

# Chapter 8

## Occurrence and Spatial Distribution of Selected Organic Substances in Germany's Forest Soils



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### 8.1 Introduction

Persistent organic contaminants are hardly decomposed in the environment. Once emitted from anthropogenic sources, these substances can accumulate in various environmental compartments, particularly in soils and sediments, and remain there for many years. In addition to their persistence, the substances can have harmful effects on humans and on the environment. They may have a cancerogenic or mutagenic effect to humans or impair the reproduction. In the environment, these substances can accumulate in organisms, have an adverse effect on them or influence their hormonal balance. Substances like polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), dichlorodiphenyltrichloroethane (DDT), and hexachlorobenzene (HCB) have been emitted from anthropogenic sources for several decades and are now ubiquitously distributed. The worldwide distribution of the persistent organic substances is caused by transport through air and water, leading to the detection of the substances on places far away from their emission sources, e.g. in polar regions (Kallenborn 2007; Lohmann et al. 2007; Jones and de Voogt 1999). Some persistent organic substances can naturally arise under certain conditions, but these sources are negligible compared to the anthropogenic emissions. Due to their proven harmful properties for humans and the environment, the use of these substances was governed and partly totally forbidden by the international Stockholm

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Convention on Persistent Organic Pollutants. Twelve organic substances known as “dirty dozen” were banned worldwide by the Stockholm Convention (UNEP 2001; Lohmann et al. 2007).

The investigated substances are briefly described in the following:

### **Polycyclic Aromatic Hydrocarbons: PAH**

PAHs consist of hydrocarbon rings (usually benzene rings), which are connected to one another via common sides. Due to the combination of the rings, there are approximately 10,000 different PAH. For the present study, the 16 indicator PAHs (EPA) were selected using established analytical methods for this substance group.

The PAHs have been the focus of science and the public for decades because of their harmful properties for humans and the environment. Many PAHs are assessed in European chemicals legislation (REACH) as so-called “PBT” substances because of their negative environmental behaviour. They decompose very slowly or not at all in the environment (P, persistent), accumulate in organisms and food chains (B, bioaccumulating), and are toxic to organisms (T, toxic) even at very low environmental concentrations. Once released, such substances remain very long, accumulate, and can thus develop their toxic effect in the environment over a long period. Additionally, numerous PAHs are also carcinogenic and therefore belong to the “CMR” substances (C, carcinogen; M, mutagenic; R, toxic for reproduction). The ubiquitous occurrence of PAHs in the environment makes them a particularly problematic substance group in combination with their properties (UBA 2016).

### **Polychlorinated Biphenyls and Dioxin-Like Polychlorinated Biphenyls: PCB and dl-PCB**

PCBs are chlorinated hydrocarbons with a similar chemical structure to dioxins. On the backbone of a biphenyl (two benzene rings linked via a single bond), one or more hydrogen atoms are replaced by chlorine atoms. In total, there are 209 possible compounds (congeners). In the present study, six indicator congeners were analysed.

Polychlorinated biphenyls are thermally and chemically stable, non-flammable, non-conductive, and hydrophobic. They are technical chemicals that have been used extensively in various applications since 1929 until the early 1970s, including the use in transformers, electrical capacitors, and hydraulic systems as hydraulic fluids, as softeners in paints, sealants, insulation materials, and plastics. In addition, PCBs can originate from combustion. The use of PCBs has been banned in Germany since 1989, but polluting the environment by disposing PCB-containing waste (transformers, capacitors, and hydraulic systems) is still a major problem worldwide. Because of accidents, improper waste management, and diffuse inputs, PCBs have continued to spread throughout the environment. They accumulate as persistent and bioaccumulative substances in the food chain and can now be detected even in fish in the Antarctic, in mother’s milk, and in human fat tissue. The chronic effects of PCBs on humans can be very diverse (e.g. chloracne, liver damage, teratogenicity, immune system damage). PCBs are amongst the 12 organic substances known as “dirty dozen” (Batool et al. 2016; UBA 2017).

Twelve of the possible 209 PCB congeners (see above) have a similar structure as well as properties as the dioxins and are therefore called dioxin-like PCB. The most toxic one is PCB 126 (UBA 2017).

**Dichlorodiphenyltrichloroethane: DDT and Its Metabolites (DDx)**

DDT is an insecticide that has been used since the early 1940s. Because of its good protection against insects, its low toxicity to mammals, and its low-cost manufacturing process, it was the most used insecticide for decades. DDT is degraded, beginning with the conversion into the very long-lived metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) (Aislabie et al. 1997; Boul 1995). Because of their good fat solubility, DDT and its metabolites accumulate in the fat tissue of humans and animals through the food chain (Aichner et al. 2013). The use of DDT in most industrial countries was banned in the 1970s. It also belongs to the “dirty dozen”. In countries that have ratified the Stockholm Convention, the production and use of DDT are only permitted for the control of disease-transmitting insects, particularly the carriers of malaria (Wang et al. 2016; Batool et al. 2016; Lohmann et al. 2007; Boul 1995).

**Hexachlorobenzene: HCB**

HCB consists of an aromatic benzene ring in which all hydrogen atoms are replaced by chlorine atoms. HCB has a high vapour pressure and is stable in the air. In addition to the persistence, HCB has several harmful properties for humans and the environment. It accumulates in organisms and along the food chain because of its high fat solubility, and this might lead to harmful effects to humans.

HCB was used as a fungicide, being stopped between 1981 and 1984 due to the negative properties in both parts of Germany (Heinisch et al. 2006a). In addition, HCB also belongs to the “dirty dozen”. HCB is a by-product or waste product in numerous chemical production processes, including chlorine-containing products (Fiedler et al. 1995). Therefore, many chlorinated pesticides and other chemicals contain traces of HCB contamination. HCB can also arise from combustion processes of chlorine-containing compounds.

**Polychlorinated Dibenzo-*p*-Dioxins, Polychlorinated Dibenzofurans: PCDD/F**

PCDD/F are composed of 75 polychlorinated dibenzo-*para*-dioxins (PCDD) and 135 polychlorinated dibenzofurans (PCDF). They consist as mixtures of single compounds (congeners) with different composition. For the toxic effects of the 210 dioxins and furan congeners, 17 compounds are relevant since they are strongly enriched in living organisms. Therefore, only the concentration of these 17 indicator congeners is generally analysed. The most toxic dioxin of them is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), which is widely known since the chemical accident in Seveso, Italy, in 1976. Dioxins are already highly toxic in small amounts. They accumulate mainly in fat tissue due to their lipophilicity (fat solubility). Dioxins have been classified as cancerogenic. They can arise as unwanted by-products in the presence of chlorine and organic carbon during combustion processes and thus be present as impurities in chemicals and products, e.g. in PCB, in pentachlorophenol, and in other chloro-organic pesticides. They may also be present as impurities in materials, e.g. in asphalt, in building site rubble, or in PCB sealing compounds. Dioxins can also arise from fires of forests, coal seams, dumps, and peats and during volcanic eruptions (UBA 2017; Dopico and Gomez 2015).

For the unified risk assessment of PCDD/F and dl-PCB mixtures, the World Health Organization introduced toxicity equivalence factors (TEF) in 1998, which were modified in 2005. The concentration of a given congener is multiplied by its TEF to calculate the equivalence concentration related to 2,3,7,8-TCDD (normalized to 1). The total value of the PCDD/F and dl-PCB equivalents (TEQ) is then calculated from the sum of these concentrations (van den Berg et al. 2006).

Studies show that forests have a higher air/soil distribution coefficient due to their scavenging effect (the “Auskämmeffekt”, i.e. trees filter out airborne pollutants) than agricultural or urban areas. Furthermore, soils with high total organic carbon (TOC) concentration act as a sink for persistent organic substances (Wania and Mackay 1996; Meijer et al. 2003; Posado-Baquero and Ortega-Calvo 2011; Horstmann and McLachlan 1998; Nizzetto et al. 2006; Sweetman et al. 2005). On the other hand, soils can also act as a source for some of these substances, particularly for highly volatile substances.

Numerous publications deal with the occurrence of volatile organic substances in the atmosphere and the deposition from the atmosphere (Hafner et al. 2005; Hageman et al. 2010) as well as their occurrence in agricultural and urban soils. However, there are only a few studies on forest sites, and they are often restricted to smaller areas or small sample numbers (Manz et al. 2001; Aichner et al. 2007; Wilcke 2007; Maliszewska-Kordybach et al. 2008). Exceptions to this are, for example, a study from Austria (Weiss et al. 2000) as well as studies from Bavaria, Switzerland, Great Britain, and Norway (Schmid et al. 2005; Belis et al. 2009; Offenthaler et al. 2009; Desaulles et al. 2008; Schuster et al. 2011) and a recent study from Pandelova et al. (2018), dealing with PCDD/F and PCB in German forest soils. Some of these studies discuss the relationships between environmental parameters or local conditions such as altitude, population density, precipitation, or the concentration of organic matter in soil. However, a systematic comparison of the results of these studies is difficult because they differ in their sampling methods, the investigated soil horizons, and investigated substances.

