Development of a Soil Fugacity Sampler for Determination of Air−Soil Partitioning of Persistent Organic Pollutants under Field Controlled Conditions

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Soils are the main reservoir of persistent organic pollutants (POPs) and thus air−soil exchange and partitioning are key processes controlling the fate and transport of POPs at regional and global scales. To date, soil fugacity has been estimated from models of the soil−air partition coefficients, with the associated unavoidable uncertainties; or by experimental procedures in the laboratory with uncertain application in field conditions. The development of an operational soil fugacity sampler is presented here; one which ensures optimal field data of the POP fugacity in soil and environmentally relevant surface (soil+grass, etc.) and therefore ensuring accurate soil−air partition coefficients and surface−air fugacity gradients. The sampler flow rate is optimized, sampler reproducibility is assessed, and equilibrium between the gas and soil concentrations of polychlorinated biphenyls and polycyclic aromatic hydrocarbons is demonstrated. The development and comprehensive validation of a soil fugacity sampler opens the door for the first time to field studies that accurately determine the variables driving the soil−air partitioning and fluxes of POPs.

1. Introduction

Quantification of diffuse sources and atmospheric deposition of persistent organic pollutants (POPs) along with the understanding of the variables governing these processes are important issues and need to be taken into consideration to understand the occurrence, long-range transport, and impact of POPs (*1*). Soil is the main reservoir of POPs globally (*2−4*) and the long-term sinks and environmental occurrence trends depend on atmosphere−soil partition and exchanges. There are several processes for the exchange of POPs between the atmosphere and soil (*5*). Dry deposition of aerosol-bound POPs and wet deposition of POPs onto soils have received significant attention (*6−8*). However, diffusive air−soil exchange of organic pollutants has received much less attention due to lack of appropriate methodologies for the determination of air−soil partition constants and fugacity gradients.

Field determinations of partition coefficients of POPs have seldom been assessed previously and were done only for a few chemicals such as organochlorine pesticides (*2*, *9*). Currently, the understanding of air−soil partitioning and

exchange of POPs, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), is limited by the lack of a robust and reproducible method for their measurement in field conditions. These limitations result in important uncertainties in current predictions of fate and transport of pollutants in the biosphere, and thus their risk assessment.

Soil fugacities have previously been determined in the laboratory by stripping soils with air, though with results of difficult extrapolation to field conditions, due to the impossibility of determining the extent of the layer of surface soil in contact with the atmosphere, and the dependence of fugacity on environmental conditions (temperature, relative humidity). The few previous attemps to measure soil−air partitioning and fluxes in field conditions are the studies performed by Jones, Bidleman, and co-workers (*2*, *9*, *10*). Indeed, the use of simultaneous measurements of POP concentrations at different heights and meteorological conditions allows for estimated air−soil exchange fluxes and thus the gradient in fugacities. While it may be appropriate to estimate fluxes providing the concurrent meteorological information is available, it is not clear that air−soil partition can be assessed because the gas phase concentrations determined close to the soil may not be equilibrated with the soil surface and thus are not a "true" measure of soil fugacity. In this sense, the development and validation of a sampling methodology of soil fugacity is required to understand and quantify the mechanisms involved in air−soil exchange and partition of POPs.

The purpose of this paper is to (i) develop a sampling procedure to determine air−soil partitioning and fugacity gradients of POPs and (ii) validate the procedure for field conditions including the evaluation of the equilibrium between the soil and gas phase concentrations, the reproducibility of the sampling device, and evaluation and minimization of all potential sampling artifacts. The system is applied to the study of air−soil partitioning and fugacity gradients of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

2. Materials and Methods

2.1. Sampler Development and Theoretical Background.
Soil Fugacity and Soil−Air Partitioning. Fugacity is a measure of the tendency of a chemical to escape from its medium (*11*). For a gas-phase POP, its fugacity (f_G, pa) is given by

$$f_G = 10^{-9} C_G RT / M_W \tag{1}$$

where R is the universal gas constant (Pa m^3 K^{-1} mol^{-1}), M_W is the POP molecular weight (g mol^{-1}), T is the temperature (K), and C_G is the gas phase concentration (ng m^{-3}). POP fugacity in soil (f_S, pa) is given by:

$$f_S = 10^{-3} C_S RT / (K_{SA} \times M_W) \tag{2}$$

where C_S is the POP concentration in soil (ng g^{-1}), and K_{SA} is the soil−air partition coefficient at equilibrium (L kg^{-1}), which is given by

$$K_{SA} = C_{S,eq} / C_{G,eq} \tag{3}$$

where $C_{S,eq}$ and $C_{G,eq}$ are the POP soil and gas phase concentrations at equilibrium. Therefore, when the POP fugacity is the same in the two phases, POP soil fugacity can be viewed, as the gas phase concentration equilibrated with the soil; this is the operational principle used to measure the

soil fugacity. Fugacity and concentrations are proportional to each other (linearly), where the proportion is the soil or gas fugacity capacity (see eqs 1 and 2). In most modeling studies, f_S is predicted from C_S using available models for the value of K_{SA} (12, 13). One of these models is that suggested by Finizio et al. (13, 14).

