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Halogenated Flame Retardants in the Great Lakes Environment

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CONSPECTUS: Flame retardants are widely used industrial chemicals that are added to polymers, such as polyurethane foam, to prevent them from rapidly burning if exposed to a small flame or a smoldering cigarette. Flame retardants, especially brominated flame retardants, are added to many polymeric products at percent levels and are present in most upholstered furniture and mattresses. Most of these chemicals are so-called "additive" flame retardants and are not chemically bound to the polymer; thus, they migrate from the polymeric materials into the environment and into people. As a result, some of these chemicals have become widespread pollutants, which is a concern given their possible adverse health effects. Perhaps because of their environmental ubiquity, the most heavily used group of brominated flame retardants, the polybrominated diphenyl ethers (PBDEs), was withdrawn from production and use during the 2004−2013 period. This led to an increasing demand for other flame retardants, including other brominated aromatics and organophosphate esters. Although little is known about the use or production volumes of these newer flame retardants, it is evident that some of these chemicals are also becoming pervasive in the environment and in humans.

In this Account, we describe our research on the occurrence of halogenated and organophosphate flame retardants in the environment, with a specific focus on the Great Lakes region. This Account starts with a short introduction to the first generation of brominated flame retardants, the polybrominated biphenyls, and then presents our measurements of their replacement, the PBDEs. We summarize our data on PBDE levels in babies, bald eagles, and in air. Once these compounds came off the market, we began to measure several of the newer flame retardants in air collected on the shores of the Great Lakes once every 12 days. These new measurements focus on a tetrabrominated benzoate, a tetrabrominated phthalate, a hexabrominated diphenoxyethane, several brominated benzenes, and a highly chlorinated norbornene compound called Dechlorane Plus. Most recently, we have begun measuring the atmospheric concentrations of several organophosphate esters, which are an increasing part of the flame retardant market.

The interesting feature of this story is how one compound or set of compounds has followed another out of and into the marketplace even though none of them have been officially regulated. This replacement of one commercial product by another with similar functions shows that the chemical industry does respond to scientific environmental measurements and to the resulting bad publicity. This is a good thing. The problem is that often the replacement chemicals also become environmentally ubiquitous.

■ INTRODUCTION

Halogenated flame retardants, particularly brominated flame retardants (BFRs), are important commercial chemicals that are added to many consumer and commercial products to inhibit them from burning when they are exposed to a spark or a smoldering cigarette. In fact, in the early 1970s, the State of California created a flammability standard (Technical Bulletin 117) mandating that many household products, such as textiles, furniture, and electronics, be flame-resistant. To meet these regulations, many manufacturers added BFRs to their products. For example, BFRs have been added to polyurethane foam that is used in the furniture found in most homes and offices and to commercial fabrics used in auditorium seating and carpeting. BFRs save lives by reducing fires, but some BFRs have become environmentally ubiquitous, and their adverse health effects on humans and biota have been questioned.[1] This story starts in the 1970s in Michigan and continues to this day.

■ POLYBROMINATED BIPHENYLS

Polybrominated biphenyls (PBBs) were the first generation of brominated flame retardants, and they were produced by Michigan Chemical Corporation at a plant in St. Louis, Michigan. This company manufactured several products from brine, which was pumped from wells under the town. The anionic components of this brine included bromide, which was converted to elemental bromine and used to brominate biphenyl to make PBBs. This PBB mixture was marketed as a flame retardant under the trade name FireMaster, and the most abundant congener present in this mixture was 2,2′,4,4′,5,5′-hexabromobiphenyl (abbreviated PBB-153; see Scheme 1).

This same chemical plant also produced magnesium oxide (MgO), which was used as a nutritional supplement for dairy cows and marketed under the trade name of NutriMaster. Sometime in May 1973, apparently as a result of a shortage of the color-coded, printed paper bags in which FireMaster and NutriMaster (note the similarity of the names) were packaged, some FireMaster was accidentally shipped to a cow-feed-producing mill. The exact details of this mixup will probably never be known, but it is likely that something in the range of

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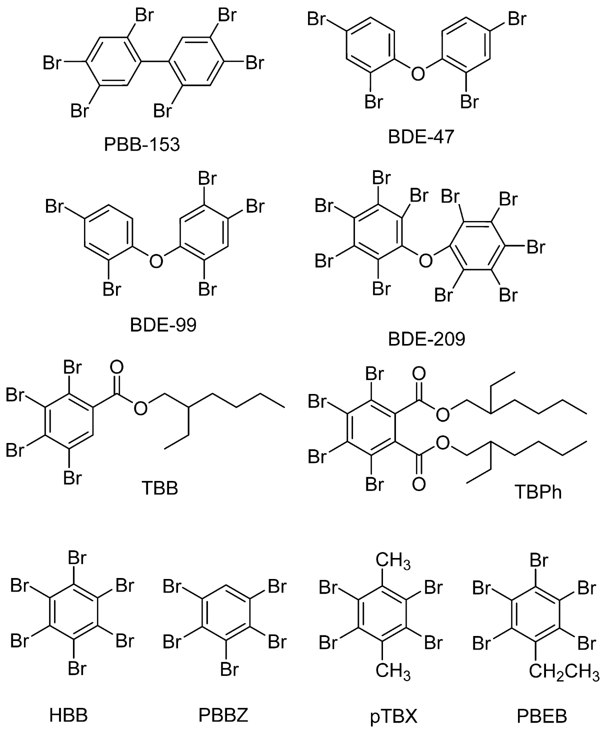
Scheme 1. Structures of the Major Brominated Flame Retardants (BFRs) Discussed in This Account and Their Abbreviations



100−300 kg of FireMaster was shipped to this feed mill. Unfortunately, the feed mill operators mistakenly added FireMaster to dairy cow feed as though it were NutriMaster.

