Brominated Flame Retardants in the Atmosphere of the East-Central United States

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Air samples were collected at five sites (urban, semiurban, agricultural, and remote) from Lake Michigan through the U. S. Midwest to the Gulf of Mexico every 12 days during 2002–2003 using high-volume samplers so that we could study the spatial trends of brominated flame retardants (polybrominated diphenyl ethers (PBDEs), hexabromo-cyclododecanes (HBCDs), and 1,2-bis(2,4,6-tribromophenoxy)-ethane (TBE)). The mean ΣPBDE atmospheric concentration was 100 ± 35 pg/m^3 at the Chicago site, which was 3–6 times higher than that at the other sites. The ΣPBDE atmospheric concentrations at the Chicago site were significantly higher than previous measurements made in 1997–1999. Unlike these former measurements, BDE-209 is now relatively abundant. Lower BDEs (tri- through hex-BDEs) were detected in both the particle and the gas phases, and the partitioning of these compounds between phases was highly dependent on atmospheric temperature. Higher BDEs (hepta- through deca-BDEs) were mostly detected in the particle phase. On the basis of the congener distributions in the samples, the concentrations were divided into three groups: penta-BDEs, octa-BDEs, and deca-BDEs. Penta-BDEs were the most concentrated at the Chicago site and the least concentrated at the Louisiana site; octa-BDE concentrations were low at all of the sites; deca-BDEs were the most concentrated at the Chicago site and notably high at the Arkansas site. High concentrations of deca-BDEs, HBCDs, and TBE at the Arkansas site suggest that manufacturing areas in southern Arkansas could be the source regions. Backward trajectories for air masses with high concentrations of deca-BDEs coming to the Arkansas site suggest that deca-BDEs bound to particles can move long distances from source regions to nonsource regions.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been used in a variety of consumer and commercial products such as furniture, textiles, polyurethane foam, and thermoplastics as a brominated flame retardant (BFR). The use of PBDEs has increased over the last 20 years, and now ~35 000 tons/year (half of the global use) are used in North America (*1*).

Three PBDE commercial products were available until the end of 2004: The penta-BDE product is mainly composed of tetra- and pentabromodiphenyl ethers, the octa-BDE product is composed of higher brominated diphenyl ethers (hexa- to nona-BDEs), and the deca-BDE product is almost entirely composed of decabromodiphenyl ether (also called

BDE-209) (*2*). Because of their frequent detection in the environment and people, the penta- and octa-BDE products have faced government regulation in Europe and in the United States (*3*), and perhaps as a result, a major BFR producer, Great Lakes Chemical Corp., voluntarily stopped production of these two products in December 2004 (*4*). However, the goods containing the penta- and octa-BDE products will remain in use for years, and the deca-BDE product and other brominated flame retardants will continue to be produced and used.

The PBDE concentrations in people from North America were >10 times higher than those in people from other regions, probably as a result of the relatively high use of the penta-BDE product in North America (*5*). Other brominated flame retardants are also contaminating the environment. For example, BDE-209 was recently detected in biota and in ambient air samples (*6–8*), hexabromocyclododecanes (HBCDs) were detected in biota (*9–11*), and 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) was detected in a sediment core and in ambient air samples (*12*). These occurrences of BDE-209 and other BFRs in the environment may reflect the shift of the BFR market from older to newer products. In addition, photolytic and microbial debromination of BDE-209 has been observed in laboratory studies, which indicate that BDE-209 could degrade to less brominated PBDEs in the environment (*13–16*).

Previously, Strandberg et al. investigated PBDEs in the atmosphere of the Great Lakes region, but their study used a limited number of archived samples collected during the late 1990s (*17*). In our study, we collected air samples every 12 days from August 2002 to January 2004 at five sites ranging from the shore of Lake Michigan through the Midwest to the Gulf of Mexico. Our goal was to understand the spatial and temporal behavior of PBDEs in the atmosphere of the east-central U. S. In addition, we analyzed other BFRs such as HBCDs and TBE. To identify sources of these compounds, we have used backward air trajectories.

Experimental Section

Sample Information. Air samples were taken at five sites: (a) the Integrated Atmospheric Deposition Network (IADN) site located near Sleeping Bear Dunes National Lakeshore on the northeastern shore of Lake Michigan (44°48.78′ N, 86°03.53′ W), (b) the IADN site located at the Illinois Institute of Technology in Chicago (41°50.07′ N, 87°37.48′ W), (c) Indiana University in Bloomington, Indiana (39°10.00′ N, 86°31.28′ W), (d) the University of Arkansas Southeast Research and Extension Center near Rohwer, Arkansas (33°45.65′ N, 91°16.53′ W), and (e) the Louisiana Universities Marine Consortium in Cocodrie, Louisiana (29°15.23′ N, 90°39.07′ W) (Figure 1). The Chicago site is highly urbanized, the Michigan and Louisiana sites are in remote areas, the Arkansas site is in an agricultural region, and the Indiana site is a college town with a population of ~60 000. The detailed descriptions of the sampling and analytical procedures have been given elsewhere but are summarized here (*18–20*).

A modified Anderson high-volume air sampler (General Metal Works, model GS2310) fitted with XAD-2 resin (Sigma, Amberlite, 20–60 mesh) and with a Whatman quartz fiber filter (QM-A) was used to collect air at the Chicago site. High-volume air samplers equipped with a polyurethane foam (PUF) adsorbent (Tisch Environmental, Inc., Cleves, OH) and a glass fiber filter (Whatman, Florham Park, NJ) were used to collect air at the other four sites. All of these samplers
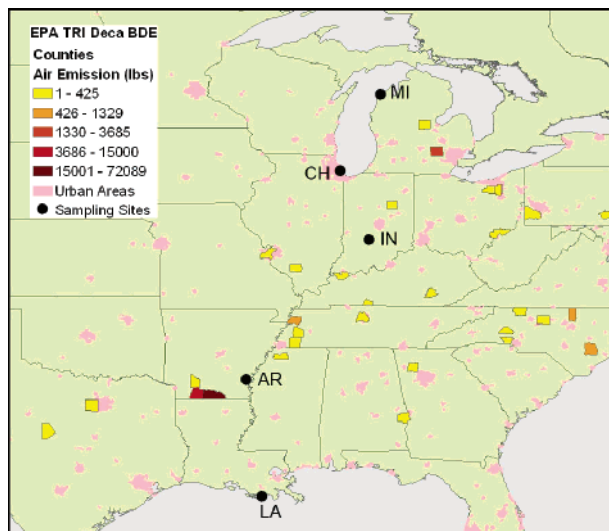
FIGURE 1. Map of air sampling sites, deca-BDE air emission sites (data from the 2002 U. S. EPA toxics release inventory database, http://www.epa.gov/triexplorer/), and major urban areas. The red and black region in southern AR includes Great Lakes Chemical (El Dorado, AR) and Albemarle (Magnolia, AR) plants where BFRs are manufactured. Abbreviations for the sampling sites: MI, Sleeping Bear Dunes in Michigan; CH, Chicago in Illinois; IN, Bloomington in Indiana; AR, Rohwer in Arkansas; LA, Cocodrie in Louisiana.

draw air through the filter to collect the particle-bound compounds and then through a PUF adsorbent or XAD-2 resin to collect the gas-phase compounds. No breakthrough was observed with either media.

