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Factors Influencing the Soil—Air Partitioning and the Strength of Soils as a Secondary Source of Polychlorinated Biphenyls to the Atmosphere

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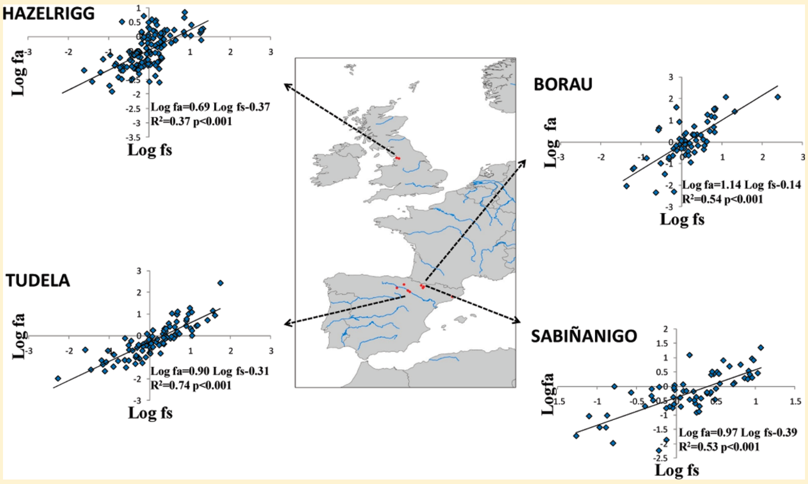
Supporting Information

ABSTRACT:



Soils are a major reservoir of persistent organic pollutants, and soil—air partitioning and exchange are key processes controlling the atmospheric concentrations and regional fate of pollutants. Here, we report and discuss the concentrations of polychlorinated biphenyls (PCBs) in soils, their measured fugacities in soil, the soil—air partition coefficients (K_{SA}) and soil—air fugacity gradients in rural background areas of N-NE Spain and N-NW England. Four sampling campaigns were carried out to assess seasonal and daily variability and differences between sampling sites. K_{SA} values were significantly dependent on soil temperature and soil organic matter quantity, and to a minor extent organic matter type. All the PCB congeners in the soil are close to equilibrium with the atmosphere at rural Ebro sites, but soil fugacities tend to be higher than ambient air fugacities in early and late summer, consistent with the influence of temperature on soil—air partitioning. Therefore, during warm periods, soils increment their strength as secondary sources to the atmosphere. The mixture of PCBs found in the atmosphere is clearly strongly influenced by the mixture of PCBs which escape from soil, with significant correlations between them (R^2 ranging between 0.35 and 0.74 and p-level <0.001 for the Ebro sampling sites). Conversely, the close-to-equilibrium to net sink status of rural UK sites, suggest a close coupling of air and soil concentrations, but it is not possible to elucidate the importance of these soils as secondary sources yet, and presumably there are still significant primary sources to the regional/global environment.

1. INTRODUCTION

Soils are the major terrestrial environmental reservoir and one of the major sinks for persistent organic pollutants (POPs) and make a major contribution to the global inventory of these compounds.[1,2] The availability for biological degradation, burial, revolatilization, and toxic effects of POPs are strongly affected by the soil organic matter content (SOM) due to its high capacity to retain POPs.[1,2] Few papers have addressed the influence of organic matter type or quality on soil—air partition coefficients of POPs, and these papers deal mainly with nonpersistent pollutants such as polycyclic aromatic hydrocarbons (PAHs),[3−5] even though it has been recognized that SOM composition could account for a factor of 2.5 of the variability of the soil—water

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partition coefficient normalized by organic carbon (K_{OC})[6] for polychlorinated biphenyls (PCBs). Although PCBs are one of the priority pollutants listed by the Stockholm Convention on POPs, and were banned decades ago, they continue to be found in the environment as a consequence of releases from primary (buildings, old electrical equipment, etc.) and diffuse secondary sources ("old" PCBs reemitted from soils and oceans).[7−9] Even though some soils may have received direct inputs of PCBs, all soils, even in remote areas, receive inputs of POPs from atmospheric deposition.[10] For this reason, background soils are a key environmental compartment to consider when assessing soil−air partitioning and the relevance of secondary sources.[1,11,12] The magnitude and direction of soil−air exchange of PCBs have also varied over time as production restrictions and emissions controls were introduced, and it also depends on climatic/environmental factors, magnitude of sorption to SOM and compound properties. The understanding of the factors controlling the magnitude of sorption of POPs to soils, and their exchanges with the atmosphere, has been a central research issue in environmental chemistry.[1,13,14] In the present paper, we investigate in detail the factors controlling PCB concentrations in soils, their fugacities and fugacity gradients between soil and the atmosphere, by using the soil fugacity sampler.[15] Therefore, the main objectives of this study were (i) to investigate the influence of environmental and soil−related variables on soil PCBs burden, (ii) to study the effect that temperature and soil organic quantity and quality have on soil PCB fugacity and soil−air partition coefficients (K_{SA}), (iii) to determine the direction of soil−air exchange, by means of soil/air fugacity ratios, in rural and semirural areas of the Ebro river basin (Spain) and northwest England. This work is a companion study of the recently reported study on polycyclic aromatic hydrocarbons.[16]

