PERSISTENT ORGANIC POLLUTANTS IN BOREAL AND MONTANE SOIL PROFILES: DISTRIBUTION, EVIDENCE OF PROCESSES AND IMPLICATIONS FOR GLOBAL CYCLING

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2 3 4	1	PERSISTENT ORGANIC POLLUTANTS IN BOREAL AND MONTANE SOIL
5 6	2	PROFILES: DISTRIBUTION, EVIDENCE OF PROCESSES AND
7 8 9	3	IMPLICATIONS FOR GLOBAL CYCLING
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41 42	17	Abstract
43 44	18	The distribution of persistent organic pollutants (POPs) within background soil profiles
45 46 47	19	was investigated in boreal (Norway) and montane (Italy) areas. The typical build-up of
48 49	20	slowly mineralizing humus layers, containing high amounts of soil organic matter (SOM)
50 51	21	makes soils of such ecosystems an important global sink for POPs released to the
ວ∠ 53 54	22	environment. The study focused on evidence and implications of processes influencing
55 56 57 58	23	the fate of POPs in soil. POP deposition, interaction with SOM, volatilization, leaching,

degradation and bioturbation are discussed. Results indicate that the less volatile POPs such as hexa- and higher chlorinated biphenyls (CBs) or polybrominated diphenyl ethers are very stable in soil profiles, undergoing little translocation or (re-)transfer to other environmental compartments. In contrast, more volatile compounds (e.g. tri- and tetra-CBs) were found in soil layers below those formed from vegetation ever directly exposed to airborne POPs. This suggests the occurrence of downward transport and hence limited surface-air exchange of more volatile POPs as they are removed from the top layers. Such soils may therefore be able to retain higher amounts of these compounds than just addressed by the capacity of their surface layers.

34 Introduction

Background soils can be stores, sinks and sources of persistent organic pollutants (POPs) and make a major contribution to the global inventory of these compounds (1, 2). The net direction of fluxes between soils and air is key to the global cycling of POPs, while storage and processing within soil profiles is critical to their overall environmental persistence and global burden (1, 2). The strong affinity between POPs and SOM will be important in determining their fate (2-4), with relative rates of POP and SOM decomposition and association with soluble and insoluble SOM fractions likely to be controlling factors (5). Profile distributions and processing of POPs will be influenced by: the historical atmospheric emissions of POPs; climatic/environmental factors affecting air-surface interactions, vegetation and soil type, bioturbation and decomposition rates of organic carbon and POPs; compound properties which influence phase partitioning and

46 persistence (2, 6-8). Figure 1 summarizes some of the complex and highly variable
47 processes which will determine the fate of POPs in different soil systems.

Temperate and boreal ecosystems are particularly important for the global inventory and processing of POPs, because they: are often close to source regions; vegetation canopies enhance POP scavenging from the atmosphere; contain a high proportion of the global terrestrial carbon stock; often have low temperatures, enhancing cold condensation and slow decomposition (9-14). Several studies have drawn attention to these systems and the importance of the profile distribution and within-soil processing of POPs in impacting their global fate (e.g. 2, 15-17). However, very few have reported profile distribution data for these ecosystems and interpreted it with respect to the processes acting on POPs (5, 18, 19). It is necessary to distinguish between such processes, to understand and predict POP fate in the environment. This is difficult in laboratory or field experiments, which may not mimic key natural processes very effectively and would need to be run over many years/decades. This paper therefore reports POP profile distributions in different soils from the Italian Alps and Norway and interprets them with respect to the processes introduced above. These regions are 'natural laboratories' with relevant environmental gradients (e.g. of temperature and ecosystem type) which have been used previously to investigate the air and terrestrial ecosystem distribution and processing of POPs (4, 12, 20).

66 Methods

Sampling: Topsoil-profile samples were collected in Norway (6 profiles) and Italy (3
sites, profiles in triplicate) (see Table SI-1 for details and Figure SI-1 for location map),

away from towns, roads or other human activity. Four of the Norwegian locations were open areas (i.e. soil under short vegetation such as heather, grasses and dwarf shrubs – coded G) and two in forests (F) close to the G-sites. The Italian profiles represent soils from three different forest systems along an orographic alpine transect - deciduous broadleaf (I-1100), mixed broadleaf-needle (I-1400) and deciduous needle stands (I-1800). A detailed description of these sites can be found elsewhere (12).

