The Atmospheric Concentrations of Brominated Flame Retardants at Extreme Remote Locations: The Canadian High Arctic and the Tibetan Plateau

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Introduction

Brominated flame retardants (BFRs) have been heavily used in industrial and commercial products for fire prevention since the 1970s. Due to the rising concerns about their toxicity and ubiquitous occurrences in the environment, the production and usage of some more conventional BFRs, such as the polybrominated diphenyl ethers (PBDEs) have been subjected to bans or regulations at the national or international level (de Wit et al, 2006). However, due to the continued demand for fire safety, the manufacturing industry is replacing these banned substances with other BFRs (Hoh et al, 2005). Environmental data on these replacement compounds is scarce and their environmental behavior and the risk they pose mostly unknown.

Most BFRs belong to the group of semi-volatile organic compounds (SOCs), which can volatilize in relatively warm source regions, undergo efficient atmospheric transport over considerable distances, and deposit in very remote locations, in particular in places with low temperatures, such as the Arctic. Atmospheric transport and deposition has been identified as the predominant pathway for PBDEs present to rural/remote locations (Ter Schure et al., 2004). Monitoring the atmospheric concentrations of new BFRs is essential to improve the understanding of their environmental occurrences, long range atmospheric transport (LRAT) and temporal variation.

The Arctic has been used for monitoring the global background of airborne organic contaminants because of its remote location and negligible local emissions. The Northern Contaminants Program (NCP) has conducted air monitoring of SOCs in the Canadian High Arctic since 1992 (Fellin et al., 1996). SOCs detected in Arctic air are highly likely to undergo LRAT.

Known as the “Roof of the World” or the “Third Pole on the Globe”, the Tibetan Plateau is the largest and highest plateau on Earth, with an average elevation of 4200 meters and a spatial extension of 2.5 million km^2. Due to the plateau’s high altitude, sparse human population, and minimal to nonexistent industrial activities, LRAT is believed to be the dominant source of SOCs to the area (Loewen et al. 2007) and mountain cold-trapping may be particularly pronounced in the Himalaya.

This study presents data for year-round continuous BFR measurements in air at these two remote locations. The objective of the study is to address knowledge gaps regarding the occurrence and concentrations of BFRs in remote sites. Furthermore, data analysis may help to identify important factors influencing the air concentrations of BFRs, such as ambient temperature, and to provide insights into potential sources of BFRs to global background sites.

Materials and Methods

The Arctic samples were collected in Alert, Nunavut (82° 30′ N / 60° 20′ W). Air sampling was conducted using a high-volume air sampler with one glass fiber filter (GFF) followed by two PUF plugs. Approximately, 13,000 m^3 of air was sampled over a 1-week period, continuously throughout the study period. The GFF and PUF samples were Soxhlet-extracted with dichloromethane and hexane, respectively. Extracts of the GFF and PUFs for individual samples were combined to form one composite sample prior to cleanup. The sampling, extraction, cleanup and instrumental analysis of PBDEs is identical to those described in an earlier study (Su et al., 2007). BFRs were analyzed by a gas chromatograph (Agilent 6890) equipped with a mass spectrometric detector (MSD; Agilent 5973). An injection volume of 1.0 μL was applied in the pulsed splitless mode with a pulse pressure of 25.0 psi and a pulse time at 1.25 min. Purge flow of 60 mL min^{-1} started at 1.25 min. Thirteen BFRs (Allyl 2,4,6-triBromophenyl Ether (ATE), Pentabromotolune (PBT), 2-Bromoallyl-2,4,6-tribromophenyl Ether (BATE), PentabromoBenzene (PBBe), Hexabromobenzene (HBB), 1,2-Bis(2,4,6--tribromophenoxy)ethane (BTBPE), Tetrabromo-o-chlorotoluene (TBCT), 2,3-dibromopropyl--2,4,6-tribromophenyl Ether (DPTE), 2,2',4,5,5'-Pentabromobiphenyl (BB-101), Pentabromobenzyl Acrylate (PBBA), 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTeBB), bis(2-ethyl-1-hexyl)-tetrabromophthalate (BEHTBP) and Octabromotrimethylphenylindane (OBIND)) were separated on a DB-5MS column (30m×0.25 mm i.d., 0.1 μm film thickness). The carrier gas was helium at a constant flow rate of 1.2 mL min^{-1}. Samples were injected at an inlet temperature of 250 °C. The initial temperature was 80 °C for 2 min, 5 °C min^{-1} to 250 °C, 15 °C min^{-1} to 300 °C and held for 15 min. All BFRs were analyzed by MSD in NCI mode with methane as a reagent gas at a flow rate of 2.0 mL min^{-1}. Temperatures were 290, 230, and 150 °C for interface, ion source, and quadrupole, respectively. The BFRs were quantified by 79/81 m/z and checked with other ions in selected ion monitoring mode. The PBDE standards were purchased from Cambridge Isotope Laboratories, Inc., Andover, MA, USA.

