Drivers of atmospheric deposition of polycyclic aromatic hydrocarbons at European high altitude sites[§]

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[§]Dedicated to the memory of Unai Pérez de Arenaza and Gaspar Giner-Abati

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) were analyzed in bulk atmospheric deposition samples collected at four European high mountain areas, Gossenköllesee (Tyrolean Alps), Redon (Central Pyrenees), Skalnate Pleso (High Tatra Mountains) and Lochnagar (Grampian Mountains) between 2004 and 2006. Sample collection was performed monthly in the first three sites and biweekly in Lochnagar. The number of sites, period of study and sampling frequency provide the most comprehensive description of PAH fallout in high mountain areas addressed so far.

The average PAH deposition fluxes in Gossenköllesee, Redon and Lochnagar ranged between 0.8-2.1 µg m^{-2} mo^{-1}, and in Skalnate Pleso it was 9.7 µg m^{-2} mo^{-1}, showing the influence of substantial inputs from regional emission sources. The deposited distributions of PAH were dominated by parent phenanthrene, fluoranthene and pyrene, representing 32-60% of total. The proportion of phenanthrene, the most abundant compound, was higher at the sites of lower temperature, Gossenköllesee and Skalnate Pleso, showing higher transfer from gas phase to particles of the more volatile PAHs. The sites with lower insolation, e.g. those located at lower altitude, were those with higher proportion of photooxidable compounds such as benz[a]anthracene.

According to the data analysed, precipitation is the main driver of PAH fallout. However, when rain and snow deposition were low, particle settling also constitutes an efficient driver for PAH deposition. Redon and Lochnagar were the two sites receiving highest rain and snow and the fallout of PAH fluxes was related to this precipitation. No significant association was observed between long-range backward air trajectories and PAH deposition in Lochnagar, but in Redon PAH fallout at higher precipitation was essentially related with air masses originating from the North Atlantic, which were dominant between November and May (cold season). In these cases, particle normalized PAH fallout was also associated to higher precipitation as these air masses were concurrent with lower temperatures, which enhanced gas to particle partitioning transfer. In the warm season (June-October), most of the air masses arriving to Redon originated from the south and particle deposition was enhanced as consequence of Saharan inputs. In these cases, particle settling was also a driver of PAH deposition despite the low overall PAH content of the Saharan particles.

In Gossenköllesee, the site receiving lowest precipitation, PAH fallout was also related to particle deposition. The particle normalized PAH fluxes were significantly negatively correlated to temperature, e.g. for air masses originating from Central/Eastern Europe, showing a dominant transfer from gas phase to particles at lower temperatures, which enhanced PAH fallout, mainly of the most volatile hydrocarbons.

Comparison of PAH atmospheric deposition and lacustrine sedimentary fluxes showed much higher values in the latter case, 24-100 µg m^{-2} yr^{-1} vs. 120-3000 µg m^{-2} yr^{-1}, respectively. A strong significant correlation was observed between these two fluxes which is consistent with a dominant origin related with atmospheric deposition at each site.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are semivolatile organic compounds (SOCs) originating from incomplete combustion and pyrolysis of carbonaceous materials. In addition to natural sources, the global emissions of these compounds are dominated by anthropogenic activities such as fossil fuel combustion (Wild and Jones, 1995; Pacyna et al., 2003), which are responsible for their ubiquitous occurrence in the environment, especially in urban/industrial regions. In Europe, the emission of PAH in 2004 was estimated about 5.1×10^4 tons (calculated for 16 PAHs), with residential combustion representing 88 % of the total contribution, followed by industrial activities (van der Gong et al., 2007).

The widespread distribution of PAHs is of great environmental concern, since several parent (non-methylated) compounds of this group of hydrocarbons are human carcinogens and priority pollutants (Baek et al., 1991; IARC, 1983; Armstrong et al., 2004). Moreover, the Convention on Long-range Transboundary Air Pollution included PAHs in the list of persistent organic pollutants (POPs) (UNECE, 1998) whose emissions should be reduced to 1990 levels (EC, 2001). Implementation of regulatory activity caused an initial decrease of PAH emissions (Meijer et al., 2008) but recent studies showed that PAH have increased globally as consequence of higher urban population, energy consumption and vehicle use (van Metre and Mahler, 2005)

Once in the atmosphere, PAH may remain in the gas phase or associate to particles (Gustafson and Dickhut, 1997; Park et al., 2001; Simcik et al., 1998), be degraded by direct and/or indirect photolysis (Masclet et al., 1986; Wang et al., 2011a), and be deposited by wet and dry processes (Golomb et al., 2001; Halsall et al., 2001; Dickhut and Gustafson, 1995). Deposited PAHs may re-volatilize, be transported over long distances and be deposited again on soil and water surfaces far from the emission sources (Fernández et al., 2003), e.g. in high altitude areas (Fernández et al., 2002; Fernández et al., 2000; Vilanova et al., 2001; Vives et al., 2004; Grimalt et al., 2004; Grimalt et al., 2001; Halsall et al., 2001; Arellano et al., 2011; van Drooge et al., 2010).

Atmospheric deposition is one of the main mechanism of transport of PAHs to all ecosystems (Leister and Baker, 1994). Direct measurements of the atmospheric deposition of these pollutants have mostly been performed in industrial/urban areas (Halsall et al., 1997; Franz et al., 1998; Golomb et al., 2001; Park et al., 2001; Garban et al., 2002; Gigliotti et al., 2005; Gocht et al., 2007; Esen et al., 2008; Wang et al., 2011b; Bari et al., 2014). Only in a few cases has deposition been considered in remote areas such as high altitude regions (Fernández et al., 2003; Offenthaler et al., 2009; Foan et al., 2012). However, high mountain areas provide the reference background information of the pollution impact, in this case PAHs, of the overall anthropogenic activities in large regions. The study of the processes of transport and pollutant incorporation into these remote ecosystems shows the basic mechanisms of action of these compounds far from direct human influence. Understanding of these processes provides the basic knowledge for description of the air-to-soil transfer mechanisms in all ecosystems. Furthermore, these remote areas may also act as secondary sources of toxic substances as a consequence of re-emission from terrestrial and aquatic ecosystems by air-water or air-soil exchange or ice/glacier melting (Ma and Cao, 2010; Ma et al., 2011).

To improve the knowledge on how PAH move through the atmosphere and partition between air and the terrestrial and aquatic environments, bulk atmospheric deposition was collected at four high altitude sites over

two years, covering different European climatic and source regions: Redon (2235 m above sea level, Pyrenees), Gossenköllesee (2413 m, Alps), Skalnate Pleso (1787 m, Tatras) and Lochnagar (790 m, Grampian mountains).

115 Bulk atmospheric deposition (dry+wet) was collected monthly in the three former sites and biweekly in Lochnagar. The samples were analyzed to determine seasonal, spatial and temporal trends of atmospheric PAHs inputs and to identify the main processes determining PAH fallout at each site. Backward air mass trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for assessment of the air sources during sampling. To the best of our knowledge, the number of sites and sampling

120 frequency and period of study constitute the most comprehensive approach performed so far on PAH deposition in high mountain areas.

