

# FLAME RETARDANTS IN THE ATMOSPHERE OF CITIES NEAR THE NORTH AMERICAN GREAT LAKES

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**Introduction.** Cities tend to be sources of POPs to the atmosphere. For example, the concentrations of PCBs in air sampled in cities are very much higher than in rural or remote areas<sup>1</sup>. The uses of polybrominated diphenyl ether (PBDE) flame retardants parallel those of PCBs; in addition, PBDEs are environmentally stable and bioaccumulative. As a result, one might expect that their urban concentrations would be higher than their rural or remote concentrations, but this has not been studied systematically.

In this study, we report on the concentrations of 35 PBDE congeners at two urban sites (Chicago, Illinois and Cleveland, Ohio) and at three rural or remote sites. All five of these sites are part of the United States Integrated Atmospheric Deposition Network (IADN) and are located in the North American Great Lakes basin. These samples were collected from October 2003 to December 2006. The goal of this study is to provide insights on the temporal and spatial distributions of PBDE concentrations in the atmosphere of this region. We also analyzed other emerging BFRs, including 1,2-*bis*(2,4,6-tribromophenoxy)ethane (TBE) and decabromodiphenyl ethane (DBDPE). To explain the measured concentrations, we modeled the concentrations using environmental parameters such as local human population density, backward air trajectories, and the locations of emission sources.

**Material and methods.** The United States IADN sampling sites are shown in Figure 1. Details of the sampling procedures and site operations can be found elsewhere<sup>2</sup> and only a brief summary will be given here. Air samples were collected for 24 hours every 12 days using a high-volume air sampler. Precipitation samples were integrated for an entire month using MIC wet-only samplers. The extracts were analyzed using electron capture negative ionization gas chromatographic mass spectrometry.

**Atmospheric PBDE concentrations.** PBDEs are present in the atmosphere in both the gas and particle phases; for example, BDE-47 is present in both phases at about equal amounts, and BDE-209 is present almost exclusively in the particle phase. Thus, to present overall information, the PBDE concentrations in both phases have been added together. These total PBDE concentrations (notated here as  $\Sigma$ PBDEs) are shown in Figure 2 as box-plots. The highest mean and median concentrations were detected at the two urban sites; Chicago (CH) and Cleveland (CL) had concentrations of  $65 \pm 4$  pg/m<sup>3</sup> (mean  $\pm$  standard error) and 58 pg/m<sup>3</sup> (median) and  $87 \pm 8$  pg/m<sup>3</sup> and 66 pg/m<sup>3</sup>, respectively. The higher average  $\Sigma$ PBDE concentration in Cleveland was due to the presence of several samples with relatively high BDE-209 concentrations; these results will be discussed more later. The mean and median concentrations at the rural sites of Sturgeon Point (SP) and Sleeping Bear Dunes (SB) were  $9.2 \pm 0.6$  pg/m<sup>3</sup> and 8.1 pg/m<sup>3</sup>, and  $8.4 \pm 0.8$  pg/m<sup>3</sup> and 6.0 pg/m<sup>3</sup>, respectively. The lowest  $\Sigma$ PBDE concentrations were found at the remote site at Eagle Harbor (EH) with mean and median concentrations of  $5.8 \pm 0.4$  pg/m<sup>3</sup> and 4.8 pg/m<sup>3</sup>, respectively.

Among the other studies that measured PBDEs in the atmosphere, only a few reported the concentration of BDE-209, allowing for a direct comparison with our results. Strandberg et al. investigated the concentrations of PBDEs at the same sites near the Great Lakes, except Cleveland, for the years 1997-1999<sup>3</sup>. At that time, the  $\Sigma$ PBDE concentrations averaged  $\sim 50$  pg/m<sup>3</sup> in Chicago and 5-15 pg/m<sup>3</sup> at the other rural/remote locations. Our results for Chicago are also similar to the concentrations reported in a previous study from our laboratory<sup>4</sup>, where the average was  $100 \pm 35$  pg/m<sup>3</sup>. The mean  $\Sigma$ PBDE concentration measured in two duplicate samples taken at the University of California, Davis<sup>5</sup> was  $93 \pm 27$  pg/m<sup>3</sup>, which is close to our urban site values. Median atmospheric  $\Sigma$ PBDEs levels in Houston, Texas<sup>6</sup> were reported to be 126 pg/m<sup>3</sup>, again similar to our values.

