SPATIAL DISTRIBUTION AND SEASONAL VARIATION OF PBDES IN ARCTIC AND GREAT LAKES AIR

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Introduction:

Polybrominated diphenyl ethers (PBDEs) are a group of halogenated aromatic organic compounds used as flame-retardants. The annual usage of PBDEs rose from 40,000 in 1992[1] to 67,000 in 1999[2]. Similar to European data, recent data from North America indicated that PBDEs are ubiquitous environmental contaminant. PBDEs in particular BDE-47, 99, 100, and 153 have been detected in various environmental compartments. For example, Hales et al[3] reported concentrations up to 57 μg/g lipid weight PBDEs in carp composite samples from rivers in southern Virginia. These are among the highest concentrations of PBDEs reported to date in biota[4]. The main concern in North American environment is the sharp increase in the concentrations of PBDEs that has been observed over the past 20 years. Luross *et al.*[5] reported that the levels of PBDEs increased by 300 fold over the past twenty years in lake trout from Lake Ontario. The increase in concentration is not limited to the industrialized areas such as Lake Ontario basin, but similar increase have been observed in ringed seal from Holman Islands (Northwest Territories)[6] and in beluga whale from Baffin Island (Nunavut)[7].

Atmospheric transport and deposition has been identified as a major source of persistent organic pollutants such as PCBs to pristine areas such as the Arctic.[8] Recent data on congener specific determination indicated that the vapor pressure of PBDEs ranged between 1.28×10^{-1} for BDE-2 and 8.43×10^{-6} for BDE-153[9] are within the same range as PCBs[10]. Lower brominated BDEs such as BDE-47 are predominately in the vapor phase at ambient temperatures, whereas higher brominated BDEs such as BDE-209 are predominately on the particulate phase, and some other BDE congeners such as BDE-99 and -153 can exist in both phases. Gas/particle phase distribution is the key factor, which controls the transportability and deposition of contaminants to the water bodies.

In this study, concentrations of PBDEs in air samples (vapor and particulate bond) collected at Alert, Tagish and Point Petree in 1994 are presented. Spatial distributions, seasonal variations, and gas particulate distributions are also discussed.

Methods and Materials:

Air samples were collected from Alert on Ellesmere Island (82°30'N, 62°20'W) and Tagish in the Western Yukon (60°20'N, 134°12'W). Weekly samples have been collected at these

two sites since 1992. At each site a high volume air samples was operated year round. Each sample was collected over the course of a week (6 days). The Flow rate was maintained at 1.13 m^3/min resulting in approximately 11000 m^3 of air aspirated. The polyurethane foam plug and filters were extracted with hexane and DCM respectively. Half of the samples were used for classical POPs, and the other half of the extracts were archived for future use. As part of this study, a sub sample from the archive was retrieved and analyzed for PBDEs.

As part of the Integrated Atmospheric Deposition Network (IADAN), weekly samples were collected in duplicate at Point Petre master station (Lake Ontario), and were stored as backup for the routine analysis of POPs. These samples were collected using a Sierra Anderson PS-1 PUF sampler. Initially PUFs and filters were extracted with hexane and DCM respectively. Filters were subsequently extracted with toluene to ensure that the extraction of BDE-209 was complete. The extracts were analyzed with HRGC/HRMS without any further clean up.

Premixed standard solution of Br_2-Br_7 PBDE congeners was purchased from Cambridge Isotope Laboratories (EO-4980). PBDE determinations were performed on a Micromass Ultima HRGC/HRMS, equipped with a HP 6890 gas chromatograph and CTC A200 auto-sampler. The GC injection port was configured for 1 uL splitless injections, held at a temperature of 280°C, and operated in constant flow (1.2 mL/min) mode. Gas chromatographic separation prior to MS was achieved using a 60 m X 0.25 mm X 0.25 μm Restek Rt_x5 capillary column. The initial oven temperature was 80 °C, held 1.5 min, raised to 180 °C at 15 °C/min, raised to 280 °C at 2°C/min and held for 35 minutes. Ionization was performed by electron ionization (EI) at an electron voltage range of 30 to 40 eV depending on the optimization parameters of the instrument. Source temperature was 230°C and the resolving power of the analyzer was 10 000. The instrument operated under selected ion recording (SIR) conditions.