2 Materials and Methods

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2.1. Sampling

Bulk atmospheric deposition samples were regularly collected at four high mountain European areas (Table 1) over the same period: monthly between 2004 and 2006 in Gossenköllesee (Tyrolean Alps), Redon (Central

130 Pyrenees) and Skalntate Pleso (Tatra Mountains) and biweekly between 2004 and 2007 in Lochnagar (Grampian Mountains) (Figure 1). All lakes are located in remote areas under special protection. Lake Redon is situated within the Aiguestortes area belonging to Natura 2000 European network. Lochnagar is located within the Deeside and Lochnagar National Scenic Area, which definy protected landscapes in Scotland with the same category as National Parks. Gossenköllesee and its catchment area constituted one of the UNESCO

135 Biosphere Reserve from 1977 until 2014, while Skalnate Pleso is situated in the area of the Tatra National Park.

Meteorological parameters, i.e. air temperature and precipitation, were provided by automatic weather stations (AWS) located at each site except in Skalnate Pleso where data were provided by the Meteorological observatory of the Earth Science Institute of the Slovak Academy of Science. In summer, precipitation was collected with a polyethylene funnel (different diameter depending on the sampling site) connected to stainless

140 steel or Teflon coated reservoirs by a tube. In winter, precipitation occurs as snow and sampling was performed either with a wider tube assembled to the top of a tank or with cylindrical collectors. These devices were equipped with windscreens around the collector's mouth to prevent wind disturbance. The samplers were placed 1.5 m above ground level.

Samples were filtered on site using pre-weighed Whatman glass fiber filters (GF/B, 45 mm diameter, 1

145 μm pore size) at each field station and the filtrates were solid-phase-extracted with C18 Empore disks (47 mm diameter, 0.5 mm thickness) as described elsewhere (Carrera et al., 1998). After sample removal, the bulk collectors were rinsed with Milli-Q water which was filtered and solid-phase-extracted with the same disk used for the corresponding deposition sample. Glass fiber filters and disks were wrapped in aluminium foil and transported frozen to the laboratory. More details on sampling procedures are reported elsewhere (Arellano et

150 al., 2015).

2.2. Extraction and clean-up

Glass-fiber filters were freeze-dried and weighed for measuring total particle content in bulk atmospheric deposition. PAHs were extracted from the filters by sonication with dichloromethane:methanol (2:1) (3 x 10 mL, 20 min each). The pollutants adsorbed in the C_{18} disks were eluted sequentially with methanol, cyclohexane and dichloromethane.(Carrera et al., 1998). Both phases were combined and purified by column adsorption chromatography with aluminium oxide after adding a recovery standard mixture of perdeuterated anthracene-d_{10}, benz[a]anthracene-d_{10}, benzo[b]fluoranthene-d_{12} and benzo[ghi]perylene-d_{12} (Dr. Ehrenstorfer; Augsburg, Germany). Prior to instrumental analysis, samples were spiked with an internal standard mixture of pyrene-d_{10} and perylene-d_{12} dissolved in isooctane.

2.3. Instrumental analysis

PAHs were analysed by gas chromatography-mass spectrometry (GC-MS; Trace DSQ II Instrument Thermo Austin USA.) using a 60 m HP-5MS column (0.25 mm i.d. x 0.25 µm film thickness). The oven temperature program started at 90°C (held for 1 min) and increased to 120°C at 10°C min^{-1}, and then to 310°C at 6°C min^{-1} (final holding time 25 min). Injector, transfer line, and ion source temperatures were 280ºC, 270ºC and 250℃, respectively. Helium was used as carrier gas (1.2 ml min^{-1}). The injector operated in splitless mode. Data were acquired in electron impact and selective ion monitoring modes. Further details on the ions selected for quantification and mass spectrometric conditions are reported elsewhere (Fernández et al., 1999).

2.4. Quality control and assurance

Quantification was performed by the internal standard method. Recoveries of the analytical procedure were evaluated using surrogate standards. The reported values were corrected by these recoveries, which varied between 76% for benz[a]anthracene-d_{10} and 53% for benzo[ghi]perylene-d_{12}.

Field and procedural blanks were collected at each sampling site and processed together with the samples. For field blanks, Milli-Q water was filtered and solid-phase adsorbed, transported and stored for subsequent analysis. In general, blank values represented less than 10% of bulk deposition sample concentrations. These values were used to determine method detection limits (MDL) that were established as average blank values plus 3 times the standard deviation. These limits ranged between 0.45 pg and 28 pg depending on the compound.

2.5 Back air mass trajectory calculations

Three-day back trajectories were calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT data available at http://ready.arl.noaa.gov/HYSPLIT.php) modelling system developed by the National Oceanic and Atmospheric Administration (NOAA)'s Air Resources Laboratory (ARL) (Draxler and Hess, 1998;Draxler and Rolph, 2013).

The meteorological data used to compute the 6-hourly back-trajectories were obtained from the National
190   Centre for Environmental Prediction (NECP) Global Data Assimilation System (GDAS) and from Eta Data
Assimilation System (EDAS). The trajectories were calculated for those days with precipitation (rain or snow)
and every 2 days when no precipitation was recorded by the AWS.

Different altitudes were used to calculate the trajectories. Usually, they did not show differences, thus
altitudes representing the air mass above the sampling point were selected, 3000 m above sea level (asl) in
195   Redon and Skalnate Pleso, 3500 m asl for Gossenköllesee and 2000 m asl for Lochnagar. The total number of
backward trajectories was 1968, being 335, 475, 598 and 560 for Redon, Gossenköllesee, Lochnagar and
Skalnate pleso, respectively. More details on air mass trajectory determination can be found in Arellano et al.
(2014)

200   **3 Results and Discussion**

3.1 Atmospheric PAH deposition fluxes. Spatial and temporal variability.

Mean, minimum and maximum atmospheric deposition fluxes of the PAHs at the four sampling sites during
205   the studied period are summarized in Table 1. A strong contrast is found between the total PAH mean fluxes
found in Lochnagar, Gossenköllesse and Redon, 0.80-2.1 μg m^{-2} mo^{-1}, and Skalnate Pleso, 9.7 μg m^{-2} mo^{-1}, the
latter showing PAH deposition fluxes between 5 and 10 times higher than the others. In Table 2, these deposition
fluxes are compared with those observed in different environments, e.g. remote, rural, coastal, industrial,
suburban and urban areas. In addition, the deposition fluxes of benzo[a]pyrene are also included in this Table
210   for comparison. This hydrocarbon is a known carcinogen taken for reference in regulatory pollution values of
PAH concentrations. As observed for total PAHs, the benzo[a]pyrene mean deposition fluxes in Skalnate Pleso,
280 ng m^{-2} mo^{-1}, are much higher than those observed in Lochnagar, Gossenköllesee and Redon, 20-61 ng m^{-2}
mo^{-1} (Table 2).

The observed PAH deposition fluxes in these high mountain European areas, 0.02-0.28 μg m^{-2} d^{-1}, range
215   among the lowest values reported in the literature (Table 2). Thus, PAH deposition fluxes of 0.40-0.55 μg m^{-2}
d^{-1} have been recorded (in remote sites from USA (Su et al., 2007; McVeety and Hites, 1988; Leister and Baker,
1994; Dickhut and Gustafsson, 1995), whereas Foan et al. (2012) reported mean deposition fluxes of PAHs of
0.18 μg m^{-2} d^{-1} in remote areas of North Spain. The reported PAH depositions in background areas are again
higher than those observed in the high mountain European sites, 0.19-0.82 μg m^{-2} d^{-1} (Brorstrom-Lunden et al.,
220   1998; Horstmann and McLachlan, 1998; Garban et al., 2002). Higher PAH deposition has also been measured
in rural areas, 0.09-3.9 μg m^{-2} d^{-1} (Kiss et al., 2001; Garban et al., 2002; Menichini et al., 2006; Gocht et al.,
2007; Wang et al., 2011b) or in coastal sites, 0.4-6.8 μg m^{-2} d^{-1} (Lipiatou et al., 1997; Golomb et al., 2001; Park
et al., 2001; Brun et al., 2004; Poor et al., 2004; Gigliotti et al., 2005; Tsapakis et al., 2006). As expected, the
PAH deposition fluxes measured in industrial areas, 0.3-19.5 μg m^{-2} d^{-1} (Esen et al., 2008), in suburban, 0.13-
225   39 μg m^{-2} d^{-1} (Bae et al., 2002; Motelay-Massei et al., 2003; Fang et al., 2004; Gigliotti et al., 2005) and in
urban, 0.63-49 μg m^{-2} d^{-1}, locations (Halsall et al., 1997; Bae et al., 2002; Garban et al., 2002; Ollivon et al.,

2002; Fang et al., 2004; Gigliotti et al., 2005; Pekey et al., 2007; Wang et al., 2011b) are higher than those in the remote European mountains.