2. MATERIALS AND METHODS

Soil and Air Sampling. Samples from ten nonagricultural sampling sites were taken and analyzed. There were six rural sites: Borau, Alfaro, Nájera, Lasieso, Uruñuela located along the Ebro river basin (N-NE Spain) and Langden (near Lancaster, UK); and three semirural: Tudela, Sabiñanigo (Ebro river basin-Spain) and Hazelrigg (near Lancaster, UK). Three sampling campaigns were carried out in June 2006, November 2006, and September 2007 in the Ebro river basin. Sampling in the UK sites was performed during August−September 2008. A map of the sampling sites and information of sampling events is shown in the Supporting Information (SI) (see Figure S1 and Table S1). PCBs fugacity in surface soils was measured by analyzing the PCB concentrations in air that had been equilibrated in situ with the soil surface using the soil fugacity sampler.[15] Ambient air concentrations, hereafter defined as the PCB concentrations in air at a height of 1.5 m, were sampled with a low volume sampler (total air volume between 10 and 14 m^3) with glass fiber filters and polyurethane foam (PUF) plugs identical to those used to determine soil fugacities. Measurements of fugacity in soil and ambient air were done during 24 h. Since there is a diurnal variability in temperatures, the uncertainty associated with these measurements was estimated to be lower than 70% (see Annex 1, SI). Soil samples were taken after measuring the fugacity in soil, by gently collecting the soil surface layer (top 0.5−1 cm approximately). For this study, a total of 44 soil fugacity measurements, 41 ambient air concentrations, and 20 top surface soils were sampled and analyzed. After sampling, air and soil samples were stored in freezers at −20 °C until analysis.

Analytical Methods. Briefly, soil and air samples were Soxhlet extracted for 24 h in dichlorometane:methanol (2:1) and acetone:hexane (3:1) respectively. Extracts were cleaned and fractionated using alumina chromatography. Soil samples were also treated with activated copper to avoid chromatogram interferences. Samples taken in the Ebro river basin (Spain) were analyzed by GC/ECD and those taken in the UK by GC/MS with an EI+ source operating in selected ion mode (SIM). Details of the temperature programs and monitored ions are given elsewhere.[15,17,18] The following PCB congeners were analyzed in samples collected at the selected rural/semirural sites of the Ebro river basin (Spain): tri-PCB 18, 17, 31, 28, 33; tetra-PCB 52, 49, 44, 74, 70; penta-PCB 95, 99/101, 87, 118; hexa-PCB 110, 151, 149, 153, 132/105, 138, 158, 128, 169; hepta-PCB 187, 183, 177, 171/156, 180, 191, 170; octa-PCB 201/199, 195, 194, 205; nona-PCB 206, 208, 209. The following PCB congeners were analyzed in samples collected at the selected rural and semirural UK sites: tri-PCB 18, 31/28, 22; tetra-PCB 52, 54, 49, 44, 41/64, 60/56, 74, 70; penta-PCB 95, 90/101, 99, 87, 104, 105, 110, 114, 123, 118; hexa-PCB 151, 149, 155, 156, 157, 153/132, 141, 138, 158, 167; hepta-PCB 174, 187, 188, 183, 180, 170, 189; octa-PCB 199, 203, 194. Reference to the sum of homologue groups or the total sum of PCB (ΣPCBs) considers the aforementioned congeners.

Quality Assurance/Quality Control. All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks and field blanks constituted 21% of the total number of samples processed. PCB 52, 70, 118, 149, and 153 were routinely detected in blanks and field blanks showing low concentration, ranging between 3 and 10%, indicating minimal contamination during storage, sampling, transport and processing, so samples were not blank corrected. Method quantification limits derived from the lowest standard in the calibration curve, ranged from 0.50 to 2 pg m^{-3} and 0.33 to 2.65 pg g^{-1} for air and soil samples processed with GC/ECD and between 2.5 to 5 pg m^{-3} and 1.67 to 3.34 pg g^{-1} for air and soil samples processed with GC/MS. Recoveries were routinely monitored using PCB65 and PCB200 in samples analyzed with GC/ECD and $^{13}C_{12}$−PCBs (28, 52, 101, 138, 153, 180, 209) for those injected in GC/MS. They ranged from 53 ± 17 to 76 ± 14 and from 58 ± 3 to 101 ± 26 for soil and gas phase, respectively.

