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Life surfing

GOBIERNO DE ARAGON

Índice

Block 1.
LIFE SURFING SESSION

LIFE SURFING: SURFACTANT ENHANCED CHEMICAL OXIDATION FOR REMEDIATING DNAPL

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ABSTRACT

The Government of Aragon leads the LIFE SURFING project, a pilot test whose aim is to demonstrate the field feasibility of a soil decontamination technique in fractured aquifers containing residual Dense Non-Aqueous Phase Liquid (DNAPL) of a high pollutant mixture of multicomponent organic contaminants and POPs.

The LIFE SURFING project, developed in the framework of the European LIFE Programme, and with whole title "SURFactant enhanced chemical oxidation for remediatING DNAPL" (LIFE17 ENV/ES/000260), has a budget of 2.1 million euros and a duration of 60 months.

The project will develop a field test in the fractured aquifer of the old Bailín landfill.

This old landfill was used by the Inquinosa factory for the disposal of the waste. The factory produced lindane. As well as solid HCH, Inquinosa dumped liquid residues there.

DNAPL was found in 2004 during the site monitoring activities and, since then, it has been pumped in Bailin boreholes. Nowadays, it does not accumulate any more, thus, it can be considered exhausted. Nevertheless, this dense residue remains attached to the walls of the rock fractures and keeps present in a residual way. The objective of LIFE SURFING is to eliminate this residual phase, and to establish a methodology that can be transferred to a full scale level and even other sites with different DNAPLs and different geological conditions.

The consortium is formed by five partners: the Government of Aragon, coordinating the project; the Complutense University of Madrid, carrying out the preliminary analysis and the design and assessment of the field test; the University of Stuttgart, carrying out a large-scale laboratory test; the IPHA, in charge of the study of transferability to other locations, and SARGA, for the implementation of the infrastructures and fieldwork.

In short, this contribution from the EU, via LIFE funds, will make it possible to increase safety conditions in the old Bailín landfill by removing an important amount of pollutants.

KEYWORDS

LIFE, Demonstration test, Remediation, DNAPL, Lindane, HCH, POP, Bailin landfill

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LIFE SURFING: FACILITIES, EQUIPMENT, CONSUMABLES, AND RESOURCES IN THE TEST EXECUTION

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ABSTRACT

The Government of Aragon has undertaken an innovative pilot test for the elimination of residual DNAPL in a fractured aquifer under the LIFE SURFING project (Life LIFE17 ENV/ES/000260), which has entailed a complicated task of planning and quantifying both, costs and resources.

The organization has been integrated by an interdisciplinary work team with knowledge on the geomorphological and hydrological characteristics of the site. Based on it, they defined the scope of the test, the design of the installation, and the execution of the works. Preventive and corrective measures have been applied to control the test performance in case of deviations in the development of the works.

The pilot test has been developed in a vertical layer of fractured rock where the pumpable dense phase (DNAPL) was already exhausted. The LIFE SURFING test has consisted of several phases of in situ tests (SEAR injections and S- ISCO injection) and on-site treatments of the SEAR extraction, which involved and intense with laboratory and fieldwork. The works have been carried out on an area of 380 linear meters of the so-called "M layer". For this, three different facilities were implemented:

Injection Zone, close to the dismantled Bailin landfill, constructed for the purpose of carrying out the injections in the test cell. Mixture, injection and recirculation tanks, as well as pumps, flow-meters, and a complex circuit of pipes were placed there.

Test area, where the equipment for developing the on-site treatments (Fenton oxidation, alkaline hydrolysis and adsorption on activated carbon of the volume extracted by the SEAR injections) was installed.

Barrier Zone, located downstream of the tested cell, where equipment for the treatment of the volumes going out the test cell was installed.

The test had 14 months duration which was necessary to carefully manage the material (electromechanical equipment and chemical reagents) and human resources. Once the work has been completed, a global analysis of the pilot test has been carried out focused on the improvements to be made for future application at a large scale.

KEYWORDS

Life Surfing, equipment, facilities, chemical products, pilot, test, feasibility

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LIFE SURFING PROJECT, PREPARATORY WORKS FOR THE INJECTION OF SURFACTANTS AND OXIDANTS

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ABSTRACT

The LIFE SURFING Project has tested the application of SEAR and SISCO techniques in a fractured aquifer affected by a dense phase from lindane manufacturing residues. After 16 years of pumping the dense phase (DNAPL) in the Bailín landfill aquifer (Sabiñánigo, Huesca), a situation has been reached in which physical extraction is already inefficient, which makes it necessary to address the application of chemical techniques that allow cleaning the residual DNAPL.

The lithostratigraphic and hydrogeological conditions of the aquifer are the major determining factors for the application of these techniques, controlling the distribution of the reagents, the contact time and the risk that the mobilization of Persistent Organic Pollutants (POPs) reaches the Gállego River.

During the execution of the boreholes in the test area a detailed test of both lithologies and fracturing has been carried out, in addition, samples have been taken from the fractures of the borehole cores to delimit the distribution of the DNAPL.

Seven hydrogeological tests (injection, pumping and combined) have been carried out to establish connectivity between boreholes, estimate response speeds to level changes, establish conditions for flow and connectivity (lithological, structural, barriers, etc.), and allowable injection and pumping flows.

Six tracer tests have been carried out, with sodium chloride to achieve a conductivity contrasted with that of the aquifer, which allows detailed monitoring of the vertical evolution of conductivity in control boreholes, and with sodium bromide to estimate recovery rates and adjust the necessary volumes and injection and pumping strategies.

Finally, downstream, a barrier zone has been equipped to minimize the mass and toxicity of POPs that could be mobilized in the application of surfactants. In this area, the application of caustic soda, sodium persulfate, temperature and aeration are combined. With this joint treatment, the dehydrochlorination of the heavier chlorinated substances and the oxidation and volatilization of the less chlorinated substances are favoured. The operation of the barrier has been verified by simulating a flow with the predictable concentration of surfactant and POPs, reaching a performance greater than 99% in the elimination of HCH, and greater than 90% in benzene and chlorobenzene, which are the most abundant compounds.

This set of tests constitutes the essential methodology to carry out SEAR and SISCO treatments in a heterogeneous fractured aquifer with the presence of DNAPL. Its implementation has allowed us to successfully address these treatments, which results will be communicated during this Forum.

KEYWORDS

Lindane, DNAPL, fractured aquifer, surfactants, persulfate, tracer test, hydrogeological test.

LIFE SURFING PROJECT, IN SITU CHEMICAL OXIDATION ENHANCED WITH SURFACTANTS (SISCO) IN A FRACTURED AQUIFER

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ABSTRACT

The LIFE SURFING project has tested the application of SEAR and SISCO techniques in the fractured aquifer of the Bailín landfill (Sabiñánigo, Huesca). After applying surfactant to minimize the presence of a dense organic phase (DNAPL) composed of more than 28 Chlorinated Organic Compounds (COCs), a test combining surfactants and oxidants (SISCO) was carried out. A solution of persulfate (40 g/l), surfactant (E-Mulse 3 ®, 4 g/l) and NaOH (10 g/l) as an activator have been injected in two wells. The pH of the injected fluid was strongly alkaline (pH>12). A volume of 21.6 m^3 was injected in 1 m^3 pulse over two days. This procedure allows for an increase in the contact time between the injected fluids and the subsoil to reach the target groundwater levels and increase the injected fluid dispersion. Immediately downstream of the test cell, the groundwater is pumped and recirculated back to the cell. In addition, the foam has been generated in a well downstream by injecting a solution of xanthan gum (2 g/l) and E-Mulse 3 ® (5 g/l) and an airflow to minimize the flow rate of injected fluids escaping downstream.

To maintain the aquifer's strong alkaline pH and prolong the persulfate activation time, a NaOH aqueous solution has been injected into various boreholes downstream, compensating for the buffer effect of the carbonated medium.

In the test cell, the contact time of the reagents in the vadose zone was limited. In contrast, in the saturated zone, the oxidation reaction has been maintained until the exhaustion of persulfate.

POPs solubilization and oxidation continued downstream until the surfactant and oxidants were exhausted, maintaining the oxidation reaction in the saturated zone. The injected fluid that escaped from the test cell reached the barrier zone without a dense organic phase and with low solubilized COCs.

It is estimated that around 20 kg of DNAPL has been degraded without noticing a significant rebound in concentrations after two months; however, it is necessary to wait for the high water situation to verify the effectiveness of the treatment above the low water level. To extend this treatment to the rest of the site, improving the measures to increase the contact time, particularly the recirculation rates and the foam barrier, is necessary.

KEYWORDS

Lindane, DNAPL, fractured aquifer, surfactants, SISCO, persulfate

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LIFE SURFING PROJECT, ENHANCED SURFACTANTS EXTRACTION (SEAR) IN A FRACTURED AQUIFER

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ABSTRACT

The LIFE SURFING project has tested the application of SEAR and SISCO techniques in the fractured aquifer of the Bailín landfill (Sabiñánigo, Huesca). After 16 years of pumping and treatment, the dense phase (DNAPL) from lindane manufacturing residues is in the residual phase, with very low pumping performance.

After several hydrogeological and tracer tests, two tests have been designed and carried out in which a solution of a non-ionic surfactant (E-Mulse 3 ®) with a concentration of 20 g/l, sodium chloride (5 g/l) and sodium bromide (0.2 g/l) as tracers to facilitate monitoring and mass balances, and hydrogen peroxide (1% by volume) to favour the dispersion of the reagents.

The injections have made it possible to reach the vadose zone, where the presence of DNAPL was detected in some fractures, as well as sufficient dispersion and contact time (minimum 6 hours). In the first test, 9.3 m^3 were

injected, and 7.1 m^3 were extracted. The maximum concentration of POPs in the recovered volumes was 7 g/l, with an average concentration of 0.4 g/l. In the second test, 6 m^3 were injected, and 2 m^3 were recovered, with a maximum concentration of POPs of 5 g/l and a mean value of 2.5 g/l.

A caustic soda solution was injected into the downstream flow from the test cell to prevent the polluted volumes released from reaching the Gállego River. NaOH addition favours the dehydrochlorination of the heavier chlorinated substances and the breaking of the surfactant emulsion. In the barrier zone, located between the injection zone and the river, the application of caustic soda, sodium persulfate, temperature and aeration has been combined. The surfactant released downstream disappeared from the aqueous phase by hydrolysis, dilution and absorption and did not reach the barrier zone. The POPs downstream of the barrier zone have not exceeded 40 ppm of the total sum in any borehole, representing the heaviest chlorinated compounds between 1 and 5% of the total POP mass.

Once the tests were finished, the boreholes were cleaned using a self-pumping tanker truck to eliminate the abundant accumulation of fines. In this operation, more than 100 kg of DNAPL have been recovered. The area where the injections were made was left with minimal concentrations of DNAPL in conditions to execute the assay of joint application of oxidants and surfactants (SISCO).

KEYWORDS

Lindane, DNAPL, fractured aquifer, surfactants, SEAR, persulfate.

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LIFE SURFING PROJECT: CONTAMINATED EMULSION TREATMENT BY ADSORPTION IN GAC AND ADSORBENT REGENERATION

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ABSTRACT

The LIFE SURFING Project has tested the application of Surfactant Enhanced Aquifer Remediation (SEAR) and In Situ Chemical Oxidation enhanced by Surfactant addition (SISCO) in the Bailin Landfill (Sabiñanigo, Spain). The fractured aquifer was contaminated by discharges of a dense organic phase produced as residuum in the lindane manufacture nearby. This DNAPL comprises a complex mixture of more than 28 Chlorinated Organic Compounds, COCs. Physical extraction of DNAPL is already inefficient, and more advanced techniques were required for either DNAPL extraction or in situ degradation. SEAR has been successfully applied in the LIFE SURFING project to extract the residual DNAPL from the most polluted area of the landfill. The injected fluids are extracted in the SEAR treatment, and contamination is transferred from the subsoil to the extracted emulsion. This polluted emulsion containing dissolved COCs and surfactant needs to be treated to eliminate the COCs and, if possible, recover the surfactant. In this context, adsorption on Granular Activated Carbon (GAC) has been proposed as an on-site treatment of the polluted fluids extracted in SEAR application in the landfill. In the circular economy scenario and to avoid transporting contaminated residues out of the landfill, on-site regeneration of spent GAC has been studied using Thermal Activated Persulfate (TAP). A column filled with 20 g of GAC used in the wastewater treatment plant of Bailin Landfill has been built and operated at a lab scale. A volume of 280 mL of a polluted emulsion obtained in the SEAR event of the LIFE SURFING project carried out in May 2022 was adsorbed on GAG (COCs and surfactant, E-Mulse 3®, concentrations being 9100 and 12000 mg/L, respectively). The saturated GAG was regenerated with TAP at 60°C (PS concentration 40 g/L) and a new adsorption cycle was carried out. This procedure was repeated three times to determine the recovery of the adsorption capacity and the selective oxidation of COCs in the GAG surface. It was found that GAG adsorbed about 115 mg COCs/g_{GAC}, being this value stable in successive adsorption-regeneration cycles. The unproductive PS consumption decreases in the presence of adsorbed organic compounds, and the surfactant adsorption decreases with the regeneration cycles (from 144 to 47 mg E3/g_{GAC}). Therefore, the adsorption-regeneration cycles tested allow selective removal of COCs from the emulsion, partially recovering the surfactant used and reusing the GAC without generating a secondary residuum.

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ON SITE REMEDIATION OF FLUIDS EXTRACTED IN SEAR TREATMENT IN THE LIFE SURFING PROJECT AT BAILIN – SABIÑÁNIGO (HUESCA): SELECTIVE POLLUTANTS OXIDATION AND ADSORPTION

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ABSTRACT

A soil remediation pilot test was carried out at the Bailin landfill within the LIFE SURFING project. Various techniques for on-site decontamination of aqueous phases generated in the cited project, highly polluted with chlorinated organic compounds (COCs) and also containing surfactants, are evaluated. These on-site treatments aim to reduce the contaminant load of the aqueous phase to pollutant concentration values that allow the discharge in the wastewater treatment plant located at the Bailín landfill or to recover the fluids with surfactant capacity for their reuse. The techniques applied to achieve these objectives in the on-site pilot plant were treatment by activated carbon and its regeneration by persulfate, advanced oxidation processes (Fenton Reagent) and thermal alkaline hydrolysis with aeration with retention of volatiles on granular activated carbon. In this work, an emulsion containing 5.166 g/L of solubilized COCs and 10 g/L of non-ionic surfactant E-mulse 3 ® has been treated at room conditions and pH=3 with stoichiometric H_2O_2 concentration and ratios H_2O_2/Fe^{2+} of 45/1 (Fenton Reagent). More than 95% of COCs were selectively eliminated at 48 h. Besides, an emulsion containing 16 g/L of surfactant and 8 g/L of COCs has been successfully adsorbed on GAG, and GAG has been regenerated with thermally activated persulfate at 45°C. However, an unproductive consumption of PS was found with GAG. The treated fluid can be discharged in the Bailin WWTP or be reinjected in the subsoil.

KEYWORDS

Lindane, COCs, HCH, Fenton oxidation, surfactant, GAC adsorption and regeneration

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ON-SITE TREATMENT OF LIFE SURFING PROJECT WASTEWATER IN BAILIN – SABIÑÁNIGO (HUESCA)

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ABSTRACT

Included within the LIFE SURFING project, a soil remediation pilot test carried out at the Bailin landfill, various techniques for on-site decontamination of water and leachate with a high polluting load and presence of surfactants generated in said project are evaluated. The objective of these treatments is to reduce the contaminant load to adequate concentrations for the final treatment in the Bailín's treatment plant and/or to recover the fluids with surfactant capacity for their reuse. The techniques to be carried out to achieve these objectives in the on-site pilot plant were the following: treatment by activated carbon and its regeneration by persulphate, advanced Fenton oxidation and alkaline hydrolysis with aeration.

The depuration of wastewater by active carbon treatment could not be carried out due to problems of splashes and leaks from the carbon filter. There were also reactor sealing problems in the Fenton oxidation. Finally, three alkaline hydrolysis tests were carried out with degradation results of 99.8% in the sum of HCH and 93-98% of the total COCs.

KEYWORDS

Lindane, COCs, HCH, Fenton oxidation, alkaline hydrolysis, surfactant, dehydrochlorination

Block 2.
STRATEGY-INFRASTRUCTURE-MONITORING SABIÑANIGO MEGA-SITE

CASE STUDY OF THE INFLUENCE OF GEOLOGY AND THE PRESENCE OF DIFFERENT MATRICES ON THE APPLICABILITY OF HCH REMEDIATION TECHNOLOGIES

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ABSTRACT

Inquinosa factory (Sabiñánigo, Huesca) produced lindane (γ-HCH) from 1975 to 1989. Per each ton of lindane, 8 to 10 tons of other HCH isomers were produced and sent for disposal to two landfills: Sardas landfill, which received Inquinosa waste from 1975 to 1983 and Bailín landfill, which received it from 1984 to 1989. As well as solid waste, the factory dumped liquid waste that has been found in the form of DNAPL. None of the sites had proper isolation measures. Thus, the solid and liquid wastes leaked into the ground causing soil and water pollution.

The Government of Aragon has been working on the control, containment and remediation of these orphaned polluted sites since 1992.

The three sites (Inquinosa, Sardas and Bailin) are close to each other, distributed around the axis of the Santa Orosia anticlinal. Whereas Inquinosa and Sardas bedrocks, separated 400 m by the Sabiñanigo reservoir, are composed of tertiary fractured marls of the anticline axis, Bailin, which is 2 km south from Sardas landfill, is composed by an alternation of siltstones and fractured sandstones in vertical layers. In spite of their proximity, Sardas and Inquinosa present also geological differences, due to the diversity of the quaternary deposits present at each margin of the river. As a consequence of this variety, each of the three sites has its own groundwater behaviour. Such is the case that there is a free detrital aquifer in Inquinosa, a semi-confined detrital aquifer in Sardas influenced by the tidal effect of the reservoir, and a fractured aquifer in Bailín.

But a part of the natural geological materials, sediments and sludge are generated within the control and remediation activities.

The diversity of materials, aquifers and matrices together with the existence of DNAPL and solid HCH, makes it impossible to solve the problem with only one remediation technology, nor to replicate the same methodology in all sites. A site-specific train of techniques is needed to remediate all matrices. Dedicated studies and pilot tests are currently undergoing progress on its implementation.

KEYWORDS

Lindane, hexachlorocyclohexane (HCH), DNAPL, fractured aquifer, detrital aquifer

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UNIQUE STRATEGIC PROJECTS IN THE SITES AFFECTED BY HCH IN ARAGON

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ABSTRACT

In October 2015, a Management Unit for the Comprehensive Decontamination of Lindane was created, agreed by the Governing Council, which was integrated into the Contaminated Soil Service in accordance with Decree 25/2020, of February 26, of the Government of Aragon, which approves the organic structure of the Department of Agriculture, Livestock and the Environment (BOA No. 43 of March 3). In 2016, the "The Strategic Environmental Action Plan against the lindane waste in Aragon" was approved. The Plan includes five priority actions, and organizes them in a Roadmap. Action I is the isolation of waste, which began with the transfer of waste from the old Bailin landfill to the new security cell. This action will be completed with the "DEFINITIVE CLOSURE OF THE BAILÍN SECURITY CELL", which to date and since 2014 has been provisionally sealed in anticipation of receiving the waste from the dismantling of the old Inquinosa factory and the waste at that time stored in those facilities.

Included in Action III of the Strategic Plan is the so-called "HYDROLOGICAL CORRECTION AND BIOREMEDIATION PROJECT OF NORTH ZONE OF THE OLD BAILÍN LANDFILL" (CORHIBA) whose aim is the decontamination and restoration of a relevant part of the surface of the north zone of the old Bailin landfill.

As Action III, the decontamination of surface soils and restoration was established. This that has led to the drafting of the "PROJECT FOR THE DISMANTLING AND DEMOLITION OF THE OLD LINDANO FACTORY, SABIÑANIGO (HUESCA)" which address the dismantling of the facilities and structures of the old Inquinosa factory as a prior step to enable the subsequent decontamination of the soil and its restoration.

KEYWORDS

Strategic Plan, Security cell, Corhiba, dismantling, Inquinosa, Bailin

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MULTIDISCIPLINARY PERSPECTIVE OF THE ENVIRONMENTAL MANAGEMENT OF THE SARDAS SITE

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ABSTRACT

For over two decades the Sardas landfill (Sabiñánigo, Spain) was used for the uncontrolled disposal of industrial waste as well as municipal and construction & demolition waste. In total, approximately 400,000 m^3 of waste have been deposited directly onto the ground, consisting of Eocene marls. As a consequence, the landfill had no base liner or any other waste mitigation systems installed. The industrial waste contained residues from chlorine production and in particular, approximately 70,000 tonnes of waste isomers from the hexachlorocyclohexane (HCH) production for the manufacture of lindane (γ-HCH). Lindane production was carried out by chlorination of benzene in a photochemical process using ultraviolet radiation. For the production of one tonne of lindane approximately ten tonnes of HCH waste isomers were generated and were largely dumped in the past around the former lindane productions. These wastes are present in the Sardas landfill both in solid and in liquid form (as Dense Non Aqueous Phase Liquid, DNAPL).

The landfill site was assessed through a governmental project supported by joint funding from the European, National and Regional environmental authorities. Currently, the environmental monitoring of the site, the extraction of the DNAPL phase by pumping, the control and treatment of leachate and research of different remediation techniques are ongoing.

Hydrogeology, chemistry, microbiology and mathematical modeling, are just some of the areas in which research is carried out on the site. In addition to the resources of the Government of Aragon, SARGA and EMGRISA, work is being done on the site with five university research groups.

This study will address the way to solve the environmental problem of the Sardas landfill from a multidisciplinary point of view in which different materials or soils, impacted to a different degree, require very different remediation techniques (SEAR, ISCO, pump & treat, electroremediation, bioremediation, phytoremediation), even in the same location.

KEYWORDS

HCH, lindane, DNAPL, POPs, Sardas landfill, Sabiñánigo

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PURIFICATION, ANALYSIS AND LABORATORY MANAGEMENT SERVICE, TECHNICAL ASSISTANCE TO THE FACULTY MANAGEMENT AND MONITORING FOR SPACES AFFECTED BY HCH CONTAMINATION

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ABSTRACT

The public company SARGA, as an instrumental company of the Autonomous Community of Aragon, assists the Contaminated Soil Service of the General Directorate of Climate Change and Environmental Education to guarantee the control and monitoring of contamination by HCH, and other residues derived from the manufacture of lindane in Aragón, in the locations of Bailín, Sardas and Inquinosa and other affected areas.

The purpose of these activities is to avoid affecting the environment and the existing population in the surroundings, while guaranteeing the quality of the waters in the Gállego River after the possible incorporation of pollutants from the aforementioned locations.

This assistance includes the exploitation, management and maintenance services of the different existing facilities, as well as environmental monitoring which includes the analysis of the data offered by climatic parameters, the sampling and analysis of surface water and groundwater, the evolution of the quality of the soils in the affected environment, and the monitoring of atmospheric dispersion and gasses. An integral part of this monitoring are the surveillance services of the Gállego River and the ecological study of its riverbed.

This assistance includes the drafting of projects and technical valued reports for the improvement of existing infrastructures, as well as the health and safety coordination service, coordination of business activities and occupational risk prevention.

KEYWORDS

HCH, contaminated soils, environmental monitoring, Gállego river

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ENVIRONMENTAL MONITORING IN THE SURROUNDINGS OF THE SPACES AFFECTED BY THE RESIDUE FROM THE MANUFACTURE OF THE HEXACHLOROCYCLOHEXANE PESTICIDE IN THE TOWN OF SABIÑANIGO

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ABSTRACT

The Government of Aragon, from its public company Sarga S.L.U., carries out environmental monitoring of the surroundings of the spaces affected by the manufacture of γ-Hexachlorocyclohexane (Lindano), in Sabiñanigo. Environmental monitoring includes surveillance of surface water quality (rivers, reservoirs, canals, ravines, and lakes), groundwater quality (piezometers), soil quality (soils and sediments in rivers and reservoirs), quality of ichthyofauna, macroinvertebrates and birds, vegetation quality (trees, shrubs, riverside forest and macrophytes) and air quality (sedimentable particles and gases).

The Government of Aragon has a surveillance protocol on the Gállego river (early warning), which defines the actions to be carried out in case of contamination by lindane and which covers from the municipality of Sabiñanigo to the mouth of the Ebro river and coordinates the different organisms affected (General Directorate of Climate Change and Environmental Education, 112 Aragón, General Directorate of Public Health, Aragonese Water Institute).

The samples that involve both environmental monitoring and the surveillance protocol of the Río Gallego are analyzed at the HCH laboratory in Sabiñanigo, a reference centre for research on persistent organic compounds.

KEYWORDS

Lindane “ɣ-hexachlorocyclohexane” (ɣ-HCH)

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AIR QUALITY MEASUREMENT TASKS IN RELATION TO THE DECONTAMINATION WORKS OF MANUFACTURING WASTE OF THE HEXACHLOROCYCLOHEXANE PESTICIDE IN THE TOWN OF SABIÑÁNIGO

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ABSTRACT

The Government of Aragon, from its public company, Sarga S.L.U., monitors and assesses the air quality in the surroundings of the locations affected by the manufacture of the pesticide ɣ-Hexachlorocyclohexane (Lindano), within the municipality of Sabiñánigo. It is located on the Pyrenean axial and communication axis, linking the autonomous communities of Aragon with Catalonia and Navarre. Here are shown the main works and equipment used, the results of the particulate matter and the updates that have been carried out since the start of the actions for the remediation of the sites, adjusted to the regulatory requirements, and analyzing the main assessments and limitations around the limit thresholds and campaigns executed. The main objective is the design of a control and surveillance network, which allows for future remediation work (such as the dismantling of the Inquinosa Factory, the definitive sealing of the Bailín Landfill, etc.), coupling the experiences of the monitoring carried out in Bailin and Sabiñánigo, according to historical data. However, there are still important uncertainties that should be taken into account for future actions, without clear reference limit thresholds for some of the sedimentable particles, PM10 and/or PM2.5 in the case of Lindane, only the data indicated for exposure professionals. For this reason and taking into account the actions from 2009 to 2014 in the surroundings of the Bailín Landfill and the measurements between 2015 and 2022 in the surroundings of the sources of the Sardas Landfill, the Inquinosa Factory (abandoned), and the Bailín Valley, the Government of Aragon wants to consolidate a particulate matter surveillance network to control dispersion in relation to the works in progress and HCH isomers.

KEYWORDS

Lindane “ɣ-hexachlorocyclohexane” (ɣ-HCH), Particulate matter; surveillance network, settleable particles, PM10, spatial dispersion

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LABORATORY HCH SABIÑÁNIGO-REFERENCE CENTER IN RESEARCH ON PERSISTENT ORGANIC COMPOUNDS

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ABSTRACT

The Government of Aragon has the Pirenarium laboratory in the municipality of Sabiñanigo, a reference center for research on persistent organic compounds, for carrying out the analytical monitoring of the samples taken in the surroundings of the spaces affected by the manufacture of ɣ- Hexachlorocyclohexane (Lindane), in Sabiñanigo.

The number of samples analyzed annually is in continuous growth, reaching seven thousand units in 2022. The complexity of the work carried out in the laboratory is the wide range of concentrations depending on the origin, being less than 0.02 ugr/l in clean samples from the channel and reaching gr/l in DNAPL samples taken in piezometers within the dumps. A variety of matrices are also analyzed, such as solids (sediments, plants and animals), gasses (retained in active carbon) and liquids.

The laboratory has different equipment, the most relevant being gas chromatography equipment. The laboratory works with different work methods adapted for the compounds under analysis, within the complexity of the matrices to be treated, and conditioning said methods to the accuracy and speed required.

The chromatography equipment undergoes periodic calibrations with standardized standards, in addition to participating in intercomparison exercises with other accredited external laboratories.

KEYWORDS

Lindane "ɣ-hexachlorocyclohexane" (ɣ-HCH), dense non-aqueous phase (DNAPL)

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INTEGRAL MANAGEMENT OF THE PREVENTION OCCUPATIONAL RISKS IN THE EXPLOITATION, EXECUTION OF WORKS AND SPECIAL ACTIONS, INVESTIGATION, AND REMEDIATION OF SOILS AND/OR SITES CONTAMINATED BY HCH

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ABSTRACT

The investigation and remediation of soils and/or sites contaminated by HCH, as well as all the works associated with the control of the contamination plume, such as water treatment works, hydrogeological monitoring, construction works of essential facilities, execution of special actions, etc., frequently raises situations that may endanger the safety and health of people, property and environmental resources involved or not in such work.

Uncertainty about the harmful substances present in soil, water or air, and, in many cases, their state and spatial distribution, are factors that condition the prevention measures to be established, as well as the actions to be carried out, which differ from the that, are normally implemented in common work environments.

For adequate management of prevention in all work carried out on soils and/or sites contaminated by HCH, a document must be produced that serves as an effective prevention instrument, the Health and Safety Plan.

Next, some recommendations and examples on the contents of the Safety Plan available at the HCH contaminated sites in Sabiñanigo (Huesca). In addition, as an extension to the risk assessment method, the system of indications of risk levels implemented in the HCH contaminated sites in Sabiñanigo (Huesca) will be described, which includes risk assessment and prevention measures for areas established with contamination risks, activities and/or operations and safe work protocols.

Specific aspects and own experiences related to industrial hygiene control, health surveillance and applicable regulations will be explained.

The main characteristics of personal protective equipment, personal protective equipment management system, "black and white" installations, self-protection and emergency measures will also be explained.

