Deposition of atmospheric polycyclic aromatic hydrocarbons in rural areas: Current data and historical record from an ombrotrophic peatland

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ABSTRACT

Atmospheric concentrations of 18 polycyclic aromatic hydrocarbons (PAHs) were measured in a rural area in northern Spain. Both the gas phase and particulate fraction were determined to evaluate the types and abundance of PAHs taken up by vegetation and the historical record of PAH deposition in an ombrotrophic peatland over the last 300 years. The total atmospheric PAH concentration was ca. 2.5 ng m^{-3}, a value that is slightly lower value than those found in other rural areas, consistent with those of remote areas (Pyrenees, Alps, and Caledonian Mountains), and much lower than those recorded in urban areas. The particulate fraction showed a greater content of high molecular weight PAHs, whereas the gas phase was enriched in low molecular weight homologues. The concentration of total PAHs in the gas phase was higher than that in the particulate fraction (ca. 80%) and similar to that found in other localities in remote areas. PAHs showed seasonal variability. In this regard, the highest concentrations in the gas phase occurred in winter and autumn, whereas in the particulate fraction they were found in winter and spring. Of note, the concentrations of PAHs increased in the particulate fraction during the years in which fires occurred. The PAH content in peat-forming plants in this area showed a similar distribution to that of the gas phase. The historical record of the depositional fluxes of PAHs in an ombrotrophic peatland in the study area, which was dated radiometrically, allowed to reconstruct the changes in pollutant content between 1775 and the present. In general, the PAHs detected were of pyrogenic origin (fossil fuels and wood combustion). The concentrations of these pollutants increased from uniform background levels at the turn of the second half of the 19th century, which were linked to industrial development, to maximum values during the first half of the 20th century until the beginning of the 21st century, when the extraction and combustion of coal was extensive close to the study area. In contrast, in the uppermost part of the record, PAH concentrations decreased. This reduction is attributed to the implementation of environmental policies, although the concentrations of these pollutants were still greater than during the preindustrial period. To gain a detailed understanding of the deposition and evolution of PAHs in the study area, here it is reported on a new method that integrates current atmospheric data on PAHs with information on their accumulation in plants and the historical peat record of a rural area in Spain. The methodology described herein could be applied to other scenarios in the context of PAH pollution.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to the category of persistent organic pollutants (POPs), which have carcinogenic and mutagenic properties (Menzie et al., 1992; Readman et al., 1986; Magi et al., 2002; Lang et al., 2012; Wang et al., 2014; Cai et al., 2016) and are ubiquitously present in the environment.

PAHs are found in petroleum and coal and can also be derived from incomplete combustion processes. These can be either natural, such as forest fires, although their contribution to the total PAH concentration is

relatively low (Wegener et al., 1992; Wilcke, 2000), and natural petroleum seeps, or anthropogenic, such as the combustion of fossil fuels (Harvey, 1998; Howsam and Jones, 1998).

PAHs can be classified into three types, namely petrogenic, biogenic, or pyrogenic. Those of petrogenic origin (e.g., naphthalene and phenanthrene), including crude oil and its refined products, are related to petroleum. PAHs of biogenic origin are generated by biological processes (e.g., plant- and microbial-related sources of naphthalene, phenanthrene, and perylene) (Wilcke, 2000; Krauss et al., 2005), or by the early stages of diagenesis in marine sediments (e.g., perylene) (Venkatesan, 1988). Those of pyrogenic origin come about from the combustion of fossil fuels and recent organic material (Page et al., 1999). Therefore, the origin of PAHs can be inferred from their characteristics and types, i.e., petrogenic PAHs, including oil seeps, petroleum refined products, and terrestrial precursors, are characterised by the predominance of 3 or fewer benzene rings (Benner Jr et al., 1990; Porte et al., 2000). In contrast, pyrogenic PAHs have significant percentages of 4 or more rings (Benner Jr et al., 1990). In this regard, some indexes allow the identification of pyrogenic sources, thereby allowing differentiation between coal combustion, petroleum combustion, gasoline and diesel emissions from vehicles, forest burning, and others (Boente et al., 2020; Yunker et al., 2012; Liu et al., 2012; Zhang et al., 2008; Lehndorff and Schwark, 2004).

Thus, PAHs are released into the atmosphere. They are more abundant within urban areas or zones close to industrial sites and they can be transported over long distances (Fernández et al., 2002, 2003; Van Drooge et al., 2010). PAHs may occur in the gas phase or association with atmospheric particulate matter, mainly in the submicron particle fraction (Aceves and Grimalt, 1993; Allen et al., 1996), which favors their long-range transport and global distribution (Laflamme and Hites, 1978; Atlas and Giam, 1981; Grimalt et al., 1988; McVeety and Hites, 1988). PAHs in both fractions are deposited into aquatic and terrestrial ecosystems by dry depositional processes (gas absorption, gravitational settling, eddy diffusion) and rainfall (Baker and Eisenreich, 1990; Leister and Baker, 1994; Fernández et al., 2002, 2003). They can also be incorporated into sediments as a result of runoff (Hoffman et al., 1984; Brown et al., 1985).

In addition, vegetation can take up PAHs from the gas phase or particulate fraction. From the former, they can enter vegetation by deposition onto the waxy cuticle of leaves or by uptake through the stomata and subsequent translocation by the phloem (Meredith and Hites, 1987). In contrast, particle-bound pollutants stick to the leaf surface or are partly downwashed by rain, depending on particle size and leaf surface (Hosker Jr and Lindberg, 1967). Thus, these pollutants can accumulate in living plants (Holoubek et al., 2000; Johnsen and Karlson, 2007; Lehndorff and Schwark, 2004; Vuković et al., 2014; Wang et al., 2019).

Once deposited, PAHs are highly sorptive to organic matter, but their post-depositional mobility is assumed to be negligible (Sanders et al., 1995; Eriksson et al., 2000; Johnsen et al., 2005; Zaccone et al., 2009). In the acidic and anoxic conditions of peat, and consequently a low overall metabolic activity in zones below the water table, PAH degradation is very slow (Lei et al., 2005; Zaccone et al., 2009; Thuens et al., 2013).

Ombrotrophic mires receive water only from rainfall and are characterised by the accumulation of peat in a raised mass over the groundwater table. Given these characteristics, these peatlands are natural archives of atmospheric pollution and their records allow the study of the deposition history of harmful contaminants (e.g., Zaccone et al., 2009; Martínez Cortizas et al., 2002; Pontevedra-Pombal et al., 2012; Gallego et al., 2013, 2019). Furthermore, allochthonous inputs of chemical compounds to ombrotrophic mires originate exclusively from the atmosphere. Therefore, peat cores from these environments are among the best archives of temporal changes in the deposition rates of organic pollutants (Zaccone et al., 2009). Indeed, these peatlands are ideal archives for research into palaeoenvironmental changes (Martínez

Cortizas et al., 1999; Pontevedra-Pombal, 2002). On the other hand, peat is a very immature sediment, has a relatively low amount of aromatic compounds and the ones present are strongly functionalized with the typical configuration of the biological precursors (Hajje and Jaffé, 2006). Therefore, PAHs identified in the sediment can be confidently attributed to external sources. However, few studies have addressed the historical temporal deposition of PAHs from cores drilled in peatlands (Berset et al., 2001; Dreyer et al., 2005; Zaccone et al., 2009; Cong et al., 2016), and except for Pontevedra-Pombal et al. (2012), no such studies have been carried out in the Iberian Peninsula.

Here it is sought to delve into the processes affecting historic PAH accumulation rates over the past 300 years. To this end, an undisturbed ombrotrophic peatland called Las Conchas was selected, located in a remote rural area in Asturias (Northern Iberian Peninsula). Thus, 18 PAHs included in the US Environmental Protection Agency (EPA) priority list were analysed. The atmospheric input of these PAHs to this area (gas phase and particulate phase) was determined, together with their uptake by living plants. In addition, a core was drilled to examine the abundance of these pollutants in the uppermost part of the record, whose biomarker and trace element content was studied previously (Ortiz et al., 2016; Gallego et al., 2019). A detailed analysis of the data collected is provided and discuss the temporal changes in the content, accumulation rates, and composition of PAHs in Las Conchas mire, as well as their potential sources.

2. Geographical setting

Located to the east (Llanes county) of the Asturias Province (N. Spain), Las Conchas mire (UTM 30360.627, 4.803.642; 363 m) covers ca. 100,000 m^2 (Fig. 1a). This region has an Atlantic-type climate with humid temperate winters and occasional droughts in the summer.

Las Conchas mire lies on the Ordovician quartzites of the Barrios Formation, at the top of an ancient marine abrasion platform (Martínez García, 1980). This platform laterally leans on the Cuera Range (Fig. 1a), made of karstified carboniferous limestone (Barcaliente, Valdeteja, and Cuera Formations).

The area has an annual mean temperature of 13.1 °C, July and August being the warmest months, and an annual mean precipitation of 1136 mm/year. July and August are the driest months and December is the most humid (Rivas-Martínez and Rivas y Sáenz, 2006).

