CHLOROPHENOL SITES IN SWEDEN – A MAJOR DIOXIN RESERVOIR WITH COMPLEX CONTAMINATION PATTERN

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Introduction

Surveys of dioxins and related compounds focused on identification and quantification of sources in Sweden show that a major reservoir of dioxins is connected to the use of chlorophenol (CP) based wood preservatives (*1,2*). In Sweden, CP preservatives have been used at approximately 400 – 500 sawmill sites. The total accumulated amount of dioxins at these sawmill sites, expressed as toxic equivalents (TEQs), is estimated to be in the range of 2-50 kg TEQ (*1*). Today, soil at these sites are contaminated not only with CPs, but also with by-products in the technical formulations, *viz.* polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), diphenyl ethers (PCDEs) and phenoxy phenols (PCPPs) (See Figure 1).

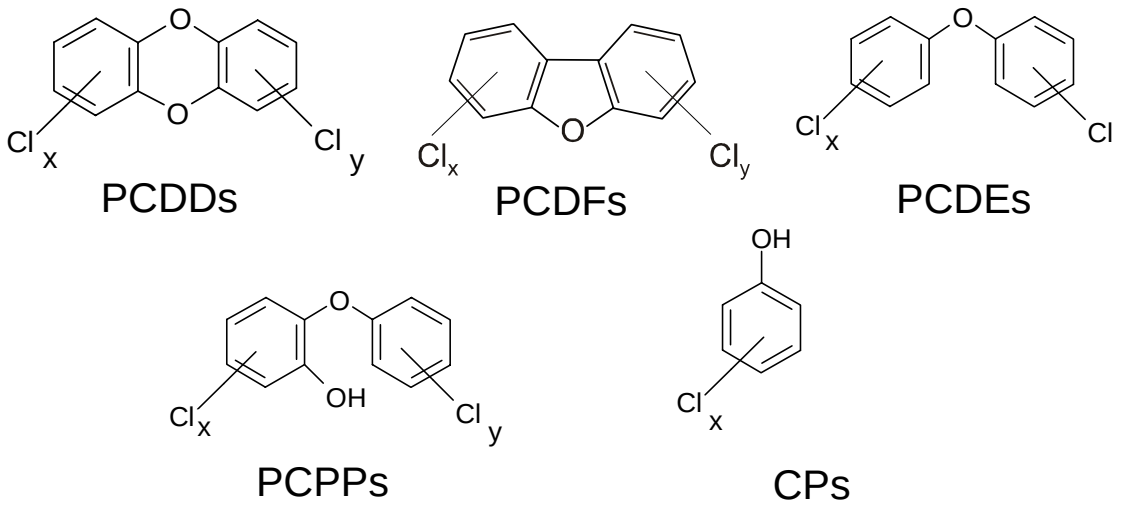

Figure 1. Structural formulas of chlorophenols (CPs) and contaminants found in technical CP-formulations, *viz.* polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), diphenyl ethers (PCDEs) and phenoxy phenols (PCPPs).

Typically, the concentrations of PCDD/Fs found at specific sawmill sites are in the range 100 – 1000 ng WHO-TEQ/kg dw, obviously concentrations depend on previous activities. Hot spots however, have shown concentrations up to 100.000 – 200.000 ng WHO-TEQ/kg dw with corresponding total concentrations of PCDD/Fs in the mg PCDD/F/ kg range. The total concentrations of PCDEs and PCPPs reported in soil samples from sawmill sites in Sweden were up to mg PCDE/kg soil and g PCPP/kg soil (*3,4*). Thus, the total concentrations of the complex mixture of chloroaromatic compounds are in the g/ kg dry soil which has to be considered in the risk assessment prior to possible soil remedial actions. One important aspect is that that different group of chloroaromatic compounds will show different potential for mobilisation and are thus subject to different potential environmental risks.

The aim of the present study was to investigate the potential mobility of CPs, PCDEs, PCPPs, PCDFs and PCDDs at sawmill sites in Sweden as one important factor in the risk assessment procedure. Special interest was given the role of organic matter and particles as carriers of hydrophobic compounds.

Materials and Methods

Soil samples were collected at several sawmill sites, also representing the use of different technical CP formulations. In the field, the samples were sieved through a 2 mm sieve and homogenised. Potential transport via particles was studied by fractionation of particles in ground water samples (*5*). Collected groundwater samples were fractionated in three particle size fractions, *viz.* filter size 0.7µm, 0.4 µm, and 0.2 µm (Whatman International Ltd and Millipore). The fraction passing 0.2 µm was defined as the dissolved fraction. Further, the distribution of the different classes of chloroaromatic compounds between particulate organic matter (POM) and dissolved organic matter (DOM) as well as dissolved fraction was studied in experiments with soil samples from three sawmill sites (*6*). Soil slurries were equilibrated for 48 hours and filtrated (0.7 µm).

All soil samples and fractions were analyzed for CPs, PCPPs, PCDEs, PCDFs, and PCDDs. The extraction and clean-up procedures used are described elsewhere (*5,6,7*). The determinations were performed using HRGC-LRMS as well as HRGC-HRMS.

Results and Discussion

This study showed extraordinary high levels of chloroaromatic compounds that are not normally included in characterizations of contaminated sawmill sites. The observed concentrations of the different classes of compounds in the saw mill soil samples were 0.3 – 4,800 mg CPs/kg d.w., <38 - 6,800 µg PCDEs/kg d.w., <0.01 - 940 mg PCPPs/kg d.w., 7.4 – 18,000 µg PCDFs/kg d.w., and 9.8 – 35,000 µg PCDDs/kg d.w (*4*). The compositions of homologue groups revealed characteristic profile of chloroaromatics in different technical formulations, *e.g.* Ky-5 was dominated by specific PCDFs and Dowicide G was dominated by specific PCDDs.

