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Mosses as an integrating tool for monitoring PAH atmospheric deposition: Comparison with total deposition and evaluation of bioconcentration factors. A year-long case-study

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HIGHLIGHTS

- Spatial and temporal trends of PAH atmospheric deposition were studied in a remote area.
- Biomonitoring via moss was compared to PAH fluxes in total deposition.
- Total deposition was determined via throughfall samples.
- Seasonal variations of PAH content in moss and PAH fluxes followed a similar trend.
- PAH fractionation between total deposition and the mosses occurs.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) atmospheric deposition was evaluated at a remote site in Northern Spain using moss biomonitoring with *Hylocomium splendens* (Hedw.) Schimp., and by measuring the total deposition fluxes of PAHs. The year long study allowed seasonal variations of PAH content in mosses to be observed, and these followed a similar trend to those of PAH fluxes in total deposition. Generally, atmospheric deposition of PAHs is greater in winter than in summer, due to more PAH emissions from domestic heating, less photoreactivity of the compounds, and intense leaching of the atmosphere by wet deposition. However, fractionation of these molecules between the environmental compartments occurs: PAH fluxes in total deposition and PAH concentrations in mosses are correlated with their solubility ($r = 0.852$, $p < 0.01$) and lipophilic properties (K_{ow} , $r = 0.768$, $p < 0.01$), respectively. This annual study therefore showed that atmospheric PAH fluxes can be estimated with moss biomonitoring data if the bioconcentration or 'enriching' factors are known.

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1. Introduction

Long range transport through the atmosphere and deposition of persistent organic pollutants (POPs) leads to uncontrolled exposure of human populations and biota to these toxic and

bioaccumulating substances (UNECE, 1998). The 1998 Aarhus protocol (LRTAP convention) and 2001 Stockholm convention on POPs, aim to eliminate and/or restrict the production and use of selected POPs.

Polycyclic aromatic hydrocarbons (PAHs) are POPs composed of fused aromatic rings and originate from fossil or non fossil fuels by pyrolysis or pyrosynthesis. The main sources of PAHs in the environment are aluminium production, coke production from coal, wood preservation and fossil fuel combustion (traffic, domestic heating, electricity production) (Ravindra et al., 2008).

The biosphere intercepts these contaminants during atmospheric deposition: wet deposition and dry deposition (Finlayson Pitts and Pitts, 2000). In this way, biomonitors like conifer needles (Ratola et al., 2010), deciduous leaves (De Nicola et al., 2013), lichens (Blasco et al., 2011) and mosses/bryophytes (Foan et al., 2014) can be a useful strategy to monitor the exposure of wildlife and human populations to these pollutants. Due to the lack of root system and cuticle, as well as their high cationic exchange capacity and surface area to volume ratio, mosses are excellent subjects for biomonitoring (Harmens et al., 2013). Atmospheric deposition can also be evaluated by collecting total deposition (dry + wet) via bulk deposition (Fernández et al., 2003; Esen et al., 2008) and throughfall deposition.

The results described in this study are the first to be based on year long measurements of PAH concentrations in biomonitors and in total deposition. The purpose of our study was to (i) determine atmospheric deposition at a remote site in a Nature Reserve in Northern Spain by biomonitoring, (ii) assess monthly and annual PAH atmospheric deposition fluxes, (iii) compare biomonitoring with measurements of contaminants in total deposition and, (iv) identify the emission sources.

2. Materials and methods

2.1. Sampling

Bertiz Nature Reserve (43.14°N, 1.61°W) is located in the North west of Navarra (Spain), near the French border and has an oceanic climate with average annual temperatures of 13.7–15.0 °C (Aldabe et al., 2012). Vegetation is mainly beech forest (*Fagus sylvatica* L.), although there are some patches of oak woods (*Quercus robur* L.) and a few pastures. Sampling devices were set up in an 'intensive plot' within the Bertiz catchment, which is part of the International Cooperative Programme Integrated Monitoring network (ICP IM).