Sampling took place for 1 day every 12 days from 9:00 a.m. to 9:00 a.m., and the sampling dates followed the IADN sampling schedule. Sample volumes were ~800 m³ for Chicago, ~1300 m³ for Michigan and Indiana, and ~400 m³ for Arkansas and Louisiana (although the air volume for the latter two sites was increased to ~800 m³ after October 2002 by doubling the running time to 2 days). We analyzed Chicago gas-phase samples collected between August 2002 and December 2003 and Chicago particle-phase samples collected between January 2003 and December 2003. At all other sites, we analyzed both gas- and particle-phase samples collected from September 2002 to January 2004.

Materials. A PBDE standard mixture solution (EO-5103, from Cambridge Isotope Laboratory (CIL), Andover, MA) was used for the analysis of the following PBDE congeners: 2,2′, 4-TrBDE (BDE-17), 2,4,4′-TrBDE (BDE-28), 2,2′,4,4′-TeBDE (BDE-47), 2,3′,4,4′-TeBDE (BDE-66), 2,3′,4′,6-TeBDE (BDE-71), 2,2′,3,4,4′-PeBDE (BDE-85), 2,2′,4,4′,5-PeBDE (BDE-99), 2,2′,4,4′,6-PeBDE (BDE-100), 2,2′,3,4,4′,5′-HxBDE (BDE-138), 2,2′,4,4′,5,5′-HxBDE (BDE-153), and 2,2′,4,4′,5,6′-HxBDE (BDE-154). The following congeners were purchased individually: 2,2′,4,5′-TeBDE (BDE-49); 2,3,4,4′,5,6-HxBDE (BDE-166), 2,2′,3,4,4′,5,6-HpBDE (BDE-181), 2,2′,3,4,4′,5′, 6-HpBDE (BDE-183), 2,3,3′,4,4′,5,6-HpBDE (BDE-190), 2,2′,3,4,4′,5,5′,6-OtBDE (BDE-203), 2,2′,3,3′,4,4′,5,5′,6-NoBDE (BDE-206), 2,2′,3,3′,4,4′, 6,6′-OtBDE (BDE-207), and deca-BDE (BDE-209) from CIL; 2,2′,3,3′,4,4′,5,6′-OtBDE (BDE-196) and 2,2′,3,3′,4,4′,6,6′-OtBDE (BDE-197) from Wellington Laboratories (Guelph, ON, Canada); 2,2′,3,3′,4,5,5′,6-OtBDE (BDE-198), 2,2′,3,4,4′,5, 6,6′-OtBDE (BDE-204), 2,3,3′,4,4′,5,5′,6-OtBDE (BDE-205), and 2,2′,3,3′,4,5,5′,6,6′-NoBDE (BDE-208) from Accustandard (New Haven, CT). In addition, we also used a polybrominated biphenyl (PBB) congener, 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153), a standard of which was purchased from Ultra Scientific (North Kingston, RI). 1,2-Bis(2,4,6-tribromophenoxy)ethane (TBE) was purchased from Wellington Laboratories (Guelph, ON, Canada), and γ-hexabromo-

cyclododecane (HBCD) was from CIL. The internal standard, 3,3′,4,4′-TeBDE (BDE-77), and the quantitation standard, 2,3′,4,4′,5-PeBDE (BDE-118), were purchased from CIL. These compounds are not present in the ambient environment. All of the HBCD isomers (α, β, and γ) and γ-^{13}C-HBCD used for HBCD isomer analysis by LC/MS/MS were purchased from Wellington Laboratories. All of the solvents used for the extraction and cleanup procedures were residue-analysis grade. Technical mixtures (DE-71, DE-79, and DE-83) were obtained from Great Lakes Chemical Corp.

Sample Preparation. Before use, the PUF and XAD-2 resin were washed with water and then sequentially Soxhlet-extracted for 24 h with each of following solvents: methanol, acetone, hexane, dichloromethane, hexane, and 1:1 acetone–hexane. Filters were heated at 450 °C for 6 h. After being sampled, the PUF and XAD-2 samples and the filters were prepared separately. Each sample was spiked with a known amount of 3,3′,4,4′-tetrabromodiphenyl ether (BDE-77) and then Soxhlet-extracted for 24 h with 1:1 acetone–hexane. After extraction, the solvent was exchanged to hexane, reduced in volume to about 1 mL by rotary evaporation, and fractionated on 1% water-deactivated silica gel with the following solvents: hexane, 3:2 hexane–dichloromethane, and dichloromethane. The second fraction and the third fraction were combined. The combined fraction was reduced to 50 μL by N₂ blow down. The final extract was spiked with a quantitation standard, 2,3′,4,4′,5-pentabromodiphenyl ether (BDE-118) prior to analysis. In the case of the Chicago air samples, PBDEs were detected in both fractions; thus, 3.5% water-deactivated silica gel was used for fractionation with hexane and 1:1 hexane–dichloromethane, and each fraction was spiked with the same quantitation standard (BDE-118) and analyzed. For the organochlorine pesticide analysis, γ-^{13}C$_{10}$-chlordane (from CIL) was used as an internal standard, and 2,2′3,4,4′,5,6,6′-octachlorobiphenyl (PCB-204) (Accustandard) was spiked into the final extracts as a quantitation standard. Only the gas-phase samples were analyzed for the pesticides.

Seven of the particle-phase samples were analyzed for the relative amount of α-, β-, and γ-HBCD isomers. The analyses were done at the National Institute of Standards and Technology (NIST). The internal standard γ-^{13}C-HBCD was added to the samples and calibration standards. The four calibration standards contained between 0.25 and 3.0 ng of each of the three HBCD isomers. The samples and standards were solvent-exchanged into methanol and concentrated by N₂ blow down to approximately 150 μL.

