

Elevated Mobility of Persistent Organic Pollutants in the Soil of a Tropical Rainforest

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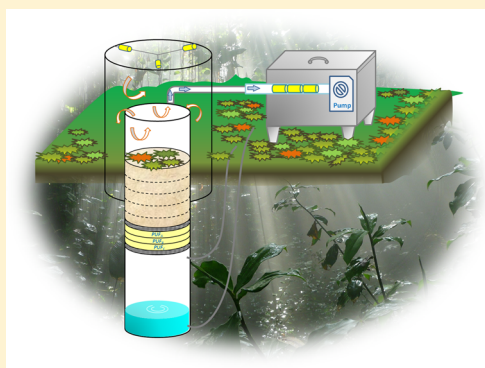
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Supporting Information

ABSTRACT: Semivolatile persistent organic pollutants (POP) are bioaccumulative and toxic contaminants. Their global distribution depends on source distribution, atmospheric transport, degradation, and the exchange with ocean and land surfaces. Forests are crucial terrestrial reservoirs due to the commonly envisaged high capacity of their surface soils to store and immobilize airborne contaminants bound to soil organic matter. Our results show that POPs can be unexpectedly mobile in the soil of a tropical rainforest due to fast litter turnover (leading to rapid POP transfer to the subsoil) and leaching rates exceeding degradation rates especially for more hydrophobic congeners. Co-transport in association with leaching fine particulate and dissolved organic matter appears as a relevant driver of this PCB export. A markedly different distribution pattern is displayed in this soil in comparison to soils of colder environments with lower overall storage capacity. These findings show that biogeochemistry of organic matter degradation and weathering can influence POP soil fate. Because tropical forests represent 60% of the global terrestrial productivity, the highlighted dynamics might have an implication for the general distribution of these contaminants.



Persistent organic pollutants (POPs) are globally distributed pollutants recalcitrant to degradation and with elevated affinity for the organic matrix, including biota. Following emission to the atmosphere, POPs undergo long-range transport engaging in continuous temperature-dependent deposition and revolatilization processes with the different environmental media.¹ POPs are efficiently accumulated by organic carbon (OC)-rich reservoirs such as soils and sediments. In these compartments, they can persist during many decades undergoing very slow degradation processes.²

Forest soils are important reservoirs of POPs emitted in the past decades. Primary net production in forest canopies efficiently scavenge airborne hydrophobic pollutants and deliver them to soil mainly through litter fall.^{3–6} Soil organic matter serves as a long-term reservoir or even as a definitive sink, dynamically controlling the atmospheric pool and ultimately delaying long-range atmospheric transport.⁷ A number of studies conducted in temperate and boreal environments have shown that POPs are very stable in undisturbed soils, and their largest pool is associated with litter and organic top layers at the interface with the atmosphere.^{2,5,6,8–10} High affinity of POPs

for the slow-degrading pool of OC, high-retention capacity, and degradation half-lives in soil in the range of several years to several decades, underpin the long residence time of POPs in these soils.¹¹

Available information on POP fate in soils almost entirely derives from studies conducted in boreal or temperate ecosystems. Data from tropical or subtropical soils are notably lacking in the literature, even though over 60% of global terrestrial productivity and a considerable fraction of the terrestrial pool of organic matter are in these environments.¹²

Tropical rainforests are characterized by rapid turnover of organic matter, intense precipitation, high temperatures, and low capacity of soils to retain nutrients and organic matter. Organic matter is lost by these soils through runoff and leaching in both the particulate and dissolved form.¹³ Studying the fate of contaminants under these markedly different

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conditions is therefore needed to improve our knowledge of the processes controlling the coupling between contaminant and organic matter fate.¹⁴

We focused here on the experimental assessment of the dynamics controlling POP fate in a tropical rainforest soil. We spiked in situ a set of polychlorinated biphenyls (PCBs) labeled with ¹³C stable isotope to the fresh litter matrix above structured soil cores of a primary rainforest and follow their distribution over one year to experimentally determine the influence of different fate process rates and compare POP vertical distribution and storage capacity with those of soils from colder environments.

