Atmospheric deposition of semivolatile organic pollutants in European high mountains: Sources, settling and chemical degradation

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ABSTRACT

Bulk atmospheric deposition samples, including wet and dry deposition, were collected during 2004–2006 in four high mountain European lakes: Skalnate Pleso (Tatra mountains, Slovakia), Gossenköllesee (Alps, Austria), Redon (Pyrenees, Spain), and Lochnagar (Grampian Mountains, Scotland). Samples were analysed for polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), endosulfans, and polybromodiphenyl ethers (PBDEs).The deposition of PCBs, HCHs, and low brominated BDEs reflected baseline contributions from long range atmospheric transport. This was also the case for PAHs in Redon and Gossenköllesee, endosulfans in Lochnagar and Gossenköllesee and HCB in these three lakes. However, Skalnate received PAHs, endosulfans, and HCB from regional sources as it was the case for endosulfans in Redon. The distinct origin of these pollutants was reflected in the relative composition of some metabolites such as the proportion of endosulfan sulfate vs α- and β-endosulfans or the relative composition of BDE47 and BDE99.Wet deposition was the main process for atmospheric removal of PAHs, HCHs, and HCB. In addition, warm season revolatilization from soils and melting snow with subsequent condensation at low temperature were significant for volatile PAHs, HCB, low chlorinated PCBs, and endosulfans. Reaction with OH radicals was not a significant loss process of HCHs and HCB in remote areas, dominated by wet deposition, whereas PCBs and PAHs were significantly removed by both wet deposition and OH radical oxidation, the latter dominating in the highest altitude sites. Photolysis was the main atmospheric removal process of PBDEs, dominating over atmospheric deposition and OH depletion in all sites.

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1. Introduction

Semi-volatile organic contaminants (SOCs) encompass a variety of compounds of different origins and common physical-chemical properties. They include already banned or severely restricted organohalogenated pollutants such as polychlorobiphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and polybromodiphenyl ethers (PBDEs), all of them belonging to the list of persistent organic pollutants regulated by the Stockholm Convention (UNEP, 2020). Other compounds such as the polycyclic aromatic hydrocarbons (PAHs), unintentionally emitted from incomplete combustion of organic matter, share similar properties. Semi-volatility and environmental persistence make these compounds prone to long range atmospheric transport (LRAT) and global distribution, being detected far from their emission sources.

In the last decades, numerous studies have documented the accumulation of these pollutants in soil, aquatic systems, and snow/ice in remote cold areas owing to their temperature-dependent physical-chemical properties. Indeed, significant SOC levels have been found in high altitude alpine and polar sites, such as PCBs, HCB, and organochlorine pesticides (Blais et al., 1998; Cabrerizo et al., 2018; Davidson et al., 2003; Estellano et al., 2008; Grimalt et al., 2001a; Halsall, 2004; Liu et al., 2010), PBDEs (Arellano et al., 2014b; Wang et al., 2009), and PAHs (Fernández et al., 2000; Ren et al., 2017; Usenko et al., 2010), as consequence of their preferential partitioning onto condensed phases at low temperatures.

SOCs can be removed from the atmosphere by diffusive gas-surface exchange (Gioia et al., 2008; Ma et al., 2013), wet and dry deposition (Carrera et al., 2002; Feng et al., 2017; Fernández et al., 2003; Jurado et al., 2005), and direct and/or indirect photolysis (Raff and Hites, 2007; Wang et al., 2011; Zhang et al., 2018). The last two represent an effective removal of SOCs from the atmosphere limiting their atmospheric transport, while air-surface exchange exhibits a seasonal reversal effect, which can result in net deposition or volatilization, mainly depending on temperature. The relative importance of these processes is strongly related to the distribution of these compounds between the gas and particulate phases, e.g. degradation of gas phase compounds generally occurs faster than those associated to atmospheric particles (Keyte et al., 2013). The knowledge of the relative importance of these processes is relevant for adequate design of

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regulatory measures of SOCs production and use, which should lead to reducing their environmental concentrations. However, as emissions from primary sources decrease, re-volatilization of previously deposited pollutants may gain importance on their global environmental cycling (Nizzetto et al., 2010).

Besides physical-chemical properties, atmospheric and meteorological conditions have great influence on the removal of these pollutants from the atmosphere. High mountain regions have specific features, which can influence on the relative importance of the elimination processes. These sites are characterized by high levels of precipitation with a significant fraction of snow, which is more efficient in scavenging atmospheric pollutants than rain (Franz and Eisenreich, 1998). They receive greater insolation than lowland sites and are often constituted by poor soils (mainly bare rocks) and sparse vegetation, with low SOC retention capacity. Moreover, the aquatic systems in these sites are small oligotrophic lakes that remain ice-covered for much of the year. All these features are relevant for the accumulation of SOCs in these areas. Understanding the processes of transport, deposition and degradation of these compounds in these regions is important as mountains can become secondary sources of SOCs accumulated in soils and ice surfaces (Grimalt et al., 2001b). Indeed, recent studies have reported evidences of SOC re-volatilization in polar (Ma et al., 2011; Wong et al., 2011) and Alpine regions (Bogdal et al., 2009).

