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Atmospheric deposition of polybromodiphenyl ethers in remote mountain regions of Europe

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Abstract. Polybromodiphenyl ethers (PBDEs) were analyzed in bulk atmospheric deposition collected in four European remote mountain areas over a period of two years (2004–2006): Lake Redon (Pyrenees, Catalonia, Spain), Gossenköllesee (Alps, Austria), Lochnagar (Grampian Mountains, Scotland) and Skalnate (Tatras, Slovakia). In all sites, the PBDE distributions were dominated by BDE209. BDE47 and BDE99 were the major low-brominated congeners, followed by BDE100 and BDE183. This composition is consistent with predominant inputs from the commercial mixtures decaBDE and pentaBDE. The total congener site-averaged fluxes ranged between $100\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ (Alps) and $190\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ (Tatras).

Significant correlations between PBDE deposition and percent of North Atlantic backwards air mass trajectories in the collected samples of the westernmost sites, Lochnagar and Redon, suggested an impact of transcontinental transfer of these pollutants from North American sources into Europe. Skalnate, and to a lower extent Redon, recorded another main PBDE source from central Europe corresponding to secondary emissions of the pentaBDE commercial mixture. The fluxes of these secondary emissions were temperature dependent and correlated to total particle deposition and

rainfall. Higher PBDE fluxes were observed at increasing temperature, particle deposition and precipitation. Another specific PBDE source was observed in United Kingdom and recorded in Lochnagar.

Photolytic degradation during transport decreased the relative abundance of BDE209 and modified the emitted pentaBDE technical mixtures by depletion of the relative composition of BDE99 and, to a lower extent, BDE47. The transformations were more intense in the sites located above 2000 m (Redon and Gossenköllesee) and, particularly, during the warm periods.

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1 Introduction

Polybromodiphenyl ethers (PBDEs) have been used as flame retardants in a variety of commercial products including polyurethane foam, plastics, electronics, and textile coating in furniture (de Wit, 2002). These additives are mixed with the product during manufacture, not being chemically bound to the material. Thus, they can be released into the environment during use and disposal (Prevedouros et al., 2004a; Batterman et al., 2009). They have been applied in three

technical mixtures, pentaBDE, octaBDE and decaBDE. The former primarily consists of ten isomers dominated by the congeners BDE47 and BDE99 (> 70 %), the second contains BDE183 as major congener and the latter consists primarily of the fully brominated BDE209 (La Guardia et al., 2006). Commercial use of PBDEs began in late 1970s, with a global demand in 1999 of about 70 000 tons (Alaee et al., 2003). Russia, Germany and the United Kingdom were the countries emitting most PBDEs in Europe. Total emissions in Europe were estimated to be 9.87 tons in 2000 (Vestreng et al., 2006). The estimated global emission of these compounds due to the e-waste production was 280 tons at the end of the last decade (Robinson, 2009).

These compounds have been documented to have strong environmental persistence, lipophilicity and tendency to bioaccumulate in animals (Vives et al., 2004; Wan et al., 2013; Xia et al., 2008) and humans (Carrizo et al., 2007; Vizcaino et al., 2011). In the last decades their environmental levels have increased significantly (Renner, 2000; Ikonomou et al., 2002; Usenko et al., 2007; Ma et al., 2013), although recent studies indicate no clear temporal trends in their concentrations in the environment during the last years after their regulation (Birgul et al., 2012; Kirchgeorg et al., 2013; de Wit et al., 2010; Law et al., 2014). Health concerns with these compounds are growing as consequence of reported results on developmental neurotoxicity in mice (Moser and Gee, 2007), hormonal disruption (Legler, 2008; Darnerud, 2008) and some evidences of impaired neuropsychological development in infants (Gascon et al., 2012). Initial studies suggested that BDE209 was too large to bioaccumulate and had a limited transport capacity (Wania and Dugani, 2003) being associated to the particle phase in the atmosphere (Gouin et al., 2006). However, recent studies have documented the widespread occurrence of this compound in the environment, even in locations far from the sites where it was produced or used (Breivik et al., 2006; Arellano et al., 2011; Bartrons et al., 2011). In addition, it has been observed to accumulate in organisms (Wan et al., 2013; Koenig et al., 2013; Tomy et al., 2009), including humans (Zhu et al., 2009; Vizcaino et al., 2011), and can be transformed into lower brominated congeners either in the environment (Schenker et al., 2008; Söderström et al., 2004) or in organisms (Roberts et al., 2011; Stapleton et al., 2004; Bartrons et al., 2012) giving rise to mixtures dominated by low-brominated congeners such as those typically found in the pentaBDE and octaBDE mixtures.

In view of these properties, international regulatory actions have been implemented to restrict or eliminate the use and production of these compounds. PentaBDE and octaBDE were banned by the European Union (EU) in 2004, while decaBDE use was restricted in 2008 (EBFRIP, 2013). In 2004, the major US manufacturer voluntarily stopped production of pentaBDE and octaBDE, which were finally banned in several US states in 2006. A voluntary phase-out of decaBDE production is also expected in the USA by 2013 (EPA DecaBDE Phase-out Initiative, 2013). Moreover, the main congeners of penta and octaBDE have been included in the list of new persistent organic pollutants (POPs) under the Stockholm Convention in 2009 (Stockholm Convention on POPs, 2013).

Atmospheric deposition is an important pathway for the incorporation of semivolatile organic compounds into aquatic and terrestrial ecosystems. This pathway has been shown to be relevant for the transfer of POPs, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), to remote background regions (Carrera et al., 2002; Fernandez et al., 2003; Usenko et al., 2010; Sun et al., 2006) but data on atmospheric deposition of PBDEs to remote sites is scarce (Meyer et al., 2012; Newton et al., 2014). Preliminary information on the occurrence of these compounds in remote regions far from their production and use sites provided evidence for their capacity for long-range transport, even in the case of BDE209, underlining the need for better understanding on atmospheric PBDE transfer modes and incorporation into terrestrial and aquatic environments. In this context, high mountain regions are useful sentinel environments for the characterization of the atmospheric pollution load, since these areas receive pollutant inputs primarily from regional or distant sources by means of long-range atmospheric transport (Fernandez and Grimalt, 2003; Fernandez et al., 2000).

The present study aims to determine the PBDE fluxes and composition in bulk atmospheric deposition in four European high altitude mountain areas. These sites were chosen because they contain lakes which have been studied in the past (Grimalt et al., 2001; Gallego et al., 2007) and these previous studies provide complementary information on the long-range air transported pollutants in these areas. Seasonal and geographical trends, as well as the environmental and meteorological factors determining PBDE deposition fluxes have been investigated. Potential source regions for each site have been evaluated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.

The selected sites are representative of the full range of climate and pollution gradients across Europe: Redon (Pyrenees, Catalonia, Spain) and Lochnagar (Grampian Mountains, Scotland) situated in the south- and north-western periphery of the continent, respectively, and Gossenköllesee (Tyrolean Alps, Austria) and Skalnate Pleso (Tatra Mountains, Slovakia) in central/eastern Europe. This four-site strategy provided a comprehensive description of the sources and processes influencing PBDE deposition in remote high altitude European areas.

2 Materials and methods

2.1 Sampling

Bulk atmospheric deposition samples were regularly collected at four remote European areas (Table 1): the Pyrenees, Alps, Tatras and Grampian mountains. Monthly samples were taken at all sites from May 2004 to August 2006 except at Lochnagar where sampling was performed biweekly from June 2004 to March 2007. Meteorological parameters, namely air temperature and precipitation, were provided by automatic weather stations (AWS) located at each site. Atmospheric deposition was collected with polyethylene funnels (the diameters were different depending on the sampling site) connected to stainless steel or Teflon coated reservoirs by tubes. In winter, when precipitation was in the form of snow, wider tubes assembled on the top of tanks or cylindrical collectors were used for sampling. Bulk atmospheric deposition samplers were placed 1.5 m above ground. Samples were filtered on site using pre-weighed Whatman® glass fiber filters (GF/B, 47 mm diameter, 1 μm retention size) and the filtrates were solid-phase extracted with C_{18} Empore disks (47 mm diameter, 0.5 mm thickness) as described elsewhere (Carrera et al., 1998, 2002). After sampling, each collector was carefully cleaned with MilliQ water and acetone.

2.2 Chemicals

Trace organic analysis solvents SupraSolv® isooctane, n-hexane, cyclohexane, methanol and acetone, and UniSolv® dichloromethane were from Merck (Darmstadt, Germany). Anhydrous sodium sulfate (analytical-reagent grade, Merck) and alumina were cleaned by Soxhlet extraction with dichloromethane : hexane (1 : 1, v/v, 24 h) and were activated by overnight heating at 450 °C and 120 °C, respectively. Glass fiber filters (47 mm diameter, 1 mm, GF/B, Whatman, Maidstone, UK) were kiln fired at 400 °C for 12 h, weighted and wrapped into solvent prewashed aluminum foil until use. Empore C18 extraction disks (47 mm diameter, 0.5 mm thickness) were from 3M Co. (St Paul, MN, USA). Previous to SPE extraction, the disks were cleaned by elution with 10 mL of dichloromethane : cyclohexane (1 : 1) and conditioned with 10 mL of methanol.

