



Critical evaluation of a new passive exchange-meter for assessing multimedia fate of persistent organic pollutants at the air-soil interface



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ABSTRACT

A new passive exchange meter (PEM) to measure inter-compartment fluxes of persistent organic pollutants (POPs) at the interface between soil and the atmosphere is described. The PEM uses labeled reference compounds (RC) added in-situ to vegetation litter deployed in open cylinders designed to trap the vertical downward export of the RCs while allowing free exchange of POPs between litter and air. Fluxes of native compounds (bulk deposition, volatilization and downward export) are quantitatively tracked. One scope of the PEM is to investigate the influence of biogeochemical controls on contaminant re-mobilization. The PEM performance was tested in a subtropical forest by comparing measurements under dense canopy and in a canopy gap; conditions in which deposition and turn-over of organic matter (OM) occur at different rates. Significant differences in fate processes were successfully detected. Surprisingly, mobilization by leaching of more hydrophobic compounds was higher under canopy, possibly as a result of canopy mediated enhancement of OM degradation.

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1. Introduction

Many chemical pollutants of major environmental and human health concern, including the persistent organic pollutants (POPs) are semivolatile and engage in partitioning among air and solids including soil organic matter (SOM). Such a diffusive exchange provides the conditions for soils and vegetation to behave as natural reservoirs and potential secondary sources. Re-emissions from soils and vegetation are believed to represent an important contribution to the total atmospheric sources of POPs (e.g. Komprda et al., 2013), while the mechanisms controlling the air-surface exchange may significantly influence contaminant fate and distribution (Dachs et al., 2002; Wania and Mackay, 1993). Gaining knowledge on these mechanisms is pivotal for the compilation of source inventories, interpretation of monitoring data and the assessment of emission control measure effectiveness.

The re-mobilization of semivolatile organic pollutants (SVOCs) depends on compound specific properties, environmental conditions

and environmental media characteristics. In terrestrial environment, SOM and vegetation represents major reservoirs of POPs (Meijer et al., 2003). Vegetation litter and soil organic carbon synthesis and turn-over are under strict climate control. Theoretically, high temperatures, rapid turn-over of SOM, and enhanced precipitations are expected to favor re-emission of SVOCs from soil surface (AMAP, 2003; Nizzetto et al., 2010; UNEP/AMAP, 2011). Available technology does not allow a direct field-based experimental assessment of this exchange and the analysis of the re-emission drivers mainly remains a theoretical exercise.

Although at least some notable example exists (Kurt-Karakus et al., 2006; Perlinger et al., 2005), active micrometeorological based SVOC air-surface exchange measurements in background conditions, are still at an embryonic stage. Other active sampling approaches have been tested to assess the biogeochemical control on POP re-emission from soils, mainly aimed at measuring air-surface fugacity gradients (Cabrerizo et al., 2009, 2011a,b; Hippelein and McLachlan, 2000). These approaches lacked capacity of resolving mass transfer and fluxes. In addition, active methods focused on the air-surface exchange, neglecting other mobilization processes such as, for example, leaching.

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In this study we present a new design of a passive exchange meter (PEM) for the simultaneous measurement of the time integrated air-surface exchange and leaching of SVOCs from the material constituting the soil-air interface. The goals of this critical evaluation were i) to introduce the design and conceptual framework of the PEM, and ii) to demonstrate the performance of the PEM in a particularly dynamic scenario: a sub-tropical system forest, comparing flux measurements under dense canopy and in a small canopy gap during a deployment period of two months.

2. Materials and methods

2.1. Introducing the exchange meter

This evaluation of the PEM focuses on forest litter. Vegetation litter is a ubiquitous matrix covering large part of global soil surface and represents a highly dynamic pool of OM. The mass and properties of this pool are controlled by dynamics of production and mineralization, which in turn may affect multimedia exchange of SVOCs.

The framework presented here to measure SVOCs mobilization assumes that isotopically labeled (^{13}C) reference compounds (RCs) added to environmental matrices in the field can be used to trace the fate of their “native” homologues. This assumption is regularly and successfully applied in lysimeter studies for pesticide fate (e.g. Laabs et al., 2002) or in the field of SVOC passive air (e.g. Moeckel et al., 2009; Pozo et al., 2004) and water (e.g. Booij et al., 2002) sampling. In addition, optimized spiking method for studying bio-availability and mobility of SVOCs in SOM are available, which ensure low level of disturbance and preservation of the organic matter properties (Doick et al., 2003).