Year long biomonitoring of PAH deposition requires a high surface area of mosses, and the quantity available near the intensive plot was insufficient. Therefore an active biomonitoring study was set up. *Hylocomium splendens* (Hedw.) Schimp. moss was collected on 11 June 2010 from a site located only 35 km from the Bertiz Nature Reserve, in the Aralar Range, showing low levels of contamination and covered in bryophytes. The mosses were transported to the Bertiz site in polyethylene trays and left for a year under the beech forest canopy similar to their natural habitat. The high number of trays (18) ensured the greatest spatial variability. The mosses were sampled every month from June 2010 until May 2011, using a predetermined random plan (1/6th of 8 different trays to sample ~0.3 m²), and transported in an icebox to the laboratory, where they were placed in darkness at 20 °C.

A total of 6 collectors were distributed over the intensive plot under the beech forest canopy to collect total deposition. The collection device consisted of glass funnels fitting into 2 L dark glass bottles (described in Foan et al., 2012). Total deposition samples were recovered every 15 days from June 2010 to May 2011.

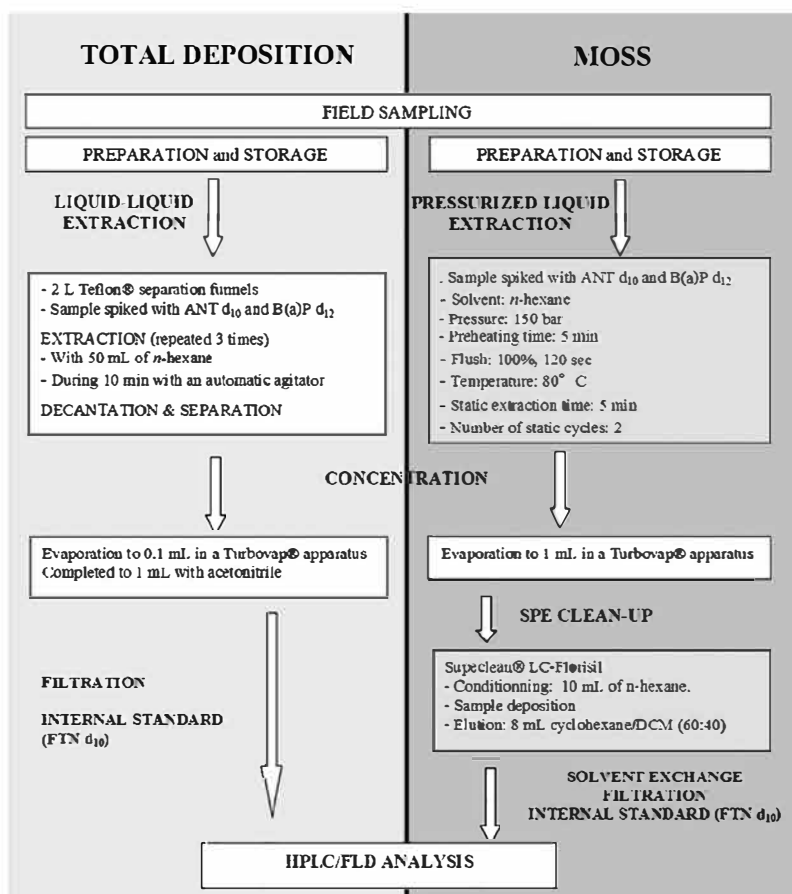


Fig. 1. Diagram illustrating all operations of the analytical procedure to determine PAH concentrations in total deposition and moss samples by solvent extraction.

Table 1
Quantification limits and reproducibility obtained during validation of the analytical procedure of PAH determination in total deposition and in mosses. Quantifiable compounds are in bold type.

Compounds	Mosses			Total deposition	
	LOQ ^a (pg)	LOQ ^b (ng g ⁻¹ DW)	RSD ^c (%)	LOQ ^d (ng L ⁻¹)	RSD ^e (%)
Acenaphthene (ACE)	22	1.0	5	3.2	ND ^f
Fluorene (FLR)	52	2.5	9	7.6	15
Phenanthrene (PHE)	27	1.3	11	4.0	18
Anthracene (ANT)	4	0.2	22	0.6	6
Fluoranthene (FTN)	28	1.3	4	4.1	4
Pyrene (PYR)	13	0.6	1	1.9	7
Benzo(a)anthracene (B(a)A)	15	0.7	18	2.0	6
Chrysene (CHR)	16	0.8	12	2.1	6
Benzo(b)fluoranthene (B(b)F)	6	0.3	9	0.8	ND
Benzo(k)fluoranthene (B(k)F)	3	0.1	18	0.4	8
Benzo(a)pyrene (B(a)P)	12	0.6	12	1.6	5
Dibenzo(a,h)anthracene (D(ah)A)	7	0.3	7	0.9	ND
Benzo(g,h,i)perylene (B(ghi)P)	6	0.3	9	0.8	13
Indeno(1,2,3-c,d)pyrene (IND)	22	1.0	ND	2.9	ND