Meteorological Data. Concurrent meteorological data were monitored where possible using a wireless weather station or were provided by the nearest weather station to the sampling site by the Spanish Meteorological Agency (AEMET). The following physicochemical characteristics of samples were measured by standard methods described elsewhere[16]: soil temperature (Soil T), ambient air temperature (Air T), soil water content (SWC), and precipitation, soil organic carbon (TOC) or organic carbon fraction (f_{OC}), surface soil pH and redox potential, fraction of nitrogen (f_N) and altitude. As pH and redox potential and soil T and SWC were significantly correlated with each other, only redox potential and soil T (variables explaining higher fraction of variability of K_{SA}) were considered in the multiple regressions shown below in order to avoid double use of parameters. No correlation was found between soil T and altitude, probably due to the short range of altitudes of the sampling sites. Therefore, f_{OC}/f_N and soil redox were considered here as indirect parameters related to organic matter quality.

3. RESULTS AND DISCUSSION

Occurrence of PCBs in Ambient Air. All the measured concentrations, Air T and precipitation in the Ebro river basin and UK sites' Air-sheds are listed in the SI (Tables S2a−d). Individual PCB congener, Σ_{41}PCBs, Σ_{46}PCBs, and ICES congener (Σ_7PCBs) average concentrations are also presented. The range of Σ_7PCBs in the Ebro river basin, during the sampling period, varied from 0.04 to 0.44 ng m^{-3}. The highest concentrations occurred in June, with the exception of the Alfaro site. Σ_7PCBs at Hazelrigg and Langden were 0.065 ng m^{-3} and 0.069 ng m^{-3}, respectively. These ambient air concentrations reported here were in agreement with other previous field studies.[19,20] Ambient air concentrations for the sites in the Ebro river basin are shown in Figure S2, SI, and presented below as fugacities (or partial pressures in Pa) estimated by

$$f_a = 10^{-9} C_A RT/\mathrm{MW} \qquad (1)$$

where C_A is the measured air concentration in ng/m^3, R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), MW is the chemical molecular weight (g mol^{-1}), and T is the temperature (K).

Occurrence of PCBs in Soils. Results for individual PCB congeners, the sum of the tri-to-nona homologue groups and the total PCB concentration (ng g^{-1}dry weight) at each site are shown in the SI (Tables S3a, b). Overall, Σhexa-PCBs were the most abundant homologue group followed by the Σpenta- and Σhepta-PCB. Σ_{41}PCB concentrations ranged from 0.09 to 22 ng gdw^{-1} for Ebro's sites and Σ_{46}PCBs between 0.66 and 5.20 for UK sites. These observations are consistent with other studies on global background soils.[1,21,22] The influence of soil and environmental properties on PCB concentrations in soils, was assessed by regression analysis using SPSS 15.0. Regressions were calculated between the soil PCB congener concentration and the following variables: Soil T, Air T, SWC, precipitation, SOM quantity and quality. Soil organic matter quantity is generally considered as the main descriptor of the sorption of hydrophobic pollutants[23] and has been recognized as an important variable that influences the concentrations of POPs at local, regional and global scales.[1,24] Figure 1 shows the significant dependence of PCB homologue groups and total PCBs concentrations on f_{OC}. ΣPCB concentrations were significantly positively correlated with another class of organic pollutants (ΣPAHs) determined in these soils[16] with $R^2 = 0.47$ and p-level < 0.001. This was also observed by Nam et al.[25] in other European background soils, and it is due to the common role of organic matter quantity as a descriptor of the burden of hydrophobic pollutants. To study the role of SOM quality on PCB soil concentrations, concentrations were normalized by f_{OC} and regressed against f_{OC}/f_N and soil redox by ($\log \mathrm{Cs}/f_{OC} = a + b(\log f_{OC}/f_N) + c\,(\log \mathrm{redox})$). Table S4, SI, shows the significant influence of both variables on most congener groups and ΣPCBs, showing a greater influence on concentrations of penta-to-hepta congeners, compared to low chlorinated congeners, with R^2 ranging between 0.32 and 0.73 (p-level < 0.05). Concerning temporal trends, there were no statistically significant differences in soil concentrations of PCBs with respect to soil or ambient air temperature for the three sampling periods in the Ebro. No statistically significant correlations were found when regressing soil PCB concentrations against soil pH, altitude, SWC or precipitation.

PCB Fugacity in Soils. Due to the lack of direct measurements, soil fugacity is often estimated from the soil fugacity capacity, which governs the potential of soil to emit or retain pollutants and is dependent on f_{OC} and K_{OA}, the octanol-air partition coefficient, which is temperature-dependent. The recent development of a soil fugacity sampler[15] allows for directly determining the pollutants fugacity in soils. In this study, PCB fugacity in soil was determined directly under field controlled conditions by:

$$f_s = 10^{-9} C_{SA} RT/\mathrm{MW} \qquad (2)$$

where C_{SA} (ng m^{-3}) is the gas phase concentration that has been equilibrated with the soil surface as measured using the soil fugacity sampler. To establish the role of the SOM and the magnitude of the emission of PCB in soils, a least-squares regression of $\log f_s = a + b\,(\log f_{OC})$ was applied to individual congeners and homologue groups (see Table S5, SI). Results show that lower soil fugacities correspond to higher amounts of SOM, with R^2 ranging between 0.10 and 0.59 (p-level < 0.05), thus suggesting that SOM is an important parameter retarding the emission of PCBs to the atmosphere and therefore soils with high concentration of SOM are favored in the accumulation of POPs as described in previous studies.[26]

