PBDE levels in German forest soils

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Introduction

Polybrominated diphenyl ethers (PBDE) are a class of the widely used brominated flame retardants (BFRs) in electronic devices and residential products. The atmosphere is the primary transport media of these compounds and subsequent wet or dry deposition is one of the most important means of entry PBDEs into the terrestrial environment[1]. Since some PBDE are also persistent and bioaccumulate in certain biota (including human) in May 2009 the Parties of the Stockholm Convention for Persistent Organic Pollutants (POPs) took the decision to list commercial penta-BDE and commercial octa-BDE as POP substances[2]. It has been shown that forest regions can efficiently filter POPs from the atmosphere and increase contaminant deposition in forest soils[3]. For example, in Germany 70% of soil-borne POPs could be present in the soils of forests, which cover 30% of the country's land area[4]. Since several studies focused on the environmental fate of existing "traditional" POPs as PCBs and PCDD/Fs in forest soils, there are not much data published on PBDE levels and distribution. Higher concentration of $\sum_{ALL}$PBDE in forest soils than grassland was assessed[5] and manifested that some differences in the congener pattern are observed depending on soil composition and latitudinal fractionation. Therefore, the aim of this work is to identify and quantify the PBDEs levels in forest soil samples of the second national forest soil inventory in Germany. In addition, PBDE composition patterns are aimed to be assessed with respect to various numbers of parameters as vegetation cover, the total organic carbon (TOC), pH, the soil–water partitioning coefficients (Kd), and latitude in order to provide an insight on their occurrence in the study region.

Material and methods

Soil samples

A subset of 86 humic topsoils (Oh/Of horizon) has been selected from a set of 470 samples taken in a 16 km x 16 km grid[6]. Additionally, a subset of 11 forest soil samples from the German federal 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, were selected and two layers with depth of 0-5cm and 5-10 cm of the mineral horizon were collected within the subset. Details about the sampling campaign are described elsewhere[7,8]. In total 45 coniferous-, 21 deciduous-, and 16 mixed, and 4 soil samples of unknown type were included. The octanol/water partition coefficient (Kow) value for 11 PBDE congeners and the organic carbon/water partition coefficient (Koc) as Koc=0.411* Kow[9] are calculated. The Kd value for selected 11 topsoils and mineral soils regarding the compounds of PBDE was expressed as Kd=Koc*TOC(%)/100%.

Determination of PBDE levels in soil samples
Extraction of 20 g of fresh weight (fw) soil sample was carried out on Accelerated Solvent Extractor (ASE 300, Dionex GmbH, Idstein, Germany) using a mixture of n-hexane:acetone (75:25, v/v) at 120°C and pressure of 12 MPa. Clean-up encompassed sandwich, carbon and alumina chromatographic columns. PBDE analyses were performed by HRGC/HRMS. A Restek Rtx-1614 capillary column was used with a length of 15 m, ID 0.25 mm and film thickness 0.1 µm. The temperature program was as follows: 100°C, 1.5 min, 10°C min-1, 230°C, 5°C min-1, 325°C, 6 min. 11 BDE- congeners including BDE-15, -28, -47, -99, -100, -153, -154, -183, -197, and -207 were identified and reported in pg/g dry weight (dw). The analytical laboratory involved is quality assured according to DIN EN ISO/IEC 17025.

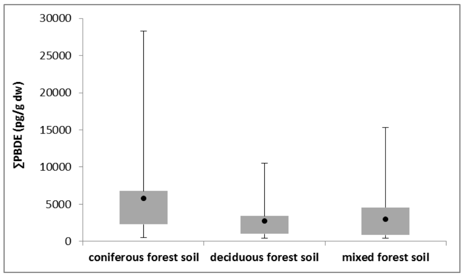
Results and discussion
Levels of PBDE in 86 forest humus topsoil and 11 mineral topsoil samples on dw basis are summarized in Table 1. The data show a considerable high variation for each congener and decreased PBDE abundance with increasing forest topsoil depth. Among the 11 PBDEs analysed, five congeners such as BDE-15, 28, 183, 197, and -207 were found below the limit of quantification (LOQ) in all topsoil samples with depth of 5-10 cm. The dominant PBDE congeners in all samples within the subsets were BDE-47, followed by BDE-99, and BDE-100. This finding of PBDE fingerprint in regard to the highest concentration was also found in Scottish surface soils[1]. Furthermore, another study[10] found out that BDE-209 could debrominate to lower brominated BDE congeners as BDE-99 and BDE-47 by solar photolytic decomposition.

Table 1: Concentration of PBDE (pg/g dw) in 86 humus topsoil and 11 mineral topsoil samples at depths of 0-5cm and 5-10 cm, respectively.

