



Black carbon-dominated PCDD/Fs sorption to soils at a former wood impregnation site

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ABSTRACT

The influence of black carbon (BC) on the sorption of 17 native polychlorinated-*p*-dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was studied in five soil samples from a sawmill site where wood used to be impregnated with chlorophenol preservatives. The presence of BC caused measured total organic carbon (TOC)–water distribution ratios (K_{TOC}) to be a median factor of 51 (interquartile range 18–68, $n = 85$) higher than modeled amorphous organic carbon (AOC)–water distribution ratios (K_{AOC}). K_{TOC} was a factor of 73 ± 27 above K_{AOC} for PCDFs ($n = 10$) and a factor of 20 ± 13 ($n = 7$) for PCDDs. The reason for this difference is probably that attaining a planar configuration after sorption to BC is less thermodynamically favorable for PCDDs than for PCDFs. BC–water distribution ratios were calculated from K_{TOC} , K_{AOC} and BC contents, and ranged from $10^{9.9}$ (2,3,7,8-Tetra-CDD) to $10^{11.5}$ l kg⁻¹ (Octa-CDF). More than 90% of the PCDD/Fs in the soil was calculated to be BC-sorbed. Dissolved organic carbon (DOC)–water distribution ratios were measured to be in the same order of magnitude as K_{AOC} . This study shows that strong sorption to BC should be included when assessing ecotoxicological risk or modeling transport to groundwater of PCDD/Fs in soil.

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1. Introduction

Soil pollution as a result of wood impregnation with tetra- and penta-chlorophenol preservatives occurs at hundreds of locations in various countries such as Sweden, Finland and Canada (Jensen, 1996). The contamination usually consists of chlorophenols, polychlorinated dibenzofurans (PCDFs), polychlorinated-*p*-dibenzodioxins (PCDDs), chlorinated phenoxyphenols and chlorinated diphenylethers (Persson et al., 2007). Total PCDD/Fs contents in such soils can amount up to three mg World Health Organization Toxic Equivalents (WHO-TEQ) per kg dry weight (Persson et al., 2007). As a result, PCDD/Fs can leach to groundwater (Frankki et al., 2006) and accumulate in organisms. Leaching (Huang et al., 2003; Cornelissen et al., 2005; Frankki et al., 2006), bioaccumulation (Moermond et al., 2005) and toxicity (Knauer et al., 2007) can be reduced by the strong binding of PCDD/Fs to carbonaceous geosorbents (CGs) including black carbon (BC), unburned coal and kerogen. Since no coal mining has existed in the area, BC is expected to dominate possible strong PCDD/F sorption to CG.

For PAHs and PCBs in sediments, BC and other carbonaceous geosorbents have been shown to enhance sorption by a factor of up to 100 (Jonker and Koelmans, 2001; Barring et al., 2002; Huang et al., 2003; Cornelissen et al., 2005; Lohmann et al., 2005). For PCDD/Fs in soils, the observations are scarce. Three studies indicate that BC could enhance sorption of these compounds as well. First, the BC–water distribution ratios (K_{BC}) of spiked mono-, di-, tri- and tetra-substituted PCDD/Fs in diesel soot were 20–300 times higher than amorphous organic carbon (AOC)–water distribution ratios (K_{AOC}) (Barring et al., 2002). Second, the K_{BC} s of native di-CDD and tri-CDD in New York Harbor sediment were two orders of magnitude above K_{AOC} (Lohmann et al., 2005). Third, the TOC–water distribution ratios (K_{TOC}) of native tetra-, penta-, hexa-, hepta- and octa-chlorinated CDD/Fs in Norwegian Mg-smelter contaminated sediments were a factor of 40–3330 above K_{AOC} (Persson et al., 2002). In the third study freely dissolved aqueous concentrations ($C_{\text{w,free}}$) were not measured directly but determined by correcting total aqueous concentrations ($C_{\text{w,total}}$) for dissolved organic carbon (DOC) sorption, using non site-specific literature K_{DOC} -values.