The current vegetation in the mire includes mainly species of *Sphagnum* (*Sphagnum denticulatum* being especially abundant) and Gramineae (Ortiz et al., 2016). Other types of moss (*Calliergonella cuspidata, Polytrichum commune, Campylopus flexuosus, Aulacomnium palustre, Kindbergia praelonga*) and vascular plants, including the gorse *Ulex europaeus*, and the rush *Juncus effusus,* are found. The heathers *Erica mackaiana*, endemic to northern Spain, and *Erica tetralix* are also common.

The peat record of Las Conchas mire is 3.2 m deep. The stratigraphy and main characteristics of the core were described in detail in previous work by Ortiz et al. (2016). The column consists of bryophytic spongious reddish and brownish peat, with clearly recognisable plant remains. The core gets darker towards the bottom, except for the last centimeters, which consist of grey and light-coloured silt (Fig. 1b).

The geochronology of the uppermost 20 cm of the core was calculated from the ^{210}Pb profile, through alpha spectroscopy, using the constant rate of supply method (CRS) supported by ^{137}Cs and ^{226}Ra activities (Gallego et al., 2019). In addition, 12 peat samples were taken at greater depths for radiocarbon dating (Ortiz et al., 2016). Thus, the chronological model for the whole record (Fig. 1B) was created with the Bayesian R-code package "Bacon 2.3.7" (Blaauw and Christen, 2011), using the IntCal13.14C calibration curve (Reimer et al., 2013) for radiocarbon samples.

In this regard, estimates of the sedimentation rate indicate that the uppermost 20 cm of the record were deposited over ca. 300 years (Fig. 1A), and no signs of major mixing or disruption of the
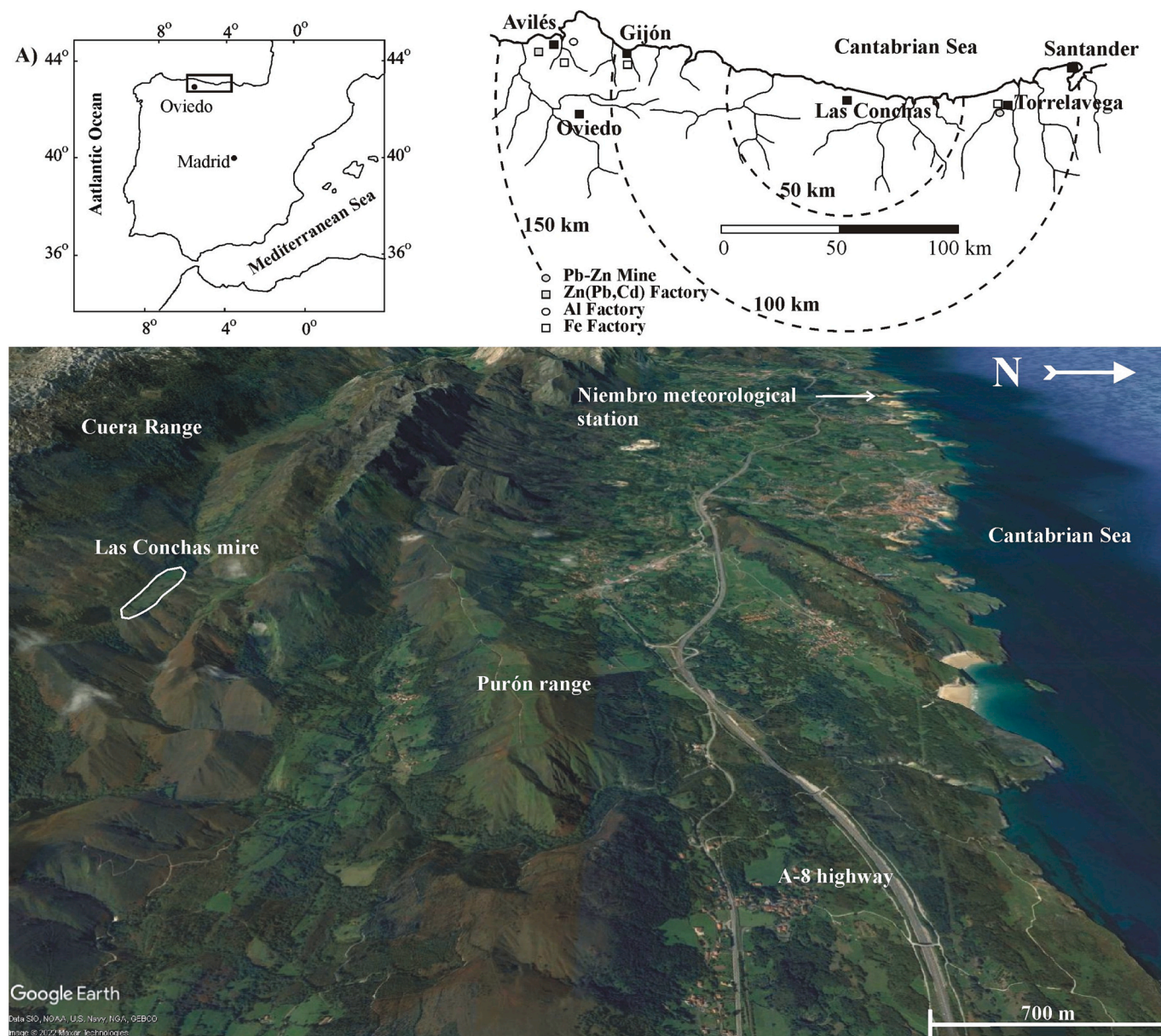
Fig. 1. Geographical location of Las Conchas mire.

sedimentation were observed.

3. Methodology

3.1. Atmospheric PAHs

3.1.1. PAHs in the gas phase

Samples from gas phase deposition were collected regularly from rainwater monthly or bimonthly from March 2018 to April 2019 in Las Conchas mire. A bottle, with a mouth of 5 cm^2 was used, placed 1.5 m from the surface.

Samples were filtered through preweighed glass fiber filters onsite (Whatman, GF/B, 45 mm diameter, 1 μm pore size). PAHs were extracted in a Dionex AutoTrace Solid-Phase Extraction instrument for liquid samples using dichloromethane and ethylacetate and following EPA method 3545 (El Comercio, Spain, 2017). Prior to PAH extraction, 1-fluoropyrene (20 μL of 10 μg/L surrogate standard) was added to the samples to check the effectiveness of the process (resulting in a final concentration of 0.2 μg/L).

Each extract was concentrated using a rotary evaporator and a TurboVap II concentrator under N$_2$. The solvent was switched to cyclohexane before analysis. Also, to test the reliability of the extractions, control samples consisting of 1 L water with a concentration of 1 μg/L of the different PAHs were used. PAH recoveries were above 70%.

PAHs were analysed using a gas chromatograph (Agilent-7890) coupled to a mass spectrometer (Agilent-5975a) with a PTV injector (90–275 °C in 0.5 min) and a DBS-5MS column (0.25 mm × 30 m × 0.25 μm). Helium was the carrier gas and the oven temperature was programmed from 60 to 300 °C (held 10 min) at 5 °C/min. Prior to PAH analysis, an internal standard (20 μL of 1 μg/L 3-fluorochrysene) was added to the extracts (resulting in a final concentration of 0.02 μg/L).

3.1.2. PAHs in the particulate fraction

PAHs in the particulate phase were considered from data collected in the Niembro meteorological station, located 5 km from Las Conchas mire, in 2018 (Red EMEP/VAG/CAMP, 2018). For comparison purposes, available data from 2010, 2011, 2012, and 2017 for the same station (Galán Madruga et al., 2013; Orío Hernández et al., 2013; Red EMEP/

VAG/CAMP, 2017, 2018**)** were also examined. PAHs were regularly extracted and analysed from the PM10 fraction.

3.2. Living plants

Living plants, including various mosses and stems from vascular plants, from Las Conchas mire were selected for PAH analysis. To avoid degradation and contamination, plant samples were preserved at low temperatures immediately after collection. Prior to analysis, they were washed independently with distilled deionised water, classified, and examined following the same procedure as that used for peat samples.

Mosses, including *Sphagnum*, and grasses (Gramineae) are currently the main plant inputs to the mire, although other plants, such as Ericaceae, also contribute to peat composition. The plant specimens were selected on the basis of their current abundance in the mire (*S. denticulatum*, Gramineae, *J. effusus,* and *U. europaeus*) and their diversity (non-*Sphagnum* mosses).

3.3. Coring and sample preparation

A 3.2 m-long core was drilled in the central part of Las Conchas mire with a manual probe (5 cm diameter). The core was split in half longitudinally, photographed, and sliced into portions after the profile had been described. Before analysis, samples were freeze-dried at −18 °C using a lyophiliser to prevent any alteration.

Peat samples were taken at 1-cm intervals in the uppermost 20 cm of the core, and three samples were taken at 2-cm intervals between 20 cm and 26 cm, covering the last 300 years, according to the chronology of Las Conchas record (Gallego et al., 2019).