It has been shown in previous studies that PBDE concentrations in the United States were generally higher than in Europe and Asia, reflecting substantial differences in the use of these chemicals<sup>7</sup>. Ambient air concentrations of

$\Sigma$ PBDEs were 13-35 pg/m<sup>3</sup> in Vienna<sup>8</sup>, 106 pg/m<sup>3</sup> in Ispra, Italy<sup>9</sup>, and 6.2-150 pg/m<sup>3</sup> at an industrial site in Izmir, Turkey<sup>10</sup>. Only a few studies of East Asian air have included the measurement of BDE-209. Of those, a mean  $\Sigma$ PBDE concentration of 58 pg/m<sup>3</sup> was reported for airborne particles collected from the Bohai Sea to the high Arctic<sup>11</sup>, and 4.5-110 pg/m<sup>3</sup> was reported for an urban site in Kyoto, Japan<sup>12</sup>. These European and Asian levels were similar to the concentrations we measured in Chicago and Cleveland, but higher than at our other sites. In a recent study, Harrad et al. showed that concentrations of BDE-209 in indoor dust in Europe were similar to, if not higher than, those in the United States<sup>13</sup>. The statistically supported sequence for atmospheric concentrations of PBDE in the Great Lakes basin was CL > CH > SP  $\approx$  SB  $\approx$  EH.

**Precipitation PBDE concentrations.** To compare our results with previously reported precipitation values, volume weighted mean concentrations (VWM) of total PBDEs were calculated as the sum of the concentrations of the seven most abundant congeners (BDE-28, 47, 99, 100, 153, 183, and 209) for all the sites, and these data are plotted as box-plots in Figure 2.

As expected, the highest  $\Sigma$ PBDE concentrations were found in precipitation at the two urban sites at Chicago and Cleveland with  $94 \pm 19$  ng/L (VWM  $\pm$  SEM) and  $4.4 \pm 1.4$  ng/L, respectively, followed by the rural/remote sites of Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point with  $1.00 \pm 0.28$  ng/L,  $0.73 \pm 0.13$  ng/L, and  $0.65 \pm 0.14$  ng/L, respectively. While there was a statistically significant difference between the concentrations at the two urban sites ( $t = 4.78$ ,  $P < 0.05$ ), a significant difference could not be detected among the rural/remote sites. Therefore, the statistically supported sequence for precipitation concentrations of PBDEs in the Great Lakes basin was CH  $\gg$  CL > EH  $\approx$  SB  $\approx$  SP.

**Dependence of ambient air concentrations on local human population.** A strong positive correlation ( $P < 0.05$ ) was observed between the geometric mean of the total PBDEs concentration at each site and the human population within a 25 km radius of each site [see Hafner et al.<sup>14</sup> for details on this calculation], see Figure 3 (top). The same correlation was significant for BDE-47 and BDE-99 but not for BDE-209. It is not surprising that large industrial or urban centers such as Chicago and Cleveland represent sources of PBDEs to the atmosphere, as previously demonstrated for PAHs and PCBs<sup>1,14</sup>. Eagle Harbor and Sleeping Bear Dunes are both located where the human population density is very low, and the PBDE concentrations at these remote sites are very low. Perhaps long range atmospheric transport from the Chicago/Milwaukee corridor is bringing these flame retardants to these remote areas. The average total PBDE concentration at Sturgeon Point was relatively lower than one would expect from the local population density, which may indicate that the influence of Buffalo, NY, which is located  $\sim$ 25 km northeast of this sampling site, was not particularly important at that site.

