

PCDD/F AND PCB LEVELS IN GERMAN FOREST SOILS

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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. Being lipophilic compounds and having a high organic carbon-water partition coefficient, PCDD/F and PCB can easily adsorbed by soils rich of organic carbon. Despite the number of international measures which successfully lowered the atmospheric levels of toxic compounds in recent years, this positive trend has not been convincingly identified in soils yet. The aim of this study is to illustrate the historical burden of Dioxin and PCB emissions. Forest soils are an effective trap of POPs due to their high content of total organic carbon (TOC), which has a strong ability to absorb chemicals¹. Even though the leaf/needle area in forest surfaces has often been subject of different investigations^{2,3}. Trees with leaves of broad-leaved species with rough surfaces were considered as more effective type of vegetation in capturing particulate matter (PM) than those with smooth surfaces⁴. In a recent study the spatial distribution of the concentrations of POPs in German forest soils was clearly attributed to historic application⁵. The purpose of this study is to assess PCDD/F and PCB distributions in topsoils in different German forest regions and to interpret the results with respect to vegetation cover, TOC, and altitude data and to correlate the experimental findings with the emission inventories.

Materials and methods

Soil samples

As part of the second forest soil survey in Germany (BZE II) a subset of 86 top soil (humic layer) samples, has been selected from a set of 470 samples taken in a 16 km x 16 km grid⁵. This subset of samples represents approximately a grid (by 64 km x 64 km), and covers all German federal states (with the exception of the 3 city states). In total 45 needle-, 21 foliage-, 16 mixed, and 4 unknown soil samples were included.

The sampling campaign was done in the period of 2007 to 2008. Directly after sampling the soil material was stored in cooled brown glass bottles and kept at about 0 °C for some hours until it was transferred to a freezer for intermediate storage and kept at -20 °C. Subsequently, the samples were sieved by a 4 mm cross diameter stainless steel sieve and homogenized by a Tyler divider and bottled in brown glass bottles. The pretreatment of the samples was performed at about -10 °C. The laboratory samples were stored at less than -20 °C.

Calculation of stocks of humic soil and pollutants and of loads of pollutants

Drying of the investigated samples was not performed to avoid loss of volatile contaminants. The dry weight (d.w.), TOC and altitude data was in a range of 25-81%, 5-49%, and 3-1180 m a.s.l., respectively.

The stocks (as g/m²) of dioxins are calculated by multiplying the contents (as ng TEQ/g) by the stock of humic soil (as t/ha) investigated for each sampling plot. Finally, to estimate the total load of Dioxins and PCBs of Germany the mean stock of each state was multiplied by the forested area and integrated for all federal states.

Stocks of the humic top layer are determined as follows. At each sampling plot the depth and density of each separate horizon was experimentally determined at up to eight different locations by volumetric sampling using a metal sampling cutting frame and subsequent weighing of the excavated soil. If possible the litter (L horizon) and the organic horizons (Oh and Of) were sampled separately, however in case of low depth a separation could not be performed. As the analytical data refer to the content of pollutants in the organic layer (Oh, Of) only the litter has to be subtracted. Therefore, the sum of humus and litter stock was calculated for each plot and an average portion of 13 % litter stock was subtracted from the sum of the stock of L+Oh+Of. The estimated error of this approach is presumably small compared to the total sampling error.

Determination of PCDD/F and PCB 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 MPa⁶. Two static cycles of 10 min were applied for a complete extraction. Clean-up encompassed sandwich, carbon and alumina chromatographic columns. PCB and PCDD/F analyses were performed by HRGC/HRMS. Detailed information on the clean-up procedure and instrumental parameters are given elsewhere⁶. The 17 PCDD/F, 6 indicator PCB and 12 dioxin-like PCBs (dl-PCBs) were identified and are reported in pg/g d.w. Dioxins, furans and dl-PCBs are also reported in pg WHO-TEQ/g d.w. considering WHO 2005 toxic equivalency factors (TEFs). The analytical laboratory involved is quality assured according to DIN EN ISO/IEC 17025 and accredited for the analysis of PCDD/F and PCB.

Results and discussion

Spatial distribution of PCB and PCDD/F

The average fingerprint of our data set regarding the PCB-TEQ and PCDD/F-TEQ concentration range is shown in Figure 3. The results reveal that the main load of total WHO-TEQ is aggregated in the topsoil of the eastern (the Free State of Saxony, lower Saxony and Brandenburg) and western states (North Rhine-Westphalia, Rhineland-Palatinate, Hesse, and Saarland). In the 1950s and 1960s North Rhine-Westphalia was known as the land of coal and steel and the most important industrial region in Europe particularly in metal and iron working industry. The significant POP amounts observed in the eastern region are derived from historic emissions of the former GDR. The lowest total TEQ values were detected in Baden-Württemberg and Bavaria (southern Germany) and in Mecklenburg-Western Pomerania (northern Germany).