Bulk atmospheric deposition samples, including wet and dry deposition, were collected during two years in four high mountain European lakes and analysed for PAHs (Arellano et al., 2018), organochlorine compounds (OCs) (Arellano et al., 2015), such as PCBs, HCB, HCHs and endosulfans, and PBDEs (Arellano et al., 2014a). The present study is concerned with the description of the factors controlling the atmospheric deposition of SOCs in these areas, namely regional sources versus LRAT, spatial and temporal trends and the relative significance of photochemical degradation and wet deposition, whether rain or snow, in the removal of these compounds from the mountain atmospheres.

2. Material and methods

2.1. Chemicals

Isooctane, n-hexane, dichloromethane, cyclohexane, methanol and acetone were for trace analysis (Merck; Darmstadt, Germany). Glass fiber filters (47 mm diameter, 1 mm, GF/B) were supplied by Whatman (Maidstone, UK) and Empore C_{18} extraction disks (47 mm diameter, 0.5 mm thickness) were from 3 M Co. (St Paul, MN, USA). Internal standards, surrogates and standard solutions purchased from Dr. Ehrenstorfer (Ausburg, Germany).

Table 1
Sampling site characteristics and meteorological condition over the sampling period.

	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 Mts	Pyrenees	Tyrolean Alps	Tatra Mountains
Country	Scotland (UK)	Spain	Austria	Slovakia
Latitude (N)	56.9591	42.6421	47.2253	49.18993
Longitude (E)	−3.2313	0.7795	11.0139	20.23422
Altitude (m ASL) [a]	790	2235	2413	1787
Temperature (°C) [b]	4.9	5.3	−1.4	2.2
Precipitation (mm mo^{-1}) [b]	129	79	66	120

[a] Meters above sea level.
[b] Mean values for the whole sampling period.

2.2. Sampling

Bulk (dry and wet) atmospheric deposition samples were regularly collected at the four remote high mountain areas selected for study (Table 1 and Fig. 1) over different time periods: monthly (one sample for the whole month deposition) from 2004 to 2006 in Gossenköllesee, Lake Redon, and Skalnaté Pleso, and biweekly (one sample for the whole two weeks' deposition) from 2004 to 2007 in Lochnagar. Further information concerning sampling devices and conditions is reported elsewhere (Arellano et al., 2014a, 2018).

Samples were filtered on site using pre-weighed glass fiber filters. The filtrates were solid-phase-extracted with C_{18} disks as described elsewhere (Carrera et al., 1998). After sample removal, the bulk collectors were rinsed with Milli-Q water which was filtered, solid-phase-extracted, and the extracts combined with those of the corresponding atmospheric deposition sample. Glass fiber filters and disks were wrapped in aluminium foil and transported frozen to the laboratory. Meteorological parameters, namely air temperature and precipitation were provided by automatic weather stations (AWS) located at each site.
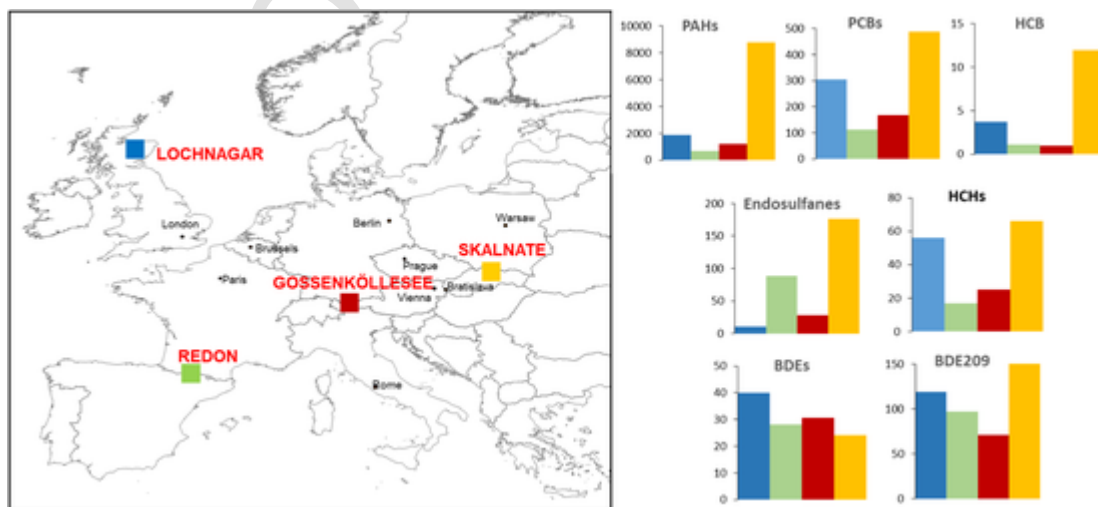

Fig. 1. Spatial distribution pattern of studied pollutants in atmospheric deposition of remote lakes of Europe (values in ng m^{-2}mo^{-1}).