Instrumental Parameters. The samples were analyzed on an Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC/MS) with helium as the carrier gas. The 2-μL injections were made in the pulse splitless mode, with a purge time of 2.0 min. The injection port was held at 285 °C. For the determination of the lower PBDEs (tri- through hexa-), the GC column used was a 60 m × 250 μm (i.d.) fused silica capillary tube coated with DB-5-MS (0.25 μm film thickness; J&W Scientific, Folsom, CA). A 60-m column was used to ensure separation of BDE-154 from BB-153. The GC oven temperature program was as follows: isothermal at 110 °C for 1.90 min, 15 °C/min to 180 °C, 1.85 °C/min to 300 °C, and held at 300 °C for 45 min. The GC to MS transfer line was held at 280 °C. The mass spectrometer was operated in the electron capture negative ionization (ECNI) mode using methane as the reagent gas and an ion source temperature of 150 °C. Selected ion monitoring of the two bromide ions at m/z 79 and 81 was used to detect the lower PBDEs. The response factors for all compounds were determined using a quantitation standard with known amounts of all of the target compounds and an internal standard. BDE-118 was used to quantitate all of the PBDE congeners.

All of the samples were quantified for the higher BDEs (hepta- through deca-) separately on a shorter DB-5-MS column (15 m × 250 μm i.d.; 0.25 μm film thickness; J&W Scientific) with the following temperature program: 110 °C for 1 min, 15 °C/min to 300 °C, held at 300 °C for 15 min, 10 °C/min to 325 °C, and held at 325 °C for 2 min. ECNI selected ion monitoring was used. The ions at m/z 486.60 and 488.60 were used to detect and quantify BDE-204, BDE-208, and BDE-209, m/z 408.80 and 410.80 were used to detect and quantify BDE-197, and m/z 79 and 81 were used for quantitation of the other octa- and nonabrominated BDEs and TBE. BDE-118 was also used as a quantitation standard. Under these GC conditions, we observed slight but insignificant thermal degradation of deca-BDE and no degradation at all for octa- and nona-BDE.

For the determination of the total concentration of all HBCD isomers, all samples were run separately on the same 15-m column with the same temperature program but with a lower injection temperature of 230 °C. ECNI selected ion monitoring of the ions at m/z 79 and 81 was used to detect and quantify HBCDs, and m/z 560.80 and 562.80 were monitored for identification. BDE-118 was used as a quantitation standard. To reduce degradation of HBCDs, we removed 25 cm from the front of the column and changed the injection port liner after every 30 samples.

To determine the relative amount of each HBCD isomer, an Agilent 1100 series liquid chromatograph coupled to an Applied Biosystems/Sciex API 4000 triple quadrupole mass spectrometer was used. An Eclipse XDB-C18, 250 × 4.6 mm², HPLC column (Agilent) was used for separation. The injection volume was 20 μL. The mobile phase was a water−methanol mixture (10:90 by volume). The flow rate was 0.5 mL/min; the total run time was 25 min. The temperature of the HPLC column was 20 °C. The mass spectrometer was operated in negative mode electrospray ionization with multiple reaction monitoring. The $(M−H)^- \rightarrow Br^-$ transition at m/z 640.8 → 78.8 was monitored for the three unlabeled HBCD isomers. The $(M−H)^- \rightarrow Br^-$ transition at 652.8 → 78.8 was monitored for γ-$^{13}C_{12}$-HBCD. The amount of each HBCD isomer in the sample vials was calculated using calibration curves. The different HBCD isomers have different relative response factors; therefore, using the chromatographic peak areas to determine the percent of each isomer would have been less accurate than using calibration curves.

The organochlorine pesticides were analyzed using electron capture negative ionization gas chromatographic mass spectrometry. These methods are described in elsewhere (18, 19).

Quality Control. Four quality control criteria were used to ensure the correct identification of the target compounds: (a) The GC retention times matched those of the standard compounds within ±0.1 min. (b) The signal-to-noise ratio was greater than 3:1. (c) The isotopic ratio between the ion pairs was within ±15% of the theoretical value. (d) The recovery of the internal standard (BDE-77) was over 80%. Either a procedural blank or a spike recovery sample containing PBDEs (BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154) was run with every batch of eight samples. Field blanks were collected at each site seasonally. The PBDE levels in the blank samples were low enough so that we did not correct the concentrations in the samples. A few PUF samples for the southern sites (AR and LA) collected during the 2003 summer might have been contaminated, so these samples were excluded from our analyses. The recoveries of the lower BDEs (tri- through hexa-) were between 85% and 110%. The recovery for each homologue of the higher BDEs (hepta- through deca-) was determined separately to check for potential debromination of higher BDEs through sample treatment. The recoveries of these higher BDEs were 50−60%; the recoveries of HBCDs and TBE were about the same.
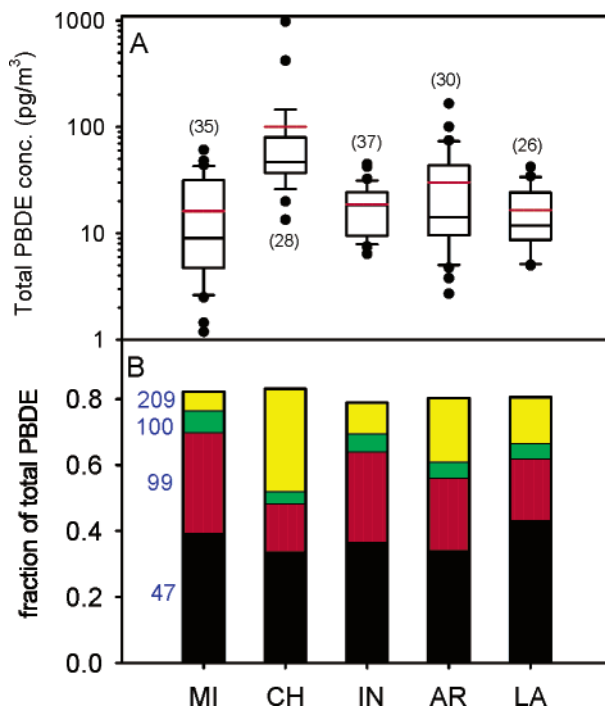
FIGURE 2. (A) ΣPBDE concentrations (pg/m³) at each sampling site. The horizontal lines represent the 10th, 50th, and 90th percentiles; the boxes represent the 25−75th percentiles; the red lines represent the means; individual points are outside of 90th and 10th percentiles. The number of samples is given in parentheses. (B) Congener fractions for those composing ∼80% of the ΣPBDE concentration; BDE-47, BDE-99, BDE-100, and BDE-209 are indicated.