Soils were sampled according to sub-horizons of the organic (O-) horizon (see SI for brief description) and from mineral horizons if they contained visible amounts of organic carbon (oc). In Norway a square of about 25 x 25 cm was collected from each layer using a large cleaned knife. Care was taken to avoid cross-contamination between layers. The Oi layer was not sampled at these sites. In Italy, each horizon was sampled from pits. Details about sample locations and soil properties are given in Table SI-1. The samples were wrapped separately in two layers of aluminum foil and sealed in zip lock plastic bags for transport to the laboratory where they were stored at -20 °C until extraction. At the Italian sites superficial litter (i.e. <1 year old) was collected during five campaigns between April and October 2005 (for details see Table SI-2) and was handled and analyzed in the same way as soil samples.

Sample processing and analysis: The Norwegian soil samples were extracted and cleaned as described by Meijer et al. (4). The Italian samples were extracted and cleaned according to the procedure used by Nizzetto et al. (7) for vegetation samples. A brief description of these methods and details on the gas-chromatographic analysis of the extracts for PCBs and organochlorine pesticides (OCPs) are given in the Supplementary Information.

C/N and pH analysis: Total C and N were determined using method SOP 3102 (Total carbon and nitrogen in biota, vegetation, soils, sediments and particulates from waters by
elemental analyzer) accredited to ISO/IEC 17025:2005 on an Elementar Vario EL
elemental analyzer. Soil pH was measured potentiometrically in water (1:2.5 w/v). *Quality Control:* Blanks (Na₂SO₄ filled cellulose thimbles) were included at a rate of 1
per 5 soil samples and extracted in the same way as samples. The detection limit (LOD)
was calculated as three times the standard deviation of the mean blank or the amount of

99 analyte per sample corresponding to the lowest calibration standard, whichever was the 100 greater. In all samples dry weight-based LOD was 0.004 - 0.69 ng g⁻¹ for different PCBs,

101 0.004 - 0.94 ng g⁻¹ for pesticides and 0.011 - 0.31 ng g⁻¹ for PBDEs (Norwegian samples 102 only). All reported values are blank corrected but not corrected for the recovery rates of 103 PCB-40 and -128 (70 – 100%) (Italian samples), ${}^{13}C_{12}$ PCBs (52 - 110%) and PBDEs (36

104 - 145%) (Norwegian samples).

Three separate profiles at the Italian sites were sampled and analyzed. On average, results showed relative standard deviations of 61% (5% - 160%), 47% (1% - 145%) and 49% (1% - 155%) at sites I-1100, I-1400 and I-1800, respectively. Lower variations between triplicates were generally observed in the top layers.

Results and Discussion

General remarks: All the chemical data for the soils are presented in Table SI-3.

112 An Oe horizon was present in most profiles and could therefore be compared between 113 sites. It contained between 0.42 and 28 ng Σ PCB g⁻¹ dry weight (dw) soil, with 114 significantly higher concentrations in the Italian samples. Hexa-CBs were the most

abundant homologue group in the Oe-layer, followed by the penta- and hepta-CBs. These observations are all consistent with other studies on global background soils (1, 21). The Italian samples were taken close together on valley sides, differing in altitude (and therefore in climate and ecosystem type) (7). These factors may influence the soil's POP burden because of the different litter deposition rates, and the different efficiency in vegetation and SOM to take up and retain such pollutants. Concentrations of the less volatile compounds (several penta- and all higher CBs, DDD, DDE and DDT) significantly increased with increasing altitude whereas little or no difference was observed for more volatile substances (see Table SI-3). This may be related to the different forest types (12) but also the orographic temperature gradient will cause semi-volatile compounds which are present in the vapor phase at lower altitudes, to partition to surfaces such as litter/soil and vegetation at higher altitudes (13). This temperature dependence is stronger for higher chlorinated PCBs (22).

Initial remarks on profile distributions: Concentrations of selected compounds in the soil profiles are presented in Figure 2. In both Italy and Norway, the highest concentrations of the penta- and higher CBs and the pesticides occurred in the organic (O) layers (expressed on both a dw and oc basis). However, tri- and several tetra-CBs showed highest oc-based concentrations in deeper, more mineral layers (and in some cases also on a dw basis). Such observations support the suggestion that lower molecular weight POPs can be preferentially transported to mineral layers in a truly dissolved form (5, 22). This is a form of 'fractionation' affecting the POP composition of surface soils.