Concerning the benzo[a]pyrene deposition fluxes, again those observed in the European high mountains, 20-280 ng m^{-2} mo^{-1}, range among the lowest described (Table 2). However, the values reported for different types of sites do not show such uniform trends as those observed when considering total PAH deposition. Thus, benzo[a]pyrene deposition fluxes ranged between 225 and 500 ng m^{-2} mo^{-1} in remote sites (Su et al., 2007; McVeety and Hites, 1988; Leister and Baker, 1994; Dickhut and Gustafsson, 1995; Foan et al., 2012). In forested and rural areas, the benzo[a]pyrene deposition has been measured to account between 140 and 15000 ng m^{-2} mo^{-1} (Horstmann and McLachan, 1998; Garban et al., 2002; Kiss et al., 2001; Garban et al., 2002; Menichini et al., 2006). Finally, benzo[a]pyrene fluxes between 42 and 9000 ng m^{-2} mo^{-1} have been reported in urban sites (Halsall et al., 1997; Gigliotti et al., 2005; Pekey et al., 2007).

The differences between Lochnagar, Gossenköllesee and Redon and Skalnate Pleso cannot be explained by differences in precipitation (e.g. 120 mm mo^{-1} in Skalnate Pleso and 66-129 mm mo^{-1} in the other sites) (Table 1) or particle flux (330 mg m^{-2} mo^{-1} in Skalnate Pleso and 145-320 mg m^{-2} mo^{-1} in the other lakes) (Table 1). The higher PAH deposition in Skalnate Pleso compared to the other sites is in agreement with atmospheric PAH concentrations and probably reflects regional contributions from industrial emissions by factories located in southern Poland and other areas as the Black Triangle (Figure 1) (van Drooge et al., 2010). This geographical difference is consistent with PAH concentrations reported in air at European scale, which identified high PAH emissions in Eastern Europe (Jaward et al., 2004).

Comparison of the PAH deposition measured in Gossenköllesee and Redon in 2004-2006 with those found in 1996-1998 (Fernandez et al., 2003) shows nearly the same values at Gossenköllesee (Table 2) but statistically significant differences in Redon (p> 0.05), involving lower fluxes in the 2004-2006 period. In both cases, the deposition fluxes range among the lowest measured in remote sites (Table 2), which suggest that they correspond to background concentrations of long-range transported PAHs and not to direct pollution inputs. Very similar deposition of total particles has been measured in Gossenköllesee in the two sampling periods, 145 mg m^{-2} mo^{-1} between June 04-August 06 (Table 1) and 130 mg m^{-2} mo^{-1} in October 1996-October 1998 (Fernandez et al., 2003), whereas total precipitation shows a strong difference, with lower values in 2004-2006, 66 mm mo^{-1} (Table 1) vs 110 mm mo^{-1} (Fernandez et al., 2003) in 1996-1998 period. Precipitation in the recent period is quite low suggesting that the PAH fallout fluxes at Gossenköllesee were mainly determined by particle deposition. By contrast, in Redon both decreases in particle deposition, 320 mg m^{-2} mo^{-1} (Table 1) vs 420 mg m^{-2} mo^{-1} (Fernandez et al., 2003) and atmospheric precipitation, 79 mm mo^{-1} (Table 1) vs 110 mm mo^{-1} (Fernandez et al., 2003), are observed when comparing the recent (May 04-September 06) and previous sampling periods (March 1997-October 1998), respectively. The differences in the deposition of particles and wet precipitation are consistent with the lower PAH fallout from the atmosphere observed at this site in 2004-2006.

3.2 PAH composition

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Overall, the PAH composition in the atmospheric deposition samples was dominated by parent compounds and, among these, the low molecular weight fraction (LMW-PAH, from acenaphthene to pyrene). Phenanthrene, fluoranthene and pyrene were the most abundant, representing between 32% to 60% of the total PAH mixture

270 (Fig. 2). These compounds are also the most abundant in the atmosphere, namely in the gas phase (Fernández et al., 2002). Dominance of LMW-PAH in atmospheric deposition and, particularly, phenanthrene, fluoranthene and pyrene, is a common feature of studies in Europe (Halsall et al., 1997; Holoubek et al., 2007; Fernández et al., 2003; Cetin et al., 2016), America (Gigliotti et al., 2005; Brun et al., 2004) and Asia (Li et al., 2009; Wang et al., 2011b; Sharma et al., 2018).

275 In the present study, no significant differences in qualitative composition between sites were observed, except for the relative proportion of phenanthrene, the most volatile and abundant compound. The PAH distributions from the sites with lower annual mean temperature, Gossenköllesee and Skalnate Pleso, -1.4°C and 2.2°C, respectively (Table 1), were those with highest proportion of this compound (31-32%) whereas the lowest was observed in Redon (12%, 5.3°C). Lochnagar (4.9°C) also showed a low but intermediate proportion

280 of phenanthrene (18%). Higher local temperatures likely involve lower condensation of the most volatile PAHs and therefore lower deposition fluxes.

Consistently with these differences in phenanthrene content, the coldest sites, Gossenköllesee and Skalnate Pleso, were those with highest deposition of low vs high molecular weight PAH, 0.89 vs 0.40 µg m^{-2} mo^{-1} and 5.6 vs 3.9 µg m^{-2} mo^{-1}, respectively (Table 1), whereas this proportion was inverse in Redon, 0.30 vs

285 0.49 µg m^{-2} mo^{-1} and about the same in Lochnagar, 1.1 vs. 0.97 µg m^{-2} mo^{-1} (Table 1).

Further assessment on the qualitative changes in PAH composition between samples can be obtained from the study of diagnostic ratios (Table 3; Sicre et al., 1987). The pyrene/(fluoranthene+pyrene) ratios showed a uniform composition between samples and therefore no environmental dependence. In contrast, the sites located at lower altitude, e.g. Lochnagar (790 m) and Sklanate (1787 m) were those with higher relative proportion of

290 benz[a]anthracene to its less labile to photooxidation isomer, chrysene (Ding et al., 2007; Xing et al., 2016). The lower altitude sites receive less insolation than those located at higher altitude. Accordingly, the average benz[a]anthracene/(chrysene + benz[a]anthracene) ratios were higher in Skalnate (1787 m asl) and Lochnagar (790 m asl), between 0.28-0.31, than in Gossenköllesee (2413 m asl) and Redon (2230 m asl), 0.17-0.18 (Table 3). Furthermore, the average benz[a]anthracene/(chrysene + benz[a]anthracene) ratio in Skalnate Pleso (0.28;

295 1787 m) was even lower than the one in Lochnagar (0.31; 790 m). Thus, insolation and not local temperature was the main driver of the relative changes between benz[a]anthracene and chrysene in all sites. Differentiation between the cold (from November to May) and the warm (June-October) sampling periods, involving higher insolation in the latter, did not show significant differences in this ratio in Gossenköllesee, Redon and Lochnagar (Table 3). However, in Skalnate Pleso higher benz[a]anthracene/(chrysene + benz[a]anthracene)

300 ratio was observed in the cold season (Table 3), which confirmed a predominant insolation effect in the relative concentrations of these two PAH.