Air Trajectory Generation. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to generate backward trajectories (http://www.arl.noaa.gov/ready/hysplit4.html). Four-day backward trajectories were generated at four different starting times during the sampling period for each sample (6 h intervals for 24 h sampling or 12 h intervals for 48 h). In each case, the trajectories were calculated at three different starting altitudes: 10, 100, and 500 m above ground level. Thus, 12 backward trajectories were generated for each sample. The calculations used the Eta Data Assimilation System database of archived meteorological data.

Results and Discussion

The atmospheric total concentrations (particle plus gas phases) of PBDEs (ΣPBDEs) analyzed here are summarized in Figure 2A as box plots by sampling locations. The major congener distributions are given in Figure 2B. Full data for each sample are given in the Supporting Information.

The ΣPBDE concentrations at the Chicago site (CH) were significantly higher than those at the other sites; the mean Chicago concentration (100 ± 35 pg/m³, mean ± standard error) was 3−6 times higher than those at the other sites. Surprisingly, the ΣPBDE concentration once reached 980 pg/m³ at the Chicago site. These high ΣPBDE concentrations make it clear that this urban region is a source of PBDEs. The ΣPBDE concentrations were similar among the other sites, although several high ΣPBDE concentrations were detected at the Arkansas site (AR), which is more agricultural than urban. The ΣPBDE concentration range at the Michigan site (MI) was larger than that at the Louisiana site (LA), even though the two sites were in remote coastal areas.

At all sites, BDE-47, BDE-99, BDE-100, and BDE-209 composed ∼80% of the ΣPBDE concentration, and BDE-47 was the most abundant congener. The average fraction of
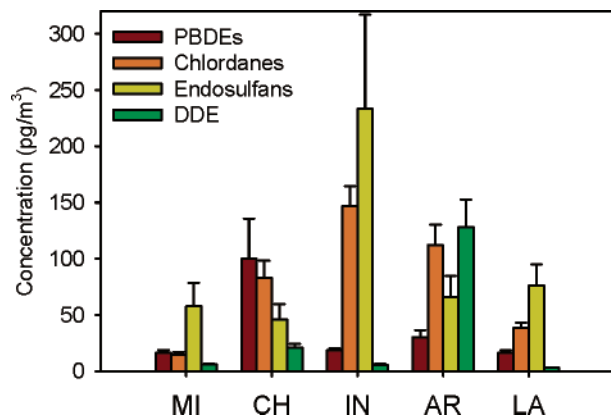
FIGURE 3. Average concentrations (pg/m³) of ΣPBDEs, chlordanes (sum of α- and γ-chlordanes and *trans*-nonachlor), endosulfans (endosulfan I and II and endosulfan sulfate), and *p,p'*-DDE at each sampling site. The error bars indicate the standard errors of the means.

FIGURE 4. Atmospheric particle- to gas-phase partition coefficients (K_p, m³/μg) for six BDE congeners as a function of the reciprocal sampling temperature (1000/T) for the Chicago samples.

BDE-209 ranged from 6% to 31%, and it was associated with the atmospheric particle phase. The following congeners composed the remaining 20% of the PBDE load: BDE-17, BDE-28, BDE-49, BDE-66, BDE-85, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-198/203, BDE-206, BDE-207, and BDE-208. No other unknown PBDE congeners were observed.

In a previous study, Strandberg et al. reported ΣPBDE concentrations in a few samples collected during 1997−1999 at the IADN sites, which included the Chicago and Michigan sites used in this study (*17*). Our ΣPBDE concentrations are about a factor of 2 higher than the previously reported value at the Chicago site but similar at the Michigan site. The notable difference is that BDE-209 is relatively abundant at both sites in our study, while BDE-209 was found at trace levels for only the Chicago site in the previous study. Therefore, the higher concentrations at the Chicago site in our study may be the result of increasing usage of PBDEs, especially BDE-209, between 1997−1999 and 2002−2003.

Figure 3 shows the concentrations of gas-phase organochlorine pesticides and ΣPBDE in the air samples at each site. At the Chicago site, ΣPBDE was the most abundant compound class, and ΣPBDE concentrations were a factor of 2 higher than those of the in-use pesticide, endosulfan. ΣPBDE was 3−5 times more concentrated than *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE) at all of the sites, except the Arkansas site, where dichlorodiphenyltrichloroethane (DDT) had been used heavily for cotton farming (*18*). Figure 3 clearly indicates that PBDEs have urban sources, but even at sites distant from these sources, PBDE concentrations are as high as those of some organochlorine pesticides.

Gas−Particle Partitioning of PBDEs. In the previous study, Strandberg et al. reported that some PBDE congeners (tetra- through hexa-) were present in both the particle and the gas phases, except for BDE-209, which was only present in the particle phase (*17*). The partitioning of semivolatile organic compounds between the particle and gas phases is described by a partition coefficient (K_p)

$$K_p = \frac{F/\text{TSP}}{A} \qquad (1)$$

where F and A are the particle-associated and gas-phase concentrations (pg/m³) and TSP is the total suspended particle matter level in air (μg/m³) (*21*). Strandberg et al. demonstrated a strong linear correlation between the subcooled liquid vapor pressure of a PBDE congener (expressed as log P_L°) and the ratio of its concentrations in the particle
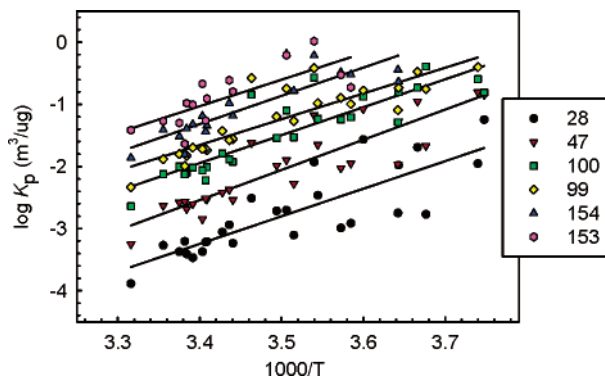
and gas phases (expressed as log K_p). Thus, it follows that (*21, 22*)

$$\log K_p = a_0 + \frac{a_1}{T} \qquad (2)$$

where T is the atmospheric temperature (in K) on the day of sampling and a_0 and a_1 are fittable constants. Using a whole year's data, covering the temperature range of 263−302 K and eq 2, we found a strong temperature dependence of log(K_p) for BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 for the Chicago samples; see Figure 4 and Table 1. As expected (*17, 21*), the log(K_p) values at 298 K track the common logarithms of the vapor pressures of each congener ($r^2 = 0.987$).

