Altitudinal distributions of BDE-209 and other polybromodiphenyl ethers in high mountain lakes

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A R T I C L E   I N F O

Article history:
Received 3 November 2010
Received in revised form 25 March 2011
Accepted 26 March 2011

Keywords:
Polybromodiphenyl ethers
Organohalogen compounds
High mountains
Temperature dependence
Microbial biofilms
Long-range transport

A B S T R A C T

The present study shows the occurrence of 2,2',3',3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209) in microbial biofilms of Pyrenean and Tatra high mountain lakes despite its low vapor pressure and high hydrophobicity. Aerosol air transport is therefore a feasible mechanism for BDE-209 accumulation in sites up to 2688 m above sea level. This compound and other PBDEs exhibit altitudinally-dependent distribution involving higher concentrations with increasing mountain lake elevation. However, the apparently very high enthalpies of the concentration gradients observed, including BDE-209, suggest that bacterial anaerobic debromination also plays a significant role in the resulting altitudinal distributions. This microbial mechanism explains the relative abundances of PBDEs and their within lake differences between rocky and sediment microbial biofilms, thereby showing that the altitudinal pattern observed is not purely due to water temperature control on bacterial activity but also to changes in the availability of anaerobic microenvironments which increase with increasing lake productivity at lower altitudes.

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1. Introduction

Polybromodiphenyl ethers (PBDEs) are common flame-retardant products currently in use in household and workplace materials. They have been produced commercially in the form of diphenyl ether mixtures with three degrees of bromination: nominally penta-, octa- and deca-BDE. The last formulation currently involves 83% of the PBDE global market demand, followed by penta- and octa-BDE at 11% and 6%, respectively. Due to health concerns and their widespread occurrence in environmental and human samples, the penta-BDE and octa-BDE technical mixtures were banned by the European Union (EU) in 2004 and their production ceased in North America. Recently, the Stockholm Convention on Persistent Organic Pollutants (SCPOPs) decided to include the following mixtures in their list: tetraBDE (defined as BDE-47), penta-BDE (defined as BDE-99), hexa-BDE (defined as BDE-153 and BDE-154) and heptaBDE (defined as BDE-175 and BDE-183) (SCPOPS, 2010). Deca-BDE is essentially composed of 2,2',3',3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209) where it constitutes more than 97% of the congener mixture (Sjödin, 2000). Almost half of the annual global deca-BDE demand (more than 56,000 metric tonnes in 2003; Bromine Science and Environmental Forum, 2007) is used in flame retarding high impact polystyrene, the plastic resin commonly used in TV and radio cabinets. Other applications of deca-BDE include use in polyester fibre additives, coatings for automobiles and acrylonitrile-butadiene-styrene rubber, in which deca-BDE can be found in concentrations between 6% and 22% (Environmental Health Criteria, 1994). Production and use of deca-BDE has continued although in 2009 its use was restricted in Europe (EBFRIP, 2009).

In the environment, BDE-209 is susceptible to degradation via debromination, due to exposure to UV light (Bezares-Cruz et al., 2004), to reaction to radicals (Ter Schure et al., 2004) and/or by microorganism activity (Rayne et al., 2003; Gerecke et al., 2005; He et al., 2006; Vonderheide et al., 2006; Tokarz et al., 2008, La Guardia et al., 2007). These three debromination pathways can all potentially lead to the formation of PBDE congeners, which are similar to the congeners found in the now banned penta- and octa-BDE commercial mixtures. Nevertheless, the occurrence of BDE-209 has been reported in air, sediments, biota, and house dust (Stapleton et al., 2005; Webster et al., 2009).

Generally, it is believed that the large molecular size, low vapor pressure (subcooled vapor pressure = 10–8.3 Pa; Wania and Dugani,
high hydrophobicity (log Kow = 8.7; Wania and Dugani, 2003) of BDE-209 will result in limited capacity for long-range atmospheric transport (Wania and Dugani, 2003; Strandberg et al., 2001) and low bioavailability (Hardy, 2002). However, recent studies suggest that BDE-209 is also likely to be transported to remote areas in association to particles under dry conditions and high wind speed (Brevik and others, 2006) or, perhaps less likely, via the temperature-dependent grasshopper effect (Gouin and Harner, 2003). The presence of this compound in Arctic mosses and marine organisms has recently been reported (de Wit and others, 2006).

