BFR Concentrations and Trends in Abiotic Media

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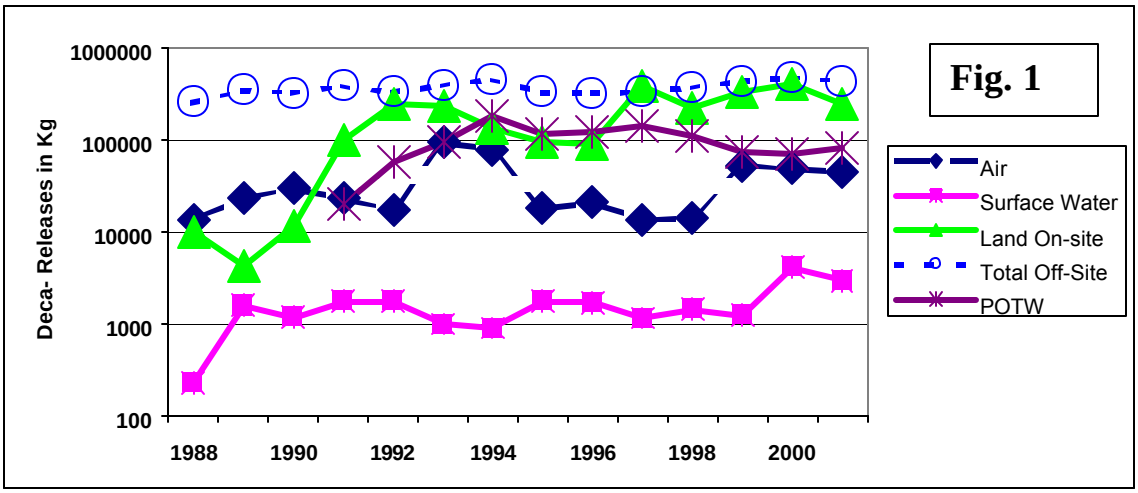
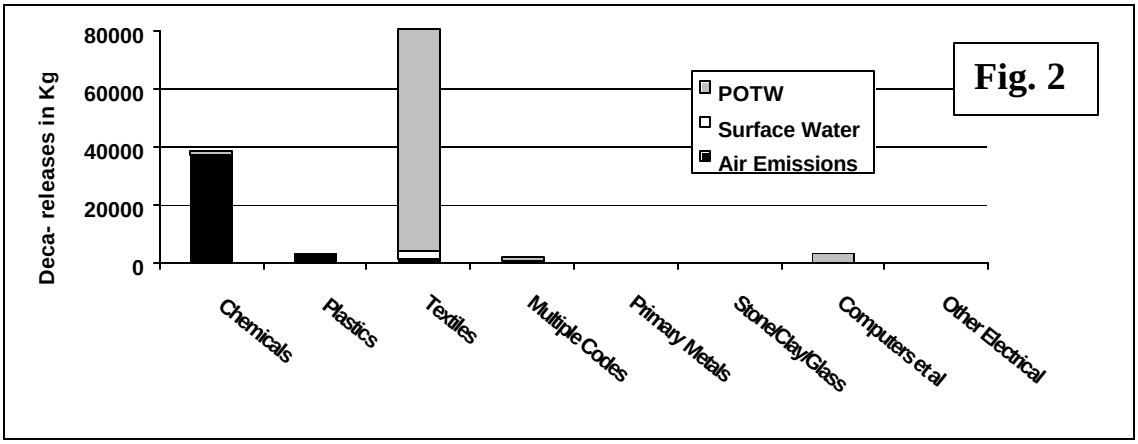
It was once widely held that brominated flame retardant (BFR) applications were nondispersive and environmental burdens would thus be minimal. However, growing evidence indicates that some BFRs are released in significant amounts. Despite low volatilities and water solubilities, BFRs are generally environmentally persistent, permitting eventual long-range transport, particularly the lower molecular weight polybrominated diphenyl ethers (PBDEs). Abiotic media are their primary recipients, transporters and sinks. Hence, examination of these media is crucial for identifying important BFR sources, trends and exposure scenarios. While most available data pertain to the PBDEs, the BFR market is dynamic and other less-studied materials are beginning to be tracked. This short review emphasizes BFR burdens with an eye towards potential sources. BFRs constitute several % by weight of treated finished products and are widely disseminated via trade. Hence, products themselves merit consideration as significant release vectors. Abiotic media in the indoor environment are included here, as BFR burdens therein are often higher, provide clues to sources/release mechanisms, are in proximity to humans and are themselves eventually released to the outdoor environment.