The average benzo[a]pyrene/(benzo[e]pyrene + benzo[a]pyrene) ratios found in Gossenköllesee, Redon and Skalnate Pleso were also consistent with insolation differences, since the proportion of benzo[a]pyrene, the compound more labile to photooxidation, was higher at the lower altitude sampling sites, 0.38, 0.42 and 0.45,

305   respectively (Table 3). However, this trend was not observed in Lochnagar, the lowest altitude site, which showed the lowest average benzo[a]pyrene/(benzo[e]pyrene + benzo[a]pyrene) ratio. In general, the benzo[a]pyrene/(benzo[e]pyrene + benzo[a]pyrene) ratio is less sensitive to photooxidation than the benz[a]anthracene/(chrysene + benz[a]anthracene) ratio (Behymer and Hites, 1988).

310   **3.3 Meteorological drivers of PAH atmospheric deposition**

The influence of particle deposition, precipitation and temperature on PAH fallout fluxes at these remote sites was investigated. Pearson correlation coefficients between the log-transformed PAH monthly deposition fluxes and these variables were calculated at each site. The statistically significant correlations found at 95% ($p < 0.05$)

315   and 99% ($p < 0.01$) confidence levels are shown in Table 4.

In Redon and Lochnagar, the two sites receiving highest precipitation, the fallout fluxes of most of these hydrocarbons were directly correlated to wet deposition, e.g. higher precipitation involving higher PAH fallout. At these two sites, no significant correlations between PAH fluxes and particle deposition or temperature were observed. Normalization of PAH fallout to particle deposition also showed significant positive correlations with

320   precipitation ($p < 0.01$) which corroborated the dominant role of rain and snow in the transfer of PAH from atmosphere to soil. These results are also consistent with reports indicating that particle scavenging processes are significant mechanisms of PAH removal from the atmosphere (Gocht et al., 2007; Li et al., 2016).

In Gossenköllesee, the site receiving lowest precipitation, 66 mm mo^{-1} (Table 1), PAH fallout was significantly correlated to particle deposition for the higher molecular weight PAH ($p < 0.05$; Table 4) and no

325   correlation was observed between PAH fluxes and precipitation. Normalization of the PAH fluxes to particle deposition showed significant negative correlations with precipitation for some compounds in the low molecular weight range, e.g. fluoranthene, pyrene and chrysene ($p < 0.05$; Table 4). The particle normalized deposition flows of these compounds were also negatively correlated to temperature. Lower temperatures enhance the PAH transfer from gas phase to particles and this effect is stronger among the PAH of higher

330   volatility, such as fluoranthene, pyrene and chrysene. This association to the particulate matter increases the deposition of these compounds.

Previous studies considering the gas-particle partitioning of these compounds in Gossenköllesee, Redon and Skalnate Pleso showed that the observed distributions in Gossenköllesee and Skalnate followed more closely the theoretical slope constants of the correlations between gas-phase partition coefficients and octanol-

335   air constants (Fernandez et al., 2002; van Drooge et al., 2010), which was consistent with a temperature-dependent reversible transfer between gas phase and particle adsorption. Moreover, the significant negative correlations of the particle-normalized deposition fluxes of these compounds in Gossenköllesee with precipitation may be explained by the significant positive correlation between precipitation and temperature at

340 this site. Accordingly, in the cold period lower precipitation and higher particle-normalized PAH deposition was observed.

Skalnate Pleso has some specific features since this location is receiving enhanced PAH inputs from regional emissions. These emissions involve the release of large amounts of particulate matter containing PAH. This site was the one receiving highest particle deposition flux, 330 µg m^{-2} mo^{-1} (Table 1), and PAH fallout was significantly correlated with particle deposition ($p < 0.05$; Table 4). Some PAHs, e.g. benzo[a]pyrene,

345 benzo[ghi]perylene and coronene, also showed significant negative correlations with temperature ($p < 0.05$; Table 4) which may reflect the effects of higher winter production of electric power or other combustion processes in the region. These results are consistent with previous studies in urban and rural areas (Schifman and Boving, 2015; Birgul et al., 2011; Gaga et al., 2009; Gocht et al., 2007; Brun et al., 2004; Shahpoury et al., 2015) which also found higher PAH fluxes in winter. The observed seasonal trend in Skalnate Pleso could

350 reflect direct impacts of regional sources, while Redon, Lochnagar and Gossenköllesee received PAH mixtures from more distant areas and no significant seasonal influences were recorded.

Normalization of the PAH fallout to particle deposition showed that precipitation is not a main driver of the transfer of these hydrocarbons from atmosphere to soil in Skalnate Pleso. However, temperature appeared as a significant parameter that was negatively correlated with PAH deposition fluxes ($p < 0.05$; Table 4). As in

355 the case of Gossenköllesee, these negative correlations may reflect the higher adsorption of PAH to particles at lower temperatures, involving higher particle PAH content and therefore higher deposition fluxes of these hydrocarbons. Lower temperatures enhance the capacity of settling particles for the transfer of PAHs from atmosphere to soil.

360 **3.4 Correlation with air mass back trajectories**

Determination of the PAH source regions for each site was performed by 72-hour backward trajectory analyses using the HYSPLIT model for the entire sampling periods (Table 1). A detailed description of the back trajectory analyses performed in each study site is reported elsewhere (Arellano et al., 2014). Air mass back

365 trajectories and their contributions to the total trajectories measured in each sampling period were assigned to each monthly deposition sample. The number of trajectories calculated in each sampling site is indicated in Table 5.

The relationship between air mass trajectories and PAH deposition was investigated for each sample. No trend was observed at Lochnagar, indicating diffuse PAH inputs from unspecific sources in this site.

370 In Skalnate Pleso, a negative dependence between particle normalized PAH fluxes and air masses from the south was observed, which may indicate that particles from this origin were depleted in PAH content (Table 5).

In Gossenköllesee, total particle mass was negatively correlated with air masses from the North Atlantic (Table 5). These air masses were also negatively correlated with total PAHs, including LMW-PAHs and HMW-

375 PAHs (Table 5), which is consistent with the predominant role of particle deposition at this site (Table 4).

Normalization of PAH fallout to particle deposition showed a positive correlation with air masses from Central/Eastern Europe (Table 5).

The two main air mass trajectories arriving to Redon are clearly different in terms of meteorological characteristics and PAH deposition fluxes. As reported elsewhere, backwards air mass trajectories in Redon showed a well-defined seasonal pattern (Arellano et al., 2014). South-trajectories were dominant during the warm season (June-October; 59 %, see Figure 3 as an example), while North Atlantic trajectories prevailed during cold periods (November-May; 48 %). The central/east European trajectories identified in this site were less frequent and did not show any seasonal trend.

Southern air masses in this site are characterized by high temperature and particle content (positive correlation with T and particle deposition flows, Table 5), which is consistent with Saharan dust inputs and the well-known geographical characteristics of the North African regions. In this case, a significant negative association was observed between particle normalized PAH flows and air masses from this origin, mainly for the LMW-PAH (Table 5), which may respond to both, a gas phase-aerosol displacement towards the former and a low PAH content of the Saharan dust in comparison to the PAH concentrations in particles from other areas. Despite this, the overall result is an increase of PAH loads to Redon during the warm periods due to the high amount of particles arriving to this site in spring-summer (Table 1). Air masses originating from the North Atlantic involved higher precipitation and lower particle content (significant positive and negative correlation with these variables, respectively). Particle normalized PAH fallout was positively correlated with air masses of this origin (Table 5), which was consistent with the dependence of PAH deposition on precipitation at this site (Table 4), likely enhanced by gas phase-aerosol partitioning of PAH at low temperatures and increased scavenging efficiency of snow compared to rain (Fernandez et al., 2002; Arellano et al., 2011). Finally, air masses from central/east Europe are negatively correlated with PAH deposition fluxes, mainly for HMW-PAHs. Air masses from this origin were therefore not significant for PAH fallout.