Factors Affecting the Soil−Air Partitioning of PCBs. The soil organic carbon−air partition coefficient (K_{OCA}) was calculated from the soil−air partition coefficient (K_{SA}). K_{SA} describes the equilibrium partitioning of a chemical between the air and the soil and was calculated as

$$K_{SA} = C_S/C_{SA} \qquad (3)$$

where C_S is the PCB concentration in surface soil (ng gdw^{-1}), while K_{OCA} is given by

$$K_{OCA} = K_{SA}/f_{OC}$$

Soil retention capacity governs how much chemical is able to accumulate in soil during primary emission and deposition and how much is released back to the atmosphere (secondary emission) for transport and eventually deposition elsewhere. Due to the lack of consensus about the effective surface depth of soil compartment available for soil−air exchange (in this study, approximately, the top 0.5−1 cm soil surface was sampled), it is possible that results presented here, and to a large extend to previous studies,[7,8,13] may contain soil which is not available for soil−air exchange. Therefore the results on K_{SA} and K_{OCA} reported in this and previous studies are operational estimates. We have considered almost negligible the vertical transport of PCBs in the soil samples considered here due to the temporal scale of our sampling events and campaigns, but it will be an important mechanism on the long-term (scale of years), as previous studies have assessed.[27,28] The influence of T and organic matter quality and quantity were initially studied separately by single least-squares regressions between K_{SA} and f_{OC}, f_{OC}/f_N, soil redox potential, altitude, etc. Most of them were statistically significant ($p < 0.001$ level) so we decided to use a multiple parameter least-squares regression since the variability of K_{SA} could be explained by more than one descriptor. The following multiparametric least-squares regression was obtained using all the samples and all analyzed PCB congeners:

$$\log K_{SA} = a + b(1/T) + c(\log \mathrm{redox}) + d(\log f_N) + \mathrm{e}(\log \mathrm{altitude}) + f(\log f_{OC} K_{OA}) \qquad (4)$$

Where $a-g$ are the regression parameters which were all significantly different from zero ($p < 0.05$). The fitted eq 4 explained 39% of the variability ($R^2 = 0.39$, $p < 0.05$, $n = 682$). The fitting