Finally, examples of processes where the HAZOP analysis (HAZard and OPeratibility study) has been applied to analyze risks and identify potential hazards and operational problems will be explained.

KEYWORDS

Health & Safety Plan, HAZard and OPeratibility study, HCH

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PERSISTENT PESTICIDES IN AIR FROM A FORMER HCH PRODUCTION SITE IN SPAIN

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ABSTRACT

The landfilling and dumping of persistent organic pollutants (POPs) and other persistent hazardous chemicals, such as hexachlorocyclohexane (HCH) isomers can have significant adverse environmental consequences and cause contamination in soil, water, and atmosphere systems. The Government of Aragón implemented remediation and containment measures at derelict production facility (INQUINOSA Factory) and landfill sites located in Sabiñánigo (Aragón, Spain). To protect and assess the local environment, the concentrations of HCH isomers in air were periodically monitored in the Bailín and Sardas landfills and surroundings. Important differences were found between sampling locations (geographic distribution) and sampling campaigns (temporal trend). HCH concentrations obtained during dismantling works at Bailín landfill were statistically higher for all isomers compared to those obtained afterwards. Nevertheless, the levels obtained in Bailín and Sardas landfill and INQUINOSA Factory highlights that even after dismantling works, these facilities are currently HCH air pollution sources.

KEYWORDS

POPs, HCH, PeCB, HCB, air monitoring, passive air samplers

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ATMOSPHERIC HCH CONCENTRATIONS (2008-2019) FROM THE SPANISH MONITORING PROGRAM ON POPs

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ABSTRACT

In Spain, notorious environmental and human health awareness issues related to lindane and other HCH forms have been documented mostly in the north of the country (e.g. Aragón, Basque Country or Galicia regions). Yet, aside from the scientific data available from pointed polluted areas, the presence of HCH in atmospheric air across Spain has been and continues to be systematically investigated since the 2008 inception of the Spanish Monitoring Program on POPs (SMP-POPs). In the SMP-POPs, passive air sampling by means of polyurethane foams (PUFs) is conducted seasonally (winter, spring, summer, fall) at representative urban and background sites scattered through the peninsular and insular Spanish national territory.

In this study we present and evaluate data on HCHs (α, β, ɣ) since 2008 to 2019 from half of the monitoring sites of the SMP-POPs (those investigated by our group at the Spanish National Research Council, IQOG-CSIC), corresponding to seven background and five urban sites made up almost entirely of coastal locations.

Obtained data for over a decade showed greater HCH air concentrations in urban sites than in background locations when splitting all data (n=484) into those two categories. These differences were statistically significant (Mann-Whitney, $p<0.05$) for the three HCH isomers as well as for ∑HCHs. Among the twelve study locations, two cities stood out among the urban sites with median concentrations of 42.2 pg/m^3 (Azpeitia) and 50.3 pg/m^3 (Barcelona). Likewise, two background sites stood out from the rest of them; namely, Mahón (30.0 pg/m^3) and Cap de Creus (39.3 pg/m^3). In all these sites, ɣ-HCH was the most abundant species contributing up to ≈75% to ∑HCHs. The predominance of ɣ-HCH was consistently observed over the whole study period in the five urban sites while in background locations the α-HCH was predominant in 3 of them, and in a forth one the relative contribution of the α and ɣ isomers measured about the same.

Conversely to what was found for other airborne POPs such as PCBs and PCDD/Fs targeted as well in the SMP-POPs, the seasonality did not influence either the total air concentration nor the isomeric profile of HCH.

Furthermore, it is worth noting the results on HCH air concentrations showed no clear pattern from a temporal perspective, making it necessary to widen the number of monitoring years to crystalize the expected decline in Spain of airborne HCHs. The fact that HCH air concentrations seem to remain stable over the reported years along with the predominance of the ɣ isomer -the least persistent of them-, highlight the ongoing existence of HCH sources in the Spanish territory. All in all, SMP-POPs results build on numerous international scientific studies that call for attention on these chemicals, for which despite being POPs, further and concrete action is needed.

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2D MODEL OF GROUNDWATER FLOW AND DISSOLVED HCH TRANSPORT THROUGH THE GÁLLEGO RIVER ALLUVIAL AQUIFER DOWNSTREAM THE SARDAS HCH LANDFILL (HUESCA, SPAIN)

Samper, J.[1], Sobral, B.[1], Montenegro, L.[1], Guadaño, J.[2], Gómez, J.[2], Delgado, F.[3], San Román, J.[3] & Fernández, J.[4]

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ABSTRACT

INQUINOSA produced more than 150 000 t of waste with a high content of HCH (hexachlorocyclohexane) and other chlorinated compounds. Here we present a 2D finite element groundwater flow and dissolved HCH transport through the alluvial aquifer of the Gállego river. The model extends from 250 m north of the N-330 road bridge to the Sabiñánigo dam. Groundwater inflows include aerial recharge, inflows from the surrounding fluvioglacial terrace on the right bank, inflows along the left bank from the surrounding marl formation and inflows from the Sabiñánigo reservoir. The aquifer discharges to the Gállego river, the Sabiñánigo reservoir and underneath Sabiñánigo dam. The oscillations of the level of the reservoir produce a tidal effect in the hydraulic heads in the alluvial aquifer. These oscillations are transmitted in a damped way with some delay to the piezometric oscillations in the aquifer The offset and the damping of the hydraulic heads attest that the alluvial aquifer is not in direct hydraulic contact with the Sabiñánigo reservoir. The silting sediments of the reservoir and the natural silts of the terrace are interposed between the alluvial and the reservoir. The flow direction changes quickly in a daily basis in response to the oscillations of the reservoir level. Model results confirm the validity of the conceptual model and reproduce the measured hydraulic heads in the aquifer. A contaminant transport model in the alluvial aquifer has been performed to simulate the total dissolved HCH. The model is based on the hypothesis that HCH is partitioned between dissolved and sorbed phases by using a constant distribution coefficient, K_d. The computed plume of the concentrations of total dissolved HGH is very sensitive to changes in the distribution coefficient. The “effective” distribution coefficient is smaller than the values derived from lab tests by Lorenzo et al. (2020). The calibrated model has been used to calculate the flux of dissolved HCH leaving the site towards the Sabiñánigo reservoir. The flux of dissolved HCH is very sensitive to K_d and is estimated to be equal to 2.1 kg/year for K_d = 10 L/kg. The lack of measured HCH data in the siltation sediments prevents a validation of this estimate. However, this flux estimate is consistent with the HCH fluxes recorded downstream the Sabiñánigo reservoir at the hydropower channel and at the Jabarrella reservoir.

ACKNOWLEDGMENTS

This study was performed within the framework of research contracts funded by Ebre Water District and EMGRISA (Company for the Management of Industrial Waste) which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

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TRACER TESTS IN THE HCH-AFFECTED ALLUVIAL AQUIFER DOWNSTREAM THE SARDAS LANDFILL (HUESCA, SPAIN)

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ABSTRACT

HCH and other COCs have migrated through the Gállego river alluvial aquifer downstream the Sardas landfill, which is located on the left bank of the Gállego river, less than 500 m from the Sabiñánigo reservoir. Tracer tests were performed in 2022 to quantify groundwater velocity under ambient conditions and characterize aquifer parameters and heterogeneities. A dilution test was performed on Feb 8th by adding salt water in borehole PS16H and recording electrical conductivity logs. Darcy velocity was estimated to range from 0.04 m/d to 0.06 m/d. A long-term tracer test was performed from June 30 to September 23 by injecting 300 L of traced NaBr solution in 1 hour into PS16H borehole. Tracer concentrations were monitored periodically for three months in downstream boreholes PS16K and PS16L located around 4 m from the injection borehole. The test was successful in providing the tracer breakthrough curves in boreholes PS16K and PS16L. The peak tracer concentration in PS16L occurred after 18 days. The average water velocity was estimated to be about 0.25 m/d. A numerical model of the tracer test was performed to support the design of the tracer test and provide guidance during its execution. The transport parameters and boundary conditions of the numerical model were dynamically updated during the test by incorporating the measured tracer data. The best fit of the numerical model to measured tracer concentration data lead to the following results: 1) Darcy velocity which fluctuated during the test due to the oscillations of the reservoir level ranged from 0.01 m/d to 0.09 m/d); 2) The porosity of the alluvial deposits ranges from 0.15 to 0.25; and 3) The longitudinal dispersivity ranges from 1 to 2 m while the transverse dispersivity varies from 0.25 m to 0.5 m. The results of the tracer test confirm the conceptual model of the flow through the alluvial aquifer and provide useful information about the heterogeneities of the sands and gravels.

ACKNOWLEDGMENTS

This study was performed within the framework of research contracts funded by EMGRISA (Company for the Management of Industrial Waste) which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

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3D GROUNDWATER FLOW AND CONTAMINANT TRANSPORT MODEL OF THE SARDAS LANDFILL (HUESCA, SPAIN)

Samper, J.[1], Sobral, B.[1], Pisani, B.[1], Montenegro, L.[1], Guadaño, J.[2], Gómez, J.[2], & Fernández, J.[3]
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ABSTRACT

INQUINOSA's lindane factory in Sabiñánigo (Spain) operated from 1975 to 1992 and produced more than 150 000 t of waste with a high content of HCH (hexachlorocyclohexane) and other chlorinated compounds. This waste, in the form of powder and liquid, was dumped in an uncontrolled manner at the Sardas landfill, located on the left bank of the Gállego river, less than 500 m from the Sabiñánigo reservoir. The landfill was poorly sealed in 1997. In 2009 the presence of a DNAPL was detected at the foot of the landfill near the Sabiñánigo reservoir. Here we present a 3-dimensional (3D) transient groundwater flow and contaminant transport model of the Sardas landfill performed with MODFLOW 6. The model includes the landfill and the surrounding bedrocks and extends from October 1, 2011 to September 29, 2022. The most important water inflows into the landfill occur in the lowest areas of the landfill

perimeter where drainage-collected waters flow into the landfill. The daily values of the water inputs were estimated with a hydrological water balance model performed with VISUAL-BALAN. Most of the water discharge from the landfill takes place underneath the frontal bentonite wall through the shallow layer of altered, fractured and decompressed marls. Other outflows include cyclic water pumping in well S37 and discharge in perimeter ditches constructed in 2018 and 2021. Flow model parameters were calibrated with hydraulic head data collected at 40 boreholes drilled in the landfill and its surroundings. The results of the 3D flow model confirm the previous hypotheses about the water inflows and outflows. The contaminant transport model simulates the transport of total dissolved HCH. The contaminant transport model has been used to quantify the fluxes of contaminants leaving the landfill.

ACKNOWLEDGMENTS

This study was performed within the framework of research contracts funded by EMGRISA (Company for the Management of Industrial Waste) which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

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DIAGNOSIS OF LINDANE CONTAMINATION OF THE SARDAS LANDFILL (SABIÑÁNIGO) IN THE GÁLLEGO RIVER AND PROPOSAL FOR ACTION

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ABSTRACT

A study of the effect of lindane on the Gállego river was commissioned to the CEDEX by the CHE during 2021. The study focused on the knowledge of the system formed by the Sabiñánigo reservoir, the Sardas landfill facilities, located on its left bank, and the geological substratum. The work consisted of the compilation and analysis of the information generated over decades by centres of the Central Administration, through the CHE, by the Government of Aragón, and by experts in multiple disciplines.

The results obtained include: 1) a better definition of the hydrogeological functioning of the low permeability substrate of the Sardas landfill; 2) the evaluation of the landfill sealing system and its stability; 3) the mass balances of water and HCH in the reservoir and the distribution of pollutants in the seasonal episodes analysed; and 4) the selection and preliminary evaluation of the most plausible hypotheses to explain these pollution episodes.

A series of future actions are proposed to evaluate these hypotheses, and to prioritise HCH pollution containment techniques over clean-up activities and treatment of contaminated soil and water. These are:

1) a modification of the water monitoring network, based on a better knowledge of the water renewal time in the reservoir and of the mass balances of circulating HCH;
2) the additional characterisation of the silts at the top of the lower terrace of the Gállego river and the sediments filling the reservoir on its right bank with non-destructive techniques;
3) the reinforcement of the screen and passive leachate drainage in front of the Sardas landfill; 4) the application of retention techniques that enhance the natural biodegradation of lindane in the aquifer and the materials that confine it.

KEY WORDS

Landfill, lindane, contamination, surface water, groundwater, conceptual modelling

ACKNOWLEDGEMENTS

CEDEX acknowledges the attention received by the Government of Aragon (GA), EMGRISA, SARGA and AECOM during the field visits to the Sardas landfill site on 26 November 2019, 15 April 2021 and 11 November 2021, and that received by the representatives of the Demarcation of State Roads in Aragon of the Ministry of Transport, Mobility and Urban Agenda, UTE and Technical Assistance during the field visit and study of the slopes of the A-23 motorway route on the Sabiñánigo East - Sabiñánigo West section in Huesca. The invitation of the CHE and the GA to the meetings to present the results of the Hydrogeological Monitoring is also acknowledged.

MASS DISCHARGE TEMPORAL EVALUATION IN A TRANSECT LOCATED IN THE DISCHARGE ZONE TO THE GALLEGO RIVER IN BAILIN LANDFILL, SABIÑANIGO (HUESCA)

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ABSTRACT

Since 2015, Mass Flux (J) and Mass Discharge (Md) studies have been conducted in a control area of the former lindane landfill in Sabiñanigo, Huesca (Spain) close to the Gallego River, by using the methodology of Passive Flux Meters (PFM).

Lindane and other Persistent Organic Pollutants (POP) dumped in the landfill created a dissolved plume in a complex fractured bedrock media that contains, in order of amount in the groundwater, monochlorobenzene, benzene and HCH (lindane and non-commercial isomers). This plume reaches the Gallego River in a zone called Discharge Zone, and the knowledge of the scope of its discharge to the river is the main objective pursued with the calculations of the Mass Discharge, in order to implement control and corrective actions during the increasingly frequent remediation activities that are being carried out on the site in recent years.

PFM devices consist of a permeable sorbent infused with soluble tracers packed in nylon mesh tubes. They are placed in the boreholes or monitoring wells for a known exposure period where they intercept the groundwater flow, causing dissolved contaminants to be sorbed and the soluble tracers to leach out. Measurements of the contaminant concentration and remaining resident tracers can then be used to estimate groundwater and contaminant fluxes. The integration of these fluxes throughout a control area (transect) is used to calculate the total Md of each contaminant.

The results obtained for Mass Discharge estimations have shown an increase in Mass Flux and, consequently, in the Mass Discharge of the Discharge Zone transect, and suggest that some remediation tests, especially those involving intensive injection events, have been able to produce a 'washout' effect process in the fractures that favors the contaminant mass to move downgradient with a higher velocity within the groundwater flow. In addition, the evaluation of the Mass Discharge in those situations in which the aquifer is not in equilibrium highlights that it could increase when carrying out on site remediation activities that have a direct impact on the hydraulic head of the aquifer, e.g., injection events from the source zone that push the most contaminated groundwater downstream.

KEYWORDS

Mass Discharge, Mass Flux, PFM, benzene, monochlorobenzene, HCH, mass balance

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Block 3.
WASTE AND SOIL TECHNOLOGIES SESSION. WASTE MANAGEMENT EXPERIENCES, DESTRUCTION TECHNOLOGIES

TREATMENT AND RECOVERY OF HAZARDOUS WASTE MANAGEMENT

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Séché Environnement / Trédi Global Solutions, Saint-Vulbas, France

ABSTRACT

Séché Environnement is the benchmark player in the treatment and recovery of all types of waste, including the most complex and hazardous, and in pollution control operations, serving the environment and health. **Trédi** is a wholly owned subsidiary of the Séché Environnement group and a reference in the management and treatment of hazardous industrial waste.

Our French industrial sites of **Trédi Salaise** and **Trédi Saint-Vulbas** aim to process all types of waste in complete safety, whatever their volume and packaging. With a capacity of treatment of 344,000 tons a year, facilities are receiving hazardous waste from all around the world for disposal. Specialized in the elimination of hazardous waste, and also in the recovery of materials, particularly high-added value materials such as solvents, chlorine, bromine, PCB transformators, ...

Offering a **global management solution for hazardous waste disposal** to meet our clients demands and find the most appropriate and efficient solution for the waste disposal is our priority. We establish transportation plans, from the country of origin to our facilities for final disposal in compliance with the Basel Convention and hazardous transport regulations.

Séché and Trédi have expanded their range of specifications in recent years. These include the mass treatment of polluted soils with obsolete pesticides from Ukraine (10,000 tons), HCH waste from Turkey (730 tons) and Egypt (230 tons), and other POPs from Bulgaria (3,500 tons).

Thousands of tons of hazardous waste have been exported and disposed with the purpose of reducing further increase and pollution of the environment.

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COMMERCIAL ORGANIC CHEMICAL WASTE DESTRUCTION USING SUPERCRITICAL WATER OXIDATION

Follin, J.
General Atomic

ABSTRACT

Supercritical water oxidation (SCWO) is a destruction process for organic compounds that makes use of the unique properties of water exhibited under supercritical conditions, that is, temperatures above 374€ and pressures above 22MPa.

General Atomics introduced a commercialized a SCWO process that is called iSCWO (Industrial Supercritical Water Oxidation) in 2014 based on extensive use in prior years of the SCWO process for destruction of energetics (explosives and propellant) and nerve agents for the US Government.

GA has been developing SCWO technologies and delivering SCWO/iSCWO systems to the US Government since 1991.

The GA iSCWO operating temperature is 650€ and the operating pressure is at 23.5MPa for excellent organic waste destruction efficiencies. The oxidant is high-pressure air to minimize issues (both operational and permitting) associated with high-content oxygen supply systems (e.g., liquid oxygen). Organics and oxidants are miscible with supercritical water, creating excellent conditions for oxidation with minimal mass transport limitations resulting in organic materials are quickly destroyed to yield carbon dioxide and water.Heteroatoms such as chlorine, fluorine, phosphorus and sulfur are converted to inorganic acids or to salts if sufficient cations such as sodium or potassium are present. If present, metals such as iron and copper will produce metal oxides. Typical iSCWO gaseous discharge composition when oxidizing organic compounds consists of depleted oxygen, carbon dioxide and water vapor.

GA's iSCWO systems are perfect for onsite organic waste destruction, does not require any afterburner or complex secondary off-gas processing system, is a simple system that is easily maintainable, and designed for little or no liquid post-treatment prior to discharge to a publicly owned treatment works. Of recent interest is the use of GA's iSCWO system for the destruction of PFAS (Per- and Polyfluoroalkyl Substances) and AFFF (Aqueous Film Forming Foam) waste and waste streams. Tests have been performed by the EPA on GA's iSCWO system and the results have shown that this system is excellent for the destruction of PFAS material.

GA's iSCWO systems are offered either as transportable systems that can be moved from site-to-site or skid systems that can be permanently installed.

This presentation will review GA's experience with SCWO for military waste destruction and iSCWO for commercial waste destruction.

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CAN LOW TEMPERATURE THERMAL DESORPTION BE CONVERTED TO DESTRUCTION AND BE MORE SUSTAINABLE THAN TRADITIONAL INCINERATION

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ABSTRACT

Can thermal remediation be designed to be more than a simple separation of contaminants from soil?

High temperature thermal conductive heating (TCH) remediation at 300 - 350 °C has been utilized for decades to remediate contaminated soils both in situ and ex situ. TCH has a documented effect for a range of persistent organic pollutants like Dioxin, PCBs, Lindane and PFAS as well as mercury and PAHs. A literature study suggests that DDT can also be treated successfully.

Tailoring the remediation process to favour thermal degradation of contaminants can greatly reduce the risk of operation, simplify the treatment system and associated costs and limit the need for disposal of waste products like spent activated carbon.

Full scale remediation projects have demonstrated significant thermal degradation of the contaminants in the soil during the heat treatment process, e.g. dioxins (99%) even where thermal degradation processes were not believed to be a major removal mechanism.

In order to reduce operator risk arising from the highly toxic pesticide parathion, a 40 ton pilot scale project was designed to optimise thermal degradation. During operation 99.99% destruction of parathion in the soil was achieved.

Recently a lab scale study has implemented a similar approach to PFOS remediation and has demonstrated near complete conversion of PFOS to inorganic (water soluble) fluoride 25% and insoluble species (75%) with only 0.05% left as PFOS. The investigation of the reactions and the insoluble fluorine species formed is ongoing.

A common feature of the high temperature processes is that the thermal degradation forms more volatile degradation byproducts, that more easiæy can be removed by simple evaporation. The chemical reactions need to be controlled and monitored, to ensure that all reaction products are accounted for and included in the monitoring program. The degradation reactions can potentially be optimised to result in complete degradation or even mineralization if sufficient reaction time at elevated temperature is obtained.

The presentation will show examples of how in-situ or on-site thermal desorption can be operated towards thermal destruction in a far more sustainable way than traditional incineration. Using this approach it is likely to ease the stress on fixed incineration facilities as well as avoiding long and sometimes cross bordering transports of highly toxic substances.

Some sites will contain high mass pure substances where a combination of handling pure chemicals combined with in-situ or on-site thermal desorption/destruction of contaminated soils will be a safe and sustainable approach.

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HYDROGEN REDUCTION OF HCH, PCBS, AND PLASTIC

Douglas J. Hallett

True Energy Incorporated, Kingston, Ontario, Canada – Chairman and CEO, Founder, PhD.

ABSTRACT

Gas Phase Chemical Reduction of PCBs was presented by ELI Eco Logic International Inc., at the 1998 conference in Bilbao, Spain. I was the founder of that company, and inventor of the GPCR process.

In 2023, **True Energy Incorporated** presented Hydrogen Reduction of Organic waste Molecules which was published under the Patent Convention Treaty in 2020. This work reflects the continual development of a chemical process using hydrogen to destroy toxic organic molecules such as HCH and PCBs, breaking them down into methane and halogenated salts. Non-halogenated molecules and particularly polyethylene or plastic produce even higher volumes of methane and hydrogen. The overall mass and energy balance of this process is positive due to the release of energy during hydrogenolysis. This is an efficient, low-cost process. The methane produced is saleable as Renewable Natural Gas. There is a considerable quantity of this gas produced which more than offsets the operating cost and Capex of the plant. The process still operates with **no direct atmospheric emission** and the aquatic effluents have met Surface Water Discharge Criteria in Canada which are equivalent to WHO drinking water standards.

In recent years we have discovered that hydrogen can also be produced by catalysis of the methane produced, reacting with water or steam in our reactor. More than half of the hydrogen is produced from the water added making this a carbon neutral net producer of hydrogen at low cost. Carbon is converted to primarily CO and elemental carbon which are collected. The amount of hydrogen that is produced is much higher than the amount of methane. The production of this hydrogen meets the specification recently published by the US DOE. Production of methane or hydrogen from waste organic molecules using Hydrogen Reduction has finally achieved **Cyclic Management** of plastics, halogenated pesticides, still bottoms, solid municipal and commercial waste and sewage, providing a local source of fuel and energy.

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PROGRESS IN ENVIRONMENTALLY SOUND MANAGEMENT AND DISPOSAL OF PESTICIDE POPS WASTES IN CHINA

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ABSTRACT

China, the largest developing country in the world, had widely used pesticides containing persistent organic pollutants for the pesticides and disease prevention and control in the fields of agriculture, sanitary and epidemic control, termite prevention and antifouling. Such POPs pesticides include DDT, HCB, toxaphene, chlordane and mirex. Pesticide POPs wastes are mainly original production process wastes, pesticide stockpiles and contaminated matters. In China, pesticide POPs wastes were mainly distributed in original manufacturing plants and original sales, use and distribution areas; pesticide POPs wastes were mainly concentrated in the area of agricultural area, with the DDT wastes in largest percentage. As the Chinese life-cycle management system of hazardous wastes is gradually improved, corresponding environmental management and disposal requirements are established for pesticide POPs wastes. Nowadays, Chinese government has disposed of pesticide POPs wastes leftover historically, including environmentally sound disposal of 4147.93 t pesticide POPs wastes via cement kilns co-incineration, which provides experiences and references for the management and disposal of pesticide POPs wastes in various developing countries.

KEYWORDS

POPs pesticide wastes; status quo; environmentally sound; co-incineration in cement kiln

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HIGH TEMPERATURE INCINERATION OF POPs AND HAZARDOUS WASTE IS THE PROPER TREATMENT TO DESTROY THEM

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SARPI Spain

ABSTRACT

Nowadays, there is a revolution to change from a linear economy to a circular economy. We have to reuse waste as many times as possible, we have to develop technologies to increase the circularity of the waste, following the

action plan of the Green Deal. But taking into account this legislative package, we cannot reintroduce the pollutants into the economy to avoid any dispersion of hazards into the environment and to ensure that the public health is protected and according to this, on 4th October 2022 the European Parliament voted to reduce the concentration limit values for POPs in the waste, existing in the previous POPs Regulation

The high temperature rotary kiln is the best tool for hazardous waste, this treatment is based on a rotary kiln and post combustion chamber that incinerates at temperatures around 1.100° C or higher. And it is possible to incinerate different types of wastes: liquids with a wide range of viscosity, solids, gases, drums, IBC, etc and different calorific values.

According to the waste there are different ways to feed it into the kiln, in addition to the burners for liquid and sludge waste, it is possible to feed the kiln directly from the truck (like toxic, corrosive, mutagenic or other extremely dangerous waste streams) . It is also possible to put in whole or crushed drums and crushed big bags or IBCs.

Sarpi Constantí in Spain is one of the most reliable incinerators for treating POPs and is the only HWI that exists in Spain with these features. It can provide a service not only to Spain but also to European and International Markets.

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DDT DISPOSAL IN BANGLADESH

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ABSTRACT

The Food and Agriculture Organization of the United Nations (FAO) has supported the Government of Bangladesh in disposing of the DDT safely and cleaning up the storage site in a complex international operation. What is thought to be the world's largest remaining stockpile of the now-banned pesticide Dichlorodiphenyltrichloroethane (DDT), left in Chattogram city for 37 years, has finally been removed.

In 1985, the Government of Bangladesh (GoB) imported DDT and stored it in the urban part of Chattogram, Government Medical Sub-depot (MSD). The adverse effect of a humid tropical climate on DDT, and floods, caused the stock to become severely degraded and entirely obsolete. The stockpile poses a high risk to human health and ecosystem functions.

An international company did the DDT repackaging process. The DDT disposal is a complex and highly technical operation that took considerable expertise and planning and was the first of its kind in Bangladesh. Fourteen countries had to give their permission for the ship carrying the waste to transit through their territorial waters. France is one of only a handful of countries that has the capacity to dispose of DDT safely and also allows the import of hazardous waste from other countries according to international guidelines (Stockholm Convention).

The project team and government counterparts faced challenges with multiple approval processes with multiple regulatory agencies, decision-making bodies and inter-ministerial coordination with technical teams, which led to the formation of a multi-stakeholder committee with more than 22 government regulatory bodies supporting the smooth operations of the disposal process.

The project is supporting the GoB in strengthening its compliance with the Stockholm Convention on Persistent Organic Pollutants and developing the national capacity for the management and safe disposal of hazardous wastes in order to safeguard people and the environment by addressing the reduction of risks from ongoing exposure and illegal uses of pesticides in dry fish production, and public health protection.

To achieve the project goals, FAO conducted several training on contaminated site risk assessment, Pesticide Registration Toolkit, and Highly Hazardous Pesticides. Collection, recycling, and environment-friendly disposal of empty pesticide bottles have been initiated, and an action plan is being prepared to identify a future course of action in. A documentary on disposal is also being finalized to raise mass awareness and to ensure documentation for future references in similar environmentally sound disposal processes.

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OBSOLETE PESTICIDES MANAGEMENT AND DESTRUCTION IN MOLDOVA

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ABSTRACT

This communication presents the results of the actions undertaken in the Republic of Moldova during the last 20 years in the management of obsolete and prohibited pesticides, including POP pesticides, and elimination of the risks caused by them in relation to the environment and human health.

Concrete measures to solve this problem began in the early 2000s, following a special decision of the Government, and carried out in accordance with the NIP of the Stockholm Convention on Persistent Organic Pollutants ratified by the Moldovan Parliament in 2004. These actions have been funded by the Government and substantially supported by international organizations and Governments of development partner countries.

As a result, to date all known obsolete pesticides stockpiles, including POP pesticides, which constitute over 3,800 tons, were collected, evacuated abroad and destroyed. Parallel to these actions the national inventory and mapping of OP and POPs contaminated areas (around 1,600 sites) were conducted.

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 at all levels increased substantially.

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 were involved. Over 20 projects funded from various sources have been implemented in this area.

The main next steps to be taken in reducing the impact of OP and POPs waste are to ensure a sustainable management of chemicals in agriculture and industry, to find and eliminate any unknown stocks of pesticide waste and remediation of contaminated sites.

KEYWORDS

Obsolete pesticides (OP), persistent organic pollutants (POPs), POPs management, contaminated sites, Stockholm Convention on POPs.

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MANAGEMENT OF POPs CONTAMINATED SITES IN MOLDOVA: CISMICHIOI LANDFILL

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ABSTRACT

Here we present the evolution of the situation at the largest pesticide waste storage location in the Republic of Moldova – the Cişmichioi landfill.

The Chismichioi burial site was built in 1977 and put into operation in 1978, according to a special decision of the Government, on the territory of Cismichioi [Chishmikioy] community in the south of Moldova. The operations of burial of obsolete pesticides under the Ministry of Agriculture supervision have been carried out in several stages. According to the available documents, by 1987 approx. 4,000 tons of waste, including POP pesticides, were buried in 14 pits on an area of 2.3 ha.