2.3. Extraction and clean-up

Glass-fiber filters were freeze-dried and weighed for total particle content measurement. SOCs were extracted from the filters by sonication with dichloromethane:methanol (2:1) (3×10 mL, 20 min each). Pollutants adsorbed in the C_{18} disks were eluted sequentially with methanol, cyclohexane, and dichloromethane (Carrera et al., 1998). Both filter extracts and C_{18} disk eluates were combined and purified by column adsorption chromatography with aluminium oxide after adding a recovery standard mixture. Prior to instrumental analysis, samples were spiked with internal standards.

2.4. Instrumental analysis

PCBs, HCB and HCHs were analysed by gas chromatography with micro-electron capture detector (GC-μECD) (Agilent Technologies 6890 N). Endosulfans (α- and β- isomers and endosulfan sulfate) and PBDEs were determined by gas chromatography coupled to mass spectrometry in negative ion chemical ionization (GC-MS-NICI) and selective ion recording modes (Trace DSQ Instrument Thermo Electron). This technique was also used for structural confirmation of all OCs and for their quantification when the interferences in GC-μECD did not allow their determination. PAHs were analysed by gas chromatography coupled to mass spectrometry in electronic impact and selective ion recording modes (Trace DSQ Instrument Thermo Electron). Further details on instrumental analysis conditions and quantification of each pollutant family are described elsewhere (Arellano et al., 2014a, 2015, 2018).

2.5. Quality control and assurance

Field and procedural blanks were obtained at each sampling site and processed together with the samples. In general, blank values represented less than 10% of bulk deposition sample concentrations. These values were used to determine method detection limits (LODs), which were established as the average blank values plus 3 times the standard deviations. Efficiency of the analytical procedure was evaluated from recoveries of the surrogate standards. All reported values were recovery corrected.

2.6. 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's Air Resources Laboratory (Draxler, 2013; Draxler and Hess, 1998).

The meteorological data used to compute the 6-hourly back-trajectories were obtained from the National Centre for Environmental Prediction Global Data Assimilation System and from Eta Data Assimilation System. The trajectories were calculated for those days with precipitation (rain or snow) and every 2 days when no precipitation was recorded by the AWS. The altitudes representing the air masses above the sampling sites were selected as follows: 3000 m above sea level (asl) in Redon and Skalnate Pleso, 3500 m asl for Gossenköllesee and 2000 m asl for Lochnagar.

3. Results and discussion

3.1. Spatial deposition fluxes

The monthly mean atmospheric deposition fluxes of SOCs over the studied sites are shown in Fig. 1. PAHs were dominant in all sites, with deposition fluxes between one and two orders of magnitude higher than the other contaminants. In general, the concentrations of the other

SOCs followed PCBs > BDE209 > endosulfans > HCHs > low brominated BDEs > HCB.

All compounds were found in highest levels in Skalnate, the easternmost site, while different spatial distributions were observed in Lochnagar, Redon and Gossenköllesee, depending on the pollutant class. Thus, Lochnagar showed higher concentrations of PBDEs, while Redon was characterized by significant inputs of ensodulfans. The highest differences in atmospheric deposition fluxes between sites were observed for PAHs and endosulfans, whereas legacy compounds such as PCBs, HCHs or even HCB showed similar levels at all three sites in contrast with the high amounts in Skalnate. PBDEs were the compounds with more uniform deposition fluxes, with differences of twofold at the most.

3.2. Principal component analysis (PCA)

This multivariate method was used to identify correlations between atmospheric deposition fluxes of the selected pollutants and environmental variables, namely temperature, precipitation, particle deposition, sampling site characteristics, and prevailing backward air mass trajectories for each sampling period (data reported in the supporting information). These calculations were performed on normalized data (subtraction of average value and division by the standard deviation) using statistical software IBM SPSS Statistics v. 26. Individual compounds were taken as representative of each pollutant family when they were present in more than 90% of the analysed samples. Missing values were replaced by LOD/2.

Four PCA components accounted for 69.8% of the total variance of the data set. PC1, which explained 32.8% of the total variance, was highly dominated by PAH (Fig. 2), mainly by the high molecular weight compounds. PC2, 18.6% of total variance, was represented by the more volatile pollutants, e.g. low molecular weight PAH, endosulfans, HCB and the low chlorinated PCB congeners, and also showed a significant loading of particle deposition and temperature. PC3, 9.4% of total variance, was highly dominated by low brominated BDEs. This component also had a positive association with North Atlantic air mass trajectories. PC4, 9.0% of total variance, consisted of BDE209, HCHs, precipitation and, to a lesser extent, temperature.

The score plots of the deposition samples in each component (Fig. 3) showed that the samples from Skalnate Pleso had a large positive loading on PC1, mainly those collected during the cold season. Some winter samples collected in Lochnagar also contributed to this PC in a minor proportion. PC2, representing the more volatile compounds, was contributed by samples from Skalnate Pleso collected in the warm season, and, to a much lesser extent, from Redon and Lochnagar. The samples from Lochnagar collected during 2004 and the winter of 2005 showed the highest scores on PC3, followed by those from the warm period of 2004 in Skalnate Pleso (Fig. 3). This component, representing low brominated BDEs was also positively associated with North Atlantic air masses coming from North America. This influence was more pronounced in Lochnagar, the westernmost of the studied regions. A PCA considering only samples taken in this region showed a component with similar composition to PC3, but with a contribution of North Atlantic air masses of 0.87 instead of 0.24 as observed when considering all sites (Fig. S1). Samples taken during warm seasons in Skalnate Pleso, Lochnagar and Gossenköllesee had a large loading on PC4, representing the HCHs, the more water soluble pollutants among the studied compounds, and had a significant positive association with precipitation.