By the late summer of 1973, the contaminated feed produced by this mill had been shipped, both directly and through retailers, to dairy farms, where it was consumed by hundreds of cows. Shortly after, it was clear that the cows eating this feed were not healthy. There was a drop in their milk production, their hooves grew unnaturally, and they were generally malnourished. PBBs were identified as the cause of these health problems in April 1974,[2] and by the end of May, all dairy herds with relatively high levels of PBB contamination were identified and quarantined. Eventually, about 30 000 cows were destroyed by the State of Michigan. Because some farm families continued to consume milk and meat from contaminated cows, these families were especially contaminated with PBBs. Over time, the milk supply of the entire state of Michigan became contaminated with PBBs, and virtually everyone in Michigan became contaminated to some extent. Litigation and legislation ensued. The production of FireMaster in Michigan stopped in November 1974. Michigan Chemical Corporation was purchased by Velsicol Chemical Corporation, and the plant in St. Louis, Michigan, was closed in 1978. The plant was dismantled, and this site was declared a hazardous waste site and eventually remediated. Our recent work, however, shows that it is still emitting PBBs into the atmosphere.[3]

■ POLYBROMINATED DIPHENYL ETHERS

After the production of PBBs stopped, the brominated flame retardant industry introduced a new generation of BFRs, polybrominated diphenyl ethers (PBDEs), the structures of which were not too dissimilar from those of PBBs. PBDEs were widely marketed, and by 2001 about 67 000 tons per year was being sold throughout the world.[4] PBDEs were commercially available as three products, all of which were mixtures of several congeners. The so-called Penta product contained primarily 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) and 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99) (Scheme 1). The Octa product was the least used of the three products, and it contained several hexa- to nonabrominated congeners. The Deca product was also widely used, and it was almost entirely composed of decabromodiphenyl ether (BDE-209) (Scheme 1). In 2001, about 7100 tons of the Penta product was used in North America, representing about 95% of its global use.[4] In 2001, about 24 500 tons of the Deca product was used in North America and about 23 000 tons was used in Europe, representing about 44% and 41%, respectively, of its global consumption.[4] Because of their chemical stability and widespread uses, PBDEs too became ubiquitous in the environment and in people.

Once PBDE measurements of human and environmental samples began to be published in the scientific literature and to a lesser extent in the popular press, the flame retardant industry decided that it was easier (and probably cheaper) to simply abandon the production and sale of PBDEs and to move on to alternative BFR compounds. Thus, the production of the Penta- and Octa-BDEs stopped in 2004, and the production of the Deca-BDE product stopped in 2013. In the meantime, these compounds have been added (or are under review to be added) to the Stockholm Convention's list of restricted substances,[5] and the environment remains contaminated.

Human Samples

The first inkling that PBDEs were becoming ubiquitous contaminants in people was presented by Meironyte et al.[6] in 1999, who measured the concentrations of these compounds in archived samples of Swedish human milk and found that their concentrations were exponentially increasing with doubling times of about 5 years. By 2004, a large number of samples from people had been analyzed for PBDEs. Omitting occupationally exposed people, total PBDE concentrations ranged from <0.03 ng/g of lipid for adipose tissue from Japan in 1970 to >190 ng/g of lipid for milk from Austin, TX, and Denver, CO, in the United States in 2000. A plot of these concentrations versus sampling year (see Figure 1)[4] shows an exponential increase with a doubling time of about 5 years. In general, the PBDE concentrations in people have increased by a factor of about 100 during the last 30 years. The regression of these concentration data as a function of year is good despite the disparate sample types (blood, milk, and tissue), the different continents of origin, and the various congeners measured. This analysis showed that the North American concentrations were always above the regression line (in more recent years by a factor of >10) and that the Japanese concentrations were always below the regression line (by a factor of about 5). This observation suggests that people in the United States were exposed to higher levels of PBDEs than Europeans and that the Japanese were exposed to less than the Europeans.

Our laboratory's work on this subject began with measurements of PBDEs in neonates and in their mothers.[7] Blood from the neonates was obtained from the umbilical cord after delivery of the placenta, and blood from the mothers was obtained from a vein.[7] These data are shown in Figure 2 along with other human data from North America and Sweden.[4] The median concentrations in the Indiana neonate and maternal

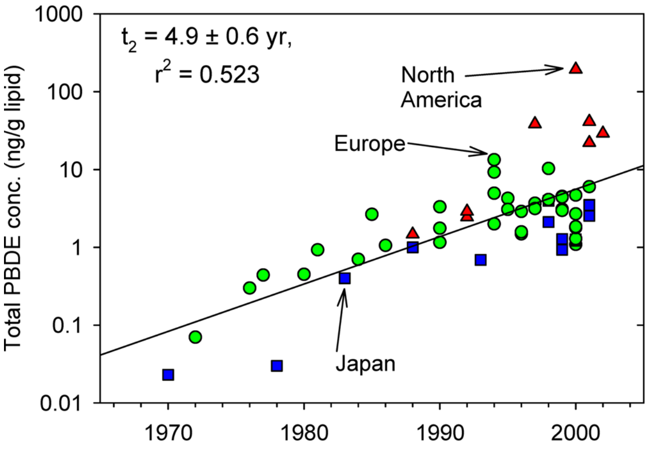


Figure 1. Total polybrominated diphenyl ether (PBDE) concentrations in human blood, milk, and tissue samples.[4] Data from occupationally exposed individuals are excluded. Data are normalized to lipid levels with units of ng/g of lipid and are from the literature up to May 2004. Red, green, and blue symbols are for data from North America, Europe, and Japan, respectively. Reproduced from ref 4. Copyright 2004 American Chemical Society.