The ecological situation at this landfill has been periodically evaluated with participation of different interested institutions from Moldova. Also, some repair and consolidation works on the site were carried out. The conclusions on the ecological situation was that over the years the impact of this object on the environment is minimal.

However, considering the age of the landfill and the uncertainty regarding the amount of buried obsolete pesticides and packaging materials, as well as the growing concerns of the residents of this area regarding the

harmlessness of this object, it was considered necessary to carry out an extensive assessment of the situation at the site and to take measures in order to disposal or conservation of this wastes.

Consequently, in the period 2016-2018, with the support of the Government of the Czech Republic, a series of investigation activities, risk assessment and a feasibility study were carried out, followed by the execution of extensive reconstruction and consolidation of the landfill infrastructure, and establishing of a monitoring system of this site.

Currently the Cismichioi landfill is under the management of the National Agency for Food Safety (ANSA).

KEYWORDS

Obsolete pesticides (OP), OP landfill, persistent organic pollutants (POPs), POPs management, contaminated sites.

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PESTICIDE INFORMATION SOURCES AND WASTE MANAGEMENT – SURVEY RESULTS FROM AZERBAIJAN COMPARED TO GEORGIA

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[4]Department of Soil Geography, Ivane Javakhishvili State University, Tbilisi, Georgia;

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ABSTRACT

Both Azerbaijan and Georgia inherited a legacy of obsolete pesticides like DDT and HCHs from Soviet times. In this contribution, results of a small survey (30 participants) with a standardized questionnaire from Azerbaijan are compared to results obtained from a survey in Georgia with 100 participants living in the surroundings of a former pesticide store. The results show that both countries share similar challenges e.g. with regard to risk communication about pesticide use. An important issue is repackaging of pesticides into alternative containers without labels or reliable instructions on safe handling of pesticides. Also, prolonged use of pesticides well beyond recommended shelf life is common. In addition, environmental legislation in both countries is still developing or weak. The situation of environmental legislation and its implementation is reflected in the survey results regarding safe management options for hazardous waste for both countries. Especially in rural areas, safe waste management of hazardous waste needs further efforts in both countries in the future.

KEYWORDS

Pesticide label, risk communication, pesticide use, waste management

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Block 4.
DEALING WITH CHLOR ALKALI AND MERCURY: SYNERGY BETWEEN MINAMATA AND STOCKHOLM CONVENTION: PRACTICAL CASES

MINAMATA CONVENTION AND THE UNEP GLOBAL MERCURY PARTNERSHIP: MERCURY MANAGEMENT IN THE CHLOR-ALKALI SECTOR

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ABSTRACT

The Minamata Convention on Mercury aims to reduce and where feasible eliminate mercury from products and processes around the globe. Having entered into force in 2017, the Minamata Convention includes a phase-out date for mercury cell chlor-alkali facilities by 2025. The Convention also requires each Party to take measures to ensure that mercury waste from these facilities is disposed of in ways that do not lead to recovery, recycling, reclamation, direct reuse, or alternative uses of mercury. Supporting these goals of the Minamata Convention, the UNEP Global Mercury Partnership's Chlor-Alkali Partnership Area, co-led by the US EPA and UNIDO, provides technical, and educational information to chlor-alkali production facility partners, governments, and other stakeholders. It promotes commercially competitive and environmentally responsible solutions for eliminating mercury use in chlor-alkali production. This presentation by the Global Mercury Partnership's Chlor-Alkali Partnership Area will explain the role of the Convention and the Partnership in reducing mercury use and releases from the chlor-alkali, progress in these efforts, and perceived challenges and opportunities moving forward.

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RELEVANCE OF MERCURY CONTAMINATED SITES FOR GLOBAL MERCURY RELEASE AND IMPLEMENTATION SYNERGY OF THE MINAMATA & STOCKHOLM CONVENTION

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ABSTRACT

Mercury contaminated sites considerably contribute to environmental pollution & release of mercury today and will become the most important emission source in future. Major releases stem from (former) mining sites of Hg and sites where mercury has been used in manufacturing of products (e.g., pesticides, medical devices, thermometers, light bulbs). Also, sites of gold/precious metal mining including artisanal gold mining (AGM) as well as sites of non-ferrous metals processing can be contaminated with mercury and have associated releases. Furthermore, mercury storage/disposal sites, mercury recycling sites and sites where mercury pesticides have been used can be contaminated and continuously release mercury. Last not least sites of former mercury use in industry (chloralkali sites; acetaldehyde; vinyl acetate; certain PVC) can be highly contaminated with mercury with current and future release and need systematic assessment and appropriate securing and remediation.

Chloralkali production sites can also be contaminated with PCDD/Fs and other unintentionally POPs listed in the Stockholm Convention with large legacies from the former use of graphite electrodes from 1890 to 1980s and in some developing countries longer. Additionally, a range of chloralkali sites were also production sites of chlorinated POPs (e.g. lindane/HCHs, PCP, DDT) partly with large contaminated sites from POP production and disposal. Therefore for chloralkali site assessment there is a strong synergy for Minamata and Stockholm Convention implementation. Therefore when assessing chloralkali production sites, the technologies used in the past need to be assessed including the management of wastes. In addition, the organochlorine/POPs production portfolio at these sites needs to be assessed including the disposal practice.

The current study gives a short overview on mercury contaminated sites and highlights the need of a synergistic approach to assess mercury and POPs pollution for certain sites for a synergistic implementation of Minamata and Stockholm Convention where appropriate.

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MERCURY CONTAMINATION AS A LEGACY OF CHEMICAL PRODUCTION IN THE CEE REGION

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ABSTRACT

The Minamata Convention was adopted in 2013 to protect the environment and human health from mercury. Mercury has been known as a pollutant for decades, and the effects on human health associated with its presence in the environment are well known. This toxic metal bioaccumulates particularly in aquatic environments, and through the food chain and, especially through fish and seafood, enters the human body. Even before the Minamata Convention, a threshold by WHO (0.5 mg/kg wet weight) for mercury concentrations in fish was established which should not be exceeded for human consumption. The results of our study show that this concentration is commonly exceeded in fish from the vicinity of former and operating factories using mercury in various processes, chlor-alkali plants in particular. Fish from these areas poses a serious health risk. It also shows that the mercury problem is of global concern due to its transportation from hotspots to distance of tens of kilometres in aquatic environment. Remediation of these sites is also complicated due to the presence of other contaminants such as e.g. POPs.

KEYWORDS

Chlor-alkali contamination, mercury, Minamata Convention, chemical industry, remediation, contaminated sites

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WHERE STOCKHOLM MEETS MINAMATA – MERCURY AND HCH ISSUES AT CHLOR-ALKALI FACILITIES

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ABSTRACT

The legacy of HCH production has been long known. World-wide an estimated 4.8 to 7.4 million tonnes of waste isomers from lindane production was disposed as waste. Within the EU alone 54 production sites were present. With few exceptions, hexachlorocyclohexane was produced at mercury cell chlor-alkali plants. The Stockholm Convention banned Lindane and all HCH isomers in 2009 and the Minamata convention has set the goal to phase out all mercury cells chlor-alkali facilities world-wide by 2025. This phase out gives renewed attention to the clean-up and remediation of these facilities where both HCH and Mercury are serious issues. This article will showcase the best environmental practices and project risk management for the assessment and remediation of HCH wastes and contamination at mercury cell (i.e., Castner–Kellner process) chlor-alkali plants.

First, the production process of HCH will be discussed, including the connection between the production of HCH and the use of mercury at these facilities. Within this description, we will show where both the HCH and mercury wastes and contamination are present, what investigation techniques are recommended, where the main risks lie, and how the presence of both HCH and mercury influences the remediation and disposal options for the soil, wastes and groundwater. This outline is supported by examples from site investigations and site remediations in both the Netherlands and North-Macedonia. The article finishes with recommended actions for site owners and authorities who want to start addressing these legacy sites.

KEYWORDS

Mercury, hexachlorocyclohexane, lindane, HCH, Minamata Convention, Stockholm Convention, XRF, chlor-alkali.

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ECON INDUSTRIES: VACUDRY® TECHNOLOGY. CASE STUDY: MERCURY AND HCH WASTE TREATMENT FROM CHLOR-ALKALI PLANTS

Ibarz, X.

ABSTRACT

Currently, the demand for remediation of obsolete chlor-alkali plants that used elemental mercury during the manufacturing process has increased considerably, due to the emissions that these facilities cause to the environment. During these remediation works, large quantities of contaminated waste with high concentrations of both mercury and HCH are obtained. Due to the hazardous nature of these wastes, it is necessary to treat them using the best available technologies for remediation and subsequent use of the decontaminated land, discarding landfill as an option.

With its VacuDry® technology, a low-temperature vacuum distillation process, Econ Industries offers the leading solution to recover resources from hazardous industrial wastes. VacuDry® units are available starting from 1 ton/day up to 100 tons/day and just require less than 20% of the energy compared to other thermal treatment systems. The option for electrical heating can reduce the carbon footprint of the entire process to zero. In the VacuDry® process, contaminants are separated and concentrated in a closed process under the influence of heat and vacuum.

This treatment process aims to separate the recyclable soil components from the pollutants and send them for recycling. Finally, in the case of the mercury obtained in the remediation process, it has to be properly treated as stipulated in the Minamata Convention. Therefore, Econ Industries has developed an advanced mercury stabilisation process, where the toxic mercury is converted into mercury sulphide, a non-toxic and stable compound for its safe final disposal.

KEYWORDS

VacuDry®, Econ Industries, hazardous industrial wastes, remediation, recycling, Minamata Convention, mercury sulphide

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BATREC: TREATMENT OF MERCURY AND MERCURY WASTES: MERCURY STABILIZATION AND SAFE DISPOSAL

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ABSTRACT

BATREC, a subsidiary of the Veolia group, part of Sarp Industries, is a leading specialist in the treatment and recycling of industrial hazardous wastes, particularly those containing Mercury.

MERCURY TREATMENT

Mercury is present in many industries including oil & gas and non-ferrous metal industry. Parties that have ratified the **Minamata Convention** are committed to taking action to eliminate Mercury from its use in both everyday products and industries (e.g. chlor-alkali units or mines).

BATREC has developed a **patented solution to stabilize metallic mercury** (Hg) to mercury sulfide (HgS) for a permanent and safe disposal in a salt mine. **HgS** is the safe, most stable and most non-soluble non-toxic mercury compound. In addition, the BATREC process is a wet process and thus not prone to gaseous mercury emissions, improving operational safety.

BATREC offers in addition **other treatment technologies** according to the different types of waste:

- **Reactivation unit with a thermal treatment step** for the decontamination of mercury absorbents, allowing these products to be returned into industrial processes.
- **Distillation unit** for Mercury waste (any type of waste contaminated with mercury: lamps. Thermometers, button batteries), to recover the Hg in metallic form, followed by a stabilization of liquid mercury.

Sludges, residual material, soils, from old-industrial sites are processed at our facility to extract Hg in several stages. At the end of the process, the recovered Hg is stabilized.

BATREC contributes to the progressive global removal of mercury by treating **all types of mercury waste**, rendering them safe in an environmentally sound way in compliance with international legislation.

KEYWORDS

Mercury treatment, Minamata Convention, patented solution to stabilize metallic mercury, all types of mercury waste

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BATREC: HG DECONTAMINATION: CASE STUDIES IN SPAIN AND ABROAD, INCLUDING MERCURY BASED CHLOR-ALKALI PLANT DECOMMISSIONING

Castellnou, A.

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ABSTRACT

Parties that have ratified the **Minamata Convention** are committed to taking action to eliminate Mercury from its use in both everyday products and industries (e.g. chlor-alkali units or mines).

Today, the use of mercury-based chlor-alkali production has been phased out and this technology is no longer used in Europe.

Projects accomplished in Chlor-Alkali Industry and Gold Mines:

1. Decommissioning of European Hg based Chlor-Alkali plants.

   More than 1500 T as of 2016 (Spain, Belgium, France, Italy, Hungary, Slovakia, Czech Republic, Switzerland). A
2. Industrial gold mines**.** *Continuous production worldwide*.

   More than 500 T as of 2016 (Latam Region).

Two Case Studies are provided with a detailed examination within a real-world context. BATREC offers a turnkey solution providing:

- transfrontier shipment formalities according to **Basel Convention** on the control of transboundary movements of hazardous waste;
- local operations (e.g on-site supervision for packing, labelling, shipping into maritime containers, health and safety protocol);
- road and maritime transport according to **ADR/IMDG** regulations;
- mercury stabilization through the patented Batrec process to HgS, safe transport and permanent disposal of the HgS in the salt mine;
- **full traceability chain** is ensured from the on-site to the final disposal in the salt mine – including the provision of a final report tracking the waste.

KEYWORDS

Mercury decontamination, Minamata Convention, Basel Convention, ADR/IMDG regulations, chlor-Alkali plants, industrial gold mines, traceability chain

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ASGM (ARTISANAL AND SMALL-SCALE GOLD MINING) PROJECT INDONESIA

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ABSTRACT

Artisanal Small scale Gold Mining (ASGM) is responsible for a large part of mercury contamination on earth. Indonesia is the third largest contributor of the global mercury pollution by ASGM. NEXUS3 and Durham University developed a polymer that binds heavy metals including mercury. A consortium formed by NEXUS3 and TAUW was granted by the TAUW Foundation for a ASGM pilot remediation project. The pilot intends to apply sustainable remediation techniques including the above-mentioned technique when applicable. The Consortium subcontracted the Lombok Mataram University and engaged PT Amman Mineral at Sumbawa, the Durham (England) and Flinders (Australia) University as project partners. PT Amman Mineral donated an analyzer to measure total mercury and its various compounds including methylmercury. The pilot has the following four phases: (1) inception, including site investigations of ASGM sites and selection of a pilot site to be remediated (2) the site remediation, (3) the remediation monitoring and (4) outreach including the development of a toolkit to remediate ASGM sites in Indonesia. This abstract summarizes the findings of the inception.

Eleven ASGM sites were preliminary assessed. From these, two were selected for a detailed site assessment. One is the Kayu Putih site at Lombok. ASGM using mercury was practiced in nearly all of the twelve family compounds of this site (section of a village). The detailed site assessment concludes that mercury contamination of the soil and groundwater is present. The primary source is the ASGM using mercury. The secondary sources are the sedimentation ponds, the diffuse contaminated topsoil around the rod-mills and the groundwater as a result of the mercury use and mercury vapor deposits. The other selected site was an abandoned ASGM site in the city Kuang, Taliwang, at West Sumbawa. This site comprises a family house with a shop, a shallow well and a garden with the remains of a platform that supported the ASGM rod-mill and a backfilled sedimentation pond. All ASGM installations were removed two years before. Mercury contamination of the soil and groundwater is present. The sources of contamination are the contaminated topsoil, the soil in the backfilled sedimentation pond and the water and sludge in the on-site domestic shallow well. In the water sample of the on-site and the surrounding domestic shallow wells the mercury concentrations are above the Dutch intervention value but just above, equal and below the EU/WHO drink water norm. Although ASGM activities have stopped, people living here are exposed. For both sites (Kayu Putih and Taliwang) the pathways are in direct contact with the contaminated topsoil and the water from the domestic shallow wells used in the households and kitchen gardens. From these two sites the Taliwang site is selected to be remediated as all on-site ASGM activities have stopped and therefore recontamination with mercury is excluded.

The health risks for the Taliwang site using the tier 3 risk models RBCA and RAIS are assessed to justify remediation. This tier 3 risk assessment concludes that human health risks cannot be excluded at the site. The most critical exposure routes are in order of magnitude: (1) consumption of vegetables grown on-site, (2) consumption of meat from livestock feeding on-site, (3) groundwater exposure (in case of using groundwater as drinking water), (4) Indoor air exposure and (4) Soil exposure (mainly soil and vegetable ingestion). The people at the Taliwang sites, as the majority of the villagers in the ASGM villages, are not drinking the water from the domestic wells, they use bottled water.

Soil remediation of the Taliwang site is justified as: (1) the identified mercury concentrations in the soil are above guideline values, (2) the tier 3 risks assessment confirmed that human health risks cannot be excluded and (3) ASGM activities have stopped, excluding recontamination. The Taliwang site will be remediated by excavation of the mercury contaminated soil. The excavated soil will be mixed Biochar and contained in an off-site depot planted with Vetiver grass. Both the Biochar and the Vetiver grass immobilize mercury. As the groundwater has mercury levels around the drinking water norm over a large area and the people are not drinking this water, a groundwater remediation is not justifiable.

In the villages where ASGM is still practiced remediation is not justifiable instead, the awareness should be raised with a focus on phasing out the use of mercury in ASGM. Only when the use of mercury has stopped, remediation should be considered. Based on the experiences gained with this TAUW Foundation pilot project a blueprint/tool kit will be developed to remediate ASGM site where the mercury is not anymore used.

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REMEDIATION OF MERCURY CONTAMINATED SITE. THE CASE OF ALMADEN DUMP AND THE ANTIQUE MERCURY METALLURGY FACILITIES OF ALMADENEJOS CERCO

Conde Ana I. Carrasco, F. Javier
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ABSTRACT

Almadén is the area with the largest mercury deposit in the world. Almadén and MAYASA, the state-owned company that has exploited and marketed these resources since time immemorial, are closely and historically linked to the mining-metallurgical activity of Hg production and marketing. Due to the health and environmental problems caused by Hg, the evolution of social sensitivity and the subsequent regulations, Almadén's cinnabar extraction ceased in 2001, its metallurgical activity in 2003 and its Hg trading activity in March 2011 as per Regulation 1102/2008. Once all Hg related activities ceased, MAYASA carried out the environmental restoration of its facilities, with the objective of minimising the environmental effects of 2,000 years of mining and metallurgical operations.

Of all environmental remediation activities developed by MAYASA in recent years, the San Teodoro waste heap restoration is far away the most important. This heap was for centuries the deposit for both sterile from the mining, and slag of the metallurgical processes, reaching a size of 3.5 million tons and occupying an area of 10 hectares. The restoration process consisted of encapsulation of the "in situ" encapsulation to ensure the waterproofing preventing water recharge and to minimize the effects on both groundwater and surface water, to reduce the dispersion of the material deposited on the tip that could affect the surrounding soils, and the emissions of Mercury. The restoration work lasted 3 years (2005-2008), and an environmental monitoring program was included in the design that allows to check the degree of achievement of the target set by performing the restoration works. After the completion of the restoration work of the dump, the values of mercury in surface water and groundwater show that the encapsulation of the dump has allowed the recovery of the area and its surroundings because both surface water and groundwater fulfill the legal limits of mercury in water.

MAYASA following its policy of remediation of the Almadén and its surrounding area has worked on possible solutions for the enclave "Cerco de Almadenejos", located 12 km from Almaden. The site is a historic metallurgical site operational in the 18th-19th centuries, and has the remains of the old Hg extraction furnaces and storage buildings. The studies of the site show that the enclosure acts as a gaseous Hg emitting source, constituting a contamination point and a potential danger for the area. MAYASA are working on the proposal *"Demonstration of new process of decontamination on mercury contaminated sites improving soil management and land use",* whose main objective is to demonstrate an innovative and environmentally friendly technology for the decontamination of mercury contaminated soil, by means of its *in situ stabilization*. The project combines the well-known soil remediation technology with the new material stabilizer, a "low-grade MgO", contributing significantly to reduction of Hg contamination in the site by reducing Hg dispositions in soil, as previous experiences have shown. Field tests were carried out, on a pilot scale in an international project, and laboratory tests with soil samples of the site, which have been able to achieve up to 80% reduction in the concentration of mercury in the soil eluate. The project increases environmental quality in the site due to the soil stabilization treated by physical and thermal insulation as it will decrease the re-suspension of dust downwind and mercury evaporation from the soil. The proposal is a sustainable solution, and allows an integral solution in the site with special restrictions on historical and cultural features.

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Block 5.
BIOREMEDIATION

MICROBIOME BASED REMEDIATION AND OTHER NATURE BASED TECHNIQUES

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ABSTRACT

There is an immense task on soil & groundwater remediation of contaminated sites in the EU, amongst which HCH-sites. This paper gives a compact overview of the current research and development progress regarding potential nature based solutions (NBS) for HCH in the EU. These NBS are focused on the use and support of natural processes, like the natural flowrate of (ground)water, sorption to green adsorbents, degradation by bacteria, atmospheric oxygen/UV and phytoremediation.

The search for HCH-specific microbiomes to subsequently upscale them for depollution purposes at contaminated sites has just started within the framework of EU-Horizon project MIBIREM. The quality improvement of surface water impacted by contaminated groundwater has just been shown by the use of a reactive mat filled with green adsorbents in another EU-project: RESANAT.

For HCH-contaminated sites, which are frequently large and sometimes remote, NBS have a high potential and fit into the current philosophy that the environmental, social and economic value of a remediation work should be optimized.

KEYWORDS

HCH, EU, sustainable remediation, nature based solutions, microbiome, MIBIREM, Natural Catch[TAUW]

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INTEGRATED SUSTAINABLE APPROACH TO LINDANE BIODEGRADATION

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ABSTRACT

Background/Objectives. Lindane was used in the second half of the 20th century as pesticide, until in 2000 it was banned in the EU. Its production was inefficient as 8 to 12 tons of waste isomers were produced per ton of lindane. These wastes were dumped near the production sites, usually creating uncontrolled landfills. Lindane and its isomers are POPs difficult to biodegrade. The project presented here aims at identifying and studying microbial population and species that can degrade effectively lindane and its isomers as well as testing their efficiency in laboratory and pilot scale trials in order to find a sustainable and cost-effective approach for widespread diffused contamination.

Approach/Activities. A model site in Italy, Colleferro industrial area and Valle del Sacco, has been studied and characterized. Microorganisms have been isolated based on their capacity to degrade lindane and HCH isomers. Both single strains and mixed culture are being tested for in-situ and ex-situ remediation treatments. Microbial community analysis will be performed by a molecular approach, to identify the bacterial and fungal communities and to predict their functional behavior. At a later stage, the ex-situ on-site testing will be conducted using the proprietary pilot testing plant RoboNova®.

Results/Lessons learned. Based on the results of the site characterization and on the aim of the project to define a strategy for bioremediation of lindane and its isomers, it was decided to proceed with isolation of microbiota and strains to be later tested at lab scale and pilot scale using RoboNova®. Three fungal and five bacterial strains have been isolated from cultures grown on medium with HCH as sole carbon source. One microbial community has also been established and is currently being tested at lab scale for its abilities to degrade HCH.

KEYWORDS

Lindane, HCH, isomers, sediments, groundwater, contamination, bioremediation, pilot testing

ASSISTED-BIOREMEDIATION FOR THE DEGRADATION OF ORGANOCHLORINE COMPOUNDS

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ABSTRACT

For several decades, the organochlorine pesticide lindane (γ-hexachlorocyclohexane, γ-HCH) has been used in agriculture and medicine due to its wide field of application. Its high toxicity and low degradation have caused negative effects on the environment and the human health, resulting in the presence of contaminated sites that must be remediated. In this sense, bioremediation can be a sustainable alternative to recover sites by favouring the degradation and detoxification of lindane and other HCH isomers. The bioremediation process is highly influenced by environmental conditions, the functional capacity of the soil microbiota and the properties of the contaminant and the soil. The object of study was to evaluate bioremediation assisted with compost in a soil contaminated with organochlorine compounds. The soil comes from a site located in Sabiñánigo (Huesca). The initial analysis showed concentrations of chlorinated compounds above the legislative limits, with the majority being compounds 1,2,4-trichlorobenzene and the α-HCH and β-HCH isomers. The experiment was carried out in mesocosms with 500 g of soil under controlled conditions of temperature (26°C) and humidity (60% field capacity) for 60 days. The effect of natural attenuation (NA) was compared with the application of a compost from sewage sludge with pruning waste (B-CP), and a mineral treatment from a NPK fertilizer (B-NPK). After 60 days of incubation, the organochlorine compounds detected in the soil underwent a degradation process under the experimental conditions. The NA achieved degradation around 45%, not observing a positive effect when providing soluble nutrients (B-NPK). The application of compost (B-CP) induced an increase in degradation to values around 57% in the 60 days of incubation probably due to the double effect of biostimulation by the contribution of nutrients and organic matter and a potential bioaugmentation due to the incorporation of exogenous microorganisms. The application of compost showed a positive effect in the recovery of soil functionality, observing increases in biological activity of the soil as well as the decrease of its phytotoxicity.

KEYWORDS

Polluted soil, lindane, HCH, biostimulation, natural attenuation, biological activity

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DEGRADATION OF LINDANE BY BIOLOGICAL TECHNOLOGY

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ABSTRACT

The gamma isomer of the hexachlorohexane (γ-HCH) or lindane, is an organochlorine compound included in the list of persistent organic pollutants (POP) of the Stockholm Convention. Lindane was produced in Spain in four factories. One of them is the INQUINOSA - factory in Huesca. Lindane production wastes were dumped, solid and liquid, in an almost non-controlled fashion in the area.

The key to biodegradation of lindane is removal of a halogen (Cl) atom. During this step, the halogen atoms, which are usually responsible for the toxic and xenobiotic character of the compound, are most commonly replaced by hydrogen or a hydroxyl group. Gram negative bacteria (such as our Rhodopseudomonas and nitrifying bacteria) and gram positive bacteria (as our three Bacillus species) will be responsible for carrying out the degradation in this assay. The method is a Preparation tanks (aerated and with controlled temperature) will be used to acclimatize the product to lindane and generate enzymes, favoring bacterial growth in a hostile environment through an adaptation mechanism.

Three efficiency tests were carried out at the landfill facilities during our collaboration with the UELA.

In the first one, a stable bacterial population was generated, achieving a bioaugmented high-yield product with evolved transfer over several generations. Adaptive and degradative efficacy of lindane was verified.

During the second test, trials were extended to 16 individualized tests, generating different scenarios variating conditions, bacteria mix (using Blue Planet bacteria), different substrates and inoculums.

Finally, the third test consisted of a Biopiles system to create aerobic, anaerobic, and mixed environments, using different substrates, seeking effective methods of decontamination of soils.

All the tests carried out, both aerobic and anaerobic, presented a significant reduction in total HCH using Blue Planet technology.

KEYWORDS

Hexachlorohexane, lindane, biodegradation, bacteria, decontamination, soils, biopiles

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LAB STUDIES LEADING TO DECISION-MAKING FOR *IN SITU* BIOREMEDIATION OF ORGANOHALIDES

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ABSTRACT

Bioremediation is an economical and environmentally friendly technology that can degrade a wide variety of persistent pollutants, such as pesticides, hexachlorocyclohexanes (HCHs), and chlorinated benzenes, with high specificity and efficiency. In this lab study, we evaluated the feasibility of applying bioremediation to the polluted groundwater of Sardas (Spain) and tested different conditions to select the best treatment to apply at field scale. Microcosms experiments were set up in different conditions and satisfactory bioremediation results were achieved. Aerobic treatment biostimulated with phosphate presented degradation of less chlorinated compounds (monochlorobenzene, dichlorobenzene and trichlorobenzene) in short period of time (3 d) and the degradation of the most chlorinated pollutants (tetrachlorobenzenes, pentachlorobenzenes, hexachlorobenzenes and hexachlorocyclohexanes) were almost completely achieved after 15 d. In addition, the anaerobic treatment biostimulated with phosphate led to the degradation of the most chlorinated compounds including all hexachlorocyclohexanes isomers, but no dechlorination of the less chlorinated pollutants was obtained. The presence of aerobic and facultative anaerobic bacteria known to dechlorinate these pollutants were identified in the different stages of the lab studies. Our findings pointed out that oxygen and phosphate integrate a suitable biostimulation alternative to be carried out in the alluvial groundwater.

KEYWORDS

Aerobic, anaerobic, biostimulation, microcosms, microorganisms, lindane, treatment train.

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SOURCE ALLOCATION AND DEGRADATION EVALUATION OF HCHs WITHIN A CONTAMINATED AQUIFER USING COMPOUND-SPECIFIC STABLE CARBON ISOTOPE ANALYSIS (CSIA)

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ABSTRACT

Hexachlorocyclohexane (HCH) isomers are pollutants of particular concern because of their widespread distribution in the environment, toxicity and persistence. Especially at sites of pesticide production, formulation and dumping, significant soil and groundwater pollutions of HCHs have been detected. For cost-efficient and highly productive remediation strategies of contaminated sites, it is necessary to investigate pollutant sources and sinks. In recent years, compound-specific stable isotope analysis (CSIA) has gained more and more attention as a tool for characterizing and assessing contaminant sources and *in situ* degradation of organic pollutants, respectively.

The applicability of compound-specific stable carbon isotope analysis (CSIA) for assessing degradation of hexachlorocyclohexane (HCH) isomers was investigated in a contaminated aquifer at a former pesticide processing

facility. A CSIA method was developed and tested for efficacy in determining carbon isotope ratios ($^{13}C/^{12}C$) of HCH isomers in groundwater samples using gas chromatography - isotope ratio mass spectrometry (GC-IRMS).

The carbon isotope ratios of HCHs confirmed contaminant source zones at former processing facilities, a storage depot and a waste dumpsite. This finding was confirmed by the concentration patterns of the contaminants and historical information.

The ^{13}C-enrichment in HCHs provided evidence for degradation of HCHs especially downstream of the contaminant source zones. CSIA from monitoring campaigns in several years revealed temporal trends in HCH degradation. Thus, the impact and progress of natural attenuation processes could be evaluated within the investigated aquifer. Conservative calculations based on the Rayleigh equation approach yielded extends of HCH degradation ranging from 30 to 86 %. Moreover, time- and distance-dependent *in situ* first-order degradation rate constants were estimated.

In summary, our study highlights the applicability of CSIA for evaluating sources and sinks of HCHs within contaminated aquifers located at sites of pesticide production, formulation and dumping.