3.5. Atmospheric PAH deposition and lacustrine sedimentary fluxes

The atmospheric deposition samplers are located close to high mountain lakes. Previous studies of sediment cores in these lakes allowed to determine the average PAH sediment fluxes in the top cores from Redon and Gossenköllesee, 120 µg m^{-2} yr^{-1}, and 125 µg m^{-2} yr^{-1}, respectively (Fernandez et al., 1999). The sedimentation flux in Lochnagar was calculated from the PAH concentrations (4000 ng g^{-1} dw; data not published) using a sedimentation rate of 0.012 g cm^{-2} yr^{-1} (Rose, 2001), which resulted in a PAH flux of 480 µg m^{-2} yr^{-1}. No lake sediment was available for Skalnate Pleso. Therefore, PAH fluxes from two nearby lakes in the Tatra mountains were therefore considered, e.g. Starolesnianske Pleso with 3000 µg m^{-2} yr^{-1} (Fernandez et al., 1999) and Ladove Pleso with 1400 µg m^{-2} yr^{-1} (Drooge et al., 2011).

Comparison of the PAH atmospheric deposition and lacustrine sedimentary fluxes showed much higher values in sediments, i.e. 24-100 µg m^{-2} yr^{-1} and 120-3000 µg m^{-2} yr^{-1}, respectively (Table 6). All lakes considered in this comparison are located in high mountain areas and their hydrological regime is determined

by atmospheric precipitation into the watershed. The strong difference in flux values of the direct PAH
415 atmospheric and sedimentary measurements may respond to processes such as the sediment focusing (Rowan
et al., 1995) or lake sediment concentration of these hydrocarbons falling into the surface of the lake catchment.
In this sense, an estimated sediment flux was calculated considering that the total amount of atmospheric PAHs
deposited in the lake and its catchment area were accumulated in the lake sediments (Table 6). Interestingly, in
the case of Lochnagar, Redon and Ladove, the ratio between calculated and measured sediment fluxes varied
420 between 0.5 and 0.6. This consistency between atmospheric and sedimentary PAHs in high altitude areas
situated in different areas of Europe is remarkably, taking into account that it has been considered that sediment
area equals lake area, and confirm the predominant atmospheric PAH origin in all studied sites. In
Gossenköllesee, calculated sediment fluxes are six-fold higher than measured values, which indicates that a
small fraction of the PAH deposited in the lake watershed accumulate in the surface sediments. On the contrary,
425 calculated sediment fluxes in Starolesnianske Pleso are one order of magnitude lower than measured fluxes.
The difference between Ladove and Starolesnianske Pleso, both situated in the same region could be related to
orographic and hydrological characteristics of the latter that enhanced the PAH inputs and accumulation in
Staroleniasnke Pleso sediments. This would explain the high concentration of PAH found in this site in
comparison with other lakes from the same area (Fernández et al., 1999 and 2000). Another possibility for these
430 differences could be related to a decrease in PAH atmospheric concentrations in this region during the last
decades. Atmospheric deposition fluxes were measured between 2004 to 2006, whereas sedimentary fluxes
correspond to 2001 in Ladove, but ten years before in the case of Starolesnianske Pleso (1991).

   Representation of the PAH sedimentary settling fluxes and average atmospheric deposition from each high
mountain site showed a strong significant correlation ($r^2 = 0.9958$; $p < 0.01$; Figure 4). The standardized residual
435 of this correlation fulfilled the normality conditions according to the Shapiro-Wilk test. Representation of the
same dataset excluding the area of highest PAH deposition, High Tatras, also showed a strong correlation ($r^2 = 0.8559$; $p < 0.20$) but in this case there was no statistical significance given the small statistical freedom resulting
from the number of cases considered. In any case, the values of both datasets (Table 6) followed parallel
distributions.

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4. Summary and Conclusions

The PAH and benzo[a]pyrene deposition fluxes recorded in the studied high mountain areas of Europe (790-
2413 m) range among the lowest described in remote, rural, coastal, suburban, urban or industrial areas.
445 Nevertheless, a strong contrast is observed between the PAH deposition fluxes in Lochnagar, Gossenköllesee
and Redon, 0.80-2.1 µg m^{-2} mo^{-1}, and Skalnate Pleso, 9.7 µg m^{-2} mo^{-1}, the latter showing PAH deposition fluxes
between 5 and 10 times higher than the others as consequence of inputs from Southern Poland and other areas.

   Low molecular weight compounds from acenaphthene to pyrene dominate the atmospheric deposition of
PAHs, with phenanthrene, fluoranthene and pyrene representing 32-60% of total. The proportion of
450 phenanthrene, the most abundant compound in the PAH distribution of each sample was higher at the sites of

lower temperature, Gossenköllesee and Skalnate Pleso, indicating higher transfer from gas phase to particles of the more volatile PAHs.

Insolation was another local property determining the deposited PAH distributions. The sites with lower insolation, e.g. those located at lower altitude, were those with higher proportion of photooxidable compounds 455 such as benz[a]anthracene.

Precipitation was the main driver of PAH fallout. However, when rain and snow deposition were low, particle settling also constituted an efficient driver for PAH deposition. Accordingly, in Redon and Lochnagar, the two sites receiving background long-range transported PAHs and highest precipitation, the fallout PAH fluxes were related to precipitation. Whereas no significant association was observed between long-range 460 backward air trajectories and PAH deposition in Lochnagar, enhanced PAH fallout at higher precipitation essentially occurred for air masses originating from the North Atlantic in Redon. In these cases, particle normalized PAH fallout was also associated with higher precipitation as these air masses were concurrent with lower temperatures, which enhanced gas to particle partitioning transfer. In the warm season (June-October), most of the air masses arriving to Redon originated from the south and particle deposition was enhanced as 465 consequence of Saharan inputs. In these cases, particle settling was also a driver of PAH deposition despite the low overall PAH content of the Saharan particles.

In Gossenköllesee, the site receiving lowest precipitation, PAH fallout was related to particle deposition, namely in the case of higher molecular weight homologues. No correlation was observed with precipitation and PAH deposition. However, the particle normalized PAH deposition fluxes were significantly negatively 470 correlated to temperature according to the transfer of these compounds from gas phase to particles at lower temperatures, which enhanced PAH fallout, mainly for the most volatile hydrocarbons. These dependences were observed to occur when air masses originated from Central/Eastern Europe. Lower deposition of total particles and PAHs were observed in this site for air masses originating from the north.

Comparison of PAH atmospheric deposition and lacustrine sedimentary fluxes showed much higher 475 values for the latter, 24-100 µg m^{-2} yr^{-1} compared with 120-3000 µg m^{-2} yr^{-1}, respectively. However, the representation of the PAH settling fluxes and average atmospheric deposition at each site showed a strong significant correlation. Moreover, estimated sediment fluxes calculated from the PAH atmospheric deposition measured in each site, taking into account inputs from the lake catchment, showed slightly lower values than measured fluxes, which indicates that the PAH accumulated in the lacustrine sediments of high mountains 480 reflect the atmospheric fallout of these hydrocarbons.

Author contributions. L. Arellano carried out sample processing and OC analysis of the samples taken between 2004 and 2007 and performed the backward air mass trajectory calculations. Sampling and other field work were designed and performed at each site by N. Rose (Lochnagar), U. Nickus and H. Thies (Gossenköllesee), 485 E. Stuchlík (Skalnaté), and L. Camarero (Redón). P. Fernández performed data interpretation and prepared the paper with contributions from all co-authors, especially J.O. Grimalt.

Competing interests. The authors declare that they have not conflict of interest.