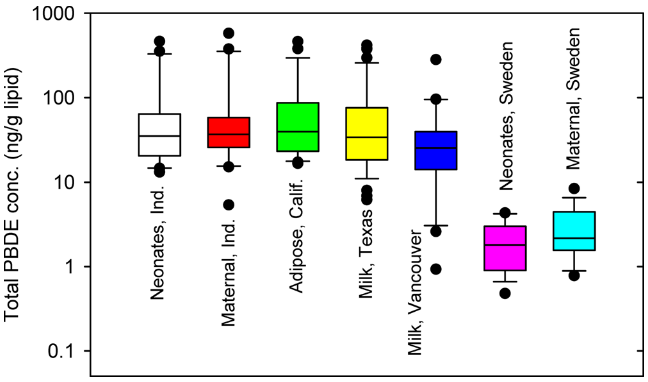


Figure 2. Total polybrominated diphenyl ether (PBDE) concentrations (ng/g of lipid) in various human samples from Indiana, California, Texas, Vancouver, and Sweden.[4] The boxes show the 25th and 75th percentiles, and the whiskers show the 10th and 90th percentiles. The high and low outliers are shown as dots, and the line in each box is the median concentration. The interlaboratory measurement variations are much less than a factor of 2. Reproduced from ref 4. Copyright 2004 American Chemical Society.

sets of samples (the two leftmost boxes) and in the samples from California and Texas were about the same, averaging about 35 ng/g of lipid. The median concentration in the Vancouver (Canada) milk samples was somewhat lower than the United States value, and the Swedish neonatal and maternal blood concentrations (the two rightmost boxes in Figure 2) were much lower at about 2 ng/g of lipid. In other words, the concentrations of PBDEs were about 20 times higher in Americans compared with Swedes. It is likely that the North American samples show relatively high concentrations because of the focused use of the Penta-BDE product in North America.

Environmental Samples

After 2003, our laboratory's research on PBDEs began to focus on the North American Great Lakes (Figure 3), and the rest of this Account will present some of these results. Why the Great Lakes? These five lakes are the largest freshwater reservoir on Earth; they are an important part of North America's ecosystem; the drainage basin is the home to 10% of the population of the United States and 30% of the population of Canada; there are important commercial centers in the region (18% of the combined GDP of the two countries); the lakes are a major recreational resource for both countries; and they are a major transportation route for intralake and (through the St. Lawrence Seaway) global shipping. Thus, it was important to determine the spatial and temporal variations in flame retardant levels in the Great Lakes environment. We started with fish.

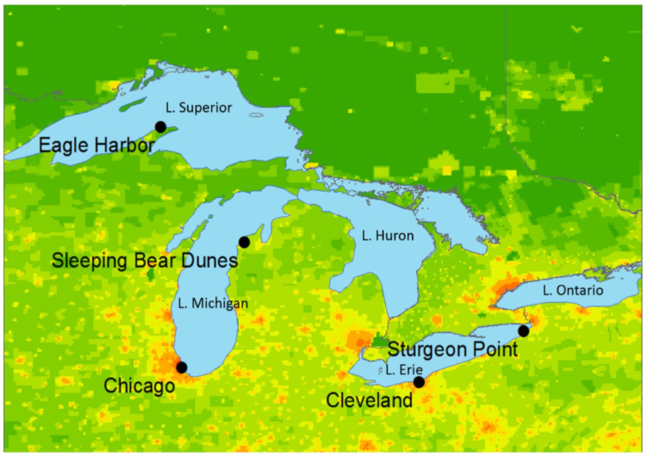


Figure 3. Map of the North American Great Lakes showing the five Integrated Atmospheric Deposition Network sampling sites. The yellow- and orange-colored locations indicate areas of relatively high population density.

Historically, one measure of the environmental health of the Great Lakes has been pollutant concentrations in lake trout, which is a top salmonid predator. Thus, these fish have been collected from the five lakes by the U.S. Government, and composites have been ground together, frozen, and archived. Past studies of these samples have focused on classic chlorinated organic compounds, such as DDT and polychlorinated biphenyls (PCBs), and it is now known that the concentrations of these compounds decreased by a factor of ~10 between 1970 and 1990.[8] In our flame retardant research, we used these archived fish samples to explore the historical and geographical distributions of PBDEs in the Great Lakes.

Our measurements of total PBDE concentrations in these fish as a function of the year when they were collected, covering the period 1980–2000, are shown in Figure 4.[9] The statistically significant linearity of the regressions suggests that the concentrations of these compounds in Great Lakes trout increased exponentially between 1980 and 2000, much like those in human samples. In this case, the rate of increase suggests doubling times of 3–4 years. In these samples, Lake Michigan and Lake Superior generally showed the highest PBDE concentrations, which is surprising given that Lake Superior is thought to be the most pristine of the Great Lakes. Perhaps the relatively high PBDE concentrations in Lake Superior are a result of the slow contaminant removal processes at work in the very cold water of this lake. Our finding that trout from Lake Michigan were generally the most contaminated with PBDE was expected given the large population residing on the shores of this lake and the intense industrial processes associated with the large urban regions (from Milwaukee, WI, through Gary, IN) on Lake Michigan. Although the doubling times we measured in these samples are not statistically distinguishable among the lakes, there are

