13TH HCH INTERNATIONAL HCH & PESTICIDES FORUM IN ZARAGOZA

3TH to 6TH NOVEMBER 2015

Key messages of the 13th International HCH & Pesticides Forum, held in Zaragoza 3-6 November 2015, organized by the International HCH & Pesticides Association, the Aragon Government and SARGA

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History of the International HCH and Pesticides Forum

The first International HCH and Pesticides Forum took place in 1992 in Provincie Overijssel - Zwolle in The Netherlands. Since 1992 the Forum has been organised as a biannual meeting to create a platform for discussing the national and regional strategies, action plans and financial resources for elimination of obsolete pesticides. The 14th Forum will be organized in Astana, Kazakhstan in the second half of 2017.

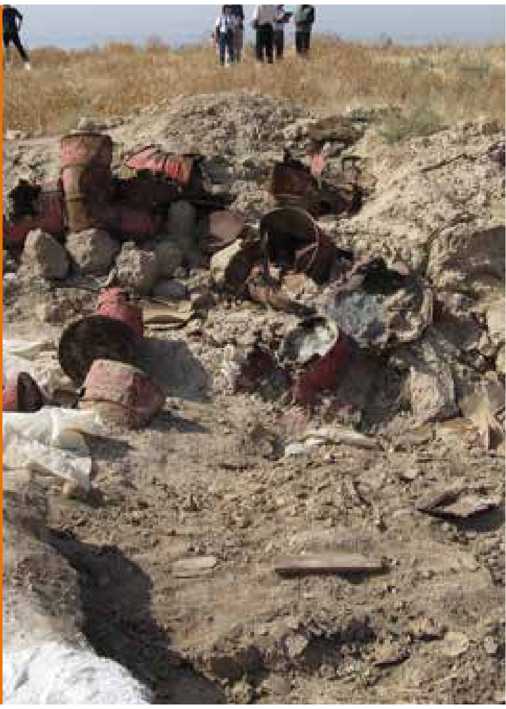
About IHPA

The International HCH and Pesticides Forum is initiated by IHPA, the International HCH and Pesticides Association, an independent and non-political network of committed individuals that wants to draw international attention to the worldwide problems stemming from the production and use of HCH and other obsolete pesticides and its dangers for human health and the environment. Visit our website www.ihpa.info or contact IHPA, director John Vijgen at john.vijgen@ihpa.info and Chairman of the Board Bram de Borst at bram.deborst@ihpa.info for more information.

About the 13th International HCH and Pesticides Forum

The International HCH and Pesticides Forum represents a platform for discussion between stakeholders of all kinds, working on implementation of projects related to POPs, obsolete pesticides and hazardous chemical waste. It acts as a catalyst in the exchange of information for the implementation of the Stockholm Convention and other chemicals related multilateral environmental agreements, and the environmentally sound management of pesticides, pesticide waste and other chemicals, and has today developed into an important event for national as well as international decision-makers and stakeholders

Its special focus is and has always been to contribute to the solution of the problems in the EECCA (Eastern Europe, Caucasus, Central Asia) countries.



At the 13th Forum the results of the EU financed and FAO coordinated project "Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union" have been presented. This project is an important strategic study that has been implemented by IHPA on the assessment of legislation and waste management practices related to obsolete pesticides for the 12 EECCA countries.

A summarizing Roadmap dealing with the development of environmentally sound management of hazardous waste in the EECCA countries has been worked out.

The 13th Forum was organized in Zaragoza to draw international attention to the enormous environmental and financial problems in the region of Aragon (Spain) created by the former production of Lindane by Inquinosa and the legacies created by the wild dumping of huge quantities of HCH-waste in the area surrounding Sabiñánigo and the Gállego River.

The Forum agenda also included the dissemination of experiences made by Aragon authorities on solving of this problem and the transfer of these unique experiences to the countries of the EECCA region and other interested regions in the world with similar problems.

THE ZARAGOZA DECLARATION

endorsed November 5, 2015 by the participants of the
13th HCH and Pesticides Forum

The Participants at the 13th International HCH and Pesticides Forum representing governments, sponsors, donors, intergovernmental organizations, NGOs, private sector, civil society, media, universities and research centres, meeting in Zaragoza on 3-6 November 2015, expressed their gratitude to the Government of Aragon, SARGA and IHPA for its hospitality and generous contribution in organizing this Forum.

The participants recognized that the elimination of POP pesticides, POPs and associated waste is at the same time a local, national and transnational issue that threatens the environment, health, local economies and the sustainability of agricultural products, and that the importance and urgency require a multidisciplinary approach developed and supervised by Governments under the highest possible level and with the participation of all relevant institutions.

Specifically, the participants identified and concluded on three areas of further development,

1 Firstly, the Road Map developed under the EC-FAO partnership programme project “Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union (FAO/GCP/RER/040/EC)’ was endorsed as an efficient framework for building the necessary leadership and capacity for sound environmental management of hazardous waste in the EECCA region. The Road Map will prove its value during implementation, and reports of experiences will be made on the 14th Forum.

2 Secondly, being informed of the situation in Aragon, and visiting the HCH dump sites in Sabiñanigo and Sardas from the Lindane-plant of Inquinosa, and based on previous reports to the IHPA Forum, it is clear that mega-sites exist, where the contamination is so large and complex that no region and/or country alone can fund the necessary remediation. The Inquinosa facility and connected landfills in Aragon is such a mega-site (See under Consequences of the legacies created by the Inquinosa factory for the affected area of Sabiñánigo and more specifically Bailín and Sardas landfill and the former Inquinosa factory).

3 Thirdly, reviewing the inventories and calculation of the cost of eliminating POP pesticides, POPs and associated waste, it was noted that the total cost of clean-up of the known legacy sites is less than 0,1% of the 2014 GDP of the EECCA countries. Hence elimination of the legacy of POP pesticides, POPs and associated waste should be affordable in all EECCA countries given that the political awareness and leadership are present; and will prevent a further increase of the costs because of in-action.

Based on the above and on the discussion and recommendations from the Forum participants, the following declaration is brought forward:

Call upon all ***National Governments*** to take leadership in the elimination of POP pesticides, POPs and associated waste and

Understand and discuss the increasing negative socio-economic, environment and human health impacts of non-action and the associated damages and losses slowing down economic development

Strengthen environmental institutions on all levels, build capacity through training programs and ensure that existing capacities are maintained.

Strengthen the custom regulations and monitoring in order to avoid substandard and counterfeit products entering the countries

Allocate funding for awareness raising through media and education as well as to advance sustainable technologies for elimination of obsolete pesticides and associated wastes, contaminated soils and water in an environmentally sound manner (ref. Secretariat of the Basel Convention guideline)

Specifically for ***POP mega-sites***, including HCH mega-sites,

Identify POP mega-sites, assess and control their risks to human health, the environment and the socio-economic development; prepare midterm containment and long term plans for remediation of POP mega-sites in dialogue with GEF and supported by international partners

Specifically for the Governments in the ***EECCA region***,

Establish the elimination of POP pesticides, POPs and associated waste as a national priority and ensure intra-governmental cooperation, e.g. through an interdisciplinary project implementation approach.

Develop and implement the Road Map including the principles of environmental management, required policies and legal frameworks and their proper implementation and enforcement thereof and create the conditions for proper investments in destruction capacity.

Use the implementation of the Road Map to comply with the requirements for international financing, more specifically the requirements regarding implementation of environmental policies and legislation.

Facilitate the transboundary transport of hazardous waste, including customs procedures in alignment with the Basel Convention.

Calls upon the ***European Union*** to recognise that non-action has immediate and long-term negative consequences to the European Community and the European health, environment and economy as well as to the food safety of the European citizens, and specifically call upon

The European Parliament to

Acknowledge its major role in elimination of POP pesticides, POPs and associated waste for the benefit of the food safety of the European citizens and for the health, environment and economic development of the wider Europe

Recognise the results of the EC-FAO partnership programme project ‘Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union (FAO/GCP /RER/040/EC)’ as a basis for further regional technical assistance and encourage the European Commission to continue to support the EECCA countries.

Assist the Parliamentarians in the EECCA region in developing and implementing policies to eliminate POP pesticides, POPs and associates waste in an environmental sound manner

The European Commission to,

Establish a regional technical assistance programme for the elimination of POP Pesticides, POPs and associated waste supporting the Road Map activities in the countries in the EECCA region

Establish a dedicated facility for funding technical assistance to Governments who are responsible for the risk reduction and possible remediation of mega-sites in the wider Europe

Call upon the ***International Organisations and International Financial Institutions*** to

Replenish GEF funding in support for financing projects related to Stockholm Convention

Facilitate the Governments' action plans especially in implementing the Road Map in EECCA region

Assist countries in assessing the damages and losses in economic terms from obsolete pesticides, POPs and associates waste on public health and environment

Ensure short term and well as long term funding of necessary remediation of the threats from POP mega-sites

Specifically call upon ***FAO*** to,

Support the implementation the Road Map for the elimination of obsolete and POP pesticides and associated waste in the EECCA region.

Assist countries to prevent the entry of substandard and counterfeit pesticides through the implementation of the Rotterdam Convention and the International Code of Conduct on Pesticide Management, and raise awareness among all stakeholders of the importance of integrated pest management as part of sustainable agricultural production.

Specifically call upon ***GEF and in cooperation with GEF agencies and other relevant partners*** to,

To consider the funding of potential projects emerging from the 'framework of the Road Map' as per GEF pertaining rules and policies.

Explore possible means of support to establish a global inventory of POP mega-sites in preparation for assessing the global risk to human health and the environment.

To further encourage the development of partnership with private sector to help co-financing of GEF projects.

To further emphasise the role of concerned NGOs as key participants in implementation GEF funded projects.

Call upon the ***Waste Sector*** to

Continue to work on innovative and effective technologies for the environmental sound management

Support the process of building destruction capacity by participation in public private partnerships

Call upon ***local NGOs and the civil society*** to

Continue their large effort in creating political pressure and raise awareness of the importance to eliminate obsolete pesticides in the environment, food cycle and human bodies and to follow-up on Government policies and assist in their implementation in line with the Aarhus Convention

Consequences of the legacies created by the Inquinosa factory for the affected area of Sabiñánigo and more specifically Bailín and Sardas landfill and the former Inquinosa factory

Regarding the affected area of Sabiñánigo and more specifically Bailín and Sardas landfill and the former Inquinosa factory, no region and/or country alone can fund the necessary remediation that is why we:

Call upon the ***Parliament and Government of Aragon*** to fulfil the commitments made by all political groups in the documentary "Discovering Lindane" presented at the forum.

These commitments are:

1. TO ACHIEVE the decontamination of the area surrounding Sabiñánigo and the Gállego River as soon as possible and with the backing of all political groups, as well as by locating other points which may cause environmental or health-related problems.
2. TO PROVIDE the necessary means, on a technical, financial, and legal level, to undertake the decontamination tasks.
3. TO DESIGN a transparent communication, information and participation system which includes the involvement of institutions, researchers, specialist companies, NGOs and citizens
4. TO PROMOTE technological innovation as an indispensable tool for the decontamination of the affected area, in turn creating an opportunity for local development based on a sustainable and technologically pioneering industry.
5. TO FACILITATE the exchange of knowledge and the technological transfer of HCH and lindane decontamination actions carried out in Aragon so that this knowledge can be transferred to other regions with similar problems.
6. TO CARRY OUT a Public Health study which assesses the exposure of the general public, and those exposed in an occupational context, to the pollutants dumped in the Gállego river basin.
7. TO ESTABLISH mechanisms which allow for evaluation of the efficacy of the actions carried out and the public investments made.
8. TO TAKE LEGAL ACTION against the company INQUINOSA so that they cover the reparation costs.

Call upon ***the National Administration of Spain***

9. TO RECOGNISE the seriousness of the problem and therefore provide the necessary financial support.
10. TO COMMIT, as a national environmental priority, to cleaning up lindane, HCH and other POPs in the Sabiñánigo area and the Gállego river basin.

Call upon ***the European Commission***

11. TO SUPPORT, on an institutional level, the clean-up of lindane, HCH and other POPs in the Sabiñánigo area and the Gállego river watershed, and to provide the necessary funding.
12. WE REQUEST that, within the framework of H2020 funding, a specific financial line be included for research into this topic, as well as the allocation of more FEDER funds for the operation.

Call upon ***the parties involved and corresponding administrations***

13. TO ESTABLISH ongoing cooperation to achieve a definitive solution to the problem of pollution caused by the Inquinosa factory in Aragon.
14. TO GUARANTEE and provide an alternative supply of clean and safe water to all of the people whose drinking water comes from the Gállego.

The 13th Forum recognised the effort of IHPA as an important contributor in building awareness in governments and civil society in the EECCA region, and urged IHPA to continue working towards the fulfilment of the objectives of Stockholm Convention and in bringing together scientists, industry and policy-makers to support the implementation of the Road Map and contribute to the remediation of the large and complex POP mega-sites starting with the Inquinosa site in Aragon.

Opening John Vijgen

Director IHPA

Dear friends, colleagues and honourable Excellencies,
We are extremely happy to be here in the beautiful capital of Aragon, Zaragoza with its warm-hearted inhabitants.
Many people asked me why is an association like the International HCH & Pesticides Association, which is solely focussed on the problems of obsolete pesticides in EECCA coming to Aragon?? What do you want to do there?

About 4 years ago the Aragon authorities approached IHPA to jointly address the issue of the terrible impact of the legacy of the Inquinosa factory by means of an EU-Life project and when I came here and visited the site, I was shocked about the extent of the problem, but also impressed by the dedication and the enormous specific know how that has been developed here over the last years and this know how is unique and needs to be spread all over the globe including the EECCA region. Also the high level of dedication in spite of a very bad economic situation to solve this issue inspired us to join forces!

The Inquinosa case is certainly one of the largest POPs legacies in Europe, and needs to be solved!

IHPA's view is perhaps different than others but we feel, and I speak on our own behalf that the disaster left behind by Inquinosa is also an opportunity!

Why?? The Location in Huesca brings the confrontation of old chemical industries, large number of jobs lost and talented people that have left the region at the one hand and a nature so splendid that you feel being in paradise at the other hand. Only a MASTERPLAN focussing on the complete conversion and clean-up of the contaminated land can be the target: the factory, the 2 landfills and the surroundings to be converted in a new green industrial area with intelligent industry creating a high added value for the region in and around Huesca. A proper socio-economic feasibility study at Huesca should lead to innovative green business investments on top of this former disaster.
For this moment, I leave further discussions to all experts and politicians that join their strengths to solve this issue. But we are ready to support Aragon in its battle to gain both moral and financial support in the EU parliament and from the EU Commission. I propose to get a special public session in the EU Parliament organized.

Because this is the focus of IHPA: to assist and support countries who have made a genuine commitment to eliminate obsolete pesticides and who are willing to allocate money and who will not rest before they have established the funding required for the elimination of their problem of obsolete pesticides. Over the past more than 25 years this has been our approach, even before the Stockholm convention was in place.

We are proud that we could contribute in such a sense to countries that show the good examples: we started in the Netherlands, followed by the Eastern part of Germany and the Basque country here in Spain. We developed a joint learning process with Poland and supported over the past more than 10 years our friends from Moldova. We asked for the commitment of the international community to contribute to the Kalush project in Ukraine and the Nubarashen project in Armenia, as we are requesting today commitment for the Inquinosa case. And there has been achieved a lot in more countries than mentioned.

We are proud but not satisfied. When we look at the global problem, the progress is clearly not sufficient. If we don't speed up it will take many decades to free our planet from obsolete pesticides. And if we lose momentum the elimination of obsolete pesticides will fade out. Therefore active countries should speed-up; inactive countries should follow the examples of the active countries and start action. Because delay is not without consequences: still more than one million tons of obsolete pesticides are

to be eliminated, the contaminants continue to spread, affecting soil and groundwater, wild life and crops. But there is also a growing impact on human health: effects on food quality, long term effects on health. It should scare us: how do obsolete pesticides contribute to increased cancer risks and decrease of human fertility? Why does it seem that we don't want to invest to know these answers?

And even for those who want to close their eyes for the impact on environment and human health we have an economic message. One day you will have to agree that the increased risks and effects, the damages and losses have to be restored and compensated and at that time at higher costs than today. Penny-wise will turn out to be pound-foolish. This is our message as IHPA and we hope that you take this message and spread this message after this forum.

Looking back at the 12th forum in Kiev in 2013 and I come back to all our EECCA friends, just before the Ukrainian revolution, we have addressed there the issues on:

Damages and losses: IHPA proposed an approach that combines identification of damages, including increased illness, loss of life, failing ecosystem services and polluted agricultural products. We have not worked on this issue. Instead we worked, on request of FAO on the development of a Road Map for the elimination of obsolete pesticides, POPs and other hazardous wastes. The outcomes thereof will be presented in the next session of this Forum. But we will come back on damages and losses in the Forum statements of this Forum.

The Forum declaration of the 12th Forum addressed issues to:

National Governments to create in an open dialogue awareness for the size and impact of the problem and the need for action, to allocate funds for the elimination of obsolete pesticides, to adopt sustainable agriculture practices and to strengthen the environmental institutions.

As these issues are also part of as well the recommendations in the National Reports on Legislation and Waste Management and the Road Map, we are happy to see that we received endorsement letters on our Road Map report from Belarus, Moldova, Azerbaijan, Kazakhstan, Kyrgyzstan and Tajikistan. We also welcome the increased commitments in Kyrgyzstan and Tajikistan. And Georgia is now working on a concerted plan for improvement of the waste legislation.

We addressed to the ***European Union*** to give political support to politicians from the EECCA region and to continue their efforts based on the joint project with FAO (National reports and Road Map). It is more than disappointing to see that the European Commission has decided not to allocate any further funding and due to that decided not to address to this Forum a stimulating message. Therefore, with even more energy IHPA will prepare for the first quarter of 2016 a new public hearing in the European Parliament.

The ***International Organisations and Financial Institutions***:
We specifically addressed a recommendation to the GEF to continue their support to the elimination of obsolete and POPs pesticides and suggested a contribution to a regional facility for destruction projects and capacity.

We are happy to welcome Ms Lulwa Ali from GEF in our conference and are convinced that her presence will led to follow up actions for continued support.

We called upon the ***NGOs and civil society*** to continue their efforts in creating political pressure and raise awareness at governments and civil society to eliminate the obsolete pesticides. We are impressed that you did not rest to raise your voice and work on this.

The coming days IHPA will challenge you to reconfirm your commitment to the elimination of obsolete pesticides, leading to personal commitment, seeking for funding and perseverance till the moment that obsolete pesticides have been eliminated.

And finally, let me show you now some impressions on the video on the Vaksh Pesticides Landfill in Tajikistan that show you why we need to act.

Video Vaksh Pesticides Landfill on youtube:
https://www.youtube.com/watch?v=DhH2F72TAn4

I wish you a good Forum!

Key note speech Ms. Sandra Ortega Bravo

Director General for Sustainability of the Government of Aragon

Good morning and welcome to everyone.

This forum in Zaragoza is an excellent opportunity and has great importance for the Government of Aragon and all the people and institutions that have been working on finding a solution to one of the greatest environmental challenges that we face in Spain.

Contamination by obsolete pesticides is a global problem that is clearly reflected in the participation of over 150 experts from 35 different countries in this Forum, sharing their experiences related to the problems of pesticides manufacturing as well as the stocks of obsolete pesticides. It is an undeniable fact that these environmental problems cannot be solved without concerted action at EU and international level.

The use of pesticides has been a double-edged sword. For decades the mass manufacture and use to combat vector diseases and to fight pests that substantially detracted the productivity of agricultural crops, has been responsible for numerous harmful effects on human health and renewable resources. The serious environmental problems are on the one hand related to the characteristics of these compounds, due to their persistence, bioaccumulation and dispersion capacity, and on the other hand the consequences of mass production, enormous amounts of waste generated and the huge amounts of stocks of obsolete pesticides found in many countries.

After long years of negotiations the Stockholm Convention on Persistent Organic Pollutants was adopted in 2001, which currently has 179 signatories. The agreement defined initially a dozen compounds for priority actions. This list is periodically revised and in 2010 the pesticide LINDANE was included, whose mass production led to serious environmental pollution as we are currently suffering in the Sabiñanigo area in Aragon.

Between 1975 and 1988 the Inquinosa factory produced Lindane, using a production process where for each tonne of the pesticide produced between 8 to 10 tonnes of waste were generated, which were deposited in the landfills of Sardas and Bailín. Although its manufacture was stopped more than 25 years ago, the problems associated with the waste deposits remain unresolved. In the three most affected areas, the total volume of HCH solid waste exceeds 130,000 metric tonnes, 3,000 metric tonnes of liquid waste, 1 million metric tonnes of contaminated land, 50 hectares of contaminated soil and three contaminated aquifers.

The project Comprehensive Decontamination of Lindane in the Bailín Ravine is a priority of the Government of Aragon through the Department of Rural Development and Sustainability, and must also become a priority at the highest political and economic level for both the Spanish Government and the European Commission.

Since 1990, the Government of Aragon has developed a set of numerous actions and provided funding of millions of euros to address this problem of pollution. These actions include specialist studies to analyse the situation, surface sealing works on the landfills in Sardas and Bailín, leachate purification, the location and removal of the free phase of the waste at the different points affected, the establishment of action protocols and health and safety protocols, the development of operation models for the landfills, and the implementation of pilot tests and remediation techniques applicable to in situ rock and soil decontamination, such as the Discovered LIFE project, whose awareness-raising activities are part of this Forum. They also include the establishment of the Monitoring and Control Plan of the HCH landfill in Bailín, the implementation and monitoring of the network of hydrogeological monitoring of the aquifers affected, the Plan for Monitoring, Control and Removal of HCH, the Environmental Assessment and analysis of alternatives in Sardas, surveys and removal of free phase, and a wide range of laboratory and mathematical modelling tests on the landfill.

It is a challenging combination of high investments and complex engineering, project development and R&D work. We have made a tremendous effort in the control and monitoring of this pollution, but there is still a long way to go to reach a final solution.

Achieving the objective of comprehensive decontamination of Lindane in Aragon requires a serious commitment of the Ministry of Agriculture, Food and Environment of Spain and the European Commission. The solution to this problem not only involves a very high financial cost and political responsibility, but also requires the development of a comprehensive and detailed Action Plan.

We at the Government of Aragon are aware of the importance of the collaboration of all the stakeholders, since comprehensive decontamination involves the direct participation of all the institutional and private actors, scientists, associations and environmental NGOs, along with involvement by members of the public. Therefore, it is a priority for the Department of Rural Development and Sustainability in the short term to enforce its management structure and create a framework for communication and collaboration with all its stakeholders.

We not only have to deal with the solution of a serious decontamination problem, we also have an obligation to learn from what happened and to redesign our approach of global food needs, while maintaining the ecosystems and resources on which also other essential elements of health and life depend.

We have a responsibility to advocate the rational management of chemicals and the sustainable management of industrial production and agriculture. Promotion of integrated pest and vector management and alternatives to POP pesticides will enable a reduction in pesticide use. It is not simply a matter of "replacing one pesticide for a similar one", nor is it enough to just replace POPs with other pesticides; it is necessary to take a broader view and consider more sustainable alternative practices. The key aspect is the ability to integrate a global vision throughout the whole chain.

The year 2015 has been declared by the United Nations as the International Year of Soils, which offers a special occasion to remind ourselves of the key importance of maintaining and protecting this non-renewable resource and its crucial role in agricultural development and the functions of ecosystems.

All of us here today share the same challenge to find solutions for pesticide contamination that threaten our regions and countries. We are aware of the necessity to join forces between institutions, private entities, researchers and citizens. And above all, we know that responsibility and personal commitment are prerequisite to reaching the necessary solutions to these worldwide problems.

I would like to give my sincere thanks to all the participants, to the technicians who are involved in the hard work of controlling and containing the problem of pollution, to the people organising this 13th International Forum on HCH and Pesticides for all their efforts, and to all the people and entities who are working and collaborating on solving the environmental problem of pollution.

I hope that these four days of intense work will be productive and allow a great ferment of knowledge, exchange and cooperation between all the participants.

A big thank you to everyone.

Official Forum Statements at the 13th International Forum HCH and pesticides

Zaragoza- Spain, 3 November 2015

Global Environment Facility

The senior Environmental Specialist at the Global Environment Facility (GEF), ***Ms. Lulwa Ali*** highlighted the GEF support to the EECCA countries for the implementation of several projects covering a wide spectrum of chemicals and waste issues including obsolete POPs pesticides. Acknowledging the unique situation and major challenges faced by them with regard to managing huge amounts of obsolete and legacy pesticides, she emphasised the need for developing a more focused integrated strategy coupled with feasible national/ regional action plan based on adequate economic and financial policy incentives as key determinants for moving forward. Ms. Ali also underlined the key factors necessary for accelerating the elimination process in the region including ownership which is supported by a solid political will and commitment, replication of successful experiences within the region, and availing the latest and most appropriate technology options that could help the countries in disposing the obsolete pesticides in a safe and environmentally sound manner.

Ministry of Environment, Moldova

The Deputy Minister of Environment of the Republic of Moldova, ***Mr. Adrian Delinschi*** explained that Moldova has a long tradition in agricultural production and hence used large amounts of pesticides in the past. It is estimated that between the 1950s and 1990s about 560,000 tons of pesticides were used in the Moldovan agricultural sector, including 22,000 tons of organochlorine pesticides.

In the absence of an adequate pesticides management strategy, more than 3,000 tons of now banned and useless pesticides have been accumulated over the years in storage facilities all over the country.

In 2002, the Moldovan Government initiated a strategy on additional measures for centralized storage and neutralization of obsolete pesticides.

Over the last 14 years more than 20 projects in the area of management and elimination of POPs and other dangerous chemicals and wastes have been or are currently implemented. The amount of funds used for these purposes up to now is approximately US$20 million.

The conclusions and lessons learnt over more than one decade of experience in the management and disposal of POPs in Moldova can be summarized as follows.

A comprehensive assessment and establishment of a detailed inventory leading to a comprehensive strategy and action plan is the fundament for cooperation and communication with as well the relevant stakeholders in the country and the international donors. Other key elements are continuity in time and trained personal, that agreed commitments and activities are respected and tasks are completed within the set time frame. The establishment of a Project management team that continued to ensure the effectiveness of implemented projects has proven to be very important. Streamlining of the existing policies in the field of POPs management, development of legislation and permanent awareness raising activities at all levels of society are crucial throughout the entire process of approaching and solving of POPs issues.

Given the results obtained, the international institutions and experts involved in POPs management consider Moldovan results as a success by the fact that most of the objectives set in recent years have been achieved.

Ministry of Natural Resources and Environmental Protection, Belarus

The Deputy Minister of Natural Resources and Environmental Protection of the Republic of Belarus, ***Mr. Igor Kachanovskiy***, stated that today in Belarus almost 7 thousand tons of obsolete pesticides is located in the temporary storage warehouses and five burial sites. Over the past years Belarus has spent large efforts to implement the application of the Stockholm Convention. As important achievements can be mentioned that all stocks of obsolete pesticides in Belarus are repacked and environmentally safe stored.

In addition, Belarus created a large storage facility for hazardous waste in the Gomel region. This facility is unique for the CIS countries and provides the bulk of the safe storage of obsolete pesticides. In the creation of this complex the Belarus State has invested more than US $ 25 million.
Also, using the GEF financial support, in 2012 the Ministry of Natural Resources and Environmental Protection of the Republic of Belarus completed the elimination of 2,103 tons of obsolete pesticides in Slonim. From this amount, 1,800 tons were exported and disposed in Germany.

Despite this progress, it is necessary in the near future to create the technological capacity for environmentally sound disposal of the remaining obsolete pesticides and other hazardous chemical waste. The storage facility in the Gomel region could be an excellent location for such developments. We hope that international investors and donors will provide financial and technical support for this project.

This facility is intended not only for obsolete pesticides from Belarus and other CIS countries, but we believe that this disposal facility can also serve other countries in the region.

Investors and donors are invited to discuss during this Forum such investment developments.

Ministry of Energy, Kazakhstan

From Kazakhstan, ***Mr. Kerey Bekbergen***, director of the Department of Green Technologies and representative of the Ministry of Energy of the Republic of Kazakhstan, stressed that the heritage stemming from the use of large volumes of pesticides over the last century has created problems for human health and the environment worldwide.

This is also a problem for Kazakhstan. Obsolete Pesticides and POPs waste has been stored in stores or dumpsites. Many of these stores have been destroyed. Currently, information about their number and the composition of the content are not always reliable because of the lack of documentation. This requires in a first step a complete inventory to be made.

He underlined the importance of this Forum as an excellent opportunity to share experiences and make use of the expertise of other countries. He also stipulated that Kazakhstan has sent a letter of endorsement to confirm the acceptance of the Road Map as a guideline for the elimination of pesticides, POPs and other hazardous waste.

Being aware of the fact that most countries in Central Asia are confronted with similar challenges in the approach of these problems, Kazakhstan proposes the creation of a council for the countries of Central Asia in order to enforce co-operation.

In addition, Mr. Bekbergen recalled, on behalf of the government that the Republic of Kazakhstan has offered to host the next 14th International HCH and Pesticides Forum in Astana, Kazakhstan.

Ministry of Agriculture and Melioration, Kyrgyz Republic

Mr. Janybek Derbishaliev, Director of Chemistry and Plant Protection of the Ministry of Agriculture and Melioration of the Kyrgyz Republic, highlighted the problems of Central Asia in dealing with these accumulated pesticides and the ongoing need for external support from international institutions in implementation of future projects.

Based on the adherence of the Kyrgyz Republic to the Stockholm Convention, a national inventory of old stocks of pesticides have been carried out. For some urgent situations, first actions of repackaging, containment and destruction have been taken.

The Kyrgyz Republic supports the Road Map as developed by IHPA as a tool for the development of environmentally sound management of hazardous waste and is preparing its implementation.

He requested for the ongoing support of international and donor organizations in the future actions regarding repackaging, storage and destruction of obsolete pesticides and other POPs and afterwards the remediation of the affected soil and groundwater.
The Kyrgyz Republic is ready to fulfill its obligations under the international conventions and has the means and political will to do so. This will contribute to the sustainable development of the country.

Committee of Environmental Protection under the Government of the Republic of Tajikistan

The representative of Tajikistan, ***Mr. Abdusalim Juraev***, Head of the office for POPs, appealed to international institutions to make them aware of the serious problem facing his region. “Tajikistan has a lack of own resources and is therefore depending on international funding and support to create and develop projects. Since 2007 we have adapted the laws of our country and we have reconditioned the areas that are most polluted by pesticides. But without additional funding we can not apply more projects, so we appeal to the European Parliament and other international institutions to provide us the required support”.

Ministry of Natural Resources and Environment, Vietnam

“Until a few years ago, the government of Vietnam was not aware of the problem of obsolete pesticides. International organizations have helped us to understand the size and seriousness of the problem and to develop and propose solutions. As a result, we are now struggling to implement the required improvements in Vietnam,” stated ***Mr. Hoang Thanh Vinh***, the representative of the Ministry of Natural Resources and Environment and director of the Project Persistent Organic Pollutants (POPs) in Vietnam. In the meantime we are making important progress. We had to start from scratch to develop our methodology but our project-oriented way of working has in the meantime led to an integrated programmatic approach.

Food and Agriculture Organization of the United Nations

The Project Coordinator of the project “Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union” ***Mr. Richard Thompson*** highlighted the role that FAO developed since 2009 to solve the problem with obsolete pesticides.

“The role of FAO is to build capacity to manage disposal of obsolete pesticides and all the harmful substances produced. Therefore we make use of the mechanisms as provided by the related international Conventions as Stockholm, Basel and Rotterdam and more specifically also work with World Health Organization. We look at each of the countries to know how to apply disposal technologies and to eliminate these obsolete pesticides. Part of our project was to create a Road map to provide guidance for institutions, both public and private how to implement concerted actions and arrive at environmentally sound management of obsolete pesticides and other hazardous waste in the next 10 to 20 years”.

Member of European Parliament (MEP)

Mr. Miguel Martínez Tomey Head of European Affairs of the Aragonese Union and Local Assistant to MEP Jordi Sebastià (European Free Alliance)

“When the lindane problems in the area surrounding Sabiñánigo and the Gállego River came in the spotlight, now a bit more than a year ago, after a long and strange period of non-action, we went to the European Parliament and raised this issue. The European Commission did not know what to say. At that moment we realized that Europe is not up to the commitments sustaining the Stockholm Convention. Our conclusion is that we need to persuade the European Union that we have identified a problem calling for a budget and the definition of a programmatic approach. We must create a permanent financial line in the general budget of the European Union for it”.

Member of European Parliament (MEP)
Mr. Jeroen Lenaers (European People's Party Group)

The Members of the European Parliament, independent of their political background, have already been involved since 2001 in supporting the efforts of IHPA to create more awareness on the immense and urgent problems of obsolete pesticides in the EECCA countries, and on the need to eliminate the dangerous chemicals completely from this region. In 2007, former colleague Wieslaw Kuc organized a first Public Hearing and a large exhibition with impressive photos that showed the real situation on the ground. In 2010, a Mini hearing led by former MEPs Ria Oomen-Ruijten together with Esther de Lange was organized.

Due to our persistence, the EU Commission has carefully listened to the pleas of the politicians of the EECCA countries that showed willingness and strength to make all possible efforts in their countries and therefore EC Commission financed the project "Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused chemicals in the Former Soviet Union".

The deliverables of this project are important anchors for future action: assessment of legal frameworks, identification of actions to improve the progress under Stockholm, quantification of as well legacy volumes as annual arisings of POPs pesticides, POPs and other hazardous wastes per country and the definition of a Road Map for the development of environmentally sound management of hazardous waste in the EECCA region.

This Road Map enables a structured approach with concerted actions, facilitates co-operation between countries in the region and is a basis for countries, donors and international financial institutions to discuss investment options for destruction capacity in the region.

Based on the experiences of other parts of the world, **it will take at least 10 to 20 years to arrive at full implementation.** The international donors have initiated this process and will continue to give support to the countries. But it is the responsibility of the governments to make the necessary commitments, to allocate resources, to define principles and create a firm legal basis, with effective enforcement and open communication in order to arrive at a well-managed implementation.

And finally we want to invite all participants to come to the European Parliament in Brussels at the beginning of next year to discuss how we can realize the elimination of obsolete pesticides in the near and long-term in the EECCA region

The 13th International HCH and Pesticides Forum

The 13th International HCH and Pesticides Forum created a platform for discussing the national and regional strategies, action plans and financial resources for elimination of obsolete pesticides with a special focus on the need for accelerated action. Valuable scientific results and best practices were exchanged; and the progress of EECCA region was showcased in special sessions, emphasizing the importance of Government determination and focus. On November 3-6th the 13th Forum on HCH and Pesticides Forum was held in Zaragoza, Spain with participation of more than 230 experts from more than 35 countries.

The International HCH and Pesticides Forum in Zaragoza was sponsored by:

- EU LIFE + Programme, project “Lab to field, soil remediation demonstrative project: new ISCO application to DNAPL Multicomponent environmental problem” (DISCOVERED LIFE),
- the European Union and FAO through the project “Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union”,
- Antipollution, Greece,
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- Emgrisa, Empresa para la gestión de residuos industriales S.A., Spain,
- GreenTox, Switzerland,
- University of Applied Sciences of Northwestern Switzerland, School of Life Sciences
- POLYECO S.A., Greece,
- SI Group Consort Ltd., Israel,
- SARPI-VEOLIA,
- Tradebe, United Kingdom,
- UTE FCC Ambito – Adiego Hnos, Spain.

IHPA is grateful for the support given from all companies and organisations. This support facilitated the 13th Forum in Zaragoza and enabled access for experts from the EECCA countries and other international experts to travel to Zaragoza and to participate in the discussions.

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HCH: A PROBLEM SOLVED IN THE BASQUE COUNTRY

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Abstract

Over 450,000 m3 of contaminated soil and the dumping of 5,000 Tn of pure HCH waste were at the root of one of the most serious environmental health problems detected in the Basque Country at the end of the 1980s. Significant social pressure along with obvious concern among politicians spurred the Basque Administration on to define a global strategy to solve this environmental liability. Ten years and over €52 million were necessary to implement the measures included in this strategy. These measures ranged from different administrative formalities focused on closing down once and for all the two companies that produced HCH to preparing different market and benchmarking studies to search for more effective solutions. Yet, particularly noteworthy among these measures was the construction of three cutting-edge infrastructures aimed at the final elimination of the problem: a physical-chemical plant to treat pure waste and two safety landfills to confine the contaminated soil caused by the uncontrolled dumping of HCH. Apart from the technical rigour when implementing the solutions adopted, fundamental aspects of the success of this strategy was the involvement of the different authorities and of the different agents and stakeholders affected, and interested parties, along with the numerous public participation processes that were conducted over those 10 years. This has all meant that the solution adopted in the Basque Country continues to be an international benchmark in the search for solutions to manage the waste from producing lindane.

Key Words

HCH, the Basque Country, Ihobe, strategy, lindane, contaminated soil, safety landfill, Based Catalyzed Decomposition, public participation.

The problem of HCH in the Basque Country

There were two companies in the Autonomous Community of the Basque Country that produced the pesticide commercially known as lindane: Bilbao Chemicals and Nexana (subsequently called Celamerck). Both companies operated from the 1950s until the end of the 1980s. They were located in the province of Bizkaia, in municipalities close to Bilbao.

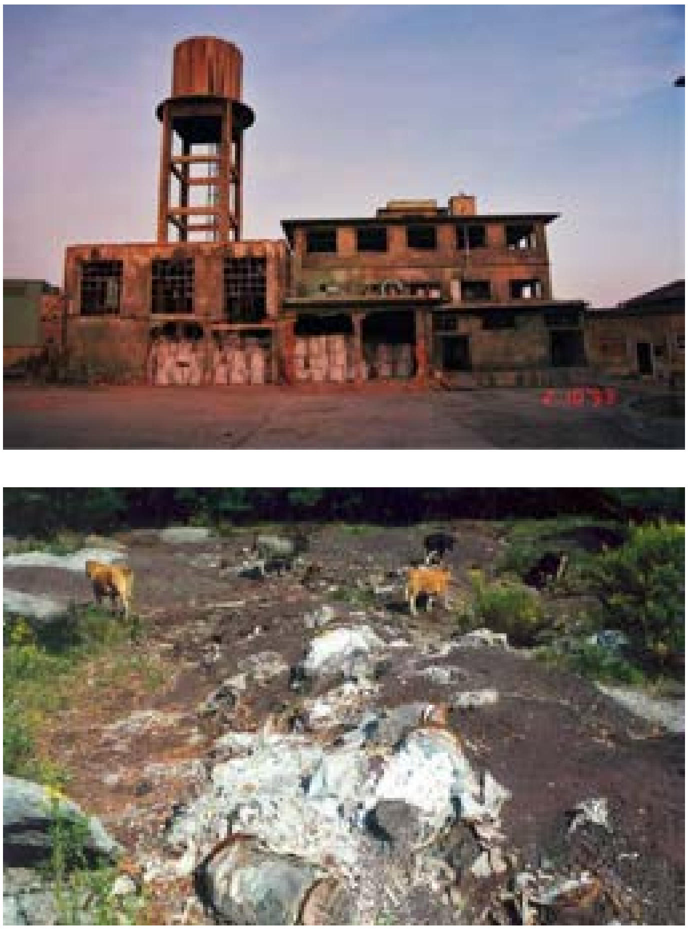

Fig 1.- Top: Photo of the Bilbao-Chemicals premises.
Down: uncontrolled dumping of HCH.

During the productive process, a total of 82,000 tons of waste were generated, 77,000 Tn of which were dumped in an uncontrolled way at different sites close to the companies and which caused a very serious environmental problem. The rest, a further 5,000 Tn, were stored at one of the facilities after the Ministry of Health of the Basque Government banned the uncontrolled dumping of waste in 1987. This ban led to the closure of the two companies producing lindane in that same year.

Producers	2
Production period	1947-1987
Estimated amount of waste produced	82,000 Tn
Amount of raw waste	5,000 Tn
Amount of waste dumped with no controls	77,000 Tn
Number of contaminated sites	36
Land surface area affected	410 Ha
Volume of contaminated soil	450,000 m3

Fig. 2.- Key data to calculate the scale of the environmental problem generated by lindane production.

The solution adopted

The Ministry for the Environment of the Basque Government, through its Publicly-owned Environmental Management Company Ihobe, S.A., began to design a global strategy that would allow an ambitious goal to be reached: the elimination once and for all of the environmental problems associated to HCH waste.

Numerous administrative formalities were introduced as initial measures and which sought to involve producers to search for solutions. It was an expensive process due to the limitations of the legal instruments existing at that time. The involvement and coordination of the different local authorities and the different ministries of the Basque Government with jurisdiction regarding the environment and public health were necessary in order to implement those formalities.

On the other hand, and in order to grasp the size of the problem, different studies were conducted that highlighted the existence of unacceptable risks both for human health and for the ecosystems, which sped up the implementation of corrective measures. Thus, in 1992, and pending a final solution being found, the raw waste that had been abandoned in the old warehouses was stored safely. It was therefore packed into 1m3 big-bags and stored inside the warehouses and isolated from the environment by means of high density polyethylene sheets. The HCH contaminated soil that was being excavated in the immediate vicinity for urban development reasons was stored in those same facilities, pending a final solution being found.

In 1993, numerous studies on the quality of the soil and the associated risks were conducted on the sites where HCH waste had been illegally dumped and over 30 HCH contaminated sites were identified.

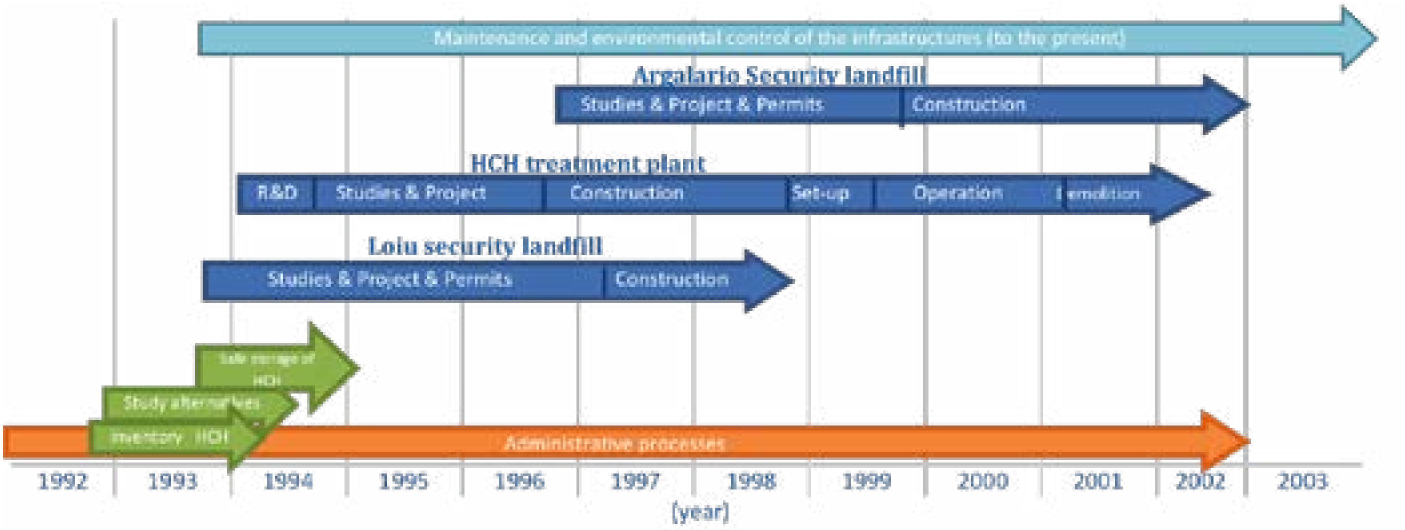

Fig. 3.- Timeline summary of the most important measures implemented by the Basque Administration to solve the environmental problem arising from the HCH.

Given this really worrying situation, and in order to find for an appropriate and final solution for the problems existing in the Basque Country, several meetings were held with international experts and countries were visited where this problem had already been tackled. Forums and specialist meetings were likewise held, including the organisation of the III and V International HCH Forum. Both events were held in Bilbao in 1994 and 1998 respectively.

Finally, and after the alternatives had been studied exhaustively, the Basque Government opted to build a treatment plant to eliminate the pure HCH waste and two safety landfills to confine the contaminated soil. The budget needed to be able to embark on these actions was in excess of €52 million and therefore European Commission funding was fundamental to finance part of the projects.

The HCH treatment plant

A study was conducted to select the most appropriate treatment technology for the final elimination of the raw waste. Technologies such as thermal desorption, soil washing, phyto-remediation and even incineration were assessed among the options studied. However, finally, and for environmental, economic and technical feasibility reasons, a soft technology for the destruction of organochlorine compounds, developed by the US Environmental Protection Agency and known as BCD (Based Catalyzed Decomposition), was chosen. Thus in 1999, and after the satisfactory results obtained in the tests conducted in a pilot plant, an industrial plant was built in the former premises of Bilbao Chemicals. This plant operated from June 1999 to October 2001 and all the pure HCH found was treated there.

Basically, the treatment consisted of mixing HCH with different substances that encouraged a chemical reaction in which trichlorobenzene (TCB) and sodium chloride (ClNa) were generated. The TCB was used for commercial purposes as a reagent product and the soda was dumped in the river in the tidal area, after undergoing the relevant quality controls and once adapted to the composition of the brine.

$$C_6H_6Cl_6 + 3NaOH \xrightarrow{cat} C_6H_3Cl_3 + 3H_2O + 3ClNa$$

Fig. 4.- Basic reaction of the BCD process to treat pure HCH.

Construction of the safety landfill

At the same time, the treatment of the soils affected using the different technologies was ruled out for the HCH contaminated sites and after a new analysis of alternatives, mainly due to the fact that they were mixed with other earth and with other types of different waste. This heterogeneous mix means that its treatment using any of the technologies available at the time was unfeasible. Therefore, and pending new technological developments leading to effective treatment, the decision was taken for the controlled confinement of that earth in two safety cells constructed for that purpose.

Fig. 5.- Top: Construction of the Argalario safety landfill.
Down: Inferior seal of the safety landfill

Thus, in 1998, a safety cell able to hold 113,000 m^3 of HCH contaminated soil was built in the municipality of Loiu. In turn, a second cell was built in the municipality of Barakaldo between 1999 and 2002, and simultaneously to the recovery of a former municipal waste landfill existing in the Mount Argalario area. Over 340,000m^3 of contaminated soil was deposited there, along with the waste from the demolition of the former premises of the two lindane producers. Over 400 hectares of contaminated land was thus cleaned up thanks to those measures.

Associated to both cells, two plants were designed and commissioned to treat the leachates generated in the cells and the contaminated water from the sites that had been recovered. Those plants continue to operate today, even though the flow generated in time has significantly dropped since the cells closed.

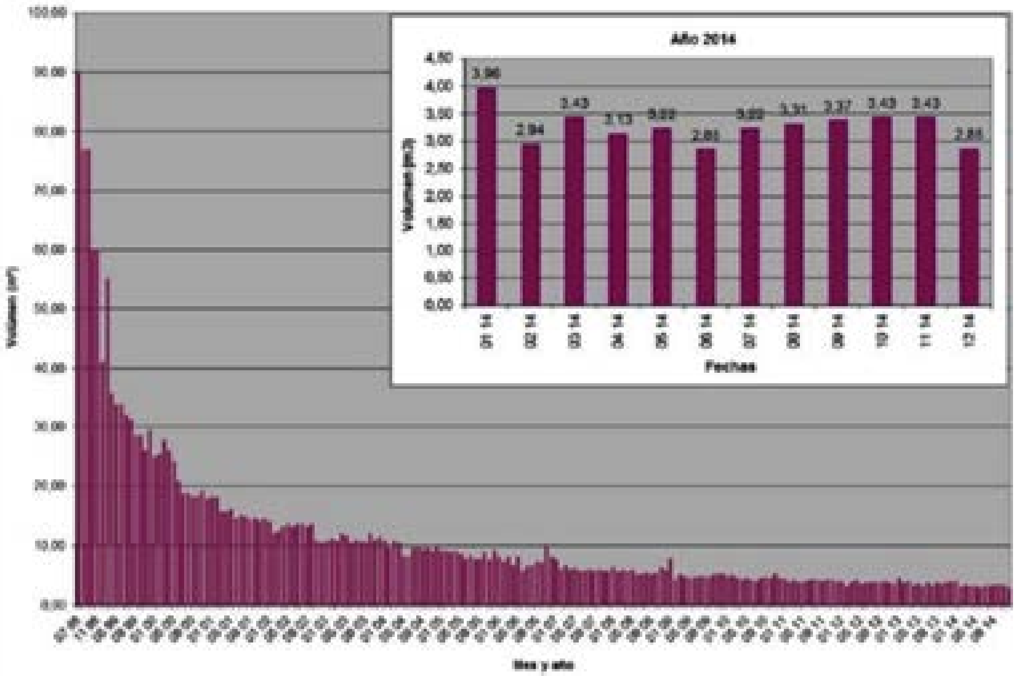

Fig. 6.- Evolution of the flow generation in the Loiu safety landfill closed in 1998.

On the other hand, different devices and a variety of instruments were installed in the cells and in the surrounding area, as well as in the treatment plant at the time. An exhaustive environmental control could therefore be carried out during pre-operational phase and during the construction and operating phase. Those controls have continued to the present and the more than 30,000 analytical results obtained so far endorse, apart from the cells functioning smoothly, the environmental improvement achieved at the 36 sanitized sites. That improvement has allowed those sites that had been overlooked in the past due to their longstanding major environmental problem to be integrated in the local urban development plans. Examples of how they have been used include an important area for recreational and commercial use, a leading exhibition centre or even a residential area.

Environmental quality thresholds	
Surface water	50ug/l
Underground water	50ug/l
Sub-surface water	50ug/l
Land	10-100 mg/kg
Air emission	20mg/Nm3
Air inmission	16,700 ng/l
Discharge to the sewer	10ug/l
Discharge to waterways	50ug/l

Fig. 7.- Environmental quality thresholds established in the relevant administrative permits granted between 1999 and 2002.

Key points of the designed strategy

Undoubtedly, and having analysed the current situation, the strategy driven by the Basque Country can be said to have met the initial target set to eliminate the risks associated to the waste from the production of the lindane pesticide. Some of the key points that have helped with this are as follows:

- An overview of the problem that allowed a final solution to be designed for the problems generated by two independent facilities.
- Medium-term planning that would allow all the measures to be implemented with sufficient guarantees for them to be effective.
- Constant coordination between the different authorities and stakeholders involved.
- Input from international experts.
- The public participation processes held in the different phases, involving ecologist groups, neighbour's associations and political representatives of the municipalities in question.
- Transparency towards society regarding the actions undertaken, by creating, for example, a citizen information office and technical monitoring committees, daily publishing online of the results of the environmental inspections carried out, publishing information material (leaflets and DVDs) on the measures implemented, or even setting up an environmental education learning centre at the Argalario cell, along with organising technical visits to the worksite aimed at different profiles.

- The technical rigor followed in the constructed infrastructures with special mention of the strict inspections established both for the health and safety at work of the workers and of the local inhabitants, as well as for the environmental monitoring and for the overseeing of the quality of the waterproofing of the safety landfillss.
- The economic and financial support by the European Commission subsidising around 80% of the cost of the Argalario safety cell and the HCH treatment plant projects.

Fig 8.- Left: HCH contaminated site. Right: final situation of the site after its recovery (source: geoeuskadi.eus)

It should likewise be noted that the actions implemented give impetus to the development of legal arbitration instruments and measures aimed at protecting the environment, at correct waste management and at preventing soil contamination, thanks to which it would be impossible to return today to a situation such as the one that existed at the end of the 1990s. This legislative development, along with other instruments created, is similarly the reason for the Basque Country being an advanced region and even a European benchmark as regards the management of contaminated soils.

Acknowledgements

Legal, administrative and technical team of Ihobe and of the Basque Government's Ministry for the Environment involved in each and every one of the measures implemented to sole the HCH environmental problem. A special mention must go to Maribel Martinez, Head of the Hazardous Waste Unit of the Basque Government, and to Enrique Martinez Lorenzo, a technician from the Ihobe contaminated lands division.

GENERAL STRATEGY FOR THE HCH LANDFILL POLLUTION. THE SINGULAR PROBLEM REGARDING THE DNAPL PRESENCE

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Abstract

The manufacture of lindane in the decades of the 70s and 80s in Sabiñánigo (Spain) generated among other sources, three highly contaminated sites: the landfills located in Sardas and Bailín and the factory itself. The use of poor environmental practices involved the direct disposal of more than 120,000 t. isomers of HCH in the field and the consequent pollution of soil and water. It is noteworthy the presence in the three locations of dense non-aqueous phase (DNAPL) which generated a pollution plume with high concentrations of organochlorines that can affect the river Gállego, a watercourse intensively exploited. Among all the pollutants, it must be highlighted the presence of at least 5 compounds listed in the Stockholm Convention (αHCH, βHCH, γHCH, pentachloro benzene, dioxins and furans).

The decontamination strategy is conditioned by the presence of DNAPL and the scarce margin to act due to the proximity of the pollution sources to the receiver watercourse. Since 2005 it has been applied pump-and-treat methods and several remediation techniques (improved surfactant extraction, thermal destruction in situ, chemical oxidation, chemical reduction, nanoparticles, steam extraction...) are being tested in field and laboratory. Additionally, one of the contamination focuses, the landfill located in Bailín, has been shifted to a security cell. This measure has led to the transference of 64,000 t. of HCH and 360,000 t. of contaminated soil. In the Sardas dump, it has been designed isolation measures and it is foreseen the dismantling of the industrial ruins of INQUINOSA, as well as the soil affected beneath them. In the near future it is intended to address the research and design of different techniques (chemical destruction, modified soils, plant and bioremediation, etc.) focused on the decontamination of the matrix rock (in surface and vadose zone) and the most affected soils.

Concerning the relevance that implies the presence of DNAPL in aquifers, this paper addresses some guidelines focused on the detection of other sites potentially affected. It has been concluded that, bearing in mind the manufacturing process of technical-grade HCH and lindane, as well as environmental practices carried out during long periods of time in most of the countries where these compounds have been manufactured, it is highly probable that exist DNAPL diffuse sources on those places. Therefore, its identification and study is a key factor for the remediation of industrial and disposal areas in those countries where HCH has been manufactured.

Key Words

HCH, lindane, DNAPL localization, organoclorate megasites.

Background

Between 1975 and 1989 the company Industrias Químicas del Noroeste (INQUINOSA) produced lindane in Sabiñanigo, a small industrial town in the Aragonese Pyrenees.

The waste produced during the operation period of the factory Inquinosa generated an amount of 6,800 t/year of solids (several isomers of HCH) and between 300 and 500 t/y of liquid residue.

The synthesis of HCH was performed by adding chlorine to benzene by a photocatalysis process with ultraviolet radiation. Through the removing of the excess of benzene, it was obtained a solid made up by a mixture of HCH isomers. This mixture is known as technical HCH and was widely used as a pesticide since the early 1940s until the early 1970s.[1,2]

In the 1950s, once known that the insecticidal properties of HCH are obtained from the gamma isomer, there was a change in the market of pesticides with the progressive increase in the production of lindane replacing the manufacture of technical-HCH. In Inquinosa, the production was focused, from the beginning, on the obtention of γHCH, i.e, lindane.

The photochlorination process, at least in the factory of INQUINOSA, was carried out in glass reactors (figure 1). According to the reports of former workers, this process was frequently interrupted, generating a pasty-liquid residue made up by a highly variable quantity of every substance from the product chain between benzene and benzene heptachlor.

Figure 1. Reactors for the photochlorination in the factory of INQUINOSA

Once photochlorination process is completed, the direct cooling of the solution allows separating the alpha isomer by crystallization and the surplus of benzene by stripping. The presence of this pollutant, with a high content of αHCH isomer, has been verified in the landfill of Bailín and in the laboratory of INQUINOSA.

Finally, once the excess of benzene has been separated, it is produced a solid with the other isomers and other impurities. In order to separate and enrich the γHCH isomer, the solid obtained is dissolved in methanol and subjected to fractional distillation processes. The end-product obtained in this process is lindane (isomer γHCH 99%), a solid residue made up of the mixture of disposable isomers and liquid-paste distillation bottoms, known as greasy substances or delta phase.

All this waste (solids: αHCH, mixture of disposable isomers; pasty liquids: failed reactions in the head of production, greasy substances), along with other materials generated in the process (activated carbon already consumed, sludge, treated water, out of use reagents, production surplus of γHCH, etc.), were poured indistinctly in landfills without adequate isolation conditions or in scattered locations without control.

The Spanish environmental legislation during those years and until the entry into the European Union, as well as the lack of environmental awareness, made such actions easier, which bearing in mind what has happened in other countries[3] it was not an exception in the usual practices of these industries.

The legacy of INQUINOSA. A complex contamination emplacement.

In the case of Sabiñánigo and the factory of INQUINOSA, the practices outlined in the previous section have ended up in the presence of two large landfills (Bailín and Sardas), an abandoned factory and a damp directly affected (figure 2), as well as probably scattered spaces affected by uncontrolled dumping.

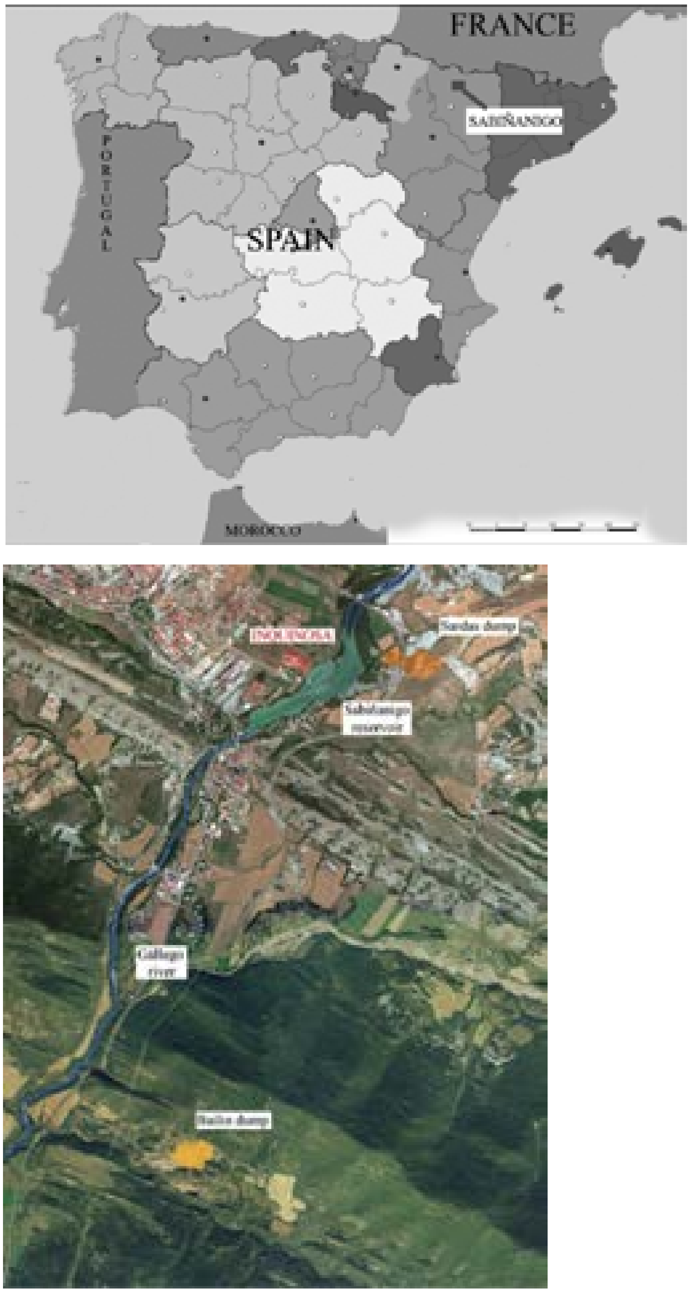


Figure 2. Location of the areas affected by the production of HCH in Sabiñánigo.

Unlike the storages of obsolete pesticides, the pollution linked to the manufacture of pesticides, and in particular to the manufacture of lindane, has the particularity of being a multi-component contamination that affects several matrixes.

In the case of Sabiñánigo, with significant concentrations in different matrixes, the presence of benzene, polychlorobenzenes, polychlorophenols, HCH isomers, methanol and other alcohols as well as dioxins and furans among other compounds[4] was found.

These compounds can appear in a solid state, in an aqueous phase or in a dense phase (dense non-aqueous liquid phase: DNAPLs). Moreover, they can appear as pure residues, in a mixture, or contaminating solid (soil and rock) and liquid (surface and underground water) matrixes. To the complexity arising due to the variety of compounds and matrixes, it must be added the large volumes involved in the pollution episode, the surface affected and the geological complexity of the area.

Need for a global strategy

The complexity of this environmental and health problem caused by bad practices (which in some cases could be classified as criminals), involve expensive and lasting decontamination works, which forces to establish priorities when addressing the several compounds and matrixes affected (figure 3).

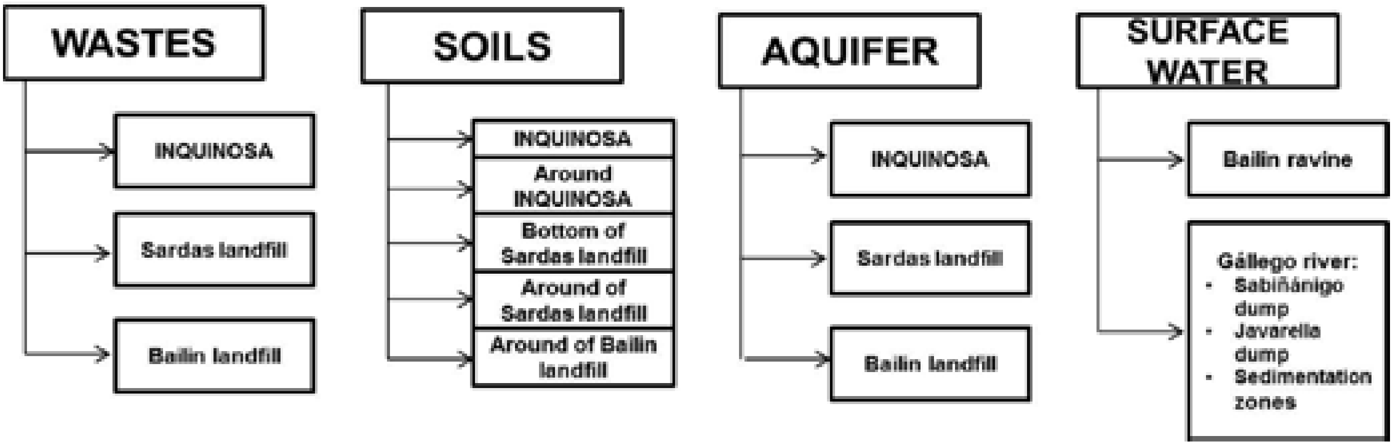


Figure 3. The matrixes affected by HCH residues.

They are mainly based on the risk level and are restricted by the available budget, the technical state of the art and the multiple connections among affected areas and matrixes.

There are two kinds of residues generated by INQUINOSA:

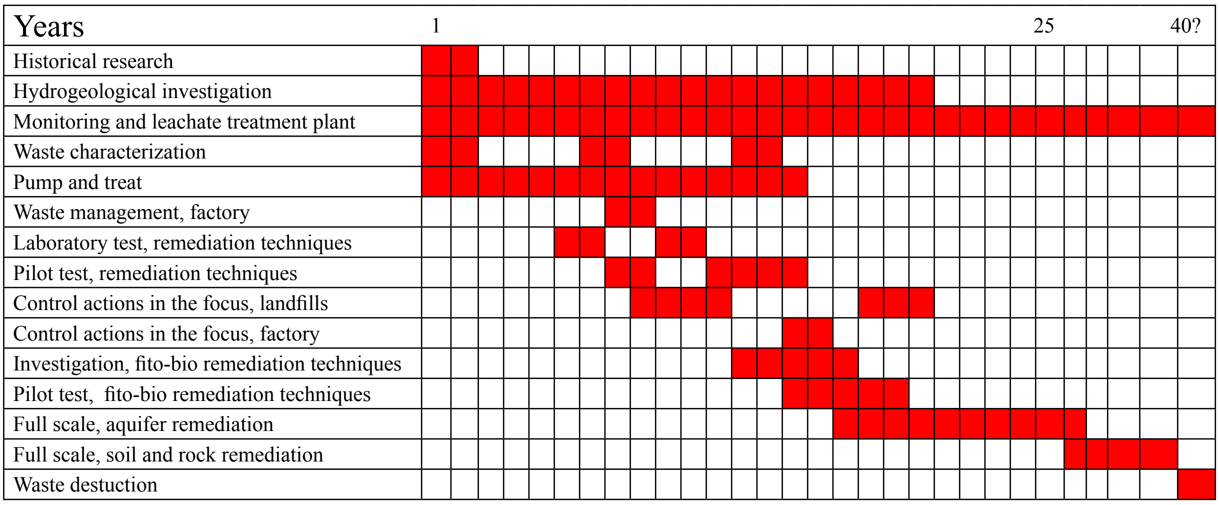
- Solids: mainly isomers of HCH with different types of impurities.
- Liquids: greasy substances or delta phase, a DNAPLs (figure 4) with a high concentration of HCH and other pollutants.

Figure 4. DNAPL in landfills and aquifers in the areas affected by residues from the manufacture of lindane in Sabiñánigo.

Parameter g/Kg	Max.	Min.
Water	9	2,2
Benzene	11,16	9,4
Cholorobenzenes	305,06	145,09
Phenol	1,72	**
Chlorophenols	4,86	1,21
Tetrachlorociclohexenes	18,64	1,97
Pentachlorociclohexenes	130,69	74,3
Hexachlorohexadieno	65,1	**
Hexachlorociclohexano	167	**
a-HCH	60,92	48,3
b-HCH	1,91	**
g-HCH	148,86	134
d-HCH	129,05	102,2
e-HCH	35,9	21,43
Other HCH isomers	39,97	**
Heptachlorocicloexano	96,38	1,39
Alcohols, others	148, 85	136,1
Viscosity 25° Cps	12,1	14,2
Density Kg/l	1,543	1,3662

The presence of large amounts of pure solid wastes or mixed with soil or other type of wastes are affecting the landfills of Bailín and Sardas, with 64,000t of HCH in the first case and a similar estimation in the second one. The absence of an adequate isolation system of this waste poses a major risk on the underground and surface water affecting the aquifers linked to the dumps of Bailín and Sardas, the ravine of Bailín and finally the watercourse of the Gallego river. In the case of the former factory of INQUINOSA, the amounts of residues accumulated are minor (around 100 t.) and they are located under covered areas without implying an immediate risk.

The presence of a free phase or DNAPL was detected in the landfill of Bailín and Sardas, in the aquifers linked to these sites and in the factory of INQUINOSA. The presence of this substance entails the highest risk because of their mobility, their impact on groundwater and its easy solubility in surface water, which can reach very high concentrations in these contaminants.



Years	1																							25					40?
Historical research	🟥	🟥																											
Hydrogeological investigation	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥										
Monitoring and leachate treatment plant	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Waste characterization	🟥	🟥					🟥	🟥					🟥	🟥																
Pump and treat	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥															
Waste management, factory								🟥	🟥																					
Laboratory test, remediation techniques						🟥	🟥			🟥	🟥																			
Pilot test, remediation techniques								🟥	🟥			🟥	🟥	🟥	🟥															
Control actions in the focus, landfills									🟥	🟥	🟥	🟥						🟥	🟥	🟥										
Control actions in the focus, factory															🟥	🟥														
Investigation, fito-bio remediation techniques													🟥	🟥	🟥	🟥	🟥													
Pilot test, fito-bio remediation techniques															🟥	🟥	🟥	🟥	🟥											
Full scale, aquifer remediation																	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥				
Full scale, soil and rock remediation																										🟥	🟥	🟥	🟥	
Waste destuction																														🟥

Figure 5. Approximate timetable in the decontamination plan since 2005.

In fact, this compound has come out into the surface in the landfills Sardas and Bailín, although it could have been intercepted before it reached the surface waters.

On the contrary, the concentrations achieved in the soils are minor, except for very specific areas, with less than a ten mg/kg.

Its little impact compared to other matrixes and potential receiving areas limits the risk.

Regarding the groundwater of the aquifers affected, although they have no direct use, in all the cases DNAPL is present in some points and the point of discharge in the Gallego river is very close, so the risk is quite high.

Finally, the surface water, the ravine of Bailin and the Gallego river itself, play a double role as receptors and secondary pollutant sources due to the sediments accumulated in dams and backwater areas. However, the concentrations detected so far in the accumulated sludge are quite low; therefore, they are mainly considered as a receiving area.

Bearing in mind the above considerations, among others, since 2004 and after the detection of DNAPL in the landfill of Bailín, the priority has been to limit the extent of DNAPL and hinder its progression or even reduce its scope (figure 5).

In relation to the presence of active sources DNAPL, it has been addressed the control of original sources, of the landfills, through their transference to other safe location in the case of Bailín[5,6], or in the near future through the increase of the extraction capacity using surfactants[7,8] and isolating the landfill with screening techniques like the ones applied in Sardas.

With the aim of decontaminating the aquifers, several laboratory tests[9,10] are being carried in order to select suitable remediation techniques, with a minimum forecast of 5 years before developing pilot tests and their later large-scale application .

The presence of DNAPL. General guidelines for its location.

The presence of DNAPL linked to the production of HCH and lindane or to its waste disposal, is scarce and shortly detailed; it is referred the presence of delta phase in Skopje[11], the presence of DNAPL in the aquifer associated to the factory in Hamburgo[12], and is likely to be related to the of residues in Rudna-Gora[13] according to their typology.

It is not the purpose of this article to carry out a detailed description of the methodology for the detection and research based on dense non-aqueous phases, already detailed in several scientific papers[14,15,16,17,18,19,20], but rather providing some general guidelines for its location, highlighting some particularities of the presence of these compounds in Sabiñánigo that can help to the location of DNAPL in other areas. In both sites, the landfill of Bailín and the landfill of Sardas, the presence of DNAPL was detected almost accidental. In the landfill of Bailín, the analysis carried out in the boreholes installed in 1996 showed saturation in groundwater. During 2004, a certain number of new boreholes were added in order to assess the situation and the possibility of running a drain under the landfill to make the extraction of leachate easier. In the first borehole executed the presence of DNAPL was already detected. In the case of the landfill of Sardas in 2009, the DNAPL rised to the surface in the bottom of the landfill. Its presence was detected before it reached the surface waters. In INQUINOSA, the detection of this compound, was carried out through a borehole close to the storage tanks of raw materials (benzene), later used for the discharge of liquid waste.

Historical analysis of the activity

The first criterion to be followed for the search of the free phase should be the historical analysis of the industrial activity, its processes, the operational mode and the waste management activities. In this sense, it must be highlighted that, in the case of Spain, prior to its EU membership, the industrial activity had not environmentally concerns, as it may have occurred in other countries, and still happens in some countries such us India[21]. The DNAPLs manufacture is linked to the storage of raw materials, mainly benzene and methanol and to two manufacturing processes or HCH or lindane: photochlorination and final distillation with methanol.

In the case of INQUINOSA, it has been found that the benzene storage tank has generated a dissolved-phase plume and the presence of free phase of this compound has been detected. According to the experience in administrative monitoring of polluted soils, the majority of the buried tanks, especially those older than from 20 years, have losses of greater or lesser importance.

The photochlorination process may fail, leaving a complex mixture of organochlorine compounds that will depend on the stage of the reaction at the moment of failure . This fact leads us to consider the possibility of generating wastes able to produce DNAPL even before the beginning of the enriching process in γHCH in the 50s.

The enrichment process of lindane generated greasy substances known as “grasillas” or delta phase, which constitute the largest volume of waste that can generate DNAPL. In the case of Sabiñánigo, its presence has been found in the alluvial aquifer linked to the premises of the former factory of INQUINOSA. Its presence is related to the waste storage areas in the facility itself and to the possible pouring of this waste in the storage tanks of raw materials after the end of the production of lindane.

In the dump of Bailín, the discharge of these compounds directly and by the use of barrels became evident due to the review of historical photos. During the dismantling of the landfill those barrels appeared much corroded or, in some cases, they have vanished completely even leaving the waste stored inside of them with the shape of the mold. It has been found that a significant part of the delta phase got solidified, another part with waxy appearance was liquefied when exposed to the sun and the last part of the barrels remained empty or contained traces of free phase or DNAPL.

The experience acquired in the landfills was indicative that the generation of a plume of DNAPL occured since the beginning of the spilling and was increased in the early years with the degradation of the barrels. It has also been verified that, in the case of having kept the residues volume exposed, the volume of free phase mobilized would have been larger.

In any case, it is highly probable that the access to historical documents and information of the manufacturing facilities will be difficult. However, it is likely that a certain amount of liquid wastes have been produced and, either in the industrial premises or in the locations where the removal of this waste was carried out, have generated a pollution source of DNAPL, reaching groundwater.

Even considering that the disposal of this waste has been carried out in spaces with waterproofing systems, it must be taken into account that these residues are extremely aggressive, being able to dissolve the concrete, and as it has been checked in the landfill of Bailín, they may end up degrading a large number of plastic products.

Direct observation

Direct observation is not easy, considering the long lapse of time since the stop of the lindane manufacturing in most countries. Nevertheless, in those areas where waste may have been collected and stored, it is possible that the soils remain affected, in which case the techniques listed in those scientific papers referred can be a guide on how to proceed.

In the case of the landfills of Bailín and Sardas, the free phase has been detected directly rising to the surface naturally, which, although it simplifies its location, reveals that the advance of DNAPL is very important.

During the execution of boreholes, in the case of guessing the presence of free phase, the progress must be slow enough to be able to observe both control sampling points and drilling water. It must be discarded the use of destructive techniques (percussion, rotopercussion), despite being possible to identify DNAPL, due to the high risk of deepening the free phase. In this case, the DNAPL was observed in both fractures and water drilling, although sometimes a severe washing occurs and makes the detection of DNAPL not possible until a reasonable period of time. In these cases and despite the caution that advises the adequate safety measures for the workers, the odor is a remarkable indicator.

Depending on the lithology of the soil, the observation can be very difficult. As it is highlighted in another paper of this forum[16], in which the procedure followed in the execution of the boreholes is also detailed. In the control samples placed in marl soils, it has been observed the presence of DNAPL droplets in micro-fractures that couldn't be observed in the boreholes. It has been helpful, in the case of Bailin and Sardas, the performing of extractions with methanol (MERCK) in the first centimetres of fracture zones in the boreholes, where, despite the low permeability of the rock, it can be seen the spreading of volatile and semi-volatile compounds, with higher concentrations when getting closer to the focus of DNAPL.

The solubility of organochlorine compounds in the dissolved plume associated

In the literature it is frequently used the figure of 1% related to the effective solubility in a water sample in order to consider the presence of DNAPLs. This value may be valid for single-component pollutants or simple mixtures. It is not in the case of HCH waste.

In the following tables are gathered the different trials carried out over the years with HCH residues from INQUINOSA.

				αHCH	βHCH	γHCH	δHCH	
Chlorobenzene	35.9	gr/kg		αHCH	βHCH	γHCH	δHCH	
1,3-Dichlorobenzene	0.4	gr/kg	0% Methanol	1,637	144	2,472	16,273	µg/l
1,4-Dichlorobenzene	0.9	gr/kg	1% Methanol	4,363	780	3,117	19,836	µg/l
1,2-Dichlorobenzene	0.4	gr/kg	10% Methanol	7,365	1,078	5,405	31,549	µg/l
1,2,3-Trichlorobenzene	0.4	gr/kg						
Pentachlorcyclohexane	1.0	gr/kg	0%Acetone	1,637	144	2,472	16,273	µg/l
αHCH	763.1	gr/kg	1%Acetone	2,032	226	3,041	19,967	µg/l
βHCH	148.0	gr/kg	10%Acetone	5,724	587	5,070	29,879	µg/l
γHCH	13.8	gr/kg						
δHCH	24.7	gr/kg						
εHCH	11.4	gr/kg						

Table 1. Composition of technical HCH from INQUINOSA and its solubility in water and co-solvents at 20 °C.

Parameter	Units	DNAPL	DNAPL	Units	Water	Methanol		Acetone	
						1%	10%	1%	10%
Viscosity 25ºC	Cps	1.4							
Density	Kg/l	1.21							
Water	g/Kg	90	9.27 %						
Benzene	g/Kg	10.83	1.12 %	µg/l	33,947	18,234	45,563	20,202	31,124
Chlorobenzene	g/Kg	75.53	7.78 %	µg/l	79,781	59,574	144,232	68,121	110,219
Dichlorobenzenes	g/Kg	2.64	2.94 %	µg/l	2,957	3,603	6,896	4071	6,228
Trichlorobenzenes	g/Kg	3.74	4.27 %	µg/l	1,232	2,269	2,409	2,427	2,495
Tetrachlorobenzenes	g/Kg	13.49	2.51 %	µg/l	51	75	127	100	163
Trichlorophenols	g/Kg	0.9	0.36 %	µg/l	2,903	3,186	4,775	2,525	4,754
Pentachloro benzene	g/Kg	0.8	0.08 %						
Tetrachlorocyclohexenes	g/Kg	2.21	0.23 %						
Pentachlorocyclohexenes	g/Kg	130.69	13.47 %	µg/l	2,521	3,636	4,625	3,701	4,727
Hexachlorohexadiene	g/Kg	1.47	0.15 %	µg/l	135	141	208	160	301
αHCH	g/Kg	48.3	4.98 %	µg/l	1,275	1,465	1,696	1,632	1,711
βHCH	g/Kg	1.58	0.16 %	µg/l	292	620	212	740	310
γHCH	g/Kg	136.52	14.07 %	µg/l	4,439	5,449	6,164	5,751	6,122
δHCH	g/Kg	107.33	11.06 %	µg/l	12,647	10,834	17,593	8,606	17221
εHCH	g/Kg	21.93	2.26%	µg/l	1,723	1,347	1,863	1,031	1,857
Total HCH	g/Kg	351.66	32.53 %	µg/l	20,377	19,715	27,528	17,760	27,221
Heptachlorocyclohexane	g/Kg	96.38	9.93 %						
Other compounds	g/Kg	148.85	15.34 %						

Table 2. Composition of DNAPL from the landfill of Bailín and its solubility in water and co-solvents at 20 ° C

	Units	DNAPL	CT-11-11-1	CT-16-11-1	CT-18-4-3	CT-38-8-1	CT-45-7-2	CT-X-11
Waste weight	g	1.3091	0.9826	0.9983	0.9896	0.9958	0.9982	1.0137
Benzene	µg/l	238,207.24	168.95	69.32	58.92	41.2	1.09	6.55
Chlorobenzene	µg/l	158,436.13	621.72	162.54	268.16	1,270.29	168.06	391.25
Dichlorobenzenes	µg/l	64,439.59	82.61	26.27	53.77	2,508.64	458.79	1,401.74
Trichlorobenzenes	µg/l	27,711.04	97.34	118.83	157.02	716.39	515.63	3,737.54
Tetrachlorobenzenes	µg/l	1,180.59	18.75	29.18	13.97	57.81	60.73	121.05
Phenol	µg/l		<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichlorophenols	µg/l	4,932.13	<0.1	<0.1	<0.1	10,989.69	35,822.81	4,951.9
Tetrachlorophenols	µg/l		<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pentachlorobenzene	µg/l	130.5	<0.1	<0.1	<0.1	0.7	<0.1	<0.1
a-HCH	µg/l	14,315.36	15,001.73	6,504.75	40,785.93	45,306.87	4,257.83	3,877.22
b-HCH	µg/l	52,089.96	8,054.9	13,769.05	15,724.06	42,893.98	13,855.33	20,695.51
g-HCH	µg/l	18,435.36	12,666.49	3,709.65	4,129.12	10,168.66	4,163.29	<0.02
d-HCH	µg/l	95,658.99	45,213.81	50,479.34	65,125.53	336,966.94	85,506.43	50,322.06
e-HCH	µg/l	7,673.73	5,179.83	2,097.16	<0.02	<0.02	<0.02	5,153.18
Total HCH	µg/l	188,173.4	86,116.76	76,559.95	125,764.64	435,336.45	107,782.88	80,047.97

Table 3. Aqueous solubility of organochlorine compounds from DNAPLs and of solid residues coming from the landfill of Bailín. The test consisted in the solution in 100 ml of water with stirring for 24 hours of the amounts indicated in the table. In all cases the dissolved phase was analysed after its filtration on glass filter of 0.25 microns.

Table 4. The first part of the table shows the range of concentrations detected in one of the layers polluted in the landfill of Bailín, in the area where DNAPL is accumulated and in the dissolved-plume downstream of the former area. The second part of the table shows the concentration of the second zone in which alcohols and fatty acid have been analysed.

	Dissolved-plume zone		DNAPL zone	
November 2014	Max	Min	Max	Min
Benzene	139,735.08	20,580.09	97,495.04	6,621.06
Chlorobenzene	101,311.46	29,482.05	100,363.68	26,425.38
Dichlorobenzenes	5,278.04	1,823.18	4,096.62	684.04
Trichlorobenzenes	1,205.06	320.65	2,127.31	110.77
Pentachlorobenzenes	37.65	13.03	79.59	3.53
Tetrachlorobenzenes	1.2	0.42	2.75	0.3
Phenol	0	0	0	0
Chlorophenol	1,794.46	315.45	1,320.93	132.83
Dichlorophenol	251.61	143.65	337.97	207.69
Trichlorophenols	4,532.18	782	15,586.11	815.36
Tetrachlorophenols	608.9	305.01	881.39	573.71
α-HCH	391.16	11.23	1,215.04	117.5
β-HCH	176.92	2.53	215.15	1.93
γ-HCH	1,542.33	114.2	2,841.06	116.1
δ-HCH	7,061.29	618.26	9,628.1	1,570.5
ε-HCH	695.08	38.19	829.4	259.85
Total HCH	9,866.78	784.41	14,361.09	2,113.46

Parameter	Units	
Benzene	µg/l	15,500
Chlorobenzene	µg/l	25,000
Dichlorobenzenes	µg/l	753
Trichlorobenzenes	µg/l	855
Tetrachlorobenzenes	µg/l	70
Phenol	µg/l	530
Chlorophenol	µg/l	130
Dichlorophenols	µg/l	330
Trichlorophenols	µg/l	6175
α-HCH	µg/l	590
β-HCH	µg/l	1,200
γ-HCH	µg/l	1,100
δ-HCH	µg/l	5,000
Acetone	µg/l	7,500
Methanol	mg/l	4,197
Acetate	mg/l	1,222
n-Butyrate	mg/l	503

As shown in tables 3 and 4, the solubility of the HCH isomers coming from the solid waste is far superior to that of isomers separately or of technical HCH. Even in the case of sample CT-38-8-1, which is a solidified phase from a barrel of greasy substance (delta phase), certain isomers, particularly the δHCH, has a solubility greater than that of DNAPLs.

According to this fact, the overcoming of 1% of the effective solubility is not a valid criterion for concluding the presence of DNAPLs, since the presence of other compounds acting as co-solvents greatly increases the water solubility of the solid waste, even beyond of what would be expected with water and methanol or acetone (table 1). A marker that has worked properly in the case of the landfill of Bailín is the comparative assessment of samples with higher concentrations of HCH with and without filtration or centrifugation (table 5), showing concentration differences of up to 90%, what reveals the presence of DNAPLs microdroplets.

Summarizing, it is clear that all the water masses that have been in touch with DNAPL achieve a very high levels of volatile and lighter semi-volatile compounds, what can be used as a key marker of DNAPL.

This procedure has been tested in the three pollution sources located in Sabiñánigo systematically in the analysis carried out in the boreholes that cross the plumes linked to the presence of DNAPL, even when the concentrations of HCH are in the order of hundred of ug/l. It can also be detected in upwellings, although in these cases is less reliable due to the volatilization speed of some compounds.

Indirect detection

The results obtained with indirect detection methods have also been positives in the case of the landfill in Sardas, where the dumping area and the accumulation of greasy substances by measuring with PID equipments in the degassing wellhead have been delimited. This method can also be used for direct measurements in the soil, especially in those areas with unconfined aquifers, using probes, small diameter boreholes in unsaturated area or other gas sampling techniques through the use of indirect measures such as PID or gas capture in absorbents or tedlar bags.

		piezometer 55, Bailin				piezometer 16, Sardas		
october-15	Units	unfiltered	with filter 0.45 μ	with filter 10 μ	centrifuged 4,000 rpm	unfiltered	with filter 2.7 μ	centrifuged 4,000 rpm
1,1-Dichloroethane	μg/l	<2.5	1,056.43	<2.5	<2.5	<2.5	<2.5	<2.5
Trichloroethylene	μg/l	290.43	<2.5	287.66	285.66	144.48	88.62	63.25
Benzene	μg/l	8,973.03	13,793.75	7,142.69	7,147.04	32,687.6	28,643.57	22,638.25
Chlorobenzene	μg/l	21,672.3	24,507.35	12,106.94	10,352.74	63,841.39	53,942.74	41,672.35
Dichlorobenzenes	μg/l	1,612.29	1,259.36	444.94	986.53	13,312.95	11,569.9	8,858.14
Trichlorobenzenes	μg/l	1,037.1	142.01	581.9	518.97	2,714.74	1,495.4	1,329.98
Tetrachlorobenzenes	μg/l	62.02	<2.5	<2.5	22.98	54.54	7.5	10.75
Phenol	μg/l	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorophenol	μg/l	233.33	205.79	152.99	154.68	16.74	18.54	20
Dichlorophenol	μg/l	82.09	52.58	68.15	28.8	<0.1	<0.1	<0.1
Trichlorophenols	μg/l	1,094.24	608.37	568.51	1,051.17	<0.1	<0.1	<0.1
Pentachlorobenzenes	μg/l	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tetrachlorophenols	μg/l	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
α-HCH	μg/l	881.75	243.98	428.3	834.98	570.69	594.39	506.61
β-HCH	μg/l	111.36	<0.02	27.92	99.91	119.83	59.7	60.7
γ-HCH	μg/l	3,281.44	833.95	1,863.46	3,191.32	2,006.06	2,058.86	2,075.67
δ-HCH	μg/l	9,231.89	446.96	5,752.33	9,302.59	2,407.36	2,467.49	2,521.4
ε-HCH	μg/l	1,001.96	62.91	618.52	925.77	794.44	736.64	786.52
Total HCH	μg/l	14,508.4	1,587.8	8,690.53	14,354.57	5,898.38	5,917.08	5,950.90

Table 5. Samples of the contaminated dissolved-plume in the landfills of Bailín and Sardas with different pre-treatment carried out prior to its chromatographic analysis.

Sampling methodology in boreholes

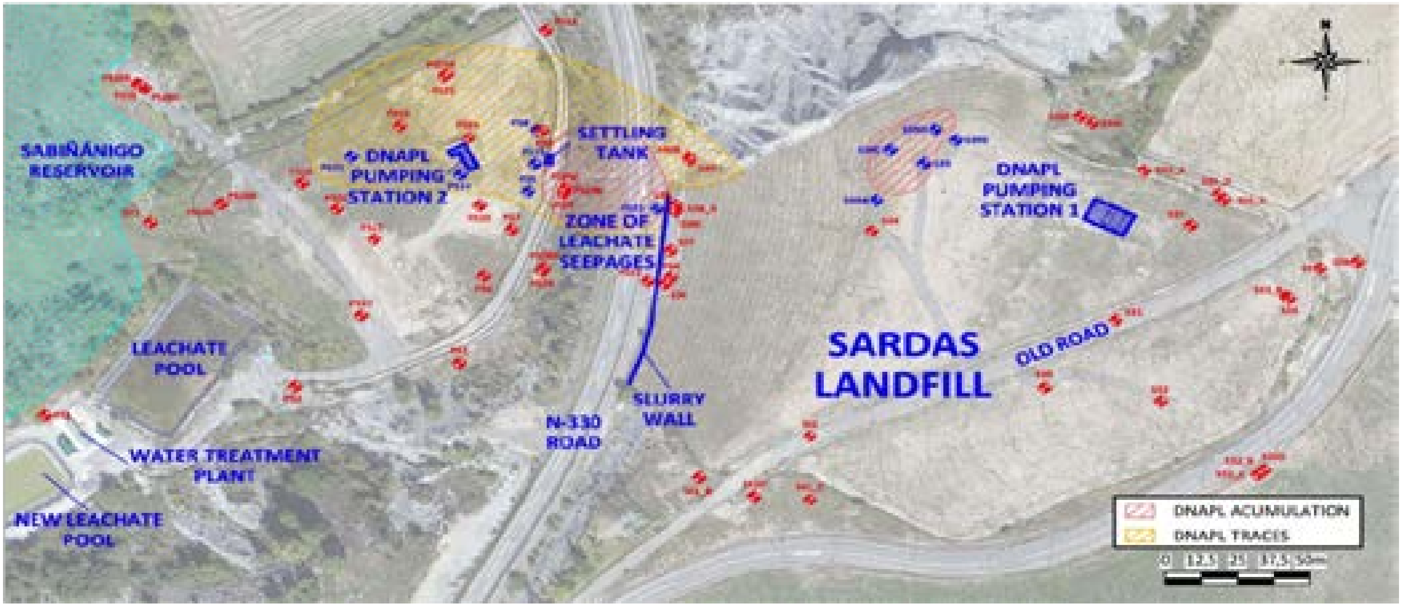
Regarding the sampling methodology used, the performing of vertical conductivity profiles allows in some occasions to identify both preferential paths and density stratification. The sampling is usually carried out without any renewal of water in the borehole regarding the fact that it can cause the mixing of different levels. The sample is obtained using a bladder pump in order to test the specific levels of interest.

The location of DNAPLs

With regards to the location of primary polluting sources or the storage sites of DNAPL, it is necessary to insist again in the historical knowledge, documents and the testimonies of workers or local people. The location of primary pollution sources is not always easy, especially due to the large period of time that has gone since the end of the industrial activity.

In the case of the sites in Sardas and Bailín, the main source of pollution is obviously the dump, but due to the large area they cover, it is necessary to delimitate where the DNAPL has been spilled.

The availability of degasification chimneys in the landfill of Sardas allowed focusing the working area through the detection of volatile compounds concentrations in these chimneys. Then, a photogrammetric restitution in detail carried out using historical aerial pictures prior to the disposal, has allowed locating new boreholes for the extraction of DNAPL, following the topographic axis of one of the ravines used as landfill (figure 6).



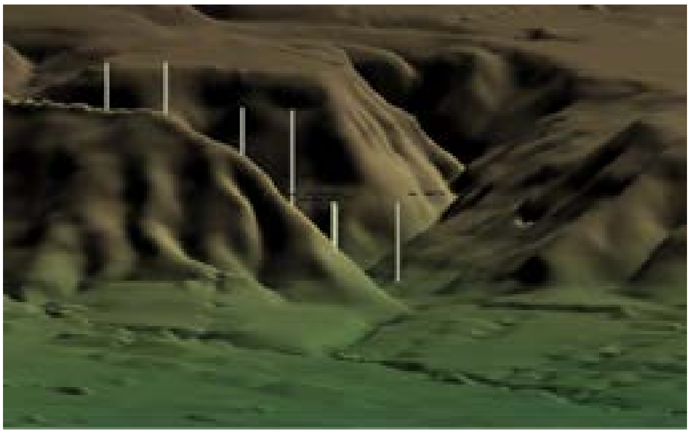


Figure 6. Photo restitution of gullies in the landfill of Sardas from an aerial picture of 1956, layout of the boreholes to locate the accumulation of DNAPL.

The use of geophysical techniques, in particular the electrical tomography, was not suitable in the case of the landfills due to the presence of an upper sheet of HDPE.

In the case of the INQUINOSA premises, the geophysical techniques (electrical tomography and GPR) allow drawing the outlines of the base of the Quaternary terrace where it is placed. Nevertheless, the level of definition is not enough for the location of small depressions in the paleo-relief, where DNAPLs may be accumulated. In those cases, a very high density of boreholes would be required in order to locate the main sources, what can be palliated through the execution of small superficial boreholes for the detection of volatile compounds prior to the setting of boreholes in areas of major concentration. In any case, it will not always be possible to locate the sources of DNAPL without a significant economic effort.

Once the main substrate has been reached mobilization will occur either following the slope direction until a barrier (i.e. a spill with abundant clay materials) or until a natural depression that allows its storage. On the other hand, if the substrate is fractured or if its permeability allows it, the DNAPL will move controlled by gravity and the existence of structural or stratigraphic lineations driven by the gravitational movement, without being related this movement to the flow direction of the aquifer affected. A detailed picture of the stratigraphy and structure is essential to determine the movement and accumulation of DNAPL in the aquifer.

As an example, the landfill of Bailín is located on a detrital formation with alternating siltstones, sandstones and conglomerates within a subvertical structure. The limestones are fractured in the surface section while sandstones have a deeper and wider fracture. The DNAPLs poured reached the substrate and was infiltrated towards the layers of sandstones until a depth at which fracturing is closed. Once the accumulation started, it was expanded in the direction of subsurface flow forming a decreasingly power plume and delimitated by the width of each layer of sandstone affected. In order to define the scope of the plume in each layer, a borehole was executed at a random distance of the landfill, by undertaking the next one at half distance upstream or downstream depending on whether DNAPLs has been detected or not.

In the case of the landfill in Sardas, the boreholes were set along the axis of the anticline that crosses the landfill and going deeper in each borehole while getting away towards north and along the preferential fracture planes in the marl.

Conclusions

The manufacture of lindane in Sabiñánigo during the decades of the 70s and 80s led to three major sources of pollution due to the waste disposal and the presence of the factory itself.

The large volumes of waste involved, the effects in different matrixes (pure pollutants, soil, rock, vadose setting and aquifer) and the existence of a free phase which is the DNAPL, requires the implementation of a long-term decontamination, restricted by the risks related to health and environmental and linked to contamination episodes and by the economic availability.

The fact that the DNAPL has reached groundwater requires focusing efforts first to contain their advance and secondly to remove the primary and secondary sources of these compounds.

The final removal of the large volumes of waste is postponed pending the availability of suitable techniques at affordable costs. Meanwhile, the efforts are focused on the isolation of these wastes to prevent the generation of leachate that could reach ground and surface waters.

The complexity of the matrixes and the multi-component nature of the pollutants force to test previously in laboratory the different options of techniques for decontamination, bearing in mind that it is expected the necessity of using the combination of more than one treatment technique. These laboratory tests and the field trials carried out later at a pilot scale should start well before the moment at which they can be applied on a large scale. In the case of Sabiñánigo, the testing has been addressed with an advance of approximately 5 years to its application, since it is necessary to adapt the technologies and work on its R&D component. Therefore, the decontamination techniques in the aquifer began when the implementation of pump-and-treat techniques for DNAPL were forecasted for 5 years. Currently, they are about to begin the testing and research for the treatment of rocks, soils and vadose zone, foreseeing the extensive application in a period of not less than five years.

The generation of DNAPLs is associated with the storage of raw materials, mainly benzene and methanol and to two manufacturing processes of HCH or lindane: the photochlorination and the final distillation with methanol.

The photochlorination process may fail, leaving a complex mixture of organochlorine substances depending on the stage of the reaction at the time of failing. This fact leads to consider the possibility that these wastes can be generated DNAPL even before the enrichment process begins in γHCH in the 50s.

The presence of DNAPL linked to the manufacture of HCH and lindane or to the waste disposal, is scarcely detailed and gathered in literature. Bearing in mind that the manufacture of these products was largely developed in the EU before the 90s, and that both the legislation and the environmental awareness of society were not of major concern, it is likely that the presence of DNAPL in the EU and other countries is much more widespread than currently known.

This situation makes advisable that, in those areas where technical HCH or lindane has been produced, the presence of these compounds should be studied, either in the industrial premises or in areas where residues have been removed. In this sense, any action preventing the arrival of DNAPL, HCH residues or obsolete pesticides to groundwater would be cheaper, quicker and more efficient from an environmental point of view.

For the location of DNAPL, the first criterion to be followed should be the historical analysis of industrial activity, processes, operating procedures and waste management activities.

In the case of Sabiñánigo, its presence has been found in the alluvial aquifer of the premises of INQUINOSA, linked to the waste storage areas in the facilities itself and to the probable dumping of this waste in the storage tanks for raw materials after the end of the activity.

Once the DNAPLs has reached the aquifers, depending on the lithology crossed, its surveillance can be very difficult. In addition to the methods gathered in literature about free phases, for the location of DNAPL in the case of the landfills of Bailín and Sardas, it has been helpful to perform extractions with methanol (MERCK) in the first centimetres in the markers of the zone of fracture, where despite the low permeability of the rock, it can be verified the presence of volatile and semi-volatile compounds, with higher concentrations at closer distances of the DNAPL focus.

In literature, it is usual to find the figure of 1% related to the effective solubility in a water sample in order to consider the presence of DNAPLs. This value may be valid for single-component pollutants or simple mixtures but it is not in the case of HCH waste. The presence of other compounds acting as co-solvents greatly increases the water solubility of solid waste reaching saturation concentrations.

One indicator that has worked well in the case of the landfill of Bailin is the comparative assessment of samples in the dissolved plume area with higher concentrations of HCH with and without ultrafiltration. Differences of up to 90% in concentration have been obtained, which is indicative of the presence of DNAPLs microdroplets.

Summarizing, it is clear that all the water masses that have been in touch with DNAPL achieve a very high levels of volatile and lighter semi-volatile compounds, what can be used as a key marker of DNAPL.

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LABORATORY EVALUATION OF MIXED SURFACTANTS SOLUTIONS TO MOBILISE HEXACHLOROCYCLOHEXANE (DNAPL) FROM SARDAS LANDFILL (ARAGÓN, SPAIN)

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Abstract

A laboratory study was conducted to evaluate the suitability of a mixed surfactant solution for removal DNAPL of hexachlorocyclohexane (HCH) and different organochlorinated compounds from a landfill site at Sardas (Aragón, Spain). The commercial surfactants (ionic and nonionic) used for making mixed surfactant solutions were Sorbitan monooleate (Span 80), Polyoxyethylene (20) sorbitan monooleate (Tween 80), Octoxinol (Triton X-100), Dioctyl sodium sulfosuccinate (Aerosol OT), Dihexyl sodium sulfosuccinate (Aerosol MA80), Envirosurf and Envirosurf CC. Based on the properties (hydrophilic/lipophilic balance and emulsifying capacity) of individual and mixed surfactants, the preferred composition for an aqueous mixed surfactant solution was Span 80 (65%) - Tween 80 (35%). The HLB (Hydrophilic-Lipophilic Balance) for HCH DNAPL was calculated and corresponds to a value of 8.0 (lipophilic compound). The emulsion stability tests have shown that mobilisation of free product through micellar solubilisation (stable emulsion) was higher with mix surfactants than with individual surfactants. In addition, we concluded that the best surfactant composition candidates to mobilise HCH DNAPL (higher emulsifying capacity and absence of free product) were Envirosurf CC, Aerosol OT (25%) - Triton X-100 (75%); Span 80 (65%) - Tween 80 (35%). Bath experiments have shown that the sequence of DNAPL removal efficiency was Span 80 (65%) - Tween 80 (35%) > Envirosurf CC and Aerosol OT (25%) - Triton X-100 (75%) > water. The ability of aqueous surfactant solutions to recover DNAPL leachate entrapped in silica soil matrix was evaluated in column experiments. The column studies involved the injection of: a) 5% solution of (Span 80 (65%) – Tween 80 (35%); b) 5% solution of Aerosol OT (25%)-Triton X-100 (75%); c) clean water (Control). Treatment with Aerosol OT (25%)-Triton X-100 (75%) showed high washing efficiency (water solubilisation) after passing 5 volumes of solution though the column. On the other hand, treatment with the surfactant mixture Span 80 (65%) – Tween 80 (35%) mobilise DNAPL in a highly stable emulsion form (micellar solubilisation), although free phase removal was not as effective. Micellar solubilisation of organochlorinated DNAPL is the chosen recovery system for the test trial to be carried out at the Sardas landfill. The tests have revealed a reduction on the DNAPL removal in fine-grained soils. The potential for displacement of HCH DNAPL in natural conditions may be limited due to the presence of high content of silt and clay; therefore, this is a key factor to consider for aquifer remediation. The aim of this study is to choose the best surfactant solution and dosage (concentration and volumes) to develop a field trial test in Sardas landfill.

Key Words

Contaminated site, DNAPL, Emulsifier, Groundwater, HCH, DNAPL, Sardas Landfill, Surfactant.

Materials and methods

Sampling

Soil samples from the unsaturated zone nearby the Sardas landfill were collected including brown silt and marly clays. The two different soil types were mixed (50% each) and physical and chemical properties were determined. Samples of contaminated groundwater (borehole S-37) from the landfill and tap water were collected and chemical properties were determined. DNAPL was collected from the settling tank installed on the landfill site and analysed ate the lab in Bailin. The most common DNAPL compounds are chlorobenzene (21%), Total HCH (17,8%), hexachlorccyclohexane (7,3 %), dichlorobenzene (6,41%), pentachlorocyclohexane (5,8 %), trichlorobenzene (4,8%) and tetrachlorobenzene (3,8%) and benzene (1,2 %).

Surfactant selection

A previous bibliographic study was carried out to select suitable surfactants for DNAPL clean up among different commercial brands according to key characteristics including solubility, emulsification, critical micelle concentration (CMC) and effects on soil dispersion. The following surfactants (ionic and nonionic) were used: Polyoxyethylene (20) sorbitan monooleate (Tween 80), sorbitan monooleate (Span 80), dihexyl sulfosuccinate (Aerosol MA80), dioctyl sulfosuccinate (Aerosol OT), Triton X-100, Envirosurf and Envirosurf-CC.. Tween 80 and Aerosol MA 80 were purchased form Sigma-Aldrich; Span 80 was obtained from Fluka Analytical, Triton X-100 was obtained from Alfa Aesar GmbH and Aerosol OT from Molekula. Envirosurf and Envirosurf CC were obtained from Envirotecnics Global Servicies. All surfactants purchased were laboratory grade. All aqueous solutions were prepared with deionised and distilled water. The properties of the surfactants used are shown in the Table 1.

Glass bottles (250 ml) were prepared, adding 5 ml of DNAPL leachate, 200 ml of tap water from the site and 5,0 ml of emulsifier solution. The glass bottles were stirred at 50 r.p.m for 1 hour at room temperature. HLB was determined comparing solution stability after leaving to settle for 24 hour.

Surfactant commercial name	Abbreviation	Surfactant type	HBL	Molecular Formula
Sorbitan monooleate	Span 80	Nonionic	4,3	$C_{24}H_{44}O_6$
Polyoxyethylene (20) sorbitan monooleate	Tween 80	Nonionic	15	$C_{32}H_{60}O_{10}$
Octoxinol	Triton X-100	Nonionic	13,5	$C_{16}H_{26}O_2$
Dioctyl sodium sulfosuccinate,	Aerosol OT	Anionic		$C_{20}H_{37}NaO_7S$
Dihexyl sodium sulfosuccinate	Aerosol MA80	Anionic		$C_{16}H_{29}NaO_7S$
Ethoxylated fatty alcohol Benzenesulfonic acid	Envirosurf	Nonionic	14	-
Ethoxylated fatty alcohol Benzenesulfonic acid	Envirosurf-CC	Nonionic	9,5	-

Table 1. Properties of the test surfactants

HLB determination

To determine the HLB (Hydrophilic-Lipophilic Balance) value for the DNAPL leachate, seven emulsions tests were prepared using different proportions of Sorbitan monooleate (Span 80) and Polyoxyethylene (20) sorbitan monooleate (Tween 80) proportion as shown in Table 2.

HLB	Sorbitan monooleate (Span80)	Polioxietilen 20 sorbitan monooleate (Tween80)
4	100%	0%
6	83%	17%
8	65%	35%
10	46%	54%
12	28%	72%
14	8%	91%
15	0%	100%

Table 2. Determination of HLB requirement

Figure 1. Series of jars of nonionic surfactant blends used in the HLB determination

The glass bottles were stirred at 50 r.p.m during 1 hour at room temperature. HLB was determined by solution stability after settling for 24 hours.

Emulsion stability experiments

Emulsion stability experiments were performed in order to determine the best surfactant composition candidate to mobilize DNAPL. Glass bottles (250 ml) were prepared, adding 5 ml of DNAPL leachate, 200 ml of tap waterfrom the site and 5,0 ml of emulsifier solution (see Table 3).

Number	Surfactant 1	%	Surfactant 2	%
1	Aerosol OT	100		
2	Aerosol MA80	100		
3	Triton X-100	100		
4	Envirosurf	100		
5	Envirosurf-CC	100		
6	Aerosol OT	50	Triton X-100	50
7	Aerosol MA80	50	Triton X-100	50
8	Triton X-100	25	Span 80	75
9	Aerosol OT	75	Triton X-100	25
10	Aerosol OT	25	Triton X-100	75
11	Aerosol MA80	75	Triton X-100	25
12	Aerosol MA80	25	Triton X-100	75
13	Span 80	65	Tween 80	35

Table 3. Emulsion Stability Test

Batch experiments

Batch test were conducted using 350 ml glass bottles, where 100 g of silica sand (20-30–mesh size fraction) or soil from the site previously passed through a 2,0 mm (10-mesh) sieve was added, with 5 g of DNAPL leachate and 300 ml of surfactant solution. The glass bottles were stirred on a rotary stirrer for 3 hours at room temperature. After leaving to settle for 24 hours, the supernatant was decanted and analysed for DNAPL concentration, and then the amount of DNAPL extracted was calculated. From to the previous experimental results (HLB determination and the emulsion stability test), the following surfactant formulations were used in the batch experiments: (1): Span 80 (65%) – Tween 80 (35%); (2) Aerosol OT (25%)-Triton X-100 (75%); (3) Envirosurf CC (100%).

Column experiments

Soil column experiments were conducted to measure the capacity of 5% (w/w) mixed surfactant solutions (Span 80 (65%) – Tween 80 (35%) and Aerosol OT (25%)-Triton X-100 (75%)) to recover DNAPL leachate from calibrated sand.

The experiments were carried out in glass columns (90 mm diameter, 400 mm high, glass thickness 3,3 mm) with a filter disc (Duran- Porosity 0; 160-250 µm) at the bottom. Three soil columns (2 treatments, 1 Control) were packed with 2000 g of nonporous, 20-30–mesh size fraction silica sand acting as a solid matrix. The sand was rinsed with deionised water before use. The soil columns were saturated by adding of 1000 ml of contaminated groundwater from the Sardas landfill (borehole S-37). DNAPL leachate (100 g) was added to the columns to reach an initial concentration of 50.000 mg/kg (DNAPL/soil).

The water level in the columns was kept constant (water saturation conditions) by adding surfactant solution (Treatment 1 and 2) or clean water (Control) at a rate of 3,5 ml/min with a peristaltic pump (inlet) and pumping out the effluent at the same flow-rate (outlet). The effluent was collected and analysed by GC-MS. Soil samples were collected (three samples per column) at the end for lindane analysis. Tests were performed at room temperature (22°C).

The experimental work was conducted at the Environtecnics Laboratory (Girona, Spain) and analytical determinations were carried out at the SARGA laboratory (Bailín, Spain) using internal methods.

Results and discussion

HLB determination

Prior to surfactant tests, the HLB requirements of the HCH leachate were determined. Different HLB solutions were prepared (from 4 to 15), adding purified water, DNAPL and HLB solutions, and were shaken for 1 hour. The results after leaving to settle for 24 hours showed good emulsion stability in HLB mixtures 6, 8 and 10. HLB mixtures 7 and 9 were prepared following the same experimental procedure to select the most stable emulsion. It was found that HCH leachate (mixture of chlorobenzene, dichlorbenzene, pentachlor cyclohexene and hexachlorocyclohexane) has an HLB value of 8,0.

Figure 2. Determination of the required HLB for HCH DNAPL

Emulsion stability experiments

Emulsion stability experiments were conducted using different types of surfactant (ionic and nonionic) and surfactant mixtures with contaminated water from the site amended with DNAPL to a final concentration of 0,25%. The most stable mixture from the HLB determination (Span 80 -65%- + Tween 80 – 35%) was also tested (Table 3, number 13). The solutions were gently mixed on a shaker at 50 r.p.m for 1 hour in a temperature-controlled room maintained at 23 ± 0,1°C. The results were assessed following equilibration and settling for 24 hours.

The test resulted in the formation of a stable emulsion when nonionic surfactants were used, except for Triton X-100 which gave a brownish solution with a high HCH concentration. Additionally, the solutions were tested for the absence or presence of organochlorinated mixture as a free product (DNAPL) at the bottom of the glass flasks.

The best surfactant composition candidates to mobilize DNAPL (higher emulsifying capacity and absence of free product) were Envirosurf CC, Aerosol OT (25%) + Triton X-100 (75%); Span 80 (65%) + Tween 80 (35%).

Batch experiments

Batch experiments were conducted using the best surfactant candidates from the emulsion stability tests, modifying surfactant concentration (0%, 2,5% and 5,0%), solid matrix (natural soil and silica sand) and aqueous phase (deionised water and groundwater contaminated from S-37). The properties of surfactants used (surface tension, HLB, solubility) and environmental characteristics (soil properties, sorption of surfactants on soils, temperature and flow velocity of the surfactant solution) impacted on the effectiveness of the removal efficiency of DNAPL in soil.

Free lindane showed up in glomerular form in the silica soil matrix in control samples (without surfactant solution). In natural soil, lindane is sorbed by the silt and clay and is not visible in the soil matrix. The batch tests also revealed that higher surfactant concentrations were required when natural soil was used as compared to silica soil. We can conclude that silt and clay content in natural soil may represent a key limiting factor in the effectiveness of the lindane removal process.

During the batch testss we observed that the surfactant solutions with the highest emulsion capacity were Span 80 (65%) - Tween 80 (35%), followed by Envirosurf CC and Aerosol OT (25%) - Triton X-100 (75%). We will confirm these observations after reception and study of analytical results from the aqueous samples. Although Aerosol OT (25%) - Triton X-100 (75%) didn’t show DNAPL mobilisation through the formation of a stable emulsion, we believe this particular surfactant mixture could be highly efficient when the decontamination method of choice is dilution in the aqueous phase.

Column experiments

Columns experiments were conducted to assess the effect of adding different surfactant solutions to mobilise DNAPL in water saturated conditions. Soil columns (silica soil matrix) contaminated with DNAPL were tested using 5% (w/w) of mixed surfactant solutions (Span 80 (65%) – Tween 80 (35%) and Aerosol OT (25%)-Triton X-100 (75%) and compared to a control column (clean water). The effluent throughout testing and soil samples resulting after the tests were monitored by GC-MS in order to compare the DNAPL removal efficiency.

Treatment with an Aerosol OT (25%)-Triton X-100 (75%) surfactant mixture showed a high washing efficiency after passing 5 volumes of solution though the column, as DNAPL could not be detected visually in the soil column. Effluent samples did not show evidence of an emulsion, leading to the conclusion that lindane had been removed through solubilisation in aqueous phase. The use of Span 80 (65%) – Tween 80 (35%) solution (nonionic surfactant mixture) to remove lindane was seen to be less effective as lindane drops were detected in the soil column. However, the effluent from this column was a stable emulsion. Studies are under progress to break up the emulsion for subsequent laboratory analysis. Mobilization was shown to be an effective means of removing residual HCH from silica soil by using different surfactant mixtures. Based on the efficient recovery of HCH from the lab experiments, we considered the appropriate surfactant for the Surfactant Enhanced Aquifer Remediation (SEAR) in situ trial in the Sardas landfill, the surfactant solution Span 80 (65%) – Tween 80 (35%) at 5%. Further investigation of the de-emulsion process will be required to design properly the effective surfactant remediation strategy.

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DNAPL DETECTION, IDENTIFICATION & CHARACTERIZATION TECHNIQUES AND DISTRIBUTION IN THE SARDAS LANDFIL. SABIÑANIGO (SPAIN)

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Abstract

From the seventies to the early nineties, the Sardas landfill (Sabiñánigo, Spain) was used to dispose of municipal, construction and industrial wastes, which were deposited directly onto Eocene marls without any leachate collection system or bottom liner. The industrial wastes consisted of residues derived from the production of chlorine and lindane, including various hexachlorocyclohexane (HCH) isomers, present both in powder and free phase form as Dense Non Aqueous Phase Liquid (DNAPL). This DNAPL is currently seeping as leachate from the landfill to the surrounding area. The DNAPL on site is a mixture of multiple compounds, mainly chlorinated organic compounds, among which the following contaminants may be outlined: hexachlorocyclohexane (HCH) present as lindane (gHCH) and several isomers; lindane production byproducts such as benzene and chlorobenzenes, etc.; and degradation products of the above, such as chlorinated cyclohexenes, chlorophenols and others. DNAPL consists of poorly soluble and semi-volatile compounds (with exceptions such as benzene), highlighting the fact that it has a density of about 1.5 g / cm3. There are different techniques for the detection of free phase, ranging from visual contact on field works during drilling supervision, data collection from monitoring wells, pumping works, to geophysic techniques, those of visu field well for witnessing the perforations or through data collection or work in piezometers installed pumps, making geophysical techniques thickness measurement levels etc. The aim of this work is to present the techniques for detection, identification and characterization of DNAPL used, as well as showing the distribution of such DNAPL at the site.

Key Words

DNAPL, lindane, HCH, marls, landfill, groundwater, reservoir, Sabiñánigo, Spain.

Introduction

From the seventies to the early nineties, the Sardas landfill (Sabinanigo, Spain) was used to dispose of the municipal, construction and industrial wastes, which were deposited directly onto Eocene marls without any leachate collection system or bottom liner. The industrial wastes consist of waste derived from the production of chlorine and lindane, including various hexachlorocyclohexane (HCH) isomers, both in powder and free phase form as Dense Non Aqueous Phase Liquid (DNAPL). This DNAPL is currently seeping as leachate from the landfill to the surrounding area. Waste generated by the Inquinosa factory during its production years amounted to 6,800 t / year of solid waste (various isomers of HCH) and between 300 and 500 t / year of liquid waste, in addition to sewage sludge, spent activated carbon and minor amounts of other reagents and used containers. Much of these wastes were dumped in the Sardas landfill, located on the gullies system modeled in the Larrés marls (middle Eocene -Luteciense-) by the erosion of the tributary hydrographic network on the left bank of the Gállego River, near Sabiñánigo. When the landfill reached its maximum capacity and, once the alternative route to the N-330 road as it passes by Sabiñánigo was built, the sealing of the front of the landfill with a screen bentonite - cement anchored in the rock formation was performed. In February 2009, DNAPL was detected emerging in the plot of land at the foot of the road and next to its batter. Chemical analysis revealed the similarity with the liquid waste present in the landfill (Figure 1). Since then, characterization, monitoring and decontamination works in the Sardas have intensified, in order to prevent the advance of the DNAPL and disolved plumes towards the Sabiñanigo reservoir, which is the mosto sensitive receptor and is located barely a few meters from landfill reservoir.

Figure 1. Upwelling of DNAPL in a N-330 road batter.

Materials and methods

Extensive field and laboratory works have been performed in order to determine potential areas of DNAPL accumulation and mobilization. The most significant works are detailed below.

Trabajo de gabinete

All the available information and data regarding the site and works performed has been thoroughly reviewed. These include several geophysical studies conducted by TME (electrical tomography), previous environmental characterization works, the landfill design project, and others.

Photogrametric Restitution[8]

Photogrammetric restitution has provided information on the original topography of the site. We have identified the lowlands where the flow of DNAPL is most likely and appropriate for the location of certain boreholes.

Drilling of Boreholes

It is the main field tool for both DNAPL detection and recovery as well as to its extension and progress. A total of 76 monitoring wells have been built along several characterization surveys, by hollow-stem augering, using high density poliethylene (HDPE) pipe due to the highly corrosive fluids.

Detailed logging of boreholes

During the drilling of the boreholes, a thorough supervision has been done in order to detect any sign of DNAPL, since its detection in many cases, is limited to the appearance of a simple stain / drop along the whole borehole. Once the monitoring well is installed and developed is when the accumulation of DNAPL at its bottom occurs. This is why logging has been critical to know the exact location of free phase presence, since once the monitoring well is installed, it is no longer possible. Moreover, detailed logging avoids potential contamination of lower clean levels due to vertical migration of unidentified DNAPL.

Annular seal installation

The high density of DNAPL implies that during the drilling works, sealing of the monitoring wells has been performed using cement grout as drilling technique. This technique prevents contamination of deep clean levels while drilling. Moreover it is the only way to know environmental quality of deep levels when DNAPL if detected at higher levels.

The process involves sealing the annulus with cement down to the contaminated section before continuing the drilling. The deeper drilling is performed after drilling through the seal Once the contaminated section is passed through, cement grout is injected under pressure. After 24-48 hours the drilling is continued with a smaller diameter down to the final required depth. (Fig 2).

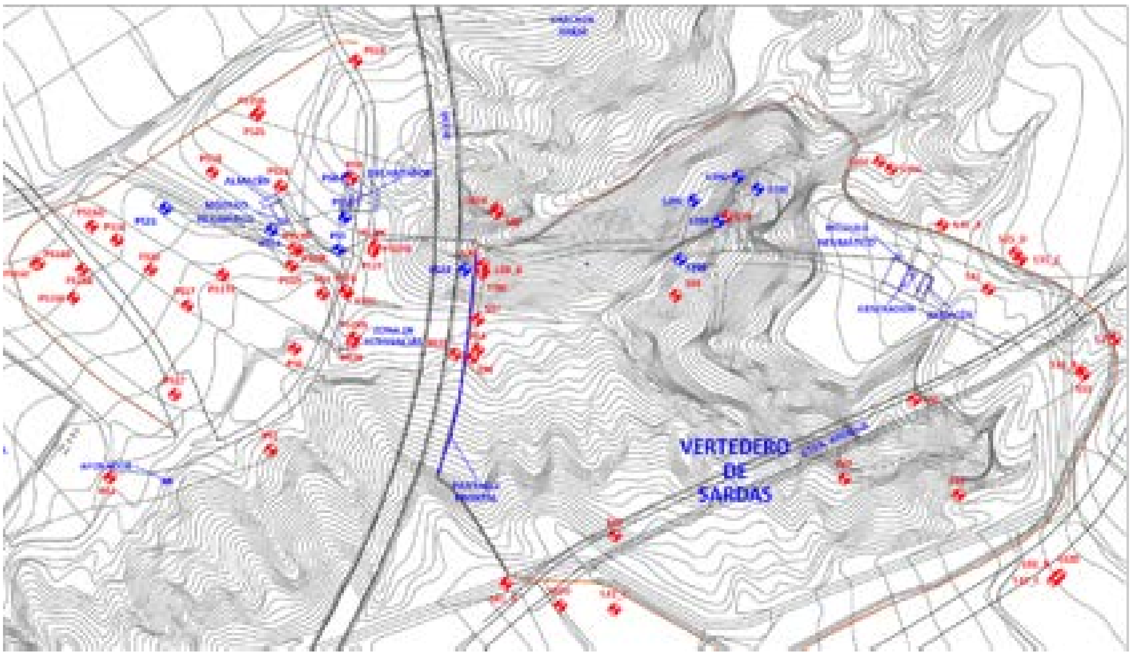

Figure 2. Drilling conducted on topographical restitution.

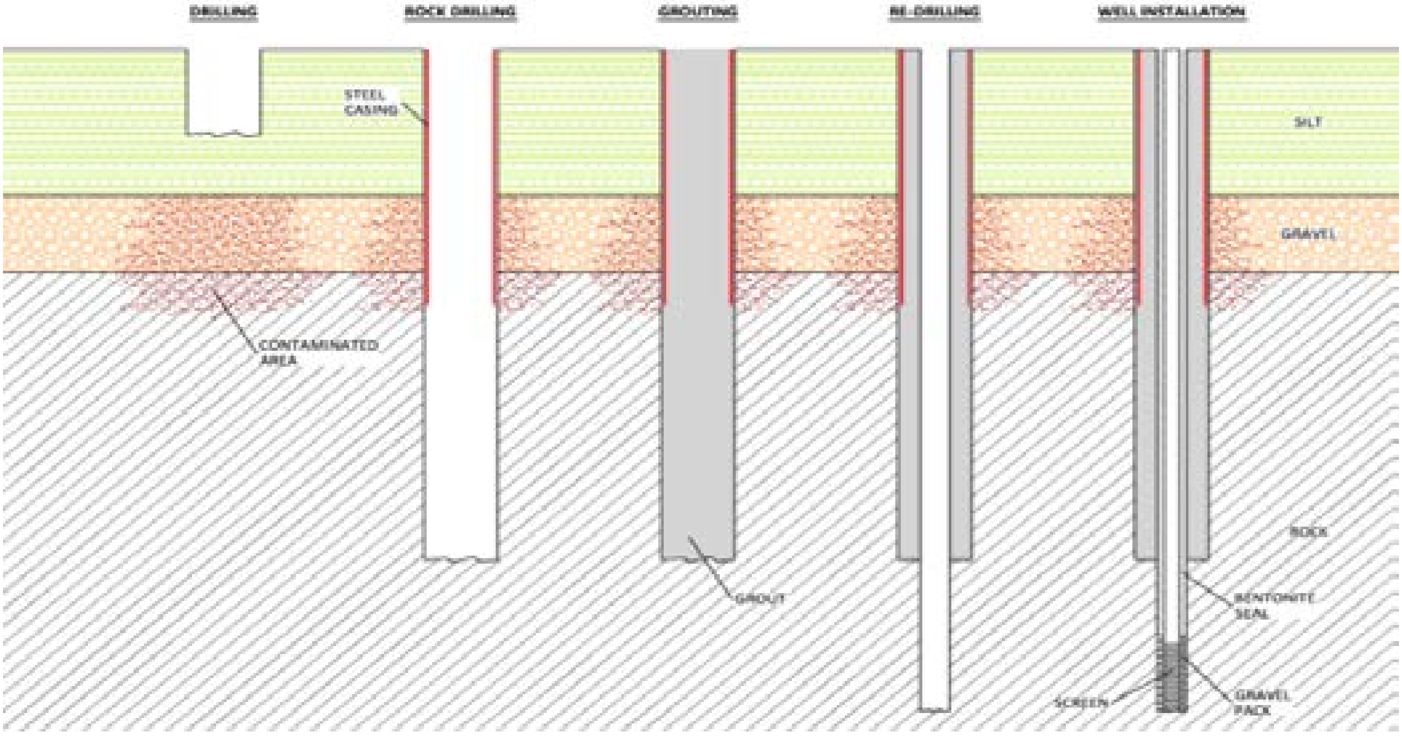

Figure 3. Drilling with cement grout sealing

Hydrogeological monitoring [4-9]

After the monitoring wells installation, a thorough hydrogeological monitoring has been conducted with many campaigns in which DNAPL presence and thickness was checked and measured. Groundwater and DNAPLS levels were measured both manually and by pressure sensors which output continuous measurements. Physicochemical parameters were also measured and soil, groundwater and DNAPL were sampled.

Figure 4. Detection of DNAPL during fieldwork.

Different field equipment have been used for data collection have been used (interface probes, multi-parameter probes etc.) For fluid sampling, pneumatic low flow samplers (bladder pumps) were used, since they allow targeting a specific sampling depth. Once the areas and sampling points with most free phase were defined, we proceeded to the installation of different pumping systems in order to pump the most of it out until stronger measures are undertaken. During pumping, detailed logging of free phase levels in the monitoring well before and after the pumping; DNAPL removed and any data which may help to detect any trend in DNAPL behavior is registered.

DNAPL chemical aggressiveness test[8]

There have been several studies aimed at understanding the behavior of the free residue in contact with the crossed materials and its ability to penetrate fractures. To this effect, among others, MERC type tests, “Methanol Extraction Core Rock”, have been performed to semi-quantitatively determine the processes of diffusion into the rock from the contact area with the organochloride free phase (DNAPL), simulating the processes that could take place in the fractures of the rock mass in which free phase is present and its possible penetration into the rock (diffusion). The test has consisted in sinking rock test pieces in DNAPL during a certain period of time taking samples of fractured zones to detect whether cracks have advanced or are wider.

Results and discussion

With the drilling of boreholes the distribution of the different subsoil material can be described as follows [4-9]:

- At the head of the gully and marl lays a formation of glacis with a variable thickness between 3 and 7 m and with poor hydraulic properties.
- Filling materials in the landfill are heterogeneous with a thickness of 30-35 m directly deposited on the marl formation.
- The subsoil of the plots of land at the foot of the landfill consists of:
    - fillers composed of heterogeneous waste dump up to 3 m thick.
    - compact sandy silt and fairly homogeneous up to 12 m thick
    - alluvial gravels and sands with a maximum thickness of 4 m
    - gray marls with fracturing and/or alteration following the original gully drain line.

Both during the drilling works and the subsequent data collection, waste recovery campaigns, etc., at some point the presence of DNAPL has been detected at 26 on site monitoring wells.

The presence of free phase has been detected in the contact of the fills with the altered marl along an east-west line from the northern area of landfill bottom reaching the historical area of DNAPL upwelling.

Free phase has been detected in the alluvial gravels or the silts in contact with altered layer in up to 4 points located in the central area of the plot of land located at the foot of the landfill.

The presence of DNAPL in the altered rock layer was detected mainly in an east-west axis, reaching the monitoring wells close to the original gully drain in the lowest area of the site.

Finally, DNAPL has been detected outside the landfill at the northern area of the above east-west axis, associated to rock fracture zones at a maximum depth of 38 m.

From the pumping works performed and the DNAPL recovery rates, we can infer that most of the DNAPL seems to be still in the vessel itself, mainly in the north by the adjacent gully. Once the DNAPL has advanced through the screen within 20 meters west, the plume decreases as it moves away from the landfill.

The analyses carried out for DNAPL characterization reveal a percentage of around 15-25% water, 15-25% of the various isomers of HCH, 30-45% of chlorobenzenes and 5-40% of other compounds.

DETERMINACIONES	**UNIDADES**	PS15	PS23	S39B	S39F
Volatile organic compounds (VOC)					
Benceno	% w/w	0.84	1.4	1.3	1
Clorobenceno	% w/w	21.64	21.61	19.14	21.5
1.3-Dichlorobenzene	% w/w	4.19	0.51	0.41	0.2
1.2- Dichlorobenzene	% w/w	4.44	2.86	2.47	1.8
1.4- Dichlorobenzene	% w/w	0.61	3.47	2.79	1.9
Semivolatileorganic compounds (SVOC)					
1.2.3 Trichlorobenzene	% w/w	0.32	0.16	<0.1	0.8
1.2.4 Trichlorobenzene	% w/w	5.21	3.94	2.28	2
1.3.5 Trichlorobenzene	% w/w	2.41	1.36	0.61	0.15
1.2.3.5 Tetrachlorobenzene	% w/w	2.14	1.4	0.4	0.9
1.2.4.5 Tetrachlorobenzene	% w/w	4.73	3.2	1.18	1.17
Pentachlorophenol	% w/w	<0.1	<0.1	<0.1	<0.1
Phenol	% w/w	<0.1	<0.1	<0.1	<0.1
Chlorophenol	% w/w	<0.1	<0.1	<0.1	<0.1
2.4 Dichlorophenol	% w/w	<0.1	<0.1	<0.1	<0.1
2.6 Dichlorophenol	% w/w	<0.1	<0.1	<0.1	<0.1
Trichlorophenols (Sum.)	% w/w	<0.1	0.14	0.25	1.15
Tetrachlorophenols	% w/w	<0.1	<0.1	<0.1	<0.1
Pentachlorobenzene	% w/w	0.77	0.37	0.15	0.17
Tetrachlorohexenes	% w/w	<0.1	<0.1	<0.1	<0.1
Pentachlorhexenes (1)	% w/w	3.53	6.07	5.39	8.22
Hexachlorociclohexene	% w/w	4.85	5.86	8.35	10.15
a-HCH	% w/w	3.15	2.8	2.87	3.32
b-HCH	% w/w	0.23	0.26	0.17	0.19
g-HCH	% w/w	7.28	6.95	6.71	7.86
d-HCH	% w/w	3.35	5.4	6.36	7.46
e-HCH	% w/w	1.41	1.6	1.83	2.05
Rest of isomers and metabolites	% w/w	2.61	3.42	4.2	6.15
Heptachlorocicloheptane	% w/w	0.28	0.38	0.75	0.98
H_2O	% w/w	18.2	25.9	27.3	1.5

Table 1. Composition of DNAPL (%)

The results of the tests performed to assess the aggressiveness of the free phase towards the marls have been inconclusive. The “poor quality” of the tested rocks did not allow performing numerous tests because rocks disintegrated when in contact with the DNAPL.

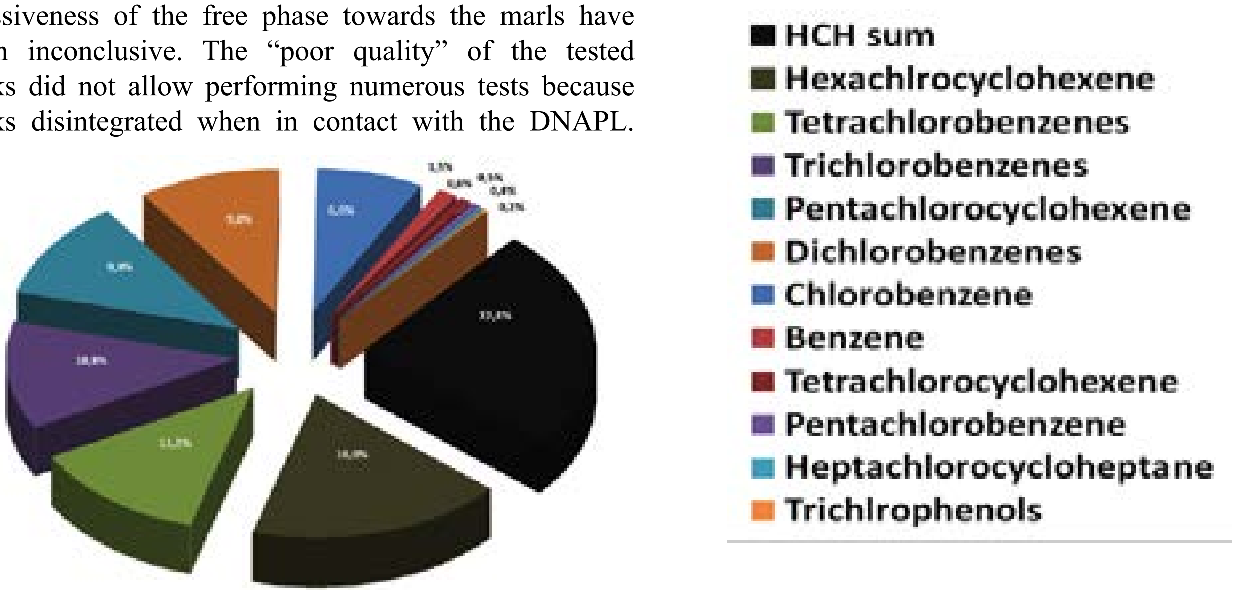

Figure 5. DNAPL Composition

The percentages of each of the compounds present in the detected DNAPLs reveal an amount close to 50% of chlorobenzenes and 20% HCH isomers.

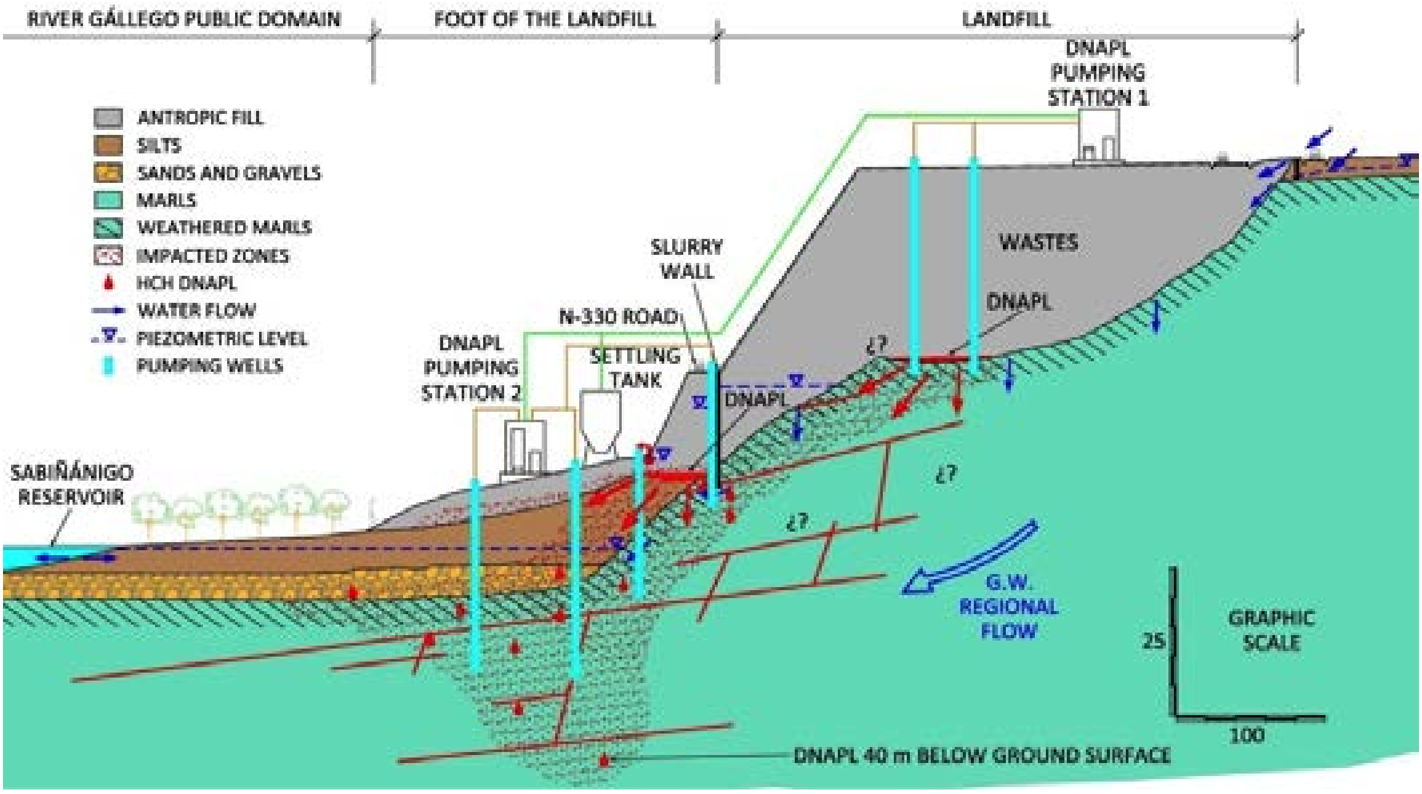

Figure 5. DNAPL distribution cross-section

Conclusions

The main sources of DNAPLs at the site are located both inside the landfill body, and outside. These sources are associated with anthropogenic fillings in contact with the layer of altered rock and enable free phase accumulations conditioned by the low permeability of the marl. These accumulations probably existed before sealing the landfill and are currently being pumped. On the other hand, there has been a migration of the free phase to deeper levels through the fractured rock (and through the bedding planes) following typical mobilization patterns of this type of free phase.

Current efforts are addressed to improve DNAPL pumping rates with the construction of new wells and the use of techniques such as SEAR (Surfactan Enhanced Aquifer Remediation)

Acknowledgements

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ISCO LABORATORY TESTS FOR THE REMEDIATION OF A COMPLEX MIXTURE OF POPs IN THE UNCONTROLLED LINDANE LANDFILL OF BAILÍN (HUESCA, SPAIN)

SUBMITTED PAPER

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Abstract

This paper describes part of the treatment laboratory program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located over a complex fractured geological media where lindane and other Persistent Organic Pollutants (POP) were dumped. These compounds have formed a multi-component Dense Non Aqueous Phase Liquid (DNAPL) which has spread in response to the geological layers and the fracture network.

The complete rehabilitation of the site comprises the dismantling of the landfill and the subsequent implementation of subsoil remediation technologies. Within this context, In-Situ Chemical Oxidation (ISCO or chemox) was identified as a potentially applicable technology for the treatment of plume areas (dissolved phase contamination).
This paper presents the methodology and results of the chemical oxidation treatability tests performed for the treatment of the Contaminants Of Concern (COC) by activated persulfate (Klozur®), using bedrock and groundwater samples from the site.

The ChemOx testing program comprised two different phases:

- A first phase consisting of a treatability test based on alkaline activated persulfate (ISCO 1), planned to assess the feasibility of the test as well as estimating the dosing requirements.

  A high organic load was detected in the site's groundwater in addition to the organochlorinated compounds: elevated concentrations of oxygenates (mainly methanol), named to the purpose of this paper as "matrix" compounds were identified (some 6,000 mg/l). The oxidant demand exerted by these matrix compounds, different to the target COC´s, led to an underestimation of persulfate dosing in the first steps of the test.

- A second test (ISCO 2), which studied three different activation methods (thermal, Fe-EDTA and alkaline activation) and the development of treatability tests considering decreasing concentrations of the optimum dose of persulfate (OPT, ¾ OPT, ½ OPT and ¼ OPT) with both alkaline and thermal (40ºC) activation. The optimal dose was established as 155 g/L in a small excess of the theoretical stoichiometric oxidant demand considering both COCs and matrix compounds. This treatability test results confirm the effectiveness of chemical oxidation by alkaline activated persulfate for the elimination of POPs and other target contaminants detected at the Bailín site.

Keywords

Lindane, HCH, POPs, persulfate, thermal, alkaline, activation, PEN.

Introduction and objectives

This paper describes the chemical oxidation treatment laboratory program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain).The site is a former unlined landfill located in the Bailín creek, over a complex fractured geological media. At this location the former company Inquinosa dumped, between 1984 and 1992, lindane (γ-HexaChloro-cycloHexane - γHCH) and other POPs (Persistent Organic Pollutants), namely: (i) non-commercial HCH isomers; (ii) chlorobenzenes and chlorophenols; (iii) benzene and; (iv) other organics from the lindane production process.
These compounds have formed a multi-component DNAPL (Dense Non Aqueous Phase Liquid) which has spread in response to the geological layers and the fracture network. Since 2004, interim remedial measures consisting of "pump and treat" techniques in the surroundings of the landfill have extracted more than 20 tn of DNAPL and have treated thousands of cubic meters of dissolved phase contamination.

The complete rehabilitation of the site comprises the dismantling of the landfill and removal of the wastes to a new location, which has been already performed and constitutes the major contaminant mass reduction measure.

Parameter	Unit	Value / Concentration	% w/w
Density	g/cm^3	1,3662	-
Water (Karl Fischer)	g/kg	2,2	0,2%
COC (GC/MS, FID, TIC)			
Benzene	g/kg	9,4	0,9%
Monochlorobenzene	**g/kg**	**140,0**	**14,0%**
1-chloro-2-Etilbenzene	g/kg	3,6	0,4%
1,2-Dichlorobenzene	g/kg	15,7	1,6%
1,3-Dichlorobenzene	g/kg	2,2	0,2%
1,4-Dichlorobenzene	g/kg	20,5	2,1%
1,2,3-Trichlorobenzene	g/kg	6,1	0,6%
1,2,4-Trichlorobenzene	**g/kg**	**41,0**	**4,1%**
1,2,3,5-Tetrachlorobenzene	g/kg	5,1	0,5%
1,2,4,5-Tetrachlorobenzene	g/kg	5,3	0,5%
1,2,3,4-Tetrachlorobenzene	g/kg	11,1	1,1%
Pentachlorobenzene	g/kg	1,7	0,2%
alpha HCH	**g/kg**	**59,4**	**5,9%**
delta HCH	**g/kg**	**102,2**	**10,2%**
gamma HCH	**g/kg**	**136,7**	**13,7%**
Pentachlorociclohexenes	**g/kg**	**74,3**	**7,4%**
Tetrachloropyridines	g/kg	32,0	3,2%
1,1,2,4,5-Hexachloro-1,5-hexadiene	**g/kg**	**65,1**	**6,5%**
Other organochlorinated compounds non resolvable by chromatography*)*	g/kg	136,1	13,6 %
Total	**g/kg**	**869,8**	**87,0%**

Table 1 Chemical characterization of the Bailin's DNAPL.

As expected, such a challenging site as Bailín, involving organochlorinated DNAPL and extensive dissolved phase contamination in a fractured environment, requires the subsequent implementation of remediation techniques for the treatment of residual subsoil impact.

Within this context, during the past years a remedial option appraisal has been performed for the fractured bedrock in order to address the most suitable remediation technique. The evaluation of different remedial options started with an in-depth bibliographical review of the "state of the art" regarding remediation of POPs in fractured bedrock. This research confirmed lack of available experiences worldwide, with just a few examples of comparable sites reported.

During the assessment, a limited number of remedial techniques were identified to be potentially capable of successfully treating the complete spectrum of contaminants at the fractured bedrock, driven in part by the complex nature of the mixture: (i) volatile and non-volatile compounds; (ii) differential biodegradation pathways of the COC's - reductive and oxidative -; (iii) high contrasts in the physical properties of the constituents (i.e solubility, adsorption potential, Henry's constant); etc.
The identified technologies to be potentially applied, by themselves or forming part of a treatment train at the Bailin site were: (i) thermal treatment; (ii) surfactant flushing; for the treatment of source areas (presence of DNAPL at bedrock fractures) and (iii) ISCR - *In Situ Chemical Reduction* – and; (iv) ISCO - *In Situ Chemical Oxidation*, for plume areas (high dissolved concentrations in groundwater).

Whilst some of these approaches proved to be effective for partial and/or complete removal of the COC's, chemical oxidation appeared to be the most balanced approach regarding efficiency and potential costs involved. This paper presents the development and results of the chemical oxidation treatability tests performed for the treatment of the Contaminants Of Concern (COC) by activated persulfate (Klozur®), as one of the best technologies to achieve project objectives.

The selection of activated persulfate was driven, among others, by the following factors:

1. Sufficient oxidation potential for destruction of the complete range of contaminants.

2. Durability of the reagent vs. other strong oxidants such as Fenton or ozone. Furthermore, these alternatives would present additional constraints such as pressure build-up in the fractures, which would limit the distribution and effective contact of the oxidant with the COC's.

3. Other pros would include: (i) high aqueous solubility of persulfate; (ii) concentrated solutions are denser than water and density driven migration of the oxidant

could be expected at some degree, matching that of the DNAPL and; (iii) better diffusion to the rock matrix vs. other oxidants.

The main objectives of the ChemOx treatability tests developed were the following:

- Evaluation of the effectiveness of chemical treatment with activated persulfate in the reduction of VOC and SVOC constituents of DNAPL.
- Activation methods performance assessment.
- Study of persulfate dosing effect in the reduction of contaminants of concern.

The laboratory tests comprised two different phases:

- A first phase (ISCO 1) consisting of a preliminary test of the chemical oxidation using activated persulfate oxidation. This test was performed using alkaline activation in order to assess the feasibility of the technology and identifying potential constraints. The following steps were included in the study:
    a. Establishment of activating requirements.
    b. Determination of the Soil Oxidant Demand (SOD) exerted by the rock.
    c. Estimation of dosing requirements associated to the dissolved phase contamination
    d. Final development of the treatability test by alkaline activation

A high organic load was detected in groundwater, mainly exerted by matrix compounds different to the target COC, These matrix compounds were not initially considered for the dosing estimation which led to an underestimation of the oxidant demand.

- A second phase meant to test re-evaluated dosing of persulfate (ISCO 2). A study of different activation methods was also performed as a first step of this second phase test. The development of this second phase considered the following steps:
    a. Re-assessment of dosing requirements associated to the dissolved phase contamination and the matrix compounds.
    b. Study of different activation methods.
    c. Final development of the treatability test by thermal and alkaline activation as a result of the outcome of previous testing steps.

The current paper summarizes the experimental procedure implemented during the bench scale tests performed in the framework of the Bailin's project, as well as the obtained results.

Materials and methods

The materials used for the test included site's soil and groundwater, sodium persulfate, sodium hydroxide and deionised water. Site's soil and groundwater was collected at the site by URS. Sodium persulfate was supplied by FMC and contained ≥ 98% $Na_2S_2O_8$. Sodium hydroxide of 10 M strength was supplied by Fisher. Deionised water was purified using D700 and C750 cartridges supplied by Purite Limited.

Phase 1 – ISCO 1

Alkaline activation requirements

Alkaline activation requires pH in the range of 10.5 and 12. The demand of sodium hydroxide for the sustainment of such pH conditions throughout the reaction period was empirically determined for both fine and coarse site's material by the means of continuous pH monitoring.
Additionally, every mole of persulfate added requires 2 moles of NaOH to neutralize the persulfate-generated acid (HSO_4^-).

Soil Oxidant Demand (SOD)

Soil oxidant demand was tested for both coarse and fine material in microcosmos containing site's soil treated with 15g persulfate per kg of soil. Sodium hydroxide was added for activation purposes. Total testing period was 7 days and persulfate was determined by colorimetric method at specified times (0, 2, 4 and 7 days - all determinations in duplicate). No significant change was registered in persulfate concentration. Thus, the SOD was proven to be negligible.
The colorimetric determination method was validated by further testing over easily oxidized material, namely glucose and granular soil from the site, as well as over site´s rock samples. Both glucose and the granular soil exerted an important persulfate demand resulting in persulfate concentration reduction, while persulfate concentrations during the testing period hardly varied when rock samples were studied.

ISCO 1 Treatability test development

ISCO 1 was performed in microcosmos containing site's soil and groundwater. Tested concentrations of sodium persulfate included increased concentrations of the stoichiometric demand determined for the oxidation of COC's (0,5g/l).
The treatability test included the establishment of 36 microcosms divided into two groups of treatment microcosms – high dose and low dose- and one group of control microcosms (all in duplicate).
The low dose and the high dose were each established as 1,2 and 2,2 g/L, in a small excess of the 2x & 4x theoretical stoichiometric quantity (which yielded 1 and 2 g/L). The only activation method tested was alkaline activation.
Microcosms were established in baked glass bottles. For each microcosm, the required amount of soil was weighed into the bottle (Table 2). Subsequently, the specified amount of groundwater was measured and approximately half of the volume was transferred to the bottle. The test-

ed dose of sodium persulfate was then added (excluding control microcosms) and the bottle closed and shaken for a few seconds to dissolve the sodium persulfate. The prescribed amount of sodium hydroxide was added to both treatment and control bottles and the bottles closed and shaken for a few seconds to mix the contents. Then, the remaining amount of the measured groundwater was added, the bottle closed and shaken again for 15 minutes to equilibrate. The bottles were sealed with an air tight lid. The prepared microcosms were then stored until sacrificed at the pre-established reaction times in order to analytically determine the progress of the oxidation processes.

	EXPERIMENTAL SET-UP					MONITORING PROGRAM	
Test / Type	**Soil (g)**	**Groundwater (ml)**	**Sodium Persulfate Dose (g/L)**	**Activation Method**	**Addition of NaOH 20% (mL)**	**Monitoring periods (d)**	**Analytical program**
CONTROL	80	400	0	-	-	Baseline t = 0, 7, 14, 28, 71, 170	Persulfate COV + SCOV + TIC VFA + Formaldehyde
LOW DOSE	80	400	1,2	Alkaline	1,5		
HIGH DOSE	80	400	2,2	Alkaline	2,0		

Table 2: Treatment and control microcosms – ISCO 1.

Phase 2 – ISCO 2

Reassessment of dosing requirements associated to the dissolved phase contamination and matrix compounds.

The stoichiometric demand determined for the oxidation of all COC's and matrix compounds (named as Optimum dose - OPT -) yielded 130 g/L and that estimated from the COD analysis yielded 145 g/L.

Almost 99% of this oxidant demand is associated to the matrix compounds present in groundwater rather than to the COC's.

Study of activation methods

A screening study of applicable activation methods different to alkaline activation was developed prior to the ISCO 2 treatability test. The activation methods under consideration were thermal activation and Fe-quelate activation, namely:

- Thermal activation at 40ºC

Fe-EDTA activation with a persulfate to Fe ratio of 4:1 and a Fe to EDTA ratio of 5:1.

The test outcome discarded the use of Fe-EDTA due to its low performance for site specific COC's.

ISCO 2 Treatability test development

ISCO 2 test considered the establishment of different microcosms with site's groundwater only, as previous SOD results showed to be negligible vs. the demand exerted by the dissolved phase contamination.

The test included the establishment of 42 microcosms divided into eight groups of treatment microcosms and three groups of control microcosms (all in duplicate). Each treatment microcosm group included jars containing one of the four tested doses of sodium persulfate combined with one of the tested activation methods.

The tested sodium persulfate activation methods were heat treatment at 40 ˚C and alkaline conditions in the pH range 10.5 – 12. Previous testing discarded the use of FeEDTA due to its low performance for site specific COC's.

Tested concentrations of sodium persulfate included the stoichiometric demand determined for the oxidation of all COC's and matrix compounds (named as Optimum dose - OPT -), and decreasing concentrations of ¾, ½ and ¼ of this, due to the high oxidant demand exerted by site's groundwater. The optimum dose was established as 155 g/L, in a small excess of the theoretical stoichiometric quantity and that estimated from the COD analysis.

The addition of sodium hydroxide to alkaline activation treatment jars resulted in a varying degree of contamination dilution that was homogenized by the addition of compensatory volumes of deionized water to ensure comparable COC's and the matrix compounds concentrations in all tested microcosms.

A summary of the treatments and controls tested and details of the composition of the microcosms for each of the groups are described in Table 3.

Microcosms were established in baked glass bottles with a total volume of 540 mL when filled to the rim. For each microcosm, the required amount of groundwater was measured and approximately half of the volume was transferred to the bottle. The specified amount of sodium persulfate was added (excluding control microcosms) and the bottle closed and shaken for a few seconds to dissolve the sodium persulfate.

For the treatment microcosms with alkaline activation and for the alkaline control, the prescribed amount of sodium hydroxide (Table 3) was added to the bottle and the bottle closed and shaken for a few seconds to mix the contents. Then, the remaining amount of the measured groundwater was added, the bottle closed and shaken for a few seconds to mix the contents. Subsequently, the prescribed amount

Test / Type	Sodium Persulfate Dose (g/L)	Activation Method	Addition of 10 M NaOH (mL)	Addition of Deionised Water (mL)
CONTROL	0	-	0	32.8
CONTROL @40°C	0	Thermal	0	32.8
ALK CONTROL	0	Alkaline	2.6	30.2
OPT @40°C	155	Thermal	0	32.8
¾OPT @40°C	116	Thermal	0	32.8
½OPT @40°C	78	Thermal	0	32.8
¼OPT @40°C	39	Thermal	0	32.8
OPT ALK	155	Alkaline	32.8	0.0
¾OPT ALK	116	Alkaline	24.6	8.2
½OPT ALK	78	Alkaline	16.4	16.4
¼OPT ALK	39	Alkaline	8.2	24.8

Table 3: Treatment and control microcosms – ISCO 2.
Thermal = microcosms placed into temperature conditions of 40°C. *Alkaline = pH in microcosms maintained within range of 10.5 – 12.0.*

of deionised water (Table 3) was added to the bottle and the bottle was closed and shaken again for 15 minutes to equilibrate. The bottles were sealed with an air tight lid. The prepared microcosm was then placed into the prescribed temperature conditions.

Microcosms with thermal activation of sodium persulfate and related control microcosms were placed into an incubator, set to maintain a temperature of 40 ˚C. Microcosms with alkaline activation and the related control microcosms were placed on a bench in a room at a temperature of 20 ˚C.

During the period of the test, the pH of the microcosms with alkaline activation was checked daily and the pH was maintained within the desired range of 10.5 - 12.0 by the drop wise addition of 10M NaOH.

Due to the addition of sodium hydroxide to microcosms with alkaline activation and the resulting dilution of the added groundwater, a calculated amount of deionized water was added to the microcosms. This means that due to the varying degree of dilution of the groundwater resulting from the addition of differing amounts of NaOH, it was necessary to add a compensatory volume of deionized water (Table 3) to ensure that the -concentration of the COC's and the matrix compounds was comparable in all tested microcosms.

A number of jars from each set of microcosms were sacrificed and submitted for analysis at the specified time points after the start of the test (0, 7, 21 and 42 days). The analytical program is summarized in Table 4.

Analysis	Time Point of Analysis			
	Baseline (Day 0)	Day 7	Day 21	Day 42
Sodium persulfate		✓	✓	✓
Sulfate	✓	✓	✓	✓
Total Organic Carbon (TOC)	✓	✓	✓	✓
Chemical Oxygen Demand (COD)	✓	✓	✓	✓
Volatile compounds (SW 846 8260B)	✓		✓	✓
Semivolatile compounds (SW 846 8270C) including HCH isomers	✓	✓	✓	✓
Alcohols	✓		✓	✓
Volatile Fatty Acids	✓		✓	✓
Formaldehyde	✓	✓	✓	✓
Chloride	✓	✓	✓	✓

Table 4. Analytical program of the ISCO test.

Results and discussion

ISCO 1 Treatability test development

The tested doses accomplished the depletion of HCH isomers within the first 7 days of treatment. Such a reduction is believed to be consequence of both the oxidation with persulfate and the hydrolysis of HCH to Trichlorobenzene under alkaline conditions. High and low treatments yield removal efficiencies for the remaining SCOVs around 90% and in the range of 90 to 95% for both total SCOVs and HCH.

However, the registered removal rates for COVs were slower and only a 45% of COVs removal was accomplished even when the testing period was extended from 14 to 170 days.

A high organic load was detected in the site's groundwater related to the presence of elevated concentrations of oxygenates (mainly methanol). Persulfate tested doses considered only the expected oxidant demand exerted by the organochlorines (up to 65 mg/l), and not that exerted by these "matrix" compounds (some 6,000 mg/l). Thus, persulfate was strongly under-dosed (two orders of magnitude) and its effect in COC's removal and persulfate consumption rates led to inconclusive results.

Alcohols may be frequently present in Lindane impacted sites since γ-HCH is separated from other isomers by an extraction with alcohols as part of the production process. This test outcome has proven the consideration of the oxidant demand exerted by the total organic load to be essential in oxidant dosing estimations.

ISCO 2 Treatability test development

General observations during operation of the systems

pH of the control microcosms was found to be stable and within the below described range during the period of the test:

Treatment	Average min pH	Average max pH	10 M NaOH added (mL)
OPT ALK	10.6	11.3	10.6
¾OPT ALK	10.6	11.4	9.1
½OPT ALK	10.8	11.5	6.3
¼OPT ALK	11.0	11.7	3.2

Table 5. pH values and NaOH added to maintain pH within the prescribed range for alkaline activation treatments.

pH of control microcosms without addition of sodium hydroxide was determined to be within range of 6.8 – 7.0; pH of control microcosms with added sodium hydroxide was determined to be within range of 11.2 – 11.5.

In addition, treatment microcosms under thermal activation showed a decrease of pH from initial value of 6.8 to less than 2 within 48 hours of the start of the activation and remained below this level.

Finally, treatment microcosms with alkaline activation showed a tendency for the pH to drop below the prescribed range. The pH of these microcosms was close to 12 at the establishment and it reached a value of 10.5 at 5 days from the start of the test. Since this time pH was maintained within the prescribed range by drop wise addition of 10 M NaOH. Average minimum pH values of microcosms with alkaline activation before correction of pH and average pH values immediately after the correction are listed in Table 5. The pH had dropped to below the prescribed value of 10.5 for a total period of 48 hours during the duration of the test. The amount of sodium hydroxide added to maintain pH within the prescribed range during the test is showed in Table 5. Microcosms under thermal activation of the sodium persulfate showed the formation of bubbles resulting in a build-up of pressure in the bottles. White needle-shaped crystal-like structures were formed on the bottom of the bottles of these microcosms with similar amount deposited for each dose of sodium persulfate tested (visually evaluated). A strong chlorinated odour was noticed when the microcosms were opened. These observations were not observed neither in the control microcosms related to this activation method nor for the other treatment microcosms using alkaline activation and their relevant control microcosms.

Analytical results

This section presents the results and performance of the oxidation processes on the main COC's and matrix compounds for both activation methods. To facilitate the interpretation and assessment the data has been grouped as follows:

a) Sodium Persulfate concentrations

b) Pesticides (HCH) and SVOC's

c) VOC's

d) Methanol

e) Persulfate Efficiency Number - PEN -

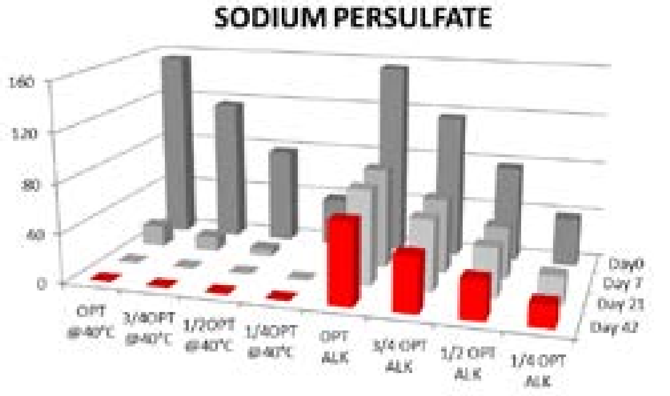
All reported results have considered microcosms preparation and operation steps and are dilution corrected.

a) <u>Sodium Persulfate</u>

Persulfate monitoring results throughout the test are shown both in Table 6 and Graph 1.

Sodium Persulfate (g/L)	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Baseline (t=0 d)	155	116	78	39	155	116	78	39
t = 7 days	17	12	5.6	--	81	60.5	41.8	--
t = 21 days	0.13	<D.L	<D.L	<D.L	77	58	40	23
t = 42 days	0.03	0.04	0.1	0.02	66	45	31	18
Consumption (%)	**100%**	**100%**	**99.9%**	**99.9%**	**58%**	**62%**	**59%**	**53%**

Table 6: Persulfate concentrations results of the treatability test (g/l)



Graph 1: Persulfate concentrations (g/l)

b) <u>Pesticides (HCH) and SVOC's</u>

Table 7 and Graph 2 depict the results of the sum of **HCH isomers** (α, β, γ, and δ) concentrations.

All treatments achieve good performance for HCH isomers, with reductions close to 100 %. Contaminant removal is more gradual in the thermal activation treatments, requiring 21 days for the more concentrated treatments (OPT and ¾ OPT) and 42 days for the lower concentrations (½ OPT and ¼ OPT). On the contrary, for the alkaline activation treatments kinetics are much faster, with complete removal within the first seven days in all treatments independently of the oxidant concentration. This suggests that not the oxidation but other process could be the predominant elimination mechanism (i.e hydrolysis of HCH in alkaline conditions).

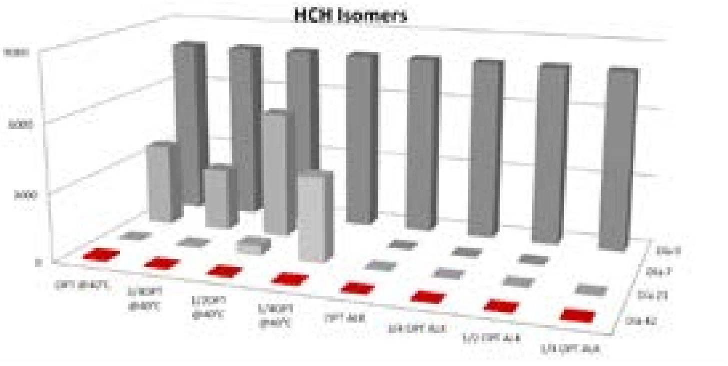
Total HCH (µg/L)	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Baseline (t=0 d)	7,890	7,890	7,890	7,890	7,890	7,890	7,890	7,890
t = 7 days	3,621	2,765	5,575	-	<D.L	<D.L	12.5	-
t = 21 days	9	60.5	433	3,740	2	7.5	13.5	24
t = 42 days	110	36	43	55	4	8	15	36
Reduction (%)	**98.6%**	**99.5%**	**99.5%**	**99.3%**	**99.9%**	**99.9%**	**99.8%**	**99.5%**

As can be observed, the pattern of persulfate consumption differs depending on the type of activation method. Persulfate consumption in thermal activation treatments is more than 90% within the first 7 days of testing, and after 21 days persulfate is at trace level or < D.L; whereas the alkaline activation treatments display a more progressive consumption rate, with approximately 40-50% of the initial dose remaining after 42 days of treatment.

The described behaviour implies that, for the thermal activation method, occurrence of contaminant oxidation is not expected after the first three weeks of treatment, since the oxidant is no longer available.

Persulfate decomposition rate increases with temperature and, as a result, a higher presence of available persulfate radicals is expected in initial treatment stages. Nevertheless, the fast depletion of the oxidant and the boosting effect of temperature and acidic conditions (which promote the occurrence of competitive radical - radical reactions and inhibit contaminant - radical reactions) could influence the oxidation rates of the COC's in thermal activation treatments.

***Table 7**: Total HCH concentration results throughout the treatability test (µg/l)*



Graph 2: Total HCH isomers concentrations (µg/l)

This aspect was confirmed by the results obtained from the controls and in side experiments performed with standards prepared at the laboratory with HCH isomers and deionised water (Table 8).

	t = 0 days	t = 42 days			t = 0 days	t = 5 days
Total HCH (µg/L)	**Baseline**	**Control @20°C**	**Control @40°C**	**ALK Control**	**HCH Standard**	**HCH Standard**
α-HCH	590	570	520	<D.L	-	-
β-HCH	1,200	1,700	1,500	35	460	<D.L
γ-HCH	1,100	660	700	17	170	<D.L
δ-HCH	5,000	5,600	3,800	<D.L	1,100	<D.L
1,2,4 Trichlorobenzene (1,2,4 TriCB)	<D.L	<D.L	160	3,100	<D.L	2,100

Table 8: Total HCH concentration results in the ISCO test (µg/l)

The control treatments at the end of the test present clear differing behaviors. Controls with no pH modification (@20 ºC and @40 ºC) do not undergo significant variations of HCH concentrations nor 1,2,4 TriCB generation throughout the test, whereas in the alkaline control (ALK) HCH isomers practically disappeared and 1,2,4 TriCB concentrations increased importantly. This phenomenon is also observed in the standards prepared at the laboratory in which, after 5 days, all HCH has converted in 1,2,4 TriCB. These results confirm the instability of HCH isomers in basic conditions, where alkaline hydrolysis (dehydrochlorination and aromatization reactions of the HCH ring to yield 1,2,4 TriCB) is the predominant elimination mechanism.

As such, alkaline activation of persulfate presents synergetic effects for the elimination of HCH (oxidation and alkaline hydrolysis), not observed in thermal activation treatments.

With regards to other **SVOC´s Phenols and Chlorophenols** also achieved important reductions throughout the test (Table 9 & Graph 3).

These results show removal of these compounds within the first seven days of treatment, regardless the persulfate dose and type of activation applied. Only residual concentrations are detected in thermal activation treatments, greater at low concentrations of persulfate. The presence of electron donating groups (-OH) in the aromatic ring explains the fast removal of these compounds, as it increases the reaction rates due to the electrophilic character of the persulfate radical.

c) <u>VOC’s</u>

The results corresponding to the main volatile organic compounds are displayed separately depending on whether they are contaminants originally present in the baseline groundwater and/or partial oxidation intermediates.

Table 10 and Graphs 4 and 5 show the concentration results of **Benzene and Chlorobenzene**, most representative VOC’s originally present in groundwater.

Phenols & chlorophenols(µg/L)	**OPT @40°C**	**¾ OPT @40°C**	**½ OPT @40°C**	**¼ OPT @40°C**	**OPT ALK**	**¾ OPT ALK**	**½ OPT ALK**	**¼ OPT ALK**
Baseline (t=0 d)	7,335	7,335	7,335	7,335	7,335	7,335	7,335	7,335
t = 7 days	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L
t = 21 days	<D.L	<D.L	87,5	<D.L	<D.L	<D.L	<D.L	<D.L
t = 42 days	<D.L	57	155	238	<D.L	<D.L	<D.L	<D.L
Reduction (%)	**100%**	**99.2%**	**97.9%**	**96.7%**	**100%**	**100%**	**100%**	**100%**

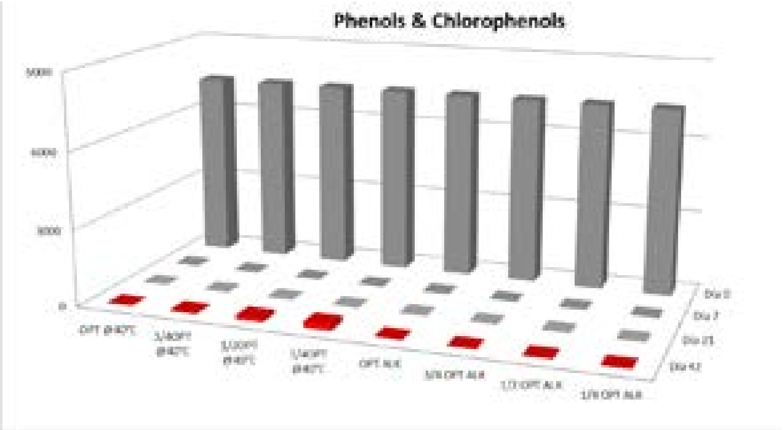
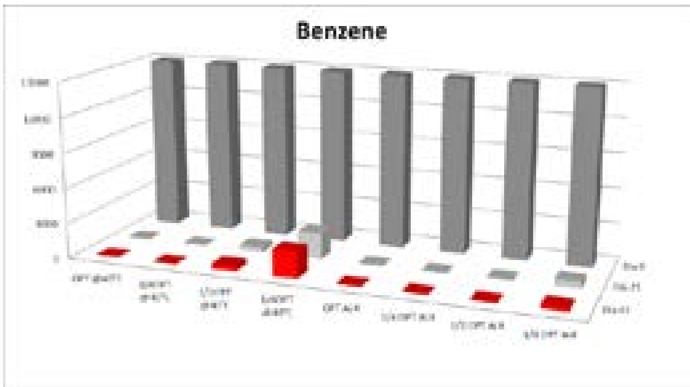


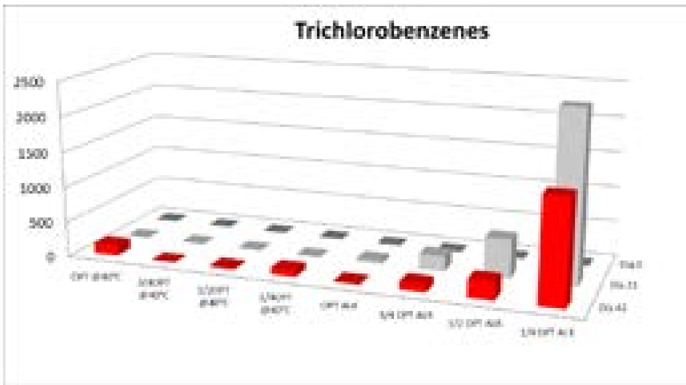
Table 9: Phenols and chlorophenol concentrations throughout the test (µg/l)
Graph 3: Total phenols and chlorophenols concentrations (µg/l)

Compound	Sampling	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Benzene	Baseline (t=0 d)	15,500	15,500	15,500	15,500	15,500	15,500	15,500	15,500
	t = 21 days	<D.L	<D.L	435	2,200	5	25.5	82.5	570
	t = 42 days	<D.L	<D.L	450	2,300	<D.L	<D.L	28	330
	Reduction (%)	**100%**	**100%**	**97.1%**	**85.2%**	**100%**	**100%**	**99.8%**	**97.9%**
Chlorobenzene	Baseline (t=0 d)	25,000	25,000	25,000	25,000	25,000	25,000	25,000	25,000
	t = 21 days	<D.L	<D.L	200	1,800	10.5	26.5	130	1,300
	t = 42 days	<D.L	<D.L	190	1,700	<D.L	5	23	720
	Reduction (%)	**100%**	**100%**	**99.2%**	**93.2%**	**100%**	**99.9%**	**99.9%**	**97%**

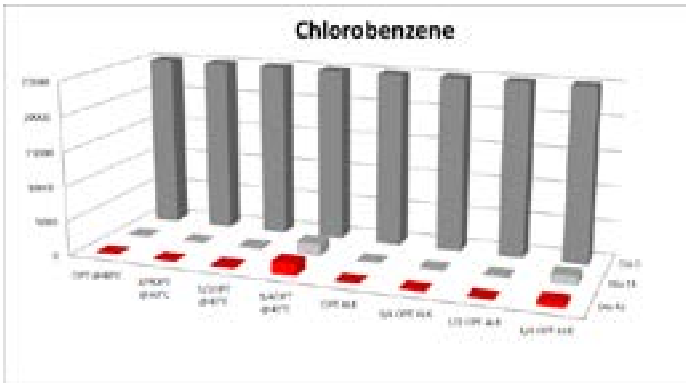
Table 10: Benzene and Chlorobenzene concentrations throughout the test (µg/l)



Graph 4: Benzene concentrations (µg /l)



Graph 6: Trichlorobenzene concentrations (µg/l)



Graph 5: Chlorobenzene concentrations (µg /l)

These compounds present a similar behaviour throughout the test. Removal rates of nearly a 100% were obtained with both types of activation at high persulfate doses (OPT and ¾ OPT). Lower doses present slower oxidation kinetics, resulting this in lower elimination yields.

On the other hand, **Trichlorobenzene**, as a partial oxidation intermediate, behaves differently depending on the type of activation, as shown in Table 11 and Graph 6.

Thermal activation microcosms show a small generation of TriCB as a reaction intermediate (low concentrations), probably related the oxidation sequence of other precursors. However, generation of trichlorobenzene in alkaline activation treatments (1,2,4 TriCB) is more important and confirms the alkaline hydrolysis of the HCH isomers. Accumulation of TriCB is greater at low persulfate doses (½ and ¼ OPT ALK), where the oxidant is the limiting reagent taking into account the organic load present in groundwater and is reduced as persulfate concentrations approach the optimum dose (¾ and OPT ALK), where the available oxidant oxidizes the generated TriCB, preventing its accumulation.

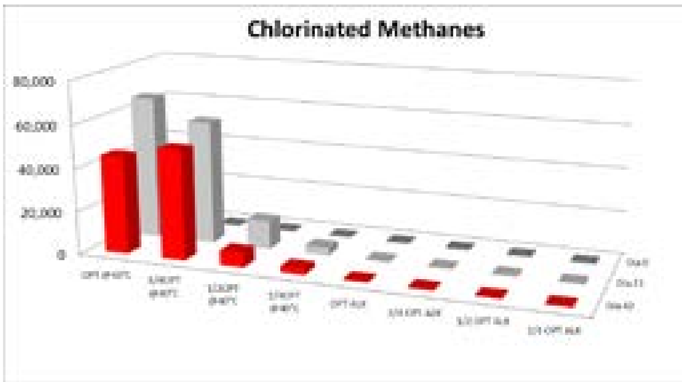
Other relevant oxidation intermediates are short chain chlorinated aliphatics, coming from the oxidation sequence of higher molecular weight precursors, such as HCH and chlorinated aromatics. Table 12 and Graph 7 depict the concentration trends of chlorinated methanes during the test, which are mainly related to chloroform and dichloromethane.

Trichlorobenzenes (µg/L)	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Baseline (t=0 d)	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L
t = 21 days	<D.L	<D.L	<D.L	<D.L	46.5	213	546	2,390
t = 42 days	150	<D.L	24	94	18	113	259	1,460
Reduction (%)	-	-	-	-	-	-	-	-

Table 11: Trichlorobenzene concentrations throughout the test (µg/l)

Chlorinated Methanes (µg/L)	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Baseline (t=0 d)	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L	<D.L
t = 21 days	66,500	57,200	13,075	3,520	255	165	105	62
t = 42 days	45,400	50,800	6,740	2,700	227	147	120	120
Increase (order of magnitude)	**5**	**5**	**3 - 4**	**3**	**2**	**2**	**2**	**2**

Table 12: Chlorinated methanes concentrations throughout the test (µg/l)



Graph 7: Chlorinated methanes (µg/l)

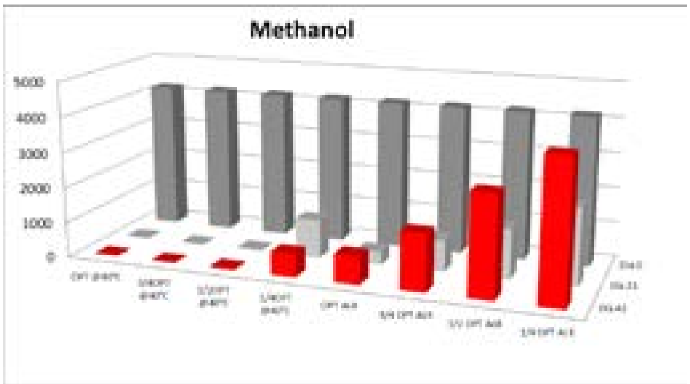
These specific intermediates present a clear differing pattern between both treatments (thermal and alkaline activation methods). Chlorinated methanes are mostly generated in thermal treatments at high persulfate concentrations (OPT and ¾ OPT) and exhibit a maximum at 21 days of treatment, with a slight decreasing trend from then till the end of the test. This behavior is coherent with the observed rapid depletion of persulfate (see Graph 1). Absence of available persulfate allows anticipating lack of oxidation processes of these and/or any other compound thereafter, in thermal activation treatments.

Rapid dissociation of the oxidant and abundance of persulfate radicals produced in early stages of the treatment result in intense oxidation processes of parent compounds which, in turn, produce an increase in the generated oxidation intermediates. The concentrations of these chlorinated methanes are sustained in time as no persulfate is available for complete oxidation of these intermediates to CO2 during the final stages of the treatment.

This important accumulation of chlorinated methanes is not observed in the alkaline activation treatments, suggesting that these intermediates are subsequently oxidized, yielding better elimination rates and superior performance of alkaline activation with respect to mineralization of short chain chlorinated aliphatics.

d) Methanol

The results of methanol concentrations, as principal matrix compound present in groundwater, are depicted in Table 13 and Graph 8.



Graph 8: Methanol concentrations (mg/l)

Significant variations of the elimination rates are observed depending on the activation method and the dose of persulfate applied. In both treatments the reaction rates increase with increasing persulfate dose. Thermal activated treatments present significantly higher performance, whereas kinetics of the alkaline activation treatment is much slower. Given the fact that the alkaline activation treatments still present significant concentrations of available persulfate (approx. 50 % of initial concentrations) it is foreseen that achievement of complete mineralization of methanol in high dose treatments (OPT and ¾ OPT) is just a matter of time.

e) PEN

The Persulfate Efficiency Number (PEN) is an indicator of the overall efficiency of the oxidation process and it is estimated as the ratio between the amount of contaminant degraded and amount of persulfate used.

Compound	Sampling	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
Methanol	Baseline (t=0 d)	4,197	4,197	4,197	4,197	4,197	4,197	4,197	4,197
	t = 21 days	10.6	6.1	42.1	1,091	372	891	1,392	2,164
	t = 42 days	9	10	35	658	793	1,602	2,842	3,958
	Reduction (%)	**99.8%**	**99.8%**	**99.2%**	**84%**	**81%**	**62%**	**32%**	**6%**

Table 13: Methanol concentrations throughout the test (mg/l)

$$\text{PEN} = \frac{\%\,\text{Contaminant Degraded}}{\%\,\text{Persulfate Used}}$$

A PEN ≥ 1 indicates that the persulfate is dosed properly and the contaminants are being destroyed at a sufficient rate. A PEN in great excess of 1 may indicate an over-dosing of the persulfate, and a PEN less than 1 indicates an under-dosing of the persulfate and/or the occurrence of unproductive reactions different to those leading to the target contaminant removal. The PEN allows to evaluate the efficacy of the oxidation process independently of the time of testing.

For the testing program and due to the complexity of the contamination present at the site, two different PEN's have been estimated, one including the entire organic load (organochlorines and matrix compounds) and a second one with the initial COC's only (POP's and other VOC/SVOC's).

Treatment	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
% Contaminant degraded	97.2%	87.3%	72.4%	63.9%	72.2%	54.6%	28.4%	3.6%
% Persulfate used	99.9%	99.9%	99.9%	99.9%	57.6%	61.4%	59.7%	53.5%
Total PEN	0.97	0.87	0.72	0.64	1.25	0.89	0.48	0.07

Table 14: PEN values - contaminants of concern (COC´s) and matrix compounds

As expected, treatments with higher persulfate dose (OPT ALK and OPT @40ºC) present the higher PEN's. The results above suggest better elimination rates of the alkaline activation (1.25) versus the thermal activation (0.97). This may be due to the performance of a greater number of unproductive reactions as a result of faster activation and dissociation of the persulfate in thermal treatments. Scavenging reactions with chloride ions are foreseen to be one of the main competitive, given the fact that a high baseline concentration of chloride was detected (1.6 g/L) and due to the boosting effect of temperature, which can increase competitive scavenging reactions of persulfate radicals with chloride and promote the following sequence of reactions:

$$\begin{aligned}
&SO_4^{\cdot\,-} + Cl^- \text{ --> } SO_4^{2-} + Cl^{\cdot}\\
&Cl^{\cdot} + Cl^- \text{ --> } SO_4^{2-} + Cl_2^{\cdot -}\\
&Cl_2^{\cdot -} + Cl_2^{\cdot -} \text{ --> } 2Cl^- + Cl_2\,(\text{gas})
\end{aligned}$$

Chlorine gas generation would explain the formation of bubbles and the strong chlorinated odour noticed when thermal activation treatments were opened for analyses, which was not observed in the alkaline activation treatments.

For a closer look at the efficacy of the activation methods in the oxidation of the POPs and VOC/SVOC's, the PEN values were estimated for these COC's, excluding the matrix compounds.

Treatment	OPT @40°C	¾ OPT @40°C	½ OPT @40°C	¼ OPT @40°C	OPT ALK	¾ OPT ALK	½ OPT ALK	¼ OPT ALK
% Contaminant degraded	21%	2%	78%	69%	95%	97%	97%	93%
% Persulfate used	99.9%	99.9%	99.9%	99.9%	57.6%	61.4%	59.7%	53.5%
Total PEN	0.21	0.02	0.78	0.69	1.66	1.58	1.63	1.74

Table 15: PEN values - contaminants of concern (COC's)

Based on the estimated PENs the effectiveness of the alkaline activation treatment is much greater for all doses tested. The high PEN values estimated for the alkaline activation treatments at low persulfate doses (½ and ¼ OPT ALK) suggest that the efficacy of the treatment on the initial target is not directly related to the oxidant concentration. This aspect can be of interest for up scaling of the technology, as doses significantly lower than the theoretical stoichiometric demand would still achieve important reductions on POPs and VOC/SVOC concentrations.

On the contrary, the efficiency of thermal activation treatments regarding the priority contaminants can be considered very low. Especially at high doses of persulfate, where the oxidation processes appear to be focused on the matrix compounds (methanol) and where the occurrence of competitive unproductive reactions significantly reduces the elimination rates of the organochlorines.

Conclusions

Chemical oxidation treatability tests have been performed to investigate the effect of activated persulfate in the treatment of a complex mixture of contaminants from the Bailin's lindane landfill. As part of the testing program, several activation methods and persulfate doses have been studied. The main findings gathered as a result of the chemox program outcome are the following:

- At this site, methanol and other matrix compounds exert most (99 %) of the high oxidant demand required for the complete oxidation of the organic load, while only 1 % of the demand is associated to the COC's (organochlorines).
- Alkaline activation has been considered more suitable for a potential field application for the following reasons:
    - Higher POP's (HCH) and SVOC degradation rates have been obtained as a result of the synergistic effect of the oxidation and the alkaline hydrolysis on the elimination of HCH.
    - No significant accumulation of

intermediates has been observed as opposed to thermal activation (short chain chlorinated aliphatics). Therefore VOC oxidation rates are greater.

- Much greater PEN values for the main target contaminants (POPs and other VOC/SVOC organochlorines) and equivalent performance for the complete range of constituents when compared with thermal activation (especially at high doses). Some factors leading to this best performance of alkaline activation are:
    1) More progressive dissociation of the persulfate in alkaline activation appears to minimise unproductive side reactions (scavenging).
    2) Oxidative processes in alkaline activation treatments focus on the target contaminants whereas in the thermal activation appear to be focused on matrix compounds.
    3) The fast depletion of available persulfate observed in the thermal activation method.
- Longer lifespan which would allow a better radius of influence and effective contact of the oxidant with the contaminants.
- Easier and cheaper field implementation of the alkaline activation method for up scaling of the technology at the site.

- Treatability test results confirm the effectiveness of chemical oxidation by alkaline activated persulfate for the elimination of POPs and other target contaminants detected at the Bailín site. Nevertheless, the potential elevated oxidant demand if chemical oxidation is targeted for treating the complete groundwater organic load may increase the implementation and reagents costs significantly.
- Further field testing and adjustment of operational requirements is needed prior to implementation of the technology at the site, including the careful definition of the ultimate goal to be achieved by the chemical oxidation treatment.

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ISCR LABORATORY TESTS FOR THE REMEDIATION OF THE ORGANIC CONTAMINANTS ASSOCIATED WITH THE UNCONTROLLED LINDANE LANDFILL IN BAILÍN (HUESCA, SPAIN)

SUBMITTED PAPER

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Abstract

Bailín's lindane landfill in Huesca (Spain) is a former unlined landfill located over a complex fractured geological media where lindane and other Persistent Organic Pollutants (POP) were dumped. These compounds have formed a multi-component Dense Non Aqueous Phase Liquid (DNAPL) which has spread in response to the geological layers and the fracture network.

The complete rehabilitation of the site comprises the dismantling of the landfill and the subsequent implementation of subsoil remediation technologies. Within this context, In-Situ Chemical Reduction (ISCR) was identified as a potentially applicable technology for the treatment of plume areas (dissolved phase contamination). Reductive dechlorination is one of the primary attenuation mechanisms by which chlorinated hydrocarbon groundwater plumes can be stabilized and/or remediated.

The chemical reduction experimental setting considered the study for three dosing scenarios –control (no-dose), low dose and high dose - of both the chemical reduction and reductive dechlorination aimed by EHC® micro-particles of Zero Valent Iron (mZVI) treatment alone, and the complete process of COC's mineralization aimed by the subsequent treatment EHC-O® Oxygen Slow Release Compound (OSRC). Tested concentrations of mZVI were 0,25% for the low dose and 0,5% for the high dose, whereas those of OSCR were 1,5% for the low dose and 2,5% for the high dose, all doses referred to the mass of soil considered.

The concentration reduction as a result of adsorption over crushed bedrock has proven to be significant for all Contaminants of Concern (COC´s), particularly Hexachlorociclohexane (HCH) isomers. However, adsorption on bedrock is enhanced by the crushing of samples and is, therefore, thought to occur in a lesser extent in the fractured media bedrock of Bailín.

The mZVI treatment accomplished increasing reductive conditions (negative ORP values) throughout the test. The combination of adsorption of contaminants on the crushed rock and the degradation process yield HCH removal rates ranging from 64 to 93% for the low dose and 81-97% for the high dose. The estimated HCH mass removal rate by degradation with the low dose treatment was 71% and 85%. No effective degradation of SCOVs is registered in the tested EHC-EHC-O treatments due to the unsuccessful achievement of oxidant conditions by EHC-O reagent.

Keywords: Lindane, HCH, POPs, in-situ, thermal, desorption, ISCR.

Introduction and objectives

This paper describes the chemical reduction treatment program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located in the Bailín creek, over a complex fractured geological media. At this location the former company *Inquinosa* dumped, between 1984 and 1992, lindane (γ-HexaChlorocycloHexane - γHCH) and other POPs (Persistent Organic Pollutants), namely: (i) non-commercial HCH isomers; (ii) chlorobenzenes and chlorophenols; (iii) benzene and; (iv) other organics from the lindane production process.These compounds have formed a multi-component DNAPL (see This paper describes the chemical reduction treatment program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located in the Bailín creek, over a complex fractured geological media. At this location the former company Inquinosa dumped, between 1984 and 1992, lindane (g-HexaChlorocycloHexane - gHCH) and other POPs (Persistent Organic Pollutants), namely: (i) non-commercial HCH isomers; (ii) chlorobenzenes and chlorophenols; (iii) benzene and; (iv) other organics from the lindane production process.These compounds have formed a multi-component DNAPL (see Table 1) which has spread in response to the geological layers and the fracture network.Table 1) which has spread in response to the geological layers and the fracture network.

Parameter	Unit	Value / Concentration	% w/w
Density	g/cm^3	1,3662	-
Water (Karl Fischer)	g/kg	2,2	0,2%
COC (GC/MS, FID, TIC)			
Benzene	g/kg	9,4	0,9%
Monochlorobenzene	**g/kg**	**140,0**	**14,0%**
1-chloro-2-Etilbenzene	g/kg	3,6	0,4%
1,2-Dichlorobenzene	g/kg	15,7	1,6%
1,3-Dichlorobenzene	g/kg	2,2	0,2%
1,4-Dichlorobenzene	g/kg	20,5	2,1%
1,2,3-Trichlorobenzene	g/kg	6,1	0,6%
1,2,4-Trichlorobenzene	**g/kg**	**41,0**	**4,1%**
1,2,3,5-Tetrachlorobenzene	g/kg	5,1	0,5%
1,2,4,5-Tetrachlorobenzene	g/kg	5,3	0,5%
1,2,3,4-Tetrachlorobenzene	g/kg	11,1	1,1%
Pentachlorobenzene	g/kg	1,7	0,2%
alpha HCH	**g/kg**	**59,4**	**5,9%**
delta HCH	**g/kg**	**102,2**	**10,2%**
gamma HCH	**g/kg**	**136,7**	**13,7%**
Pentachlorociclohexenes	**g/kg**	**74,3**	**7,4%**
Tetrachloropyridines	g/kg	32,0	3,2%
1,1,2,4,5-Hexachloro-1,5-hexadiene	**g/kg**	**65,1**	**6,5%**
Other organochlorinated compounds non resolvable by chromatography*)*	g/kg	136,1	13,6 %
Total	**g/kg**	**869,8**	**87,0%**

Table 1: Chemical characterization of the Bailin’s DNAPL.

Since 2004, interim remedial measures consisting of “pump and treat” techniques in the surroundings of the landfill have extracted more than 20 tn of DNAPL and have treated thousands of cubic meters of dissolved phase contamination.

The complete rehabilitation of the site comprises the dismantling of the landfill and removal of the wastes to a new location, which has been already performed and constitutes the major contaminant mass reduction measure.

As expected, such a challenging site as Bailín, involving organochlorinated DNAPL and extensive dissolved phase contamination in a fractured environment, requires the implementation of remediation techniques for the treatment of residual subsoil impact. Within this context, during the past years a remedial option appraisal has been performed for the fractured bedrock in order to address the most suitable remediation techniques.

The remedial option appraisal started with an in-depth bibliographical review of the “state of the art” regarding remediation of POPs in fractured bedrock. This research confirmed lack of available experiences worldwide, with just a few examples of comparable sites reported.

During the assessment, a limited number of remedial techniques were identified to be potentially capable of successfully treating the complete spectrum of contaminants at the fractured bedrock, driven in part by the complex nature of the mixture: (i) volatile and non-volatile compounds; (ii) differential biodegradation pathways of the COC’s - reductive and oxidative -; (iii) high contrasts in the physical properties of the constituents (i.e solubility, adsorption potential, Henry’s constant); etc.

The identified technologies to be potentially applied, by themselves or forming part of a treatment train at the Bailin site were: (i) thermal treatment; (ii) surfactant flushing; for the treatment of source areas (presence of DNAPL at bedrock fractures) and (iii) ISCR - *In Situ Chemical Reduction* – and; (iv) ISCO - *In Situ Chemical Oxidation,* for plume areas (high dissolved concentrations in groundwater).

Subsequently, a comprehensive program of treatability tests was implemented at laboratory scale. The focus of this program was to evaluate the performance of each technology to address most of the contaminants within the mixture.

Reductive dechlorination is one of the primary attenuation mechanisms by which chlorinated hydrocarbon groundwater plumes can be stabilized and/or remediated. This naturally occurring biological/abiotic reaction takes place when a chlorine atom is replaced by a hydrogen atom (electron donor) in a chlorinated hydrocarbon molecule (electron acceptor).

Chemical formulations containing microparticles of Zero Valent Iron and organic substrates (EHC® commercialized Adventus Americas) are commonly used with the purpose of promoting an on-going reductive dechlorination of chlorines by two synergic and complementary pathways:

direct chemical reduction (short-term effect) and anaerobic biodegradation (long-term effect). The addition of organic substrates to the surface enhances anaerobic bioremediation by changing naturally aerobic or mildly anoxic aquifer zones to anaerobic and microbiologically diverse reactive zones.

Chemical reduction and reductive dechlorination of HCH occurs under anaerobic conditions and results in the generation of certain reaction, such as cyclohexenes, chlorobenzenes, chlorophenols and benzene. Biodegradation of such compounds preferably happens under aerobic conditions. Therefore, the removal of contamination concerning HCH isomers ISCR requires a treatment sequence consisting of an anaerobic reaction zone (partial or complete dechlorination and aromatization of HCH isomers) followed by an aerobic reaction zone, so as to achieve the complete mineralization of the reduction intermediates. These aerobic processes were enhanced by adding oxygen slow released compounds (EHC-O® commercialized Adventus Americas).

In order to evaluate the effectiveness of ISCR treatment in addressing Bailin's impact, a specific treatability test was implemented with the following objectives:

- Assessment of the effectiveness in the reduction of HCH isomers, Volatile Organic Compounds (VOC) and Semi-Volatile Organic Compounds (SVOC) constituents of DNAPL, of a treatment sequence consisting of chemical reduction/anaerobic bioremediation followed by an aerobic reaction stage.
- Verification of whether these two different reaction zones can be efficiently accomplished to achieve the complete mineralization of COC´s
- Evaluation of the two tested remediation substrates requirements (EHC and EHC-O).
- The bench treatability test included different phases of testing, namely:

a. Bedrock and groundwater samples collection,

b. Preparation and conditioning of field samples,

c. Determination of the baseline conditions,

d. Development of the chemical treatment.

The current paper summarizes the experimental procedure implemented during the bench scale test performed in the framework of the Bailin's project, as well as the obtained results.

Experimental setting

The experimental setting used intended to reproduce Bailín's subsoil occurring bio-chemical processes in the case of the tested treatments were applied on field. For this purpose, a dynamic column system was designed in order to simulate the different elements taking part in the subsoil treatment process (Figure 1.- General experimental settingFigure 1).

A peristaltic pump was used to feed site's groundwater from a Tedlar® bag to the base of the first treatment column. This column was prepared with crushed rock collected from the site mixed with mZVI reagent (EHC®) and reproduced the anaerobic reaction zone meant to accomplish the degradation of HCH, trichlorophenols and polychlorobenzenes. These targeted compounds have higher oxidation numbers and are, therefore, more likely to experience chemical or biological reduction.

The two attenuation jars downstream to the mZVI column, containing only crushed rock collected from the site, were prepared with the aim of simulating the attenuation zone downgradient to the injection. Throughout this attenuation zone, the reductive conditions conferred to groundwater as a result of the mZVI treatment should be attenuated before arriving to the aerobic reaction zone.

The second treatment column was prepared with a mixture of an oxygen slow release compound (EHC-O®) and crushed rock collected from the site. This column reproduced the aerobic reaction zone established as a result of the oxygen release to the aquifer. The targeted compounds are the biodegradation intermediates generated in the anaerobic reaction zone and other already present compounds, such as benzene and chlorobenzenes, whose biodegradation require aerobic conditions. Prior to the effluent accumulation jar, two additional attenuation jars were set so that

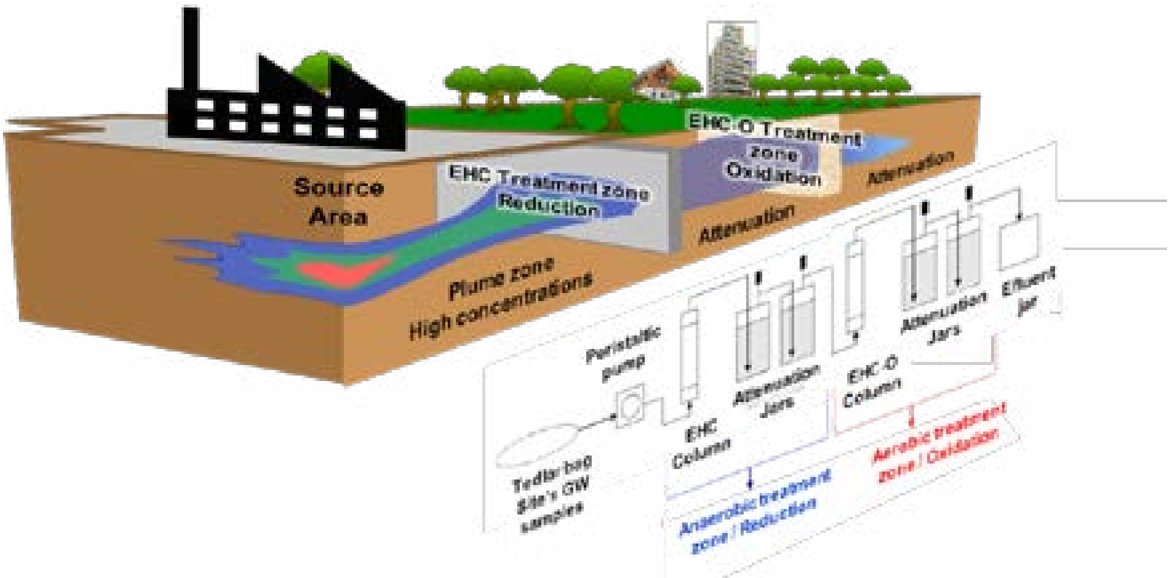


Figure 1.- General experimental setting

the effluent collected reproduced groundwater conditions downgradient to the treatment area, after oxygen depletion.

The final development of the experimental setting considered the study for three dosing scenarios –control (no-dose), low dose and high dose - of both chemical reduction and reductive dechlorination aimed by mZVI treatment (treatment line 1), and the complete process of COC's mineralization aimed by the combined and sequential treatment of mZVI and oxygen slow release compound (treatment line 2). This experimental scope required the establishment of two experimental lines per dosing scenario tested (Figure 2). Tested concentrations of EHC were 0,25% for the low dose and 0,5% for the high dose, whereas those of EHC-O were 1,5% for the low dose and 2,5% for the high dose, all doses referred to the mass of soil considered.

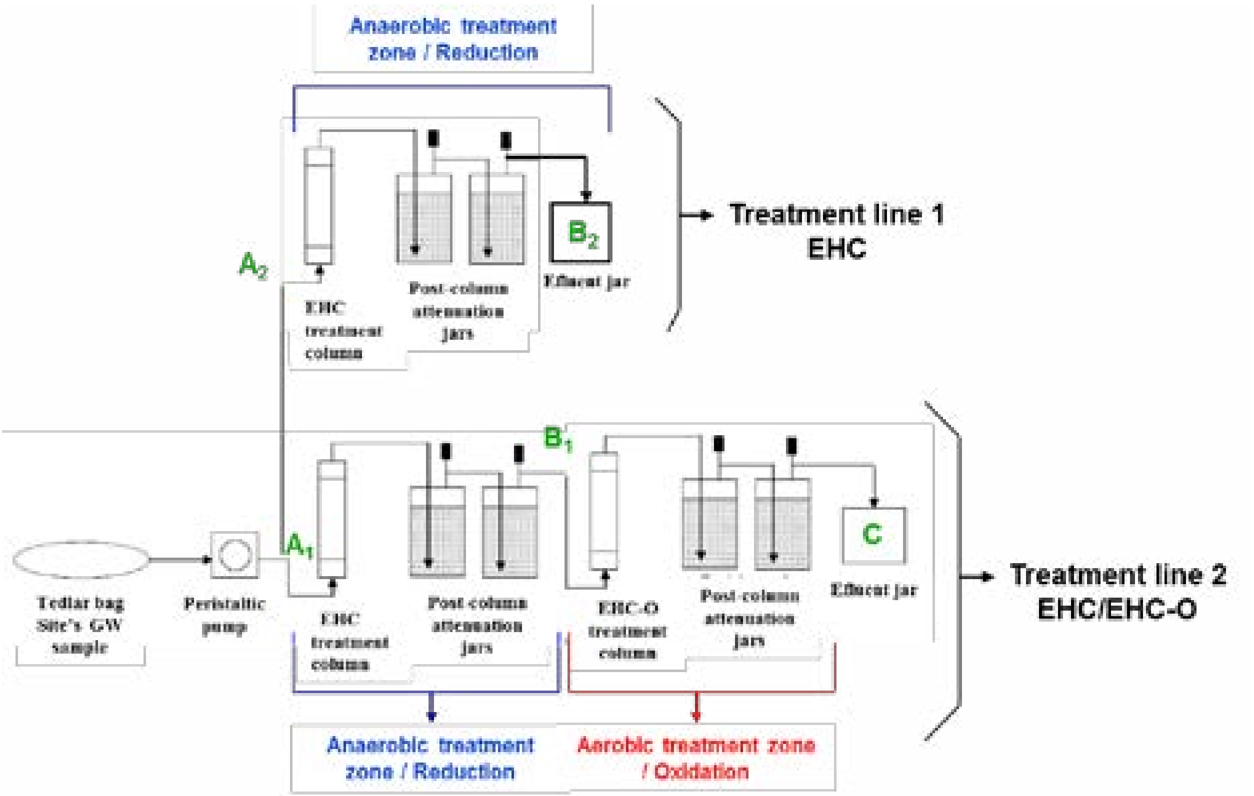


Figure 2.- Final experimental setting

Monitoring events were established at: (i) the feed of the mZVI columns (A_1 and A_2), (ii) after the attenuation jars following the mZVI treatment columns (B_1 and B_2), and (iii) after the attenuation jars following the oxygenation columns (C). COC's concentration, pH and ORP were monitored at the designated monitoring points for the specified treatment periods (49, 62, 76 and 91 days from the start of the test).

Results and discussion

In general, the identified variations in COC's concentration in the feed are considered negligible. The registered values are similar to those detected in the site's groundwater samples prior to the test development.

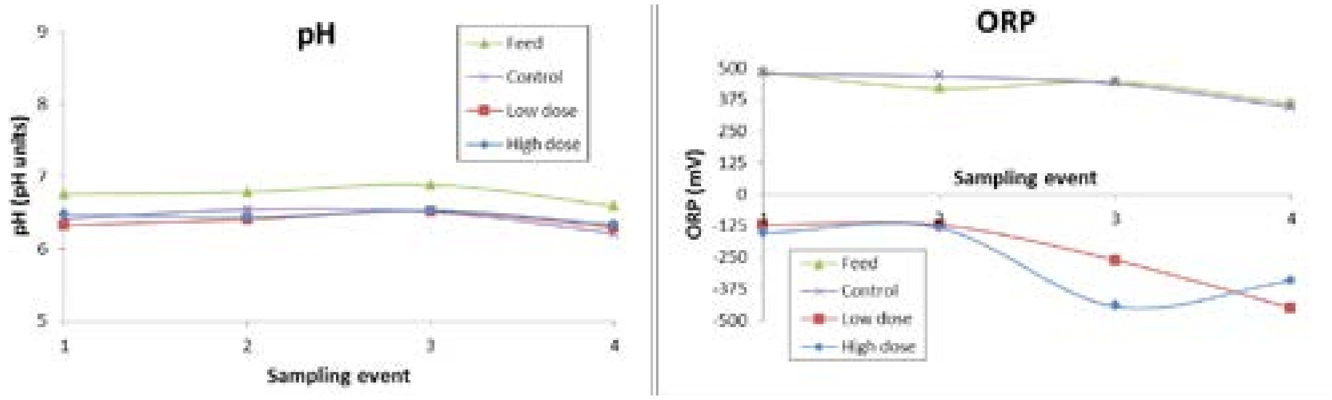
According to the analytical determinations of the column's outlet in the control systems, the reduction of COC´s concentration as a result of adsorption over crushed bedrock has proven to be significant, particularly for HCH isomers. Thus, estimation of removal yields associated to the tested treatments must consider the contamination reduction yielded in the control samples. However, adsorption on the bedrock is enhanced by the crushing of the samples and it's, therefore, thought to occur in a lesser extent if the tested treatments were to be implemented on field.

Parameter	Treatment feed		Post EHC-Treatment		Post EHC-O
	A_1	A_2	B_1	B_2	C
COC's Concentration	X	X	X		X
pH	X	X	X	X	X
ORP	X	X	X	X	X

Table 2: Laboratory test analytical program.

Tested line	Parameter	Test development – Monitoring events (days)			
		1	2	3	4
		49 d	62 d	76 d	91 d
Feed	pH	6,75	6,78	6,88	6,59
	ORP (mV)	488	421	449	361
Control	pH	6,41	6,54	6,51	6,21
	ORP (mV)	480	470	441	347
Low dose	pH	6,32	6,40	6,52	6,29
	ORP (mV)	-120	-120	-259	-448
High dose	pH	6,48	6,43	6,53	6,33
	ORP (mV)	-152	-131	-443	-341

Table 3: pH and ORP evolution – mZVI treatment

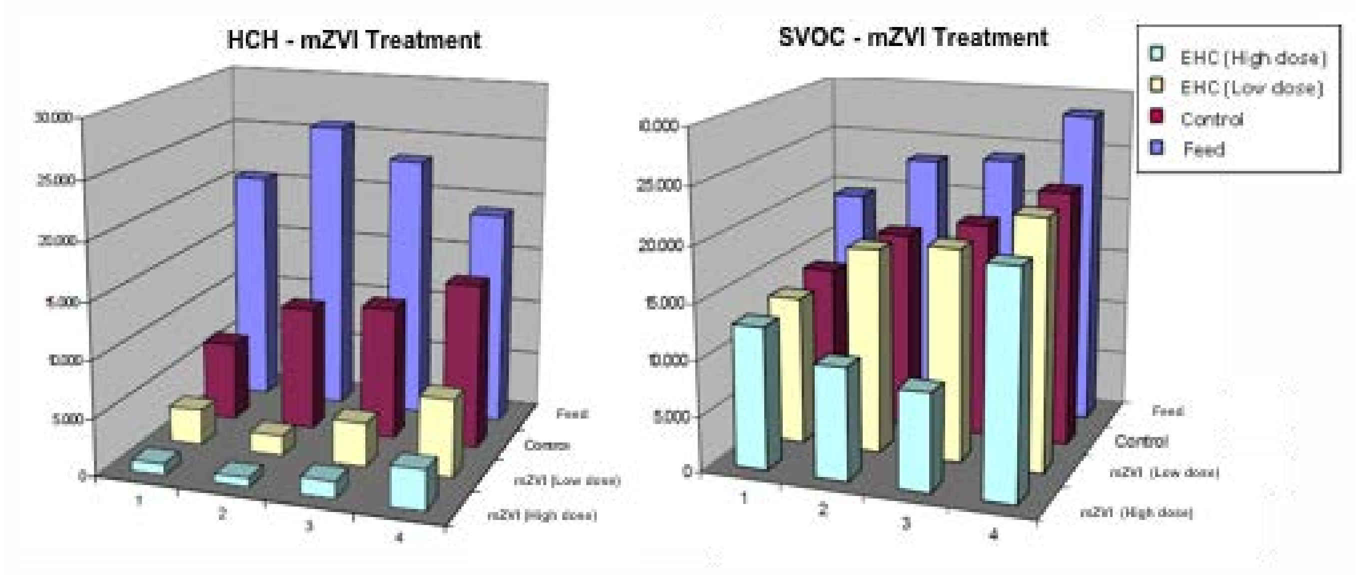


Graphic 1: pH and ORP in mZVI treatment columns

mZVI treatment

The pH and ORP measures in the column feed and after control and treatment columns are registered in Table 3: pH and ORP evolution – mZVI treatment and Graphic 1

The mZVI treatment accomplished increasing reductive conditions (negative ORP values) throughout the test. mZVI depletion may be behind the ORP increase registered in the high dose outlet on the fourth monitoring event. As expected no significant change in pH is identified due to the presence of mZVI.



Graphic 2: HCH and SVOC concentration in EHC treatment test

The analytical results for HCH isomers and SVOC are shown in *Graphic 2.*

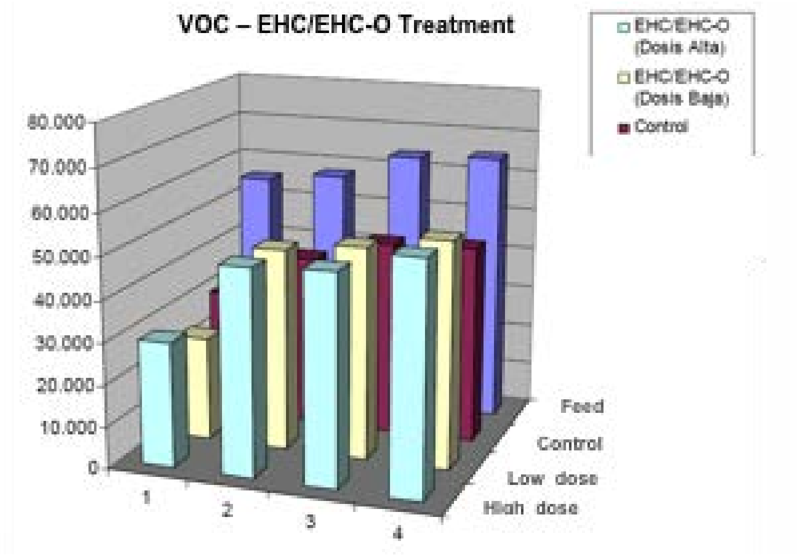
Removal rates increased with the reagent dose applied: the low dose treatment yielded removal rates ranging from 64 to 93% and the high dose treatment yielded removal rates in the range of 81-97%. The achieved reductions of HCH concentrations in the treatment systems are due to the combination of contaminants' adsorption on the crushed rock (see difference between feed and control series) and the degradation processes.

After the development of the mZVI test, the concentration of HCH isomers in the rock contained in each column was determined in order to perform mass-balance of the complete system (rock and groundwater). These side experiments concluded that adsorption alone achieved an estimated average of 33% mass removal of HCH from groundwater for the control line. However adsorption effects for treatment lines where significantly lower. Then the effective HCH removal yield, at the end of the test ranged from, 71% for lower dose line to 85% for the higher dosing.

With regards to other SVOC´s (mainly Poly-chlorobenzenes, Phenols and Chlorophenols) the achieved reductions are significantly lower, partly due to their higher solubility and therefore lower tendency to get adsorbed to the rock surface. The similar rates yielded by the control system and the low dose system would imply that the removal achieved by the latter is mainly associated to the adsorption process.

A higher dose of EHC yielded removal rates that ranged from 34 to 63% within the first 76 days of treatment. Such rates are thought to be related to the progressive degradation of 2,4,6-Trichlorophenol. The removal rate achieved at the end of the test (91days) was lower than expected probably due to mZVI depletion.

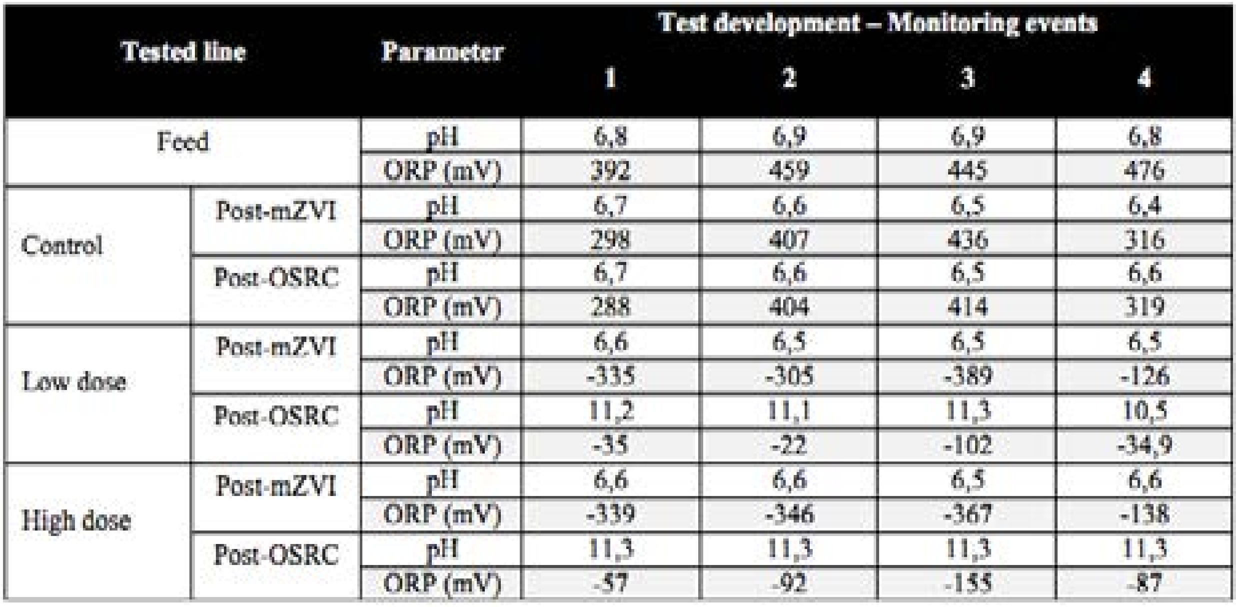
The analytical results for VOC (mainly benzene and chlorobenzene) are shown in Graphic 3.



The results corresponding to the main volatile organic compounds showed a similar behavior. The lesser removal rates achieved was partly due to their increased solubility. Although total VOCs concentration hardly changed throughout the test, both treatments showed progressive reduction of Chlorobenzene and a consequent gradual increase of Benzene1. In any case it should be taken into consideration that the compounds are preferably degraded through aerobic processes.

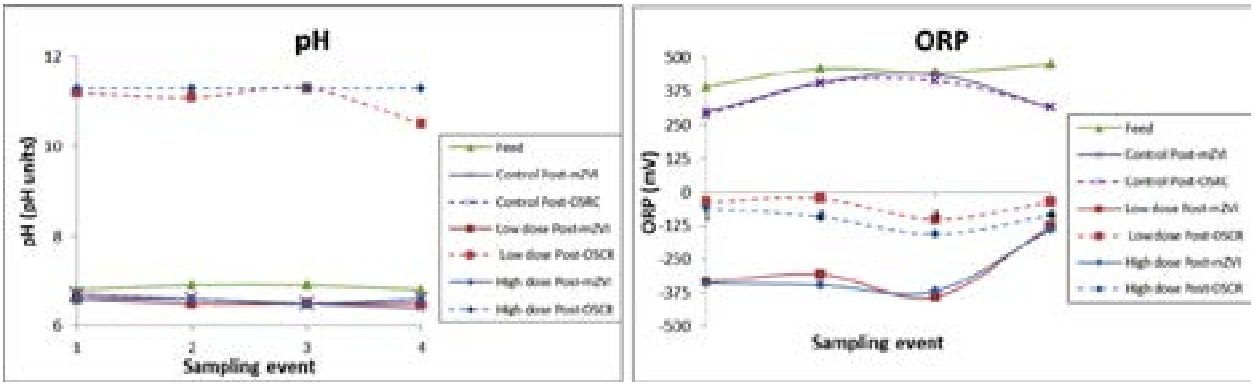
mZVI/Oxygen Slow Release Compounds

The pH and ORP measures in the column feed, control and treatment columns are registered in Table 4 and Graphic 4.



