

## Changes of Persistent Organic Pollutants in Atmospheric Concentration and Soil Load in the UK and Norway over 10 Years

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**Abstract**—Persistent organic pollutants (POPs) are mainly defined by their physical-chemical properties and toxicity. A number of POPs was listed under the Stockholm Convention and signing parties declare the voluntary restriction or elimination of those compounds. In order to gain more insight in the long-term changes for POP loads and trends in the soils compartment, about 40 remote soil sampling sites from 1998 in the UK and Norway were revisited in 2008. 70 surface soil samples were collected and analyzed for the legacy POPs like polychlorinated biphenyls (PCBs) and selected organochlorine pesticides (OCs), as well as the current-use POPs polybrominated diphenyl ethers (PBDEs). POP loads in the soils collected 2008 were compared to those found in 1998. POP concentrations from both sampling campaigns were also correlated to soil characteristics (soil organic matter, black carbon content) and site characteristics (land use, vegetation type, remoteness) as well as atmospheric POP concentration monitored at selected sampling sites. The data shows that there was significant decline of PBDE concentrations in soils from 1998–2008, but less significant decline for PCBs and OCs. The air concentrations for PCBs are still defined by primary source emissions, while in background soils this influence has decreased from 1998–2008.

**Keywords:** polychlorinated biphenyls, polybrominated diethyl ethers, background soil

### INTRODUCTION

Persistent organic pollutants (POPs) are mainly defined by their toxicity, slow

degradation in the environment and their semi-volatile character which enables them for long range atmospheric transport. They can be found in all environmental compartments. While air and water mainly have a transport function for those compounds, the role of the soil compartment should be considered as reservoir. The question arises whether soil acts as a secondary source of POPs, revolatilising them to the atmosphere, or rather an infinite sink, especially for semi-volatile compounds with high molecular weight.

Next to the direct air-soil gas exchange other processes are involved in the POP transfer between soil surface and the atmosphere. POPs from the gaseous phase can adsorb to the particle phase and then be transferred to the soil surface via dry or wet deposition. The same applies to POPs that condense from the vapour phase to aerosols. Furthermore POPs can partition into biomatter and vegetation and are transferred to the surface via leaf litter (or wax shed). (Moeckel *et al.*, 2008a, b).

The processes in the soil layer are rather complex, mostly due to the heterogenic nature of soil. The removal of POPs via degradation is possible (biological, chemical and close to the surface also photolysis). POPs can be associated with particles, dissolved organic matter or be freely dissolved in the stored moisture. Rainwater might have a flushing effect and wash off POPs from the soil surface or leach them to deeper layers. They might also be transported to deeper layers via bioturbation caused by organisms. It is not clear if POPs associated with biomatter will be released when it degrades to soil organic matter (SOM).

In 2008, 70 surface soil samples were collected at sites, following the method and locations as reported in a previous study from 1998 (Meijer *et al.*, 2002). The sampling sites are located in the UK and Norway covering an area from 50.6–70.4°N and 6.2°W–27.9°E and a mean temperature gradient of –12–5.3°C and 10.4–16.0°C for winter and summer respectively. The sampling sites are all located in rural or remote areas and can be distinguished by grassland and woodland vegetation. The samples were analysed for polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCs). The POP concentrations in soil were reported as pg per g SOM instead of dry weight, to allow for comparisons between individual sites as well as sampling years. Atmospheric data, acquired with the passive air samplers semi-permeable membrane devices (SPMDs), is available for 11 sites along the transect from previous sampling campaigns (Ockenden *et al.*, 1998; Meijer *et al.*, 2003; Jaward *et al.*, 2004; Gioia *et al.*, 2006; Schuster *et al.*, 2010).

## METHODS

Soil cores were collected with a bulb planter for 5 cm depths. Soil samples were mixed with anhydrous sodium sulfate and Soxhlet extracted with dichloromethane for 16 h. Clean-up included alumina/silica column, acid digestion and gel permeation chromatography. Samples were analysed using gas-chromatography-mass-spectrometry (GC-MS) with an EI+ source operating in selected ion mode for PCBs (PCB 44, 49, 52, 70, 74, 87, 90, 95, 99, 101, 105, 110,