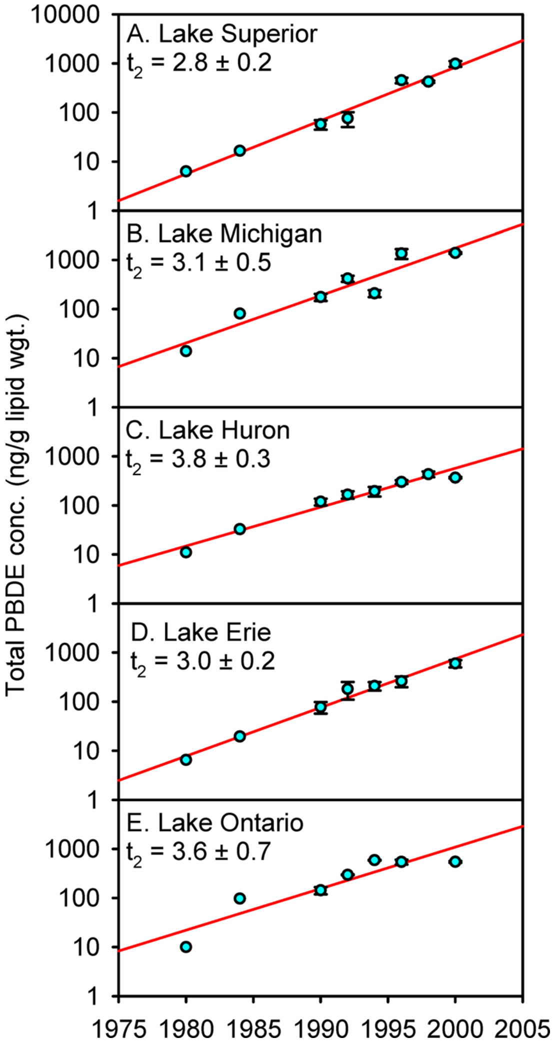


Figure 4. Total polybrominated diphenyl ether (PBDE) concentrations in ng/g of lipid in archived lake trout from the five North American Great Lakes (walleye from Lake Erie) as a function of collection year.[9] The concentrations from 1990 to 2000 were measured in triplicate, and the standard errors of these measurement are shown. All of the regressions with time are significant at $P < 0.05$. The times for the concentrations to double (t_2, in years) are shown in each panel. Replotted from ref 9.

some preliminary indications that PBDE concentrations may have leveled off in Lake Huron and Lake Ontario since 1996. These earlier findings have been confirmed by more recent work of Crimmins et al.[10]

We also measured PBDEs in Great Lakes bald eagles.[11] Bald eagles are top predators in the food web, which makes them susceptible to accumulation of high levels of lipophilic environmental contaminants such as PBDEs. We collected eaglet plasma samples in 2005 from six nests in the Lake Michigan basin, six in the Lake Huron basin, and three in the Lake Superior basin. PBDEs were detected in all 15 samples, but there were no statistically significant differences in the total PBDE levels among these three areas. The geometric mean concentration was about 6 ng/g wet wt. With the assumption of a lipid concentration of 0.5% in human serum,[12] the median North American PBDE levels shown in Figure 2 convert to about 0.2 ng/g wet wt. Thus, our measured levels in bald eagle nestlings are about 30 times higher than in people from North America. The most abundant congeners were BDE-47 and BDE-99, but BDE-209 (the fully brominated congener, which was thought to have very low bioavailability) was detected in one-third of the samples. More recently, using a contiguous population of bald eagle nestlings, Route et al.[13] obtained PBDE concentrations similar to our measurements and reported that these levels had decreased by “5.5% annually from 2006–2011”, which is good news given the relatively high concentrations in eagles.

Perhaps as a result of these and many other studies showing that people and the environment were contaminated with PBDEs, the flame retardant industry decided to withdraw the less brominated BDE products (Penta-BDE and Octa-BDE) from the marketplace at the end of 2004 and the fully brominated product (Deca-BDE) at the end of 2013. Nevertheless, the regulations requiring that flame retardants be added to many consumer goods remained in place, and in fact, the elimination of these regulations was opposed by the flame retardant industry.[14] In any case, it was clear that other BFRs would be entering the market as replacements for the unavailable PBDEs and that the environmental levels of these PBDE replacements should be tracked as a function of time. Thus, after about 2005, the questions turned from enumerating PBDE concentrations in the environment to determining whether removing them from the market would be effective in eliminating them from the environment, and if so, how fast these changes were taking place. We addressed these questions by repeated measurements of PBDEs (and their replacements) in the atmosphere of the Great Lakes.

We focused on the atmosphere because it is a critical pathway for the input of pollutants into the Great Lakes. By about 1990, many of the direct sources (so-called point sources) of pollutants to the Great Lakes had been eliminated, and many contaminants were entering the lakes through atmospheric deposition. In this process, pollutants from many sources (an entire city, for example) can move through the atmosphere (in some cases for considerable distances) and then be deposited either by vapor exchange with the surface water, direct particle deposition on the water (dry deposition), or scavenging by rain or snow (wet deposition). Fish exposed to these contaminated waters (and sediment) bioaccumulate these contaminants in their flesh.

Our five atmospheric sampling sites are shown in Figure 3. These sites range from the highly populated Chicago area to the very remote tip of the Keweenaw Peninsula at Eagle Harbor, MI. These sites are part of the Integrated Atmospheric Deposition Network (IADN), which is a joint United States—Canadian project. At each location, we collect about 820 m^3 of air over a 24 h period once every 12 days. The air is first drawn through a quartz fiber filter with a 0.2 μm cutoff to collect the atmospheric particle phase and then through a bed of XAD-2 resin to collect the atmospheric vapor phase. This project has been operating continuously since 1991, although our measurements of flame retardants started in 2005.[15] By now, we have enough data that we can use rigorous statistical methods to determine whether the spatial and temporal differences we see among the sites are significant.

