Non-PBDE Flame Retardants in the Environment and in People

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We are all aware of the ubiquity of polybrominated diphenyl ether (PBDE) flame retardants in the environment and in people; indeed, there have been several reviews on the subject (among others, see Hites, 2004; Hale et al., 2006; Law et al., 2006). In addition to PBDEs, there is a developing body of knowledge on the environmental presence of hexabromocyclododecanes (HBCDs) (see Covaci et al., 2006) and of tetrabromobisphenol A (TBBPA) and its dimethylated derivative. In addition to these more well-known flame retardants, other flame retardants, some highly chlorinated, are now beginning to be identified in the environment. The following paragraphs summarize some information about these compounds. Their structures and abbreviations are given in Figure 1.

Polybrominated biphenyls (PBBs). These compounds were popular flame retardants in the early 1970s, especially in the United Sates. Because of an accidental poisoning of dairy cows in Michigan in 1973, PBBs were taken off the market by the late 1970s. Presumably PBBs were never manufactured in Europe, but they were likely to have been used in products sold in Europe. Despite the passage of 30 years since PBBs were taken out of commerce, these compounds (particularly congener 153) are still present in birds and fishes collected from Europe and North America. PBBs are even present in fishes and birds from the Arctic (de Wit et al., 2006). PBBs are also present in human blood collected from Europe and North America, although the concentrations seem to be decreasing slightly over time (see Figure 2). What is really quite remarkable is that these compounds have spread from an industrial accident in Michigan to become globally ubiquitous; clearly, they will be with us for the foreseeable future.

Decabromodiphenylethane (DBDPE). This compound is a relatively new flame retardant (introduced in 1990s) and its applications are same as deca-BDE. Two reports have appeared identifying this compound in sewage sludge from Sweden and Canada (Kierkegaard et al., 2004; McCrindle et al., 2004) with concentrations of 10-100 ng/g dry weight. Hoh (2006) has also observed DBDPE at air sampling sites around the Great Lakes with relatively high concentrations in Chicago (up to 120 pg/m^3). DBDPE was also present in tree bark at low levels (Zhu & Hites, 2006). This compound may be on it way to becoming environmentally widespread.

Pentabromotoluene (PBT). This is a relatively unknown flame retardant manufactured under the trade names of Bromcal 81-5 T (Huber & Ballschmiter, 2001) and Flammex 5 BT (Norstrom et al., 1976) . It has been found in air in the U.S. (Hoh et al. 2005) and in sediment from Germany (Schwarzbauer et al., 2001). Interestingly, a related compound, pentabromoethylbenzene (PBEB), has also been found in air, with an especially high concentration on one day in Chicago (Hoh et al., 2005). This later compound is a flame retardant that is manufactured by the Albemarle Corp. in France. It is not yet clear if either of these compounds will become environmentally ubiquitous.

1,2-*Bis*(2,4,6-tribromophenoxy)ethane (TBE). This compound has been suggested for use as a replacement for the octa-BDE product that is no longer being manufactured. TBE has been found in the environment in the atmosphere and in air from ambient indoor and occupational settings. The environ-

mental data for TBE are from Sweden and North America. For example, Hoh and Hites (2005) reported atmospheric concentrations on the order of 0.1-10 pg/m^3 in the east-central U.S. with the highest levels in Arkansas, not too far from where TBE is manufactured. Indoor air in Sweden had concentrations of 4-40 pg/m^3, while an electronics disassembly plant had air concentrations on the order of 10,000 pg/m^3 (Pettersson-Julander et al., 2004). TBE has also been found in sediment from the Great Lakes (Hoh et al., 2005) and in tree bark from North America (Zhu & Hites, 2006). Clearly this compound warrants further attention.

Chlorinated paraffins (CPs). We should not forget that chlorinated compounds have also been used (in some cases quite widely) as flame retardants. One prevalent class of such a chlorinated flame retardant is the chlorinated paraffins, which are complex mixtures of chlorine substitution patterns and paraffin chain lengths. CPs have been found in air, fishes, and sediment from all over the world (see Santos et al., 2006, for an up-to-date review). In many cases, the concentrations of the CPs are similar to those of PBDEs in the same type of sample matrix (Hites, 2004).