Tested line		Parameter	Test development – Monitoring events			
			1	2	3	4
Feed		pH	6,8	6,9	6,9	6,8
		ORP (mV)	392	459	445	476
Control	Post-mZVI	pH	6,7	6,6	6,5	6,4
		ORP (mV)	298	407	436	316
	Post-OSRC	pH	6,7	6,6	6,5	6,6
		ORP (mV)	288	404	414	319
Low dose	Post-mZVI	pH	6,6	6,5	6,5	6,5
		ORP (mV)	-335	-305	-389	-126
	Post-OSRC	pH	11,2	11,1	11,3	10,5
		ORP (mV)	-35	-22	-102	-34,9
High dose	Post-mZVI	pH	6,6	6,6	6,5	6,6
		ORP (mV)	-339	-346	-367	-138
	Post-OSRC	pH	11,3	11,3	11,3	11,3
		ORP (mV)	-57	-92	-155	-87

Table 4: pH and ORP evolution – mZVI/OSCR treatment

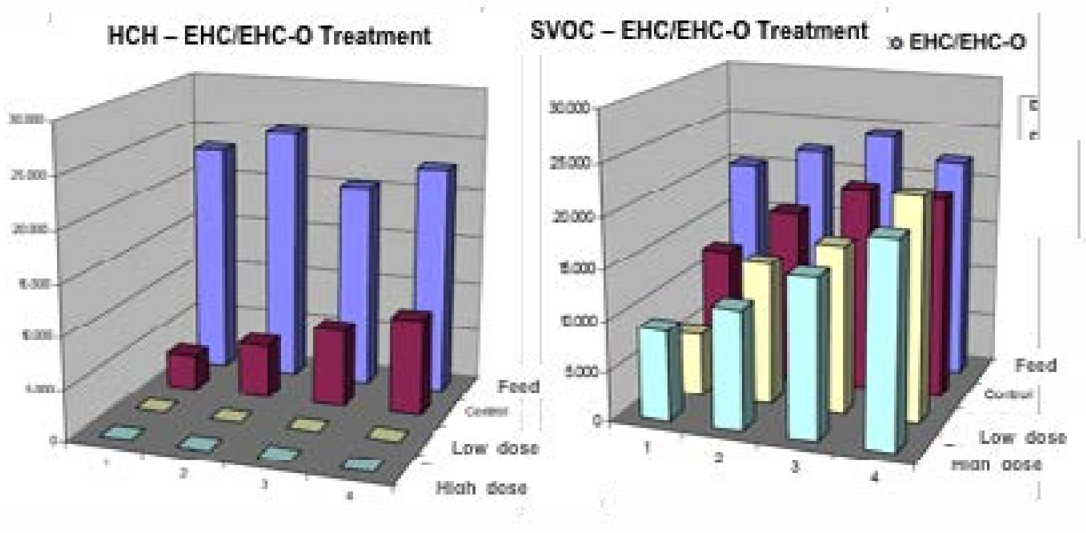


Graphic 4: pH and ORP in mZVI/OSRC treatment columns

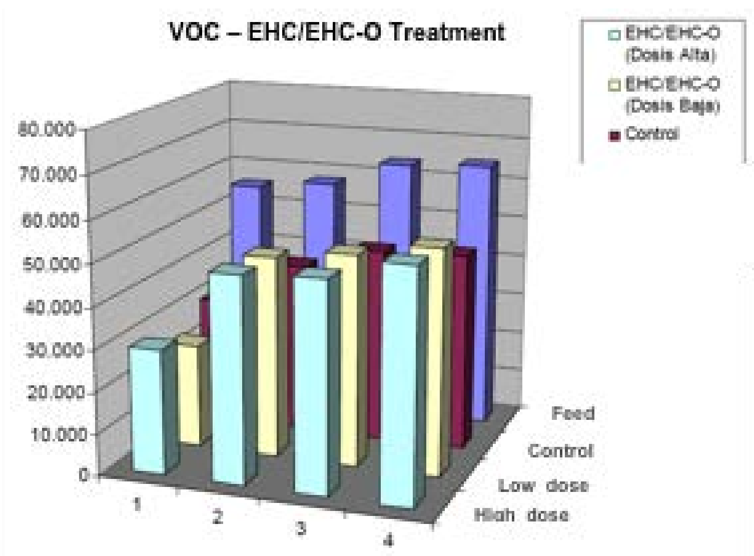
No significant change in pH was registered in the feed control and mZVI column outlet. However, OSRC increased pH values to 11, due to calcium hydroxide generation as a result of calcium peroxide (EHC-O® constituent) hydrolysis.

The mZVI column outlet (anaerobic reaction zone) exhibited strong reductive conditions, whereas OSCR's column outlet (aerobic reaction zone) showed increased ORP positive values, although still quite reductive. Such a behavior highlights the need of a more competent attenuation zone after EHC treatment to achieve the dissipation of reductive conditions in groundwater before entering the aerobic reaction zone. This situation together with the conceptual site model's estimated high velocity of groundwater within the bedrock fractures and the fact that the test columns and attenuation jars were prepared with crushed rock, constitute an important limitation for the field implementation of ISCR technology.

The analytical results for HCH isomers, SVOC and VOC are shown in Graphic 5 and Graphic 6.



Graphic 5: HCH and SVOC concentration in EHC/EHC-O treatment test



Graphic 6: VOC concentration in EHC treatment test

The inclusion of a second stage aerobic reaction zone has no theoretical effect in HCH degradation. Thus, HCH removal rates for both treatment systems should be similar. However, mZVI/OSRC treatments yielded higher removal rates due to the increased rock surface to which HCH isomers can get adsorbed to as a result of the three additional jars containing crushed rock (an aerobic reaction column followed by two attenuation jars) of the mZVI/OSRC treatment line (Figure 2, treatment line 2) compared to the mZVI-treatment line (Figure 2, treatment line 1).

The detected SCOVs and VOCs concentrations gradually increased throughout the test towards balanced concentrations in the inlet and outlet lines. This behavior is indicative of an on-going adsorption process and consequent progressive reduction of available adsorption centers. No effective degradation of SCOVs was registered in the tested treatments due to the unsuccessful achievement of oxidant conditions in the aerobic reaction column (Table 4).

Conclusions

The main observations obtained during the ISCR Laboratory test are the following:

- Relevant adsorption processes on the crushed rock (employed due to test set-up conditioning) have being observed for the main COCs, especially for HCH isomers.

However it should be considered that the specific contact surface between rock and groundwater is considerably lower at the site than during the test. Therefore it can be anticipated than the sorption processes will be significantly lower in case of a field implementation.

- High reductive conditions have been attainted using mZVI (EHC®). Such reducing conditions are optimal for the chemical reduction and anaerobic dehalogenation of the main COCs.

A relevant reduction of HCH concentrations was observed as consequence of both adsorption and degradation processes. The mass balance performed to the treatment columns indicated effective removal rates for HCH ranging 71% to 85% (low and high dosing respectively).

- However COVs and SVOCs concentration haven't shown an important reduction trend as consequence of the addition of OSRC (EHC-O®). These low performance ratios can be related to the failure to reach enough oxidant potential as consequence of the low efficiency of the post attenuation columns located between mZVI and OSCR treatment columns.

Based on these results, it can be concluded that the mZVI/OSRC (EHC®/EHC-O®) treatment train has been efficient for the degradation of the dissolved HCH isomers but has presented a limited performance for the rest of the COCs. This can be due to the failure in reaching oxidant condition to effectively degrade the HCH chemical reduction intermediates via aerobic biodegradation.

In the case of site escalation of the technology, it can be anticipated that the adequate oxidant condition would not be reached, as observed during the laboratory test.

The hydrogeological feature of the site, specifically the high groundwater seepage velocity in the fracture network, would difficult the effective implementation of separated anaerobic/aerobic treatment zones.

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9th International HCH and pesticides Forum for CEECCA countries, Chisinau, Republic of Moldova

SURFACTANT ENHANCED AQUIFER REMEDIATION LABORATORY TESTS FOR THE REMEDIATION OF THE ORGANIC CONTAMINANTS ASSOCIATED WITH THE UNCONTROLLED LINDANE LANDFILL IN BAILÍN (HUESCA,SPAIN)

SUBMITTED PAPER

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Abstract

This paper is part of the treatment laboratory program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located over a complex fractured geological media where lindane and other Persistent Organic Pollutants (POP) were dumped. These compounds have formed a multi-component DNAPL (Dense Non Aqueous Phase Liquid) which has spread in response to the geological layers and the fracture network.

The complete rehabilitation of the site comprises the dismantling of the landfill and the subsequent implementation of subsoil remediation technologies. Within this context, In-Situ Thermal Desorption was identified as a potentially applicable technology for the treatment of source areas (zones with presence of DNAPL within the fracture network).

This paper presents the development and results of the surfactant enhanced aquifer remediation treatability test, which was established as preliminary approach to evaluate the efficiency of this technology for the treatment of the Bailin's contaminants of concern. The main objectives of the test were: (i) to evaluate the applicability of the SEAR technology during the remediation of the site and (ii) finding an appropriate surfactant formulation considering the site features and conditionings.

In this regard, the particularities of the site hydrogeology (fractured rock) as well as the contaminant distribution in the subsoil DNPAL (present at high depths) advise looking for a surfactant formulation which empowers the solution of the DNAPL versus its mobilization.

This test, which was performed using bedrock, groundwater and DNAPL samples collected at the source areas of the site and, comprised two phases:

Phase 1 – Solubilization study: the DNAPL solubilization achieved by a number of surfactant formulations was analytically determined. Based on the obtained results, 5 of these formulations were selected and evaluated in the next phase.

Phase 2 – Mobilization: five lysimeters were implemented in order to evaluate potential increases in the migration capacity of the DNAPL caused by the selected formulations (no desirable effect).

Based on the results and observation performed during this test it was concluded that the SEAR technology can be an applicable technology for the Bailin site. In addition it was determined that the formulation showing the higher solubilization rates as well as a low mobilization capacity was the one containing 1% of sorbitan monooleate (Span 80; CAS# 1338-43-8) and 1% of dioctyl sulfosuccinate sodium salt (SDS octyl, CAS# 577-11-7)

Key Words

Lindane, HCH, POPs, in-situ, Surfactant, Solubilization, Mobilization, DNAPL, SEAR

Introduction and objectives

This paper describes the Surfactant Enhanced Remediation treatment program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located in the Bailín creek, over a complex fractured geological media. At this location the former company Inquinosa dumped, between 1984 and 1992, lindane (g-HexaChlorocycloHexane - gHCH) and other POPs (Persistent Organic Pollutants), namely: (i) non-commercial HCH isomers; (ii) chlorobenzenes and chlorophenols; (iii) benzene and; (iv) other organics from the lindane production process.

These compounds have formed a multi-component which has spread in response to the geological layers and the fracture network (see Table 1). Since 2004, interim remedial measures consisting of "pump and treat" techniques in the surroundings of the landfill have extracted more than 20 tn of DNAPL and have treated thousands of cubic meters of dissolved phase contamination.

Parámeter	Unit	Value / Concentration	% w/w
Density	g/cm3	1,3662	-
Water (Karl Fischer)	g/kg	2,2	0,2%
COC (GC/MS, FID, TIC)			
Benzene	g/kg	9,4	0,9%
Monochlorobenzene	**g/kg**	**140,0**	**14,0%**
1-chloro-2-Etilbenzene	g/kg	3,6	0,4%
1,2-Dichlorobenzene	g/kg	15,7	1,6%
1,3-Dichlorobenzene	g/kg	2,2	0,2%
1,4-Dichlorobenzene	g/kg	20,5	2,1%
1,2,3-Trichlorobenzene	g/kg	6,1	0,6%
1,2,4-Trichlorobenzene	**g/kg**	**41,0**	**4,1%**
1,2,3,5-Tetrachlorobenzene	g/kg	5,1	0,5%
1,2,4,5-Tetrachlorobenzene	g/kg	5,3	0,5%
1,2,3,4-Tetrachlorobenzene	g/kg	11,1	1,1%
Pentachlorobenzene	g/kg	1,7	0,2%
alpha HCH	**g/kg**	**59,4**	**5,9%**
delta HCH	**g/kg**	**102,2**	**10,2%**
gamma HCH	**g/kg**	**136,7**	**13,7%**
Pentachlorociclohexenes	**g/kg**	**74,3**	**7,4%**
Tetrachloropyridines	g/kg	32,0	3,2%
1,1,2,4,5-Hexachloro-1,5-hexadiene	**g/kg**	**65,1**	**6,5%**
Other organochlorinated compounds non resolvable by chromatography)	g/kg	136,1	13,6 %
Total	g/kg	869,8	87,0%

Table 1: Chemical characterization of the Bailin's DNAPL.

The complete rehabilitation of the site comprises the dismantling of the landfill and removal of the wastes to a new location, which has been already performed and constitutes the major contaminant mass reduction measure.

As expected, such a challenging site as Bailín, involving organochlorinated DNAPL and extensive dissolved phase contamination in a fractured environment, requires the implementation of remediation techniques for the treatment of residual subsoil impact. Within this context, during the past years (while before the dismantling), a remedial option appraisal has been performed for the fractured bedrock in order to address the most suitable remediation techniques.

The remedial option appraisal started with an in-depth bibliographical review of the "state of the art" regarding remediation of POPs in fractured bedrock. This research confirmed the lack of available experiences worldwide, with just a few examples reported of comparable sites. During the assessment, a limited number of remedial techniques were identified to be potentially capable of successfully treating the complete spectrum of contaminants at the fractured bedrock, driven in part by the complex nature of the mixture: (i) volatile and non-volatile compounds; (ii) differential biodegradation pathways of the COC's - reductive and oxidative; (iii) high contrasts in the physical properties of the constituents (i.e solubility, adsorption potential, Henry's constant); etc.

The identified technologies to be potentially applied, by themselves or forming part of a treatment train at the Bailin site were: (i) surfactant flushing; and (ii) thermal treatment, for the treatment of source areas (presence of DNAPL at bedrock fractures), as well as (iii) ISCR - In Situ Chemical Reduction – and; (iv) ISCO - In Situ Chemical Oxidation, for plume areas (high dissolved concentrations in groundwater). Subsequently, a comprehensive program of treatability tests was implemented at laboratory scale. The focus of this program was to evaluate the performance of each technology to address most the contaminants within the mixture.

Surfactant Enhanced Aquifer Remediation was identified as a potentially applicable technology for the treatment of the source area since it has been used as an enhancement to conventional pump-and-treat systems, which often are inefficient for recovering contaminants that are trapped as an immiscible-phase liquid.

This technology is based on the activity of surfactants (acronym of “surface active agents”), which are chemical agents that enhance the effective solubility of the low solubility organic compounds in water. Surfactants tend to adsorb at the interface between two immiscible fluid phases. This behavior occurs because surfactant molecules consist of two components, a water-liking (i.e., hydrophilic) group and a water-disliking (i.e., hydrophobic) group.

Surfactants work to enhance contaminant mass recovery in the subsurface by reducing the interfacial tension of the fluid phases contacting the residual DNAPL. The extent of interfacial tension reduction will determine whether the primary mechanism of contaminant removal is via:

1. Solubilization of the residual DNAPL into the surfactant solution, or
2. Mobilization of entrapped DNAPL as free product.

The prevalence of one of these effects over the other one for a given organic phase depends on the hydrophilic- lipophilic mass ratio of the surfactant formulation. This ratio is commonly known as Hydrophilic Lipophilic Balance (HLB), which is a specific parameter of each surfactant formulation, which characterize the behavior activity of these compounds 1 2 3.

Given the hydrogeological features of the site (complex fracture matrix, DNAPL vertical migration risks, effective hydraulic control of the site, etc.) the SEAR treatment should be based on the DNAPL solubilization will be preferred for the remediation of the Bailin site, versus a mobilization approach.

A specific treatability test with the following objectives was implemented in order to evaluate the effectiveness of surfactants in addressing Bailin’s impact in source areas:

- Evaluating whether the application of surfactant formulations may significantly enhance the removal contaminant mass via hydraulic extraction, as consequence of an increase of the solubilization of the DNAPL constituents in groundwater.
- Finding an appropriate surfactant formulation considering the chemical and hydrogeological features and conditionings of the site (DNAPL composition, fractured aquifer, DNAPL distribution, etc.).
- Estimating the optimal dosages in case of further on-site application.

The bench treatability test included two different phases of testing, namely:

- **Phase 1 – Solubilization study:** the DNAPL solubilization achieved by a number of surfactant formulations was analytically determined. In the following steps of the test and based on the obtained results, 5 of these formulations were selected and evaluated.
- **Phase 2 – Mobilization column tests:** five lysimeters were implemented in order to evaluate potential increases in the migration capacity of the DNAPL caused by the selected formulations (no desirable effect).

The current paper summarizes the experimental procedure implemented during the bench scale test performed in the framework of the Bailin’s project, as well as the obtained results.

Materials and methods

Sampling

The first step includes the collection of site bedrock, groundwater and DNAPL samples to be used during the bench test (see Picture 1 and Picture 2). These samples were taken at the identified target areas for this technology, namely areas where DNAPL is present within the bedrock fractures and high dissolved phase concentrations of contaminants of concern have been identified. Concretely, up to 50 Kg of bedrock, 25 liters of groundwater and 10 liters of DNAPL were collected in the landfill body, within the formation underlying the dumped HCH manufacturing wastes. These samples were adequately sealed and cooled until their arrival to the laboratory in charge of the performance of the test.

Picture 1: Groundwater and DNAPL Sampling

Picture 2: DNAPL bottling

Phase 1.- Solubilization study

The first step has the aim of selecting a limited number of formulations (those with higher solubilization capacity) that can potentially be applicable for the treatment of the Bailin DNAPL and that will be used in next stage of the current lab test. This selection is based on both analytical results as well as visual observations.

A series of 32 vials were set up, comprising surfactant solutions or mixed surfactant solutions with HLB values mostly ranging between 5 and 15. Each vial had 1 mL of DNAPL and 10 mL of the surfactant solution, which were shaken four times a day for three weeks. Duplicate vials were also set up, which were left undisturbed for the same duration (see Picture 3).

Picture 3: Test Phase 1: preparation of the surfactant formulations

A sample of each of the shaken surfactant solutions were taken in order to determine its DNAPL solubilization capacity.

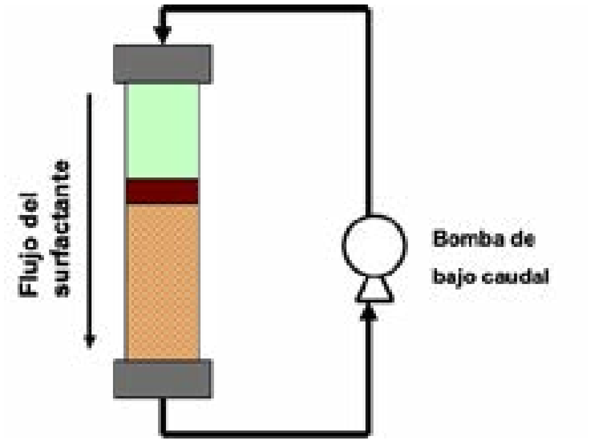
Phase 2 – Mobilization column tests:

Column tests were prepared for the best surfactant mixes identified in the first phase of the works (mixes 7, 14, 16, 31 and 32). In addition, the testing of a series of sands with varying permeability, the material chosen for the columns was silver sand (0.17 - 0.44 mm in size), due to this material having the best ability to just hold a thin layer of DNAPL (2 ml per 20 ml of material) yet allowing liquid to flow through it.

The columns were prepared by placing 1 kg of silver sand at the bottom of a column which was then saturated with surfactant solution to approximately 20 cm above the top of the sand's surface. In order to create a suspended DNAPL layer on the sand's surface 250 g of DNAPL was then slowly poured through the aqueous surfactant solution, allowing the DNAPL to slowly sink into the sand. An additional amount of silver sand was placed on top of the DNAPL layer, followed by the remainder of the 1 L surfactant solution (see Picture 4).

Picture 4: Test Phase 2: preparation of the test columns

The columns were left saturated and observed over a 14 day period. After this equilibration period two litres of surfactant solution were pumped in down flow through the columns at a rate of 3 l/h (50 ml/min). This down flow configuration was to encourage the DNAPL to migrate vertically down through the soils. This cycle was repeated three times , recycling the surfactant each time.



Picture 5: Test Phase 2: surfactant recirculation

A continuous monitoring of the DNAPL layer behavior was done during both the stabilization and pumping process, logging any kind of relevant information. This is a key information in order to understand the mobilization behavior of the DNAPL under the influence of the surfactant and consequently for the selection of the optimal formulation.

In addition, up to 4 sand samples per lysimeter were collected at different segments of each column, with the aim to evaluate analytically the mobilization of DNAPL. A groundwater aliquot was also collected for analytical determination.

Analytical considerations

In order to determine the solubilization capacity of the surfactant solution, a test was done considering the total amount of solved DNAPL, instead of the individual compounds. This is due to the complex mixture of compounds present in the Bailin's free phase

In this case High Performance Liquid Chromatography (HPLC) was used and site specific calibration standards prepared with DNAPL of the site were used to determine the calibration line which was lately applied for the determination of the DNAPL concentration in both soil and groundwater samples. This approach did not allow the separated quantification of the individual compounds contained in the DNAPL but quantifies the totality of grams of DNAPL per liter of surfactant solution.

Among others, the following are the main reasons behind the application of this analytical approach:

1. The presence of surfactants may interfere in the gas chromatography methods commonly used for individ-

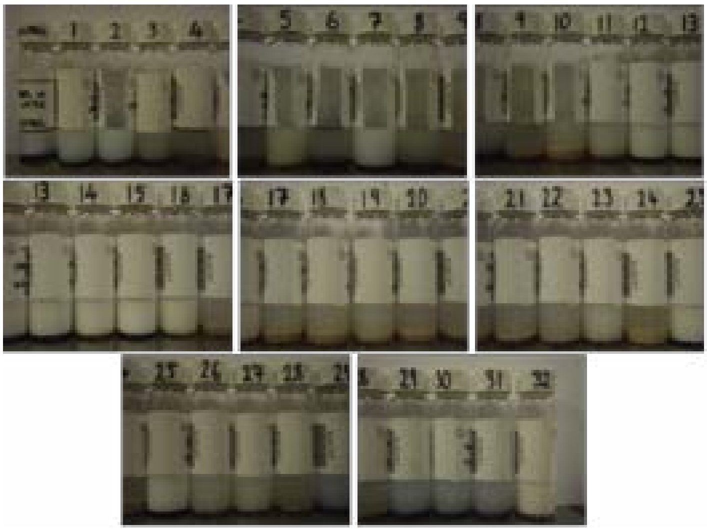
ual compounds determinations, preventing its use or at list significantly increasing the detection limits.

2. Common methods may underestimate the COCs concentrations due to the incapacity of quantifying the molecules that are inside the surfactant micelles.
3. HPLC methodology is a robust technology which will be applied in case there is an eventual field escalation of the technology (i.e. field pilot tests and/or full-scale implementation).

Results and discussion

Phase 1.- Solubilization study

DNAPL Solubilization rates attained by the 32 studied formulations are recorded in Table 2. In addition Picture 6 depicted the visual aspects of the surfactant mixtures.



Picture 6: Solubilization microcosms

The selection of the surfactant formulations, to be studied in the next stage, were considered by both of the analytical results and the observations related to the DNAPL behavior to the presence of the different surfactant formulations.

Based on the analytical results the surfactant mixtures that presented higher solubilization were obtained by formulation with medium HLB values, ranging (6 to 16). Concretely, the highest values were those numbered as 1, 2, 7, 16 and 31. However, formulations 1 and 2 presented were dismissed because of its multiphase behavior. Therefore the selected formulations to be studied in the next step of the test were those numbered as: 7, 14, 16, 31 and 32.

Surfactant formulation #	HLB	Solubilization rate (g/l)
1	14,90	63,57
2	16,70	36,00
3	10,80	10,25
4	>40,00	2,64
5	8,0	6,40
6	4,30	1,31
7	15,00	48,95
8	13,40	3,62
9	40,00	7,44
10	8,00	9,31
11	5,04	3,58
12	5,21	2,51
13	6,12	2,96
14	6,15	28,73
15	7,03	3,39
16	7,07	40,45
17	8,27	7,50
18	8,35	19,28
19	9,05	27,34
20	9,08	7,07
21	10,16	3,12
22	10,10	23,30
23	11,15	19,99
24	11,20	8,13
25	12,03	11,97
26	12,20	17,24
27	12,90	17,14
28	13,13	0,69
29	14,12	18,81
30	14,04	12,733
31	14,92	45,61
32	15,01	29,33

Table 2: HLB of used surfactant mixtures and attained solubilization rate.

Phase 2 – Mobilization column tests:

The five formulations which presented the higher DNAPL solubilization behavior during the first stage were lately studied in order to specifically asses its potential mobilization (undesirable). For that, five lysimeters (one per selected formulation) were prepared using DNAPL from the site, silver sand (holding material) and the surfactant formulation prepared with site's groundwater.

After a former equilibration period of 15 days, a sequential low flow pumping program started. In addition to the analytical determinations, a detailed observation of the DNAPL solubilization and mobilization process was performed during the entire process. The main recorded observations are summarized in tables Table 3 to Table 7, which include the following pictures of the process:

(i) During the start-up of the Phase 2.
(ii) After 2 weeks of equilibration and just before

the pumping step.
(iii) At the end of the pumping period.
(iv) Dismantling of the different sand segments of the lysimeter.

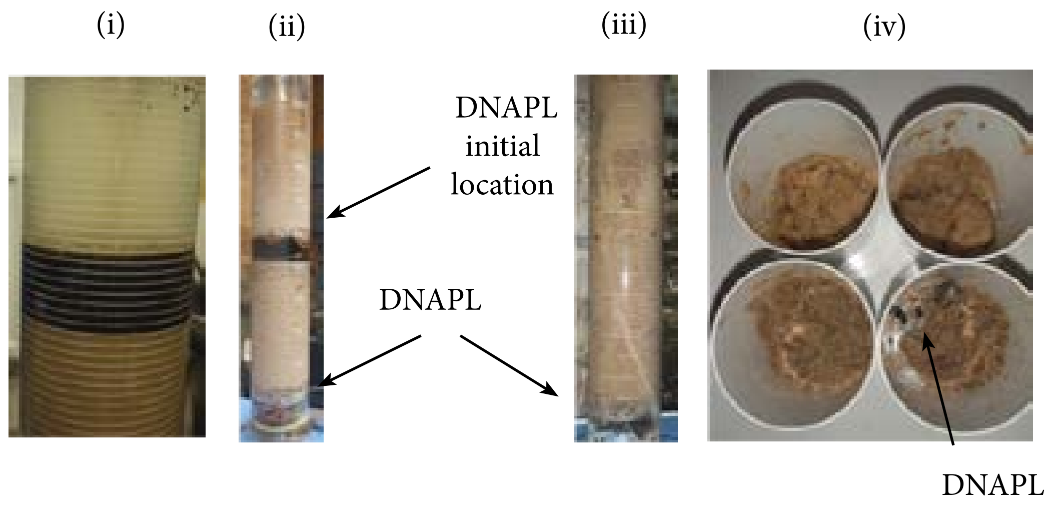
Column 1 (Formulation # 7)	Observations
Start-up	DNAPL layer 13.5cm from base of column, 2.5cm thick.
1st Pumping cycle	DNAPL started migrating through column after 2 minutes. Globules of DNAPL started flowing out of column 20 minutes into pumping.
2nd Pumping cycle	DNAPL globules in surfactant flowing out
3rd Pumping cycle	Small globules of DNAPL still in surfactant. DNAPL in surfactant visible at bottom of the column
Pictures	
SUMMARY	*Even during the first stages of the pumping, a relevant mobilization of the DNAPL layer was observed (Pictures ii y iii).* *After pumping and dismantling processes (pictures iii and iv) signs of relevant migration were observed as evidenced by the presence of free phase at the bottom of the lysimeter.*

Table 3: Observations of column 1 (formulation #7)

Table 4: Observations of column 2 (formulation #14)

Column 2 (Formulation # 14)	Observations
Start-up	DNAPL appears to have solubilized into surfactant solution.
1st Pumping cycle	Some globules of DNAPL seen in column.
2nd Pumping cycle	No DNAPL globules observed within the surfactant solution
3rd Pumping cycle	No DNAPL globules observed within the surfactant solution
Pictures	
SUMMARY	*Since the former stages an efficient solubilization of the DNAPL was observed (Picture ii)* *No evidences of DNAPL were observed in any of the steps, that means that the mobilization process can be considered as negligible when compared to the solubilization. (Pictures ii, iii y iv).*

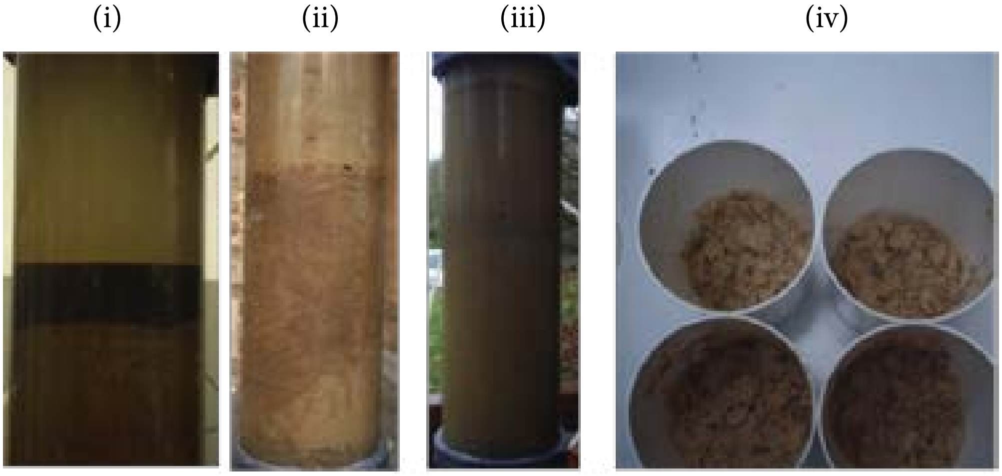
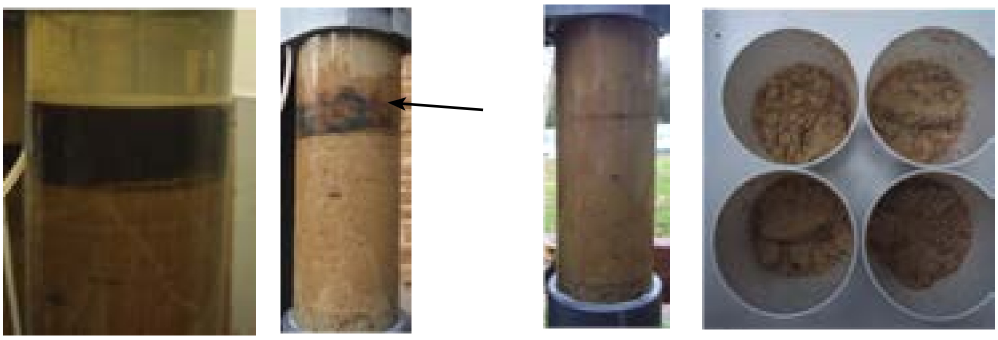
Column 3 (Formulation 16)	Observations
Start-up	No distinct DNAPL layer. A dark brown DNAPL/surfactant solution has dispersed through most of the sand
1st Pumping cycle	Some small DNAPL globules evident in surfactant. Insufficient to measure volume
2nd Pumping cycle	No DNAPL globules observed within the surfactant solution
3rd Pumping cycle	No DNAPL globules observed within the surfactant solution
Pictures	 (i) (ii) (iii) (iv)
SUMMARY	*After the stabilization process, DNAPL globules appeared but they seem to be solubilized during the pumping cycles. Therefore, it can be concluded that mobilization occurs during the former stages but in a lower extent tan for column 1.*

Table 5: Observations of column 3 (formulation #16)

Table 6: Observations of column 4 (formulation #31).

Column 4 (Formulation 31)	Observations
Start-up	Obvious DNAPL layer, 13.5cm from base, 3cm thick. Slight dispersion of DNAPL in bubbles in sand.
1st Pumping cycle	DNAPL migrated down column instantly. Small band of DNAPL left (<0.5cm) in original position.
2nd Pumping cycle	DNAPL came out first before surfactant (2 ml).
3rd Pumping cycle	Small globules of DNAPL in surfactant after 1L of pumping. DNAPL visible in bottom of column
Pictures	
SUMMARY	*An important mobilization of the DNAPL was observed from the earlier stages. This effect increases during the pumping stage.*

Column 5 (Formulation # 32)	Observations
Start-up	All DNAPL appears to have solubilized.
1st Pumping cycle	DNAPL sitting at bottom of column - subsequently flowed out before surfactant. 43 ml of DNAPL flowed out.
2nd Pumping cycle	No DNAPL evident in surfactant.
3rd Pumping cycle	No DNAPL evident in surfactant.
Pictures	(i) (ii) (iii) (iv) 
SUMMARY	*DNAPL seemed to be solubilized at the beginning of this phase. However at the beginning of the first pumping cycle mobilization evidences were observed.* *A significant quantity of DNAPL flowed out of the column during the first pumping cycle, which indicates that most of the DNAPL was located at the bottom of the column even if not visually identified.*

Table 7: Observations of column 5 (formulation #32).

Once this process ended, the following samples were collected:

- Silver sand samples: The sand contained in the lysimeter was split in for subsamples depending of its location within the column (10 cm segments). These subsamples were homogenized before the analytical quantification of the DNAPL content. Obtained results are recorded in Table 8

Segments	DNAPL (g)
Column 1	
0-10 cm	8,7
10-20 cm	37,7
20-30 cm	52,8
30-40 cm	78,4
Column 2	
0-10 cm	14,6
10-20 cm	53,0
20-30 cm	27,4
30-40 cm	32,0
Column 3	
0-10 cm	10, 7
10-20 cm	36,9
20-30 cm	40,3
30-40 cm	74, 6
Column 4	
0-10 cm	25,5
10-20 cm	24,5
20-30 cm	60,0
30-40 cm	68,1
Column 5	
0-10 cm	22,5
10-20 cm	21,3
20-30 cm	23,4
30-40 cm	18,2

Table 8: Sand samples concentrations

The columns # 1, 3 and 4 showed higher DNAPL concentrations on the 4th segment (located at the bottom of the column). Such results indicate an important contribution of the mobilization behavior of the surfactant.

For column # 5, low DNAPL concentrations reported could be related to the high amount of free product that flowed out of the column (43 ml).

- Surfactant solution samples: the analytical determination of the amount of DNAPL dissolved in the surfactant solution (Table 9).

Column	Surfactant formulation	Waste solubilization [g/l]
1	7	69
2	14	44
3	16	44
4	31	69
5	32	63

Table 9: Surfactant solution samples concentrations

The higher DNAPL solubilizations were detected for the columns # 1, 4 and 5. However, columns # 1 and 4 presented traces of DNAPL embedded in the column. These droplets could have interfered in the analytical results, overestimating the dissolved phase.

Regarding column nº 5, during the pumping periods, a very significant mobilization and high solubilization rates have been observed. This effect has to be avoided for this specific site.

Columns nº 2 and nº3 obtained the most representative solubility, since no noticeable DNAPL was detected during the last two pump cycles, which suggests that the given concentrations must been in an effective dissolution.

The DNAPL mass distribution in the sand sections of columns nº2 and nº3 indicate that column nº3 has caused a vertical migration of DNAPL higher than nº2, since the concentrations of the lower sections are higher.

In other words, column number 2 presents, a priori, fewer DNAPL vertical mobilization effects than the rest of the columns and a proper effective solubilization ratio.

Conclusions

During the execution of the test, an important enhancement of the waste solubility ratios has been observed, as a result of the surfactants activities. Therefore, this technology is considered applicable for the remediation process in this site.

The obtained observations and the results indicate that mixture number 14 has given the best results according to the upcoming criteria:

Proper effective solubilization rates,

No vertical mobilization was induced, minimize the effects in the generation of drops (separation of phases) and presents a better balance between solubility and multiphase behavior that the other formulations studied, maximizing the waste solubilization versus mobilization.

It can be the concluded that the optimal formulation for the Bailin's site (higher solubilization rates as well as a low mobilization capacity) was the one containing 1% of sorbitan monooleate (Span 80; CAS# 1338-43-8) and 1% of dioctyl sulfosuccinate sodium salt (SDS octyl, CAS# 577-11-7)

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SPANISH EXPERIENCES

Part 2: Air monitoring and water monitoring during the dismantling of the Bailín landfill

ENVIRONMENTAL MONITORING OF THE DISMANTLING WORKS IN THE HCH BAÍLIN LANDFILL, SABIÑÁNIGO, SPAIN

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Abstract

The dismantling of the HCH landfill in Bailín (Sabiñánigo, Huesca, Spain) carried out between the months of May and October 2014, has exposed the excavation and transfer of 65,000 t of HCH waste and 342,000 t of polluted lands. To minimize the environmental risks of these works, an Exhaustive Environmental Monitoring Plan has been developed, based on the specific procedures for the monitoring of the different aspects.

The efforts to minimise the impact on the environment has been focused specially on the control of the atmospheric dispersion and of the generated leachate and runoffs. For this, multiple prevention measures have been applied, planned in the Project, adopting the specific action Procedures: laying of temporal covering sheet in case of precipitations and/or wind limits (8mm/day and 11 m/s=40 km/h); protocol for the monitoring of the particles dispersion; management procedure, maintenance and cleaning of infrastructure for leachate and surface runoffs evacuation; procedure for the management of affected waters and generated leachate during the works and monitoring of surface waters.

It has been confirmed that the Environmental Monitoring has been a key tool to direct the attenuation measures planned in the Project, allowing also to detect the changes that, as a consequence of the transfer of great waste volumes in a very reduced period of time, were happening in the surroundings. Thanks to it, it has been possible to implement additional corrective measures in the Project, to reduce the effects of some punctual episodes of surface waters affection, generated as a consequence of very unfavourable climatological circumstances.

Key Words

HCH, Chlorinated pesticide, lindane, transfer of landfills, environmental monitoring, environmental follow-up, dust dispersion control.

Results and discussion

The Bailín landfill received the Lindane fabrication wastes of INQUINOSA between 1984 and 1992. These wastes were directly deposited on the land without any isolation measure.

The detection of a dense free phase in the aquifer with elevated HCH concentrations and other organochloride made the environmental authority contemplate the dismantling of the landfill as the only option to approach the extraction of the free phase and the decontamination of the aquifer, as the dissolved feather reaches the río Gállego (Fernandez et al., 2013).

The “Dismantling of the current HCH landfill, excavation, transfer and deposit in the new cell, waste management and dismantled surface cleaning” (Stage 2) works developed between the 19 May and 29 October 2014, in which the complete sealing of the new cell was reached, affected a total of 429,000 t of materials that correspond to 65,000 t of HCH waste, 342,000 t of polluted lands, 12,600 t of breakwater, 1,700 t of voluminous waste (plastic sheets), 327 t of muddy waste, 473 t of solid urban waste and 7,000 t of broken rocks.

Environmental monitoring plan

The Environmental monitoring programme designed for the dismantling stage of the old HCH landfill in Bailín (Stage 2), observed the following means and environmental aspects to monitor: meteorology, surface waters, groundwater, leachate, soils, dust and gas in environment and settlement and stability; and defined the group of monitoring and environmental follow-up tasks and their frequency in conformity with what has been established in the Integrated Environmental Authorisation (IEA), summarised in the enclosed table.

Aspect	Frequency	Monitoring
Weather Data	Daily	Precipitation volume measure, temperature, average evaporation, atmospheric humidity
		Measurement of dominant wind direction and strength
		Daily prediction up to 3 days of precipitation, wind speed and direction intensities
Leachate composition and volume Purification performance	Daily	Leachate volume in rafts of the current landfill **(*)** and in the rainwater tanks*
	Weekly	Sampling and leachate analysis before and after the purification in each treatment line and in the rainwater tank **(*)**
Volume and composition of surface waters	Daily	Registry of rain level inside the monitoring rafts of the new cell and rainwater tank(*)
	Monthly/Quarterly and always after rain or intense wind periods	Sampling and analysis of the surface waters monitoring points
		Volume, flow and composition monitoring of surface waters
	Quarterly	Additional analysis of the main water ions
Groundwater monitoring	Monthly	Piezometric level measure in environment piezometers of the old landfill and in the monitoring network of the new cell
	Monthly	Flow and composition measurement in the monitoring rafts of the draining systems
Soils	At the start (in some points) and at the end of the Stage 2	Sampling and analysis of the soils (previous) and of the remaining soils in the surroundings of the current HCH landfill and of the surrounding soils of the safety cell and transportation roads
Gas and dust	At the beginning of the Stage 2	Establishment of operation conditions (wind intensity module) for the prevention of the HCH dispersion
	Daily	Planning of the dismantling works as a consequence of the wind prediction (module and intensity) for 3 days and with the former conditions
	Monthly	Monthly measurement in two collectors of sediment particles and two suspension particles and HCH high volume pick-up units, in a day in which the weather previsions advise to adopt the minimisation measures
	At the end of the Stage 2	During the RSU retreat phase of the current landfill, CH4, CO2 and O2 in air concentration measurement in the surroundings of the current urban landfill and new safety cell
Topographic monitoring	Before the beginning of the	Survey monitoring of the new safety cell
	At the end of the Stage 2	Current HCH landfill survey, once dismantled
	Fortnightly	Acknowledgements and inspections of cracks, subsidence and erosion in the new cell
	Monthly	Survey monitoring of the new safety cell
		Determination of the occupied land volume and the new cell's available volume
		Evolution of the topographic references coordinates for the new cell's seats and subsidence monitoring

(*) Executed by the property

Table 1. Summary of environmental monitoring and follow-up during the Stage 2

These measurements and monitoring were carried out in accordance with the environmental procedures approved by the Project Management, based on the Guides, Technical Standard and Regular use sampling manuals (ISO, Community of Madrid, IHOBE, Ontario, etc). The localisation of the monitoring points of the different environmental aspects, was extreme in the immediate surrounding of the Bailín Ravine (fig. 1) and extended all along the río Gállego riverbed and in the Sabiñánigo municipality.

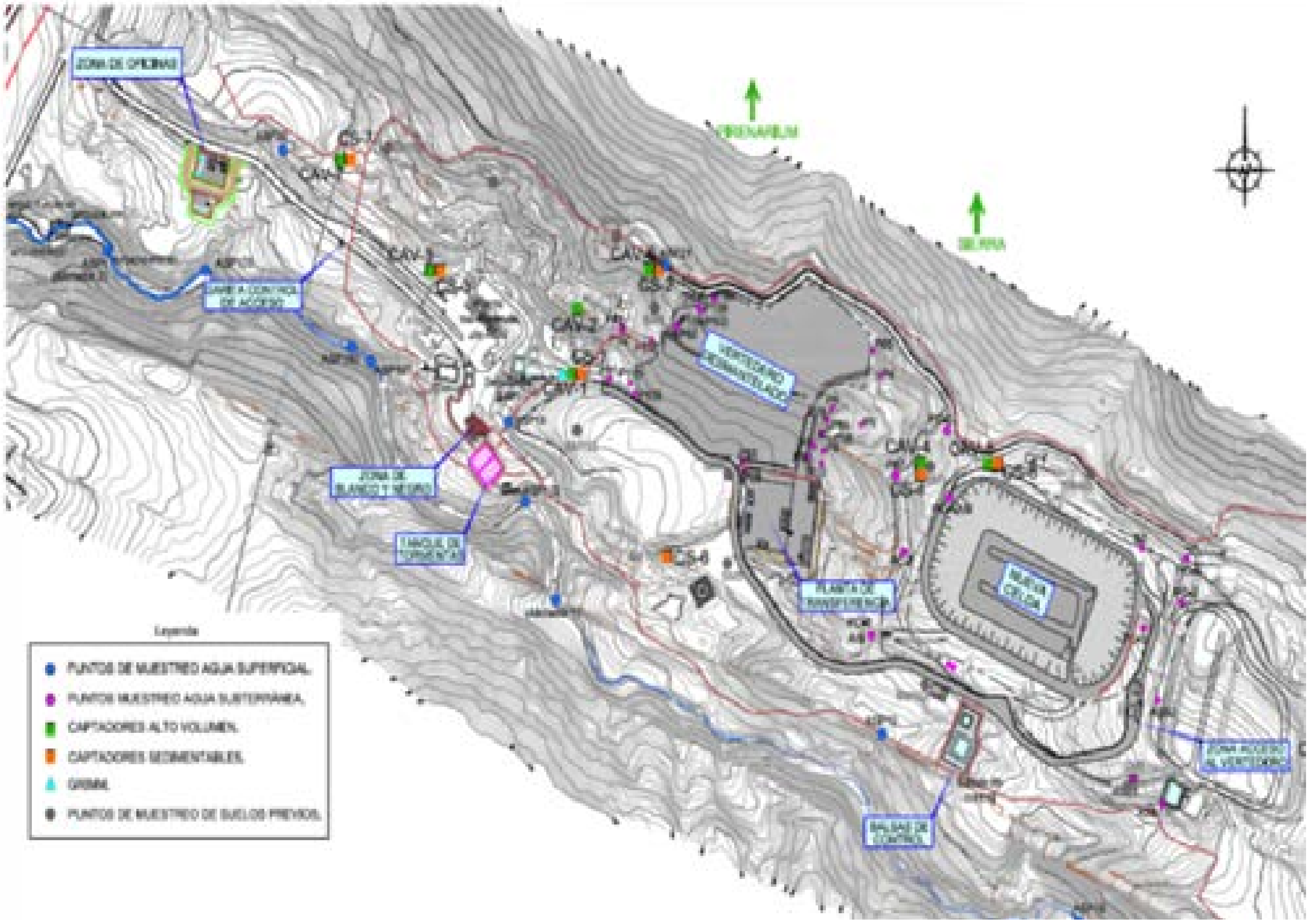

Figure 1. Localization of the environmental follow-up monitoring points

Meteorology

The meteorological conditions in the location have been one of the most critical factors of the works development, that is why the dismantling was programmed between the months of May and September, period in which the precipitation conditions and winds' regime are supposedly more favourable.

The analysis of the meteorological previsions of regional scope and of the observations in the meteorological station of Bailín showed a bad correlation, especially for the direction and speed of the wind. In order to improve the adjustment on the winds, key aspect for the monitoring of the particles dispersion, a statistic model was carried out that improved the previsions, even though there was an important uncertainty. The development of this model is the object of a communication in this same Forum (Pelegrin et al.).

For the precipitations prediction a specific short scale model for the Bailín emplacement has been placed, with 10 days hour forecasts and additionally there has been a short term prediction follow-up (12 hours) since the last hours observations.

The work regime established limit conditions that obliged to stop the works if:

- more than 8 mm/day precipitation
- wind of more than 11 m/s (40 Km/h).

In these situations, environmental protection measures were applied, consisting of covering with impermeable sheet of the work front to avoid the runoff, dragging and/or dispersion of waste particles and in the new discharge cell the usual procedure was intensified for the filling which consisted of covering the lindane wastes with land.

Because of rain prevision it has been necessary to cover the front and excavation surface in 25 occasions to which are added 29 other days of weekends in which it was kept covered to avoid any risk of rains and/or particles dispersion because of wind. Also, East winds, in occasions close to 11 m/s and the development of works in the action area limits, has obliged to stop the works up to two occasions and modify the type and/or work zone to avoid the increase of particles generation in other 8 occasions.

Also it should be highlighted that during the works period a total of 377.8 mm precipitations have been accumulated, 27% more that during the same period in 2013. See graphic of figure 2.

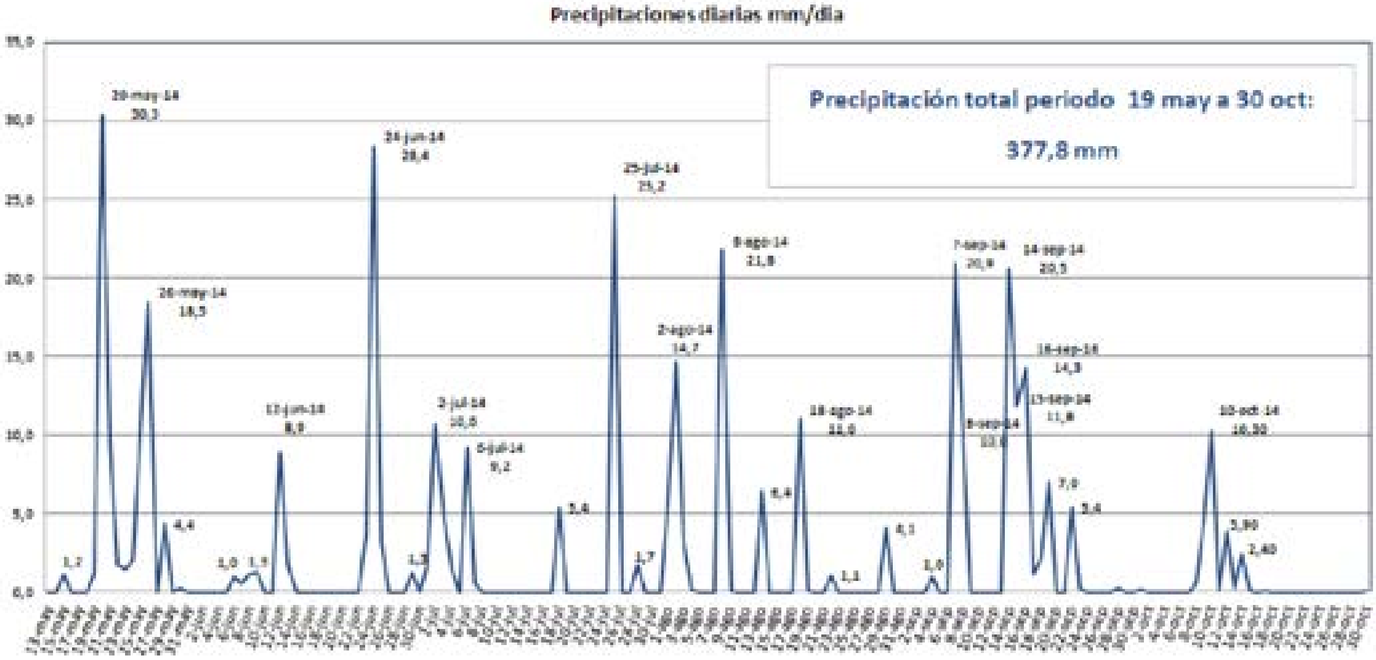

Figure 2. Graphic of daily precipitations

Some of them are highlighted because of their quantity and other also because of their intensity, among others: in the early morning of 25 July, 15.6 mm fell in 10 minutes of the total (25.2 mm); on 8 August (21.8 mm) 19.8 mm concentrated in only 1 hour (8 p.m.); on 7 September (20.9 mm) 7.6 mm fell in 10 minutes (11 p.m.) to which added 10 mm on the day 8; and on 14 September (20.5 mm) fell in 10 minutes at 9 p.m. (20.3 mm in 30 min) to which added in the early morning of 15 September the 10.4 mm that fell in 30 minutes. In all these episodes, the old landfill was covered with an impermeable sheet and the new discharge cell with soil. Additionally, an emergency equipment was place at night and/or weekends to control the correct flow of the runoff waters and the operation of the pumps installed in the new cell that in both cases are evicted by the ditches network to the storm rafts for their treatment in the Bailín purification plant. The winds regime during the dismantling works period of the landfill (Stage 2) presents a daily scheme in which the valley warmth influence provokes NW-SE winds during the days and winds of SE-NW direction at the end of the day and during the night owing to its cooling. The winds have been of moderated speed between 0 and 10.6 m/s. Depending on the wind regime function, the GRIMM continuous particles measurer that was incorporated by the Project Management as an additional monitoring measure for the surveillance of the air quality, has been located in the West limit of the black action area that is also the limit of the works with other industrial activities that take place in the valley, which has allowed the determination of the stopping and/or slowing down of the works to minimise the particles dispersion.

Surface waters

The generated runoff in the work area among both landfills (fig. 1) and the roads are drained thanks to the ditch that directs all the flows affected by the pollution to stormrafts, for their ulterior treatment in the Purification plant. During the dismantling, concentration of 50 mg/l were reached, which made it necessary to reinforce the treatment system of the purification plant.

In the monitoring and follow-up of the surface waters context, the Environmental Monitoring Plan of the works has counted with a total of 14 inspection and sampling points located in important natural or artificial draining points in relation with the possible dispersion of pollutants, in the immediate surrounding of the works (See Figure 1 Location of monitoring points). In the receiving riverbed, the río Gállego, there were two fixed sampling points and up to seven points to monitor the evolution of the water concentration points under the riverbed. During the works period, in the immediate surroundings, only the Bailín Ravine has presented a permanent water sheet. The concentration time of the rain episodes in of approximately 1 hour, and since June, after the rains, the riverbed goes immediately back to its base level after the exhaustion of the underground reserve. In the rest of inspections points, the circulation of the surface water was directly associated to precipitation episodes, with a length of circulating flows scarcely larger than its own precipitation episodes' length. Great part of the sampling campaigns were linked to precipitation episodes.

The surface waters monitoring included the content in HCH isomers. Regarding the results, a uniform behaviour is observed during the monitoring period in the ASP16 located upstream of the activity area with indexes of HCH indicating a background level in the Ravine associated with the historic impact of the location. In the Ravine monitoring points (AFO1 and AFO2) the HCH concentration curves when the time passes present a pat-

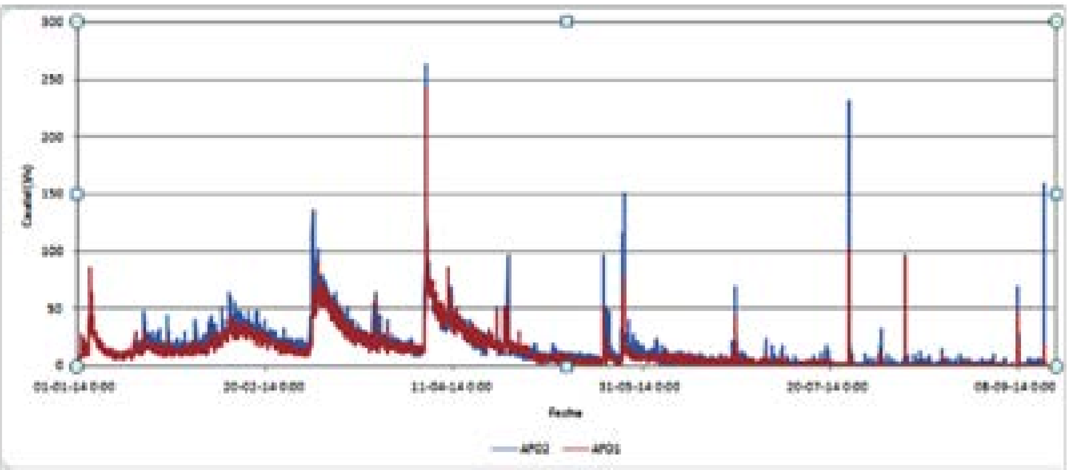

Figure 3. Graduated flow in the Bailín Ravine (AF01 intermediate point and AF02 lower section of the Ravine)

tern with a saw-tooth shape, establishing an apparent correlation between the peak records and the highest intensity precipitation episodes (Fig. 4). In both sampling points, the concentration peaks correspond to punctual registries, followed by fast decreases in the monitoring carried out afterwards. Excluding these concentration peaks, a basal representative concentration line can be esteemed of the Bailín Ravine's conditions during the works in absence of intense precipitation events around the reference threshold established of 50 µg/l of HCH.

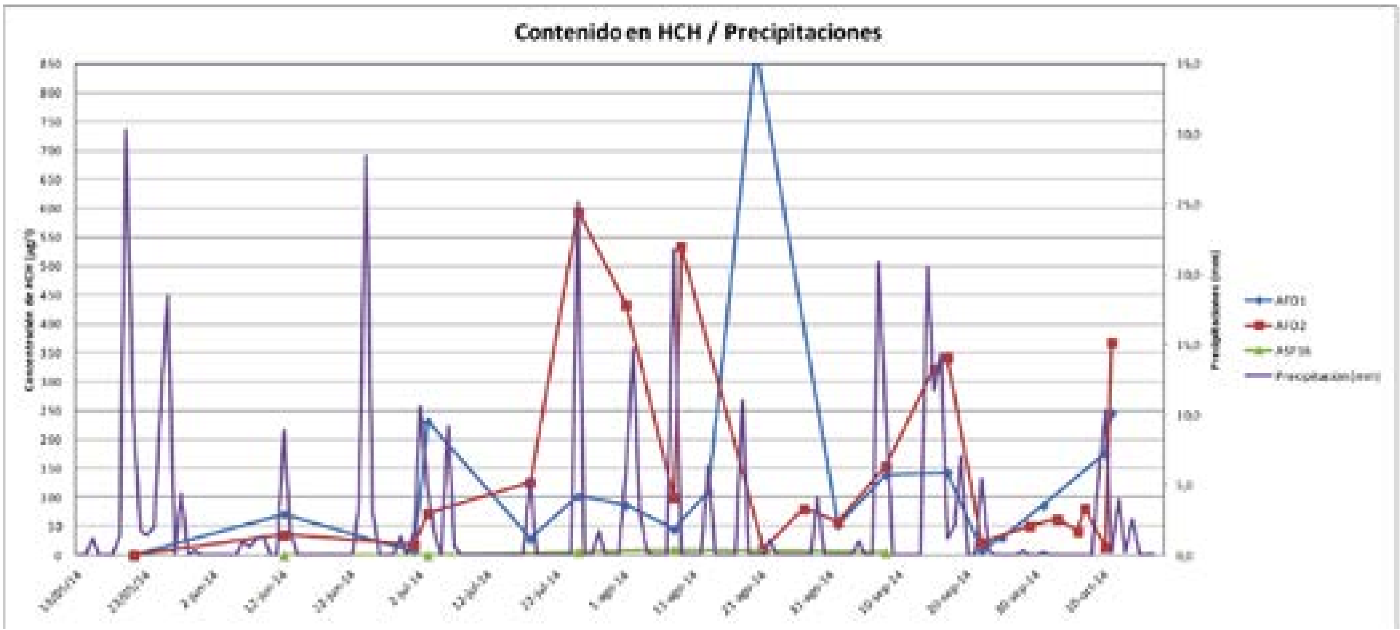

Figure 4. Evolution of HCH in the surface waters in relation with the precipitations

As a consequence, observing the increase of the HCH concentrations base and the punctual increases with the rains, during the dismantling actions of the Bailín landfill, the planned attenuation measures were progressively increased.

The presence of COV in the ravine, outside of the precipitation period is associated with underground inputs, owing to the increase of the reload when discovering the old landfill.

In the río Gállego, 500 m downstream of the mouth of the Bailín Ravine, along the period of 19 May - 29 October 2014, 122 analytic monitoring were carried out (Figure 5). Presenting 99.96% of these samples, HCH concentrations under the alert threshold (5 µg/l), overcoming it in a unique sample taken on 8 September 2014, the intervention threshold value (30 µg/l), established in the landfill Self-protection Plan. After this sampling point, an important dilution of the flow happens, with the intake of the circulating flows through a channel that nourished the hydro-electrical central systems. Despite this dilution, values of up to 1 ppb were reached in the flow, obliging the suspension of the supply of the riverside communities.

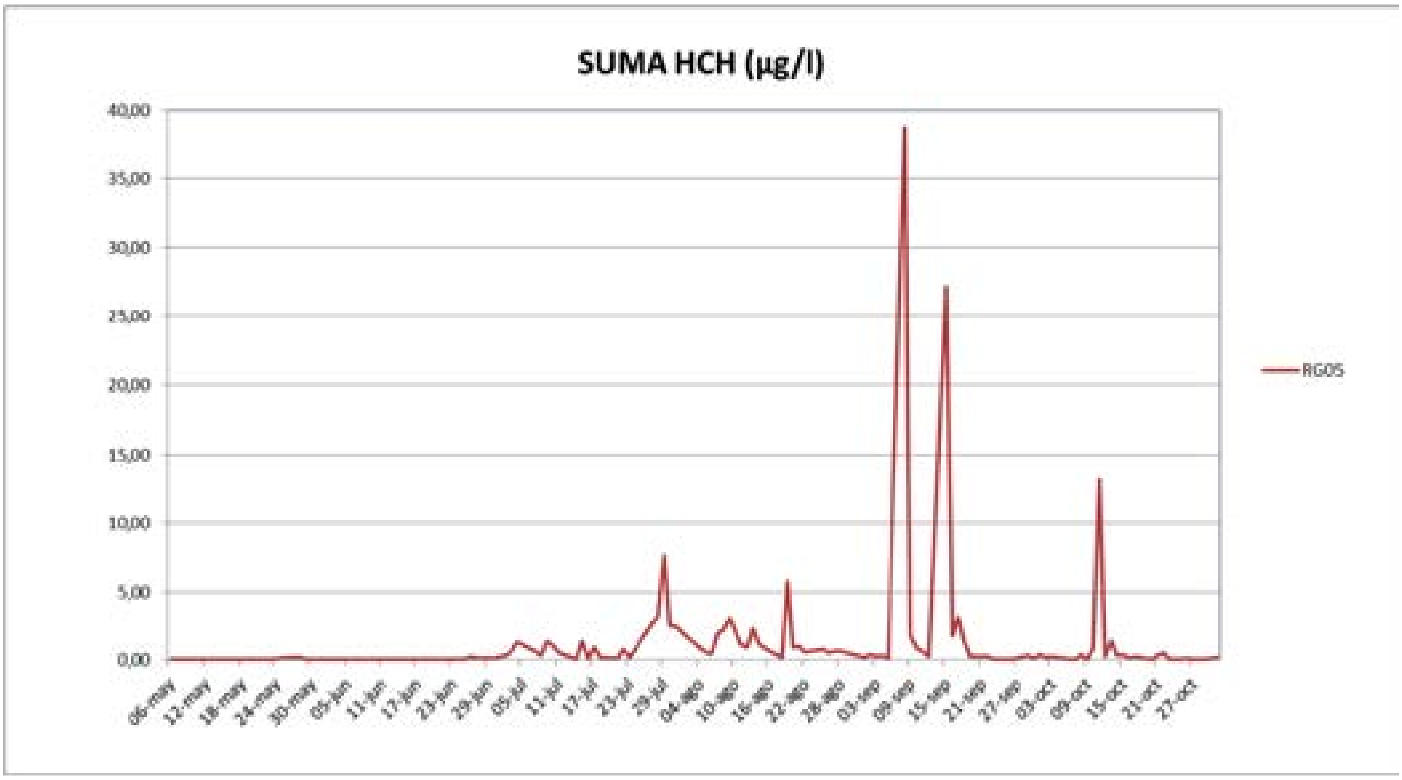

Figure 5. Evolution HCH in RG05 in Río Gállego

Groundwater

The Bailín ravine is part of the south side of the Santa Orosia anticline, with an alternation of sandstone, conglomerates and subvertical shales and with E-W orientation. This formation constitutes a permeable aquifer by fracturing, with low storage capacity and a heterogeneous behaviour. The sandstones and conglomerates more fractured than the shales constitute the preferential circulation roads E-W towards the río Gállego, with a transversal component towards the Bailín ravine favoured by the presence of N-S fractures (Fernandez et al., 1993).

Therefore, the water (and the liquid waste) circulate, mainly, in E-W direction through the permeable strata of sandstones and conglomerates, in the río Gállego direction. The low storage capacity provokes that with efficient rains, the phreatic level increases very fast, which has the consequence of increasing the transversal flow towards the Bailín ravine in the most superficial and fractured zone, as well as the appearance of upwelling when cutting to the phreatic level the topographic surface.

A piezometric and groundwater quality monitoring was carried out in points of the periphery of the dismantled cell and of the new cell that was used to value the level variations and of pollution load and therefore to ensure the watertightness of the new cell.

Regarding the chemical evolution of the groundwater registered in 8 monitoring points in the surrounding of the new landfill, a slight increase of the HCH has been observed (values of less than 5 µg/l with a punctual maximum of 18.76 µg/l in PC5) associated with the particles dispersion during the works.

Soils

In order to know the quality of the soils in the activity areas surrounding before the beginning of the dismantling works of the HCH landfill (Stage 2) a series of soils samples have been taken (11) and the analysis in the laboratory, which except in areas in which an activity was developed in the former stage (Stage I of infrastructures execution), do not show the presence of HCH and/or TPH.

At the end of the dismantling actions, a series of samplings were carried out to defined the quality of the soils and determine the need of carrying out cleaning operations, the areas and depths. The samplings were carried out in the 5 and 15 higher cm, in order to value the importance of the sedimentation of particles and the effect of the leachate in the depth. An important increase in the 5 higher cm was noticed in the transportation roads and surroundings of the landfills in a lateral strip of 5 to 9 m, as well as punctually in the affected sections because of dragging where the depth has been slightly higher.

When the dismantling works finished, the affected soils were taken until the concentrations were lower than 1mg/kg.

Atmospheric monitoring

The atmospheric dispersion, of particles and gases, constitutes one of the most important risks of these kind of actions.

The integrated environmental authorisation established a series of monitoring during the works. This approach supposed that the possible affections would be known afterwards they had happened, once the analytic results of the samplers were available.

Facing this situation, the development of a prevision system was planned. In the first place, a dispersion model was developed for particles and gases, which development is the object of a presentation in this forum (Mantilla et al.). This model was compared with dispersion tests in the placement and with real data at the beginning of the works. With the data observed and the models of the dispersion a simplified model was prepared based on the continuous monitoring with a GRIMM particles spectrometer (See Figure 1 Location of monitoring points), and an action protocol was established depending on the evolution of the concentrations in the GRIMM not to exceed the work values of particles' concentration outside the work's direct zone.

The observance of the dispersion criteria was monitored through 5 PM10 particles high volume collectors and 6 sediment particles collectors, located in significant points of the works surroundings according to the dispersion model.

The atmospheric surveillance is carried out through the analysis of particles in the air, concretely the analysis of the presence of PM 10 Particles, PM 2.5 Particles and Sedimentable particles (>30 µm). The particles of 10 and 2.5 µm size, mobilise to higher distances and are the ones that present a risk for health. The sedimentable particles however are related with the presence and deposition of dust in the surroundings of the work site.

The data continuously taken by the GRIMM (a measurement every 10 seconds) show that the daily average of PM10 and PM2.5 particles has been during the period of the works lower than the legal limit value 50 µg/m3 of PM10 particles and 25 µg/m3 PM 2.5 particles ("Royal Decree 102/2011, of 28 January, in relation with the improvement of the air quality"). The results of the determination of the content in PM10 particles through collectors, confirm that in no case it surpassed the value of 50 µg/m3 daily average of PM10 particles and the HCH content was lower than the reference value of 0.5 mg/m3 (HCH daily exposition limit value established by the INHST .Instituto Nacional de Higiene y Seguridad en el Trabajo).

Regarding the samplings of particles bigger than 30 µm for its gravimetry and speciation, distributed in "white area" (outside the fencing with controlled access) did not exceed 300 mg/m2 day, limit value taken as a reference despite of what is being currently derogated and no other value has been established in the legislation. The HCH content was shown under the reference value of 60 µg/m2 day defined in the IEA in 18 of the 21 campaigns. In all the cases the attenuation measure were maintained and, following the guidelines defined in the protocols, as no outstanding incidences were detected in real time in the GRIMM continuous measurement equipment, the works were not stopped on those occasions, the analysis results term being of 15 days. In any case, the collectors' results were always compared with the continuous data, to validate the results.

The monitoring was complemented with the location of an atmospheric monitoring station in the urban nucleus of Sabiñánigo, which included PM10 and PM2.5 particles collectors. The HCH speciation analysis in this station have been maintained under the analytic detection limit.

Vapour and gas measurements

The monitoring of the gas dispersion was carried out under three scales: work control for the operators of the black zone (zone directly affected by the works), work and environmental control in the surroundings of the works zone in the Bailín ravine, and environmental control in the municipality of Sabiñánigo.

In the black zone a total of four campaigns of hygiene measurements of the workers have been carried out by placing dedicated operators of different tasks a series of impingers or bubblers with specific HCH, benzene and chlorobenzene in period of 4 hours. The reports issued by the Prevention Service indicate that all the measurements are lower to the limit work values and therefore all the positions are complying.

In the surroundings of the work, inside the ravine, 4 work monitoring were carried out following the same protocol that in the black zone, two environmental samplings (July and August) with fixed impingers, and tedlar bags in periods of 4 hours and monthly monitoring with fixed collectors (polyurethane foam) The results shown were under the admissible limit values of hygienic measures for the workers (VLA-ED).

In the urban nucleus two campaigns were carried out (with morning and afternoon samplings) with the same techniques and all the results were under the limits of analytic detection values. In any case, despite the values in the urban nucleus samplings were under the detection limits, it has to be informed that in 4 occasions, with south winds, a smell of "lindane" was detected, which generated some social alert.

Leachate

All the generated leachate on the work site were collected and conducted to storm rafts for their ulterior treatment in the Bailín purification plant, through physical-chemical treatment and active charcoal absorption. The level of leachate in the new cell was monitored every day, carrying out periodical pumping until the purification plant.

During the work, concentration points in the rafts of more than 50,000 ppb of total HCH were reached, the averaged high concentration being 15,000 ppb. These values manifest the importance of the co-solvents present in the waste (methanol, benzene, etc.) and of the particle fraction. To this regard, filters were installed before the entry of the leachate to the purification plant to reduce the particle fraction as well as the pollution load in the water and allow better performance in the purification process.

Corrective measures

During the dismantling works of the old HCH landfill (Stage II), apart from the measures and protection mechanisms of the environment planned in the Project, a series of additional corrective measures have been applied, designed from the evaluation of the results of the environmental monitoring and in order to mitigate the impact of the work on the environment.

The application of the corrective measures has been carried out in conformity with the protocols established with this goal: laying of temporal covering sheet with precipitations and/or wind limits (8mm/day and 11 m/s=40 km/h); protocol for the monitoring of the particles dispersion; management procedure, maintenance and cleaning of infrastructure for leachate and surface runoff evacuation; procedure for the management of affected waters and generated leachate during the works.

In relation with this, the corrective measures carried out during the Stage 2 of the old HCH landfill dismantling are the following:

Attenuation of the dust dispersion measures

- Use of wheel washers at the exit of the area being dismantled and of the new landfill body.
- Use of pulverised water cannons in the excavation points.
- Cleaning with road and plant platforms sweeper of transfer and scale.
- Irrigation of roads and work zones; between 3 and 7 irrigations by turn (approx. 6-14 irrigations/day).
- Cleaning of ditches with water pressure equipment and suction extractor weekly and before and after the rain.
- Alternation in the gorges to avoid the generation of HCH dust, under persistent wind conditions that could generate particles above the limit values (monitoring of the GRIMM).
- Slowing down of the works with the same goal (10 occasions), including the total stop of the excavation works, transportation and waste deposition in the new cell (3 occasions), to stop the particles dispersion.

Surface water management in the work site

- Deviation of non-affected rainwater before its entrance to the action area.
- Ditches in the advancement of the excavation to avoid the waste logging and direct the affected runoffs to the storm rafts.
- Covering of the gorges with a plastic sheet in the precipitation conditions above 8 mm, which was required during 25 days to which add up 29 days in the weekends as a preventive criteria.
- Collection of potentially polluted waters of all the work area, by the ditches/pipes system that direct waters to the storm rafts from where they are pumped for their treatment in the landfill.
- Cleaning of sediments of the storm rafts.
- Punctual pumping of the affected groundwater and subsurface water that appeared in the surface of the old landfill as the waste were being withdrawn. In its case collected with mineral absorbers.
- Leachate pumping in the new cell.
- Maintenance operations weekly of the ditches network and additional monitoring systems of the rainwater and depending on the needs.
- Emergency equipment of two/three individuals in the precipitations' episodes outside of working hours to check and monitor the correct operation of the work site draining network, the filling of the storm rafts and the operation of the installed pumps in low points in contact with wastes.

Temporary covering of exposed areas during the dismantling

It was essential to minimise the contact of the rainwater with the waste, therefore it was decided to temporary cover the work platforms during the rain periods of more than 8 mm/day and/or winds of more than 40 km/h, with pre-cut polyethylene sheet panels and rolled to ease the handling.

Water quality improvement actions of the Bailín Ravine

As a consequence of the apparition of HCH concentration peaks in the Bailín ravine waters that coincide with the strong precipitation episodes, the need to adopt treatment measures of the ravine waters was established at the exit of the working area before its incorporation in the río Gállego. These measures consisted in the installation of two passive filtration systems with activated charcoal (A.C.) in the last section of the Bailín Ravine. One of them consisted in the placement of a series of metallic cells filled with active charcoal that intercepted the ravine flow obliging the water to pass through the inner part of the cells. Its installation supposed an improvement of the water quality, mainly in normal flow conditions of the ravine, even if the precipitation events that would bring fine sediments would reduce its performance.

A second filtering system consisted in two active charcoal filters with capacity of 1600 litres that work at the pressure that the ravine water collector pump brings. The HCH average reduction in the waters measured in the ravine was of 45% (98% analysing directly from the exit of the filters).

Additionally to this ravine water quality improvement action, the withdrawal of fine sediments has been carried out in the flume surrounding and the previous area in many occasions as well as manual cleaning of fine sediments in secondary ravines and the main ravine water inputs areas.

After the works, a water treatment plant has been installed (sand filters and active charcoal filters) at the exit of the ravine, with a capacity of 10l/sec, and the static barrier of the active charcoal has been improved.

Figure 6. Treatment plant. Decanter and washing deposit and static active charcoal barrier.

Surface cleaning of the surrounding soils

Once the work ended the surface of the surrounding grounds of the two landfills, the transportation roads and other defined areas based on the representative samplings of these areas at different depths that have defined the areas and thickness to submit to cleaning operations has been sanitised. Afterwards, the sanitised areas were sampled to establish the final quality of the Work surroundings, which has an optimal quality (1mg/Kg).

In the surface of the old Bailín landfill, once the waste retired, additional sanitising tasks of the rocks have been carried out through different procedures: withdrawal of the possible wastes in the slope though retro-excavation machinery and cleaning ladle, breaking of the rock in the areas in which it had contact with HCH waste, manual withdrawal of little fragments of HCH waste (even smaller than 0.5 cm) and sweeping of waste fragments. Afterwards, this surface has been sampled to establish the final quality of the dismantled area surface, observing that even if the stone matrix is maintained at adequate levels (under 1 mg/kg), in the fracture zones, the concentrations are high (until 50 mg/kg) and the presence of multiple upwelling conditions that when it is raining the concentration in the runoff is close to 10,000 ppb.

Conclusions

In the Bailín landfill, in order to monitor and decontaminate the aquifer, 65,000 t of HCH isomers and chlorine components associated to the manufacturing of lindane and the degradation of the original components have been transferred to a new landfill.

The dismantling works of the old HCH landfill in Bailín have been carried out with strict observance of the terms planned in the IEA. This requirement was essential to mitigate the potential effects that the transfer of waste in unfavourable weather conditions could have over the environment.

It has been confirmed that the environmental monitoring has been a key tool to modulate and monitor the use of attenuation measures planned in the Project and has allowed to detect the changes that as a consequence of the transfer were taking place in the surroundings and the subsequent implementation of new measures for its monitoring and/or attenuation, measures that were not initially planned.

The modelling of the atmospheric dispersion and the implementation of a prediction system, versus an afterwards monitoring system have been effective tools for the preventive monitoring of the environmental conditions of the site. The incorporation from the beginning of the works of a continuous particle measurement system (GRIMM) has been a basic tool for this preventive monitoring.

The new safety cell, once sealed, has been provided with an improved monitoring network and collection of surface runoff waters, which improves the segregation of flows and will minimise the amount of water to treat, reducing the dragging effects and potential instability.

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SECURITY AND HEALTH PROTOCOLS FOR THE DISMANTLING WORKS IN THE HCH BAILÍN LANDFILL, SABIÑÁNIGO, SPAIN

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Abstract

Dismantling works of the former HCH landfill in Bailín (Sabiñánigo, Spain) and waste relocation into a new security cell have posed a challenge due to the amount of waste to be managed (65,000 tons of HCH containing wastes and 342,000 tons of contaminated soil), the short execution time frame and the need of an adequate level of protection for the environment and human health.

Specific security and health protocols were designed and implemented to ensure adequate levels of protection for the work personnel, as well as providing solutions to optimize performance and ergonomic conditions. The scheme of actions on health and safety during the execution stage of the dismantling work was organized based on three lines of action: 1) Ensuring the site personnel health and safety; 2) Establishment of protection zones and areas of control, by defining a system of white / black to prevent the transfer of pollutants outside the control limits, and 3) Periodic health checks for staff involved, in conjunction with sanitary measures on site.

The selection of adequate personal protective equipment (PPE) was of critical importance to ensure high standards of protection but at the same time allowing an acceptable comfort level compatible with stressful conditions associated with the nature of the works. Selected equipment included a portable breathing assistance apparatus with a pumping device for air influx and two A2P filters connected to a full face polyamide/plyurethane screen. Other PPE garments included the use of a hooded Type 5 and 6 full head-to-toe disposable overall for dermal protection and footwear rubber (Wellington) boots to protect against the influx of liquids.

Working procedures included the installation and use of a B/W unit in order to control the access to the working area, and to provide a systematic procedure prior to access to the potential risk zone. The unit comprised two distinct and physically separate areas (the white or clean area, outside the restricted working area boundaries, and the black area inside the risk zone where all personnel were forced to carry the PPE and workwear).

To monitor the health of workers, two medical protocols were defined; depending on whether the individual intervened directly and continuously in the dismantling works (direct contact protocol), or whether the worker was associated with short, point-type visits (sporadic visits or work without direct contact).

The health surveillance results during and after the works showed no increase in HCH levels for the workers in comparison to those obtained in the initial medical exams. These results proved the overall security and protection plan to be effective, in terms of PPE selection and working procedures. Personnel specialization and workers awareness about the work environment were considered key factors for the project success.

Key Words

HCH, chlorinated pesticide, lindane, health protocols, portable respiration protection system, protection zones, black and white unit.

Materials and methods

The uniqueness of the work of dismantling the old HCH landfill in Bailin, the special configuration of the site and its surroundings, as well as the hazardous nature of the waste present in the landfill, made the implementation of clear lines of action essential to ensure to health and safety of workers.

In order to guarantee the safety of all activities during the

development of the works, a team of specialized staff designed health and safety measures and work protocols to control the exposure of the pollutants to the work personnel and to ensure their safety.
The scheme of actions on health and safety during the execution stage of the dismantling work was organized based on three lines of action: 1) Ensuring the site personnel health and safety; 2) Establishment of protection zones and areas of control, by defining a system of white / black to prevent the transfer of pollutants outside the control limits, and 3) Periodic health checks for staff involved, in conjunction with sanitary measures on site.

Protection of health of workers in the workplace

The choice of the correct personal protective equipment (hereinafter PPE) required to carry out the different tasks was crucial to the success of this work. It was necessary to select PPE garments that combined high standards of protection but were at the same time compatible with stressful conditions (hot weather), mobility (working on steep gradients) and ergonomics (manual/physical work) associated with the nature of the various tasks that were to be undertaken. Therefore, external factors such as the type of work being performed, the hot summer weather forecast, the mountainous terrain and conditions of mobility and work areas were analyzed before choosing the most appropriated PPE.

The respiratory protection system was one of the key elements in response to environmental conditions of the work area (presence of large amounts of dust and volatile pollutants). Further, equipment that was breathable but watertight was required - to allow for comfortable breathing in strenuous situations without hampering visibility by misting protective eyewear. The solution adopted was a portable breathing assistance apparatus comprising a helmet with face fit screen comprised of polyamide and polyurethane to combat against dust, spraying and volatile chemicals. This PPE had two mixed type A2P filters to protect against organic gases and vapors, solvents and particles, and an engine that pumped outside air through said filter to the helmet screen. This configuration facilitated breathing, avoiding the additional effort of forced breathing through filters directly, thus greatly decreasing the feeling of fatigue when performing physical work or walking on steep terrain.

To protect the operator from any dermal contact with the particles, a hooded Type 5 and 6 full head-to-toe disposable overall was selected to act as a barrier against chemical splashes and dangerous particles. Prior to carrying out the work, the option of providing full overalls that provide greater protection against splashes was investigated, since it was likely that organic liquid phases would be encountered during the dismantling process. However, the high ambient temperature and limited breathability of this outfit were key factors that justified their dismissal as standard work clothes, considering that the hot conditions and lack of perspiration could generate an additional risk to the health of workers. In the end, the result was a protection system that adapted to the hot and physical working conditions, but a safe working protocol was defined whereby, in case of detecting non-aqueous liquid phase during the dismantling process, the worker appointed for the treatment of this phase was obliged to change in the locker-room into a head-to-toe waterproof overall resistant to chemical spills before proceeding with the task at hand.

For footwear, rubber (Wellington) boots were chosen to protect against the influx of liquids. A double hand protection system was chosen whereby a pair of disposable nitrile gloves was worn under the outer gloves, that were commensurate with the type of task.

Protection perimeter and control zones."Black and White" Areas.

During the works a Black/White (B/W) facility was designed, used and managed. This facility was of compulsory use for all personnel within the protection perimeter of the site.

The B / W unit defined two distinct and physically separate areas; white or clean area, where to leave personal belongings and clothes, and change to disposable Workwear. Once staff access black area in disposable Workwear there was a PPE check up and also footwear and respirators supply previous access to site.

This B/W facility was divided in three rooms, a first one that provided a first access control, registering workers to enter the site and provided a set of Workwear (disposable overall, gloves, socks and underwear). A second room in the facility was divided in two dressing rooms (male and female), this room was for the staff or visitor to get changed into workwear ad keep personal belongings in their personal locker. And a third room where B/W staff provided site staff with personal artificial respirator equipment for each one and sealed their cuffs with tape. Once correct PPE equipment was verified and breathing equipment was on, entry was allowed to the site. In order to minimize the entry of site dust in the facility, safety footwear was stored in locked containers outside, next to the entry door.

Due to the maximum working time defined in the Health and Safety Plan (4 hours), The B/W facility also served as a restful stay. For this purpose the entry room of the facility was conditioned with tables and benches, coolers, water fountains and air conditioning. Once the statutory hours worked, workers entering from the black zone should conduct a reverse procedure for admission to the work area with a number of additional points. The procedure for re-entry to the white area began with the washing of footwear in a device with pressurized water area located next to the access to the B / W facility, placing footwear in the locked container. Without work footwear, site staff access the facility, turning off the respirator. B/W staff collects breathing apparatus for site workers and proceeds to cleaning external dust and storage them. At that point, worker take of overall, socks and underwear and places them in containers located next to the access door of the dressing room. This process was also standardize, making the inner disposable gloves the latest to take off, avoiding skin contact with the exterior of the PPE exposed to chemical agents. Once in the dressing room, they proceeded to a compulsory shower before proceeding to putting on their clothes. In order to optimize transition times throughout the zones Tyvek suits were made available to the workers, these were called "rest" to be used during rest periods throughout the workday. These overalls had no protective function against external agents, as they can be used within the white area of the installation. These two ways, coming in and out of the site, were repeated again in the next 4 hours and once the working day finished.

A member of staff was in this facility throughout the day and was responsible for registering site staff entry, PPE delivery to staff and storage of disposable PPE and maintenance of non disposable PPE (charging batteries, cleaning, calibration, etc).

Health surveillance program

To monitor the health of workers, two medical protocols were defined; depending on whether the individual intervened directly and continuously in the dismantling work or parallel tasks within the safety zone (direct contact protocol), or whether the worker was associated with short, point-type visits (sporadic visits or work without direct contact).

The first (direct contact) protocol required deadlines to be established for performing routine medical examinations: initially, 40 days after starting work on site, within the black zone and at the end of the work period. In the case of the odd jobs (sporadic visits/work without direct contact), the protocol was similar, but without the medical examination 40 days after starting work: these employees were only required one exam upon starting work and another upon completion. These protocols possessed a number of key medical markers that, if detected, would qualify the workers "unfit" to perform any task within the black area. These incompatibilities included those with respiratory diseases (incompatible with the continued use of computer assisted breathing), skin problems, or pregnant or lactating mothers.

Within this health surveillance program hygienic measures were taken for all personnel involved within the scope of work. For the duration of the work, a total of four hygienic measurements were made, selected from a sample group of no less than 25% of all affected staff working on site. The sample groups included workers that were directly involved in the dismantling work, as well as operators from other partner companies in the area of the landfill, regardless of their access to the black zone. External Prevention Service (hereinafter EPS) hired for these previously defined positions to monitor and analyze parameters were marked after the first measurement and carried out routinely from one week after the start of the dismantling operation. The spectrum analysis measurement program was based on pollutants that had been detected previously at the site (primarily lindane, benzene, dichlorobenzene, trichlorobenzene and policlorobenzene). The measurements were made using sampling equipment coupled to workers during a normal working day. The location of the measuring equipment was available both outside and inside screens breathing apparatus, allowing the comparison of the performance of filters against particulate and volatile organic compounds.

In parallel several environmental measurement campaigns at the site were made, whose results were made known to the EPS hygienists, in order to take into account the findings for the design of the next health surveillance campaign. With these data, the EPS could set new measurements, target certain positions or define additional areas of risk.

The procedures and protection schemes developed formed the basis of standard work during the daily operation of dismantling the old HCH Bailin landfill site. The development work that led to situations had to be analyzed and, in some cases, resulted in adjustments or alternatives to standard protocols. One of the main principle problems was the high ambient temperatures (the work was performed during Spanish summer time) meaning that workers routinely worked under suffocating heat that caused severe perspiration, which was exacerbated by the limited breathability of protective clothing and breathing apparatus. The study of this situation led to several possible alternatives, such as the incorporation of hydration packs attached to the costumes or the reduction of continuous long periods of work in tasks with a significant physical demand.

Portable hydration systems were discarded due to the express prohibition in the security plan to drink within the working area (black zone). The hydration system caused a limitation of movement and was a nuisance when performing certain key tasks during a test. Furthermore, the need to make an opening in the overall to bring the suction of water into the hull screen meant a loss of the watertight protection.

Given the need to facilitate regular hydration to workers without protection and degree of exposure to potential contaminants, we opted for a modification of the work protocol which included increasing the number of short breaks during the workday. Thus, at any time workers could approach the B / W installation and, after shedding the PPE, drink water and cool off before returning to the task. This solution was supplemented with the provision of shaded areas in the work areas that served as a shelter for break times. Note that these solutions applied only to workers on foot, since the machinery and truck drivers had air conditioned cabins to protect them from the hot summer weather.

As an additional element to make the day more bearable to operators, the installation of shaded areas provided refuge spots that could be used at specific times when the temperature was extremely high. Given that the work was carried out in an open space devoid of vegetation, there were no areas of natural shade from the sun. For this reason, a number of occasional rest decks for the workers were installed at defined points of the installation, i.e. vessel dismantling, transfer plant and the new vessel. Although this solution was effective in certain moments, it did not provide definitive results, so the only way to be considered valid was the slowdown of production and increase of partial operator breaks.

In conclusion, the PPE defined for the implementation of the work of dismantling the old HCH landfill in Bailin was adequate, as shown in the results of health surveillance carried out both during the decommissioning and afterwards, since no worker gave HCH values higher than those obtained in the initial medical exams. Similarly, the high temperatures and lack of shade in open areas of the site created significant problems for workers on foot, for which the only measure that was found to be effective for avoiding detrimental effects to their health was to increase the number of short rest breaks each day. This had the knock-on effect of decreasing productivity levels.

Finally, in works of this scale, avoiding contact with contaminants is considered essential, to ensure this, a large enough B/W facility and protocols for management and usage are necessary. This particular installation itself generates an image of a dangerous site work environment, thus all workers were increasingly aware of the correct use of PPE to carry out the work.

DISMANTLING OF THE OLD LINDANE WASTE LANDFILL OF BAILÍN (SABIÑÁNIGO-HUESCA)

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Abstract

In the area of Bailín, in Sabiñánigo-Huesca (Spain), different waste of lindane and other materials contaminated with chlorinated organic compounds were dumped during years on a landfill without the necessary environmental control measures. The old landfill is located on a geological setting that is characterized by an alternation of sandstone and lutites. The local aquifer is a complex fractured system where groundwater circulation depends on the fractures connectivity.

As a result of the waste dumping in Bailín, a serious environmental impact was produced both in surficial and underground media. DNPL and high concentration of dissolved HCH in groundwater, flowing towards the nearby Gállego River, were detected in previous environmental monitoring plans.

After several years in which DNPL extraction and some aquifer control plans were conducted, between 2009 and 2015 an ambitious remediation project has been developed by the Environmental Authorities to eliminate the source of contamination, as a result of which the old landfill has been dismantled. More than 400,000 tons of waste and contaminated soil have been excavated, in-situ treated and removed to a new safe confining cell that finally was provisionally sealed with a geo-synthetic liner. In the work of dismantling several innovative and effective operating procedures they were used, f.e., the waste encapsulation in 14m^3 big-bags suit to the size of the transport lorries.

For the dismantling work, a very demanding environmental control plan has been carried out to prevent significant adverse effects to the environment. These control measures included the use of an in-real-time dust measuring instrument (GRIMM) that allowed taking immediate decisions at work based on the dust dispersion data.
Also, due to the hazardousness of contaminants involved in this project, the most strict safety and hygiene measures for the protection of the workers were adopted.

However, once the dismantling of the landfill, several new environmental problems have been revealed which has forced the completion of additional work.

Key Words

Chlorinated pesticide; lindane waste treatment; selective excavation of HCH contaminated soil; DNAPL recovery; groundwater and soil protection; dust dispersion control; geo-synthetic liner of landfills

Introduction

The Bailín landfill was operated from 1984 to 1991-2. Wastes dumped in the landfill were mainly associated with the activity of INQUINOSA, a lindane-production facility located in the municipality of Sabiñánigo (Huesca, Spain). Other waste present in the landfill included construction and demolition debris, as well as urban solid waste. The lindane manufacturing process needed of an easily accessible point for waste treatment due to process inefficiency and high rates of waste generation, up to 85% per unit of final product in weight. The produced waste included non-commercial HCH (hexachlocyclohexane) isomers and other waste from distillation process with benzene and chlorinated organic compounds.

The Bailín landfill lacked of sealing of supporting surface, leachate collection system, surface run-off drainage or any other protection measures according to the hazardous condition of waste accumulated. The improper landfill construction and uncontrolled dumping procedures have resulted in a major threat for the environment and human health.

Preliminary figures estimated an amount of some 30,000 Tons of solid waste including lindane and HCH-isomers waste. Hazardous liquid waste was also present, with an estimated amount of 1,000 to 2,000 Tons of a mixture of wastes including benzene, HCH and other chlorinated organic compounds.

Lindane is a chlorinated pesticide that has been broadly used as an agricultural insecticide, and also for the treatment of lice and scabies in humans and a range of parasites in livestock. Highly concentrated lindane is hazardous to human health and to the environment.

The Bailín landfill is located in the Bailín ravine also named "*El Paco*" ravine, 2 km southeast from Sabiñánigo. The geological setting is characterized by an alternation of sandstone and lutites. These materials belong to the Guarga synclinal folding system, composed of detritic rocks of continental origin and Oligocene age (conglomerate, sandstone, limolite and lutites). Erosion processes have caused a characteristic structure where rocky outcrops of highly resistant materials (sandstone and conglomerates) in almost vertical layers alternate with depressed areas of softer materials (fine-grained sandstone, clays, lutites and limolites).

The geological setting of the site shapes the complexity of the groundwater hydrology and hinders the contamination control in deep levels. The local aquifer in the sandstone and conglomerate layers is a fractured system that results in an anisotropic and heterogeneous media. Groundwater circulation depends upon fractures connectivity. The almost vertical layers promote vertical infiltration through the fractured media, with a fractures density inversely proportional to the depth. The ground topography causes a high gradient between recharge and discharge areas, with a virtual piezometric surface that correlates with ground contour, and identification of water springs during rainy season.

The HCH landfill of Bailín is on the right slope of "*El Paco*" ravine. The basin has an irregular morphology as a result of the original topography, characterized by the existence of rocky outcrops with lateral continuity along the E-W axe. The aquifer of Bailín is a complex system formed by the alternation of almost vertical sandstone and lutite layers, with a fracture network reaching dozens of meters (see Figure 1).

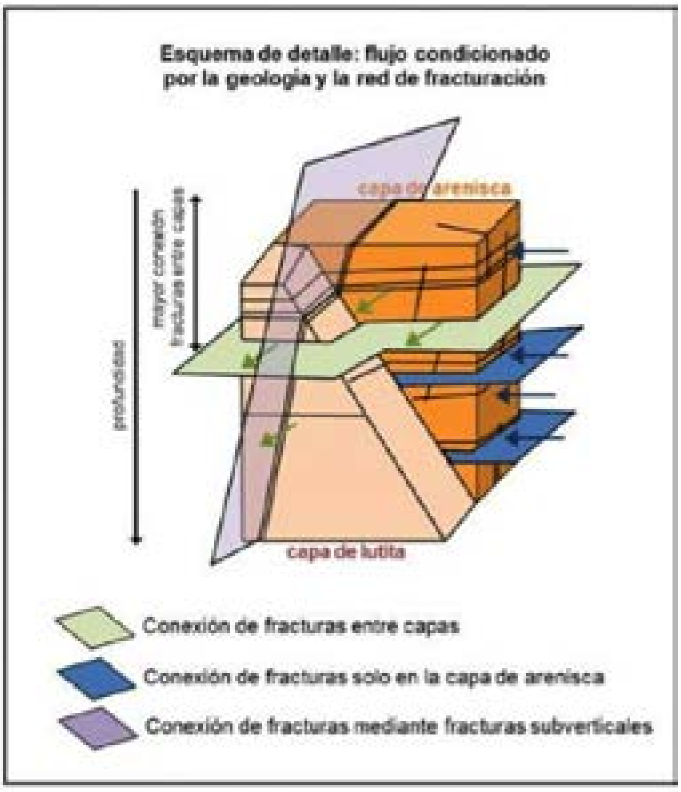

Figure 1 – Conceptual scheme of groundwater flux patterns conditioned by fracture network in the Bailín system. Source: www.lifediscovered.es.

Investigation and monitoring results have identified the contamination pool preferentially located in the sandstone layers. One of these layers, known as M layer, hydraulically connects the landfill with the Gállego River. Orientation and fractures connectivity are critical factors to define recharge conditions, preferential and secondary groundwater flows, plume mobilization and potential migration pathways towards the Gállego River, which is the main discharge point of the system and located 1 km west from the landfill (see Figure 2).

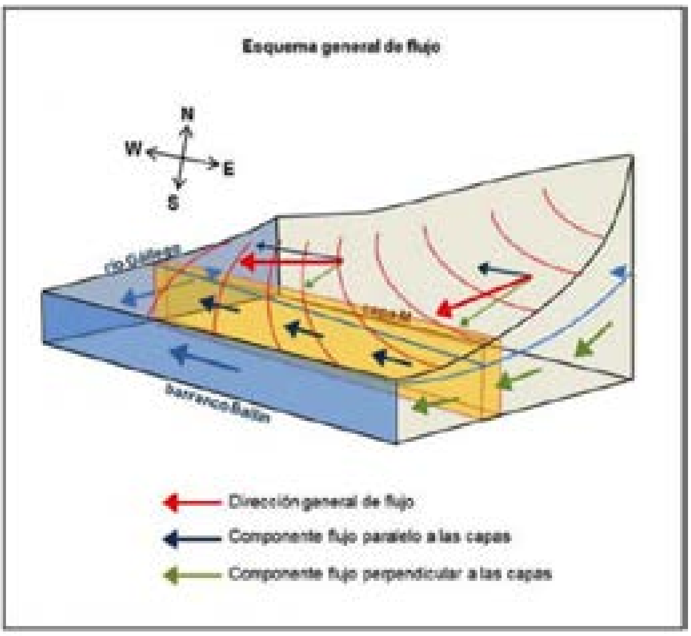

Figure 2 – Conceptual flux scheme for the Bailín system. Source: www.lifediscovered.es.

Materials and methods

Since 1980´s the Regional Government of Aragon has conducted successive investigation and monitoring projects, as well as DNAPL recovery programs to address the environmental issue resulting from the Bailín Landfill and to manage the related potential risks to the environment and human health. In 2009, a public contract is developed in order to safely remove the waste dumped in the former landfill to a new security disposal cell to be built upstream of the "*El Paco*" ravine.

The project scope includes all necessary works to ensure proper confinement and the stability conditions for the wastes to be transferred according national and regional regulations. Specific procedures for waste segregation, handling, treatment and transportation to disposal, were defined, as well as an environmental program to guarantee safe work protocols and to minimize environmental impacts during works execution.

The overall project was structured in three stages:

- Stage 1. It included the construction of the new security cell according to technical specifications more restrictive than those set by legislation. This stage also

included the construction of complementary infrastructures to be used during the waste transfer process, including a waste transfer plant.
- Stage 2. It was focused on the waste transfer process to the new security cell. Works were undertaken in 2014.
- Stage 3. This final stage is not yet ongoing, and it will comprise the removal of the unnecessary infrastructures built during previous stages, and the execution of a landscape restoring project.

The Stage 1, performed between 2010 and 2012, basically consisted on the construction of the new confinement cell, the waste transfer plant and the ancillary infrastructure for the dismantling work.

The design of the new disposal cell included specific reinforcing measures for the safe containment of waste and protection of site, above the requirements of the legislation, focused on groundwater and soil protection, as well as leachate minimization during operation period. So, it has two independent drainage layers for groundwater control, located at different depth, ensuring that the groundwater level is always far away from bottom of landfill. The lining system of the new landfill is a double composite liner, with an intermediate leakage detection layer. Both the top and the bottom liner are multilayer, based on a confinement reinforced pattern of geomembrane, geosynthetic clay liner and geomembrane. The leachate collection and removal system has been divided in three sectors with an independent drainage net, in order to minimize volume of leachate production during the operational phase.

This design, unlike the usual designs of landfills, increases the permeability of the rock substrate with a dual purpose; on one hand to favors the drainage of groundwater, removing them from the base of the landfill to ensure its stability; and secondly, the drained water is leading to a ponds that control the chemical quality, and in the unlikely event that a leaking occurred, the preferred drainage to the control the ponds minimizing contamination of the aquifer.

The transfer plant is a facility, with the waterproof surface, where the different waste is treated for their classification and packing to permit the transport to new cell in proper conditions well as ensuring its stability in the future. This facility has different environmental control systems like: covered loading hoppers with dust dispersion control device, encapsulation machine for powdered waste (big-bags), wheel wash, contaminated surface water drainage, etc.

The Stage 2 performed in 2014 included the dismantling itself of the old waste landfill. All the waste and contaminated soil were transferred to the new confinement cell, and the cleaning up of the original surface underneath the landfill was conducted.
Basically, the works consisted of the selective excavation of the HCH waste and the contaminated soil of the old landfill, its on-site treatment in the transfer plant, depending on the type of waste, and the loading & transport for disposal in the new disposal cell.

The materials that were classified into different categories:
- Industrial waste: powder HCH or mixed with other materials,
- Soil contaminated with HCH,
- Liquid waste from the lindane manufacturing process,
- Semi-solid waste related to one of the lindane isomers,
- Solid urban waste
- Voluminous waste (blocks of rocks, rests of geo-membranes, etc.)

The waste treatments consisted of:
- Encapsulation of HCH powder waste in special big-bag of $14m^3$ capacity, suited to the size of the transport lorries
- Physical-chemical stabilization of semi-solid materials
- Decanting of liquid waste for final elimination in incineration facilities

The selective excavation was carried out in thin layers, no more than 2.5m thick, based on a waste distribution 3D Model developed with data obtained from borings of the Stage 1 and previous works.

Due to the special conditions of hazardousness of waste and contaminants involved in this project, the most demanding safety and hygiene measures for the protection of the workers were adopted. So, all workers and visitors had to obey a strict protocol requiring that everyone on site was equipped with the necessary personal protective equipment, including respiration mask and wearing working overalls.

During dismantling work numerous environmental control measures were taken to prevent pollutants mobilization, among them:
- “Dry fog” dust suppression systems.
- Monitoring devices for dust dispersion control, including an in real-time dust measuring instrument (GRIMM).
- Protocols for temporary covering of the excavation areas under adverse weather conditions.
- Systematic cleaning of roads and other paved surfaces, and watering of unpaved surfaces.
- Groundwater and surface water monitoring plan

The polluted water during the dismantling operations was taken to a storm water tank, from which it was pumped to the existing water treatment plant, located on the site.

In the dismantling procedure, among others, the following materials were excavated, treated and disposed:
- 65,000 tons of industrial HCH waste
- 342,000 tons of contaminated soil
- About 14,000 tons of voluminous waste
- Approximately 325 tons of semi-solid material

- More than 450 tons of solid urban waste.

In addition, more than 7,000 tons of surface rock were broken with hammer, excavated and disposed in the new cell. Finally, more than 30,000m2 of old landfill surface were cleaned by hand.

After finishing the dismantling work in October 2014, the new disposal cell was provisionally sealed with a geo-synthetic liner. The definitive sealing will be undertaken in the future in the Stage 3.

Thanks to the activities and works conducted during Stage 2, the surface of old landfill stayed free of waste and contaminated soils but several environmentally problems were revealed due to that works had changed hydrogeological conditions. So, in 2015 several additional actions were performed to improve the environmental safety conditions of the area: the rock surface was covered with gunite to reduce the surface water infiltration, the capacity of the surface drainage system was increased to absorb large rainfall and several groundwater upwelling points were directly connected to the drainage system to drive the waters to the treatment plant. In addition, other actions were carried out in order to increase the capacity of treatment and control of the potentially contaminated waters, for instance, a bigger storms tank was constructed and a water filtering plant was designed and installed close the "*El Paco*" ravine.

Results and discussion

As conclusion of the work, mention should be that the actions of dismantling the old landfill Bailín have eliminated the major source of pollution that represented waste deposited there, moving them to final and safe area, using selective excavation and in-situ treatment procedures that have been adapted during the development of the work. In addition, a very demanding environmental control plan has been carried out to prevent that the movement of waste, in a quantity exceeding 400,000 tons, adversely affects the environment. However, once the dismantling of the landfill, several new environmental problems have been revealed which has forced the completion of additional work and have shown that there are still challenges to face in the old landfill of Bailín.

FLOW SIMULATION MODELING OF THE GROUNDWATER INTERCHANGE BETWEEN QUATERNARY AQUIFER AND SABIÑÁNIGO RESERVOIR

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Abstract

Groundwater contamination by Persistent Organics Pollutants, henceforth POP, is a major problem in the surrounding areas of Sardas landfill, in the Sabiñánigo region (Aragón, Spain). In the nineties decade, the landfill was abandoned and superficially sealed. Some years later, a road was built through the toe of the landfill, resulting in the removal of impacted material which was deposited at an unprepared site down-gradient and adjacent to the River Gállego Reservoir. The building of the road through the landfill, involved the installation of a slurry retaining wall, both to provide slope stability and to serve as a hydraulic barrier in order to retain the leachate.

The aforesaid reservoir is down-gradient to the site and its water rests upon quaternary alluvial materials, consisting of silts, sands and gravels which are linked with the reservoir's level. Both the reservoir and the alluvial aquifer are the principal receptors of the leachate plume.

Water level control network and hydrochemical analyses were performed to assess the quality of the water in the quaternary aquifer level and in the reservoir. A mathematical modeling flow simulation was developed applying the finite difference method. The Model designed deal with the flow as three-dimensional and unsteady. The results obtained include determining the levels of water and a first approach to define the hydraulic interchange flow rate between reservoir and aquifer. The groundwater model software Modflow was used to manage the hydrodynamics of the flow through porous media. Gaining in more in-depth knowledge about the hydraulic behavior of the relationship among aquifer and reservoir is a primary objective, leading to the estimation of the pollutant mass balance coming from the landfill.

Key Words

Groundwater quality; Flow modeling; Modflow; Finite difference; DNAPL

Materials and methods

The Sardas landfill is situated near the town of Sabiñánigo, in the Autonomous Community of Aragón, close to the northern border of Spain with France. This landfill was used for over two decades for the uncontrolled disposal of heterogeneous wastes, from both local industries and municipal urban waste. The total waste volume is estimated at around 350.000 m^3, including organ chlorine waste, Chlor-alkali wastes, wastes containing heavy metals, oils, hydrocarbons and urban waste. This environmental problem is one of the issues of greatest concern in Spain, associated to the presence of DNAPL and lindane.

The landfill is located along a geological ridge structure of folded rock layers. The northern flank of this anticline dips at approximately 30º to the north, while the southern flank is orientated south and is almost vertical. The base of the landfill consists of Eocene marls (*Larrés marls formation*), which is weathered at the surface and fractured in depth.

The industrial and municipal wastes were deposited directly onto the weathered marls without any prior basal impermeabilisation system or a leachate collection system in place. During the period of operation, twenty years, since early seventies decade to nineties, it is estimated that between 30,000 and 80,000 tonnes of HCH in powder form and approximately 2,000 tonnes of liquid waste (Dense non-aqueous phase liquid, DNAPL) were deposited into the landfill. The DNAPL waste is currently seeping as leachate from the landfill to the downstream area.

At the beginning of the nineties, the landfill was abandoned and superficially sealed. Some years later, a road was built through the toe of the landfill, resulting in the removal of impacted material which was deposited at an unprepared site down-gradient and adjacent to the River Gállego Reservoir. The building of the road through the landfill, involved the installation of a slurry retaining wall, both to provide slope stability and to serve as a hydraulic barrier in order to retain the leachate.

The reservoir is down-gradient to the site and its water rests upon quaternary alluvial materials, consisting of silts, sands and gravels which are linked with the reservoir's level. Both the reservoir and the alluvial aquifer are the principal receptors of the leachate plume.

Figure 1. Schematic view of the site

Several campaigns of monitoring water level using data loggers both in the reservoir and aquifer show the existence of a hydraulic relationship. All the oscillations in the reservoir have a quick response in the aquifer level.
Depending on the rises and falls of the reservoir level, an interchange of flow between both systems is taken place. Due to this oscillation, pollutants might be able to reach the reservoir, generating an impact in the environmental quality of the water.

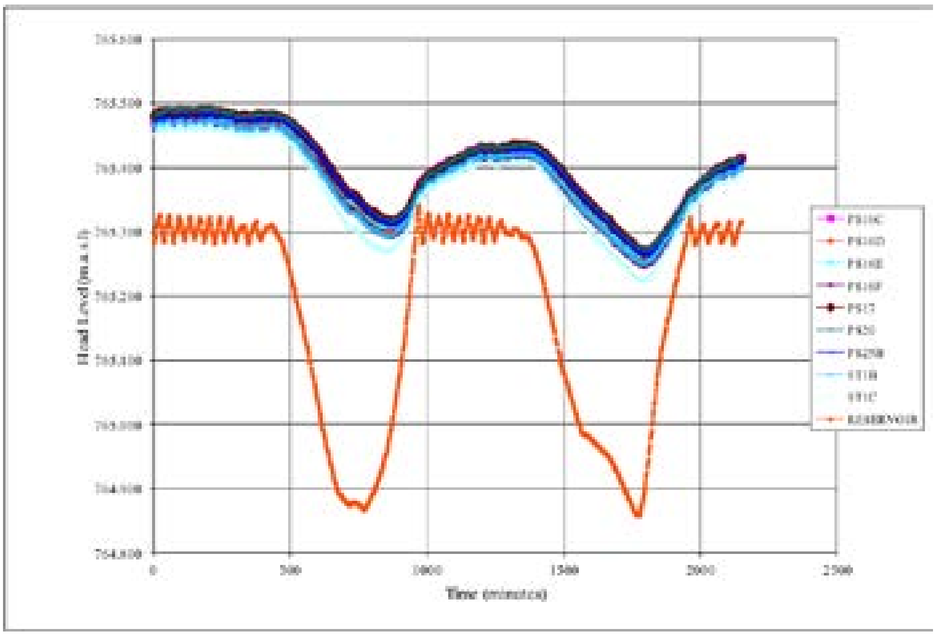

Figure 2. Head level oscillations measured in reservoir and observation points in quaternary aquifer

It was considered as a necessity to develop a flow model to evaluate the preexistent conceptual site model, simulate and calculate the amount of water interchange between both systems (aquifer and reservoir) and, secondarily, to define the mass balance of pollutants provided.
Model assumptions considered to simulate geometry were no flow boundary provided by the presence of marls substrate below quaternary levels, as bottom. Lateral boundaries considering presence of marl substrate and no flow conditions. From top to bottom geological distribution is formed for the presence of fillings, deposited during construction of a road which intersected landfill with an approximate 4 m thickness focused in a central area down the landfill. Clay silt quaternary deposits with a 5 m media thickness, and gravel and sands level from 3m to 5m. According to that, three layers were considered layer 1 (*fillings*), layer 2 (*clay-silt deposits*), layer 3 (*sand and gravel*). The area considered in the model was 400 m x 480 m, divided in 29 columns and 31 rows. The grid design was developed considering different cells size 20x20m, 20x10m and 10x10m.

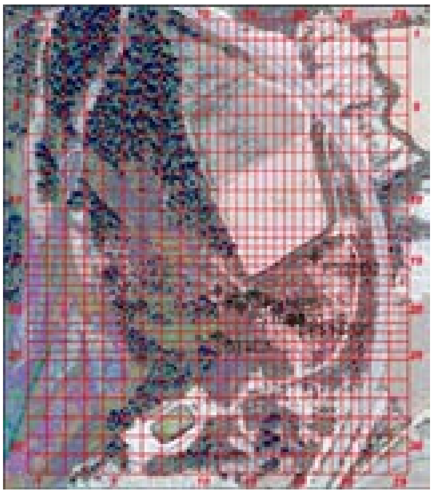

Figure 3. Grid model design

The horizontal hydraulic conductivity ranges, considered in steady state, were $1x10^0$, $1x10^{-1}$, $1x10^2$, measured in m/day, respectively for layers from top to bottom. The recharge from rainfall assumed was 112 mm/year, being increased in the proximities of the roadway (136 mm/year), considered a main way of rainfall recharge. The Reservoir was simulated as a general head boundary (GHB) in layer 2 silts. The conductance assigned was 25 m^2/day for 20x20 size cells, and 12,5 m^2/day for 20x10 cells. A medium head level considered was 765.298 m.a.s.l. Depending level head oscillations in the reservoir, it acts as a discharger of the aquifer or recharging it. In addition, seepage from the front of landfill was considered as an inflow, estimated in 20 m^3/day based on level head changes measured in the landfill control network.

Two pre and post processor based in *Modflow* were used to solve the mathematical models numerically, applying the finite difference method for the solution of groundwater movement issue, being able to predict future changes of heads and changes in flow direction.

After steady state run successfully, the model is prepared to run in transient conditions (time dependent). The heads obtained in the steady state simulation were used as starting values in transient simulation. A simulation period of 2.150 minutes was applied. Simulation time was subdivided in thirteen intervals of time. The model was calibrated using head levels measured with levelogger devices. Nine observation wells and reservoir control point were employed as observation points.

The horizontal hydraulic conductivity ranges considered in steady state were modified in transient simulation after pre simulations in transient state. $1x10^0$ m/day as assigned to layer 1 as general value, except in the seepage area near front of landfill where $1x10^{-1}$ m/day was fixed. General value in layer 2 $1x10^{-1}$ m/day, except down reservoir cells where $1x10^0$ m/day was considered. In layer 3, a general value of $6x10^1$ m/day was considered, with the exception of the reservoir whose value was 30 m/day. The Reservoir was simulated as a general head boundary (GHB) in layer 2 silts. Conductance assigned was 25 m^2/day for 20x20 size cells, and 12.5 m^2/day for 20x10 cells. Seepage from the front of landfill was considered as an inflow estimated in 20 m^3/day based on level head changes measured in the landfill control network. Specific storage assigned from top to bottom layers was 0.006 m^{-1}, 1.8 $x10^{-4}$ m^{-1} cell down active cells in layer 1, 2.0 $x10^{-3}$ m^{-1} cells down the reservoir and 3.0 $x10^{-3}$ m^{-1}. 4.56 x 10^{-5} m^{-1} assigned all layer. Storage coefficient assigned was 3.0 x 10^{-2} layer 1, 9.0 $x10^{-3}$ down active cells in layer 1, 3.0 x 10^{-2} cells of layer 2 and 3.21 x 10^{-4} layer 3.

Results and discussion

The quaternary aquifer in the studied area shows a direct hydraulic answer to head level changes in the Sabiñánigo reservoir. In the simulated period the outflow system reach a maximum 475 m^3/day, with a medium 173 m^3/day. A range of inflow maximum value 362 m^3/day with a medium value 75 m^3/day these values are a first approach to quantify the interchange flow, considering all the size of the model developed.

After run transient state simulation, model was able to play hydraulic behavior in reservoir considering head level oscillations and flow interchange rates between reservoir and aquifer. In 6, 7 and 8 simulation periods when reservoir level was at its peak, interchange flow rate was going down until reaching the hydraulic equilibrium between both media. The time estimated to reach an equilibrium was six hours.

The results obtained allow to confirm a hydraulic connection between both media: reservoir and quaternary aquifer. The behavior predicted beforehand in the conceptual site model considered was confirmed.

The model does not reject flow presence in the base level (Eocene Marls), but considering conductivity values contrast with quaternary deposits, this flow may be considered irrelevant in the hydraulic balance.

Water level changes in the system are produced by the filling and emptying processes in the reservoir.

To enhance results obtained in this first approach, some improvements must be taken: increasing the simulation period including several phases of level head rise and fall, testing the model sensibility to surface recharge effect including several rain periods and developing and running a transport model, using specific software focused in main impacted area.

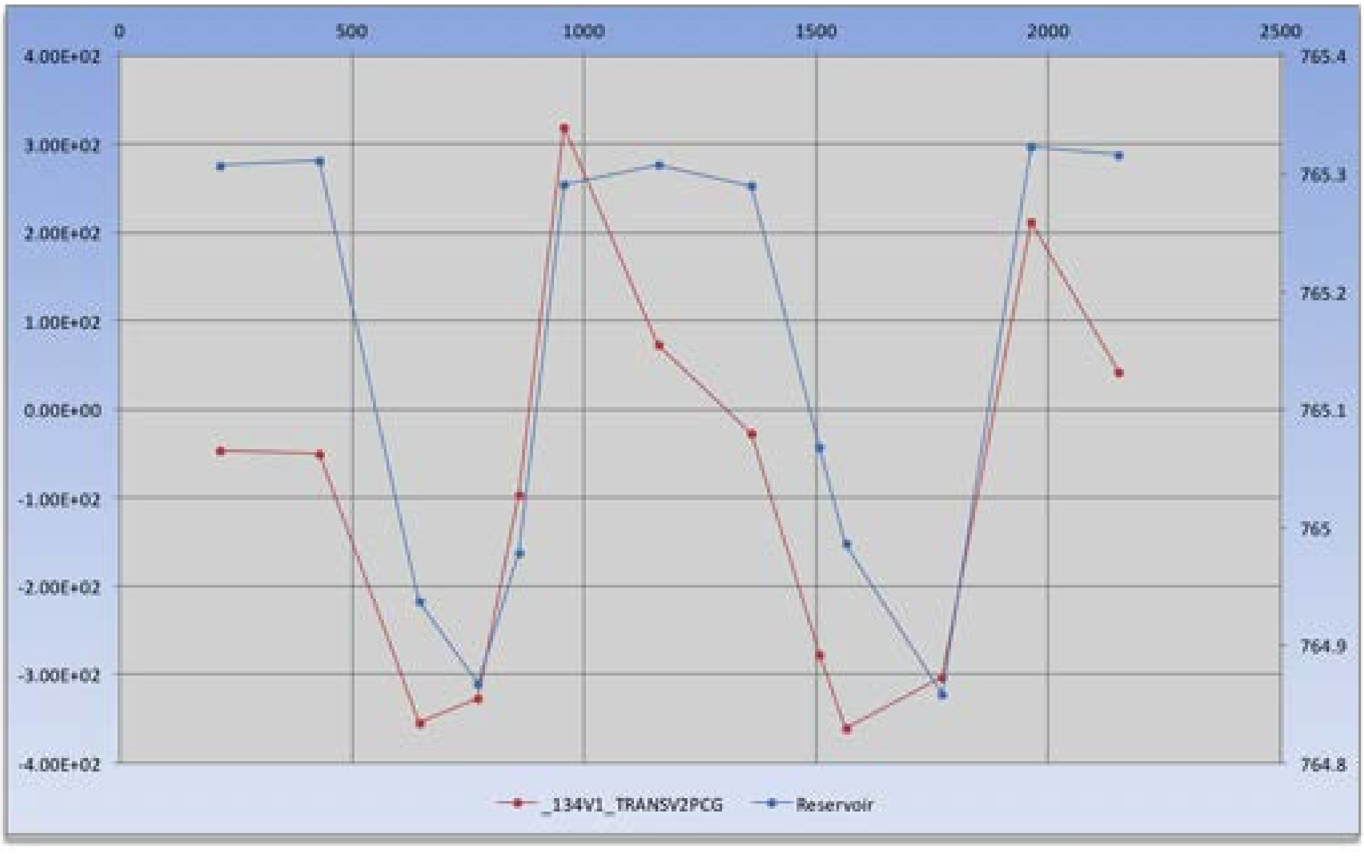

Figure 4. Flow interchange between reservoir and aquifer(m^3/day) vs reservoir's head level changes (m.a.s.l) in time period simulation (minutes).

Acknowledgements

Aragón Government, especially Jesús Fernández with his personal effort to gain more in-depth knowledge of the Sardas site problem, has provided this team the opportunity to develop this investigation.

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WASTE SHIPMENT IN SABIÑÁNIGO (HUESCA, SPAIN) AND ITS EFFECT ON THE GÁLLEGO RIVER CONTAMINATION DURING LATE 2014

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Abstract

Gállego River is a main tributary of the Ebro River, northeast Spain, by the left side. It flows through 192 km from the Pyrenees, at the French border to the city of Zaragoza. Historically has been used for irrigation. At Sabiñanigo city, from 1975 to 1989 the company INQUINOSA (Industrias Químicas del Noroeste) produced the insecticide lindane (γ-hexaclorocicloxane). Its production generates approximately 115,000 tons of toxic waste, which was accumulated in two main dump sites: Bailín and Sardas, both placed near the factory and close to the Gállego River, in addition of an unknown number of minor sites.

Through the summer of 2014, the HCH waste from Bailín dumpsite was transferred to a close and new convenient place. Unfortunately, an unknown mass of HCH waste was spilled into Bailín creek, producing a subsequent contamination to the Gállego River after heavy rains. The use of the public water supply of several populations was forbidden and agriculture and adventure tourism activities were also affected. Water quality was monitored by the Confederación Hidrográfica del Ebro and Gobierno de Aragón.

The present paper analyzes the evolution of the HCH spill in three sampling points located in Gállego River. The first one, named Caseta del Gállego, is situated at the Gallego River, some hundred meters down Gallego River after the Bailín creek confluence. The second and third sampling points are located at 37 and 61 km kilometers downstream at La Peña dam outlet and Ardisa dam (start of the Gállego canal). The relationships between the HCH concentration in these last two sites and that measured in the first one have been studied taking into account rainfall and river flow. This study will serve to understand the pollutant fate and mitigate future contaminant episodes in Gállego River. The work should be considered as a preliminary study. The results show a general relationship between the HCH isotopes indicating a common origin of the pollution. However, the October 10 peak shows an unusual concentration of α-HCH, suggesting a different pollution origin. The velocity of transport of the HCH through the river seems be higher than expected in some episodes. Indeed, it is too sort a forewarning of one day after a heavy rain fall episode, in order to avoid than the HCH pollutans reach the public water supply facilities.

Key Words

Gállego River, HCH pollution, HCH isomers, correlation, linear regression

Introduction

With a watershed of 4000 km^2, the Gállego River is a main affluent of the Ebro River by the left side (Figure 1). The river flows through 192 km from the Pyrenees to the city of Zaragoza. Traditionally was used for irrigation. Log transport, the nabatas, ended at the beginning of XX century when La Peña dam (14 Hm^3) was build. During the XX century a number of hydroelectric facilities, composed by a small diversion dam, an usually long canal and the subsequent chute to the turbines, were also build to supply electricity to cities and the chemical facilities of the city of Sabiñánigo, located in the upper part of the watershed. At 1930, a large diversion, the Gállego canal (90 m^3/sg) was built connecting Ardisa with Sotonera dam, where Monegros channel supplies water for the irrigation system of Riegos del Alto Aragón. It covers more than 130.000 ha and is the biggest of the Ebro valley. From 1970, two big dams (Bubal (64 Hm^3) and Lanuza (17 Hm^3) were built in the upper part of the watershed for irrigation and hydroelectricity.

Figure 1. Gállego River location and studied sampling points. (From Wikipedia and Iberpix)

From 1975 to 1989, the company INQUINOSA (Industrias Químicas del Noroeste) produced lindane (γ-hexaclorocicloxane), by direct reaction of chlorine and benzene. Its production generated approximately 115,000 tons of waste[1], which was accumulated in two main dumping sites: Bailín and Sardas, both placed close to the Gállego River. Inadequate disposal produced the pollution of underground waters that reach the Gállego River[1,3,6]. A number of actions have been performed in order to quantify, and mitigate the problem, but unfortunately is far to be solved.

Through the summer of 2014, the HCH waste from Bailín dumpsite was transferred to a close and new convenient place. See Figure 2. Unfortunately, an unknown mass of HCH waste was spilled by water and/or wind into Bailín creek, producing a subsequent contamination to the Gállego River following heavy rains. The use of the public water supply of several populations was forbidden and agriculture and adventure tourism activities were also affected.

Figure 2. Bailin dumpsites. (From Iberpix)

The goal of the present paper is to give a first approach on the movement of the contaminants through the river.

Materials and methods

In order to asses the effect of HCH spill, a number of systematic analysis were performed at several points at Bailin creek, Gállego River and local water supply facilities by authorities as Confederación Hidrográfica del Ebro (CHE)[2], and Gobierno de Aragón (DGA).

Three sampling points located in Gállego River were selected for the present study. The first one, named Caseta del Gállego, is situated at the Gállego River, some hundred meters after the Bailín creek confluence to the Gállego River. The second and third sampling points are located at 37 and 61 km kilometers downstream at La Peña dam outlet and Ardisa dam (start of Monegros canal). Discharge between Sabiñánigo and Ardisa is affected by the production of hydroelectricity, which uses to be irregular in time. An important percentage of the discharge is diverted through the hydroelectric channels, changing the speed of the flow. No important tributaries are located between sites one to three in order but Guarga, Garoneta Asabón and Subién Rivers may play an important role in dilution during heavy rain episodes. La Peña lake is the only damned mass of water that may play an important paper in dilution of single episodes but it is bypassed through Carcavilla canal. Figure 3 presents a sketch of the studied area, showing the complexity of the hydrology of this reach of the Gállego River.

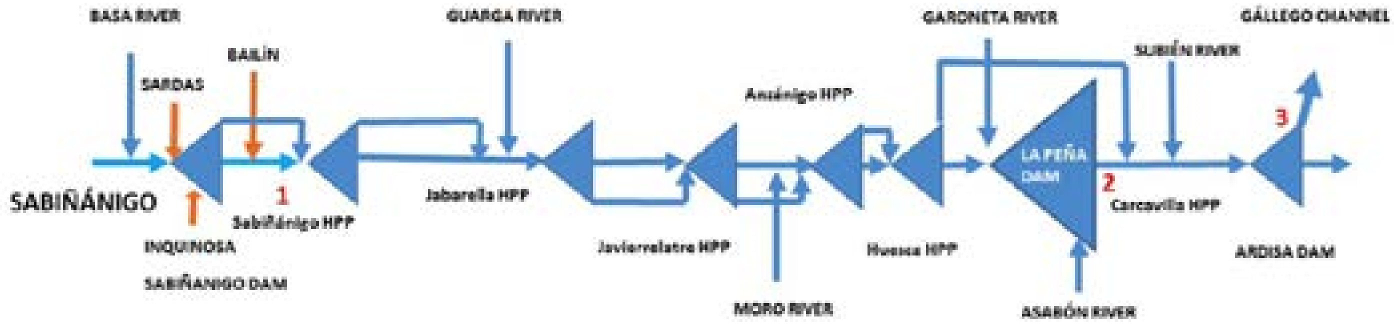


Figure 3. Sketch of the studied reach of the Gállego River. Not to scale.

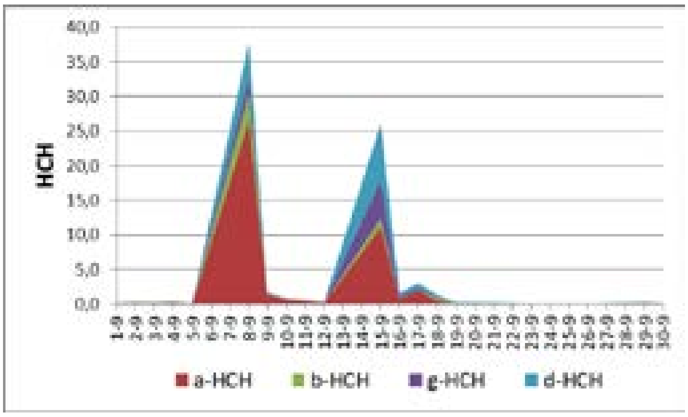
In the present paper, we study the period ranges from September 1st to November 30th, 2014, in which there were four contaminant episodes affecting the environmental state of the Gállego River. Daily samples were kept and analyzed for the different HCH isomers (except for weekends) for Caseta del Gállego sampling site and from every 2 to 5 days for La Peña and Ardisa. The datasets include the concentration of α, β, δ and γ HCH-isomers and their relationships as well as their sum in µg/l in the three mentioned sampling sites. There exist several censored data when the level of the HCH-isomers is under 0.02 µg/l in Caseta del Gállego and under 0.015 µg/l in La Peña (base of dam) and Ardisa. These data are considered equal to the upper limit unless explicitly stated.

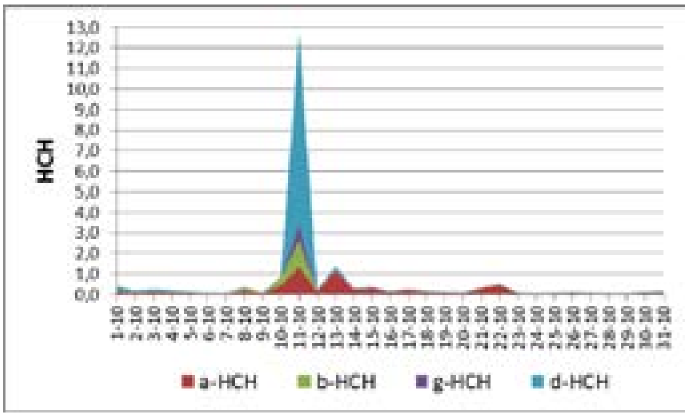
Spearman correlation coefficients are computed for all pairs of isomers concentration since neither normality nor linear relationship of data can be assumed due to the presence of extreme values, which cannot be discarded. If assumed, regression models to represent the linear relationship between isomers would also present heteroscedasticity problems. Statistical analysis has been done with R statistical environment[4] and graphics with Microsoft Excel (2010).

Results and discussion

Figures 3 and 4 show HCH concentration in the three sampling sites. Colors indicate HCH-isomers concentration. Graphs corresponding to Caseta del Gállego are separated by months and scale of the vertical axe is different to facilitate visualization. However, scale is the same in graphs corresponding to La Peña (base of dam) and Ardisa for allowing comparisons. In Caseta del Gállego (Figure 3), maximum values of HCH concentration are over 35 µg/l and 25 µg/l in September; over 12 µg/l in October and over 5 µg/l in November. Maximum values in La Peña (base of dam) and Ardisa are always under 1.4 µg/l but mostly seriously over the health allowed limit 0.5 µg/l[5]. In fact, this limit is exceeded 21.4% of the days in Caseta del Gállego, 38.1% in La Peña and 24.5% in Ardisa.

With regard to the presence of the isomers, concentration of α isomer is usually higher than the rest. Also δ and γ isomers exhibits high values in some periods. The same occurs in La Peña (base of dam) and Ardisa.





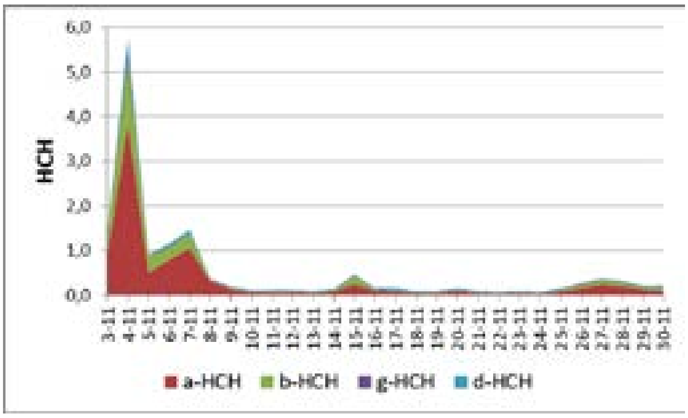


Figure 3. HCH concentration in Caseta del Gállego from September, 1st to November, 30th 2014.

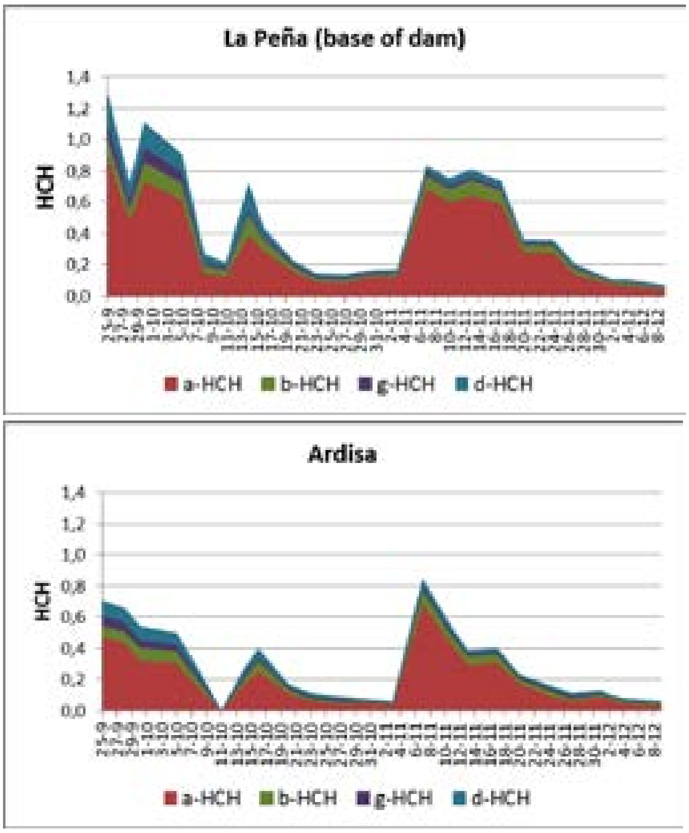


Figure 4. HCH concentration in La Peña (outlet) (left) and Ardisa (right) from September, 25th to December, 9th 2014.

All Spearman correlation coefficients indicate moderate to strong correlation between HCH-isomer concentrations in Caseta del Gállego and very strong correlation in La Peña outlet and Ardisa (see Table 1). They are significantly different from 0 with pair-wise two-sided p-values all under 0.001.

Figure 5 shows sum of HCH in Ardisa and La Peña and the effect of the high peaks observed in Caseta del Gállego, which have been highlighted. The highest concentrations where registered in September 8th (38.8 µg/l) and 15th (27.16 µg/l), but unfortunately our first registers in this month for La Peña and Ardisa are for 25th. Second critical spill detected in Caseta del Gállego occurs on October 11th (13.12 µg/l), which has effect in the concentration registered in La Peña and Ardisa on 14th and 16th, respectively. Finally, in November 4th, 5.75 µg/l are registered in Caseta del Gállego. This peak is replied in November 7th in both La Peña and Ardisa, and even thou in Ardisa the concentration decrease quickly, in La Peña the problem remains at least until November 17th. It is worthy to notice that daily data are used in Caseta del Gállego but not in La Peña and Ardisa.

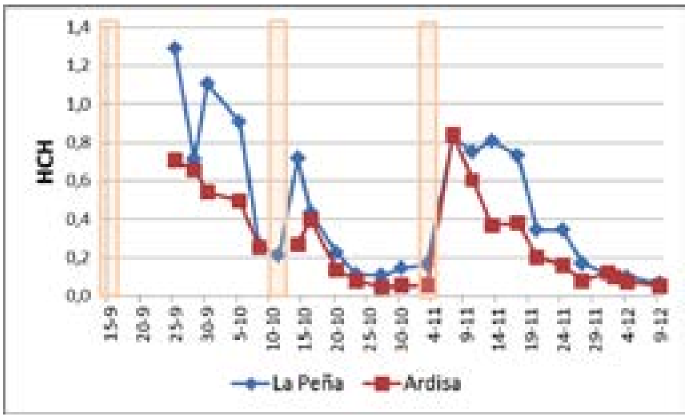


Figure 5. HCH concentration at La Peña (base of dam) and Ardisa. High peaks in Caseta del Gállego are highlighted in orange.

Then, taking this fact into account it can be estimated that the effect of a peak takes from 1 to 3 days to affect the downstream sites considered. For a distance of 37 km between points 1 to 2 to 1, it gives a speed from 12 to more than 37 km/day. The last value is higher than expected for a river to the characteristics of the medium reach of the Gállego River. An average timing of two days between points 2 to 3 means a value around 15 km/day.

Theoretically, the sharp highest values of every pollution episodes from point 1 should to wide the base and smooth the peak values, by dilution, advection and dispersion. Figure 5 shows that HCH concentration in Ardisa is always under HCH concentration in La Peña but very close during the second half of October

Table 1. Spearman correlation matrices for the concentration of the HCH-isomer concentration in Caseta del Gállego, La Peña (base of dam) and Ardisa.

	Caseta del Gállego		
Spearman ρ	α	β	δ
β	0.6557		
δ	0.6337	0.3974	
γ	0.5154	0.4549	0.6110

	La Peña (base of dam)				**Ardisa**		
Spearman ρ	α	β	δ	**Spearman ρ**	α	β	δ
β	0.9293			β	0.9426		
δ	0.8578	0.9259		δ	0.8520	0.9316	
γ	0.8919	0.8912	0.9373	γ	0.7985	0.8705	0.9666

and November. This must be due to the almost nul contribution of the existing tributary creeks between the two sites during a dry period. Evidently, more information is needed on the timing of the use hydroelectric power plant and the relative relations between the discharges through the natural river and the hydroelectric channels.

Conclusions

The work should be considered as a preliminary study. The results show a general relationship between the HCH isotopes indication a common origin of the pollution. However, the October 10 peak shows an unusual concentration of a HCH, suggesting a different pollution origin. The velocity of transport of the HCH through the river seems be higher than expected in some episodes. Indeed, is too sort a forewarning of one day after a heavy rainfall episode, in order to avoid than the HCH pollutans reach the public water supply facilities.

Acknowledgements

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LINDANE AND OTHER ORGANIC POLLUTANTS RECORD IN THE PYRENEAN SABOCOS TARN WATER MASS

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Abstract

High mountain lakes are excellent proxies, or sentinel ecosystems, for assessing the airborne persistent organic pollutants (POPs) impact as they record enhanced POP levels due to altitudinal distillation[1]. Nowadays, production and use of most of those compounds are banned or severely restricted in many countries by several national and international laws and/or treaties (*e.g.*, The Stockholm Convention). This study examines for the first time the occurrence of a large number of airborne POPs in a Pyrenean mountain lake after the 2004-2009 banning enforcement period to use a number of pesticides and chemicals. With the aim to examine POP transport and accumulation dynamics, along with long- and short-term consequences of POP regulated uses, we report concentration levels of 48 POPs (*i.e.,* pesticides, industrial chemicals and by-products) in Sabocos, a Spanish Pyrenees glacial cirque lake, from 2011 to 2014. High resolution analyses were based on Gas Chromatography/Mass Spectrometry techniques, using isotope-labeled standards to obtain the lowest detection limits and ensure results accuracy. Most banned chemicals such as dichlorodiphenyl trichloroetanes (DDTs), aldrins, most polybromodiphenyl ether (PBDE) congeners, endosulfans, triazine and simazine were detected in relatively low and uniform concentrations, whereas chemicals still in use such as BDE-209, terbutilazine, diuron, metolachlor and chlorpyrifos were found in higher and more variable amounts. Sabocos water mass recorded a HCH waste isomers pollution peak in the 2014 summer, related with the HCH residues transfer operation at the nearby (20 km) Bailín landfill site (Sabiñánigo, Huesca province, Spain). All analyzed POPs showed common depth and seasonal trends. Higher concentration levels were reported at the surface water layer when sampled at two different depths. Opposite seasonal trends were found for gas- (higher levels in summer) and particle- (higher levels in winter) phase associated POP compounds.

Key Words

High mountain lakes; persistent organic pollutants; airborne pollutants; altitudinal distillation; organochlorine pesticides; lindane; hexachlorocyclohexane

Materials and methods

Study Area

The Sabocos tarn is a cirque glacial lake located 1905 m of altitude, in the axial zone of the Spanish Pyrenean mountain range (Fig. 1; Universal Transversal Mercator -UTM-, Zone 30, European Datum -ED- 1950, coordinates: 724.800 - 4.730.500)[2]. Sabocos is a medium-large (9.3 Hm^2 of area) and deep (maximum depth of 25.9 m) lake that stores a rather large water volume (1.02 Hm^3). Water inputs calculation brought a mean result of 3.13 Hm^3year^{-1}, with a renewal time of 9.12 months[2]. Details of lake water mass chemical properties and dynamics can be found elsewhere[2].

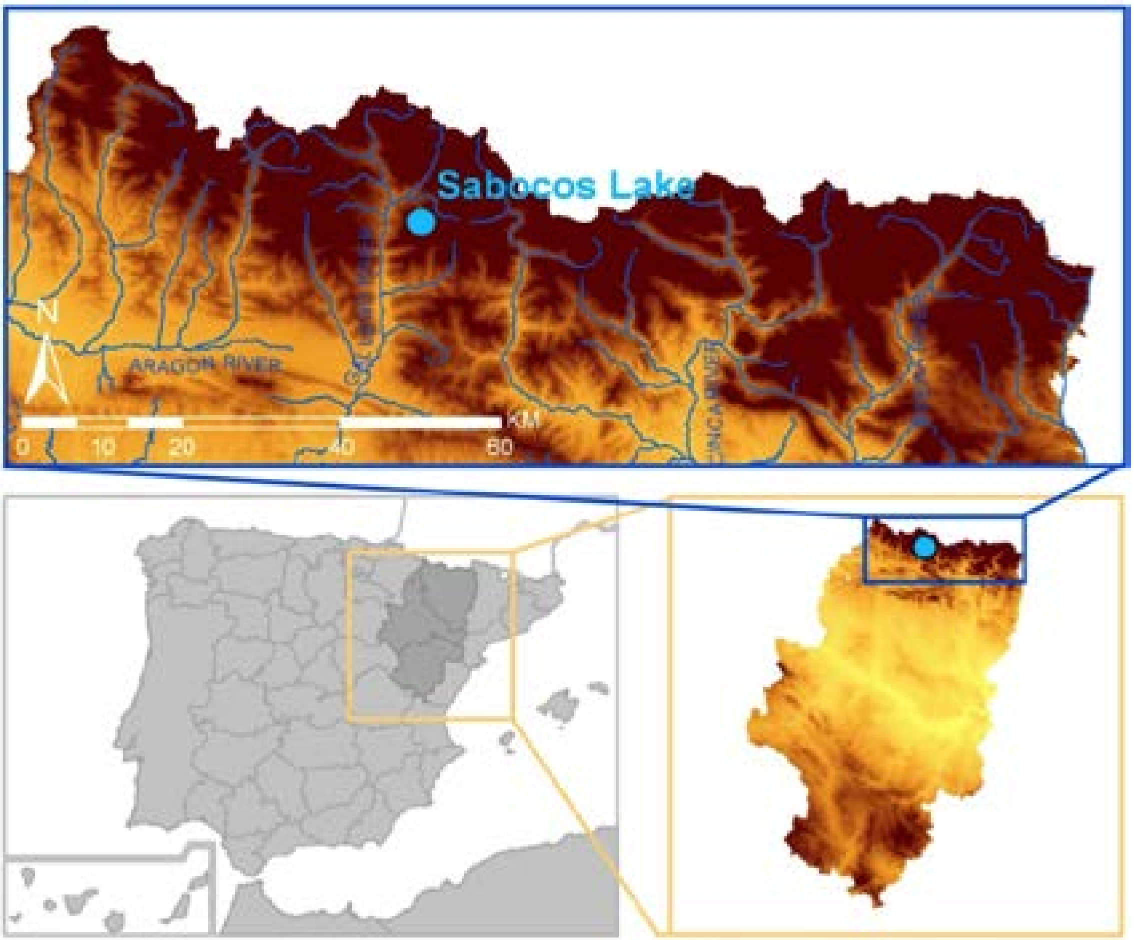

Figure 1. Location zoom of the Sabocos lake[3].

Sampling strategy

Field work was performed on July 2011, July 2012, April 2014 and August 2014. Lake water samples were collected near the lake centre by scientific scuba divers in 5 L Pyrex borosilicate amber glass bottles following underwater scientific and safety protocols[4]. In July 2011, two water samples were collected at different depths to check possible depth variations: near the surface (1-2 m) and at an intermediate depth (15 m). As POP concentrations were higher in the surface sample, only this water layer was sampled thereafter. After collection, samples were sent refrigerated to the Laboratory of Mass Spectrometry-Organic Pollutants in Aquatic Systems, IDAEA-CSIC, for their analysis.

Analytical methods

Samples were extracted based on US-EPA 1625 method and cleaned-up. Prior extraction, a set of isotope-labeled standards was spiked to each sample for quantitative isotope dilution analyses. For recovery checking, another labeled standard set was added to each extract prior to injection. Polybromodiphenyl ethers (PBDEs, 9 congeners), polychlorobiphenyls (PCBs, 7 congeners), and a group of 20 organochlorine pesticides including hexachlorocyclohexanes (HCHs, 4 isomers), dichlorodiphenyl trichloroethanes (DDTs, 6 isomers), aldrins (aldrin, isodrin, dieldrin and endrin) and endosulfans (endosulfan I, endosulfan II and ensofulfan sulfate) were analyzed by High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC-HRMS) using a Fisons 8060 gas chromatograph (Thermo Instruments) and a AutoSpec-Ultima Series V double focusing mass spectrometer, magnet sector (Micromass). Another group of 15 conventional pesticides including organophosphates (chlorfenvinphos, chlorpyrifos, dimetoato, diazinon, azinphos and fenitrothion), triazines (simazine, atrazine, desetilatrazine, terbutilazine), ureas (isoproturon, diuron) and anilines/anilides (trifluralin, alachlor, metolachlor) were analyzed by Gas Chromatography coupled to Tandem Mass Spectrometry (GC-MS/MS) with a Bruker SCION 320 triple quadrupole device. Gas chromatographic and mass spectrometry analyses conditions regarding each compound family have been previously described[1].

Results and discussion

Concentrations levels of the several POPs analyzed in the Sabocos tarn are summarized in Table 1. Compounds not detected in any of the samples were not included in the table.

	July 2011 surface	July 2011 deep	July 2012	April 2014	August 2014
2,4,4’-Tribromodiphenyl ether (BDE-28)	0.002	0.002	nd	nd	0.003
2,2’,4,4’-Tetrabromodiphenyl ether (BDE-47)	0.023	0.018	0.009	0.009	0.015
2,2’,4,4’,5-Pentabromodiphenyl ether (BDE-99)	0.014	0.012	0.003	0.003	0.009
2,2’,4,4’,6-Pentabromodiphenyl ether (BDE-100)	0.005	0.003	0.002	0.002	0.003
2,2’,4,4’,5,5’-Hexabromodiphenyl ether (BDE-153)	nd	nd	nd	nd	0.001
2,2’,4,4’,5,6’-Hexabromodiphenyl ether (BDE-154)	nd	nd	nd	nd	0.001
2,2’,3,4,4’,5’,6-Heptabromodiphenyl ether (BDE-183)	nd	nd	0.002	nd	0.007
2,2’,3,3’,4,4’,6,6’-Heptabromodiphenyl ether (BDE-197)	nd	nd	nd	nd	0.013
Decabromodiphenyl ether (BDE-209)	0.037	0.021	0.009	0.201	0.130
Sum polybromodiphenyl ethers (PBDEs)	**0.081**	**0.056**	**0.024**	**0.214**	**0.180**
2,4,4’-Trichlorobiphenyl (PCB-28)	0.031	0.021	0.013	0.008	0.012
2,2’,5,5’-Tetrachlorobiphenyl (PCB-52)	0.046	0.026	0.024	0.009	0.016
2,2’,4,5,5’-Pentachlorobiphenyl (PCB-101)	0.028	0.028	0.040	0.014	0.015
2,3’,4,4’,5-Pentachlorobiphenyl (PCB-118)	0.041	0.015	0.006	0.003	0.009
2,2’,3,4,4’,5-Hexachlorobiphenyl (PCB-138)	0.057	0.019	0.031	0.013	0.013
2,2’,4,4’,5,5’-Hexachlorobiphenyl (PCB-153)	0.041	0.016	0.019	0.007	0.011
2,2’,3,4,4’,5,5’-Heptachlorobiphenyl (PCB-180)	nd	0.005	0.004	0.001	0.008
Sum polychlorobiphenyls (PCBs)	**0.243**	**0.129**	**0.138**	**0.056**	**0.084**
α-Hexachlorocyclohexane (α-HCH)	0.051	0.025	0.053	0.016	0.460
β-Hexachlorocyclohexane (β-HCH)	0.013	0.008	0.021	0.005	0.073
γ-Hexachlorocyclohexane (γ-HCH)	0.141	0.095	0.138	0.093	0.050
δ-Hexachlorocyclohexane (δ-HCH)	0.022	0.010	0.022	0.008	nd
Sum hexachlorocyclohexanes (HCHs)	**0.226**	**0.138**	**0.234**	**0.122**	**0.583**
p,p’-Dichlorodiphenyl dichloroethylene (*p,p’*-DDE)	0.015	nd	0.016	nd	nd
p,p’-Dichlorodiphenyl trichloroethane (*p,p’*-DDT)	0.019	0.023	nd	nd	nd
Sum dichlorodiphenyl trichloroethanes (DDTs)	**0.034**	**0.023**	**0.016**	**nd**	**nd**
I-Endosulfan	nd	nd	nd	0.010	nd
II-Endosulfan	nd	nd	nd	0.070	nd
Endosulfan Sulfate	0.028	0.011	nd	nd	nd
Dieldrin	0.020	0.014	0.035	nd	nd
Terbuthylazine	2.27	0.81	1.93	0.47	0.32
Atrazine	nd	nd	0.30	0.18	0.09
Desethylatrazine (DEA)	0.47	0.45	0.38	0.21	0.30
Simazine	nd	nd	0.31	0.20	nd
Diuron (3-(3,4-diclorofenil)-1,1-dimetilurea)	1.09	0.92	0.40	0.12	nd
Metolachlor	0.17	0.04	0.31	0.15	0.05
Chlorpyrifos	0.62	0.19	0.39	0.62	0.12

nd=not detected/ below the detection limits

Table 1. POP concentration levels in the Sabocos tarn (units: ng L^{-1}).

Results indicate that chemicals banned in the 1970 decade such as DDTs and aldrins were in the lowest amounts, below detection limits in most of the water samples (Table 1). Only PCB overall concentration levels were higher than expected, although declining trends were detected. More recently banned pollutants such most PBDE congeners, endosulfans, triazine and simazine were detected in rather low and uniform levels. In contrast, currently used chemicals such as BDE-209, terbutilazine, diuron, metolachlor and chlorpyrifos were found in higher and more variable concentrations (Table 1).

In July 2011 sampling camping, all chemicals were analyzed at two different depths and recorded higher concentration levels at the surface water layer sample (Table 1). This may be related to surface air-water exchange at the surface water layer and deep water column stratification processes. Opposite seasonal trend are found for high and low volatility POPs (Table 1). Most POPs present high volatilities and therefore record lower concentration levels in winter due to lower evaporation rates at lower temperatures. Conversely, PBDEs and PCBs show lower volatilities and higher affinity for atmospheric particulate matter, recording higher concentrations in winter samples, due to dust and particle trapping effects by snowflakes[1].

HCH results in this study are particularly intriguing. Although overall HCH concentration levels were rather low during most of the sampling period, a remarkable HCH pollution event was recorded in the 2014 summer (Table 1) caused by α-HCH and β–HCH concentration peaks. Both HCH isomers are the main waste products of the lindane production that took place in the INQUINOSA chemical plant, located in the nearby (about 20 km from Sabocos) Sabiñánigo town (Figure 2)[5]. From 1975 to 1988, INQUINOSA chemical waste was dumped into Sardás and Bailín unlined landfills, near to the lindane production site (Figure 2). Both dumping sites are nowadys among the largest HCH waste deposits worldwide, causing severe environmental pollution in the sourounding areas[6]. As part of the remediation strategy, the Aragón government performed from June to September 2014 a solid residues transfer from the original unlined Bailín landfill to a new secured landfill site located 600 m SE. Therefore, α-HCH and β–HCH concentration peaks recorded in the August 2014 Sabocos water mass samples might be attributed to HCH atmospheric transport consequence of the HCH waste operations at the Bailín landfill site.

Figure 2. Location of the INQUINOSA HCH waste landfil sites[1].

Overall results in this study highlight the importance of POP concentration continuous monitoring at remote sites to investigate levels of these substances into the environment, and the impact and consequences of the use banning policies to POP environmental accumulation and dispersal trends.

Acknowledgements

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A STATISTIC WINDSPEED PREDICTION MODEL FOR THE DISMANTLEMENT OF THE HCH LANDFILL IN BAILÍN (SABIÑÁNIGO, HUESCA, SPAIN)

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Abstract

This study was developed before the Bailín landfill dismantlement in Sabiñánigo (Huesca, Spain) and its waste transfer to a new and safe location. The aim of the work was creating a tool that allowed to prevent extreme wind event effects, which could produce pollution dispersion and which will aggravate the environmental situation in the area.

First, an exploratory analysis of the wind regime of Bailín showed that the AEMET (*Agencia Estatal de Meteorología, Spanish Meteorological Office*) prediction model did not reflect the observed wind speed in the area of interest. Then, a regression model (RM) was developed to downscale the AEMET wind speed predictions, adapting them to the real wind conditions in Bailín. The model provides the wind speed prediction in the Bailín area, 24 hours in advance. The construction of the RM was carried out within the R statistical environment, through the following steps: 1) Study of the useful atmospheric parameters to be included into the model, and construction of a database. 2) Development of a model-building and model-selection strategy (with and without interactions). 3) Study of the prediction ability of the selected models in the area and period of interest. 4) Final best-model selection.

The model finally selected was able to increase the explanation of the real wind speed variability up to a 57%, with regard to the 14% explained by the AEMET predictions. The developed methodology pretends to provide an extensible tool for solving similar prediction problems.

Key Words

HCH, Bailín dismantlement, wind speed, prediction, regression model, particle dispersion.

Introduction

In Spain, one of the main places polluted by lindane is located around Sabiñánigo (Huesca), where INQUINOSA poured around 115,000 mt of organochlorine toxic wastes, most of them as HCH isomers[1,2] without any kind of environmental concerns.

One of the main deposition points was the Bailín ravine, our study area, where from 30.000 to 80.000 mt of solid HCH-wastes[1] were poured between 1984 and 1988, as well as 2.000 mt of liquid DNAPL waste (dense non-aqueous phase liquid). In 2005, the DNAPL was discovered to be percolating towards the Gállego river, which is just 800 meters far away. For that reason, in 2007 the Bailín landfill was decided to be dismantled and transferred into a safe location at a nearby place at the same valley. The construction of the new landfill began in 2010 and had a capacity of 250.000 m^3, enough to keep the Bailín wastes, those that were still inside the old INQUINOSA factory, as well as the polluted soils around Sardás landfill, another point with HCH wastes. The dismantlement and transfer of Bailín landfill was planned to be carried out at the summer 2014, between May and October, when the precipitations are lower. One of the challenges of the process was to avoid the lindane-aerosol dispersion, because of its environmental and health risks[3]. For that reason, the transfer works should stop for wind speed predictions over 40 km/h.

The main objective of this work was to make a statistic model of wind speed prediction, for the Bailín area and for the summer period. This new model was supposed to adjust the AEMET predictions to the Bailín landfill area, and it should be able to show in an instant t_0, the wind speed that will be registered 24 hours after. This paper is organized as follows. The first section presents the dataset and the methodology used; then, the main results will be showed. Summary and conclusions are provided in the last section.

Data

Two data base (DB), with data from May to September 2012, were available. The first one contained 22,032 records of observed wind data at the Bailín area. They were collected by a meteorological station situated in the ravine every 5 seconds, and its data-logger generated records every ten minutes. These DB contained records of average and maximum wind speed (in km/h), as well as the corresponding average and maximum wind direction (in degrees) for each ten minutes interval, that means, measured at the same point in time.

The second DB contained AEMET hourly wind predictions for the Sabiñánigo area and contained 3,672 records.

Methodology

An *exploratory analysis* was developed to study the behaviour of the Bailín wind regime and the predictive ability of the corresponding AEMET predictions. First, a pre-treatment and selection of variables will be done; then, a comparison of the real and predicted wind regimes, as well as of the season and daily cycles. The analysis will be carried out by using different graphics and wind roses. The results will also be contrasted by a correlation analysis between pair of variables.

Then, some *regression models (RM)* will be fitted in order to downscale the available AEMET predictions to the area and period of interest. The models will be constructed with an adequate transformation of the observed-wind-speed as response variable and 31 potential useful covariates, which are described in Table 1, associated with the wind speed and direction prediction, as well as harmonic terms that reflect the seasonality and daily cycle.

A methodology was developed to construct those RM and to select the best one, namely, the one that offers the best forecast. That methodology included the next steps:

1. Construction of models, which includes: a) Study and construction of potential-useful-variables. b) Study of variable transformations. c) RM construction strategy, including stepwise for terms-selection. d) Study of linear and non-linear effects of covariates. e) Goodness-of-fit criteria based on adjusted R^2, number of covariates and the result of ANOVA tests.
2. Study of the adequacy of the selected models, carried out by cross-validation.
3. Best candidate-model selection, following different criteria.

Results and discussion

Exploratory Analysis

The exploratory analysis studied the differences between the observed and predicted DBs, being noteworthy the difference between their wind speed records, which was anyway expected because of the smoothing of the AEMET model.

This first analysis showed the existence of different wind behaviours during the day, with a maximum value at 15 hours and a minimum at 8 (both in the observed and predicted DB, see Figure 1 left). It was also observed that the seasonality of the real records was not correctly captured by the AEMET predictions (see Figure 1 right). For a deeper study of that wind daily cycle, the wind speeds during the day (8 to 19 hours) and the night (20 to 7 hours) were compared, paying special attention to the day times, since it was when the dismantlement process at Bailín landfill would be carried out. It was observed that during the day time and for wind speeds over 20 km/h, just 10% of the AEMET predictions were accurate; however, they worked correctly for the night period (see Table 2). The difference between the wind directions was studied by wind roses, which showed a slight phase-shift between real records and predictions (see Figure 2).

The difference between real and predicted wind directions was checked through a correlation analysis, obtaining a maximum autocorrelation at lag -2 (see Figure 3 left). That result implies the idea of creating "new" covariates from the AEMET wind speed and direction predictions, 4 hours around the point of interest (t_0-4, t_0+4), since for that time interval the cross-correlation stays over 0.2 (see Figure 3 right).

Source	**No. of covariates**	**Covariates**
AEMET **Wind speed** prediction	**9**	
	1	*x* at t_0.
Delays	4	*x* at t_0-1, t_0-2, t_0-3, t_0-4.
Forwards	4	*x* at t_0+1, t_0+2, t_0+3, t_0+4.
AEMET **Wind direction** prediction *wd*	**18**	
Sin and cos of the first harmonic[(a)]	2	*sinwd* and *coswd* at t_0.
Delays	8	*sinwd* and *coswd* at t_0-1, t_0-2, t_0-3, t_0-4.
Forwards	8	*sinwd* and *coswd* at t_0+1, t_0+2, t_0+3, t_0+4.
Daily cicle	**2**	sin(2π *hour* /24) and cos(2π *hour* /24)[(b)]
Seasonality	**2**	sin(2π *day* /366) and cos(2π *day* /366)[(c)]

[(a)] The first harmonic of the wind direction prediction is 2π *wd* /360. [(b)] *hour* stands for the exact time the data has been registered. [(c)] *day* stands for the day number the data has been registered considering that May 1st, 2014 is the day number 123.

Table 1. Variables used in the RM models where the response variable is the observed wind speed in Bailín.

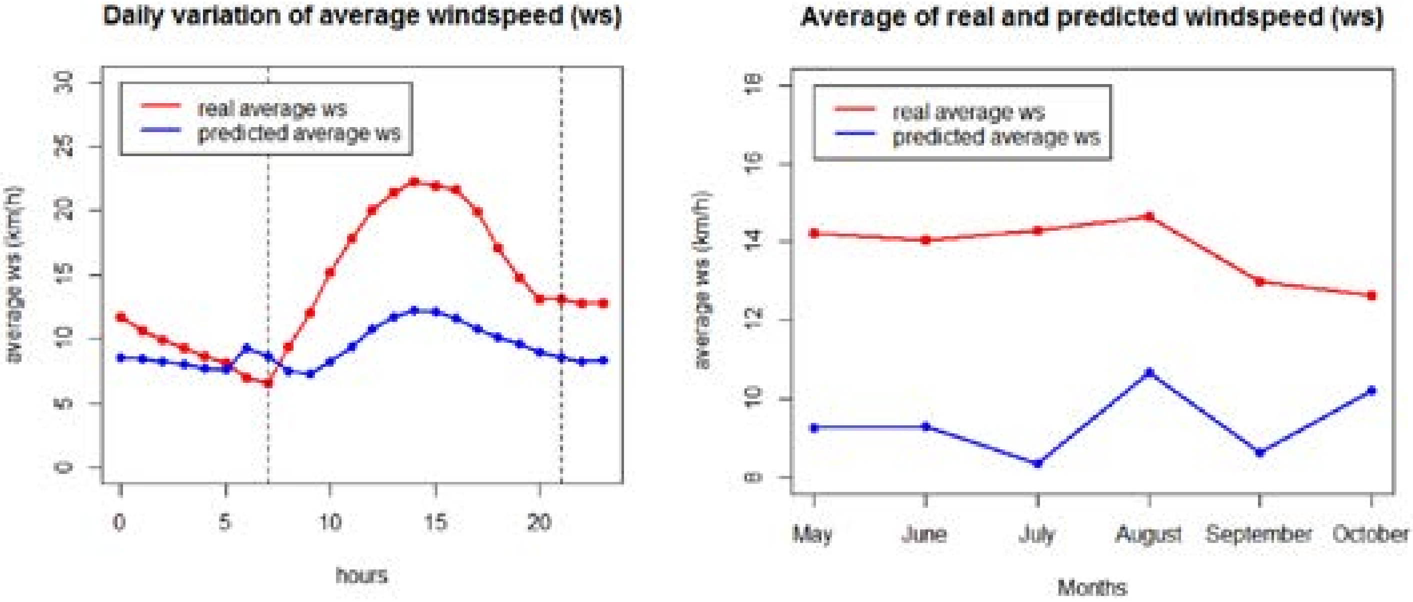


Figure 1. Daily variation of wind speed average (left) and variation during the period of interest (right).

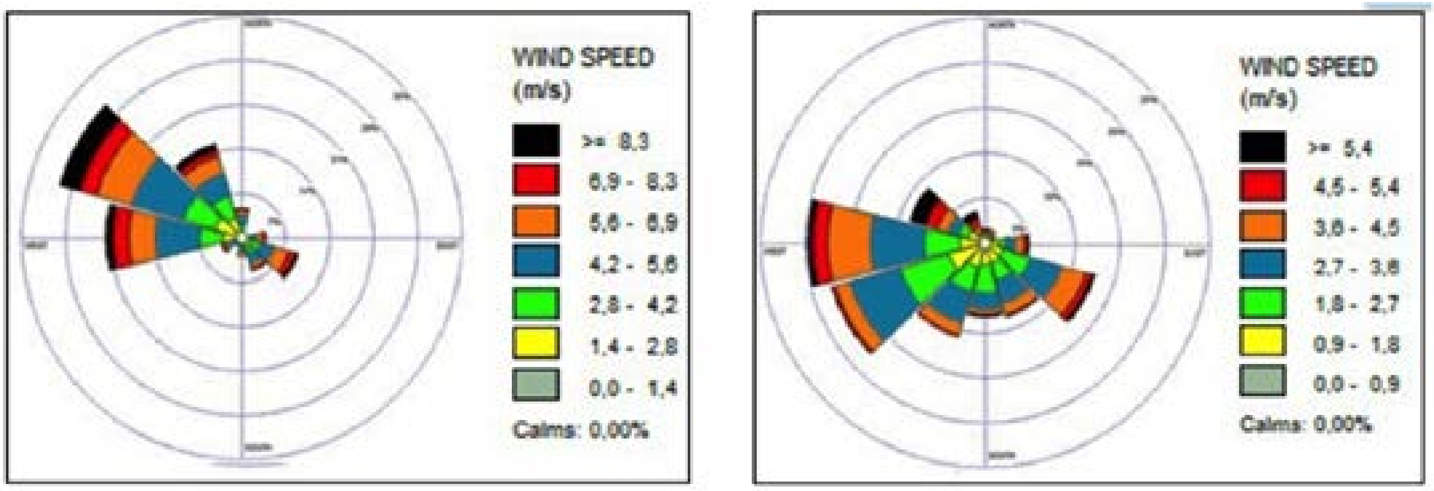


Figure 2: Daytime wind roses. Real (left) and predicted wind speed (right). In order to compare both figures, the smoothing of the AEMET model has been taken into account for the scale.

Daytime	Frequency		Night time	Frequency	
Windspeed interval (km/h)	Observed	Predicted	Windspeed interval (km/h)	Observed	Predicted
5 to 10	-	34.2%	5 to 10	51.7%	27.1%
10 to 15	-	35.7%	10 to 15	24.7%	25.2%
15 to 20	28.0%	11.4%	15 to 20	-	-
> 20	34.5%	3.7%	> 20	14.7%	14.4%
> 30	6.8%	.7%	> 30	1.0%	-

Table 2: Distribution of wind speed in DB with observed data and AEMET prediction, for day and night time.

In general, the exploratory analysis showed a lack of accuracy of the AEMET predictions to the area and period of interest. A new statistic model had to be developed in order to downscale the wind speed AEMET predictions, and it should include covariates that would reflect the seasonality and daily cycle observed at the real data, as well as interaction-terms due to the observed relationship between wind speed and direction, daily cycle and seasonality.

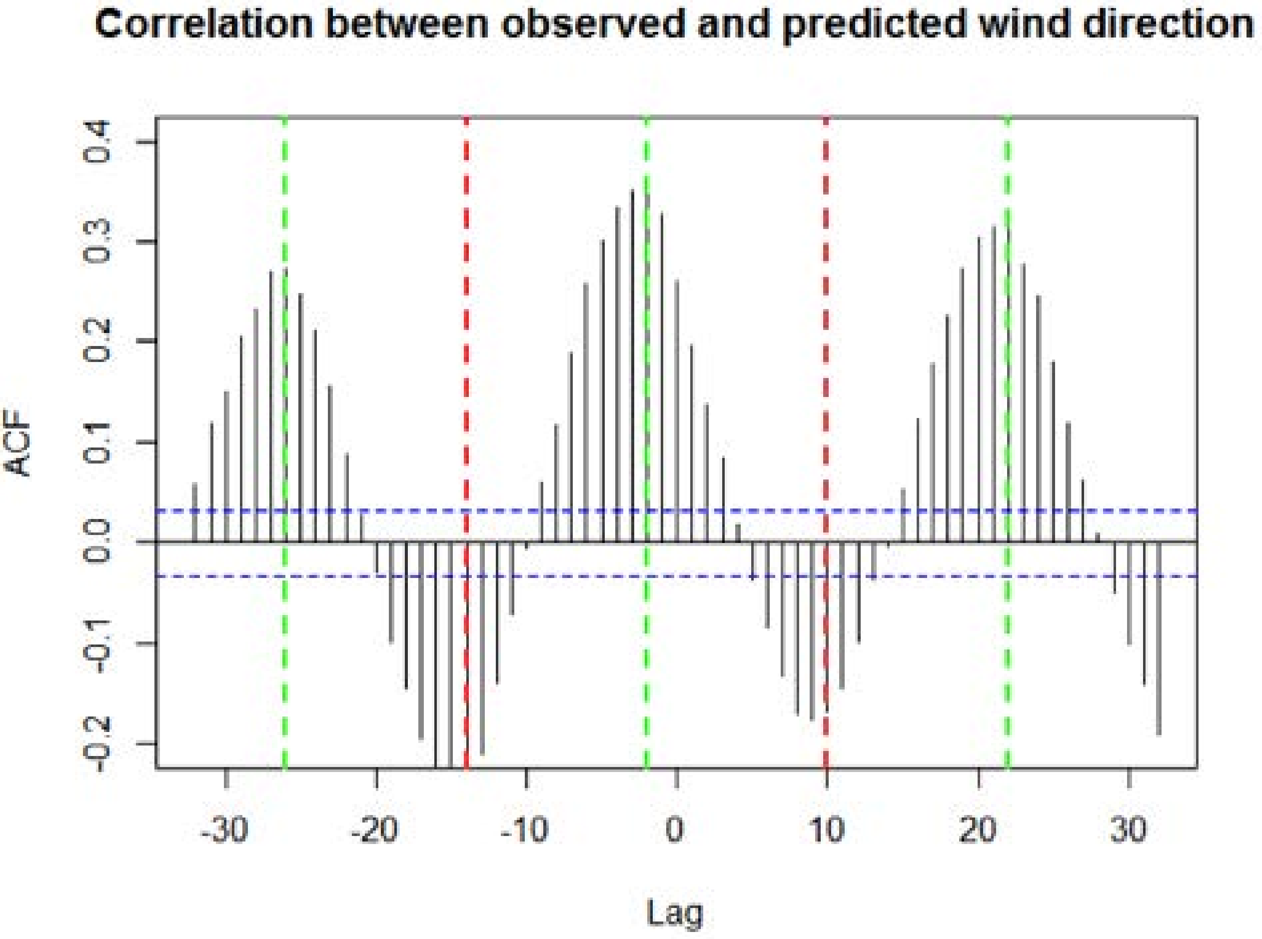


Figure 3: Cross-correlation graph between observed and predicted wind direction (left). Auto-correlograms of real and predicted wind speed (right).

Estimation of Regression Models

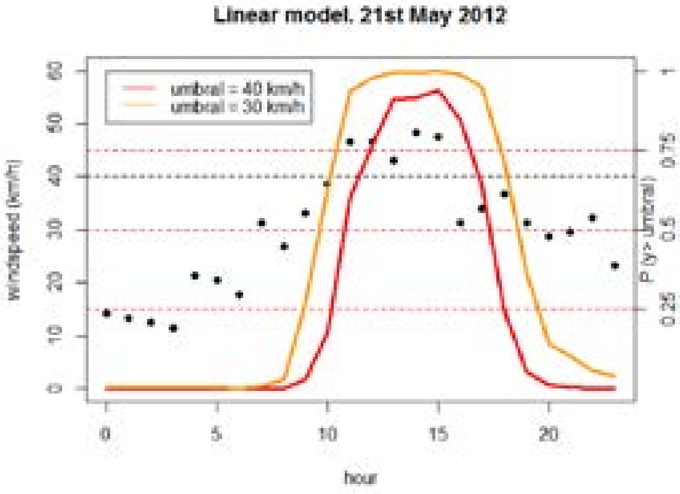
A linear regression model (LRM) between the real records and the AEMET predictions showed their accuracy for the winter but not for the summer (with a goodness-of-fit measure of R^2 equal to 17%). The residual study showed that the model-response should be transformed, and a root square transformation of the response was finally used to develop the new model.

The RM without interactions obtained a R^2 up to 48%. The covariates linked to the wind direction representation were responsible of the 18% of the R^2 increase, while 13% was due to the daily cycle harmonics.

In order to improve the model adjustment, interaction-terms were also included. The use of some loops developed on R statistical language[4] allowed to study a huge different amount of interaction-and-model combinations. The most significant interactions were those between the wind speed and the daily cycle. Also, the use of new harmonics (for the daily cycle and the seasonality) allowed to eliminate some complicated interactions (i.e. triple interactions), to decrease the number of parameters as well as to improve the adjusted R^2 of the models.

The final selection of two models (a linear and a polynomial one) was carried out taking into account the results of different ANOVA tests, the models' simplicity (in terms of number of covariates and interactions) and the models' adjustment to the months of interest (May to September). Both models were validated statistically by a cross-validation process; the difference between the standard deviation of the model and that of the cross-validation was less than 0.7%, which showed that both models would work for a new DB. Also, the residuals were analysed, showing correct linearity and homocedasticity in both models.

In order to select the final best model, the operational work and forecast of both models was studied. The proceeding protocol of the Bailín dismantlement postulates that these works should stop when the wind speed predictions overcome the 40 km/h. That happened 27 times during the period of study, mainly during the day time. As set at the methodology, the models' forecast was studied by graphs (see an example in Figure 4) and classification tables. Both models showed similar results, so the simplest one was finally selected. These model was linear, had 23 parameters (13 covariates and 10 interactions), and was able to explain 57% of the wind speed variability. The judgement of that percentage should take into account the difficulty of working with mountain-meteorological data, whose intrinsic characteristics make its prediction very hard.



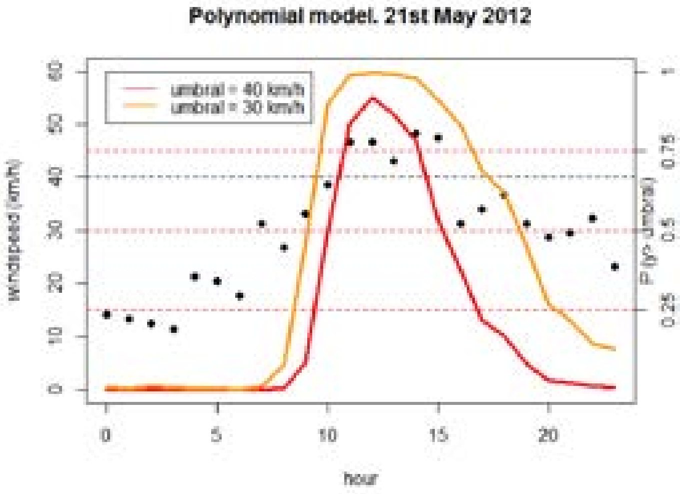


Figure 4: Example of the graphic study of the models forecast at 21st May 2012. Dots represent the hourly observed wind speed, red dashed lines the probability intervals of the models to overcome certain speed thresholds, defined by the colour code. Vertical right scale shows the probabilities and the left one the wind speed.

Conclusions

From the model-forecast study, the following conclusions were established:

(i) In case that the model forecasts wind speed over 40 km/h for at least one hour during the day, it can be assumed that the prediction will come true.

(ii) When the model forecasts wind speeds over 30 km/h, it should be updated with new AEMET predictions, since those observations are susceptible to overcome the 40 km/h limit.

(iii) The model behaviour is not accurate for point situations, as storms. For that reason, is important to pay attention to the storm AEMET forecasts.

As a final review, a methodology of the construction of a wind-speed prediction model has been developed. The finally selected model allowed to downscale the AEMET predictions at Bailín area with satisfactory results. The model pretended to be a predictive tool to avoid the atmospheric dispersion of HCH, which would increase the environmental problems in Bailín area. In situations when isolation measures are not available, the use of statistical models is an alternative to minimize health and environmental risks since instrumental controls during the work of mobilization of contaminants can only propose corrective measures once the unwanted dispersion effects have been produced.

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LINDANE LANDFILL IN BAILÍN (HUESCA): DESIGN, DEVELOPMENT AND PERFORMANCE OF THERMAL TREATMENT TESTS

SUBMITTED PAPER

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Abstract

This paper is part of the treatment laboratory program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located over a complex fractured geological media where lindane and other Persistent Organic Pollutants (POP) were dumped. These compounds have formed a multi-component DNAPL (Dense Non Aqueous Phase Liquid) which has spread in response to the geological layers and the fracture network.

The complete rehabilitation of the site comprises the dismantling of the landfill and the subsequent implementation of subsoil remediation technologies. Within this context, In-Situ Thermal Desorption was identified as a potentially applicable technology for the treatment of source areas (zones with presence of DNAPL within the fracture network).

This paper presents the development and results of the thermal desorption treatability test, which was established as preliminary approach to evaluate the efficiency of this technologies for the treatment of the Bailin's contaminants of concern.

This test was performed using Bedrock and DNAPL samples collected at the source areas. Due to the site rock features and in order to assure the representativeness of the bench test, bedrock cores were spiked using site DNAPL. An exhaustive analytical characterization was performed after the spiking process in order to establish baseline pre-treatment conditions.

Four different tests were implemented with temperatures ranging from 100ºC to 325ºC and treatment periods ranging from 3 to 7 days. A subsequent chemical characterization of the treated specimens, including the all the COCs of the site, was carried out in order to evaluate the performance of thermal treatment. Satisfactory removal rates were obtained for all the families of contaminants present in the site's subsoil.

Key Words

Lindane, HCH, POPs, in-situ, thermal, desorption, ISTD.

Introduction and objectives

This paper describes the thermal treatment program performed within the context of the remediation project of the Bailín's lindane landfill in Huesca (Spain). The site is a former unlined landfill located in the Bailín creek, over a complex fractured geological media. At this location the former company *Inquinosa* dumped, between 1984 and 1992, lindane (γ-HexaChlorocycloHexane - γHCH) and other POPs (Persistent Organic Pollutants), namely: (i) non-commercial HCH isomers; (ii) chlorobenzenes and chlorophenols; (iii) benzene and; (iv) other organics from the lindane production process.

These compounds have formed a multi-component which has spread in response to the geological layers and the fracture network (see Table 1). Since 2004, interim remedial measures consisting of "pump and treat" techniques in the surroundings of the landfill have extracted more than 20 tn of DNAPL and have treated thousands of cubic meters of dissolved phase contamination.

Parámeter	Unit	Value / Concentrtió	% w/w
Density	g/cm^3	1,3662	-
Water (Karl Fischer)	g/kg	2,2	0,2%
COC (GC/MS, FID, TIC)			
Benzene	g/kg	9,4	0,9%
Monochlorobenzene	**g/kg**	**140,0**	**14,0%**
1-chloro-2-Etilbenzene	g/kg	3,6	0,4%
1,2-Dichlorobenzene	g/kg	15,7	1,6%
1,3-Dichlorobenzene	g/kg	2,2	0,2%
1,4-Dichlorobenzene	g/kg	20,5	2,1%
1,2,3-Trichlorobenzene	g/kg	6,1	0,6%
1,2,4-Trichlorobenzene	**g/kg**	**41,0**	**4,1%**
1,2,3,5-Tetrachlorobenzene	g/kg	5,1	0,5%
1,2,4,5-Tetrachlorobenzene	g/kg	5,3	0,5%
1,2,3,4-Tetrachlorobenzene	g/kg	11,1	1,1%
Pentachlorobenzene	g/kg	1,7	0,2%
alpha HCH	**g/kg**	**59,4**	**5,9%**
delta HCH	**g/kg**	**102,2**	**10,2%**
gamma HCH	**g/kg**	**136,7**	**13,7%**
Pentachlorociclohexenes	**g/kg**	**74,3**	**7,4%**
Tetrachloropyridines	g/kg	32,0	3,2%
1,1,2,4,5-Hexachloro-1,5-hexadiene	**g/kg**	**65,1**	**6,5%**
Other organochlorinated compounds non resolvable by chromatography*)*	g/kg	136,1	13,6 %
Total	**g/kg**	**869,8**	**87,0%**

Table 1: *Chemical characterization of the Bailin's DNAPL.*

The complete rehabilitation of the site comprises the dismantling of the landfill and removal of the wastes to a new location, which has been already performed and constitutes the major contaminant mass reduction measure.

As expected, such a challenging site as Bailín, involving organochlorinated DNAPL and extensive dissolved phase contamination in a fractured environment, requires the implementation of remediation techniques for the treatment of residual subsoil impact. Within this context, during the past years (while before the dismantling), a remedial option appraisal has been performed for the fractured bedrock in order to address the most suitable remediation techniques.

The remedial option appraisal started with an in-depth bibliographical review of the "state of the art" regarding remediation of POPs in fractured bedrock. This research confirmed lack of available experiences worldwide, with just a few examples of comparable sites reported.

During the assessment, a limited number of remedial techniques were identified to be potentially capable of successfully treating the complete spectrum of contaminants at the fractured bedrock, driven in part by the complex nature of the mixture: (i) volatile and non-volatile compounds; (ii) differential biodegradation pathways of the COC's - reductive and oxidative; (iii) high contrasts in the physical properties of the constituents (i.e solubility, adsorption potential, Henry's constant); etc.

The identified technologies to be potentially applied, by themselves or forming part of a treatment train at the Bailin site were: (i) thermal treatment; (ii) surfactant flushing; for the treatment of source areas (presence of DNAPL at bedrock fractures) and (iii) ISCR - *In Situ Chemical Reduction* – and; (iv) ISCO - *In Situ Chemical Oxidation,* for plume areas (high dissolved concentrations in groundwater).

Subsequently, a comprehensive program of treatability tests was implemented at laboratory scale. The focus of this program was to evaluate the performance of each technology to address most the contaminants within the mixture.

According to the revised bibliography, thermal treatment proved to be effective for the removal of the most, if not all COC's. Table 2 includes the boiling points of the main COCs.

Compound	Boiling point range (ºC)
Benzene	80
Chlorobenzene **(MCB)**	132
Dichlorobenzenes **(DCBs)**	173-180
Trichlorobenzenes **(TCBs)**	208-220
Dichlorophenols	209-218
Trichlorophenols	246-253
Hexachlorocyclohexanes **(HCHs)**	228-323

Table 2: *Boiling point ranges for COCs.*

In order to evaluate the effectiveness of thermal treatment in addressing Bailin's impact, a specific treatability test was implemented with the following objectives:

- Evaluation of the effectiveness of thermal treatment in the reduction of VOC and SVOC constituents of DNAPL.
- Study of the influence of treatment temperature and treatment duration in the reduction of contaminants of concern.

The bench treatability test included different phases of testing, namely:

a. Bedrock and DNAPL samples collection

b. Preliminary Physical and Chemical Characterization

c. Preparation and conditioning of field samples

d. Determination of the baseline condition

e. Development of the thermal treatment

The current paper summarizes the experimental procedure implemented during the bench scale test performed in the framework of the Bailin's project, as well as the obtained results.

Experimental methodology and obtained results

Samples collection and preliminary Characterization

The first step includes the collection of site bedrock and DNAPL samples to be used during the bench test (see Picture 1 and Picture 2). These samples were taken at the identified target areas for this technology, namely areas where DNAPL is present within the bedrock fractures. Specifically these samples were collected in the landfill body, within the formation underlying the dumped HCH manufacturing wastes.

Picture 1: Bedrock sample

Picture 2: DNAPL sample

After its collection, aliquots of the rock cores were subjected to specific physical and chemical analyses. A summary of these results are recorded Table 3 and 4.

Parameter	Analytical Method	Unit	Result
Density	ASTM D2937	g/cm^3	2,68
Dry density	ASTM D2937	g/cm^3	2,66
Moisture	ASTM D2216	%	0,6
Apparent Specific weight	ASTM C-97	-	2,67
Porosity	Calculated.	%	0,4
Permeability	ASTM D5084	m/s	$< 1 \times 10^{-12}$

Table 3: *Results of physical characterization of the Bailin's bedrock samples*

Compunds	Concentration (mg/kg)
alpha-HCH	3,1
delta-HCH	9,2
gamma-HCH (Lindane)	26,0

Table 4: Chlorinated Organic Pesticides in Bedrock

The physical properties of the rock cores displayed reveal a very dense core with low porosity, water content and permeability. The analyzed rock core didn't show significant cracks or fissures. Regarding chemical properties, HCH isomers are the predominant compounds present in the bedrock (38,3 mg/kg, versus 0,2 mg/kg of the rest COC).

Chemical characterization of the rock core samples revealed significantly lower COC concentrations than expected. Being such an heterogeneous site, the possibility of identifying concentration discrepancies was anticipated and DNAPL samples were collected for rock core DNAPL spiking purposes. Thus, source area conditions were artificially reproduced avoiding further sampling campaigns limited by project economic constraints.

Preparation and conditioning of field samples

Prior to DNAPL spiking, six cores were cut to approximately 15 cm in length and weighed to determine weight and density of the core material. The cores were then placed into a pressure chamber together with an aliquot of the site DNAPL (see Picture 3: Spiking chamber).

Picture 3: Spiking chamber

Spiking of DNAPL was performed under pressurized conditions to increase DNAPL diffusion inside the rock core. For this purpose, an airline was connected the chamber and the pressurized conditions sustained for 2 weeks. After this period the soaked cores were extracted, drained, visually evaluated and then weighed to determine the quantity and extent of DNAPL saturation.

The spiked rock core exhibited staining (Picture 4 and Picture 5) and a weight increase of 2.4 grams (0.25%) when compared to the original as-received

Picture 4: Spiked vs original cores

Picture 5: Detail of spiked cores

Determination of the baseline condition

After spiking, a chemical determination was performed over several rock aliquots to determine the COC content of the cores. Table 5 compares the COCs concentrations in the rock cores before and after the spiking process.

Compound)	Baseline (pre-spiking)	Spiked core 1[a] (post-spiking)	Concentration increase ratio (x)
Pesticidas clorados			
alpha HCH	3,1	42	14
beta HCH	< DL	1,3	-
gamma HCH	26	310	12
delta HCH	9,2	100	11
HCH (sum)	38,3	453,3	12
COV			
Benzene	0,019	0,38	20
Chlorobenzene	0,061	29	475
1,2 Dichlorobenzene	0,020	11	550
1,3 Dichlorobenzene	0,0012	1,1	917
1,4 Dichlorobenzene	0,01	12	1200
1,2,3 Trichlorobenzene	0,01	3,6	360
1,2,4 Trichlorobenzene	0,091	53	582
SCOV			
2,4,5 Trichlorophenol	<DL	2,4	-
2,4,6 Trichlorophenol	0,00034	2,2	6471
TIC			
Tetrachlorobenzenes	-	104,7	-
Pentachlorobenzenes	-	70,7	-
Pentachlorociclohexenos	-	327	-
TOTAL	**38,5**	**1.274**	**33**

Table 5: *Pre and post spiking concentrations (mg/kg)*

COCs concentrations show increases that range from of 1 to 3 orders of magnitude due to the spiking process. The estimated contaminant mass average increase is 33 times the baseline.

Concentration values achieved as a result of DNAPL spiking are considered representative of source areas and are therefore set as baseline conditions for the thermal treatability test.

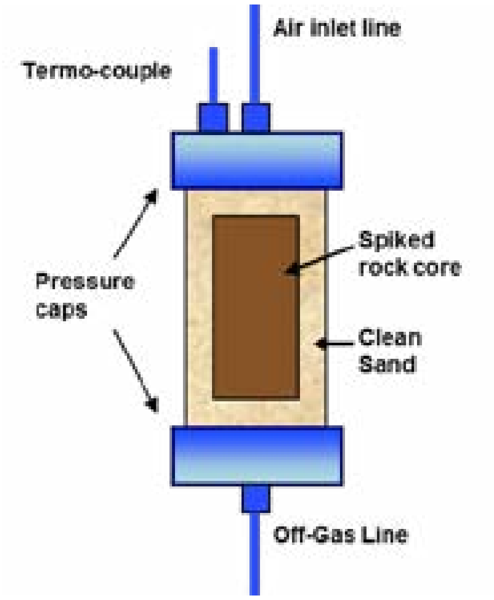
Development of the thermal treatment

Tested temperatures and periods were selected according to the main COCs boiling points ranging from 80 ºC - 325 ºC (see Table 2). The treatability test program is showed in Table 6.

Test #	Duration (days)	Treatment temperature (ºC)
1	3	100
2	7	100
3	7	200
4	7	325

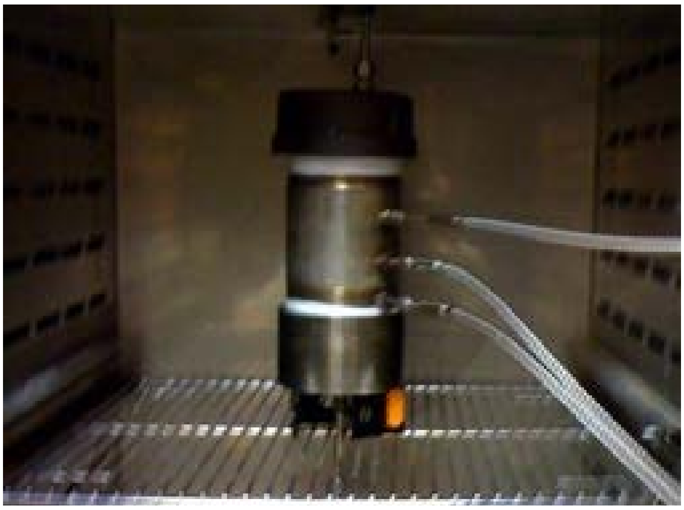
Table 6: *Treatability test program*

Each treatment was tested in a stainless steel cylindrical reactor, were the spiked core sample was embedded within clean sand. Both ends of the reactor were closed with caps, each fitted with ports for inflow and outflow gas lines. The test reactor was placed into muffle furnace for heating. Stainless steel air injection and off-gas tubing were attached to the reactor end caps, and a thermocouple connected to a data-logger was inserted along the body of the reactor (see Picture 6).



Picture 6: Thermal reactor set-up scheme

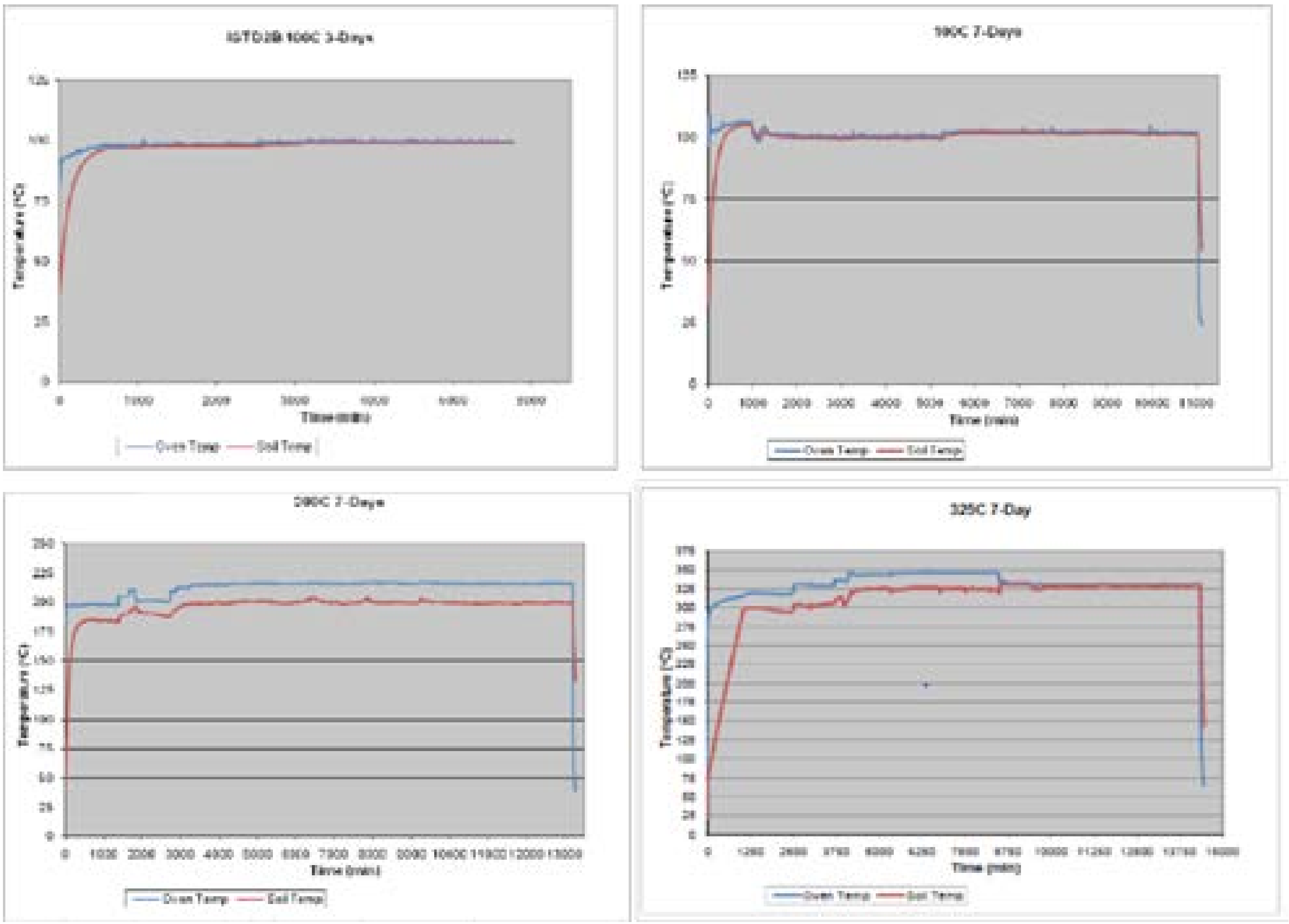
The treatment program tests (Table 6) were performed under controlled heating conditions using a *muffla* oven. During the treatment, air was injected into the reactor at a rate of approximately 10 milliliters per minute (ml/min). A 10 ml/min regulated vacuum pump was attached to the off-gas system to ensure airflow through the system. The reactor off-gas vapor stream was sent to a cold water condenser where desorbed COCs vapors were collected for mass determination. Soil and ambient oven temperatures were recorded at 10 minute intervals throughout the treatment process (see <u>*Picture 7*</u> and <u>*Picture 8*</u>).



Picture 7: Thermal reactor details

Once thermal treatments ended, soil reactors were removed from the oven and chilled to 4ºC prior to analytical sampling. Aliquots of the treated core samples were then collected and crushed prior to analysis, following the same procedure than for baseline analyses. The following paragraphs include a discussion of the obtained results.

Picture 8: Treatment temperature records



Discussion of Results

The analytical results before and after the thermal treatment are recorded in Table 7. A discussion of the main results of each treatment is included in the following paragraphs.

3 and 7 day treatment @ 100ºC

No significant changes have been identified for most of the main compounds after 100ºC treatments. Higher concentration decreases were detected for those compounds determined through *Tentatively Identification Compound* (TIC) analytical techniques, which are considered semi-quantitative and therefore less accurate. Consequently, it cannot be discarded that the abovementioned decreases are due to analytical bias rather than to thermal treatment itself.

As expected, Volatile Organic Compounds (VOCs) with lower boiling points have experienced higher decreases than Semi-Volatile Organic Compounds (SVOCs), which have experienced no significant concentration change.

Consequently, thermal treatments at 100ºC are proven to be inefficient for the removal of Bailin's DNAPL impact.

7 day treatment @ 200ºC

The 7-day treatment at 200ºC yielded important concentration decreases of all the families of compounds. The estimated average reduction achieved was 97.5%.

Regarding HCH isomers removal, concentration decreases over 99% were achieved, except for beta-HCH. The baseline concentration of the latter is low and its low reduction may be related to analytical bias rather than the thermal treatment itself.

Removal rates for Trichlorobenzenes (TCB), ranging from 33 to 62%, are far lower than expected according to its lower boiling point and higher volatility when compared to HCH isomers. Such results can be due to the thermal generation of TCB from HCH isomers at 200ºC - 250ºC[1].

Given the above-mentioned results, thermal treatment at 200ºC achieves satisfactory contamination removal rates.

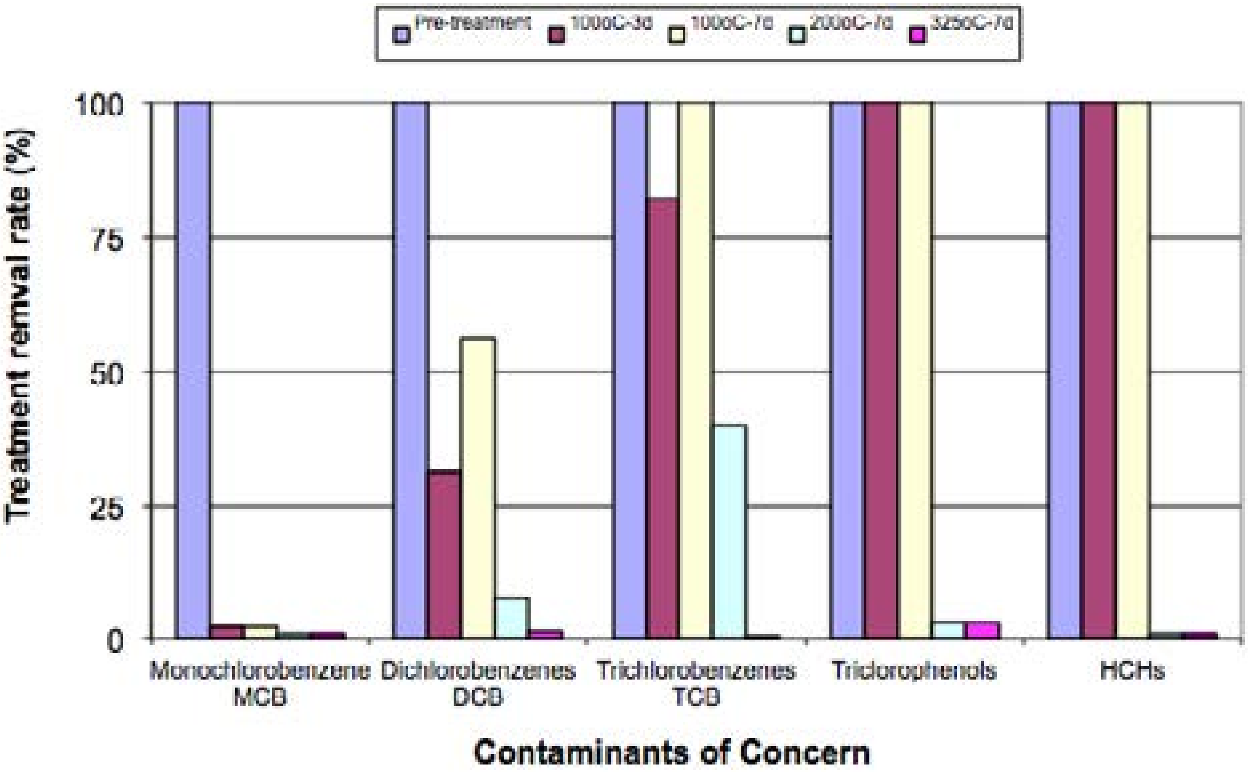
7 day treatment @ 325ºC

The efficiency of the thermal treatment at 325 ºC is over 99.9 % and efficient removal is accomplished for all the families of compounds.

Compounds	**Pre-treatment Conc.**	**Post-treatment (100°C - 3 days)**		**Post-treatment (100°C - 7 days)**		**Post-treatment (200°C - 7 days)**		**Post-treatment (325°C - 7 days)**	
		Conc.	**Removal rate**	**Conc**	**Removal rate**	**Conc.**	**Removal rate**	**Conc.**	**Removal rate**
PESTICIDAS CLORADOS									
Alpha-HCH	42	92	**	84.50	**	0.21	100%	<LD	100%
Beta-HCH	1	-	**	-	100%	0.78	40%	<LD	100%
delta-HCH	100	185	**	195.00	100%	1.00	99%	0.01	100%
gama-HCH (Lindano)	310	625	**	595.00	100%	0.14	100%	<LD	100%
VOC									
Benzene	0.38	-	100%	-	100%	<LD	100%	0.15	61%
Chlorobenzene	29.00	0.45	98%	0.57	98%	0.30	99%	0.13	100%
1,2-Dichlorobenzene	11.00	4.05	63%	6.30	43%	0.90	92%	0.12	99%
1,3-Dichlorobenzene	1.10	0.29	74%	0.55	50%	0.11	90%	0.04	96%
1,4-Dichlorobenzene	12.00	3.15	74%	6.60	45%	0.79	93%	0.13	99%
1,2,3-Trichlorobenzene	3.60	4.35	**	8.50	**	2.40	33%	0.03	99%
1,2,4-Trichlorobenzene	53	42	21%	71.50	**	20	62%	0.19	100%
SVOC									
2,4-Dichlorophenol	<LD	2.40	**	3.20	**	<LD	100%	<LD	100%
2,4,6-Trichlorophenol	2.20	5.00	**	5.80	**	<LD	100%	<LD	100%
2,4,5-Trichlorophenol	2.40	4.55	**	10.05	**	<LD	100%	<LD	100%
Other VOC & SVOC (TIC)	**770**	**50**	**94%**	**63**	**92%**	**5**	**99%**	**<LD**	**100%**
Sum	**1278**	**1018**	**20%**	**1046**	**18%**	**32**	**97%**	**16**	**98%**

Table 7: *Treatability test results (mg/kg)*
*** increase of COC concentration: related to soil heterogeneities*
<DL concentration lower than detection limit

Graphic 1 specifies the treatability removal effectiveness for the main COCs of the site.



Graphic 1: Treatability removal effectiveness for the main COCs

The graphic above displays the main findings of the thermal treatment tests, namely:

- Treatments at 325 ºC and 200 ºC achieve removal rates over 90 % for the main COCs except for TCBs in the 200 ºC treatment, due to thermal degradation of HCH to TCB at 200 - 250 ºC. This behavior has not been identified during the treatment at 325ºC.
- Treatments at 100 ºC do not accomplish significant removal ratios except for highly volatile compounds such as MCB (> 90 %), and in a lower extent for DCBs (30–50%).
- MCB (the most volatile compound detected) is completely removed in all tested treatments.
- Estimated DCBs and trichlorophenols removal ratios achieved at 200 ºC are over 90 %, while TCBs are only efficiently removed at 325 ºC.

Conclusions

According to the obtained test results it can be concluded that:

- Thermal treatment can be an applicable technology for the treatment of source areas at the Bailin's site, whenever the appropiate temperatures can be achieved:
  - Working temperature over 100 ºC is requiered.
  - Thermal treatments at 200ºC and 325ºC have shown high removal rates for all the contaminants of concern (97,5 and 99.9% respectively).
- An eventual field application of this technology could yield higher efficiency and removal rates as a consequence of the *stripping* effect of groundwater evaporation. This removal mechanism is usually on the most effective during in-situ thermal treatments.
- Effective thermal treatments for the site require temperatures over 100ºC. This means treatment areas will require water table depletion to dry them out in order to achieve such temperature conditions. A filed implementation will therefore require intensive hydraulic control of the treatment area to avoid excessive energetic requirements.

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USE OF PASSIVE FLUX METERS FOR MASS FLUX AND MASS DISCHARGE ESTIMATION IN BAILIN

SUBMITTED PAPER

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Abstract

This paper describes the passive flux meters technology used in Bailin for mass flux and mass discharge estimation in a specific area of the site, called Emergency Zone, where a plume of benzene, monochlorobenzene, and HCH is present.

Bailin site is a former unlined landfill where lindane and other Persistent Organic Pollutants (POP) were dumped, and formed a multi-component DNAPL (Dense Non Aqueous Phase Liquid) that has created a dissolved plume in a complex fractured media. Previous studies were carried out in order to characterize the main flow pathways in the fracture network[1], and it was proposed to estimate the mass flux of the contaminants of concern (COC) through these fractures, in differenced areas of the site that show a different behavior depend on the distance to the source zone; and calculate the total mass discharge of the COC through each area. Use of Passive Flux Meters (PFM) technology[2] was proposed for these measurements. While this year this methodology is going to be implemented all over the site, last year a pilot test of this technology was carried out in the middle area of the site, the Emergency Zone.

PFM consists of a permeable sorbent infused with soluble tracers packed in a nylon mesh tube. The device is placed in a borehole or monitoring well for a known exposure period where it intercepts the groundwater flow, causing dissolved contaminants to sorb to the sorbent and the soluble tracers to leach out. The measurements of the contaminants and the remaining resident tracer can then be used to estimate groundwater and contaminant fluxes. By using several PFM across a transect, the average mass flux and total mass discharge through the control plane can be estimated[3].

COCs Mass flux through the main fractures in the transect object of this study was calculated, as well as COC mass discharge across the Emergency Zone, showing an important vertical variation of the fluxes, and therefore the relevance of the preferential fracturation pathways in the control of the pollution migration.

Key Words

Mass flux, mass discharge, PFM, fracture, COC.

Materials and methods

4 Passive Flux Meters were used for this study. The PFM is a passive sampling device that provides simultaneous measurements of a time-average contaminant mass flux and water flux[4]. These devices were composed of a sorbent matrix of activated carbon mixed with water-soluble tracers with a wide rank of solubility coefficients (Figure 1). Each PFM was designed according to the monitoring well specifications, especially with the proper diameter to fit the well lining. The devices had a length of 1.5 m, and a diameter of 7.62 cm, and they were sectioned into 37.5 cm segments separated from each other. This division allows avoid vertical flows and permits to obtain up to 4 measurements at different depths. PFM were placed in the wells facing the existing fractures at the object depth, intercepting the groundwater flow for an estimated exposure time. In this time, the dissolved contaminants present in the groundwater were captured by the sorbent matrix, and the tracers were leached at rates proportional to the groundwater flux.

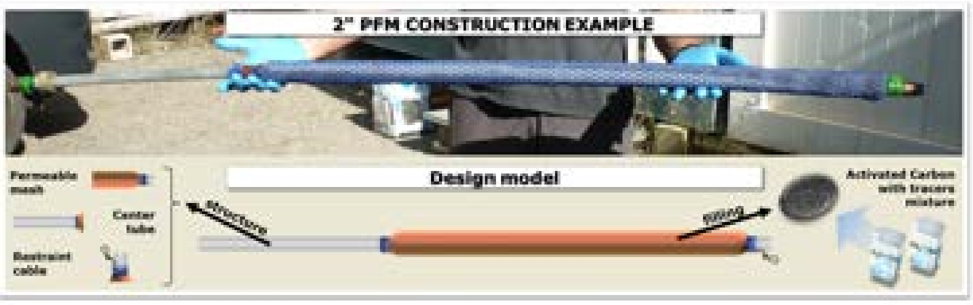

Figure 1. PFM construction example. The illustration represents the elements of a PFM device. The body of the PFM is made of a center tube where the permeable mesh filled with the sorbent mixture is fixed.

Results and discussion

Bailin site is a former unlined landfill where lindane and other POP were dumped and generated a multi-component DNAPL that has created a dissolved plume that reaches the Gallego river, located about 800 m downgradient. The COC present in the plume, in order of amount in the groundwater, are monochlorobenzene, benzene and HCH (lindane and non-commercial isomers). The plume migrates through a fissured aquifer formed by a sequence of vertical fractured sandstone and mudstone layers. These layers are parallel to a stream (Bailin stream) that delimit the south boundary of the site and drains to the Gallego river. There´s only one sandstone layer, called “M layer”, that has enough longitudinal continuity to connect the landfill and the river. This lithological discontinuity has favored a natural funnel and gate distribution of the plume (Figure 2).

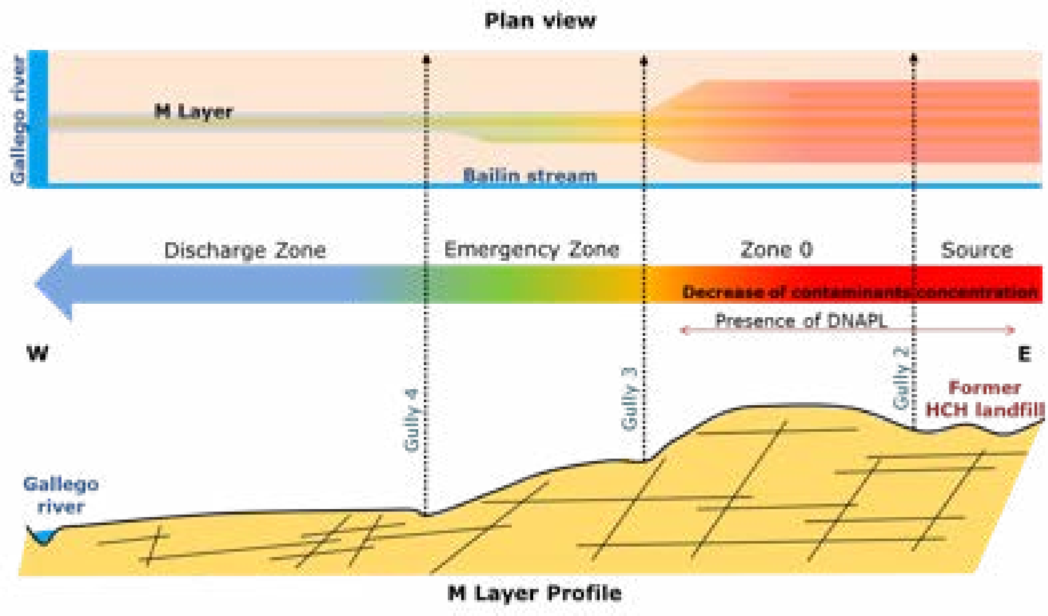

Figure 2. Distribution of the contaminant plume across Bailin site. Figure shows the natural funnel and gate distribution of the plume and the decrease of the contaminants concentration from the former HCH landfill to the Gallego river.

Important topographic gradients control runoffs and infiltration rates, and groundwater flows towards Bailin stream and Gallego river within a shallow fracture network in the first meters of the mudstone and sandstone layers. In depth, the lithological alternation with different fracture distributions controls the preferential groundwater pathways. The understanding of the relationship among fractures, hydraulic conductivities, hydrochemistry and depth was crucial to develop the conceptual site model (Figure 3). Although the principal contaminated area is close to the source zone, sandstone layers constitute the main pathways that contribute to spread the plume[5].

Nowadays, the control of the contaminant plume is a priority in the monitoring and remediation activities performed in the site. Even though there is available a huge quantity of groundwater quality records in depth of the main layers that constitute the aquifer, it was needed to know in detail the behavior of the plume in order to determine its evolution, and delimit the critical areas for a focused remediation work, allowing to optimize the efficiency of the treatment and reducing costs. Previous studies were carried out in order to characterize the main flow pathways in the fracture network[1]; and for characterizing the detail required, an estimation of the mass flux in the main fractures in the middle area of the site, Emergency Zone, and the calculation of the total mass discharge of each COC were conducted.

The mass flux (J) is the mass of a chemical compound passing through a perpendicular plane to the groundwater flow (transect) per unit time (e.g., g/d/m^2); that is, the mass flux determines the amount of a contaminant mass moving in the groundwater based on the groundwater flow velocity, and it´s delimited in a defined area. Mass discharge (Md) represents the total contaminant mass transported by groundwater (e.g., g/d) (Figure 4). Mathematically, mass flux (J) is the product of the contaminant concentration in the groundwater and the groundwater flux: $J = q_0 \cdot C = -K \cdot i \cdot C$, where q_0 = groundwater flux, $L^3/L^2/t$ (e.g., volume/area/d), K = saturated hydraulic conductivity, L/t, (e.g., m/d), i = hydraulic gradient, dimensionless (e.g., m/m), and C = contaminant concentration, M/L^3 (e.g., mg/volume); and mass discharge is the integration of the contaminant mass fluxes across the selected transect:

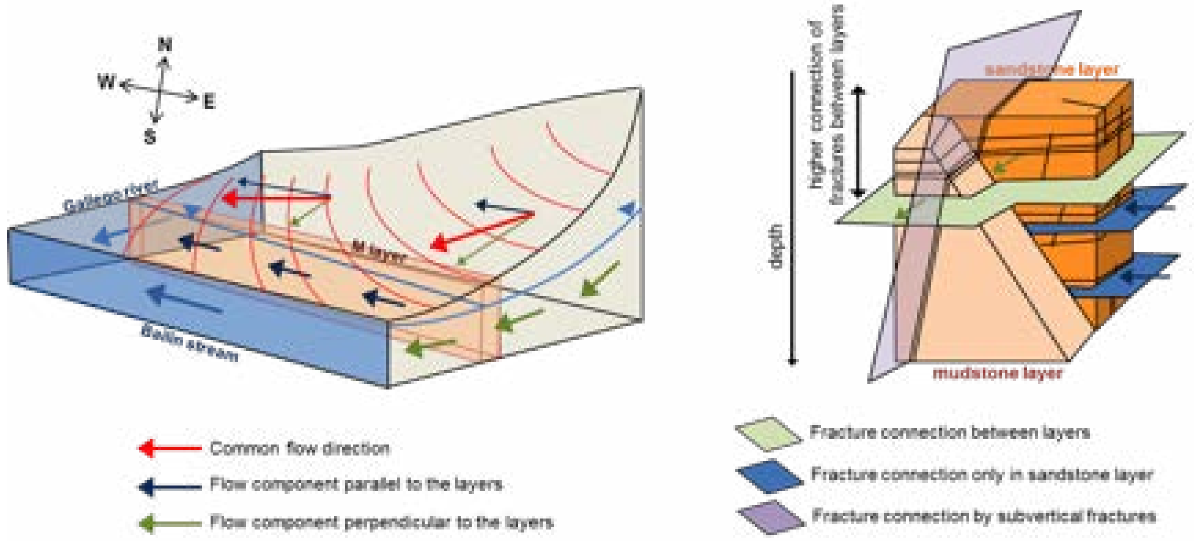

Figure 3. Conceptual Site Model of Bailin. The CSM was developed regarding to the hydrogeological and hydrochemistry data recorded in the site, and shows the importance of the lithological control.

$Md = \int_A J \cdot dA$, where A = area of the control plane, L^2 (e.g., m^2), and J = spatially variable contaminant flux, as previously defined[2].