Let us first look at the concentration variations among the five sampling sites. Figure 5A–C shows the geometric mean concentrations (and their standard errors) of BDE-47, BDE-99, and BDE-209 at each of the five United States sampling sites on the shores of the Great Lakes. Our first step in analyzing these data was to add the concentrations we measured in the particle

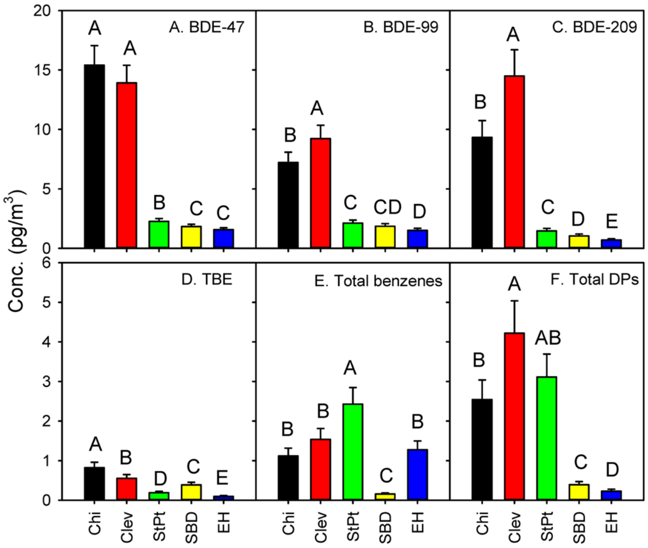


Figure 5. Concentrations of various brominated flame retardants (BFRs) and Dechlorane Plus (DP) in the atmosphere (in pg/m^3) at five sites around the Great Lakes. See Figure 3 for site locations; the abbreviations are Chi, Chicago; Clev, Cleveland; StPt, Sturgeon Point; SBD, Sleeping Bear Dunes; EH, Eagle Harbor. The concentration data are geometric means ± standard errors for samples collected every 12 days from 2005 to 2012 (inclusive). The concentration scale is different for the upper and lower panels. The compound abbreviations are given in Schemes 1−3. The letters A to E are from an analysis of variance (ANOVA) of the logarithmically transformed concentrations; sites sharing a letter are statistically indistinguishable from one another with $P < 0.05$.

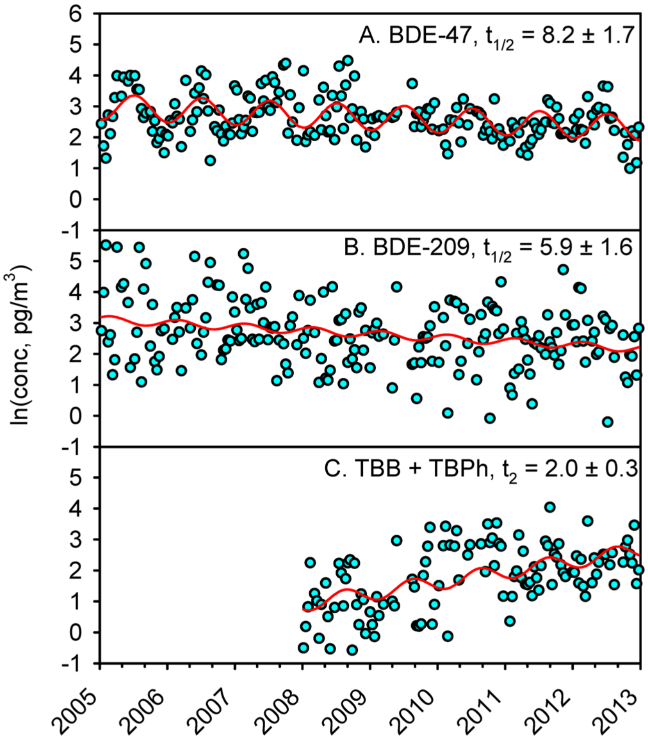


Figure 6. Vapor plus particle phase, atmospheric concentrations of (A) BDE-47 and (B) BDE-209 measured at Cleveland, OH, every 12 days starting in January 2005 and ending in December 2012 and (C) TBB and TBPh (concentrations summed together) measured at Cleveland starting in January 2008 and ending in December 2012. The values are given as the natural logarithms of the concentrations in pg/m^3. The regression lines (red) were fitted using eq 1, and all were significant at $P < 0.001$. The compound abbreviations are given in Scheme 1. The halving times ($t_{1/2}$) and doubling times (t_2) are given in years.

phase to those we measured in the vapor phase to get total atmospheric concentrations. In addition, because environmental concentration measurements are log-normally distributed,[16] all averages presented here are geometric means. Data over the entire sampling period, from January 2005 until December 2012, were averaged to eliminate seasonal effects, which are sometimes large (see below). It is very clear that the atmospheric concentrations of PBDEs at Chicago and Cleveland are significantly higher than the others. This is expected given that flame retardants are used in products that are common household items, whose abundance increases with population density. What is surprising is that the BDE-99 and BDE-209 concentrations at Cleveland are significantly higher than those at Chicago even though the population of greater Chicago is about 3-fold that of Cleveland. We attribute this result to a higher degree of industrialization in Cleveland compared with Chicago. The BDE-47, BDE-99, and BDE-209 concentrations at the other three sites are much lower than in the cities, with the lowest levels usually found at Eagle Harbor, which is our most remote and least populated site.