3.3. Long range atmospheric transport (LRAT) versus regional sources

The pollutants deposited in the sampling sites arrive by atmospheric transport from outlying sources, which may be regional or from very distant areas, reflecting LRAT.

The large positive loading on PC1 of the deposited PAHs from Skalnate Pleso, mainly those collected in the cold season, likely reflect
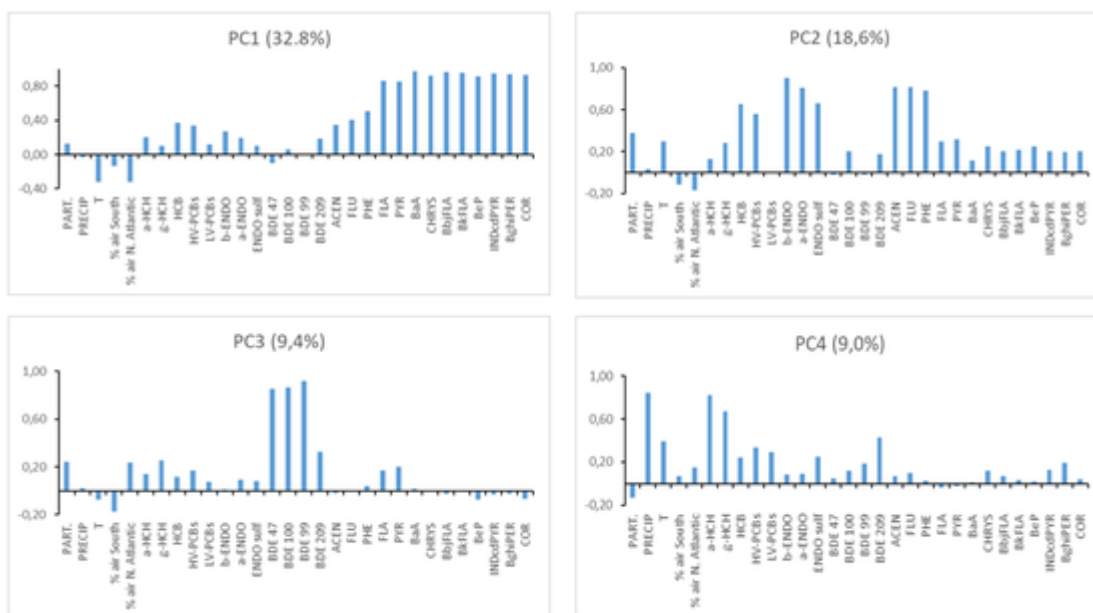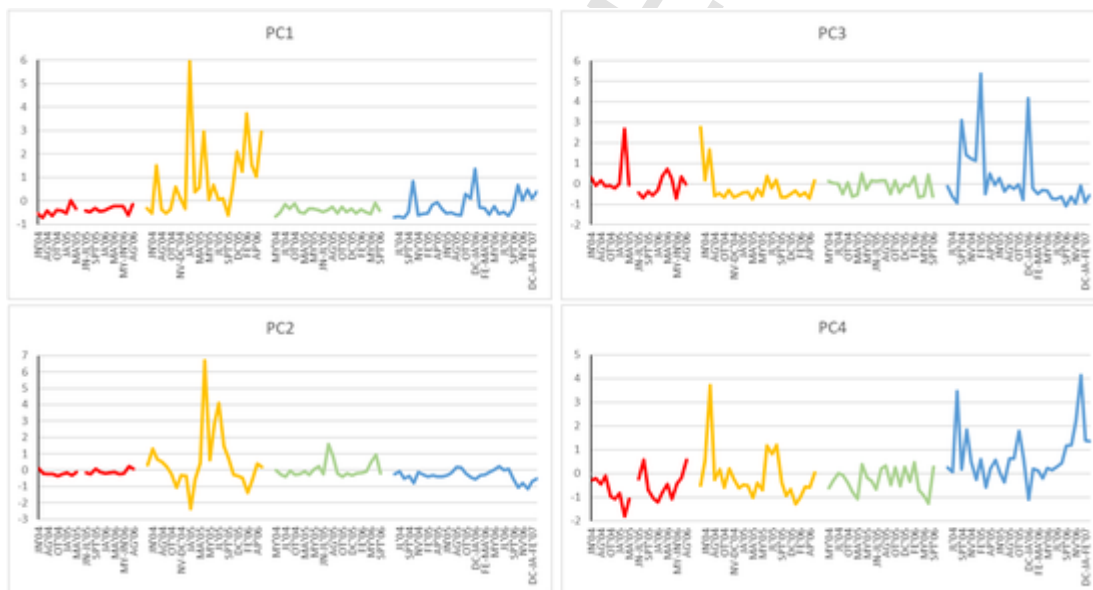
Fig. 2. Loadings of selected variables in each component. In brackets, the percentage of total variance explained. x-axis label identification: Part, particle deposition; Precip, percipitation rate; T, temperature; % air South, percentage of air masses from the South; % air N. Atlantic, percentage of air masses from Nort Atlantic; HV-PCBs, high volatility PCBs (Σ(PCB 28, PCB 52, and PCB 101)); LV-PCBs, low volatility PCBs (Σ(PCB 118, PCB 138, PCB 153, and PCB 180)); Acen; Acenaphthene; Flu, fluorene; Phe, phenanthrene; Fla., fluoranthene; Pyr, pyrene; BaA, benz[*a*]anthracene; Chrys, chrysene; BbjFla, sum of benzo[b] and benzo[*j*]fluoranthene; BkFla, benzo[*k*]fluoranthene; BeP; benzo[*e*]pyrene; Indcdpyr; indeno[1,2-*cd*]pyrene; Bghiper, benzo[*ghi*]perilene and Cor, coronene.

