Contaminated Sites – Cases, Remediation, Risk and Policy

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The contemporary scientific discussion regarding PCDD/PCDF sources focuses mainly on thermal emissions (e.g. waste incineration, sinter plants, secondary metal production etc.), however, the history of contamination with dioxins and dioxin-like chemicals is closely related to the chlorine industry and the production of chlorine and chlorinated organics and their application. While the majority of such contamination occurred in the past, contaminated sites and hot spots of POPs are major legacies from this history and, as can be seen from the presentations of this session, remain of contemporary and future interest and relevance. The cases of contaminated site presented from all over the world demonstrates that attention needs to be drawn to tackle a problem of global dimensions, and thereby call for a concerted action of all international stakeholders to work jointly towards sustainable solutions.

A total number of 22 short papers are presented in this session. The major finding of these papers are briefly summarizes here:

**Contaminated megasites polluted by mainly chloroalkali process are presented in 4 papers:**

Pless-Mulloli et al describe a complex case study of an area contaminated by a former chloroalkali electrolysis plant, in the vicinity of which a school and housing ground exist now. The case is discussed in the context of current UK legislation on contaminated land and requirements for remediation with the objectives to establish the spread of contamination, to carry out the risk assessment in line with UK contaminated land exposure assessment guidance, and to inform a remediation strategy.

Der-Kau Soong et al reports on a contaminated site with high mercury and PCDD/PCDF levels due to a former chloroalkali process and PCP production in Taiwan. The presented part of the project focused on the investigation of contaminants distribution outside the plant, and on the human risk assessment of residents in the neighbourhood. Results of this investigation indicate the pollution by dioxins (the Taiwan EPA had found high dioxin level in the blood of residents) and mercury could have affected the health of residents in the neighbourhood. Based on the investigation results, three possible options for the next remediation phase are suggested.

The contamination of the Tittabawassee River with a comprehensive effort to understand the impact of dioxins and furans from certain production processes during the early 20th century is presented by researchers from the Dow Chemical Company (Wilken et al.). The paper describes the contribution of the 2,3,7,8-substituted congeners for the floodplain and sediment samples, and how patterns found are consistent with chloroalkali production in the first decades of the 20th century (dominated by PCDFs) and a change in the pattern consistent with the production of chlorophenols from the 30s onwards (with a dominance of PCDDs).

Verta, Kiviranta et al. reports on the evaluation progress on a POPs and Hg contaminated megasites in the Kymioki region in Finnland and the Gulf of Finland, polluted mainly by chloroalkali electrolysis and PCP (KY5) production and additionally impacted by paper mill effluents. 10 years of research has been carried out to examine the spatial extent of the contamination, elucidate and model the transport of the sediment and pollutants, predict future changes, investigate ecotoxicological effects and assess risks on aquatic biota, human health risks and to find out restoration needs and preconditions. The studies form the basis of the risk management strategy and the possible remediation of contaminated sediments. It is concluded that the risks posed by Hg (from the chloroalkali electrolysis and use as slimicide) exceeded those from PCDD/Fs and also need to be addressed in decision making regarding remediation actions.

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In the study of Otto et al., a city in Germany (Rheinfelden) was contaminated by a chloroalkali electrolysis and PCP production. The case reveals the possible dimensions of contamination by the chloroalkali process and strategies on investigating and remediation of contaminated sites originating from the chloroalkali process. A total mass balance demonstrates that several kg PCDD/PCDF TEQ can be generated by one chloroalkali process and reveals that these deposits have high contemporary and future relevance. Furthermore, the case shows that these deposits can contaminate wide areas by construction activities. Some key conclusions for remediation and secure containment of PCDD/PCDF residues are summarized.

**Contaminated megasites from the large scale production of chlorinated organics are addressed in 6 papers:**
The total remediation of chemical landfills in Switzerland and the relevance of PCDD/PCDF hot spots in remediation planning is reported by Martin Forter. According to the paper, the chemical landfill in Bonfol containing 114000 tons chemical waste endangered drinking water and contaminated and presently continues to contaminate groundwater. Therefore, the Basel Chemical Industry (Roche and the predecessor companies of Novartis, Ciba, Syngenta and Clariant) is forced to fully remediate the landfill, i.e. to remove and incinerate the chemical waste. The paper concludes that water-soluble compounds in chemical landfills often result in high contamination of groundwater and that containment solutions, which were often used for isolation of such wastes readily fail after 10-20 years as in the case of Bonfol. The author further concludes that, considering the soluble compounds and their likelihood for contamination of groundwater, it is reasonable to remove and destroy these wastes, as is required in Switzerland, and that also from an economic point of view, complete remediation is often the most cost effective solution in the long-term. The author demonstrates that during complete remediation, the less water-soluble compounds such as PCDDs/PCDFs and PCBs - present in hot spots in Bonfol and estimated in kg TEQ scale - are relevant as health risk for staff operating the remediation and for potentially contaminating the environment if improper remediation technologies are applied.