Having measured these concentrations every 12 days at these sites, we can determine whether there has been a change in these levels since 2005 (when our measurements began). We have published a series of papers on these temporal trends using an increasing number of data.[15,17,18] In this Account, we have updated these results with data through 2012 for BDE-47 and BDE-209. Figure 6A,B shows these results for Cleveland only, where the PBDE atmospheric concentrations are the highest. These time-series data have been fitted with an equation that describes the seasonality of the concentrations (many of which tend to be higher in the warmer summer months) and the long-term trends (if any) of the concentrations:[19]

$$\ln(C) = a_0 + a_1 \sin(zt) + a_2 \cos(zt) + a_3 t \tag{1}$$

where the a_i are fitted constants, $z = 2\pi/365.25$ (which sets the periodicity to 1 year), and t is the sampling date. This multiple regression also tells us whether the coefficients are statistically significant. It should be noted that a_3 is a rate constant, and from its value we can calculate a halving time ($t_{1/2}$) or a doubling time (t_2), which are the times required for the atmospheric concentration to decrease or increase, respectively, by a factor of 2:

$$t_{1/2} = -\frac{\ln(2)}{a_3} \tag{2}$$

$$t_2 = \frac{\ln(2)}{a_3} \tag{3}$$

For both BDE-47 and BDE-209, the fitted values of a_3 are statistically significant with $P < 0.001$. From this analysis, we determine that the concentrations of BDE-47 are significantly decreasing with a halving time of 8.2 ± 1.7 years (Figure 6A). Thus, it appears that abandoning the production of the less brominated PBDEs (including BDE-47) at the end of 2004 is having a slow but significant effect, at least in Cleveland. Interestingly, the temporal trend data and the regression for BDE-209 also show a significant decrease with a halving time of

5.9 ± 1.6 years (Figure 6B). This halving time is not significantly different than the one for BDE-47. In fact, it is surprising that these concentrations are decreasing at all given that BDE-209 was pulled from the market at the end of 2013. It is noteworthy that the seasonality for BDE-209 is very much less than for BDE-47 and that it is not statistically significant. This is a result of the much lower vapor pressure of BDE-209 (Br_{10}) compared with that of BDE-47 (Br_4), which indicates that BDE-209 is more particle-associated than BDE-47.

The temporal trends at the other sites are not as clear as at Cleveland. For example, at the more remote sites of Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point, the concentrations of BDE-47 are actually increasing with doubling times of 7−11 years.[17] This observation suggests that the elimination rates of BDE-47 are much higher at the most contaminated sites (the cities) than at the remote sites. In other words, taking BDE-47 off the market in 2004 has had the largest effect at the locations where this compound was used the most. We expect to eventually see decreasing atmospheric concentrations of BDE-47 at all of the sites as the atmospheric effects become more homogeneous. This is what we observed for PCBs, which were banned in 1976; the atmospheric levels of PCBs at the five Great Lakes sites are now all decreasing at the same rate.[20] Unlike Cleveland, the atmospheric concentrations of BDE-209 are not significantly changing (one way or the other) at Chicago, Sleeping Bear Dunes, or Eagle Harbor.[17] As BDE-209 was only recently removed from the market, it may be too early to see the full effect (if any) of this market shift.

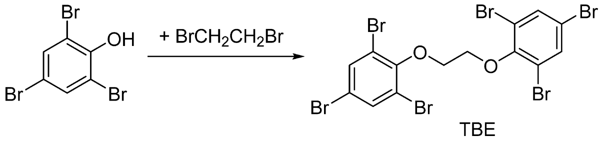
■ TETRABROMINATED BENZOATE AND PHTHALATE

When the PBDEs were pulled from the flame retardant market, they were replaced by other brominated compounds that could serve the same function. The most important of these newer flame retardants are 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB or EH-TBB) and di-2-ethylhexyl tetrabromophthalate (TBPh or BEH-TEBP) (see Scheme 1). These two compounds are the two brominated components of FireMaster 550, a commercial flame retardant mixture, which also includes some arylphosphate esters (more on these below). Our atmospheric measurements of these two newer compounds began in 2008,[21] and these data for Cleveland are shown in Figure 6C as the sum of the concentrations of TBB and TBPh in the vapor and particle phases. Even though we have only five years of data for these compounds, it is clear that their atmospheric concentrations—at least at Cleveland—are increasing significantly with a doubling time of about 2 years, which is rather rapid. The seasonal component of this regression is not significant, probably because, like BDE-209, TBB and TBPh are mostly bound to atmospheric particles. The comparison of the concentration data shown here for BDE-47 and BDE-209 on the one hand and for TBB + TBPh on the other clearly shows the succession of one chemical product (the PBDEs) by another (FireMaster 550)—at least at Cleveland—and that this effect is easily noted by careful environmental measurements. Incidentally, TBB and TBPh have recently been detected in human serum and milk samples collected in Canada.[22]

■ BROMINATED PHENOXYS AND BENZENES

Other brominated compounds have also been used over the years as flame retardants, and our atmospheric data have uncovered some of them. One of the first ones we detected was 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE or BTBPE), which was advertised by the flame retardant industry as a replacement for the Octa-BDE mixture.[23] This is one of a series of BFRs made from 2,4,6-tribromophenol (see Scheme 2).[24]

Scheme 2. Industrial Synthesis of 1,2-Bis(2,4,6-tribromophenoxy)ethane (TBE) from 2,4,6-Tribromophenol



The geometric mean concentrations of TBE are shown in Figure 5D. These concentrations correlate well with the population densities of the sampling sites, with Chicago > Cleveland > Sleeping Bear Dunes > Sturgeon Point > Eagle Harbor. In general, however, the atmospheric concentrations of this compound are low compared with those of the PBDEs.

