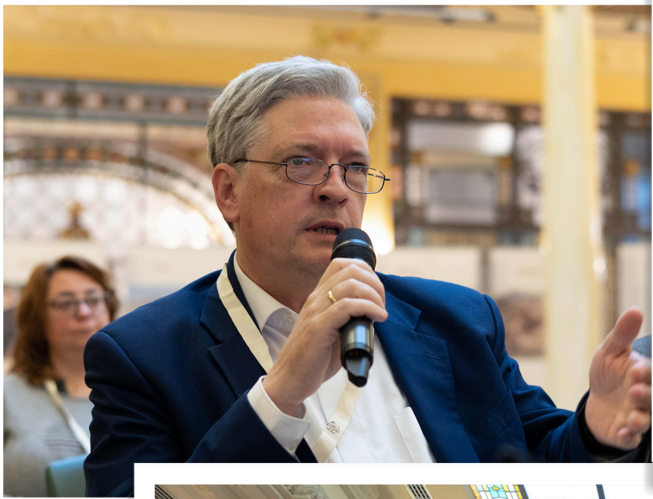
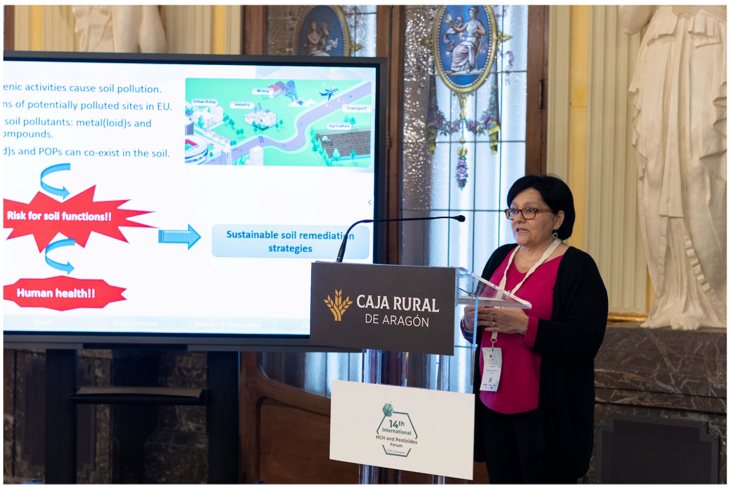
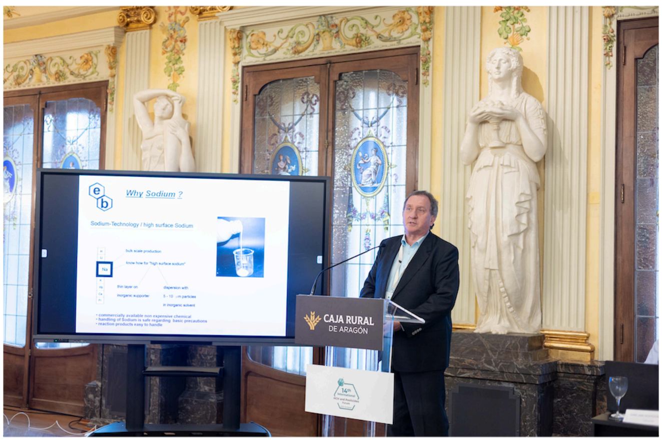
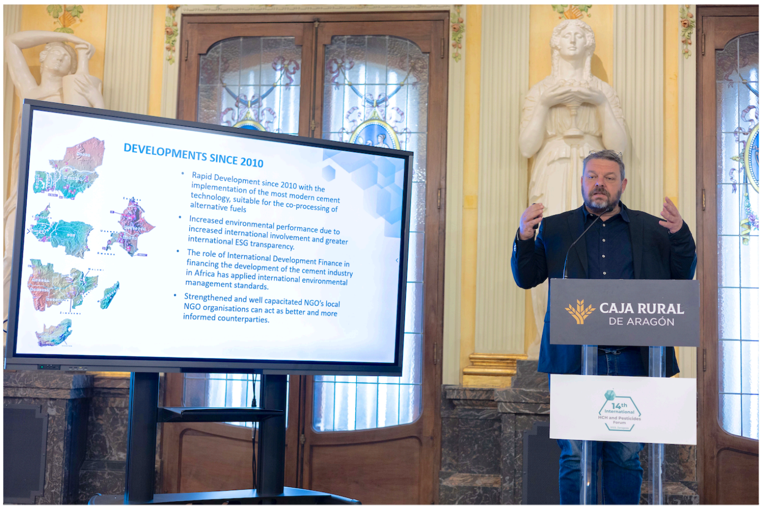
Block 13

PCB MANAGEMENT








DEVELOPMENTS SINCE 2010
Rapid Development since 2010 with the implementation of the most modern cement technology, suitable for the co-processing of alternative fuels
Increased environmental performance due to increased international involvement and greater international ESG transparency.
The role of International Development Finance in financing the development of the cement industry in Africa has applied international environmental management standards.
Strengthened and well capacitated NGO's local NGO organisations can act as better and more informed counterparties.
CAJA RURAL
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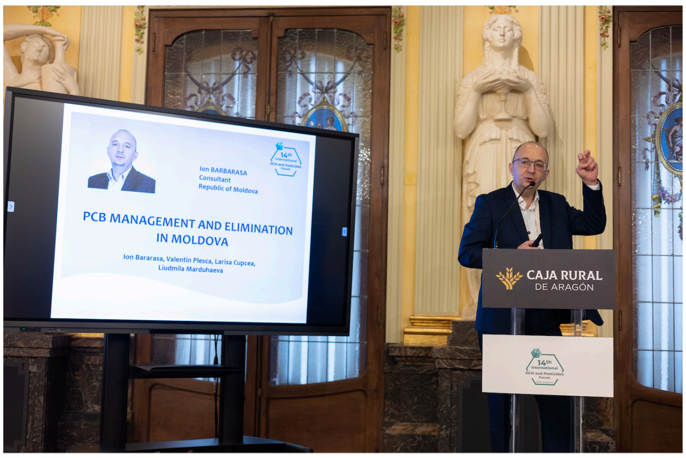
Ion BARBARASA
Consultant
Republic of Moldova
PCB MANAGEMENT AND ELIMINATION IN MOLDOVA
Ion Bararasa, Valentin Plesca, Larisa Cupcea, Liudmila Marduhaeva
CAJA RURAL
DE ARAGÓN

SUMMARY OF THE PCB MANAGEMENT SESSION

Zaragoza, 23 February 2023

Chaired by ***Dirk Jan Hoogendoorn*** (Orion b.v., the Netherlands) and ***Ed Verhamme*** (Alternate Resource Partners, the Netherlands)

1. Given the remaining estimated amounts of PCB liquids (1.5 million ton) and PCB equipment (4.5 million ton) worldwide the current deadlines for Parties to the Stockholm Convention to eliminate the use of PCB in equipment by 2025 and to ensure the environmentally sound waste management of liquids containing PCB and equipment contaminated with PCB by 2028 cannot be achieved;
2. The PCB waste treatment capacity in Europe is not sufficient to treat the waste worldwide and also the transport cost are prohibitive;
3. Using existing local capacity for licenced high temperature treatment of liquid PCB's and POP's in emerging economies 80% to 95% of the PCB problem can be treated local in many countries, with only 5% of the remaining PCB waste to be exported for treatment abroad. In the past years this proposition has been developed with licensed cement kilns and PCB oil treatment technologies;
4. A proven and feasible Sodium technology for oil treatment was presented by Dr. Bilger Umweltconsulting GmbH. It is implemented and in use in several countries for de-chlorination and in one case for desulfurization of oil. Very high quantities of oil can be recovered. It is very effective for PCB containing mineral oils and can be applied also for any kind of chlorine- and fluorine-containing compounds as long as they are in liquid phase or diluted in organic solvent;
5. Life cycle management and product re-use is an important additional positive effect if inventory and sampling programs allow for additional oil quality analyses apart from PCB in oil testing. First of all in this way also PCB free transformers may benefit from the sampling efforts. Secondly the stability and the reliability of the electric distribution grid can be assessed and if necessary improved. Thirdly the low-PCB contaminated transformers with otherwise good technical conditions can be cleaned and re-used, thus moving the PCB treatment up on the Waste Hierarchy. In the past years electricity boards in emerging economies have expressed much interest in this concept and proposed to integrate the PCB treatment in the regular maintenance schedules immediately instead of postponing treatment to 2025.
6. PCBs and POPs treatment and disposal should be incorporated in the general waste treatment infrastructure (holistic approach) and not on a (demonstration) project basis for reasons of efficiency and the high capital expenditure for a project based approach.
7. Cement kiln coprocessing is only economical feasible when they are allowed to become part of the (hazardous) waste infra structure;
8. Cement kiln coprocessing can only be done under complete transparency and strict environmental, receiving, handling, storage, feeding and emission control. BAT and BEP are available and proven: UNEP/Basel convention technical guideline for co-processing of hazardous waste;
9. Basel convention notifications are faced with a number of practical problems:
   - 9.1. Routes for shipping waste can be changed every 6 months and the submitting and approval process typically takes more then 6 months. This results in more (possible) transit countries and ports being included in the notification to anticipate on any future route changes that may occur;
   - 9.2. Transit countries that do never consent;
   - 9.3. Transit countries will only consent if all other countries consent (potential deadlock situation);
   - 9.4. Transit countries that act as if they are importing the waste and review the notification as such (for example reviewing the environmental licence for the treatment company) instead of following the importing countries competent authorities decision and approval;
10. A review of 20 year egg monitoring of the International Pollutant Elimination Network (IPEN) presented by Roland Weber for contamination in eggs of free roaming chicken shows that the PCB (and PCDD/F) contamination is wide spread in areas near for example waste treatment, metal recycling, e-waste management, metal smelters, shredder plants, open burning sites, and dump sites. This showed that PCB equipment including contaminated metals and small capacitors often containing < 5 dl has not been managed appropriately resulting in widespread contamination of soils. PCB contamination was also detected in remote rural areas including farms and the point sources appear to be open applications like paints, and caulk . Therefore PCB open applications and small capacitors need to be better addressed in the Stockholm

convention implementation, metal waste need to be better cleaned and areas where PCB have been managed in the past 50 years need to be better assessed for exposure via free range chicken and other livestock (https://doi.org/10.1016/j.emcon.2022.05.001) ;

11. Based on local and country specific needs the general preference for 100% local treatment of PCB waste is usually not the economic and environmentally sound solution. However an important part of available budgets is spend on (studying and coordinating) these projects without always achieving results. Best practices and bench marks are available for feasibility scans for organizations wishing to use the available budgets effective and efficient. The project studies in past years have shown how high the local investment and operational cost actually are for full local PCB treatment as opposed to the relative low cost for the 95% local solution.
12. Nano soil remediation was presented by Dra. Mª Carmen Lobo Bedmar: PCBs 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; being necessary the use of effective remediation techniques. Recently, nanotechnology has enabled the generation of new cost-effective and environmentally friendly remediation strategies, compared with traditional physico-chemical technologies. According to experimental assays, the use of nanoscale zero valent iron (nZVI) and pseudo-anaerobic conditions could be used for the recovery of soils co-contaminated with Cr and PCBs. PCB projects in emerging economies.