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LIST OF FIGURES

Figure 1. Location of the high altitude areas included in this study. Lake identification: LN, Lochnagar; RDN, Lake Redon; GKS, Gossenköllesee and SKP, Skalnate Pleso. Situation of the Black Triangle between Germany, Poland and Czeck Republic is indicated by a shaded area.

Figure 2. Qualitative distribution of PAH mixtures in atmospheric deposition samples. Compound identification: Acnphlene, acenaphthylene; Acnphtene, acenaphthene; Flu, fluorene; Phe, phenanthrene; Ant, anthracene; Fla, fluoranthene; Acephe, acephenanthrilene; Pyr, pyrene; B[a]A, benz[a]anthracene; Chrys+Triph, chrysene+triphenilene; B[b+j]Fla, benzo[b]fluoranthene + benzo[j]fluoranthene; B[k]Fla, benzo[k]fluoranthene; B[e]P, benzo[e]pyrene; B[a]P, benzo[a]pyrene; Per, perylene; IndChrys, indeno[7,1,2,3-cdef]chrysene; IndPyr, indeno[1,2,3-cd]pyrene; B[ghi]Per, benzo[ghi]perylene; DB[ah]A, dibenz[a,h]anthracene; Cor, coronene.

Figure 3. Prevalent back trajectories in Redon from 1st to 29th June 2006, mainly originating from southern areas.

Figure 4. Average PAH sediment and atmospheric deposition fluxes at the high altitude lakes considered in this study. Units in µg m^{-2} yr^{-1}.
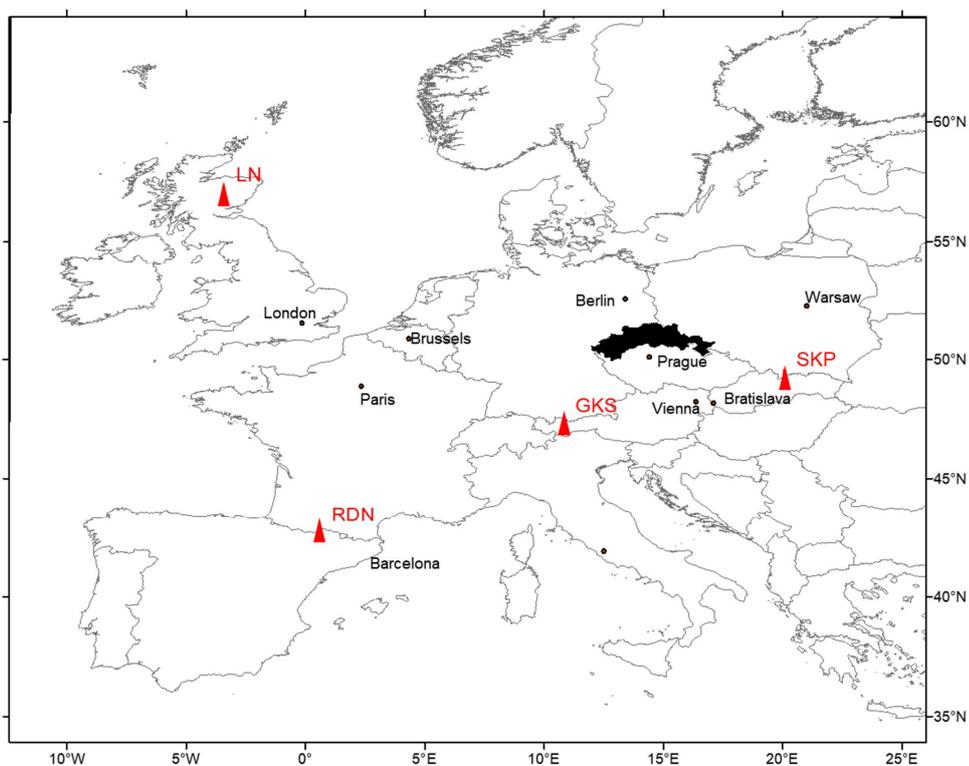
Figure 1.

Figure 2.
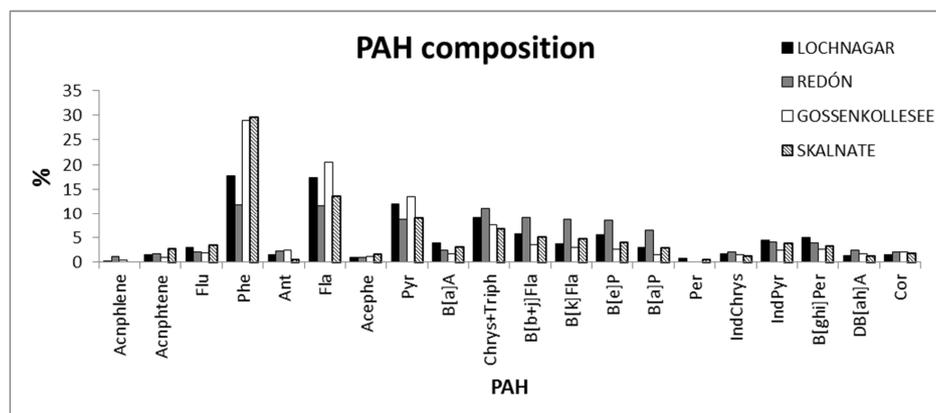
Figure 3.
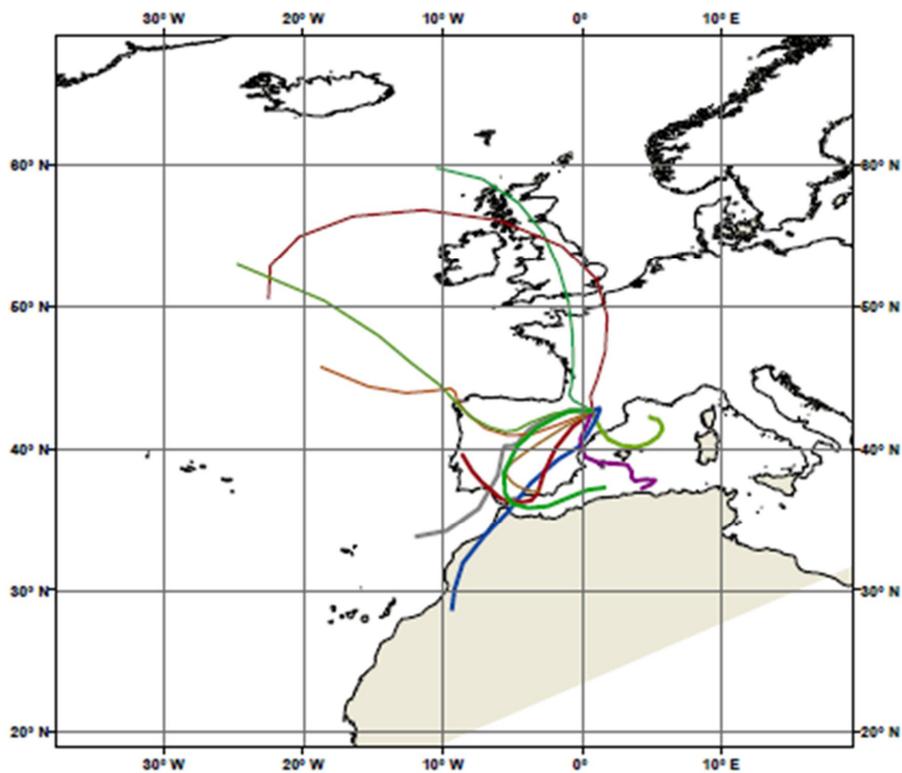
Figure 4.
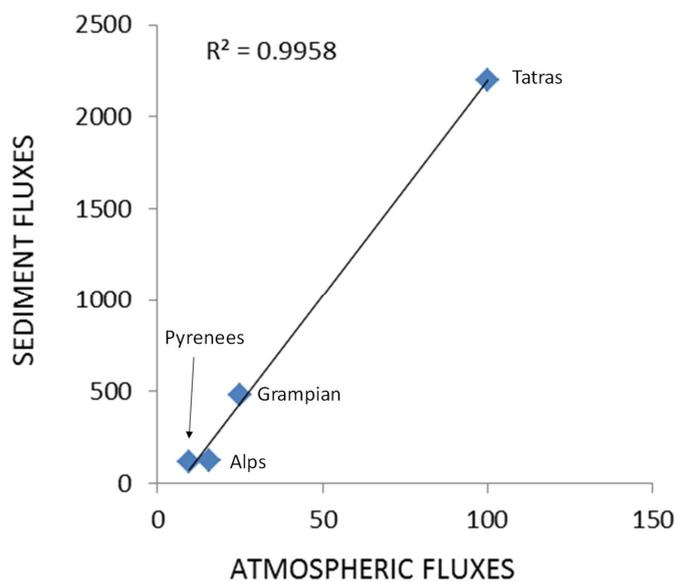
Table 1. Average temperature, atmospheric precipitation and particle (mg m^{-2} mo^{-1}) and PAH (µg m^{-2} mo^{-1}) monthly deposition fluxes in the European mountain areas considered in the present study.

