CASE STUDY ON REMEDIATION OF A GERMAN CITY CONTAMINATED BY A CHLOROALKALI PLANT AND PCP PRODUCTION

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1. Introduction

Experiences in Germany, Sweden and the USA demonstrated that the chloroalkali process can generate large amounts of polychlorinated dibenzofurans (PCDFs)[1-3], polychlorinated naphtalenes (PCNs)[3] and other organic and inorganic hazardous contaminants[4,5]. However, up to now there was no documentation on the possible extent of these types of contaminations, the dimension of remediation efforts it can take, and the strategies of investigation and remediation employed with these contaminated sites.
In Rheinfelden, a small town (32000 inhabitants) in South Germany, a chloroalkali plant operated since 1898 for 87 years. Furthermore, a PCP and PCP-Na production facility operated from 1970 to 1986. An investigation of topsoil and deep soil samples starting in 1989 revealed an extensive PCDD/PCDF contamination of several contaminated sites also impacting the inner city area. In the following years, investigation and remediation efforts of the city council, with support from state, the production company, two Universities, experienced engineering and remediation companies, resulted in securing and remediation of the contaminations. The case in Rheinfelden reveals the possible dimensions of contamination by the chloroalkali process and strategies on investigating and remediation of contaminated sites originating from the chloroalkali process.

2. History and discovery of the contamination case

2.1 History

Industrialisation and settlement started in Rheinfelden with the construction of the first European hydroelectric power station in 1895. In the same decade some industries developed. One of the companies was Griesheim Elektron starting operation of a chloroalkali plant in 1898. Already in the first years of operation the health hazard of the process and the residues was discovered due to the development of severe chloracne of the operation staff[1]. Nevertheless during 87 years these toxic residues of the chloroalkali process together with other industrial waste and construction waste were disposed of without any safety measures in different small gravel pits in the vicinity of the plant. During this time the ownership of the company changed to IG Farben then to Dynamit Nobel, Sivento, Hüls, Degussa-Hüls and finally to Degussa AG today.

2.2. Discovery of PCDD/PCDF contamination

A specific PCDF contamination was discovered around the production site in 1989 during an investigation of a widely distributed PCDD contamination (mainly OCDD (20 to 8000 ng/kg); <40 ng TEQ/kg) originating from atmospheric deposition from the PCP production process[A]. The PCDF contamination levels in some locations were, however, considerably higher compared to the atmospheric PCDD deposits and it was not known from which industrial process the PCDF originated. The quantification of the PCDF dominated samples, revealed peak concentration in topsoil of 26 000 ng TEQ/kg and 3 800 000 ng TEQ/kg in deep soil[5]. The tremendous PCDF values in different locations indicated that several heavily PCDD/PCDF impacted areas exists which needed to be classified as contaminated sites. As first measure, the potential contaminated areas where blocked off and the population was alerted and provided with instructions.

3. Assessment of the contaminated sites

The German legislation set a remediation limit for soil in populated areas of 1000 ng TEQ/kg[6]. Therefore, the contaminated sites in Rheinfelden needed remedial actions. However for these activities, detailed knowledge of the contaminated sites in the deeper soil layers was necessary since the higher contamination in deep soil would

[A] This was one of the first PCDD/PCDF soil analysis ordered by state authority in Germany.

have increased the health hazard by excavation activities. Furthermore the risk for the population and groundwater contamination needed to be assessed. For clarification of these questions, detailed investigations and assessments where necessary:

- About the extent, the composition and the origin of the contamination
- About the resulting/actual potential for health and contamination risk
- About the necessity and possibilities of remediation

In this early stage, neither the source of contamination nor the extent or if further areas were contaminated were known. Therefore, an investigation strategy had to be developed including historical investigations and evaluation of production processes, as well as technical and scientific investigations of potentially contaminated sites.

3.1 Historic investigation

Based on information from the population and the evaluation of historic maps and land registers it became apparant that some of the production residues have been deposited before 1920. This restricted the contamination origin to three companies. The responsible companies were ordered to open all information related to their production portfolio. This investigation covered in particular also the chloroalkali electrolysis (amount of chlorine and applied technology), the history of production portfolio of chlorinated organics and production amount, as well as the knowledge on deposited sites.

3.2. Technical and scientific investigation and discovery of the source

In the first phase (3 months) of technical investigation for localisation and evaluation of deposits, 100 locations where sampled with 303 core probes resulting in 500 samples. For the first overview 40 representative mixed samples were analysed on PCDD/PCDF, heavy metals, organic sum parameters and general contaminated site-specific parameters.