NEED FOR LOCAL TREATMENT, STOCKHOLM CONVENTION DEADLINE 2028, TRANSPORT AND EXPORT OBSTACLES

Dirk Jan Hoogendoorn Msc.

Orion b.v. Towards a cleaner world, CEO

Summary

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

Orion B.V. is an internationally operating company specialized in the treatment and handling of Polychlorinated Biphenyl's (PCB's). Orion was founded in 1985.
Orion's mission is to be recognized as a reliable partner in safeguarding the environment by safe and cost-effective removal and destruction of PCB containing equipment.
Our procedures foresee in packing the PCB-waste on location and sending it in containers to the Netherlands for destruction in our treatment facility in Drachten or to deliver the waste at local PCB waste treatment facilities.
Orion is not unique in providing this kind of service, however as a dedicated and specialized company we have (a need for) an unique and different philosophy.
Our vision is to transfer know-how and expertise to local partners aiming to enable each country to have a company trained in the handling of PCB waste. In our experience the advantages are:

- "In country" competence to offer transformer life cycle management and to handle PCB waste and PCB calamities;
- Trust, understanding and good communications between the local company, the environmental authorities, the owners of the PCB waste and Orion;
- Much employment and revenues remain in the local economy;
- Local temporary storage is created, so PCB waste disposal is also available to owners of small PCB waste amounts;
- Fast and professional domestic intervention in case of a calamity;
- Local processing of PCB liquids assures that 95% of the hazardous substances does not have to be exported;
- Combination of "end of life" treatment with "life cycle management" for transformers in order to re-use as much resources at the highest possible level in the "Waste Hierarcy".

Our treatment technology is comparatively low cost to build and to operate. Orion is using this technology already for over 20 years. One of Orion's unique features is to use no heating for the rinsing/washing nor for the distillation of the solvents. This is safe, easy to use and very cost effective.
Through international partnerships and cooperation we realize high economic value at low environmental impact, all in line with modern Corporate Social Responsibility (CSR) through strategic partnerships and innovative business models.
In the past years Orion and her local partners studied the feasibility of building a local treatment facility in emerging economies.

The following table shows the treatment cost estimates:

Typical estimated local treatment cost - summary	**Amount**
Capital expenditure	€ 3.500.000
Fixed cost	€ 830.000
Variable cost per kg	€ 0,23
Margin	30%
Total cost per kg, annual volume 500 000 kg typical project guarantee	**€ 2,46**
Total cost per kg, annual volume 1 000 000 kg	€ 1,38
Total cost per kg, annual volume 1 500 000 kg	€ 1,02
Total cost per kg, annual volume 2 000 000 kg	€ 0,84
Typical estimated export treatment cost	€ 0,50
Typical estimated sea transport cost	€ 0,35
Total cost per kg for export	**€ 0,85**

These number are based on a 10 year depreciation of the capital expenditure.

The conclusion is that local treatment cost can match the cost of export at an annual treatment volume of transformers for disposal (out of use) of 2 000 000 kg for 10 years.

However the typical capacity building project for PCB waste (out of use transformer disposal) has a size of 500 000 kg transformers for 1 or 2 years with no guarantee or budget for the following 8 years required to earn back the capital expenditure.

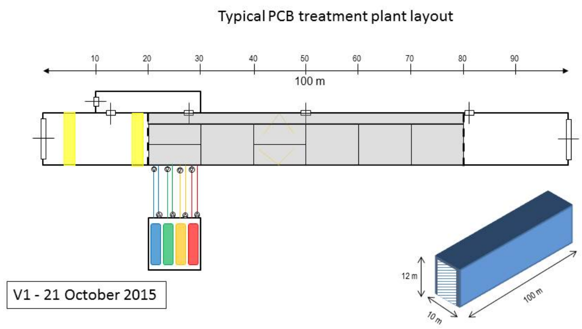

FIGURE 1. TYPICAL PCB TREATMENT PLANT LAYOUT

How to avoid the capital expenditure and get 95% local treatment of the PCB waste instead of 100% local treatment

The strategy to avoid a euro 3 500 000 investment in a treatment facility for PCB transformers and still have 95% of all the PCB's treated locally consists of three approaches:

1) **Re-use of low PCB contaminated oil transformers** by changing the contaminated oil for clean oil. This operation typically reduces the PCB content in the transformer to 10% of the original PCB concentration. In a country with a PCB limit of 50 ppm PCB in oil the oil change operation is economically feasible up to levels of 500 ppm PCB in oil.
   The majority of PCB contaminated oil transformers contains PCB levels below 500 ppm. However this treatment is only effective for transformers that are in use because the PCB contamination in the active part (the core) of the transformer will only leach out during operation in approximately 6 months. For that reason it is important to start this treatment as soon as possible as part of the regular transformer maintenance.
2) **The use of local cement kilns for co-processing** the PCB containing oils from transformers in use and from "end of life" transformers.
3) **Export the metallic parts** (drained transformers) that contains only 5% of the PCBs in the wood and the paper for treatment.
   The oil in the transformer contains 95% of the PCB's. By only treating this PCB containing oil locally the country is already processing 95% of the PCB's. The additional benefit of re-using the transformers < 500 ppm PCB contamination that are still in the electricity grid, on average 50% of the population of PCB transformers, raises the local treatment percentage even more.

At an additional investment of typically euro 800 000 an oil treatment plant can be used to remove the PCBs from internal transformer oils. This oil can then be used to change the oil in PCB contaminated mineral oil transformers for re-use.

PCB MANAGEMENT AND ELIMINATION IN MOLDOVA

Barbarasa, I., Plesca, V., Cupcea, L., Marduhaeva, L.

Chisinau, Republic of Moldova

Summary

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 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 was developed and approved in 2009 with a view to provide a legal framework for environmental sound management for PCBs and equipment containing PCBs, 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 26,000 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 550 units of PCB contaminated equipment were detected, the total amount of contaminated oil making up about 180 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.

Alongside these activities, PCB-containing electrical capacitors from 13 transformer stations of Moldelectrica State Enterprise were eliminated and the remediation of contaminated site carried out. 18,660 PCB-containing capacitors (934 tons in total) were dismantled, shipped abroad and disposed of. Based on a results of the feasibility study, remediation works were carried out on the contaminated area at the Vulcanesti 400 kV transformer station. Approx. 15,000 square meters were cleaned and about 3,500 cubic meters of PCB-contaminated soil were isolated in two cofferdams built on the territory of the station.

Keywords

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

Introduction

Polychlorinated Biphenyls (PCBs) are one of the leading members in the group of POPs identified by the international community for immediate international action by means of the Stockholm Convention. PCBs and PCB-containing equipment have never been produced in Republic of Moldova, but until 2000 the country had had an unusually high amount of PCBs requiring disposal. It was cause by the fact that in the soviet period it was an energy hub transmitting electricity to Balkans. Most of the PCBs were concentrated in electrical power installations, i.e. in dielectric oils in transformers and especially in capacitors.

Large power capacitors were used by the power transmission companies and large consumers of electricity. According to the inventory undertaken as part of the NIP preparation, almost 20,000 PCB-containing capacitors were located in 20 electrical substations throughout the country. All substations with capacitors were owned by the two transmission companies "Moldelectrica" and "Dnesterenergo" (Transnistria region, uncontrolled by the Moldovan authorities).

For the development of a PCB management system a detailed inventory of PCBs in transformers, switches and other electrical equipment (closed systems) was also needed. According to an inventory of the electrical equipment in use, carried out as part of the NIP preparation, approximately 23,000 power transformers were in use in the country. Of these about 2,500 belongs to large consumers of electricity. The total content of oil in the transformers is approximately 18,000 tons and about 5,400 tons in switches, inductors and other equipment. Besides transformers originally filled with PCBs, an unknown number of the transformers in use could be contaminated by PCBs by cross-contamination during the maintenance of transformers.

Moldova started solving the PCB issues in 2004 after ratification of the Convention and approval of the NIP, with both own means and international support.

The actions undertaken for the sound management and elimination of PCBs were focused on strengthening of regulatory framework, national inventory of PCBs in transformer oils and disposal of electrical capacitors with PCBs – actions carried out within the GEF/WB "*Persistent Organic Pollutants Stockpiles Management and Destruction Project"*.

Strengthening of regulatory framework on PCBs

The basic document providing a legal framework for environmental sound management for PCBs and equipment containing PCBs is the *Regulation on Polychlorinated Biphenyls* that was developed and approved by the Government in February 2009. This regulation was developed based on the Governmental Decision 1155/2004 on the Strategy on the reduction and elimination of POPs and on the National Implementation Plan for the Stockholm Convention on POPs.

The main elements established by the Regulation on PCBs are:

- production, placing on the market, use and maintenance of PCBs and equipment containing PCBs. It implements the deadline for phasing out of PCB-containing equipment set in the UNECE POPs Protocol;
- for what, by whom and how inventory of PCB-containing equipment shall be made;
- labelling;
- provisions for storage, decontamination and disposal of equipment containing PCBs. It implements the deadline for disposal/ decontamination of PCB-containing equipment set in the UNECE POPs Protocol;
- analyses of PCBs;
- permitting requirements including how to apply and the condition for obtaining a permit;
- administrative provisions, including enforcement;
- penalties for non-compliance with the Regulation.

This Regulation is part of an overall legislation package for hazardous chemicals and waste management implementing international POPs Treaties and key EU chemicals and waste legislation.

As part of the legal framework for PCBs management, in order to support public and private organizations and enterprises dealing with PCB-containing equipment and PCB wastes within an environmentally sound management, the *Handbook "Environmental Sound PCB Management in Electrical Equipment"* was developed.

The handbook supports the introduction of a management system for recording, monitoring and environment-friendly disposal of PCB-contaminated electrical equipment in Moldova. It is intended for technicians and engineers from the Republic of Moldova who professionally handle equipment and products suspected to contain or containing PCBs.

The Handbook provides assistance from identification to maintenance of respective equipment, phase-out of contaminated installations as well as transport, interim storage and final disposal of PCB-containing materials or wastes. Furthermore, safety aspects and emergency actions form an integral and essential part of the document.

Inventory of PCBs in electrical equipment

An inventory registration system and national database for electrical equipment containing or contaminated with PCBs above a concentration of 50 ppm have been developed and will serve for its further management and gradual elimination, as required by the international agreements and national legislation.

Objectives of the inventory

The inventory of PCBs in Moldova was launched in September 2008. The goal of the inventory was to create a reliable database that would describe the electric power equipment which contains dielectric oil of PCBs type in concentrations higher than 50 ppm for a volume of more than 5 liters. The PCB inventory can therefore be regarded as a basis for all future PCB management decisions.

