Novel Flame Retardants, 1,2-Bis(2,4,6-tribromophenoxy)-ethane and 2,3,4,5,6-Pentabromomethylbenzene, in United States' Environmental Samples

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Two brominated flame retardants, 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) and 2,3,4,5,6-pentabromomethylbenzene (PEB), were detected and identified in ambient air samples from various sites in the United States. The identifications were confirmed by comparing the gas chromatographic retention times and mass spectra of the compounds found in the environment with those of authentic materials. Generally, the TBE concentrations in air were comparable to those of tetra- through hexabrominated diphenyl ethers (PBDEs) and often higher than those of decabromodiphenyl ether (BDE-209). The atmospheric TBE concentrations at locations in the southern United States were higher than those in the northern United States. TBE was also found in a sediment core from Lake Michigan; the concentrations of TBE increased with time, were lower than those of BDE-209, but were ~10 times higher than the sum of BDE-47, -99, and -100. The maximum PEB concentration in Chicago air was 550 pg/m³, which was 10 times higher than the concentration of total PBDEs in this sample. In general, the concentrations of PEB in air samples were low but detectable and were less than those of PBDEs. PEB was not found in the sediment core from Lake Michigan. These occurrences of relatively high concentrations of TBE and PEB in environmental samples may reflect the increasing usage of these compounds as flame retardants.

Introduction

Brominated flame retardants (BFRs) have been heavily used in many domestic and industrial products for fire prevention. Although there are over 50 different BFRs, the main commercial BFRs are tetrabromobisphenol A, hexabromocyclododecane, decabromodiphenyl ether (deca-BDE), octabromodiphenyl ethers (octa-BDE), and pentabromodiphenyl ethers (penta-BDE). In 2001, the total global production of these five types of BFRs was over 200 000 t (1).

Perhaps as a result of their widespread use, BFRs are now ubiquitous in the environment. Specifically, polybrominated diphenyl ethers (PBDEs) have now been found in most environmental compartments, including air, water, sediment, fish, and people; in addition, the environmental concentrations of these compounds are doubling every 3–5 years (2). Some PBDEs are facing governmental regulation: penta-

and octa-BDEs are subject to bans in Europe, California, and Maine, and in fact, the BFR industry will soon stop producing these two products (3). Decabromodiphenyl ether and the other BFRs are not included in these bans, and the BFR market is still growing, presumably because of increasingly stringent fire safety standards. Thus, penta- and octa-BDEs are likely to be replaced in the marketplace with other BFRs (4). For example, one of the major BFR manufacturers, Great Lakes Chemical, has recently announced that they will replace octa-BDE with 1,2-bis(2,4,6-tribromophenoxy)ethane (5).

During the course of analyzing air samples for PBDEs in our laboratory, we noted relatively high concentrations of brominated compounds, the GC retention times and mass spectra of which did not agree with those of any PBDEs. Subsequent efforts (summarized here) showed that these compounds were 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) and pentabromomethylbenzene (PEB). Thus, the goal of the work reported here is to elucidate the identities of these compounds and to quantitate these compounds in selected air samples collected at various sites in the eastern United States and in a sediment core from Lake Michigan.

Experimental Section

Sample Information. Air samples were collected at five sites: (a) the Integrated Atmospheric Deposition Network (IADN) site located at the Illinois Institute of Technology in Chicago (41°50.07′N, 87°37.48′W); (b) the IADN site located near Sleeping Bear Dunes National Lakeshore on the northeastern shore of Lake Michigan (44°48.78′N, 86°03.53′W); (c) Indiana University in Bloomington, IN (39°10.00′N, 86°31.28′W); (d) the University of Arkansas Southeast Research and Extension Center near Rohwer, AR (33°45.65′N, 91°16.53′W); and (e) the Louisiana Universities Marine Consortium in Cocodrie, LA (29°15.23′N, 90°39.07′W). The Chicago site is highly urbanized, the Michigan and Louisiana sites are in remote areas, the Arkansas site is an agricultural site, and the Indiana site is in 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 (6, 7).

