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### ► To cite this version:

Louise Foan, Caroline C. Sablayrolles, David Elustondo, Esther Lasheras, L Gonzalez, et al.. Reconstructing historical trends of polycyclic aromatic hydrocarbon deposition in a remote area of Spain using herbarium moss material. *Atmospheric Environment*, 2010, 44 (26), pp.3207-3214. 10.1016/j.atmosenv.2010.05.019 . hal-02668360

**HAL Id: hal-02668360**

**<https://hal.inrae.fr/hal-02668360>**

Submitted on 31 May 2020

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## Reconstructing historical trends of PAH deposition in a remote area of Spain using moss material from a herbarium

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20 **“Capsule”:** *Herbarium moss samples can contribute to the reconstruction of past PAH deposition.*

### Abstract

Herbarium mosses from 1879-1881, 1973-1975 and 2006-2007 were used to investigate the historical changes of atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) at a remote site located in Northern Spain. Natural abundance of nitrogen and carbon isotopes was also measured in order to assess the evolution of emissions from anthropogenic sources.

5 Nitrogen concentrations,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and PAH levels were significantly higher in 19<sup>th</sup> century samples with respect to the present century samples. Moreover, PAH distribution varied over the centuries, following a tendency of light PAH enrichment. The carbon, nitrogen and PAH levels measured in the mosses tally with the historic evolution of anthropogenic emissions in the area, mainly influenced by changes of economic activities, domestic heating and road traffic

10 density. Mosses provided by herbaria seem to offer the possibility to study long-term temporal evolution of atmospheric PAH deposition.

*Keywords:* Atmospheric deposition; Biomonitoring; Herbarium moss; PAH; N, C isotope signatures

## 15 **1. Introduction**

Air quality is generally monitored by physico-chemical detectors supplying numerical information. However, these direct measures face problems such as low sample representativeness, analytical difficulties (trace levels), cost and maintenance of

20 equipments. Biological monitoring is an alternative consisting in an integrative technique able to assess the environment contamination based on studies of living organisms exposed to pollution episodes. Because of their capacity to act as efficient interceptors and accumulators of chemicals, plants are used widely as passive biomonitors in urban and rural environments (Garrec and Van Haluwyn, 2002), the

25 most common being persistent trees (Lehndorff and Schwark, 2009a, b), lichens (Blasco et al., 2008) and mosses (Migaszewski et al., 2009).

Bryophytes in particular have been employed over the past decades as biomonitors for the assessment of airborne pollutant deposition, including heavy metals (Harmens et al., 2007; Rühling and Tyler, 1969; Tyler, 1990), radionuclides (Sawidis et al., 2009; Sumerling, 1985), persistent organic pollutants (Carlberg et al., 1983; 5 Migaszewski et al., 2009) and nitrogen (Poikolainen et al., 2009; Solga et al., 2006; Wilson et al., 2008). Characteristics of mosses make them excellent subjects for biomonitoring. Their lack of root system as well as their well-developed cuticle forces them to obtain most of their nutrient supply from the atmosphere. Moreover, their high cationic exchange capacity and surface area to volume ratio favours the accumulation of 10 great amounts of pollutants (Gerdol *et al.*, 2002).

Persistent organic pollutants (POPs) remain in the center of scientific attention due to their slow rates of degradation, their toxicity and potential for both long-range transport and bioaccumulation in living organisms (Holoubek et al., 2007). Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants formed by 15 incomplete combustion of organic material through pyrolysis and pyrosynthesis mechanisms (Kiss et al., 2001) and emitted into the atmosphere from both anthropogenic and natural sources (Simonich and Hites, 1995). Anthropogenic sources are generally referred to sources that produce energy such as domestic heating, traffic exhaust, incinerators and natural gas (Mastral et al., 2003). Some of the PAHs are also produced 20 commercially. Acenaphthene, acenaphthylene and anthracene may be used in dye, explosive and fiber production, and in pharmaceutical industry (Hawley, 1987). Natural sources are usually volcanic eruptions and biomass burning. Several PAHs are hazardous to living organisms due to their mutagenic, carcinogenic, teratogenic, immunosuppressive and/or neurotoxic properties (Garuszka, 2000) and eight PAHs are

classified by US EPA (1997) as possible human carcinogens. Therefore it is important to monitor and regulate the occurrence of PAHs in ambient air.

To further investigate the quantitative importance of different sources of deposition, the use of stable isotopes at natural abundance levels in mosses provides a powerful approach for understanding environmental interactions. Isotopic composition of elements, such as carbon and nitrogen, changes in predictable ways during their course through the biosphere, which makes them ideal tracers of the pathways and origins of these elements (Liu et al., 2008; Solga et al., 2005).

Mosses preserved in herbaria should be highly suitable for determining environmental conditions in past times since mosses are largely dependent on the atmosphere for their nutrition. It is safe to assume that the concentrations in the herbarium moss samples correlate with atmospheric inputs in the corresponding periods provided that disruptive factors such as soil particles and leaching processes, contamination during sampling and certain preservatives or storage conditions can be excluded (Ross, 1990).

Naturally growing mosses have been extensively employed for studying spatial variations of atmospheric PAHs (Migaszewski et al., 2009) and temporal variations of these pollutants over periods of 10 years at the most (Holuoubek et al., 2007). The originality of the present study is to use herbarium moss samples to reconstruct temporal tendencies of PAH deposition over the last 125 years in a Natural Park located in Navarra, North Spain. Moreover, we propose to investigate the historical changes of natural abundance of nitrogen and carbon isotopes in order to detect the evolution of emissions from anthropogenic sources. The temporal variations were measured with

four different mosses in aim to study the inter-species variability. This study will assess the value of herbarium mosses for reconstructing past PAH deposition trends.

## 2. Experimental section

5

### 2.1. Study area

The Natural Park of the “Señorío (Estate) de Bertiz” is located in the northwest of Navarra (Spain), near the French border. The Park occupies the eastern side of Bertizarana Valley, covering 2040 hectares.

