

Soil-water partition coefficients (Kd) and translocation of POPs in soils

Pandelova M^{1*}, Bussian BM², Henkelmann B¹, Schramm K.-W.^{1,3}

¹Helmholtz Zentrum München, German Research Center for Environmental Health (GmbH), Molecular EXposomics, Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany, pandelova@helmholtz-muenchen.de; ²formerly Federal Environment Agency, Section Soil Quality and Soil Monitoring, Am Wörlitzer Platz, 06844 Dessau, Germany, Germany; ³Department für Biowissenschaftliche Grundlagen, Technische Universität München, Weihenstephaner Steig 23, 85350 Freising, Germany

Introduction

Persistent Organic Pollutants (POPs), including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and some polybrominated diphenyl ethers (PBDE) and organochlorine pesticides (OCP), are groups of chemicals possessing the following characteristics: persistence in environment, harmfulness to humans and wildlife, long-range transport through air and water, and bioaccumulation in the food chain¹. The chemical properties of POPs, such as low water and high fat solubility, low vapor pressure and high organic carbon-water partition coefficient (Koc) indicate their persistence in soil organic carbon typically used as a measure of sorption capacity². Specifically, forest soils are effective sinks of these chemicals due to their high content of total organic carbon (TOC)³ and the scavenging properties of trees⁴. The aim of this study was to investigate the phase-partitioning behavior described as the soil–water partitioning coefficients (Kd) of POPs between the dissolved and the absorbed phases in soils and their partition between soil horizons.

Material and methods

Soil samples

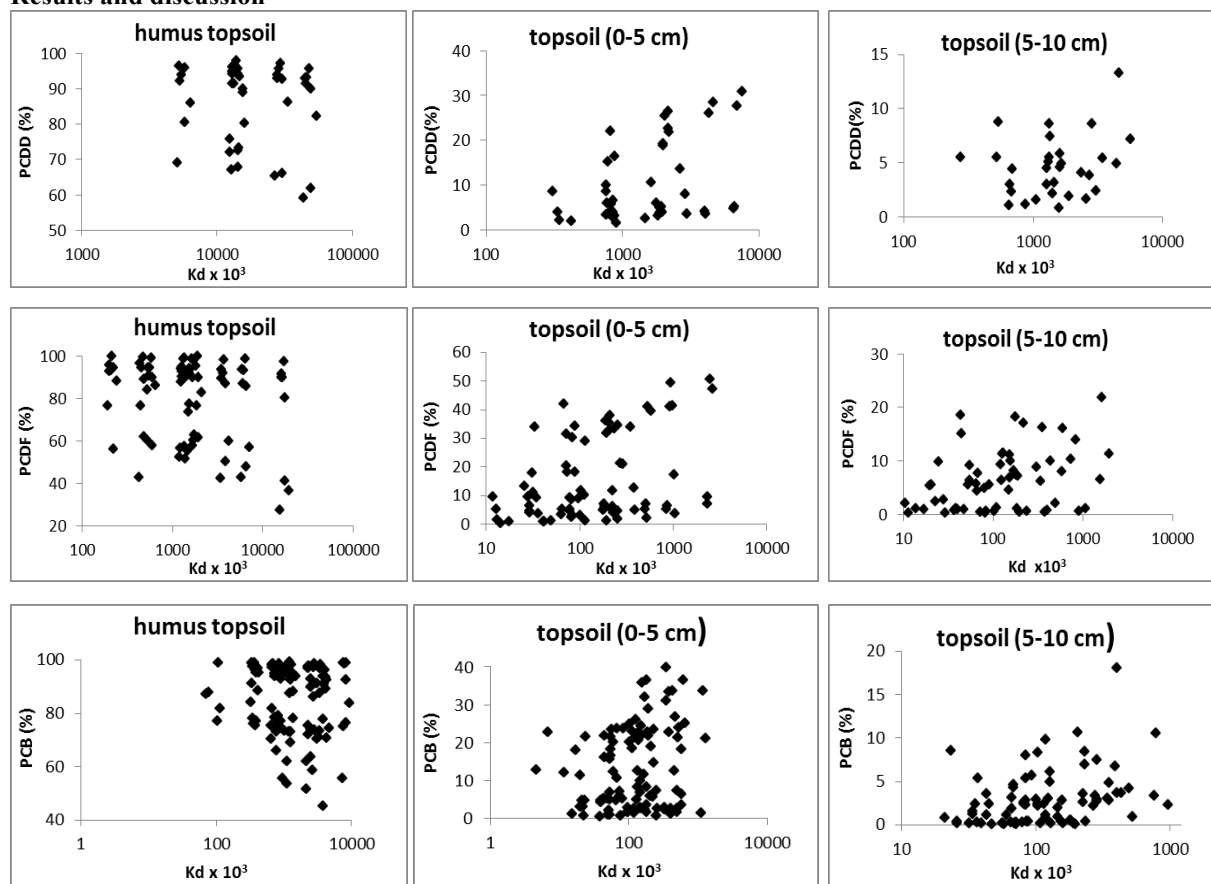
A subset of 86 humic topsoils (Oh/Of horizon) has been selected from a set of 470 samples taken in a 16 km x 16 km grid⁵. Additionally a subset of 8 coniferous forest soil samples from the German federal states Brandenburg, Bavaria, North Rhine-Westphalia, Lower Saxony, Baden-Württemberg, Thuringia, Hesse, and Mecklenburg-Western Pomerania, 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 elsewhere⁶. The soils were analyzed in Helmholtz Zentrum München⁷. The octanol/water partition coefficient (Kow) for 7 PCDD, 10 PCDF, 18 PCB, 29 OCP and 11 PBDE congeners and the organic carbon/water partition coefficient (Koc) as $Koc = 0.411 * Kow$ ⁸ were calculated. The Kd value for selected 8 coniferous topsoils and mineral soils regarding all compounds was expressed as $Kd = Koc * TOC(\%) / 100\%$. The ratio (%) of the $\sum PCDD$, $\sum PCDF$, \sum indicator-PCB, $\sum OCP$, $\sum PBDE$ within the topsoil and the two mineral soil horizons (0-5 cm and 5-10 cm), respectively was calculated. In case the resulted ratio was 0% or 100% the value was excluded from the study.