In eq 2, the slope, a_1, is related to the energy needed to move a molecule from the sorbed state on an atmospheric particle into the vapor phase (*23*)

$$\Delta H = Ra_1 \ln(10) \qquad (3)$$

where R is the gas constant (8.3 J/mol). The ΔH of each BDE congener was calculated and compared to ΔH_{vap} measured in the laboratory by Tittlemier et al. (*24*) (Table 1). While the ΔH values that we measured are somewhat lower than the heats of vaporization, these values are roughly compatible and in the range of 80−110 kJ/mol (*24*).

On the basis of this regression, log(K_p) for BDE-47 is −2.76 at 298 K and −1.59 at 278 K, which corresponds to a ~15-fold increase in the affinity of BDE-47 to particles over a 20 °C decrease in temperature. This observation suggests that it is important to measure both the gas and the particle phases to obtain an accurate measurement of the concentrations of PBDEs in the atmosphere.

The atmospheric concentrations (actually partial pressures) of PBDEs depend on atmospheric temperature, and this dependence can be parametrized by the Clausius−Clapeyron equation (*25, 26*)

$$\ln P = -\frac{\Delta H'}{R}\left(\frac{1}{T}\right) + \text{const} \qquad (4)$$

where P is the partial pressure of the compound (in atm). In this case, $\Delta H'$ is a composite value, representing the energy needed to move a molecule from soil, vegetation, particles, water, or unknown surfaces into the gas phase. We applied the Clausius−Clapeyron equation to only BDE-47 because this congener composed 50−70% of ΣPBDE in the gas-phase samples at all the sites. The natural logarithms of the partial pressures versus reciprocal atmospheric temperature for each of the samples collected at all of the sites are plotted in Figures 5A and 5B, and the regression results are summarized in

TABLE 1. Results of Equations 2 and 3 and Literature Values of the Enthalpies of Vaporization and Vapor Pressure (23) for Six BDE Congeners; See Figure 4[a]

BDE congener	slope	intercept	r^2	N	ΔH(kJ/mol)	ΔH_{vap} (kJ/mol)	P^0_L (Pa), 298 K
BDE-28	4440 ± 600	-18.3 ± 2.1	0.673	27	85 ± 11	79.7	2.19×10^{-3}
BDE-47	4860 ± 490	-19.1 ± 1.7	0.787	27	93 ± 9	94.6	1.86×10^{-4}
BDE-100	4500 ± 470	-17.3 ± 1.7	0.775	27	86 ± 9	102	2.86×10^{-5}
BDE-99	4150 ± 490	-15.8 ± 1.7	0.741	26	80 ± 9	108	1.76×10^{-5}
BDE-154	4550 ± 650	-16.8 ± 2.3	0.738	18	87 ± 12	113	3.80×10^{-6}
BDE-153	4270 ± 1020	-15.5 ± 3.5	0.543	15	82 ± 20	110	2.09×10^{-6}

[a] The listed errors are standard errors.
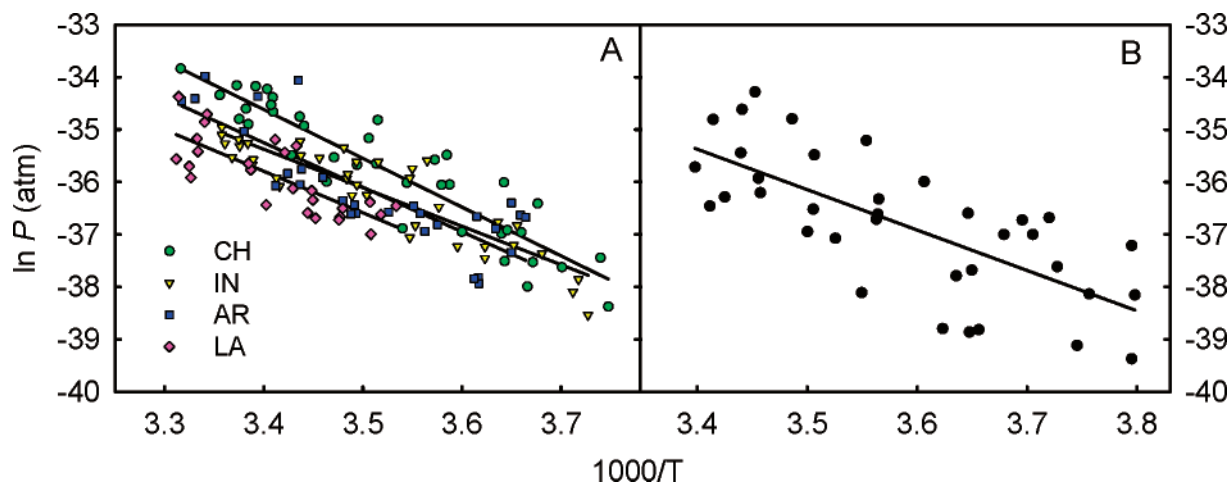
FIGURE 5. Clausius−Clapeyron temperature dependence of BDE-47 partial pressures at the five sampling sites: (A) CH, IN, AR, and LA; (B) MI.

TABLE 2. Summary of Clausius−Clapeyron Regression Results for BDE-47 from Each Sampling Site; See Figure 5[a]

site	$\Delta H'$ (kJ/mol)	temperature range	N	r^2
MI	64 ± 11	263−294	36	0.502[b]
CH	77 ± 5	265−302	39	0.854
IN	61 ± 5	268−298	38	0.800
AR	71 ± 9	273−301	29	0.684
LA	66 ± 11	283−302	26	0.594

[a] The listed errors are standard errors. [b] All of the regressions between the natural logarithms of the partial pressures of BDE-47 and $1/T$ are significant at the 99% confidence level.

Table 2; the regression for the Michigan samples was plotted separately because, for reasons that are not yet clear, these data showed more scatter.