Bertiz has oceanic climate, with an average annual temperature of 13.7-15 °C, not very hot summers, mild winters and not much difference between the average monthly maximum and minimum temperatures. This is due to the influence of the Biscay Bay, only several kilometres away. The rainfall is one of the highest in Navarra, with an annual average of about 1800 mm distributed all over the year, especially between October and May.

The vegetation mainly consists in a beech forest (*Fagus sylvatica* L.), although there are some patches of oak woods (*Quercus robur* L.) and a few pastures.

Due to its ecological richness, the Señorío de Bertiz was declared as a Natural Park during March 1984 (92/43/CEE Directive) and has become since part of the Natura 2000 Network.

### 2.2. Herbarium specimens

The following species of bryophytes were studied: *Dicranum scoparium* Hedw., *Hypnum cupressiforme* Hedw., *Thamnobryum alopecurum* Hedw. Gangulee and *Thuidium tamariscinum* Hedw. Schimp. The mosses had been conserved in the Herbarium PAMP of the University of Navarra, which contains specimens of bryophytes collected in the Natural Park of Bertiz since 1879. Samples were separated into three periods: 1879-1881 (Lacoizqueta, 1885), 1973-1975 (Fuertes & Álvarez, 1982) and 2006-2007. A total of 28 specimens of the species mentioned above were found in the herbarium.

Leaves or stem tips were taken from a similar terminal position on each specimen using plastic tweezers. Any extraneous material was removed. After that, the unwashed samples were oven-dried at 30°C to constant weight (dry weight) and finally ground to a fine powder in a mill.

### 2.3. Elemental analysis and isotopic determination

Moss samples were analysed for their carbon and nitrogen content and their respective isotopic signatures ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). Tissue C and N contents (% , dry weight) were determined by an elemental analyzer (EA1108, Carlo Erba, Milano, Italy) with an analytical precision of 0.1%. The calibration was performed using atropine (ThermoQuest Italia, Milan, Italy). Stable C and N isotopic ratios were measured with an isotope ratio mass spectrometer (CONFLO II interface, Thermo Finnigan MAT, Bremen, Germany) operating in continuous flow mode. The calibrations were performed using interspersed international isotopic standards of carbon and nitrogen (IAEA, Vienna, Austria). Isotope data are reported as  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values, which

represent relative difference expressed in per mil (‰) between the isotopic composition of the sample and that of a standard (Pee Dee Belemnite (PDB) for carbon and atmospheric N<sub>2</sub> for nitrogen):

$$\delta^{13}\text{C} (\text{‰ vs V-PDB}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

5

$$\delta^{15}\text{N} (\text{‰ vs at-air}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R<sub>sample</sub> represents the isotope ratio (<sup>13</sup>C/<sup>12</sup>C) or (<sup>15</sup>N/<sup>14</sup>N) and R<sub>standard</sub> the isotope ratio for the standard. The accuracy of the measurements was ± 0.15‰ for δ<sup>13</sup>C and ± 0.3‰ for δ<sup>15</sup>N.

## 10 2.4. Polycyclic Aromatic Hydrocarbons

### 2.4.1. Chemicals and standards

A standard mix containing acenaphthene (ACE), fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FTN), pyrene (PYR), benzo(*a*)anthracene (B(a)A), benzo(*b*)fluoranthene (B(b)F), benzo(*k*)fluoranthene (B(k)F), benzo(*a*)pyrene (B(a)P), dibenzo(*a,h*)anthracene (D(ah)A), benzo(*g,h,i*)perylene (B(ghi)P) and indeno(*c,d*)pyrene (IND) at 10 μL/mL of acetonitrile was used for calibration (PAH Mix 9, Supelco, France). Deuterated PAHs were used as extraction standards (anthracene d<sub>10</sub> and benzo(*a*)pyrene d<sub>12</sub> at 300 ng/mL of acetonitrile) and as an internal standard (fluoranthene d<sub>10</sub> at 1000 ng/mL of acetonitrile) (Supelco, France). Anthracene d<sub>10</sub> was chosen as a reference for the light PAH fraction (ACE to PYR) and benzo(*a*)pyrene d<sub>12</sub> for the heavy PAH fraction (B(a)A to IND).



All solvents were HPLC grade: *n*-hexane and acetonitrile were provided by VWR Scharlau (Spain), cyclohexane and dichloromethane (DCM) by VMR Merck (France) and Milli-Q water by VWR Millipore (France).

#### 5 2.4.2. *Extraction and clean-up procedure*

In order to analyse the PAHs in mosses by High Pressure Liquid Chromatography coupled with fluorescence detection (HPLC-FLD), Soxtec extraction and Solid Phase Extraction (SPE) clean-up were carried out. The analytical procedure is described with figure 1.

10 The extractions were performed with a Soxtec System HT2 (Tecator, France). Cellulose thimbles were filled with approximately 1 g of spiked moss, anhydrous sodium sulfate and Florisil (U.S. Silica Company, USA). The extract was concentrated with a rotary evaporator at 30°C (Rotavapor, Büchi, Switzerland), then by nitrogen flow (Alpha 1, Air Liquide, France). A clean-up procedure was carried out with normal phase  
15 Florisil SPE cartridges (Supelclean LC-Florisil SPE 1g, Supelco, France) placed on a Supelco manifold. After solvent exchange, the samples were filtered and an internal standard was added. The extracts were stored at -20°C.

The global recoveries of the extraction/purification procedure extend from 25 to 71 % with an average of 54 % for light PAHs (ACE to PYR) and from 27 to 79 % with  
20 an average of 60 % for heavy PAHs (B(a)A to IND).