The polybromodiphenyl ether analytical standard solution EO-5103 was purchased from Cambridge Isotope Labs (CIL, Andover, MA, USA). The standard solution contains 14 PBDEs congeners being two tribromo BDEs (BDE17, and BDE28), three tetrabromo BDEs (BDE47, BDE66, and BDE71), three pentabromo BDEs (BDE85, BDE99, and BDE100), three hexabromo BDEs (BDE153, BDE154, and BDE138), two heptabromo BDEs (BDE183, and BDE190) and the decabromo BDE (BDE209) (Table S1 and Fig. S1 in the Supplement). PCB 142 and PCB 209 were used as internal standard and recovery standard, respectively, both purchased from Dr. Ehrenstorfer (Ausburg, Germany).

2.3 Analytical methodology

Frozen glass fiber filters were freeze-dried using an Edwards K4 Modulyo Freeze Dryer (Edwards High Vacuum International Ltd., West Sussex, England) during ca. 6 h before weighing to obtain the total mass of the collected particles. PBDEs were extracted from the freeze-dried filters by sonication with dichloromethane : methanol (2 : 1) (3 × 10 mL, 20 min each), while compounds adsorbed onto the membrane extraction disks were eluted sequentially with methanol (5 mL), cyclohexane (5 mL) and dichloromethane (5 mL) as described elsewhere (Carrera et al., 1998; Quiroz et al., 2008). The filter extracts and eluates were mixed and dried by passing through glass columns filled with anhydrous sodium sulfate.

A recovery standard PCB 209 was added to the extracts. After that, they were vacuum evaporated to near dryness with a rotatory evaporator equipped with a vacuum regulator (membrane pump CVC2, Vacuubrand GMBH, Wertheim, Germany) and further purified by adsorption chromatography with alumina. Organohalogenated compounds were eluted with dichloromethane : hexane (1 : 19) and dichloromethane : hexane (2 : 1). The fractions were vacuum evaporated to 1 mL and transferred to vials by a gentle stream of nitrogen. Prior to instrumental analysis, samples were spiked with the internal standard PCB 142 dissolved in isooctane.

PBDE congeners were analysed on a gas chromatograph (Trace GC Ultra-Thermo Electron, Milan Italy) coupled to a mass spectrometer (MS DSQ Intrument Thermo Electron Corp., Austin, Texas, USA) in negative ion chemical ionization (GC-MS-NICI) and selective ion recording modes. 2 μL of each fraction were injected in split/splitless mode into a low bleed SGE-BPX5 MS fused silica capillary column (15 m long, 0.25 mm internal diameter and 0.10 μm film thickness; SGE Analytical Science, Milton Keynes, UK) containing 5 % phenyl polysilphenylene-siloxane. A Siltek® deactivated retention gap from Restek Corp (Bellefonte, PA, USA) with a length of 1.5 m and an inner diameter of 0.32 mm was used for column protection. The oven temperature was programmed as follows: initial temperature 90 °C during 1.5 min, a temperature increase of 20 °C min^{-1} up to 200 °C, followed by 5 °C min^{-1} up to 275 °C and a final ramp of 30 °C min^{-1} up to 300 °C; final time of 10 min. Injector, transfer line, and ion source temperatures were 270, 300 and 250 °C, respectively. Helium and ammonia were used as carrier and reagent gases, respectively. More details about selected ions and other instrumental conditions used to prevent BDE209 degradation are described elsewhere (Vizcaino et al., 2009).

2.4 Quality control

The target PBDEs were quantified with the above-mentioned internal standards. A short chromatographic column with

Table 1. Sampling site location and meteorological conditions.

Sampling site	Mountain region	Latitude (N)	Longitude (E)	Altitude (m a.s.l.)[a]	Temp. (°C)[b]	Precipitation[c] (mm)	Sampling period	Particles flux (mg m^{-2} mo^{-1})[d]
Gossenköllesee	Tyrolean Alps (Austria)	47.2253	11.0139	2413	−1.38[e]	1722	Jun 2004–Aug 2006	132 (18–750)
Lake Redon	Pyrenees (Spain)	42.6421	0.7795	2235	5.34	2224	May 2004–Sep 2006	323 (14–2750)
Lochnagar	Grampian Mts. (Scotland, UK)	56.9591	−3.2312	788	5.09[f]	4398	Jun 2004–Mar 2007	126 (14–1570)
Skalnate Pleso	Tatra Mts. (Slovakia)	49.1899	20.2342	1787	2.3	3001	May 2004–May 2006	328 (43–1815)

[a] Metres above sea level. [b] Mean temperature for the whole sampling period. [c] Total precipitation measured for the entire sampling period. [d] Mean particle deposition flux and range in brackets.
[e] From October 2004 to August 2006. [f] From June 2004 to November 2004 and October 2005 to March 2007.

0.10 µm film thickness was used in order to prevent BDE209 degradation during chromatographic analysis. This degradation was controlled by measuring the percentage of nonabromoBDEs, BDE206, BDE207 and BDE208, the main BDE209 degradation products, which did not exceed 8 % of the total BDE209 concentration in any case. A series of field and procedural blanks were conducted at each sampling site and processed together with the samples. For field blanks, bulk atmospheric deposition samplers were filled with 1 l of Milli-Q water, which was filtered and solid-phase extracted like a real sample. Extraction and analytical efficiency were evaluated by surrogate standard recoveries, ranging from 51 % to 94 % (mean 70 %). Reported values were corrected by surrogate recoveries. Method detection limits (MDL) for each congener were determined as the average of blank values plus 3 times the standard deviation. They ranged from 0.66 to 41 ng m^{-2} (from 0.002 to 0.22 ng for low-brominated compounds and 0.51 ng for BDE 209). Likewise, the method quantification limits (MQL) were determined as the average blank values plus 5 times the standard deviation of the signal corresponding to each congener in the blank samples. They ranged between 0.85 and 42 ng m^{-2} (Tables S2 and S3 in the Supplement).

2.5　Data analysis

The monthly PBDE deposition fluxes were calculated by division of the total PBDE amounts measured in each sample (ng) by the surface area of the collection sampler (m^2) and the sampling period (days). Finally, the data were reported after normalization to one calendar month.

All statistical tests and correlations were performed using IBM SPSS® Statistics 21 (IBM Corp.©, Armond, NY, USA). The data series were tested for normal distribution using the Kolmogorov–Smirnov test. In general, the data distributions differed significantly from normality and were log-transformed to obtain normally distributed values. One-way ANOVA analysis was carried out to investigate the differences between sites and seasons, while Pearson correlation test was used to examine relationships among BDE congeners and environmental and meteorological parameters.

2.6　Back trajectory analysis

The 3-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 Air Resources Laboratory (ARL) from the National Oceanic and Atmospheric Administration (NOAA) (Rolph, 2013; Draxler et al., 1998, 2013). The meteorological data used for computing the 6-hourly back trajectories come from the FNL archive at the National Centre for Environmental Prediction (NECP) Global Data Assimilation System (GDAS) and from the Eta Data Assimilation System (EDAS).

The backward trajectories were calculated for each site every time that there was a precipitation event recorded by the AWS at the different sampling sites and every 2 days in the absence of precipitation. In all, 72 h back-trajectories consisting of 12 end-points corresponding to the air mass location (longitude, latitude and altitude) at 6 h intervals were obtained for the four sampling sites. The selected altitudes to compute the trajectories were representative of the air masses above the sampling sites (3000 m above sea level (a.s.l.) at Redon and Skalnate, 3500 m a.s.l. for Gossenköllesee and 2000 m a.s.l. at Lochnagar).

A hierarchical clustering (HC) method was used to classify horizontal trajectories using SPSS 15.0 software package, grouping the data into clusters. Altitude trajectories were classified according to their mean elevation into high altitude trajectories (more than 50 % of time above 1000 m a.s.l.) and low altitude trajectories (more than 50 % of time below 1000 m a.s.l.). The type of HC method used was agglomerative, and the result was calculated to provide the minimum variance within cluster and the maximum variance between clusters. Cluster means were obtained using HYSPLIT model (Version 4) installed on a PC and run using its graphical user interface.

Table 2. Percent contributions of air mass trajectories to the studied sites.

