Comparison of Multi-Year Air Measurements of Polybrominated Diphenyl Ethers (PBDEs) Between the Arctic and the Great Lakes

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a type of flame retardant additives used in commercial products like polyurethane foams, textiles, and plastics. They are ubiquitous in the environment, presumably the result of release from PBDE-treated commercial products (Hale et al. 2003). PBDEs are being considered as a candidate for persistent organic pollutants (POPs), since they appear to have similar properties of POPs, being persistent, bio-accumulative, toxic, and subject to long-range transport (LRT).

Long-term air monitoring of organic contaminants has been conducted at Alert, Nunavut, since 1992 under the Northern Contaminants Program. Fifteen PBDEs were added to the chemical target list starting from 2002. Air concentrations of PBDEs in 2002-2004 at Alert showed increasing trends for major PBDE congeners with doubling-times of 2-6 years (Su et al. 2006), which are similar to growth rates found in biotic samples (Hites 2004). During the same sampling period (2002-2004), gaseous and particle-bound concentrations of 15 PBDEs were measured continuously at Point Petre in the Great Lakes region. Point Petre is in the mid-latitude and close to source regions, whereas Alert locates in the remote Arctic. Comparison of multi-year measurements between these two locations could shed light on LRT potential of PBDEs to the Arctic. Moreover, similarity and difference of seasonality and inter-annual trends may provide insights into important factors controlling air concentrations of PBDEs.

Materials and Methods

Alert (80°30'N/62 °20'W) is located in the Canadian High Arctic. Approximately 13,000 m^3 of air was sampled weekly using a high volume air sampler, which is composed of a tray of one glass fiber filter (GFF) and two polyurethane foam (PUF) plugs. GFF and PUF blanks were taken once every four weeks in the field. The GFF and PUF samples were Soxhlet-extracted by dichloromethane (DCM) and hexane, respectively. Extracts of the GFF and PUFs were combined to form one composite for each sample and subject to clean-up and fractionation by a deactivated Florisil column. Prior to sample cleanup, $^{13}C_{12}$-BDE-209 was added to monitor recovery between sample clean-up and instrument analysis. Details in sampling, extraction, and cleanup were reported in previous papers (Fellin et al. 1996; Su et al. 2006). Samples were analyzed by a gas chromatograph (Agilent 6890) equipped with an auto-sampler (Agilent 7683) and a mass spectrometric detector (MSD, Agilent 5973). Fourteen PBDE congeners (namely, BDE-17, 28/33, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, and 190) were identified using by 79/81 *m/z* (target/qualifier) in selected ion monitoring (SIM) mode. BDE-154 was additionally monitored by 484 *m/z* to avoid coelution with polybrominated biphenyl 153. The target/qualifier ions for BDE-209 and $^{13}C_{12}$-BDE-209 were 487/485 *m/z* and 495/493 *m/z*, respectively. The procedural blanks were either non-

detectable or much lower than the field blanks. Recovery of the spiked blanks was in the range of 68±10%-97±28% (*n*=11) for PBDE congeners of interest, except for BDE-183 with a recovery of 44±28%. A good internal recovery of 87±23% (*n*=90) was achieved for $^{13}C_{12}$-BDE-209. Compounds below the instrument detection limits (IDLs) were substituted with ⅔IDLs. Data reported here were not blank-corrected or adjusted by recoveries.

