

REMEDATION MEASURES IN A RESIDENTIAL AREA HIGHLY CONTAMINATED WITH PCDD/PCDF, ARSENIC AND HEAVY METALS AS A RESULT OF INDUSTRIAL PRODUCTION IN THE EARLY 19th CENTURY

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Abstract

Soil from a residential area, which was established on a past chemical production site, was found to be highly contaminated with PCDD/Fs (~1-10 kg TEQ load), arsenic (12 to 80 tons load) and heavy metals. The contamination resulted from a *LeBlanc* chemical sodium carbonate decahydrate (sal soda or washing soda) production facility, which operated during the 19th century. The discovery of PCDD/F levels up to 100,000 ng/kg TEQ on the residential site resulted in extensive remediation and monitoring measures which are accompanied by extensive monitoring and safety measures.

This case demonstrates for the first time that PCDD/Fs were formed at high concentrations during production processes of inorganic chemicals involving chloride/chlorine already in the early phase of industrialization at the beginning of the 19th century, i.e. several decades before the first chloroalkali electrolysis started around 1890². The case further demonstrates that these contaminated sites can be of contemporary relevance including contamination of humans and the environment.

Introduction

The contemporary scientific discussion regarding PCDD/F 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, dating back to the start of the chloroalkali process around 1890^{1,2}. While the majority of such contamination occurred in the past, contaminated sites and hot spots of POPs are major legacies from this history and remain of contemporary and future interest and relevance. It has been reported that the production of certain inorganic chemicals also resulted in PCDD/F contaminated residues¹. In this respect, there are a number of little investigated questions such as a) which inorganic chemical processes can/could have lead to formation and release of significant PCDD/F levels, b) from when on these chemical production processes have emitted elevated PCDD/F and other toxic emissions, c) whether significant anthropogenic PCDD/F emissions occurred before 1900³ and d) what the contemporary relevance of these releases and historic contaminations is.

During the late 1980s, highly elevated levels of arsenic and lead were discovered in subsurface soil during the construction of a child care facility and play ground in Lampertheim, South Hessen/Germany (approximately 60 km south of Frankfurt/Main). Random and coincidental investigations of surface soils in residential gardens of the estate during the 1990s also showed highly elevated levels of PCDD/Fs. Based on these findings, the state of Hessen commissioned investigations into the history of the estate and extensive soil and groundwater analysis were carried out. These investigations revealed that highly PCDD/F contaminated residues were formed during the production of Sal Soda (sodium carbonate) associated with the *LeBlanc* process, and that this formation process was already relevant several decades before the start of the chloroalkali processes in 1890. Elevated PCDD/F levels in humans living now on the area of the former factory highlight that these contaminations are of contemporary relevance and require extensive remediation and other measures.

Site History

The historical investigations revealed that the residential estate was established on a previous chemical production site (Figure 1 and 2) which produced solely inorganic products since 1827, including sodium carbonate decahydrate (also commonly known as sal soda or washing soda) after the *LeBlanc*-process, sodium

sulphate, sulphuric acid, calcium hypochlorite, chlorine (but not with the chloralkali process) and phosphate fertilizers⁴. After cessation of production in 1927/28 the factories' facilities were demolished and partially levelled on the estate. Until the end of the 2nd World War, the ~80,000 m² area of the previous factory site was unused and from 1950 underwent successive development for residential housing, in particular for immigrants and refugees of the 2nd World War as well as their descendants. Today, 125 blocks of land contain residential housing and approximately 600 people live within the estate. A forested waste deposit site of the previous factory is now located directly adjacent to this housing estate, which also contains high levels of heavy metal and PCDD/Fs.