The PCDD/PCDF congener pattern is like a "fingerprint" and represents one important tool to identify PCDD/PCDF sources in combination with information on technical processes and specific products or product residues. The congener pattern of the main contamination in Rheinfelden was comparable to the pattern reported by Rappe for a chloroalkali process in Sweden[2a,b]. Therefore, the heavy PCDF contamination could be attributed to the chloroalkali process.

3.3 Formation of PCDD/PCDF and other contaminants from the chloroalkali process

The formation of high levels of PCDF and other chlorinated organic compounds is tied to the use of coal or graphite electrodes (sludge from electrolysis cells resulting mainly from reaction of chlorine with the pitch binder of graphite anodes[4]). These electrodes have been used since the beginning of industrial chlorine production via chloroalkali electrolysis in 1890 and have been partly replaced[B] from the seventies onwards. However some companies still use this type of electrodes today.

Further, relevant contaminants[C] in the deposits from these chloroalkali residues were PAHs (with concentrations up to 4345 mg/kg) Lead (up to 1425 mg/kg), Barium (up to 60 g/kg) and mercury (max. 24.4 mg/kg Hg).

[B] It is most probable that lower PCDD/PCDF and other chlorinated organic compounds are generated by the chloralkali technologies used today. However detailed investigations on other plant types are missing.

[C] In addition, these contaminants were also deposited from other industrial processes.

3.4. Mapping of the entire city

Based on the first phase of investigation, an assessment of the type of contaminants were given. In the second assessment phase it was discovered that during the development of the town in the 20th century contaminated solid residues from some of the waste deposits in gravel-pits (which included highly PCDD/PCDF contaminated sludge from the chloroalkali process) were partly used as filler materials at many individual estates within the town. This resulted in the potential contamination of wide areas of the city by PCDD/PCDF, heavy metals and the other contaminants. Therefore, the entire inner city of Rheinfelden (ca. 290 ha) had to be assessed: a total of 1878 land estates were mapped and soil samples were collected and screened from 1615 estates (3566 individual drillings). Finally a soil map of the entire city (Figure 1) was produced in collaboration with the University Hohenheim[5], using indicator heavy metals as guiding parameters and PCDD/PCDF analysis for confirmation[7]**.** It was demonstrated that, with one exception, levels above 100 ng TEQ/kg soil could be tracked by screening samples for optical characteristics (screening for electrode sludge residues) and soil mapping based on the heavy metal fingerprints in these soils. During this investigation, 36 estates were found to have PCDD/PCDF contaminations exceeding the limit values for remediation (1000 ng TEQ/kg).

4. Remedial actions

The investigation and remediation of contaminated grounds within housing estate areas brings specific challenges for environmental agencies. First, the evaluations and decisions on contamination levels in soils of sensitive areas such as gardens with home-grown food or areas where children play are delicate. In addition the cooperation with owners of private grounds – which were not the polluters but were now the owner of the pollution – requires tact. In particular, the legal succession for the pollution could not be clarified, since the company has changed ownership (see 2.1.) and one of the former company went bankrupt, and therefore the actual owners of the estate and not the polluters were responsible for remediation. To avoid financial hardness, a public remediation fund was established to cover 75% of the cost of remediation of the private ground while a maximum of 25% was planned to be covered by the owner of the ground. All private owners of the ground agreed in the remediation since the maximum costs for the owners for remediation were fixed and where low compared to the value of the restoration of the areas. Furthermore the possible financial risk of remediation was covered by the remediation fund. Therefore the principle of “voluntary remediation” could be applied for all private estates. The costs for the owners of the private estates could finally be minimized by reasonable cost management to below 10% of the respective remediation cost.

The company areas around the chloroalkali process and organochlorine productions, a second deposit area and landfill A, where most of the residues were deposited, were secured on the cost of the company (ca. 15 Mio Euro).

For another deposit area, where the bankrupt IG Farben is responsible for the contamination, the remediation is presently ordered by city authority. For one remaining deposit area (Fecampring) the remediation strategy has not been decided to date.

4.1. Remediation in dependence of contamination level

The heavily contaminated soils (> 1000 ng TEQ/kg)[6] were substituted and removed or, in some cases were contained by removing of the top soil, fitting a geo textile and covering the bottom soil again with non-contaminated soil. All 36 “hot spot estates” with a PCDD/PCDF-contamination (of 1000 ng TEQ/kg to 10000 ng TEQ/kg) have been remediated. The largest share of contaminated soil below 10000 ng TEQ/kg was deposited on the company landfill A of Dynamit Nobel (today Degussa AG). The landfill A was already heavily contaminated with deposits from chloroalkali electrolysis and production residues.