As expected, highly significant regressions ($P < 0.01$) were observed at all sites, and the $\Delta H'$ values of the regression lines are about the same at all of the sites despite the relatively narrow temperature range at the Louisiana site (283−302 K) and a relatively small number of samples at the southern sites. This consistency among sites suggests that the atmospheric behavior of BDE-47 is similar at all of the sites and suggests an average phase transition energy ($\Delta H'$) of 68 $\pm$ 8 kJ/mol. There are a few studies that have reported these $\Delta H'$ values for BDE−47: Lee et al. reported variable $\Delta H'$ values for two different sites in England during the summer of 2001 (77 $\pm$ 21 and 115 $\pm$ 18 kJ/mol); Gouin et al. reported a $\Delta H'$ value of 41 kJ/mol) in southern Ontario during 2002 (27, 28). The $\Delta H'$ from our study is between these two previous studies and is probably not significantly different from them.

Congener Distributions. The congener distributions of the three Great Lakes Chemical technical mixtures, DE-71 (the penta-BDE product), DE-79 (the octa-BDE product), and DE-83 (the deca-BDE product) were measured in our

laboratory; see the Supporting Information. The congener distributions of some of these technical mixtures have already been investigated (29−31), but this is the first report that BDE-183, BDE-197, and BDE-207 are the main congeners in DE-79. On the basis of these congener distributions, we have divided the congeners into two classes: First, the less brominated congener class is made up of the tri- through hexa-BDEs; second, the more brominated congener class is made up of the hepta- through deca-BDEs.

Figure 6A shows that the less brominated congener distributions in the atmospheric particle phase are similar to those in the two penta-BDE product technical mixtures. Interestingly, the fraction of BDE-47 measured at the Chicago site is somewhat higher than that at the other sites, suggesting that the source of the less brominated congeners at this site may include several kinds of technical mixtures. For example, note that the congener distribution of Bromkal 70-5DE (BK) is different from that of DE-71 but similar to that at Chicago. The similarity between the particle phase and the technical mixture congener distributions suggests that the sources of the less brominated BDE congeners in the particle phase at these sites are the penta-BDE product technical mixture.

Figure 6B shows the congener distributions for the less brominated PBDEs in the gas phase at all of the sites. With the exception of BDE-183, which was detected in only a few samples, BDEs with seven or more bromines were not detected in the gas phase at any site. Assuming that PBDEs are volatilized from the particle phase and that the congener distributions of the particle phase are the same as those of the two technical mixtures, BDE congener distributions in the gas phase can be calculated by using K_p for each congener based on the regression lines in Figure 4. The calculated gas-phase congener distributions (at an atmosphere temperature of 288 K) for the two technical mixtures are shown in Figure 6B. These K_p corrected congener distributions indicate that BDE-47 is the most abundant congener in the
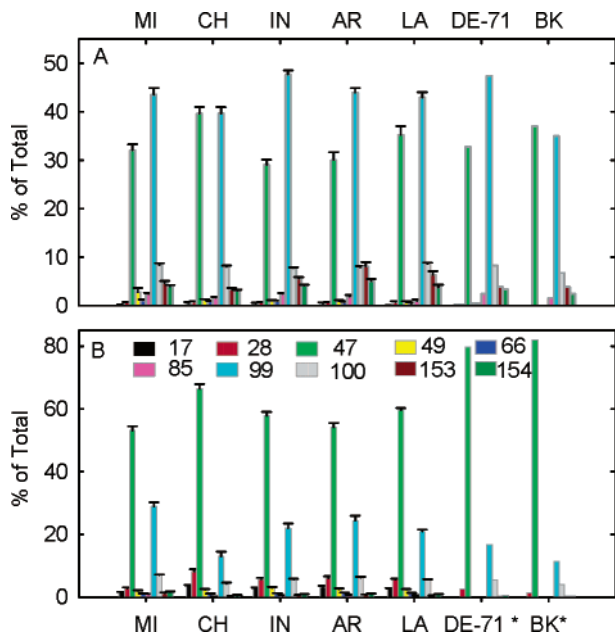
FIGURE 6. Congener distributions, given as the percent of total tri-through hexa-BDEs, for particle-phase (A) and gas-phase (B) samples at each sampling site. Two commercial penta-BDE products (DE-71 and Bromkal 70-5DE (BK)) are included. The congener distribution for BK was from the literature (30). DE-71* and BK* represent K_p corrected congener distributions from the original distributions shown in part A. The error bars indicate the standard errors of the means.
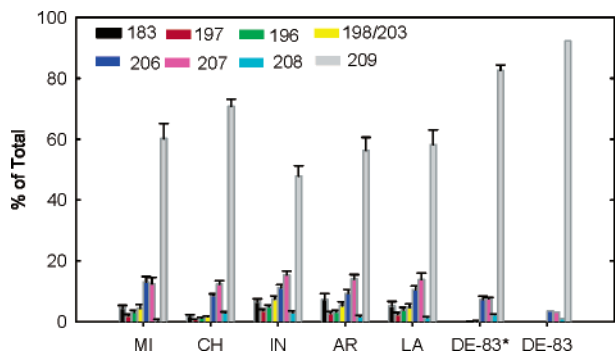
FIGURE 7. Congener distributions, given as the percent of total BDE-183, BDE-197, BDE-196, and BDE-198/203, nona-BDEs, and BDE-209 for the particle phase. A commercial deca-BDE product (DE-83) and this product after it had been through our sample preparation procedures (DE-83*) are included.

gas phase, and the similarity of all of the congener distributions suggests that volatilization of the penta-BDE product may be a source of these compounds to the atmosphere.

Figure 7 shows the congener distributions for the more highly brominated PBDEs. The rightmost set of bars is for the deca-BDE commercial product, DE-83. Note that there are small amounts of nona-BDEs in this product. To see if the commercial product could be debrominated during our analytical procedure, as observed in some laboratory experiments (13−16), we spiked the commercial product onto filters and analyzed these samples as though they were environmental samples. These data are shown in Figure 7 as DE-83*. The relative amount of nona-BDEs increased slightly. In addition, BDE-196, BDE-198/203, and BDE-208 were produced in very small amounts, but there was no production of BDE-183 or BDE-197.