	Warm	Cold	Total	Air masses > 1000 m a.s.l.
Gossenköllesee				87
North Atlantic	12	22	17	
North Continental	30	27	28	
Eastern Europe	11	11	11	
West Europe/ Atlantic Ocean	11	10	11	
South/south-west	37	29	33	
Lake Redon				92
North Atlantic	32	48	38	
Eastern/central Europe	9.8	14	11	
South	59	37	51	
Lochnagar				82
North polar	16	19	18	
North Atlantic	31	31	31	
Eastern Continental	8.5	9.4	9.0	
England/Scotland	7.2	3.8	5.2	
South	37	37	37	
Skalnate				94
North polar	12	8.1	9.7	
North Atlantic	44	37	40	
East	16	15	15	
West	6.7	10	9.0	
South-west	21	30	26	

Warm period from June to October. Cold period from November to May.

3 Results

3.1 Backwards air mass trajectories during the sampling periods

Air mass origin varied considerably between sites and within each site during sampling. Following the above-mentioned calculation criteria, 465 trajectories were obtained for Gossenköllesee. They were classified into five groups (Fig. 1, Table 2): North Atlantic (air masses flowing from the North Atlantic Ocean, Greenland and north/north-west areas) which represented 17 % of the total calculated air masses during the studied period, north (United Kingdom, Sweden or/and Norway; 28 % of total), eastern Europe (mainly from Russia, Ukraine and Romania; 11 % of total), west (Atlantic Ocean and France; 11 % of total) and south/south-west (North Africa, South Atlantic Ocean, Mediterranean Sea and/or Iberian Peninsula; 33 %).

In Redon, 339 air mass trajectories were obtained and were classified into three groups: North Atlantic (from the North Atlantic Ocean, Greenland and north/north-west, which represented 38 % of the total calculated trajectories), eastern/central Europe (mainly from Germany, Czech Republic and Hungary; 11 % of total) and south (from North Africa,

the Mediterranean Sea and/or the Iberian Peninsula; 51 %). In fact, the North Atlantic trajectories arriving to this site may be separated in two, one for air masses from the west, over the Atlantic Ocean, and the other crossing over the British Isles and France before arriving to Redon (Fig. 1).

The 598 trajectories obtained for Lochnagar were classified into five different groups: north polar which contributed 18 % to the total air masses, North Atlantic (north-west/west, North Atlantic, Canada and USA; 31 % of total), eastern continental (Sweden, Russia and Poland; 9 %), cyclonic and anticyclonic trajectories over England/Scotland (5 % of the total air masses) and south (Africa, the Mediterranean Sea or the Iberian Peninsula; 37 % of total).

For Skalnate, 560 air mass trajectories were determined and classified in five groups: north polar (from the Arctic region and the Barents Sea; 10 % of total), North Atlantic (from Canada, Greenland, Iceland, Sweden and Norway; 40 %), east (mainly from Russia, Ukraine, and Romania; 15 %), west (from the Atlantic Ocean, France and Germany; 9 %) and south/south-west (Italy, the Mediterranean Sea and the Iberian Peninsula; 26 %) (Fig. 1, Table 2).

In all sites, more than 80 % of the calculated air masses corresponded to high altitude trajectories, flowing at high elevations (more than 50 % of time above 1000 m a.s.l.).

3.2 PBDE concentrations and temporal trends

Fourteen PBDE congeners were analysed in bulk atmospheric deposition, BDE17, BDE28, BDE47, BDE66, BDE71, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154, BDE183, BDE190 and BDE209. Only ten were consistently found above the limit of detection in the four sampling sites, BDE28, BDE71, BDE47, BDE99, BDE100, BDE66, BDE154, BDE153, BDE183 and BDE209. Mean concentrations, ranges, and frequencies of PBDE detection are summarized in Table 3, while the temporal variations of atmospheric deposition fluxes of ΣPBDEs, BDE209 and particles over the entire sampling period at each site are shown in Figs. 2 and 3.

The mean deposition PBDE fluxes were similar at all studied sites with differences of twofold at the most. The most abundant PBDE congener was BDE209, with fluxes ranging from $71\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ in Gossenköllesee to $162\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ in Skalnate, involving between four and sixfold higher values than the other detected PBDEs (Table 3). BDE47 and BDE99 were the dominant low-brominated congeners, followed by BDE100 and BDE183. The mean deposition fluxes of these four BDE congeners (Σ4BDEs) varied between $24\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ (Skalnate) and $40\,\mathrm{ng\,m^{-2}\,mo^{-1}}$ (Lochnagar). Redon and Gossenköllesee showed intermediate levels, 28 and $31\,\mathrm{ng\,m^{-2}\,mo^{-1}}$, respectively. Despite these similarities in mean values, high variability in PBDE deposition fluxes over the studied period was observed in each site, with coefficients of variation ranging from 53 % to 85 %.
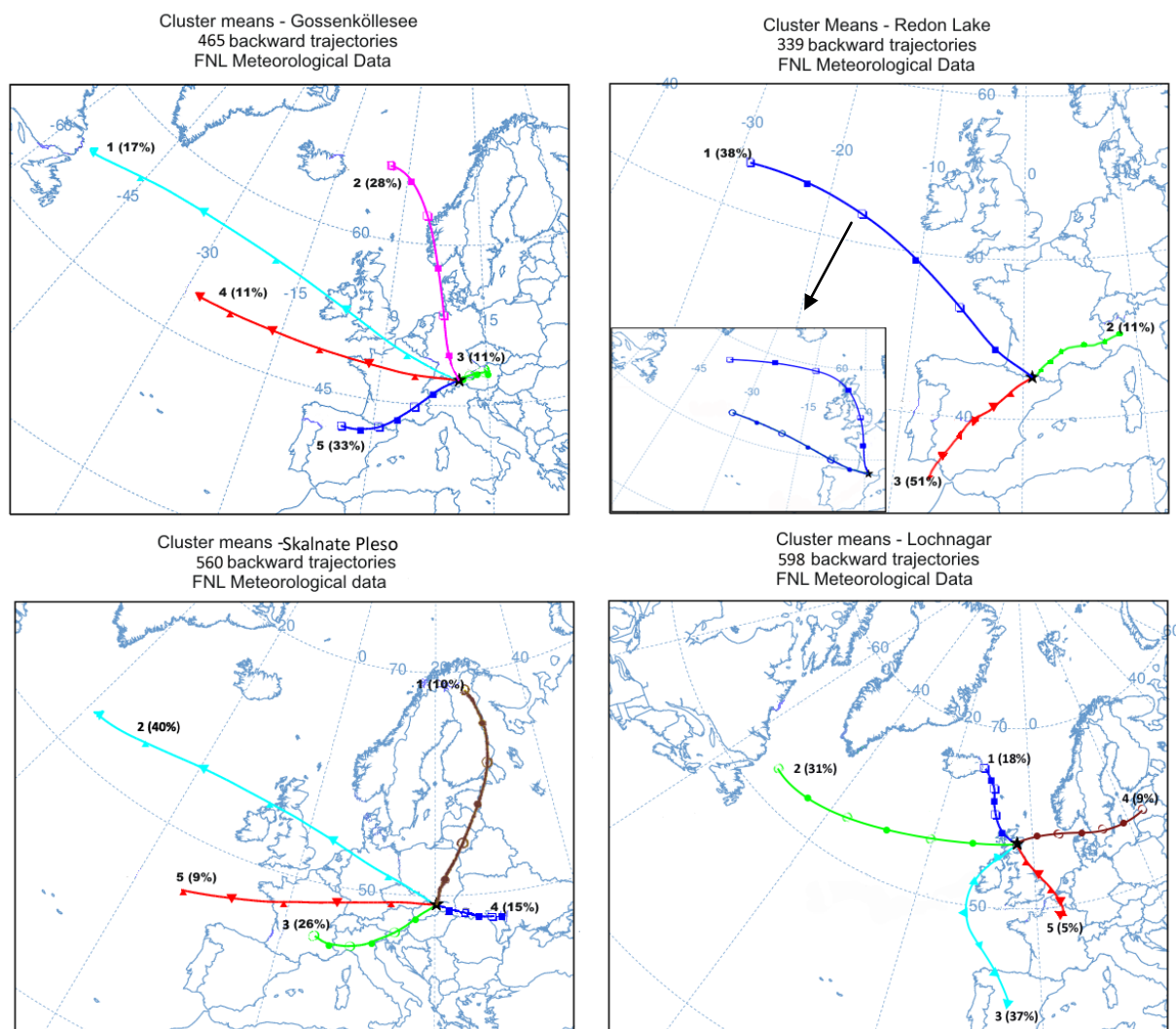
Fig. 1. HYSPLIT 72 h back trajectories to the studied sites. Values in parenthesis showed total contribution of each trajectory during the entire sampling period.

Table 3. Mean depositional fluxes, range, and frequency of detection (FD) of BDE congeners in bulk atmospheric deposition to high mountain regions of Europe.