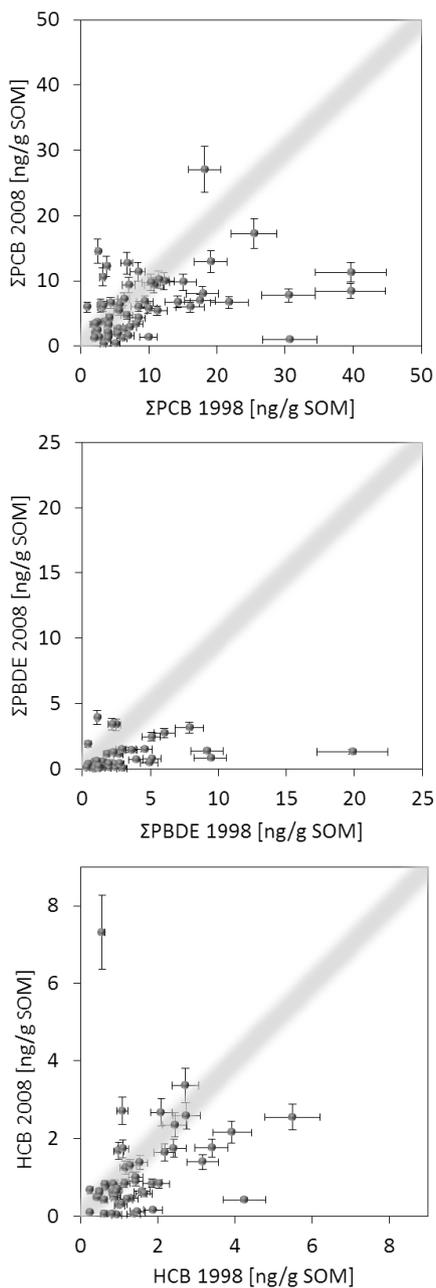


Fig. 1. The POP concentrations in soil showed a strong shift between 1998 and 2008 for PBDEs. For PCBs and OCs such as HCB, significantly less sites showed a decline in concentration between the sampling years.

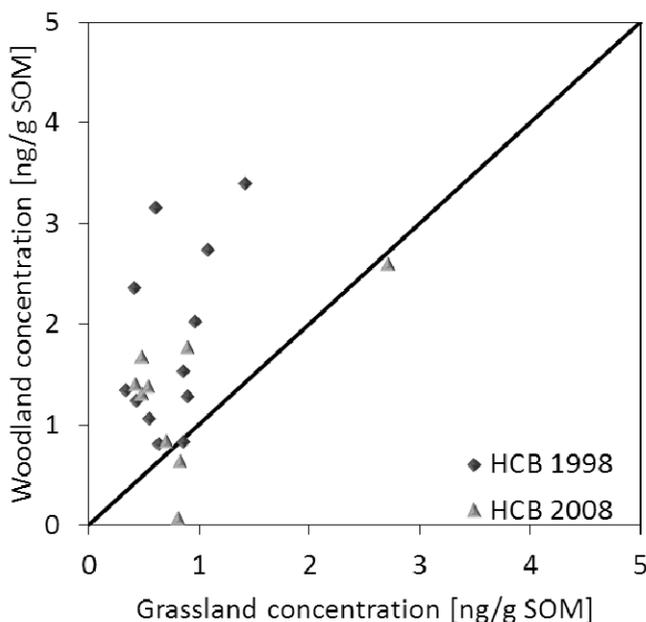


Fig. 2. The forest filter effect can be observed from higher concentrations of POPs in woodland areas compared to adjacent grassland sites.

118, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 170, 174, 180, 183, 187, 194, 203), PBDEs (PBDE 47, 99, 100, 153, 154) and OCs (hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (*p,p'*-DDT, *o,p'*-DDT), dichlorodiphenyldichloroethylene (*p,p'*-DDE, *o,p'*-DDE), dichlorodiphenyldichloroethane (*p,p'*-DDD),  $\alpha$ -/ $\gamma$ -chlordane. Chiral analysis for PCBs 95, 132, 149 and 174 was performed with GC-GC-MS-MS as described by Bucheli and Brändli (Bucheli and Brandli, 2006). SOM content was determined gravimetrically by loss-on-ignition at 450°C. Further details for the methods can be found in the literature (Meijer *et al.*, 2002; Hassanin *et al.*, 2004; Schuster *et al.*, 2011).

## RESULTS AND DISCUSSION

In general lower concentrations were observed in the data sets from 2008 compared to 1998 for PCBs and PBDEs, and no significant difference for most of the OCs (Fig. 1). This difference was more pronounced for PBDEs with 79% of the samples showing significantly lower concentrations in 2008 and for PCBs only 56% of the samples. This could be explained by higher degradation rates for PBDEs in soil. No significant differences were noted for concentration increase or decrease between woodland and grassland sites, nor between UK or Norwegian sites.