#### 2.4.3. *HPLC-FLD analysis*

The PAH analyses were performed on reversed-phase high-performance liquid chromatograph DIONEX RF 2000 (Pump P680 HPLC) (Dionex, USA) equipped with a  
25 C18 column Supelcosil™ LC-PAH (250 mm X 4.6 mm X 5 µm) and a precolumn (20

mm X 4.6 mm X 5  $\mu$ m) (Supelco, France) and a fluorescence detector (DIONEX RF 2000, Dionex, USA) at a flow rate of 1.5 mL/min with a water/acetonitrile elution gradient. The details of the analytical parameters are given in table 1.

The linearity range for the PAH analysis extends from 0 to 58 ng/L with regression coefficients from 0.9992 (B(k)F) to 0.9999 (ANT and B(a)A).

To study the repeatability of the analysis, a standard solution containing low PAH concentrations (2 ng/mL) was injected 10 times. The standard deviation, determined for each PAH (from 3% for ACE to 14% for PHE), appeared to be lower than 20%.

The reproducibility of the method was tested by repeating 7 times the entire extraction-purification-analysis procedure on a recent moss sample (collected during October 2008). The results are shown in figure 2. The standard deviation determined for each PAH was lower than 20% except for ACE, FLR, D(ah)A and B(ghi)P with a maximum of 81% for ACE.

Limits of detection (LOD) and limits of quantification (LOQ) were determined by studying the chromatogram obtained with a 2 ng/mL standard solution. The LOD was calculated as equal to 3 times the background and the QL as 10 times the background (Tranchant, 1995). The limits of quantification appear in table 1.

Finally, the accuracy of the analytic procedure was verified by applying the whole extraction-purification-analysis procedure 5 times to a reference material of organic contamination (IAEA-1400C Fucus (35 g) from ANALAB) which contains 9 of the 13 researched PAHs. All determined concentrations entered the reference concentrations 95% confidence interval, except for PYR, overestimated because of interferences with other reference molecules (PCBs or pesticides).

## 2.5. Statistical analysis

One way analysis of variance (ANOVA) was performed to determine the effects of the factors time and species on the variables. For examining associations between the different variables Pearson's correlation coefficients were calculated. The statistical analysis was conducted by using SPSS 15.0 (SPSS Science, Chicago, USA) and XLSTAT 2008 (Addinsoft, Paris, France).

## 3. Results

### 3.1. Elemental analysis and isotopic determination

#### 3.1.1. Nitrogen and carbon concentrations

Tissue nitrogen concentrations in the herbarium specimens ranged between 0.8 % and 1.8 %. Nitrogen concentrations were significantly higher ( $p < 0.05$ ) in 19<sup>th</sup> century with respect to the present century (Figure 3).

The moss *Thamnobryum alopecurum* exhibited the highest nitrogen concentrations, showing significant differences ( $p < 0.05$ ) with the other species.

Concerning carbon, concentrations ranged between 30.9% and 43.9% and in this case values did not show significant differences between species or along the centuries.

#### 3.1.2. Nitrogen and carbon isotope signatures

Mean  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values for the moss species studied ranged between -30.5‰ and -25.1‰ and between -9.3‰ and 0.6‰ respectively. The average  $\delta^{13}\text{C}$  showed a significant ( $p < 0.05$ ) decrease along the three studied centuries, while in the case of  $\delta^{15}\text{N}$  only mosses collected in the 19<sup>th</sup> century exhibited values significantly higher ( $p < 0.05$ ) than those collected in the 21<sup>st</sup> century (Figure 4).

No significant differences were observed in  $\delta^{13}\text{C}$  values between the four studied moss species. However, in the case of  $\delta^{15}\text{N}$  significant differences were detected between *Dicranum scoparium* and *Thamnobryum alopecurum*, species that respectively showed the lowest and highest  $\delta^{15}\text{N}$  values.

10

### 3.2. PAH levels

Except for anthracene and dibenzo(*ah*)anthracene levels which remained low, all PAH concentrations significantly decreased in the mosses between 1879-1881 and 1973-1975 ( $p < 0.01$ ). Solely levels of the heavy PAHs benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, benzo(*g,h,i*)perylene and indeno(*c,d*)pyrene significantly decreased between 1973-1975 and 2006-2007 ( $p < 0.01$ ) (Table 2).

As a consequence, total PAH levels decreased significantly between the 19<sup>th</sup> and 20<sup>th</sup> century ( $p < 0.01$ ) but not between the 20<sup>th</sup> and 21<sup>st</sup> century. The average total of the 13 PAHs was 172 ng/g (dry weight) in the current century samples against 1219 ng/g (dry weight) in the 130 year old samples.

Phenanthrene showed the highest PAH levels whatever the moss age. It appears to be the major compound as its accumulation accounted for 47% of the total PAHs measured in the 2006-2007 samples and this percentage increased over time (24% and

39% respectively in the 19<sup>th</sup> and 20<sup>th</sup> century samples). Fluoranthene and pyrene are the other major compounds measured in Bertiz mosses accounting for 33 to 39% of the total PAHs.

Heavy PAHs (benzo(*a*)anthracene to indeno(*c,d*)pyrene) accounted for approximately half of the total PAH levels in mosses of the 19<sup>th</sup> century but appeared to be minor compounds in the recent samples (12%) with individual concentrations of less than 6 ng/g (dry weight).

Three groups of PAH levels appeared to be positively correlated ( $p < 0.01$ ,  $R^2 = [0.913-0.978]$ ):

- 10 - acenaphthene and fluorene (2-benzene ring PAHs).
- phenanthrene, fluoranthene and pyrene (3-benzene ring PAHs).
- benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene and indeno(*c,d*)pyrene (4- and 5-benzene ring PAHs).

The individual and total PAH levels measured in Bertiz moss did not vary significantly from one species to another.