The objectives of the inventory were:

1. identification of the holders of electrical equipment with dielectric oil, mainly in the electricity sector;
2. sampling and laboratory analysis of dielectric oil;
3. informing the holders of electrical equipment with dielectric oil about the impact of PCBs and the necessity of the inventory;
4. establishing a database containing information on PCB equipment.

Organizing and coordinating the inventory process

An established Steering Committee, which included representatives of the Ministry of Environment, the Ministry of Economy (energetic sector), electricity enterprises and consumers, was responsible for coordination and supervision of the inventory in accordance with national regulations and procedures, and for providing the necessary support in organizing the project implementation process and carrying out field works.

Full management related to the PCB inventory in the energy sector, focused on closed systems (i.e. power electrical transformers and capacitors), was ensured by the POPs Sustainable Management PMT, Ministry of Environment, assisted by two consultants, one local and one international, as well as the State Energy Inspectorate, which plays an important role in the inventory of the electrical

equipment owned by small consumers and private companies.
The basic document that has guided the process was the *Regulation on Polychlorinated Biphenyls.* The practical activities carried out by the personnel involved in the inventory process were facilitated by the *PCB Management Handbook* that describes all stages of inventory and management of potential PCB contaminated equipment, including requirements of the international conventions and national legal framework, general information and hazard potential of PCBs, identification and monitoring of PCB, PCB management, maintenance of equipment containing PCB, safety, emergency actions and clean up, phase out, packing, temporary storage, transport and disposal.

FIGURE 1. L2000DX ANALYSER

The inventory in the electricity sector covers four power production companies, one power transportation company and three power distribution companies.
At each company from the energy sector inventory teams were created, trained on sampling procedure and supplied with the necessary equipment. A special inventory form containing information about the type of equipment, its owner, placement etc., was filled in for each sample according to PCB Regulation.
The samples were examined in two stages: by screening all samples using the L2000DX Analyzer at the first stage, when the results can be negative or false positive, and in the second stage, by gas-chromatographic analysis of the false positive samples, after which we obtain negative or positive results, i.e. the samples which contain PCBs above 50 ppm.
To train personnel in the use of the analyzer and to ensure the quality of data, a training workshop took place with the participation of international experts. Three analytical centers were established at the biggest electricity companies and personnel was trained. Another analytical laboratory, at the State Hydrometeorological Service, was responsible for screening the samples taken from small consumers and other private companies as well as for gas-chromatographic analysis of all false positive samples identified.
Food processing, construction, light industry, telecommunication enterprises, water supply and treatment companies and public institutions represent the second major group of holders of potentially PCB-contaminated electrical equipment. The risk of exposure in these companies could be much higher than in the electricity sector, as these entities do not have trained maintenance or repair staff.
To identify holders and carry out the inventory, three trained consultants were equipped with all necessary tools and automobiles and accompanied by the territorial energy inspectors during site visits. Samples were taken by the person responsible for the equipment, under the supervision of the consultant, who filled in the inventory form, took pictures and registered the GPS data of the equipment. The selected samples were analyzed by the laboratory of the State Hydrometeorological Service.

Results of the inventory

The national inventory of PCBs included about 26,000 units of electrical equipment owned by 4 production companies (CET-1, CET-2, CET-Nord, CHE Costesti-Stanca), one transport company (S.E. "Moldelectrica") and 3 electricity distribution companies (RED Union Fenosa, RED Nord, RED Nord-Vest), as well as over 7,800 electricity consumers.

TABLE 1. RESULTS OF PCBS INVENTORY IN THE ELECTRICAL EQUIPMENT

Întreprinderea Undertaking	Samples taken and tested	Detected false positive samples	Samples containing PCBs > 50 ppm	Amount of oil in contaminated equipment, kg
RED Union Fenosa	7831	715	158	76207
RED NORD	3455	87	4	8685
RED NORD-VEST	1849	5	2	948
S.E. MOLDELECTRICA	4212	622	300	86960
CET-1, Chisinau	71	7	0	
CET-2, Chisinau	184	0	0	

Întreprinderea Undertaking	Samples taken and tested	Detected false positive samples	Samples containing PCBs > 50 ppm	Amount of oil in contaminated equipment, kg
CET-Nord, Balti	159	5	0	
CHE Costesti-Stanca	80	15	1	2700
Consumers	7849	380	81	785
TOTAL	25770	1836	546	176285

The inspected equipment was then labeled with red labels for contaminated equipment and green for PCB free units.
The electrical equipment contaminated with PCBs is to be managed during the period of operation in safe conditions, taken out of use and disposed of in accordance with the provisions of the Regulation on Polychlorinated Biphenyls.

Elimination of PCB-containing capacitors

According to the preliminary data, before starting the elimination of PCB-containing capacitors, the State Enterprise "Moldelectrica" owned about 20,000 capacitors at 13 transformer stations. Of these, 12,000 capacitors were kept in one assembly consisting of 18 capacitor batteries at the Vulcanesti 450 kV Station. About 300 discarded capacitors were kept in closed containers at the station. Also, two dumps with approximately 1000 broken capacitors each were located at this substation giving a total of 13,000 spent capacitors in Vulcanesti.
The capacitors at the Vulcanesti station were taken into use in 1972. Due to voltage surges in two incidents in 1974 and 1978 approximately 1,000 capacitors exploded in each incident and the contents were partly dissipated on the ground below the batteries. The remaining parts of the capacitors from each incident were buried in a pit of reportedly 6-10 meters in depth. The pits were without any lining. The location of the two pits on the territory of the substation was approximately known.
By the explosions of capacitors in the 1970'ies and releases from corroded capacitors during the last 30 years, the ground below the capacitor assembly in Vulcanesti has been highly contaminated. The capacitor assembly covers an area of about 10,000 m^2; of this about 2,700 m^2 just below the 18 capacitor batteries.
In Vulcanesti substation and most of the other substations the capacitors have not been in operation since the collapse of the Soviet Union around 1990, however, some of the batteries have been used periodically during wintertime. The total PCB content in 20,000 capacitors (excluding the pits at Vulcanesti) were estimated at 380 tons while the total weight of the capacitors was considered at approximately 1,080 tons.
Elimination PCB capacitors was carried out in 2006-2007 under the *POPs Stockpiles Management and Destruction Project*. At that time the priorities were established on the evacuation and destruction of all PCB-containing electrical capacitors from 13 transformer stations. As a result, 18,660 electrical capacitors containing PCBs found in the country (934 tons, including highly polluted soil from Vulcanesti station) have been dismantled/ excavated, shipped and disposed of in France.


Also, at Vulcanesti station approx. 2,000 m^3 of less contaminated soil were isolated in two cofferdams on the territory of the station, applying the techniques described in /1/. Later, in 2010, based on a feasibility study, the broader remediation works of the contaminated area at this station were carried out. All the metal constructions left after removing the capacitors were dismantled and evacuated and the concrete supports were excavated. An area of approx. 15,000 m^2 was cleaned and about 3500 m^3 of soil contaminated with PCBs were isolated in a third cofferdam built on the territory of the station. The cleaned area was covered with a 50 cm layer of clean soil and planted with trees and shrubs.

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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) and nano-magnetite (nFe_3O_4)) for the remediation of an industrial soil co-contaminated with Cr and PCBs. Iron nanoparticles were extensively characterized prior 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 was 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.

Introduction

Soil pollution is a worldwide issue due to its adverse effects on the ecosystem and human health (FAO and ITPS 2015). The majority of pollutants have anthropogenic origins, such as industrial processes, mining, transport, use of agrochemicals, and land application of sewage sludge. Among the most common soil pollutants are persistent organic pollutants and metal(loid)s (van Liedekerke et al., 2014). In many cases metal(loid)s and organic pollutants co-exist in the soil (Baragaño et al., 2020). Among metal(loid)s, Cr is widely used in many industrial activities because of its corrosion-resistant properties. It generally exists in two forms, an immobile Cr(III) species under reducing conditions and a highly mobile and toxic Cr(VI) species under oxidizing conditions (Choppala et al. 2013). 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 (Lobo and Gil-Díaz 2021). There are about 209 possible congeners depending on the substitution of the chlorine atoms around the biphenyl molecule, but PCBs research has been mainly focused on a few number of representative congeners which largely contribute to the total amount found in the environment, such as PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180. The exposure to PCBs, metals and metalloids poses a serious risk for both human health and the environment, thus the development of effective remediation techniques is very important and should be prioritized.

Recently, nanotechnology has enabled the generation of new cost-effective and environmentally friendly remediation strategies, compared with traditional physico-chemical technologies. Nanoparticles have a large specific surface area which contributes to increase the rate of reaction with pollutants (Wang and Zhang, 1997). In this regard, nanoscale zero valent iron (nZVI) has been found to be effective in the immobilization of metals and metalloids in water and soil samples (Gil-Diaz et al. 2017, 2019, 2021), and some researches have shown its potential for degradation of organic pollutants. The use of bimetallic nZVI, obtained from the addition of small amounts of a transition metal such as Pd, increases the reactivity of nZVI. Nanomagnetite (nFe3O4) shows important adsorption capacities which can be interesting in decontamination strategies (Pérez et al., 2015).

The main objective of this study was to evaluate the ability of three types of commercial iron nanoparticles (nZVI, nZVI-Pd, and nFe_3O_4) for the remediation of an industrial soil co-contaminated with Cr and PCBs.

Methodology

Soil samples from an industrial area historically polluted with PCBs were collected from the surface layer (0-30 cm), air-dried and sieved (<2 mm) before characterization (Table 1).

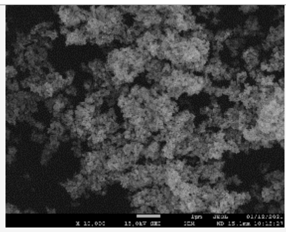
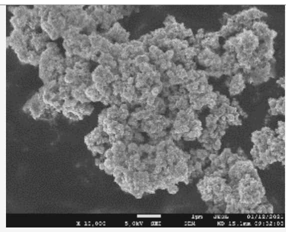
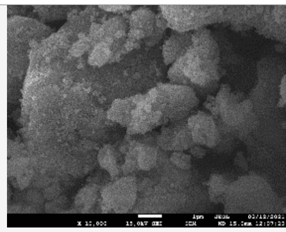
TABLE 1. PHYSICO-CHEMICAL CHARACTERISTICS OF THE SOIL

pH	EC	N	OM	Ca	Mg	Na	K	Cd	Cr	Cr^{6+}	Cu	Ni	Pb	Zn	Sand	Silt	Clay	PCB28	PCB52	PCB101	PCB138	PCB153	PCB180
	dS/m	%		mg/kg											%			ng/g					
6.29	2.7	0.06	0.81	594	90	31	155	<LD	214	65	9.1	<LD	10	30	64	25	11	33.9	193	512	719	531	292

Fifteen grams of soil sample was weighted in a plastic tube (50 mL Falcon) and mixed with the iron nanoparticles at 10% (20 g Fe/kg) dose for nZVI and nZVI-Pd, and 5% for nFe_3O_4 (36.2 g Fe/kg). The mixture was homogenized, and 35 mL of water was added to completely fill the tube and minimize the presence of oxygen to prevent nanoparticle oxidation. Tubes were incubated at 28ºC in a climatic chamber, at darkness for 15, 45 and 70 days. Experiments were carried out in triplicate. In each sampling time, tubes were centrifuged, and supernatant was collected with a Pasteur pipette, filtered and stored at 4ºC until PCBs and Cr analysis were carried out. Soil was air dried before analytical determinations. PCBs was analyzed after extraction with ethyl acetate in a Florisil column followed by quantitation by GC-MS (Gil-Díaz et al., 2022). Hexavalent chromium was determined using ion chromatography with an UV-VIS detector. Cr leachability in soil were performed according to the TCLP (Toxicity Characteristic Leaching Procedure) test (USEPA 1311). Iron nanoparticles were characterized prior use (Table 2). More details can be found in previous studies (Gil-Díaz et al., 2021, 2022).