In this paper, we report the presence of BDE-209 in high mountain lakes situated far from pollution emission sources, with hydrology dominated by atmospheric processes: Llebreta (42.55°N, 0.89°E, 1620 m.a.s.l.), Llong (42.57°N, 0.95°E, 2000 m), Xic de Colomina (42.52°N, 0.99°E, 2425 m) and Vidal d’Amunt (42.53°N, 0.99°E, 2688 m) from the Pyrenees (Catalonia, Spain) and Vel’ké Hincovo (49.18°N, 20.06°E, 1946 m) from the Tatras (Slovakia) (Fig. 1). They are softwater oligotrophic lakes, with long ice-cover periods (from ca. 4–7 months) and cold water temperature during ice-free periods. These conditions involve relatively scarce biomass and simple food webs. The lakes from the Pyrenean transect are situated in a maximal planar projection distance of 9.2 km. Thus, their differences in PBDE accumulation capacity will essentially depend on altitudinal differences, e.g. 1068 m between those two situated at highest and lowest elevation.

BDE-209 could only reach these sites by long-range atmospheric transport (Vilanova and others, 2001; Grimalt and others, 2001; Carrera and others, 2002; Ribes and others, 2002), thereby providing solid proof of the feasibility of the transfer of this compound from sources to remote areas through the atmosphere. In addition, we found that PBDE increases in accordance with lake altitude. We studied the presence of PBDE in microbial biofilms at an altitudinal gradient of lakes (Fig. 1) and within each lake we studied biofilms on different substrates, namely rock and silt biofilms. Rock biofilms are present in littoral lake areas, whereas silt biofilms are mostly found in the top sediment of deep lake areas. In these relatively shallow mountain lakes, even the deep layers receive enough light for light-based autotrophic growth; thus all microbial biofilms are an amalgam of microalgae (mainly diatoms) and heterotrophic bacteria. However, they differ in the relative proportions of these components or, in terms of processes, in the intensity and duration of autotrophic vs. heterotrophic activities and particularly in the time periods in which bacterial activity takes place under anoxic conditions. Anaerobic bacterial activity has been identified as the main pathway for PBDE biodebromination (He and others, 2006; Tokarz and others, 2008). Therefore, comparison of PBDE distribution in biofilms of lakes at different altitudes enables us to elucidate between air–water exchange and biodegradation as the main mechanism responsible for the altitudinal patterns observed.

2. Materials and methods

2.1. Chemicals and materials

Trace analysis (SupraSolv) isooctane, n-hexane, dichloromethane, and acetone were from Merck (Darmstadt, Germany). Concentrated sulfuric acid ProAnalysis grade 95–97% was also purchased from Merck (Darmstadt, Germany). PB-209 and PCB-209 were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The standard solution EO-5099 and BDE-209 in isooctane were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Helium and ammonia were from Air Liquide (Barcelona, Catalonia, Spain). Their purity was 99.999%.

Copper for desulphurization was activated by sonication with 35.5% hydrochloric acid (3 × 3 mL), and then it was rinsed several times with Milli-Q water to neutral pH and, subsequently, with acetone for water removal. This powder was stored under n-hexane prior to use (not later than 2 days after activation).

The gas chromatograph used for the PBDE analyses was a Trace GC Ultra (Thermo Electron, Milan, Italy). This instrument was coupled to a negative ion chemical ionization mass spectrometer MS DSQ (Thermo Electron, Austin, Texas, USA; Eljarrat and others, 2004). The DBS-MS capillary column was from J&W Scientific, Folsom, CA, USA.

2.2. Sampling

A full description of the analytical method used for analysis of PBDEs is described elsewhere (Vizcaino and others, 2009). Sampling in the Pyrenean and Tatra lakes was performed in July 2004 and September 2005, respectively. Two main types of samples were considered: rock and silt biofilms. Each rock biofilm sample was obtained by scraping ten stones representing the littoral shore of each lake, at 1 m deep in the shoreline of the lake. A metallic ultra – cleaned brush was used. Stone tops and bottoms were scraped separately in order to identify potential effects due to exposition to UV radiation. Silt biofilms were sampled with an Uwitec gravity core sampler (Mondsee, Austria). Top layers of 1 cm thickness were sliced from the sediment cores. Samples were kept frozen (-20 °C) until analysis. Sample dry weight was estimated by drying in a vacuum sealed-drier at 20 °C until constant weight. Sediment loss on ignition was carried out at 550 °C, as an estimation of the organic content of the sediment samples (Heiri and others, 2001).

