

A CONTAMINATED SITE FROM THE CHLORINE/ORGANOCHLORINE INDUSTRY AS SOURCE OF PCDD/F CONTAMINATION OF CITRUS PULP PELLETS USED AS ANIMAL FEED IN EUROPE DURING THE LATE 1990's

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Introduction

Polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) and other persistent organic pollutants (POPs) emitted from historical sources can persist in soil/sediments and waste reservoirs for decades or even centuries. In this respect the US EPA estimated in 1994 that the relevance of PCDD/Fs from contaminated sites/hot spots will soon become the major source¹ of contemporary pollution. Therefore problems associated with PCDD/Fs should be considered to a large extent a legacy issue and contaminated sites are likely to remain a problem not only now, but also in the future².

One important issue to consider are the pathways through which PCDD/Fs and POPs enter the food web. Special attention must be paid to how these compounds might be introduced into the industrial food products. Here, in addition to entering the food chain through the standard mechanisms of bioaccumulation and biomagnification, of environmental PCDD/Fs and other POPs can enter the food chain through a range of "short cuts" directly contaminating feeds and foods³⁻⁵. One such documented case occurred in 1997 when dioxin concentrations in milk from different farms in Baden-Württemberg (SW Germany) suddenly increased. After years of slowly declining values, the mean dioxin content in milk rose from 0.62 pg I-TEQ/g fat to 1.41 pg I-TEQ/g fat within half a year. The peak concentration in this sample was almost 8 pg I-TEQ/g fat. Soon, similar concentrations in milk and dairy products were reported from several regions of Germany and other European Union member states⁶⁻⁸. The first step was to find the contamination source, which turned out to be citrus pulp pellets (CPP) imported from Brazil used for cattle feed. Citrus pulp, a former residue of orange juice production, nowadays is added in the form of pellets to feed for ruminants due to its high energy content. Dioxin concentrations in the contaminated CPP samples ranged from 5 to 10 ng I-TEQ/kg⁶⁻⁸. The PCDD/F contamination source for the CPP was the 2% lime added to the wet peels corresponding to about 7–8% of the dry CPP weight⁶. Following the ban on CPP exports, Brazilian CPP producers lost at least USD 40 million, according to the Brazilian Association of Citrus Exporters (Abecitrus, Associação Brasileira de Exportadores de Cítricos)⁹. 40 thousand tons of contaminated pulp stored in the Netherlands were destroyed at a cost of USD 6 million⁹.

This embargo was lifted by the European authorities only after the source of the contamination was eliminated, and the Brazilian Ministry of Agriculture had implemented a dioxin regulation for CCP and lime with the limit of 0.5 ng I-TEQ/kg complying with the European standard (European Directive 98/60/EC) and had established a continuous monitoring program of PCDD/Fs in CPP and lime.

The contaminated lime was purchased from one supplier using lime from a contaminated site. However, details about the origin of the PCDD/Fs in the contaminated lime were not revealed. This paper further investigates the contamination origin and describes the link between lime milk from the dumpsite of a chlorine/organochlorine industry and the contaminated hydrated lime.

Material and methods

323 samples were taken from the landfill where the contaminated lime milk and other residues from the company were deposited. The sampling was done with 1 m transparent PVC cores (pre-cleaned with dichloromethane) in a systematic quadrat grid over the site (GIS/GPS).

After Soxhlet extraction (toluene, 24 h) the extracts were subjected to clean-up and analysed by HRGC (HP 6890) and HRMS (VG Autospec Ultima). As GC-column a 30 m J&W DB5-ms was used (0.25 µm film thickness, 0.25 mm i.d.).

Results and discussion

Contaminated lime from the landfill of the chlorine/organochlorine industry

The contaminated lime was supplied from one supplier, (Carbotex Ind Com de Cal Ltda) (Carvalhoes 2000; EU Report). Carbotex Ltda took the lime from the landfill owned by Solvay Indupa do Brazil (Solvay Indupa) which operated also under the same address as Solvay Indupa. Since 1997 the lime milk from the site has been sold to the construction and CPP market. After the PCDD/F contamination was discovered, the sales for the CPP and construction markets were stopped. Since then there has been a lot of discussion about what kind of remediation measures for the PCDD/F contaminated site are necessary and a range of securing measures of this site have been enacted.

