

Ubiquitous Net Volatilization of Polycyclic Aromatic Hydrocarbons from Soils and Parameters Influencing Their Soil–Air Partitioning

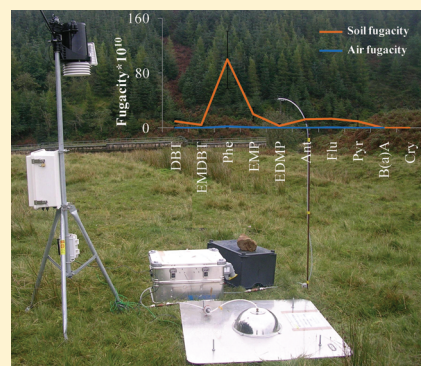
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S Supporting Information

ABSTRACT: Soils are a major reservoir of organic pollutants, and soil–air partitioning and exchange are key processes controlling the regional fate of pollutants. Here, we report and discuss the soil concentrations of polycyclic aromatic hydrocarbons (PAHs), their soil fugacities, the soil–air partition coefficients (K_{SA}) and soil–air gradients for rural and semirural soils, in background areas of N-NE Spain and N-NW England. Different sampling campaigns were carried out to assess seasonal variability and differences between sampling sites. K_{SA} values were dependent on soil temperature and soil organic quantity and type. Soil fugacities of phenanthrene and its alkyl homologues were 1–2 orders of magnitude higher than their ambient air fugacities for all sampling sites and periods. The soil to air fugacity ratio was correlated with soil temperature and soil redox potential. Similar trends for other PAHs were found but with lower fugacity ratios. The ubiquitous source of PAHs from background soils to the atmosphere found in all temperate regions in different seasons provides an indirect evidence of potential in situ generation of two to four ring PAHs and their alkyl homologues in the surface soil. We discuss this hypothetical biogenic source and other potential processes that could drive the high soil to air fugacity ratios of some PAHs.



1. INTRODUCTION

Soils are the major reservoir and one of the major sinks for persistent organic pollutants (POPs) due to their strong affinity to organic matter. The fate and toxic effects of POPs are strongly affected by the quality and quantity of soil organic matter (SOM),^{1–3} which controls POPs availability for biological degradation, burial or revolatilization from soil. Indeed, the amount of organic matter plays an important role in soil–air and soil–water partitioning of polycyclic aromatic hydrocarbons (PAHs), as derived from the widely accepted paradigm of hydrophobic interactions of POP with organic matter.^{4–6} Several studies^{7–9} have pointed out that SOM quality, usually related to its aromatic content, also influences chemical partitioning that enhances the soil sorption capacity for PAHs. Some authors^{10–12} have assessed recently the potential role of black or soot carbon on the sorption of PAHs to soil, but these studies have concluded that carbonaceous particles account for a negligible fraction of the overall sorption capacity of most background soils, due to the low black to organic carbon ratio.

The occurrence of PAHs in soils and other environmental media has received much attention since these chemicals were first found by Blumer 1961.¹³ Combustion of fossil fuels such as coal or petroleum in domestic and industrial applications or biomass combustion are major anthropogenic sources of PAHs to the environment. In addition to combustion processes, there is some evidence for biogenic PAH formation in the environment.

Perylene is believed to be produced biologically from pigments of fungi, insects, or marine organisms¹⁴ and other authors have described field evidence for in situ formation of phenanthrene, methylphenanthrene, retene (1-methyl-7-iso-propylphenanthrene), and pimanthrene (1,7-dimethylphenanthrene) in remote soils and sediments.^{15,16} More recent studies^{17–21} found large amounts of phenanthrene and naphthalene in tropical soils, *Magnolia* flowers and termite nests, highlighting the biological production of some PAHs. Despite the potential importance of biogenic PAHs in the environment, it is still usually assumed that most PAHs, including phenanthrene, are predominantly anthropogenic.

The recent development of a soil fugacity sampler^{22,23} makes it possible to unequivocally determine soil–air partition coefficients and gradients, and to study the relevant variables affecting them. The main objectives of this study were therefore to (i) study the temporal and spatial variability of soil PAH fugacity and soil–air partition coefficients (K_{SA}) in a range of rural, semirural and urban locations; (ii) determine the soil/air fugacity quotients and the variables affecting them, in different soil types, under field conditions; (iii) consider the field evidence for possible in situ

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production of lighter PAHs in temperate areas to improve the understanding of PAH cycling and their implications.