A modified Anderson high-volume air sampler (General Metal Works, model GS310) fitted with XAD-2 (Sigma, Amberlite, 20–60 mesh) resin and with a Whatman quartz fiber filter (QM-A) was used to collect air at the Chicago site. High-volume air samplers equipped with polyurethane foam (PUF) adsorbent (Tisch Environmental, Inc., Village of Cleves, OH) and a glass fiber filter (Whatman, Clifton, NJ) were used to collect air at the other four sites. All of these samplers drew air through the filter to collect the particle-bound compounds and then through polyurethane foam (PUF) adsorbent or XAD-2 resin to collect the gas-phase compounds. Sampling took place for 24 h 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 48 h). The Chicago samples...
were collected throughout 2003, and the samples at the other four sites were collected from September 2002 to December 2003.

A sediment core was taken from Lake Michigan at the end of April 2004 at site MI 47 (45°10.70' N, 86°22.52' W). A box core (30 cm × 30 cm × 52 cm depth) was taken from the U.S. EPA’s ship, the R/V Lake Guardian. Once the box core was back on the deck, several subcores were taken by inserting subcore tubes (10 cm i.d. × 60 cm); care was taken to avoid distortion of the sediment. The cores were cut into 0.5 cm slices down to 10 cm depth and into 1 cm slices below 10 cm. The samples were immediately frozen, transported to our laboratory, and stored at −30 °C until analysis.

Materials. 1,2-Bis(2,4,6-tribromophenoxy)ethane (TBE) was purchased in nonane solution from Wellington Laboratories, and 2,3,4,5-tetrabromodiphenyl ether (BDE-118) prior to further use. The 1,1,1,3,3-pentabromodiphenyl ether (BDE-118) was purchased from Philipsburg, NJ, which was used to remove elemental sulfur. After spiking with a known amount of the internal standards, the GC retention times matched those of the standard compounds within ±0.3 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. For the air samples, the recovery of the surrogate standard (BDE-77) was over 80%. The recoveries for both 13CDE-156 and 13CDE-194 were also over 80% for the sediment samples.

Sample Preparation. Before air sampling, the PUF and XAD-2 resins were washed with water and then sequentially Soxhlet extracted for 24 h with each of following solvents: methanol, acetone, hexane, dichloromethane, and hexane, and 1:1 acetone—hexane. Filters were heated at 450 °C for 6 h. After sampling, 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’,5-tetabromodiphenyl ether (BDE-77) and then Soxhlet extracted for 24 h with 400 mL of 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 a 1% water deactivated silica (Grace Davison, Columbia, MD) column (0.6 cm i.d. × 6 cm) with 8 mL of each of the following solvents: hexane, 3:2 hexane—dichloromethane, and dichloromethane. The second and third fractions were combined. The hexane fraction and the combined fraction were reduced in volume to 50 μL.

For the sediment samples, ~15 g of wet sediment was mixed with 100 g of precleaned, anhydrous Na2SO4, and 20 g of precleaned granular copper (20–30 mesh; J. T. Baker, Phillipsburg, NJ), which was used to remove elemental sulfur. After spiking with a known amount of the internal standards, 13C12-2,3,3’,4,4’,5-hexachlorodiphenyl ether (CDE-156) and 13C12-2,2,3,3’,4,4’,5,5’-octachlorodiphenyl ether (CDE-194) (Cambridge Isotope Laboratories), the samples were Soxhlet extracted for 24 h with 300 mL of 1:1 acetone—hexane. Throughout the extraction and analysis procedure, the analytes were protected from light by wrapping the containers with aluminum foil or by using amber glassware.

After evaporating most of the solvent, approximately 4 mL of concentrated H2SO4 (EM Science, Gibbstown, NJ) was added to remove any lipsids present in the sediment samples. After centrifugation for 10 min, the upper hexane layer was recovered and combined with 5 mL of hexane used to wash the sulfuric acid residue. After reducing the volume to ~1 mL, the samples were loaded onto a 3% water-deactivated silica column (1.9 cm i.d. × 20 cm). Only one fraction of 150 mL of dichloromethane was collected. The solvent was evaporated to 500 μL, and the samples were fractionated on an alumina (ICN Biomedicals GmbH, Eschwege, Germany) column (0.6 cm i.d. × 6 cm). The column was first eluted by 8 mL of hexane followed by 8 mL of 2:3 acetone—hexane. The PBDEs eluted in the second fraction. After solvent exchange to hexane, BDE-118 and decabromodiphenyl (BB-209, purchased from Dr. Ehrenstorfer, GmbH, Augsburg, Germany) were added as recovery standards, and the samples were analyzed by GC/MS.