3.4. Analysis of PAHs in sediments and plants

PAHs were extracted following EPA method 3545 (EPA, 1998), which indicates that their extraction is most effective on dry sediment (2–5 g). PAHs were extracted in an accelerated solvent extractor (Dionex ASE 200) with 1:1 acetone/dichloromethane at 2000 psi and 100 °C. The heating phase and static extraction time were both 5 min. Prior to PAH extraction, the following five surrogate standards (50 µL of 10 µg/L surrogate standard) were added to the samples to check effectiveness of the process (resulting in a final concentration of 0.1 µg/g): naphthalene *d*-8 for compounds with signals at *m/z* 128; acenaphthene *d*-10 for those at *m/z* 152, 153, and 166; phenanthrene-*d*10 for those at *m/z* 178, and 202; chrysene-*d*12 for those at *m/z* 228; and perylene-*d*12 for those at *m/z* 252, 276, and 278.

Each extract was concentrated using a rotary evaporator and a TurboVap II concentrator under N_2. The solvent was changed to cyclohexane prior to analysis. Also, to test the reliability of the extractions, control samples consisting of 5 g silica sand and a concentration of 1 µg/L of the different PAHs were used. PAH recoveries were above 80%.

PAHs were analysed by gas chromatography (Agilent-7890) coupled to a mass spectrometer (Agilent-5975a) with a PTV injector (90–275 °C in 0.5 min). PAHs were eluted using a DBS-5MS column (0.25 mm × 30 m × 0.25 µm) and He as carrier gas. The oven temperature was programmed from 60 to 300 °C (held 10 min) at 5 °C/min and the injector was at 275 °*C. prior* to analysis, an internal standard (10 µL of 100 µg/L decafluorobiphenile) was added to the extracts (resulting in a final concentration of 1 µg/L).

To test the effectiveness of the analysis, a blank was run after six samples. For PAH quantification, six standards (containing all the PAHs) with concentrations between 0.001 and 0.1 µg/L were run, which were used to calculate a calibration curve. The standard relative deviation of the calibration curve was <20% for all PAHs.

4. Results

4.1. PAHs in the atmosphere

The concentrations of PAHs in the gas phase are shown in Table 1. Low molecular weight PAHs were dominant, phenanthrene, fluorene, fluoranthene, and pyrene being the most abundant. In contrast, 5- to 6-ring PAHs were present almost only in winter rainfall but at low concentrations. Of note, the highest concentrations of these pollutants were observed in winter, followed by autumn, spring and summer.

PAH concentrations in the particulate phase in the PM10 fraction recovered in the Niembro station (Llanes, Asturias) over several years are shown in Table 2 (Galán Madruga et al., 2013; Orío Hernández et al., 2013; Red EMEP/VAG/CAMP, 2017, 2018). The total concentrations differed between the years with available records, 2017 being the year with the highest abundance, followed by 2012, 2011, 2010, and 2018. The most abundant homologues were benzo[*b,j*]fluoranthene, indene [123-*cd*]pyrene, benzo[*k*]fluoranthene, and benzo[*ghi*]perylene, whereas chrysene, phenanthrene, fluoranthene, and pyrene had the highest presence in the group of 2- to 4-ring PAHs.

4.2. PAHs in plants

To discern the origin of PAHs in the sediment, the PAH content in living plants in Las Conchas mire was analysed (Table 3). They all showed low molecular weight PAHs, phenanthrene, fluorene, fluoranthene, and pyrene being predominant. PAHs with higher molecular weights than chrysene were not detected. Of note, mosses showed the highest concentrations of these compounds.

4.3. PAHs in Las Conchas record

The logs with the sum of PAH concentrations arranged by the number of benzene rings are shown in Fig. 2, together with the total concentration of PAHs. Of note, in all cases, the values showed few

Table 1
Annual concentration of PAHs in rainwater collected in Las Conchas mire during 2018–2019.

PAH	Spring 2018 (ug/L = ng/m³)	Summer 2018 (ug/L = ng/m³)	Autum 2018 (ug/L = ng/m³)	Winter 2018/19 (ug/L = ng/m³)	2018/19
Naphtalene	0.015	0.039	0.064	0.046	0.165
Acenaphtilene	0.002	0.011	0.049	0.049	0.112
Acenaphtene	0.002	0.009	0.005	0.014	0.030
Fluorene	0.005	0.018	0.025	0.053	0.101
Phenanthrene	0.032	0.068	0.151	0.452	0.703
Anthracene	0.001	0.001	0.007	0.019	0.028
Fluoranthene	0.011	0.041	0.069	0.308	0.429
Pyrene	0.008	0.028	0.042	0.180	0.258
Benzo[*a*]anthracene	–	–	–	0.019	0.019
Chrysene	0.001	0.003	0.004	0.050	0.058
Benzo[*b*]fluoranthene	0.002	0.002	0.005	0.022	0.022
Benzo[*k*]fluoranthene	0.001	0.002	0.002	0.007	0.007
Benzo[*e*]pyrene	–	–	–	0.009	0.009
Benzo[*a*]pyrene	0.001	0.002	0.002	0.005	0.005
Perylene	–	–	–	0.001	0.001
Dibenzo[*ah*]anthracene	–	–	–	0.005	0.005
Indene[123-*cd*]pyrene	–	0.002	0.002	0.003	0.003
Benzo[*ghi*]perylene	–	0.001	0.002	0.005	0.005
Total	**0.081**	**0.228**	**0.430**	**1.245**	**1.984**

Table 2

Mean annual concentration of PAHs in the atmospheric particle fraction (PM10) in the Niembro station during diverse years (Orío Hernández et al., 2013; Red EMEP/VAG/CAMP, 2017, 2018).

PAH	2010 (ng/m³)	2011 (ng/m³)	2012 (ng/m³)	2017 (ng/m³)	2018 (ng/m³)
Naphtalene	0.090	0.090	0.085	0.0023	0.004
Acenaphtilene	0.070	0.070	0.065	–	0.001
Acenaphtene	0.090	0.090	0.085	0.00075	0.002
Fluorene	0.030	0.030	0.024	0.00017	0
Phenanthrene	0.040	0.110	0.033	0.027	0.020
Anthracene	0.030	0.030	0.009	0.0018	0.002
Fluoranthene	0.050	0.190	0.150	0.035	0.016
Pyrene	0.080	0.160	0.100	0.022	0.011
Benzo[a]anthracene	0.020	0.120	0.034	0.0078	0.007
Chrysene	0.040	0.200	0.087	0.046	0.026
Benzo[b + j]fluoranthene	0.020	0.190	0.720	2.300	0.248
Benzo[b]fluoranthene	0.050	0.300	–	–	–
Benzo[k]fluoranthene	0.050	0.100	0.094	0.300	0.031
Benzo[a]pyrene	0.030	0.090	0.044	0.019	0.011
Indene[123-cd]pyrene	0.030	0.250	0.330	0.390	0.057
Dibenzo[ah]anthracene	0.020	0.070	0.031	0.061	0.003
Benzo[ghi]perylene	0.030	0.150	0.200	0.270	0.027
Total	0.680	2.150	2.006	3.480	0.466
	March–May	Oct-Dec	All year	All year	All year

variations and low concentrations below 11 cm. In contrast, in the uppermost 10 cm, the abundance of PAHs showed a sharp increase, with a maximum concentration at 8 cm. Of note, 5-ring PAHs were the most abundant compounds, followed by 4- and 3-ring homologues.

Selected PAHs, such as phenanthrene, benzo[a]pyrene, dibenzo[a,h] anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, and chrysene were also plotted (Fig. 3), which provide valuable information about pollution sourcies.

5. Discussion

5.1. Atmospheric deposition of PAHs

The total atmospheric PAH concentration (gas phase + particulate phase) in Las Conchas mire was ca. 2.5 ng m^{-3} (Tables 1, 2), which is slightly lower than those measured in rural areas, such as the Chesapeake Bay (2.7–5.3 ng m^{-3}; Leister and Baker, 1994; Gustafson and Dickhut, 2009) and Lake Superior (2.9–3.9 ng m^{-3}; McVeety and Hites, 1988; Baker and Eisenreich, 1990), but consistent with those of remote areas (Pyrenees, Alps, and Caledonian Mountains): 1.3–3.7 ng m^{-3} according to Fernández et al. (2002, 2003) and 0.2–5.1 ng m^{-3} accoding to Van Drooge et al. (2010). In urban areas, much higher concentrations of atmospheric PAHs occur. In this regard, the following concentrations were recorded: 166 ng m^{-3} in London (Halsall et al., 1994); 127 ng m^{-3} in Strasbourg and 149 ng m^{-3} in Schiltigheim (Morville et al., 2011); ca. 100 ng m^{-3} Harbin (China) (Ma et al., 2010); 23.8–44,5 ng m^{-3} in atmospheric particles PM10 Hong Kong (Guo et al., 2003); 93.0 and 55.1 ng m^{-3} in urban and industrial areas of Flanders (Belgium), respectively (Rockens et al., 2000); and 24.5–38.8 ng m^{-3} in Mumbai (India) (Kulkarni and Venkataraman, 2000).