To compare these congener distributions to those from the five sites, we only used those samples in which BDE-209

TABLE 3. Summary of the Concentrations (in pg/m³) and Frequency of Detection for HBCD and TBE at Each Sampling Site

	limit of detection	range	frequency of detection	mean	median
		HBCD			
MI	<0.07	0.2−8.0	29/35	1.2	0.5
CH	<0.13	0.9−9.6	28/28	4.5	4.2
IN	<0.07	0.2−3.6	33/37	1.0	0.75
AR	<0.13	0.2−11	20/30	1.6	0.4
LA	<0.13	0.16−6.2	10/26	0.6	<dl
		TBE			
MI	<0.015	0.03−1.4	35/35	0.16	0.08
CH	<0.025	0.025−11	27/28	1.6	0.66
IN	<0.015	0.08−3.6	37/37	0.53	0.24
AR	<0.025	0.06−70	30/30	3.4	0.30
LA	<0.025	0.026−19	25/26	1.1	0.16

TABLE 4. Relative Abundances of HBCD Isomers (Percentage of Total) Analyzed by LC/MS/MS in Some Particle-Phase Air Samples at the Sampling Sites[a]

		percent of total (LC/MS/MS)		
sample	total HBCD (GC/MS) pg/m³	α-HBCD	β-HBCD	γ-HBCD
MI 10/12/2003	8.0	81	8.7	10
CH 8/1/2003	9.6	11	6.4	83
IN 7/9/2003	3.6	78	12	9.7
IN 10/12/2003	2.9	46	7.3	47
IN 12/11/2003	2.1	32	6.1	61
AR 9/11/2002	11	62	10	28
LA 12/23/2003	2.4	17	17	66

[a] For the HBCD isomer analysis, a known amount of γ-^{13}C-HBCD was spiked as a quantitation standard after part of each sample had been used for GC/MS analyses; thus for accuracy, GC/MS data for total HBCD concentrations are given here.

was detectable; the percentages of BDE-209 detectable in the samples were: MI, 37%; CH, 100%; IN, 66%; AR, 77%; LA, 73%. Figure 7 shows that the relative amounts of BDE-183, BDE-197, BDE-196, and BDE-198/203 are higher in the atmospheric samples compared to those in the deca-BDE product. This result suggests that these congeners could originate from small amounts of the octa-BDE product that are released into the environment. The fraction of hepta- and octa-BDE congeners was somewhat lower at the Chicago site, suggesting that the deca-BDE product is relatively more abundant, compared to the octa product, at this site.

Hexabromocyclododecanes and 1,2-Bis(2,4,6-tribromophenoxy)ethane. Hexabromocyclododecanes (HBCDs) and 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) were detected only in the particle phase, and their concentrations are summarized in Table 3. The mean and median values of the HBCDs were by far the highest at the Chicago site, suggesting that urban areas are the source of this compound. However, the highest individual HBCD concentration was observed at the Arkansas site for the sample collected on September 11−12, 2002. In Sweden, HBCD concentrations were 2−5 pg/m³ in background air (11), which is somewhat higher than our observations at the remote sites in Michigan and Louisiana. The reason for this difference may be that HBCDs replaced the penta- and octa-BDE products earlier in Europe than in North America.

Hoh et al. previously identified and quantified TBE in a few air samples (12); however, in this study, we quantified TBE in all of the air samples. The mean value of TBE was highest at the Arkansas site, but the median value of TBE was highest at the Chicago site. High TBE concentrations occurred in the four southern samples when the BDE-209 concentra-
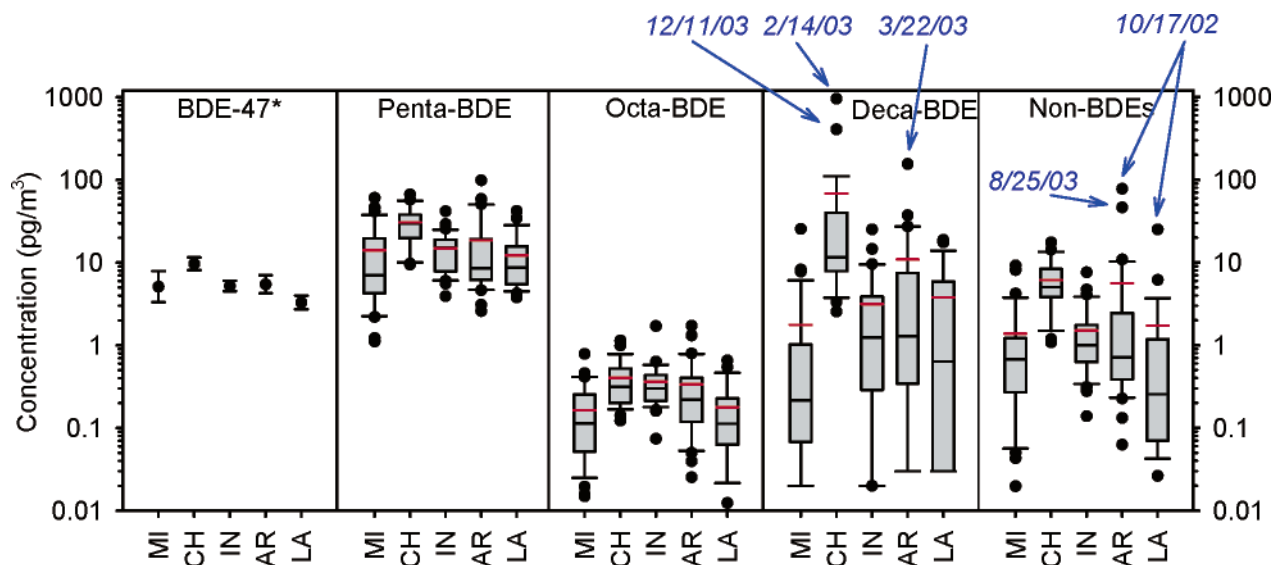
FIGURE 8. PBDE concentrations (pg/m³) at each sampling site. See Figure 2 for format information. BDE-47* is the temperature-corrected (to 288 K) BDE-47 concentration in the gas phase; penta-BDE is the sum of tri- through hexa-BDE concentrations; octa-BDE is the sum of BDE-183 and BDE-197 concentrations; deca-BDE is the sum of nona-BDEs and BDE-209 concentrations; non-BDE is the sum of the TBE and HBCD concentrations. In the leftmost panel, the error bars represent the 95% confidence intervals of the mean. The dates for six outliers are indicated.

tions were also relatively high. This suggests that TBE and deca-BDE may have the same source.

The relative abundance of each HBCD isomer for seven samples was determined by LC/MS/MS. These results are summarized in Table 4, and the chromatograms for the samples are given in the Supporting Information. While γ-HBCD is a dominant isomer in the technical mixtures (*32*), the percent composition of the air samples was variable. Three of the seven samples were dominated by γ-HBCD, one had approximately equal amounts of α-HBCD and γ-HBCD, and three were dominated by α-HBCD. Even the three samples from the Indiana site had different compositions. The percentage of β-HBCD (6−17%) was low and not as variable as the other isomers. The HBCD isomer distribution has been analyzed in aquatic biota and sediments from Europe and in aquatic biota from Lake Ontario; sediment samples were dominated by γ-HBCD, and biota were often dominated by α-HBCD (*10, 33*).