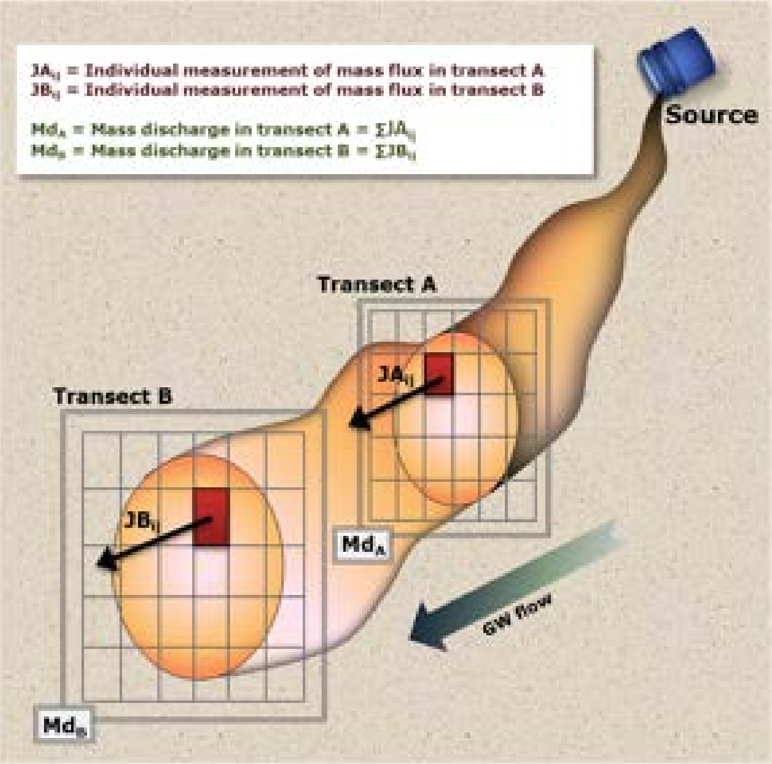

Figure 4. Concepts of mass flux (J) and mass discharge (Md). Flux is the mass moving past a plane of given area per unit time (e.g., g/d/m^2). Each square in the transect represents the mass flux for that unit area (cell ij) of the transect. Mass discharge is the total mass flux integrated across the entire area of a transect (e.g., g/d). It is therefore the sum of the cells in the transect. There would be two mass discharge values for this example (Md_A and Md_B) at different distances downgradient from a source. (Adapted from ITRC – Use and Measurement of Mass Flux and Mass Discharge, 2010).

In order to make a first estimation of mass flux and mass discharge in a specific area of the site, a PFM pilot test was performed. While this technology has been mostly applied in porous media, and it´s being perfected for fracture rock formations at present, most of the uncertainties were studied and assumed[6], as it is discussed in Table 1.

The pilot test was carried out in the Emergency Zone, in the monitoring wells P130, P127, P79 and P57, situated on the M layer. This area has good features because: (a) perpendicular groundwater flow component to the Bailin stream is insignificant in contrast to the principal groundwater flow direction to Gallego river, (b) distribution and characteristics of the fractures going through the wells are well known and the preferential flow pathways are well delimited in the zone, as it was recorded in the previous fracturation study[1], (c) fracture network knowledge also allows to evaluate individual mass flux moving through each fracture as well as the total mass discharge in the zone of study, (d) contaminant concentrations are high enough to be representatives, and (e) the area is easy to access and it is good prepared to perform the test.

The PFMs were placed in the wells at the proper depth, where each segment of the device was facing the main fractures individually (Figure 5), and they were exposed to the groundwater flow for 10 days. Figure 6 illustrates the PFMs usage in the wells.

Uncertainties	Assumptions
Temporal and spatial variability of hydrogeological conditions due to the heterogeneity of the fractured rock formations.	Well knowledge about the fracture network and the location and features of each single fracture.
Presence of vertical flows in the water column could compromise the results.	PFM are sectioned and constructed to fit the well lining leaving no space between them.
Packers could be needed in order to minimize the entrance of undesirable flows.	Minimum water column at the moment of the test implementation. Groundwater flow limited to the preferential pathways at the depth of the PFM location.
Presence of non-conductive fractures and diffuse transport processes.	PFM only measures through active fractures. Diffuse transport is assumed to be negligible against the advective fluxes.

Table 1. Discussions of the PFM implementation in the site.

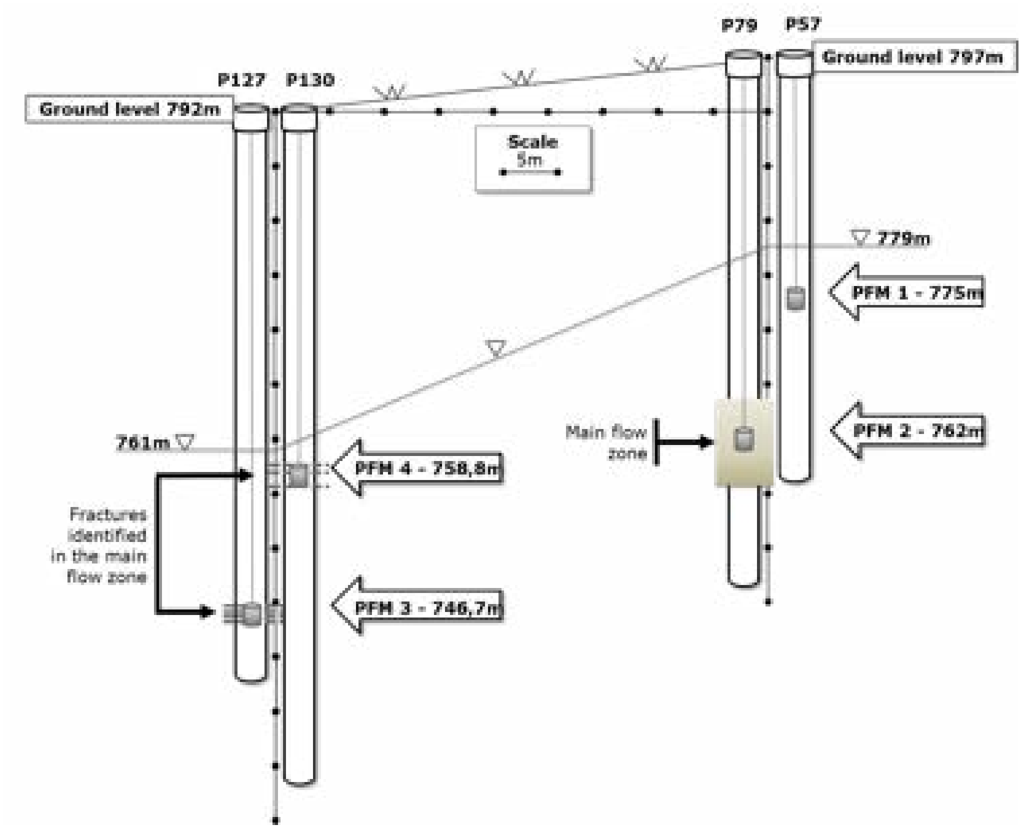

Figure 5. PFM well installation. The PFM were placed in the wells in the Emergency Zone intercepting the groundwater flow moving through the main fractures in the preferential flow pathways. PFM #1 was placed in the well P57 at 775 m a.s.l, PFM #2 was placed in the well P79 at 762 m a.s.l., PFM #3 was placed in well P127 at 746,7 m a.s.l., and PFM #4 was placed in the well P130 at 758,8 m a.s.l.

After the previours planned time of exposure, PFMs were removed from the wells and sampled. Samples were sent to the corresponding labs and results of the groundwater fluxes, mass flux and mass discharge were given. These results were adapted to the particular conditions of the fractured media.

Two assumptions were evaluated in the study, illustrated in Figure 7: (1) it was considered that mass flux only occurs in the preferential flow pathways identified in the previous fracturation study, where the PFM were placed. This assumption considers there are no fractures between these main zones, or there are fractures without relevance enough (non-conductives) against most fractured zones. In the calculations, each segment of the PFM is intercepted by 1 fracture (4 fractures per PFM) with an openess between 4-10 mm (real data obtained from the fracturation study); and (2) there is an aditional mass flux between preferential flow pathways, considering there are active fractures that allow mass flux. In this assumption, it was considered the existence of 1 fracture per meter in the saturated zone, with an openess of 4 mm (larger openess are only detected in the preferential flow pathways). Considering these assumptions, maximum and minimun values for mass discharge estimation were calculated.

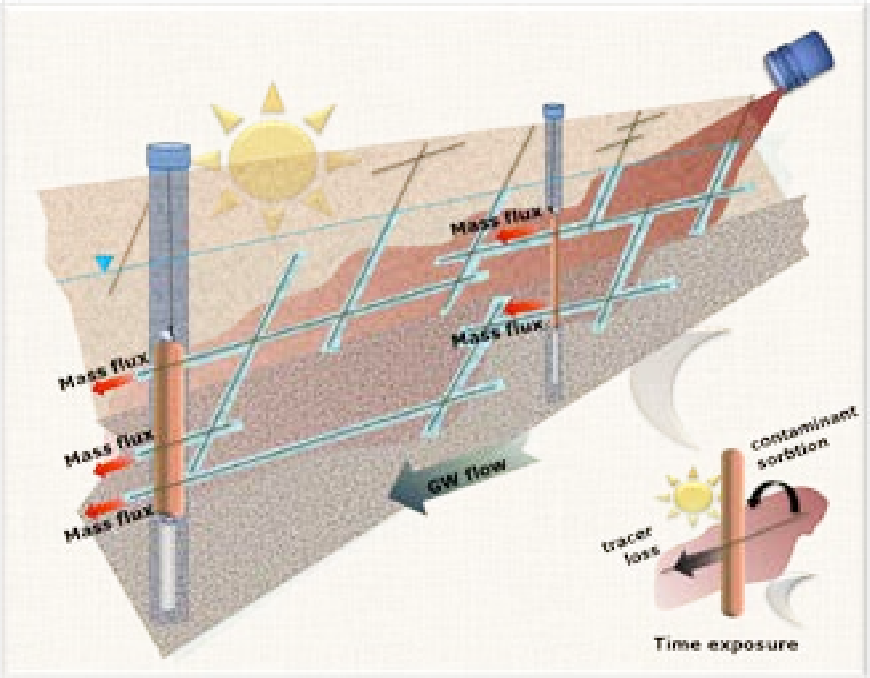

Figure 6. Example of PFM working in the site. During the time of exposure, PFM sorb the contaminants moving in the groundwater flow through the fractures while soluble tracer loss is happening.

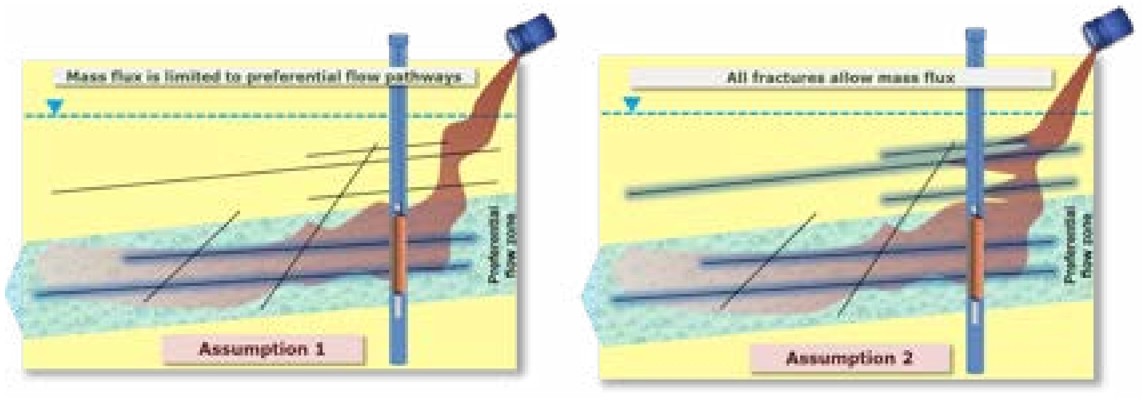

Figure 7. Assumptions for mass discharge estimation in the Emergency Zone. Assumption 1 considers that mass flux is limited to the main fractures in the preferential flow zone, and assumption 2 considers all fractures allow mass flux in the saturated zone.

Fluxes and Darcy velocitiy estimations are shown in Figure 8. The highest groundwater flow velocity estimated was 25 cm/d, and it belongs to fractures located at 761 m a.s.l. In the remaining fractures located in the preferential flow zone, groundwater flow velocity average calculated was 6 cm/d. However, an important vertical variation of the mass flux, showing the relevance of the preferential fracturation pathways that control the COC mass migration, was identified.

The behavior of benzene and chlorobenzene is similar, and mass flux mainly occurs in the preferential flow zone, between 775 and 760 m a.s.l., due to the existence of higher flow velocities together with high groundwater contaminant concentrations. However, HCH behavior is the opposite, and main mass flux occurs at lower levels (760 m a.s.l.), although flow velocities are also lower. This distribution responds to the physicochemical properties of the compounds, fundamentally due to their solubility and density.

Mass discharge estimations obtained in the Emergency Zone were 330-1470 g/year for chlorobenzene, 180-800 g/year for benzene, and 53-203 g/year for HCH. Even though dissolved concentrations in the groundwater are high in the zone, mass discharge is not as high as it was to be expected, because there are a few fractures with high groundwater flow velocity, and they do not always coincide with the highest contaminant concentration distribution. It is considered that values obtained in the

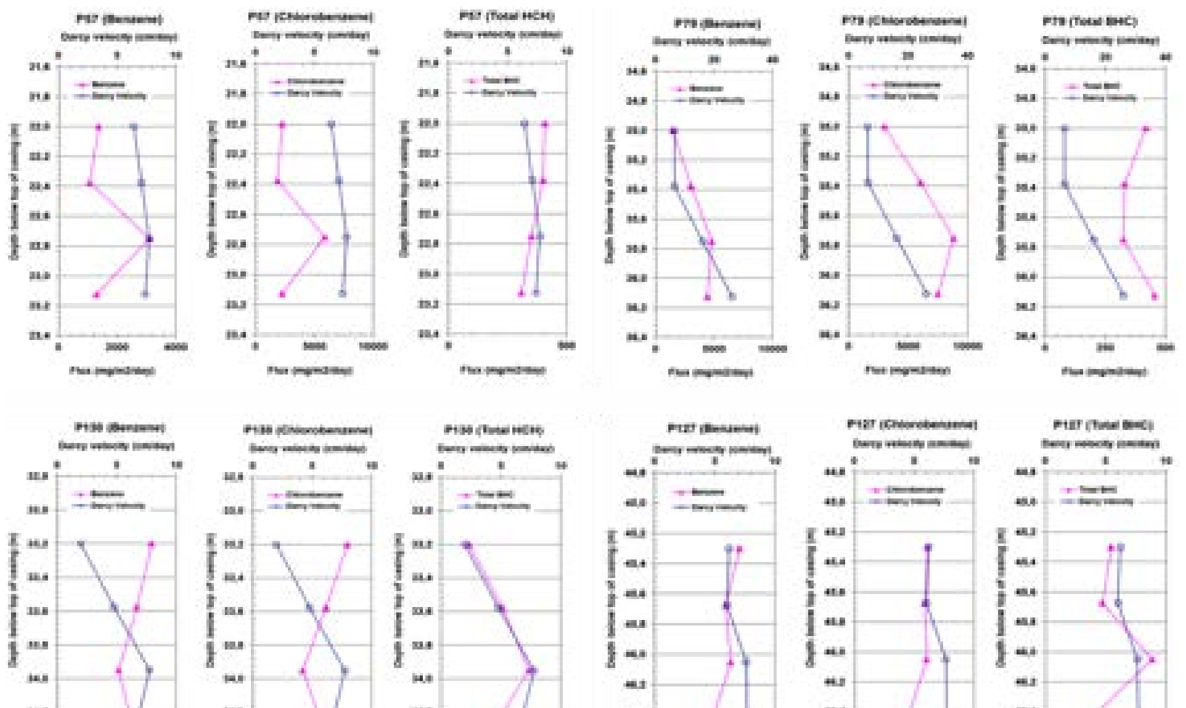

Figure 8. Mass flux data for monitoring wells. Darcy velocity and mass flux is represented for each well related to the installation depth below top of casing.

assumption 1 are closer to reality, because the proportion of fractures that controls the preferential mass flux is relatively low regarding to the main fracturation network. Results have been also compared to the historical analytical results and hydraulic parameters obtained in pumping test and the mathematical groundwater model of the site; and it can be concluded that pilot test results are very satisfactory, and the viability of the use of PFM in the site for mass flux and mass discharge estimations has been proved.

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COUNTERFEIT PESTICIDES AND EMPTY CONTAINERS

Counterfeit pesticides and empty containers, improvement on pesticides management

EXPERIENCES ON ILLEGAL AND COUNTERFEIT PLANT PROTECTION PRODUCTS IN POLAND

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Abstract

Presence of illegal and counterfeit pesticides in the market is now a global problem. Data published in 2012 by European Crop Protection Association (ECPA) indicate that illegal products represent over 10% of the global market of plant protection products. The main reason for the prevalence of this practice is to derive a financial benefit.

Counterfeit and illegal pesticides may contain substances inconsistent with the label and the registration dossier and are likely to pose a threat to the environment, crops, animals and people. In Poland, parties in charge of working against illegal and counterfeit plant protection products include the Main Inspectorate of Plant Health and Seed Inspection (as part of the official control), the police, prosecutor's office and pesticide producers. Results of chemical analyses carried out by the Pesticide Quality Testing Laboratory at the Institute of Plant Protection – NRI, Sosnicowice Branch, indicate that most of illegal pesticides in Poland belong to herbicides. Majority of irregularities are detected among pesticides from parallel trade.

The aim of this article is to present the organization of pesticide quality control system in Poland and to describe the analytical methods and test results for pesticides suspected of being counterfeit.

Key words

Counterfeit pesticides/plant protection products, illegal pesticides/plant protection products, registration dossier, quality control of pesticides/plant protection products, parallel trade, analytical methods.

Introduction

In recent years, presence of illegal and counterfeit pesticides on the market has become a global problem. The first case of illegal pesticides in Europe was uncovered in Spain in 2000 when authorities found unregistered pesticides without labels being imported from China[1]. Over the next five years, other attempts of introducing illegal pesticides into the market were uncovered in Germany, Italy, the Netherlands and Poland. Estimated data published by the European Crop Protection Association – ECPA in 2012 and included in the document by the European Commission of 2 March 2015 titled: *Ad-hoc study on the illegal and counterfeit pesticides in the UE: Executive summary* indicate that worldwide the illegal and counterfeit pesticides account for over 10% of the market share for crop protection products. For the European countries ECPA talks about 8 - 10% of the market share and for Poland of about 10 - 15%. There is some evidence suggesting that the amount of illegal pesticides may depend on the geographic location of a EU country and it is higher for states bordering countries that are not EU members. We should also remember that some member states may report a lower amount of illegal pesticides due to inadequate systems of control in place in a given country. The phenomenon is growing mainly because of the profit gained from introducing the illegal pesticides on the market. The estimated value of global sales for pesticides is 44 mld €. In the case of Poland, the value of this market is around 2 mld zloty (450 – 500 mln €).[1,2,3] We are talking about high amounts of money and due to legal loopholes and relatively low fines charged for engaging in trade involving illegal pesticides made them a fast growing area of organized crime. Presence of illegal and counterfeit pesticides on the market brings losses to the National Treasury, chemical manufacturers who produce pesticides and farmers who grow crops. At this point we should explain what illegal pesticides are, what risks are involved and how they are different from legal products. The composition of legal pesticides is precisely determined. Prior to their registration, which allows for their use and sales on the market, legal pesticides undergo comprehensive testing and evaluations designed to assess, among others, phytotoxicity of active ingredients they contain, any effects they could have on humans and the environment and the ways to use them properly and safely. The trials take a long time and are very expensive. In the case of illegal pesticides, the basic purpose behind putting them on the market is to gain the highest profit at the lowest expense, this is why illegal pesticides do not undergo any studies and their ingredients come from unknown sources. This way we have a situation where illegal pesticides are in price competition with original products. [3].Studies related to quality of crop protection products, including their original source have been conducted at IOR-PIB Sosnicowice for a number of years. The experience gained by the Pesticide Quality Testing Department (LBJŚOR) of Plant Protection Institute - National Research Institute, Sosnicowice Branch (IOR-PIB Sosnicowice) allows to group illegal pesticides into the following groups:

- pesticides that do not contain an active ingredient,

or contain a different active ingredient
- pesticides whose composition was changed - composition is different from what the label says (e.g. diluted, formulation is different from the one declared on the label)
- not registered in a given country
- illegally manufactured (products coming from unregistered sources, which imitate a legal product) - mainly from Asia.
- pesticides in unoriginal packaging, and/or with unoriginal label.
- pesticides smuggled in, with a label in a foreign language or no label at all.

The above list shows that mere organoleptic evaluation of the container or its contents can raise suspicions of dealing with an illegal product (Figure 1).

Fig. 1. Example of visual analysis of suspected PPPs against reference product (first from the left).

We should also mention that illegal pesticides create some serious threats, which can be divided into three different groups.

I. Danger to crops through:
- decreased efficacy or no efficacy at all,
- damage or destruction of a plantation in the case of pesticides with a phytotoxic effect of impurities or other irregularities in the contents of pesticide formulation.
- improper use on protected crops resulting in damage to crops,

II. Danger to humans and animals through:
- increased amounts of residues due to overdosing
- occurrence of unknown, uncontrolled residues in plants which can be harmful if consumed by people or animals,
- potential for direct adverse effect on sprayer operators

III. Danger to the environment through:
- toxic substances getting to the soil and underground water
- potentially long-term contamination
- potentially contamination of the adjacent crops.
- potentially a side effect involving beneficial organisms. [5]

Materials and methods

In Poland, there is a number of institutions involved in activities against introducing illegal pesticides on the market which include manufacturers of legal products (Polish Society for Plant Protection - PSOR) , police, customs offices, prosecutor's office and last but not least the National Plant Protection and Seed Inspection Service (PIORiN) in collaboration with IOR-PIB Sosnicowice. Regulation of the European Parliament and of the Council (EC) No. 1107/2009 requires the EU member states to conduct independent quality control of pesticides.[4] Poland has performed official quality control of pesticides for a number of years. Since 2006 it has been implemented under the so called Multi-year Programme (currently for the years of 2011 – 2015) by PIORiN and LBJŚOR IOR-PIB Sosnicowice. The main purpose of the control is to uncover any irregularities related to pesticide quality and in particular to look for any products suspected of having been illegally introduced on the market and to verify where they came from. Pesticides are sampled at the points of sale according to pre-determined guidelines by PIORiN inspectors and then forwarded to the lab at LBJŚOR IOR-PIB Sosnicowice for testing. Polish law requires quality control labs to be GLP certified. The LBJŚOR lab has implemented the necessary system in 2008. Annually, the LBJŚOR lab tests from 300 – 350 samples, including around 260 from the official basic control. The rest of the samples are those suspected of some irregularities, e.g. no effective activity, activity different from intended, no documented source (for points of sale), samples detained by the police, border patrol, or collected during interventions. The cost of pesticide quality control is covered by the National Treasury. Until 2011, sample collection for the basic control was very spotty and largely unplanned. In 2012 a new system of sample collection was introduced. Taking into account the data on the number of irregularities and sales of pesticides in the previous years, the total number of samples included in the basic control scheme (260) is randomly assigned among the provinces in Poland, depending on the crop area, amount of pesticides used and the number of points of sale. A special software is used for the random assignment of samples among the provinces. Statistical calculations and findings from each year the control was performed allow to turn the next year's control efforts to the groups of products which are most prone to irregularities. Pesticide quality tests carried out at the LBJŚOR lab consists of verifying the content of active substances as well as the basic physical and chemical properties which are characteristic for a product and set forth in the registration process, including: density, pH, suspension/emulsion/dispersion stability, sieve residue, wetting time and foam stability. The lab uses methods approved by the Collaborative International Pesticides Analytical Council (CIPAC)[5], manufacturer's methods included in the registration dossier as well as its own internal methods. For most cases, however, the tests are not sufficient to verify the legal source of a product, because the "quality" of fakes is getting better and better and very often the content of active substances and majority of physical and chemical properties correspond to the specifications of a legal and genuine product. A full analysis of a pesticide suspected of coming from an illegal source is practically impossible because it is time consuming, and requires a number of expensive testing techniques. This is why the LBJŚOR lab developed a number of methods for comparative analysis utilizing different analytical techniques, like GC, HPLC, GC/MS, HS-GC/MS, NIR. The methods aim at obtaining the analytical image (a chromatogram or spectrum) of the original product, supplied directly by its producer, along with a certificate verifying that it is a quality product from a legal source. The analytical images of the original products are then compared with images obtained for the samples of suspected products. This approach allows for a quick, inexpensive and effective method of verifying the source of pesticide samples tested by the lab. A fake is usually different from a genuine product in that it contains active substances which come from unknown sources, obtained through unknown process of synthesis, therefore contaminated with unknown chemicals, which could dangerous, e.g. due to their potential toxicity. The same is true for other ingredients of a fake formulation, when we know nothing about the type or source of these ingredients. A counterfeit product may also not include other ingredients like safeners and synergists which have an effect on the proper performance of a product. Exaples of the use of comparative methods are shown in Figures 2-3.

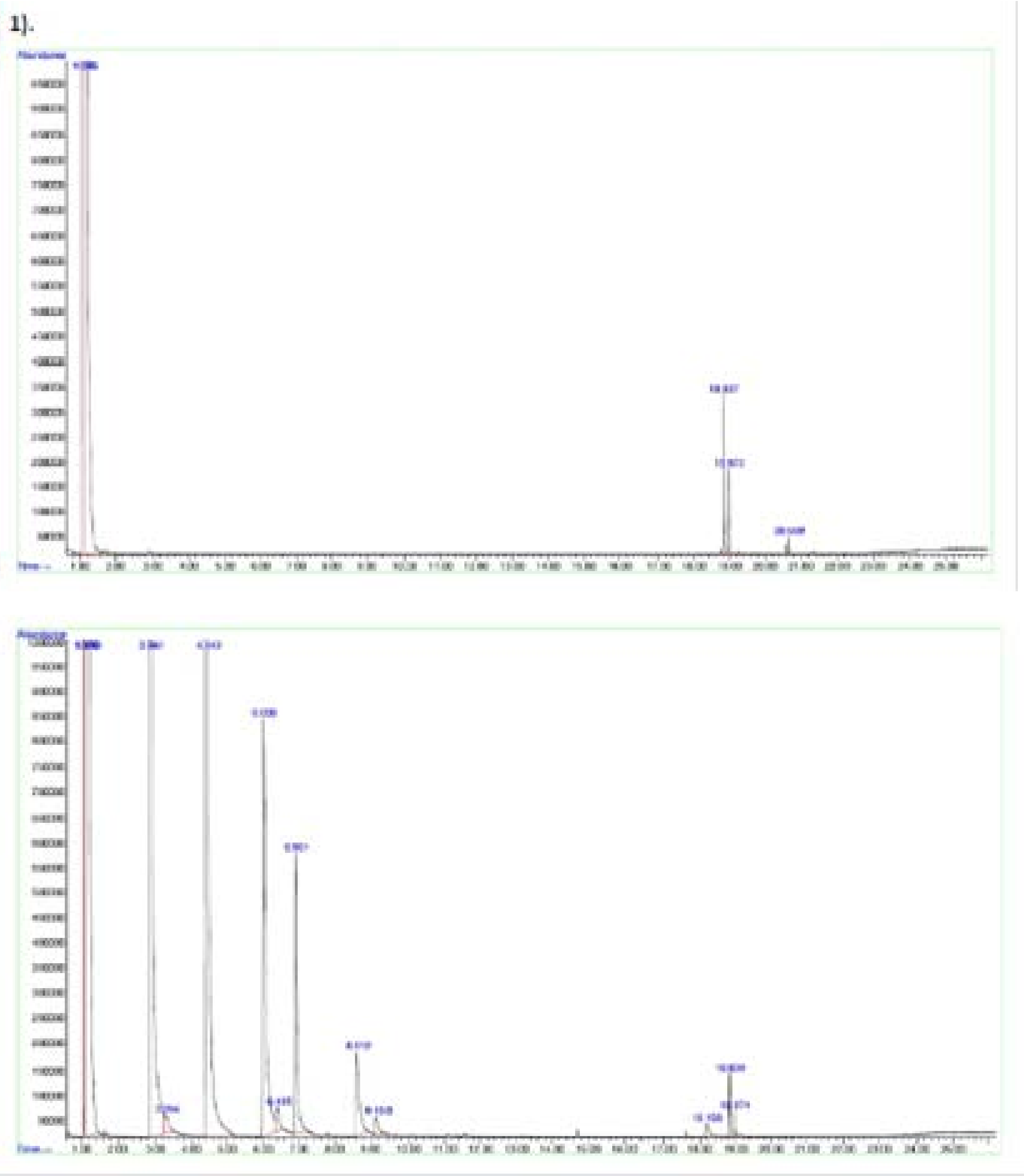

Fig. 2 Example of use comparative methods by HS-GC/MS technique to verify the originality of the suspect PPP (2) against reference product (1).

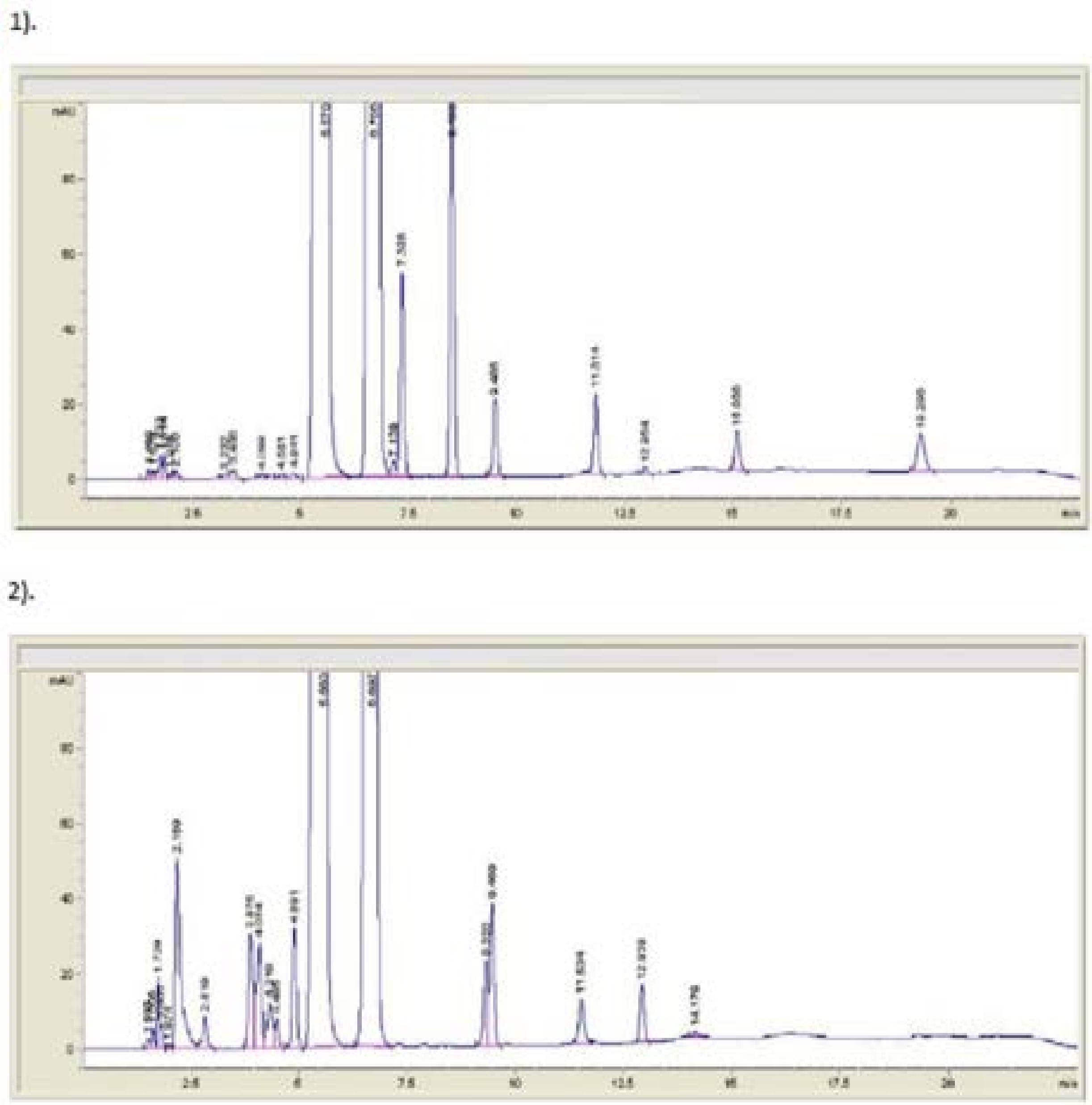

Fig. 3 Example of use comparative methods by HPLC UV DAD technique to verify the originality of the suspect PPP (2) against reference product (1).

Results and discussions

In 2011, official inspections tested a total of 308 samples, including 268 as part of the basic control and 40 interventions. In general, 30 certifications issued were negative, including 20 for illegal and counterfeit pesticides.

Tables 1 – 3 include results of official controls for 2012 – 2014 (after introducing the new system of sample taking), taking into account the number of uncovered illegal and counterfeit pesticides.

Type of control	No. of samples investigated per year		
	2012	2013	2014
Basic control	275	266	262
Interventions	79	45	48
Total	354	311	310

Table 1. Number of pesticide samples tested as part of the official control in 2012-2014

Type of control	No. of negative certificates issued in the following years		
	2012	2013	2014
Basic control	11	6	7
Interventions	40	30	34
Total	51	36	41

Table 2. Number of negative certificates issued for samples tested as part of the official control in 2012-2014

Type of control	No. of samples investigated per year		
	2012	2013	2014
Basic control	6	4	3
Interventions	30	23	20
Total	36	27	23

Table 3. Number of cases of illegal or counterfeit pesticides negative uncovered during the official control in 2012-2014

Pictures 1-3 show examples of visual comparison of suspected counterfeit samples with the original products

The effectiveness of the new sampling system used in the process of basic control to uncover illegal and fake pesticides was considered in reference to the results of lab analyses conducted in 2009-2011.

A review of test results for 2009-2011 and 2012 - 2014 indicates a tendency for a higher detection rate of illegal and counterfeit products. In 2009-2011 the number of samples tested annually ranged from 261 to 271 and the number of illegal and fake cases uncovered in the process ranged from 0 to 6, which was around 1%. In 2012-2014, however, the average percentage of illegal and counterfeit pesticides was 1.6% in relation to the total number of samples tested. The number is higher by more than a half in comparison with the years before the new system was introduced. The total number (for basic control and interventions combined) of illegal and fake pesticide cases was 36 in 2012, 27 in 2013 and 23 in 2014, which in relation to the total number of samples taken in the course of official control each year is 7.4 – 10%. The rate of illegal and fake pesticides in relation to the number of negative certifications issued in 2012 to 2014 ranged from 56 – 75%. In 2012 to 2014 the highest number of fakes was found among herbicides and the lowest for insecticides and other products. In 2012, most irregularities related to illegal source of pesticides were uncovered among products in parallel trade which makes it possible to sell pesticides between the EU member states as long as a product is properly registered in one of them (a product registered in a given state is the reference product). The basic reason for disqualifying a product under parallel trade is that it is not considered identical, in accordance with Article 52 of Regulation No. 1107/2009. Article 52.3 says that: “Plant protection products shall be considered as identical to the reference products if: (a) they have been manufactured by the same company or by an associated undertaking or under licence in accordance with the same manufacturing process;(b) they are identical in specification and content to the active substances, safeners and synergists, and in the type of formulation; and(c) they are either the same or equivalent in the co-formulants present and the packaging size, material or form, in terms of the potential adverse impact on the safety of the product with regard to human or animal health or the environment.” Unfortunately, the Article allows for misinterpretation of the regulations regarding parallel trade (especially section c of Article 52) which makes it hard to impose adequate sanctions on companies engaging in introducing illegal pesticides on the market. [6] Most of the samples found to come from illegal sources are collected as a result of intervention. In 2013-2014, among the products permitted under parallel trade there was a decreasing tendency to detect irregularities in relation to previous years. Pesticide quality control, including uncovering of illegal and fake products is quite a challenge for a control lab because the activities are time- and labour-consuming, and cost-intensive, it requires advanced equipment to use a variety of analytical techniques, as well as qualified and experienced personnel, able to face still increasing challenges.

We should underline that different campaigns and awareness initiatives directed at food producers and public officials, including police, border patrol agents and prosecutor's office personnel play an important role in the fight against illegal and counterfeit pesticides. Preventing illegal pesticides on the market is a task for proper public authorities. Collaboration of individual farmers, sellers and legal producers with those authorities makes the fight much more effective. It is also important to harmonize the regulations in place across the EU member states to ensure consistent interpretation of the laws governing the process of registration, introduction on the market, use and quality control of pesticides. Even the best system of control will fail to protect us against the threats from illegal pesticides without the vigilance and common sense of the consumers and users of crop protection products.

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A NEW APROACH FOR MODELING INORGANIC PESTICIDES: ADAPTATION OF LIFE CYCLE ASSESSMENT TOOLS TO COPPER FUNGICIDES

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Abstract

Pesticides are applied to agricultural fields to protect and enhance crop yield and their generalized use is substantial. Life Cycle Assessment (LCA) is a method to quantitatively assess the environmental impacts of goods and processes from ”cradle to grave”. LCA models are underpinned by cause-effect relationships in different environmental compartments, which allow understanding the environmental consequences of human actions[1]. In LCA, the inventory phase (LCI) provides emission data to the different environmental compartments and the impact assessment determines the final distribution, fate and effects[2].

Regarding the LCA application to agricultural systems one of the main drawbacks is in one hand the lack of agreement in how to handle with Cupper products, and on the other hand, to grasp the specificity of toxicity according to edaphoclimatic traits in the stage of Life cycle Impact Assessment (LCIA). This study focuses on the fate and effect of Cupper compound active substance on agricultural systems in the frame of LCA studies. The final goal is to characterize and evaluate the potential environmental damage of the Copper emissions produced by the use of these fungicides . In addition a model of geographic specificity for establishing the impact of the use of Copper as active substance in pesticides will be developed.
Methods The main and most advanced LCI model for quantification of organic pesticide PestLCI 2.0, is customized and tailored for its use to cupric pesticide emissions. That customization is also integrated with the regional archetypes for the consensus USEtox model used for the LCIA.
Results and discussion The proposed framework provides a starting point for authorities, public and private researchers and developers to be able to better estimate and quantify cupric pesticide emissions due to application in agricultural systems. The model customization addresses the issue of accounting inorganic substances for inventory analysis. Furthermore for the impact assessment phase taking into account specific geographic distributions (regional archetypes) helps to describe in a more accurate way the human toxicity and environmental ecotoxicity, considering that Cu toxicity depends mainly to its capacity of interact with the surrounding environment.

Key Words

Inorganic Pesticides, cupric fungicides, environmental control, Life Cycle Assessment (LCA), Life Cycle Inventory (LCI), emissions, Life Cycle Impact Assessment (LCIA).

Methods

Life Cycle Assessment is a tool to assess the potential environmental impacts and resources used throughout a product’s life cycle, i.e., from raw material acquisition, by way of product and use phases, to waste management[3]. In contrast to monitoring assessments, LCA is not used to analyze product risk or safety, but instead supports to establish and inform environmental performance profiles aiming to identify the most environmentally sustainable ways of providing a product or service between different options[5].

There are four phases in an LCA study: i) the goal and scope definition: includes the reasons for carrying out the study, the intended application, and the intended audience. ii) Life Cycle Inventory Analysis (LCI): The result from the LCI is a compilation of the inputs (resources) and the outputs (emissions) from the product over its life-cycle in relation to the functional unit (quantitative measure of the functions that the good provide)[4], iii) Life Cycle Impact Assessment (LCIA): intended to understanding and evaluating the magnitude and significance of the potential environmental impacts of the studied system, iv) and interpretation: the results from the previous phases are evaluated in relation to the goal and scope in order to reach conclusions and recommendations[4].

The typical difficulty in LCA studies with respect to pesticides is to quantify the proportion emitted to the different environmental compartments, while usually only the amount applied to the agricultural field is known[6].

Life Cycle Inventory LCI

In order to provide emission estimates, LCA practitioners and developers proposed generic assumptions regarding varying percentages of applied active ingredient emitted to environmental compartments[5]. Furthermore, there are very different approaches and assumptions that are currently applied in quantifying life cycle emission inventories of pesticides in any LCA studies involving agricultural systems, for example: Ecoinvent database, the US Life Cycle Inventory Database and the organic pesticide emission model PesLCI 2.0.

PestLCI 2.0 model

The pesticide emission model PestLCI 2.0[7] is an inventory model intended to provide an estimation of organic pesticide emission fractions to the environment. After calculating the primary distribution of pesticides between crop and soil, specific modules calculate the pesticide emission for the application. It employs a local model that estimates emitted amounts (meaning here leaving the agricultural field) to air, surface water, and ground water (see figure 1) through the soil, respectively, based on application methods, local meteorological conditions, crop types, and other influencing factors[5].

Life Cycle Impact Assessment LCIA

It characterizes potential impacts on human health and the environment attributable to chemical emissions. LCIA assesses impacts at midpoint or endpoint level and relies on substance-specific characterization factors (CFs) that combine exposure potential and toxicity to represent the relative contribution of the substance to health and environmental impacts[8]. All current LCIA characterization models for toxicity, such as IMPACT 2002, USES-LCA and USEtox consider the fate (transport, distribution and degradation) of a pesticide once is emitted to the natural environment (air, water, and soil) outside the agricultural field[9].

USEtox model

We choose USEtox as characterization model since it was developed as a scientific consensus model, to better represent application practice for characterization of toxic impacts of chemicals including metals and pesticides in LCA[8]. The model calculates CFs for human toxicity and freshwater ecotoxicity, linking emissions to impacts through three steps: environmental fate, exposure and effects.

For special scales, USEtox spans two different special measures, the continental scale, which consists of six environmental compartments (urban air, rural air, agricultural and industrial soil, freshwater and coastal marine water) and the global scale that has the same structure as the continental scale, but without the urban air, and accounts for impacts outside the continental scale[9].

Copper Active Ingredients

Conventional pest management relies on generic farming organic pesticides active ingredients (AI) most of them included in both models described above. But also conventional agriculture, viticulture and more over organic production relies on inorganic pesticides, more specifically copper fungicides. Under the new pesticide package five different copper compounds (copper (I) oxide, copper (II) hydroxide, Bordeaux mixture, copper oxichloride, and tribasic copper sulfate), were approved in 2009 by the European commission and are ours substance of interest.

Results and discussion

New model approach

PestLCI 2.0 is designed for modeling of organic pesticides emission. Thus, we consider a new framework to customize the model taking into account the complex chemistry of metals in order to properly reflect the behavior of these chemicals in the environmental compartments.

We identified specific needs for copper pesticide emission modeling looking at the current PestLCI model structure, and a large number of processes need a major change given the nature of copper. First the module on wind drift during application can be used as it is because it depends of the applications methods and field characteristics. All processes of degradation, uptake, and volatilization are no significant for metals and can be ignored due to the nature and behavior of copper (and metals in general). In soil processes (runoff and leaching) we need to consider also speciation processes vital to describe the behavior of metals. And finally, a new module of erosion needs to be included, because for cupric fungicides, as well as other metal compounds, erosion of soil particles to which pesticide is bound is a large source of emissions to surface water. The resulting new approach and model customization is illustrated in figure 2.

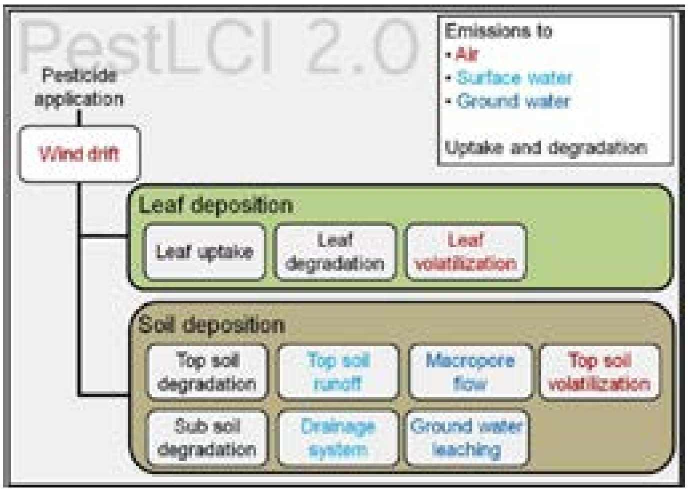

Figure 1. PestLCI 2.0 modules

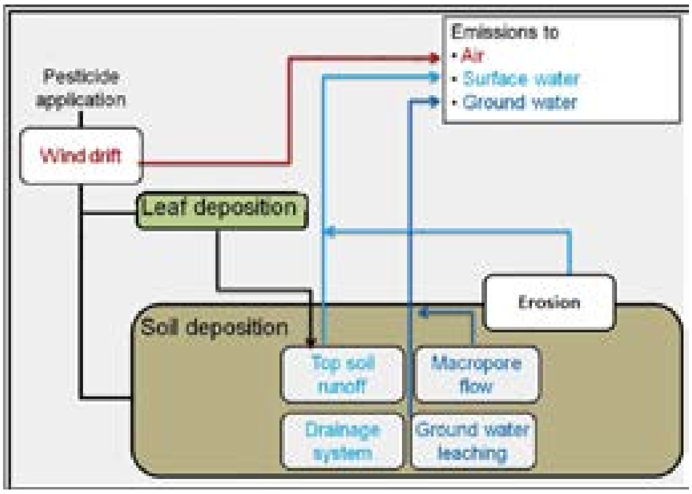

Figure 2. New LCI Cu model approach

USEtox new land scape data

It is well known that copper toxicity depends mainly on its capacity to interact with the surrounding environment; in this sense, evaluating primary distribution is as important as the evaluation of geographical distribution in order to determine the impact of these pesticides.

The new regional archetypes should account for wind speed, rain, human population, human intake[9], for better describe fresh water ecotoxicity of copper (and metals in general). This also led to the use of parameterized freshwater archetypes with, for example, the characterization for cationic metals.

Finally this proposed framework provides a starting point for LCA practitioners, researchers and developers to better estimate cupric pesticide emissions and environmental impacts using in combination the resulting fractions of the customized model with characterization factors for emissions to off-fiel environment compartments of USEtox that take into account the regional land scape archetypes.

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LESSONS LEARNED IN REDUCING PESTICIDE RISKS IN ETOP MANAGEMENT THROUGH INNOVATIVE APPROACHES

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Summary

Conventional pest control tools such as pesticides, are meant to incapacitate, kill or destroy unwanted living things called pests, the classification of which is rather broad and includes, microbial, insects, plants, and other animals such as fish, birds, rodents, and even those in the higher taxonomic and strata.

The use and handling of pesticides are among the most difficult tasks to effectively monitor and regulate. Considerable numbers of users in low income countries (LIC) often transport, distribute, store, use, and/or dispose pesticide products in a manner that reflects their ability, skills and knowledge, perception, behavior, immediate needs and/or resources available at their disposal.

Many pesticide users, particularly those in the LIC, are barely cognizant of the presence of "best practices" described in several places, such as the manufacturers' material safety data sheet (MSDS). Best practices and procedures stipulated in documents prepared and made available by own national authorities, international organizations such as the United Nations Food and Agriculture Organization (UN/FAO), the World Health Organization (UN/WHO), bilateral and international donors, including the United States Agency for International Development (USAID), Organization for Economic Cooperation and Development, Inter-African Phytosanitary Council, academia and many entities are alien to low income farmers (LIF) in LIC.

In contrast to high income countries (HIC), the pesticide market in LIC and, to a certain extent, in some middle income countries (MIC), has been difficult to regulate. The magnitude of counterfeit products penetrating the pesticide market by far exceeds the national capacity to curtail the movements. This has caused effective enforcement of applicable laws and procedures on safe use and handling of these products often hard to implement. Obsolete, unusable and dangerous pesticides that are least desirable in their countries of origin, but much cheaper and affordable compared to the legally imported products to LIF easily penetrate the LIC pesticide market through the porous borders and further exacerbate the pesticide delivery problem. Empty pesticide containers are much thought after commodities in rural areas in LIC where they are inappropriately recycled and indiscriminately used without the pesticide residues removed.

Diversions of pesticides, including those that are considered highly hazardous products and banned or have strictly limited use in many countries (e.g., *DDT, Lindane, Endosulfan, Paraquat…*) or may have been allowed for time limited and restricted use fall in the hands of poor farmers and households. While the adverse impacts of these products have not been systematically and exhaustively documented in LIC, the human health impacts and the damage they may have caused or continue causing to the environment can be immense.

This paper attempts to look at the key limiting factors in the pesticide delivery system (PDS) in LIC as an element in the overall integral part of the pest management practices. It explores lessons learned from the innovative alternative approaches that USAID/OFDA supported to reduce the risks associated with the use of conventional pest control tools and draws conclusions and suggests recommendations.

Lack of Information on Safe Use and Management

Lack of appropriate and easily palatable information among grassroots users is often one of the key issues that undermine pesticide delivery system in LIC and extends the impact to pest management operations. The information contained in most MSDS are useful and relevant, but they seldom reach the LIF or is written in languages that are not comprehensible to the grassroots end users or are written in small fonts making them too hard to their eyes. Some labels may also lack adequate safety and warning information as opposed to the MSDS targeting users in HIC. For instance, the label on the product *Nativo* (a fungicide) targeted for the European market contains a warning statement that the product is "suspected of damaging the unborn child", whereas the label for the same product marketed in parts of southwestern Asia lacks this critical information. Similarly, the product label for *Gramoxone* (*Paraquat*) in the US warns that the product is "fatal if inhaled", but the label lacks this critical information on the same product which is marketed in parts of southwestern Asia. Even if it contained such information, there is no guarantee that the text could not be obscure to the end user LIC. These are just some of the overlooked critical messages that fail to reach the end users in LIC whose literacy rate is far below those of the HIC.

Reducing and/ or Managing Pesticide Risk

While all pesticides are by their inherent nature toxic to humans, some are more toxic than others. For instance, due to their inherent high toxicity to humans and non-target organisms, some pesticides that are classified as highly hazardous products (HHP) necessitated inclusion of Article 3.6 in the 2014 UN/FAO-WHO International Code of Conduct on Pesticide Management. The Article recommends that pesticides whose handling and application require the use of personal protective equipment that is uncomfortable, expensive or not readily available should be avoided, especially in the case of small-scale users and farm workers in hot climate. These kinds of pesticides are often categorized under restricted use products (RUP) and require extra precaution and their production and sale may have even been targeted for banning.

Pesticide risk reduction (PRR) and pesticide risk Management (PRM) are mutually inclusive and complementary interventions that can save life, alleviate human sufferings and reduce economic stress. While PRR and PRM can be implemented independently, their functionality is synergized through integration and concurrent interventions. Through these mechanisms, responses to ETOP can potentially avoid or mitigate pest and pesticide related crises and even disasters. The modus operandi of these interventions can be independent, mutually inclusive or simply tangential. The procedures and methods employed to address effectively execute PRR and PRM can be custom tailored as shown below or remain generic depending on circumstances.

Efforts to Explore Innovative Approaches for Pest and Pesticide Risks

Mindful of the severity and importance of the adverse effects that crop pests in general and emergency transboundary outbreak pests (ETOP) in particular cause to crops and pasture and significantly undermine food security and livelihoods of vulnerable populations, USAID's Office of US Foreign Disaster Assistance (OFDA) supported the launching of multipronged DRR initiatives as related to pest and pesticide management (PPM). These initiatives took into account ideas and tools considered innovative - not widely practiced or tried out - to explore alternatives to the conventional PPM practices to develop tools and methods that can support and complement the existing systems, methodologies and tools.

Key aspects of the above mentioned initiatives and lessons learned are examined in this paper. The benefits and complementarity of these approaches to explore how they will ensure safer and effective means of managing pesticides and preventing/controlling pests is explored. Attempts were made to investigate and evaluate the feasibility, viability, effectiveness, and sustainability of these initiatives. The roles of the various actors and their collaborative engagements at all levels are emphasized.

1. AAW Project in Ethiopia, Kenya and Tanzania

Armyworm, *Spodoptera exempta (Lepidoptera: Noctuidae)* (AAW) is one of the most devastating ETOPs that constantly threaten food security and livelihoods of tens of millions of LIF across sub-Saharan Africa, Arabian Peninsula, Asia, Australia and the Pacific, including Hawaii (Rose, Dewhurst and Page, 2000) and elsewhere around the globe. In a plague year, adult AAW moth can migrate over hundreds of thousands of miles following the seasonal winds and rainfall patterns producing caterpillars (larvae) covering thousands of square miles over vast areas.

AAW prefers crops in the Graminae or Poacea family such as maize, sorghum, millets, *teff*, barley, rice, wheat and sugarcane as well as a large variety pasture grass species. A single AAW outbreak can completely wipeout an entire crop field and severely damage pasture subjecting farmers to a seasonal poverty. While its primary host plants are grasses, in the absence of them, the pest can move to adjacent cropping areas and cause considerable damage. The pest often feeds on tender and younger plants and plant parts and later moves to older plants or plant parts when it has decimated younger plants. A subsistence farmer can lose his entire crop for the year to an armyworm outbreak not having additional assets to re plant his field unless the government or other partners step in and provide extra seeds or planting materials. Even then, the optimum sawing period will have been lost after the armyworm has damage the field and late planted seeds will at best produce a lot less yield, exposing the farmer to severe resource strain and food insecurity. In addition, AAW infested fields can also cause a disease to livestock and kill cattle.

Taking these recurring problems into account, USAID/ OFDA supported a three year fixed obligation grant as part of its assistance to disaster risk reduction (DRR) strategy. The grant provided assistance to implement a project to strengthen the capacity of rural communities and empower them to establish a community level armyworm monitoring, information collection, early warning and reporting (CBAMFEW) mechanism. Through this project, rural communities

– farmers, village chiefs, local government officials and extension agents received training in AAW identification, monitoring, reporting and executing preventive and curative control interventions. The farmer/community forecasters also received training on a mobile apparatus- based data entry, analysis and reporting system on AAW situation, weather and vegetation. This approach significantly improved early warning and effective and timely preventive and curative control interventions. This website http://bit.ly/1C782Mk contains maps of the 300 CBAMFEW monitoring sites as well as multiple data layers such as demographics, agricultural activities, land use pattern, infrastructure, and rainfall in two of the three countries that participated in the project. This link CBAMFEW monitoring sites contains detailed maps of the AAW monitoring sites and multiple data layers in Kenya. The maps are developed by USAID/OFDA's in-house Geographic Information Unit.

CBAMFEW project has proven effective and useful in enabling farmer forecasters to collect, analyze and disseminate important AAW information and alert local famers and neighboring villages. In 2014, farmer forecasters that were trained through the CBAMFEW project in a remote area in eastern Ethiopia were the first to issue warnings and alert neighboring villages and the regional agricultural office on a potentially devastating AAW outbreak. Thanks to these farmer forecasters' early warning, local administration and farmers in neighboring villages were

able to effectively abate what could have otherwise become a major outbreak and could have destroyed a year's worth of farmers' maize and sorghum crops and cause a serious damage to and their pasture or otherwise require large quantities of pesticides and substantial financial and technical resources to put the outbreak under control.

Through the CBAMFEW initiative, rural communities in all three participating countries

have been able to effectively prevent AAW outbreaks before they reach a level where abating

them would require considerable amounts of resources – pesticides, material, technical and monetary. The above field photo shows community-forecasters in Tanzania demonstrating the procedures for collecting and reporting AAW moth catches, using pheromone traps, and rain gauge readings as part of the AAW forecasting, prevention and control tools (photo: courtesy Yeneneh Belayneh).

2. PSMS – Pesticide Stockpile Management System

PSMS – pesticide stock management system PSMS is a computerized data-base system that enables participating countries to collect, analyze and document pesticide data where pesticides are frequently utilized as the primary means of controlling pests, including ETOPs and non- ETOPs. USAID/OFDA supported the creation and establishment of the system through UN/FAO's pesticide management program. To date, more than 63 countries, including score of ETOP-prone countries around the globe utilize the system to track their stockpiles, monitor transactions and make informed decisions as to what they ought to do with their existing stocks. Thanks to the system, a number of ETOP-prone countries have been able to easily retrieve up to date information on their pesticide inventories and make informed decisions whether they should use, donate, store for a later use or dispose them safely. Through these, a number of countries have been able to minimize human health impacts, reduce environmental contamination, and save considerable amounts of resources in health costs, environmental remediation, as well as storing and disposing of unusable, obsolete and dangerous stocks. This tool has proven very valuable for countries where the current state of their PDS has yet to be fully developed and incorporate important national and international standards, regulatory procedures and best practices.

3. PSN – Pesticide Stewardship Networking Initiative

PSN is a dynamic tool that aims at improving PDS in and around countries. The system is established in collaboration with national and regional entities that provide/produce, handle, sell, regulate, use, transport, research and/or training to those in need. The primary goal of the PSN initiative is to bring together all stakeholders that play an important role in subject country's PDS or may have a regional influence along this line. With the PDS in most LIC poorly structured or not structured at all, engagement of key stakeholders to establish and ensure effective sharing of skills and knowledge among the various actors remains to be an important element in proper development, strengthening and nurturing the PDS. The networking which is aimed at linking institutions and individuals responsible for pesticide management in country as well as neighboring countries can not only improve professional relationships among key stakeholders, but also raise awareness among the broader consumer sectors and significantly reduce movement of counterfeit and obsolete pesticides across political borders. This link was established in two sub-regions in Eastern Africa and the Horn of Africa. It is shown that the effectiveness and sustainability of such practices require champions in participating countries to get the ballrolling. Without dedicated champions, effective implementation of the overarching goal of the initiative is quite a challenge. Participating countries are encouraged to designate full-time champions to strengthen widespread implementation of the PSN initiative and improve the existing PDS. There is a strong demand for collaborations among neighboring countries to curtain free movement of elicit and dangerous pesticides through their shared porous political borders.

4. Safe Management and Removal of Empty Pesticide Containers

Empty pesticide containers and other packaging materials are often used for unintended purposes in LIC. These containers and packaging materials are, if at all, rarely properly cleaned and sanitized. They are almost always left with considerable amount of pesticide residues which contaminate food stuff or drinking water and animal feed that are often stored in them. Although not much is done on the documentations of incidences related to these containers, human and animal poisoning as well as contaminating the environment are frequent and can result in significant health costs, loss of labor, and adverse economic impacts.

In order to address the issue of empty pesticide containers, USAID/OFDA supported an innovative approach through a grant to the UN/FAO and assisted dozens of countries by installing drum crushers. The drum crushers not only enabled countries to crush metal and plastic drums, but also provided facilities to triple rinse the empty containers in situ. The drums that were puncher and crush were no longer attractive to LIF and rural communities in LIC. With the help of this tool several countries are now able to minimize inappropriate reuse and accumulation of empty pesticide containers and thereby reduced unnecessary health costs, avoided environmental contamination and contributed to the countries' economy.

5. ETOP Information Analysis, Dissemination and Management for Early Detection, Early Warning and Early Intervention Through in-House Expertise

USAID/OFDA's in-house expertise with considerable experiences in researching, collecting, analyzing and disseminating crucial information on ETOP and associated pesticides encourages and promotes ETOP prevention and control through early detection, early warning and timely and appropriate interventions. This crucial piece of information plays an important role to save lives, alleviate health and environmental impacts as well as reduce economic impacts of ETOPs. OFDA-issued ETOP monthly reports and alerts continue helping many countries to keep abreast with current thinking and approaches on PPM. The analytical PPM monthly updates and dekadal alerts reach partners and beneficiaries in the four corners of the globe via **free email subscription** and posted on the Agency PPM website: USAID ETOP - PPM website. These documents can be easily accessed and downloaded on the above website as PDF files. In addition, the Agency PPM website also contains a sizeable photo gallery that depicts PPM activities that OFDA has been supporting in dozens of countries across multiple continents. The Agency PPM website has been running for more than a decade and will remain to be around for years to come. These information pieces have been valuable to hundreds of thousands of users across the globe and will continue serving them.

OFDA's in-house PPM expertise has proven invaluable in evaluating ETOP situations and advising management and staff on the need for interventions in an effort to address ETOP. The expertise that provides important and timely advices on ETOP, DRR, PRR, PRM and PPM consistent with OFDA's overarching goal in food security, livelihoods, economic needs, health and the shared environment of vulnerable populations and communities is uniquely USAID. No other international organization has such capability or its equivalent. The presence of sector specific in-house expertise has proven invaluable and is highly encouraged to be maintained and expanded. In the absence of such essential capability, an institution or organization can be severely incapacitated in its strategic planning and implementation of a short-, medium- or long- term ETOP, PRR, or PRM responses, be it preventive or curative interventions.

6. USAD/OFDA Sponsored Capacity Strengthening in Acridid ETOP Management

Efforts made by USAID/OFDA to strengthen capacities of national and regional entities in Africa, Southwest and Central Asia as well as the Caucasus have helped raise awareness and perceptions of PPM among key players. ETOP-prone countries have been able to experiment and practice effective and safer innovative approaches, such as community- engagements, cross-border joint surveillance and information exchange, use of naturally occurring pest control tools, biological control, real-time information collection, reporting and sharing joint PPM operations and many more.

As an example of a unique collaborative venture initiated among experts in neighboring countries, the project funded by USAID/OFDA and managed by the UN/FAO launched joint training, workshops, and border surveillance among the Central Asia and Caucasian (CAC) countries. As part of this initiative, locust experts in Uzbekistan and Kyrgyzstan and other CAC countries were, for the first time, able to jointly monitor and survey locust breeding sites in their respective countries. The above photo shows Uzbek and Kyrgyzstan colleague jointly surveying locust breeding sites in Uzbekistan (photo credit: L. Nutsubudze).

The project has successfully created viable collaborative interventions among neighboring countries that were once doubtful of each other for not being the source of locusts that invade their respective countries. The initiative also enabled CAC countries to identify and maintain a roster of *acridid* and PPM expertise in the region that could be called on when needed. Through these collaborative interactions among technical staff, countries in the region have been able to contribute to the reduction in the use of pesticides and thereby improve PPM for the region as a whole and individual countries in particular.

CONCLUSIONS AND RECOMMENDATIONS

There is an increasingly continued need and demand for appropriate training and technical assistance in the implementation of safer and effective pest control tools and practices, all the more so in LIC. Exploring alternative approaches through naturally occurring products, improved pest management practices and safer and effective indigenous knowledge and skills is all the more relevant.

The use of hardcore, highly hazardous conventional pesticides does not give the best bang for the buck as it is not the most viable means available to avert ETOP outbreaks and avoid the damages they can cause to crops or prevent public health threats from *arbo*-diseases (arthropod-borne diseases) such as malaria, dengue, lieshmaniasis, and many more.

There is no a single tool (a silver bullet) that can effectively control crop pests and/or prevent public health pests and at the same time readily available at an affordable cost as well as ensure human health and safety of the environment. Combinations of a variety of tools and methods can create a synergy that can significantly contribute to effective prevention and control of crop pests as well as public health pests while saving time and minimizing costs incurred, not to mention improve human health. Such approaches can help avoid environmental pollution by eliminating the need to deal with unusable old leftover pesticide stocks, tedious collects and costly dispose of large amounts of dangerous empty pesticide containers.

With inherent synergy among various kinds of pest prevention and control tools, effectiveness and efficacy of the combined interventions can be maximized and help frontline LIC manage both crop pests and public health pests in a manner that maintains the balance between the major factors that play an important role in sustainable pest management practices.

With new pesticides entering the market and the gap in the skills and knowledge of small-scale farmers in pest prevention and management widening and the ability of LIF to access these new products evermore shrinking, the need to strengthen community-based alternative interventions have become ever more critical. To this effect, a USAID/OFDA funded CBAMFEW (community-based armyworm monitoring, forecasting and early warning) made significant contributions to improve farmer's perception and knowledge of the AAW source, origin and impacts as well as safer and affordable means of preventing and controlling them with minimal to no adverse effects.

In most LIC, empty pesticide containers and packaging materials are frequently recycled for unintended purposes. These containers and packaging materials are rarely properly cleaned or sanitized and they are left with considerable amounts of pesticide residues before they are used by LIF and low income rural communities for unauthorized purposes. The residues in the containers or packaging materials contaminate food, drinking water and/or animal feed that are often stored in them. Such practices often cause health hazards to humans and domestic animals as well as contaminate the environment and result in significant health cost, loss of labor, economic impacts and irreversible environmental damage. A USAID/OFDA-funded project provided metal crushers that come with the ability to triple rinse and clean empty pesticide containers and crush making them unattractive to LIF and rural communities. These drum crushers have been installed in dozens of LIC. A number of ETOP-prone countries where the crushers are installed have been able to collect, crush and safely remove large quantities of empty pesticide containers and significantly reduce the quantities of empty containers that fall in the hands of LIF and rural communities. Although not properly documented, it is highly likely that this has saved considerable amount of lost work hours from sick leave, caregiver need, health costs and death of domestic animals due to feeding from contaminated containers. This tool has proven useful and its installation is recommended in other LIC.

Regional collaborations were encouraged and promoted through OFDA funded project and successfully demystified unsubstantiated blame games in *acridid* pest invasions that were once considered the outcome of intentional send-off or the result of negligent behavior among the next the neighboring countries. The project sufficiently understands that ETOP are not a single- country issue and so are the interventions required to curtail their migration and abate their negative impact on crops and/or health and the shared environment. For this, joint planning and coordinated operations are strongly promoted, encouraged and recommended.

It is shown that the effectiveness and sustainability of the PSN initiative requires dedicated champions to get the ball rolling in participating countries. Without dedicated champions, effective implementation of the overarching goal of the initiative is quite a challenge.

Participating countries are encouraged to designate full-time champions to strengthen widespread implementation of the PSN initiative and improve the existing PDS. There is a strong demand for collaborations among neighboring countries in jointly patrolling their porous political borders and sharing relevant information to curtail uncontrolled and free movement of elicit and dangerous pesticides, including HHP. Without a fully operational and enforced monitoring and control tools put in place, a viable PDS cannot be established or become fully functional at the national or regional level. Lack of such tools will continue encouraging free flow of illegal, counterfeit and obsolete pesticides along the LIC borders.

The presence of sector specific in-house PPM expertise has proven critical for regularly monitoring, assessing and evaluating ETOP situations and providing relevant updates on the situation on the ground and operational advice to management and staff on the needs for effective response and preventive interventions for the existing and ensuing ETOP problems. With OFDA's strategic objectives and its overarching goal primarily revolving around food security, livelihoods, economic needs, health and the shared environment of vulnerable populations and communities, the presence of such expertise has proven invaluable and needs to be bolstered to ensure continued timely, rapid and effective response and preventive interventions. In the absence of such crucial capability, a response institution or organization could be severely incapacitated to strategically plan for a short-, medium or long-term response or DRR interventions.

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CENTERS OF ASSISTANCE TO THE FARMERS, SUFFERED FROM USE OF COUNTERFEIT PESTICIDES (CAF)

Mikhail Malkov

The idea of development of the network of CAFs as a sustainable instrument on combating illegal pesticides trade was proposed by Mr. Mikhail Malkov and Mrs. Larysa Petriv during the XIII IHPA Forum in Zaragoza in 2015. Traditionally comprehensive counteracting to any crimes consists of three major stages: prevention, preparedness and response. However, when we are speaking about committed environmental crimes – such as production and distribution of fake pesticides - recovery stage must be taken into consideration. In the areas of different crops production, it becomes even more important due to possible social tension because of financial losses and long-term natural resources degradation. The main purpose of the CAFs is to help the farmers to mitigate these losses.

Core vulnerable group is small- and medium-scaled farmers. In major countries (probably except developed states) such agribusiness has similar characteristics: (i) low access to finance; (ii) poor land consolidation – many different plots in one field; (iii) low or no crop rotation on each particular plot and, in many cases, (iv) – farmers cannot cooperate regarding sort of crops and joint purchase of seeds and plant protection products even within one area (or big field). It is clear, that promotion of agricultural cooperatives for small-scale farmers will be the strategic aim of CAFs but main activities should be done ASAP.

As a first step, in case of application of the farmer to CAF (preferably – an NGO), Center should organize the legal support to the farmer in order to get compensation for the losses. For this to happen the applicant will have to bring all documents related to purchase of the pesticide with maximum information about the distributor, and preferably the empty drum with the label. CAF, normally well connected with the representative of local business associations (eg. CropLife), will be in position to organize the chemical analysis in order to get the evidence whether container is original or not, and whether the product has been purchased from the proper supplier, confirm the labeling and marking of the drum. All this info can afterwards be used in the court. Cooperation with top lawyers is a must and can be arranged either by the business associations or through other stakeholders (eg. Involved UN Agencies). The CAF will facilitate the farmer in getting better conditions during the arrangements with these lawyers.

As a hidden benefit, it will also allow to collect the data about illegal suppliers as well as to open at least some elements of the criminal supply chain and provide this information to the law enforcement and/or security advisors of the plant protection companies. On the other hand, in order to achieve this goal, CAFs will have to be involved not only in information exchange but also in capacity building of law enforcement and other stakeholders like customs, tax police, ecological inspectorates and food safety authorities.

CAFs may be also involved in monitoring the collection and disposal of empty containers and organize relevant awareness company. It is extremely important as the lack of Empty Container Management System is accounting to counterfeiting.

Another big task is the support in remediation of the polluted land. This work is pure business and requires certain investments for soil analysis and further activities. Clear that CAFs neither technically nor financially can deal with this problem. However, they should establish partnership relationships with the specialized organizations and financial institutions in order to support the farmer in getting better conditions and achieving reasonably fast results.

Finally, the Centers must work sustainably. It means that after the end of the donor's program CAFs should continue their activities. It can be easily afforded, as these organization will certainly become the analogue of traditional extension services – Centers of Excellence where the farmers can get the advice where to get original pesticides, seeds, vet medicines etc. from the people to whom they trust.

The Proposed concept was warmly welcomed during the XIII IHPA Forum. After one year of intensive discussions UN Environment Program has decided to launch the pilot project in Ukraine which, besides all, will cover development of three Centers of Assistance to the Farmers in three critical areas: (i) Zakarpatska oblast bordering with 4 EU countries; (ii) Odeska oblast with the main Black Sea ports and (iii) Donetska oblast (Government controlled areas), affected by ongoing military conflict. The project will be implemented by the Ministry of Ecology and Natural Resources of Ukraine in close cooperation with other Governmental Stakeholders, Green Cross Switzerland and several Ukrainian NGOs. Link to the project press release is: http://web.unep.org/chemicalsandwaste/special-programme/news/unep-help-ukraine-crack-down-illegal-trafficking-fake-pesticides

Mikhail Malkov

TOXICOLOGY

Part 1: HCH and POP Pesticides in Spain and South America

HEALTH AND ENVIRONMENTAL RISKS OF THE LINDANE WASTE DUMPING IN SABIÑÁNIGO (SPAIN)

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Abstract

The company Inquinosa produced Lindane between 1975 and 1989 in the town of Sabiñánigo (Spain). The factory, which has still not been dismantled, is located just on shore of the Gállego river, as well as most of the over 100.000 tonnes of hazardous wastes it generated. Since 1987 environment protection organizations have been denouncing the risks for the human health and the environment posed first by the uncontrolled dumping of the HCH production waste and later by the abandonment of the waste deposits and their mismanagement. This has resulted in the contamination with a mixture of POPs, heavy metals, and other substances of high concern of the soil, subsoil, and underground waters of the area, together with the contamination of the Gállego river and its reservoirs over a stretch of more than 100 km. During these years, authorities have considered the issue an environmental waste management problem, denying any human health risk. During the summer of 2014, the poor managed transfer of the waste from an old deposit to a new landfill in Bailín resulted in the presence of high concentrations of HCH isomers in the water of the Gállego river, leading to the cut off of drinking water supplies of 40000 inhabitants of the area and of the irrigation system to more than 7000 users. Water, sediment and fish analysis show that the environment and the population have been and are exposed to low levels of a mixture of dozens of toxic substances. On account of this, about ten environmental, trade union, health and community organizations have presented a set of ten urgent measures that the responsible administrations should apply in order to reduce the exposure of the population and the environment to these substances, including a biomonitoring program of the exposed population.

Key Words

Lindane, pollution, water, NGO, POP,

Introduction

It seems incredible that one of the most severe episodes of pollution with a persistent organic pollutant in Western Europe is so unknown and that, still, 40 years after the beginning of the spills, the pollution sources remain active and nobody has been kept responsible for this situation.

The company Inquinosa produced lindane, this is, gamma hexachlorocyclohexane (δ- HCH) in the city of Sabiñáni go (Huesca) between the years 1975 and 1989. 22 years after the company completely ceased its activities (in 1989 the regional government ordered the cessation of lindane production, but the company continued grinding and packaging activities until 1993) the factory has not been decontaminated, and its soil and undersoil are polluted as well as the nearby Sabiñánigo reservoir. HCH waste pollutants are also leaching into the soil and groundwater of the dumpsites where the waste has been disposed and unfortunately also into the river Gállego (tributary of the Ebro river). The contamination of the water has left thousands of inhabitants of its basin without drinking supplies. Furthermore, production waste was dumped in several sites in the vicinity of Sabiñánigo, however the exact locations still remain unknown. Public authorities have spent already over 62 million Euros in controlling the situation.

Industrial waste is generally a fraction of the transformation processes, but in the production of lindane this is not the case. Lindane is obtained by reacting chlorine and benzene. The useful fraction is only 15%. The remaining 85% is a solid waste composed of a mixture of different organochlorinated substances. During a second refining step, a liquid residue with high δ- HCH concentration is produced. It is estimated that during the production of lindane, Inquinosa produced and dumped in its surroundings a total of 115.000 t of waste (Polanco M., 2012).

In this article we are going to describe the health and environmental risks of the lindane waste dumping in Sabiñánigo (Spain) from an NGO perspective and the proposals put forward by civil society and trade union organizations of Aragón to improve the situation.

Results and discussion

The first denounces of the impact that the factory was causing to the health and the environment are dated in 1987, when ADEPA a local environmental group denounces the odours that the factory caused in the city, the emissions from the factory to the Gállego river and the dumping of the production waste together with the city's garbage in the landfill. Their claims would be supported afterwards by regional and national NGO, such as Ecologistas en Acción, ANSAR, Greenpeace, SEO Birdlife, and COAGRET among others.

The first dump site that the company used, with the knowledge of local and regional authorities, was the municipal waste landfill of Sardas, where it is estimated that between 30.000 and 80.000 t of solid waste and 2000 t of liquid waste (DANPL) were dumped. The total volume of waste in this landfill is estimated to be 350.000 m^3.

The waste deposited in this site also contains high levels of metals and hydrocarbons. This landfill is located 200 meters from the Sabiñánigo reservoir and 500 meters from the first houses of the city of Sabiñánigo. It doesn't have any lining nor a leachate collection and treatment system. Leachates and dispersion of waste have contaminated soils, groundwater, and surface water. It is estimated that the Gállego River receives 120 k of HCH each year through polluted surface water inputs (Fernández J et al., 2013).

The Sabiñánigo reservoir received during decades the direct emissions from the the factories located in Sabiñánigo and is still receiving the leachates of the Sardas landfill and of the Inquinosa plant. Its sediments have a high concentration of lindane, mercury, arsenic, PAH, etc.

Its undersoil contains hexachlorocyclohexane and, in lower levels, chlorobenzene, 1,2 dichlorobenzene, 1,4 dichlorobenzene, cadmium and mercury have been detected. Benzene, naphtalene, antracene, and other metals such as selenium, copper and lead have also been detected in several spots (Confederación Hidrográfica del Ebro, 2010).

The second site where the company was allowed to dump its waste was the Bailín landfill, located 3000 m from the city and 800 m from the Gállego river. It is estimated that between 1984 and 1992, Inquinosa dumped here also between 30000 and 80000 t of solid waste and 2000 t of liquid waste, that were also mixed with urban waste. The site contained a total amount of 180.000 m3 of waste. (Fernández J et al., 2013). Analysis of the HCH waste performed in 1991 showed that it contained such high concentrations of dioxins (2633 ng/k) that it should be considered dioxin waste (Técnicas de Protección Ambiental ,1991).

Furthermore, an undetermined quantity of pure lindane was also dumped in this site, as during its last years of activity, Inquinosa had problems to market its lindane due to social and judiciary pressure as a consequence of NGO denounces (Polanco, M, 2012).

This landfill also lacked bottom lining and leachate collection and treatment systems. In 1996 a superficial lining system was installed.

The location of this landfill couldn't be more inadecuate. It is placed in the Bailin creek, tributary to the Gállego river. The geological setting is formed by vertical sequences of sandstone, limestone and conglomerates that present several discontinuities and fractures that have facilitated the infiltration of the waste into the undersoil and groundwater. It is estimated that the underground stores already 15 t of a dense nonaqueous phase liquid (DNAPL). The leachate plume in the groundwater has reached the Gállego River. An average concentration of 0.5μg/L and peaks of 1 μg/L of HCH have been measured 0.5 km downstream in the river. Additionally, it is estimated that the river receives 20 k of HCH through surface water inputs. Other diffuse sources are not considered (Polanco, M, 2012, Fernández J et al., 2013).

Nevertheless, the Government of Aragón and the Spanish State Authorities decide to move the waste from the Bailín landfill to a new one, equipped with bottom lining and leachate collection and treatment system, located in the same area as the former landfill. The cost of the new landfill is estimated to be 19 million Euros.

The construction of the new landfill ended in 2014 and the waste began to be transferred. After visiting the works several times, Ecologistas en Acción denounced publicly the negligence and unfulfilment of basic security measures.

Workers walked around the most polluted areas without wearing their masks, with the pressuring equipment of their protective clothing disconnected and hanging from their shoulders, disdaining basic security norms and putting their health under risk.

Trucks loaded with waste remained hours parked with their load uncovered, allowing its dispersion. Although a waste sorting plant was constructed, it was used as a parking space for the trucks, and the waste was deposited in the new landfill without any classification. Liquid waste was also mixed together with the solid waste, although it is known that it will accelerate the deterioration of the bottom lining.

Each time the trucks were loaded with the waste a cloud of dust was formed and dispersed by the wind. No equipment to avoid this situation was used, although it was in place.

The unloading of the waste in the landfill also formed clouds of dust that the wind moved towards Sabiñánigo, as the intense lindane odour in the city revealed. Repeated complaints from the neighbours to the emergency service are derived to the Municipality of Sabiñánigo, who assured them there was no problem, after consulting the regional authorities **(Ecologistas en Acción, 2014)**.

The negligence and unfulfilment of the security measures is later confirmed by the police (**DiarioAragonés.com, 2015)**.

Shortly before the end of the transfer of the waste, in September of 2014, regional authorities had to cut the drinking water supply to 40000 inhabitants and 7000 users (irrigators, farmers, etc.) of the basin of the river Gállego as analytical results performed by the Hydrographic Confederation of the River Ebro (CHE), show levels of HCH isomers in the water up to 1.5 μg/L well over the average HCH limit in surface water (0.02 μg/L) specified by the Council Directive for priority substances under the Water Framework Directive (Directive 2008/105/CE). Previous analysis from the regional authorities had delivered the same results but were not published, allowing the population to drink water with high levels of these pollutants at least during two months, between July 1st and September 17th 2014.

The high levels of HCH isomers that appear in the river come from the new landfill. The summer rain storms overflow the tanks that should collect the leachate and the waste flows with the rainwater through the Bailin creek to the Gállego river. The new landfill has not been inaugurated yet, but it already has severe design and management problems.

To avoid alarming the population, The Government of Aragón assures that these levels do not pose any helath

risk. The Food Segurity Agency of Aragón publishes a report on the toxicity of lindane (δ- HCH) that states that the acute toxicity level for this chemical is 10 mg/kg. This is, a child with a weight of 15 kg, would need to ingest 150 mg to be intoxicated and therefore would need to drink 7500 liters of water polluted with 2pbb of lindane (Ferrer A y Badiola JJ, 2014).
Unfortunately, these predictions are made only for one substance and forget that human exposure is concomitant to several chemicals at the same time that may act with common toxicity mechanisms.

We understand that, with the exception of some workers exposed during the factory's activities and during the management of the waste, the population of Sabiñánigo and its surroundings and the population of the Gállego river's basin has been and is still being exposed, on an ongoing basis, to low levels of dozens of toxic substances, therefore, chronic toxicity has higher relevance that acute toxicity.

Many of the substances detected in the water, soils, and sediments by the regional authorities and the CHE are pollutants with well known toxic properties, while there is scarce toxicological information for many others.
Lindane is restricted in Europe and in process of being banned worldwide under the Stockholm Convention. A report from the United Nations Environmental Program (UNEP) list among its adverse health effects: damage to the liver, immune and reproductive systems; adverse developmental effects (growth, sperm count, reduction of testosterone levels); and genotoxicity. It also recalls that the international Agency for Research on Cancer (IARC) has classified alfa, beta and gamma HCH as possible human carcinogens (UNEP, 2006).
Recent studies relate the exposure to organochlorinated pesticides, including lindane, with hypothyroidism, breast cancer, malformation of urogenital tract of boys exposed in-utero and also with male fertility problems (Ibarluzea et al, 2004; Goldner et al., 2013; Fernández et al., 2007).
As Table 1 shows, many organochlorinated substances are present in Sabiñanigo's wastes, including chloropenols, chlorobenzenes, chlorocyclohexanes, etc. En general, the chronic effects of these substances include damage of the neurological, immune and reproductive systems.

Table 1. Pollutants detected in samples of soils, water, sediments and leachates (Fernández J et al., 2013; CHE, 2010).

Group	Substances	Leachate	Soils	Water	Sediments
AROMATIC VOC	Benzene	X	X	X	X
	Toluene	X	X	X	X
	Ethylbenzene	X			
	Xylenes	X			
PHENOLS	phenol	X		X	X
	monochlorophenols	X	X		
	dichlorophenols	X	X		
	trychlorophenols		X		
	tetrachlorophenols	X	X		
	pentachlorofenols		X		
	cresol				X
CHLORINATED ORGANIC HYDROCARBONS HIDROCARBUROS	Chlorometane	X			
	Dichlorometane	X	X		
	Trichloroethylene	X			
	Tetrachloroethylene	X			
CHLOROBENZENES	monochlorobenzene	X	X	X	X
	Dichlorobenzenes	X	X	X	X
	Trichlorobenzenes	X	X	X	
	Tetrachlorobenzenes	X	X	X	
	Pentachlorobenvenes	X	X	X	
CLOROFENOLES	Monochlorophenol	X		X	
	Dichlorophenol	X		X	
	Trichlorophenol	X		X	
	Tetrachlorophenols	X		X	
	Pentachlorophenols			X	
PAH	Naphtalene		X	X	
	Antracene		X		X
	Chrysene				X
	Benzo(k)fluorantene				X
ORGANOCHLORINATED PESTICIDES	Alpha-HCH	X	X	X	X
	Beta-HCH	X	X	X	X
	Gamma-HCH	X	X	X	
	Delta-HCH	X	X	X	X
	Epsilon-HCH		X	X	X
OTHER ORGANIC COMPOUNDS	Acetone		X		
	p-Chloroaniline		X		
	Trichlorocyclohexane			X	
	Tetrachlorocyclohexane	X	X		X
	Pentachlorocyclohexane	X		X	
	Hexachlorocyclohexanes	X			
	Heptachlorocyclohexanes	X			
	Hexachlorohexadienes	X		X	
	Heptachlorohexadiene	X			
METALS	Arsenic		X	X	X
	Selenium		X	X	X
	Tin		X	X	X
	Antimony		X		X
	Cadmium		X	X	X
	Cobalt		X		X
	Copper		X		X
	Chromium		X		X
	Nickel		X		X
	Lead		X	X	X
	Zinc		X	X	X
	Mercury		X	X	X
	Barium		X	X	X
	Vanadium		X		X

In addition to organochlorinated substances, the wastes contain polycyclic aromatic hydrocarbons (PAH) such as naphthalene and antracene, wich are carcinogens and neurotoxicants; carcinogen volatile organic compounds (VOC) such as benzene and reprotoxic VOC such as toulene, ethylbenzene and xylenes; carcinogenic (arsenic, cadmium, chromium, lead, nickel), neurotoxic (mercury, lead) and reprotoxic (lead, cadmium, mercury) metals. Many of these substances are also highly toxic for aquatic organisms and wildlife (ISTAS, 2015; ECHA, 2015).

Organochlorinated substances, PAH and heavy metals are persistent, this is, they may remain in the environment during years, polluting the soils and sediments. They are also able to bioaccumulate and biomagnify along the food chain. Substance that are persistent and bioaccumulative pose severe risk to human health and the environment. Therefore European legislation, such as te REACH Regulation, consider that Persistent, Bioaccumulative and Toxic substances (PBT) or very Persistent and very Bioaccumulative (vPvB) substances do not have a safe exposure threshold.

It is also important to recall that HCH isomers and other chemicals that are present in the wastes (PAH, cadmium, mercury) are endocrine disrupters, this is, substances that are able to interfere with the normal functioning of the endocrine system. They can disrupt the hormonal system at extremely low levels, causing a wide range of adverse heath effects that depend on the timing of exposure. Foetal development, early childhood and puberty are periods of high vulnerability to the exposure to these substances (TEDX, 2015).

Furthermore, the toxicity of a mixture of substances is quite different to the toxicity of a single substance. In the case of endocrine disrupters it has been shown that mixtures can have more potent effects than single substances (Kortenkamp, 2009). In summary, to assess the health risks of the lindane wastes we should take in account that the environment and the population are exposed to a mixture of dozens of substances that not only are toxic by there own, but that combined may have more potent adverse effects.

In order to control the pollutants entering the river Gállego through the Bailín creek urgent works have been implemented, to enlarge the storm water containment capacity of the new landfill and to try to contain and treat the water from the creek before it reaches the river.

However, summer storms during 2015 have resulted again in high pollution levels in the river. On June 13th 2015, spills from the new landfill to the river have HCH isomer levels of 528µg/L , well over the 50 µg/L established in its discharge permit. (Ecologistas en Acción, 2015).

Members of Ecologistas en Acción visiting the area, realised that the water treatment facility that had been built to treat the creeks water was not working at all, and that the polluted water was flowing again directly to the river. They were unable to find anybody to whom inform in the landfill facilities, although the storms had been predicted. Actually, Civil protection authorities had recommended the towns of the Gállego basin not pump water from the river as storms were expected during those days (Ecologistas en Acción, 2015).

The Environment department of the Government of Aragón has announced the end of the emergency works in the Bailín creek. However, the pollution of the sides of the creek is so high that even after two clean-ups of the sediments, in some areas the levels of pollutants are over 5000 µg/k sediment (Ecologistas en Acción, 2015).

The Spanish Ministry of the Environment and the Government of Aragón have agreed recently on a Decontamination Plan of the Gállego River . The plan, intends to clean-up the factory site, control the pollution from the Sardas and the two Bailín landfills (budgeted in 8 million Euros) and derive and clean the water from the Bailín creek (budgeted in 3.5 million Euros). In addition, this year, the Environment Department of Aragón is proving a new groundwater decontamination system through chemical oxidation, in the frame of an EU Life Plus project named DISCOVERED LIFE (Gobierno de Aragón, 2015).

Proposals

Environmental, trade union and civil society organisations of Aragón have developed a set of ten urgent measures that the responsible administrations, this is the Government of Aragón, the Confederación Hidrográfica del Ebro and the Spanish Ministry of the Environment, should implement in order to ensure the health of the population and of the environment of the basin of the Gállego river:

1. Provide alternative supplies of clean drinking water to the population of the Gállego river's basin.
2. Identify all the sites where Inquinosa or other companies from Sabiñánigo have dumped industrial waste.
3. Clean-up all the polluted sites, including the Sardas and Bailín landfills, the factory of Inquinosa, the Sabiñánigo reservoir and other sites where waste has been dumped, as well as the basin of the Gállego river.
4. Transparency and information. Publish, in real time, through the Web page of the Government of Aragón and through other media, the results of all the analysis on the state of the pollution of the river and its basin, including surface water, groundwater, soil, sediments, flora and fauna, crops, etc.
5. To search for an adequate site for a secure and stable storage of the waste, dismissing its incineration.
6. To guarantee the participation of all environmental, trade union and civil society organisations, as well as the population of the Gállego river basin in the monitoring and solution of the crisis.
7. To carry out a study to assess the exposure of the population to the pollutants that have been discharged to the Gállego river basin through a biomonitoring program.
8. To monitor the health of the workers of Inquinosa and of the workers participating in the works on the Bailín landfills.
9. To prosecute Inquinosa and demand responsibilities (political, penal, administrative) to those involved in the spills from the new landfill. To control the money that has been invested in the Bailín works and demand responsibilities to the companies that might have not complied with their functions or might have acted with negligence.
10. To elaborate a Environmental Health Plan for Aragón, that includes all the previous proposals and establishes a framework for the establishment of objectives and the adoption of the measures that are needed to guarantee the health of the population

against the risks posed by the pollution of the environment in Aragón.

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PERSISTENT ORGANIC POLLUTANTS AND REPRODUCTIVE FAILURES IN SPAIN

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Background

Persistent organic pollutants (POPs) are a wide group of highly lipophilic environmental contaminants that tend to accumulate and biomagnify in food chains, resulting in the considerable exposure of living organisms. POPs include, among others, organochlorine pesticides (OCs), which have long been widely used in agricultural activities and public health programs as highly effective pest control agents, and polychlorinated biphenyls (PCBs), employed as dielectric and heat exchange fluids among other commercial applications (WHO, 2014). Although the production and handling of many organochlorine POPs are in decline worldwide, human exposure to these chemicals remains of relevance to public health.

Organochlorine POPs, like dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB), and some PCBs, polybrominated biphenyls (PBBs), dioxins and furans are identified as endocrine disrupting chemicals (EDs) because they are able to disrupt the endocrine system of humans, mimicking or otherwise interfering with naturally produced hormones that control the development and functioning of an organism, and consequently causing adverse health effects. EDCs may interfere with the synthesis, secretion, transport, binding, action, and/or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior. Exposure to EDs has been implicated in certain adverse health effects, and some new prospective birth cohort studies have yielded suggestive results on these exposure-effect relationships.

Prenatal Exposure

The impact of EDs exposure on human health strongly depends on the age at which exposure occurs. Thus, the effects of exposure in utero can be expected to differ from those of exposure during adulthood. Both embryos and neonates are highly sensitive to ED exposure and suffer more severe adverse effects than do adults. Experimental and epidemiological studies have suggested that pre- and perinatal periods constitute a “time window of especial vulnerability” to the harmful effects of those toxicants.

Pregnant women are daily exposed to a wide selection of those exogenous agents and transfer of EDs from mother to fetus has been demonstrated by their detection in several biological matrices such as maternal blood, umbilical cord blood, placentas, and newborn blood.

Our research group has confirmed prenatal exposure to numerous persistent EDs, including OCs, PCBs, dioxins, furans, and heavy metals, in a mother-child birth cohort recruited at the San Cecilio University Hospital (one of the two reference public hospitals serving Granada province in southern Spain), from October 2000 to July 2002. This cohort is part of the INMA (Environment and Childhood) study, a population-based cohort study in Spain that focuses on prenatal environmental exposures in relation to growth, development, and health from early fetal life until childhood. The INMA-Granada cohort includes 668 mother-newborn pairs. Thus, we have demonstrated the presence of several persistent EDCs in the umbilical cord blood of newborns as well as in placenta tissue and in maternal urine during pregnancy.

Because mothers are not exposed to a single chemical but to a complex mixture of compounds, investigation of toxic impact should not be limited to the individual effects of single agents but should rather consider the combined effects of chemicals. For this purpose, our research group has also developed of the total effective xenoestrogen burden (TEXB), using a specific bioassay for the combined estrogenicity in placenta samples, as a reliable marker of the cumulative effect of mixtures of xenoestrogens in the organism. TEXB assesses the estrogenicity of biological samples in two fractions: that largely attributable to environmental organohalogenated xenoestrogens (TEXB-alpha), and that mostly due to endogenous estrogens (TEXB-beta). Exposure to mixtures of (anti-)androgenic chemicals during pregnancy was also explored using the biomarker total effective xenobiotic burden of anti-androgens (TEXB-AA).

Reproductive failures

It has been hypothesized that the rise in male reproductive disorders over recent decades may at least be partially attributable to environmental chemical exposures. Both experimental and human data point toward a causal relationship between exposure to OCs during pregnancy and the development of male congenital malformations, such as cryptorchidism (failure of one or both testicles to descend into scrotum) and hypospadias (urethral opening on ventral side of penis).

First, we explored the possible association between exposure to xenoestrogens of the male fetus to endocrine disruptors and sex differentiation disorders in the INMA-Granada cohort. A case–control study was nested in INMA-cohort comparing 50 newborns with diagnosis of cryptorchidism and/or hypospadias with 114 boys without malformations matched by gestational age, date of birth, and parity. All placentas had measurable concentrations of at least one of the 16 OCPs quantified, reflecting the ubiquity of exposure in the population, although the number of quantifiable residues was significantly higher in cases than in controls (9.34 ± 3.19 *vs*. 6.97 ± 3.93). Our results showed an excess risk of malformation associated with the presence of pesticides (lindane, among them). Interestingly, the conditional regression analysis after adjusting for potential confounders, odd ratios (ORs) for cases with detectable levels of lindane was (OR = 3.38; 95% CI, 1.36–8.38).

In addition, we explored the relationship between exposure to mixtures of xenoestrogenic chemicals of the embryo-fetus and the risk of cryptorchidism and/or hypospadias by estimating TEXB in placentas. Three of four placentas from boys with cryptorchidism and/or hypospadias and one of two placentas from control boys had a measurable level of estrogenicity due to xenoestrogens (TEXB-alpha). Compared with controls, cases had an OR for detectable versus non-detectable TEXB-alpha of 2.82 (95% CI, 1.10-7.24). No single chemical could be positively and significantly associated with the biologic effect measured by TEXB-alpha.

Second, we also analyzed the relationship between exposure to mixtures of (anti-)androgenic chemicals during pregnancy and the risk of cryptorchidism and/or hypospadias in offspring, using the total effective xenobiotic burden of anti-androgens (TEXB-AA) biomarker, in a subsample of 29 cases and 60 healthy controls nested in the cohort. The TEXB-AA biomarker is combined with a bioassay-directed fractionation protocol that separated endogenous hormones from most (anti-)androgenic chemicals by normal-phase HPLC. The bioassay measures the androgen-induced luciferase activity and the inhibition of this pathway by (anti-)androgens. We collected 27 HPLC fractions from each placenta extract, which were all tested in the bioassay. The multivariable statistical analyses indicated a statistically significant positive dose-response association between the potent anti-androgenic activity of the HPLC fraction collected during minutes 1-2 (F2) and the risk of malformations (OR: 2.33, 95% CI: 1.04-5.23).

Fetal exposure to EDs may also increase the risk for other reproductive outcomes at birth or growth later in life. Our findings suggest that prenatal exposure to xenoestrogens may increase birth weight in children, which might have an impact on child obesity and other later health outcomes. To analyze the relationship between TEXB and child birth weight, early rapid growth and body mass index (BMI) at 14 months, we randomly selected 490 placentas collected in the whole INMA prospective birth cohort. Multivariate models showed that higher TEXB-alpha levels (third tertile) were associated with increased birth weight in boys but not in girls ($\beta = 148.2$ g, 95% CI: 14.01, 282.53, $p_{int} = 0.057$). Additionally, higher TEXB-alpha values in boys were related with a lower risk of early rapid growth (OR = 0.37; 95% CI: 0.15, 0.88) and with a larger BMI z-scores at 14 months of age ($\beta = 0.29$; 95% CI: − 0.11, 0.69).

Conclusion

Although the complexity of human biology makes it very difficult to establish a relationship between ED exposure and harmful effects of those toxicants, our data suggest that environmental chemicals play a role in the risk of some reproductive outcomes.

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HUMAN EXPOSURE TO PERSISTENT ORGANIC POLLUTANTS AND CHRONIC DISEASES: AN OLD PROBLEM FOR CURRENT GENERATIONS. FOCUS ON METABOLIC SYNDROME

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Abstract

Because of their high resistance to degradation and their potentially harmful effects on human health, the manufacture and use of most organochlorine pesticides and polychlorinated biphenyls have been banned in most countries. However, despite these restrictions, human exposure to these contaminants remains prevalent and it occurs on a daily basis, with important differences in exposure levels among populations and individuals. In addition to the dose, timing of exposure is critical, given the particular vulnerability of humans to the effects of pollutants during fetal life and infancy, effects that may manifest not only during childhood but also during adulthood. On the other hand, recent decades have seen a marked increase in the prevalence of chronic non-infectious diseases, and five of them (cardiovascular disease, stroke, cancer, respiratory diseases, and diabetes) are considered responsible for 63% of deaths worldwide. The term "metabolic syndrome" has been defined as a cluster of conditions (hypertension, high glucose levels, obesity, and dyslipidemia) that are commonly associated with an increased risk of heart disease, stroke, and diabetes. In the present manuscript, we present a short review of the potential link of POPs exposure and the development of metabolic syndrome.

Several recent studies reported a positive association between exposure to low doses of organochlorine pesticides and the risk of obesity, dyslipidemia, cardiovascular disease, and hypertension. Several mechanisms of action have been suggested, including the disruption of the insulin production ability of pancreatic beta cells, interaction with insulin receptors, or partial agonist interaction of androgenic and/or estrogenic receptors. A contribution of these contaminants through non-hormone dependent mechanisms is also suspected, given their capacity to induce mitochondrial alterations and the release of free radicals. However, the epidemiological evidences are still controversial.

Further investigation is warranted into the role of organochlorine pesticides and other POPs in the development of metabolic syndrome.

1. Introduction

Recent decades have seen a marked increase in the prev alence of chronic non-infectious diseases, which were responsible for the death of 36 million people worldwide in 2008 (29% under 60 years of age). In fact, a group of five chronic diseases (cardiovascular disease, stroke, cancer, respiratory diseases, and diabetes) is considered responsible for 63% of deaths worldwide (http://www.who.int/topics/chronic_diseases/es/). In this regard, researchers have proposed a cluster of pathophysiological conditions that are commonly associated with an increased risk of heart disease, stroke, and diabetes, called the "metabolic syndrome", which includes dyslipidemia, obesity, hypertension, and insulin resistance and affects 20-30% of the European population (Branca et al., 2007).

Cardiovascular diseases (CVDs) are among the most frequent causes of adult mortality in developed countries (Goncharov et al., 2008). In Spain, cardiac and cerebrovascular diseases were, respectively, the 2nd and 3rd causes of death in 2010 (Regidor E and Gutiérrez-Fisac JL., 2013). Main risk factors for CVD include high-fat diet, stress, smoking, genetic susceptibility, obesity, dyslipidemia, diabetes, or hypertension (Goncharov et al., 2008; Meigs, 2000). Additionally, hypertension is considered the most prevalent treatable risk factor for stroke, coronary artery disease, and renal disease (August, 2004), as well as a direct cause of 7.6 million deaths worldwide (Lawes et al., 2008). It is also believed to be related to certain cancers, premature death, and cardiovascular disease (Joffres et al., 2013; World Health Organization, 2014).

The mentioned increasing prevalence in metabolic syndrome risk factors cannot solely be explained by the aging of the populations or improved diagnostic methods, and there is growing evidence that the environment plays a major role in the development of many of these diseases. In this regard, it is suspected that long-term human exposure to low doses of environmental pollutants may have a relevant impact in relatively frequent chronic diseases, including diabetes mellitus (Taylor et al., 2013), dyslipidemia (Aminov et al., 2013), cardiovascular disease (Lind and Lind, 2012), obesity (Sharpe and Drake, 2013), and hypertension (Lind et al., 2014). It is important to note that the mentioned exposure might occur at levels traditionally considered "safe" (United Nations Environment Programme and World Health Organization, 2013). However, the mechanisms underlying this action have not yet been fully elucidated.

Persistent organic pollutants, such as organochlorine pesticides and polychlorinated biphenyls (PCBs), are synthetic chemicals that are highly resistant to biodegradation. Due to their persistence and lipophilicity, persistent organic pollutants tend to bioaccumulate and biomagnify in the food chain, resulting in the considerable exposure of living organisms (Porta et al., 2008; Rollin et al., 2009). Dichlorodiphenyltrichloroethane (DDT) is an organochlorine pesticide that has been used extensively worldwide in agriculture and for vector control since 1939 (Turusov et al., 2002). Once in the environment or living organisms, DDT is mainly metabolized to *p,p´*-dichlorodiphenyldichloroethylene (*p,p´*-DDE), which is even more persistent than its parent compound (UNEP, 1999). Other examples include the organochlorine pesticide hexachlorobenzene (HCB), a fungicide used until 1980s-90s and now mostly released as a by-product of different industrial activities, and the insecticide lindane, primarily used on crops, timber, and grain and in lotions for personal use (U.S.Department of Health and Human Services, 2011). PCBs, manufactured since 1929, have been used in numerous industrial and commercial applications, including transformer and capacitor oils, hydraulic and heat exchange fluids, and lubricating and cutting oils (La Rocca and Mantovani, 2006).

Because of their high resistance to degradation and their potentially harmful effects on human health, the manufacture and use of most organochlorine pesticides and PCBs have been banned or severely restricted in most countries. The mentioned restrictions on the use and production of POPs have caused a progressive reduction in exposure of the general population. However, the fact that virtually all populations still show detectable internal levels of POPs is a matter of concern (Porta et al., 2003). In fact, it is estimated that 100% of the general population have detectable levels of POPs in their bodies, including people residing in regions where these chemicals were banned or never applied (Dewailly et al., 1999; Salihovic et al., 2012).

It is known that the general population is commonly exposed to POPs at low doses on a daily basis. Fatty food is considered the main route of exposure for non-occupationally exposed populations, although other sources have also been identified, such as inhalation or dermal absorption. These factors are responsible for major differences in exposure among different populations and within individuals in the same population. Thus, relative concentrations of individual POPs in the environment and humans vary widely as a function of the population studied, probably attributable to regional differences in the use of these chemicals and in the specific dietary habits of exposed populations. In fact, we recently reported very different POP exposure levels in people living in urban and rural Bolivian populations (Arrebola et al., 2012; Mercado et al., 2013). Interestingly, Greenlandic Inuit, that live in a region were organochlorine pesticides were scarcely applied, are considered among the highest exposed populations to POPs, mainly because of their diet (rich in animal fat) and the contamination of the Arctic environment by emissions from other regions (Rusiecki et al., 2008).

2. POP exposure and chronic disease

Several recent studies with distinct designs in different populations reported a positive association between exposure to low doses of organochlorine pesticides and the risk of health conditions related to metabolic syndrome, including obesity (Sharpe and Drake, 2013), dyslipidemia (Lee et al., 2011), cardiovascular disease (Ha et al., 2007), and hypertension (Lind et al., 2014). However, there are controversies in the results, both in the type of associations found and in the chemicals responsible for the effects observed.

2.1 POPs and diabetes

Research in highly exposed populations has suggested that certain POPs may alter the insulin production ability of pancreatic beta cells (Grandjean et al., 2011), interact with insulin receptors (Hectors et al., 2011), or even induce an immunotoxic response by binding to estrogen receptors. Our research group recently reported linear associations of exposure to three PCB congeners (138, 153 and 180) and HCB with both hepatic and peripheral insulin resistance (measured as HOMA2-IR and ISI-gly indices), in a cohort of women that suffered from gestational diabetes mellitus (Arrebola et al., 2014). These results appear to indicate that POP exposure is related to a slight degree of insulin resistance, which could be subclinical in many cases. These results were consistent with observations of a positive association between serum PCBs (including congeners 138, 153 and 180) and the risk of diabetes or insulin resistance, in general (Gasull et al., 2012) and non-diabetic populations (Lee et al., 2011).

In a study of non-diabetic individuals, Faerch et al. (2012) found that POP exposure was associated with altered substrate oxidation patterns, lower glucose oxidation, and higher lipid oxidation. Other reported mechanisms include interactions with the insulin signaling pathway or lipid metabolism (Marchand et al., 2005) and alterations in glucose transport (Tonack et al., 2007).

2.2 POPs and hypertension

The mechanisms of action by which POPs may cause hypertensive disorders are poorly understood (Ha et al., 2009). It has been suggested that POPs may cause hypertension through a mechanism involving the androgen receptor, given that many OCPs have been shown to act as anti-androgens (Freire et al., 2014). Thus, high OCP concentrations have been found to be inversely correlated to testosterone levels (Blanco-Munoz et al., 2012), which are associated with hypertension (Akishita et al., 2010). Furthermore, it is believed that female sex hormones may confer protection against cardiovascular disease. In fact, 2-hydroxyestradiol, a hydroxylated metabolite of estradiol, is considered a potent inhibitor of vascular smooth muscle cell proliferation (Masi et al., 2006), and chemicals with (anti-) estrogenic potential (such as certain organochlorine pesticides and PCBs) may interact with this mechanism. *In* *vitro* research has also suggested that PCB-126 can stimulate the production of vasoconstriction factors and reactive oxygen species, as well as inhibiting the release of nitric oxide (Andersson et al., 2011).

2.3 POPs as obesogens

There is scientific evidence that human exposure to some POPs might be involved in lipid homeostasis disorders, and several action mechanisms have been proposed at different levels, including the down-regulation of insulin-induced gene-1 (Insig-1) and Lpin1, two master regulators of lipid homeostasis (Ruzzin et al., 2010). Additionally, dioxin- and non-dioxin-like PCBs have been reported to induce P450 enzymes, causing an over-reactive liver that synthesizes increased levels of cholesterol and triglycerides (Goncharov et al., 2008). Moreover, PCBs can induce oxidative stress in endothelial cells by stimulating inflammatory processes (Choi et al., 2003). Previous research found that high serum PCB levels were associated with elevated serum lipids and CVD risk in a native American population (Goncharov et al., 2008), while others have also described these associations in subpopulations highly exposed to PCBs (Baker, Jr. et al., 1980; Chase et al., 1982; Kreiss et al., 1981; Tokunaga and Kataoka, 2003). Furthermore, Lee et al. (2011) described significant associations between low POP exposure levels and various lipid metabolism parameters (e.g., triglycerides and HDL) in a sample of non-diabetic individuals.

Additionally, there is scientific evidence that some POPs may act as obesogens, i.e. capable of altering lipid accumulation and promoting adipogenesis (Grun and Blumberg, 2007). This effect might take place through the enhancement of adipocyte hyperplasia, disruption of energy balance controlling systems, or interaction with the nervous system, among other mechanisms (Grun and Blumberg, 2009; Heindel and vom Saal, 2009; Newbold et al., 2009). However, despite numerous epidemiological and laboratory findings of a potential role for POPs in the development of many of these conditions, these relationships remain unclear. Some researchers have argued that POPs accumulated in adipose tissue (commonly higher in obese individuals) may in part explain the role of obesity in the development of cardiovascular disease. In fact, Lee and colleagues found that obesity was associated with the prevalence of diabetes, but only in individuals with high levels of POPs (Lee et al., 2006), similar to later findings by our group on the prevalence of hypertension in the *"GraMo"* Spanish adult cohort (Arrebola et al., 2015).

3. Conclusions

Environmental levels of organochlorine pesticides are now significantly lower than those recorded in previous decades. However, the generations currently suffering the increased prevalence of metabolic syndrome-related diseases were born and raised during a period of maximum POP use and were therefore exposed to elevated levels at very critical stages of their development. This is of great importance, given the particular vulnerability of humans to the effects of pollutants during fetal life and infancy, effects that may manifest not only during childhood but also during adulthood (Smink et al., 2008).

A review of the scientific literature reveals numerous uncertainties and controversies around the role of human exposure to low doses of POPs in the development of chronic diseases. However, the fact that most of the general population is exposed to persistent organochlorine pesticides and PCBs on a daily basis is compatible with the gradual development of chronic diseases, which are typically characterized by long subclinical stages and a greater prevalence in the elderly. It is also possible that the associations found with single chemicals were caused by exposure to mixtures of POPs, given their similar physicochemical properties. Further investigation is warranted into the role of organochlorine pesticides and other POPs in the development of chronic diseases with a high prevalence worldwide, such as obesity, diabetes and cardiovascular disease.

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EVALUATION OF HUMAN EXPOSURE TO HEXACHLOROCYCLOHEXANE (HCH) IN SANTOS AND SÃO VICENTE ESTUARY, SÃO PAULO, BRAZIL

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Abstract

The Santos and São Vicente Estuary suffers from contamination by toxic industrial waste that has affected the local population health. This study aims to measure the concentration of Hexachlorocyclohexane (HCH) in hair samples of exposed members from contaminated areas in Santos and São Vicente Estuary, and Bertioga. The distribution of HCH in the five studied areas was statistically tested with a one-way ANOVA followed by a Kruskal Walles and the statistical significance level adopted was 5 %. Bertioga ($7.4ng.g^{-1}$) was the area with the highest HCH concentrations and Cubatão Center revealed the lowest concentration ($3.5ng.g^{1}$). There was no significant difference between the five areas (ANOVA p=0.770). These concentrations are ten times higher than the concentrations revealed in previous studies carried out in the region, and suggest a relative increase of HCH availability as well that there are still exposure routes in Santos and São Vicente estuarine populations for this organic compound.

Keywords

Environmental contamination, persistent organic pollutants (POPs), Hexachlorohexane (HCH), hair, Santos and São Vicente Estuary.

Introduction

Santos and São Vicente estuarine area, on São Paulo's coast, is one of the biggest examples of environmental degradation in Brazil due to tons of industrial hazardous waste dumped in cities during the 1970s[1]. For the last 40 years, previous studies have been shown the presence of persistent organic pollutants (POPs) in the environment, the population exposure and suggests that there are still exposure routes from estuarine people to organic pollutants until nowadays[1,2,3,4,5]. Furthermore, there is no specific attention from the public health services to the affected populations.

To try to confirm present exposure routes in the Santos and São Vicente Estuary, hair samples from members from the affected population were collected. Hair was chosen because it is easy to collect, transport, and store. It can reveal internal, external, short, and long-term exposures to organohalogenated pollutants in any population without restrictions[6,7,8].

This study aims to measure the concentration of Hexachlorocyclohexane (HCH) in hair samples of exposed members from contaminated areas in Santos and São Vicente Estuary, and Bertioga.

Materials and methods

Sampling: Four contaminated estuarine areas established around the hazardous wastes were selected (area 1: Pilões and Água Fria; area 2: Cubatão Center; area 3: Continental São Vicente; and area 4: Guarujá). One area outside the estuary without a history of contamination was sampled (area 5: Bertioga). In 2009, 121 hair samples of the studied populations were collected. The number of samples collected per area is the following: 11 in Pilões and Água Fria; 13 in Cubatão Center; 41 in Continental São Vicente; 29 in Guarujá and 27 in Bertioga. The hair samples were cut close to the root from the occipital region and storage in a plastic bag. Figure 1 shows the five selected areas.

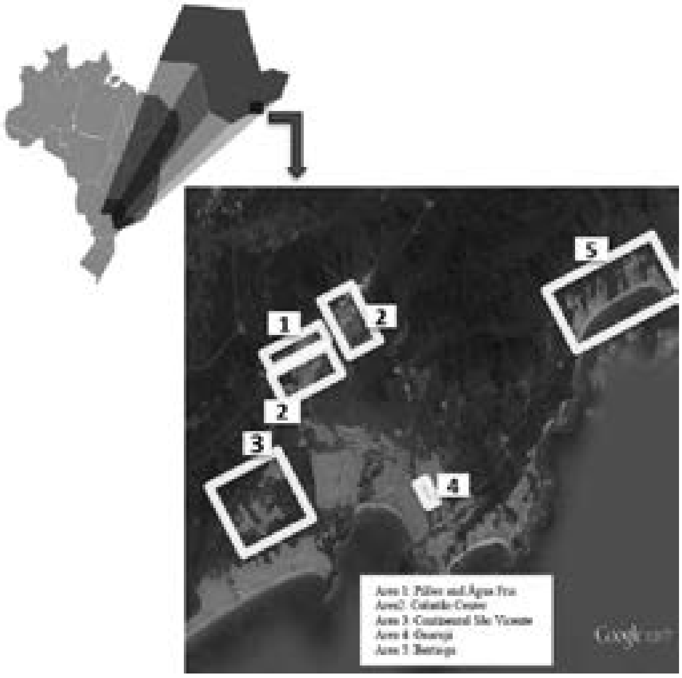

Figure 1. Five areas studied.

Chemical analysis: The preparation of the samples was based on Wielgomas *et.al.,* (2012) study[8]. About 100mg of hair was cut in small fragments and spiked with the internal standard PCBs: 103 and 198 (200ppb). Then, 4ml of HCl (4M) and 4ml of hexane:acetone (4:1vv) was added to the hair samples and there were incubated overnight at 40°C. The samples were agitated and centrifuged; then, the organic phase was transferred to another tube (three times). The clean up was done with a column of 1g of silica, 1g of acidified silica (1%), and 1g of anhydrous sodium sulfate. Samples were then eluted with 10ml of hexane and 10ml of acetone. Eluates were transferred to a vial and dried to 50µL. Lastly, the internal standard 2-4-5-6 tetrachlorometaxylene (200ppb) was added.

The instrumental analysis of the extracts was carried out by gas chromatography (Agilent GC 7890A) with a DB-5MS capillary column (60 m x 0.25 mm i.d., 0.25-µm film thickness, Agilent Technologies) coupled to a mass spectrometry (Agilent 5975CMS), using negative chemical ionization (NCI). The conditions of NCI analysis and selection of ions have been described elsewhere[9]. Injection was splitless at 265°C, and the oven program was the following: 90°C (1 min); 150°C (10°C.min^{-1}); 240°C (3°C.min^{-1}); hold for 5 minutes; and then 300°C (10°C.min^{-1}) and hold for 5 minutes. The extracts were analyzed for α-HCH; β-HCH; γ-HCH and δ-HCH.

Quality assurance/quality control: Blanks were performed during each analytical batch to evaluate interferences. The HCH metabolites limits of detection (LOD) were: 3.8ng.g^{-1} for α-HCH; 2.2ng.g^{-1} for β-HCH; 4.7ng.g^{-1} for γHCH and 6.8ng.g^{-1} for δ-HCH.

Statistical test: The distribution of HCH in the five studied areas was statistically tested with a one-way ANOVA followed by a Kruskal Walles test to compare the five sampling areas. We adopted a statistical significance level of 5 %. All statistical analyzes were performed on Statistical Package for the Social Sciences (SPSS) 17.0 for Windows.

Results and discussion

The internal standard recovery mean in the samples was 79% for PCB 103 and 92% for PCB 198. HCH was present in the five studied areas. Table 1 shows HCH concentrations per area.

	Σ HCH						
	Mean	**SD***	**1ºQ+**	**Median**	**3º Q+**	**Minimum**	**Maximum**
Pilões and Água Fria	7.2	5.6	0.0	8.4	12.9	0.0	14.0
Cubatão Center	3.5	4.8	0.0	0.0	6.4	0.0	13.8
Continental São Vicente	5.7	6.0	0.0	3.3	11.2	0.0	16.5
Guarujá	6.1	9.9	0.0	1.2	8.1	0.0	29.3
Bertioga	7.4	12.3	0.0	2.1	8.9	0.0	46.9

Table1. Concentrations of ΣHCH (ng.g^{-1}) in the five studied areas.

*SD= Standard deviation; + Quartiles.

Bertioga was the area with the highest SHCH concentrations, subsequent by Pilões and Água Fria, Guarujá, Continental São Vicente and Cubatão Center. There was no significant difference between the five areas (ANOVA p=0.770). Table 2 shows g-HCH concentrations per area.

	γ-HCH						
	Mean	**SD***	**1ºQ+**	**Median**	**3º Q+**	**Minimum**	**Maximum**
Pilões and Água Fria	4.9	3.6	0.0	5.7	7.6	0.0	9.5
Cubatão Center	0.9	2.0	0.0	0.0	0.9	0.0	5.6
Continental São Vicente	1.5	2.0	0.0	0.0	3.1	0.0	6.3
Guarujá	0.8	1.6	0.0	0.0	1.2	0.0	5.0
Bertioga	4.8	11.9	0.0	0.0	2.9	0.0	46.9

Table 2.Concentrations of γ-HCH (ng.g^{-1}) in the five studied areas.

**SD= Standard deviation; + Quartiles.*

Pilões and Água Fria revealed the highest concentrations and Guarujá revealed the lowest concentration. There was no significant difference between the five areas (ANOVA p= 0.239). Figure 2 shows the contributions of each HCH metabolite to the ΣHCH concentrations in the five studied areas.

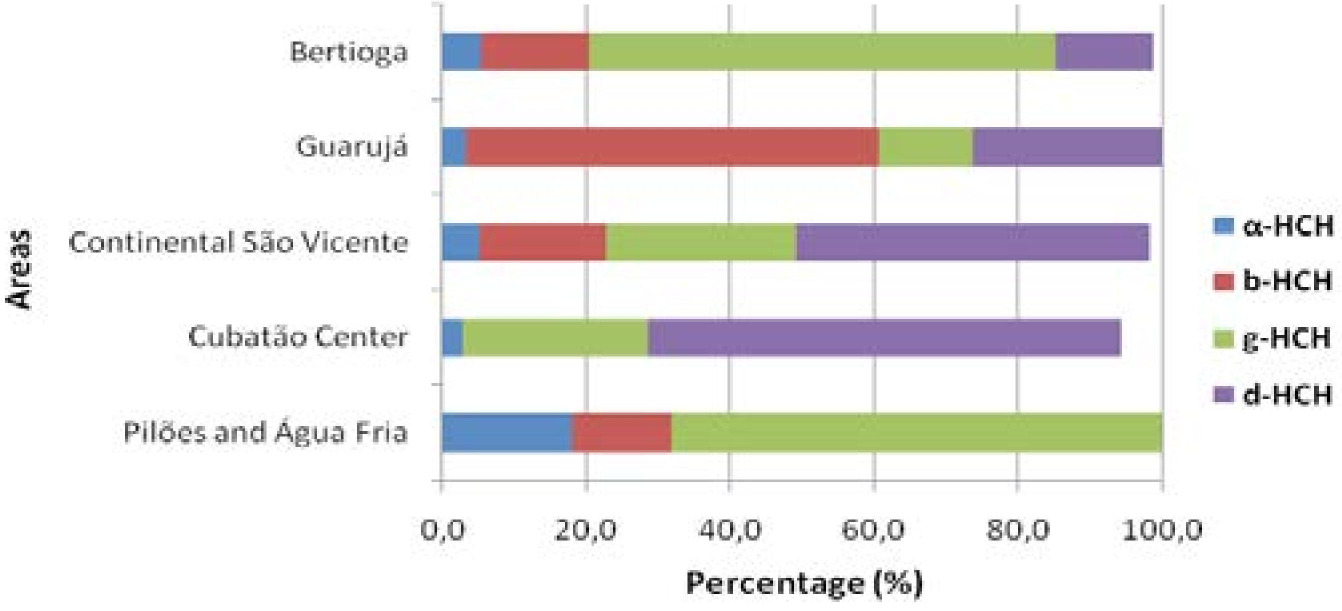

Figure 2. Contribution (%) of HCH metabolites to ΣHCH concentrations in the five areas

Figure 2 shows that, γ-HCH was the most present HCH metabolite in Pilões and Água Fria and Bertioga. δ-HCH was the most present metabolite in Continental São Vicente and Cubatão Center and β-HCH

was the most present metabolite in Guarujá.The concentrations of α, β, δ-HCH ranged from non detected to 3.5 ng.g^{-1} of β-HCH in Guarujá. There was no significant difference on HCH metabolites concentrations in the five studied areas (ANOVA α-HCH: p= 0.174; β-HCH: p= 0.330; δ-HCH: p= 0.460).

Previous study[1] describes that HCH was used as insecticide in the region, in households and in banana plantations, what could have contributed to the estuarine rivers contamination. Furthermore, HCH was also revealed in the blood of living people from Pilões[3] (0.84µg/L; n=133) and children from Cubatão[2] (0.28µg/L; n=242). These concentrations are ten times lower than the concentrations revealed in this study in the respective areas. This study revealed higher concentrations than those revealed in the hair of members from Amazon riverside[10] in 2009 (3.60ng.g^{-1}; n= 85).

But, the estuarine area concentrations are lower than the concentrations revealed in people's hair from: Poland[8] in 1968 (22.2ng.g^{-1}; n=15) and in 1989 (9.8ng.g^{-1}; n=10), Greek women[6] in 1996 (40.8ng.g^{-1}; n=35), in hair from members from Romania[6] (31.8ng.g^{-1} n=2) and Belgium[6] (14.7ng.g^{-1}; n=10) in 2000, adolescents' hair from Romania[7] in 2002-2003 (172ng.g^{-1}; n=42), and from members from Poland[8] in 2009 (12.6ng.g^{-1};n=15). The concentrations revealed in the contaminated areas investigated in this study suggest a relative increase of HCH availability as well that there are still exposure routes in Santos and São Vicente estuarine populations for this organic compound, hence, this matter deserves further investigation.

Aknowledgements

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TOXICOLOGY

Part 2: HCH and POP problems in European and EECCA countries

THE PRODUCTION OF LINDANE BY UGINE KUHLMANN HUNINGUE (FRANCE) AND THE CONSEQUENCES FOR THE CITY OF BASEL (SWITZERLAND)

Martin Forter, Basel (Switzerland)

Hexachlorocyclohexane (HCH) is persistent and bioaccumulating in fatty tisue. It was used in agriculture in Western Europe and in the US as an insecticide from World War II to around 1955. But this created the so-called Hexa-potatoes. Whole train-loads of potatoes were destroyed because the smell of HCH. There have been also smelly vegetables: The Swiss food-authorities report that the housewifes put their noses in the green salat on the farmers markeds to test if the vegetables were smelling from HCH.[1] Therefore, the Industry had to do something: As only the gamma-isomer of HCH has insecticidal properties, the industry started to separate this from the other isomers. As only 15-20% of HCH is gamma-isomer, which is the trade product Lindane, the other 80-85% of the HCH-amount became waste thus including all the other isomers. Approximately 600.000 tonnes of Lindane has been produced since the end of world war II. This means: Around 4,8 to 7,2 mio tonnes of HCH-waste exist globally. In general HCH isomers are:

1. Probably Cancerogenic (Class 2b). Here it should be noted that the international cancer agency IARC in a new assessment from June 2015 has classified Lindane – meaning the gamma-isomer of HCH – as Cancerogenic (Class 1).[2] The other isomers have not been reassessed.
2. The HCH-isomers are acting as hormones in the human body.
3. As mentioned, the HCH-isomers are persistent. It means that they are not degradable in the environment or very slowly degrading. It is worth noting here: Quite high concentrations of trichloro-benzene are now found in the area where HCH dust from the Ugine Kuhlmann Factory has precipitated in the Basel region, which was 2015 documented by the Environmental Authorities of the State Basel-Stadt.[3]
4. The isomers from HCH are also poisonous to bees, fishes and birds.[4]

Ugine-Kuhlmann started the HCH-production in 1947. It's factory was located in the tripple-point at Hochrhein. That means: It is located on French soil in Huningue at the river Rhine. There, a fence marks the border to Switzerland. On the other side of the river Rhine is Switzerland too, but also Germany (see Photo 1).

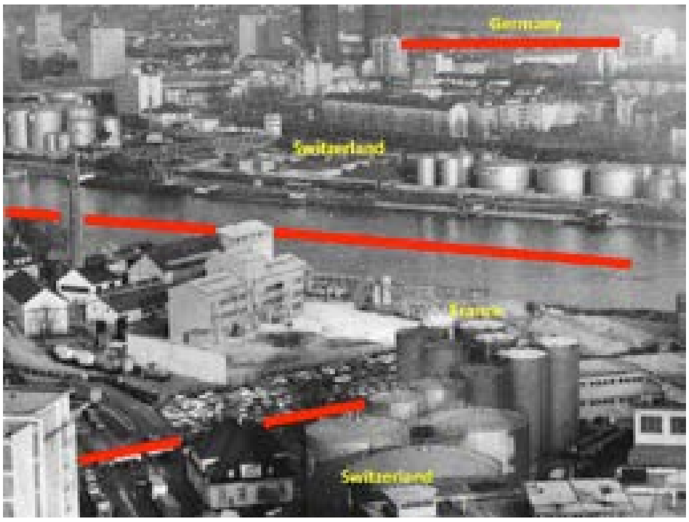

Photo 1: The location of the Lindane-Factory Ugine-Kuhlmann in Huningue in French Alsace at the border to Switzerland and Germany. Photo: Eugène Groellin, Journal «L'Alsace», St-Louis, undated, probably 1972.

Until 1972, large white mountains of HCH are being piled up on the site (see Photo 2). The prevailing nord-westernly wind transports dust from the HCH waste to Germany and Switzerland.[5] As a consequence, massive contamination

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[1] Protokoll über die Konferenz betreffend Schädlingsbekämpfung mit Gift enthaltenden Präparaten vom 11.01.1952, Teilnehmer sind verschiedene nationale Schweizer Behörden, die mit Pestiziden zu tun haben, Protokoll vom 16.01.1952 S. 4.

[2] International Agency for Research on Cancer (IARC): Agents Classified by the IARC Monographs, Volumes 1–112, 23.3.2015; IARC: IARC Monographs evaluate DDT, lindane, and 2,4-D, Press Release N° 236, 23.6.2015.

[3] Alexander Laver: Hexachlorocyclohexane. A well-known and highly explosive topic. Investigations on environmental levels of hexachlorocyclohexane in the Canton of Basel-Stadt, master thesis-Report, Fachhochschule Nordwestschweiz, in Zusammenarbeit mit dem Amt für Umwelt und Energie (AUE) des Kantons Basel-Stadt, Basel, 2.2.2015, p. 87, 88.

[4] Details on the toxicology of HCH see: U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry: Toxicological profile for aplpha-, beta-, gamma-, and delta Hexachlorocyclohexane, 8.2005; Stockholm Convention on Persistent Organic Pollutants, Persistent Organic Pollutants Review Committee (POPRC): Draft Risk Profile For Beta-Hexachlorocyclohexane, 5.2007 and Draft Risk Profile For Alpha-Hexachlorocyclohexane, 5.2007.

[5] Vgl. z.B.: Basel-Stadt, Kantonales Laboratorium: Umweltverschmutzung im Raume Basel durch Hexachlorcyclohexan (HCH), wöchentliche Niederschlagsmessungen von alpha- und gamma-HCH -RCR, ausgedrückt in ug/m2/Tag, 8.-12.1972; Martin Forter: Umweltnutzung durch die chemische Industrie am Fallbeispiel der HCH-Fabrik Ugine-Kuhlmann, Hüningen (F). Die Insektizide Hexachlorcyclohexan (HCH) und Lindan: Die Produktion und ihre räumlichen Konsequenzen in der Region Basel. Eine Untersuchung zur Veränderung der Wahrnehmung von Umweltrisiken, Basel,

of mother's milk and cow milk is found. The authorities recommended the mothers to stop breastfeeding their. babies. The cow milk was destroyed. HCH was still found in breast milk until 2007. Thereafter it has not been analysed anymore. The authorities recommended the mothers to stop breastfeeding their babies. The cow milk was destroyed. HCH was still found in breast milk until 2006.[6] Thereafter it has not been analysed anymore.

In 1976, the factory was demolished.

From the end of world war II and until 1975, Ugine-Kuhlmann has produced around 100.000 tonnes of HCH-waste.

Photo 2: 1972, Ugine Kuhlmann stores on it's factory site large mountains of HCH-waste. The wind blows the poisoning dust also to Germany and Switzerland. Photo: Staatsanwaltschaft Basel Stadt, 2.11.1972.

The larger part of it is deposited in 11 gravel pits in the French Elsass (see Table 1).

Thousands of tonnes of HCH waste is furthermore burried at the factory site.

In this way, Ugine Kuhlmann has left a large and poisonous legacy behind.

The company Ugine Kuhlmann does not exist anymore. It is first merged into the company Pechiney, which later became Alcane.

Today the moral responsibility lies with the mining company Rio Tinto after their purchase of Alcane.

Legally, is the responsibility with the French state. The cost of environmental damage is thereby brought to the French taxpayers.

The French government has not allocated any funds for the site at all. Apparently, the French government accepts the exposure from the poison to the inhabitants.

Then: Until today, this type of contaminated sites are normally only monitored. In the last decades, the French authorities have hardly done anything on this site and other similar sites.

So now, the gardens in the town of St. Louis are filled with contaminated humus and soil materials from the Ugine-Kuhlmann site, and until today no investigation and/or assessement has been made.

And the rural roads in Hagenthal le Bas are still contaminated. How is it possible things come that far, one must go back to the 1970s: The HCH-waste mountains at

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6.1995, p. 76ff; accessed on 4.1.2016: http://www.martinforter.ch/news/2013_09_25/08_19950600_Martin_Forter-Umweltnutzung.pdf; Priska Forter/Martin Forter: Reizendes Gift - Begegnungen mit HCH, Dokumentarfilm, Produktion: Fama Film AG, Bern, im Auftrag des ZDF und von SF DRS (heute: SRF), 1995.

[6] Margret Schlumpf et al.: Exposure patterns of UV filters, fragrances, parabens, phthalates, organochlor pesticides, PBDEs, and PCBs in human milk: Correlation of UV filters with use of cosmetics, Chemosphere 81 (2010) 1171–1183.

Where?	Name of the Site	possibly HCH-waste	definitelyHCH-waste	works implemented
St-Louis/Bourgfelden	Simon-Grube		demolition material of the factory	none
Gouneans-Haut Saône	-		HCH-waste	groundwater pumping
Hagenthal-le-Bas	fdirt roads		gravel and sand contaminated with HCH from the factory site	investigated
Hagenthal-le-Bas	dirt roads		gravel and sand contaminated with HCH from the factory site	investigated
Hagenthal-le-Bas	dirt road		HCH-concrete	investigated
Allschwil	road		gravel and sand contaminated with HCH from the factory site	investigated, low. concentrations; no active treatment needed
Hésingue	dredging pit	HCH-waste		none
Hochfelden			HCH-waste	groundwater pumping
Huningue	former factory site		HCH-waste HCH-concrete	under excavation
Huningue	Nouvelle Sablière de Huningue	HCH-waste		none
Kingersheim	Eselsacker		HCH-waste	groundwater pumping
Magstatt		HCH-waste		none
Village-Neuf	Stade de Huningue		HCH-waste	none
Sierentz	Brunner-Grube		HCH-waste	excavated and stored on site in a clay-bag
Sierentz	Bäumlin-Grube		excavation-material from the factory-site	None
St-Louis	Grande Sablière de St-louis	HCH-waste		None
St-Louis	garden of the building Phoenix		excavation-material from the factory-site	None
Winzenheim	Grube Ritzenthaler		HCH-waste	groundwater pumping

Table 1: A Mega-site: a toxic legacy (among others in Alsace (France)) which is spread over a very large area: Here has definitely and/or probably HCH waste, HCH-concrete, gravel contaminated with HCH and other with HCH polluted excavated material stemming from the former lindane factory Ugine-Kuhlmann, been dumped and/or has been buried (status 2015)

the factory sites in the French town of Huningue contaminate – as mentioned – mother's milk and cow milk in the region of Basel.

Therefore, Ugine-Kuhlmann *had to find* a 'solution' in the beginning of the 1970es. The socalled waterproof Concrete (Béton hydrofuge) would be the solution.[7]
This concrete was produced in a concrete mixer and comprised a showel of gravel, a showel of cement and a showel HCH-waste.

In order to be able to dispose of this waterproof cement Ugine Kuhlmann constructed a number of pits on the factory site.

For this pupose, Ugine Kuhlmann excavated around 4.000-5.000 m^3 of contaminated gravel and sand on it's site at Hunigue.[8] The gravel is however contaminated with HCH. Firstly, a part of this gravel is transported by the company Transablag to the the Swiss community of Schönenbuch, where it was used as part of road foundation. However it smelled, and Transablag had to re-excavate the material.
Hereafter it was transported across the border to the French communities of Hagenthal-le-Bas and Hagenthal-le-Haut, and was used for the rural roads in both communities.[9]
It looks hereafter as if Transablag (or other companies) in more than 10 years has worked with a storage facility, and in 1980, a Swiss community has built a road with HCH-gravel.
Finally, it is known that this material has been spread over around a dozen small roads in France and in Switzerland (see Table 1). The contamination levels in the gravel at these small roads varies a lot: We have documentation that

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[7] Martin Forter: Umweltnutzung durch HCH-Fabrik Ugine-Kuhlmann, Basel, 6.1995, p. 98-101.

[8] Martin Forter: Umweltnutzung durch HCH-Fabrik Ugine-Kuhlmann, Basel, 6.1995, p. 98-101.

[9] Martin Forter: Umweltnutzung durch HCH-Fabrik Ugine-Kuhlmann, Basel, 6.1995, p. 101-103.

shows levels varying from 0,3 to 623.000 mikro g/kg.[10]
Back again at the Factory site: Before Transablag filled the gravel pits with HCH-concrete they tested if the HCH-concrete could function and solidify. This was done on a rural road in the French Hagenthal-le-Bas. In 2011, we have documented the HCH contents on this rural road to be 750 Gramm HCH per kilo material. Yes, you read correctly: 750 grammes of HCH per kilogramme. The material is there since 1972. And the French authorities knew it.[11]
The French authorities were not even able to close this heavily continted rural road after our public protest in 2011. This is why we have this action in 2013 in cooperation with the environnmental organisation Pingwin Planet – where we used chains and locks and organised a public outcry (see Photo 3).[12]
Four years after our first public protest, the highly contaminated special waste is still lying uncovered and accessible for people and animals in 2015. Surface water is still running down the meadow into the nearby stream, which is still polluted with toxic HCH. The French authorities do not have the capacity to dispose of the highly contaminated and special waste which is still uncovered and accessible for the public..
In the community of Hagenthal-le-Bas, which is affected by the toxic gravel and the toxic concrete, the female inhabitants report on breast cancer. They are saying, in every family, you may find a woman with breast cancer.
The Swiss chemical company Sandoz bought the Ugine-Kuhlmann-site at Hunigue and established there a waste water treatment plant in 1980. It was built in the middle of the HCH-waste. The today responsible Swiss pharma-company Novartis assures that no materials have been leaving the location during the construction at the time.
Novartis closed down the waste water treatment plant on the former Ugine-Kuhlmann-site in 2012.[13] In 2013, Novartis started to excavate the HCH-waste on the factory site in cooperation with the French company Sita remediation. Low contaminated material was stored uncovered being able to emit and being accessible for public??. But: 10 samples from gravel and sand heaps will give 10 different results depending on if HCH-lumps are included in the sample or not. The material is inhomogenous and unpredictable. In addition, the primitive 'Camping'-tents that are supposed to contain the contaminated air and then collect them and treat accordingly, simply flutter in the wind, Such tents Novartis and Sita Remediation have established instead of the more stable storage facilities as being used in the Bonfol landfill project in Switzerland.

Photo 2: The French authorities are not able to close down a dirt road that is contaminated with upto 750 Grammes per Kilogram HCH. That is why the environmental organisation Pingwin Planet takes action to close the road in June 2013. The toxic waste is still present, even today. Photo: Dave Joss
Die französischen Behörden sind nicht einmal in der Lage, einen Feldweg abzusperren, der mit bis zu 750 Gramm HCH pro Kilogramm belasteten ist. Deshalb holen dies die Umweltorganisation Pingwin Planet im Juni 2013 nach. Das Gift liegt noch heute dort. Photo: Dave Joss

The primitive tents are also strongly exposed to upward winds so instead of keeping the emissions inside they can partly escape.[14]
Bonfol is another polluted site in Switzerland, which is excavated by among others Novartis.[15] In addition: When Novartis/Sita Remediation are transferring excavated HCH-material in French Huningue to a vessel on the river Rhine then a cloud of smell is covering the Swiss city of Basel. Neither the Air Quality Agency, nor the Environmental Protection Agency in the State of the City of Basel is monitoring the air pollution.
We have therefore spontaneously started action: with so-called dust-traps – normalised plastic boxes of 1,40 Euro per box – we have measured the HCH dust-precipitation in the city of Basel and have herewith a HCH-precipitation up to 4.7 mikrogramme per square meter per day in August/September 2014 in the city area.[16]

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[10] RWB analub laboratoires SA: Rapport d'essais d'échantillon n° 5079, im Auftrag von Pingwin Planet u. Martin Forter, Porrentruy, le 13.10.2011.

[11] Pingwin Planet/Martin Forter: Hagenthal: le HCH, substance très toxique, contamine progressivement la vallée du Lertzbach, Informations de fond sur le communiqué de presse du 29.11.2011, accessed on 4.1.2016: http://www.pingwinplanet.ch/index.php/hch-schleichende-vergiftung.html?file=tl_files/Themenbilder/HCH/Hintergrund%20MM%20HCH%20f.pdf

[12] Pingwin Planet/Martin Forter: Déchets chimiques HCH à ciel ouvert sur un chemin rural à Hagenthal-le-Bas (F) : La Préfecture ne se soucie pas du danger toxique, communiqué de presse du 10.6.2013, see: http://www.martinforter.ch/news/2013_06_10/soucie.html

[13] Novartis: Geschichte des Areal ARA STEIH, accessed on 4.1.2016: http://sanierung-steih.ch/geschichte/, Martin Forter: Umweltnutzung durch HCH-Fabrik Ugine-Kuhlmann, Basel, 6.1995, p. 112.

[14] Martin Forter: Lindan-Abfall-Aushub in Huningue (F): Novartis-Gestank im Unteren Kleinbasel, Medienmitteilung, Basel, 5.9.2013; eine detaillierte Dokumentation ist zu finden unter: http://www.martinforter.ch#a05_09_2013

[15] Martin Forter: Farbenspiel. Ein Jahrhundert Umweltnutzung durch die Basler chemische Industrie, , Zürich, 2010, p. 237-244; Martin Forter: Falsches Spiel. Die Umweltsünden der Basler Chemie vor und nach «Schweizerhalle», Zürich, 2010, p. 102-120.

[16] Martin Forter: Messergebnisse zeigen: Novartis kontaminiert die Stadt grossflächig, Medienmitteilung, Basel, 25.9.2013; accessed on 4.1.2016: http://www.martinforter.ch#a25_09_2013

After making our measurements public, the pharmacompany Novartis stopped the excavations.[17] Novartis then had put the work on hold for a year.

In 2015, the work was restarted by Novartis, and HCH waste and HCH concrete were excavated again. Novartis has replaced Sita Remeditation with Züblin AG and Marti AG, who have know-how and experience from Bonfol (CH).[18]

Bonfol is the already mentioned 114.000-tonnes Swiss landfill of chemical waste, which is excavated amongst others by Novartis.

According to Novartis, are all works in Huningue executed in-doors, including conditioning and loading of all materials. New tents have been erected, and the old primitive tents have been reenforced.[19]

Novartis' old project was costing 100 Mio Euro. The new project will cost 200 Mio Euro.[20] Despite these additional 100 Mio Euro, again it is in 2015 smelling in the City of Basel, and again it smells of HCH.[21]

Since End of the year 2013, also the State Basel-City started its measurements of odor and HCH-precipitation.

With extra costs of 100 Mio Euro, Novartis has reduced the HCH emissions with a factor 3-4 in comparison with my mesurements in September 2014.[22]

The resulting reduction should however be much larger: Novartis did – also because of our complaints about the smell - take action against the emissions even before we and the State Basel-Stadt had started to monitor. Novartis seems to have conducted air quality measurements in April 2013, but has not made the results available to the public.[23]

It is obvious that «an old workhorse» (primitive tents) cannot even be changed with additional 100 Mio. Euro, into a «racehorse». Or without metaphors: If the pharmaceutical company Novartis had planned carefully and responsibly from the very beginning, then today the HCH emissions and the costs of excavating the HCH would have been waste significantly lower.

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FARMERS AND VULNERABLE GROUPS AT RISK OF PESTICIDE POISONING IN EECCA REGION: A PRELIMINARY STUDY

The paper describes how farmers and their family are exposed to pesticides and how it can affect their health.

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Abstract

The pilot study, performed in six countries in the EECCA region, gathered information about risky practices and self-reported signs and symptoms of acute pesticide poisoning. The participating countries were Armenia, Belarus, Georgia, Kyrgyzstan, Moldova and Ukraine and the study was conducted 2014-2015.

Using simple questionnaires, discussions and desk research it was possible to build a picture of how pesticides are used, common exposure routes and some of the ways people experience the impact on their health. Although the surveys were based on a small sample size, with just 200 respondents in each country, they indicate that there is a potentially significant problem worthy of more research and action to reduce the risks from hazardous pesticides.

All respondents in the surveys lived or worked on farms that use pesticides. The study considered the exposure of all family members and seasonal workers. Very few respondents across all participating countries wore Personal Protective Equipment (PPE) and a high proportion of participants reported that they had suffered signs and symptoms of pesticide poisoning in the previous 12 months.

The findings indicate that women's roles and potential exposure to pesticides vary significantly. Just 4% of the women in the study in Belarus said they handled pesticides directly, while the figure was 56% in Kyrgyzstan and higher still in Moldova and Ukraine.

The data collected in Kyrgyzstan and Moldova showed that more than a quarter of participating children directly involved in using pesticides (26% and 39% respectively) as well as undertaking other tasks that may expose them to these hazardous chemicals.

Although the studies were pilot scale, they revealed a very worrying situation in which many farming households are routinely exposed to hazardous chemicals.

Key Words

Pesticide poisoning, farmers, children exposure, migrant workers, vulnerable groups.

Materials and methods

National non-governmental organisations were trained and supported to undertake studies in the six countries using desk studies; group discussions; structured and semi-structured interviews; participatory mapping exercises[1,2]. Discussions and interviews were used to explore the issues in more depth and to verify the results of the surveys. A national workshop in each country fed the results back to key stakeholders at all levels and a variety of communications materials were produced in national languages to raise awareness of the issues that emerged.

200 people living / working on farms that use pesticides within the target area were surveyed.

The survey tools were developed by PAN-UK in collaboration with the Secretariat of the Rotterdam Convention. Target areas for the surveys were selected in consultation with Ministries of Agriculture on the basis of relatively high pesticide use and high incidence of the target group.

All survey respondents lived or worked on farms that use pesticides in the target area. Four questionnaires were used:

1. Adults who handle pesticides e.g. mixing or applying them
2. Adults who don't handle pesticides directly
3. Children (under 18 years)
4. Third party incidents (this short set of questions may be added to 1 or 2 if the

person is aware of a poisoning incident that happened to someone else)

The survey for children is short, uses simple questions and pictures.

A severity score calculator was incorporated into the surveys in order to assign severity scores to each reported incident. It was loosely based on similar scoring systems used elsewhere[3,4] as a way of rapidly distinguishing the most severe incidents for potential follow up, from more minor incidents.

All national partner organisations submitted the data collected in the surveys to PAN-UK for checking and analysis.

Results and discussion

The goal of this study was to identify common exposure scenarios and self-reported incidents of pesticide poisoning for each member of the farming household and seasonal workers.

The study strongly suggests that smallholder farmers across the region are routinely using pesticides without the information or equipment they need to reduce the risks to themselves and their communities. 79% of respondents said they wear ordinary clothes when they spray pesticides, for example, and just 7% participants had received safety training in relation to handling pesticides in the previous five years.

Many respondents buy pesticides in unlicenced premises (69% respondents in Ukraine). The practice of repacking pesticides into drinks bottles and plastic bags seemed to be very common. Just 23% of respondents in Armenia said they bought their pesticides in their original containers. Buying pesticides in improvised containers is more likely to lead to spills, leaks and accidental exposure. It also means that there is no label to refer to for information regarding safety, handling, dose, post-harvest interval etc. The disposal of empty pesticides containers was also problematic. In Kyrgyzstan and Moldova the most common option was to burn empty containers or to discard them in the field.

It is often assumed that men are at greatest risk because they often take on the task of spraying pesticides. However, the studies of farming families showed that, while men are often at high risk, many women and children are also taking on this hazardous work.

The results indicated that gender roles vary significantly from one country to another, and within countries. Just 4% of the women in the study in Belarus said they used pesticides, for example, while the figure was 56% in Kyrgyzstan.

The respondents that apply pesticides were asked about signs and symptoms of acute pesticide poisoning in the 12 months prior to the survey. The proportion that reported such problems was very variable but over all 40% adults who handle pesticides reported signs and symptoms of pesticide poisoning in the previous twelve months.

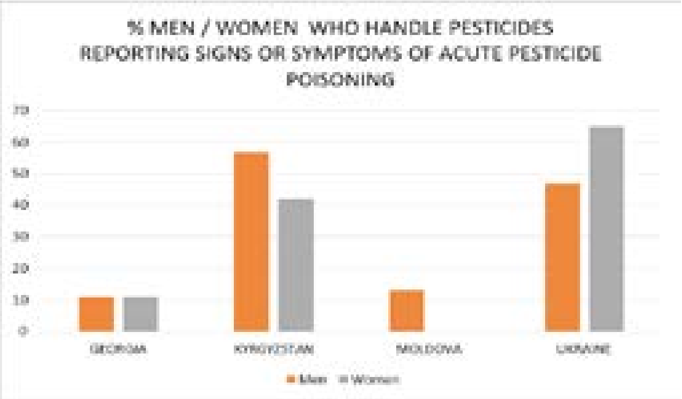
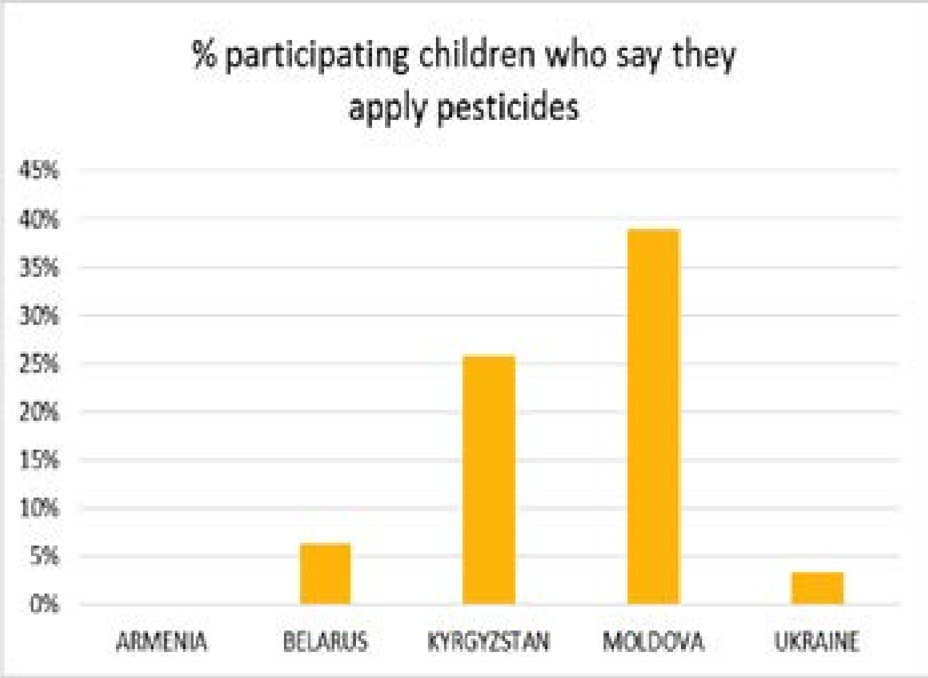


Figure 2.
% men and women who apply pesticides reporting signs and symptoms of acute pesticide poisoning over the previous 12 months.

Even family members that do not apply pesticides on the farm are often in close contact with them. 18% women surveyed in Belarus said they wash clothes that are contaminated by pesticides by hand, for example.



	Total number of children
ARMENIA	34
BELARUS	79
KYRGYZSTAN	31
MOLDOVA	121
UKRAINE	30

Figure 1. % participating children reporting that they apply pesticides

7% of participants who do said they do not handle pesticides reported signs and symptoms of pesticide poisoning in the previous twelve months.

Children who do not spray pesticides are involved in other tasks around the farm that could result in their exposure to pesticides – see Table 1. Handling sprayed produce may be particularly hazardous if label instructions concerning dose and post-harvest interval are not observed.

	ARMENIA	BELARUS	KYRGYZSTAN	MOLDOVA	UKRAINE
Total children (n)	34	79	31	121	30
Planting	32%	56%	61%	72%	83%
Weeding	29%	66%	19%	74%	83%
Harvesting / picking	50%	85%	71%	80%	73%
Handling / packing produce	18%	71%	16%	29%	30%

Table 1. % participating children reporting that they undertake listed tasks on the farm

Whether they use the pesticides or not, members of rural households are at risk of exposure to these hazardous chemicals from a variety of sources. Some groups are particularly vulnerable to the effects of pesticides on health, such as expectant and breastfeeding mothers and children. For physiological reasons their bodies may be more vulnerable to the negative effects of pesticides[5]. Since many children below the age of employment live on farms, their risk of accidents and disease associated with pesticides is significantly increased[6]. Women and children form a relatively large proportion of agricultural workers and they are often exposed to pesticides over a long period of time. Even if they do not experience signs or symptoms of acute pesticide poisoning, they may suffer long-term, chronic effects on their health[7,8].

Migrant, seasonal and casual workers are also prevalent in agriculture. In many countries, agricultural workers as a whole are poorly protected in law and often not represented by trade unions, especially casual workers[9]. Lack of job security, training or information may lead to a reluctance to question hazardous practices or to request additional safety equipment. Seasonal workers proved to be a group from whom it was difficult to capture good data[10], particularly as the studies were undertaken in winter. More work is needed to determine the risks to seasonal agricultural workers. In Georgia and Ukraine, for example, many of these workers were found to be women of reproductive age. The combination of social and physiological factors may mean that they are at particularly high risk.

An important group that had not been identified *a priori* were pesticide retailers. They seem to be at high risk of pesticide exposure due to the common practice (in Armenia, Georgia, Kyrgyzstan in particular) of repacking pesticides into plastic bags and bottles without suitable protection.

The practice, along with the poor level of advice provided by many retailers, also puts their customers at increased risk.

It is very early days for this type of work in this region. None of the participating countries yet has systems in place to collect data on pesticide practices or pesticide poisoning (although Armenia is introducing a new pesticide incident report card for health services) and the experience of collecting this type of information directly from affected communities was also new to all participants.

The studies were small scale, but they did raise important questions, challenged assumptions and clearly identified common practices that are serious cause for concern. Government authorities showed a keen interest and took positive action to reduce risk. In Georgia, for example, the authorities responded by taking steps to improve compliance with labelling standards and to tackle repackaging by retailers. The activities also served the valuable purpose of bringing key actors together and strengthening linkages between them. Several countries noted the value in this approach and are taking steps to formalise networks or cross-sectoral committees to focus on the issues raised. Further work is needed to build on this success in order to better understand the scale and nature of the problems identified; to gain a better understanding of the products most commonly associate with poisoning; and to take effective action to reduce the significant risks pesticides pose to rural families.

Acknowledgements

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THE EFFECT OF ORGANOCHLORINE PESTICIDE RESIDUES ON THE INCIDENCE OF PRIMARY MALE INFERTILITY

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Abstract

The paper presents data on the effect of organochlorine pesticides (OCPs) on the development of primary male infertility.
Semen samples collected from a total of 1211 patients (61 patients - treatment group) and 51 - control group) with male infertility were subjected to epidemiological analysis for OCPs: HCH isomers, DDT, DDE, DDD, Aldrin and Dieldrin. In the environment of the Osh Province, high prevalence rate of male infertility was reported among the residents of cotton-growing areas polluted by OCPs and former pesticides storehouses and agro-airstrips, that is 2-3 times higher than that in unpolluted areas. Primary male infertility rates were 10% higher than the same figures reported among the residents of unpolluted areas. Organochlorine pesticides were detected in 87.03 % and 57.1 % of sperm samples collected from patients with primary and secondary infertility, respectively, versus 4.3% in control group.

Key Words: Incidence, male infertility, primary, secondary, organochlorine pesticides, semen, pollution.

Background: At the moment, more attention is being paid to toxicological follow-up studies of the effects of various chemicals on humans and animals. One of the most important and widely discussed problems of modern society is the protection of reproductive health. According to WHO, there has been a complicated demographic situation in the world in the past 50 years due to the sharp increase in population, declining birth rate, significant increase in the prevalence of different diseases, exposure to adverse environmental factors, referred to as "ecological crisis" and other reasons[1].

The potential risk of many medicines, foodstuffs, cosmetics and chemicals used in veterinary and agriculture (herbicides, pesticides), as well as chemical compounds used in industry on male reproductive system has not been studied yet [2]. Males are more susceptible to pesticide contamination[3]. The potential danger of toxic chemicals is not only that many of them are highly toxic to humans and animals, but also in the fact that even a relatively low-toxic drugs have specific effects on the body.
The sterility of animals with pronounced atrophy of both male and female reproductive organs was observed in the experiment (Shitskova A.P. et al., 1970). Many chemical compounds (industrial poisons and pesticides, in particular, used as medicinal agents) may have gonadotrophic mutagenic action (Stenberg A.I. et al., 1970).

There are some scientific publications on the detection of organochlorine pesticides (OCPs) in breast milk, liver, spleen, heart, lungs, kidney, fat, etc. At the same time, there are no works on the detection of organochlorine pesticides in sperm in male infertility. The study of this problem could help to assess the impact of OCPs on the development of male infertility and develop methods of treatment and prevention.

Objective: To study the effect of organochlorine pesticide pollution on male infertility.

Materials and methods: Epidemiological and toxicological.

To conduct epidemiological studies, a total of 1211 medical cards of outpatients with male infertility (MI) living in rural areas and consulted a doctor in medical institutions of southern Kyrgyzstan were analyzed. All patients were allocated into groups depending on residential area in order to study the adverse effects of environmental pollution (various toxic chemicals, including OCPs) on male infertility. To study the effect of pesticides on male infertility, specified investigation cards were developed. Along with passport data, the cards contained information on existing environmental factors, industrial and internal environment, health history (including infectious diseases), residential area, occupation, conditions of the patient's daily activities, diet and lifestyle.
Clinical samples (blood, urine and sperm) collected from 61 patients with infertility and 51 volunteers (control group) were subjected to analysis. Sensitivity to antibiotics was also studied. Ultrasound examination of genitourinary system and other organs was performed. Samples (> 5 mL) were collected for measuring OCPs (HCH-α, HCH-γ, HCH-β, DDT, DDE, DDD, aldrin and dieldrin) concentrations in semen. All measurements were performed by using gas-liquid chromatography (chromato-

graph “Tzvet-164” in accordance with the procedures set out in the recommendations “Methods for determination of trace amounts of pesticides in foodstuffs, fodder and environment” (M .: Kolos, 1977), supplemented by regulations #1112-73 (“Guidelines on the determination of trace amounts of pesticides in foodstuffs, fodder and environment.” - M., 1992).

Results and discussion:

The incidence rate of male infertility was 20.19 per 100,000 male population in unpolluted areas of Alay district. In Kara-Kulzha district, where the local population cultivated tobacco, the incidence rate was 23.84. At the same time, in a mountainous area of Chon-Alai district, where the local population is engaged in cattle-breeding and cultivation of leguminous plants, this figure was higher (35.78). When studying causes of male infertility it was revealed that OCP (DDT) was widely used by local population to combat ectoparasites (ticks, fleas and lice). The data on the incidence rates reported in the areas (tobacco-growing areas) that were not heavily contaminated by pesticides are as follows: Nookat district - 37.3 against 33.55 in Uzgen district. In cotton-growing area (in Soviet times pesticides including organochlorine pesticides were intensively used against cotton pests), the incidence rates were as follows: Aravan district - 55.47; Kara-Suu district - 52.74. More than 60% of the total of patients with infertility lived near the former pesticides storehouses and agro-airstrips used in 1990s for treatment of cotton and tobacco against pests. Of the total of 1211, 946 patients had primary infertility accounted for 79.7% and 258 had secondary male infertility (21.3%). The data on the incidence rates of male infertility in the districts of the Osh Province were as follows: Alay district – 51. Of them, 38 (74.5%) had primary infertility, 13 (25.5%) - secondary infertility; Chon-Alai district – 28. Of them, 20 (71.4%) had primary infertility, 8 (28.6%) - secondary infertility; Aravan district – 160. Of them, 131 (81.9%) had primary infertility, 29 (18.1%) - secondary infertility; Kara Kulzha district – 60 patients. Of them, 42 (70%) suffered from primary infertility, 18 (30%) had secondary infertility; Kara-Suu district – 475. Of them, 337 (79.4%) had primary infertility, 98 (20.6%) – secondary infertility. Nookat district – 232 patients. Of them, 174 (75%) patients had primary infertility, 51 (25%) –secondary infertility. Uzgen district – 205 patients. Of them, 164 (80%) patients suffered from primary infertility and 41 (20%) had secondary infertility.

Thus, the number of patients with primary infertility living in the areas polluted by organochlorine pesticides was 81.9% as compared to 70% of patients reported in unpolluted areas.

The incidence of male infertility was correlated with concentrations of pesticides (HCH-α, HCH-γ, DDT and DDE) in semen. No traces of HCH-β, DDD, aldrin and dieldrin were detected.

The highest percentage of HCHα in semen was revealed in 34 (72.3%) patients, pesticide traces - in 2. The rest of 32 patients showed concentrations ranging from 0.0003 to 0.014 mg / l. HCHγ was found in 6 (12.76%) patients. Concentration levels ranged from 0.0003 to 0.0054 mg / l. DDT - in 6 (12.76%), concentration ranged from 0.0019 to 0.053 mg / l. DDE was detected in 27 (57.4%) patients. Pesticides traces were found in 9. Eighteen patients showed concentrations ranging from 0.0012 to 0.073 mg / l.

To prove the impact of OCPs on the development of male infertility, take a specific example: Three brothers suffered from primary infertility. Environmental studies showed that the brothers lived near the former pesticide warehouse. OCPs were detected in sperm of 2 brothers: HCHα - 0,001 mg / l, DDT - 0.011 mg / l, DDE - 0.0007 mg / l. Total - 0.0127 mg / l, HCHγ – 0.0041 mg / l, DDT - 0.019 mg / l and DDE - 0.0012 mg / l. Total - 0.0243 mg / l. One brother showed the following concentrations HCH γ – 0.0054 mg / l and DDT - 0.053 mg / l. Total - 0.0584 mg / l. Patients were treated for infertility and all three brothers now have children.

In control group (healthy males), OCPs were detected in 2 of the total of 51 males examined, accounting 3.92%. Concentrations of HCH and DDE ranged from 0.0001 and 0.0004 mg / l. Both males lived near the former pesticide warehouses.

Permissible concentration level of HCH (total isomers) in blood should not exceed 0.001 mg / kg of body weight, DDT (total isomers and metabolites) - 0.0005 mg / kg of body weight, (SanPiN 42-123-4540-87). Still there are no established standards for permissible concentration level of OCPs concentration in semen. In our opinion, there should not be any OCPs in semen considering blood-testis barrier.

Conclusion:

Thus, incidence rate of male infertility in the areas polluted by organochlorine pesticides is 2-2.5 times higher than that in unpolluted areas. The incidence is correlated with the concentrations of organochlorine pesticides in semen. The primary cause of male infertility in the environment of the Osh Province is organochlorine pesticides. The populations living near the former pesticide storehouses and agro-airstrips are suggested to cultivate technical crops and do not use DDT in order to prevent male infertility. Raising awareness on the hazardous effects of OCPs is also of great importance.

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THE EFFECT OF ORGANOCHLORINE PESTICIDE CONCENTRATIONS IN PLACENTA ON PREGNANCY AND LABOR

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Abstract

The paper presents the results of pesticide (OCPs) examination of 246 placenta samples and the results of examination of 246 newborns (including stillborn cases) with clinical and laboratory manifestations of the disease during the first six days. Organochlorine pesticides (OCPs) were detected in 39.2% of placenta samples, the concentration ranged from the traces to 2.27 mg/kg. OCPs were found in clinical samples collected from women living near the former pesticide storehouses, agro-air strips and pesticide burial sites.

The higher the concentration of OCPs in placenta, the higher the number of the recorded pathologies in pregnant and parturient women. Moreover, a correlation between the detection of OCPs in placenta and gynecological and post-parturient complications was revealed. Women living near the former pesticide storehouses, agro-air strips and pesticide disposal sites should be included in a risk group. In case of detection of OCPs in placenta, preventive treatment should be performed on parturient women and their children.

Key Words: placenta; woman; concentration; organochlorine pesticides; complications; concentration.

Background: In Soviet times, Kyrgyzstan was of the main suppliers of cotton and tobacco. A huge amount of pesticides including organochlorine pesticides (such as DDT (dichlorodiphenyltrichloroethane) banned in 1970) was used to maintain productivity and control cotton and tobacco pests. Persistent organic pollutants were mostly sprayed on tobacco and cotton fields, contaminating not only the cultivation areas but the neighboring territories[1].

Pesticide pollution affects humoral and cellular factors of homeostasis. Meanwhile, intensification and use of chemicals in agriculture are accompanied by circulation and accumulation of pesticides in the environment creating conditions for entry and deposit of pesticides in human body [2,3].

Researches carried out in the 1970s showed that pregnant women's contacts with pesticides increase the frequency of complications of pregnancy and labor, cause anomalies in newborns and lead to deterioration of integrated indicators of children's health[1]. Among the pesticides which are currently applied, OCPs are the most dangerous to the health of women and their children. First, the make up more than 50% of all pesticides used; second, they are most persistent in the environment[4]; third, pesticides accumulate in organs and tissues of people when entering the body[5], are capable of excreting with breast milk and even pass through the placental barrier [4,6]. This affects not only the children's health, but the gene pool of future generations, since there are not specific antidotes and remedies for OCPs. At the moment, in the environment of southern Kyrgyzstan, more than 95% of OCPs enter the human body through the gastrointestinal tract[7]. Moreover, pesticides deposit sites, storehouses and agro-airstrips present a serious environmental problem.

Based on the above, studies of OCPs concentration in placenta and their effect on the course of pregnancy and labor could help to answer some obstetrical and gynecological questions.

Objective: To study the impact of concentration of pesticides in placenta on pregnancy and labor.

Materials and methods: To study the effects of OCPs in placenta and umbilical cord on pregnancy and labor we examined 246 placentas of pregnant women for OCPs. Concentrations of organochlorine pesticide (HCC, DDT, DDE, DDD, aldrin and dieldrin) residues in placenta were measured by gas-liquid chromatography. Group I comprised of 96 patients with detected OCPs in placenta, Group II consisted of 150 patients (placentas were found free from pesticides).

Measurements of organochlorine pesticides in placenta and umbilical cord samples were performed by the method developed by VNIIGITOKS (Kiev) research workers, D.B. Girenko, M.A. Klisenko (1987) and supplemented by instruction #1112-73 («Guidelines on detection of trace amounts of pesticides in food, feed and environment" - M., 1992), by thin layer gas-liquid chromatography in the laboratory of toxicology, radiology, morphology and ecology of the Institute of Medical Problems, South Branch of the National Academy of Sciences of the Kyrgyz Republic (Osh) and the Osh regional SES.

For pesticide tests, 50-60 g of placental issue collected from 5 points of placenta were placed in hexane and delivered to the laboratory. Concentrations of pesticides (HCH, heptachlor, aldrin, DDT and its metabolites - DDE and DDD) were measured by gas chromatography and gas-liquid chromatography. Samples were treated with concentrated sulfuric acid and then organochlorine pesticides were extracted with hexane. The combined hexane extracts were purified with concentrated sulfuric acid, washed with distilled water, dried with anhydrous sodium sulfate and evaporated on a rotary evaporator and chromatographed on a gas-liquid chromatograph «Perkin Elmer» with an electron capture detector. 5 μL of extract was placed in evaporator. Silica capillary column (length -20 mm, inner diameter - 9.22 mm) with silicone fluid phase BP-1 was used. The temperature ranged from 180 to 230 ° C at a rate of 3 ml/min. The temperature of evaporator was 200 ° C, the temperature of detector - 300 ° C. Carrier gas - argon. Quantitative analysis was performed by the absolute calibration of the height or area of peaks.

Results and discussion:

OCPs were found in 96 (39.6%) of the 246 surveyed placentas. At the same time, OCPs were detected in all women living near the former pesticide storehouses, agro-airstrips and pesticide disposal sites. The highest concentration of OCPs was 2.27 mg/kg. Total concentration of OCPs detected in placenta ranged from 0.0001 to 2.27 mg / kg. Concentration of pesticides in umbilical cord was lower than that in placenta. Severe and moderate complications during pregnancy and labor were observed in 39 (40.6%) of the 96 samples against 3.33% in control group. The more detailed data on complications depending on OCPs concentrations are given in Table 1.

Concentration of DDT and HCH, mg/kg	M, mg/kg	No. of placenta samples with OCPs	%	Of them with complications during pregnancy and labor	
				Total No.	%
>0,1	0,75 ±0,20*	21	8,53	20	95,2
0,01 – 0,099	0,052 ±0,012**	28	11,38	14	50,0
0,001 – 0,0099	0,0042 ±0,0011**	38	15,44	4	10,5
0,0001 – 0,00099	0,00039 ±0,0001*	9	3,65	1	11,1
Total with OCPs		96	39,2	39	40,6
Control group		150	60,8	25	16,7
Total		246	100,0	64	26,7

Table 1
Complications revealed during pregnancy and labor depending on OCPs concentrations in placenta

*Note: confidence indices *P<0,05 and **P<0,001.*

As shown in Table 1, in Group I (concentrations of OCP >0.1 mg / kg), moderate and severe complications were observed in 95.2% of women. The maximum concentration of OCPs was 2.27 mg/kg, M = 0,75 ± 0,20 mg / kg (P <0.05). Subgroup 2 - M = 0,052 ± 0,012 mg/kg (P <0.001), sub-group 3 - M = 0,0042 ± 0,0011 mg / kg (P <0.001), subgroup 4 - M = 0,00039 ± 0,0001 mg / kg (P <0.05). In Group I, pathologies associated with OCPs were found in 39 (40.6%) women. Of them, gestosis in 28 (29.1%), the threat of termination of pregnancy - 52 (54.2%), anemia - 90 (93.7%), fetal abnormalities - 5 (5.2%), premature birth - 12 (12.5%), bleeding during pregnancy and labor - 8 (8.3%), late amniorrhea - 25 (26%) and children with low body mass - 18 (18.75%). Stillborn cases were reported in 2 (2.1%), renal pathology - 31 (32.3), placental abruption - 2 (2.1%), eclampsia - 7 cases (7.3%), fatal outcome – 1.

In control group, complications were found in 25 of the 150 pregnant women, accounting for 16.7%. Chronic respiratory diseases were reported in 28 (29.2%), chronic kidney disease in 13 (13.5%), chronic diseases of the gastrointestinal tract in 12 (12.5%), thyroid dysfunction in 8 (8.1%), dystonia and essential hypertension in 30 (31.25%) and hepatitis in 13 (13.5 %).

Gynecological diseases were detected in 48 (48.3%), menstrual dysfunction - in 21 (21.7%). Anemia was found in 96 out of the 93, accounting for 96.9% of cases. In control group, moderate and severe complications were observed in 25 (16.7%) cases. 81 (54%) of pregnant woman had anemia.

The most severe complications in pregnancy, labor and in postnatal period were observed in samples with aldrin and DDT.

Pathologies of newborns in Group I were observed in 30 (31.25%) of the 96 against 7 (4.7%) in control group.

Conclusion:

Thus, moderate and severe complications occurred 2-3 times more frequently when OCPs were found in placenta. Women living near the former pesticide storehouses, agro-air strips and pesticide disposal sites should be included in a risk group. Moreover, if OCPs are revealed in placenta, preventive treatment should be performed.

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THE PROBLEMS OF ORGANOCHLORINE PESTICIDE POLLUTION IN OBSTETRICS, PEDIATRICS AND ANDROLOGY

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Abstract

To study the influence of organochlorine pesticides on the occurrence of pathologies associated with pregnancy complications – stillbirth, congenital malformations of the fetus and the health state of newborns during the first 6 days of life, including lethal cases. It was found that the higher the concentration of OCPs in placenta, the higher the number of the recorded pathologies in pregnant women and newborns. At concentration of OCPs > 0.1 mg/kg in placenta, complications rate reported in pregnant women and newborns is 97. The number of complications encountered in newborns is higher than that in pregnant women. At lower concentrations, the number of complications in main group (placentas with OCPs detected) is lower than that in control group (OCPs were not detected in placentas). The incidence of male infertility (MI) in the areas that are heavily polluted with OCPs is twice higher than that in unpolluted areas. OCPs in sperm of men with MI were detected in 82% of cases and in 3.92% in control, in 87.03% of men with primary MI and in 57.1% of men with secondary MI.

Keywords: organochlorine pesticides, placenta, pregnancy, newborns, pathology, complications, sperm, male infertility, morbidity.

Background: In Soviet times, Kyrgyzstan was of the main suppliers of cotton and tobacco. A huge amount of pesticides including organochlorine pesticides (such as DDT (dichlorodiphenyltrichloroethane) banned in 1970) was used to maintain productivity and control cotton and tobacco pests. Persistent organic pollutants were mostly sprayed on tobacco and cotton fields, contaminating not only the cultivation areas but the neighboring territories [7].

Moreover, pesticide storehouses, agro-airstrips and pesticide residues still pose a great environmental problem [6].

Researches carried out in the 1970s showed that pregnant women's contacts with pesticides increase the frequency of complications of pregnancy and labor, cause anomalies in newborns and lead to deterioration of integrated indicators of children's health [7].

Among the pesticides which are currently applied, OCPs are the most dangerous to the health of women and their children. First, the make up more than 50% of all pesticides used; second, they are most persistent in the environment [1]; third, pesticides accumulate in organs and tissues of people when entering the body [2]; are capable of excreting with breast milk and even pass through the placental barrier [1]. This affects not only the children's health, but the gene pool of future generations, since there are not specific antidotes and remedies for OCPs. At the moment, in the environment of southern Kyrgyzstan, more than 95% of OCPs enter the human body through the gastrointestinal tract [6].

On the other hand, males are more susceptible to the effects of pesticides [3]. The sterility of animals with pronounced atrophy of both male and female reproductive organs was observed in the experiment [4].

Many chemical compounds (industrial poisons and pesticides, in particular, used as medicinal agents) may have gonadotropic mutagenic action [5].

At the same time, there are no works on the detection of organochlorine pesticides in placenta and sperm and their effects on the health state of pregnant women, fetus, newborns and male infertility. The study of this problem could help to assess the impact of OCPs on the development of pathologies in women, fetus, newborns and male infertility and further development of methods of treatment and prevention.

Objective: to study the effect of OCPs concentrations in placenta on the development of pathologies in pregnant women, women in labour, fetus, newborns and concentrations of OCPs in sperm on the development of male infertility.

Materials and methods: To detect the source of pesticide pollution we have studied archival pesticide data (from 1978): location of pesticide storehouses, agro-airstrips in settlements of southern Kyrgyzstan.

Measurements of OCPs (DDT, DDD, DDE, HCH ant its isomers, aldrin and dieldrin) in soil (13 soil samples taken from pesticide disposal sites, agro-airstrips and pesticides storehouses) water (2 samples) and clinical samples (246 placenta samples collected in 1995-1996 and 262 placenta samples collected in 2011-2014; 13 breast milk samples), 2 lamb and cow's milk samples, a ship liver sample, blood samples collected from 3 children who consumed poisoned fried lamb liver , ship and cow milk samples, sperm samples) were performed on the gas-liquid chromatograph "Svet-100" in the laboratory of toxicology, radiology, morphology and ecology of the Institute of Medical Problems and in the laboratory of toxicology of the Osh Regional SES.

To study the effect of OCPs pollution on male infertility (MI) epidemiological studies were performed. A total of

1211 medical cards of outpatients with MI living in rural areas and consulted a doctor in medical institutions of southern Kyrgyzstan were analyzed. Clinical samples (sperm) collected from 61 patients with MI and 51 volunteers (control group) were subjected to analysis.

Results:

Analysis of soil samples collected from 2 pesticide deposit sites and downstream the water sources showed the presence of HCH and its isomers, DDE, DDD and DDT. No traces of aldrin and dieldrin were found. Total concentration level ranged from 0.519 to 1242.69 mg/kg. Soil samples collected from pesticide storehouse and former agro air-strips also contained OCPs at concentrations of 252.16-974.89 mg/kg and 32.6-65.7 mg/kg, respectively.

Total pesticides (HCH and DDE) concentration in spring water samples was 0.00022 mg/l. Concentration of pesticides (HCH, DDE and DDT) in water samples collected from Bazar-Korgon reservoir was 0.12 mg/l.

Thus, the main sources of organochlorine pesticide pollution are soil, former pesticide storehouses and agro-airstrips.

In 2008, analysis of breast milk samples of 6 lactating women living near the pesticide burial sites revealed HCH, DDE and DDT with total concentration of 1,639 mg/l.

In 2013 (also 6 women), concentrations of HCH ranged from 0.03 to 2 mg/l and DDE - 0.03-2 mg/l. Breast milk of woman (a shepherd) living near Ak-Chabyr pesticide disposal site contained: HCHα - 0.003 mg/l, DDE - 0.04 mg/l, DDT - 0.06 mg/l. Milk sample collected from sheep grazing in 3 km from the site contained HCHα - 0.0023 mg/l, DDE - 0.023 mg/l and DDT - 0.03 mg/l.

In 1995-1996, OCPs were detected in placentas of 96 of the total of 246 observed women, accounting for 39.2%; in 2011-2014 – 144 (55%) of 262 placenta samples contained pesticides. In Group I (OCPs concentration > 0.1 mg/kg) was 8.53% and 14.4%, respectively. Gestational complications were found in 95.2 and 96.7%, respectively. Complications in newborns during the first 6 days of life - 96.7%;

At concentrations of OCPs from 0.01 to 0.099 mg/kg, gestational complications were found in 52.5% of pregnant women and in 85.0% of newborns.

At concentrations of OCPs from 0,001 to 0.0099 mg/kg, complications were detected in 13.55% of pregnant women and in 32.2% of children; at concentrations of OCPs 0.0001 - 0.00099 mg/kg, in 6.7% and 13.3%, respectively. In the group where pesticides were found, the total number of complications detected was 41.0% in pregnant women versus 9.3% in control and 58.3% in newborns versus 13.6%, i.e. infants are more susceptible to the effect of OCPs. The total number of complications in two groups was as follows: 26.7% in pregnant women and 38.17% in newborns. The total number of gestational complications reported in 1995-2014 remained unchanged (26.7%).

Severe complications were detected in Group I: threatened miscarriage- 54.2% versus 1.3% in Group II (control); fetal growth abnormalities- 5.2% and 0.7%, respectively, bleeding during pregnancy and childbirth - 8.3% versus 0.7%; stillbirth cases - 2.1% versus 0.7%; eclampsia - 7.3% versus 0.7%; placental abruption - 2.1% versus 0.7%.

The data on intrauterine complication and complications detected during the first 6 days of life (medium and severe complications in newborns) were as follows:

In Group I (144 observed), congenital malformations (CM) - 3.47%; intrauterine hepatitis - 2.08%; stillbirth cases - 2.77%. In group II (118 observed), these complications were not revealed.

Perinatal infant mortality rate in Group I was 5.55% versus 1.7% in Group II, intrauterine hypoxia - 30.5% and 9.3%, respectively; cerebrovascular disease - 9.7% and 0.84%; intrauterine hypotrophy - 9.0% and 4.23%; respiratory distress syndrome - 9.0% and 3.4%; bacterial infection - 11.1% and 1.6%; other complications - 28.5% and 2.5%, respectively. The total number of complications revealed in children in Group I was 58.3% and 13.6% in Group II.

At lower concentrations (<0.1 mg/kg), the organism of pregnant women can control the pesticide load, but a high percentage (85.0%) of abnormalities in newborns is revealed. This is probably due to the high sensitivity of newborns to pesticide loads.

Thus,

- the main sources of OCPs pollution in Kyrgyzstan are the soil, the former pesticide storehouses and agro airstrips and pesticide burial sites.
- the residues of OCPs, getting into the body of pregnant women with food, affect the health of pregnant women, women in labour, fetus and newborns.
- the occurrence of complications in pregnant women and newborns depend on the concentration of OCPs in placenta; the higher the concentration of OCPs in placenta, the higher the percentage of complications;
- OCPs are the primary cause of stillbirth cases, congenital malformations, prematurity and other severe complications.
- At concentrations of OCPs in placenta > 0.1 mg/kg, complications among pregnant women and newborns are reported in 96.7%, stillbirth cases - 10.7% and congenital malformations - 9.3%, perinatal mortality rate - 21.1%.

Physicians are advised to examine placentas of pregnant women living near the former pesticide storehouses, agro airstrips and pesticide burial sites. If OCPs are revealed in placenta, preventive treatment should be performed.

To prevent pathologies in pregnant women, women in labour, fetus and newborns it is recommended to eliminate soil sources of pesticide pollution. The local population is advised to plant poplar (used as a building material) instead of cultivating vegetables, melons, legumes and fodder crops.

To study the effect of OCPs on male reproductive function epidemiological studies on male infertility (MI) depending on the degree of OCPs pollution were performed. Incidence rate of MI in unpolluted areas ranged from 20.19 to 23.84, from 33.55 to 37.3 in tobacco-growing areas and 52.74 -55.47 per 100 000 male population in cotton-growing areas. Primary MI was diagnosed in 70 -71.4% of patients in unpolluted areas, in 75- 80% in tobacco-growing areas, in 79.4 -81.9% in cotton-growing areas.

To study the effect of OCPs on MI, sperm samples collected from 61 patients with MI (Group I) and 51 healthy men (Group II) were subjected to analysis.
The more detailed data are given in Table 1.

Table 1
Concentrations (%) of OCPs found in sperm samples

Group	No. of observed	No. of detected	%	Concentrations, mg/l
Group I	61	50	82	Up to 0,0584
Group II	51	2	3,92	0,0001 and 0,0004

Table 2
Concentration of OCPs detected in sperm samples collected from patients with primary and secondary male infertility

Male infertility	No. of observed	No. of detected	%	Concentrations, mg/l
Primary	54	47	87,03	Up to 0,0584
Secondary	7	3	57,1	0,0023 and 0,006

The incidence of male infertility correlated with concentrations of pesticides (HCH-α, HCH-γ, DDT and DDE) in sperm. No traces of HCH-β, DDD, aldrin and dieldrin were detected.

The more detailed data on OCPs detected in sperm are shown in Table 3.

Table 3
OCPs detected in sperm samples collected from patients with infertility (47 patients)

	OCPs	No.	%	Traces	Concentration of OCPs, mg/l
1	HCH-α	34	72,3	2	0,0003-0,014
2	HCH-γ	6	12,76	-	0,0003-0,0054
3	DDT	6	12,76	-	0,0019-0,053
4	DDE	27	57,4	9	0,0012-0,073

Thus, the incidence rate of male infertility in the areas polluted by organochlorine pesticides is 2-2.5 times higher than that in unpolluted areas. The incidence correlates with the concentrations of organochlorine pesticides in sperm. The primary cause of male infertility in the environment of the Osh Province is organochlorine pesticides.
The populations living near the former pesticide storehouses and agro-airstrips are suggested to cultivate technical crops and do not use DDT in order to prevent male infertility. Raising awareness on the hazardous effects of OCPs is also of great importance.

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HEALTH & SAFETY OF PESTICIDES AND THEIR COMPLEX ENVIRONMENTAL COCKTAILS

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Abstract

In several EU projects (ReProtect, ChemScreen) a panel of in vitro human reporter cell lines CALUX has been developed that allows rapid screening of hazards of pesticides, POPs, PAHs & pollutants and their complex mixtures on multiple toxicological pathways. The ultimate goal is a simple and fast method to accurately predict human and environmental hazard for known/unknown pesticides and/or their complex mixtures, based on such effect- and human cell line based profiles.

Here we will report from 30 different characteristic environmental pollutants their toxicological profile tested by using the most ten relevant human reportergene bioassay activities (such as dioxin-, endocrine disrupter-, PAHs-, genotoxicty, cytotoxicity, obesity-like activities). We will present an easy and toxic relevant way to handle complex cocktails of chemicals and their risk assessment for the environment, wildlife & human health

Key words

Bioassays, in vitro reporter reportergene assays; CALUX, pesticides, POPs, dioxins, complex mixtures

Materials and methods

CALUX bioassays

The CALUX battery of stable reporter gene assays consisted of the following human U2OS cell based lines: ERα-, PR-, GR-, AR-, PPARα-, PPARγ-, Cytotoxicity-, p53-, Nrf2- and ESRE-CALUX [1, 2]. Two additional lines were included based on rat H4IIE liver cells expressing the aryl hydrocarbon receptor (AhR) endogenously: the DR- and PAH-CALUX [3]. The CALUX cells were cultured essentially as described before [3]. Cells were seeded in transparent 96- or white 384-wells microplates. After 24h, exposure medium was prepared by adding 2% of a test compound dilution series (16 individual concentrations) in DMSO to a plate with assay medium. Of this exposure mixture, 1 volume was added in triplicate to the assay plates containing the CALUX cells, resulting in final DMSO concentrations of 1%. Positive and negative controls were included on each plate. After 24h exposure (PAH-CALUX: 4h exposure) the exposure medium was removed and cells were lysed with triton-lysis buffer. Subsequently, the luciferase signal was measured in a luminometer (Berthold), essentially as described before [2].

Results and discussion

HTP-screening on the CALUX panel

After the validation of the procedure, a list of approximately 30 reference compounds with known toxicological properties has been screened on 10 different CALUX assays. The list includes some of the ‘dirty dozen’ POPs, PCBs, heavy metals, pesticides from the ToxCast program [4], reprotoxic compounds and genotoxins.

The pesticides showed activity mainly in the endocrine assays ERα-, anti-AR- and anti-PR-CALUX, suggesting endocrine disrupting activities. This is a well-known mode of action of many pesticides.

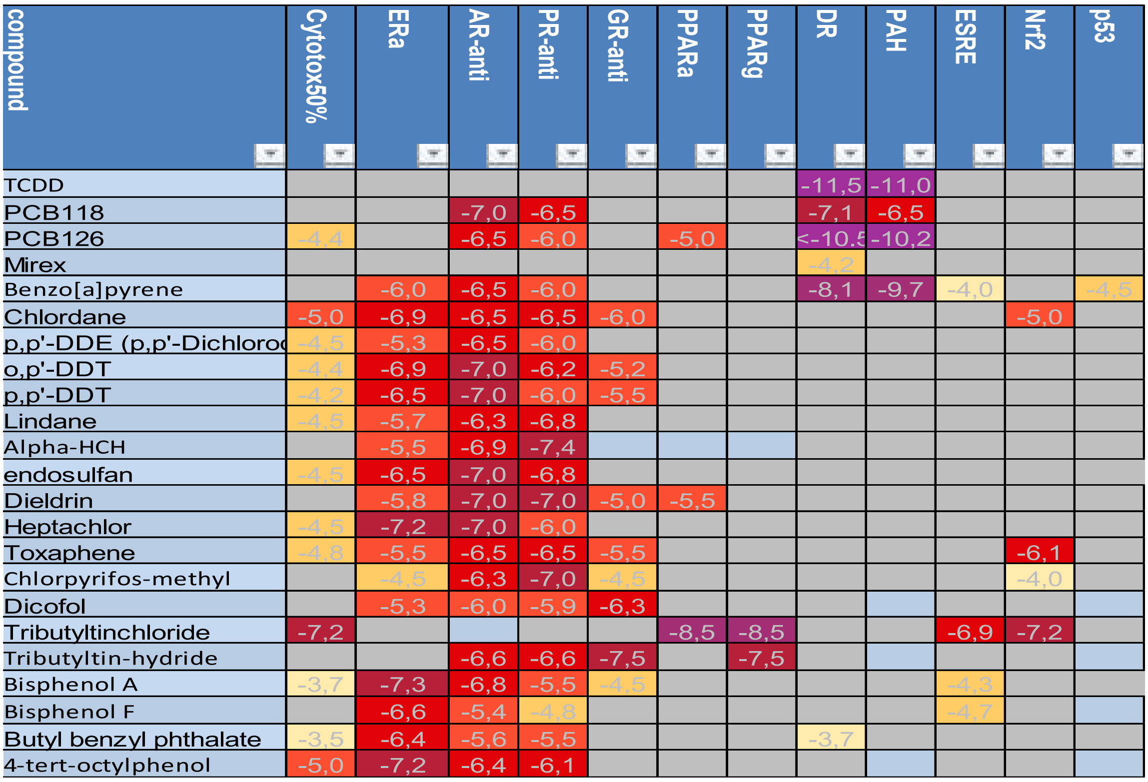
For heavy metals, activity is observed in the cytotoxicity- and stress/signaling pathway assays Nrf2- and ESRE-CALUX. This is in line with the known acute toxicity of heavy metals (figure 1).

The dirty dozen POPs can be sub-divided into pesticides and non-pesticides. The pesticide POPs showed a similar ‘endocrine’ profile as the ToxCast pesticides, while the non-pesticide POPs (PCBs, PAHs, furan, TCDD) mainly showed very high activity in the AhR-receptor mediated DR- and PAH-CALUX (figure 2). These PCBs/PAHs are indeed known to activate the dioxin (AhR)-receptor. Pesticides and plastic additives are predominantly active on endocrine assays, while heavy metals act on general tox/stress pathway assays (Nrf2, p53, ESRE).

In conclusion, the compound screening showed a different CALUX activity profile for different classes of compounds. A clearly distinct profile was observed for pesticides, heavy metals, and non-pesticide POPs.

The observed CALUX profiles can be explained on the basis of the known toxicological properties of the different compounds, which demonstrates the physiological relevance of the CALUX results.

Moreover, because of recent automation- and downscaling activities, the throughput of the CALUX assays has been increased dramatically. This enables the screening of large sample numbers in a short period of time, while requiring only small amounts of sample material. This makes the CALUX panel a promising fast, efficient and economical tool for toxicological profiling with multiple areas of application, including incidental or routine monitoring and large epidemiological wildlife and human studies.



compound	Cytotox50%	ERa	AR-anti	PR-anti	GR-anti	PPARa	PPARg	DR	PAH	ESRE	Nrf2	p53
TCDD								-11,5	-11,0			
PCB118			-7,0	-6,5				-7,1	-6,5			
PCB126	-4,4		-6,5	-6,0		-5,0		<-10.5	-10,2			
Mirex								-4,2				
Benzo[a]pyrene		-6,0	-6,5	-6,0				-8,1	-9,7	-4,0		-4,5
Chlordane	-5,0	-6,9	-6,5	-6,5	-6,0						-5,0	
p,p'-DDE (p,p'-Dichloroc	-4,5	-5,3	-6,5	-6,0								
o,p'-DDT	-4,4	-6,9	-7,0	-6,2	-5,2							
p,p'-DDT	-4,2	-6,5	-7,0	-6,0	-5,5							
Lindane	-4,5	-5,7	-6,3	-6,8								
Alpha-HCH		-5,5	-6,9	-7,4								
endosulfan	-4,5	-6,5	-7,0	-6,8								
Dieldrin		-5,8	-7,0	-7,0	-5,0	-5,5						
Heptachlor	-4,5	-7,2	-7,0	-6,0								
Toxaphene	-4,8	-5,5	-6,5	-6,5	-5,5						-6,1	
Chlorpyrifos-methyl		-4,5	-6,3	-7,0	-4,5						-4,0	
Dicofol		-5,3	-6,0	-5,9	-6,3							
Tributyltinchloride	-7,2					-8,5	-8,5			-6,9	-7,2	
Tributyltin-hydride			-6,6	-6,6	-7,5		-7,5					
Bisphenol A	-3,7	-7,3	-6,8	-5,5	-4,5					-4,3		
Bisphenol F		-6,6	-5,4	-4,8						-4,7		
Butyl benzyl phthalate	-3,5	-6,4	-5,6	-5,5				-3,7				
4-tert-octylphenol	-5,0	-7,2	-6,4	-6,1								

Figure 1. Activity profile of a selection of pesticides, plastic additives, heavy metals and other relevant environmental, wildlife and human health pollutants. Values indicate PC10 values compared to the reference compound activity.

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HISTORY OF HCH AND PESTICIDE USE IN IRAN, IMPACT ON HEALTH, SAFETY AND ENVIRONMENT

SUBMITTED PAPER

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Abstract

Expansion of industrialism, overpopulation and occurrence of two World wars in 20th century were main motivations for man to discover and make better killing agents resulting in high numbers/ types of pesticides/ chemical agents. Due to the diverse numbers of pesticides/ chemicals imported/ produced in Asian countries, used without regulations and enforcement, now people/ environment in these countries are more exposed to chemicals as compared to other parts of the World. Observing high pesticide use in three Northern Provinces of Iran (by the Caspian) during my academic studies/ teaching since 1970s, motivated me to do this comprehensive study followed by people / environmental awareness against toxic pollution. Objectives were: pesticide/ chemicals pollution reduction and regulations for Iran and other developing countries, capacity building and awareness in people and government in a national, regional and international level against toxic exposure in developing countries, in particular Iran and other Middle Eastern countries, searching and working for alternatives for pesticides in these countries, working on propagation of the neem tree, *Azadirachta indica* in the Persian Gulf area. In this paper some of my global messages, some discussions about the situation of pesticides in Iran as a developing country and a few general topics on pesticide/ chemicals pollutions for human and environment, regulations etc. are discussed briefly. Considering my work on pesticide/ chemicals regulations during the past 10 years I will discuss this important issue later separately in a more detailed paper or book.

Key Words

Pesticides, Chemicals, IRAN, Regulations, Neem tree, Persian Gulf, Natural insecticide

Introduction

In early 20th Century explosion of human population and also higher demands for better food, health and living quality forced man to advent and use pesticides. In fact it was the occurrence of 1st and the 2nd World wars and synthesis of the killing warfare agents like Sarin, Soman and Tabun which later turned to be the basis for most widely used insecticides, organophosphorus (Ops) insecticides and also eager of mankind for better/ higher agricultural production and health that guided man to develop a high array of compounds called synthetic organic insecticides and later other types of synthetic pesticides. In the meantime what added to the speed of synthesizing and wide usage of these materials was discovering of the insecticidal properties of DDT by Dr. Muller of Swiss in 1939. Rescue of man from big pests like cooties (lice) and increase in crop productions by using DDT brought a Nobel Prize for Dr. Muller but it was only after few years that resistance in different pests against DDT was observed and later the incompatibility of DDT and related compounds with nature was discovered[1]. Now in recent two decades the pesticide discoveries and science has entered its new and more sophisticated era, pesticide gens. That is about transferring of toxin producing gens like those from *Bacillus thuringiensis* (BT), *Bacillus subtilis* (BS) etc. through gene manipulations, gene transfer and engineering called biotechnology. During the past 7 decades of conventional pesticide use thousands of different types of these compounds were used in agriculture, horticulture, forest and ornamentals; in health sector and home pest control; veterinary and aquaculture; roadsides and airports as herbicides and many other uses, the last one: nonagricultural pesticides called biocides. Due to the diverse numbers of pesticides/ chemicals which are imported/ produced in developing countries and used without regulations and enforcement, now consumers[18] in these countries are more exposed to these chemicals as compared to people in developed World. Many factors helped for this higher exposure, among them less knowledge and information about these dangerous compounds[2].

Iran, a very diverse developing country with diverse climates and crops is a good end market for pesticide industries. Pesticide/ chemicals/ toxic compounds now are found in every habitat and niches and need more examination, discussion, evaluation of their effects on human, biodiversity and ecosystem services.

Materials and methods

Many papers reviewed, high internet communications with World NGOs like different sections of Pesticide Action Network (PANs), long, decades study and communications with different global regulatory agencies: EPA, DPR, OECD, PMRA, CFIA and in particular recent years with ECHA & REACH (EU). In 2003 a website created by virtualactivism in New York for my NGO: Sustainable agriculture and environment just before leaving for Canada to expand my global activities (the website was on only until 1988). Conducting many workshops/ presentations and also worldwide virtual communications with many other groups in different parts of the World to curb dangerous pesticides/ chemicals[3].

Objectives: 1- Pesticide/ chemicals/ toxic/ genetically modified crops pollution reduction and regulations in Iran/ developing countries; 2- Introducing, searching for, propagation and cultivation for alternatives for dangerous pesticides for Iran/ developing countries: case work: neem tree *Azadirachta indica* in the Persian Gulf; 3- Reducing exposure of most vulnerable groups like pregnant mothers, babies and children, elderly to dangerous pesticides and chemicals in Iran and other developing countries.

Results and discussion

Pesticides in Iran: Past and present

In Iran as a developing country like most other developing countries only use of pesticides and not the industry and real science and regulations was going until recently and considering the good oil money and diversity of crops, Iran turned to be a good end market for these dangerous compounds, wide usage with no regulations and big profits for Transnational Corporations (TNCs)[2, 4]. In Iran now by employing concepts of Integrated Pest Management (IPM) generally and our efforts in Iranian society of toxicology for regulating these compounds recently there are good science and publications going but still a big distance from sound regulations and organizations like Department of environment of Iran and the Ministry of agriculture had little to do with this progress and the infrastructure in these organizations are against regulations[4].

Past situation of pesticides in Iran:

Past history of pest control in old Iran is shiny but later by using unregulated synthetic pesticides is disastrous. Persians in old time were extracting a drug called Persian Louse Powder from *Composite* flowers and were exporting it to the World[5], later in recent time this turned to be a big science and profit for other countries extracting Pyrethrums from the species *Chrysanthemum cinerariaefolium*[5].

According to the Wikipedia: *"C. coccineum, the Persian chrysanthemum, is a perennial plant native to Caucasus and looks somewhat like a daisy. It produces large white, pink or red flowers. The leaves resemble those of ferns, and the plant grows to between 30 and 60 cm in height. The flowering period is June to July in temperate climates (Northern Hemisphere). C. coccineum also contains insecticidal pyrethrum substances, but it is a poor source compared to C. cinerariaefolium. Pyrethrum has been used for centuries as an insecticide and as a lice remedy in the Middle East (Persian powder, also known as "Persian pellitory"). It is one of the most commonly used allowed nonsynthetic insecticides in certified organic agriculture."*

Years before synthetic organic pesticides, some minerals like sulfur and dangerous compounds like arsenicals (green Paris and other arsenicals) etc. used against plant pests in Iran which still high residue of those arsenicals could be detected in Iranian soil now[2]. After advent and introduction of the synthetic organic pesticides, Iran turned to be one of biggest users of these compounds and so a good profitable market for Western pesticide industry, below I try to mention some of these heavily non-regulated pesticide use in Iran which partly of it is still continuing today:

Seed treating dangerous mercury based compounds (now banned) for many years with high human killing disasters like what happened in Iraq.

Heavy use of the fumigants like methyl bromide, aluminum phosphide etc. against stored products pests most in southern Iranian ports of the Persian Gulf in ships carrying wheat and other grains and in big storage facilities, these compounds are still in use in Iran as well as most other developing countries, methyl bromide is supposed to be banned at 2015 under Montreal protocol. Aluminium phosphide in the form of rice tablet kills hundreds of Iranians every year (please see below under the present situation of pesticides in Iran).

A few decades ago very heavy use of many types of pesticides most of them insecticides, a big special market for the World's pesticide industry TNCs: cotton pesticide use in vast (that time) Gorgan and Gonbad (now Golastan) cotton fields by the Caspian, most of these pesticides later categorized as Persistent Organic Pollutants (POPs) and now residues can be found easily in soils of our above mentioned Provinces bringing a higher rate of cancer for people and their animal herds and wildlife. Being there as a student researcher in early years of my career I was observing the big real polluting story of: ships and ships full of these compounds, DDT, Aldrin, Dieldrin, Endrin, Toxaphene and other mixed chlorinated insecticides with organophosphorus insecticides called Turbidan (with Parathion), many types of organophosphorus insecticides (Ops), different types of acaricides and fungicides and so a big list, were arriving in the Persian Gulf Ports, carried to the Caspian side by big trucks, making huge monies for pesticide mafias and finally used with big aerial spraying airplanes (light weight Pipers and heavy Bulgarian spraying planes). If you go now to the aerial spraying aviation office in Iran you will see a big salon with pictures of the fallen spraying pilots martyred to help the agriculture and health sector of Iran but also to bring money to those corporations and insider mafias. This is a scary story of heavy unregulated pesticide use in three beautiful Northern Provinces of Iran: Golastan, Mazandaran and Gillan (cotton field were in Gorgan and Gonbad now called Golastan Province and in Khuzistan South of Iran) and also some Southern Provinces like Khuzistan[6]. At the same time very heavy use of different types of pre emergence and post emergence herbicides like Trifluralin, Chloridazon, Phenmedipham etc. as well as different insecticides and fungicides was going on different crop fields of Khuzistan and many other Provinces of Iran. In Khuzistan huge multinational agricultural cropping companies called "*cultivation & industry*" were using very sophisticated spraying equipment some of them for the first time in the World and under experiment for spraying these compounds. This observations later were the motivation behind my long term activities for pesticide reductions and regulations in Iran and other developing countries, starting with my MSc studies 40 years ago[13].

At the same time that the above polluting scenario was taking place and even years before that heavy use of different insecticides like the dangerous OP compound parathion in citrus orchards of Mazandaran and mass killing of orchard owners is a famous story in Iran.

Adding to the misuse scenario of pesticides in Northern Provinces of Iran is a very heavy and long pressure of pesticide use against rice stem borer *Chilo suppressalis* Walker and other pests and diseases in paddy rice fields. Millions of kg of a wide spectrum killer insecticide called diazinon[13] was used every year in these rice paddy agro-ecosystems with high level of ground water with the resulting dramatic decrease in biodiversity now. Nearly all these rice paddies were connected to wetlands with bringing high toxic pollution to wetlands where the Ramsar (Ramsar convention) itself is located[7]. Wetlands in Asian countries are under big toxic pressure. In these countries many wetlands are connected to paddy rice fields which are the most polluted agricultural fields with different types of pesticides, fertilizers, etc. Wetlands are the most important habitat for nearly all species of birds which are the place of hunting and game birds are under different big threats some of them are already extinct. Many wetlands in Middle Eastern countries are already dried dead helping to the big dust problem[7].

According to my research and findings under a national project: ***Effects of highly used pesticides on Caspian Sea living organisms and natural enemies of pests*** (1995-2003) some fish species and also gammarids (amphipods) in the Caspian sea were effected by high usage of pesticides[8,11]. In this national project acute toxicity of some insecticides and herbicides were evaluated on Gammarids and some fish species of the Caspian Sea, many thesis were defended and few published due to different problems. Bioassays in this long research were based on scientifically safe bioassays which was designed and used in Canada during my PhD studies and final analysis by a computerized Probit analysis[14.]

Very heavy use of different insecticides most of them dangerous compounds like famous Dieldrin (H.E.O.D.) (now banned) happened widely for migratory locust control with aerial spraying most of them under pressure of pesticide companies and related pesticide mafia with no real migratory locust population make up in the field. I myself was observing one of these pesticide abuse and misuse in the Ghazvin plains (120 Km from Tehran) more than 3 decades ago with all types of wildlife killed on the scene, a crime scene against nature. One big problem in this pesticide abuse in Iran was the prescriptions and recommendation by entomologist with no knowledge about dangerous compounds like pesticides because there was no pesticide toxicologist in the country, not all entomologists can prescribe pesticides.

Heavy use of different types of insecticides against the wheat bug *Eurygaster integriceps* all over Iran is an old story and still is continuing with newly sophisticated developed Ops and synthetic pyrethroids. The wheat bug is an important pest in Iran and about half a Century ago following activities of some entomologists like Dr. Afshar (the founder of science of entomology in Iran) there appeared a good biological control against this pest employing *Scelionidae* parasite wasps but later it was destroyed by pressure of pesticide companies.

In health sector of Iran use of DDT and lindane and also mixed isomers of Benzene Hexa Chloride (BHC) called Gamexan as well as other insecticides etc. against human lice and malaria was continuing for many years. Because of these wide use now residues of these persistent compounds and their metabolites are found everywhere in Iranian environment. Adding to this is a dangerous abuse of different insecticides most from pyrethroids family for home pest control against cockroaches, flies and other household insects most by ladies and leaving a high residue on the kitchen floor and other parts of home with most residues goes to the crawling babies of the family according to a study in USA[6].

Wide use of Zinc phosphide for mouse control with lots of human mortality deliberately (suicidal) or un-deliberately. It was used widely against different species of rodents in Iran called desert mice like *Rattus rattus*, *Rattus norvegicus*, etc. as agricultural fields' pests.

Pesticide companies and their related people in government in our country were most responsible for above pesticide scenarios.

I have to add here that these pesticide use and abuse of the past in Iran mentioned above are only some of my personal observations and history of pesticide use and pollution in Iran is too much wider than this that I will try later in a long paper/ book to describe it. That longer paper or book surely will include all my years of work on regulations and also alternatives for pesticides in IRAN and other developing countries.

Present situation of pesticides in Iran:

Some of the pesticide use, abuse and misuse that were mentioned above are continuing today in Iran. Pesticide research and science in Iran at first were most about the efficacy plots supported by pesticide companies and in most cases results supported one or more particular compound and later in recent years conducting some laboratory bioassays[9]. This type of research which is continuing now in whole chemical World including pharmaceuticals, pesticides etc. now is changing in part. In recent years there are more research and publications about the side effects on human and the environment. Advent of more sophisticated toxic compounds based on biotechnology and nanotechnology is making the situation more complex and unfortunately an ever increasing harm is going to the whole life system on the planet and people in developing countries are most exposed and harmed[10]. Looking on the positive side we have to confess that drug/ pesticide/ chemicals research have added a lot to understanding of mankind for his/ her protection and also to the pure science among other things.

Every year there were about 700 (670 people according to many Iranian media) people killed recently in Iran by aluminium phosphide (Phosphine), using this dangerous poison as rice tablet, fumigant etc. or deliberately as suicidal but it is decreased this years following awareness and activities by Iranian society of toxicology including myself in many conferences in Iran. Unfortunately these types of dangerous deadly poisons are sold in many supermarkets all over Iran [19, 20].

Pesticide registration and marketing in Iran:

In developing countries pesticide registration, use, and marketing are different from developed world due to differences in regulatory issues and bad infrastructures in related government offices. This is because when you do not make something yourself you will not have the science behind it to control it and surely this is truer for very complex pesticide molecules that are carefully and scientifically designed to kill, each final marketed compound chosen from 1000s in screening. Pesticide registration and marketing in Iran now is a big part of Iranian scientific research and also a big business. Many laboratories are now involved in pesticide measurement and analysis for purpose of residue, quality control, etc.[4]. We tried to make a scientific and social basis for sound management of pesticides during past decade, many of my students now are producing a good number of ISI papers and it seems that there are winds of change coming for finally sound regulations, as I mentioned above I am going to bring all mine and others activities in this respect in a longer paper or book later.

According to the official internet site of Iran government for pesticide registration: *"Pesticide registration for new compounds in Iran now must go under a detailed, more than 30 steps procedure and only those pesticides are allowed for new registration that show better quality in respect to better pest control, less phytotoxicity, less toxicity for human, animal and the environment, less bioaccumulation in body, ease of application, less environmental persistency, less dangerous metabolites after degradation, selectivity and many other qualities"*[4].

Pesticide formulation and manufacturing in Iran:

Pesticide manufacturing in Iran which started after revolution, for most cases stopped at pilot level. About 20 years ago a faulted herbicide manufacturing factory was bought from India with price of about $30 million by Arak petrochemical company for producing two dangerous out of order herbicides: Alachlor and Butachlor!, it never worked properly and later stopped and turned to be only a manufacturing decoration. This incidence showed that Iran as a developing country still is only a high user of these dangerous compounds. After that incidence (about 20 years ago) they invited me and some others in the form of a conference! to correct the damage but it was late (only to clarify that I am not a chemist, lots of chemistry but always use it (always) to now pesticides better and their impact on life systems, I am a toxicologist). According to my studies in Canada during my PhD studies Alachlor and Butachlor are cancerogenic compounds.

One other semi successful pesticide manufacturing effort was synthesizing some basic materials for Ops insecticides in the biggest pesticide formulation company of Iran Agrochimi by a young chemist. Many other efforts were and are taking place but the fact that right now Iran is importing nearly all its pesticide from China and few other countries most not in a good quality, makes it clear that we do not have any national pesticide production industry yet in Iran. This is at the time that now there are many ISI papers written by young Iranian students and scientists, we are getting a good rank for it globally and so I as an always positive optimistic person say that there are winds of change to have our manufacturing and more important than that our sound regulations and enforcement. I myself did a different wider work especially during the past 10 years in the form of some global messages, people and environmental awareness, capacity building (many conferences and workshops), working on alternatives etc.[12].

Now in Iran about 100 registered licensed companies are involved in importing pesticides from abroad under control of Plant Pest Research Institute and Plant Protection Organization of the Ministry of Agriculture. Most of these imports are taking place from China with bad quality reputation. The bad and dangerous fact for these industries like China is that they rarely are ready to get involved scientifically with scientific people of the importing country, only like to sell their products and surely this type of bargains does not persist for a long time.

A few years ago I was invited by India to present a paper about pesticides in Iran in a conference held in Dubai (U.A.E.) and it was only there that I observed a high competition between India and China for taking over Iranian pesticide market. China and India as newly emerged industrialized developing countries are now big producers of different types of pesticide with not enough scientific and regulatory basis, India itself a big victim of these compounds in the past (Bhopal) and recent (Bihar).

In Iran now about 60 companies are involved in pesticides and agricultural oil formulations some of them had been active for more than 4 or even 5 decades. Many of these formulator companies are only involved in agricultural oil formulations. After introduction of the new Integrated Pest Management (IPM) concepts at first in academic environment and later in the field some change and reduction in use of pesticides in Iran started to happen[4].

Obsolete pesticide in Iran:

Iran stockpiles Updated Aug 12, 2010, Stockpiles of obsolete pesticides in Iran estimated at 1,138 metric tons (Source: FAO) [15].

Pesticide residues in fruits and vegetables of Iran:

A few years ago (2010) residues of nine insecticides were reported higher than MRL (determined by World food codex committee) and were given to me for analysis, interpretation, their health effects on consumers and control. I started to prepare a comprehensive report about the problem because of the importance of people's and in particular children safety, but later the related manager (executive manager of Tehran Myadin) stopped cooperation, returned the data to the laboratory! And in the best of my knowledge and according to the Iranian media this year all these higher residues are continuing now with no action yet. Thanks to the recent government of Iran that made these awareness possible[4].

Pesticide regulations in Iran and other developing countries:

There are no regulations in these countries and if there is a regulation written, unfortunately its enforcement is impossible and all these will result to a more exposure for people and more loss of biodiversity. During the past decade I examined this problem and discussed about it in a national/ international level[1, 2,3,4,6].

My work on Neem tree, Azadirachta indica as an alternative for synthetic pesticides:

Introduction, propagation and cultivation of the neem tree, *Azadirachta indica* in the Persian Gulf region as an alternative for dangerous pesticides and also helping environmental quality in oil/ petrochemical production areas of the Persian Gulf. I started to work on the neem tree more than 20 years ago in Qeshm and Bandar Abbas and finally I introduced the neem tree from the Persian Gulf region to the World more than 20 years ago. Now the tree exists in nearly all ports and Islands of the Persian Gulf but surely need more propagation and support and we are now far away from using all potential neem tree profits for the region. For now I finished doing a small project on possibilities of neem propagation in the Petro-zone in Western Persian Gulf and I look for more support to propagate this miraculous tree in all Persian Gulf area. Neem tree surely is the most important species for phytoremediation of oil polluted soils of the region[5, 16].

Pesticide/ chemicals/ toxic pollution effects on biodiversity and ecosystem services:

During my teaching years on Integrated Pest Management (IPM) going deep to the concept of IPM to be able to do it efficiently I went deep to the ecosystem services concepts (that time not under this name) and always there were a big disturbing problem called pesticides, pesticides now are everywhere and even though pesticides are only few thousands now we are facing with a real bigger problems called toxic chemicals, millions of them, and their metabolites, now in every habitat and niches with possibility of synergism on each other. Some phenomenons like cumulative exposure, bioaccumulation, biomagnifications, sequestration/ encapsulation (and then release of toxic compound in the body) and many other newly discovered ecotoxicological process need to be studied carefully. It is worth to mention that most of these process do stronger (more dangerous) in aquatic environment and so threatening whole aquatic life. The big problem of eutrophication now as a result of high N and P coming from agricultural lands is having big effects on biodiversity. The big problem of cyanotoxins as a result of eutrophication is now adding to the problems. I observed myself that they are using lots of toxic pesticides in aquaculture now[7, 17]. The Colony Collapse Disorder (CCD) mostly related to use of neonicotinoids is pushing honey bees to the verge of extinction.

How pesticides are handled in developing countries (my first message about 10 years ago):

Pesticides have a dilemma nature and because of this nature to use them safely there must be done lots of research and there should exist lots of laws and regulations and enforcement, now let say that this is followed correctly in developed countries where the industry exists but the story and scenario is quite different in developing countries. In most of these developing countries there are no research/ regulations or if there is it is not followed / enforced absolutely and this is the problem and because it deals with the life of people and health of the environment it is a real big problem. When it comes to spraying technology and worker protection it is never practiced by ordinary farmers in these countries. These are my personal experiences/ observations during more than 35 years being involved in pesticide science work. Living more than 15 years in Mazandaran, Golastan and Gillan the three beautiful Northern Provinces of Iran by the Caspian Sea I observed so many cases of pesticide intoxication. This is because people do their spraying without any protective clothing, most of times with bare foot and body because of hot weather and with any type of spraying equipment that they can find and they use lots of pesticides in their rice paddies, cotton fields and citrus orchards etc. So as a result where there is no scientific research and laws and regulations as in developing countries then most use of pesticides should stop because no rules are followed.

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TOXICOLOGY

Part 3: Consequences of human exposure to OCP’s and breast cancer

ENDOCRINE-DISRUPTING POTENTIAL OF LINDANE AND OTHER HCH ISOMERS VIA NUCLEAR RECEPTORS

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Introduction

Organochlorine chemicals (OCs) used for years in agriculture and industrial practices, are stable and strongly lipophilic, have slow degradation rates and tend to bioaccumulate in lipid-rich tissues. In the last decades, interest has focused on their reproductive effects in terms of fertility, pregnancy outcomes, long-term developmental outcomes both in wildlife and humans. More recently, some lipophilic OCs have been identified as Endocrine Disrupting Chemicals (EDCs) which may act through different hormonal mechanisms, either reacting directly or indirectly with the hormone structure to alter its function, changing the pattern of hormone synthesis, or modulating the number of hormone receptors and their affinities for specific molecules. The present review summarizes the role of Hexacholorocyclohexane (HCH) isomers as disruptors of hormonal homeostasis, both in vivo and in vitro models.

Hexachlorocyclohexane isomers

Complex and variable mixtures of HCH related compounds are produced by photochemical chlorination of benzene. HCH exists in 9 stereoisomeric forms, which include (+)- and (−)-alpha- (α), beta- (β), gamma- (γ), delta- (δ), epsilon- (ε), zeta- (ζ), eta- (η) and theta- (θ) isomers. Technical-grade HCH is comprised of 60–70% α-HCH, 5–12% β-HCH, 10–15% γ-HCH, 6–10% δ-HCH, and 3–4% ε-HCH.