Fig. 3. Score plots of deposition samples in each component. Site identification: Gossenköllesee (red), Skalnate (yellow), Redon (green) and Lochnagar (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regional contributions related with higher combustion during the cold months. On the contrary, the deposition samples taken in Redon and Gossenköllesee do not contribute to this component, which points to LRAT as the main origin of the PAHs deposited in these areas. In addition, the PAH deposition fluxes showed the highest differences between sites, with the highest levels in Skalnate, which is consistent with regional point sources impacting in the Tatras.

Although higher levels of PCBs and HCHs were detected in Skalnate, the differences among sites were not significant (Fig. 1). The occurrence of these legacy pollutants in the deposition samples was therefore most likely related to LRAT resulting from diffuse baseline pollution levels distributed throughout Europe. The similar deposition fluxes of HCB in Lochnagar, Gossenköllesee and Redon were consistent

with these uniform air concentrations and origin from remote areas as consequence of its high volatility and persistence (Jaward et al., 2004); however, Skalnate Pleso showed 4–10 times higher fluxes than other studied regions, which pointed to regional emission sources.

The endosulfan deposition fluxes also showed significant differences between sites (Fig. 1), with the highest levels found in Skalnate and Redon, and the lowest in Lochnagar. This is consistent with point sources of this pesticide in the eastern and southern European regions, while inputs of endosulfans arriving to Gossenköllesee and Lochnagar could reflect LRAT. The quantitative composition of the endosulfan mixtures found in each site provided further insight into the origin of these compounds. Thus, once emitted to the atmosphere, α- and β-endosulfan degrade to endosulfan sulfate, therefore high percent of the

degradation product is indicative of LRAT. Skalnate and Redon showed the lowest percentages of this metabolite (17% and 29%, respectively) (Arellano et al., 2015) while the higher values in Gossenköllesee (39%) and Lochnagar (53%) were consistent with a higher degree of degradation during LRAT.

The low brominated BDEs were the compounds with more uniform deposition fluxes, from 24 ng m^{-2} mo^{-1} in Skalnate to 40 ng m^{-2} mo^{-1} in Lochnagar. This uniform distribution over such distant sites is consistent with LRAT. Further evidence of the LRAT of these compounds was obtained from examination of the BDE47/BDE99 ratios, as BDE47 has longer photodegradation half-life than BDE99 (Dickhut et al., 2012). These ratios in the atmospheric deposition samples collected in Redon, Gossenköllesee, and Skalnate varied between 1.4 ± 0.42 to 2.6 ± 1.3 (Arellano et al., 2014a), which was higher than those found in the technical mixtures (0.79–1.1). These values were indicative of preferential BDE99 photodegradation and consistent with LRAT as predominant source for the low brominated BDEs deposited in these areas. The BDE47/BDE99 ratios in the deposition samples of Lochnagar (Arellano et al., 2014a) showed higher values in 2004, suggesting photolytic loss of BDE99 in this year (1.4 ± 0.19) than in 2005 (1.0 ± 0.09), and 2006 (0.88 ± 0.02), which were in the range of those reported in commercial mixtures. This difference was consistent with a declining long range transport of PBDE mixtures from North America, whose contribution may have decreased after US restrictions, leading to a higher contribution of the European sources from 2005 onwards.

In contrast to the low brominated BDEs, the deposition fluxes of BDE209 showed differences between sites. The lowest fluxes were recorded in Gossenköllesee (71 ng m^{-2} mo^{-1}) and Redon (97 ng m^{-2} mo^{-1}), while the highest levels were found in Skalnate (162 ng m^{-2} mo^{-1}) and, to a lesser extent, in Lochnagar (119 ng m^{-2} mo^{-1}). These geographical differences suggest an influence of regional sources in the deposition of BDE209 in Skalnate and Lochnagar.