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ANALYSIS OF MICROBIAL COMMUNITIES FOR THE IDENTIFICATION OF INOCULANTS FOR AN *IN-SITU* BIOREACTOR FOR TREATING HCH CONTAMINATION IN GROUNDWATER

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ABSTRACT

In situ bioremediation using microorganisms is a growing and developing discipline for clean-up sites contaminated by pollutants of different nature. Several bioremediation technologies can be applied at pilot and field scale levels based on different approaches such as natural attenuation, biostimulation or bioaugmentation. However, when applied to the field, the previous techniques do not always offer an optimal yield due to slow degradation rates, logistic limitations or difficulties to control field parameters that relate with microbial degradation of target pollutants. In those cases, bioreactors can be a more controlled, robust and effective approach that can provide more accurate and optimum conditions for microbial growth for its use in bioremediation processes.

This study evaluates the feasibility of implementation of an *in-situ* bioreactor for the groundwater bioremediation of a site impacted by a HCH spill at a former dumpsite. Comprehensive characterization of indigenous samples of different nature and collected at the site was carried out in laboratory scale experiments to identify matrices to be used as bacterial starters or inoculums in the following steps of bioreactor scale-up. For that purpose, different laboratory experiments were carried out to preliminary investigate the microbial communities in order to identify those samples with better characteristics and potentially containing HCH-degrading bacteria.

In total, 13 samples collected from locations historically impacted by HCH were characterized in four laboratory experiments, including the study of (1) viable microbial population growth in generic medium, (2) viable population of indigenous microorganisms capable of growing in minimal medium containing HCH, (3) diversity community composition and (4) tolerance to different HCH concentrations. The analysis of the samples revealed microbial populations adapted to site conditions with rather similar populations growing in the generic and minimal mediums with values of $10^4/10^5$ CFU for all the samples. Functional diversity studies showed diverse and metabolically active communities capable of growing in plate conditions which, at the same time, revealed to also be tolerant to HCH concentrations among 1 to 35 ppm.

KEYWORDS

Bioremediation, HCH, bioreactor, microbial communities, laboratory

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CHARACTERIZATION OF NATURALLY PRESENT MICROBIAL POPULATION AT SARDAS' LANDFILL AND INQUINOSA FACTORY IN SABIÑANIGO, HUESCA

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ABSTRACT

Microorganism bioremediation is a technique that is increasing its importance in recent years. The microorganisms naturally present in the soil are capable of using polluting compounds as a carbon source, contributing to their degradation and therefore, to the environment decontamination. In this essay, we have evaluated the degradation capacity of chlorinated organic compounds (COCs) by aerobic microbial colonies naturally present at strategic points in the emplacements of Sardas' landfill and Inquinosa factory, both located in Sabiñanigo, Huesca. For it, 8 samples from Inquinosa area and 29 from Sardas site, including soil, mud, water and plant material were studied. A physical-chemical and microbiological characterization was carried out for each sample. Within the microbiological analyses, the total and special bacterial biomass was determined; also, the diversity of the population through analysis with Biolog EcoPlate™ microplates and "Shannon" and "Simpon" diversity indexes. In addition, toxicity tests were carried out using Biolog MT2™ microplates, with the objective to evaluate the growth capacity of microbial populations using the organic carbon of the contaminants. From the Inquinosa area, rich population densities were obtained in 3 samples (10^4-10^5 CFU) and very rich in other 3 (≥10^6 CFU). On the other hand, 7 of 8 samples obtained high values of diversity indexes. Regarding the Sardas samples, 26 of 29 presented high diversity indexes and in terms of population density, 10 samples can be considered rich and 12 very rich. Only 3 samples from each location showed biological activity in the toxicity test.

KEYWORDS

COCs, Biolog EcoPlate™, Biolog MT2™, bioremediation, lindane, CFU (colony forming unit), microbial diversity

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APPLICATION OF MOLECULAR BIOLOGICAL TOOLS AND ISOTOPIC ANALYSIS FOR BIOGEOCHEMICAL CHARACTERIZATION OF FRACTURED BEDROCK AQUIFER IMPACTED BY DNAPL

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ABSTRACT

Biological degradation processes of target compounds are often desired in contaminated aquifers for the successful application of bioremediation strategies. However, the understanding and characterization of the occurring biological processes is still limited, since many projects rely on classical approaches just considering geochemical and hydrogeological data to support the existence of biodegradation. Those approaches would provide valuable information on reductions in concentrations, changes in inorganic species, generation of secondary products or variations in physicochemical parameters, although insights on microbial data are neglected.

In that sense, Molecular Biological Tools (MBTs) and isotopic analysis comprise a group of non-culture dependent laboratory techniques used to fill these gaps and estimate biodegradation processes in contaminated aquifers. With its application it is possible to identify key microorganisms, microbial communities and microbiological processes involved in the degradation of the contaminants of concern. It is also possible to obtain probing data that contaminant biodegradation is actually occurring and/or information about the parameters that affect microbial activity.

This work would provide a general overview on the application of commercially available MBTs at fractured bedrock aquifer impacted by DNAPL mainly composed of benzene, chlorobenzenes and HCH isomers. The combination of various MBTs and its integration with hydrogeochemical data, allowed the collection of multiple

lines of evidence to assess the biodegradation potential or degradation mechanisms existing under different site conditions. Comprehensive site characterization would facilitate understanding of microbial processes and time/spatial variations thereof for the potential selection and design of future remediation strategies and monitoring campaigns.

KEYWORDS

Bioremediation, Molecular Biological Tools, biodegradation, HCH

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PRELIMINARY STUDIES TO IMPLEMENT A PILOT REACTOR FOR THE BIOLOGICAL REMOVAL OF PESTICIDES FROM AGRICULTURAL WASHING WASTEWATER

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ABSTRACT

Agricultural washing wastewater (AWW) is an important source of pesticides that has a high potential to be treated by fungal bioremediation using white rot fungi. In the present study, two AWW treatment strategies were compared: a fluidized-bed bioreactor (FBB) with *T. versicolor* pellets and a rotating drum bioreactor (RDB) with *T. versicolor* immobilized on wood. The RDB effluent showed better results in all studied parameters compared to those of the FBB, including pesticide removal (85 %), toxicity, laccase activity, COD, absorbance and microbial communities. Additionally, the fungal assemblage showed that *T. versicolor* was successfully immobilized in the RDB, which triggered a major shift in the initial community. Afterwards, solid by-products were treated in a fungal biopile-like system reaching high biodegradation rates. Therefore, this study validates the fungal RDB as a viable alternative for AWW treatment, opening up the possibility of a further in-situ and full-scale application.

KEYWORDS

Fungal bioremediation, Pesticides, Agricultural wastewater, Fluidized-bed bioreactor, Rotating-drum bioreactor

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DESIGN, DEVELOPMENT AND SCALE-UP OF AN AEROBIC *IN-SITU* BIOREACTOR FOR REMOVAL OF HCH IN GROUNDWATER

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ABSTRACT

Lindane and other hexachlorocyclohexane isomers (HCH) are complex target pollutants for the implementation of bioremediation strategies of contaminated sites due to its persistence and low solubility. Nonetheless, microbial degradation of HCH is known to be possible through different degradation mechanisms under either aerobic or anaerobic conditions, although the implementation of these biological processes as remediation strategy is challenging.

In that sense, different bioremediation technologies are possible but its successful implementation for field-scale treatment should address multiple considerations and design parameters. One of these growing alternatives is the implementation of bioreactor systems which can be an efficient, robust and viable way to approach HCH removal from contaminated environments.

This work involves a scaling strategy for the development of an aerobic bioreactor from laboratory experiments until its implementation in a pilot field test for groundwater treatment. The first steps of the study involve the initial screening of samples of different nature using a multi-criteria approach that may allow the selection of the best candidates to be used as inoculum in the successive phases (e. g., microbial populations, diversity or tolerance to contaminant concentrations). At this stage co-inoculation of different samples to enhance microbial activity will also be addressed. Secondly, experiments in flasks will be carried out for the assessment of degradation efficiency and basic design conditions and parameters such as optimal pH, nutrients, minerals or contaminant bioavailability. At the final stages, a laboratory scale bioreactor would be carried out to optimize and adjust operating conditions that could be implemented at field scale and that support biomass growth during project lifecycle.

KEYWORDS

Bioremediation; HCH; bioreactor; microbial communities; laboratory; pilot test

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COUPLING ELECTROKINETIC SOIL FLUSHING WITH BIOREMEDIATION FOR THE REMOVAL OF CHLORINATED BENZENES AND LINDANE IN GROUNDWATER

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ABSTRACT

Bioremediation is coupled with electrokinetic soil flushing technology to check the proper performance in the degradation of chlorinated benzenes and lindane in the soil and groundwater from Sardas (Sabiñánigo, Spain). Biological barriers using microbial consortia from the site are used, and aerobic and anaerobic conditions were tested. The electric field (17 V) does not hamper biological activity and promotes a water flow that allows the pollutants to reach the biological barrier, where the pollutants can be removed.

KEYWORDS

Chlorinated benzenes, lindane, bioremediation, electrokinetic soil flushing, biological barrier, groundwater.

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APPLICATION OF THE METHOD OF PHYTOREMEDIATION OF PESTICIDE CONTAMINATED SOILS IN A FIELD EXPERIMENTAL PLOT IN CHIM-KORGON VILLAGE

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ABSTRACT

The widespread use of pesticides in agricultural practices has led to the fact that all countries of the world, in one way or another, face the problem of pesticide waste. The main problem is the elimination of unused and obsolete pesticide stockpiles, as well as the reclamation of adjacent areas. The sources of pesticides entering the ecosystem are old pesticide storage facilities, landfills, and agricultural aviation airfields. Many storage facilities are either completely or partially destroyed or converted to other needs. For the Kyrgyz Republic, the problem of disposal of obsolete pesticides is relevant, since there are more than 200 storage sites in the republic, and more than half of them are in an unusable condition, with contaminated degraded soil. In this study, an experimental site was selected - the former airfield in Chym-Korgon village (N 42049'23.9" and E 75031'49.8"); since 2021, aerobic biodegradation technology by soil bacteria has been carried out at this site. Chromatographic analysis in the spring of 2022 showed the presence of residual amounts of organochlorine compounds. Therefore, the phytoremediation method was applied at this site, which is an *in-situ* strategy, cheap and sustainable, suitable to remove this type of

pollutants, for self-remediation of soil processes. To evaluate the potential of phytoremediation of soils, we chose the seeds of agricultural plants, since the seeds of agricultural crops are easily available, and have a short growing season. It was found that in the soil-plant system, the efficiency of the process of phytoextraction of pesticides increases.

KEYWORDS

Obsolete pesticides, contaminated soil, phytoremediation, seeds of agricultural plants, types of pesticides.

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ENHANCED REMEDIATION OF SOIL CONTAMINATED WITH LINDANE, OTHER CHLORINATED PESTICIDES, AND ORGANIC EXPLOSIVES USING ZVI/ORGANIC CARBON REAGENTS

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ABSTRACT

Industrial production, agricultural and horticultural uses of organochlorine pesticides (OCPs) has resulted in contamination of soil in many countries. Lindane is the gamma isomer of hexachlorocyclohexane (γ-HCH) and it was extensively used worldwide as an insecticide for almost five decades, from the early 1950s through the late 1990s. Due to its toxicity and environmental persistence, Lindane as well as the alpha and beta isomers of HCH, are recognized as Persistent Organic Pollutants (POPs) in many countries, and the use of Lindane has been banned in more than 50 countries. HCH compounds and several other chlorinated pesticides have proven resistant to traditional soil bioremediation methods. This prompted research on alternate remediation methods and led to the development of a novel biochemical treatment using soil amendments formulated using microscale reduced iron powder, processed organic carbon, and an emulsifying agent. A key finding from the research was that greater degradation of OCPs could be achieved when the soil was treated with ZVI plus organic carbon, than when ZVI alone or organic carbon alone was used. Soils contaminated with Lindane, DDT, Toxaphene, Chlordane, and Dieldrin have been successfully remediated at many industrial and agricultural sites using this soil amendment approach. The ZVI/organic carbon soil amendment has also proven very effective for remediation of soil contaminated with organic explosive compounds, including TNT, DNT, RDX, HMX, and Tetryl. Full-scale soil remediation projects using the iron/carbon soil amendments have been successfully completed in Brazil, Canada, China, Colombia, El Salvador, and the United States. Treatment has been conducted *in situ* on surface soil (i.e., without excavation) as well as on excavated soil with attainment of common remedial goals for industrial and residential land use. Findings from bench-scale research and full-scale projects will be presented and discussed from the perspectives of performance and cost. The ZVI/organic carbon soil amendment approach provides a reliable, economical, and an environmentally sustainable alternative to excavation and off-site soil disposal, soil washing, or thermal treatment.

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PRELIMINARY STUDY OF THE BIOREMEDIATION CAPACITY OF HORSE AMENDMENT IN SOILS CONTAMINATED WITH HCHS

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ABSTRACT

One of the objectives of the REMSURFOX research project is the evaluation of bioremediation in soils contaminated by hexachlorocyclohexanes (HCHs) as the final part of a treatment train after the use of chemical

oxidation. In this work, an initial evaluation of the bioremediation capacity of organic horse amendment on soils with different HCH concentrations is carried out.

Four treatments were established: 1) soil with High Concentrations (HC) of HCH (130.27 mg/kg), 2) soil with Low Concentrations (LC) of HCH (0.97 mg/kg), 3) soil HC together with Horse Amendment (HC-HA) at 5% dry weight and 4) LC soil with Horse Amendment (LC-HA) at 5% dry weight. After an initial physical-chemical characterization of the soils, a study of the temporal evolution of the biological activity of the soils over 55 days was carried out, by determining enzymatic activities and HCH concentrations.

The application of horse amendment generated an improvement in the physical-chemical properties of the soil by reducing its pH and by increasing the content of organic matter and nutrients, which generated an increase in the biological activity of the soil. The dehydrogenase enzymatic activities (related to the quantity of microorganisms in the soil), phenol-oxidase (related to the degradation of complex organic compounds) and the phosphatase and urease activities (related to P and N, both macronutrients that are usually limiting in soils) were the most benefited from the application of the amendment. The temporal evolution of the enzymatic activities indicates a decrease in them, possibly due to a decrease in the availability of nutrients throughout the experiment.

The use of organic amendment produced a strong decrease in the concentrations of alpha, gamma, and delta HCH isomers during the first week of the experiment, reaching decrease percentages of around 90%. Regarding the beta and epsilon isomers, the horse amendment used reduced their concentrations by 50% at the end of the experiment.

The results obtained in this preliminary study point to the possibility of using the organic horse amendment studied within the treatment of soils contaminated by HCH, especially in the final phases within a treatment train.

KEYWORDS

Lindane, bioremediation, organic amendment, biological activity, enzymatic activities.

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Block 6.
WASTE AND SOIL TECHNOLOGIES.
IN-SITU REMEDIATION TECHNOLOGIES

SPIN® INJECTION TECHNOLOGY OR HOW TO PERFORM QUALITY INJECTIONS FOR AN OPTIMAL RESULT, EVEN IN LOW PERMEABILITY OR HETEROGENEOUS SOILS. EXPLANATIONS THROUGH THE CASE OF LINDANE

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Lindane, (γ-HCH, an isomer of HCH), widely used as an insecticide in agriculture since the 1930s, is a resistant and persistent molecule. It is now considered hazardous to human health and has harmful effects on the environment, due to its generally lipophilic and bioaccumulative nature. Due to the high persistence of lindane and HCH isomers, their indiscriminate and uncontrolled release has become a global concern, with heavily HCH-contaminated sites reported worldwide. Lindane has been banned by the European Union since 1991 and is classified as a Persistent Organic Pollutant (POP) under the Stockholm Convention (2009) and is listed in Group 1 of the WHO (World Health Organization) list of most hazardous substances.

Faced with this global problem, a great deal of research has been carried out to find the best treatment techniques and certain degradation pathways are beginning to be well known, whether biological, under aerobic or anaerobic conditions, or chemical - oxidation (ISCO) or reduction (ISCR) - or even physical to allow the extraction of the DNAPL (Deep Non Aqueous Phase Liquid). Most of the research done so far has been carried out under controlled laboratory conditions and there is still a lack of pilot-scale and especially full-scale field data.

Given the nature of lindane, which is easily dispersed at great depths, sometimes forming DNAPL, the remediation of Lindane/HCH contamination by in situ techniques seems almost inevitable in this context, and mainly in situ soil remediation techniques by reagents injections.

For this kind of remediation, in addition to a well-defined conceptual site model (CSM) and the appropriate choice of degradation process and reagents, a critical requirement for successful remediation is getting reagents in contact with the pollutants to be treated. Moreover, an optimal and prolonged contact between reagents and pollutants will ensure the success of the remediation, regardless of the type of soil concerned. This contact will be optimal if the reagents are injected into the natural porosity of the soil.

However, when the permeability of the soil decreases, in sandy-loamy or clayey soils or when the soil is very heterogeneous with less permeable horizons, traditional injection techniques have not yielded convincing results, or have yielded few results to date, with frequent rebounds problems after injections. The scientific literature continues to agree that injection remediation techniques are not recommended in this type of heterogeneous or in low permeable geology.

Faced with this problem and this “crucial” lack of contact, INJECTIS has developed and patented the SPIN® injection technique, which overcomes the limitations of traditional injections (direct thrust or through wells) on which the scientific literature is based. This new technology solves an essential lack when moving from pilot scale or full-scale remediation, to achieve qualitative injections in all conditions and geologies.

In addition, Spin® technology is equipped with a continuous recording system of pressure, flow rate and volume, and generates an instantaneous measurement of the hydraulic conductivity of the geology drilled. This makes it possible to adapt the pressures to allow homogeneous injection, despite the heterogeneity of the soil, by adapting to the permeability and injecting the appropriate volumes right where the pollutants are located. In addition, the technology minimizes reagent wastage and saves considerably on treatment costs in the final bill.

In this presentation we will explain in detail the SPIN® technology, the limitations of traditional techniques, their advantages, but also some of their limitations. In the context of the HCH conference, the presentation will focus on the case of lindane, trying to provide some insights into injection treatment techniques.

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INNOVATIVE HCH IN-SITU REMEDIATION USING POLYMER GEL AS A REAGENT CARRIER – RESULTS AT FIELD SCALE

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ABSTRACT

Assessing a sufficient contact time between injected reagents and contaminants is one major problem associated with in-situ remediation. Hence, the present work aimed at finding and evaluating at field-scale an innovative technique for the in-situ remediation of source zones contaminated by chlorinated compounds in high velocity aquifers. The field evaluation of the developed technique was done at a major French chemical plant, where the remediation of lindane contaminated source zone (~200 mg/kg in soils, ~0.5 mg/l in groundwater (GW)) using classical techniques is hindered by the velocity of the GW (10+ m/d).

The field work relies on the injection of a jellified reagent to ensure a sufficient contact time despite the high velocity groundwater (GW). 150 m^3 of viscous reactive gel was prepared and injected in 6 wells to target vadose and saturated zone (-8 to -15 m depth, GW table: 10 m). A comprehensive monitoring was conducted during and after injection (gel injectivity, 3D imaging using electrical resistivity tomography (ERT), reagent and dissolved lindane monitoring in GW, GW level ...) aiming at gaining knowledge over gel propagation, influence, and persistence in the aquifer. Finally, the technique efficiency was assessed on the comparison of lindane concentration in soil samples before and one month after the end of the injection of gel. The gel could be injected with very little pressure, and thanks to its high viscosity it propagated homogeneously in every direction, including upward and upstream. Radius of influence was higher than expected (> 8 meters), increasing the volume of soil treated beyond the 500 m^3 planned. ERT proved to be a very efficient tool to monitor gel propagation and persistence in-between monitoring wells. It proved that gel was still massively present in the treated area one month after the end of the injection. GW monitoring showed lindane concentrations downstream quickly dropped below LOQ after gel was injected, because of its degradation and the reduction of local permeability in the treated volume. Finally, soil sampling 1 month after the end of the injection showed excellent lindane degradation (up to 99%) in the treated area. All results acquired show that gel is a powerful fluid to homogeneously deliver reagent, increase contact time by orders of magnitude, and reduce local permeability.

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INSTALLATION, COMMISSIONING AND OPERATION OF AN INJECTABLE *IN SITU* PERMEABLE REACTIVE BARRIER TO PREVENT THE ADVECTION OF PER-AND POLYFLUOROALKYL SUBSTANCES AT A EUROPEAN AIRPORT

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ABSTRACT

An airport in Europe is divesting an area at the edge of their site for residential housing. The historic fire training area is located in the tranche of land to be divested. At this location, aqueous film forming foams containing per- and polyfluoroalklyl substances (PFAS) had been used for many years. PFAS contamination was identified in the groundwater at levels exceeding guidelines (PFOS at 320ng/L and PFOA up to 6,320ng/). A remedial options appraisal concluded the residential development precluded the use of active extraction of contamination to the surface, and the long-term costs were considered prohibitive. It was determined that a passive, *in situ* approach could match the requirements and that installing a subsurface colloidal activated carbon permeable reactive barrier should be explored to prevent further advection of the contamination.

A pilot test has been performed, completed using a 10m long barrier, with geological, hydrogeological and engineering/injection testing conducted to provide accurate information on contaminant flux zones. Direct push injection was used to emplace the colloidal activated carbon, followed by six months of monitoring.

The treatment was shown to be effective, reducing the contamination below performance criteria. Consent was given to install a 277m long full-scale barrier. Work on this started in February 2022, resulting in 7 months of installation and commissioning activities. The barrier has been warrantied for ten years to ensure ongoing efficacy and guarantee that the airport's off-site liability costs are defined and fixed.

KEYWORDS

PFAS, *In Situ*, Remediation, Colloidal Activated Carbon, PRB, Injection

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DESIGN, OPERATIONAL AND PROCEDURES FOR THE APPLICATION OF IN SITU CHEMICAL OXIDATION TREATMENTS IN FRACTURED BEDROCK AQUIFER IMPACTED BY AN OLD DNAPL

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ABSTRACT

Chemical Oxidation (ISCO) is one of the most applied in situ technologies for the remediation of soils and groundwater. It is based on applying strong oxidants under the surface able to degrade a wide variety of organic pollutants. Implementation of successful ISCO treatment depends on multiple factors such as, for example, choosing the right oxidant, distributing and achieving effective contact between the oxidant and the contaminants, understanding site specific conditions or optimizing delivery of the amendment at the right dose.

This work describes the evolution and performance over several years of the implementation of ISCO treatments as an effective remedy for the groundwater treatment in a fractured aquifer impacted by an old DNAPL. The DNAPL was formed by the lixiviation of lindane production residues, and it is continuously feeding a dissolved plume of 1.5 km length composed by chemicals of different nature (mainly benzene, chlorobenzene and HCH). The specific hydrogeology and chemical nature of contaminants of concern (i.e. chlorinated pesticides) have been a major challenge to study the effectiveness of ISCO treatments at the site.

The study covers an initial screening for the potential application of the technique including different treatability studies to address key factors as oxidant selection, activation modes and dosages. Based on the previous studies, persulfate-based injections seemed to be the most promising option for treating target contaminants at field conditions. Over the following years it has been possible to implement this technology in pilot and large-scale field tests with high yields of contaminant removal. Here we provide information on the main results obtained, operating procedures, limitations and lessons learned in applying ISCO technologies as remediation strategy in fractured bedrock.

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REMEDIATION OF HCHs-POLLUTED SOILS BY SURFACTANT-ENHANCED WASHING AND ACTIVATED PERSULFATE OXIDATION

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ABSTRACT

The existence of soils contaminated with hexachlorocyclohexanes (HCHs) represents a serious environmental problem. Their origin lies in the inadequate management of solid and liquid wastes generated during the production of lindane (γ−HCH). Solid waste consists of a mixture of HCH isomers: α-, β-, ε-, and δ-HCH, whose disposal pollutes surface soils. The remediation of these soils is limited by the low aqueous solubility of the pollutants (HCHs), which hinders their transfer to the aqueous phase and, therefore, their degradation. The use of surfactants, amphiphilic compounds able to reduce the water surface tension, can overcome this limitation.

This work focused on the remediation of real soil polluted with α-HCH and β-HCH (ΣHCHs = 373 mg/kg) by a coupled process: surfactant soil washing (SW) followed by the oxidation of the resulting emulsion with persulfate (PS) activated by alkali and temperature.

Three surfactants, one anionic: sodium dodecyl sulphate (SDS), and two non-ionic: Emulse-3® (E3) and Tween-80® (T80), were evaluated for SW experiments in batch conditions (water/soil ratio = 2, room temperature, 24 h). In order to optimize this process, the effect of the most representative variables: solution pH, reagents addition order and reagents concentration, has been studied. SW experiments have been carried out at neutral (7) and alkaline (>12) pH, with simultaneous (surfactant and NaOH) and sequential reagents addition (NaOH at zero time and surfactant after 4 h). The concentrations of surfactants tested were 2, 5 and 10 g/L, and the concentrations of NaOH: 0, 2.5, 4 and 13.5 g/L. The surfactants' capacity to solubilize the chlorinated organic compounds (COCs) of the soil was determined through the partition coefficient (Kd), which represents the ratio between COCs concentration in soil and aqueous phases. This parameter was used to select the surfactants: the lower the Kd value, the higher the surfactant solubility capacity. The use of surfactants in SW experiments increased the solubilization of COCs from the soil to the aqueous phase, decreasing Kds, especially at alkaline conditions. Neutral pH is not suitable for the SW of these soils due to the low solubility of the pollutants (HCHs). At pH>12, HCHs hydrolyze to trichlorobenzenes (TCBs), compounds with significantly higher solubility, highly decreasing Kds. However, the non-ionic surfactant T80 showed low stability at highly alkaline conditions (NaOH = 13.5 g/L), and its use was ruled out. The higher the surfactant concentration, the higher the COCs solubilization. Considering the second step of the process (to avoid excessive unproductive consumption of PS), a value of 5 g/L of E3 and SDS and an alkali concentration of 4 g/L were chosen for further experiments. At these conditions, above 70% of the initial COCs were transferred from the soil to the emulsion with both surfactants. The second step of the remediation process was the treatment of the SW emulsions by PS activated by alkali and intensified by temperature (PS = 40 g/L, NaOH:PS = 2, and T = 40 °C). COCs conversion of 30% and 96% were achieved in 72 h when treating E3 and SDS-emulsions, respectively, highlighting the suitability of SDS for the combined process.

KEYWORDS

HCHs, surfactants, soil remediation, soil washing, activated persulfate

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AIR SPARGING AND SOIL-VAPOR EXTRACTION PILOT TESTS IN BAILIN LANDFILL, SABIÑANIGO (HUESCA)

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ABSTRACT

Three air sparging and vapor extraction (AS/SVE) pilot tests have been performed in two different sites located in the middle area and source area of the dissolved plume of volatile organic compounds (VOCs) present in the former lindane (HCH) landfill of Bailin in Sabiñanigo, Huesca (Spain). The prime objectives of the pilot tests were testing and adapting several configurations based on AS/SVE technique in different sections of the plume, quantifying vapor mass removal rates, and evaluating a potential full-scale implementation. Selected configurations were a) AS/SVE, b) in-well air stripping (IWAS), c) AS/SVE with temperature increase, and d) AS/SVE combined with in-situ chemical oxidation (ISCO).

Since these methodologies could not be recommendable for its application in a fractured bedrock media such as the one that defines the site, the estimates made based on the Conceptual Model of the site and the knowledge of the hydrogeologic behavior in the pilot test areas suggested a good approach of these techniques for the evaluation of volatile mass elimination.

In 2018, configurations a), b) and c) were tested in a single well in the middle area of the plume. In 2019, configuration a) test was extended to four wells located in the same area, plus a configuration d) test using two additional wells for oxidant injection. Finally, in 2021, configuration a) test was performed in three wells located in the source area.

The design and built of the remediation equipment was conducted by the AECOM team members of the project related to the hydrogeological control and monitoring of the aquifer and remediation works in Bailin, which have been working on site for the last 14 years. The system was adapted to the particular conditions present in the test areas.

The execution of the tests was successful, and the results obtained were satisfactory and demonstrated the feasibility of these remediation techniques to be applied on site. Total mass removal rates were significant in all cases, although the methodology that showed the best results was AS/SVE with temperature increase. Nevertheless, mass removal rates obtained with the simplest configuration (AS/SVE) were favorable enough to avoid difficulties in logistics, since in a potential full-scale application it is recommendable to minimize the elements involved in the remediation system, as well as other matters such as work costs or sustainability.

KEYWORDS

AS/SVE; IWAS; ISCO; temperature; VOC; Henry's law; removal rate

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PILOT TEST SEAR APPLICATION IN SARDAS LANDFILL REMEDIATION

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ABSTRACT

Sardas Landfill at Sabiñánigo, Huesca, is polluted with Dense Non-Aqueous Liquid Phases (DNAPLs) produced as liquid waste from lindane production. DNAPL is composed of a complex mixture of more than 28 chlorinated organic compounds (COCs) from Chlorobenzene to Heptachlorocyclohexane of hydrophobic character. DNAPL dumped in the landfill migrated by gravity through the subsurface and accumulated in the contact between the alluvial and marls layers (about 16 m b.g.l.).This DNAPL is a continuous source of groundwater pollution because of the slow COCs solubilization in the aqueous phase, with the associated risk for the close Gallego river and Sabiñanigo reservoir.