A homogeneous database, which is necessary for a systematic evaluation, is not available for a large forest area. For this reason, the sampling area of the second National Forest Soil Inventory (NFSI) with about 470 sampling points of the BIOSOIL grid is ideally suited to investigate the occurrence of persistent organic substances in forest soils under climatically moderate conditions with a wide range of environmental parameters and local conditions. The aim of the present study is to show the concentrations, stocks, and spatial distribution of the investigated organic substances in forest soils across Germany.

## 8.2 Material and Methods

The soil sampling procedure is described in detail in BMELV (2006). In brief, soil was sampled in a grid at the BIOSOIL spots of  $16 \times 16$  km as systematic sampling scheme within the German forests. Additionally, about 50 sampling spots of the

**Table 8.1** Classification of humus levels according to Ad-HocAG\_Boden (2005)

Notation (humus level)	Humus concentration (mass-%)
No humus	0
Very weak humic	<1
Weak humic	1 – <2
Medium humic	2 – <5
Strong humic	5 – <10
Very strong humic	10 – <15
Extremely strong humic	15 – <30
Organic, peat	≥30

NFSI 8 × 8 km grid were selected to consider specific regional topography or emission situations. Amongst others, polychlorinated dioxins and furans and dl-PCBs were analysed in the context of a supplementary project of the Federal Environment Agency (UBA) in the humus layer at a selection of 86 sampling spots.

For details concerning the analysis of organic substances, see Aichner et al. (2013). To calculate the humus concentration, total organic carbon concentration was multiplied by 1.72 or by 2 for organic layers and peat, respectively. For discussion purposes, humus is classified according to Ad-HocAG\_Boden (2005), as is compiled in Table 8.1. At least 15 sampling sites per humus level had to be present for data evaluation.

For the evaluation of data, the lower bound assessment was chosen, i.e. values lower than the quantification limit was set to  $10^{-6}$   $\mu\text{g kg}^{-1}$  or  $\text{ng TEQ05 kg}^{-1}$  for dl-PCB and PCDD/F, respectively. Zero values, as normally required for the lower bound approach, were not used, since statistical analysis was carried out on log-transformed data and  $\log(0)$  is not defined. Scales in the figures are also on a log basis. Kruskal-Wallis (H test) and post hoc Dunn test were conducted to identify significant differences on a  $p < 0.05$  level. A nonlinear multiple regression (support vector machine, SVM) was used to investigate the driving factors explaining the concentrations of organic substances. The results of SVM were compared to a linear regression model. The factors examined were soil texture, humus level according to Ad-HocAG\_Boden (2005) representative for total organic carbon (TOC) concentration, forest type (deciduous, mixed, and coniferous), soil depth (depth increment), and western and eastern federal states for DDX.

Stocks [ $\text{g ha}^{-1}$ ] were calculated by multiplying a given concentration of a considered organic substance in soil [ $\text{mg kg}^{-1}$ ] with the considered depth increment (i.e. 0.05 m; 0–5 cm or >5–10 cm) and the soil bulk density [ $\text{g cm}^{-3}$ ] of the considered depth increment and a conversion factor of 10. The stocks of the organic layer were referred to the TOC stocks (see Chap. 6), since the organic matter mainly consists of TOC. The total stocks for a considered organic substance were calculated by summing up the stocks of the organic layer and the two depth increments.

All statistical analyses were performed with R 3.2.5 (R Core Team 2015).

### 8.2.1 Concentrations of Organic Substances in German Forest Soils

Data of organic substances in soils of forest soils are rare in comparison to urban or agricultural soils. Krauss et al. (2000) published a local study from northern Bavaria. They measured PAH (as sum of 20 congeners) concentrations from 24 to 15,056  $\mu\text{g kg}^{-1}$  in the O horizons of 15 forest sites. The range for PCB (as sum of 12 congeners) in their study amounted to 11.6–201.5  $\mu\text{g kg}^{-1}$ . In a study of Fortmann and Meesenburg (2007) from Lower Saxony, PAH concentrations (as sum of 16 congeners) from 61–18,266  $\mu\text{g kg}^{-1}$  were measured in the O horizons.

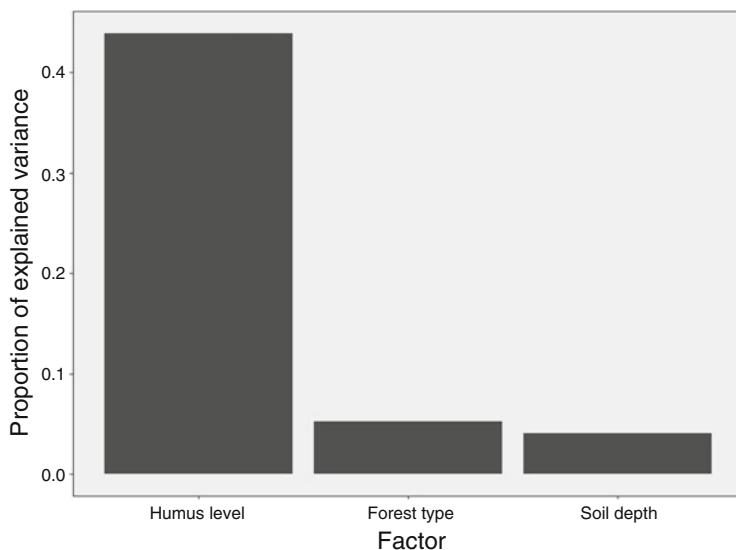
Aichner et al. (2013) evaluated the same data as in the present study and classified the organic substances concentrations as generally low. They mention studies and the respective results for organic substances from other countries, e.g. Czech Republic, France, UK, and Norway. However, due to varying sampling strategies (e.g. different horizons or depth increments) and/or different methods (e.g. determination sum of 16 PAKs versus sum of 14 PAKs, sum of 6 PCBs versus sum of 12 PCBs), a comparison from the above-mentioned studies to the present study is not appropriate. Additionally, in the present study, results were not restricted to a specific region in Germany.

For some of the organic substances considered in this study, the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung; BBodSchV (1999)) provides so-called precaution values to evaluate the organic substance concentrations in the mineral soil. In accordance with § 8 (2) of the Federal Soil Protection Act (Bundes-Bodenschutzgesetz; BBodSchG (1998)), exceedance of precaution values for soil, when taking into account the harmful substance concentration from sources that are geogenic or due to extensive settlement, generally raises concern that harmful changes to the soil have taken place pursuant to § 9 BBodSchV. The precaution values thus do not represent a danger threshold but instead indicate a threshold for concern, which, if exceeded, demands that precautionary measures such as avoiding or reducing further inputs should be taken.

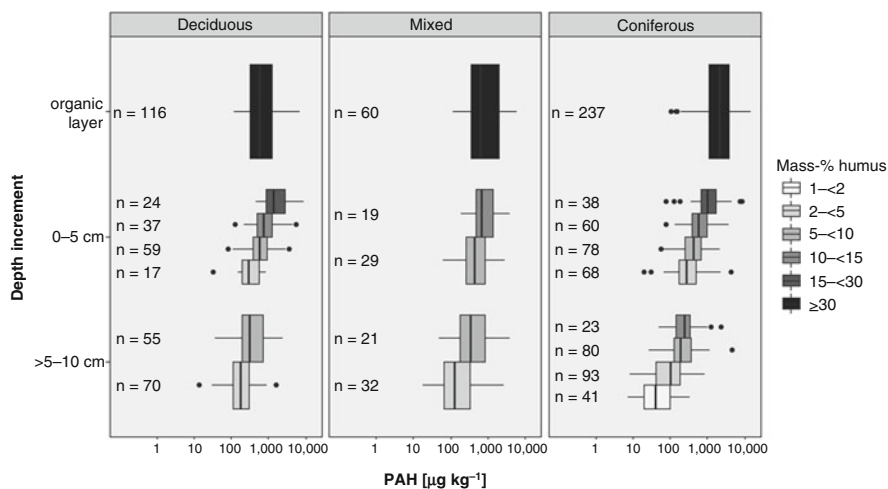
#### PAH

The nonlinear multiple regression analysis (SVM) revealed that most of the PAH concentration can be explained by the humus level classified according to Ad-HocAG\_Boden (2005). The humus level, which is representative for TOC concentration, explained 44% of the total variance followed by the forest type (5%) and soil depth (4%). In total, 53% of the variance was explained (Fig. 8.1). This was compared to a multiple linear regression, which explained 43% of the total variance, showing a nonlinear relationship between the PAH concentration and the explanatory parameters. The results for the PAH concentrations depending on the humus level, forest type, and the depth as explanatory factors are shown in Fig. 8.2.

