Brominated Flame Retardants in the Great Lakes: A Review

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There is now good evidence that non-reactive brominated flame retardants (BFRs) are widely present in the Great Lakes. These compounds include the long banned polybrominated biphenyls (PBBs), the recently restricted polybrominated diphenyl ethers (PBDEs), and the currently used decabromodiphenyl ether and hexabromocyclododecane (HBCD). This review focuses on the concentrations of these compounds in air, fishes, birds, and sediment from the Great Lakes.

Polybrominated Biphenyls

PBBs were a disaster for the State of Michigan. They were accidentally mixed into dairy cow feed in mid-1973, and as a result, the milk of much of the state and many Michiganders themselves became contaminated. The history of this accident makes an interesting lesson and is summarized here based on the account by Fries.[1]

The Michigan Chemical Corp. operated a plant in St. Louis, Michigan, on an impounded section of the Pine River. This company manufactured several products from brine pumped from wells under the center of the lower peninsula of Michigan. The anionic components of this brine included bromide, which was converted to elemental bromine and used to brominate biphenyl to make PBBs. This mixture was marketed under the trade name FireMaster FF-1, which was a white powder. The manufacturing of PBBs at this Michigan plant started in 1970 and ended in 1974, during which time about 2500-5000 metric tons had been produced. The congener composition of FireMaster was largely 2,2',4,4',5,5'-hexabromobiphenyl (also called BB-153 using the IUPAC numbering system).

This same plant also used the cationic components of the brine to produce other useful products. Among these products was magnesium oxide, which was used as a nutritional supplement for dairy cows. This material had the trade name of NutriMaster, and it was also a white powder. Sometime in May 1973, there was apparently a shortage of the color-coded, printed paper bags in which these two products were packaged, and as a result, some FireMaster was shipped to a mill, which formulated dairy cow feed, in bags that were hand-labeled "NutriMaster". The exact details of this mistaken transaction will probably never be known, but it is likely that something in the range of 100-300 kg of FireMaster was shipped to this feed mill, which was located in Climax, Michigan. Unfortunately, the feed mill believed the labeling on the bags and mistakenly added PBBs to the dairy cow feed as though it were NutriMaster.

By the fall of 1973, the feed produced by this mill had been shipped, both directly and through retailers, to dairy farms where this contaminated feed was consumed by cows. By late September 1973, it was clear that the cows eating this material were not healthy. There was a precipitous 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, and by the end of May, all dairy herds with a high level of PBB contamination (>5 ppm) were identified, quarantined, and eventually destroyed. During this period, some farm families had unknowingly consumed milk from the contaminated cows and, in some cases, had even eaten meat from the slaughtered cows. As a result, these dairy farmers and their families were particularly contaminated. Eventually, the milk supply of the entire state of Michigan (with the possible exception of the Upper Peninsula) had become contaminated with PBBs, and as a result, virtually everyone in Michigan became contaminated to some extent.

Litigation and legislation ensued, the details of which are outside the scope of this review. Suffice it to say that the production of FireMaster in Michigan stopped on November 20, 1974.[2] Michigan Chemical Corp. was purchased by the Velsicol Chemical Corp., and the plant in St. Louis, Michigan was closed in 1978. The plant was dismantled, and this site and the local county dump, which had been used during PBB production, were declared hazardous waste sites. The former plant site and the adjacent impoundment of the Pine River contained about 1 metric ton of PBBs, and the county dump contained about 80 metric tons of PBBs.[3] Even after remediation during the 1982-1985 time period, these two sites are still highly contaminated.

In addition to the contamination of the dairy industry and people of Michigan, PBBs also contaminated the environment and the Great Lakes. The concentrations of PBBs in Great Lakes fishes, birds, and sediment are summarized in the first row of Table 1. It is clear that the concentrations of these compounds are very high in the vicinity of the old plant in St. Louis, Michigan, that fishes and sediment throughput the Great Lakes are also contaminated, and that the level of this contamination is decreasing very slowly, if at all. Given that PBBs are still present in the Great Lakes 30 years after the direct input of PBBs was stopped, it seems safe to conclude that PBBs are highly persistent compounds that will be present for many years to come.

Polybrominated Diphenyl Ethers

With the demise of PBBs as a viable product, the brominated flame retardant industry turned to polybrominated diphenyl ethers (PBDEs) as a replacement. PBDEs have become a popular product; for example, furniture-grade polyurethane foam is now treated with 1-10% by weight of PBDEs to make this material safe for home use.[4] Not surprisingly, the use of PBDEs has increased over the years, and global annual sales are now ~70,000 metric tons.[4]

Despite their societal benefits, PBDEs seem to be migrating from the products in which they are used and entering the environment and people. PBDEs are now ubiquitous; they can be found in air, water, fish, birds, marine mammals, and people, and in many cases, the concentrations of these compounds are increasing exponentially over time,[4] doubling every 5 years or so. Perhaps as a result of these observations, several governments have banned the use of the penta- and octa products, and the major U.S. manufacturer of these materials (Great Lakes Chemical) has voluntarily stopped producing these two products. The deca-BDE product is, however, still in use, and the flame retardant industry shows no signs of abandoning it.[5]

The second row of Table 1 summarizes what is known about PBDEs in the Great Lakes. In the atmosphere, the concentrations of these compounds are highest in a big city (Chicago), indicating urban sources (as opposed to agricultural). In fishes, birds, and sediment, PBDE concentrations are on the rise, doubling every 3-10 years. Interestingly, in sediment the decabrominated congener predominates, as opposed to the rest of the environment, where BDE-47 dominates.