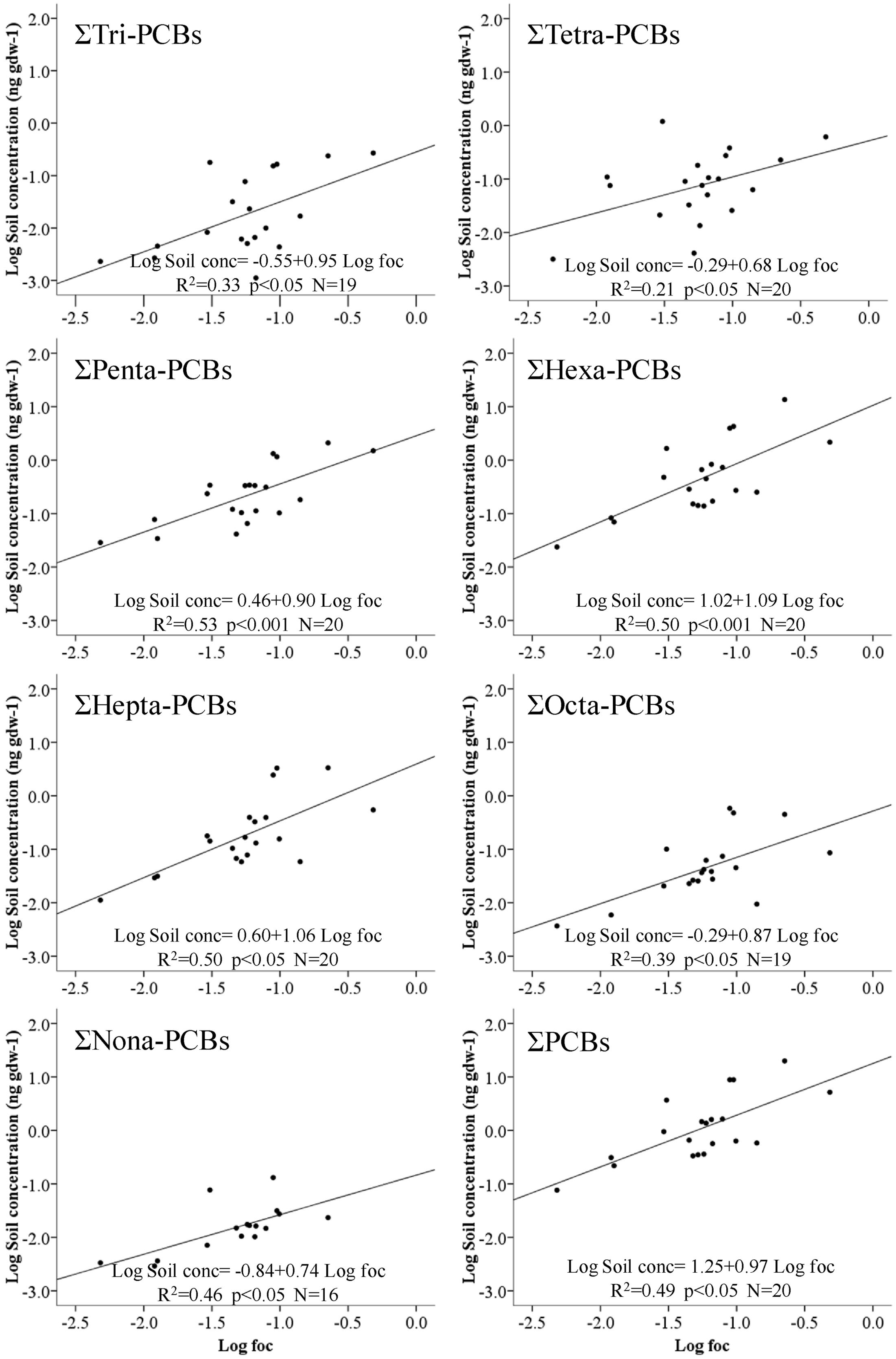

Figure 1. Correlation of log Soil PCB concentrations of homologues groups on log f_{OC}.

parameters were: $a = 0.51 \pm 2.92$, $b = 3042 \pm 931$, $c = -1.66 \pm 0.51$, $d = 1.15 \pm 0.12$, $e = -1.00 \pm 0.14$, $f = 0.45 \pm 0.04$. There is a large range of K_{OA} when considering all individual PCBs. Hence, the last term of eq 4 explains most of the variability, consistent

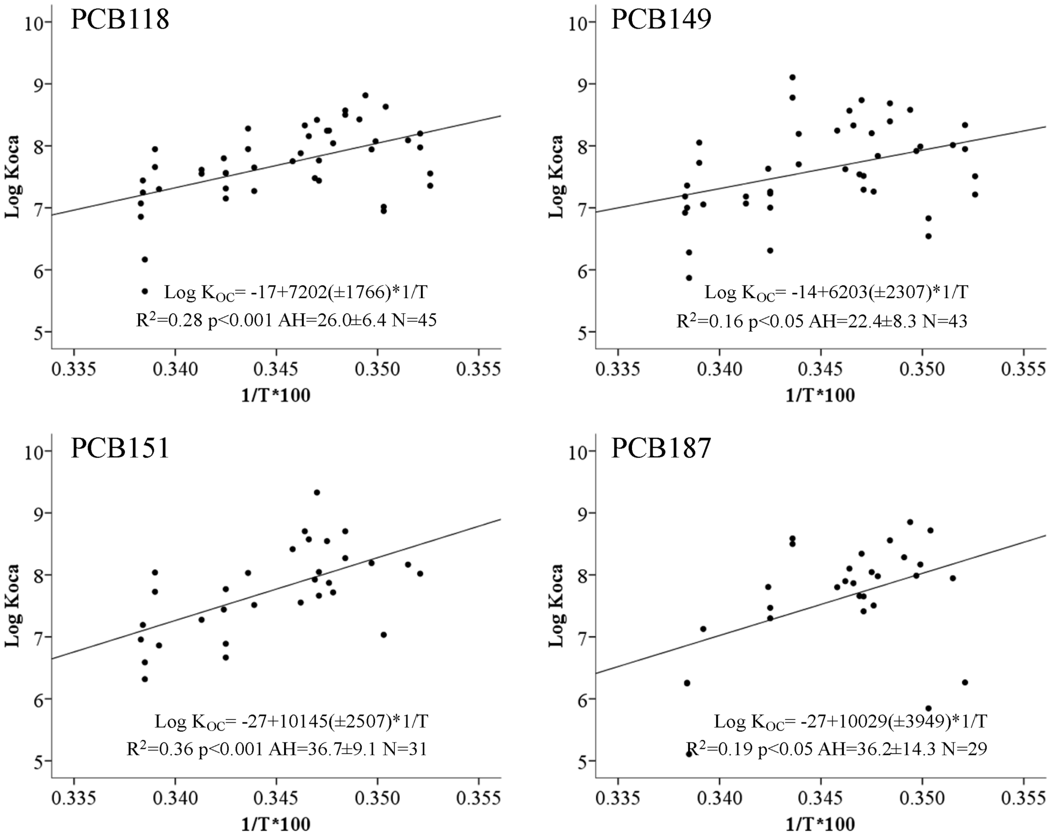

Figure 2. Regression of log K_{OC} versus $1/T$ for selected penta-PCB, hexa-PCB, and hepta-PCB congeners.