2.3. Extraction and clean-up

Samples were fortified with PCB-209 standards and extracted by sonication with 20 mL n-hexane–dichloromethane (4:1) for 15 min. This step was repeated four times and all the extracts (80 mL) were combined and concentrated to a small volumes (2–4 mL) by vacuum rotary evaporation. Samples were redissolved in n-hexane and cleaning-up was performed by four successive oxidation steps with sulfuric acid (Eljarrat and others, 2004). About 0.5 g of activated copper was added to the extracts containing sulfur. After manual stirring the suspensions were kept overnight at room temperature. Finally, the extract was concentrated to near dryness under a gentle flow of nitrogen and redissolved in 25 µL of isooctane. An internal standard of PCB-200 was added before chromatographic analysis.

2.4. Instrumental analysis

Extracts were analyzed by gas chromatography coupled to negative ion chemical ionization mass spectrometry. The system was equipped with a DB5-MS capillary column (15 m × 0.25 mm × 0.1 µm film thickness) coated with phenyl arylene.
polymer that is virtually equivalent to 5%phenyl/95%methylpolysiloxane stationary phase. The oven temperature program for GC polymer that is virtually equivalent to 5%phenyl/95%methylpolysiloxane stationary phase was 99.999% in both cases. Transfer line temperature was 300 °C.

2.5. Quality assurance

Procedural blanks were analyzed for every set of six samples which correspond to periods between 12 h and two days of sample handling, depending on the matrix. The recoveries of the surrogate standard, PCB-209, were calculated for each sample, being 69 ± 22% (average ± standard deviation). The recovery of this surrogate was used for correction of all PBDE concentrations in each sample. Identification and quantification of PBDEs was performed by injection of external standards at different concentrations. Relative responses to PCB-200 were used in order to correct for instrumental variability, and this value was also corrected by the recovery of the surrogate standards. Limits of detection and quantification were calculated from real samples as the mean of noise signal plus 3 and 5 times, respectively, the standard deviation. They ranged between 0.1–0.8 and 0.2–1.3 pg g⁻¹, respectively. Final validation was made by analysis of reference material obtained from the Arctic Monitoring and Assessment Program (AMAP). We participate regularly in the AMAP Ring Test Proficiency Program for POPs (Centre de Toxicologie Institut National de Santé Publique du Québec, Québec, Canada) and the laboratory results usually were within 20% of the consensus values, including BDE-209 concentrations.

3. Results and discussion

3.1. Biofilm concentrations

Silt biofilms are relatively similar among lakes. They are composed of large masses of mostly empty diatom valves, amorphous organic matter and bacteria. These biofilms experience large periods of anaerobiosis during long ice-cover periods, and the temperature of their overlying waters (ca. 4 °C) varies only slightly between one lake and another throughout the year. In contrast, rock biofilms are diverse and rich in microalgae. At higher lake altitudes, they undergo shorter growth periods, higher UV radiation and colder temperatures which result in less productive and thus thinner biofilms. Higher accumulation of organic matter in rock biofilms at low altitude lakes enhances the formation of anoxic microenvironments, as reflected by the presence of sulfur generated by sulfate reduction.

BDE-209 was the most abundant congener in the samples, representing about 50% of total PBDE (Table 1). BDE-47, 99, 183 and 190 were the other main congeners but their concentrations were much lower. These results evidence the long-range atmospheric transport and deposition of this low volatile and highly hydrophobic brominated compound to remote European areas, including high mountains. The BDE-209 dominance agrees with the present use of deca-BDE as the only PBDE mixture freely traded in Europe (Cox and Ethymiou, 2003).