3.4. Primary versus secondary inputs

Most of the more volatile compounds such as Acenaphthene (Acen), fluorene (Flu) and phenanthrene (Phe) for PAHs, HCB and low chlorinated PCBs, together with endosulfans, particle deposition and temperature were grouped in PC2 (Fig. 2). This component likely reflected secondary contributions of these compounds due to their volatilization from soils and snow melting at increasing temperature. In addition, the high loading of endosulfans in this component was probably related to the more intensive application of this pesticide in spring and summer. The samples showing the highest scores in PC2 were those collected during the warm season in Skalnate and, to a lesser extent in Redon and Lochnagar (Fig. 3).

For the other compounds, secondary inputs appeared to be less significant, either because of their lower volatility, like the more chlorinated PCBs, or because primary sources overcame their contribution to the atmospheric deposition, such as high molecular weight PAHs or BDE209, which were still in use during part of the sampling period.

The HCHs exhibited high loadings in PC4, which also showed high contribution of precipitation and, to a lower extent, temperature (Fig. 2). This component pointed to a deposition mechanism mediated by wet deposition after volatilization from soils and melting snow. In this respect, HCHs have much lower Henry constants than the compounds grouped in PC2 (Table S1). The samples with higher scores in PC4 were those collected during the warm periods in Skalnate, Lochnagar and Gossenköllesee (Fig. 3). Wet deposition may also enhance the deposition of the other compounds such as BDE209 or the PCBs.

3.5. Temporal changes

Volatile PBDEs were the only compounds showing a deposition decrease during the sampling period which was recorded in Lochnagar. The observed changes may reflect a decrease in the influence of

transcontinental sources as they coincided with the start of the restrictions in the production of penta- and octa-BDEs in the USA in 2004. These changes can be used for approximate calculations of halving times reflecting the decreasing LRAT. Continuously decreasing changes can be approached by (Venier et al., 2016):

$$Ln\ (C) = a0 + a1t \tag{1}$$

where C is the geometric mean concentration in year t and $a0$ and $a1$ are calculated from the linear regression fitting of the data.

Halving times can then be estimated by

$$t^{1/2} = \frac{-Ln\ (2)}{a1} \tag{2}$$

Only BDE47 and BDE99 were considered as they were the BDE congeners showing statistical significant linear correlations between geometric mean concentrations and years (from 2004 to 2006). Halving times of 0.82 ± 0.06 and 1.5 ± 0.11 years were obtained for BDE47 and BDE99. Interestingly, halving times of 2.0 ± 0.7 and 1.6 ± 0.5 years for BDE47 and BDE99, respectively, were observed in the Great Lakes for 2005–2006 (Venier and Hites, 2008), just after implementation of US restrictions of pentaBDE production in 2004. Although the BDE47 halving time estimated in Lochnagar is somewhat shorter than in the Great Lakes, the results for BDE99 are remarkably similar for the same time period in both sites, which could suggest a global effect of these production restrictions.

3.6. SOC deposition versus photodegradation in the mountain atmosphere

SOCs in mountain atmospheres undergo higher photooxidation than in low lands. These processes occur by reaction with atmospheric oxidants (OH, NO$_3$/NO$_2$ and O$_3$), although gas phase reactions with NO$_3$ and O$_3$ are usually significantly slower than with OH radicals (degradation rate constants between 2 and 7 orders of magnitude lower) (Keyte et al., 2013). Furthermore, the higher ultra violet irradiation at higher elevation results in the increase of OH in air. These SOC loss processes are two orders of magnitude higher in the gas phase than for the compounds associated to atmospheric particles (Keyte et al., 2013).

The degradation fluxes D (ng m^{-2}mo^{-1}) can be defined by Eq. (3)

$$D = \frac{(Cf - Ci)\ ABL}{t} \tag{3}$$

where Ci and Cf are the initial and final concentrations of the gas phase compound before and after a specific period of time t, and ABL is the atmospheric boundary layer height.

The Cf resulting from gas phase reaction with [OH] can be calculated as defined by the Eq. (4)

$$Ln\ \frac{Ci}{Cf} = k_{OH}\ [OH]\,t \tag{4}$$

where k_{OH} is the compound-specific degradation rate constant (cm^3 molec^{-1} s^{-1}) and [OH] is the air concentrations of OH radicals (molec cm^{-3}). This approach has been used to estimate the degradation flux of atmospheric pollutants from their concentrations in the gas phase (Ci) (Berrojalbiz et al., 2014; Ren et al., 2017).

Bulk atmospheric deposition (F_B, ng m^{-2}mo^{-1}) can be expressed by the Eq. (5)

$$F_B = F_{DD} + F_{WD} \tag{5}$$

where F_{DD} is the dry deposition, which depends on the concentration of the pollutant in the atmospheric particles and the deposition velocity ν_D, and F_{WD} is the wet deposition that can be parametrized by Eq. (6)

$$F_{WD} = P\ (W_G C_G + W_P C_P) \tag{6}$$

where P is the precipitation rate in mm, W_G and W_P are the gas and particle washout ratios, respectively, and C_G and C_P are the concentra-

tions in the gas and the particulate phases, respectively. If equilibrium conditions are achieved, W_G can be estimated from $W_G = RT / H$, where R is the ideal gas constant (Pa m^3 K^{-1} mol^{-1}), T is the temperature in K, and H is the temperature-corrected Henry's law constant of the compound (Pa m^3·mol^{-1}).

