

PCDD/Fs IN COLLOIDAL GROUNDWATER FRACTIONS AND FILTERED GROUNDWATER FROM A CONTAMINATED SAWMILL SITE

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Introduction

The aim of this study was to elucidate the partitioning and transport of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) between colloidal material and dissolved fractions of groundwater sampled at a contaminated sawmill site.

A previous study has shown sawmill sites contaminated with polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) and other organohalogen compounds (1). Soil samples from five different sites revealed a complex contamination composition with chlorophenols and chlorinated phenoxyphenols, chlorinated diphenylethers (PCDE), PCDFs and PCDDs. The chlorophenols and chlorinated phenoxyphenols usually were the most abundant. All compounds showed a high degree of chlorination, *viz.* tetra- to penta- chlorinated chlorophenols, hepta- to octa-PCDEs and PCDD/Fs.

The large number of wood preservation sites contaminated with chlorophenols and PCDD/Fs makes it important to study the risk of transport of chlorinated compounds from these sites. The low water solubility and high hydrophobicity of PCDD/Fs (2) results in low mass transport when dissolved in water. However, the hydrophobic properties may increase the importance of transport with dissolved organic matter (DOM) and colloidal material (3,4).

To study these transport processes groundwater was sampled at one of the previously investigated sites (1). The groundwater was fractionated into different particulate size fractions, thus making it possible to investigate the distribution of PCDD/Fs between colloidal material in the groundwater and the fraction dissolved in groundwater.

Materials and Methods

The groundwater was sampled at a sawmill site in the northern part of Sweden. The usage of chlorophenols at the site were during the 1960's until the sawmill closure in 1975. The chlorophenol treatment was as dipping or spraying of sawn timber with water based chlorophenol solution. Groundwater was sampled by low flow pumping (Masterflex™) from a well placed in a highly contaminated area at five occasions in the summer and autumn 2005. The groundwater had a yellow-brown colour but was transparent. After the sampling the groundwater was fractionated with filters of 0.7 µm (Whatman International Ltd.), 0.4 µm and 0.2 µm cut off (Millipore). The filtration was done filter holders (Geotech Environmental Equipment Inc.). The three filters collected colloidal fractions; the water that passed through the 0.2 µm filter was defined as the dissolved fraction.

The analytical procedure was according to Persson *et al.* (1) with Soxhlet extraction, clean up using silica (Silica 60, Merck) treated with sulphuric acid and potassium hydroxide respectively. A carbon column (AX21: Celite, Anderson Development Co and Fluka) was used to fractionate the extracts. Analyses was done with HRGC-HRMS (HP 6890 Network GC system, Waters Autospec MS), by means of an isotope dilution technique (¹³C-standards from Wellington Laboratories). The recovery of particulate samples ranged between 60 – 120 %. The water fractions recovery of ¹³C internal standard ranged between 40% and 90%; one sample (sample #4 < 0.2 µm) was excluded due to recoveries below 20 %.

Results and Discussion

Figure 1 shows the concentrations of PCDD/Fs in the colloidal fractions and in the water fractions from the five sampling occasions. All particulate samples, except sample #3-0.4, displayed a dominance of PCDDs (PCDF/PCDD < 1), while in the four water samples PCDFs were more abundant (PCDF/PCDD > 1). More than 99 % of the PCDD/Fs were associated with the colloidal fractions (0.7 – 0.2 μm). The autumn samples (#4 and #5) contained lower concentrations of PCDD/Fs compared to the summer samples (#1 – #3). A possible explanation to the lower concentrations in sample #4 and #5 could be dilution; the weeks prior to sampling had high rainfall compared to the summer samples #1, #2 and #3.