Highest and lowest PAH concentrations with 7.5–14,889.0  $\mu\text{g kg}^{-1}$  were both measured in coniferous forests. As expected, the PAH concentrations increased with

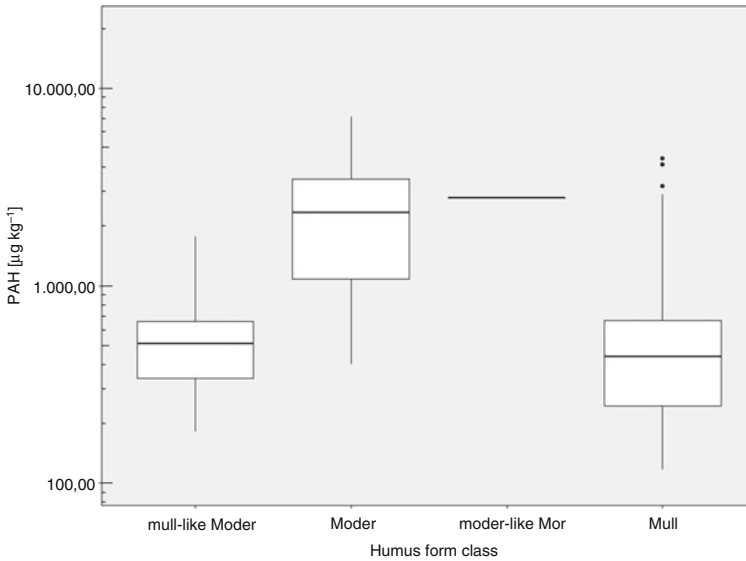


**Fig. 8.1** Proportion of the variance explained by given factors calculated by support vector machines for PAH content in forest soils



**Fig. 8.2** PAH concentrations grouped by forest type, depth increment, and humus level

increasing humus level, i.e. increasing TOC concentration. In the organic layer, PAH concentration in soils under coniferous forests (median  $2113.2 \mu\text{g kg}^{-1}$ ) was significantly higher than in soils under deciduous (median  $580.8 \mu\text{g kg}^{-1}$ ) or mixed (median  $655.6 \mu\text{g kg}^{-1}$ ) stands. Moreover, in medium humic mineral soil ( $2 \leq 5$  mass-% humus) at >5-10 cm depth, the PAH concentration under deciduous forest (median



**Fig. 8.3** PAH concentrations in the organic layer grouped by humus form classes under deciduous forest

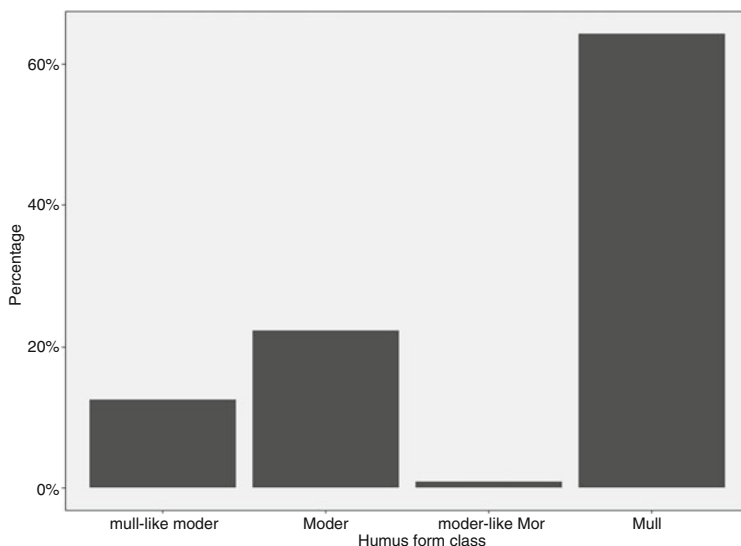
183.1  $\mu\text{g kg}^{-1}$ ) was significantly higher than under coniferous forest (median 108.0  $\mu\text{g kg}^{-1}$ ).

In deciduous forest, the PAH concentration was lower in the organic layer than in extremely strong humic mineral soil (15 –  $\leq 30$  mass-% humus) at the first depth increment from 0 to 5 cm. Figure 8.3 presents the PAH concentrations in the organic layer plotted against the humus form class. The humus form class mull showed the lowest PAH concentration. It becomes obvious from Fig. 8.4 that the biological highly active humus form mull with more than 60% had the greatest share on the observed humus form classes.

The Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999) prescribes precaution values for PAH in fine soil depending on its humus concentration. The precaution value for soils with a humus concentration equal or lower than 8% is 3000  $\mu\text{g PAH kg}^{-1}$  dry weight; the value for soils higher than 8% is 10,000  $\mu\text{g PAH kg}^{-1}$  dry weight. The precaution values do not apply to organic layers. At only two of the investigated sampling sites, the PAH concentration exceeded the precaution value in the mineral soil in the first depth increment from 0 to 5 cm.

It was expected that PAH concentrations were universally decreasing with depth, due to the (historic) deposition. In deciduous forest, the PAH concentration was lower in the organic layer than in the first layer of extremely strong humic mineral soil. Mull was the dominant humus form class under deciduous forest (Fig. 8.4). It is characterized by high biological activity, and the litter layer is not present all year. On the one hand, the very active microorganisms supported the PAH degradation.





**Fig. 8.4** Percentage of humus form classes under deciduous forest

On the other hand, biological activity supported an intensive mixing with the mineral soil. These processes presumably led to a higher PAH concentration in the mineral top soil compared to the organic layer. The same trend was observed for the other investigated substances.

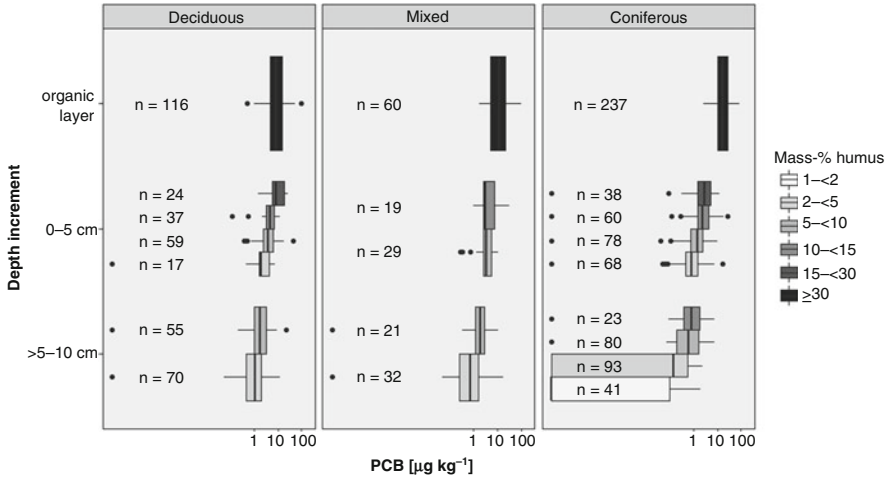
It becomes obvious that degradation and relocation might both have been responsible factors for the PAH distribution within the organic layer and mineral soil. Furthermore, these factors seemed to be driven by additional site characteristics, e.g. humus form or TOC. High PAH concentrations in the O horizons or in the organic layers reflected the current airborne deposition of PAH, whereas high concentrations in mineral soils might stem from older deposition incorporated from organic layers into the mineral soil through biological activity.

### PCB

The humus level was the factor explaining most of the PCB concentration in soils as revealed by SVM. It explained 32% of the total variance, followed by the forest type with 7% and soil depth with 5%. This made 44% of explained variance in total. A linear regression model explained only 33% of the total variance.

At some sampling sites under all three forest types, PCB was below quantification limit. This was especially obvious in weak humic soils ( $1 - \leq 2$  mass-% humus) under coniferous forest, where the median concentration amounted to  $0.0 \mu\text{g kg}^{-1}$ . Maximum PCB concentration was  $106.3 \mu\text{g kg}^{-1}$  under mixed forest in the organic layer (Fig. 8.5).

The PCB concentration in the organic layer of coniferous forest was with a median of  $16.9 \mu\text{g kg}^{-1}$  significantly higher than that of deciduous forest with  $8.6 \mu\text{g kg}^{-1}$ . In strong humic mineral soil ( $5 - \leq 10$  mass-% humus) at 0–5 cm



**Fig. 8.5** PCB concentrations in the organic layer and the first two depth increments of the mineral soil grouped by forest type and humus level

depth, the PCB concentration was significantly lower in coniferous (median  $1.4 \mu\text{g kg}^{-1}$ ) compared to deciduous forests (median  $3.8 \mu\text{g kg}^{-1}$ ). The same was true for extremely strong humic soil ( $15 - \leq 30$  mass-% humus), where the median under deciduous forest amounted to  $8.6$  and to  $3.0 \mu\text{g kg}^{-1}$  under coniferous forest.

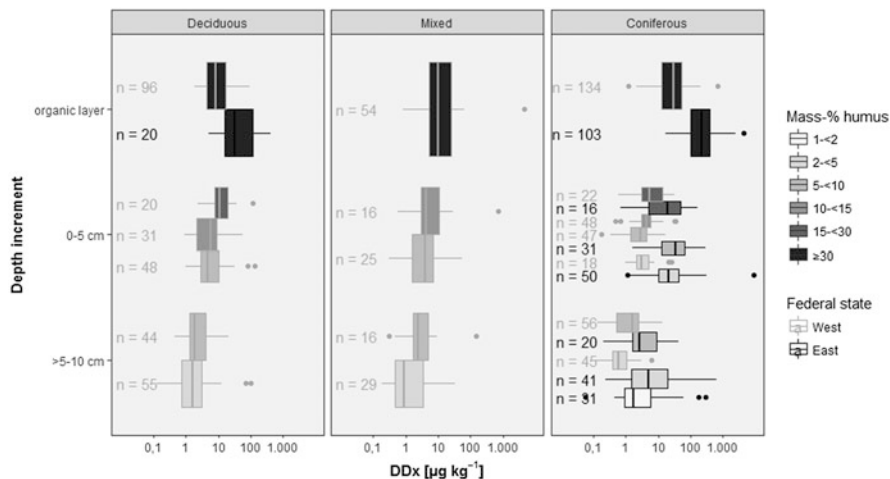
As mentioned for PAH, the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999) also prescribes precaution values for PCB6 in fine soil depending on its humus concentration, amounting to  $50 \mu\text{g kg}^{-1}$  dry weight ( $\leq 8\%$  humus) and  $100 \mu\text{g kg}^{-1}$  dry weight ( $>8\%$  humus concentration). At none of the investigated sampling sites, the PCB concentration exceeded the precaution values in the mineral soil, showing that the PCB concentration in German forest soils was universally low.

