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Results of the second national forest soil inventory in Germany - Interpretation of level and stock profiles for PCDD/F and PCB in terms of vegetation and humus type

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HIGHLIGHTS

- Elevated PCDD/F and PCB concentrations in coniferous forest soils than in deciduous and mixed forest soils
- No significant cross-correlation between PCB and PCDD/F amounts and altitude
- At coniferous forest stands pronounced decrease of POPs content from topsoils to mineral soils
- The abundance of POPs in forest soils is dependent of the humus type and forest type.
- Possible translocation within the soil layers for planar contaminants with higher Kd values

GRAPHICAL ABSTRACT

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) were detected in 86 humic topsoil layers and in a subset of 11 randomly selected top mineral forest soils at the depths of 0–5 cm and 5–10 cm collected from different federal states of Germany. The distribution of these persistent organic pollutants (POPs) in humic topsoils with respect to vegetation cover (coniferous vs. deciduous vs. mixed), total organic carbon (TOC), altitude and latitude data was investigated. There is cross correlation between the contents and TOC while the correlation with latitude indicates higher abundances of POPs in central Germany where there is high population density accompanied with industrial activities. The calculated stocks suggest that humus type (mor, mull, or moder) in conjunction with forest type can explain the relative POPs abundances in different soil layers. Generally, humic topsoils show highest contents of POPs compare to the two mineral soils with a ratio of 100:10:1. However, the stock humic layers of coniferous stands contribute about 50% to the total stock, whereas at deciduous stands the stock is mainly located in the upper mineral soil layer (0–5 cm). The soil-water distribution coefficients (Kd) were calculated to estimate the potential translocation in the different soil types. The Kd values vary among the PCBs and PCDD/Fs congeners and are most variable for humic topsoils. There is pronounced chemical abundance in the top mineral soils with increasing Kd and this points to non-water bound transport processes for superlipophilic compounds.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) recognized by the Stockholm Convention on POPs (UNEP, 2001). Being lipophilic compounds and having a high organic carbon-water partition coefficient (Koc), PCDD/F and PCB can easily adsorb on soil organic carbon. Soils tend to be higher in concentration, and take longer to decrease because the residence time for persistent compounds is extremely long, allowing for accumulation with deposition over time. Specifically, forest soils are effective sinks of these chemicals due to their high content of total organic carbon (TOC) (Wang et al., 2014). A German study performed in 1994 for PCDD/F levels in soils reported high values in forest topsoil layers compared to plowland and grassland samples (Rotard et al., 1994). Furthermore, larger POP contents in humus (O-horizon) than mineral soil (A-horizon) were reported in the study that concerns the Central European Alps (Offenthaler et al., 2009). However, there is need for details on the relationships between POPs accumulation in the O- and A-horizons, atmospheric deposition rates, and post depositional mobility.

In Germany, spatial distribution of PCB contents in forest topsoils was attributed to historic application (Aichner et al., 2013). The model known as "forest filter effect" suggests that forest canopies are able to store POPs in soils following different processes such as: rain washout, wax erosion and transport due to litter fall (Nizzetto et al., 2007). In addition, investigations on the particular leaf/needle area in humic (O-) horizon of forest soils (Moeckel et al., 2009; Terzaghi et al., 2013; Weiss et al., 2000) propose that the tree leaves of broad-leaved species with rough surfaces are more efficient in capturing particulate matter than those with smooth surfaces (Beckett et al., 2000).

In fact, different soil horizons may accumulate substances due to various processes such as adsorption, degradation, dissolution, and evaporation which are controlled by physicochemical, microbiological, and soil parameters. In order to understand the mobility of the chemicals one needs to determine the soil–water partitioning coefficients (Kd) (Jonker and Smedes, 2000; Komprdová et al., 2016).

Overall, the ability of forest soils to act as a sink is complicated, and there are many variables which affect the delivery and retention of POPs in ecosystems. The purpose of this study, therefore, is to assess PCDD/Fs and PCBs distributions between humic topsoil layers and the top mineral forest soils of a set of samples collected in different German forest regions and to interpret the findings with respect to parameters such as vegetation cover, forest type, humus type, TOC, altitude, latitude, and Kd.

2. Materials and methods

2.1. Soil samples

As part of the Second National Forest Soil Inventory in Germany (Bodenzustandserhebung (BZE) II, BZE II, 2006; Thuenen Report 43, 2016) samples of a subset of 86 sampling locations (Fig. 1) of approximately 1900 genuine BZE plots were analyzed for their content of PCDD/F and PCB in humic topsoils layer (O-horizon). This subset of samples represents approximately a grid (by 64 km × 64 km), and covers all German federal states (with the exception of the 3 city states), namely Brandenburg, Rhineland-Palatinate, Bavaria, North Rhine-Westphalia, Lower Saxony, Baden-Württemberg, Thuringia, Saxony-Anhalt, the Free State of Saxony, Hesse, Mecklenburg-Western Pomerania, Saarland, and Schleswig-Holstein.