Wycisk et al conducted an exposure route assessment of groundwater pollutants from a contaminated megasite in East Germany. At this site, the industrial production of chlorinated chemicals started at the end of the 19th century with the chloro-alkali electrolysis. The produced and dumped chlorinated organics are the main contamination source at this site. Due to incompletely sealed industrial dumps, the ground water was affected directly by prevailing chlorinated aliphatic and aromatic hydrocarbons. Due to the multi-source regional contamination of the upper and lower aquifers, risk assessment-based investigations of distinct exposure routes of the contaminated ground water have been made. The exposure assessment of contaminant pathways were performed with an appropriate GIS-based 3D spatial model for subsequent simulation. The authors concluded that for the generation of a detailed environmental impact scenario, it is necessary to gather not only high-resolution land-use information in terms of source and receptors and morphological data, but also to generate a model of the aquifer systems corresponding to the real world scenario of the geological setting, as well as the “true” regionalization of contamination data.

Amirova et al. describes the present status of the production history and present contamination of the Khimprom plant in Ufa (Russia) and lists other cities of the former USSR with chlorine industry. The factory in Ufa was focused on production of chlorine, chlorophenol products and phenoxyherbicides and produced a wide range of chlororganic products at large scale for 55 years, among them the extremely hazardous production of butyl ester of 2,4,5-T and 2,4,5-TCP. When the plant was shut down, its territory and the territory of unauthorized landfill sites became “hot spots”, and its impact on the residential zone is continuing due to dust particles transfer. The paper describes the overall status of the contaminated megasite, the contamination levels, the present status of long-term conservation and also list preliminary ideas on conservation and remediation.
Revich et al. reports on another contaminated megasite in Chapaevsk (Russia) impacted from a chemical plant with dioxins, HCH, HCB, PCB and other contaminants granting the town the special status of an “extremely polluted zone” by state environmental expertise. Higher dioxin levels in blood and mother milk were found compared to other areas in Russia and most other countries. The authors also used chicken eggs as a bio-monitoring matrix and compared the contamination values with eggs sampled at other polluted sides in Russia, Egypt, Belarus and Bulgaria confirming the high pollution originating from the chemical plant. The paper also lists measures of rehabilitation of the Chapaevsk territory through federal and regional programs.

Vijgen et al summarize the global problematic of Lindane and HCH production and the legacy of the HCH waste isomers. Based on the results obtained in a global review it is concluded that the international society is confronted with a vast legacy of 1.6 to 4.8 million tons of toxic materials in the form of by-products from lindane production. Most of these waste were found to be dumped and stored in a non acceptable manner so that environmental impacts have and are still taking place. Therefore, it is concluded that appropriate measures have to be taken as soon as possible by the international society to take action within the framework of the Stockholm Convention to nominate Lindane and HCH as a new POP and establish an environmentally sound strategy for the development of destruction strategies of HCH waste in a sustainable and economical way.

Related to the HCH problematic, Weber et al. addressed the contemporary relevance of former and present recycling attempts of HCH waste and the associated PCDD/PCDF contaminations. The distillation residue from HCH decomposition to trichlorobenzene (the key residue of HCH recycling) were analysed by CALUX bioassay and instrumental analysis and found to be highly contaminated with ca. 300 ppm TEQ. The authors concluded that the deposited, highly PCDD/PCDF contaminated residues in the respective dumps and landfills can be of contemporary relevance. Furthermore, the authors report that in India - the country with the last operating HCH productions worldwide - the HCH waste is still thermally decomposed to trichlorobenzene today and the wastes dumped in the vicinity of the factories. The authors point out that this practice calls for immediate assessment of these sites when considering the extremely high PCDD/PCDF contamination in residues from a comparable process found in this study and former investigations.