The contaminated soil exceeding 10000 ng TEQ/kg were mainly treated in hazardous waste incinerators in Holland (contamiation level <30000 ng TEQ/kg) and Germany (levels <100000 ng TEQ/kg). All resulting decontaminated soil were deposited in Germany. Some extremely high contaminated materials (around 1000000 ng TEQ/kg) were deposited in mines.

Estates with a contamination level below 1000 ng TEQ/kg remained without action[6], however, agricultural use of estates with a PCDD/PCDF contamination of more than 40 ng TEQ/kg is limited.

4.2. Limitations for complete remediation

A complete remediation of the contaminated areas (landfills, production site and lower impacted estates) with destruction of the PCDD/PCDF was considered to be not feasible due to elevated cost and was not considered necessary since the risk for groundwater contamination by PCDD/PCDF could be excluded. Also, the two contaminated deposit areas mentioned above are still awaiting remediation action.

In addition, water needs to be pumped continuously from the production site to prevent the contamination of groundwater from various chlorinated hydrocarbons. Similarly, for landfill A, water has to be pumped to guarantee that the water-level inside the secured area is below the water-level of the vicinity, in order to guarantee a water flow gradient towards the contaminated site and to exclude groundwater contamination. For the secured landfill B, the water effluents have to be cleaned by active carbon filtration. The water level in the landfill is monitored and the streams in the vicinity are regularly analysed.

Furthermore, an assessment has to be carried out for any new construction activity within the town today and in future.

Against this background as a whole, the containment of the former landfills and soil contamination on the production site and the remediative action of the private estates could minimize the risk of further environmental contamination and exposition of humans in Rheinfelden.

6. Total PCDD/PCDF mass balance

The total amount of deposited PCDD/PCDF residues of the single chloroalkali electrolysis facility in Rheinfelden is estimated to to 8.5 kg TEQ. In addition, the residues of PCP and PCP-Na produced between 1970 and 1986 is estimated to 7.7 kg TEQ (total 7 tons of PCDD/PCDF, preliminarily OCDD) mainly from PCP-Na production. The latter residues have been deposited in secured landfill B at the time of production. The dimension of the contamination (in total 16.2 kg TEQ) becomes apparent when comparing it to the estimated emission of ca. 20 kg TEQ/year of all global available PCDD/PCDF inventories today[8].

7. Conclusions

7.1. For Rheinfelden

The responsible and rational management of the contaminated estates could minimize the risk of health impact on the population of Rheinfelden as well as the costs (approximately 24 Million EURO) for remediation. The remediation and containment of the production areas and associated landfills are completed to the extent possible, however, are not finalized (chapter 4.2). Even today areas where any construction activity is planned within the city need to be evaluated for possible contamination, and two contaminated deposit areas are waiting for remediation.

7.2. Relevance for other sites

The case in Rheinfelden 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. There are a vast number of former chloroalkali plants in Europe (Figure 2) and contemporary plants around the globe. For example, today alone 300 chloroalkali enterprises are operating in China[11]. Depending on the technology used, similar high PCDD/PCDF contamination for these other sites are possible and similar burdens in (typically nearby) landfills and the production sites or - if disposal route was via water – respective river and lake sediments can be expected. However, the deposited quantity of PCDD/PCDF depends on the chloroalkali process and some other key factors, in particular the used electrodes as well as the disposal of cell sludge. Before the seventies, all residues have not been incinerated but dumped in available pits or unsecured landfills and this might be practice for some facilities still today. Therefore, these sites need strict evaluation with respect to the contemporary and former production processes and the waste management practice.

7.3. Lesions learned

The investigation and remediation of the contaminated sites in Rheinfelden can be viewed as one of worldwide precedent cases for chloroalkali electrolysis and production of organochlorine compounds[D]. One key conclusion, which can be drawn, is that it remains difficult and cost extensive to completely remediate contaminated areas[E] due to the large volume of contaminated soils and landfilled materials, and that landfilling of these type of materials is not acceptable. Some key conclusions from Rheinfelden for remediation and secure containment of PCDD/PCDF residues are:

- Detailed documentation of former production processes of the facility and transparency of type, amount and location of waste residues from these productions are important. Landfills and contaminated areas (based on detailed data from historic documentation) need to be localised.
- Assessment of the landfills and contaminated area are required, in particular with respect to:
    - Extent of contamination,
    - Geological conditions and frame of the sites,
    - Actual contamination/contamination risk of ground water;
    - Mobility of contaminants.
- Investigation schemes with respect to contaminated sites should be designed in such a way that their results are adequate for risk assessment and tracing the origin of the contaminants.
- Close cooperation of the pesticide/chemical companies and state/local authorities is required; open communication with impacted public and NGOs is important.
- Experienced engineering companies qualified in the field of remediation of contaminated areas of similar type should be consulted. The planning needs high creativity since the solutions applied are normally not the standard engineering techniques but might be rather unique.
- Assessment whether total remediation of the area is possible and necessary[D] need to be carried out.
- Timely environmental impact assessments with subsequent prompt remedial and securing actions can minimize total damage and costs.
- Evaluate how and to which extent the "polluter pays principle" can be applied.