To evaluate the extent and type of PCDD/F contamination of the landfill, 323 samples were taken from the site.

History of the site and potential processes for PCDD/F contamination

The site belongs to Solvay Indupa (formerly Industrias Quimicas ElectroCloro) at the industrial city of Santo Andre (SP) close to the Metropolitan Area of Sao Paulo. Industrias Quimicas Electrocloro was established in 1941 to produce chlorine and alkali via chlor alkali electrolysis. In 1955 acetylene/vinylchloride monomer (VCM) production began and from 1956 VCM is also produced from ethylenedichloride (EDC) via the balanced process. Since then PVC is manufactured from the VCM at this site. VCM production via the acetylene method was stopped in 1996. Currently Solvay Indupa produces chlorine, alkali, acetylene, EDC, VCM and PVC in a 175,000 square meter area. The corporate landfill at that facility was used for approximately forty years and was closed in 1996. The main bulk waste deposited at that site was lime milk from the acetylene process. Today about 1,400,000 tons of lime milk are stored at the site. Also on that site is an industrial waste incinerator that was used to destroy organochlorine waste from the EDC process and to recover the HCl for reuse in the factory.

Processes at the Electrochloro/Solvay factory involving potential release of PCDD/Fs

a) Acetylene, Ethylenedichloride (EDC) and VCM production

It is known that VCM production via the EDC process generates high PCDF concentrations, especially from the oxychlorination process¹⁰. Releases are mainly in the form of solids, particular with the oxychlorination catalyst¹⁰. A second PCDD/F release route is via aquatic effluents/sludge. The VCM/EDC process has resulted in PCDD/F contaminated sites at places such as the Venice lagoon in Italy¹¹ and the Baltic sea¹².

The process has a PCDD/F pattern with high concentration of OCDF/HpCDF and decreasing homologue pattern (Figure 1). Similar patterns were found in most of the samples from the landfill in Brazil, with concentration ranging from 0 to 81,000 ng TEQ/kg and averaging at around 1000 ng TEQ/g. PCDD were found in most samples below 10% of the PCDFs (mass and TEQ). PCDF:PCDD ratios (mass) were between 8 and 200. Patterns in the higher contaminated samples (1000 ng – 81,000 ng TEQ/kg) were similar to the EDC catalysts

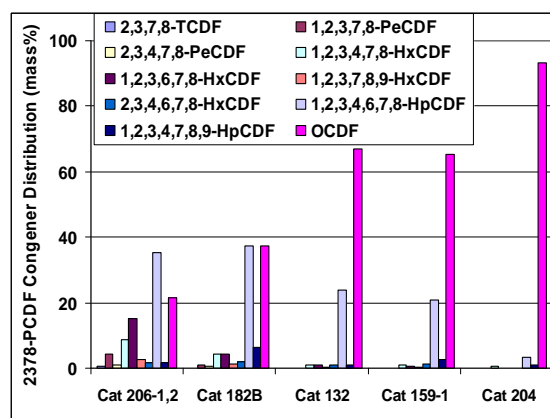


Figure 1: 2,3,7,8-PCDF distribution in some EDC catalyst samples (Carroll et al¹⁰).

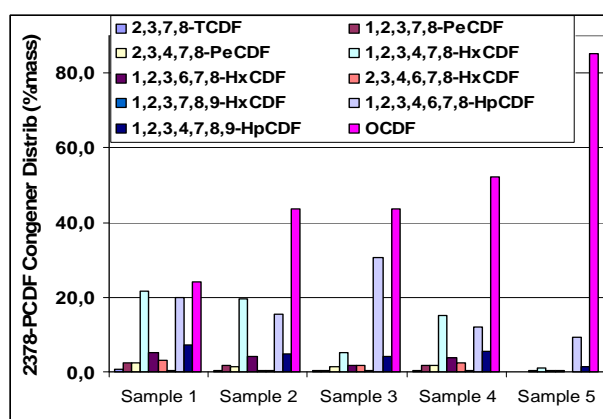


Figure 2: 2,3,7,8-PCDF distribution in high contaminated samples from the landfill in Brazil (TEQ between 1000 and 81,000 ng TEQ/kg).