Difference among treatments were determined by one-way analysis of variance at significance level of $p < 0.05$, followed by a Tukey post-hoc test (IBM SPSS Statictics 23).

TABLE 2. CHARACTERISTICS OF THE IRON NANOPARTICLES.

Characteristic	nZVI	nZVI-Pd	nFe_3O_4
Producer	NanoIron (Czech Republic)	NanoIron (Czech Republic)	IoliTec Nanomaterials (Germany)
Physical state	Aqueous suspension (80% water)	Aqueous suspension (80% water)	Solid
Composition	14-18% Fe(0) y 2-6% Fe_3O_4	14-18% Fe(0) y 2-6% Fe_3O_4, Pd 0.1%	Iron(II,III) oxide >98%
Organic stabilizer	3% polyacrylic acid	3% polyacrylic acid	-
Mean diameter (nm)	60	< 50	20-30
Specific surface area (m^2/g)	25	30	90
SEM images			

Results and discussion

Cr in water and soil samples

The addition of nZVI, nZVI-Pd and nFe_3O_4 significantly reduced Cr concentration in the aqueous extracts at the three sampling times, whereas in control samples higher Cr concentration remained constant throughout the experiment (Figure 1a).

In relation to soil samples, the three iron nanoparticles reduced Cr availability according to the TCLP test and no significant differences were observed among treatments. The immobilization was stable for at least 70 days under the experimental conditions (Figure 1b).

Treatments with nZVI and nZVI-Pd showed a reduction of Cr(VI), whereas soil from nFe_3O_4 and control samples showed similar concentration of this cation. Thus, nZVI favored Cr(VI) reduction to Cr(III). According to the reduction potential (E^0 (Fe^{2+}) = -0.41 V, E^0 (Cr^{6+}) = 1.36 V), the reduction of Cr(VI) to Cr(III) is thermodynamically favorable forming $Cr(OH)_3$ and Cr–Fe (oxy)hydroxide.

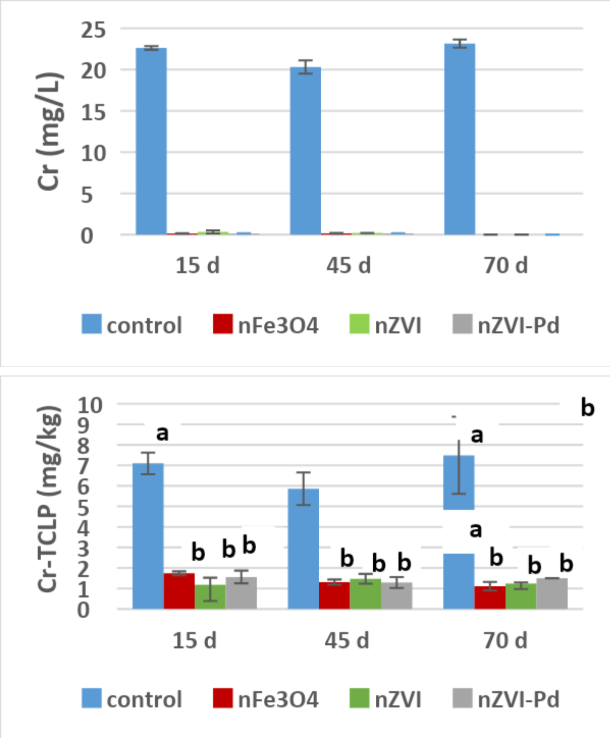


FIGURE 1. CHROMIUM CONCENTRATION IN AQUEOUS EXTRACT (A) AND CR LEACHABILITY (B) FOR DIFFERENT TREATMENTS.
For each sampling time, bars with the same letter do not differ significantly ($p<0.05$).

PCBs in water and soil samples

PCBs were not detected in aqueous fraction for any of the treatments at any sampling time, probably due to their high hydrophobicity.

After 15 days of interaction between polluted soil and iron nanoparticles, a significant decrease of PCBs was observed for all the studied PCBs (Figure 2). The three types of iron nanoparticles significantly reduced the PCBs concentration under the experimental conditions after 15 days; nFe_3O_4 and nZVI-Pd showed similar reduction results, and they were significantly more effective than nZVI for PCB101, PCB153 and PCB138.

However, the soil samples treated with nFe_3O_4 over a longer time period, 45 and 70 days, showed an increase in PCB content. We hypothesize that magnetite retains the PCBs by adsorption, but the interaction is reversible, and the PCBs are released over time. Thus, further studies are necessary to determine the optimum conditions of contact time, so as to evaluate the effectiveness of their use for reducing PCBs availability in soil, as well as the potential regeneration and reusability of the nFe_3O_4. In addition, due to the magnetic properties of nFe_3O_4, they could be easily separated from the soil under a magnetic field, regenerated and reused several times.

At short-term (15 days) nZVI-Pd proved more effective and faster than nZVI, especially for PCB101, PCB153 and PCB 138. However, after 45 and 70 days no significant differences were found in the concentration of PCBs between soils treated with nZVI and those treated with nZVI-Pd. ZVI nanoparticles can degrade PCBs by reductive dechlorination: the PCB molecule accepts the electrons from Fe0 oxidation and is reduced, replacing the Cl atoms with H atoms (Wei et al., 2006).

The study in relation to time showed the most important differences after 15 days. It was observed that the PCB concentrations did not significantly change in soils treated with nZVI-Pd after 45 and 70 days. In those treated with nZVI, only PCB101, PCB153 and PCB138 significantly decreased after 45 days, however no more reductions were observed at longer time. It can be due to iron nanoparticles (Gil-Diaz et al., 2022). This may be due to the loss of reactivity of the nanoparticles, as well as to the reduced availability of the contaminants in the soil.

The concentration of PCBs in control samples decreased after 45 days due to bioremediation process. These reductions are likely associated with anaerobic biodegradation processes because of the pseudo-anaerobic conditions. However, no more PCB reductions were observed at longer time (70 days), probably due to the lower availability of the remaining PCBs in soil matrix, which are not easily accessible for microbiota.

Conclusions

The treatment of a soil co-contaminated with Cr and PCBs with nZVI, nZVI-Pd or nFe_3O_4 significantly reduced the leachability of Cr and the immobilization was stable for at least 70 days under the experimental conditions. The nZVI and nZVI-Pd showed better results for the reduction of Cr(VI) to Cr(III) compared to that of nFe_3O_4. Regarding PCBs, they were not found in aqueous extract at any sampling time, whereas in soil, they significantly decreased after 15 days for the three types of iron nanoparticles. However, nFe_3O_4 showed a reversible behavior for PCBs adsorption. nZVI-Pd was the most effective reducing PCBs at 15 days, whereas after 45 days, nZVI and nZVI-Pd showed a similar degradation rate. PCB concentrations in control soils significantly decreased after 45 days probably due to bioremediation process reaching similar values to those found in soils treated with nZVI and nZVI-Pd. Thus, bioremediation could be the selected strategy for decontamination of soil only contaminated with PCBs but not when it also contains metal(loid)s such as Cr. Thus, the use of nZVI or nZVI-Pd and pseudo-anaerobic conditions could be a strategy for the remediation of soils co-contaminated with Cr and PCBs.

Acknowledgments

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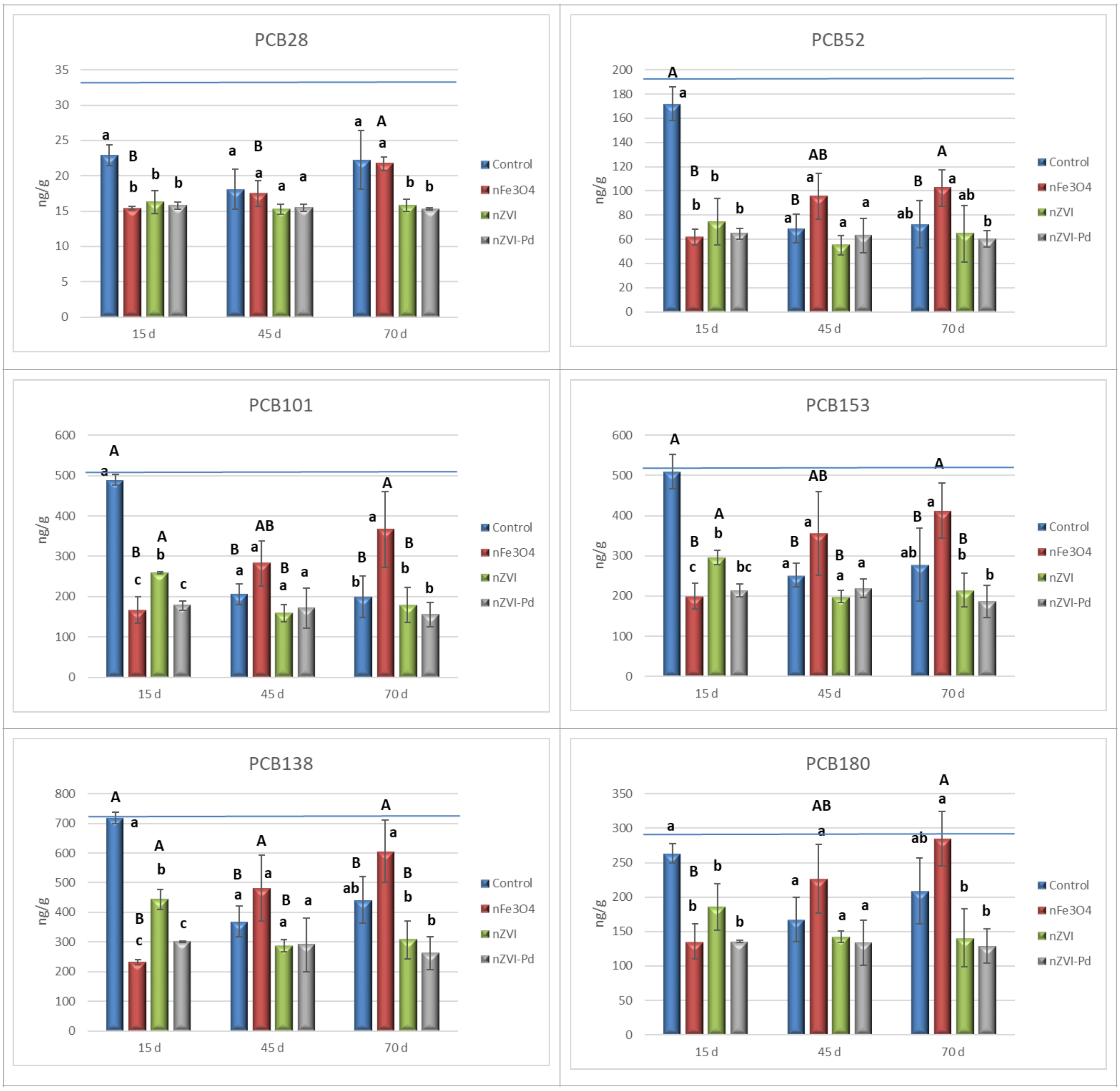