### DDT and Its Metabolites

In the knowledge of the nationwide distribution of DDX, the distinctions between western and eastern federal states were applied in the SVM. In contrast to PAH and PCB, soil depth with 28% is the factor explaining most of the total variance of the DDX concentrations. Oppositely, the humus level contributes 1% to the explanation of the total variance. In total 43% of the total variance were explained by the given factors (39% with a linear model).

Figure 8.6 provides an overview of DDX concentrations grouped by depth, forest type, federal state, and humus level. Many humus levels are excluded because they contain too less sampling sites ( $<15$ ), especially under the deciduous and mixed stands in the eastern part of Germany. For reasons of better visibility, the zero values (DDX below quantification limit) are not shown in Fig. 8.6.

As for PCB, at 14 sampling sites under all 3 forest types, DDX could not be detected and was set to  $0.0 \mu\text{g kg}^{-1}$  due to the lower bound approach. Maximum



**Fig. 8.6** DDX concentrations in the organic layer and the first two depth increments of the mineral soil grouped by eastern and western federal states, forest type, and humus level

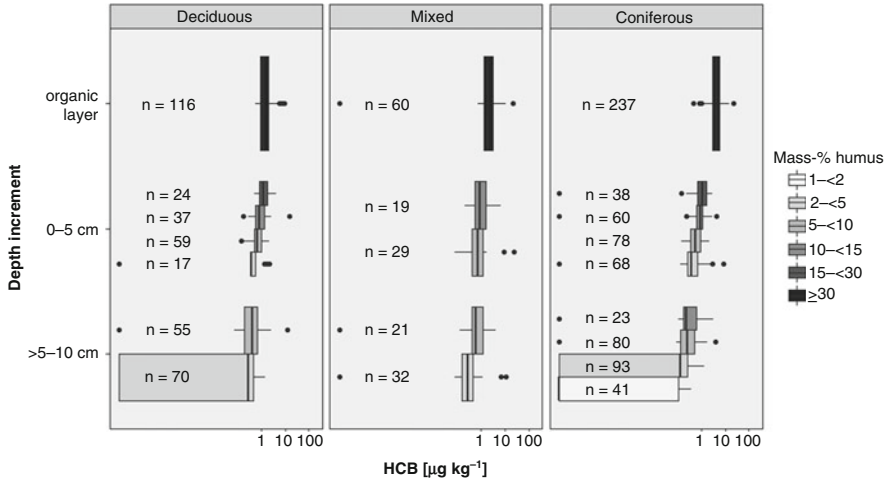
concentration reached  $8630.0 \mu\text{g kg}^{-1}$  in 0–5 cm depth of medium humic mineral soil ( $2 - \leq 5$  mass-% humus) under coniferous forest. Significant differences between DDX concentrations under coniferous forests in eastern compared to western soils were observed in the organic layer, in medium humic mineral soil ( $2 - \leq 5$  mass-% humus), and in 0–5 cm depth in strong humic mineral soil ( $5 - \leq 10$  mass-% humus). The DDX concentrations were lower under deciduous than under coniferous forest.

In the western federal states, the same pattern of explaining factors on the DDX concentrations was revealed, but only 31% (compared to 26% with linear regression) of the variance was explained by the model. In detail, soil depth had the highest proportion with 26%, forest type showed 4%, and humus level amounted to 1%. Due the lack of data in deciduous and mixed forests and because of the dominance of coniferous forests, SVM was not calculated separately for the eastern federal states.

### HCB

Similar to DDX, soil depth with 27% was the factor explaining most of the total variance of the HCB concentrations. The forest type explained 6% and the humus level 2% of the total variance. In total 35% of the total variance was explained by these factors. A linear regression model gave 29% explanation.

As for the other substances, except PAH, also HCB was below the quantification limit at some sampling sites and was consequently set to  $0.0 \mu\text{g kg}^{-1}$ . Maximum concentration amounted to  $24.4 \mu\text{g kg}^{-1}$  in >5–10 cm depth in strong humic soil ( $5 - \leq 10$  mass-% humus) under mixed forest. Significant differences between the HCB concentrations in soils were observed in the organic layer. The concentration under coniferous forest (median  $4.3 \mu\text{g kg}^{-1}$ ) was higher than that under mixed forest (median  $1.9 \mu\text{g kg}^{-1}$ ) and under deciduous forest (median  $1.2 \mu\text{g kg}^{-1}$ ) (Fig. 8.7).



**Fig. 8.7** HCB concentrations in the organic layer and the first two depth increments of the mineral soil grouped by forest type and humus level

Aichner et al. (2013) assessed the concentrations of HCB, like the other investigated organic substances, in German forest soils as low. Three main sources of HCB are given in the relevant literature. The application of HCB as a fungicide was discontinued in both parts of Germany between 1981 and 1984 (Heinisch et al. 2006b; UBA 2012). As a by-product, traces of HCB are included in various chlorine-containing chemicals. HCB can also arise from combustion processes of chlorine-containing compounds (Aichner et al. 2013).

### dl-PCB

Data were available of 86 sites, which were only sampled in the organic layer. Only the 83 locations with  $\geq 30$  mass-% humus were evaluated. The dl-PCB concentration reached from 0.7 ng TEQ05 kg<sup>-1</sup> in the organic layer under deciduous forest to 34.1 ng TEQ05 kg<sup>-1</sup> in the organic layer of a mixed forest. The median concentration of dl-PCB under coniferous forest is significantly higher than that under deciduous forest (Fig. 8.8).

### PCDD/F

As for dl-PCB, 83 sampling sites were evaluated. The PCDD/F concentration in the organic layer under coniferous forest was with 19.2 ng TEQ05 kg<sup>-1</sup> significantly higher than under deciduous forest with 11.0 ng TEQ05 kg<sup>-1</sup>. Minimum concentration was found in the organic layer under deciduous forest. Maximum concentration under coniferous forest amounted to 2.2 TEQ05 kg<sup>-1</sup> and 105.5 TEQ05 kg<sup>-1</sup>, respectively (Fig. 8.9).

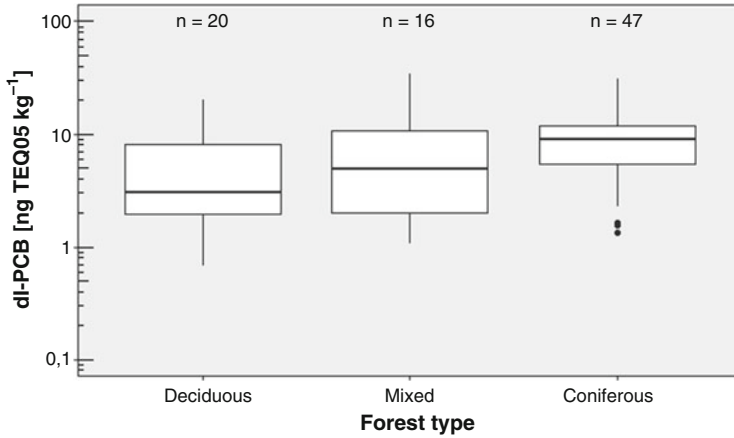


Fig. 8.8 dl-PCB concentration in the organic layer grouped by forest type

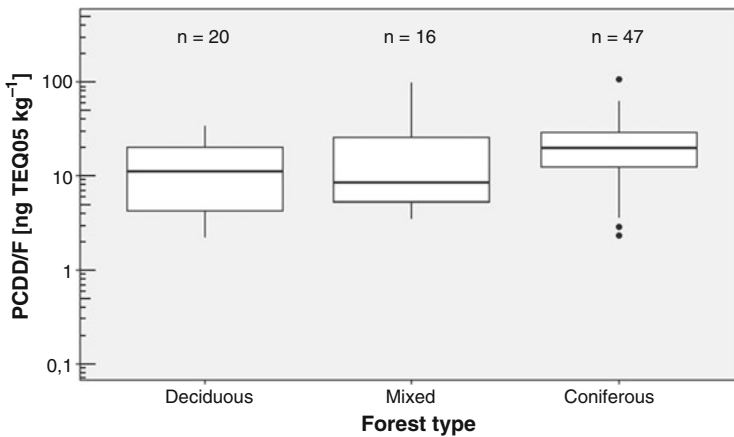


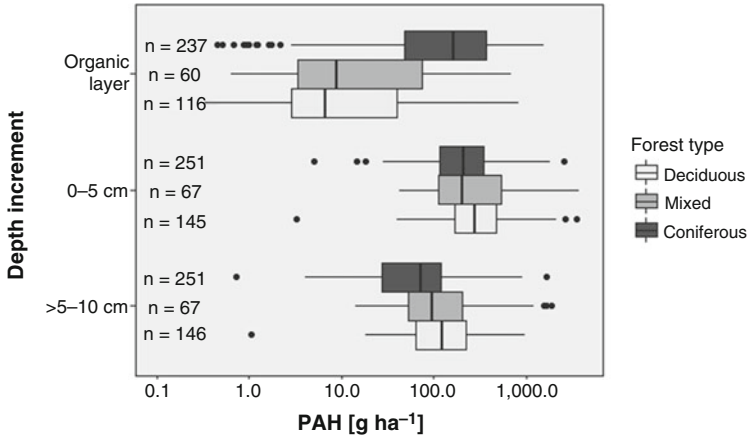
Fig. 8.9 PCDD/F concentration in the organic layer grouped by forest type

## 8.2.2 Stocks of Organic Substances in German Forest Soils

The stocks of all organic substances were differentiated according to depth increment and forest type, except for dl-PCB and PCDD/F. The stocks are also shown as total amount by forest type. The stocks of the organic layer were referred to the TOC stocks, since the organic matter mainly consists of TOC. This is also the binding agent for the organic substances.