Fig. 1: Aerial photograph of the chemical factory 1926



Fig. 2: Aerial photograph of residential area 1995

Soil investigations

Based on the historical investigations, detailed surface and subsurface soil analyses on the residential estate were undertaken from 1994 until 1999. More than 600 soil cores of a total length of 3 km were taken and more than 3,500 soil analyses were carried out for the relevant contaminants. The soil analyses confirmed that the entire surface and subsurface soil, in some locations up to a depth of approximately 8 meters, was highly contaminated with PCDD/Fs, heavy metals and arsenic, the latter in bioavailable form:

Parameter	Maximum	Parameter	Maximum
Arsenic	up to 37,000 mg/kg	Tin	up to 3,940 mg/kg
Lead	up to 79,400 mg/kg	Antimony	up to 355 mg/kg
Copper	up to 16,100 mg/kg	Selenium	up to 117 mg/kg
Thallium	up to 190 mg/kg	PAH	up to 1,117 mg/kg
Mercury	up to 618 mg/kg	Hydrocarbons	up to 8,500 mg/kg
Zinc	up to 5,500 mg/kg	PCDD/F	up to 100,900 ng TEQ/kg

Based on these investigations, it was clear that the contaminant loading of the site was very high (arsenic: ~12-80 tonnes, lead: ~50-300 tonnes, PCDD/Fs: ~1-10 kg TEQ).

The investigation of characteristic on-site materials confirmed that the production processes of the previous chemical facility were the only possible PCDD/F source. The high levels of PCDD/Fs (up to 100,900 ng TEQ/kg in the residential area, up to 500,000 ng TEQ/kg at the waste deposit site of the factory and up to 49,240 ng TEQ/kg in slag samples) were remarkable. The PCDD/F congener and homologue profiles in samples from the site were characterized by high proportions of PCDFs, in particular TetraCDF and HexaCDF (with 1,2,3,4,7,8-HexaCDF as marker congener). PCDDs contributed only little in most cases. Similar profiles were identified in all characteristic materials of the site. The PCDD/F congener profiles (Figure 3) show similarities to those reported from electrode sludge from chloroalkali electrolysis^{1,2} and some production in the chlorine industries¹.

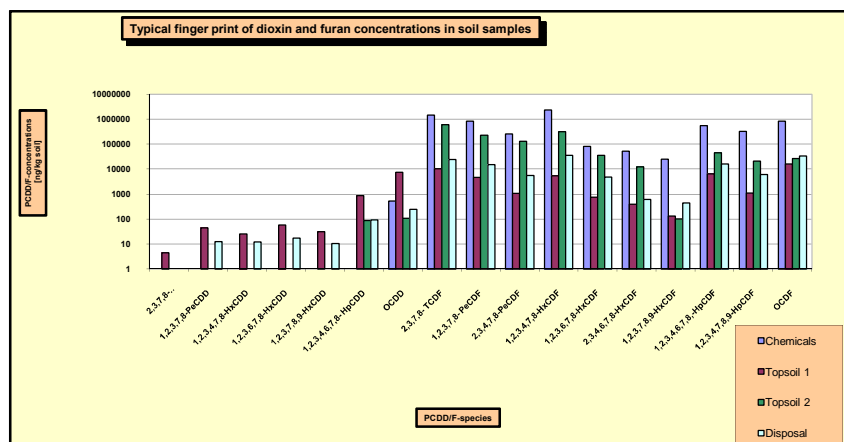


Figure 3: Typical PCDD/F congener profile in soil samples of the previous factory site.

The arsenic and heavy metal contamination was clearly associated with the production of sulphuric acid (pyrite roasting). The PCDD/F contamination, characterised by the site specific congener profiles, was conclusively linked to the sal soda production and associated processes (1840s to 1893). Therefore the known PCDD/F formation processes with similar congener profiles mentioned above can be excluded as possible sources. This means that PCDD/F formation occurred during sal soda production and associated processes long before 1890 and demonstrates that anthropogenic PCDD/Fs were formed at a kg TEQ scale during industrial processes in the early 19th century as part of production processes of inorganic chemicals involving chloride/chlorine.

