LEVELS AND PATTERNS OF CHLOROAROMATIC COMPOUNDS IN CONTAMINATED SAWMILL SOILS

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Introduction

Soil contaminated with polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) as an effect of chlorophenol (PCPh) usage is a common problem (1). For example chlorophenol preservatives were used at 400 – 500 sawmill sites in Sweden until 1978/1979.

Besides PCDD/Fs, the production of chlorophenols gave rise to a number of other chlorinated by-products (2, 3). In this study we present the results from a survey of three classes of chlorinated aromatic compounds *viz.* PCPhs, chlorinated phenoxyphenols (PCPP) and chlorinated diphenylethers (PCDE).

The compounds were selected because of their known presence in chlorophenol preservatives and because of their differing chemical properties. The PCDEs has been shown to bioaccumulate and to cause toxic responses similar to PCB (4-7). The PCPPs can undergo ring closure and form PCDDs in certain environments.

Materials and Methods

Soil samples from contaminated sawmill sites where collected, sieved through a 2 mm sieve and homogenised in the field. Approximately 2 g of soil was extracted with toluene for 17 hours using Soxhlet-Dean-Stark equipment. Prior to extraction the soil was acidified with acetic acid in order to optimise the extraction of phenolic compounds. Solvents used in extraction and clean-up were of glass-distilled purity (Burdick & Jackson). The phenolic compounds were separated by liquid-liquid extraction by using 0.5 M potassium hydroxide in 50 % ethanol (8). The organic solvent phase contained neutral compounds and the alkaline water phase contained phenolic compounds. After extraction the phenolic compounds where derivatized using acetic acid anhydride.

The extracts with neutral compounds (the organic solvent phase) went through a clean-up and fractionation using multilayered silica (neutral silica and silica mixed with potassium hydroxide and sulphuric acid respectively) (Merck), AX21 Carbon-Celite (Anderson Development Company and Fluka) and alumina oxide (Fluka). The PCDEs was collected when eluting the carbon column with hexane:dichloromethane (1:1), the PCDD/Fs was eluted from the carbon column as a reversed phase using toluene. The final fractionation of PCDD/Fs was performed with an alumina oxide column which was eluted with hexane:dichloromethane (1:1). The results of the PCDD/F analyses will be reported elsewhere.

The analyses of PCPh, PCPPs and PCDEs were made on a GC/LRMS (30 m 0.25 mm I.D., 0.25 µm stationary phase DB-5MS column (J&W)). The ionisation mode was electronic impact and the acquisition was set in SIR-mode registering two ions of each homologous group.

PCPPs were identified as homologues because reference substances are lacking and literature data are sparse. PCDEs are identified with reference substances and literature data covering retention times and mass spectral information (9, 10).

Results and Discussion

Table 1 shows loss on ignition and the total concentrations of the analysed compounds in three different soils. All three soils had high amounts of organic matter, in soil Öbacka some of the organic carbon was a contribution from saw dust. The levels of PCPh were similar in Sikeå and Hillringsberg and in the range of Swedish guideline values of soil remediation; sum of mono – tetrachlorophenols should not exceed 10 mg/kg dw and pentachlorophenol 5 mg/kg dw. In Öbacka the levels of the comparably water-soluble chlorophenols is high which could be explained by the high amount of organic material and a visually more fine particulate soil than Sikeå and Hillringsberg. Both these factors could result in a better adsorption of the compounds to the soil.

Noticeable was the high amount of PCPPs, originally contributing with up to 1-5 % (3). PCPPs were persistent in the soil and thus were not subject to as much transport as could be expected. This has lead to increased amounts of PCPPs in the soil compared to the preservative used. Since it is mostly the higher chlorinated congeners that is present (Figure 1) it is probable that the aromatic structure has a greater influence on the behaviour of the PCPPs than the hydroxyl group. Hillringsberg had an interesting distribution of chloroaromatic compounds compared to the other soils; in Hillringsberg the PCPPs constitute a much smaller amount.

Table 1. Concentration of analysed compounds in three different soils.