Purified HCH isomers, as well as technical-grade HCH are used either as insecticides and fungicides or in the synthesis of other chemicals. Lindane or technical-grade HCH containing the γ isomer is used primarily as an insecticide in the treatment of wood and wooden structures, seed grains, and livestock. Other major uses are as an insecticide for fruit and vegetable crops, in baits and seed treatments for rodent control, and for treatment of scabies (mites) and lice. The beta-isomer (β-HCH) has all chlorine atoms in an equatorial position, and thus: i) while it lacks aromatic character, its molecular shape is more similar to that of strictly planar hexachlorobenzene than those of all other isomers, and ii) it lacks any axial chlorine atom(s) which can be the site for 1,2-elimination by chemical mechanisms. This seems one reason why this isomer shows a higher bioaccumulation higher half-life in human body. Since this isomer is eliminated very slowly from human body, it makes a significant contribution to the total HCH body burden.

Although restrictions for γ-HCH use have been introduced in many European countries human exposure may represents still a concern because of the persistence in the environment and bioaccumulation in the feed and food chains.

In vivo endocrine activity of HCH isomers

Lindane is a weel-known endocrine disruptor in animals, and is associated with a range of serious effects on reproduction and development. These effects include testicular damage, reduced sperm production, disrupted estrus (menstrual) cycles, delayed puberty in females, ovarian and uterine atrophy, and infertility (Cooper et al., 1989). For example, adult male rats treated with lindane develop atrophy of their sex accessory organs, including the epididymis, seminal vesicles, and vas deferens, consistent with treatment with an anti-androgen (Chowdhury and Gautam, 1993). In addition, decreases in testicular weight and degeneration of the Leydig cells, resulting in diminished testosterone levels has been observed in adult male rats dosed with lindane (Chowdhury and Gautam, 1994).

Lindane is a weak estrogen, a more potent anti-estrogen and anti-androgen, and may also interfere with thyroid and adrenal gland function. For instance, ewes fed lindane have significantly decreased thyroid hormone (T4) and pituitary hormone (LH) concentrations and significantly increased insulin and estrogen levels (Rawlings et al., 1998). In adult female mice, administration of lindane results in atrophy of the adrenal glands and abnormalities of the gland structure. The mice also have increased cholesterol levels and decreases in ascorbic acid (Vitamin C) content of the glands (Lahiri and Sircar, 1991).

Low, environmentally relevant, doses of lindane inhibit the binding and production of androgens in the prostate, even at the lowest dose tested. The inhibition does not appear to occur via direct binding to the androgen receptor (AR). A synergistic interaction between lindane and other pesticides may result in inhibition of testosterone metabolism in the rat prostate (Simic et al., 1992; Danzo, 1997).

In sexually immature and ovariectomized rats lindane did not change the ER number or the estrogen-dependent induction of progesterone receptor (PR) in the hypothalamus, pituitary, or uterus suggesting that the effects of this chemical on the female reproductive system do not involve an alteration in the ER (Susan et al., 1994). In fact, in the rainbow trout lindane seems to act on ER and Vg gene expression no directly by through their hepatic metabolites (Flouriot et al., 1995). Since both estrogen receptor forms (ERα and ERβ) have shown to be target for endocrine disruption, the role of lindane on the development of female reproductive system was investigated in an in vivo model during prenatal period in pregnant CD1 mice which were treated p.o. on gestational days 9-16. In treated F1, lindane elicited subtle effects on female reproductive development likely mediated by ERβ-related pathway(s), without a concurrent impairment of steroid hormone metabolism (Maranghi et al., 2007). In summary, in vivo results suggest that HCH isomers may interact with ER acting either through their metabolites or *via* different gene activation pathways.

Mechanisms of HCH endocrine disruption

Mechanisms of endocrine effects of lindane and other HCH isomers have yet to be clarified, but lindane seems not to be a strong agonist or antagonist of either ERα or AR, nor is a dioxin-like agonist of the aryl hydrocarbon receptor (AhR), although a competitive binding with PR has been reported (Band et al., 2011).

Our own results are consistent with findings that attribute potential endocrine-disrupting activity to lindane through its action on either ERα or ERβ (Briz et al., 2011; Li et al., 2008; Maranghi et al., 2007). When we study the effects of lindane on nuclear ERs in primary cultures of cortical neurons (CN) and cerebellar granule cells (CGC), we observed that lindane inhibited the binding of [^{3}H]-estradiol to the ER in both CN and CGC (Briz et al., 2011). In contrast, β-HCH did not displace 17β-estradiol (E2) from its binding to ER in our cultures, as previously reported in MCF-7 cells (Coosen and van Velsen, 1989; Steinmetz et al., 1996). Nevertheless, this HCH isomer is considered an endocrine disruptor in human breast cancer cells through a non-classic ER-dependent mechanism (Steinmetz et al., 1996). We also determined the effects of lindane, using primary cultures, on protein kinase B (Akt) and extracellular-regulated kinase 1 and 2 (ERK1/2) phosphorylation, and observed that this chemical acts as ER antagonist rather than an agonist because it not only failed to activate Akt and ERK1/2 but also actually inhibited the effects of E2 on these protein kinases (Briz et al., 2011).

Altogether, these results suggest that the classic view of endocrine disruptors (EDs) as agonists or antagonists of ER may be too simplistic to describe the estrogenic effects of HCH isomers, at least in systems in which different ERs are present. In this sense, it has been demonstrated that some OCs induce a unique pattern of conformational changes in both ERα and ERβ, which is a combination of the patterns induced by E2 and the partial ER antagonist 4-hydroxy-tamoxifen (Sumbayev et al., 2005). In turn, this would allow the ligand-activated ER to bind different co-regulators or associated proteins, and therefore different effects on the signaling pathways associated can be expected depending on the relative expression of ERα, ERβ, and GPR30 and on the specific affinity for each ER that a given OC has.

In both males and females, E2 is produced by the aromatization of dihydrotestosterone (DHT) by the cytochrome P450 aromatase enzyme complex. It has been reported that lindane enhances aromatase activity at short exposure times (< 6 h) followed by mild inhibition at longer times in cell lines (Nativelle-Serpentini et al., 2003). Estrogens exert their action not only regulating the female reproductive tract but also male gonads and, in both sexes, the skeleton, the central nervous system as well as the cardiovascular and immune systems. The basis of such a pleiotropic role relies on the broad tissue-specific expression of both nuclear ERs. ERα and ERβ are nuclear hormone receptors, ligand-activated transcription factors, able to regulate gene expression in a cell- and promoter-specific way. ER-β shows major biological roles in different tissues which have not yet fully clarified.

Interestingly, the estrogenic activity of lindane was characterized using stably transfected MCF-7 and HeLa cells expressing ERα and/or ERβ together with an ER-regulated reporter gene (Balaguer et al., 1999; Lemaire et al., 2006). In these systems, lindane did not show estrogenic activity. However in a yeast two-hybrid assay used to assess the estrogenic activity of different EDCs, based on the interaction between the human ERβ ligand-binding domain and the co-activator SRC1 nuclear receptor-binding domain as the most effective to detect a xenoestrogen-dependent induction of the reporter activity, lindane showed a detectable estrogenic activity (Lee et al., 2002).

Moreover, when testing lindane ER interference in the LNCaP cell line, derived from human prostate adenocarcinoma a cell line expressing only a functional ERβ besides nuclear AR and PRs, but devoid of functional ERα, lindane revealed a concentration-related effect on cell viability and proliferation (Maranghi et al., 2007). Interestingly, the addition of a pure anti-estrogen, the ER antagonist ICI 182,780, completely reversed lindane effects indicating an ER-β-mediated action. All together, these findings indicate that lindane may act as an ED interacting with ERβ as a potential target for this compound and other EDCs.

Like lindane, β-HCH does not compete with estradiol for binding to the ER. Its chemical structure characteristics may not allow binding the classical ligand domain and thus fail to activate ER in the nucleus, but it shows affinity to the alternative pocket and consequently triggers the Src/Ras/ERK pathway. Although unable to bind the ER, β-HCH is capable of activating ER target genes and the proliferation of estrogen-responsive cell lines by other chemical and biochemical mechanisms. For example, treatment of MCF-7 cells with β-HCH resulted in strong activation of the Src kinase, ERK1 and ERK2. Thus β-HCH has been shown to induce rapid and sustained Src/ERK signaling in MCF-7 cell lines lasting for at least 30 min (Hatakeyama et al. 2002). Interestingly, β-HCH (1 μM) has mitogenic activity in MCF-7 cells but not in ERα-MDA-MB231 cells which express a non-functional ER, suggesting that a functional ER is necessary to elicit the proliferative activity. Finally, in mouse xenografted with MCF-7 cells, β-HCH significantly increased cell number and increased pS2 gene mRNA level (Mrema et al., 2013). Several studies have demonstrated the anti-androgenic action of different α-HCH stereoisomers using the MDA-kb2 cell line stably transfected with the luciferase reporter gene under the control of AR (Pavlíková et al., 2012). There was no direct effect of α-HCH on AR but both isomers significantly suppressed the activity of AR in co-exposure with the natural ligand DHT in a concentration-dependent manner. In contrast, using the stable transfected PALM cell line lindane was ineffective both in the presence and in the absence of the synthetic androgen R1881 (Lemaire et al. (2004).

Conclusions

A number of adverse health effects such as endometriosis, infertility, immunotoxicity, neurotoxicity and spontaneous abortions, breast cancer, prostate cancer and neurodegenerative disorders have been suggested as a result of the exposure to OCs, including in some cases lindane and its isomers. These chemicals may exert these effects through various mechanisms, for example, acting as agonists on ERα and/or antagonists on ERβ and also as probably antagonists on androgenic receptors. This is the case of HCH isomers which have been shown to exhibit hormonal effects by binding to nuclear receptors, competing with natural estrogens/androgens, and acting by intracellular pathways other than the one used by endogenous estrogen in mediating these actions.

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TESTING FOR DEVELOPMENTAL IMMUNOTOXICITY OF CHEMICALS

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Abstract

In recent decades, there has been an increased focus on chemical risk assessment for children as a specific subpopulation, as hazard and risk assessment in adults may not necessarily be sufficiently protective for children. Developing organs may be more susceptible to chemical-induced toxicity than mature adult organs. Especially, the nervous system, immune system and reproductive system are more vulnerable to toxicants during the developmental stages.

Different exposure and testing designs for developmental immunotoxicity exist. Examples of developmental immunotoxicity studies and their impact on regulatory measures will be presented.

Key Words

Immunotoxicity
Developmental effects
Toxicity testing

In recent decades, there has been an increased focus on chemical risk assessment for children as a specific subpopulation, as hazard and risk assessment in adults may not necessarily be sufficiently protective for children. Developing organs may be more susceptible to chemical-induced toxicity than mature adult organs. Especially, the nervous system, immune system and reproductive system are more vulnerable to toxicants during the developmental stages.

The primary aim of the immune system is to protect the host against invading pathogenic microorganisms and arising neoplasms. Many xenobiotic compounds are known to have toxic effects on the immune system and such effects may eventually result in reduced resistance and lead to enhanced incidence and/or severity of infections. The development of the immune system starts in utero and completes in early life. Immune-based diseases in the developed countries affect around 25% of the children. Early onset diseases related to malfunctioning of the immune system show a high prevalence in children in western societies, including recurrent otitis media (18-26%), asthma (15-26%), atopic dermatitis (15%) and allergic rhinitis (8-12%). Moreover, juvenile onset allergic, inflammatory and autoimmune diseases have shown an increasing prevalence in recent decades. The underlying causes are probably multifactorial, while a possible causative role of chemical exposures during pre- and postnatal development of the immune system cannot be excluded. Yet, direct evidence for a relation with chemical exposure is poor. Part of this lack of knowledge is the current virtual absence of developmental immunotoxicity testing in the regulatory requirements of chemical hazard assessment.

Guidelines for the evaluation of reproductive and developmental toxicity include the prenatal developmental toxicity study, the one- and two-generational reproductive toxicity study, and developmental neurotoxicity study. These protocols do not contain parameters for developmental immunotoxicity (DIT). Parameters indicating immune toxicity such as spleen and thymus weight, differential blood cell counts and immunohistopathology parameters could easily be incorporated into the reproductive toxicity studies. Moreover, functional assays may provide additional sensitivity to DIT testing. In 2011, OECD adopted the guideline for the extended-one-generation reproduction toxicity study (EOGRTS), with dosing from the premating period to offspring adulthood, which now includes structural and functional endpoints for developmental neurotoxicity and DIT. Besides the above mentioned structural immune parameters, a T-cell dependent antibody response assay, i.e. the primary IgM antibody response to a T-cell dependent antigen, such as Sheep Red Blood Cells (SRBC) or Keyhole Limpet Hemocyanin (KLH) should be performed.

The acceptance of the OECD TG 443, including specific attention for developmental immunotoxicity parameters, has been recognized as a significant hallmark. It confirms the importance of assessing developmental immune parameters in regulatory toxicology. However, this study is only applied for a subset of chemicals of high tonnage under the European legislation for chemical safety (REACH). Moreover, it is a logistically complicated and expensive study. Developmental immune toxicity testing could perhaps be more practical in other study designs. In the past, several research groups have embarked on defining exposure protocols considering windows of sensitivity of the developing immune system.

We have performed a series of developmental immunotoxicity in rats according various study designs and using exposure windows based on various existing protocols (pre/perinatal exposure, juvenile exposure). Collectively, these studies demonstrated that the most sensitive immune parameters showed effects at lower dose levels compared to more general developmental parameters, indicating the relevance of including them by default in protocols for DIT testing. Furthermore, functional immune parameters largely made up to the most sensitive parameter sets, demonstrating the relevance of including them by default in protocols for DIT testing.

Differences exist when comparing the different exposure designs and route of exposure (this differs per compound). Comparing the EOGRTS and juvenile model show that both exposure designs have some advantages. On the one hand, the EOGRTS model studies continuous exposure during the development of the immune system, whereas the juvenile model is limited in that sense but may allow higher sensitivity of endpoints especially vulnerable during this window of development.

Examples of developmental immunotoxicity that we have studied include effects of methylmercury, di-n-octyltin dichloride, ethanol, di(2-ethylhexyl)phtalate. The impact on regulatory measures will be presented.

THE DEVELOPING BRAIN AS A TARGET OF ENVIRONMENTAL CHEMICALS

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Abstract

Brain development is controlled by genetic programs in intensive interaction with influences from the internal milieu of maternal organism and fetus, including endocrine systems and immune system, and with the physical and social environment. While environmental stimuli are essential for brain development, certain environmental influences can have adverse effects. Among these are prenatal stress, prenatal immune stimulation, and environmental chemicals from environment, nutrition, and consumer products.

Development of behavior: epidemiological studies and animal models. Correlations between developmental exposure to chemicals and behavioral disturbances in the offspring are well documented in epidemiological studies on children and in animal models. For example, prenatal exposure of **children** to **polychlorinated biphenyls (PCBs)** has been correlated with reductions in general cognitive abilities (IQ), verbal ability, executive functions (planning, response inhibition, task switching, working memory), information processing, and short-term memory (meta-analysis: Boucher et al., 2009; see also Vreugdenhil et al., 2002; Schantz et al., 2003; Newman et al., 2009; Eubig et al., 2010). Effects on sexually dimorphic play behavior of children have also been reported (Winneke et al., 2014). Impaired cognitive functions of children have further been observed with prenatal exposure to **brominated flame retardants (PBDEs)** (Roze et al., 2009). Emotional and social behavior and attention can also be affected by prenatal exposure to environmental chemicals. Thus, attention deficits, increased scores of aggressiveness and depression, and severe conduct problems have been observed in children in relation to **phthalate** metabolite levels in maternal urine during pregnancy (Engel et al., 2010; Miodovnik et al., 2011). Maternal **bisphenol A** levels were related to reduced control of emotions, reduced impulse control, increased anxiety, and depression in girls (Braun et al., 2009, 2011). The effects of bisphenol A were sex-dependent; the only parameter affected in boys was general activity, which was reduced, whereas girls exhibited more hyperactivity scores.

Animal models mirror many of the behavioral disturbances observed in humans, even though most experimental studies were conducted at doses higher than human exposure levels (Tab.1)

Table 1. Effects of prenatal exposure to environmental chemicals in humans and animal models

Animal models	Epidemiological data in children
Learning and Memory PCB:Learning and Memory â M and F Bisphenol A: Learning and Memory âM Phthalates:(DINP, DBP) âM á Vinclozolin: âM extinction of cond. response	**Cognitive Performance, Memory** PCB: cognitive performance, verbal ability â executive functions â short-term memory â
Attention, Activity PCB: Attention â, Hyperactivity á	**Attention, Activity** PCB: ADHD-type behaviors á Bisphenol A: Hyperactivity âM áF Phthalates (DMP, DEP, DBP): Attention âM+F
Anxiety Bisphenol A: Anxiety áM Vinclozolin:Anxiety âM áF	**Anxiety / Depression** Bisphenol A: Anxiety áF, Depression áF Phthalates: áAnxiety+ áDepression (M+F combined)
Aggression, Social interactions Bisphenol A:Aggression á M Social interaction á between Females Self-grooming (non-social behavior) â F	**Aggression, Social interactions** Bisphenol A Externalizing behavior áF (Aggression) Phthalates (DMP, DEP, DBP), M+F combined Social cognition âSocial communication â Conduct problems á
References for epidemiological studies see text. Selected references for animal models: Bisphenol A: Xu & 2010, Jasarevic & 2011, Fujimoto & 2006, Wolstenholme et al., 2011, Cox et al. 2010, Kawai et al., 2003. PCBs: Roegge et al., 2000, and others.Phthalates: Boberg etal., 2011; Li et al., 2009. Vinclozolin: Andréand Markowski 2006; Hotchkiss et al., 2002; Skinner et al., 2008.	

Neuro-endocrine systems as a target of environmental chemicals. Nervous system, endocrine systems and immune system are closely interrelated. Many chemicals that circulate in the environment and in living organisms, have the potential to interfere with the action of hormones (**Endocrine disrupters,** Table 2.), and hence, can disturb functions of neuro-endocrine systems in developing and adult organisms. Neuroendocrine systems are involved in the control of reproduction and development, behavior (reproductive behaviors such as sexual behaviors and maternal behavior, as well as non-reproductive behaviors such as learning, emotional and social behaviors), adaptation to environmental changes (stress and avoidance of stress, e.g., migration, hibernation), metabolism, and immune functions. **During ontogeny**, hormones such as male and female sex hormones (androgens, estrogens) and thyroid hormones exert **organizing actions** on the developing organism, which result in persisting functional patterns. Interactions of chemicals with these organizing actions of hormones can lead to permanent functional deficits ("fetal origin of adult disease"). Endocrine disrupters comprise a wide variety of chemicals, including pesticides (organochlor pesticides (DDT, HCH, lindane, methoxychlor), epiconazole, linuron, prochloraz, procymidone, vinclozolin), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDE), alkylphenols, the plastic monomer bisphenol A, phthalates, chemical UV filters (i.a. EHMC, 4-MBC, 3-BC), parabens, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), dioxins (TCDD), the analgesic paracetamol, synthetic estrogens (ethinylestradiol), phytoestrogens.

Examples of interactions of environmental chemicals with the developing nervous system. **Thyroid hormones and PCBs.** Thyroid hormones – in particular also thyroid hormones of maternal origin prior to the development of the thyroid gland – influence major developmental processes in brain: proliferation of neuronal stem cells, commitment of neural stem cells with cell cycle exit into a differentiation program, migration of neural precursors, differentiation of neurons, differentiation of glial cells, control of myelinization, synaptogenesis (reviewed in Demeneix, 2014). PCBs interfere with the function of thyroid hormones and hence, may possibly affect all of the aforementioned processes. The interaction with thyroid hormones occurs at several different levels: Levels of triiodothyronine (T3), in some cases also of thyroxine (T4) in maternal blood are decreased in humans and animal models in relation to PCB blood levels, with differences between congeners (e.g., Koopman-Esseboom et al., 1994; Osius et al., 1999; Takser et al., 2005). PCBs bind to transthyretin (TTR) and thyroid hormone-binding globulin (TBG) and thus may displace thyroid hormones from their transport proteins (Cheek et al., 1999). Thyroxin (not T3) metabolism is enhanced by increased UDP-glucuronyltransferase (UGT) activity (Hood and Klaassen, 2000). Finally, recent studies indicate that certain hydroxylated PCB congeners bind to and activate thyroid hormone receptors in vitro and in vivo (Gauger et al., 2004. You et al., 2006; Gauger et al., 2007). The data from brain of fetal rats treated with the PCB mixture Aroclor 1254 (Gauger et al., 2004) suggest that PCBs might exert a dual action: Expression changes were seen in genes that are directly activated by thyroid hormone receptors, but also in genes known to be indirectly influenced by a hypothyroid state. This incongruence in signaling might further disturb developmental processes.

Endocrine disrupters and the organizing action of sex hormones in brain development. The sexual phenotype of brain structures and functions is established by the organizing action of sex hormones. According to the classical rodent model, differentiation of the male brain phenotype is achieved by estradiol locally generated in brain by aromatization of testosterone (MacLusky and Naftolin, 1981), but recent studies provided evidence that sexual brain differentiation is the result of estrogen receptor (ER)- as well as androgen receptor (AR)-mediated mechanisms also in rodents (Sato et al., 2004; Zuloaga et al., 2008). The latter appear to be the dominant mechanism of male sexual brain differentiation in anthropoid primates and humans (Wallen, 2005). Development of the female brain phenotype depends on estrogen (Bakker et al., 2002). Effects of endocrine disrupters on the development of sexual behavior are well documented in animal models. Male sexual behavior is affected by prenatal exposure to TCDD (Bjerke et al., 1994), PCBs (Colciago et al., 2009), bisphenol A (Farabollini et al., 2002, Jones et al., 2011), phthalates (Gray et al., 2000), and vinclozolin (Colbert et al., 2005), male-type sweet preference by PBDEs (Lilienthal et al., 2006), female sexual behavior by PCBs (Chung et al., 2001), PBDEs (Faass et al., 2013), bisphenol A (Farabollini et al., 2002), and the UV filters 4-MBC and 3-BC (Faass et al., 2009). In contrast, evidence for effects of EDCs on the development of male sexual behavior is lacking, which contrasts with the observations on adverse effects on reproductive organs. There only is some evidence for alterations of male-type play behavior in children, e.g., with respect to phthalate exposure (Swan et al., 2010). There may be several reasons for this discrepancy. On the one hand, the time interval between chemical exposure and manifestation of sexual behavior is long and hence, difficult to pursue in cohort studies, also, human sexual behavior is influenced by many confounding variables. On the other hand, observations in primates suggest that sex hormones may influence human sexual behavior at a different level of brain organization. While the performance of sexual behavior by a female rat, for example, is directly dependent on estradiol, female monkeys display female sexual behavior during the entire estrous cycle, also at low estrogen levels; they use sexual behavior for social bonding (Wallen and Zehr, 2004). In primates, estrogens appear to regulate sexual motivation (correlating it with the time of ovulation), rather than sexual behavior itself. Effects on this more complex process might be difficult to detect.

Brain regions involved in cognitive and emotional behaviors as a target of sex hormones and endocrine disrupters: Hippocampus. As described above, endocrine disrupters exhibit adverse effects on cognitive performance and emotional and social behaviors in children. This is in keeping with the fact that sex hormones also control developmental processes in brain regions involved in non-reproductive behaviors, such as hippocampus. The developing hippocampus is a target for estrogens as well as androgens, but estrogenic actions are better documented. Hippocampal neurons, e.g., pyramidal cells, express nuclear estrogen receptors (ERalpha, ERbeta), at particularly high levels during development (Solum and Handa, 2001). Additional non-nuclear ERs with so far unknown function are present in nerve terminals (Hart et al., 2007). This brain structure also is capable of *de novo* synthesis of testosterone and estradiol (Hojo et al., 2004; Prange-Kiel et al., 2009). Locally generated estradiol may play a role in synaptogenesis (Fester et al., 2009).

The **hippocampus** plays a central role in the formation of new memories and in memory consolidation (see Preston and Eichenbaum, 2013). Memory consolidation involves the participation of excitatory glutamatergic synapses (Wang et al., 2006). Glutamate released into the synaptic cleft binds to several postsynaptic receptor types. While AMPA receptors mediate fast synaptic transmission, NMDA receptors are activated only upon strong depolarization of the postsynaptic neuron, they therefore are considered to function as “coincidence detectors” identifying important inputs. Their activation is accompanied by calcium ion influx which activates signaling cascades thought to be involved in memory processes. Estradiol regulated expression of brain-derived neurotrophic factor (BDNF) (Solum and Handa, 2002; Luine and Frankfurt, 2013), one of the major growth factors in hippocampus, stimulates the formation of dendritic spines, the site of excitatory glutamatergic synapses (through effects on neuronal networks) (Cooke and Woolley, 2005), stimulates glutamatergic synapse formation (Jelks et al., 2007), regulates expression of NMDA receptor subunits and synaptic proteins (Watanabe et al., 1999; Morissette et al., 2008; Ikeda et al., 2010; Waters et al., 2009;), and alters patterns of hippocampal connectivity (Cooke and Woolley, 2005).

Acute injection of estradiol in adult rats increased the number of dendritic spines and improved working memory (Sandstrom and Williams, 2001). When bisphenol A was administered at low doses (0.04-0.05 mg/kg per day) to mice during pregnancy and lactation, adult offspring showed impaired synaptogenesis (Xu et al., 2013) and reduced expression of NMDA receptor subunits in hippocampus, and impaired learning behavior (Xu et al., 2010). In hippocampus of adult (ovarectomized) monkeys, the same dose of bisphenol A prevented the formation of dendritic spines in response to estradiol (Hajszan and Leranth, 2010). These examples taken from one endocrine disrupter, bisphenol A, illustrate the sensitivity of hormone-dependent processes in hippocampus. Developmental changes in hippocampus and other cortical areas have also been reported after exposure to other EDCs such as PCBs (Parent et al., 2011; Gauger et al., 2004), or phthalates (Li et al., 2014).

Mixtures of endocrine disrupters. In the real world, the developing brain is exposed to a mixture of different chemicals. In a study of human milk from Basle (Switzerland), PCBs, PBDEs, pesticides, phthalates (metabolites), UV filters, fragrances and parabens were simultaneously present in the same samples (Schlumpf et al., 2010). We recently investigated effects of endocrine disrupter mixtures on genome-wide gene expression patterns in two rat brain regions, involved in control of gonadal functions and sexual behavior, during the critical, sex hormone-sensitive developmental period. Mixtures composed of anti-androgenic or estrogenic chemicals, or a combination of both, elicited distinct gene expression patterns that differed also between male and female offspring (Lichtensteiger et al., 2015). However, all three EDC mixtures affected genes controlling migration and pathfinding of glutamatergic and GABAergic neurons, and the development of glutamatergic synapses, which are not only involved in cognition and emotional processes, but also in sexual brain differentiation. A number of genes linked with increased risk of autism spectrum disorder (ASD) was likewise affected by the tree EDC mixtures. This illustrates the potential for interactions between genetic background and environmental, endocrine active chemicals.

Epigenetic mechanisms Multiple processes contribute to the persistent alterations caused by exposure to chemicals during development. Long-lasting functional modifications can be achieved by changes in epigenetic regulation of gene expression, such as methylation of the base cytosine (DNA methylation) or modifications of histones in nucleosomes. The effect of cytosine methylation in CpG dinucleotides depends on their position in the gene; methylated cytosines in the promoter region block gene transcription (Jones, 2012; Moore et al., 2013). Epigenetic changes in somatic cells influence their function in the individual organism, whereas epigenetic changes in germ cells lead to inheritable functional alterations. DNA methylation and other epigenetic modifications exhibit dramatic, life stage-dependent changes from germ cells to somatic cells in the adult organism, and continue to change in adult life, in brain, e.g., in relation to memory formation, consolidation and retrieval (Guan et al., 2015). The epigenetic control of gene expression in **somatic cells** can be affected by chemicals. An example are increases in DNA methylation of CpG sites in the promoters of BDNF and of a NMDA receptor subunit, with concomitant reduction in gene expression, in the hippocampus of adult male mice after prenatal exposure to bisphenol A (Kundakovic et al., 2015). This effect was achieved with a low dose of bisphenol A, 0.2 mg/kg per day.

Another issue are chemical-induced epigenetic changes in the **germ line** that may result in transgenera-tional inheritance of functional alterations. Behavioral changes in mice of the F3 generation following prenatal exposure of the F1 generation to chemicals have been observed with vinclozolin – increased anxiety in F3 females (Skinner et al., 2008) – and with bisphenol A – changes in social recognition in F3 males and females (Wolstenholme et al., 2013). Doses administered to pregnant F0 dams were comparatively high for vinclozolin (100 mg/kg per day), but lower for bisphenol A (0.8 mg/kg per day). In line with the concept of transgenerational transmittance of alterations in structure and function, transcriptomes of peripheral tissues (genome-wide gene expression patterns from somatic cells) were found to differ between F1 and F3 generation (Skinner et al., 2012). Quite different types of environmental influences, such as stress during prenatal development of the F1 generation, can also lead to behavioral alterations in subsequent generations (F3) (Franklin et al., 2010). This supports the idea that the epigenome is sensitive to environmental factors, including chemicals. Primary target of such influences are germ cells, which transfer genetic information across generations. Germ cell DNA is de-methylated upon arrival of the primordial germ cells in the genital ridge of the embryo, prior to gonadal sex determination, and will subsequently be re-methylated. This re-methylation process could be altered. Indeed, germ cells from F3 mouse embryos descending from vinclozolin-exposed F1 mice exhibit chromosomal regions, where DNA methylation differs from that of control F3 germ cells (“differentially methylated regions (DMR)”, Skinner et al., 2013). Interestingly, the chromosomal distribution of DMR as well as the accompanying transcriptomes differ between different developmental stages of germ cells. Thus, the germ line epigenome in the mature sperm (or oocyte), which transmits epigenetic inheritance, is the result of a cascade of epigenetic and transcriptional events during germ cell development.

Conclusions

Adverse effects of environmental chemicals on brain development and behavior are well documented by animal models and epidemiological studies, also for lower doses. Humans and animal models show a common focus on cognitive, emotional and social behaviors. Chemicals have further been found to cause epigenetic modifications leading to transgenerational inheritance of alterations in structure and function, including brain and behavior. Here, more information on the low-dose range is required. By affecting epigenetic and genetic mechanisms in developing tissues, environmental chemicals can interact with the genetic background.

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HCH AND POP PESTICIDES IN SPAIN, SOUTH AMERICA, AND EECCA COUNTRIES: EXPOSURE AND HEALTH PROBLEMS

Margret Schlumpf & Walter Lichtensteiger

Exposures to obsolete POP pesticides have been observed in increasing numbers of countries. Additionally, a concomitant increase in various health risks had been reported at the 12th HCH and Pesticides Forum, 2013, in Kiev. We here briefly summarize the expanded news on exposure and effects presented at the 13th HCH and Pesticides Forum held in November 2015 in Zaragoza.

1. New data on exposure and inadequate waste deposits Exposure

Additional countries and locations were found to be repeatedly affected by inadequate waste deposits because of re-exposures of humans and animals following dislocation using unexpected pathways or caused by transportations of waste to different areas. New data were presented on Asian countries, where the majority of imported and produced pesticides had frequently been used without regulations and enforcements, resulting in severe exposure of environment and people (Romano, abstract 2015, Mahdavi et al., 2010).

Carvalho and coworkers (Carvalho abstract 2015) reported on the Brazilian Santos and Sao Vicente estuary, where contamination with toxic industrial waste is affecting the health of the local population. HCH concentrations in hair samples of exposed individuals were 10 times higher than the levels measured in earlier studies, with similar environmental values across 5 different areas. The increase in HCH availability deserves further investigations. Deficits in technical knowledge of waste handling and public health persist in many countries.

Inadequate waste deposits and re-exposure. in Sabiñanigo (Spain), the company Iquinosa, located on the shore of the Gallego river, generated over 100’000 tons of toxic waste between 1975 and 1989, when they produced the pesticide Lindane (γ-hexachlorocyclohexane, γ-HCH). γ-HCH makes up only about 15% of all HCH isomers. The toxic waste consisting of the remaining HCH isomers, of similar toxicity, and some Lindane, was dumped at several places in the environment. Contamination of the Gallego river and its reservoirs, over a stretch of about 100 km, was known for years. Almost 20 years later, during summer 2014, the transfer of the waste from the old dump site to a new landfill resulted in an additional severe HCH contamination of the Gallego river, cutting 40 000 inhabitants off drinking water supplies, because unappropriate technology was used for transportation of the waste (Romano, abstract 2015). This kind of delayed re-exposure to toxic organochlorine pesticides is to be expected whenever the pesticides are not accommodated sufficiently safe according to up-to-date waste deposit rules.

Long lasting deposition of toxic waste today remains a matter of concern (compare Sabinanigo, Romano, 2015) One of the latest examples is the hazardous-waste landfill of Koelliken (Switzerland), that was started in 1978. Following an extensive remediation with a budget of over 900 million CHF, it finally became clear only recently that additional some 10’000 tons of co-contaminated solid rock mass has to be removed.

HCH was also produced by Ugine Kuhlmann in the city of Basel, at the border to Germany. Large mountains of HCH isomers, were piling up since the remaining 80-85 % of HCH isomers was also considered as toxic waste. In 2013, the Swiss pharmaceutical company Novartis, which is responsible for the property, started excavation of HCH waste, producing rather high HCH dust precipitation (up to 4.7 µg/m^2 per day) (Forter, abstract 2015). Meanwhile, Novartis improved methodologies to reduce air pollution, doubling the total budget. But HCH dust precipitation remained unacceptably high. Novartis seemed to have conducted air pollution measurements silently, without making the results available to the public. This behavior of “Acting while producing possibly harmful consequences for non-involved people” remains debatable. An EMBO report states ”In cases, where the lives (health) of others are at stake, decision-making and the handling of uncertainties have important ethical dimensions. A prudent strategy to deal with this ethical challenge is to diminish uncertainty by acquiring (and distributing) knowledge of the issue” (Tannert et al., 2007).

2. New data on Health risks

Diverse and potentially severe health risks have increasingly been observed in additional countries/regions. Preliminary data on health effects of organochlorine pesticides were reported from EECCA (Eastern Europe and Central Asian) countries. The audience was confronted with the large knowledge gaps between toxicology labs, countries and universities with regard to education in toxicology and epidemiology.

Pesticide use and poisoning in EECCA countries. A pilot study in six EECCA countries gathered information about risky practices and self-reported signs of pesticide poisoning during 2014-2015 in Armenia, Belarus, Georgia, Kyrgystan, Moldovia and Ukraine. Questionnaires and interviews of 200 participants/country were used to find out about pesticide use, common exposure routes, and health impacts. Thus, 79% of the respondents uses to wear ordinary clothing when applying pesticides, only 7% of the participants had received safety instructions in order to handle pesticides. More than 60% of men and women applying pesticides, experienced symptoms of acute pesticide poisoning (Willis, Guadagnini, abstract 2015).

Male infertility in Kyrgystan. In the Osh province of Kyrgystan, organochlorine pesticides were detected in 57-87% of sperm samples collected from patients with primary and secondary infertility, as compared to 4.3% in the control group. The incidence rate of male infertility (MI) in unpolluted areas of Kyrgystan (Alay district) was 20.19 per 100'000 males in epidemiological studies on 1211 male outpatients.. The infertility rate raised to 35.78 in a mountain area (Chon-Alai district), where people engaged in leguminous plants cultivation and cattle breeding. The increase in MI was considered to result from the increased use of OCP pesticides to combat ectoparasites. Similar MI rates were seen in tobacco growing populations with MI numbers between 33.55 and 37.3. In Soviet times, Kyrgystan was among the main suppliers of tobacco and cotton. OCP pesticides have also been used extensively against cotton pests; in these populations, infertility rates reached 52.74 - 55.47 per 100'000 (Toichuev et al. 2015).

OCP pesticides in placenta, labor, obstetric and pediatric data in Kyrgystan. Examination of placentas revealed a clear relationship between complications during pregnancy and labor, and OCP concentrations in placenta (Toichuev et al., 2015). OCP pesticides (HCH, Heptachlor, Aldrin, DDT and metabolites DDE and DDD) were detected in 39.6 % of the placentas. In the group with highest placental levels (>0.1 mg/kg), moderate to severe complications occurred in 95.2% of women. At 10 and 100 times lower OCP concentrations in placentas, the percentage of complications diminished to 10%. The OPC pesticides in the placentas also affected dose-dependently the percentage of newborn children suffering from pathologies, such as intrauterine hypoxia, cerebrovascular accident, intrauterine hypotrophy, bacterial infections, respiratory distress syndrome, congenital malformations, hepatitis, prenatal mortality.

While the toxicological analysis of consequences of pesticide exposure is still in its beginnings in EECCA countries, excellent scientific work is ongoing in many labs in Europe, the US, Japan and other countries. In Spain, the group of Nicolas Olea (University of Granada) has presented evidence for a correlation between total effective xenoestrogenic burden in adipose tissue, and breast cancer (Fernandez et al., 2007).

Reproductive toxicity in Spain
Reproductive effects of OCP pesticides include effects on fertility, pregnancy outcomes, and long-term developmental outcomes in humans and wildlife (Fernandez,Perez-Lobato, abstract, 2015). The impact of EDC on human health widely depends on the age at which exposure occurs. Prenatal exposure to numerous EDCs including OCs, PCBs, dioxins, furans, has recently been confirmed in a mother-child birth cohort in Southern Spain that in the context of INMA (Environment and childhood study), a population based cohort study focusing on prenatal exposures to environmental OCs in relation to growth, development and health from early fetal life and childhood. The results show an excess risk of the malformations, hypospadia and cryptorchidism, associated with the presence of pesticides (lindane among others). Both, experimental and human data point to a causal relationship between OC exposure during pregnancy (placental tissue, umbilical cord blood, blood of newborn, maternal urine) and development of male congenital malformations.

Increase in cardiovascular diseases, stroke, cancer, respiratory disease, and obesity in Spain. Cardiovascular diseases, stroke, cancer, respiratory disease, and diabetes are responsible for 63 % of deaths worldwide; the increase in some of these diseases cannot be explained solely by improved methodology. Recent studies revealed positive associations between exposure to low doses of organochlorine pesticides and risk of obesity, dyslipidemia, cardiovascular disease, hypertension and cancer. In fact, the incidence of obesity has tripled over the past decades reaching epidemic proportions in US and Europe. The "metabolic syndrome", defined as a cluster of hypertension, high glucose levels, obesity and dyslipidemia, has been found to be associated with increased risk of heart disease, stroke and diabetes. Recently, exposure to POP pollutants in an adult cohort of adult Spanish citizens was found to be associated with altered serum lipids and obesity (Arrebola, abstract 2015; Arrebola et al., 2014).

3. Reviews of developmental immunotoxicity and neurotoxicity

Developmental Immunotoxicity (van Loveren, abstract 2015). Developing organs may be more susceptible to chemical-induced toxicity. Especially, nervous system, immune system and reproductive system are more vulnerable to toxicants during development. The primary aim of the immune system is to protect the host against invading pathogenic microorganisms and arising neoplasms. Many xenobiotic compounds are known to exert toxic effects on the immune system and such effects may eventually result in reduced resistance and lead to enhanced incidence and/or severity of infections. The development of the immune system starts in utero and completes in early life. This results in a high fetal vulnerability to immunotoxicants with negative effects on immune-related health outcomes and immune functionality. Immune-based diseases in the developed countries affect around 25% of the children. Early onset diseases related to malfunctioning of the immune system show a high prevalence in children in Western societies, including recurrent otitis media (18-26%), asthma (15-26%), atopic dermatitis (15%) and allergic rhinitis (8-12%). Moreover, juvenile onset allergic, inflammatory and autoimmune diseases have shown an increasing prevalence in recent decades. Because the literature reports gender specificity in the innate, humoral, and cell-mediated responses to viral vaccines, separate analysis for males and females was conducted. Genes correlating negatively with PCB and dioxin exposure in general show positive correlations with antibody levels and vice versa. The underlying causes are probably multifactorial, while a possible causative role of chemical exposures during pre- and postnatal development of the immune system cannot be excluded. Yet, direct evidence for relations with chemical exposure is poor. Within the NewGeneris cohort BraMat, a subcohort of the Norwegian Mother and Child Cohort Study (MoBa), associations were demonstrated between estimated maternal intake levels of PCBs and dioxins, and reduced measles vaccination responses in the offspring at the age of 3. One reason for the lack of knowledge on developmental immunotoxicity of chemicals is the current virtual absence of developmental immunotoxicity testing in regulatory requirements of chemical hazard assessment. An increased focus on chemical risk assessment for children is needed, as hazard and risk assessment in adults may not be sufficiently protective for children.

Developmental neurotoxicity (Lichtensteiger et al., abstract 2015). Correlations between developmental exposure to environmental chemicals such as PCBs, pesticides, polybrominated flame retardants (PBDEs), phthalates, bisphenol A, on the one hand, and behavioral disturbances in the offspring on the other hand, are well documented in epidemiological studies on children as well as in animal models. Behavioral disturbances include general cognitive abilities, verbal ability, executive functions, attention deficits, emotional behaviors (anxiety, aggressiveness) and social behaviors. Many of these environmental chemicals interfere with the action of hormones (Endocrine Disrupters, EDCs). By interacting with organizing actions of hormones (estrogens, androgens, thyroid hormones) on the developing brain, they can lead to permanent deficits in brain function ("fetal origin of adult disease"). It is important to note that hormones do not only control the development of brain regions involved in sexually dimorphic functions (sexual behavior, reproductive behaviors), but also that of brain regions involved in cognitive and emotional behaviors. Hippocampus, for example, which plays a central role in memory formation and emotional behaviors, is a prominent target of estrogens. In real life, the developing brain is exposed to a mixture of different chemicals. In a study of human milk from Basle (Switzerland), PCBs, PBDEs, pesticides, phthalate metabolites, cosmetic UV filters, fragrances, and parabens were simultaneously present in the same human milk sample (Schlumpf et al., 2010). Mixtures of chemicals with different endocrine activities have recently been shown to elicited distinct, sex-specific gene expression patterns in developing rat brain (Lichtensteiger et al., 2015). A number of genes linked with increased risk of autism spectrum disorder was also affected. This illustrates the potential for interactions between genetic background and environmental chemicals. Recent studies indicate that exposure to environmental chemicals during early development can affect epigenetic mechanisms also in brain.

4. What to do?

The contributions to the symposium disclosed large gaps among countries and regions with respect to technical problems and problem solving. Even worse is the situation with health problems. None of the participating EECCA countries has systems in place to collect data on pesticide practices or poisoning. In absence of basic knowledge about problems with obsolete pesticides, help and improvement of the conditions, if available, may require more time, in the order of many years. In the absence of unique requirements and cost-covering emoluments, adequate medical assistance often is out of reach. In this new, self-inflicted, endangering health scenario, no rules exist and no diagnosed illnesses are depicted. In the face of authorities, these people often are not considered being sick, as their disease does not meet with WHO classifications. Thus, precious time goes by and may finally be lost.

The most promising task to begin or to proceed with is organizing continuing education. Meetings/Courses in the style of IHPA HCH and pesticide should be widely proposed for offering **education and overviews** on progress in technical as well as in toxicological and medicinal matters, worldwide. There should be financial support for the participation of people working in the field. One might even familiarize with the idea of making such continuing education mandatory for them.

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PESTICIDES AND FARMERS (PILOT RESEARCH IN BELARUS)

SUBMITTED PAPER

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Abstract

Working over baseline study of pesticide exposure in Belarus, with particular focus on social dimensions of pesticides use and identification of vulnerable groups, we used such methods as desk study and stakeholders consultations; survey, with the help of questionnaires, concerning vulnerable to pesticide poisoning groups, that took place in Bragin district of Gomel region , that suffered a lot from disaster at Chernobyl ; National workshop "Protecting Farmers and Vulnerable Groups from Pesticide Poisoning"**.**

The results of our survey showed that there is a reason to mull over. The National Workshop and survey participants' basic reaction was a will of learning more information about risks, raising these issues in their regions, as they were sure that their level of awareness was low. Despite a sample of the survey was small, nevertheless, appeared new information and confidence in that there was a need for further research and the implementation of measures in order to reduce risk. Moreover, the representatives of regulators found that people on the ground knew almost nothing about the risks, and there were many unresolved issues on the safety of pesticides and disposal of containers. Some participants asked the questionnaires in order to conduct a survey in their respective regions.

During conducting survey in Bragin district, after people were asked all the questions we were interested in, we gave them leaflets on pesticide exposure and poisoning to raise their awareness in this sphere. The communication materials on pesticide exposure and poisoning were given to every Seminar participant. We put the electronic variants of communication materials on our website: www.greencross.by, into the library, section Health School, so any visitor of our site can have a look at this information and print it if needed.

Key-words

Pesticides, obsolete pesticides, POP, IPM, alternatives, exposure, public awareness raising, health, risk, safety, exposure, garden, danger, education, training, Belarus, children, vulnerable group, food quality, families.

Introduction

According to data of Ministry of Agriculture the country had in 2014 2531 private farms while at beginning of 2012 - 2338. Private farmers use 165 000 hectares of land (1,7% of total agricultural land) including 146 of agricultural ones. Farmers give 1,5% of total agriculture products and are strong in potatoes 87%, vegetables 81%, eggs 32%, milk 13%, meat 12%. Average farm has 65 hectares of land (48 ha of arable land). At the same time farms have different sizes: from 2 hectares to 200 hectares. Private gardens in rural area as a rule occupy ~0,2-0,5 hectares. According to Belarusian law the land couldn't be a private property.

General situation on usage of pesticides in Belarus

Climatic conditions favour the spread of 65 kinds of pests, 100 species of diseases and 300 – weeds over Belarus. The Institute of Plant Protection estimates that the use of pesticides results in yield increases equivalent to 1.5-2 times the budget spent on pesticides (in comparison with not using pesticides). Unfortunately, the above calculations didn't take into account comparison with application of IPM and other alternatives. They were based on chemical plant protection approach, which was used since Soviet time. They constitute a base for active use of pesticides and postpone promotion of alternatives to them.

The calculation brought a reason to agricultural sector for active use of pesticides. We should definitely take it into account. At the same time this logic doesn't take into account many consequences as well as potential less risky alternatives.

The leading method of plant protection is a chemical one - the use of pesticides. They are widely used by agricultural organizations, farmers and gardeners. The main users of course are collective farms - kolkhozes. Volumes of the used pesticides in agricultural organizations for over 50 years doubled every 5 years until the mid 80s. Then the figure was 3.52 kg / ha, and then gradually decreased and in 2002 amounted to less than 1 kg / ha of the formulation. That was a time of strong economic crisis in the country. Pesticide load per 1 ha of arable land from 2008 to 2010 increased by 0.2 kg to 2.9 kg / ha. In 2008 Belarus consumed 13.8 thousand tons of remedies, in 2012 - already 15 thousand tons for about 235 million US dollars. The main share (10.7 thousand tons) accounted for herbicides, fungicides need is 2.0, insecticides - 0.3, seed - 1.1 thousand tons. In comparison with developed countries it is not a big number. But ultimately, it is important not only the amount of used pesticide but rather safety and sustainability of their application.

In accordance with the Law of the Republic of Belarus of 2005 “On Plant Protection” in Belarus are allowed to use only those pesticides that have passed the state test and registration. Today the official Register has about 700 names of pesticides. In Belarus today the most used pesticide groups such as herbicides, insecticides, fungicides, disinfectants, growth regulators, defoliants and desiccants, rodenticides and others. 70% are herbicides. Most pesticides are used in Minsk and Grodno regions - 1.8-2 kg / ha while in Vitebsk one - only 0.9 kg / ha.

Study of exposure of pesticides on vulnerable groups

In November 2014-January 2015 Green Cross Belarus has implemented a small study on pesticides exposure for farmers in Bragin district of Belarus. The work covered 200 correspondent. It was conducted in the framework of the FAO-EC Project GCP/RER/040/EC Improving capacities to eliminate and prevent recurrence of obsolete pesticides as a model for tackling unused hazardous chemicals in the former Soviet Union with the technical support from PAN-UK and the Secretariat of the Rotterdam Convention.

Total adults handling pesticides	MILD	MODERATE	SEVERE	Not reporting signs/symptoms in the last 12 months	Reporting signs and symptoms in the last 12 months
49	6	8	7	28	21
	12%	16%	14%	57%	43%

The information received during a study demonstrates that main impact of pesticides is focused on the workers dealing with pesticides use. We should mention that safety precautions are implemented in a better way in collective farms (kolkhozes) which have agronomists and/or other specialists and arrange preliminary safety instruction of the workers. After that all workers sign in record book of safety of enterprise. Another important group is employee of pesticides producing companies. They also have similar preventive measures.

Private farmers and gardeners are in a much worse situation. As a rule they do not have proper knowledge and rely mainly on spontaneous information, advises of distributors, own logic. There are some cases when farmers know about risk of pesticides so grow agricultural products separately: “clean” one for themselves and “one with pesticides for sale. There are cases when farmers and members of their families don’t follow post-harvest interval and work in the garden with acting pesticides. Anyway private farmers and gardeners have no outside control and monitoring. This information came from communication of specialists of GCBY with private farmers in different regions of the country.

National Workshop entitled ‘Protecting Farmers and Vulnerable Groups from Pesticide Poisoning’ took place on 26 March 2015 at the Centre of Ecology and Health in Smolevichy. It involved 44 participants (representatives of ministries, NGOs, farmers, educators, school directors, teachers, specialists of ecological centres, etc.) The Workshop’s goals were:

- Raising awareness of the risks from pesticides
- Sharing experiences and lessons learned from the studies dedicated to social dimensions of pesticide use
- Strengthening/establishing linkages between various stakeholders involved

Particular attention was paid to the following points:

- Men handle pesticides in households;
- The majority of the farmers buy pesticides in unlicensed stores (63%);
- Only 2% out of 49 respondents have been trained to use personal protective equipment within the last 5 years;
- 57% of 49 respondents handling pesticides did not have signs of pesticide poisoning;
- In all cases, contaminated clothes are washed by an adult woman, only 30% of contaminated clothing are washed by hand, and 31% - with other clothes, which indicates the high underestimate of the risks;
- If containers are re-used, it is mainly done for pesticides and fuel, and the main method of disposal is triple rinsing which once again proves that there isn’t an order of handling containers’ waste;
- Some households have open water sources near treated areas;
- 74% of adult respondents who do not handle pesticides have reported that they had no signs of poisoning within the last 12 months;
- 83% of children reported that they had noticed empty containers of pesticides lying around the farm.

The results showed that there is a reason to mull over. The participants’ basic reaction was a will of learning more information about risks, raising these issues in their regions, as they were sure that their level of awareness was low. Despite a sample of the survey was small, nevertheless, appeared new information and confidence in that there was a need for further research and the implementation of measures in order to reduce risk. Moreover, the representatives of regulators found that people on the ground knew almost nothing about the risks, and there were many unresolved issues on the safety of pesticides and disposal of containers. Some participants asked the questionnaires in order to conduct a survey in their respective regions.

Conclusion

The National Workshop showed that the issue is highly pressing. There are needed further studies and accomplishment of measures related to reducing risks from pesticides. It was also noted that there is a need in trainings for informers, small farmers, personal subsidiary plots, gardeners, as well as a demonstration of successful alternatives.

Implemented survey and workshop indicated a high need in further investigation of situation and arrangement of a wide information campaign for population. In particular, there is a sense to organise regular trainings for all involved parties for awareness campaign, small farmers and agronomists of kolkhozes (of course taking into account specific of each above mentioned group of trainees). To arrange also study tours for them to see successful practices in the country. For example, in to establish at GCBY Centre alternatives technologies demonstration ground for small farmers and gardeners.

The calculation of the Institute of Plant Protection on profit due to use of pesticides (up to 100% profit) gives a reason and stimuli to kolkhozes and farmers for active use of pesticides. We would recommend to actively present the alternatives to pesticides as IPM, their efficiency and benefits as well as risk connected to pesticides. We would like also to recommend to involve international arguments like calculation by UNEP and/or other sources of comparison different system of plant protection. All together means lack of awareness raising among decision makers, administrators and population. There should be nominated a responsible institution which will promote the alternatives. Another idea is to propose economic stimulation of alternatives at the state level in particular for development of a new segment of high quality nutrition products at the national food market (for example by Ministry of Agriculture for small farmers and Ministry of Trade for different sellers networks).

There is lack of involvement of best international practices in regulation of pesticides as well as promotion of their alternatives. For this issue it is important to arrange a wide awareness raising campaign on issues related to pesticide management and risk reduction according to Code of Conduct on Pesticide Management. In fact wide population doesn't know neither understands well risks connected to use of pesticides nor worries about safety/quality of consumed food.

From the above extra recommendation: to improve cooperation with other countries, FAO and European Union, to build bridges in regulation between them and CIS / Custom Union (Belarus is a member of it) to involve best international practices (in particular in promotion of alternatives to pesticides).

In Belarus - licensing is not required in relation to pesticides management. Thus in general the whole chain of pesticides management is not controlled while only some its links are controlled. Therefore we observe the need in holistic approach with proper control and licensing for import, transport, storage, sale etc. of pesticides.

There are no 24h toxicological centres. Poisoning of population due to pesticides needs good control. Establishment of proper centres within medical universities could be in long perspective.

Available statistical health forms don't separate poisoning by pesticides. Thus real situation with such poisoning is unclear as well as available data have lack of significance. At the same time because of the majority of agricultural product is produced by kolkhozes (which in general follow safety rules and proper instructions) general situation seems not critical. Thus, main risk of poisoning is coming for small farmers and private gardeners. They and their families should be in focus of awareness raising campaign.

There is also even a more global problem – quality of food and its advertisement. As a rule advertisement presents idealistic condition of production and quality of products. We observe very high competition between food producers on Belarusian market. The main fight is going via low costs. As a result, food market is overflowed by low quality and cost products on the base of chemical taste ingredients and unnatural surrogates. According to Belarusian law producers indicate (as a rule) main taste and chemical supplies on packages (mainly by small size fonts). At the same time, wide population has very low consumer culture, doesn't understand well what means what and ignores them. Thus, we need to improve proper consumer and safety culture – to arrange a wide public campaign against food illiteracy.

Implemented survey and workshop indicated high need in further investigation of situation and arrangement of a wide information campaign for population. In particular, there is a sense to organise regular trainings for all involved parties for awareness campaign, small farmers and agronomists of kolkhozes (of course taking into account specific of each above mentioned group of trainees). To arrange also study tours for them to see successful practices in the country. Now GCBY is developing a plan to establish alternatives technologies demonstration ground for small farmers and gardeners at GCBY Center.

There is high need in the setup of a recycling system for pesticide containers. The most pesticides are liquid formulations. Thus practices like triple rinsing significantly reduce the amount of remaining pesticide in the emptied cans. Leaflets should be made available to retailers informing users how to apply triple rinsing (use rinsing water for the spray solution) thus reducing risks to the environment. The establishment of such a recycling system should therefore be considered as a high priority.

TREND OF HIGHLY HAZARDOUS PESTICIDES REGISTERED AND DISTRIBUTED IN SUBSAHARAN AFRICA

SUBMITTED PAPER

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Abstract

Registration of pesticides begun in Cameroon in 1996. Less than 5% of pesticides used in 2004 were registered and more than 80% of producers were not aware of this legal process. In 2014, 85% of pesticides used are registered. Among these licit chemicals, some are hazardous to human and environment, 40% are registered for use in bananas production (28% for nematodes control alone and 10% for control of both insects and nematodes). Moreover, 20% of highly hazardous pesticides (HHP) registered are for the control of rondents. In Subsaharan Africa, registered HHP are rondenticides, insecticides and nematocides, frequently used in banana production and for protection of stored products. Licit POP (heptachlore, chlorobenzène) and HHP (alluminium phosphide, terbufos, abamectine, ethropophos, …) are frequently used to protect stored grains. In cotton production, lindane and HCH are used.

Key Words

Cameroon, chemical pest control, highly hazardous pesticides

Materials and methods

To access the diversity of pesticides used by smallholders to protect crops from insect pest attack, since 2004, yearly sampling of names of pesticides used and collection of pesticides containers were carried out in the 3 northern regions of Cameroon. Moreover, the list of authorized pesticides was established by consulting two official releases. The first is from the Cameroon National Committee of Regulation and Quality control of inputs and agricultural products which is in charge of the registration of pesticides in Cameroon[1]. These products are also used in neighboring countries in Central Africa where no registration authority is functioning. The second list is from the Sahelian Committee of Pesticides who is in charge of the registration of all pesticides in use in the West Africa countries[2]. These lists are updated twice a year. The cited pesticides are classified according to their hazards following the Guidelines to classification[3].

1. Typology of the pesticides in the hands of smallholders for crop protection

Pesticides registered for central or for West Africa include 10 categories of products:

- avicides,
- fungicides,
- herbicides,
- insecticides,
- insecticides-acaricides,
- insecticides-nematicides,
- insecticides-fungicides,
- nematocides,
- molluscides,
- rodenticides.

Results and discussion

In Central Africa, 4 other categories are added: adjuvants, growth regulators, public hygiene products and resistant activators. A last category is that of pesticides receiving temporary authorization to be sold.

Since its first implementation of registration of pesticides in 1996, Cameroon government is improving the quality and the availability of pesticides offered to producers. Less than 5% of the farmers in 2004 used registered pesticides, 10 year after, more than 80% of the pesticides on the list are registered. In the same way the amount of users ignoring registered pesticides is reducing moving from 50% in 2004to less than 10% 10 years after.

The compilation of the pesticides names collected from users' citation or read on containers collected in their environment allow to come to a list of pesticides in use. This list was made and from year to year and regularly updated. In comparison with the list of the pesticides homologated, 3 situations were currently observed:

- That of pesticides used which are registered;
- That of pesticides used which are not registered
- That of pesticides registered which are not used or not known.

The illustration of the evolution of this situation during the last 10 years is compiled in the figure 1. It raises from there the positive change in the better use of pesticides quality in the crop protection in Sub-Saharan Africa.

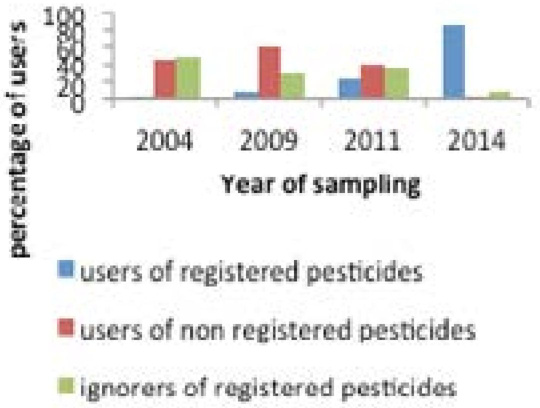

Figure I. Amelioration of the use of licit pesticides in 2004, 2009, 2011 and 2014.

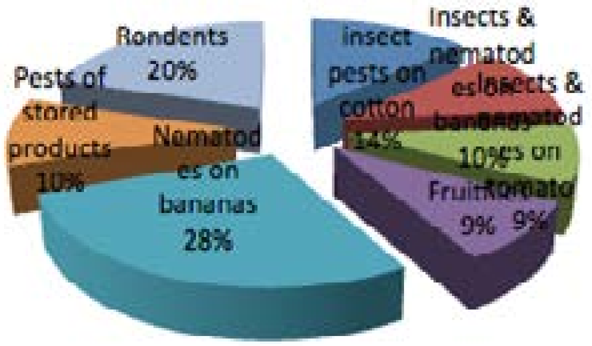

Figure 2. Pests for which hazardous and highly hazardous pesticides are registered

2. Occurrence and uses of highly hazardous pesticides

The classification active ingredients according to the WHO recommended classification of pesticides by hazard was used to categorize pesticides on the list of chemical made from year to year.

A total of 10 highly hazardous substances are currently used in Central and West Africa in the formulation of fungicides, herbicides, insecticides, insecticides-acaricides, insecticides-nematocides, insecticides-fungicides, nematocides, molluscides, rodenticides. These uses are in relationship with some phytosanitary problem occurring in targeted crops (Figure 2).

Among these licit chemicals, some are hazardous to human and environment, 40% are registered for use in bananas production (28% for nematodes control alone and 10% for control of both insects and nematodes). Moreover, 20% of highly hazardous pesticides (HHP) registered are for the control of rondents. In Subsaharan Africa, registered HHP are rondenticides, insecticides and nematocides, frequently used in banana production and for protection of stored products.

Table 1. List of highly hazardous (Ia) and hazardous (Ib) active ingredients of pesticides registered in Cameroon (1) and by the Sahelian Pesticide Committee (2).

N°	***Active ingredients** (1; 2)*	*WHO class*	*Targeted pests / Ecosystems*
1	*abamectine (1; 2)*	*Ib*	*Insects & Mites / Cotton, Fruits*
2	*bromadilone (2)*	*Ia*	*Rondents / Ware Houses*
3	*brodifacoun (1; 2)*	*Ia*	*Rondents / Ware Houses*
4	*cadusafos (2)*	*Ib*	*Insects & Nematodes/ Bananas, Tomato*
5	*ethropophos (2)*	*Ia*	*Insects & Nematodes/ Bananas, Tomato*
6	*flocoumafene (2)*	*Ia*	*Rondents / Ware Houses*
7	*oxamyl (1; 2)*	*Ib*	*Insects & Nematode / Bananas*
8	*phenamiphos (1)*	*Ib*	*Nematodes/ Bananas*
9	*aluminium phosphide (1; 2)*	*Ia*	*Insects / Stored Grains*
10	*terbufos (2)*	*Ia*	*Insects & Nematodes/ Bananas, Tomato*
11	*thiazophos (2)*	*Ib*	*Caterpilar/ Cotton*

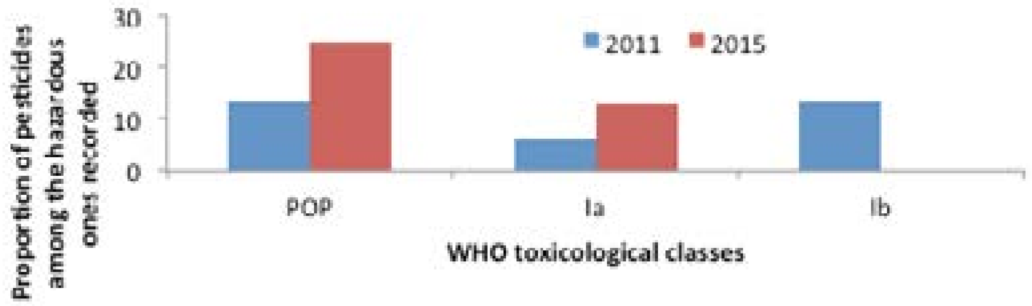

Figure 3. Numerical importance of dangerous registered pesticides by WHO toxicological classes (Ib: hazardous and Ia: highly hazardous and POP) during the years 2011 and 2015

Licit POP (heptachlore, chlorobenzène) and HHP (alluminium phosphide, terbufos, abamectine, ethropophos, …) are frequently used to protect stored grains. In cotton production, lindane and HCH are used.

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UNINTENTIONAL/ INTENTIONAL POPs

Unintentional/Intentional POPs - challenges and management

ASSESSMENT OF PCDD/Fs FORMATION IN THE ADVANCED OXIDATION TREATMENT OF MODEL SOLUTIONS OF 2-CHLOROPHENOL

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Abstract

The concern about water pollution has increased during the last few years because of the increasing domestic and industrial activities together with growing population. Amongst the possible compounds found in wastewater, chlorinated organic compounds include some of the most toxic and largest groups of hazardous chemicals. Due to their resistance to chemical and biological degradation, more effective technologies are needed. Advanced oxidation processes (AOPs) postulate as viable technologies to treat recalcitrant wastewaters by means of generating reactive oxygen species (ROS). Hydroxyl radical ($^{\bullet}OH$) is the most powerful ROS, which is not selective and reacts rapidly with organic/inorganic pollutants. Owing to the wide use of 2-chlorophenol (2-CP), it has been selected as a model chlorinated organic compound. Furthermore, chlorophenols are known to be precursors of the highly toxic polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans (PCDD/Fs). Fenton and electrochemical oxidation have been selected in this work to treat 2-CP solutions. The conventional physicochemical parameters total organic carbon (TOC) and chemical oxygen demand (COD) have been determined in order to assess the mineralization degree. Moreover, the analysis of some of the byproducts generated, including PCDD/Fs, has been carried out. The influence of several operating conditions and treatment time on COD, TOC and PCDD/Fs generation has been assessed. The selection of adequate operating conditions namely, the use of appropriate amount of H_2O_2 in Fenton treatment and avoiding the use of supporting electrolytes containing chlorine species in electrochemical oxidation is essential to achieve high degradation efficacy hindering the formation of toxic byproduct such as PCDD/Fs. Therefore, this works aims at monitoring the major parameters TOC, COD and minor byproducts such as PCDD/Fs during the advanced oxidation of 2-chlorophenol aqueous solutions providing knowledge on the influence of the operation conditions.

Key Words

Advanced oxidation processes (AOPs); polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs); Fenton oxidation; electrochemical oxidation; 2-chlorophenol; toxic equivalents (TEQ).

Materials and methods

The study of the effectiveness of two AOPs (electrochemical and Fenton oxidation) to the treatment of a model solution (2-chlorophenol) has been addressed.

Fenton oxidation experiments

Fenton oxidation experiments were performed in batch mode in glass reactors magnetically stirred (700 rpm) with a heating magnetic stirrer with temperature control. Batch experiments were carried out adjusting the initial pH of the solutions to be treated to 3.0. $FeSO_4{\cdot}7H_2O$ was added to the solution to yield the desired Fe^{2+} dose. The Fenton reaction was initiated by adding the corresponding amount H_2O_2 to the solution. Samples were withdrawn from the reaction medium when the oxidation time was reached and the excess of H_2O_2 was removed by $NaHSO_3$, after titration with sodium thiosulfate $Na_2S_2O_3$.

Electrochemical oxidation experiments

Electro-oxidation experiments were performed in batch mode in a laboratory DiaCell system (two circular electrodes: boron doped diamond (BDD) on silicon anode and stainless steel cathode, with surface area of 0.007 m^2 each and an electrode gap of 5 mm). A Feed tank magnetically stirred (1 L) and a recirculation pump that provides an operational flowrate of 9 $L\ min^{-1}$ were employed. Experiments were carried out working at 20 ºC with a current density of 900 $A\ m^{-2}$ [1,2]. The influence of the supporting electrolyte (56.3 mM NaCl or 21.1 mM Na_2SO_4, 7.5 $mS\ cm^{-1}$) was studied along the treatment of 2-CP (15.56 mM) solution.

2-CP, TOC, COD analysis

Total organic carbon (TOC) analysis was performed using a TOC-V CPH Shimadzu and chemical oxygen demand (COD) was determined according to the Standards Methods 5220C. 2-CP was quantified by means of HPLC (Waters 2690) equipped with a Gemini C-18 column (Supelco) and a PDA detector at λ= 211 nm. The mobile phase consisted of 4 mM aqueous sulfuric acid solution.

Qualitative screening of organics in the advanced oxidation of 2-CP

Qualitative screening for intermediate organic compounds formed during the advanced oxidation treatment of 2-CP solution was performed by gas chromatography-mass spectrometry (GC-MS). After an extraction and concentration steps, the final sample was analyzed using a GC-MS Shimadzu QP2010 equipped with an auto-sampler[3]. The analytes were separated using a HP5 MS column (L = 30m; Øi = 0.25 mm) with a film thickness of 0.1 mm.

PCDD/Fs analysis

The concentrations of PCDD/Fs were determined according to Standard Method U.S.EPA 1613 (1994) by isotope dilution method and high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS, Trace GC UltraTM, ThermoFisher Scientific). This method requires extraction, concentration and purification steps prior to the analysis. All sample preparation steps together with a detailed procedure of the quantitative analyses of PCDD/Fs has been previously described[2].

Results and discussion

CPs are characterized by high toxicity, bio-cummulative behavior and recalcitrant character, among others[4]. Furthermore, CPs can undergo reactions leading to the formation of even more hazardous products such as PCDD/Fs[5,6]. 2-CP has been selected as a model CP due to its wide application as intermediate in the manufacture of fungicides, herbicides, wood preservatives, etc. and also they can be formed as a result of the chlorination of phenols during water disinfection[4,7]. The initial 2-CP concentration was around 15.56 mM (2 g L^{-1}) with corresponding COD and TOC values of 101 mM (3236 mg L^{-1}) and 93 mM (1120 mg L^{-1}), respectively.

Fenton oxidation

Different operating conditions were selected in order to assess the effect of H_2O_2 dose, temperature and chloride ions (Table 1).The influence of iron concentration was also studied in the range 0.09-0.36 mM.

Fenton Experiment	$[H_2O_2]$ (mM)	T (°C)	$[Cl^-]$ (mM)	$[Fe^{2+}]$ (mM)
FE1	40.44	20	-	0.18
FE2	202.22	20	-	7.22
FE3	40.44	70	-	0.18
FE4	40.44	20	56.34	0.18

Table 1. Operating conditions applied to the Fenton treatment of 2-CP.

Fenton oxidation has been demonstrated to be an effective technology for removing 2-CP under the experimental conditions selected (Fig. 1), allowing almost complete removal during the first 5 min, especially using stoichiometric H_2O_2 doses (FE2, Eq. 1) due to the higher •OH availability (Eq. 2).

$$C_6H_5OCl + 13H_2O_2 \rightarrow 6CO_2 + 15H_2O + HCl \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (2)$$

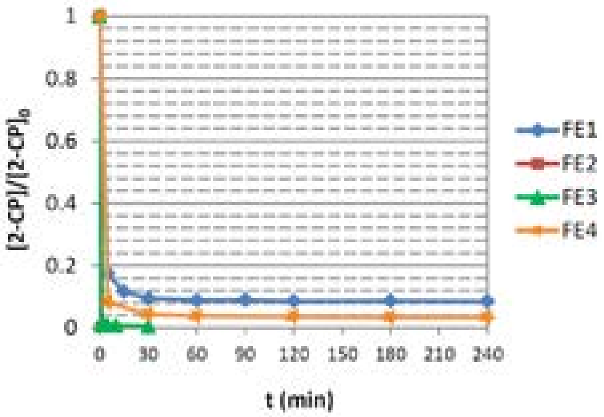

Fig. 1. Evolution of dimensionless 2-CP concentration during Fenton oxidation of 2-CP model solutions. For the sake of clarity error bars were not represented (error ≤± 10%).

On the other hand, the reduction of COD and TOC was less noticeable, mainly working at substoichiometric doses as it could be expected (Fig. 2). Nevertheless, Fenton oxidation is commonly proposed as pretreatment technology in which non-biodegradable compounds are further oxidized into short chain compounds which are susceptible of being biodegraded by conventional treatment methods[8]. Together with H_2O_2 dose, temperature showed a remarkable positive effect on the reduction of COD and TOC, whereas the presence of chloride had a little positive effect.

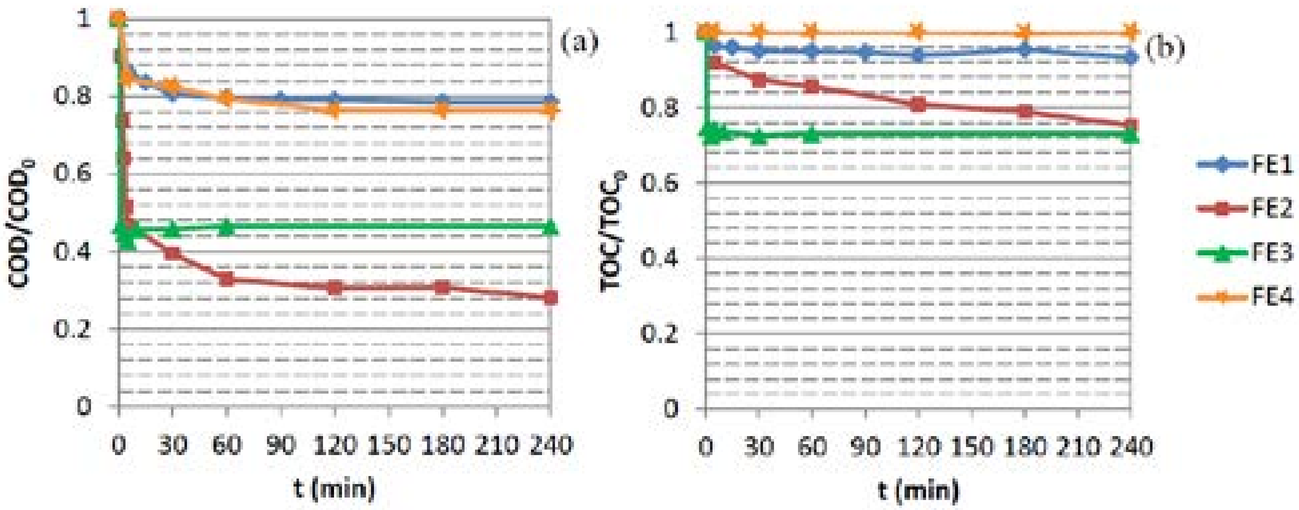

Fig. 2. Evolution of dimensionless (a) COD, and (b) TOC concentrations during Fenton oxidation of 2-CP model solution. For the sake of clarity error bars were not represented (error ≤± 10%).

Since CPs are direct precursors of PCDD/Fs, their potential formation was assessed after 4 h of treatment. The concentrations of PCDD/Fs increased regarding the untreated sample for both total and 2,3,7,8-congeners working with substoichiometric H_2O_2 doses (FE1, FE3, FE4, Fig. 3), while working with stoichiometric doses led to low PCDD/Fs generation (FE2, Fig. 3). The addition of chloride to the reaction medium (FE4) displayed a positive effect on the formation of PCDD/Fs working under substoichiometric conditions, where total PCDD/Fs and total 2,3,7,8-congeners concentrations were 20-40 and 3-4 times higher regarding to the untreated sample, respectively. Therefore, the employment of low doses of H_2O_2 does not allow the progress of the reaction to shorter chain products. In any case, toxic equivalence (TEQ) values kept under 1.96 pg I-TEQ L^{-1}, which is 15 times lower than that established by the U.S. EPA based on potential health effects from ingestion of water (30 pg TEQ L^{-1}). The obtained results evidenced the role and relevance of the chloride concentration in the formation of highly substituted chlorinated byproducts, PCDD/Fs, in the oxidation medium.

Electrochemical oxidation

The electro-oxidation process requires a conductive medium to decrease the resistance between cathode and anode. Because of this, two different supporting electrolytes have been selected, NaCl and Na_2SO_4. As it is shown in Fig. 4, the presence of chloride had a positive effect on the decrease of 2-CP, where the time required for the complete removal of 2-CP is 1 h for NaCl and around 2 h for Na_2SO_4.

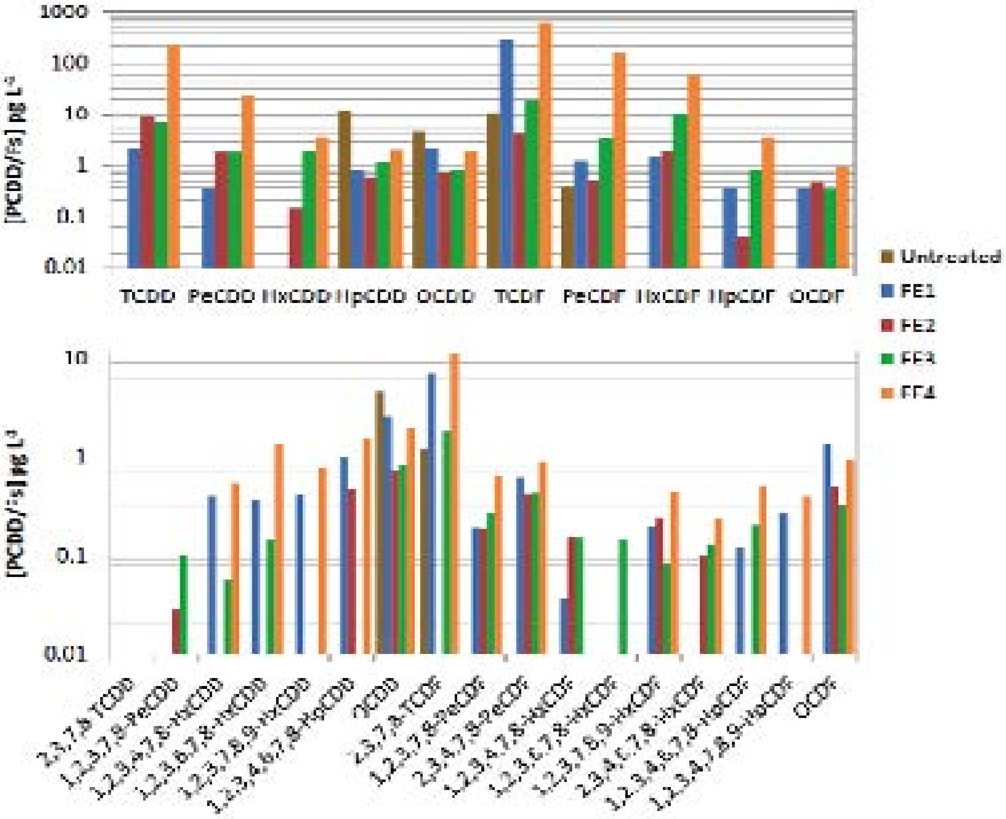

Fig. 3. PCDD/Fs concentration after 4 h Fenton oxidation of 2-CP: (a) homologue profile of total PCDD/Fs; (b) congener profile of 2,3,7,8-PCDD/Fs. For the sake of clarity error bars were not represented.

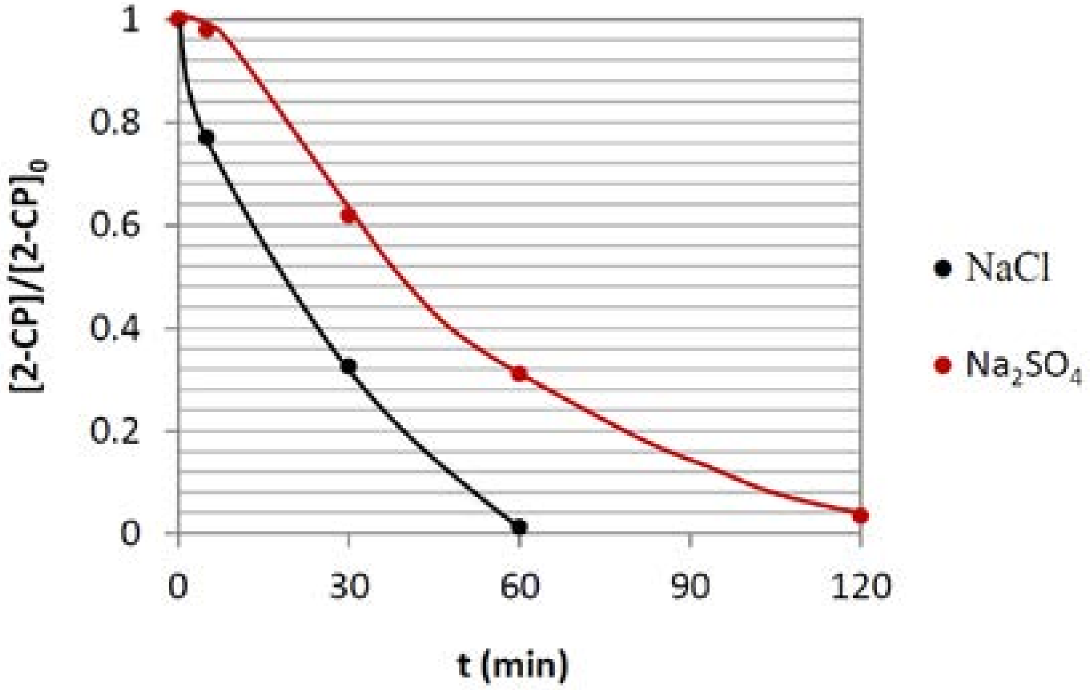

Fig. 4. Evolution of dimensionless 2-CP concentration during electrochemical oxidation of 2-CP model solution. For the sake of clarity error bars were not represented (error ≤± 10%).

Nevertheless, there is no clear influence of the electrolyte type on the decrease of either COD or TOC, which are almost removed after 2 h of treatment (Fig 5). This fact is explained by the formation of free chlorine active species when •OH reacts with chloride[9]. Free chlorine reacts with 2-CP leading to higher chlorinated compounds such as dichlorophenol and trichlorophenol[10].

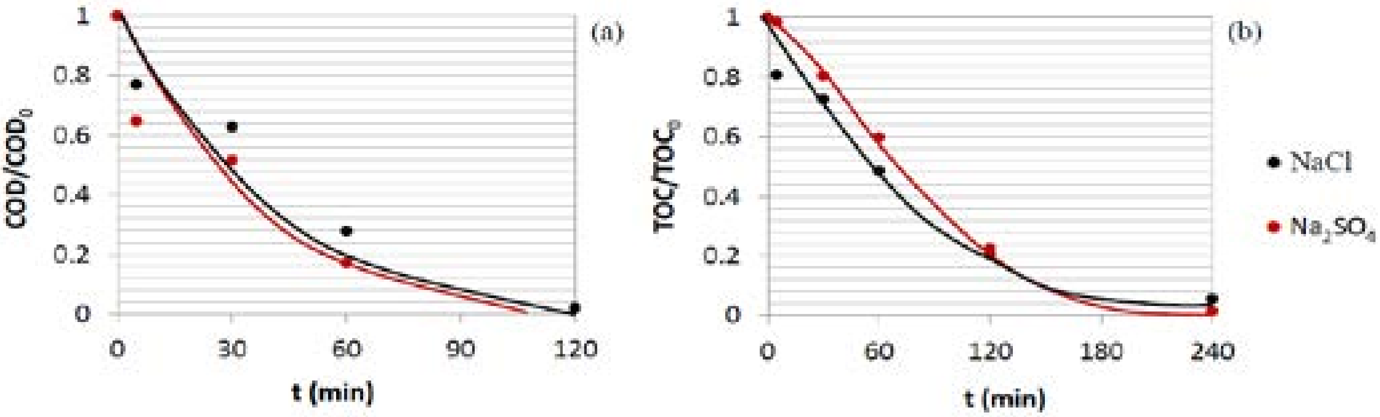

Fig. 5. Evolution of dimensionless (a) COD, and (b) TOC concentrations during electrochemical oxidation of 2-CP model solution. For the sake of clarity error bars were not represented (error ≤± 10%).

Regarding PCDD/Fs (Fig. 6), significant formation of PCDD/Fs could be observed after 4 h of treatment with NaCl as electrolyte. The total PCDD/Fs concentration in the oxidized samples was $2.68 \cdot 10^4$ times higher than in the untreated solution. On the other hand, when Na$_2$SO$_4$ was used as electrolyte, the concentration of PCDD/Fs increased by 200 times relative to the untreated sample, but such increase was 134 times lower than in the presence of NaCl. With respect to the most toxic congeners, when Na$_2$SO$_4$ was used as electrolyte, a negligible formation of 2,3,7,8-PCDD/Fs was observed whereas when NaCl was used the total 2,3,7,8-PCDD/Fs concentration increased by 828 times in comparison with the untreated solution, which only represented the 1.6% of the total PCDD/Fs concentration, showing the preferential formation of non 2,3,7,8-PCDD/Fs. In terms of toxicity, TEQ reached 220 pg I-TEQ L^{-1} after 4 h of treatment in the presence of NaCl.

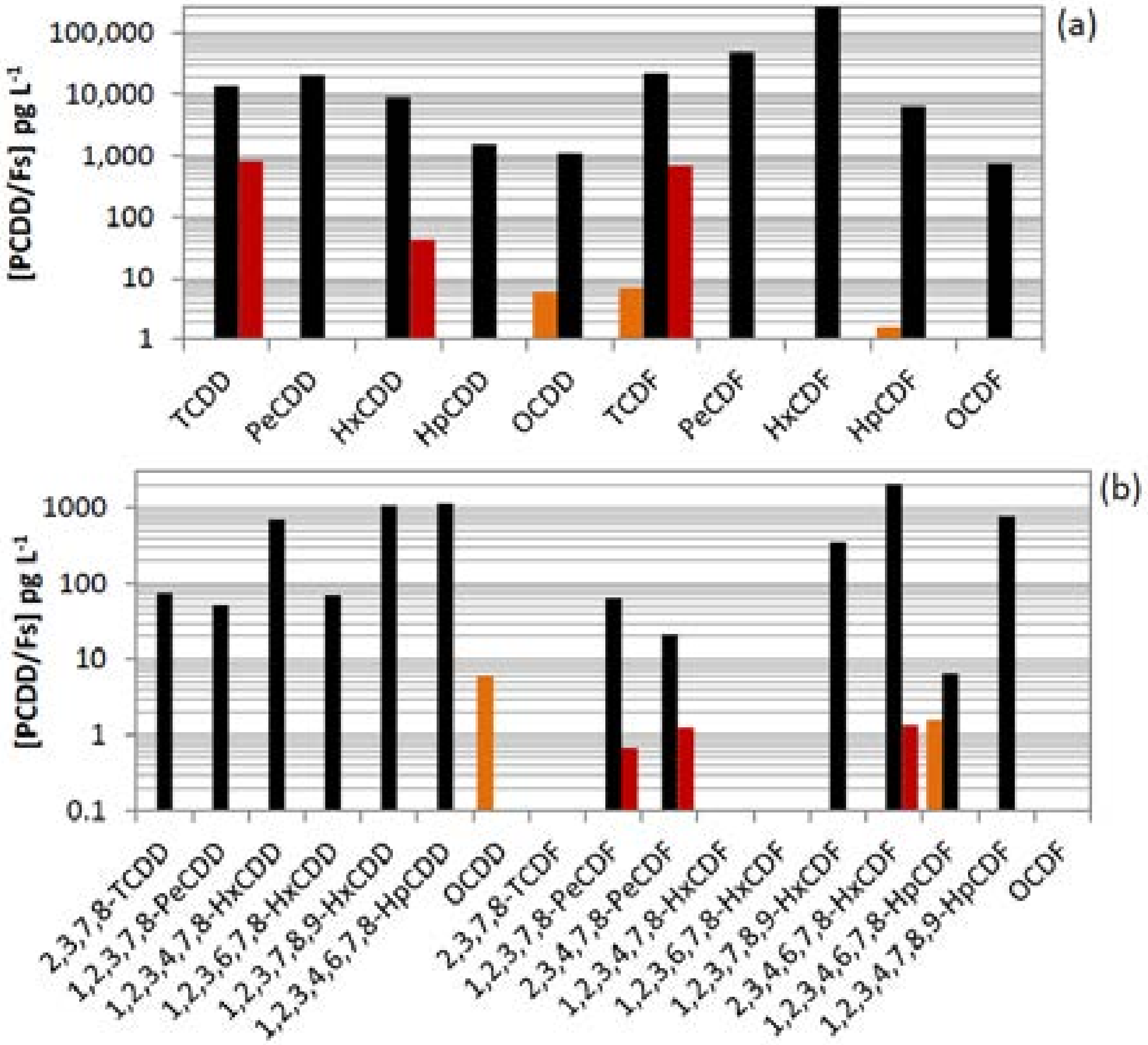

Fig. 6. PCDD/Fs concentration in the initial sample (🟧) and after 4 h of electro-oxidation employing NaCl (■) and Na_2SO_4 (🟥) as supporting electrolytes: (a) homologue profile of total PCDD/Fs; (b) congener profile of 2,3,7,8-PCDD/Fs. For the sake of clarity error bars were not represented.

Mechanisms of formation of PCDD/Fs

The cleavage of the O-H bond from 2-CP through H abstraction by •OH (Fig. 7), results in the formation of chlorophenoxy radicals (CPRs), substituted phenyl radicals and pristine/chlorinated phenoxyl diradicals which contribute to the formation of PCDD/Fs[11,12]. The oxidative coupling of these radicals and 2-CP leads to bi-aromatic intermediates whose cyclization produce PCDD/Fs. Free chlorine generated in the reaction medium may participate in the chlorination of chlorophenol and its oxidized intermediates. Therefore, highly chlorinated PCDD/Fs must have been generated not only by the oxidative coupling of CPs and their oxidation intermediates, but also by prevalent chlorination reactions[13]. The qualitative analyses carried out by GC-MS confirmed also the formation of some condensation products that may act as PCDD/Fs precursors such as 2,4'-dichloro-5-hydroxydiphenyl ether and 4,4'-dichloro-1,1'-biphenyl-3,3'-diol.

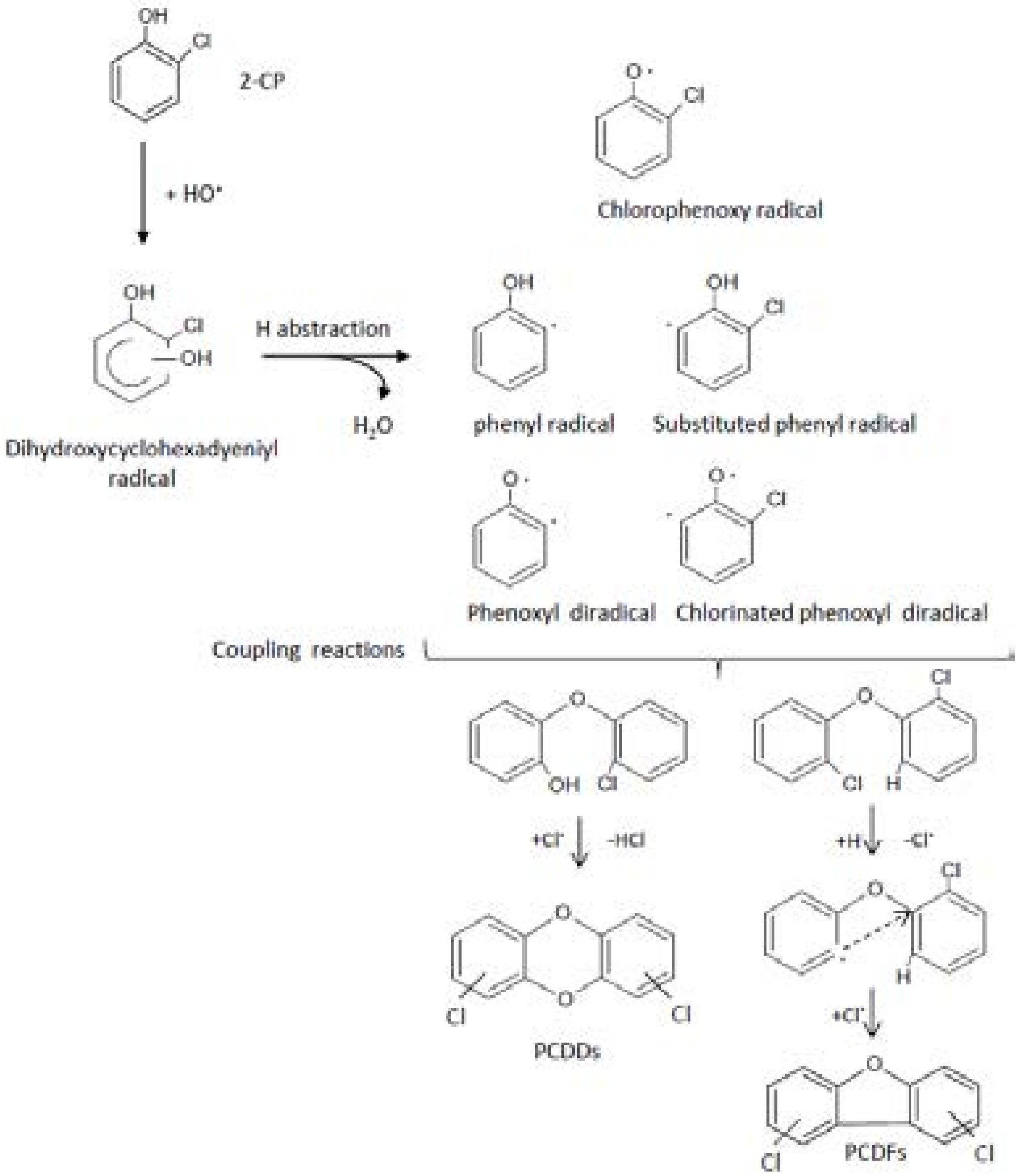

Fig. 7. Scheme for the formation of PCDD/Fs on AOPs of 2-CP

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PCDD/F, PBDD/F AND PCB CONTAMINATION IN EGGS AS SENSITIVE INDICATOR FOR SOIL CONTAMINATION AROUND POLLUTION SOURCES

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Abstract

Contamination of eggs with polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), polybrominated PBDD/F or polychlorinated biphenyls (PCBs) have been found around larger emission sources in different countries. Contaminations were found around (former) PCB-using industries, hazardous landfill, incinerators, metal industries, and e-waste treatment sites. A preliminary screening of eggs around the production site and landfill sites of the Sabiñanigo HCH production indicated no larger PCDD/F or PCB contamination.

The DRCALUX bio-assay has been used as screening tool for dioxin-like toxicity in eggs at potentially contaminated sites. If bio-assay levels were at/above EU regulatory levels then instrumental analysis were used to determine the responsible dioxin/dioxin-like contaminants.

The low PCDD/F levels in soil at which eggs from free range chicken can be contaminated above regulatory limits demonstrate that regulatory soil limit values need to be re-assessed.

Key words: Dioxin; PCDD/PCDF; PBDD/PBDF; dl-PCB; contaminated sites; monitoring; egg; DRCALUX; bioassay

Introduction

There have been an increasing number of reports on contamination of eggs with PCDD/Fs and particularly dl-PCBs in last decade[1-7]. Eggs have been found to be sensitive indicators of PCDD/F and PCB contamination in soils and are an important exposure pathway from soil pollution to humans and eggs from contaminated areas can readily lead to exposures which exceed thresholds for the protection of human health [1-4]. Chickens and eggs might therefore be ideal "active samplers" and indicator species for contaminated soils but there are, as yet, few systematic studies linking pollution sources, related soil exposures and concentrations of contaminants in eggs.

In this study, eggs were sampled at sites suspected of being impacted by PCDD/Fs or PCBs in Germany, Spain and Thailand and the relationship between the sources and contamination levels has been examined.

Materials and methods

Eggs were sampled at potential hot spots in Germany, Spain and Thailand. The first site in Germany was close to a condenser factory and the second site close to a hazardous landfill site. For both sites two individual chicken flocks were sampled. The eggs in Spain were sampled in the vicinity of INQUINOSA lindane factory and Sardas and Bailin HCH landfills.

The egg samples were pooled in each case. For the sites in Germany 10 to 20 eggs were pooled and for each flock in Thailand and Spain 2 or 4 eggs were pooled for analysis.

Bioassay.

All samples were analysed at Bio Detection System for dioxin-like activity according to the standard procedures of the DR CALUX® method from BDS[9]. The procedure for the BDS DR CALUX bioassay has previously been described in detail[8] but, briefly, H4IIE cells stably transfected with an AhR-controlled luciferase reporter gene construct, were cultured in α-MEM culture medium supplemented with 10% (v/v) FCS under standard conditions (37ºC, 5% CO_2, 100% humidity). Cells were exposed in triplicate on 96-well micro-titerplates containing the standard 2,3,7,8-TCDD calibration range, a DMSO blank Following a 24 hour incubation period, cells were lysed. A luciferine containing solution (Glow Mix) was added and the luminescence was measured using a luminometer (Berthold Centro XS3).

Instrumental analysis.

All samples were analysed by gas chromatography high resolution mass spectrometry (HRGC/HRMS) in ISO 17025 accredited laboratories with a resolution >10,000 using ^{13}C isotope labelled standards. PCDD/F and dl-PCB analysis followed the European Union's methods for the control of levels of PCDD/Fs and dl-PCBs for levels in certain foodstuffs (Commission Regulation (EC) No 252/2012)[9]. The sample from Thailand was also analysed for PBDD/F using ^{13}C isotope labelled standards.

Results and discussion

Levels of PCB in chicken eggs around a former capacitor factory (Germany)

Hens eggs were sampled from two private chicken farmers (A and B) close to a capacitor factory in Teningen, a small town in South-West Germany. The factory produced capacitors from 1932 on including PCB-containing capacitors for some time. The ground-water below the former production site and the associated dumping area is contaminated with PCBs and a PCB plume contaminates the ground water of the nearby town[10].

Bioassay screening for dioxin-like toxicity was conducted for eggs from the two flocks/sites with DR CALUX. The BEQs from the bio-assays were 18 pg BEQ/g fat at both sites. PCBs were the main contributor to the BEQ for both samples and the levels considerably higher than the regulatory limit of 5 pg TEQ/kg fat for the sum of PCDD/F and dl-PCB. For confirmation the eggs were also analysed by instrumental analysis (HRGC/HRMS). The same egg samples from chicken holder A were highly contaminated (36.4 pg TEQ/kg fat) mainly from dl-PCB (25 pg TEQ/g fat). The levels in eggs from chicken farmer B were nearly as highly contaminated with 31.9 pg TEQ/kg fat. Again this was mainly due to dl-PCB (25.5 pg TEQ/g fat).

The competent authority tested the soils in the area for PCDD/F and PCB and found 2.3 ng PCB-TEQ (0-5 cm) and 3.3 ng/kg (5-10 cm) at farm A and 4.4 ng/kg PCB-TEQ (0-5 cm) and 3.8 ng/kg (5-10 cm) at farm B - significantly above German background levels of approx. 0.5 ng PCB-TEQ/kg. The upper levels of the soil contamination would be sufficient to explain the PCB-contamination in the chicken eggs via exposure from soil ingestion at high soil intakes.

Levels of PCB in soil and chicken eggs around a hazardous landfill (Germany)

The BEQ levels in chicken eggs from two farms (C and D) close to the Eyller Berg hazardous waste landfill close to the city of Kamp-Lintfort in Germany were found to be 7.1 pg BEQ/g and 6.4 pg BEQ/g fat in a screening with DR CALUX. Both samples exceeded the EU limit for egg consumption of 5 pg TEQ/g fat. The instrumental analysis (HRGC/HRMS) in these cases samples confirmed the contamination with levels of 10.4 and 8.7 pg TEQ/g fat (sum of PCDD/F and dl-PCB) in the two egg samples respectively stemming mainly from dl-PCBs.

The competent authority of the federal state had already conducted a soil screening for PCDD/F around the hazardous landfill in 2012 and found dl-PCBs between 3.1 und 6.6 ng WHO-PCB-TEQ/kg dm[11] which was therefore about 6 to 10 times above background soil levels in German pasture land. These PCB soil levels were sufficiently elevated to explain the contamination levels in the eggs (see below).

Levels of dioxin toxicity around hot spots of a former HCH-production site and related landfills (Spain)

Chicken eggs were sampled from six flocks in the vicinity of the former HCH production site in Sabiñanigo and related landfills. The screening with DRCALUX assay showed that in none of the analysed flocks high PCDD/F or dl-PCB levels were present. Only in the egg sample around the Sardas landfill (1 Km from the landfill, 1.4 Km from the INQUINOSA factory) the Bio-TEQ levels were at the regulatory limit for PCDD/F (2.5 pg BEQ/g fat) with low levels of dl-PCB (0.6 pg TEQ/g fat). Overall the preliminary study indicates that there seems no major PCDD/F or dl-PCB contamination around the sites but that further assessment is needed around the Sardas landfill. The results are in agreement with a preliminary study of PCDD/F in wastes and soils were PCDD/F levels of 20 ng TEQ/kg were detected in soils and 500 ng TEQ/l were detected in leachates near the landfill, which would be problematic for accumulation of PCDD/F in chicken eggs (see below).

HCH determination by GC-MS made on some of these samples in the Bailin landfill laboratory yield values below the detection limits (<0.1 µg/g for each isomer of HCH).

Levels of dl-PCBs and chlorinated and brominated dioxins/furans in eggs at a metal recycling site of informal sector (Thailand)

Egg samples in Thailand were taken at a site where metals containing waste including e-waste were recovered by simple approaches including open burning. Such recycling frequently take place in developing countries and in countries of economies in transition.

The bio-TEQ in eggs from the site showed extreme high levels of 100 pg BEQ/g fat with 83 pg TEQ/g in the dioxin-fraction and 17 pg TEQ/g in the PCB-fraction. The instrumental analysis for PCDD/F showed 55.6 pg TEQ/g fat and for PBDD/F 22.9 pg TEQ/g fat. This demonstrate that also PBDD/F can be transferred to chicken and into eggs and accumulate.

PBDD/F are formed from the brominated flame retardants present in e-waste plastic[13]. Such pollution can be expected at sites with e-waste plastic or cable burning and likely result in contamination of free range animals at these sites. It has recently been established in a UK food survey that PBDD/F can also contribute significantly to total dioxin exposure for the UK population[14]. This is possibly linked to the UK having set exacting flammability standards for furniture and thus having been a major user of brominated flame retardants including PBDEs.

Need for further assessment and management - currently assessed sites and potential contamination around emission sources

The chicken flocks investigated need further assessment. E.g. the PCDD/F, PCB and PBDD/F levels in soils at the site in Thailand have not yet been measured as well as other sites of the study of IPEN.

While the high levels of PCDD/F and PBDD/F in eggs in Thailand indicates high contamination levels at the site, the carry-over of PBDD/F compared to PCDD/F or PCBs has not yet been assessed and need detailed carry-over studies. Since a large number of e-waste recycling sites exists with increasing recycling volumes and contamination, a detailed assessment of these sites and exposure of the people living at and around these sites are needed including chickens and cattle raised at and around these sites.

The case study around the German factory demonstrate that soils around PCB using industries are likely to be polluted with PCBs at levels where eggs contamination might exceed regulatory limits and is thus of concern for human health impacts. The egg contamination around the hazardous waste landfill site indicates that PCB and PCDD/F levels in soil around such hazardous landfills might be impacted by these contaminants at levels of concern for human exposure via chicken/egg pathways.

For both sites in Germany, however, further assessment of the scale of the pollution is needed. For the former production site a key question is the extent of the pollution of the soils and the distance over which soils have been impacted by either atmospheric PCB deposition over the decades of production and/or also by migration of PCBs in the ground water. It therefore needs to be established at what distance from the site the soil is polluted to the extent that chickens (and other livestock) can not be safely kept - or can only be kept with particular management measures including, for example, special feeding regimes, restrictions on movement or substitution of the upper soil layer. Another study showed high level of PCBs (259 pg PCB-TEQ/g)[15] in an eel from a creek receiving drainage water from the former German capacitor factory. Fish and eels from the creek are consumed by members of a local fishing club which is worrying when it is considered that a single (200 g) portion of eel would exceed the Tolerable Daily Intake (TDI) for a whole year in a 70 kg adult. This case also demonstrates that in spite of contamination of the site being known for 35 years - and whilst Germany has had adequate PCDD/F and PCB monitoring capacity for more than 30 years - there has still been no assessment of potential human exposure through the multiple pathways from this high risk PCB site.

It became clear that low levels of PCDD/F and dl-PCBs contamination in soils can result in chicken eggs being contaminated above EU regulatory limits and above levels relevant to TDI and health. This means that chickens around present and former PCDD/F and PCB emission sources are likely to be the most sensitive exposure pathways for contamination of humans and exposure assessments are urgently needed for many of these sites. A recent assessment of a former factory in Slovakia has shown that humans seems affected at distances of up to approx. 50 km from a PCB production facility[16]. Therefore the distances of concern could be very large depending upon the source strength and the local dispersion. A recent German study showed that more than 50% of smaller chicken flocks raised in an industrialised areas in South Germany had PCDD/F and PCB levels above EU limits while most of the flocks from rural areas were significantly below regulatory limits[2] with only two exemptions both of which were likely a result of high PCB levels from point sources at the farms[2]. Another study in the Netherlands similarly warns that PCB contamination from historic PCB use in open applications such as paints and sealants can be responsible for exceedance of regulatory limits in eggs and potential on farm contamination sources should be carefully assessed[6]. Therefore when assessing contamination sources for a flock, potential local sources on the farm should be considered together with larger emission sources in the vicinity. It is therefore useful to assess at least two independent flocks around pollution sources together with detailed soil investigations including assessments of fingerprints of sources and soils before any firm conclusions are reached.

Indication of critical soil levels from other studies and consequences for soil limit values

The IPEN global egg studies on PCDD/F levels from developing countries sampled eggs around industrial emission sources including e.g. non-BAT incinerators and metal industries revealed that in many areas soils are already polluted with PCDD/F levels at which eggs can be highly contaminated. Other studies on chicken eggs such as those in the Netherlands have indicated that eggs from free-range chicken on soils with levels of 2 to 4 ng PCDD/F-TEQ/kg dm frequently exceed EU limits[4]. Calculations taking into account the soil intake of chicken (up to 36 g/day) and the regulatory levels of the eggs indicate that soil levels around and even below 2 ng TEQ/kg for PCDD/F or dl-PCB can be sufficiently high to reach the EU standards of 2.5 pg TEQ/g fat for PCDD/F or 5 pg TEQ/g fat for the sum of PCDD/F and dl-PCB. This is particularly relevant for flocks of chickens spending a lot of time outside with associated higher soil exposures/intake.

The soil-chicken-egg exposure pathway is therefore probably the most sensitive exposure path for PCBs and PCDD/Fs from soil to humans. This pathway is relevant in many contaminated sites in both developing and industrial countries and it needs to be carefully considered in the development of regulatory soil limits for PCDD/Fs and PCBs. People – and especially young children - consuming contaminated eggs can easily exceed health based standards and may be subject to very high exposure levels. In conclusion the contamination levels in soil used for the production of free-range eggs should ideally be less than 2 ng TEQ/kg dm for the sum of PCDD/F and dl-PCBs (and certainly less than 5 ng TEQ/kg dm). Further studies generating larger datasets of egg levels and related soil contamination are recommended for statistically determining problematic soil limits. There are different bio-accumulation factors for dl-PCBs and PCDD/F in eggs and the current EU legislation for eggs has an individual limit for PCDD/F but a combined limit for PCDD/F and dl-PCB. Therefore soil limits for PCDD/F and dl-PCB might have to be determined individually for PCDD/F and for dl-PCB. Furthermore the particular sensitivity of dl-PCB accumulation in beef[17] reinforces the importance of defining dl-PCBs limits in soils independently of PCDD/F limits and not just as the sum of both. To our knowledge there is not yet any soil standard for dl-PCBs.

Monitoring approach using bioassay

This study demonstrates the utility of using bioassay for monitoring of chicken eggs. Specifically bioassays have the dual benefit of being both a cheap and useful tool to measure PCDD/F and PCB in eggs and are also a sensitive tool to measure pollution in soils via the egg levels. Furthermore the bioassay approach can also detect PBDD/F and mixed-halogenated PXDD/F in eggs (and associated soils). Due to the complexity of instrumental analysis of the mixed halogenated PXDD/F currently only total dioxin-toxicity measured by appropriate bioassays can adequately address this challenge. Therefore the bioassay approach is the only method yet available to assess overall environmental and food contamination with dioxin and dioxin-like contamination in a comprehensive way at reasonable costs.

The chicken eggs from Thailand show that brominated PBDD/F can be a main contributor to total Dioxin-toxicity. PBDD/F and PXDD/F are not yet regulated in foodstuffs or soils and this is a major and serious regulatory omission which needs to be addressed especially considering the increase in PBDD/F precursors in the material and waste flow.

Consequences for industrial emissions and for controlling ashes from thermal processes

The low PCDD/F and PCB levels in soil at which chicken/eggs can become contaminated above regulatory limits and health based limits highlights the need to strictly control industrial and other emissions. It is also particularly important to ensure the safe treatment and disposal of residues from waste incinerators and even ashes from residential sources where waste plastics/PVC or contaminated wood are co-incinerated. Residual ashes with contamination levels as low as 50 ng TEQ/kg can be a risk sources. Even if such ash is "diluted" on soils the PCDD/F can re-accumulate over time with repeated applications. In this respect it needs to be highlighted that the current provisional low POPs limit established by the Basel Convention for dioxin contaminated waste of 15,000 ng TEQ/kg is much too high and needs urgently to be re-evaluated and reduced. A single kilogram of ash meeting the Basel "low POPs" level could contaminate 7 tonnes of soil to a level where eggs would not meet EU regulatory limits if laying chickens were kept on it.

Need for re-evaluation of soil limit values and compensation of farmers and private owners

A major challenge is that the levels of contamination in the soil which result in excessive levels of contamination of chicken/egg (and other livestock) are below the current regulatory soil limits. In Germany, for example, the regulatory limit for soil for residential areas/private estate is 1,000 ng PCDD/F-TEQ/kg dm. If chickens were kept on land with these levels this could result in eggs with approx. 800 pg TEQ/g fat! For a 16 kg child a single egg (10 g fat) would exceed the TDI by 250 times. Farmer and private owners have legitimate grounds to expect the original polluters to compensate them for loss of the use of land and in some cases for historic (and current) exposure. The regulatory framework therefore needs to be updated by the establishment of much lower thresholds for soil contamination reflecting the levels at which land uses need to be restricted if excessive exposure via soil-chicken-egg pathways are to be reduced. More stringent emission standards and residue treatment can reduce long-term costs associated with the loss of productive land close to emission sources.

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EXPERIENCES WITH (NEW) POPs & EDCs IN THE ENVIRONMENT, WILDLIFE AND HUMANS BY EFFECT & QUANTITATIVE BASED BIOANALYSIS

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Abstract

The use of effect and cell based screening methods for monitoring POPs and endocrine disrupting chemicals (EDCs) in the environment, wildlife and humans allows the (pre)-selection of samples suspected of being contaminated above limit values, as well as the discovery and evaluation of so far not regulated POPs/EDCs.

In case of dioxin-like POPs, many mixed halogenated PXDD/Fs, PXBs, PXNs, N-dioxins and X-PAHs (X= Cl, Br, J and F) exist. Certainly, several hundreds of them have dioxin-like toxic properties. Many of them may also classified as persistent organic pollutant (POP), while only 29 PCDD/PCDF/dl-PCB congeners are routinely measured and monitored by mostly chemical analysis methods[1,2].

Many of the pesticides found in contaminated sides are known to be endocrine disrupting chemicals (EDCs). We will report here relative equivalent potencies (REP) values and their implementation to calculate here toxic equivalents factors (TEQs) for dioxins as well as EDCs and compare the calculated chemical based data with the real-toxicity bioanalysis results.

Some studies in soil from e-waste burning sites showed already that effect-based analysis tools for dioxin-like compounds such as DR CALUX show much higher levels than the chemical analysis of the 29 PCDD/PCDF/dl-PCB congeners[3]. Cell based bioassays such as the CALUX technology have been evaluated, accepted and used in International guidelines[4-5].

In this presentation we show several examples from polluted environmental samples (soil, sediments, water) with POPs & EDCs and their impact to wildlife and humans.

Key words

Effect-based analysis, bioassays, in vitro reporter reporter gene assays; CALUX, endocrine disrupting chemicals, POPs, dioxins, human, wildlife

Methods and materials

Environmental, wildlife and human samples

All samples were analyzed in the laboratory of BioDetection Systems bv (BDS). The procedure for the DR CALUX® bioassay by BDS is described in detail previously[6]. All other bioassays done are as previously reported[10, 14, 16].

Results and Discussion

Several earlier studies did show already that effect and cell based tests such as DR CALUX have similar quantitative results for dioxins than chemical analysis tools for environmental samples[10-12] as well as feed/food samples[13-14].
Winkler et al (2014) showed recently that environmental samples such PCB contaminated roofs can impact significantly food samples (such as eggs from free ranging chickens)[13]. Here he presented a strategy to use at first DR CALUX screening to sort out the negative samples and to focus than on the few positive samples by chemical analysis.

Also Arkenbout et al (2014)[14] showed several examples of PCB/Dioxin contaminated soils, their impact to chicken eggs and finally to consumers of these contaminated eggs. Here an excellent correlation occurred between the dioxin screening test DR CALUX and for chemical analysis of the suspected egg samples.

Recently also the study of Dubugnon (2015)[15], did show that human bio monitoring is needed for the safety of workers involved in the remediation of landfills. Here all workers before and after the remediation did show low levels of non-dioxin-like PCBs as well as for dioxins/dl-PCBs analyzed by DR CALUX. Therefore it was proven that the way the workers handled this waste was in a safe and healthy way.

In the last decade such effect- and cell-based quantitative analysis tools for POPs (by DR CALUX) and EDCs have been several times used for different kinds of populations (see Table 1):

Publication	N	PCDD/F/ PCB-BEQ Range	PCDD/F/ PCB-BEQ Mean	Info
Pliskova (2005)	Male: 144		92	Worker
Ayotte (2005)	40	37-287	102	Fish eater
De Angelis (2009)	158		19-21	Women
Halldorsson (2009)	100		46	Pregnant women
Brouwers (2011)	50	32-85	54	Workers
Merlo (2013)	Cord blood: 725			Mother/Baby
Vafeidi (2014)[16]	Cord blood: 269 Mother blood: 791	Cord: 13-82 Mothers: 13-50	Cord: 33 Mothers:32	Mother/Baby
Dubugnon (2015)[15]	2 x 10	13-32	20-22	Workers

We also present results from blood samples for mothers and their newborn babies, which have been monitored by ER and AR CALUX for estrogenic and androgenic activities in their blood samples (EU project NewGeneris)[16].

Additionally, Perret (2015)[17] showed the importance of monitoring dust samples at municipal waste incinerators for dioxins/dl-PCBs for the safe handling of ashes and workers in such facilities.

Conclusions

The demand for monitoring for POPs in contaminated environment, wildlife and human will continually rise due to more national and international legislation with the ultimate goal to reduce these dioxins/POPs/EDCs significantly. More efforts will be promoted by international organisations (see also EU Effect-based analysis tools; Technical Report 2014)[18] to receive more data analysed by effect-based and cost-efficient HTPS bioanalysis tools. Our results shows that the CALUX bioassay for screening of POPs/EDCs and not yet regulated new POPs/EDCs in environmental, wildlife and human is an important tool to separate the bulk of unpolluted samples from the few percentage of polluted samples exceeding limit values. Such effect- and cell based screening technologies are most efficient way to know more about the unknown pollutants in complex mixtures.

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SURVEY AND RISK ASSESSMENT EVALUATION OF AN AREA CONTAMINATED BY DIOXINS IN VIETNAM, PHONG MY COMMUNE AND A SO SITE

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Summary

Between 2006 and 2009 a detailed survey of PCDD/PCDF contamination in Phong My Commune has been carried out. Based on the results a human health risk assessment was elaborated and later second risk assessment has been done for A So site a former US military air base in Dong Son Commune. Both Communes are located in Thua Thien Hue province in central Vietnam which was heavily affected by the herbicide spraying during the war between 60s and in the beginning of 70s of the last century. As a consequence of herbicides spraying a significant amount of PCDD/PCDF has been released into the environment and is still present in the basic environment matrices (soil, sediment) and has already entered various food chains. Local inhabitants have limited information about the potential threat they are faced with and are continuously exposed to the increased concentrations of PCDD/PCDF mainly in the locally produced foodstuff.

Based on the findings of both risk assessments, dietary exposure is the most risky one and represents carcinogenic and non-carcinogenic risk at both sites. Dermal contact with contaminated soil shows increased carcinogenic and non-carcinogenic risks too at A So site. Comparison of the two sites shows some important differences in the level of risks and contamination of the environment. Higher contamination and risks were identified at the A So site, where the herbicides were stored and handled. However; Phong My Commune as a typical area affected by herbicide spraying shows significant and non-acceptable carcinogenic and non-carcinogenic risks arising from the dietary exposure.

Key words: PCCD/PCDF, Dioxins, Agent Orange, Vietnam, Risk Assessment

Introduction

The company DEKONTA, a.s. in cooperation with the unincorporated association DWW (Development Worldwide) implemented in the years of 2006-2009, in the framework of official development cooperation of the Czech Republic in the Social Republic of Vietnam a project "Rehabilitation of Thua Thien Hue province affected by dioxins". This project, which was implemented in Phong My Commune was focused on rehabilitation of an area, which was heavily affected by spraying of herbicide preparations during the Vietnam war in the end of 60s and in the beginning of 70s of the last century.

Spraying affected approximately 10% of the Southern and Middle Vietnam (approx. 1.2 million ha) A number of military defoliants were used for these purposes, most of all the substance called "Agent orange", the mixture of 2,4-Dichlorphenoxyacetic acid (2,4-D) and 2,4,5 Trichlorphenoxyacetic acid (2,4,5-T). The dioxins and particularly the most toxic congener TCDD (2,3,7,8-Tetrachlorodibenzo-p-dioxin) coming from the herbicidal mixture was identified as a contaminant in the given area. Unlike the substances 2,4-D and 2,4,5-T, which decompose relatively fast (during several months), dioxins are more stable and persist in the environment for dozens of years.

Phong My Commune

In the years of 2006 and 2007 a detailed survey of the selected area was carried out, in the framework of which 246 samples of various matrices including basic elements of environment (soils, sediments, surface and groundwater), food (meat, fat tissue, fruits and vegetables), as well as human blood. PCDD/PCDF, or as the case may be, 17 monitored congeners were analyzed in the collected samples. Apart from these substances, selected organochlorinated pesticides, PCB and heavy metals were also monitored.

Based upon average detected PCDD/PCDF concentrations in food components and results of questionnaires focused on lifestyle and eating habits of inhabitants in the Phong My commune, the average lifetime daily consumption was derived in WHO-TEQ units, ranging at the level of 5 to 7 times bigger in comparison to chronic exposure to these substances in industrial countries of the Western Europe, or North America. Based upon these data a risk analysis was elaborated, which was primarily focused on a dietary exposure, with regard to significant cumulative nature of dioxins.

In the framework of assessment of health risks resulting from the PCDD/PCDF exposures of inhabitants of the Phong My commune, several key exposure scenarios were identified, for which model calculations were made on the quantitative assessment of average and lifetime exposure doses of PCDD/PCDF and non carcinogenic health risks and risks of rise of cancer diseases resulting from them.

Matrices	Unit	Average concentration	Maximal concentration
Soil and sediments	[pg.kg^{-1}]	1678 ± 863	5100
Fish	[pg.kg^{-1}]	780 ± 1090	4800
Poultry	[pg.kg^{-1}]	640 ± 450	1700
Other meat	[pg.kg^{-1}]	57 ± 38	130
Vegetables (sweet potatoes, casawa)	[pg.kg^{-1}]	16 ± 2	18
Fruit (bananas, papaya)	[pg.kg^{-1}]	25 ± 5	30

Table 1: Average and maximal concentration of PCDD/PCDF in the mayor matrices, Phong My Commune

The dietary exposure was clearly the most risky scenario, most of all with regard to detected PCDD/PCDF concentrations in foodstuffs, especially in fish and poultry, which exceeded the maximum permissible limits determined for these substances by the European legislation by order of magnitude. The most risky foodstuffs from the perspective of PCDD/PCDF intake were especially fish, poultry and wild animals (snakes, frogs). Consumption of vegetables and fruits insufficiently cleaned/peeled from soil particles containing contaminants were also potentially risky. This concerns above all root vegetables, underground bulbs, low growing foliage vegetables, etc.).

Calculations were made according to standard equations for calculation of exposure and health risks, for which exposure parameters recommended by the US EPA and the Ministry of Environment of the Czech Republic were used. Further to this, results of a questionnaire were used for more detailed specification of exposure parameters, these questionnaires served as the most crucial source of information on a monitored population of inhabitants, including their dietary habits (e.g. a number of individual meals during the day and their composition).

The results of model calculations proved that prerequisites connected with this exposure scenario were justifiable and both the noncarcinogenic and carcinogenic risk coming from the dietary exposure was confirmed for all studied groups of inhabitants.

Ascertained values of the HI risk index in the case of noncarcinogenic risk in the monitored age categories ranged from 13.3 to 17.7 for the maximum PCDD/PCDF concentrations in foodstuffs, while the ILCR values (Incremental Lifetime Cancer Risk) in the monitored population groups ranged from 2.8.10^{-5} to 1.5.10^{-3},, which corresponds to the probability of development of cancer disease approximately in the range of 28 individuals out of the group of 1,000,000 of inhabitants to 15 individuals out of 10,000. The cumulative lifetime risk of development of cancer diseases in the monitored population corresponded to the value of 2,1.10^{-3} for the maximum ascertained PCDD/PCDF concentrations in foodstuffs.

Age category	Noncarcinogenic risk		Carcinogenic risk	
	CID [mg.kg^{-1}.den^{-1}]	HI	LCD [mg.kg^{-1}.den^{-1}]	ILCR
1 – 2	4,6E-09	**4,6**	6,5E-11	**9,8E-06**
2 - 6	5,1E-09	**5,1**	2,9E-10	**4,4E-05**
6 – 10	5,7E-09	**5,7**	3,3E-10	**4,9E-05**
10 – 18	6,1E-09	**6.1**	7,0E-10	**1,0E-04**
18 – 70	4,6E-09	**4.6**	3,4E-09	**5,1E-04**
Lifetime exposure	-	-	4,8E-09	**7,2E-04**

Table 2: Total exposure dose and health risks from dietary PCDD/PCDF exposure derived from average values of concentrations of PCDD/PCDF in foodstuffs, Phong My Commune

Age category	Noncarcinogenic risk		Carcinogenic risk	
	CID $[mg.kg^{-1}.den^{-1}]$	HI	LCD $[mg.kg^{-1}.den^{-1}]$	ILCR
1 – 2	1,3E-08	**13,3**	1,9E-10	**2,8E-05**
2 - 6	1,5E-08	**14,6**	8,4E-10	**1,3E-04**
6 – 10	1,7E-08	**16,6**	9,5E-10	**1,4E-04**
10 – 18	1,8E-08	**17,7**	2,0E-09	**3,0E-04**
18 – 70	1,3E-08	**13.3**	9,9E-09	**1,5E-03**
Lifetime exposure	-	-	1,4E-08	**2,1E-03**

Table 3: Total exposure dose and health risks from dietary PCDD/PCDF exposure derived from maximum values of concentrations of PCDD/PCDF in foodstuffs, Phong My Commune

A So site

A So site is a forms US military air base in Dong Son Commune where the herbicides and number of agents were stored and later pumped into the planes and sprayed. This site is reported as one of the contaminated sites with "Agent Orange" e.g. PCDD/PCDF. As a part of the project a risk assessment has been done for the site. No site survey was done; however previously the site has been investigated by Hatfield Consultants (1998).

Data presented in this report were used for the calculation of the identified human health risk scenarios (same as for Phong My Commune). Risk Assessment was primarily focused on a dietary exposure. A questionnaire campaign has been done the same way as in Phong My Commune to specify exposure parameters, especially their dietary habits.

According to the calculation done both dietary and dermal exposure represent a carcinogenic and non-carcinogenic risks to local inhabitants. Significant non-carcinogenic and carcinogenic risk for all population groups studied from dietary exposure, primarily from the consumption of fish and poultry has been proved. The lifetime risk of cancer development for the studied population corresponds to the maximum detected concentrations of PCDD / PCDF in food value of $9.25 \ . \ 10^{-3}$. Contact with contaminated soil, where transport through dermal contact and incidental ingestion of contaminated soil pose a significant exposure pathways of PCDD / PCDF in terms of non-carcinogenic and carcinogenic health risks. Especially for children non-carcinogenic risk and carcinogenic risk arise from lifetime exposure.

Matrix	Unit	Average concentration	Maximal concentration
Soil	$[pg.kg^{-1}]$	44610	897000
Sediments	$[pg.kg^{-1}]$	2520	17600
Fish	$[pg.kg^{-1}]$	7610	51300
Poultry	$[pg.kg^{-1}]$	4710	82000
Beef	$[pg.kg^{-1}]$	280	1800
Eggs	$[pg.kg^{-1}]$	2400	12900
Vegetables (sweat potatoes, cassava)	$[pg.kg^{-1}]$	16	18
Fruits (bananas, papaya)	$[pg.kg^{-1}]$	25	30
Rice	$[pg.kg^{-1}]$	150	-

Table 4: Average and maximal concentration of PCDD/PCDF in the mayor matrices, A So site (Dong Son Commune)

Age category	**Noncarcinogenic risk**		**Carcinogenic risk**	
	CID [mg.kg^{-1}.den^{-1}]	**HI**	**LCD** [mg.kg^{-1}.den^{-1}]	**ILCR**
1 – 2	3,68E-08	**36,8**	5,26E-10	**7,90E-05**
2 - 6	2,46E-08	**24,5**	1,40E-09	**2,11E-04**
6 – 10	1,84E-08	**18,4**	1,05E-09	**1,58E-04**
10 – 18	1,23E-08	**12,2**	1,40E-09	**2,11E-04**
18 – 70	6,72E-09	**6,7**	4,99E-09	**7,48E-04**
Lifetime exposure	-	-	9,38E-09	**1,41E-03**

Table 5: Total exposure dose and health risks from dietary PCDD/PCDF exposure derived from average values of concentrations of PCDD/PCDF in foodstuffs, A So site

Age category	**Noncarcinogenic risk**		**Carcinogenic risk**	
	CID [mg.kg^{-1}.den^{-1}]	**HI**	**LCD** [mg.kg^{-1}.den^{-1}]	**ILCR**
1 – 2	2,43E-07	**243,3**	3,48E-09	**5,22E-04**
2 - 6	1,62E-07	**162,2**	9,27E-09	**1,39E-03**
6 – 10	1,22E-07	**121,6**	6,95E-09	**1,04E-03**
10 – 18	8,11E-08	**81,1**	9,27E-09	**1,39E-03**
18 – 70	4,40E-08	**44,0**	3,27E-08	**4,91E-03**
Lifetime exposure	-	-	**6,17E-08**	**9,25E-03**

Table 6: Total exposure dose and health risks from dietary PCDD/PCDF exposure derived from average values of concentrations of PCDD/PCDF in foodstuffs, A So site

Conclusion

As expected the level of contamination is much higher at the site where the herbicides with trace content of PCDD/PCDF were stored and handled (A So site) to sprayed areas (Phong My Commune). However; the level of contamination in sprayed areas is still increased and accumulated PCDD/PCDF in some of the animals exceed significantly the limit values for these chemicals in foodstuff according to the EU standards and WHO recommendation of daily intake. At both sites dietary expose scenario shows unacceptable carcenogenic and non-carcenogenic risks for local inhabitants.

Fairly low PCDD/PCDF concentration in soil and sediment in Phong My Commune doesn´t represent any human health risk, however; much higher concentration at A So site represents a serious carcenogenic and non-carcenogenic risk for dermal contact with contaminated soil/sediment.

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OPEN BURNING: MAIN SOURCE OF DIOXINS/FURANS EMISSIONS IN ARMENIA

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Abstract

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) were never produced intentionally, but are undesirable by-products of many industrial processes and all processes of burning. Open burning of household and industrial wastes at landfills is an important and significant source of Dioxins emission to the environment. This issue gains a prime urgency under conditions of the Republic of Armenia, where wastes combustion plants, special polygons for waste recycling, utilization and combustion, as well as specialized polygons for toxic wastes treatment are lacking, wastes are generally burnt, thus aggravating the state of environment and worsening the health of the general population.

Within the "Open burning" source group fires at waste dumps make the most important source for PCDD/PCDFs releases, while other sources include agricultural residues burning in the fields, forest/bush fires, open burning of household wastes.

Key words: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), emissions, environmental pollution, wastes, open burning.

Materials and methods

Recent years are characterized by the ecological mentality of the Globe that aims to protect the environment and mankind against the harmful impact of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) (Aleksandryan et al. 2003). These chemicals were never produced intentionally, but are undesirable by-products of many industrial processes and all processes of burning [1-4; 6; 8].

The threat of PCDDs/PCDFs-related effects is conditioned by their physical and chemical properties, such as environmental stability, good fat solubility and poor water solubility, ability to cumulate in different ecological systems, i.e. biomagnification, as well as extreme toxicity for humans and other representative species of the biosphere.

For identification and quantitative determination of PCDDs/PCDFs potential sources and transfer vectors to air, water, soil, products, and residues the United Nations Environment Programme (UNEP) elaborated the calculation procedure and Toolkits, which were used in this research work.

Open burning of household and industrial wastes at the landfills is an important and significant source of PCDDs/PCDFs emission to the environment. This issue gains a prime urgency under conditions of the Republic of Armenia, where wastes combustion plants, special polygons for waste recycling, utilization and combustion, as well as specialized polygons for toxic wastes treatment are lacking and the wastes are generally burnt, thus aggravating the state of environment and worsening the health of the general population.

The "Toolkits for identification and quantification of dioxin and furan releases" [9;10] developed by UNEP facilitated identification of industrial and non-industrial processes as a result of which the substances are released to air, water, soil, waste and products. To quantify the emission it is supposed to use "emission factor" describing dioxins and furans entry into the environment/media per unit of activity characterizing the enterprise, such as "toxic equivalent per ton" (TEQ/t). TEQ indicates the potential toxicity of the particular substance itself as related to the most powerful poison among all the dioxins – 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The sum of emission factors allows us to estimate the total "dioxin" toxicity of the given source. Usually the international system (I-TEQ) is used.

In all countries, including the Republic of Armenia, where an inventory of dioxins was previously conducted, the coefficients given in UNEP Toolkits[9; 10] were used. The results obtained show that the share of uncontrolled combustion processes account for the majority of dioxin releases. Further studies, including direct measurements of combustion processes, showed that emission factors are significantly lower than coefficients of UNEP.

In 2013 an updated Methodological Guidance – "Toolkit for Identification and Quantification of Releases of Dioxins, Furans and other Unintentional POPs" (Toolkit 2013) was published under which the emissions were estimated by the new mode and the inventories have been updated.

Results and discussion

In Armenia releases of dioxins and furans increased from 2002 to 2006. Since 2006 there was a steady decline in their releases (Figure 1; Table 1). The highest release was observed in 2005, when it reached 66 g I-TEQ. From 2006 to

2012 the estimated releases of unintentionally produced persistent organic pollutants reduced by 93% to 4.65g I-TEQ.

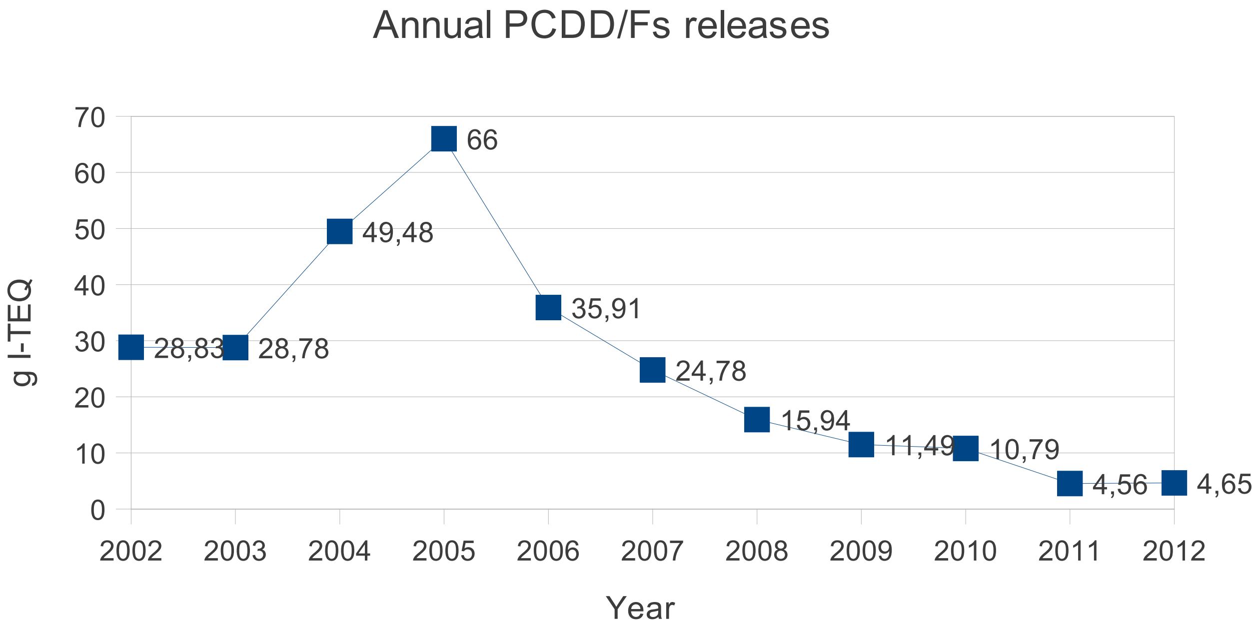

Figure 1. PCDD/Fs release trend between 2002 and 2012

Initially, up to 2011, the most significant source group was waste incineration. Since 2011 open burning processes became the second most important source for releases of unintentionally produced persistent organic pollutants, as the waste incineration has stopped in Armenia. In accordance with the new UNEP publication, Armenia carried an inventory update for Category 6 "open burning processes". The data obtained are presented below; Table 1 shows that the "'new" UNEP coefficients are significantly lower than previous ones.The most significant PCDDs/PCDFs release route is via emissions to air which are followed by releases to residues; the third route is to water and the fourth is land depositions. Releases to products were found to be negligible (Figure 2).

TEQ coefficients, mcg/t	**Media**	**According to UNEP Toolkits 2001; 2005**	**According to UNEP 2013 new factors [**
Forest fires	air	5	1
	soil	4	0.15
Agricultural residue burning in the field	air	30	0.5
	soil	10	0.05
Fires at waste-dumps	air	1000	300
	soil	-	10
Open burning of household waste at waste-dumps	air	300	40
	soil	600	1
	residue	600	

Table 1. Toxic equivalency (TEQ) coefficients

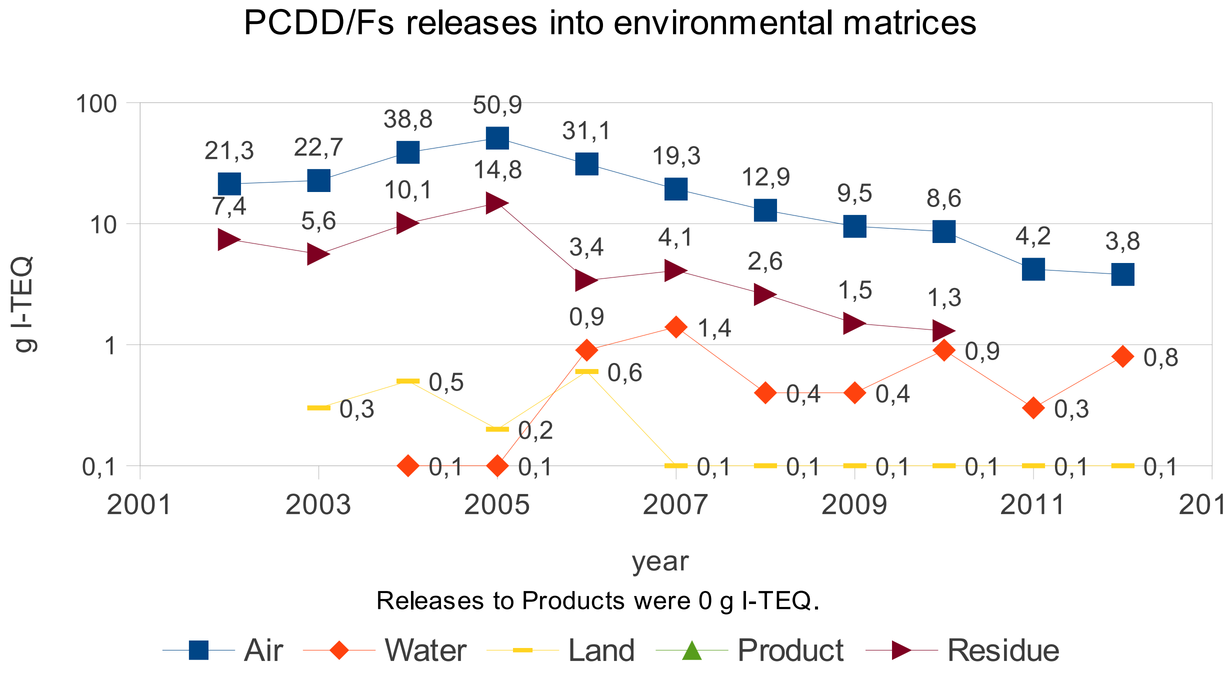

Figure 2. Trends of PCDD/Fs releases into various environmental matrices

Approximately 79% of the PCDDs/PCDFs are released to the air. Because air can transport pollutants to large distances this release route requires strong attention in future planning. The research also allowed to conclude that 18% of the releases occur to residues. These two release routes show strong decline as waste incineration has stopped in Armenia.

Releases to water increased in the past years mainly due to increased sewage generation and better statistical reporting (Figure 3).

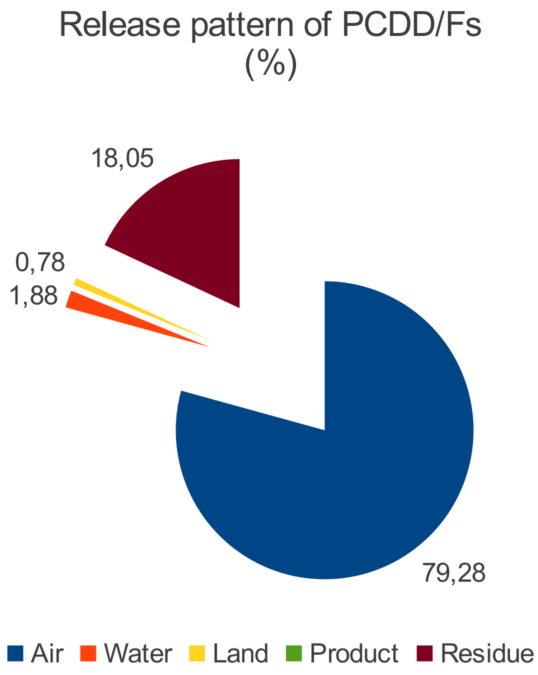

Figure 3. Release pattern of Annex C POPs PCDDs/PCDFs

Within the "Open burning" source group fires at waste dumps make the most important source for PCDD/PCDFs releases. Other important sources are: agricultural residues burning in the field; forest/bush fires; open burning of household wastes.Fires happen commonly in both municipal landfills and on illegal waste dumpsites. Fires on open-air dumpsites are among the main sources of dioxins and furans releases. Currently, in Armenia the majority (if not the entire number) of those sites do not correspond to sanitary requirements. This is the main source of pollution by dioxins and furans. Deep fires occur constantly at almost all dumpsites, and practically it is impossible to extinguish them. These landfills regularly contain significant amounts of polyvinyl-chloride as well as polychlorinated biphenyls (PCBs). The concentration of PCBs in different dumpsites varies from 22.3 to 369.9 mcg/kg of waste. During the burning of these chemicals dioxins and other hazardous compounds may be generated, polluting various environmental media, mostly air. From the polluted areas migration of hazardous compounds occurs into underground and surface waters, plants, agricultural products. These pollutants can enter and biomagnify in the food chain and subsequently expose wildlife and humans.

Table 2 demonstrates that PCDDs/PCDFs releases continuously increase from dumpsite burning. Due to the recent modification in the emission factors of the Toolkit release estimates in this sector were changed significantly. In order to better understand the pollutant release trends release estimates of the first NIP were recalculated with the new emission factors.

Table 5 demonstrates the release estimates with both the old and the new emission factors.

Year	Amount of waste, t	Emissions, g TEQ/year	
		According to UNEP Toolkit, 2013	
		air	land
2002	2 756	0,827	0,028
2003	30 203	9,261	0,302
2004	42 893	12,868	0,429
2005	22 369	6,711	0,224
2006	54 072	16,222	0,541
2007	5 569	1,671	0,056
2008	3 767	1,130	0,038
2009	6 418	1,925	0,064
2010	6 376	1,913	0,064
2011	7 494	2,248	0,075
2012	6 546	1,964	0,065

Table 2. Dioxin emission caused by fires at dumpsites

The next most significant source of PCDDs/PCDFs releases in open burning sector is presented by the forest and bush fires. The figures vary considerably, probably due to drier or rainy summers, but since 2010 a steady decline is observed which might be due to better fire response measures.

In the past six years there were no significant changes in the amount of burned agricultural residues, therefore the releases were in the same range (Table 4.). This was due to the fact that the size of agricultural land and farming practices did not change. It was assumed that burnings happen on approximately 56-57% of the cultivated area and the amount of burned biomass is 2.5 t/ha. The contribution of this sector to the total PCDDs/PCDFs releases is less important.

Indicator	2006	2007	2008	2009	2010	2011	2012
Amount of burnt biomass, (t)	3680	125	228	299	9077	5240	3082
Dioxins release to air TEQ/year	3.68	0.125	0.228	0.299	9.077	5.240	3.082
Dioxins release to soil TEQ/year	0.552	0.01877	0.03422	0.0448	1.362	0.768	0.462

Table 3. PCDDs/PCDFs releases of forest/bush fires
(calculated according to UNEP Toolkit 2013 emission factors)

Indicator	Values						
	2006	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
Area of agricultural residue burning, ha (56%)	173.6	171.36	170.52	168.0	158.82	160.55	170.35
Burnt biomass, thousand tons	434.0	428.4	426.3	420.0	397.05	401.37	425.88
Emission, mg TEQ/ year, air	217.0	214.2	213.15	210.0	198.52	200.68	212.94
Emission, mg TEQ/ year, land	21.70	21.42	21.315	21.0	19.85	20.07	21.294

Table 4. PCDDs/PCDFs releases in agricultural residue burning (calculated according to UNEP Toolkit 2013 emission factors)

Open burning is the most inexpensive, easy-to-implement and the most applicable means to destruct household wastes. This is especially true for people who have to remove the wastes by themselves. Nevertheless, open burning of household wastes is the environmentally unacceptable process, at which chemicals, which pollute the environment, are generated. Therefore, open burning should be minimized or eliminated, where possible.

Of course, when sanitary-hygienic removal of wastes is required in order to fight with diseases or pests, then open burning is absolutely necessary, if there are no alternative ways to dispose (destruct) wastes. In no case household wastes can be burned in household conditions: in kitchen stoves, fireplaces, ovens or furnaces. Despite the character of burnt materials open burning is always accompanied by smoke and unpleasant smells, odours, which irritate and might be hazardous for human health [7].

Dioxins generation at household wastes burning depends on wastes composition and combustion conditions. These factors might vary to a very wide extent. For emissions assessment and evaluation the emissions factors, which are mostly close (appropriate) according to composition and conditions of burning, should be selected.

In Armenia, as a rule, unsorted wastes are burnt; apart from combustible (inflammable) materials there are tins and aluminum cans, glass, ceramics, food waste, different types of plastics, packaging, paper, cardboard (carton), textile fabrics, biologically decomposed wastes. The household wastes open burning issue was assessed based on data of the National Statistical Service. As a rule, in Armenia the wastes are not recycled and are entirely burnt in bonfires at random places, sometimes near the residential buildings.

The available data is presented in Table 5. Emissions to air and land were assessed taking into account coefficients of UNEP Toolkit of 2013[11]. Table 5 also involves comparative data on emissions calculated with the use of coefficients from UNEP Toolkit of 2005[10]. We observed a steady decline of the pollutant releases from this sector. It has roughly been reduced by one order of magnitude, which is a success (Table 5).

Total Releases	Year	Amount of waste	Emissions, mg TEQ/year			
			air		land	
			Toolkit 2005	Toolkit 2013	Toolkit 2005	Toolkit 2013
	2006	2284.1	685.23	91.364	1370.40	2.284
	2007	2513.6	754.08	100.544	1508.16	2.514
	2008	1462.4	438.72	58.496	877.44	1.462
	2009	463.1	138.93	18.524	277.86	0.463
	2010	300.3	90.09	12.012	180.18	0.300
	2011	17.3	5.19	0.692	10.38	0.0173
	2012	167.4	50.22	6.696	100.44	0.1674

Table 5. PCDD/PCDF releases in domestic waste burning (calculated with UNEP Toolkit 2005 and 2013 emission factors

Taking into consideration the results of initial studies and PCDDs/PCDFs inventory of 2003-2005, the country have taken measures to decrease emissions generated at open burning. The current research was aimed to evaluate the achievement obtained as a result of carrying-out the above-mentioned actions. The results presented in this paper demonstrate that in Armenia no significant changes are observed in respect of open burning.

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RESULTS OF INVENTORY AT PESTICIDES CONTAMINATED SITES AND IDENTIFICATION OF CONTAMINATION LEVELS IN DIFFERENT PROVINCES OF ARMENIA

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Abstract

The stocks of obsolete pesticides and other POPs pose serious and long-term threat for human health and the environment at both local level and on the global scale. In Armenia the problem is aggravated by the lack of necessary financial resources and absence of efficient and environmentally sound technologies and capacities for their destruction in Armenia, where areas contaminated by organochlorine pesticides are those of former warehouses and storehouses of pesticides and the surrounding sites.

Detailed investigation was undetaken to identify and quantify POPs stocks. All of the 550 former storage facilities, which have been used to store POPs or other hazardous pesticides, have been revisited. The condition of these storages were found to be substandard. The inventory on obsolete pesticides concluded that approximately 140 700 kg obsolete pesticides are stored in various storage facilities. It was not possible to collect samples from and around all these storages; these locations have been classified as potential contaminated sites

Removing the stocks of obsolete pesticides from the former warehouses and remediation of the contaminated sites are necessary.

Key Words: pesticides; persistent organic pollutants (POPs); contaminated sites; hazardous chemicals; wastes.

Materials and methods

In Armenia, likewise other countries, special warehouses were intended to store pesticides: chemicals used for pest control. Until 1985 Armenia received DDT, HCH, Hexachlorobenzene among other organochlorine pesticides. These products were stored in warehouses of the former administrative areas and regions, each region had central and rural warehouses. At that time 550 warehouses were functioning in the country. Accumulation of organochlorine pesticides in mentioned warehouses began after the ban of their use. DDT was prohibited for use since 1971, but Armenia received this pesticide up to 1978, when Aragatsotn, Ararat, Vayots Dzor, Syunik, and Gegharkunik provinces received the last batches of DDT. The use of HCH was banned from 1980, but the import and storage continued up to 1985: the last batches of HCH were delivered to all provinces with the exception of Lori and Shirak. Unused pesticides imported after the ban accumulated and over time became unfit for use.

The first “National Implementation Plan for the Stockholm Convention on the Persistent Organic Pollutants”[1] (2005) requested the identification/clarification of the amounts of obsolete pesticides stocks on the territory of Armenia. Within the NIP update process detailed investigation was undetaken to identify and quantify POPs stocks.

Results and discussion

All of the 550 former storage facilities, which were previously used to store POPs or other hazardous pesticides, have been revisited. The condition of these storages was found to be substandard. At many locations the storages are used as cattle sheds, or storages for grains. At some locations the pesticides are still there spilled out on the ground with contaminated soils or construction materials. It is highly probable that the buildings of these storages and the surrounding environment, where the pesticides were loaded or mixed, are potential contaminated sites. This poses significant threat to the environment and humans. The table below presents the distribution of the storage locations in Armenia including the stocks of the obsolete pesticides and other potentially contaminated materials.

Provinces of Armenia	Number of storehouses	Approximate amount of pesticides, kg
Kotayk Province	39	
Aragatsotn Province	48	8 200
Gegharkunik Province	33	3 250
Lori Province	40	18 550
Vayots Dzor Province	37	1 000
Shirak Province	89	2 750
Syunik Province	41	2 750
Tavush Province	48	5 500
Ararat Province	89	28 700
Armavir Province	86	69 500
TOTAL:	550	140 700

Table. Former pesticide storage locations and identified stocks

The inventory on obsolete pesticides concluded that approximately 140 700 kg obsolete pesticides are stored in various storage facilities. Relatively large quantities of organochlorine pesticides were received and used in Armavir, Aragatsotn, Ararat, Lori, Syunik, and Tavush provinces. In order to better demonstrate the distribution of the stocks in the country Figure 1 presents distribution of the obsolete pesticides stocks in the provinces. In Armavir province alone half of the total stocks is stored, approximately 70 tons. The second most affected province is Ararat, the third is Lori province. These three provinces are still the most important agricultural regions in Armenia.

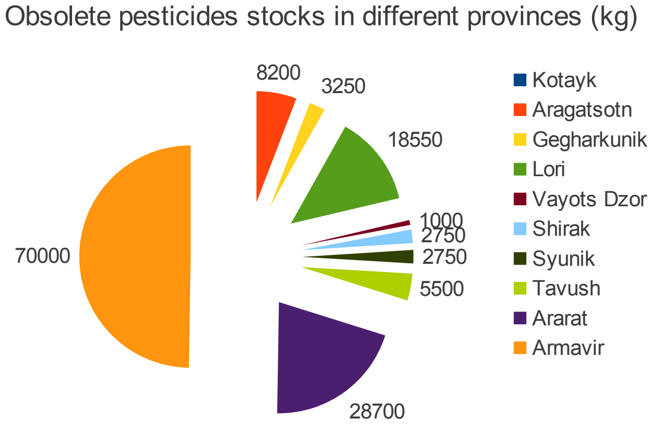

Figure 1. Obsolete pesticides stocks in different provinces of Armenia.

Potential pesticides contaminated sites

The inventory exercise could not collect samples from and around these storages, all of these locations have been classified as potential contaminated sites. Figure 2 presents the distribution of the contaminated pesticides locations in Armenia. The largest number of potential contaminated sites with pesticides is in Ararat (89), Shirak (89) and Armavir (86). In each of the other provinces there are approximately 40 contaminated sites.

The relative content (%) of HCH isomers, isomers and metabolites of DDT in samples of soil taken in the vicinity of pesticides shops and store-houses, as well as samples of arable soil taken near these sites is reflected by Figure 3.

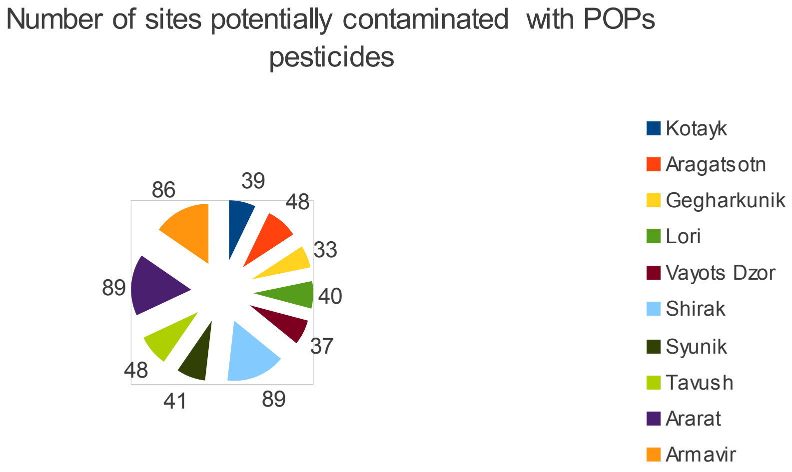

Figure 2. Distribution of potential POPs pesticide contaminated sites in provinces of Armenia.

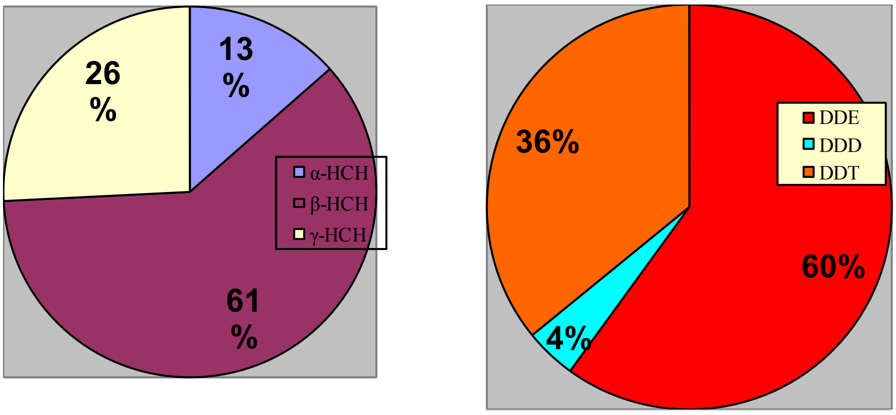

Figure 3. Percentage of HCH isomers, isomers and metabolites of DDT in samples of soil from the vicinity of pesticides shops and store-houses, as well as soil taken near these sites.

The residual amounts of the following compounds were revealed [2]:

- Hexachlorcyclohexane (α-, β-, γ- isomers);
- Hexachlorbenzene;
- Heptachlor;
- Aldrin;
- DDT and its metabolites (o,p-DDT, pp-DDT, p,p-DDE, o,p-DDE, o,p-DDD, p,p-DDD);
- Dieldrin;
- Endrin;
- Mirex.

According to analyses performed the amounts of revealed pesticides varied:

- Hexachlorcyclohexane (α-, β-, γ- isomers): 1.3-5.8 mcg/kg (0.0013-0.0058 mg/kg) *versus* the Maximum Alowable Concentration (MAC) of 0.1 mg/kg;
- Hexachlorbenzene: 1.6-67 mcg/kg (0.0016-0.067 mg/kg) versus MAC of 0.08 mg/kg
- Heptachlor: 2.2-59 mcg/kg (0.002-0.059 mg/kg) versus MAC of 0.05 mg/kg;
- Aldrin: 1.4-39 mcg/kg (0.0014-0.039 mg/kg) (not regulated);
- pp-DDE: 1.8-608 mcg/kg (0.0018-0.608 mg/kg) versus MAC of 0.1;
- o,p-DDE: 2-12.5 mcg/kg (0.002-0.0125 mg/kg);
- o,p-DDD: 2-36.8 mcg/kg (0.002-0.0368 mg/kg);
- p,p-DDD: 0.9-64 mcg/kg (0.0009-0.064 mg/kg);
- o,p-DDT: 0.6-54 mcg/kg (0.0006-0.054 mg/kg);
- p,p-DDT: 0.9-346 mcg/kg (0.0009-0.346 mg/kg);
- Dieldrin: 0.5-2.1 mcg/kg (0.0005-0.0021 mg/kg);
- Endrin: 0.9-16.3 mcg/kg (0.0009-0.163 mg/kg);
- Mirex: 0.8-21 mcg/kg (0.0008-0.021 mg/kg).

Previously, in compliance with the List of pesticides imported to Armenia and according to results of the studies performed, limited amounts of Dieldrin, Endrin, Mirex were imported. According to analyses, either no residual amounts of these pesticides were revealed or they were very low. The revealed amounts of DDT and its metabolites indicate that mainly technical preparation of obsolete (inappropriate for use), degraded DDT was used and, in all probability, this formulation is used at present.

The comparison of residual amounts found in samples with the appropriate MACs, which were approved by Sanitary Rules and Standards No.2.1.7.003-10 "Hygienic requirements to soil quality" allows to state that the revealed residual amounts were below the MACs, except the sample of arable land taken from the area of Masis, in which o,p-DDE makes 0.346 mg/kg. All in all, the analyses demonstrated that the summary content of Hexachlorocyclohexane did not exceed the MAC.

The content of DDT and its metabolites in the studied samples taken from the sites of pesticides shops was as follows:

- in Artashat: 0.3 mg/kg;
- in Masis: 0.66 mg/kg;
- in Mkhchan: 0.196 mg/kg,
- in Nor-Kharberd: 0.023 mg/kg;
- in Armavir: 0.74 mg/kg.

At the site of former pesticides store-house in Armavir the residual amount made 0.8 mg/kg; there was exceeding of MAC.

Summary content of DDT and its metabolites (0.66 mg/kg) in samples of arable land earlier taken from Masis (0.66 mg/kg) and Mkhchyan (0.196 mg/kg) exceeded MAC levels. Summarizing the results of study it is possible to suppose that, according to the current state, DDT is used in the Ararat Valley.

Figures 4-5 visually present the average and maximum values of OCPs and PCBs in soil samples.

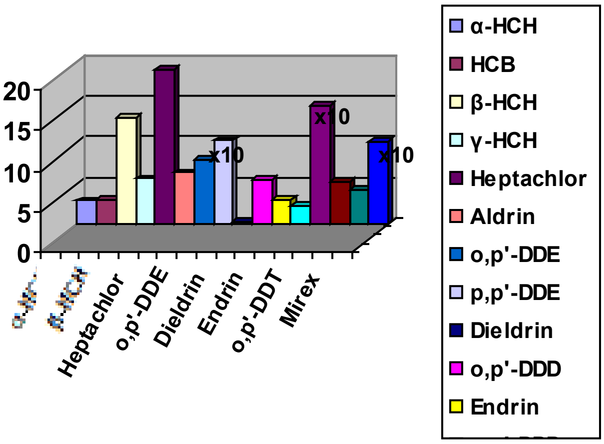

Figure 4. Average values of OCPs and PCBs in soil samples (mcg/kg).

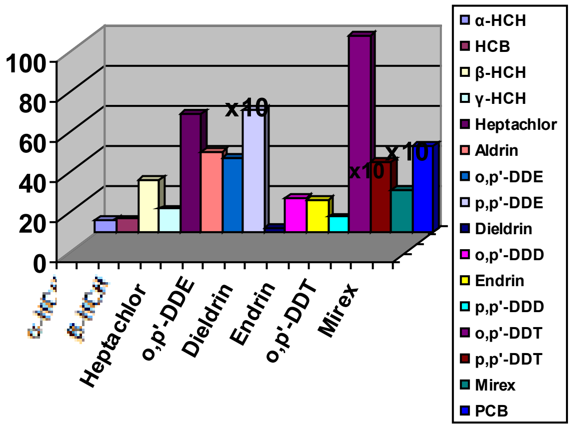

Figure 5. Maximum values of OCPs and PCBs in soil samples (mcg/kg).

The trends observed for residual amounts of α-, β-, γ-HCH in soil samples from different regions of Armenia are presented in Figure 6.

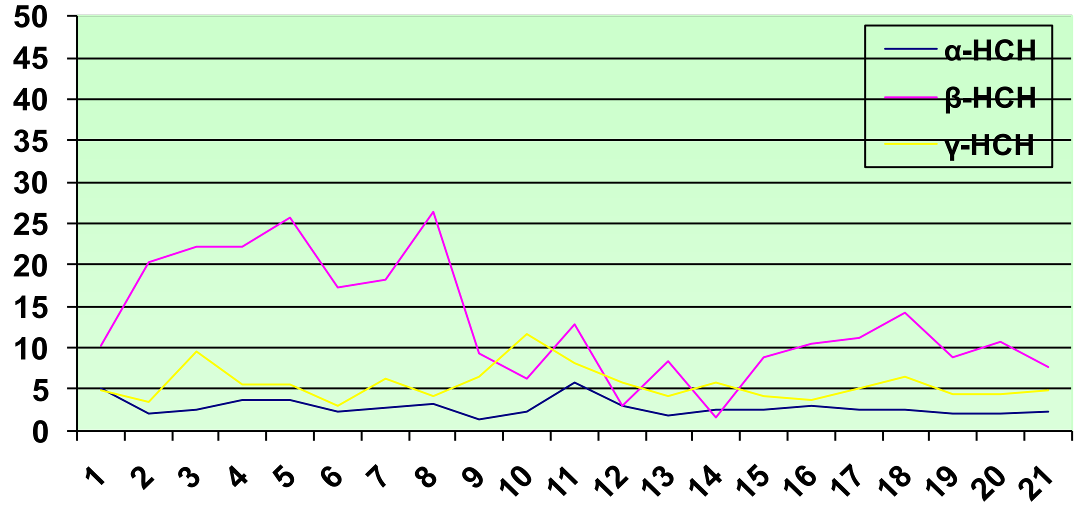

Figure 6. Residues of α-,β-, γ-HCH in soil samples from different regions of Armenia (mcg/kg)

Notes: Sampling point descripion

1. Soil, Kotayk Marz, Eghvard, area of pesticides shop
2. Soil, Kotayk Marz, Eghvard, arable land
3. Soil, Aragatsotn Marz, Ashtarak, arable land
4. Soil, Aragatsotn Marz, Byurakan, arable land
5. Soil, Aragatsotn Marz, Agarak Village, arable land
6. Soil, Ararat Marz, Aintap Village, arable land
7. Soil, Ararat Marz, Artashat town, area of pesticides shop
8. Soil, Ararat Marz, arable land between Burastan and Azatavan villages
9. Soil, Ararat Marz, arable land at the road to Masis
10. Soil, Ararat marz, arable land from Mkhchyan Village
11. Soil, Ararat Marz, arable lands from Marmarashen Village
12. Soil, Ararat Marz, vineyard at the highway Yerevan- Artashat
    (Masis – Artashat section)
13. Soil, Ararat Marz, arable lands of Nor-Kharberd Village
14. Soil, Yerevan, Erebuni Community, middle section of the highway (between Mushavan Village and pesticides burial)
15. Soil, Yerevan Erebuni Community, Jrashen Village, area of the former pesticides storage
16. Soil, Yerevan, Mushavan Village, area of former pesticides shop
17. Soil, Yerevan, Erebuni Community, arable lands between Jrashen and Mushavan Villages
18. Soil, Yerevan, Erebuni Community, area of "Erebuni" nature reserve of the Ministry of Nature
    Protection, Armenia
19. Soil, Armavir Marz, Armavir town, area of pesticides shop
20. Soil, Armavir Marz, area of the former pesticides storage
21. Soil, Armavir Marz, arable lands of Khanjyan Village

The main conclusion that might be drawn**:** **r**emoving the stocks of obsolete pesticides from the former warehouses and remediation of the contaminated sites is necessary.

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HEXACHLOROBUTADIENE IN THE DRINKING WATER OF THE CITY OF BASEL (SWITZERLAND), THE RHINE AND THE CHEMICAL LANDFILL „FELDREBEN” OF BASF, NOVARTIS AND SYNGENTA

Martin Forter, Basel (Switzerland)

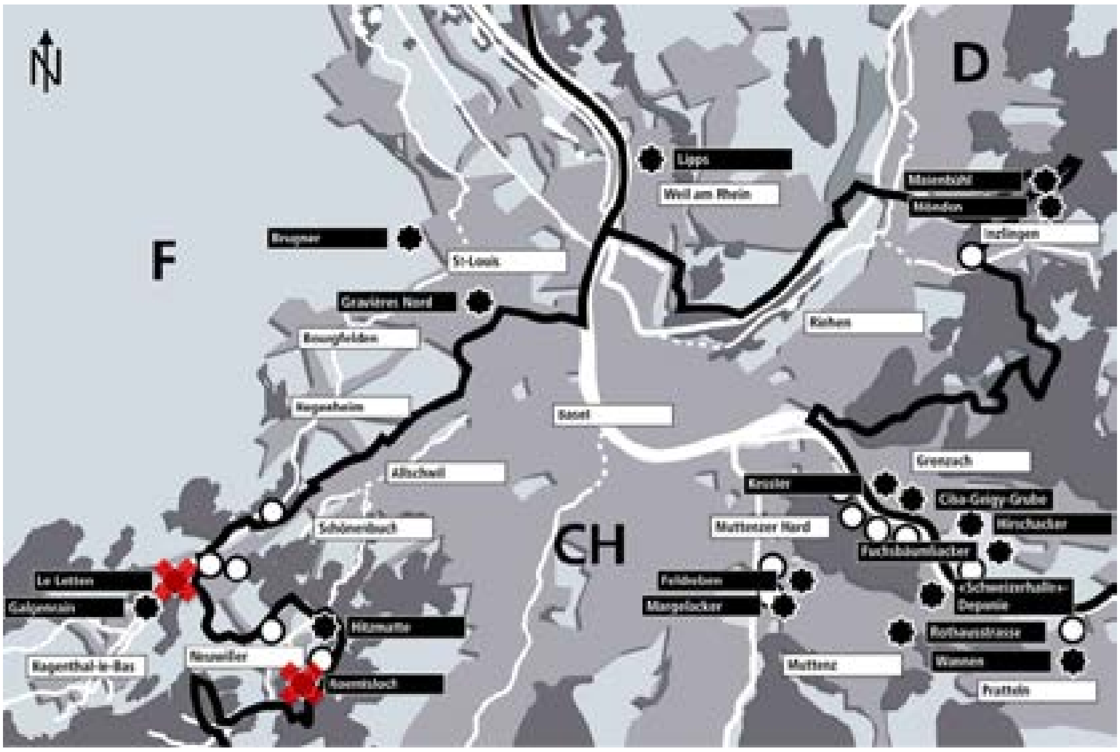
Today, the Basel region at the Upper Rhine is a centre of the pharmaceutical industry. But: In the past it was a centre of classical chemical industry. The classic chemical industry left behind in the three countries of the Basel Region – France, Germany and Switzerland – 18 chemical landfills. They are often close to drinking water wells.[1]

Only 2 of these 18 chemical landfills have been completely eliminated (by excavation) by the today responsible companies among others BASF, Novartis and Syngenta.

In the following, I will focus on the case of the chemical landfill Feldreben in the Swiss State Basel-Land.

According to industry estimates this landfill – a former exploited gravel pit – contains 13,500 to 25,000 tonnes of chemical waste.[2] The predecessor company of today's BASF, Novartis and Syngenta has dumped these wastes between approximately 1940 -1957. It is waste from for example the production of dyes, pigment, textile auxiliaries, pesticides and plastics.[3] In the immediate vicinity of the chemical waste dump is a drinking water reservoir. From there, 240,000 people in the Swiss states Basel-Stadt and Basel-Land obtain their drinking water.

The 18 chemical landfills in the three countries of the Basel Region – France, Germany and Switzerland, also with the landfill Feldreben in Muttenz (CH) close to the drinking water wells of 230'000 people.



Legend: **O** Drinking water supply; ● **Feldreben** Chemical Landfill; ▬ National border

In 2006, Greenpeace Switzerland analysed this drinking water by GC / MS screening and found a range of chemicals including Hexachlorobutadiene and Tetrachlorobutadiene.[4] Hexachlorobutadiene is a high-boiling solvent and a persistent organic pollutant listed as POP in the Stockholm Convention.[5] It is also unintentionally formed

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as a byproduct in the production of chlorinated solvents such as tetrachloroethane and present there as impurity.[6]

Greenpeace considers already in 2006 that the chlorinated budatienes and other pollutants in the drinking water most likely stem from the neighbouring chemical landfill Feldreben.[7] This, because chlorinated butadienes as well as other pollutants detected in the drinking water had previously been detected in the wastes of this chemical landfill and the surrounding groundwater. Shortly after the results of the Greenpeace analysis in 2006, it was revealed that the drinking water supplier “Hardwasser AG” had already detected hexachlorobutadiene and tetrachlorbutadiene in the drinking water in 2005[8] – this means even before the Greenpeace study.

But that is not all: The Swiss Federal State of Basel-Land and the drinking water supplier Hardwasser AG had already detected chlorinated butadienes in this drinking water in 1980 without publishing the results.[9] The authorities judged internally in 1981 as follows: “The burden of water consumers” stands “disproportionate to the burden with the same substances” in everyday life. So, for example, “In the workplace, from solvents and colors, from the road, from smoking, etc.”.[10]

However hexachlorobutadiene is not formed in thermal processes such as cigarette smoke.

The authorities of the two cantons Basel-Land and Basel-Stadt – where people drink this water – never assessed the toxicology of these pollutants by any national authority. This only happened after the Greenpeace analysis.[11]

Due to the suspicion of genotoxic effects of the chlorinated butadiene, the national authorities determined a limit value for drinking water of 75 ng/l.[12] Now the authorities forced the drinking water supply company to treat the drinking water. In the meantime the genotoxicity of chlorinated butadiene is confirmed. Today the limit is set at 100 ng /l.

In the chemical landfill, Feldreben, chlorinated butadienes were detected in high concentrations. Now the question arises: Do these chlorinated butadienes from the Feldreben dumpsite enter and contaminate the drinking water? That is not simple to answer. Because the drinking water is mainly made from Rhine water, which the drinking water supplier Hardwasser AG filters through gravelly and sandy soil. The Rhine water enriched groundwater supplies the 240,000 inhabitants with drinking water. In the underground, the pumped Rhine water forms a kind of groundwater mountain. This is supposed to keep the pollutants from the Feldreben landfill away from the drinking water wells. Whether this is a reliable barrier has, however, never been tested by the authorities.

Today, the government of the state Basel-Land does not see the chemical landfill as the cause, but two historic sources:

1) Before the Rhine water pumping started in 1959, polluted groundwater from the landfill flowed into the drinking water.

2) Until 1982, the Rhine was also contaminated with chlorinated butadienes. This – according to the authorities - had led to reservoirs in the soil, which are still mobilizing today to contaminate the drinking water.[13]

Until 1982 the company Dynamit Nobel (later Hüls-Werke) produced tetrachlorethylene and was located upwards the Rhine in the German Rheinfelden. This resulted in the release of hexachloro-, tetrachloro- and pentachlorobutadiene into the Rhine. The water supplier Hardwasser AG, 25 km downstream, used this loaded Rhine water for the production of drinking water. Also for this reason the Basel drinking water was until 1982 loaded with chlorinted butadienes, which is demonstrated by measurements from 1976.[14]

The arguments in favour of a “historical storage” are, however, inconclusive. Already with the monitoring results from 1981, it can be shown that the entry via the Rhine water was approximately 7 times smaller than the discharge via drinking water and wastewater.[15]

In addition, the chlorinated butadiene is not the only contaminant in this drinking water. So far, 36 substances have been detected in the drinking water.

1. 34 of these substances were also found in the groundwater at the Muttenzer chemical landfills. These are 94%.

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lutants, Seventh meeting, Geneva, 4–15 May 2015, 7.5.2015; Earth Negotiations Bulletin: Summary of the meetings of the conferences of the parties to the Basel, Rotterdam ans Stockholm Conventions, 4-15 may 2015, Vol. 15, No. 230, p. 14-15, p. 35

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2. 27 substances - or 75% - are also found in waste samples from the landfill.[16]

We assume that the normal operation probably takes place via upper aquifer (Rhine gravel and pulverized limestone) to the east and west edges and via deeper layer from dirty groundwater from the chemical landfills Feldreben can get into the drinking water.

In case that the Rhine water is not available for a longer period, for example, due to an accident in a nuclear power plant or because of a chemical accident upstream of the Rhine, the contaminated groundwater from the landfill flows directly back to the drinking water wells - same as before the pumping of Rhine water in1959. Probably this leads to a strong pollution, if not destruction of the now-built drinking water treatment plants, which were built for around 40 Million Euros after the Greenpeace monitoring results in 2006 where published.

In Switzerland, chemical landfills which have a negative impact for more than two future generations are supposed to be fully excavated. What is almost completed in Bonfol and Kölliken - excavation, w´should also happen at their predecessor's landfill, namely the chemical landfill Feldreben in the canton of Basel-Land.

But: the industry does not want a complete excavation at the Feldreben landfill for about 700 Million Swiss francs. How they want to avoid a total remediation was described by one representative of the Chemical and Pharma companies in an industry-internal Mail from December 2002: «Important is [...] the Canton has its share for further clarifications.» Then «the Canton will consider twice [...] what it requires in the Environment Department Basel-Land, if they have to co-finance (from the same directorate).»[17]

And indeed in 2010 the following actions take place:

1. The canton of Basel-Land buys in 2010 the chemical landfill Feldreben for 22 million euros from a small company.[18] With this acquisition the state takes over the risk for a total remediation of 500 to 700 million euros.
2. At the same time, the state received from Ciba (now BASF), Novartis and Syngenta EUR 20 million for the drinking water systems.[19]

The canton of Basel-Land aims now for the chemical dump Feldreben only a partial excavation.[20] In this way BASF, Novartis and Syngenta have (almost) achieved their goal: The canton does not want to excavate the entire chemical waste quantity. But this partial excavation does not solve the problem of the Feldreben landfill. The threat for the drinking water still exists, for example, due to the estimated 1.4 tons of chlorinated butadienes, which remain as a continuing leaking reservoir inside the landfill.[21]

Therefore, we will in the next step initiate legal steps to enforce a complete excavation of the chemical waste of Feldreben landfill. It is the only way to definitively and permanently solve the problem.

By the way: The residents of the state Basel-Stadt are drinking most of this drinking water. This population has consumed for at least 30 years Hexachlorobutadiene and Tetrachlorbutadiene (and other pollutants) via drinking water. Hexachlorobutadiene and Tetrachlorbutadiene are persistent and accumulate in the fatty tissue. This was the reason to list hexachlorobutadiene in May 2015 in the Stockholm POPs Convention. The government of the canton Basel-Stadt refused in December 2014 to carry out mother's milk analysis.[22] Thus, although, this is most unlikely, it remains unknown, whether the mother's milk in the Basel region is contaminated with chlorinated butadienes via drinking water.

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NATIONAL POPS INVENTORIES AND NIPS – USEFUL TOOLS OF THE STOCKHOLM CONVENTION VS. PROBLEMS WITH PREPARATION AND REALISATION

SUBMITTED PAPER

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Abstract

We have a lot of problems with the state of our planet's environment, we have problems with chemicals on the planet with their often highly complex mixtures.These problems pose a risk to the long-term environment and human health. Addressing these issues requires a broad and highly effective international cooperation. Despite tremendous efforts, a number of activities and projects well done, the key question is whether the effectiveness of activity of the international community in the UN would not be significantly higher. It is extremely important to have perspectives from the current economic crisis, critically evaluate the relationship between funds spent and the results obtained. It is necessary to critically evaluate the relationship between the resources embedded in the organization of conferences, expert meetings, workshops, tours (sitting time) and resolution procedure in individual countries (resolution time). How to carry the participation of representatives of each country largely funded from international resources to solve problems in these countries. It is necessary to critically assess whether it would be possible these (sitting) resources better invested in solving problems, solving specific problems in individual countries.

Key Words

Effectiveness evaluation of the Stockholm Convention measures, inventories, NIPs

Materials and methods

The effectiveness evaluation of the POPs inventories and national implementation plans as very important tools of the Stockholm Convention on persistent organic pollutants were analysed. This analysis represents the overview of personal experiences of author from the evaluation of the different inventories and NIPs.

Results and discussion

Effectiveness evaluation:

- elimination (destruction) of obsolete amounts of chemicals (OCPs, PCBs)
- elimination of sources of POPs
- remediation of contaminated sites
- decreasing levels of POPs in environmental matrices and human (global, regional, local scales)

Possible objective indicators:

- produced amounts
- imported amounts
- used amounts
- unused, obsolete amounts
- emitted amounts, releases
- contaminated sites
- environmental levels

Evaluation of the POPs inventories:

- availability and validity of the information concerning to the old POPs
- quality of the source inventories – availability of information concerning to:
  - industrial production
  - agricultural usage
  - industrial usage
  - emission of by-products
- validity of emission inventories
- relevance of the historical information concerning to the production, export/import, usage
- quality of available concentration data
- ability of country to evaluate effectiveness of the SC measures on the national level
- availability and validity of the information concerning to the new POPs
- very limited number of countries prepared upgrade and actualization of the inventories – annually from 2002 the Czech Republic only.
- in some countries we have separate POPs inventory, in some countries the inventory is a part of NIP,
- in very limited number of countries the national POPs inventories are publicaly available – agan the CR – every year upgrade is presented as a part of POPs portal GENASIS.
- validity of the inventory and NIP information – availability of the fundamental information concerning to the production, usage, disposed and obsolete wastes, quality of statistical parameters, usage of expert judgment, default values of emission factors for the emission inventory; validity of information concerning to environmental and human levels – in some cases the analysis which were used for the national inventory were performed by the unacceptable analytical methods – packed columns for the determination of PCBs and OCPs or without any QA/QC system etc.
- effectiveness of the using of the financial budget –

how is the ration between financial input and quality of results ?

The results of inventories:

The use and releases of chemicals in agriculture is proportional to the land for farming in the recipient countries – valid for the fertilizers, herbicides; POPs pesticides were/are mainly insecticides with limited area of application which is not connected with the agricultural productive land.

The consumption and/or environmental releases of industrial chemicals and un-intentionally produced chemicals is linearly correlated with industrial development (with the value added in industrial sectors) – valid generally for PCBs, in the case of HCB the industrial production and application is connected with the existing chemical industry, other HCB sources is agricultural application, emission from waste combustion and military application.

In the case of new POPs – PeCB – similar case as a HCB; chlordecon – pesticides with the limited application; opposite case – HCHs – very broad production, application, a huge amount of obsolete HCHs, very broad range of production and application from the global point of view; brominated compounds and PFOS – different case – production and direct application is connected with the industrially developed countries; the rest of globe – the use of products with the limited and specific contents of these chemicals (computers, carpets, many other very specific application).

Other problem is connected with the un-intentionally produced POPs (PCDD/F) from the open burning (illegal, accidental) – more important in the less developed countries without legislative approaches to the home open burning of any wastes, garden wastes, etc. Emission factors based on the experimental measurements are probably overestimated. Number and range of forest and bush fires is unpredictable.

The use of chemicals in other sectors such as commercial and transportation sectors linearly correlated to the industrial sectors of the countries – no direct correlation with POPs with exception of PCDD/F – emission from old cars. Other uses of chemicals such as in the health sector will be captured by above mentioned indicators – DDT, HCH, anti termites substances – connected with some campaigns or limited areas of application.

Different range of POPs concentrations – million tons of HCHs, huge amounts of DDTs and some other OCPs, near to two millions of PCBs which were produced and used with small application amounts of PFOS, PBDEs – very problematic for any parameterisation or comparison.

Statistical information – different temporal and spatial validity – some OCPs were phased-out sometimes even decades ago and we have now in some cases less relevant data connected with former producers or distributors, continuous releases. Similarly for PCBs.

NIP evaluation

Elements for evaluation:

- Legislative and regulatory framework in place for the management of POPs, and the sound management of chemicals in general, in supported countries
- Strengthened and sustainable administrative capacity, including chemicals management administration within the central government in supported countries
- Strengthened and sustainable capacity for enforcement in supported countries
- NIPs submitted to the Stockholm Convention
- POPs phased-out from use (tons and cost per ton per compound)
- POPs phased-out from production (tons and cost per ton per compound)
- POPs destroyed in an environmentally sound manner (tons and cost per ton per compound and per mode of destruction)
- Reduced exposure to POPs, measured as number of people living in close proximity to POPs wastes that have been disposed of or contained
- Number of environmentally sound alternative products, practices, or techniques demonstrated that are efficacious and cost effective, out of the total number demonstrated

NIPs evaluation considerations:

- acceptance
- realization
- evaluation
- WEOG – using of experiences
- CEECs – EU/non EU members + big/small countries
- Asia – big countries with intensive production and application/small countries without any own production
- South and Central America – big continental countries/small ones/islands
- Africa – north/equatorial/south part – my limitation – language – I am able evaluate only English written NIPs.
- the fundamental indicator – if the NIP is a living document – periodic review or actualization based on the 4th COP conclusions; if the NIP is respectable document which was accepted by the national authorities and the measures and conclusion are realized and control

NIPs evaluation

Very different levels of the available NIPs – a lot of formalisms

One the other hand some countries did not describe this introductory part so detailed and in these cases NIPs are much more comprehensive with adequate level of information and readable.

Other problem is in many cases very high overestimation of potential financial support, quite unrealistic, out of eco-

nomical reality of the countries and globe. The evaluation of NIPs conclusions will be useful to focus on the realism of the conclusions, in many cases a lot of meetings and trainings is mentioned, in many cases with overestimated proposed budget. Only small number of countries performed as a part of NIP any broader set of analysis.
Essential conclusion for the future similar project – it is a necessary very carefully and strictly evaluate the effectiveness of the use of budget, in this step of NIPs development it was very formal from the side of implementing agencies. The level of NIP action plans and activities realisation is very low – in many countries less than 10 %. NIP is prepared but nobody worked with this document – there is no regular, annual control. In many countries – organisation structure is missing or non-effective.

Conclusions

Inventories:

- A lot of uncertainties in the inventories
- Uncertainty in activity rates of some sources (secondary metal production, open burning processes, fire accidents etc.)
- Uncertainty in some illegal activities (use of waste oils, open burning of agricultural residues and wastes)
- Uncertainty in some emission factors (lack of national data)
- Uncertainty in national statistics
- Lack of recent data
- Establish the permanent inventory teams and defined their work including time schedule of their work with define outputs

NIPs:

- Lot of formalism
- Absolutely unrealistic conclusion prepared using the copy-paste of Guidelines
- Absolutely unrealistic financial considerations
- No country financial contribution, only waiting for the international support
- Bad ratio between the financial input and process outputs
- Very low level of NIP measures realisation
- Departmentalism in the countries

General:

- How many times were POPs discussed in these bodies ?
- How many times were discussed the NIP 2010 during the meetings of Government including the budget discussion.
- In the many countries the POPs issue is based on the project base – how is the effectiveness of the use of these projects measures and results, what happens with the project topics after end of project
- How many percentages of action plans/activities form the first phase of NIP were realised – how many times it was evaluated on the Governmental/ministerial levels
- Long is recognized very bad work of the National Focal points – how this problem was solved ?
- Have the countries developed effective environmental inspection system including the financial penalty system ?
- Do countries prepare annual POPs situation report for Government
- How is the feedback of the participation of the country representatives on the COP, SC expert bodies etc.

Acknowledgements

Thanks to all round the Globe who participated on the development of the national POPs inventories and National implementations plans.

WASTE & SOIL TECHNOLOGIES

RNIP (REACTIVE NANO-SCALE IRON PARTICLES) SUCESSFULL CASE APPLICATION FOR HCH DECHLORATION IN SARDAS CONTAMINATED SOIL. SABIÑÁNIGO (ARAGÓN, SPAIN)

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Abstract

RNIP (Reactive Nano-scale Iron Particles) have been used for several years for soil and water decontamination. Their performance is similar to iron microparticles barriers but due to their nano-size they can be injected as a liquid and act as an active decontaminant.

Each RNIP particle has an inner core composed by reactive zero-valent iron. Inner core is coated by an iron oxide shell which provides oxygen insulation making it safe handling. Once nanoparticles are spread or injected in the polluted soil or water, each iron atom from the inner core oxidizes yielding 2 or 3 electrons. By this way a highly reductive medium is getting where RNIP was injected. Under these conditions, oxidized heavy metals are reduced to their elemental state and organo-chlorinated solvent molecules suffer a dechlorination by link breakdown between Chlorine and organic part of the molecule; by this way, dangerous and recalcitrant pollutants as HCH are decomposed into non recalcitrant and non bioaccumulative substances.

In this paper we expose main lines of the RNIP applications we have been doing in Sabiñánigo area (Spanish Pyrenees, Huesca), where huge amounts of Lindane production residues were dumped till 90´s.

Different concentrations of RNIP slurry have been applied in different soil lots. Soil material was obtained from the Sardas dump site lowest area. Each lot has been insulated by using high density PET and separated from each other. RNIP slurry application technique was sprinkling showing while mechanical mixing of soil was done till full homogenization by backhoe and/or rotovator machine.

First pilot tests gave results about 85% total HCH isomers degradation during first 30 days.

New RNIP applications are being done in Sardas dump site area during 2015 summer. These applications have been designed and calculated based in first applications experience. In September 2015 pilot applications will be ended and it is expected that the conclusions from this application let to calculate a total remediation of the Sardas dump site lowest part, the most vulnerable site in the area due to its proximity to Gállego River.

Key Words

RNIP, HCH, Lindane, Sabiñánigo, Sardas, chemical reduction, dechlorination, nanoparticle.

Materials and methods

Zero-valent iron particles have been used successfully in the past as passive reactive barrier to control or restrict organochlorinated soil contaminated areas. Reactive Nano-scale Iron Particles arise as an active method which let to use zero-valent iron as a liquid, injecting or mixing it with contaminated soil or water. Wider range of chlorinated hydrocarbons may be dechlorinated by using RNIP: Chlorinated methanes, ethanes, benzenes, phenols and other.

Product´s reactivity is due to its Fe0 core. The 2 or 3 electrons each iron atom yields when it´s oxidized generate a chemical reductive medium, decomposing organochlorinated solvents into most elemental, non recalcitrant and non bioacumulative substances.

Due to their extremely small size (70 nanometers diameter), RNIP nanoparticles have a huge specific surface (30m^2/g) which confers them an extremely reactive properties.

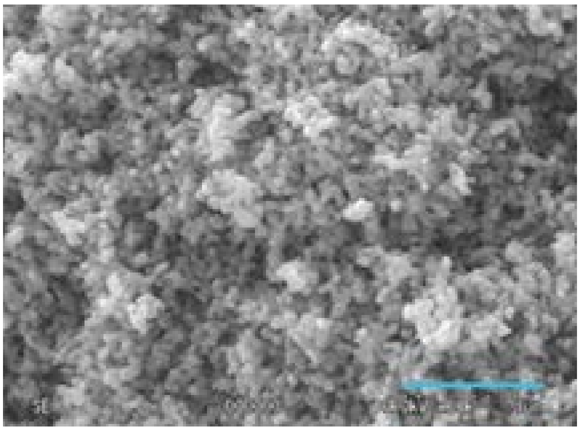


Figure 1: TEM picture of RNIP.

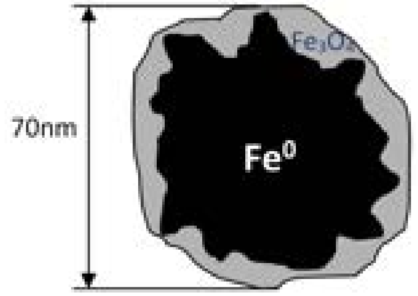


Figure 2: Schematic RNIP nanoparticle structure

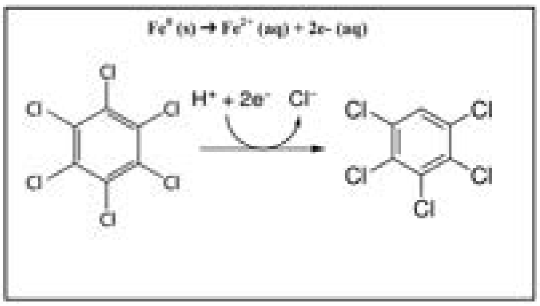


Figure 3: Dechlorination process due to two electrons yielding because of an iron atom oxidation.

During 70´s, 80´s and early 90´s several tons of Lindane production residues were dumped in Sabiñánigo surrounding area. One of the most affected dumping areas was Sardas landfill where thousands tons of HCH isomers where mixed with all kind of industrial and domestic waste. Nowadays, this dump is partially covered but lower area is constricted between general road and Gállego River (Sabiñánigo Reservoir). In this lower area, HCH residues are mixed with soil in concentration 1,000-2,000 mg/kg.

Subsoil is formed by a variable depth brownish silt soil demarcated by a grey tertiary marl bedrock extensively fractured.

During 2011 summer, a 100 soil tons pilot test was disposed in the area using contaminated brownish silt from the area. The homogeneous amount of silt was separated into three sectors, 33 tons each one. Each sector was analyzed in order to characterize organ chlorinated compounds initial concentration. Sectors were denominated as "Sector A", "Sector B" and "Sector C".

RNIP was provided by Toda-Kogyo Corp. (Japan), 73.5 kg of RNIP in total. Product was spread in two different applications. First dispersion of RNIP in water was 49 kg and initial produced slurry was 17.5 Kg in total and were dispersed in water by using a special device for correct and homogeneous dispersion. Initial slurry concentration was 17% in water. It was stored in 30 liter steel barrels under N2 protective atmosphere and transported to Sardas. Water used to produce initial dispersion was just fresh drinkable tap water (Approximate properties: Conductivity 800µS/cm; free Chlorine 0.5mg/ l).

AMOUNTS OF RNIP APPLIED			
	Sector A	Sector B	Sector C
First Application	25Kg RNIP	16Kg RNIP	8Kg RNIP
Second Application	12,5Kg RNIP	8Kg RNIP	4Kg RNIP
Total Applied	37,5Kg RNIP	24Kg RNIP	12Kg RNIP

Table 1: Amounts of RNIP applied per each Sector and per each application done.

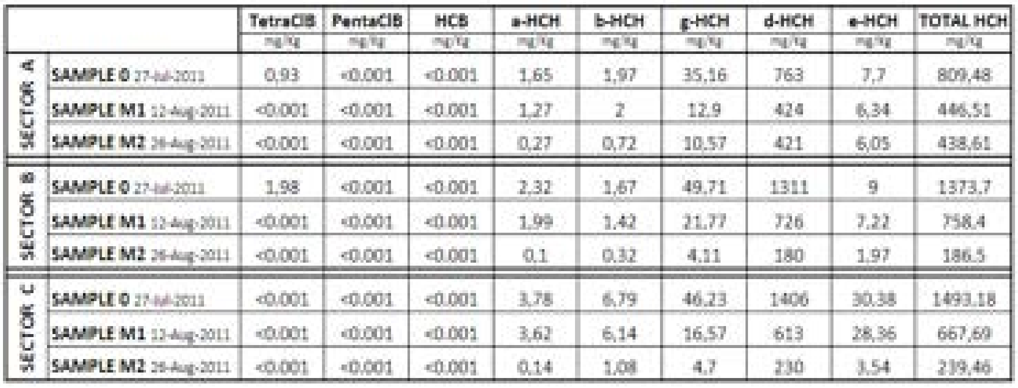
Once in Sardas site, 17% RNIP Slurry was diluted till 0.8% RNIP in water by using a portable dispersion unit equipped with an electric mixer. 0.8% concentration product was directly used for showering pilot test as Table 1. Portable dispersion unit pump was also used for pumping slurry during showering process.

Second application was done 15 days after first application.

Soil samples from each sector were taken into 1x1 meter net knots as a representative sampling of every Sector. Just before second RNIP application, Sectors were sampled. 15 days after second application Sectors were already sampled.

Analytical method used for soil samples was gas chromatography and were done by *Inserco Laboratorios* (Zaragoza, Spain).

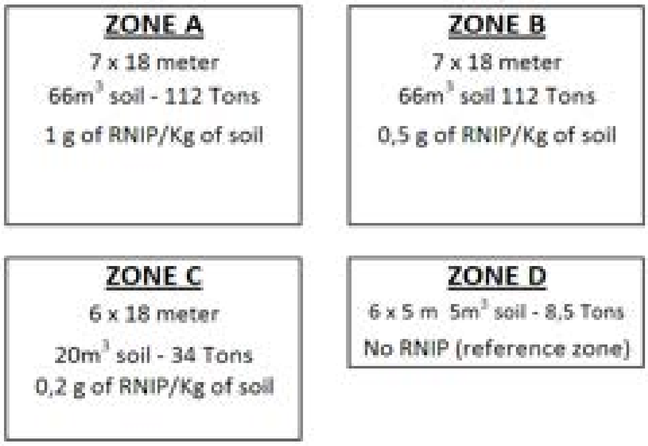
Total experiment was designed for three months but was needed to be dismantled because of external causes. Despite of this, in just one month, total HCH degradation rises 85%, as can be compared in Table 2.



		TetraClB mg/kg	PentaClB mg/kg	HCB mg/kg	a-HCH mg/kg	b-HCH mg/kg	g-HCH mg/kg	d-HCH mg/kg	e-HCH mg/kg	TOTAL HCH mg/kg
SECTOR A	SAMPLE 0 27-Jul-2011	0,93	<0.001	<0.001	1,65	1,97	35,16	763	7,7	809,48
	SAMPLE M1 12-Aug-2011	<0.001	<0.001	<0.001	1,27	2	12,9	424	6,34	446,51
	SAMPLE M2 26-Aug-2011	<0.001	<0.001	<0.001	0,27	0,72	10,57	421	6,05	438,61
SECTOR B	SAMPLE 0 27-Jul-2011	1,98	<0.001	<0.001	2,32	1,67	49,71	1311	9	1373,7
	SAMPLE M1 12-Aug-2011	<0.001	<0.001	<0.001	1,99	1,42	21,77	726	7,22	758,4
	SAMPLE M2 26-Aug-2011	<0.001	<0.001	<0.001	0,1	0,32	4,11	180	1,97	186,5
SECTOR C	SAMPLE 0 27-Jul-2011	<0.001	<0.001	<0.001	3,78	6,79	46,23	1406	30,38	1493,18
	SAMPLE M1 12-Aug-2011	<0.001	<0.001	<0.001	3,62	6,14	16,57	613	28,36	667,69
	SAMPLE M2 29-Aug-2011	<0.001	<0.001	<0.001	0,14	1,08	4,7	230	3,54	239,46

Table 2: Analytical results of pilot test.

Currently (June 2015) a new pilot test is being done in Sardas dump by pooling and improving previous experiences from last pilot test:
Four different sectors have been disposed with similar soil as in previous tests, isolated with high density polyethylene HDPE sheet as shown:



ZONE A
7 x 18 meter
$66m^3$ soil - 112 Tons
1 g of RNIP/Kg of soil

ZONE B
7 x 18 meter
$66m^3$ soil 112 Tons
0,5 g of RNIP/Kg of soil

ZONE C
6 x 18 meter
$20m^3$ soil - 34 Tons
0,2 g of RNIP/Kg of soil

ZONE D
6 x 5 m $5m^3$ soil - 8,5 Tons
No RNIP (reference zone)

Project will be finished at the end of September 2015.

Soil samples free of organochlorinated compounds but geologically and edaphologically identical have been taken from an adjacent plot for total Fe analysis and Fe^0 consumption in absence of HCH.

Results and discussion

Stoichiometric calculations tell us 1 g of RNIP is composed by 0.9 g of Fe0 approximately (1.8066x1022 electrons yielded) and Sardas soil decontamination has a standard concentration of 1.000 mg organochlorinated compounds per kg of soil (1,27x1022 links chlorine-cyclohexane).
It´s necessary to remark that soil homogenization process stimulates decontamination process and reductive medium generated also stimulates bacteria and other microorganism growth which can contribute to organochlorinated compounds degradation. Previous experiences tell us all of this factors work synergistically to generate organochlorinated compounds degradation higher than can be expected just by stoichiometric calculations.
Despite of this, organochlorinated compound degradation experimented in first experience in Sardas pilot test was the best for 0.73g of RNIP per kg of soil (Sector B); better results than for the case of Sector A, with a concentration of 1.13g of RNIP applied per kg of soil. Because of those results, in 2015 pilot test clean soil is being taken into account for total Fe inherent concentration and a small area with same polluted soil has been considered in the test for natural soil evolution control.
Laboratory tests have been done by adding small amounts of Transition Metal catalyst; chlorinated compounds degradation is much faster but catalyst price only allows use it for special treatments as emergencies or uncontrolled escapes in exceptional cases. But this possibility confers an added value and opens a new door for RNIP applications.

Acknowledgements

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SOIL RE-USE AFTER THERMAL DESORPTION TREATMENT. THE DUTCH APPROACH

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Abstract

Many people view hazardous waste as a considerable threat to our environment. However, this is an unavoidable consequence of our way of life. Since we want to live in a clean world, this waste must be managed and treated in an appropriate manner and this is what ATM has made its particular area of expertise. Although this is not an activity with an attractive image, it does have major social importance.

ATM, located in Moerdijk, The Netherlands, operates 24 hours a day and primarily processes contaminated soil, hazardous waste, such as household chemical waste, industrial waste and ship-generated waste, as well as wastewater/sludge. ATM processes 1.8 million tons of waste every year, more than 90% of which is made suitable for reuse as a product or raw material. The quantities processed make ATM one of the biggest processors of hazardous waste in the world. Waste processing at ATM is all about achieving the right balance between safety, expediency, efficiency and care for the environment.

Contaminated soil is the biggest waste stream cleaned and remediated at ATM. Contaminated soil is released when remediating old factory sites, such as gas works and oil-storage buildings, but also from current-day contamination caused by spillage and leaks involving oily products. ATM also processes sand, soil and bricky waste streams. Examples are contaminated rubble, blasting grit, sieve sand, RKGV (sewer sand, drain sand, ground sand and sweeping sound) and matured dredge spoil.

ATM owns a thermal cleaning installation consisting of a rotating drum that is 49.5 meters long and 4.5 meters wide. The drum operates at a high temperature, enabling organic contamination to be separated from the soil, and be completely destroyed in the after burner. The gas scrubbing system removes dust and inorganic components. After treatment the clean soil will be used as an official certified material. The treatment capacity is 1.2 million tons.

As far as waste management is concerned, the Netherlands has one of the strictest regulations in the world. Lack of space and a growing environmental awareness forced the Dutch Government to take measures early on to virtually eliminate land filling of waste. This in turn gave companies the confidence to invest in environmentally friendly solutions. The Dutch approach resulted in technological progress and gave Dutch companies a head start to commercialize their products around the world. Today more than 80% of the waste in the Netherlands is recycled, 16% incinerated and only a small fraction of 4% of the waste produced is land filled.

Key Words

Thermal desorption; contaminated soil; recycling; re-use; hazardous waste; thermal cleaning; site remediation;

Results and discussion

TECHNOLOGY EMPLOYED: THERMAL DESORPTION.

The thermal decontamination plant (TRI) has been designed for the thermal treatment of soil, rubble, asphalt containing tar (granulate and lumps) and other materials that have become contaminated with organic components (e.g. oil, solvents, PAHs (polycyclic aromatic hydrocarbons), BTEX (benzene, toluene, ethyl benzene and xylenes) etc.) or cyanide. Examples include petrol stations, underground oil tanks, former gasworks and industrial areas zones. Even today, soil contamination still happens occasionally, particularly as a result of incidents. Much of this contaminated soil has been contaminated with oil and chemical substances that have to be ‘burnt clean’ at a high temperature in a thermal plant.

Another waste substance that has to be cleaned in a thermal plant of this nature is Tar Asphalt Granulate (TAG), which is used in road building. This is the asphalt that is released when asphalt roads are removed or repaired, when tar has been used as the binding agent in the asphalt. There are also other contaminated mineral waste substances that have to be thermally remediated; these include sweeping sand and sieve sand.

ATM has had a thermal remediation plant for the remediation treatment of these waste substances since 1985. In 2003, the capacity of the thermal remediation plant was increased to one million tons per year, making it the biggest plant in Europe. The core of the plant is formed by a centrifugal furnace that is 49.5 meters long and has a diameter of 4.5 meters. Oil heaters are placed on both sides of this furnace, which ensures that a high temperature is achieved in the furnace. Conveyor belts are used to feed the contaminated soil into the furnace and the turning movement ensures that the soil moves slowly towards the other end of the furnace. The heat causes the water and the contamination from the soil to evaporate, which means that only remediated soil is left. This remediated soil is suitable for use as sand or as a building material, particularly in road building and groundworks. Any rubble or gravel present is sieved out and collected separately and is also reused as building material. Both the process and the remediated products are certified in line with national assessment guidelines (Nationale Beoordeling Richtlijn (BRL)) 7510 and 9335. This means that ATM is a processor that has been recognised by the Ministry of Housing, Spatial Planning and the Environment in the context of the statutory regulation on quality assurance in soil management (KWALIBO-regeling).

The contamination and waste gases are exhausted out of the furnace and are incinerated in an after-burner, after which the waste gases in dust filters and gas washers are cleaned. As such, all permit requirements applicable for the emissions into the air are met; this is measured continuously for the various substances. The contamination from the waste gases is bound together in the so-called waste-gas residue. This is the only residue from the plant; it is transported to a tip as a waste substance.
The thermal remediation plant uses fuel, which is recovered entirely from oily waste and paint waste that are processed in the other plant at that ATM has. Because of this synergy between the different plants at ATM, no new fuel is needed to heat the thermal remediation plant. Heat is also recovered using a steam boiler; the steam generated is used in the other plant as well

QUALITY ASSURANCE

ATM is certified in accordance with National Evaluation Guideline 7510 for Soil Processing. ATM is recognized by the Netherlands Ministry of Housing, Spatial Planning and the Environment as an approved processor in accordance with the KWALIBO scheme and is registered under the following number: MEM-00161-03403.

PROCESSING METHOD AND ADDITIONAL USE OF DECONTAMINATED SOIL

Following acceptance checks, contaminated soil is mixed with similarly contaminated soil to form processing clusters. These are then decontaminated using the thermal cleaning plant. Once decontamination has taken place, the soil is then tested and the possible uses of the decontaminated soil are determined.
There are three possible uses for decontaminated soil:

- Use of the decontaminated soil on, or in, the ground (see Picture 1) .In this case, the decontaminated soil must satisfy the applicable regulations (Construction Materials Decree or Soil Quality Decree)

- Use of the decontaminated soil in the production of pre-shaped building components (decontaminated earth is rendered immobile). In this case, the pre-shaped building components must satisfy the applicable regulations (Construction Materials Decree or Soil Quality Decree).
- Use of the decontaminated soil outside the Netherlands. This may well take place in the country of origin, or another country. In this case, the decontaminated soil involved must satisfy the relevant national regulations. A separate permit under the European Regulation on the Supervision and Control of Shipments of Waste is also required.
- All three of these applications comply with the indicated methods of recovery (R12 + R5) and disposal (D10) (this applies in the case of material that is contaminated with PCBs > 3.5 mg/kg).

Picture 1. Use of decontaminated soil in civil engineering works

DESCRIPTION OF IMMOBILISATION

"Contaminants" in the relevant consignments of soil are immobilized through the addition of additives. This means that the contaminants are held in place through the use of chemical and/or physical techniques. This occurs by binding the contaminants to additives in the soil or by reducing the water permeability of the soil itself.

In this way, the relevant consignments of soil are rendered suitable for recovery within the framework of current legislation and regulations. The additives employed are typically made up of natural substances that are comparable to cement.

Note: "immobilisation is accorded equal status to soil cleaning in the National Waste Management Plan [Landelijk Afvalbeheerplan] (LAP 2005).

Recovery

The thermal cleaning of contaminated soil does not generate any residual waste. Based upon the assertion that the contaminated soil represents 100%, 90% of it is recovered (recovery may account for only round about an average of 90%, because the soil is contaminated with approx. 2% organic substances (Hydrocarbons, PAH, etc), which will be fully incinerated in our thermal soil cleaner during the cleaning of the soil. Next to the organic substances there will be some water and dust (8%) which will be fully incinerated as well The organics, water and dust will evaporate and the gasses will be treated in our gas cleaning system. In this case 90% of the total amount of material is recovered.

After cleaning, the soil is used in civil engineering projects, such as the construction of embankments. Any rubble that is dislodged from the ground and then occurs in the soil is graded according to size and is also used in civil engineering projects.

Decontaminated soil that is used in road-building projects forms a replacement for primary raw materials, the price of which can vary according to supply and demand. Normally, decontaminated soil is supplied at around two-thirds the cost of the price of primary raw materials, which normally have a cost price between € 5,00 up to €20,00 per ton.

Picture 2. General view contaminated soil.

DESCRIPTION OF THE PROCESS. MAIN STEPS.

The thermal purification process is divided in the following phases:

The contaminated soil is dried and heated. As a result of this, the contaminants are evaporated from the soil and then transported to a post-combustion step where they are fully degraded.

- After pre-treatment (if necessary), the contaminated soil and broken rubbles are transported to the rotary kilns by conveyor belts. Transport between the kilns is made by screws and gravity.
- In the drying kiln, the soil is heated and then evaporated to avoid any moisture present in the contaminated soil. The main purpose of the drying kiln is to increase the effectiveness, for the heating process that comes after. Any contaminants with a low boiling point are also evaporated at this early stage. The possible gases coming out of this first stage are sent to the gas incinerator.
- The actual purification takes place in the heating kiln, where soil and rubble are heated to temperatures between 450 ºC and 650 ºC. The contaminants are vaporised and partially decomposed. This is due to the fact that the temperature in the kiln is higher than the self-ignition temperature of the contaminants. The flue gas extraction system ensures an under pressured environment that allows to bring the gases to the gas incinerator.
- After cleaning, the hot materials are mixed with water in order to cool and to prevent dust formation.
- The flue gases from the kilns are transported to the incinerator, where the contaminants are decomposed completely.
- After cooling the flue gases via heat exchangers, they go through an electrostatic filter to remove dust.
- Acid contaminant gases, especially sulfur dioxide, are removed by atomization of lime milk into the lime spraying tower.
- Most lime particles are separated in the cyclone and then re-circulated back to the line reactor in order to increase lime use efficiency.
- After the cyclone, activated carbon can be injected in the flue gases to remove specific contaminants like mercury or dioxins.
- Dust, lime and active carbon are removed from the flue gases in the baghouse filter.
- The flue gas fans maintain a slight under pressure environment in the whole installation.

DETAILS OF THE PROCESS DESCRIPTION

- Soil preparation
  The process starts with pre-processing, during which coarse components are sieved out and iron is removed using a magnetic conveyor. Large pieces

of rubble are broken up, in order to prevent coarse materials and solid pieces of metal from disrupting the process or damaging the plant. For the sake of convenience, the term 'soil' will be used, but this also includes TAG/blasting grit and other solid materials.

- In-feed
  The sieve and conveyor belts have been designed for an input of up to 250 tons/hour. The nominal supply rate is 80-200 tons/hour. The moisture content of the input will be 5-40%.
- Calcining kiln
  The calcining kiln is a rotating drum in which soil is placed for one to two hours depending on the speed of rotation. The materials to be remediated are heated directly with burners fuelled by (waste) oil and gas, on both the input and output sides. The final temperature will vary from 450 to 650ºC. The drum has heat-resistant masonry and the required underpressure is maintained by means of the smoke and fire vent, so that all gases and the dust from the calcining kiln are extracted to the after-burner.
  At the end of the drum, a sieving stage takes place, during which the rubble fraction is separated from the sand fraction. (Picture 3)
- Cooling
  In the so-called plough share mixer, the remediated soil is cooled and moistened by the addition of water. This prevents the occurrence of dust emission when the remediated soil leaves the plant. When cooling the soil, steam is generated, which leaves the plant via a dust filter (rotoclone).
  The sieved out rubble is also cooled with water before it leaves the plant.

- After-burner
  The gas exhausted from the calcining kiln passes into the after-burner. This is heated by burners, which are both oil and gas fuelled. The flame temperature in the after-burner is approximately 1500ºC, while the temperature at the after-burner outlet will be at least 850ºC. The oxygen concentration in the waste gases is higher than 6% and the waste gases will remain in the after-burner for at least two seconds.

- Waste gas remediation system
  Emissions from the plant must comply with the norms laid down in the Waste Incineration Decree (Besluit Verbranden Afvalstoffen). A waste gas remediation system is present for this, which guarantees these low emissions. Waste gas treatment consists of a large number of steps.
  After the after-burner, an air cooler and water cooling are used to cool the waste gases to a temperature of <200ºC. Cooling the waste gases rapidly in this way means that the formation of dioxins is prevented.
  The heat from the waste gases is largely recovered using the air cooler (LUVO). This heat is reused for the production of steam and to heat the burnable air required for the burners for the thermal remediation plant.
  After cooling the waste gases, these go through an electrostatic filter, where the dust is removed from the waste gases. This dust is the fine fraction from the remediated soil, which has been transported with the waste gases. The dust collected is mixed with water and taken to the soil cooler.
  After the electrostatic filter, the waste gases are led through a number of washers, which are designed to remove acidic components like CO2, HCl, HF and Hg. After each washer, the waste gases pass through a drip tray. Here, the waste gases are again stripped of dust particles and of droplets of moisture. Ultimately, the waste gases leave the chimney via the smoke and fire vent (Picture 3).
  The thermal remediation plan and waste-gas remediation are carried out in under pressure atmosphere. This is achieved by means of the smoke and fire vent. The waste gases that are discharged via the chimney are monitored continually for CO, SO2, dust, CxHy, NOx, HCl, moisture and O2.

- Emission standards
  Since 2005, concentrations of the components indcated in the table below have not been permitted to exceed the limits stated when off-gassing the thermal remediation plant at the measurement point intended for this purpose:


Picture 3. General view of the TRI

	Daily average standard **mg/Nm3 (11% O2)**
Continuous measurement	
NOx	250
Carbon monoxide (CO)	50
CxHy	10
Hydrochloride (HCl)	10
Sulphur dioxide (SO2)	50
Dust	10 (5)
Discontinuous measurement	
Sum of Cd + TL	0.1
Hg	0.05
Heavy metals	1
Sum of PCDDs and PCDFs	0.1 ng 1-TEQ/Nm3

Picture 4. General view chimney.

- The laboratory
  The laboratory has an important role during the whole process. Analyses are carried out in the laboratory both before and during the process. The final approval of the cleaned soil is given by a third organization in accordance with the Buildings materials regulation.
  The contaminated soil is analyzed in the laboratory for oil, PAH, cyanides, EOX and heavy metals.

Examples of analysis methods:

- total hydrocarbon determination by GC
- cyanide determination after destruction using an auto analyzer
- PAH by HPLC
- EOX using a micro-coulometer
- Heavy metals by XRF or after destruction by ICP.

Picture 5. Sampling on top of a truck at the arrival on the site for delivery.

The contaminated soil delivered to ATM for treatment may contain a maximum concentration of pollutants, to be determined on beforehand (Picture 7)

Picture 7. Truck delivering contaminated soil.

Picture 6. Soil samples in the laboratory for test.

MOBILE THERMAL DESORPTION UNIT:
Small scale contaminated sites solution

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Summary

Laboratory semi-pilot tests of thermal desorption proved its high efficiency in removal of different types of contaminants from different types of matrices. It can be also used for treatment of dangerous substances but for that detailed laboratory research is needed to prevent dangerous situations. Based on results of semi-pilot tests mobile thermal desorption pilot plant with indirect heating system was designed, constructed and tested. Modular system allows high variability especially for off-gas treatment system. Dimensions of the system, its capacity of 1 – 2 tons per hour and low demand of electric power make the unit useable also as a full scale system for remediation of smaller contaminated sites. Functional tests of pilot unit were carried out with pesticides contamination with promising results.

Keywords: thermal desorption, pesticides, mobile unit, POPs

Introduction

Besides of commercial activities DEKONTA is working on development of new innovative technologies. Through years several research projects focused on thermal desorption have been carried out. Based on results of the research projects a mobile unit of continuous indirectly heated thermal desorption technology was designed and constructed. This system has low demand of electrical power and can be powered by diesel generator set.

Thermal desorption is very effective and fast remediation technology which can be used for treatment of various types of contamination – petroleum hydrocarbons, PCBs, pesticides, mercury etc. It removes contaminants from soil, sludge or sediments by heating the input material in “hermal desorber” to evaporate the contaminants. Evaporation changes the contaminants into vapors (gases) and separates them from the solid material. The final temperatures vary from relatively low temperatures up to 600 °C. Thermal desorption itself doesn’t deal with vaporized contaminants so additional technology for off-gas treatment is needed - mostly the incineration or condensation. Incineration destroys evaporated substances, condensation enables to concentrate contaminants and reuse them, recycle them or just radically cut down the amount of toxic waste. In case of chlorinated substances as pesticides or PCBs dechlorination methods as base catalysed dechlorination (BCD) or gas phase catalytic reduction (GPRC) can be used as part of whole technological system.

Research and Development

Thermal desorption research and testing in DEKONTA is mainly focused on system upgrade and lowering of initial and operational costs. Different types of samples are tested to find out if the thermal desorption would be suitable or not. Laboratory or semi-pilot testing can bring valuable information about material behavior, e.g. its tendency for lumping or sintering, and about off-gas quality which can be very important in case of safety.

Set no.	Incoming concentration ENP (mg.kg^{-1})	Pressure (mbar)	Final temperature (°C)	Efficiency (% wt.)	Condensate pH	H_2S (ppm)	SO_2 (ppm)	CO (ppm)
1	166 500	150	355	75	3.2	> 13 000	2 100	5 000
2	203 800	150	352	79	1.6	> 13 000	3 000	2 600
3	102 300	150	356	93	2.7	> 13 000	150	2 500
4	91 400	50	356	98	2.5	> 13 000	3 000	4 000
5	144 700	50	356	99	1.8	> 13 000	500	2 700
6	59 300	50	357	99	3.3	> 13 000	3 100	5 000
7	155 100	50	360	99	3.0	> 13 000	3 000	4 500
8	176 500	800	355	15	2.1	> 13 000	100	1 600

Tab. 1: Semi-pilot desorption trials of acid oil sludge.