Silt biofilms showed lower BDE-209 concentrations than rock biofilms (Table 2). This difference could reflect dilution effects due to sediment slicing, since 1 cm of top sediment sections in these lakes could represent an interval between 5 and 40 years, probably including long sedimentation periods in which deca-BDE was not used. The silt sediment concentrations of BDE-209 in the lakes of these two mountain ranges (Table 2) are similar to those found in Arctic lake sediments such as Char and AX-AJ lakes (Canada; de Wit et al., 2006), 0.042 and 0.075 ng g⁻¹ dw, respectively, and lower than those found in Lake Winnipeg (0.63 ng g⁻¹ dw; Law et al., 2006). Comparison of the BDE-209 concentrations in the lake biofilms of these European mountains with those found in Arctic mosses from Skogarvarre and Valvik (Norway), 0.025 and 0.12 ng g⁻¹ dw (de Wit et al., 2006) respectively, show comparable levels in the case of the Pyrenean sites (Table 2). However, the biofilm BDE-209 concentrations in Velké Žihovo (Table 2) are between one and two orders of magnitude higher than in these mosses. All PBDE congener concentrations in all biofilms were higher in Velké Žihovo than in the Pyrenean lakes (p < 0.01, Wilcoxon rank-sum test).

Comparison between top and bottom rock surfaces, i.e. between exposed and protected biofilms respectively, does not show consistent significant differences in BDE-209 concentrations (Table 2). Thus, UV radiation of lake surfaces does not seem to be a major cause of the concentration differences of this flame retardant after deposition.

3.2. Altitudinal dependence

The biofilm concentrations of the most abundant PBDE congeners in the Pyrenean lakes exhibit altitudinal gradients in most cases. These gradients involve concentration increases of about two orders of magnitude between the highest and the lowest altitude lakes but in some compounds and types of samples it may be four orders of magnitude. The compounds represented in Fig. 2 are those with mean PBDE concentrations higher than 0.015 ng g⁻¹ OM.

Representation of the logarithmic transformation of these concentrations vs. lake altitude (Fig. 2) shows a linear trend with statistically significant correlation coefficients in several cases, e.g. BDE-47 (p < 0.05) and BDE-173/190 (p < 0.05) in silt biofilms and BDE-183 (p < 0.05) and BDE-209 (p < 0.001) in top rock biofilm and

<table>
<thead>
<tr>
<th>Br Structure</th>
<th>Pyrenees Mean ± SD</th>
<th>Pyrenees Range</th>
<th>Tatra Mean ± SD</th>
<th>Tatra Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-209</td>
<td>10</td>
<td>2.3,3,4,5,5',6'</td>
<td>0.19 ± 0.20</td>
<td>&lt;0.0008–0.65</td>
</tr>
<tr>
<td>BDE-190/173</td>
<td>7</td>
<td>2.3,3,4,5,6</td>
<td>0.018 ± 0.18</td>
<td>&lt;0.0004–0.74</td>
</tr>
<tr>
<td>BDE-183</td>
<td>7</td>
<td>2.3,4,4,5,5'</td>
<td>0.052 ± 0.07</td>
<td>&lt;0.0004–0.23</td>
</tr>
<tr>
<td>BDE-138</td>
<td>6</td>
<td>2.3,3,4,5'</td>
<td>0.025 ± 0.04</td>
<td>&lt;0.0004–0.13</td>
</tr>
<tr>
<td>BDE-153</td>
<td>6</td>
<td>2.3,4,4,5,5'</td>
<td>0.006 ± 0.01</td>
<td>&lt;0.0004–0.04</td>
</tr>
<tr>
<td>BDE-154</td>
<td>6</td>
<td>2.2,4,4,5,6</td>
<td>0.010 ± 0.02</td>
<td>&lt;0.0001–0.08</td>
</tr>
<tr>
<td>BDE-85</td>
<td>5</td>
<td>2.2,3,4,4'</td>
<td>0.015 ± 0.03</td>
<td>&lt;0.0004–0.10</td>
</tr>
<tr>
<td>BDE-99</td>
<td>5</td>
<td>2.2,4,4,5</td>
<td>0.026 ± 0.03</td>
<td>&lt;0.0003–0.12</td>
</tr>
<tr>
<td>BDE-100</td>
<td>5</td>
<td>2.2,4,4,6</td>
<td>0.042 ± 0.07</td>
<td>&lt;0.0003–0.19</td>
</tr>
<tr>
<td>BDE-66</td>
<td>4</td>
<td>2.3,4,4'</td>
<td>0.006 ± 0.02</td>
<td>&lt;0.0003–0.08</td>
</tr>
<tr>
<td>BDE-47</td>
<td>4</td>
<td>2.2,3,4,4'</td>
<td>0.059 ± 0.08</td>
<td>&lt;0.0003–0.25</td>
</tr>
<tr>
<td>BDE-71</td>
<td>4</td>
<td>2.3,4,4'</td>
<td>0.015 ± 0.02</td>
<td>&lt;0.0004–0.06</td>
</tr>
<tr>
<td>BDE-28</td>
<td>3</td>
<td>2.4,4'</td>
<td>0.002 ± 0.001</td>
<td>&lt;0.0004–0.01</td>
</tr>
<tr>
<td>BDE-17</td>
<td>3</td>
<td>2.2,4</td>
<td>0.003 ± 0.001</td>
<td>&lt;0.0007–0.01</td>
</tr>
</tbody>
</table>
BDE-183 in bottom rock biofilm ($p < 0.05$). These results must be considered tentative in view of the small numbers of cases defining the correlations. Altitudinal gradients encompassing more cases should be undertaken for confirmation. In these cases, the altitudinal concentration gradients involve two orders of magnitude for a difference of 1060 m (Fig. 2). These gradients evidence the feasibility of PBDE including BDE-209 for long-range atmospheric transport. Thus, despite its low volatility (Wania and Dugani, 2003), this decabrominated compound can be found in remote mountain lakes situated at 2688 m above sea level.