Several short papers reported on contaminated sites by application of chlorinated organics or treatment of materials containing persistent halogenated compounds:

Tysklind et al discussed the potential mobility of CPs, PCDEs, PCPPs, PCDFs and PCDDs at saw mill sites in Sweden as one important factor in the risk assessment procedure, since the Swedish surveys of dioxins and related compounds revealed that one major reservoir of dioxins is connected the use of chlorophenol based wood preservatives: the accumulated PCDD/PCDF amount from CP preservatives at total sawmill sites in Sweden is estimated to be in the range of 2-50 kg TEQ. The study demonstrated that soil organic matter and colloidal particles have an important role for the transport and fate of these organic contaminants with low water solubility. The authors also suggest that, due to the limited knowledge of potential effects of several classes of chloroaromatic compounds, e.g. PCPPs and PCDEs, found at sawmill sites and their proven persistency, that these compounds should be included in future risk assessment of contaminated sawmill sites.

A related study of Persson et al. showed potential transport of PCDD/Fs from sites contaminated with PCDD/Fs from usage of chlorophenols. Considerable amount of PCDD/Fs was found bound to mobile colloids in groundwater. The results demonstrate that PCDD/Fs may potentially be transported in groundwater from contaminated wood preservation sites where chlorophenols have been used. The authors suggested that further studies of the mobility of PCDD/Fs associated with colloids needs to be done at other contaminated sites for confirmations of the results presented in this paper.
Nguyen Van Minh et al. present some initial results of research on active landfill bioreactor for dioxin decontamination in soil in hot spots in Vietnam. The background of the research was that the US army had sprayed about 80 million liters of herbicides including 45 million liters of Agent Orange with an estimated PCDD/F concentration of 170-600 kg TEQ during the Vietnam war. These activities had resulted in hot spots in e.g. former herbicide storages, loading bases for air crafts and craft washing bases. The dioxin decomposition rate in the contaminated soil by the active landfill bioreactor lay between 50-70% (calculated in total TEQ). Beside dioxin decomposition, other toxic chemicals such as 2,4-D, 2,4,5-T, chlorophenols were degraded by microorganisms and undetectable in the tested soil after 2 years.

In a second study related to the high PCDD/PCDF contamination in Vietnam, Trinh Khac Sau et al. investigated on the possibility of applying certain domestically produced activated carbons for water treatment in heavy PCDDs/PCDFs contaminated sites. In the laboratory study some of the local activated carbons showed adsorption efficiencies between 97.2 to 99.4%.

Yu and colleagues from the Baptist University Hong Kong investigated the distribution, concentration and profile of PAHs, PBDEs and PCDD/Fs in soil of Guiyu city, a blooming Chinese E-waste processing center since 1995, affected by E-waste recycling. In this first investigation on PTS in soil from an E-waste site the authors investigated a wide range of persistent toxic substances in soil resulting from E-waste processing.

Duh et al. utilized the contents of heavy metals and the fingerprinting database of dioxin congeners and principle component analysis (PCA) statistical technique to establish a decision-making flow diagram and the identification technique for tracking the sources of fly ash illegally dumped by steel factories in Taiwan. With the established approach the research team was able to find out the steel factory responsible for illegally dumping of fly ash at four contaminated sites.

Ruus and colleagues discovered a PCB contamination by using blue mussels (Mytilus edulis) and Cod (Gadus morhua) for bio monitoring of environmental contamination at the Sørfjord (Norway) (one time considered as one of the most metal polluted fjords in the world). As source for the PCB contamination an old paint containing high concentrations of PCBs (336030 ng/g) was discovered which were removed from approximately 1500 m² of a building facade (although measures were taken to prevent release of waste material to the environment). The described case shows the potential for old PCB-containing paint to contribute to serious local pollution if not enough care is taken during remediation.

Voie et al used a semipermeable membrane devices for the sampling and quantification of PCB leakage from contaminated sites to sea. The study monitored the leakage by introducing a physical barrier in the water just outside the contaminated site and measured water samples inside and outside the physical barrier and compared the concentrations of PCBs estimating then the daily release of PCBs from the contaminated site.

Further, some papers reports on remediation experiments of POPs:

Noma et al investigated the structures of the degradation products of 4-chlorobiphenyl by the sodium dispersion method in a laboratory scale experiment. The monochlorinated biphenyl was degraded without detection of chlorinated intermediates resulting in biphenyl, phenylcyclohexadiene, phenylcyclohexene, and phenylcyclohexane as main degradation products. Some polymerised compounds were detected as minor side-products.

Takahashi et al performed a preliminary feasibility study in laboratory scale on bio-degradation system for PCDD/PCDF in contaminated soil and sediments.