Point Petre (43°50'N/77 °09'W) is a rural site of the Integrated Atmospheric Deposition Network (IADN) in the Great Lakes region. A GMW PS1 high-volume air sample consists of one GFF and a glass cartridge containing *ca.* 20 g of Supelpak-2 (XAD-2 resin, 20-60 mesh, Supelco). Approximately 950 m^3 of air was collected over 72 hours every month. Field blanks of GFF and XAD were taken each time when samples were collected. GFF and XAD samples were Soxhlet-extracted with DCM separately for 24 hr. Prior to extraction, 10 ng of PCB-30 and 204 were added as surrogates to monitor recoveries. The extracts were dried using anhydrous granular sodium sulphate and passed through a GFF, and further reduced in volume to 1 mL. The samples were cleaned up by a Florisil column. Details in sampling, extraction, and cleanup can be found in a previous paper (Shoeib et al. 1999). Fifteen PBDEs (i.e., BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) were separated by a DB5 column (15m length × 0.25 mm i.d. × 0.25 µm thickness, J&W Scientific), and quantified using GC-ECD. Confirmatory analysis of PBDEs was carried out for 2 selected samples by using GC-electron capture negative ion mass spectrometry (HP5989B MS) (GC-ECNI-MS). PBDEs were separated by a longer column (DB5, 30m length × 0.25 mm i.d. × 0.25 µm thickness, J&W Scientific), and monitored by 79/81 *m/z* (target/qualifier) in the SIM mode. Analytical results agreed well between GC-ECD and GC-ECNI MS for the 2 samples. However, relatively poor response was found for non-volatile PBDE congeners (e.g., BDE-209), presumably the result of less sensitivity of MS for this compound. External recovery tests were carried out by spiking GFF and XAD with 10 ng of PBDEs, and results showed good recoveries of >80% for all target congeners. Internal recovery obtained from PCB-30 and 204 was in the range of 60% - 110%.

Results and Discussion

PBDEs had been quantified for all samples collected in 2002-2004 at Point Petre. Data in 2003-2004 at Point Petre are being subject to quality control currently; therefore, only 2002 measurements are reported here. However, the full set of data will be presented in the BFR 2007 Meeting.

Congener profiles of atmospheric PBDEs in 2002 are displayed in Figures 1A and 1B for individual sampling event at Alert and Point Petre, respectively. For the sake of simplicity, air concentrations of different congeners are averaged over 2002, and an "average" of congener profile is shown for each site. Congener profiles appear similar – dominant congeners at both sites were BDE-47, 99, and 209 (Su et al. 2006). Major congeners at Point Petre also include BDE-100, 153, 154, and 183. It indicates that both sites were strongly affected by usage of "penta-BDE" and "deca-BDE" technical mixtures. At Point Petre, the 7 PBDEs consisted of 97% (93%-99%, *n*=14) of Σ_{15}BDE. However, differences were also found between the two sites. Firstly, BDE-28/33 were frequently observed at Alert, but BDE-28 was detected in none of the 14 samples at Point Petre. Alaee et al. (2003) suggested that presence of mono-, di-, and tri-BDE in Arctic air was likely related to photo-degradation of PBDEs when they are transported through atmosphere. This is consistent with the difference of BDE-28 between Alert and Point Petre, since Point Petre is close to source regions whereas Alert locates in remote area. Secondly, BDE-183 was more often detected and showed relatively higher abundance at Point Petre than Alert (Figure 1). This suggests that

air at Point Petre was influenced by applications of "octa-BDE" mixture as well. Ratios of BDE-47/99 and 99/100 were 1.1 ±0.26 and 5.4±1.4 (n=104) at Alert, and 1.4 ±0.48 and 6.9±3.5 (n=14) at Point Petre (Table 1). Table 1 also includes ratios of BDE-47/99 and 99/100 in vapour phase, which are equilibrated with technical "penta-BDE" mixtures at reference temperatures (0 °C at Alert and 20 °C Point Petre). It is apparent that observed ratios of BDE-47/99 were lower than predicted ones in vapour at both sites, whereas that of BDE-99/100 were higher than predictions, suggesting aging sources of "penta-BDE" technical mixtures.

