Concentrations of decabromodiphenyl ether in air from Southern Ontario: Evidence for particle-bound transport

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Introduction

Decabromodiphenyl ether (mainly BDE-209) was the most widely used brominated flame retardant in North America in 1999[1]. It is mostly used in plastic housings for small household appliances and office equipment[1]. Recently, restrictions regarding the use of the commercially available pentabrominated diphenyl ether and octabrominated diphenyl ether mixtures have been initiated in the State of California[2] and the European Union (EU)[3]. However, BDE-209 was not included. In the EU, action regarding the use of BDE-209 is dependent on the outcome of a Risk Assessment[4]. Our understanding of the environmental fate and distribution of BDE-209 is limited by the paucity of environmental data. Because the atmosphere is the most important transport route for many organic pollutants it is important to assess levels of these substances in the air. This is especially relevant for assessing transport to remote regions such as the arctic and for assessing loadings to the environment. Butt *et al.*[5] recently showed that BDE-209 dominated the PBDE congener profile in organic films on windows along an urban-rural gradient in Southern Ontario. These results are consistent with ter Schure *et al.*[6], who reported a dominance of BDE-209 in air over the Baltic Sea, with 71% of BDE-209 associated with the particle phase. In this study two complementary efforts were undertaken to compare levels and trends of BDE-209 in relation to other PBDEs: (i) the collection of high volume air samples over several months, at a background forested site, to assess temporal trends and (ii) the collection of passive air samples (PAS), which were deployed at several sites along an urban-rural transect to investigate spatial trends.

Materials and Methods

A PS1-type high-volume air sampler was operated during the winter and spring of 2002 within a young hardwood forest at the James McLean Oliver Ecological Centre (JMOEC) (Fig. 1), located 115 km NE of Toronto. 24-hour samples, corresponding to total air volumes between 250 and 400 m^3, were taken every 6 days from January 23 to April 11, 2002, daily from April 11 to 28, 2002 during a period of rapidly warming temperatures, and again every 6 days from May 4 to June 6, 2002. The particulate fraction of the high-volume air samples was trapped on a Whatman glass microfiber filter (GMF) (grade

GF/A, 10 cm dia., to retain particles above 1.6 µm in diameter) and the gas-phase on a PUF plug (length 8 cm, diameter 6.25 cm, density 0.035 g cm^{-3}). Meteorological data were collected at JMOEC, and for each sampling event two-day back trajectories were acquired from the HYSPLIT transport and dispersion model, using the NOAA Air Resources Laboratory's READY web server [7].

PAS consisting of a PUF disk (14 cm diameter; 1.35 cm thick; density 0.0213 g cm^{-3}; PacWill Environmental, Stoney Creek, ON) were placed inside a stainless steel sampling chamber similar to the one described by Harner et al.[8], and were deployed at several sites along an urban-rural transect (Fig. 1) for two, one-month periods in April and May 2002.[9]

GMFs, PUF plugs and disks were extracted and cleaned-up following the method described by Gouin *et al.*[9]. BDE-209 was analyzed by GC-ECD using a 15 m DB5 column and splitless injection at 260°C. BDE-181 was used as an internal standard. All other PBDEs were analyzed with a Fisons MD800 GC-MS with separation on a 0.18 mm id DB5 MS 30 m column. The MS was run with an NCl source in SIM mode, using ammonia as reagent gas.