	GOSSENKÖLLESEE ($n = 18$)			REDON ($n = 23$)			LOCHNAGAR ($n = 47$)			SKALNATE PLESO ($n = 25$)		
ng m^{-2} mo^{-1}	Mean	Min.–Max.	FD (%)	Mean	Min.–Max.	FD (%)	Mean	Min.–Max.	FD (%)	Mean	Min.–Max	FD (%)
BDE28	1.54	1.10–7.30	43	BDL	na	0	1.63	BDL–8.88	32	4.47	BDL–39.8	24
BDE71	0.69	BDL–5.00	29	3.66	BDL–28.3	31	0.83	BDL–3.05	17	0.65	BDL–6.13	28
BDE47	18.6	3.49–89.7	100	12.9	2.27–29.7	81	15.9	0.07–77.7	64	8.91	2.32–44.1	100
BDE99	7.63	BDL–29.7	95	9.09	3.11–17.8	73	15.0	BDL–95.7	74	7.44	2.44–19.9	68
BDE100	2.45	BDL–6.29	90	2.50	0.57–5.77	46	3.42	BDL–16.5	72	4.13	0.59–26.0	64
BDE66	6.82	BDL–26.9	86	0.58	BDL–5.96	8	0.24	BDL–5.39	4	2.12	BDL–14.6	32
BDE153	0.71	BDL–3.05	43	1.81	BDL–6.77	61	4.35	BDL–22.4	70	1.84	BDL–8.41	44
BDE154	0.40	BDL–2.80	33	1.11	BDL–6.99	57	1.96	BDL–8.71	68	0.21	BDL–0.86	52
BDE183	2.11	BDL–9.67	48	3.22	BDL–10.4	50	5.38	BDL–19.3	66	3.71	2.63–16.8	56
BDE209	71.2[a]	BDL–247	60	97.1	BDL–409	62	119	BDL–318	55	162	BDL–704	84
Σ4PBDEs[b]	30.7	10.4–64.6	na	28.1	9.83-141	na	40.0	0.43–214	na	24.2	6.45–74.0	na

[a] Average of ten samples from September 2005 to August 2006. [b] Sum of those BDE congeners found in more than 50 % of the samples at all sites excepting BDE209 (BDE47, 99, 100, and 183).
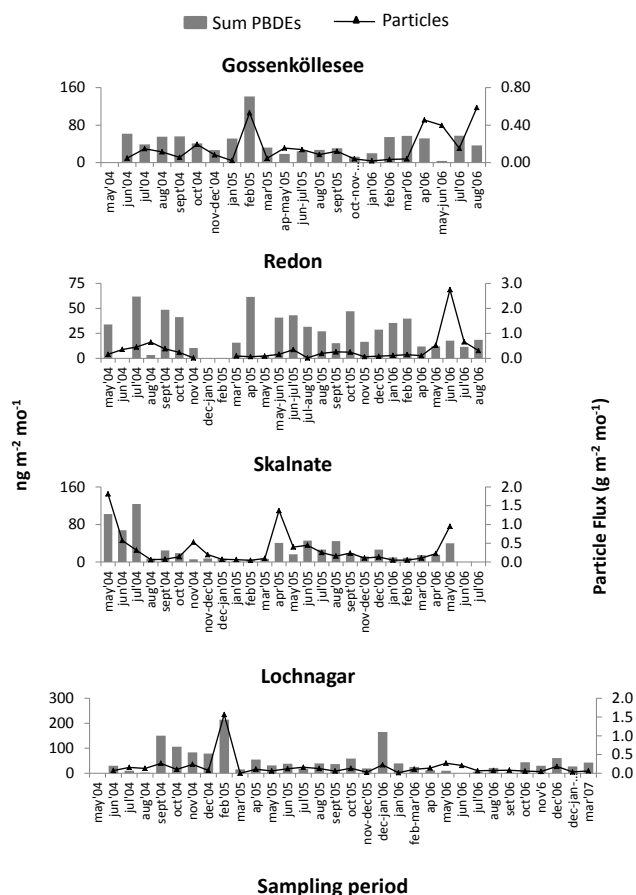BDL: below detection limit. na: not applicable.

Fig. 2. Temporal variation of particle (straight line) and ΣPBDE (excepting BDE209) deposition fluxes to the studied sites.

Fig. 3. Temporal variation of particle (straight line) and BDE209 deposition fluxes to the studied sites. Data from Gossenköllesee precluded due to the large number of samples with levels below the detection limit.

Previous information on atmospheric deposition fluxes of PBDEs is scarce. Most studies were performed in urban and industrial areas involving shorter sampling periods than in the present study (e.g. one week, one month or one year at the most). As expected, the Σ4BDE fluxes found in the four remote high mountain areas considered here exhibited lower values than those reported in urban and industrial sites, e.g. in China (Tian et al., 2011), Japan (Hayakawa et al., 2004), Turkey (Batterman et al., 2009) or Korea (Moon et al., 2007) (Table 4). They were similar to those found in Gotska Sandön, an island situated in the Baltic Sea far from pollution sources (Ter Schure et al., 2004b) (Table 4) and to mean deposition fluxes estimated from PBDE levels measured in a firn core from the Swiss Alps (Kirchgeorg et al., 2013). In contrast, the observed BDE209 deposition fluxes were similar or even higher than those reported in rural and remote sites (Venier and Hites, 2008; Moon et al., 2007; Kirchgeorg et al., 2013; Arinaitwe et al., 2014).

Comparison of the average annual values measured between 2004–2005 and 2005–2006 generally showed a decrease of lower molecular weight PBDEs and BDE209 and an increase of BDE183 in most of the sites (Table 5). How-
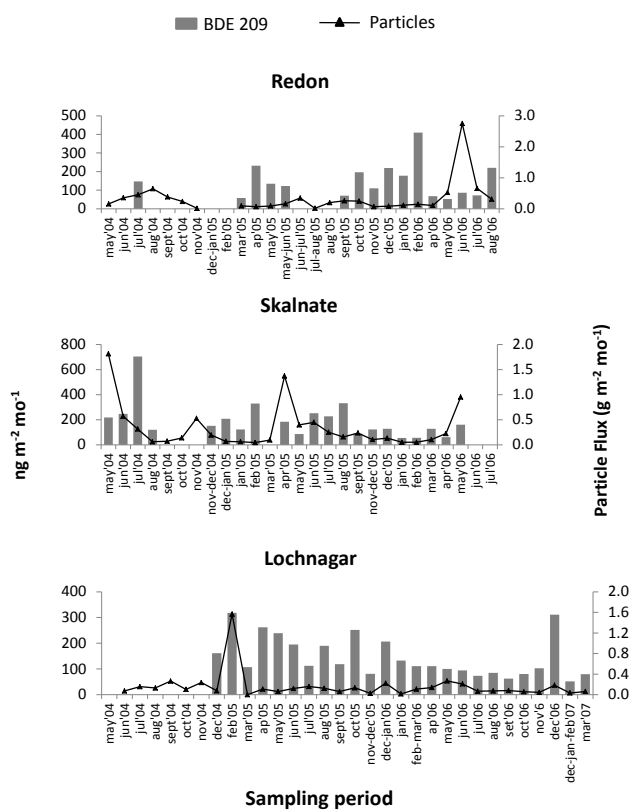
ever, these differences were only statistically significant in Lochnagar (95 % confidence level) for all compounds but BDE100. In the other sites, the differences were only significant for BDE47 in Gossenköllesee and for BDE209 in Skalnate. This PBDE deposition flux decline may reflect decreasing emissions as a consequence of the implementation of the restrictions in PBDE use and production which occurred during the sampling period (Meyer et al., 2012). Recent studies have observed similar declines of PCB and PBDE concentrations in European background air and soils that have been attributed to emission reduction (Schuster et al., 2010, 2011).

3.3 PBDE profiles and sources

As mentioned above, only five of the 14 PBDE congeners were consistently found above the limit of quantification in all sampling sites (BDE47, BDE99, BDE100, BDE183 and BDE209), while BDE28, BDE66, BDE71, BDE153 and BDE154 were only detected occasionally. BDE209 was the dominant congener in all sites, contributing from 61 % (Gossenköllesee) to 82 % (Skalnate) of the total PBDEs, followed by BDE47, BDE99 and BDE100. The observed

Table 4. Comparison of PBDE deposition fluxes in high mountain sites of Europe with those reported in the literature (units: $\mathrm{ng\,m^{-2}\,mo^{-1}}$).