SEAR (Surfactant Enhanced Aquifer Remediation) technology was applied in a test cell of the Sardas Landfill (wells PS14x) from 2018 to 2021. Removal rate of residual DNAPL (in the contact between the alluvium and marls and adsorbed in the alluvial) was remarkably increased by injecting an aqueous solution of non-ionic and biodegradable surfactant (E-Mulse 3 ®). Different injection strategies have been studied, analyzing the effect of variables such as surfactant concentration (5-50 g/L), injection volumes (0.2-7 m^3), injection and extraction flow rates (0.08-0.85 m^3/h and 0.3-4.5 m^3/h, respectively), number of injection wells (1-3), time elapsed between injection and extraction (16 h to 70 h), simultaneous or consecutive injection and extraction stages and the ratio of extracted volume to injected volume (1-8) on DNAPL recovery by solubilization or mobilization as an organic phase.

Higher DNAPL mass was recovered as a mobilized organic phase by injecting low flow rates of the surfactant solution (less than 0.3 m3/h) and higher extraction flow rates of the injected fluid (> 3 m3/h), with mass ratios of DNAPL recovered to surfactant injected higher than the unity. The interfacial tension between aqueous and DNAPL phases decreases in the surfactant presence and promotes DNAPL extraction by mobilization. Surfactant adsorption in the alluvium and surfactant absorption in the residual organic DNAPL increase when the time between injection and extraction increases. The strong surfactant adsorption is due to the clay presence in the alluvial. It causes the drop in dissolved COCs concentration (from about 2000 mg/L to 70 mg/L) in the aqueous phase over time, controlling the dispersion of contamination. If washing actions of the alluvial soil are needed, the time between injection and extraction should be reduced, being carried out almost immediately after injection. The extracted fluids were managed on-site before they were sent to the landfill wastewater treatment plant. SEAR treatment is a better choice until the residual contamination drops to a sufficient value and other methods, such as ISCO or bioremediation, could be applied.

KEYWORDS

Lindane, DNAPL, Surfactant; alluvium; groundwater remediation, SEAR

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ISCO AND S-ISCO EVALUATION IN THE REMEDIATION OF SARDAS ALLUVIUM

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ABSTRACT

Sardas Landfill at Sabiñánigo, Huesca, is polluted with Dense Non-Aqueous Liquid Phases (DNAPLs) produced as liquid waste from lindane production. DNAPL is composed of a complex mixture of more than 28 chlorinated organic compounds (COCs) from Chlorobenzene to Heptachlorocyclohexane. DNAPL dumped in the landfill migrated by gravity through the subsurface, being adsorbed in the alluvial soil, which is the permeable layer, contaminating the groundwater (GW) flow, with the associated risk for the Gallego river and Sabiñanigo reservoir in the vicinity.

In Situ Chemical Oxidation (ISCO) and ISCO enhanced by Surfactant addition (S-ISCO) are promising in situ technologies able to transform the chlorinated toxic compounds in the subsoil into less toxic and biodegradable compounds. Both technologies have been studied at the lab scale using real polluted soils obtained at 14.5 m.b.g.l. from boreholes PS14B and PS14D, drilled in 2018 in the Sardas Alluvium. Soils corresponding to the alluvial layer were dried, sieved and characterized, with contamination levels of up to 9622 mg COCs/kg soil.

The oxidant selected was Persulfate activated by alkali. This selection was made taking into account the pollutant nature, the high stability of Persulfate in the alluvial soil (with high carbonate content), the unaffordable and high risk of soil acidification, and the advantages of using strong alkaline pH in the transformation of the most toxic and chlorinated compounds (Hexachlorocyclohexanes and Heptachlorocyclohexanes) into less toxic and biodegradable compounds (Trichlorobenzenes and Tetrachlorobenzenes, respectively). The surfactant selected was a non-ionic and biodegradable one, Emulse®, commercialized by EthicalChem.

Experiments were carried out at batch and column scales with different oxidant and surfactant concentrations. A moderate improvement was found when surfactants and oxidants were added simultaneously, due to the higher solubilization of COCs to the aqueous phase in the surfactant presence. However, a high contribution of COCs oxidation on the soil surface to the total COCs removal was found, explained by the high surface created by the interbedded clays. This high surface also explained the high surfactant adsorption found in the alluvial soil and the slight increase in the oxidation rate found in the surfactant presence. After 8 Pore Volumes (PS 210 mM and molar PS/NaOH ratio 1:1) were added, more than 95% of COCs in soil (3680 mg/kg) were oxidized with ISCO and S-ISCO (5 and 10 g/L of surfactant in the aqueous solution were fed to the column in S-ISCO) to non-toxic compound, confirmed by results of Microtox® bioassay.

KEYWORDS

Lindane, DNAPL, ISCO, S-ISCO, Sardas Alluvial, Microtox®

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DESIGN AND VALIDATION OF ELECTROKINETIC TECHNIQUES FOR THE REMEDIATION OF THE ALLUVIAL SILT OF THE SARDAS LANDFILL (SABIÑANIGO) CONTAMINATED WITH HCHs

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ABSTRACT

In this work, electrokinetic soil remediation techniques will be evaluated for the treatment of COCs polluted silts located in the Sardas landfill (Sabiñanigo, Spain). Electrokinetic treatment is suitable for working at great depths and in poorly permeable media and it is based on the application of an electric field among electrodes

sited in the soil to induce different transport mechanisms such as electroosmosis, electromigration, electrophoresis as well as volatilization to gas phase due to the heating of the soil. Additionally, the electrolysis of water can take place on the electrolyte wells, leading to the generation of acid and basic fronts which may cause side processes such as dehalogenation. The present study ranges from laboratory scale tests (1 kg of soil) through bench scale tests (5 kg of soil) to real on-site tests at the Sardas landfill (full scale). Additionally, a conceptual 1-D model has been developed to validate the experimental results and to determine the extent of the pollutant transport mechanisms from the soil to the liquid and gas phases. Results point out that during the treatment, the resulting intensity decreases due to the silt undergoing the depletion of ions. Electro-osmotic fluxes are very low and do not depend importantly on temperature and other operation variables, and the amounts of pollutants collected in electrolyte wells is always negligible. Regarding the effect of the electric field applied, it influences the final speciation of pollutants because of the higher extension of the basic and acidic fronts that promote the dehalogenation of HCHs. Iron electrodes and the use of SDS solutions (as flushing fluid) also allow a more intense dehalogenation of COCs. There is an important volatilization of the COCs but effective dragging of pollutants by gas is not very efficient as the amount of pollutants collected in the GAC adsorption column is very limited. However, the grasshopper effect may explain the depletion of these pollutants from soil and their accumulation in the walls and pipes of the mockups.

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DISMANTLING STRATEGIES FOR HIGHLY HCH-POLLUTED LANDFILL LEACHATE DUMP USING ELECTROCHEMICALLY ASSISTED TECHNOLOGY

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ABSTRACT

This work will evaluate electrokinetic-assisted remediation for the restoration of sludge accumulated in the Sardas landfill pond as a previous step for its dismantling without causing any leakage in case of HDPE film rupture. The sludge contains a very heterogeneous concentration of HCH, ranging from a few mg/kg to less than a dozen g/kg. At this point, electrokinetic soil remediation technology is presented as a good option, both to dry the sludge due to the induced water transport and to reduce the hazardousness of the sludge by inducing dehalogenation as well as evaporation processes. In this work, different strategies have been evaluated at bench scale prior to its implementation in the Sardas landfill pond (full scale). In a first stage, several tests were carried out using mock-ups in which a portion of sludge was placed into a silt matrix to study the transport of pollutants through a clean silt to the liquid and gas phases. Results point out that the mobilization of species to the electrolyte wells is negligible as compared to the compound dragged with air, which is also promoted by the temperature. Then, in a second stage, mock-ups were filled with polluted sludge and the effect of electric field, surfactant addition and type of electrode material were evaluated. Results showed that dewatering of the sludge varies around 15-20 % depending on the operation conditions. Iron electrodes, the use of SDS solutions as flushing fluid and high electric field allow to attend a more intense dewatering. Finally, an integrated in situ treatment will be carried out, consisting of the application of an electric field directly in the pond and the subsequent treatment of the liquid and gaseous effluents generated. For this purpose, a 5x5 m area will be delimited with a plastic barrier. This will be followed by 9 cylindrical carbon iron electrodes with grooves to allow the accumulation of the liquid removed from the sludge. A cover will be installed to lead the gases produced to a granular activated carbon (GAC) column or to a condensate extraction system for those that condense. The latter, together with the liquid extracted from the electrodes, will be treated by the well-known Advanced Oxidation Processes (AOP), such as electrolysis or electrofenton. Additionally, the regeneration of the GAC column will be carried out by desorption with methanol, which will then be treated again by an oxidation process.

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Block 7.
LIFEPOPWAT SESSION

WETLAND+® TECHNOLOGY: TREATMENT OF HCH CONTAMINATED WATER BY A PASSIVE BIOLOGICALLY BASED REMEDIATION SYSTEM

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ABSTRACT

LIFEPOPWAT is a European project focusing on innovative technology based on constructed wetlands for the treatment of pesticide contaminated waters. This transnational cooperation project is funded by the European Union LIFE Programme under grant agreement number LIFE18 ENV/CZ/000374.

The Wetland+® system is a robust, low maintenance, and sustainable treatment that can be deployed in remote locations, where access to infrastructure may be limited. This is based on integrated reactive zones with wetland as polishing step. The first prototype was installed at Hajek (the Czech Republic).

The Wetland+® technology for the treatment of water containing HCH substances, developed by the Technical University of Liberec and AQUATEST a.s., is based on the use of oxidation-reduction and biosorption methods. Contaminated drainage water at the Hajek pilot site contains a high concentration of dissolved iron, which is oxidized by air oxygen and precipitated in the form of Fe(III) oxides and hydroxides. Due to a negative impact on the whole process, oxide-hydroxides are removed in the first stage of the technology - *the sedimentation tank*. No significant sorption of HCH substances was detected on sedimenting iron oxides. The water enters the first reactive stage - *a permeable reactive barrier* filled with Fe chips, where it is deoxygenated and converts back to the reduced state. Subsequently, HCH are partially dechlorinated, and chlorinated cyclohexenes and chlorobenzenes are formed.

The second reactive step is the *biosorption unit*, where both HCH compounds are sorbed and subsequently degraded by present microorganisms. The last step is the *aerobic wetland*, where the plant root system purifies the water, and the concentration of HCHs and their daughter products decrease below specified limits. The individual hydrocarbons are a source of energy and carbon for the microorganisms, which disintegrate the chemical bonds. The technology does not need additional chemicals and energy, and the whole process is naturally based. In the case of Hajek site, only one pump is required to pump water from a drain well at the base of the spoil heap to the first sedimentation tank. The project also foresees the system´s regular maintenance, including the eventual replacement of the iron chips in the permeable reactive barrier; the whole technology is without further input.

The system was finished in September 2021 with a capacity of 2 L/s. The initial efficiency of our systems was 97.3% for chlorobenzenes and 81.5 % for HCHs. During next months due to a tunning of the system the efficiency was increased to almost 100% for chlorobenzenes and 97 % for HCHs.

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ADAPTATION OF METHODOLOGICAL ASSUMPTIONS FOR DESIGN OF PILOT SCALE WETLAND+ INSTALLATION FOR WATER TREATMENT FROM HCH TAKING INTO ACCOUNT PRACTICAL LESSONS FROM DIFFICULT FIELD CONSTRUCTION PROCESS IN JAWORZNO, POLAND (LIFEPOPWAT PROJECT)

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ABSTRACT

The construction of the pilot scale Wetland+ installation for water treatment from HCH in Jaworzno, Poland is one of the key elements of international project LifePOPWAT implemented by 7 partners from 4 countries

(Czech Republic, Poland, France and Denmark) under coordination of Technical University of Liberec (CZ). The Municipality of Jaworzno (PL) is responsible for design and installation of the pilot scale treatment installation while PhotonWater (CZ) and Central Mining Institute (PL) provide methodological assumptions for the design. The original design developed in late 2020 have been the subject of construction works performed from August 2021 till June 2022 by contracted company. However, the contracted company finally failed to deliver the proper installation according to the design from 2020. Therefore, there was an urgent need to adapt at first the methodological assumptions and then to develop the updated design. The updated methodological assumptions had to take into account the lessons from the previous failed construction of the pilot system. The current conference paper describes the lessons learnt while transferring the methodology developed in Czech Republic into a real field pilot scale installation in Poland. The finally adapted methodological assumptions developed for the construction design are also presented. The design changes concerned technical aspects such as adapting the installation design to the materials available on the Polish market, improving the connection between the tanks, implementing solutions to protect against vandalism and damage. Technological aspects were also refined to increase the functionality of the Wetland+ system: a change of the installation control system, a change of the installation monitoring system, an adjustment of the filling of the chambers with reactive material to Polish conditions, a change of the aeration and sedimentation system, a verification of plant species for planting.

KEYWORDS

design, wetland, permeable reactive barrier, PRB, implementation, scaling up, construction

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EXPERIENCE FROM OPERATION AND TUNING OF WETLAND+® TECHNOLOGY FOR TREATMENT OF HCH-CONTAMINATED WATER

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ABSTRACT

At the Hájek site (Czech Republic) approximately 5,000 tons of HCH residue were disposed of in a dump of overburden of a kaolin pit mine in the 1970's. Dump leachate impacted mainly by hexachlorocyclohexane (HCH) isomers and chlorobenzenes (ClB) discharged into the Ostrovsky Creek and contaminated its ecosystem. Within the LIFEPOPWAT project Wetland+® demonstration prototype for treatment of the dump leachate has been installed. The Wetland+® cascade contains 4 sequential stages: (A) aeration and sedimentation module, (B) permeable reactive modules with zerovalent iron fill, (C) biosorption module, and (D) aerobic wetland module.

During the testing period of 14 months (the test is ongoing) the total concentrations of HCH isomers at the inlet to the Wetland+® varied from 52 to 265 µg/l, total concentrations of chlorobenzenes (ClB) varied from 103 to 1330 µg/l.

During the first 5 months of operation the removal efficiency of HCH showed a descending trend from 97% to 54%. The analysis of chemical data and geochemical modelling revealed that the descending efficiency is mainly the result of prevailing aerobic conditions in the B modules that led to clogging of the reactive fill by ferric hydroxide and oxyhydroxide precipitates. In addition, the original design of the B modules led to improper flow pathways of contaminated water through these modules. Bypassing the A module and modification of B modules suppressed the unwanted geochemical processes and resulted in an increase in the overall HCH removal efficiency of Wetland+® to 95%. Removal efficiency was not uniform for individual HCH isomers but exhibited the trend: $\alpha = \gamma = \delta > \beta = \varepsilon$. As a consequence, while δ-HCH isomer dominates in the inflow, ε-HCH prevails in the outflow from Wetland+®. The operation of the Wetland+® led to decrease in HCH mass discharge to the Ostrovský Creek from 23 to 25 g/day prior to the Wetland+® down to 0.8 – 0.9 g/day (approximately 97% decrease).

KEYWORDS

hexachlorocyclohexane, lindane, treatment, wetland, ZVI

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BENTHIC DIATOMS AS INDICATOR OF ENVIRONMENTAL IMPACT OF WETLAND+® TECHNOLOGY FOR TREATMENT OF HCH-CONTAMINATED WATER

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ABSTRACT

Wetland+® demonstration prototype for treatment of the HCH-contaminated dump leachate has been installed at the Hájek site (Czech Republic). Among other indicators phytobenthos, namely benthic diatoms are used as indicators of the environmental impact of Wetland +® on water environment. Benthic diatoms are suitable indicators of water quality due to a good knowledge of the autecological preferences of many diatom species. The species composition of the diatom community is influenced by local environmental conditions; e.g. in oxygen concentration, salinity, temperature, pH, shading, types of substrates, nutrient and organic matter concentration, pollution with toxic substance (heavy metals, pesticides). However, the phytobenthos community is also affected by various disturbances such as higher flow rates, turbidity, drying, mud cover, etc. This must be taken into account when evaluating the results.

Phytobenthos samples were surveyed along the Ostrovský Creek that is the recipient of HCH-contaminated leachate as well as in the Wetland+® prototype. Already before Wetland+® was put in operation the results showed increasing trend of number of diatom species identified in profiles along the Ostrovský Creek (in direction of surface water flow: 0, 3, 30, and 35 species in profiles 1, 2, 3, and 4, respectively). It fits well with the descending trend of HCH concentration in surface water due to dilution and attenuation processes. The monitoring campaign performed after the year of Wetland+® operation exhibited a noticeable higher number of diatom species in Ostrovský Creek profiles 1 and 2 (3 and 14 species in profiles 1 and 2, respectively) where the effect of HCH removal was the most significant. The numbers of diatom species at sites 3 and 4 were similar before and after the start of Wetland+® (30 and 35 species before and 28 and 30 species after in profiles 3 and 4, respectively). Monitoring of the Wetland+® prototype showed an increasing trend of diatom species along the flow path in correlation with the decreasing trend of HCH concentration.

In sum, phytobenthos acts as a suitable indicator of water quality and of impact of the operation of Wetland+® on water ecosystems.

KEYWORDS

hexachlorocyclohexane, treatment, wetland, phytobenthos, diatoms, diversity

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BENEFITS OF THE PRESENCE OF PLANTS IN WETLAND+® SYSTEM, TREATING HCH POLLUTED SITES

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ABSTRACT

Hexachlorocyclohexane (HCH) is an insecticide banned around the world, but it is still a worldwide problem since there are many legacy sites that are leaching polluted waters to the environment. The most common solution to limit the leaching has been confining the site to retain the pollutant, but the solution does not treat the source and no actual treatment results from the procedure. Pilot plant studies have shown the capacity of treatment wetlands to remove HCH, and as result a LIFE EU project, LIFEPOPWAT has financed the establishment of two sites, one in the Czech Republic and one in Poland as well as the performance of parallel studies to assess the capacity of planted system to treat the pollutant. Treatment wetlands take advantage of the combination of process through the intervention of water, media, biofilm and plants to remove pollutants.

The LIFEPOPWAT project has developed a wetland system (WETLAND+®), where the combination of planted anaerobic and anaerobic environment speed up the removal of HCHs. The systems are planted with selected

species of plants to improve the performance. The presence of plants in wetlands is known to contribute to treatment since they perform processes that speedup the removal process including: the transport of oxygen to the root zones, improving hydraulics in the reactors, while the roots can release a cocktail of low molecular carbon compounds (exudates) that benefit the removal of the pollutants. Additionally, the presence of plants increases the density of the biofilm community attached to roots and stems, which results in an increase biological activity and the presence of degrader microorganisms and therefore, increases the rate at which the pollutants are removed. Furthermore, plants can uptake, translocate the pollutants to the plant organs, metabolise, and store the compounds, and in case of further treatment, the management becomes easier that dealing with diffuse pollution. Another advantage of the plants in the system is the increase of biodiversity, since plants attract pollinators and increase the presence of fauna. The presence of plants in the system helps to integrate the sites to the landscape, resulting in acceptance from the local populations and can be used as a site for research, education and leisure.

The talk will present the results of the evaluation of the roll of plants and the contribution in the removal of HCH in one of the sites as well as a mesocosms study, where different plants were tested for the removal of HCH.

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GROUNDWATER HCH INDICATION VIA PHYTOSCREENING OF TREES

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ABSTRACT

The topic of this paper is the detection of HCH contamination in groundwater. The term phytoscreening can be used for pharmaceutical search for phytochemicals with potential medical use. However, this topic will not be covered, nor will the topic of using plants for HCH phytoremediation. Briefly, the paper will focus on an indirect and non-invasive alternative to reach groundwater level, which is the use of trees - HCH phytoscreening. Phytoscreening typically precedes drilling and indicates where groundwater survey probes need to be placed to fully confirm HCH plume delineation.

In this sense, the term “phytoscreening” was established by the work of Sorek et al in 2008 to indicate VOC contamination. Since then, more than 30 scientific papers have appeared describing the sampling methodology, data interpretation, and specific outcomes from tree studies at pilot sites. Looking closely, we see that the authors have studied the patterns of VOC uptake by plants, the distribution of VOCs in woody plants and its age/height/seasonal dependence, the applicability of phytoscreening to delineate the contamination plume, and the involvement of green analytical techniques (e.g., SPME).

In the case of HCH, the scientific literature and groundwater contamination investigations using phytoscreening are very limited. Some historical manuals even listed HCH as a pollutant unsuitable for phytoscreening. In fact, phytoscreening of trees for the purpose of indicating HCH in groundwater is a very viable approach. Our data from the growth chamber and from 2 pilot sites in the Czech Republic and Poland confirm that (i) trees uptake and phytoaccumulate HCH in their stem biomass, (ii) that HCH phytoscreening can be used to delineate contamination plumes, (iii) that different tree species and different cultivars differ in their physiological response to HCH exposure, that (iv) HCH phytoaccumulation is species-, age-, seasonal-, and height-dependent, that (v) SPME is a useful green technique for HCH analysis in woody biomass, and (vi) that birch sap monitoring has only limited applicability. All of these aspects of HCH phytoscreening will be demonstrated using data from sites with HCH contamination.

Acknowledgement: EC LIFE Programme within the framework of project “Innovative technology based on constructed wetlands for treatment of pesticide-contaminated waters (LIFEPOPWAT)“, registration number LIFE18 ENV/CZ/000374

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ASSESSMENT OF SOCIO-ECONOMIC IMPACT FOR WETLAND+®

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ABSTRACT

Sustainable remediation is the practice of demonstrating that the benefit of undertaking remediation is greater than its impact and that the optimum remediation solution is selected through the use of a balanced decision-making process. Assessing sustainable remediation is site and project specific, and is strongly multifactorial across a wide range of categories, which may or may not be readily quantifiable. The applied socio-economic survey framework is based on the 2020 SuRF-UK guidance (CL:AIRE 2020 A & B). The 15 broad categories of indicators, which revolve around three main elements of sustainability (environment, society, and economy) were established. The approach develops the guidelines set out in the 1987 Brundtland Report (UN 1987) and subsequent UN Sustainable Development Goals or SDGs (UN 2015). The chosen framework considered both input and output effects within the sustainability assessment. According to the methodology used, the socio-economic analysis was divided into 15 broad categories. In the initial assessment, out of a total of 73 criteria, 15 from the Environment category, 19 from Economic and 11 from Social were identified as relevant.

Figure 1 provides summaries of the sustainability assessment rankings. In this initial qualitative assessment Wetland+® outranked the use of conventional WWTP for most of the 15 general categories shown in Table 2, and where it did not outrank the ranking was the same. Adoption of WWTP outranked no intervention, so the general trend of sustainability is:

Wetland+ > WWTP > no intervention.

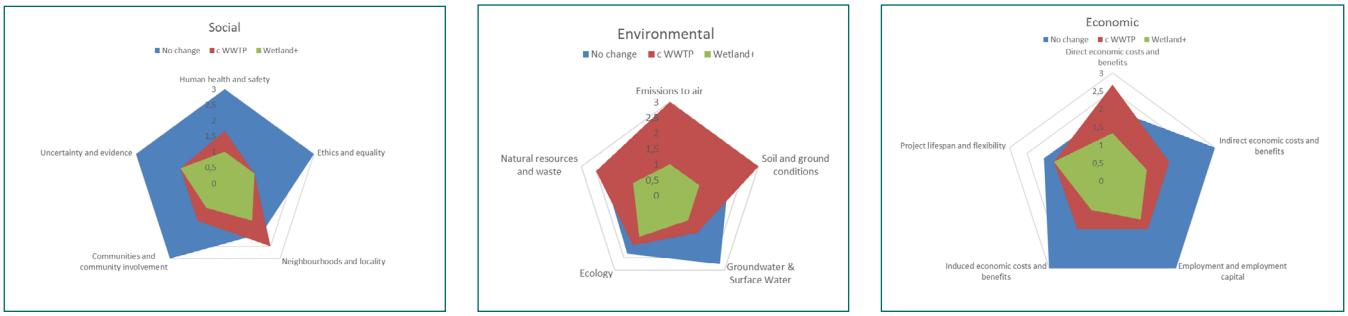

Figure 1: Sustainability assessment outcomes from Hajek (the initial assessment).

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PROTOCOLS OFFER TO THE CLIENTS FOR WETLAND+® REPLICATION

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ABSTRACT

For partners and clients interested in Wetland+® technology, iteratives service packages are proposed in order to go step-by-step from laboratory tests up to scale 1. Also, GO/NO GO are present along this iterative reflexion to check the relevance of Wetland+® techniques vs other techniques (like coagulation/precipitation, activated carbon) in order to propose the best solutions in terms of costs but also in terms of sustainability for the treatment of an effluent (resurgence, GW, surface water) impacted in HCH or pesticides.

The cost for CAPEX roughly depends on the compartments needed (anaerobic with permeable reactive barrier with ZVI and/or biosorption wetland / aerobic wetland) and the total surface necessary (directly dependent on flow rate and pollutant concentrations). OPEX is relative to operational monitoring that should be low as Wetland+® is a robust and rustic passive treatment.

Block 8.
HCH IN EUROPEAN UNION SESSION

INTRODUCTION HCH IN EU PROJECT

***Fokke, B.*[1,2]**
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ABSTRACT

The two objectives of the HCH in EU project were (1)obtain an overview of the legacy of Lindane and Technical HCH production in Europe (2) assist six site authorities to sustainably manage HCH-contaminated sites. The main project deliverables are an EU-wide inventory of sites that may be contaminated with HCH and Lindane, as well as consultancy services for authorities in relation to six HCH contaminated sites. Other deliverables are a report about the use and legacy of HCH in the EU, support in developing an EU-wide strategy for sustainably managing HCH-impacted sites and feedback on the selected remedial approach of the Vrakuňa site in Slovakia.

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INVENTORY RESULTS FOR GERMAN

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ABSTRACT

The inventory demonstrates that Germany has 80 sites for which handling of HCH/Lindane could be confirmed or where sufficient evidence existed for such actions. Another 23 sites were identified, where handling of HCH/Lindane could be confirmed or sufficient evidence existed, but which could not be located due to different reasons (e.g., lack of data). For 81 sites it was not possible to clarify whether these sites were relevant for this inventory (e.g., distinction between formulator and supplier). It can be assumed that the available results of the site research in Germany are not complete. Sites, for which certain data use restrictions apply, were not considered. Also, the main focus was on the use of HCH/Lindane as a pesticide. Due to the wide range of possible uses for this substance, focusing on a different area of application (e.g., wood preservatives, hygiene) may result in additional relevant sites and sub-sites (e.g., various waste deposit sites associated with a production site).

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THE GEOGRAPHIC INFORMATION MODEL

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ABSTRACT

One of the tasks of the HCH in EU project was to compile an inventory for sites that may have been potentially affected by HCH. The sites in this inventory include Lindane and HCH production and processing sites, waste deposits and landfills, storage facilities, and waste treatment plants. The inventory has been incorporated into a custom-made Geographic Information Model (GIM), which identifies sites that are known to have handled HCH and may thus have been impacted. For each EU member state, a report featuring a country-specific list of such sites was prepared. The 'HCH in EU' project has identified a total of 299 sites where HCH and Lindane were handled. 54 of these sites are expected to be high-risk sites, with significant potential impact on people and the environment. All consultancy deliverables are supplied on the EU website, together with the Geographic Information Model (GIM).

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ROAD MAP TO SUSTAINABLY MANAGE HCH CONTAMINATED SITES

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ABSTRACT

Based on the needs assessment an overview of what is needed to come to a complete sustainably managed (HCH-impacted) site is presented in a road map for the Sardas Landfill site and a road map for the O Porriño site in Spain. The activities of the Road Map are discussed through the four main aspects as discussed in the needs assessment and included actions that will be included in the Action Plan of the HCH in EU project and actions that could not be covered by this project:

1. What is needed to complete the CSM / to fully understand the contamination situation
2. When and how much funds are needed to enhance the sustainable management
3. What is needed to make decision makers aware of the situation and the necessity to act

SARDAS LANDFILL

This site is a waste deposit in a ravine next to the Gállego river. The waste includes industrial waste of lindane production and other chemical industries; such as solid and liquid waste of HCH, mercury, caustic soda, hypochlorite, dichromates, dithiocarbamates, solid urban waste, construction and demolition wastes, etc. The estimated quantities are 50,000 to 80,000 m^3 of solid waste of HCH isomers in the form of dust, and 3,000 m^3 in liquid form (DNAPL). In the 1980's, the Sardas landfill reached maximum capacity, with a waste volume above 400,000 m^3. Between 1985 and 1988 a road was built and its trajectory cut off the front of the landfill. Because of these works, approximately 50,000 m^3 of waste from the landfill was moved to the bottom of the site.

O PORRIÑO SITE

The O Porriño site concerns an extensive distribution of solid waste buried and disseminated throughout the Municipality of O Porriño. The buried solid waste has impacted the surface water and the groundwater. Through the surface and groundwater, the pollutants have spread throughout the entire basin of the Louro.

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GUIDELINES SC POP CONTAMINATED SITE MANAGEMENT

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ABSTRACT

The BAT & BEP Guidance for Management of POPs Contaminated Sites has been developed by the Expert Group on BAT & BEP under the Stockholm Convention, for use by parties and others seeking to implement sustainable and environmentally sound management of POPs contaminated sites. The guidance is structured into 10 Modules in a stepwise manner to allow the reader to build on their understanding of the approaches required to address POPs contaminated sites. Module 1 provides the background to POP contaminated sites. Module 2 is on the site assessment and the use of a Conceptual Site Model. Module 3 explains the rationale behind risk-informed decision making at contaminated sites and introduces the reader to the Tier 1, Tier 2 and Tier 3 risk assessment. Module 4 gives the principles and approaches for POPs Contaminated site Management and Remediation. Module 5 presents remediation technologies and techniques compiles information on technologies and techniques that are available to destroy POPs waste, treat contaminated soils, sediments, and solids and groundwater. Module 6 explains the technology Selection Tool for Remedial Options. Module 7 elaborates on the Stakeholder Engagement, Public and Worker Safety and Health. Module 8 is on how to get started providing information on the necessary Legislation, Policy, Inventory Development and Financing Remediation. Module 9 is a case study of a DDT remediation in Lâm Hoá site, Viet Nam.