Determination of PCDD/F, PCB, OCP and 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, C18-modified silica and alumina chromatographic columns. The analyses were performed by HRGC/HRMS. For detailed information on the clean-up procedure and instrumental

parameters, see Pandelova et al., 2018⁷. The mass-concentrations of 17 2,3,7,8-chlorosubstituted PCDD and PCDF, 6 indicator PCB (PCB 28, 52, 101, 138, 153, and 180), 12 dioxin-like PCB (dl-PCB) including non-ortho-dl-PCB (PCB 77, 81, 126, and 169) and mono-ortho-dl-PCB (PCB 105, 114, 118, 123, 156, 157, 167, and 189), 29 OCP (α -, β -, γ -, δ -, and ϵ -hexa-chlorocyclohexane (HCH), pentachlorobenzene (PeCB), hexachlorobenzene (HCB), pentachloroanisole (PCA), octachlorostyrene (OCS), isomers of DDT, DDE, and DDD (namely 4.4'-,2.4'-DDT, 4.4'-,2.4'-DDE, and 4.4'-,2.4'-DDD), trans-, cis-, and oxy-chlordane (CLH), heptachlor (HC), cis- and trans-heptachlor epoxide (HCE), aldrin, dieldrin, endrin, α - and β -endosulfan (Endo), endosulfan-sulfate (Endo-sulfate), methoxychlor, and mirex) and 11 BDE- congeners (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