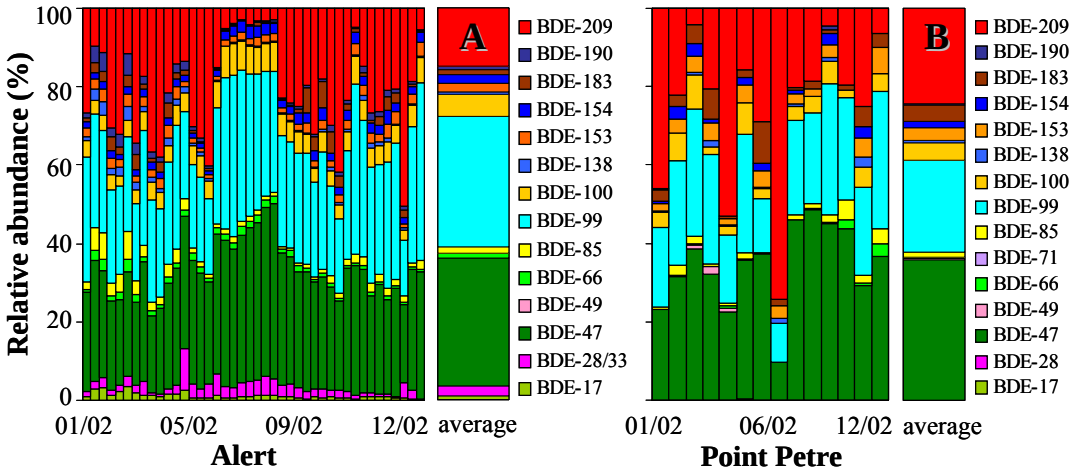

Figure 1. Relative abundance (%) of PBDE congeners in 2002 at Alert (A) and Point Petre (B).

Table 1. Ratios of BDE-47/99 and 99/100 at Alert and Point Petre, and those in technical "penta-BDE" mixtures and equilibrated vapour phase after being adjusted at ambient temperatures.

	Alert (n=104)	"penta-BDE" mixture [a]		adjusted at 0 °C [b]	
		DE-71	Bromkal 79-8DE	DE-71	Bromkal 79-8DE
BDE-47/99	1.1±0.26	0.79	0.96	14	17
BDE-99/100	5.4±1.4	3.7	5.7	1.9	2.9

	Point Petre (n=14)	"penta-BDE" mixture [a]		adjusted at 20 °C [b]	
		DE-71	Bromkal 79-8DE	DE-71	Bromkal 79-8DE
BDE-47/99	1.4±0.48	0.79	0.96	9.2	11
BDE-99/100	6.9±3.5	3.7	5.7	2.2	3.4

[a] Data of "penta-BDE" mixtures are from La Guardia et al. 2006 (Environ Sci Technol 40: 6247).
[b] Data of vapor pressure are from Tittlemier et al. 2002 (Environ Toxicol Chem 21: 1804).

Mean and median concentrations of PBDEs in 2002 at the two sites are shown in Table 2. Concentration ranges for individual congeners are also listed as reference. It appears that dominant congeners (i.e., BDE-

47, 99, and 209) had similar concentrations at the two sites. Total concentrations of 15 PBDEs (Σ_{15}BDE) were also fairly comparable between the two sites.

Table 2. Mean and median concentrations (pg·m^{-3}) of PBDEs, and concentration ranges in 2002 at Alert and Point Petre.

		Alert			Point Petre		
		mean	median	range	mean	median	range
Tri-BDE	BDE-17	0.055	0.029	0.022-0.20	0.0012	BDL	BDL-0.017
	BDE-28	0.17	0.11	0.020-0.72	BDL	BDL	BDL
Tetra-BDE	BDE-47	2.2	1.3	0.21-11	2.6	1.6	0.42-7.2
	BDE-49	---	---	---	0.018	BDL	BDL-0.089
	BDE-66	0.086	0.041	0.021-0.42	0.026	0.022	BDL-0.082
Penta-BDE	BDE-85	0.11	0.059	0.045-0.71	0.10	0.095	BDL-0.20
	BDE-71	---	---	---	BDL	BDL	BDL
	BDE-99	2.2	1.0	0.19-15	1.7	1.3	0.44-3.6
	BDE-100	0.40	0.19	0.031-2.1	0.31	0.28	BDL-0.98
Hexa-BDE	BDE-138	0.034	0.032	0.024-0.097	0.043	0.040	BDL-0.14
	BDE-153	0.14	0.078	0.025-1.2	0.25	0.20	BDL-0.83
	BDE-154	0.16	0.086	0.015-0.81	0.12	0.065	BDL-0.37
Hepta-BDE	BDE-183	0.081	0.037	0.018-0.53	0.30	0.13	0.042-2.0
	BDE-190	0.046	0.044	0.034-0.079	0.0068	BDL	BDL-0.066
Deca-BDE	BDE-209	1.0	0.82	0.091-2.4	1.8	1.4	0.16-5.6
Σ_{15}BDE		6.7	4.7	0.78-32	7.3	6.4	2.5-19

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