■ EXPERIMENTAL SECTION

Field Site and Soil Characteristics. The experiment was carried out in a primary tropical rainforest at Jianfengling (Hainan Island, South China (18°44' N, 108°50' E)). Climate is controlled by the tropical monsoon regime. Average temperature, relative humidity, and yearly precipitation are 19.8 °C, 88%, and 2449 mm, respectively, and 80–90% of the rainfall is mainly concentrated between May and October.¹⁵

The soil studied here was an Oxisol, typical of tropical rainforests. These soils develop under relatively intensive weathering and leaching conditions and are characterized by the lack of a defined horizon structure with OC fractions typically being in the range of 1–2% homogeneously distributed along depth.¹³ A full description and characterization of the soil properties for this site is presented elsewhere.^{16,17}

Lysimeters. Lysimeters have been extensively and successfully used for studying mobility and persistence of other type of contaminants in soils throughout the world, including tropical soils (e.g., ref 18). Three relatively undisturbed soil cores (namely, C1, C2, and C3) were collected by introducing metal cylinders (i.d. 15 cm) at a depth >10 cm into the forest floor. The cores were extracted by removing the soil surrounding the cylinder and carefully inserting a metal blade at its base. The 10 cm deep cores were then individually placed into special metal frames (stainless steel 304) supporting (at the base of the core) three polyurethane foam disks (PUF_A, PUF_B, and PUF_C, from top to bottom) piled between two metal nets (1 mm mesh; Figure S1, Supporting Information (SI)).

The frames with the soil cores and the PUFs were then inserted into respective three lysimeters (Lysimeter 1, 2, and 3) created using 80 cm long metal (stainless steel 304) cylinders (i.d. 14.5 cm) closed at the base, as described in Figure S1 (SI). Below the frames supporting the cores and the PUFs, a basal reservoir collecting leaching water was included with the necessary piping (in polytetrafluoroethylene, PTFE) and hoses to allow equilibration of the pressure in the reservoir with atmospheric pressure and collection of the leachate. The three PUFs piled at the bottom of the soil core were included to extract labeled PCBs from the leaching water. PUF is a reliable sorbent to extract truly dissolved hydrophobic compounds from water;¹⁹ however, it is not suitable to quantitatively trap particulate and dissolved organic matter which is expected to carry a significant pool of the leaching PCBs.^{20,21} Organic matter is lost in heavily weathered tropical soils both in the dissolved form and as fine particulate.²² To keep track of the total leaching flux, we periodically quantitatively collected and analyzed the leachate from the reservoir, assuming that the fraction of labeled PCBs detected in this compartment was primarily that co-transported in association to leaching fine

particulate and dissolved organic matter. The lysimeters were finally placed back in situ, as shown in Figure S1, SI.

Native forest litter was collected and spiked with 30 ng (of individual congeners) for every 20 g of litter using a mixture of isotopically labeled PCBs (EC-4058, Cambridge Isotope Laboratories, Tewksbury, MA, containing ¹³C-labeled PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180, and PCB-209) diluted in 10 mL toluene, as described elsewhere.^{23,24} Then, 20 g of litter (entire leaves) were added to the top of the soil core in each lysimeter. The representativeness of the behavior of labeled compounds added in this way compared to that of native contaminants associated with litter was analyzed in detail and demonstrated in a previous study.²⁴ The mass of labeled PCBs measured at Day 0 in the litter (24 h after spiking) was used as reference for the mass budget assessment (more details on spiking performance are reported in Text S3, SI).

A larger metal (stainless steel 304) cylinder (i.d. 25 cm, open at both sides) was deployed concentrically to the lysimeter (Figure S1, SI) to further reduce the possibility of wind entrainment of the spiked litter and lower the risk for uncontrolled losses. Such an aerodynamic “protection” was also used to optimize conditions for the implementation of low-volume active air sampling at the core head (Figure S1, SI) to trap potential volatilization.

Sampling from the Lysimeters. The three lysimeters were deployed on November 18, 2008. Following a procedure optimized in earlier studies^{24,25} an aliquote of the spiked litter sample from each lysimeter was collected using metal tweezers 24 h after the deployment to determine the initial mass of the labeled PCBs present in the litter at the beginning of the experiment.

Sequential destructive sampling from individual lysimeters was carried out along one year time. Lysimeters 1, 2, and 3 were sampled after 120 days (t_{120}), 270 days (t_{270}), and 360 days (t_{360}), respectively, to capture the progression of translocation and loss processes of the labeled compounds. In particular, the following pools and cumulative fluxes of labeled PCBs were monitored over time:

Potential Volatilization (U_{vol} , ng). To preserve high levels of environmental realism with regard to the influence of litter fall, wet deposition, gaseous exchange, and latent and sensible heat exchange controlling biogeochemical processing in the soil core, the assessment of the volatilization flux was conducted using an open-system approach. Volatilization measurements under realistic environmental conditions are a real challenge in POP research.^{24,26–29} Such an assessment is normally performed through coupling of concentration measurements and modeling which provides flux estimates with a level of uncertainty hardly quantifiable and therefore insufficient for the scopes of this study. The method adopted here to track potential volatilization is deliberately semiquantitative and include a set of ancillary measurements and a thorough analysis of uncertainty to demonstrate confidence boundaries of the volatilization estimates which are suitable for the scopes of the mass budget conducted to determine fate process rates.