Main research testing is carried out in semi-pilot laboratory unit which can be mobilized if needed. Besides standard samples dangerous materials are also tested, e.g. highly flammable samples, acid sludge from petro chemistry with risk of high concentrations of methane and hydrogen in off-gas, NORM containing samples when tests must be carried out on site, PCDD/F containing samples when tests should be carried out on site. Examples of obtained data are shown in tables below - Tab. 1 shows results obtain from testing of acid oil sludge, Tab. 2 show data from testing of pesticides containing soil.

Methane and hydrogen concentrations were held under 2 % vol. by continuous dosing of nitrogen so they are not mentioned in the table.

Set no.	**Incoming concentration** S **OCP** (mg.kg^{-1})	**Pressure** (mbar)	**Final temperature** (°C)	**Efficiency** (% wt.)
1	180	50	350	97
2	365	50	352	98
3	230	50	350	99
4	80	50	351	> 98
5	415	50	353	98

Tab. 2: Semi-pilot desorption trials of pesticides containing rubble.

Mobile unit description

Mobile thermal desorption unit which was constructed in DEKONTA was designed as modular system. This makes the transport and the use of the unit easier because the system is now more variable – condensation module or catalytic oxidation module can be used for off-gas treatment or if needed they can be connect in series. With this the unit can be used for treatment of various types of contaminants without any significant changes in the whole system.

Pilot plant consists of these main parts:

- rotary kiln (Fig. 1)
- off-gas pretreatment (Fig. 2)
- supply unit 1 – nitrogen supply, water supply
- supply unit 2 – control room.

Rotary kiln can continuously process 1 – 2 tons of input material per hour. Off-gas is dusted off by cyclone and fine filter. If needed, off-gas can be cool down by quenching system. Endpoint of this technology can vary according to contaminant type and aim of the pilot test as mentioned above. System can be inertized by nitrogen from one of supply units.

Unit was designed as pilot testing unit and its size is determined by demand of mobility. Still even as pilot scale unit it can be effectively used as smaller sites where excavating and transport of thousands of tons wouldn't be possible. Contaminants can be handled (destroyed or concentrated) on site.

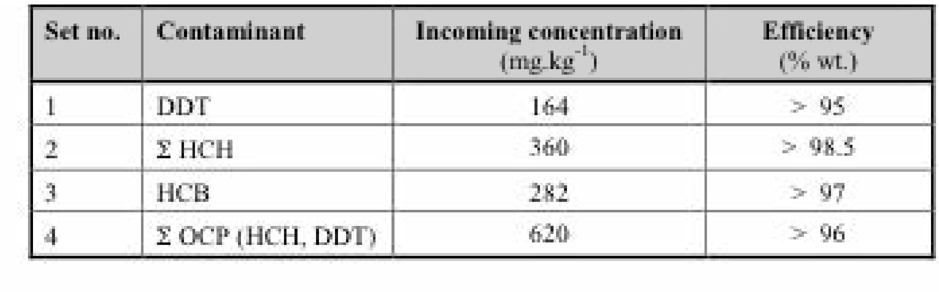
Rotary kiln has these parameters:

- capacity: 1 – 2 tons per hour
- diameter: 1.2 m, length: 8 m
- rotation: 0 – 10 rpm
- indirect heating system
- temperature: 400 -500 °C

Fig. 1 Rotary kiln of continuous thermal desorption pilot unit.

Fig. 2 Off-gas pre-treatment module of continuous thermal desorption pilot unit.

Functional tests prove sufficient efficiency for treatment of different types of matrices contaminated by various types of contaminants. Results from pesticides contamination are summarized in Tab 3. As end-pipe technology condensation was used. Condensate was then treated by incineration. Depending of input properties as moisture content and contamination type pilot unit can be effective solution for some contaminated sites. It can't be used as full scale application for oil sludge lagoons remediation but for some local mercury, PCB or pesticide contamination pilot unit can be very promising – it offers relatively fast and very efficient solution with low initial costs because the unit can be used repeatedly. Operational costs depend on many factors and are specific for each site – mainly on fuel price and its availability, transportation distance and costs and availability of competent subsuppliers.



Set no.	Contaminant	Incoming concentration ($mg.kg^{-1}$)	Efficiency (% wt.)
1	DDT	164	> 95
2	Σ HCH	360	> 98.5
3	HCB	282	> 97
4	Σ OCP (HCH, DDT)	620	> 96

Tab. 3: Desorption pilot trials for pesticides contamination.

Conclusion

DEKONTA has experience with various types of contamination even with dangerous materials explosive or poisonous. Experiences gained through semi-pilot tests were turned into design and construction of mobile pilot thermal desorption unit with indirect heating system. Functional tests proved that unit can be effectively used for treatment of soil contaminated by chlorinated pesticides and other POPs.

PESTICIDE DESTRUCTION USING SUPERCRITICAL WATER OXIDATION

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Article

Supercritical water oxidation (SCWO) is an excellent process for the destruction of old or obsolete pesticides, obsolete paints, petroleum product manufacturing waste streams, pharmaceutical waste, energetic materials (explosives or propellants), flame retardants (containing BTBPE, TBECH, PEBE, TBBPA, and TCEP) and contaminated waste waters.

As described in the abstract, GA uses SCWO as a destruction technology for organic compounds and toxic wastes that makes use of the unique properties of water exhibited at supercritical conditions, that is, temperatures above 374°C and pressures above 22 MPa. Under these conditions, oxidation reactions occur rapidly and to completion with by-products consisting of clean water or brine, clean gases, and inorganic ash with essentially no airborne particulates.

Based on experiences with destruction of chemical agents, GA has developed a simplified, small and compact version of SCWO called Industrial SCWO (iSCWO). The iSCWO process flow diagram is illustrated in Figure 1 and an operational system is shown in Figure 2.

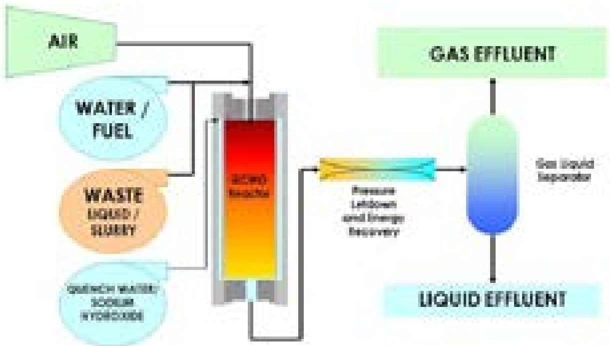

Figure 1 – iSCWO Process Flow Diagram

Figure 2 – iSCWO System Equipment Skid

High pressure air is combined with water, fuel (if required by the specific application) and the waste liquid/slurry that is pumped into the iSCWO reactor where high temperature and pressure will destroy the organic compounds via oxidation reactions. The reaction by-products exit the reactor through a pressure letdown system and discharge into a gas-liquid separator. The gases (CO2, excess O2, and steam) are exhausted through a stack and the liquids (water, dissolved salts, oxidized inorganics) are discharged either into a holding tank or into a commercial sewer system (Public Owned Treatment Works).

A number of these simplified iSCWO systems have been supplied to US Government entities as well as commercial users for the destruction of various chemical and hazardous wastes. The iSCWO system is available as a compact, transportable unit (see Figure 3) or available to be installed in a new or existing facility as a final installation (see Figure 4). The benefits of utilizing SCWO far outweigh the use of alternative waste destruction approaches especially if onsite treatment (or for transportable systems, multiple sites) use is desired. In addition, SCWO systems do not require pollution abatement systems for gaseous effluent cleanup.

Figure 3 – Transportable iSCWO System

Figure 4 – Embedded iSCWO System

GA has demonstrated the destruction of hundreds of organic compounds and mixtures with SCWO technology including pesticides and compounds containing flame retardants (Figures 5 and 6). Shown in Figure 7 is GA's test facility located in San Diego, California, which utilizes a 3gpm iSCWO system. This system is used to test customer wastes in order to demonstrate operability and waste destruction. Effluent analyses (gas and liquid) are performed to confirm high waste destruction efficiencies. The systems built for our customers are put through rigorous acceptance tests prior to shipment. Figure 8 shows a transportable system undergoing final acceptance testing for a European commercial client.

The iSCWO system has a limited number of components which makes maintenance and operation very easy. The control system uses off-the-shelf computer components such as programmable logic controllers (PLC), variable frequency drives (VFD), gas and liquid monitors, and workstation graphic displays for automated operation (calibrate, startup, operation, shutdown) complete with alarms and interlocks. The control system is highly intuitive and can be configured for English or Metric Units, and customized for specific languages.

The installed size of the iSCWO skid is 7.3 meters long by 4.5 meters high and 2.4 meters wide. For the transportable version, the iSCWO fits inside an ISO container that is 8.3 meters long by 2.9 meters high and 2.4 meters wide. Once the transportable unit is at the site, only a small number of equipment components need to be assembled before operation (e.g., heat exchanger).

To adequately treat powdered pesticides, flame retardants and other solid wastes, a front-end feed processing system would need to be incorporated. Preprocessing steps could include size reduction, slurrying, blending, filtering, and other waste preprocessing technologies to produce pumpable mixtures. Once in an acceptable form, the waste feed would be pumped into the iSCWO reactor as shown in Figure 1. The majority of iSCWO systems that GA supplies require some type of up-front pre-processing system to create mixtures that can be delivered to the process in a reliable manner.

Evaluating the implementation of iSCWO as either a transportable system or a fixed site system involves the identification and inventory of the pesticide and other wastes to be processed as well as logistical studies to determine the optimum remediation strategy. This includes performing a mass and energy balance evaluation along with economic, safety and feasibility studies.

The next step would be to perform tests to demonstrate that the iSCWO system can process and destroy the waste, and to collect the test data to support design and permitting activities. While SCWO destruction efficiencies typically exceed 99.999%, the actual requirement is driven by site specific needs especially if the liquid effluent is to be disposed of via the site sewer system. The collected test data will be used to characterize gas and liquid effluent compositions, determine operating conditions, and to quantify utility requirements (electrical power, water, fuel). Included in this analysis is the capital and operating costs of the iSCWO system for the specific waste(s) to be processed.

Organic Chemicals

Acetic Acid
Acetone
Acetylsalicylic acid(aspirin)
Adumbran
4[(2-Amino-3, 5-dibromophenyl)-methylamino]cyclohexanol
Ammonium acetate*
Ammonium formate*
Ammonium oxalate*
Benzene
Biphenyl
Butanol*
Calcium acetate*
Carbon tetrachloride*
Carboxylic acids
Carboxymethyl cellulose
Cellulose
Cerium Acetate*
Chlorinated dibenzo-p-dioxins
6-chloro-2,3,4,5-tetrahydro-3-methyl-1H-3-benzazepine hydrochloride
Chlorobenzene*
Chloroform*
2-Chlororphenol*
o-Chlorotoluene*
Cobalt acetate
m-Cresol*
Cyanide*
Cyclohexane
DDT
Decachlorobiphenyl
Dextrose
Dibenzofurans
3,5-dibromo-N0cyclohexyl-N-methyltoluene-,2-diamine
Dibutyl phosphate
Dichloroacetic acid
Dichloroanisole

Dichlorobenzene
4,4-Dichlorobiphenyl
Dichloroethylene
Dichlorophenol
Diethanolamine*
Dimethylformamide*
Dimethyl methyl phosphonate (DMMP)*
Dimethyl sulfoxide*
4,6-denitro-o-cresol
2,4-Dinitrophenol
Dinitrotoluene
Dipyridamole
Diisopropyl ethanolamine
Diisopropyl ethylamine
Ethanol
Ethyl acetate*
Ethylene chlorohydrin
Ethylenediamine tetraacetic acid
Ethylene glycol
Fluorescein*
Freon 22
Glycerol
Hexachlorobenzene
Hexachlorocyclohexane
Hexachlorocyclopentadiene
Iron acetate*
Isooctane
Isopropanol*
Lead acetate*
Mercaptans
Mercaptoethanol
Methanol*
Methyl acetate*
Methyl cellosolve
Methylene chloride*
Methyl ethyl ketone
Methylphosphonic acid (MPA)
Monoethanolamine*

Nitrobenzene*
2-nitrophenol
4-nitrophenol
Nitrotoluene
Octachlorostyrene
Octadecanoic acid magnesium salt
Paracetamol
Pentachlorobenzene
Pentachlorobenzonitrile
Pentachlorophenol*
Pentachloropyridine
Phenol
Polychlorinated biphenyls (PCB*)
Polychlorotrifluoroethylene*
Sodium acetate
Sodium formate
Sodium hexanoate
Sodium isethionate*
Sodium propionate
Sucrose
Surfactant
Tetrachlorobenzene
Tetrachloroethylene*
Tetrapropylene H
Thiodiglycol*
Toluene
Tributyl phosphate
Trichlorobenzenes
1,1,1-Trichloroethane*
1,1,2-Trichloroethane*
Trichloroethylene
Trichlorophenol
Trifluoroacetic acid
1,3,7-Trymethylxanthine
Unsymmetrical dimethyl hydrazine
Urea
o-Xylene*
Zinc acetate*

Figure 5 – Chemicals Successfully Treated by iSCWO

Complex Feeds

Activated carbon (spent)*
Adhesives*
Aqueous Cleaning Solution*
AFFF
Antifreeze*
Aroclor 1242
Aroclor 1254
Aroclor 1260*
Bacillus stearothermophilus (heat resistant spores)
Brake fluid*
Bran cereal
Caprolactam wastewater
Casein
Chlorinated plastics (shredded)*
Class 1.1 solid propellant*
Class 1.3 AP-depleted solid propellant
Coal
Coal waste
Corn flakes*
Corn oil
Corn starch
Diesel fuel
E. coli
Endotoxin (pyrogen)
Explosives/energetics/propellants (hydrolyzed RDX, TNT, Tetryl, NG, NC)*
Fermentation byproducts*
Fuel oil
GB chemical agent (neat, hydrolyzed*)
Gray water*
Greases (mixed)*
Human waste
Hydraulic fluid*
Industrial biosludge
Ion exchange resins (styrene - divinyl benzene)
Kerosene*
Lube oil (molybdenum disulfide oil)*
Malaria antigen
Motor oil*
Mustard chemical agent (neat, hydrolyzed*)
Navy shore-based wastes*
Olive oil
Organic salts (complex mixtures)*
Paint, paint sludges*
Paper
Paraffin oil
Pesticide manufacturing wastewater
Pharmaceutical waste*
Photographic developer paste
Photographic developer solutions*
Polychlorotrifluoroethylene (PCTFE)*
Pig manure
Propellants (hydrolyzed)*
Protein
Pulp/paper mill sludge
Sewage sludge (black water)*
Soil contaminated with organics
Soybean plants
Sulfolobus acidocaldarius
Transformer oil*
Trimsol cutting oil*
VX chemical agent (neat, hydrolyzed*)
Waste oils (chlorinated and non-chlorinated)*
Wheat straw*
Wood fibers
Yeast

Inorganic Substances

Aluminum hydroxide*
Aluminum metal
Aluminum oxide sodium
Ammonia*
Ammonium chloride
Ammonium nitrate*
Ammonium nitrite*
Ammonium perchlorate*
Ammonium sulfate
Ammonium sulfite*
Boric acid
Bromides
Calcium carbonate
Calcium chloride
Calcium oxide
Calcium phosphate
Calcium sulfate
Cerium chloride*
Copper chloride
Fluorides
Hydrochloric acid*
Hydrofluoric acid
Iron chloride
Iron oxide*
Lead chloride*
Lead sulfate*
Lithium hydroxide
Lithium sulfate
Magnesium nitrate
Magnesium oxide
Magnesium phosphate
Magnesium sulfate
Mercuric chloride
Molybdenum disulfide lube oil*
Nitric acid*
Phosphoric acid
Potassium bicarbonate
Potassium carbonate
Potassium chloride
Potassium hydroxide
Potassium sulfate
Silica
Sodium bicarbonate*
Sodium carbonate
Sodium chloride*
Sodium fluoride*
Sodium hydroxide*
Sodium nitrate
Sodium nitrite
Sodium phosphate*
Sodium sulfate*
Sodium sulfite*
Sulfur, elemental
Sulfuric acid*
Titanium dioxide
Zinc chloride*
Zinc sulfate*

Figure 6 – Chemicals Successfully Treated by iSCWO

Figure 7 – iSCWO Waste Test System

Figure 8 – Final Acceptance Test

Once deemed acceptable, the final step would be the design and fabrication of an iSCWO system(s) based on the test results and specific customer requirements (e.g., safety and fabrication standards). Prior to shipment to the customer site, the system would be subjected to final acceptance tests to demonstrate operability and waste destruction efficiencies.

In summary, SCWO technology is an exceptionally clean waste destruction process suitable for destroying all classes of hazardous and nonhazardous wastes especially pesticides and flame retardants. SCWO systems can provide onsite waste treatment at an affordable cost.

IN SITU CHEMICAL OXIDATION FOR PESTICIDES: A REVIEW

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Abstract

In situ chemical oxidation (ISCO) is a developing tool for treating soils, sludges, sediments, and groundwater impacted by pesticides. Its successful use is a function of four factors: the particular oxidant system used; the chemical structure of the pesticide being treated; the presence and nature of other contaminants; and the lithology and mineralogy of the impacted media. There are four oxidants commonly used for ISCO: permanganate (sodium and potassium), hydrogen peroxide, sodium persulfate, and ozone gas. Each of these four oxidants has a variety of application conditions such as pH, or the use of activators (e.g., metal catalysts) that promote oxidant reactivity with particular pesticides. The selection of the correct oxidation conditions is key to the success of ISCO.

The chemical structure and properties of the impacting pesticide have a big role in determining its reactivity to the oxidants employed.. Pesticides that have carbon-carbon double bonds or aromatic rings tend to be more amenable to oxidation than saturated "C-C" structures. The key property of pesticides most affecting oxidation is solubility. Oxidants, for the most part, react in the aqueous phase of the site with the contaminants being treated.

During ISCO, the presence of co-contaminants (e.g., aromatic solvents used as carriers for pesticides) may compete for the oxidant. Treatment of the pesticide may require pretreatment/removal of the carrier to facilitate the effective oxidization of the target pesticides.

Finally, the lithology and mineralogy of the impacted media influence the use of ISCO by affecting oxidant distribution or by affecting the stability of the oxidant. Successful application of ISCO for pesticides is defined as "having enough oxidant in contact with the pesticide for a long enough period of time for it to react effectively."

This paper will discuss these four factors of ISCO use and will provide a weighting of their relative importance to successful application of ISCO. This paper provides a framework for evaluating the use of ISCO for treating different types of pesticides. It discusses laboratory and field data that illustrates successful use of ISCO and its limitations.

Key Words: ISCO, permanganate, persulfate, hydrogen peroxide,

Oxidant Properties

Each of the four potential oxidants may generate a variety of reactive species that can be used to oxidize pesticides. These are summarized in Table1.

Permanganate is the simplest of the oxidants. It has only one reactive species, the permanganate anion (MnO_4^-). Permanganate comes as either the potassium salt or the sodium salt. The only difference in the reactivity of the two salts is their solubility; potassium permanganate has a solubility of 6.8 g/L; sodium has a solubility of 900g/L. There are, based on pH, three reaction pathways for permanganate which are

$3e^{-} + 2H_2O + MnO_4^{-}$ à $MnO_2 + 4OH^{-}$ basic conditions,

$3e^{-} + 4H^{+} + MnO_4^{-}$ à $MnO_2 + 2H_2O$, mildly acidic conditions

$5e^{-} + 8H^{+} + MnO_4^{-}$ à $Mn^{2+} + 4H_2O$,strongly acidic conditions.

Permanganate is generally stable but it can react with reduced species in the soil such as natural organics (humic and fulvic acids) or reduced metals (Fe^{+2}, Mn^{+2}). This can limit its effectiveness. The organic carriers used in crop spraying are aromatic solvents such as xylene which can also consume the permanganate and limit its effectiveness in treating pesticides.

Hydrogen peroxide is a more complex oxidant which can generate a series of free radicals, a number of peroxy-anions based on pH and the presence of transition metals such as iron. The mixture of reactive species is quite complex and can contain both oxidizing and reducing species. Hydrogen peroxide can also form solid peroxygen adduct compounds (e.g., a perhydrate) which can act as slow-release sources of hydrogen peroxide or oxygen.

A primary limitation to the use of hydrogen peroxide is its, often, rapid decomposition. The half-life of peroxide can be as short as a few hours.

Oxidant	**Formula**	**Equivalent Weight**	**Redox Potential**	**Application Conditions**	**Active Species**	**Non-Beneficial Consumption**
Hydrogen Peroxide	H_2O_2	34	1.77	pH = 5 to 10 Activater (Fe)	$HO^\bullet$, HO_2^-, $^1O_2$,	Decomposition
Calcium, Magnesium peroxide	CaO_2 MgO_2	36 – Ca 28 - Mg	0.9^* 0.9^*	pH = 9-11 hydrolyzes to H_2O_2	H_2O_2, O_2	Decomposition
Sodium percarbonate	$2Na_2CO_3$●$3H_2O_2$	52	0.9*	hydrolyzes to H_2O_2	H_2O_2, O_2	Decomposition
Sodium, Potassium Permanganate	$NaMnO_4$ $KMnO_4$	52.7 Na 47.3 K	1.7	Ambient pH	MnO_4^-	Soil Oxidant Demand Reduced C, Metals
Sodium Persulfate	$Na_2S_2O_8$	119	2.01	Ambient pH	$S_2O_8^{-2}$	Decomposition
Sulfate Radical	$SO_4^{\bullet -}$	96	2.6	Heat >40^0 High pH Fe	$SO_4^{\bullet -}$, $HO^\bullet$, HO_2^-,$^1O_2$, $S_2O_8^{-2}$	Decomposition
Ozone	O_3	24	2.07	Gas injection, H_2O_2 Activation	$HO^\bullet$, HO_2^-, $^1O_2$, O_3	Decomposition

**Alkaline pH*

Table 1: Oxidation Systems

Sodium persulfate is the third oxidant system. It is a peroxygen similar to hydrogen peroxide. The hydrogens on hydrogen peroxide are replaced by sulfate:

$$H\text{-}OO\text{-}H \rightarrow O_4S\text{-}OO\text{-}SO_4$$

Like hydrogen peroxide. persulfate can produce a mixture of free radicals including both the hydroxyl radical $HO^\bullet$ and sulfate radical $SO_4^{\bullet -}$It can be activated by heat, high pH, the addition of metals (Fe) and also hydrogen peroxide.

Also, like hydrogen peroxide, decomposition is a limit to the use of persulfate. However, persulfate is much more stable than is hydrogen peroxide. Its half-life is on the order of weeks to months. This allows for more effective distribution.

The two most common persulfate systems are base-catalyzed persulfate and thermally activated persulfate. Both react with a wide range of organics.

Ozone is the fourth oxidation system. Ozone is applied as a gas mixture. Typical concentrations range from 3 to 10% in air or oxygen. A variation on the use of ozone is to mix it with a solution of hydrogen peroxide to generate hydroxide radicals:

$$2\ O_3 + H_2O_2 \rightarrow 2\ HO\bullet + 3\ O_2$$

For this process, a solution of hydrogen peroxide is first applied and then ozone is injected.

Ozone has a very short half-life, on the order of a few hours. It does,however react quickly. Ozone sparging distributes ozone over the desired area.

Application to pesticides

The structure and properties of the pesticide being treated have a significant impact on its oxidizability. Based on a review of chemical oxidation results for SVOCs and pesticides, the following generalizations can be made as to amenability to oxidation based on chemical structure:

Amenable to Oxidation

Double bonds (C=C, C=N), Aromatic Rings, Heterocyclic rings with unsaturated bonds, Phenolic compounds

Resistant to Oxidation

Saturated Compounds, Highly chlorinated compounds, Cyclic ethers.

In addition, the chemical properties of the pesticide will also affect its amenability to oxidation, in particular, solubility. With the exception of ozone, oxidants react primarily in the aqueous phase. Ozone also reacts in the vapor phase. The higher the solubility of the pesticide, the greater is the contact between the oxidant being used and the pesticide being treated. This results in greater destruction.

The applicability of the oxidation systems discussed above is variable. Permanganate is the most narrowly applicable, reacting primarily with pesticides having carbon-carbon double bonds. Hydrogen peroxide is highly reactive but is often unstable. The oxidant that shows the best overall performance for pesticides is sodium persulfate. Persulfate generally requires an activator. Table 2 summarizes a study of the oxidation of Lindane (HCH)[1] with persulfate.

Table 2
Oxidation of HCH wit Persulfate

Activator	% destruction of HCH @ 1 day
No persulfate or activator (control)	0
Iron EDTA	4
Temperature 40^0C	95
Hydrogen Peroxide	99
High pH (11)	99

HCH is readily oxidized with the proper activator. The study of HCH oxidation examined a number of persulfate activators including FeEDTA (200 mg/L iron), elevated temperature at 40^0C, hydrogen peroxide with a10:1 mole ratio of H_2O_2 to persulfate, and pH 11.

ISCO was evaluated in a field application for a pesticide formulation site where pesticides were blended with xylene for aerial crop spraying. The site was contaminated with a number of pesticides with chlordane and heptachlor having the highest concentration. Persulfate and hydrate lime were applied on the surface and blended by shallow soil mixing. Soil samples were taken one month after treatment. The results of the treatment are summarized in Table 3.

The site showed substantial decreases in the pesticide levels relative to the untreated controls. Based on these results, alkaline persulfate would appear to have broad applicability to a range of pesticides. It appears to be less dependent on the pesticide structure than other oxidant systems. The other lesson learned for the application of alkaline persulfate is the benefit of using mechanical soil mixing. Soil mixing provides a more uniform application of the alkaline persulfate.

CONSTITUENTS	SOIL REMEDIATION STANDARD (mg/kg)	PRE-REMEDIATION AVERAGE SOIL CONCENTRATION (mg/kg)	POST-REMEDIATION AVERAGE SOIL CONCENTRATION (mg/kg)	REDUCTION (%)
VOCs (SW846 8260B)				
Xylene (total)	12,000	204,600	28,432	86.1%
Pesticides (SW846 8081A)				
Aldrin	40	20,427	10,555	48.3%
alpha-BHC	2	2,048	0	100.0%
gamma-BHC (Lindane)	2	6,043	0	100.0%
Chlordane	100	199,633	32,007	84.0%
Dieldrin	30	8,080	3,166	60.8%
4,4'-DDD	1,000	20,867	5,916	71.7%
4,4'-DDE	1,000	2,489	1,258	49.5%
4,4'-DDT	1,000	97,100	42,887	55.8%
Endrin	600	61,900	22,243	64.1%
Heptachlor	100	104,233	38,073	63.5%
Methoxychlor	390,000	70,033	30,247	56.8%
Total Pesticides		**592,854**	**186,352**	**68.6%**

Table 3 Application of Alkaline Persulfate @ Pesticide Formulation Site

Acknowledgements

The shallow soil mixing data was provided by Kevin Morris of ERM.

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EXPERIENCES WITH IN SITU REMEDIATION OF HEXACHLOROCYCLOHEXANE IN SOIL AND GROUNDWATER

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Abstract

HCH production waste contains liquid benzene, monochlorobenzene and alcohols from the Lindane production process. HCH-isomers and other chlorinated benzenes and cyclohexenes are dissolved in the liquid that has a density of more than 1,3 kg/dm^3, resulting in typical DNAPL behavior. DNAPL-HCH source areas pose a long term threat for aquifer contamination and may threaten surface water quality. MIP (Membrane Interface Probe) measurements were demonstrated as an effective tool for HCH-DNAPL source identification. Most in situ remediation field scale applications focus on the shallow contamination or down gradient groundwater plume treatment. Several chemical oxidation technologies were tested for treatment of HCH DNAPL source with persulfate as most effective oxidant. In our experiments radical scavenging by carbonates naturally present in soil and chlorides may have limited the effectiveness of chemical oxidation in more shallow zones of the subsurface on a test site. On another test location several ZVI formulations were tested for groundwater treatment, and granular ZVI was most effective in chemical reduction of HCH, leading to exclusively benzene as identified end product.

Key Words

HCH, DNAPL, Chemical oxidation, Chemical reduction, Zero Valent Iron, MIP

Introduction

HCH (Hexachlorocylcohexane) is a mixture of isomers, produced by the chemical reaction of benzene and chlorine gas. The gamma isomer, also known as lindane, is a pesticide that is used as insecticide. It is extracted from the mixture of HCH isomers. A high volume of solid and especially liquid toxic waste is produced in the form of HCH isomers and mother- and by-products that are ineffective as insecticide, and has been stored on or near production sites. Liquids have migrated into the subsurface and pose a long term threat to groundwater and surface water quality.

Behavior of HCH in soil and groundwater

HCH-isomers are solid compounds with a low solubility in water and a high affinity for sorption on soil particles. Based on the physical properties of HCH a deep penetration in the subsurface is not expected. However the migration potential of HCH is correlated with the source of the HCH. Two major characteristic sources of soil pollution with HCH can be distinguished, HCH production sites and sites where HCH stored and was applied as a pesticide.

On application in agriculture HCH the migration potential of HCH in the subsurface is limited. 12-30 % of HCH is volatilized after application as a pesticide. Part of the HCH is taken up by crops and distributed into the food chain. Residual HCH is sorbed to soil particles and plants and soil bacteria will take up or transform HCH in the root zone. A study into natural attenuation of HCH[1] on sites with ppb level of HCH in soil revealed only limited migration of HCH and its main degradation products benzene and chlorobenzene into the subsurface.

Production sites pose a different challenge. Residual waste from the separation of HCH isomers and reactor batches have mostly been stored on site. The waste contains liquid benzene, monochlorobenzene and alcohols from the production process. HCH-isomers and other chlorinated benzenes and cyclohexenes are dissolved in the liquid and control the density of the liquid. Generally the mixture of chlorinated compounds has a density of more than 1,3 kg/dm^3 and hence behaves as a DNAPL (Dense Non Aqueous Phase Liquid) in the subsurface. DNAPL may penetrate deep into the subsurface depending on the volume of DNAPL and hence the amount of waste product stored on site. The large amounts of lindane production waste generally stored on production sites result in a high infiltration risk potential.

Once present in the subsurface as a residual DNAPL, HCH will slowly dissolve in groundwater. The DNAPL will act as a long term source of HCH groundwater contamination. Also, the composition of the DNAPL will alter in time. Benzene and monochlorobenzene will tend to dissolve and will be transported down gradient. If a sufficiently low redox potential can be achieved by biological anaerobic degradation of benzene and alcohols, anaerobic degradation processes will lead to dechlorination of chlorinated hexanes, resulting in the production of additional dissolved chlorobenzenes and benzene. In an anaerobic aquifer a plume of predominantly stable monochlorobenzene will grow.

In aerobic aquifers such as weathered and fractured rocks with low bacterial growth capacity a plume of HCH, high chlorinated chlorobenzenes and chlorophenols will be created.

On several sites the groundwater migration of HCH and infiltration of HCH on surface water has resulted in poor surface water quality as a result of the ppt level of EU Water Framework Directive Environmental Quality Standards (Maximum Allowable Concentration 40 ppt). The interface between surface water/sediments and groundwater (hyporheic zone) is capable of acting as a contaminant sink as a result of natural processes. Many hyporheic systems cannot deal with the low biodegradable HCH, and surface water quality may become a trigger for remedial action.

In situ remediation experiences

DNAPL-HCH source areas pose a long term threat for aquifer contamination, yet there have been limited attempts for in situ remediation of these source areas. Most field scale applications focus on down gradient groundwater plume treatment. The presence of DNAPL on HCH production sites poses serious remediation challenges. Biological treatment is not likely to be effective for in situ source zone treatment due to the high contaminant load and the possible toxic effect of the contamination on soil bacteria. As in situ remediation focuses on contaminant elimination by bringing the contamination into contact with materials that react chemically or physically, distribution and contact of injected materials with the contamination is the key issue for a successful remediation. On laboratory scale, under ideal mixing conditions, technologies may appear feasible, but for a succesfull in situ application a thorough understanding of DNAPL and injected material behavior is essential.

The Daramend technology, using a cycled anoxic/oxic and biological/chemical treatment, was used to treat hexachlorocyclohexane (HCH)-contaminated soil on several sites[4]. Although the technology is effective, the application is not considered an in situ treatment source zone methodology. Also phytoremediation has been applied with considerable success, however not in DNAPL source zones.

Remediation of the groundwater from Marzone Inc., Chevron Chemical Company at Tifton (USA) contaminated with α-HCH (60 $mg.L^{-1}$), β-HCH (98,5 $mg.L^{-1}$) and lindane (54,6 $mg.L^{-1}$) has been achieved with a funnel and gate barrier filled with 780 kg activated carbon. The residual concentrations of α-HCH, β-HCH and γ-HCH below the gate are 0,03, 0,1 and 0,77 $\mu g.L^{-1}$ respectively[2].

In the Netherlands a bioscreen for the treatment of HCH contaminated groundwater was tested on a pilot scale in 2001-2004. The 150 meter wide screen for infiltration of organic substrates was installed on a depth of 5 m bgl to create an anaerobic zone in groundwater. The field test demonstrated that the enhanced biodegradation of all HCH isomers resulted in a successful decrease of HCH concentrations and an increase of monochlorobenzene and benzene concentrations in down gradient groundwater. Down gradient groundwater infiltrated on a canal and benzene and monochlorobenzene concentration was effectively degraded in the hyporheic zone[3].

Several in situ source zone technologies have been tested on laboratory scale. Bioremediation of HCH has been studied for groundwater and low concentration source zones. Physico-chemical in situ feasibility treatment studies of HCH have focused on application of zero valent iron and chemical oxidation. Zero valent iron (ZVI) has been applied on several occasions[5] for chemical dechlorination of HCH. The reaction with ZVI results in (chloro)benzene production, and on occasion results in the exclusive end product benzene, which has to be dealt with separately. The technology was tested on pilot scale in Oltchim and TMUCB in Romania[6].

Chemical oxidation focuses on the application of oxidants to in situ chemically destruct HCH and its degradation products. Several oxidants have been applied to test the feasibility but thermally or alkaline persulfate appear most effectively on laboratory scale for HCH. A field scale pilot with alkaline activated persulfate in a fractured bedrock is in preparation at the Bailin site in Spain [EU Life+ DISCOVERED project]. On the site also a DNAPL extraction has been in operation since 2006 and has extracted more than 20 m^3 DNAPL.

Sites under study

At two sites under study HCH was produced and liquid and solid waste of the lindane production was stored on site. Infiltrating DNAPL liquids and rainwater caused a soil and groundwater contamination. The groundwater contamination migrates off site and needs to be captured and treated. The effectivity of two HCH treatment processes were investigated in a laboratory study on the two sites with different approaches:

A. Source remediation by chemical oxidation
B. Plume remediation by chemical reduction by Zero Valent Iron (ZVI).

The results of the laboratory study are presented.

Remediation case A

Site A was characterised by a MIP study (Membrane Interphase Probe). The hypothesis was that not only benzene but also monochlorobenzene would be detected by the MIP sensors that can detect volatile organics and specifically chlorinated volatiles. After the measurements were completed and MIP detectors were withdrawn, the boreholes were filled with a bentonite seal to prevent migration of HCH-DNAPL in the MIP boreholes.

The MIP study clearly indicated the presence of the source areas of the DNAPL contamination (see figure 1 for an example). The DNAPL was distributed heterogeneously under the site.

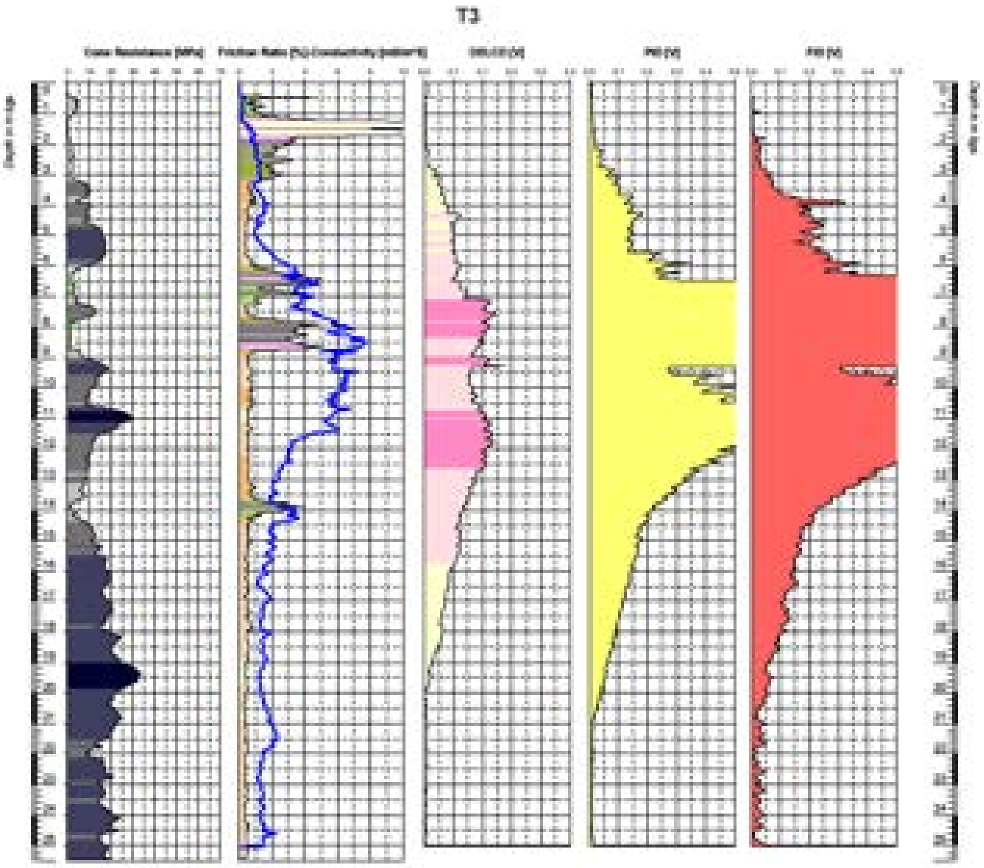

Figure 1 MIP response on a HCH DNAPL. DELCD detector identifies volatile chlorinated compounds, PID detects photo ionisable compounds (most volatile organic hydrocarbons, however not methane) and FID detects flame ionisable compounds (all volatile hydrocarbons)

For a treatment study two different soil samples (B1 at 3,7 – 5.2 m bgl and and B2 at 9,8-12,4 m bgl) were selected to determine the effectiveness of source treatment by chemical oxidation. The soil samples contained 480 mg/kg and 890 mg/kg HCH and were treated in slurry batch experiments by Fentons Reagens (10 % and 20 % H_2O_2), Modified Fentons Reagens (10 % H_2O_2) and persulfate (10, 20 and 40 g/l, non-activated, heat activated and H_2O_2 activated). The maximal reduction of HCH levels is 94 % obtained in the deep sample B2 with 40 g/l (4 %) heat activated persulfate. A reduction of 95 % was obtained by 20 % Fentons Reagens. Modified Fentons Reagens demonstrated a similar reduction. Chlorobenzenes and benzene were removed under these conditions at 93 to 97 %. Sample B1 however demonstrated a very low reduction of HCH, which was contributed to calcium carbonate levels in soil of 8–11 %. Carbonates are well known scavengers of radicals. Furthermore high chloride levels in the shallow groundwater may have contributed to radical scavenging in sample B1.

Remediation case B

On site B the effectiveness of treatment of HCH contaminated down gradient groundwater by chemical reduction with Zero Valent Iron (ZVI) was investigated in a laboratory study. Of three different types of ZVI tested to determine the effectivity of chemical reduction of the HCH isomers in groundwater (granular ZVI, fine ZVI, and nanoscale ZVI) granular and fine ZVI were most effective. The batch tests have shown that ZVI can bring about a fast reduction of HCH to almost exclusively benzene. Using the aqueous phase data from the batch tests, an average half-life of 0.46 day can be estimated for total HCH. Furthermore considerable adsorption of HCH on iron was observed. Granular ZVI was selected for testing in column experiments. After 110 days and 62 pore volumes of flushing, the HCH level was still below the detection limit (0,01 µg/L) and benzene was present in a concentration of 2 µg/L, accounting for only 7.5% of the HCH in the influent. Adsorption to the solid phase will have influenced the effluent levels of HCH and degradation products in experiments.

Conclusions

HCH DNAPL zones can be characterized by MIP measurements. Chlorobenzenes present in the DNAPL can be detected by the MIP sensors. In situ technologies to in situ treat HCH in DNAPL source zones have not yet been demonstrated on field scale. Technologies based on chemical oxidation with activated persulfate are most promising for source zone treatment.

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MCS^{TM} TECHNOLOGY THERMAL TREATMENT SYSTEM DEMONSTRATION TRIAL ON DIOXIN CONTAMINATED SOIL AT BIEN HOA AIRBASE, VIETNAM

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Background

Thermodyne Technologies, Inc. ("TTI"), a specialized environmental remediation technology company based in Charlotte, North Carolina USA and its proprietary Matrix Constituent Separator ("MCS^{TM}") Technology, a unique, award-winning thermal desorption system design, qualified to participate in the Global Environment Facility ("GEF") funded "Environmental Remediation of Dioxin Contaminated Hotspots in Viet Nam" Project. Specifically, TTI and the MCS^{TM} Technology were jointly selected by the United Nations Development Program ("UNDP") as the GEF Implementing Agency in partnership with the Vietnam Ministry of Natural Resources and Environment ("MONRE") acting as the GEF National Executing Agency for the "Treatability Study of Dioxin Remediation Technology to Treat Soil/Sediment in Bien Hoa Airbase, Viet Nam" project. Subsequently, the implementation of the Bien Hoa Airbase Technology Demonstration Trial Project was directly managed by MONRE's Office of National Steering Committee 33 ("Office 33"), Dioxin Project Management Unit ("PMU").

A significant deciding factor for the selection of the MCS^{TM} Technology was its very relevant, real world successful full-scale experience involving the treatment of over 24,000 tons of Agent Orange ("HO")/Dioxin contaminated soil/dredged coral at the United States Air Force Base on Johnston Atoll ("US AFB"), United States Environmental Protection Agency ("US EPA") Region IX Superfund Site. Johnston Atoll AFB, located in a remote region of the South Pacific, was the final resting place for all of the chemical agents (HO and its chemical derivative relatives) removed from Viet Nam during the armed conflict in the 1970's.

Consequently, the MCS^{TM} Technology's proven successful performance on this project treating the same source chemicals responsible for the contaminated soil at the Bien Hoa Airbase provided strong real world supporting evidence to provide TTI the opportunity to demonstrate the MCS^{TM} Technology's capability to replicate these results.

Demonstration trial project objectives

The GEF, UNDP, and Office 33 PMU's major specific objectives of the Demonstration Trial Project were as follows:

- To test the feasibility of the proposed technology to reduce Polychlorinated dibenzodioxins and polychlorinated dibenzofurans ("PCDD/PCDF") in contaminated soil down to the stipulated cleanup targets in an environmentally sound manner;
- To strengthen national capacity to assess, by means of a consolidated Proof of Performance Test, a treatment technology specially addressed to reduce PCDD/PCDF contamination in soil/sediment at Agent Orange/Dioxin hotspots;
- To facilitate the possibilities to further develop more appropriate options for potential remediation technologies that can be applied in Viet Nam in the near future.

Equally important, TTI's primary specific objectives for the Demonstration Trial Project were as follows:

- To demonstrate the MCS^{TM} Technology's capability to replicate and confirm the proven successful treatment results of over 24,000 tons of Agent Orange/Dioxin contaminated soils/dredged coral at the Johnston Atoll AFB located in the South Pacific.
- To utilize our "Lessons Learned" experience successfully treating the same chemical constituents at the Johnston Atoll AFB to exceed the performance objectives established for the Bien Hoa Airbase project;
- To provide a proven, environmentally sound, economically viable full-scale commercial option for the treatment of PCDD/PCDF contaminated sites in addition to other Persistent Organic Pollutants ("POPs") project sites throughout Vietnam;
- To provide a strategic technology transfer framework to collaborate with Vietnam in building its national capacity to address its contaminated land and waste management issues.

MCS^{TM} Technology general description

The MCS^{TM} Technology is a portable, modular, low profile batch thermal treatment system design that efficiently and economically achieves the successful desorption of organic and volatile inorganic compounds from a solid or semi-solid matrix utilizing the combined operational benefits of infrared heating, convective/conductive heat transfer, heated air stripping effect, vacuum conditions, fluidized bed, boiling point reduction and chemical volatilization principles.

The MCS^{TM} Technology thermal treatment process involves the following basic steps. The pre-treatment soils are mechanically conveyed directly from the material handling or agglomeration equipment into the MCS^{TM} Technology treatment trays. The soil treatment trays are then loaded into the thermal chamber onto an infrared heater. An extraction hood containing the air exhaust manifold assembly is then lowered onto the treatment trays creating an air-tight seal. An extraction fan is started which will draw ambient air into the thermal chamber and through the matrix. The thermal chamber's burners are ignited and their associated emitter tubes begin to emit infrared radiation. The target chemicals are heated to their reduced boiling point and/or significant vapor pressure and stripped from the matrix. The combined effect of the operating principles within the treatment chamber reduces the boiling point of the chemicals, thereby reducing the energy required to remove them from the matrix.

The MCS^{TM} Technology's basic air emission control system design package can consist of a series of particulate filtration, condensation system, coalescing filtration, air impingement systems and activated carbon purification prior to final discharge to the atmosphere. Additional treatment devices are utilized as needed depending on the target chemicals of concern. At each of these devices, the air is further purified until acceptable final discharge limits are achieved.

MCS^{TM} technology thermal treatment system components

The specific Demonstration Trial Project MCS^{TM} Technology thermal treatment system design consisted of two (2) major equipment transport skids. The first skid consists of one, full scale, five (5) ton capacity MCS^{TM} Technology thermal treatment chamber unit equipped with six (6) kerosene-fired burners, hydraulic power supply system pipework, negative pressure process air exhaust ductwork, various air filtration units, condensing units, cooling water piping manifold, a primary condensate storage tank and various electronic process monitoring probes, wiring channels and connection boxes. The dimensions of the primary MCS^{TM} Technology thermal treatment system skid is approximately 8' x 20'.

The second skid contains the remaining MCS^{TM} Technology thermal treatment system negative pressure process air exhaust ductwork, the main vacuum extraction fan, recirculation and positive pressure process air exhaust ductwork, hydraulic power supply system pipework and pump, cooling water recirculation pumps and supply pipework, various electronic process monitoring probes, wiring channels and connection boxes, and the PLC shed containing all electrical and electronic process control panels. The dimensions of the secondary MCS^{TM} Technology thermal treatment system skid is also approximately 8' x 20'.

These two (2) equipment skids are connected end to end to each other to form the main MCS^{TM} Technology thermal treatment system component setup with an overall dimension of approximately 8' x 40'.

The list of MCS^{TM} Technology thermal treatment system ancillary equipment consisted of: 5 ton fork lift for loading the treatment trays into the thermal chamber; vapor-phase granulated activated carbon ("GAC") vessel with final process air exhaust stack; condensate diaphragm pumps; pre-treatment condensate storage tank (1,000 liters); aqueous-phase GAC treatment drum (205 liters); treated condensate storage tank (1,000 liters); thermal treatment unit burner system fuel storage tank (1,000 liters); fuel supply transfer pump, hosing and piping; electrical power supply generator and cabling; fully enclosed decontamination trailer for input soil sample preparation and agglomeration; portable mixer for soil agglomeration; cooling towers and associated non-contact cooling water transfer pipework; and mobile staircase for thermal chamber probe monitoring.

Photographs of the Demonstration Trial Project MCS^{TM} Technology thermal treatment system module are provided on Page 3.

Demonstration trial project introduction

The MCS^{TM} Technology Demonstration Trial Project was conducted at TTI's project partner, Cape PLC's ("Cape") licensed facility in Paisley, Scotland. Office 33/PMU provided TTI with three (3) 20kg discrete Bien Hoa Airbase pre-treatment soil samples packaged in sealed plastic containers. The pre-treatment soil samples were identified as 0314VN4.1, 0314VN4.2, and 0314VN4.3. These input samples contained "Low Range" concentration "Hot Spot" soils with PCDD/PCDF levels ranging between 10,000 and 15,000 parts per trillion ("ppt") WHO TEQ.

Based on the excellent treatment results achieved on the "Low Range" concentration soils, UNDP/Office 33 PMU extended the project to include supplemental demonstration tests for the treatment of "Medium Range" and "High Range" concentration soils from Bien Hoa Airbase. Subsequently, TTI was provided a discrete 20kg sample of "Medium Range" concentration soil (PCDD/PCDF levels up to 40,000 ppt WHO TEQ) identified as 0515VN-02 and another discrete 20kg sample of "High Range" concentration soil (PCDD/PCDF levels up to 130,000 ppt WHO TEQ) identified as 0515VN-01.

TTI conducted multiple individual trial tests for each discrete soil sample to demonstrate the MCS^{TM} Technology's capability to replicate treatment results.

Photo 1 MCS^{TM} Technology Thermal Unit - Closed - Front Angle View

Photo 2 Side View of MCS^{TM} Technology Thermal Unit Open With Treatment Trays

Demonstration trial project test procedures

A soil volume weighting approximately 5kg was collected from the discrete pre-treatment soil sample containers for each treatment test. A representative pre-treatment soil sample was obtained from each treatment test's entire soil volume for independent laboratory analysis to demonstrate a direct correlation of treatment efficiencies for each test. The remaining volume was placed into a portable mixer with the addition of approximately 5% by weight of water acting as a binding agent and the application of simple centrifugal forces for soil particle size agglomeration. The agglomeration process is important to ensure uniform air flow and heat transfer throughout the entire matrix within the thermal chamber.

The entire agglomerated pre-treatment soil sample volume was then transferred into a dedicated stainless steel test scale soil sample tray measuring 12" in width by 12" in length by 16" in height. The agglomerated soil sample filled the treatability test tray to approximately 6" in depth. The treatability tray containing the pre-treatment soil sample was then placed into a full scale MCS^{TM} Technology thermal treatment tray for processing. Each demonstration test consisted of two (2) discrete demonstration test soil sample trays, one each installed within the two (2) full-scale treatment trays.

Prior to the placement of the test scale soil sample trays into the full-scale treatment trays, the full-scale trays were filled to an approximate depth of 6" with 1" diameter inert catalyst spheres. The inert catalyst spheres were used to simulate a treatment tray of approximately 1" agglomerated soil spheres. Each MCS^{TM} Technology thermal treatment chamber unit contains two (2) full-scale treatment trays. The thermal treatment chamber unit's extraction hood is then hydraulically lowered onto the trays to provide an airtight seal. These procedures are repeated for each demonstration trial test.

The MCS^{TM} Technology thermal treatment system's temporary generator power source was activated and the PLC main process control system energized for operation. The cooling towers and the entire cooling water recirculation system was then switched on for operation. The main extraction fan and its entire negative pressure process air system were activated. Once all systems were tested to be operating properly, the MCS^{TM} Technology thermal treatment system's fuel supply and burner system was energized and the official demonstration test was started.

Batch treatment cycles for the various demonstration tests ranged from four to six hours in duration with maximum soil temperatures reaching between 560 to 675 degrees Celsius. Upon batch completion, the burner system was turned off and the thermal chamber began a cool down cycle. When the cool down period was complete, the extraction hood was hydraulically raised to gain access to the full-scale treatment trays. The test scale soil sample trays were removed from each full-scale treatment tray. The contents of each treatability test soil sample tray were emptied onto a stainless steel sheet in separate discrete piles.

The entire soil volume of each sample was then crushed with a stainless steel spoon to achieve a relatively uniform particle size. The entire post-treatment soil sample volume was then homogenized. Grab samples were then randomly obtained from the entire soil volume with a stainless steel spoon and placed into a 500 ml amber glass jar for laboratory analysis.

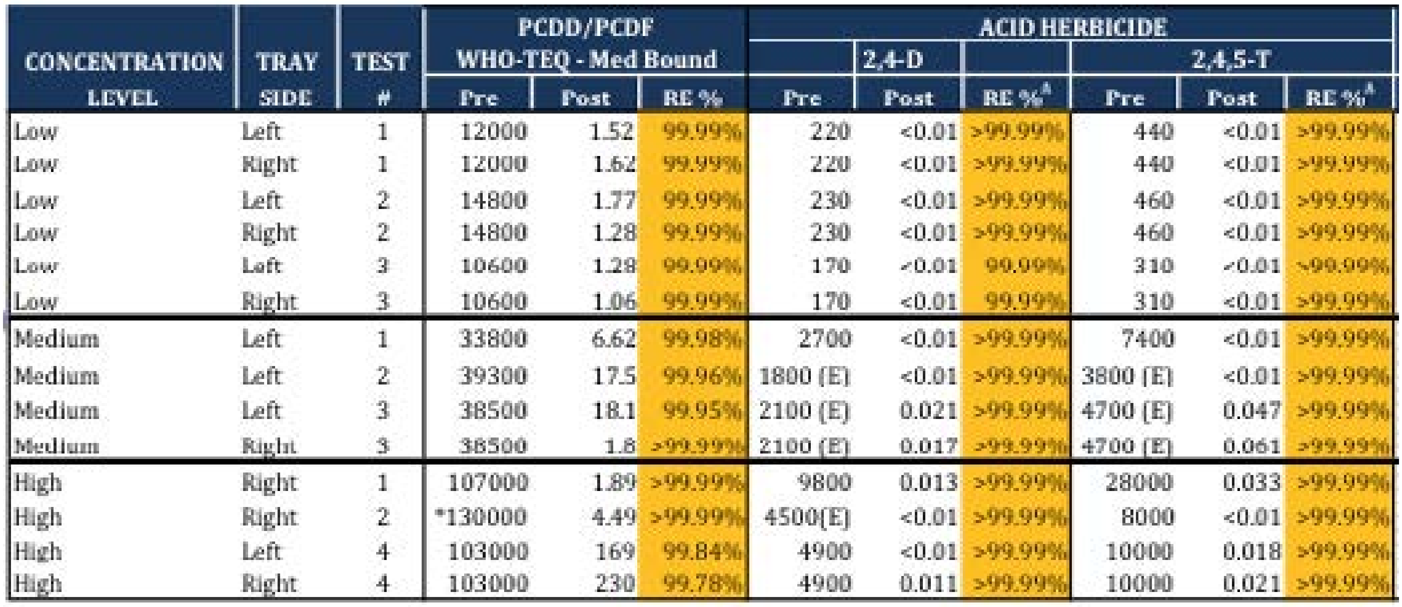
This same post-treatment soil sample collection procedure was completed for each test scale soil sample tray for the entire demonstration trial project.

Demonstration trial test results

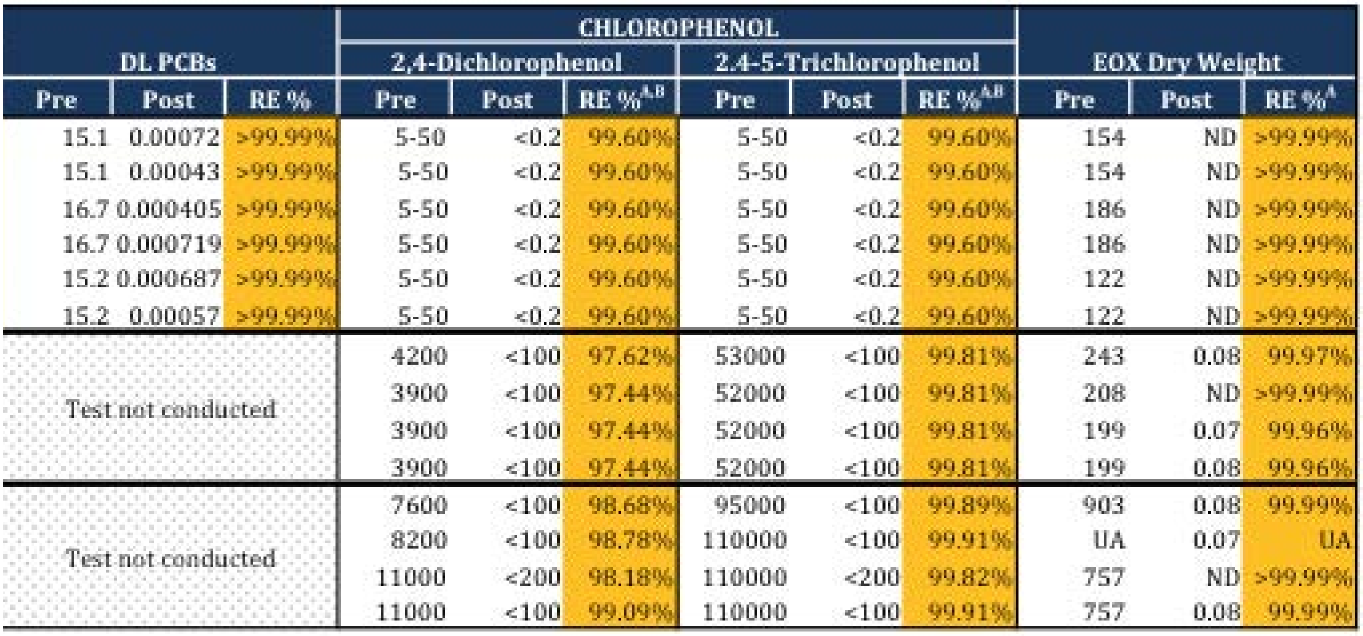
The table below provides a comprehensive summary of analytical results for the entire MCS^{TM} Technology Demonstration Trial Project for all of the principle chemicals of concern at the Bien Hoa Airbase project site. The data clearly illustrates excellent treatment results and RE% were consistently achieved for all ("Low Range" to "High Range") pre-treatment PCDD/PCDF concentration levels. The detailed laboratory analytical report illustrates the MCS^{TM} Technology's capability to consistently replicate the removal of all 17 toxic PCDD/PCDF congeners to below each analyte's respective laboratory method detection limit ("MDL") for "Low Range" concentration soils. The % RE values reported in the table for these tests were calculated using the applicable laboratory MDL for each toxic congener since the reported result was Non-Detectable ("ND") or below the MDL. All results for the "Low Range" concentration soil effectively achieved a WHO-TEQ RE of >99.99%, virtually eliminating the toxic PCDD/PCDF congeners from the matrix.

The table below further illustrates post-treatment results between 1.80 and 18.1 ppt WHO TEQ for Total PCDD/PCDFs with RE's ranging from 99.95% to >99.99% for all "Medium Range" concentration soil and post-treatment results between 1.89 and 230 ppt WHO TEQ for Total PCDD/PCDFs with RE's ranging from 99.78% to >99.99% for all "High Range" concentration soil. All results for the "Medium Range" and "High Range" concentration soil far exceed the <1,000 ppt WHO TEQ post-treatment cleanup criteria for the project. Indeed, all "Medium Range" and "High Range" post-treatment test results, bar one, indicate residual levels at or approaching virtual elimination of the toxic PCDD/PCDF congeners from the matrix. Using the calculation methodology mentioned above, all post-treatment soil samples from the entire MCS™ Technology Demonstration Trial Project collected for PCDD/PCDF analysis achieved actual post-treatment performance levels essentially at or approaching 99.99% RE Total WHO-TEQ.

MCS™ Technology Demonstration Trial Project
Entire Treatment Test Program Result Summary Table
Principle Chemicals of Concern



CONCENTRATION LEVEL	TRAY SIDE	TEST #	PCDD/PCDF WHO-TEQ - Med Bound			ACID HERBICIDE					
							2,4-D		2,4,5-T		
			Pre	Post	RE %	Pre	Post	RE %[A]	Pre	Post	RE %[A]
Low	Left	1	12000	1.52	99.99%	220	<0.01	>99.99%	440	<0.01	>99.99%
Low	Right	1	12000	1.62	99.99%	220	<0.01	>99.99%	440	<0.01	>99.99%
Low	Left	2	14800	1.77	99.99%	230	<0.01	>99.99%	460	<0.01	>99.99%
Low	Right	2	14800	1.28	99.99%	230	<0.01	>99.99%	460	<0.01	>99.99%
Low	Left	3	10600	1.28	99.99%	170	<0.01	99.99%	310	<0.01	>99.99%
Low	Right	3	10600	1.06	99.99%	170	<0.01	99.99%	310	<0.01	>99.99%
Medium	Left	1	33800	6.62	99.98%	2700	<0.01	>99.99%	7400	<0.01	>99.99%
Medium	Left	2	39300	17.5	99.96%	1800 (E)	<0.01	>99.99%	3800 (E)	<0.01	>99.99%
Medium	Left	3	38500	18.1	99.95%	2100 (E)	0.021	>99.99%	4700 (E)	0.047	>99.99%
Medium	Right	3	38500	1.8	>99.99%	2100 (E)	0.017	>99.99%	4700 (E)	0.061	>99.99%
High	Right	1	107000	1.89	>99.99%	9800	0.013	>99.99%	28000	0.033	>99.99%
High	Right	2	*130000	4.49	>99.99%	4500(E)	<0.01	>99.99%	8000	<0.01	>99.99%
High	Left	4	103000	169	99.84%	4900	<0.01	>99.99%	10000	0.018	>99.99%
High	Right	4	103000	230	99.78%	4900	0.011	>99.99%	10000	0.021	>99.99%



DL PCBs			CHLOROPHENOL						EOX Dry Weight		
			2,4-Dichlorophenol			2.4-5-Trichlorophenol					
Pre	Post	RE %	Pre	Post	RE %[A,B]	Pre	Post	RE %[A,B]	Pre	Post	RE %[A]
15.1	0.00072	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	154	ND	>99.99%
15.1	0.00043	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	154	ND	>99.99%
16.7	0.000405	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	186	ND	>99.99%
16.7	0.000719	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	186	ND	>99.99%
15.2	0.000687	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	122	ND	>99.99%
15.2	0.00057	>99.99%	5-50	<0.2	99.60%	5-50	<0.2	99.60%	122	ND	>99.99%
Test not conducted			4200	<100	97.62%	53000	<100	99.81%	243	0.08	99.97%
			3900	<100	97.44%	52000	<100	99.81%	208	ND	>99.99%
			3900	<100	97.44%	52000	<100	99.81%	199	0.07	99.96%
			3900	<100	97.44%	52000	<100	99.81%	199	0.08	99.96%
Test not conducted			7600	<100	98.68%	95000	<100	99.89%	903	0.08	99.99%
			8200	<100	98.78%	110000	<100	99.91%	UA	0.07	UA
			11000	<200	98.18%	110000	<200	99.82%	757	ND	>99.99%
			11000	<100	99.09%	110000	<100	99.91%	757	0.08	99.99%

* - Pre-Treatment Soil Sample for the 0515VN01 Test #2 was broken during transport to Assure Quality Laboratory, Pre-Treatment data is based on Baseline analytical results for Sample 0515VN01

A: Analyte was reported as non-detected (ND) or below method detection limit (MDL). However, the % Removal Efficiency (RE) was calculated using the analyte's laboratory MDL.

B: The RE% for the chlorophenols for the low concentration soils was calculated using the upper limit of the concentration range provided by the laboratory

E: Laboratory methodology estimated concentration

Conclusions

The MCS^{TM} Technology successfully and consistently far exceeded the anticipated Bien Hoa Airbase project clean-up goal of <1,000 ppt Total WHO TEQ for the primary contaminants of concern, PCDD/PCDFs. The MCS^{TM} Technology also achieved a RE of >99.99% for all other organic chemicals of concern, such as DL-PCBs; Acid Herbicides; Chlorophenols; and, EOX for this project. These high performance levels were achieved consistently on input soil sample PCDD/PCDF concentrations ranging from “Low Range” concentrations of approximately 10,000 ppt to “High Range” concentrations of up to 130,000 ppt.

In conclusion, the MCS^{TM} Technology’s performance for the entire Technology Demonstration Trial Program successfully meet and far exceeded GEF/UNDP/MONRE’s project objectives as well as TTI’s project objectives. As a result of these excellent results, the MCS^{TM} Technology has been officially approved and certified as suitable for use in Vietnam by MONRE’s Office 33/PMU for the treatment of PCDD/PCDF contaminated soil in addition to the treatment of other POP contaminated sites. The MCS^{TM} Technology is now also an accepted and approved treatment technology for use on PCDD/PCDF and POP contaminated soil site remediation projects funded by GEF and UNDP worldwide.

PCB MANAGEMENT

ASSESSMENT OF EFFORTS MADE AND STATUS OF PCB INVENTORIES AND ELIMINATION TOWARDS THE 2028 DEADLINE

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Abstract

This presentation provides critical insight into the status of international PCB identification and elimination towards the 2028 deadline of the Stockholm Convention, highlighting both achievements and obvious gaps.
It will further introduce the use of Polychlorinated Biphenyls (PCBs) in open applications in public buildings and industrial facilities (for example hydro power plants).

Assessment of PCB Inventories as of 2015

According to the latest assessments the today existing national PCB inventories are still very limited in scope and coverage. Even for closed applications of PCB, comprehensive data are still lacking. However, national PCB inventories should cover **all** types of equipment, industrial sectors and geographical areas, in order to provide a basis for all future elimination or treatment activities.

Unfortunately, it is still very common that national PCB inventories only focus on transformers in the electricity generation, transmission and distribution sector. Based on these incomplete and unreliable data, total PCB quantities are often estimated or calculated. Typically, such estimations are either too high or too low.

Example Country A: 15 out of more than 30 states were selected for the national PCB inventory. In these regions mainly transformers as well as a small percentage of capacitors from the electricity generation, transmission and distribution sector were sampled and screened. Based on the received data, the national PCB inventory report was elaborated, although many regions, different types of potentially PCB containing equipment and a large number of possible stakeholders (e.g. industries and small consumers, railways, the shipbuilding industry, the army, navy and air forces, etc.) had not been considered in the first place.

Example Country B: PCB transformers were sampled, and the oils were subsequently screened by common PCB test kits. Positive samples were later screened by another similar screening method, instead of being verified by laboratory analysis. Therefore, the samples were tested twice without revealing any new results, and the available funds could have been used differently.

In conclusion, it is essential that steps are taken to ensure that comprehensive, clear, reliable and well-structured data on the amounts of PCB to be eliminated (and already eliminated) are available. Existing data must be (re-)evaluated and inventories must be re-assessed.

Finally, the PCB databases should also cover open applications of PCBs, which have so far rarely been given attention despite the provision in Annex A, Part II, para (f) of the Stockholm Convention. Sites contaminated with PCBs have also not yet received the attention that would be needed given the large potential for releases into soil, water and air.

Elimination of PCB Wastes as of 2015

Existing data on already eliminated quantities of PCBs are severely limited. Information from the countries on already eliminated PCB equipment and wastes is incomplete. For some countries, no information is available at all.

The Chemicals Branch of UNEP/DTIE summarised the elimination status in their *Preliminary Assessment of Efforts Made Toward the Elimination of Polychlorinated Biphenyls* as follows:

The total amount of worldwide produced PCB is estimated between 1 to 1.5 million tonnes. It was produced by a small number of countries (12) and companies (17) since the late 1920s. It is important to note that due to mixture, use, dilution and cross-contamination, the mass of equipment and materials containing or contaminated with PCB is much larger than the amounts of PCB produced.

According to the data provided in the national reports, only less than 600 thousand tonnes of PCB and PCB containing equipment have been eliminated to date. This report, including the above-mentioned additional sources, estimates that between 1.6 and 3.1 million tonnes have been destroyed. Expert judgment suggests that the actual amounts destroyed are in the upper part of the range or possibly even beyond. According to available data, almost 50 % of the total was eliminated between 2002 and 2006, with a sharp increase after 2001.
The steady decline from 2007 onwards may suggest that disposal activities are losing momentum as the ‘low-hanging fruits’ have already been picked. It is estimated that GEF-funded projects account for the elimination of at least

15’000 tonnes to date. In addition to the amounts that have already been eliminated, an estimated 0.5 to 3.7 million tonnes are scheduled for elimination through national or regional action plans as well as GEF-funded projects.

The progress in eliminating PCB varies considerably across the UN regions. About 87 % of the eliminated mass was from the Asia-Pacific Region and the Western European and Others Group (WEOG). The regions also followed different approaches in disposing of PCB wastes. While the Latin American and Caribbean Group (GRULAC), the African Region, and - to a lesser extent - the Central and Eastern Europe(CEE) Region exported most of their waste for destruction in other regions, WEOG and -slightly less pronounced - the Asia-Pacific Region destroyed almost all of their waste either domestically or within the region.

The total mass of PCB equipment and materials that still needs to be eliminated is estimated at about 9.3 million tonnes. Transformers account for the largest share, followed by capacitors.

Data on the amounts of PCB in open applications are very scarce and limited to very few developed countries. This estimate is at best indicative, given the many limitations discussed above. It is difficult to judge whether it is more likely to underestimate or overestimate the amounts still in need of elimination.

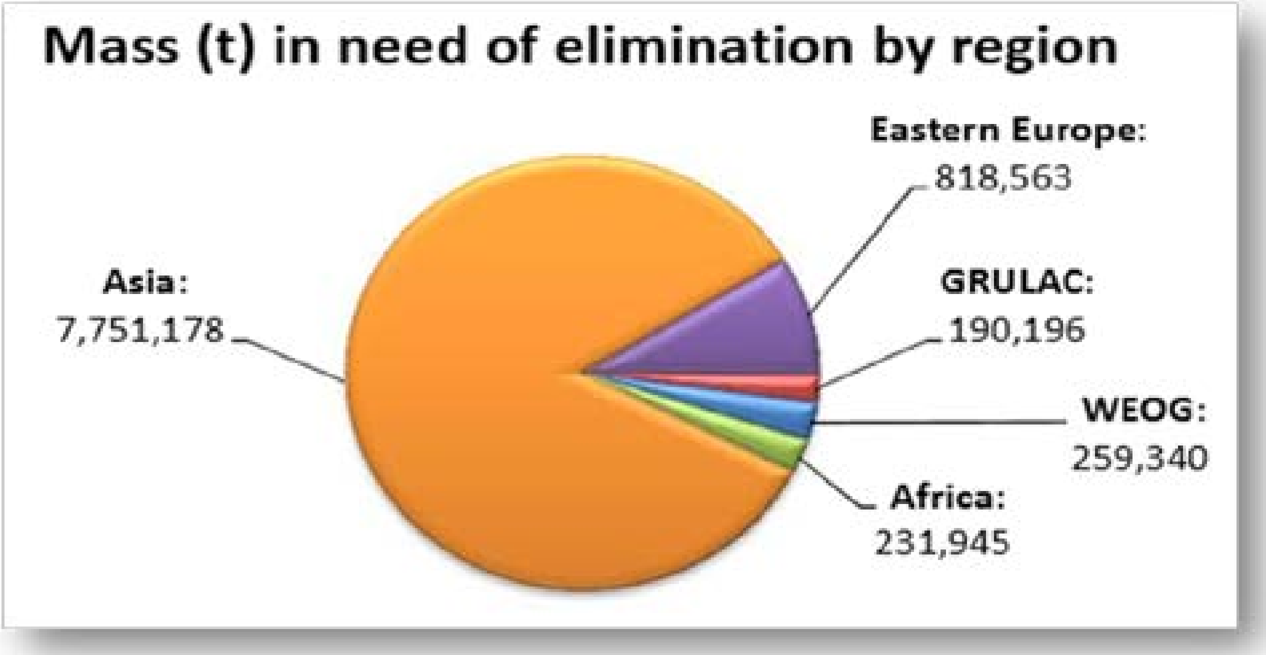
Almost 84 % of the total mass of equipment and materials containing or contaminated with PCB has been reported by the Asia-Pacific Region, followed by the CEE Region at about 9%, WEOG and the African Region at 3%, and GRULAC at 2%. This large discrepancy between the Asia-Pacific Region and the other regions can to a far extent be explained by varying quality in reporting. For the African Region in particular, data are incomplete and need improvement. Meanwhile, in the case of WEOG, only small amounts in closed applications remain to be eliminated.

The African Region has the longest way ahead towards achieving the goal of eliminating PCB. About 97 % still need to be eliminated. The approximate shares lie at 89 % for the Asia-Pacific Region, 81 % for the CEE Region, 64 % for GRULAC and 19 % for WEOG.

Considering the 2025/2028 deadlines of the Stockholm Convention, it would be high time that projects focused on the elimination of the PCBs.

While technologies and capacities for the destruction or treatment of PCBs are available, with many countries already having eliminated substantial amounts of PCB, additional financial resources are needed, in particular for developing countries and countries in transition.

As stipulated before, reliable inventories are the basis for every future BAT/BEP disposal or treatment activity - and reliable inventories are scarce. In most countries it seems too late to redo national inventories. Thus, each future PCB project should always include an assessment of the PCB inventory as a first component.



Based on these data, it is estimated that approximately 20 % of the total amount of PCB has been eliminated to date and about 80 % remain to be destroyed.

The Problem of PCBs in Open Applications

Experiences in US and Europe show that many public buildings, constructed between 1955 and 1983, often contain PCBs in their caulks (elastic sealants) and anti-corrosion coatings. In 2003 the Swiss Federal Office for the Environment published a directive requiring investigations about the PCB content in such buildings, calling for special measures to protect workers and the environment. The thresholds were set at 50 mg/kg of PCBs in the caulks, or an average concentration over one year of more than 6 resp. 2 µg PCB per m^3 indoor air. Buildings frequented by many people (e.g. schools, hospitals, etc.) or with long duration of stay (e.g. flats) pose the greatest risks.

Only an analytical investigation can give information about possible present contaminants. Screenings of buildings should not only focus on one particular chemical but provide an overall picture of the situation. Dangerous chemicals and materials like PAH, CPs, Asbestos, etc. can be found in many buildings, both public and private, in various applications and materials. PCBs can also be found in combination with other hazardous substances. For example, parallel installations of PCB small capacitors and Asbestos cardboard for fire protection reasons were very common.

Many European and US regulations e.g. require that a screening of a building and the necessary analyses are performed before a building is renovated or knocked down. Such screenings and analyses often reveal the presence of different PCB applications like paints, anti-corrosion coatings or small capacitors, which can influence the PCB content in indoor air.

Since the early 2000, PCB screenings in buildings and consequently their remediation have increased significantly - at least in the public sector. A professional and environmentally sound remediation of a building requires careful planning and investigation, appropriate techniques, skilled and reliable specialists both for the remediation as well as the supervision of the works and achievable and sustainable clean-up targets.

EXPERIENCE OF PCB REMOVAL IN THE FIELD

Nick Morgan
Managing Director, Veolia ES Field Services Limited, UK

Abstract

As a World leader in environmental services, VEOLIA has a wealth of experience in the environmentally sound treatment of hazardous waste including PCBs. Our specialist International Field Services business unit based in the UK has >20 years direct experience in handling POPs in field conditions throughout the world.

Having worked in Africa, Asia, Latin America and Eastern Europe we have developed a successful model for the safe and effective management of POPs including safeguarding, removal, transportation and effective treatment through a network of state of the art treatment facilities. Our project model is based on a sustainable, collaborative approach, working with waste producers/holders, countries and international organisations to remove POPs safely and to provide a lasting skills legacy for the country.

This approach was implemented recently in Ghana on a POPs disposal project undertaken on behalf of The Environmental Protection Agency (EPA) of Ghana in conjunction with the United Nations Institute for Training and Research (UNITAR).

Background to Veolia Environmental Services

Environmental issues are a concern throughout the world, but even more so where there are no local resources or infrastructures in place to effectively manage these concerns. At Veolia Environmental Services, we are committed to delivering sustainable, responsible and economically viable waste management solutions and services, whilst protecting and caring for the welfare and development of the environment and local communities in which we operate.

Offering a truly worldwide service in specialist hazardous waste and clean-up solutions, Veolia Environmental Services has an unrivalled reputation for practical and economical solutions, with a dedicated international team to advise on the best practical environmental options and an enviable track record in the responsible handling of hazardous materials.

Our operations are delivered in the field with the utmost care for the environment, the law and the health and safety of those directly or indirectly involved.

With extensive project management experience, a range of treatment technologies and full logistical support, we provide turnkey solutions for the removal, treatment and disposal of all hazardous substances, including PCBs and pesticides, plus land and building remediation, clean up and decommissioning.

Introduction

Over a period extending back to the early 1990s Veolia Field Services has undertaken POPs clean-up projects throughout the world including extensively in Africa, Latin America, the Far East and across the entire European area. Over this time we have worked together with other stake holders including waste producers, international organisations, governments and partners to foster and promote a sustainable added value solution for POPs destruction projects. Central to this approach has been a partnering strategy to ensure that as well as ensuring the safe destruction of POPs materials that there is a legacy of skills transferred from Veolia to the country from which the waste has been removed. These two aspects, destruction and skills transfer are central to the aims and requirement of the Stockholm Convention. They are also fundamental to the strategy of Veolia Field Services in relation to POPs clean-up.

This paper will describe how training of local staff can benefit the successful implementation of a disposal project and develop national capacity for chemical management via technical assistance.

Project Background

Polychlorinated Biphenyls (PCBs) belong to a broad family of man-made organic chemicals known as chlorinated hydrocarbons. PCBs have adverse effects to both human health and the environment. They are highly stable compounds that can last for years or decades before breaking down. They have a long range transportation characteristic in the environment. They were included in the initial list of globally managed Persistent Organic Pollutants (POPs).

Ghana is committed to safe management of PCB as demonstrated by her signing of the Stockholm Convention and its subsequent ratification. Therefore, Ghana is committed and already taking concrete steps for planning appropriate action in the management of POPs substances and releases as well as fulfilling its reporting requirements of the Convention. In this regard, the Government of Ghana developed an Action Plan for PCB management as a part of its draft National Implementation Plan (NIP) on POPs.

A GEF funded project has developed and implemented a strategy, and the required steps, from the current unsustainable management of PCB-containing equipment to sound management and disposal practices. The strategy commences by strengthening the legal framework and the management capacity both within government institutions and among PCB holders. The project will also eliminate, as a first step, the PCB-containing equipment, mainly transformers, and in a second step start phasing out PCB-contaminated equipment. The project is the first major step to meet the obligations of Ghana under the Stockholm Convention.

The project has the overall goal of protecting human health and the quality of the environment by eliminating the risk of exposure to PCB oil and PCB contaminated oils from capacitors and transformers. The project has safely disposed of approximately 160 tonnes of POPs including: pure PCB oils, PCB contaminated wastes, obsolete pesticides along with Ozone depleting substances from Ghana. The introduction of in-country safe management practices will contribute to achieving these goals and it is expected that the remaining PCBs in Ghana will be responsibly managed and disposed as well. UNITAR is the executing agency under this project and provides its technical expertise while delivering the project inputs.

As part of project activities, utility companies such as Electricity Company of Ghana (ECG), Ghana Grid Company Limited (GRIDCo), Volta River Authority (VRA) and the Mines possess equipment which contains PCBs (capacitors and transformers) and these have been identified, collected and stored at a central storage facility in Tema.

Objectives of Disposal Project

The objective of the project is to strengthen the capacities and capabilities of government officials and stakeholders outside of government to address PCB identification, and manage existing sources of PCBs as well as their elimination/destruction, as identified as a priority in the National Implementation Plan for Persistent Organic Pollutants for the Republic of Ghana.

Another objective is to enhance the capacity for the safe management of PCB oil and PCB containing equipment at all stages of the PCB management cycle.

Collaborative Project Management

Veolia Field Services has over more than 20 years worked with stakeholders including waste producers and trade organisation such as Croplife International, International Organisations such as FAO and other partners to develop and promote a collaborative approach to delivery of POPs clean-up projects. A key strategy has been to use local staff as part of the core project team at all levels including project management, technical, administrative and operational roles.
In Ghana Veolia had worked previously with CropLife International to Safeguard pesticides that have now been exported under this project. As part of this Safeguarding operation, local staff where trained and utilised in the repackaging and centralisation of pesticides to the Government store at Pokuase. The same staff were utilised during the latest operation using experienced local personnel to supplement the Veolia team. Additionally at the start of the project in 2014 a regional workshop was organised in Ghana by UNITAR and EPA involving stakeholders and experts from 10 countries to provide technical information and share experience in the field of PCB Management.

Skills Legacy

In order to ensure that local inputs contribute fully to the safe and successful outcome of the project extensive training and on-going supervision and support is provided by Veolia. This ensures that all staff working on the project do so safely and effectively. In addition it ensures that following completion of the specific disposal operation that there is a legacy of trained, skilled and experienced national staff. This retained resource can contribute to or even act as a national focal point for responsible chemical management going forward.
The strategy of assigning local staff to active project roles ensures that they can apply the training provided in a “real world” situation which allows skills to be practiced and developed with expert support and supervision to ensure safe operations. Only by combining training with practical experience in a controlled environment can competency be achieved in the key areas of project management, administration, handling, storage and transport of hazardous chemicals including wastes.

Conclusion

A POPs disposal project provides a great opportunity to ensure a legacy of local competence in chemical management. If projects are designed and delivered applying a collaborative project management approach between key stakeholders from the private, public and international sectors they can deliver a sustainable outcome combined with secure POPs destruction. Accordingly this approach ensures that the key aims of the Stockholm Convention can be cost effectively achieved in practice.

CO-PROCESSING PCB & OTHER POP'S IN CEMENT KILNS A LOCAL SOLUTION

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About ARP

The main priority of Alternate Resource Partners is to aid industry and government in their effort to efficiently recover valuable resources from their waste guided by the Waste Hierarchy using strict environmental and safe practices.

A growing attention of the public over the effects of climate change, the search for alternative energy sources and the drive towards sustainable development has led to great improvements in the recycling of waste materials. However, there are numerous sources of residual waste from fabrication processes that await transformation into useful energy and materials which will allow for a significant reduction in the requirement of fossil fuels and other raw materials.

To allow this transformation to happen, it is essential that a different approach is taken towards waste. Instead of thinking of waste as useless and disposable material, there should be a mindset of investigating possible uses of waste and application of found possibilities. To accommodate such a re-setting of minds, it imperative that a three layered approach is used:

- Education of the government, industry and investors;
- Identification of the opportunities for possible reuse or recycling of waste; and
- Implementation of the identified opportunities with or for the customer.

As a consultant, coach or sparring partner Alternate Resource Partners is well-positioned and experienced to provide you with the right approach and tools.

Manufacturing of cement

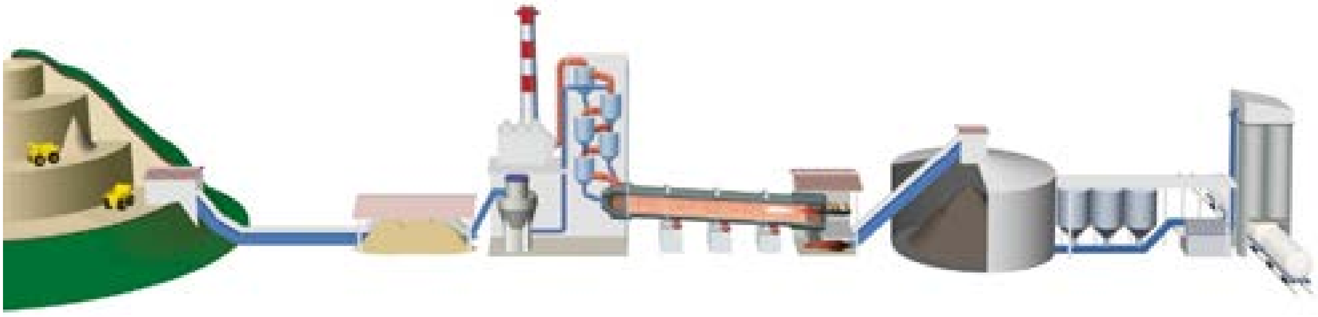
Manufacturing of cement has 3 different phases:

- Preparation of raw materials into raw meal
Extraction – Crushing – Pre-homogenisation - Dosing – Grinding - Homogenisation

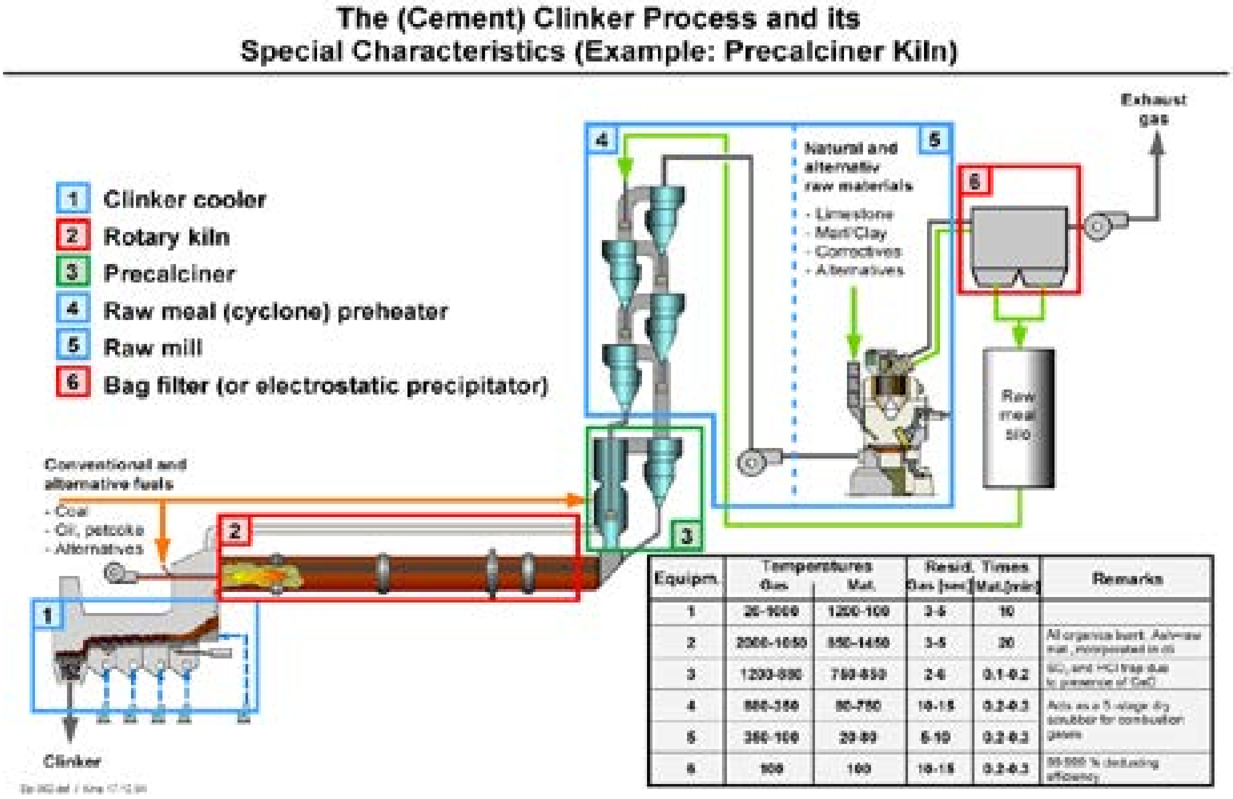
- Clinker production – pyro-processing of raw materials
Calcination of the raw meal into the rotary kiln – energy supplied by burning fuels

- Cement production
Grinding of clinker and mineral components to obtain cement

In the figure represented below, you can see the different components of a cement kiln and the introduction points for raw materials and Alternative fuels. The table contains the various temperatures in the different stages of the manufacturing process.



Schematic picture of the 3 phases of cement manufacturing


The (Cement) Clinker Process and its Special Characteristics (Example: Precalciner Kiln)

Equipm.	Temperatures		Resid. Times		Remarks
	Gas	Mat.	Gas [sec]	Mat.[min]	
1	20-1000	1200-100	3-5	10	
2	2000-1050	850-1450	3-5	30	All organics burnt. Ash=raw mat., incorporated in cl.
3	1200-850	750-850	2-6	0.1-0.2	SO2 and HCl trap due to presence of CaO
4	850-350	80-750	10-15	0.2-0.3	Acts as a 5-stage dry scrubber for combustion gases
5	350-100	20-80	5-10	0.2-0.3	
6	100	100	10-15	0.2-0.3	99.999 % dedusting efficiency

Co-processing in cement kilns

What is co-processing?

Co-processing is the use of waste or by-products from one industrial process, as fuel or raw material substitutes in another manufacturing process.

In the cement community, these materials are referred to as **alternative fuels and raw materials** or **AFR**.

In the following industries, co-processing could be applied:

- Cement manufacturing
- Thermal power industry
- Steel industry
- Lime production
- Ceramics, bricks, glass
- Chemical industry
- Petroleum industry

What are the benefits of co-processing?

Benefits of co-processing are as follows:

- Provides a permanent solution to waste management problems
- Lessens reliance on fossil fuels
- Preserves natural resources
- Reduces emissions and greenhouse gases
- Saves on fuel costs

In short . . .

Co-processing is the environmentally-friendly alternative for responsible industries and communities

Co-processing (treatment) of POP's in cement kilns

Technical characteristics of cement kiln

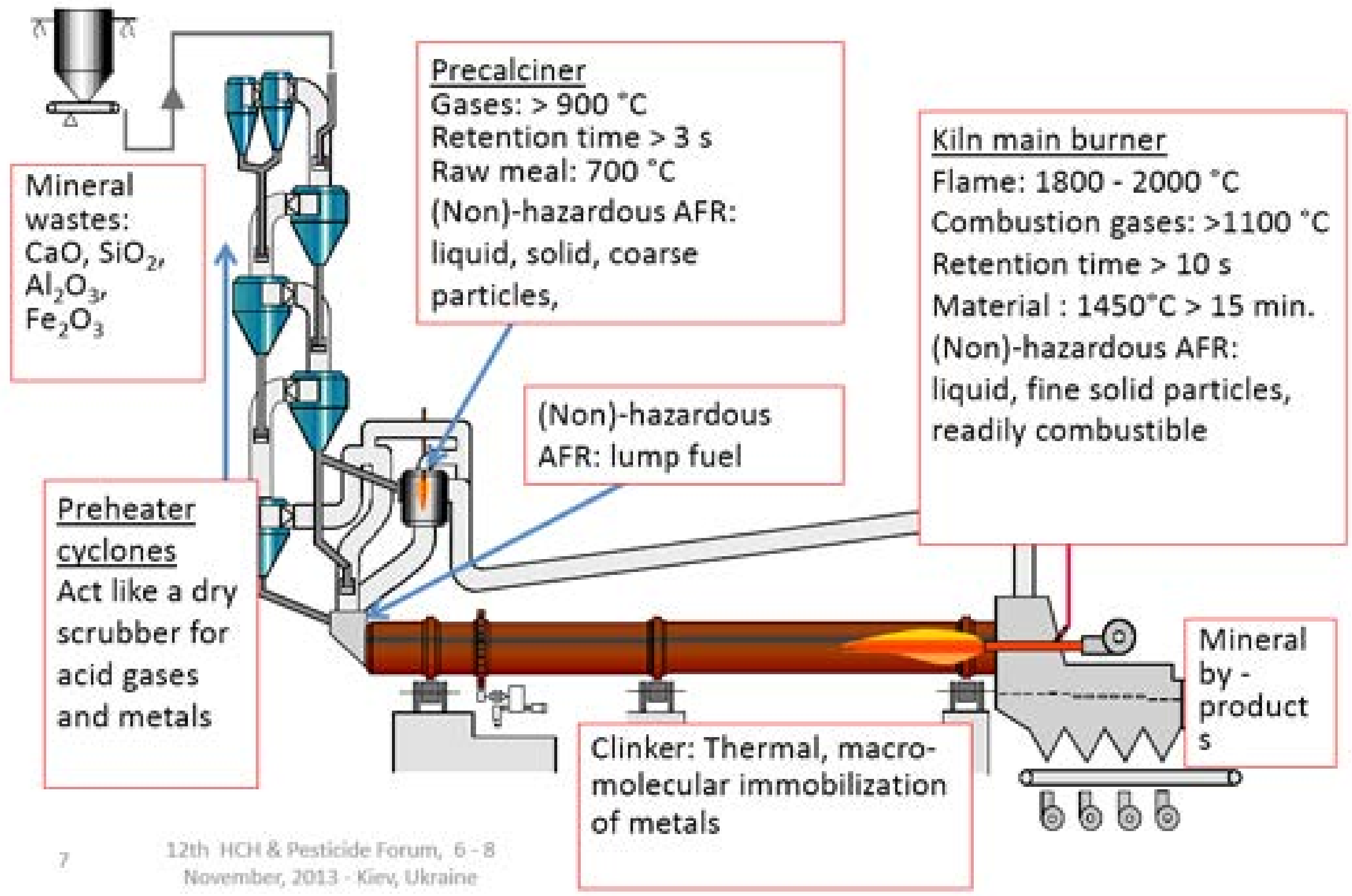
In the figure illustrated below, you find the details on characteristics and feeding points of the various AFR – hazardous and non-hazardous, lump and fine, fuels and raw materials of :

- Pre-calciner
- Pre-heater
- Kiln main burner
- Feeding of nonhazardous lump fuels
- Feeding of (non) Hazardous liquids, solids

Furthermore, you will find the temperatures of gas and materials in the kiln stages as well as be able to understand what is actually happening in these parts of the kiln.

POP's, depending on their chemical and physical properties, will be fed to the kiln at the appropriate feeding points.

In the acceptance procedures for the AFR, the necessary analyses are made on both chemical and physical properties to have enough information to judge which feeding point to use, in the next part of this paper we will also explain more on the trial burns which might be part of the acceptance procedures if not enough information is available on the destruction behavior in the specific kiln where the POP's are being treated.



Main test results of co-processing PCB’s

When PCB’s are treated in a cement kiln for the first time and not enough data on the destruction efficiency is available, trial burns will be made.

In all kilns that co-process AFR an Emission monitoring and reporting scheme(EMR) has to be installed, the EMR should, at a minimum, contain the following components:

- **Implementation of continuous emission measuring equipment** for dust, SO2, NOx and VOC (and O2) on all cement kiln stacks
- At least a **once per year measurement** of HCl, NH3, C6H6, PCDD/DF and heavy metal emissions
- At least a **once per year calibration** of the CEM equipment
- The **yearly report** of results in a CSR report in a standardized form (Normal conditions, 10% O2, dry)

PCB Trial burn

A (PCB) trial burn testing scheme takes typically 3 days.

Day 1 Baseline emission testing in Compound mode of operation (with raw mill on) & no PCB

Day 2 AFR trial burn emission testing in Compound mode of operation (with raw mill on) and Burning of PCB, 2 ton/h (approx.10% fuel replacement) at main kiln burner

Day 3 Baseline emission testing, Direct mode of operation (with raw mill off) and no PCB.

Parameter	Unit	How the value is obtained
Mass flow rate concentration of PCB	g/min	Measured during test & calculated from flow and density
Flow volume of PCB	l/min	Measured during test
Density of PCB	g/ml	Density analysis from lab
Concentration of compound in stack sample	Nm3	Calculation from sample train
Stack flow volume	Nm3/h	Normative and current values

Besides the abovementioned parameters, the following operational parameters need to be collected:

- Temperature in kiln inlet
- CO content in kiln inlet
- O2 content in kiln inlet
- Waste feed rate, energy and chlorine content
- Energy efficiency
- Primary combustion air flow rate
- Total fuel feed rate
- Raw meal consumption, clinker production, quantity and quality

With respect to the Baseline emission testing, the table depicted below is giving the necessary information on the parameters.

These samples have to be analyzed on the following parameters:

- PCB's
- Heavy metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl, V, Zn)
- Cl, F, K, Na, NH3

The samples have to be taken during

- Baseline testing 1 – No PCB, raw mill on
- Trial burn – With PCB, raw mill on
- Baseline testing 2 – No PCB, raw mill off

Parameter	Mode of Operation	Note
Heavy Metals	Direct & Compound	
HCl, NH3, C6H6	Direct & Compound	(1)
PCDD/PCDF	Direct & Compound	(2)

Notes:

(1) Generally the emission of these substances is higher in direct operation.

(2) The PCDD/PCDF emission of a dry kiln is very low.

Sampling solids during PCB trial burn:

The following solid materials samples need to be taken during the trail brum

- Raw meal
- Clinker
- Coal (fine)
- EP dust
- Cement (from bag filter)

Some pictures on a trial burn at a cement plant & Results in local plant

Emptying PCB drums for trial burn

Emission testing facility on kiln stack

Trial burn of PCBs -Pyralene oil with 56-62% of PCB's, 33-38% tri-chloro-benzene, 5-6% tetra-chloro-benzene

Results of trial burn
DRE
>99.99999998% & 99.999999995%
In 2 different scenarios
Emissions not effected by PCB

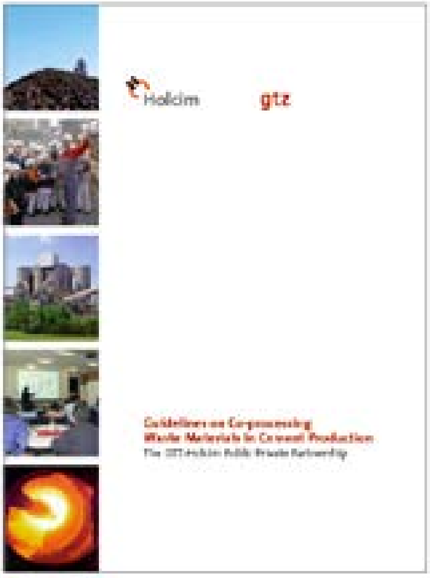
Notes: these results respect BAT/BEP guidelines of Stockholm Convention and Basel Convention, i.e. a DRE of 99.9999%.

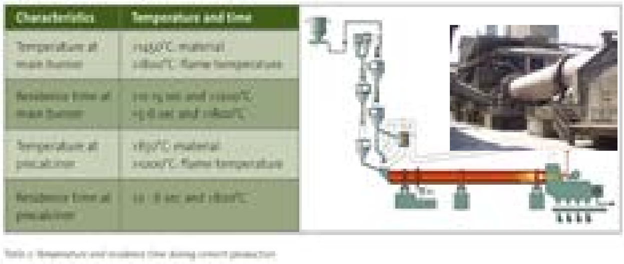
Main Conclusions:

- Burning of AFR does not significantly affect the emission of the cement kiln
- The hazardous wastes destructed well in the kiln
- No additional pollution generated with burning of AFR
- Quality of clinker and cement products not changed

International development & recognition of solution

- GTZ – Holcim Alliance : Co-processing Guidelines, more info on www.coprocem.ecs.ch





International Technical Guidelines Basel Convention

UNITED NATIONS

UNEP

BC

UNEP/CHW.10/6/Add.3/Rev.1

Distr.: General
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Original: English

BASEL CONVENTION

Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal
Tenth meeting
Cartagena, Colombia, 17–21 October 2011
Item 3 (b) (i) of the provisional agenda*
Matters related to the implementation of the Convention: scientific and technical matters: technical guidelines

Technical guidelines

Note by the Secretariat

Addendum

Technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns

At its tenth meeting, the Conference of the Parties adopted, as amended, the technical guidelines on the environmentally sound management co-processing of hazardous wastes in cement kilns on the basis of the draft contained in document UNEP/CHW.10/6/Add.3, which was prepared by the Government of Chile. The text of the final version of the technical guidelines is set out in the annex to the present document

For full tekst of guidelines visit website www.basel.int/TheConvention/Publications/Technical-Guidelines/tabid/2362/Default.aspx

Observations & Conclusions on way forward

- The cement kiln offers a highly advantageous system for co-processing because…..
  - high gas and material temperatures in addition to long residence times in the kiln, virtually destroy all organic materials potentially present in alternate fuels, and
  - alternative raw materials supply necessary chemical constituents of cement (calcium carbonate, silica, alumina, and iron).
- Cement companies have a local sustainable solution for PCB containing liquids & contaminated solids like PPM's, cleaning materials etc.),
- No long transport routes with these waste materials lower risk and lower cost or bigger volumes for same budget
- No investments needed in waste disposal infrastructure so budget can be used for other also much needed infrastructure in emerging countries materials.

Take home messages

- There is a great and urgent global need for the services of the cement industry based on general sustainability principles but in particular for hazardous waste co-processing in emerging countries
- The principles and philosophy/policy developed & adopted by Holcim on AFR practices are currently among the most responsible and advanced in the industry
- The "*only*" way forward is to document and publish the performance and practice, especially from well-designed studies in emerging countries.

SODIUM TECHNOLOGY
– THE CHOICE FOR TREATMENT OF POP`S

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Dr. Bilger Umweltconsulting GmbH, Freigericht, Germany

Abstract

The Sodium Technology was initially developed for the treatment of PCB-contaminated oils, such as transformer oils.

The Sodium Technology involves the complete mineralization of organic chlorine containing compounds (such as PCBs and further POP`s) by sodium.

POP`s in liquid or dissolved form are destroyed, and only non dangerous compounds such as rock salt and organic polymers remain as final products.

The efficiency of the Sodium Technology is at > 99.9999%. There is no fear of formation of dioxins and furanes as compared to incineration.

Further advantages are as follows: the low investment costs, the inexpensive nature of reagent sodium, the likelihood of stationary as well as mobile detoxification units.

Key words

Sodium, PCB-destruction, POP-Destruction, operating temperature, mobile unit, approved technique, high efficiency.

Materials and methods

The handling of sodium is well-understood from industrial application since many decades. In the field of environmental technology, sodium is used for the dechlorination especially for PCB-destruction in transformer oil. Due to the high reactivity, additional fields, such as treatment of any of the POP`s up to chemical warfare agents of application, can be identified .

Both stationary and mobile units can be set up and operated with very high efficiency.

The chemical principle in any reaction with sodium is the cleavage of the C-Cl- bond to yield sodium chloride and a mixture of organic molecules without any chlorine.

The overall chemical reaction of halogenated compound with sodium will follow

$$2\,R-X \quad + \quad 2\,Na \;\rightarrow\; R-R \quad + 2\,NaX$$
with $X = F, Cl, Br$

and is valid for any kind of halogenated organic compound within the POP`s and all other organic chemical compounds. Even halogenated gases can be treated in a modified way of the sodium treatment process.

The required efficiency of > 99.9999 % can be achieved in any case, when:

- operating temperature meets the requirements (approx. 120-150°C)
- sodium-dispersion in sufficient quantity is offered.

Preconditions for the success are the following:

1. POP dissolved in mineral oil, or
2. grinded and mixed with mineral oil

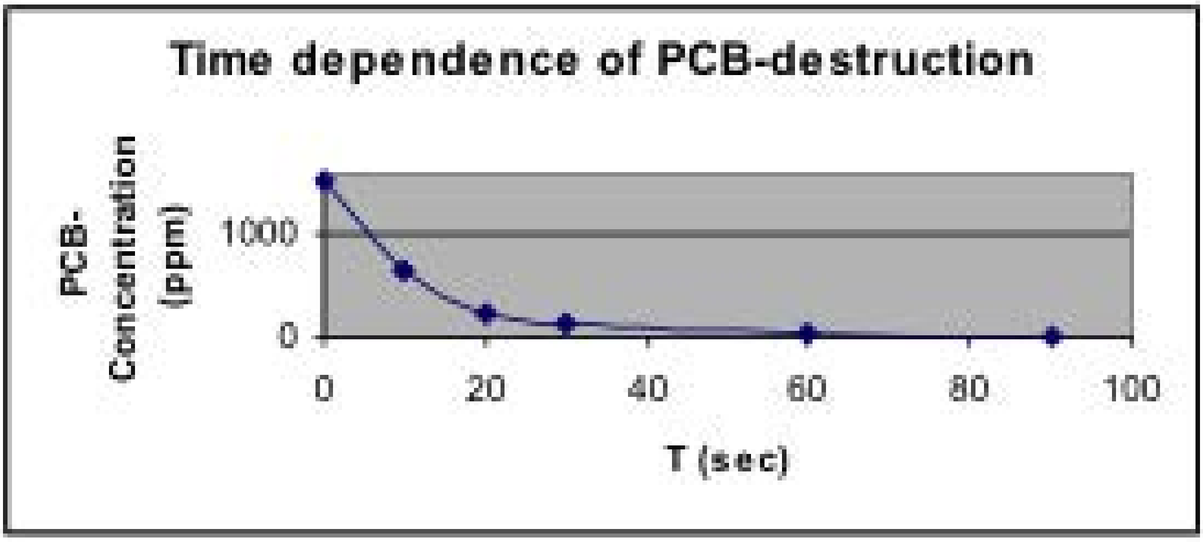
General operation path

Pre-treatment:

Pre-treatment includes filtering and de-watering to avoid violent reactions with metallic sodium. Drying of oil/organic solvent is sufficient if moisture content is about 100 ppm.

The Sodium Technology is applied by adding the sodium dispersion to the oil stream (particle with a diameter of approximately 2 to 10 µm) at low temperatures. Generally the operating temperatures vary from 100°C to 150°C, depending on the compound being destroyed, with temperatures of 130°C to 140°C being more typical. This relatively low temperature provides an important safety feature for application of the technology, since the formation of reaction heat can be quickly reduced in an emergency case by removing the applied heat and cooling the treatment vessel. The technology operates at atmospheric pressure.

The efficiency of the process is revealed in the diagram depicted below:



Practical experience

Operating units have been set up in Germany, the Netherlands, France, the United Kingdom, Czech Republic and South Korea.
The size of the unit can be adapted to the specific requirements and can be realised either in stationary or mobile units.

The most experienced industrial operation unit has been in process since 1989 until today without any alterations in mechanical equipment. In all cases, the operating company was able to guarantee a limit of < 2 ppm for their clients. More than 20,000 tons of transformer oil have been processed up to now.

A semi-continuous plant in the U.K. was able to treat 5 m³ per batch a total quantity of 10,000 tons of transformer oil processed with a limit of < 2 ppm after treatment with sodium.

In South Korea, Seoul, the limit of < 2 ppm has been approved by the Ministry of Environment in as well as the South Korean Institute for Science and Technology (KIST) at the day of the first start of the unit covering a capacity of 1000 lt/h. The unit can operate 24 hrs per day.
Even the very low Japanese limits of < 0.5 ppm can be guaranteed.

Most recent positive results could be obtained from a transportable Dechlorination Unit set up in Columbia. An overview will be presented during the Forum 2015.

Vast own experience has been made with POP`s from effluents of a local landfill in Hamburg. A wide range of POP`s have been found in the effluent in high concentrations. After the treatment with sodium, no organic compound with chlorine could be found.

The cumulated results are given in the table below:

compound	before	after treatment
PCB	80 ppm	< 0.0001 ppm
PCDD	17 ppm	< 0.0002 ppm
PCDF	8 ppm	< 0.0002 ppm
HCH	2000 ppm	< 0.1 ppm
Chlorobenzene	30000 ppm	< 0.1 ppm
Chlorophenole	900 ppm	< 0.1 ppm

Conclusions

The Sodium Technology is a straightforward and widely approved method for the safe decomposition of any kind of POP`s, especially PCB`s with final products that are easy to be handled.
Due to long lasting experience in handling of sodium specific solutions for the decomposition of POP`s can be evaluated and realised.

OIL & PCBs FREE PROGRAM 2015 : INVENTORY, CONTROL, MANAGEMENT, INTEGRATED DECONTAMINATION & DEHALOGENATION OF PCBS & OIL AND TRANSFORMERS - SOME CASE HISTORIES

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Abstract

This paper describes the Oil & PCBs Free Program 2015 for inventory, control, management, decontamination of electrical equipment and insulating liquids containing PCBs according with European (CENELEC) and International Standards (IEC).

For this scope are used the Best Available Techniques (BAT) and Best Environmental Practices (BEP) for Life Cycle Management (LCM) of electrical equipment impregnated with insulating liquids, such as *CENELEC CLC/TR 50503 February 2010 "Guidelines for the inventory, control, management, decontamination and/or disposal of electrical equipment and insulating liquids containing PCBs."*[1]*; IEC 60296 Ed.4-2011"unused mineral insulating oils for transformers and switchgear"*[2]*; IEC 60422 Ed.4-2013"mineral insulating oils in electrical equipment-supervision and maintenance guidance*"[3];*; CIGRE 413 Working Group D1.01(TF 12) April 2010"Insulating Oil Regeneration and Dehalogenation* [4]*"; IEC 60475 "Methods of sampling liquid dielectrics*[5]*;"*
IEC/EN 61619 Insulating liquids - Contamination by polychlorinated biphenyls (PCBs) - Method of determination of PCBs by capillary column gas chromatography (IEC 61619) [6]*; EN 12766-1 Petroleum products and used oils - Determination of PCBs and relatedproducts - Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD)*[7].

In this standards is indicated the Dehalogenation in continuous mode by closed circuit process for transformer decontamination and PCBs in oil detoxification.

This technique is CDP Process (patented by Sea Marconi), is a unique solution (since 1992) in compliance with BAT/BEP definition of the Italian Ministry of Environment, - D.M. 29/01/2007 - G.U. no. 133 of 7/06/2007 art. D.2.2.2.3 and art. E.3 [8], applicable for transformers and electrical equipment contaminated by PCBs. The CDP and DMU units (Decontamination Mobile Unit) are capable to decontaminate PCBs-containing oils to concentrations below legal limits such as by local regulation, international standards and technical guidelines (such as re-classification of oil and transformers as "PCBs-FREE" according local regulation). The case history of decontamination and dehalogenation of PCBs by mean of on-load and off-load "CDP Process" is compared with other techniques.

Key Words

Oil, PCBs, Transformer, Dehalogenation, Decontamination, CDP Process.

Materials and methods

This paper reports on the results of a four decades long expertise by Sea Marconi (since 1968), an independent third party company with respect to electrical equipment and insulating fluid manufactures, in the field of diagnostics for the prevention of failures and integrated treatments of insulating liquids for Smart LCM - O&T (Life Cycle Management of Oil & Transformers).

This solution satisfies the European regulations and standards in terms of BAT/BEP and sustainability (technical feasibility, economic-cost/benefits, environmental benefits and social-green jobs), safety (for workers, public health and environment-emissions CO2 etc.), proximity, self-sufficiency and functional recovery through the integrated treatments (off load and on load conditions) for Life Cycle Management (LCM) of insulating mineral oil and transformers, and includes the following key aims:

a) Dehalogenation and detoxification of PCBs in oil below the limits prescribed by local regulations or internal specifications (< 50; < 25; < 10; <2; < 0,5 mg/Kg of PCBs, determined with IEC 61619 Ed.1-1997). This process uses a solid reagent (S/CDP) consisting of a high molecular weight glycol mixture, a mixture of bases and radical promoter or other catalyst for chemical conversion of organic halogen to inert salts on a high surface area particulate support. This process normally runs typically at 80-100 °C and has the capability to decontaminate equipment on site, through continuous circulation of the oil in a closed system (without draining the oil or using auxiliary tanks), using the solvent capability of the oil for continuous extraction of PCBs from solid materials inside the equipment (IEC 60422 Ed.4- 2013-01 art.11.4.4;CENELEC

CLC/TR 50503 – 2010 art. 8.4.2.3; CIGRE 413 – 2010 art. 10.1.4.);

b) Selective depolarization of oil, with the reagents S/CDP and S/CHED, through elimination of oxidation by products, corrosive sulfur compounds-DBDS and organic-metal compounds with improvement of oil properties (electrical, physical and chemical according IEC 60422 ed. 4 2013-01; § Table 5);

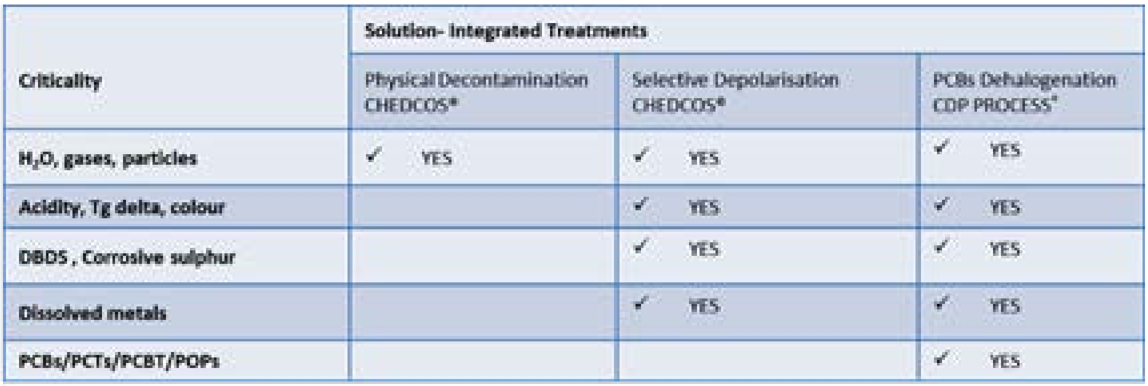
c) Decontamination of transformers and electrical equipment (extraction of PCBs, DBDS, moisture, sediments and sludge from solid materials inside the equipment).

Decisional matrix for the various available techniques (Refer- Table E3- Italian Ministry of the Environment, the Territory and the Seas Decree 29/01/2007 – Published on the Official Gazette n.133)

METHODS	Functional Safety	Environmental safety	Operator Safety	Eco-balance and Emissions	Global Cost/Benefit Ratio
Retrofilling	***	**	***	*	**
Sodium, Lithium and Derivates	*	*	*	**	*
KPEG	**	***	***	**	**
Continuous Closed-Loop Dehalogenation (CDP Process®)	***	***	***	****	****

***** = OPTIMUM; *** = GOOD; ** = AVERAGE; * = CRITICAL*

This solution provide in the same way the integrated treatments of insulating mineral oil for to guarantee properties according with IEC 60422 Ed.4 for oil and transformer in operation:



Criticality	Solution- Integrated Treatments		
	Physical Decontamination CHEDCOS®	Selective Depolarisation CHEDCOS®	PCBs Dehalogenation CDP PROCESS®
H_2O, gases, particles	✓ YES	✓ YES	✓ YES
Acidity, Tg delta, colour		✓ YES	✓ YES
DBDS , Corrosive sulphur		✓ YES	✓ YES
Dissolved metals		✓ YES	✓ YES
PCBs/PCTs/PCBT/POPs			✓ YES

Key Factors	Sea Marconi Closed loop treatment*	Replacement of Oil
On-Load Operation	Yes ✓	✖ No Off-Load for Draining and Refilling
Requirement of Unused Oil	No ✓	✖ Yes 125%/150% of original mass of oil**
Compatibility of Unused Oil vs original	Safety ✓	⚠ Warning base Oil, additives, others**
Recovery: Physical Properties KV, DSA, H_2O	Yes ✓	⚠ Warning*** only after reconditioning of Unused Oil in closed loop §11.2.3 (IEC 60422 Ed. 4 2013)
Recovery: Chemical Properties TAN, DF, IFT	Yes ✓	⚠ Warning*** only after reconditioning + reclamation treatments of Unused oil in closed loop §11.3 (IEC 60422 Ed. 4 2013)
Removal: DBDS & Corrosive Sulfur	Yes ✓	⚠ Warning*** only if initial DBDS is < 80 mg/Kg or reclamation with special adsorbent
Desludging & Dehydration Solid insulation	Yes ✓	⚠ Warning*** only after reconditioning + reclamation of Unused oil in closed loop §11.3 (IEC 60422 Ed. 4 2013)
Decontamination: Dissolved Metals	Yes ✓	⚠ Warning*** only after reclamation with special adsorbent if initial value is 8/10 times higher than the target limit
Dehalogenation: PCBSs/POPs in Oils	Yes ✓	⚠ Warning*** only if initial PCBs is 8/10 times higher than the target limit
Self-cleaning unit from: DBDS, PCBs/POPs	Yes ✓	✖ No cross contamination***
Cross contamination by DBDS, PCBs/POPs	Safety ✓	⚠ Warning depending upon the used oil impregnated mainly in the solid insulation
Partial Discharges: bubble air & moisture inlet	Safety ✓	⚠ Warning especially for wet insulation
Environmental Risks for Oil handling	Safety ✓	⚠ Warning high logistical impact
Oil & PCBs Waste disposal	No ✓	✖ Yes especially if PCBs is higher than limit

* Integrated treatments with DMU (Decontamination Mobile Unit) using closed loop process patented by Sea Marconi

Sea Marconi Integrated Treatments" vs "Replacement of Oil

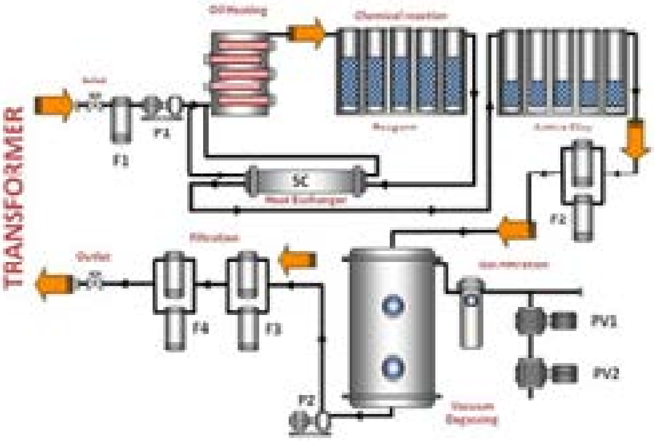
This approach is implemented during the ten steps of Smart LCM - O&T (Life Cycle Management and Oil & Transformers):

I. **Inventory of oils and transformers;**
II. **Requirements and General Specifications;**
III. **Acceptance;**
IV. **Factory Test;**
V. **Commissioning and Prior Energization;**
VI. **Energization;**
VII. **Infancy;**
VIII. **Operation – Oils & Transformer:**
IX. **Aging**
X. **End of Life - Post Mortem: decontamination, material recovery and waste disposal, etc.**
DMU (Decontamination Modular Unite) - typical scheme

This type of integrated treatments performed in a continuous manner by the closed-loop circulation of the oil, without draining the contaminated equipment; the latter is simply connected to a DMU, with a variable flow from 500 through 5.000 l/h. These mobile units are modular systems with compact dimensions equipped with automatic safety and process control systems capable of operating under all operational conditions (power generating stations, primary and transformation cabins, bunkerised substations etc.). Also, the modular units can be equipped with spill protection systems (Spill Guard), self-cleaning systems also capable of eliminating critical emissions into the atmosphere (Emx-Clean) and automatic supervision and control systems for all the safety parameters of the process to prevent the origin of possible critical conditions (functional and environmental).

During the continuous circulation, the insulating oil is subject to decontamination operations proceeding simultaneously, as described here below:

- heating of the oil at a temperature between 80 and 100 °C;
- chemical dehalogenation by percolation under pressure on the solid reagent, pre-prepared in filtering cartridges contained in appropriate containers (columns);
- depolarisation by percolation under pressure on adsorbent particle supports with a high surface;
- decontamination with degassing, dehumidification under vacuum and micro filtration



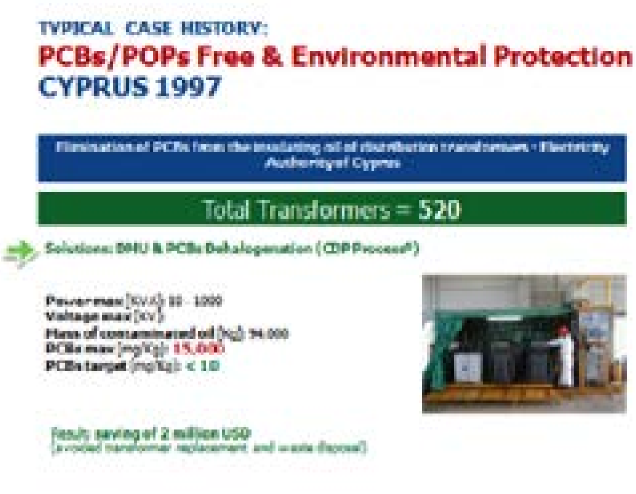
CDP Process ® and DMU-Plant flow diagram

CDP Process ® and DMU -Typical configuration rendering and pictures

CDP Process ® and DMU- Containerized unit connected with shunt reactor (500 kV) on-load treatment (Brasil 2010)

Results and discussion

Case History Cyprus - 1997: CDP Process ® and DMU- Typical applications for distribution transformers on-site



TYPICAL CASE HISTORY:
PCBs/POPs Free & Environmental Protection
CYPRUS 1997

Elimination of PCBs from the insulating oil of distribution transformers - Electricity Authority of Cyprus

Total Transformers = 520

Solutions: DMU & PCBs Dehalogenation (CDP Process®)

PCBs max [mg/Kg]: 15,000
PCBs target [mg/Kg]: < 10

Result: saving of 2 million USD
(avoided transformer replacement and waste disposal)

Case History France - 2004/2012: CDP Process ® and DMU- Typical applications for power transformers on-site

TYPICAL CASE HISTORY:
PCBs/POPs Free & Environmental Protection
FRANCE 2004-2012

Total Transformers = 1,093

Case History France - 2012: CDP Process ® and DMU- Typical applications for power transformers on-site and on-load

TYPICAL CASE HISTORY:
PCB + «C2 - NON DBDS & Corrosive Sulfur»
FRANCE 2012

TYPICAL CASE HISTORY:
PCBs + «C1 - DBDS & Corrosive Sulfur» SWEDEN 2012

Primary alluminium factory: 8 Rectifier Transformers

Solutions: DMU & PCBs Dehalogenation (CDP Process®) + Selective Depolarisation (Chedcos®) On Load

Manuf.: Brown Boveri
Year: 1930
Power [MVA]: 19
Voltage [kV]: 13
Oil Mass [kg]: 15.000
Oil type: mineral blended

	PCBs [mg/kg]	DBDS	IFT [mN/m]	CCD test	TAN [mg KOH/g]	DF
Before treatment	29	18	24	corrosive	0,14	0,230
After treatment	0,37	< 5	42	non corrosive	0,01	0,002

GUARANTEE: PCBs < 2 mg/Kg

Case History Sweden - 2012: CDP Process ® and DMU-Typical applications for power transformers on-site and on-load

Conclusion

Oil & PCBs Free Program 2015 for loss Prevention and Environmental protection provide the Best Available Techniques (BAT) & Best Environmental Practice (BEP) according the European (CENELEC) and International standards (IEC) for:

- PCBs Inventory
- PCBs Control
- PCBs Decontamination

References

[1] CENELEC CLC/TR 50503 Guidelines for the inventory, control, management, decontamination and/or disposal of electrical equipment and insulating liquids containing PCBs;

[2] EN60296 Fluids for electrotechnical applications - Unused mineral insulating oils for transformers and switchgear (IEC 60296);

[3] EN 60422 Ed.4 -2013 Mineral insulating oils in electrical equipment - Supervision and maintenance guidance;

[4] CIGRE Insulting oil regeneration and dehalogenation Brochure 413 Working Group D.1.01 (TF 12);

[5] IEC 60475 Methods of sampling liquid dielectrics;

[6] *IEC/EN 61619 Insulating liquids - Contamination by polychlorinated biphenyls (PCBs) - Method of determination of PCBs by capillary column gas chromatography (IEC 61619);*

[7] *EN 12766-1 Petroleum products and used oils - Determination of PCBs and relatedproducts - Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD);*

[8] Italian Ministry of the Environment, the Territory and the Seas Decree 29/01/2007 – Published on the Official Gazette n.133 titled Guidelines for the identification and utilisation of the Best Available Techniques on Treatment of PCBs, apparatuses and wastes containing PCBs and stocking systems

SARPI CONSTANTI: EFFECTIVE MANAGEMENT OF POPs AND HAZARDOUS WASTE TREATMENT IN SPAIN

Montse Papiol
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Abstract

The incineration plant in Constantí was founded as Public Service Industry in 1998 to treat hazardous waste. It was acquired by Sarp Industries in 2014.

The plant is composed of rotary kiln, post combustion chamber, boiler, and different equipment to purge the combustion gas i.e. filters, catalyser, quench, scrubber and effluent treatment.

The plant can handle pesticides, herbicides, fungicides, and insecticides, and also waste from chemical formulation industries, waste containing heavy metals and PCBs.

The plant can accept a wide variety of waste conditions and the capacity of storage is more than 1.000 tons of toxic waste.

Our incineration plant is one of the most reliable for treating POPs and is the only plant that exists in Spain and we can provide a service not only to Spain but also to European and International Markets.

Introduction

Sarpi Constantí is a Spanish incineration plant located close to an industrial area in Tarragona. It is next to the motorway and just 10 km away from the Port of Tarragona and 100 km from Barcelona.

After sixteen years providing service as a Public Service Company, the incineration plant was acquired by Sarp Industries and, under the name Sarpi Constantí, the plant continues to carry out sustainable waste management, including POP treatment by high temperature incineration, which is certainly the most reliable disposal option for this type of waste.

Having developed a large experience in hazardous wastes and POPs proceeding from a wide range of sectors and industries, such as chemical, pharmaceutical, healthcare and clinical, cosmetics and drugs, Sarpi Constantí is offering its services throughout Spain, and on the international market, in countries like Portugal, Tunisia or Malta.

Our experience is not only based on the handling of pesticides, herbicides, fungicides, and insecticides, but also on waste from chemical formulation industries, waste containing heavy metals and PCBs.

The treatment is based on High Temperature Incineration in a rotary kiln and post combustion chamber. There is also a boiler, and different equipment to purge the combustion gas i.e. filters, catalyser, quench, scrubber and effluent treatment. These elements configure the whole process as a proven solution for the safe disposal of POPs and most of the other hazardous waste, serving the market requests, providing a sound technical solution in compliance with legislative requirements.

The whole process is focused on safety and now that we form part of Sarp Industries, our company is becoming a very effective, safe company highly committed to the environment.

Waste Reception

The current facility in Constantí allows the reception of the waste in bulk liquid with a wide range of viscosity, and packed waste in drums, big bags, IBCs, etc.

The plant has a very well equipped laboratory that can carry out an exhaustive analysis of the waste. With these values it is possible to decide the best place to store the waste and the best way to introduce it into the kiln.

It is possible to store the liquid waste on the tank farm with 1.700 m3 of capacity or in the packaged and flammable waste storage area of 800 tons and especially for POPs the plant has the capacity to store 1.200 tons of toxic waste.

There are different ways to feed the waste into the kiln, in addition to the burners for liquid and sludge waste, it is possible to feed the kiln directly from the truck. It is also possible to put in whole or crushed drums and crushed big bags or IBCs.

Rotary Kiln and static combustion chamber

With a twelve meter long and 4 meter diameter rotary kiln, the facility can treat liquids and solids received in multiple formats. It usually operates 1.100 degrees, and even higher temperature can be achieved. With a proper rotation speed, an oxygen excess, and more than 3 seconds of residence time, a complete combustion and volatilisation of organic compounds is ensured.

Even the solid waste inside the drums is absolutely burnt out after a minimum of 30 minutes inside the kiln.

After the kiln, gases pass through the secondary combustion chamber, in which liquid waste is injected by four different burners, providing vortex turbulences that allow a high mix of waste and air, necessary to achieve the maximal removal efficiency.

Heat recover

After the post combustion chamber gases flow through a three-pass boiler, which provides 40 bar and 350 degree steam. A little part of the steam is used for internal utilities, the rest goes to the turbine and is recovered.

Gas Cleaning

- The gas cleaning is performed by four different equipment:
- Electrostatic precipitator: This High voltage filter holds and precipitates the fly ash with an efficiency higher than 99,99%.
- DeNOx Catalyser: The gas free of ash exits the Electrostatic precipitator and passes through a three layer Dioxin Catalyst, in order to destroy the dioxins and NOx.
- Quench: After the catalyst, gases pass through a Saturate Venturi, where most of the chlorine is dissolved in a water solution, and the temperature decreases to 68 degrees.
- Scrubber: A three stage scrubbing tower removes hydrochloric acid, oxides of sulphur, bromine, heavy metals and the traces of solid particles that could remain in flue gas.

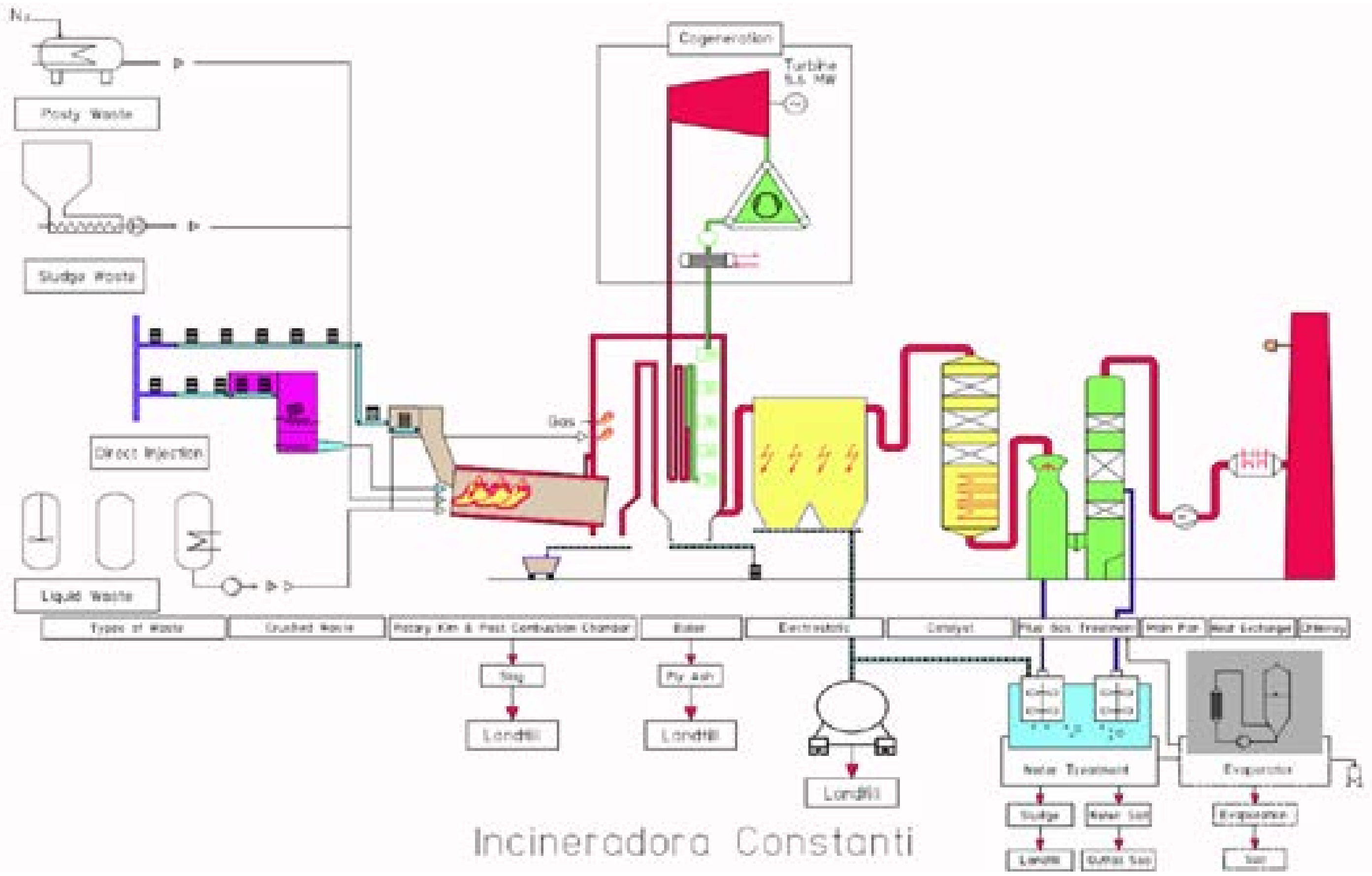
Waste water treatment

From the Quench and Scrubbing tower two different effluents flow, one acid with most of the hydrochloric acid and metals, and the other one with sulphur. These effluents are treated and purified on our own plant through a process which consists of four stages:

- Neutralisation in reactors.
- Precipitation of sulphates and metal hydroxides.
- Filtration on a press filter.
- Heavy metal Nano filtration.

Serving the Environment

Our plant obviously complies with the emission limit values for PTS, TOC, HCl, HF, SO2, CO, NOx and Hg, and it is important to remark that we are analysing Hg in continuous, and we also measure heavy metals and dioxins. But we also went further using a blank sample to measure the contents of heavy metals and dioxins in soils, flora and adipose tissues, before the plant was built. We are carrying out these analysis regularly to know the concentration of these pollutants in the population. The results show that the values are the same as the population areas that are not under the influence of an incineration plant.



BASEL CONVENTON ON THE CONTROL OF TRANSBOUNDARY MOVEMENT OF HAZARDOUS WASTE AND THEIR DISPOSAL & REGULATION (EC) 1013/2006 TRANSFRONTIER SHIPMENT OF WASTE

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Abstract

FTA logistics ltd, a forwarding company, has organised since it was founded in 2003 on behalf of various principals the transportation of hazardous waste. As such has to arrange that the transportation is carried out in compliance with the various rules & regulations. Besides arranging that the shipments comply to the inter- and or national regulations on dangerous cargo fi. IMDG code (sea) and/ or ADR (road) also have to comply to the specific regulations regarding transportation of hazardous waste as per Basel Convention Regulation and the adapted EU Directive 1013/2006 'Transfrontier Shipment of Waste Regulation'.

In this capacity has noticed over the years that it is getting harder and sometimes even impossible to obtain the permits and transit consents from the Competent Authorities required under the Basel convention &/or EU Directive. The current regulations are counter-productive and need to be adjusted.

Key words

Basel Convention, Transportation, Hazardous Waste, Competent Authority, transit consent

One of the aims of the Basel Convention on the control of Transboundary Movements of Hazardous Waste and their disposal into force on May 1992 adopted by the EU regulations of which 1013/2006 is the latest version was & is to control illegal trafficking of waste.

The regulations states that under certain conditions the wastes can be exported to another country equipped to dispose of the waste, either by recycling (much preferred) or final disposal or combination thereof.

To bring the waste from the exporting country to the importing country, involves transport.

If you are not that lucky the transport involves 1 border crossing, requiring only an import and respective export consent, the Transboundary Movement of Waste gets more complicated due to the involvement of transit countries.

Definition of 'transit' as per EU 1013/2006 directive: a shipment of waste or a planned shipment of waste **through** one or more countries other than the country of dispatch or destination.*

Besides the import and export permit, each competent authority of the transit country has to give their consent to planned Transboundary Movement of Hazardous Waste.

The transports of waste within the EU is already complicated enough. Some of the competent authorities of the EU transit countries will give their consents rather quickly. Though there are some, who don't respond at all. However, art 9 = tacit consent (30 days) of EU Directive 1013/2006 will be applicable and export consent can be given.

** there are EU countries having incorporated in their national legislation a different definition! Defining transit to be import and export*.

Transportation involving none-EU countries

However to import into the EU from overseas can put your patience to the test. As also the Basel Convention Regulations incorporated in the various national laws kick in.

For the Transboundary Movement application you have to identify

- The carriers, hauliers
- The routing incl. the transit countries

If the hazardous Waste is to be shipped overseas, you will have to look for carriers willing to accept the hazardous waste on board their vessels.

First you will have to classify the hazardous Waste as per IMDG code: International Maritime Dangerous Goods Code being the regulations for the carriage of dangerous goods by sea.

Classifying hazardous waste

Hazardous waste is considered dangerous goods when substances which, already in small amounts, due to their characteristics can cause risks to human health and environment in unforeseen circumstances **during movement, storage and handling of these substances**.

Characteristics of these substances can be:
- toxic, poisonous
- flammable
- combustible
- explosive
- corrosive
- radioactive
- gases

or a combination there of.
The classification is based on analysis results of the waste.

Note that not all hazardous waste is considered to be dangerous goods. There is a distinctive difference, which can make a world of difference.

With the classification an UN number & IMO class with respective Packing Group can be assigned to the hazardous waste. Giving you the information on how, in what kind of package the required labelling etc the waste has to be made ready for transportation.

You are 'ready' to contact the carriers in order to have the waste moved from the export location to the disposal and/or recycling site.

Carriers

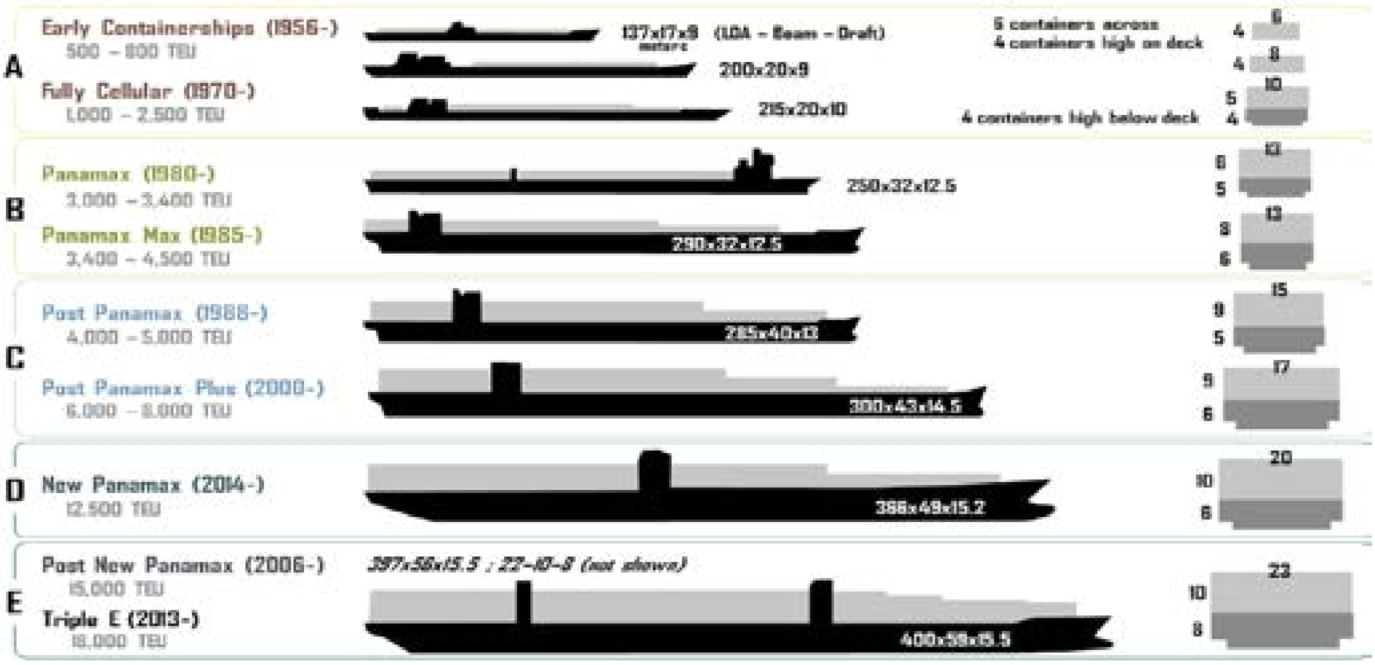
***Carrier means any person who carries out the transportation of hazardous waste or other wastes* (Basel convention).**

Transportation, can be by road, sea, rail, air or combination thereof.

In the past it was easier to obtain acceptance by the carriers for the sea-voyage. The service between port of loading & port of discharge, was mostly carried out with their own and/or long term chartered vessels on which the operator had full control.

The carriers representative (agent0 checked with the headquarters or with the DG (IMO)-desk, whether the vessels were equipped to take the hazardous waste on board their vessels and whether the P&I coverage (insurance coverage) allowed it. When no objection, they would give you a quote and advice on the routing the vessels take from the port of loading to the final port of discharge including the ports of call en route (=transit).

Nowadays, difficulty starts already with determining whether a shipping line carrying out a service of a specific trade line (f.i. Far East to NW Europe) maintains it with their owned and/or managed vessels.
In the last 3 decades the container vessels 'grew' from a mere 3000 TEU to the earlier this year introduced 19000 TEUs vessels.



And it’s expected the capacity might go up to 24.000 TEU.

TEU = Twenty foot Equivalent Unit = a box of roughly 6.00 x 2.40 x 2.40 m.

With the vessels getting bigger and bigger, it required whole new strategy of the carriers in order to get these filled in order to survive.

One of the strategies was forming an **alliance:**
An Alliance being an operational co-operation between container shipping companies in various

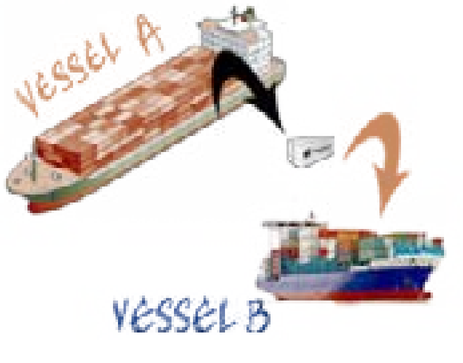
forms, ranging from slot-chartering and vessel-sharing agreements to multi-trade strategic alliances.

With the ‘growing’ vessels, acceptance of dangerous goods in general by the carriers got more complicated. Even more so, by adding ‘Waste’ to the description of the dangerous goods.

You can imagine, the people in the dangerous goods department, having to consider the various characteristics of the different dangerous goods container loads offered, to plan the stowage of these containers on board a vessel, in such way to safeguard all the cargo on board and the vessel during her voyage or whilst in the ports. (f.i. not stow acids near corrosives) Where in the past the vessels were making direct calls in the various ports, now due to the size of the ships the ports of call are limited to the so-called Main Ports.

To services the surrounding ports and/or countries, the containers are taken to & from the main ports smaller by vessels the so-called feeders. mostly operated by a third party (= an other vessel operator=other carrier). In that case a transhipment is involved.

Transhipment where containers are taken from one mode of transport, in this case ex feeder vessel A to a 2nd mode of transport, in this case the main ocean carrier B via a terminal (land=territory)



Waste on the whole as a bad reputation let alone hazardous Wastes. As soon you mention waste this is what the carrier's representative 'sees' to be packed in their containers. They will refuse immediately.

Stating that the cargo is all duly packed/marked labelled in accordance by the IMDG regulations, they will still refuse because of fear of their vessels being blocked by the 'greens', which has happened whether or not justified in the past.

Was it that about 10 years ago 60% of the shipping lines had incorporated in their policy that they not accept any kind of waste on board their vessels. Nowadays it has been become even close to 95%, due to accidents and/or incidents with wastes, causing them too much complications and hassles. If not due to the nature of the cargo, then caused by the paperwork and/or fear of negative publicity.
In the end a sea-carrier is found willing to accept the hazardous waste under certain conditions on board their vessels.
The other carriers for transport by road, inland waterway and/or rail are also 'on board'.
The 'fun' of the Transboundary Movement application starts for the exporter by obtaining all the consents.

Example

take a consignment of
Transformers with the transformer oil contaminated Polychlorinated Biphenyls (PCB) over 50ppm
The country of export is : Paraguay
The country of import is : Netherlands
It has been decided that for safe transport, the transformers are drained of the oil. The oil packed in drums.
Giving:
The empty/drained transformers contaminated with PCB = UN 3432 WASTE POLYCLORINATED BIPHENYLS, SOLID
The oil contaminated with PCB = UN 2315 WASTE POLYCHLORINATED BIPHEYNILS, LIQUID
both Class 9 PACKING GROUP II MARINE POLLUTANT as per IMDG code.

Cargo is ready to go: August 2015
TRANSPORT ROUTING PARAGUAY – NETHERLANDS
The transformers are located San Lorenzo not far from Asuncion and the final destination is in Drachten/Netherlands.

Transboundary Notification requires that you have to advise the

- Details of the carriers involved and that these are registered as Waste carriers by the national regulations (box 8)
- Advise the full routing including border crossings (box 15)

Definition of 'transit' as per Basel Convention & EU 1013/2006 means a shipment of waste or a planned shipment of waste through one or more countries other than the country of dispatch or destination;

Transport routing

The nearest port in Paraguay (a landlocked country) is Asuncion. From Asuncion there are river vessels (barges) taking the containers to Buenos Aires/Argentina where the containers can be loaded on board the ocean carriers to take it across the Atlantic to Rotterdam, Netherlands. Avoiding international road-haulage to nearest sea-port. The first carrier is the trucking company, to take the packed containers from San Lorenzo to the port Asuncion.

The 2nd carrier is the barge operator from Asuncion to Buenos Aires on the river connecting both cities.

The 3rd carrier is the shipping line from Buenos Aires/Argentina to Rotterdam/Netherlands.

The routing the vessels normally take from Buenos Aires to Rotterdam is advised to be: Buenos Aires – Montevideo (Uruguay) - Santos, Rio de Janeiro (Brasil) - Antwerp (Belgium) then Rotterdam (Netherlands).

The 4th carrier is the trucking company to take the containers from Rotterdam to the facility in Drachten.
The total route ex San Lorenzo/Paraguay to Drachten/Netherlands:

Truck: San Lorenzo – Asuncion

Barge: Asuncion – Buenos Aires/Argentina

Ocean : Buenos Aires (AG) – Montevideo (UY) – Santos & Rio de Janiero (Brasil) – Antwerp (BE) – Rotterdam(N)

Truck: Rotterdam(NL) – Drachten (NL).

In the Transboundary Movement documentation the complete detailed routing including the various carriers full details and registration numbers are incorporated.

All the documents required are submitted to the competent authorities in Paraguay where the application process is to start. You indicated that you would like to start the transportation by December 2015. The documents are verified by Paraguay and when all in order they will send out the notifications to all the other mentioned countries.

Problems with transit consents

The competent authorities of Uruguay will not give a transit consent for the Hazardous Waste transport for the port of call of the vessel in Montevideo even though the cargo remains on board the vessel while in the port. And notifies the EPA in Paraguay in cc all the other authorities refusing to consent to transit based on their ***national regulation***.
You need to restart your application where Uruguay is avoided as transit country. Time lost.
You find an alternative carrier/routing skipping Montevideo ex Buenos Aires/Argentina but still calling the Brazilian Ports then Antwerp to discharge in Rotterdam/Netherlands.
Documents are resubmitted. After some time the import consent from the Netherlands. Now you have to start chasing the consents of the transit countries.
Article 4 of the Basel convention states:

Each State of transit which is a Party shall promptly acknowledge to the notifier receipt of the notification.

It may subsequently respond to the notifier in writing, within 60 days, consenting to the movement with or without conditions, denying permission for the movement, or requesting additional information.

The State of export shall not allow the transboundary movement to commence until it has received the written consent of the State of transit.

However, if at any time a Party decides not to require prior written consent, either generally or under specific conditions, for transit transboundary movements of hazardous wastes or other wastes, or modifies its requirements in this respect, it shall forthwith inform the other Parties of its decision pursuant to Article 13.

In this latter case, if no response is received by the State of export within 60 days of the receipt of a given notification by the State of transit, the State of export may allow the export to proceed through the State of transit.

After some pushing the transit consents are finally received. Meanwhile months have passed from the moment you have submitted the papers. By now it is already February 2016.
You set everything in motion to get the transformers already since August 2015 exported as quickly as possible to the Netherlands.
You contact the named carrier for the sea-voyage to book the containers for export to the Netherlands.
You submit them copies of all the permits & consents under the Transboundary Notification..
They check the papers, come back to you advising that as per January 1st, 2016 the routing to Rotterdam has changed. Before discharging in Rotterdam the vessels go first to Hamburg, Germany. Hamburg/Germany is not mentioned and there is no transit consent of the German Authorities. Cargo is rejected.
You immediately inform all concerned that the routing has changed and that a new port/country has to be inserted as transit country in the notification for which you need to obtain a transit consent .
You send an official request to the German Authority and copy all the authorities in this message together with supporting documents advising them of the changed routing and you ask if the German authority is willing to give their transit consent for the Port of Hamburg. Also asking the 'existing' authorities for their non-objection to the changed routing under the existing notification. Hoping that the EU- authorities will apply art 17.2 disregarding art 17.3
If you are lucky all the competent authorities on the existing notification give their non-objection and that Germany consents as well.

EU 1013/2006 directive art. 17

art 17 ***Changes in the shipment after consent***
1. If any essential change is made to the details and/or conditions of the consented shipment, including changes in the intended quantity, route, routing, date of shipment or carrier, the notifier shall inform the competent authorities concerned and the consignee immediately and, where possible, before the shipment starts.

2. In such cases a new notification shall be submitted, unless all the competent authorities concerned consider that the proposed changes do not require a new notification.

3. Where such changes involve competent authorities other than those concerned in the original notification, a new notification shall be submitted.

However, if one of the authorities does not consent to the revised routing by f.i. applying art. 17.3 you will have to re-apply and start the whole procedure over again. You can only hope that there will no more change in the routing by the time you receive the consents under the new notification.

The whole process from starting the notification procedure till all the consents we experienced in average takes 6 months. We even had to arrange transports under Notifications were there was only 1 month left on the expiry date for transport. Or even where exporters had to re-apply because of the difference in interpretation on ‘expiry date’ by the importing country.

Complications

You want to transport the hazardous waste in the proper way, in accordance with the Basel Convention & EU regulations. However,

- All the time the notification process takes, you are stuck with the waste requiring safe storage as per national safety and environmental regulations.
- The transport charges you pay a premium for hazardous waste, specially due to the few carriers willing to transport it.
- The costs for the financial guarantee and notification consents have to be added. Some transit countries charge high administrative fees and/or require additional financial guarantees to be placed in their country.
- Difficulties encountered delaying and/or complicating international transport of hazardous waste with the various **transit countries**:
  - refusing consent either on
    - § their national regulations not allowing hazardous waste within their territories. It has been noted that sometimes they use this when there is some other feud with the exporting and/or importing country.
    - § For certain hazardous waste not being allowed within their territory.
  - o giving their transit consent but stipulating that cargo may not be offloaded,. even though in the notification it is mentioned that transhipment is to take place in the named port
    - § not responding to the notification even when reminded on various occasions;
      - when can it be considered tacit consent ?
      - does the national legislation stipulate you need a written consent at all times?

    stipulating that a separate transit consent has to be applied for by a local party. So you have to find a local party willing to do this for you f.i. Singapore, Australia.

    Problems with the routing and/or carriers due to :

- changes in the routings before starting the transport. Carriers based on supply and demand review the routings of their vessels minimal once a year.
- Changes during transport. f.i. a trucking company chooses another border crossing.. A sea- carrier has to discharge in another port because of expected delays in the foreseen port of discharge; f.i. due to strikes or has to skip the port to make up their ‘lost’ days in the schedule.
- Last minute refusal by the carriers even though the booking was accepted on submitted paperwork (consents, Dangerous Goods Note etc) due to change in policy.
- Refusal due to circumstance with incidents involving Dangerous Goods like recently in Tanjin/China

Various problems due to the inconsistencies between the Basel Convention; EU 1013/2006 Directive and the various national legislations.
The EU 1013/2006 is only applicable for the EU-countries and even then it should be incorporated fully in the national law not adjusted like some have done. On other other countries, you need to check the national legislation regarding the transportation of hazardous waste. Maybe available on the website of Basel.int otherwise you have to check with the respective country.
As potential exporter of the hazardous waste will be tempted to consider other solutions; cheaper, quicker, less hair-pulling to get rid of the wastes some way or other.

> F.i. on contaminated transformers, sell it to a local or maybe international scrap buyer, not disclosing that it is PCB contaminated. Might be that the scrap buyer is so keen to buy, that they disregard this information, even when informed. It was noted that even governmental organisations has ‘sold’ off their contaminated transformers/capacitors in this way.
> Still export to a facility in order to get it disposed of in the environmentally accepted way, but never informing any of the carriers, that it is hazardous waste and even more so that it is dangerous goods. Just declare it to be transformers and/or oil. Transportation will be carried out as NON dangerous cargo. If the carrier’s representatives, don’t question the description, they will not know unless cargo gets inspected somewhere en-route and the changes of that are slim, especially if you don’t mention it to be IMO cargo. But what if there is an incident ?

Where legislation counter the aims and purpose

Over the years the transboundary notification process is becoming more and more complicated for the respective exporters and/or importers to have the hazardous transported in accordance with the Basel convention and/or EU regulations and/or national regulation.

he aims of the Basel Convention and consequential EU regulation 1013/2006 is to

- Control the transboundary movements of hazardous waste and their disposal. Not to make it impossible
- To reduce as much as possible the movement to a minimum. Not to make it complicated in order to avoid transit countries, refusing consents for various 'national' reasons.
- Attack illegal trafficking. Not to increase it due to the stringent, impossible legislation.

  A waste disposer in order to comply to the various regulations you have to be strong minded, have deep pockets and have a lot of patience, which will be tested over and over, before the hazardous waste shipment has arrived finally at the disposal site.

Solutions

The Basel Convention and the various national or international regulations incorporating or adapting the Basel Convention regulations have to be changed regarding the requirement for consent of a transit country. The EU 1013/2006 can be adapted in such way, that if you have an import permit of an EU-country and the export permit, that you automatically have a transit consent for all the EU-countries. Some EU-countries already applied this in their national regulations, like Spain & United Kingdom.

If a transit consent of 1 or more EU-countries is required, that this can be applied for with a central bureau f.i. in Brussels. No need to go to each and every competent EU-authority, chasing them for outcome.

Basel Convention to clearly define when a consent of a transit country can be considered tacit.

Basel Convention & EU Regulations to clearly define transit (=pass through) and transhipment.

A port of call where cargo remains on board a carrier to take discharge and/or take on board other cargo, should not be considered to be a transit (= passing through a country).

In some countries, even in the EU, transit is defined as import & export but that is not the case when cargo remains on board, as NO import and/or export customs formalities on the waste takes place.
This requires a strong lobbying of the waste industry.
The legislative authorities must be made aware that regulations should not counter the aims and the purpose for which the regulations were made in the first place.

PCB PROJECTS IN EMERGING ECONOMIES: FEASIBILITY OF LOCAL TREATMENT

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Abstract

In the past years Orion and her local partners studied the feasibility of building a local treatment facility in emerging economies.

The conclusion is that local treatment cost can match the cost of export at an annual treatment volume of transformers for disposal (out of use) of 2 000 000 kg for 10 years. However the typical capacity building project for PCB waste (out of use transformer disposal) has a size of 500 000 kg transformers for 1 or 2 years with no guarantee or budget for the following 8 years required to earn back the capital expenditure. And the quantities of PCB containing transformers in the countries involved usually are not sufficient to start and operate an economically viable PCB waste treatment facility for 10 years.

Orion B.V. is an internationally operating company specialized in the treatment and handling of Polychlorinated Biphenyl's (PCB's). Orion was founded in 1985.

Orion's mission is to be recognized as a reliable partner in safeguarding the environment by safe and cost-effective removal and destruction of PCB containing equipment.

Our procedures foresee in packing the PCB-waste on location and sending it in containers to the Netherlands for destruction in our treatment facility in Drachten or to deliver the waste at local PCB waste treatment facilities.

Our vision is to transfer know-how and expertise to local partners aiming to enable each country to have a company trained in the handling of PCB waste and in reconditioning and cleaning PCB contaminated transformers.

Our treatment technology is comparatively low cost to build and to operate. Orion is using this technology already for over 20 years. One of Orion's unique features is to use no heating for the rinsing/washing nor for the distillation of the solvents. This is safe, easy to use and cost effective.

Keywords

PCB transformer disposal, PCB transformer cleaning, local treatment, PCB waste export

About Orion

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Our procedures foresee in packing the PCB-waste on location and sending it in containers to the Netherlands for destruction in our treatment facility in Drachten or to deliver the waste at local PCB waste treatment facilities.

Through international partnerships and cooperation we realize high economic value at low environmental impact, all in line with modern Corporate Social Responsibility (CSR) through strategic partnerships and innovative business models.

Of course Orion is not unique in providing PB waste treatment service, and as a dedicated and specialized company we have (a need for) an unique and different philosophy.

Our vision is to transfer know-how and expertise to local partners aiming to enable each country to have a company trained in the handling of PCB waste and in reconditioning and cleaning PCB contaminated transformers. In our experience the advantages are:

- "In country" competence to offer transformer life cycle management and to handle PCB waste and PCB calamities;
- Trust, understanding and good communications between the local company, the environmental authorities, the owners of the PCB waste and Orion;
- Much employment and revenues remain in the local economy;
- Local temporary storage is created, so PCB waste disposal is also available to owners of small PCB waste amounts;
- Fast and professional domestic intervention in case of a calamity;
- Local co-processing in licensed cement kilns or high temperature rotary kilns of PCB liquids and solids like PPE and absorbents assures that 95% of the hazardous substances does not have to be exported;
- We offer our technology and experience to build a local treatment facility in order to reduce or eliminate the requirement for waste export;
- Combination of "end of life" treatment with "cleaning and reconditioning" for transformers in order to re-use as much resources at the highest possible level in the "Waste Hierarchy":

Figure 1 Waste Hierarchy

Feasibility of local treatment

In the past years Orion and her local partners studied the feasibility of building a local treatment facility in emerging economies.

The following table shows the treatment cost estimates:

Typical estimated local treatment cost - summary	**Amount**
Capital expenditure	€ 3.500.000
Fixed cost	€ 830.000
Variable cost per kg	€ 0,23
Profit	30%
Total cost per kg, annual volume 500 000 kg typical project guarantee	**€ 2,46**
Total cost per kg, annual volume 1 000 000 kg	€ 1,38
Total cost per kg, annual volume 1 500 000 kg	€ 1,02
Total cost per kg, annual volume 2 000 000 kg	€ 0,84
Typical estimated export treatment cost	€ 0,50
Typical estimated sea transport cost	€ 0,35
Total cost per kg for export	**€ 0,85**

These number are based on a 10 year depreciation of the capital expenditure.
The conclusion is that local treatment cost can match the cost of export at an annual treatment volume of transformers for disposal (out of use) of 2 000 000 kg for 10 years.

However the typical capacity building project for PCB waste (out of use transformer disposal) has a size of 500 000 kg transformers for 1 or 2 years with no guarantee or budget for the following 8 years required to earn back the capital expenditure. And the quantities of PCB containing transformers in the countries involved usually are not sufficient to start and operate an economically viable PCB waste treatment facility for 10 years.

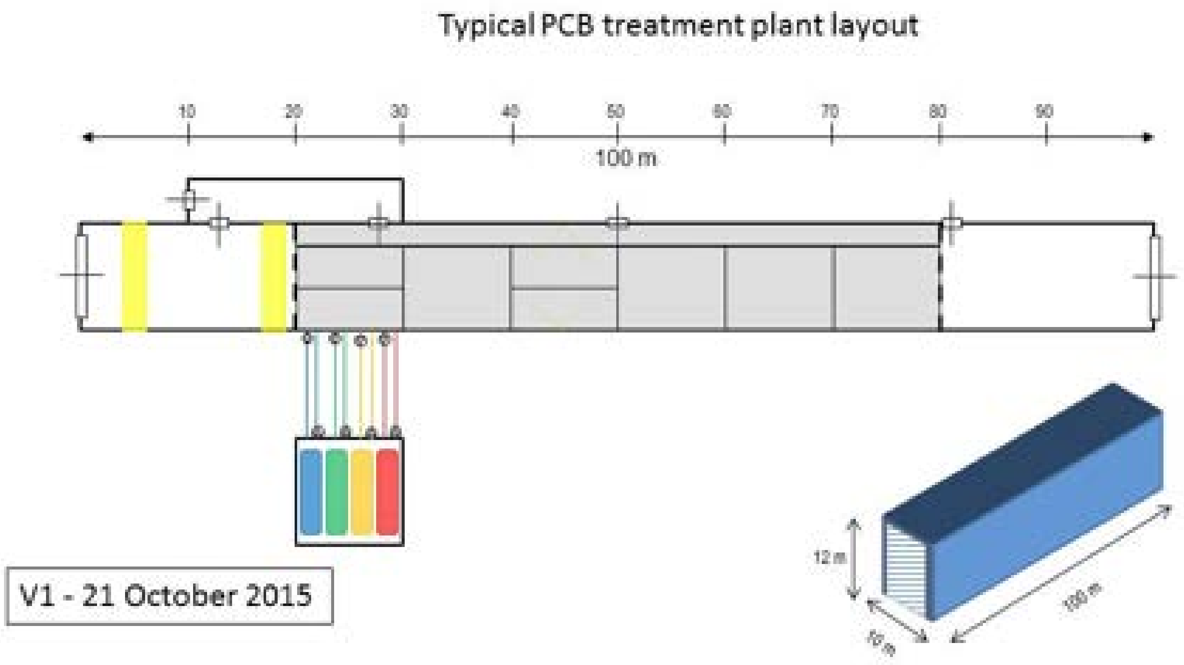

Figure 2 Typical PCB treatment plant layout
The details for the numbers in the treatment cost summary table are given in the following three tables.

Typical requirements for a local treatment facility and the estimated capital expenditure

Typical estimated capital expenditure, maximum treatment capacity 4.000.000 kg per year	**CAPEX**
land 3.000 m2	€ 200.000
Engineering	€ 80.000
Technology license and training	€ 600.000
Concrete floor 1.000m2, Geomembrane 3.000 m2, Fences, liquid proof parking and roads 2.000 m2	€ 300.000
Building steel construction 1.000 m2, 10.000 m3	€ 332.000
Basic equipment (cranes, forklift truck, transport containers, storage tanks, PCB analyses, transformer testing, pumps and hoses, copper shredder)	€ 618.000
Oil treatment technology (Bilger or Sea Marconi)	€ 800.000
Inventory (PPE, process liquids, other consumables)	€ 50.000
Electric power 630 kVA and installation	€ 80.000
Building project management	€ 60.000
Offices and equipment (3 workplaces)	€ 20.000
Environmental analysis (air, water, soil) baseline	€ 30.000
Environmental impact assessment	€ 20.000
Environmental license	€ 30.000
Decommissioning of the building; dismantling /cleaning and scrapping equipment and steel floor, making the building ready for other waste activities	€ 90.000
Develop a training module in local languages for the project (customers, workers, drivers) + write all the operational procedures/work instructions	€ 16.000
unforeseen 5%	€ 166.300
Total capital expenditure	**€ 3.492.300**

Typical fixed and variable operational annual cost

Typical fixed operational annual cost	**Amount**
Office cost	€ 2.600
Guards (full time, 5 shifts)	€ 9.000
cleaning offices and toilets, showers, changing area	€ 3.000
Director	€ 50.000
Office assistant	€ 12.000
Manager Logistic and SHEQ	€ 18.000
Site supervisor	€ 18.000
leasing 3 cars	€ 16.000
Gasoline for cars	€ 10.000
maintenance (10% of CAPEX equipment)	€ 142.000
Telecommunication, internet	€ 8.000
Utilities (electricity, water)	€ 6.000
Food for fixed personnel	€ 18.000
Environmental analysis (air, water, soil) - 2 times/year	€ 40.000
Insurance (environmental, liability, fire)	€ 60.000
Depreciation 10% of CAPEX	€ 350.000
Professional services (Accounting, HR, SHEQ, waste collection, auditing)	€ 26.000
unforeseen 5%	€ 39.430
Total fixed cost	**€ 828.030**

Typical Variable operational annual cost	**Quantity**	**Amount**
Treatment volume transformers (90% low PCB, 10% Askarel) kg per year	**1.000.000**	**€ 0,23**
workers in the facility	4	€ 20.000
workers for transformer collection	2	€ 10.000
Personal protection equipment for workers	6	€ 27.000
Weight bridge service	200	€ 2.000
Laboratory services	100	€ 9.000
Utilities (electricity, water)		€ 8.000
Waste water disposal (washing overalls, floors)	9	€ 8.550
Food for the workers	6	€ 10.800
Consumables (small tools, absorbents)	1.000.000	€ 8.000
Reagents for oil treatment equipment for kg of oil	250.000	€ 37.500
Solid waste (paper/wood) treatment	50.000	€ 100.000
Askarel (PCB 60%) treatment (3.5 % of volume)	35.000	€ 245.000
unforeseen 5%		€ 24.293
Scrap metal revenue kg (80% copper winding transformers)	690.000	€ -276.000
Total variable cost		**€ 234.143**

How to avoid the capital expenditure and get 95% local treatment of the PCB waste instead of 100% local treatment

The strategy to avoid a euro 3 500 000 investment in a treatment facility for PCB transformers and still have 95% of all the PCB's treated locally consists of three approaches:

1. **Re-use of low PCB contaminated oil transformers** by changing the contaminated oil for clean oil. This operation typically reduces the PCB content in the transformer to 10% of the original PCB concentration. In a country with a PCB limit of 50 ppm PCB in oil the oil change operation is economically feasible up to levels of 500 ppm PCB in oil. The majority of PCB contaminated oil transformers contains PCB levels below 500 ppm. However this treatment is only effective for transformers that are in use because the PCB contamination in the active part (the core) of the transformer will only leach out during operation in approximately 6 months. For that reason it is important to start this treatment as soon as possible as part of the regular transformer maintenance.

2. **The use of local cement kilns for co-processing** the PCB containing oils from transformers in use and from "end of life" transformers.

3. **Export the metallic parts** (drained transformers) that contains only 5% of the PCBs in the wood and the paper for treatment. The oil in the transformer contains 95% of the PCB's. By only treating this PCB containing oil locally the country is already processing 95% of the PCB's. The additional benefit of re-using the transformers < 500 ppm PCB contamination that are still in the electricity grid, on average 50% of the population of PCB transformers, raises the local treatment percentage even more.

4. At an additional investment of typically euro 800 000 an oil treatment plant can be used to remove the PCBs from mineral transformer oils. This oil can then be used to change the oil in PCB contaminated mineral oil transformers for re-use.

Finding a local partner

Orion looks for partnership with existing local companies in the area of hazardous waste collection and treatment. This way we use the local expertise and capacity in a country and we avoid to disturb the local market.

When Orion starts business in a new country we introduce our company to the local government (Competent Authorities) and ask them for a list of suitable and licensed organizations for the treatment, collection, storage and transport of PCB containing waste. Most of the time the Dutch government is able to support Orion during this introduction.

The next step is to ask PCB-waste owners like the local power companies and the industry for recommendations of PCB-waste collectors. By matching these lists we aim to find licensed and service oriented partners in each country outside the Netherlands.

The type of company that we usually form a partnership with are industrial & hazardous waste collectors, PCB waste treatment companies or transformer-service companies.

Cooperation between Orion and her local partners

The local partner is supported by Orion when needed. Mostly this will be in the field of marketing, technical support and logistic services. During the first projects Orion will send a specialist to assist to local partner. When the local partner has demonstrated sufficient know how and technical skills the projects will not be supervised by our specialists.

The period of extra support typically is 1 to 3 projects. This depends on the level of existing experience at the local partner and the speed of the market development.

Also personnel from the local partners comes for training to Orion's facility.

Export documents

TFS documents

Orion opens Trans Frontier Shipment (TFS) Documents for a country for one year from our local partner to Orion. The procedures for obtaining these documents are very familiar to Orion and our requests have been rewarded by all the different competent authorities up till now.

Duly Motivated Request

To obtain the TFS documents for a project, the competent authorities have to give their written statement in which they allow export of PCB-waste to the Netherlands, because there is no capacity for destruction of PCB-waste in their own country. To obtain this statement the assistance of the local partner is very welcome.

Example from Bulgaria – working with a local partner for export

In 2004, to prepare for the enlargement of the EU the Dutch trade minister has visited all the potential new country-members of the EU, so also Bulgaria.

During this visit, Orion, among other Dutch exporting companies, joined the minister. In this week we were introduced to the Bulgarian ministry for environment. The ministry has introduced us to Balbok. After two more visits to Bulgaria, Orion has signed the contract for partnership with Balbok in 2005 and the first PCB-project is finished in 2006.

Balbok is specialized in hazardous waste in Bulgaria. For PCB-waste they did not have a partner with the recycling options Orion could offer.

During the last 3 years Orion and Balbok developed a very nice cooperation. Exchange of logistic and technical knowledge, both ways is working out very nicely. Orion has assisted Balbok during the first project with a sales visit at the client and supervision of the first PCB-project at the client's factory.

Balbok has assisted Orion in obtaining the TFS documents and the transport permits.

Balbok works according to the high international standards for the handling, treatment and storage of hazardous waste. Because of their impeccable reputation, the PCB-project runs very smooth and the confidence of the clients and the authorities is very high. This partnership helps to strengthen the reputation and the services of both partners.

Both companies are very enthusiastic about this partnership and both the economy and the environment of Bulgaria and The Netherlands benefit from this cooperation.

PCB treatment and transformer life cycle management

Our treatment technology is comparatively low cost to build and to operate. Orion is using this technology already for over 20 years. One of Orion's unique features is to use no heating for the rinsing/washing nor for the distillation of the solvents. This is safe, easy to use and very cost effective. In cooperation with our partners we also offer insulating oil treatment technology and services for transformers in-use.

Transformers during use stage

Since 2012 we have an international cooperation with transformer oil analyses laboratories and transformer oil (mobile) treatment solution providers in order to offer life cycle management for mineral oil transformers during the use stage. Life cycle management is not restricted to PCB contaminated oil transformers. It is applicable to all mineral oil transformers and allows the transformer owners to monitor the quality and remaining thermal life of their capital equipment using all the data and experience available today. Modern life cycle management allows the owners to better assess the quality and the reliability of their transformers and make the optimal investment and maintenance decisions.

If a transformer owner and/or a governmental organization performs a PCB inventory study much money and effort is required. In that case it makes sense for transformers which are in use to:

1. collect additional technical data about the transformer and
2. do additional analyses (not only PCB content but also quality parameters) on the oil samples

in order to assess the quality and remaining thermal life of the transformers. Based on that information a life cycle management plan can be drafted.

Low PCB contaminated oil transformers can be treated by retro-filling for small oil transformers or direct treatment for large transformers with more then 15 000 liters of oil inside.

In case of high shut-down cost it is also possible to do the direct oil treatment on-load (energized) with only a short shut down time of 2 to 4 hours to connect the oil treatment equipment. This option is used often at power generation plants where a shut-down of 1 line can cost Euro 400 000 per day. Also in industries without sufficient backup capacity the on-load option may be used. Treatment time on-load is typically 2 to 3 times as long as off-load due to the reduced oil flow rates.

When PCB is removed from the oil the oil quality is also improved as all the other parameters (water, particles) are treated at the same time and also problems like corrosive sulfur are eliminated.

For transformers without PCB contamination but other oil quality and thermal life issues the same oil treatment procedure can be applied where necessary.

In the figures 3 and 4 the process flow for oil treatment for small and large transformers is shown:

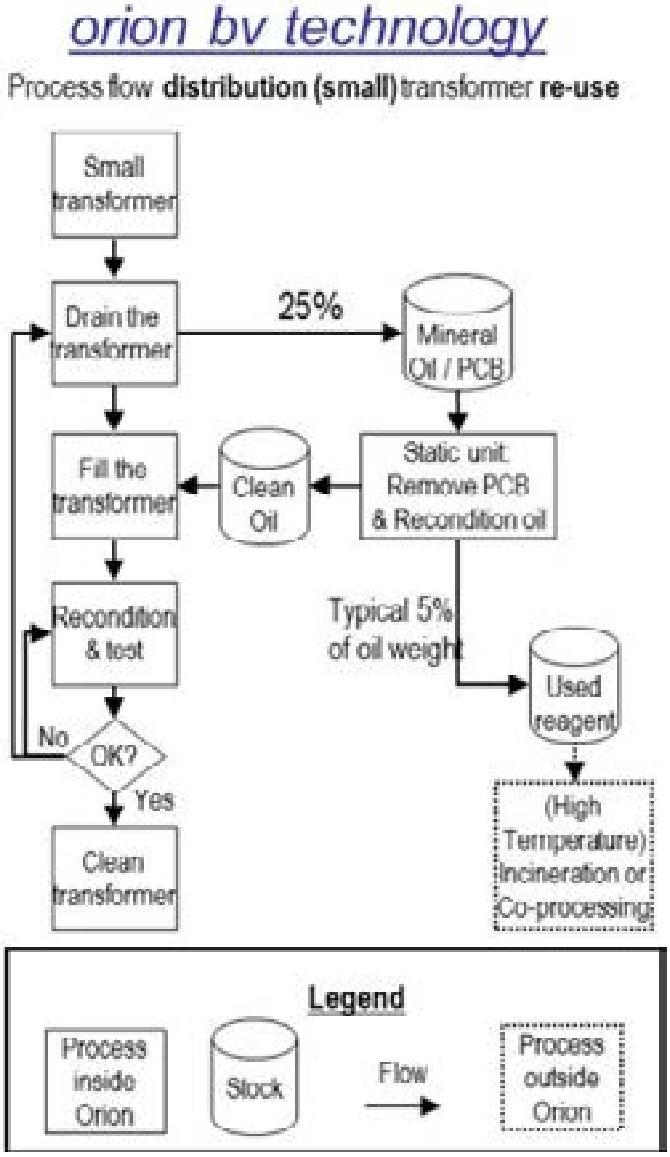

Figure 3

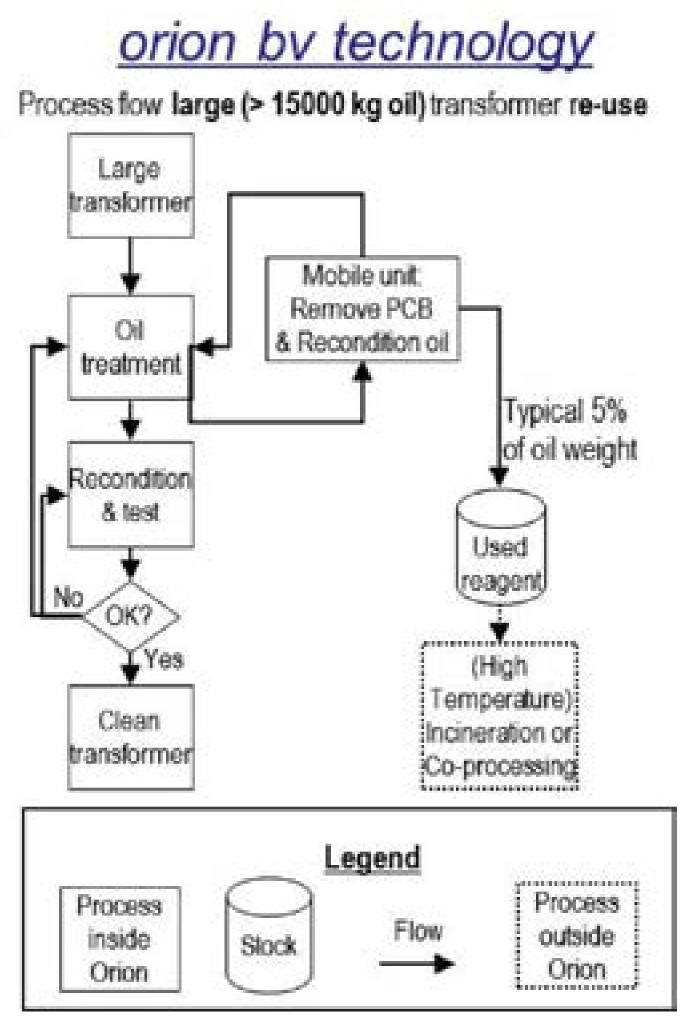

Figure 4

Transformers in the waste stage

If a transformer cannot be used anymore it is in the waste stage. At this stage oil treatment is typically more expensive then dismantling and cleaning for several reasons:

1. Oil treatment creates additional waste like used reagents and in the case of washing with oil extra contaminated oil
2. If the transformer is not in use during or after the treatment the internal (active) part / core material will not be cleaned and will retain the high PCB levels. The core contamination will only be reduced after some months of use (typically 3 to 6 months) after the oil treatment where the PCB level in the oil will rise again from < 2 ppm to higher levels. The final level will depend on the original PCB contamination level.
3. Even if we take into account the transport cost and the scrap (copper / iron) revenues the dismantling treatment is less expensive than the oil treatment. The economic advantage of the oil treatment is only when the transformer can be re-used because it saves the cost for a new transformer and its installation

The PCB transformer dismantling treatment is done as follows: PCB-containing transformers are drained and the inside is cleaned with solvents. After this cleaning operation, the transformer is opened and all the parts are separated. Copper, aluminum and sheet metal are rinsed with fresh solvents. The cleaned metal parts are sent to smelters as base materials for new metals, and the solvents are cleaned by vacuum distillation. We can recover approximately 95% of all materials, the only exception being insulating materials, which cannot be cleaned.

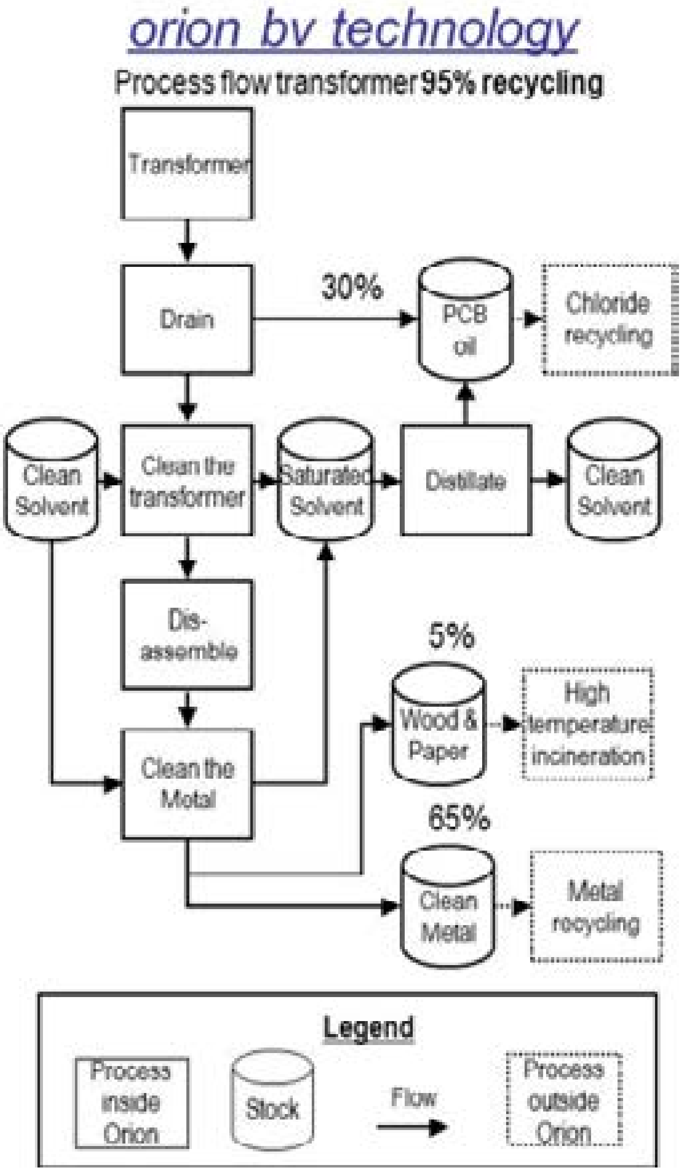

Figure 5

PCB-containing capacitors are recycled in a similar fashion to transformers. The capacitors are drained and opened, after which the metal case is rinsed with solvents. Approximately 50% of the materials are recovered. The remaining 50% consists of insulating materials and aluminum foil, which cannot be cleaned.

Technology and know-how that Orion licenses or sells:

Orion has developed a mobile solution in cooperation with one of our technology partners for on-site dismantling for low contaminated transformers if export is not possible and quantities are limited (between 5 000 000 and

10 000 000 kg).

For higher quantities and pure PCB transformers also a fixed installation can be offered in case export is not feasible. However, including amortization of the capital expenditure required, the total treatment cost per kg is typically higher than if the PCB waste can be exported to the EU. This is mostly caused by the fact that the EU treatment centers have already absorbed the capital expenditures in the past en are now operating at variable cost plus revenue only.

Orion's technology as it is used in our plant at Drachten for dismantling of transformers, capacitors and cleaning of the metal parts

1) Access to Orion's proven and approved technology and know-how for the following facilities:

- Specifications for liquid proof and PCB resistant floors as used at our plant;
- Specifications for construction of cranes as used at our plant;
- Specifications for ventilation and air treatment systems as used at our plant;
- Specifications for Fire protection measures and detection systems as used at our plant;
- Lay-out of our treatment centre with area's for:
    - PCB-waste reception,
    - draining and rinsing,
    - (intermediate) storage for liquids, metals and solids,
    - dismantling,
    - solvent distillation,
    - offices,
    - locker rooms, showers and restrooms for workers

- Specifications of required personal protection equipment as used at our plant;

- Specification of the equipment and materials we use at our plant in Drachten like:

    - shredders and separators
    - shears
    - cutters
    - tap-sets
    - pumps
    - hoses
    - sawing machines
    - vacuum chambers
    - solvents
    - distillation equipment for solvent recuperation
    - monitoring systems
    - tanks
    - containers for storage and ADR transportation
    - etceteras

- Safety plans and procedures for *environmental* protection as used at our plant;

- Safety plans and procedures for *worker* protection as used at our plant;

- Emergency and contingency plans and procedures as used at our plant;

- Quality control plans and procedures as used at our plant;

2) Education, training and visits to Orion's dismantling facility at Drachten, the Netherlands. Travel and housing expenses to be paid by the client.

3) 200 hours of advice during the first year after purchasing the license are included for each client. Travel and housing expenses to be paid by the client.

CO-PROCESSING PCB & OTHER POP'S IN CEMENT KILNS - A LOCAL SOLUTION

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Abstract of Paper

The paper is presenting the role a cement kiln could play in the waste management structure of an emerging country and how the kiln with some minor investments could become part of the solution needed to remove historical stock of POP's including PCB's
The paper talks about the following topics:

- Manufacturing of cement
- Co-processing in cement kilns
- Co-processing (treatment) of POP's in cement kilns
- Main test results of co-processing PCB's
- PCB Trial burn
- International development & recognition of solution
- International Technical Guidelines
- Basel Convention

The main observations, conclusions and take home messages are:

Observations & Conclusions on way forward

The cement kiln offers a highly advantageous system for co-processing because…..

- high gas and material temperatures in addition to long residence times in the kiln, virtually destroy all organic materials potentially present in alternate fuels, *and*
- alternative raw materials supply necessary chemical constituents of cement (calcium carbonate, silica, alumina, and iron).

Cement companies have a local sustainable solution for PCB containing liquids & contaminated solids like PPM's, cleaning materials etc.),
No long transport routes with these waste materials lower risk and lower cost or bigger volumes for same budget
No investments needed in waste disposal infrastructure so budget can be used for other also much needed infrastructure in emerging countries materials
.

Take home messages

There is a great and urgent global need for the services of the cement industry based on general sustainability principles but in particular for hazardous waste co-processing in emerging countries
The principles and philosophy/policy developed & adopted by Holcim on AFR practices are currently among the most responsible and advanced in the industry
The "*only*" way forward is to document and publish the performance and practice, especially from well-designed studies in emerging countries.

SPECIAL COUNTRY SESSION

Special country session on Tajikistan: status, problems, action plans, know how and technology needs

FORGOTTEN OBSOLETE PESTICIDES BURIAL SITES IN TAJIKISTAN HOW TO AVOID LAND DEGRADATION AND SECURE THE FOOD PRODUCTION IN A DENSELY POPULATED MOUNTAINOUS COUNTRY

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Abstract

In 2004 the University of applied sciences, North Western Switzerland together with the Regional Environmental Centre of Central Asia (CAREC) launched the implementation of the regional project "ToxCare" related to the management of hazardous substances and goods. The project is financed by the Swiss Government, Federal Office for Environment, as part of its efforts to foster cooperation and environmental protection within the GEF Constituency that unites Azerbaijan, Kazakhstan, the Kyrgyz Republic, Switzerland, Tajikistan, Turkmenistan, and Uzbekistan.

In 2009 the ToxCare project managed by the University of Applied Sciences, North Western Switzerland (FHNW), organised a workshop in Dushanbe on sound obsolete pesticides and PCB management. In parallel, the Dutch environmental consulting company Tauw carried out an 'Obsolete Pesticides Technical Study' for the World Bank to analyse the environmental and health risks from obsolete pesticides in Kyrgyzstan, Tajikistan and Uzbekistan.

On the territory of the municipalities of Vaksh (Southern Tajikistan close to the Afghan border) and Kanibadam (Northern Tajikistan close to the Uzbek border) major obsolete pesticides burial sites are located. The sites contain thousands of tonnes of stocks of obsolete pesticides, including DDT. Both burial sites Vakhs and Kanibadam were constructed in 1973, when Tajikistan still was part of Soviet Union.

The outdated Soviet stocks, however, were not only disposed of in the past by underground storage in the two Tajik polygons. Large quantities were dumped as well on a rather ad-hoc basis in mini burial sites, especially during the chaotic times of civil war (1992- 1997) after the collapse of the Soviet Union. These mini burial sites are often located close to villages and reportedly contain large quantities of obsolete and POP's pesticides. Unfortunately the exact volume of the wastes in these sites can, at present, only be estimated. Village # 1 in the Khatlon Oblast of Southern Tajikistan is a striking example of such a mini-burial site. At least 2000 tonnes of obsolete pesticides are reportedly buried under Village # 1. Six families are living on top of the toxic hot-spot.

Project teams of Tauw, Witteveen+Bos, Milieukontakt International, IHPA and FHNW carried out preliminary inventories and risk assessments at Vakhs and Kanibadam burial sites in close cooperation with the Committee for Environmental Protection under the Government of the Republic of Tajikistan. From 2012 to 2015 different initiatives for short term risk reduction and protection of the population have been carried out.[1]

To really tackle the problem, large projects financed by international donors are needed for collection, repackaging and disposal of the stocks. In line with international best practice the waste should be disposed of in state of the art destruction facilities such as high temperature incineration plants abroad and or co-incineration facilities at modern cement plants in Tajikistan itself. Such larger projects are currently being prepared by different agencies. In none of these projects, however, the burial site in Kanibadam and Village #1 are included.

The University of North Western Switzerland, the International HCH and Pesticides Association and Milieukontakt International are looking for ways to cooperate with the Tajik Committee for Environmental Protection, UNDP Tajikistan and possible donors to reduce the risks for human health and the environment from these two forgotten burial sites. Urgent action is needed to avoid environmental and health emergencies.

Key Words

Tajikistan, obsolete pesticide burial sites, risk assessment, risk reduction, remediation, DDT, awareness raising, venerable groups.

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[1] *Especially the UNEP GEF project Demonstrating and scaling up sustainable alternatives to DDT for the control of vector borne diseases in Southern Caucasus and Central Asia* with co-funding initiatives from OSCE, UNDP and the Tajik Committee for Environmental Protection has been instrumental for reducing environmental and health risks from Vakhsh Burial site. Project results of this project, however, are discussed in other sections of this publication.

Full Article

In 2012, the environmental condition of the abandoned Kanibadam burial site in the Sughd province of northern Tajikistan was extremely bad. The fence, that once protected the site, was taken away already many years earlier, by locals in need of construction materials. Nobody was guarding the place and contraband groups regularly raided the site to dig up DDT and other obsolete pesticides to sell them at the local market. As a result chemicals migrated off site through wind and water run-off erosion. Trespassers (mostly children) with cattle, flora and fauna were exposed to hazardous toxic waste from the burial site.

Generally the contraband groups used to manually dig out the pesticides using a backhoe. Sometimes such groups organised themselves in a more professional way and large equipment was brought to the site in order to get to the outdated but still valuable stocks more efficiently. All over the territory empty metallic and plastic containers were scattered around. Erosion control measures such as terraces and a sluice (built in Soviet times, in the polygon for reducing run off; collecting rain and controlling gully erosion) were destroyed. The soil erosion processes contributed to the contamination of lower laying territories with obsolete and POPs pesticides.

Project teams of Tauw, Witteween+Bos, Milieukontakt International, IHPA and FHNW established inventories and risk assessments at Kanibadam burial site in 2013.

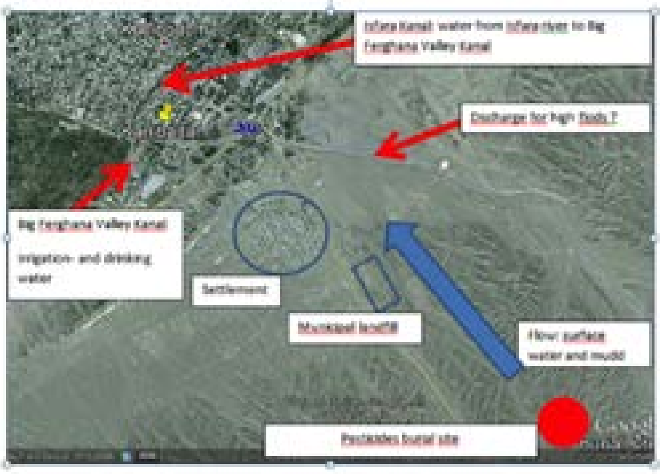

Figure 1: site investigations, sampling, risk mapping and risk zone description (pictures courtesy of TAUW, Milieukontakt, IHPA,FHNW)

Still today there is open access to Kanibadam burial site; there is no fence to keep out people and cattle. The GEF Small Grants Programme in Tajikistan supported an initiative of the Dushanbe based NGO Bono that covered the site with layers of fresh soil to stop further contamination via wind erosion and rainwater run-off. Unfortunately the works were not carried out fully in line with international best available practices, but a positive result is that obsolete stocks are not accessible anymore for contraband groups, cows cannot drink standing water from pits and toxic chemicals do not enter directly into the food chain.

Expanding neigbourhoods

The site, however, continues to be an environmental hotspot and urgent environmental and health risks remain. The city of Kanibadam is gradually expanding and especially the people from the newly build neighbourhoods at only a couple of kilometres located from the site are at risk. Well-designed risk reducing measures are urgently needed to avoid public health and environmental accidents.

The problem for the smaller sites containing leftovers from DDT and other POPs pesticides is their location. As a matter of fact many of them are situated close to settlements. People living and working near or even at such sites are nearly in daily contact with the toxic substances. Children are playing in highly contaminated soil.



Figure 2: dumpsites with open access, no fences, no warning signs, no cover, illegal waste extraction, children playing with pesticides. (Pictures courtesy of Tauw, Milieukontakt, IHPA, FHNW).

Houses build on top of pesticide waste

Village # 1 is one of these mini burial sites. The six families that build houses on top of at least 2000 tonnes of obsolete pesticides settled in the village as refugees. They moved to the village from other Tajik regions because of landslides, flooding and other emergency situations in their native settlements. The estimated tonnage buried in the village, however, is not based on a detailed site investigation and the amounts need to be verified. Run-off water from the territory of Village # 1 ends up in an irrigation canal that is used, amongst others, by the population of downstream villages for drinking water.

The outcomes of a risk-assessment carried out during a ToxCare mission in 2012 to Kanibadam are summarised in an action plan. The proposed measures for risk reduction are based on international recognized best practises. These actions should be implemented as soon as possible in order to protect the local population and environment from further negative impacts of emissions and the spreading of contaminants from the burial site.

Prioritized action

The ToxCare mission in 2015 prioritised the actions listed below and started to carry them out during the mission

- Get support from local, regional and national authorities and the Committee of Environmental Protection (CEP) for the implementation of short and long-term measures to remediate the obsolete pesticides burial sites in Kanibadam and Kumsangir (Village # 1);
- Raise the awareness of the local population on how to protect themselves from the negative impacts of the toxic chemical stored at the burial sites;
- Identification of possible donors for the implementation of mid-term risk reduction measures and complete remediation of the obsolete pesticides burial sites in Kanibadam and Kusamgir.

Kyrgyz approach

During the mission in March 2015 the sites of Kanibadam and Kumsangir where visited. A concept for final remediation of Kanibadam burial site was presented to the mayor's office and to local environmental protection experts.
In the Northern Sughd Oblast (Kanibadam) and in the Southern Khatlon Oblast (Village # 1) meetings where organised with the heads of the regional environmental departments. The successful implementation of a Milieukontakt International, Tauw, Green Cross Switzerland, Ekois, Green Light risk reduction project at the Kyrgyz burial site Suzak A. was presented. Tajik stakeholders welcomed the adoption of a similar strategy to lower the risks from Kanibadam and Village # 1 burial sites.

In short the strategy prioritizes:

1. Protection of the population (awareness raising amongst the local population and resettlement of groups at direct risk);
2. Protection of groundwater (top cover including HDPE plastic, avoid surface run-off by a drainage system);
3. Avoid wind erosion (top cover including HDPE plastic);
4. Avoid contraband excavation (Installation of a fence

and appointment of guards, CCTV);
5. Elaboration of a control a maintenance concept including a budget needed for implementation.

Figure 3: A reference project from Kyrgystan: fencing, covering and guarding the contaminated site, developed and implemented by Milieukontakt International (Pictures courtesy of Milieukontakt International).

During the same March mission several workshops where organised in Kanibadam to inform the local population. In collaboration with the authorities the population was informed about the risks they, and especially their children, are facing because of the obsolete pesticides burial side close to their homes. Simple rules on how to protect themselves and how to avoid risks were explained in detail. In separate meetings with school children the same message was conveyed.

Figure 4: Awareness rising workshops for authorities, school children, local population

Abstract health worries

Awareness raising is very important and actually need to be carried out constantly. The problem is that people do not get sick overnight, when exposed, but eventually somewhere in a distant future. Especially in regions were people have urgent daily worries on how to maintain their families, long-term health risk can appear as an abstract and only theoretical risk to the local population.

To really tackle the problem of Kanibadam and Village # 1, large projects financed by international donors are needed for collection, repackaging and disposal of the stocks. In line with international best practice the waste should be disposed of in state of the art destruction facilities such as high temperature incineration plants abroad and or co-incineration facilities at modern cement plants in Tajikistan itself. Such larger projects are currently being prepared by different agencies. In none of these projects, however, the burial site in Kanibadam, and Village #1 are included.

Urgent action

The University of North Western Switzerland, the International HCH and Pesticides Association and Milieukontakt International are looking for ways to cooperate with the Tajik Committee for Environmental Protection, UNDP Tajikistan and possible donors to reduce the risks for human health and the environment from these two forgotten burial sites.

If there will not be an interaction within reasonable time environmental and health emergencies can happen. Through ongoing surface and groundwater the contaminants can enter the food chain and poison local communities. Large areas of fertile soil will get polluted and will degrade. Only small surfaces of the mountainous republic of Tajikistan are suitable for agriculture and ultimately the food security of a densely populated country is at risk.
Both sites, Kanibadam and Kumsangir are directly exposed to groundwater pollution and surface water runoff from the obsolete pesticides sites.

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RECOMMENDATIONS FOR FUTURE RISK ASSESSMENT AND ACTION PLANS FOR FINAL DISPOSAL OF OBSOLETE PESTICIDES IN TAJIKISTAN

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Abstract

First data of pesticide inventory were obtained in 2005 by Environmental Research and Protection Center (Ufa, Russia) when realizing the project GEF\UNEP GEL-2328-2761-4708. Samples of soil and of mixture of unidentified pesticides from Sagdijskaya, Khatlonskaya and Kulyabskaya regions and from the area of the city of Tursunzade (the Tadjik aluminium production plant) were analyzed. The sum total of pesticides in soil samples made from 2 to 70000 mg/kg, and general pollution was from 14 to 73000 mg/kg of soil: in the soil of Kulyabskaya zone it was 10000-75000 mg/kg, in that of the waste burial site in Vakhsh and Kanibadam - 2000-20000 mg/kg.

Implementation of subsequent international projects in Tajikistan in 2009-2015 permitted to reveal most hazardous storage places, to evaluate waste volumes and to start planning work on hazardous waste decontamination.

The phase of pesticide repacking is being carried out. Quick risk assessment (ICARO) for the Kanibadam site was made. The city of Kanibadam is situated within the risk zone. The main path of population exposure is transfer of polluted particles with dust for the distance of up to 20 km. Aquatic path has not yet been sufficiently studied. Stocks of obsolete pesticides still represent a hazard in many countries, in particular if storage or disposal is inappropriate or delayed. Connection between the volume of used pesticides, death rate and infectious diseases of the population was found.

To obtain information on risk assessment for the population living close to waste landfill sites it is recommended to use economically acceptable methods proven in our practice of monitoring of the area of complex pollution by dioxins-pesticides-oil products in risk zones in Russia (Ufa, Chapayevsk). Effectiveness was shown by the methods of passive air sampling, screening-methods of assessment of dioxin-like toxicity of soil and food using the Calux system. Positive results were displayed by methods of soil rehabilitation with the use of modified aboriginal bacterial component. Promising is the use of semi-field test methods. Soil micro- and mesofauna (e.g., nematodes, microarthropods, enchytraeids) and microorganisms are the main groups targeted by this particular system.

Key Words

Pesticides, risk assessment, contaminated soil, passive sampling, test-systems, Tajikistan

Materials and methods

International organizations such as WHO, FAO, IARC, **CAC** as well as national standards state the limits of pesticide content in the environment and food[1]. Thus in Russia beginning from 01.01.2015 there is in force a national standard concerning the waste containing POP[3]. Toxicity parameters for obsolete pesticides are also well known, instructions for risk assessment are worked out[3]. It is obvious that for risk assessment the determination of toxicants coming via all possible ways – air, water, food, inhaling, through skin, in everyday life - is required. A wide range of methods may be used for this.

Determination of composition of soil pollutants in Tajikistan was carried out by the GC/LRMS method and the system of preliminary extraction of components (TRIO-1000, GC 8000 serias, DB-MS, 60 m*0.25mm*0.1µm). PCDD/Fs determination and dl-PCB was carried out in compliance with the methods of USEPA 1613 and 1668, HRGC/HRMS.

Method of air passive sampling is introduced into the list of methods for analysis of Stockholm convention POPs. The effect of long-term accumulation on PUF filters of polluted dust containing pesticides and POPs is being used, this is applied in GAPS and MONET[4,5] programs for air monitoring.

Calux methods are good for screening of wide areas of pesticide pollution, for assessment of soil toxicity, including the dioxin-like one, for risk assessment of pollutants contribution with food. Semi-field methods based on the use of soil biota are fit when designing schemes of cleaning polluted soils. They apply the effects on the organisms predominantly inhabiting the soil profile[6]. Methods of pesticides biological destruction with the use of aboriginal bacterial component (Patent of the RF No. 2562156) were tested under the conditions in-situ and ex-situ on real polluted soils in Ufa and Chapayevsk[7].

Results and discussion

In many countries there is the experience of elimination of obsolete pesticides stocks and rehabilitation of polluted soils. In terms of Tajikistan the tasks of 3 levels were stated:

1. Elimination of direct risks: destruction of stock masses of determined and undetermined complex mixtures of pesticides (the project TOX CARE).
2. Limitation of potential risks in medium-term period: monitoring in the area of high pollution of soil as a result of long storage period.
3. Reducing risks in long-term period: rehabilitation of soils of agricultural lands and residential zones brining them to admissible levels by biotechnological methods.

Even the primary inventory in 2005 of obsolete pesticides stocks in regions of Tajikistan revealed a wide range of pesticides of different structures, primarily chlororganic and organophosphorous compounds, pyrethroids, carbamates, including POPs-related pesticides from 0.08 to 7.18 mg/kg of soil. These data were used when developing NIP in Tajikistan[8].

Evidently there is no universal solution for different zones depending on the pollution level.

After destruction of repacked pesticides there remain zones of residual impurity that require monitoring. As far as the main way is propagation of contamination with dust particles it is quite probable that the method of passive sampling will be suitable to reveal the ways of secondary emission around the landfill sites Vakhsh, Kanibadam planned for elimination and what is more important – in residential zone. The data are also needed for risk assessment.

As an example we'll give the data found in the course of realization of the MONET-CEEC project[3]. Experimental data were obtained at the University of Masaryk, Brno. Including Tajikistan into MONET monitoring programs will permit to make assessment of the air pollution level in hazardous zones, of intensity of transfer from landfill sites, and also to make a prognosis.

POP component	Bishkek	Karaganda	Ufa (background)
α-HCH	49.3-340.7 (166.8)	189.5-798.5 (426.7)	50.9-65.3 (56.1)
β-HCH	20.3-103.1 (62.2)	12.1-103.9 (39.2)	3.6-8.4 (5.9)
γ-HCH	37.4-308.7 (66.7)	27.2-124.5 (79.9)	15-23.9 (20.15)
o,p-DDD	0.25-0.25 (0.25)	9.21-5.2 (3.5)	0.25-2.4 (1.75)
o,p-DDT	0.25-0.25 (0.25)	2-4.6 (3.2)	0.25-3.8 (1.78)
o,p-DDE	11.9-73.8 (51.7)	20.6-31.2 (21.6)	7.6-12.3 (9.1)
PCB, 6 indicator	160.9	313.82	64.35
HCB	31.3-40.5 (37.5)	33.2-73.3 (36.4)	27.6-33 (30.6)
PnCB	11.9-105.9 (53.8)	7.4-23.3 (10.2)	6.5-9.8 (7.7)

Table 1. POPs in the air of the cities of Kyrgyzstan, Russia and Kazakhstan, pg/m^3
Minimum and maximum values are given, in brackets – median value of data.

The results of a model experiment of biodegradation of pesticides in soil when processed by microorganisms *Rhodococcus wratislaviensis* in combination with application of a complex of fertilizers are given in Table 2.

Experiments with biological preparations in Chapayevsk demonstrated efficiency in the process of treatment of soil polluted with PCDD/Fs and PCBs (TEQ PCDD/Fs 331.1 pg/g and 5.32 pg/g dl-PCBs) in the experiment ex-situ up to 104.1 PCDD/Fs and 1.99 pg/g PCBs. Polluted soils in Ufa in the model experiment revealed tendencies to changes of concentrations of some PCDD/Fs congeners by 25-35% at the average. However in the experiment in-situ an inconsiderable change is shown, there are some results falling out of the general tendency. There may be present the influence of additional physical factors (sludge washing, transfer to the depth when watering the site, transfer of polluted dust, emission).

Compound	Level	Start	15 days	45 days	75 days	105 days
lindan	Low	2.48±0.37	1.43 ± 0.21	1.24 ±0.19	1.17±0.18	1.05±0.16
HCB		2.99±0.45	1.51 ± 0.23	1.41± 0.21	0.62±0.09	0.45±0.07
DDT		2.51±0.38	1.17 ± 0.18	0.92 ±0.13	0.32±0.05	0.25±0.03
lindan	Medium	25.2 ±3.8	11.4 ± 1.7	11.3 ±1.69	5.11±0.77	4.84±0.73
HCB		31.7 ± 4.8	16.6 ± 2.5	11.4 ±1.71	4.20±0.63	3.42±0.51
DDT		25.4 ± 3.8	12.9 ± 1.9	12.2 ±1.83	8.13±1.22	7.88±1.18
lindan	High	98.8 ± 14.8	47.8 ± 7.2	45.4 ± 6.8	38.6±5.8	20.0±3.0
HCB		148 ± 22	101 ± 15	92.9 ±13.9	85.3±12.8	54.8±8.2
DDT		99.1 ± 14.9	60.8 ± 9.1	56.5 ± 8.5	45.9±6.9	37.2±5.6

Table 2. Periodical checking of the degree of pesticide destruction, mg/kg

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ENVIRONMENTAL RESPONSIBILITY

CONSUMERS' COMPENSATION FOR DAMAGE CAUSED IN THE CONTEXT OF ENVIRONMENTAL CONTAMINATION – INPUTS FROM EU PRODUCT SAFETY LEGISLATION[1],*

[1] This contribution is a revised version of a presentation made by the author at the 13th HCH & Pesticides Forum «20 years after the 3rd Forum in Bilbao: the legacy of the Lindane production in Spain and lessons learned», held in Zaragoza from 3rd to 6th November 2015.

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Résumé

L'inventaire des directives adoptées par les institutions européennes en vue de protéger les consommateurs contre les risques liés à l'usage de produits de consommation et, en cas d'accident, de faciliter l'obtention de dommages compensatoires par la mise en place d'un régime de responsabilité sans faute mène au constat d'une fracture. Les instruments législatifs en place dans le domaine de la politique de protection des consommateurs d'une part, et dans celle de la protection de l'environnement, d'autre part, ne se rejoignent pas. Les directives «consommateur» restreignent la définition du défaut de sécurité des produits à l'atteinte à l'intégrité physique du consommateur ou à sa propriété, sans l'étendre aux dommages causés à l'environnement. Quant à la directive sur la responsabilité environnementale, elle ne confère aux consommateurs aucun droit à indemnisation à la suite d'un dommage environnemental ou d'une menace imminente d'un tel dommage.

Comme c'est trop souvent le cas, la politique de protection du consommateur et celle de protection de l'environnement évoluent sur des chemins parallèles sans se rencontrer. Une préoccupation partagée de longue date par notre collègue Mary Sancy et moi-même et à laquelle nous avons tenté d'apporter des réponses dans plusieurs contributions et manifestations scientifiques. La présente analyse poursuit un même but et entend susciter une première réflexion sur la complémentarité des régimes de responsabilité consacrés par le droit européen pour les dommages liés à l'usage de produits de consommation et leur application dans le contexte d'une contamination environnementale.

L'analyse identifie certains ponts possibles entre les textes en vigueur ; elle souligne aussi les obstacles à un tel rapprochement. Elle appelle à confirmer dans les normes légales une vision inclusive, globale et intégrée de la notion de sécurité des produits qui inclue la protection du consommateur, la santé, le développement durable et la protection de l'environnement.

Building bridges between consumer protection policy and environmental policy

This short contribution, which still is a preliminary attempt, focuses on the relevance of the liability regimes that have been defined by the European Union legislator with a view to protect the safety of users of consumer products in relation to safety hazards created by such products in the context of long-term environmental contamination.

For years, I shared with our colleague Mary Sancy the strong willingness to build bridges between consumer protection policy and environment protection policy. Obviously there are conflicts of interests between these two policies, as mass-consumption is a main source of pollution and consumer choices remain most often based on hedonist, materialist and short-term price-related considerations. However, if one takes distance from a «consumerist» perception of consumer policy rationales, one soon realizes that there are more converging interests, goals and tools than diverging ones between the concerns for consumer protection at one hand, and environment protection on the other.

Both policies share the general objective of improving the quality of life of the citizens. Among other specific goals, they both aim at protecting consumers against hazards to their health and safety. Health or safety risks faced by consumers as a consequence of damage caused to the environment fall in the scope of consumer policy concerns. Similarly, sustainable production and consumption patterns have become a major policy area of consumer protection policy. The Guidelines on consumer protection adopted by the UN General Assembly in April 1985, as amended in 1999 and more recently in December 2015[1], explicitly state that the guidelines have the objective «*to promote sustainable consumption*» (Par.1, h). Responsibility for sustainable consumption is placed upon «*all members and*

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[1] United Nations General Assembly, Resolution A/C.2/70/L.28 entitled «*Consumer protection*», doc. A/70/470/add.1, 15 December 2015.

organizations of society, with informed consumers, member States, business, labour organizations and consumer and environment organizations playing particularly important roles» (Par. 50).
While rationales for consumer policy include strong economic considerations, they also put forward social policy concerns, among which the protection of collective and long-term interests, such as environmental health, quality of life and sustainable development.

Legal tools referred to for implementing both policies are also quite similar, in particular, regulatory patterns, information and education measures, specific liability rules and collective redress procedures. Both policies rely heavily on the active involvement of non-governmental organizations, such as consumer associations and environmental groups.

The protection of consumers against unsafe pesticides is one of these areas where consumer protection and environmental protection converge. Indeed, the presence of pesticides in consumer products – food or non-food – may prove hazardous both to human health and safety and to the environment. Harmful effects on consumer health and safety may be immediate or short-term ones; they may also result from the long-term contamination of the environment.

In order to prevent such hazardous situations and, in case of damage, to allow for fair compensation of victims, EU policy-makers have introduced safety obligations and liability rules that fall in the scope of application respectively of consumer protection policy and of environmental policy. Unfortunately, these safety rules and liability regimes apply to the one or to the other policy field. None of the adopted legislation provides for a common set of obligations that could be equally applicable to the protection of consumers against unsafe products and to damage caused to the environment. The liability rules that are applicable in case of damage caused by unsafe consumer products to individual consumers and in case of damage caused to the environment remain separate.

Both liability systems, as defined at the level of the European Union, evolve in parallel, as consumer protection policy and environmental policy too often do. Under EU consumer legislation, the definition of a safe product will not include damage to the environment. As to Directive 2004/35, it does not give consumers a right of compensation because of environmental damage or of an imminent threat of such damage (Art.3.3).

Therefore, it is worthwhile investigating whether the tools that are available under EU consumer legislation in order to fight against unsafe products could be usefully referred to in case of damage caused to consumers in the context of a long-term environmental contamination, such as soil, food or water pollution.

Applicable rules

The Directive states a rule of complementarity that makes it applicable to all products available on the market "*in so far as there are no specific provisions with the same objective in rules of Community law governing the safety of the products*" (Art.2). It acts as an umbrella legislation, which complements EU vertical or sector-specific legislation in place, such as safety rules applicable to chemicals and pesticides.

(i) *Directive 1999/44/EC of 25 May 1999 on certain aspects of the sale of consumer goods and associated guarantees*[2]: this Directive deals with implied warranties and express guarantees associated with the sale of goods to consumers. Defects covered under the legal or implied warranty scheme are these making the product unfit for use or of lower quality than ordinary, hence including quality, performance and safety defects.

As shown in the Table below, the main features of these three directives are far from being uniform.

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[2] *Official Journal* L171, 7th July 1999, p.12.

Directive	Scope	Person protected	Liability based on	Person liable	Recoverable damage	Prescription period
Product liability	Product = any movable (e.g., finished, component)	Any victim (buyer, user, bystander)	No-fault/ strict liability: safety defect.	Producer, importer. By default, distributor, retailer.	Death, injury, damage to *private* property, consequential and immaterial damages (according to national laws)	10 years
General safety of consumer products	Product = any movable (e.g., finished, component) intended for consumers or likely to be used by them under reasonably foreseeable conditions.	Consumer (non-professional user)	Fault: violation of the general obligation to place only safe products on the market, and of the other general obligations set out in the directive.	Producer, importer. distributors within the limits of their respective activities.	Death, injury, damage to *private and business* property, consequential and immaterial damages (according to national laws)	Time limits as defined under national laws.
Legal/ implied warranty	Product = any movable (e.g., finished, component)	Non-professional buyer	No-fault/ strict liability: product unfit for use because of a safety defect.	Professional seller and/or producer	Death, injury, damage to *private and business* property, consequential and immaterial damages (according to national laws)	2 years

Positive features

The multiplicity of regimes that are applicable leads to a highly complex and confuse legal framework to deal with unsafe consumer products. However, for the purpose of this contribution, it presents positive features that should be pointed out.

(1) The very broad definition of «*product*» under the above liability regimes makes these applicable to pesticides, chemical substances, residues, waste or by-products.
The definition of product includes all movable goods, whatever their form or nature. Movable goods containing pesticides or chemical substances are included, i.e. feed and food, drugs, drinking water, raw materials, finished products or component parts, all non-food products, whether new, used or reconditioned. In addition, pesticides, chemical substances, residues of pesticides, waste, by-products singled out as such without being integrated into another product are included either.
It does not matter whether the product is still on the marketplace or has been withdrawn, removed, partially destroyed or discarded, as long as there is still likelihood that it is available or accessible to consumers under one form or another, such as residues, waste or by-products, and presents safety hazards.
It could be argued that pesticides or chemical substances, identified as such, are products «*not intended for consumers or likely to be used by them under reasonably foreseeable conditions*». We do not share

that opinion, as these are products the use of which by consumers remains likely as long as they have not been fully eliminated, and this is precisely the case in the context of environmental contamination and related consequences on feed and food, milk or water. Besides, long-term risks and risks associated with waste, residues or by-products must be held reasonably foreseeable by the economic operators making such products available to consumers.