	Min	Max	P10	Median	mean	P90	SD	n<LOQ
	86 humus topsoil							
BDE-15	<2.6	34.9	4.49	9.56	11.4	23.3	34.9	65
BDE-28	<5.5	938	8.0	18.0	40.9	59.9	938	5
BDE-47	177	85043	332	1149	2942	4417	85043	0
BDE-99	79.9	28025	237	945	1671	2920	28025	0
BDE-100	20.8	5973	69.3	240	429	853	5973	0
BDE-153	<9.5	1018	25.8	91.0	146	301	1018	6
BDE-154	2.4	1043	25.3	79.3	119	216	1043	1
BDE-183	<23.6	2926	46.0	138	242	569	2926	11
BDE-197	<10.4	1019	18.8	48.2	91.6	212	1019	10
BDE-207	<30.1	2822	71.1	150	266	433	2822	16
HBB	<3.8	603	12.4	34.0	66.4	101.3	603	49
	11 mineral topsoil with depth of 0-5 cm							
BDE-15	<1.7	2.0	0.0	0.0	0.4	2.0	0.8	9
BDE-28	<1.0	4.6	0.0	1.4	1.4	3.4	1.6	5
BDE-47	<10.4	179.7	28.7	81.8	81.5	152.2	57.1	1
BDE-99	<2.9	96.2	6.7	35.3	42.2	95.9	36.1	1
BDE-100	<0.7	36.4	1.7	10.6	12.9	25.2	11.5	1
BDE-153	<2.9	9.4	0.0	0.0	2.9	9.4	3.8	6

BDE-154	<0.8	17.1	0.0	1.8	5.0	13.4	5.9	3
BDE-183	<10.8	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-197	<4.0	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-207	<6.1	18.6	0.0	0.0	5.9	17.1	7.6	6
HBB	<1.7	7.3	0.0	0.0	1.6	5.5	2.6	7
	11 mineral topsoil with depth of 5-10 cm							
BDE-15	<1.7	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-28	<0.9	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-47	<9.6	40.4	0.0	0.0	10.6	26.1	13.8	6
BDE-99	<2.7	44.7	0.0	4.3	7.6	9.7	12.8	4
BDE-100	<0.6	9.5	0.0	1.4	2.0	3.4	2.8	4
BDE-153	<2.9	13.1	0.0	0.0	2.3	12.8	5.2	9
BDE-154	<0.3	3.8	0.0	0.9	1.4	3.7	1.5	3
BDE-183	<8.2	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-197	<3.8	0.0	0.0	0.0	0.0	0.0	0.0	11
BDE-207	<5.8	0.0	0.0	0.0	0.0	0.0	0.0	11
HBB	<1.7	3.0	0.0	0.0	0.3	0.0	0.9	10

The data for the ∑PBDE (pg/g dw) grouped by the three different vegetation types of forests (coniferous, deciduous, and mixed stands) is shown on Figure 1. Although, great variations within the values and the different numbers of samples included in the groups are present, the results show that soils of coniferous forests tend to accumulate more PBDE than deciduous and mixed forest soils. Similar results were also found in the previous study for the sum of PCDD/F and sum of PCB in this subset of soil samples (Pandelova et al., 2018), whereas the relationship was more pronounced for PCBs than for PCDD/Fs. The process behind this is possibly associated with the retention of POPs in wet and dry deposition by the conifer needle[11]. In fact, several other studies have suggested that the retention of POPs in the soils of boreal forests is highly efficient[12,13].



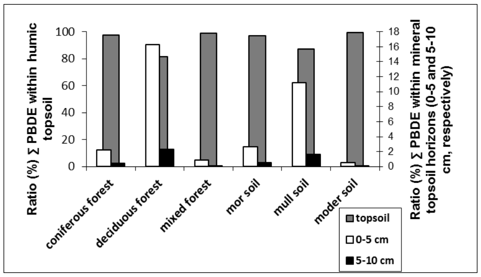


Figure 1 (left). Boxplot for∑PBDE (pg/g dw) in humic topsoils differentiated according the forest type, namely coniferous (n = 43), deciduous (n = 21) and mixed (n= 16). Vertical bars represent the error bars and the mean is presented as a point.

Figure 2 (right). Ratio (%) of the ∑PBDE within humus topsoil and mineral topsoil with depth of 0-5 cm and 5-10 cm in respect to vegetation cover (coniferous, deciduous, and mixed stands) and soil type (mor, moder or mull), respectively.

Figure 2 shows the ratio of ∑PBDE (pg/g dw) in humus topsoils and topsoil horizons with depth of 0-5cm and 5-10 cm in respect to vegetation cover (coniferous, deciduous, and mixed stands) and soil type (mor, moder or mull), respectively. In general, the ∑PBDE were almost completely distributed in the humus topsoils, followed by negligible amounts in the mineral topsoils with depth of 0-5 cm and 5-10 cm. However, about 14% of the total ∑PBDE were found in topsoils with depth of 0-5 cm of deciduous forests or mull types, respectively. It can be explained by the fact that mull-type humus is characterized by aeromorphic and less acidic properties and intense biologically driven mixing of organic matter with the lower soil horizons[8].

No clear relationship was observed for the distribution of ∑PBDE across the soil TOC(%) and pH within the humus- and mineral forest soil horizons (data not shown). The spatial distribution of ∑PBDE (pg/g dw) on topsoils in regard to the latitude of the 86 sample locations was studied. No correlation was found between the data of northing and the PBDE level, whereas the most abundant levels were determined in the samples collected from the area with latitude between 51°00’00’’ and 53°00’00’’ which reflects an intensively industrialized and highly populated belt of 250 km width in central Germany.

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