Instrumental Parameters. TBE and PEB in the air and sediment samples were identified using GC/MS (an Agilent 5973 system) operating in the full-scan electron ionization (EI) and electron capture negative-ionization (ECNI) modes. The quantitation of TBE and PEB as well as of the PBDEs, except for BDE-209, used ECNI selected ion monitoring of the bromide ions at m/z 79 and 81 for the target compounds and of the ions at m/z 351.9, 349.9, 457.8, and 455.8 for the internal standards, CDE-156 and CDE-194. BDE-118 was used as the quantitation standard for the PBDEs, TBE, and PEB. 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. The GC separation used a 60 m × 250 μm (i.d.) fused silica capillary column coated with DB-5-MS (0.25 μm film thickness; J&W Scientific, Folsom, CA). 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 ion source temperatures were 230 and 150 °C for the EI and ECNI modes, respectively.

The BDE-209 measurements were performed separately on the same GC/MS instrument, but a shorter GC column (15 m) was used with the following temperature program: 110 °C for 1 min, 15 °C/min to 300 °C, and held at 300 °C for 17 min. ECNI selected ion monitoring of the ions at m/z 486.6 and 486.6 was used to detect BDE-209. BDE-118 was also used as a quantitation standard for the air samples. BB-209 was used as the quantitation standard for BDE-209 in the sediment samples. TBE measurements were also included with this BDE-209 measurement to confirm the TBE measurements using the 60-m GC column.

Quality Control. Three 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 ±0.3 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.

Sediment Dating. One of the subcores was used for dating by measuring the specific activities of the isotopes 137Cs and 210Pb. All samples were air-dried for 2 weeks, ground in a mortar, and sieved through 2-mm mesh; each sample was loaded into a Petri dish (50 mm o.d. × 9 mm). The 137Cs and 210Pb activities were measured by γ spectrometry at 661.62 and 46.54 keV, respectively, using a high-purity germanium detector (Canberra Gl. 2820R, Canberra Industries, Meriden, CT). At each depth, the 210Pb activity was corrected by subtracting the background activity from the observed activity, and the sedimentation rate was then determined using the constant initial activity model. The 137Cs activity was used for confirmation of the resulting sedimentation rate.
Result and Discussion

1,2-Bis(2,4,6-tribromophenoxy)ethane in Ambient Air and Sediment. During the analysis of PBDE in the particle phase of atmosphere samples from various sites in the United States, we noted a significant, unknown bromine-containing GC peak with a retention time of ~91 min (relative retention time = 1.574, relative to BDE-77 on a 60-m column) in some samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. The presence of bromine was known because of the equal responses of samples. 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the average TBE concentration was 20,000 pg/m³ in the air of the dismantling hall, and it was even higher near the shredder. Sjödin et al. (15) measured TBE in the air from other occupational environments and found concentrations of 41 pg/m³ in a factory assembling circuit boards, 5.8 pg/m³ in an office with computers, 3.1–11 pg/m³ in a computer repair facility, and 3.4–8.4 pg/m³ in a computer teaching hall. Sjödin et al. (15) measured TBE in outdoor air in a suburban area close to Stockholm, but this concentration was under their limit of quantitation (~3 pg/m³). Comparing these values with our data, we note that the TBE concentrations in our ambient air samples were similar to or higher than the TBE concentrations Sjödin et al. (15) found in some occupational indoor air samples.

TBE was also found in sediment samples from Lake Michigan; see Figure 3 for a typical gas chromatogram from one of these samples. TBE’s identity was confirmed by comparing its GC retention time and mass spectra with those of the authentic material. To our knowledge, this is the first time TBE has been found in sediment samples. The levels of TBE in this sediment core were lower than those of BDE-209 but much higher than those of the other PBDE congeners; for example, Figure 4 (note the logarithmic scale) shows the pattern of major BFR congeners found in the segment of this sediment core dated as 1987. The concentration of TBE was almost 10 times higher than the total concentration of BDE-47, -99, and -100, which are the major components of the penta-BDE commercial product.