These equations have been used elsewhere to estimate atmospheric SOC deposition (Jurado et al., 2005; Ren et al., 2017, among others). They can also be used to estimate atmospheric concentrations from the measured wet atmospheric deposition fluxes. Bulk atmospheric deposition samples do not allow for discrimination between dry and wet processes. However, wet deposition can be assumed as the dominant process for those compounds mainly found in the gas phase.

Accordingly, this approach was used in the present study for estimation of the atmospheric gas phase concentrations of α-HCH, γ-HCH, HCB, Flu, Phe, PCB 52, BDE47 and BDE99 using Henry's law constants corrected by the ambient temperature in each site and the measured atmospheric deposition fluxes (Table S1).

The C_G values obtained from Eq. (6) are listed in Tables S2 and S3. They show remarkable agreements with those measured experimentally in the same sites in earlier periods for Flu, Phe, HCB, α- and γ-HCH (Table S2) or slightly higher than in other remote sites for PBDEs (Table S3). However, in the case of PCB 52, the difference was two orders of magnitude. This high disagreement was not associated with H values used in Eq. (6), since C_G of PCB 52 estimated from different H values and methods for their temperature correction were similar (Table S6), with a coefficient of variation of 30%. In this sense, the enrichment of PCBs in the dissolved phase of rainwater related to atmospheric gas concentrations has been observed, which resulted in higher gas washout ratios W_G determined from field concentration of PCBs than those predicted from the Henry's law (Mandalakis and Stephanou, 2004; Poster and Baker, 1996). Several explanations have been proposed for these discrepancies (Gioia et al., 2010; Mandalakis and Stephanou, 2004), including sampling artefacts or non-equilibrium partitioning of PCBs between rain drops and gas phase compounds during scavenging, among other. Regardless of the cause of these differences, the results obtained for this compound can only be taken as very tentative.

The selected k_{OH} constants for each compound are reported in Table S4. The concentrations of OH radicals in each site were estimated from Spivakovsky et al., 2000, taking into account the differences in altitude, latitude and seasons. Values ranged between 2.0×10^4 in Lochnagar in winter and 2.6×10^6 molec cm^{-3} in Redon in summer. The ABL heights were estimated taking into account the differences between warm sunny months (between 1200 and 1800 m above ground level (agl)) and cold periods with snow cover (between 300 and 600 m agl) (Serafin et al., 2018).

The estimated degradation fluxes are reported in Table 2 where they are compared with the measured deposition fluxes. HCHs showed the lowest degradation fluxes of OCs, 0.08–0.19 ng m^{-2} mo^{-1} and 0.32–1.1 ng m^{-2} mo^{-1} for α-HCH and γ-HCH, respectively, while HCB had values from 0.34 to 3.7 ng m^{-2} mo^{-1}. These values were significantly higher than those reported for these compounds over a remote lake in the Tibetan Plateau (0.009–0.027 ng m^{-2} mo^{-1})(Ren et al., 2017). The HCH degradation fluxes in the European mountains were between two and three orders of magnitude lower than the atmospheric deposition fluxes in the same sites (Table 2), indicating that reaction with OH radicals were not a significant atmospheric loss process for these compounds in remote areas. In the highest altitude sites, the atmospheric deposition and degradation fluxes of HCB were comparable in magnitude indicating that both removal processes were of equal importance, whereas atmospheric deposition dominated in Lochnagar and Skalnate. In any case, the HCB atmospheric deposition and degradation fluxes in these sites were low.

PBDE OH depletion was showing similar values to those of HCHs, 0.48–3.5 ng m^{-2} mo^{-1} and 0.06–0.88 ng m^{-2} mo^{-1} for BDE47 and BDE99, respectively. These fluxes were between one and two orders of magnitude lower than atmospheric deposition. For PBDEs with 2–6 bromides, direct photolysis has been reported as the main degradation mechanism in the atmosphere, which is defined by the gas-phase photolysis rate constants (k_{PHOTO}) reported by (Raff and Hites, 2007) (Table S4). In contrast with the other selected SOCs, BDE47 and BDE99 partition between gas and atmospheric particles. Thus, the C_G values and photodegradation rate constants were corrected using the fractions of these compounds associated to atmospheric particles indicated elsewhere (Raff and Hites, 2007), 0.17 and 0.42 for BDE47 and BDE99, respectively.

This process was one order of magnitude higher than atmospheric deposition and two-three orders of magnitude higher than OH degradation (Table 2). The degradation fluxes of the PBDEs found in the lower altitude lakes of this study were lower than those reported in Lake Superior, both for OH depletion, 7 ng m^{-2} mo^{-1} and 1 ng m^{-2} mo^{-1} for BDE47 and BDE99, respectively (Raff and Hites, 2007), and photolysis, 220 ng m^{-2} mo^{-1} and 170 ng m^{-2} mo^{-1} for BDE47 and BDE99, respectively, whereas the degradation fluxes in the lakes situated at highest altitude were similar to those reported in the Great Lakes region, with differences of twofold at the most.