## 4. Discussion

### 4.1. Isotopic signatures and atmospheric N, C sources

20

In contrast with other studies (Peñuelas and Filella, 2001; Solga et al., 2006; Wilson et al., 2008), N concentrations in mosses collected at Bertiz significantly decreased ( $P < 0,05$ ) between the 19<sup>th</sup> and 21<sup>st</sup> century. A plausible explanation may be found in the 19<sup>th</sup> century history of the Señorío de Bertiz. At that time, the use of wood

burning stoves was the main procedure for heating houses and the accomplishment of coal bunkers inside the forest was very frequent, in order to obtain charcoal to feed the numerous existing foundries of the surrounding valleys (Erdozáin and Mikelarena, 2002). All these activities emitted high amounts of NO<sub>x</sub> and consequently, it is very  
5 probable that a remote place such as Bertiz was more contaminated in the past than nowadays. Taking into account that these activities decreased (wood burning) or disappeared (coal bunkers and foundries) at the end of the 19<sup>th</sup> century, it seems logical that N concentrations are lower at present.

Moreover, Peñuelas and Filella (2001) suggested that the decrease in foliar N  
10 from 1940-1950 to 1960-1970 observed in vascular plants and mosses collected in Spain was the result of increased global CO<sub>2</sub> concentrations. Thus, the pattern of N decrease observed in this study could also be explained by growth dilution as a response to large increase of CO<sub>2</sub> availability.

The highest N concentrations found in *Thamnobryum alopecurum* may be  
15 explained by the different life-form of this bryophyte with respect to the others (Dierssen, 2001; Mägdefrau, 1982). *Thamnobryum* is a hygrophytic moss that grows on rocks by streams and rivers, just above mean water level. In consequence, the main water and nutrient source for this moss is groundwater, which is much more N enriched than rain water.

20 The other three moss species are mesophytic, growing on forest soils. In this case, the main water source is precipitation, being *Dicranum scoparium* the species with lesser ability to retain water, fact that would explain the lower tissue N concentrations found in this moss. Regarding *Thuidium tamariscinum* and *Hypnum cupressiforme*, both

mosses have a wet life-form that allows them to hold considerable quantities of rain water by capillarity action, thus showing intermediate N concentrations.

Concerning  $\delta^{15}\text{N}$ , isotopic signatures measured in this study were substantially lower than values found by Peñuelas and Filella (2001), but similar to those registered  
5 by Liu et al. (2008) and Solga et al. (2006).

As mentioned above, the highest  $\delta^{15}\text{N}$  values were detected in *Thamnobryum alopecurum*, while *Dicranum scoparium* showed the most negative signatures. This behaviour may be also related to the opposite ecological life-forms of both species. It is known that N absorbed from rain is depleted in  $^{15}\text{N}$ , while N taken from groundwater is  
10 enriched in the heavy isotope (Asada et al., 2005; Heaton et al., 1997). Thus, the different water sources for both species would explain the  $\delta^{15}\text{N}$  values observed.

A clear trend towards  $^{15}\text{N}$  depletion was observed, in agreement with Peñuelas and Estiarte (1997), who observed a  $\delta^{15}\text{N}$  decline in moss over the past century that was attributed to an increase over time of the uptake of anthropogenic N, which is depleted  
15 in  $^{15}\text{N}$ . This pattern may be related with the increase of N inputs in the reduced form, which is consistent with the gradual intensification of agriculture in the studied area.

Likewise, Turekian et al. (1998) have shown that the combustion of organic material as vegetation produce aerosol particulate material and ashes higher in  $\delta^{15}\text{N}$  than the source vegetation, material which can be retained by mosses. This could explain the  
20 significative higher values of  $\delta^{15}\text{N}$  recorded in Bertiz during the 19<sup>th</sup> century, when burning beech branches (coal bunkers) was a frequent activity in the forest, supporting the idea that N fractionation is a good indicator for the isotopic characterization of combustion-derived nitrogenous material.

In spite of the obtained results, it is obvious that the atmospheric concentrations of N have significantly increased all over the world since the Industrial Revolution. In fact, the Ellenberg ecological values calculated from 187 species of mosses collected in Bertiz since 1879, suggest an increasing trend for anthropogenic nitrogen in this area  
5 (Ederra and Villaroya, 2009). This means that several factors, such as the local influence of coal bunkers and foundries mentioned above, the increased growth and biomass production of mosses or the seasonal variations of N tissue concentrations, could mask the real increase of anthropogenic N deposition.

With respect to  $\delta^{13}\text{C}$ , values were in agreement with the range of  $\text{C}_3$  plants (Liu  
10 et al., 2008). The observed decreasing tendency of  $\delta^{13}\text{C}$  through the time was consistent with the depletion of  $^{13}\text{C}$  detected in the atmosphere during the last centuries due to the increase of anthropogenic emissions, as well as the fractioning by mosses against the heavy isotope of carbon (Fletcher et al., 2006).

#### 15 4.2. Temporal variations of PAH levels in the mosses

Bertiz mosses sampled in 2006-2007 presented total PAH levels of the same order as other background passive moss biomonitoring studies carried out during the past decade in Austria (Krommer et al., 2007; Zechmeister et al., 2006) and Czech  
20 Republic (Holoubek et al., 2007). The PAH distribution is also similar, with phenanthrene, fluoranthene and pyrene as major contaminants. It appears that Holoubek et al. (2000, 2007) measured a significant decrease of total PAH concentrations between mosses from 1988-1994 and 1996-2005, which confirms the temporal trend of PAH depletion in Bertiz mosses.



The significant decrease of individual PAH levels since 1879 ( $p < 0.01$ ) can be explained by the evolution of the emissions in the area throughout the past centuries. During the 19<sup>th</sup> century, charcoal production with the coal bunkers located in the forest, charcoal burning in the local foundries and wood burning in stoves for domestic heating were activities that emitted significant amounts of PAHs as they involved biomass burning under sub-optimum combustion conditions (Freeman and Catell, 1990). Thus, PAH emissions dropped significantly during the 20<sup>th</sup> century due to the abandon of charcoal associated activities and to the evolution of domestic heating towards systems powered by oil or gas, which emit less PAHs. Indeed, Smith (1987) estimated that PAHs emission factors from wood combustion in small-space heating stoves exceed those from furnace-oil combustion by a factor of 100 on an energy equivalent basis and Rogge et al. (1993b) showed that gas home appliances have low total fine particulate organic carbon mass emission rates.