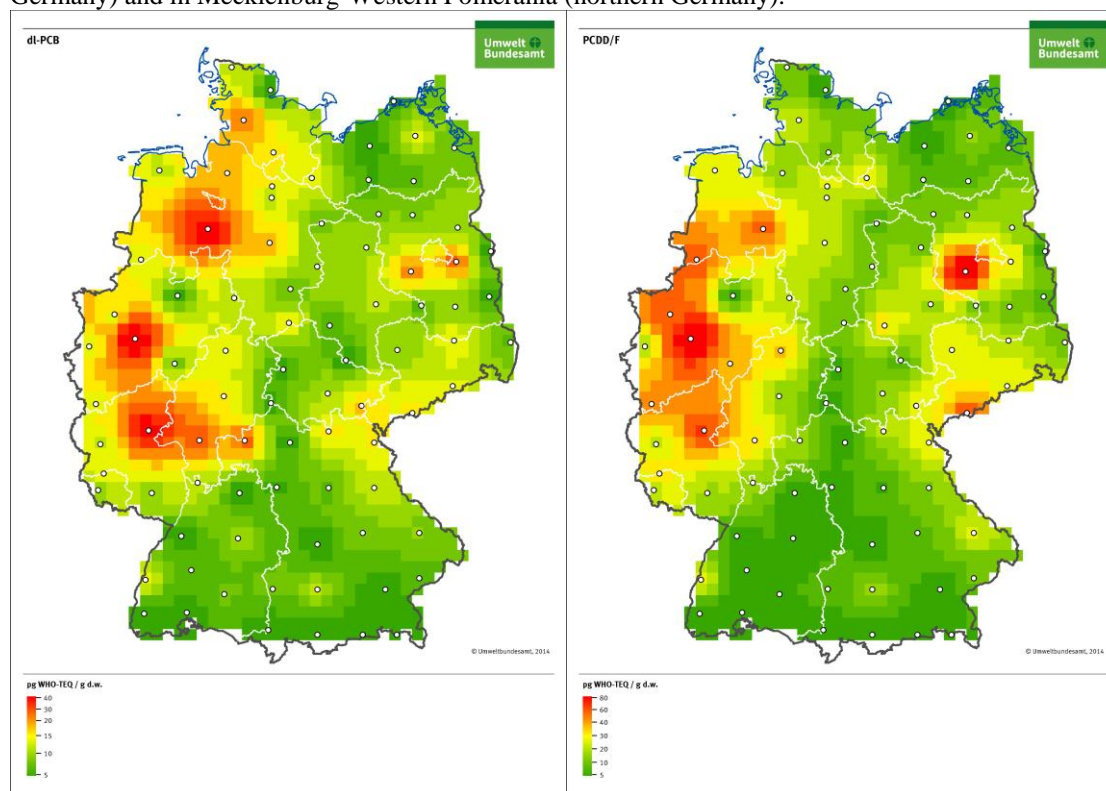


Figure 1: Average fingerprints of PCB-TEQ (pg/g d.w.) and PCDD/F-TEQ (pg/g d.w.) in the O-horizons of forest soils

Effect of total organic content (TOC)

The cross correlation plots between TOC (%) and the sum of PCB (ng/g d.w.) are shown in Figure 2. The results suggest that high POP concentrations are only found for samples with higher TOC content. However, low sums of PCB or PCDD/F can be observed throughout to the whole range of TOC contents in our data set. A correlation of PCDD/F contents with TOC could not be found which is in agreement with the literature⁷.

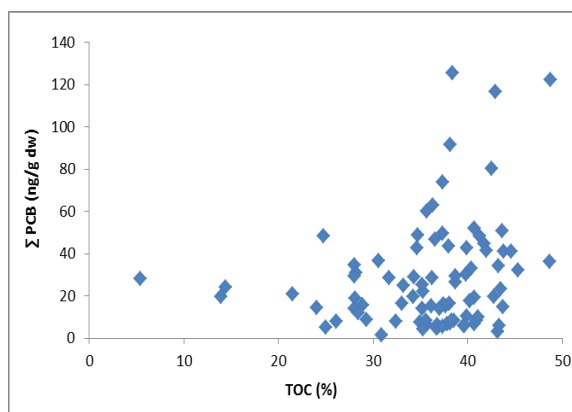


Figure 2: Cross correlation plots between TOC (%) and sum PCB (ng/g d.w.) for all soil samples

Altitude dependence and TOC correlation

Since Bavaria was represented with the highest number of topsoil samples (n=17) only this sampling area was considered to correlate with altitude or TOC data. The concentration levels of 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF and the 6-indicator PCB were normalized by TOC value and its correlation to the altitudes of the sampling sites was investigated. From 400 m a.s.l. to about 1200 m a.s.l., the concentrations showed an inverse relationship with the altitude, however very weak relation was found (data not shown). Similarly, results from passive air samples exposed in forests showed no significant differences between PCB amounts sequestered with increasing altitude⁸.

