



Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005–2013



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ABSTRACT

Air (vapor and particle phase) samples were collected every 12 days at five sites near the North American Great Lakes from 1 January 2005 to 31 December 2013 as a part of the Integrated Atmospheric Deposition Network (IADN). The concentrations of 35 polybrominated diphenyl ethers (PBDEs) and eight other halogenated flame retardants were measured in each of the ~1,300 samples. The levels of almost all of these flame retardants, except for pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), and Dechlorane Plus (DP), were significantly higher in Chicago, Cleveland, and Sturgeon Point. The concentrations of PBEB and HBB were relatively high at Eagle Harbor and Sturgeon Point, respectively, and the concentrations of DP were relatively high at Cleveland and Sturgeon Point, the two sites closest to this compound's production site. The data were analyzed using a multiple linear regression model to determine significant temporal trends in these atmospheric concentrations. The concentrations of PBDEs were decreasing at the urban sites, Chicago and Cleveland, but were generally unchanging at the remote sites, Sleeping Bear Dunes and Eagle Harbor. The concentrations of PBEB were decreasing at almost all sites except for Eagle Harbor, where the highest PBEB levels were observed. HBB concentrations were decreasing at all sites except for Sturgeon Point, where HBB levels were the highest. DP concentrations were increasing with doubling times of 3–9 years at all sites except those closest to its source (Cleveland and Sturgeon Point). The levels of 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) were unchanging at the urban sites, Chicago and Cleveland, but decreasing at the suburban and remote sites, Sturgeon Point and Eagle Harbor. The atmospheric concentrations of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) and bis(2-ethylhexyl)-tetrabromophthalate (BEHTBP) were increasing at almost every site with doubling times of 3–6 years.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) were added to numerous household and commercial products to slow the spread of fire and to save human lives. Once it became obvious that these compounds were environmentally persistent and potentially toxic, their manufacturers voluntarily stopped producing and selling them in the United States. Two major commercial PBDE products, penta- and octa-BDE, were withdrawn from the market at the end of 2004, and the other major PBDE product, deca-BDE, was withdrawn at the end of 2013 (Ma et al., 2013). Other halogenated flame retardants have been introduced to replace these PBDE products. For example, FireMaster 550, FireMaster BZ-54, and DP-45 entered the market in the early 2000s to replace the penta-BDE mixture (Ma et al., 2012a). The major halogenated components of these newer flame retardant formulations are 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) and bis(2-ethylhexyl)-tetrabromophthalate (BEHTBP). As a result of this market shift, EHTBB and BEHTBP are now being widely detected in the environment and in

biota (Dodson et al., 2012; Guerra et al., 2012; Li et al., 2016; Ma et al., 2012a; Peverly et al., 2015; Zhou et al., 2014). Other brominated compounds such as hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE or BTBPE) and decabromodiphenylethane (DBDPE) have also come into their own as replacements for PBDEs, and these compounds are now being found in the environment and in biota (Barón et al., 2014; Cequier et al., 2015; Guerra et al., 2012; Ma et al., 2013; Ricklund et al., 2008; Wu et al., 2011).

TBE is an additive flame retardant marketed under the trade name of FF-680, and it was introduced into the market in the mid-1970s by the Great Lakes Chemical Corporation, now known as Chemtura. Since 2005, TBE has been used as a replacement for octa-BDE by Chemtura (Hoh and Hites, 2005). It is used in acrylonitrile-butadiene-styrene, high-impact polystyrene, thermoplastic elastomers, thermoset resins, coatings, adhesives, polycarbonate, and textiles (Covaci et al., 2011). DBDPE was introduced into the flame retardant market in the early 1990s as a replacement for deca-BDE (Covaci et al., 2011). It is an additive flame retardant marketed under the trade names Saytex 8010 (Albemarle, 2016) and FireMaster 2100 (Chemtura, 2016). The applications of DBDPE include acrylonitrile-butadiene-styrene, high-impact

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polystyrene, polypropylene, engineering resins, wires, cables, elastomers, plastics, foams, and construction materials (Albemarle, 2016). Dechlorane Plus (DP), a highly chlorinated flame retardant produced by OxyChem, is used in nylon, polypropylene, polybutylene terephthalate, phenolic laminates, elastomer substrates, thermosetting resins, and ethylene vinyl acetate wire and cable insulation (OxyChem, 2016). DP is widely detected in the environment (Sverko et al., 2011).

Given these changes in the flame retardant market over the past decade, it is appropriate to ask if the environmental levels of these flame retardants are changing, and if so, at what rate. One way of doing this is to use data from the Integrated Atmospheric Deposition Network (IADN), which is a long-term atmospheric monitoring program that has been in operation since 1990. IADN is a joint United States-Canadian project, which focuses on measuring the spatiotemporal trends of the concentrations of persistent organic pollutants in the atmosphere around the North American Great Lakes. The analysis of 35 PBDE congeners and other brominated or chlorinated flame retardants began in 2005 after PBDEs and some other halogenated flame retardants had been found in atmosphere around the Great Lakes (Hoh and Hites, 2005; Strandberg et al., 2001). EHTBB and BEHTBP were added to this analyte list in 2008.

Some spatial variations and temporal trends of selected flame retardants have been reported previously in IADN samples (Ma et al., 2013; Ma et al., 2012a; Salamova and Hites, 2011a,b; Venier and Hites, 2008; Venier et al., 2012; Venier et al., 2015). Salamova and Hites (2011a) and Ma et al. (2013) reported the spatiotemporal trends of *syn*-DP and *anti*-DP concentrations in air samples collected from 2005 to 2009 and of PBDEs, PBEB, HBB, TBE, and DBDPE in air samples collected from 2005 to 2011, respectively. Ma et al. (2012a) reported the concentrations of EHTBB and BEHTBP in air samples collected from 2008 to 2011. None of these publications presented a unified picture of the behavior of all of these compounds over time. That is the goal of this paper.