2. MATERIALS AND METHODS

Air Sampling and Soil Sampling. Ten nonagricultural sampling sites (i.e., sites never used for agricultural activities) were selected; six rural: Borau, Alfaro, Nájera, Lasieso, Uruñuela located along the Ebro river basin (N-NE Spain) and Langden (near Lancaster, UK); three semirural: Tudela, Sabinanigo (Ebro river basin-Spain) and Hazelrigg (near Lancaster, UK) and one urban at the garden of the Institute of Environmental Assessment and Water Research, IDAEA-CSIC, in Barcelona (NE Spain). Table S1 in the Supporting Information (SI) summarizes the sites and the duration of the sampling campaigns.

PAH fugacity in surface soils (f_s), was measured by analyzing the PAH concentrations in air that had been equilibrated in situ with the soil surface using the soil fugacity sampler described by Cabrerizo et al.²³ (see SI Figure S1). Ambient air concentrations, hereafter defined as the PAH concentrations in air at a height of 1.5 m were determined using a low volume sampler with glass fiber filters and polyurethane foams identical to those used to determine soil fugacities. These concentrations were used to determine ambient air fugacities (f_a). Samples used to calculate f_s and f_a were an integration of 24 h of sampling time. The uncertainty associated to integrate the fugacity during a 24 h periods, due to diurnal variation of temperatures, is lower than 70% (see Annex 3, SI) Soil samples were taken after air sampling by gently collecting the soil surface layer (top 0.5–1 cm). For this study, a total of 48 soil fugacity measurements, 47 ambient air concentrations, and 22 top surface soils were sampled and analyzed (Table S1, SI). After sampling, air and soil samples were stored in freezers at $-20\text{ }^\circ\text{C}$ until analysis. 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 in the SI: soil temperature (Soil T), ambient air temperature (Air T), soil water content (SWC); precipitation, soil organic carbon (TOC) or organic carbon fraction (f_{OC}), surface soil redox potential, pH, 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 multiple parameter regression analysis shown below to avoid double use of parameters. No significant 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 potential were considered here as indirect parameters of mineralization and aromaticity to assess the influence of the organic matter quality.

All samples were analyzed for the following parent PAHs: phenanthrene (Phe), anthracene (Ant), fluoranthrene (Flu), pyrene (Pyr), benzo(a)anthracene (B(a)ant), chrysene (Cry), benzo(b and k)fluoranthene (B(b and k)f), benzo(e)pyrene (B(e)pyr), benzo(a)pyrene (B(a)pyr), perylene (Pery), dibenzo(a,h)anthracene (Dib(a,h)ant), benzo(g,h,i)perylene (B(g,h,i)per), indeno(1,2,3-cd)pyrene (In(1,2,3-cd)pyr), dibenzothioophene (DBT) and alkyl homologues, methyl dibenzothioophenes (Σ MDBT), methylphenanthrenes (Σ MP), dimethylphenanthrenes (Σ DMPD).

Details of sampling procedures are given elsewhere²³ and the specific details on QA/QC for the set of samples considered here are given in Annex 1, SI.

3. RESULTS AND DISCUSSION

Occurrence of PAHs in Ambient Air. Ambient air concentrations for the sites in the Ebro river basin, Barcelona and the UK rural sites are shown in Figure 1 (and SI Figure S2) as fugacities (Pa) estimated by

$$f_a = 10^{-9} C_A R T / MW \quad (1)$$

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

All C_A and Air T in the Ebro river basin and UK sites airshed are listed in the SI (Tables S2a–S2e and Figure S2). PAHs with molecular weights higher than those of chrysene could not be quantified in the gas phase due to their low concentrations and low sampling volumes (14 m^3). Consequently, only PAHs that range from Phe to Cry are considered here. The PAH pattern is dominated by the low molecular weight PAHs, such as Phe, Σ MP, and Flu. On average, Phe was the most abundant compound in all the samples, independent of the sampling site, contributing up to 44% of the total PAHs. The ranges of ambient air concentrations of Phe, Σ MP and Flu in background rural areas of the Ebro river basin were $0.74\text{--}2.20\text{ ng m}^{-3}$, $0.16\text{--}1.03\text{ ng m}^{-3}$; $0.09\text{--}0.79\text{ ng m}^{-3}$, respectively. At the semirural sites in the Ebro river basin, the range of concentrations were $1.43\text{--}3.27\text{ ng m}^{-3}$, $0.22\text{--}0.68\text{ ng m}^{-3}$, $0.33\text{--}2.04\text{ ng m}^{-3}$ for Phe, Σ MP and Flu, respectively, and the concentrations in Barcelona's urban atmosphere were $1.66\text{--}4.67\text{ ng m}^{-3}$, $1.03\text{--}2.17\text{ ng m}^{-3}$, $0.57\text{--}1.16\text{ ng m}^{-3}$. Ambient air concentrations at the selected rural and semirural sampling sites in NW England were in the same range as those in NE Spain: $1.55\text{--}1.74\text{ ng m}^{-3}$, $0.29\text{--}0.38\text{ ng m}^{-3}$, and $0.28\text{--}0.37\text{ ng m}^{-3}$ for Phe, Σ MP and Flu, respectively. Data found in rural European regions are similar to those reported here.^{24,25}