### PAH

PAH stocks ranged from 0.3 g ha<sup>-1</sup> in the organic layer under deciduous forest to 3758.6 g ha<sup>-1</sup> in mineral soil from 0 to 5 cm under mixed forest. In the organic layer and in both depth increments, the PAH stocks were significantly different between



**Fig. 8.10** PAH stocks in the organic layer and the first two depth increments of the mineral soil grouped by forest type

coniferous and deciduous forest (Fig. 8.10). In the organic layer, the PAH stock under coniferous forest was clearly higher (median  $6.8 \text{ g ha}^{-1}$ ) than under deciduous forest (median  $162.3 \text{ g ha}^{-1}$ ). In contrast, in 0–5 cm of the mineral soil, PAH stocks were significantly lower (median of  $209.0 \text{ g ha}^{-1}$ ) under coniferous forest than under deciduous forest with  $282.1 \text{ g ha}^{-1}$ . The stocks in the soil depth increment from >5 to 10 cm were also significantly lower under coniferous (median  $72.4 \text{ g ha}^{-1}$ ) than under deciduous forest (median  $124.1 \text{ g ha}^{-1}$ ).

Regarding the total stocks without differentiating by depths, there are no significant differences between the forest types. The median PAH stock was  $483.2 \text{ g ha}^{-1}$  (Fig. 8.11).

### PCB

PCB stocks showed the same pattern as PAH: stocks under coniferous forest were significantly higher than under deciduous forest (median  $1.2$  vs.  $0.1 \text{ g ha}^{-1}$ ) and vice versa in both depth increment of mineral soil (median  $0.7$  vs.  $1.9 \text{ g ha}^{-1}$  and  $0.1$  vs.  $0.7 \text{ g ha}^{-1}$ , respectively) (Fig. 8.12).

Figure 8.13 shows significantly higher total PCB stocks under deciduous forest than under coniferous forest, amounting to  $3.4 \text{ g ha}^{-1}$  and  $2.4 \text{ g ha}^{-1}$ , respectively.

### DDx

As for the DDx concentration, the stocks are shown separately for eastern and western federal states. Stocks were significantly higher in the organic layer under coniferous forest than under deciduous forest (median  $17.1$  vs.  $0.5 \text{ g ha}^{-1}$  in the eastern federal states, median  $2.1$  vs.  $0.1 \text{ g ha}^{-1}$  in the western federal states) and under mixed forest in the western federal states.

In the eastern federal states, no significant differences between the forest types in the mineral soil were detected. In the western federal states, the DDx stocks were significantly higher in 0–5 cm under deciduous forest than under coniferous forests

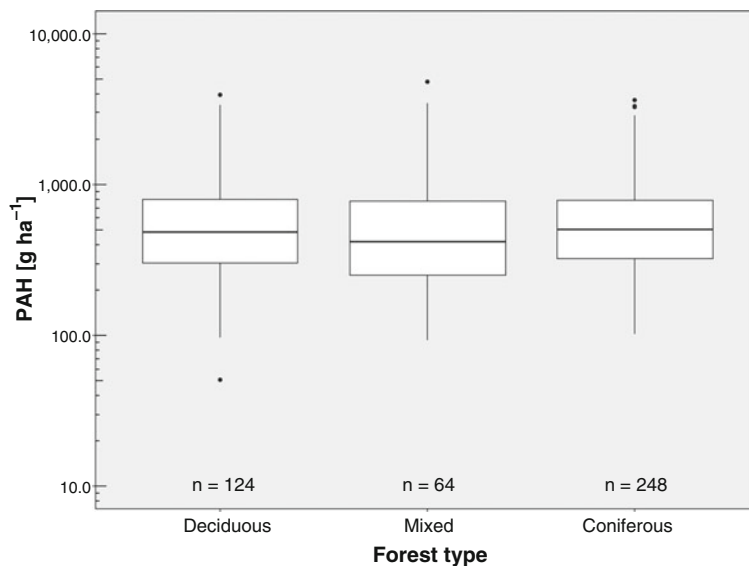


Fig. 8.11 Total PAH stocks grouped by forest type

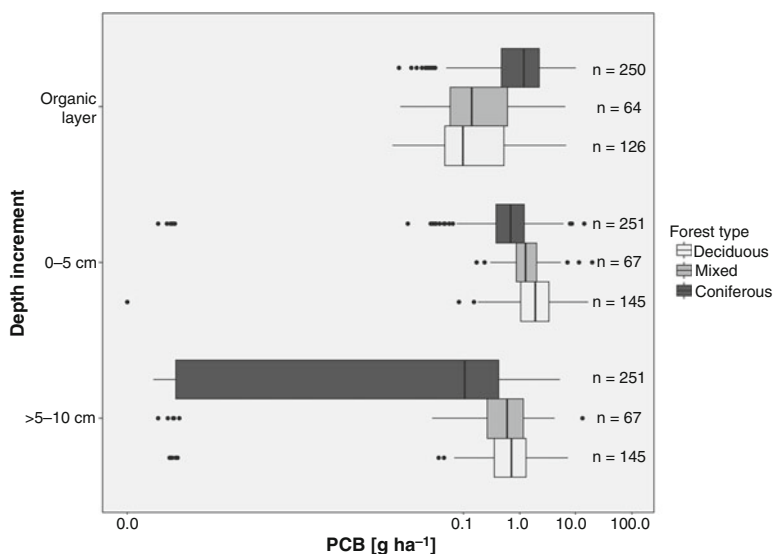


Fig. 8.12 PCB stocks in the organic layer and the first two depth increments of the mineral soil grouped by forest type

(median  $2.7\text{ g ha}^{-1}$  vs.  $1.5\text{ g ha}^{-1}$ ). In  $>5-10\text{ cm}$  depth, DDx stocks under deciduous forest with a median  $0.8\text{ g ha}^{-1}$  and mixed forest with  $0.7\text{ g ha}^{-1}$  were significantly higher than under coniferous forest with  $0.4\text{ g ha}^{-1}$ .

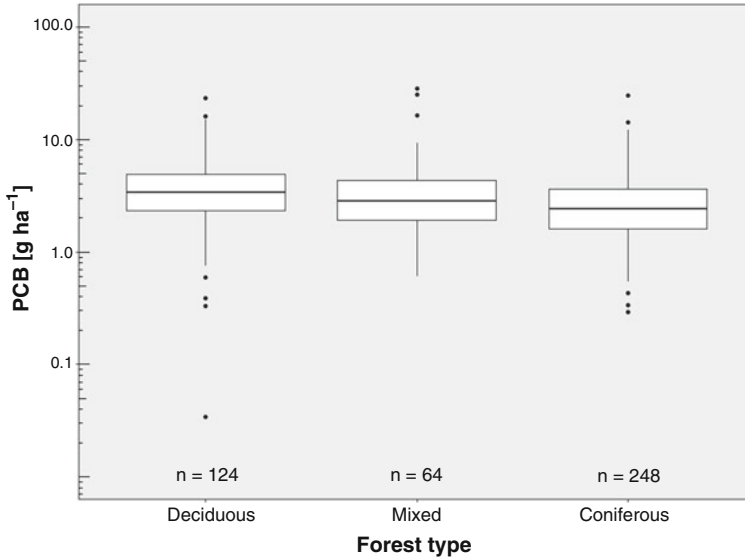


Fig. 8.13 Total PCB stocks grouped by forest type

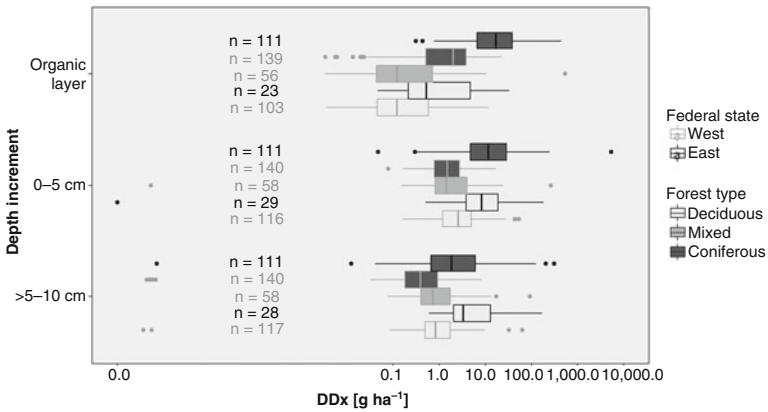


Fig. 8.14 DDX stocks in the organic layer and the first two depth increments of the mineral soil grouped by federal states and forest type

The stocks in the respective forest types were significantly higher in the eastern than in the western federal states (Fig. 8.14). Consequently, the total DDX stocks were significantly higher under deciduous and coniferous forests in the eastern than in the western federal states, as shown in Fig. 8.15. The differences within eastern and western federal states between the forest types were not significantly different and amounted to 38.3 g ha<sup>-1</sup> in the eastern and to 4.4 g ha<sup>-1</sup> in the western federal states.