The PEM consists of an open metal cylinder (i.d. 147 mm, Interception area $A = 0.0154 \text{ m}^2$) with a coarse metal net (1 mm mesh) in proximity of the base (Fig. 1). Below the net, three pre-extracted polyurethane foam (PUF) disks are piled supporting another metal net. The material constituting the interface between air and soil of the area selected for the measurements (forest litter, top SOM or grass, taken as examples) is collected in situ and spiked (see details in Section 2.2) with a range of isotopically labeled RCs covering the window of properties of the targeted “native” compounds (in this study a range of PCBs and their ^{13}C isotopes was selected (see chemical analysis section)). A given amount of the spiked material is then added to the PEM above the upper metal mesh to mimic characteristics and abundance of the material naturally present at site. For example, in the case of forest litter the same mass of litter present in a forest floor surface equivalent to A is added into the PEM.

Re-equilibration of the spiked litter was carried out during 2–3 days (from the moment of the spiking and at least 5 h from the moment of the deployment in field). During this phase the readily exchangeable mass of the RCs is re-distributed in the mass of the litter or rapidly lost after deployment in the field. An aliquot of the spiked material in the PEM is then collected and concentrations measured to determine the amount of labeled and native compounds at the beginning of the sampling period (U_0 and U_0^* (ng), respectively). The starred symbols identify parameters for the RCs.

The PEM is then left in the field, in close contact to the ground, for a selected period of time (e.g. one month or more). During this period a number of processes (including aging of the OM, atmospheric dry and wet depositions, leaching, gaseous exchange, litter deposition, and virtually, chemical degradation) affect the fate of native and labeled chemicals.

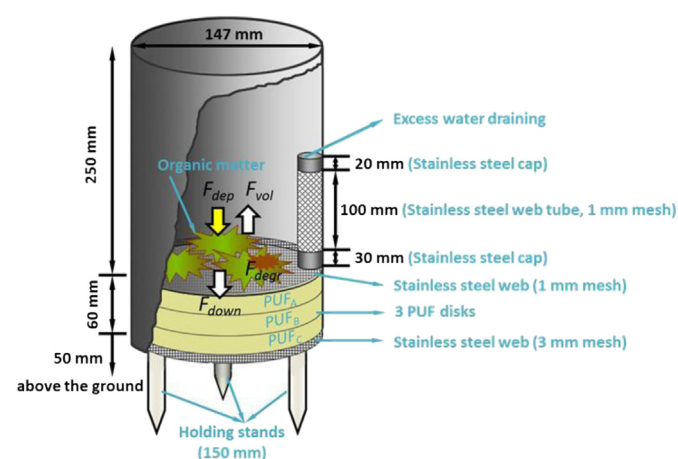


Fig. 1. Design of the exchange meter (EM) and scheme of fluxes of POPs in the organic matter (litter).

A simple device (named infiltration excess collector) is included. This collects the potential superficial run-off resulting from the off-set between infiltration rate through the litter and precipitation rate and prevents overflowing from the PEM during intense precipitations. Collected run-off is then directly address to the sorbing PUFs (Fig. 1). The PUF disks added at the bottom of the PEM, instead are used solely to measure the mass U_{PUF}^* of RC that underwent downward export.

The spiked litter and the PUF disks are retrieved and analyzed at the end of the exposure period (t_1) to determine U_{t_1} and $U_{t_1}^*$ (namely the amount (ng) of native and labeled compounds in the organic material). Based on this set of information the mass balance of both natives and labelled POPs in the PEM can be tracked as described in the theory Section 3.1.

2.2. Sampling

The particularly dynamic pool of forest litter in a humid subtropical forest was considered in this assessment. Subtropical forests during humid periods are characterized by high productivity and rapid turn-over of organic carbon in litter and soil. The choice of a forest site allows accessing PEM measurement resolution by looking for differences of exchange fluxes under canopy and in canopy gaps. A previous study (Zhang and Zak, 1995) performed in a Chinese subtropical forest site with similar species composition and climate to that of the site selected for this study, showed that degradation rate and substrate induced respiration of litter significantly differed between dense canopy conditions and canopy gaps, with the canopy enhancing faster degradation of litter OM. This is due to the different exposure conditions to direct solar radiation resulting in different dynamic of the water mass balance and OM degradation. In this scenario, the PEMs deployed in the understory and the gap will experience similar atmospheric concentrations air temperature and precipitation while variance in conditions will be expectedly associated to the occurrence of litter deposition and faster litter OM turn over in the understory (Zhang and Zak, 1995).

The sampling site is located in the Dinghushan Biosphere Reserve ($112^\circ 30' 39'' - 112^\circ 33' 41'' \text{E}$ and $23^\circ 09' 21'' - 2311' 30'' \text{N}$) in the mid-part of Guangdong Province in south China. A mixed pine and broad-leaved forest plot and an adjacent gap (with no canopy cover in the range of 20 m, and completely surrounded by tall trees) were selected.