Occurrence of PAHs in Soils. Individual PAH concentrations in soils (ng g^{-1} dry weight) and soil physicochemical properties for all the sampling locations are reported in the SI (Tables S3a–S3c and Figure S3). The PAH profile in soil was dominated by high molecular weight (HMW) compounds. The most abundant compounds are those having four (Flu, Pyr, and Cry) and five aromatic rings (B(b and k)f and B(a)pyr). This distribution is consistent with previous studies in temperate soils.²⁶

The influence of the physicochemical properties on PAH concentration in soils was assessed by means of multiple regression analysis using SPSS 15.0. The regression parameters considered were Soil T , Air T , SWC, precipitation, SOM quantity and quality. Initially we tested soil PAH concentrations against each individual parameter for all sites in UK and Spain (see Annex 2, SI), and only f_{OC} and f_{OC}/f_N were significantly correlated (p -level < 0.05) with individual PAH soil concentrations (SI Table S4a,b and Figure S4), explaining 18–45% of the variability depending on the individual PAH. The use of multiple parameter regression did not improve the significance of regression with other variables. The lower the f_{OC}/f_N ratio, the lower the PAH concentration, suggesting that not only organic matter quantity, but also organic matter quality affects the PAH reservoir in soils. Concerning temporal trends, there was no statistically

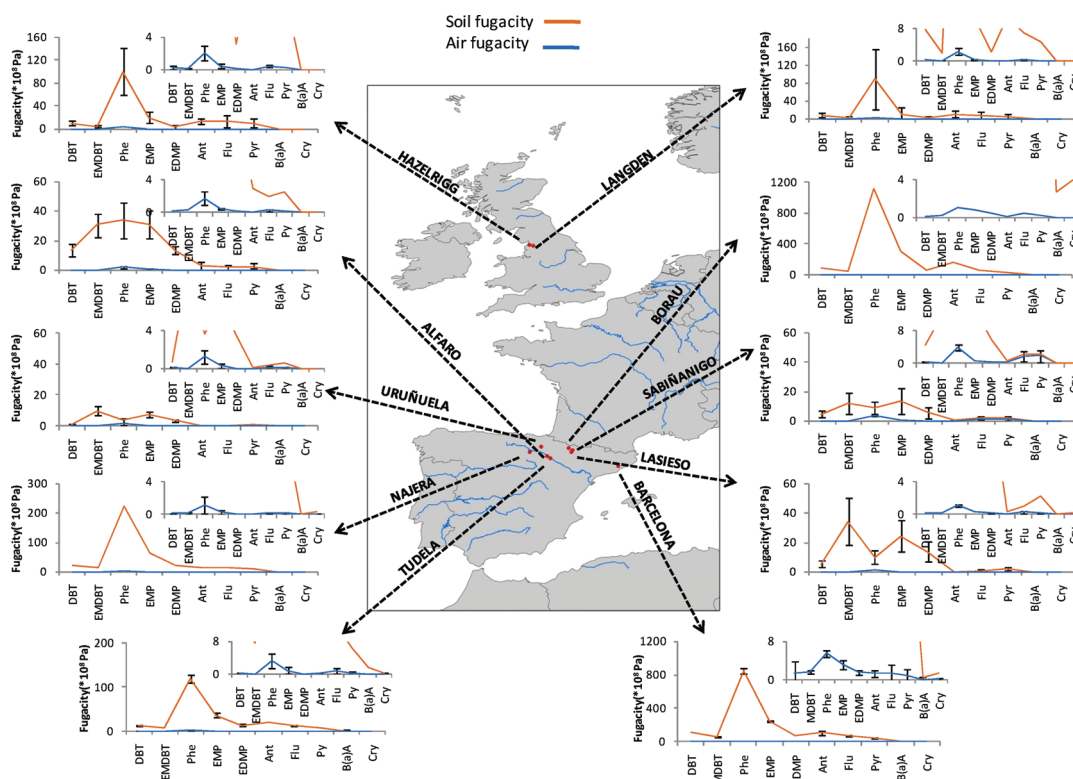


Figure 1. PAH fugacity in soil and ambient air PAH (Pa) for the different sampling sites. Note that the small figure inside the larger one is the same figure showing the soil and air fugacities of 4–5 ring PAHs with a different scale.

different soil PAH concentrations with respect to soil temperature or ambient air temperature for the three sampling periods in Ebro’s watershed soils.