In practice, a low-volume active air sampler (AAS) deployed in proximity to the head of the soil core was used to trap losses of labeled PCBs from the head of the lysimeter. For PCBs, these are expected to occur mainly through degassing; however, aerosol formation (e.g., due to wind erosion or impacting rain drops entraining small fragment of spiked litter

and soil), can, in principle, contribute to headspace losses. For this reason, it is appropriate to adopt the definition of potential volatilization when referring to the volatilization losses measured here.

The sampling system and approach is described in details in Text S1 (SI). The gentle suction applied in the proximity of the soil core top (Figure S1, SI) produced a regime in which renewal of the air over the lysimeter was controlled by the sampling during most of the time with sporadic events in which air renewal was instead controlled by turbulent eddies propagating from the canopy boundary layer especially during stormy episodes. In this case, turbulent eddies can drive volatilized labeled compounds to escape from the AAS. To monitor for the occurrence of such an event, we deployed three small PUF sorbent (7 cm long, 2.5 cm diameter) at the level of the external cylinder opening (30 cm above the litter, and about 25 cm above the AAS inlet) as passive air samplers to capture the signal of volatilized compounds that “escaped” AAS. The cumulative projected surface of the small passive samplers was only 20% of the total lysimeter opening area. Diffusion in the horizontal plane and through the laminar boundary layer surrounding the passive samplers can be much smaller than the vertical advective component driving volatilized contaminants to escape AAS. This prevents any possibility of quantifying the losses based on the contaminant masses accumulated by the small passive samplers at the lysimeter head. To fully acknowledge such a confounding factor, we included a uniformly distributed random factor q ranging across 2 orders of magnitude (namely, 0.01–1) in the mass balance model as described in Text S4 (SI) to be simultaneously estimated by the Markov Chain Monte Carlo (MCMC) frame described below with other process rates and correct volatilization rate for sampling artifacts.

There is no claim here that the measured volatilization flux directly reflects the on-site volatilization of native PCBs. As previously discussed, other processes might have influenced the losses from the head of the lysimeter, and the geometry of the parts of the cylinders exceeding the ground level may have affected soil boundary layer dynamics. On the other hand, very high variability of volatilization fluxes can be expected when measurements are performed at such small spatial scales due to stochasticity of soil characteristics and surface roughness elements distribution. The measurement performed here can therefore be regarded as an assessment of a pseudo- or potential revolatilization from the litter–soil system. Active and passive mini-PUFs from all the lysimeters were collected at each sampling time. The three mini-PUFs used in the active sampler were analyzed individually. New pre-extracted active and passive mini-PUFs were deployed in the air sampler and lysimeters and sampling continued during the following period.

PCB Mass in Litter (U_{litter}). The spiked litter from lysimeters 1, 2, and 3 was collected at t_{120} , t_{270} , and t_{360} , respectively, using tweezers and spoons, placed in aluminum foil bags, sealed in plastic bags, frozen, and immediately transported to the laboratory for analysis.

PCB Mass in Soil Core (U_{SC}). Consistent with the litter sampling, cores C1, C2, and C3 were sampled at t_{120} , t_{270} and t_{360} , respectively. At the appropriated time, each core was carefully removed from the respective lysimeter and placed on a clean pallet. The soil core was carefully sliced using a metal knife into 5 layers of ~ 2 cm thickness (namely, from top to bottom, layers A, B, C, D, and E) directly at the field site.

Chemical analysis was conducted separately on each individual layer.

Leaching (U_{leach}). The three PUF disks (PUF_A, PUF_B, and PUF_C) deployed at the base of the soil cores were retrieved consistently to their relative core, transported to the laboratory folded in aluminum foil and plastic bags and analyzed individually. During each sampling period, the leaching reservoir was emptied regularly or immediately after intense precipitation events using a peristaltic pump equipped with PTFE piping and fittings. In addition, to recover residual particles, we wiped the reservoir with glass fiber sheets at the moment of the destructive sampling of the soil core. The leachate was transferred into clean amber glass bottles cooled and transported to laboratory. Particles were separated by filtration through a glass fiber membrane (GF/F, 14.2 cm diameter). Particulate and dissolved phase were analyzed separately, as described in Text S2 (SI).