Before the deployment of the PEMs, 500 g of forest litter were collected from the forest site. A small fraction was assessed for water and organic carbon content, and analyzed for selected PCBs (more details are available on line (Text S11)). The remaining fraction was homogenized by cutting large leaves using a scissor to achieve a texture with the largest pieces in the order of 1 cm^2 , and spiked with a solution containing ten ^{13}C congeners covering di- to deca-PCBs (see details in Text S11). Spiking was carried out following a validated procedure (Doick et al., 2003). Briefly, this widely employed technique consists of spiking (using a small volume of carrier solvent) only to 20% of the sample while mixing for several minutes using a stainless steel spoon to allow solvent evaporation and homogeneous distribution of the spiked material. The rest of the sample is then added while continuously mixing. The sample is left for at least 1 day (in our study 2 days) in a close jar to favor redistribution and homogenization of RCs. This technique guarantees that most of the native contaminants in the litter are not directly exposed to the carrier solvent and prevents alteration of their distribution and binding to the OM. The effectiveness of this method was widely tested against several endpoints, including: reproducibility, extractability, bio-availability and soil microbial activity (Doick et al., 2003), showing high level of consistency, homogeneity of RC distribution in the sample and no alteration of distribution and mobility of the native contaminants present in the sample or significant alteration of its biophysical integrity.

In total, 0.5 ng of each congener was added per each g of dried litter to obtain a concentration of the RCs in the range of that of native PCBs. All spiked litter was transferred into a 10 L brown glass jar and rehydrated at about 30% level. The bottle was vigorously shaken by hand for several minutes and kept closed at room temperature for 48 h to allow reequilibration/redistribution of the added ^{13}C PCBs and water.

On the 10 June 2011, back in the field, the equivalent of 20 g (dw) of the spiked litter were deployed in each 10 PEMs (5 in the understory and 5 in the canopy gaps) and three pre-extracted PUF disks (diameter 15 cm thickness 1.5 cm) (Fig. 1) were placed in each PEM. After the period of time required to set up the experiment (about 5 h), 5 g sub-aliquots were collected from each PEM, wrapped in aluminium and plastic bags, cooled, immediately brought back to the lab and analyzed for the determination of U_0 and U_0^* .

After 2 months of deployment, the remaining spiked litter and the PUF disks were collected and transported to the lab. There, a sub-aliquote of each replicate was freeze dried and weighted to determine mass and water content. The remaining samples were stored at -20°C until chemical analysis for the determination of U_{t_1} and $U_{t_1}^*$.

2.3. Chemical analysis and QA/QC

Details of the analytical method and quality assurance and control are reported in the supplementary information available on-line (Text S1). In summary, 34 PCB including di- to octa-chlorinated congeners were measured.

2.4. Ancillary data

Five litter deposimeters (diameter = 60 cm, mesh = 1 mm) were used to collect the litter fall in the canopy plot during the PEM deployment. Deposited litter was collected and its dry weight (dw) determined to calculate the bulk litter deposition flux. Similarly a known mass of litter (equivalent to about 100 g dw) was deployed in triplicate litter bags directly on the soil surface of the forested plot. Litter mass loss was determined by recovering the litter in the bags after the deployment time and measuring again its dry weight. Litter mass loss in the PEM was also estimated both under canopy and the gap, by the change in litter dry weight corrected for the contribution of litter fall calculated from the litter deposimeters.

3. Theory

3.1. Flux determination

The net exchange flux F_{net} ($\text{ng m}^{-2} \text{d}^{-1}$) is defined as follows:

$$F_{\text{net}} = \frac{U_{t_1} - U_{t_0}}{A \cdot t} = F_{\text{dep}} - F_{\text{loss}} \quad (1)$$

where t (d) is the deployment time (set as 60 days in this pilot study). F_{dep} represents the entering flux of native atmospheric pollutants deposited to the PEM organic matter through various deposition processes during the sampling period. F_{loss} represents the net loss of either native or labeled compounds from the material in the PEM and can be expressed as the sum of three processes:

$$F_{\text{loss}} = F_{\text{down}} + F_{\text{vol}} + F_{\text{degr}} \quad (2)$$

where, F_{down} is the downward export flux (e.g. leaching (including run-off) + downward diffusion from the litter), F_{vol} is the volatilization flux from the organic matter, and F_{degr} is the degradation of chemicals in the litter.

In the case of POPs (e.g. the PCBs, targeted in this paper) it can be assumed that degradation is not relevant during the 2 months of deployment time and it is therefore considered as negligible. This assumption has been previously used in similar studies (Horstmann and McLachlan, 1998; Nizzetto et al., 2008). Half-lives of PCBs in soils or litter are in the order of several years (Sinkkonen and Paasivirta, 2000). Following this assumption, F_{loss} can be simplified as:

$$F_{\text{loss}} = F_{\text{down}} + F_{\text{vol}} \quad (3)$$

The downward transport (F_{down}^*) of RCs from the litter to the PUF can be estimated from the amount of the labeled congeners sequestered by the PUFs during the deployment time, as follows:

$$F_{\text{down}}^* = \frac{U_{\text{PUF}}^*}{A \cdot t} \quad (4)$$

Assuming negligible atmospheric depositions of the labeled compounds (since ^{13}C PCBs are rare in the environment) Equation (1) for the labeled chemicals can be further simplified as:

$$F_{\text{net}}^* = -F_{\text{loss}}^* = -(F_{\text{down}}^* + F_{\text{vol}}^*) \quad (5)$$

therefore the volatilization flux of the RCs F_{vol}^* can be calculated as follows:

$$F_{\text{vol}}^* = -(F_{\text{net}}^* + F_{\text{down}}^*) \quad (6)$$

It is useful to introduce now the function $f_{\text{loss}(t)}$ describing the instantaneous value of F_{loss} . If the concentrations of labeled compounds in the medium added to the PEM are in the order of, or lower than that of the native ones and assuming that the labeled

compounds behave similarly to their native homologues, the following relationship can be written:

$$f_{\text{loss}(t)} = r_{(t)} \cdot f_{\text{loss}(t)}^* \quad (7)$$

where $r_{(t)} = U_{(t)}/U_{(t)}^*$ is the ratio between the amount of native and labeled compounds in the PEM organic matter and $f_{\text{loss}(t)}^*$ is the function describing the instantaneous value of F_{loss}^* .

The r values of those compounds lacking a labeled isotope were calculated considering the labeled isomer within the same congener group. In spite the occurrence of similar losses of native and labeled compounds, native compounds (unlike the RC) continuously receive fresh inputs from the atmosphere. This means that r is not constant. Since the shape of the functions $r_{(t)}$ and $f_{\text{loss}(t)}^*$ are not known, it is not possible to analytically derive the aggregated value F_{loss} , integrated over the deployment period. However it can be argued that $r_{(t)}$ is a growing function of time (since native compounds receive inputs while labeled ones do not) and its minimum $r_{(t_0)}$ and maximum $r_{(t_1)}$ values are experimentally known. Therefore, assuming in first approximation that $r_{(t)}$ is linearly growing during the time of the sampling, the following equivalence can be demonstrated:

$$\int_{t_0}^{t_1} r_t dt \approx \frac{r_{(t_1)} + r_{(t_0)}}{2} \cdot \theta = \theta \quad (8)$$

and

$$F_{\text{loss}} = \theta \cdot F_{\text{loss}}^* \quad (9)$$

Similarly (and remembering Equations (3) and (4)) the downward export flux and volatilization flux of native pollutants from the organic matter can be expressed as:

$$F_{\text{down}} = \theta \cdot F_{\text{down}}^* \quad (10)$$

$$F_{\text{vol}} = \theta \cdot F_{\text{vol}}^* \quad (11)$$

Finally, from Equation 1, 5 and 8, F_{dep} for the native compounds can be calculated as follows,

$$F_{\text{dep}} = F_{\text{net}} - \theta \cdot F_{\text{net}}^* \quad (12)$$

This framework allows separating deposition and volatilization fluxes. For this reason, the PEM does not require that air and litter are far from the partitioning equilibrium. In fact, in theory, equilibrium conditions for gaseous compounds will be detected by the PEM by displaying F_{dep} values similar to F_{vol} values.

4. Results

4.1. Results for ancillary data

Detailed information on litter fall, litter degradation, and meteorological parameters during the deployment are reported in Table 1.

Consistently to (Zhang and Zak, 1995), litter dry weight loss was higher under canopy (33%) plot compared to the gap (26%), and was consistent with the measurement performed using the litter bags (38%) under canopy, suggesting the manipulation of the litter during spiking did not significantly alter litter OM properties and microbial activity.

Table 1
Ecological and meteorological parameters.

	Forest	Clearing
Dry weight at t_0 (g)	15	15
Dry weight at t_1 (g) ^a	11.2 ± 1.55	11.1 ± 0.32
Water content of the PEM litter at t_1 (%)	49.0 ± 5.68	2.76 ± 2.03
Litter fall deposited into the PEM (g dw)	1.2 ± 0.4	–
Dry weight loss of litter in the PEM (g)	4.96 ± 1.55	3.87 ± 0.32
Calculated dry weight loss rate in the PEM (% in 2 months)	33.2 ± 10.3	25.8 ± 2.1
Dry weight loss measured in litter bags (% in 2 months)	37.9 ± 9.2	–
Water content in the litter in litter bags (%)	62.1 ± 15	–
Litterfall measured in litter depositors (g dw)	15.8 ± 3.5	–
Average air temperature (°C)	25.5	–
Average precipitation (mm)	219	–
Average air humidity (%)	90.8	–

^a Including litterfall deposited during exposure.

4.2. PUF efficiency in sampling F_{down}^*

The quality of the measurement of the downward export flux F_{down}^* depends on the ability of the three PUFs deployed below the spiked litter in the PEMs to quantitatively trap the RC downward transport. Separate analysis of the three PUF disks demonstrated that more than 90% of the leaching RCs was trapped by the upper PUF (more details in text S12 and Fig. S11).