PAH Fugacity in soils. Because of a lack of direct field measurements, soil fugacities of POPs have traditionally been estimated from the soil concentration and the K_{SA} , which can be derived from the octanol-air partition constant K_{OA} .^{10,27} Traditionally, the consideration of PAH concentrations in soil to calculate soil fugacities overestimates the value of soil fugacity, since both extractable and unextractable forms of pollutants are considered. Only those pollutants present in the extractable form would be able to escape from soil and would be sampled by the soil fugacity sampler. Nonextractable PAHs, strongly bound to SOM, may not contribute, in this study, to the PAH fugacity in soil measurements. The PAH fugacity in soil was determined directly under field controlled conditions by

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

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.²³ Figure 2 shows the soil fugacity, on natural logarithmic scale, for the three sampling campaigns in selected sites of the Ebro river basin and at Barcelona. Among the PAHs detected, Phe and Σ MP always had the highest fugacity independently on the season and soil type. No statistically significant correlations were found between individual PAH fugacity in soil and reciprocal Soil T , organic matter quantity, and other variables (redox potential, f_N , etc) when tested by a multiple parameter regression model, probably because soil and atmosphere are closely coupled and it is necessary to study them together using the K_{SA} . K_{SA} describes

the equilibrium partitioning of a chemical between the air and the soil and was calculated as follows:

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

where C_S is the PAH concentration in surface soil ($ng\ gdw^{-1}$).

Factors Affecting Soil–Air Partitioning of PAHs. The influence of T and organic matter quantity and type on K_{SA} was studied separately using single least-squares regression. Except for T , the variables were not statistically significant (see Annex 2, SI) when their influence was assessed individually, so we used a multiple parameter least-squares regression equation, since variability in K_{SA} could depend on more than one descriptor, whose effects could mask each other. A multiple parameter regression of the following type was used on all the samples (from Spain and UK) and PAHs analyzed:

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

where $a-e$ are the regression parameters which were significantly different from zero ($p < 0.001$). The term f_N was selected instead of f_{OC}/f_N to avoid double entry of f_{OC} in the equation. The fitted eq 4 explained 56% of the variability ($r^2 = 0.56$, $p < 0.001$, $n = 341$). The fitting parameters were $a = -2549 \pm 352$, $b = 7028 \pm 1147$, $c = -148 \pm 53$, $d = -90 \pm 19$, $e = 99 \pm 5$. Because there is a large range in K_{OA} for different PAHs the last term of eq 4 explains an important fraction of the variability (48%), consistent with the fact that organic matter quantity and K_{OA} are the key variable and descriptor, respectively, to account for soil–air partitioning.^{10,27} Results here are in agreement with previous studies²⁸ that show that a variability of only a factor of 2.5 in the OC-water partition coefficients is due to quality (composition)