$$\text{predicted } K_{SA} = 1.5 f_{OC} (\xi_{oct}/\xi_{OM})(MW_{oct}/MW\delta_{oct}) K_{OA} \tag{4}$$

where f_{OC} is the fraction of organic carbon in soil ($g_{OC}\,g_{Soil}^{-1}$), and ζ_{oct} and ζ_{OM} are the activity coefficients in octanol and organic matter, respectively. MW_{oct} and MW_{OM} are the molecular weight of octanol and organic matter; δ_{oct} is the density of octanol ($kg\,L_{Oct}^{-1}$) and K_{OA} is the octanol–air partition coefficient ($L_{Oct}\,L_A^{-1}$); 1.5 is the conversion from organic matter to organic carbon. The units of the predicted K_{SA} are the same as those of the K_{SA} shown in eqs 2 and 3. These estimations are limited by uncertainties in the knowledge of several of these parameters and the appropriateness of octanol as a surrogate for organic matter sorbing phase.

If a robust method is developed for measuring soil fugacity of POPs, which is the gas phase POP concentration equilibrated with the soil, then it will be possible to directly determine K_{SA} as the ratio of measured POP concentrations in the soil and gas phases, and inferences on the values of activity coefficients and other parameters appearing in eq 4, or other models, will be obtained. However, such a soil fugacity sampler should provide reproducible results and gas phase concentrations of POPs in equilibrium with the surface soil.

Air Sampler Design. To measure the soil fugacity, the sampled gas phase must have been in contact with the soil for sufficient time to equilibrate. A chamber located above the soil that forces air to have a laminated flow parallel to the soil surface has been used previously for sampling air in contact with soil surface (2). However, these authors recognized that equilibration between air and soil could not have been achieved. This eventual lack of equilibration may have happened because in the original configuration the air sampling flow-rate was high, resulting in contact times of air and soil of only a few seconds. Therefore, even though air was sampled near the air–soil interface, as done with other approaches (9), it was not possible to ensure that the air mass had enough time to equilibrate with the soil.

The residence time of the air in contact with the soil below the sampler will depend basically on the operating flow rate of the sampler pump and the volume of air between the sampler and the soil surface. Previously, this kind of sampler was operated with flow rates of 200 L min^{-1}, which had the advantage of large samples, but the disadvange of short air–soil contact times. Besides this potential sampling artifact, the innovative approach by Meijer and co-workers (2) could be adequate to attempt the determination of soil fugacity, if the sampling device is modified, leading to longer contact times between air and soil.

We have designed a new sampler (see Figure 1) to determine POPs in gas and soil samples in equilibrium. It is fully portable and can be operated in field conditions. This has been possible by (i) reducing the flow rate of the pump more than 20-fold down to 2–10 L/min (see below), (ii) increasing the surface of the sampler to 1 m^2, and (iii) adapting the cleanup and concentration procedure allowing analysis of POPs in small volumes (12–15 m^3) of air, (iv) assessing the occurrence of air–soil equilibrium, and (v) assessment of the accuracy and reproducibility of the sampling method.

The soil fugacity sampler consists of a stainless steel plate with a surface of 1 m^2 which is located a few cm above the soil surface (the height can be regulated between 1 and 6
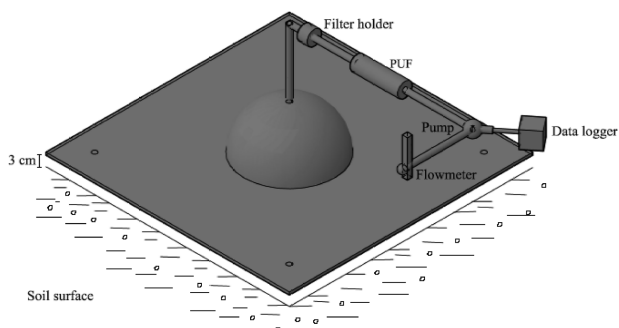

FIGURE 1. Sampler device scheme for determining soil–air partitioning in field conditions.