Determination of Fate Process Rates. Optimization of process parameters was performed by applying a MCMC simulation (Texts S4 and S5, SI, for methodological details) to estimate posterior distributions of the process rates in a set of equations dynamically describing the mass balance of labeled POPs in the litter–soil system. For a formal description of the frame, we remand to Text S4 (SI). The framework simultaneously searches for values of rates of volatilization, leaching, litter-to-soil transfer, degradation and the volatilization uncertainty factor q which minimize the squared deviation between modeled and time-dependent observed results of volatilization, leaching, and evolution of PCB masses in litter and soil.

Chemical Analysis and QA/QC. Details of the analytical method and quality assurance and control are reported in Text S2 (SI). In summary, 7 ¹³C-PCB congeners were analyzed in all samples, while a set of 27 native PCBs were measured in the litter, soil core, and leachate samples.

Statistical Methods. Statistical methods are described in Text S5 (SI).

RESULTS

Distribution of Labeled PCB in the Soil Core. The distribution of the labeled PCBs among different phases varied depending on both compound and time, usually with the litter and soil core being the phases containing the highest fractions (Figure 1 and Table S1, SI). A steady decline of all labeled PCBs from the litter was observed with similar dissipation rates for all congeners and half-lives in the range of only 110–150 days. At the first sampling period (day 120), the increase of labeled PCBs in the upper soil layer accounted for about 62 and 87% of the labeled compound mass lost from the litter (Figure 1 and Table S1, SI). The remaining losses from the litter were primarily due to volatilization, and (to a much lower extent) leaching and degradation. At this stage (day 120), about 50% of the total labeled PCBs that had migrated to the soil core were found in the top 2 cm (Figure 1 and Table S1, SI). During the same stage, traces of all labeled PCBs could be detected in all layers of the soil core (down to a depth of 10 cm; Figure S2 and Table S1, SI), demonstrating an unexpectedly rapid mobility of these persistent hydrophobic contaminants in the soil of the rainforest. During the subsequent stages (day 270 and day 360) the mass of all labeled POPs progressively tended toward a homogeneous distribution with depth, which was influenced by the distribution of soil OC (Figures S2 and S3, SI). At days 120

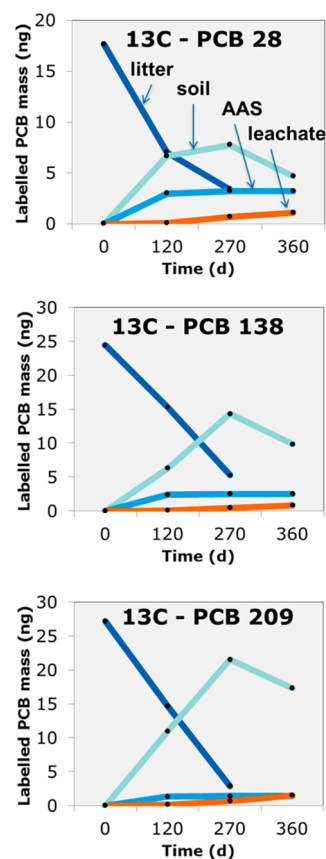


Figure 1. Time trends of PCB masses measured in litter, the whole soil core, and cumulative masses in the active air sampler (AAS) and leaching samples for three representative congeners. The lack of observation in litter at day 360 is due to a field accident resulting in the loss of the sample.

and 270, in fact, no significant relation was found between ^{13}C POPs and soil organic matter vertical distribution. At the end of the experiment (day 360), however, a significant ($P < 0.05$) positive relationship with soil OC was established for all congeners (Figure S3, SI). In summary, the spiked labeled POPs underwent a relatively rapid net downward displacement, resulting (in a time frame less than 1 year) in a distribution influenced by the horizon-specific OC content. Such a distribution was consistent with that observed for the native (C12) PCBs measured in the soil core (Figure S3, SI). The slope of the linear regression curve was higher than 1 (1.2–1.8) for the labeled congeners and lower than 1 (0.4–0.6) for the native congeners. Similarly, the intercept of the regression line of the labeled compounds was always negative, while it tended to be 0 for the native ones.

Leaching Fluxes. Data on leaching from the base of the soil core into the polyurethane foam (PUF) traps (capturing the POP dissolved component) and directly by leachate analysis (assumedly mainly accounting for the leaching particulate and dissolved organic matter fraction) (Figure S1, SI) confirmed the occurrence of elevated vertical mobility of POPs in this soil. A small fraction of the initial mass of the labeled POPs (0.3–0.5%, depending on compound) was lost by leaching from the bottom of the soil core after only 120 days (Table S1, SI).