Increased precipitation and snow accumulation at higher mountain altitudes may be potential sources for the enhanced deposition of this compound and the less brominated PBDEs. However, studies in this geographic area have found no consistent patterns corresponding to altitude or depth of the snow layer in the distribution and chemistry of major components in winter snowpack in the altitude range of 1820–3200 m above sea level (Bacardit and Camarero, 2010). This result is consistent with a previous study in the area showing lack of altitudinal influence in the amount and chemistry of precipitation in an altitude range of 1600–2200 m above sea level (Camarero and Catalán, 1996). These previous results make unlikely that altitudinal changes in precipitation and snow deposition with altitude may determine the PBDE concentration increase along this Pyrenean lake profile.

Previous studies reported altitudinal distributions of organohalogen compounds in remote mountain areas, either in aquatic organisms (Grimalt et al., 2001; Gallego et al., 2007; Demers et al., 2007) or adsorbed in soils (Ribes et al., 2002), snow (Blais et al., 1998; Carrera et al., 2001) or plants (Grimalt et al., 2004), explained by the partial condensation of their atmospheric gas phase standing reserve. The process is consistent with the global distillation effect (Wania and Mackay, 1993) and requires gas phase transport of semi-volatile compounds (Grimalt et al., 2001, 2004; Daly et al., 2007) such as the organochlorine pollutants of these previous mountain studies. These compounds have volatilities of $10^{-2.5}$–$10^{-3.9}$ Pa (Grimalt et al., 2001) which are similar to those of BDE-47 and BDE-99, $10^{-3.5}$ and $10^{-4.2}$ Pa (Chen et al., 2003) respectively and are higher than those of BDE-183 and BDE-173/190, $10^{-6.1}$ and $10^{-6.6}$ Pa respectively.

In this context, BDE-209 stands out for its low volatility, $10^{-8.3}$ Pa (Wania and Dugani, 2003), i.e. more than four orders of magnitude lower than that of the organochlorine range. Accordingly, this compound predominantly occurs in the particulate phase (Gouin and Harner, 2003; Hoh and Hites, 2005; Strandberg et al., 2001; Ter Schure et al., 2004; Breivik et al., 2006). Despite this association mode, evaluations based on experimentally determined deposition velocities have pointed to a much higher capacity for long-range atmospheric transport of this compound than initially estimated (Breivik et al., 2006). In addition, the association to particles may protect it from significant UV-decomposition on its way to high mountain lakes, as occurs with polycyclic aromatic hydrocarbons (Fernandez et al., 2000, 2002). In any event, the BDE-209 vertical gradient observed (Fig. 2) is challenged by the predominant particle-association of this compound.

### 3.3. Transport and transformation mechanisms

The cold condensation theory referred to above is consistent with the annual average air temperatures of mountain sites in Europe (Grimalt et al., 2001; Vives et al., 2004; Gallego et al., 2007) and the Andes (Grimalt et al., 2004). Transformation of the altitudinal distributions of Fig. 2 into equivalent temperatures using the annual average temperatures of each lake shows concentration gradients in line with temperature dependence (Fig. 3). This approach allows joint representation of the BDE concentrations from both the Pyrenean and Tatra lakes vs. the reciprocal of temperature (Fig. 3). Vel’ke Hincovo is the lake with lower air temperatures and consequently higher PBDE concentrations. In nearly all cases, lower temperatures correspond to higher BDE concentrations.
Enthalpies calculated from the log-transformed concentrations of PBDEs in the Pyrenean and Tatra samples for the congeners exhibiting statistically significant temperature dependence in the Pyrenean series alone can be explained by loss of statistical power because of the lower number of lakes and elimination of the case with highest concentrations from the correlations. However, in practically all cases, PBDE concentrations increase with the altitude of the lake.