A flow-through sampler (FTS), which consists of a horizontally oriented, aerodynamically shaped, stainless steel flow-tube mounted on ball bearings which allow it to turn into the wind with the help of vanes (Xiao et al. 2007), was deployed to monitor BFR concentrations at a remote Chinese research station located close to Nam Co Lake, Tibet (30° 46.44′ N, 90° 59.31′ E, 4730 m asl). Two P10z PUF disks (Pinta Foamtec, Minneapolis, MN) of 7.62 cm thickness and one 2.54 cm PUF disk were arranged in series inside the sampling cylinder. Fifteen consecutive 1 month-long samples were taken between October 2006 and February 2008. The collected air volume for a single 1-month sample ranged from 4,500 m^3 to 16,000 m^3. Sample preparation and extraction are identical to those described in earlier studies using the FTS (Xiao et al., 2007). Twenty-six PBDE congeners (BDE-30, 17, 28, 49, 71, 47, 66, 100, 119, 99, 154, 153, 139, 140, 138, 156/169, 184, 183, 204/197, 203, 196, 205, 207, 208, 206 and 209) and three BFRs (BTBPE, EHTeBB and BEHTBP) were quantified used GC-HRMS. The instrumental configurations are identical to those in Kolic et al. (2009).

Results and Discussion

Total air concentrations of gaseous and particle-bound phases of BFRs were derived for these two sampling campaigns. BFR levels in Nam Co air were general very low, normally below a few pg/m^3. The dominant PBDE congeners at both sites were always BDE-47, 99 and 209, which are the three major components of the “penta-BDE” and “deca-BDE” technical mixtures (La Guardia et al. 2006),

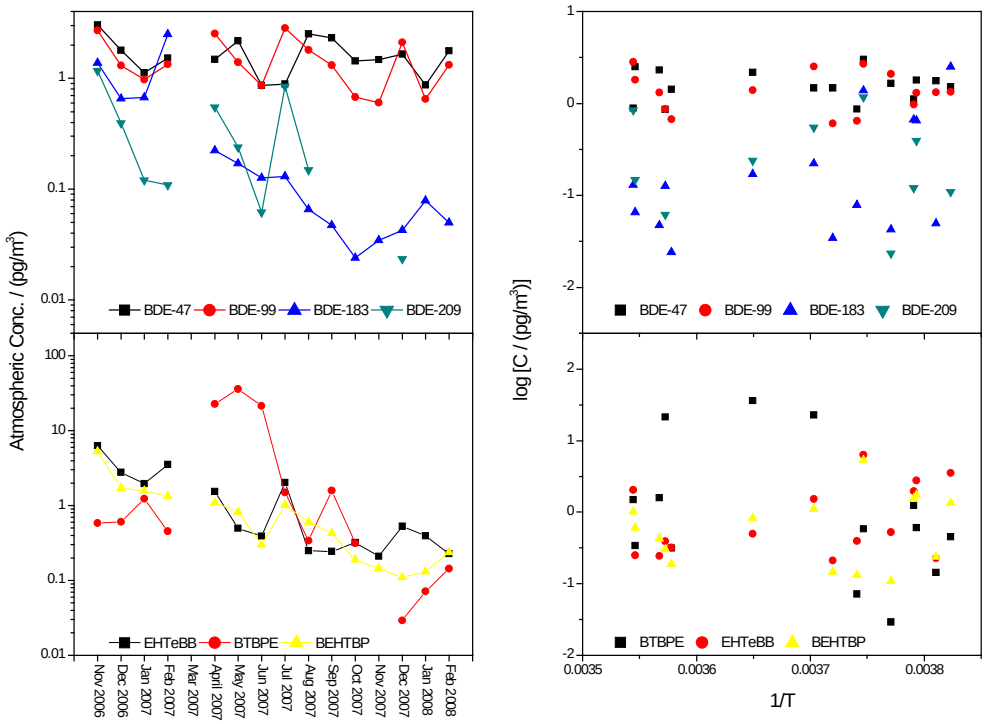

Figure 1. Seasonal variation and temperature dependence of the atmospheric concentrations of PBDEs and other BFR substances at Nam Co.