The significant decrease of heavy PAHs between the 1973-1975 and 2006-2007 mosses ( $p < 0.01$ ) can be put in relation with the political incitements to limit POP emissions after the signature in 1982 of the Geneva Convention on Long-range Transboundary Air Pollution. In particular, the most toxic compounds, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene and indeno(*c,d*)pyrene were regulated by the Aarhus Protocole (1998). Thus, their emissions were reduced by 56% in France between 1991 and 2007 (CITEPA, 2009) due to the control of industrial emissions, the commercialization since 1990 of catalytic converters in transportation and the recent efficiency improvement of biomass combustion heating systems. Rogge et al. (1993a) showed for example that the total PAH emission rate was 25-fold lower

for vehicles fitted with catalytic converters. The simultaneous limitation of these heavy PAHs may explain why their levels are significantly correlated ( $p < 0.01$ ).

Phenanthrene, fluoranthene and pyrene, which levels were significantly correlated ( $p < 0.01$ ), were the major contributors to PAH contamination in Bertiz mosses along the centuries. These compounds are important markers of wood combustion (Khalili et al., 1995; Smith and Harrison, 1998). Thus, the very high levels of each of these PAHs ( $> 200$  ng/g, dry weight) in the 1879-1881 samples and their significant decrease in the 1973-1975 samples can be explained by the charcoal associated activities and the dominance of domestic heating with wood stoves in the area during the 19<sup>th</sup> century.

However, in mosses from the 20<sup>th</sup> and 21<sup>st</sup> century, phenanthrene, fluoranthene and pyrene remained the major contributors to PAH contamination in Bertiz moss, probably due to the presence of local traffic, in particular because of the closeness of the Pamplona-Irun main road (N-121A). Indeed, these three compounds are markers of traffic emissions as diesel emission has a high factor loading for phenanthrene, fluoranthene and pyrene and petrol emission for fluoranthene and pyrene (Duval and Frieland, 1981; Ho et al., 2002; Khalili et al., 1995; Masclet et al., 1986; Omar et al., 2002; Orlinski, 2002; Ravindra et al., 2006).

The fact that phenanthrene levels in moss increased relatively to fluoranthene and pyrene between the 20<sup>th</sup> and 21<sup>st</sup> century suggests that diesel-engined traffic is predominant nowadays. Moreover, Marr et al. (1999) showed that light-duty vehicles contribute significantly to 4- and 5- benzene ring PAHs, whereas heavy-duty vehicles, which are diesel powered, are the dominant source of 3-benzene ring PAHs, i.e. phenanthrene, fluoranthene and pyrene. Thus, the high density of trucks that transits

locally between France and Pamplona (Navarra's capital city) appears to be the main current PAH contamination source for Bertiz moss.

#### 4.3. Limits of the method

5

Air quality passive biomonitoring, i.e. with specimens sampled in-situ, meets general disruptive factors due to species variability and to environmental conditions, particularly meteorological conditions and altitude (Liu et al., 2005; Niu et al., 2003). Moreover, bryophytes can be contaminated by the soil, which can either emit particles or light volatile PAHs, and can lose PAHs through precipitation leaching (Steinnes et al., 1992).

In the case of this study, the number of herbarium samples available was limited and the total quantity of each sample was low. Moreover, the only data available on the samples was their age. Hence, no inter-species variability was observed for PAHs. Yet moss morphology and growth conditions appear to have an influence on contaminant accumulation in mosses as was shown for nitrogen stable isotopes in this study and for PAHs in other studies. For example Galuszka (2007) observed higher PAH accumulation in *Hylocomium splendens* than in *Pleurozium schreberi* moss species.

For a more thorough statistical interpretation, more information would be necessary on the exact sampling localisation, dating and meteorological conditions as well as the storage conditions (temperature, preservatives...).

## 5. Conclusion

This study has assessed the value of herbarium moss samples as biomonitors of atmospheric PAH deposition at a Spanish remote site. The high levels of PAHs, N and  $\delta^{15}\text{N}$  in 19<sup>th</sup> century mosses of Bertiz Natural Park appear to be related with the historical production of charcoal for local foundries in coal bunkers located in the forest and to the exclusive use of wood stoves for domestic heating before the 20<sup>th</sup> century. The disappearance of the coal bunkers and foundries at the end of the 19<sup>th</sup> century, associated with evolution of domestic heating towards less pollutant systems during the 20<sup>th</sup> century, explain the significant PAH, N and  $^{15}\text{N}$  depletion in the 1973-1975 mosses. Between the 20<sup>th</sup> and 21<sup>st</sup> century mosses, PAH distribution changed noticeably with a tendency towards 3-ring PAH enrichment, due to political limitation of heavy PAH emissions during the last 30 years and a regular increase of traffic in the area, in particular of heavy-duty vehicles, confirmed by significant  $\delta^{13}\text{C}$  decrease. Thus, in this study, knowledge of nitrogen and carbon signature in Bertiz mosses helped to identify the evolution of anthropogenic emissions in the area and furthermore explain the evolution of PAH deposition since the 19<sup>th</sup> century.

Herbarium moss sample analysis meets certain limits due to low sample availability and poor data on sampling and storage. Thus, no evidence of PAH accumulation variability between species could be brought to light in this study. However, relevant information was obtained during this study on past PAH deposition at Bertiz and it consisted with the measured carbon and nitrogen signatures. Therefore, herbarium moss samples appear to be an effective tool for reconstructing historical tendencies of atmospheric PAH deposition.

## Acknowledgments

This work was supported by the Communauté de Travail des Pyrénées / Comunidad de Trabajo de los Pirineos (CTP). We thank Audrey Breton and Christine Raynaud from the LCA (Toulouse, France) for their technical and scientific support, as well as the University of Navarra (Pamplona, Spain) for giving us access to their herbaria.