The PAHs showed the highest degradation fluxes, 80–565 ng m^{-2} mo^{-1} and 200–3700 ng m^{-2} mo^{-1}, for Flu and Phe, respectively (Table 2). These fluxes were similar to those reported in the air of remote sites of the Atlantic Ocean (Nizzetto et al., 2008), 210–3600 ng m^{-2} mo^{-1} for Phe, or in the central Tibetan Plateau (Ren et al., 2017), 54–330 ng m^{-2} mo^{-1} and 120–5520 ng m^{-2} mo^{-1}, for Flu and Phe, respec-

Table 2
Degradation and atmospheric deposition fluxes of selected compounds in high mountain areas. Values in ng m^{-2} mo^{-1}.

	PCB 52	α-HCH	γ-HCH	HCB	Flu	Phe	BDE47	BDE99	BDE47	BDE99
[OH] degradation photolysis										
Lochnagar	140	0.08	0.32	0.34	80	355	0.48	0.06	100	75
Redon	450	0.19	0.75	0.91	103	199	3.48	0.88	190	90
Gosenköllesee	340	0.14	1.06	0.83	138	613	3.03	0.43	275	80
Skalnate	445	0.18	0.88	3.66	565	3700	0.77	0.23	80	50
Deposition										
Lochnagar	70.5	19.0	37.0	3.70	54.5	332	15.9	15.0		
Redon	19.4	5.70	12.0	1.10	15.0	81.3	12.9	9.09		
Gosenköllesee	28.0	4.60	20.0	1.00	25.1	435	18.6	7.63		
Skalnate	108	16.0	50.0	12.0	253	2155	8.91	7.44		
Deposition/degradation ratios										
Lochnagar	0.50	49	115	10.8	0.69	0.94	33	235	0.16	0.20
Redon	0.04	67	16	1.21	0.15	0.41	3.70	10.3	0.07	0.10
Gosenköllesee	0.08	29	19	1.21	0.18	0.71	6.15	18	0.07	0.09
Skalnate	0.24	97	57	3.28	0.45	0.58	11.6	32	0.11	0.15

tively. The PAH degradation fluxes in the European mountains were slightly higher than the atmospheric deposition fluxes. The ratios between deposition and degradation ranged between 0.15 and 0.18 for Flu and 0.41–0.71 for Phe in the highest altitude sites, Redon and Gossenköllesee (Table 2), and between 0.45 and 0.58 in Skalnate, whereas the lowest ratios were found in Lochnagar, 0.69–0.94, the easternmost site situated at the lowest altitude.

PCB 52 exhibited OH degradation fluxes comparable to those of Flu, 140–450 ng m^{-2} mo^{-1}. They were significantly higher than atmospheric deposition in the highest altitude sites (the deposition to degradation ratios ranged between 0.04 and 0.08 (Table 2)), whereas differences of twofold were observed in Lochnagar.

Wet deposition was therefore the main removal process for HCHs and HCB in high mountain regions, while degradation by direct photolysis was the dominant loss process for PBDEs. PAH were significantly removed by both wet deposition and reaction with OH radicals. The dominance of wet deposition in the removal of these SOCs has not been observed in low land environments such as marine systems (Berrojalbiz et al., 2014; González-Gaya et al., 2016; Nizzetto et al., 2008), where reaction with OH radicals and diffusive gas exchange were reported as the main loss processes of atmospheric SOCs. In general, wet deposition has not been considered relevant for the atmospheric deposition of these compounds at a global scale (Jurado et al., 2005); however, high altitude areas are characterized by high precipitation rates, frequently in form of snow, which has been recognized to be a more efficient air scavenger of non-polar organics than rain (Franz and Eisenreich, 1998; Lei and Wania, 2004). In addition, air-surface gas exchange of atmospheric pollutants in high mountain regions is restricted to a short period of time, since lakes in these areas remain ice-covered for several months, which prevents gas-water exchange. Moreover, the presence of snow has also a significant effect over gas exchange process owing to its lower storage capacity of organic pollutants than soils and vegetation (Stocker et al., 2007). Therefore, it is expected that wet deposition of gaseous contaminants gains importance in relation to other atmospheric loss processes in these sites.

4. Conclusions

The deposition of PCBs, HCHs, and low brominated BDEs in the European high mountains reflects baseline contributions from LRAT. This is also the case for PAHs in Redon and Gossenköllesee, endosulfans in Lochnagar and Gossenköllesee and HCB in these three lakes. However, Skalnate receives PAHs, endosulfans and HCB from regional sources as it is the case for endosulfans in Redon.

Reaction with OH radicals was not a significant loss process of HCHs and HCB in remote areas, dominated by wet deposition, whereas PCBs and PAHs were significantly removed by both wet deposition and OH radical oxidation, the latter dominating in the highest altitude sites. Photolysis was the main atmospheric removal process of PBDEs, dominating over atmospheric deposition and OH depletion in all sites.

CRediT authorship contribution statement

Pilar Fernandez: Conceptualization, Validation, Formal analysis, Writing – original draft, Visualization, Supervision. **Barend L. van Drooge:** Methodology, Formal analysis. **Lourdes Arellano:** Methodology, Validation, Investigation. **Joan O. Grimalt:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147099.

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