^a Instrumental quantification limits (LOQ), determined with a standard solution of PAHs at 2 ng mL⁻¹ in acetonitrile, are expressed as mass of injected compound (pg).
^b As a rough guide, the equivalent concentrations in mosses (ng g⁻¹ DW) have been calculated for 1.5 g samples submitted to average extraction recoveries of 70%.
^c Relative standard deviations (%) obtained for the evaluation of the reproducibility of the moss analytical procedure (n = 6).
^d As a rough guide, the equivalent concentrations in total deposition (ng L⁻¹) have been calculated for 500 mL samples and with global average PAH recoveries of 68% for light PAHs (ACE to PYR) and 75% for heavy PAHs (B(a)A to B(a)P).
^e Relative standard deviations (%) obtained for the evaluation of the reproducibility of the total deposition analytical procedure (n = 3).
^f Nondetermined.

Table 2
Mean and median individual and total concentrations (ng g⁻¹ DW) and corresponding standard deviations (SD) of 13 PAHs in *Hylocomium splendens* (Hedw.) Schimp. sampled at a remote site in the Aralar Range (n = 8).

PAH	Concentrations (ng g ⁻¹ DW)		
	<i>Hylocomium splendens</i> (Hedw.) Schimp.		
	Mean value	Median value	SD
Acenaphthene	3.5	3.1	0.4
Fluorene	30.3	30.1	2.8
Phenanthrene	19.2	19.8	1.3
Anthracene	1.3	1.1	0.2
Fluoranthene	15.5	15.5	0.8
Pyrene	26.3	25.8	4.0
Benzo(a)anthracene	4.4	4.1	0.7
Chrysene	8.2	7.9	0.9
Benzo(b)fluoranthene	8.5	8.2	0.8
Benzo(k)fluoranthene	3.5	3.5	0.4
Benzo(a)pyrene	5.2	5.0	0.5
Dibenzo(a,h)anthracene	1.6	1.5	0.3
Benzo(g,h,i)perylene	5.8	5.5	0.6
Total	133.3	131.2	4.8

2.2. Analytical procedure

The green shoots from the last three years growth were with drawn using stainless steel tweezers and scissors. The unwashed samples were freeze dried and ground to a fine powder in a stainless steel mill (particle size <0.5 mm). PAH extraction was carried out by pressurized liquid extraction (PLE).

The deposition sample volume was estimated gravimetrically, then transferred to 1 L polyethylene bottles and subsequently stored at -20 °C until analysis. Fortnightly samples from each collector were combined to form average monthly samples of 0.1–1.6 L. PAH extraction was performed by liquid/liquid extraction (LLE).

PAH extraction in both matrices, and PAH analyses performed by HPLC FLD, have been reported elsewhere (Foan et al., 2012; Foan and Simon, 2012). The analytical procedure is summarized in Fig. 1.

2.3. Quality assurance/quality control (QA/QC)

Reproducibility of the sample treatment/analysis procedure and limits of quantification (LOQ) are shown in Table 1. Accuracy of moss and total deposition analyses have been evaluated with reference material and spiked solutions, respectively (Foan et al., 2012; Foan and Simon, 2012). For this study, the content of 13 PAHs was studied in mosses, while 10 PAHs were evaluated in total deposition (identified in bold type in Table 1). The other compounds were not considered due to low accuracy or presence of interfering compounds.

2.4. Evaluation of PAH fluxes

Atmospheric daily fluxes for the individual PAHs were calculated for each sampling period using the expression (Eq. (1)):