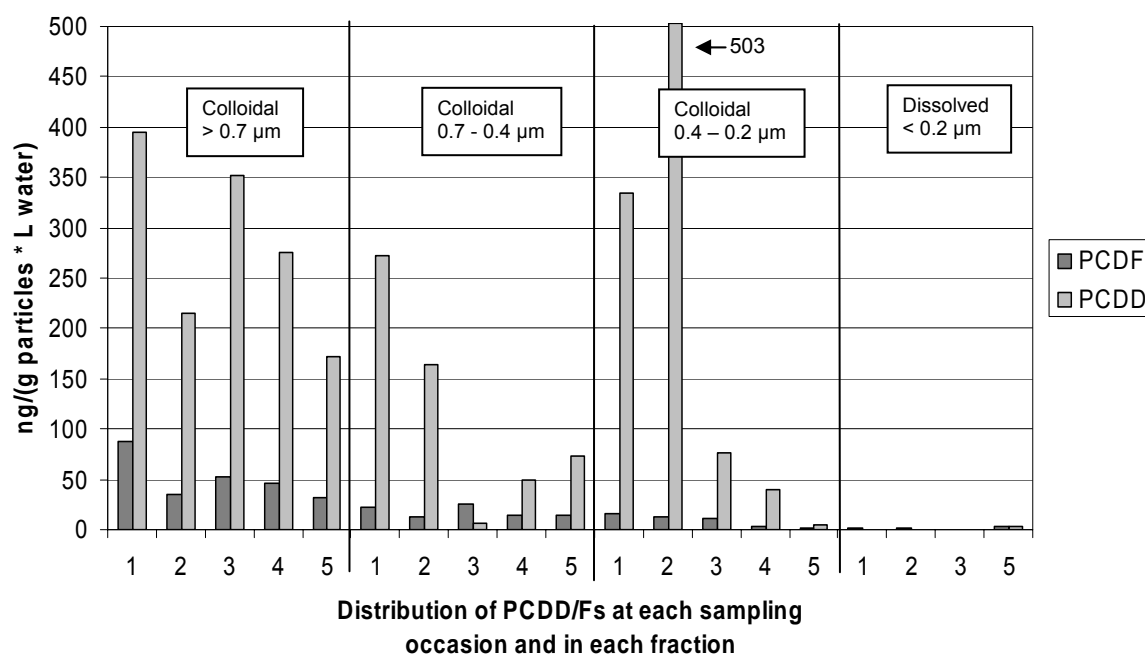


Figure 1. Sum of seventeen 2,3,7,8-substituted PCDD/Fs at each sampling occasion. Sample #4 <0.2 μm has been excluded due to low recovery and an indication of contamination from particulate material. The samples are displayed as amount of PCDD/Fs associated with particles in one litre of water (> 0.2 μm) or dissolved in one litre of water (> 0.2 μm).

No distinct difference in distribution of PCDD/Fs was seen between the three colloidal fractions. At sampling occasions #3, #4 and #5 most PCDD/Fs were associated with the coarse fraction (> 0.7 μm). In contrast, at sampling occasion #1 and #2 a more even distribution of PCDD/Fs between the colloidal fractions was observed. The coarse fraction (> 0.7 μm) had an even distribution of PCDD/Fs between the five sampling occasion. The sum of PCDD/Fs in fraction > 0.7 μm ranged between 200 and 480 $\text{ng}/(\text{g particles} * \text{L water})^{-1}$ compared to 32 – 290 $\text{ng}/(\text{g particles} * \text{L water})^{-1}$ in fraction 0.7 – 0.4 μm and 6 – 510 $\text{ng}/(\text{g particles} * \text{L water})^{-1}$ in fraction 0.4 – 0.2 μm . The coarse fraction (> 0.7 μm) contained the least amount of particles (20 – 300 mg L^{-1}), while the 0.7 – 0.4 μm fraction contained 150 – 600 $\text{mg particles per litre}$ and the 0.4 – 0.2 μm fraction contained 30 – 500 $\text{mg particles per litre}$.

Though the concentrations of PCDD/Fs differed between sampling occasions, the composition of congeners of PCDD/Fs was similar within each fraction ($>0.7\mu\text{m}$, $0.7\text{-}0.4\mu\text{m}$, $0.4\text{-}0.2\mu\text{m}$ and $<0.2\mu\text{m}$). An average composition of PCDD/Fs congeners in each fraction was calculated based on this concordance between sampling occasions. Figure 2 shows the congener distribution of 2,3,7,8-substituted PCDD/Fs in the different fractions, expressed as a percentage. PCDDs, and in particular OCDD, dominated in the colloidal fractions. The second most abundant congener was 1,2,3,4,6,7,8-HpCDD or 1,2,3,7,8,9-HxCDD. No large differences in congener composition between the colloidal samples could be seen. However in the water fraction 1,2,3,4,6,7,8-HpCDF dominated with OCDF as the second most abundant congener. In water sample #4 ($<0.2\mu\text{m}$) OCDD was the dominating congener. The composition showed similarities with the colloidal samples. Thus, water sample #4 was excluded from Figure 2 and Table 1.