with the fact that organic matter quantity and K_{OA} are the key variable and descriptor, respectively, to account for soil—air partitioning.[29] In order to obtain compound specific values for the fitting parameters explaining the role of temperature and organic matter quality, K_{OCA} values were correlated with the various variables. Statistical analyses were only done for those PCB congeners having at least $n = 20$ pairs of air-soil measurements. Altitude, f_{OC}/f_N and soil T were statistically correlated ($p < 0.001$) when regressed individually against K_{OCA} in single regressions (SI Tables S6a—b) for selected congeners. However, a multiple regression analysis of all parameters considered together (eq 5),

$$\log K_{OCA} = a + b(1/T) + c(\log \text{redox}) + d(\log f_{OC}/f_N) + e(\log \text{altitude}) \tag{5}$$

where

$$\log K_{OCA} = \text{Log}(K_{SA}/f_{OC})$$

revealed that T and altitude or T and f_{OC}/f_N were the only significant terms, while redox potential did not explain any significant additional variability of K_{OCA} (Tables S7a and b, SI). Altitude and f_{OC}/f_N are negatively correlated ($R^2 = 0.35$ and $p < 0.05$), and thus only one of them can be used in eq 5. This suggests a small contribution of the OM quality explaining the total variability of the K_{OCA} and it is masked by the altitude, which may be related to a change of composition. Similar behavior has already been observed in a previous study by Zhu et al,[30] in which they showed dependence of the soil type in the K_{OC} for electron-rich aromatic compounds (i.e., phenanthrene, naphthalene), but not for PCBs. Characteristic examples of the influence of temperature on K_{OCA} for selected congeners are shown in Figure 2. K_{OCA} was significantly positively correlated with $1/T$, in agreement with previous studies.[31] From the values of slope of the regression, it is possible to estimate the enthalpy of volatilization (ΔH) by:

$$\Delta H = \frac{\text{slope}}{2.3} R \tag{6}$$

where R is the gas constant and 2.3 the conversion factor from decimal to natural log. The values of ΔH ranged from 22.4 ± 8.3 to 36.7 ± 9.1 kJ mol^{-1}. These phase change enthalpies are consistent with, but in the lower range, of those derived from other field measurements. Brunciak et al.[19] reported enthalpies of volatilization ranging between 19 and 87 kJ mol^{-1}, ΔH values observed by Currado and Harrad[32] varied from 27 to 112 kJ mol^{-1}.

Soil—Air Exchange and Extent of Background Soils as Secondary Sources of PCBs. Comparison of the fugacities of PCBs in soil and ambient air makes it possible to infer the direction of air—soil exchange. When fugacity in soil is higher than in ambient air there is a net volatilization of chemical. In contrast, if the fugacity in ambient air is higher than in soil, there is a net deposition of the chemical. Figure 3 shows soil/air fugacity ratios (f_s/f_a) versus K_{OA} for the three sampling campaigns in different seasons, at the rural and semirural Ebro basin sites. K_{OA} values for individual PCB congeners were estimated from the vapor pressure and corrected by the measured temperature as proposed by Falconer and Bidleman.[33] Regressions from Harner and Bidleman[34] were used to estimate K_{OA} for