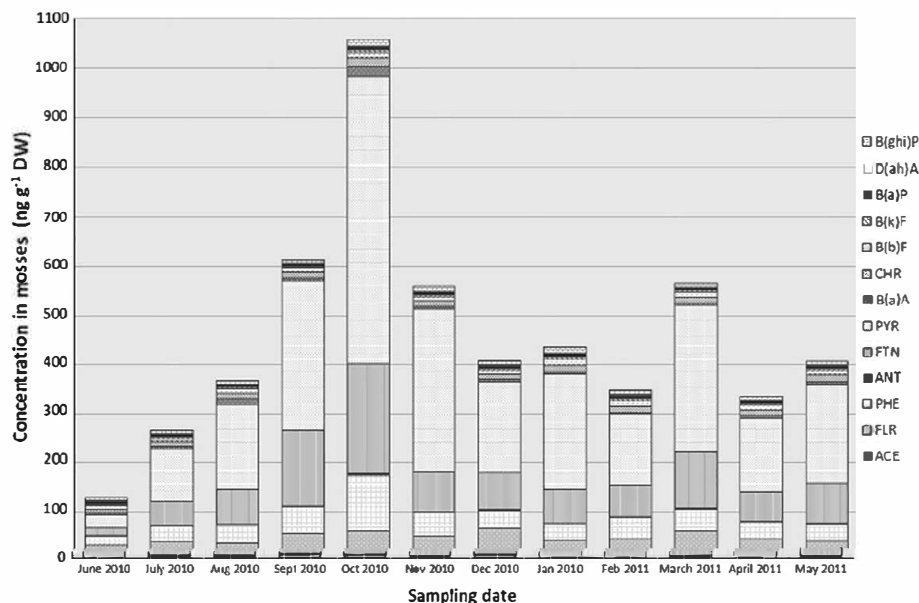


Fig. 2. Seasonal trends in PAH concentrations ($\text{ng g}^{-1} \text{DW}$) in the *Hylocomium splendens* (Hedw.) Schimp. mosses collected from the Aralar Range and exposed from June 2010 to May 2011 to atmospheric deposition in a Bertiz Nature Reserve beech forest. For clarity, the error bars have been excluded.

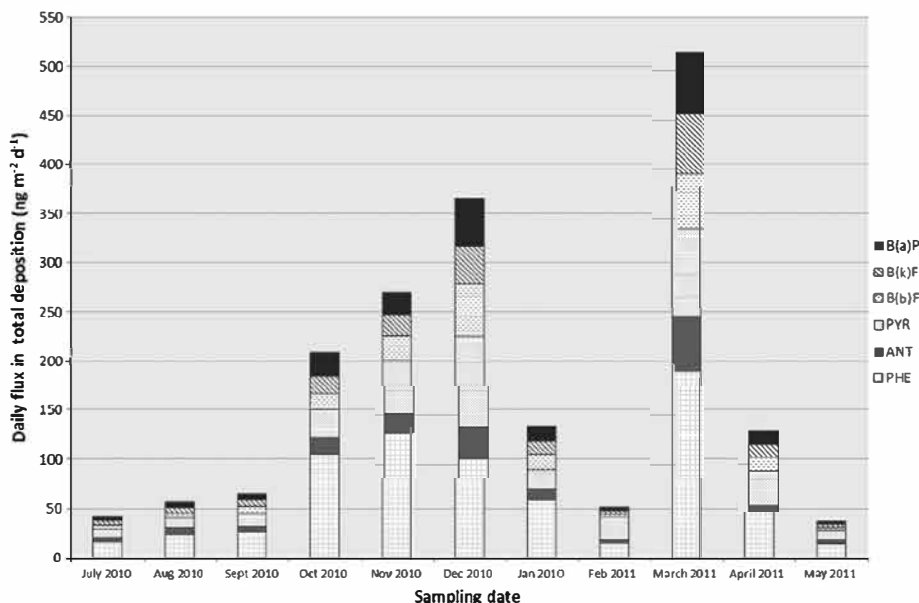


Fig. 3. Temporal variations of PAH daily fluxes ($\text{ng m}^{-2} \text{d}^{-1}$) in throughfall deposition between July 2010 and May 2011. For clarity, the error bars have been excluded.

$$\Phi(\text{PAH}) = [\text{PAH}] * V / (S * T) \quad (1)$$

where $\Phi(\text{PAH})$ is the daily PAH flux ($\text{ng m}^{-2} \text{d}^{-1}$), $[\text{PAH}]$ the PAH concentration measured in total deposition (ng L^{-1}), V the volume of total deposition collected (L), S the surface area of the collector (m^2) and T the length of the sampling period (d).

2.5. Statistical analysis

The significance of PAH seasonal variations was studied by analysis of variance (ANOVA) and by Newman Keuls tests. To study correlations between the variables, Pearson's correlation coefficients were calculated (after checking normality of data). They were performed using XLSTAT 2008 (Addinsoft, Paris, France) software.