Above 160 °C, γ-HBCD can be converted to α-HBCD (*32*), and incorporating HBCD into plastic sometimes requires this temperature. Therefore, the dominant isomer may be converted from γ-HBCD to α-HBCD during this process. Leaching of HBCD from the treated products followed by atmospheric transport may also account for air samples that have relatively high levels of α-HBCD. Clearly, to determine the fate of HBCD isomers, more air samples should be investigated.

Intracomparison and Intercomparison. On the basis of the congener distribution study, we divided the BDE congeners to three groups: penta-BDEs, the sum of the tri- through hexabrominated congeners, octa-BDEs, the sum of BDE-183 and BDE-197, and deca-BDEs, the sum of the nona-BDEs and BDE-209. We also summed the HBCD and TBE concentrations together as the non-BDE group. The concentrations of these groups are summarized in Figure 8. In addition, we generated temperature-corrected (to 288 K) gas-phase BDE-47 concentrations using the Clausius−Clapeyron plots in Figure 5, and these values are shown in Figure 8.

The mean and median penta-BDE concentrations (31 and 30 pg/m³) were the highest at the Chicago site, and these values are 2−4 times higher than those at the other sites. The penta-BDE concentrations are similar among the other sites, but the temperature-corrected BDE-47 concentration is

significantly lower at the Louisiana site ($p < 0.05$ between MI and LA and $p < 0.0025$ between the other sites and LA). The octa-BDE concentrations were relatively higher at the inland sites (CH, IN, and AR) than those at the near-shore sites, but these concentrations were generally very low at all of the sites, reflecting the small amount of the octa-BDE product marketed. The deca-BDE concentrations were highest at the Chicago site, where very high concentrations of 960 and 410 pg/m³ were measured on February 14, 2003, and December 11, 2003, respectively. At Chicago, the mean and median concentrations were 68 and 12 pg/m³, which are about 10-fold higher than those at the other sites.

The mean and median concentrations of the non-BDEs (6.1 and 5.2 pg/m³) for the Chicago samples were generally higher than those at the other four sites, but the two highest concentrations (78 and 46 pg/m³) were observed for samples collected at the Arkansas site on October 17, 2002, and August 25, 2003, respectively. These high concentrations at this nonurban site may be the result of emissions from the plants where these compounds are manufactured. Our Arkansas sampling site is located 150 km east of major production plants of Great Lakes Chemical and Albemarle (Figure 1). Interestingly, the non-PBDE concentrations that we observed were similar to deca-BDE concentrations at all sites except in Chicago, where the deca-BDE concentration exceeds that of the non-BDEs by about 10-fold.

The ΣPBDE levels in our study are comparable with literature data. The average ΣPBDE concentration was 10 pg/m³ (BDE-209 comprising 60% of the total) in air from an urban area in southern Sweden, 8.6 pg/m³ (BDE-209 comprising 70% of the total) in air from an island in the center of the Baltic Sea, and 34 pg/m³ (BDE-209 was detected in three samples among five samples and the range was 19−74% of the total) in air from Kyoto (urban area) in Japan (*8, 34, 35*). The ΣPBDE levels that we measured in air from Chicago are higher than those in the urban areas outside of the U. S. Unlike the remote site in the Baltic Sea, BDE-209 was not the most abundant congener at our rural and remote sites. This difference may indicate the continued use in the U. S. of the penta-BDE product during our sampling period. The average ΣPBDE, except BDE-209, was 12 pg/m³ at semirural sites, 2.6 pg/m³ at a remote site in England, and 31 pg/m³ at a rural site in southern Ontario, Canada (*27, 28*).

The penta-BDE concentrations at the remote sites in our study are higher than those in England but lower than those in southern Ontario.

Backward Trajectories. Figure 8 shows six significantly high outlier concentrations: two for deca-BDEs at CH, one for deca-BDEs at AR, two for non-BDEs at AR, and one for non-BDEs at LA. The dates for these outlier samples are given in Figure 8. We investigated the cause of these outliers using four-day backward air trajectories.

The highest deca-BDE concentrations were observed in Chicago on February 14, 2003, at 960 pg/m^3 and on December 11, 2003, at 410 pg/m^3. The backward trajectories for these days (Supporting Information, Figures SI-4 and SI-7) show that the air parcels sampled on those days largely came to Chicago from Iowa and Wisconsin and the north-central United States—areas where there are no major PBDE sources (Figure 1). Thus, it seems likely that the high deca-BDE levels measured in Chicago on these days are a result of local sources in the city itself, although it is not clear why the concentrations would be particularly high on these 2 days. The March 22, 2003, sample at the AR site showed the third overall highest deca-BDE concentration at 160 pg/m^3. The backward trajectories for this sample (Figure SI-5) show that all 12 trajectories of air parcels coming to this site at this time passed through the major BFR manufacturing region in southern Arkansas (Figure 1). Our AR site is relatively close to these locations, and it is possible that air from these manufacturing facilities may be a source of deca-BDEs to our Arkansas site.

The two highest non-BDE concentrations were measured on October 17, 2002, at 78 pg/m^3 and on August 25, 2003, at 46 pg/m^3 at the AR site. The backward trajectories for these two dates and location are shown in the Supporting Information in Figures SI-2 and SI-6. On the earlier date, these air parcels passed near the production site in southern Arkansas (Figure 1), and on the later date, the air was virtually stagnant, not leaving Louisiana or Mississippi. Interestingly, the third highest non-BDE concentration of 25 pg/m^3 was also observed on October 17, 2002, at the LA site (Figure 8). The backward air trajectories for this date and location (Figure SI-3) also passed near the manufacturing site in southern Arkansas. This observation may suggest that the October 17, 2002, samples at both the AR and the LA sites may have the same non-BDE source, namely, the location where these compounds are manufactured.

Acknowledgments

Supporting Information Available

Full data for each sample, congener distribution in the three Great Lakes Chemical technical PBDE mixtures, chromatograms of HBCD isomer analysis by LC/MS/MS, and NOAA HYSPLIT backward trajectories. This material is available free of charge via the Internet at http://pubs.acs.org.

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