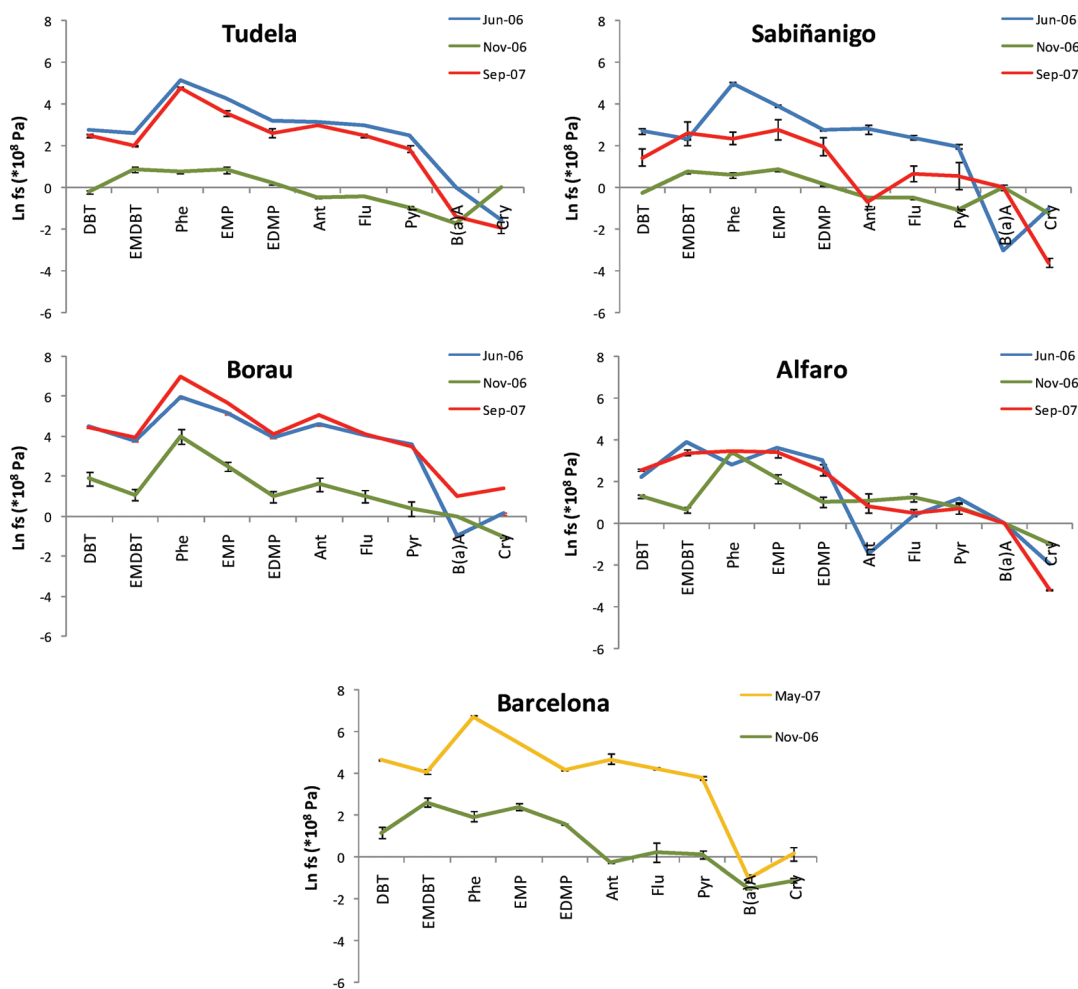


Figure 2. PAH fugacity in soil in selected sampling sites of the Ebro's River Basin and Barcelona for different seasons.

of organic matter but the remaining variability is explained by the K_{OW} . Nguyen and co-workers²⁹ estimated, using a polyparameter LFER, that the contribution of hydrophobicity to the variability of the SOM–water partition coefficient, was between 41 and 54% for aromatic hydrocarbons, with the remainder explained by differences in polarizability, basicity, etc. In order to obtain compound specific values for the fitting parameters explaining the role of organic matter quality such as soil redox potential, f_N (f_N was selected instead of f_C/f_N to avoid f_{OC} to appear in both sides of equation) and temperature on measured soil organic carbon–air partition constant (K_{OCA}), the empirical eq 5 was applied to individual compounds:

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

where

$$K_{OCA} = K_{SA}/f_{OC} \quad (6)$$

Table 1 provides the values of the fitting parameters a – e for individual PAHs in the multiple parameter linear least-squares regressions and the level of significance (p) for each parameter considered. The parameters a – e are, for most compounds, significantly different from zero (p -level < 0.05) and were able to explain between 45% and 62% of the K_{OCA} variability. When K_{OCA} was regressed against each individual parameter (see SI),

there were no significant correlations for the parameters considered, except T (SI Figure S5), presumably because these parameters are affecting the soil–air partitioning at the same time thus masking the effects of other variables. The significant influence of $1/T$ on K_{OCA} is in agreement with previous studies.³⁰ From the values of parameter b it is possible to estimate the enthalpy of volatilization (ΔH) by

$$\Delta H = \frac{b}{2.3} R \quad (7)$$

where R is the gas constant. The values of ΔH ranged from 30 to 49 kJ mol^{-1} . These are lower or in the lower range of the reported vaporization enthalpies from the pure compound, suggesting that POPs sorption to SOM is weaker than sorption to the pure compound (SI Table S5). Other studies have shown the high affinity of POPs to form clusters in lipid-like phases due to the strong PAH–PAH affinity.³¹ K_{OCA} was negatively correlated with soil redox potential and f_N . These results confirm a relationship between PAH sorption and organic matter composition. Indeed, several studies over the last decades^{9,32,33} have reported variations in the sorption potential of organic compounds for different fractions of organic matter such as humin and fulvic acids or humins. Here, the influence of redox potential may be related to the aromatic content of SOM (not measured) consistent with other studies.⁹

Table 1. Multiple Parameter Least Squares Regression of K_{OCA} for Individual PAHs^a