3. Results and discussion

3.1. Atmospheric deposition estimation by active biomonitoring

All 13 target PAHs were quantified in the *H. splendens* (Hedw.) Schimp. moss samples collected from the Aralar Range (Table 2). A total average concentration of $133 \pm 5 \text{ ng g}^{-1}$ (dry weight, DW) was measured in the samples ($n = 8$), and this level is the same order of magnitude as that already found in mosses collected from other rural European sites (Harmens et al., 2013). Fluorene, phenanthrene, fluoranthene and pyrene were the major PAH compounds and probably originated from road traffic around the Aralar Range (Khalili et al., 1995; Simon et al., 2012). The native moss was interesting for active biomonitoring, due to the low PAH concentrations and the poor variability between samples.

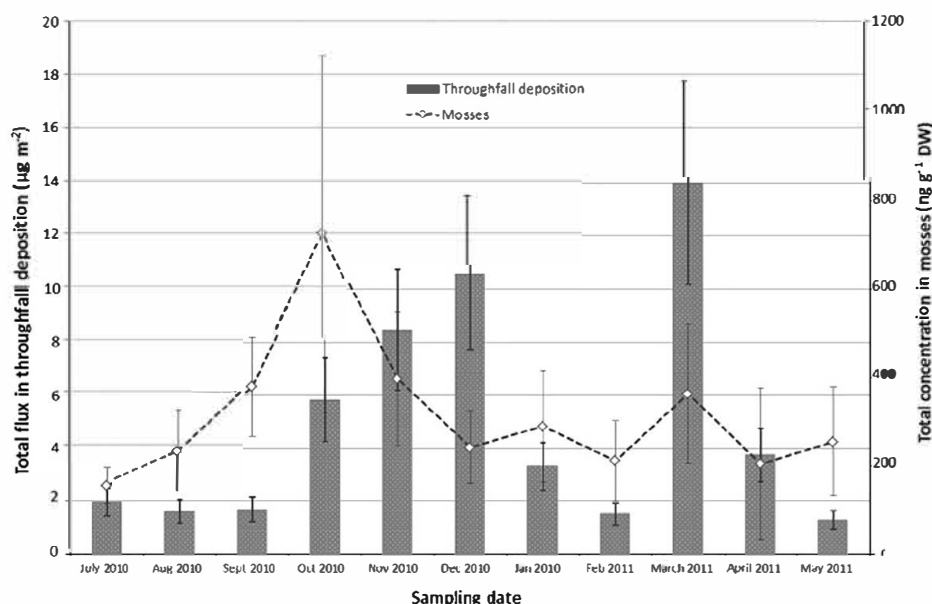


Fig. 4. Seasonal variations between July 2010 and May 2011 of the atmospheric deposition flux of 6 PAHs (PHE, ANT, PYR, B(b)F, B(k)F, B(a)P) measured in total deposition (ng m^{-2}) and of the concentrations of the 6 PAHs in the mosses (ng g^{-1} DW). The error bars represent the uncertainty ($P = 95\%$) evaluated with Student's t -test for $n = 8$ samples of mosses and $n = 6$ deposition samples per sampling month.

Table 3
Pearson correlations ($p < 0.01$) between PAH physico-chemical properties, concentrations in total deposition and in the mosses, and the bioconcentration factor. Significant coefficients are in bold type.

	$\log K_{OA}$ at 25 °C	$\log K_{OW}$ at 25 °C	sol (mg L^{-1}) at 25 °C	[PAH] _{deposition} (ng L^{-1})	[PAH] _{mosses} (ng g^{-1} DW)
$\log K_{OA}$ at 25 °C	1				
$\log K_{OW}$ at 25 °C	0.446	1			
sol (mg L^{-1}) at 25 °C	-0.469	-0.418	1		
[PAH] _{deposition} (ng L^{-1})	-0.313	0.106	0.852	1	
[PAH] _{mosses} (ng g^{-1} DW)	-0.095	0.768	0.083	0.550	1
BCF	-0.072	0.794	-0.076	0.371	0.960

K_{OA} : octanol/air partition coefficient; K_{OW} : octanol/water partition coefficient; sol: solubility in water; [PAH]_{deposition}: PAH concentration in total deposition; [PAH]_{mosses}: PAH concentration in the mosses; BCF: bioconcentration factor.