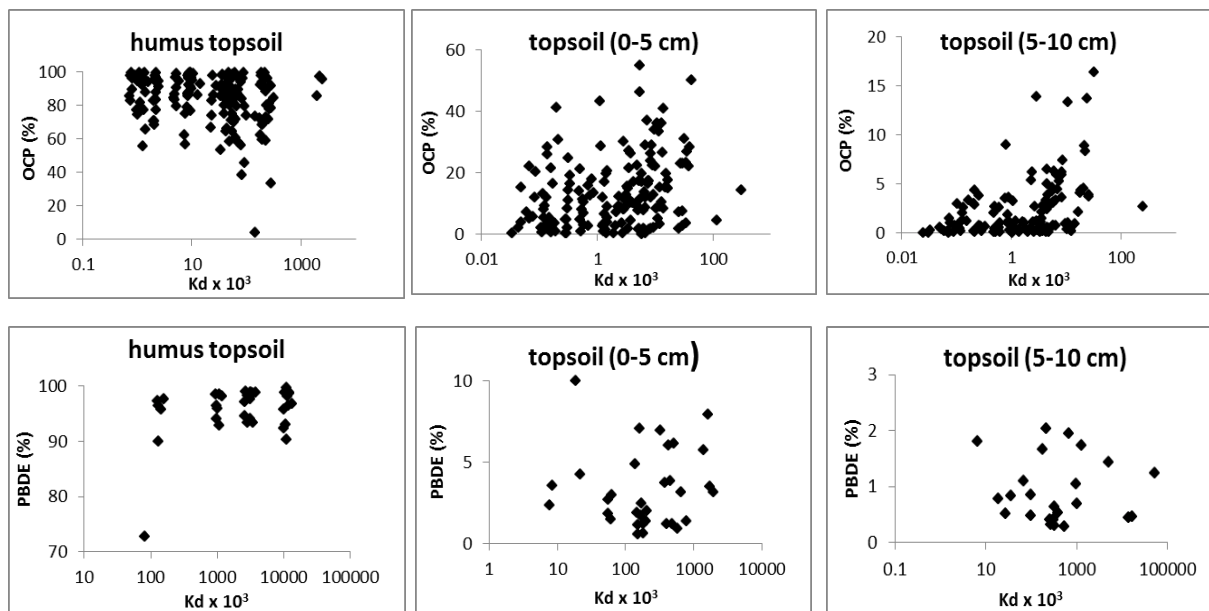


Figure 1: Relationship of the calculated K_d of 8 samples including the humic topsoil horizon and the top mineral soils at two depths (0–5 cm and 5–10 cm, respectively) to the calculated PCDD, PCDF, PCB, OCP and PBDE ratio (%).

The proportion (%) of the Σ PCDD, Σ PCDF, Σ PCB, Σ OCP, and Σ PBDE within the topsoil and the two mineral soil horizons (0–5 cm and 5–10 cm), respectively were calculated. Largest part of POP stored in forest soils was found in upper humus layer suggesting that the deposition of these contaminants in organic carbon is crucial. However, the ratio (%) of investigated compounds decreases sharply with increasing soil depth. No significant relationship could be determined for K_d plotted against the corresponding ratios (%) for all PCDD, PCDF, PCB, OCP and PBDE congeners in humic topsoils and the top mineral soils at two subsequent, respectively. Theoretically, it should be expected that especially at very high K_d values a transport in solution of the very lipophilic compounds should be subordinated in comparison to compounds with low K_d values. However, surprisingly the opposite is shown in Fig. 1 for the cases of PCDD, PCDF and OCP where almost all observations in the K_d range between $K_d 1 \times 10^5$ and $K_d 1 \times 10^7$ exhibit losses in the topsoil towards the lower soil layers investigated. A recent study⁹ indicated that adsorbed organic carbon may desorb easily and in this way can release dissolved organic carbon (DOC) quickly without being dependent on mineralization and degradation. Solubilization via DOC and mobilization of nanosized TOC mediated solid transport of e.g. black carbon seems more likely since compounds with very high K_{oc} values might partition intensively towards these materials and are being carried downwards. As outlined earlier⁷, the theoretical distribution between the total concentration C_{wT} (water+DOC+ nanosized TOC) of compounds in solute, including the amount bound to DOC and/or TOC, versus the compound in solution of water C_w only at a given soil concentration in relation to K_d and increasing concentrations of DOC and/or TOC partitioning with C_w on the basis of K_{oc} reveals that at K_d values higher than about 100,000 and at DOC/TOC concentrations above 1 mg/L C_{wT} is increasing exponentially. Those conditions attenuate translocation of compounds into lower soil horizons as observed. DOC concentration in soils of Northern Russia is reported at

several tens of mg/L in O-horizons and still at several mg/L in Ah and B horizons⁹. In addition, a correlation between TOC in soil and DOC which then will lead to attenuated transport of pollutants in carbon rich soils. Similar DOC values are observed in German soils as well¹⁰. The translocation of superlipophilic compounds associated with high K_d values seem to become pronounced at K_d values beyond at least about 10⁶ in some soils which puts doubt on the conclusion that groundwater is not endangered for compounds which exhibit log K_{oc} values higher than 4.5¹¹. Taking high level of TOC in the soils at 40% as a conservative value for calculation K_d will result in K_d values for compounds being not translocated of about 13000. However, all groups of compounds exhibit translocation at higher K_d than 13000 for many soils and compounds of log K_{oc} values higher than 4.5. In conclusion, the study shows that risk of transport of POP into groundwater cannot only be related to aqueous translocation.

Acknowledgements

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