cm). In the center of the stainless steel plate there is a chamber from which air is sampled. Air goes through a 47-mm glass fiber filter (GFF, Whatman filter) into a polycarbonate holder and then through polyurethane foam (PUF). The air pump, operating at a range from 1 to 10 L min^{-1}, is located after the filter and PUF holders to avoid any potential contamination. Traditional high-volume air samplers (Hi-Vol Samplers) work at a flow rate of about 300–600 L min^{-1} which allows a sample of hundreds of m^3 in a 24-h period to be obtained. With a flow rate of 8–10 L min^{-1} or lower, in 24 h a sample of 12–14 m^3 is obtained and therefore the polyurethane foam and filter should be significantly smaller than in a high-volume air sampler configuration, which dramatically reduces the blanks. Here a PUF, 10 cm long by 2 cm in diameter, is used and held inside a metallic tube. To set up the desired flow rate, a flowmeter at the end of the circuit and a data logger allow the control and register of the flow rate and sampling volume during the sampling period. The sampler can be operated with either electrical power or using portable 12 V batteries; therefore the system is fully autonomous to be operated in remote environments. After sampling, PUFs are stored inside amber vials at 4 °C prior for analysis.

In this study, the soil fugacity sampler was always located 3 cm above the soil surface. In addition to the air sample taken with this sampler, a simultaneous second air sample has been taken at 1.5 m height (height used traditionally for Hi-Vol Samplers) using the same PUF and sampling conditions. This allows for determining the gradient of gas phase concentrations between the surface and the atmosphere at a height of 1.5 m and comparing soil fugacities with ambient gas-phase concentrations used previously for soil–gas partitioning studies. Inferences on the direction of air–soil exchange can also be determined. If concentrations from the soil fugacity sampler at 3 cm are higher than those at 1.5 m, there is a net volatilization of POPs. Conversely, if the POP concentration at 1.5 m height is higher than that at 3 cm, there is a net absorptive deposition to the soil. Here, the soil fugacity is defined operationally and in fact, the sampler measures the surface fugacity; in case there is grass on the soil, the fugacity measured will be that of the soil-grass system.

Soil Sampling. It is a common practice to determine the occurrence of POPs in soil by sampling the top 3 or 5 cm (10, 13, 15); however, only the top 0.5 or 1 cm is in direct contact with the atmosphere and thus subject to air–soil partitioning (16). After the air sampling, surface vegetation samples (grass) were obtained by carefully cutting the grass and storing it in aluminum foil for future analysis. Surface soil below the sampler device was collected by gently removing the top 0.5 cm soil with a stainless steel spatula (cleaned before and after each sample with acetone) and bulked together to form one sample. Both soil and vegetation samples were kept frozen at −20 °C until analysis.

2.2. Analytical Procedure. *Total Soil Organic Carbon.* Soil samples were extracted with HCl (7%) to remove inorganic carbon. Subsequently, they were cleaned with Milli-Q water

until neutral pH and freeze-dried (24 h; Edwards High Vacuum International). The determination of total organic carbon (TOC) was performed by flash combustion at 1025 °C followed by thermic conductivity detection in a CHNS Elemental Analyzer EA1108. This analysis was done by the Laboratory for Microanalysis (IDAEA-CSIC, Barcelona, Spain). Limit of detection was 0.1% of carbon content.

To have simultaneous measurements of temperature, wind speed, humidity, etc., a wireless vantage Pro2 weather station with UV and solar sensors (Davis Instruments) was deployed close (1 m) to the sampler device, to better record the meteorological conditions during the sampling period. Soil temperature was continuously measured below the sampler.

Soil Extraction and Fractionation for POP Analysis. Approximately 10 g of surface soil samples were homogenized and dried by mixing with anhydrous sodium sulfate and ground using a mortar and a pestle. The whole sample was transferred into a Soxhlet cellulose thimble (Whatman) and extracted in a Soxhlet apparatus during 24 h, using dichloromethane/methanol (2:1 v/v) (Merck, Darmstad, Germany). Prior to the extraction, samples were spiked with PCB congeners 65 and 200 and per-deuterated PAHs standards (anthracene-d10, crysene-d12 and perylene-d12) which were used as surrogate standards.

The extracts were reduced in a rotary evaporator to 1 mL and then solvent-exchanged to isooctane. All samples were then fractionated on a 3% deactivated alumina column (3 g) with a top layer of anhydrous sodium sulfate. Each column was eluted with a first fraction of 6 mL of hexane eluting the organochlorine compounds, and a second fraction of 12 mL of dichloromethane/hexane (2:1 v/v) (Merck, Darmstad, Germany) eluting PAHs. About 0.5 g of activated copper (size <63 μm; Merck, Darmstad, Germany) was added to the first fraction to eliminate the sulfur interferences. Both first and second fractions were concentrated in a rotary evaporator and solvent-exchanged to isooctane under a gentle stream of nitrogen.