Results and Discussion:

PBDEs were observed in all atmospheric samples collected in 1994. The total PBDE levels in Alert ranged between 10 and 700 pg/m^3 presented in Figure 1. There are only limited values reported on the concentrations of PBDEs in ambient air. Ambient air concentrations of PBDEs from USA ranged between 77pg/m^3 for air samples collected in Chicago (Illinois) 6.9 pg/m^3 for air samples collected at Eagle Harbor (Michigan) [11]. Concentrations of PBDEs in ambient air from Japan and Taiwan which ranged between 7.1 and 53 pg/m^3.[12] On the other hand, much higher levels were observed in Tagish (31-2000pg/m^3). The high levels of PBDEs in Tagish can possibly be attributed to local burning of the garbage in the vicinity of the sampling site. These values are much lower than those reported by Sjöden et. al[13] from an electronic disnaturing plant (66,690 pg/m^3 of PBDEs in ambient air samples from dismantling hall and 284,770 pg/g in BFR shredder area).

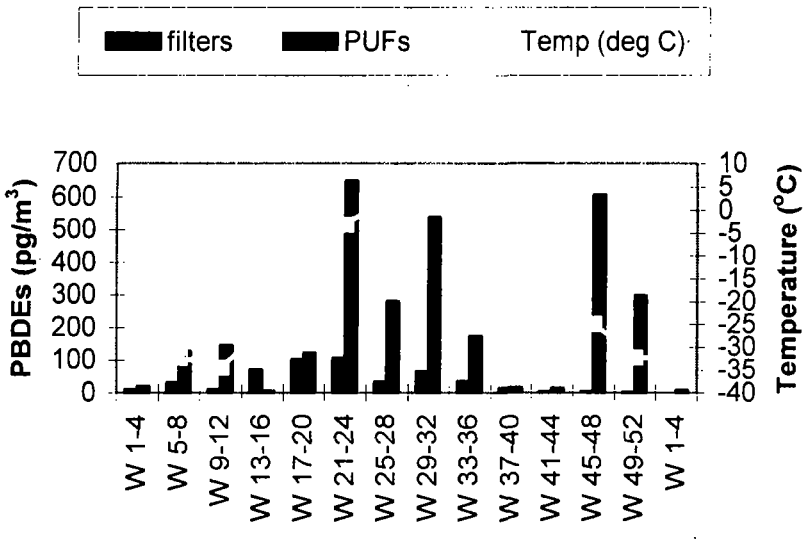

Figure 1. Concentration of PBDEs in 4 week composite samples from Alert in 1994.

In these samples, Penta-BDEs homologue group predominated by BDE-99 had the highest concentration followed by tetra-BDE group predominated by BDE-47. Hexa-BDEs homologue group had the third highest concentration observed in these samples. Hepta-BDEs were only observed in a limited number of samples. Octa-, nona-, and deca- BDEs were not detectable in these samples.

The ratio of BDE-153 in vapor phase and particulate bound in air samples from Tagish is presented in Figure 2. More than 50% of BDE-153 is bound to particulate phase during the colder periods of the year. In contrast, to BDE-47 this is predominantly in vapor phase throughout the year.

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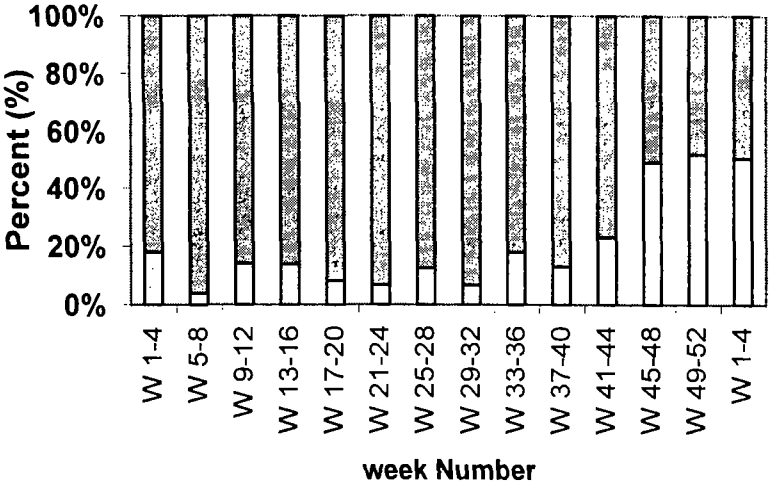

Figure 2. Distribution of BDE-153 in 4 weeks composite samples from Tagish in 1994.

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