4.3. Behavior of labeled RCs

Fig. 2 shows the amount U^* (ng) of labeled PCBs present in the litter deployed in the PEM at t_0 ($N = 10$) and t_1 for the forest ($N = 5$) and gap ($N = 5$) in comparison with the nominal spiked amount. A rapid loss of labeled PCBs occurring between the time of the spiking and that of the beginning of the field deployment accounted for 11.7–42.7% of the nominal added amount. This is likely due to rapid volatilization of the less bounded fraction of the RCs during preliminary equilibration time, transport and the set-up procedures in the field. All further calculations and parameters presented here were therefore based considering the data of t_0 determined from the analysis of the 5 g aliquots rather than the nominal spiked amount.

A major implicit prerequisite of the present experimental framework is that $U_{t_0}^* > U_{t_1}^*$. Without such a condition no flux calculation could be performed using the PEM. This condition was always verified (Fig. 2). The residual amount $U_{t_1}^*$ of PCBs from ^{13}C -

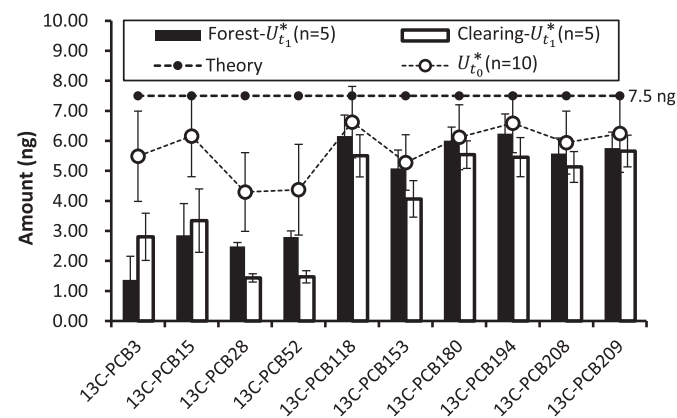


Fig. 2. Comparison of the amount (ng) of ^{13}C labeled PCBs in the EM litter at t_0 ($n = 10$), and at t_1 in the forest ($n = 5$) and clearing ($n = 5$), in relationship to the nominal added amount (theory).

PCB28 to ^{13}C -PCB209 in the PEM litter was in average 71% of the initial amount $U_{t_0}^*$ for the forest plot. As expected, the most volatile and soluble PCBs (such as ^{13}C -PCB3 and ^{13}C -PCB15) showed the highest loss (and therefore mobility), with $U_{t_1}^*$ representing only 12% and 30% of $U_{t_0}^*$, respectively.

For these compounds, volatilization represented the main pathway driving to bulk loss of RCs (Fig. 3). Volatilization typically represented between 60% and 80% of total loss also for the heavier compounds (Fig. 3).

EMs in the gap, instead, experienced: i) a lower overall loss of ^{13}C -PCB3 and ^{13}C -PCB15 (being $U_{t_1}^*$ about 55–60% of $U_{t_0}^*$); ii) a significantly higher loss of compounds with intermediate volatility (namely: ^{13}C -PCB28 (32%) and ^{13}C -PCB52 (40%)) and; iii) a significantly lower loss of the heavier compounds (^{13}C -PCB153 and higher) ($U_{t_1}^*$ 90% of $U_{t_0}^*$).

In general, mobilization of labeled chemicals (with the exception of ^{13}C -PCB28 and ^{13}C -PCB52) appeared to be favored under canopy conditions (Fig. 3).

4.4. Fluxes of “native” PCBs below and outside the canopy

Solutions for the fluxes of “native” PCBs (namely: F_{dep} , F_{down} and F_{vol}) are represented in Fig. 4 and reported in Table S2.

In the gap site, F_{net} was negative for all compounds indicating net release of contaminants from litter towards the atmosphere or the underlying soil. Also the litter deployed under canopy behaved mainly as a source of PCBs with some exceptions (PCB49, PCB169 and PCB189 and to a lower extent PCB44, PCB114, PCB156 and PCB189). Concerning the more volatile compounds (namely: tri- to penta-CBs) the overall losses of PCBs from the litter in the gap always exceeded that under canopy of an average factor of 4, being these differences significant ($P < 0.05$) in 64% of the cases. Concerning higher chlorinated compounds, the net loss from the litter tended to be higher under canopy, but the differences were not significant. This is an interesting result since it shows the tendency of enhanced mobility of more hydrophobic compounds in the understory compared to the gap conditions.

The detail analysis of loss processes highlighted dramatic differences between the canopy and the gaps. As expected, average F_{dep} values were higher under the canopy for most of the analyzed congeners of a factor ranging between 1.8 and 4.4, with the highest factors measured for the hexa- and hepta-CBs. Only for 8% of the congeners these differences were statistically significant. Despite the sampling period did not coincide with the period of maximum litter deposition (only few grams (Table 1) of litter fall were intercepted by the PEMs), the PEMs allowed detection of forest canopy influence on F_{dep} .