The total leaching flux was at a maximum between day 120 and 270 coinciding with the rain season. This trend was consistent between artificially added labeled and native

contaminants ($P < 0.05$) (Figure S4, SI). Also, in terms of absolute losses, at the end of the study (day 360), the cumulative amount lost by leaching was typically between 1 and 3.4% of the total mass of contaminants present in litter and soil at day 120, for both native and labeled congeners. Interestingly, the more hydrophobic congeners were those experiencing the highest leaching fluxes (Figure S5, SI). In particular, the extremely hydrophobic PCB 209 was the congener displaying the highest cumulative leaching flux at the end of the study. The highest fraction of the leaching POPs was trapped by the PUFs; however, the fraction of PCBs detected in the leachate (in association to particulate and dissolved organic matter phase) was relevant (between 18 and 29% of the total leached mass, depending on congener) with the particulate associated fraction representing around 10% for the lighter congeners and 20% for the heavier ones (Table S1a,b and Figure S4b, SI). These data suggests that the dissolved organic matter and in particular the leaching particles can have played a role in enhancing the leaching of the highly hydrophobic congeners compared to more soluble congeners. It must, however, be acknowledged that the PCB phase distribution in the leaching assessed here might be sensitive to artifacts caused by the possible trapping of part of the leaching particles and dissolved organic matter by the basal PUFs. As a consequence, leachate analysis results might underestimate the real dimension of the particulate and dissolved organic matter-bound PCB export.

Potential Volatilization. The AAS used to gently sample air in proximity of the core surface, sequestered a total of ~ 16 ng of the labeled congeners during the first 120 days of the study. Traces of the labeled POPs (86 pg, sum of labeled POPs) detected by the small passive traps deployed a few cm above the AAS inlet (Figure S1, SI), demonstrates however that a fraction of the total volatilization escaped AAS (Figure S6, SI). We fully considered this source of uncertainty when setting constraints for the estimation of the process rates in the mass balance model (Text S4, SI). Resulting volatilization rate estimates ranged over 1 order of magnitude following a log-normal distribution. These results confirm that the method was sufficiently accurate to capture (within 95% credibility intervals) the order of magnitude of the real PCB loss from the headspace. Estimated total potential volatilization (over 1 year) represented about 5 and 60% of the initially added mass (depending on compound and considering lower and upper boundaries; Table S1, SI). The expected pattern with volatile compounds (tri- and tetra- chlorinated biphenyls) experiencing highest losses was highlighted by the data (Table S1, SI). Potential volatilization losses were concentrated during the first 4 months of the study. In this period, we observed between 93 and 96% (depending on compound) of the total potential volatilization of labeled congeners over the full year of the experiment (Table S1, SI). This is an expected behavior because, during the first phase of the study, the bulk of the contaminant was associated with forest litter at the soil surface and therefore was readily available for engaging in diffusive exchange with the atmosphere.

Estimates of Fate Process Rates. Quality of process rate estimates and their distribution are depicted in Figure 2 (summary data are provided in Table S2, SI). Potential volatilization was the process with the fastest rate, determining an average loss of POPs from the system with half-lives ranging from 169 to 315 days. The median of potential volatilization rate estimates were not dependent on compound octanol-air equilibrium partitioning coefficients (K_{oa}). In contrast, the

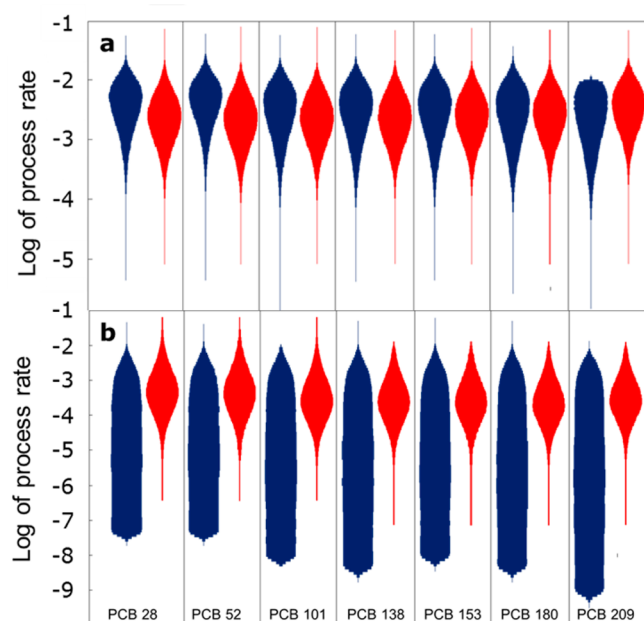


Figure 2. Violin distribution plots comparing the distribution of estimated process rates from the Bayesian framework. (a, blue) Volatilization and (red) litter–soil transfer; (b, blue) degradation and (red) leaching. The width of the violin plot along the *x* axis is proportional to the likelihood of the parameter value scoring on the *y* axis. Rates are expressed in d^{-1} .