As shown in Figure 3, the average concentration of PBDEs at the Cleveland site was relatively higher than one would expect considering only the population density, suggesting that a strong urban source might be enhanced by significant contributions from atmospheric transport. To verify the above hypothesis, backward air trajectories were obtained for Cleveland on the dates with the two highest and the two lowest concentrations of BDE-209, and these backward air trajectories were overlaid on a map of BDE-209 sources obtained from the EPA's Toxic Release Inventory (TRI). The air masses corresponding to low BDE-209 concentrations were mainly coming from Lake Erie, while those corresponding to high BDE-209 concentrations were mainly coming from directions with facilities emitting BDE-209 into the atmosphere. Even without considering distant sources, the area surrounding Cleveland seems to have a high density of facilities emitting BDE-209, as opposed to Chicago, where the TRI indicated that there were none.

**Decabromodiphenylethane (DBDPE).** This flame retardant was introduced to the market as an alternative for BDE-209<sup>15</sup>. In this study, the concentrations of DBDPE were generally higher than those for TBE, with a maximum average concentration of  $22 \pm 13$  pg/m<sup>3</sup> in Cleveland and a minimum average concentration of  $1.0 \pm 0.5$  pg/m<sup>3</sup> in Eagle Harbor. The concentrations of DBDPE are related to the local population density (see Figure 3), although the correlation is not statistically significant. In Cleveland, the concentrations of DBDPE roughly tracked those of BDE-209 ( $r^2 = 0.325$ ,  $P < 0.001$ ). This observation suggests that DBDPE and BDE-209 were likely coming from the same sources. For the other sites, more data are needed to be able to draw any conclu-

sions on the relationship between DBDPE and BDE-209. The only study that measured the concentration of DBDPE in ambient air reported a value of 700 pg/m<sup>3</sup> in an electronics dismantling facility in Sweden<sup>15</sup>.

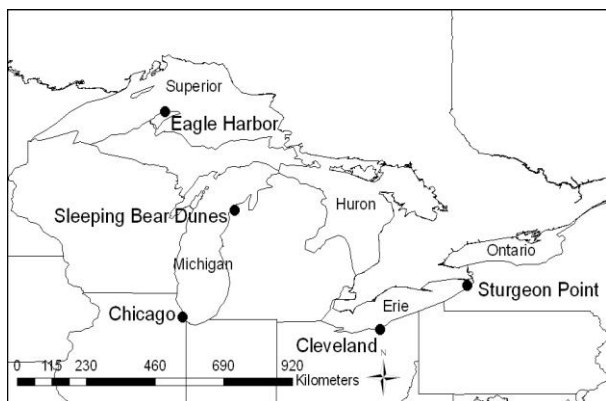
**1,2-Bis(2,4,6-tribromophenoxy)ethane (TBE).** This compound was heavily produced in the United States from 1986 to 1994<sup>16</sup> but it may have been re-introduced to the market as a substitute for Octa-BDE, the production of which was stopped in the United States in 2004<sup>17</sup>. At all the sites, the concentrations of TBE were generally low and comparable with those of Octa-BDE congeners. The highest average TBE concentration was found in Chicago (1.2 ± 0.3 pg/m<sup>3</sup>) and the lowest in Sturgeon Point (0.4 ± 0.1 pg/m<sup>3</sup>). The concentrations of TBE are very roughly related to the local population density (see Figure 3), although the correlation is far from statistically significant. Although there are few studies that have measured TBE, our levels are comparable with concentrations measured in a suburban area close to Stockholm (< 3 pg/m<sup>3</sup>)<sup>18</sup>, in Bloomington, IN (2.8 pg/m<sup>3</sup>), and in Chicago (4.0 pg/m<sup>3</sup>)<sup>16</sup>.

**Conclusions.** As expected, the urban sites of Chicago and Cleveland showed higher concentrations of PBDEs than the rural and remote sites. A strong positive relationship was observed between median atmospheric concentrations of PBDEs and local human population, confirming the hypothesis that urban areas act as sources of these flame retardants. Long range transport might be responsible for the PBDEs detected at the rural and remote sites. Similar, but statistically insignificant, spatial trends were observed also for two emerging flame retardants, DBDPE and TBE.