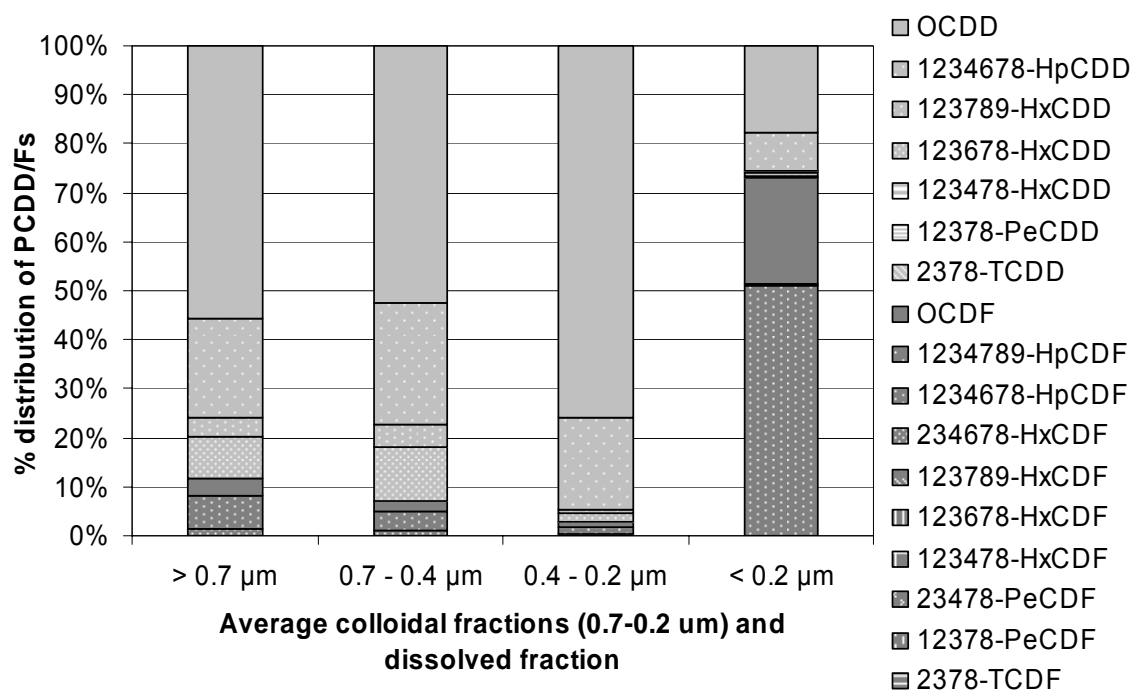


Figure 2. Distribution of 2,3,7,8-substituted PCDD/Fs in four fractions of groundwater based on average calculations of five samples. The colloidal fractions are derived from filtration of groundwater with filter cut-offs of $0.7\mu\text{m}$, $0.4\mu\text{m}$ and $0.2\mu\text{m}$.

In table 1 the concentration of PCDD/Fs expressed as toxic equivalents (WHO-TEQ)(5) are summarized. As mentioned earlier most PCDD/Fs were associated with the colloidal fractions ($0.7\text{--}2.3\text{ ng WHO-TEQ/L}$ compared to $0.001\text{--}0.015\text{ ng WHO-TEQ/L}$). In the colloidal fractions the contribution from different congeners to the WHO-TEQ were as follows: $1,2,3,6,7,8\text{-HxCDD} > 1,2,3,4,6,7,8\text{-HpCDD} > 1,2,3,7,8,9\text{-HxCDD} > 1,2,3,4,6,7,8\text{-HpCDF}$. In the filtered water fraction ($<0.2\mu\text{m}$), dissolved $1,2,3,4,6,7,8\text{-HpCDF}$ contributed the most to the WHO-TEQ. The amounts of PCDD/Fs found in groundwater in this study are considerable, though the bioavailability of particle associated hydrophobic compounds are lower compared to compounds in a dissolved fraction(6).

Table 1. Concentrations of PCDD/Fs expressed as WHO-TEQ of 2,3,7,8-PCDD/Fs in water and particulate samples from five sampling occasions.

Sampling occasion	PCDD/Fs in colloidal fractions (> 0.7 – 0.2 µm) (ng WHO-TEQ L ⁻¹)	PCDD/Fs in filtered water fraction (< 0.2 µm) (ng WHO-TEQ L ⁻¹)
1	2.3	0.001
2	1.8	0.015
3	1.8	0.002
4	1.1	-
5	0.70	0.005

The results show that a significant amount of PCDD/Fs is associated with colloids in the groundwater. Thus, PCDD/Fs may potentially be transported in groundwater from contaminated wood preservation sites where chlorophenols have been used. An estimate of the groundwater outflow at the specific site is 3000 m³ per year. Thus, the outflow of PCDD/Fs would be less than 2 mg WHO-TEQ/year. However, the sampling well was placed in a hot spot and not all soil at the site could be expected to be highly contaminated. Therefore, a true value for the yearly outflow of PCDD/Fs from the site will be less than 2 mg WHO-TEQ. The coarse fraction 0.7 µm was included in these calculations; this fraction will be subject to more adsorption to surrounding soil compared to the colloidal fraction 0.4 – 0.2 µm due to the size of colloids.

A potential transport of PCDD/Fs has been shown from sites contaminated with PCDD/Fs from usage of chlorophenols. Considerable amount of PCDD/Fs was found bound to mobile colloids in groundwater. Further studies of the mobility of PCDD/Fs associated with colloids and confirmations of the results presented in this paper needs to be done at other contaminated sites.

Acknowledgements

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