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EU WIDE STRATEGY TO MANAGE HCH CONTAMINATED SITES

Vijgen, J.
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An outlined for a strategy to resolve the legacy of Lindane production in the EU is made. This outline is meant to serve as input for developing an EU-wide strategy to manage the 299 sites that are potentially impacted by HCH and Lindane. The outline sketches the steps that must be taken at EU, country and/or regional as well as site level to, once and for all, resolve problems concerning the legacy of historical Lindane production in the whole of the European Union.

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STATUS OF THE IMPLEMENTATION OF THE EU WIDE STRATEGY

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Presentation-response on email to stakeholders.

The responses, to a survey asking what follow-up actions are taken, based on the results of the HCH in EU project, will be presented.

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EUROPEAN COOPERATION TO TACKLE THE LEGACIES OF HEXACHLOROCYCLOHEXANE (HCH) AND LINDANE

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ABSTRACT

Hexachlorocyclohexane (HCH) waste isomers from lindane production are the largest single POPs legacy, with an estimated 4.8 to 7.4 million tonnes of disposed waste. A large part of this waste –1.8 to 3 million tonnes– was disposed in Europe, where many lindane producers were located. This short paper provides an overview of the project supported by the European Union (EU) to address this waste legacy and to implement the Stockholm Convention for the POP group of HCH (lindane/gamma-HCH, alpha-HCH and beta-HCH) with associated protection of soil, ecosystems and human health. We summarise the results of this EU financed project called the "HCH in EU project", which aimed to develop a systematic inventory of sites where HCH was handled and potentially resulted in contamination. The compiled information provides guidance for competent authorities to further develop their national inventory of potentially HCH contaminated site and to further develop a strategy to address this large POP legacy in future. The systematic inventory revealed that there were at least 299 sites where HCH was handled. These sites include 54 former production sites, 76 pesticide processing plants that used lindane, 59 uncontrolled HCH waste isomer deposits, 29 landfills with HCH waste, 34 former or current storage sites for stocks of obsolete pesticides including technical HCH and/or lindane, and 16 HCH sites with a POP treatment or disposal facility. Additionally, at 31 of these sites lindane/technical HCH was used in applications with significant risk of soil pollution, such as wood treatment. The number of sites in this latter category is likely higher and will need further assessment. In addition to this inventory, the "HCH in EU project" produced detailed country inventory reports, a guidance

document for how to find potentially HCH-impacted sites, and a strategy document for implementing the sustainable management of these sites EU-wide, with proposed actions at the EU, country, and site level. Furthermore, the project has facilitated information exchange and –together with other related EU projects– has led to sharing information and best practices among member states. The project also enhanced the formation of an informal network of authorities and other stakeholders working on the lindane/HCH waste legacy. This collaboration will facilitate a more systematic and better coordinated process to further assess, secure, and remediate the large HCH waste legacy and reduce and control lindane/HCH releases in the EU and possibly beyond. Such a coordinated effort and exchange of information for inventorying and managing contaminated sites might also be useful for other POPs such as PFOS/PFOA or dioxins.

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Block 9.
HCH CASES – LINDANE NETWORK AND OTHERS

LINDANET: EUROPEAN NETWORK OF LINDANE WASTE AFFECTED REGIONS WORKING TOGETHER TOWARDS A GREENER ENVIRONMENT

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[3]General Directorate of Environmental Quality and Climate Change, Xunta de Galicia, Spain;
[4]Regional Development Agency of South Bohemia, RERA a.s., Czech Republic;
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ABSTRACT

Lindane (γ-hexachlorocyclohexane or γ-HCH) was a pesticide widely produced during the second half of the 20th century around Europe and worldwide. Lindane production generated a huge amount of waste consisting of other HCH isomers and other organochlorinated compounds.

Lindane production and use has been prohibited in EU regulation from 2007, but lindane and its waste still constitutes a very important risk for the human health and European environment. An estimated 4,000,000 tons of HCH waste are present in Europe in at least 299 polluted sites (*HCH in EU project*).

LINDANET was a project of the Interreg Europe Programme that constituted the first network of regions affected by the HCH pollution committed to progress together towards the improvement of the HCH remediation solutions. With a budget of 1,3 M €, it started in August 2019 and finished in January 2023. The Interreg Europe Programme is addressed to policy makers with the purpose of improving public policies, in the case of LINDANET, related to the HCH waste management.

The consortium of regional bodies participating in the project was formed by the Government of Aragon (Spain, lead partner), Xunta de Galicia (Spain), the Regional Environmental Agency of South Bohemia (Czech Republic), the State Office for Contaminated Soils of Saxony-Anhalt (Germany), the Central Mining Institute (Poland), and the Zooprophylactic Institute of Lazio and Toscana (Italy).

The project was divided in two phases:

- Phase one, of five semesters duration, for the interchange of experiences and the interregional learning. Lessons learnt were used for the design of regional action plans whose aim was to improve a specific policy instrument.
- Phase two, of one-year duration, for the implementation and monitoring of the actions that each region had designed in one's action plan.

The regional stakeholder groups were involved and informed in both phases of the project.

A description of the results achieved during the project is presented in the current paper.

KEYWORDS

LINDANET, Interreg Europe, soil pollution, Lindane, hexachlorocyclohexane (HCH), POP

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HCHS IN BRAZIL – SOCIALIZING CHEMICAL RISKS AND SO ON...

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ABSTRACT

This work discusses the representations of the toxic risks of hexachlorocyclohexane, an active ingredient of many pesticides commonly used in Brazilian fields during the second half of XX century. Emphasis is placed on the practices that visibilized and invisibilized these risks, seeking to establish the actors that promoted them and the mechanisms they used. From the perspective of the Public Health System, we analyze the generation of ignorance and uncertainty related to this compound. Likewise, we examine the most prevalent rhetorical strategies used in print source to uncover the present situation of a well-known case of Environmental and People Contamination

the “Cidade dos Meninos Chemical Factory” in Duque de Caxias, Rio de Janeiro State, that produced HCHs for 5 year around 1955. To do so, we consulted several main primary sources like Academic Documents, like Master and Doctoral Thesis, besides Scientific Articles as well as Local Newspapers and media coverage on the Issue.

KEYWORDS

Obsolete pesticides, Contaminated Sites, Environmental (in)justice

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SPATIAL DISTRIBUTION OF HEXACHLOROCYCLOHEXANE ISOMERS IN OAK LEAVES AND TOPSOIL FROM O PORRIÑO (NW SPAIN)

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ABSTRACT

Topsoil (0-20 cm) and pedunculate oak leaves (*Quercus robur*) were collected from O Porriño (NW Galicia) to establish the current superficial contamination of hexachlorocyclohexane (HCH) in the territory. The concentrations of α-, β-, γ- and δ-HCH in soil samples were determined by accelerated solvent extraction, while in leaf samples by ultrasound-assisted extraction. No isomer was detected in 93% of the soil samples and 29% of the oak leaves collected. The total concentrations of SumHCH (sum of α-, β-, γ- and δ-HCH) in soils ranged from <0.09 to 27.50 mg kg^{-1}(dry weight) with a mean value of 0.86 mg kg^{-1} (SD = 4.30 mg kg^{-1}). The total concentrations of SumHCH in the oak leaves ranged from <0.04 to 2.79 mg kg^{-1}(d. w.) with a mean value of 0.33 mg kg^{-1} (SD = 0.49 mg kg^{-1}). The predominant isomer was α-HCH in soil samples, while in leaves it was γ-HCH followed by α-HCH. Trace levels of HCH were generally detected and high levels of HCH were only detected in the two matrices in a former dump site. Ratios of γ/α and α/β confirmed its historical use as a dump site. This dump site was surveyed 10 years ago and was therefore selected in this study to determine the evolution of the pollutant. Results indicated a drastic reduction of contamination (*e.g.* levels decreased from 353 mg kg^{-1} to 27.5 mg kg^{-1} in the soil at the most polluted site). Differences observed between soil and leaf samples reflect the capacity of *Q. robur* to accumulate HCH from the atmosphere and demonstrate its potential use as a biomonitor of atmospheric pollution. More research is needed to understand the behaviour of the pollutant in the plant-air-soil system and the influence of other factors.

KEYWORDS

Hexachlorocyclohexane, lindane, POPs, biomonitoring, *Quercus robur*

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CHARACTERIZATION AND MANAGEMENT OF LINDANE-CONTAINING WASTE AT AN ABANDONED LINDANE PRODUCTION FACILITY IN HUESCA PROVINCE (SPAIN). A SITE SPECIFIC PROTOCOL DESIGN FOR WASTE CONDITIONING AND HANDLING FOR EX SITU FINAL TREATMENT

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ABSTRACT

The remaining raw chemicals and uncontrolled waste after closure of Inquinosa, a lindane-production facility located in the municipality of Sabiñánigo (Huesca, Spain) in 1991 has caused a major concern regarding health and

safety conditions and potential environmental risk. Different action programs have been undertaken by the Regional Government of Aragón to ensure proper waste conditioning and handling for final treatment.

A fraction of these hazardous wastes was found scattered within the former plant boundaries. Therefore, in 2017 these uncontrolled wastes were encapsulated to prevent further dispersion and environmental risks. Some of the remaining buildings of the former plant with a better state of conservation were used as a temporary storage unit until transportation for final management was executed.

A process of waste repackaging from original 1-m^3 big bags to 60-liter capacity drums approved for hazardous waste was carried out on site for proper conditioning and to meet transportation standards. To accomplish this project, strict safety measures were mandatory to ensure safe working conditions and environmental protection.

The selected building for these operations was conditioned with a new concrete base coupled with a system for leachate collection, the construction of a negative pressure containment enclosure (softwall plastic bubble), and the installation of airline supplied respirators for the workers.

The lindane containing waste conditioning included a pH control to meet the acceptance criteria for final treatment. The pH measures were done in a zone prior to access the containment bubble, allowing the marking and segregation of those wastes with different pH.

As a result, a site-specific management protocol was developed for complex lindane containing waste types in order to guarantee maximum compliance with safety standards during handling, conditioning and transportation, as well as to meet the acceptance criteria at the facility for final treatment. Consecution of the waste reconditioning plan prioritized actions to prevent further environmental and human health impact, according to potential hazardousness of the waste in the current conditions of the site.

KEYWORDS

Lindane, repackaging, pH

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THE EXAMPLE OF UGINE-KUHLMANN HUNINGUE/F: THE REMEDIATION OF NOVARTIS AND THE QUESTION: DOES THE FRENCH INVENTORY FULLY COVER THE LINDANE WASTE OF THIS LINDANE FACTORY?

Forter, M.

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ABSTRACT

The French chemical company Ugine-Kuhlmann produced the insecticide lindane in Huningue/Haut-Rhin/F from the end of World War II until 1974. This resulted in about 100,000 tons of lindane waste, which the company management deposited on the factory site or mostly in gravel pits in the region. In addition, several thousand tons of gravel contaminated with lindane waste from the factory site ended up on dirt roads and in road beds in Switzerland and France.

In 1976, the factory was demolished. The Swiss chemical company Sandoz bought the factory site in Huningue/F, which was contaminated with large amounts of lindane waste. Sandoz built a wastewater treatment plant on it also for the chemical wastewater from its factories in Basel/CH.

Sandoz merged with Ciba-Geigy in 1996 to form Novartis.

Novartis demolished the wastewater treatment plant in 2012. After that, the pharmaceutical company, together with the French remediation company Sita Remediation, started to excavate the lindane waste on the site. Novartis describes everything that went wrong in the process in a surprisingly open and transparent way in a book that the pharmaceutical company published after the remediation ended in 2019. This comprises the first part of my presentation. The second part reviews the French HCH/Lindane inventory using the example of lindane waste from the same lindane factory, i.e. Ugine-Kuhlmann Huningue. Does the 2020 TAUW/CDM Smith and Sarga inventory cover all sites where lindane waste from Ugine Kuhlmann is located?

Dr. Martin Forter (59) is a geographer and communications scientist. He has been researching and investigating the production of lindane or lindane waste by Ugine-Kuhlmann in Huningue/F since 1990. He inventoried not only most of the waste dumps of this lindane factory, but also those of the Basel chemical companies Ciba SC (today

BASF), Lonza, Novartis and Syngenta (ChemChina) or their predecessor companies especially in the three countries of the Basel region.

Martin Forter is also the Executive Director of Ärztinnen und Ärzte für Umweltschutz/AefU-Médecins en faveur de l'Evironnement/MfE (Doctors for the Environment Switzerland) since 2011.

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POLLUTION BY PESTICIDES, LINDANE AND SIMILAR SUBSTANCES IN SLOVAKIA

Plch, J.
Ministry of the Environment, Slovakia

With the changes after 1989 in the agricultural sector (land restitution, price increase, reduction of intensification, legislative measures) there was a significant decrease in industrial fertilizers and pesticides consumed in agriculture.

As part of the improvement of the environment, a survey program of locations - industrial areas, where pesticide production was carried out, was launched. At the same time, a geological survey of environmental loads was carried out. In parallel with the aforementioned, a monitoring network was completed to monitor pollution by pesticides and their degradation products in groundwater. Currently, the number of facilities in Slovakia for monitoring pesticide substances is 156. The state of pollution can be considered reviewed.

At the same time, geological and geochemical mapping of pollution sources, which include industrial facilities, warehouses of old agrochemicals and the like, was carried out. At the same time, mathematical and prognostic models of the spread of pollution were implemented at selected sources and in locations where increased environmental protection is needed.

So there are well-known locations with heavy pollution and endangered places of polluted groundwater. Among the most threatened places is Bratislava, where before 1989 there was a massive chemical production, landfilling of waste products from the production of pesticides. Intensive agricultural activity also contributed to the pollution. At the same time, it is a place with a highly permeable gravel bed, where pollution can spread very quickly.

It is possible to state that solving the mentioned problems is one of the priorities of the Department of the Environment.

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REMOVAL OF TECHNICAL AND ECONOMIC BARRIERS TO INITIATING THE CLEAN-UP ACTIVITIES FOR ALPHA-HCH, BETA-HCH AND LINDANE CONTAMINATED SITES AT OHIS

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ABSTRACT

The HCH waste isomers generated during the lindane production conducted in the period 1964-77 were dumped in two locations within the production facility of Organic Chemical Plant (OHIS), on so-called big dump (alpha-beta) and small dump (delta). In the frames of the Community Assistance for Reconstruction, Development and Stabilisation (CARDS) 2007 project for development of the National Waste Management Plan with Feasibility Studies, 16 Industrial Contaminated Sites - "hotspots" were identified and ranked according to environmental indicators. The OHIS Chemical Industry site was ranked as number one priority for remediation. In 2015 the Ministry of Environment and Physical Planning (MoEPP) of the Republic of Macedonia, in cooperation with United Nations Industrial Development Organization (UNIDO) as an implementing agency started with the implementation of a project "Removal of Technical and Economic Barriers to Initiating the Clean-up Activities for Alpha-HCH, Beta-HCH and Lindane Contaminated Sites at OHIS".

The project was funded by the GEF with USD 3.1 million and committed co-finance was USD 12,450,000. The project has been designed to address a variety of barriers (legal, institutional, technical, financial) in order to ensure

its successful execution and achievement of project objectives, with the final aim to have the OHIS contaminated site free from HCH waste and other hazardous contaminants for future industrial use. Achievements of the project:

- Rulebooks on contaminated sites management developed;
- Guidelines, tools and procedures for contaminated site management prepared; relevant stakeholders trained on contaminated site management;
- Technical personnel from two laboratories trained on POPs monitoring issues;
- Detailed site investigation conducted, resulting in the estimated quantities of pure HCH waste of 41,000 tons in the “big” dump and 1,600 tons in the “small” dump and of 10,000 tons of HCH contaminated soil in the “big” dump and 5,000 tons in the “small” dump;
- Risk assessment analysis prepared;
- Cost-benefit analysis prepared; public awareness campaign conducted;
- Site remediation/clean up mechanism established, resulting in the excavation, packing, exportation and disposal of 477 tons of HCH waste and 127 tons of HCH contaminated soil;
- Supervision of the site remediation activities established, evaluating the contractor’s clean-up performances;
- Environmental monitoring system/programme established for monitoring the level of contaminants in the environmental media (air, soil and water) and the humans (blood serum);
- Financial mechanism to sustain the continuation of the remediation activities developed, by establishing a fund, called Multi-Partner Environmental Fund with the aim to mobilize funds from different donors to finalize the clean-up of the OHIS site.

KEYWORDS

HCH, dumpsite, site characterization, risk assessment, remediation, monitoring

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REMOVAL OF TECHNICAL AND ECONOMIC BARRIERS TO INITIATING THE CLEAN-UP ACTIVITIES FOR ALPHA-HCH, BETA-HCH AND LINDANE CONTAMINATED SITES AT OHIS

Avramikos, I., Tsaimos, G., Prekas, K.

POLYECO SA, Attica, Greece

ABSTRACT

In 2020, Polyeco SA was awarded through international tendering the UNIDO funded project for the remediation of a small dump at OHIS area in North Macedonia. The 1st LOT comprised the excavation and identification of 127 t contaminated soil and of 477 t HCH waste in OHIS plant, Skopje, North Macedonia. More than 6.000 t of HCH and HCH associated waste are estimated to have be disposed in the area as a result of OHIS former industrial activities (production of organochlorine pesticides) and the successful remediation of the small dump area will form a good example for extension of the remediation activities to the bigger dump. The remediation area is located in a nearby populated area and specific environmental mitigation and monitoring activities took place to minimise the impact during the works. The scope of services included the erection of a 2500 m^2 environmental enclosure, installation of specialized equipment (Negative Pressure Units), construction of water collection systems, excavation, segregation and packing of HCH waste into UN packaging and HCH contaminated soil into specialized BK2 bulk containers along with their transportation and final disposal to EU thermal treatment facilities.

The objective of this article and respective presentation is to share the experience gathered during the execution of the project, the obstacles and contingencies that occurred, and the flexibility that Polyeco showed in order to provide prompt solutions. Covid-19 pandemic restrictions, the actual erection and construction of the environmental enclosure of such magnitude, the identification and segregation of additional contaminants hindering the treatment options are some of the challenging tasks that will be presented for consideration in the implementation of future OPs management projects.

KEYWORDS

Obsolete Pesticides, Lindane, HCH, OHIS, POPs, Basel Convention, safeguarding.

Block 10.
LIFECYCLE MANAGEMENT OF PESTICIDES AND DISPOSAL IN CENTRAL ASIA COUNTRIES AND TÜRKIYE

ARE PESTICIDES OBSOLETE?

Davis, M.
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ABSTRACT

The mountains of HCH isomers and other obsolete pesticide stockpiles around the world that demand huge financial, technical and natural resources to manage safely, are one of several symptoms of a heavy reliance on pesticides for agricultural production and public health protection that has evolved over the past seven decades. While pesticide use globally has consistently increased over this period, estimates of crop losses to pests and diseases have not gone down and yields are plateauing. Understanding of the impacts of pesticides on health and the environment is evolving and shows significant damage in areas previously not well understood such as the soil microbiome and global suicides. Removing synthetic chemical pesticide has been shown to be feasible without additional crop losses where farmers are provided with viable alternatives. The trajectory for policy and regulation, private sector investment and agricultural advisory services should be towards the elimination of synthetic chemical pesticides and their replacement with sustainable alternatives that benefit human health, environmental protection, biodiversity and food safety.

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IN SITU IMPLEMENTATION OF TRIALS ON MICROBIOLOGICAL REMEDIATION OF POPS CONTAMINATED SOILS IN KYRGYZSTAN

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ABSTRACT

This study aimed to develop a bioaugmentation and bioremediation technology that can be used in situ at contaminated sites. For the bioaugmentation, three bacterial species were used: *Stenotrophomonas sp. (*Ps-B strain)*, Lysinobacillus fusiformis (*SA-4 strain) and *Esherihia cloacae* (SB-2 strain).

A former pesticide store in Chem–Korgon village (N 42049'23.9" and E 75031'49.8") in Kyrgyzstan was a suitable place for testing the efficacy of the bioremediation technology.

Three conditions were tested: application of fertile soil and bioproduct, application of fertile soil and no bioproduct (Control 1) and no fertile soil and no bioproduct (Control 2).

The most effective condition, in terms of pesticide degradation, was the application of fertile soil and the bioproduct. The degradation using this condition was 1.5 to 2 times higher than when only fertile soil was added (and no bioproduct) and five times higher than when no fertile soil and no bioproduct were added. Based on the results, we could state that the degradation of pesticides by microbes depends not only on the bacterial enzyme system but also on the conditions like temperature, pH of the soil, moisture contents and nutrients.

Further research will optimize the degradation conditions in a variety of soil types, and ex-situ conditions with high concentrations of pesticides, using the bacterial strains selected for this study.

KEYWORDS

Obsolete pesticides, bioaugmentation, bioremediation in situ, biodegrading bacteria, degradation conditions

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PHYTOREMEDIATION OF POPS-CONTAMINATED SOILS: SOLUTIONS AND DEVELOPMENT POTENTIAL IN KAZAKHSTAN

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Organochlorine pesticides, especially those belonging to persistent organic pollutants, are causing rising concern. Environmental monitoring investigations identify polluted sites regularly, limiting their utilisation. Kazakhstan is facing increasing problems of soil pollution caused by unutilised obsolete pesticides. In 2012, 1500 tons of obsolete pesticides and their mixtures across the country along with 602 pesticide warehouses were recorded whereas 64 out of 602 are located in the Almaty region. For recovering soils damaged by the aforementioned substances, phytoremediation has great potential. Remediation of such sites is a crucial step in preventing the damaging effects of contaminants on the environment and human health. Since existing technologies are exceedingly energy-intensive and need a significant financial commitment, phytoremediation is a real alternative interacting harmoniously with the surrounding environment. This technology relies on plants to allocate, degrade, immobilize, and uptake toxic compounds from soil. However, in spite of the obvious benefits, phytoremediation has significant limits such as a lengthy remediation duration, climatic differences, and the use of non-native species that might lead to a biodiversity violation.

The current study aimed to assess the phytoremediation potential of *Miscanthus sp*. concerning organochlorine pesticides, as intensive agricultural practices, notably disposal and former storage facilities of obsolete pesticides in the 1960s, have been documented to damage the Kazakhstan environment. The soil was collected at the former pesticide storage facility in Kyzylkairat, Almaty region, Kazakhstan. The analysis showed the presence of 24 OCPs in the research soil and concentrations of chlorobenzilate, DDT, 2.4-DDD, 4.4-DDD, endrin, and heptachlor significantly exceeded (up to 100 times) the permitted levels for those substances established by Kazakh legislation. Despite the high concentrations of OCPs in the soil and significant differences in the agrochemical parameters of the polluted and controlled soils, *Miscanthus* sp. showed minimal changes in growth in the polluted soil (95% of the control), the dry weight of aboveground biomass decreased by 23%. The results of chemical analysis illustrated that only ten (α-HCH, β-HCH, γ-HCH, 2.4-DDD, 4.4-DDE, 4.4-DDD, 4.4-DDT, aldrin, dieldrin, and endrin) out of 24 OCPs detected in the historically contaminated soil were presented in *Miscanthus* sp. tissues. Optimising the growth conditions of the second-generation crops *Miscanthus* sp. with activated carbon showed that cultivating plants on pesticide-contaminated soils produced comparatively clean biomass for conversion into bioproducts.

Thus, the second-generation crop *Miscanthus* sp. as a novel phyto plant can be used for remediation of the pesticide-contaminated soil. Plants acquired a physiological resistance mechanism during adaptation to POP-pesticides, i.e., the accumulation and migration of POP-pesticides in the “soil-root-aboveground biomass” system via phytostabilization and phytoextraction processes.

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AWARENESS RAISING WORK IN MINI-LANDFILL AREAS IN TAJIKISTAN, PLANNING FOR REMEDIATION OF VILLAGE #1 MINI-LANDFILL

Ulugov, U.
NGO “Peshsaf”, Dushanbe, Tajikistan

ABSTRACT

Tajikistan has to deal with a legacy of about 200 so-called mini-landfills. Many of these highly contaminated sites are today located within populated areas. A series of awareness raising seminars was organised in 2022 in affected communities, showing the need for further such meetings. In parallel, detailed site assessment and planning for the remediation in 2023 of one of the high-risk mini-landfills in Village #1 has been completed.

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EMPTY CONTAINER MANAGEMENT

Efimkin, A.
FAO, International Consultant on empty pesticides packaging management

ABSTRACT

Pesticide containers are mostly made of high-quality plastic. Thus, there is a risk that, once they are empty, they are not disposed of properly but reused for various purposes including storage of food. Many countries have, therefore, introduced Container Management Systems (CMS). An overview on the efforts to introduce CMS in the Central Asia region will be provided.

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REDUCTION OF PESTICIDES USE

Keresztes, Z.
FAO, Specialist on IPM and Climate Resilient Agricultural Practices

ABSTRACT

So called Highly Hazardous Pesticides (HHP) pose above-average risks to farmers and food safety. An assessment of the pesticide registration lists of the project countries showed that all of them still have a number of HHPs permitted for use. To allow phase-out of HHPs, the project is promoting various types of agriculture relying on reduced use of pesticides. E.g. in apple production in Türkiye, pesticide use against codling moth could be reduced on average by 70 % by the use of pheromone traps. These efforts are key to reaching the global goal of reducing by half both excess nutrients and the overall risk posed by pesticides and highly hazardous chemicals pesticide application (Biodiversity Convention, December 2022).

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Block 11.
NEW APPROACHES TO TESTING OF CHEMICALS BASED ON OMICS AND EPIDEMIOLOGY: EXAMPLE DEVELOPMENTAL NEUROTOXICITY

DEVELOPMENT OF APPROACHES TO REMOVE TOXIC SUBSTANCES FROM THE ENVIRONMENT

Vijgen, J.
IHPA, Holte, Denmark

ABSTRACT

Photographical journey starting from the situation in the 1980s onwards on the problems of HCH in the Netherlands from scratch confronting huge regional problems with people living in houses in HCH landfills and a famous farmer with dying cows and being accused from not feeding their cows and being brought to court. But nobody wanted to know that these cows were grazing for years on highly contaminated fields and farmers lost their property all leading finally to huge clean-up for more than 15 years.

Another pictorial travel to Central and Eastern Europe and Central Asia, where in Western Europe unknown obsolete pesticide stockpiles were all over the countries as a consequence of the collapse of the Former Soviet Union. Inventories were organized mainly by FAO, where the experiences made in Africa were used to start to get first impression of the huge number of stockpiles in the region. The many pictures show old sheds and stores with cows running around right through the obsolete pesticides and children playing in villages in contaminated DDT. The process of solutions, starting with inventories, take years and slowly with mainly help of The GEF and UN agencies part by part slowly move forward but still can take decades as project often deal with hundred of tons or sometimes a couple of thousand tons in areas where are still tens and hundreds of thousands of tons present

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CONCEPT: EPIDEMIOLOGY- AND OMICS-BASED DEVELOPMENT OF A TEST BATTERY FOR DEVELOPMENTAL NEUROTOXICITY INDUCED BY ENDOCRINE DISRUPTION

Rüegg, J.
Environmental Toxicology, Uppsala University, Sweden

Clear evidence supports associations between exposure to endocrine disrupting chemical (EDC) and impaired neurodevelopment. Yet, current hazard assessment of EDCs does not address developmental neurotoxicity. This is due to lack of scientific knowledge on how endocrine disruption is linked to developmental neurotoxicity (DNT). Thus, there is an urgent need for novel testing and screening tools to address endocrine disruption (ED-)induced DNT, based on new scientific knowledge.

The ENDpoiNTs[1] project is designed to address the scientific and regulatory gaps with regards to ED-induced DNT. ENDpoiNTs is a H2020 research and innovation action involving 16 participants in Europe, USA and Australia. It integrates expertise in ED and DNT and combines state-of-the-art *in silico* and *in vitro* tools, innovative experimental designs and technologies, and advanced biostatistics on human epidemiological and biomonitoring data. This enables the ENDpoiNTs consortium to generate the necessary scientific insights on the correlative and causal links between ED and DNT, and to develop *in silico* and *in vitro* tools for chemical screening as well as novel OMICs endpoints for existing animal-based test guidelines.

In this first part, I will present the concept on which ENDpoiNTs is built on, namely the interaction between epidemiology and experimental toxicology to link changes in OMICs signatures and cellular key events to human relevant exposures and health outcomes.

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1. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 825759

GLOBAL EFFECTS OF POLLUTANTS AND OTHER RISK FACTORS ON INVERTEBRATE FAUNA

Cardoso, P.
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ABSTRACT

Biodiversity is eroding at an increasing pace, with current species extinction rates being up to 1000x higher than background rates. The causes for these are multiple, from habitat loss, degradation, and fragmentation, use of polluting and harmful substances, the spread of invasive species, global climate change, direct overexploitation, and co-extinction of species dependent on other species. The relative importance of each is however taxon- and context-dependent.

Insects and other invertebrates constitute the vast majority of species at any spatial scale, from small habitat patches to the global level. In agricultural areas they provide fundamental ecosystem services, including pollination, soil formation, nutrient cycling, and pest control. There has been a recent interest in their fate, as recent research suggested alarming rates of species extinctions and population reductions across the world. The causes for such are however less clear. Some authors suggest that pollution, including pesticides, herbicides and others, are causing most of these effects on invertebrates.