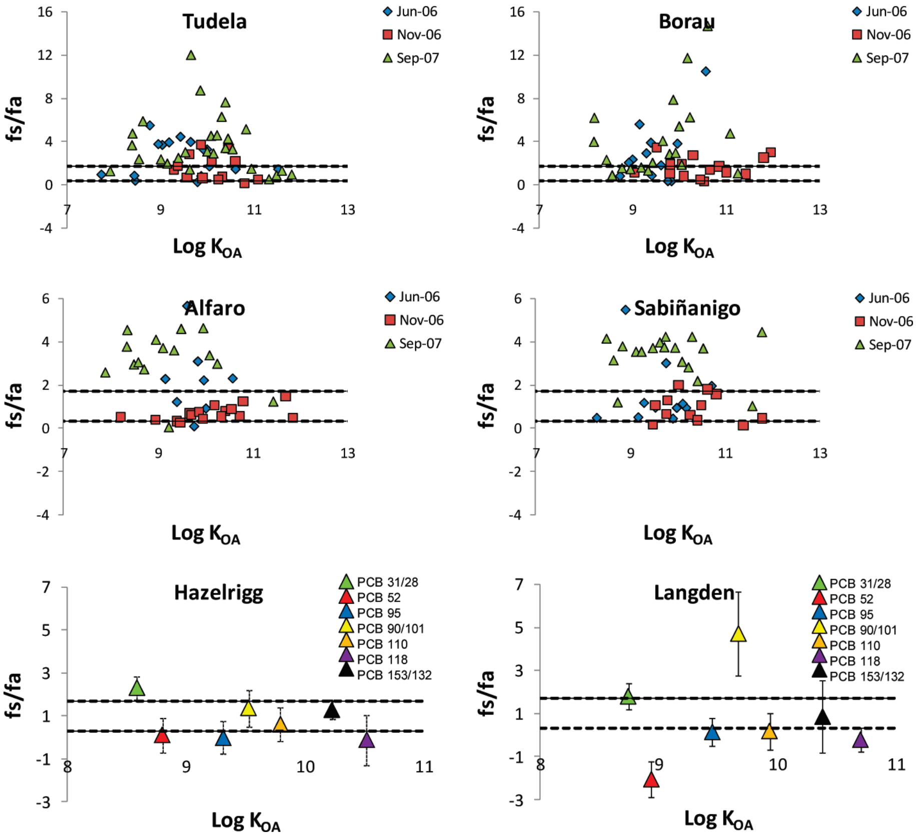

Figure 3. Seasonality of f_s/f_a versus log K$_{OA}$ in rural and semirural Ebro river sites (year/month/day) (top four graphics) and daily f_s/f_a versus log K_{OA} for selected individual congeners at the UK sites (bottom two graphics). f_s/f_a is indicated in mean and error bars indicate the SD of consecutives samples taken from 08/08/12 to 08/08/29 for Hazelrigg ($N = 9$) and from 08/09/17 to 08/09/24 for Langden ($N = 6$). Dash lines indicate the equilibrium interval.

non/mono-ortho and multi-ortho PCBs. Since there is an analytical uncertainty of 20% when analyzing gas phase concentrations with the low volume of sampled air[15,16] and the soil fugacity sampler is averaging the signal for 24 h, there is an uncertainty associated to the soil−air fugacity ratios, estimated to be lower than 70% (see Annex 1, SI). With this in mind, equilibrium would be represented by f_s/f_a in the range of 0.30 and 1.70. Four graphics at the top of Figure 3 show that all the PCBs appear to be close to equilibrium between the soil and air, even though some seasonal variations of f_s/f_a for individual PCBs were observed. In general, larger f_s/f_a values were observed for Tudela, Alfaro, and Borau in June 2006 and September 2007 than in November 2006, which demonstrates that during warm periods, soils increment their strength as a source, even for PCB congeners with higher K_{OA}. However, there is a higher predominance of the lighter PCBs at the soil surface air than in ambient air, which suggests that a vertical gradient of concentrations exists for the lighter congeners. In those sampling events where there is net volatilization, and to a lower extent when air and soil are close to equilibrium, it is possible that soils act as significant sources controlling the atmospheric occurrence of PCBs. Indeed, Figure 4 shows the strong relationship between soil and air PCB fugacity for the Ebro sampling sites, where air and soil are close to equilibrium or there is a net volatilization of PCBs. The mixture of PCBs found in the atmosphere is significantly correlated with the mixture of PCBs which escape from soil (fugacity in soil) with R^2 ranging between 0.35 and 0.74 ($p < 0.001$), independent of the season. This indicates that atmospheric levels of banned PCBs in Ebro river basin are now controlled by soils, although the magnitude of this re-emission is mostly controlled by seasonal variations. This trend is not as clear at UK sampling sites, where it explains a small fraction of the variability (from 0.1 to 0.37). Therefore, it is possible that the fact that regressions of f_s versus f_a only explain a small fraction of the variability is due to the importance of other sources, presumably primary, contributing to the atmospheric occurrence of PCBs. When there is net deposition, as in a scenario dominated by primary sources, net deposition from the air-to-soil cannot drive, in the short term, a variation of PCB concentrations in surface soils (and their f_s values) that are correlated to the atmospheric concentrations (or f_a values). This is explained by the PCB reservoir capacity, or the fugacity capacity, of the surface soil, that is hundreds of times that of the atmosphere.[10] Average f_s/f_a versus the K_{OA} for the UK sites is presented at the bottom of Figure 3. From the range of f_s/f_a for representative PCBs it can be concluded that air-soil exchange fluctuated from net sources to net sinks, with soils acting as sinks for PCB 52, 95, 110, and 118 and as a source for PCB 31/28 and 90/101 especially in Langden. Congeners PCB153/132 were close to equilibrium. Therefore, soils appear to act as sinks even in the summer in the NW England environment. This points to regional differences, since the equilibrium behavior in these Spanish and UK environments is different. These data support those obtained in a recent study by Li and co-workers,[35] who studied differences in air-soil equilibrium status of PCBs in China, the West Midlands of the UK and Central and Southern Europe. From a large database,