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[D] Other cases are e.g. treated in the US in the frame of the Superfund site[9] and cases in Switzerland [10a,b, 11].

[E] Switzerland exemplifies the requirement of total remediation of chemical waste landfills (based on a polluter pays principle). Two large-scale remediation projects are currently undertaken in Kölliken (estimated remediation cost 500.000.000 SFr) and Bonfol (estimated remediation cost 300.000.000 SFr) [10a,b, 11].

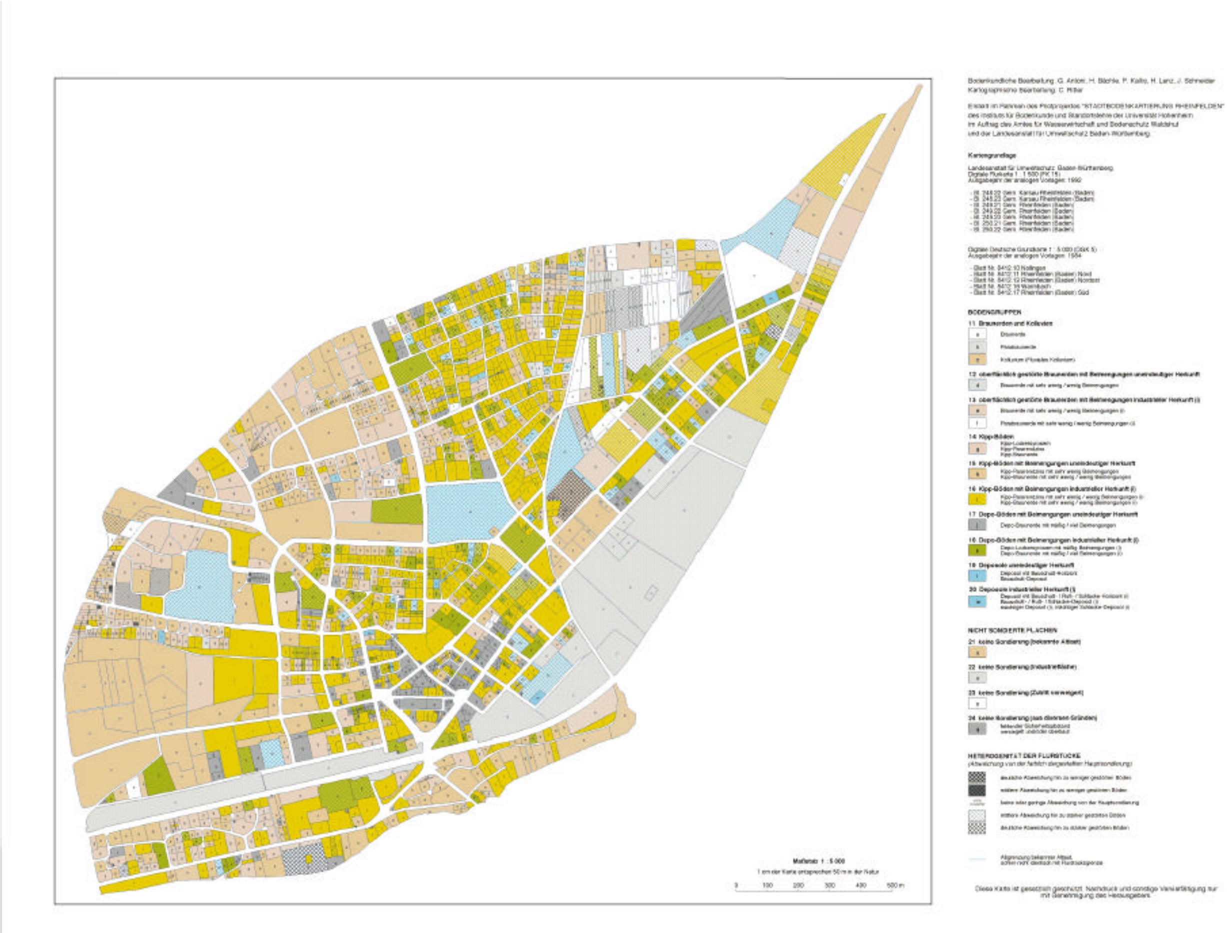

Figure 1: Soil map Rheinfelden (Baden, Germany) (published by the environmental ministry Baden Württemberg).[5]

Figure 2: Chloroalkali plants operated 1910 in Europe.