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## Table captions

Table 1. Analytical parameters for PAH analysis by HPLC/FLD. Excitation (Exc.  $\lambda$ ) and emission (Em.  $\lambda$ ) wavelengths were chosen in function of the analyzed compounds.

5 The limits of quantification (LOQ) are expressed in mass of injected compound (pg). As a rough guide, the average equivalent concentrations in moss (ng/g, dry weight) have been calculated (for 1 g of moss sample and with the average PAH recoveries).

Table 2. Means and ranges of PAH concentrations (ng/g dry weight) in mosses sampled

10 in Bertiz Natural Park during the 19<sup>th</sup>, 20<sup>th</sup> and 21<sup>st</sup> centuries. The table indicates the individual PAH levels and the total PAH level ( $\Sigma$ PAHs) for each sampling period

## Figure captions

15 Fig. 1. Diagram illustrating all operations of the analytical procedure to measure PAHs in mosses.

Fig. 2. Means and standard deviations of polycyclic aromatic hydrocarbon concentrations (ng/g dry weight) in a *Hypnum cupressiforme* sample collected at Bertiz

20 in 2008. The results were obtained by repeating the extraction/purification/analysis procedure 7 times on the moss sample.

Fig. 3. Temporal variation of nitrogen concentrations (% dry weight) in mosses from Bertiz Natural Park. The nitrogen content is represented for the 3 sampling periods:

1879 – 1881 (XIX<sup>th</sup> century), 1973 – 1975 (XX<sup>th</sup> century) and 2006-2007 (XXI<sup>st</sup> century). The boundary of the box indicates the 25<sup>th</sup> and 75<sup>th</sup> percentile and the line within the box the median. Boxes with different letters are significantly different at level of  $P < 0.05$ .

5

Fig. 4. Temporal variation of  $\delta^{13}\text{C}$  (‰) and  $\delta^{15}\text{N}$  (‰) in mosses from Bertiz Natural Park. The isotope signatures are represented for the 3 sampling periods: 1879 – 1881 (XIX<sup>th</sup> century), 1973 – 1975 (XX<sup>th</sup> century) and 2006-2007 (XXI<sup>st</sup> century). The boundary of the box indicates the 25<sup>th</sup> and 75<sup>th</sup> percentile and the line within the box the median. Boxes with different letters are significantly different at level of  $P < 0.05$ .