Possible changes in retention capacity of the lake catchments at increasing altitude could be considered for washout differences into the lakes and therefore causes of altitudinal dependence in PBDE accumulation. However, the altitudinal pattern of relative abundances of these compounds (Fig. 4) and the differences in PBDE distributions between biofilm types (Fig. 4) cannot be explained by this hypothesis. Conversely, they are consistent with a temperature-dependent effect.

Calculation of the apparent enthalpies derived from the slopes of the statistically significant correlations and comparison with the theoretical vaporization and solubilization enthalpies provides further insight into the processes involved in these altitudinal trends. In most cases, the experimental values are much higher than the theoretical estimates from the physical-chemical constants of the compounds, e.g. 980–760 kJ mol\(^{-1}\) for BDE-209 or 500–690 kJ mol\(^{-1}\) for BDE-47 (Table 3). The differences between theoretical and apparent enthalpies are extremely high, e.g. 570–780 kJ mol\(^{-1}\) in the case of BDE-209 (Table 3), indicating that processes other than condensation and solubilization must

**Table 3**

<table>
<thead>
<tr>
<th>Lakes</th>
<th>(r^2)</th>
<th>(p)</th>
<th>Slope</th>
<th>(\Delta H^e)</th>
<th>(\Delta H^{\text{theoretical}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P × T</td>
<td>P</td>
<td>P × T</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>BDE-209</td>
<td>Rock biofilm (top)</td>
<td>0.98</td>
<td>0.99</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Rock biofilm (bottom)</td>
<td>0.86</td>
<td>0.86</td>
<td>0.023</td>
<td>0.023</td>
</tr>
<tr>
<td>BDE-190</td>
<td>Rock biofilm (top)</td>
<td>0.85</td>
<td>0.93</td>
<td>0.028</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Silt biofilm</td>
<td>0.85</td>
<td>0.93</td>
<td>0.028</td>
<td>0.03</td>
</tr>
<tr>
<td>BDE-183</td>
<td>Rock biofilm (top)</td>
<td>0.83</td>
<td>0.96</td>
<td>0.031</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Rock biofilm (bottom)</td>
<td>0.91</td>
<td>0.94</td>
<td>0.012</td>
<td>0.02</td>
</tr>
<tr>
<td>BDE-154</td>
<td>Rock biofilm (top)</td>
<td>0.95</td>
<td>0.95</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Rock biofilm (top)</td>
<td>0.88</td>
<td>0.88</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td>BDE-47</td>
<td>Silt biofilm</td>
<td>0.90</td>
<td>0.89</td>
<td>0.012</td>
<td>0.012</td>
</tr>
</tbody>
</table>

a P × T: Pyrenean and Tatra lakes (\(n = 5\)), P: Pyrenean lakes (\(n = 4\)).
b Enthalpies (kJ mol\(^{-1}\)) calculated following the equation: \(\Delta H = SR\ln(10)\), where \(S\) = slope of the regression straight lines, \(R = 8.314\) J K\(^{-1}\) and \(\ln(10) = 2.303\).
c Summed condensation (Fernandez et al., 2002; Tittlemier et al., 2002) and solubilization theoretical enthalpies. Solubilization enthalpies for PBDE were estimated from (Dickhut et al., 1986).
d Octanol–air exchange (Harner and Shoheib, 2002).
determine the air temperature-dependent accumulation of PBDE in the biofilms of high mountain lakes.

Microbial reductive debromination is one of the most important routes for environmental transformation of persistent halogenated compounds. Penta-BDE (Vonrheide et al., 2006), octa-BDE (He et al., 2006; Robrock et al., 2006), deca-BDE (He et al., 2006; Vonrheide et al., 2006) technical mixtures or individual congeners such as BDE-15 (Rayne et al., 2003) and BDE-206, BDE-207, BDE-208 and BDE-209 (Gerecke et al., 2005) have been reported to be degraded under anaerobic conditions. These processes may also occur in lake biofilms after long-range atmospheric transport of these compounds to these sites.