samples reported from Carroll et al¹⁰ (Figures 1 and 2). The background pattern at the landfill in most of the samples had an “EDC pattern” with a characteristic OCDF dominance known from literature^{11, 12} (Figure 2, sample 5). This resembles probably the effluent pattern from the EDC/VCM process and was detected also at the contaminated sites such as Venice lagoon¹¹ and the Baltic sea¹². While the homologue distribution of the EDC catalysts have displays some variation between the “EDC pattern” (Figure 2, sample 5) and patterns with considerable impact of HpCDF and HxCDF (Figure 1 and 2). Up to now there has been no data on the PCDD/F release/patterns from the acetylene/VCM process using mercury chloride as a catalyst. Since the patterns on the landfill are similar to the known EDC releases we suspect that the PCDD/F formation from the acetylene/VCM process was rather small.

b) Chlorine production via chlor-alkali process

Past experiences in China, Germany, Sweden and the USA have demonstrated that the chlor-alkali process can generate large amounts of PCDFs^{13, 14} with a specific chlor-alkali pattern. Electrocloro (and its successor, Solvay Indupa do Brasil) operated and still operates a chloralkali plant to produce chlorine for VCM/EDC production as well as alkali. The original company (Industrias Quimicas ElectroCloro) was established in 1941 and started chlorine and soda production in 1949 using mercury cells and graphite electrodes. In order to reduce mercury releases, a membrane technology was installed during the late 1990’s and that now handles approx. 50% of the chlorine production. No information was available regarding the changes of the electrodes over time (e.g. to metal electrodes). Therefore high PCDD/F release can be expected at least for the time when graphite electrodes were used. In the 323 samples analysed from the site, no higher contaminated samples with a chlor-alkali pattern were found. However 5-10% of the samples were impacted by a PCDF pattern similar to the chlor-alkali pattern with 2,3,7,8-dominating the TCDF (~30%), PeCDF (~70%) and HxCDF (~80%) with 1,2,3,4,7,8-HxCDF as a marker congener. The maximum concentration in samples dominated by this pattern was however only 310 ng TEQ/kg. In all these samples, the EDC background pattern were found in various concentrations as depicted in Figure 3. Other than by the chlor-alkali process, this pattern could have been formed from another process in which chlorine and dibenzofuran/PAHs were present. Up to now it has not been clarified where the residues from the chlor-alkali process have been deposited.

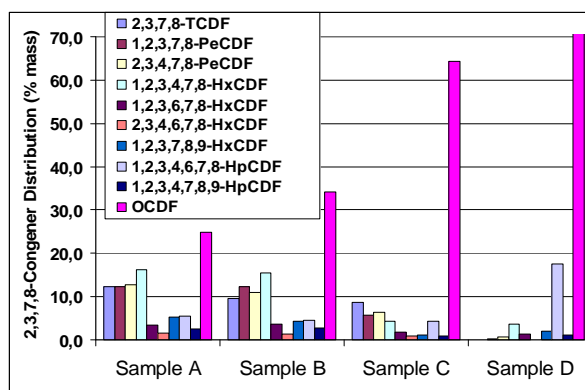


Figure 3: 2,3,7,8-PCDF distribution pattern of site samples with TCDF-HxCDF isomer patterns similar to chlor-alkali process (high 2,3,7,8-congener contribution within the homologues) with varying impact of EDC pattern).

PCDD/F pattern in the lime milk/landfill compared to and treated lime/CPP

The PCDD/F pattern in the treated lime and citrus pellets were dominated by the EDC pattern. However a higher share of 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD were responsible for approx. 50% of the TEQ in the CPP. In the original lime 2,3,7,8-TeCDD/PeCDD were present only as minor component. This difference in the TEQ distribution can not be explained by the second PCDD/F source present at the landfill with the specific 2,3,7,8-TCDF to HxCDF. The main impact on the pattern change can only be explained by the thermal dehydration treatment of the lime milk in the lime converters as has been speculated before⁸. Here are three processes that may have contributed to the pattern change.