	Sampling period	$\Sigma 7\mathrm{PBDEs}$[a]	BDE209	Reference
Lake Maggiore (North Italy)	1 week (Mar 2005)	273	255	Mariani et al. (2008)
Venice Lagoon	36 days (May–Nov 2005)	5.1–2670[b]	n.r.	Gambaro et al. (2009)
Kyoto (Japan)	Three periods of 2 weeks (Aug 2000–Sep 2001)	81–3000[c]	250–45000	Hayakawa et al. (2004)
Urban/industrial (China)	Monthly (Oct to Sep 2007–2008)	485[d]	6175	Tian et al. (2011)
Near e-waste industry (China)	Monthly (Oct to Sep 2007–2008)	1750[d]	12000	Tian et al. (2011)
Rural (China)	Monthly (Oct to Sep 2007–2008)	460[d]	360	Tian et al. (2011)
e-waste (Southern Sweden)		640[e]	1914	Ter Schure et al. (2004a)
Pearl River region			2750–160 000	Li et al. (2010)
Urban site (Southern Sweden)		210[e]	440	Ter Schure et al. (2004a)
Rural Site (Southern Sweden)		24[e]		Ter Schure et al. (2004a)
Urban site (Lund, Southern Sweden)	Two weeks (Aug–Sep 2000)	60[f]		Ter Schure et al. (2002)
Gotska Sandön (Baltic Sea)	40 days (Sep–Nov 2001)	23[g]	54	Ter Schure et al. (2004b)
Southern Ontario (Canada)	Oct 2001–Nov 2002	460–2100[h]	n.r.	Su et al. (2007)
Urban site (Turkey)	Sep 2004 and Feb–Mar 2005	1900[g]	2580	Cetin et al. (2007)
Urban/suburban (Korea)	Monthly Jan–Dec 2004	128–167	1680–4000	Moon et al. (2007)
Rural (Korea)	Monthly Jan–Dec 2004	40.1	1410	Moon et al. (2007)
Lake Superior (USA)	2005–2006	80[i]	41	Venier and Hites (2008)
Lake Michigan (USA)	2005–2006	412[i]	43	Venier and Hites (2008)
Lake Erie (USA) 2005–2006	350[i]	250		Venier and Hites (2008)
Lake Victoria region (eastern Africa)	Ca. monthly	11.4	7.6	Arinaitwe et al. (2014)
Remote (Arctic and southern Sweden)	Bimonthly (2009–2010)	7.3–20[j]		Newton et al. (2014)
High mountain sites (Europe)				
Scotland	Biweekly (Jan 2004–Mar 2007)	47.6	119	This study
Pyrenees	Monthly (May 2004–Sep 2006)	30.6	97.1	This study
Alps	Monthly (Jun 2004–Aug 2006)	33.4	71.2	This study
Tatra Mountains	Monthly (May 2004–May 2006)	30.7	162	This study

[a] Otherwise noted, it is referred to the sum of BDE congeners 28, 47, 99, 100, 153, 154, and 183. [b] $\Sigma 7\mathrm{PBDEs}$ plus BDE85 and 138. [c] $\Sigma 7\mathrm{PBDEs}$ plus BDE49, 66, and 77. [d] Include 18 BDE congeners. [e] $\Sigma 7\mathrm{PBDEs}$ plus BDE66. [f] $\Sigma 7\mathrm{PBDEs}$ plus BDE66 and 209. [g] $\Sigma 7\mathrm{PBDEs}$ minus BDE183. [h] Sum of BDE28, 47, 66, 99, 100, 153 and 154. [i] $\Sigma 7\mathrm{PBDEs}$ plus BDE209. [j] Sum of BDE47, 99 and 100. n.r.: not reported.
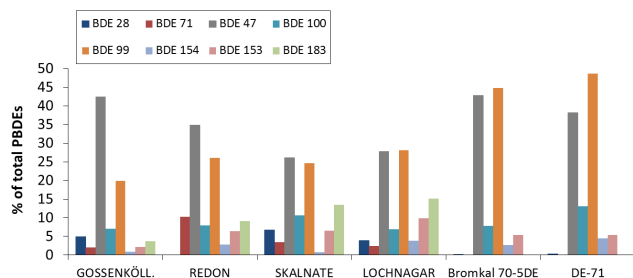

Fig. 4. Relative distribution of PBDEs in atmospheric deposition samples from the studied sites. The distributions were dominated by BDE209 in all cases but this compound is not included in the plots. The composition of the pentaBDE technical mixtures is included for comparison.

average congener distributions (Fig. 4) are similar to those reported in deposition samples from the Great Lakes (Venier and Hites, 2008), Baltic Sea (Ter Schure et al., 2004b) and Sweden (Ter Schure et al., 2002), among others.

The composition of the lower brominated PBDE congeners in these remote sites is generally consistent with the technical pentaBDE mixture, although some differences in the relative proportions of BDE99 and BDE100 can be observed (Fig. 4 and Table 6). In general, atmospheric deposition samples analysed in this study showed lower per cent contribution of BDE99 and BDE100 relative to their pro-

portions in pentaBDE formulations. Photooxidation during long-range transport may modify the composition of these mixtures. The observed photodegradation half-lives of the main congeners are as follows: BDE100 > BDE47 > BDE99 (Dickhut et al., 2012). Accordingly, high BDE47/BDE99 and low BDE99/BDE100 ratios are indicative of photolytic debromination. The average values of these ratios observed in Gossenköllesee are 1.5 and 2.1, respectively, which are higher and lower than those characteristic of the technical mixtures, 0.79–1.1 and 3.7–5.4, respectively (Table 6) and indicate photolytic loss of BDE99. In Redon, the average values of BDE47/BDE99 and BDE99/BDE100 are 1.4 and 4.1, respectively, reflecting some degree of transformation but lower than in Gossenköllesee (Table 6). In the other sites the above-mentioned ratios follow closely that of the pentaBDE mixture (Table 6). These results suggest that PBDE mixtures arriving at Redon and Gosseköllesee have been partially photodegraded during their long-range atmospheric transport from distant sources, while in Lochnagar and Skalnate, they may be originated from a nearby source area. This difference could be related to altitude. Redon and Gossenköllesee are the sites located at higher altitude, 2235 m and 2413 m above sea level, respectively, whereas Lochnagar and Skalnate are situated at 788 m and 1787 m, respectively. Highest photodegradation is expected to occur at highest altitude and the results of the above-mentioned ratios consistently show highest transformation in the highest sites.

Table 5. Temporal variations of mean atmospheric deposition fluxes of PBDEs to remote sites. Values expressed in $ng\,m^{-2}\,mo^{-1}$.

	BDE47	BDE99	BDE100	BDE183	BDE209	PBDEs tot[a]
Gossenköllesee						
Jun 2004–May 2005 ($n = 10$)	25.3[c]	8.40	1.86	2.48	n.a.	46.6
Sep 2005 –Aug 2006 ($n = 8$)	10.3[c]	6.68	3.18	1.66	71.2	34.9
Lake Redon						
May 2004–Apr 2005 ($n = 8$)[b]	15.4	10.4	2.25	2.35	54.9	41.2
May 2005–Apr 2006 ($n = 12$)	13.2	9.33	2.78	4.01	132	34.7
Skalnate						
May 2004–Apr 2005 ($n = 12$)	12.2	8.32	4.15	1.02	170[c]	41.1
May 2005–Apr 2006 ($n = 11$)	5.95	7.56	3.55	6.57	137[c]	27.3
Lochnagar						
Sep 2004–Aug 2005 ($n = 11$)	29.8[c]	22.9[c]	4.56	3.84[c]	136[c]	67.6
Sep 2005–Aug 2006 ($n = 10$)	8.45[c]	10.9[c]	3.99	6.38[c]	120[c]	39.7

[a] Sum of all PBDEs determined except BDE 209. [b] Do not include from December 2004 to February 2005 due to problems with the sampling equipment. [c] Indicate statistically significant differences in the BDE composition of the atmospheric deposition collected in the two sampling periods of the same station ($p < 0.05$). n.a.: not analysed.

Table 6. Mean PBDE ratios in pentaBDE technical mixtures and atmospheric deposition samples from remote regions of Europe. Technical mixture data from La Guardia et al. (2006) and Sjödin et al. (1998).

	Technical mixtures		Gossenköllesee	Redon	Skalnate	Lochnagar
	DE-71	Bromkal 70				
BDE47 / BDE100	2.9	5.5	3.1 ± 1.2	6.1 ± 3.9	3.0 ± 1.8	5.5 ± 3.7
BDE47 / BDE99	0.79	~ 1.1	1.5 ± 0.57	1.4 ± 0.42	1.1 ± 0.47	0.96 ± 0.44
BDE99 / BDE100	3.7	5.4	2.1 ± 0.08	4.1 ± 2.0	2.6 ± 1.3	5.5 ± 4.0
BDE153 / BDE154	>1	>1	3.7 ± 5.3	3.3 ± 3.5	9.5 ± 4.7	3.7 ± 3.9

These photochemical degradation processes of some PBDE congeners, especially BDE209, contrast with the presence of these compounds at significant concentrations in remote high altitude sites. Nevertheless, several studies have observed longer half-lives of BDE209 in the environment than those measured under laboratory conditions (Ahn et al., 2006; Lagalante et al., 2011). Significant photolysis of BDE209 in the gas phase has been reported (Raff and Hites, 2007) but BDE209 is mostly associated to particles, which makes this compound more resistant to photochemical transformation, as observed for other organic pollutants such as PAHs (Simó et al., 1997). Accordingly, BDE209 has been found in diverse types of environmental samples from remote sites in addition to those considered in the present study indicating that a significant fraction of the BDE209 emitted to the environment can persist enough in air to be transported over long distances (Bartrons et al., 2011; Breivik et al., 2006; Wang et al., 2005).