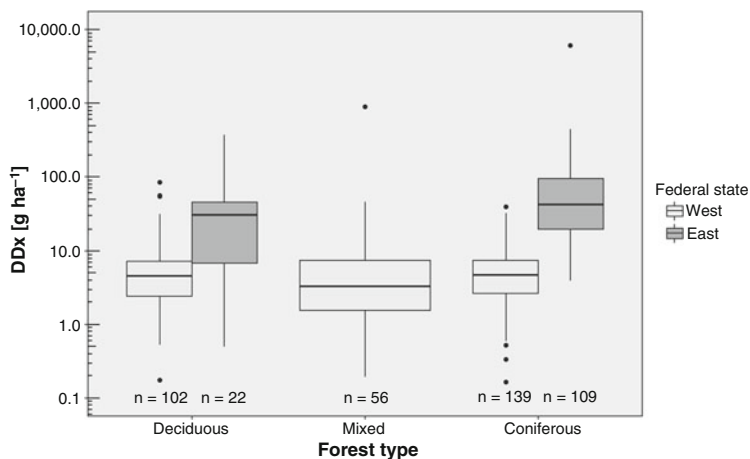


Fig. 8.15 Total DDX stocks grouped by federal states and forest type

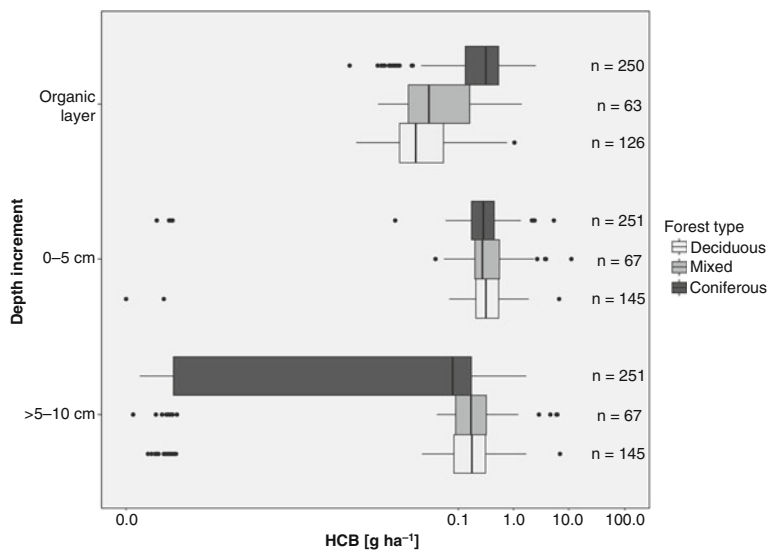


Fig. 8.16 HCB stocks in the organic layer and the first two depth increments of the mineral soil grouped by forest type

### HCB

The HCB stocks were significantly higher in the organic layer under coniferous than under deciduous and mixed forest (median  $0.3 \text{ g ha}^{-1}$  vs.  $<0.1 \text{ g ha}^{-1}$ ). Oppositely, stocks in mineral soil from 5 to 10 cm were significantly lower under coniferous (median  $0.1 \text{ g ha}^{-1}$ ) than under deciduous and mixed forest (median  $0.2 \text{ g ha}^{-1}$ ). In the depth increment from 0 to 5 cm, no significant differences were detected (Fig. 8.16).

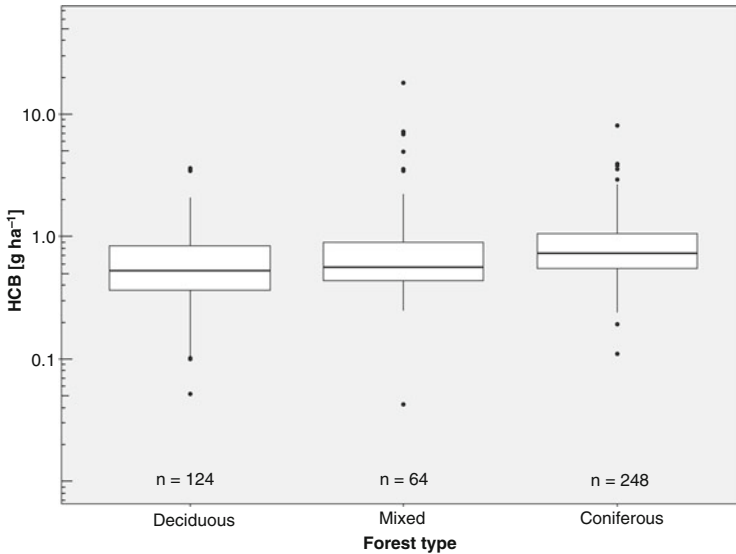


Fig. 8.17 Total HCB stocks grouped by forest type

Figure 8.17 illustrates the total HCB stocks irrespective of soil depth, showing no significant differences between the forest types. Median HCB stock amounted to 0.6 g ha<sup>-1</sup>.

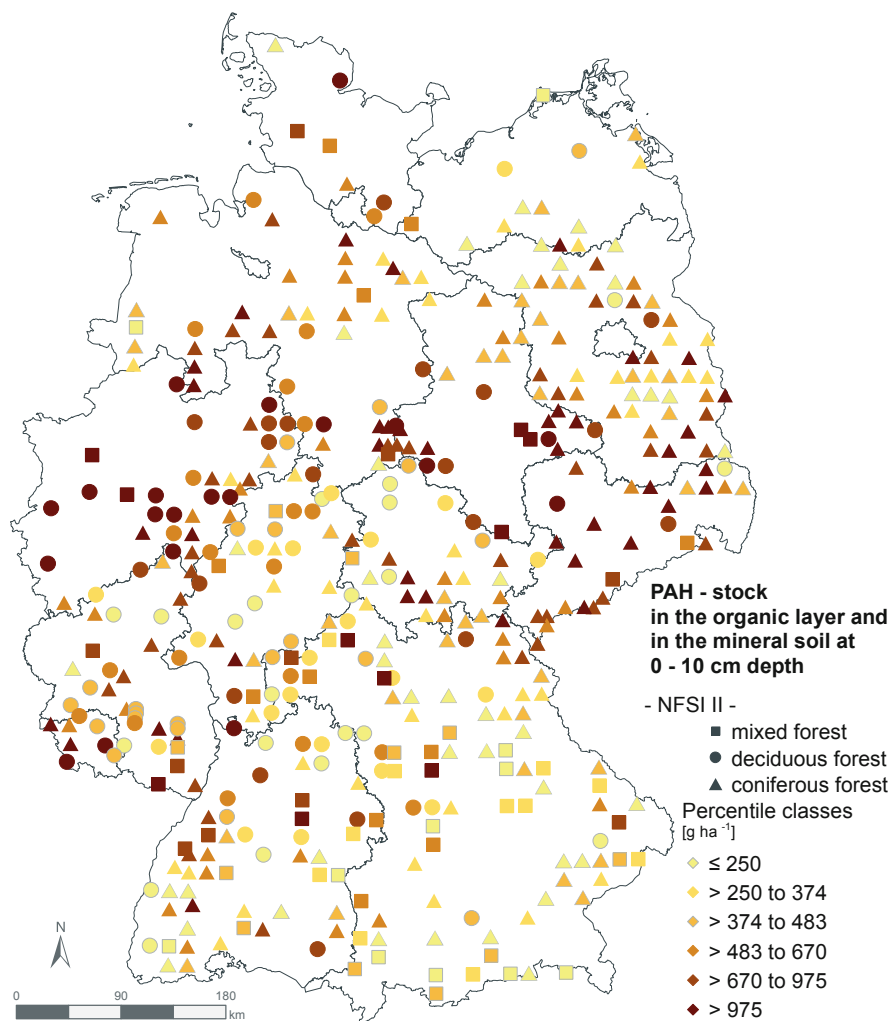
### 8.2.3 Spatial Distribution of Organic Substances in German Forest Soils

The burden of German forest soils with the organic substances described above was classified with six percentile classes for total stocks in the following maps. For dl-PCB and PCDD/F, the concentrations instead of the stocks are presented, since stocks were only available for the organic layer and not for the mineral soil.

#### PAH

Relatively low PAH stocks were found in the northern and southern part of Germany. High PAH stocks were present in the central German Uplands (Fig. 8.18).