Processes potentially influencing profile distributions: The main processes expected to influence compound distributions in the soil profiles are: variability in deposition fluxes over years/decades (6); loss processes which may vary with depth (degradation, volatilization) (e.g. 24-26); vertical transport (in the dissolved phase, with dissolved organic matter (DOM) or particulates) (23); and bioturbation (8). Their potential influence is considered here in two different stages of soil formation: firstly, the initial pedogenesis (including aging of living vegetation, litter deposition and aggregation into the Oi layer); secondly, the degradation and evolution of SOM through the O layers and mineral horizons. The forest soils are the focus of this discussion, because they are more highly resolved regarding the degree of SOM decomposition from fresh litter at the surface to deeper, older layers.

150 Initial pedogenesis:

Examining changes in POP composition: The Italian forest study yielded data on fresh canopy vegetation collected at various times in a growing season (27), fresh litter (<1 year on the ground), and the top (Oi) litter layer. The Oi layer is estimated to be typically 3-9 years old in these soil systems (see SI for details). The POP composition ('fingerprint') could vary in these layers as it ages from leaves – fresh litter – aged litter. Selected PCB congeners (28+31, 52, 101, 138 and 153) were therefore 'normalized' relative to the stable congener PCB-180 for the 3 compartments - vegetation (R_{veg}); superficial litter (R_{litt}) (i.e. the top part of the Oi layer, < 1 year old); and the Oi layer (R_{Oi}) (i.e. the whole litter layer):

160
$$R_x = \frac{C_{PCB-i}}{C_{PCB-180}}$$
 1)

where x is a generic compartment or soil layer and C the concentration of the selected congener *i* or of PCB-180.

163 The mean canopy concentrations at the end of the growing season were used to calculate 164 R_{veg} (7), while the averages from superficial litter samples collected in June and 165 September were used to calculate R_{litt} . These data are presented in Table SI-4. The shift 166 (*S*) in the PCB fingerprint between compartments was then calculated as:

167
$$S_{x/x+1} = \frac{R_x}{R_{x+1}}$$
. 2)

Interpreting the change in POP composition: S values of consecutive compartments (from the top downward) are presented in Figure 3, and plotted against compound log K_{OW} . They were >1 for all congeners. This indicates either higher loss fluxes than for PCB-180 from the compartment under consideration or greater increases in PCB-180 concentrations. In order to investigate which processes drive the observed phenomenon the following factors were considered: i) the high K_{OW} and low volatility of PCB-180, ii) the very slow degradation of PCB-180 (14), iii) as it was shown for the same forest stand that PCB-180 does not approach air-canopy equilibrium during the lifetime of leaves and needles (unlike lighter congeners e.g. PCB-28 and -52) (27), litter still presents residual capacity to take up PCB-180 during the initial phase of decomposition. PCB concentrations were measured in superficial litter at all the sites at 5 different periods between April and October. The R_{Litt} of selected PCBs varied only by a factor of <2 from the mean value for the whole season, with the lowest values recorded during the warmer periods.

For the more volatile (tri- to penta-CB) compounds R_{Veg} and R_{Litt} were clearly $>R_{Oi}$, resulting in $S_{Veg/Oi}$ and $S_{Litt/Oi} > 1$ with the strongest shifts observed for the forest at 1800

m (Figure 3). A marked change in *R* appears to occur relatively soon after litter fall, since $S_{Veg/Litt}$ are of similar magnitude or even significantly higher than $S_{Litt/Oi}$. The weight loss of needle/leaf biomass is typically < 70% (dw-based) in the first 6 years after litter fall (28). The dw-based concentrations of lighter PCBs in superficial litter (average for all 5 sampling campaigns) were up to 3 times higher than in the vegetation, and up to 10 times for heavier compounds (compare Table SI-2 and reference 7). This indicates that the shift in R-values cannot be entirely explained by a loss in lighter congeners (e.g. due to temperature driven volatilization), but may also be caused by some preferential increase of the heavy compounds. The process behind this is possibly associated with the retention of POPs in wet and dry deposition by the litter. If particles (airborne and originating from vegetation surfaces) deposit to the ground, a shift toward less volatile POPs compared to the air will occur due to compound specific equilibrium status reached in this material.

Changes through the organic and mineral horizons: The fractions of individual PCB congeners in each layer compared to the summed concentrations of the whole profile were calculated. Figure SI-2 shows the fractions calculated for all the PCB congeners analyzed in each profile plotted against log K_{OW} (29). The observed trends are schematically represented in Figure 4. In upper horizons, the fractions of individual PCB congeners increase with increasing log K_{OW} (i.e. with decreasing water solubility and increasing organic matter-water partition coefficient (K_{OC}) , whereas deeper horizons show the opposite trend. This behavior is discussed here taking into consideration the different aforementioned processes.