In 2018, the PAH concentrations in the gas phase in Las Conchas mire were higher than those in the particulate fraction, i.e., the contribution of particle-associated homologues to the total PAH content in Las Conchas mire (ca. 20%) was similar to that in other localities in remote areas, e.g. ca. 10–30% (Fernández et al., 2002) and 5–20% (Van Drooge et al., 2010). Ma et al. (2010) found similar concentrations of PAHs in

Table 3

Concentration of PAHs (µg/g) in plants from Las Conchas mire.

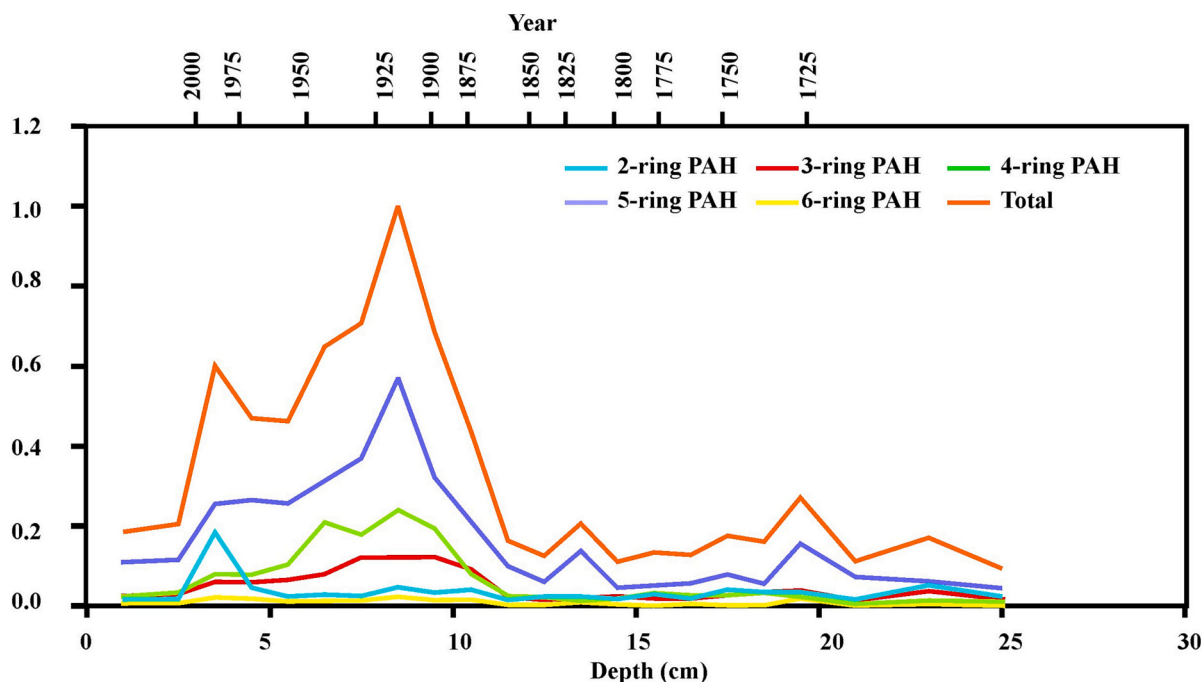| PAH	Ulex europaeus (gorse)	Juncus effusus (rush)	Gramineae 1 (grass)	Gramineae 2 (grass)	Calliergonella cuspidata (moss)	Polytrichum commune (moss)	Campylopus flexuosus (moss)	Sphagnum denticulatum (moss)	Aulacomium palustre (moss)	Kindbergia praelonga (moss)
Naphtalene	0.045	–	–	–	0.008	0.007	–	–	–	–
Acenaphtilene	0.150	0.003	–	0.096	0.243	0.060	0.016	0.011	0.041	0.092
Acenaphtene	0.122	0.001	–	–	0.080	0.039	0.043	–	–	–
Fluorene	0.229	0.003	–	0.047	0.048	0.013	0.030	0.016	0.047	0.105
Phenanthrene	0.095	0.002	0.001	0.009	0.026	0.025	0.013	0.009	0.039	0.083
Anthracene	–	–	–	0.002	–	–	–	–	–	–
Fluoranthene	0.039	0.004	–	0.006	0.028	0.023	0.005	0.006	–	0.057
Pyrene	0.056	–	0.001	0.011	0.027	0.019	0.010	0.007	–	0.057
Benzo[a]anthracene	–	–	–	–	–	–	–	–	–	–
Chrysene	–	–	–	–	0.006	0.011	0.001	–	–	–
Benzo[b]fluoranthene	–	–	–	–	–	–	–	–	–	–
Benzo[k]fluoranthene	–	–	–	–	–	–	–	–	–	–
Benzo[e]pyrene	–	–	–	–	–	–	–	–	–	–
Benzo[a]pyrene	–	–	–	–	–	–	–	–	–	–
Perylene	–	–	–	–	–	–	–	–	–	–
Dibenzo[ah]anthracene	0.446	–	–	–	–	–	–	–	–	–
Indene[123-cd]pyrene	–	–	–	–	–	–	–	–	–	–
Benzo[ghi]perylene	0.301	–	–	–	–	–	–	–	–	–
Total	1.483	0.013	0.002	0.171	0.466	0.197	0.118	0.049	0.127	0.394

Fig. 2. Content and distribution of 2 to 6-ring polycyclic aromatic hydrocarbons (PAHs) in Las Conchas record over the past 300 yr.
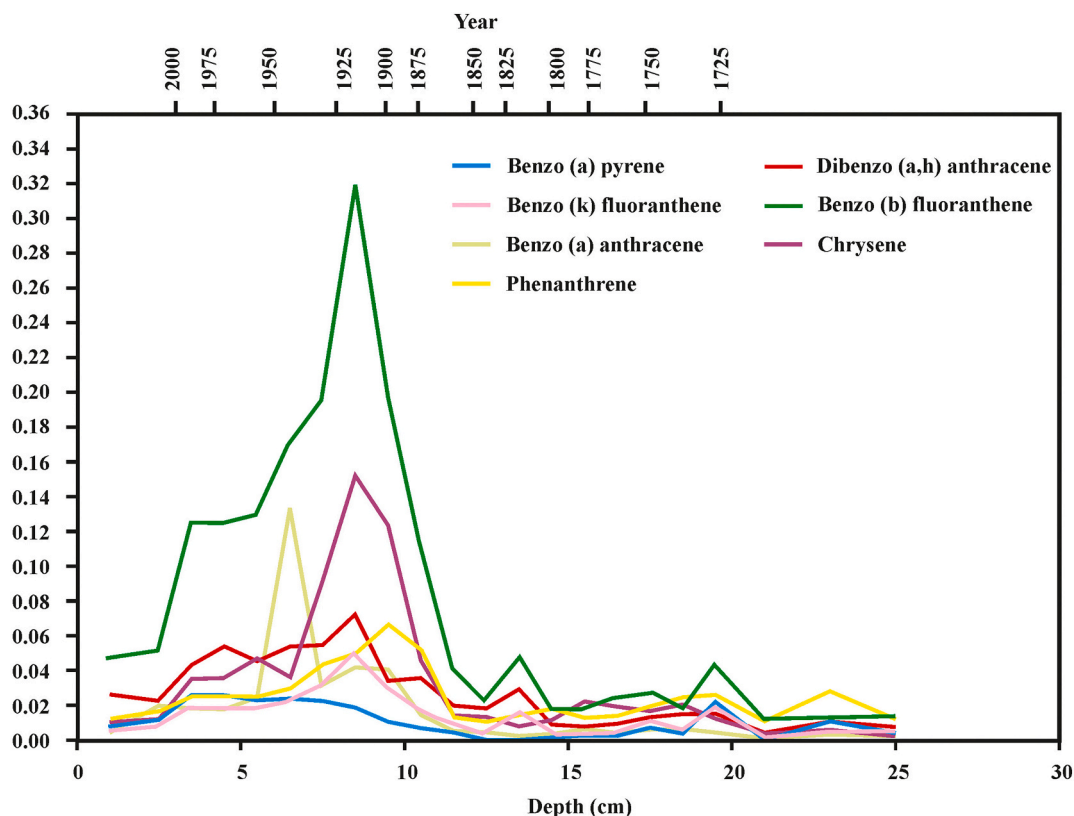

Fig. 3. Content and distribution of selected PAHs in Las Conchas record over the last 300 yr, namely: phenanthrene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo [*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]anthracene and chrysene.

the gas and particulate fractions in urban areas. In contrast, Paloluoglu et al. (2016) observed that PAH concentrations in the particulate fraction were higher.

In this regard, total PAHs in the gas phase from Las Conchas mire (1.9 ng m^{-3}) were similar to those reported in other remote localities,

for example, 0.16–4.44 ng m^{-3} (Fernández et al., 2002; Van Drooge et al., 2010). In addition, the concentration of PAHs in the particulate fraction in Las Conchas mire was similar (0.46 ng m^{-3}) to that of other sites, e.g., 0.05–0.70 ng m^{-3} (Van Drooge et al., 2010).

Of note, the concentration of PAHs in the particulate fraction in 2018

was markedly lower (0.46 ng m^{-3}) than in 2017 (3.48 ng m^{-3}), which can be explained by the important fire that affected this area in 2017 (El Comercio, 2017; La Nueva España, 2017). Likewise in 2011 and 2012, there were fires close to the Niembro station and these would have caused an increase in the abundance of PAHs in the particulate fraction (2.0–2.1 ng m^{-3}), although the increase was not as big as that caused by the fire in 2017 (Table 2).