Doubts may also arise from the fact that the Directive 2008/98/EC of 19 November 2008 on waste[3] does not define waste as a «*product*», but as «*any substance or object which the holder discards or intends or is required to discard*» (Article 3.1). «*Object*» and «*substance*» are without any doubt movable goods and hence products.

(2) None of the above regimes excludes the application of the other. They are separate but complementary liability rules and they all have an impact on both the prevention of risks and hazards and the correction thereof.

While the main goal of the Directive on product liability and the Directive on sales of consumer goods and associated guarantees is to facilitate compensation of damage caused by a defective product, they also act as a strong deterrent for economic operators making unsafe or non-compliant products or substances available on consumer markets.

While the Directive on general product safety and the Directive on environmental liability, whose main goal is prevention, do not give private parties a right of compensation because of a product-related accident or environmental damage[4], the general obligations set out in the directives create new grounds for admitting and extending the liability of economic operators.

(3) Defences used to escape liability remain few.

Third-party liability defence, by which the economic operator would invoke the liability of the distributor, transporter, testing body, certification body, waste producer, waste holder, dealer or broker (as defined by Article 3 of the Directive of 2008 on waste) is not a valid defence (Article 8, par. 1, of the Directive of 1985 on product liability).

In case of several liable persons, liability will be joint and several.

No disclaimers of liability are allowed and such disclaimers will be declared unfair contract terms in consumer transactions.

With respect to development risks, i.e. risks that could not have been known or foreseen by the economic operator in the state of scientific and technical knowledge at the time of placing the product on the market, Article 15.1.b of Directive 85/374/EEC on product liability leaves the option open to member States to admit development risks as a valid defence or not. The fact that development risks are not a valid defence in several EU countries, while they are in others, forces economic operators to consider, assess and insure these risks when placing on the market products that are likely to have long-term safety hazards, such as pesticides and chemicals.

Besides, the follow-up obligation stated in Article 5 of the Directive 2001/95 on general product safety imposes upon economic operators to monitor the long-term risks associated with products that they have placed on the market and to take appropriate action when they become informed of such risks or damage:

« (…) *Within the limits of their respective activities, producers shall adopt measures commensurate with the characteristics of the products which they supply, enabling them to:*

(a) be informed of risks which these products might pose;

(b) choose to take appropriate action including, if necessary to avoid these risks, withdrawal from the market, adequately and effectively warning consumers or recall from consumers.

(...) Where producers and distributors know or ought to know, on the basis of the information in their possession and as professionals, that a product that they have placed on the market poses risks to the consumer that are incompatible with the general safety requirement, they shall immediately inform the competent authorities of the Member States thereof (...) giving details, in particular, of action taken to prevent risk to the consumer».

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Shortcomings

While the above positive features of the liability regimes applicable to consumer product safety create potential for action in case of damage caused by a product, of any kind and whatever its form, in the context of environmental contamination, such as soil, food or water contamination, they also have severe shortcomings.

(1) The very short prescription period of 10 years from the date on which the producer put into circulation the product which caused the damage, as provided by Article 10 of Directive 85/374/EEC[5] may have the effect to exclude liability for long-term safety hazards and associated risks. At the time of introduction of the EU directive, no-fault was admitted only against such a strict time limitation. This compromise solution severely undermines the impact of the introduction of the strict liability regime,

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[3]. *Official Journal* L312, 22 November 2008, p.3

[4]. The Directive explicitly states that national laws may give private parties such a right of compensation (Art.3.3).

[5]. Under the directive on environmental liability, the prescription period is 30 years (Art.17).

especially for products such as drugs, pesticides and chemicals, as well as for waste, residues and by-products.

(2) While no-fault liability is the rule under product liability law, it is not under general product safety law.

However, in most EU countries, case law confirms that strict liability is predominant when safety of consumers is at stake. Where damage was caused to consumers by a defective product and there is uncertainty about the source of damage, courts prove to be flexible as to the obligation of the victim to prove the causal link between the defect or lack of safety and the damage. Either they declare the person who did create the risk liable without fault, or they broaden the scope of what constitutes a negligent behaviour. As for example, the following acts will be held negligent:

- To put into circulation a product that does not comply with safety requirements, including mandatory standards.
- To put and maintain into circulation a product that is or becomes unsafe, whatever the moment of the product lifecycle.
- Not to have adequately foreseen or assessed the long-term risks linked to the product, including those likely to subsist or to appear during the product elimination, destruction or reuse.
- Not to take appropriate action to prevent, reduce or remove any known or foreseeable (by professionals) safety hazards or risks linked to the product, even if the risk is not immediate.
- Not to have adequately informed consumers about the actual or potential long-term impact of the product or components thereof on their safety.
- Not to have adequately notified or informed the market surveillance/environment protection authorities about the actual or potential risks involved.

(3) None of the EU legislation on consumer product safety and product liability provides for recovery of damage caused to the environment.

This highlights the restricted or fragmented vision of the concept of safety that prevails in consumer safety legislation. Recoverable damage are limited to damage to physical integrity (death, injuries) and property.

It also reflects the predominance of individual interests rather than public or collective concerns in consumer policy.

Conclusions and recommendations

The above observations reveal that in case of environmental damage, the liability regimes that are applicable for unsafe or defective consumer products under EU law are useful complements to the Directive 2004/35 on environmental liability, which indeed introduces new grounds of liability for economic operators but does not include remedial action directed at compensating damage suffered by individual consumers.

Still, this conclusion needs to be further substantiated and the way to build a bridge between the liability rules that are applicable to product safety and the one that applies in case of environmental damage must be further explored.

It is our opinion that the following three legal reforms will help reaching that goal:

(1) To broaden the definition of unsafe or defective products under Directives 2001/95, 1999/44 and 85/374 in order to include damage to the environment and serious (rather than ‘imminent’, as used in Directive 2004/35/EC, Art. 2.9) threat of such damage.

The cornerstone of this new approach is an all-inclusive or crosscutting understanding of the concept of safety, which combines consumer protection, health, sustainable development and environment protection considerations.

(2) To confirm that no-fault liability is the common rule in case of damage caused by unsafe or defective products. The one who creates the risk pays, exactly as the one who pollutes pays.

(3) To ensure that long-term safety risks are actually included in the scope of these new liability rules, namely by extending the prescription period under Directive 85/374 to 30 years.

The above recommendations will help in designing an integrated and coherent regime applicable in case of damage caused to consumers by consumer products in general as well as in the context of environmental contamination. For sure, effective consumer redress will remain an issue, especially in case of mass-damages. Hence, building bridges between consumer protection policy and environmental policy will be needed also in respect to private and public enforcement tools available to put the newly defined regimes in action.

LINDANE, THE HUNGARIAN CASE ADJUSTED

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Abstract

This paper explores the liability schemes related to Lindane at the time of the replacement of DDT and after its ban, taking into consideration the concept of damage prevented by use and also damage caused. It argues that there is a great difference in liability schemes when life-cycle analysis (from invention through production to use) is introduced. It demonstrates that economic and scientific evaluation both of risks related to use, and also of the attributes, of Lindane has changed over the years and has affected policy decisions and, as a consequence, the liabilities. It shows that damage caused by the use of artificial chemicals such as Lindane is not necessarily recognised under liability schemes and may be turned into a cost element of agricultural production. It demonstrates that the first decision on use of chemicals such as Lindane is political in nature and does not fall within the scope of classical legal liability. It claims that scientific evidence is considered on economic grounds by policy makers and that damage caused to nature and to its capacity for self-protection is not given full consideration even though it is acknowledged by scientists; as a consequence liability schemes fail to integrate such evidence. Furthermore, individuals affected by the hazards of Lindane are part of different communities depending on when and where they are affected, thus the risk to society as a whole is usually not clearly outlined and externalities are not fully integrated. The paper demonstrates that the use of Lindane and of other artificial chemicals is overtaking traditional knowledge and methods based on ecological thinking. As a result, users of chemicals cannot make good choices in line with ecological rationality; thus the paper calls for the development of an educational policy regarding the application of pesticides.

Key Words

lindane, liability, damage, costs, public interest

Introduction

Synthetic insecticides have been part of plant protection against pests since the 1940s in Hungary. After the ban on DDT in 1968, Lindane was introduced as one of the most important replacements. By an overview of scientific papers, articles, this paper reviews on what grounds

Lindane was chosen as the best substitute and what kind of side effects and damages related to its usage were recognised at that time. Policy documents prepared by public policy and research institutions allowed to summarise the use and the effect of Lindane. They were published as appendices to the project summary on implementing the Stockholm Convention. For the liability chapter, legislation over the last hundred years with regard to plant protection was reviewed to see how liability schemes alter and what are the new elements that are introduced as a result of chemical protection.

Why Lindane?

In 1968 Hungary was the first State to ban DDT. It was preceded by an extensive debate on the health hazards and negative health impacts on humans and other living organisms. In 1967 the General Assembly of the Hungarian Academy of Science devoted a full day to discussing the options and alternatives to replacing DDT, Dieldrin and Aldrin. The need to ban the most persistent chemicals was commonly accepted, due to the health hazards they represent not only through direct contact but also by bioaccumulation and even biomagnification. In 1968 a special report on the subject matter was published by the Information Centre of the Agricultural and Food Ministry (Report 68).[1] It summarized the up-to-date scientific information on choices for substituting chlorinated hydrocarbons in plant protection. Josepovits and Nechay collected, reviewed and evaluated 150 scientific articles and reports from 43 establishments in 18 countries. The first chapter of the report summarized the hazards, and negative side effects of chlorinated hydrocarbons, the second chapter listed and evaluated the potential active components (phosphoric acid esters, carbamate derivatives, and natural plant compounds) with a view to making them as replacements, and the third chapter was dedicated to chlorinated hydrocarbons substitution for the purposes of public and animal health. The fourth chapter provided an overview of administrative measures and economic aspects.

It is clear from the report that one of the most important aspects in finding replacements was to achieve less persistence. Even if Lindane was known to be more toxic than DDT and represented higher risks to bees when not applied properly, it was considered a good substitute due to its faster disappearance from the body and its shorter half-life time as demonstrated by data. It was noted, however, that its presence in plants varied by species (e.g. fodder, cabbage) and, when applied with other pesticides, its persistence could increase. Furthermore, it was affected by the formulation used, granule formulation lasting longer than powder.

The Report 68 noted, with reference to various studies (including Hungarian), chlorinated hydrocarbons' very strong impact on insect biome. It was argued that the impact on the fauna of insects is very difficult to assess. Usually it was recognised only after the damage had occurred in terms of loss of balance. It was observed that predator bugs, predator mites and other beneficial species could be more susceptible to insecticides. Their disappearance allowed uncontrolled growth of other insect populations turning them into plant-damaging insect populations. It was observed that greater damaged was caused by Aphids due to DDT treatment killing the lady beetle population. A similar outcome was observed as a result of lost natural pest control in apple orchards treated with DDT. According to the Report, the elimination of "natural enemies" by insecticides caused an estimated 100 million HUF[2] in plant damage each year in Hungary. Phytotoxic impact was observed especially when chlorinated hydrocarbon was applied as soil disinfectant. It had a damaging impact on sensitive plants by changing germination, deforming sprouts, etc. In addition, evidence showed that some insecticides (including DDT) could change the biochemistry of plants, manifesting in a trophic impact on pest mites by speeding up their growth and fertility. Lindane was considered safe in this respect if used under normal conditions that is, if used as instructed by the makers

Lindane was odourless and tasteless and that made it suitable for treating orchards or even using it as a soil disinfectant because it did not affect the taste of fruit and vegetable products. However, it was proposed to monitor results when Lindane was more extensively used.

Lindane was also considered as a substitute for DDT for public and animal health measures. It was used for treating storage places and keeping animals healthy. (Lindane was used as a spray or a bathing/washing lotion against parasites of cattle.)

Using Lindane as a replacement was also justified by the fact that its impact in practice was known at the time, and it was an effective insecticide with shorter persistence. It was considered to become the main substitute to protect plant parts above ground, against pests in soil, and also as a disinfectant in storage places and to protect crops. Compared to the other choices Lindane was a sort of all-purpose insecticide. The Report68 listed the substitute chemical products and their descriptions including their main properties in comparison to the chemicals they replaced and details of where and how to use them.

Based on the Report 68, 2000 tons of DDT manufactured in Hungary, 150 tons of Dieldrin and 300 tons of Aldrin both imported, had to be replaced. DDT was very cheap (330 USD/ton) compared to the other agents (Aldrin: 1174 USD/ton, Dieldrin: 1860 USD/ton) especially compared to Lindane (2300-2400 USD/ton). In economic term it meant that domestic DDT had to be replaced within the cost-frame of 660,000 USD. (Note, that the availability of foreign currency was limited at that time.) This served as a justification for enhancing the Hungarian production of phosphoric acid esters. However, concerns were raised regarding occupational health and safety and cost effects. Due to higher toxicity of phosphoric acid esters, they represented much higher health hazards not only to workers but to consumers as well.

The Report 68 included a detailed list for chlorinated hydrocarbon (with special reference to Aldrin and Dieldrin) and for Phosphoric acid esters setting out the costs related to personal protective equipment. When all relevant costs are added up, data show that the cost of protective equipment regarding Lindane is 30 percent of Aldrin's or Dieldrin's and 29 percent of that of Phosphoric acid esters. Additional costs of safety measures were also indicated, though not in figures but by listing them including preventive and curative measures.

Based on the Report 68 and other sources, giving up use of chemicals was not an alternative to DDT. In his book on Plant protection[3] Nechay referred to FAO calculations that rapid population growth in the world required an increase in food production by 35 percent by 1975. He stated that there were only two options to increase production: a) increasing territory of cultivated land, or b) increasing productivity of agriculture. He argued that the first option was not a real alternative in Europe except in the Soviet Union[4], and noted that in Europe in general and in Hungary in particular, land for agriculture was constantly shrinking due to land being taken for alternative uses such as industry, infrastructure and settlement development. Furthermore, air, soil and water pollution made land unsuitable for agricultural production or only suitable to a limited extent especially around industrial plants. He stated that plant protection (primarily chemical) could ensure and secure such rapid growth. He pointed to the positive effect of using chemicals since each HUF spent on chemical protection resulted in 5-7 HUF worth of increased production. In 1963 34 percent of the cultivated territory was treated with chemicals, in 1964 it grow to 40 percent. He stated that due to application of chemicals, the value of pest damage prevention amounted to 3.5 billion HUF and 5 billion HUF, respectively and that the damage caused by pests could be as high as 6 billion HUF on untreated territories. He assessed the main requirements against pesticides: a) they should not damage plants while they should be effective against the damaging living organisms, b) should not be persistent in unwanted ways, c) and should not harm beneficial organisms when applied under normal conditions. He called for research to shed light on the biological impact of plant protective chemicals, and to develop an effective educational policy that drew attention to the direct link between following instructions during application on the one hand and prevention, mitigation of hazards on the other. The impact on pests due to ecological, and agro-management organisational changes and the need to develop new methods were acknowledged by him and recommended. All of these showed how chemicals were gaining ground in plant protection even if importance and cheapness of biological protection was undebated.[5] In this context it is not surprising that, based on scientific evidence, the political decision was made to ban DDT, Aldrin, Dieldrin and technical HCH and the choice for their substitute included Lindane which is still a POP.

Lindane at work

The usage and the impact of Lindane can be summarised by studies attached as appendices to the reports on implementation of the Stockholm Convention on POPs. Hungary joined the Stockholm Convention in 2001. The Ministry of Environment, with the participation of public organisations including scientific bodies and NGOs, launched a programme (between 2000-2004) with the objective of summing up the evidence related to POP production and usage. As one of the first steps, inventories of sources were made and available data on POPs were evaluated. The report published in 2005[6] included an overview of POP presence in soil, water, air, the health impact of POPs, special chapters on plant protection chemicals, monitoring along with research and development, capacity regarding the elimination of hazards, macroeconomic concerns, legal background, assessments by public stakeholders and NGOs.

The usage of Lindane was shown mainly by adding up sales data for each year in which it had a permit.[7] Lindane and its different formulations had been on the Hungarian market till 1999. Sales data show the impact of the political decision on the production of chemicals. Figure 2 illustrates sales of Lindane between 1950s-2000 in tons of active compound.

Figure 1
Sale of Lindane between 1950-2000 (in tons)
Source: Table 11 in Pethő-Ocskai (2003)

In Hungary during this 50 years 2 3706 005 tons of plant protecting chemicals had been used out of which 446 881 tons (that is 18.8 percent) consisted of POPs. However, the active compound of those was only 66 459 tons. In this DDT was the leading agent amounting to 39 480 tons (59.4 percent). (It should be noted that it had been used for a limited time only between 1950-1970). Lindane was in second place with approx. 13 300 tons (20 percent) mainly sold between1960-1980. [8]

After the banning of DDT and the other POPs, all remaining products unsold became hazardous waste. The Ministry of Agriculture and Rural Development organised a collection campaign in the early 70s. About 100 tons of residues were collected mainly with chlorinated hydrocarbon and arsenic components. The waste was first placed in the nuclear waste landfill of Püspökszilágyi, then moved to the hazardous waste landfill of Aszód. Later some more collection programmes were pursued and the waste collected was taken to the hazardous waste incinerator of Dorog.[9]

As part of the implementation of the Stockholm Convention, evidence on pesticides residues and packaging materials left untreated was collected with the support of the environmental NGO Reflex.

Data produced by the soil monitoring system demonstrate a decreasing presence of Lindane in soil. Samples were taken from three layers. There was a steady decrease in the number of samples where presence of Lindane was above the detection limit, and while in 1993 it could still be detected in 7 samples at the second and third level, no sample was found in 1997 at those same levels.[10]

Data between 1990-2001 on water show that Lindane could be traced in surface water mainly at points of discharge of liquid waste by chemical companies. However, Lindane had not been found in ground waters.[11]

The impact on public health was assessed by analysing human and animal fat tissues, breast milk and in milk production of dairy animals.[12] The presence of DDT and other pesticides in them has been monitored since 1960. While data till 2002 still indicates the presence of DDT in breast milk the authors argued that it was mainly due to DDE metabolite and not due to new exposure.[13] It was observed that the regional distribution of samples containing HCH isomers varied. While they could not be traced in all samples, the number of contaminated samples was higher in agricultural regions, demonstrating a direct link between exposure and contamination.

In 1996 in Hungary the Government decided to launch a programme for the rehabilitation of contaminated fields.[14] It started with a survey that summed up contaminated sites. As a result a national programme was introduced. The number of contaminated sites and polluting sources amounted to approx. 30-40 thousand, and the estimated costs of rehabilitation were calculated to be 1000 billion HUF, within a 30 year time frame. The progress report of 2004 summed up the results reached between 1996 and 2004. The rehabilitated sites numbered 200, and related costs more than 82 billion HUF. The Ministry of environment managed the rehabilitation of 60 sites with a budget of 11.15 billion HUF. In 2004 the national budget contained 14.380 billion HUF.

In 2009 the Ministry of Environment and Water Affairs published the national action plan to reduce POP in the environment[15]. No new information on Lindane was published in it. Concerning site rehabilitation it was stated that site pollution by POPs was less significant and for that reason it did not require the inclusion of projects aimed at their recovery and cleaning up into the national rehabilitation programme.[16]

Snap-shots of liability schemes at the time of Lindane[17]

The liability schemes of the time when Lindane had been in use reflect the nature of the political regime, and also the changing role of chemicals in plant protection. In the 50s very detailed general and product specific rules provided for whom, how and under what conditions could apply chemicals including how to warn bees' owner. Along with the rules on chemicals detailed provisions set the obligations for protective measures, such as means of biological protection, managing monitoring and warning systems. Biological protective measures were very practical and concrete (e.g. having at least one turkey per hectare on alfalfa field, the obligation to placing out given number of birdhouses per hectare, to place a T shape sitting tree for predator birds at every hectare during moppet invasion or to get pigs on stubble fields within ten days after harvest against weevils). Reporting on the appearance of pests listed in pieces of legislation was the obligation of everyone involved in agricultural production. This information was collected by local authorities and the public was regularly informed on pests and what kind of pest control measures should be taken. Rules had to be strictly followed and non-compliance was penalised under public administration law of offence or even criminal law. It was the head of the cooperative or the state farm, which was held liable under criminal law if rules were not enforced by him/her.

Besides penalizing non-compliance, the public authority had the obligation to give a warning on the measure to take and if obligor failed to perform then the authority had to take over the obligation at the cost of the obligor. Cost was to be recovered by the authority like taxes.

If threats of invasion of pests were predicted by authorities then for ensuring public interest citizens could be called in for participating in searching for and collecting pests. Rules on how to manage public involvement was highly elaborated in laws, e.g. people were organised in groups of ten per hectare, thus every hectare had its own "supervising" team, tools and their use were provided for, etc. Schools and scout teams were also involved in the "public defence" operations against pests and the laws required cooperatives and state farms to give rewards to the most dedicated and most effective groups.

It is important to note that the substance of rules on plant protection especially on biological protection and the pronounced public interest in taking preventive measures were present and inherent part of agricultural management.[18] Thus not the substance of the rules but the ways in which they were formulated and enforced reflected the political regime.

Over the years the main approach of the above rules had not been changed, however, separate pieces of legislation were compiled into one main piece of legislation and there was a shift in the role of individuals and public bodies in plant protection. Along the way, the rules on public involvement became less and less detailed and by 1968 they were mainly limited to how costs of operation could be recovered by cooperatives and state farms from state budget of the regional public administration bodies of plant protection. Also, mainly public administrative state bodies organised at regional or local level took over the responsibility for and relieved individuals from monitoring and reporting of pests or participating in actions enforcing public interest. It showed that technical tools and chemicals had gained priority over manpower. Also, it reflected on the change in ownership structure of agricultural lands, agricultural policy, and management.

The concrete biological protective measures became general obligations and they were removed from plant protection laws in 1988 because provisions on protecting beneficial animals (mainly birds) were viewed as part of laws on nature protection. Similar separation of rules by substance could be witnessed when terms and conditions (upon which sanctions for failing to comply with provisions regarding plant protection) became part of Acts on public administration law, or criminal law. Standards and guides were compulsory by law till 1994. Civil law liability for environmental damage had been decided by courts on the basis of strict liability by using the provision on dangerous activities even when they could come to that conclusion only through interpretation of law. Strict liability rules for environmental damage were introduced by the Act on the Environment in 1972. It was a framework act compiling the most important general rules of environmental protection based on the principles such as prevention and the polluter pays principle. It stated that environmental aspects should be considered in settlement development and site designations for economic operators. The environmental act of 1995 reinforced the comprehensiveness of environmental legislation and state liability for damages caused by state owned economic actors. The first comprehensive act on waste was passed only in 2000. While legal liabilities for damage caused to the environment were well established, cases of that time shows that enforcement was very much dependent on political decisions[19]. As various environmental cases demonstrate, political decisions could be manifested in various forms, including directly or indirectly influencing public authorities, not ensuring adequate public financial resources and manpower for supervision and on-site inspection, not taking immediate action when should have been done to prevent damage originating from non-compliance of economic actors.

Conclusions

Based on the above facts and findings some conclusions can be drawn.

The decision on plant protection schemes is political in nature. Even if political decisions are taken based on scientific evidence, environmental harm is not necessarily avoided. Harm implies a value judgement that is not necessarily expressed in terms of money. The "use of natural enemies" in plant protection requires ensuring and respecting the natural conditions of beneficial living organisms and adjusting man's behaviour to them. Thus the behaviour of man in relation to nature in itself is an expression of a value judgement. However, acknowledgement of the role of beneficial organism in plant protection is a prerequisite for respect, without it, decision makers would not attach a value to it and could not consider it as an alternative. When a value is not expressed in terms of money but only acknowledged and its appreciation is shared by the whole society then decision makers are taking it into consideration even if it is not apparent. When this knowledge or appreciation is shared only by some parts of the society then it is usually turned into professional, political or legal debate and often requires finding a way in which this special value could be assessed and expressed in terms of money. From this it follows that liability issues in relation to the environment are only raised when decisions are based on values not commonly shared or accepted by the whole society.

The word "damage" refers to a relationship. In this relationship there has to be someone whose interest is harmed. The negative impact of chemicals including Lindane on beneficial living organism were recognised and noted by scientists. For them it is a well-known fact that most parasites and pathogens, and many predators, are highly specialized on pest species. Also, similar specialisation has been known between insects and plants.[20] However, this negative impact was not considered as a damage in legal terms, because there was no one who would claim damage except when bees were concerned. But even in that case when bees were killed by pesticides the damage was not calculated on the ground of loss in pollination but on loss in honey production. Damage in the capacity for playing a balancing role in the agro-ecosystem was not recognised by farmers. If they knew about it they could not claim damage because it was their intentional behaviour that caused it. Clearly, the intention was not to kill beneficial insects, it would have been illegal any way, however, by using an all-purpose kind of pesticide it was at least an acceptance of the unintentional outcome. Instead of claiming damage farmers accepted the disappearance and elimination of "natural enemies" of pests and its consequence (unexpected increased population of some pests species) and bought additional chemicals to do the job. It demonstrates that the use of Lindane and other synthetic chemicals were overtaking traditional knowledge and methods based on ecological thinking and as a result users of chemicals could not make a good choice that is in line with ecological rationality. Thus damage to the ecosystem was turned into a cost element of agricultural production. There was no liability scheme that could prevent it from happening.

The history of DDT and Lindane shows that each property of a chemical could be evaluated individually and the result of this evaluation may change over time depending on the objective of the evaluation. When chemicals are used in order to ensure food security it is essential to review its impact not only on human health but along the food-chain to see whether there is a potential risk of bioaccumulation or biomagnification. This question belongs to the terrain of science, thus it is the obligation of the scientists to provide evidence on those issues.[21] Could a scientist be kept liable for damage caused if crucial evidence was withheld from decision makers? In the Report 68 the authors referred to Herrick's article noting on the existence and availability of evidence on DDT being present in meat products since 1940[22]. (Note, that this was before the time of getting the Nobel Prize for DDT) Liability is a question related to behaviour. It is the behaviour and not the knowledge for which someone can be held liable for. Scientific knowledge is often withheld from decision makers on the ground of intellectual property rights or commercial secrets. The question is whether scientific evidence on health hazards and risks either on humans or on living organism could be kept secret from the affected by the right holder or by the decision maker.

There is no single liability scheme that merges all hazards of Lindane or other chemicals due to the differences in hazards along its life-cycle. Different people at different places at different times are affected by different impacts. The sale curve of Lindane is a good demonstration of this variety. Lindane was present on the market since the 50s however; its sale boom was in 1970 and disappeared in 2000. However it disappeared only from the market, and not entirely from the environment. People affected by Lindane falls at least under four categories: affected a) by its production, b) its application, c) through consumption of products, d) by its waste treatment. As a result, individuals affected by the hazards of Lindane became part of different communities depending on when and where they were. Producer's liability is an attempt to integrate relevant costs for preventing health and environmental damage caused during production, usage and waste treatment of pesticides. Despite efforts, the risk of the society as a whole is usually not clearly outlined and externalities are not fully integrated. As evidence shows illegal operations, and non-compliance with protective rules are often behind the damage and its magnitude. Thus public control, public enforcement of laws and the role of state, regional and local public administration are crucial. In order to prevent the negative impacts of synthetic chemicals a complex liability scheme has to be developed and elaborated that covers the life-cycle of such chemicals.

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2. The following official exchange rate for HUF (a so called „currency HUF") was used for the purpose of statistics till the end of 1968: 1 USD = 11,74 currency HUF, 1 Rubel = 13,04 currency HUF. (Marton, Á. (2012) Infláció, fogyasztói árak Magyarországon a második világháború után I. (1945—1968) p 383, In *Statisztikai Szemle*, vol. 90. no. 5 pp373-393)

3. Nechay, O. (1966), Növényvédőszerek, pp 11-14, Mezőgazdasági Kiadó, Budapest

4. Note that the book was published when the Soviet Union still existed.

5. Nechay argued that biological protection together with good agro-technology was better and cheaper in respect to those measures being preventive and long lasting. Nechay (1966), p 40.

6. Beside the summary reports of each themes, concrete data and maps on POPs were published in more than 70 appendices to the report. A környezetben tartosan megmaradó szerves szennyezőanyagok kibocsátásnak országos katasztere (National cadastre for POP emmissions) http://www.kvvm.gov.hu/index.php?pid=4&sid=74&hid=758

7. Detailed information on sale is available for all POPs. see tables 4-8, 11 in Pethő, Á. Ocskó, Z.: (2003) *POP hatóanyagot tartalmazó növényvédőszerek hazai felhasználása 1950-2000* Növényvédőszerek 1. Függelék http://www.kvvm.hu/cimg/documents/Noveny_1_fugg.pdf

8. ibid. p 24

9. ibid. p 12

10. See tables 2-4 in Marth, P (2003): *A hazai talajok POP szennyezõdéseinek mérési eredményei a Talajvédelmi Információs és Monitoring Rendszerben*, Talaj függellék 2., http://www.kvvm.hu/cimg/documents/Fugg_2_Talaj.pdf

11. See the summary appendix on water. Ferenc, L. Bagi, M. Csáki, F. Kovács, P: *Felszíni és felszin alatti vizek POP szennyezésének felmérése* (KvVM)http://www.kvvm.hu/cimg/documents/Osszefoglalo_3.pdf

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13. ibid. 5

14. Government Decision 2205/1996. (VII. 24.)

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16. ibid. p 103

17. Statements of this chapter are based on the review of relevant acts, government decrees and decrees of the minister in charge of agriculture.

18. Local ordinance was passed in the interest of the public by the Senate of Debrecen in 1760 on how to fight against caterpillars; also the beneficial role of birds in controlling plant-damaging insects were recognised by Nagyváthy in his book on good farmer published in 1791 (Penyigey, D. (1935) *A hernyók tömeges megjelenésének és írtásának adatai a mezőgazdaság és a kertészet múltjából* pp10-11Városi Nyomda, Debrecen

19. Szirmai gave an overview of environmental cases and their social and political background. She analysed the case on production waste of one of the main producers of pesticides Szirmai, V. (1999) *A környezeti érdekek Magyarországon (Environmental Interests in Hungary),* pp. 57-63, Pallas Stúdió, Budapest

20. Note that in the XVII century Gáspár Miskolcy a Calvinist priest wrote that there were as many butterflies as many species of plants. (Penyigey, (1935), pp 5-6)

21. In the preface Béla Darvas gave such reason that justified his work in writing a book on ecotoxicity. Darvas, B. (2000) *Virágot Oikosnak*, p 16, L'Harmattan, Budapest

22. Josepovits, Nechay (1968) p 6 The cited article is: Herrick, J.B. Meat and chemical residues, Iowa Fm Sci., Ames, 1965. Vo. 20., No. 5., pp 270-272

CONTAMINATED SITES – A LEGACY OF ECONOMIC GROWTH IN GERMANY IN THE 20TH CENTURY: THE BOEHRINGER CASE

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1. Brownfields in Germany

The official statistics of the Federal Environmental Agency (*Umweltbundesamt*), based on the regional contaminated sites register of the German Länder, reports for whole Germany 317.036 so called "suspicious contaminated sites" (*Altlastenverdächtige Flächen*) for 2014.[1] 95.889 of these potential brownfields had been used as old dump sites ("Altablagerungen") and 221.793 are considered to be old industrial (production) sites ("Altstandorte")[2], a distinction that is made by the German Soil Protection Act. 15.837 sites are considered as brownfields (pollution has been proven), in 26.679 cases rehabilitation measures had been terminated, in 93.991 cases a risk assessment had been done, 4.686 sites are currently undergoing a rehabilitation procedure and in 3.966 cases the site is under monitoring of the competent authorities. More than 30 years after the beginning of a systematic approach to deal with the brownfield issue, polluted sites of the past are still a truly important subject. A full rehabilitation of all sites is economically impossible. Although in theory the polluter of the site should be liable and bear the costs, in reality this is often not the case. The public sector therefore pays an important part of the rehabilitation and assessment measures. In order to illustrate this, we give just one figure: Only the Land Baden-Württemberg has paid, from 1988 to 2014, the amount of 748 Million Euro to support municipal rehabilitation measures of polluted sites.[3]

The "Boehringer" case is just one of these over 300.000 cases, but certainly one of the most prominent ones. It was a major environmental scandal that can be considered as a "typical" case for the 1980s. Yet, it can also be considered as a positive example, where a company has late, but not too late, assumed its responsibility.

2. The Case of the Lindan production in Hamburg Moorfleet

2.1. The history of the site

Since 1923 the Boehringer company had a production site in Hamburg near the Moorfleet channel. The main site of the company was and is still today in Ingelheim near Mainz at the periphery of the Rhine-Main-region. In 1951 the production of the insecticide Lindan (Hexachlorcyclohexan) started in Hamburg. HCH was one of the high toxic hazardous wastes that had been generated in a quantity of thousands of tons over the years. Later, in the administration, they just called the wastes BSS: "Boehringer specific contaminants" (*Boehringer-Spezifische-Schadstoffe*). Workers of the plant were exposed to high concentrations of toxic substances such as dioxines, furanes and HCH. Different studies showed significantly increased cancer mortality among men.[4] A particularly problematic production plant was the Trichlorphenol production that was used as basic element of the herbicide "T-Acid". 1955 Boehringer had to interrupt the production of T-Acid as it became public, that the high toxic 2,3,7,8-TCDD was generated as a by-product and workers became sick. 1957 the T-Acid-Production restarted with a new process. Since 1979 the site was under inspection and continuous control of the competent authorities. The control measures – including market restrictions of polluted fruits and vegetables produced in the surroundings of the site - are described in detail in the official document of the Regional Parliament, the Citizen Council of the State of Hamburg, called *Umweltbeeinträchtigungen durch die Firma C.H. Boehringer Sohn, Werk Hamburg-Moorfleet*.[5] Pollution decreased in the following time, but extremely high polluted soil and groundwater already existed due to heavy emission in the 1970. The groundwater was polluted up to 1000 m outside the plant and the sediments of the Moorflet channel were also highly polluted.[6]

During control measures in 1983/84 the environmental authority found, that still high emissions of dioxin were generated by the Trichlorbenzol production plant. The authority therefore issued an administrative order, stating that no further waste of 2,3,7,8 TCDD was allowed

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[1] http://www.umweltbundesamt.de/sites/default/files/medien/384/bilder/dateien/
2_tab_altlastenstatistik_2014-12-11_0.pdf

[2] Partially, one site has been used for both purposes, therefore the figures are not equivalent.

[3] Landesanstalt für Umwelt Baden-Württemberg, Altlastenstatistik 2014, p. 27. https://www.lubw.baden-wuerttemberg.de/servlet/is/249772/altlastenstatistik_2014.pdf?command=downloadContent&filename=altlastenstatistik_2014.pdf.

[4] Mortality study of chemical workers exposed to dioxins: follow-up 23 years after chemical plant closure, Ulf Manuwald, Marcial Velasco Garrido, Jürgen Berger, Alfred Manz, Xaver Baur, in: Occup Environ Med 2012;69:636–642. doi:10.1136/oemed-2011-100682.

[5] Bürgerschaft der Freien und Hansestadt Hamburg, Drs. 11/2864, vom 21.8.1984.

[6] See in detail the Report of the City Council of Hamburg, Drs. 11/2864.

to be generated. As the plant was not able to comply with this order, it had to be closed on 18 June 1984. This was the end of the Boehringer site in Hamburg Moorfleet. For the first time in Germany, an industrial site had been closed by an environmental authority[7] for environmental reasons. Meanwhile, the site had become one of the best known brownfields in Germany. Parts of the technical equipement of the plant have been sold in 1990 to "Industrias Quimicas del Noroeste S.A., Inquinosa in Spain,[8] a contaminated site where also HCH was produced.

2.2. Rehabilitation and monitoring measures

After the closing of the plant in Hamburg the question was how to remediate the site in order to reduce the risk for human health and the environment. There was no technical blueprint to rehabilitate a contaminated site of such a dimension.

A first plan was to incinerate the toxic waste. The installation "Prometheus" was built, a special hazardous waste incineration plant. However, the practice was too complex: In 1994 the installation had to be closed down as the agressive toxic substances eroded even the incineration plant.[9]

As this first conception failed, the authorities decided to establish a massive barrier so as to avoid further introduction of the contaminants into the groundwater. To that extent, 1997/1998 a protecting wall of concrete was built in the underground around the 8.5 ha site: 80 centimeter thick, up to 50 Meter deep in the ground.[10] An impermeable layer of clay constitutes the bottom of this construction. On the top, a cover of asphalt protects the site against rainwater. Five pumps, four inside and one outside the actual site, every hour pumping 20 m^3 of contaminated groundwater that is treated by a special treatment plant located directly on the site, 24 hours a day.

Thus, from 1998 to 2012 about 20 tons of toxic waste have been excavated and cleaned from the soil. Today these pumps are working still, and they will do so for the next 20 years. The site itself is used today, after the containment was successfully established, for commercial purposes (market for commercial vehicles).

3. The legal situation

The legal framework today is determined by the Federal Soil Protection Act and its implementing regulations. This Act establishes according to the polluter-pays-principle a fault based polluter liability. A natural or legal person who contaminates the soil or the groundwater has to pay for the rehabilitation measures (Art. 4 para 3 of the Act). Moreover, a strict, non-fault based liability of the owner of the real estate is established. Even the *former* owner can be held liable (Art. 4 para. 6 of the Act), if he knew or by negligence did not know, that the site is polluted. Thus, selling a polluted site does not exclude legal liability, if the pollution is known or should have been known by the landowner. The liability is, by law, not limited. As this could have extremely severe consequences in practice, even for owners that are in good faith, the Constitutional Court limited the liability of the landowner to the market value of the land.[11]

Yet, in 1984, when Boehringer closed the door of its polluting site in Hamburg, this legal framework did not exist. The Federal Soil Protection Act came into force on 1 March 1999 only. The preceding years, brownfield liability was regulated by the general law on police and public order of the Länder. Diverse court decisions on the extent of this liability and different regional laws led to a general insecurity on the question if, when and to what extent polluters could be held liable for historical pollution. This is one reason, why public authorities were reluctant in taking rehabilitation measures at the beginning of the 1980.

In the Boehringer case, the Authorities concluded a remediation contract with the company in 1990. This contract aimed at an exhaustive rehabilitation of the site with a complete decontamination (by incineration).[12] As mentioned above, this plan failed for technical reasons. Instead, the "containment solution" was set into practice. A new agreement was reached in 1995, this time with participation of the public.

4. The costs

According to the information given by the public authorities and by Boehringer[13], more than 160 million Euros have been spent by the company for security, rehabilitation and monitoring measures in the last 30 years.[14] The monitoring and decontamination of the still heavily polluted groundwater will take a further 40 years. Boehringer has just recently (in 2014) concluded a new agreement with the administration of Hamburg and the environmental group BUND (the German branch of friends of the earth) to pay further 17 million Euros for monitoring and decontamination of the groundwater.[15]

5. Lessons learnt

The major environmental scandals in the 1970 and 80ies had far reaching consequences: The environmental movement grew to an important political movement. As far as technological innovation is concerned: It seems to be a bit

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[7] Drs. 11/2864, p. 4.

[8] Der Spiegel, 9.4.1990.

[9] Geo.de, 25.3.2014,

[10] See in detail: J. Schwarz/K. Günther/J. Maier-Erbacher/F.-W. Gerressen, Sicherung eines Werksgeländes mit 50 m tiefen Einphasen-Dichtwänden, https://www.unibw.de/bauv8/institut/mitarbeiter/2003_christianvederkolloquium_langfassung.pdf.

[11] Federal Constitutional Court, 16. 2. 2000 - 1 BvR 242/91, Neue Juristische Wochenschrift 2000, p. 2573.

[12] See the information of the competent authority in: http://www.hamburg.de/contentblob/142908/data/boehringer.pdf.

[13] 30 Jahre Werksschließung Hamburg-Moorfleet, https://www.boehringer-ingelheim.de/unternehmensprofil/geschichte/hamburg-moorfleet.html

[14] http://www.hamburg.de/contentblob/142908/data/boehringer.pdf.

[15] Entgiftungskur für Moorfleet, Die Tageszeitung, 25.2.2015, http://www.taz.de/!5018878/

cynical, but it is a fact that due to the thousands of brownfields in Germany we gained a lot of technical experience in solving the problems. The legal response was better regulation of contaminated sites and soil protection.

Finally the Boehringer case can also be considered as a positive example in terms of operator responsibility: Boehringer assumes its responsibility. Already in 1984 Boehringer founded a daughter company that had the task to develop appropriate decontamination techniques for the site. The City of Hamburg presents the Boehringer case as a "good practice" example for land redevelopment on its web site.[16] And even the environmental movement acknowledges that Boehringer is a cooperative partner.[17]

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[16] http://www.hamburg.de/contentblob/142908/data/boehringer.pdf.

[17] See note 14 above.

THE LINDANE OF INQUINOSA, 25 YEARS OF ACTION IN THE COURTS

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Key Words

Lindane, Toxics Waste, Inquinosa, Courts, Liability.

Materials and methods

This paper shows the evolution of the Inquinosa´s cases in Courts and its current situation; and has been write on the bases of the Judgements listed in “References”

Abstract

The company “Inquinosa” (*Industrias Qumicas del Noroeste* S.A.) produced lindane from 1975 to 1988 in the city of Sabinanigo, Aragonian Pyrenees (Spain), and formulated lindane products until 1992. It had bad environmental practices associated with the dumping of the solid waste generated in their industries. About 150,000 tonnes of HCH mixture remain today located at three main sites that lack an adequate liner system to stop leaking. The drinking water of 40.000 people is still today contaminated or at risk to being contaminated.

More than 40 millions of Euros has been spent trying to restore the sites, but more than another 200 millions, as minimum, will be necessary for an appropriated management of the toxic wastes.

Actions in Court have taken place during 25 years, and there is not still an effective mandatory duty to pay the six millions and half of Euros the company must pay. In the meanwhile the company has disappeared from Spain and has been declared “insolvent”

The company “Inquinosa” (*Industrias Qumicas del Noroeste* S.A.) produced lindane from 1975 to 1988 in the city of Sabinanigo, Aragonian Pyrenees (Spain), and formulates lindane products until 1992.

Until the closure of Inquinosa at the end of the 80´s, it’s bad environmental practices associated with the dumping of the solid waste generated in the city and its industries left several contaminated sites. Total waste generation data differs upon the information source used but probably about 150,000 tonnes of HCH mixture remain today located at the three main sites that lack an adequate liner system.

At these sites, a DNAPL (Dense Non-Aqueous Phase Liquid DNAPL) groundwater plume has been found, containing benzene, chlorobenzenes and chlorophenols and a mixture of HCH isomers. With a density of 1.5 cps and 950 g/kg of contaminants it constitute a serious risk due to the vicinity of the Gallego river and also the complex aquifer system which consist of alternating verticals sandstones and marls. 2009. Currently, the river pollution affects more than 40.000 people living in the area of the river basin.

Without taking account of several small dumps sites, four sites remain contaminated: the Sardas and Bailin dumping sites, the industrial ruins of INQUINOSA, and the dam of Sabinanigo. In the first three sites the Regional Government of Aragon is executing remediation works, while the dam is supervised by a national authority
Inquinosa was compelled to stop its Lindane production in 1988. During the following years the company continued manipulating and packaging this product and after that tried to management the toxics wastes in its own facilities, although this task never was finished because they did not follow the instructions received from the regional government.
In 1996 Inquinosa declared it self “insolvent”.
In 1998 Inquinosa reached an trade agreement with the Romanian national company “Oltchim” in order to continued producing Lindane in Romania , and also sold 50,1% of it´s stock for the price of near two millions of Euros to JLM, a chemical company with a large record of infractions in the USA. So, in fact, Inquinosa is still the main Lindane producer in the world.
From 2004, the technical experts of the regional government were able to extract around 20 tones of this waste from the ground waters of the area. Is a dangerous activity since the product is very inflammable. This waste is sent to France, and there is destroyed in a specialized plant of incineration.

Process is being very slow because of the lack of funds. The option of the Aragon Government is to build his own plant of incineration but this could cost more than 100 millions of Euros, plus another 100 millions in the task of restoration which are needed. In the meanwhile, each year the regional and national governments spend around one million and half Euros to minimize the toxics leaks. By now, the amount spended is more than 40.6 millions of euro

The administrative proceedings

Once the production of Lindane was prohibited, the company shows his acceptance to ahead the tasks of storage and Management of the toxics wastes under the law. According to that, the regional authorities required in 1990 (1) to carry on an Environmental Impact Assessment, proceeding which finished with an "Environmental Impact Declaration" which imposed some requirements and technical systems. The company took actions in the courts losing all this cases until the Supreme Court. (2)

The company also lost the cases they took against the regional government, to have no licence to use certain technical systems as evidence of a good practices in the management of the toxics wastes. (3)

And finally, the company lost the cases against the punishments imposed by the regional government for a total value of 15 millions of "pesetas" (around 100.000 Euros)

The criminal proceeding

In 1995 the Provincial Court of Huesca (4) the General Director of Inquinosa, was condemned to two months of prison and 6.000 Euros of punishment as main responsible of the production and dissemination of toxics wastes without permit from the authorities. This judgement was confirmed by the Supreme Court in 2000 (5) and the issue arrived even to the Constitutional Court (6) since Inquinosa appealed this action, saying it was a infringement of his rights. The judgement of the environmental crime declared also Civil Liability for an amount which was determinate in another civil proceeding (see in net paragraph)

The liability proceeding

In 1996, the Aragon government takes an action of Civil Liability against Inquinosa and won (7). The judgement was confirmed by the upper courts (8), and the Court established an indenisation of six millions and half Euros (9).

Finally, the last Judgement is the one confirming this indenisation by the Supreme Court (10). This judgement is interesting because:

> Declared the evidence of "the facts" through the rest of the judgements as sufficient evidence without needing to consider them once more time, and took this action even without any legislation of environmental liability, using the Civil Code to support the indenisation.
>
> Declared the no expiration of the deadline for the legal action – which was argued by Inquinosa- due to the idea that there is not such a expiration in a case of environmental damages, "*until the authorities can have a total overview of the damages*".

In 2014, the regional government announced they had asked the Court for the *"ejecución de la sentencia*" (Which means to have it accomplish in a effective manner) They are now clamming now for the six millions and half of Euros plus another 14 millions of Euros in interest for the delay in the payment.

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SOIL BIOREMEDIATION

USING MIXED BACTERIAL CULTURE TO DEVELOP A BIOLOGICAL LOW COST TREATMENT OF PESTICIDES

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Abstract

Agriculture is the major pollution sources by pesticides of contaminated soils and waters. In France, to limit this pollution, farmers have obligation to treat waters coming from washing pesticides containers and application equipment. Global concentration of pesticides in these effluents is estimated between 10 to 100 mg/L by Ballesteros[1]. So, the aim of this study is to treat these residuals waters by developing a biological treatment process on bioreactor based on inoculation of a selected mixed bacterial culture[2] and addition of an adsorption support composed of crushed corn cobs.

The first part of this work was to create a representative mixture of pesticides based on a watershed model and to focus on the behavior and stability of the bacterial culture when confronted with the pesticide mixture. Then we study corn cobs as a sorbent material and bacterial growth support.

In a second part, treatment parameters have been optimized at laboratory scale. Then, the efficiency was assessed on a 5 liters bioreactor.

Results showed that the model mixture containing 10 pesticides (6 herbicides, 3 fungicides, 1 insecticide), change initial bacterial culture diversity but allow a stable production of an inoculum composed of *Pseudomonas putida, Pseudomonas multiaromavorans et Delftia sp.* Pesticides dissipation experimentations concluded to the development of an 28 days batch aerobic process, inoculated with 10^7 CFU / mL and with 20g / L crushed corn cobs, without regulation of pH nor nutrients complementation. This process performs with a global reduction of 72% of pesticides concentration on treated effluents.

Key Words

Pesticide dissipation, biodegradation process, corn cobs, bacterial inoculum

Materials and methods

Pesticides products were used on their commercial form with additives. They were supplied by an agricultural cooperative (CA, Hochfelden, France). The referent mixture contains 11 actives molecules, copper and adjuvants (composition not known). Concentrations used are : benoxacor (0.47mg/L) ; S-metolachlor (9.61mg/L) ; Copper-cuprous oxide (12.50 mg/L) ; Dicamba dimethylamin salt (2.40 mg/L) ; diflufenican (0.75 mg/L) ; isoproturon (6.00 mg/L) ; epoxiconazole (0.62 mg/L) ; flumioxazin (3.00 mg/L) ; glyphosate isopropylamin salt (14.40 mg/L) ; mancozebe (9.38 mg/L) ; nicosulfuron (0.30 mg/L) and dimethoate (1.50 mg/L).

To study additives impact, bacterial growth was also carried with analytical grade Standard molecules corresponding to the molecules contained in pesticides. Its were all purchased from Sigma-Aldrich Laborchemikalien GmbH (Germany).

The bacterial mixed culture used was isolated from sediment of a stormwater basin from the vineyard of Rouffach (Haut-Rhin, France) contaminated with many phytosanitary products[3].

Inoculum preparation was made by introducing 100µL of the original bacterial culture, into a growth culture medium containing 25 percent of autoclaved LB medium, pesticides at final referent concentration (mixed and sterilized) and sterilized water. Incubation was done into sterilized 100 mL glass flasks agitated on a rotary shaker at 200 rpm, at 20°C, in the dark for 48 hours.

Inoculum is quantified and identified after enumeration and phenotypic isolation on solid LB-agar medium (10 g/L agar) incubated at 28°C for 4 days. Bacterial identifications were performed after PCR amplification of 16s rDNA with universal primers and by sequencing of DNA products. DNA sequences obtained were treated with N-Blast software (BLASTn) and compared with the NCBI and LEBIBI databases.PCR-TTGE (temporal temperature gel electrophoris) method was also used to assess the impact of pesticides on the structure of the bacterial community, regardless of culture on petri dishes. PCR was made using universal primers 1401r and 968f corresponding to V6-V8 area of bacterial 16S rDNA and TTGE was performed as previously described[2]

For evaluating impact of pesticides and actives molecules forms on bacteria, we compared bacterial growth kinetics on microplates using Bioscreen system at 600nm wavelenght[5]. Microplate wells were filled with 300µl of 25 % LB liquid medium, inoculated with the bacterial culture and contaminated with following modalities: each pesticide form, singly or mixed at referent concentration; each standard molecule, singly or mixed at referent concentration and each products spiked with its associated standard molecule, both at referent concentration.

Microplates were at constant temperature of 20°C during 14 days.

Corn cobs came from the INRA center of Colmar to the year 2013 and are crushed using a simple grinder (BOSCH grinder 2200 W AXT RAPID 2200). Their pesticides adsorption capacity was evaluated in terms of adsorption isotherms. Erlenmeyers were filled with 150mL of model pesticides mixture at 5 different levels of referent concentration (RC) (RC/10; RC/5; RC/2; RC; RCx5) with a corn cobs concentration of 20g/L. Erlenmeyer were at constant temperature of 20°C and under stirring at 200 rpm during 48h.

For degradation experiment, small scale experiments were made on Erlenmeyer filled with pesticides mixture referent concentration, crushed corn cobs at 20g/L and inoculated with 10^7 CFU / mL of our mixed bacterial culture. Then we used two bioreactors of 5 liters to confirm efficiency of chosen parameters and scale changes.

We tested the duration of treatment, aeration, pH control or the provision of co-substrates. Parameters evaluation was based on the dissipation of the active molecules of pesticides after batch treatment.

Pesticide concentrations were measured by HPLC-MSQ (Agilent 1100 series and Agilent G1956B Single Quad Mass Spectrometer) using two methods on a Zorbax Eclipse XBD-C18 column with a water gradient (0,1 % formic acid) / acétonitrile (0,1 % formic acid) : Méthode 1 : 75/25 to 0/100 water/acetonitrile gradient on SIM positif mode for all molecules except glyphosate and méthod 2 : 90/10 to 0/100 10 water/acetonitrile gradient on SIM négatif mode for glyphosate.

Accelerated Solvent Extraction (ASE) on a Thermo Scientific Dionex ASE 150™ was used to evaluate residual pesticides concentration on corn cobs. Extraction by acetonitrile was made during 20 minutes at 150°C under 5 bars.

Results and discussion

Inoculum characterization

For inoculum production on our define culture medium, experimentations didn't show any inhibition of pesticides compared to control on diluted LB medium (see figure 1).

Moreover bioscreen study showed there was no impact of additives on global bacterial growth and growth kinetics were quite similar between pesticides and standard molecules, as well as they were used alone or mixed.

Nevertheless, using phenotypic isolation of colonies on LB agar (10g/L) petri dishes, we showed that the model mixture containing 10 pesticides changes the bacterial structure community. Indeed, original culture was composed of 5 cultivable bacterial species: *Arthrobacter sp, Methylobacterium extorquens, Micrococcus luteus, Pseudomonas putida* and *Microbacterium pumilum*. After 48h growing on the model medium with pesticides, species found were, *Pseudomonas putida, Pseudomonas multiaromavorans* and *Delftia sp.* Only *Pseudomonas putida* was present before and after intake of pesticides.

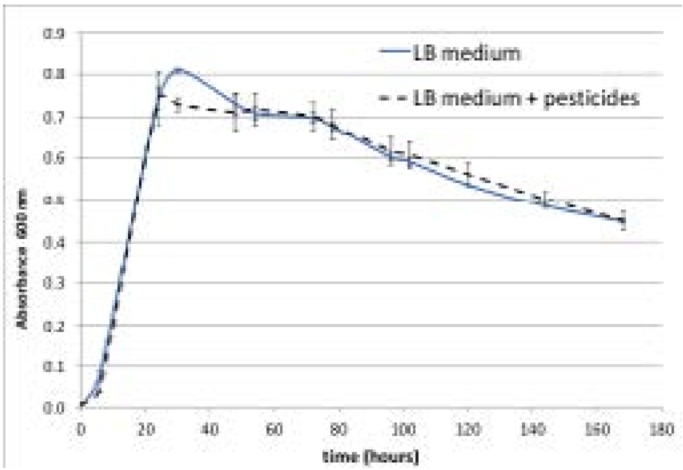

Figure 1: Growth kinetic of bacterial culture on diluted liquid LB medium (LB 25%) contaminated or not with pesticides filtered at CE concentration

These changes were confirmed by gel profil obtained by TTGE method which also showed a stability of composition of the culture after 48 h of growth in LB medium with pesticide

Inoculum study permitted to show that the model mixture containing 10 pesticides reduce initial bacterial culture diversity but allow a stable production of an inoculum with a concentration of 10^8 CFU / mL.

Sorbent study

Adsorption capacities of corn cobs showed that this sorbent, when is crushed, have an average pesticides sorption of 40% (see figure 2). We didn't observe difference of sorption of pesticides if there are used one by one or mixed, except for glyphosate. For this molecule, sorption is better when it was mixed. 2 pesticides molecules, flumioxazine and diflufenican were not quantifiable.

Furthermore, isotherm study (figure 3) demonstrated there were no significantly impacts of pesticides concentrations studied on crushed corn cobs adsorption capacity. However, we observed than dicamba adsorption tends to increase with higher concentration, while those of dimethoate and metolachlor tends to decrease. These phenomena could be due to competition for adsorption sites on corn cobs or presence of additives products[6] which can reduce or increase adsorption of organic compounds.

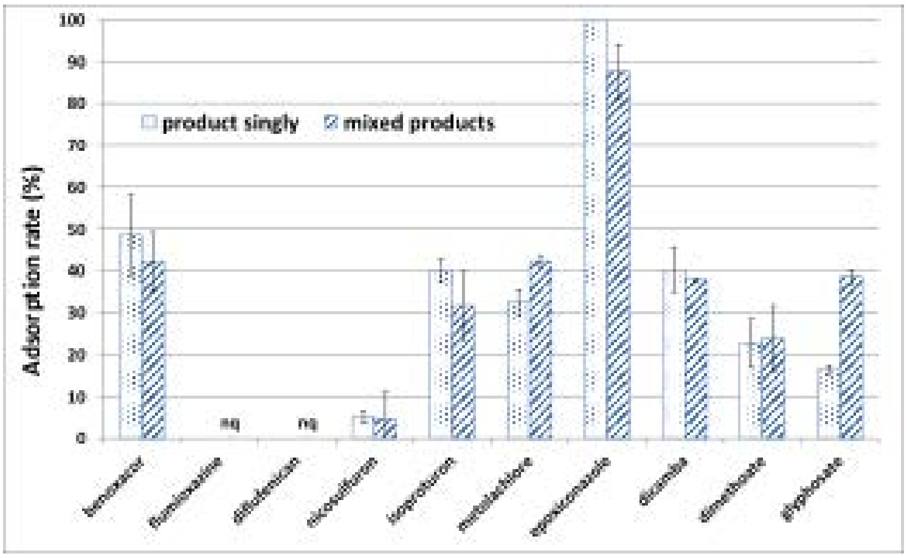

Figure 2: Comparison of adsorption rate by crushed corn cobs of pesticides used singly or mixed at referent concentrations

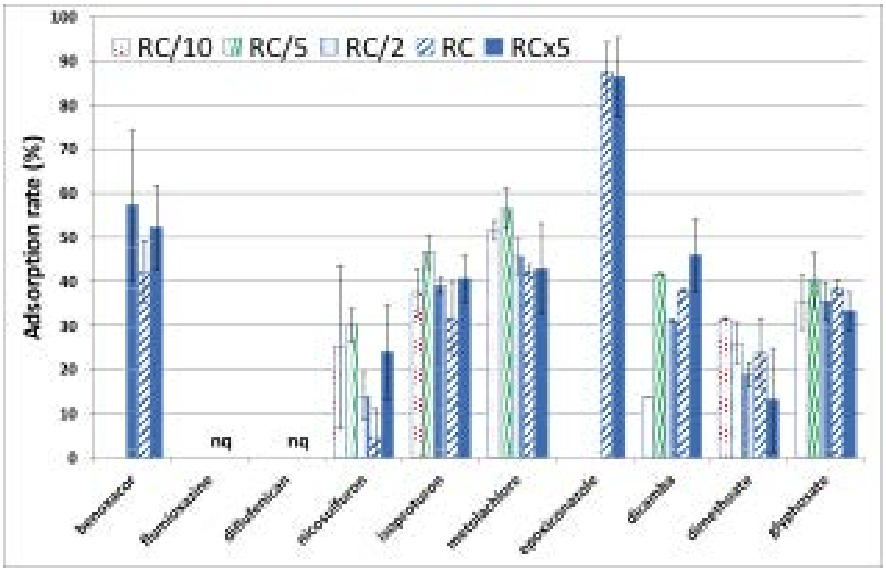

Figure 3: Evolution of sorption capacities of crushed corn for mixed pesticides at 5 different concentrations.(RC correspond to referent concentration; RC/10 : correspond to referent concentration diluted by a factor 10; RC/5 : correspond to referent concentration diluted by a factor 5; RC/2 : correspond to referent concentration diluted by a factor; RCx5 : correspond to referent concentration concentrated by a factor 5).

Dissipation experiment

Batch dissipation tests on erlenmeyer showed that pH regulation and nutrient complementation were not necessary to optimise pesticides dissipation.

Batch treatment duration was also tested at 7, 14, 21 and 28 days. Better dissipation rates were measured at 28 days.

Finally, bioreactors validation concluded, for now, at maximum dissipation with following parameters : a 28 days batch aerobic process (50L per hour aerated and 200 rpm stirred), inoculated with bacteria mixed culture concentrated at 10^7 CFU / mL and with addition of 20g / L of corn cobs There are no regulation neither pH nor nutrients complementation.

This process performed with a global reduction of 72% of pesticides concentration on treated liquid effluents (see figure 4). Degradation rates, depending pesticides, vary from 66% to 97% for 8 of the 10 active molecules contained in the mixture. But nicosulfuron and dicamba are few dissipated with respectively 2.6 % and 16.4 %.

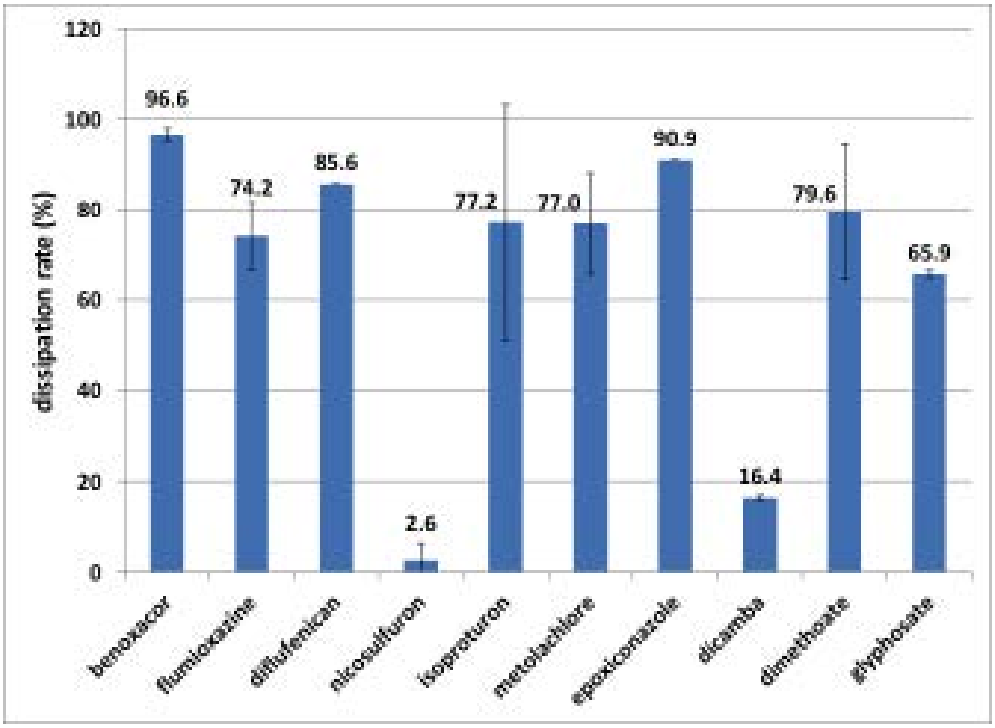

Figure 4: pesticides dissipation rates on treated liquid phase on a 28 days batch aerobic process (50L per hour aerated and 200 rpm stirred), inoculated with bacteria mixed culture concentrate at 107 CFU / mL and with addition of 20g / L of crushed corn cobs

Conclusion

These works showed that a low cost-treatment using biodegradable matters as sorbent permit to reduce significantly pesticides concentration on residual water and can help to reduce punctual pollution. But results need to be completed by ASE extraction of pesticide adsorbed on corn cobs to validate the degradation process. Moreover some pesticides are not impacted by this process, so post-treatment of effluent treated on bed planted with reeds is being investigated to optimize this system.

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USE OF NATURAL ZEOLITE AS SUPPORT OF PENDIMETHALIN-DEGRADING BACTERIA IN BIOREMEDIATION ASSAYS

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Abstract

The use of pesticides is a common practice in intensive agriculture that can produce adverse effect on soil and groundwater quality depending compound chemical characteristics and its behaviour in the soil. Depending soil characteristics pesticides can be adsorbed by the soil colloidal particles which could lead to inactivation of the product and can move through the soil with the risk of groundwater pollution. Pesticides can also suffer different chemical transformations in the soil inducing the degradation of the product or its transformation into other compounds than can be sometimes more persistent and more toxic than the original product.

Pendimethalin (N-(1-ethylpropil)-2, 6-dinitro-3, 4-xylidine) is a herbicide often used for pre-emergence or early post-emergence control of weeds in cotton, wheat, maize, tomato and onion crops. Belongs to the group of dinitroanilide herbicides which are sensitive to photodegradation and relatively volatile. Due to its hydrophobic nature, the persistence of this herbicide in soil represents an environmental hazard. The strong adsorption of pendimethalin to most soils, owed to its physical and chemical characteristics, can build up the concentration of the herbicide, which needs to be removed.

Decontamination techniques commonly applied to organic pollutant removal, such as thermal desorption or vapour extraction, turn out extremely expensive not being feasible processes in the case of agricultural soil, due to the dispersion of pesticides over large areas of land. Bioremediation is an *in situ* strategy, cheap and sustainable, adequate for the removal of this type of pollutants. The potential capacity of the soil microorganism for degrading organic compounds, is the main mechanism to prevent the accumulation of these chemical in the soil. In this sense, numerous studies have been focused to the use of bacterial inoculum to degrade pesticides (bioaugmentation). However, in some cases, the inoculum added to soil does not promote the biodegradation as it was expected. The objectives of this work are: 1) to test the use of zeolite (mordenite) for immobilize degrading bacteria of pendimethalin. 2) to evaluate the efficiency of cell immobilization to render longer viability and higher density of the inoculum and favor the bioremediation process.

Key Words

Herbicides, soil pollution, bioremediation, microorganisms, pendimethalin, zeolite.

Materials and methods

Bioremediation assays.

Soil samples were collected from the surface layer (0–30 cm depth) of an agricultural soil in Alcalá de Henares (Madrid). Samples were air-dried and sieved (<2mm) before analyses. Soil properties (Table 1) were determined according to Spanish official methodology for soil analysis[1]. In brief, pH and electric conductivity (E.C) was measured in 1:2.5 soil-to-water ratio; organic matter (O.M) and total nitrogen content (N) were determined using the Walkley–Black and Kjeldahl methods, respectively; the percentage of carbonates was measured using the Bernard calcimeter. The soil texture was analysed using a Bouyoucos densimeter.

Soil was spiked with pendimethalin (GmbH, Reference Materials ISO 9001 certified) at the dose of 5 µg g^{-1} in microcosm (500 g soil). Microcosms were kept in an incubation chamber at 25ºC and 65% air humidity during 35 days. Soil moisture was checked daily and maintained at 18%. Different treatments were tested:

Texture			% O.M	%N	%CaCO3	pH	E.C.(dS/m)
%Sand	%Silt	%Clay					
73,41	11,79	14,8	1,41	0,09	6,6	8,2	0,24

Table 1.- Soil characteristics

- Natural attenuation (NA)
- Bioaugmentation with a single inoculum (B)
- Bioaugmentation, inoculum application every 3 or 4 days. (B+)
- Bioaugmentation, immobilized cells in zeolite. (BIC)

Bacteria strain capable of degrading pendimethalin were isolated from a plant nursery soil with a history of exposure to different herbicides including pendimethalin. This strain was identified as *Pseudomonas fluorescens* VSE. Cultures of *Pseudomonas fluorescens* strain VSE (capable of metabolizing pendimethalin) were added to soil microcosms. Natural zeolite (mordenite) was used to immobilize the bacteria cultures.

Herbicide extraction and determination.

Pendimethalin in soil was extracted by 15 min sonication of 5 g soil samples in 8 ml of acetone and 8 ml of aqueous solution of sorbitan trioleate (180 µg ml^{-1}); then, 16 ml of isooctane were added for a liquid-liquid extraction. Isooctane was then evaporated to a volume of 2-4 ml in order to concentrate the sample.

Quantification of pendimethalin in isooctane is performed by Gas Chromatography with Electron Capture Detector (Varian CP-3800). Silica column has a composition of 5% phenyl, 95% of dimethyl polysiloxane. Column CP Sil 8B (Varian) presents this characteristics: 30 m length, 0.25 mm internal diameter and 0.25 µm of thickness. 0.1 µl of isooctane's extract was injected with splitless. Chromatography conditions were: 100 ºC initial temperature during 1 min, then temperature increases up to 250 ºC with a speed of 6 ºC min^{-1} and this temperature remains during 7 min. Carrier gas was helium. Injector's temperature was 270 ºC and detector's temperature was 300 ºC.

Results and discussion

The kinetic parameters of degradation of pendimethalin in soil are shown in table 2. They are fitted to the exponential equation: $C=C_i e^{-kt}$ where C_i is the initial concentration of the herbicide, t is the time of operation (days) and k the rate constant of degradation. Pendimethalin in the assay temperature and humidity conditions, treatment NA, shows a TD_{50} of 78 days. Temperature and humidity allows pendimethalin degradation by abiotic mechanisms and by the soil native microbial population. In real conditions, pendimethalin can have a TD_{50} higher than this value[2]. In all the bioaugmentation treatments, TD_{50} decreases significantly.

Treatment	C_i(^{N}g/g)	K(d^{-1})	TD_{50}	r^2	%Pend (*)
NA	4,6	0,0089	78	0,904	>75
B	4,38	0,0345	20	0,988	25
B+	4,41	0,0527	13	0,998	16
BIC	4,33	0,0476	15	0,996	18

Table 2.- Kinetic parameters for degradation of pendimethalin. (TD_{50} is the half life of pendimethalin under different treatments)

(*) Percentage of pendimethalin in the soil at the end of the assay.

Single inoculation with *Pseudomonas fluorescens* VSE (10^7 CFU g^{-1} soil) decreases TD_{50} from 78 days to 20 days. Bioaugmentation should increase the rates of degradation of the herbicide. However, at the end of the assay, still remains 25% of the initial concentration of pendimethalin. Thus, inoculation fails on the soil. Bacteria functionality can decrease along the time in free-cells inoculations (Figure 1).

The main cause pointing by Ramadan[3] for the inactivation of the inoculum is the low inoculum charge. In this case, the added bacteria are not able to compete with indigenous microorganisms.

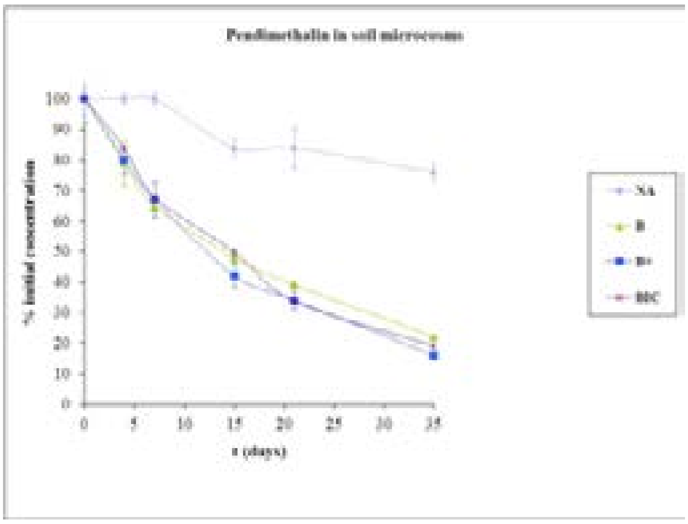

Fig. 1.- Degradation of pendimethalin in soil with different treatments of bioremediation.

Other factors responsible for the inactivation of the inoculum could be a too low pollutant concentration, the presence in the soil of certain substances that inhibit the activity of the added microorganism and the use of other carbon sources than the pollutants by the added microorganisms[4]

The limited viability of the VSE strain is opposed to the renewal of the inoculum every 3-4 days (10^7 CFU g^{-1} soil). These results indicate that the repeated inoculations should ensure keep the amount inoculum viable and metabolically active. TD_{50} of this treatment is only 13 days and the final concentration of herbicide is only 16% of the initial concentration. Immobilization of the bacteria on the zeolite achieves similar results than with successive inoculations although the initial inoculum load is less (4x10^6 CFU g^{-1} soil). This suggests the increased survival of immobilized inoculum and better adaptation to the natural soil conditions, and which would maintain the renovated cell-free inoculum in successive inoculations. Stealing et al.[5] showed that zeolite-immobilized *Pseudomonas* sp. strain ADP retained full functionality to degrade atrazine after 10 weeks in sterile soils in contrast with free-cells. Martín et al.[6] found similar results with propachlor. They found that bioaugmentation with microorganisms notably accelerated propachlor biodegradation but they did not find differences among suspended and immobilized cells.

In our study, *Pseudomonas fluorescens* VSE strain was immobilized successfully onto a zeolite carrier. These results demonstrated that the tolerance of this strain to pendimethalin could be enhanced by cell immobilization.

Other fact we want to point is the importance of obtain microorganisms from soils with long-term record of pollutants. These microorganisms were adapted to soil pollution, then the zeolite used as support improves the implementation of bioremediation process.

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MICROBIAL COMMUNITIES IN PESTICIDE-CONTAMINATED SOILS IN KYRGYZSTAN AND BIOREMEDIATION POSSIBILITIES

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Abstract

In almost every region of Kyrgyzstan, there are former storehouses and dumping zones for obsolete pesticides. In recent years in Kyrgyzstan (2009, 2010), an inventory and assessment of these dumping zones, and the risk of environmental hazard that they pose, has been performed by international organizations (FAO, World Bank) and experts (Project 100 020 592, for which the team leader was John Vijgen and the project manager was Boudewijn Fokke). Chromatography analyses have revealed a high concentration of persistent chlorinated-hydrocarbon-based pesticides in the soils of these dumping zones, including A-BHC, B-BHC, Heptachlor-epox, 4.4 DDD, Dieldrin, Endosulfan-2 and others.

The main purpose of this research was to study the microbial structural complexes of the pesticide-contaminated soils in these dumping zones, and to search for and select microorganism destructors for these chlorinated pesticides. In this study, both culture-dependent and culture-independent approaches were used to determine the taxonomic composition of the bacterial communities taken from the contaminated soils, and to compare them with the bacterial communities in a non-contaminated soil. The universal primer set for 16S rRNA gen, and the specific primer set P450R, were used to amplify the cytochrome P450 hydroxylase gen.

In light grey soils (Suzak A and B plots) and grey-brown soils (Balykchy dumping plots), the bacteria from the *Actinobacteria* phylum (particularly bacteria species of the *Micrococcus* genus) were dominant. These bacteria made up 32- 47, 0% of the indigenous local microflora; bacteria species from the *Pseudomonas* genus (*Gammaproteobacteria* phylum) made up 23% in Suzak , 12,0% in Balykchy soils. *Bacillus* species from *Firmicutes* phylum were found only in Suzak soils, their content made from 21, 0% to 71, 0%.

The 16S rRNA analyses and the specific primer set P450R have relieved bacteria with cytochrome genes which are directly involved in degradation process of organic carbon compounds.

The model experiments were carried out to help select active destructors from among the bacterial populations isolated from heavily and chronically contaminated soils. Destructors designed for the degradation of chlorinated hydrocarbons like Aldrin enrichment cultures were arranged. Degradation rate of Aldrin by *Pseudomonas fluorescens* + *Bacillus polymyxa* + *Micrococcus sp* + *Flavobacterium sp* in association in a mineral medium over 12 days was higher than in single cultures.

So, 50mg of Aldrin was degraded up to 32, 0%, 25mg – 32, 3% and 10mg- 54, 0% by association of these bacteria. Single culture of *Bacillus polymyxa* was able degrade 50mg of Aldrin about 20, 0%, 25mg – 23, 0% and 10 mg- 48, 2%. Single culture of *Pseudomonas fluorescens* has shown second position on degradation efficiency. So in 12 days 50mg of Aldrin was degrade about 14, 0%, 25mg – 18, 3% and 10 mg- 43, 1% by single culture of this bacteria.

Key words: dumping of obsolete pesticides; microbial consortia in contaminated soil; aerobic bioremediation of pesticides.

Introduction

Pesticides are widely used in agricultural production to prevent or reduce the losses caused by pests. At present, around 2.5 million tons of pesticides are used annually and the number of registered active substances is higher than 500. Classes of organic pesticides (consisting of organic molecules) include organochlorine, organophosphate, organometallic, pyrethroids, and carbamates among others [Gilden et al.2010; http://chm.pops.int/Convention/ThePOPs/tabid/673/default.aspx]. However, their chemical structures, along with their incorrect preparation, application and storage, may pose a serious toxicity risk to other organisms and to the environment.

Despite the fact that, Kyrgyzstan is a unique country with a rich natural and agro-biodiversity in almost every region of Kyrgyzstan, there are former storehouses and dumping zones for obsolete pesticides. In recent years in Kyrgyzstan (2009, 2010), an inventory and assessment of these dumping zones, and the risk of environmental hazard that they pose, has been performed by international organizations (FAO, World Bank) and experts (Project 100 020 592, for which the team leader was John Vijgen and the project manager was Boudewijn Fokke). In total in the territory of Kyrgyzstan exist 50 storage facilities of obsolete pesticides, which store about 5000 tons of these chemicals. In many places, the local people are trying to dig out. They pose a greater threat to the people living there, for livestock and the environment [The Interim Report on the Technical Investigations of Obsolete Pesticides in the Kyrgyz Republic 2010].

Pesticide presence in environment determines the dose and time at which an organism is exposed and could represent a hazard for worldwide life due to their mobility. Hence, the persistence in the environment leads to a risk for life: the more persistent a pesticide is, the worse its environmental impact. Pesticide persistence in environment is caused by either their physico-chemical properties or the lack of organisms able to degrade them. Degradation caused by organisms (biodegradation) could help decreasing considerably the pesticides persistence in environment [Velázquez-Fernández et al. 2012].

The microbial degradation of xenobiotics, a process known as bioremediation, is a cost- effective method of removing pollutants from the environment. Biodegradation involves the biological reactions that modify the chemical structure of the compound, so, this implies a decrease in toxicity. When pesticide degradation occurs, it usually involves more than one microorganism, i.e. each microorganism contributes to biodegradation reactions on pesticides, but no example of mineralization by a single strain has been described. Bacteria have been used extensively for bioremediation purposes. Bacterial classes: gamma-proteobacteria (v.gr. *Pseudomonas*, *Aerobacter*, *Acinetobacter*, *Moraxella*, *Plesiomonas*), beta-proteobacteria (v.gr. *Burkholderia*, *Neisseria*), alpha-proteobacteria (v.gr.: *Sphingomonas*), Actinobacteria (Micrococcus) and Flavobacteria (*Flavobacterium*) are considered as active microbiodegraders

[Geetha and Fulekar 2008; Matsumoto et al. 2008].

Bacterial biodegradation could take place in anaerobic or aerobic conditions.

Although different enzymes participate in each condition, it seems that both, aerobic and anaerobic degradation should happen if a mineralization is expected to occur [Langerhoff et al. 2001]. It seems that anaerobic metabolism is more adequate for dechlorination [Barragán-Huerta et al. 2007; Baczynski et al. 2010] and aerobic metabolism produces a cleavage in aromatic or aliphatic cyclic metabolites. The higher persistence of organochlorine in aerobic conditions [Singh et al.1999] compared to anaerobic might be caused by the absence of enzymes or more likely by the oxidative damage following organochlorine metabolism. The removal of heteroatoms (like halogens) or heteroatom-containing groups are frequently among the first steps in biodegradation. These steps are catalyzed by monooxygenases, dioxygenases or peroxidases [Singh et al.1999; Wackett 1995], which in aerobic conditions could generate large quantities of free radicals. Thus, anaerobic conditions are more adequate for biodegradation of organochlorine pesticides, while aerobic are better for biodegrading hydrocarbon metabolites from pesticides [Environmental Protection Agency. In situ treatment technologies for contaminated soil 2006]. In spite of such requirements, some examples of organochlorine pesticides bioremediation could be accomplished *in situ* [Langerhoff et al. 2001; Qureshi et al. 2009].

Among oxidoreductases, the most frequent are monooxygenases (like cytochrome P450), dioxygenases, peroxidases and oxidases, hydrolases like A-esterases are involved in biodegradation pathways. Cytochrome P450 (CYP**)** can catalyze reactions of oxidation, reduction or oxidative breakdown of xenobiotics [Lamb et al.2009; Yang et al. 2010; Thies et al.1996; Cools et al.2011; Leitao 2009; Kullman et al.1996; Stegeman and Lech 1991; Bolwell et al.1994; Pelkonen and Raunio 1997; Gonzalez and Lee 1996].

The main purpose of this research was to study the microbial structural complexes of the pesticide-contaminated soils in these dumping zones, and to search for and select microorganisms- destructors with cytochrome P450 genes for pesticide degradation.

Materials and methods

Environmental samples:

Environmental soil samples (from a depth of 5–10 cm below the surface) were collected from sites located around three dumping plots (Suzak A, B and Balykchy) that have long been exposed to pesticide contamination (Table 1). The same types of soil, taken from natural and virgin plots, were used as uncontaminated soil samples. The soil was air-dried, ground and passed through a sieve with 2-mm pores, before being stored in sealed containers at room temperature. The soil organic carbon, cation exchange capacity and other physico-chemical parameters were analysed. Soil samples from the uncontaminated and contaminated sites served as an inoculum source for the enrichment cultures in subsequent experiments.

Geographic position, elevation and locality	Zone/ecosystem and Soil source type	Physical and chemical characteristics of the soils
Dumping plot Suzak A and B: N 40° 59.625′, E 72° 53.796′ 1136 m elevation above sea level; Jalalabad province, Suzak region The dumping plot has an area of about 0.9 hectares. It has free access and contains nine separate tranches with a total of 2000–3000 tons of pesticides dumped.	The plot is located on the bank of the Kougart River, in the northeastern part of the Fergana Valley. **Light sierozem soils:** These soil types are formed by vegetation from the ephemeral desert steppes. Parent rocks are loess-like loams. The climate of this zone is continental. In summer, the air temperature can reach up to 43°C, and in winter up to - 25°C.	Mechanical composition is silt-loam, sandy loam and loamy loess. Humus content: 0.7–1.7% Total nitrogen: 0.1–0.14% The soils are calcareous at the surface: the CO_2 in the upper layer is about 2–3%. C: N - 6.3 Mechanical fraction, %: 1.0–0.25 mm: 5.34; 0.25–0.05 mm: 17.5; 0.05–0.01 mm: 47.73; 0.01–0.005 mm: 13.73; 0.005–0.001 mm: 12.97; <0.001 mm: 5.32; 0.001 mm: 32.02 Soil pH: 8.0
Dumping plot Balykychy N 42°28′, E 76°11′ 1900 m elevation above sea level; **Issyk-Kul** province A former pesticide storage location is located in Balykchy city. Seven or more barrels of liquid pesticide are stored in the crumbling buildings, in poor storage conditions.	The plot is located 300 m from the Issyk-Kul lake. There is a residential area within 200 m of this site, and livestock are sometimes grazed here. **Mountain/valley grey-brown desert rocky soils:** These soil types are formed under extreme continental desert climate conditions. The surface is composed of rocky and gravelly soils. The climate is dry; rainfall varies within 100–250 mm. The weather here is dominated by constant winds.	Humus content: 0.5–1.5% Total nitrogen: 0.1–0.14% Mechanical fraction, %: 1.0–0.25 mm: 5.34; 0.25–0.05 mm: 17.5; 0.05–0.01 mm: 47.73; 0.01–0.005 mm: 13.73; 0.005–0.001 mm: 12.97; <0.001 mm: 5.32; 0.001 mm: 32.02 Soil pH: 7.6

Table 1. Environmental sites for the collection of soil samples

Chemical analyses: Soil samples taken from the contaminated sites were analysed for their pesticide concentration at the Chemical Laboratory of the ‘’ILIM” Ltd Scientific Production Association, Bishkek, Kyrgyzstan (Chromatography, Master GC).

Extraction of total DNA and DNA extraction from pure cultures: DNA was extracted from the enrichment cultures during the active phase of microbial growth, using the UltraClean™ Soil DNA Isolation Kit and an alternative protocol by the MO BIO Laboratories. The purified bacteria were incubated in MPM medium for two days at 25ºC. Cells were harvested at the early exponential growth phase, and their DNA was then extracted by the alternative protocol of the MO BIO Laboratories.

Characterization of isolated bacteria: Isolated bacteria were grouped on the basis of their morphological, biochemical and physiological characteristics. The bacteria’s catalase activity, NO_3 reduction, indole production from tryptophan, fermentation of 12 different organic carbon compounds, urease activity, and hydrolysis of gelatin and starch were determined. Fluorescent, diffusible pigments, and growth at 4ºC, 27ºC and 37ºC, were also determined.

PCR amplification: Amplification was performed with a Multigene Thermal Cycler (TC9600-G/TC, Labnet International), using a (25 µl) mixture containing the following: 15 µl of PCR Master Mix (Taq DNA polymerase, $MgCl_2$, deoxyribonucleotide triphosphate and reaction buffer), 2 µl of each primer, 1 µl of template DNA and 1 µl of H_2O.

Primers: Almost-full-length fragments of the 16Sp RNA gene were amplified using the following primers: 16S-27F and 16S-907R. Fragments of genes encoding the subunits of monooxygenases were amplified using specific sets of primers. The primer set of P450R was used to amplify the cytochrome P450 hydroxylase.

Sequence analysis: Sequence analysis was performed by Macrogen (World Meridian Venture Center 10F, #60-24, Gasan-dong, Geumchun-gu, Seoul, Korea), and the sequences were edited using Applied Biosystems 3730XL sequencers.

Pesticide: Aldrin was obtained from Private Agrochemicals Companies of China in Bishkek, Kyrgyzstan.

Biodegradation Experiments

Biodegradation of pesticides in a liquid medium:

A mineral medium was prepared, containing $(NH_4)_2SO_4$ –1, 0; K_2HPO_4 – 0, 8; KH_2PO_4 – 0, 2; $MgSO_4*7H_2O$ – 0, 2; $CaCl_2*2H_2O$ – 0, 1; $FeCl_3*6H_2O$ – 0, 05; $(NH_4)Mo_4O_2*4H_2O$ – 0, 01 and water (1000 ml, pH: 7.0).

In this medium microbial cultures were incubated with various concentrations of pesticide in the following scheme:

1. *Pseudomonas sp.* + 10mg Aldrin in 100 ml of mineral medium:
Pseudomonas sp. + 25 mg Aldrin in 100 ml of mineral medium*:*
Pseudomonas sp. + 50 mg Aldrin in 100 ml of mineral medium;

2. *Micrococcus sp.* + 10 mg Aldrin in 100 ml of mineral medium*:*
Micrococcus sp + 25mg Aldrin in 100 ml of mineral medium;
Micrococcus sp + 50 mg Aldrin in 100 ml of mineral medium;

3. *Flavobacterium sp* + 10mg Aldrin in 100 ml of mineral medium:
Flavobacterium sp + 25 mg Aldrin in 100 ml of mineral medium*:*
Flavobacterium sp + 50 mg Aldrin in 100 ml of mineral medium;

4. *Bacillus sp.* + 10 mg Aldrin in 100 ml of mineral medium;
Bacillus sp. + 25 mg Aldrin in 100 ml of mineral medium
Bacillus sp. + 50 mg Aldrin in 100 ml of mineral medium

5. The association of these bacteria + 10 mg, 25 mg and 50 mg Aldrin in 100 ml of mineral medium

6. Control: 50mg Aldrin in 100 ml of mineral medium without microbial culture.

At first pesticide was added to a pre-sterilized 100-ml Erlenmeyer flask, at a concentration of 50 µg/ml in acetone. After evaporation of the acetone, 50 ml of mineral medium were placed in 100-ml Erlenmeyer flasks and the flasks were shaken for 48 hours. The medium was inoculated with a suspension of cells from *Bacillus polymyxa, Micrococcus sp, Flavobacterium sp.* or *Pseudomonas fluorescens* grown on nutrient media for 48 hours with a final density of about 2×10^8 CFU (colony-forming units) ml^1. Another medium without a bacterial suspension inoculation served as a control. Both the inoculated and uninoculated samples were incubated under intermittent shaking (180–200 rpm) to provide aerobic conditions. After two, four, six and 12 days, duplicate flasks from the inoculated and uninoculated samples were withdrawn aseptically and analysed for pesticide residues by HPLC, after their extraction in hexane [Barceló 1991].

Results and discussion

Pesticide residues in the soil of dumping zones

Chromatography analyses of soil samples, selected from contaminated sites around the Suzac A plot, have revealed a high content of obsolete pesticides, including D-BHC (52.661 mg/kg); B-BHC (52.740 mg/kg); 4.4 DDD (35.621 mg/kg); Endrin-aldehyde (43.469 mg/kg); Dieldrin (17.778 mg/kg); and others (Table 2). The soils of the Suzac B plot also contained a very high concentration of obsolete pesticides, including Heptachlor-epox (15,418.160 mg/kg); Aldrin (1326.939 mg/kg); D-BHC (2283.103 mg/kg); Heptachlor (1371.921 mg/kg); and others (Table 3).

Soil sample number	Quantity (mg/kg)	Substance name
1	13.801	A-BHC
2	52.740	B-BHC
3	19.079	G-BHC
4	52.661	D-BHC
5	4.537	Heptachlor
6	7.353	Aldrin
7	18.000	Heptachlor-epox
8	12.122	Endosulfan-1
9	27.567	4.4 DDE
10	17.778	Dieldrin
11	35.621	4.4 DDD
12	25.601	Endosulfan-2
13	43.469	Endrin-aldehyde
14	73.873	Endosul-sulf+4.4 DDT

Table 2. The pesticide content of the soil from around the Suzac A dumping zone

(*Method of external std. 201_13_07_2015-ECD*)

Soil samples number	Quantity [mg/kg]	Substance name
1	979,504	A-BHC
2	577,502	B-BHC
3	910,548	G-BHC
4	2283,103	D-BHC
5	1371,921	Heptachlor
6	1326,939	Aldrin
7	15418,160	Heptachlor-epox
8	462,358	Endosulfan-1
9	654,768	4.4 DDE
10	268,031	Dieldrin
11	266,593	4.4 DDD
12	743,211	Endosulfan-2
13	567,780	Endosul-sulf+4.4 DDT

Table 3. The pesticide content of the soil from around the Suzac B dumping zone

(*Method of external std. 201_13_07_2015-ECD*)

Chromatography analyses of soil samples, selected from contaminated sites around the Balykchy dumping zone, have shown a high content of the following pesticides: Heptachlor-epox (23.956 mg/L), A-BHC (20.764 mg/L), Endosulfan (16.527 mg/L), Endosul-sulf+4.4 DDT (14.379 mg/L), 4.4 DDD (8.836 mg/L), Dieldrin (5.549 mg/L), and others (Table 4).

Soil samples number	Quantity [mg/kg]	Substance name
1	20,764	A-BHC
2	4,995	B-BHC
3	7,133	G-BHC
4	1,813	D-BHC
5	4,121	Heptachlor
6	23,956	Heptachlor-epox
7	5,024	Endosulfan-1
8	4,629	4.4 DDE
9	5,549	Dieldrin
10	8,836	4.4 DDD
11	16,527	Endosulfan-2
12	14,379	Endosul-sulf+4.4 DDT
Accumulated Value	1,000	

Table 4. The pesticide content of the soil from around the Balykchy dumping zone
(Method of external std. 201_13_07_2015-ECD)

These obtained results confirm the technical studies of experts [e.g., the Interim Report on the Technical Investigations of Obsolete Pesticides in the Kyrgyz Republic, from April 22, 2010], claiming that the dumping plots Suzak A and Suzak B are essential “hot spots”. These areas are very dangerous for any living organisms, since the content of persistent and obsolete pesticides in these soils exceed the normal limits many times. Illegal digging further increases the potential for contaminants to enter the environment (Fig.1). In terms of environmental protection, there is importantly also a former pesticide storage unit located in Balykchy, 300 metres from Lake Issyk-Kul. High levels of obsolete pesticides have also been found there.

Fig. 1. View from Dumping plot Suzak A and B: N 40° 59.625', E 72° 53.796' 1136 m elevation above sea level; Jalalabad province, Suzak region; open pit, people dig out a trench in search of pesticides

Cultivable microbial diversity of contaminated soils

Classical microbiological analysis revealed cultivable forms of microorganisms on different nutrient media. The poorest microflora was identified in pesticide-contaminated soils, composed of only one or two physiological groups. Specifically, in light grey soils (Suzak plot) and mountain-valley grey soils (Balykchy plot), bacteria from Actinobacteria phylum were the dominant. In particular, bacteria species of the Micrococcus genus were predominant in soils from around the Suzak and Balykchy dumping places (Figure 2 and 3). These bacteria made up 32- 47,0% of the indigenous local microflora; bacteria species from the *Pseudomonas* genus (*Gammaproteobacteria* phylum) made up 23% in Suzak , 12,0% in Balykchy soils. *Bacillus* species bacteria were found only in Suzak soils, their content made from 21, 0% to 71, 0%. Bacteria of *Flavobacterium sp* were obtained only in *Balykchy* soils ((Figure 4).

Fig.2. Cultivable microbial diversity of contaminated soils of Balykchy plot on mineral medium: Colonies of Micrococcus , Flavobacterium and Pseudomonas genera bacteria

Fig.3. Cultivable microbial diversity of contaminated soils of Suzak plots on mineral medium: Colonies of Micrococcus , Bacillus and Pseudomonas genera

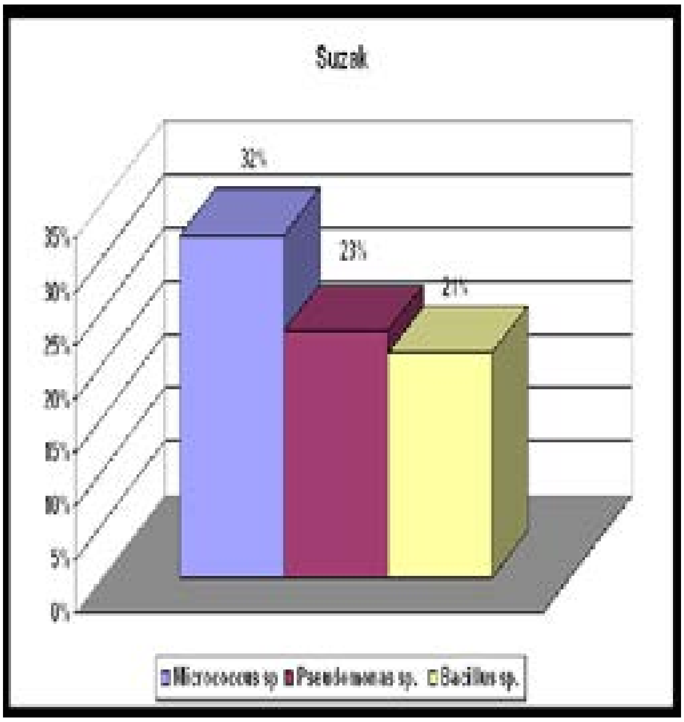


Fig.4.Cultivable diversity of bacteria in Suzak soils; and cultivable diversity of bacteria in Balykchy soils

Fungi as representatives of the soil biota were found in both soils. In Balychy plot soils fungi from *Botrtys, Phialophora and Plectosphaerella genera were dominated.* In Suzak plot soils fungi from *Penicillium and Acremonium genera were relieved (*Figure 5 and 6).

A

B

Fig.5.Cultivable diversity of fungi of contaminated soils (on mineral medium): A) Colonies of fungi found in Balychy plot soils (Botrtys, Phialophora and Plectosphaerella genera). B) Colonies of fungi found in Suzak plot soils (Penicillium and Acremonium genera).

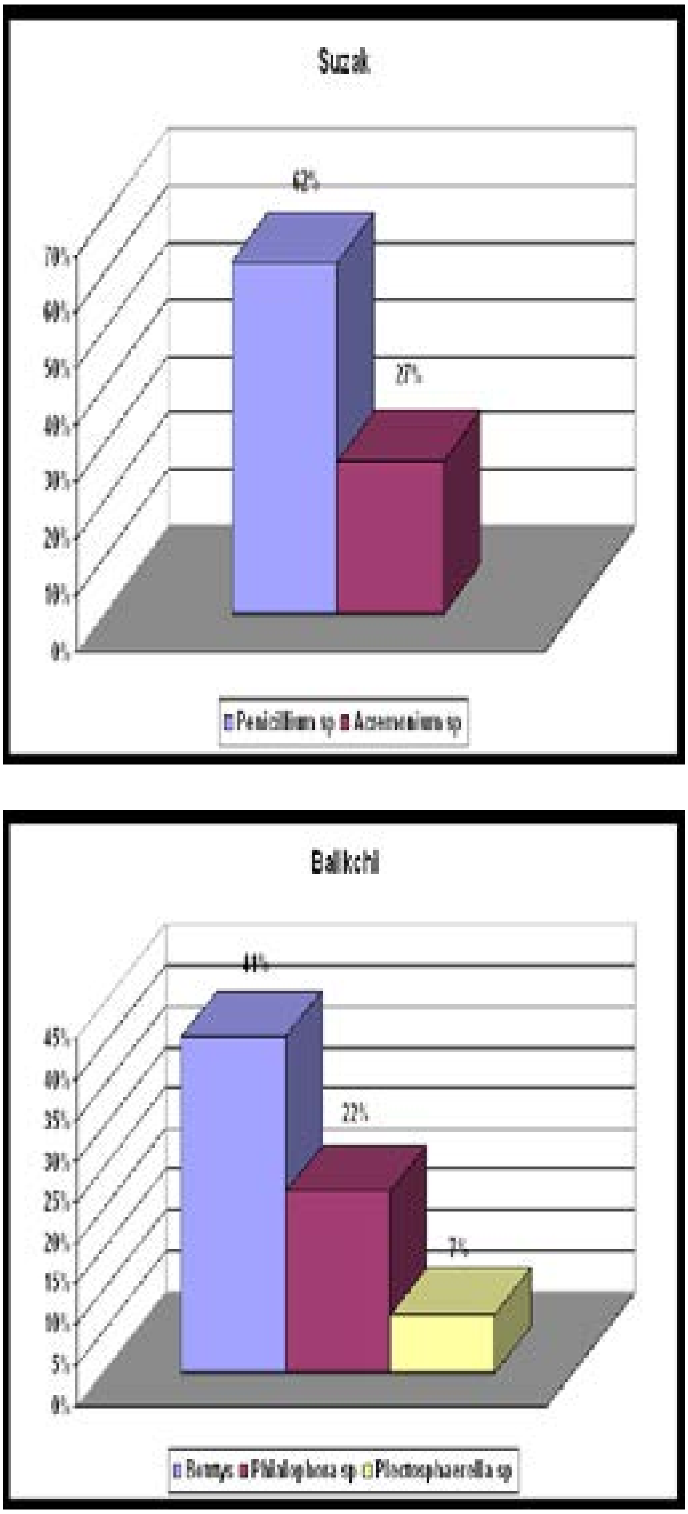


Fig. 6. Cultivable diversity of fungi in contaminated soils

Biodiversity of uncultured bacteria isolated from contaminated soils by PCR analysis

The 16S rRNA gene sequences taken from uncultured soil samples confirmed that most of the bacteria belonged to classes of *Beta, Alpha* and *Gamma Proteobacteria* and *Firmicutes*. Representatives of the *Actinobacteria, Firmicutes* and *Gammaproteobacteria* phyla were predominant in contaminated soils (Table 5). Among uncultivable forms the 16S rRNA analyses has found the bacteria with cytochrome genes which are directly involved in degradation process of organic carbon compounds. This indicates to a natural process of pesticide biodegradation in these soils carried by local natural microflora (Figure 7).

Groups	Contaminated soils		Uncontaminated soils	
	Cultivable isolates, %	16S rRNA sequence, %	Cultivable isolates, %	16S rRNA sequence, %
Alphaproteobacteria	-	1.3	5.1	-
Firmicutes	30. 8	47,2	1,2	10,2
Gammaproteobacteria	3–4	32.8	-	12–15
Betaproteobacteria	-	1–1.4	-	28.5
Bacteroidetes	0.5–0.7	1.0–1.2	7.0	12–17
Actinobacteria	50,3	47,3	12,8	14.2

Table 5. Percentages of bacterial taxa detected in pesticide -contaminated and uncontaminated soil samples. The taxonomic affiliation of bacteria was determined by BLAST and by neighbour-joining analysis.

Pesticide contamination seemed to encourage the propagation of Actinobacteria, *Firmicutes* and *Gammaproteobacteria*; that bacterial groups are known to be commonly associated with hydrocarbon degradation processes**.** Reported microbiodegraders, obtained by researchers from different countries, belong to the following bacterial classes: gamma-proteobacteria (e.g., *Pseudomonas*, *Aerobacter*, *Acinetobacter*, *Moraxella*, *Plesiomonas*), beta-proteobacteria (e.g., *Burkholderia*, *Neisseria*), alpha-proteobacteria (e.g., *Sphingomonas*), actinobacteria (*Micrococcus*), and flavobacteria (*Flavobacterium*). Indeed, bacteria related to the *Pseudomona*s, *Neisseria*, *Moraxella* and *Acinetobacter* genera are able to degrade DDT almost completely [Carrillo-Pérez et al. 2004], while microorganisms from the *Pseudomonas*, *Bacillus*, *Trichoderma*, *Aerobacter*, *Muchor*, *Micrococcus* and *Burkholderia* genera have been shown to biodegrade dieldrin and endrin [Matsumoto et al.2009; Hayatsu et al.2000; Matsumoto et al.2008].

Most of the DNA samples extracted from the soil in the enrichment culture were amplified with P450 fw1 and P450 rv3 primers, showing by the presence of cytochrome P450 genes (Figure 8). This confirms the presence of pesticide-degrading bacteria genes, which catalyse the degradation pathways of the organochloride compounds in these soils.

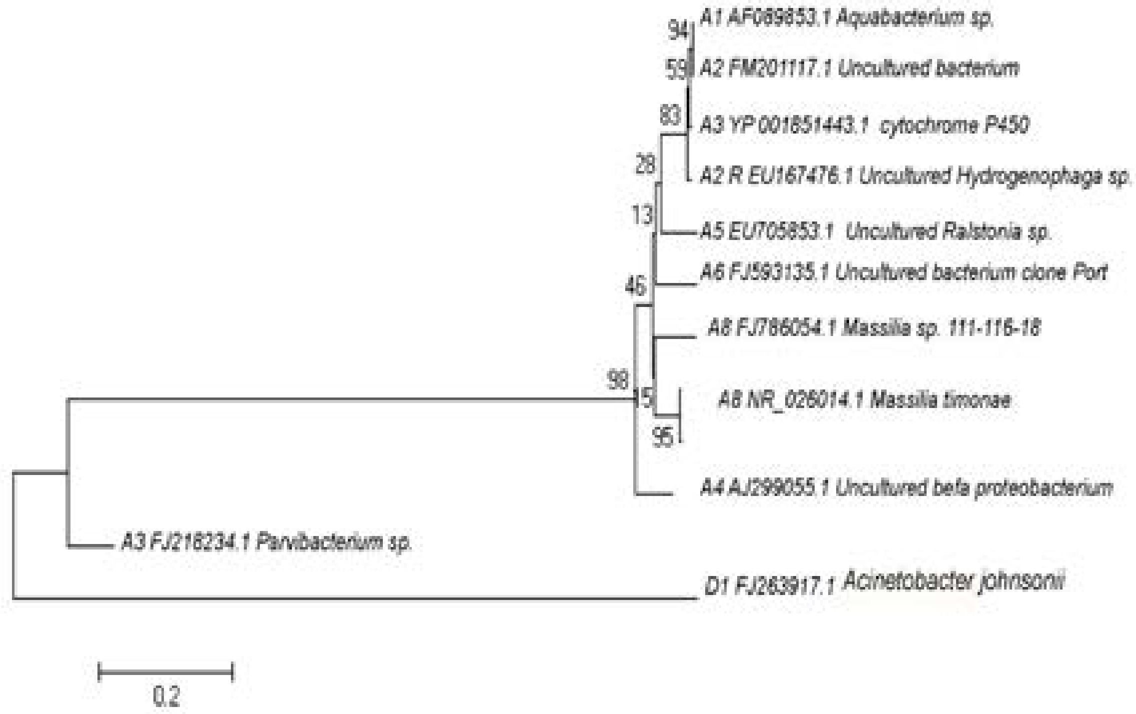


Fig.7. Phylogenetic tree based on 16SrRNA gene sequences showing the position of isolated bacteria strains from contaminated sites.

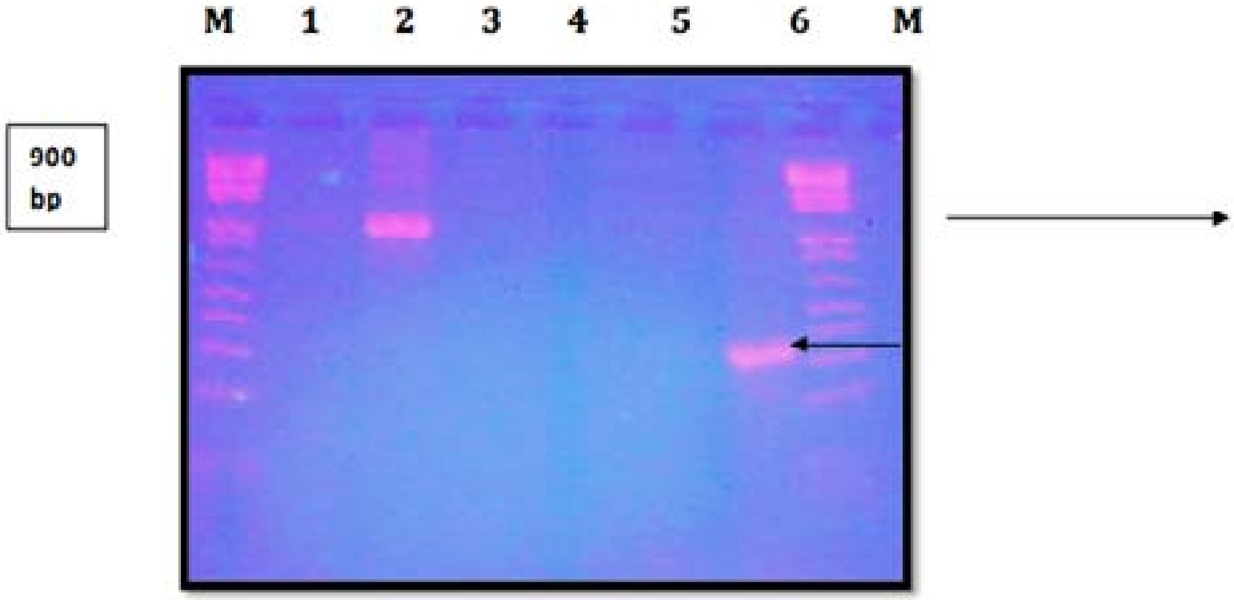


Fig 8. Agarose gel (1.0 %) electrophoresis of some PCR products of DNA samples extracted from enrichment culture obtained with universal and specific primers : lanes M- molecular weight markers ; lanes 1,3 and 5 – negative controls; lane 2 – DNA sample (A-3) amplified with 16SpRNA gene; lane 4 - DNA sample (A-3) no amplified with alkane hydroxylase genes (alkB-F and alkB-R); lane 6 - DNA sample (A-3) amplified with cytochrome P450 hydroxylase genes (P450F and P450R).

Biodegradation experiments. Degradation of aromatic compounds requires the opening of the aromatic ring. Bacteria must possess enzymes that either cleaves the ring of the aromatic halogen compound (PCP). Organochlorine insecticides, including Dieldrin and Aldrin are still found in the environment more than 30 years after their prohibition. We have studied biodegradation of Aldrin in the polluted soils.

The *Bacillus polymixa, Pseudomonas fluorescens, Micrococcus sp. and Flavobacterium sp.* cultures in association utilized the Aldrin in the mineral salts media as their sole carbon and phosphorus sources. After 12 days of incubation, the 0.1% aldrin was degraded up to 55.1%, the 0.5% aldrin – 32,2%, the 1,0 % aldrin – 32,0 % by these bacteria in association in aerobic conditions. During the same period, in the uninoculated control, the abiotic dissipation rate of Aldrin was 2.27% ((Figure 9). *Bacillus polymixa* single culture appeared to be more effective than the other bacteria in degrading of tested organochloric pesticide. After 12 days of incubating the degradation efficiency of *Bacillus polymixa* was 48,2 % for 0,1% Aldrin; for 0,5% Aldrin - 21,3%; for 1,0% Aldrin – 18,7%. In the same days 0,1% Aldrin was degraded up to 43,2 % by single culture *Pseudomonas fluorescens;* 0,5% Aldrin – 17,7%; 1,0% Aldrin – 13,9% (Figure 10). The degradation efficiency of *Flavobacterium sp. and Micrococcus sp.was* lower than previous bacteria, so in 12 days their single cultures were able to degrade 27,0% and 24,2% respectively of 0,1% Aldrin (Figure 11).

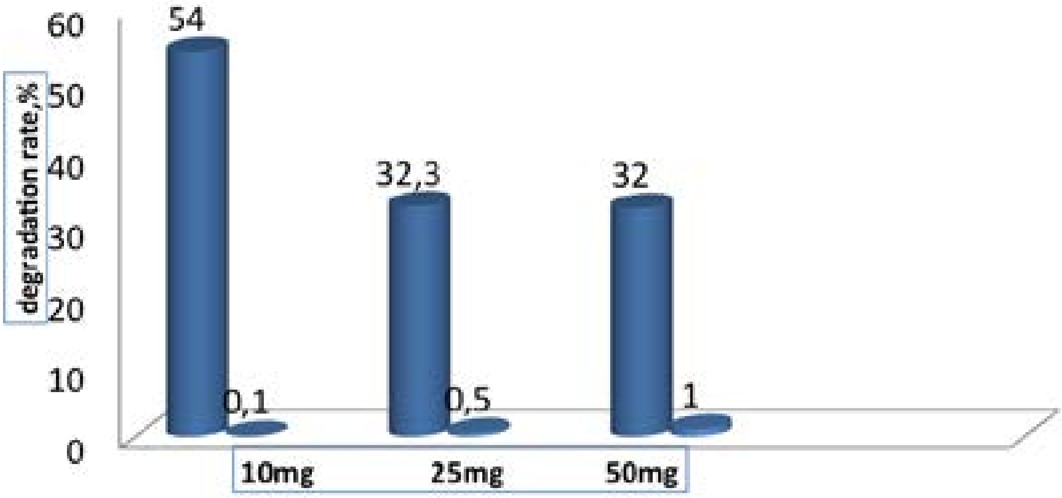
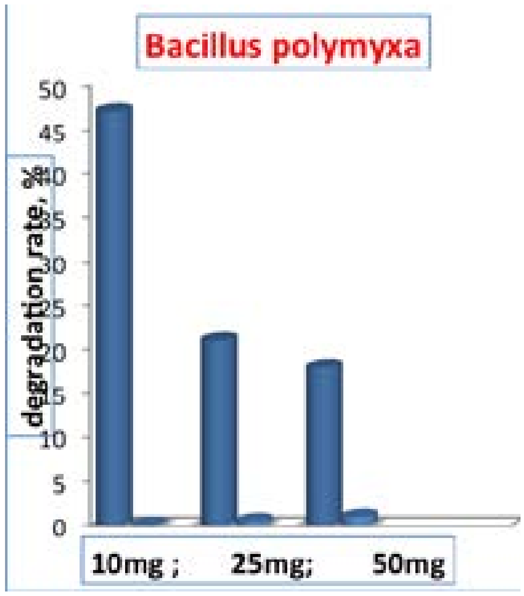


Fig 9. Degradation rate of Aldrin by Pseudomonas fluorescens + Bacillus polymyxa + Micrococcus sp + Flavobacterium sp. in association, in a mineral medium over 12 days



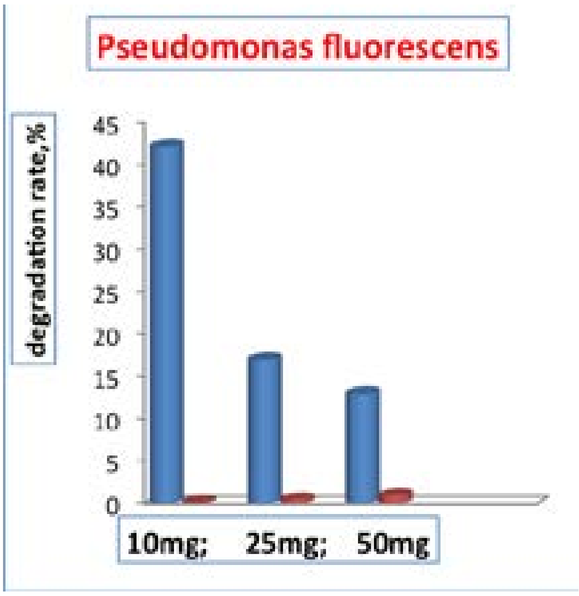


Figure 10. Degradation rate of Aldrin by single cultures of Bacillus polymyxa and Pseudomonas fluorescens in mineral media over 12 days

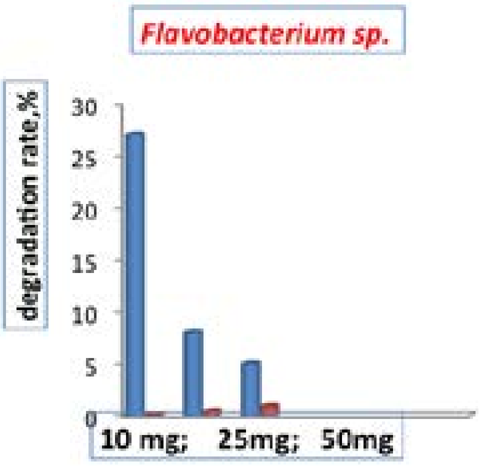


Figure 11. Degradation rate of Aldrin by single cultures of Flavobacterium sp. and Micrococcus sp. in mineral media over 12 days

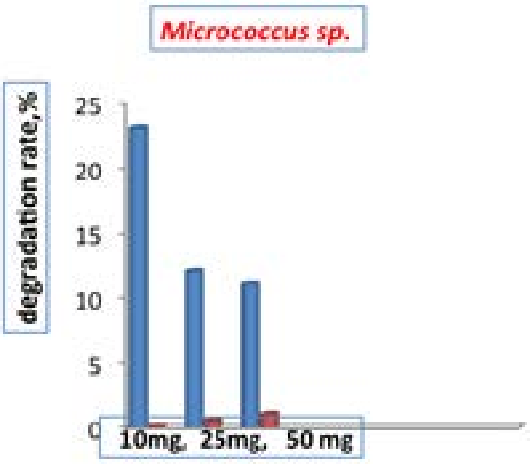
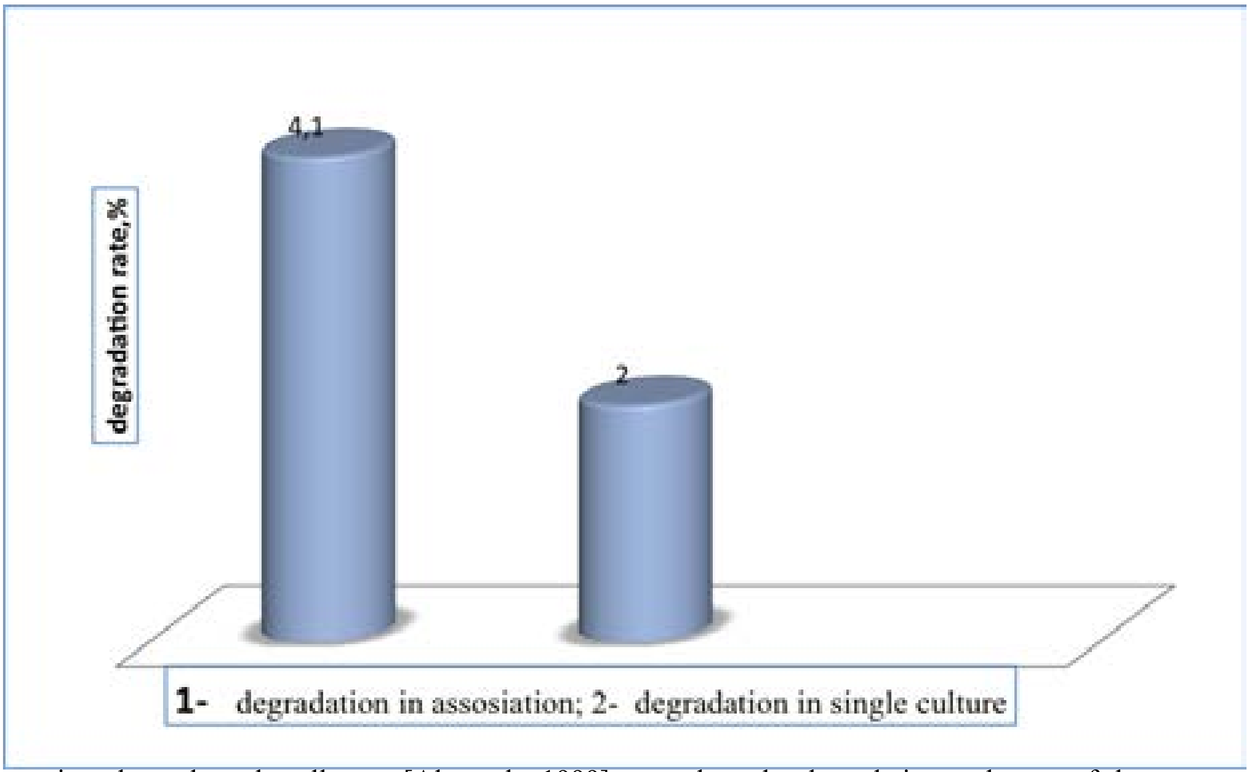


Figure 12. Degradation of Aldrin in control

The degrading capacity of the bacteria increased only in co-cultivation, which shows that these bacteria naturally coexist and are dependent on each other for the utilization of environmental substances. Some researchers have noted two further factors worth mentioning: co-metabolism and consortia conditions. Some biodegraders require other



substrates in order to degrade pollutants [Alexander 1999]. This phenomenon is called co-metabolism and is especially necessary for organochlorine compounds. In contrast, it has been shown that the presence of other carbon sources decreases the rate of organophosphate biodegradation [Hayatsu et al.2000].

When pesticide degradation occurs, it usually involves more than one microorganism, i.e., each microorganism contributes to the biodegradation reactions on the pesticides, while no example of mineralization by a single strain has been reported. It seems that the presence of different microorganisms is essential for adequate biodegradation to occur [Velázquez-Fernández et al. 2012; Romeh et al.2014].

Conclusions

Studying the microbial diversity of soils contaminated with pesticides has an undoubted practical significance. The changes in the structure of soil microorganisms caused by the toxic effects of pesticides have a biodiagnostic potential. At the same time, the resistant populations of microorganisms in such soils are capable of the active degradation of pesticides. The selection and cultivation of the most promising microorganism populations for the degradation of different types of pesticide is a basic strategy for the bioremediation of a contaminated environmental matrix. Among uncultivable forms the 16S rRNA analyses has found the bacteria with cytochrome genes which are directly involved in degradation process of organic carbon compounds. Most of the DNA samples extracted from the soil in the enrichment culture were amplified with P450 fw1 and P450 rv3 primers, showing by the presence of cytochrome P450 genes. This confirms the presence of pesticide-degrading bacteria genes, which catalyse the degradation pathways of the organochloride compounds in these soils.

Active bacterial strains from the *Pseudomonas fluorescens and Bacillus polymixa* were selected in this research. They have demonstrated high rates of degradation activity on chlorinated hydrocarbon pesticide, both in association and in single cultures. Our future research will focus on optimizing the pesticide degradation conditions in a variety of soil types, using these selected bacterial strains. It is necessary to optimize all the physical and chemical parameters, taking into account the type of pesticide and the metabolism of the microorganism itself.

Acknowledgements

This research was supported by the project "Bioremediation of environmental contaminants by microorganisms" (Science Foundation of the Ministry of Education and Science of the Kyrgyz Republic).

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STIMULATION IN THE BIODEGRADATION OF LINDANE AND OTHER HEXACHLOROCYCLOHEXANE ISOMERS BY SPHINGOMONAS D4 WHEN GROWN IN CO-CULTURE WITH BIOSURFACTANT-PRODUCING STRAINS

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Abstract

Lindane, the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane (g-HCH) was extensively used as an insecticide. The industrial production, by chlorination of benzene and posterior purification of lindane, generated massive amounts of residues containing other HCH isomers (mainly alpha and beta). Moreover, the mixture of isomers (technical lindane) was also used as a cheap and effective insecticide, mainly in developing countries[1,2]. Nowadays all HCH isomers are included in the list of persistent organic pollutants (POPs) of the Stockholm Convention (2009)[3] and their use is banned or restricted to specific applications in most countries. However, these contaminants are still present worldwide in soils and waters and constitute a particularly important environmental problem in the previous dumping sites close to production centres[4,5].

The HCH isomers differ in their physic-chemical properties (hydrophobicity, volatility, structural stability, etc.)[6]; determining their interactions with organic and inorganic soil components and their persistence in the environment. Beta isomer is the more hydrophobic and recalcitrant of the major HCH isomers. Biodegradation is considered the main degradation pathway of HCHs in the environment and is influenced by their availability. Several bacterial strains able to degrade HCHs have been isolated and studied. In aerobic environments members of the family *Sphingomonadaceae* are considered particularly important for the elimination of HCHs although other degraders have also been isolated and described [4,5,7],.

In the present study the biodegradation of HCHs residue in slurries of two soils with contrasting organic matter contents (4% and 0.4% organic C) was studied. The soil slurries were inoculated with the HCH-degrading *Sphingomonas* D4[8], alone or in co-culture with *Streptomyces* M7[9] or *Rhodococcus* ET54b[10], strains which are able to produce biosurfactants. In all soil slurries inoculated with D4 the HCHs content decreased by more than 95%. Co-inoculation of the degrader with either M7 or ET54b stimulated the dissipation of HCHs. The positive effect of the co-culture on the dissipation was mainly observed in the soil with a lower organic matter content and for the major isomers present in the HCHs residue (alpha and beta). In soil with a higher organic matter content the degradation of HCHs was very fast and the stimulating effect of co-inoculation was only significant for the beta isomer after 2 days of incubation. The results indicate that biodegradation of HCHs in the environment may probably be improved by bioaugmentation with selected bacterial consortia including HCHs degraders and strains which are able to increase the bioavailability of HCHs.

Key Words

Lindane, hexachlorocyclohexane, HCHs, biodegradation, Sphingomonas D4, Streptomyces M7, Rhodococcus ET54b, biosurfactants, co-culture, soil, organic matter.

Materials and methods

Two soils A and B with similar characteristics (sandy-loam texture, pH 4.5-5 and cation exchange capacity < 5 $cmol_c$ kg^{-1}), except for their contrasting organic matter content (4% and 0.4% of organic C, respectively) were selected. Aliquots of 0.5 g soil were sterilized in glass tubes (3 cycles in autoclave in three consecutive days) and contaminated with HCHs residue from the production of lindane, mainly composed of alpha (80%) and beta (15%) isomers. The contaminant was allowed to *age* in contact with the soil for 1 month. Thereafter slurries were prepared adding 4 ml of sterile minimal salt medium and the selected bacterial strains were inoculated alone or in combination. Five different inocula were prepared: D4 = HCH degrader *Sphingomonas* D4[8]; M7 = *Streptomyces* M7[9]; ET54b = *Rhodococcus* ET54b[10], D4+M7 and D4+Et54b. The dose of inoculum used was 10^6 colony forming units (cfu) ml^{-1} slurry, in the case of D4 and ET54b, and 1g biomass ml^{-1} slurry, in the case of M7. Control tubes containing sterile slurries were also prepared. The tubes were incubated at 28ºC with agitation (150 rpm). After 1, 2, and 9 days of incubation, 4 replicates of each treatment and of the control were taken for analysis. The bacterial proliferation was determined by plating appropriate dilutions of the slurries in rich media, and the cfu were counted after 2 weeks of incubation at 28 ºC. HCHs were extracted with hexane (10 ml hexane/4 ml slurry) in an ultrasonic bath for 60 min and the different isomers were identified and quantified using a gas chromatograph coupled to an ion-trap mass spectrometer (450 GC and 220MS, Varian Inc., Australia)[8]

Results and discussion

All 3 strains inoculated alone or in combination survived in the slurries of soils A and B. *Sphingomonas* D4 proliferated faster and the density reached was slightly higher in soil A than in soil B. The proliferation of D4 was not affected by the growth in co-culture with M7 but, in general, the presence of ET54b significantly decreased the density of D4, particularly in soil A (around 0.5 logarithmic units). The density of M7 in the slurries tended to increase during the incubation, particularly in soil B, but the increment was not significant, which may be because the time of incubation was too short for this slow growing *Actinobacteria*. Moreover Streptomyces growing in liquid culture tend to form cell aggregates, which reduces precision of counts determined by plating. ET54b proliferated fast in slurries of soil A but its density did not change or slightly decreased in slurries of soil B.

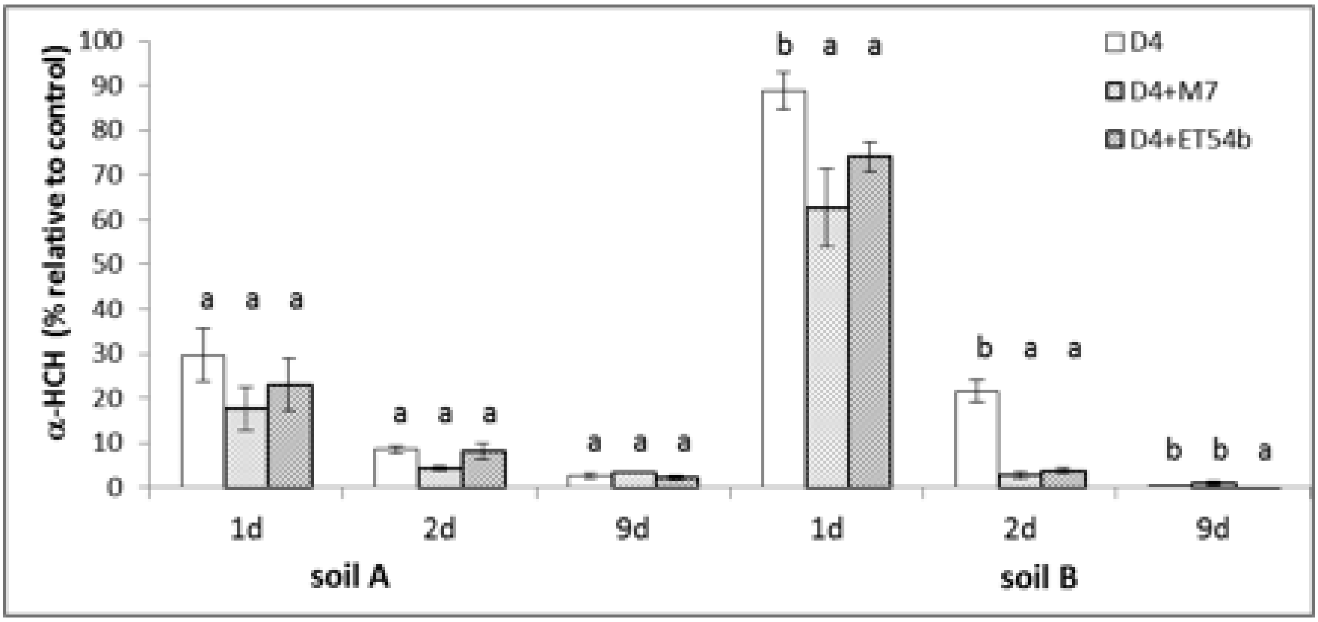
In all soil slurries inoculated with D4 the HCHs content decreased by more than 95% (Fig. 1A and 1B). Co-inoculation of the degrader D4 with either M7 or ET54b stimulated the dissipation of HCHs. The positive effect of the co-culture on the dissipation was mainly observed in the soil with a lower organic matter content and for the major isomers present in the HCHs residue (alpha and beta).

In soil with a higher organic matter content the degradation of HCHs was very fast and the stimulating effect of co-inoculation was only significant for the beta isomer after 2 days of incubation (Fig. 1B).

Both *Streptomyces* M7 and *Rhodococcus* ET54b are able to produce biosurfactants, which may increase the bioavailability of HCHs and stimulate the degradative efficiency of Sphingomonas D4. HCHs, particularly the beta isomer, are highly hydrophobic[6] and adsorb to soil organic matter[4]. A more pronounced positive effect of biosurfactants on HCHs biodegradation could be expected in soils with higher organic matter content. Surprisingly, the stimulating effect of the co-culture of the degrader D4 with biosurfactant producers was higher in slurries of the soil B, with much lower organic matter content than soil A. The rapid degradation of HCHs in slurries of soil A probably hampered the detection of any positive effect of the biosurfactant producing strains. It could be interesting to carry out further studies in soils with HCHs strongly adsorbed to organic matter due to long time of contact of the contaminant with soil components or in soils with higher concentration of contaminant.

The results indicate that biodegradation of HCHs in the environment may probably be improved by bioaugmentation with selected bacterial consortia including HCHs degraders and strains which are able to increase the bioavailability of HCHs.

A



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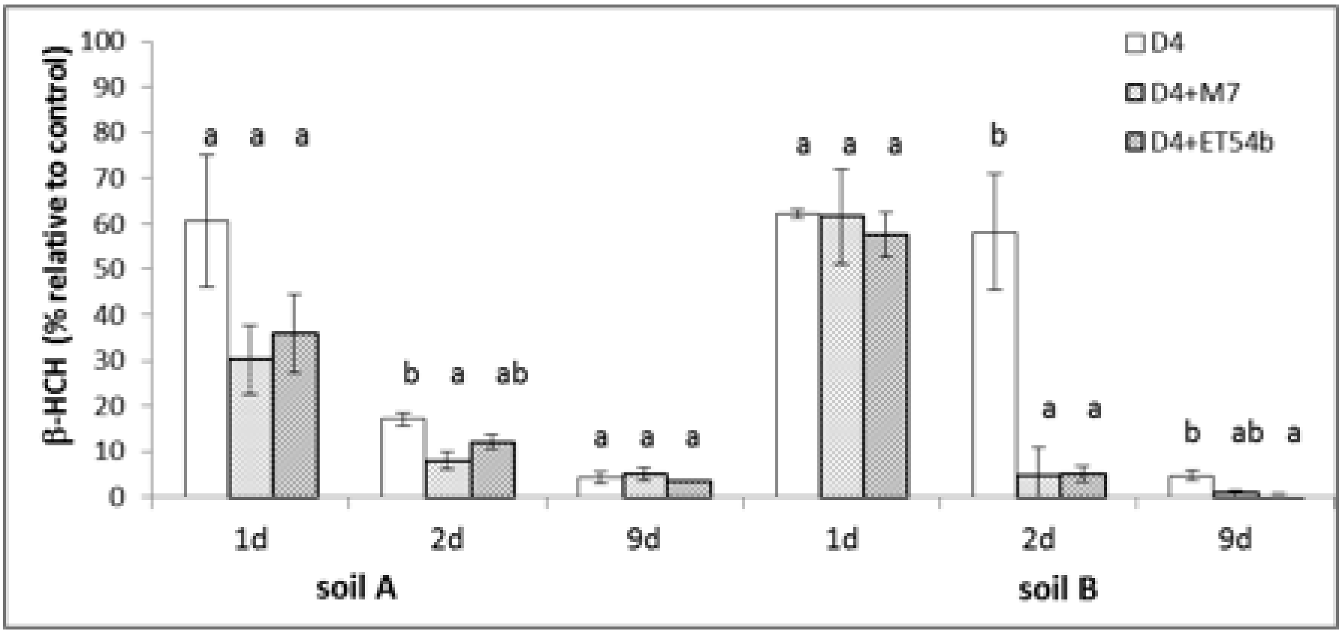

Fig 2.
α-HCH (A) and β-HCH (B) remaining in soils A and B inoculated with Sphingomonas D4 alone (D4) or in co-culture with Streptomyces M7 (D4+M7) or Rhodoccocus ET54b (D4+ET54b). Results (mean±standard error) are expressed as percentage relative to the HCH amount in control slurries (sterile). 1d, 2d, 9d: days of incubation after inoculation. At each incubation time different letters indicate significant differences between treatments (p≤0.05).

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MONITORING OF HALOGENATED POLLUTANTS USING DEHALOGENASE-BASED BIODEVICES

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Abstract

The essential component of remediation technologies developed for removal of unwanted chemicals from the environment is monitoring of the contaminant levels in the treated soil or groundwater. Analysis of the multiple samples collected at a locality and transported to a laboratory has to be conducted to describe changes in pollutant concentration. This process can be very time-, labour- and resource-demanding. One possible solution to this problem is development of on-line monitoring systems for continuous on-site analysis of the contaminants. This idea has driven the development of biodevices (biosensors and bioassays) as the new analytical tools that can be an alternative or a complement to conventional analytical techniques. Applications of biosensors and bioassays in environmental monitoring are very promising owing to their sensitivity, low costs, user-friendliness and adaptability for on-site field measurements. One of the largest groups of harmful environmental pollutants are halogenated hydrocarbons. These compounds result from their extensive use as pesticides (e.g., γ-hexachlorocyclohexane) and industrial solvents (e.g., 1,2-dichloroethane). The most recent biodevices based on dehalogenase enzymes for detection of toxic halogenated compounds were developed in collaboration among Masaryk University (www.muni.cz), Enantis (www.enantis.com) and Photon System Instruments (www.psi.cz). These biodevices have proven to be fast, reliable, simple and cost-effective tools for detection of halogenated aliphatic hydrocarbons under laboratory as well as field conditions. Developed systems are particularly suited for continuous on-site monitoring, where sample removal is inconvenient, difficult or dangerous.

Key Words

biosensors, bioassays, biodevices, environmental monitoring, haloalkane dehalogenases, halogenated pollutants, hexachlorocyclohexane, γ-hexachlorocyclohexane dehydrochlorinase, lindane

Materials and methods

All chemicals were of analytical grade and used without further purification. Fluorescence indicator dye was purchased from Fluka (Switzerland). All other chemicals were purchased from Sigma-Aldrich (USA). Dehalogenase enzymes were overexpressed in *Escherichia coli* BL21(DE3). The His-tagged enzymes were purified using a chromatographic column with nickel nitrilotriacetic acid Sepharose attached to a fast protein liquid chromatography system (GE Healthcare) as described earlier[1]. The prepared enzymes were lyophilized using an ALPHA 1-2 LD freeze dryer (Martin Christ). Biosensor tips were prepared as previously described[2]. Electronic parts of biodevices were obtained from the Photon System Instruments (Czech Republic).

Results and discussion

Biosensors and bioassays

According to IUPAC definition, biosensor is a self-contained integrated device capable of providing specific analytical information using a biorecognition element, which is retained in direct spatial contact with a transducer. Bioassays are distinct from biosensors, as the biorecognition element is not fixed to the transducer[3]. However, in both cases, the chemical compound to be detected (an analyte) interacts selectively with the biorecognition element. This interaction causes a change in the physicochemical properties of the bio-layer, e.g., changes in optical properties. The altered properties are converted to an electronic output signal by the transducer. The signal, which is proportional to the analyte concentration is processed and evaluated using a computer system.

Our fully functional biodevices are suitable for rapid detection of halogenated hydrocarbons and consist of: (i) a cofactor-free dehalogenase enzyme as biorecognition element, (ii) a derivative of fluorescein as pH indicator dye, and (iii) sensitive optoelectronic instrumentation[2]. The enzymatic reaction with halogenated hydrocarbons is accompanied by release of protons, which is followed by a change in fluorescence of the pH indicator. The light directed into a photomultiplier is then transformed into an electrical signal. The optoelectronic instrumentation part was recently significantly miniaturized to be simple, cost-effective, user and environmentally friendly (Fig. 1).


Figure 1. Two fully functional miniaturized optical biodevices based on dehalogenase enzymes.

As biorecognition elements we use several different enzymes from haloalkane dehalogenase (HLD) family and γ-hexachlorocyclohexane dehydrochlorinase LinA. HLDs are hydrolytic enzymes able to catalyse cleavage of a carbon-halogen bond in a wide range of chlorinated, brominated and iodinated aliphatic hydrocarbons, including alkanes, cycloalkanes, alkenes, alcohols, esters, carboxylic acids, ethers, epoxides, nitriles and amides[4].

The products of the reaction are alcohols, halide ions, and protons. Brominated compounds are generally better substrates than chlorinated ones. Nevertheless, also anthropogenic-chlorinated compounds, such as 1,2-dichloroethane and 1,2,3-trichloropropane, were identified as possible substrates of HLDs[5]. The substrate range as well as the rate of conversion of individual substrates differs among HLDs. The HLDs LinB, DhlA, DhaA and DbjA exhibiting the highest level of activity and ability to convert otherwise resistant compounds represent particularly useful biocatalysts (Table 1).

Enzyme	**LinB**	**DhlA**	**DhaA**	**DbjA**
Source organism	*Sphingobium japonicum* UT26	*Xanthobacter autotrophicus* GJ10	*Rhodococcus rhodochrous* NCIMB 13064	*Bradyrhizobium japonicum* USDA110
pH optimum	8.5	8.2	8.0-9.5	9.7
Temperature optimum	40 °C	37 °C	30-37 °C	50 °C
Attractive substrates	1,3,4,6,-tetrachloro-1,4-cyclohexadiene, bis(2-chloroethyl) sulphide	1,2-dichloroethane 1,2-dibromomethane	1,2,3-trichloropropane bis(2-chloroethyl) sulphide	1,2-dibromoethane
Applications	biosensing bioremediation decontamination	biosensing bioremediation	biosensing bioremediation biocatalysis decontamination molecular imaging	biosensing biocatalysis

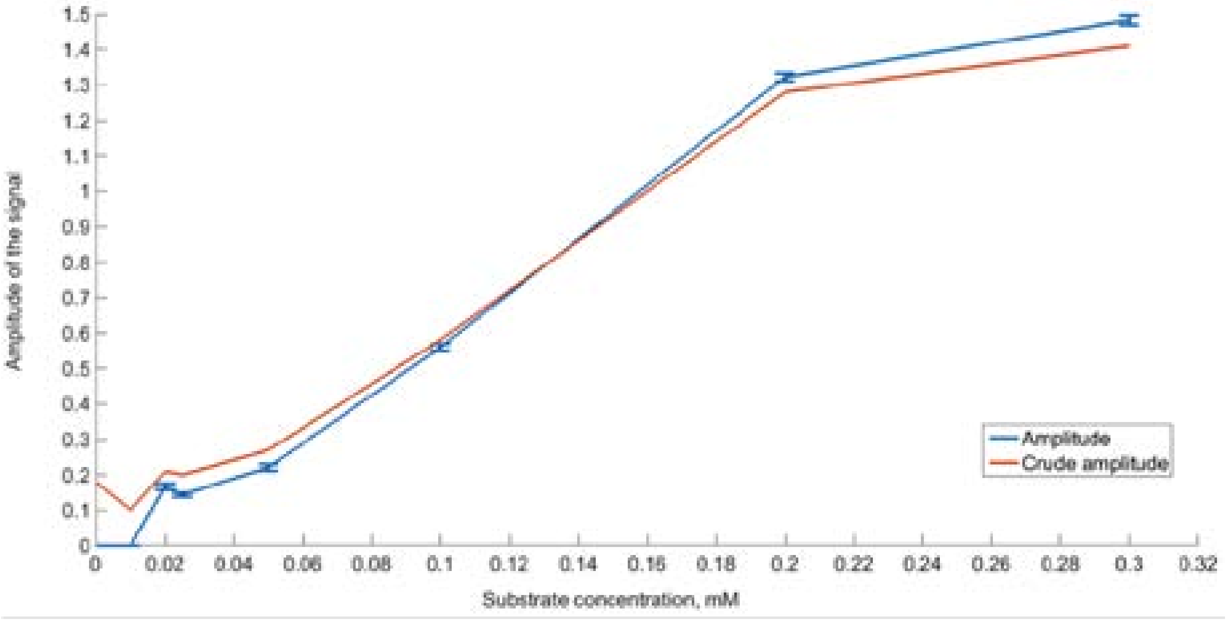
Table 1. Characteristics of four HLDs exhibiting the highest application potential[5].

Under aerobic conditions, the enzyme LinA from *Sphingomonas paucimobilis* UT26 catalyses the elimination of chlorine atoms from the molecule of γ-hexachlorocyclohexane (lindane), a recalcitrant pesticide[6]. The *linA* gene product is the first enzyme of a catabolic pathway that dechlorinates lindane and makes the carbon backbone utilizable in the general metabolism of the bacteria[7]. As in the case of HLDs, this reaction is followed by a change in pH. Due to quite narrow substrate specificity, the LinA-based sensor was found to be specific to hexachlorocyclohexane and did not respond to several other organic halogenated compounds studied. Commonly used chloropesticides like DDT did not interfere with the sensor response.

Detection of halogenated compounds

Evaluation of the HLD-based biosensor was performed with the pesticide 1,2-dibromoethane, the ground water pollutant 3-chloro-2-(chloromethyl)-1-propene and the oxygen yperite bis(2-chloroethyl) ether. As a biorecognition element was used dehalogenase LinB. The HLD-based biosensor showed an excellent linear dependence with the detection limits of 2.4, 1.4 and 4.6 mg/l, respectively. Evaluation of the LinA-based bioassay was performed with lindane (Fig. 2). This bioassay was found to detect lindane with the detection limit of 2.9 mg/l. With both biodevices, detection of halogenated compounds was possible within 5 min of measurement time.

Figure 2. Calibration plot of the biodevice utilizing LinA for the analyte lindane. Amplitude (blue line) was obtained by fitting. Crude amplitude (red line) is equal to the difference between maximal and minimal points of the smooth segment of the curve. The detection limit was calculated to be 0.01 mM (2.9 mg/l).



Field-testing of biosensor

The field-testing of HLD-based biosensor was performed at the locality Pancevo in Serbia with chemical factories bombarded during the Yugoslav war in 1999[8]. As a consequence, 2,100 tonnes of toxic industrial solvent 1,2-dichloroethane leaked into the soil and to a wastewater canal that flows into the river Danube. High concentration of this chemical can be still detected in surroundings of a petrochemical complex. Data measured by DhlA-based biosensor were compared with those measured by gas chromatography-mass spectrometry (Fig. 3). The profile of the biosensor response to collected water samples exhibited patterns similar to the conventional chromatographic analysis. The field trials with LinA-based bioassay for the detection of lindane are currently in progress.

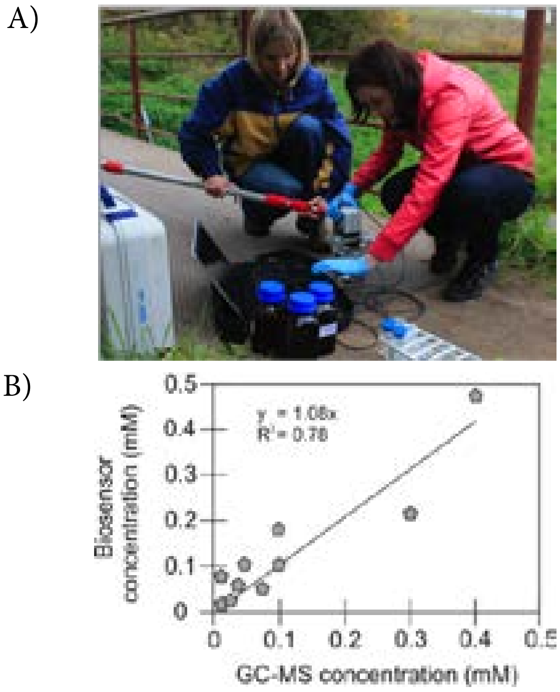


Figure 3. A) Sample photo taken during measurement at the contaminated locality. B) Comparison of 1,2-dichloroethane concentrations measured by DhlA-based biosensor and by gas chromatography-mass spectrometry (GC-MS).

Conclusions

Biosensors and bioassays are highly useful tools for monitoring of long-term changes in contaminant concentrations or preliminary screening of contamination from landfills with inappropriate protective barriers, old sewers, sewage or industrial effluents, before applying more costly techniques. Small size and robustness enables the usage of biodevices for on-site detection of surface and groundwater contamination, where sample removal is inconvenient, difficult or dangerous. The HLD-based biosensors will be in the next step amended by GSM system to construct a device enabling distant on-line monitoring of pollutants without repeated visits of the operator to the locality. The ongoing identification and isolation of novel dehalogenases from extremophilic organisms is expected to significantly broaden the application spectrum of the biodevices. Particularly, biocatalysts showing good activity at lower temperatures are attractive for biosensing. Moreover, we are constantly striving to further decrease the detection limit of the biodevices by application of protein engineering improving the catalytic performance of employed enzymes.

Acknowledgements

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ECOTOXICOLOGICAL ASSESSMENT OF LINDANE-POLLUTED SOILS ON BACTERIAL COMMUNITIES AND EARTHWORMS AND THE USE OF THESE ORGANISMS AS A BIOREMEDIATION TOOLS

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Abstract

During its activity (1975-1992), a lindane factory located in Sabiñánigo (Huesca, NE Spain), wasted tons of industrial residuals in a nearby urban landfill, provoking the contamination of the surrounding soils with lindane isomers and other organic compounds. This study has assessed the physiology of the bacterial communities and earthworms in soils exposed to land-fill leachates and others from the surroundings (i.e. just exposed to atmospheric deposition from the landfill). Soils were characterized including the analysis of pollutant concentrations (by HPLC) and endocrine disruption potential and stimulation of cytochrome P450 (CYP) dependent detoxification activities. The physiology of the bacterial communities –assessed as the ability of degrading different carbon sources- was analyzed using Biolog Ecoplates; avoidance experiments were used to assess the earthworm response to the different soils. Soils presented a long list of organic compounds, including all the lindane isomers, and elevated content of chlorophenols and toluene. Soils presenting the higher lindane concentrations were those presenting the highest endocrine disruption activities. These soils were the most toxic for earthworms, presenting an acute toxicity (lethal after a few hours of contact). However, under mixture conditions (50% of the most contaminated and 50% of the less contaminated), earthworms survived up to 30 days. Moreover, its activity as soil engineers increased the extractability of pollutants and reduced the endocrine disruption activity on soil extracts.

Key Words

Lindane, earthworms, soil bacteria, carbon sources degradation, landfill, endocrine disruption

Materials and methods

Soil selection and characterization. Soil samples L1 and L2 were collected immediately downstream (in the direction of groundwater) from the landfill, in close proximity to it (see Fig. 1). Historically these soils could be affected by the air dispersion from the landfill, although it was sealed in 1996. These soils are affected directly by surface leachates from groundwater. L3 sample is located in an area that receives runoff from the landfill. The L4, L5 and L6 samples are located east from the landfill, in a region that forms a topographic barrier to the wind and certainly receive the dispersion of waste dust during operation on the landfill. These soils were characterized and their content in pollutants by analyzing water and n-hexane extracts by HPLC. A complete analysis of the compounds present in the leachates of this landfill are available in a previous study [1].

Endocrine disruption activity was measured on n-hexane soil extracts. Particularly, we assessed the (anti-)estrogenic,(anti-)androgenic, (anti-)thyroidal activities using different fish and human cells. Moreover, the CYP1A dependent ethoxyresorufin-*O*-deethylase (EROD)activity and the CYP3A dependent benzyloxy-4-[trifluoromethyl]-coumarin-O-debenzyloxylase (BFCOD. It must be noted here that some recent reports associate BFCOD with CYP1A) of soil extracts was also assessed.

Figure 1. Area of study ("Vertedero original" = original landfill; "Celda seguridad" = new and secure landfill to which, recently, the content of the original one has been transferred).

Bacterial physiological activity. Microbial population and diversity changes can be detected with Biolog™ microplate test, which is based in 31 microbial C-source substrates, which are plant root exudates [2] and were identified as highly discriminant substrates for soil microbial community characterization. Each microplate contains 96 wells with the substrates (3x32 substrates). Microbial respiration is detected by a colour change in the well for each substrate, and a fingerprint of the microbial community is thus obtained and used for comparison with other microplates.

Samples were obtained by taking soil from different depths (S= 0-10 and P=10-20 cm). Bacteria were extracted as described in a previous study [3]. A Biolog microplate was used for each one. An Anthos 2010 microplate reader (Biochrom) was used for automatic optical reading of absorbance in each well of the microplates at 590 nm. There is sigmoid relationship between OD590 and time [4]. Data from the microplates reading were normalized and degradation curves are fitted to a sigmoid growth model where all the curves are then compared. This process is known as average well color development (AWCD). Later, three parameters were compared for each curve to test for statistical differences between soils: slope, maximal degradative capacity and time to reach half of the slope (TM50).

Earthworms activity. The earthworm used was *Allolobophora chlorotica* by adapting the ISO 17512-1:2008 procedure. Toxicological endpoints include from lethality to sublethal changes (e.g. weight loss). Short-term avoidance tests were performed[5], later long-term exposure experiments were done under sub-lethal conditions (lethal soils for earthworms, detected in the short-term experiments, were not used).

Pollutants in soils. Analyses were performed in the laboratory of the Government of Aragon located in Bailin, by GC / MS (Agilent 7890A) and has held high-level analysis of procedures for QA / QC, including interlaboratory comparisons (AquaCheck program) . The volatiles compounds were analyzed by HS-GC/MS whereas for semivolatile compounds and phenols, a solid phase extraction with subsequent organic solvents dissolution and determination by GC/MS were used. The uncertainty in intercomparison exercises were less than 10 % for all parameters with the exception of chlorophenols which reaches 70% due to the absence of a specific method of extraction.

Results and discussion

Soil characterization. In general, the n-hexane was able to extract higher amounts of almost all toxic compounds than distilled water; between 5 and 30 times depending on the compound (see Tab. 1). The exceptions were the m- and p- xylene and o- xylene; in these cases the amount extracted with distilled water was between 1.5 and 10 times the amount extracted with n-hexane. Other compounds, as toluene, were extracted with similar performance for both solvents (water and n-hexane).

Compounds	Extraction with n-HEXANO (µg/kg suelo seco)									Extraction with distilled water (µg/kg suelo seco)						
	L1		L2	L3		L4	L5	L6		L1		L2	L3		L6	
	L1S	L1P	L2S	L3S	L3P	L4S	L5S	L6S	L6P	L1S	L1P	L2S	L3S	L3P	L6S	L6P
BENCENE																
TOLUENE				218	304	124	180	188	91			193	167	302	138	58
ETILBENCENE												3		1		
m y p-XILENE				25	18	13	14	16	12		3	37	33	29	28	31
o-XILENE		4	2	13	9	5	6	9	5		11	19	21	14	13	14
2 Y 4-CLOROPHENOL				29	3											
2,4-DICLOROPHENOL				3	1											
2,6-DICLOROPHENOL				1												
1,2,4,5-TETRACLOROB	7	8		14	30											
2,4,6-TRICLOROPHEN.	1			1761	274							1	12	2		
PENTACLOROB.	10	9		465	270											
TETRACLOROFEN.				197	45		28	27	26				0			
a-HCH	201	50		39	3								0			
b-HCH	992	363	20	294	274			223	43	30	31		37	7		
g-HCH				73	64								11	14		
d-HCH	128	70		73	530					22	54		2			
e-HCH	2359	1640		4126	3917					77	80	8	487	379	5	
Total HCH	3681	2123	20	4604	4789			223	43	129	164	8	537	400	5	

Table 1. Analysis of compounds present in the soil samples. The blank cells are values below the detection limit. Samples of soils from 6 different locations (L1-L6) were collected at two different depths (S 0-10 cm and P 10-20cm).

Regarding the tests using human cells, all soil extracts (from soils used in the long-term exposure to earthworms) showed different levels of estrogenicity, ranging from values around 15-25 E_2Eq/g (pM) for L1/L6 soils to 127 E_2Eq/g for the L3/L6 (the mixture including the most polluted soil, L3). This sample was the only presenting anti-androgenic activity (26 ProcEq/g (µM)). No anti-estrogenic or androgenic activities were detected in these samples.

Regarding the tests using fish cells, the extract from soils L3/L6 was the only inducing EROD activity and BFC -O- Debenciloxilase activity, being the first stronger than that the second. None of the soils presented estrogenic or androgenic or thyroidal activities. However the presence of compounds able of blocking androgen and thyroid receptors was detected in all samples. This anti-androgenic and anti-thyroidal activity was particularly high in L3/L6 soil extract. The presence of earthworms decreased anti-androgenicity of L6/L6 and anti-thyroidal activity in L1/L6. Regarding the anti-estrogenic activity, it was observed only in L1/L6 soils without earthworms. It is possible thus to hypothesize, that the activity of these organism may reduce the soil anti-estrogenicity.

Bacterial physiological activity. After 7 days of incubation on the Biolog microplates, there were no significant differences in the TM50 due to soil depth (0-10 and 10-20cm) in L1 , L3 or L6. When comparing the soils collected from 0-10 cm depth of the TM50 L3S was significantly higher than the L1S , L2 and L6S ($p < 0.05$) and higher than L5 ($p = 0.057$). However, differences between L1S, L2 and L5 L6S were not significant. Regarding soil collected between 10-20 cm, the TM50 of L3P was also significantly higher than those of L1P and L6P, while between these last two there were no significant differences. Regarding the upper limit of the curves, or the maximum capacity of degrading all substrates (and related to the amount of active bacteria), L1S, L2 and L6S presented significantly higher ability of degrading C sources than L5. There were no significant differences between L3 and L6.

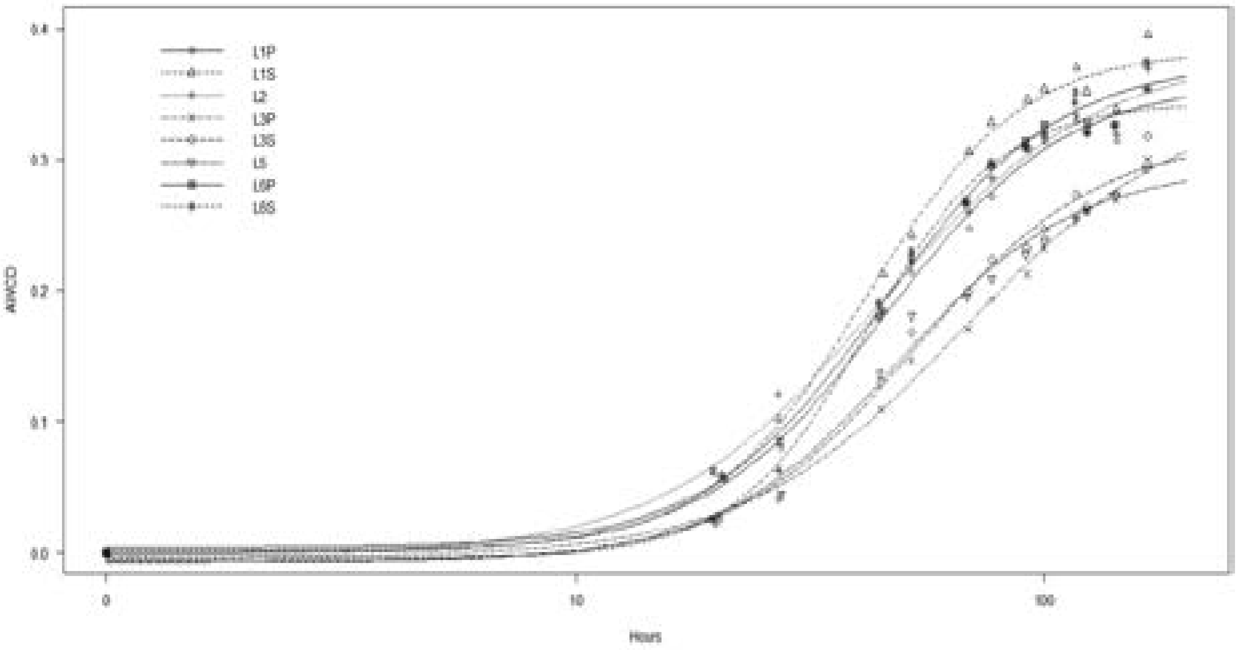

Figure 2. AWCD represented as a function of time for all soils sampled (at both depths S and P). All data fits to sigmoidal curves.

Earthworms activity. Short-term exposure of earthworms to the most polluted soil (L3, see Tab. 1) resulted in the death of all individuals after 48 h. Accordingly, in the long term experiments, earthworms exposed to the mixtures of soils containing 50% of L3, presented avoidance behavior. During the long-term exposure, the earthworms in contact with L6 and with a mixture of mixtures of soils from L1/L6, presented a weight loss, being significant in the case of L1/L6. L1 is, indeed, the second most polluted soil. The L3, the most polluted, was not used because its lethality. The L6 can be considered the less polluted one. Moreover, the activity of earthworms as soil engineers increased the extractability of pollutants (data not shown) and reduced the endocrine disruption activity on soil extracts (data not shown).

Summary. Soils presented a long list of organic compounds, including all the lindane isomers, and elevated content of chlorophenols and toluene. Soils presenting the higher lindane concentrations were those presenting the highest endocrine disruption activities. These soils were the most toxic for earthworms, presenting an acute toxicity (lethal after a few hours of contact). However, under mixture conditions (50% of the most contaminated and 50% of the less contaminated), earthworms survived up to 30 days. Moreover, its activity as soil engineers increased the extractability of pollutants and reduced the endocrine disruption activity on soil extracts.

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TRANSFER OF EXPERIENCES

Landfills: Transfer of experiences from Aragón, Vietnam and EECCA Countries

Part 1: Transfer of experiences from Bailín and POP pesticides landfills in EECCA Countries

EXPERIENCE OF THE HCH BAILÍN LANDFILL DISMANTLING: CHARACTERISTICS OF THE SCENARIO, CONTROL AND ACTIONS

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Abstract

The production of HCH as a by-product in the pesticide industry in the mid eighties in Aragon, led to the accumulation of toxic substances in uncontrolled landfills. This work describes the techniques used for the removal of the main source of active pollution caused by the HCH landfill placed in Bailín through the transfer and encapsulation in a new safety cell.

In this landfill, the products generated in the manufacturing of HCH, HCH pure and DNAPL (Dense Non-Aqueous Phase Liquid) were dumped during several years, generating a focus of active pollution in a particular site with a special hydrogeology and topography.

To carry out the dismantling work was necessary to implemented health and safety measures to ensure no affection to workers and nearby population through the dispersion of Persistent Organic Pollution (POP). Likewise, a thorough environmental control and monitoring was implemented, aimed at ensuring the minimum dispersion of HCH and other organochlorines.

It is also described the waste management process used, as well as the main measures implemented, to ensure a proper transfer of the pollutants until their encapsulation in the new safe confining cell.

During the dismantling, 65,000 Tons of pure HCH and 342,000 Tons of contaminated soil have been transferred and 25 Tons of DNAPL have been removed.

Key Words

Dismantling HCH landfill; Environmental control systems; health and safety control systems; Lindane; HCH; DNAPL; Waste management process.

Materials and methods

1 Background

From the mid 80s until early 90s, the old Bailín landfill was used for the storage of by-products generated in the production of lindane and the liquid waste from distillation process (DNAPL), as well as others types of industrial and urban waste. The wastes were stored without the right conditions to ensure the isolation of the landfill, enabling both the input of groundwater and the infiltration of contaminated fluxes. So it became a source of pollution for the soil, groundwater and surface water in the area.

The Bailín landfill was sited in a geological scenario constituted by an alternation of almost vertical layers formed by sandstones and mudstones. The sandstones layers form a lithology that stand out in the landscape forming bars. The mudstone layers form the depressed areas between said bars (figure 1).

Figure 1.
HCH landfill site.

The sandstone layers, at higher rates, and the mudstones layers, presents a fractures system, which decreases with depth, creating a fissured aquifer with a preferential flow towards the Gallego river and, to a lesser extent, in the direction of the Bailin ravine (figure 2).

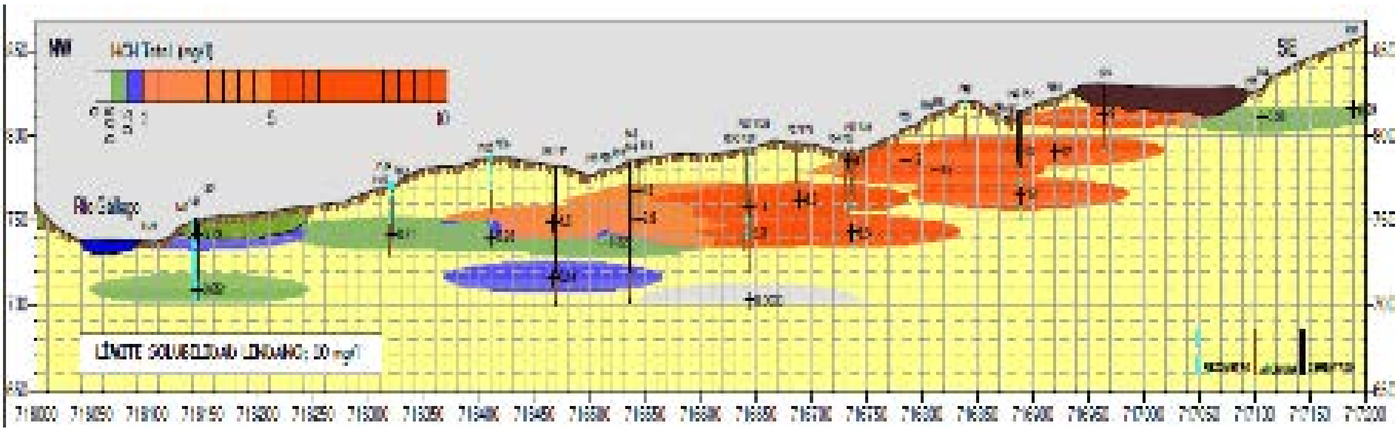

Figure 2. HCH pollution plume. Final report of monitoring year 2010. Government of Aragon.

The particular topography of the area is also remarkable with the landfill place in the middle of the hillside where waters run into the Bailín ravine, which is an effluent of the Gallego River.

2. Scope of the problem and preliminary actions

Once the Bailín landfill was closed down, some studies and monitoring of groundwater and runoff began to be held which let detect the presence of contaminated groundwater by HCH and DNAPL at the bottom of some boreholes.

The detection of this contaminated groundwater, downstream from the HCH landfill, rushed two first courses of action: on the one hand, the monitoring and extraction of contaminated groundwater through the realization of boreholes and, in the other hand, the development of a treatment plant for the water extracted.

From 2008, samples began to be taken periodically in the Gallego River, downstream from Bailin, to determine the possible presence of organochlorines in the River. In some of the cases, this substance was detected.

It also was proceeded to make a characterization of the amount and type of waste stored at the landfill by the execution of boreholes, estimating the presence of around 45,000 tons of residues of HCH, 220,000 tons of contaminated soil and DNAPL from the distillation of lindane.

Bearing in mind the characteristics of the site in which was located the landfill, as well as the large amounts of stored waste and its high toxicity, it was considered as the most appropriate solution, to remove the active focus of pollution that had been detected, the dismantling of the landfill in order to encapsulate the waste in a new safety cell that would have guarantees suitable for storage. In this way, the main sources of pollution would be removed and it will also allow the implementation of measures for decontamination of the polluted aquifer by lindane and DNAPL under this focus.

It should be noted that given the characteristics of the site, it was necessary to consider a system of dismantling that minimizes the periods of exposure of the mass of waste to prevent their uncontrolled dispersion due to the weather effects.

3. Preparatory actions for the dismantling of the landfill

The actions required to undertake the transfer of waste were detailed in the Building Project of Bailin: phase B (2007), in which the action was divided into three different stages:

- Stage 1: construction of a new cell and previous infrastructure required.
- Stage 2: dismantling of the old cell and transfer to the new one.
- Stage 3: sealing of the new cell and landscape restoration.

The stage 1 includes all the infrastructure required to undertake the dismantling of the landfill in safe conditions, the execution of the building works in the new safety cell and auxiliary infrastructure which comprised additional measures for the runoff control and later treatment, as well as vials and waste transfer facilities.

Noteworthy is the waterproofing system laid out in the new safety cell (Figure 3) made up by a double sandwich of geomembrane (HDPE) - geosynthetic clay liner – geomembrane (HDPE), a system well above the legal requirements for this type of landfill.

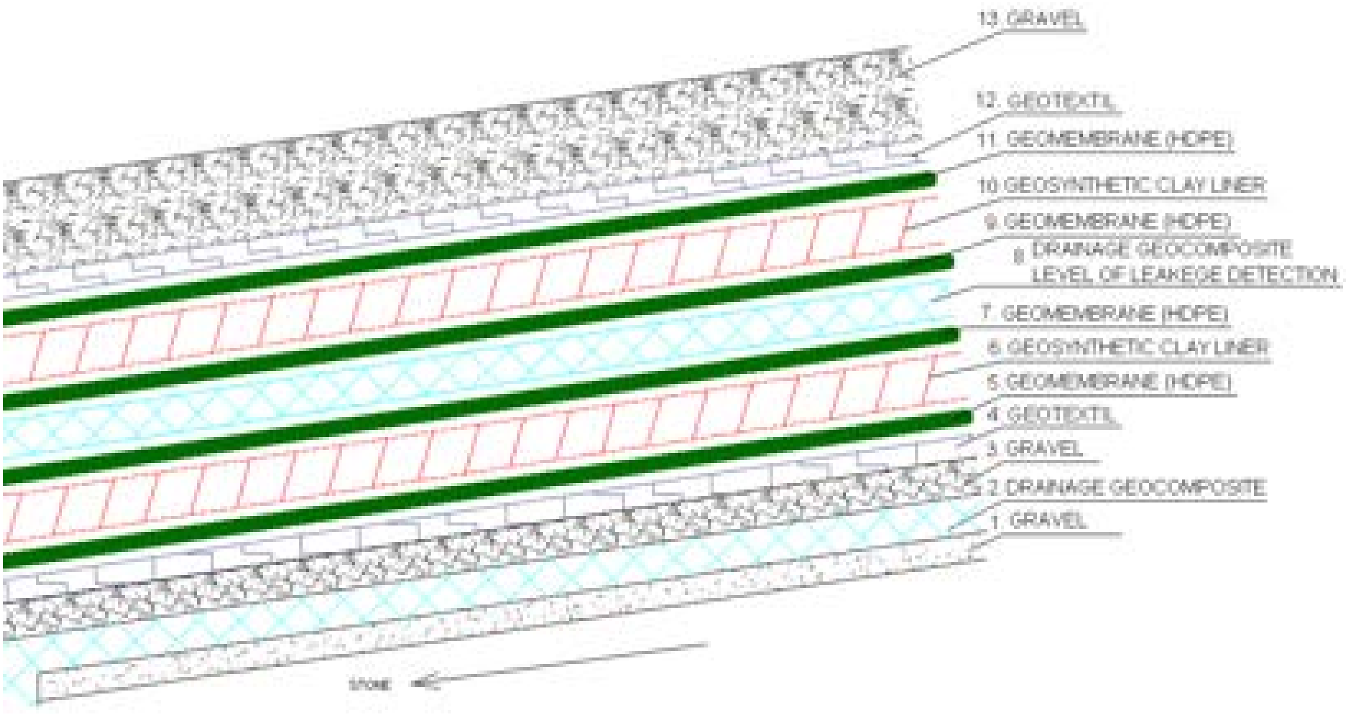

Figure 3: Detail waterproofing new cell

In the use of waterproofing composite is of major priority the adequate control during the installation of the material, preventing the generation of filtrations which are difficult to control once the cell has been filled. Additionally, it should be studied in detail the possible appearance of sliding circles in the own waste-mass as well as in skin landslides, which can be caused by the reduction of friction coefficients due to the use of such materials.

As an additional security measure, it was planned in layer number 8 of the leakage control level between the waterproofing sandwiches installed, a working control system of the waterproofing with three checkpoints to control the presence of leakage, allowing the extraction of leakage by pumping if it was necessary.

During the building works of the new cell, a series of probes carried out in the old HCH landfill allowed modeling the distribution of the different types of waste (figure 4), as well as its quantification, in order to estimate and identify the volumes to be managed during the dismantling works.

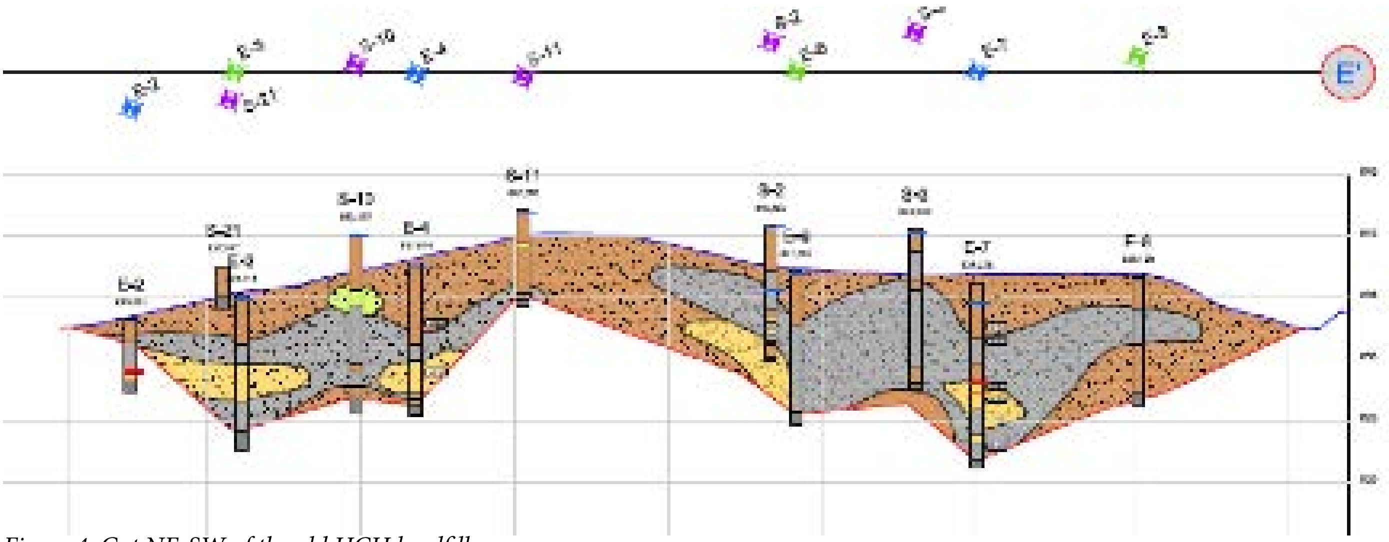

Figure 4: Cut NE-SW of the old HCH landfill.

4 Landfill dismantling.

It is stage 2 of the building project of Bailin: phase B, planned for the drier season, from May to September, with the aim of reducing the risk of pollutants dispersion due to adverse weather conditions.

Noteworthy is the implementation of special health and safety measures and the thorough environmental monitoring required to avoid any condition in the workers, nearby population and environment due to the special hazardousness of this waste.

From the point of view of health and safety, it has been implemented several measures aimed at protecting all the workers involved in dismantling as well as the nearby population:

- Protocols have been established to regulate medical skills (at both levels, health and physical capacity to used special protective equipments) required for the development of works on this contaminated sites. In addition, medical protocols have been carried out to check the absence of health conditions in people who have already completed their work there, in order to validate the adequacy of the protective equipment. At this point, the protocols include the daily maximum exposure times during the performance of the work in the presence of pollutants, as well as the rest periods required and exposure levels to pollution based on the legal requirements.
- Personal and collective protective equipments have been provided concerning the hazardousness of pollution. In terms of personal protective equipment, workers have been equipped with overalls tyveck with an adequate level of safety according the works with solid or liquid waste as well as with integrals masks with filters (figure 5).

Figure 5. Personal protective equipments.

- It has been provided a special facility for the access to the contaminated site, which regulates the entry and exit of workers in accordance with the protocol established for the personal protective equipments delivery and to ensure no dispersion of pollution in the transfer of workers.
- Protocols have been developed to carry out hygienic sampling campaigns using impingers placed inside and outside of the personal protective equipments, before, during and after the development of the work at the contaminated sites. By these samples have been validated the suitability of the personal protective equipments.

At the end of the work of dismantling, it was confirmed, based on the medical checks carried out to all workers, that any of them suffered any affection from exposure to contamination, which was the validation of the health and safety measures.

An environmental monitoring and control plan was developed in order to minimize impacts to the environment during the work of dismantling, as well as monitoring of the appropriateness of the corrective measures established and the implementation of new ones for the adequate development of the works. The environmental monitoring plan is essentially based in the following controls:

- Daily weather monitoring, establishing stop conditions in the dismantling work by forecasts of precipitation or wind that may cause pollution dispersion. In this case, not only transfer works are stopped but also are covered the fronts of excavation.
- Modelling of the dispersion of sedimentary particles, PM.10, PM-2.5. Starting point to establish the control points in air by instrumental monitoring consisted of high volume samplers for PM10 and a GRIMM automatic PM monitor for 2.5.
- Runoff and groundwater monitoring, establishing sampling procedures, sampling points, frequency and control parameters.
- Soils and sediments monitoring, establishing sampling procedures, sampling points, frequency and control parameters.
- Gas monitoring, establishing sampling procedures, sampling points, frequency and control parameters.

Previous to all the work of dismantling, an internal and external emergency plan was developed with different accidental situations such as fire with toxic emissions or uncontrolled discharges which may arrive at Bailín ravine. This plan establishes the warning and action protocols to be followed in each case considered.

The work of dismantling consisted on a selective excavation and different management of the different typologies of waste and contaminated soil management in the waste transfer plant built to effect. The excavations were carried out following a downward direction and at the level of every work esplanade. They were carried out from the landfill boundaries until the final rock slope so as to make sure that all runoff could be recovered for their treatment (figure 6).

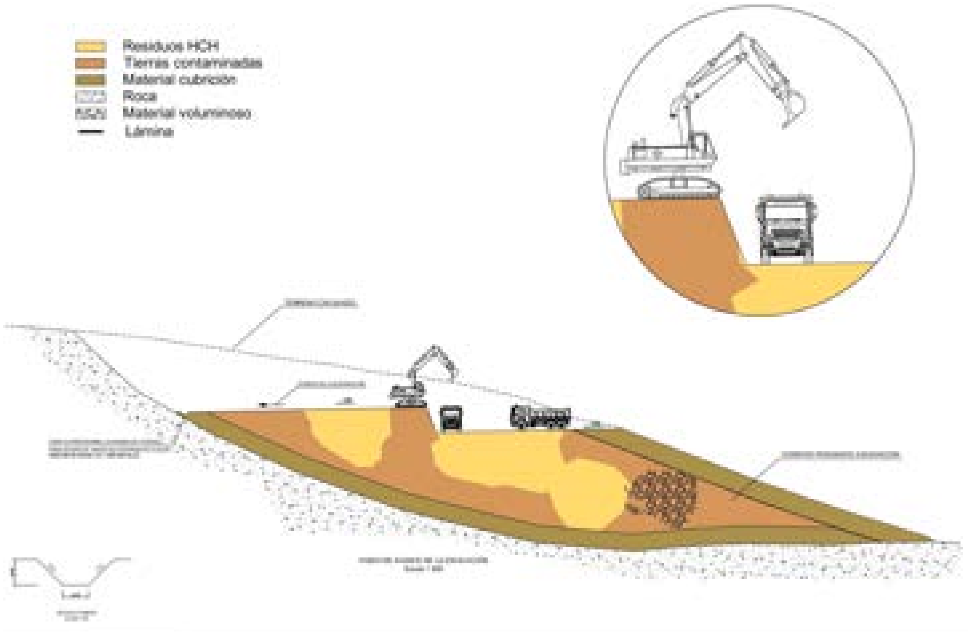

Figure 6: Profile of excavation scheme.

Prior to the start of each excavation level, and as a complement to the modeling of the distribution of waste, a series of tastings of progress were carried out in order to identify the type of waste to be excavated. The following types of waste are managed mainly:

- Pure HCH: 65,000 tons
- Contaminated soils: 342.000 Tn.
- DNAPL: 25 tons.
- Voluminous waste: 14,500 tons
- Solid urban waste: 473 tons.

The excavation was performed selectively according to typology of waste, transporting the dug material to the transfer plant for its separated management (figure 8) and transported to its final storage in the new safety cell or to its external management in the case of DNALP.

The transfer plant constitutes the management unit of the excavated waste, as well as a point of transfer of the residue to the new cell. There are available in it car wash facilities to minimize the dispersion of pollution in the vials of the work during transportation. Equally, they set out equipment for cleaning of road and equipment of dry fog for the settling of sediment particles in the excavation and discharge processes.

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Figure 7: detail of the excavation advance differentiating by type of residue.

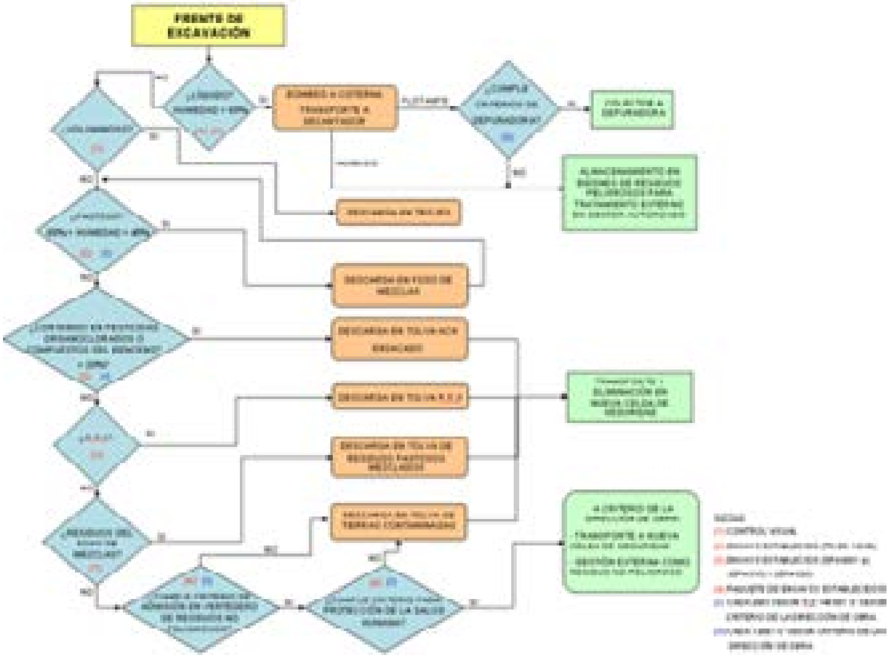

Figure 8: Flow chart of the waste management by type.

The waste transfer into the plant was performed through hopper discharge and truck load. During the dismantling work, it was found that passing through the hopper implied a double waste transfer which involves increasing the dispersion of pollution and the risks associated with it. Therefore the direct load on truck in the excavation face was prioritized in order to reduce this effect.

During the dismantling work, all runoff were captured and stored in tank of storms available to the effect. Then, it was treated in the sewage treatment plant of Bailin, consisting of active carbon filters. Such a runoff achieved HCH concentrations of up to 50,000 µg/l.

The waste stored in the new safety cell has been temporarily sealed (figure 9) with a geomembrane liner (HDPE) and a drainage geocomposite, this last one with the aim of increasing the puncture resistance and drain gases.

Figure 9. New safety cell sealed temporarily.

The definitive sealing is a later stage (stage 3) which is going to develop in a next future, as well as the landscape integration of the new cell.

5. Later actions to the dismantling.

Since the end of the sealing of the new safety cell, it has been done a series of monitoring actions of the correct waste encapsulation with the level leakage detection, with the leached liquid level and with the control ponds (figure 10). They confirmed the absence of leaks or external recharges, that the wastes were stored in appropriate conditions without generating any pollution to the environment and that the main objective of dismantling was achieved.

Figure 10. Leached liquid level and control ponds.

In the same way, once the principal pollution focus has been removed from the old landfill, there is a work area available that will allow applying techniques of decontamination and removal of the still active pollution focus caused by the presence of contaminated mass in groundwater and DNAPL in the fractured sandstone. The Life Discovered Project, co-financed by the European Union, is aimed at applying techniques of decontamination to remediate soils polluted with pesticides by chemical oxidation.

In addition to the above, on the rock of the old dismantling cell, a series of monitoring boreholes are being set up to increase the capacity of study of the contaminant plume and introduce new elements of control, measures and extraction.

Results and discussion

Given the characteristics of the site and the high amount of material contaminated by HCH, the dismantling of HCH landfill through the encapsulation in a new safety cell and the DNAPL removal was considered as the most suitable solution.

The HCH waste management process, forcing the implementation of specific health and safety measures that ensure no affections to the workers and nearby population. Equally, it obliges the adoption of an environmental monitoring plan, in order to minimize the impacts to the environment during the dismantling work, as well as the implementation of appropriate corrective measures. At this point, it is essential to know the meteorological conditions that can lead to dispersion of pollution, as well as establish adequate means of containment and stop of work conditions.

The actions described in this work have achieved to remove the main HCH pollution focus on the site of Bailín with its encapsulation in a new safety cell. The control and monitoring work carried out have confirmed that the wastes have been encapsulated under safety condition without generating further pollution episodes.

Once the principal contamination focus has been removed, there is a work area available that will allow applying techniques of decontamination and removal of the still active pollution focus caused by the presence of contaminated mass in groundwater and DNAPL in the fractured sandstone

Acknowledgments

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SUSTAINABLE MANAGEMENT OF POP PESTICIDE CONTAMINATED LANDFILLS IN ARMENIA AND GEORGIA

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Abstract

This paper presents the 'lessons learned' with regard to sustainable project management when applying our methodology for site characterization and remediation design of two POP and obsolete pesticide landfills in Armenia and Georgia.

The key objective of both projects was to design sustainable measures to mitigate the human health, the ecological and off-site migration risks. Two major phases distinguished in these projects are detailed site assessment and the development of a remediation plan.

Sustainable management in these phases is highlighted through the added value of using Conceptual Site Models in the site assessment phase (anybody can pick up the CSM and extract or add information to it at any moment in time, safeguarding knowledge). Further, in the remediation design/planning phase, Multi Criteria Decision Analysis is used to select the remediation scenario that enjoys most support from the stakeholders. Consideration of the aspect 'time' is also important when choosing a certain solution; in case funds (for related follow-up activities) become available at a much later moment in time, another approach or solution may be more beneficial in the end as compared to the more obvious solution in the short-term.

Taking these aspects into consideration allows for more sustainable management of these sites, noting that in the authors perception 'management' starts with the very first action or investigation of a site and continues until the site has been fully remediated.

Key Words

POPs, pesticides, landfill, remediation, site assessment

Materials and methods

The 4.4 hectare Iagluja[1] dumpsite is situated in Georgia and contains an estimated 2,800 tonnes of POP and obsolete pesticides and other agrochemicals from the Soviet era in sarcophagi, pits and trenches. The site was investigated by Tauw in 2014, finally resulting in a preferred jointly agreed remediation option.

The Nubarashen[2] dumpsite is situated in Armenia and consists of a landfill body of some 3,900 m^2 that is currently capped and reportedly contains a total of 512 tons of pesticides originating from the Soviet era. The Nubarashen dumpsite is situated in a valley subject to severe erosion processes. The site was investigated by Tauw in 2013, finally resulting in a preferred jointly agreed remediation option.

The methodology for sustainable management of these landfill sites entails two major phases that each consist of sub-phases:

- Site assessment, phased as follows:
  1. Reviewing of all available site information with compilation of an Initial Conceptual Site Model (ICSM)
  2. Performing a gap analysis of the ICSM to update the Conceptual Site Model (CSM)
  3. Design a sampling and analyses plan including detailed work plan
  4. Conduct an on-site detailed site assessment by surveying, sampling and chemical analysis to establish the quality the type, extend, volume and tonnage of waste, and the extent to which contaminants have spread in the vicinity.
  5. Draft a final (updated) CSM, carry out a Tier 2 risk assessment and prepare site assessment report

- Design of a site remediation plan, phased as follows:
  1. Determine the remediation objectives and strategy by selecting feasible remediation techniques and strategies for each site component or situation
  2. Conceptual design of at least three feasible remediation scenarios
  3. Select preferred option with a Multi Criteria Decision Analysis
  4. Detailed technical design of the preferred remediation scenario

Results and discussion

This section presents the 'lessons learned' with regard to sustainable project management during the execution of the two projects, following the methodology outlined above.

Site assessment

For both projects it is concluded that the cycle preliminary/ available information –>ICSM –> gap analysis –> field investigations to fill in the identified knowledge gaps –> updated CSM, is the essential backbone for performing the site assessment cycle in a logical, structured way.

During the ICSM stage, high resolution satellite images (LANDSAT) are sufficient, but in the following stages 3D images are required which were obtained by 3D laser scanning (Armenia case) or with the use of an unmanned aircraft equipped with an advanced 3D camera (Georgia case). With high resolution 3D images, a Digital Terrain Model (DTM) can be designed that allows for quick integration of data, such a combining calculated surface areas or volumes with analytical results from recorded sample depths resulting in, for example, estimated volumes of contaminated soil.

As anybody can extract or add information to the continually developing CSM (i.e. understanding of the situation), this is considered a sustainable approach (illustrated below). For both projects, a dynamic work plan was found to be very useful. Instead of sending field staff to a site with a fixed work plan (e.g. sampling location that have been determined up-front), it is beneficial to allow for ad-hoc deviations. This also entails allowing for delineation of contamination in the field, based on field observations.

Design of a site remediation plan

In order to identify a suitable remediation campaign, it is recommended to review feasible remediation techniques and strategies for each site component or situation, followed by designing three scenario's that each contain a (selection of) feasible approaches.

For example, in the Georgia case, the following three scenarios were conceptually designed:

A. POP pesticides destruction
B. Soil remediation training centre annex experimental station
C. POP pesticides containment

The client and stakeholders can then select the preferred option from these three scenarios by means of Multi Criteria Decision Analysis (MCDA). Each stakeholder can attribute a weight ('points') to all relevant aspects in each scenario, which in the end results in a weighed score that is an average of the stakeholders, hence a democratic decision is taken – crucial for a sustainable remediation approach.

In both projects it was concluded that the aspect of time is very important in deciding which remediation scenario (or approach) would be most effective.
For example, in case not all site remediation funds will be available on the short term (1-2 years), short and mid - long term (2-20 years) risk reduction measures will be needed to temporarily safeguard/contain the situation until funds become available. Hence this requires different measures as compared to a situation in which actual remediation commences directly after issuing the remediation plan.

In any case it is required that in order to reach the remediation objective all risks are contained on the short-term in each of the proposed scenarios.

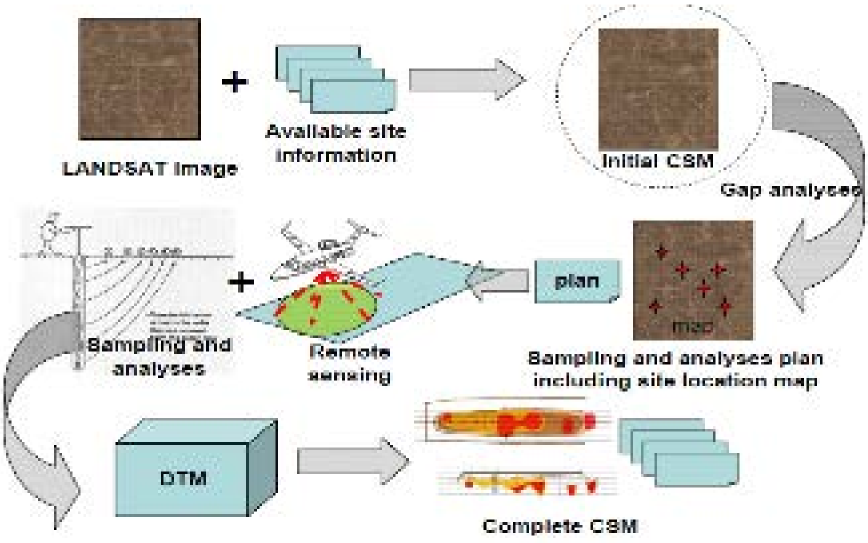

Figure 1. Site assessment logical framework featuring the use of a developing CSM

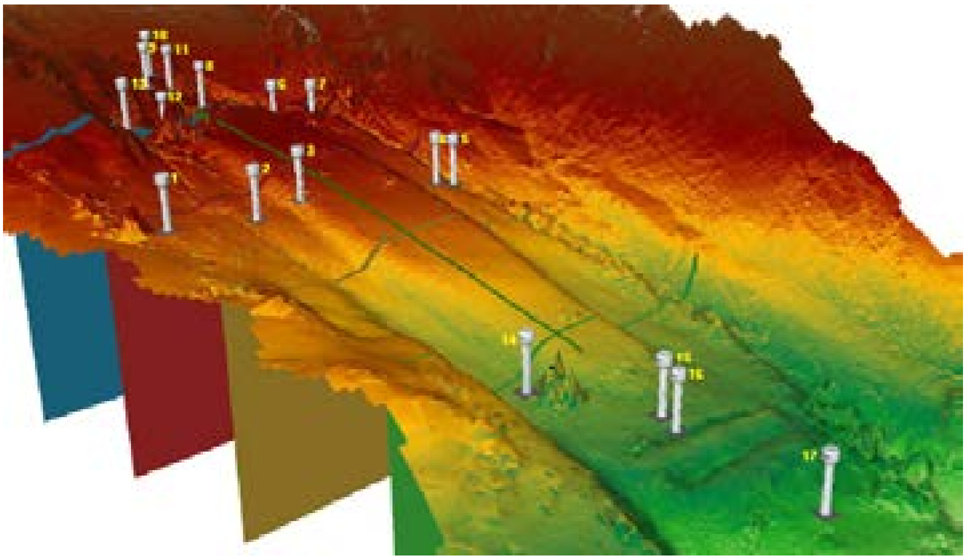

Figure 2. Example of a Digital Terrain Model integrating 3D Imagery with field observation (Armenian Nubarashen case)

Example of a remediation approach (Georgian Iagluja case)

Following the site assessment it was concluded that four categories of contaminated soil/ product exist at the site in quantities as presented in Figure 3.

After review of feasible remediation techniques and strategies, three scenarios were conceptually designed, out of which one preferred option was chosen by means of MCDA.

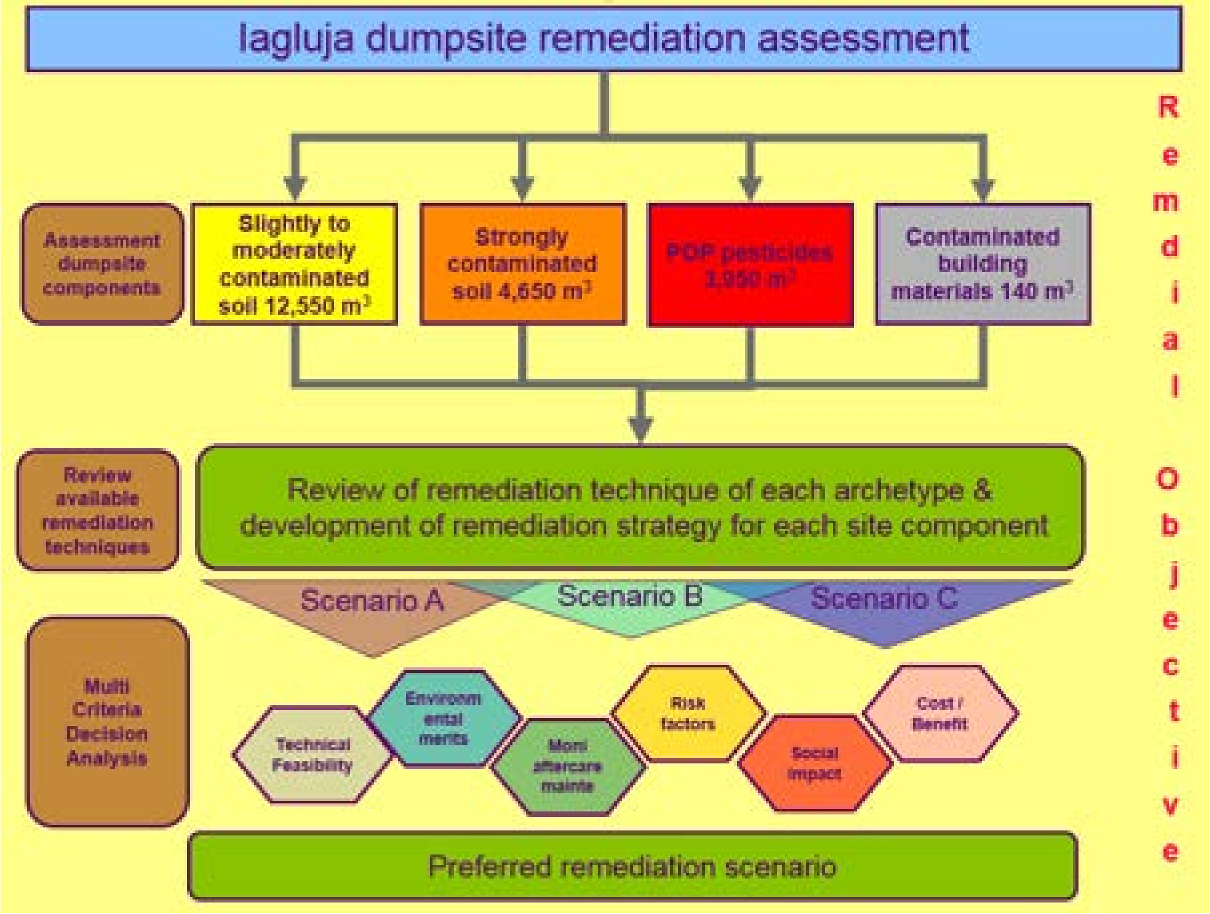

Figure 3. The remediation assessment approach aims at arriving at a sustainable solution, a preferred scenario that is supported by the majority of the stakeholders

In the Georgian project, emergency measures were designed and implemented directly after the site assessment was reported (December 2014).

In the long-term, it is proposed that the Iagluja dumpsite will be transformed into a soil treatment centre annex hazardous waste storage and landfill site. The idea is that parts of slightly to moderately POP pesticides contaminated soil (1,500 – 2,000 m^3) will be remediated with a variety of in-situ and/or on-site, ex-situ soil remediation techniques. The remaining contaminated soil and the soil mixed with POP pesticides and agrochemicals will be excavated, sorted and transferred to a new (to be constructed) on-site landfill. This should ensure a long lasting containment of the contaminants. In this scenario the Iagluja site is also used to build a hazardous waste storage facility to store POP pesticides coming from other parts of the country and for the POP pesticides coming from the Iagluja dumpsite itself. These POP pesticides will be stored temporarily awaiting final destruction. This storage facility can also be used to store hazardous waste coming from other sources.

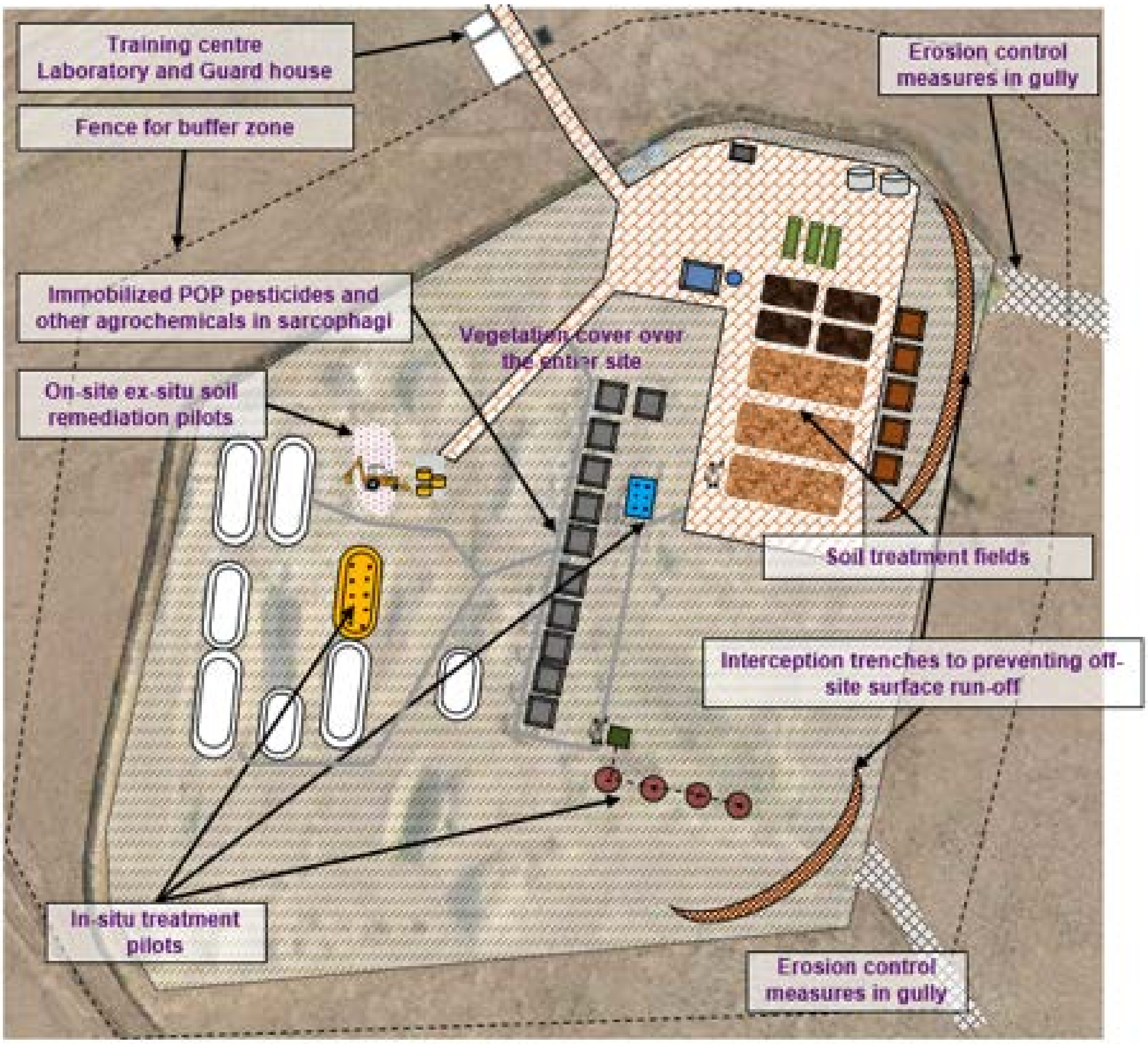

Figure 4. Summarized design of the preferred remediation approach for Iagluja

Acknowledgements

We would like to thank the governmental bodies and local project teams in Armenia and Georgia for their support. The project in Georgia was GEF funded and UNDP executed. The project in Armenia was OSCE funded and executed.

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THE CISMICHIOI LANDFILL: ECOLOGICAL STATUS AND MANAGEMENT

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During the second half of last century Moldova served practically as a large experimental field for use of chemicals in agriculture. Between 1950 and 1990 about 560 thousand tons of pesticides were imported in Moldova.

Due to the lack of an adequate management of pesticides, such as preventing the accumulation of unused stocks, more than 3,000 tons of pesticide wastes have been accumulated over the years in warehouses throughout the country. Others 4,000 tons (according to available documents) of obsolete or prohibited pesticides were collected during the period from 1977 to 1987 and stored in a specially constructed for this purpose landfill in the south the country near the village of Cismichioi [Chishmikioy].

During the last years the Government of Moldova with the support of international organizations removed 2760 tons of pesticide wastes kept in warehouses. These activities continue and it is expected that by the end of 2016 all pesticides from warehouses will be definitively eliminated. After this, as one of the priority issues, along with the contaminated areas, it highlights the OP stocks from the Cismichioi landfill. This site is located on the border with Ukraine and not far from the border with Romania, and thereby represents a cross-border environmental problem.

The official data on the amount of pesticide stored in this landfill are incomplete. In fact this amount could be 4-5 times higher. A study conducted in 2014 within a project financed by the National Ecological Fund, and according to information presented by plant protection specialists, who participated in the construction of the landfill, show that the total volume of 14 bunkers at this landfill is about 26 thousand cubic meters, which indicates a much higher amount of waste, estimated over 16 thousand tons.

In this situation, the initiation of activities on evacuation and destruction of these stocks must be preceded by a feasibility study to determine more accurately the quantities and categories of substances stored, to estimate costs, technical and equipment needs, etc.

Key Words

Persistent organic pollutants (POPs), obsolete pesticides (OP), contaminated sites, risk assessment, remediation, landfill.

MODERN PROJECT MANAGEMENT IN LAND REHABILITATION – APPLICATION OF PRINCE2 METHODOLOGY

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Abstract

Project management is a vital element to the success of projects. In the 1990s it became clear that project management is a profession in itself and different methodologies were developed for professional project management. A well known and widely used methodology nowadays is PRINCE2. It encompasses the high level management, control and organization of a project, but not lower level activities such as scheduling. PRINCE2 is also used to refer to the training and accreditation of authorized practitioners of the methodology who must undertake accredited qualifications to obtain certification.
In this paper a number of merits of PRINCE2 are discussed in land rehabilitation and redevelopment projects, the authors of this paper being PRINCE2 practitioners since 2012. This is done using specific elements of recent projects carried out in the framework of POPs-Pesticides inventory and remediation projects in Viet Nam, Georgia and Armenia. The conclusion is that PRINCE2 offers much room for thought on project setup, organization and budgeting, and a number of lessons to be learned are defined.

Key Words

Project management, PRINCE2, business case, project brief, project plan, exception report.

Materials and methods

PRINCE was named as an acronym for “PRojects IN Controlled Environments”. It was originally developed in UK for IT environments, but was soon applied in other types of project environments. PRINCE2 was released in 1996 as a generic process-driven project management method and has become increasingly popular since. The authors of this paper are authorized PRINCE2 practitioners since 2012. Both the Foundation and Practitioner Examinations are based on the 2009 revision ‘Managing Successful Projects’ manual[1].

As far as we know PRINCE2 is not a much used standard for project management across the United Nations organizations, GEF and World Bank. These organization use project management tools that are to some extent comparable, e.g. the GEF Project cycle with four stages and four related decision points. The Logical Frame used by UN organizations in fact defines the different sub-stages of the Implementation, monitoring and evaluation stage.
PRINCE2 is based on seven principles, seven themes and seven processes (or stages). The seven principles are: Continued business justification, learn from experience, defined roles and responsibilities, manage by stages, manage by exception, focus on products, and tailored to suit the project environment. The seven themes are: business case, organization, quality, plans, risk, change and progress. The principles and themes come into play in the seven processes:

- *Starting-Up a project (SU).* In this process the project team is appointed and a *project brief* is produced. In addition the overall approach to be taken is decided and the next stage (initiation) of the project is planned. Once this work is done, the Project Board is asked to authorize this stage.

- *Initiating a Project (IP).* This process builds on the work of the start-up process, and the project brief is used to prepare other management documents that will be needed during the project. For example, the approach taken to ensure quality throughout the project is agreed. The business case is refined. A plan for the next stage of the project is also created. The resultant information is put before the Project Board for them to authorize the project.

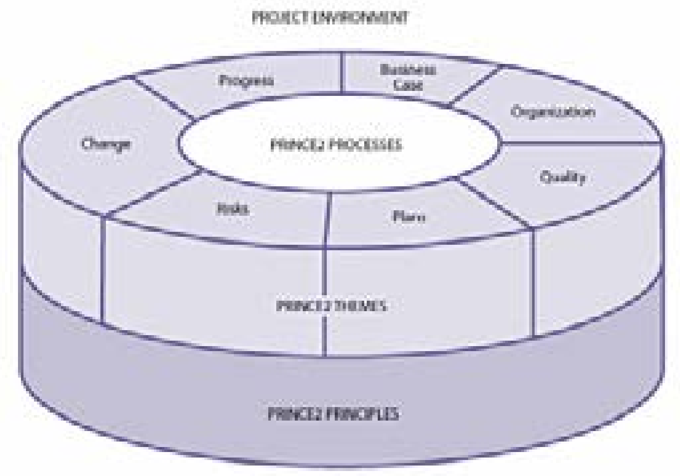

Figure 1. PRINCE2 structure[1]

- *Directing a Project (DP).* This process dictates how the Project Board (which comprises such roles as the Executive, Senior User and Senior Supplier) should control the overall project. As mentioned above, the Project Board must authorize the initiation stage and also authorize the project. Directing a project also dictates how the Project Board should authorize a stage plan, including any exception plan that replaces an existing stage plan due to scope change or other unforeseen circumstances. Also covered is the way in which the Board can give ad hoc direction to a project and the way in which the project should be closed down.

- *Controlling a Stage (CS).* PRINCE2 suggests that projects should be broken down into stages and this process dictates how each individual stage should be controlled. Most fundamentally this includes the way in which *work packages* are authorized and received. It also lays down the method by which certain project issues should be escalated to the Project Board.
- *Managing Stage Boundaries (SB).* Whereas the CS process dictates what should be done within a stage, the SB process dictates what should be done towards the end of a stage. Most obviously, the next stage should be planned and the overall project plan, risk register and business case amended as necessary.
- *Managing Product delivery (MP).* This process has the purpose of controlling the link between the Project Manager and the Team Manager(s) by placing formal requirements on accepting, executing and delivering project work. The objectives of the MP process are to ensure that: work on products allocated to the team is authorized and agreed; Team Manager(s), team members and suppliers are clear as to what is to be produced and what is the expected effort, cost, timescales and quality; the planned products are delivered to expectations and within tolerance; accurate progress information is provided to the Project Manager at an agreed frequency to ensure that expectations are managed.
- *Closing a Project (CP).* This covers the activities that should be carried out at the end of a project. The project should be formally de-commissioned (and resources freed up for allocation to other activities), follow-on actions should be identified and the project itself be formally evaluated. An important follow-on plan is the benefits review plan that indicates when the benefits of the end product may be measured and how, and what resources will be required.

PRINCE2 maintains several management products throughout a project, which may be formal paper documents, word processor files, data in specialized PRINCE2 software, informal notes by managers, or even communi-

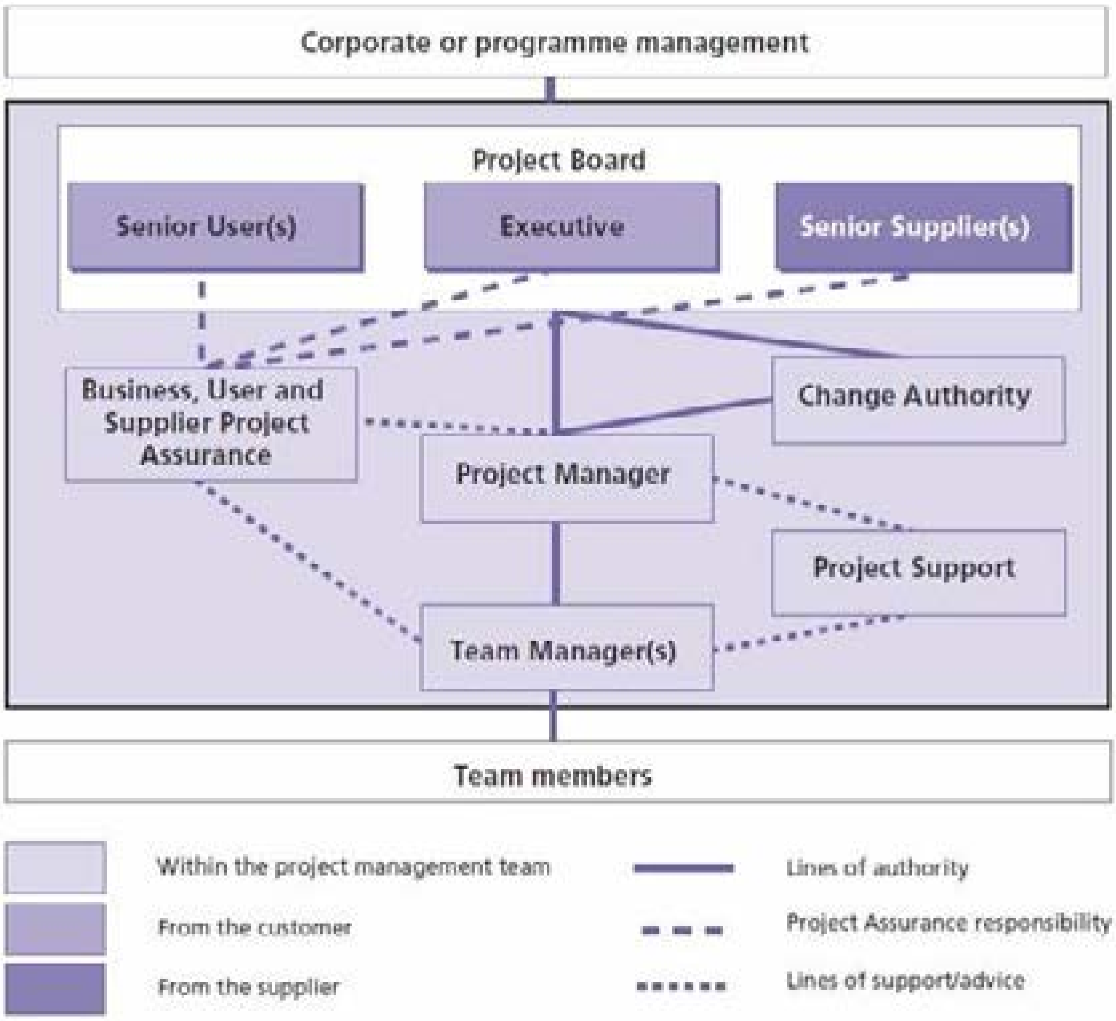

Figure 2. Project management and team structure in PRINCE2[1]

cated orally. The following are examples of the PRINCE2 management products:

- *Project brief.* A short explanation of the need for the project, the management team, the structure and goals.
- *Business case.* The justification for a project also containing the expected costs and benefits. The business case is adjusted at every project stage boundary.
- *Project plan.* A plan describing the most important project products to be delivered, the delivery dates and the costs. An initial Project plan is presented as part of the Project Initiation Documentation (PID). The plan is adjusted in the course of the project and is an important information source for the Project Board to compare planned and real project progress.
- *Benefits review plan.* A plan that describes how and when the business case benefits will be measured.
- *Exception report.* A description and analysis of an identified deviation outside tolerance levels, including impacts and options, and recommendations. Exception reports are normally prepared by the Project Manager for the Project Board, who will after approval order the Project Manager to adjust the Project plan.

Much of the methods above are derived from the mentioned seven principles of which we want to highlight here *Continued business justification.* The business case is the most important document, and is updated at every Stage of the project to ensure that the project is still viable. Early termination can occur if this ceases to be the case. At lower levels, use of time and resources should be justified, such as the need to have (expensive) meetings.

PRINCE2 knows a formal registration, candidates who have passed the PRINCE2 Practitioner exam may call themselves a Registered PRINCE2 Practitioner for 5 years after which they must pass a Re-registration examination every 5 years to maintain their Registered Practitioner status.

Results and discussion

PRINCE2 should not be applied in a dogmatic, bureaucratic form as this would lead to wasted time on paperwork and create false senses of security. The most interesting thing about PRINCE2 in the context of land (remediation and) rehabilitation projects is its conceptual framework and flexible approach allowing for project changes (*scope changes* for that matter) in the course of the project's turn around, as well as the constant check and update of the business case. We will illustrate this with examples from three recent projects in which Tauw was involved as Team Manager/Team in respectively Viet Nam, Armenia and Georgia.

Sustainable management of POP pesticides contaminated sites in Viet Nam

In 2010 the Vietnamese Ministry of Natural Resources and Environment (MONRE) started a country wide action for the elimination of POP pesticides stockpiles and remediation of POP pesticides contaminated sites in Viet Nam. Tauw was involved in the development of technical Guidelines and Standard Operation Procedures (SOPs) for this project. This also involved the development of site specific Environmental Management Plans and related pilots in the Nghe An, Ha Tinh and Thai Nguyen provinces. The Guidelines were completed in April 2015 and cover all five phases of sustainable management of a POP pesticides contaminated site: Preliminary Site Assessment; Site Assessment; Site Remediation Assessment; Site Remediation Management; Site Monitoring and Aftercare[2].