Potential role of leaching: In all cores except I-1100, the highest concentrations of tri-and tetra-chlorinated CBs were found below the horizon with highest burdens of higher chlorinated congeners. This can be attributed to leaching of these more water soluble congeners, most likely in the dissolved phase (23). Transport associated with DOM may favor the more hydrophobic compounds, but since it is always linked to a downward flow of water, this effect will be masked by transport of freely dissolved chemicals. The same is true for particle associated transport induced by preferential flow. The soil column thus appears to act as a chromatographic column, separating compounds according to their organic matter-water partition coefficient, which is linked to their water solubility. However, above a log $K_{OW} \sim 6.3$, the PCB fractions do not show K_{OW} dependence. This suggests that downward dissolved phase transport does not occur with these substances sufficient to influence their profile distribution.

Water-mediated downward transport depends on the amount of rainwater percolating through the profile. Based on the average annual precipitation, it was estimated that about 0.1 to 3% of the total amount of PCBs present in the organic horizons have leached into deeper layers every year in the truly dissolved phase and associated with DOM (details in Text SI-3), depending on the different compound physical chemical properties and sites (see Table SI-5a). The greater precipitation at the Norwegian sites than at the Italian ones (30) may explain the greater translocation of light PCBs in the Norwegian soil profiles. These fluxes are apparently small but they are sufficient to explain the amount of POPs currently found in the deeper mineral layer (see later).

Influence of the timing of peak emissions on profile distribution: PCB emissions (and hence air concentrations) peaked in the 1970s and have been historically re-constructed (31); variations in deposition, fluxes to vegetation and soil are expected to be related to such emission rates. In the absence of bioturbation peak concentrations would be expected in the layer whose genesis started in the period of maximum emissions. Such a distribution was observed for heavier PCBs that showed significantly higher oc-normalized concentration in the O_a layers. Unfortunately data on the age of these specific soils are note available. However, applying the SOM decomposition rates reported by Liski et al. (32) it is possible to estimate that current O_a layers in the soils selected for this study contain organic matter produced during the decade of 1960-70s. The PBDE dataset can be used for comparison, since PBDE emissions started (1960s) and peaked (1990s) ca. 20 years later than for PCBs (33). PBDE concentration peaks were always observed in soil layers above and therefore younger than those with highest concentrations of heavier PCBs (see Table SI-3). This confirms that at least for compounds with log $K_{OW} > 6.3$ (i.e. those with stronger affinity to SOM), vertical transport and transformation processes do not significantly alter the distribution in the soil profile. For these compounds, the soils broadly 'recorded' the historical emission pattern (although with a low resolving power).

247 Potential role of bioturbation: An important observation made in the Norwegian profiles 248 is that one layer generally accounted for 60 - 80% of the summed oc-normalized 249 concentrations in the profile. Bioturbation is negligible in these systems, since 250 earthworms and other large, soil-mixing invertebrates do not inhabit these acidic boreal 251 soils (pH values given in Table SI-1). In the Italian soils the distribution of PCB

congeners between the horizons was slightly more homogeneous. Bioturbation or other transport processes indifferent to partitioning and volatility, such as particle associated transport induced by preferential flow, appear to play more of a role here. Faster litter decomposition compared to the boreal sites may also account for the difference, at least in profiles I-1100 and I-1400.

Potential role of volatilization: Assuming that the sorptive capacity of SOM dominates that of the soil and varies only negligibly between different stages of SOM decomposition, the highest oc-normalized concentrations would correspond to the highest fugacities. For compounds that were able to reach equilibrium between the air and vegetation, SOM decomposition would therefore increase compound fugacity for persistent molecules, potentially resulting in a fugacity gradient back to the surface and the overlying air and/or into downward percolating waters. Potential mobilization is more likely for the lower molecular weight PCBs, partly because of their higher volatility and K_{QC} , but also because they are more likely to have approached equilibrium between air and vegetation before leaves or needles fall (27). Volatilization, however, is kinetically limited as older layers become buried by younger material, and in absence of substantial bioturbation it soon becomes negligible.

Potential role of SOM degradation: Lower degradation rates of POPs relative to SOM 272 are another factor resulting in their relative enrichment with depth. Organic layers at 273 different stages of decomposition can be classified by their C/N ratio. The C/N value 274 decreases as decomposition proceeds; it can indicate the decomposition rate in soil

ecosystems since high rates result in a more rapid decrease in the ratio than low ones do (34). Plots of oc-normalized PCB concentrations against C/N (Figure SI-3 shows examples) may indicate the presence of this process as the concentrations increase with proceeding SOM decomposition. However, as discussed above, evidence of such trends is confounded by variable inputs of PCBs over time.