Fluoranthene and pyrene rather than benzo[*ghi*]perylene, dibenzo[*a*, *h*]anthracene, and indene[123-*cd*]pyrene are considered the dominant PAHs in airborne particulate matter derived from the burning of vegetation (Freeman and Cattell, 1990). In this regard, the abundance of all these compounds markedly increased in 2017, especially benzo[*b*]fluoranthene, indene[123-*cd*]pyrene, and benzo[*ghi*]perylene. These compounds could be considered important markers of wood and grass combustion.

Low molecular weight PAHs (2–4 rings) were present mainly in the atmospheric gas phase (compounds from fluorene to pyrene), while PAHs with 5 and 6 rings were associated principally with particulate matter (from benz[*a*]anthracene to benzo[*ghi*]perylene) (Orío Hernández et al., 2013; Red EMEP/VAG/CAMP, 2017, 2018), in coincidence with Fernández et al. (2003).

Atmospheric gas phase deposition was dominated by low molecular weight PAHs, namely phenanthrene, fluoranthene, pyrene, and fluorene, as reported in the Pyrenees and the Alps (Fernández et al., 2002, 2003; Van Drooge et al., 2010), and other sites in Europe (Gevao et al., 1998; Halsall et al., 1994; Van Drooge et al., 2010) and the United States (Golomb et al., 1997). Furthermore, compounds with molecular weights exceeding that of chrysene were not present in the gas phase, except for some PAHs in winter rainfall, while in remote areas they are present only in the particulate phase (Fernández et al., 2002, 2003; Van Drooge et al., 2010).

In the particulate phase, benzo[*b,j*]fluoranthene, indene[123-*cd*] pyrene, benzo[*k*]fluoranthene and benzo[*ghi*]perylene were the most abundant high molecular weight PAHs, while chrysene, phenanthrene, fluoranthene, and pyrene were the dominant lower molecular weight homologues, in agreement with the predominant PAHs reported in remote areas of Europe (Fernández et al., 2002, 2003; Van Drooge et al., 2010). Of note, benzo[*e*]pyrene, one of the most abundant PAHs in the particulate phase (Fernández et al., 2002, 2003; Van Drooge et al., 2010), was not measured at the Niembro station. PAHs are generally associated to the combustion of fossil fuels but have not a high specificity as source indicators: typically benzo[*b*]fluoranthene and benzo[*k*] fluoranthene are typical indicators of diesel exhaust emissions (Sienra et al., 2005; Ravindra et al., 2008), whereas benzo(*ghi*)perylene and indene (123-cd) pyrene are characteristic of gasoline engines (Miguel et al., 1998; Hien et al., 2007; Ravindra et al., 2008; Tian et al., 2009). Chrysene, phenanthrene, pyrene, and fluoranthene are typical markers of diesel vehicles (Rogge et al., 1993; Masclet et al., 1986; Guo et al., 2003; Hien et al., 2007; Zheng et al., 2017), but also of wood combustion (Khalili et al., 1995; Bourotte et al., 2005; Ravindra et al., 2008; Wang et al., 2008).

The highest gas-phase PAH deposition to Las Conchas mire was observed during winter and autumn, consistent with the findings of other studies (Brun et al., 1991; Golomb et al., 1997; Polkowska et al., 2000; Leuenberger et al., 1988; Fernández et al., 2002). The highest particle-associated PAH concentrations occurred in winter and spring (Galán Madruga et al., 2013), with 5-ring homologues accounting for the main contribution (52.84%), followed by 6-ring (33.26%) and 4-ring (13.91%) compounds. These observations could be explained by increased emissions and lower atmospheric mixing heights in winter and, consequently, a higher atmospheric concentration of pollutants (Golomb et al., 1997). In contrast, Dickhut and Gustafson (1995) and Fernández et al. (2003) reported that the main PAH deposition in the Chesapeake Bay, Estany Redó (Pyrenees) and Gossenköllesee (Alps) occurred during spring and summer, probably as a result of the redistribution of these pollutants to larger particles under increasing

temperature and higher convective storms and precipitation events during the warm seasons. Of note, these sites are located in high mountains with different altitudes and climates to those of Las Conchas mire.

In this regard, at lower temperatures, a larger fraction of the atmospheric PAHs is associated with air particles, which are more efficiently scavenged than those in the gas phase (Dickhut and Gustafson, 1995; Poster and Baker, 1996; Baker et al., 1997). In this context, positive linear correlations have been described between total washout and particulate phase PAHs (Franz et al., 1998). Furthermore, exponential increases in PAH gas washout coefficients at decreasing temperature are expected due to the exponential dependence of the Henry law constants of these pollutants on temperature (Dickhut et al., 1995).

Therefore, the atmospheric PAH profile of Las Conchas mire was similar to that reported in other remote or rural sites, being typical of PAH mixtures after certain atmospheric transport (Fernández et al., 2002, 2003; Van Drooge et al., 2010). Differences may be due to temperature during the gas/particulate phase partitioning, and differences in concentrations suggest the geographical influence of regional emissions. Also, the contribution of particle-associated homologues to the total PAH content (20%) was similar to that reported in other localities in remote areas (Fernández et al., 2002; Van Drooge et al., 2010). However, in some years affected by fires (2011, 2012, and mainly 2017), an increase in particulate-phase PAHs was detected, especially those with 5 or 6 rings (Table 2). Of note, Umlauf et al. (2010) observed high concentrations of PAHs (mainly 5- and 6-ring PAHs) in southern Poland in winter, which was attributed to wood and coal combustion for domestic heating. Likewise, high concentrations of vapour- and particle-associated compounds can also be found in fog water (Bidleman, 1988), which is a typical feature of Las Conchas mire.

In brief, the main input of PAHs in Las Conchas mire may be due to the proximity of small villages (with a total population of 10,000 inhabitants), in which biomass and fossil fuels are used for heating, and the A-8 motorway (< 5 km), in addition to controlled fires commonly used in agricultural and cattle farming practices in the area. In this regard, the most important sources of PAHs in this area are diesel emissions and vegetation (Galán Madruga et al., 2013). In this regard, industrial sources of PAHs (Fe, Al and Zn factories and mining activities) must be considered secondary in Las Conchas given that they are located around 100 km to the west or the east of the study area.

5.2. PAH uptake by plants

The PAH concentrations in living plants from Las Conchas mire are shown in Table 3. Phenanthrene, fluoranthene, fluorene, and pyrene were the predominant homologues found in the plants. Although PAHs can be originally present in unpolluted plants, the PAHs present in Las Conchas mire plants coincide with the most abundant ones in the atmospheric gas phase (Table 1), although the total concentrations differed. In contrast, 5- and 6-ring PAHs were not detected in the plants. In this regard, it has to be considered that the particulate matter from the surface of plants, which was more enriched in high molecular weigth PAHs (Table 2), was removed.

Of note, mosses are the most common plants that have been considered in PAHs intake studies. Moreover, mosses, including *Sphagnum*, together with grasses are the main peat forming plants in Las Conchas mire.

These results obtained here are in agreement with Orliński (2002), who measured the PAHs in moss samples from the highly polluted city of Warsaw (Poland) and its surroundings. That study found that the dominant compounds were phenanthrene, fluoranthene, and pyrene.

Likewise, the mosses of the Holy Cross Mountains (south-central Poland) and two National Parks (Alaska) showed a predominance of 3-ring PAHs, followed by 4-ring compounds (Migaszewski et al., 2009), in all cases linked to the atmospheric distribution of PAHs influenced by the emission sources (combustion of wood, vehicle particle emissions,

residential and industrial combustion of coal). Phenanthrene, fluoranthene, and pyrene were found to be the major components.

Dołęgowska and Migaszewski (2011) reported the predominance of phenanthrene, fluoranthene, and pyrene in mosses from the Kielce area (south-central Poland). They found that the highest PAH concentrations occurred at sites located close to the potential emission sources, thus allowing inference of the distance and type of pollution sources.

In this regard, deposited PAHs are easily absorbed by foliar surfaces. Therefore, leaves such as those of *Sphagnum* are ideal for estimating the degree of atmospheric PAH contamination (Lehndorff and Schwark, 2004; Vuković et al., 2014). However, in some cases, the morphology and species, rather than organic components in leaves, may be important in regulating PAH accumulation (Augusto et al., 2015; Dias et al., 2016).

Recently, Wang et al. (2019) found similar concentrations of PAHs in *Sphagnum* and *Ledum*, thereby indicating that these two plant species have comparable accumulation capacity by adsorption and uptake. For instance, in moss, a high surface-to-mass ratio and cell wall characteristics, such as specific surface area, seem to be the major mechanism through which PAHs are taken up (Boileau et al., 1982; Giordano et al., 2005; Tretiach et al., 2011).