Dechlorane. This compound (a dimer of hexachlorocyclopentadiene) was also known as Mirex, an insecticide that was used to kill fire ants in the southern U.S. It was also sold under the name Dechlorane as a flame retardant, and in fact, the amount sold for this later application was much greater than that sold as an insecticide (see Figure 3). Dechlorane was manufactured by OxyChem (formerly known as Hooker Chemical) in Niagara Falls, New York, and perhaps as a result, this compound is relatively abundant in the sediment of Lake Ontario, which is downstream of the manufacturing site (for a review see Kaiser, 1978). Dechlorane is now off the market, but it is still found occasionally at low levels in the environment; for example, it is present in farmed salmon from all over the world (Hites et al., 2004).

Dechlorane Plus (DP). This is a highly chlorinated flame retardant that was detected and identified in ambient air, fish, and sediment samples from the Great Lakes region by Hoh et al. (2006). This compound exists as two gas chromatographically separable stereoisomers (*syn* and *anti*), and they were detected in most air samples, even at remote sites; see Figure 4. The atmospheric DP concentrations were higher at the eastern Great Lakes sites (Sturgeon Point, New York, and Cleveland, Ohio) than at the western Great Lakes sites (Eagle Harbor, Michigan, Chicago, Illinois, and Sleeping Bear Dunes, Michigan). At the Sturgeon Point site, DP concentrations once reached 490 pg/m^3. DP atmospheric concentrations were comparable to those of BDE-209 at the eastern Great Lakes sites.

DP was also found in sediment cores from Lakes Michigan and Erie. The peak DP concentrations were comparable to BDE-209 concentrations in a sediment core from Lake Erie, but were about 20 times lower than BDE-209 concentrations in a core from Lake Michigan. In the sediment cores, the DP concentrations peaked around 1975-1980, and the surficial concentrations were 10-80% of peak concentrations. Higher DP concentrations in air samples from Sturgeon Point, New York and in the sediment core from Lake Erie suggest that DP's manufacturing facility in Niagara Falls, New York, may be a source. DP was also detected in archived fish (walleye) from Lake Erie, suggesting that this compound is, at least, partially bioavailable.

Dechlorane Plus is an example of a relatively old compound that has apparently slipped under the United States' regulatory radar and that is still currently being used without attracting public attention. DP was introduced as a substitute for Dechlorane by OxyChem in the mid-1960s. Major applications are indus-

trial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material. DP falls under the U.S. EPA's high production volume challenge program. An environmental test plan for DP was generated by OxyChem in 2005 (Hoh et al., 2006). According to this plan, DP has the typical characteristics of a persistent organic pollutant: high lipophlicity (its estimated K_{ow} is $10^{9.3}$), resistance to photo- and biodegradation, and accumulation in fish. DP appears to have ecotoxicological effects in fish, and a dermal study with rabbits showed potential effects on reproduction. However, the studies presented in this test plan were limited in terms of DP's environmental fate (only laboratory tests were performed) and in terms of DP's toxicity (no chronic studies were performed). Otherwise, there is no scientific literature about the fate or toxicity of this compound in the environment.

DP was recently quantitated in archived suspended sediment samples from the mouth of the Niagara River (which connects Lakes Erie and Ontario); these concentrations ranged from 90 ng/g dry wgt in 1980 to 7 ng/g dry wgt in 1999. The concentrations at this location were about twice those reported by Hoh et al. (2006) in Lake Erie sediment, indicating the presence of a source between Lakes Erie and Ontario.