Potential role of compound degradation: So far the discussion has focused mainly on PCBs which may experience degradation in soil (14), but this process could not be distinguished from others (e.g. volatilization) which could also result in losses from the soil profiles. Here OCPs may provide information, because ratios between certain chemicals have been used in the literature to indicate whether (bio-) degradation has occurred. The most common example is the decreasing ratio between DDT and its very persistent metabolite DDE, as degradation proceeds (18). However, no clear trend could be seen in the DDT/DDE ratios found in the soils investigated (see Table SI-3). Similar observations were made for the α/β -HCH ratio which also decreases as degradation occurs, due to the greater persistence of β -HCH (18) (see Table SI-3, β -HCH was determined in Norwegian samples only). The results suggest that these background soils are repositories for POPs with degradation being very limited. Low temperatures and unfavorable soil properties (low pH and litter degradability), resulting in low metabolic rates, and leaching of some compounds into deeper, biologically inactive soil layers explain this finding. However, pesticide ratios must be interpreted with care because they will also depend on changing emission patterns, particularly as pesticides are emitted from contaminated soils where they may have experienced degradation.

PCB degradation rates in soil, recommended for modeling (14), exceed leaching rate estimates performed here by a factor of up to 40 for tri-PCBs, while for heavier congeners both are of similar magnitude (see Table SI-5) with degradation rates being up to two orders of magnitude lower than those of lighter PCBs. Accordingly, compound degradation-although slow-appears to be a key factor in controlling the fate of PCBs in these soils. However, as such values may depend strongly on environmental conditions, soil type and compound specific degradation data are needed to more thoroughly evaluate the impact of these processes

307 Comments on the inventory and persistence of POPs in the surface soils

The discussion above has shown that PCB congener ratios change during the transition from living vegetation to soil litter. Losses of lighter congeners via volatilization and transfer to deeper soil horizons were implicated.

Here, an attempt is made to evaluate the significance of these losses, by estimating the absolute amount U (µg m⁻²) of selected compounds (PCBs 18, 28+31, 49, 52, 101, 118, 138, 153, 180, 194, α - and γ -HCH, p,p'-DDE, p,p'-DDT) present in each layer, as follows:

 $U_i = C_i \cdot BD \cdot l$

where C_i (ng g⁻¹) is the concentration of a certain compound (i) in soil (dw-based), *BD* (g

 m^{-3} dw) is the soil bulk density and l (m) is the layer depth. BD was estimated according

3)

to Huntington et al. (35) (see Table SI-1). The data are presented in Table SI-6.

According to the discussion above, heavier compounds (e.g. PCB-180) were assumed to be less affected by loss processes in the soils. This is supported by comparing U_{180} in the 321 Oi layer with amounts deposited during its formation (U_d) (see SI for details of the 322 calculation).

Estimated $U_{d,180}$ -values of 0.24, 1.2 and 1.2 µg m⁻² in Oi layers at sites I-1100, I-1400 and I-1800, respectively, are in good agreement with U_{180} determined (0.32, 1.2 and 1.4 µg m⁻² at 1100, 1400 and 1800 m), showing that PCB-180 experienced little if any losses from the Oi layer. The slight under-prediction of PCB-180 amounts at sites I-1100 and I-1800 may be attributed to trapping of particles subject to surface run-off.

In contrast, lighter PCBs and HCHs showed substantial fractions of the profiles' total burden in layers formed from vegetation at a time when concentrations of these chemicals in the air were lower. This emphasizes the importance of considering the range of compound-specific processes when modeling the fate of POPs in terrestrial systems.

Regional and global multi-media fate models generally do not attempt to model the within-profile processes investigated in this study (i.e. transfer to deeper layers, interaction with ageing SOM) (36) because this requires knowledge of a number of scenario-specific parameters. However, it is clear that these processes are important in long-term soil fate and hence the global inventory and cycle of POPs.

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341 Supporting Information Available

342 Details about sampling sites and soil profiles, analytical methods, the full concentration
343 data set, congener ratios, the distribution of PCBs within the profiles, estimates of PCB

fractions leached and area specific amounts of POPs in the soil layers. This material is

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477 Figure 3.





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- 483 Factors influencing the fate and behavior of persistent organic pollutants within organic
- 484 matter-rich soils from boreal and montane regions are investigated.