1,2,5,6,9,10-Hexabromocyclododecane

This compound is an additive BFR used in polystyrene. The commercial product contains three isomers, among which the g isomer is the most predominant at 75-90% of the total, the a isomer is next at 10-13%, and the b isomer is least at <0.5-12%.[6] The third row of Table 1 summarizes the little that is known about these compounds in the Great Lakes. In general, HBCD concentrations are 100-fold lower than those of PBDEs.

1,2-*Bis*(2,4,6-tribromophenoxy)ethane

During the analysis of PBDE in the particle-phase of atmosphere samples from various sites in the United States, Hoh et al.[7] noticed a significant, unknown, bromine-containing GC peak in some samples. This compound was identified as 1,2-*bis*(2,4,6-tribromophenoxy)ethane (TBE). The fourth row of Table 1 summarizes the concentrations of TBE in air and sediment of the Great Lakes. In general, in these samples, the TBE levels are on the order of a few percent of the levels of the PBDEs, which is a significant amount.

It is interesting to note that the only producer of TBE in the United States, Great Lakes Chemical, produces this compound at a facility located in El Dorado, Arkansas, and it is likely that the production of TBE will increase at this site given that Great Lakes Chemical has announced that they will market TBE (trade named FF-680) as an additive flame retardant to replace the discontinued octa-BDE product.[7]

2,3,4,5,6-Pentabromoethylbenzene

PEB was found by Hoh et al.[7] in gas- and particle-phase atmospheric samples collected in the summer of 2003 in Chicago. Its identity was verified by comparison of the unknown mass spectra and GC retention times with those of authentic material. In the Chicago sample collected on July 20, 2003, the PEB concentration was 520 pg/m^3 in the gas-phase and 29 pg/m^3 in the particle-phase. In the same sample, the total PBDE (tri- through hexabrominated)

concentration was 47 pg/m^3, and the BDE-209 concentration was 22 pg/m^3. PEB was present in most other Chicago atmospheric samples, but its abundance was low. The reason for a relatively high concentration of PEB in the Chicago atmosphere on this one summer's day is unclear.

Recommendations

Table 1 shows that there is reasonably good data at hand for the PBDEs, but there is much less information for the other BFRs. While the PBBs are no longer in production or use, it is clear that these compounds are persistent in the environment and in people; thus, it would be a good thing to continue to monitor the concentrations of these compounds in (at least) the sediment and fishes of the Lakes. The other BFRs (HBCD, TBE, and PEB) are not now abundant in the Lakes, but the likelihood of their increased use in the future suggests that they too be monitored in the sediment and fishes of the Lakes. Of course, the PBDEs are not a closed issue either. Even though the penta and octa products are no longer produced, the deca product (BDE-209) is still being marketed aggressively, and the residues of the penta and octa products are still out there and are not going away soon. Given the increasing concentrations over time for these compounds, continued work on all of them is certainly warranted.

Table 1. Summary of Available Data for Five Brominated Flame Retardant Classes Found in the Great Lakes.[a]

	Air (pg/m^3)	Fishes (ng/g lipid)	Birds (ng/g lipid)	Sediment (ng/g dry wgt)
PBBs		>>1000 upstream of Tittabawassee R.; 100-1000 downstream this river; <<100 in open Lakes No significant decrease 1980-2000, except L. Huron where $t_{1/2}$ = 19 yr	100-500 in eggs from Green Bay	1000-100,000 near plant; 100-1000 after plant but upstream of Saginaw Bay; 0.01-0.1 in eastern L. Erie & 0.03-0.1 in northern L. Michigan
PBDEs	5-15 near Lakes Michigan, Superior, & Erie; ~50 in Chicago Present in both the atmospheric gas and particle phases	400-3000 in top predators in 2000; 1-10 in 1980 Lakes Michigan and Superior now highest; Lake Huron now lowest Strong trend with time; t_2 = 3-4 years in all five Lakes Systematic changes in congener ratios with time	In herring gull eggs from all Lakes: 5000-10,000 in 2000; 100-300 in 1980-1985 t_2 = 3 years Systematic changes in congener ratios with time	Almost all is the deca congener 200-400 in northern L. Michigan; 20-100 in L. Erie; 5-20 in L. Superior Burdens: 100 tons in northern L. Michigan; 10 tons in L. Erie; 4 tons in L. Superior t_2 = 5-8 years in L. Michigan & Erie; 45 years in L. Superior
HBCDs		4-20 in fishes & ~4 in zooplankton from L. Ontario a-isomer dominated		6 in Detroit R. suspended solids g isomer dominated
TBE	4-9 in Chicago			1-5 in northern L. Michigan
PEB	500-600 in one Chicago sample			Not present in Lakes Michigan or Erie

a. $t_{1/2}$ is half-life and t_2 is doubling time.

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