Increasing air temperatures generate longer growing seasons and ice-free periods; productivity rises and littoral environments become richer in organic matter. Higher biofilm thickness and organic matter content increase the formation of anoxic microenvironments during less productive periods of the year in the rock biofilms of the lower lakes. Higher PBDE biodegradation may therefore occur in the lower altitude lakes paralleling the temperature differences. Alternatively, higher rock biofilm thickness could be attributed to higher PBDE dilution and therefore lower concentrations at lower altitudes. However, this hypothesis contradicts the observations of silt biofilms whose thickness is not altitudinal-dependent and their PBDE concentrations also show altitudinal concentration gradients. In this context, the differences in PBDE distributions between silt and rock biofilms are key findings suggesting that reductive dehalogenation of PBDE by anaerobic bacteria, e.g. Dehalococcoides sp., is responsible for the patterns observed. In fact, silt biofilms with higher periods of anaerobiosis and similar organic matter content along the altitudinal gradient (Bartrons et al., 2010) show the same PBDE distribution than rock biofilms from low altitude lakes.

Further insight into this degradation effect is obtained when considering the qualitative PBDE changes by compilation of the ratio between each PBDE and total PBDE concentrations for the rock biofilms analyzed in the lakes considered for study shows a clear temperature dependence, i.e. more than 80% BDE-209 at annual average air temperatures of 1 °C, and less than 20% BDE-209 at temperatures higher than 4 °C (Fig. 4). Since anaerobic microbial degradation of BDE-209 involves the formation of most PBDEs listed in Table 1 (Tokarz et al., 2008) the changes in these ratios may reflect the extent of transformation of BDE-209 at different temperatures. In contrast, silt biofilms do not show this temperature dependence, as they are characterized by long anoxic periods, irrespective of the altitude at which the lake is located, and thus high degradation occurs in all of them (Fig. 4). This higher degradation in silt microbial biofilms is also consistent with their PBDE concentrations, which are much lower than in rock biofilms (Table 2).

BDE-209 may reach high mountain sites in association to particles and be better preserved at low temperatures (high altitude) than at warm temperatures (low altitude). Since PBDE microbial degradation involves transformation of the more brominated congeners into others less brominated, e.g. nona-, octa-, hexa-bromodiphenyl ethers (Bezares-Cruz et al., 2004; Tokarz et al., 2008; La Guardia et al., 2007), BDE-47 (He et al., 2006; Tokarz et al., 2008) and others, this process may also account for the enhanced thermal dependence of BDE-47, BDE-100, BDE-154 and BDE-173/190 observed in mountains. For compounds such as BDE-47, the convective diurnal cycles in mountains during summer may add an upwards transport mechanism to the preservation mechanism.

4. Conclusions

Climate-related processes which generate altitudinal and latitudinal concentration gradients of PBDE include biodegradation as well as global distillation long-range transport effects, e.g. volatilization, cold condensation and lipophilic phase-transfer which depend on the physical—chemical properties of the compounds. Biodegradation enhancement or depletion may respond to both direct thermal dependence and availability of anaerobic (micro) environments. This microbial mechanism is needed to explain the relative abundances of PBDEs and their within lake differences between rocky and sediment microbial biofilms, thereby showing that the altitudinal pattern observed is not purely due to water temperature control on bacterial activity but also to changes in the availability of anaerobic microenvironments which increase with increasing lake productivity at lower altitudes. To a significant degree, these microbial processes may also influence the global distribution of other organohalogen pollutants.

Acknowledgments

This work has been supported by the EU Projects Euro-Limpacs (GOCE-CT-2003-505540) and ArcRisk (FP7-ENV-2008-1-226534), Spanish MEC project Trazas (CGL2004-02989) and Consolider Ingenio “GRACCIE” program (CSD2007-00067). Technical assistance in instrumental analysis by R. Chaler, D. Fanjul, and R. Mas, analytical advice by J. López and P. Fernández, field help by L. Camarero, M. Bacardit, G. Mendoza, E. Gallego, and S. Jarque is acknowledged. One of the authors, M.B., thanks a FPU grant of the Spanish Ministry of Education and Science.

References