Atmospheric Samples Extraction and Fractionation for POP Analysis. The methodology for concentration and cleanup proposed for the gas phase has been modified if compared with what is commonly done (*17, 18*); mainly due to the small volume of atmospheric samples (approximately 12−14 m³) that requires the use of a small polyurethane foam plug (PUF) (2 cm diameter × 10 cm length) to minimize blanks. PUFs were Soxhlet-extracted for 24 h in 100 mL of hexane/acetone (1:1 v/v; Merck, Darmstad, Germany). Extracts were concentrated by rotary evaporation to 1 mL and then fractionated on a 3% deactivated alumina column (1.5 g). PCBs and PAHs were both eluted in a fraction with 12 mL of dichloromethane/hexane (2:1 v/v; Merck, Darmstad, Germany). The collected fraction was concentrated in a rotary evaporator and solvent-exchanged to isooctane under a gentle nitrogen stream.

POP Identification and Quantification. PCB congeners were analyzed by a gas chomatograph equipped with an electron capture detector (GC-ECD, Agilent Technologies, model 6890N) with a 60 m × 0.25 mm i.d. DB-5 capillary column (Varian, Scharlab S.L) coated with 5% phenyl−95% methylpolysiloxane (film thickness 0.25 μm). The instrument was operated in splitless mode (close for 1.5 min) and the oven temperature program started at 90 °C (held for 2 min) to 190 at 20 °C/min, and then to 310 at 3 °C/min (holding time 18 min). Injector and detector temperatures were 280 and 320 °C, respectively. Helium and nitrogen were used as carrier (1.5 mL/min) and makeup (60 mL/min) gases, respectively.

PAHs were analyzed on a gas chromatograph (CG) coupled to a mass spectrometer (MS). A Fisions MD800 instrument (quadrupole-detector, THERMO Instruments, Manchester, UK) operating in selected ion monitoring (SIM) mode was used. The GC system was equipped with a 30 m × 0.25 mm × 0.25 μm i.d., Tecknokroma, TRB-5MS (5% phenyl−95% dimethylpolysiloxane) capillary column with a film thickness of 0.25 mm. The oven temperature was increased to 90 °C and held for 1 min, then increased to 120 at 10 °C/min, and then increased from 120 to 315 at 5 °C/min, and finally held at 315 °C for 5 min. Injector and transfer line temperatures were 280 and 300 °C, respectively, and 2 μL of sample was injected.

Quality Control. Field PUF blanks (one for every 5 PUFs extracted) were inserted between the samples for monitoring the possible contamination during the transport and processing, and also analytical blanks for soil samples (one for every 5 soils extracted) were prepared by filling precleaned extraction thimbles with precleaned and muffled at 400 °C sodium sulfate. Phenanthrene, anthracene, fluoranthene, and pyrene were detected in both PUF and soil blanks, but they account for less than 6% of the total sample concentration. PCB 70, 191, and 199/201 among the 41 congeners analyzed were also found in PUF and they account for between 0.04 and 21%, so samples were blank corrected for PCBs.

Instrumental detection limits (IDLs) were determined from linear extrapolation from the lowest standard in the calibration curve; using the area of the peak having a signal-to-noise ratio of 3. IDLs varied between 0.01 and 0.25 ng mL⁻¹ for PAHs and between 0.003 and 0.040 ng mL⁻¹ for PCBs. Method detection limits (MDLs) were defined as mean blank plus three times the standard deviation. MDLs in soil and air varied between 0.01−1.83 ng g⁻¹ and 0.01−1.32 ng m⁻³ for PAHs and between 0.001−0.059 ng g⁻¹ and 0.004−0.04 ng m⁻³ for PCBs. A mean air sampling of 14 m³ and 10 g of soil was applied to derived MDLs for air and soil concentrations.

More than 40 air and 40 soil samples were taken in different sampling locations using the methodology previously described and recoveries higher than 80% for PCBs and PAHs were obtained. For the subset of samples comprising the optimization of the soil fugacity sampler, the surrogate recoveries were (mean ± SD) 70.5% ± 15 for PCB65 and 90.8% ± 6.5 for PCB200 for PUF samples (*n* = 20), and 72.4% ± 3.1 for PCB65 and 78.2% ± 4.9 for PCB 200 for soil samples (*n* = 4). The surrogate percent recoveries of PAHs from the same subset of PUF plugs and for soil samples were (mean ± SD) 101.8% ± 17.5 for anthracene-d10, 97.3 ± 17.9 for crysene-d12, 79.3 ± 20.9 for perylene-d12 for PUF samples, and 72.9 ± 4.9 for anthracene-d10, 104.6 ± 4.9 for crysene-d12, and 92.9 ± 5.1 for perylene-d12 for soil samples.