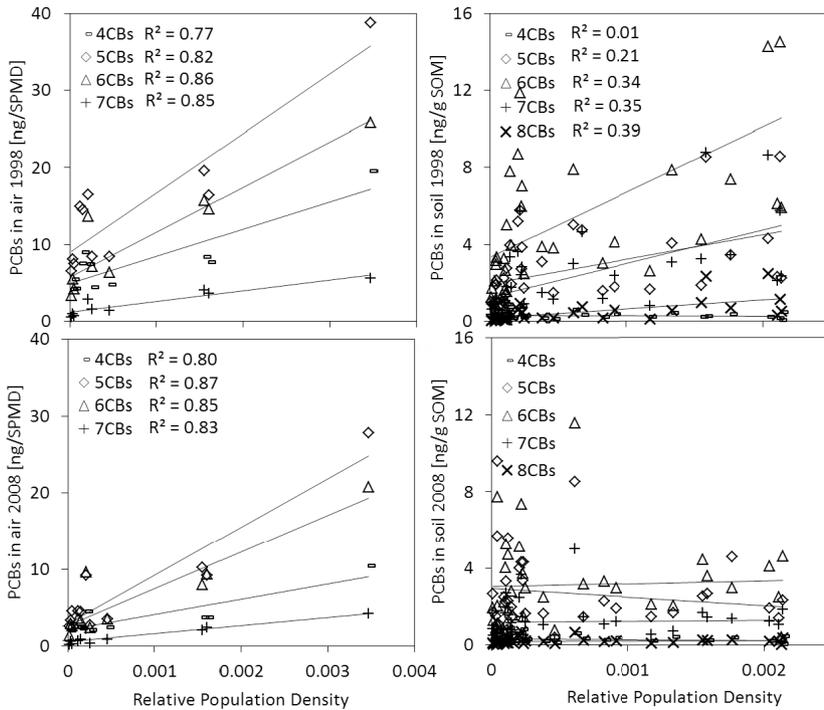


Fig. 3. Correlations between PCB concentrations and relative population density at the sampling site indicate a strong influence of ongoing primary source emissions. This influence is stronger for atmospheric concentrations than in soil.

Concentrations in 2008 ranged from 720–39,700 pg/g SOM, 140–19,900 pg/g SOM and 90–5,500 pg/g SOM for  $\Sigma_{31}$ PCB,  $\Sigma_5$ PBDE and HCB respectively. It was found that in general woodland sites showed higher concentrations than grassland sites. Figure 2 presents the data for HCB concentrations in 1998 and 2008 for adjacent woodland and grassland sites. Adjacent sites are located in less than 1 mile distance from each other; therefore differences in sources should be negligible. This observation is explained by the forest filter effect at woodland sites (Maddalena *et al.*, 2003; Su and Wania, 2005; Nizzetto *et al.*, 2006).

The correlation between POP concentrations and SOM was noted in both the 1998 data and the 2008 data. But there was a shift in the POP load for PCBs observed between the years. In 1998 plotting log POP against log SOM shows a break in the linear curve at 40–60% SOM content. This indicates a saturation of soils with an SOM content of less than 60% or rather an air-soil equilibrium. The SOM content of the “saturated” soil decreases with increasing chlorine substituents of the PCB congeners. This was no longer observed for the 2008 data, indicating an approach of the air-soil equilibrium during the last 10 years for soils with a

SOM content higher than 60%. This was only observed for woodland sites, due to the fact that grassland sites in general only had SOM contents of less than 60%. The fact that this was not observed for the PBDEs might be explained with their higher degradability in the soil compartment.

The data from 1998 displayed a PCB fractionation pattern along the latitude/temperature gradient, with increasing or decreasing fractions along the latitude for the lower and higher chlorinated PCB respectively. This fractionation pattern was no longer observed in the soil data in 2008. As observed in a previous study by Schuster *et al.*, atmospheric data monitored along the same transect shows unchanged fractionation slopes from 1998–2008, regardless of the generally declining atmospheric concentrations (Schuster *et al.*, 2010).

Similar to this, correlations to the relative population density (RPD) shifted between the years. Figure 3 shows the correlation between the RPD and PCB concentrations in soil and air. Significant correlations were observed for all PCB homologue groups (4CBs, 5CBs, 6CBs, 7CBs) in the air data 1998–2008. Correlations between RPD and the PCB concentrations in woodland soil from 1998 were less strong than those observed in the atmosphere. The correlation was not noted for 4CBs, but increased for the other homologue groups with degree of chlorination. For the soil data of 2008 correlations were only found significant for the higher chlorinated congeners (6CBs, 7CBs, 8CBs) at the Norwegian woodland sites.

Among the PCBs there are 19 axially chiral congeners (PCB 45, 84, 88, 91, 95, 131, 132, 135, 136, 139, 144, 149, 171, 174, 175, 176, 183, 196, 197). Chlorine-substituents in ortho-locations (positions 2, 2', 6, 6') on the phenyl-rings limit the rotation along the phenyl-bond (Kaiser, 1974). Chiral PCB signatures were reported in sediments and soil. The enantio-selective biodegradation of PCBs is considered to be rather complex and an enantio-selectivity for one of the isomers (which is often observed for pesticides) is missing in the biodegradation process (Koblickova *et al.*, 2008; Lehmler *et al.*, 2009). To gain information on the influence of possible PCB re-emissions from soil on atmospheric concentrations the chiral signature in soil and air data along the transect was compared. It was noted, that while PCB mixtures in soils were definitely non-racemic, the corresponding air samples showed racemic mixtures. Therefore possible revolatilisation of non-racemic PCBs cannot yet be observed in the air data.

In conclusion, the stronger decline for the PBDEs in soil can be explained by the higher biodegradation rates than for other POPs. That raises the possibility that the environmental life span of PCBs is actually increased by the partitioning into the soil compartment. While the data indicates that air-soil equilibrium is approached, the influence of soils as secondary sources for PCBs to the atmosphere is still negligible compared to ongoing primary source emissions even in background sites. It has to be considered though, that soils have to be considered as a reservoir for PCBs that may gain more influence on atmospheric PCB concentrations with the ongoing decrease of primary emissions.

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