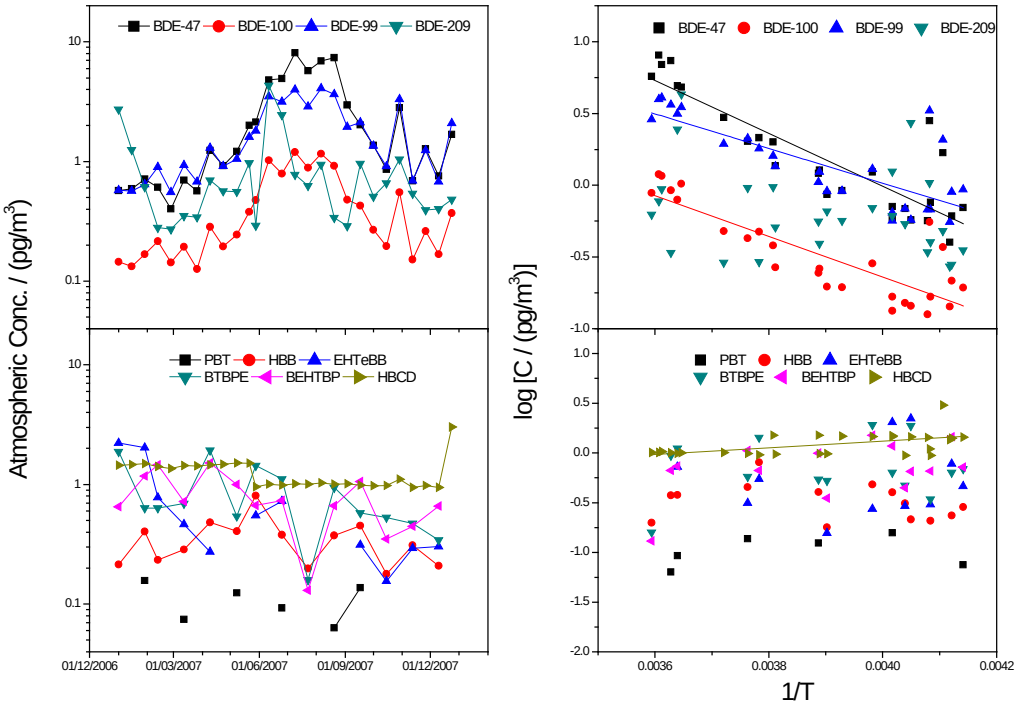

Figure 2. Seasonal variation and temperature dependence of the atmospheric concentrations of PBDEs and other BFR substances at Alert.

while other congeners, such as BDE-100, 183, 153 and 196 were also frequently detected. BTBPE, EHTeBB and BEHTBP were generally detected at both sites as well with concentrations similar to those of the dominant BDE congeners. PBT, HBB and HBCD were sometimes detectable in the Alert atmosphere. Figure 1 and 2 present the seasonal variation and temperature dependence of the atmospheric concentrations of these commonly detectable compounds at Nam Co and Alert, respectively. Although back trajectory analysis has shown that air mass origin at Nam Co was distinctly different during winter and summer, the PBDE concentrations neither show any significant seasonality nor temperature dependence. Meanwhile, the PBDE concentrations at Alert are only slightly higher than those at Nam Co; however, significant seasonal variations and temperature dependence were apparent, which is consistent with previous results (Su et al. 2007). The lack of seasonal variability thus may suggest that PBDEs at Nam Co do not have regional sources, but are reflective of truly global background contamination. A BFR detected in the Tibetan atmosphere thus should be regarded as having a very high potential for long range atmospheric transport.

In contrast to PBDEs, no significant temperature dependence of the new BFR air concentrations was found at either site. However, interestingly the EHTeBB and BEHTBP concentrations at Nam Co show obvious decreasing trends during the sampling campaign.

Considering that air concentrations of new BFRs are similar to those of the PBDEs at both remote sites, suggest that the study of the toxicology and risk of PBDE substitutions should have a high priority.

Acknowledgement

Thanks to the Natural Sciences and Engineering Research Council of Canada and the Northern Contaminant Program for funding.

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