	Lochnagar	Redon	Gossenköllesee	Skalnate Pleso
Sampling period	June 04-March 07	May 04-Sept. 06	June 04-Aug. 06	May 04-May 06
Mountain range	Grampian Mountains	Pyrenees	Tyrolean Alps	Tatra Mountains
Latitude (N)	56.95914	42.64208	47.22528	49.189933
Longitude (E)	-3.23128	0.77951	11.01390	20.234217
Altitude (m ASL)[a]	790	2235	2413	1787
Temperature (ºC)[b]	4.9	5.3	-1.4	2.2
Mean precipitation (mm mo^{-1})	129	79	66	120
Particle flux *(min.-max.)*	130 *(15-1600)*	320 *(14-2800)*	145 *(18-590)*	330 *(43-1800)*
$\sum$PAH[c] *(min.-max.)*	2.1 *(0.53-10)*	0.80 *(0.24-1.4)*	1.3 *(0.19-3.7)*	9.7 *(2.3-32)*
warm	1.8 *(0.53-4.4)*	0.89 *(0.24-1.4)*	1.3 *(0.22-3.7)*	8.4 *(2.3-15)*
cold	2.25 *(0.74-10)*	0.63 *(0.24-1.2)*	1.3 *(0.19-3.7)*	8.8 *(3.6-32)*
LMW-PAH[d] *(min.-max.)*	1.1 *(0.25-7.6)*	0.30 *(0.06-0.74)*	0.89 *(0.09-3.1)*	5.6 *(1.4-22)*
warm	0.94 *(0.25-2.2)*	0.30 *(0.07-0.74)*	0.86 *(0.10-3.1)*	5.7 *(1.4-10)*
cold	1.2 *(0.39-7.6)*	0.28 *(0.06-0.66)*	0.90 *(0.09-2.8)*	4.2 *(1.7-22)*
HMW-PAH[e] *(min.-max.)*	0.97 *(0.08-2.6)*	0.49 *(0.18-0.94)*	0.40 *(0.10-0.84)*	3.9 *(0.73-11)*
warm	0.82 *(0.20-2.6)*	0.57 *(0.21-0.94)*	0.42 *(0.11-0.98)*	2.3 *(0.73-4.1)*
cold	1.1 *(0.08-2.5)*	0.34 *(0.18-0.55)*	0.41 *(0.10-0.84)*	4.5 *(1.6-11)*
PAH ($\sum$15 PAH-EPA)[f] *(min.-max.)*	1.9 *(0.48-9.6)*	0.70 *(0.22-1.3)*	1.2 *(0.17-3.5)*	8.8 *(2.2-29)*

[a]Meters above sea level. [b]Mean temperature for the whole sampling period. [c]Sum of all PAH analysed from acenaphthylene to coronene.
[d]Sum from fluorene to pyrene. [e]Sum from benz[a]anthracene to coronene. [f]Sum of PAH included in the EPA list (excluding naphthalene).

Table 2. Comparison of PAH deposition fluxes with those reported in the literature.

Sampling site	Sampling period	Site type	∑15 PAH-EPA (μg m^{-2} day^{-1})	benzo[a]pyrene (ng m^{-2} mo^{-1})	Reference
Skalnate Pleso	May 2004- May 2006	remote	0.28	280	This study
Lochnagar	June 2004-March 2007	remote	0.06	61	"
Gossenköllesee	June 2004-Aug. 2006	remote	0.04	20	"
Redon	May 2004-Sept. 2006	remote	0.02	51	"
Gossenköllesee	Oct. 1996-Oct. 1998	remote	0.038	22	(Fernandez et al., 2003)
Redon	March 1997-Oct. 1998	remote	0.052	59	(Fernandez et al., 2003)
Øvre Neadalsvatn	Dec. 1997, April-Aug. 1998	remote	0.063	41	(Fernandez et al., 2003)
Chesapeake Bay	June 1990-Dec. 1991	remote	0.55	500	(Leister and Baker, 1994)
Chesapeake Bay	1991	remote	0.4-0.55	500	(Dickhut and Gustafson, 1995)
Siskiwit Lake (Lake Superior, USA)	1983-1984	remote	0.46	225	(McVeety and Hites, 1988)
Natural Park (North Spain)	June 2010-May 2011	remote	0.18		(Foan et al., 2012)
Southern Ontario (Canada)	Oct. 2001-Dec. 2002	remote	0.41	345	(Su et al., 2007)
Southern Italy	Dec. 2003-Jan. 2004	rural	0.09 (0.07-0.15)	140	(Menichini et al., 2006)
Southern Germany	Aug. 2001-Aug. 2002	rural	0.55		(Gocht et al., 2007)
Beijing-Tianjin region	June 2007-May 2008	rural	3.9		(Wang et al., 2011b)
Pleumeur-Bodou (France)	Oct. 1999-Oct. 2000	rural	0.14	15000	(Garban et al., 2002)
Balaton Lake (Hungary)	1996-1997	rural	0.51-0.81	1000-1500	(Kiss et al., 2001)
Abeschviller (France)	Oct. 1999-Oct. 2000	forest	0.19	15000	(Garban et al., 2002)
Bayreuth (Germany)	May 1995-April 1996	forest	0.42-2.4	620-1700	(Horstmann and Mclachlan, 1998)
Gardsjon (Sweden)	1991-1994	forest	0.51		(Brorstrom-Lunden et al., 1998)
Western Mediterranean Sea	1989-1990	coastal	0.13	183	(Lipiatou et al., 1997)
Eastern Mediterranean	Nov. 2000-July 2002	coastal	0.46		(Tsapakis et al., 2006)
Atlantic Ocean (Canada)	1998-2000	coastal	0.12	25-75	(Brun et al., 2004)
New England coast	Dec. 1998-May 2000	coastal	0.22		(Golomb et al., 2001)
Galvesston Bay (Texas, USA)	Feb 1995-Aug. 1996	coastal	0.63		(Park et al., 2001)
New Jersey	June 1999-Aug. 2002	coastal	1.0	1.6	(Gigliotti et al., 2005)
New Jersey	Feb. 1998-Jan. 2003	coastal	0.4-6.1	1.3-24	(Gigliotti et al., 2005)
Tampa Bay	May-August 2002	coastal	6.8	120	(Poor et al., 2004)
Beijing-Tianjin region	June 2007-May 2008	background	0.82		(Wang et al., 2011b)
Western Greece	Jan. 2001-Oct. 2002	background	0.19		(Terzi and Samara, 2005)
New Jersey	Feb. 1998-Aug. 2002	suburban	0.81-3.1	1.7-12	(Gigliotti et al., 2005)
Evreux (France)	March 2001-Feb 2002	suburban	0.13		(Motelay-Massei et al., 2003)
Yangsuri, Yangpyoung	Feb.-May 2000	suburban	5.5-24		(Bae et al., 2002)
Taichung (Taiwan)	Aug.-Dec. 2002	suburban	39		(Fang et al., 2004)
Izmit Bay (Turkey)	Sept. 2002-July 2003	urban	8.3	1500	(Pekey et al., 2007)
Manchester	1991-1992	urban	5.2	9000	(Halsall et al., 1997)
Cardiff	1991-1992	urban	4.1	6600	(Halsall et al., 1997)
Taichung (Taiwan)	Aug.-Dec. 2002	urban	49		(Fang et al., 2004)
Beijing-Tianjin region	June 2007-May 2008	urban	8.3		(Wang et al., 2011b)
Paris	Oct. 1999-Oct. 2000	urban	0.63		(Garban et al., 2002)
Paris (France)	Nov. 1999-Oct. 2000	urban	0.64 (0.2-2.0)		(Ollivon et al., 2002)
Seoul and Inchon	Feb.-May 2000	urban	5.5-24		(Bae et al., 2002)
New Jersey	Feb. 1998-Aug. 2002	urban	11-16	42-54	(Gigliotti et al., 2005)
Bursa (Turkey)	July 2004-March 2005	industrial	0.3-19.5		(Esen et al., 2008)