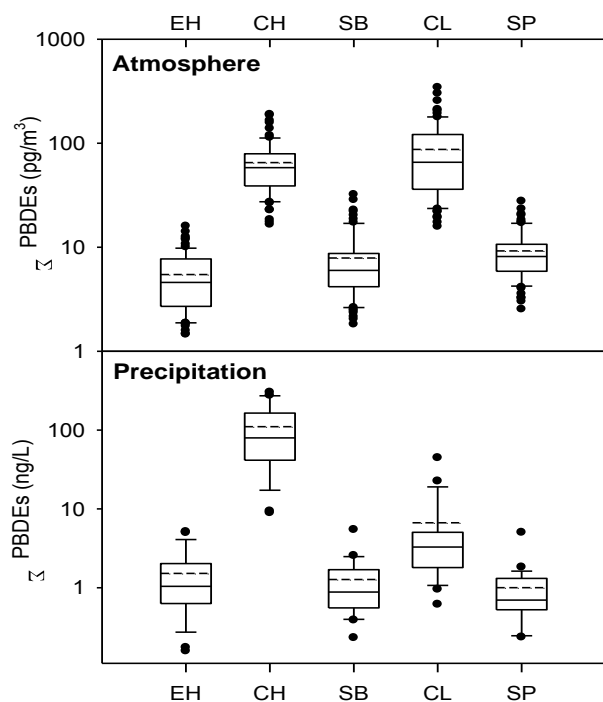
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## References

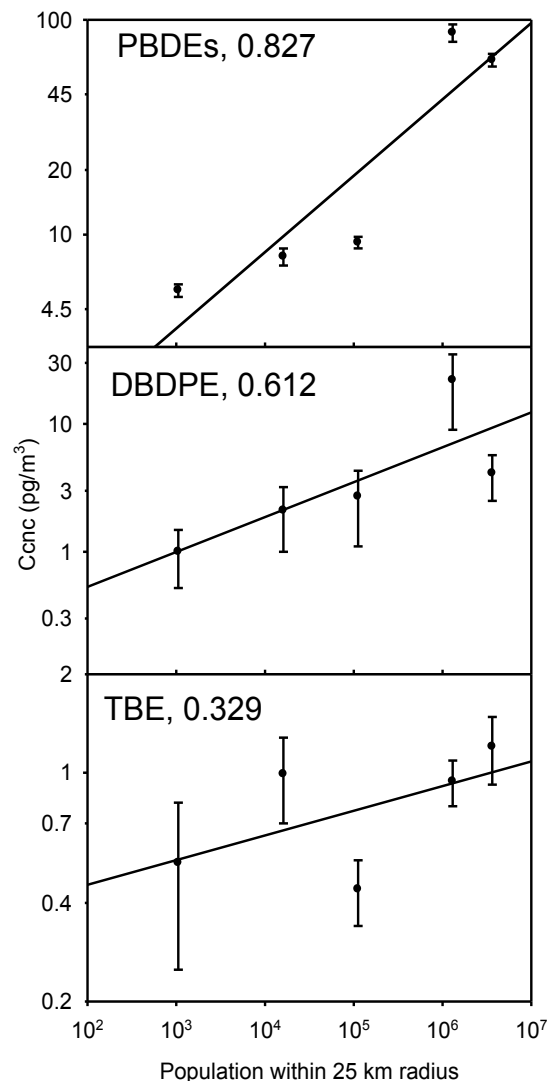
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**Figure 1.** The locations of the five air and precipitation sampling sites discussed in this paper



**Figure 2.** Total PBDE concentrations in the atmosphere (top) and in precipitation (bottom) at the five IADN sites ordered from east to west. The solid horizontal line represents the median, and the dashed line represents the mean. The box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles, and the whiskers represent the 5<sup>th</sup> and the 95<sup>th</sup> percentiles.



**Figure 3.** Average concentrations of total polybrominated diphenyl ethers (PBDEs, top), decabromodiphenylethane (DBDPE, middle), and 1,2-bis(2,4,6-tribromo-phenoxy)ethane (TBE, bottom) in air collected near the North American Great Lakes as a function of the human population living within a 25 km radius of the collection site. The data points in all plots are given in the following sequence: Eagle Harbor, Sleeping Bear Dunes, Sturgeon Point, Cleveland, and Chicago. The correlation coefficients ( $r^2$ ) are given in each plot; the critical value for 3 degrees of freedom at  $P = 0.05$  is 0.771. The error bars are standard errors.