However since the basic conditions for PCDD/F formation – chlorine and/or hydrochloric acid as a chlorination source, organic compounds, metallic catalysts and elevated temperatures – were prevailing in a range of production processes in the chemical factory, the main process of PCDD/F formation on site could not yet be identified conclusively. Following processes related to the sal soda process could have contributed to PCDD/F formation/emission:

- The production of chlorine and chlorinated chalk,
- The processes for condensation and purification of hydrochloric acid,
- The production of sodium sulphate and sal soda in so called sulphate ovens, or special flame ovens,
- Maybe also the production of sulphuric acid after the so called “Bleikammer process”

The most probable main formation source in the chemical factory was the chlorine production process (through washing of hydrochloric acid gas with brown coal), which operated since at least 1848, i.e. several decades before the introduction of chloralkali electrolysis around 1890. As formation mechanism, *de novo* formation from coal tar as carbon source (including dibenzofuran² and PAHs² known as excellent carbon source for PCDD/F formation^{5,6,7}) widely utilized for protection of materials in ovens and other production installations of the factory and therefore present in most processes, can be considered. This is supported by the high PCDF/PCDD ratio and the similarities to the congener pattern of PCDD/F formation from oxychlorinative degradation of PAHs^{6,7} and chlorination of dibenzofuran^{1,5}.

Human biomonitoring

Due to the high contamination and bioavailability of contaminants, human biomonitoring was carried out on selected individual residents and control groups from outside the factory grounds in collaboration with toxicologists and physicians⁸. The biomonitoring consisted in essence of analysis for PCDD/Fs in blood lipids of a total of 18 people (6 long term residents, 6 new residents and 6 control individuals from non impacted surroundings). Although relatively low blood PCDD/F levels were present, the results demonstrated that the site contamination lead to PCDD/F exposure, in particular in long term residents which consumed mainly vegetable and animal products grown on site.

Evaluation of dust deposition

In addition to the above investigations, dust associated PCDD/F wet and dry deposition was monitored on the site since 1995. The results demonstrated a clear influence of the soil contamination on the PCDD/F deposition

rates on site. In general, 2 to 3 fold higher PCDD/F deposition rates were observed on site, which were characterized by the site-specific congener profile. Often, the LAI guidelines⁹ (15 pg I-TEQ/m² x d⁻¹) were exceeded in the deposits. As an immediate measure, the use of home-grown vegetables and fruit, ground water and animal products were suspended. Additionally, the non-stabilized and bare soil areas were covered.

Remediation measures

Based on the surface contamination, the elevated levels of contaminants, and the use of the site for residential housing urgent action was required for remediation. Various scenarios regarding remediation efficiency and costs were investigated and compared, ranging from evacuation of the site (including demolition of the residential housing and complete remediation) to less invasive measures (exchange of the top 30 cm of soil).

According to the German legislation¹⁰ and under consideration of costs and benefits, a remediation plan was developed jointly with the state government, the city administration, the affected citizens and professionals¹¹. This plan involved soil exchange to a depth of 1 meter at most locations. For protection of groundwater, subsurface "hot-spots" of soil contamination were to be exchanged to a depth of 3-4 meters and larger scale contaminated areas were to be secured through pore water sealing to prevent continuous contaminant transport to groundwater. These remediation actions commenced in 2003 and are predicted to be completed by 2010. The costs incurred are estimated at 65 million Euros.

Particular importance was placed on logistic measures to minimise dust in order to protect residents and workers during the remediation activities. For this purpose, the dust levels in the atmosphere are continuously monitored (evaluation of dust deposition, diffractometrical online measurements of dust concentration). Based on these monitoring activities, the health and safety requirements for residents could be substantially reduced.

Conclusions

This case highlights that PCDD/Fs of anthropogenic origin were formed in kg TEQ scale during production processes of inorganic chemicals involving chlorides/chlorine in the early phase of industrialization beginning of the 19th century, several decades before the chloroalkali process started in 1890. It is unknown how many similar production facilities existed at that or earlier times in Europe, however, an initial investigation indicated that 10 to 15 similar factories existed in Germany during the 19th century. The extremely high levels of PCDD/F emission from these processes and potential wide distribution of production facilities highlight that PCDD/F contamination found in soils/sediments prior to the 1900s³ may in fact reflect such or similar anthropogenic processes.

The present case further highlights that these contaminated sites can be of contemporary relevance including contamination of humans and the environment and that these areas need to be assessed.

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