Brominated benzenes have also been used as flame retardants, although the exact applications of most of these compounds remain obscure. In our Great Lakes atmospheric data, we have observed hexabromobenzene (HBB), pentabromobenzene (PBBZ), tetrabromo-*p*-xylene (pTBX), and pentabromoethylbenzene (PBEB) (see Scheme 1).[25] For simplicity, we have added the concentrations of these four compounds together in both the vapor and particle phases, and the geometric means of this total are shown in Figure 5E. The ANOVA results indicate that these concentrations at Chicago, Cleveland, and (surprisingly) Eagle Harbor are statistically indistinguishable from one another and that the concentration is highest at Sturgeon Point. We suspect that this spatial variation is related to the presently unknown usage patterns of these compounds.

■ DECHLORANE PLUS

In the course of making these quantitative measurements by gas chromatographic mass spectrometry, two GC peaks were observed that did not correspond to any of our targeted analytes. The power of mass spectrometry was especially suited to identifying these previously unsuspected compounds, and we proceeded to do so. The portions of the gas chromatograms and the corresponding electron capture negative ionization (ECNI) mass spectra of these unknown peaks are given in Figure 7 (the mass spectra of the two peaks were identical). The isotopic pattern clearly indicated the presence of 12 chlorine atoms and a monoisotopic molecular weight of 648. The 12 chlorine atoms suggested to us that this molecule might be made from the common cyclic intermediate hexachlorocyclopentadiene (C_5Cl_6). Thus, subtracting the mass of 2 moles of this compound from a monoisotopic molecular weight of 648 left us with 108, which could correspond to C_9 or more likely C_8H_{12}. Putting this together suggested the elemental composition of the unknown compounds to be $C_{18}H_{12}Cl_{12}$. Consulting the literature led us to a commercially available compound with the trade name of Dechlorane Plus (DP), which interestingly enough is marketed by OxyChem as a flame retardant for hard plastics and is manufactured in the city of Niagara Falls, NY.[26] Scheme 3 shows the synthetic process that results in two DP conformers (called syn and anti). We obtained (surreptitiously) a sample of the commercial product,

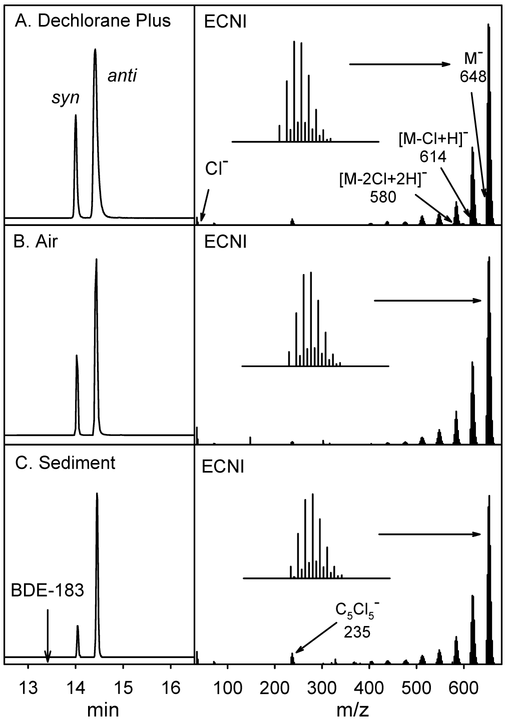
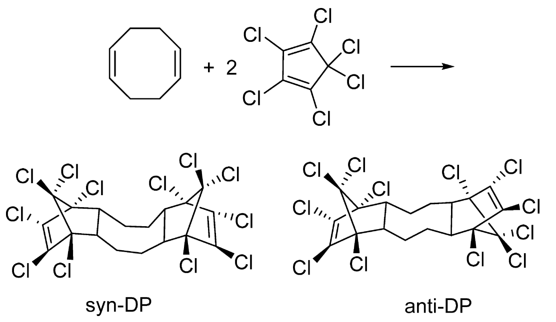


Figure 7. (left) Electron capture negative ionization (ECNI) gas chromatograms (monitored at *m*/*z* 652) and (right) ECNI mass spectra of *anti*-Dechlorane Plus (DP) from (A) the commercially available material, (B) a particle-phase atmospheric sample collected at Sturgeon Point, NY, in July 2004, and (C) a sediment core section (sediment depth = 39 cm) taken off Long Point in Lake Erie at a water depth of 62 m.[26] The mass spectral insert shows the molecular ion isotopic distribution. Reproduced from ref 26. Copyright 2006 American Chemical Society.

Scheme 3. Industrial Synthesis of Dechlorane Plus (DP) Showing the Conformations of the Two Resulting Conformers



and the GC retention times of the two peaks and the corresponding mass spectra (see Figure 7A) perfectly matched those of the compound we had found in the air at Sturgeon Point (Figure 7B) and subsequently found in sediment from Lake Erie (Figure 7C). In the commercial product (and in the environment), the anti conformer is about 3 times more abundant than the syn conformer. These two conformers can be easily separated by gas chromatography (Figure 7, left panels), and their ratio is characteristic.