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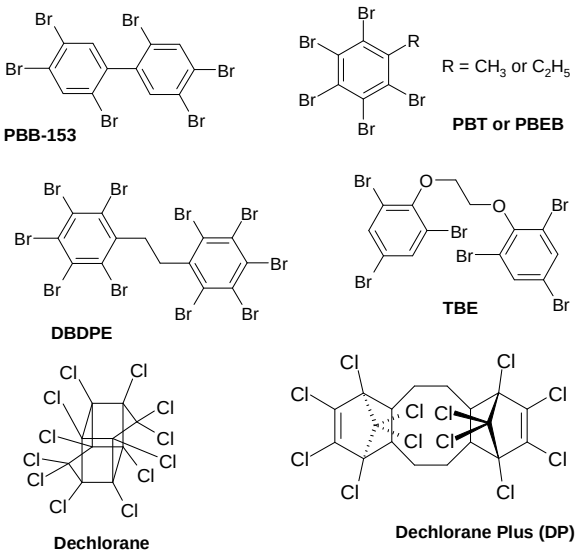

Figure 1. Structures of some unusual flame retardants that have been found in the environment.

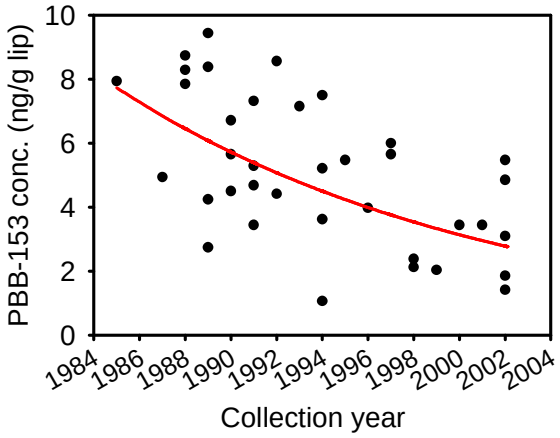

Figure 2. Concentrations of PBB-153 in human serum from the United Sates; re-plotted from Sjodin et al., 2004 (one high outlier removed). These concentrations are decreasing significantly with time ($p < 0.01$) with a half-life of ~12 years. The global median PBB-153 concentration in human blood is now about 1-3 ng/g lipid.

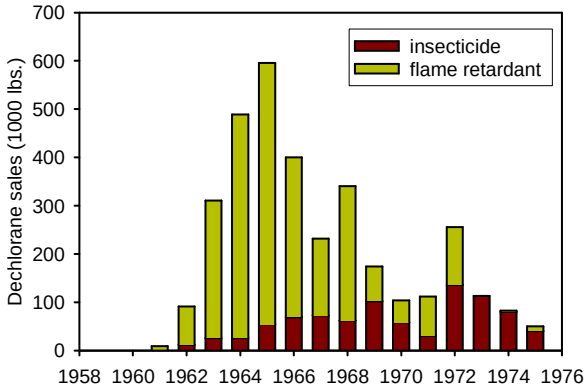

Figure 3. Annual sales of Dechlorane as an insecticide and as a flame retardant between 1959 and 1975; plotted from Kaiser, 1978.

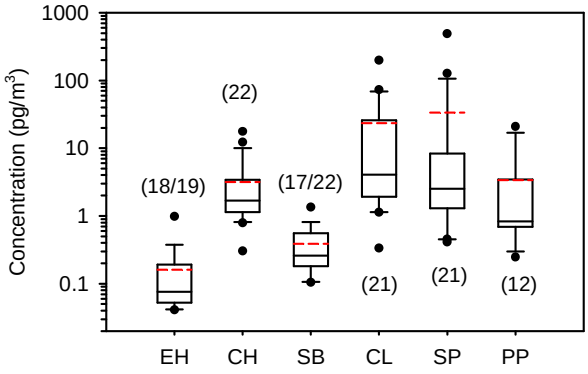

Figure 4. Total Dechlorane Plus concentrations (pg/m^3) at air sampling sites around the Great Lakes. The number of samples detectable and the total number of samples are given in parentheses. The sampling locations are sequenced from west to east. Abbreviations for the sampling sites: EH, Eagle Harbor in northern Michigan; CH, Chicago in Illinois; SB, Sleeping Bear Dunes in Michigan; CL, Cleveland in Ohio; SP, Sturgeon Point in New York; PP, Point Petre in Ontario.