	R^2	a	b	p	ΔH	c	p	d	p	e	p	N
DBT	0.56	-27.64	13551	<0.001	49 ± 8	-6.33	<0.001	-1.47	<0.001	-0.85	<0.05	41
ΣMDBT	0.59	-29.68	12738	<0.001	46 ± 10	-5.45	<0.05	-2.40	<0.05	-0.97	>0.05	30
Phe	0.51	-21.65	11659	<0.001	42 ± 9	-6.15	<0.001	-1.57	<0.001	-0.82	<0.05	41
ΣMP	0.45	-19.82	8170	<0.001	30 ± 8	-1.50	>0.05	-1.06	<0.05	-0.51	>0.05	39
ΣDMP	0.59	-28.85	9491	<0.001	34 ± 10	-0.77	>0.05	-1.14	<0.05	-0.99	<0.05	41
Ant	0.51	-12.67	11160	<0.001	40 ± 12	-8.89	<0.001	-1.98	<0.001	-1.44	<0.05	41
Flu	0.46	-16.25	11069	<0.001	40 ± 11	-6.41	<0.05	-1.64	<0.001	-1.51	<0.05	41
Pyr	0.52	-26.33	13552	<0.001	49 ± 10	-6.03	<0.05	-1.72	<0.001	-1.44	<0.05	41
Cry	0.62	-1.80	4670	>0.05		-2.48	>0.05	-1.45	<0.001	-1.56	<0.001	35

^a $a-e$ are the fitting parameters in the equation: $\log K_{OCA} = a + b(1/T) + c(\log \text{redox}) + d(\log f_N) + e(\log \text{altitude})$, p is the level of significance for each parameters, ΔH the enthalpy of volatilization in kJ mol^{-1} , and N the number of samples considered.

Ubiquitous Soil to Air Volatilization of PAHs. The comparison of fugacities in soil and ambient air makes it possible to infer the direction of air-soil exchange (see Figure 1). When fugacity in soil is higher than fugacity in ambient air, there is a net volatilization of chemical. In contrast, if fugacity in ambient air is higher than fugacity in soil there is net deposition of the chemical. Figure 1 shows large fugacities in soil compared with fugacities in ambient air for PAHs with 2–3 aromatic rings and their alkyl derivatives at all sampling sites. These gradients were much smaller or close to unity for PAHs with 4–5 aromatic rings (note that in Figure 1, the small graph inside the larger one represents soil/air fugacities but with a different scale so differences are discernible for the 4–5 ring PAHs).

It is also relevant to evaluate if these gradients are maintained during different sampling periods (diurnal variability) or seasons. Figure 3 shows soil/air fugacity ratios ($\ln f_s/f_a$) for three different campaigns in three different seasons versus K_{OCA} in the rural and semirural Ebro sites, urban Barcelona and the daily $\ln(f_s/f_a)$ for sampling sites in the UK. Since there is an analytical uncertainty of 20% when analyzing gas phase concentrations with the low volume of sampled air²³ 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 3 of the SI). Therefore equilibrium would be represented by $\ln(f_s/f_a)$ in the range of +0.53 and -1.20 (see Annex 4, SI for methods used to estimate K_{OCA} for individual PAHs).

The general trend was that values of $\ln(f_s/f_a)$ decreased with increasing K_{OCA} , confirming that the soil is an important source of lighter PAHs to the atmosphere at the rural, semirural and urban sites. Cousins and Jones³⁴ reported the soil as a source of lighter PAHs for all the combinations of SOM and temperature studied and suggested the possibility of biological formation of some lighter PAHs in the soil. Seasonal variation of soil/air fugacity quotients for individual PAHs was observed in the Ebro river watershed and in Barcelona. The values of $\ln(f_s/f_a)$ were larger in early and late summer (June 2006 and September 2007) than in early winter (November 2006). Most of the individual PAHs were close to, or at, equilibrium in November 2006 in Sabiñánigo, Alfaro and Tudela, while in Borau and Barcelona $\ln(f_s/f_a)$ indicates the soil as a continuous source of PAHs through the year. Similarly, daily $\ln(f_s/f_a)$ for sampling sites in the UK show a decrease of $\ln(f_s/f_a)$ with increasing K_{OCA} , indicating that the soil is an important source of lighter PAHs. The equilibrium status for higher molecular weight PAHs (Flu, Pyr, B(a)p and Cry) is not clear. Soil is moving from equilibrium toward net volatilization. This is in agreement with previous work³⁴

suggesting that air concentrations of the low molecular weight PAHs in the temperate areas are may be controlled by the re-emissions of these chemicals from the soil. It seems that for the heavier molecular weight PAHs, soils in transition between being a sink and a source, thus close to air–soil equilibrium.