In this talk I will review what is known at a global scale, how pollutants are affecting communities in multiple settings, and how much still must be done to cover our knowledge gaps. I will finally cover the importance of dialogue between interested parties, which are often in conflict but whose cooperation is essential for averting future species extinctions and population declines, with consequences on our own well-being.

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EPIDEMIOLOGY IN CHILDREN AS A BASIS FOR TEST DEVELOPMENT

Bornehag, C.-G.
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ABSTRACT

Humans are constantly exposed to complicated mixtures of chemicals with suspected or proven endocrine-disrupting properties. Prior epidemiology literature also demonstrates that prenatal exposure to numerous of such EDCs may adversely influence neurodevelopment in children such as cognition and behavioral outcomes. In order to identify EDCs to be used in the ENDpoiNTs project, we used the SELMA study, a Swedish pregnancy cohort following around 2,000 families from early pregnancy over birth and up in puberty age. A mixture of 26 EDCs was analyzed in maternal urine and serum during the first trimester, neurodevelopmental outcomes were measured in children at 2.5 and 7 years of age, and data for co-factors were collected by the use of questionnaires and national registers. To assess the association of the EDC mixture on neurodevelopmental outcomes in children and identify the chemicals of concern in that mixture, we used Weighted Quantile Sum (WQS) regression. Briefly, WQS index is regressed on the outcome in a multivariable linear model providing an overall mixture effect estimate. Weights are expressed as percentages that sum to one and indicate the relative strength of each compound within the mixture. In this part, we will present epidemiological results from the SELMA study, i.e., chemicals of concern for neurodevelopmental outcomes in children, to be used in the ENDpoiNTs project.

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USE OF COMPARATIVE TRANSCRIPTOMICS FOR TEST DEVELOPMENT

Lichtensteiger, W.
GREEN Tox, Zurich, Switzerland

ABSTRACT

Interactions of endocrine disrupting chemicals with brain development can impair cognitive, emotional, and social behaviors, as shown by human epidemiology and experiments in animal models. Genome-wide analysis of

effects of chemicals on gene expression in developing brain of rodents (rats) allows to identify genes with particular roles in developing processes and signaling pathways that are targeted by chemicals. In animal models, the effect of chemicals on molecular processes in developing brain can further be related to behavior of adult offspring and molecular deficits in their brains, as evidence of adversity. The information can be used in the development of new in vitro models for the assessment of chemical risks for brain development, and to better link test systems with adverse effects in humans as well as wildlife.

In the context of the ENDpoiNTs project, we are investigating effects of 6 chemicals out of the chemical mixture identified in children of the SELMA study, on brain development in a rat model. Bisphenol F (plastic monomer), butylbenzylphthalate (plasticizer), 1,2-Cyclohexane dicarboxylic acid diisononyl ester (DINCH, phthalate replacement), perfluorooctanesulfonic acid (fluorosurfactant), permethrin (pesticide), and triphenylphosphate (flame retardant) have been administered to parent (F0) female rats in the feed from premating through mating and pregnancy until end of lactation. Transcriptomic, epigenomic, and metabolomic analyses are performed in developing hippocampus of their offspring (postnatal day 6). Adult offspring are studied for hippocampus-dependent (memory) and other behaviors and transcriptomics in hippocampus. Examples of chemical-specific gene expression patterns in developing hippocampus with possible links to adverse behavioral outcome will be discussed in relation to their use in test development.

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CONTRIBUTION OF EPIGENETICS TO TEST DEVELOPMENT

Rüegg, J.
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ABSTRACT

Experimental studies have shown that early life (pre- and early postnatal) exposure to EDCs can induce epigenetic changes that might underlie long-lasting adverse effects of these chemicals in one or over several generations. Epigenetic marks are molecular modifications that regulate temporal and spatial patterns of gene activity and are propagated across generations of cells or organisms, independent of changes in the underlying DNA. They play a critical role in cell differentiation and tissue organisation during development, not least of the brain. Due to its heritable nature, the epigenome is less transient and less tissue specific than other OMICs layers. Thus, epigenetic changes could be highly valuable markers to predict chemical-induced disease risk. However, there is still a lack of conclusive links between exposure, epigenetic changes, and adversity in humans.

In this part, I will present first results on epigenomic patterns indicative for ED-induced DNT, and illustrate how we can link such findings back to human data in order to establish epigenomic markers for exposure-induced adverse outcomes of human relevance.

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ROLE OF METABOLOMICS IN TEST DEVELOPMENT

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ABSTRACT

Exposure to endocrine-disrupting chemicals (EDCs) in humans during pregnancy and early stages of life can impair normal brain development and reproductive function patterns, leading to severe pathologies later in life. We study the molecular mechanism of endocrine disruption linked to developmental neurotoxicity (ED-linked DNT) using a metabolomics approach. Metabolomics studies endogenous small molecules, such as steroid hormones or neurotransmitters, in tissues or cells. We study which molecular pathways are affected by EDCs in in vitro and in vivo models. This information is of great significance for deeper understanding the relationship between affected endocrine systems and developmental neurotoxicity of EDCs. We, therefore, applied targeted steroid and thyroid hormones analysis to map the hormonal endpoints mostly influenced by the exposure to six EDCs, namely bisphenol F (BPF), permethrin (PMT), butyl benzyl phthalate (BBzP), triphenyl phosphate (TPHP), perfluorooctane sulfonic acid (PFOS), and 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) in neonatal rats. Hormone levels measurements will be primarily useful for in vivo mechanistic evaluation of EDCs' mechanism

of action and for assessing neuro-endocrine toxicity EDCs mediated at early stages of life, but also at which exposure levels effects occur.

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BRAZILIAN PEOPLE STILL UNDER INCREASED RISK OF CANCER DEVELOPMENT DUE TO HEXACHLOROCYCLOHEXANE INHALATION EXPOSURE

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ABSTRACT

Organochlorine pesticides (OCPs) have been restricted in most countries worldwide for being toxic, persistent, bioaccumulative and prone to long-range transport. In Brazil, OCPs were produced and used in industrial scales for both agricultural and public health purposes for several years, but most of them were restricted in the late 1980's and 1990's. Nevertheless, their environmental occurrence due to secondary sources still plays a key role on the environmental contamination and human health in the country. Therefore, we aimed to investigate the occurrence of some OCPs in outdoor air of urban sites from two major regions of southeast Brazil known to be impacted by industrial irregular dumpings of hazardous chemicals, such as OCPs. Inhalation cancer risk (ICR) assessments were performed following measurements of OCP concentrations in ambient air during winter and summer seasons. Ambient air was mainly affected by Σ-HCH (median = 340 pg m−3) and Σ-DDT (median = 233 pg m−3), the only two OCPs registered for public health purposes (fight insect-borne diseases) in Brazil. OCP concentrations were higher in summer than in winter and were associated with known secondary sources, such as industrial dumping sites. Both deterministic and probabilistic assessments indicated an increased risk of hepatic cancer for people living in the studied regions. Infants and toddlers (0 < 2 y) were exposed to the highest ICRs compared to other age groups. More studies covering other exposure pathways, such as ingestion and dermic uptake, are needed for a more comprehensive risk assessment. Moreover, those people are exposed to several OCPs and other hazardous chemicals that may have synergistic effects on human health. Finally, we reinforce a need to review the human inhalation exposure to OCPs and their associated risk in other impacted areas worldwide, especially where high levels of OCPs are still found.

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Block 12.
EMERGING POLLUTANTS. PFAS SESSION

PFAS CONTAMINATED SITES – A PERSONAL JOURNEY AND SOME LESSONS LEARNED

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ABSTRACT

One of the first large PFAS contaminated sites in Europe was discovered 2006 in North Rhine Westphalia/ Germany, where the drinking water of several million citizens had been impacted by PFOA and other PFAS.[1] The source of the PFAS was contaminated sludge from Belgium, imported via Netherlands by a small German company and given to farmers as "soil improver" dozens of agricultural areas.[1] Similarly, at one of the first discovered PFAS contaminated city in the United States (US), surface and groundwater were found contaminated in the early 2000, with releases from production and from landfills of production waste.[2] Based on these and further experiences of large contaminated sites from PFAS production, associated landfilling of PFAS waste and mismanagement of PFAS contaminated sludge causing all contamination of land and water resources, recommendations for risk reduction measures of PFOS and related compounds were developed in the frame of the Stockholm Convention when PFOS and related compounds where listed as first fluorinated POPs in 2009 for global action.[3]

Further assessment by the scientific community in the following years documented the huge ecological and health risks of the several thousand PFAS substances and consequently scientists published in 2014 the Madrid Statement[4] calling on policy makers, the industry and scientists for phasing out PFAS in any non-essential uses.

Meanwhile systematic drinking water monitoring or compilation of drinking water data in some countries such as the US[5] and China[6] have revealed that several hundred millions people are at or above drinking water limits considering the tolerable daily intake established by the European Food Safety Authority in 2020[7] calling for global assessment and action.

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PFAS IN SOIL AND GROUNDWATER – PROGRESS AND COMPREHENSIVE CHALLENGES IN GERMANY

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ABSTRACT

The substance group of PFAS poses challenges for the protection of the environment and also for their regulation. The talk focuses on the current knowledge, management and policy issues and progress regarding PFAS in soil and groundwater in Germany and in Europe.

With regard to PFAS levels in soils in Germany, the greatest attention is paid first to groundwater protection. In 2017, so-called insignificance thresholds values were derived for PFAS in groundwater. The insignificance threshold values for PFAS are therefore based throughout on human toxicological impacts and on the provisions of the German Drinking Water Ordinance. In view of the solubility of many PFAS and their associated relevance to the soil-groundwater pathway, the insignificance threshold values are directly connected to the values applied to classify soil material. The 2021 revision of the German Federal Soil Protection and Contaminated Sites Ordinance includes the insignificance threshold values as trigger values for the soil-groundwater pathway. Moreover, in Germany some large areas of agricultural land were found, polluted with high PFAS. Authorities implemented a so-called pre-harvest monitoring to make sure that highly contaminated crops were not put on the market. Until today a lot of research was done to find out which plants easily take up PFAS and which crops are suitable to be grown on polluted land.

A strategy change is necessary in order to elaborate more promising approaches through improved soil monitoring and more data. PFAS-background levels in soil will be used to derive further measures to assess PFAS levels in soil and groundwater. Until the implementation of legally binding values and their verified derivation a German guideline for PFAS assessment provides currently available media-related assessment bases and criteria.

European chemical regulation is controlled via REACH. Some PFAS the manufacture, use, and import are restricted with derogations. However, still a number of uses are allowed, emissions of PFAS into the environment still occur or are caused by contaminated sites. European Environmental administrations are lacking legal binding values and regulations for PFAS and in particular for soil. On the other hand, the thresholds for PFAS in drinking water and food are at such a low level, that environmental concentrations are often already above those levels. The best way forward seems to be a PFAS group restriction connected with strict regulation of industrial emissions for the remaining uses. Otherwise, gaps between the development and release of new chemical substances and mixtures and successful approaches to protecting environmental media like soils and groundwater cannot be narrowed. The European Green Deal the EU has set an ambitious sustainability plan. PFAS have been incorporated into a specific action plan for a Zero Pollution Ambition for a future of a non-toxic environment.

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INVESTIGATIVE SOIL AND WATER ANALYSIS AT AN OUTSTANDING LARGE-SCALE CONTAMINATED SITE: HOW NOVEL APPROACHES CAN HELP TO SOLVE THE PFAS PUZZLE

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The sheer number (estimated ≈ 5000) of existing poly- and perfluorinated substances (PFASs) the application of target analysis by liquid-chromatography-tandem mass spectrometry to samples from PFAS contaminated sites is limited, predominantly due to the lack of available analytical standards. Novel analytical approaches have been developed within the past decade, aiming at an integral assessment of PFASs with the ambitious goal to measure “total PFAS”.

At the example of the region Rastatt/Baden-Baden in southwest Germany, where a large scale contamination of agricultural soil (>1200 ha) and groundwater exists, the subsequently combined application of analytical tools is demonstrated. The contamination was caused predominantly by soil amendment of agricultural land with compost mixed with paper-fiber biosolids. Since the first findings about a decade ago, proceedings have been achieved in the development and application of novel trace-analytical methods for PFASs in soil and groundwater. The innovations comprise the extension of target analysis to additional active ingredients of grease-proofing chemicals for food-contact materials. These are precursors that can degrade in soil to perfluoroalkyl acids (PFAAs) as persistent and mobile final products, and leach into groundwater. Another useful tool is the oxidative digestion of unknown/not analyzable precursors to detectable PFAAs in the total oxidizable precursor (TOP) assay. Fluorine specific sum parameters, such as adsorbable organic fluorine (AOF) for water samples and extractable organic fluorine (EOF) for soil samples also complete the picture. Extraction methods for soil play a key role. By comparison of extractable PFAS/organofluorine in soils with CF_2-/CF_3-group specific organofluorine directly measured by ^{19}F nuclear magnetic resonance (NMR) spectrometry >80% of PFAS-related organofluorine turned out to originate from yet inaccessible, non-extractable residues (NER).

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THE BELGIAN 3M CASE FROM A HEALTH PERSPECTIVE

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ABSTRACT

Since 1970, the 3M plant has produced PFAS in Zwijndrecht (Belgium), in the neighbourhood of the Antwerp harbour. In 2002, the production of C8 PFAS chemicals was voluntarily stopped by the company, while the production of short chain PFAS continued. During soil excavations to build a tunnel under the river Scheldt, soil near the 3M site was discovered to be highly contaminated with PFAS. This raised awareness of local residents and action groups. In response, samples of soil, groundwater, locally grown vegetables and chicken eggs were analysed. PFAS were also measured in serum samples of about 800 residents living within 3km of the 3M site. Results showed that living closer to the 3M plant and consuming more home-grown products were risk factors for increased serum levels of mainly PFOS. Some individuals had high serum levels (P95 of linear and branched PFOS up to 145 µg/L serum). The health concerns and lack of knowledge and transparency on the current PFAS emissions opted the authorities to take immediate action. The 3M company had to stop the production process of PFAS. The infrastructure works were halted. The residents received targeted advice to limit further exposure to PFAS. A coordinator was appointed to bring the stakeholders together and streamline further research, policy actions and communication. Advisory expert groups were installed. A parliamentary inquiry commission was established to find out what went wrong, who was responsible and to deduce lessons learned and propose solutions. In 2022, an agreement was obtained between the Ministry of Environment and the 3M company about financial compensation and remediation of the area.

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PFAS POLICY FOR SOIL AND GROUNDWATER IN FLANDERS (BELGIUM)

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ABSTRACT

In Flanders, standards were published in the spring of 2021 for PFAS for soil and groundwater. During the same period, measurements in a residential area near a 3M site in Antwerp (Zwijndrecht) found elevated PFAS levels in the soil. This was the beginning of a PFAS crisis, which meant that these forever chemicals dominated the news and the political world in Flanders for several months. The experiences and the knowledge gained are explained in the presentation.

A large number of locations in Flanders were flagged for further investigation on PFAS. Typically, the most worrying of these are industrial sites where PFAS is/was produced and used, as well as the training grounds of fire departments and sites of historical fire incidents where extinguishing foams containing PFAS have been used.

The OVAM started a campaign to map and investigate the locations with suspected PFAS contamination. From the many studies on PFAS and the ongoing social debate, it became clear that the existing Flemish standards frameworks must be tightened.

Several gaps in knowledge remain in order to arrive at a conclusively human risk assessment framework: transfer from soil to crops/eggs, contribution of inhalation, uncertainty on measured values at very low concentrations, mixture toxicity. The background exposure through food already leads to the threshold value being exceeded. The experiences lead to a tightening of the action framework for soil and groundwater.

In Flanders, a great deal of attention and effort went into measuring and mapping PFAS contamination in the past year. This went hand in hand with the gathering of new knowledge about the risks and spread of PFAS. The presenter brings the insights that these experiences have yielded.

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THE CRITICAL ROLE OF CHEMICAL REFERENCE STANDARDS IN THE RISK GOVERNANCE OF CHEMICALS

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ABSTRACT

Access to pure reference standards for chemicals is key to generating the hazard and exposure data for risk assessment, and to enforce and monitor for the effectiveness of legislation. A recent case where the producer and sole vendor of C604, a newer type of PFAS, obstructed unlimited access to this chemical for scientific purposes illustrates the need for scientists to have access to reference standards for conducting scientific studies. In this presentation I will outline (i) that information used for regulatory purposes relies heavily on the access to reference standards to generate data for determination of human and environmental hazards, occurrences, exposure/uptake, fate and (ii) the impact of the C604 case for scientists to support policy makers, regulators and society as a whole. Possible ways forward include (a) suggestions for improving and guaranteeing access to reference standards e.g. by revision of chemical regulations, (b) technical solutions for improving/agreeing on sufficient levels of confidence when reference standards are not available and (c) the risk governance of chemicals in absence of reference standards. Following this presentation I will briefly mention a new EU HORIZON EUROPE project ARAGORN, which we are pleased to have been invited to negotiate with the EU. It is a project under The Soil Mission/ Farm-to-Fork research initiatives under the European Green deal, and is foreseen to start in October 2023 and run for four years. The project aims to enable the decision making of landowner across Europe to remediate hot-spot polluted soils and restore the nature on it, with a focus on persistent contaminants. ARAGORN is led by University of Copenhagen, and consists of 17 partners, across 12 countries, and collaborates with 22 identified polluted sites. It will build on existing networks and knowledge and we are therefore interested in reaching out to other networks working on analysis, remediation, cost-benefit analyses, stakeholder processes and regulations of metal, organochlorine, PFAS and PETCO pollutants at business, local, regional and national levels.

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"FOREVER CHEMICALS" VS. "ONE HEALTH" – PFAS, A CALL TO RETHINK HOW WE MANAGE CONTAMINATED LAND

Müller-Grabherr, D.
COMMON FORUM on Contaminated Land in Europe

ABSTRACT

The new scientific findings published by the European Food Safety Authority in 2019 have caused an unexpected tipping point in contaminated land management. Since then PFAS is turning out as a "perfect" challenge in risk management. Accordingly COMMON FORUM took action in 2020 and as a result published its **PFAS-Memorandum** calling for a policy dialogue of all stakeholders and defining 5 key requirements which are

i. to establish improved high standard risk assessment,
ii. to refine and validate risk-based modelling by biomonitoring,
iii. to coordinate transnationally the development of remediation methods and integrated management approaches,
iv. to develop and integrate alternatives to active technical solutions into policy frames, and
v. to harmonise regulatory approaches for soil, water and waste within EU and national regulatory approaches.

We not only need to deal with still increasing uncertainties, but enhanced complexity in risk characterisation, and unforeseen ambiguities as well. To overcome it needs a new momentum at science-policy interfaces, in technology development and cooperation of all societal actors.

The European Human Biomonitoring Initiative (HBM4EU) started in 2017 to coordinate and advance human biomonitoring studies as a joint effort at European level. Among the results published until 2022 it established baselines for the internal exposure to 12 PFASs for European teenagers in 9 countries, evidencing that 14,3 % exceed the guideline value for a tolerable weekly intake, with a country-specific maximum exceedance found at 23,8 %. (HBM4EU 2022). Higher PFAS blood levels were found linked to the consumption of fish, seafood, eggs, offal and locally produced food (Richterová et al., 2023). Like the European Commissions first Zero Pollution Monitoring and Outlook report (EC, 2022) reveals that EU policies have contributed to reduce environmental pollution, still to reach mid-term targets envisaged for 2030 much stronger action is needed.

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PFAS CONTAMINATION AND PRESUMPTIVE CONTAMINATION SITES IN EUROPE – WHAT NEEDS TO BE KNOWN BY THE PUBLIC AND BY GOVERNMENTS

Journalist Consortium of The Forever Pollution Project

ABSTRACT

For more than 10 years PFAS contaminated sites gained attention in the research community and especially in some authorities which are affected by a PFAS contaminated site. For the United States an EPA assessment showed the country wide pollution of drinking water affecting millions of people and the presidents Trump and Biden had to include PFAS in their priority to-do list. Meanwhile a public map of presumably contaminated sites has been published for the United States with more than 57,400 possibly affected areas. **A similar compilation of PFAS contaminated sites and a priority on the upper political level is missing in Europe.** Therefore "The Forever Pollution Project" has been developed as a cross-border journalism collaboration whose objective is to map known and presumed PFAS contamination sites across Europe for the first time and to inform governments and the public on this pressing issue for drinking water safety and will be published soon.

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PER- AND POLY-FLUORALKYL SUBSTANCES (PFAS) AND THE GLOBAL DIMENSION OF SOIL POLLUTION

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ABSTRACT

At the initiative of the FAO Global Soil Partnership, the International Network on Soil Pollution (INSOP) was established in 2022. Its mission is to support and facilitate joint efforts to reduce soil pollution risks globally and effectively remediate already polluted areas.

PFAS, in particular, are a fast-evolving issue receiving increasing governmental and public attention, as the presence of these contaminants in the environment is ubiquitous. Soil pollution impacts the critical zone of soil ecosystems and their ecosystem services, which supply not only agricultural products but a wide range of functions and services that benefit our societies and citizens.

INSOP works on the full cycle of soil pollution, from assessment to remediation, as well as environmental and human health effects. Data from around the world on PFAS are alarming. They are everlasting contaminants and require increased efforts and budgets for risk analysis, control, adaptation and rehabilitation to restore soil ecosystem functions and services and limit damage.

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Block 13.
PCB MANAGEMENT SESSION

PCB PROJECTS IN EMERGING ECONOMIES: NEED FOR LOCAL TREATMENT, STOCKHOLM CONVENTION DEADLINE 2028, TRANSPORT AND EXPORT OBSTACLES

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ABSTRACT

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.

At the PCB workshop during the 14th forum a dialog will be held about the need for treatment capacity and local treatment due to:

- Refusal of many shipping lines to carry PCB containing wastes;
- Substantial numbers of equipment still in use;
- PCB waste stockpiles / storage;
- Stockholm Convention treatment deadlines: out of use 2025 and disposed 2028;
- How feasible is an investment in 100% local treatment if the deadline for disposal is 5 years?

KEYWORDS

PCB's, Local treatment, Transport, Export; Transformer Life Cycle Management; Re-use; Recycling

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PCB MANAGEMENT AND ELIMINATION IN MOLDOVA

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ABSTRACT

The bases of the PCB management system in the Republic of Moldova were laid in the framework of broader actions for the management of persistent organic pollutants, initiated and carried out after the ratification of the Stockholm Convention on POPs. Those activities included the creation of the regulatory framework for PCB management, national inventory of equipment in the power sector and disposal of PCB-contaminated waste.

In this respect, the Regulation on Polychlorinated Biphenyls has been developed and approved in 2009 with a view to provide a legal framework for environmental sound management for PCB and equipment containing PCB, and to ensure effective implementation of the Strategy on the reduction and elimination of POPs and of the NIP for the Stockholm Convention on POPs.

Based on this document, the national inventory of transformer oils in the power equipment, which included approximately 28,000 units, was carried out. The analysis of the oil samples was carried out in two stages, by testing the chlorine content and then by gas chromatography analysis. As a result, around 300 units of equipment contaminated with PCBs were detected, the total amount of contaminated oil constituting approximately 330 tons. The respective equipment is to be safely managed during the period of operation, removed from use and disposed of in accordance with the provisions of the Stockholm Convention.

Parallel to this, activities on elimination of electrical capacitors with PCBs from 13 transformer stations of Moldelectrica State Enterprise, and the remediation of contaminated site were carried out. 18,660 PCB capacitors (934 tons in total) were dismantled, transported abroad and destroyed. Based on a feasibility study, on the contaminated area at the Vulcanesti 400 kV transformer station remedial works were carried out. Approx. 15,000 square meters were cleaned, about 3,500 cubic meters of soil contaminated with PCBs were isolated in two cofferdams built on the territory of the station.

KEYWORDS

Polychlorinated Biphenyls (PCB), persistent organic pollutants (POPs), POPs management, PCB contamination, contaminated sites, Stockholm Convention on POPs.

NANOREMEDIATION OF A SOIL POLLUTED WITH PCBs AND Cr

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ABSTRACT

Polychlorinated biphenyls (PCBs) are a broad group of POPs due to their high potential for bioaccumulation and resistance to degradation, with toxic, mutagenic, and carcinogenic effects. They have been found in all environmental media, especially in soils and sediments due to their hydrophobic character. In many cases, metals and organic pollutants co-exist in the soil, which poses a serious risk for both human health and the environment, thus the development of effective remediation techniques should be prioritized. Recently, nanotechnology has enabled the generation of new cost-effective and environmentally friendly remediation strategies, compared with traditional physico-chemical technologies. The main objective of this study was to evaluate the ability of three types of iron nanoparticles (nanoscale zero valent iron (nZVI), nZVI with Pd as catalyzer (nZVI-Pd), nano-magnetite (nFe_3O_4)) for the remediation of an industrial soil co-contaminated with Cr and PCBs. Iron nanoparticles were extensively characterized prior to the experiment. Soil (15 g) was mixed with iron nanoparticles at 10% (20 g Fe/kg) for nZVI and nZVI-Pd, and 5% for nFe_3O_4 (36.2 g Fe/kg), and water (35 mL) was added to minimize the presence of oxygen and prevent nanoparticle oxidation. Tubes were incubated and at 15, 45 and 70 days, samples were collected. PCBs, Cr and Pd were analyzed in soil and aqueous extract. The leachability of Cr in treated soil samples decreased and was stable throughout the experiment. PCBs were not detected in the aqueous fraction for any sampling time. In soil samples, PCBs significantly decreased (up to 68%) after 15 days for the three types of nanoparticles. However, nFe_3O_4 evidenced reversible adsorption of PCBs after 45 days. nZVI-Pd reduced PCB concentration in soil faster than nZVI. Control soils showed a similar reduction in PCBs concentration as those obtained with nZVI and nZVI-Pd, after a longer time (45 days) probably due to bioremediation processes. In this regard, bioremediation would be feasible for soil polluted exclusively with PCBs. In conclusion, nZVI or nZVI-Pd and pseudo-anaerobic conditions could be used for the recovery of soils co-contaminated with Cr and PCBs.

KEYWORDS

POPs, metal, nZVI, magnetite, soils, bioremediation

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MONITORING PCBS IN EGGS AS SENSITIVE INDICATORS FOR ENVIRONMENTAL POLLUTION AND CONTAMINATED SITES

Weber, R.[1], Petrlik, J.[2,3], Bell, L.[2,4], DiGangi, J.[2], Kuepouo, G.[5], Ismawati Drwiega, Y.[6], Behnisch, P.[7], Herold, C.[1]
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[7]BioDetection Systems BV (BDS), The Netherlands

ABSTRACT

This study compiles information on PCB-contaminated eggs from 20 years of global egg monitoring around emission sources conducted by the International Pollutants Elimination Network (IPEN) and Arnika as well as a compilation of data from scientific literature. IPEN monitored 127 pooled egg samples including samples from 113 chicken flocks at potential PCB- and PCDD/F-contaminated sites around priority sources listed in the Stockholm Convention (e.g. storage sites, e-waste sites, waste incinerators, metal industries, and landfills). More than 85% of pooled egg samples were above the EU maximum limits for the sum of dioxin-like PCBs and PCDD/Fs (5 pg PCDD/F-PCB-TEQ/g fat). This demonstrates that close to 90% of these areas were not safe for the production of free-range eggs. In 58 (51%) pooled egg samples the PCB-TEQ was above 5 pg TEQ/g fat exceeding the EU maximum limit by dioxin-like PCBs alone. This highlights the important role of commercial PCBs for global contamination with dioxin-like compounds. It was discovered that around metal industries, shredder plants, open burning sites of

e-waste and dump sites, a high share of contamination was caused by dl-PCBs. This clearly shows severe PCB release from the end-of-life management of PCB-containing equipment in developing countries.

KEYWORDS

dl-PCBs; PCDD/PCDF; contaminated sites; monitoring; egg; DR CALUX

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SODIUM TECHNOLOGY – THE CHOICE FOR TREATMENT OF PCB AND POP'S

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ABSTRACT

The Sodium Technology, developed by our team, involves the complete mineralization of organic chlorine containing compounds (such as PCBs in transformer oil) by sodium metal. Any kind of halogenated chemical compound will be attacked by sodium and converted to inorganic sodium chloride and organic follow up products. In the case of transformer oil the challenge is to recover at least 99% of the highly valuable oil for future applications.

Within a project in Medellin, Colombia 2015/2016 a unit was constructed to treat transformer oil from (today) 10 of the 32 Colombian "Departamentos". Until November 2022 a total of 1227 equipment (mainly distribution transformers with 175,000 litres of PCB contaminated dielectric mineral oil have been dechlorinated.

The decontaminated oils are used as diluents for hydraulic oil bases, lubricants and greases.

The efficiency of the Sodium Technology is very high so the target of < 2ppm PCB was achieved in any case.

Advantages are as follows: the moderate investment costs, the inexpensive reagent sodium metal and the choice of stationary as well as mobile detoxification units.

Basically the same type of equipment for the Application of the Sodium Technology may be used for the treatment of POP`s and also sulphur compounds in diesel fuel.

KEY WORDS

Sodium, PCB-destruction, POP-Destruction, mobile unit, approved technique, high efficiency.

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PCB DECONTAMINATION: AUTOCLAVE TECHNOLOGY CASE STUDY: TREATMENT OF PCB CONTAMINATED TRANSFORMERS

Wauters, J.

SARPI

ABSTRACT

In accordance with Stockholm Convention, the use of PCB in equipment must be eliminated by 2025 to ensure the environmentally sound waste management of liquids containing PCB and equipment contaminated with PCB by 2028. Currently, large quantities of transformers need to be removed within the next 3 years which will require significant resources and expertise.