FIGURE 2. MEAN CONCENTRATION OF PCBS (NG/G) IN SOIL SAMPLES AT THE DIFFERENT SAMPLINGS. BARS WITH THE SAME LETTER DO NOT DIFFER SIGNIFICANTLY ($P < 0.05$); LOWER LETTERS COMPARE AMONG TREATMENTS FOR THE SAME SAMPLING; UPPER LETTERS COMPARE AMONG SAMPLING TIMES FOR THE SAME TREATMENT. BLUE HORIZONTAL LINE INDICATES THE INITIAL PCB CONCENTRATION.

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

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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

1. Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) or polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) elicit toxic effects including e.g. adverse reproductive effects, neurodevelopmental impairment, damage to the immune system, and endocrine disruption as well as cancer (Carpenter et al. 2003; IARC 2015).

Food is a major exposure pathway for PCBs to humans (Rose and Fernandes 2013; Weber et al. 2018a,b). Food producing animals and related products (meat, milk and eggs) can become PCB contaminated along the life cycle of PCBs and related soil contamination the past nearly 100 years (Figure 1; Weber 2018a,b). Free range livestock ingest soil or grass contaminated with PCBs with related human exposure. Therefore site where PCBs were produced, used or disposed need to be assessed and exposure pathways need to be reduced and eliminated (Weber et a. 2018a,b).

PCB production sites were large emitters of PCBs with associated contamination of the production sites, the landfills and the wider environment including animals and population (ATSDR 2015; Kocan et al. 2001; Turrio-Baldassarri et al. 2009; Watson 2017; Wimmerova et al. 2015). Also factories formerly using PCB in production processes have contaminated the environment (Weber et al. 2018a,b). While in industrial countries PCB productions, PCB use sites and PCB management and disposal sites are all relevant for environmental and human contamination, developing countries did not have PCB production but are in particular contaminated from end of life management of PCBs.

Eggs as food are of importance in feeding the population, as they are a relatively inexpensive and a rich food source of very high biological value. The daily animal protein requirement for the human body can be covered with eggs in the cheapest way and with the lowest environmental impact (Molnár and Szőllősi 2020). Eggs are a highly nutritious food containing vital vitamins (A, D, E, B1, B2, B3, pantothenic acid, B6, folic acid, vitamin B12), are very rich in minerals (Fe, Zn, Cu, Mg, I, Se, Ca, P, K) and contain 18 amino acids, nine of which are essential (Molnár and Szőllősi 2020).

Contaminated soil is a high risk for global food production (FAO and UNEP 2021). Assessments of levels of PCBs and PCDD/Fs in chicken eggs and soil have shown that surprisingly low concentrations of PCBs or PCDD/Fs in soil can result in exceedances of regulatory limits in chicken eggs and meat due to the chicken's behaviour of ingesting higher amount of soil than other farm animals per body weight (Schuler et al. 1997; Weber et al. 2018a, 2019). Due to the high soil intake ratio of free-range chickens and transfer of POP pollutants into egg, chicken eggs are ideal “active samplers” and indicators for PCB and other POP contaminated soils.

In this study we compiled information on the PCB contamination of eggs from free-range chickens in a systematic manner in respect to contamination sources and areas in a wide range of countries. A major resource for this review were the studies of the International Pollutants Elimination Network (IPEN; formerly International POPs Elimination Network), an international network of more than 600 public interest NGOs from more than 120 countries (https://ipen.org/about) and Arnika Association which monitored POPs in eggs near 100 potential pollution sources since the beginning of the Stockholm Convention in 2004 (Petrlik et al 2022). This monitoring filled many of the large gaps in egg data from developing countries. This review also includes data of eggs from peer reviewed literature in particular for sites where POP levels in eggs were above regulatory limits.

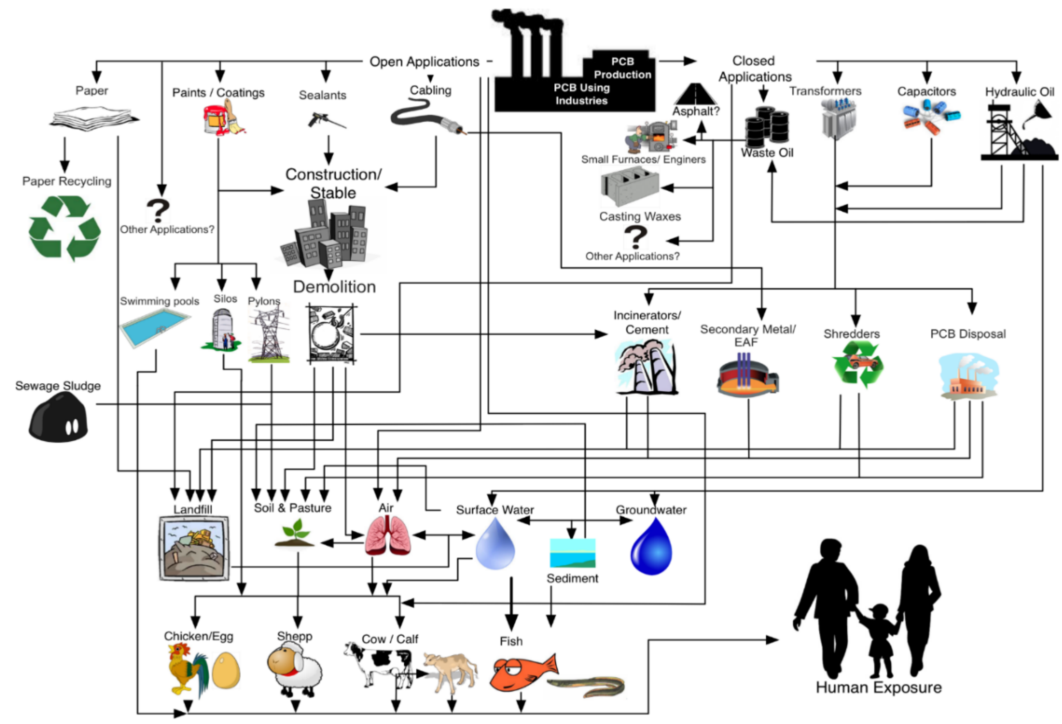

FIGURE 1: LIFE CYCLE OF PCBS AND RELATED RELEASES TO THE ENVIRONMENT AND EXPOSURE TO FOOD PRODUCING ANIMALS (WEBER ET AL. 2018B)

2. *Materials and methods*

2.1. Information from global monitoring of IPEN/ Arnika POPs in eggs project

At the start of the Stockholm Convention, IPEN and Arnika, in cooperation with many public interest NGOs, started sampling of free-range chicken eggs in many developing countries and countries with economies in transition from four continents (Asia, Africa, Europe and America). The sampling focused on different industrial sites and sites influenced by waste management or known or suspected contaminated sites. Their results were published in a range of reports focused on Africa (Cameroon, Ghana) (Petrlik et al. 2019a); Armenia (Petrlík and Straková 2018, Grechko et al. 2021), Bosnia and Herzegovina, Montenegro, Serbia (Petrlik and Behnisch 2015), China (Petrlik 2015), Indonesia (Petrlik et al. 2019a,b, Petrlik et al. 2020), Kazakhstan (Petrlik 2016b), Moldova (Petrlik et al. 2022), Ukraine (Petrlik et al. 2018b), Thailand (Petrlik et al. 2017), and sites specifically affected by waste incineration residues in Asia and Europe (Petrlik and Bell 2017). Normally between 2 to 6 eggs were pooled for analysis of one flock.

In total, the egg survey of IPEN included 127 pooled egg samples which were analysed for PCDD/Fs and dl-PCBs. This included 113 pooled egg samples from free-range chickens taken in the vicinity of various industrial/commercial sites and dumpsites mainly in developing and emerging economies. Some eggs were analysed with DR CALUX bioassay for total dioxin-like toxicity.

The TEQ values were calculated according to the 2005 WHO re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds (van den Berg et al. 2006).

3. *Results and discussion*

3.1. Exposure of chicken to PCBs and PCDD/Fs

Chickens have several exposure pathways to POPs like PCDD/Fs and PCBs. The major exposure pathways are: soil, feed, animal bedding as well as specific point sources on a farm (Figure 1). Some specific information on the exposure sources are briefly introduced here while the main focus of the review is on free-range poultry around pollution sources and contamination of eggs which is mainly triggered by soil pollution (Kijlstra et al. 2007; Weber et al. 2018a,b; 2019).

The average exposure to soil and pollutants strongly depends on the size of the chicken flock. Soil ingestion is high for smaller chicken flocks spending a lot of time outside (Kijlstra et al. 2007).

3.2. Overall outcome of chicken eggs screening of IPEN around selected pollution sources

In total IPEN monitored 113 chicken flocks around potential PCB- and PCDD/F-contaminated sites near industries and other sources listed in the Stockholm Convention Annex C Part II (waste incinerators, secondary copper, secondary alumina and secondary zinc industry, sinter plants and cement kilns incinerating hazardous waste) and Part III (e.g. other metal industries, power plants, open burning/smouldering of copper cables).

The measured contamination levels were compared to the European Union maximum levels for PCDD/Fs and dioxin-like compounds in eggs of 2.5 pg PCDD/F-TEQ/g fat and 5 pg PCDD/F-PCB TEQ/g fat. In the IPEN monitoring, from the 113 sampled flocks around the potential pollution sources only 14 egg samples were compliant with the EU maximum limits and 99 egg samples were not. This means that 88% of egg sampled in the vicinity of emission sources were above regulatory limits for PCDD/Fs or the sum of PCDD/Fs and dl-PCBs. This demonstrates that close to 90% of these areas are not safe for the production of free-range eggs and that in 14% of the cases, a very high exposure risk exists and may even present a danger to health if such eggs are frequently consumed over an extended period of time (as is normally the case with families keeping chicken for private consumption). This also indicates that close to 90% of soils in the monitored suspect areas had PCDD/F or dl-PCB levels unfit for free-range chickens which is already reached at 2 to 4 ng TEQ/kg soil (Weber et al. 2019). Therefore soils at these sites are a major source for contamination of eggs by PCDD/Fs and PCBs. On some sites, hens had access to unsafely stored/distributed ashes from waste incineration and/or metal smelters (Petrlik et al. 2019a; Petrlik et al. 2020).