In order to study the influence of soil characteristics and temperature on fugacity gradients, the compound specific f_s/f_a were regressed against the different parameters describing the soil properties (as described above) and only Soil T and redox potential resulted in significant correlations, thus f_s/f_a is given by eq 8:

$$\log f_s/f_a = a + b(1/T) + c(\log \text{redox}) \quad (8)$$

Values of $a-c$ for each PAH are given in SI Table S6. Fugacity ratios increase at higher temperatures and higher soil redox potential. The influence of temperature is consistent with the seasonal variability (Figure 3) and demonstrates that during warm periods soils increment their strength as a source. The influence of redox potential can be related to soil organic matter quality, more oxidized soils have lower capacity to retain PAHs. However, redox potential is also closely related to soil microbiology, an important factor that could be related to in situ production of PAHs from degradation of organic matter.

For phenanthrene and its alkyl compounds soil fugacity was between 10 and 600 times higher than the ambient air fugacities, thus indicating a large net volatilization gradient. It is difficult to determine which environmental process can support these large volatilization gradients over time. Potential entries of PAHs in soils are atmospheric deposition through wet deposition, aerosol-bound dry deposition and diffusive exchanges, while the potential losses of PAHs are volatilization, degradation, and leaching to deeper soils. The large soil to ambient air fugacity gradient implies an important source of these compounds to the soil surface. The candidates are (i) exchange of compounds from deeper soils, which is unlikely due to low diffusivity in soil, (ii) dry and wet deposition of aerosol bound PAHs could account for inputs to surface soils. If such atmospheric deposition was important for the low MW PAHs in addition to the high MW PAH (for which it may be important), then the gradient would also be observed for the heavier PAHs, which is not true (Figures 1 and 3). (iii) Soil to air fluxes are so low that gradients due to historical inputs cannot be erased. If this was true, the flux would also be low for the high MW PAHs, but a large gradient is not observed. In addition, the soil–air gradients for polychlorinated biphenyls,³⁵ compounds with physical-chemical properties