The sampling campaign was performed in the period of 2006 to 2008 and details regarding the sampling procedure are described elsewhere (BMELV, 2006; Aichner et al., 2013). In total 86 locations (45 coniferous, 21 deciduous, 16 mixed and 4 unknown forest types) were included (Table 1S). Additionally, samples of the mineral topsoil (A-horizon) at two subsequent depths (0–5 cm and 5–10 cm) were collected

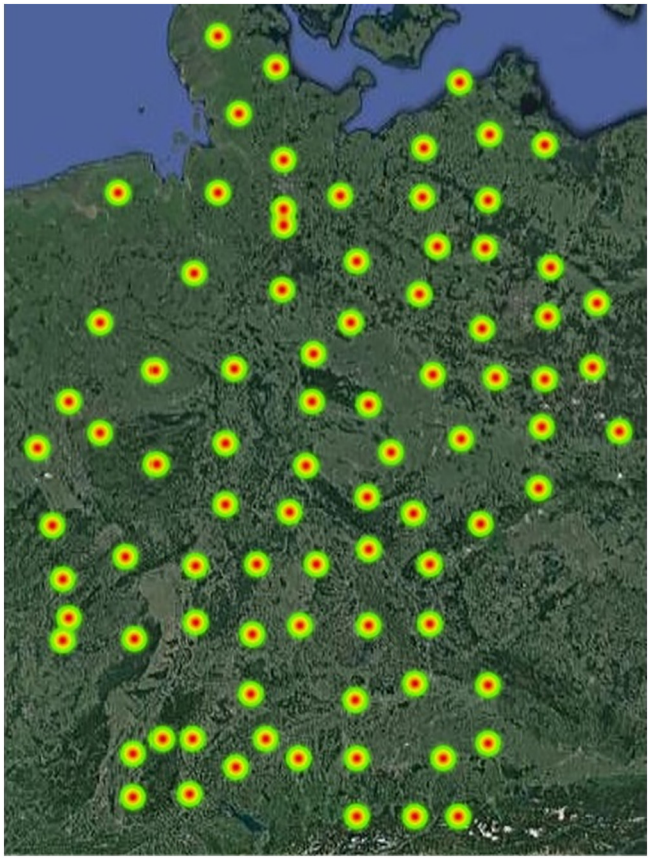

Fig. 1. Map with the 86 sampling sites. Illustrated sampling points were based on geographical coordinates.

from 11 out of 86 sampling locations. This selection was made so that nearly every federal state is represented and that samples of high pollutants abundances are provided. The ratio of coniferous- deciduous- and mixed forest soil samples of the 11-subset is 8 vs. 2 vs. 1 which is similar to the 86-subset (45 vs. 21 vs.16).

Drying of the investigated samples was not performed to avoid loss of volatile contaminants. The TOC (%), dry weight (dw) (%), and pH data was in a range of 5.4–49/1.2–6.2/0.9–5.4% for the 86 samples of humic topsoils; 25–81/62–97/69–96% for the 11 samples of top mineral forest soils at depth of 0–5 cm; and 2.9–4.9/2.6–4.5/2.6–4.3% for the 11 samples of top mineral forest soils at depth of 5–10 cm, respectively (Aichner et al., 2013). The data which also encompass altitude as meters above mean sea level (m a.s.l.), sum of humus stock (t/ha), forest type (coniferous, deciduous, and mixed) and humus type (mor, mull, and moder) are presented in Table 1supplementary. The log K_{ow} and the organic carbon/water partition coefficient (Koc) values for 17 PCDD/F and 18 PCB congeners are shown in Table 2S. The Koc was expressed as $0.411 \times K_{ow}$ (Karickoff, 1981). The Kd value for selected 11 humic topsoil layers and top mineral soils regarding the compounds of PCDD/F and PCB was further calculated as Kd = Koc * TOC (data can be calculated on the basis of information Tables 1S and 2S).

After sampling, the soil material was stored in cooled brown glass bottles and left on ice until transfer to −20 °C freezer. Subsequently, the samples were sieved by a stainless steel sieve (4 mm cross diameter in case of humic topsoil and 2 mm cross diameter in case of top mineral soils) and homogenized by a Tyler divider and bottled in brown glass bottles. The pretreatment of the samples was performed at about −10 °C. The pretreated samples were stored at less than −20 °C at the Federal Institute for Materials Research and Testing (BAM), Berlin. Hereinafter, the samples were transported to Helmholtz Zentrum München where the storage temperature was −28 °C.