In conclusion, the PAH content in the peat-forming plants of Las Conchas mire showed a similar distribution to that of the PAH composition of the gas phase, in coincidence with other studies (Orliński, 2002; Migaszewski et al., 2009; Dołęgowska and Migaszewski, 2011), and also the same predominant homologues. Therefore, the PAH uptake of the peat-forming plants would contribute to the distribution of these pollutants along Las Conchas record.

However, plants can differ in PAH degradation rates rather than in PAH accumulation capacity (Wang et al., 2019).

5.3. PAH record

For the study of the PAH profile in Las Conchas record, it is worth noting that the comparison of the atmospheric concentration of PAHs with those of lake sediments and soils in mountain sites shows good correspondence (Fernández et al., 1999; Grimalt et al., 2004; Van Drooge et al., 2010). Therefore, in mountainous sites, atmospheric transport determines the concentration of PAHs, which are influenced mainly by proximity to potential emission sources and whose distribution is governed by temperature.

Moreover, ombrotrophic bogs, such Las Conchas (Ortiz et al., 2016), receive water exclusively from rainfall and are characterised by the accumulation of peat in a raised mass over the groundwater table, with no additional input from other sources. In this regard, the PAH record of Las Conchas mire showed the characteristics of atmospheric deposition (during dry and wet periods) over time.

Furthermore, given that PAHs are not degraded in peat and there are no signs of vertical mobility, these peatlands are suitable environments in which to infer long-term trends over time (Thuens et al., 2013). Moreover, these findings reveal that the peat-forming plants of Las Conchas mire provided a similar PAH content and distribution to those found in the atmosphere (gas phase). Finally, it was found that plant uptake of PAHs from the particulate fraction was not significant. Therefore, it is inferred that the presence of high molecular weight PAHs in the peat record came directly from the particles deposited directly in the mire, together with those of petrogenic origin.

PAH concentrations in sediments from Las Conchas mire ranged between 0.09 mg/kg (25 cm; 1760 CE) and 1.14 mg/kg (8 cm, 1920 CE), these results being consistent with those found in sediments from other sites (Zaccone et al., 2009; Pontevedra-Pombal et al., 2012; Cong et al., 2016; Ortiz et al., 2017), and slightly lower than those reported by Leorri et al. (2014).

The maximum PAH concentrations in peat (ca. 1.14 µg/kg) were found at 8–9 cm, which corresponded to ca. 1920–1930, when coal extraction activity in northern Spain peaked. Of the 18 PAHs measured

in the peat samples, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*e*]pyrene, dibenzo[*ah*]anthracene, benzo[*a*]anthracene, phenanthrene, fluoranthene, and chrysene were the predominant homologues. In this regard, most of these compounds were the most abundant PAHs in the gas and particulate fractions (Tables 1, 2). Of note, most PAHs were detected in all samples, except acenaphthene and acenaphthene, which were below the detection limit in some samples located at greater depths.

Fig. 2 shows the concentration of PAHs grouped by the number of benzene rings in Las Conchas record. In all cases, the values were lower at the bottom of the record and increased in the uppermost 11 cm (ca. 1870), being especially noticeable between 8 cm (ca. 1920–1930) and 3 cm (ca. 1995). In contrast, in the upper 3 cm, the concentration of these contaminants decreased but did not reach the previous low values.

Similar behaviour was observed in the Urdaibai (N Iberian Peninsula) record (Leorri et al., 2014), which showed an increase in PAH concentrations since 1850, with a maximum between 1940 and 1990, due to the increase of fossil fuels and biomass consumptions, and development of industrial activities. However, in this case, the maximum concentration exceeded 4 mg/kg, whereas in Las Conchas it did not reach 1.4 mg/kg. As in Las Conchas, the PAH concentration decreased in the upper part of the Urdaibai record. Likewise, in the Penido Vello peat record (NW Iberian Peninsula), the PAH content has risen since the industrial revolution (Pontevedra-Pombal et al., 2012).

The following 2-ring PAHs in the record of Las Conchas were detected: naphthalene; acenaphthene; acenaphthene and fluorene. These accounted for 2–10% of total PAHs. Naphthalene was the most abundant but at a low concentration when compared with to PAHs with more rings. The main 3-ring PAHs in the record were fluoranthene, phenanthrene, and anthracene, the former two typically with high concentrations. In most samples, they accounted for 10–15% of total PAHs. The main 4-ring PAHs were pyrene, benzo[*a*]anthracene, and chrysene, accounting for 15–30% of the total PAHs in the uppermost 11 cm and 2–6% in the lower part of the record. With regard to 5-ring PAHs, benzo[*b*]fluorantene, benzo[*k*]fluorantene, benzo[*e*]pyrene, benzo[*a*]pyrene, perilene, and dibenzo[*a,h*]anthracene were found, all of which were markedly abundant in the uppermost 11 cm of the record. Finally, the 6-ring PAHs detected were indene[1,2,3-*cd*]pyrene and benzo[*ghi*]perilene, which accounted for considerable percentages of the total PAH content in the lowermost part of the record.

Thus, PAHs with 5 rings were the most abundant in the uppermost 12 cm, accounting for approximately 50% of the total content, followed by PAHs with 3 and 4 rings. In contrast, below 12 cm, the concentration of PAHs with >3 rings decreased sharply, with 2-ring compounds being important at some levels.

5.3.1. Origin of PAHs in las conchas record

In general, low molecular weight PAHs (2–3 rings) are linked to combustion at low to moderate temperatures (residential coal heating and small industry) and petrogenic sources (Mai et al., 2001, 2003). In contrast, PAHs with more rings are associated with combustion at high temperature (coal and oil combustion, heavy industry, vehicle emissions) (Mai et al., 2003; Khalili et al., 1995).

Crépineau-Ducoulombier and Rychen (2003) observed high concentrations of PAHs associated with motorways and airports, 86% of the PAHs in soil at these sites having >4 rings. Similarly, Hewitt and Rashed (1991), Pathirana et al. (1994) and Golomb et al. (2001) detected PAH pollution in soils related to vehicles. Beasley and Kneale (2001) reported a 5- to 6-fold increase in the concentration of PAHs in industrial areas and along roads with respect to rural zones.

It must be highlighted that the most abundant PAHs in Las Conchas record since 1870 were those with 5 rings, together with phenanthrene, fluoranthene, chrysene, and pyrene, which were the most abundant homologues in the atmospheric (gas and particulate phases) deposition (Tables 1, 2) and in polluted soils close to roads (Boxall and Maltby, 1997; Crépineau-Ducoulombier and Rychen, 2003). Nevertheless, they

are persistent PAHs in the natural environment, being frequently linked to organic matter, and mainly phenanthrene is resistant to microbial degradation (Belviso et al., 2005).

In brief, the pattern of PAH concentration observed in the uppermost 12 cm of Las Conchas record was comparable with that observed in the present-day atmospheric distribution of these pollutants in this zone, especially those of the particulate phase. These observations thus indicate pollution derived from industrial activities and also from grass and

wood combustion in the area. During this period, Pontevedra-Pombal et al. (2012) also reported an increase in high molecular weight PAHs, which they attributed to the mining and use of coal.

Thus, a pyrogenic origin of PAHs in the Las Conchas record since 1870 was interpreted. This interpretation was confirmed by a complementary approach to characterise the source of these contaminants in sediments. In this regard, the PAH isomeric ratios, namely benzo[*a*]anthracene/(benzo[*a*]anthracene+chrysene) (BaA/(BaA + Chrys))
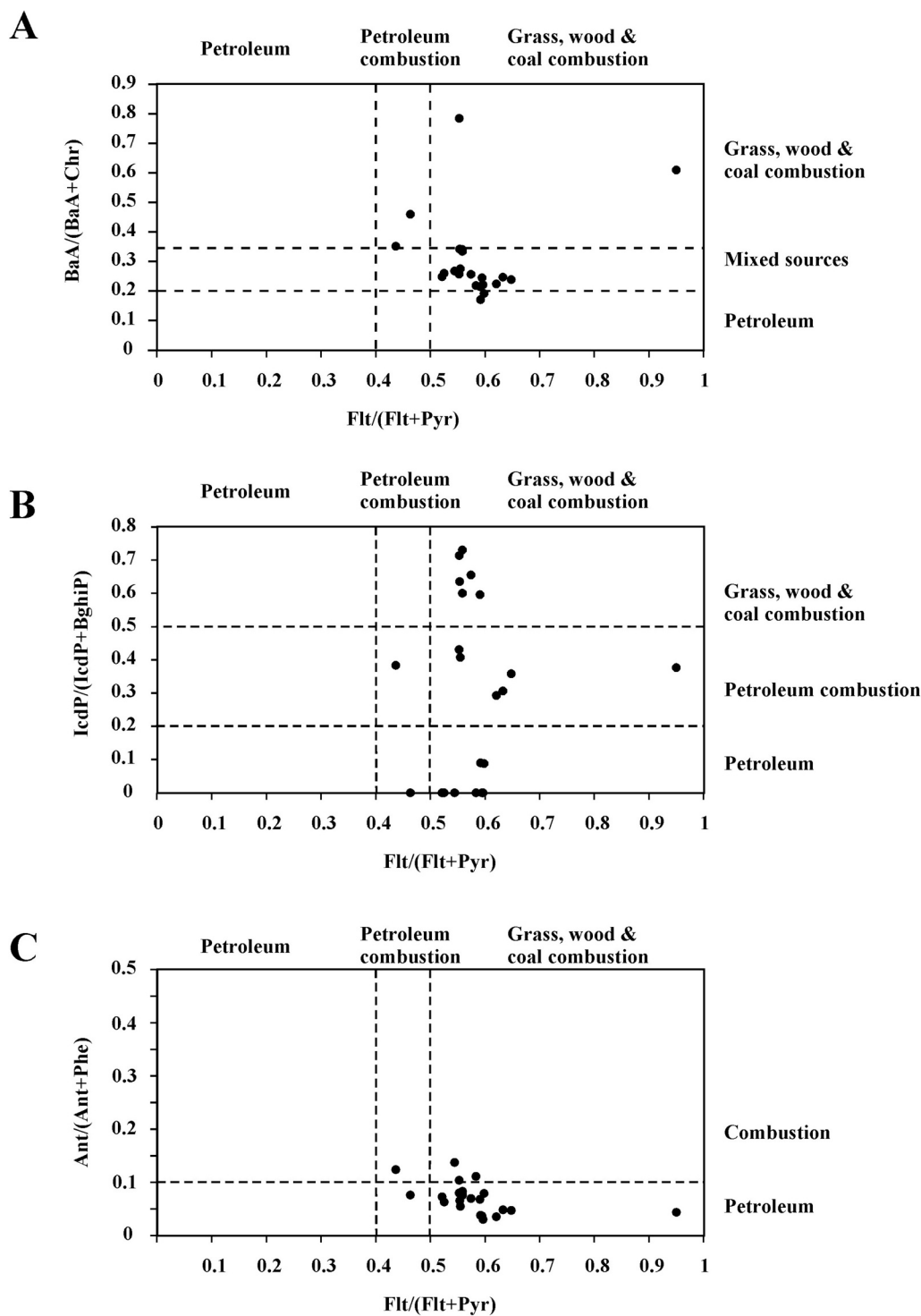

