

Identification of interferences during PCDD/DF analysis in soil from a chlor-alkali facility

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Introduction

Soil samples originating from the Eka-Chemicals (Akzo Nobel) chlor-alkali plant at the Göta River close Gothenburg at the Swedish west coast were investigated in this study. The production of chlorine at this facility started in 1924, the maximum production volume was approximately 100 000 tonnes/year. Up to the end of the 1970s the process included the use of graphite electrodes. Electrode sludge from such electrodes has been reported to contain high levels of PCDFs (1,2), up to 13 000 pg TEQ/g. The amount of the contaminated soil in the landfill is approximately 13 000 m³. The soil from this site will be used to test several destruction and degradation methods. Before doing this, a thorough screening of the soil with respect to organochlorine compounds was performed. The results of this screening are presented in this paper.

Materials and methods

Samples from the landfill were collected in barrels. The content of one such a barrel was homogenised by mixing in a cement mixer. The soil was then transferred in 10 kg portions to plastic containers and shipped to the laboratory. Here 70 kg of the soil was sieved (0.3 cm), mixed and stored at +4 °C. Before analysis the soil was air dried for 3 days and ground using a rotary mill. Five samples of each 3 g were Soxhlet extracted for 18 hours with toluene after the addition of 100 µl of an internal standard solution containing several ¹³C labelled PCDDs and PCDFs. After the addition of 50 µl tetradecane the extract was evaporated to near dryness, re-dissolved in 1-3 ml hexane and applied on a silica column. The silica column consisted of the following absorbent material from top to bottom: sodium sulphate, 40% H₂SO₄/silica, activated silica and NaOH/silica. The silica column was eluted with 50 ml hexane which was evaporated until near dryness and transferred to auto sampler vials. Before GC injection two ¹³C labelled recovery standards were added.

From the sample, 2 μ l was injected on a non polar DB5 column using helium as the carrier gas. Holding the injector at 250°C, the GC was temperature programmed as followed: initial temperature 200°C for 2 minutes, 3°C/minute to the final temperature of 300°C, hold at 300°C for another 10 minutes. The gas chromatograph, a Fisons GC-8000, was coupled to a Fisons MD800 mass spectrometer. Full scan mass spectra were obtained in the EI mode, scanning in the range 100-700 amu in 1 second.

Results and discussion.

The full scan chromatogram between 14 and 24 minutes of the soil extract is given in Figure 1. Several major peaks were identified in this full scan run. The spectra from the most abundant peaks are given in Figure 2 and 3. Unexpectedly, from these spectra ortho and para substituted DDT, DDE and DDD isomers were identified.

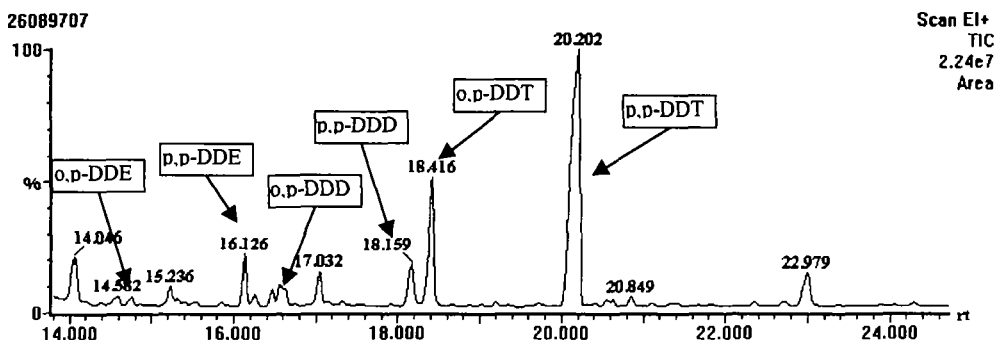


Figure 1. Full scan chromatogram of the contaminated soil, major peaks are identified as DDT, DDD and DDE

The typical mass spectrum of DDE was found at 15.1 and 16.1 minutes (Figure 2). For the two isomers, p,p-DDE was found to be the most abundant in the soil sample. The typical chlorine cluster can be seen at both mass 316 (Cl_4) and 246 (Cl_2).

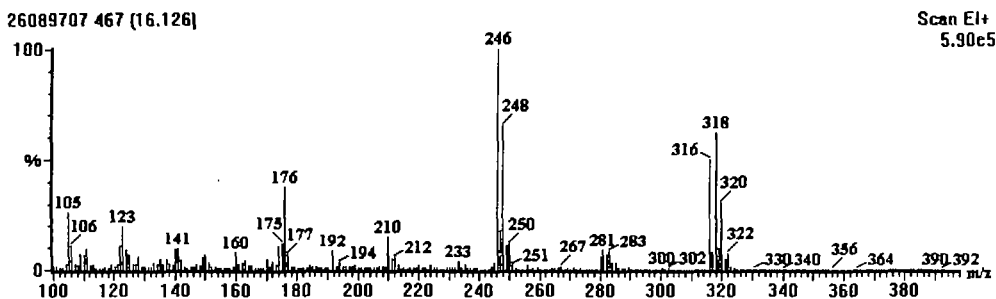


Figure 2. Mass spectrum 100-400 amu from the full scan of the soil extract; p,p-DDE.