Site	LOI (%)	PCPh (mg/kg)	PCPP (mg/kg)	PCDE (mg/kg)
Sikeå	14	8.1	50	1.3
Hillringsberg	9.7	8.3	3.3	0.28
Öbacka	52	66	940	1.9

Congener patterns of PCPhs, PCDEs and the homologue profiles of PCPPs are shown in Figure 1. Only congeners that contribute to more than 2 % of the total amount of each class of compound are included. 2,3,4,6-tetrachlorophenol and pentachlorophenol dominates among the PCPhs. Among the commonly used impregnating agents used in Sweden 2,3,4,6-tetrachlorphenols was the dominating active substance. In these agents pentachlorophenol and 2,4,6-trichlorophenol often contributed with 5-10 % each. These agents contained substantially more PCDFs than PCDDs. However PCDDs were most common when pentachlorophenol was the dominating active agent. Pentachlorophenol has the lowest water solubility of the chlorophenols and therefore present in the soil in higher amounts compared to the composition of the impregnating agent. In these soils it is possible that agents with either 2,3,4,6-tetrachlorophenol or pentachlorophenol have been used.

The PCPPs showed a pattern resembling the scarce data described in literature (2), consisting mostly of hexa- to octachlorinated PCPPs. The Öbacka soil showed a slightly different pattern with mostly hexachlorinated and pentachlorinated PCPP. At Öbacka this deviating pattern was also seen with the PCDEs, with a minor shift towards hepta- and octachlorinated PCDEs instead of octa- and nonachlorinated PCDEs as shown in the other soils. PCDE #196 is the most dominant congener in the PCDE pattern, it contributes to approximately 50 % of the amount of PCDEs in each soil. Compared to literature data of PCDEs in sediment (5), these soils have a larger amount of octa and nonachlorinated PCDEs compared to sediment analyses which have shown hexa and heptachlorinated PCDEs to be the largest homolouge.

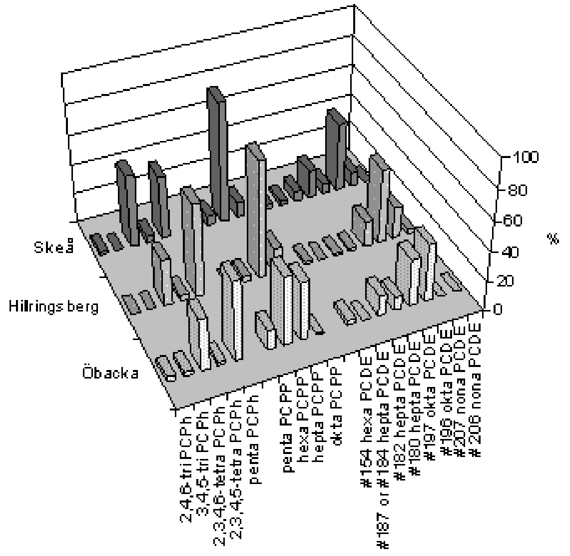

Figure 1. Congener patterns of PCPhs, PCDEs, and homologue profile of PCPPs.

The composition of PCDFs and PCDDs is known from previous analyses in these soils (data not shown here). These results shows a small contribution of 2,3,7,8-substituted congeners to the total amount of PCDD/Fs, *e.g.* the TEQ-concentration were approximately 20 µg TEQ/kg and a the total PCDD/F concentration were 4600 µg/kg in a soil with comparable contamination (1). The profile in Öbacka and Hillringsberg were dominated by PCDDs and particularly OCDD. The profile in Sikeå was more divergent with large amounts of both heptachlorinated PCDFs and PCDDs.

The large amount of natural organic matter at Öbacka has probably contributed to the elevated levels 30 years after the discharges to the soil. The large amount of natural organic matter has contributed to good possibilities for adsorption of contaminants and thereby a lesser transport of the contaminants.

This study has shown high levels of chloroaromatic compounds in soil that are not normally included in characterizations of contaminated sawmill sites. Due to the limited knowledge of their toxicity and their shown persistence it is desirable to include these compounds in future research of contaminated sawmill sites.

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