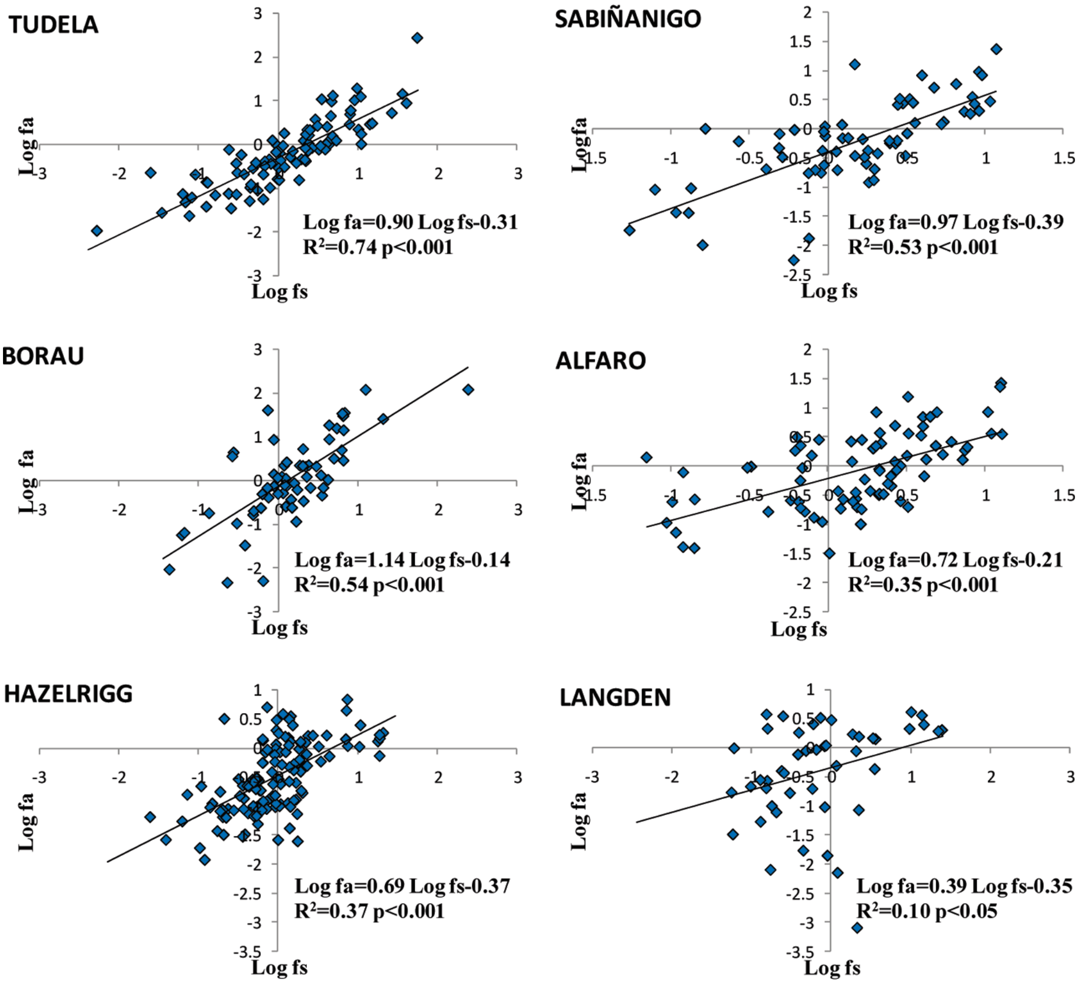

Figure 4. Log fugacity in soil (f_s) versus log fugacity in air (f_a) for Ebro and UK sampling sites.

they concluded that regions with low-moderate log K_{SA} values, as is the case of samples taken in the Ebro river basin, will be temporary or transient sinks of PCBs and actively involved in soil—air exchange and secondary emission. This study indicates that soils are now controlling the emissions of PCBs to the atmosphere in this region, to a greater extent during warmer periods than in colder ones. This means that secondary sources are beginning to play an important role, and PCBs are freely exchanging between the soil and the atmosphere. In contrast, regions where log K_{SA} values are elevated, due to higher SOM content or lower temperatures, as is the case at the UK sampling sites, soils will act as larger traps and accumulate more PCBs. They will need more time to reach equilibrium and become significant secondary sources. This finding is important since after decades of restriction in the use of PCBs, soils at higher latitudes and in cold environments are still far from approaching equilibrium with the air. According to Harner,[36] the maximum concentration in cold polar regions for some classes of POPs, such as more volatile PCBs are still to be attained. If Li et al.'s[35] hypothesis is correct, then K_{SA} should be inversely correlated with the f_s/f_a ratio. For the data set reported here, this only happens for some low chlorinated PCBs such as PCB 31, 52 and 74, but not for the high chlorinated PCBs (Figure S3, SI). This indicates that secondary sources are more relevant for the lower MW congeners.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details about sampling sites, soil, and air concentration tables and statistical analyses of soil concentration, soil fugacity and K_{OC} are also included. This material is available free of charge via the Internet at http://pubs.acs.org

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