Fig. 4. Combustion origin indexes a) fluoranthene/(fluoranthene + pyrene) ratio [Flt/(Flt + Pyr)] compared with benzo[*a*]anthracene/(benzo[*a*]anthracene + chrysene) ratio [BaA/(BaA + Chr)], b) [Flt/(Flt + Pyr)] compared with indene[123-*cd*]pyrene/(indene[123-*cd*]pyrene+benzo[*ghi*]perylene) ratio [IcdP/(Icdp+BghiP)] and c) [Flt/(Flt + Pyr)] compared with anthracene/(anthracene+phenanthrene) ratio [Ant/(Ant+Phe)].

compared with fluoranthene/(fluoranthene+pyrene) (Flt/(Flt + Pyr)) (Fig. 4A), and indene[123-*cd*]pyrene/(indene[123-*cd*]pyrene+benzo[*ghi*]perylene) (IcdP/(Icdp+BghiP)) compared with (Flt/(Flt + Pyr)) (Fig. 4B) were used to discriminate between PAHs of petrogenic and pyrogenic origin (Yunker et al., 2002; Lehndorff and Schwark, 2004). The anthracene/(anthracene+phenanthrene) ratio (Ant/(Ant+Phe)) compared with (Flt/(Flt + Pyr)) was also used (Fig. 4C).

In products derived from petroleum, pyrene is more abundant than fluoranthene, while in combustion at high temperatures there is a predominance of fluoranthene (Wise et al., 1988; Benner Jr et al., 1989; Baumard et al., 1999). An Flt/(Flt + Pyr) ratio higher than 0.5 is characteristic of coal, wood or grass combustion and defines pyrogenic sources of PAHs (Yunker et al., 2002; Lehndorff and Schwark, 2004; Lu et al., 2012). Values between 0.4 and 0.5 indicate combustion linked to vehicles (gasoline, diesel, and fuel oil combustion), also linked to pyrogenic sources, while values lower than 0.4 indicate a petrogenic origin (Yunker et al., 2002; Lu et al., 2012).

Lehndorff and Schwark (2004) also suggested that BaA/(BaA + Chr) ratios lower than 0.20 indicate a petroleum origin and values higher than 0.35 combustion. Nevertheless, a BaA/(BaA + Chr) ratio between 0.38 and 0.64 has also been reported for diesel emissions and between 0.22 and 0.5 for gasoline emissions (Sicre et al., 1987; Simcik et al., 1997). In Las Conchas mire, all the samples showed a BaA/(BaA + Chr) ratio of >0.20 and Flt/(Flt + Pyr) values of >0.5, indicating a pyrogenic origin of PAHs (Fig. 4A).

The IcdP/(IcdP+BghiP) to Flt/(Flt + Pyr) isomeric plot showed that all the sediment samples of the uppermost 10 cm were plotted within the pyrolytic quadrant (either petroleum combustion or grass/wood/coal burning), thereby supporting the notion that the PAHs were derived mainly from high-temperature processes (Fig. 4B). Indeed, high values of the IcdP/(IcdP + BghiP) ratio (ca. 0.72) have been reported for diesel and gasoline emissions (Rogge et al., 1993; Caricchia et al., 1999; Guo et al., 2003). In contrast, samples of the lowest 11 cm of the record fell within the petrogenic quadrant, with two samples originated from combustion. The plot using BaA/BaA + Chrys and Flt/(Flt + Pyr) ratios confirmed that the PAHs were from pyrogenic sources, such as petroleum, grass, wood, and coal combustion, although in this case, even the samples below 11 cm indicated a certain degree of grass/wood/coal combustion (Fig. 4B). This finding is not uncommon in the area as controlled fires are frequently used in agricultural and cattle farming activities to gain land.

The Ant/(Ant+Phe) ratio is also used to discriminate between PAHs of petrogenic and pyrogenic origin (Yunker et al., 2002; Lu et al., 2012). In this regard, phenantrene is thermochemically more stable than anthracene, and therefore it is preferentially originated at lower temperatures (Alberty and Reif, 1988). Thus, Ant/(Ant+Phe) values of >0.1 are indicative of processes at high temperature (pyrogenic) such as the incomplete combustion of organic materials (wood and coal, vehicle emissions), whereas Ant/(Ant+Phe) values of <0.1 are linked to petrogenic origin (Yunker et al., 2002; Lu et al., 2012). The Ant/(Ant+Phe)
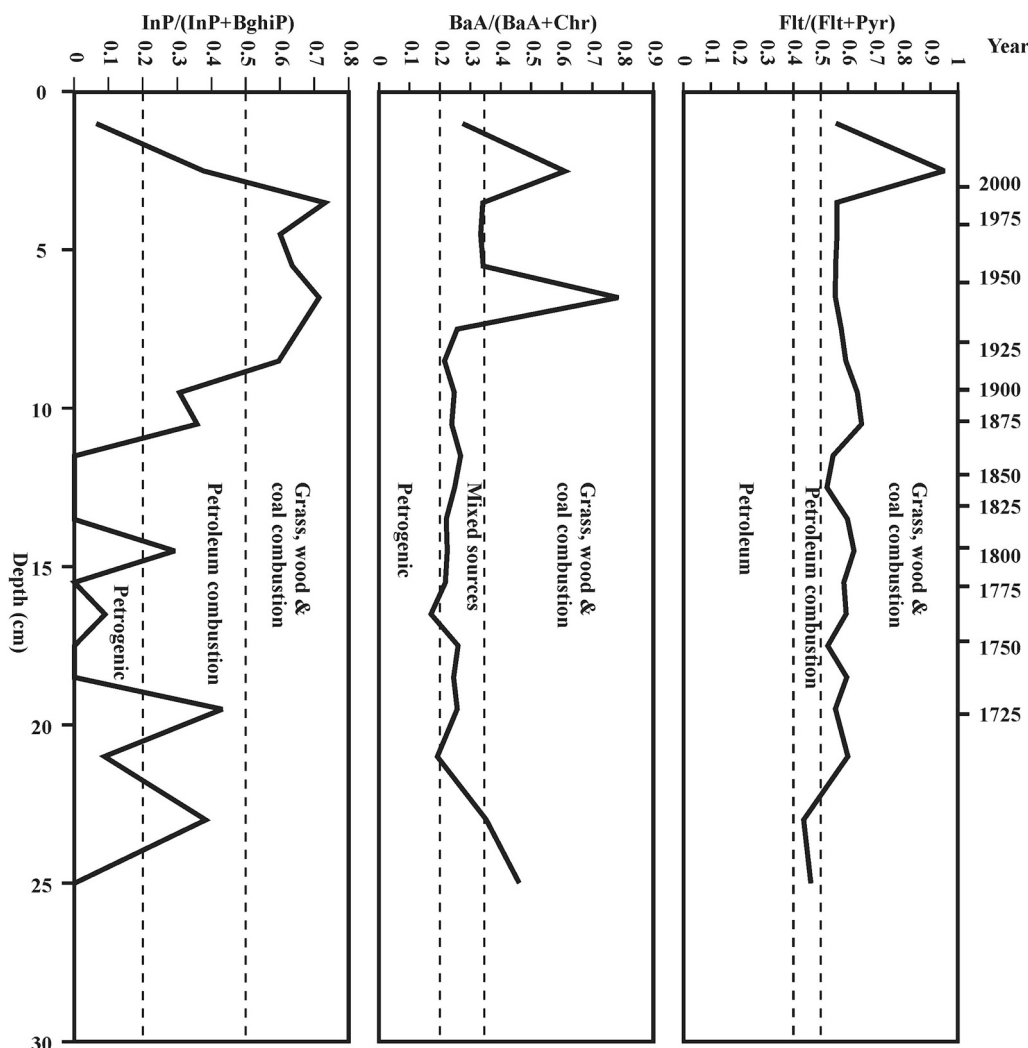