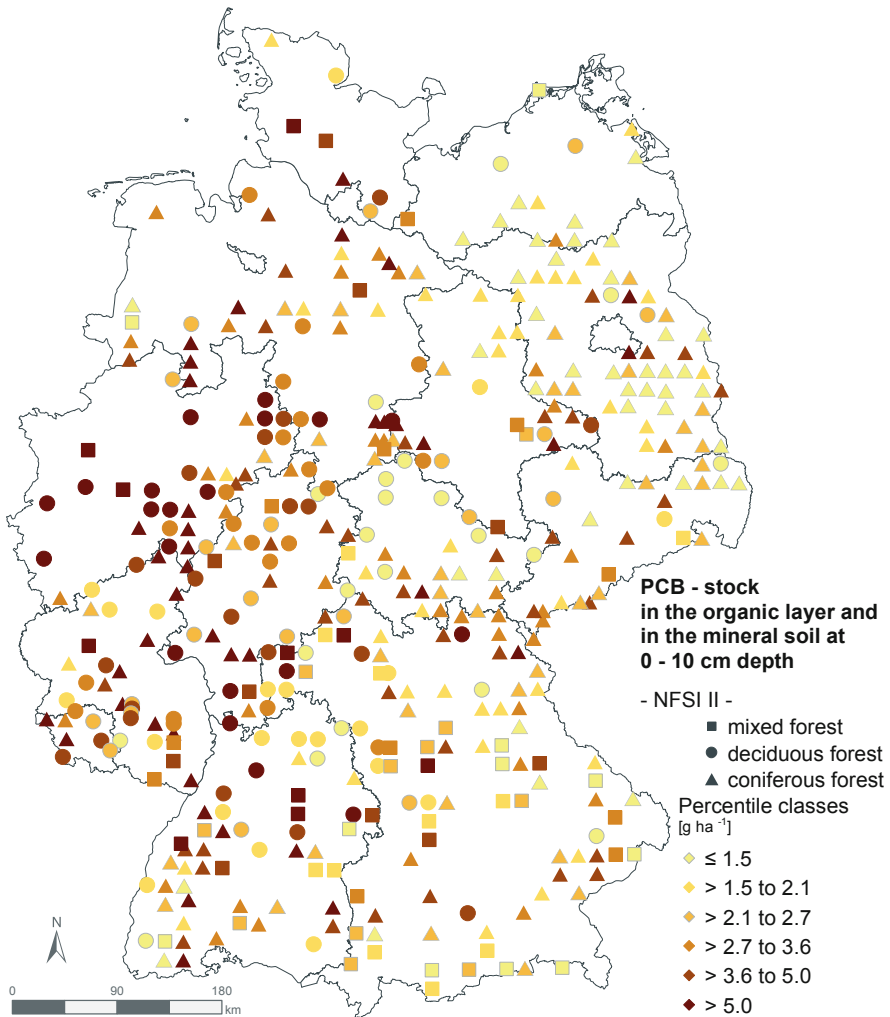
The incomplete combustion of organic substances produces PAHs. Thus, their occurrence was due to various sources such as traffic or industrial exhaust fumes. Aichner et al. (2013, 2015) investigated in their studies with the same data as in the present study the PAH congeners. Based on a study of Khalili et al. (1995), they used the two- and three-ring PAHs as indicator for coal-borne sources. According to this, they assigned lignite opencast releasing coal by mining and (brown) coal-fired power plants as responsible sources for the relatively high low molecular weight PAH



**Fig. 8.18** Spatial distribution of total PAH stocks (organic layer and the first two depth increments of the mineral soil) classified with six percentile classes under different forest types

concentration in eastern Germany. Moreover, they hypothesized that the central German Uplands were a barrier for regional PAH emissions.

The topographic situation induced a distinct microclimate, i.e. high precipitation together with a change in temperature leading to a high PAH deposition rate. The two impact factors, namely, the vicinity to a main emitter and the topography inducing a distinct microclimate, were also reflected on the PAH stock distribution in German forest soils, as can be seen from the map in Fig. 8.18.



**Fig. 8.19** Spatial distribution of total PCB stocks (organic layer and the first two depth increments of the mineral soil) classified with six percentile classes under different forest types

### PCB, dl-PCB, and PCDD/F

PCB stocks show a high gradient in the spatial distribution between the (south-) western part of Germany, with relatively high values, and the north-eastern and eastern part, with lower values. Particularly high stocks were found in different regions in West Germany (Fig. 8.19).

Aichner et al. (2013) could not detect a specific distribution pattern from the congeners, regarding the same PCB data as in the present study. They explain the low PCB concentrations by re-evaporation and microbial degradation at least for tri- and tetrachlorinated PCB.

The PCB stock distribution seemed to be dependent upon regional emissions in former times. Aichner et al. (2013) mentioned studies of Breivik et al. (2002, 2007) who calculated a balance of PCB disposal from population density data. They estimated lower PCB emission in the eastern federal states. In combination with the tenfold higher PCB-containing waste disposal in the western federal states, this might explain the difference between higher stocks in the western compared to the north-eastern and eastern part of Germany. Additionally, it is under discussion that cities might contribute to recent PCB emissions (Jamshidi et al. 2007; Desborough and Harrad 2011).

Since stocks are not calculated for dl-PCB due to lacking data of mineral soil, only the concentration in the organic layer was regarded (not shown). The distribution of dl-PCB was like that of PCB: a gradient with relatively high values in the western part of Germany and lower values in the north-eastern part.

As for dl-PCB, stocks were not calculated for PCDD/F. There was a similar distribution pattern for PCDD/F concentrations in the organic layer as for dl-PCB, except for the south-western part of Germany, where low PCDD/F concentrations could be found (not shown).

The concentrations and consequently stocks of PCDD/F and dl-PCB were significantly higher in organic layers under coniferous soils compared to deciduous or mixed forests, respectively. The concentrations varied across Germany and depended most likely on the sources of emission, like discussed for the other organic substances.

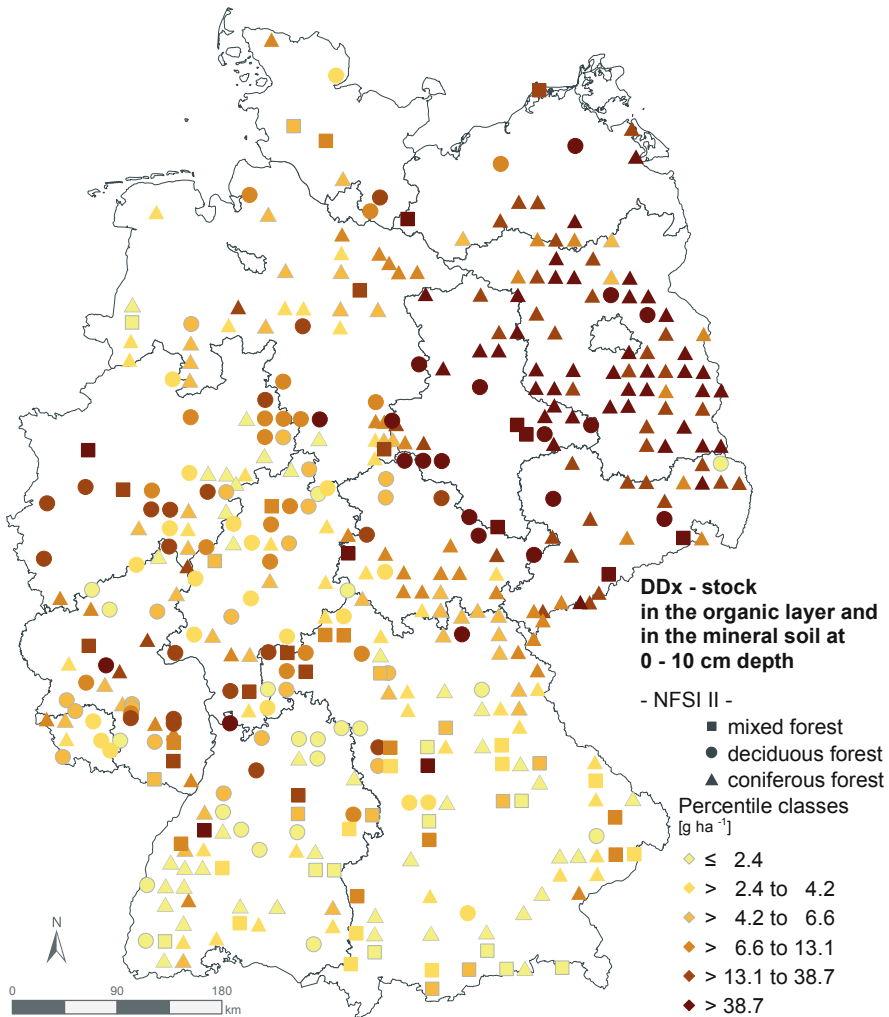
The results for dl-PCB correlated well with these of PCB. Highest concentrations appeared mostly at sites of historical emissions from industrial applied PCB in the western federal states. Furthermore, sampling sites with higher PCB concentrations coincided with sites with elevated PCDD/F.

Note that stocks of dl-PCB and PCDD/F were only calculated for the organic layer. It might be misleading to conclude that stocks under coniferous forests were higher than under deciduous forest for the whole soil profile. It becomes obvious from the other investigated organic substances in the present study that total stocks (organic layer and mineral soil to 10 cm depth) were not significantly different in soils under a given forest type, except for PCB.

## **DDx**

Opposite to PCB stocks, highest DDx stocks were found in the north-eastern part of Germany, while relatively lower stocks were present in western Germany. However, there were some hotspots mostly located in North Rhine-Westphalia (Fig. 8.20).