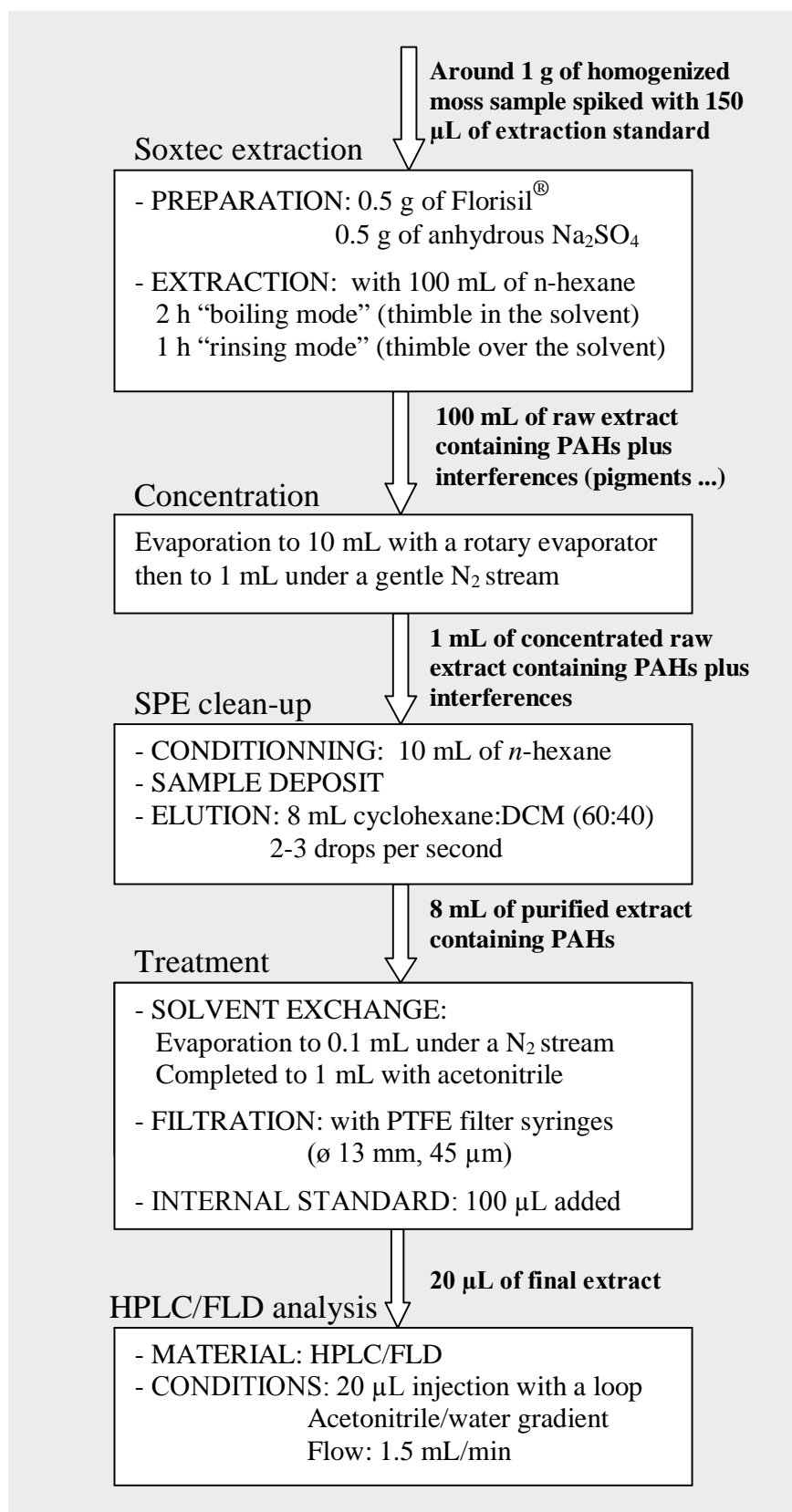
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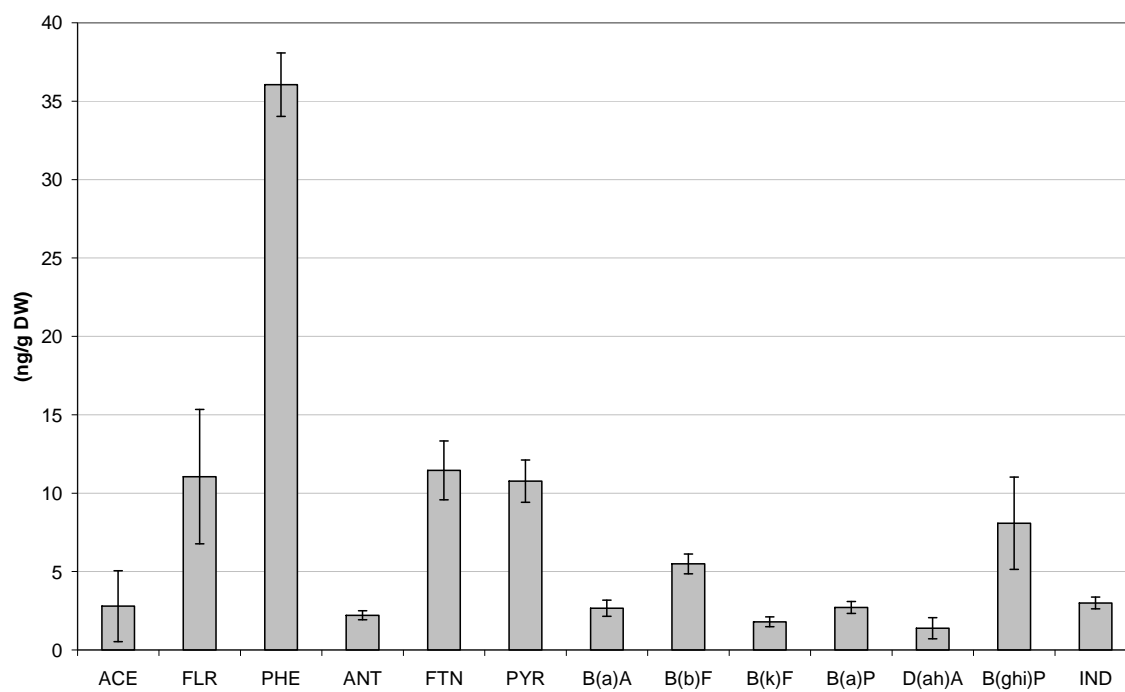
Time window	Time (min)	Exc. $\lambda$ (nm)	Em. $\lambda$ (nm)	Compounds	Retention time (min)	LOQ (pg)	Moss average LOQ (ng/g DW)
1	8.0	233	320	ACE	9.2	22	2.2
				FLR	9.7	52	5.3
2	10.5	260	380	PHE	11.4	27	2.8
3	12.0	250	375	ANT-d <sub>10</sub>	12.5		
				ANT	13.1	4	0.4
4	13.8	365	462	FTN-d <sub>10</sub>	14.3		
				FTN	14.9	28	2.8
5	15.6	275	380	PYR	16.4	13	1.3
6	18.0	270	300	B(a)A	21.3	15	1.4
				B(b)F	26.5	6	0.6
				B(k)F	28.4	3	0.3
7	22.1	302	431	B(a)P-d <sub>12</sub>	29.0		
				B(a)P	30.0	12	1.1
				D(ah)A	32.3	7	0.6
8	33.4	302	419	B(ghi)P	33.9	6	0.6
9	34.8	300	500	IND	35.8	22	2.1

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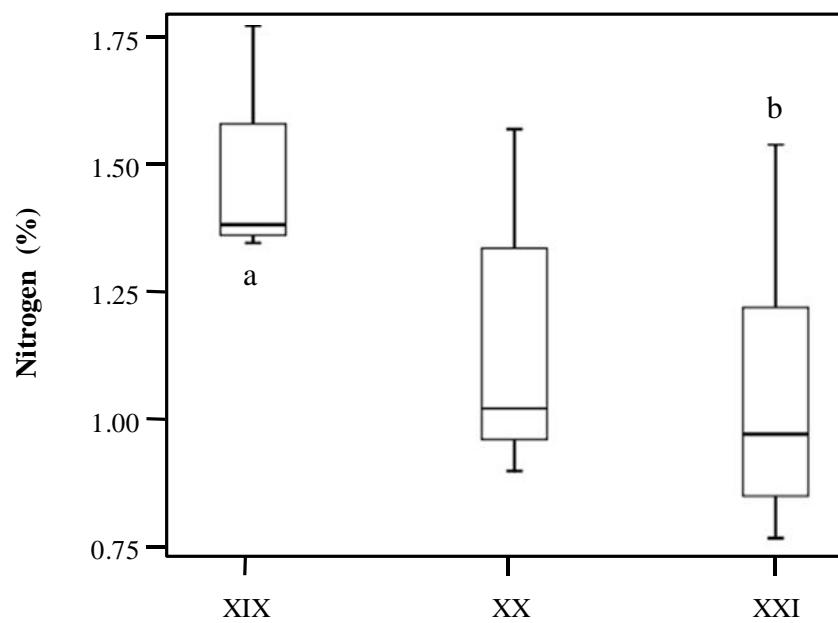
Foan, L., Sablayrolles, C., Elustondo, D., Lasheras, E., Gonzalez, L., Ederra, A., Simon, V. (Auteur de correspondance), Santamaria, J. (2010). Reconstructing historical trends of polycyclic aromatic hydrocarbon deposition in a remote area of Spain using herbarium moss material. *Atmospheric Environment*. 44 (26). 3207-3214. . DOI : 10.1016/j.atmosenv.2010.05.019