PCDD/F and PCB distributions in forest topsoils with respect to vegetation cover

Data on the sum of PCDD/F and PCB (pg/g d.w.) accumulated in soils of three vegetation forests (needle, foliage, and mixed) in Germany are presented in Figure 3. Each of the three soil groups exhibited normal distributed data according to Kolmogorov-Smirnov t-test ($p \geq 0.05$).

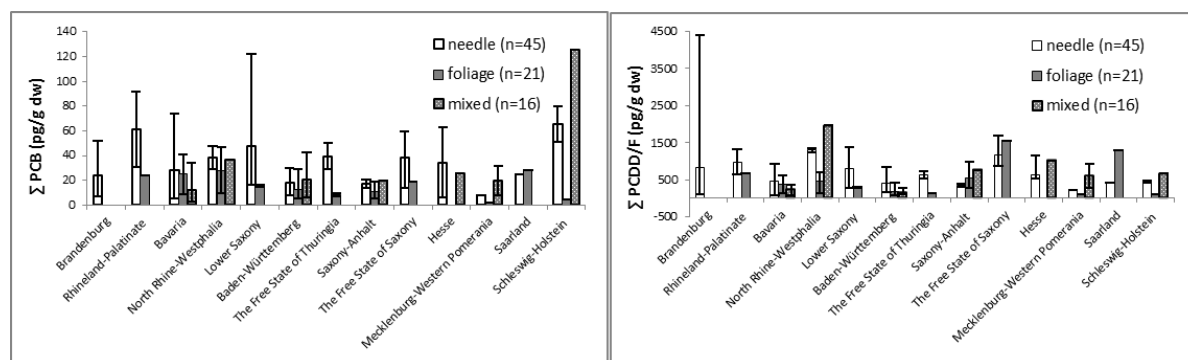


Figure 3: Sum PCDD/F and PCB (pg/g d.w.) in topsoils of needle, foliage and mixed forest, respectively for 13 states of Germany.

The results showed that soils of needle forests tend to accumulate more PCB compounds than foliage forest soil. Not as obvious was the tendency found for the sum of PCDD/F prevailed in needle than foliage forest soils since, Saxony-Anhalt, the Free State of Saxony, and Saarland showed the opposite relation. Regarding the accumulation of PCDD/F in mixed forest soils indefinite behaviour was noticed. Significant amount of PCB was detected in Schleswig-Holstein but the result based on only one sample.

Another research showed that needles of coniferous trees, which produce a thicker epicuticular wax layer, are more effective in PM accumulation than broad-leaved species⁹. Moreover, the quantity of smaller particles known to be harmful for human health was dominated in wax layer than on the surface. Since spruce trees can store PCDDs and PCDFs in the needles and discard them by the tree after 4-6 years in the case of deciduous trees this occurs within one year¹⁰. Apparently, due to needle fall that had accumulated PCB and PCDD/F from the atmosphere higher concentration values were detected in the needle forest soils. Some authors proposed that

another part of deposition could be accounted by portions of the spruce needle cuticle which are shed or eroded, thus carrying PCDD/F accumulated in the cuticle from the atmosphere to the forest¹¹.

The stocks and loads of dioxins and PCBs show significant differences for the eastern and western states, named the new and the old federal states. Due to the different economical situation the old and the new states differed significantly in terms of the emitted pollutants.

The experimental data allow estimating the stocks and loads of Dioxins and PCBs deposited in Germany which are in relationship with the documented emission inventory of Germany¹².

The mean stocks of dioxins and dl-PCBs are 132 ng TEQ / m² and 67 ng TEQ / m², respectively. In case of Dioxins the load for the total area of German forests is estimated to 12 kg TEQ where the ratio of old to new German states is 2 to 1. Compared with the reported annual emissions of Dioxins of some 60 g TEQ the amount of Dioxins stored in the soil is about 2.5 magnitudes higher than the actual reported emission¹². Taking into account the fact that the emissions of dioxins have been significantly reduced by a tenth within the last 25 years the load of dioxins in German forest soils can be explained by the persistency of formerly emitted dioxins.

The load of dl-PCBs is about 6 kg for the forest area of Germany, where about 4 kg are found in the old federal states and 2 kg were found in the new federal states. This ratio reflects the fact that PCBs were not used as extensively in the former GDR as in the BRD. The ratio of Dioxins (PCDD/F) to PCBs in Germany is found as 2 to 1, which corresponds with monitoring data of the federal states.

Current conclusions about POP persistence and mobility in soils need to be applied to other families of chemicals, which have similar properties and diffusive uses. The global annual production of polybrominated diphenyl ether (PBDEs) exceeded 67,000 metric tonnes in 1999 comparable to the peak production of PCBs around 1970¹³. Although the European Union banned PBDEs in 2006, probably relatively high residue concentrations close to source will be measured for the next decades.

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