pattern of PCBs observed in the small passive samplers deployed at the head of the lysimeter to trap volatilization escaping AAS, showed a very different behavior, with the level of the lighter congeners exceeding by more than 1 order of magnitude those of heavier ones. This result suggests that the AAS might have recorded the influence of other processes rather than pure degassing, including, for example, losses associated with aerosol formation in proximity to the soil surface, which could have actually enhanced the losses of less volatile congeners.³⁰

Export from litter to soil was also a rapid process (half-lives ranging from 272 to 337 days) and was independent of compound properties. Leaching occurred with rates about 1 order of magnitude lower than volatilization. Rates of more soluble congeners were only a factor of 2 higher compared to those of highly hydrophobic substances.

Using the mass budget model presented in Text S4 (SI), we could generate estimates for degradation rates. Degradation was by far the slowest process. The uncertainty in air measurements had a strong influence in determining very broad credibility boundaries of degradation rates. Degradation rates estimates ranged several orders of magnitude but were confined in the domain of the infinitely small. As a result, we could only provide useful information on the lower boundary of degradation half-lives, estimated to be >3 and >6 years for low- and high-chlorinated PCB congeners, respectively.

DISCUSSION

Evidence of a relatively high mobility of POPs in the soil of the tropical rain forest emerges from the data. The pattern of vertical distribution influenced by the OC content for both labeled and native compounds and the consistent trends and magnitude of leaching fluxes suggest that a hypothetical higher mobility of labeled compounds compared to native homologues

could have only a minor influence on our results and confirms previous findings on the robustness of the adopted experimental approach.^{24,25}

An important and so far understudied mechanism controlling POP fate in forest soils is the coupled incorporation of contaminants and litter organic matter into the top soil. Previous studies in boreal and temperate environments evidenced high stability of POPs in litter and a very tight association to the OC-rich superficial horizons in structured soils.^{2,5,6,31} The conditions of tropical rainforests with highly weathered soils, characterized by poor retention capacity for organic matter and other nutrients, resulted in a very different fate of POPs. The downward export of POPs from litter to top soil occurred with rates comparable to those observed for volatilization (Figure 2 and Table S2, SI) and was similar across all congeners. Such a compound-independent process appears to be under the control of the biogeochemistry of litter degradation. Studies conducted in rainforest stands of southern China (including this same site) gave litter degradation rates ranging between 0.0036 day^{-1} (half-life ($t^{1/2}$) = 190 days) and 0.0049 day^{-1} ($t^{1/2}$ = 141 days),^{32–34} consistent with the rates of the litter–soil transfer measured here (Table S2, SI). On the top of the soil core, litter is decomposed by leaching (water driven transfers of soluble materials including minerals and organic matter into the soil matrix), fragmentation (by soil animals breaking large pieces of organic matter), and chemical alteration of organic matter as a consequence of the activity of bacteria and fungi. Such a process proceeds until degraded litter structures become undistinguishable from that of the underlying soil core.¹³ This results in a net loss of litter dry mass with environmental conditions controlling the aforementioned degradation processes.¹³ In boreal and temperate environments, litter may take several decades to “become” soil, while in tropical rainforests, this typically occurs within the course of a single year. Unlike boreal and temperate stands, there typically is no multiannual accumulation of litter above the rainforest soil. Litter mass is lost essentially due to mineralization and leaching; however, the associated POPs are subject to a different fate. Because they are recalcitrant to degradation, they are either mainly incorporated to the top soil core or lost by volatilization. In this experiment, effective incorporation from litter into soil is demonstrated by the parallel rapid POP enrichment of the upper soil layer observed at day 120 (Figure 1 and Table S1, SI). An important implication of such a rapid incorporation is that POPs transferred to the soil core become rapidly buried by fresh litter fall and therefore are segregated from direct contact with free-air above the soil surface. If on one side the rapid turnover of litter on the soil surface prevents multiannual accumulation, on the other side litter production in tropical rain forest is very high.¹³ The rapid renewal of the litter layer and the fast vertical translocation of POPs in the soil core provides a strong kinetic limitation to the gaseous exchange, preventing further revolatilization of the contaminants from taking place. Nearly all the volatilization of labeled POPs, in fact, occurred during the first 120 days of the experiment (Table S1, SI). In contrast, systems (such as boreal and temperate forests) where contaminants accumulate and persist during several years in the litter at the interface with the atmosphere, shifts in temperature and atmospheric levels can drive to re-emission to air of previously deposited contaminants, during longer time.