The Henry's law constants (H) decrease in the sequence of BDE47 > BDE99 > BDE100 (Wania and Dugani, 2003). Lower H should result in higher association to particles and higher deposition fluxes. Higher washout ratios of BDE99 and BDE100 than BDE47 have been reported in remote atmospheres (Ter Schure et al., 2004b) indicating higher efficiency in the deposition of these congeners than BDE47. If the volatilization effect would be important, decreases in the BDE47 / BDE99 and BDE47 / BDE100 ratios in atmospheric deposition should be observed. Comparison of the measured PBDE composition with those in the technical mixtures shows that this is not the case. As mentioned above the average mixtures in Lochnagar and Skalnate follow closely the composition of the technical products (Table 6) and the average values of BDE47 / BDE99 in Gossenköllesee and Redon are higher than in pentaBDE which is consistent with photolytic degradation.

The PBDE composition in atmospheric precipitation from these sites is consistent with the PBDE distributions found in liver and muscle from fish sampled in twelve high altitude lakes distributed throughout Europe, which showed higher contribution of BDE99 than BDE47 in Lochnagar and the lakes from the Tatra mountains when compared with the typical PBDE distribution of the other European lakes

(Vives et al., 2004; Gallego et al., 2007). The high BDE99 content in Lochnagar deposition is also consistent with the increase of BDE99 relative composition detected in some atmospheric samples analysed in UK which have been attributed to episodic anthropogenic sources (Lee et al., 2004).

The relative contributions of octaBDE can be assessed from the relative proportion of BDE183 and the BDE153 / BDE154 ratios which should be higher than 1 (La Guardia et al., 2006). In the samples considered for study the average values for this ratio were higher than 1 in all cases (Table 6) and the relative proportion of BDE183 was low (Table 3), indicating a low contribution of octaBDE technical mixtures in the European atmospheric deposition.

Examination of the Pearson correlations of the log-transformed deposition fluxes of the individual PBDE congeners shows significant correlations in many cases (Table 7, Fig. S2 in the Supplement). These high coefficients point to common long-range transport and settling processes for the atmospheric deposition of all congeners in each site. The highest number of significant correlations between congeners was observed in Skalnate and the lowest in Gossenköllesee, the site in which PBDEs were photodegraded to the highest extent. In addition, correlations between BDE209 and low-brominated compounds in Skalnate show an increase of determination coefficients with the number of Br atoms in the molecule, which indicates that debromination of decaBDE technical mixtures partially contributes to the levels of low-brominated congeners found in this site (Meyer et al., 2012; Wang et al., 2005). This result is also consistent with the higher concentration of BDE209 and higher contribution of the more brominated PBDEs detected in Skalnate (Fig. 4).

4 Discussion

4.1 Influence of atmospheric and meteorological parameters in PBDE deposition

Significant correlations between deposition of total particles and most BDEs were observed in Skalnate and Lochnagar (Table 7). In the former they concern all compounds but BDE209 and in the latter BDE47, BDE99, BDE100, BDE154 and BDE209. In contrast, no associations between PBDE and particle deposition have been found in Redon and Gossenköllesee except for BDE47 in this latter site (Table 7). The results observed in Skalnate and Lochnagar are consistent with previously reported preferential association of these compounds to the atmospheric particulate phase (Ter Schure et al., 2004b). Thus, previous study on trans-Pacific air masses reported more than 50 % of PBDE concentrations sorbed to atmospheric particles, and up to 90 % in the case of BDE209 (Noel et al., 2009). Moreover, particle scavenging processes have been found to dominate the deposition mechanisms of PBDEs (Gouin et al., 2006; Ter Schure et al.,

2004b), especially BDE209 (Breivik et al., 2006), which contrast with the lack of correlation between this BDE congener and particle deposition observed in three of the four studied sites.

In some cases the lack of correlation between total particle deposition and BDE209 could be due to photodegradation. Previous results on BDE 209 deposition in Skalnate measured in snowpack collected in April 2005 (within the sampling period of the present study) showed strong correlation between particle content in the snowpack and BDE 209 concentrations (Arellano et al., 2011). The discrepancy between BDE209 concentrations in atmospheric deposition and snowpack from the same site may be due to high photodegradation during the warm periods when solar irradiation is high. In winter, solar irradiation is low and snow preserves photolabile compounds. Previous studies have shown this preservation capacity of snow for other photochemically labile compounds such as PAHs (Arellano et al., 2011).

Rainfall enhances the deposition of both particle and gas phase PBDEs. Good correlations between precipitation and PBDE deposition have been observed in Skalnate (Table 7, Fig. S2 in the Supplement), one of the sites receiving highest precipitation among those considered for study, 3001 mm (Table 1). Significant correlations between precipitation and the deposition of BDE100, BDE183 and BDE209 are also observed in Redon. The correlations identified in these two sites are consistent with previous observations in the Great Lakes (Venier and Hites, 2008) and Izmir (Turkey) (Cetin et al., 2007) reporting wet deposition as the main deposition process for PBDEs. The lack of correlation between rainfall and PBDE fluxes in Gossenköllesee and Lochnagar may reflect diverse precipitation origins that are unconnected to the main air mass trajectories for PBDE inputs.

Statistically significant correlations between PBDE deposition and mean air temperatures were observed in Skalnate for all congeners except BDE209, with increasing deposition levels at increasing temperature (Table 7, Fig. S2 in the Supplement). The increases in low-brominated congener deposition with higher temperature are consistent with higher volatilization of compounds stored in environmental compartments such as soils, that is, PBDE emissions from secondary sources, while decaBDE reflects emissions from primary sources (Moon et al., 2007; Gouin and Harner, 2003). The same effect has been observed for the atmospheric deposition of organochlorine compounds such as hexachlorobenzene and polychlorobiphenyls in Gossenköllesee and Redon (Carrera et al., 2002). These compounds are also found at higher concentrations in the atmosphere of European mountain sites at warmer temperatures (van Drooge et al., 2004) which reflects secondary emissions of these legacy pollutants from the environmental compartments where they were formerly retained by cold trapping (Grimalt et al., 2001).

In the case of the PBDEs measured in the present study the temperature trends are more complex because these compounds are still in use. Significant increases of the more

Table 7. Pearson correlation coefficients between individual BDE congeners (ng m^{-2} mo^{-1}), particle fluxes (mg m^{-2} mo^{-1}) and meteorological variables. Correlations calculated from log-transformed values, excepting for temperature and precipitation. Only statistical significant correlations are indicated.

		BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	BDE209	T (°C)	Precip. (mm)	Particles
GOSSENKÖLL.	BDE 47			0.751[b]	0.884[b]						0.464[a]
	BDE 100			0.693[a]		0.792[a]	0.889[b]	0.998[b]			
	BDE 99	0.751[b]	0.693[b]					0.998[b]			
	BDE 154	0.884[b]									
	BDE 153		0.792[a]								
	BDE 183		0.889[b]		0.980[a]						
	BDE 209		0.998[b]	0.998[b]							
REDON	BDE 47			0.886[b]	0.731[b]			0.635[b]			
	BDE 100			0.610[a]		0.703[b]	0.842[b]	0.622[a]		0.425[a]	
	BDE 99	0.886[b]	0.610[b]		0.693[b]			0.667[b]			
	BDE 154	0.731[b]		0.693[b]				0.728[b]			
	BDE 153		0.703[b]				0.847[b]				
	BDE 183		0.842[b]			0.847[b]		0.670[a]		0.558[a]	
	BDE 209	0.635[b]	0.622[a]	0.667[b]	0.728[b]		0.670[a]			0.544[a]	
LOCHNAGAR	BDE 47		0.719[b]	0.909[b]	0.661[b]			0.749[b]			0.408[a]
	BDE 100	0.719[b]		0.724[b]				0.751[b]			0.523[b]
	BDE 99	0.909[b]	0.724[b]		0.739[b]	0.411[a]		0.769[b]			0.506[b]
	BDE 154	0.661[a]		0.739[b]		0.408[a]					0.435[a]
	BDE 153			0.411[a]	0.408[a]		0.781[b]				
	BDE 183					0.781[b]					
	BDE 209	0.749[b]	0.751[b]	0.769[b]							0.510[a]
SKALNATE	BDE 47		0.806[b]	0.853[b]	0.971[b]	0.948[b]	0.962[b]	0.753[b]	0.642[b]	0.919[b]	0.553[b]
	BDE 100	0.806[a]		0.929[b]	0.971[b]	0.993[b]	0.998[b]	0.462[a]	0.535[b]	0.750[b]	0.618[b]
	BDE 99	0.853[b]	0.929[b]		0.979[b]	0.980[b]	0.992[b]	0.577[b]	0.609[b]	0.852[b]	0.630[b]
	BDE 154	0.971[b]	0.971[b]	0.979[b]		0.955[b]	0.964[b]	0.876[b]	0.744[b]	0.977[b]	0.614[a]
	BDE 153	0.948[b]	0.993[b]	0.980[b]	0.955[b]		0.995[b]	0.942[b]	0.664[a]	0.945[b]	0.711[a]
	BDE 183	0.962[b]	0.998[b]	0.992[b]	0.964[b]	0.995[b]		0.928[b]	0.692[b]	0.960[b]	0.577[a]
	BDE 209	0.753[b]	0.462[a]	0.577[b]	0.876[b]	0.942[b]	0.928[b]			0.815[b]	