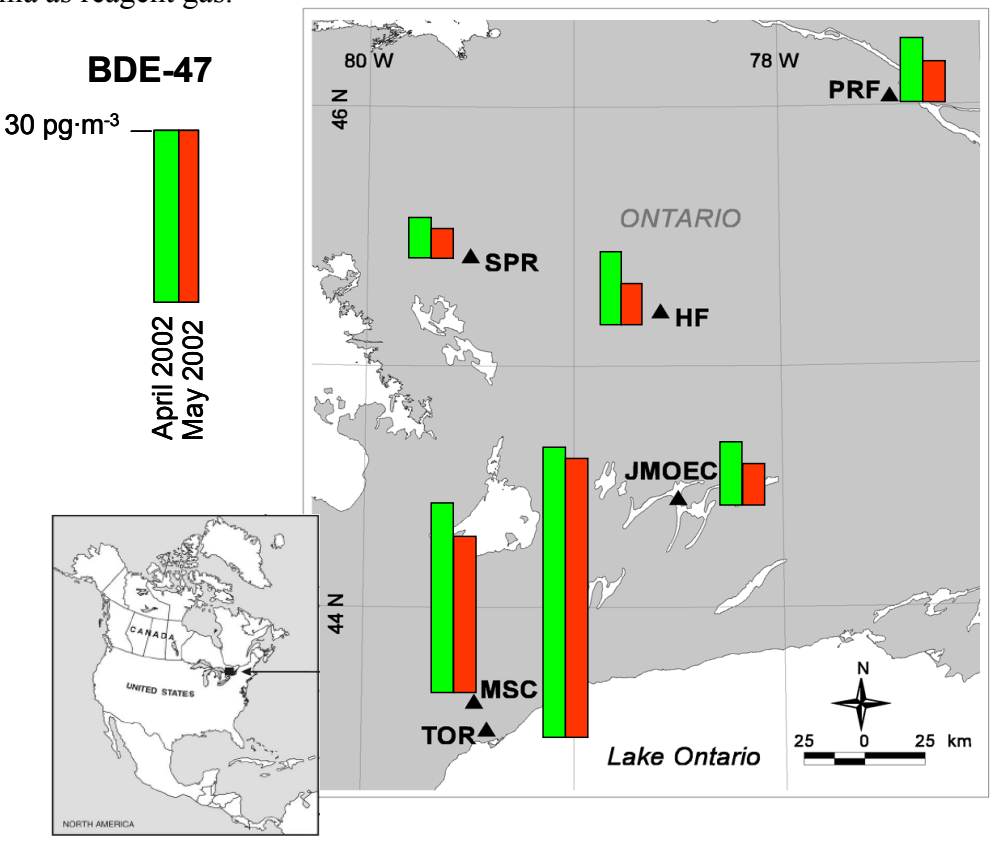

Figure 1: Location of passive air samplers (University of Toronto (TOR), Meteorological Services Canada, Downsview (MSC), JMOEC, Haliburton Forest (HF), Sprucedale (SPR), and Petawawa Research Forest (PRF)) and air concentrations of BDE-47.

Field and method blanks (i.e. solvent blanks) were collected throughout the study. The field blanks for the PUF plugs were characterised by higher levels for the PBDEs than was found in the method blanks, while little difference was observed between method blanks and field blank GMFs. The limit of detection (LOD) values for BDE-209 in the PUF plugs, defined as the mean blank plus 3 times the standard deviation of the blank values, was 9.4 pg·m^{-3}, whereas the GMFs and method blanks were typically below the instrument quantification limit (approximately 0.35 ng total per sample). The LOD for BDE-47 was 0.4 pg·m^{-3}. Analysis of the other PBDEs is presented elswhere[9].

Results and Discussion

Air concentrations for deca-BDE were dominated by the particulate fraction, represented by the concentration in the GMF, and ranged from below the detection limit to 105 pg·m^{-3}, with an average concentration in the particulate phase of approximately 19 pg·m^{-3}, whereas, concentrations in the gaseous phase, represented by the concentration in the PUF plugs were typically <LOD. The concentrations in the gas phase of the remaining PBDE congeners ranged from below the detection limit to 19 pg·m^{-3}, and were dominated