The volatilization fluxes F_{vol} were higher for most of the congeners in the gap by a factor ranging between 1.4 and 9 (with the biggest differences observed for penta-CBs) and differences statistically significant for 50% of the congeners.

The downward export F_{down} measured under canopy exceeded that in the gap basically for all compounds (with exclusion of PCB28 and PCB37) of a factor ranging between 2.3 and 3.6 and significant differences observed for 85% of the dataset. In particular the largest differences were observed for the more chlorinated congeners. To our knowledge this is the first time this behavior was documented.

5. Discussion

5.1. Assessing the quality of the flux measurement method

In order to assess the quality of PEM derived flux measurements the basic assumptions adopted in the quantitative framework

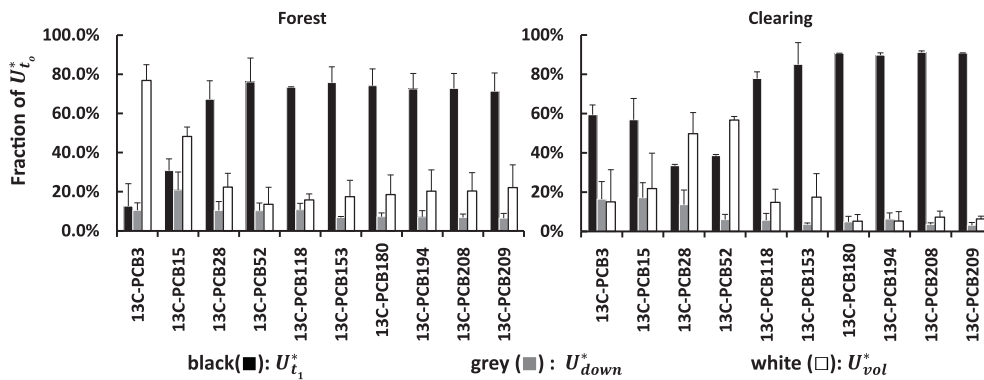


Fig. 3. The amount of ¹³C labeled PCBs in litter ($U_{t_1}^*$), PUF disks (U_{down}^*) and calculated loss by volatilization (U_{vol}^*) at t_1 relatively to t_0 .

presented in section 3 will be critically challenged in order to gather evidences of their validity.

5.1.1. Values of r and their change with time

Two important assumptions underpinning the quantitative framework introduced here are: i) the concentration of ¹³C PCBs in the litter was in the order or lower of that of native PCBs; and ii) $r(t)$ is a growing function of time and therefore the condition $\int_{t_0}^{t_1} r(t) dt \approx \theta$ (see Equation (8)) is verified.

Assumption i) can be assessed by looking at the r values representing the ratio of concentrations between the native and the labeled congeners. At t_0 r ranged for all compounds between 0.05 and 1.53 (Fig. 5, Table S3). These data support the validity of

assumption i) for most of the investigated congeners. Despite in general, a higher ratio between native congeners and RC would have been preferable, a further reduction of RC concentration would have resulted in challenging analytical conditions. In fact the native PCBs were already present at trace levels.

Concerning assumption ii) the value of the difference Δr between $r(t_1)$ and $r(t_0)$ was expressed in fractional terms as follows:

$$\Delta r = \frac{r(t_1) - r(t_0)}{r(t_0)} \tag{13}$$

Δr was always positive (Fig. S12, Table S3) confirming the validity of the assumption. In addition Δr values indicated that the change in r between $t(1)$ and $t(0)$ was generally <50% of the $t(0)$ value. It can