[a] Significant at 95 % confidence level. [b] Significant at 99 % confidence level.

brominated congeners during the colder months in UK have been described (Prevedouros et al., 2004b; Lee et al., 2004), being attributed to direct PBDE emissions as consequence of the increase of combustion processes. Skalnate is the site closer to potential pollution sites among those considered in the present study. For the other European remote regions degassing of PBDEs from secondary sources is not still strong enough to define the dominant input trend of these compounds while this is the case of several organochlorine compounds which are no longer in use.

4.2 Influence of air mass origin

The predominant air mass trajectories arriving at each sampling site calculated from the HYSPLIT data from FNL archive and GDAS are summarized in Fig. 1 and Table 2. No statistically significant relationships between air mass origins and PBDE deposition fluxes in Gossenköllesee and Skalnate have been observed. This lack of correlation is consistent with unspecific European continental sources as main determinants of the PBDE load arriving to these sites. In contrast, in the westernmost sites, Redon and Lochnagar, 0.7795° E

and −3.2313° E, respectively, significant changes in PBDE deposition fluxes are observed in relation to prevailing air mass origins.

In Redon, higher fluxes are found with a higher proportion of air mass trajectories from the North Atlantic in the monthly collection periods (Fig. 5). This trend is observed for all PBDE congeners, although the correlations are only statistically significant for BDE154, BDE183 and BDE209. For this site, consideration of the proportion of North Atlantic trajectories without passing over the British Isles and France (west North Atlantic) (Figs. 1 and 5) shows even stronger correlations with the PBDE deposition fluxes, indicating that this increase is not related to regional sources. The congeners exhibiting statistically significant correlations are BDE100, BDE154, BDE183 and BDE209. As in the previous case, BDE99 and BDE47 also exhibit a positive correspondence between proportion of west North Atlantic trajectories and deposition fluxes but the correlations are not statistically significant probably because of lack of enough samples to obtain sufficient statistical power. These two congeners are those of highest environmental background since many processes (e.g. photo-oxidation) may generate them by
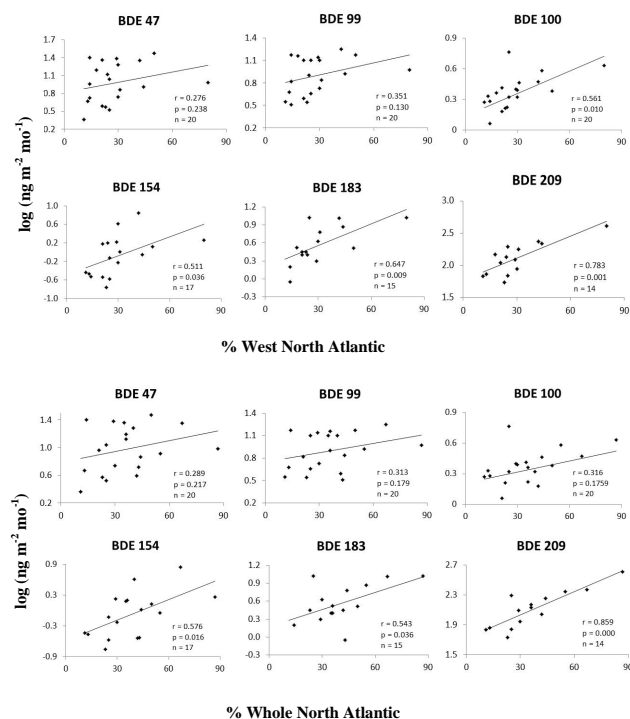
Fig. 5. Relationship between % of North Atlantic air masses during the collection period of each sample and PBDE atmospheric deposition fluxes in Redon. Western North Atlantic trajectories only consider those air masses flowing from the west without passing over British Isles and France. Whole North Atlantic includes all air masses coming from the North Atlantic arriving to this site.

transformation of more brominated BDEs (Bartrons et al., 2011; Bezares-Cruz et al., 2004). As mentioned above, photooxidation processes can affect PBDE composition at Redon because of its high elevation.

At Lochnagar, a positive correlation between air mass trajectories from North Atlantic and PBDE fluxes is also observed (Fig. 6). The correlations are statistically significant for less brominated compounds BDE47, BDE99 and BDE100. As mentioned above, no photooxidation effects have been observed at this site and the composition of PBDE in atmospheric precipitation matches closely that of the pentaBDE mixtures. The lack of significant correlation of BDE209 fluxes with North Atlantic trajectories in Lochnagar suggests an additional contribution of decaBDE from Scotland or the British Isles that reached this remote site.

The correlations of PBDE fluxes with the contributions from western trajectories are consistent with the reported prevailing wind regimes from west to east (Halse et al., 2011) and the known higher degree of PBDE pollution in USA than in Europe (Hites, 2004; Harley et al., 2010; Sjödin et al., 2003). These results, identified in two western sites separated by 1600 km, suggest a transcontinental PBDE contribution into Europe that may be long-range transported from North American sources.
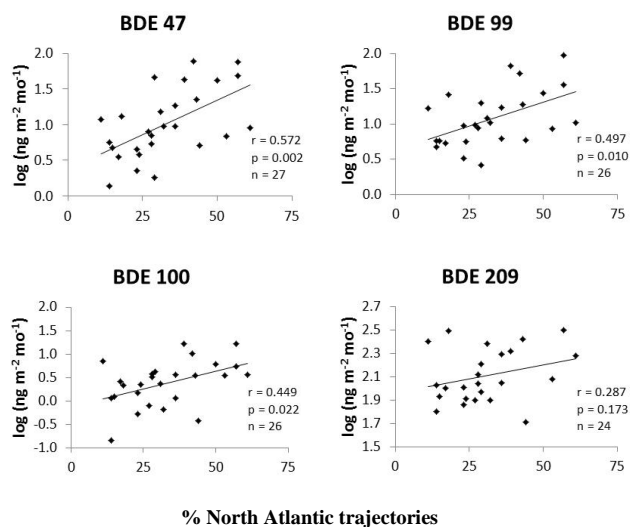

Fig. 6. Relationship between % of North Atlantic air masses during the collection period of each sample and PBDE atmospheric deposition fluxes in Lochnagar.

At the eastern locations, 11.0139° E and 20.2342° E for Gossenköllesee and Skalnate, respectively, the influence of PBDE inputs carried by the North Atlantic air mass trajectories is not observed. The PBDE inputs in these sites may respond to the high complex circulation patterns resulting from competing influences of air masses and pollution sources (Beniston et al., 2005; Ostrozlik et al., 2007).

In the southernmost site, Redon (42.64208° N), a positive correlation between particle levels in bulk deposition and air masses flowing from the south is observed ($r = 0.498$, $p < 0.025$; Fig. 7), which is consistent with previous studies reporting transport of large quantities of dust from northern Africa across the Mediterranean basin to Europe, mainly in summer (Escudero et al., 2005). African dust is the largest PM_{10} source in regional background southern sites of the Mediterranean (35–50 % of PM_{10}) with seasonal peak contributions up to 80 % of the total mass (Pey et al., 2013). These southern contributions can explain the lack of correlation observed between PBDE deposition fluxes and particle content in this site. The southern air trajectories corresponded to relatively clean air masses, which transport significant amount of particles with low PBDE concentration.

On the other hand, a negative correlation between BDE47 / BDE99 ratios and percent of air mass trajectories flowing from central/eastern Europe has been observed at Redon ($r = -0.453$, $p < 0.05$) and Gossenköllesee ($r = -0.476$, $p = 0.05$) (Fig. 8). These coefficients are only statistically significant in the former and at the limit of statistical significance in the latter. The coincident trends observed in these two sites and the agreement of the low values with the characteristic ratio of the technical pentaBDE mixtures that accumulate in Skalnate, the easternmost site, suggest that this region may be a major source of these compounds.