After being incorporated into the top soil layer, the labeled contaminants underwent redistribution, resulting in the time

frame of 1 year in a vertical profile partially influenced by the thermodynamics of hydrophobic interactions with soil organic matter. This is supported by the linear relationship between both labeled and native PCBs established with soil OC content. The different slopes of such a relationship observed for the labeled congeners, however, show that elevated mobility of PCBs within the soil core can significantly influence such a relationship. Differences in slopes and intercepts between labeled and native congeners are likely related to the different conditions in which the two classes of compounds were added to the litter-core system. The mass balance of native compounds may in fact be approximated to a system at the steady state because native contaminants were already present in the soil core before the beginning of the experiment and are added continuously to the top of the soil core by atmospheric depositions. In contrast, labeled compounds were added in a single spike event configuring a highly unsteady system. In simplistic qualitative terms, one can imagine that due to the lack of reiterated inputs capable of replenish losses, labeled congeners are more rapidly depleted from soil layers with lower OC content compared to layers with higher OC content, resulting in a steeper slope and negative intercept. The change in distribution of PCB 209 in the soil core between t_{270} and t_{360} , for example, appears to be consistent with this mechanism (Figure S2, SI). Furthermore, such an elevated mobility may be at the base of the lower dependence of PCB distribution on soil organic carbon observed in previous studies for lower latitude soils and never fully elucidated, so far.^{35,36}

Leaching (both in association to the truly dissolved phase and in particular to the leaching of both fine particulate and dissolved organic matter phase) appears to play an important role in influencing the fate of POPs in the rainforest soil. The crucial role of organic matter efflux is supported by a range of evidence: (1) the total leaching flux increased with compound hydrophobicity,³⁰ (2) leaching rates were relatively similar for compounds with different K_{ow} , and (3) a considerable fraction of the leaching of more hydrophobic PCBs was found to occur in association with leaching particulate and dissolved organic matter. Such a behavior is not surprising. The efflux of leaching organic matter from tropical rainforest top soil in fact represents a crucial process controlling soil OC mass balance,³⁷ therefore likely affecting capacity for accumulating hydrophobic contaminants, too.

Microbial activity in tropical environments is enhanced by the conditions of high temperature and high humidity. It can be hypothesized that these conditions may also enhance POP degradation. To the authors' knowledge, the data presented here are the first experimentally derived estimates of degradation half-lives of PCBs in the soil of a tropical rainforest. Our approach could only provide useful information on the lower boundary of the degradation half-lives. Obtained values for tri- to hepta-CBs (derived here considering the upper 85th percentile of estimated degradation rates (Table S2, SI)) are consistent with previously proposed data on soil degradation³⁸ obtained from observations performed in colder environments (e.g., ref 5). The conditions of the tropical rainforest therefore did not appear to significantly boost degradation of the contaminants in our samples. Such a conclusion however must be taken cautiously since it is sensitive to the large uncertainties affecting both degradation rate estimates reported here and those reported in the literature.

Leaching rates from the top 10 cm of the soil core were significantly ($P < 0.05$) higher than estimated degradation rates, especially for the more hydrophobic substances (Figure S5, SI). Such a situation is of concern because it represents a risk for leaching to groundwater, the occurrence of which was previously tuned-down for these hydrophobic contaminants in forest soils.⁵ Available data on currently used pesticide fate from lysimeter studies also suggested a higher potential for leaching of these more hydrophilic substances in tropical soils compared to other type of soils.¹⁸

Accumulation of "Native" Airborne POPs in Tropical vs Boreal Soils. The process dynamics elucidated here through the use of artificially added labeled contaminants have a major influence on the vertical distribution of "native" airborne POPs in the soil core and on the bulk capacity of soil to accumulate them. Figure 3 shows the typical vertical