3. Results and Discussion

Assessment of Equilibration between Soil and Gas Phase POPs. An important issue to evaluate is whether this sampler can provide reproducible results in terms of the soil fugacity sampled and gas phase concentrations at soil surface, thus assuring that these are equilibrated with the soil; also it is important to make sure that a sufficient volume of air is sampled. The higher the flow rate, the higher the volume sampled per day, though the residence time of the air-mass below the sampler is shorter and therefore it is important to compare to which extent the flow rate will affect the gas-phase POP concentrations.

Initial experiments were performed using 2 samplers operating under the same sampling conditions, side by side, to test the reproducibility and accuracy of the methodology. The presence of equilibrium conditions between air in contact with the soil surface was evaluated by modifying the residence time of the air in contact with the surface soil. Duplicate samples with sampling times of 30 (at 8 L min⁻¹), 48 (at 5 L min⁻¹), and 120 (at 2 L min⁻¹) hours, were taken during consecutive days at the IDAEA's campus garden in Barcelona. The samples were all taken with the flow rate regulated to
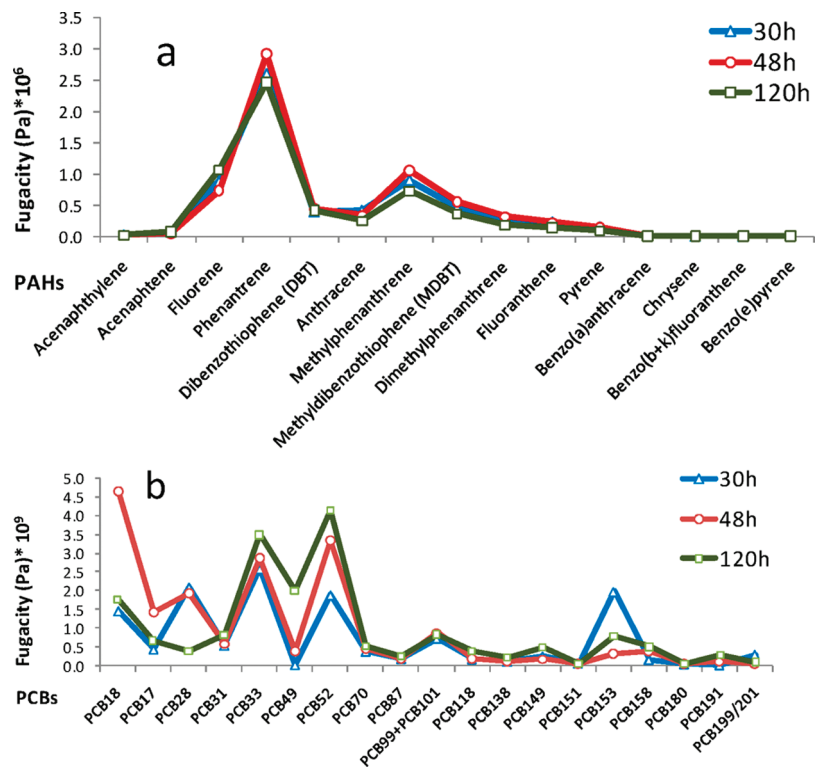
FIGURE 2. Soil fugacities of PAHs (a) and PCBs (b) for different sampling flow rates (residence times).

sample a total volume of 14.4 m³ in each experiment, regardless of the sampling time. Information about the air and soil sampling conditions is shown in Tables SI-1a and b of Supporting Information. During the longer periods, the sampler was operating with a lower flow rate, thus increasing the residence time of the air in contact with the soil. If equilibrium is not achieved, the measured soil fugacity would be expected to vary as the residence time of the air in the sampler increases, since the air would have more time to approach equilibrium with the soil. Conversely, equilibrium is achieved if the POP fugacity in soil does not vary significantly with increasing the residence time.

Figure 2 illustrates the measured soil fugacities of PAHs and PCBs. Note that the fugacities shown for PAHs and PCBs are an average of 4 samples for experiments at 30 and 48 h and of 2 samples for experiments at 120 h (from the two parallel samplers). Only the lower molecular weights PAHs and the more volatile PCBs were detected; mainly due to the small volume of atmospheric samples taken and the higher abundance of these compounds in the gas phase. The profile and concentration obtained in the 30, 48, and 120 h experiments are similar in the case of PAHs and for most PCB congeners, except for PCB 49, 52, and 153 which showed large variability during the three experiments. For these three PCB congeners a variability of 30−68% is unexplained by the analytical uncertainty and thus concentrations differ significantly. Equilibrium conditions may not be achieved for these three congeners. There are also some differences for some other volatile congeners, but it is just for one of the experiments, which is related to the difficulties in determining the low chlorinated PCBs for the small sampled volumes. The similarity of the gas phase concentrations for the rest of PCBs and PAHs with differences lower than 10% for most compounds, thus independent of flow rate, suggest that even with a flow rate of 8−10 L min⁻¹, the residence time of the air mass in contact with the soil (about 4 min) is enough to reach equilibrium with the soil. Indeed, for lower flow rates with longer residence times the soil fugacity is not significantly different.
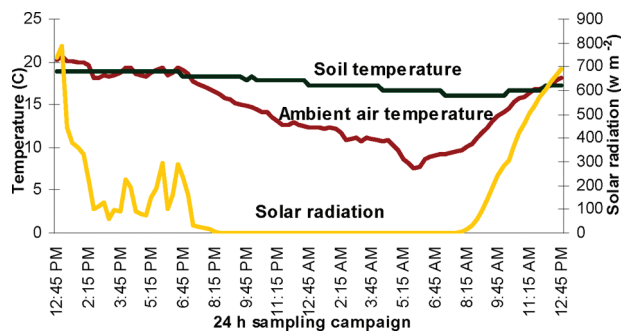