- Dehalogenation and degradation: It is known that a range of metal oxides including Ca(OH)₂ has a strong potential to dehalogenate PCDD/F in thermal treatment¹⁵. Further PCDF can be converted to PCDD under alkaline conditions. Both mechanisms can lead to the observed pattern changes.
- PCBs, OH-PCBs and chlorobenzenes were present in high concentrations in the lime samples¹⁶. These and other precursors present in the lime milk can convert to PCDD/F in the thermal treatment. Since the process is operated in an alkaline media, temperatures around 150°C or lower can be sufficient for especially PCDD formation.

c) The oxychlorination catalyst is the main PCDD/F formation source in the plant. Heating of the catalyst during lime milk dehydration might have formed PCDD/F during the thermal treatment.

Current situation at the site

In December 1999, Solvay Indupa signed an agreement with the Public Prosecutor, CETESB and Greenpeace, in which they agreed to decontaminate the Rio Grande riverbed and the lime deposit (landfill) (Greenpeace intern, 2002). During the last ten years securing measures were installed including the construction of a hydraulic barrier and pump and treat. Further the site was capped. These securing measures will need to be monitored for their effectiveness in the future.

Lessons learnt

The Solvay/Citrus pellet case demonstrates how PCDD/F from reservoirs can enter the food chain by short-cuts directly into cattle feed and human nutrition. Therefore PCDD/F reservoirs need to be identified as requested by the Stockholm Convention (Article 6(1)e SC 2001) by appropriate strategies. The identification of sites is a first necessary step for better controlling these legacies. In a second step appropriate strategies for the remediation of such sites need to be developed for each case.

References

1. US EPA. (1994) . Estimating Exposure to Dioxin-like compounds, Vols 1-3. Office of Health and Environmental Assessment, Office of Research and Development. EPA/6006-88/005. Washington, USA.
2. Weber R., Gaus C. and Tysklind M. *Env Sci Pollut Res.* 2008; 15:96.
3. Fiedler H., Hutzinger O., Welsch-Pausch K., Schmiedinger A. (2000) . Evaluation of the Occurrence of PCDD/PCDF and POPs in Wastes and Their Potential to Enter the Foodchain. Study on behalf of the European Commission, DG Environment http://ec.europa.eu/environment/dioxin/pdf/001_ubt_final.pdf
4. Behnisch P. *Food*, Spring 2005/1 13-17; 6 .<http://www.gfa-b.de/qualitaet/publikationen/pdf/246.pdf>
6. Malisch R. *Chemosphere* 2000; 40:1041-1053.
7. Carvalhaes G.K., Brooks P., Marques C.G., Azevedo J.A.T., Machado M.C.S. and Azevedo G.C. *Chemosphere* 2002; 46:1409-1411.
8. European Commission 1999, MISSION REPORT on a mission carried out in BRAZIL from 11 to 15 January 1999 concerning the ORGANISATION OF OFFICIAL INSPECTIONS IN THE FIELD OF ANIMAL NUTRITION: DIOXIN CONTAMINATION OF CITRUS PULP PELLETS
9. Greenpeace International, Corporate crimes. June 2002.
http://archive.greenpeace.org/earthsummit/docs/corpcrimes_1of3.pdf
10. Carroll et al *Chemosphere* 2001; 43:689-700.
11. Fattore E, Benfenati E, Mariani G and Fanelli R. Patterns and sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments. from the Venice Lagoon, Italy. *Environ. Sci. Technol.* 1997;.31:1777 -1784
12. Isosaari P, Kohonen T, Kiviranta H, Tuomisto J, Vartiainen T. Assessment of Levels, Distribution, and Risks of Polychlorinated Dibenz-*p*-dioxins and Dibenzofurans in the Vicinity of a Vinyl Chloride Monomer Production Plant. *Environ. Sci. Technol.* 2000; 34:2684-2689.
13. Rappe C, Kjeller L-O, Kulp S E, and de Wit C. *Chemosphere* 1991; 23:1629-1636.
14. Otto W., Schönberger H, Burger D., Weber R. *Organohalogen Compd.* 2006; 68, 880-885.
15. Weber R., Nagai K., Nishino J., Shiraishi H., Ishida M., Takasuga T., Kondo K. and Hiraoka M. . *Chemosphere* 2002; 46: 1255-1262.
16. Carvalhaes GK, Brooks P, Marques CG, Azevedo JAT, Machado MCM and Azevedo CG. *Chemosphere* 2002; 46: 1413–1416.