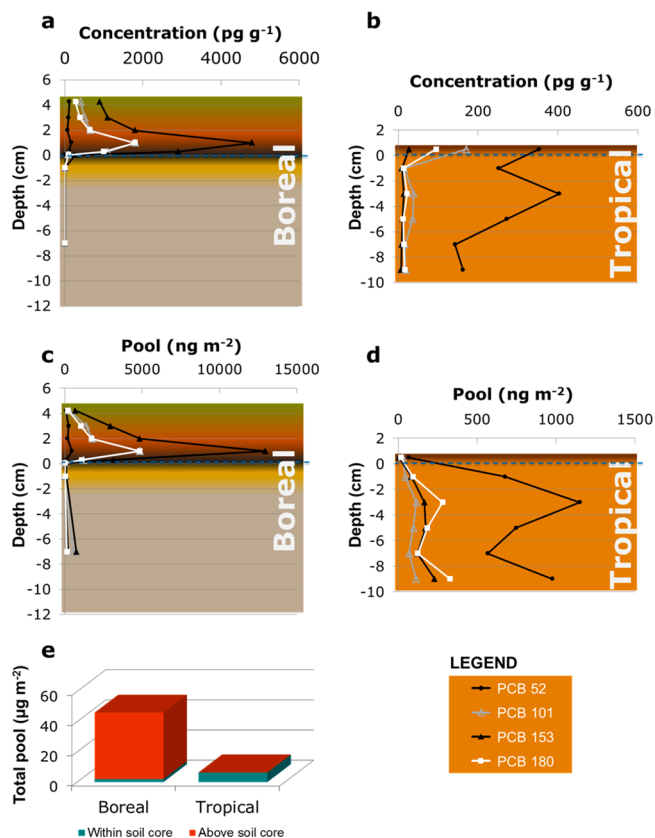


Figure 3. Vertical distribution of (a) concentration and (c) pools of selected representative "native" PCBs in the undisturbed soil core of a boreal forest⁵ in comparison with (b) mean concentrations and (e) mean pools observed in the analyzed tropical soil cores used in this study (Table S3, SI). (e) Total pool (sum of selected congeners) in the upper 10 cm soil core and litter. The rapid turnover of organic matter at the surface of the tropical soil prevent the building of capacity to store pollutants at the interface with the atmosphere. As a result, contaminants are transported more efficiently at a deeper level in soil by leaching of organic matter.

distribution of selected representative native PCBs in the soil of a boreal forest in comparison to that observed here in the tropical rainforest. Data on boreal soil contamination were taken from Moeckel et al.⁵ The POP contamination profile in the boreal forest soil core presented in this study is representative of the general distribution pattern of soils observed in other studies from both boreal and temperate

environments.^{2,6} Similar to the tropical forest sampled here, the boreal forest in reference 5 is located in a semirural region exposed to background contamination levels from long-range atmospheric transport; therefore, differences in soil contamination can only to a small extent be related to differences in atmospheric inputs. This assumption is substantiated by available data from these sites (or nearby locations) displaying atmospheric concentrations of individual congeners differing maximum by a factor of 2 between the two sites.^{39,40} Data from these studies were generated using the same technique (PUF-based passive air samples with integration time of 40 and 60 days), and samples were analyzed by the same laboratory. As shown in Figure 3a,c, the litter and organic horizons (O-horizons) of the boreal forest display a high storage capacity to retain POPs. Soil organic matter constitutes the bulk capacity for the accumulation of POPs in soils.³⁵ Large O-horizon PCB pools in the boreal forest can only be explained as the results of several years of cumulative depositions demonstrating the very high stability of POPs in the soil of this environment. Cesium-based soil core dating confirmed that the humus layer of this boreal forest is constituted by organic matter deposited during the 1980s.⁵ A considerable fraction of the PCB deposition occurred during the last 30 years are therefore still found at this level.⁵ The total pool of the four representative PCBs shown in Figure 3c in the top 12 cm of the boreal forest soil was about $46 \mu\text{g m}^{-2}$ (Figure 3e). In contrast, the pool in the tropical forest was about 1 order of magnitude lower ($6.5 \mu\text{g m}^{-2}$). Differences in soil temperatures of up to 20°C between the two systems may have a substantial role in determining this variability; however, the markedly different vertical distribution in the two soil cores highlights the fundamental role of biogeochemical controls. About 96% of the PCB pool in the boreal forest ground was present above the mineral soil ("O" level, Figure 3c), in association with the humus and litter layer. In contrast, in the tropical forest, only 2% of the pool was associated with the litter while stored amounts tended to be higher deeper in the soil core (Figure 3d). The set of process rates estimated above, in particular, litter–soil transfer rates similar to volatilization rates, and leaching rates higher than degradation rates for all congeners can explain such a behavior. In the tropical rainforest, the fast turnover of organic matter and heavy weathering prevents the formation of an OC-rich horizon at the top of the soil with high capacity for storing POPs. Despite high productivity, the pool of organic matter reaching the soil through litter fall undergoes rapid degradation and is efficiently incorporated into soil through leaching. This rapidly draws down associated POPs.

Differences in turnover of the labile organic matter pool appear to underpin the variability in POP accumulation pattern observed between soils from different climates. The dynamics highlighted here shed light on processes that are not fully included in the current conceptual frame of global POP fate and distribution. Because tropical environments encompass over 60% of the terrestrial primary production, the implications of these findings may be relevant to our general understanding of current and future POP global distribution.

■ ASSOCIATED CONTENT

■ Supporting Information

Fully detailed data sets of labeled and native PCBs, ancillary data, and estimated process rates; information on chemical analysis and statistical methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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