FIGURE 3. Ambient air and surface soil temperatures during a characteristic 24 h of sampling period (9/18/2007−9/19/2007) in the Ebro river watershed. Soils conditions were measured below the sampler.

Soil concentrations of POPs do not change significantly for time periods of only a few days due to the fact that the reservoir capacity of soil is much higher than that of the gas phase (4). Soil concentration of PAHs and PCBs for the soil under the 2 samplers is shown in Table SI-2 of the Supporting Information. If air equilibrates with the soil, the concentration will not change in consecutive samples if the soil concentration and meteorological conditions do not change during this time period. However, soil−air partitioning is strongly influenced by both soil temperature and ambient temperature, mainly affecting vapor pressure (19, 20). The little differences in soil fugacity between the experiments could be attributed to slight variation in meteorological conditions. Various studies (21, 22) have shown that soil sorption is increased at lower water content, thus reducing the soil−air partition coefficients.

Therefore it is important, in order to determine the air−soil partitioning, to have a concurrent monitoring of soil and atmosphere meteorological conditions under the sample. Due to solar radiation, it could be thought that the sampler surface could act as a greenhouse increasing the temperature of the soil surface during the sampling, thus introducing an artifact in the measure of soil fugacity. However, Figure 3
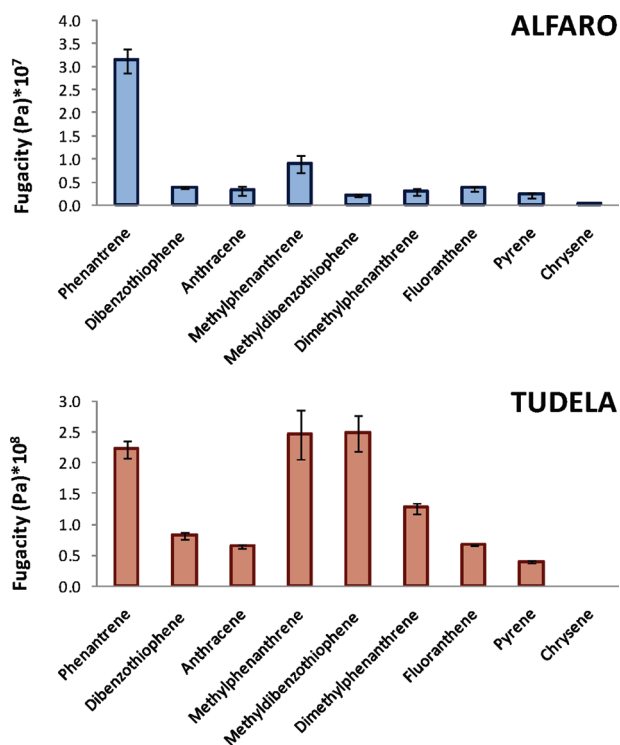
FIGURE 4. Two examples of replicate measures of PAHs soil fugacities. Replicates are taken at the same sampling site on consecutive days. Latitude and longitude of the two sampling sites are Alfaro (42°11′ N, 1°47′ W) and Tudela (42°04′ N, 1°36′ W).

illustrates that the soil temperature varies by only few degrees during the 24 h of a sampling period due to the buffering effect of humidity. For a characteristic sampling period for a sunny day in late summer, when there was a strong day−night fluctuation (from 22 to 7 °C) in atmospheric temperature as measured at 150 cm height, the fluctuation in soil temperature was minimal (17.6 °C ± 0.98). Therefore, there is not a significant modification of soil temperature due to solar radiation heating the sampler. This lower temperature excursion of the soil decreases the air−soil partitioning variability, which would be much higher if the temperature at the interface was that of ambient air. However, the extrapolation of the results for air−soil partitioning obtained need to be adequately extrapolated to field conditions by considering changes in temperature and humidity.