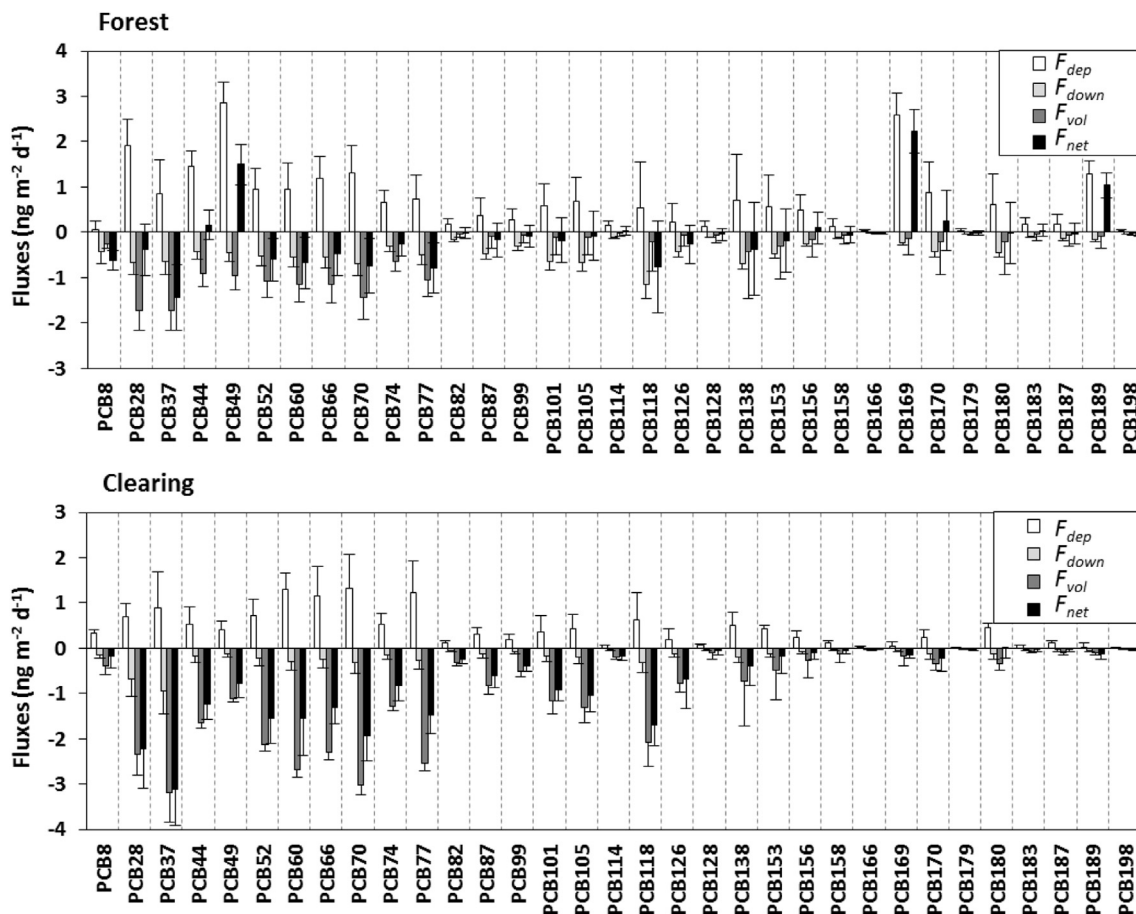


Fig. 4. Air-surface and vertical export fluxes of native PCBs during 2 months of deployment in the Dinghu Mountain forest ($n = 5$) and clearing ($n = 5$).

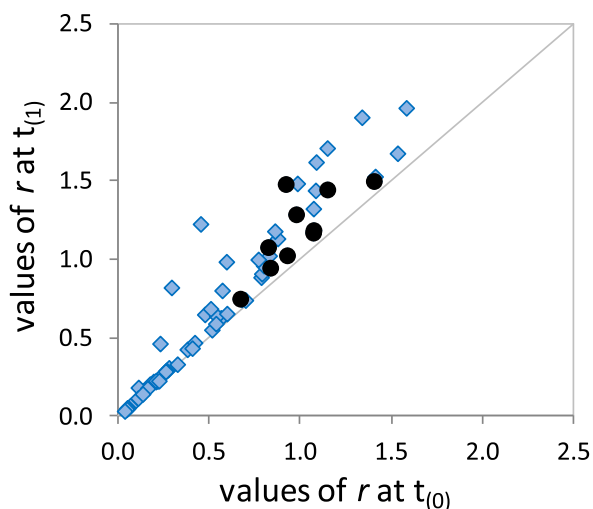


Fig. 5. Relationship between mean value of compound specific $r(t_0)$ and $r(t_1)$. The points highlighted with dark circles represents the target congeners for which a labeled homologue was present in the RC mixture.

be demonstrated that with such a limited variation in time of r , the maximum theoretical error introduced by Equation (7) affecting measurement accuracy (for example assuming an unlikely highly nonlinear growth of $r(t)$) – in percentage terms – is about $\pm 18\%$ for the high chlorinated congeners and $\pm 38\%$ for the low chlorinated congeners.

5.1.2. Consistency of behavior between labeled and native PCBs

A possible major source of error for the quantitative framework introduced here is the possible different behavior of labeled and native compounds. In particular, one may hypothesize that added ^{13}C PCBs have higher mobility than native ones due to the different pathways which drove to their enrichment in the organic matter (being the RCs added through an artificial spiking procedure).

We checked for this possible artifact by analyzing the correlation of r values at t_0 and t_1 . Results are depicted in Fig. 5, showing the occurrence of a statistically significant correlation ($P < 0.05$) and therefore considerably consistent behavior of labeled and native compounds.

Three outliers were identified (namely PCB49, PCB169 and PCB189) for which, relatively high concentrations were found in the litter of the forest plot at t_1 . Since there is no reason to exclude these data from the dataset due to analytical quality assurance/quality control criteria we concluded that the high r values measured at t_1 is the result of efficient canopy scavenging and litter fall transport, or alternatively, a fraction of these congeners may have derived from de-chlorination of higher chlorinate PCBs in the litter. Unfortunately this dataset does not allow testing such hypothesis.