Table 3. Average PAH isomeric ratios in atmospheric deposition.

	Pyr/(Fla+Pyr)	BaA/(BaA+Chrys)	BaP/(BaP+BeP)
Gossenköllesee			
Mean	0.40±0.03	0.18±0.04	0.38±0.10
Warm[a]	0.41±0.04	0.19±0.04	0.31±0.13
Cold[b]	0.39±0.02	0.17±0.04	0.39±0.06
Redon			
Mean	0.43±0.02	0.17±0.04	0.42±0.05
Warm	0.42±0.02	0.18±0.03	0.41±0.05
Cold	0.43±0.02	0.17±0.05	0.43±0.05
Skalnate Pleso			
Mean	0.40±0.02	0.28±0.07	0.45±0.12
Warm	0.41±0.01	0.22±0.04	0.51±0.18
Cold	0.40±0.02	0.32±0.05	0.42±0.07
Lochnagar			
Mean	0.41±0.06	0.31±0.06	0.33±0.12
Warm	0.42±0.08	0.32±0.06	0.36±0.10
Cold	0.40±0.04	0.30±0.06	0.31±0.11

[a]June-October, [b]November-May.

Table 4. Pearson correlation analysis between atmospheric deposition fluxes of PAHs and environmental variables.

	GOSSENKÖLLESEE			REDON			SKALNATE PLESO			LOCHNAGAR		
	Particles	Precipitation	T(ºC)	Particles	Precipitation	T(ºC)	Particles	Precipitation	T(ºC)	Particles	Precipitation	T(ºC)
Particles	-			-	-0.495*	0.460*	-	0.550**	0.529**	-		
Precipitation		-	0.559*	-0.495*	-		0.550**	-	0.613**		-	
Temperature		0.559*	-	0.460*		-	0.529**	0.613**	-			-
∑PAH					0.720**		0.481*					
LMW-PAH					0.616**		0.509*					
HMW-PAH	0.547*				0.635**						0.416*	
Phe					0.472**		0.531*					
Fla					0.679**		0.444*					
Pyr					0.661**		0.457*					
Chrys	0.644*				0.645**						0.409*	
BaP					0.562**	0.482*			-0.466*		0.378*	
IndPyr	0.521*				0.510**				-0.448*		0.559*	
BghiPer	0.619*				0.557**						0.475*	
Cor	0.624*				0.603**				-0.488*	-0.390*	0.444*	
Normalised by particle deposition												
∑PAH		-0.449*	-0.492*		0.544**				-0.608**		0.394*	
LMW-PAH		-0.471*			0.564**				-0.490*			
HMW-PAH			-0.488*		0.517**				-0.731**		0.443*	
Phe					0.537**							
Fla		-0.531*	-0.485*		0.556**				-0.654**			
Pyr		-0.522*	-0.489*		0.553**				-0.637**			
Chrys		-0.440*	-0.597*		0.510**				-0.684**		0.411*	
BaP					0.484**				-0.765**		0.418*	
IndPyr					0.594**				-0.738**		0.530**	
BghiPer					0.497**	-0.407*			-0.718**		0.508**	
Cor					0.562**	-0.433*			-0.749**		0.501**	

All data have been log-transformed except precipitation and temperature. Only those correlations statistically significant at 95% (*) and 99% (**) are shown.

Table 5. Pearson correlation analysis between PAH deposition fluxes and percentage of air mass trajectories recorded during sample collection.

Otherwise noted, all correlations are statistically significant at 95% or 99% confidence level.

	n[b]	Particles	Precipitation	T (ºC)	∑PAH	LMW-PAH	HMW-PAH	∑PAH/part[c]	LMW-PAH/part[c]	HMW-PAH/part[c]
Gossenköllesee	465									
North Atlantic (17%)[a]		-0.493			-0.580	-0.573	-0.558			
Central/East Europe (11%)								0.573	0.573	0.479
Redon	339									
North Atlantic (38%)		-0.440*	0.491	-0.601				0.558	0.564	0.513
South (51%)		0.498		0.805				-0.483	-0.524	-0.431*
Central/East Europe (11%)					-0.541		-0.611			
Skalnate Pleso	560									
South (26%)								-0.493	-0.534	

[a]Percentages of air mass trajectories from the specific origin with respect to total air mass trajectories calculated during the sampling periods (Table 1). Only the air mass trajectory origins involving significant correlations with PAH deposition are included. A full description of the origins of the air mass trajectories is available in Arellano et al. (2014). [b]Total air mass trajectories calculated during the sampling period. [c]Normalised to particle deposition. *Statistically significant at 90% confident level.

Table 6. Comparison between atmospheric deposition and lacustrine sediment fluxes of PAHs in the study regions ($\mu g\ m^{-2}\ yr^{-1}$).

	Lochnagar	Redon	Gossenköllesee	Skalnate Pleso[a]	
Atmospheric deposition					
Sampling period	June 04-March 07	May 04-Sept. 06	June 04-Aug. 06	May 04-May 06	
∑PAH	25	9.6	16	100	
Sediment fluxes					
Sampling year	2001	1991	1998	1991	2001
Sampling site	Lochnagar	Redón	Gossenköllesee	Starolenianske Pleso	Ladove Pleso
Catchment area (ha)	109	155	85	3.2	14.4
Lake area (ha)	10.4	24	1.7	0.71	1.7
∑PAH conc. ($ng\ g^{-1}\ dw$)	4000	680	780	18000	8700
∑PAH tot fluxes	480	120	125	3000	1400
∑PAH tot fluxes (estimated)[b]	260	62	780	452	850
∑PAH ratio (meas./calc.)[c]	0.54	0.52	6.2	0.15	0.61

[a] Sediment data from Skalnate Pleso were not available. Sedimentation rates from two nearby lakes in the Tatra mountains are shown for comparison. [b] Calculated considering that all atmospheric inputs in the lake and its catchment area accumulate in the lake sediments (atmospheric deposition x catchment area)/ lake area. [c] Ratio between measured sediment fluxes and those calculated from the atmospheric deposition considering the lake and its catchment area.