This paper will present complete data on the atmospheric concentrations and trends of PBDEs, PBEB, HBB, TBE, DBDPE, and *syn*-, and *anti*-DP over the time period 2005–2013 (inclusive), and EHTBB and BEHTBP over the time period 2008–2013 (inclusive) as measured at five sites on the United States shores of the North American Great Lakes every 12 days. In this paper, we will present a full picture of the spatiotemporal variations of the concentrations of all of these compounds – those that have been phased out of the market and those that have more recently entered the market.

2. Materials and methods

2.1. Sampling and extraction

The United States' IADN sampling sites include two urban sites at Chicago, IL, and Cleveland, OH; one rural site at Sturgeon Point, NY; and two remote sites at Eagle Harbor, MI, and Sleeping Bear Dunes, MI. The locations of these sites are shown in Fig. S1. Air samples were collected for 24 h every 12 days from 1 January 2005 to 31 December 2013 using a high-volume air sampler (General Metal Works, model GS2310) at each sampling site. The air samplers were equipped with a 2.2 μm quartz fiber filter (Whatman QM-A) to collect the particle phase followed by a cartridge containing XAD-2 resin (40 g, 20–60 mesh) to collect the vapor phase. Detailed information on the sample treatment and chemical analyses is given elsewhere (Team IADN, 2011). Briefly, after being spiked with a known amount of surrogate recovery standards (BDE-77, BDE-166, and $^{13}\text{C}_{12}$ -BDE-209), the vapor and particle samples were separately extracted in a Soxhlet apparatus for 24 h with a 1:1 (v:v) *n*-hexane and acetone mixture. The extracts were concentrated and then purified on a 3.5% water deactivated silica (Fisher Scientific Inc.) column. The column was eluted consecutively with 25 mL of *n*-hexane and with 25 mL of a 1:1 (v:v) *n*-hexane and dichloromethane mixture. The fractions were rotary evaporated, blown down with N_2 to 1 mL, spiked with internal standards (BDE-118 and

BDE-181), and further blown down to $\sim 100 \mu\text{L}$. Target compounds were quantitated using the internal standards.

2.2. Instrumental analysis

Thirty-five PBDE congeners (7, 10, 15, 17, 28, 30, 47, 49, 66, 85, 99, 100, 119, 126, 138–140, 153, 154, 156, 169, 180, 183, 184, 191, 196, 197, 201, and 203–209), 6 other brominated flame retardants (PBEB, HBB, EHTBB, BEHTBP, TBE, and DBDPE), *syn*-DP, and *anti*-DP were measured on an Agilent 7890 series gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) operating in the electron capture negative ionization (ECNI) mode. Chromatographic separation was accomplished with an Rtx-1614 (15 m, 250 μm i.d., 0.1 μm film thickness) fused silica capillary GC column (Restek Corporation, Bellefonte, CA). High purity helium (99.999%; Liquid Carbonic, Chicago) was used as the carrier gas and high purity methane (99.97%, Praxair) was used as the reagent gas. Details on the instrumental analysis procedures have been previously reported (Ma et al., 2013).

2.3. Quality assurance and quality control

Samples were processed following standard operating procedures and quality assurance and quality control measures, all of which are available on the IADN website (Team IADN, 2011). These sampling and analytical procedures have been unchanged throughout the project. Either a procedural blank or a matrix spike recovery sample was run with every other batch of ~ 8 samples throughout the project. The surrogate recoveries were $104 \pm 14\%$, $90 \pm 15\%$, and $61 \pm 20\%$ for BDE-77, BDE-166, and $^{13}\text{C}_{12}$ -BDE-209, respectively. Field blanks were collected at every site seasonally. Concentrations below the field blank levels, which were averaged over the entire sampling period, were treated as non-detects and replaced with empty cells in the data spreadsheet. None of the concentrations were corrected for surrogate recoveries. Method detection limits (MDL) were calculated as the average procedural blank plus two times its standard deviation and normalized to an air volume of 815 m^3 . The MDLs for the compounds in Table 1 ranged from 0.002 pg/m^3 for PBEB to 0.71 pg/m^3 for EHTBB.

3. Results and discussion

3.1. Concentrations and spatial distributions

Because many of the analytes of interest are found in both the vapor and particle phases, the first step in our data analysis was to add the concentrations in these two phases together. We believe that this sum provides the best measurement of the atmospheric loads of these compounds. The geometric means and medians of these concentrations (in pg/m^3) are given in Table 1 as a function of sampling location. Geometric means are used here because Hites (2015) has recently shown that these sort of atmospheric concentration measurements are log-normally distributed. Table 1 also gives the detection frequencies (in percent) of each compound at each site. Fig. 1 shows the results of the analyses of variance (ANOVA) of the logarithmically transformed concentrations of each compound at each of the five sites.

The geometric mean concentrations of Σ PBDE (sum of 35 PBDE congeners) in air sampled around the Great Lakes ranged from 5.7–52 pg/m^3 . These levels are at the low to medium end of the range when compared with global atmospheric PBDE levels (see Table S1); higher than those in Polar Regions, the oceans and seas, and Australia; comparable to those in Europe; and lower than those in Asia. A complete list of available atmospheric PBDE data is provided in Table S1.

The concentrations of the three most abundant PBDE congeners (BDE-47, -99, and -209) and of all the other flame retardants are plotted as a function of sampling site in Fig. 1. As expected, the atmospheric concentrations of the PBDEs and of most of the other flame retardants

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