Higher amounts of DDD but especially DDT were found. Figure 3 shows the spectrum for p,p-DDT, clearly visible is the chlorine cluster at mass 235 (Cl_2). The levels of p,p-DDT were among the highest measured on the soil ($\mu\text{g/g}$ range), only HxCBz was found at higher concentrations.

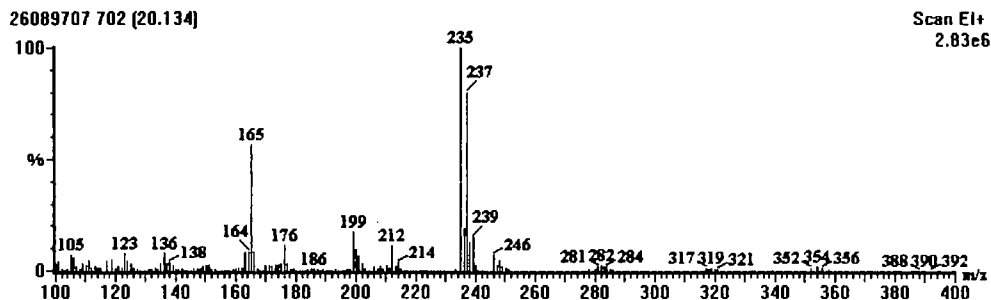


Figure 3. Mass spectrum 100-400 amu from the full scan of the soil extract; p,p-DDT

The full scan spectra also revealed the presence of several polychlorinated naphthalenes (PCNs). A large number of Tri- to Octa PCN congeners were identified. In Figure 4 the reconstructed chromatogram as the sum of the most abundant ions in the chlorine cluster for the Tri- to Octa-PCNs is given. After the detection of PCNs in the soil, the sample was re-run in the selective ion recording mode (SIR) and isomer specific quantification was performed by using relative response factors of the ^{13}C labelled PCDF internal standards and a PCN congener at each chlorination level. Isomer specific identification was done by using a mixture of equal quantities of Halowax 1001, 1014 and 1051 and assignment of the congeners in the literature (3,4). The isomeric pattern closely resembles commercial Halowax mixtures and differs from a typical incineration pattern (3,4,5).

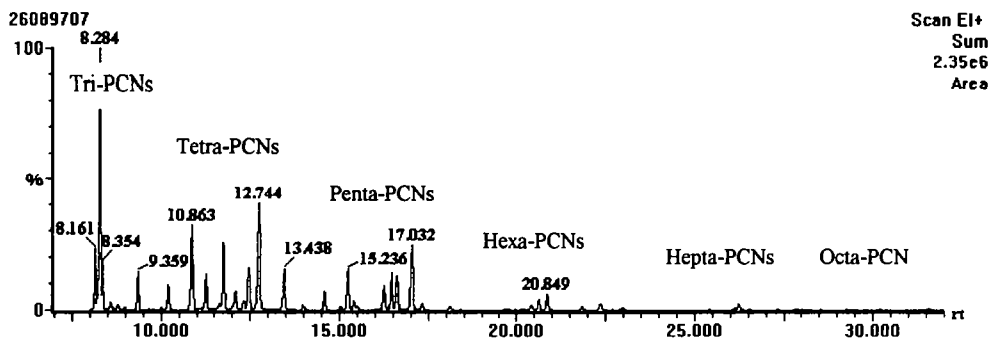


Figure 4. Reconstructed chromatogram: sum of mass 229.9, 265.9, 299.9, 333.8, 367.8, 403.7

PCNs are structurally similar to the likewise planar PCDDs and PCDFs and toxicological studies have also shown that lateral substituted PCNs induce EROD activity (6) indicating 'dioxin-like' toxicity. Recently also a high bioaccumulation potential of several of the PCN

congeners present in the soil, viz. 1,3,5,7-TeCN, 1,2,4,5,7-PeCN, 1,2,4,8-PeCN, 1,2,3,4,5,8-HxCN, 1,2,3,5,7,8-HxCN, 1,2,3,4,5,6,7-HpCN and 1,2,3,4,5,6,8-HpCN (Table1), has been established (7). Although relatively large amounts of the PCDFs are present in the soil (8 ng TEQ/g dw)(8) the even larger amounts of the structurally similar PCNs in the soil should be evaluated both from a risk evaluation and remediation point of view.

Table 1. Concentration of PCNs with a high bioaccumulation potential in the soil.

	Concentration (ng/g)dw
1,3,5,7-TeCN	150
1,2,4,5,7-PeCN	320
1,2,4,6,8-PeCN	310
1,2,3,4,5,8-HxCN	110
1,2,3,5,7,8-HxCN	130
1,2,3,4,5,6,7-HpCN	29
1,2,3,4,5,6,8-HpCN	120
Total PCN	6400

Conclusion

Using full scan mass spectrometry several persistent organo-chlorine compounds were discovered on contaminated soil from a chlor-alkali production facility. In addition to relatively high levels of PCDFs (8 ng TEQ/g dw) high amounts of the pesticides DDT, DDD, DDE and HxCBz ($\mu\text{g/g}$ range) were identified. Also large amounts of PCNs, structurally similar to PCDDs and PCDFs were found in the soil. Both pesticides and PCNs are unlikely to be formed during chlor-alkali production and it was confirmed that production of these compounds had taken place on the site during World War II. The presence of PCNs and pesticides in addition to PCDFs complicates both risk evaluation and remediation of this site.

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