In the year between June 2010 and May 2011, the total concentrations of the 13 PAHs measured in the *H. splendens* mosses placed under the Bertiz forest canopy varied greatly, from $129 \pm 6 \text{ ng g}^{-1}$ (DW) in June 2010 to $1059 \pm 600 \text{ ng g}^{-1}$ (DW) in October 2010 (Fig. 2). The higher concentration variability observed over the summer period (July to mid October) can be explained by the variable structure of the canopy during this season. Indeed, the Leaf Area Index (LAI) of the study trays ranged from 3.9 to $5.4 \text{ m}^2 \text{ m}^{-2}$ in the summertime, as winter values ranged between 0.8 and $0.9 \text{ m}^2 \text{ m}^{-2}$. However, ANOVA has demonstrated that the seasonal variations of the total PAH concentrations are significantly more important than variability during sampling ($p < 0.05$).

Analysis of variance also showed that there is significant seasonal variations in the concentrations of the different PAHs studied, even the minor ones ($p < 0.05$). The main components in decreasing order of importance are: pyrene, fluoranthene, phenanthrene and fluorene. Pyrene's contribution in particular represents 41–59% of the total concentration of the 13 PAHs.

3.2. PAH deposition fluxes

Fluorene, fluoranthene, benzo(a)anthracene and chrysene concentrations in total deposition were under the quantification limits (Table 1). Thus daily fluxes were determined for 6 PAHs: phenanthrene, anthracene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene (Fig. 3). All compounds showed significant variations throughout the year (ANOVA, $p < 0.01$), and

the seasonal trends were significantly more important than spatial variations due to sampling (ANOVA, $p < 0.01$).

The total daily fluxes varied from $37 \pm 10 \text{ ng m}^{-2} \text{ d}^{-1}$ (May 2011) to $517 \pm 140 \text{ ng m}^{-2} \text{ d}^{-1}$ (March 2011). Firstly, PAH emissions increase during the cold season because of domestic heating using fossil fuels or biomass (Khalili et al., 1995; Dejean et al., 2009). Secondly, there is intense photochemical degradation of PAHs in the summer (Dabestani and Ivanov, 1999). Finally, high levels of precipitation induce good clearance of airborne PAHs (Sicard, 2006). Indeed, PAH fluxes showed temporal trends correlated to the volume of precipitation collected ($r = 0.7206$, $p < 0.01$).

Total annual flux of the 6 target PAHs was $60.5 \pm 16.4 \mu\text{g m}^{-2}$ (based on 326 d sampling), giving an equivalent daily flux of $166 \pm 45 \text{ ng m}^{-2} \text{ d}^{-1}$, a characteristic level for a rural site. Indeed, this value is the same order of magnitude as measures previously obtained in the Pyrenees mountains in Northern Spain (Fernández et al., 2003), and significantly lower than those obtained in a Turkish urban area (Esen et al., 2008). Phenanthrene and pyrene were the major compounds in total deposition, representing 39% and 20% of the total annual flux of the 6 PAHs.

3.3. Comparison between PAH atmospheric deposition and PAH contents in mosses

Seasonal variations in the monthly atmospheric deposition of the 6 PAHs (PHE, ANT, PYR, B(b)F, B(k)F, B(a)P) and their total contents in the mosses, are shown in Fig. 4. Overall, the trends are similar ($r = 0.464$, $p < 0.01$). The Newman Keuls test has shown that

concentrations in mosses were significantly higher in October 2010 than during the rest of the study year, as significantly higher values for the monthly fluxes appeared from October to December 2010 and in March 2011 ($p < 0.05$). The less important amplitudes of PAH concentrations in moss are probably the result of surface leaching of PAHs and dilution of PAH contents during moss growth. Moreover, the low correlation between the PAH levels in the two environmental compartments can be explained by relatively different levels in the mosses (Fig. 2) and in total deposition (Fig. 3).

In order to study PAH fractionation in the bryophytes during the accumulation of atmospheric deposition, bioconcentration factors have been calculated from the following expression:

$$\text{BCF} = [\text{PAH}]_{\text{mosses}} / [\text{PAH}]_{\text{deposition}} * \rho_{\text{water}} \quad (2)$$

where BCF is the bioconcentration factor (), $[\text{PAH}]_{\text{mosses}}$ the individual PAH levels measured in the mosses ($\text{ng g}^{-1} \text{ DW}$), $[\text{PAH}]_{\text{deposition}}$ the individual PAH levels measured in the total deposition collected (ng L^{-1}), ρ_{water} the density of water (1000 g L^{-1}).