Once we had identified these compounds, we began to measure their concentrations in our regular atmospheric samples, and the resulting geometric means of the syn and anti conformer concentrations in the vapor and particle phases, all added together, are shown in Figure 5F. The levels were especially high at Cleveland and Sturgeon Point, which are the two sampling sites closest to the DP manufacturing facility in Niagara Falls, NY. We also found that DP levels in sediment from Lake Ontario were relatively high compared with the other Great Lakes,[27] a result confirmed by Yang et al.[28] After this compound was "sighted" in the Great Lakes, subsequent work has shown that it is a global contaminant, and it has been found in air from Alaska to Tasmania.[29] DP is also present in human serum collected from people in France, China, and Canada.[30]

■ ORGANOPHOSPHATE ESTERS

In addition to these brominated and chlorinated compounds, several organophosphate esters (OPs) have also been used as organic flame retardants, and in fact, their use as flame retardants may increase as the brominated compounds are taken off the market. In this case, there are many such compounds that have been used for these and other applications, such as plasticizers and antifoaming agents in hydraulic fluids; thus, interpreting data on their concentrations in the environment is more complex than for the BFRs. Several of these compounds are present in water, sediment, indoor air and dust, fish and biota, and human blood and milk,[31] but there have been only a handful of measurements of these chemicals in the ambient atmosphere. Some of the most recent such data are from our laboratory.

We measured several halogenated and nonhalogenated OPs in particle samples collected on the shores of the Great Lakes (see Figure 3) from March 2012 to December 2012 (inclusive). On average, the most abundant OPs in the samples were tri-*n*-butyl phosphate, tris(1-chloro-2-propyl) phosphate, and tris(butoxyethyl) phosphate.[32] By way of summary, in Figure 8 we show box plots of the total concentrations of the 12 OPs measured in this study as a function of location. These levels are relatively high, ranging from about 1500 pg/m^3 in Chicago and Cleveland down to about 100 pg/m^3 at Eagle Harbor. For comparison, we have included in Figure 8 the concentrations of total PBDEs, TBB, and TBPh measured over the same time period. A one-way ANOVA of total OP, total PBDE (the sum of about 35 congeners), TBB, and TBPh concentrations at each site showed that the total OP concentrations were consistently

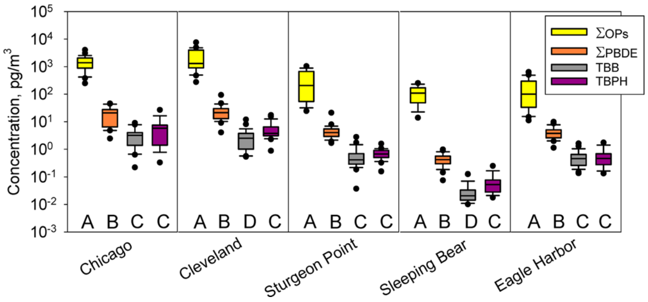


Figure 8. Atmospheric total organophosphate ester (OP), total polybrominated diphenyl ether (PBDE), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), and di-2-ethylhexyl tetrabromophthalate (TBPh) concentrations in the particle phase at five sampling sites around the Great Lakes (see Figure 3).[32] The box and whisker scheme is the same as used in Figure 2. ANOVA results using logarithmically transformed concentrations are shown; concentration distributions sharing the same letter are not statistically different at $P < 0.05$. Reproduced from ref 32. Copyright 2013 American Chemical Society.

higher ($P < 0.001$) at all five Great Lakes sites compared with the corresponding total PBDE, TBB, and TBPh concentrations at the same sites. The total OP concentrations are about 100, 1200, and 600 times higher (on average) than the PBDE, TBB, and TBPh concentrations, respectively. These are relatively high levels, but it is too early to tell whether these concentrations are increasing or decreasing with time. Nevertheless, in view of these high concentrations, their environmental behavior bears watching.

CONCLUSIONS

The interesting feature of the flame retardant story is how one compound or set of compounds has followed another out of and into the marketplace even though none of these compounds had been regulated in any way, at least in the United States. The PBBs were followed by the PBDEs, which were in turn followed by TBB and TBPh, and many of the brominated compounds are now being replaced (to some extent) by the organophosphate esters. This replacement of one commercial product by another with similar functions, and in some cases similar structures (PBBs vs PBDEs), shows that the chemical industry does respond to scientific environmental measurements and to the resulting bad publicity. This is a good thing. The problem is that often the replacement chemicals also become environmentally ubiquitous. This cycle will eventually stop as new chemical products are developed that do not leak into the environment from their intended applications.

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Notes

The authors declare no competing financial interest.

Biographies

Marta Venier was awarded her Laurea degree at the University of Trieste (Italy). She received a doctoral degree and postdoctoral training at Indiana University and is now an Assistant Scientist there. She has published about 30 papers on topics ranging from in vitro toxicology to environmental chemistry and has worked on legacy persistent organic pollutants and flame retardants in humans, biota, and the environment.

Amina Salamova is an Assistant Scientist at Indiana University. She received her doctorate and postdoctoral training there and has three other degrees from Indiana University and Baku State University (Azerbaijan). Her research focuses on persistent organic pollutants in various environmental media, emphasizing the determination of spatial and temporal trends in regional and global environments and the investigation of human exposure routes.

Ronald A. Hites received a Ph.D. from the Massachusetts Institute of Technology, and he remained on the staff and faculty of MIT until 1979, when he became a Professor of Public and Environmental Affairs at Indiana University. In 1989, he was appointed a Distinguished Professor. He is a Fellow of the American Chemical Society (ACS), of the American Association for the Advancement of Science (AAAS), and of the Society for Environmental Toxicology and Chemistry (SETAC). He is the winner of the 1993 Founders Award from SETAC and the 1991 Award for Creative Advances in Environmental Science and Technology from ACS.

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