Polybrominated Diphenyl Ethers in Ambient Air across North America

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardant additives that are used in a variety of commercial and household products to reduce their flammability. As a result of their use in a wide range of materials and their detection in numerous environmental samples, PBDEs have been identified as important emerging contaminants[1]. Their concentrations in the environment are increasing with times, even in remote regions[2,3,4]. Many studies on PBDEs focus on their occurrence in sediments, fish, marine mammals, and human samples[5]. There are only a few investigations reporting concentrations in the atmosphere (e.g.[6,7]). The aim of this study is to investigate levels and spatial trend of PBDEs in air across North America using passive air samplers (PAS) to identify potential sources of PBDEs to the atmosphere.

Materials and Methods

The PAS employed in this study consists of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a steel can with an open bottom[8]. The PAS is deployed at 1.5 m above ground except in locations with a deep snow pack, where deployment height is increased to ensure that the PAS is not covered by snow. Contaminants are taken up in the resin from the atmosphere by diffusion, whereby previous experiments established independence of the sampling rate over a wide range of wind speeds[8]. Previous studies confirmed that most of persistent organic pollutants of environmental concern do not reach equilibrium between the atmospheric gas phase and the XAD-2 resin during 1 yr sampling period. This makes it feasible to interpret the amounts of PBDEs quantified in the PAS in terms of volumetric air concentrations, using a sampling rate that is largely independent of chemical, wind speed and temperature[8].

PAS were deployed at forty sampling stations across North America. Thirty-one were in Canada, five in the USA, and four in Central America (Southern Mexico, Belize, Costa Rica) (Figure 1). A north-south transect in the eastern part of the continent covers 72 degrees of latitude (10° to 82°N) from the Arctic to Central America. An east-west transect in southern Canada ranges from eastern Newfoundland to Vancouver Island covering 72 degrees of longitude (53° to 125°W). Four of these stations constitute an altitudinal transect in the Southern Canadian Rocky Mountains, covering a range of elevation of more than 1500 m. The criteria used in the selection of the sampling sites are given in Shen et al.[9]. Duplicate PAS were deployed at each station in May to July 2000 by shipping the samplers to local contact people or by visiting the sites. After one year,

the PAS were retrieved and stored frozen until analysis. Eight of the stations received additional XAD-mesh cylinders, which remained in the shipping containers throughout the 1-yr deployment period, during which they were taped to the posts holding the sampling shelters. These samples served as field blanks[9].

The XAD-2 from the sampling container was transferred to an elution column and solvent extracted and fractionated as described in detail in Wania et al.[8]. The extracts were analyzed for PBDEs on a Agilent 6890 series gas chromatograph (GC) connected to a Agilent 5973 mass spectrometer (MS) that was operated in the negative chemical ionization (NCI) mode with selected ion monitoring (SIM), using methane as the reagent gas. The two bromide ions at m/z 79 and 81 were monitored. The separation was undertaken on a DB-5MS column (60 m × 250 μm × 0.10 μm) with the following temperature program: 140 °C for 1 min, 20 °C /min to 220 °C, and 2 °C/min to 280 °C. BDE-congeners 47, 99, 100, 153, and 154 were quantified using an internal standard method. The PAS concentrations (in units of $ng{\cdot}PAS^{-1}$) were blank corrected using the averages of field blanks. Time-averaged volumetric air concentrations (C_A; in $pg{\cdot}m^{-3}$) were estimated by dividing the sampler concentration (in $pg{\cdot}PAS^{-1}$) by the product of the deployment period (365 d) and the PAS sampling rate ($0.52\ m^3{\cdot}day^{-1}{\cdot}PAS^{-1}$) [8].

Results and Discussion

BDE-47, 99, 100, 153, and 154 are detected in almost all samples from across North America. Concentrations of the sum of these five PBDE congeners ranged from below the detection limit to 28 $ng{\cdot}PAS^{-1}$ (150 $pg{\cdot}m^{-3}$) and displayed a large variation with latitude and longitude, and between urban, rural and remote areas. The continental distribution pattern for the sum of the five congeners is presented in Figure 1, showing that they are widely dispersed in the North American atmosphere. BDE-47 and 99 are predominant in passive air samples accounting for 73 to 94% of the sum of the five congeners; and their concentrations vary from 0.30 to 13 $ng{\cdot}PAS^{-1}$ for BDE-47 and 0.068 to 11 $ng{\cdot}PAS^{-1}$ for BDE-99. This corresponds to volumetric air concentration between 1.6 to 71 $pg{\cdot}m^{-3}$ and 0.36 to 61 $pg{\cdot}m^{-3}$, respectively.

There are only a few data available on PBDE levels in the North American atmosphere. Strandberg et al.[6] reported that total levels of PBDEs between 1997 and 1999 in rural air of the Great Lakes region ranged from 4.4 to 21 $pg{\cdot}m^{-3}$, and 33 to 71 $pg{\cdot}m^{-3}$ in urban air of Chicago. Gouin et al.[10] reported that PBDE levels in rural air of the southern Ontario ranged from 10 to 230 $pg{\cdot}m^{-3}$ after the bud burst in 2000. Total air concentrations of PBDEs at Alert varied between 10 to 726 $pg{\cdot}m^{-3}$ from January 1994 to January 1995[11]. Our PAS-derived concentrations are comparable with those findings. Levels of the sum of the five congeners in vapor phase in rural air of Ontario ranged from 0.4 to 20 $pg{\cdot}m^{-3}$; and the air concentrations were 44 $pg{\cdot}m^{-3}$ at Toronto and 22 $pg{\cdot}m^{-3}$ at Alert. These results suggest that the PAS provides information sufficiently reliable for the identification of PBDEs over a large scale.