In contrast, no effect of BC on PCDD/F sorption was observed for native PCDD/Fs in a soil sample from a wood impregnation site in Northern Sweden (Sikeå) (Frankki et al., 2006). Possible

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explanations for the apparent lack of BC-sorption observed in this study are discussed later in the manuscript.

In the present study, sorption of PCDD/Fs to TOC, BC and DOC was studied in five soils affected by chlorophenol wood impregnation. All 2,3,7,8-chlorinated PCDD/F congeners were included in the study. These congeners show extremely high toxicity through a specific mode of toxic action through binding to the aryl hydrocarbon receptor. Novel elements were added to the knowledge presented in the abovementioned studies by (i) providing K_{BC} -values for 2,3,7,8-substituted PCDD/F congeners in soils, (ii) measuring freely dissolved aqueous concentrations with a passive sampler method, avoiding effects of incomplete phase separation, and (iii) measuring both $C_{W,free}$, $C_{W,total}$ and DOC concentrations, providing reliable data on K_{DOC} for these compounds. Sorption to environmental BC has not been studied before for 2,3,7,8-substituted tetra- to octa-CDD/Fs, and PCDD/F sorption to BC has not been studied before for soil samples.

2. Materials and methods

2.1. Materials

All solvents used were of glass-distilled purity (Burdick and Jackson, Muskegon, MI, USA). All ^{13}C -labelled and ^{12}C -PCDD/Fs were obtained from Wellington Laboratories, Ontario, Canada. Polyurethane foam (PUF) adsorbents were obtained from Ekornes, Norway, and pre-cleaned by twice 24-h extraction in subsequently toluene and acetone. POM (polyoxymethylene) of 55- μm thickness (POM-55, obtained in ~ 1 -kg cylinder-shaped blocks and sliced on a lathe equipped with a high-precision razor blade) from Astrup AS (Norway) was pre-cleaned by washing in hexane and methanol followed by drying overnight at 60 °C. Seventeen ^{13}C -labelled PCDD/Fs (all 2,3,7,8-substituted) were used as internal standards. The quantification was made by the isotope dilution method and by using a ^{12}C -mixture of 17 PCDD/Fs (all 2,3,7,8-substituted). Quantification methods from Danielsson et al. (2005) were exactly followed.

2.2. Soil samples

Samples were collected at a former sawmill site at Marieberg, Sweden (62°59'8", E 17°47'51"), where around 260 kg WHO-TEQ PCDD/F are present. Samples I and II consisted of soil from the inner sawmill area (<50 m from the sawmill), sample III of sawdust from the inner sawmill area, and samples IV and V of soil from the outer sawmill area (350 and 450 m from the sawmill, respectively). Samples (0–50 cm depth; >5 kg) were collected in summer 2006 with a spade, sieved over a 5-mm steel sieve, homogenized using a blender, and analyzed fresh, without prior drying.

2.3. BC and TOC contents

Total organic carbon (TOC) contents were determined with catalytic combustion elemental analysis at 1030 °C after micro-acidification (1 M HCl) to remove inorganic carbonates. Black carbon (BC) contents were determined using the same method on small samples (10-mg) that were ball-ground to optimize oxygen access. Samples were combusted at 375 °C for 18 h under abundant oxygen access, following exactly the procedures outlined by Gustafsson et al. (1997). The temperature was controlled independently and shown to be 375 \pm 1 °C.

2.4. POM calibration for PCDD/Fs

All POM calibration studies were carried out in triplicate, in 1000-ml all-glass flasks, in the presence of 1 g NaN_3 (biocide also providing a constant ionic strength). The principle of the POM

equilibrium passive sampling method is that one can deduce freely dissolved aqueous concentrations (C_W) from the PCDD/F contents in POM with concentration-independent POM–water distribution ratios (K_{POM}) (Jonker and Koelmans, 2001).