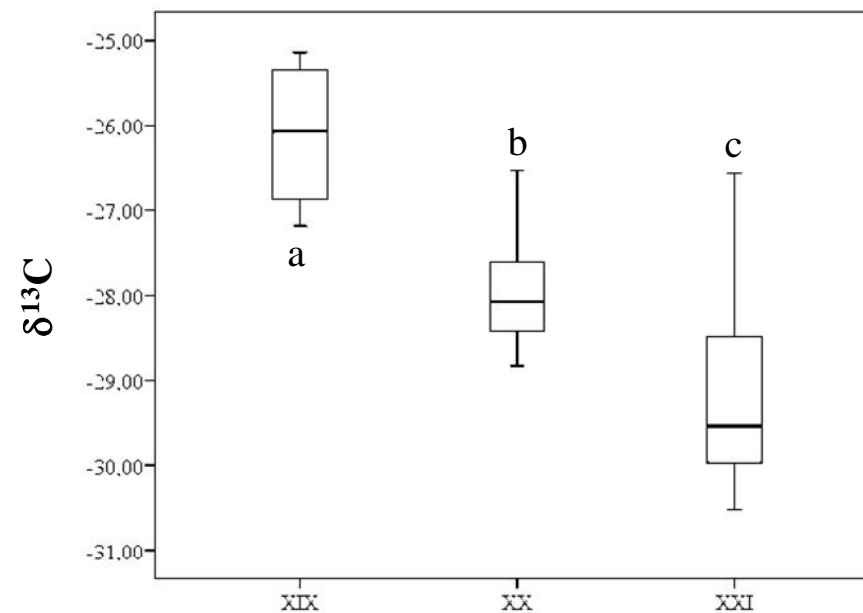
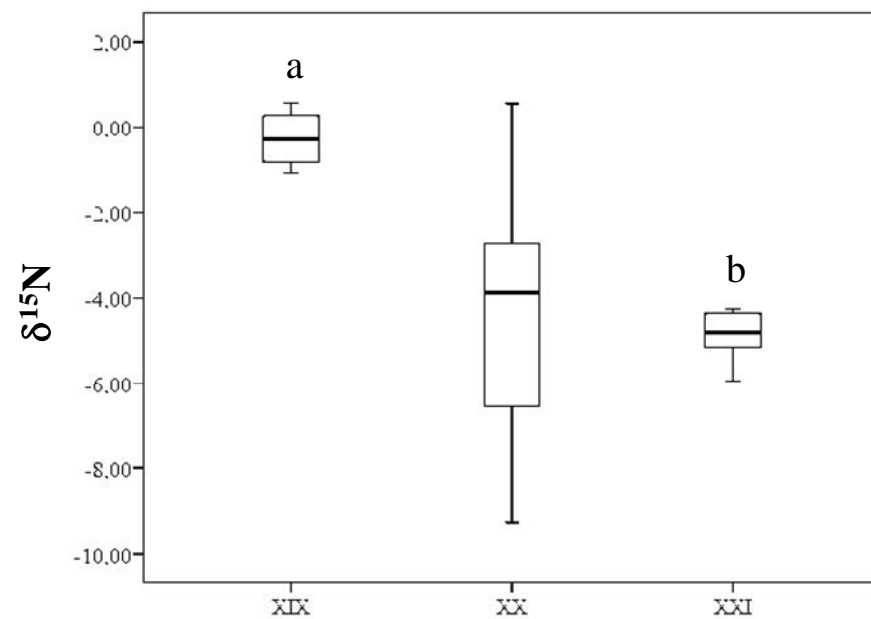
Sampling period	1879 – 1881	1973 – 1975	2006-2007
<i>Observed compounds (ng/g)</i>			
Acenaphthene (ACE)	39.0 12.2 – 62.4	2.5 < 1.5 – 3.3	4.1 < 1.5 – 12.7
Fluorene (FLR)	85.5 37.9 – 143.2	13.9 < 10.4 – 18.7	15.1 < 10.4 – 21.3
Phenanthrene (PHE)	298.8 118.9 – 622.0	127.9 98.6 – 174.3	81.1 26.9 – 142.2
Anthracene (ANT)	6.2 2.9 – 9.4	4.7 3.2 – 9.6	3.2 1.2 – 9.9
Fluoranthene (FTN)	252.2 145.5 – 466.4	65.4 32.7 – 123.0	38.1 10.2 – 152.7
Pyrene (PYR)	220.9 127.4 – 436.7	44.8 29.1 – 66.4	18.5 6.8 – 39.0
Benzo(a)anthracene (B(a)A)	97.0 66.9 – 120.1	8.3 4.2 – 11.9	3.1 < 1.2 – 7.0
Benzo(b)fluoranthene (B(b)F)	86.8 65.6 – 95.5	18.8 9.3 – 40.9	3.0 1.8 – 5.5
Benzo(k)fluoranthene (B(k)F)	40.6 29.6 – 49.1	6.6 3.2 – 14.3	0.8 < 0.5 – 1.8
Benzo(a)pyrene (B(a)P)	31.6 28.5 – 34.8	9.7 < 1.4 – 17.8	2.4 < 1.4 – 1.7
Dibenzo(a,h)anthracene (D(ah)A)	3.6 3.0 – 4.6	1.8 < 1.3 – 3.3	4.2 < 1.3 – 7.8
Benzo(g,h,i)perylene (B(ghi)P)	31.2 21.7 – 55.1	18.5 10.9 – 35.3	5.6 2.0 – 16.1
Indeno(c,d)pyrene (IND)	25.2 17.5 – 35.0	9.9 5.8 – 21.0	2.0 < 2.0 – 2.5
ΣPAHs	1218.6 782.8 – 2009.1	328.2 206.1 – 464.6	171.8 86.0 – 372.5











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