The concentrations of TBE and BDE-209 as a function of year of deposition in the core are shown in Figure 5 (note the logarithmic scale). TBE first appeared in this core at a depth corresponding to 1973, which was 4 years later than when BDE-209 was first found in this core. Although the details are hazy, Great Lakes Chemical seems to have first produced TBE 25–30 years ago (9), a time which is compatible with the 1973 advent date we found in this core. The levels of TBE in this sediment core increased rapidly after 1973, with a doubling time of ~2 years until 1985, after which time the TBE concentrations were relatively constant. This increase of TBE concentration with time was much faster than the rate of increase of BDE-209, the concentration of which doubled every 5 years between 1968 and 1982, with a relatively constant concentration after that time. TBE was not found in this core’s top layers corresponding to 0–3.0 cm, which represented 1993–2004 for reasons that are not clear.

According to the U.S. EPA Inventory Update Rule 2002 (16), Great Lakes Chemical produced 4500–22,500 t each year of TBE from 1986 to 1994, but the production decreased to 450–4500 t per year after 1998. This diminution in production may be the cause of the relatively constant

| TABLE 1. Summary of Concentrations (in pg/m³) of TBE and PBDEs in the Atmosphere at Various Sites |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| sampling site                   | beginn | TBE   | BDE-209 | BDE-47 | BDE-99 | BDE-100 | BDE-154 | BDE-153 | BDE-183 | ∑PBDE |
| Bloomington, IN                | 11/22/02 | 6.6  | 0.20   | 2.7   | 2.2   | 0.41   | 0.16   | 0.26   | 0.41   | 13    |
| Bloomington, IN                | 4/15/03  | 2.8  | 7.3    | 7.7   | 4.9   | 1.1    | 0.28   | 0.24   | 0.32   | 17    |
| Rohwer, AR                      | 10/17/02 | 70   | 20     | 2.8   | 4.1   | 0.28   | 0.28   | 0.45   | 0.57   | 79    |
| Rohwer, AR                      | 8/25/03  | 45   | 22     | 23    | 13    | 2.9    | 0.50   | 0.57   | 0.43   | 85    |
| Cocodrie, LA                   | 10/17/02 | 19   | 9.7    | 11    | 5.1   | 1.3    | 0.30   | 0.30   | 0.32   | 37    |
| Cocodrie, LA                   | 1/9/03   | 5.4  | 12     | 2.7   | 1.2   | 0.30   | 0.08   | 0.12   | 0.30   | 10    |
| Chicago, IL                    | 4/15/03  | 6.7  | 65     | 21    | 9.0   | 2.1    | 0.56   | 0.57   | 0.32   | 40    |
| Chicago, IL                    | 5/9/03   | 6.0  | 16     | 31    | 3.8   | 1.6    | nda    | nda    | 0.20   | 43    |
| Chicago, IL                    | 8/25/03  | 9.0  | 17     | 41    | 12    | 3.9    | 0.58   | 0.44   | 0.41   | 67    |
| Chicago, IL                    | 11/17/03 | 4.0  | 15     | 21    | 4.4   | 1.2    | 0.23   | 0.24   | 0.18   | 31    |

a nda, under the limit of detection.
concentrations in the sediment core in sections dating after 1985. However, since Great Lakes Chemical plans to replace the octa-BDE product with TBE, there may be an increase in the production of TBE, which will show up as increased concentrations in surficial sediments in the future. Only time will tell.

2,3,4,5,6-Pentabromoethylbenzene in Atmosphere. To analyze PBDEs in the air samples from the Chicago site, we had to analyze both the hexane and the 1:1 dichloromethane–hexane fractions because PBDEs were present in both fractions (see details in the Experimental Section). In the ECNI GC/MS chromatograms for the hexane fractions, several unknown peaks with early retention times were detected at relatively high abundances in the 2003 summer Chicago samples. These unknown peaks were especially large in both the gas- and particle-phase samples collected in Chicago on July 20, 2003. Figure 6A shows the gas chromatogram of this sample in which the intensities of these unknown peaks (a–f) were 100 times higher than those of the PBDEs in this sample.