In the present study, K_{POM} was measured in POM–water systems with spiked PCDD/Fs, without soil. K_{POM} was measured for eight non-2,3,7,8-substituted congeners of variable degree of chlorination (2,8-DiCDF, 1,6-DiCDD, 2,4,8-TriCDF, 1,3,6,8-TetraCDF, 1,3,6,8-TetraCDD, 1,2,3,8,9-PentaCDF, 1,2,3,4,6,9-HexaCDD and 1,2,3,4,6,7,9-HeptaCDD), and deduced K_{POM} for the toxic, 2,3,7,8-substituted congeners from the K_{POM} – K_{OW} linear free-energy relationship (LFER) obtained by linear regression of measured K_{POM} vs. K_{OW} for the non-2,3,7,8-substituted congeners.

K_{POM} was measured at a range of methanol–water ratios (0–50% methanol) and derived K_{POM} for pure water by extrapolating to 0% methanol. Measurement in methanol–water cosolvent systems, similarly to Smedes (2007), was chosen because of the difficulty in measuring aqueous PCDD/F concentrations at pg to ng per l ranges in 1 l pure water.

PCDD/F stock solution (prepared by dissolving the compounds in acetone and spiking <500 μl acetone per l water) and POM (25–250 mg) were shaken horizontally (180 rpm; 20 \pm 1 °C; 100 d). This 100-d equilibration time is longer than equilibration times of around 30 d used for similar experiments with nine times thicker POM (500 μm) in earlier studies (Jonker and Koelmans, 2001; Cornelissen and Gustafsson, 2004). After equilibration, individual PCDD/F concentrations were 0.1–20 ng l⁻¹, depending on congener and methanol content. The POM-strips were taken out of the water–methanol solutions using tweezers and treated exactly as described in Cornelissen and Gustafsson (2004). Briefly, POM strips were dried with a tissue and extracted by horizontal shaking (180 rpm; 20 \pm 1 °C; 48 h) with 20 ml hexane in the presence of internal standard (see above). The aqueous phase was extracted with 2 \times 25 ml hexane. Hexane extracts were cleaned and analyzed according to the procedures described below.

2.5. Freely dissolved concentrations and K_{TOC}

All sorption studies were carried out in triplicate, at 20 \pm 1 °C, in 250-ml all-glass flasks, with NaN_3 (1 g l⁻¹). Soil (non-dried, 2 g dry weight) was shaken horizontally (180 rpm, 14 d) with distilled water (250 ml). Subsequently POM (2 g) was added and the systems were shaken for another 30 d. No PCDD/Fs were added as native *in situ* compounds were studied. It was assumed that 30 d was long enough for equilibration of the systems where soil and water were pre-equilibrated. The equilibration time of 14 + 30 d was longer than the 10 d earlier shown to be sufficient for equilibration of native six-ring PAHs in a sediment–water–POM-55 system (Cornelissen et al., 2008). Fourteen days sufficed for equilibration of PAHs, PCBs and trichloro-PCDD/Fs in 51- μm thick LDPE (Lohmann et al., 2005). After equilibration, the POM strips were extracted with hexane as described above. Cleanup and analysis of the extracts was as described below.

Freely dissolved soil porewater concentrations ($C_{W,free}$) were deduced from the PCDD/F contents in the POM samplers with the concentration-independent K_{POM} values determined in the POM calibration experiments. The passive samplers turned out to deplete 0.1–5% (average < 1%) of the PCDD/Fs in the soil phase. The reported aqueous concentrations were corrected for this depletion. No correction of K_{TOC} for the “salt effect” caused by the biocide concentration (0.015 M), as the correction was <0.005 log-unit and thus within the experimental error.

2.6. Total dissolved concentrations and K_{DOC}

Soil (1000 g) was slowly percolated with 0.01 M $CaCl_2$ in water (50 ml/h) for 14 days in a 10-cm glass column until a L/S (liquid/

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