The spatial distribution of DDx in the investigated forest soils was generally attributed to the former use as insecticide and the different application times in eastern and western Germany. The application ended in the western federal states in 1972. In the eastern federal states, DDT was used until 1988 (Daly and Wania 2005; Heinisch et al. 2005, 2006a; Taniyasu et al. 2005; Breivik et al. 2007; Gasic et al. 2009). The high stocks in the eastern federal states, particularly in Brandenburg, were most likely due to the application of DDT between 1982 and 1984, in order to combat the dark beetle and the pine moth (*Lymantria monacha*; Heinisch et al.



**Fig. 8.20** Spatial distribution of total DDx stocks (organic layer and the first two depth increments of the mineral soil) classified with six percentile classes under different forest types

(1993, 2005)). Dimond and Owen (1996) estimated the half-life of DDT in soils to about 20–30 years in temperate climates, supporting the assumption for the DDx recovery in the mentioned regions today.

Aichner et al. (2013) differentiated with the same data as in the present study between technical (direct application) DDx, consisting mainly of 4,4'-DDT, and deposit-borne (degraded) DDx, consisting mainly of 4,4'-DDE. They used the specific proportion of DDT and DDE as a regionalized DDx fingerprint. Based on the results, they explained the exceptional high DDx concentration at some sampling sites in western Germany, particularly in North Rhine-Westphalia, with former

emissions of the chemical industry. Moreover, in south-western part of Germany, the DDx fingerprint showed an advanced microbial breakdown of DDT. On the other hand, they found evidence from the DDx fingerprint for the application of technical DDT in the eastern part of Germany. These findings are very well reflected in the spatial DDx stock distribution in the present study.

### **HCB**

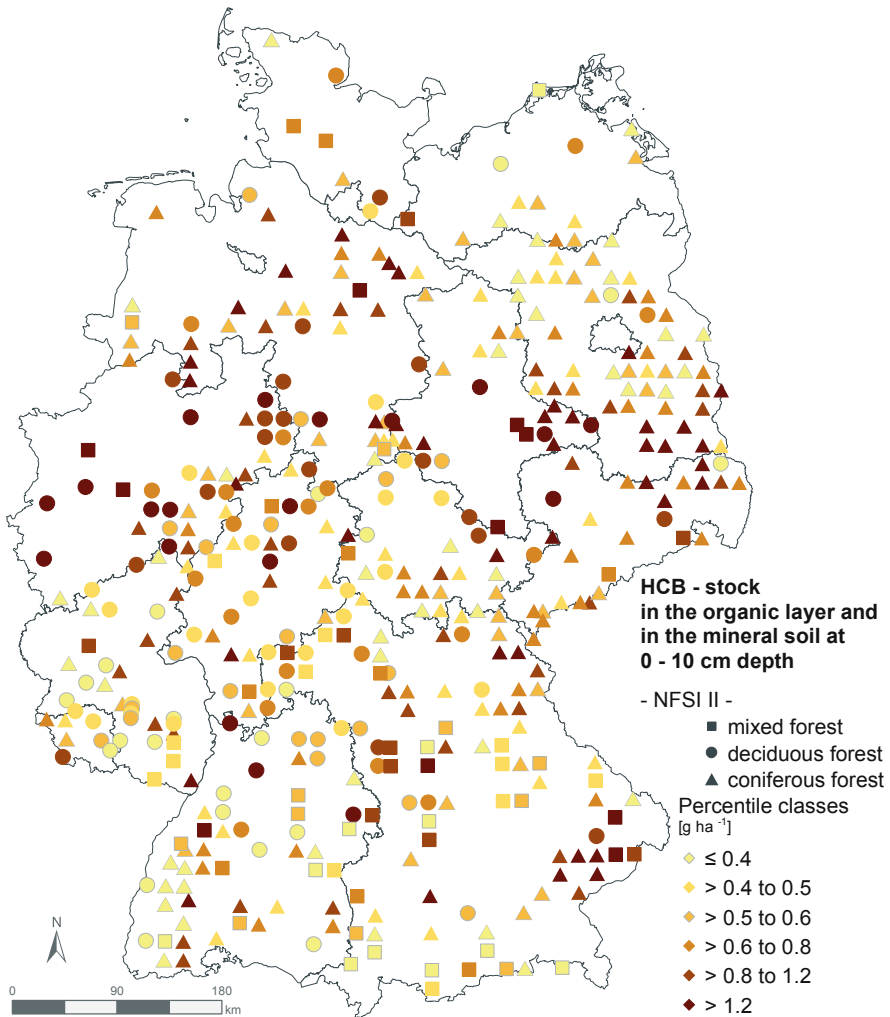
The distribution of highest total HCB stocks was scattered across Germany. Hotspots were detected, e.g. in the south-eastern part of Bavaria, in the Rhein-Ruhr region of North Rhine-Westphalia, and, like PAH stocks, in north of the central German Uplands (Fig. 8.21).

Aichner et al. (2013) assessed the concentrations of HCB, like the other investigated organic substances, in German forest soils as low. Three main sources of HCB are given in the relevant literature. The application of HCB as a fungicide was discontinued in both parts of Germany between 1981 and 1984 (Heinisch et al. 2006b; UBA 2012). As a by-product, traces of HCB are included in various chlorine-containing chemicals. HCB can also arise from combustion processes of chlorine-containing compounds (Aichner et al. 2013). It is difficult to assign one specific main source to the detected HCB stock hotspots. For HCB concentrations, Aichner et al. (2013) named especially industrial combustion processes in the eastern federal states. In addition to this process, they suggested former HCB production as an additional source for the relatively high HCB concentrations in Bavaria and in the industrial regions along the river Rhine and in the Ruhr district. These suggestions also apply to the HCB stocks, as they were calculated from the concentration values.

### **8.2.4 Environmental Factors for the Distribution of Organic Substances**

Aichner et al. (2013) pointed out the importance of local environment parameters for the distribution of organic substances. This is especially true if regional sources of organic substances are to be compared to atmospheric transport with subsequent deposition. The same authors performed a principal component analysis on the same data as in the present study with additional available environmental factors, e.g. climate, soil, and vegetation parameters. They found only weak statistical relationship between environmental parameters and the concentrations of organic substances. They concluded that concentrations of organic substances in German forest soils were mainly driven by former and current emission sources. Moreover, other factors as discussed above such as changing microclimate with altering topography can be decisive to explain pollution pattern on a regional scale.

In this context, it was expected that with decreasing temperatures because of increasing altitude, semivolatile organic compounds condense and precipitate. This effect suggests higher concentrations of organic substances depending on the topography as deposition barrier for organic substances. However, this is discussed



**Fig. 8.21** Spatial distribution of total HCB stocks (organic layer and the first two depth increments of the mineral soil) classified with six percentile classes under different forest types

controversially and is not supported in general (Navarro-Ortega et al. 2012; Guzzella et al. 2011; Daly and Wania 2005; Kirchner et al. 2009; Hangen et al. 2011). Another temperature effect on the organic substances is the potential re-evaporation from soils, thereby reducing their concentrations (Brorström-Lundén and Löfgren 1998). Beside temperature, the amount of precipitation might influence the wet deposition and consequently the concentrations and stocks of organic substances.

In the present study, it is also concluded from the explained variance of the nonlinear regression analysis (SVM) that other factors than depth increment, TOC concentration, and forest type play a significant role in explaining the organic



substances' concentrations and stocks as well as their distribution. More than half or half for PAH, respectively, of the variance remains unaccounted. It seems therefore reasonable to include regional characteristics into statistical models of future investigations in order to explain a greater share of the variance, particularly topography with changing climate parameters and distance to emitters.

### 8.3 Conclusion

To our knowledge, this is the first study to show stocks of organic substances in forest soils on a nationwide basis. As stock calculations took soil mass and soil volume by means of the bulk density, the depth of the investigated soil profiles, and the area into account, it was possible to compare the masses of organic substances per hectare in soil profiles to 10 cm depth under different forest types. The results showed that the organic substances stocks were not dependent on forest type for the investigated substances, except for PCB, showing higher stocks under coniferous than deciduous forest. This indicated that other factors than forest type explained the differences in total stock amounts across Germany, e.g. deposition or vicinity to emission sources.

The concentration of the investigated organic substances in German forest soils seemed to be generally low. This was underpinned by the values of PAH and PCB, which were lower than the precaution values prescribed in German soil protection legislation (BBodSchV). Nevertheless, soils store organic substances over long periods. Still, DDx applied as pesticide in the 1980s was detected in the organic layer, particularly in the eastern federal states. Additionally, deposition stemming from various sources cannot be ruled out and might become a problem in the future due to the persistence of organic substances. It is therefore recommended to find appropriate measures to reduce depositions, e.g. from fuel combustion, mineral, and metal industry. On the other hand, further soil samplings to study the development of organic substances concentrations under forest should be conducted.

The sampling campaign should include the search for impact factors responsible for the spatial distribution of organic substances (e.g. on a regional scale). Besides this, factors for the distribution within the soil profile can also be uncovered, i.e. the prevailing process of historic vs. current deposition. In this study, a greater share of the variance was explained with nonlinear regression compared to linear methods. It seems therefore reasonable to consider nonlinear trends in the evaluation of data from future studies. The outcome will improve models that forecast the distribution of organic substances in forest soils. Eventually, the results can contribute to further develop background, precaution, trigger, and action values in the German soil protection legislation.

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