The five different phases can be seen as 'stages' in PRINCE2 terminology. Between the different phases gate controls (*Controlling a Stage/Managing stage boundaries*) have been built in before a new phase can be started. Gate controls are checks if all tasks ('work packages' in PRINCE2) defined in a phase have been completed. In PRINCE2 stages are controlled by the authorization and delivery of the 'work packages'. If one or more work packages have not been finalized, no next stage can be started and if budget or technical problems arise to complete a work package and a stage, escalation means are described to tackle the problem, e.g. the Exception report for presentation to the Project Board (for project products going outside agreed tolerance levels). In PRINCE2 this could even lead to a scope change and adjustment of the Project plan. In this way PRINCE2 provides for a flexible but controlled work plan. To give an example, the cyclic process of completing a CSM (Conceptual Site Model) in the Viet Nam project (see Figure 3) proved difficult to fit in the strict structure of fixed budgets per phase or task ('work package') within a phase. Where a cycle to come to a complete CSM had to be ran several times, budget frictions occurred that were not catered for by the overall project structure. In a PRINCE2 environment these aspects can easily be catered for by Exception reports and Exception plans for presentation and approval by the Project Board.

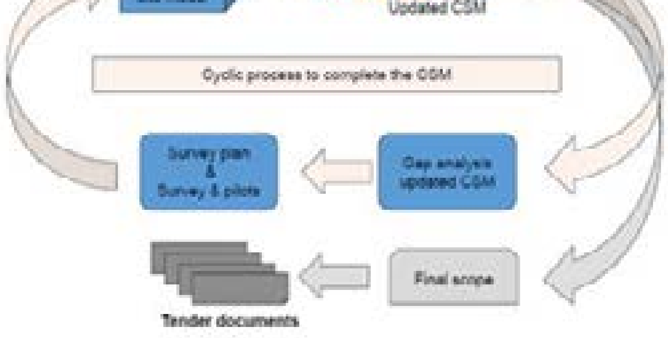

Figure 3. Cyclic process in CSM (Conceptual Site Model) completion

Management of POPs and obsolete pesticides burial site in Nubarashen, Armenia

The Organization for Security and Cooperation in Europe (OSCE) contracted Tauw for the site assessment and remediation feasibility study of the POP and obsolete pesticides burial site (consisting of a number of pits) in Nubarashen in Armenia. In the framework of this project Tauw recommend to repack pure pesticides and strongly contaminated soil in adequate and approved UN repackaging and to store these in a proper intermediate storage facility awaiting final destruction[3]. This project was a follow-up of the FAO emergency capping after the landfill was confronted with high migration risk due to looting.

In this project securing future remediation funding was identified as an issue. It was demonstrated that funding possibilities over time would be largely determining what remediation approaches could be adopted. Five scenarios using previously determined preferred remediation techniques in combination with funding schedule, were distinguished and offered to UNDP for decision making. For all relevant components of the site (slightly contaminated soil, strongly contaminated soil, pure pesticides and contaminated building materials), the possible remediation techniques were reviewed using a Multi Criteria Decision Analysis. For the strongly contaminated soil, the contaminated building materials and the pure pesticides ex-situ destruction was considered the most appropriate option. For the slightly contaminated soil, containment and phyto-remediation were considered the most appropriate techniques.

Five funding schedule options were defined as follows:

- 1. Merely minimal funding is directly available. Only after a significant period of time (more than ten years) the funding for full clean-up is available
- 2. Funding is available over the years in several intervals, until the site has been fully remediated. It is assumed that full remediation is achieved after 20 years
- 3. Within a short timeframe (two years) significant funds are available but not sufficient to fully remediate the site. To complete site remediation a second tranche of funding becomes available after a period of more than ten years
- 4. Delay in the availability of funds of several years after which full funding becomes available
- 5. Funding for the complete site remediation is available within the next two years

Figure 4 illustrates the different schedules for funding set out against the progress of the remediation in five remediation scenarios.

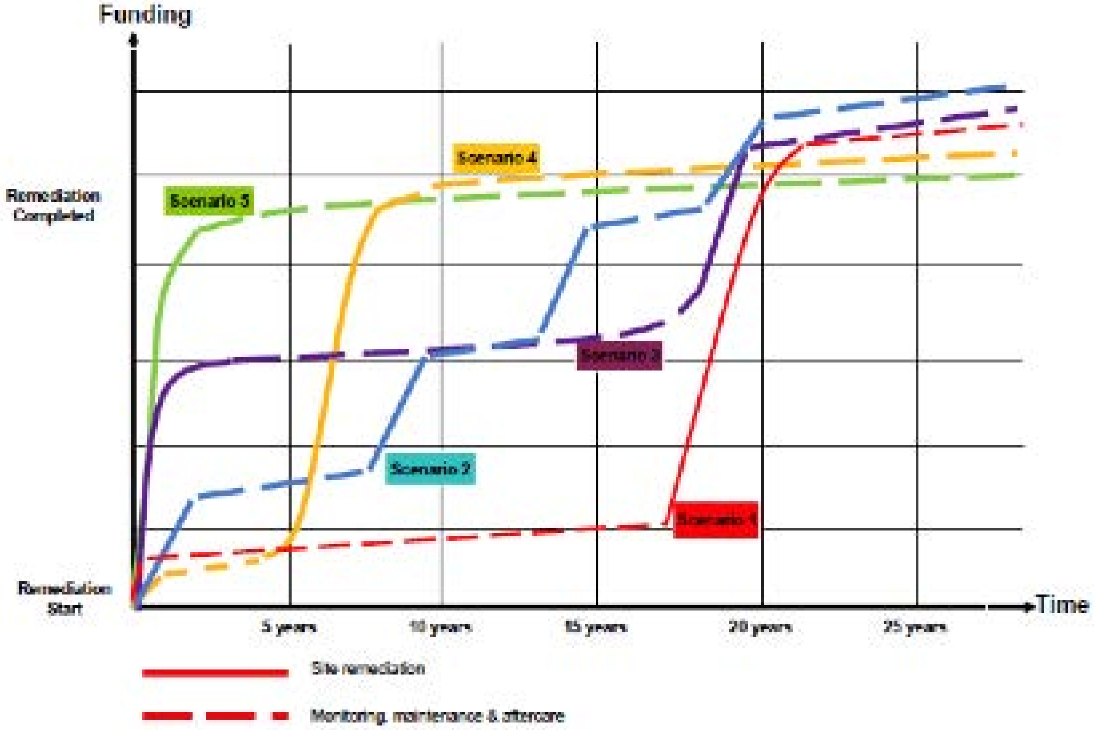

Figure 4. Funding schedule options against remediation progress (Armenia project)[3].

The main conclusion of the scenario review was that the steps required for the final clean-up of the site can be done in accordance with availability of the funding. Even if on the short term only very limited funding is available steps can be made to improve the site and mitigate the current risks. Based on the review it became clear that the technical measures needed for the landfill are quite similar for all scenarios. The timing of the funding will determine when, which steps can be taken. Specifically scenarios 2 and 4 contained nearly all elements of importance and therefore give a good insight into the costs and remediation feasibility:

- *Scenario 2*. The precondition of Scenario 2 is that the funds are available in tranches over the years. In this scenario the pure pesticides and strongly contaminated soil are excavated, re-packaged and stored on-site or off-site in purposely built storage.
  A Centralized Intermediate Collection Centre to be constructed within the larger scope of the implementation of the Stockholm Convention, has preference over storage on-site.

The storage of the re-packaged strongly contaminated soil and pure pesticides allows for secure storage until funds are available for the final destruction of the pure pesticides and the cleaning of the strongly contaminated soil. The slightly contaminated soil is re-distributed in a new landfill site to be constructed on the then empty former site area.
- *Scenario 4.* In Scenario 4 only limited measures are implemented until all funds for the complete site remediation become available. After that the pure pesticides and strongly contaminated soil are excavated, re-packaged and transported to an off-site destruction and soil cleaning facility. The slightly contaminated soil is re-distributed in a new landfill site constructed on the then empty former site area.

In conclusion, the remediation-funding scenarios should be seen as an opportunistic way to get some grip on unsecure funding having a big impact on the overall business case. In remediation and redevelopment projects of this kind, land investigation/inventory data have a short-term validity (few years), mainly because of potential manipulation of the stored pesticides by locals (in spite of stakeholder involvement), and, in this particular case, the progressive erosion of the landfill. This means that when follow-up funding is pending too long, the land investigation has to be updated, requiring additional funds. There are examples of projects elsewhere that have known several cycles of re-investigation over the years without actual remediation. In this way the business case is seriously threatened by inefficiency. This was also demonstrated by Harmsen *et al.*[4] in Mali, Africa.

The Nubarashen Landfill was inventoried in 2013 and funds for project implementation (remediation) have not been released so far. At an early stage of project planning, already in the project brief, projects such as these should try to look far ahead, and enough stages should be defined to come to a closed overall project cycle from preliminary investigation to remediation to monitoring and aftercare. Splitting up projects into investigative and implementation parts may be justified from an organizational point of view, but these should be linked planning and budget-wise, otherwise the business case is seriously at risk and may turn negative on the way. One solution to maintain a positive business case is to look for added value at an early stage (project conception, project brief), e.g. to combine investigation efforts with training and institution building creating local capacity to take the project forward. In this way the focus would not be on the individual problem site, but rather on the issue of POPs and obsolete pesticides at a national scale. In this approach the individual site serves more as pilot, much like the approach adopted in Viet Nam.

Iagluja Dumpsite remediation project in Georgia
As commissioned by UNDP Tauw was involved in one of the first steps to minimize the release of POP pesticides from the large Iagluja Dumpsite (consisting of sarcophagi, pits and trenches), through detailed site assessment and development of a plan for long-term sustainable remediation[5]. The project consisted of the following phases: Phase 1, detailed site assessment and the design of the emergency measures; Phase 2, detailed site remediation plan based on the site assessment; Phase 3, selection of the best location for the construction of a hazardous waste storage facility; Phase 4, stakeholder analysis. The project was closed after all project draft deliverables were presented and discussed in a validation workshop. After the validation workshop and approval by UNDP the project deliverables were finalized.

This project is in a way comparable with the Armenia project when it comes to complete funding from investigation to implementation and aftercare. In PRINCE2 a project is defined as a temporary organization with the aim to deliver one or more products on the basis of an agreed business case forming the justification for the project. Hence PRINCE2 does not require to comprise a full project cycle, it just depends on the agreed business case. However when long-term funding also including the implementation (remediation) stage, is not secured at the start, the particular business case is at risk anyway, specifically post-project when the investigation data get outdated as may be identified in a so-called Post-project-benefits-review. In PRINCE2 these unfavourable developments are seen as valuable learning points for other projects. This positive aspect in the case of the Georgia (and Armenia) project, where funding at once for the entire project cycle is unrealistic (as this may be in the range of EUR 10 Million), is that in the initial budget for investigation also emergency measures were included to halt imminent environmental damage and to control direct human health risks. Given the (inconvenient) reality of piecemeal budgeting, this appears to be a good way forward and keeps the business case valid. But also here, looking for added value during project conception/project brief preparation, is important. This means that upfront fundamental questions need to be answered, such as: What is really needed in this country when it comes to an effective elimination of POPs/obsolete pesticides? In this way and by effectively involving stakeholders much more goodwill and firm public support can be achieved, enhancing the business case.

Based on the described land rehabilitation projects the added value of PRINCE2 and related lessons learned can be summarized as:
- Importance of and continuous link with the business case. PRINCE2 requires an explicit business case description, with well documented benefits against costs over time, that needs to be updated and validated along the way to demonstrate that a project is still viable.
- Clearly defined stages and stage boundary definitions to mark project progress and change.
- Flexible work plan through issue and escalation management.

- Project Board consisting of Executive (this is the client/customer, i.e. UNDP or OSCE in the three project cases), Senior Users (e.g. MONRE in the case of the Viet Nam project), but also a representative of the Senior Supplier(s). This would be Tauw in all three project cases. The PRINCE2 Project Board model whereby also the suppliers are represented, is challenging and the big advantage of this model is that it provides a vehicle for effective escalation and overhead consultation. In this way it would enhance communication at all levels of the project.

Hence PRINCE2 offers room for thought about modern project management in various ways.

Acknowledgements

We would like to thank the governmental bodies and local project teams in Viet Nam, Armenia and Georgia for their support. The projects in Viet Nam and Georgia were GEF funded and UNDP executed. The project in Armenia was OSCE funded and executed.

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TRANSFER OF EXPERIENCES

Landfills: Transfer of experiences from Aragón, Vietnam and EECCA Countries

Part 2: Transfer of experiences from Vietnam

SUSTAINABLE MANAGEMENT OF POP PESTICIDE CONTAMINATED SITES IN VIET NAM

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Abstract

Viet Nam has started a ban on import and use of POP pesticides since 1993. However, lack of appropriate management of existing POP pesticides has led to serious contamination in the country.

In 2009, 1,153 pesticides contaminated sites in Viet Nam were discovered through provincial inventories and increased to 1,562 sites in 2014 inventories, mostly at the center of Viet Nam. Among those, more than 200 sites exceed Viet Nam National Technical Regulation on Remediation Target Values of Persistent Organic Pesticides According to land use (QC 54:2013/BTNMT).[1]

The Project "Building capacity to eliminate POP Pesticides stockpiles in Viet Nam" is funded by Global Environment Fund (GEF), and implemented under the management and coordination of United Nations Development Programme (UNDP) and Food and Agriculture Organization (FAO). Total GEF fund is $4.150.800.[2]

The project has been implemented by Ministry of Natural Resources and Environment (MONRE) in 5 years (2010 - 2015). The main goal is to "remove capacity barriers to the sustainable elimination of POP pesticides in Viet Nam". This project has three components: *1) Improved capacity facilitates the elimination of POP pesticides stockpiles; 2) All known POP pesticide stockpiles destroyed and impacts on human health relieved; 3) Improved chemicals management prevents importation and use of POPpesticides*[2].

Figure 1. Left a pit with buried pesticide and right an old pesticide store

Key Words

POP Pesticides, Viet Nam, GEF fund, Capacity building.

Materials and methods

The main achievements of the project are in line with the assumed project Outcomes formulated in the Logical Framework during the inception mission in 2010. Preliminary and detailed site assessment of Pilot sites are used to adapt the project Logical Framework in the course of the project execution and develop project deliverables.

Results and discussion

Results

After 5 years of implementation, the Project gained significant successes in all three components which are presented below:

Improved capacity facilitates the elimination of POP Pesticide Stockpiles

Technical Guidelines and a set of Standard Operation Procedures (SOPs) for the sustainable management of POP pesticides contaminated sites were developed. The Guidelines cover all five phases of the sustainable management of contaminated sites, which are: 1) Preliminary Site Assessment; 2) Site Assessment, 3) Site Remediation Assessment; 4) Site Remediation Management, 5) Site Monitoring and Aftercare. In the purpose of providing guidance on the sustainable management of contaminated sites, Technical Guidelines were transferred to Department of Natural Resources and Environment (DONRE) in 63 provinces.

The Project supported the development and promulgation of *Viet Nam National Technical Regulation on Remediation Target Values of Persistent Organic Pesticides According to land use (QC 54:2013/BTNMT*). It is the first time "land-use" issue is integrated in a Regulation on remediation target values.

A site database, integrated with monitoring and evaluation indicators, for the sustainable management of POP pesticides contaminated sites was developed. It is an important tool which helps to quickly assess and quantify for instance the status of the site management or the status of site remediation of pesticide contaminated sites. The site database can be accessed via the link: http://caithienmoitruong.vea.gov.vn

Nearly 500 professional staffs of DONREs were trained through 12 courses on "Sustainable management of POP pesticide contaminated sites" and "Sampling and Mapping of pesticides contaminated sites"

The Project, in coordination with local authorities, develops *a provincial strategy/plan on environmental management of pesticide contaminated sites, integrated with land use planning.*

Figure 2. left fieldwork training and right capacity building on site remediation

All known POP pesticide stockpiles destroyed and impacts on human health relieved

More than 900 tons of POP pesticides and highly POP pesticides contaminated soil in 10 sites in Thai Nguyen, Nghe An, Ha Tinh, Nam Dinhand Quang Binh were destroyed.

Figure 3. packaging of POP Pesticide waste

3.480m^2 of contaminated soil was remediated and/or contained in Hon Tro, Mau II (Nghe An) and Thach Luu (Ha Tinh) to remove or contain and control potential risks, and to reduce impacts on the surrounding environment and people.

Figure 4. Left a remediated site, with containment of POP residues in the soil, restricted site-use and, monitoring and aftercare and right preparation of anoxic phase of the soil remediation Pilot to test bio-degradation of POP pesticides in soil using Daramend[3].

Three non-combustion technologies, including Zero-Valent-Nano-Iron (ZVNI), soil washing and bio-degradation with Daramend technologies, has been demonstrated in Hon Tro to remediate POP pesticide contaminated soil. ZVNI and Daramend technologies have showed positive results when POP pesticides levels in soil decreases after testing time. However, soil washing technology, which is successful in lab scale, is not effective under field conditions.

Improved chemicals management prevents importation and use of POP pesticides

More than 500 customs, market inspectors and local staff were trained on risk of POP pesticides in 5 provinces (Thai Nguyen, Hai Duong, Bac Ninh, Hau Giang and Lam Dong).

The Project supported to improve two stores for confiscated pesticides. In addition, a guideline on the improvement of pesticide stores was also developed under the project's scope.

Discussion

After five years, the Project has significant results. In order to gain this success, the Project thanks to supports from related governmental policies, such as a *National Action Plan on treatment and prevention of POP Pesticides* ratified by a Prime Minister Decision No.1946 QĐ –TTg in 2010, and *National Target Program* approved by Viet Nam National Assembly in 2012. These policies allocated state funds which are very important in implementing activities on the sustainable management and remediation of POP pesticide contaminated sites. Moreover, their issuance awakes the awareness of governmental officials, from central to local levels, on POP Pesticide management and remediation.

Although the Project is going to be wrapped up at the end of 2015, its long-term results, such as the handover of soil and groundwater sampling equipment to local authorities, long-term measure applied in contaminated site, the lessons learned from project's remediation activities, 500 professional staff trained, will sustain the project achievement and support the sustainable management and remediation of POP Pesticide Contamination in Viet Nam in the future.

Acknowledgements

We gratefully thank the Global Environment Facility to fund for the project "Building Capacity to Eliminate POP Pesticides Stockpiles in Viet Nam" as well as the supports from United Nations Development Programme (UNDP), Food and Agricultural Organization (FAO) and related stakeholders during the implementation of project.

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THE FIVE PHASES OF SUSTAINABLE MANAGEMENT OF POP PESTICIDE CONTAMINATED SITES IN VIET NAM

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Abstract

Experiences with pilot projects on site assessment, site remediation management, and monitoring and aftercare management were used to prepare Guidelines on sustainable management of POP pesticides contaminated sites in Viet Nam including a set of Standard Operational Procedures (SOPs). The Guidelines facilitate a country wide program to manage in an environmentally sound manner the more than 1,000 POP pesticides contaminated sites. The implementation of the program started with a country wide training introducing the Guidelines and SOPs. This paper explains how the Guidelines and SOPs were designed and implemented.

Key Words

Sustainable management of POP pesticides contaminated site, flexible work plan, environmental risks, Conceptual Site Model.

Introduction

In 2010 the Vietnamese Ministry of Natural Resources and Environment (MONRE) started a country wide action for the elimination of POP pesticides stockpiles and the remediation of POP pesticides contaminated sites in Viet Nam following Decision No. 1946 / 2010 / QD-TTg. To this end, pilot Environmental Management Plans (EMPs) were developed for a selected number of POP pesticides contaminated sites in Nghe An, Ha Tinh and Thai Nguyen provinces. These pilot EMPs were developed using a model that addresses all relevant environmentally sound site management aspects, from Preliminary Site Assessment to the development of a site Remediation Plan, actual remediation and the development of an Aftercare and Monitoring Plan. Based on these pilot EMPs, technical Guidelines and Standard Operation Procedures (SOPs) were prepared for the sustainable management of POP pesticides contaminated sites and the development of site specific EMPs. The Guidelines were completed in April 2015 and cover all five phases of sustainable management of POP pesticides contaminated sites. The Guidelines[1] are divided in the following five Phases/Volumes (see Figure 1):

- Phase 1 Guidelines: The Preliminary Site Assessment
- Phase 2 Guidelines: The Site Assessment
- Phase 3 Guidelines: The Site Remediation Assessment
- Phase 4 Guidelines: The Site Remediation Management
- Phase 5 Guidelines: The Site Monitoring and Aftercare

Organization is such that the Phases 1, 2 and 3 are executed under the responsibility of the Department of Natural Resources and Environment (DONRE). After review and approval of Phases 1, 2 and 3 (as a set) by the MONRE the Phases 4 and 5 are implemented under the responsibility of the DONRE (see Figure 2).

The objectives of the Guidelines

The Guidelines are designed as an easy-reference manual to assist implementing sustainable management of POP pesticides contaminated sites and to develop a site specific EMP. An EMP contains five reports, each describing a site-specific phase of the sustainable site management. An EMP is part of the site specific Environmental Dossier that also includes the required formal documents of the competent authorities as illustrated in Figure 1.

The Guidelines guide the user through the different standardized phases of the sustainable site management allowing:

- Easy verification of the site data
- Easy monitoring of the environmentally sound management processes
- Saving time and money in implementing environmentally sound management
- Easy knowledge transfer, thus facilitating training and capacity building

The Guidelines also propose formats for reporting the gathered data and their interpretation.

The Guidelines have been translated in Vietnamese. The Vietnamese version provides the same content as in the English version but the Vietnamese version groups the five Phases in three Volumes. The Vietnamese version is issued/published by the MONRE (see figure 3).

Organization of the Guidelines

The sustainable site management is a stepwise process from Phase 1 through Phase 5 (see Figure 2). A general introduction is included in all phases and is followed by the introduction of the given phase, constituting Chapter 1. The next chapters in each volume give the technical and methodological instructions. The Guidelines are accompanied by a set of supplementary documents including Standard Operating Procedures (SOPs), providing supporting information for better understanding and execution of the different management phases. Throughout the Guidelines reference is made to these SOPs and supplementary documents. The supplementary documents are listed in the introductory chapter of each Phase.

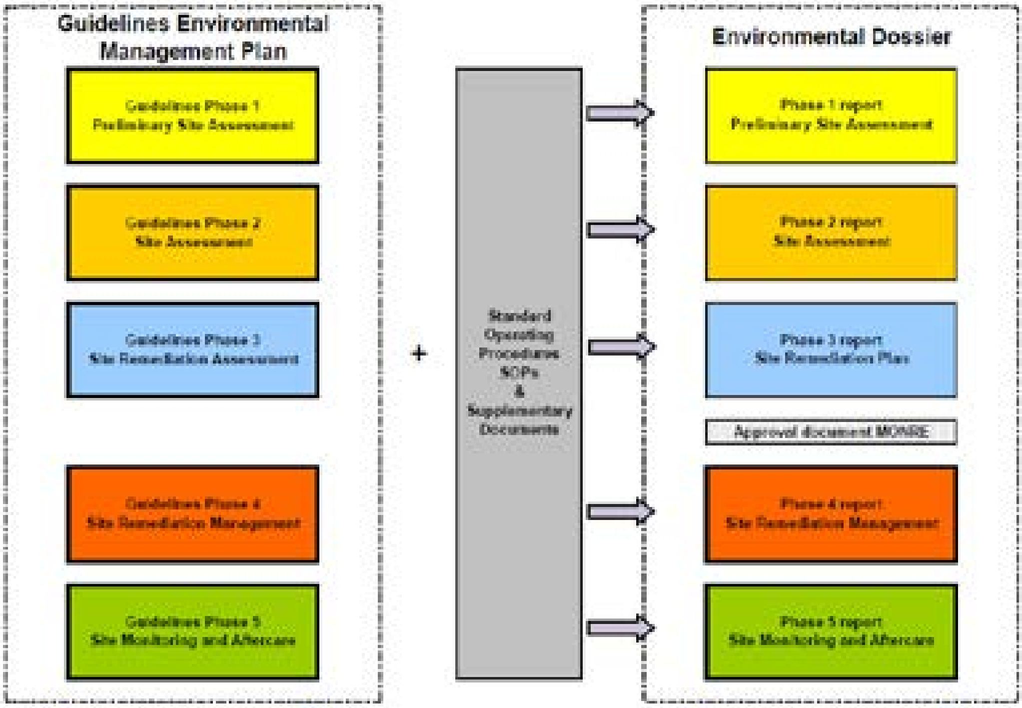
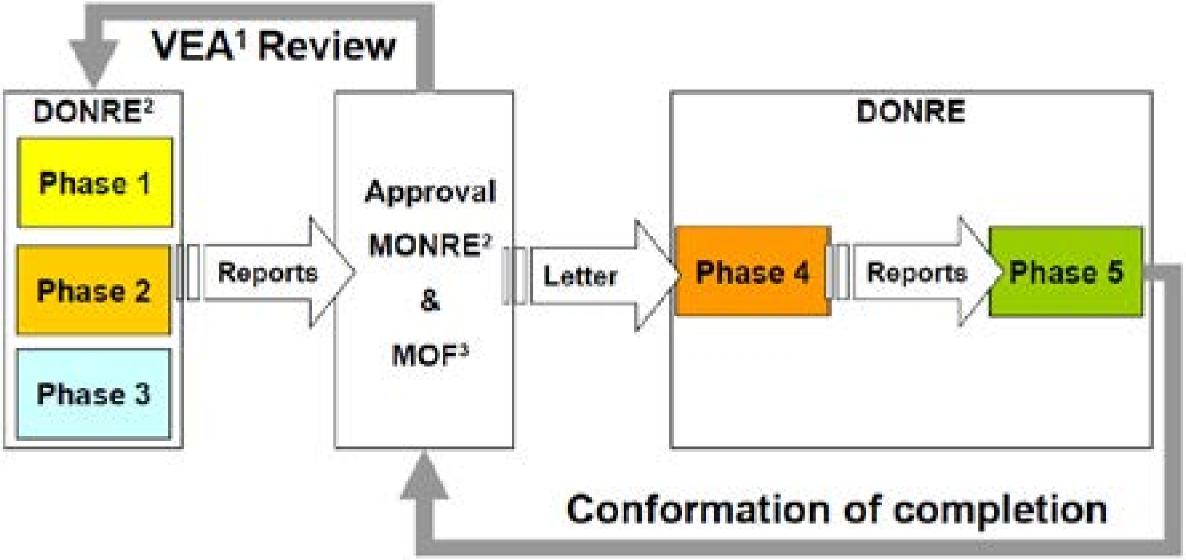


Figure 1. Process for the compilation of a complete site-specific Environmental Dossier



1 Viet Nam Environmental Agency
2 Department of Natural Resources and Environment
3 Ministry of Natural Resources and Environment
3 Ministry of Finance

Figure 2. Responsible partners of the different Phases of the sustainable management of POP pesticides contaminated sites in Viet Nam

The five Phases of sustainable site management

Each of the five Phases has phase-specific tasks and deliverables. Figure 4 presents a flow diagram with the deliverables of each phase.

The Phase 1 (Preliminary Site Assessment) tasks are:

1. Collect information through Desktop Study
2. Visit the Site and collect site data
3. Conduct a Site Reconnaissance Survey
4. Carry out a Swift Site Assessment - Draft an Initial Conceptual Site Model (ICSM)
5. Preliminarily assess the human health risks, the risks for contaminant migration and ecological risks (hereafter referred as environmental risks) to categorize and prioritize the site based on environmental risks
6. Collate all data and report Phase 1

The Preliminary Site Assessment identifies possible source areas, potential receptor pathways and potential receptors of contamination at a site. The factual contamination and exposure levels are not determined during this phase, but are investigated in detail during Phase 2, the Site Assessment.

Figure 3. Vietnamese version of the Guidelines on sustainable management of POP pesticides contaminated sites

The Phase 2 (Site Assessment) tasks are:

1. Carry out a Gap Analysis of the ICSM made in Phase 1
2. Design a Site Investigation Plan to fill the knowledge gaps in the ICSM
3. Carry out Fieldwork in line with the Site Investigation Plan
4. Interpret all (desktop & field) data
5. Refine the ICSM to make an improved / completed Conceptual Site Model (CSM)
6. Carry out Tier 2 Risk Assessment
7. Report Phase 2, the Site Assessment, results

The objectives of the Site Assessment are to establish quantitatively the contamination situation of a site and the associated environment risks. Phase 2 is time consuming and costly and it needs a trained team. At the end of Phase 2, an improved / completed Conceptual Site Model (CSM) and Risk Assessment allow for the drafting of adequate remediation measures or the substantiated discharge of the site from further measures.

The Phase 3 (Remediation Assessment) tasks are:

1. Select the best remedial techniques for the different site components
2. Conceptual design of at least three feasible remediation options
3. Select the best remedial option
4. Present the preliminary design of the best remedial option in a Remediation Plan
5. Obtain approval for the site remediation in Phase 4

The aim of Phase 3 is to give the user a structure to be followed when the Site Assessment, Phase 2, has identified environmental risks. The Remediation Assessment is divided into the Remediation Assessment proper and the design of the Remediation Plan.

The Phase 4 (Site Remediation Management) tasks are:

1. Tendering the remediation project
2. Detailed design of the remediation
3. Remediation of site components
4. Remediation closure and evaluation
5. Reporting the remediation

The aim of Phase 4 is to give the user a structure to follow when the Site Assessment (Phase 2) has identified site environmental risks and the preferred remedial option has been selected and preliminarily designed in Phase 3. Following the description of the selection of the most suitable remediation option, Phase 4 describes all tasks of the Remediation Management of the POP pesticides contaminated site with a focus on health and safety. Figure 5 is an excerpt from the English version of the Guidelines showing the lay-out of a decontamination unit.

The main objectives of the Site Remediation Management are to:

- Remove the direct environmental risks on the short-term
- Reduce and remove the potential environmental risks on the mid-term
- Contain and monitor the latent environmental risks on the long-term

Phase 5 (Site Monitoring and Aftercare) tasks are:

1. Monitoring the effects of the mid and long-term remediation measures on the residual soil, bottom sediment and/or groundwater contamination
2. Aftercare of the mid and long-term risk reduction measures

The objectives of the Monitoring and Aftercare measures are to:

- Sustain and improve the remediation results in the soil, bottom sediment and groundwater
- Make sure that environmental risks remain under control and gradually reduce
- Prove that also the residual contamination is remediated

Results and discussion

To implement the Guidelines and SOPs country wide, several training sessions were held around the country. The training commenced with explaining the significance of a CSM and the cyclic process to update or complete a CSM. About 250 professionals have been trained to carry out assessments, and prepare and implement remediation measures using the Guidelines. Current project initiatives concentrate on pilot remediation, database development and preparation of a review of remediation techniques. The use of a flexible work plan to be able to update and complete a CSM was extensively propagated and discussed.

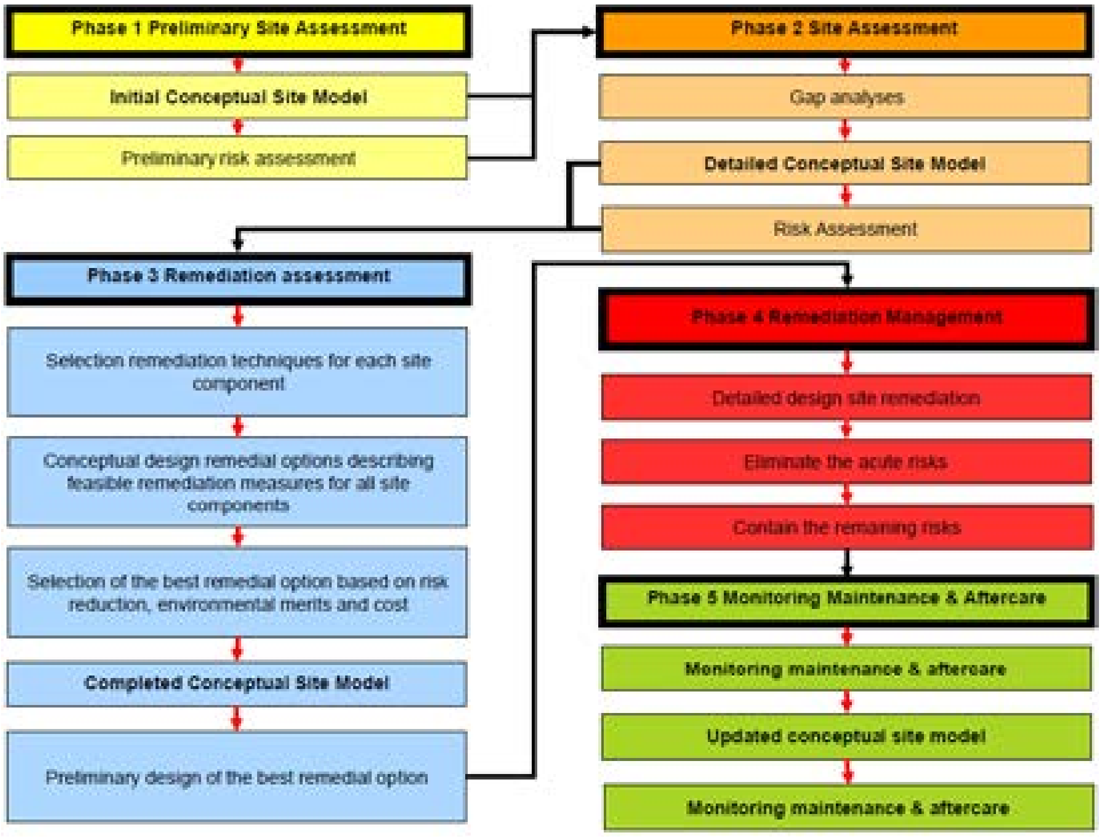


Figure 4. The five Phases of the sustainable management of contaminated sites and the deliverables

A specific bottleneck is that applying a flexible work plan is not a common practice for the competent authorities. This is caused by the practice to tender governmental projects with fixed budget and planning, and the idea that a project is considered successfully completed when all tasks in the contract have been carried out within the available budget and time frame. In case environmental risks remain often new resources have to be employed for mitigation of these risks.

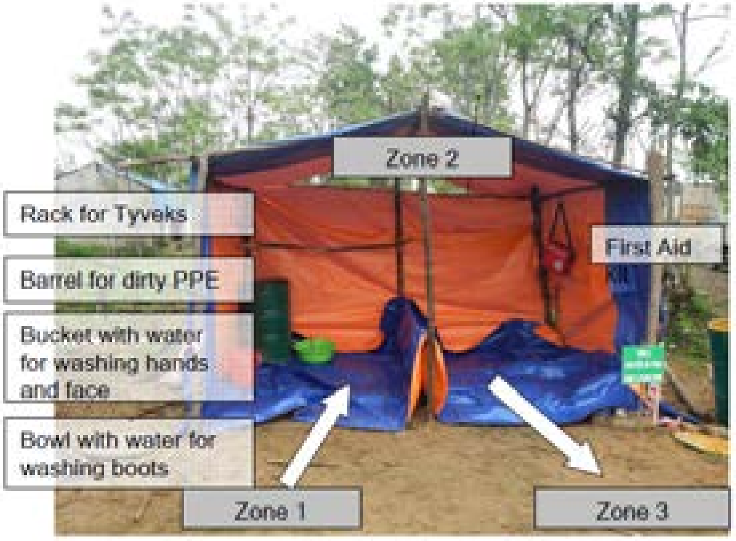


Figure 5 Excerpt from the English version of the Guidelines illustrating the lay-out of a decontamination unit

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These Guidelines were developed in the scope of United Nations Development Program 'Building capacity to eliminate Persistent Organic Pollutants (POPs) pesticides stockpiles in Viet Nam'. This Global Environmental Facility (GEF) funded project is executed by the Project Management Unit (PMU) of the Vietnamese Ministry of Natural Resources and Environment (MONRE). We thank the GEF and UNDP to make this important project possible. We also thank our colleagues from the PMU - MONRE (Mr. Vinh Hoang Thanh Vinh Project Manager, Building Capacity to Eliminate Pop Pesticides Stockpiles in Vietnam; Dao Nhat Dihn Thanh Nguyen Quang as Technical specialist) and Mr. Guido Van de Coterlet, colleague at Tauw, as co-editors of the Guidelines. They provided insight and expertise that greatly assisted the development of the Guidelines.

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1. EMP Guidelines for Sustainable Management of POP pesticides contaminated sites, containing five volumes as follows:

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1.2. Volume 2 EMP Guidelines for Sustainable Management of POP pesticides contaminated sites - *PHASE 2 The Site Assessment*, 30 April 2015. UNDP Viet Nam, Project ID 0060927. Reference R102-1217441BFF-beb-V03-NL

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REMEDIATION TECHNOLOGY DEMONSTRATIONS ON DIOXIN CONTAINATED SITES IN VIETNAM AND THEIR POTENTIAL BROADER APPLICATION TO POPs CONTAMINATED SITES

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Abstract

This paper describes the independent evaluation of a series of remediation technology demonstrations undertaken as part of a Global Environmental Facility (GEF) project in the Republic of Vietnam. These demonstrations are specifically directed to addressing residual dioxin and furan (PCDD/F) site contamination legacies from the handling and use of defoliant herbicides during the period of armed conflict in the 1960s and 1970s. The paper describes demonstration work at a full scale and/or pilot scale level on three non-combustion remediation technologies employing ball milling, enhanced thermal desorption, and bio-chemical techniques. Overall, the results on the MC-D™ ball milling and MCS™ enhanced thermal desorption demonstrate capability to reduce PCDD/F concentrations well below the specified 1,000 ppt TEQ clean-up level from initial concentrations over 70,000 ppt TEQ and offer a high potential to do so on high capacity full scale commercial units for unit costs less than most if not all other available options. The bio-chemical techniques, demonstrated on a laboratory scale showed promise but required additional laboratory and pilot demonstration work. All three technologies are considered suitable for practical application in Vietnam and developing countries generally, inclusive of being amenable to commercial technology transfer and acquisition arrangements. The paper concludes with a discussion of the results of this work in terms of lessons learned and recommendations, including general observation on the practical application of the methods used in this work to site remediation challenges on pending POPs and obsolete pesticide projects based on the author's involvement in their design and implementation planning.

Key Words

Dioxins and furans, Site remediation, POPs pesticides, Ball milling, Thermal Desorption, Bio-chemical treatment, Remediation standards

1.0 Introduction and Background

Vietnam was heavily impacted by the widespread use of defoliant herbicides during the period of armed conflict in the 1960s and 1970s and today still retains one of the world's largest POPs contamination legacies as a consequence[1]. The principle focus of this concern has been on a number of "hot spots" located on several large air fields that were used for storage, handling and delivery of these chemicals (Bien Hoa, Da Nang, and Phu Cat). These sites are now major airports near heavily populated urban areas, and are or are becoming critical infrastructure in a rapidly industrializing developing country. At these locations, this contamination has spread into the broader environment with resulting heath impacts occurring over several generations notably in the form of birth abnormalities and excessive cancer rates. They represent one of the relatively few situations where POPs legacies are having both major acute health impacts, as well as contributing to globally distributed chronic impacts which are more commonly associated with POPs.

These sites have and continue to be the subject of extensive site assessment programs undertaken by national and international investigators[1]. In general they can be characterized as being broadly contaminated by several organic herbicides and derivatives as well other contaminates such as arsenic and heavy metals. However, the primary impacts are associated with the high residual levels of the associated PCDD/F production by-products contaminating the original defoliant herbicides used (primarily 2,4-D and 2,4,5-T mixtures). The most common of these was known as Agent Orange. In total it is estimated that 336,000 m^3 of PCDD/F contaminated soil and sediment above acceptable levels exist on these three sites. PCDD/F Concentrations up to 1,000,000 ppt TEQ have been encountered although this is typically in the range of 10,000 to 30,000 ppt TEQ.

Focused work on this problem dates back to the late 1970s and early1980s principally through national efforts by the Ministry of Defence and the national academic community, along with international assistance principally from the Soviet Union and Eastern European countries. More recently there has been extensive international bi-lateral support for investigation, containment and monitoring of these sites and strengthening of national capacity from a variety of countries, including the United States, Canada, Japan, Germany, and the Czech Republic, as well as the Ford and Gates Foundations and a number of NGOs.

Currently, USAID and the Ministry of Defence have a remediation initiative is underway at Da Nang which will treat approximately 75,000 m^3 of contaminated soil using the TerraTherm In-Pile Thermal Desorption (IPTD) technology. The first phase involving 45,000 m^3 is understood to have been completed. USAID has also initiated planning and EIA work in preparation for future remediation activities at Bien Hoa.

The other major initiative undertaken in recent years has been a GEF project[2] entitled "Environmental Remediation of Dioxin Contaminated Hotspots in Viet Nam" that began preparation in 2009 and has been is implemented between 2011 and early 2015. It has been administered by Office 33 within the Ministry of Natural Resources and Environment under the supervision of UNDP acting as the GEF Implementing Agency. One of its principle objectives has been to provide the Government of Vietnam with guidance on the selection and evaluation of prospective commercial remediation technologies that could be practically applied to these sites. During the preparation and inception phase of the project, this has involved identification and screening of various candidate technologies[3]. Subsequently during implementation, work focused on finalizing clean up and environmental performance standards applicable to such technologies and to undertake demonstrations on prospective candidate technologies on a pilot and full scale level. With respect to the demonstration work, independent evaluations have been undertaken[4,5] and are the basis for what is reported in this paper.

The following reports the results of these demonstration programs undertaken on three selected non-combustion remediation technologies; i) the mecano-chemical dehalogenation (MCD™) ball milling technology proposed by Environmental Decontamination Limited (EDL); ii) an enhanced batch thermal desorption technology named Matrix Constituent Separation (MCS™) proposed by Thermodyne Technologies Inc. (TTI), and iii) several bio-chemical treatment strategies proposed by HPC-Envirotec.

Additionally some more general observation on the practical application of the methods used in this work and results to more general POPs and obsolete pesticide (OP) remediation challenges on pending projects is provided.

2.0 Nature of the Problem

As indicated above three major "hot spots" are the focus of attention with the immediate priority being the Bien Hoa airfield which is the largest, arguably the most contaminated, essentially located adjacent to a rapidly expanding urban area in the greater Ho Chi Minh City region, and is the subject to immediate commercial re-development pressure. Figure 1 illustrates this location and critical areas of interest.

PCCD/F along with other organic and inorganic contamination to a greater and lesser extent is generally encountered over the whole airfield and existing military base, in associated ponds and into the populated offsite residential and agricultural lands adjacent to the airfield boundaries. However, the major hot spots occur in two specific areas: i) Z1 which was the primary area of defoliant herbicide storage, handling and flight operations; and ii) Pacer Ivey which was used as clean up consolidation and removal area during closure operations. The following summaries the general characteristics relevant to planned remediation activities:

Figure 1: Bien Hoa Airfield illustrating areas of high PCDD/F contamination

- The estimated amounts of PCDD/F contaminated soil and pond sediment requiring remediation is 200,000 -220,000 m^3 of soil over 174,000 m^2, 30,000 m^3 of sediment over 73,000 m^2, with the majority of the contamination typically occurring in the first 150 cm but in some cases to a depth of 4.5 m.
- Containment of priority contaminated material has been undertaken in engineered landfill structures (93,000 m^3) including a relatively small quantity of very highly contaminated concentrated spill material from the Z1 area. Additionally, part of the Pacer Ivy area has been subject to temporary containment arrangements.
- The distribution of dioxin contamination concentration level is highly variable across each area of the site, particularly in the Z1 and Pacer Ivey areas with a wide range of concentrations (from low levels to over 1,000,000 ppt), unpredictable variance with depth and concentrations in the extremes from high to low occurring within close proximity (several metres).
- Approximate average concentrations for a number of the key areas are estimated as follows: Z1 contained material – 36,000 ppt TEQ (94,000 m^3), Other Z1 – 2,200 ppt TEQ (5,000 m^3), Pacer Ivy PI2 – 25,650 ppt TEQ (66,000 m^3), Pacer Ivy PI3 – 3,000 ppt TEQ (36,000 m^3), Pond/Lake Sediments – 1,160 ppt TEQ (30,000 m^3) with other areas on or around the airbase containing significant volumes having average concentrations in the range of 1,000 ppt TEQ or less.
- The contaminated surface area is estimated to be expanding at a rate of 0.3 ha per year from the original Z1 and Pacer Ivy hot spots and now extending to and beyond the airfield boundaries.
- In terms of secondary contamination, arsenic contamination in both Z1 and the Pacer Ivy areas up to levels of 273 ppm is observed and other organic contaminants (dioxin like PCBs, chlorophenols, 2,4-D and 2,4,5-T) as well as heavy metals are observed.

3.0 Remediation Technology Evaluation Criteria

Typically, an evaluation of remediation technologies focuses on what is required of the technology in terms of technical and environmental performance as demonstrated which is the primary focus of what is reported below. However, the evaluation should also address at least directionally a number of other factors related to moving it from the scale and conditions of demonstration to a practical full scale commercial application all of which need to be considered in the final decision making. Additionally a cost and policy related considerations also need to be factored in. The following lists and briefly discusses the evaluation criteria used in this work.

a) Technical and Environmental Performance

i) *Clean-up targets for PCDD/F contaminated soil:* In site remediation work, the primary performance criteria is meeting some specified remediation target typically expressed as a maximum allowable residual contaminant concentration as determined by specification of land use specific default action or remediation standard, or alternatively a site specific risk assessment. In Vietnam, two relevant national soil quality/clean-up standards have been established for PCDD/F. The first was specified in a 2009 standard for “hot spots” that set target clean-up standards of 1,000 ppt TEQ for soil based on the prevailing US EPA default soil quality action standard for commercial and industrial land use[6]. It also set 150 ppt TEQ as an action standard for excavation and treatment of sediment in water bodies. A subsequent national general soil quality standard that covers six land uses including industrial/commercial set at 1,200 ppt TEQ, recreation at 600 ppt TEQ, urban land use (residential) 300 ppt TEQ and rural land use (agricultural) at 120 ppt TEQ[7]. As context it should also be noted that the Stockholm Convention specifies the interim low POPs content for PCDD/F at a much higher level of 15,000 ppt TEQ. For purposes of this evaluation work, the 1,000 ppt TEQ is taken as a minimum acceptance level applicable to industrial commercial land use with achievement or potential thereof also being considered important to accommodate higher value land uses, particularly potential residential development.

ii) *Remediation Efficiency (RE):* RE is a complementary parameter to the actual clean-up level achievable and is defined as the % ratio of output and input concentration of a specific contaminant. It is analogous to but not strictly equivalent to the parameter of destruction efficiency (DE) or destruction removal efficiency (DRE) typically applied as a primary acceptance criteria for POPs destruction in prevailing international standards[8,9], noting that RE only accounts for contaminants removed from the media being remediated and does not account for the ultimate destruction or irreversible transformation of the subject contaminant. Further comment on this will be made below in the context of the specific technologies evaluated.

iii) *Environmental Release Performance:* Following from the above, acceptance of a technology will also depend on meeting release and/or emission requirements of both the primary contaminants of interest and any process by-products or fugitive emission that a given process may generate. For this work, the main point source release standards that would apply to PCCD/F remediation technologies are a national standard based on international standards, namely: i) air – 0.1 ng I-TEQ/Nm^3 ;

and ii) water – 10 pg I-TEQ/l[10]. While not necessarily feasible or practical to assess in these demonstrations, other potential process and fugitive emissions such as VOCs, particulate, NO_X, SO_X, CO, and volatile metals might also apply in operational performance testing.

iv) *Treated Soil and Residuals Management Issues:* A key issue for remediation technologies where the process removes contaminants and essentially concentrates them is what further steps need to be taken to destroy or otherwise dispose of them in an environmentally sound manner. This is particularly applicable to residuals in air pollution control (APC) devices such as granulated activated carbon filter material. Likewise, a consideration is also the final disposition or use made of the treated soil which could range from return to its original location, deposition in dedicated containment in recognition of its residual contaminant content, or removal to a further treatment stage that upgrades its properties for some specialized use or in some cases further treatment of a secondary contaminant of concern.

v) *Impact on Secondary Contaminants:* The impact the technology has on other contaminants needs to be considered. Nominally, the technologies being evaluated are intended to deal with organic contaminants and would be expected to also treat secondary organics such as chlorophenols and acid herbicide residuals. However, the presence of arsenic in both organic and inorganic forms complicates this assumption and the impact of a process on the proportion of each is of interest given the difference in toxicity between organic and inorganic forms. Established national soil quality standards predating the GEF project exist for heavy metals including arsenic for various land uses[11].with the main one of interest being total recoverable arsenic which is set at 12 ppm for all land uses.

b) Scale up and Full Scale Application Prospects

i) *Requirement for further scaling-up, demonstration and commercialization:* Technology demonstrations are typically done at best with a less than complete full scale configuration and more commonly on a pilot scale. A key factor in an evaluation is assessing the prospects and risks associated with scaling up that experience to a full scale configuration both in terms of practicality and performance. In this case national experts have set minimum annual capacity levels as 20,000 m^3 per year for a selected technology. As a consequence, it is important to: i) review relevant full scale commercial projects undertaken including lessons learned; ii) determine what is involved the required scale up; iii) potential process performance impacts; and iv) defining "proof of performance" testing requirements to be built into technical, regulatory, and commercial documentation applicable at the start of a full scale operation. Additionally, there may be issues respecting actually commercializing the technology both technically and in terms of having a viable business structure that have to be assessed.

ii) *Pre-processing Requirements and Infrastructure:* All remediation technologies generally require some degree of analytical site assessment and civil works at the front end of application of the specific technology. Firstly, this involves confirmatory site assessment work followed by excavation and transport to the actual site of technology application, although this is generally assumed to be in close proximity to the site of interest in this case. However, different technologies will require varying degrees of soil preparation prior to treatment. Specific to this site, the soil involved is highly disturbed and inhomogeneous in terms of physical characteristics and contaminate concentration. Preliminary processing steps involving the removal of foreign material, size reduction, and mixing to enhance homogeneity and uniformity.

iii) *Operational Applicability Factors:* As critical issue in assessing the applicability and practicality of a specific technology generally and particularly in a developing country is the feasibility of placing it and operating on a site in that country. This covers an assessment of need for supporting infrastructure, transportability, access, availability of process and operating consumables; energy requirements and its reliable supply; availability of suitable labour and technical support; training requirements, and demobilization/post project requirements.

iv) *Performance Validation and Monitoring Requirements:* Recognizing the large volumes of material to be processed as well as the fact that all required environmental performance issues cannot readily be demonstrated in advance, there is the need to assess the feasibility of a full scale performance testing step prior to initiating full scale production remediation operations. Likewise, there needs to be provision for validating ongoing technical performance (i.e. achieving soil quality specified) and ensuring that point source and ambient air and water quality standards are maintained.

c) Commercial Factors

i) *Indicative Unit, Capital and Operating Costs:* The evaluation of any remediation or destruction technology needs to include an assessment of indicative cost. This will typically be expressed in unit cost per m^3 or ton which to the maximum degree possible should internalize all input costs and ideally be reflective of what might be offered on a competitive basis against a well define specification for turn key provision of services. However, it is also useful to document indicative capital and operating costs to the degree practical, particularly if there are national expectations related to acquisition and/or transfer of technology.

ii) *Commercial Availability and Preference:* As suggested above not all technologies that may be considered are in fact available on a fully commercial basis in the context of being able to be presented as viable commercial competitive proposal. This should be assessed and considered in the evaluation process. Similarly, there will also potentially be external preferences that while not necessarily influencing an objective evaluation need to be understood. One that is relevant in Vietnam in particular is the inevitable relationship between technology selection and donor countries that may provide the principle financing for the main remediation effort.

iii) *Technology Acquisition/Transfer Potential:* A final but very important consideration in Vietnam is a very strong national interest in including provision for the acquisition and transfer of remediation technology for use in the country by a national operator. Recognizing the long term needs for remediation in the country this is a very reasonable expectation. As a result, the evaluation considers the technology vendor's position on this.

4.0 Technology Descriptions

a) <u>EDL MCD™ Ball Milling:</u> MCD™ is a tribology based technology, involving a mecano-chemical de-halogenation process where steel balls collide with the contaminated soil particles at high speeds in a rotating ball mill reactor. Highly reactive new free molecular surfaces are generated, a highly localized triboplasma is created giving energy for chemical reactions, and free radicals are created which can then go on to react with neighbouring compounds. In the case of contaminant compounds containing chlorine, when a physical energy greater than a specific strength of the chemical bond involved is exerted, the process will be chemically activated resulting in chlorine and carbon being separated to provide a de-chlorination reaction. The MCD™ configuration of this process is involves continuous feeding of dry soil with the principle process variables being feed rate, residence time, ball numbers and weight, and rotational speed.

A full scale commercial configuration of the technology typically has 4 or 5 reactors in a process train operating in series with additional trains either operating in parallel or, if longer residence times are required, again in series. A single full scale train can nominally process up to 8 tons /hour with proportional incremental capacity obtained by adding parallel trains. Various additives can be used to enhance collision efficiency and de-chlorination reactions. It is classed as closed non-combustion process technology with both capability for soil remediation and chlorinated chemical destruction such as required under Article 6 of the Stockholm Convention for POPs. It also has internalized capability to recycle captured contaminated organic dryer air pollution control (APC) residuals and other fugitive emissions products for destruction.

Generally, the technology is considered commercial and relatively mature with a significant R&D effort supporting it and an expanding commercial experience base. It is proprietary but available under licensing and joint venture operating arrangements. However, it's ultimate potential in terms of the materials and contaminants that it can address and optimization of performance and operating conditions remains subject of ongoing development. Application experience covers relatively small commercial niche applications and demonstration projects covering soil contaminated by PCDD/F, PCBs, DDT, HCH, other pesticides and chemical contaminates, and speciality waste streams such as fly ash, granulated carbon filter material and asbestos.

It is a transportable ex-situ technology that requires excavated and bulk packaged material to be bought to a plant set up for purposes of its treatment, normally on or adjacent to the site under remediation. Preparation requirements as a minimum would involve screening/size reduction and drying with a recommended homogenization step to ensure relatively even distribution of contaminant concentration. The technology is transportable and suitable to establishment on site subject to availability and/or construction of basic infrastructure (access, cover, utilities etc.).

Figure 2: MCD™ process reactors in pilot and full scale configurations (courtesy of EDL)

b) <u>TTL MCS™ Enhanced Thermal Desorption:</u> The MCS™ technology is described as transportable, modular, batch thermal treatment system that accomplishes desorption of organic compounds and volatile inorganics from a solid or semi-solid matrix utilizing the combination of infrared heating and convective/conductive heat transfer, with an enhanced air stripping effect under vacuum conditions that provide boiling point reduction and increased chemical volatilization. Its operating components consist of: i) a two box tray thermal treatment chamber (capacity of 5 ton); ii) infrared radiant heat source; iii) dry particulate filtration; iv) condensing/closed loop cooling water system; v) coalescing filtration and air impingement system; vi) condensate treatment system; vii) vacuum extraction fan; and viii) APC systems. The APC system operates by the carrier gas passing through a series of particulate filtration, condensation system, coalescing filtration, air impingement systems and vapour and condensate activated carbon units prior to final discharge to the atmosphere or condensate water collection. Operationally, it involves: i) soils being mechanically conveyed directly from the material handling and agglomeration stage into pre-staged treatment trays; ii) loading of the treatment trays into the thermal chamber with an infrared heater base; iii) lowering/sealing of the extraction hood/ air exhaust manifold assembly onto the treatment trays; iv) and operation of the extraction fan to move air through the matrix as the target chemicals are heated to their reduced boiling point and/or significant vapour pressure and stripped from the matrix. After the matrix is treated to the pre-determined temperature, the burners are shut off and the manifold assembly is lifted off of the heater base and the treatment trays are removed from the unit. The normal batch change out timeframe is less than 10 minutes with pre-loaded trays staged for insertion and treated trays stored for a cool down period.

The technology is considered fully commercial and proprietary but available under licensing and joint venture operating arrangements. The nature of the current demonstration is not considered commercial given the small size of the test sample but the scale of the actual process equipment used including the APC system is that of a single commercial full size unit and with all associated operational infrastructure except the input soil preparation (agglomeration) equipment and materials handling infrastructure. It involved a full 5-ton batch process unit with associated air pollution control (APC) system and effectively represents one module of an incrementally developed commercial system. An eight unit configuration is estimated to provide on average 50,000 ton/year of soil remediation capacity with variations above and below this depending on operating period assumptions and site conditions.

MCS™ is considered a relatively mature technology with the basic thermal desorption principle being widely applied for many years. It deviates from most such units in that it is a batch process, involves indirect heating and has the ability to accelerate removal by use of forced air and vacuum extraction to enhance stripping of volatile contaminants from the matrix. Its application experience to large scale PCDD/F contaminated sites involves treating 24,000 tons of coral soils having contaminates of the same origin as those being addressed in Vietnam to soil quality levels less than 1,000 ppt. Likewise it has had commercial application in a number of countries for a variety of complex organic chemicals including PCBs, PAHs, hydrocarbons and volatile heavy metals such as mercury.

The technology is an ex-situ technology that requires excavated and bulk packaged material to be bought to a plant set up for purposes of its treatment. It is transportable and suitable for onsite application subject to availability and/or construction of basic infrastructure (access, cover, utilities etc.). It is nominally classed as a non-combustion remediation technology given that does not involve temperatures that result in oxidation. However, viewed in terms of chlorinated chemical destruction such as required under Article 6 of the Stockholm Convention it would not be destruction technology but rather a pre-treatment technology that captures and concentrates the POPs for onward destruction by another true destruction technology, hence involves following destruction stage for the concentrated contaminates.

Figure 3: MCS^{TM} Unit used for pilot testing (Courtesy of TTI)

c) <u>HPC Envirotec Bio-Chemical Techniques:</u> The techniques demonstrated by HPC Envirotec involved a series of five bio-chemical soil treatment strategies applied as laboratory scaled experimental treatability screening tests. Two of the test runs involved reductive based treatment strategies utilizing Zero Valent Iron (ZVI) with nutrient or electron donor additives. Two were oxidative based treatment strategies involving persulfate additions (including one supplemented by an electron donor addition), and one biological treatment involving proprietary additives marketed by HPC Envirotec.

The nature of the demonstration was essentially laboratory rather than pilot scale although generically bio-chemical treatment techniques are widely used commercially in site specific applications by HPC and others using similar customized treatment strategies. As a generic technique it would be considered non-proprietary with the types of additives used being generally available and described in the open literature on soil and in-situ ground water treatment, although chemical and microbiological additives (bacteria consortium, etc.) are considered proprietary. Direct application to PCDD/F contaminated soils appears limited and in general these types of strategies and techniques are site specific and involve soil specific experimentation and piloting as preparatory steps to full scale project design and cost determination.

HPC Envirotec suggests that this technique can be applied as an in-situ technique where surficial contamination can be managed with conventional tilling and additional operations using conventional agricultural equipment without excavation. It also would potentially be applied ex-situ in contained custom designed cells or using a land farming approach applied to excavated material. Generally, in a field application the time requirements are open-ended and variable from site to site but would likely be measured in a number of months if not longer. Capacity is large but practically limited by the land base available.

Figure 4: HPC Envirotec bio-chemical laboratory treatability testing (Courtesy of HPC)

5.0 Technology Demonstration Design

The demonstrations undertaken involved two separate but linked initiatives as described in the following.

a) MCD^{TM} Full scale Demonstration at Bien Hoa(2012): The first demonstration initiative was undertaken under a contractual arrangement between EDL and UNDP involving funding from the GEF, the government of New Zealand, EDL, and the Ministry of Defence and involved a basic full scale unit being set up for operation on the Bien Hoa air base site. Overall cost excluding local in-kind contributions was approximately US$1.2 million.

The overall scope of the demonstration is summarized in the above referenced independent evaluation report[4]. It involved the processing of 100 tons of soil excavated from several locations on the Bien Hoa airbase site in a basic 4-reactor MCD ball mill train equipped (Figure 2) with a dryer and basic pre-process air pollution control system. This basic system was transported in five containers and set up in a vacant aircraft maintenance building supplied for the purpose.

The test soil was excavated from several locations on the Bien Hoa site and nominally targeted three ranges of contamination concentration: >10,000 ppt TEQ, 2,000 -10,000 ppt TEQ), and <2,000 ppt TEQ. The contaminated soil assumed to be in these ranges based on past site assessment data and limited screening was excavated and processed directly in 42 test runs over a 72 day period across in 2 to 6 ton lots per run. These involved various operating conditions. A target remediation level of <1,000 ppt and a reference remediation efficiency (RE) of 99% was nominally applied. Sampling and analysis covered characterization of the excavated soil, in-feed and out-feed soil analysis for PCDD/F (complete congener profile) and selected expanded analysis for chlorophenols (2-Chlorophenol, 2,4-Dichlorophenol, 2,6-Dichlorophenol, 2,4,6-Trichlorophenol, 2,3,4,6 –Tetrachlorophenol, Pentachlorophenol), EOX, TOC, arsenic (total recoverable, inorganic, organic) and heavy metals (Cd, Cu, Pb, Hg, Zn, Ni), all undertaken by an internationally accredited laboratory in Canada. Additionally some APC device, fugitive environmental release, and ambient workplace air quality analysis was undertaken. The demonstration product also included preparation of a design and indicative commercial proposal for a fully configured commercial facility inclusive of required support and emission control infrastructure inclusive of costs capable of providing the specified 20,000/m^3 per year capacity.

b) Pilot Scale Demonstrations on Three Technologies (2014-15): These technology demonstrations had their origins with the above initial large scale technology demonstration work above and specifically discussions on the EDL MCD^{TM} technology's operating conditions and capabilities being optimized for related to treating higher PCDD/F concentrations using a single reactor pilot unit operated for that purpose. This was concept was extended by UNDP/Office 33 to include two competitively selected proposals from TTL and HPC-Envirotec for similar pilot demonstrations.

Recognizing the lessons learned respecting inhomogeneity and predictability of as-excavated soil observed in the initial demonstration work with resulting impacts on the reliability of demonstration results, the pilot program used an approach of manufacturing and pre-screening a number of 20 l. soil lots such that these would reliably fall into the three target ranges of PCDD/F concentrations (low- 10,000-15,000 ppt TEQ, medium –approximately 30,000 ppt TEQ and high approximately 70,000 ppt TEQ). This was done by blending very high concentration material (540,000-580,000 ppt TEQ) from a segregated stock pile in the Z1 area with other low concentration material from the Pacer Ivy area at Bien Hoa to produce homogenized test sample lots samples. Six 20 kg lots of the low concentration material, four 20 kg lots of medium concentration material and two 20 kg lot of high concentration material were assembled and distributed to the three technology partners as required. A baseline analysis along with the input and output sample analysis was undertaken by an accredited international laboratory in New Zealand covering the same scope as for the 2012 demonstrations plus dioxin like PCBs, original acid herbicides (2,4,D and 2,4,5T), and more detailed speciation of organic and inorganic arsenic.

i) EDL MCD^{TM} Pilot Scale Demonstration: EDL's MCD^{TM} pilot was undertaken at a licensee's facility in South Africa (Envirosafe Waste Management) operating a single ball mill reactor of full commercial size (Figure 2). Based on the results of the 2012 full scale demonstration, the focus was on verifying previous results on the medium range material (30,000 ppt TEQ) material and demonstrating capability with increased energy input and residence time on the high concentration (70,000 ppt TEQ) material with three 1 hour test runs on each concentration with variations in operating conditions (RPM, ball weight, additives) and output sampling at 15 minute intervals to assess the progressive levels of organic destruction with residence time as summarized in Table 2.

Run No	Soil Sample Label	Soil Sample Wt. (kg)	PCDD/F Conc. Level (ppt TEQ)	Reactor Ball Wt. (kg)	RPM	Reagent	Quartz	Sampling Interval (minutes)
1	0314VN	6	28,500	120	450	No	No	15/30/45/60
2	0314VN	6	28,500	120	450	Yes*	No	15/30/45/60
3	0314VN	6	28,500	120	450	No	Yes	15/30/45/60
4	0714VN	6	71,700	120	350	No	No	15/30/45/60
5	0714VN	6	71,700	120	450	No	Yes	15/30/45/60
6	0714VN	6	71,700	120	450	No	No	15/30/45/60

Table 2: EDL - Pilot Test Conditions
**38g Bentonite, 25 g TiO_2*

ii) <u>TTL MCS™ Pilot Scale Demonstration:</u> TTL's MCS™ demonstration was undertaken at a licensee's facility in Scotland (Cape Environmental) with an initial set of 3 low concentration test runs in January 2015 and a second set of 4 test runs on medium and high concentration material in August 2015. In all cases two trays (labelled Tray A and B) were used and a 5 kg soil sample with the tray labels were prepared in agglomerated form was centrally placed in the respective process trays, the remainder of which was filled with an inert material intended to simulate the soil agglomerate in a fully loaded tray. For the low concentration test runs, material labelled Sample A and B were taken from a common soil sample while for the medium and high concentration material the first and second test runs had the medium concentration sample in Tray A and the high concentration material in Tray B, while a common sample was used for separate medium and high concentration test runs in the third and fourth runs. Table 3 below summaries the conditions for each test run along with the treatment and cool down times, and maximum temperature.

iii) <u>HPC Envirotec Laboratory Scale Treatability Demonstration:</u> This demonstration involved a series of six experimental laboratory treatability screening tests using standard controlled environment test boxes and 14 l. stainless steel trays.

Test #	Soil Sample Label	Input PCDD/F Conc. ppt TEQ	Tray Configuration	Thermal Treatment Time (Hours)	Maximum Temperature (°C)	Cool Down Period
Low Concentration Test Program - January 2015						
Trial Test #1	0314VN4.1	12,000	Sample A & B	4.25	560	Overnight
Trial Test #2	0314VN4.2	14,800	Sample A & B	4	560	Overnight
Trail Test #3	0314VN4.3	10,600	Sample A & B	5.5	>560	Late Evening
Medium and High Concentration Test Program – August 2015						
Trial Test #1	0515VN02	. 47,300	Sample A – Med. Conc.	5	675	2.5 hours
	0515VN01	130,000	Sample B – High Conc.			
Trial Test #2	0515VN02	47,300	Sample A – Med. Conc.	5.5	675	3.5 hours
	0515VN01	130,000	Sample B – High Conc.			
Trial Test #3	0515VN02	. 47,300	Sample A – Med. Conc.	5.5	626	3 hours
	0515VN02	47,300	Sample B – Med. Conc.			
Trial Test #4	0515VN01	130,000	Sample A – High. Conc.	6.25	661	2.5 hours
	0515VN01	130,000	Sample B – High Conc.			

Table 3: TTI - Pilot Test Conditions

Generally the experiments involved regular wetting as required to replicate conditions in Vietnam, subject agent additions, raking, and measurement of pH and oxidation reduction potential (ORP) or redox potential as appropriate. The test soil samples used were limited the low concentration (<15,000 ppt TEQ) category ranging from 11,200 to 15,000 ppt TEQ which upon mixing into a common sample was assumed to have an average concentration of 13,330 ppt TEQ. The work was done in two stages, the first extending over a 3 month at which time analysis was done and then extended for an additional 3 months for the three most prospective treatments. A summary of the tests and their duration is listed below.

- Sample/Test MP-2-1: Original soil mixture plus ZVI*: Zero Valent Iron with water and addition of Nutriments (lactates) to optimize wetting and electron transfer - 6 months
- Sample/Test MP-2-2: Original soil mixture plus Persulfate and neutralization to destroy persulfate (otherwise no biological reaction is possible) – 6 months
- Sample/Test MP-2-3: Original soil mixture, no further addition but storage under the same conditions as samples MP-2-1 and MP-2-5 (i.e. temperature, moisture, handling etc.) – 3 months
- Sample/Test MPD-2-4: Original soil mixture plus ZVI: Zero Valent Iron with water and addition of Electron donators (Rape Seed oil emulsion & additives) – 3 months
- Sample MPD-2-5: Original soil mixture and addition of proprietary agents for microbiological degradation – 6 months
- Sample MPD-2-6: Original soil mixture plus Persulfate and addition of electron donators (Rape Seed oil emulsion & additives) with neutralization to destroy persulfate (otherwise no biological reaction is possible) – 3 months

6.0 Remediation Technology Demonstration Results

The following summaries the results of the one full scale demonstration and three pilot scale demonstrations with technology/demonstration specific observations and conclusions.

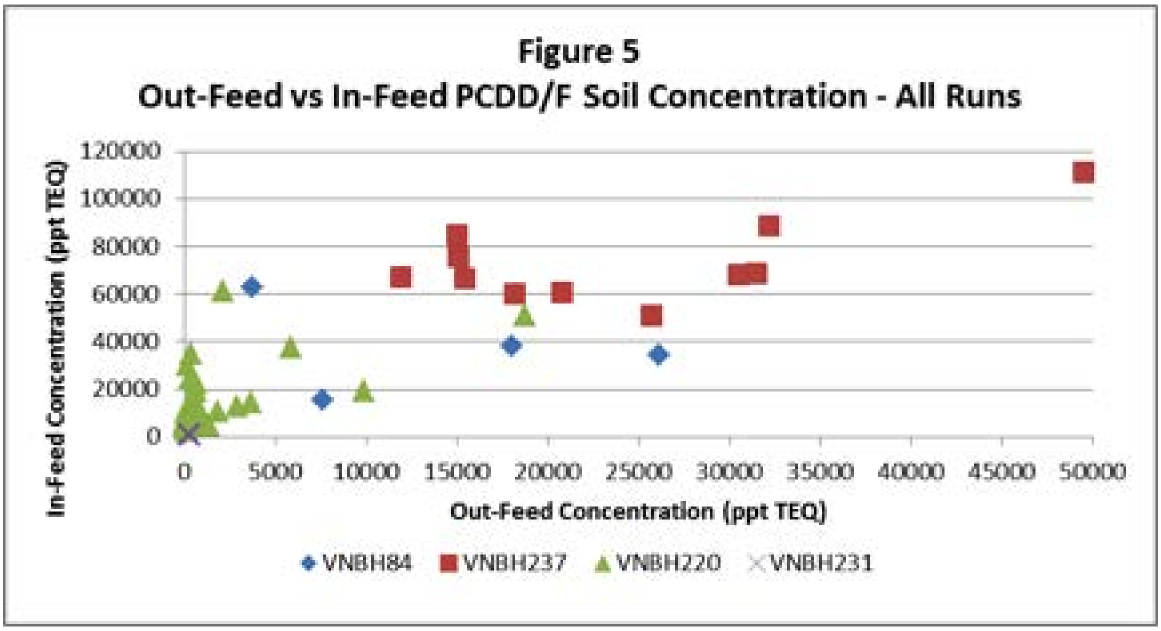
α) MCD^{TM} Full scale Demonstration at Bien Hoa (2012): The results for these test runs are briefly summarized as follows, noting that the detailed results are documented in the above referenced evaluation report[4]

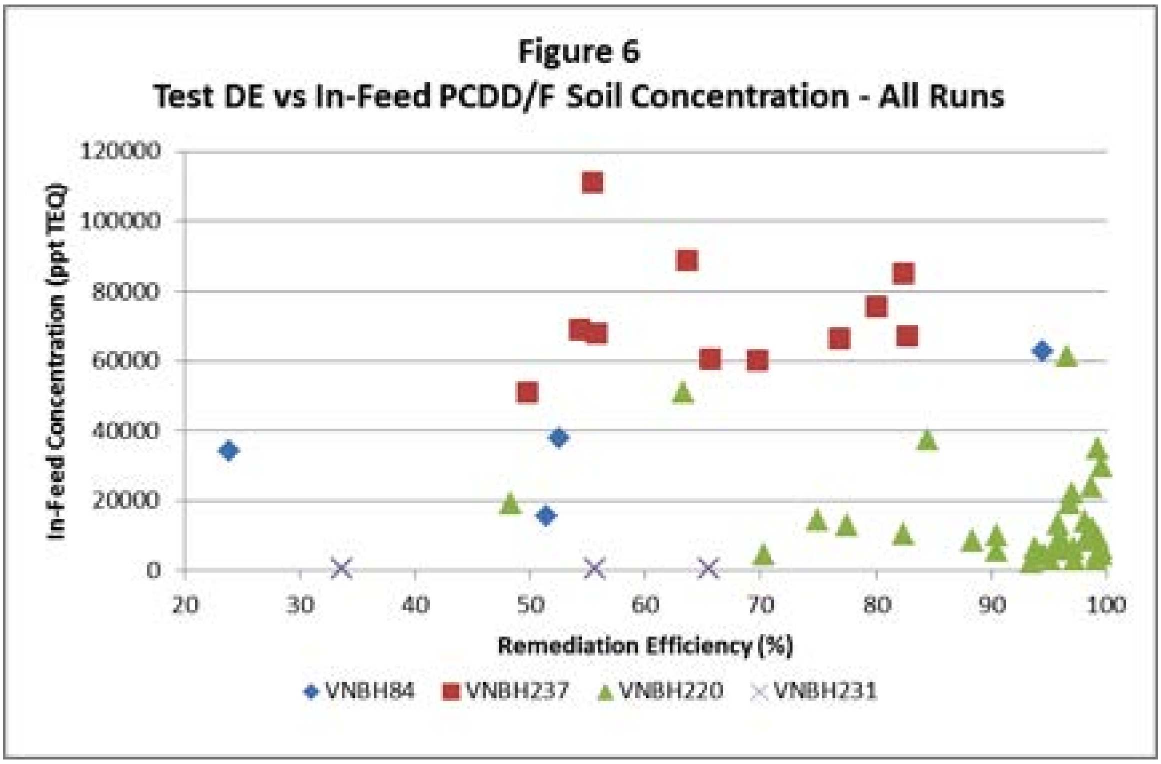
i) General Observations

- Due coordination issues related to excavation of samples and contracting of analysis, early test runs were undertaken without the benefit of accurate baseline input information needed to set process parameters.
- The above, combined with the fact that there was substantial variation between predicted and actual in-feed concentrations for the individual runs limited the value of early test results.
- It was also evident that the excavated soil is highly inhomogeneous in terms of PCDD/F concentration and basing process operating parameters on such high level site assessments and limited baseline sampling and analysis also leads inconsistent and unreliable results.
- Funding constraints on the demonstration program as implemented only provided for a basic process unit that was not fully equipped in terms of pre-treatment infrastructure and fugitive emission release management.

ii) PCDD/F Remediation Effectiveness(Figures 5 and 6)

- PCDD/F concentrations in the range 5,000 -30,000 ppt TEQ show that 33 out of 42 results were below 1,000 ppt TEQ of which 20 were below 300 ppt TEQ, and 30 out of 40 results were over 90% RE, 25 over 95% RE and 8 over 99% RE.
- All but one of the PCDD/F concentrations <5,000 ppt TEQ were below 300 ppt TEQ but significantly less than 90% RE.
- However for PCDD/F concentrations >30,000 ppt TEQ typically are only treated to a level well above 1,000 ppt and to REs well below 90%.





iii) Other Contaminants:

- No systematic impact, positively or negatively, is observed between untreated and treated soils for any of the metals profiled other than perhaps arsenic.
- For the higher arsenic concentration locations there is a marginal trend to decreased organic arsenic levels after treatment which suggests some small negative impact of the process in relation to toxicity of the contaminant.
- For chlorophenol, there is evidence that some stripping to the exhaust air stream occurs in the dryer prior to mecano-chemical processing and there is either no effect or perhaps a trend to increased chlorophenol after treating, potentially due to generation of chlorophenol intermediates during destruction of retained original herbicide compounds.
- Fugitive emissions associated with chlorophenol upon exit from the reactor as VOCs need to be managed along with residual herbicide active ingredients and aromatic by-products that appear to be present.

iv) Environmental Performance:

- Limited PCDD/F monitoring of potential point source release points (dryer exhaust air and condensate water) showed the process met national and international standards but this needs more systematic sampling.
- The sampling of bag house dust and GAC material in the air pollution control system demonstrated that the capture of PCDD/F something that underlined the need for a robust APC system in a full scale configuration.

- Limited sampling of workplace air indicated fugitive dust and VOC emission at levels of concern and suggests the need for capture and return capability being part of a full scale configuration.
- No effective external ambient air quality monitoring was done but anecdotal evidence suggests that odour and visible dust release occurred and requires inclusion of environmental monitoring in a full scale configuration.

The main overall conclusion that can be drawn from these results at this point is that the MCD™ process has the capability of destroying the PCDD/F contaminated soils representative of the hot spot contaminated sites at Bien Hoa. The range of contaminated soil where the 1,000 ppt TEQ and potentially the 300 ppt TEQ soil quality standards should be reliably achievable with this configuration of the technology is < 30,000 ppt TEQ. This should also cover the majority of PCDD/F contaminated soil in terms of volume anticipated. With respect to ability to treat higher concentrations, the results also suggest that while destruction of organic contaminants is occurring, the destruction process remains incomplete and would benefit from longer residence times and greater collision frequency and force (energy input), all of which are controllable operating variables.

β) <u>EDL MCD™ Pilot Demonstration:</u> This demonstration was undertaken to directly test the gaps suggested by the initial full scale demonstration using a pilot reactor. The results for these pilot test runs are briefly summarized as follows, noting that only the results for organic contaminants are provided in Table 4 and the detailed results are documented in the above referenced evaluation report[5]

i) PCDD/F Remediation Effectiveness

- All test runs showed substantive and progressive PCDD/F (and other organic contaminates) concentration reduction over each time interval sampled suggesting a continuous, time dependent, destruction process with no trend to a final limit.
- For medium PCDD/F concentrations (30,000 ppt TEQ) reduction/destruction was achieved to concentration levels below 1,000 ppt TEQ in all runs and in two runs achieved levels below 200 ppt TEQ with the best result being 110 ppt TEQ when a TiO_2 reagent was used.
- For high PCDD/F concentration (70,000 ppt TEQ) one run at higher RPMs without additives achieved a concentration level below 1,000 ppt TEQ, one run with higher RPM and a quartz additives approached achieved 1,000 ppt TEQ at 60 minutes, and one run with reduced RPM had somewhat poor results after 60 minutes but was trending to the 1,000 ppt TEQ level.
- Overall the results demonstrated that the nominal medium range of soils should be well within the capacity of the process to achieve the minimum acceptable soil quality with flexibility to go to levels below any applied in Vietnam for reasonably contemplated land use.
- For the high concentration range which generally would be a relatively infrequent occurrence in practice if preparatory soil mixing was employed, the results show that the process can achieve the required level and would likely do so consistently with minor adjustment of additives and resident times, while maintaining the higher rotational speeds.
- The PCDD/F RE performance achieved was in the range of 97. 4% to 99.6% for medium soil contamination levels with the best results achieved with the TiO_2 additions, and for high concentration soils the range of RE's was 97.8% and 98.7 % with high rotational speed runs.

ii) Other Contaminants:

- For other secondary chlorinated organic contaminants, the results generally tracked those for PCDD/F with reductions of dioxin-like PCBs down to negligible levels, 2,4-D/2,4.5-T showing significant reductions for the medium concentration runs particularly with TiO_2 enhanced de-chlorination with all results below international screening standards for commercial/industrial land use.
- For arsenic and heavy metals, the process does not appear to have any significant impact as anticipated although this is being further investigated by the company and a potential future refinement might be the use of zeolite to immobilize inorganic arsenic.
- The REs for 2,4,-D and 2,4,5-T approached or exceed 99% for the medium PCCD/F soil concentration runs and with the exception of the low RPM run the RE performance is in the 96 % to 98% range for 2,4-D and 98% to 99 % range for 2,4,5-T on the high PCCD/F soil concentration runs.

Substance/ Parameter	Input	Run 1 - Medium				Run 2 – Medium				Run 3 - Medium			
		A-15	B-30	C-45	D-60	A-15	B-30	C-45	D-60	A-15	B-30	C-45	D-60
PCDD/F - ng/kg (ppt)													
WHO TEQ	28,500	8,350	5,300	1,200	172	6,050	1,180	72	110	9,660	6,060	2.390	731
RE/DE (%)		70.7	81.4	95.7	99.4	77.8	95.7	99.8	99.6	66.1	78.7	91.6	97.4
Dioxin-Like PCBs –ng/kg (ppt)													
Total TEQ	15.9	5.45	5.85	1.07	0.557	5.83	0.809	0.79	0.37	5.35	5.55	2.24	0.310
RE/DE (%)		65.7	63.2	93.3	96.5	63.3	94.9	95.0	97.7	66.3	65.1	85.9	98.1
Acid Herbicides – mg/kg (ppm)													
2,4-D	990	450	220	33	8	88	11	1.5	2.3	630	220	57	20
2,4-D RE/DE (%)		54.5	77.8	96.7	99.19	91,1	98.9	99.8	99.8	36.4	77.8	94.2	98.0
2,4,5-T	2,300	930	400	53	13	94	11	1.6	3	1,500	380	88	30
2,4,5-T RE/DE (%)		59.6	82.6	97.6	99.3	95.9	99.5	99.9	99.9	34.8	83.5	96.2	98.7
Principle Chlorophenols –mg/kg (ppm)													
2,4.2,5-DiChlorophanol	15	37	120	140	110	36	8.6	1.4	0.84	35	40	17	4.6
2,4.5-Trichlorophenol	53	110	70	9.4	1.2	44	7	1.3	1	99	73	20	4.5

Substance/ Parameter	Input	Run 4 - High				Run 5 – High				Run 6 – High			
		A-15	B-30	C-45	D-60	A-15	B-30	C-45	D-60	A-15	B-30	C-45	D-60
PCDD/F - ng/kg (ppt)													
WHO TEQ	71,700	34,100	30,300	22,300	14,000	26,700	18,100	6,510	1,580	26,300	15,500	5,200	914
RE/DE (%)		52.4	57.7	68.9	80.5	62.8	74.8	90.9	97.8	63.3	78.4	92.8	98.7
Dioxin-Like PCBs –ng/kg (ppt)													
Total TEQ	18.2	10.4	8.33	7.65	7.14	7.12	7.08	3.75	0.53	8.45	7.72	2.16	0.467
TE/DE (%)		42.9	54.2	57.9	60.8	60.9	60.7	79.4	97.1	53.6	57.6	88.1	97.4
Acid Herbicides – mg/kg (ppm)													
2,4-D	2,100	1,700	1,400	1,000	410	1,300	680	200	86	1,300	1,000	110	27
2,4-D RE/DE (%)		19.0	33.3	62.4	80.5	38.1	67.6	90.5	95.9	38.1	62.4	94.8	98.7
2,4,5-T	5,100	3,900	2,900	2,000	720	3,000	1,400	310	130	2,700	1,600	130	41
2,4,5-T RE/DE (%)		23.5	43.1	60.8	85.9	41.2	72.5	93.9	97.5	47.1	68.6	97.5	99.2
Principle Chlorophenols –mg/kg (ppm)													
2,4/2,5-DiChlorophanol	31	110	120	140	110	36	8.6	1.4	0.84	35	40	17	4.6
2,4.5-Trichlorophenol	110	300	370	380	180	330	270	110	20	300	240	74	14

Table 4 EDL- Summary of Pilot Test Results for "Medium" and "High" Concentration Test Samples at 15, 30, 45 and 60 min resident times– Primary Organic Contaminants (PCDD/F, Dioxin-Like PCBs. Acid Herbicides and Principle Chlorophenols)

χ) TTL MCS^{TM} Pilot Scale Demonstration: The results for these pilot test runs are briefly summarized as follows, noting that the results for organic contaminants are provided in Table 5(a), 5(b) and 5(c) for the low , medium test runs with the detailed results are documented in the above referenced evaluation report[5]. It should be noted that international laboratory results indicated concentrations for the high concentration test material significantly higher that the nominal target ranges (>100,000 ppt TEQ as opposed to 70,000 PPT TEQ), making the demonstration somewhat more severe than originally planned.

i) PCDD/F Remediation Effectiveness

- The PCDD/F concentration test runs dramatically lowered PCCD/F from the all test samples with residual PCDD/F soil concentration to between 1 and 2 ppt TEQ for low concentrations, between 2 and 18 ppt TEQ for medium concentrations and between 2 and 230 ppt TEQ for the very high concentrations.
- Likewise all test runs demonstrated PCDD/F RE performance that was greater than 99.99% except for except for two high concentration results that were slightly less.

ii) Other Contaminants (Table 5)

- For the three low concentration test runs, results for 2,4-D, 2,4.5-T, and chlorophenols showed that these contaminants are almost totally removed with only trace amounts remaining well below any soil quality standards that might be applied. The same result was observed for dioxin-like PCBs in the low concentration runs and a similar result would be anticipated for higher concentrations noting the low initial concentrations.

- For the three low concentration test runs, the RE performance for these other organic contaminates was greater than 99.99%.
- For arsenic the results available at time of writing, they indicate that the thermal treatment process appears to alter the nature of arsenic concentrations through effectively reducing the organic arsenic and AS (III) component levels to non-detectable levels but a general increase occurred in inorganic As (V) and in total As, as well as recoverable As which suggests that the thermal treatment process may have a marginal non-beneficial effect on the potential toxicity of the As levels.
- No effect is noted on other heavy metals

iii) Environmental Performance:

- The limited analytical results related to PCDD/F stack emissions indicate the APC system is effectively capturing stripped PCDD/F primarily in the GAC as evidenced by stack sampling results meeting international point source release standards.
- Likewise PCDD/F capture is occurring in the condensate water that showed relatively high PCCD/F concentrations above release standards.
- As a consequence the technology cannot be considered to qualify as a POPs destruction technology per say and its application would require additional provision for environmentally sound destruction of concentrated residuals such as GAC and contaminated condensate water such that it would have reasonable prospect of being part of an integrated system that would meet the 99.99% DE level required in Convention and GEF guidance documents[8,9].
- TTI has indicated that a separate dedicated train could be used to extract accumulated contaminants from GAC material and destroy the resulting vapour phase in a stack thermal oxidizer (incinerator).

Parameter	**0314VN4.1 Test Conc. Results**			**0314VN4.2 Test Conc. Results**			**0314VN4.3 Test Conc. Results**		
	Input	**Sample A Output**	**Sample B Output**	**Input Conc.**	**Sample A Output**	**Sample B Output**	**Input Conc.**	**Sample A Output**	**Sample B Output**
PCDD/F - ng/kg (ppt)									
WHO TEQ	12,000	1.52	1.62	14,800	1.77	1.28	10,600	1.28	1.06
RE (%)		99.99	99.99		99.99	99.99		99.99	99.99
Dioxin-Like PCBs –ng/kg (ppt)									
Total TEQ	15.1	0.00072	0.00043	16.7	0.00040	0.00072	15.2	0.00069	0.00057
RE (%)		>99.99	>99.99		>99.99	>99.99		>99.99	>99.99
Acid Herbicides – mg/kg (ppm)									
2,4-D	220	<0.01	<0.01	230	<0.01	<0.01	170	<0.01	<0.01
2,4-D RE (%)		>99.99	>99.99		>99.99	>99.99		>99.99	99.99
2,4,5-T	440	<0.01	<0.01	460	<0.01	<0.01	310	<0.01	<0.01
2,4,5-T RE (%)		>99.99	>99.99		>99.99	>99.99		>99.99	>99.99
Arsenic - mg/kg									
Total Recoverable As	18	27	23	17	24	22	17	23	21
Inorganic As (III)	0.4	ND	ND	0.5	ND	ND	0.4	ND	ND
Inorganic As (V)	1.2	4.44	3.33	1.4	2.9	3.73	1.0	3.51	3.29
Organic As DMA	0.2	ND	ND	0.4	ND	ND	0.2	ND	ND
Organic As MA	n/a	ND	ND	n/a	ND	ND	n/a	ND	ND
Total As	1.7	16.15	16.46	2.6	15.97	17.48	1.8	15.18	17.69

Table 5: TTI- Summary of Pilot Test Results – Primary Organic Contaminants and Arsenic
5(a) Low Concentration Test Runs

Parameter	**Test #1 – 0515VN02**		**Test #2 – 0515VN02**		**Test #3 - 0515VN02**		
	Input	**Sample A**	**Input**	**Sample A**	**Input**	**Sample A**	**Sample B**
PCDD/F - ng/kg (ppt)							
WHO TEQ	33,800	6.62	39,300	17.5	38,500	18.1	1.80
RE (%)		99.98		99.96		99.95	99.99
Acid Herbicides – mg/kg (ppm)							
2,4-D	2,700	<0.01	1,800	<0.01	2,100	0.021	0.017
2,4-D RE (%)		>99.99		>99.99		>99.99	>99.99
2,4,5-T	7,400	<0.01	3,800	<0.01	4,700	0.047	0.061
2,4,5-T RE (%)		>99.99		>99.99		>99.99	>99.99
EOX (mg/kg dw.)	**n/a**	0.08	208	n/a	199	0.08	0.08
Arsenic - mg/kg							
Total Recoverable As	19	27	23	22	22	21	23

5(b) Medium Concentration Test Runs

Parameter	Test #1 - 0515VN01		Test #2 - 0515VN01		Test #4 - 0515VN01		
	Input	Sample B	Input	Sample B	Input	Sample A	Sample B
PCDD/F - ng/kg (ppt)							
WHO TEQ	107,000	1.89	130,000	4.49	103,000	169	230
RE (%)		>99.99		>99.99		99.84	99.78
Acid Herbicides – mg/kg (ppm)							
2,4-D	9,800	0.013	4,500	<0.01	4,900	<0.01	0.011
2,4-D RE (%)		>99.99		>99.99		>99.99	>99.99
2,4,5-T	28,000	0.033	8.000	<0.01	10,000	0.018	0.021
2,4,5-T RE (%)		>99.99		>99.99		>99.99	>99.99
EOX (mg/kg dw.)	**n/a**	n/a	**n/a**	n/a	757	ND	n/a
Arsenic - mg/kg							
Total Recoverable As	31	33	25	31	33	33	31

<u>5(c) High Concentration Test Runs</u>

Notes: 1) ND – Non-detectable 2) Additional As results pending for medium/high test runs 3) Input data for Test #2 High concentration based on Baseline characterization of Sample 0515VN01

δ) <u>HPC Envirotec Laboratory Scale Treatability Demonstration</u>: The results for these laboratory scale test runs are briefly summarized as follows, noting that he results for organic contaminants are provided in Table 6 and the detailed results are documented in the above referenced evaluation report[5]

i) PCDD/F Remediation Effectiveness(Table 6)

- A reduction in PCDD/F occurred for all five treatment strategies but was substantially higher than the minimum target soil quality level of 1,000 ppt TEQ after 3 months.
- For the three treatment strategies continued for 6 months, the results for all but the aggressive oxidative de-chlorination treatment with persulphate showed no further reductions.
- The persulphate treatment shows reductions down to a level of 1,475 ppt TEQ which approaches but is still above the target minimum soil quality level using output results from a European laboratory and 5,890 ppt TEQ for the designated independent laboratory results
- If extrapolated to longer times these would be predicted to would meet the 1,000 ppt TEQ level (Figure 6).
- All the treatment strategies only achieved modest REs for PCDD/F except the aggressive persulphate based treatment strategies which after 6 months approached a 90% level when the European laboratory results were used but remained less than 60% for the Office 33 designated laboratory results.

ii) Other Contaminants (Table 6):

- For 2,4-D/2,4.5-T, the results show reductions for all treatment strategies with the best results obtained for treatment strategies involving persulphate based treatment.

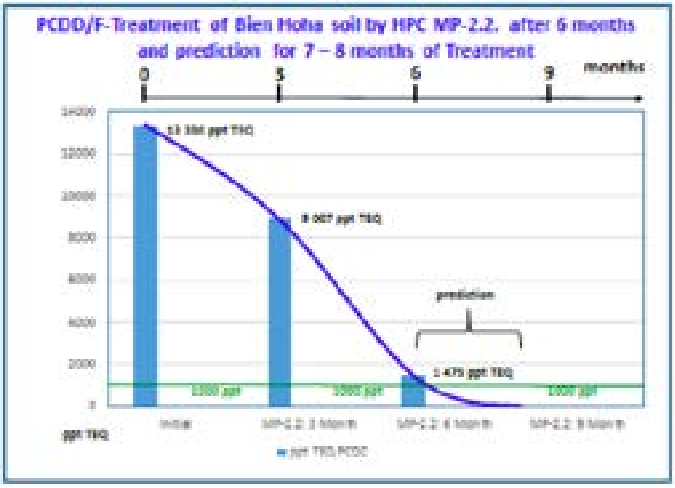


Figure 6 Projection of Persulphate Treatment MP-2.2
(Courtesy of HPC)
Based on HPC/SGS Analysis

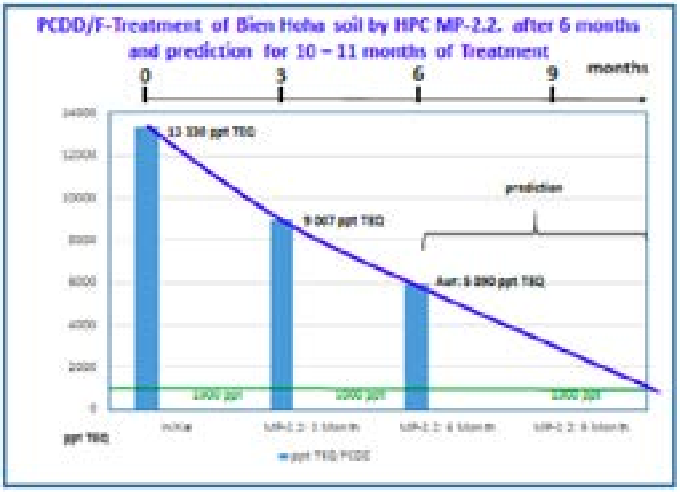


Figure 6 Projection of Persulphate Treatment MP-2.2
(Courtesy of HPC)
Based on HPC/SGS Analysis

- Reductions were achieved with several of the other biological and combined bio-chemical treatment strategies with reductions occurring primarily early in the treatment period suggesting that these treatment strategies may have a relatively short effectiveness life.

- In the case of chlorophenols, reductions are achieved for all treatment strategies.
- Impacts on arsenic or other heavy metals were not assessed

Table 6: HPC Envirotec - Summary of Laboratory Test Results for Three Extended Term (6 Month) Tests with Analysis from both HPC and PMU Designated Laboratories

Substance	Composite Average	Zero Valent Iron/Lactates			Persulfate Treatment			Microbiological Degradation		
		MP-2.1 July/14 HPC/ SGS	MP-2.1 Oct/14 HPC/ SGS	MP-2.1 Oct/14 Asure	MP-2.2 July/14 HPC/SGS	MP-2.2 Oct./14 HPC/SGS	MP-2.2 Oct/14 Asure	MPD2.5 July/14 HPC/SGS	MPD2.5 Oct/14 HPC/SGS	MPD2.5 Oct/14 Asure
PCDD/F - ng/kg (ppt)										
WHO TEQ	**13,330**	**8,723**	**8,584**	**8,780**	**9,007**	**1,475**	**5,890**	**7,013**	**8,114**	**8,580**
RE/DE (%)		**34.6%**	**35.6%**	**34.0%**	**32.4%**	**88.9%**	**55.7%**	**47.4%**	**39.2%**	**35.5%**
Acid Herbicides – mg/kg (ppm)										
2,4-D	360	11	48		0.37	0.33		57	120	
2,4,5-T	677	95	110		22	1.7		150	180	
Total 2,4-D/ 2,4,5-T	**1,037**	**106**	**157**		**22.37**	**2.03**		**207**	**300**	
RE/DE (%)		**89.8%**	**84.8%**		**97.8%**	**99.8%**		**80%**	**71.7%**	
Chlorophenols –mg/kg (ppm)										
2,4-Dichlorophenol	150150	38	2.1		6.9	<0.01		0.37	0.18	
2,4.5-Trichlorophenol	15-150	29	54		36	0.02		0.23	0.04	
Total 2,4-DCP/ 2,4,5-TCP	**15-150**	**67**	**56.1**		**42.9**	**0.02**		**0.60**	**0.22**	
RE/DE (%)		**<55.3%**	**<62.1%**		**<71.4%**	**<99%**		**<99.6%**	**<99.9%**	

Overall, while it appears that the impact of reductive and biological treatments is modest, the impact of aggressive de-chlorination treatment with persulphate appears to sustain the reduction in PCCD/F concentration with sufficient time beyond 6 months.

7.0 Conclusions, Recommendations, Lessons Learned, and Future Application

Overall the demonstration program described above should achieve its objective of providing the Government with guidance in the management of PCDD/F contaminated sites in Vietnam and, as it may choose, a sound basis to move forward with a commercial process of selecting, potentially acquiring, and applying cost effective remediation technology options to pending large scale remediation of these sites.

An overarching finding of this work is that the sites involved should be viewed as highly disturbed industrial sites exhibiting a variety of contaminants that no single remediation strategy or associated technology could realistically address all issues. As a consequence, this fact will limit future land use expectations. The approaches to remediation and associated technology applied will need to recognize this through pursuit of strategies that focus on the principle high risk contaminants and tailoring clean up requirement to appropriate land uses that can mitigate and accommodate any residual risks.

Following from the above, it is apparent that an effective strategy in addressing these sites would benefit from prioritizing areas of the overall sites in question in terms of both risk, and by differentiation between the need for immediate remediation, and those that could be addressed with longer term approaches. Within that, a basic initial strategy and one demonstrated on the Vietnam sites is to prioritize containment of high risk areas with relatively simple conventional transitional engineered landfills, surface capping, and surface water management. The next phase would be direct aggressive remediation of priority areas as defined by risk and more immediate future land use demands with larger but less contaminated areas being subject to longer term and potentially lower cost technology options that can be sustained on land not otherwise being used in the near term.

Of the three technologies demonstrated in this work, EDL MCD™ and TTL MCS™ are suitable for the more immediate rapid remediation type priorities while the HPC Envirotec work is characteristic of that which might have more long term application. In the following application of these are discussed separately:

a) Short Duration Applications

Both the EDL MCD™ and TTL MCS™ technologies as demonstrated are viewed as qualified for full scale commercial applications in future aggressive remediation initiatives, such as at Bien Hoa where the remediation requirement needs to be accomplished over a relatively short period due the demands of pending development or financing availability windows. In that regard they would logically join technologies like the IPTD in a competitive process.

The following highlights the basis for this and associated conditionality that in fact would largely apply to all such technologies and applications:

- *Organic contaminant remediation capability:* These two technologies have demonstrated the capability of reducing high levels of PCCD/F soil contamination to below the prevailing standards applicable to reasonably contemplated land use requirements with MCS™ generally offering lower achieved concentrations and higher REs. Likewise, they both destroy or remove other secondary organic contaminants to levels that would not be of concern in such land uses.
- *Full scale commercial application:* Neither technology has significant scaling issues, given that they were demonstrated on full scale process configurations and similarly offer throughput capacities that can be scaled by addition of incremental, parallel process trains to meet a wide range of capacity demands in a relatively short implementation period as required by specific commercial remediation projects.
- *Cost effective:* Both technologies offer quoted indicative unit costs of less than US$400/t for high volume projects which is would be generally very competitive with offsite alternatives and comparable remediation experience with IPTD in Vietnam to date.
- *Application in Vietnam:* Both technologies should be capable of being readily applied on site in Vietnam utilizing national operational and technical support expertise, and without significant constraints related to access or basic infrastructure. The one significant limitation both would have to address is the need for a reliable uninterruptable power supply to ensure continuity of the process, something that could be readily addressed by inclusion of dedicated electrical generation capacity in the full scale package supplied.
- *Transferable technology:* Both technologies could be offered under commercial arrangements ranging from a turnkey arrangement through to partnerships and transfer/acquisition involving qualified national service providers.
- *Residuals management:* The technologies differ somewhat in their management of residuals. MCD™ is a true destruction technology and has the capacity to recover and treat the relative small amounts of potentially released contaminants by returning it to the process. MCS™ in its demonstrated form is pre-treatment/contaminant separation process that requires a following step of destruction/environmentally sound disposal of concentrated contaminated materials, noting that potential to integrate that capability into the system exists, subject to environmental performance qualification.
- *Operational "Proof of Performance" testing requirement:* As would normally be the case at the beginning of a major project, the final acceptance of these technologies in a full scale configuration should be subject to a "proof of performance" testing phase in that configuration as part of its commissioning and start up where it would be demonstrated for regulatory and specification compliance as part of the commercial arrangements made for its use. This would cover technical and environmental performance demonstration in accordance with a specification defined in the commercial tender documents used.
- *Process flexibility for high very concentration situations:* Subject to further demonstration, both technologies should offer sufficient process flexibility in terms of the basic operational variables of residence time and energy input to adapt to a wide range of contaminant concentrations including relatively small quantities of very high concentration soils that otherwise would be considered POPs waste subject to offsite and potentially exported treatment by high temperature incineration.
- *Screening and feed homogenization benefits:* Given the highly inhomogeneous and random distribution nature of the principle contaminants on the PCDD/F sites in Vietnam, both technologies (and likely any potential candidate technology) would benefit from both pre-excavation/pre-processing analytical screening and a homogenization pre-processing stage after excavation such that a relatively uniform feed concentration is obtained and process parameters can be optimized and tailored to the feed PCDD/F concentrations.
- *APC system and fugitive emission management:* Both technologies when applied in a full scale configuration require robust, regularly monitored APC systems as well as infrastructure to capture, treat and/or return fugitive emissions, inclusive of those generated in pre-treatment handling and process activities.
- *Operational QC/QA and general environmental monitoring:* Provision needs to be made for regular onsite QC/QA analytical monitoring of treated batches of soil in accordance with the specified remediation criteria prior to disposition, with provision for return and retreatment as required, as well as workplace and surrounding ambient monitoring against a pre-defined base line.

b) Longer Term Applications

The HPC Envirotec bio-chemical laboratory scale demonstration of various bio-chemical strategies provide a starting point for further consideration of such strategies for potential application in long terms applications, typically in areas of lower level contamination on the boundaries of heavily contaminated "hot spots", where lower level contamination has been dispersed to and possibly in areas that were historically exposed to war time defoliant application and contamination remains. The following discusses the current results in such applications:

- *Prospective strategies site specific:* The current results indicate that only modest reductions in PCDD/F concentrations are achievable with the reductive zero valent iron and biological strategies even at extended application times but greater potential exists with the oxidative persulphate strategies options within a reasonable treatment time.

- *Front end laboratory and piloting requirements:* In any event, a continuing experimental program is required to optimize the application of any of these strategies or possibly combinations thereof. This would logically be followed up with pilot scale on-site trials that would allow refinement of the application techniques and additive usage, as well as properly cost the strategies if successful for full scale general application.
- *Application of overall remediation requirements:* More generally, in an ultimate full scale application such strategies would be subject to a number of the same recommendations and conditions applicable to the short term technologies discussed above. This would include provision for pre-treatment analysis, soil homogenization practices and an analytical QA/QC compliance protocol.
- *Transferable but long term national commitment:* Operationally, the application of such strategies are well suited for application in countries such as Vietnam in terms of their being readily transferable to local service providers and use of national technical support capabilities. However, this is tempered by the need for sustained financing likely primarily from national sources and a long term policy commitment to sustain the program.

c) General Application of Demonstration Results to POPs and Obsolete Pesticide Sites

The results of this work should have broader application to POPs and particularly POPs and general obsolete chloro-organic pesticide contaminated sites including the large numbers of burial sites used for disposal of such materials in many CIS countries. The following will link this to several of these situations that are now active GEF projects. Additionally, a number of key findings and lessons learned are linked to informing how such sites generally might be approached in the implementation of these projects.

i) General Lessons and Principles

- *Balance between practicality and perfection:* As an overarching lesson and recommendation from this work and the author's experience on similar projects is the need to have realistic expectations on what can be achieved. Technical practicality and financial reality generally makes it unrealistic to eliminate all contamination. In planning, designing and selecting clean up and destruction technology there will be an inevitable trade-off between perfection and scientific rigor, against the practicality of getting the job done and its cost effectiveness.
- *Environmental benefit and cost effectiveness:* Following from the above, the importance of cost should not be underestimated in the context of the ultimate environmental impact that a project it might deliver. As a general principle, there will almost always be a greater volume of material requiring remediation than financial resources available to the task. This leads to a need to first prioritize what material is treated and to also recognize that a lower unit cost that meets the specified requirements will usually have greater positive impact in comparison to a high unit cost and perhaps more sophisticated or experimental technologies that ultimately will take longer to mobilize and be able to treat less material due to cost constraints.
- *Importance of front end and operational site assessment, analytical screening of input soil:* Money invested in site assessment and application of modern analytical and modelling tools such as described in another papers this conference[12,13] is generally well spent. Likewise there will always be surprises both in terms of quantities and concentration distributions so a requirement will remain to provide on-site screening capability to define where to excavate and when to stop. This is well illustrated in this work given the variability in of in-situ and as-excavated soil
- *Consider multiple remediation strategies and technologies:* Generally the sites involved should be considered industrial or "brownfield" sites with variety of contaminants that will not be entirely cleaned up. As such, part of the remediation design will require tailoring it to appropriate future land use. This suggests the remediation approach involving more than one technology or technique ranging from containment and prevention of contaminant spread to the broader environment, through aggressive removal/treatment of high priority contaminants and more passive long term remediation strategies.
- *Importance of project specific technology demonstration as part of the commercial process:* The current work demonstrates the effectiveness of having a pilot demonstration stage that serves to screen candidate remediation technologies for further consideration. This can be integrated into a transparent competitive practice nominally required (or should be) in most internationally and national commercial selection processes. This would involve a two stage procurement process, the first being a prequalification stage where sample material is supplied to interested technology vendors/service providers to undertake a well-defined demonstration on actual soils that are involved. In the second stage where a selected service provider and technology is being contracted, the specification would also include an on-site "proof of performance" demonstration as a condition of proceeding and potentially national regulatory approval. Additionally the technical specification would include for validating ongoing technical performance (i.e. achieving soil quality

specified) and ensuring that point source and ambient air and water quality standards are maintained.

- *Commercialization and maturity as a factor in technology selection:* Ultimately, a selected technology should be capable of being presented commercially inclusive of execution program/work plan meeting a technical specification at a guaranteed cost, typically some unit rate in currency/quantity. This effectively limits technology/service provider combinations that have the experience, technical depth and financial capability to make such proposals based on assuming the technical and environmental performance risks involved (although not necessarily quantity risks). This inherently limits the viability of prospective technologies that, while showing promise, remain at an experimental and pilot stage. If those are to be considered for whatever reason, there will need to be a transfer of both financial and technical risk to the buyer and/or funding source.
- *Financing as a factor in remediation approach and technology selection:* A basic principle in site remediation is that the starting a project should ensure that it has sufficient financing to finish it, recognizing that in many cases starting and not finishing creates a larger environmental risk. Therefore, the amount of financing largely dictates the scope that can be realistically undertaken. Likewise the source of financing may dictate the approach and scope. Typically international funding such as GEF grant financing is capped without contingency provisions, often up front demonstration of substantive co-financing, and is to be disbursed over a fixed period such as 4-5 years. For application in developing countries this limits longer term options, tends to favour containment and "pack and ship" strategies versus development of on-site treatment strategies unless well-defined and financed. Consistent with that the selection of technology may well be dictated by the party bringing the external financing where this is tied to donor national preferences as has the situation to date in Vietnam.
- *National policies as a factor in selecting remediation approach and technology selection:* In many cases national interests may be dominant factors in the selection of approach if tied directly to conditionality related to limiting ant export options of POPs waste and a requirement that the technology be established in a beneficiary country including transfer and acquisition requirements by national service providers. These are legitimate factors but need to be balanced by the potential this has to limit external financing (and increase national contribution), potentially be more expensive and less efficient, and would perhaps raise questions of sustainability.

d) Application to Current Obsolete contaminated Site and Burial Projects

There are number of GEF projects being undertaken that are either starting implementation, are in the final approval stages in the GEF for detailed preparation, or are anticipated to be developed in the near future. In each case there are potentially direct applications of the knowledge base and lessons learned from the work in Vietnam, both as reported here and as has been described by others at this conference in this session[12,13,14] and in other sessions. The following provides some brief notes on how this might occur.

- *Armenia:* Armenia[15] is starting implementation of a US$24 million (US$4.7 million GEF Grant) project the major part of which is the clean-up of a degraded Soviet era OP burial site at Nubarashen near Yerevan. This originally containing primarily DDT and HCH in engineered containment cells but due to site instability and vandalism is now a more generally contaminated site. While emergency containment works have been undertaken there has been and continues to be contaminant releases into surround land and water resources. The initial site assessment and clean up strategy assessment has been described by Tauw in other papers in this session[12,14]. The final approach and conceptual design as approved by the GEF involves the division of the site into three categories of contaminated material: i) Category 1 – 900 ton of >30% pure pesticides: ii) Category 2: 7,000 ton of soil >1,500 ppm based on a risk based health impact assessment: and iii) Category 3: 12,600 t of soil > 2 ppm (average of 50 ppm) based on an agricultural land use risk assessment. The baseline project design involves i) export of Category 1 material as POPs stockpiled waste for destruction; ii) remediation of Category 2 material at a national hazardous waste site being established under the project; and iii) engineered landfill containment of Category 3 material on the stabilized Nubarashen site. The application of technologies such as MCD™ or MCS™ to Category 2 material inclusive of replicating pilot scale demonstrations on representative material would be pursued. An alternative scenario might involve the broader application of these technologies to all three categories and/or introduction of bio-chemical techniques to the Category 3 material.

- *Turkey:* Turkey[16] is likewise starting implementation of large GEF POPs legacy elimination and release reduction with UNDP and UNIDO jointly acting as implementing agencies. This project includes elimination of a large (approximately 2,500 tons) HCH stockpile which also as associated off-site HCH/DDT soil and building material contamination. The project also includes another component directed at developing and addressing POPs and chemicals contaminated sites. Additionally, at least one additional GEF project addressing sectoral site contamination and clean-up of waterfront brownfield sites is under preparation. The current work in Vietnam would be anticipated to potentially have application as these initiatives move forward, noting that Turkey, as an industrial upper middle income country represents a major market for remediation technologies and related technical services.

- *Belarus:* Belarus has eliminated its major POPs pesticide stockpiles in a World Bank GEF project that eliminated the large Soviet Era burial site at Slonim where they were concentrated by excavation and shipping 1,800 tons of such material for high temperature incineration. However it retains large but well organized stockpiles of other obsolete pesticides in storehouses, and there are 5 remaining Soviet era burial sites containing OPs being or planned for excavation and clean up by the government. A current UNDP GEF-6 project[17] at the stage of having received GEF technical clearance will address these stockpiles and support the development of in-country contaminated soil treatment capability in association with the national development of an integrated hazardous waste management facility. The current technology demonstration work may contribute lessons and candidate technologies for this work, particularly recognizing the accumulating OP contaminated soil inventory in secure storage and experience with the clean-up work to date that indicates larger volumes than assumed are involved in these sites.

- *Georgia:* As has been described in another paper at this conference[12], a completing small GEF project[18] has undertaken the site characterization and clean up option assessment for clean-up of Soviet era burial site at Iagluja, which is anticipated to lead to a follow on larger investment project involving its clean up and potentially establishment of sustaining capability for remediation and general hazardous waste management in the country. The significant estimated quantities of moderately contaminated soils (19-22,000 tons) and highly contaminated soils (8-8,500 tons) plus residual POPs pesticides (6-8,000 tons) would potentially be a match for some of the lessons learned in Vietnam and the technology demonstration.

Acknowledgements

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HCH & DDT CASES AND ISSUES

HISTORICAL STUDY OF THE SARDAS LANDFILL AND SITE CONCEPTUAL MODEL. SABIÑANIGO (ARAGÓN, SPAIN)

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Abstract

For over two decades the Sardas landfill (Sabiñánigo, Spain) was used for the disposal of industrial waste as well as municipal and construction waste[1]. In total approx. 400,000 m^3 of waste were deposed directly onto the ground, consisting of Eocene marls without a bottom liner[1]. The industrial waste contained residues from the chlorine production and in particular approximately 70,000 tonnes of waste isomers from the hexachlorocyclohexane (HCH) production for the manufacture of lindane (γ-HCH).[1] Lindane production was carried out by chlorination of benzene in a photochemical processes using ultraviolet radiation. For the production of 1 tonne of lindane approximately 10 tonnes of HCH waste isomers were generated and were largely deposited in the past around the former lindane productions [1]. These wastes are present in the Sardas landfill both in solid and in liquid form (as Dense Non Aqueous Phase Liquid, DNAPL).[1]

The landfill site was assessed through a governmental project supported by joint funding from the National and Regional environmental authorities. Part of the work consisted in the drilling and construction of more than eighty monitoring and pumping wells including the environmental characterisation of soil and groundwater. Currently, the environmental monitoring of the site, the extraction of the DNAPL phase by pumping and the control and treatment of leachate is ongoing.

This study will look at the environmental problem of the Sardas landfill with respect to its historical evolution and within the framework of the conceptual model of the site.

Key Words

HCH, lindano, DNAPL, POPs, Sardas landfill, Sabiñánigo,

Materials and methods

Due to the historic nature of this study and in order to complete this work, apart from the references listed at the end of this article, information has been obtained from many diverse sources such as historical photographs, photogrammetric restitution of historical aerial photography, works done by different companies in and around the site, analyses of journalistic information, etc.

The development of the site conceptual model required the inclusion of numerous technical characterisations completed during various phases of work at the site. The study integrated the information obtained from: borehole logs, trial pit excavations, geophysics (electrical and seismic), pump tests, tracer tests, physical and chemical analyses, mathematical modelling of the groundwater flow, etc. Additionally, various pilot treatment tests were completed such as chemical oxidation, thermal desorption, SEAR (Surfactant Enhanced Aquifer Remediation). Various commercial laboratories from different countries have been employed to analyse hundreds of soil samples, waste samples, groundwater samples, leachate samples, etc. A large number of liquid analyses were completed in the laboratory of the Aragón Government located in Bailín, near Sardas.

A multitude of chemical parameters were analysed for both in liquids and in solids: organocloride compounds (HCH, chlorobenzenes, chlorophenols, PCDD, PCDF, etc.), Total Petroleum Hydrocarbons (TPH), heavy metals, ions, etc.

Results and discussion

History of the landfill

The gully close to the River Gállego began to be filled in during the 60's with diverse types of wastes including industrial waste from the production of Lindane (HCH in powder, organochloride DNAPL), solid urban waste, construction and demolition waste, etc.

Figure 1 exhibits the original topography. The waste was dumped directly upon the natural ground.

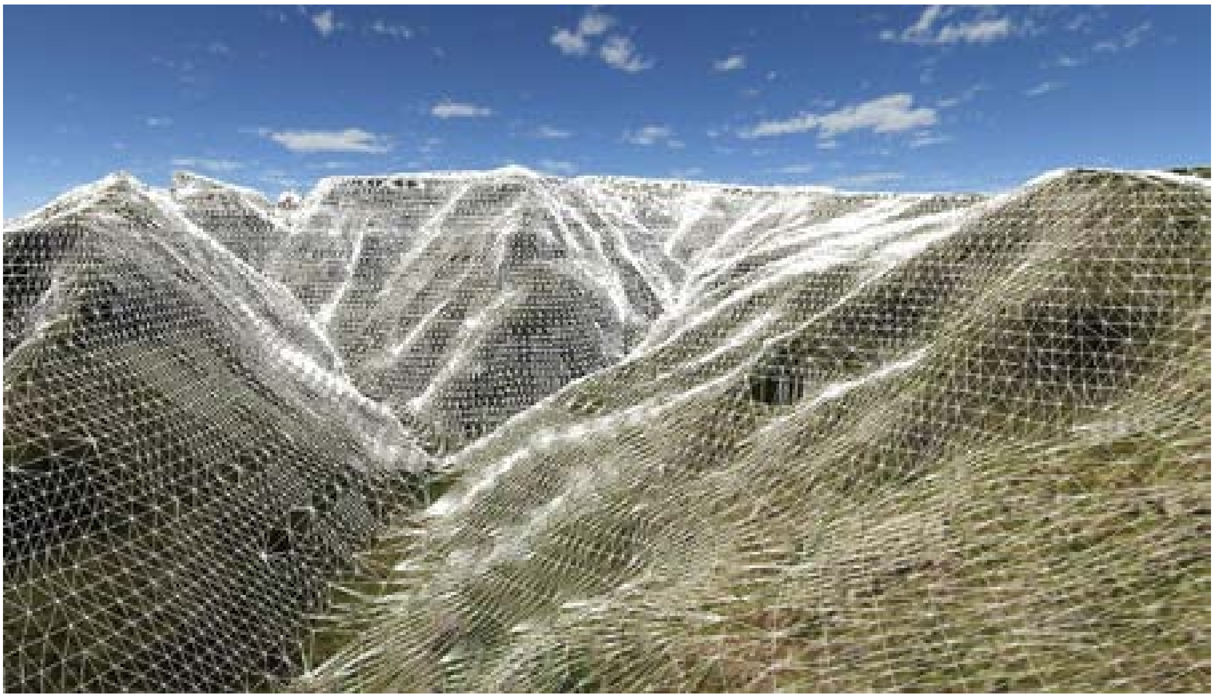

Figure 1. 3D model. The Sardas landfill location in 1956. Photogrammetric restitution [7]

The Sardas landfill was completely filled in during the 80's and was abandoned. A new landfill located nearby in Bailín was then used to deposit the waste generated from the production of Lindane.

It is estimated that between 30,000 and 80,000 tonnes[1] of solid HCH waste isomers and 2,000 t in liquid form (DNAPL) were dumped in the Sardas landfill.

Figure 2 shows the situation of the landfill completely filled in the 80's. Ever since the commencement of the exploitation of the Sardas landfill and in accordance to the available graphical information, the leachate generated within the landfill flowed in the direction of the Sabiñánigo reservoir.

In the early 1990's the N330 bypass was constructed and its trajectory intersected with the foot of the Sardas landfill. Due to these works, approximately 50,000 m^3 of waste material was removed and dumped in the lower part of the site as can be appreciated in Figure 3.

Figure 2. The Sardas landfill in the 80s

Figure 3. Dumping of excavated waste from the road construction in the lower part of the Sardas landfill site. Sealing and stabilisation of the foot of the landfill.

After the construction of the N330 bypass, the landfill was sealed as can be observed in Figure 3. The sealing consisted in the construction of side screens and a frontal cement-bentonite slurry wall. The surface was covered with HDPE geotextile thermally welded sheets, with natural vegetation placed on top.
The approximately 50,000 m^3 of waste material deposited in the lower part of the Sardas site were not sealed and are located very close the Sabiñánigo reservoir, Figure 4.

The landfill appeared to be correctly sealed, however since 2009 when DNAPL was first detected seeping to the surface, both groundwater and leachate have been under permanent periodic environmental controls. These controls also included the initiation of a hydrogeological study of the site. This initial work focused on identifying viable confinement and treatment options for later implementation.[1]

The characterisation and remediation works completed to the present date has resulted in the creation of a network comprising of 80 monitoring and pumping wells in and around the landfill. Eleven pumping wells are connected to a pumping station for DNAPL extraction. Currently, the DNAPL is also controlled in these eleven wells. The pumped DNAPL waste after decanting, are sent to an incinerator. The aqueous phase is pumped into two holding ponds that are connected to a wastewater treatment plant (physicochemical and activated carbon treatment).[1,3,4,5,6,7,8]

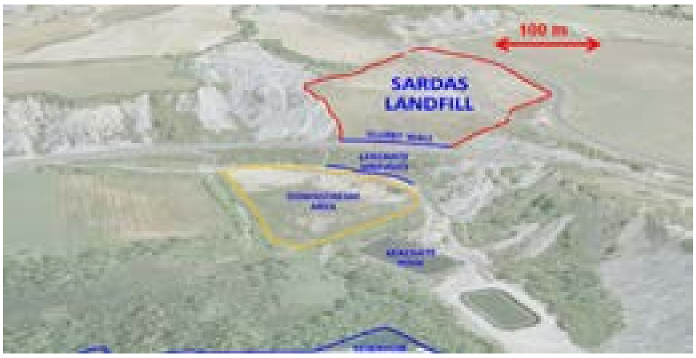

Figure 4. The landfill today

In order to avoid leachate generated within the landfill and also through seepage at the foot of the N330 bypass from reaching the Sabiñánigo reservoir, the former is pumped from wells installed within the landfill and the latter is pumped from an interception drainage trench. In both cases the leachate is allowed to decant for posterior waste management and the aqueous phase is sent to the holding ponds for posterior treatment in the wastewater treatment facility.

Site conceptual model

Figure 5 presents a schematic of the site conceptual model where it can be observed that the most sensitive receptor is the Sabiñánigo reservoir situated adjacent to the site.

The most important aquifer is the quaternary gravels associated with the River Gállego whose phreatic surface is conditioned by the oscillation of the level of the surface water of the Sabiñánigo reservoir. The gravels are covered by a layer of silt (6-8 m) that begins from the ground surface, (fields). The quaternary material rests upon a marl substrate which also forms the base of the landfill.

The landfill took advantage of the eroded gully of the marl substrate and the frontal sealing was completed by a bentonite-cement slurry wall which helped to accumulate the leachate within. It would appear that leachate escapes from the sides of the slurry wall and seeps to the surface at the foot of the slope and occasionally next to the frontal screen. It has been estimated that the seepage flow rate of the leachate is between 10 and 20 m^3/day [5].

The migration of the dissolved phase with elevated concentrations of HCH and diverse chloride compounds appears to originate from the fill material within the landfill and also from those situated below the N330 bypass. These compounds reach the quaternary silt layer and finally arrive to the alluvial gravel layer which is the principal receptor.

Important accumulations of DNAPL exist within the landfill and the lower zone of the site.

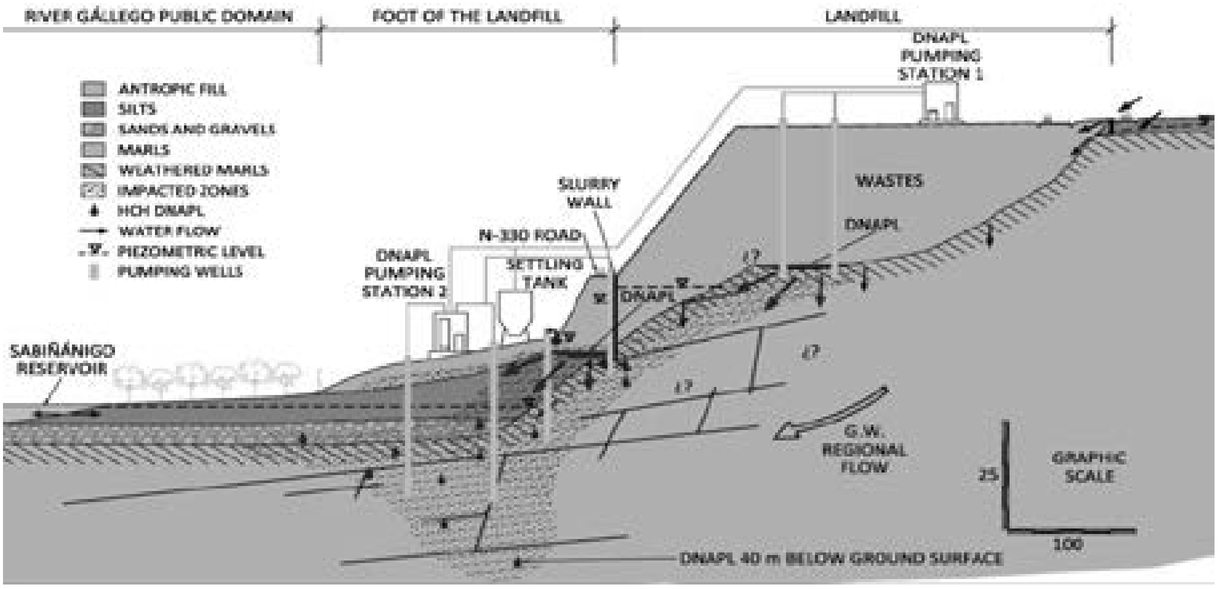

Figure 5. Site conceptual model

Conclusions

The volume of waste, the persistence and hazardous nature of the waste, the existence of DNAPL, the mixture of diverse compounds, the proximity of the site to a sensitive receptor as well as the complex topographical structure of the site consists in a technical and economic challenge to minimise and reduce the environmental risks.

Current efforts are focusing on increasing the capacity of DNAPL extraction, increasing the number of pumping points, evaluating suitable surfactants for the types of waste and specific site conditions that might allow a cost effective in situ remediation. Furthermore work is underway to increase the hydrogeological knowledge of the site through mathematical flow models.

Acknowledgements

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GEF PROJECT ON HISTORICAL HCH CONTAMINATED SITE AT THE ORGANIC CHEMICAL INDUSTRY SKOPJE (OHIS)

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Abstract

All conference papers should start with a half page introduction or abstract with the following contents: brief description of background and the aim of the study. The abstract should state briefly (half page) and specifically what the paper reports and summarize the conclusions. Point out new information and indicate the relevance of the work.
All the abstracts of the papers received with the title, name(s) of author(s) and key words will be included in the Abstract Book which will be available at the Forum materials. It will be distributed to Forum participants at the beginning of the 13th Forum.
Use Times New Roman, size 12. Abstract must be written in English.

Key Words

Chemicals, POPs, Hexachlorociklohexane, Legacy, Contaminated site, Decontamination

Materials and methods

The creation of this paper is based mainly on data collected from the previously developed feasibility studies along with the material compiled for the project development purposes, such as:

1. National implementation plan on reduction and elimination of POPs, 2014
2. CARDS-2006 Feasibility study Volume-I OHIS-Plant
3. OHIS Feasibility Study – ENACON,
4. OHIS HCH Decontamination Project Document ,
5. Chemometric assessment of the semivolatile organic contaminants content in the atmosphere of the selected sites in the Republic of Macedonia[3],
6. Organochloride pesticides in Macedonian girls with premature sexual development[1].
7. Global Monitoring Plan for Persistent Organic Pollutants Under the Stockholm Convention Article 16 on Effectiveness Evaluation. First Regional Monitoring Report Central and Eastern European and Central Asian Region[2],

Results and discussion

The Republic of Macedonia is facing with a historical problem with huge quantities (app 35.000 tones) of obsolete stocks of technical mixture of HCH (α, β) and app 3.000 tones of δ HCH stored for more than 30 years in the Organic Chemicals factory “OHIS”.
The location is identified as an Industrial Hot Spot No.1 in the country.
The Organic Chemical Industry of Skopje AD (OHIS) was affected by the historical production of lindane, an organochlorine pesticide. The lindane plant was gradually put into operation since 1964 and manufactured lindane until 1977, when its production ceased due to changing market conditions and negative environmental impact. Lindane, the gamma isomer of hexachloro-cyclohexane (HCH) was produced by the process of photo-chlorination of benzene. The produced mixture also contained other HCH isomers, i.e. α, β - and δ - HCH. Approximately 38,000 cubic meters of α, β - and δ - HCH were ‘temporarily’ stockpiled in open dumpsites, consisting of a concrete pool covered with a layer of soil (2008).

Figure 1. OHID HCH storage site

There were several scientific investigations that examined the current situation with the pollution and exposure to HCH in the country. The results of these studies were elaborated in different publications, and they additionally raised the attention of the decision makers and other relevant stakeholders to take action for decontamination of the HCH contaminated site.
According to the above mentioned studies, extremely high levels of HCH in air were detected in Skopje, particularly close to the OHIS factory. The average value at this spot was 297.2 ng/filter, which is close to 3 ng/m^3 and is among the highest in the region [7].
The averages and standard deviations of the total atmospheric concentrations of the analyzed semi volatile organic compounds (SVOCs) at six sampling locations during the period 14 May 2003 - September 2007 [5].
In addition, elevated levels of Lindane were shown in the

blood serum of the examined group for puberty development of young Macedonian girls, but unexpectedly much higher levels were detected in the control group. [6]
The Republic of Macedonia signed the Stockholm Convention on 23rd May 2001, ratified it on 19th May 2004 and endorsed its NIP on 2 nd September 2005. After the inclusion of ten new POPs in the Stockholm Convention Annexes, the Republic of Macedonia updated the existing NIP, giving a basis for realization of activities linked with priorities and action plans for new POPs. Lindane and its isomers have been added to the Stockholm Convention as POPs in 2009, and this OHIS site is now recognized as POPs contaminated site. Among others, one of the priorities in the „old“ and „new“ NIP is solving the problem with HCH-isomers in OHIS, Skopje.

The **Strategic Approach into International Chemical Management (SAICM)** project (2008-2010) resulted in the preparation of the National Action Plan for SAICM implementation. This document identifies national priorities in the area of chemical management, among which elimination and soil remediation restoration of the historical waste Lindane (HCH) at the OHIS plant and elimination of mercury containing waste and complete remediation of the OHIS plant, and defines action plans addressing these priorities for the environment, as well as decontamination of contaminated site.

The Government of the Republic of Macedonia has undertaken several steps in the process of finding proper solution for this dump site. A number of feasibility studies were developed, separate on-site investigations and laboratory analysis were conducted and most of them with a substantial assistance from the international community- Czech and Italian Governments. In the last 14 years several studies were conducted with a purpose to identify the real situation and found the most applicable solution. Starting from 2008 up to 2012 the POPs Unit in close colaboration with UNIDO developed a project proposal that was submitted to the Global Environment Facility (GEF) .The project proposal was reviewed by GEF and upgraded in several ocassions , the national contribution was raised from 2 up to 4 times according to the GEF 5 strategy criteria.
The project is in consistency with CHEM-1 of the GEF-5 Strategy "Phase out POPs and reduce POPs releases", Outcome 1.4 "POPs waste prevented, managed, and disposed of, and POPs contaminated sites managed in an environmentally sound manner",

The project objective is to set up a sustainable mechanism to ensure a sustainable clean up operation at the selected HCH contaminated site for future industrial use, and to protect human health and the environment from their adverse effects by reducing and eliminating the releases of and exposure to HCHs (6,000 m^3 or 10,700 tons to be disposed within the project period).

The Project includes the following components:

- Legal framework and institutional capacities:

This component will prepare, enhance and enforce regulatory acts and technical tools for environmentally sound management of the contaminated sites that are in compliance with the Stockholm Convention and EU requirements, and internationally accepted standards and practices. Institutional and technical structures will be enhanced and capable for site identification, risk assessment and management/clean-up of the contaminated sites.

Box 1: Foreseen activities within the Component: Legal framework and institutional capacities

Ø Preparation of legal acts and institutional and technical tools to ensure the completion of the OHIS site clean up operations and building capacities towards contaminated sites management in general;

Ø Preparation of technical tools (guidelines, procedures, instructions) for contaminated site management;

Ø Training of the environmental officers, specialists, contaminated site owners and the potential contaminated site clean up operators on practical usage of the prepared guidelines, procedures and instruction;

Ø Training of laboratory personnel for sampling and analyses standards and protocols for POPs/HCH

- Characterization of the site and risk assessment:
This component will determine the scope of contamination, the risk to human health and the environment will be assessed and the risk management options for the OHIS contaminated site defined by performing detailed site investigation, including sampling, analyses and interpretation of the results.

Box 2: Foreseen activities within the Component: Characterization of the site and risk assessment

Ø Performing of site characterization, i.e. detailed site investigation completed by sampling and analyses based on the sampling plan developed during the PPG;

Ø Survey of groundwater for drinking and irrigation purposes;

Ø Updating of the risk assessment analyses and definition of the risk management options

<u>- Clean up strategies and plan:</u>
This component will develop clean up plan and strategies that are effective in securing adequate human health and environmental protection and in providing local community cooperation.

Box 3: Foreseen activities within the Component: Clean up strategies and plan

Ø Preparation of contaminated site clean up operation/remediation plan and groundwater management plan for prevention of further contamination and adverse human health impact;

Ø Building of consensus among the general public and major stakeholders for the establishment/improvement of the OHIS contaminated site;

Ø Revision of the city development plan and zoning of OHIS site

<u>- Establishment of clean up mechanism and operations:</u>
This component will establish a remediation option which is appropriate for the d- HCH site remediation and will secure conditions for setting up an execution mechanism sufficient to sustain the clean up operations beyond the project period. There are two main key roles to be taken up: technology provider and operation service provider for the execution of the project's clean-up activities (see Table 1). Two options will be proposed in the bidding process: i) to seek a technology/operation service provider to accomplish the full scope of services or ii) to acquire technology to be operated by the operating entity (service provider) which will be separately set up following governmental due diligence. The scope and structure of the clean-up execution mechanism is illustrated in Figure 1. The bidders will be requested to submit their offers taking into consideration the two options. After the evaluation of the offers, the Government of the Republic of Macedonia/Ministry of Environment and Physical Planning in the cooperation with UNIDO will make the final decision on the option that is to be employed.

Box 4: Foreseen activities within the Component: Establishment of clean up mechanism and operations

Ø Preparation of ToR for the selection of the technology/service providers for the HCH contaminated site remediation;

Ø Selection of technology/ service provider;

Ø Identification of parties (private sectors, state owned companies or PPP contractual agreement form) interested as potential operators;

Ø Selection and establishment of the Operating entity

Ø Preparation of operation and business plan by the selected operating entity in consultation with the technical providers and all stakeholders;

Ø Obtaining of the needed permits for the technology treatment installation (EIA, IPPC);

Ø Establishment of a monitoring program, system at the location;

Ø Execution of the clean up operation

Items	Responsibilities and roles	
	Technology provider	**Service Provider/Operating entity**
Alpha and beta HCH dump site	Capping of the alpha and beta HCH dump	Ensuring the capping operation by the technology provider meets the international and national standard
Installation of HCH contaminated soil remediation technology at OHIS site	Delivery and installation of HCH contaminated soil remediation technology at OHIS site Training of the service provider/operating entity personnel by treatment of the HCH contaminated soil in quantities of 500 tons	Ensuring the technology delivered meets the technical specifications described in the Terms of Reference and UNIDO's contract Selecting qualified engineers/technicians who will operate the technology Accommodating and making logistical arrangement for smooth demonstration of remediation of 500 tons of the HCH contaminated soil
δ-HCH dump site	Developing and execution of a monitoring plan related to the remediation of 500 tons of the HCH contaminated soil (monitoring of the successfulness of the treatment, environmental media monitoring for eventual pollution during the remediation)	Treatment of the δ-HCH contaminated soil in quantities of 9,760 tons Packing and temporary storage of around 930 tons of the HCH waste and the quantities of the treatment by-products for final disposal at licensed facility Shipment of around 930 tons of the HCH waste and the quantities of the treatment by-products for final disposal at licensed facility abroad Final disposal of the HCH waste and the treatment by-products

Table 1: Roles and responsibilities of technology provider and service provider/operating entity

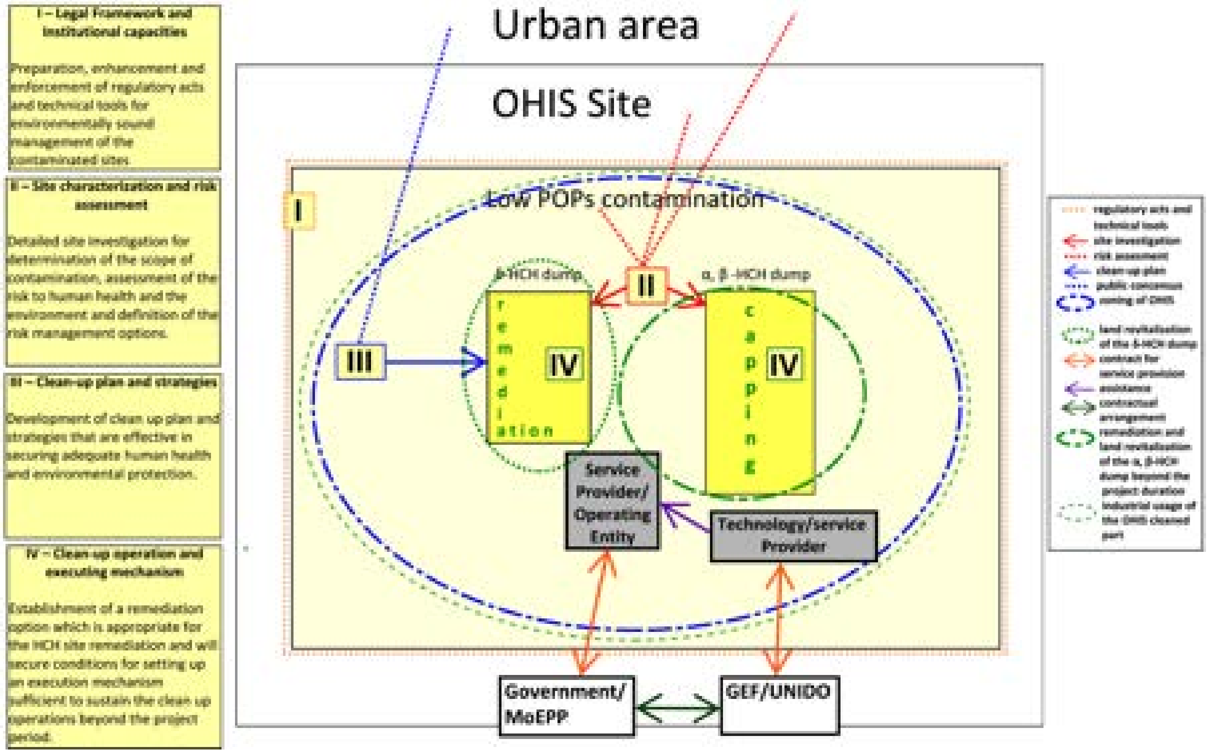

Figure 2: Illustration of the scope of each project component at the OHIS site

Acknowledgements

The POPs Unit under the Ministry of Environment and Physical Planning acknowledges appreciation to GEF for the financial support to realize the full size project:

Special acknowledgement is dedicated to UNIDO/ Environment Branch for supporting the POPs Unit in the early phases of mobilization of international and national funds to provide certain amount of contribution necessary for the project to be approved by GEF.Special acknowledgement to the Government of the Republic of Macedonia and the President of the Republic of Macedonia that showed full commitment and support to this project.

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SAFEGUARDING OF DDT AND ASSOCIATED WASTE IN GEORGIA, KYRGYZSTAN AND TAJIKISTAN

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[1] Milieukontakt International, The Netherlands, [2] Milieukontakt International, The Netherlands, [3] Green Cross Switzerland , [4] WHO/Euro and Ministries of Health of Tajikistan, Kyrgyzstan and Georgia

Between 2011-2015, the GEF funded UNEP project *Demonstrating and Scaling Up Sustainable Alternatives to DDT for the Control of Vector Borne Diseases in Southern Caucasus* is being implemented, with Green Cross Switzerland, WHO/Euro and Milieukontakt International as partners.

WHO/Euro has been working on the health component of the Project, demonstrating suitability, efficiency and cost-effectiveness of (non-chemical) alternatives to the use of DDT for malaria vector control in three pilot areas in Georgia, Kyrgyzstan and Tajikistan. The tested alternatives included 1) use of indoor residual spraying (IRS) with pyrethroids, and 2) a combination of non-chemical factors like use of mosquitoe fish (gambusia), environmental management, netting of beds and windows, plug-in evaporators for mosquitoe repellents, and/or old PET-bottles transformed into mosquitoe traps. The field tests have showed that the use of (non-chemical) alternatives is effective for ensuring disease baseline control. Based on the results, national Integrated Vector Management (IVM) programmes have been developed. Tajikistan has approved its IVM programme in November 2014, the Kyrgyz programme is currently under review and should tentatively be approved by November 2015.

One of the main aims of the environmental component of the DDT project is to build capacity within the Project countries on inventory, risk prioritisation, repackaging and disposal of obsolete pesticides in line with international best practices, as well as to raise awareness within ministries and the local public about the risks of continued use of DDT and of obsolete pesticides. Several trainings have been held over the course of the project on all these elements following guidance from FAO's EMTK-series.

In parallel to capacity building, 17.15 t of DDT-containing pesticides were repacked in December 2013 Kyrgyzstan and another 77.81 t of DDT and contaminated materials were repacked in June 2015 in Tajikistan. In Tajikistan, in parallel to repackaging, the Project built a new Central Store at the Vakhsh landfill, in order to provide safe temporary storage of the repacked materials until a final disposal solution becomes available in Central Asia. Further safeguarding of 400-450 t of DDT and contaminated materials is currently (October/November 2015) underway in Georgia and Kyrgyzstan, in close cooperation with FAO in their EU funded project.

As a recommendation, future projects should focus on the development of regional treatment options for wastes, implement trial destruction by thermal and non-thermal treatment options, use the new disposal capacity for clean-up and remediation of large burial sites as well as taking measures for immediate risk reduction of smaller sites.

STATUS OF THE HCHS ISSUES IN BRAZIL IN 2015 – ARE WE ADVANCING ON THE UNDERSTANDING OF THE ENVIRONMENTAL HEALTH EFFECTS?

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Abstract

Data from the National Inventory of Contaminated areas and of the National Implementation Plan of the Stockholm Convention (NIP/Brazil) is presented together with a SCOPUS scientific literature survey on the current literature on Brazilian studies on the health effects of HCH near some of our contaminated areas.

Key-words

Lindane, Brazil, Environmental Health, Environmental justice

Introduction

In Brazil, the production and use of chlorinated pesticides in the past was marked by a successive reporting of environmental health scandals. Not only the quality of land, but several watercourses, air quality and mangroves were affected, with an almost compulsory exposure of low income populations to residues of such pesticides. More than 25,000 tons of Technical HCH was produced and imported by Brazil between 1955 and 2003[1]. The historical efforts of IHPA are of extreme importance for the present knowledge. For example, 20 years ago, most of the selected areas that I presently report here, where officially already known, and the critical situation were reported by Lopez and co-workers in 1999[2] during the Bilbao Forum. Most of them were representative of illegal dumping of chemical wastes in the vicinity of slums ("favelas").

HCHs in the Preliminary Inventory of Contaminated Areas of Brazil

In the list of the preliminary report for contaminated areas, HCHs residues appear in around 19% of them (22 in 117 areas). Official storage for old vector control uses represents half of them and confirmatory and/or remediation measures were only taken for a few of this areas, with a clear difference between São Paulo and other states, since in São Paulo, the monitoring and remediation activities are much more advanced.

HCHs in the Stockholm Convention National Implementation Plan of Brazil

The first info regarding POPs on our NIP[3], states that some 20 foods, including different livestock and other food sources, are frequently tested for more than 200 types of pesticides, including alpha-; beta-HCH and lindane. However, results of these investigations never come out for the general public easily or in a sound manner. Most of the time, since this products a forbidden in the country, they represent a snapshot of the overall environmental contamination, and none mitigation measures can be taken in place. Although no registered use of alpha- or beta-HCH, lindane was only phased out for wood control less than 10 years ago. The use in medication was banned in 2000, and veterinary and agricultural uses stopped in 1986 and 1985 respectively.

At the most recent breast milk survey, as expected by its greater persistence, beta-HCH presented positive hints raging from 0.6 to 6.8 ng/g of fat[4]. In air samples, (e.g.: atmospheric deposition studies using PUF disks), HCHs concentrations is often found in levels that can be as high as 36 ug/m^3, in mountain areas of the southeastern part of the country[5].

Brazilian Public Health Studies on Contaminated Areas

Blood levels of beta-HCH in insecticide sprayers for vector control could be as high as 130 ug/l[6], which is one order of magnitude higher and in non-exposed population. At the same time, mangrove animals near Salvador at Bahia State had measurable levels of gamma-HCH. There is at least one important pesticide producer in this area[7].

More recently, biota survey on HCH in biota of impacted rivers of São Paulo indicates that these compounds are easily found[8]. Again, IHPA played a key role in spreading the message on the critical issues of the health status of several exposed populations in Brazil, Oliveira-Filho, from UFRJ, was one of the first Brazilian experts to report at our Bilbao Forum, secondary data on the contamination of the environment after the use of such pesticides in health campaigns[9].

Oliveira and Brilhante[10], (1996) and Brilhante and Franco[11] (2006) studying the Cidade dos Meninos (near an abandoned HCH factory), showed that case as notorious environmental injustice situation, that should receive immediate attention, according to the ATSDR standards.

In São Paulo, at Araras municipality, compost concentrations of HCH isomers was found near old pesticide depots[12] and cow´s milk at São Paulo State, more than 10 years ago showed a reducing trend for alpha-HCH[13], but for Rio Grande do Sul State, at that same time, 90% percent of milk produced on could found Lindane and alpha-HCH at a somewhat higher concentrations[14]. Accordingly, lindane and alpha-HCH were present in soils and water collected at the densely populated area of north-eastern São Paulo State[15].

In 2012, Torres and co-workers[16] compiled data on four cases where the legacy of HCH production was widespread environmental contamination.

More recently, phyto-remediation studies using potential biodiesel species like *Ricinus comunis sp*. are being developed, and indicated that for HCHs the potential uptake by the roots may play a role in decontamination of polluted soils[17].

These studies, besides the observations of altered liver, hematological, sexual hormones and cognitive functions in heavily exposed populations[18, 19, 20, 21] clearly show that this problems, although seeming to be ubiquitous, like there are all of the POPs pesticides, are not being neglected neither by the Environmental Authorities of Brazil nor by the Academia. We hope that the critical economical crisis faced by Brazil creates new opportunities for the international community to continue help Brazil to achieve a cleaner environment in the near future.

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AIR MONITORING (SETAC)

EUPHORE CHAMBERS AS A TOOL FOR STUDYING FATE OF PESTICIDES IN THE ATMOSPHERE

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Abstract

Pesticides are the most widely used chemical compounds. Once a plant protection product is applied to the field, the active ingredient can be partitioned into the soil, water and the atmosphere. The active ingredient can be emitted into the atmosphere through either dispersion during spraying or post-application volatilization from ground or leaf surfaces. In the atmosphere, pesticides are distributed among the gas, particle and aqueous phases, depending on their physicochemical properties and environmental conditions. Knowledge of the fate of pesticides and their degradation products following their use is required in order to assess the potential environmental impact of pesticides. As for other organic compounds, the gas-phase degradation of pesticides in the atmosphere is controlled by reaction with ozone, OH and/or NO_3 radicals. Pesticides, once released to the atmosphere, may be also subject to direct photolysis if its UV-visible absorption spectrum shows absorbance above 290 nm.

In general terms, studies of the gas-phase degradation of pesticides are problematic because of their low vapor pressures and usually, only theoretical information is used when it is necessary to know the degradation in the air compartment. However, theoretical models usually only provide information about the OH radical reaction, and in most of the cases, the values highly differ from the experimental values. In that sense, one advantage of large outdoor simulation chambers, such as those at the European Photoreactor (EUPHORE), is that compounds with relatively low vapor pressures can be introduced into the chamber in the gas-phase. In addition, these facilities allow to work under realistic atmospheric conditions, particularly as regards solar radiation intensity and wavelengths.

In this work we present results about experimental atmospheric degradation of several types of pesticides including: halogenated, organophosphorous, acetanilides, and dinitroaniline pesticides carried out at the EUPHORE chamber. Direct photolysis of pesticides was investigated under natural solar radiation, and the photolysis rate coefficient determined. The rate coefficients for the reactions of ozone in the dark and photo-oxidation with hydroxyl radicals were also measured under atmospheric conditions using absolute and relative rate techniques, respectively. Products of reaction were also determined by means of different analytical techniques, and degradation mechanisms were proposed. Knowledge of the specific degradation products, including the formation of secondary particulate matter, could complete the assessment of their potential impact. In fact, the fingerprint chemical composition analysis has indicated that they are a relevant source of multi-oxygenated molecules. The formation of those types of degradation products is important because they play a significant role in the atmospheric chemistry, global climate change, radiative force, and are related to health effects.

Key Words

Pesticides, atmospheric degradation, life time, gas-phase, EUPHORE

Materials and methods

The outdoor European Photoreactor (EUPHORE) is located in Valencia, Spain (longitude = -0.5º, latitude = 39.5º N). The EUPHORE chamber (volume ~ 200 m3) is fabricated of FEP foil, which transmits greater than 90% of the solar radiation in the wavelength range 290 to 500 nm. This material is transparent to UV light, allowing simulation of real conditions with a low ratio of wall-effects due to the shape and to the large volume of the chambers. The time of exposure to solar radiation is controlled with a retractable steel housing which surrounds the chamber.

A schematic representation of the simulation chamber is shown in Figure 1.

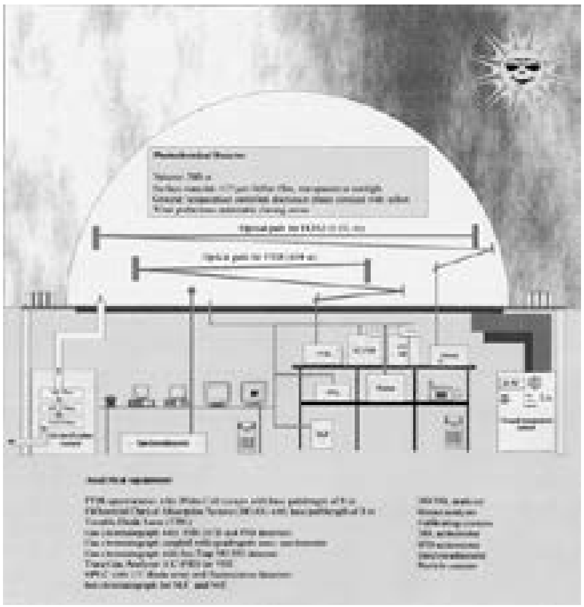

Figure 1: Schematic representation of the EUPHORE simulation chamber.

An air drying and purification system supplies the chambers with oil vapor, hydrocarbon and NOx free dry air. The dilution rate of the chamber, due to small leaks, is determined by measuring the decay of SF_6 added at the start of the experiments (monitored using its IR absorption). For the detection of the compounds, the chambers are equipped with a wide number of analytical techniques, ranging from different types of chromatographs, monitors and particles instrumentation to sophisticated in-situ optical devices. Therefore, wide number of species can be measured, e.g. Volatile Organic Compounds (VOCs), semi-VOCs, nitrates, ozone, NOx, particles (size distribution and chemical composition), OH and HO_2 radicals, solar radiation, etc. Among these instruments, some are on-line (e.g. Infra-red spectroscopy FTIR, gas chromatography coupled to mass spectrometry GC-MS (I), gas chromatography with flame ionization or photoionization detectors GC-FID/PID, monitors, differential optical absorption spectroscopy DOAS, Laser induced fluorescence LIF, proton transfer reaction mass spectrometry PTRMS etc) and others as HPLC and LC-MS or GC-MS (II), are used off-line. In addition, physical parameters such as temperature, humidity, etc. are also monitored during the course of the experiments. Table 1 shows the list of the available permanent instrumentation at the EUPHORE chambers.

To perform a photolysis experiment, the target chemicals are introduced inside the chamber together with SF_6 and kept in the dark for a while to study their wall losses. The chamber is then opened and the gas mixture is exposed to the sunlight irradiation for several hours taking samples periodically with the available instrumentation. Combining the information obtained from different instruments it is then possible to calculate the photolysis rate, the half-life time and the products formed in the reaction. Those are important inputs to suggest reaction mechanisms.

Taking into account equation (1):

$$k_{\text{total}} = J + k_{SF6} + k_{\text{wall}} \qquad (1)$$

$k_{\text{total},}$ the total rate coefficient, can be derived from the slope of the representation of ln[compound_int]$_0$/[compound_int]$_t$ versus photolysis time, where compound_int is the compound of interest studied, being J the photolysis rate, k_{SF6} the dilution rate and kwall accounting for the wall losses.

Another type of experiments to get relevant information on the pesticide studied are photooxidations. In this case, the production of the OH radical can be done by the photolysis of a precursor in the presence of NOx (e.g. addition of HONO) or without NOx (i.e. adding H_2O_2). The well-known relative method, i.e. using reference compounds (such as 1,3,5-trimethylbenzene or cyclohexane among the most used ones), is used to obtain the rate constant of OH with the key compound. Assuming that the OH reaction is the only significant loss process for the compounds

Gas chromatography		**Monitors**	
GC-FID	VOCs	NO/NO2 monitor	NO, NO2, NOx
GC FID/ECD	VOCs/PAN/Nitrates	CO monitor	CO
GC PID/FID	VOCs / Semi-VOCs	SO2 monitor	SO2
Gas Chromatography- Mass Spectrometry		O3 monitor	O3
GC-MS varian (on-line)	VOCs / Semi-VOCs	HONO monitor	HONO
GC-MS-TD	VOCs / Semi-VOCs. Multioxigenated compounds, pesticides	NH3 monitor	NH3
GC-MS thermo (off-line C18, filters, tenax)	VOCs / Semi-VOCs. Multioxigenated compounds, pesticides	**Others**	
Liquid Chromatography		Radiometer and actionmeters	Solar intensitu, J(NO2) Actinic flux
HPLC (UV-Fluorescence)	Ketones, aldehydes, hydroperoxides, phenols	Barometer	Pressure
LC/MS	Ketones, aldehydes, pesticides	Hygrometers	Dew point, Humidity (RH), temperature
Mass Spectrometry		Temperature sensors	Temperature
PTRMS	Higg temporal resolution VOCs	Diesel Engine	
Optical Instrumentation		Horiba	Fume emissions (CO, CO2, CH4, NOx, THC, O3)
DOAS (UV-Visible)	VOCS, NO2, HCHO, O3, etc	Test Bed (for diesel engine)	
LIF (Laser)	OH and HO2 radicals	Control NOx	
FTIR	VOCs, inorganic	Control RH	
Particulate matter		HONO generator	
SMPS	Number and size distribution	N2O5 Generator	
TEOM	Mass concentration	Ionic chromatography	Ions,
Particle Generator		General Analytical Instrumentation	

Table 1: Instrumentation available at the EUPHORE laboratories.

of interest and the references, it can be shown that:

$\ln[\text{compound int}]_0/[\text{compound int}]_t = k/k_R * \ln[\text{reference}]_0/[\text{reference}]_t$ (2)

Where the subscripts *0* and *t* indicate the concentrations at the beginning of the experiment and at time *t*, respectively, and k_R is the k_{OH} of the reference compound and k is the k_{OH} to obtain. After the corrections required (photolysis, leakage and wall loss, if necessary), the representation of $\ln[\text{compound int}]_0/[\text{compound int}]_t$ versus $\ln[\text{reference}]_0/[\text{reference}]_t$ should exhibit straight line where the slope is k/k_R. The k_R of the reference compound is well-documented in literature, thus the rate coefficient of OH reaction with the compound of interest can be calculated according to the equation (2).

In addition to the calculation of the OH constant of reaction, it is possible to study the product formation due to the photooxidation in the presence or in the absence of NOx.

Table 2 shows the main type of experiments and examples of pesticides studied at the EUPHORE chambers. In table 3, some of the pesticides or derivatives are shown.

Results obtained from the experiments have been also used to derive lifetimes, and provide information on particle and gas phase product formation (Table 4). Photolysis by natural sunlight has been shown to be the main degradation pathway for several pesticides, whereas the OH radical reaction is a more important degradation pathway for others. Moreover, in some cases, the reaction products are more toxic and stable than their precursor. For example, phosgene, $Cl_2C(O)$, a toxic compound, is one of the main products obtained from the reaction of chloropicrin with light (by direct photolysis) whereas the oxons are products obtained from the reaction of organothiophosphate compounds.

Results and discussion

Type of experiment	Main objective	Usual conditions
Photolysis	Determination of Photolysis rate constant and degradation products	Experiments carried out in the presence of OH and/or Cl scavenger in order to prevent the reaction with those radicals
Reaction with OH radical. Determination of rate constants	Determination of the rate constant for the OH reaction with pesticides	Relative kinetics.
Reaction with OH radical. Determination of reaction products	Determination of degradation products of the reaction of OH. Reaction mechanism	Gas and particle phase analyisis Experiments carried out in the presence or in the absence of NOx
Reaction with Ozone	Determination of Ozone rate constant and degradation products	Dark conditions. Pseudo-first order conditions. OH radical scavenger used

Table 2: Main type of experiments

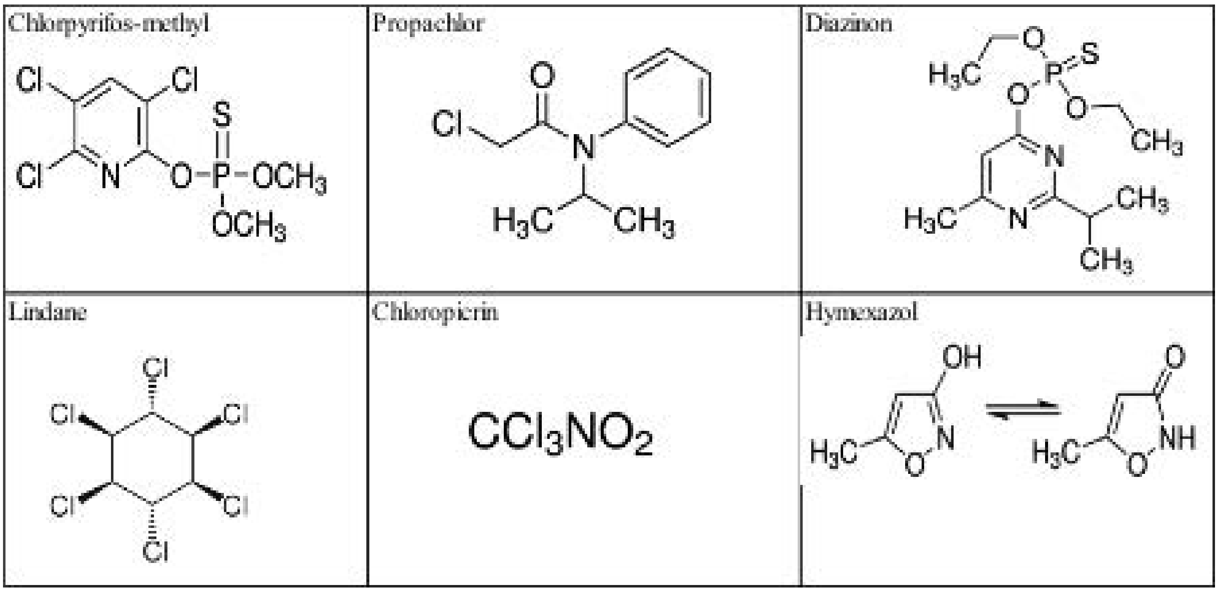

Table 3: Examples of pesticides studied at the EUPHORE chambers.

COMPOUND	J $[s^{-1}]$	k_{OH} $[cm^3\ molec^{-1}\ s^{-1}]$	k_{O3} $[cm^3\ molec^{-1}\ s^{-1}]$	Lifetime /Main degradation pathway
Chlorpyrifos oxon (1,2)	$< 4.8\times10^{-5}$	$(1.6 \pm 0.8)\times10^{-11}$	-	11 hours / Reaction with OH
Chlorpyrifos-methyl (2)	$< 2\times10^{-5}$	$(4.1 \pm 0.4)\times10^{-11}$	$<2.0\times10^{-18}$	3.5 hours / Reaction with OH
Diazinon (3)	$< 1\times10^{-5}$	$(9.6 \pm 1.8)\times10^{-11}$	-	1.8 hours / Reaction with OH
Diazoxon (3)	$< 4.8 \times10^{-5}$	$(3.0 \pm 1.0)\times10^{-11}$	-	5.9 hours / Reaction with OH
Hymexazol (4)	$< 5.1\times10^{-6}$	$(4.9\pm0.4)\times10^{-12}$	$(3.2\pm0.6)\times10^{-19}$	30 hours / Reaction with OH
Propachlor (5)	$<(2\pm0.5)\times10^{-5}$	$(1.5\pm0.3)\times10^{-11}$	$<1.5\pm0.4)\times10^{-19}$	20 hours / Reaction with OH
Chloropicrin (6)	$(5.1\pm0.5)\times10^{-5}$	-	-	5.4 hours / Photolysis
Lindane (7)	$<3.5\times10^{-5}$	$(6.4\pm1.6)\times10^{-13}$	-	20 days / Reaction with OH

Table 4: Kinetic parameters and tropospheric lifetime

On the other hand, rate coefficients are important to assess the impact of the pesticides on air quality and on human health.

Acknowledgements

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SPANISH AIR MONITORING OF PERSISTENT ORGANIC POLLUTANTS UNDER THE STOCKHOLM CONVENTION

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Summary

The present study is framed in the Spanish Implementation Plan (SIP) of the Stockholm Convention, managed by the Ministry of the Agriculture, Food and Environment since 2007 to date. The main objective of the SIP is to establish a national environmental monitoring network to characterize the current status and temporal trends of POPs and to evaluate the effectiveness of practices adopted to reduce POP emissions. In 2008 this network began monitoring POPs in air but, afterwards, it has been extended to other matrices such as soil and water.

This work has been focused on investigating POP levels in Spanish air, to elucidate background concentrations and their potential sources. Target analytes were polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) that include non-ortho PCBs (TnoPCB), mono-ortho PCBs (TmoPCB) and indicator-PCBs (TmPCB), organochlorine pesticides (DDT and their metabolites, hexaclorobenzene (HCB) and hexachlorocyclohexanes (HCHs) and polybrominated diphenyl ethers (PBDEs).

Results revealed HCB, DDTs and HCHs as the major pollutants, followed in decreasing order by PCBs, PBDEs and PCDD/Fs, when urban and remote locations are evaluated together. However, this pattern varies when samples are evaluated separately. In addition, urban areas presented statistically significant ($p<0.05$, Mann-Whitney U test) higher levels for all families studied, except for HCB, compared to remote locations. Data obtained in this study are very important for the correct evaluation of the measures taken to diminish POP levels in the environment.

Keywords

Persistent organic pollutant; air monitoring network; ambient air; passive air samplers; remote locations; urban areas.

Introduction

The Stockholm Convention on Persistent Organic Pollutants, is an international environmental treaty that aims to eliminate or restrict the production and use of persistent organic pollutants (POPs)[1]. Initially, twelve POPs were recognized as causing adverse effects on humans and ecosystems. Currently the number of POP families included in the Convention amounts to twenty three because Parties agreed to a process by which toxic compounds can be reviewed and added to the treaty, if they meet certain criteria for persistence and transboundary threat. All Parties are required to prepare a plan on how they are going to implement the obligations under the Convention and make efforts to put such plan into operation.

The present study is framed in the Spanish Implementation Plan (SIP) of the Stockholm Convention, managed by the Ministry of the Agriculture, Food and Environment since 2007 to date. The main objective of the SIP is to establish a national monitoring network to characterize the current status and temporal trends of POPs and to evaluate the effectiveness of practices adopted to reduce POP emissions.

The aim of this study was to investigate POP levels in Spanish air both in remote locations and urban sites. Target analytes were PCDDs, PCDFs, non-ortho PCBs, mono-ortho PCBs, i-PCBs, DDTs, HCB, HCHs and PBDEs.

Materials and methods

Since summer 2008 a total of 26 sampling campaigns have been conducted. Data shown in the present study correspond to the first seventeen campaigns, including 167 samples. Seven remote locations from an existing sampling network in Spain (European Monitoring and Evaluation Program (EMEP) / Global Atmospheric Watch (GAW) / Control Atmospheric Monitoring Program (CAMP)), and four urban sites close to the remote locations were chosen as sampling points (Figure 1).

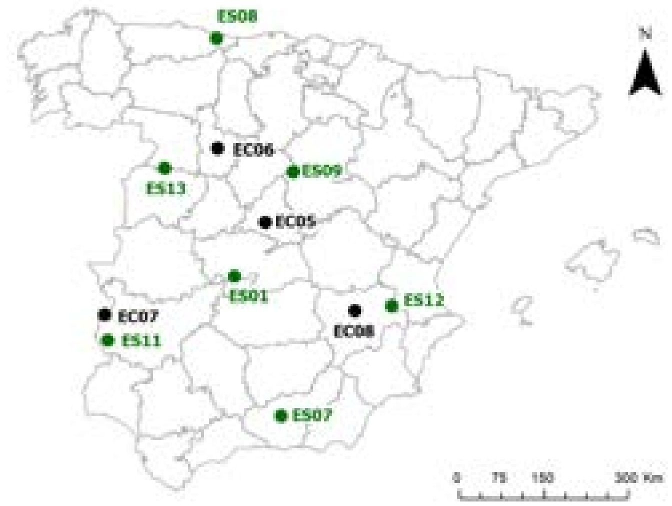

Figure 1. Geographical location of sampling points evaluated: Remote points (ES; Green) and urban points (EC; Black)

Passive air samplers (PASs) with polyurethane foam disks (PUF disks) as the sorbent media were used. These PASs are advantageous because of their low cost, simple construction, and electricity-free operation[2]. At each sampling point, four PUFs were deployed for 3 months, corresponding with each season, and then, collected after exposure. Three of them were used for PCDD/Fs, PCBs and PBDEs determinations. The fourth one was used for analysis of organochlorine pesticides (DDTs and their metabolites, α-, β- and γ-HCHs and HCB). A field blank at each station and each sampling period was also deployed.

Prior to deployment, PUF disks (14 cm diameter, 1.2 cm thickness, and 0.03 g/cm^3 density) were precleaned by Soxhlet extraction, wrapped in aluminum foil and stored in polyethylene bags at -20ºC.

Samples were spiked with ^{13}C isotope labeled internal standards before Soxhlet extraction. Purification and fractionation stages were performed in an automated Power Prep™ System. PCDD/Fs, PCBs, HCB, HCHs and DDTs were analyzed on a high resolution mass chromatograph, connected to a high resolution mass spectrometer while PBDEs were determined with a low resolution mass spectrometer. Identification and quantification were carried out using isotopic dilution[3]. All data are blank corrected. Final results are expressed as concentration, considering 4 m^3/day as the volume sampled by each PUF disk[2,4].

All statistical analyses were performed with SPSS 17.0 software. In order to represent together the levels of the different pollutant families, data were logarithmically transformed (Log X= 1 + log [X +1], where X is the concentration measured). Results have been discussed both overall and related to remote and urban locations independently.

Results and discussion

Figure 2 sumarizes concentration levels for all families considered, according to remote and urban locations. Data are plotted in two separate diagrams due to the difference of concentration between dioxins and the other pollutants.

From the global data (n=167), it can be observed the following pattern of concentration (as pg/m^3): HCB ≈ TDDT ≈ THCH > TPCB > TPBDE >> TPCDD/F. However, this pattern varies when samples collected in urban areas (TDDT > TPCB ≈ THCH > HCB > TPBDE >> TPCDD/F), are evaluated separately of those associated with remote locations (HCB ≈ TDDT > TPCB > THCH > TPBDE >>TPCDD/F). In both cases PCDD/Fs were the minor pollutants.

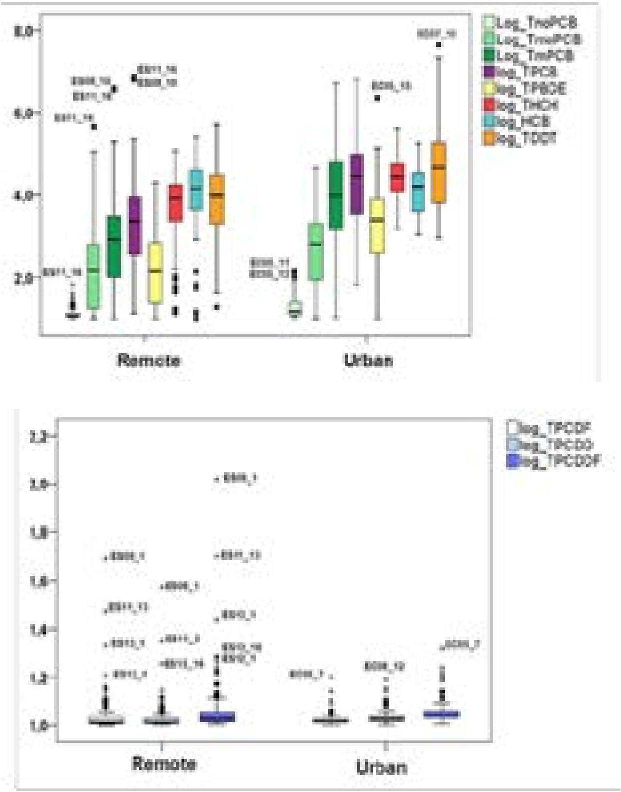

Figure 2. *Concentration levels for all families analysed represented according to remote and urban areas (log_X = 1 + log (1+ X), where X is the concentration in pg/m^3).*

The differences in the POP levels between urban and remote areas have been evaluated by using a Mann-Whitney U test. Urban sites presented higher (p<0.05; Mann-Whitney U test) levels of TPBDE, TPCBs, TDDT and THCH in comparison to remote locations.

Average congener and isomer patterns have been also established for each sampling point independently and additionally for the sum of remote and urban locations. In all cases, a common pattern has been identified: OCDD/F > HpCDD/F > HxCDD/F, TmPCB > TmoPCB >> TnoPCB, BDE 209 >> BDE 47≈ BDE 99, γ-HCH > α-HCH >> β-HCH, DDE > DDD >> DDT. No differences in terms of pattern could be found between urban and remote sampling sites.

POP levels reported in this study have been compared with those from the Global Atmospheric Passive Sampling Network (GAPS)[5]. This comparison is feasible because the GAPS Network uses similar passive sampling systems and performs sampling campaigns also every three months. Thus, it has been concluded the levels of ΣPBDE (sum of BDE 47, 99 and 100), ΣHCH and ΣDDE/T evaluated in this study are in the same order of magnitude as those obtained in the GAPS Network. Unfortunately, GAPS Network does not report PCDD/F air concentrations.

Up to date, the number of sampling campaigns performed (n=17) could be considered low, however, a cyclical trend in the HCB concentrations has been observed. Concentrations of this pollutant increase in autumn and winter and decrease in spring and summer. As indicated previously, HCB data do not present statistically significant differences between remote and urban sites. No temporal trends were found for any of the other POPs.

In order to reach reliable conclusions, including spatial and temporal trends, the maintenance of this POP monitoring plan, involving periodic air samplings throughout the Spanish territory, is consider essential for a proper evaluation of the measures taken to reduce POPs levels.

Acknowledgements

This work has been supported by the Spanish Ministry of Agriculture, Food and Environment under the project "POP monitoring in some matrices and areas of interest". The authors thank The State Meteorological Agency (AEMET) for allowing the use of their sampling stations and AFC Ingenieros SA and Ingenieros Asesores SA for the diligence and willingness to establish the sampling dates.

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EVALUATION AND MANAGEMENT OF THE ATMOSPHERIC IMPACT CAUSED BY PARTICULATE MATERIAL DURING THE PROCESS OF MOVING THE OLD BAILÍN (SABIÑÁNIGO) LANDFILL

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Summary

The works presented here collect the previous studies on the expected impact of particulate material resulting from the process of moving the old Bailín landfill to its new site. Given the potentially dangerous nature of the particle emissions with their anticipated HCH content, the study needed to manage the uncertainty inherent to the atmospheric dispersion of diffuse dust emissions in order to ensure a safety margin for personnel in the immediate vicinity of the established black area. Similarly, the study should provide the underlying basis for creating a plan monitoring all aspects of the moving process, allowing for an assessment of the levels of exposure the workers were subject to at all times.

These studies, based on numerical simulation tools and backed by experimental data, exposed the strong impression of the unique site on the pattern of surface concentrations, with respect to both the spatial distribution and seasonal variability. In general, the characteristic circulation in the valley follows a longitudinal pattern with a strong day/night alternation that results in a notable seasonal variability, with short-term peaks of elevated concentration and long-term seasonal averages that tend to be very low.

Key words

Atmospheric diffusion, particulate matter dispersion, particle emissions, diffuse emissions, particle deposition, environmental impact.

Introduction

The production of lindane by INQUINOSA in the town of Sabiñánigo (Huesca, Spain) between 1975 and 1992 left behind a sad legacy of several spaces damaged by the manufacturing of the pesticide or the elimination of its waste products in unsafe conditions.

One of the key points in this pernicious legacy is the Bailín landfill, where today we know 64,000 tons of HCH waste was eliminated. Following the detection of a dense, non-aqueous phase liquid (DNAPL) in the groundwater associated with this landfill, composed of assorted isomers of HCH, benzene, polychlorinated benzenes and polychlorinated phenols, with a maximum water level of 10%, the conclusion was reached that elimination of the source was essential in order to address treatment of the ground waters. The DNAPL plume was advancing towards the Gállego River less than one kilometer from the landfill, and the plume in its dispersed phase had been affecting the river for several years.

It was decided that transferring the waste materials from the old landfill to a new secure landfill cell also located in the Bailín ravine was the best option for achieving those goals. It was estimated at the time that up to 80.000 tons of HCH waste material and a total volume of around 200.000 m^3 between pure waste and contaminated soils would have to be moved.

To minimize the risks of this complicated operation, the waste materials transfer was scheduled for the season with less precipitation (June to October). It was a very short period to move the volume of materials involved, which in turn required that the entire operation be carried out with the standard machinery used for public works.

The main danger to the immediate environment associated with the operation clearly seemed to be the dispersion of pollutants, whether through run-offs (aqueous medium) or through the air (fundamentally as particulate matter).

The high degree of uncertainty regarding the potential atmospheric impact of the planned action required a preliminary risk assessment (in terms of the ambient concentration levels that could be expected in the different areas that were occasionally affected). That would not only define those levels 'a priori' but also permit the development of a surveillance strategy which would enable people to verify in real time that the pollution levels in the entire area were sufficiently low during the operation (within the ranges established as acceptable). If the opposite was true, they would be able to modify (and even interrupt) the operations with the intention of reducing its impact.

The need to define a perimeter within which special health protection measures would be adopted emerged from that, as did the need to minimize the area where the dispersion of pollutants could create a secondary source by affecting the soils.

A potentially significant contribution, at least locally, of particle concentrations in the atmospheric environment originates in some kind of handling of particulated material exposed to the air. The dust created from these open sources is called fugitive in that it is not released through a channeled air current.

The size of this contribution to the atmospheric environment is strongly dependent on each situation: the condition of the material (principally the granulometric texture and composition of the material, as well as its level of moisture), the kind of operations it is subjected to (excavation, loading/ unloading, etc.), the mechanical equipment used, and environmental conditions (derived from the dragging effect of the wind), etc. Specifically, the wind's influence as a source for the re-suspension/release of material displays great fluctuations derived from the strength, gustiness and turbulence of the air as well as its interaction with surface areas subject to erosion (exposure, texture, disintegration, etc.).

Handling the materials is also a significant source of emissions into the atmosphere at the different points in the handling cycle: extraction from the ground, loading and unloading the transportation vehicles, relocation of the piles. The movement of the trucks, excavators and other vehicles themselves during these processes make up another significant source of emissions (direct from the material and by resuspension of deposits on the roads and shoulder areas). The amount of the emissions produced by handling the deposits of granulated material varies naturally with the amount of material itself processed, and generally by three main factors that affect a particular pile: its age, moisture content and granulometric composition. In this way, the knowledge of the emissions due to the presence and handling of dust materials is one of the primary uncertainty factors in assessing its potential impact on the atmospheric environment.

Once in the atmosphere, the particles are subjected to turbulent dispersion processes that make the small particles behave roughly like gases. Whenever they become larger, they are affected by gravitational deposition due to the weight of the particle now suffering the effects of friction with the air current, to the extent that the movement of very large particles can be viewed as unaffected by turbulence.

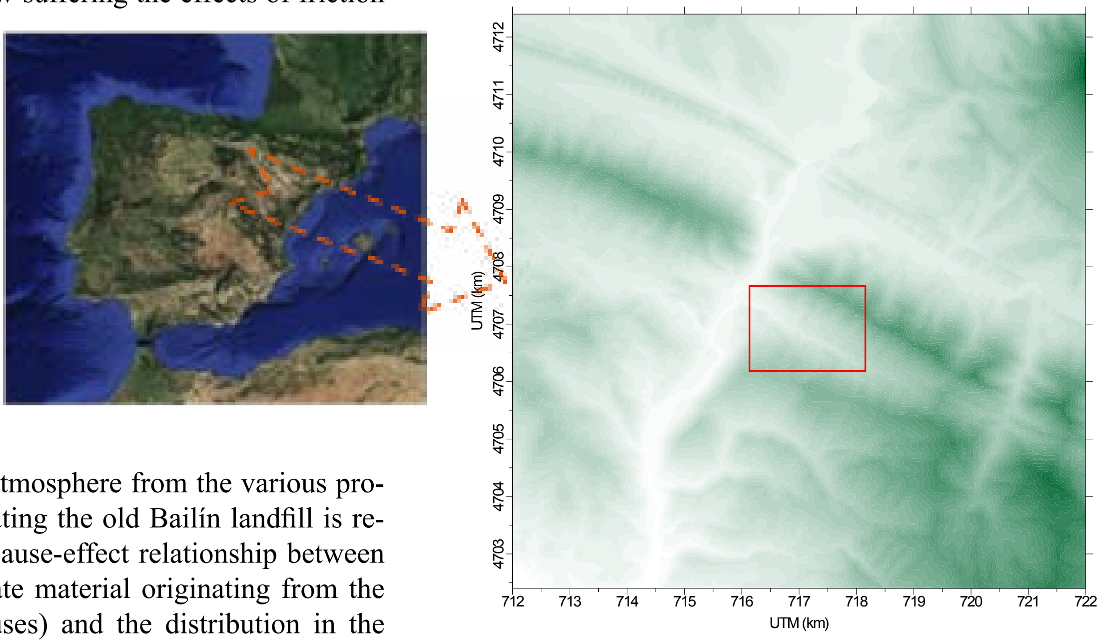

Figure 1: Principal orographic features of the Bailín valley (red box of right figure) located to the south of the Pyrenean axis, where the north/south axis runs along the Gállego riverbed.

Methodological approach

As in any dispersion problem, the preliminary assessment of the expected impact on the atmosphere from the various processes involved in relocating the old Bailín landfill is reduced to establishing a cause-effect relationship between the emission of particulate material originating from the previous operations (causes) and the distribution in the area of the atmospheric concentration levels (effects), where that "relationship" is determined by the *dispersion and transportation processes* of the released material through the atmospheric environment.

Managing the dispersion of particulate material emission is necessarily done using a *numerical tool* which incorporates the physical details of the transportation and atmospheric diffusion of the emissions (dispersion model). Two important limitations arise from this approach: the uncertainty associated with the lack of information about the emissions and the strong variability of the complex atmospheric system (turbulent), which in turn introduces noise and unpredictability (highly non-linear behavior).

One way to minimize this complexity consists of using a mixed procedure that resorts to continuous experimental measurements of the immission level at one or more locations combined with a dispersive model including both the primary characteristics of the sources and emissions as well as their transportation and dispersion by the wind.

The result obtained is an estimate of the impact on the surface area (in terms of levels of concentration) with a determined spatial distribution. The pattern turns out to be variable over time, insomuch as the factors determining it are (emissions, wind, etc.). Evaluating the map of concentrations will necessarily form the criterion for assessing the potential risk of the impact, which includes taking into consideration at least two critical aspects: the strength of the ground concentration levels and their spatial spread.

The site

The site is located in a very complex orographic context (figure 1). On the large scale, a clear slope of the north/ south elevations can be observed, established by the presence of the Pyrenees mountain range on the northernmost edge, which causes a strong channeling in that direction derived from the layout of the main transversal river valleys born from its summits (e.g., the Gállego). On a smaller scale, the pre-Pyrenean corridors form a grid of longitudinal valleys, where the Jaca-Sabiñánigo axis forms an important air basin, as does the Bailín basin, albeit on an even smaller scale.

The wind rose for the Bailín station (figure 2) reflects the strong channeling of surface winds in the site along a WNW-ESE axis that closely follows the bed of the arroyo. The influence of the basin, short in length but very narrow, translates into an air circulation of alternating breezes, up valley/down valley, during daylight hours, as shown by the hourly frequencies of directions (figure 2 top-left).

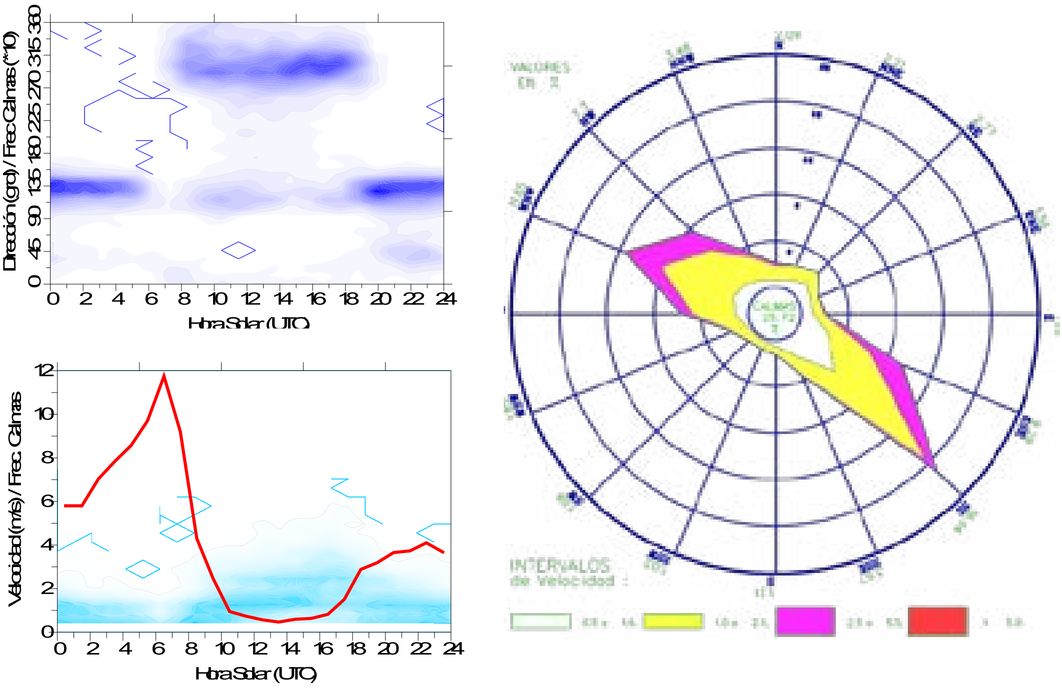

Figure 2: Aereological characteristics of the site for the summer period: frequencies of occurrence by directions by hour of the day (upper left), of wind strengths and calms (lower left) and wind rose (right).

One characteristic of the wind records is the high number of calm periods, naturally more frequent during the night (figure 2 bottom-left) and in the transitional period towards sunrise. They are clearly associated with a poorer atmospheric cleaning (and therefore potentially of greater risk from the perspective of dispersion of pollutants). The winds, highly collimated around the main directions of the axis valley, are generally stronger from the WNW direction during the daylight period of the breeze, as well as coinciding with advective situations of greater magnitude. Meanwhile the down-valley flows are almost exclusively during the nighttime circulation, always weaker and not as well developed.

The wind circulations in the Bailín valley show strong restrictions (few degrees of freedom), a result of being tightly contained by the natural environment (a narrow and sufficiently deep valley, closed in both directions). It appears to maintain a dynamic fairly independent of that recorded for the wider Sabiñanigo valley to the north, which in turn is more affected by other local elements (e.g., the effects of the flows in the Gállego basin) as well as the influence of large-scale external forces (e.g., entrance of general air circulations from the west)

Procedure for estimating atmospheric impact

Numerical simulation strategies

Reproduction of the atmospheric impact of dust emissions derived from the earthmoving works being performed on site requires the identification and characterization of the sources (areas and emission rates), and simulation of both the wind and dispersive processes fields in the selected period.

Here the transportation and dispersion models have to be able to reproduce, on the one hand, the strength of the emissions coming from the most important potential sources (previously identified) and, on the other, the transportation and mixing processes (and, if applicable, the transformation and elimination mechanisms) for the pollutants throughout the transportation process.

The variability of dust emissions created mechanically by handling of open sources of material is extremely high and tend to fluctuate greatly even within the same site. The main factors causing this variability can be grouped together into:

- those due to the nature of the exposed material itself starting from the original source;
- the variability caused by the nature and intensity of the mechanical handling of those exposed materials.

The wind action must be added to the previous factors, since it is capable of producing re-suspensions of the material itself while simultaneously increasing the emissions during the handling of the material involved in the loading/unloading and transportation processes.

An important source of uncertainty in estimating the potential impact comes from the value of the emission rates being worked with. Widely fluctuating quantitative values can be taken, depending on the factors previously alluded to, while at the same time the results will be predictably variable over time. In creating the dispersion models, the emission rate acts linearly, so that the emissions at each moment will have a multiplier effect on the entire spatial distribution obtained after its dispersion.

The possibility of comparing the results with experimental measurements would facilitate the adjustment of the simulated fields to the real impact, providing validity to the numerical estimates where no measurements are available. As a general strategy for addressing the estimate of the atmospheric impact of the operations, the numerical simulations are adjusted to the following guidelines:

- simulation of the particulate material dispersion over a small area of high resolution around the center of operations, all within the Bailín basin;
- several potential sources were evaluated related to the dismantling operations, refilling of the new container and the onsite transportation, with individual emission readings for each source, but uniform in the time;
- the results were corrected based on the values obtained experimentally on site with the goal of bringing the simulated results closer to those obtainable in operation.

Modeling tools

Initially the option of the RAMS (Regional Atmospheric Modeling System) Mesoscale Meteorological model was choosen for the simulation of the winds fields at the site; it is a numeric code for weather simulation very versatile and widely used as a limited area model since many of their parameterizations were designed for the study of mesoscale phenomena or high resolutions space. However, cold and superficial nature of particulate matter emissions suggested from the beginning a confinement in the Valley, so it was preferred a diagnosis meteorological model for the three-dimensional representation of the wind within the basin (RAMS simulations were used for potential gas releases, where transport outside the valle was easily expected, and not included here).

At small spatial scales, and especially if meteorological information 'in situ' is available, numeric diagnostic codes provide better results than more sophisticated codes, in the sense that incorporates experimental information, fully adapted to the constraints of the terrain. So, for the purpose of particulate matter dispersion analysis, the thredimensional wind field was constructed from a weather module that incorporates the base of the Nuclear Energy Agency model MATHEW (Lawrence Livermore Laboratory).

The model uses a variational analysis technique to determine a mass-consistent velocity field based on an interpolation of surface and upper air wind measurements. The process of adjusting the interpolated winds under effects of local topography is controlled through the used of Gauss Precision Moduli parameters. These parameter values depend upon the atmospheric stability, which determines the relative adjustments of the horizontal and vertical velocities during the variational procedure. So it manages explicity complex topography, does not depend on the site, uses simple meterological data usyally avalible and is computationally stable, needig not too much time to get·3D solutions.

The specific particulate material diffussion it computed directly from classical expressions for a turbulent fluid, where any formulation should respect that concentrations are proportional to the rate of emission of the focus ('Q') and inversely proportional to the average velocity ('Ū'), in which the mixing function of the material into the atmosphere responds to a simple Gaussian scheme of the type,

$$\bar{C} = \frac{Q}{2\pi \bar{U} \sigma_y \sigma_z} \exp\left\{ -\frac{1}{2} \left[\left(\frac{y}{\sigma_y} \right)^2 + \left(\frac{z - \bar{z}_0}{\sigma_z} \right)^2 \right] \right\}$$

being 'z0' the effective emission height and 's_y', 's_z' dispersion functions, dependent on atmospheric stability and distance from the source (down wind 'x'). In this generic representation ('Q') emissions are related with immission levels ('C') through the atmospheric factors ('U', 's_y', 's_z'), provided at all times by experimental measurements and numerical simulations. In the first phase of works deposition schemes of material were discarded and, as it is written in the strategies, experimentally estimated emission rates were used in a first approximation.

Selection of scenarios

The selection of a "representative" time period for the atmospheric dynamics at the site is one key for obtaining accurate results. Analyzing the measurements available at the site reveals such great repetitiveness in the cycles that the choice was made to work over a real summer time period, continuous and long enough to collect the essence of the predictable occurrence of the different atmospheric conditions during the works. The selected time frame, from August 15-28, 2013, was dominated by very stable, stationary atmospheric conditions, where the valley functions as the engine for creating the local wind circulations that prevailed during practically the entire time period. From an atmospheric impact perspective, these are the conditions which would potentially create episodes of elevated surface concentrations of materials released by the debris removal operations. Synoptic conditions of stronger winds (that break down these local cycles) generally would lead to a greater dilution rate of the emissions, and predictably at levels of lesser concentration (although this was partially compensated for by a possible increase in direct emissions and the re-suspension of already deposited material).

Spatial range

Selection of the work area determines the spatial resolution and scale of the processes to evaluate. It is important those mechanisms responsible for the dispersion of particulate material are sufficiently represented. Figure 3 shows two "windows" around the site, measuring 10 km by 2 km per side, respectively. The larger area covers the natural formations which define the Sabiñánigo and Bailín valleys as well as the transversal riverbed of the Gállego and was used in the simulation of gaseous emissions (not presented here). Meanwhile the smaller "window" covers the Bailín basin around the site in greater detail, with the primary elements that will presumably interact in the most decisive way with the emissions released by the planned activity. The strong channeling of the winds analyzed in the meteorological section enables us to estimate an obviously longitudinal pattern of impacts, where the major barrier of the mountain range to the north of the site implies a strong restriction on any exchange of solid material between the two valleys.

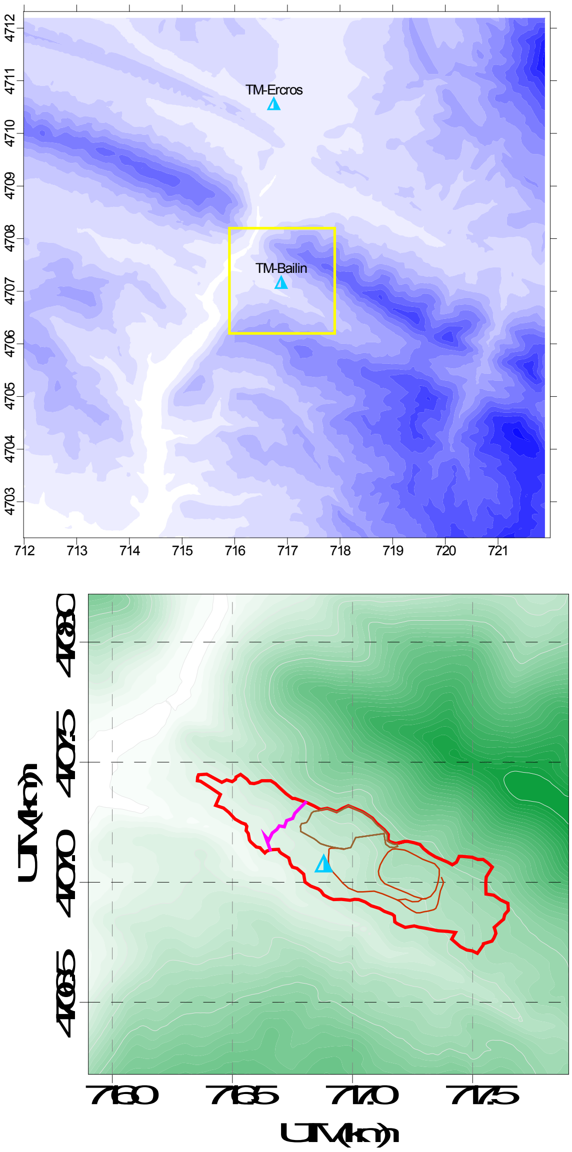

Figure 3: Orography around the site on two different scales, showing the position of the meteorological station of the site (triangle) and the perimeter area of the facilities (red line).

Five sources of emissions were studied in the exercise, including the two simultaneous extraction activities involved in the dismantling operations of the old landfill, another two sources in the new basin related to the unloading and reordering of the waste materials in their new location, and finally the emissions derived from transportation over the road that joins both sites. The first four were all identified as extensive sources, in accordance with circles with a radius of roughly 15 meters and located in the positions closest to the facilities in a conservative fashion for the simulation exercises; the road is portrayed as a linear source.

Again taking the most conservative hypothesis, in every case it was assumed that its operation was uninterrupted and uniform over time.

Figure 4 outlines the area of the plant, portraying the border of the exclusion or danger area, outside of which it is required to maintain certain concentration levels, letting the normal development of tasks without adopting special personal protection measures.

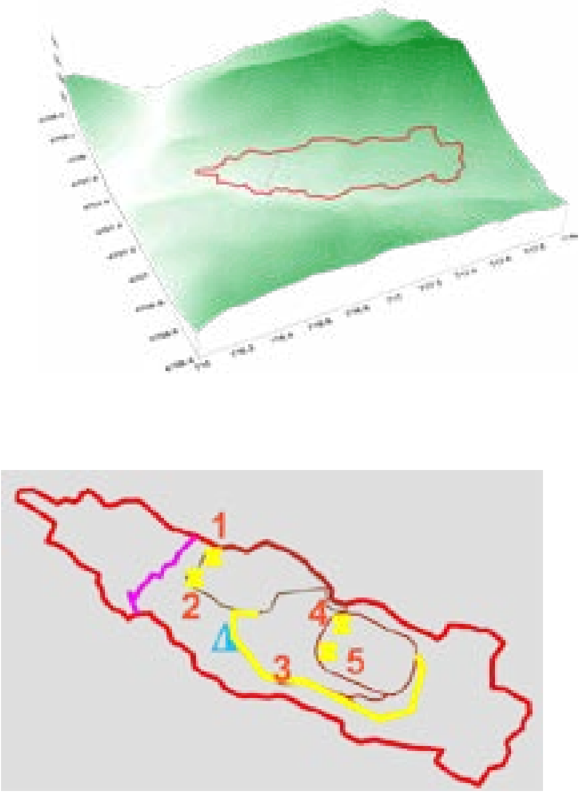

Figure 4: Orographic detail of the site and its overlap on the surrounding orography (left) next to the detailed outline of the site, including the sources considered (circular, 1 and 2 located in the old landfill, 4 and 5 in the new one, and 3 as the road between them.

Preliminary experimental estimate of emissions

In order to make the experimental adjustment to the numerical simulations, several prior experiments were performed with the goal of obtaining a preliminary estimate of the emission rates associated with the tasks of loading and unloading a truck and their circulation on the road, employing a material with granulometric characteristics similar to those expected in the dismantling process (limestone crusher filler). The instrumental monitoring of the dust dispersion impact in these tests consisted of placing four (4) high volume samplers for PM10 located at 50 and 100 meters to the east and west of the source, and a GRIMM automatic PM monitor for 1, 2.5 and 10 mm resolution, located 50 meters from the source in the direction of the prevailing wind direction at the time of the tests. Figure 5 shows a sequence of those immission measurements during one of the tests with the instruments actively deployed. The real experiences made clear the great variability of the immissions, both over time and in their relative strengths.

	FINALES	emisión	%
Carga	PM10	**153.4**	
	PM2.5	**14.7**	23.7
	PM1	**3.7**	14.1
Descarga	PM10	**53.5**	
	PM2.5	**8.0**	25.6
	PM1	**2.9**	15.4

Table 1: Estimate of the gross emission rates from loading and unloading a truck as an average of the three experiments performed (units in mg/m³). The percentages of smaller sizes relative to emitted material are shown in the rear column.

For each test, the concentration values were recorded (along with the wind -speed and direction-) continuously and with minutal resolution at one point (GRIMM system) and accumulated for the whole period for the high volume samplers. The differentiation of the time periods for the three operations made an estimate possible through using an inverse procedure on the emission levels recorded during those operations. Table 1 summarizes the average emission values obtained from the loading and unloading activities in the three tests performed.

Analysis of the emissions during the road journey of the trucks turned out to be too complex (with great interference due to re-suspension from the roads) so that employment of the instruments was not sufficient to quantify this aspect.

Results

The dispersion simulation was performed every 10 minutes over the biweekly period studied, obtaining the individual contributions of each of the five sources to the spatial window (specified as a matrix of receptors of 100x100 elements, 20 m side each). No deposition speed was introduced in the model and it was also not referenced for a specific granulometric range (generically PM10).

An initial approach then worked with uniform rate readings that were constant over time:

1 mg/m²/s, for the extensive sources;

1 mg/m/s, for the linear source;

A sequence of "instantaneous" immission fields are created that way, when the ground concentrations respond to the effects of the emissions coming from each source and their interaction with the prevailing meteorological conditions.

Analysis of the measurements show that the changes of direction induce strong fluctuations in the impact area. Superimposing them provides the average level of interest, which would represent the level of exposure. The wind strength and atmospheric stability conditions are the main factors that modulate the pattern and intensity of the

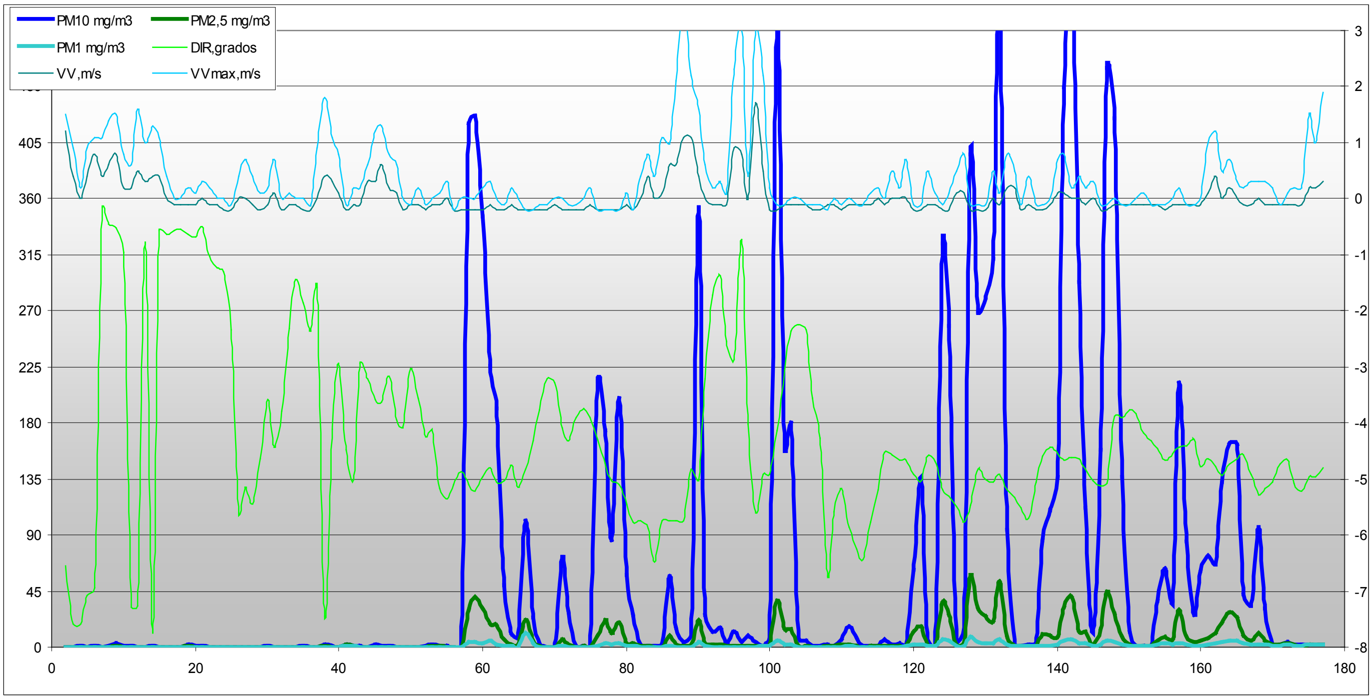

Figure 5: Immission measurements (three granulometric raqnges) against the wind parameters (speed on the right scale) recorded during the first test characterizing the emissions.

spatial distribution of these concentrations, with the orographic configuration also playing a role.

The abundance of numerical solutions offers great potential for analysis, whether by individual sources, combining sources in different formats, etc. With the goal set on establishing a monitoring program for health protection, and therefore necessarily conservative, different possibilities of spatial distributions were explored:

- **distribution of average levels**, the result of averaging the predicted levels for each node of the network at the same point for all the simulated time intervals (highly reduced values);
- **maps of maximum levels distribution**, obtained for each point of the network the absolute maximum value (hourly/every 8 hours) obtained for each point of the network against the value predicted for each node throughout all the simulations over time. That method yields a representation of the worst case scenarios (although they do not simultaneously occur at all the points, and therefore is not a real situation).
- **perimeter impacts**, represented as the expected levels of concentration on the perimeter of the danger area, with a special interest from the monitoring perspective (see figure 9).

At short distances, the position of each source is critical in its impact on a specific area. That is reflected in figure6, where the simulated concentrations for each source at the monitoring point based on wind direction are represented. Proximity to the source frequently causes stronger impacts, although more collimated, extending the range of influence towards sources that are progressively farther away.

Absolute levels average

The dynamic of pollutants characteristic of summer in a valley like the one housing the site makes the averages over extended periods appear to be very moderate, due to the alternating flows for night and day. That leaves any site alternately upwind and downwind from the source, and consequently in alternating conditions of non-impact and impact. The "stain" obtained in figure 7 thus turns out to be very limited quantitatively. The emphasized isocurve of 20 *mg*/m^3 remains completely within the area of exclusion, and the levels are immediately positioned below the level 1 *mg*/m^3.

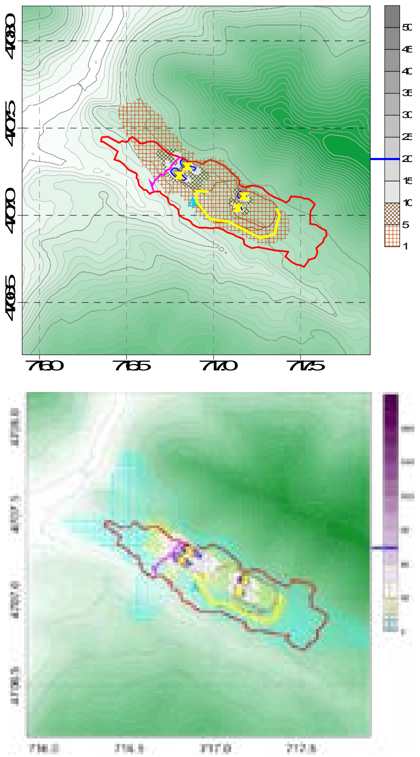

Figure 7: Spatial distribution of the simulations of the average concentrations of PM10 (left) and the daily maximum levels (right) obtained over the entire time period.

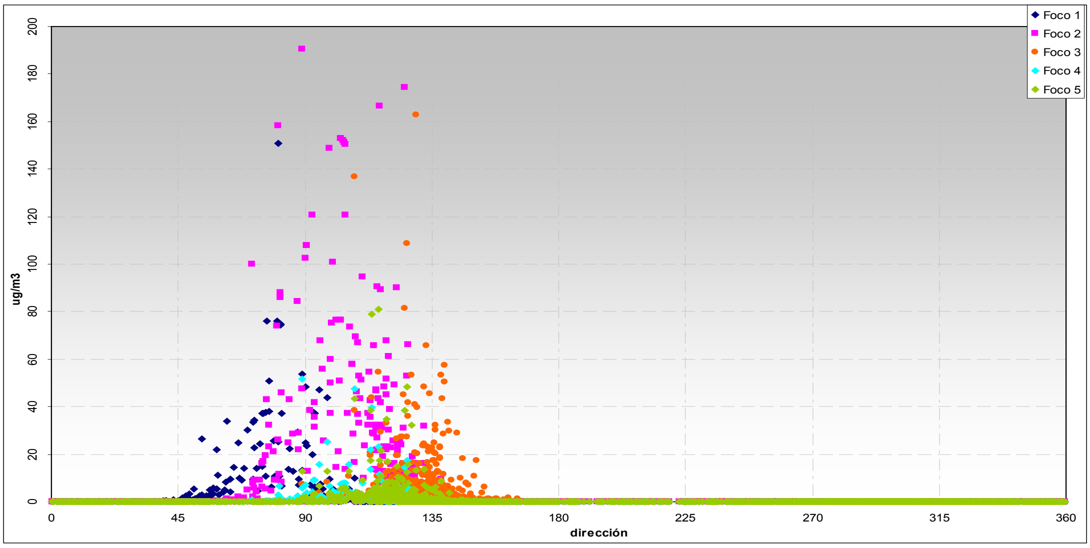

Figure 6: Simulation of the contribution of different sources (abscissa axis) based on the wind direction (ordinates) at the level of concentration of one point (location of automatic monitoring device).

Daily maximum levels

The daily averages also present the previously indicated mitigating circumstance of the alternating wind pattern. Nonetheless, any change in that cyclical wind pattern could have an adverse impact on the average concentrations in some area. The attached figure shows the distribution of the average daily maximum levels obtained at each point of the landscape. The level of 50 *m*g/m^3 has been emphasized. As can be seen in the figure, it remains completely within the safety area (the RD 102/2011 air quality regulation allows this average daily value to be exceeded a maximum of 35 times).

8-hour maximum levels.

The 8-hour value is the objective for monitoring as detailed in the workplace safety and hygiene regulations and establishes a maximum exposure limit of 0.5 mg/m^3 for a worker during an 8-hour workday. In this way, the numerical simulation solutions of the 8-hour maximum levels presented in the figure below also show the predicted levels are above the reference level only within the restricted area.

Absolute maximum levels

Without any legal reference, the figure below presents the maximum values for the simulated 10-minute concentrations obtained for the spatial area and time period of the test. The level in those short time intervals clearly can be considerably higher (as was evident in the experimental measurements for estimating the emission rates), and individual values greater than 1 mg/m^3 were reached at some points outside the control area. However, they were frequently of short duration, so that their contribution to longer periods of exposure were strongly diluted, as shown in the previous results.

Perimeter impacts

The estimated average values on that perimeter were represented, based on the assumption that all five sources would be active, as well as where the automatic meter would be placed on site (it is depicted as "control" in the figure and, even though its real position was close to the perimeter fence, its value is emphasized in the upper part of the figure –the legend refers to intervals of concentration in *m*g/m^3-).

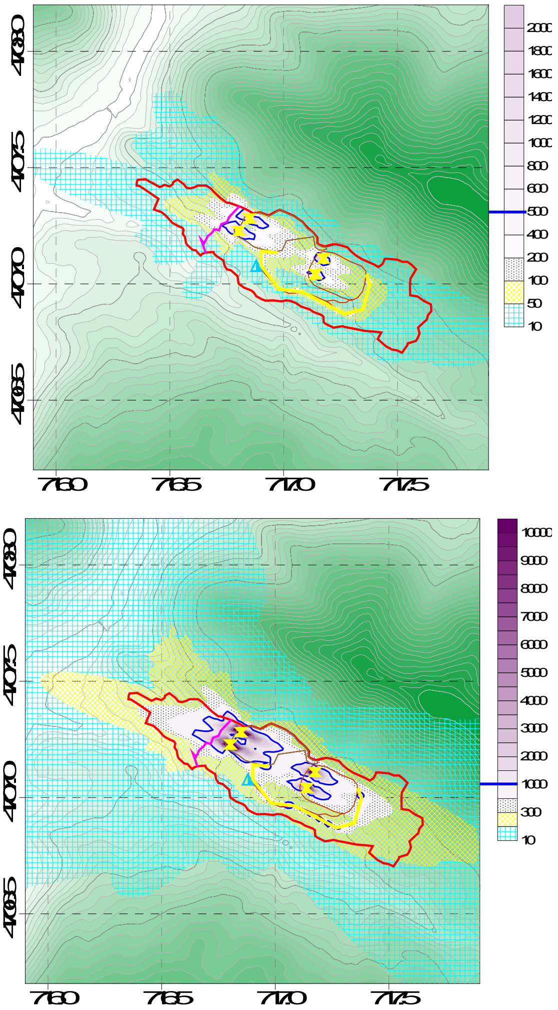

Figure 8: Spatial distribution of the simulations of the 8-hour maximum concentrations of PM10 (left) and the absolute maximum levels (right) obtained over the entire time period.

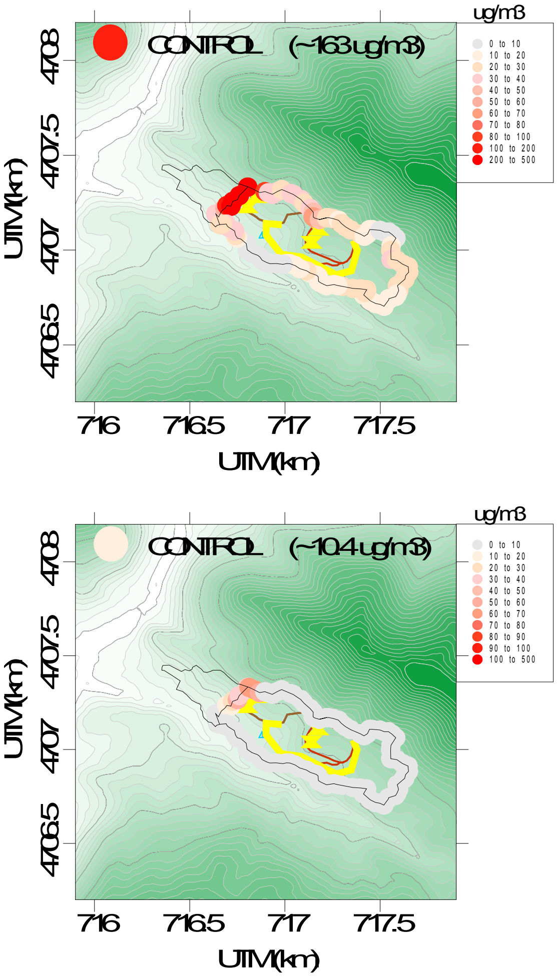

Figure 9: Simulation of the expected 8-hour maximum levels of concentration (left) and daily maximum levels (right) on the exclusion perimeter and the control point.

Surveillance program

The results of the numerical modeling of the atmospheric impact of potential emissions of particulate material derived from the planned action show patterns of spatial distribution of concentrations with the maximum levels limited within an exclusion perimeter (introduced in the previous point), but extending outside that area primarily on its west-northwest border, as the concentration maps show. That is the location where the automatic monitor unit of the particle immission levels (GRIMM model with three granulometric fractions, for PM10, PM2.5 and PM1) was placed and established a control point for recording the atmospheric concentration in a particularly unfavorable area. Starting from this experimental value and the meteorological tower measurements (wind readings), the simulation results enabled estimates to be made of the maximum values possible at those sensitive points of the site, taking the appropriate control actions if the readings indicated there was a risk of exceeding the permitted levels (in a conservative procedure of surveillance and monitoring the operations).

Similarly, two high volume samplers (PM10 and PM2.5) were deployed next to total settling particle samplers at fixed points on the site (see figure 10) to simultaneously capture samples taken over 37 active time periods during the five months the operation lasted. Its goal, not included in the present work, is to obtain an experimentally adjusted balance of the total amount of solid material in the environment resulting from the atmospheric dispersion caused by handling of the deposits.

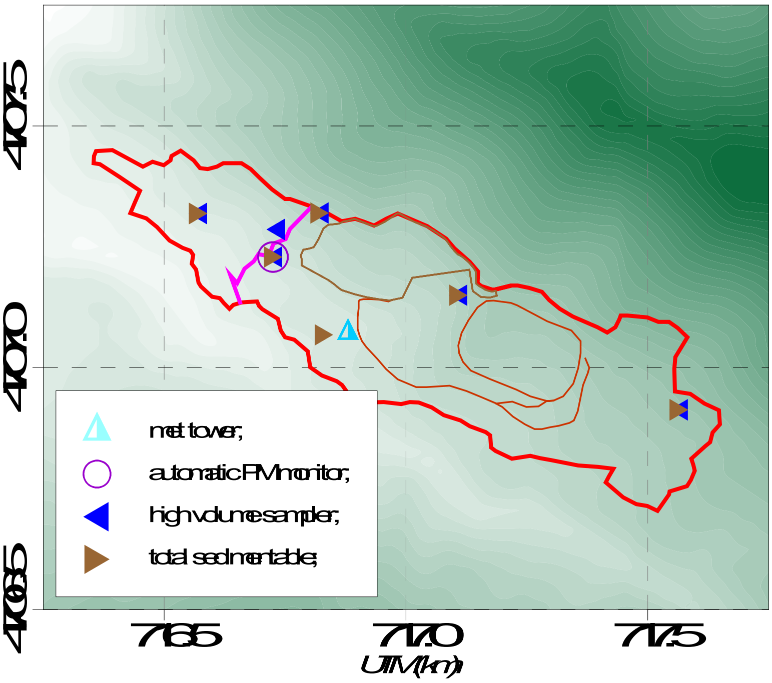

Figure 10: Monitoring deployment during operation.