Due to the hazardous nature of these wastes, it is necessary to treat them using the best available technologies.

PCB DECONTAMINATION has developed a **solvent autoclave treatment technology.** The fully closed process uses high quality degreasing solvents and with the right combination of solvent rinsing, vapor degreasing at defined temperature and pressure settings, this technology aims at separating the metals from the other contaminated materials. These metals are then completely cleaned and are recycled. The quality of the metals is checked on a regular basis by a licensed laboratory. The solvent is recycled internally. All residual PCB's fractions (liquids and solids) are fully destroyed with high temperature incineration at our shareholder Indaver.

Veolia offers an innovative recycling technology for a significant reduction in CO2: for each ton of treated waste, we recycle more than 75% of metals and contribute to a CO2 saving of 2,2 tons.

THE SUB-SAHARAN CEMENT INDUSTRY POTENTIAL FOR THE DESTRUCTION OF POP'S, PCB AND OTHER HAZARDOUS CHEMICALS

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ABSTRACT

The need for a local management and destruction solution in Sub Saharan Africa remains crucial as the local stocks of PCB's and POP's still need to be cleaned up.

The Southern African cement industry has undergone a tremendous transformation since the unsuccessful attempts in the 1990's to implement local pesticide and POP's disposal capacity in Africa.

Some co-processing demonstration tests were successful but did not proceed due to public pressure, mainly the NGO community, from reported concerns about the environmental efficacy of cement kiln co-processing and also about capacity for regulation, monitoring and enforcement in Africa. Other demonstration tests were poorly executed and harmed the potential of cement kilns as a disposal option for obsolete pesticides and POP's.

Thirty years later the situation has changed. The cement industry in Africa has undergone a dramatic development surge since 2006, with the implementation of the most modern cement kiln technology in most African countries and with the entry of large multinational cement companies into African cement markets.

Further, the environmental governance of African cement kilns has changed considerably. Most modern cement kilns are subject to much stricter environmental controls than the country they operate in. Increased ESG reporting requirements on international cement companies have also resulted in a dramatic improvement in the environmental performance of the African cement industry.

Sub-Saharan Africa is worth another look when considering disposal options for hazardous waste and obsolete PBC and POP's stockpiles in Africa.

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CO-PROCESSING PCB & OTHER POP'S IN CEMENT KILNS A LOCAL SOLUTION

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ABSTRACT

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:

- 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.

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INVESTIGATION FOR DIOXINS / FURANS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN ARMENIA

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-furans (PCDD/PCDFs) were never produced intentionally, but are revealed practically omnipresent at residue amounts as undesirable by-products of many industrial and burning processes. PCDD/PCDFs never possessed any useful features, unlike other persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) or DDT.

Dioxin-like polychlorinated biphenyls (DL-PCB) DL-PCB are a sub-group of the wider class of PCBs, which demonstrate a similar toxicity to PCDD and PCDF.

Samples of land were taken on the boundary of landfills and agricultural lands near some settlements of and analyzed for dioxin-like PCBs (DL-PCBs).

In all investigated soil samples DL-PCBs were detected.

In view of the ecological / hygienic positions, special attention was paid to summary amounts of polychlorinated biphenyls, as the total amounts of these compounds correlate with the hygienic standards, which are integral values.

The obtained results signify to necessity of further studies on less chlorinated PCBs: mono-, di-, tri-chlorobiphenyls, as well as other organic compounds, in particular, chlorine-substituted cyclohexanes and chlorine-substituted benzenes.

KEYWORDS

Dioxins, furans, persistent organic pollutants, polychlorinated biphenyls, dioxin-like polychlorinated biphenyls

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Block 14.
TOXICOLOGY: CHEMICAL EXPOSURE OF WILDLIFE AND HUMANS

PESTICIDES AND WILDLIFE FRIENDLY FARMING

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ABSTRACT

Pesticides, agrochemicals used to protect humans from various diseases, are also known by their ability to cause a large number of negative health and environmental effects. We now know that some pesticides disrupt food webs, killing plants and insects and removing weed seeds from the environment, which may be essential food or habitat for some bird species and thus represents a high risk for their conservation.

On the other hand, we are living in a biodiversity crisis and there are multiple threats facing our wildlife, including habitat loss, pollution, and climate change. In order to tackle biodiversity crisis, we must look critically at every aspect of our lives, and see if what we are doing is compatible with nature.

SEO/BirdLife is very concerned by the environmental impacts of the widespread use of pesticides. We believe that if they must be used, it should be subjected to appropriate scrutiny, in a targeted way, and with respect to the environment. To do so, Governments should provide more support for farmers to reduce their reliance on chemicals, including the implementation of a national pesticide reduction target, encouraging the putting into practice schemes that assist farmers on improving the natural health of our countryside and providing independent advice and training to farmers.

The purpose of this conference paper is to set out whether our relationship with pesticides is safe for wildlife and the environment, and what we can urgently do to limit their harm.

KEYWORDS

Pesticide, wildlife, farmland birds, biodiversity, impacts and management.

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TOXICOLOGICAL EVALUATIONS OF GLYPHOSATE IN ZEBRAFISH EARLY-LIFE STAGES

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ABSTRACT

The glyphosate is now considered the most widely used herbicide in the world. It is a systemic, non-selective, post-emergency herbicide. Its use in agriculture determines the destruction of unwanted weeds. Its mechanism of action is to block the enzyme 5-enolpyruvylshikimate 3-phosphate synthase (EPSPS) which is involved in the shikimic acid pathway. The high persistence and its widespread determine the presence of traces of this herbicide increasingly frequently in soil, water and air. The present study aimed to evaluate the glyphosate potential effects on the development of zebrafish early-life stages. The research focused on the acute toxicity, evaluated by “Fish Embryo Acute Toxicity Tests” and the tested concentrations are 25 mg/L, 50 mg/L, 100 mg/L and 125 mg/L of glyphosate. Zebrafish larvae exposed to glyphosate showed mortality and developed sublethal alterations including yolk sac and pericardial oedema, blood stasis, impaired blood flow and alterations in head development, suggesting a neurological involvement.

The results of the previous study confirm the developmental toxicity of glyphosate in zebrafish early stages. For this reason, the aim of future studies is to evaluate the toxicological mechanisms of action of glyphosate through histology to evaluate the physiological changes that occur in exposed Zebrafish larvae.

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HIGHLY HAZARDOUS PESTICIDES (HHP) IN THE EU COMPARED TO DEVELOPING COUNTRIES, CASE STUDY: HHP HISTORY AND USE IN IRAN

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ABSTRACT

Highly Hazardous Pesticides (HHP) in the EU. EU Bans Pesticides in Parks, Playgrounds, and Playing Fields; Fails to Set Organic Transition Goals in Ag (Beyondpesticides, July 2022). HHPs nearly banned in all EU countries are still found easily in some developing countries doing tremendous harm to people, environment and wildlife. Mass killing of people in Bhopal India, Iran, etc. mass killing of children in Peru a few decades ago and about 10 years ago in Bihar Province of India both due to eating HHP polluted food are some examples at the time big pesticide corporations just thinking about their own profits.

According to the UNEP report in 2015, SAICM Fourth International Conference of Chemicals Management (ICCM4) adopted a resolution that recognizes HHPs as an issue of international concern and calls for concerted action to address HHPs.

Highly Hazardous Pesticides (HHP) History and use in Iran. There are many people killed by pesticides despite our decades of efforts to stop it. Biggest obstacle is lack of cooperation between different sectors and people for enforcement issues. HHP are taking lives in many developing countries including Iran.

Death scenarios with HHP Ops in Iran: highly toxic POPs plus HHP Ops like parathion, .etc. in cotton fields, other agricultural fields and citrus orchards of Mazandaran and Golestan Provinces. HHP like Parathion, Diazinon, Sevin, Paraquat.

Effects of HHP on wildlife, honey bees and pollinators. HHP are known to be prominent drivers of pollinator decline with long term risk for pollinators. Now bits and pieces of pesticides/ chemicals and their metabolites are found in all niches and habitats preventing the natural processes of speciation responsible for the development and diversification of animals since 100s millions of years ago. A pesticide is designed to kill, when pesticide molecules and later their metabolites enter agroecosystems they are against whole biodiversity. In recent years I had some talks for SWS, RAMSAR COP 13, etc. about loss of biodiversity in wetlands due to connection between agricultural lands. Wildlife poisoning is a big problem everywhere, particularly in wetlands (A. Mahdavi, 2017, Toledo Spain, 2018 RAMSAR COP13, many other related references).

Overuse and misuse of agrochemicals particularly HHP and POPs during the past 100 years destroyed agricultural biodiversity in many developing countries due to lack of regulations and enforcement. Handling toxic compounds like pesticides in developing countries has been under lots of discussions due to lack of proper methods, infrastructures, etc. with 3-4 decades of experience as a pesticide toxicologist in Iran and globally I would like to present a detailed discussion about the situation of pesticides regulations and enforcement in developing countries as compared to developed world. There are big differences and gaps for toxic pollution reductions and regulations between Northern and Southern countries, industries in developed countries but more sufferings in developing countries.

KEYWORDS

Highly Hazardous Pesticides, enforcement, Wildlife, Developing countries.

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TOMATO AND OLIVE MICRONUTRIENTS AS "HUMAN BODY REMEDIATION" IN PEOPLE LIVING IN CONTAMINATED AREAS: FOCUS ON β-HEXACHLOROCYCLOHEXANE

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ABSTRACT

The beta-isomer of hexachlorocyclohexane (β-HCH) is one of the most widespread and environmentally persistent organochlorine pesticides, accounting for about 7.2 tons illegally buried worldwide. Due to its physicochemical properties, β-HCH exhibits high energetic stability and bioaccumulating potential thus representing a significant health hazard in contaminated sites. Epidemiological surveillance programs on a global scale demonstrated a high plasmatic concentration of β-HCH in exposed subjects. Previous cellular and molecular studies performed by our group on both normal and transformed human continuous cell lines (i.e. breast, liver, prostate) demonstrated that β-HCH activates a wide range of signaling pathways and act as an endocrine disruptor, promoting cellular processes related to carcinogenesis, tumor progression, and chemoresistance. In spite of its small size, β-HCH has a relevant impact on cellular homeostasis, making it mandatory to explore defense strategies against its multifaceted biological effects. Our purpose is identifying a balanced combination of natural chemoprotective/chemo-sensitizing compounds to modulate β-HCH intracellular effects.

A screening of natural substances was carried out on the above-enlisted cell targets to test their capability to counteract β-HCH actions by performing viability assay, flow cytometry, and western blot analysis.

Micronutrients from tomato and olive show a dose-dependent significant chemoprotective activity in the considered cell lines by contrasting β-HCH-induced intracellular responses such as anti-apoptotic and pro-metastasizing events, increase in ROS production and DNA damage.

These experimental outcomes identified the chemoprotective effects of tomato and olive-derived micronutrients. For these reasons, we hypothesize that these compounds could be an excellent starting point for a "green therapy" approach as a system of remediation or prevention of the human organism against POPs and other pollutants.

This study was supported by *Fondazione Federico Calabresi*.

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THE USE OF THERAPEUTIC AGENTS DERIVED FROM THE PLANTS AND FRUITS GROWING IN KYRGYZSTAN FOR THE ELIMINATION OF ORGANOCHLORINE PESTICIDES FROM GASTROINTESTINAL TRACT OF NURSING WOMEN

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ABSTRACT

The paper presents the results of analysis for organochlorine pesticides (OCPs) presence in breast milk, blood and urine of urban nursing women residents of Kyrgyzstan before and after the treatment with therapeutic agents derived from local medicinal plants and fruits. The first test group included 27 women who were treated with a concentrate derived from local medicinal herbs for the neutralization and elimination of OCPs from gastrointestinal tract (GT), and the second test group involved 24 mothers who didn't administered the concentrate. The breast milk, blood and urine samples were examined for the presence of OCPs: hexachlorocyclohexane (HCH) in the form of its α-, β-, γ-, and δ-isomers; 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT), 4,4'-dichlorodiphenyldichlorethylene (4,4'-DDE), 4,4'-dichlorodiphenyldichloroethane (4,4'-DDD), aldrin, dildrin, and heptachlor, eventually, eight of them were detected, excluding δ-HCH and dildrin.

A 10-12 day administration of therapeutic agents produced from local medicinal plants, including endemic herbs and fruits made it was possible to reduce the concentration rates of hexachlorocyclohexane (HCH) - α-, β-, γ isomers and dichlorodiphenylethylene (DDE) in breast milk. Concentration level of HCH decreased by 2.05 times, but the detection rates remained unchanged, DDE rates decreased from 88.9% before the start of the treatment up to 66.7%, P = 0.551 after the course of treatment, concentration level decreased by 2.01 times. The level of HCH in blood samples decreased from 33.3% to 22.2%, P = 0.29, concentration decreased by 53.5 times. DDE levels remained at 55.5% even after the course of treatment, but its concentration decreased by 28.5 times.

The level of HCH in urine samples increased from 11.1% before the treatment to 22.2% after the course of treatment, but concentration level decreased by 58 times, DDE - from 33.3% before the treatment to 3.7% after the treatment, and only DDE traces were detected, P=0.0004. In the second group (control group), the levels HCH and DDE in breast milk samples and HCH level in blood samples remained at 66.7%, in urine samples -remained unchanged. DDE level in breast milk, on the contrary, increased from 50.0% to 66.7%, in urine- the level of HCH remained at 50%, and DDE - increased from 12.5% to 16.7%.

Thus, the use of therapeutic agents obtained from medicinal plants, including endemic plants and fruits, as well as a tincture of the golden root (*Rhodiola Rosea*), an analogue of ginseng growing in Kyrgyzstan, showed good efficacy in neutralization and elimination of OCPs from GT. But further targeted experimental studies on a larger number of patients are required.

KEY-WORDS

organochlorine pesticides, women, breast milk, pathology, therapeutic agents.

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OUR EXPERIENCE OF APPLYING THE RESULTS OF RESEARCH AND EVIDENCE-BASED MEDICINE FOR IMPROVING THE AWARENESS, ACHIEVING COMPLIANCE WITH SAFETY MEASURES AND IMPLEMENTING RECOMMENDATIONS BY THE POPULATION LIVING IN THE AREAS POLLUTED BY ORGANOCHLORINE PESTICIDES

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ABSTRACT

The paper presents the results of the effectiveness of seminars, lectures, talks, and meetings to raise the awareness and knowledge of the Stockholm Convention by using evidence-based medicine in the areas polluted by organochlorine pesticides (OCPs). This approach proved to be effective in raising population awareness regarding OCPs pollution and their health effects. Recommendations for those who are planning to conduct seminars, webinars are as follows: to carry out a comprehensive study of the environment and local population and use the data obtained when conducting seminars and webinars.

KEYWORDS

Awareness, population, the Stockholm Convention, organochlorine pesticides, science, evidence-based medicine

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Block 15.
POSTERS

REMEDIATION OF GROUNDWATER POLLUTED WITH HCHs USING SOLAR LIGHT IRRADIATION

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ABSTRACT

Nowadays, pesticides in groundwater are a major concern to scientists because of the serious problems these compounds can cause for human health. Pesticides are commonly used in agricultural activities to prevent weeds in crops and are spread on the soil. One of the most used pesticides until the 90s was lindane (γ-hexachlorocyclohexane, $C_6H_6Cl_6$), an organochlorine compound with high toxicity and bioaccumulative. Several companies produced this pesticide for many years until its use was banned. In the particular case of Spain, the INQUINOSA company operated in the north of the country, producing this compound. However, different isomers of hexachlorocyclohexane (α-, β-, δ- and ε-hexachlorocyclohexane, HCHs) were also produced as wastes. These compounds, together with lindane, were uncontrolled dumped in Sardas and Bailin landfills, promoting the occurrence of HCHs in groundwater. Currently, a physical-chemical process is carried out to treat the extracted effluents or rainwater runoff. This process separates these pollutants from water but does not degrade them. Hence, subsequent treatment is necessary to destroy HCHs completely.

In this context, Advanced Oxidation Processes (AOPs) can be considered an excellent alternative for removing HCHs from groundwater. These processes are based on producing large amounts of free radicals that significantly contribute to eliminating organic pollutants. Hydroxyl radical is the most common species generated in these processes due to their high oxidation potential (2.8 V). However, it is demonstrated that the ability of these radicals to degrade aliphatics can be limited, and the total mineralization of HCHs could be incomplete. With this background, this work proposes the use of solar light irradiation for the degradation of HCHs from groundwater in the presence of persulfate (oxidant) and ferrioxalate (catalyst). To do this, actual effluents from Sardas and Bailín landfills polluted with different HCHs were treated using a solar simulator and different dosages of oxidant and catalyst. Furthermore, a compound parabolic collectors (CPC) solar reactor was also used under direct sunlight to evaluate the technical viability of the technology at a large scale. During the process, free sulfate radicals are expected to be generated from the activation of persulfate by iron. These radicals can contribute to the degradation and mineralization of HCHs contained in groundwater. The use of ferrioxalate as a catalyst allows working under circumneutral pH conditions. Results show that it is possible to attain a total HCHs conversion up to 75 % in 600 min with the solar simulator (q_w: $1.12 \cdot 10^{-7}$ E $cm^{-2}s^{-1}$) using 250 mg dm^{-3} $Na_2S_2O_8$ and 3.5 mg dm^{-3} Fe. This value is slightly reduced when using the CPC reactor, suggesting that different amounts of oxidant and catalyst could be required to increase the process efficiency at large scale.

KEYWORDS

Lindane, groundwater, solar light, HCHs, CPC reactor

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COUPLING ELECTROKINETIC SOIL FLUSHING WITH BIOREMEDIATION FOR THE REMOVAL OF CHLORINATED BENZENES AND LINDANE IN GROUNDWATER

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ABSTRACT

Bioremediation is coupled with electrokinetic soil flushing technology to check the proper performance in the degradation of chlorinated benzenes and lindane in the soil and groundwater from Sardas (Sabiñánigo, Spain). Biological barriers using microbial consortia from the site are used, and aerobic and anaerobic conditions were tested. The electric field (17 V) does not hamper biological activity and promotes a water flow that allows the pollutants to reach the biological barrier, where the pollutants can be removed.

KEYWORDS

Chlorinated benzenes, lindane, bioremediation, electrokinetic soil flushing, biological barrier, groundwater.

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SNI SACCO RIVER VALLEY – CENTRAL ITALY: CHARACTERIZATION OF AGRICULTURAL AREAS

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ABSTRACT

The Sacco River Valley is included by the Italian Ministry of the Environment among the sites of national interest (SNI), for which the reclamation process is a priority for the Italian State (National Decree 152/2006). The perimeter of the area includes 19 municipalities, 4 of which in the province of Rome and 15 in the province of Frosinone. Among the numerous environmental problems, the greatest is the contamination of soil and river sediments by β-HCH, which has since 2005 the prohibition of all agricultural activities in riparian areas up to 100 m from the riverbanks, and in the floodable zones. In 2019, the regional authority signed a framework agreement with various competent public bodies, in order to finance interventions for the promotion of citizen health and for environmental characterization, preparatory to the reclamation of the area.

In this context, the Istituto Zooprofilattico Sperimentale (IZSLT), together with the Istituto Superiore di Sanità (ISS), have been charged with planning, organizing and coordinating the "Characterization of Riparian Agricultural Areas". The main objectives of the Plan are: i. determine soil contamination levels at a very detailed scale; ii. remove the ban on agricultural activities for non-contaminated areas; iii. contribute to the assessment of the exposure risk for soils, plants, animals and humans.

For this purpose, an executive project was approved. The three main pillars of the plan are: 1. soil sampling and analysis; 2. sampling and analysis of wild plants; 3. sampling and analysis of bulk milk from livestock farms. Dedicated and trained personnel will work on a total of approximately 700 "land-plots" covering an area of 1,700 hectares. In each "land-plot", a variable number of soil and plant samples representative of the land surface will be collected. A single pooled sample of soils and one of plants will then be created for each land-plot. Two samples of bulk milk will be taken during the year.

The analyses of soil will detect the presence and concentration of an extended spectrum of contaminants; POPs, metals and PAHs will be searched for in plants; bulk- milk will be examined only for b-HCH, unless other critical issues emerge from the other matrices. This is the very first experience in Italy of such an extended characterization plan, foreseen by the recent Italian legislation (DM 1 marzo 2019 n. 46).

KEYWORDS

Italy, Sacco River Valley, soil pollution, Lindane, hexachlorocyclohexane (HCH), characterization.

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INTEGRAL INVESTIGATION ON THE COUNCIL OF O PORRIÑO, LOOKING FOR SOLUTIONS TO THE GREAT DISPERSION OF THE CONTAMINATION

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ABSTRACT

We have been working for many years with the problem of lindane contamination in the area of O Porriño. We have carried out actions such as the removal of contaminated soils and their management in hazardous waste landfill, a safety cell was built in the area of Torneiros and several phytoremediation studies were carried out throughout all these years.

But the reality is that even today uncontrolled sources of contamination continue to appear as occurred in 2017 in the area of O Contrasto in which, during the performance of sanitation works a continuous layer of lindane was found under the pavement of the road, which had previously been used to smooth the surface of the road.

This last episode showed the need to investigate the existence of other potential sources distributed throughout the territory, so an investigation was commissioned to cover the entire municipality of O Porriño.

Now with this work, we want to present to you the results of the integral investigation of the city council of O Porriño, what were the results, conclusions and recommendations of this study.

KEYWORDS

Lindane, O Porriño, dispersion, integral investigation, public administrations, coordination.

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DISPOSAL OF PRODUCTION WASTE FROM LINDANE MANUFACTURING: COLLABORATION BETWEEN UNIVERSIDAD DE ZARAGOZA AND GOBIERNO DE ARAGÓN

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ABSTRACT

Collaboration between the University of Zaragoza (UZ) and the Regional Government of Aragon since 2017 has been devoted to bibliographic search, sample analysis, and research on the chemical or physical transformation of different stereoisomers of HCH and waste from lindane manufacturing into harmless and industrial-valuable compounds. Benzene, biphenyl, and other non-chlorinated compounds have been obtained, either directly or involving intermediate isolation of a mixture of chlorinated products, which could be used as platform molecules in industrial synthesis. High yields were obtained by modifying reaction conditions at a laboratory scale, which allow scaling these results up in the next future. Non-conventional techniques such as laser irradiation for HCH transformation are also currently under study.

KEYWORDS

Benzene, Bibliographical Search, Dehydrochlorination, HCH Analysis, Hydrodechlorination, Hydrogen, Laser

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ASSESSMENT OF IN-SITE DIOXIN DEGRADATION IN WASTE, 1995-2021

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ABSTRACT

The period of maximum contamination of the industrial zone of the city of Ufa - soil, sewage, and sludge with toxic waste containing PCDD/Fs is the 70s of the 20th century. In 1964-67 "Ufakhimprom" organized a pilot production of 2,4,5-T butyl ether, 2,4-D herbicide, and operated an organochlorine waste incinerator. It is these industries that make the main contribution to dioxin pollution of "hot spots"[1]. There are no analytical data on the content of dioxins in products and the environment during this period of time. After the cessation of production of the most dioxin-hazardous products, the level of pollution of the territory did not increase significantly, and now we are dealing with the consequences of pollution 60 years ago[2]. The main depot of dioxins is sludge reservoirs, territory and industrial buildings. Some of the previously completely filled sludge reservoirs were not exposed to any impact, and the results of monitoring dioxins in sludge can serve as field studies of dioxin degradation in "natural" conditions. It is believed that the half-life of dioxins in soil depends on soil type, mineral content and climatic conditions. Estimates vary widely from 1-3 years at the surface and to tens of years at depth[3]. Under in-situ conditions in a contaminated area, based on information for 1992-2021, we estimated the half-life of dioxins in the mass of sludge reservoirs as 10-14 years, in the soil of the plant – 8-10 years.

KEYWORDS

Dioxins, half-life, sludge, soil, accumulated damage

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ASSESSING PERSISTENT ORGANIC POLLUTANTS IN SPANISH AIR

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ABSTRACT

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 (currently named Ministry for the Ecological Transition and the Demographic Challenge) since 2007 to date. 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), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides such as DDT and their metabolites, pentachlorobenzene (PeCB), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs) and endosulfan.

Samples collected in remote areas presented the following pattern of concentration: HCB > ΣPCBs > ΣDDTs ≈ ΣHCHs > ΣEndo > PeCB > ΣPBDEs > ΣPCDD/Fs. However, this pattern varied for urban areas: ΣPCBs > HCB > ΣDDTs > ΣHCHs > ΣPBDEs > ΣEndo > PeCB > ΣPCDD/Fs. Urban sites presented statistically higher concentrations for ΣPBDEs, ΣPCBs, ΣDDTs and ΣHCHs than remote locations. This result revealed anthropogenic activities as potential sources for these chemicals.

Data obtained in this study are necessary to evaluate properly the effectiveness of practices adopted to reduce POP emissions.

KEYWORDS

POPs, air monitoring network, passive air samplers, remote locations, urban areas.

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IMPACT OF ORGANIC MATERIALS ON HEXACHLOROCYCLOHEXANE VOLATILIZATION FROM CONTAMINATED SOILS

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ABSTRACT

Addition of organic materials such as compost is a common practice for the remediation of contaminated soils. Numerous studies have shown that this practice improved soil quality and reduced the leaching of contaminants into groundwater. However, studies of its effect on the transfer of pollutants to the atmosphere are not available. The objective of this work was to evaluate the impact of organic materials, used as soil amendments, on the volatilization of hexachlorocyclohexane isomers (α, β, δ and γ-HCH) from contaminated soils. For this, a laboratory test was carried out using a soil sample contaminated with residues obtained from an old lindane factory. The amendments tested were derived from organic residues of different nature (compost and biochar) and were applied at different doses. An active sampling system and solid phase microextraction (SPME) were used for monitoring HCH isomers in air. Results were different depending on both the characteristics of the specific soil amendment and dose, but volatilization was reduced by up to 85%. The application of soil amendments may be a promising practice to mitigate the transfer of HCH isomers to the atmosphere and the risk of long-distance transport in areas contaminated with lindane residues.

KEYWORDS

Hexachlorocyclohexane, Lindane, Volatilization, Organic soil amendments

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PESTICIDE EXPOSURE AND PREMATURE IDIOPATHIC THELARCHE IN GIRLS: THE PEACH PROJECT

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Several pesticides are recognized as endocrine disruptors (EDs) since they can interfere with the dysregulation of sexual, thyroid and neuro-endocrine hormones contributing to earlier pubertal onset. Exposure to pesticides can be considered an important factor associated with precocious puberty and premature thelarche in girls. Children are particularly vulnerable to the effects of EDs due to their developmental stage, peculiar lifestyle and dietary habits.

The main objective of the PEACH project is to evaluate the association between exposure to pesticides and idiopatic premature thelarche in girls, through the measurement of pesticides in urine and the dietary intake, by analysing locally produced foods.

Girls living in an agricultural area of the Marche region (Centre of Italy) and with idiopathic premature thelarche (2-7 years old), matched to healthy subjects (controls), were enrolled (N=60+60). They are asked to fill in the food frequency questionnaire (FFQ) and to deliver urine samples. Furthermore, sampling of locally produced foods was performed. Food and urine were analysed by LC or GC-MS/MS to detect the pesticide levels. The FFQ was organized in three parts: the first part included personal information on their area of residence, the second part the eaten food, as well as their place of purchase or local production (farm or private garden), the third part concerned the food diary.

All the urine samples analysed (N=60 premature thelarche and N=60 controls) showed pesticide levels below the quantification limit of the method. Otherwise, several pesticides were detected in fruits and vegetables (N= 11 samples consumed by cases and N=11 by controls) sampled in the local farms. Small fruits and berries, in particular grape and strawberry, and stone fruits (apricots, peaches, cherries, and plums) reported the highest number of pesticides including carbamates, pyridinylethylbenzamide, benzamide, phenylpyrrole and triazole fungicides and

also insecticides as neonicotinoids and carbohydrazide. The pome fruit and cucurbits (melon and watermelon) reported only the presence of neonicotinoids. Leafy vegetables reported the presence of a systemic fungicide, the metalaxyl.

Otherwise, all vegetables and fruit from private gardens reported pesticide levels below the quantification limit except for kiwi group that resulted contaminated by boscalid.

The olive oil group coming from private garden resulted contaminated by several pesticides fenazaquin, fosmet and deltamethrin while no pesticides were detected in all other commodity categories such as meats (red and white), eggs and honey coming from local and private gardens.

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DESIGN AND EVALUATION OF TEST BY OXIDATIVE METHOD FOR DECONTAMINATION OF THE WALLS OF THE OLD INQUINOSA FACTORY

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ABSTRACT

TALANTIA carried out a study of lindane (γ-HCH) decontamination in the walls of an old factory by applying oxidative techniques. The study was promoted by SARGA-Gobierno de Aragón and was part of a larger project focused on testing different cleaning methods of the building prior to its demolition.

Three methods were chosen to check their effectiveness in a pilot test. First of them consisted of spraying activated persulfate after alkalizing the wall with soda. The other two consisted of spreading a photocatalytic suspension of photosensitive titanium oxide (TiO2) in two concentrations: 10% and 20%. The results show that the persulfate treatment reduced the concentration of HCH in the coat of paint more than 80% and by 70% in the plaster underneath. Regarding the TiO2 treatment, it was concluded that the 10% concentration was too low, while the solution at 20% concentration reduced the concentration of HCH in the wall paint by more than 80% and by more than 90% in the underlying plaster.

KEY-WORDS

HCH, lindane, decontamination, wall, oxidation.

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