Fig. 5. Distribution of the combustion indexes [BaA/(BaA + Chr)], [IcdP/(Icdp+BghiP)] and [Flt/(Flt + Pyr)] in Las Conchas core over the last 300 yr.

to Flt/(Flt + Pyr) isomeric plot (Fig. 4C) showed that most of the sediment samples were within the pyrolytic quadrant (mostly grass/wood/coal combustion), thereby supporting the notion that the PAHs were derived mainly from high-temperature processes, although many Ant/(Ant+Phe) values were < 0.1 indicating petrogenic origin. In contrast to anthracene and phenanthrene, fluoranthene and pyrene have comparable physicochemical properties and are present in the gaseous as well as particle-transported PAHs (Masclet et al., 1986; Behymer and Hites, 1988; Orecchio, 2007) and therefore fluoranthene/pyrene persist and are more reliable parameters when interpreting the origin of PAHs (Yunker et al., 2002).

The high values of these ratios in the upper part of Las Conchas record (Fig. 5) confirmed the pyrogenic origin of PAHs, which had good correspondence with the industrial development that began in the 19th century and with vehicle emissions, as well as additional direct pyrogenic inputs from biomass combustion. The industrial areas of the region of Asturias in which coal from local mines was used, whose origin dates back to ca. 1860, released significant amounts of PAHs into the atmosphere. This release left a significant fingerprint recorded in soils and sediments in the surroundings of the industrial cities of Avilés (Baragaño et al., 2022), Gijón (Boente et al., 2017), and Langreo (Gallego et al., 2016; Boente et al., 2020).

This interpretation was confirmed by the increase in the concentration of benzo[*b*]fluoranthene, chrysene, dibenzo[*a,h*]anthracene, phenanthrene, and benzo[*a*]anthracene, which are linked to diverse sources of combustion, in the upper 12 cm of the record (Fig. 3). It has been shown that benzo(*ghi*)perylene is characteristic of gasoline engines, followed by dibenzo[*ah*]anthracene and indene[(123-cd]pyrene (Miguel et al., 1998; Hien et al., 2007; Ravindra et al., 2008; Tian et al., 2009). Diesel exhaust is found to be enriched in phenanthrene, fluoranthene, chrysene, and pyrene (Rogge et al., 1993; Masclet et al., 1986; Guo et al., 2003; Hien et al., 2007; Zheng et al., 2017), while fluorene, pyrene, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are typical emissions of heavy-duty diesel vehicles (Sienra et al., 2005; Ravindra et al., 2008). Anthracene, phenanthrene, fluoranthene, and pyrene have been identified as fingerprints of wood combustion (Khalili et al., 1995; Bourotte et al., 2005; Ravindra et al., 2008; Wang et al., 2008), as have fluorene and benzo[*a*]pyrene (Bourotte et al., 2005).

Benzo[*a*]anthracene and chrysene (Khalili et al., 1995), and anthracene, phenanthrene, fluorene, pyrene, benzo[*a*]anthracene and chrysene (Ravindra et al., 2008; Wang et al., 2008; Tian et al., 2009) have been considered markers of coal combustion, and phenanthrene and fluorene of coke production (Khalili et al., 1995; Ravindra et al., 2008). Anthracene, phenanthrene, benzo[*a*]pyrene, benzo(*ghi*)perylene, and chrysene are characteristic of steel industry emissions (Ravindra et al., 2008). Benzo[*a*]anthracene, chrysene and benzo[*a*]pyrene have been associated with the combustion of natural gas (Rogge et al., 1993; Simcik et al., 1997; Kulkarni and Venkataraman, 2000), together with fluoranthene and pyrene (Daisey et al., 1986), and benzo[*a*]anthracene has been considered a marker for this source (Simcik et al., 1997).

Thus, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, indicators of diesel exhaust emissions, showed a marked increase in the upper part of the record, and, similarly, benzo[*a*]anthracene, chrysene, and phenanthrene, markers of coal combustion, were high (Fig. 3). Indeed, the typical pyrogenic PAHs, namely pyrene + fluoranthene + benzo[*a*]pyrene + benzo[*jbk*]pyrene + benzo[*ghi*]pyrene (Zaccone et al., 2009), accounted for 39–82% of total PAHs, confirming additional anthropogenic sources of these organic contaminants (e.g., residential heating, road traffic, industrial waste incinerators, mid-distance sources of intensive coal combustion). In addition, given the increase in the concentration of 5- to 6-ring PAHs in the particulate atmospheric fraction in years affected by fires in the area, wood and grass burning has to be taken into account when explaining the increase in PAHs in the uppermost 12 cm of the record (Table 2).

It must be highlighted that the anthropogenic profile of Pb in Las Conchas mire (Gallego et al., 2019) shows some similarities with the

PAH distribution. The vehicle emissions that produced a marked increase in Pb concentrations in sediments deposited during the second half of the 20th century showed good correspondence with the PAH profile, thereby indicating similar sources of these contaminants. Both profiles showed a decrease in the upper part of the record corresponding to the late 20th century and the beginning of the 21st century, which may be attributed to the implementation of environmental policies, although the concentrations were still higher than those measured further down the record. A similar recent decrease has also been reported in Penido Vello (NW Iberian Peninsula) (Pontevedra-Pombal et al., 2012) and at other sites in Europe (Berset et al., 2001; Rose and Rippey, 2002; Sanders et al., 1995; Zaccone et al., 2009).

Another isomeric ratio is the anthracene/ (anthracene+phenantrene) (Liu et al., 2012). However, phenanthrene is photochemically more stable than anthracene and this ratio should be used with caution.

On the whole, the significant contribution of high molecular weight homologues, which are associated mainly with atmospheric particles and PAH depositional processes in the area, was linked principally to anthropogenic sources, namely coal, petroleum and wood combustion.

6. Conclusions

Here the first evaluation of the atmospheric deposition of PAHs, separating the gas phase from the particulate fraction, in a rural area in northern Spain is reported. These results were used to infer the uptake of PAHs by peat-forming plants and to gain a better understanding of the processes involved in the accumulation of these compounds in an ombrotrophic mire. In this regard, Las Conchas mire was selected because it receives water mostly from rainfall, thus, the historical record can be related to the characteristics of atmospheric deposition.

Significant concentrations of PAHs were found in the gas and particulate fractions of the study area (rural area). However, the concentrations found were slightly lower than those reported in other rural areas in Europe and America but comparable to those of remote mountains. On the basis of these findings, it is proposed that these PAHs had a pyrolitic origin linked to coal and petroleum combustion and fires.

PAHs were more abundant in the gas phase than the particulate fraction, the former showing the highest concentrations during winter and autumn, whereas in the latter peak concentrations occurred in winter and spring, an observation that is consistent with findings in other localities. High molecular weight PAHs were markedly more abundant in the particulate fraction. These compounds were also the most common ones in the sedimentary record of Las Conchas mire over the last 300 years, thereby indicating a preferential pyrolitic origin of these pollutants over time.

The PAH content of the peat-forming plants in this area provided a similar distribution as the atmospheric gas phase composition, with only high molecular weight homologues present in one species, thereby indicating that the 4- to 6-ring PAHs in the sedimentary record were derived mainly from atmospheric deposition in the mire.

The total concentration of PAHs increased significantly in the second half of the 19th century, and homologues typical of a pyrolytic origin were dominant. It is consider that the latter observation is attributable to the industrial revolution. The maximum concentrations of PAHs occurred during the 20th century, especially in the first half, which was marked by significant extraction and combustion of coal from mines in the region (Asturias). In the 21st century, the abundance of PAHs decreased, which may be linked to the implementation of environmental policies, although the concentrations still exceeded those of the preindustrial period.

Overall, these results revealed that different sources of pollution influenced the peatland record. In this regard, fossil fuel (coal, oil, and oil derivatives) and wood combustion produced pyrolytic PAHs that were incorporated into the sediments. Furthermore, fires (sometimes controlled for agricultural practices and cattle farming) may have also influenced the PAH record of Las Conchas mire.

CRediT authorship contribution statement

José E. Ortiz: Conceptualization, Investigation, Writing – original draft. **Yolanda Sánchez-Palencia:** Data curation, Writing – review & editing. **José L.R. Gallego:** Investigation, Writing – review & editing. **Ángeles G. Borrego:** Investigation, Writing – review & editing. **Diego Baragaño:** Investigation. **Trinidad Torres:** Investigation, Resources.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
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Data availability

Data will be made available on request.

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