Conclusions

The works presented here collect the actions involved in evaluating the potential atmospheric impact due to particulate material derived from the activities planned for the transfer of the old Bailín landfill to its new site. As a typical atmospheric dispersion problem, the specific needs of the jobs involved (the intrinsic risk of the material being handled, the need to ensure sufficiently low levels of concentration outside the exclusion area, the uncertainty regarding diffuse emissions under real operating conditions, the particular orography of the site, ...) required the creation of a plan of action adapted to the nature of the activities themselves and the unique surroundings of the site, always conditioned by limitations of means and time. Providing the supporting justification and design of a monitoring plan was also a fundamental part of the study.

Methodologically, the reproduction of the atmospheric impact of the dust emissions covered various aspects:

ü identification and characterization of the sources (areas and emission rates)

ü selection of time periods that were representative of the air conditions of the environment;

ü simulation of the wind fields and dispersive processes in the selected period;

ü manage the different sources of uncertainty inherents in the nature of the tools and information being handled;

initially the simulations were performed considering single emission rates for each source, which enabled the qualitative assessment of the patterns of the impacts created;

various field experiments provided an initial estimate of the emissions rates associated with the sources being studied, which quantitatively corrected the estimates;

the placement of a monitor for continuous measuring of the concentration levels allowed for a realistic way to adjust the immisions field with real measurements;

ü formulate the results in terms useful to the manager/operator;

- *average levels of concentration over the entire simulation period (with reference to the air quality regulations establishing an annual net limit of 40 mg/m^3 of PM10);*
- *average daily maximum levels of concentration (with reference to the same regulation, setting a limit of 50 mg/m^3 of PM10 for this parameter);*
- *average maximum levels of concentration over an 8-hour period (with reference to the workplace health and hygiene regulation setting a limit of 0.5 mg/m^3 of HCH).*

Specific analysis of the summer pattern shows high regularity in the daily cycles, with a well-defined wave in every month and for all magnitudes considered; the thermal winds of the valley/ mountainside govern the movement of air currents on the surface levels, assuring good ventilation of the basin in general; the frequency of calm periods, fewer of them during the summer, introduce periods of the day with frequencies greatly above the normal averages, and coinciding exactly with the transition of the night/day flows.

The results shows a strong channeling effect through the entire axis of the riverbed, with a pattern of markedly longitudinal impacts and strong restriction to any lateral dispersion given the significant orographic barriers:

Over short distances, the variable environmental conditions prompt abrupt changes in the individual levels of concentration; they turn out to especially unfavorable with respect to the accumulation of high concentrations during calm periods as well as at night, as the steady outflow winds favor the down valley impacts (important when the greater part of unprotected activity is found in this area).

The expected levels of concentration which may exceed the legally allowed parameters generally do not appear to go outside the maximum protection area. Nevertheless, short-term impacts are estimated that can reach substantial values.

Regarding estimates of the impact of particulate material strictly speaking,

- ü the *absolute average levels* of concentration over longer time periods are reduced, given the alternating flows between night and day, characteristic of the atmospheric dynamics in a site like the one studied;
- ü the maximum daily levels, as in the prior case, show an important mitigating factor, quantitatively placing them around the lowest values;
- ü the *maximum 8-hour levels* (a special target for monitoring in the workplace safety and hygiene regulation, with a maximum limit of exposure of 0.5 mg/m^3 for a worker during an 8-hour workday) above the reference limit were only obtained inside the restricted area;
- ü the *absolute maximum levels*, lacking any explicit legal reference, for these short time intervals could be considerably elevated although of short duration;
- ü the *perimeter impacts* permitted an analysis of the sensitive zone, as well the preferred "export" route of the potential emissions outside the restricted area. In all cases, they adjust to the wind dynamics analyses in the other experiments performed; the area that potentially would suffer the greatest harm was chosen as the site for the continuous measurement unit.

The implementation of a monitoring plan was based in the placement of an automatic multiparticle continuous monitor at a sensitive point of the site, as well as six high volume and total deposition samplers deployed at significant places around the operating area. The combination of immission and meteorological measurements (coming from the tower on site) with the normalized solutions of the model for the spatial distributions of the concentrations, quantitatively adjusting the concentration values present at each point, sufficiently to enable decision making (including the use of dust reduction systems, temporary interruption of particular jobs and/or protection of the excavation faces).

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MONITORING OF POPs IN CZECH RIVERS BY PASSIVE SAMPLERS. INTERPRETATION OF RESULTS BY ADVANCED INFORMATION ANALYSIS BY ROBUST ALGORITHMS

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Abstract

Advanced techniques of sampling have been introduced especially for suspended sediments and biota. A combination of several biotic matrixes were selected to give a proper assessment of existing pressures and definition of programs of measures. Passive samplers as screening devices have been used within a Czech National water quality monitoring network since 2003 (SPMDs and DGTs). The monitoring of polar substances in surface water was introduced in 2005. This comprehensive design was selected to get total impact on a given location, representing the whole catchment and enabling identification of the biologically available phase for source identification. In order to secure a representative dataset, an appropriate quality system (ISO 17025) was adopted for the methods used, e.g. method validation, using reference materials, duplicate samples, PRCs for SPMDs, etc.. Along with SPMDs, several other matrixes were used: suspended sediments, sediments and various biota samples. The bio-monitoring program has been set up at 44 locations of the surface quality monitoring network since 2000, whereas a whole set of matrixes mentioned above has been monitored at 21 selected locations since 2003. In terms of monitored parameters, the main attention has focused on the PCB, OCP, PAH, PBDE, or PCDD/F.

Data were evaluated by classical and robust data analysis, called Advanced Information Analysis. Basic ideas of AIA is based on the theory mathematical gnostics, that are briefly described as a methodology comprising:

1. gnostic theory of individual uncertain data and of their samples,
2. methods of data analysis based on this theory,
3. programs realizing these methods,
4. examples of applications of the methods.

Key Words

Passive samplers, advanced information analysis, POPs

Materials and methods

For all experimental work, following standard design of SPMDs was used: the lay flat thin-walled tube of non-porous (with transient cavities) material LDPE, filled with 1 ml of synthetic lipid – triolein, neutral triglyceride (1,2,3-tri-[cis-9-octacenoyl]glycerol) of high purity (>97%), which makes a thin film in membrane. The parameters: width 2.5 cm (lay-flat), overall length 91 cm and wall thickness 75 -90µm, overall sampling area is about 460 cm^2, total about 4.5 g. Exploded view of overall SPMDs is given in Figure 1. Transports of contaminants were through transient pores, with specific diameter approx. 10^{-9}m (similar to postulated size of transient cavities in biomembranes as 9.8 10^{-9}m). The use is confronted with non-standard PS, in spite of some attempts for their calibration[1]. On the other hand, the use as a tool for effective method of separation of organic contaminants from lipids, based on SPMDs is demonstrated. The Figure 2 brings used sampling arrangements. For underground water, the protective shroud was developed within this thesis. This new design (to be soon patented) allows installation two (instead one) SPMDs (e.g. 1 for toxicity and 1 for chemicals).

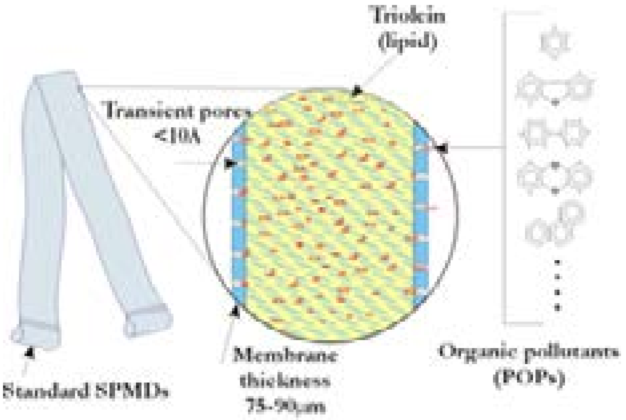

Figure 1 Exploded view of standard SPMDs

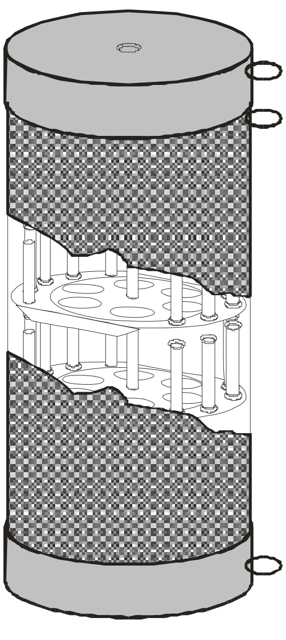

Figure 2 Sampling arrangements – protective shrouds for SPMDs for surface water

Based on detailed insight of chemical uptake, the ambient concentration was estimated from:

$$C_{W,i} = C_{S,i} V_S / R_{S,i} t$$

The term $R_{S,i}$ is the *sampling rate* parameter of contaminant *i* and provides a conceptual link between classical extraction techniques and passive sampling with SPMDs. Term $R_{S,i}t$ can be understood as a volume of water, in which contaminant $C_{W,i}$ is dissolved. Sampling rate is in L.d^{-1}, which can be interpreted as the volume of water (L), dialysed per day, for particular contaminant (*i*) and time(*t*), found in SPMDs(denoted as $C_{S,I}$), having total volume $V_{S.}$ Sampling rates were used for calculation of ambient concentration of contaminant $C_{W,i}$. They were used for a large number of compounds: PAHs, PCDDs/PCDFs[2-7], PCBs[1, 5-10] and a number of polar pesticides[6-8, 10]. The calculations were adopted from recent publications[1, 9]. At latter phase, the PRCs (Performance Reference Compounds) approach was used, based on the principle of use the kind of internal standards (PRCs), added prior the exposure into SPMDs devices, considered SPMDs as calibrated *in-situ*. Evaluation is then based on the amount of dissipated PRCs and those found at the beginning of the sampling[2, 4, 6]. Adopted general requirements for deployment were recently described[1, 3].

Used biota, bioassays

Biotic organisms, *Dreissena polymorpha* were used for comparison to SPMDs; they were collected in sand-pit with very clean water. Small shells were placed in polypropylene cages (100 pieces/cage) and fixed at the same float as SPMDs.

The toxicological response was based on EC$_{50}$, expressed as the V_{TOX} parameter that was developed during our research recently[11]. There were used following tests: *Vibrio-fischeri*, acute toxicity test with cladophora *Daphnia pulex*, test with rainbow trout *Oncorhynchus mykiss* and test of inhibition of algal growth of *Scenedesmus subspicatus* and/or *Selenastrum capricornutum*[11-14]. Test with bioluminescent bacterium was carried out following the standard procedures (ISO 11348)[12].

Novel approach to data samples

To actually realize estimation one needs more than one piece of data because all gnostic characteristics are parameterized by two parameters, the true (unknown) and observed (known) datum's value. The fundamental problem is that of composition of data and of their uncertainties. The most logical process is to make use of the proved isomorphism between uncertain data and relativistic energies and moments of some particles. It is well-known that the composition problem of special relativistic mechanics is solved by the Energy and Momentum Conservation Law which requires the energies and moments of a system of particles to be composed additively. If the correspondence of a data sample with the system of particles is to be consistent with the correspondence of individuals then the quantifying irrelevances and weights of individual data must also be added to result in gnostic characteristics of the sample. The second gnostic axiom accepts this composition law for not only quantifying but also for estimating irrelevances and data weights. The following results are derived from this axiom:

1. Formulae of both kinds of irrelevances and data weights of a data sample and analysis of their robustness.
2. Four types of probability distribution functions: global estimating, local estimating, global quantifying and local quantifying d.f. along with analysis of their features, robustness and application fields.
3. Relations between irrelevances, probabilities and robust estimates of covariance.
4. The role of finiteness of a distribution's domain (data support) and the data transformations necessary for estimation of the domain's bounds.
5. Estimation of several types of scale and location parameters.
6. Impacts of censored data onto distribution functions.
7. Applicability of the estimating d.f. to a detailed analysis and classification of sub-samples and to evaluation of the degree of similarity of two samples.
8. Testing of homogeneity of a data sample.
9. Objective estimation of unique bounds of membership intervals of a homogeneous data sample.
10. Making use of gnostic characteristics of uncertainty as criterion functions in estimation of parameters of distribution functions and for a robust multidimensional modelling. A detailed analysis4) of the latter problem shows the broad field of its applicability. Using the information as a criterion for optimization of estimation ensures the best possible information in results.

As already mentioned, gnostic characteristics can be thought of as path integrals over some curved (Riemannian) spaces. It is of fundamental importance that the metric of these spaces (the way of measuring distances, angles and curvature) result not from some a priori (and subjective) assumptions but solely determined by the data to be treated.

The original mathematical background of gnostics5) was extended and completed6) with respect to the fast growth of the world's information industry in which information became a scarce economic good. Proper measuring of information born by data and maximization of its yield is therefore an important task.

RESULTS, DISCUSSION

Advanced information analysis

The foregoing has prepared the way to introduce the concept of Advanced Information Analysis (AIA) which will be interpreted as an analysis which respects the objectivity of data and aims to draw out the maximum of information while letting the data decide the fundamental problems of their treatment. The basic rules of advanced data analysis include following:

1. Do not violate the data by subjecting them to unjustified a priori models or distribution functions such as:
    - trimming the data sample, imposing on them some a priori chosen distribution functions and other requirements,
    - not respecting the data finiteness.
2. Make use of all available data by:
    - including censored data,
    - including suspected adequately weighted outliers and inliers,
    - excluding data only after proving their negligible impact on results.
3. Let data decide the:
    - bounds of data supports,
    - outlier/inlier (`membership') problem,
    - sample's homogeneity,
    - structure of inhomogeneous data samples,
    - the metric of data space,
    - determination of individual data errors and weights,
    - proper choice of a data model.
4. Do not shun the use of good non-statistical methods when statistics fails or when its application is not appropriate.
5. Use distribution functions instead of point estimates for data characteristics to get more information from data.
6. Take as similar/comparable only objects which behave in accordance with the same mathematical model.
7. Do not blame randomness for effects. Try to explain their causes by using the data.
8. Prefer robust estimation and identification methods over no robust ones.
9. Select the desired kind of the method's robustness (inner/outer) with respect to any given task..
10. Apply realistic criteria (information/entropy) to optimization.
11. Respect theoretically proved optimal paths for data transformation by using gnostic formulae to measure data errors and data weights.
12. When in doubt on interpretation of results of analysis do not hesitate to return to the original data and in case of necessity look for a priori information to explain the "strange" or unexpected results and to confirm them.

AIA programs

Programming of gnostic methods has been running all the time in parallel to the development to verify the viability of the concept by applications to solving real problems. After a long series of academic versions, a commercial user-friendly Gnostic Analyzer for Windows was introduced to the Czech market in 1995.

Currently, the most advanced version recently exists programmed in the R-project®, that is platform independent interface is used in Web environment.

Programs meet the requirements to the advanced data analysis.

One-dimensional Analysis (Marginal analysis)

AIA marginal (one-dimensional) analysis is based on a consequent usage of the program for estimation of four types of gnostic distribution functions. Its features include:

- Applicability without any a priori assumptions on the distribution function.
- Applicability to both additive and multiplicative data.
- Applicability to three types of censored data.
- Applicability to compressed data (such as a histogram).
- Applicability to homoscedastic and heteroscedastic data (constant or variable scale parameter).
- Robust estimation of the scale parameters.
- Robust estimation of bounds of the data support.
- Test of data homogeneity and classification of outliers.
- Robust estimation of the location parameter (mode).
- Robust estimation of probabilities and densities of probability for arbitrary data.
- Robust estimation of quantiles to given probabilities.
- Objective robust estimation of membership bounds of a homogeneous sample.
- Robust monitoring, filtering and prediction of time series.
- Robust cross-section filtering of data.
- Robust marginal cluster analysis.
- Classification of data sub-samples.
- Evaluation of the degree of similarity between two samples.
- Robust estimation of covariance and correlations.

The problem of membership bounds deserves a special comment because of its relation to diagnostics.

Quantitative diagnostics

This problem is important in decision making based on measurements in many fields like medicine, environmental control, production quality assessment, rating of financial positions, etc: "Can this observed value be accepted as a member of a set of values attached to a certain diagnosis?" A frequent method of establishing the bounds of the membership interval for a data set is to accept values where is the mean and the standard deviation of the set. A crucial role is played by the multiplier dependent on the probability of rejected candidates for membership (significance of the test). Such a method is subjective not only because of the hidden assumption of normal (Gaussian) data distribution but also due to a "freedom" in choosing the multiplier. The outcome of such a test is not what data say but what the user wishes.

Gnostic membership intervals are based on the unique feature of the global distribution function of a homogeneous data sample: its density function has only one maximum. If one considers a fixed data sample extended by another (variable) piece of data ( ) then there exist exactly two 's values (the lower and upper bound) at which inflexions appear in the density of the extended sample. The procedure includes: extraction of a homogeneous sub-sample of the data sample, optimization of its data support bounds and of its scale parameter and finally finding the values of the fictitious extension causing the density's inflexions. Results of these operations are determined only by data, they are objective. Each of the found bounds are unique characteristics of the data sample.

AIA Multi-dimensional Analysis

As already mentioned, usage of gnostic criterion functions opens the way to robust estimation of parameters of both linear and non-linear multi-dimensional models. Gnostic programs have been developed for solving the most frequently tasks of MD-analysis

1. Robust estimation of parameters of an MD linear regression of four types:
- Explicit regression of data.
- Implicit regression of data.
- Explicit regression of data probabilities.
- Implicit regression of data probabilities.
2. Robust estimation of correlation matrices.
3. Robust extraction of homogeneous kernels from non-homogeneous MD objects applicable to the cluster analyses in MD space. Robust cluster analysis of inhomogeneous objects.
- Cross-section analysis and monitoring of MD objects.
- Robust monitoring and prediction of MD time series.

The ordinary (explicit) form of the regression model is based on a (hidden) assumption: it is possible to choose one variable (that is to be explained) and which is "only dependent" on the other variables assumed to be explanatory ones. Such an assumption can rarely be applied to real multi-dimensional objects or processes because of feed-back existing between all variables.

The probabilistic regression is also worth attention: if data are interdependent so their probabilities do as well, but in a non-linear way. Gnostic probability is a simple linear function of the estimating irrelevance so that . It follows that probability evaluates irrelevance's deviation from its zero value. It can be interpreted as a non-linear (Riemannian) generalization of the error measured (in the Euclidean way) by data's deviations from zero (recall that estimating irrelevance is a non-linear function of a datum robust with respect to outliers). As shown in gnostics, the robust estimate of a covariance can be obtained as a product of irrelevances (in an analogous manner like in classical non-robust case). It is well known that the classical solution of the linear regression task is determined by covariance. It is therefore natural to use the gnostic method of the regression in probabilities instead of traditional data regression. An additional advantage is obtained in that all variables as well as the model coefficients are dimension-less. This makes the interpretation and usage of results easy.

All four mentioned regression models are robust when a gnostic criterion function is applied to calculate them instead of the classical applications of the Least Squares method.

Assessment of Environmental data

In recent years, many efforts have been focused on the threats from harmful effect of chemicals on the environment and consequently on human health. The biomonitoring, along with other environmental chemistry and toxicology are very complex, covering both classical chemistry, toxicology, as well as branches like biochemistry, limnology and ecology. As a basement for evaluation, both generic and monitoring data reflecting the actual state of the environmental and health status indicators are used. Final point of the assessment is an evaluation of all those complex data to yield information for practical environmental management of chemicals, with such practical aims as their identification, description and allocation of their sources, definition of the policy for continuous limitations, and conditions of sustainable development.

The group of unwanted chemicals playing toxicological relevance due to their properties includes persistent toxic substances (PTS), with a sub-group of persistent organic pollutants (POPs). This group is composed of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), organochlorinated pesticides (OCPs), as well as hexachlorobenzenes (HCBs). Heavy metals also belong to important parameters contributing to toxicity . All these chemicals are characterized by persistence, bioaccumulation and bio-concentration (including the effect of bio-magnification) and long-range transport in the environment. In consequence of input by various pathways, they are readily absorbed in fatty tissue. Fish, predatory birds, mammals, and humans are high up in the food chain and absorb the greatest concentrations.

As a result from some important UN actions (e.g. Stockholm Convention for POPs), we have performed several studies for monitoring of POP in various environmental compartments. It is worth saying that routine monitoring data had often a typical feature: small data set for which the statistical approach was difficult to apply, so that gnostic analysis (GA) played an important role for proper interpretation of measured data. Demonstrations presented as examples stem from monitoring selected POPs and heavy metals in Czech rivers in biotic organisms. There were following analyses considered:

- distribution functions (d.f. or DF): empirical (EDF), estimating local (ELDF), and estimating global (EGDF),
- homogeneity test of a data sample,
- bounds of a data sample,
- weights of data,
- cross-section data filtering,
- data censoring,
- heteroscedasticity,
- robustness of used distribution functions,
- interval analysis of a data sample,
- analysis and comparison of used sampling methods,
- comparison of contamination profiles.
- It is important to say that this list of tasks is to be understood as an example of gnostic approach to data evaluation, not as a complete review of results.

Conclusions

AIA methodology based on mathematical gnostics represents a powerful instrument for a deep and reliable data analysis yielding maximum information.

It can also be useful for environmental applications. It results from experience with both uni- and multivariate gnostic analysis that this methodology is suitable for complex chemical analyses and toxicity problems. The package of presented methods should not universally replace statistical approach, which has its own broad application field. However, gnostic methods are especially efficient in cases of small samples of strongly uncertain data.

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A CONTEMPORARY ASSESSMENT OF POLYBROMINATED DIPHENYL ETHER (PBDE) IN THE AMBIENT AIR AND SOIL OF AZERBAIJAN

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Abstract

PBDEs were measured in air and soil across Azerbaijan to establish contemporary concentrations at 13 urban and rural sites. Polyurethane foam passive air samplers (PUF-PAS) were deployed for a period of a month with surface soil samples collected at the same sites. Unlike organochlorine pesticides previously surveyed by our group, PBDE concentrations in both contemporary air and soil were low in comparison to recent European and Asian studies. For example, mean $\sum_{10}$PBDE concentrations in air and soil were 26.9±15 pg m^{-3} and 168±57 pg g^{-1}, respectively. Surprisingly, the fully brominated BDE-209 was the most abundant congener observed in both air (25.21 ± 15 pg m^{-3}) and soil (174.8 ± 58.5 pg g^{-1}), comprising ~93% and 96% of $\sum_{10}$PBDE in air and soil, respectively. However, the PAS-derived air concentrations for this congener and other highly brominated congeners must be viewed with caution as there is uncertainty over the uptake rates of particle-bound chemicals using these devices. Some of the highest concentrations in air were observed at sites with the highest wind speeds and at several remote locations in the north of the country and this requires further research. Levels of BDE-47 and 99 (the two most abundant congeners in the widely used penta-formulation) were lower than levels reported elsewhere suggesting limited use/import of the penta-BDE formulation in Azerbaijan.

MODIFICATION OF PASSIVE SAMPLERS FOR NARROW DRILL - HOLES

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Abstract

Monitoring of pesticides is challenging area. However, current approaches are connected with description of the contamination status on compounds identified in the monitored objects. Particular systematic improvement is connected with target identification of those chemicals that have been used and their traces caused contamination. For the case of pesticides, use in agriculture emphasizes the importance of saving drinking water reservoirs. The methodology is carried out with target principle, e.g. using screening methods for identification of contamination. The range of parameters are set-up with the knowledge of used chemicals from the time and spatial distribution; the interconnection is realised by transport characteristics, used for prediction of chemical behaviour and the description of greatest risk to drinking water. A modification of standard sampling tools based on two-phase passive sampling systems was performed, called micro-PS.

Key Words

Passive samplers, pesticides, monitoring, drinking water

Materials and methods

A screening tool was based on the passive sampling tool for polar and non-polar chemicals, based on POCIS and SPMDs respectively. Those techniques have been recently used in many environmental applications for assessment of contamination of broad scale compounds. SPMDs were used for non-polar organics like OCPs[1-4], PCBs[1, 2, 5, 6], PCDD/Fs[7, 8], PBDEs[9, 10], whereas POCIS was used for numerous polar compounds like pesticides, pharmaceuticals and other similar compounds[11-16]. Particular construction with appropriate modification was designed for a placement of drill narrow wells with diameter 32x25mm, and lengths of individual segment 1m, used with bentonite collar. That system was chosen as developed by Eijkelkamp™ made from HDPE and considered as good standard for ground water quality monitoring, used worldwide. Novel construction of modified passive sampling devices, denoted as micro-SPMD and micro-POCIS is placed into groundwater monitoring, with screw-thread connection.

Individual segments of micro-SPMDs has 30 cm length whereas micro-POCIS has 10 cm.

Sampling arrangement

Individual segments are mounted according to end applications, and are defined by following parameters: the nature of the substances, required detection limits and sensitivity of the used analytical methods. During exposure, they are usually placed in configuration of 2-3 segments micro-SPMD side by side, one to three segments of micro-POCIS above. Segments also defines the resolution of elevation layers. For most applications, there is sufficient resolution layers about 50 cm, comprising the detection of polar and non-polar substances. Kit segments is quite variable, with a fixed anchor, enabling their application from the bottom to the neck of drill hole.

Exposure time depends on the anticipated level of contamination; usually from two to four weeks, as is the case with standard systems.

Overall schematic layout is on the figure below.

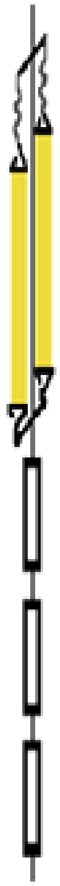
Arrangement	Configuration/position
	micro-SPMD non-polar compounds 1-3 pcs, efficient mounting
	micro-POCIS polar compounds 1-3 pcs, screw-thread connection

Figure 1 General scheme, with exploded micro-passive samplers as to be placed into the well pipes

Performance tests

Prior the use, suitability of that method and chemical based passive samplers to determine exposure to these compounds was tested by deploying them in selected Waste water treatment plant effluent, to provide measurable levels of target contaminants. There, following comparisons were performed:

- Standard PS and micro-PS,
- Comparability of micro-PS, expressed as RSD%.

For underground water, simulation tests for low flows and sampling rates, comparable to column tests. Under that test, PS were exposed in water with known amounts contaminants, to verify marginal conditions for micro-PS applications and linearity.

Analytical methods

A conventional, validated and accredited methods were used for measurement of selected compounds. Exposed PS were dialysed with appropriate solvents (hexane for micro-SPMDs, methanol for micro-POCIS). PRCs based on PCBs and PAHs were used for quantitation and Rs of non-polar compounds, polar compounds were quantified without using of PRCs due to used sorbents in micro-POCIS. Analytical methods based on liquid and gas chromatography fitted with mass detection (namely GC-MS/MS, LC-MS/MS ThermoFisher Scientific) were used for analysis[16].

Results and discussion

Detailed construction of the system is under patent pending and cannot be fully revealed.

However, reproducibility of novel micro-PS were observed. Majority of polar and non-polar compounds has revealed RSD in the order of magnitude of 20-30% (N=5). In general micro-SPMDs for non-polar organics exhibited more reproducible results (Me=17%), than micro-POCIS (Me=29%). That is in good agreement in standard PS arrangement.

Selected results for both micro-PS are given on the tables 1 and 2 below.

	micro-POCIS ng/POCIS	micro-POCIS ng/POCIS	micro-POCIS ng/POCIS	micro-POCIS ng/POCIS	micro-POCIS ng/POCIS	Average ng/POCIS	RSD ng/POCIS
PFOA	3.5	3.4	3.9	2.3	2.1	**3.0**	**26%**
MCPA	4.0	3.3	4.8	5.4	11	**5.7**	**54%**
Mecoprop	3.1	2.9	4.9	3.8	6.2	**4.2**	**33%**
Dimethoat	1.0	0.57	1.8	0.88	1.1	**1.1**	**42%**
Hexazinon	1.2	1.1	1.7	1.1	1.4	**1.3**	**20%**
Atrazin	4.5	4.0	7.3	3.0	3.7	**4.5**	**37%**
Diuron	21	15	26	12	18	**18**	**29%**
Azoxystrobin	1.5	1.1	2.1	1.5	1.7	**1.6**	**23%**
Terbuthylazine	13	11	18	8.1	15	**13**	**29%**
Metolachlor	5.1	4.3	6.6	3.6	5.7	**5.1**	**23%**
Acetochlor	2.0	1.3	1.5	1.8	2.5	**1.8**	**26%**
Terbutryn	16	14	26	13	18	**17**	**30%**
Tebuconazole	11	10	18	11	15	**13**	**26%**
Propiconazole	7.8	6.0	11	5.2	6.7	**7.3**	**31%**
Metazachlor	1.1	0.73	1.2	0.36	1.2	**0.92**	**40%**
Carbamazepin	420	320	610	310	500	**432**	**29%**
Sulfametoxazol	33	26	56	27	41	**37**	**34%**
Diclofenac	370	280	470	260	400	**356**	**24%**

Table 1: Selected polar compounds sampled by micro-POCIS; multiple sampling

	micro-SPMD ng/SPMD	micro-SPMD ng/SPMD	micro-SPMD ng/SPMD	micro-SPMD ng/SPMD	micro-SPMD ng/SPMD	Average ng/SPMD	RSD ng/SPMD
Naftalen	2.7	3.9	4.8	5.9	6.4	**4.7**	**32%**
Acenaftylen	7.4	7.5	6.9	6.5	8.1	**7.3**	**8%**
Acenaften	58	59	56	67	78	**64**	**14%**
Fluoren	7.5	7.6	6.9	8.9	10.9	**8.4**	**19%**
Fenantren	0.57	0.57	0.19	0.48	0.44	**0.45**	**35%**
Antracen	0.49	0.87	0.58	0.54	0.61	**0.62**	**24%**
Fluoranten	18	17	17	17	16	**17**	**4%**
Pyren	0.60	0.83	0.67	0.28	0.63	**0.60**	**33%**
Chrysen	10	10	8.9	9.0	9.0	**9.4**	**6%**
Benzo(a)antr.	8.0	8.1	7.5	7.0	7.6	**7.6**	**6%**
BBF	78	67	74	56	50	**65**	**18%**
BKF	39	34	32	32	29	**33**	**11%**
Benzo(a)pyren	47	41	35	36	30	**38**	**17%**
TriclosanMe	130	120	140	120	130	**128**	**7%**
Triclosan	180	180	170	220	250	**200**	**17%**
124triClBz	0.47	0.68	0.39	0.66	0.49	**0.54**	**23%**
1234tetraClBz	0.25	0.16	0.20	0.14	0.14	**0.18**	**26%**
PeClBz	0.82	0.80	0.97	0.76	0.52	**0.77**	**21%**
HxClBz	3.1	2.1	2.3	3.1	2.3	**2.6**	**19%**
PBDE28	0.035	0.056	0.025	0.005	0.020	**0.028**	**67%**
PBDE47	0.49	0.54	0.45	0.47	0.57	**0.50**	**10%**
PBDE100	0.047	0.053	0.048	0.060	0.041	**0.050**	**14%**
PBDE99	0.32	0.34	0.25	0.31	0.25	**0.29**	**14%**
opDDE	0.19	0.22	0.22	0.11	0.20	**0.19**	**24%**
ppDDE	1.5	2.1	1.8	1.7	1.7	**1.8**	**12%**
opDDD	3.9	4.2	4.0	3.7	3.3	**3.8**	**9%**
ppDDD	0.58	1.0	1.0	0.69	0.58	**0.77**	**28%**

Table 2: Selected non-polar compounds sampled by micro-SPMD; multiple sampling

As for calibration, there are on the graphs below, as representative for non-polar and polar compounds. In general, for both SPMDs and POCIS, there were well correlated responses to calibrating solutions.

Conclusions

Newly developed monitoring system for assessment used pesticides and their leakage from various sources was used. That system allows sufficient flexibility for both special and multilevel contamination of drinking water. Innovative approach uses the structural design of the borehole. The solution was compared to standard design and exhibit high reliability of data for further use in transport modelling: sensitivity, reproducibility, time-weighted evaluation of target contaminants in drinking water. Using that technique with robust multivariate methods can reveal spot of contamination. The calibration shows linearity response between found concentrations and those found in PS. However, for broader applicability, we need to understand well fluxes in the well that is challenging for further development.

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GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS UNDER STOCKHOLM CONVENTION - SECOND CENTRAL AND EASTERN EUROPEAN REGIONAL MONITORING REPORT

SUBMITTED PAPER

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Abstract

Article 16 of the Stockholm Convention requires the Conference of the Parties to evaluate periodically whether the Convention is an effective tool in achieving the objective of protecting human health and the environment from persistent organic pollutants. This evaluation is based on comparable and consistent monitoring data on the presence of POPs in the environment and in humans, as well as information from the national reports under Article 15 and non-compliance information under Article 17. The global monitoring plan for POPs introduced under the Convention is a key component of the effectiveness evaluation and provides a harmonized framework to identify changes in concentrations of POPs over time, as well as information on their regional and global environmental transport.

The 2nd Central and Eastern European monitoring report is synthesizing information from the first and second phase (i.e. until 2008 and until 2014 respectively) of the global monitoring plan and presents the current findings on POP concentrations of all listed chemicals in the Central and Eastern European Region - including baseline concentrations and trends where available.

Key Words

Global POPs monitoring Plan, Stockholm Convention on POPs, Central and Eastern European monitoring report

Materials and methods

This second regional monitoring report synthesizes information from the first and second phase of the global monitoring plan and presents the current findings on POPs concentrations in the Central and Eastern European Region. The UN region of the Central and Eastern Europe covers 23 countries of the Central and Eastern Europe. In addition, five countries of the Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan) were also included to the regional report, as agreed in discussion between relevant Regional Organization Groups due to similar pattern of production and use of POPs, geographical proximity and language issues. Thus, this regional report covers 28 countries.

The second phase of the global monitoring plan was undertaken in the period 2009-2014 to determine trends in concentration of persistent organic pollutant in humans and in the environment, and to obtain baseline data on the persistent organic pollutants that have been listed in the Convention after the year 2009. Data available in this report cover 1996-2014 for air and 1987-2014 for breast milk.

It has to be noted that for ambient air monitoring a relatively small amount of international/regional programmes cover the whole CEE GMP region such as EMEP, MONET, and GAPS. Some of the monitoring activities are lasting for decades (since 1980s), however they cover a limited scope of Stockholm Convention chemicals (seven or eight chemicals). Other air monitoring activities were only initiated simultaneously with the end of the first phase of GMP data collection round (from 2006 onwards) or by the very end of that period (post-2008). Nevertheless, the long-term sustainability of both the long-term and the most recently established programmes remains crucial for the production of representative and comparable data in the CEE region in the future. This fact is also valid for any future effectiveness evaluation of the implementation of the Stockholm Convention.

For ambient air monitoring, both active sampling and passive sampling techniques organized in the pan-European or global monitoring networks are used to generate data under the global monitoring plan in the CEE region.

For human tissues, the WHO surveys and UNEP/WHO surveys serve are the core data provider, however a number of national monitoring programmes/activities exist, but cover a limited range of chemicals.

Other matrices, such as water, or other media are not regularly monitored in a regional scale programme. A diverse and limited information exists from various sources that are rather of episodic than of the regular nature. Relevant information is provided through research publications and report, however they do not represent a regular and regional scale activity.

Sampling, analyses and data management procedures are instrumental arrangements to produce quality reports. Global analysis of the first regional reports2 revealed that to allow maximum comparability, sampling, data handling and data analyses need to be undertaken in the uniform manner, structure and with globally agreed standards, both retrospectively (where possible), but most importantly towards the future. Any changes in the methodology need to capture also previous data. For the above, the CEE region therefore fully supported development and use of the global electronic data collection system and strict coding of data format, range of additional information covered. Moreover, the CEE region continues using standard/validated methodologies for sampling, analyses and data handling, so that maximum comparability of collected information is ensured.

Finally, all relevant available representative data for POPs levels in the CEE region are stored in the GMP Data Warehouse in the required format (annually aggregated), covering the maximum time span and diversity (range of chemicals) of available representative data.

Though access to this instrument was restricted to experts only in the preparatory phase of this report, the information will be publicly available also in the electronic format (www.pops-gmp.org/visualization) once the report is finalized.

Nevertheless, the CEE region decided to share its monitoring information with its stakeholders continuously. More detailed and gradually updated information on levels of POPs collected in the CEE region is also publicly accessible and permanently available online through the GENASIS database (www.genasis.cz, the Global Environmental Assessment Information System) operated by the Research Centre for Toxic Compounds in the Environment, host of the Stockholm Convention Regional Centre in the Czech Republic.

Results and discussion

POPs GMP data availability and comparability in the CEE region increased since the first phase. EMEP and RECETOX strategic partnerships for air monitoring were expanded and significantly contributed to the establishment of monitoring stations in other countries of the region. The good cooperation among EMEP, GAPS and MONET was highlighted and will be continued in the future. Air data are available for the region for 21 chemicals. The air monitoring activities currently cover 21countries out of 28 that are followed in this GMP region (no information is available for Albania, Azerbaijan, Bosnia and Herzegovina, Georgia, Tajikistan, Turkmenistan, and Uzbekistan). The monitoring combines active and passive sampling and despite the fact that the longest time series are available for chlorinated POPs, more recent information on one site (Košetice, 2011-2013) is available for 97 parameters related to 19 POPs listed in the Stockholm Convention.

Human tissues data are available only through the WHO and UNEP/WHO surveys, with certain information gaps identified for South European and Central Asian part of the region. Data on the newly listed POPs are limited. Information related to POP levels in human blood and in water is not at all available in the region in this report, PFOS levels in water only cover western part of the CEE region.

Results indicate decreasing trends in air concentrations on sufficiently long passive sampling time series (minimum 5 years) for HCB, PCB, DDT, alpha, beta and gamma HCH and PeCB. Data from active sampling of air in Košetice also confirmed decreasing trend for HCB, sum 6 PCB, DDT, alpha HCH and PeCB. Series collected for beta and gamma HCH in Košetice, Czech Republic did not provide a statistically significant trend.

For human milk data, due to limited information, trends are not quantifiable. Likewise for water and other media, where no regular monitoring is conducted.

Long range transport was assessed based on the NILU-MSC-EAST reports for HCB, PCBs and PCDD/PCDFs.

Plans for the future include continuing the strategic partnerships for air monitoring with MONET Europe, GAPS and EMEP, support the operation of the 2nd active sampling station in Leova, Moldova, and further support the information collection from Southern Europe, Central Asia and promote greater involvement of the Russian Federation institutions. The newly developed electronic GMP data warehouse, which was used to support regional data storage, analyses, and presentation, was helpful in preparation of the regional monitoring report and should be used also in further campaigns.

Acknowledgements

Air monitoring activities are implemented in the Central and Eastern Europen Region in cooperation with strategic partners: the Arctic Monitoring and Assessment Programme (AMAP), the Global Atmospheric Passive Sampling (GAPS) Network, the European Monitoring and Evaluation Programme (EMEP) and the MONET Programme of the Research Centre for Toxic Compounds in the Environment (RECETOX).

The human milk survey draws on the collaboration between the Secretariat of the Stockholm Convention, the United Nations Environment Programme (UNEP) Division of Technology, Industry and Economics (DTIE) Chemicals Branch and the World Health Organization (WHO). The State Institute for Chemical and Veterinary Analysis of Food (CVUA), Freiburg, Germany, is acknowledged for the analytical work related to human milk samples. The MTM Research Centre, Örebro University, Sweden, is acknowledged for the analysis and provision of data on perfluorinated chemicals in human milk. Thanks are also expressed to the national coordinators of the joint WHO/UNEP exposure study for the work to collect and process the human milk samples. As well as to the officers of the Stockholm Convention Secretariat who run the survey between 2008-2014 and encouraged wider participation of the countries in the CEE region.

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Last but not least, the authors of this report would like to express their gratitude an acknowledge contribution of all partners and country experts in countries of the CEE region and Central Asia, who supported POPs monitoring endeavours in their countries through MONET-Europe network.

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STATUS OF EECCA COUNTRIES ON OPs AND POPs

ADVANTAGES IN MANAGEMENT OF PESTICIDES AND HAZARDOUS WASTES IN AZERBAIJAN

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Abstract

The pesticides and other hazardous waste management activities carried out in the Azerbaijan in the last 3 years are described. It has been shown that is not specific changes in the legislation. In the National Plan on Environmental protection and rational use of natural resources included plan on OP management problems. The institutional capacity, human resources and administrative management of OP in the Services for State Phytosanitar Controle of Ministry of Agriculture have been improved. The results of last inventory of OP conducted by interministerial commission were analyzed and included into PSMS system. The capacity of the landfill for obsolete pesticides have been increased. More significant work has been done in the field of hazardous wastes treatment technology. Thermodesorption technology for treatment of the oil sludge are applied for utilisation of oil industry wastes. The de-chlorination technology for treatment of PCB-containing transformator oils is used in the National Hazards waste Center. The information about waste centers for OP and other hazards wastes are adduced.

Key Words

Pesticides, inventory, landfill, Waste Center, de-chlorination , Termodesorption

Materials and methods

The analytical methods are used in the researches. Information and Reports from industry, Ministry of Ecology and Natural Resources, Ministry of Agriculture, Ministry of Emergency Situations and other related organizations have been received. State Statistical Committee, Scientific research sector data and the results of the projects carried out by various international organizations have been analyzed comparatively, reliability of the results was provided.

Results and discussion

The results given in this paper is divided into 4 sections: Legislation and policy documents, institutional infrastructure, inventory, storage and treatment of wastes

1.Legislation and policy

Main national Laws on the management of hazardous wastes are:-“On Industrial and municipal wastes”, -“On Phytosanitary Control”, -“On Ecological Safety” and -“Radiation safety of population”.

According to these Laws, there are relevant regulations on the management of hazardous wastes (collection, transportation, storage, neutralization, disposal, etc.).

In the “Action Plan for 2015-2020 on the improvement of ecological condition and rational use of natural resources in Azerbaijan Republic” included the measures of neutralization and removal of pesticides, biological substances, their combinations and packages which are inappropriate for usage and whose usage was prohibited by taking back from their owners were appointed to the State Phytosanitary Control Service under Ministry of Agriculture[1].

2. Institutional capacity

State phytosanitar controle Service (SPSCS) is main actor in management of pecticides, including OP. The significant changes in the structure of SPSCS was carried out in 2014-15. Currently, the organization has a following divisions:

-Plant protection and sertification sector
- Plant products quality control sector,
-Information resource and public relation sector,
-International relation, standards and methodical support sector,
- Financial and technical support sector,
-Justice, Human resource, clerical work,
-Economy and planning sector ,
-Quarantine expertise center
-Toxicology and Quality Control Center,
-Plant protection Center,
-Jangi polygon for OP,
-Regarding regional centers on plant quaranty and biological laboratory

Totally staff number of Service is 528.

State Phytosanitary Control Service and MENR are responsible for developing and implementing pesticides waste management plans. Relevant plans and programs are developed and implemented based on the rules about the participation and involvement of public, environment safety, ecological protection, phytosanitary control, ecological education of population as well as there are certain programs to involve the home owners in the collection and transportation of pesticides wastes[4-6].

Jangi Pesticide Polygon was given to the balance of State Phytosanitary Control Service under Ministry of Agriculture and it was reorganized. Initially Central Storage capacity at the Jangi polygon was 183 containers, each with a content of about 30 m³. The polygon has been reconstructed and additionally 60 containers were constructed, with a total capacity of 7,290 m³. Now 227 containers are filled with a total capacity of 6810 m³. There are 16 empty containers with capacity 480 m³. At the moment it is very difficult to estimate amount in tons. There are pesticides waste final storage facilities constructed and operated in accordance with the environment standards and they meet in 70-80% volume. Equipments are regularly replaced or repaired. Material technical base related to wastes are strengthened year by year.

The Regulation of this polygon was adopted by the Ministry of Agriculture. Material and technical support for the application of instructions on the reduction of waste is provided. Financial support is provided on the expense of state budget and other financial means by government for the purpose of application of new technologies and practices.

Waste disposal plant (incinerator) was established in Baku city (2012). Another plant near to this plant – waste sorting institutions has been built. Waste is sorted here, and appropriate waste for re-usage and processing is sent to other processing institutions, remaining part is incinerated; in this case the obtained heat energy is turned into electrical energy.

Disposal capacities in Country is following:
Jangi polygon for OP -7,290m³.
National Waste center for hazards wastes -250,000 m³
Municipal waste polygons, about 60 with a total capacity more than 3 mln ton. These are not regular poligons, but are waste dicharge areas
Polygon BP-Saranja for BP operational wastes only
SOCAR's polygon Akhtarma for oil industry wastes, mainly for oil sludges.

Each of these disposal facilities, besides of item 3 has a special Regulation document and has environmental safeguard documents, such as EIA, Environmental passport, etc.

3. Inventory of OP

Inventory of OP conducted by interministerial commission determined that in the 18 districts of country there are about 2000 tons OP and 76000 m^2 polluted area. Information about the OP is listed in Table 1. This information was included into PSMS system in 2014.

Location area	**Amount of OP**	**Polluted area,** m^2	**Content of OP**
Salyan	200ton+300 m3+500 rotten	23775	Polidofen , etc
Neftchala	5 ton		natrium propinat
Jalilabad	50 ton	5840	
Agcabedi	40 ton	2500	
Beylaqan	60	900	
Fizuli-Horadiz	500 ton	16100	DDT, HCH, izofen
Goranboy-Dalmammadli	-	10500	
Ucar	50 ton	3450	
Ucar-Mususlu		2400	
Yevlakh	100 ton	1000	
Agdash	100 ton	5600	
Khachmaz	163 m3		
Siyazan	5 ton	876	unknown
Samukh		300	
Kolayir village	98 m3 +100 ton		Izofen, xlorofos, hexakhloran
Shamkir	120 ton	30 cm thick	
Agstafa	60 ton	600	
Yevlax, Ujar, Zardab	3084 ton	-	
Agcabedi	1036 ton	-	
Ganja	1180 drums+200 pieces	-	
Zardob	1143 m3	-	

Table 1. Results of inventory of OPs in Azerbaijan (2012-2013)

Anually about 2.5 mln tonnes total, including 2.2 mln tonnes municipal wastes are generated. At the end of the 2011 amount of accumulated hazardous wastes was 1,764,400 tonnes, annual hazardous waste generation is 185,400 tonnes/year, Recycling of hazardous waste-24,900 tonnes/year, hazardous waste disposal-113,000 ton/year[2].

Industrial chemicals: In the oil industry there are 71,659 tonnes wastes, including 61,420 tonnes hazardous chemicals and 10,239 tonnes non-hazardous chemicals.

There are also 500 tonnes oil contaminated with PCB contented transformers in energy sector. Inorganic wastes identifed in content of the municipal wastes. In Azerbaijan about 6% of municipal wastes is inorganic. So the annual amount is 132,000 tonnes.

Hazardous wastes amount is 44,000 tonnes /year in municipal wastes (accumulators, lamps, medical wastes, etc), about 61,420 tonnes/year in oil industry

BP waste production 2012: 138,367 tonnes of solid and liquid waste. from which:

118,435 tonnes hazardous waste (including sewage) 28% increase to 2011. 19,932 tonnes were non-hazardous waste, 89% increase to 2011. , from 35,611 tons drilling cuttings processed at Serenja hazardous waste management facility by indirect thermal desorption. Other hazardous solids are stored at Serenja hazardous waste management facility.

Note that all waste of BP is properly disposed by approved contractors :

All waste BP disposes at the Serenja landfill . Some non-hazardous waste (5,793 tons – 29%) and some hazardous waste (3,923 tons – 3.3%) were recycled or reused by local companies. The remaining wastes were either treated and disposed of by BP approved waste disposal contractors using approved methods and routes, sent to a regulator-approved non-hazardous waste. In addition to 2012 non-hazardous waste 4,080 tonnes of drill cuttings were disposed of in a non-hazardous waste landfill.

Process of inventory, feasibility study, EIA and other issues regarding wastes were considered in the projects:

1. Strengening capacity to management of obsolete and POPs pesticides in the EECCA countries (GEF-FAO)-2010-2013
2. Solid Waste Management Improvement in Azerbaijan. UNDP/Norwegian Government 2009-2012.[3]

4. Storage and treatment of wastes

Till present has not yet selected one or more technology for elimination, but the technologies like modern cement kiln, incinerator and thermal desorption are available in the country and should be assessed on possible use for treatment of OPs and with OPs contaminated soil. More than 1000 empty metallic containers are in the OP temporary storage areas, lot of empty packaging cardboard and paper materials. No collection centres for containers from current pesticide.

1.Jangi Polygon for storage of hazards wastes**,** mainly OP wastes. OPs transported here from the former regional chemicals Storages points during 2006-2013. These are mixed POPs and OP wastes. Center has a Safeguard documents such as EIA, Environmental passport,etc

2. *Garadagh cement production Company "Holcim"* at the high-temperature rotating kiln burning hazardous waste, including burning of oil sludge and car tires. For last 10 years the question has been discussed about the opportunity of using waste of the petroleum industry (oil sludges) and tire covers by the Holcim cement plant. It was proposed that oil sludges to be used as additives on initial raw material for reception of a product, and additives on fuel. An EIA project has been developed on use of these wastes at the Holcim plant. However, the Ministry of Ecology and natural resources has not approved this project

3. *Recycling facilities in the Balakhany landfill* **.** Incinerator for combustion of Municipal wastes with capacity 500,000 ton/year and production electricity 300 mln kWh/year working since 2012 in the near of Baku. There are sorting and utilization (disposal) and re-use of wastes institutions. At present, complex (echotechnopark) is being established in Baku on the re-use of larger volume wastes, ecpecially plastic wastes.[3]

4. Serenja Hazardous Waste Management Facility (HWMF), where the drilling cuttings are received, temporarily stored, and treated. The treatment plant includes a rotary furnace for treatment of the drilling cuttings and other industrial wastes . Hazardous products resulted from the waste combustion are buried in the landfill of this polygon.

- *Indirect Thermal Desorption* (ITD) includes a rotary furnace treating at up to 450 °C. 35,611 tons of BP's drilling cuttings from offshore were processed and generating 3,751 tonnes of recovered base oil for reuse. At present constructing a new plant and soon there will be 4 ITD-plants with total capacity 160 ton/day (40 ton/day each). 20,000 ton wastes have been collected for last 10 years and waiting for ITD- treatment. So with the new plant all wastes will be treated within 1.5 years.

- *bioremediation*
  Bioremediation processes are conducting by microorganisms. Oil sludges are mixed with soils and straw and manure are added for activation of microorganisms. Organic part of sludges is destroyed by microorganisms, inorganic part content oil less than 1%. This technology is non-applicable for POPs, but may be tested for some of OPs. The residues of the bioremediation processes are transported and disposed of at the non-hazardous landfill at the National waste center in Sumgayit.[7]
- The hazardous wastes from the BP landfill are transported to this polygon and treated here. Hazardous products resulting from the waste combustion are buried in the landfill of this polygon.

5. Sumgayit – Hazardous Waste Ltd facility

In 2013, BP started landfilling hazardous drill cutting stored at the Serenja facility from previous years by sending 6,745 tonnes to Sumgayit waste landfill. BP continued disposal of non-hazardous drill cuttings at the Sumgayit non-hazardous landfill site.

Ministry of Ecology and Natural Resources according to the UNIDO Project conducted the inventory of PCB wastes and all PCB will be transported to the National Waste Center. The project is a component of the pilot project for the destruction of PCB's. In the presence of metallic sodium at the temperature of 110°C in PCB de-chlorination process occurs. This plant will have capacity of 20 tons per month. There are 500 tons of PCB wastes that will be refined during 25 months. The actual installation is now nearing completion.

6. SOCAR Akhtarma landfill

The center of Karadag region, 10-12 km away from the nearest residential area, "Akhtarma" is in an area of the mountain north of the plain of smooth and sediments. The total area of 10 hectares in the center, administrative building area is 123.3 m².

Concreted sections of the waste consists of 6 units, the total volume of 45,000 m³ (99,000 tons) of the vessels. Production of electricity (KTM-160 kVA transformer) and backup generator ("Gen Power," 22 kVA) is provided.

Monitoring **.**The monitoring for various hazardous wastes is implemented in accordance with the relevant rules adopted by the Cabinet of Ministers. Monitoring group is established by the participation of specialists of relevant bodies for this purpose.

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OBSOLETE PESTICIDES MANAGEMENT IN MOLDOVA: CURRENT STATUS AND PERSPECTIVES

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This article presents the results of actions undertaken by Moldova in the last 14 years in OP stockpiles management and elimination of the risks caused by them in relation to the environment and human health.

Practical measures in this regard started in 2001, following a special decision of the Government, and concur with signing and ratification of the Stockholm Convention on Persistent Organic Pollutants by the Republic of Moldova. These actions have been funded by the Government, and have been substantially supported by international organizations and Governments of development partner countries.

During this period, all known stockpiles of obsolete pesticides including POP pesticides were collected and approx. 3,500 tons of wastes were temporary stored in guarded warehouses. Of these, 2,760 tons evacuated abroad and destroyed. These activities are at the final stage and in the next year all OP stocks from warehouses should be eliminated.

An inventory of POPs polluted areas as well as mapping of those areas using the GIS tool has been carried out. About 1600 contaminated sites were identified, described and included in the database available on the Ministry of Environment website: http://pops.mediu.gov.md. It can effectively support the policy and decision making process in the field of contaminated sites management. Two techniques – isolation in controlled soil stockpiles and biological treatment have been tested at several pilot demonstration sites in order to identify the most appropriate methods for Moldova.

Progress is being made in the modernization of the legal framework on chemicals and waste management. As a result of extensive information and awareness campaigns on POPs, the level of education and awareness increased substantially.

Two other priority issues to be addressed in Moldova in the following period are: the contaminated areas requiring initiation and implementation of national measures for their remediation, and elimination of OP stocks from the Cismichioi landfill for which a preventive feasibility study is necessary to determine more accurately the quantities and categories of substances stored, environment risks assessment including cost estimation, technical and equipment needs.

In achieving these objectives, the Ministry of Environment, Ministry of Agriculture and Food Industry, Ministry of Defense, Ministry of Economy, local authorities, research institutes, international and local consulting companies and experts, NGOs are involved.

Key Words

Persistent organic pollutants (POPs), obsolete pesticides (OP), contaminated sites, POPs database, Stockholm Convention on POPs, risk assessment, remediation, landfill.

STATUS OF OBSOLETE AND POP's PESTICIDES IN BELARUS

Solovjev, Y.

Belarus has been active in the implementation of the Stockholm Convention since it accession in 2004. Using international support and with its own resources it developed and approved a detailed National Implementation Plan (NIP) in 2007.

This NIP has been updated with a current program inclusive of funding in place for the period 2010 to 2015, and a following plan for a five year period is currently in preparation. Since accession to the Convention the country has invested in POPs related activities including securing and elimination of POPs and obsolete pesticide stockpiles and developing and supporting hazardous waste management infrastructure in Chechersk, Gomel region.

A major part of the NIP implementation to date has been the successful implementation of a GEF FSP over the period 2009 to 2013 in association with the World Bank. This project involving US$5.5 million and an estimated US$30 million in co-financing was directed primarily at elimination of priority POPs pesticide landfill in Slonim along with technical assistance in an number of key areas to facilitate the country's ongoing POPs and broader chemicals management support.

Upon closing the combination of GEF and national resources had been provided for the secure containment and storage of 5,130 t of obsolete pesticides, the environmentally sound destruction of approximately 1,800 t of POPs pesticide waste (primarily DDT). This process involved the elimination and restoration of a large DDT burial site at Slonim as well as similar undertakings at two other Soviet era obsolete pesticide burial sites.

Notwithstanding these major achievements, the country still retains significant remaining POPs and obsolete pesticide legacies that it needs to address which include the 5,130 t of securely stored obsolete pesticides, an estimated 1,850 t of obsolete pesticides remaining in monitored burial sites.

In particular, country need international expertise and financial assistance to set up a disposal facility for obsolete pesticides in Chechersk complex where more than 4 000 tons of OPs are stored. Creation of such facility will help Belarus to eliminate all obsolete pesticides existing in the country.

“ELIMINATION OF OBSOLETE PESTICIDE STOCKPILES AND ADDRESSING POPS CONTAMINATED SITES WITHIN A SOUND CHEMICALS MANAGEMENT FRAMEWORK” FULL SIZED PROJECT IMPLEMENTED BY UNDP WITH GEF FINANCING, ARMENIA

Gayane Gharagebakyan, Project Coordinator

Background - Upon independence in 1992, Armenia had accumulated environmental hazardous waste legacies operating under command economies that had fallen behind in terms of balancing gross production with environmental quality. The Government of Armenia has signed in 2001 the Stockholm Convention and ratified it in 2005 thus committed to clean the legacy of obsolete persistent organic pollutants (POPs) including pesticide stockpiles in the country. To assure timely and respective measures for fulfilment of the country’s commitment the RA Prime Minister referred in 2010 to international donor community with a request to provide expert and funding support. Through UNDP and the RA Government joint efforts GEF has allocated 4,7 million USD grant to run a relevant project to be co-financed from the Government and other sources. UNDP-GEF “Elimination of obsolete pesticide stockpiles and addressing POPs contaminated sites within a sound chemicals management framework in Armenia” full-sized 4-year Project, has been launched since May 26, 2015.

Project Objective and Outputs - The major objective of the project is to protect human health and environment through elimination of obsolete pesticide stockpiles, particularly POPs across contaminated sites in Armenia. The Project will meet this objective by eliminating the large POPs pesticide waste in Nubarashen burial site (locate within the administrative territory of capital city) that represents the major POPs stockpile and waste legacy for the country.

On the one hand, the site is located in a landslide area and, on the other, it was built back in 1980s without proper engineering and geological assessments and required technical norms.” In the Soviet Union, Armenia, with its highly developed agriculture, had one of the highest application rates of pesticides, particularly organochlorine pesticides (OCPs). When the pesticides were banned in 1970-80s, together with expired chemicals they were disposed in landfills or in burial sites, such as the Nubarashen site. Moreover, around 600 pesticides storehouses/distribution centers existed in Armenia, with 13 regional storages containing POPs. During the 2-year preparatory phase, UNDP, in partnership with the Ministries of Nature Protection, Agriculture, Emergency Situations, and the OSCE Office in Yerevan, carried out a detailed investigation and feasibility study at Nubarashen burial site.

Through the Project in total:

Ø 1,050 tons of POPs pesticides and other OP will be removed and destroyed in an environmentally sound manner

Ø approximately 7,100 tons of POPs waste in the form of heavily contaminated soil, will be recovered, secured and ultimately treated

Ø a further 12,700 tons of less severely POPs contaminated soil will be securely contained.

Additionally the Project will support with the development of critically needed HW infrastructure and national technical capability for the ongoing management of POPs and other chemical HW, as well as will contribute to the strengthening of institutional and regulatory capacity.

STATUS OF OBSOLETE PESTICIDES IN GEORGIA

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Georgia has signed and ratified the Association Agreement with the EU (Agreement with the EU Association Agreement between the European Union and the European Atomic Energy Community and their Member States, of the one part, and Georgia, of the other part and Association Agenda between the European Union and Georgia). According to this Agreement, the parties shall develop and strengthen their cooperation on environmental issues, thereby contributing to the long-term objective of sustainable development. Policy objectives concerning management of chemicals (to implement the Regulation (EC) No 689/2008 of the European Parliament and of the Council of 17 June 2008 concerning the export and import of dangerous chemicals, by 01.09.2019 and Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures -to be implemented by 01.09.2020 for substances and by 01.09.2021 for mixtures) are included in the 2014 Association Agreement with the EU. Also, Georgia is a party to the Multilateral Environmental Agreements (MEAs) in the field of chemicals management (The Stockholm Convention on Persistent Organic Pollutants and The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade).

In order to translate the EU Association Agreement into more specific actions, the Government adopted the 2014 National Action Plan for the Implementation of the Association Agreement. The National Action Plan for the Implementation of the Association Agreement presents a road map for development of legislation that is necessary for the implementation of EU directives that are relevant for chemicals management.

The Ministry of Environment and Natural Resources Protection is responsible for the chemicals management planning. The responsibilities of the ministry include general chemicals management planning and elaboration of legislation. The Ministry of Environment and Natural Resources Protection is responsible to implement international obligations, mainly control and management of chemicals according to the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade and Stockholm Convention on Persistent Organic Pollutants. Also, Georgia has signed The Minamata Convention on Mercury on October 10, 2013, but not yet ratified it.

In 2003-2007 the Government of Georgia with assistance of GEF/UNDP developed draft National Implementation Plan (NIP) on Stockholm convention on "Persistent Organic Pollutant" (POPs). In 2011 NIP was adopted by the Order of Government of Georgia.

In 2007 state project "Inventory, repackaging and safety store the outdated and obsolete pesticides in Georgia" was carried out and 50t of OP from 12 top priority sites were repacked, transported and stored in central storage. 200t of contaminated soil was disposed in Iagluja Polygon.

The ongoing Global Environmental Facility (GEF) funded project "Review and update of the national implementation plan for the Stockholm Convention on Persistent Organic Pollutants (POPs) in Georgia" is implemented by United Nations Environment Programme (UNEP) in cooperation with the MENRP. Project envisages the new POPs inventory, assessment of the existing plan and development and adoption of the new plan, as well as public awareness raising regarding POPs.

Within the UNDP project "Disposal of POPs Pesticides and Initial Steps for Containment of Dumped POPs Pesticides in Georgia" 230 tones POPs Pesticides were collected, packed and exported to Belgium and France for disposal in 2014. The territory of Iagluja Dumpsite was fenced and the warning signs has been installed, Iagludja chemicals landfill remediation action plan is elaborated (for site remediation and environmental improvement three conceptual scenarios). Also, POPs inventory and Awareness raising activities has been carried out.

Additional 208 tones POPs Pesticides were collected, packed and sent to France for disposal in April 2016 within the FAO/EU project "Improving capacities to eliminate and prevent recurrence of obsolete pesticides as model for tackling unused hazardous chemicals in the former Soviet Union".

Furthermore, it is agreed that UNIDO will implement in Georgia project on PCB management (inventory, collection, packaging, disposal, public awareness raising).
In the scope of the GEF/UNDP project "Demonstrating and Scaling up Sustainable Alternatives to DDT for the Control of Vector Borne Diseases in Southern Caucasus and Central Asia" the demonstration of viability and cost-effectiveness of the use of sustainable alternatives of DDT was held on the selected sites and DDT was replaced by pyrethroids.

Additionally, to meet the the requirements and procedures of Rotterdam and Stockholm Conventions, and to implement the Regulation (EC) No 689/2008 of the European Parliament and of the Council of 17 June 2008 concerning the export and import of dangerous chemicals the the Decree of the Government "on Rule of Import and Export of Certain Hazardous Chemicals and Pesticides and Implementation of Prior Informed Consent Procedure" was Adopted on 13.06.2016 (Governmental decree N263).

ASSESSMENT OF THE CURRENT SITUATION WITH REGARD TO DISPOSAL OF BANNED PESTICIDES AND OTHER TOXIC CHEMICALS IN THE REPUBLIC AZERBAIJAN

SUBMITTED PAPER

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The article deals with inventory and transportation of pesticides which are kept in former chemical warehouses, as well as other measures conducted by Ministry of Emergency Situations in cooperation with other government agencies.

In recent years, a number of important measures have been taken to improve the environment in the country. Socio-economic reforms were carried out successfully, such as protection of environment and rational use of natural resources for survival and well-being of people. Collection of different types of waste, including toxic chemicals and pesticides in densely populated cities and regions can cause environmental pollution. In this regard depending on riskines, the full inventory and disposal of chemical hazardous substances by obeying proper rules are main issues and also works for cleanup of contaminated areas should match with demands of modern time.

Azerbaijan was one of the developed republics in terms of agriculture during former Soviet Union period. In 1970-1980 annually 700-800 million tons of cotton, 1.4 million tons of wheat, more than 1 million tons of grapes, 1.2 million tons of vegetables, 400 thousand tons of fruits were produced in the country. Climatic condition in Azerbaijan is very risky for diseases spread by insects and agricultural pests. Therefore, a wide range of pesticides was used in agriculture against pests. The Republic was one of the top consumers in Soviet Union according to the amount of pesticides used per hectare. Despite 20 times reduction in the amount of pesticides used after the collapse of the Soviet Union, obsolete and prohibited pesticide remnants still remain a threat to the environment and public health. Extensive use of pesticides in agriculture leads all countries to deal with their waste problem. The cause of these problems in developed countries are generation of waste, contamination of ground waters, pollution of river waters, liquidation of packaging equipment for pesticides, remediation of contaminated soil.

The following steps have been considered by the Food and Agricultural Organization of the United Nations, FAO for management and liquidation of a large amount of useless pesticides :

- The inventory of resources;
- To define area for temporary storage of resources;
- Removal of resources;
- Prevention of re-use and accumulation of pesticide resources .

Planting, thermal, physical, chemical and biological methods are used in special ranges for prevention of hazardous waste. These methods can be conducted in specialized places like special warehouses and ranges. Utilization of toxic chemicals should be carried out by accredited staff .

Based on international practice re-treatment of pesticides are known for 3 methods: chemical, physical and biological.

By physical and chemical methods toxic chemical items can be neutralized and converted into less hazardous chemical s.

Based on experiences, the physical and chemical methods requirer too high financial and energy costs. Also, through this method it is impossible to solve the problems of environmental security.

Biological method means burying of microorganisms. The biological treatment method is to ensure environmental safety. The complexity of this method is its selectivity, high demand of financial resources and also it covers small areas .

Currently, the burning and electrochemical methods are widely used for destruction of pesticides. Burning in high-pressure ovens is a widely used method for destruction of toxic chemical waste in the industry. However, burning creates toxic chemicals that causes environmental pollution. The main disadvantage of this method is that it generates toxic substances in the atmosphere. Another method is decomposition of pesticides with 50 % thickness sulfuric as a result of electro-chemical process. Despite the universality of this method, it causes serious problems in industrial level as it is conducted in severe environment (sulfuric environment). Burial method differs according to the universality and efficiency. Burying of waste in ranges- wells covers large areas and these areas are not being used. It has hazardous ecological effects with regard to pollution of soil and ground water. Toxic-chemical items can be neutralized with chemical methods. But these methods have also high demand of financial resources and it is impossible to solve the problems of environmental security through these methods.

Azerbaijan Republic joined to the Stockholm Convention on «Persistent Organic Pollutants » by the Law No.554 PQ dated December 09, 2003. Persistent Organic Pollutants (POPs) covered by the Stockholm Convention conditionally divided into 3 groups: expired and prohibited the use of pesticides, polychlorinated biphenyl (PCB) which are used in industry, hexachlorobenzene, produced but isn't used, dioxins and furans that found as a result of the conversion of chlorine organic combinations. Azerbaijan's strategy for a long-termed safety of POPs is removal of PCB and DDT ecologically friendly, changing equipment containing PCB, inventory of dioxin / furans and 9 new POPs substances.

Only DDT, PCBs and dioxins / furans DDT are available in the first 12 articles included in the Stockholm Convention and only DDT have been produced in the country, although since 1982 the use and production of it was suspended and prohibited.

Ministry of Emergency Situations is engaged along with other state agencies in obligations such as "Comprehensive Action Plan about improvement of ecological situation in the Azerbaijan Republic for 2006-2010" that approved by Order No. 1697 dated 28 September 2006 of the President of the Republic of Azerbaijan, decisions made by the Republic of Azerbaijan on the protection of the environment, joined international Conventions and agreements including Stockholm Convention on "Persistent Organic Pollutants " that ratified by the Republic of Azerbaijan in 2003 and cares for usage control of pesticides, fertilizer and other such type of drugs, Basel Convention on "Control of cross-border transportation and disposal of hazardous waste "(2001), Rotterdam Convention on "International trade permit of certain hazardous chemicals and pesticides in advance". According to 8.48.1 paragraph of the Regulation Ministry of Emergency Situations collaborates with relevant state bodies for keeping state control on production and preservation of plant protection substances (pesticides and biological).

At the same time according to fulfillment of the Order of President of Azerbaijan Republic dated 29 June, 2000, No . 357 of the Law of Azerbaijan Republic "Technical safety" dated November 2, 1999 No. 733-IQ state control of technical safety on danger potential objects as if exploitation of these objects match with technical safety requirements are implemented which mentioned in 1st paragraph of 17th article of this law .

Objects engaged in purchase, use, processing, production, storage, transportation and abolish of the chemicals were included in the list of potential dangerous objects approved by the Decision No. 94, dated 10 May 2001 of Cabinet of Ministers.

The examinations are being held according to safety norm and requirements in storages, selling points and regional supply market of pesticides, agricultural chemicals, biological and veterinary drugs that are registered in the territory of Azerbaijan Republic and allowed for production, exportation, importation and usage by representatives of State Agency for Safe Working in Industry and Mountain-Mine Control and State Fire Control Service.

During examination it was defined that toxic, explosive substances are kept in fertilizer storages of the republic in unsatisfactory conditions without following fire and other safety regulations, sometimes in the open air, close to residential areas and water sources. Also protection is not organized properly and transportations are made without rules and the use of special vehicles. During investigations conducted by regional civil defense troops of the Ministry of Emergency Situations and Civil Defense departments, useless toxic pesticides and other chemicals have been found in some regions of the country. According to the information received from Shirvan civil defense department, mixed pesticides with total capacity of 44 ton 335 kg have been found in Saatli district branch of "Aqrolizinq" LTD and fertilizer storages of Daykend and Salyan Logistic LTD. Pesticides mixed with large amount of soil were found in the territory near Hindarch village of Agcabedi that is on the balance of the State Property Committee.

A working group consisting of representatives of the relevant ministries created by the ministry to give proposals on rendering pesticides harmless which discovered on the instruction of Cabinet of Ministers as they are very dangerous for human health and environment. Working group discussed current situation and final plan of "Inventory commission for rendering harmless of useless, banned toxic pesticides and agricultural chemicals" with participation of one representative of Ministry of Emergency Situations. It was revealed that in 1990s in 4,5 hectare area built by "Azerkendkimya" Manufacturing Association in the territory of Absheron 4 km away from Jangi village and in a range consisting of 183 bunkers up to 8000 tons useless and banned pesticide remnants (DDT,calcium arsenat, calcium cyanamide, hexachloran, xomesin, Sineb etc.) were buried that were brought from different parts of the republic till cancellation of "Azerkendkimya" Manufacturing Association. Concrete covers of bunkers in a range were opened and more than 4000 tons of pesticide remnants were carried away and used as they kept in there till 2005 without any control. During initial inventory it was found that 3,500-3,700 tons of pesticide remnants were in a bunker and some of them had been scattered around range area.

During 2008-2010, 3154 ton powder-like pesticide remnants and 1200 m3 land contaminated by toxic substances have been re-packed and transported to the Jangi Pesticide Polygon (in 2008 2048 tons from the regions Agcabedi,Yevlach,Ucar, Zerdab and in 2010 1036 tons from Agcabedi). Liquid polidofen in Jangi was again packed (1180 barrels and 200 contaminated containers), carried to the Jangi Pesticide Polygon and intended to remain temporarily there till they are harmless as a whole. According to the dated 25 january 2010 No. 21s order of the Cabinet of Ministers 1143 m^3 of earth contaminated with different types of chemical substances in surroundings of buildings constructed in 10th district of Zardab region for disabled persons, was evacuated and carried tothe Jangi Pesticide Polygon and exchanged with new layer of earth. In November 2011 a pilot project named “Re-packing of pesticides that are old, high toxic and banned for use” was implemented in our Republic.During seminar and trainings with participation of delegates from 7 states approximately 70 ton pesticide remnants from 3 regions of the Republic packed and transported to the Jangi Pesticide Polygon according to FAO standards and under control of an international expert. According to the results of the monitoring process of inventory commission implementing the following activites: 1520 ton powder-like pesticides, 1064 m3 buried unknown pesticides and liquid pesticides to the Jangi Pesticide Polygon in 1000 barrels, cleaning surface of the warehouse floors contaminated with 28428m^2 toxic chemicals and rendering 73116 m^2 layers of earth considered expedient. As we don’t have enough information on unknown and illegally buried small pesticide ranges, their discovery in the future during excavation in the regions is not an exception.

As a result of the inventory at an early stage, specification of the composition of soil that is contaminated with useless, unknown substances and pesticide remnants can be made by the necesarry analyses. The re-packaging of discovered useless liquid, powder-like and in wells buried pesticides can be made according to international standards, safety and sanitary rules, legislation statements, normative-technical documents. In this way define the amount of useless, banned POP pesticides is definded by the help of detailed inventory. Finally, a report has been prepared, after the total collection and re-packing have been approved by the members of the working group.

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6. 76“Technical safety” Law of Azerbaijan Republic dated 2 november 1999 No.733-IQ

7. Order dated 29 June 2000 No.357 by President of Azerbaijan Republic about execution of “Technical safety” Law of Azerbaijan Republic dated 2 november 1999 No. 733-IQ

ASSESSMENT OF SURFACE WATER AND SOIL CONTAMINATION BY ORGANOCHLORINE PESTICIDES IN UZBEKISTAN

SUBMITTED PAPER

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Abstract

Pollution of environment by persistent organochlorine pesticides still remains a problem both in the world and in Uzbekistan. Persistent substances are remaining in the soil for up to 10 years or more. Persistent pesticides can spread over a large distance migrating with the surface water. Therefore, monitoring of pesticides content in surface water and soil is very important. In this paper the results of pesticides monitoring in surface water and soil at agriculture areas in Uzbekistan have been analyzed for some years within the period from 1989 to 2014. They show tendency to decrease in surface water and soil contamination by pesticides in Uzbekistan. For the period of observations, low concentrations of HCH isomers were determined in surface water and soil. Last years, DDT and its metabolites were not determinate in surface water samples but were determined in soil mostly in amounts less than their maximal admissible concentrations.

Key Words

Organochlorine pesticides, residue, surface water, soil, contamination, assessment

Materials and methods

In the variety of chemical toxicants of anthropogenic origin, organochlorine pesticides are the most persistent and dangerous to the environment and biota. DDT and HCH as the crop protection chemicals were used extensively in the past on the territory of Uzbekistan for agricultural and perennial crops to control various insect pests[1]. In the soil pesticides are dissolved in soil moisture and are carried by it to bottom of the soil profile. Life-time of pesticides in soil depends on their composition. Persistent substances are remaining in the soil for up to 10 years or more. Persistent pesticides can spread over a large distance migrating with the surface water. Prohibitions and restrictions in use of applied in Uzbekistan organochlorine pesticides and reduction of pesticide consumption norms for agriculture crops led to a situation, that a number of stocks have been accumulated in the burial sites and storehouses throughout the country.

Control of organochlorine pesticides in soil near the storehouses and burial sites is currying out by the State Committee for Nature Protection. Monitoring of the pesticides residue in surface water and soil in all provinces of Uzbekistan is carrying out by the Center of Hydrometeorological Service of Uzbekistan (Uzhydromet).

Though application of these pesticides in Uzbekistan was banned, DDT since 1983 and Lindane (γ-HCH) since 1991, their residues have been observed in surface water and soil until present time due to their high persistency. According to monitoring data for 2000-2004 HCH isomers were detected in low concentrations, DDT and its metabolites were not determined at all surface water quality points of Uzhydromet. HCH isomers, DDT and its metabolites were identified in soil[2,3].

In this paper the results of pesticides residue monitoring in surface water and soil in Uzbekistan for the period 1989-2014 have been analyzed[4,5].

Pesticides in soil have been monitored by Uzhydromet at vineyards and horticulture. Monitoring points of surface water of Uzhydromet are located at rivers, small watersheds, irrigation canals, collectors and water reservoirs. Observation time in these points is set taking into account the hydrological regime of each watershed. In rivers, irrigation canals and collectors water sampling is carried out monthly[6].

Organochlorine pesticides analysis is carried out by gas chromatography method using electron capture detector[7].

Maximum allowable concentrations (MAC) of pesticides in surface water and soil have been used for assessment of water and soil contamination. MAC of pesticides in watersheds for sanitary-household water use amounts 0.02 mg/dm^{3}for HCH isomers, 0.1 mg/dm^{3}for DDT and its metabolites. For fishery watersheds the MAC of HCH isomers, DDT and its metabolites should be equal to zero. MAC for these pesticides in soil is 0.1 mg/kg[8].

Results and discussion

Assessment of surface water pollution with HCH isomers and DDT were curried out using monitoring data of the lowest water quality points on the main rivers of Uzbekistan, which have essential value for water resources management. Samanbay point on the Amu Darya River accounts water inflow and contaminants into the territory of Karakalpakstan; Chinaz point is lower observation point on the Syr Darya River in the Uzbekistan; Termez point is lowest observation point for water quality on the Surhandarya River; Uchtepa point is lowest observation point on the Karadarya River which located in the Fergana Valley; Tashkent point is located below the city for water quality monitoring of the Chirchik River (Tables 1,2).

River, monitoring point	1989	1990	1999	2000	2009	2010	2013	2014
Amu Darya, Samanbay	0,021	0,013	0,006	0,004	0	0	0	0
Syr Darya, Chinaz	0,012	0,006	0,005	0,003	0	0	0	0
Surhandarya, Termez	0,009	0,007	0,004	0	0	0	0	0
Karadarya,Uchtepa	0,025	0,020	0	0	0	0	0	0
Chirchik, Tashkent	0,012	0,001	0,001	0,001	0	0	0	0

Table 1. Concentration ofα-HCH in river water of Uzbekistan,mg/dm^3

River, monitoring point	1989	1990	1999	2000	2009	2010	2013	2014
Amu Darya, Samanbay	0,013	0,009	0	0	0	0	0	0
SyrDarya, Chinaz	0,009	0,002	0	0	0	0	0	0
Surhandarya, Termez	0,011	0,003	0	0	0	0	0	0
Karadarya,Uchtepa	0,023	0,008	0	0	0	0	0	0
Chirchik, Tashkent	0,025	0,011	0	0	0	0	0	0

Table 2. Concentration ofγ-HCH in river water of Uzbekistan,mg/dm^3

According to monitoring data α-HCH were detected frequently in water samples from 1989 to 2000, they were not detected from 2009 to 2000.Amount of α- andγ -HCH varied from 0 to 0.025 mg/dm^3.Detected residues of these pesticides were exceeded their maximum allowable concentration (MAC) in 1989 only, since 1990 they were lower than MAC. During observation period, DDT and it's metabolites were not detected in water samples. According to soil monitoring data both low and high concentration of DDT and its metabolite were observed in soil samples. Amount of DDT and it's metabolites varies from 0.002 mg/kg (0.02 MAC) to 0.398 mg/kg (3.98 MAC). Content of DDT and its metabolites in soil exceeded their MACs in all regions of Uzbekistan in 1989 and 1990, but during period from 1999 to 2014 amount of DDT and it's metabolites in soil were lower than their MACs. Higher concentration of DDT, than their MACs was observed in Andijan and Fergana provinces – from 0.101 mg/kg (1.01 MAC) to 0.270 mg/kg (2.7 MAC) only (Fig. 1,2).

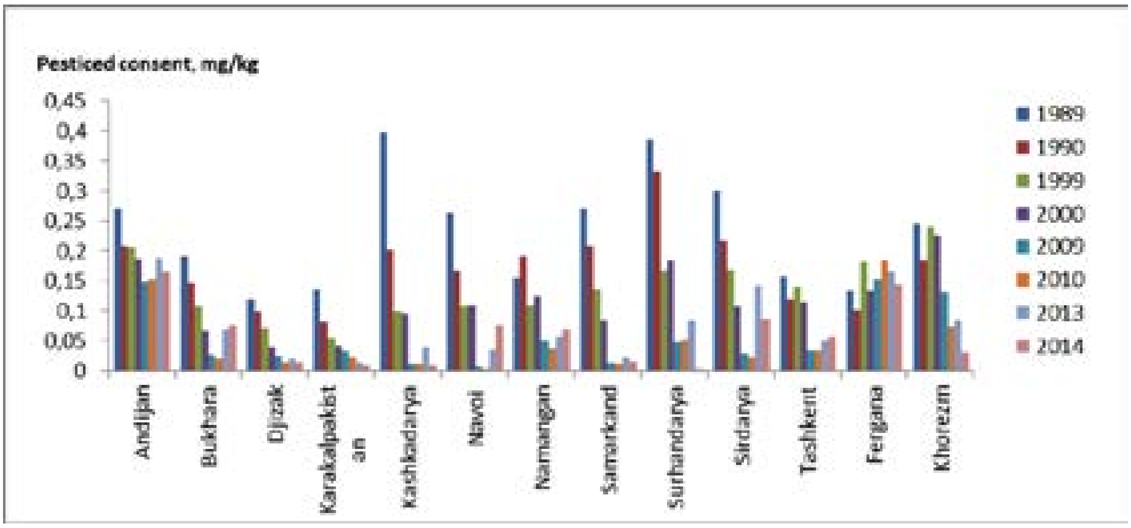

Figure 1. Mean concentrations of DDT and its metabolites in soil in provinces of Uzbekistan

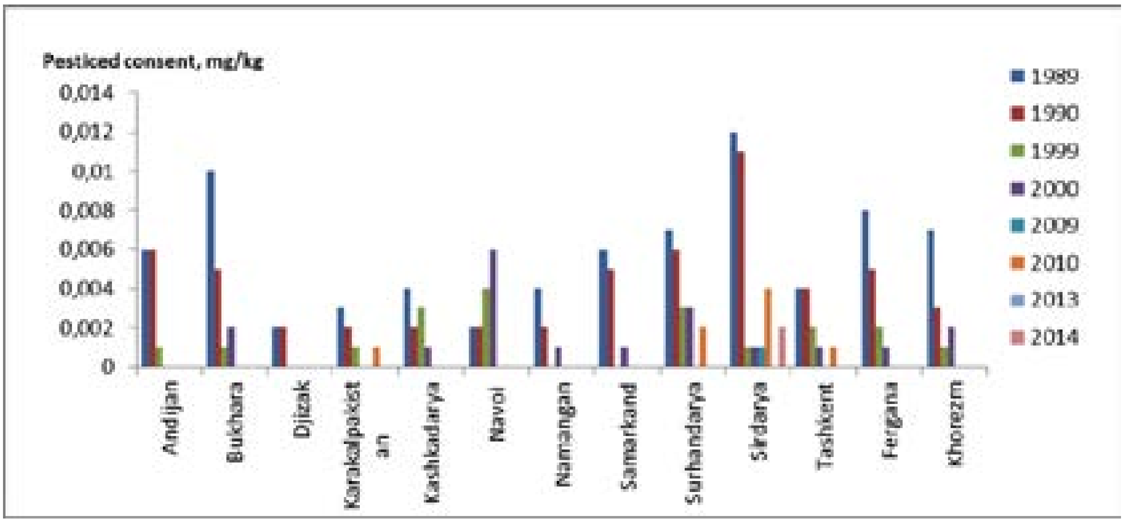

Figure 2. Mean concentrations of α-HCH and γ-HCH in soil in provinces of Uzbekistan

Mean concentrations of in soil varied from 0 to 0.012 mg/kg (0.12 MAC). Maximal concentrations of HCH isomers in soil were lower than their MACs. High concentrations of α-HCH and γ-HCHwere observed in soil of Bukhara and Syrdarya provinces in 1989 and 1990.

Surface water and soil quality monitoring data for the period of 1989-2014 shows decreasing of surface water and soil contamination by organochlorine pesticides (α-HCH, γ-HCH, DDT) in Uzbekistan. For the period of observations, low content of HCH isomers were observed in surface water and soil. DDT and it's metabolites were not determinate in lowest water quality points of main rivers of Uzbekistan. In soil, DDT and it's metabolites were observed both in small and high concentrations.

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POPs-PESTICIDES AS A JOINT ISSUE OF THE STOCKHOLM AND BASEL CONVENTIONS

SUBMITTED PAPER

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Abstract

The paper represents an overview of the latest developments achieved under the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal which concern the pesticides listed in the Stockholm Convention on Persistent Organic Pollutants (POPs). The summarized data contain the background information and the joint points covered within the scientific and technical matters, namely, in the updated technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with the POPs pesticides. It is highlighted the amendments related to the chemicals newly listed in the Stockholm Convention on POPs, including a brief description of their properties and possible use, production and wastes. It is emphasized the relevance of the joint questions for the both conventions, i.e. establishment of the levels of destruction and irreversible transformation for the chemicals and establishment of the concentration levels of the chemicals in order to define for them low persistent organic pollutant content. The conclusion reflects the status of the documents after their consideration at the triple Conferences of the Parties in 2015, as well as the decisions opening new possibilities for the countries to involve national institutions and experts to share their knowledge about newly listed POPs and experience with the implementation of low POP content.

Key Words

Persistent organic pollutants (POPs), pesticides, environmentally sound management, waste

Introduction

In 2006, the Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (Basel Convention, BC) adopted the general technical guidelines on the environmentally sound management (ESM) of waste consisting of, containing or contaminated with persistent organic pollutants (POPs) and specific technical guidelines on these wastes, including POPs-pesticides. Due to the amendments to the annexes of the Stockholm Convention on POPs (Stockholm Convention, SC), these guidelines needed revision to include the newly listed POPs and the relevant considerations obtained by the POPs Review Committee, as the SC scientific subsidiary body. The Open-ended Working Group of the Basel Convention considered the work programme on the scientific and technical matters that covered the latest developments achieved under the Stockholm Convention The special Small Intersessional Working Group (SIWG) was established by paragraph 9 of the decision OEWG-1/4, it operated under the guidance of the Open-ended Working Group of the Basel Convention and the authority of the Conference of the Parties to the Basel Convention. By its decisions BC-10/9 and BC-11/3[1], the COP to the Basel Convention extended the mandate of the SIWG to provide that the group should monitor and assist in the review and updating, as appropriate, of technical guidelines for the ESM of wastes consisting of, containing or contaminated with persistent organic pollutants, in particular, with regards to the POPs-pesticides.

Technical Guidelines: Amendments on Pesticides

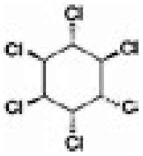
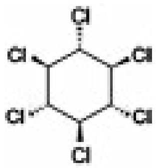
The revision of the POPs technical guidelines (TG) under the Basel Convention and their updating lead by Canada Basel Team resulted in the drafts of seven documents that were represented at the triple COPs in Geneva, April-May 2015. The paper focuses on those of them which directly concern POPs-pesticides and contain the relevant provisions from the Stockholm Convention. The specific TG on pesticides were finally updated by the UN Food and Agriculture Organization in consultation with the SIWG and with regards to the comments previously received from Parties and others, for consideration by the Conference of the Parties at its twelfth meeting among other draft TGs. Therefore, the main amendments related to POPs-pesticides were made in the following two documents (available as the drafts of April 2015):

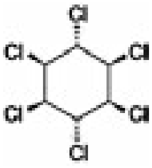
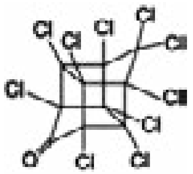
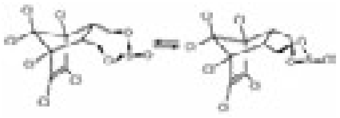
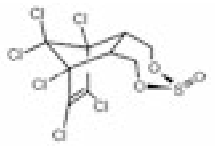
- General technical guidelines on the ESM of wastes consisting of, containing or contaminated with persistent organic pollutants[2], including the chemicals listed in Annexes A, B and C to the Stockholm Convention by decisions SC-4/10 – SC4/18, SC-5/3 and SC-6/13 of the Conference of the Parties to the Stockholm Convention, namely:
  Alpha hexachlorocyclohexane (decision SC-4/10);
  Beta hexachlorocyclohexane (decision SC-4/11);
  Chlordecone (decision SC-4/12);
  Hexabromobiphenyl (decision SC-4/13);
  Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether) (decision SC-4/14);
  Lindane (decision SC-4/15);
  Pentachlorobenzene (decision SC-4/16);

Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (decision SC-17);
Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) (decision SC-4/18);
Endosulfan[3];
Hexabromocyclododecane[4], and

- Specific technical guidelines on the ESM of wastes consisting of, containing or contaminated with pesticides aldrin, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, chlordane, chlordecone, dieldrin, endrin, heptachlor, hexachlorobenzene, lindane, mirex, pentachlorobenzene, , perfluorooctane sulfonic acid, technical endosulfan and its related isomers or toxaphene or with hexachlorobenzene as an industrial chemical[5] - should be used in conjunction with General technical guidelines as an "umbrella" document.

The table below contains the summarized brief description of the newly listed POPs-pesticides or industrial chemicals used in pesticides formulations which were included into the updated Basel Convention technical guidelines:

POPs	Description
Alpha hexachlorocyclohexane (α-HCH)  CAS No: 319-84-6	Listed under Annex A of the Stockholm Convention without specific exemptions – none use and none production One of hexachlorocyclohexane isomers By-product in the production of lindane (γ-HCH) Wastes (BC TG): - Obsolete stockpiles of pesticides (technical HCH and lindane); - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Contaminated soil; - Burials; - Stockpiles of production wastes
Beta hexachlorocyclohexane (β-HCH)  CAS No: 319-85-7	Listed under Annex A of the Stockholm Convention without specific exemptions – none use and none production One of hexachlorocyclohexane isomers By-product in the production of lindane (γ-HCH) Wastes (BC TG): - Obsolete stockpiles of pesticides (technical HCH and lindane); - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Contaminated soil; - Burials; - Stockpiles of production wastes

Lindane (γ-HCH)  CAS No: 58-89-9	Listed under Annex A of the Stockholm Convention with specific exemption for use as a human health pharmaceutical for control of head lice and scabies as second line treatment One of isomers of hexachlorocyclohexane Insecticide for seed and soil treatment, foliar applications, tree and wood treatment and against ectoparasites Wastes (BC TG): - Obsolete stockpiles of pesticides (technical HCH and lindane); - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Contaminated soil; - Burials; - Stockpiles of production wastes
Chlordecone  CAS No: 143-50-0	Listed under Annex A of the Stockholm Convention without specific exemptions – none use and none production Trade name: Kepone and GC-1189 Chemically is related to Mirex Currently, no use or production is reported Wastes (BC TG): - Obsolete stockpiles of pesticide; - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Buried pesticides
Technical endosulfan CAS No: 115-29-7  α-endosulfan CAS No: 959-98-8  β-endosulfan CAS No: 33213-65-9	Listed under Annex A of the Stockholm Convention with specific exemptions for production as allowed for the parties listed in the Register of Specific Exemptions and/or for use on crop-pexes (new Part VI) Insecticide to control crop pests, tsetse flies, and ectoparasites of cattle and as wood preservatives Wastes (BC TG): - Obsolete stockpiles of pesticides; - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Burials; - Contaminated soils

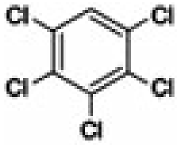
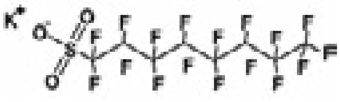
Pentachlorobenzene (PeCB)  CAS No: 608-93-5	Listed under Annexes A and C without specific exemptions – none use and none production Fungicide and a flame retardant Unintentionally produced during combustion, thermal and industrial processes By-product in production of solvents or pesticides <u>Wastes (BC TG):</u> - Obsolete stockpiles of pesticides; - Contaminated soils
Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)  CAS No: 1763-23-1 (PFOS) CAS No: 307-35-7 (PFOS-F)	Listed under Annex B with acceptable purposes and specific exemptions (Part III): among others – insect baits for the control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.* Industrial chemical Surfactant, the PFOS derivatives are used in pesticide formulations <u>Wastes (BC TG):</u> - Obsolete pesticides; - Contaminated equipment such as shelves, spray pumps, hoses, personal protective materials, and storage tanks; - Contaminated packaging materials such as drums, bags, bottles; - Contaminated soil

Table 1. Persistent organic pollutants listed in the Stockholm Convention and included in the Basel Convention updated technical guidelines on environmentally sound management of pesticides wastes

Joint Questions for Consideration

The Open-ended Working Group work programme for 2014-2015 also included the points that still remain under discussion within the both Conventions[6]:

- Establishment of levels of destruction and irreversible transformation for the chemicals necessary to ensure that when disposed of they do not exhibit the characteristics of persistent organic pollutants specified in paragraph 1 of Annex D of the Stockholm Convention;
- Determination of which disposal methods constitute environmentally sound disposal as referred to in paragraph 1 (d) (ii) of Article 6 of the Stockholm Convention;
- Establishment, as appropriate, of the concentration levels of the chemicals in order to define for them low persistent organic pollutant content as referred to in paragraph 1(d) (ii) of Article 6 of the Stockholm Convention.

As it is stated[2] in the TG, the low POP content determinations were made in accordance with the main objectives of the Basel and Stockholm conventions and the following considerations:

- Environmental and human health considerations;
- Availability of adequate capacity for analysis;
- Range of concentrations in articles, materials and waste;
- Limit values within national legislation;
- Availability of treatment capacity;
- Limitations of knowledge and data;
- Economic considerations.

As a result, the same values of the low POP content are proposed for aldrin, chlordane, chlordecone, DDT, dieldrin, endrin, heptachlor, HCB, mirex, PeCB, technical endosulfan and its related isomers and toxaphene: 50 mg/kg for each; for alpha-HCH, beta-HCH and lindane: 50 mg/kg as a sum; and for PFOS, its salts and PFOSF: 50 mg/kg as well.

Conclusion

At its 12th meeting in May 2015, the Conference of the Parties to the Basel Convention adopted the above-mentioned technical guidelines related to POPs-pesticides, as well as other specific ones dealt with the wastes from the industrial and unintentially produced chemicals newly listed under the Stockholm Convention. Besides, as a follow-up of the latest decisions of the 7th Meeting of the Conference of the Parties to the Stockholm Convention[7], the COP-12 of the Basel Convention decided to continue work on POPs, including the development or/and update of the technical guidelines for recently listed chemicals under the Stockholm Convention: chlorinated naphthalenes (industrial chemical), hexachlorobutadiene (pesticide and industrial chemical) and pentachlorophenol (pesticide); as well as work towards the review of the adopted low POP content values for each chemical, including a request for information from Parties on their experience with the implementation of low POP content.

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BAN ON THE TRANSBOUNDARY MOVEMENT OF PCBs FROM KAZAKHSTAN TO EUROPE AND AIR TRANSPORT OF THE WASTE

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Abstract

UNDP country office in Kazakhstan awarded the project for the transboundary movement and final disposal of PCB waste to Polyeco S.A. in spring 2012. The most demanding part of this project was to obtain transit permits for the transboundary movement of PCB waste from Kazakhstan to France.

The transboundary movement possibilities of the waste in the context of the Basel Convention were thoroughly investigated for one and a half year before it was finally proved that road / rail / sea transport of the waste from Kazakhstan to France was not feasible. The following countries banned the transit of PCB waste through their territories: Georgia, Azerbaijan, Russia, Turkmenistan, Iran and China.

As a result 80 tons of PCB waste was transported from Kazakhstan to France on a direct flight with a chartered aircraft. Upon the successful completion of this project, a second similar project was awarded to Polyeco and two more aircrafts were employed for the export of additional 170 tons of PCB waste.

Air transport of POPs presents the advantage of quick and safe project implementation and the disadvantage of increased costs. However, it can provide a credible solution for the incineration of hazardous waste, in cases where alternative options are not available and environmental problems must be resolved.

Key Words

Kazakhstan, PCBs, air transport, transboundary movement, transit permit, UNDP

1. Introduction

Kazakhstan ratified the Stockholm Convention on June 7, 2007. For planning appropriate action in the field of controlling POPs substances and releases as well as fulfilling the reporting requirements of the Convention, the Government of Kazakhstan developed an Action Plan for PCB management as a part of its draft National Implementation Plan (NIP) on POPs. The PCB Action Plan evolved into a project called “Design and Execution of a Comprehensive PCB Management Plan for Kazakhstan” which was a joint undertaking by the Government of Kazakhstan, private sector partners and UNDP. The Global Environment Facility provided substantive grant funding for co-financing the project.

In this context, UNDP country office in Kazakhstan issued a tender in 2011 for the final disposal of PCB oils from the Republic of Kazakhstan. The services included the handling, packaging, transboundary movement transportation and disposal of PCB oils. Transboundary movement transportation was initially planned to be undertaken in sea containers via road / rail or sea in accordance with the Basel Convention. The project was awarded to Polyeco in March 2012.

2. Transboundary movement of waste

The most challenging factor of this project was to identify a suitable export route for the transboundary movement of the waste from Kazakhstan to Europe for final disposal. Waste had to be transported to Tredi Saint Vulbas incineration facility in France.

From the beginning of this project it was identified that obtaining Basel Convention transit permits from Kazakhstan neighboring countries would be a challenging task. This issue was raised by UNDP early in 2012. Transit via China and Russia was forbidden and therefore a different gateway to Europe had to be identified.

Kazakhstan immediate neighboring countries are China, Russia, Kyrgyzstan, Uzbekistan and Turkmenistan. Kazakhstan is also connected via the Caspian Sea with Azerbaijan and Iran. A map of the geographical area is shown in Figure 1 below.

Figure 1: Map of Kazakhstan and neighboring countries

Due to the foreseen difficulty in obtaining transit permits for the export of the waste, several alternative transport scenarios were considered simultaneously and competent authorities were initially contacted without the submission of full notification files. The following potential routes were investigated:

- Kazakhstan – Russia – Turkey etc.
- Kazakhstan – Azerbaijan – Georgia – Turkey etc.
- Kazakhstan – Azerbaijan – Armenia – Turkey etc.
- Kazakhstan – Uzbekistan – Turkmenistan – Iran – Turkey etc.
- Kazakhstan – Iran (via the Caspian) – Turkey etc.

The main milestones on the efforts made by Polyeco towards obtaining transit permits for this project are described below. Discussions and meetings with Basel Convention competent authorities of various countries were taking place for one and a half year, from spring 2012 until the summer of 2013. Five alternative notification files had to be submitted in the context of the project, four of which proved to be non-feasible.

3. Communications with competent authorities

The preferred option for the export of the waste to France was through the Caspian Sea to Azerbaijan and then via road to Georgia, where it could be loaded on a container vessel to France.

Georgia

The Ministry of Environment in Georgia was contacted in March 2012. In mid-April, 2012 a reply was obtained by the Ministry that the Law of Georgia on Transit and Import of Waste bans the import or transit of PCBs through the country.

Azerbaijan

While in contact with the Georgian authorities, a meeting was arranged with the Basel Convention Competent person in Azerbaijan just upon delivery of the final ban of the waste through Georgia. Although Georgia banned the transit, Armenia was considered as an alternative route to bypass Georgia on the way to Turkey and therefore the meeting was held as planned in mid-April 2012. The meeting clarified that transit of PCBs through the country is forbidden. An official statement confirming the aforementioned ban was also received by the Deputy Minister in May 2012 further to a formal written requested submitted to the Ministry.

In the light of the above information, it was made clear that transit via Azerbaijan – Georgia or Azerbaijan – Armenia was prohibited and therefore Armenian competent authorities were never contacted. The efforts were therefore redirected towards Turkmenistan, Uzbekistan and Iran.

Turkmenistan

Polyeco tried to identify and contact Turkmenistan Basel Convention competent authority from the early stages of the project but the authority was difficult to reach. Even the Basel Convention Secretariat was contacted for this purpose, but details of the competent authority were not available at the Secreteriat database. In lack of specific information, an official letter was sent to the Minister of Nature Protection in July 2012 requesting further information about the competent person of the Basel Convention and explaining about the transit request. A formal response was received by Turkmenistan Ministry in the end of October 2012 stating that the transit of PCB waste via Turkmenistan is banned.

At that time, UNDP was also making efforts to promote the transit of the waste though Turkmenistan utilizing its local contacts. UNDP was preparing for a trip to the country, but the prohibition letter stopped the efforts.

Uzbekistan

Uzbekistan, being one of the potential transit countries, was also contacted at an early stage of the project. A response was received in May 2012 that transit of PCBs via its territory was possible in accordance with national regulations, but formal response could only be provided upon submission of the notification files

Notification files were forwarded to Uzbekistan early in September 2012 and a response was provided early in October 2012 that the files had to be translated into Russian. At the time it was decided not to proceed with the translation, since Turkmenistan had already banned the transit of the waste and therefore the route via Turkmenistan and Uzbekistan to Iran was impossible. It is therefore not known, whether Uzbekinstan would ultimately permit the transit or not.

Iran

In the light of the transit bans from all other neighboring countries, Iran presented the only remaining meaningful option for the export of the waste to Europe. A direct route to Iran via the Caspian sea without the need of transit via Turkmenistan or Azerbaijan was identified in October 2012 with a special agreement and redirection of an existing route to meet the needs of this project. Therefore all efforts were focused on obtaining transit permit through Iran.

The Ministry of Environment of Iran was first contacted in May 2012. The Ministry confirmed that there is no generic prohibition of the transit of the waste from Iranian law. An official reply to this end was also received by Iranian authorities early in July 2012 stating that an official response could only be obtained upon submission of the notification files.

Another meeting was held with the Iranian authorities after submission of the notification files and the authorities requested for some additional clarifications in mid-December 2012. Despite these efforts, the Iranian authorities unofficially informed Polyeco in the end of the year that transit through its territory would be banned.

In the effort to avoid the formal denial, UNDP Kazakhstan intervened through the Iranian UNDP office and met with the Ambassador of Iran early in 2013 to discuss the issue. Unfortunately an official denial on transit was received by the Iranian authorities in February 2013. Despite Iran's denial, UNDP kept pursuing the possibility to change this decision by organizing meetings with governmental officials in the country and by involving Iran UNDP offices until June 2013. The issue was also extensively discussed at side meetings of the Conference of the Parties to the Basel Convention held in Geneva in spring 2013 (BC COP-11).

Russia

UNDP Kazakhstan was investigating the possibility of transit via Russia from the beginning of the project. All parties were aware about the legal prohibition of the transit of PCB oils. However, there was a window of opportunity to utilize and amend the customs union regulations of Russia, Belarus and Kazakhstan, in order to make this route possible. After long communications and several meetings, transit of PCB waste via Russia proved to be non-feasible.

In the end of the summer 2013 it was formally decided that the only possible export route of the PCB oils to Europe would be via direct air transport.

4. Air transport of POPs from Kazakhstan to France

A unique operation was organized in spring 2014 for the air transportation of 80 tons of PCB waste from Kazakhstan to France. A Boeing 747 cargo aircraft was specifically chartered for this export and terminal cargo personnel in Kazakhstan and France were informed about this project well in advance.

The transportation was undertaken in accordance with the International Air Transport Association (IATA) Dangerous Goods Regulations (DGR) [1]. IATA DGR regulations are based on the same principles as the ADR and IMDG regulations, but incorporate important differences in the transportation of PCB containing dangerous goods. These differences refer to all parts of the transportation requirements, including maximum allowable quantity limitations, packaging requirements, stowage requirements, labeling and marking requirements and documentation requirements. The whole operation was undertaken under the supervision of IATA trained personnel.

Upon arrival of the waste at the airport the cargo terminal received the waste and screened each pallet separately through the security system. Once the aircraft arrived at the airport the air pallets were unloaded from the aircraft and were transferred to the cargo terminal area. The waste was loaded on the air pallets and secured in place with safety nets. The loaded air pallets were transferred to the aircraft with special vehicles for this purpose. Loading vehicles were used to lift the air pallets at aircraft deck level, where they automatically slid to their dedicated position in the deck. The exact same reverse process was followed for unloading in the French airport.

5. Second UNDP project for the export of PCB capacitors and related waste

In May 2014, upon the successful exportation of the PCB waste to France, UNDP country office issued a second tender for the incineration of 170 tons of PCB capacitors via air transportation. This project was also awarded to Polyeco in September 2014. Two additional aircrafts were chartered in the context of the second project and all waste was successfully transported to France in June 2015. Waste was incinerated in July 2015.

6. Conclusions

The transboundary movement possibilities of PCB waste from Kazakhstan to Europe in the context of the Basel Convention were thoroughly investigated in the context of a UNDP project for the disposal of 80 tons of PCB waste. The investigation proved that there is currently no road / rail / sea route available that would allow the transboundary movement of PCB waste from Kazakhstan to Europe. The following countries forbid the transit of PCB waste through their territory: Georgia, Azerbaijan, Russia, Turkmenistan, Iran and China. As a result the only possible current solution for the exportation of PCB waste from the Republic of Kazakhstan to Europe is with direct air transport without intermediate stops.

Three aircrafts were chartered for the transboundary movement of 250 tons of PCB waste in total, in the context of two separate contracts between Polyeco and UNDP country office in Kazakhstan.

Air transport of waste has the advantage of quick and safe project implementation and the disadvantage of increased costs. However, it can provide a credible solution for the incineration of hazardous waste, in cases where alternative options are not available and environmental problems must be resolved.

Acknowledgements

This work was realized in the context of the project "Design and Execution of a Comprehensive PCB Management Plan for Kazakhstan" funded by GEF and the Government of Kazakhstan and implemented by UNDP country office in Kazakhstan.

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FIELD EXPERIENCE OF POP'S MANAGEMENT IN UKRAINE

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Abstract

The company **SI Group Consort Ltd. (Israel)** is probably one of the biggest and unique operators of hazardous waste in Eastern Europe.

SI Group Consort Ltd. was established in 2008. The main purpose of establishing exercise was providing activities in several sectors :

- **environmental projects** : operators are licensed Ukrainian company " Si Bud Systems LLC " and "Sigmas Ecology Ltd", which are having all licenses, resources and experience for hazardous waste operating;
- **transportation and logistics services**: LLC "AVS Trans" - a licensed transporter having a modern fleet, its own production facilities and transport permits, including international (ADR) for a Dangerous Goods transportation;

The main activity of the company is to implement the integrated environmental programs, including and at the whole state level. And we have succeeded in this.

An integrated approach is to find and develop the best solutions for a specific customer's waste, its placement and complexity of retrieval, and ultimate disposal / destruction of the world by using modern technologies.

Now the full service hazardous waste management is practiced by S.I.Group Consort Ltd.:

- development of technological regulations and instructions in cooperation with the specialized research institutes;
- processing of permits on the international movement of hazardous wastes in close cooperation with states authorities of EU members acc. to Basel convention;
- extraction and repackaging of hazardous waste in certified packaging;
- transportation of the hazardous waste by licensed transport (trucks, vessels, railway)
- destruction / disposal of waste at the facilities of the leading European operators (Veolia, Tredi, Tradebe etc.)
- operations to eliminate the effects of environmental accidents.

All stages, without exception, the relevant documents that provide the proper level of quality control and transparency in the provision of services have been approved. Our company is certified according to international standards ISO 14001:2004 and ISO 9001:2008, as well as all subsidiaries

Key Words

POP`s, HCB, MNCB, PCB , Obsolete Pesticides, Ukraine

Materials and methods

As a National operator for dealing with hazardous waste S.I. Consort Group Consort, Ltd. with the assistance of its subsidiaries in Ukraine was able to successfully execute the national tasks for the permanent elimination of Ukraine from residues of hazardous waste left over from the Soviet era. All work performed on site of collection, packaging and transportation of hazardous waste was under control by government commission and the work of excavating, collecting, packaging and loading of HCB in Kalush (Ivano-Frankovsk region) and of MNCB in Gorlovka (Donetsk region) additionally was controlled "Institute of Environmental Geochemistry of National Academy of Sciences of Ukraine" (IEG)[1] .

We are using only certified equipment and UN approved packaging, we also use only certified transport according ADR[2], all drivers and staff passed specialized training and get permit to deal with hazardous waste.
All hazardous waste was packed and transported according European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR)[2], Regulation EC 1013/2006[3] and Basel Convention[4]

Results and discussion

Some data on the export of hazardous waste from the territory of Ukraine :

2011:

- 10 412 t – obsolete pesticides from all over Ukraine;
- 9 486 t – hazardous waste of HCB (Kalush, Ivano-Frankovsk region);
- 2351 t – hazardous waste of MNCB-mononitcrohloro-benzene (Gorlovka chemical plant, Donetsk region)
- 300 t – hazardous waste of PCB (sovtol oil)

2012:

- 13 061 t - obsolete pesticides from all over Ukraine
- 3 429 t - hazardous waste of HCB (Kalush, Ivano-Frankovsk region)
- 392 t – hazardous waste of MNCB-mononitrochlorobenzene (Gorlovka chemical plant, Donetsk region)
- 272 t – hazardous waste of beryllium (Former military plant "Zapad", Kiev)

2013:

572t - obsolete pesticides from all over Ukraine
441t – hazardous waste of MNCB-mononitrochlorobenzene (Gorlovka chemical plant, Donetsk region)
11 992 t - hazardous waste of HCB (Kalush, Ivano-Frankovsk region)

Results are that more than 52 400 t of hazardous waste has been exported and disposed from Ukraine, thus reducing further increase and pollution of the environment, reducing transboundary spread of pollution and reducing the harm to human health in regions of Ukraine which was relieved from hazardous waste as described above. It has specially to be mentioned that the Company has successfully completed four of the seven priorities in Ukraine in terms of environmental safety at the state level by the special decree of the President for 2011-2013[5].

In order to bring the scope of hazardous waste management in Ukraine in line with European standards, the company implementing own several projects, namely:

- design and construction of (hazardous) waste processing complex with high temperature incinerating based on a rotary kiln technology (up to 10 000 tones per year) and modern industrial waste landfill (up to 200 000 tones per year);
- purchased and launched the first in Ukraine self-con-

tained unit “Herborn System» (Germany) for recycling of the fluorescent and energy-saving lamps with a capacity of up to 10 million units / year.

- running and implementing social projects jointly with environmental NGOs to collect used batteries from the public in Ukraine for the following recycling in the European Union.

Acknowledgements:

The most of projects we done were funded by the government of Ukraine and local authorities.

Rapports issued by “Institute of Environmental Geochemistry of National Academy of Sciences of Ukraine” (IEG)[1] of Research work and methodological support in the implementation of environmental protection measures for collection, transportation, preparation for the transportation of hazardous waste of HCB in Kalush (Ivano-Frankovsk region) and of hazardous waste of MNCB in Gorlovka (Donetsk region).

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REMOVING THE THREATS OF OBSOLETE PESTICIDES IN MOLDOVA

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Summary

Since 2011, DEKONTA has been responsible to dispose approximately 752 tonnes of obsolete pesticides (and pesticides contaminated materials) from eight different warehouses in Moldova (Gradinita, Ciobalaccia, Clocusna, Pascani,Singerei, Oliscani, Pelivan and Paupati). The obsolete pesticides have been repacked into appropriate containers and transported abroad for final disposal in incineration facilities in Europe.

In this paper, it will be presented the process of safeguarding illustrating the challenges encountered and lessons learned from the implemented projects in Moldova.

Keywords

Persistent Organic Pollutants (POPs), Moldova, Contaminated Sites, Safeguarding, Disposal

Introduction

For decades, pesticides have been used worldwide as a mean to increase agricultural output, fight pests and control tropical diseases. Now, obsolete, these chemicals are highly toxic, highly dangerous substances that pose a direct threat to human health. In Moldova, it is not uncommon for local residents to use the dismantled warehouses as building materials for their own sheds, houses and fences and even re-use obsolete pesticides for agriculture. It is clear that obsolete pesticides lying out in the open or in ruined stores can easily pollute the environment and are a risk to human health. For this reason, Moldovan authorities with the co-operation of international donors like FAO, NATO, the Czech Government and others, have implemented several projects with the aim to remove this threat from the environment.

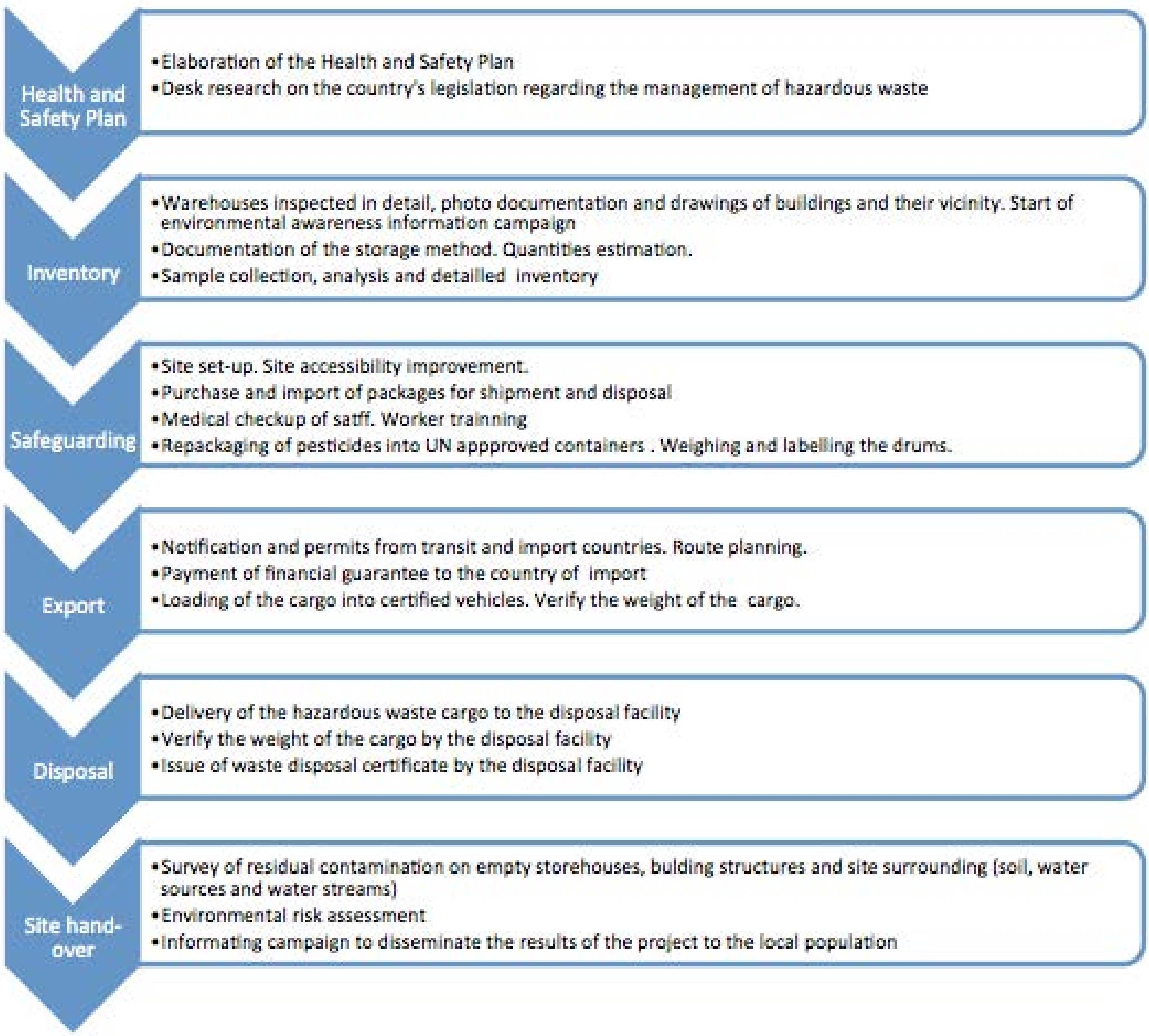
Since 2011, DEKONTA has been co-operating with the Moldavian authorities and has removed 752 tonnes of obsolete pesticide waste from several pesticides storehouses in the country.

Project Activities

DEKONTA's approach for the implementation of the projects was divided in six main phases: health and safety plan elaboration, inventory, safeguarding, transportation, disposal and site hand-over.

A summarized description of the phases is illustrated in the flowchart below.

Project	Amount (t)	Summary
Remediation of environmental burdens caused by pesticides in Moldova	202	• Gradinita, Ciobalaccia and Clocusna storehouses • Disposed in Germany
Remediation of environmental burdens caused by pesticides in Moldova II	250	• Singerei, Oniscani, Pelivan, Papauti storehouses • Disposed in Germany
Safeguarding and Disposal of hazardous chemical waste in Moldova	300 (estimated)	• Pascani storehouse • Project is running • To be disposed in Poland



Health and Safety Plan
- Elaboration of the Health and Safety Plan
- Desk research on the country's legislation regarding the management of hazardous waste

Inventory
- Warehouses inspected in detail, photo documentation and drawings of buildings and their vicinity. Start of environmental awareness information campaign
- Documentation of the storage method. Quantities estimation.
- Sample collection, analysis and detailled inventory

Safeguarding
- Site set-up. Site accessibility improvement.
- Purchase and import of packages for shipment and disposal
- Medical checkup of satff. Worker trainning
- Repackaging of pesticides into UN appproved containers . Weighing and labelling the drums.

Export
- Notification and permits from transit and import countries. Route planning.
- Payment of financial guarantee to the country of import
- Loading of the cargo into certified vehicles. Verify the weight of the cargo.

Disposal
- Delivery of the hazardous waste cargo to the disposal facility
- Verify the weight of the cargo by the disposal facility
- Issue of waste disposal certificate by the disposal facility

Site hand-over
- Survey of residual contamination on empty storehouses, bulding structures and site surrounding (soil, water sources and water streams)
- Environmental risk assessment
- Informating campaign to disseminate the results of the project to the local population

Figure 1 - Main phases of the projects

Pesticides Analysis

The results of qualitative analyses of pesticide samples and contaminated debris indicate presence of a wide spectrum of substances. The most represented pesticides in solid matrices include trifluralin, α, β, γ, δ – HCH, atrazine, carboxin, proparil (DCPA), diazinon, diphenamid, chlorobenzilat / chloropropylat / etoxinol, mefenoxam / metalaxyl, prometryn, propazine, simazine / triazine, sulfotep and triadimefon. Acetochlor, metochlor and atrazine, dimethachlor, propazine, simazine/triazine, terbuthylazine and 2,4,D were found in liquid matrices.

According to the origin and properties, the wastes were classified into three codes according to the European catalogue of wastes (Decision of the Commission 2000/532/EC) and at the same time the wastes were classified into three classes of hazardous character according to the European Agreement Concerning the International Carriage of Dangerous Goods by Road, the so-called ADR. The list of wastes and their classification is synoptically stated in the following table.

Waste code	*Waste designation*	*characteristic of risk*	*UN number*	*Name*	*Class of hazardousness*	*Packing group*
02 01 08	Agrochemical wastes containing dangerous substances	Toxicity	2588	pesticide, solid, toxic, unspecified	6.1	II
			2902	pesticide, liquid, toxic, unspecified	6.1	II
15 01 10	Containers containing the rest of dangerous substances or contaminated containers	Ecotoxicity	3077	environmentally hazardous substance, solid, unspecified.	9	III
19 13 01	Soil remediation solid wastes containing dangerous substances	Ecotoxicity	3077	environmentally hazardous substance, solid, unspecified.	9	III

Table 1 - List of wastes and their classification

Main Challenges and Lessons Learned

The implementation of these projects proved to be challenging. The main challenges encountered were:

- Lack of information regarding the pesticides stored in the storehouses. Storehouses in very poor conditions.
- Presence of strong oxidizers in the storehouses. Permanent risk of fire.
- Routes for the transportation of the pesticides should be planned considering the countries of transit/import. Some authorities are quicker to approve the movement of the waste through/to their territory.
- Maritime transportation companies may refuse to transport the waste in their vessels.

The lessons learned from these projects were:

- Insisting on maximal safe conditions during the work. The presence of unknown substances and poses a constant threat for the safety of the workers.
- Strict usage of PPE and safety equipment at the site. Due to the uncertainties regarding the identities of the chemicals present at the site, DEKONTA´s approach is to be one step ahead and use more PPE than the minimum required.
- Detailed analysis in the field, cross analysis (Raman spectography and RTG) for the identification of unknown chemicals.
- Elemental analysis of every drum for presence of limiting elements regarding incineration limits.
- Close cooperation with analytical laboratory - identification of all chemicals including the metabolites of pesticides, specific pesticides that were tested in Moldova during the Soviet times

Conclusion

The projects had very positive impact in the condition of the environment. The most benefitted group of these projects were the workers who move directly around the premises of pesticide warehouses, people who live in the surroundings of pesticide warehouses and the inhabitants of respective districts, who could be adversely affected by collected toxic substances, due to flue dust particles, improper handling, escape of liquids and etc.

As the direct benefits in the social sphere we can see the opportunity of an additional income of local inhabitants from auxiliary works associated with removal of wastes. These concerned miscellaneous small repairs (of warehouses, tools and equipment, vehicles), transport of material, manual help when loading and unloading goods, guarding of buildings, forklift operation, etc.

It is also necessary to mention that repackaging and disposal of the obsolete pesticides only removes the source of the contamination. It is common that residual contamination remains at the site (contaminated building structures, soil, water bodies and etc.) and it should also be addressed in future projects. As an example, soil samples (soil probes, surface soil) collected from the Oniscani site after the pesticides repackaging activities have been completed revealed concentrations above 50 mg/kg in soil, i.e. the level when materials are classified as hazardous waste according to the Moldavian regulations.

For these reasons, a comprehensive information campaign to raise awareness must be carried out until further projects addressing residual contamination are implemented. Situations were locals perceive the old storehouses, now empty of pesticides, as safe are not uncommon. In many cases building materials are at risk of being removed from the site and used as building material for houses or stables.

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DISPOSAL OF POPs PESTICIDES AND INITIAL STEPS OF CONTAINMENT OF DUMPED POPs PESTICIDES IN GEORGIA

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Abstract

On October 2013, Polyeco was awarded through international tendering the GEF/UNDP funded project for the management of dumped Pesticides in Lagluja landfill. The scope of services included the provision of UN packaging and protective equipment for the excavation, repackaging and final disposal of a total of 240 tn of pesticides, and the export and final disposal of two ODS cylinders stored at the premises of the Georgian Association of Refrigerating, Cryogenic and Air-conditioning Engineers (GARCAE). During the Project execution and specifically upon excavation of dumped hazardous pesticides, it was confirmed that their classification and identification was impossible either due to improper labelling of the containers or due to destruction of their initial packaging. POLYECO took action and in cooperation with the laboratory of Ministry of Environment and Natural Resources Protection of Georgia, conducted necessary chemical analysis in order to ensure their proper packaging, transportation and final disposal. The objective of this article is to share the experience gathered during the execution of the project and the obstacles and contingencies that occurred. The disposal of OPs was undertaken in two accredited incineration facilities in Belgium and France, with the aim to provide high quality services to the client at competitive prices. Lessons learnt from the challenging task, combined with the specific weather conditions and other obstacles during the export works in Georgia, will be presented for consideration in the implementation of future OPs management projects that comprise excavation and repackaging activities of unknown pesticides.

Key Words

POPs, Georgia, pesticides, ODS, Basel Convention, Iagluja dumpsite, OPs

1. Introduction

POPs pesticides, mainly DDT, started accumulating in Georgia during early 1970s due to the oversupply of pesticides as a result of the former planned economy system. The POPs pesticides were stored around the country at farming centres and smaller warehouses. From mid-1970s onwards, once it was realized that these pesticides are obsolete, a major initiative was launched to collect all obsolete pesticides into a hazardous waste dumpsite in a remote area at the Iagluja Mountain, Marneuli district of eastern Georgia. Obsolete pesticides have been dumped at the Iagluja dumpsite from 1976 till 1985, while recently and specifically the previous decade about 230 tons packed and labelled obsolete pesticides (including heptachlor, DDT) from Badiauri has been transported and disposed in Iagluja dumpsite.

The services provided within the scope of the Project comprised:

- Mobilization reports H&S, Quality , Emergency response and Working plan
- Licensing in accordance to Basel Convention
- Supply of project equipment & consumables & site preparation
- Excavation of waste, sampling & chemical analysis
- Repackaging, loading and transportation of waste to the port of Poti
- Final disposal of repacked pesticides and ODS cylinders

2. Mobilisation Activities

The kick of meeting took place in Tbilisi on 2nd of December with the presence of Project Stakeholders including representatives from UNDP Georgia and Ministry of Environment and Natural Resources Protection. Draft mobilization reports were presented during the kick off Meeting and final reports were submitted one week after.

Personal Protective Equipment (P.P.E.), consumables and UN Packaging materials were supplied from POLYECO facility in Greece and shipped to Georgia, since the equipment was not available in the country. The container loaded with consumables and equipment was loaded on a vessel on 27th of March. Shipping documentation was submitted to UNDP in order to support the custom clearance of the Goods. There was a short delay in the vessel arrival at Poti Port due to bad weather conditions and finally the equipment was custom cleared and delivered on Site on 5th of April. Indicative equipment that was finally used for the works comprised PPE, FIBCs, UN approved Drums, portable scale, pumps for drainage of liquids, Implantable Cardioverter Defibrillator (ICD) and decontamination unit.

Although the area in Lagluja was protected with fencing, additional security-guard was assigned in order to protect machineries, waste packaging-works and the site area in general during the works. Mobile office-container and chemical toilette were installed for the needs of the personnel and warning signs and strap were placed for safety reasons in order to prohibit the entrance of unauthorized persons.

3. Licensing

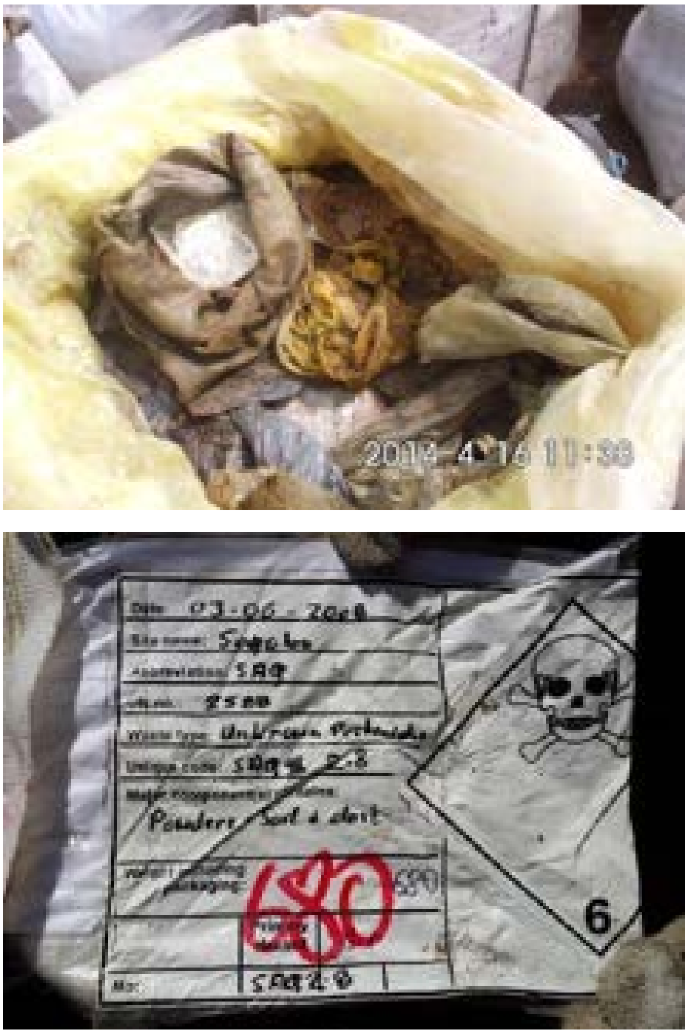
Notification documents in accordance to Basel Convention for the export of POPs to France
and Belgium were prepared and submitted to competent authority in Georgia by the end of December. Belgium provided consent for the export of waste on 18th of February. However there has been an increased delay in the licensing procedure for France, since the Ministry of Environment initially declared as waste producer was reluctant to sign the corresponding field in the TFS application. Following mutual clarification and the kind intervention of UNDP the issue was solved. TFS for France on producer field was signed on 15th of April and final consent from France was issued on April 25. The final export license from Ministry of Environment in Georgia was issued on 3rd of June.

It has to be emphasized that in accordance to Commission Decision 2005/51/EC authorizing Member States temporarily to provide for derogations from certain provisions of Council Directive 2000/29/EC in respect of the importation of soil contaminated by pesticides or persistent organic pollutants for decontamination purposes, the issuance of phytosanitary certificates export by national competent Authority is necessary. Polyeco following communication with Georgian IPPC competent authority issued the phytosanitary certificate necessary for the pesticides export.

4. Excavation activities

Excavation works for the identification of buried pesticides were initiated on 6th of April following instructions by UNDP for the potential disposal area within the fenced 4 acre area at the top of the mountain. Their disposal area was identified and covered a total 20 meters in length, 3-7 meters in width and up to 3 meters in depth. Unfortunately the condition of waste packed in non-approved equipment was poor and the majority of waste was unidentifiable. Some FIBCs had labels with generic UN numbers and info. Some others comprised several different bags with pesticides mixed with contaminated soil that had been labelled many years ago as unknown. Significant differences among the initial list of dumped pesticides and the actual excavated waste were noted, since only DDT and Chloropicrin waste fractions where visually identified.

Excavation works were finalised within 10 days and in total, 262 big bags and 42 drums of buried pesticides have been removed. Due to the poor quality of the original labelling and the actual dispersion of different unknown pesticides, it was extremely difficult to proceed with classification/ identification of waste and especially its hazard. Waste repackaging was conducted in parallel with waste inventorying and identification of the content of each FIBC. POLYECO in cooperation with Laboratory of Ministry of Environment conducted sampling plan and submitted the samples for analysis. Samples of contaminated soil from the dump were also collected in order to confirm their contamination. The method to evaluate the unknown waste included analysis on several parameters apart from visual inspection such as concentration in arsenic, mercury, phosphorous, chlorine, sulphur, pH, odour. Chemical analysis revealed increased Chlorine content in the different waste fractions, due to presence of DDT and other POPs organochloride pesticides.



Pictures 1-2: Mixed Uknown Pesticides Excavated and their old labelling

5. Repackaging & Transportation of Waste

As soon as the results of the laboratory were issued and the identification of waste was completed, repackaging works took place. New big bags type 13H3 with a total capacity of 1 m^3 and steel drums type 1A1 and 1A2 with a total capacity of 220lt were used. In total 290 FIBCs, 5 x 220 litre 1A1 UN Drums and 25 x 220 litre 1A2 UN drums were repacked. Following repackaging, the waste was transferred with truck-platforms from Lagluja Mountain to the nearest area in Marneuli in a square, large enough to host the whole quantity and the necessary truck-containers. PE-liner was applied all over the area. Nine (9) containers were loaded with pesticides and three (3) containers with soil contaminated with pesticides. GARCAE had finalized transfusion into new approved cylinders in accordance to ADR/IMDG from the beginning of April. Gas cylinders containing HCFC/HFCs were loaded on the same container with pesticides packed in FIBCs. Chloropicrin initially contained into steel drums with 100 liters capacity, was first transfused one-by-one into open head drums and then pumped with an electrical pump into steel closed head drums. After removal of the waste, the contaminated soil area was inspected by UNDP and was covered with top soil. Repackaging works of aprox 240 tn of pesticides where finalized within 22 days.

The actual maritime route for containers destined to France and Fos Sur Mer Port was the following and lasted 24 days : POTI – TRABZON – ISTANBUL (t/s)– GEBZE – GEMLIK – IZMIR – ALIAGA – VALENCIA –CASTELLON DE LA PLANA – BARCELONA – FOS-SUR-MER

The actual maritime route for containers destined to Belgium and Antwerp was the following and lasted 22 days : POTI – TRABZON – ISTANBUL (t/s)– GEMLIK – FELIXSTOWE – ANTWERP.
A significant delay occurred at the port of export in Georgia (Poti) due to extreme weather conditions. Despite the fact that containers were unloaded in the port by middle of June, the actual loading on the vessel took place 12 days later.

6. Disposal of Waste

Pesticides destined for disposal at high incineration plan of Indaver in Belgium, where delivered on 16th of July and their disposal was finalized on 15th August. Pesticides destined for disposal at high incineration plan of St Vulbas in France, where delivered until 30th of July and their disposal was finalized on 31st of August. Emissions reports from the incineration facilities depicting the efficient destruction of POPs, where submitted to the client. It has to be highlighted that the emissions reports issued by Incineration facilities always refer to the mixed fraction of several waste streams that has been disposed on the specific dates and not on the specific pesticide fraction that the client is interested in. This is due to the fact that POP waste streams are being incinerated in mixtures with other waste fractions to improve crucial operational parameters of the facility such as calorific value, Halogenated Compounds and Heavy Metal content etc.

7. Conclusions

Taking into account the obstacles and solutions provided within the project implementation, the following conclusions can be derived and taken into account in future projects that comprise excavation activities of dumped pesticides:

- Project stakeholders shall secure the prompt resolving of waste producer issue and liability. For waste fraction that is unknown and dumped under uncontrolled conditions, the national competent authority shall be initially responsible and defined as waste producer. Only following the excavation of unknown waste and the confirmation that waste beyond the scope of works is not present (e.g. radioactive, explosive etc.) can the contractor take the liability for their sustainable management.
- Hazardous waste handling works that comprise excavation activities of dumped waste comprise significant risk for the identification of their chemical characteristics. The initial list of dumped pesticides provided during tendering had significant deviations compared to the actual situation identified during the excavation waste. The majority of waste where mixed and unknown due to poor labelling, therefore stakeholders shall always foresee comprehensive sampling and analysis plan and increased disposal cost due to several contingencies.
- Combined Disposal of ODS and pesticides can reduce the overall project cost in case the same facility is eligible to receive and dispose the different waste fractions. This is due to the combined transportation of the waste streams in the same container and the reduced overall management and transportation cost.
- Maritime transportation is a component in hazardous waste management that is strongly depending on 3rd parties (Maritime Companies) and may be delayed by several parameters such as weather conditions. Stakeholders shall always take into account these contingencies while drafting their timetables for the project execution
- Disposal of hazardous waste and issuance of respective certificates in accordance to Basel Convention and EU Regulation, may be finalised even earlier than in one month, in case the disposal facility is notified early for the detailed characteristics of the waste and schedule promptly the joint disposal with other waste fractions based on the facility available capacity.

Acknowledgements

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THE DISPOSAL OF PESTICIDES AND DANGEROUS CHEMICALS IN THE REPUBLIC OF MOLDOVA UNDER NATO TRUST FUND MECHANISM

SUBMITTED PAPER

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Abstract

Surplus stocks of Pesticides and Dangerous Chemicals (PDCs) predating 1974 have left a damaging legacy in the Republic of Moldova, with around 4,000 tonnes buried and 3,300 tonnes scattered all over the country stored in over 450 poorly equipped or unfitted facilities lacking proper monitoring and security. To address and prevent increasingly high risks to population and the environment, a NATO Trust Fund mechanism was activated in 2007 to destroy the PDCs and assist Moldova to fulfil its obligations under International Conventions, agreements and protocols, especially the Stockholm Convention. A project with three distinct work packages to assist Moldova with the following objectives has been developed: repacking and centralizing, analysing and disposing the PDCs. On behalf of the lead nation Romania, the NATO Support and Procurement Agency (NSPA), NATO's logistics support management agency, is currently managing the execution of the third work package of this NATO Trust Fund in accordance with fund raising. Its objective is to dispose of 1,269 tonnes of PDCs stored at 15 Regional Central Storages repacked and centralised during work package I of the project in ready to transport containers. The work package also includes a public information and awareness campaign to ensure a permanent information flow for the general public on project activities.

Key Words

NATO, NSPA, Trust Fund, Moldova, Pesticides, Disposal.

1. NATO Support and Procurement Agency (NSPA)

1.1. What is NSPA?

The NATO Support and Procurement Agency (NSPA) is NATO's Integrated Logistics and Services Provider Agency, combining the former NATO Maintenance and Supply Agency (NAMSA), the Central Europe Pipeline Management Agency (CEPMA) and the NATO Airlift Management Agency (NAMA). The NSPA is a fully customer-funded agency, operating on a "no profit - no loss" basis. It employs some 1,200 staff and is headquartered in the Grand Duchy of Luxembourg (Capellen), with operational centres in Luxembourg, France, Hungary and Italy.

NSPA is the executive body of the NATO Support and Procurement Organisation (NSPO), of which all 28 NATO nations are members. Those nations are represented in the NSPO Agency Supervisory Board (ASB) which directs and controls the activities of the NSPA.

NSPA brings together in a single Organisation NATO's logistics and procurement support activities, providing integrated multinational support solutions for its stakeholders. Its creation falls within the framework of the new NATO approach to defence spending during austere times called Smart Defence of which Smart Support is a key element.

1.2. What is the mission of NSPA?

NSPA's mission is to provide responsive, effective and cost-efficient logistics support services for systems and operations. This support is provided – in times of peace, crisis and war, wherever required – to the NATO Alliance nations, the NATO Military Authorities and partner nations, both individually and collectively. The objective is to maximize the ability and flexibility of armed forces, contingents, and other relevant organisations to execute their core mission, in line with guidance provided by the North Atlantic Council.

1.3. NSPA support to Nations

1.3.1. Nationally Funded Support

NSPA develops multinational logistics solutions which ensure that each nation receives the logistics support it requires. NSPA hosts more than 30 different support partnerships. This is a proven concept first established in 1965, which now has a long history of success.

1.3.2. Internationally Funded Support

NATO's Partnership for Peace (PFP) Trust Fund was established in 2000 under the Ottawa Convention to assist PFP countries with the safe destruction of stocks of anti-personnel landmines.

The scope of the NATO PFP Trust Fund policy was subsequently extended to include the destruction of small arms, light weapons and surplus munitions, and to cover other and the consequences of defence reform related activities such as radioactive and chemical waste management. The area covered was later enlarged to include the Mediterranean Dialogue and Istanbul Cooperation Initiative countries.

NATO PFP Trust Funds are a transparent mechanism that allow NATO and partners to come together, collectively contributing to a project and, through NSPA management, deliver the assistance in accordance with NATO political policies and administrative procedures

NSPA has 20 years of experience in project management and is therefore well placed to provide technical and contractual support and overall project management. As executing agent, NSPA handles the following aspects:

- monitoring project implementation
- preparing statements of work
- issuing calls for tenders
- reviewing tenders and awarding contracts
- monitoring contracts
- submitting progress reports on project implementation to the Lead Nation.

In addition, NSPA is able to provide advice on matters such as the technical merit of proposals and plans for specific tasks related to the project.

During project implementation, NSPA is responsible for payment authorization, quality assurance and verification and certification of work performed.

2. Moldovan NATO PFP Trust Fund Project

2.1. Background

The use of pesticides and other chemicals, toxic to both human health and the environment grew dramatically during the last 40 years in the Republic of Moldova. Due to poor management practices and the lack of imposition of bans in the use of particular chemicals, Moldova has accumulated over the years large amounts of obsolete pesticides, in particular persistent organic pollutants (POP[1]). These substances possess toxic characteristics and are persistent. When accumulated in the tissues of living organisms, they are likely to cause adverse effects on human health and environment both close and far from their sources (Grama et al, 2012). Moldova has a population of 3.6 million people (Eurostat, 2015). Out of the total population, 57% are rural inhabitants, most of them involved in agriculture activities onto which economy heavily depends.

Despite that Moldova never produced POP pesticides[2] and prohibited POP back in early 1970s, surplus stocks of PDC have left a damaging legacy. Until 2008, the quantity of harmful pesticides was estimated at 7,300 tons, including about 4,000 tons of PDC buried (Figure 1(a)) in a 1974 built landfill and another 3,300 tons of PDC scattered all over the country (Figure 1(b)) and stored in over 450 poorly equipped or unfitted facilities lacking proper monitoring and security(Figure 1(c)).

(a) Buried pesticides

(b) Poorly packed pesticides

(c) Unregulated storage facility

Figure 1 (a-c): Obsolete pesticides scattered all over Moldova and stored in poorly equipped and unfitted facilities lacking proper monitoring and security

To address and prevent increasingly high risks to the population and the environment, NATO, in collaboration with other international organizations embedded in the Environment and Security (ENVSEC) initiative for Eastern Europe (the United Nations Environment Programme, the United Nations Development Programme and the Organization for Security and Co-operation in Europe (OSCE)), accepted supporting Moldova to achieve its objectives in the management and safe disposal of its chemical hazards and the fulfilment of its obligations under international Conventions, Agreements and protocols, especially the Stockholm Convention, signed and ratified by Moldova in 2004.

2.2. NATO PFP Trust Fund Project Scope

In February 2004, at the request of the United Kingdom delegation to NATO, NSPA developed a project proposal to assist Moldova with the disposal of PDCs. The project is to be managed under the guidelines of the NATO PFP Trust Fund mechanism and aims at the disposal of 1,269 tonnes of PDC spread over the country. Three distinct work packages (WP) within the overall requirement were

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[1] POP pesticides as addressed under the Stockholm Convention are: aldrin, dieldrin, endrin, chlordane, heptachlor, DDT, mirex, hexachlorobenzene and toxaphene.

[2] The term pesticide stands for all chemical products that serve as herbicide, insecticide, fungicide, etc.

identified, each WP focussing on the following:

- WP I: Repacking and centralization;
- WP II: Chemical analysis; and
- WP III: Disposal of PDC.

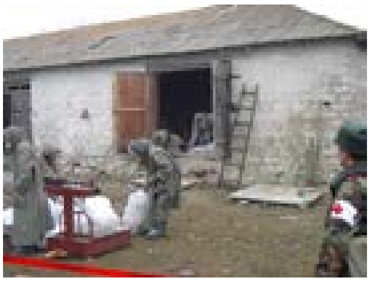
The implementation of the overall project depended on the signing of a number of agreements that were discussed, prepared and signed during the course of 2006. Each WP is summarised in a separate Implementing Agreement which is attached through amendment to the Memorandum of Understanding between Moldova and NSPO. The terms of cooperation for the execution of each WP between NSPA and the lead nation, Belgium and Romania for WP I and Romania for WP III, are set out in Executing Agent Agreements. WP II was led by the NATO Science for Peace and Security (SPS) Program.

2.3. Past achievements

2.3.1. WP I – Repacking and Centralisation

Implemented in November 2006, WP I was successfully completed in July 2007. With the support of the Moldovan Ministry of Defence (MOD), the repacking of 1,269 tonnes of both liquid and solid PDC and relocation from 228 unregistered sites to 15 regional central storages was achieved, as shown in Figure 2(a). Both public health and environment benefited immediately from the elimination of the presence of the PDC preventing also further soil pollution by various pesticides. Table 1 gives a detailed overview of the quantities of PDC stored in the regional central storages originating from different districts as well as the reduced threat on the population of each district.

(a) 228 unregistered sites were evacuated and centralised in 15 regional central storages



(b) Repacking

(c) Transport

(d) Centralization

Figure 2 (a-d): Tasks performed during the WP I of the NATO PFP Trust Fund

The PDC were packed in UN approved packaging with a 4 years validity period, i.e. metal drums for liquid PDC and plastic drums for the consolidation of solid PDC put in plastic bags (Figure 2(b)). Both the packing and the transportation (Figure 2(c)) of the packed PDC to the regional central storages (Figure 2(d)) have been entrusted to MOD's Chemical Defence Unit.

2.3.2. WP II – Chemical Analysis

In parallel with the first WP, NATO funded a 2 year SPS project, i.e. Science for Peace 98 1186 "Clean-up of Chemicals Moldova" project, to allow better decision making for the final disposal of the PDC.

Implemented in February 2005, the objective was to establish a chemical analysis laboratory for the characterization of PDC and the elaboration of a comprehensive database. Qualified personnel investigated more than 5,980 samples of 33 locations by means of analytical techniques such as GC-MS and HPLC (Grama et al, 2012). Tasks performed during this WP are shown in Figure 3. The WP ran until early 2010 with the support of the Moldovan Ministry for Environment and Natural Resources.

(a) *Sampling of buried pesticides*

(b) *Chemical analysis of the samples*

Figure 3 (a-b): Tasks performed during the WP II of the NATO PFP Trust Fund

2.4. WP III – Disposal of PDC

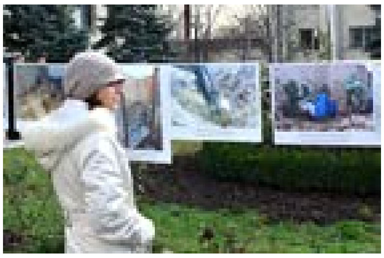
2.4.1. General

Following the successful implementation of the first and second WP of the project, NATO launched on 20 May 2010 the third WP at the NATO Political Partnership Committee in EAPC format under Romanian leadership. The aim is to dispose of the 1,269 tonnes of PDC packed and temporarily stored in 15 regional central storages.

During the first WP, an assessment was held to determine the most appropriate way for the final disposal. This assessment indicated that high temperature incineration was the most likely method for the destruction of the PDC. Options for the disposal of the packed PDC included either importing such an incineration facility into Moldova on a temporary or permanent basis or exporting the PDC to a waste incineration plant (Oltman, 2007). The latter was chosen to be the most cost effective and quickest solution.

2.4.2. Project Management

From the original 1,269 tonnes of PDC, 312.3 tonnes of PDC were destroyed under bilateral initiatives between Moldova and different institutions during 2008 and 2010. As a result, NSPA issued, in accordance with its procurement regulations of international competitive bidding, a request for proposal for the destruction of only 956.7 tonnes of PDC. Potential bidders had the chance to visit different regional central storages in order to have an understanding of the required tasks. In February 2013, an outline agreement contract for the disposal of 956.7 tonnes of PDC was awarded to the cheapest technically compliant bidder. Before contract award, NSPA undertook a pre-award survey to one of the bidder's facility located in Poland. As agreed with Moldova and the lead nation, Romania, an amendment to the outline agreement will be issued to add the 312.3 tonnes of PDC.



(a) *Inhabitants of Basarabeasca district attending the photo exhibition "Past, Present and Future" organized by the Moldovan MOD*

SOCIETY

Last batch of pesticide from district of Taraclia, to leave Moldova

(b) *Extract from a local media*

Figure 4 (a-b): Examples of the public awareness campaign held during the execution of the WP.

From a transportation perspective and in accordance with the Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal, the Moldovan MOD notified mid 2013, in writing, the different competent authorities of Moldova, as state of export, Ukraine, as state of transit, and Poland, as state of import. After providing the necessary information, the different competent authorities sent their consent with validity till end of June 2014. Upon a new notification from the MOD end 2013, the consent of the different authorities for the shipment of waste was extended till end of June 2015.

An external verification auditor was contracted to audit and verify the contractor's on-site performance on behalf of NSPA. The verification auditor performed random checks during palletising and labelling activities as well as checking the weight of the PDCs loaded on the trucks. In the framework of this WP, the Moldovan MOD in cooperation with NSPA, NATO Documentation and Information Centre and Local Public Authorities continuously coordinate public relations activities with the relevant stakeholders. This public information and awareness campaign included videos such as NATO's movie titled "NATO and Moldova tackle a silent killer"[3], press releases, ceremonies, etc. to ensure a permanent information flow for the general public on project activities. Examples are provided in Figure 4.

To ensure successful completion, the contractor provided, after an initial on-site survey, a risk based project management strategy. This is to identify the most cost effective clean-up programme according to the company's Health, Safety and Environmental Management System. Prior to commencing loading operations, the contractor trained all project staff, including the local personal of the MOD's Chemical Defence Unit working alongside the contractor in preparing and loading the shipments. The training covers basic health and safety rules including the basic principles of a risk assessment and hazard control as well as the correct use and maintenance of personal protective equipment.

2.4.3. Achievements

Although the PDCs are currently packed in adequate UN packaging, the physical characteristics were subjected to ageing and experienced environments for which they were not designed for (Figure 5(a)). Furthermore, during the years, rainwater seeped through the roofs of the temporarily storage locations. The water had made its way into the drums as the lids were damaged. Several drums have developed leaks.

To ensure safe transport of the hazardous waste, the drums with PDC are therefore repacked, palletised and properly labelled (Figure 5(b) and (c)) before being shipped (Figure 5(d)) to the incineration facility in Poland. It is the contractor's responsibility to transport the PDC in a safe and secure way from the point of loading to the place of final disposal. The contractor incinerates the PDC including the contaminated packaging according to the directive 2010/75/EU on industrial emissions (integrated pollution prevention and control).

(a) Damaged packaging

(b) Repacking of the PDC in approved packaging

(c) Repacked PDC ready to be loaded for shipment

(d) Shipment ready for transport

Figure 5 (a-d): Repacking tasks performed during the WP III before shipment

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[3] A link to NATO's movie titled "NATO and Moldova tackle a silent killer" can be found on NSPA's PFP Trust Fund website http://www.nspa.nato.int/en/organization/logistics/LogServ/ntfp.htm

Regional Central Storage	District	Population (x1,000)	Quantity (tonne)	Contracted					Disposed (tonne)	Com-pleted
				1	2	3	4	5		
Ranger Danceni	Ialoveni	84.3	112.0	☑					112.0	☑
	Anenii Noi	74.5	19.6	☑					19.6	☑
Rodina Nova	Taraclia	29.1	172.5	☑					172.5	☑
Sadaclia	Basarabeasca	16.4	44.6	☑					44.6	☑
Cahul	Cahul	85.1	63.6		☑				63.6	☑
Cosăuţi	Soroca	62.4	33.7		☑				33.7	☑
Iargara	Leova	37.8	38.3		☑				38.3	☑
Tîrnova	Donduşeni	33.7	54.9		☑				54.9	☑
Alexandreni	Glodeni	49.3	26.4			☑			26.4	☑
Călăraşi	Călăraşi	62.2	70.0			☑			70.0	☑
Budjac	Comrat	25.7	133.4				☑			
Hitresti	Făleşti	75.2	187.9				☑			
Alexandreni, Singerei	*Singerei*	*74.4*	*79.1*					☒		
	Balti	*4.9*	*54.8*					☒		
	Drochia	*68.6*	*22.8*					☒		
Edinet	*Edinet*	*56.1*	*7.8*					☒		
Gaidar	*Ceadir-Lunga*	*22.9*	*59.4*					☒		
Ungheni	*Ungheni*	*76.4*	*88.3*					☒		
Totals			1,269	349	190	96	321	312	635.4	10

Table 1: Detailed overview of the 1,269 tonnes of PDC to be disposed stored in 15 regional central storages originating from the different districts. 635.6 tonnes of PDC from 10 districts have been disposed of in Poland.

As shown in Table 1, a total of ten sites, corresponding to net 635.6 tonnes of PDCs were shipped to and disposed by means of incineration. This outcome was achieved in accordance with the fund raising allowing NSPA to award three orders on the existing outline agreement. Further contributions are necessary to dispose of the remaining surplus PDC. NSPA may need to renegotiate prices of the outline agreement with the contractor as the validity of the offer expires early 2016. Prior to any new shipment, the Moldovan MOD shall need to notify the different competent authorities to consent the shipments.

3. Conclusions

The aim of the third WP of the NATO PFP Trust Fund is the final disposal of 1,269 tonnes of surplus PDC located in various regional central storages in Moldova. The PDC which are extremely dangerous for the health of the population and environment, were previously collected, centralized and temporarily stored in regional central storages and analysed in the framework of the previous two WP of this NATO PFP Trust Fund in Moldova.

The practical activities consist in repack, transport and dispose the PDC by incineration at high temperature. Under the leadership of Romania, NSPA, acting as executing agent, has awarded an outline agreement as a result of an international open competitive bidding process with an international contractor to which it places orders. In accordance with the fund raising, 635.6 tonnes of PDC were disposed of through incineration. Further donations are necessary to achieve the aim of the targeted WP and as such diminish the adverse effect on human health and environment.

4. Acknowledgements

The 3rd phase of this NATO PFP Trust Fund is led by Romania whilst NSPA managed the project as Executing Agent. We acknowledge the financial and in-kind contributions of both Allied and Partner Nations including Romania, the Republic of Moldova, Belgium, Bulgaria, the Czech Republic, Estonia, Finland, Ireland, Italy, Japan, Latvia, Luxembourg, Norway, Poland and Turkey.

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NATIONAL IMPLEMENTATION PLAN FOR THE POPS MANAGEMENT IN TURKEY

SUBMITTED PAPER

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Abstract

Persistent organic pollutants are a subject of broad international interest on the global and regional scales. The global international agreement – Stockholm Convention on Persistent Organic Pollutants (SC) – is a global treaty focused on the protection of human and environment against this group of harmful chemicals. Very important regional activities are connected with the Convention on Long Range Transboundary Air Pollution (CRLTAP) of the United Nation Economic Commission for Europe (UN ECE) and its POPs Protocol. Both conventions are included the chemical legislation of European Union.

National implementation plan of the POPs management in Turkey as a part of the EU project of the Technical Assistance for the Implementation of the Persistent Organic Pollutants Regulation was prepared. This document is focused on the management of POPs problems in Turkey and implementation of the Stockholm Convention on POPs, CRLTAP/POPs Protocol and EU POPs Regulation. Also a draft of POPs by-law was prepared for the full implementation of POPs legislation in Turkey as a part of transposition of EU Legislation..

The existence of an institutional and organizational framework for supporting the implementation of the POPs legislation was defined with the legislative support.

The identification of competent authorities, relevant authorities and stakeholders and their participation/involvement in management process on the implementation of the legal requirements were defined in the draft by-law in order to ascertain their active participation in the management of POPs especially in decision making process.

Key Words

POPs, National Implementation Plan, Stockholm Convention, POPs Protocol, EU Regulation

Materials and methods

Turkey has signed the Stockholm Convention on Persistent Organic Pollutants on May 23rd 2001 and is approved by the Turkish Grand National Assembly as 5 871 numbered Law (14.04.2009, No.27200) then published on July 30th 2009 as approved by the Council of Ministers (30.07.2009, No.27304). The Convention officially is effective since January 12th 2010.

As stated by the Article 7 of the Convention, Turkey prepared the first NIP in 2004 to 2006 funded by GEF and revised it in 2010, submitted to the Stockholm Secretariat in 2011 which included initial 12 POPs issues of concern like uses, import, export, production, distribution in country and source related inventory, current stockpiles and its disposal options assessment, contaminated sites, POPs chemicals related infrastructure, legal instruments, monitoring, research and development capacity, monitoring system establishment and use.

As a part of the UNIDO Project, the draft of updated SC NIP was prepared. The updated NIP preparation was coordinated by the Ministry of Environment and Urbanization (MoEU) General Directorate of Environmental Management Department of Chemicals Management and conducted by establishing task teams by means of gathering previously identified relevant stakeholders. The prepared plan was finalized by remarks made by the stakeholders.

Based on the decision of the Ministry of Environment and Urbanisation, a broader document was prepared as a part of the EU project of the Technical Assistance for the Implementation of the Persistent Organic Pollutants Regulation. This document is focused on the management of POPs problems in Turkey and implementation of the Stockholm Convention on POPs, CRLTAP/POPs Protocol and EU POPs Regulation.

The title of this document is National Implementation Plan of the POPs management if Turkey (POPs NIP) and has two parts – (i) NIP as basic information, overview of country POPs problems and (ii) supporting information presented in the Annexes of the NIP.

Results and discussion

Eight main POPs priority areas of concern have been identified as follows:

- Legislative applications including regulation and enforcement
- Inventory of emissions, releases, stockpiles and contaminated sites (for POPs of both Conventions)
- Reduction of releases of intentionally and unintentionally produced POPs
- Capacity building in the regulating and permitting governmental sector and also in private sector (e.g. POPs management, BAT/BEP implementation)
- Public education and awareness raising
- Monitoring and control of public health and environment

- Information exchange and networking, inter-ministerial coordination, and
- Research into the extend of exposure of the population to POPs and the research for safer alternatives

For Turkey to full its obligations under the Stockholm Convention for POPs and CRLTAP/POPs Protocol depend on the provision of adequate financial and technical assistance. There are some implementation problems at all levels because of the complex administration system and inadequate administrative capacities due to financial restrictions and human resources.

To ensure the regular annual budget for inventories, disposal, monitoring, research and awareness raising based on the NIP conclusions and measures for technical and financial assistance.

A draft by-law is necessary for the full implementation of POPs legislation in Turkey so transposition of EU Legislation is essential.

The existence of an institutional and organizational framework for supporting the implementation of the POPs legislation should be supported with legislation.

The identification of competent authorities, relevant authorities and stakeholders and their participation/involvement in management process on the implementation of the legal requirements should be defined in the draft by-law in order to ascertain their active participation in the management of POPs especially in decision making process.

Since there are several ministries/organizations dealing with POPs a Joint Management Committee for the management of POPs is essential. Some joint management mechanisms have been formally established pursuant to the provisions of laws and regulations as Chemicals Advisory Committee. In line with the Article 8 of By-law on the Classification, Packaging and Labelling of Dangerous Substances and Preparations in order to harmonize the national policy and ensure information exchange between relavant institutions, the Chemicals Advisory Committee established under the co-odination of Ministry of Environment and Urbanization.

POPs are multidisciplinary and complex and next to the primary environmental aspect, they include a trade aspect as well as many other aspects such as the economic, health, agricultural aspects etc., therefore the involvement of the relevant authorities are essential.

One of the important implementation principle of the POPs NIP, is the inclusion of public and stakeholder participation and contribution and increased their active role in the future implementation of the POPs NIP.

In addition the POPs issue impacts on many sectors of society and economy including policy-making, the public and various interest groups. Relevant national stakeholder institutions and groups were identified, sensitized and assigned with responsibilities from the on set of the UNIDO NIP development process. During preparing the NIP the Ministry of Environment and Urbanization consulted with stakeholders and solicited their advice on the development and content of the plan. All the stakeholders supported the programs and initiatives to ensure that the obligations and the spirit of the Convention were reflected.

Stakeholders from many different institutions enounced that the Government of Turkey need to take a leadership role and to work cooperatively with the institutions in implementing the Convention as well as recognizing the existing actions to mitigate POPs as part of the NIP.

For POPs National Implementation Plan to be successful sectoral effect analysis should be carried out involving all sectors. Financial obligations should be designated accurately and realistically for related sectors to the sectors to fulfil all their obligations. Also, performing the short term activities as inventory studies and legislations are important for the other activities to be implemented.

Organisations/institutions relevant to POPs do not have adequate financial and human resources for their programmes. In order to have the adequate human and financial resources at the first instance the requirements should be designed in the NIP.

Rising awareness of public for the convention and obligations will help increasing the efficiency of short, medium and long term activities.

Evaluation and monitoring of the activities are made partly due to the lack of legal and institutional framework for evaluation plan. Evaluation should be carried out in line with the evaluation plan, and the evaluation plan should be updated regularly by using the evaluation results. In the draft by-law the measures for effective evaluations should be placed and the evaluations should be made timely and correctly and the results and experience should be used as the basis for changing activities and as insight for further implementation of activities.

Very important for the future implementation of Conventions measures is to establish and support the permanent POPs national inventory team(s) which will continue in inventory of obsolete stocks, wastes, emissions, releases, contaminated sites and potential exposure of POPs. At the same level of significance is to prepare design of the national POPs monitoring network as a part of the national environmental monitoring network established on the CRLTAP/EMEP and SC/GMP rules and considerations.

For implementation and management of POPs problems in Turkey, the control mechanism and evaluation of the effectiveness evaluation of the Convention measures have to be clearly defined and established.

Acknowledgements

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POSTERS

ATMOSPHERIC DEGRADATION OF LINDANE AND 1,3-DICHLOROACETONE IN THE EUPHORE CHAMBER

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Abstract

The gas-phase degradation of lindane (γ-isomer of hexachlorocyclohexane) towards OH radical was investigated under atmospheric conditions at the large outdoor European simulation chamber (EUPHORE) in Valencia, Spain. The rate coefficient for the reaction of hydroxyl radicals with lindane was measured using a conventional relative rate technique leading to a value of k_{OH}(lindane)=$(6.4\pm1.6)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 300±5 K and atmospheric pressure. The results suggest that the tropospheric lifetime of lindane with respect to OH radicals is approximately 20 days. The product distribution studies on the OH-initiated oxidation of lindane provided evidence that the major initial carbon-containing oxidation product is pentachlorocyclohexanone. 1,3-Dichloroacetone was employed as a model compound for pentachlorocyclohexanone, and an investigation of its photolysis and reaction with OH radicals under atmospheric conditions was carried out. The data indicate that the atmospheric degradation of pentachlorocyclohexanone would be relatively rapid, and would not form persistent organic compounds. A theoretical study was also employed to calculate possible degradation pathways. A mechanism for the reaction of lindane with OH radicals is proposed, and C-Cl bond cleavage is discussed. OH abstraction is considered to be a reasonable way for Cl to escape during degradation. The atmospheric implications of the use of lindane as an insecticide are discussed.

Key Words

Organochlorine Insecticides, Dichloroacetone, Lindane, Photo-oxidation, Tropospheric lifetime, EUPHORE

Materials and methods

Experiments were performed under sunlight conditions at the outdoor European Photoreactor (EUPHORE) in Valencia, Spain (longitude = -0.5º, latitude = 39.5º N). The EUPHORE chamber (volume ~ 200 m^3) is fabricated of FEP foil, which transmits greater than 90% of the solar radiation in the wavelength range 290 to 500 nm, allowing simulation of real conditions with a low ratio of wall-effects due to the shape and to the large volume of the chambers. The time of exposure to solar radiation was controlled with a retractable steel housing which surrounds the chamber.

The rate coefficients for the reaction of OH radicals with lindane were determined using benzene, as reference compound. The rate coefficient for reactions of OH with 1,3-dichloroacetone was measured using dichloromethane as reference compound. Hydroxyl radicals were generated from the photolysis of HONO which was obtained by the addition of a 1.5% solution of $NaNO_2$, (Fluka) to a 30% solution of H_2SO_4, (Scharlab), and flushed directly into the chamber in a stream of purified air. Cyclohexane was added to scavenge OH radicals in the photolysis experiments. All these compounds were also introduced into the chamber using a purified air stream. Reactants were allowed to mix for at least 30 minutes prior to the start of the experiments.

Results and discussion

Lindane photolysis was checked and it did not lead to any noticeable decay of the lindane concentration indicating that this process is negligible under our experimental conditions and could not be distinguished from the combined wall and dilution losses. These observations only allow an estimate for the upper limit of the photolysis rate coefficient plus wall losses, $J_{(lindane)} < 3.5 \times 10^{-5}$ s^{-1} at 300±5 K to be derived, although the photolysis rate may be expected to be much lower than the upper limit estimated, and hence less important. The UV-visible absorption spectrum of hexachlorocyclohexane has not been reported in the gas phase, however, chloroalkanes show negligible absorption at wavelengths < 300 nm.

A series of experiments was carried out at 300±5 K and atmospheric pressure in air where the initial mixing ratios of lindane and the reference compounds were in the range 180-203 ppbv and 385-390 ppbv, respectively. Benzene was employed as the reference compound. HONO, used as OH radical source, was continuously added to the chamber at a rate of approximately 2 ppbv min^{-1}. The measured dilution rate coefficients together with wall losses were in the range $(3.8\text{-}6.0) \times 10^{-5}$ s^{-1}. The kinetic studies were carried out for around 4 h.

The rate coefficient for the reaction of OH radicals with lindane provides a value of $k_{OH(lindane)}=(6.4\pm1.4)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 300±5 K. Figure 1 shows lindane decay plotted against benzene decay.

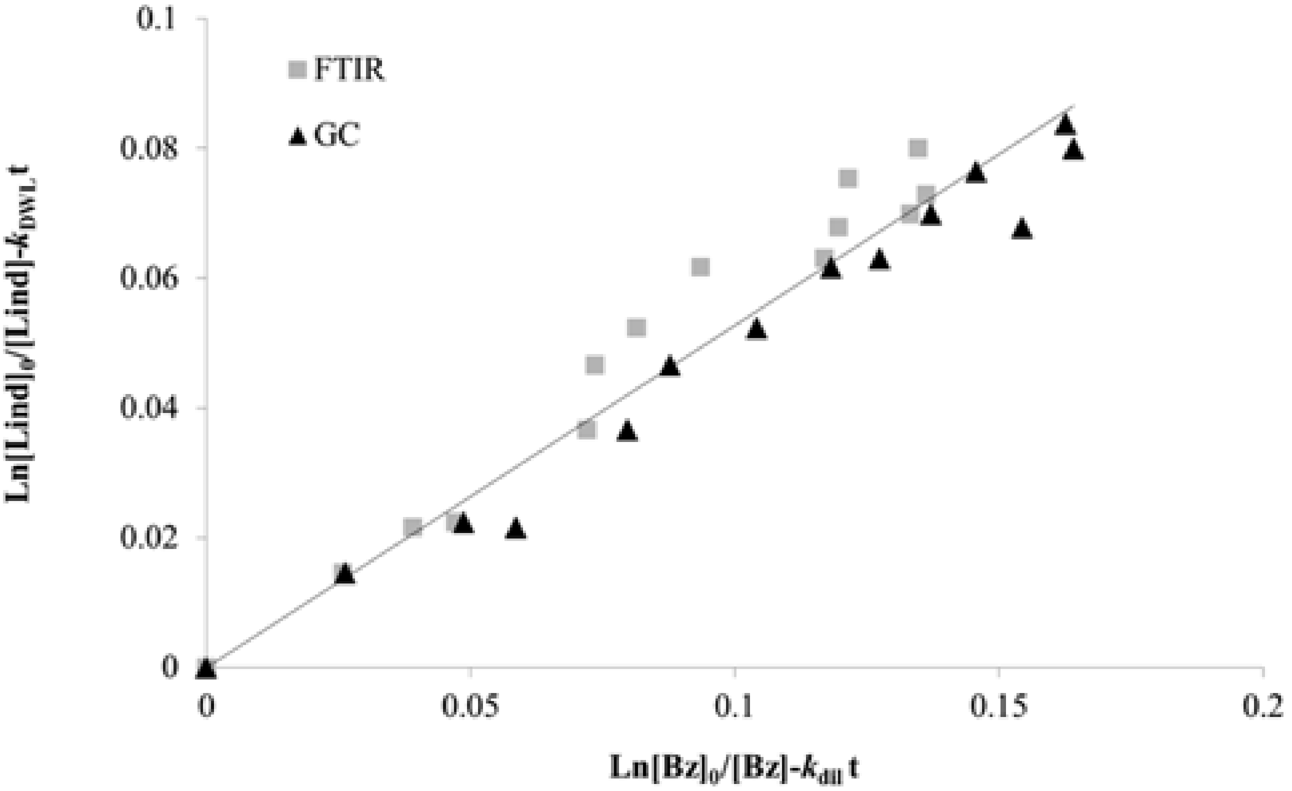

Figure 1: Concentration-time data for the decay of lindane and the reference compound benzene following reaction with OH. The concentrations of lindane and the reference compound were obtained from both FTIR and GC data, lindane was corrected taking into account the wall losses and the estimated upper limit for photolysis; benzene was corrected for dilution.

The rate coefficient determined in this work for reaction of lindane with OH radicals, $k_{OH(lindane)}=(6.4\pm1.6)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, is around a factor of three higher than that derived from elevated temperature studies. (1)
The rate coefficient determined for the reaction of OH radicals with lindane, $k_{OH(lindane)} = (6.4\times1.6)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, leads to an atmospheric lifetime of approximately 20 days.
The reactivity of saturated chlorocarbons with NO_3 radicals has been shown to be extremely low, hence reaction of lindane with NO_3 in the atmosphere is expected to be insignificant (2,3). The low reactivity of lindane suggests that it is a persistent pollutant and is transported over significant distances from the sites of application.
The mechanistic study on the OH radical initiated oxidation of lindane carried out in this work showed that pentachlorocyclohexanone was the major primary product, and that the initial yield of HCl was close to unity. Studies on 1,3-dichloroacetone suggest that under atmospheric conditions photolysis of pentachlorocyclohexanone will be the main removal process for this compound. Photolysis involves C-C bond cleavage leading to the relatively rapid stepwise degradation of pentachlorocyclohexanone producing mainly HCl and CO_2, and hence the atmospheric degradation of pentachlorocyclohexane is unlikely to form persistent organic pollutants.

Acknowledgements

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ASSESSMENT OF PCDD/Fs FORMATION IN THE ADVANCED OXIDATION TREATMENT OF LANDFILL LEACHATE

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Abstract

Advanced oxidation processes (AOPs) have arisen as promising alternative technologies to treat wastewaters, which cannot be treated by conventional methods. These processes are based on the generation of powerful oxidant species, such as hydroxyl radical ($^\bullet$OH), which reacts with organic compounds leading to partial/complete mineralization into CO_2 and H_2O. Nevertheless, because of the oxidation process, the transformation products with higher toxicity than their parent compounds may be formed, as it is the case of polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans (PCDD/Fs). Therefore, the evaluation of conventional physicochemical parameters in wastewater treatment such as chemical oxygen demand (COD) and total organic carbon (TOC) may not be enough to ensure their safely discharge. In this sense, there is shallow knowledge regarding the formation and abatement of PCDD/Fs in aqueous matrixes and, specifically, when AOPs are applied. Consequently, this work aims at providing monitoring and better understanding of PCDD/Fs formation when AOPs are applied. For this purpose, two different AOPs (Fenton and electrochemical oxidation) have been selected to treat landfill leachate, which contains not only PCDD/Fs precursors but also PCDD/Fs in its composition. The influence of the treatment time throughout Fenton and electrochemical oxidation displayed a considerable reduction of COD and TOC after 3 h, higher than 70 and 60%, respectively. The progress of PCDD/Fs over treatment time showed opposite behavior between both AOPs under the operating conditions applied: increase of PCDD/Fs concentration after Fenton oxidation and decrease when electro-oxidation treatment was applied. Hence, this work contributes to the assessment of the potential formation of PCDD/Fs during the application of AOPs to the treatment of landfill leachate.

Key Words

Advanced oxidation processes (AOPs); polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs); Fenton oxidation; electrochemical oxidation (EOX); landfill leachate; toxic equivalents (TEQ).

Materials and methods

The study of the effectiveness of two advanced oxidation processes (AOPs), namely electrochemical oxidation (EOX) and Fenton oxidation to the treatment of real wastewaters from municipal solid waste landfill has been addressed.

Electrochemical oxidation experiments

EOX experiments were performed in batch mode in a laboratory DiaCell system (two circular electrodes: boron doped diamond (BDD) on silicon anode and stainless steel cathode, with surface area of 0.007 m^2 each and an electrode gap of 5 mm). A feed tank magnetically stirred (1 L) and a recirculation pump that provides an operational flowrate of 11 L min^{-1} were employed. Experiments were carried out working at 20 ºC with a current density of 900 A m^{-2} [1,2]. The conductivity of landfill leachate was high enough (14.6 mS cm^{-1}) to directly apply EOX without addition of an electrolyte.

Fenton oxidation experiments

Fenton oxidation experiments were performed in batch mode in glass reactors magnetically stirred (700 rpm) with a heating magnetic stirrer with temperature control. Batch experiments were carried out adjusting the initial pH of the solutions to be treated to 3.0. $FeSO_4 \cdot 7H_2O$ was added to the solution to yield the desired Fe^{2+} dose. The Fenton reaction was initiated by adding the corresponding amount H_2O_2 to the solution. Samples were withdrawn from the reaction medium when the oxidation time was reached and the excess of H_2O_2 was removed by $NaHSO_3$, after titration with sodium thiosulfate $Na_2S_2O_3$.

TOC and COD analysis

Total organic carbon (TOC) analysis was performed using a TOC-VCPH Shimadzu and chemical oxygen demand (COD) was determined according to the Standards Methods 5220C.

Qualitative screening of organics in leachates

Qualitative screening (non-target analysis) for organic compounds in landfill leachates was performed by GC-MS after previous solid phase extraction (SPE). The organic compounds were extracted from the leachate matrix using a SPE procedure with Oasis HLB cartridges (Waters)[3]. The concentrated extract was analyzed using a GC-MS Agilent 6890N equipped with an auto-sampler. The analytes were separated using a HP5 MS column (L = 30m; Øi = 0.25 mm) with a film thickness of 0.1 mm.

PCDD/Fs analysis

The concentrations of PCDD/Fs were determined according to Standard Method U.S.EPA 1613 (1994) by isotope dilution method and high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS, Trace GC UltraTM, ThermoFisher Scientific). This method requires extraction, concentration and purification steps prior to the analysis. All sample preparation steps together with a detailed procedure of the quantitative analyses of PCDD/Fs has been previously described[2].

Results and discussion

Characterization of landfill leachate

Landfill leachate is a wastewater containing a large number of compounds, some of which can be expected to create a threat to health and nature if released into the natural environment. Landfill leachate composition is affected by many factors such as landfill age, precipitation, type and composition of the waste and seasonal weather variation[4]. Humic-type substances, ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts are the main substances found in leachates. Leachate samples used in this study are characterized by the following physico-chemical properties: pH, 7.8; conductivity,14.6 mS cm^{-1}; TOC, 934.2 mg L^{-1}; COD, 1981 mg L^{-1}; BOD_5/COD, 0.33; Cl^-, 2205.3 mg L^{-1}; etc[2]. The qualitative screening of organic compounds in leachate samples (Fig. 1) confirmed a contribution of 18.5% for phenolic compounds regarding the total detected compounds[3]: phenol, chlorophenol and bisphenol A derivatives, which are considered as PCDD/Fs precursors [5-9].

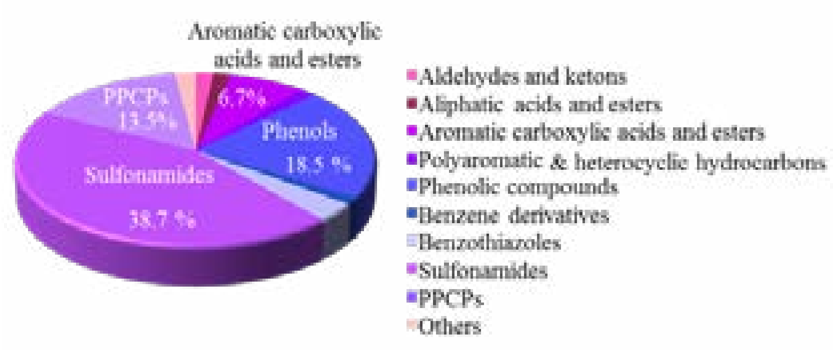

Fig. 1. Dominant groups of organic compounds found in landfill leachates.

COD and TOC abatement efficiencies of Fenton and electrochemical oxidation

Fenton oxidation of leachate sample was carried out using H_2O_2/Fe^{2+} mass ratio equal to 5.86 (H_2O_2/COD= 1.7), which was optimized in previous works of our research group[10,11]. COD and TOC concentration profiles (Fig. 2) depicted a fast degradation rate with an average removal of 50% during the first 15 min, which is consistent with a rapid H_2O_2 consumption (75%, data not shown). Although COD remaining in solution (600 mg L^{-1}) was still above the discharge limits (125 mgO_2 L^{-1}, Council Directive 91/271/EEC), the biodegradability (BOD_5/COD) increased up to 0.6 which makes biological degradation suitable as a post-treatment stage. Fenton oxidation is commonly proposed as pretreatment technology in which non-biodegradable compounds are further oxidized into short chain compounds which are susceptible of being biodegraded by conventional treatment methods[12].On the other hand, the application of EOX oxidation as an alternative treatment technology resulted in a decreased of 92 and 78% for COD and TOC (Fig. 2). The application of a 6 h EOX treatment displayed a diminishment of 95 and 90% for COD and TOC (data not shown), respectively, resulting in a COD below disposal limits.

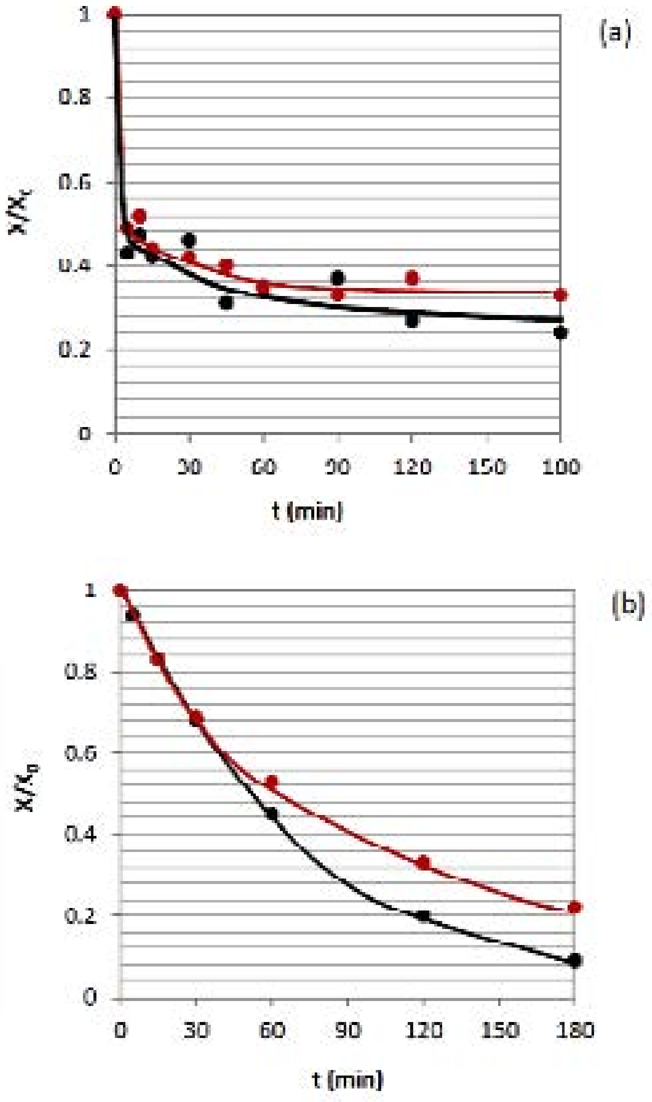

Fig. 2. Evolution of dimensionless COD (●) and TOC (●) during Fenton (a) and EOX (b) of landfill leachate. For the sake of clarity error bars were not represented (error ≤± 10%).

Monitoring of PCDD/Fs concentration during Fenton and electrochemical oxidation

During Fenton oxidation, the total concentration of PCDD/Fs increased by 29% after 3 h (Fig. 3). It may be explained taking into consideration the presence of precursors of PCDD/Fs in the media such as phenol and chlorophenols, among others. This increase was remarkable in several homologue groups and 2,3,7,8-PCDD/Fs, with special importance for OCDD, as a consequence of the formation of free chlorine species which lead to chlorination reactions causing the formation of higher chlorinated congeners[9,13]. Meanwhile, 2,3,7,8- PCDD/Fs concentration increased by 37% after 3 h treatment, whereas TEQ increased from 17.2

to 19.4 pg I-TEQ L^{-1} (12.8%), which was less than the value fixed by U.S. EPA (30 pg TEQ L^{-1}). Therefore, the presence of PCDD/Fs precursors may lead to the formation of PCDD/Fs under the Fenton operating conditions applied whereas stringent Fenton conditions could lead to further PCDD/Fs destruction since H_2O_2 was completely depleted after 1 h of treatment (data not shown).

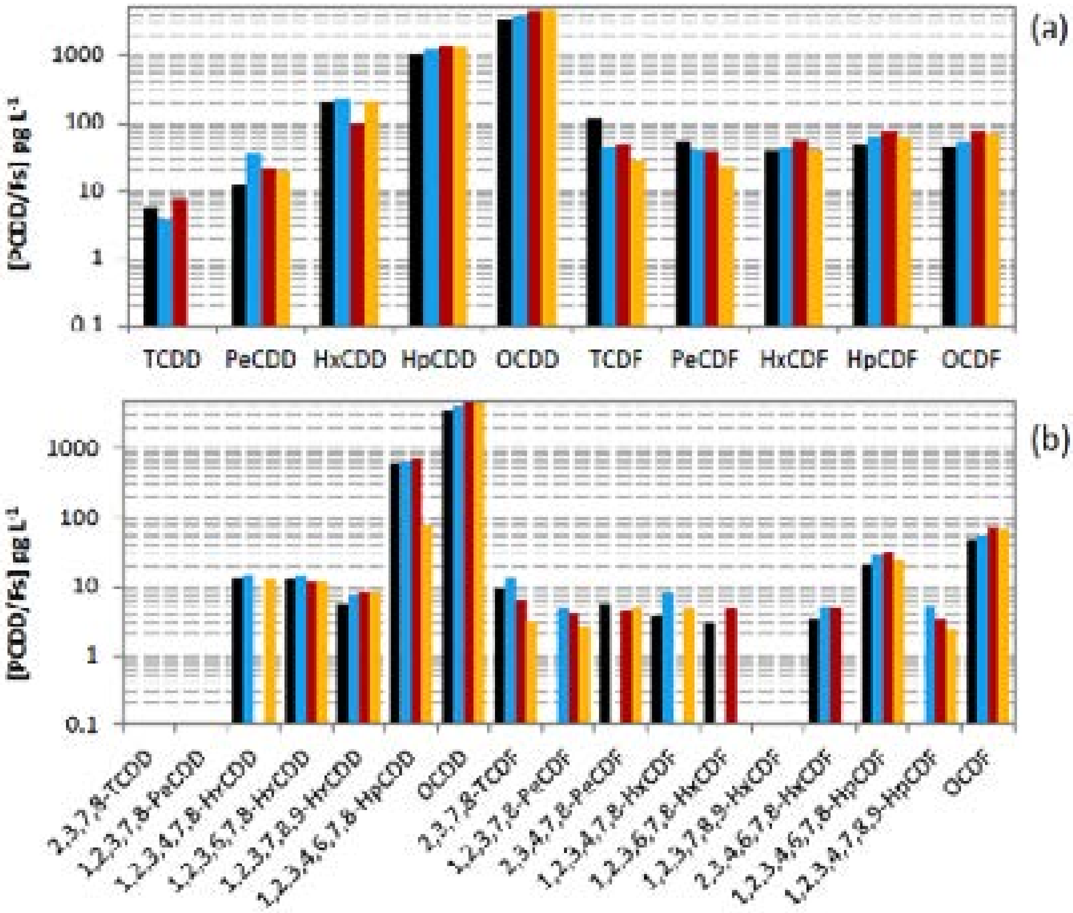

Fig. 3. PCDD/Fs concentration in leachate sample (■), after 5 min of Fenton (🟦), after 30 min of Fenton (🟥), and after (3h) of Fenton (🟧): (a) homologue profile of total PCDD/Fs; (b) congener profile of 2,3,7,8-PCDD/Fs. For the sake of clarity error bars were not represented.

Contrary to Fenton oxidation, after application of EOX to landfill leachate, the total concentration of total PCDD/Fs and 2,3,7,8-PCDD/Fs displayed a general decreasing trend (Fig. 4), specially OCDD which was the homologue found in higher concentration. After 3 h of treatment, the total concentration of the more toxic congeners 2,3,7,8-PCDD/Fs decreased by 71% and the toxicity declined by 58% (from 13.1 to 5.5 pg I-TEQ L^{-1}).

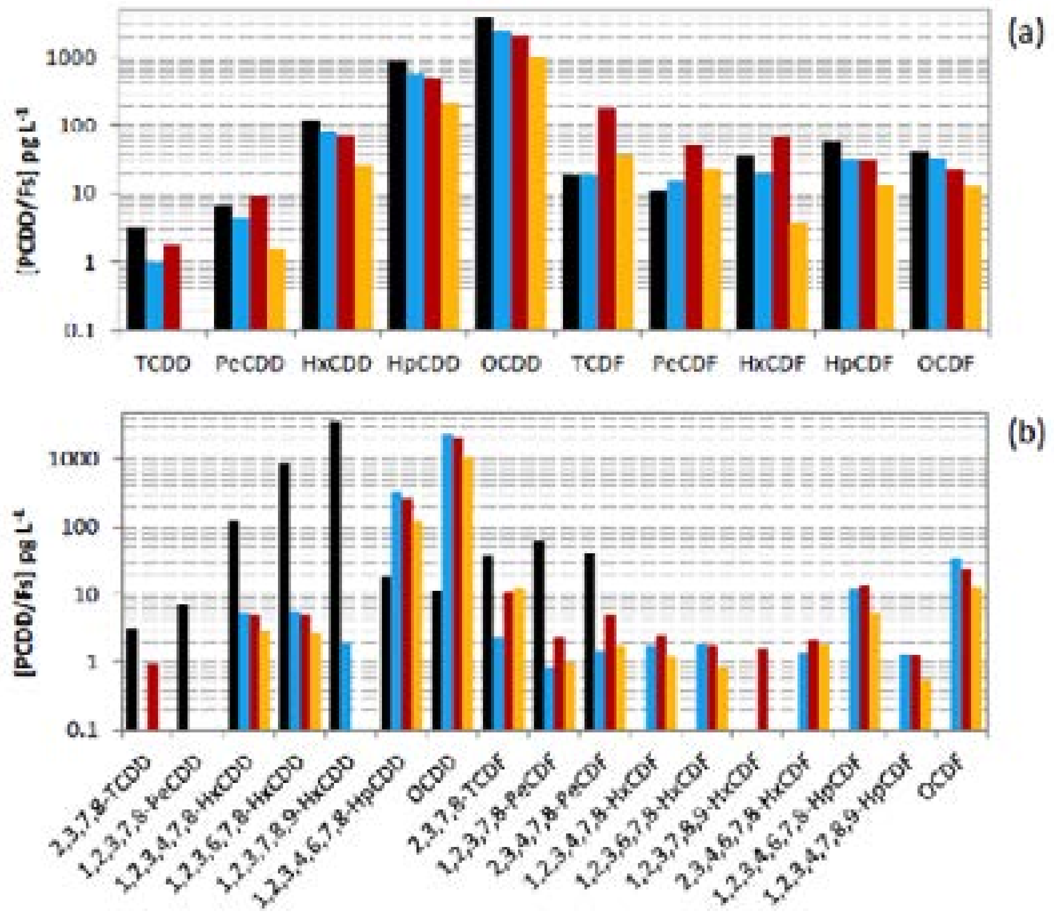

Fig. 4. PCDD/Fs concentration in leachate sample (■), after 5 min of EOX (🟦), after 30 min of EOX (🟥), and after 3 h of EOX (🟧): (a) homologue profile of total PCDD/Fs; (b) congener profile of 2,3,7,8-PCDD/Fs. For the sake of clarity error bars were not represented.

Since leachate samples had the same origin, the main difference between the results may reside in the difference of operating conditions. In the Fenton process, •OH are produced by the mixture of the catalyst Fe^{2+} with H_2O_2 under acidic pH while EOX generates •OH continuously on the anode surface. Accordingly, in the Fenton oxidation the amount of •OH generated is limited by H_2O_2 dose which is demonstrated by the plateau region shown in Fig. 2a after the complete reaction of H_2O_2 (1 h).

Acknowledgements

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AIR POLLUTION: POPS AND EMERGING POLLUTANTS IN THE CITY OF MADRID (SPAIN)

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Summary

After decades of industrialization, air pollution has become a major worldwide environmental issue. Persistent Organic Pollutants (POPs), and emerging pollutants as flame retardants, are some of the wide range of hazardous chemicals which can be found in the ambient air. Due to their toxic, bio-accumulative and persistent characteristics these chemicals are matter of great concern for human health and natural ecosystems. However there are several data gaps related to their fractionation in ambient air, which means that improving our knowledge of POPs in this matrix remains a challenge.

The present study was designed to determine the occurrence of several POPs in ambient air samples from Madrid. Analytes studied were: polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), Dechloranes (602, 603, 604, and DP) Chlordane Plus (CP) and Mirex. Gas phase and airborne particulate matter were studied separately. Results revealed i-PCBs indicators as the major pollutants, followed in decreasing order by dl-PCBs, PBDEs, DP and finally by PCDD/Fs. PCBs were mainly related to gas phase, while PCDD/Fs, DP and PBDEs were associated with particulate matter. Percentage of detection decreased form Mirex, Dec 602 and Dec 604 to Dec 603 (detected only in one sample), and finally to CP which was, in all cases, below method detection limits

Data obtained represent an important advance in the study of the behaviour of these pollutants, resulting very interesting for researching on human exposure to POPs.

Key words

Persistent organic pollutant, emerging pollutant, atmospheric pollution; high-volume active sampler; gas – particle partitioning.

Introduction

Air pollution continues to be a major health, environmental, and economic issue in Europe, because it leads to health problems, premature deaths and damage to ecosystems, crops and buildings[1]. Despite progress in reducing air pollution, certain pollutants such as particulate matter (PM) remain a significant threat. PM is a complex and heterogeneous mixture of inorganic and organic substances, and constitutes the greatest risk in terms to harm the human health, especially in urban areas where the majority of the European population lives[2]. Persistent Organic Pollutants (POPs), and emerging pollutants as flame retardants are present in the gas phase and also adsorbed on the suspended particulate matter, depending on ambient temperature and the physico-chemical properties of the chemical. Due to their toxic, bio-accumulative and persistent characteristics these pollutants are matter of great concern for human health and natural ecosystems[3]. However there are several data gaps related to their fractionation in ambient air. Therefore improving our knowledge of POPs in this matrix remains a challenge.

The aim of this study was to evaluate the presence of several POPs in ambient air samples from the city of Madrid (Spain). Gas phase and airborne particulate matter were studied separately. Levels and fractionation of the following analytes were studied: polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs: (the 2,3,7,8-substituted congeners), polychlorinated biphenyls (PCBs): dioxin-like PCBs (dl-PCBs: CB-81, -77, -123, -118, -114, -105, -126, -167, -156, -157, -169 and -189) and indicator PCBs (i-PCBs: CB-28, -52, -101, -138, -153 and -180), polybrominated diphenyl ethers (PBDEs: tri to deca-BDE) and Dechloranes (Dec 602, Dec 603, Dec 604, Dechlorane Plus (DP), Chlordane Plus (CP) and Mirex).

Materials and methods

A total of 13 sampling events were conducted between January and October 2013 in the weather station located at CIEMAT facilities in Madrid (Spain). Ambient air volumes of 1000 m^3 were drawn using high-volume samplers CAV A/M model (MCV S.A., Spain), at 30 m^3/hour flow rate. Particulate matter was collected on glass microfiber filters (GFF) (grade GF/A, 15 cm diameter, Whatman, England), and gases were adsorbed on polyurethane foam (PUF) plugs (0.029 g/cm^3) placed downstream of the filter.

Handling and sampling procedures were performed following the guidelines of UNE-EN 12341:1999 and UNE-EN 14907:2006 Standards[4,5]. The same analytic procedure was carried out for GFF samples and PUF plugs. They were Soxhlet extracted separately with toluene for 24 h. Prior to extraction samples were spiked with ^{13}C labeled recovery standards ($^{13}C_{12}$- PCDD/Fs, $^{13}C_{12}$- PCBs, $^{13}C_{12}$- PBDEs and $^{13}C_{10}$-DP: syn- and anti-DP isomers). Final extracts were concentrated to dryness and redissolved in nonane spiked with injection standards (1613-iSS, WP-ISS, i-PCBs-ISS and BDE-CVE-EISS from Wellington Laboratories Inc.) prior to instrumental analysis.

Instrumental analyses were carried out by high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC-HRMS), on a Micromass AutoSpec Ultima NT operated in electron ionization mode at resolution greater than 10,000 (10% valley). Field and laboratory blanks were analyzed and final data were blank corrected.

Results and discussion

Table 1 summarizes the descriptive statistics of POPs detected in the gas (PUF) and particulate matter (GFF) phases (Normalized conditions: 1 atm, 273° K). The profile of total concentrations (PUF + GFF) in decreasing order were: i-PCBs (349 pg/Nm^3; median) > dl-PCBs (124 pg/Nm^3) > PBDEs (11.9 pg/Nm^3) > DP (1.81 pg/Nm^3) > PCDD/Fs (0.07 pg/Nm^3). In the gas phase the major pollutants were also i-PCBs (348 pg/Nm^3; median) and dl-PCBs (122 pg/Nm^3), whereas particulate phase was dominated by PBDEs (8.85 pg/Nm^3) followed by i-PCBs (2.79 pg/Nm^3). Mirex was detected in 54% of gas phase samples (1.10 pg/Nm^3) and in 46% of GFF samples (0.94 pg/Nm^3). Dec 604 was found in three PUF samples (0.06 pg/Nm^3) and two GFF (0.15 pg/Nm^3). Dec 602 was only detected in four gas phase samples (0.01 pg/Nm^3), Dec 603 was only found in one GFF (0.008 pg/Nm^3) and CP was not detected in any of the analyzed samples.

Concentration (pg/Nm^3)	Sample	Average	SD	Median	Min	Max	Detection (%)
∑i-PCBs	PUF	372	225	348	103	872	100
	GFF	3.37	2.78	2.79	0.37	9.95	100
∑dl-PCBs	PUF	125	82.3	122	15.5	292	100
	GFF	2.44	1.88	2.62	0.06	6.32	100
∑PBDEs	PUF	3.82	3.58	2.84	0.41	11.7	100
	GFF	13.1	9.99	8.85	0.22	37.7	100
∑DP	PUF	0.66	0.59	0.38	0.02	2.07	100
	GFF	1.90	1.54	1.19	0.02	5.50	92
∑PCDD/Fs	PUF	0.02	0.02	0.01	0.002	0.07	100
	GFF	0.10	0.11	0.05	0.01	0.36	100
Mirex	PUF	0.89	0.78	1.10	0.01	1.89	54
	GFF	0.96	0.15	0.94	0.76	1.17	46
Dec 602	PUF	0.02	0.01	0.01	0.01	0.03	31
	GFF	N.D.	N.D.	N.D.	N.D.	N.D.	0
Dec 604	PUF	0.09	0.05	0.06	0.05	0.16	23
	GFF	0.15	0.09	0.15	0.06	0.23	15

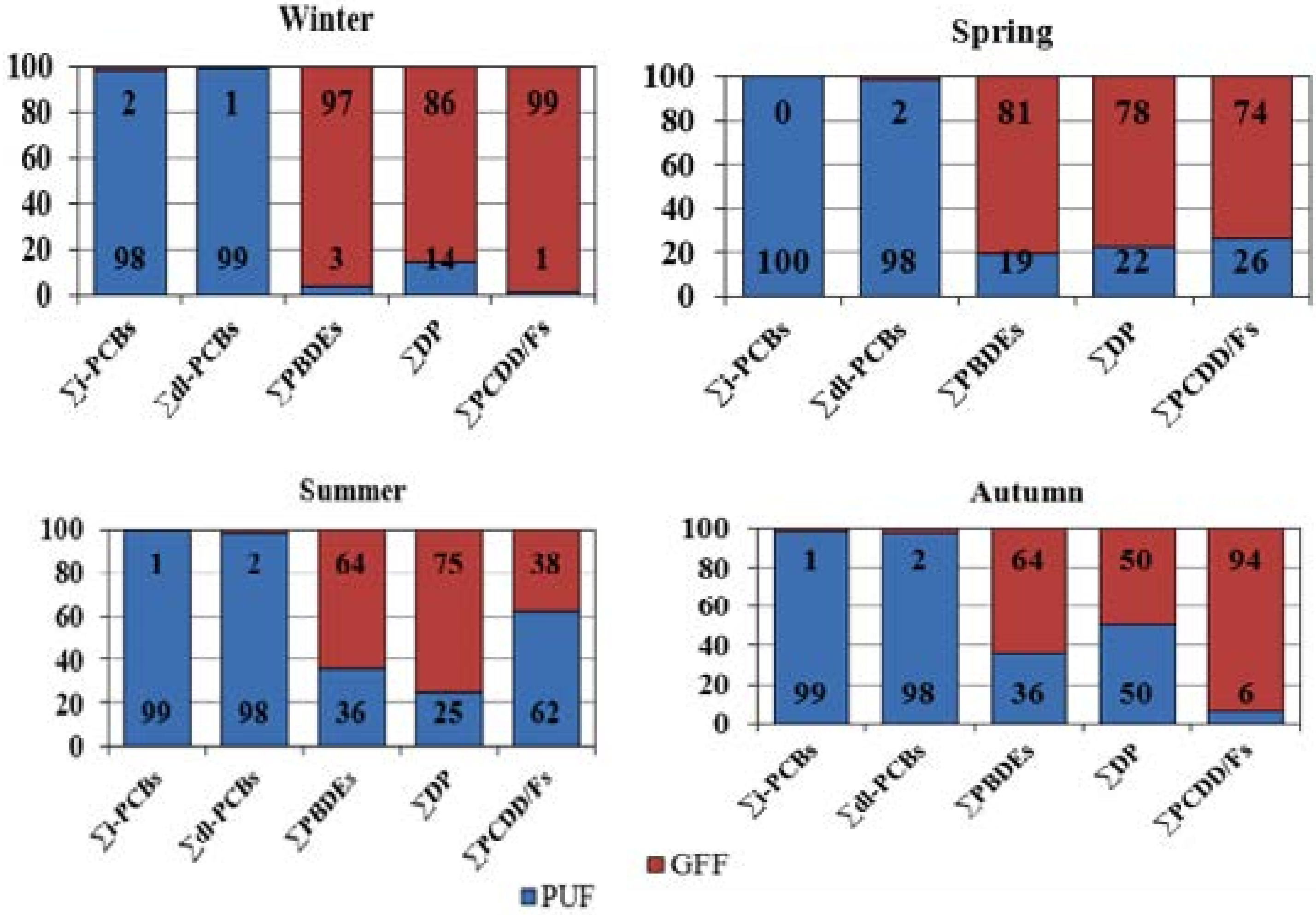
Table 1. Concentrations (pg/Nm^3) of POPs in gas-phase (PUF) and PM (GFF).

The seasonal gas-particle partitioning (% in the gas or particle phase related to the total content per season) of the major POPs in air, is plotted in Figure 1. I-PCBs and dl-PCBs were present dominantly in gas phase regardless the season (99 % and 98 % of total concentration, respectively), as published elsewhere[6,7]. On the contrary, PBDEs, DP and PCDD/Fs were mainly bounded to particulate matter (76 %, 72 % and 76 % of total concentration, respectively). The contribution to gas phase of PBDEs and PCDD/Fs showed a positive significant correlation with temperature, being this lower for PBDEs ($p < 0.05$, $R = 0.64$, where R means Pearson´s correlation coefficient) than for PCDD/Fs ($p < 0.001$, $R= 0.87$). In this way, PBDEs presented a high contribution to the gas phase in autumn (36 %), whereas the related to PCDD/Fs experienced a high decrease from 62 % in summer at 27ºC, average ambient temperature, down to 6 % in autumn at 15ºC. The increase of PBDE and PCDD/F contributions in gas phase in warm seasons has been reported in other studies[8,9].

No clear seasonal trend was observed for DP, Mirex, Dec 602, Dec 603, Dec 604 nor CP, but data are scarce to establish significant seasonal trends for these pollutants. However, it is important to highlight that Dec 602 was only detected in gas phase samples collected during sampling events exceeding 20 ºC in spring and summer. This fact may indicate some temperature dependence, however more research is needed to support this hypothesis.

Figure 1. Gas-particle partitioning (% related to total concentration) per seasons of major POPs: gas (blue) and particulate (red) phases.

Congener patterns have been established for each family of pollutants. The pattern of total PCBs was dominated by the major congeners in the PUF plugs, due to their higher presence in this phase. Similar patterns were found in France and Germany[10,11]. Related to i-PCBs, the major gas-phase contributors were PCB-101 (35 %), PCB-52 (30 %),



PCB-153 and -138 (both with 14 %). Nevertheless, in the particulate phase the most abundant congeners were PCB-138 (41 %), PCB-180 (22 %), PCB-52 (13 %) and PCB-101 (11 %). The major dl-PCB congeners were similar in gas and particulate phases, showing higher contribution of PCB-118 (71 % and 41 %, respectively), PCB-105 (18 %; 36 %) and PCB-156 (4 %; 11 %).

PBDEs showed a distinct fractionation based on their degree of bromination[8]. Deca and nonabromodiphenyl ethers (BDE-209 >> BDE-207 ≈ BDE-206) were mainly associated to PM, while gas-phase was dominated by PBDEs with low bromination degree (BDE-47 > BDE-99 > BDE-28, penta to tribromodiphenyl ethers). Considering that the production and use of Deca-BDE commercial mixture is forbidden in Europe since 2008[12], presence of BDE-209 (69 %), BDE-207 (5 %), and BDE-206 (5 %) in PM suggests the use or disposal of items containing Deca-BDE as a potential source of this pollutant into the environment.

The averaged PCDD/F profile showed a higher contribution of PCDFs compared to PCDDs. All PCDF congeners were detected in PM, but only the heaviest PCDD congeners (1,2,3,4,6,7,8-HpCDD and OCDD) showed a significant contribution to the total concentration. PCDD/Fs with a higher degree of chlorination were mainly found in the particulate phase. In parallel, a higher contribution of the lightest congeners was associated to PUF plugs. The predominant congeners in PM were OCDD (29%), 1,2,3,4,6,7,8-HpCDF (21%), and 1,2,3,4,6,7,8-HpCDD (16%). OCDD also appears as the predominant congener in gas phase (29%), followed by 2,3,7,8-TCDF (25%) and 1,2,3,7,8-PeCDF (14%), similarly to results reported for Istanbul city[9].

Conclusions

This study reported the total concentrations and fractionation of several POPs and emerging pollutants in the ambient air of Madrid (Spain). Results evidenced different gas-particle partitioning for the different compounds. PBDEs, DP and PCDD/Fs were mainly associated with particulate matter, while PCBs (i-PCBs and dl-PCBs), Mirex, Dec 602 and Dec 604 were found mainly in the gas-phase.

Gas-particle partitioning of PCDD/Fs and PBDEs was highly influenced by temperature, with increasing gas phase contributions in warmer months (Pearson test, $p<0.05$). No clear seasonal trend was observed for DP. Data related to Mirex, Dec 602 and Dec 604 are very scarce (percentage of detections are very low) and, consequently, more research is needed to draw conclusions about their presence and behavior in ambient air.

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Broekpolder
The Potential of Enhanced Biodegradation of Drins

Campus Kamp-Lintfort

Photo: DCMR

A research on the potential enhanced biodegradation of Drin contaminated harbor sludge in the Broekpolder, Vlaardingen (Rotterdam, NL)

The Broekpolder: A popular green and recreational area; highly contaminated with drins causing unacceptable ecological risks. High bioavailability of dieldrin (up to 75%) causing high concentrations in earthworms. Poisoning effects on higher organisms such as mice and singing birds that eat worms are expected.

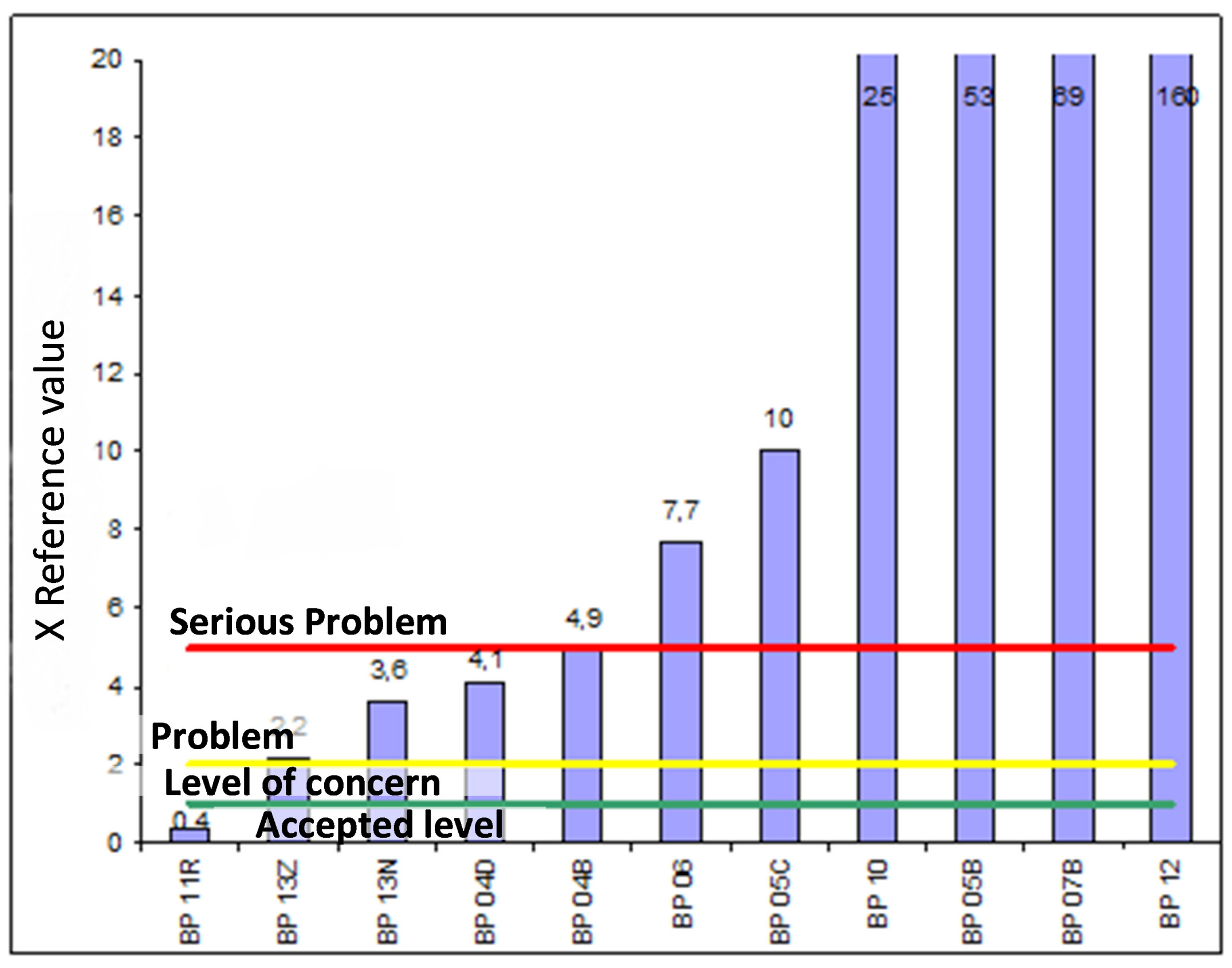

Fig.2: Site-specific remediation goal based on earthworm content of dieldrin (1)

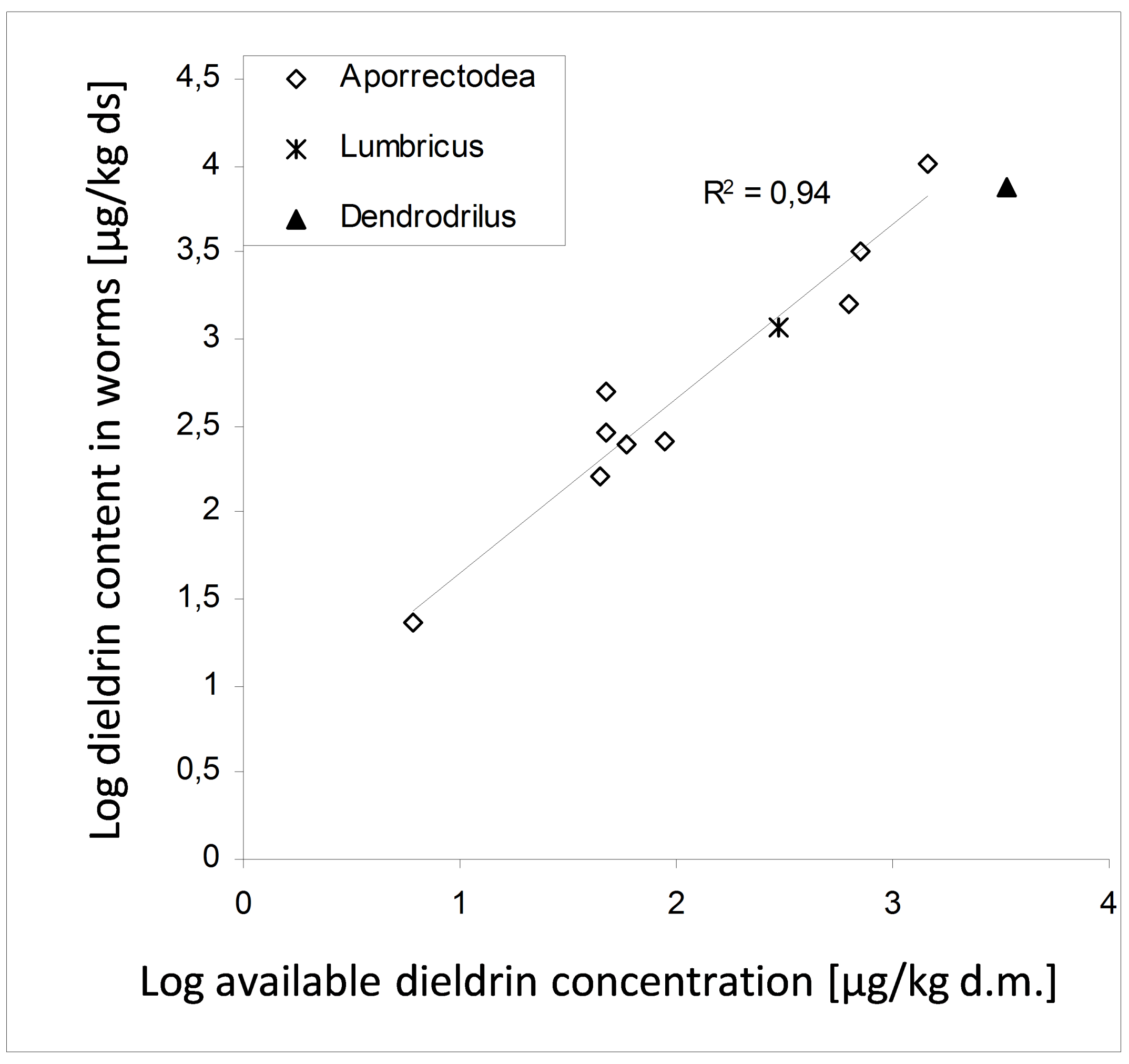

Fig.3: Good correlation with bio-available fraction [± 75% of total] of dieldrin (1)

Photo: DCMR

Fig.1: Remediation assessed to be urgent for 50% of the area [±200 ha] based on ecological risks

Drin concentrations halved within the last 25 years

Fate processes

Volatilization
Biodegradation
Bioaccumulation
Inundation and run-off?
Plant uptake
Leaching

Research question:
Is there a potential enhanced biodegradation of drins?

A literature study revealed that knowledge remains limited according to:

- Biotic and abiotic mechanisms causing decreasing concentrations of drins
- Molecular interactions between drins, soil and root matrix
- Degradation studies in soil or sediment environments

Benefits of enhanced biodegradation:

- Avoiding high remediation costs
- Current vegetation can be maintained
- This concept is more sustainable

Further input on information towards the research project is highly appreciated.

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(1) Bodemecologisch onderzoek volgens de Triade-benadering, Grondmij/AquaSense, I&M-1007086-RJ, d.d. 19-06-2009

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