To identify these unknown compounds, full-scan ECNI and EI mass spectra were obtained; see Figure 7A,B. The EI mass spectrum of peak a matched with the reference spectrum of 2,3,4,5,6-pentabromochloroethylbenzene (PEB) in the NIST MS library, but the NIST MS library search was not successful for the other unknown compounds. However, the EI and ECNI mass spectra of peak b (see Figure 8A,B) indicated the presence of four bromine and one chlorine atoms (from the molecular ion isotopic pattern of 3:13:22:18:7:1). Otherwise these mass spectra indicated the loss of one methyl group, the same as in the mass spectra of PEB (compare Figures 7 and 8). On the basis of this information, we believe that peak b is an ethyl benzene with four bromine and one chlorine atoms on the ring: a tetrabromochloroethylbenzene. The preferential loss of a bromine atom as opposed to a chlorine was observed in this spectrum (see Figure 8B) as it was in the EI mass spectrum of PEB (17). Peaks d–f may represent three different congeners of tetrabromoethylbenzene.

We quantified PEB in both the gas- and particle-phase samples from Chicago. The PEB concentration was 520 pg/m3 in the gas phase and 29 pg/m3 in the particle phase on July 20, 2003. In the same sample, the total PBDE (tri to hexa)
concentration was 47 pg/m³, and the BDE-209 concentration was 22 pg/m³. We could not quantify the other brominated compounds (the PEB byproducts) because standard chemicals are not available. However, we screened previous GC/MS (GC/MS) chromatograms of other Chicago samples. The peaks for PEB and its byproduct, tetrabromochloroethylenbenzene, were present in most gas-phase Chicago samples, but the intensities of the GC peaks were low, so they were not quantitated. We screened for PEB and its byproducts in the gas-phase samples from the four other sampling sites collected during the summer of 2003. These compounds were detected in these samples, but their intensities were low.

The reason for a relatively high concentration of PEB and its byproducts in the Chicago atmosphere on July 20, 2003, is unclear. PEB and its byproducts were not detected in the laboratory procedural blank samples associated with these Chicago gas- and particle-phase samples. Historically, PEB has been used as an additive flame retardant for thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, polyurethanes) and thermoplastic resins during the 1970s and 1980s. In 1977, the production of PEB was 45–450 t (18, 19). The U.S. EPA proposed that manufacturers and processors of PEB should test for its environmental fate and effects in 1985. The production of PEB declined to 5–225 t in 1986 (16), and in 1988, the proposed rule was withdrawn because there was no ongoing or intended manufacture or processing of this substance (18).

There is no public production information under the U.S. EPA’s TSCA inventory update rule after 1986 (16). Information on the current manufacturers or processors of PEB is not publicly available; in addition, information on the amount of PEB currently produced (if any) is confidential (private communication with EPA TSCA hotline and with the American Chemistry Council). However, PEB is listed as a low production volume chemical manufactured by Albenmarle in France according to the European Chemical Substance Information System (20). PEB production was 10–1000 t in Europe in 2002, where PEB was used in polymers as a flame retardant (21). The structurally related compound, pentabromotoluene, is a moderate production volume flame retardant with a global production of 1000–5000 t/year (22). Recall that pentabromotoluene was detected in our air samples, but it was not as abundant as PEB. There has been only one previous report about PEB in the environment; in this case, the average PEB concentration was 30 pg/m³ in the atmosphere of Chilton (United Kingdom) in 2001. This concentration was three times higher than the average total (tri to hepta) BDE-209 concentration at this site (14).

The detection of small amounts of PEB and its byproducts in our air samples could be residuals from the use of this compound 20 years ago, but the source of the relatively high PEB concentration in the atmosphere at Chicago on July 20, 2003, could be from emissions of fresh PEB used in Chicago. It is also possible the PEB is now being used as a synergistic co-additive in expandable graphite or inorganic flame retardants (23, 24). Further measurements are required to investigate the environmental sources and fates of this chemical. PEB and its byproducts were not detected in the sediment core from Lake Michigan.

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