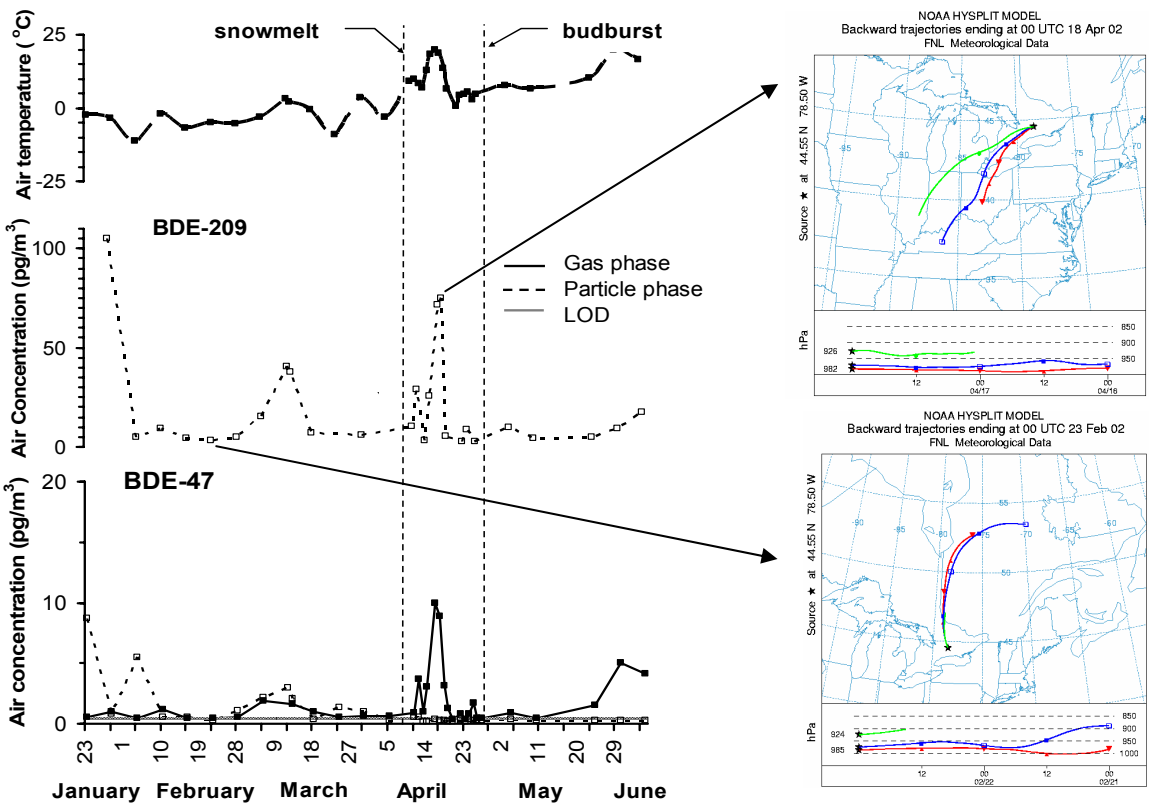

Figure 2: Atmospheric concentrations, represented by gas phase (solid line) and particulate phase (dotted line), for BDE-209, BDE -47 and ambient air temperatures observed at JMOEC between January 23, 2002 and June 06, 2002. Lines between data points have been interpolated to illustrate the overall trend.

primarily by BDE congeners 17, 28 and 47, with BDE-47 typically contributing approximately 50%, whereas, the concentrations in the GMFs ranged from below the

detection limit to 34 pg·m^{-3}, and were dominated by the heavier BDE congeners 47, 99, 100, 153 and 154 with BDE-99 typically contributing 50%. BDE-47 exhibits a strong urban-rural gradient in air concentrations (Fig. 1) suggesting that large urban centres, such as Toronto, may be a source to the surrounding rural environment[9]. The temporal trends for deca-BDE and BDE-47 in the gas and particle phase are shown in Figure 2. Also shown are lines representing complete snowmelt, defined as the date (April 11, 2002) when the depth of the snow pack could no longer be measured at JMOEC, and the date (April 27, 2002) when bud burst was first observed, as well as a line indicating the LOD. BDE-209 and BDE-47 are mostly particle-bound during the winter (Fig. 2). In the spring, BDE-47 is mostly in the gaseous phase, while BDE-209 remains particle-bound.

Between January 23 and June 6, 2002 the temperature at JMOEC showed a very large range, from -11 to 20°C. A strong correlation exists between temperature and the gas phase concentration of BDE-47. The regression of the partial pressure (P) of BDE-47 and reciprocal temperature (T^{-1}) has an r^2 of 0.6 and a p-value of 0.009. However, the temperature dependence for BDE-209 is not significant, with an r^2 of 0.1 and a p-value of 0.07.

Two-day back trajectories (Fig. 2) show that, during the period following snow melt, the air masses arriving at JMOEC had passed over source regions to the south. This period is characterized by a springtime maximum in the gas phase concentration for BDE-47, and a period of elevated atmospheric concentrations in the particulate phase for BDE-209 (Fig. 2). The pulse for BDE-47 may be due to a combination of enhanced surface-air exchange following snowmelt throughout the region and advection of contaminated air from source areas (Fig. 1). However, the elevated concentrations of BDE-209 during this period are most likely due to particle-bound transport from a source region, since this congener is fairly involatile. Interestingly, even during off-peak periods, PBDE-209 exhibited a fairly high air concentration that was not associated with advection from identified source regions (Fig.2). Thus, the abundance of BDE-209 in the atmosphere has implications for transfer to remote and sensitive ecosystems via particle-bound transport and wet and dry particle deposition.

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