

ATMOSPHERIC DEPOSITION OF POLYBROMODIPHENYL ETHERS TO REMOTE AREAS OF EUROPE: SOURCES, TRENDS AND PROCESSES

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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 furniture¹. 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 BDE209². Total emissions in Europe were estimated to be 9.87 tons in 2000³.

These compounds have been documented to have strong environmental persistence, lipophilicity and tendency to bioaccumulate in animals^{4,5} and humans^{6,7}. Health concerns with these compounds are growing as consequence of reported results on developmental neurotoxicity in mice⁸, hormonal disruption⁹ and some evidences of impaired neuropsychological development in infants. In view of these properties, international regulatory actions have been implemented to restrict or eliminate the use and production of these compounds.

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^{10, 11} but data on PBDEs is scarce¹². 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^{13, 14}.

The present study aims to determine the PBDE fluxes and composition in bulk atmospheric deposition in four European high altitude mountain 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.

Materials and methods

Sampling. Bulk atmospheric deposition samples were regularly collected at four remote European areas: Lake Redon (Pyrenees, Spain), Gossenköllesee (Alps, Austria), Skalnate Pleso (Tatras, Slovakia) and Lochnagar (Grampian Mountains, Scotland). 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. Atmospheric deposition was collected with polyethylene funnels connected to stainless steel or Teflon coated reservoirs by tubes. 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 C₁₈ Empore disks (47 mm diameter, 0.5 mm thickness) as described elsewhere^{10, 15}. After sampling, each collector was carefully cleaned with MilliQ water and acetone.

Analytical methodology. Frozen glass fiber filters were freeze-dried before weighed to obtain total mass of the collected particles. PBDEs were extracted from the freeze-dried filters by sonication with

dichloromethane:methanol (2:1), while compounds adsorbed onto the membrane extraction disks were eluted sequentially with methanol, cyclohexane and dichloromethane as described elsewhere^{15, 16}. After, they were vacuum-evaporated to near dryness 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.

Instrumental analysis. PBDE congeners were analysed on a gas chromatograph (Trace GC Ultra- Thermo Electron, Milan Italy) coupled to a mass spectrometer (MS DSQ Instrument Thermo Electron Corp., Austin, Texas, USA) in negative ion chemical ionization (GC-MS-NICI) and selective ion recording modes. 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). The oven temperature was programmed as follows: initial temperature 90°C during 1.5 min, a temperature increase of 20°C/min up to 200°C, followed by 5°C/min up to 275°C and a final ramp of 30°C/min up to 300°C, final time of 10 min. 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 elsewhere¹⁷.

Results and discussion

Of the fourteen PBDE congeners analysed in bulk atmospheric deposition, 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.

The mean deposition PBDE fluxes were similar at all studied sites with differences of two-fold at the most. The most abundant 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, involving between four and six-fold higher values than the other detected PBDEs. BDE47 and BDE99 were the dominant low-brominated congeners, followed by BDE100 and BDE183. The mean deposition fluxes of these four BDE congeners ($\Sigma 4\text{BDEs}$) varied between 24 $\text{ng m}^{-2} \text{mo}^{-1}$ (Skalnate) and 40 $\text{ng m}^{-2} \text{mo}^{-1}$ (Lochnagar). Redon and Gossenköllesee showed intermediate levels, 28 and 31 $\text{ng m}^{-2} \text{mo}^{-1}$, respectively.

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

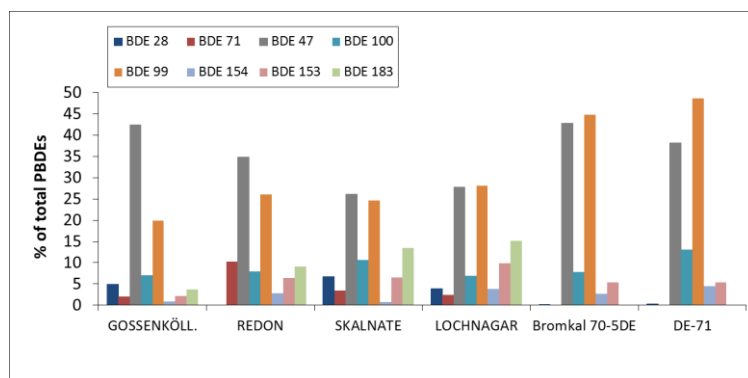


Figure 1. Relative distribution of PBDEs in atmospheric deposition samples from the studied sites. The distributions were dominated by BDE209 in all cases but this compound is not included in the plots. The composition of the pentaBDE technical mixtures is included for comparison.