The average BCF in the mosses over the study year varied from 2000 (B(b)K) to 40000 (Pyr). Pearson correlations (Table 3) showed that this factor is significantly correlated with the octanol water partition coefficients of the PAHs studied ($r = 0.794$, $p < 0.01$). The fractionation between total deposition and the mosses occurs because PAH levels in deposition are in turn, significantly correlated with the solubility of the compounds ($r = 0.852$, $p < 0.01$). Therefore pyrene is predominant in mosses, whereas phenanthrene presents the highest deposition fluxes, because pyrene has a higher affinity with organic matter ($\log K_{\text{ow}} = 8.8$ against 4.5 for PHE) while phenanthrene is very soluble in water (1.1 g m^{-3} against 0.1 g m^{-3} for Pyr). It should be noted that Ötvös et al. (2004) showed a significant correlation between the PAH levels in mosses and their octanol air partition coefficients K_{OA} , whereas we have found a better correlation with the K_{OW} . This difference is certainly due to the heavy rainfall in Navarra (1800 mm during the sampling period, Foan et al., 2012), favouring wet deposition over dry deposition.

3.4. Emission sources

Polycyclic aromatic hydrocarbon diagnostic ratios are often used as a tool for identifying and assessing pollution emission sources (Tobiszewski and Namiesnik, 2012). Studies conducted in ambient air have shown that car traffic emissions can be identified by having $\text{B(a)A}/(\text{B(a)A} + \text{CHR})$ ratios which are higher than 0.35, while the presence of emissions from coal, wood or biomass combustion leads to ratios which are lower than 0.35 (De La Torre Roche et al., 2009; Akyüz and Cabuk, 2010).

The $\text{B(a)A}/(\text{B(a)A} + \text{CHR})$ values measured in Bertiz mosses were under 0.35 from November 2010 to March 2011, and exceeded that value during the rest of the sampling year. We can therefore suppose that the main N 121 A highway situated 3 km west from the sampling site, in the direction of dominant winds, is an important source of PAHs throughout the year, and that domestic heating contributes to higher contamination during winter.

$\text{ANT}/(\text{ANT} + \text{PHE})$ and $\text{B(b)F}/\text{B(k)F}$ ratios did not show any significant seasonal variations in total deposition ($p < 0.05$), as previously observed by Wang et al. (2011). Indeed, identification of emission sources with this matrix is delicate because the solubility of PAHs with same molar mass is variable (Tobiszewski and Namiesnik, 2012).

4. Conclusions

An active biomonitoring study led in a Spanish Nature Reserve between June 2010 and May 2011 using *H. splendens*

(Hedw.) Schimp. moss has shown important seasonal variations for 13 PAHs. Pyrene's contribution represented from 41% to 59% of the total concentration. Diagnostic ratios show that the contamination comes mainly from car road traffic augmented in winter by domestic heating emissions. The average daily flux of the 6 compounds measured in total deposition is characteristic of rural areas ($166 \pm 45 \text{ ng m}^{-2} \text{ d}^{-1}$). Significant seasonal variations in PAH fluxes proved to be correlated to precipitation levels. Higher levels in winter are probably also due to important PAH emissions from domestic heating and less photodegradation of PAHs in the atmosphere. Similar trends were found for the total PAH concentrations in bryophytes ($r = 0.464$, $p < 0.01$), however with less important amplitudes, probably the result of surface leaching of PAHs by precipitations and dilution of PAH contents during moss growth. Moreover, fractionation between deposition and the mosses occurs because the PAH levels in deposition are significantly correlated with the solubility of the compounds ($r = 0.852$, $p < 0.01$), as bioconcentration factors of PAHs in the mosses are significantly correlated with $\log K_{\text{ow}}$ of these compounds ($r = 0.794$, $p < 0.01$). This study is the first to use bryophytes to measure the annual variations of atmospheric deposition of PAHs. It showed that atmospheric PAH fluxes can be estimated with moss biomonitoring data if the bioconcentration or 'enriching' factors are known.

Acknowledgments

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