The possible sources of PBDEs are thought to be factories producing brominated flame retardants, the use and recycling of PBDE-treated polymers and plastic products, and waste incineration[12,13]. However, the observed spatial distribution in this study reveals

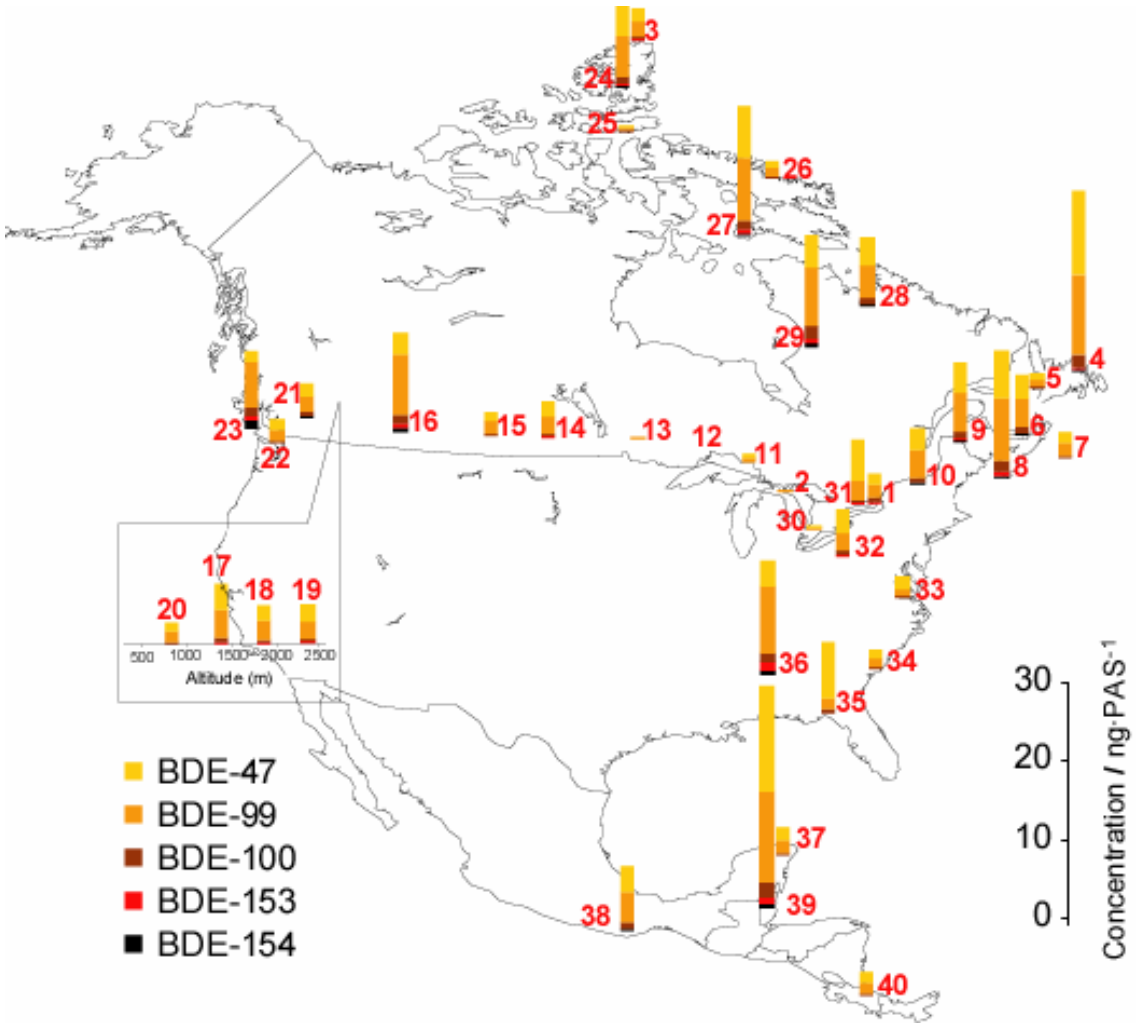

Fig. 1 PBDE concentrations in passive air samplers deployed across North America from summer 2000 to summer 2001.

that PBDE levels are not obviously related to proximity to urban and industrial centers. Although the highest level was found in Belmopan, Belize, intermediate levels were found not only at urban sites, such as Toronto, but also at most rural and remote sites. More than half of these sites even had higher levels of PBDEs than Toronto.

All samples with intermediate levels from rural and remote sites in Canada showed a congener profiles similar to the technical penta-BDE product (24-38 % tetra-BDEs, 50-60 % penta-BDEs, 4-8 % hexa-BDEs), which is used as a flame retardant in foam furniture and textiles[14]. North America accounted for 98% of the global demand for penta-BDE in 1999[15]. Dispersal of penta-containing foam is believed to be one mechanism by which PBDEs enter the environment[16]. A pronounced peak in PBDE air concentrations during a major combustion event has been observed in England[17]. Relatively high levels of PBDEs in rural and remote areas may be related to the open burning of household waste, since this activity occurs mostly in non-urban regions throughout North America,

including remote Arctic communities. Emissions from open burning are difficult to control. In contrast, the emission of PBDEs from recycling facilities and waste incinerators, which are usually located in or close to urban areas, can be reduced by technical means.

Conclusions

The results from this large scale network suggest that PAS can play a useful role in monitoring levels and distribution of PBDEs in the atmosphere. Our dataset indicates that BDE-47 and 99 are predominant throughout the North American atmospheric. Use of the penta-BDE product and residential burning of domestic waste such as plastic, construction debris, agricultural packaging, and other commercial wastes in rural and remote areas may be significant sources of PBDEs to the atmosphere.

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