The content of soil moisture has also been measured. Soil moisture measured as % water content weight per weight of wet soil was 16% on average. In 58% of cases there was an increase of soil moisture of 3% during the sampling periods, and in the remaining 42% of cases there was a decrease of 2% of soil moisture. These variations in soil−water content during sampling are minimal and smaller than the variability of soil moisture locally. Therefore, the potential variability of soil moisture during sampling does not introduce a sampling artifact.

Repeatability. It is also important to ensure that the concentrations of gas phase equilibrated with the soil are reproducible. Replicate measurements on consecutive days have been performed so far for multiple campaigns in urban, coastal, and rural sites to check the repeatability of the sampler device. Differences between replicate measures of gas phase PCBs and PAHs concentration equilibrate with the soil are lower than 10% when meteorological conditions do not change between the sampling periods (Figure 4). This is because the soil capacity to hold POPs is large (4) and thus the soil concentration does not change during a sampling period of 24 h and the sampler does provide an accurate
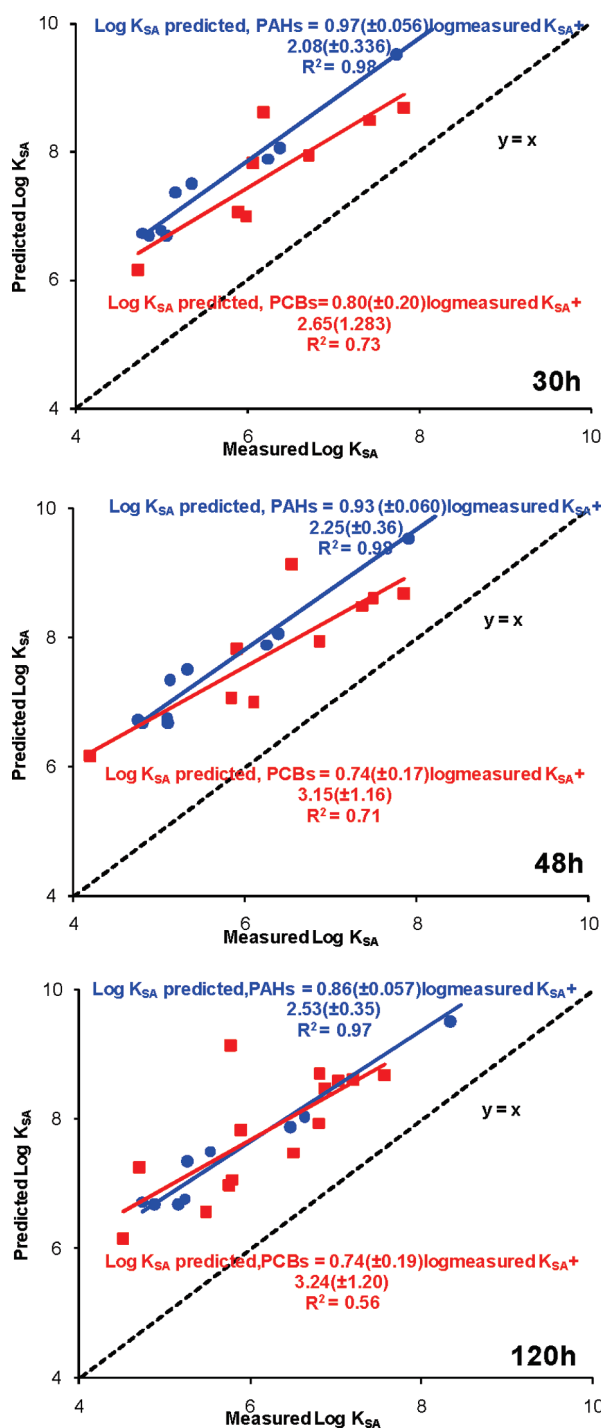

FIGURE 5. Predicted log K_{SA} versus measured log K_{SA} for PAHs (circles) and PCBs (squares) obtained with the soil fugacity sampler with different sampling flow rates, thus different sampling times (30, 48, and 120 h). Log K_{SA} predicted = β_1(±standard deviation)log measured K_{SA} + β_0 (±standard deviation).

method to measure soil fugacity. Indeed, Dalla Valle et al. (4) have shown that only the top millimeter of soil has a reservoir capacity higher than 1000 m of air column equilibrated with the soil, thus the 14.4 m³ of air sampled here is not enough to induce significant changes in POP soil concentrations. Information about soil−air sampling of Tudela and Alfaro is shown in Table SI-1c of the Supporting Information.