Table 8. Seasonal variations of BDE congener ratios in atmospheric deposition samples.

	BDE47/ BDE100	BDE47/ BDE99	BDE99/ BDE100	BDE153/ BDE154
Gossenköllesee				
Warm	3.8 ± 1.5	1.8 ± 0.7	2.1 ± 0.1	–
Cold	2.5 ± 0.7	1.2 ± 0.3	2.1 ± 0.1	
Lake Redon				
Warm	6.6 ± 4.0	1.4 ± 0.4	4.3 ± 2.0	3.8 ± 3.7
Cold	4.6 ± 3.5	1.1 ± 0.3	3.7 ± 2.0	2.9 ± 3.5
Skalnate Pleso				
Warm	3.3 ± 1.9	1.3 ± 0.6	2.7 ± 1.9	7.5 ± 5.0
Cold	2.8 ± 1.8	1.0 ± 0.3	2.6 ± 0.8	10 ± 4.6
Lochnagar				
Warm	5.5 ± 3.1	0.97 ± 0.41	4.7 ± 2.8	3.2 ± 4.1
Cold	5.6 ± 4.3	0.93 ± 0.49	6.1 ± 4.8	4.1 ± 3.8

Warm, from June to October. Cold, from November to May.
– Seasonal average values precluded due to the large number of non-detected for BDE153.

4.3 Seasonal changes

Grouping PBDE atmospheric deposition fluxes into warm (June to October) and cold (November to May) periods only shows statistically significant differences (ANOVA, $p < 0.05$) in Skalnate. The higher PBDE fluxes in the warm periods at this site are consistent with the temperature dependence and secondary source origin of these compounds. Similar seasonal differences have been observed in areas close to pollution sources in Korea (Moon et al., 2007), with higher values in spring–summer, while no seasonal pattern was observed in rural and remote sites. Higher concentrations of BDE47 in air and deposition during spring, just after snowmelt and before bud burst, have been observed in some studies (Gouin et al., 2005) but in others no evidence of this "spring pulse" (Harrad and Hunter, 2006) or any significant seasonality (Xiao et al., 2012) in remote sites, like the Canadian high Arctic and the Tibetan Plateau, has been identified. All these results indicate that seasonal trends are characteristic of areas affected by pollution sources. In this sense, Skalnate is the site closer to potential pollution areas among those considered in the present study.

No seasonal trends in percent contribution of air mass trajectories were observed in Gossenköllesee and Skalnate, although in general more trajectories from the North Atlantic and the south were found in the cold and warm periods, respectively. No trend was observed in Lochnagar (Table 2). In contrast, backwards air mass trajectories showed a well-defined seasonal pattern in Redon. South-trajectories were dominant during the warm season (59 %) while North Atlantic trajectories prevailed during cold periods (48 %). The central European trajectories to this site were much fewer and did not show any seasonal trend (Table 2), consistent

Particle flux

r = 0.498
p = 0.025
n = 20
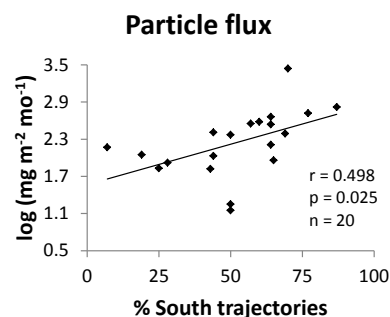
Fig. 7. Relationship between particle deposition fluxes and air mass trajectories flowing from the south in Redon.

Gossenköllesee

r = -0.476
p = 0.05
n = 17

Redon

r = -0.453
p = 0.034
n = 22
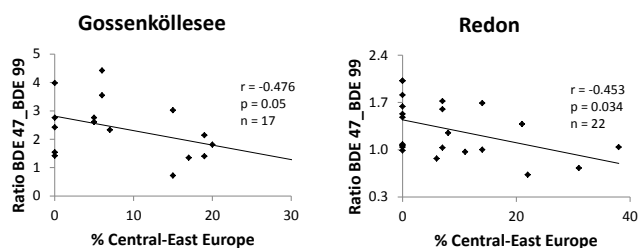
Fig. 8. Relationship between BDE47 / BDE99 ratios and air mass trajectories flowing from central–eastern Europe in Gossenköllesee and Redon.

with previous studies on air mass circulation patterns in this site (Bacardit et al., 2009). In Redon, the higher proportion of North Atlantic trajectories in cold periods, when most rainfall occurs, and the association of these trajectories with higher PBDE deposition fluxes could explain the observed correlations between deposition of some PBDEs and atmospheric precipitation at this site (Table 7). The PBDEs arriving to Redon in the cold season exhibit BDE47 / BDE99 average values of 1.1, that are close to those of the technical pentaBDE mixture (Tables 6 and 8). In contrast, those deposited in the warm season exhibit values of 1.4 that are consistent with a certain degree of photooxidation. Therefore, PBDE mixtures transported over the Atlantic Ocean arrive to Redon with a lower degree of transformation in the cold than in the warm season.

This difference between the two seasons is also observed at the other sites. Gossenköllesee is the site in which the highest BDE47 / BDE99 ratios (1.8) are observed. This is the highest altitude site in the present study with the highest insolation. Obviously, in the warm period there is higher insolation than in the cold period and the observed average BDE47 / BDE99 ratios change accordingly.

5 Conclusions

The mean deposition fluxes of PBDE were similar in all studied sites with differences of twofold at the most. The major

PBDE congener was BDE209, with fluxes ranging from $71 \, \text{ng m}^{-2} \, \text{mo}^{-1}$ in Gossenköllesee to $162 \, \text{ng m}^{-2} \, \text{mo}^{-1}$ in Skalnate, for example, between fourfold and sixfold higher values than the other detected PBDEs. BDE47 and BDE99 were the dominant low-brominated congeners, followed by BDE100 and BDE183. This composition is consistent with predominant inputs from the commercial mixtures decaBDE and pentaBDE in the atmospheric fallout of these compounds over Europe.

However, photo-oxidation modifies the composition of these mixtures, involving decreases in the relative proportion of BDE209 with respect to total PBDEs and decreases of BDE100 and BDE47 vs BDE99. These effects are much stronger in the sites situated at high elevation (2000 m a.s.l.), Gossenköllesee and Redon, than in those at lower altitude, Skalnate and Lochnagar, where photo-oxidation effects are small.

These differences in elevation are also consistent with the degree of association of these compounds to the particles collected in the atmospheric deposition samples. The low altitude sites show a significant correlation between PBDEs and total particle fluxes. At Skalnate this relates to all PBDEs except BDE209, and at Lochnagar to BDE47, BDE99, BDE100, BDE154 and BDE209. In contrast, no associations between PBDE and particle deposition fluxes were been found at Redon and Gossenköllesee except for BDE47 in the latter. The particles arriving to the studied sites above 2000 m probably have different origins and more diverse PBDE content than those transported at low altitudes. In this respect, a positive correlation between particle fluxes and air masses flowing from the south is observed in Redon, which is consistent with the transport of large quantities of dust from northern Africa across the Mediterranean basin to Europe, mainly in summer. These southern air masses are relatively clean and explain the lack of correlation observed between PBDE deposition fluxes and particle content at this site.

Statistically significant correlations between PBDE deposition and mean air temperatures were also observed at Skalnate for all congeners except BDE209. Deposition fluxes increased at higher temperature. Skalnate is also the only site at which a significant seasonal trend is observed, involving higher PBDE deposition in the warm (June to October) periods. Deposition increases at higher temperature are consistent with emissions from secondary sources involving increased volatilization of compounds stored in environmental compartments such as soils. Skalnate is the site closer to potential pollution areas among those considered in the present study.

Gossenköllesee and Redon show PBDE distributions in which the BDE47 / BDE99 ratios significantly correlate with the percent of air masses coming from central/eastern Europe. The observed values of this ratio are consistent with a predominant source of the pentaBDE commercial mixture in central Europe.

In the westernmost sites, Redon and Lochnagar, higher PBDE fluxes are found with higher percentages of air mass trajectories from the North Atlantic. This trend is observed for all PBDE congeners. At Redon, statistically significant correlations are observed for BDE100, BDE154, BDE183 and BDE209. At Lochnagar higher PBDE fluxes are also observed at higher proportion of air mass trajectories from the North Atlantic. These correlations are significant for BDE47, BDE99 and BDE100. Correlations between deposition fluxes and trajectories are consistent with reported prevailing wind regimes from west to east and the higher degree of PBDE emissions in USA than in Europe. They are observed in two western sites separated by 1600 km and suggest a transcontinental atmospheric PBDE transfer from North American sources into Europe.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/14/4441/2014/acp-14-4441-2014-supplement.pdf.

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