3.3. PCB contamination in eggs

PCBs play a specific role in the dioxin-like contamination of the world with a total dioxin-like content of 10,400 to 16,000 kg TEQ in the commercially produced 1.3 million tonnes of PCBs (Weber et al. 2008) which can be compared to approx. 100 kg TEQ release of PCDD/Fs per year from all sources and countries today (Wang et al. 2016). Furthermore PCBs are excellent precursors of PCDFs in incomplete combustion/pyrolysis processes with conversion rates in the percent range (Buser et al. 1978) and a related increase in TEQ up to 45 times (Weber 2007). The highest PCDD/F contaminated egg reported (713 pg PCDD/F-TEQ/g fat) originated from the PCB feed/food incident in Belgium which contained additionally high PCDD/Fs (van Larebeke et al. 2001). For this egg unfortunately the dl-PCBs were not measured (van Larebeke et al. 2001) but were likely in the same order of magnitude as known for the contaminated chicken fat and animal feed in this feed-food contamination incident (Covaci et al. 2002) highlighting the PCDD/F relevance of waste PCB incidents.

Figure 2 gives an overview on the highest dl-PCB-contaminated eggs (HC-PCB) measured in the study of IPEN (bars in figure striped) and literature data (bars in figure filled) and responsible sources.

From the 113 pooled eggs around pollution sources in the IPEN studies, 58 (51%) had dl-PCB content above 5 pg TEQ/g fat exceeding EU maximum limits just by PCB-TEQ alone and 20 samples had more than 14 pg PCB-TEQ/g fat (Figure 2). Therefore, the dl-PCB TEQ was a similar driver for total TEQ contamination compared to PCDD and PCDF combined which highlights the role of the commercial PCBs for contamination of eggs. This is in line with contribution of dl-PCBs to total TEQ of more than 50% in fish (Scientific Committee on Food 2000) and in butter in international studies (Weiss et al. 2005; Santillo et al. 2003) and highlights the role of industrial PCBs for global contamination of food from animal origins.

The largest share of PCBs detected in eggs originated from commercial PCBs as can be derived from the PCB patterns (see Figure 3). The PCB patterns of commercial mixtures have significant differences from the unintentionally-formed PCBs from thermal processes (see below Figures 3A-C). The high contribution of commercial PCBs can also be roughly derived from the contribution of dl-PCB to total TEQ: The TEQ contribution of PCBs formed in *de novo* synthesis in thermal processes is approx. 2 to 3% of the PCDD/Fs which can slightly increase in the air pollution control devices to a maximum contribution in the stack of approx. 7.5% (Sakurai et al. 2003). Therefore PCB-TEQ contamination in soils and eggs which exceeds approx. 7.5% of total TEQ is a strong indication that the PCBs stem mainly from commercial PCB mixtures.

PCB-TEQ had a high share of total TEQ in major source categories, in particular around metal industries (see Section 3.3.1), shredder plants and recycling (Section 3.3.2), e-waste sites (Section 3.3.3), hot spots at farms (Section 3.3.4) and around dump sites (Section 3.3.5). This highlights a very relevant PCB release in the end-of-life management/treatment of PCB containing equipment in particular in developing countries and related human exposure via the food chain. Egg monitoring around metal industries

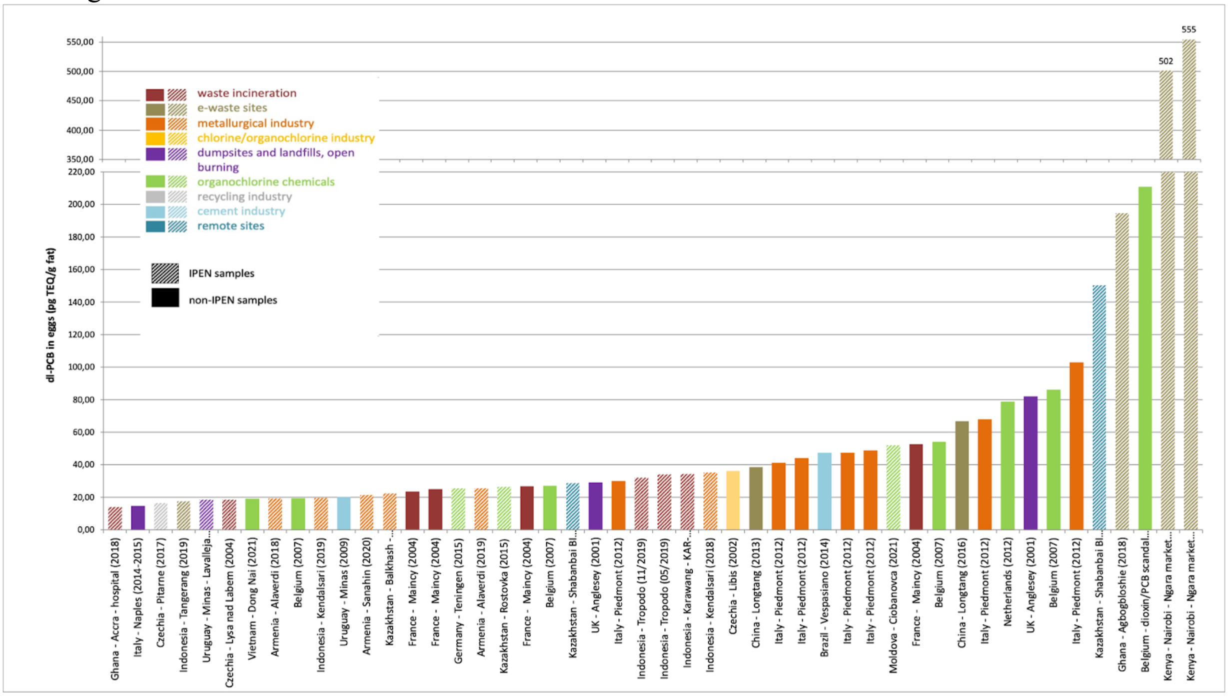

FIGURE 2. HIGHEST DL-PCB-CONTAMINATED EGGS AND RELATED SOURCES MEASURED WITHIN IPEN STUDIES (STRIPED BARS) AND FROM OTHER SCIENTIFIC LITERATURE STUDIES (FILLED BARS).
Please note that the origin for almost all sources are commercial PCBs (Figure 3) (Petrlik et al. 2022)

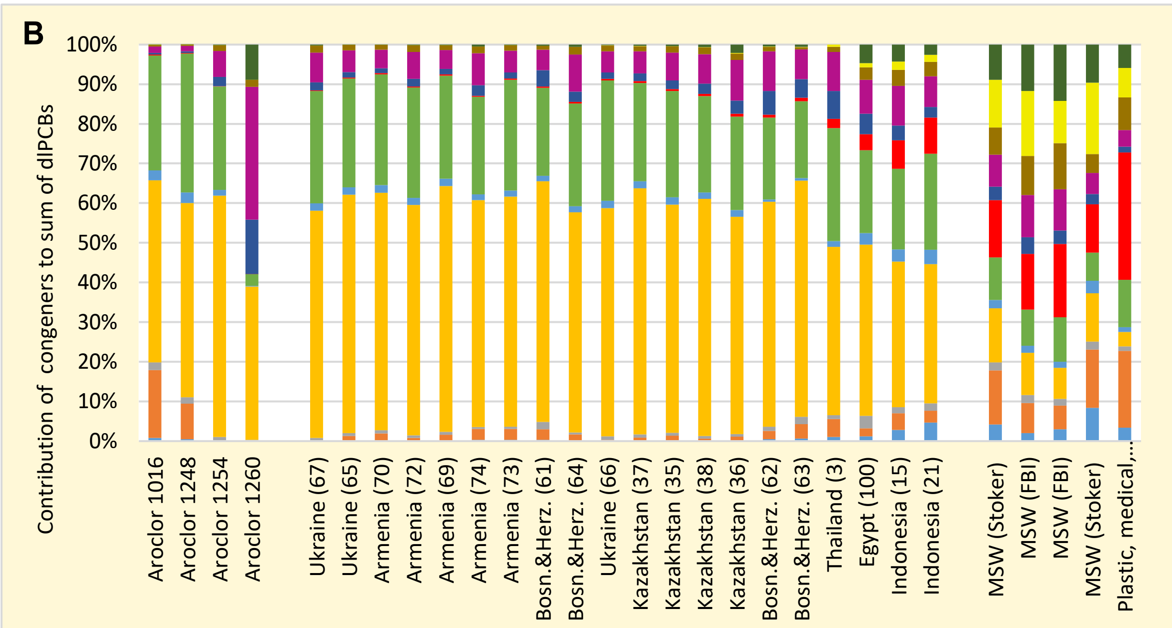

FIGURE 3. DL-PCB PATTERNS CALCULATED FOR SOILS BASED ON EGG CONTAMINATION AROUND METAL INDUSTRIES (CONCENTRATIONS OF DL-PCB CONGENERS IN EGGS FROM IPEN MONITORING WERE RE-CALCULATED TO DL-PCB CONCENTRATIONS IN SOILS BASED ON TRANSFER FACTORS).
Sites are sorted with increasing ratios of PCB-126/sum dl-PCBs, and compared to dl-PCBs in major technical Aroclor PCB-mixtures (Petrlik et al. 2022)

3.3.1. Eggs monitored around metal industries

IPEN monitored 21 pooled eggs from chicken flocks around metal industries in 7 countries (Armenia, Bosnia and Herzegovina, Egypt, Indonesia, Kazakhstan, Thailand, and Ukraine). All chicken flocks exceeded the EU regulatory limits with 4.4 to 112.6 pg TEQ/g (Figure 4), Also the median (13.5 pg TEQ/g fat) and mean (26.0 pg TEQ/g fat) TEQ concentrations were high. This indicates that 100% of areas around these secondary metal smelters or primary steel industry were unfit for free-range chicken farming. It needs to be stressed that dl-PCBs had the highest TEQ-contribution in 15 of the 21 locations exceeding

PCDD- and PCDF-TEQs (Figure 4). The median dl-PCB concentration in the eggs was 9 pg TEQ/g fat and therefore contributed 67% of the median TEQ. Similarly a study from Italian authorities on TEQ in eggs close to an aluminium smelters had dl-PCB TEQ contributions between 66 to 91% (Squadrone et al. 2015) with 5 of the analysed chicken flocks in the top 20 of dl-PCBs detected in eggs (Figure 2). This demonstrates that PCBs are major TEQ-contributors around metal industries. The PCBs can enter smelters in scrap from transformers and capacitors as well as PCB-painted and coated metals (Weber et al. 2018b). The high share of PCB-TEQ from industrial PCBs (Figure 3) reveal the relevance of PCB contamination of the input metal scrap and PCB containing equipment (see Section 3.2.2.6). It also indicates that PCBs were released partly from scrap storage areas where PCB oils can seep into the ground with further release and that the scrap was likely subjected to a de-oiling procedure at temperature where PCBs evaporate but do not significantly transform to PCDF as seen by the low TEQ contribution of PCDFs compared to PCBs.