Fig. 5 shows that (with the exception of the few outliers discussed above), the behavior of the group of compounds the fluxes of which were calculated using a different congener as RCs (highlighted as dark circles) is statistically ($P < 0.05$) undistinguishable from that of the group of compounds with labeled isotopes. For both these groups the same regression model and standard errors could be applied.

As expected r values showed a net positive deviation from the $y = x$ curve, and the slope of the regression ($S = 1.21$) was significantly ($P < 0.05$) higher than 1. This behavior is the result of deposition of native PCBs during the exposure period. However, lighter congeners showed a slightly higher positive deviation than less volatile ones (Fig. S12, Table S3). It can be argued that faster remobilization of low chlorinated RCs compared to their

homologues may also have determined such a behavior. In order to assess the magnitude of this artifact it can be assumed that the excess (equivalent to an averaged factor 0.27) between the average value of Δr of the di- to tetra-CBs ($\Delta r = 0.37$) and that of penta- to octa-CBs ($\Delta r = 0.10$) is due to the described artifact. Since the estimated excess of mobilization only affected 27% of the mass of labeled compounds in the organic matter, it can be concluded that the associated error on flux calculation for the tri- and tetra-CBs is at maximum of an equivalent proportional and does not substantially affect the outcomes of this study.

5.1.3. Differences in POP mobilization under canopy and in gap conditions

The key processes driving to the release of PCBs from the litter layer were different under canopy and the gap plots. Both in the understory and gap F_{vol} was significantly higher (factor 2–2.6, $P < 0.05$) than F_{down} for tri- and tetra-chlorinated congeners. In the gap F_{vol} dominated the loss of PCBs from the litter across all the range of analyzed compounds. It might be surprising that also congeners with high K_{OA} values experienced significant volatilization. This is due to the fact that litter collected in-situ was used in this study. Heavier congeners were therefore likely close to the equilibrium already before the spiked litter was deployed in the PEM. Under these conditions re-volatilization of these compounds is favored by their relatively higher K_{OA} dependence on temperature compared to lighter congeners (Li et al., 2003).

Under canopy, instead, F_{down} tended to be higher than F_{vol} by a factor of 1.6–5, with significant differences observed only for the penta-CB group. The enhanced leaching of PCBs below canopy could not be explained by different precipitations since the two sites were located less than 100 m one from each other. The fact that leaching flux was higher for less soluble compounds, instead, suggests biogeochemical control and a potential role of dissolved organic carbon (DOC) mediated transport.

Results of ancillary data show differences in organic matter degradation between the forest and the gap. Both the gap and the canopy sites were subjected to similar atmospheric boundary layer conditions, preventing significant direct wind flow over the PEMs (the gap site was indeed relatively small and completely surrounded by tall canopy in all directions). It is therefore very unlikely that volatilization from the gap deployed PEMs was significantly enhanced by more dynamic wind conditions. The litter in the gap, unlike that under the canopy, experienced direct exposure to solar radiation which resulted in more rapid evaporation of water and consistently significant lower litter moisture (Table 1). This determines lower bulk heat capacity and slower OM turn over in the gap deployed litter compared to the understory litter (Conant et al., 2011). Low bulk heat capacity may have implication on contaminant fugacity by means of fugacity dependence on temperature, explaining higher volatilization in the gap as a result of higher maxima in litter temperature.

Conversely, canopy conditions promoted more rapid degradation of litter organic matter (Table 1) resulting in faster remineralization and possibly larger export of DOC. This likely promoted downward export of PCBs under canopy. To our knowledge, this is the first time the possible link between POP mobilization from soil surface and organic matter turn-over dynamics is described in experimental terms and field conditions.

6. Conclusions

The precision of the PEMs derived from the variance of 5 replicates was sufficient to resolve: i) mean volatilization fluxes differing by a factor of 1.3–1.6 for the more volatile congeners (tri- and tetra-CBs) and 2.9–3.7 for the heavier compounds; ii) mean

downward export fluxes differing by a factor of 1.6–1.8 for all congeners; and iii) deposition fluxes differing by a factor of 1.4–2.2 for tri- and tetra-CBs, and 2–5 for heavier compounds.

The PEM is a relatively low cost device which does not require electric power or complex logistic infrastructures. It is fully portable and can be conveniently used in large scale spatially resolved assessments of pollutant fate. The mass balance approach allows intrinsic quality control. Unlike other types of depositometers (Brorstrom-Lunden and Lofgren, 1998; Horstmann and McLachlan, 1998), the impacting surface of the PEM mimic the natural material at the interface between air and soil, largely reducing measurement artifacts. Finally, the PEM resolve also the downward export and it is suitable for process oriented investigations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2013.06.020>.

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