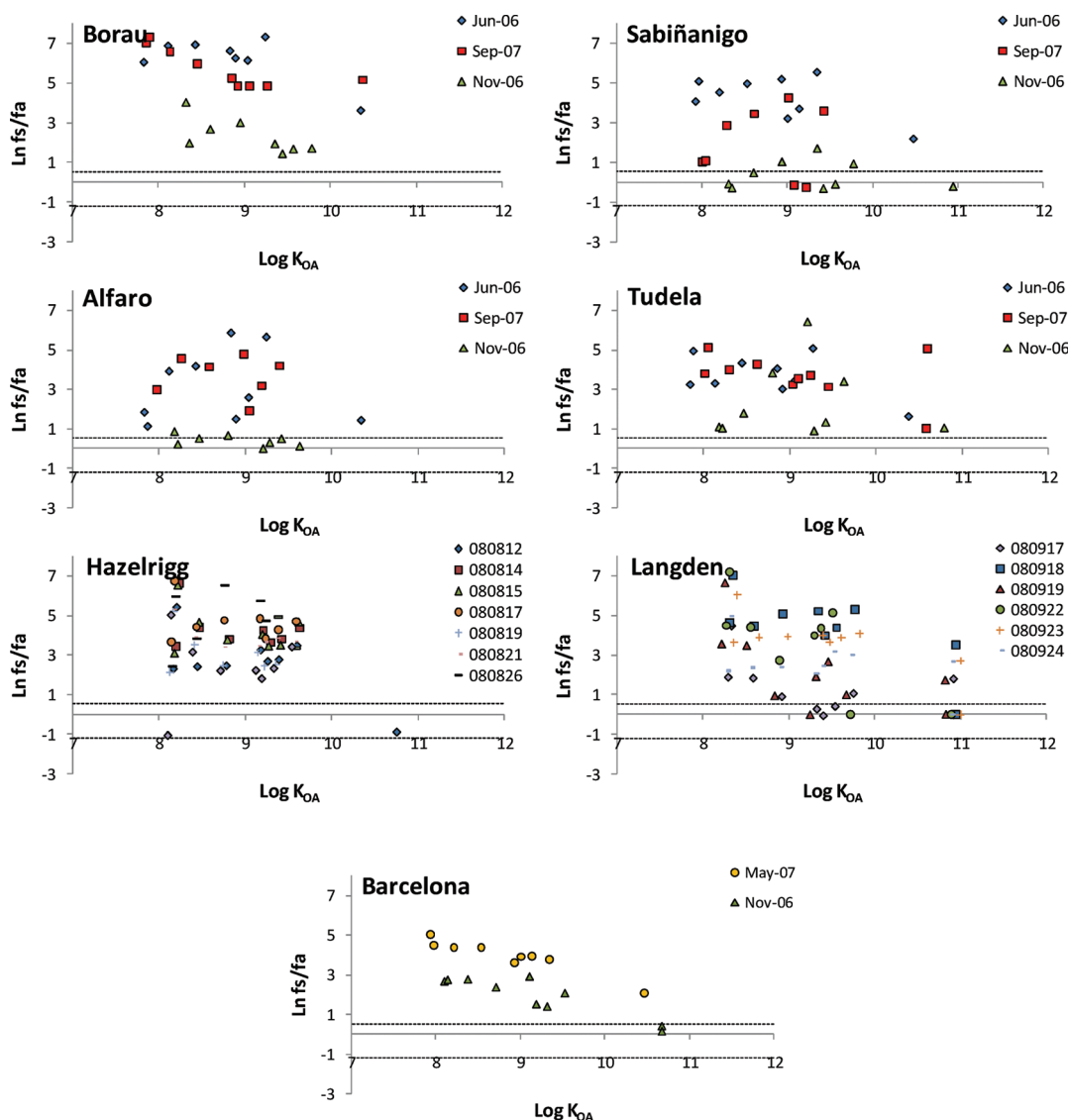


Figure 3. Seasonality of $\text{Ln}(f_s/f_a)$ versus $\text{Log } K_{\text{OA}}$ in rural and semirural Ebro river watershed sites and urban Barcelona and daily (year/month/day) $\text{Ln}(f_s/f_a)$ versus K_{OA} in UK sites. Dash lines indicate the equilibrium interval.

similar to those of PAHs, are much lower and evidence has been found that there is a close soil–air coupling which is not consistent with extremely low fluxes. (iv) The ubiquitous volatilization gradients of PAH suggest that there is possibly a biogenic production of PAHs in the soil in order to keep the observed volatilization gradients. Soil bacteria and fungi are known to be significant producers of some volatile hydrocarbons, such as isoprene which was shown to be produced by actinomycetes and by various bacterial species.³⁶ Regarding polycyclic hydrocarbons, several authors^{20,37} have found evidence for biological formation of naphthalene in termite nests of tropical forests. Wickström and Tolonen¹⁵ found phenanthrene, methylphenanthrene, and methylanthracene in preindustrial lake sediments. Laflamme and Hites¹⁶ detected the phenanthrene homologues retene (1-methyl-7-iso-propylphenanthrene) and pimanthrene (1,7-dimethylphenanthrene) in uncontaminated remote soils and sediments, and these authors suggest biogenic formation as a potential source. It is believed that microbial production of gaseous hydrocarbons has an important role in the

plant-microorganism and interspecies interactions; alkanes are involved in the synthesis of epicuticular wax layer, isoprenoids of higher plants play a role in protecting plants against herbivores and pathogens, and volatile unsaturated hydrocarbons have been implicated as possible causative agents of soil fungistasis.³⁸ Wilcke³⁹ has reviewed PAH occurrence in soils and suggests that naphthalene and phenanthrene in rural soils may be the result of background occurrence (diffuse pollution or biogenic sources), while the rest of PAHs have a clear anthropogenic source. All these previous reports and the high soil to air gradients suggest that microbial communities play an important ecological and physiological role in the synthesis of hydrocarbons, although they are frequently not quantified in existing models.

It is noteworthy that even at the urban site located at the garden of IDAEA-CSIC, in a residential/university campus area of Barcelona, there was a consistent soil to air volatilization for all the sampling events. This observation indicates that even in semiurban sites, biogenic sources of PAHs may dominate the

occurrence of PAHs in soils, or at least the fraction that is available for soil–air exchange.

Implications of Ubiquitous Net Volatilization of PAHs from Soils and Biogenic Sources. Although there is a considerable interest in quantifying PAHs emission from secondary sources such as soil (this study) or oceans^{40,41} little information is available on the total release of biogenic PAHs and it is not considered in models. Our data suggest an important entry of biogenic phenanthrene into the atmosphere that could have important effects on atmospheric chemistry and air quality since it is ubiquitous. If biogenic phenanthrene production in temperate environments is greater than currently thought, it would be necessary to reconsider the inclusion of this and other PAHs in the priority pollutant lists. At this stage, we cannot quantify the magnitude of the biogenic releases and more studies focusing on bacterial production of PAHs and isotopic characterization are needed to understand and clarify the ecological and environmental impacts of PAHs.

■ ASSOCIATED CONTENT

S Supporting Information. Details about sampling sites, samples analysis, soil and air concentration tables are included. This material is available free of charge via the Internet at <http://pubs.acs.org>

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