From the eggs sampled around metal industries almost all PCBs detected in the eggs originated from commercial PCB with negligible impact from unintentional PCBs formed from *de novo* synthesis (Figure 3). Only 3 of the eggs had some impact from unintentional thermal PCBs with 3 to 9% PCB-126 and 1 to 5% PCB-81 as thermal marker PCBs (Figure 3). In addition, 17 of the egg samples had an Aroclor 1254 pattern (Figure 3) which is the main PCB used in transformers, capacitors and cutting oils all with a high probability to partly end in metal smelters on contaminated metal parts.

The pooled egg samples from chicken flocks around secondary aluminium production in Indonesia where 136 secondary aluminium smelters operate had extremely high TEQ levels 84.6 pg TEQ/g fat (HC-PCB#22) and 60.5 pg TEQ/g fat (HC-PCB#39)) (Petrlik et al. 2020). This is comparable with the egg survey around an alumina smelter in Italy where 7 different chicken flocks sampled close to the plant had TEQ levels from 39 to 113 pg TEQ/g fat (Squadrone et al. 2015).

Eggs from 5 different flocks in Alaverdi city in Armenia where the Alaverdi copper smelting plant operated since the 18th century were highly contaminated with 40.2, 26.9 and 23.5 pg TEQ/g fat indicating a contamination of the wider city. The dl-PCB TEQ contribution ranged from 64 to 92% of total TEQ also demonstrating that industrial PCBs enter copper smelters possibly from copper coils and wiring of transformers. Furthermore metal industries have their own transformers which were considered a major PCB source for a metal plant in Italy (Liberti et al. 2014).

4 chicken flocks sampled in Balkhash city (Kazakhstan) where a large non-ferrous metals industry (including copper production) has been operating for several decades, were all contaminated from 12.7 to 30.1 pg PCDD/F-PCB-TEQ/g fat (Petrlik et al. 2016: Petrlik et al. 2018a; Figure 4). The two highest contaminated eggs (30.1 and 18.0 pg PCDD/F-PCB-TEQ/g fat) had a PCB-TEQ contribution of 74 and 76%, respectively. Also all 5 chicken flocks sampled in Zenica in Bosnia-Herzegovina where a steel complex with primary and secondary steel production operates since 1892, were contaminated from 4.4 to 8.8 pg PCDD/F-PCB-TEQ/g fat (Peterlik & Behnisch 2015). The two highest contaminated eggs in Zenica (8.8 and 8.4 pg PCDD/F-PCB-TEQ/g fat) had a PCB-TEQ contribution of 36 and 44%, respectively. Therefore, the PCDD/Fs and PCBs contamination in these two cities shows a relevant impact from the steel plant similar to the Italian steel plant (Liberti 2014).

3.3.2. Eggs monitored around shredder plants and related recycling area

High releases of PCBs have been detected from metal shredder plants with associated PCB contamination in the surrounding area areas (Bavarian LfU 2009; Gebhardt 2012).

In the IPEN global egg monitoring studies, pooled eggs from 6 chicken flocks around shredders and recycling plants were analysed from 3 countries (Belarus, Mexico and Czech Republic (4)). The PCDD/F-PCB-TEQ of the pooled egg samples ranged from 5.8 to 31.9 pg TEQ/g and therefore all chicken flocks exceeded the EU regulatory limit. This indicates that the areas around the three investigated shredder/recycling sites were unfit for free-range chicken farming.

The pooled egg from Belarus was sampled near a large car shredder plant in a small town (Gatovo) approx. 10 km south from Minsk and had TEQ levels of 15.6 pg TEQ/g fat with 73% contribution from dl-PCBs (Petrlik et al. 2019d). Also the chicken eggs close to an e-waste shredder plant and recycling workshops in Mexico (Guadalajara) were impacted with 6.8 pg TEQ/g fat with a contribution of 36% TEQ from PCB (Petrlik et al. 2021a). IPEN also sampled eggs in Pitarne village (Czech Republic) close to the Polish border near a recycling plant for cables wires and other PVC products that uses shredding to produce PVC roofing materials. Pooled egg samples from 4 flocks were sampled in the surrounding area (Petrlik et al. 2021a). All samples were above the EU maximum limit for eggs and ranged from 5.8 to 31.9 ng TEQ/g fat (Petrlik et al. 2021a). PCBs contributed between 52 to 79% which could possibly stem from PCBs formerly used as plastic additives in cables.

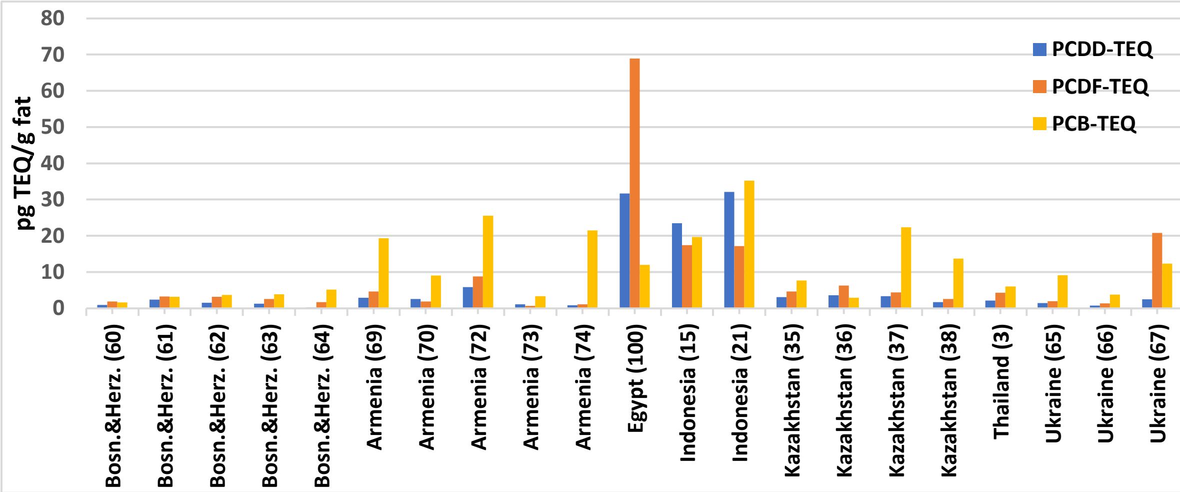

FIGURE 4. PCDD, PCDF AND DL-PCB TEQ CONTRIBUTION IN EGGS AROUND METAL INDUSTRIES SAMPLED WITHIN THE IPEN MONITORING (PETRLIK ET AL. 2022)

3.3.3. Egg monitoring at e-waste recycling sites in developing countries

E-waste recycling and dumping areas are another POP contaminated site type with increasing relevance over the past 20 years in particular where e-waste plastic and cables are openly burnt for recovery of copper and other metals (Wong et al. 2007; Labunska et al. 2015; Tue et al. 2016; Petrlik et al. 2019a) as described in BAT/BEP Guidelines of the Stockholm Convention (UNEP 2008) with high emission factors in the UNEP dioxin toolkit (UNEP 2013a).

IPEN monitored 7 pooled eggs from individual chicken flocks at such e-waste sites in 5 countries (Ghana, Kenya, Indonesia, Philippines, and Thailand). The PCDD/F-PCB-TEQs of all pooled eggs were between 20.4 to 855.8 pg TEQ/g and therefore all chicken flocks exceeded the EU regulatory limit. This indicates that such areas are frequently highly polluted with PCDD/Fs and PCBs. The median (95.7 pg TEQ/g fat) and mean (308.4 pg TEQ/g fat) TEQ concentrations were extremely high and by far the highest mean/median of all source categories. Three of the eggs from African sites had TEQ levels above 500 pg TEQ/g fat (more than 100 times above regulatory limits) with 855.8 pg TEQ/g fat in eggs from the e-waste site in Agbogbloshie (Ghana) where e-waste, including cables, is frequently burned (Petrlik e al. 2019a). The major TEQ contribution at this e-waste site came from PCDD/Fs (661 pg TEQ/g fat) with also a high contribution from dl-PCBs (194.8 pg PCB-TEQ/g fat; HC-PCB-egg#4) in agreement with the frequent open burning. On the other hand, pooled eggs from IPEN screening in Kenya at the Ngara e-waste dismantling market were contaminated with 567.4 and 519.6 pg TEQ/g fat with 97.8 and 96.6% TEQ contribution from dl-PCB which are the highest dl-PCB levels in free-range eggs ever measured (555 pg TEQ/g fat; HC-PCB#1 and 502 pg TEQ/g fat; HC-PCB#2; see Figure 2). Therefore PCB equipment is dismantled at this e-waste market but without open burning as seen with the low PCDD/F contribution of only 3% of TEQ comparable to the PCDD/F content in original PCB mixtures. This highlights that e-waste sites in Africa can be hotspots for high PCB contamination and exposure. Also from e-waste sites in China, high PCB contaminations were reported in free-range eggs (66.8 and 38.3 pg PCB-TEQ/g fat) (Zeng et al. 2018). These highly contaminated eggs from e-waste sites highlight the risk for the informal sector and related families from consuming eggs and other food produced at these sites. In addition to the urgent need to improve e-waste recycling in developing countries including stopping open e-waste and plastic burning and control of equipment containing PCB (small capacitors; transformers). The exposure from food production on these sites needs control and education.

3.3.4. PCB point sources on farms

The 4th highest dl-PCB-contaminated egg (150.4 PCB-TEQ pg/g fat; HC-PCB#4) was sampled by IPEN at a small farm in a pristine mountain area in Kazakhstan as reference background site but was obviously heavily impacted by a PCB point source on the farm (Petrlik et al. 2016). For the 9th HC-PCB egg (78.8 pg PCB-TEQ/g) the PCB point source on a farm in the Netherlands could be determined as PCB paints on the asbestos roof (Hogenboom et al. 2014). Similarly the 7th HC-PCB egg (86.15 pg PCB-TEQ/g) on a farm in Belgium without a particular industry close by was most likely contaminated by such a PCB point source, since the measured feed and soil were low in PCBs (van Overmeire et al. 2009). A range of further cases with contaminated eggs (and meat and milk) from farms with PCB paints on walls, silos and asbestos roofs have been documented in industrial countries as important point sources (Weber et al. 2018b). This highlights that PCB paints can be relevant PCB sources on farms and that within a national PCB inventory of the Stockholm Convention the assessment of past use of PCB paints and sealants is needed to understand the relevance for a particular country (UNEP 2017a; Weber et al. 2018b).