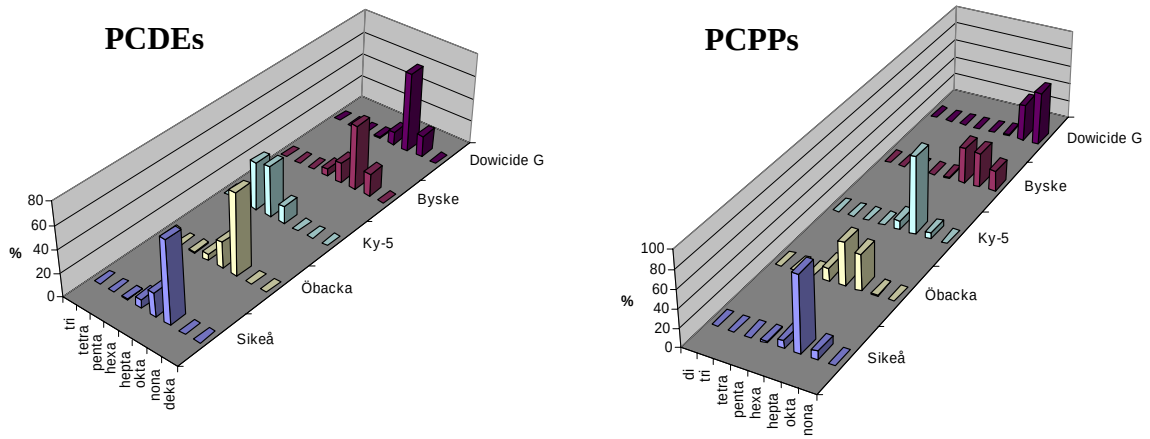

Figure 2. Relative composition of PCDEs and PCPPs in soil samples from three sawmills sites in Northern Sweden (Sikeå, Öbacka, and Byske) as well as the composition in two technical CP formulations, *viz.* Ky-5 and Dowicide G.

The relative composition of the different groups of compounds varied between sites indicating transport influenced by site specific factors. Figure 2 shows the homologue profiles of PCDEs and PCPPs , respectively. As can be seen, specific homologue groups can be found which correspond to technical formulations possibly used.

One of the most critical factors in the risk assessment of sawmill sites is the potential risk of transport from soil to groundwater or surface waters. Transport to the aquatic environment will increase the availability of the compound classes and increase the risk of up take in biota. The results of the POM:DOM distribution experiments clearly demonstrated the expected behaviour of CPs, appearing mainly in the dissolved phase. PCDD/Fs on the other hand were found the POM fraction. Figure 3 shows the partitioning of PCDF homologues between DOM and POM normalized to the amount of carbon. Mass balance calculations showed 0.04 – 27% of the CPs in aqueous phase compared to <0.001% of the PCDD/Fs. The corresponding fractions associated to the DOM for CPs, PCDF, and PCDDs were 0.5 – 17 %, 0.4 – 2.5% and 0.03 – 0.4 %, respectively. The release of DOM, *e.g.* from top soils with high organic matter content, covering the contaminated soil layers, could increase the mobility of chloroaromatic compounds, such as the PCDD/Fs [6].

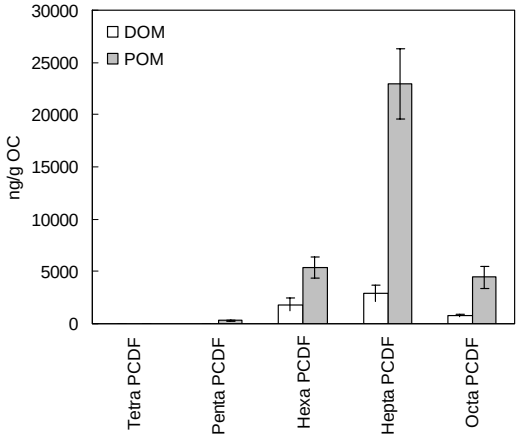

Figure 3. The partitioning between DOM and POM of homologue groups of PCDFs. Concentrations normalized to the amount of organic carbon (OC).

The possible role of particles as a carrier of contaminants was shown in the groundwater fractionation experiments. Considerable amounts of PCDD/Fs were found bound to the fine colloidal particle fraction. In the particulate fractions the PCDD/PCDF ratio was <1 and in corresponding water fraction (<2µm cut off) the PCDFs were dominated (PCDD/PCDF ratio >1)[5]. The sum of toxic equivalents in the water phase and the three colloidal fractions revealed total concentrations of 0.7 – 5.6 ng WHO-TEQs/L. Depending of ground water flow and other site specific factors, the amount associated to this mobile fraction will contribute to the transport of PCDD/Fs from the contaminated sawmill sites.

In conclusion, the total amount of dioxins at the estimated 400 – 500 contaminated sawmill sites in Sweden are in the range of 2-50 kg TEQ. Further, the soils at these sites are contaminated with over by-products, *e.g.* polychlorinated diphenyl ethers (PCDEs) and phenoxy phenols (PCPPs). The soil concentrations at hot spots can be extremely high.

Furthermore, the important role of soil organic matter and colloidal particles for the transport and fate of the organic contaminants with low water solubility was demonstrated. Due to the limited knowledge of potential effects of several classes of chloroaromatic compounds, e.g. PCPPs and PCDEs, found at sawmill sites and their proven persistency suggests that these compounds should be included in future risk assessment of contaminated sawmill sites.

Acknowledgements

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References

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