Soil−Air Partitioning. Accurate knowledge of the soil−air partition coefficients is important for modeling the fate and transport of POPs in the environment. The soil fugacity
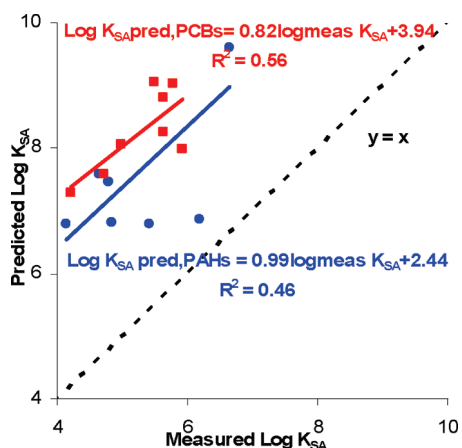
FIGURE 6. Predicted log K_{SA} versus measured log K_{SA} for PAHs and PCBs for a sampling location along the Ebro River. Latitude and longitude of the sampling location Alfaro is (42°11′ N, 1°47′ W).

sampler described here is an important step in this direction, since the measured fugacities do not depend on any physical−chemical constant or assumption. Therefore, from measured K_{SA} (eq 3) it is possible to assess the accuracy of current models for air−soil partitioning. Measured (from eq 3) and predicted K_{SA} (from eq 4) are compared in Figure 5. The values of f_{OC} used in eq 4 have been measured experimentally for the soil under the sampler device and thus introduce a negligible error. The density of octanol and K_{OA} values can be found in the literature (23−25), whereas the value of $(\zeta_{oct}/\zeta_{OM})(MW_{oct}/MW_{OM})$ is assumed, as a working hypothesis, to equal unity as done in previous studies (13, 26).

Figure 5 shows the plot of predicted versus measured K_{SA} for PCBs and PAHs at the IDAEA's campus garden when the sampler operated at different flow rates, thus needing 30, 48, and 120 h to sample 14.4 m^3 of air. If gas phase concentrations at 3 cm (soil fugacities) are considered, then the slope is similar for the three sampling times or sampling flow rates. Statistical analysis carried out on the regressions (ANOVA), showed that there are no significant differences among the three slopes at $p < 0.05$ level in soil−gas phase partitioning depending on the flow rates. These trends are logical in the sense that the air in contact with the soil can equilibrate with the soil using this soil fugacity sampler. Therefore, the soil fugacity sampler is a useful tool to determine real soil−air partition coefficients. The PCBs and PAHs studied here comprise chemicals with a wide range of physicochemical properties and thus the sampler is of generalized use for semivolatile compounds. Results of log K_{SA} for PAHs and PCBs during the three sampling times are given in Table SI-3a and b of the Supporting Information as well as the reported values from literature. The measured K_{SA} for the PAHs are in general slightly lower (less than 1 order of magnitude) than those found in the literature; which are calculated with gas-phase concentrations collected with traditional Hi-Vols at 1.5 m height and from laboratory experiments. Conversely, PCBs K_{SA} values are not significantly different from those described elsewhere.

In addition to the sampling site in an urban garden in Barcelona, the soil−air partitioning sampler has been used in other locations, providing similar results (Figure 6). For example, the predicted versus measured K_{SA} for both PCBs and PAHs in a rural area (Alfaro) can be fitted with a regression line with a slope of 0.82 and 0.99 for PCBs and PAHs respectively.

Figures 5 and 6 show that K_{SA} for PCBs and PAHs are lower than predicted values by 1−2 orders of magnitude. This suggests that the factor $(\zeta_{oct}/\zeta_{OM})(MW_{oct}/MW_{OM})$ is significantly smaller than unity because in Figures 5 and 6

it was assumed this factor was 1. Soil organic matter can have a molecular weight much higher than octanol and the POP activity coefficient in organic matter can also be different from that in octanol, therefore the present work suggests that the values of $(\zeta_{oct}/\zeta_{OM})(MW_{oct}/MW_{OM}\delta_{oct})$ should be from 0.1 to 0.01, presumably due to soil organic matter molecular weights of the order of 10,000. Furthermore, the low K_{SA} values observed are consistent with a minor role of soot carbon as a sorbing phase, even for PAHs, since the values predicted by K_{OA} are higher than the measurements. The lack of importance of soot carbon as a sorbing phase is consistent with the results of Ribes et al. (13) which showed that soot carbon was only important in high altitude soils with low OC content, though not in soils with moderate OC content and important char content as those evaluated here. However, further research is needed on this, since the results are also consistent in a scenario where sorption to OC is low due to an extremely low value of $(\zeta_{oct}/\zeta_{OM})(MW_{oct}/MW_{OM}\delta_{oct})$, though the partition coefficients are increased due to some influence of soot carbon.

Supporting Information Available

Details about soil and air temperature monitoring, soil PCBs and PAHs concentrations, and measured and literature values of K_{SA} for PCBs and PAHs. This material is available free of charge via the Internet at http://pubs.acs.org.

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