The 3rd highest dl-PCB-contaminated egg (211 pg PCB-TEQ/g fat; HC-PCB#3) stems from the PCB feed incident in Belgium (van Larebeke et al. 2001; Figure 2). In 1999 feed and food of thousands of farms in Belgium were contaminated with PCBs, because 50 kg PCB oils were not managed in an environmentally sound manner but were collected by the same companies which managed food fat and mixed with feed. This highlights the risk of mismanaged PCB for feed and food for the population of a country and beyond (van Larebeke et al. 2001; Fiedler et al. 2000).

3.3.5. Eggs monitoring at landfills and dump sites

Today dump sites receive roughly 40% of the world's waste and serve 3-4 billion people (ISWA 2016). More than 50% of PCBs were not adequately managed and were disposed in landfills and dump sites in the past (Breivik et al. 2007).

The IPEN monitoring of 20 chicken flocks around dump sites and waste burning sites in 12 developing countries revealed that most sites were contaminated (Figure 5): Mean and median TEQ of the 20 pooled egg samples were 17.7 and 14.3 pg TEQ/g fat highlighting relevant contamination and human exposure. 16 (80%) of the pooled eggs were above the EU regulatory limit for PCDD/F or sum of PCDD/F and dl-PCB. The pooled egg sample with the highest TEQ contamination (57 pg TEQ/g fat) was sampled in Moldova in the vicinity of the municipal waste landfill which serves the capital, Chisinau (Petrlík et al. 2022). PCBs contributed 91% to TEQ (51.9 pg TEQ/g fat; HC-PCB#14) indicating that PCBs have been disposed on this landfill. Also eggs from 7 other dump site areas had a higher TEQ-contribution from PCBs compared to PCDD or PCDF (Figure 5). Therefore commercial PCBs were major TEQ contributors for 35% of chicken flocks around the measured dump sites (Figure 5). This demonstrates relevant pollution and release of PCBs from landfills and dump sites in developing countries. The high TEQ-contribution of PCBs in eggs around dump sites can be explained by the large amount of PCB oils and waste having entered landfills and dump sites in the past. It is estimated that more than 50% of all PCBs produced have been disposed in landfills (Breivik et al. 2007).

Only two pooled egg samples from Koh Samui island in Thailand (1,0 and 1,3 pg TEQ/g fat) (Petrlik et al. 2018a,c) and the eggs around a landfill in Pakistan (3.3 pg TEQ/g fat) and Moldova (4.4 pg TEQ/g fat) were below the regulatory limit (5 pg TEQ/g fat).

The large differences in TEQ in eggs at landfills is in line with the large differences of PCDD/F-TEQ observed in soils around landfills in developing countries ranging from 1.5 ng TEQ/kg to 3342 ng TEQ/kg in a recent study (Martínez-Guijarro et al. 2019).

In addition, pooled eggs from two flocks close to a hazardous landfill in Germany (Eyller Berg) had twice the EU regulatory limit (10.4 and 8.7 pg TEQ/g fat) with a major contribution from dl-PCBs (Weber et al. 2018a). The dl-PCB levels in soils around this landfill were between 3.1 and 6.6 ng PCB-TEQ/ kg dm (LANUV 2012) six to ten times above background dl-PCB levels of German pastureland soil and sufficiently high to explain the contamination levels in the eggs (Weber et al. 2018a). This indicates that also in developed countries historic or long term releases from (hazardous) landfills can be a risk for chicken flocks in the vicinity.

3.4 Conclusions and policy recommendations

The large PCB (and PCDD/F) contamination along the life cycle of PCB including production, use and end of life treatment demonstrate that an overall assessment of PCB-contaminated sites along the life-cycle is needed (Weber et al. 2018b).

The large pollution detected at metal smelters, e-waste recycling sites, PCB use/storage sites and around landfills/dump sites highlights that an overall improvement of PCB management in end-of-life is urgently needed in developing and emerging economies and that care is needed when increasing PCB management pressure to meet the 2025 PCB phase-out and 2028 final PCB elimination goal of the Stockholm Convention (UNEP & UNITAR 2017; UNEP 2017b; UNEP 2018a). In addition, human exposure from the related PCB-contaminated sites and soils from past (and ongoing) PCB-releases need to be assessed. Contamination of food produced on such sites like eggs but also milk and meat needs to be assessed, controlled and eliminated.

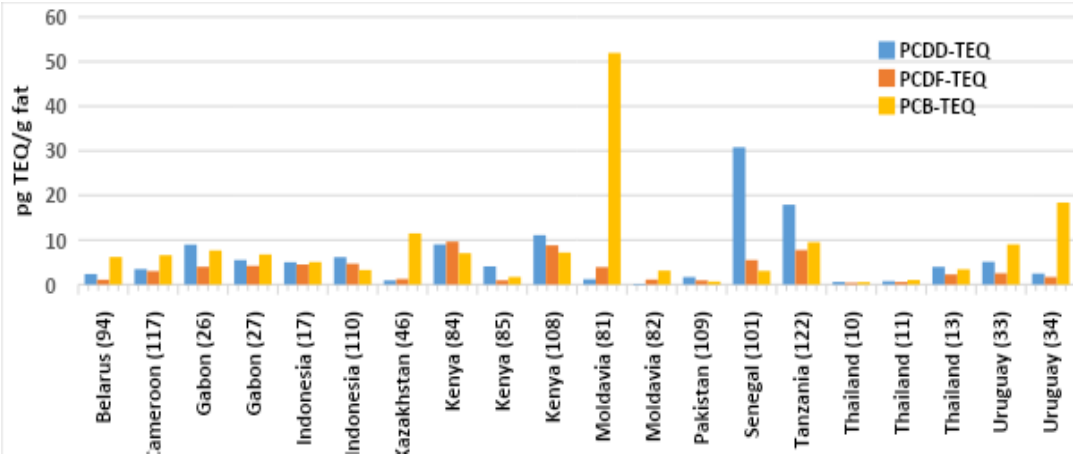

FIGURE 5: PCDD, PCDF AND DL-PCB TEQ CONTRIBUTION IN EGGS AROUND DUMP SITES SAMPLED WITHIN THE IPEN MONITORING (PETRLIK ET AL. 2022)

3.4.1. Overall conclusion on egg and soil contamination and related human exposure

The review of scientific literature and in particular the IPEN global egg monitoring in developing countries around industrial emission sources including e.g. waste incinerators, metal industries, recycling sites and dump sites, reveals that in many areas soils are polluted with PCBs and PCDD/Fs at levels at which free-range eggs can get highly contaminated (Petrlik et al. 2022).

Studies on chicken/egg - such as in the Netherlands (Kijlstra et al. 2007; Hoogenboom et al. 2016) or Germany (Weber et al. 2018a) - have indicated that eggs from free-range chickens foraging on soils with levels of 2 to 4 ng PCDD/F-TEQ/kg dm frequently exceed the EU maximum level for dioxins. This is in agreement with calculations, which also show that taking into account the soil intake of chickens (up to 31 g/day), soil levels around 2 ng TEQ/kg for PCDD/F and dl-PCB can be sufficiently high to reach the EU maximum levels of 2.5 pg TEQ/g fat for PCDD/Fs or 5 pg TEQ/g fat for the sum of PCDD/Fs and dl-PCBs. For children, daily consumption of one egg which reaches the EU regulatory limit, already leads to exceedance of the tolerable daily intake (TDI) of 2 pg TEQ/kg body weight set by the WHO (Weber et al. 2019). The soil-chicken-egg exposure pathway is therefore probably the most sensitive exposure path for PCBs and PCDD/Fs from soil to humans (Weber et al. 2019). Considering the high PCB levels (Figure 1) and PCDD/F levels (Petrlik et al. 2022) in many eggs, people – and especially young children - consuming these contaminated eggs are subjected to high exposure levels and can exceed health-based guidance values up to a hundredfold.

The contamination of free-range eggs has here an important social dimension: Eggs as the cheapest protein source (Molnár and Szőllősi 2020) are often raised by poor families and communities around the world contributing to a healthy nutrition for poor people. Raising chickens and other livestock in subsistence farming may contribute to the UN Sustainable Development Goals (SDG) (relevant to SDG1 No Poverty, SDG2 Zero Hunger, SDG11 Sustainable Cities and Communities) - but only if the eggs are not contaminated (relevant to SDG3 Good Health & Wellbeing).

We have published recommendations with open access for policy makers to systematically assess the PCB and PCDD/F contamination situation around current and past emitters and to reduce emissions and reduce and stop the exposure of populations living at or around these sites (Petrlik et al. 2022; https://doi.org/10.1016/j.emcon.2022.05.001).

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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.

Keywords

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

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

Jan Wauters

SARPI

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.

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.

Submitted paper

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

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Summary

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

Introduction

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.

The sources of environmental pollution with polychlorinated biphenyls along with the energy production/ distribution complex include landfills, which do not correspond to environmental requirements, thus bringing forth a number of problems and a great danger

Materials and Methods

Samples of land were taken in different provinces of the Republic of Armenia on the boundary of the landfills and agricultural lands or water basins near Ararat, Hrazdan, Sevan, Gavar, Dilijan, Armavir towns and Sasunik village (Aragatsotn province).

Quantitative determination was carried out using chromatograph with electron capture detectors (ECD) equipped with glass capillary column with stable phase DB–5MS UI. Column parameters: 60 m x 0.250 mm x 0.25 µm; carrier gas: high purity grade nitrogen; carrier gas velocity: 30 ml / min; temperature conditions: evaporator – 240ºC, column – 220ºC, detector – 300ºC.

Congeners determined in soil samples included: No. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189.

Results and Discussion

In all investigated soil samples DL-PCBs were detected, however, we mainly recorded PCB congeners No. 77, 81, 105, 114, 118, and 123, while No. 169 was determined very rare and at insignificant quantities.

Attention was drawn to the following:

- among 7 randomly selected soil sampling sites, a 2 to 3.5 times exceeding of the total/ summary standard level was found at four sites;
- in all cases, exceeding of standard level was due to DL-PCBs No. 81 and 114.

Of special attention is the fact that at one of the soil sampling sites (Dilijan Town, Tavush province of Armenia) along with 3.5-fold exceeding the standard, almost all dioxin-like PCBs were found.

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 (Table 1).

TABLE 1. SUMMARY VALUES OF REVEALED

	Soil sampling site	Maximum value of summary concentrations of revealed DL-PCBs, µ/kg	MAC, µg/kg
1	Ararat Town, Ararat province	181.474	60
2	Hrazdan Town, Kotayk province	18.097	
3	Sevan Town, Gegharkunik province	22.345	
4	Gavar Town, Gegharkunik province	57.023	
5	Dilijan Town, Tavush province	204.95	
6	Armavir Town, Armavir province	131.499	
7	Sasunik village, Aragatsotn province	125.614	

Conclusions

Chlorine-substituted cyclic organic substances are formed at the landfills as a result of open burning of disposed wastes.
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.

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