BDE99 and BDE100 can be observed (Figure 1). In general, atmospheric deposition samples analysed in this study showed lower per cent contribution of BDE99 and BDE100 relative to their proportions in pentaBDE formulations. These differences can be related to photooxidation of specific congeners during long-range transport. The observed photodegradation half-lives of the main congeners are as follows: BDE100 > BDE47 > BDE99¹⁸. 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 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. In the other

sites the above mentioned ratios follow closely that of the pentaBDE mixture. These results suggest that PBDE mixtures arriving at Redon and Gossenköllesee have been 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.

Examination of the Pearson correlations of the log-transformed deposition fluxes of the individual PBDE congeners shows significant correlations in many cases, pointing to common long-range transport and settling processes for the atmospheric deposition of all congeners in each site. In addition, significant correlations between deposition of total particles and most BDEs were observed in Skalnate and Lochnagar. 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. The results observed in Skalnate and Lochnagar are consistent with previously reported preferential association of these compounds to the atmospheric particulate phase¹⁹. 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 BDE209²⁰. Moreover, particle scavenging processes have been found to dominate the deposition mechanisms of PBDEs, especially BDE209¹⁹, 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 snowpacks collected in April 2005 (within the sampling period of the present study) showed strong correlation between particle content in the snowpack and BDE 209 concentrations²¹. The discrepancy between BDE209 concentrations in atmospheric deposition and snowpacks 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 photo-labile compounds. Previous studies have shown this preservation capacity of snow for other photochemically labile compounds such as PAHs²¹.

Rainfall enhances the deposition of both particle and gas phase PBDEs. Good correlations between precipitation and PBDE deposition have been observed in Skalnate and Redon. The correlations identified in these two sites are consistent with previous observations in the Great Lakes²² and Izmir (Turkey)²³ reporting wet deposition as the main deposition process for PBDEs.

The predominant air mass trajectories arriving at each sampling site were calculated from the HYSPLIT data from FNL archive and GDAS. 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, 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 (Figure 2). 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 shows even stronger correlations with the PBDE deposition fluxes, indicating that this increase is not related to regional sources. At Lochnagar, a positive correlation between air mass trajectories from North Atlantic and PBDE fluxes is also observed. 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 and the known higher degree of PBDE pollution in USA than in Europe. 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.

At the eastern locations, Gossenköllesee and Skalnate, 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.

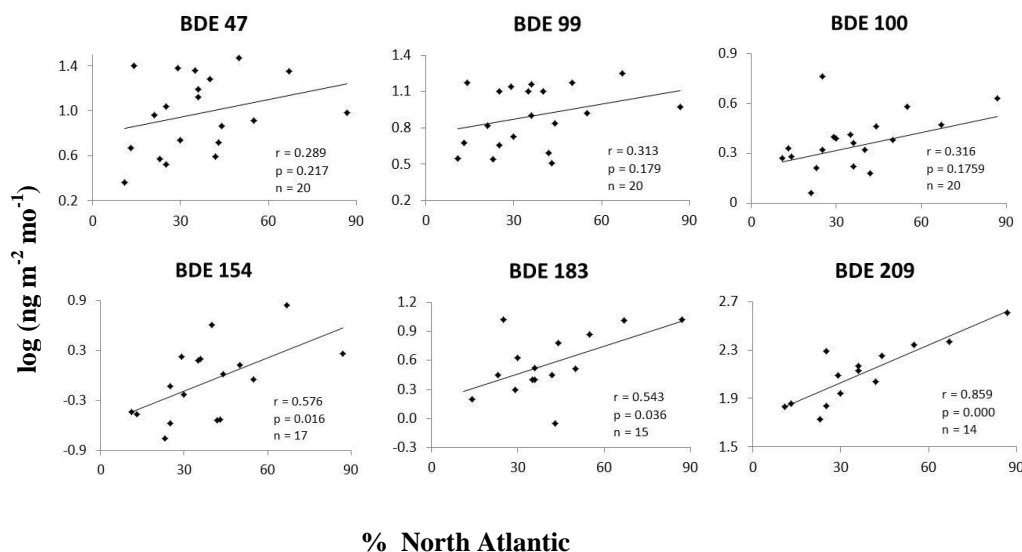


Figure 2. Relationship between % of North Atlantic air masses during the collection period of each sample and PBDE atmospheric deposition fluxes in Redon

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