Toxics Reduction Inventory (TRI) Release Estimates

The U.S. EPA's TRI provides emission estimates to abiotic media based on measured or calculated industry data. TRI information for Deca-BDE, the dominant PBDE product (tetrabromobisphenol being the only other listed BFR), suggests that industry-assignable emissions approximately doubled between 1988 and 2001. Fig. 1 indicates that most industry-related Deca- emissions were directed to land and publicly-owned wastewater treatment works (POTWs). Fate models suggest that the destinies of persistent, low volatility/solubility compounds are dominated by their point of environmental entry[1]. Disposal of BFRs to landfills and soil/sediments reduce their environmental redistribution. Discharges to surface waters in the dissolved state or to air in vapor form maximize dispersion. A plot of the 2001 TRI-estimated emissions by industry type indicates that textile production was by far the largest Deca- discharger to U.S. surface waters and POTWs (Fig. 2). The latter subsequently impacts sewage sludge burdens and effluent-receiving streams. About 98% of the air emissions were dominated by fugitive dust releases from two major Deca- manufacturing facilities. Short-range fallout of these particulates is expected and thus dispersal is anticipated to be somewhat reduced.





Outdoor and Indoor Air

Interesting data have recently emerged on PBDEs in outdoor air using high-volume, passive samplers and ambient organic surface films. PBDEs exhibit a greater propensity to partition to aerosol particulates than PCBs and their burdens now exceed PCBs in a growing number of locations.[2] The lower brominated congeners (e.g. BDE-47 and –99) dominate in the vapor state. Total PBDE burdens in outdoor air are generally <100 pg/m.[3] On aerosol particulates and near sources the less volatile PBDEs, in particular BDE-209, are increasingly found to dominate. With the exception of computer recycling[3], published BFR release data for industrial sites based on field measurements are scarce. Degradation of PBDEs via photolysis during atmospheric transport might be expected. In laboratory spiking experiments the process was rapid.[4] Congener signatures produced from photodegradation of Deca-BDE differed from those of lower brominated products (e.g. Penta-). Slower rates were observed as researchers progressed to more environmentally realistic scenarios (natural light, sediments, presence of humics). However, to date, evidence for photolytic degradation of PBDEs in field-obtained air samples is limited.

Organic window films trap airborne hydrophobics. PBDE levels in Canadian films have been reported to be 10-fold higher in urban than rural areas and to substantially exceed PCBs.[5] Surface films and air are more rapidly-responding compartments than sediments or biota. In films BDE-209 was the dominant congener reported, followed by BDE-99 and –47. Indoor windows films contained up to 20-fold higher PBDE burdens than those formed outdoors, consistent with proximity to probable sources (treated polymer products) and the contained nature of the spaces. Likewise, Penta-BDE-related congeners were ~100-fold higher in indoor than outdoor air at a UK university and concentrations in rooms correlated with the density of foam-containing furniture and electronics.[6] Chamber studies have shown that the more volatile PBDE congeners can be released into air directly from treated polyurethane foam.[7]

Indoor dust and sewage sludge

As BFRs have low volatilities, significant association with particulates is expected. Indoor dust can contain substantial (mg/kg) burdens of PBDEs, as well as hexabromocyclododecane (HBCD).[8] Whether BFRs volatile off and resorb to dust or predominantly enter dust with polymer fragments remains an open question. Resolution would provide insight into how to reduce indoor releases and to dust-associated BFR bioavailability. Preliminary data related to Penta-related PBDEs in indoor dust associated with room air filters and from dust vacuum bag samples from Virginia buildings are provided in Fig. 3. Congener profiles in the vacuum dust appear enriched in the more brominated congeners, resembling the probable parent Penta-BDE mixture.

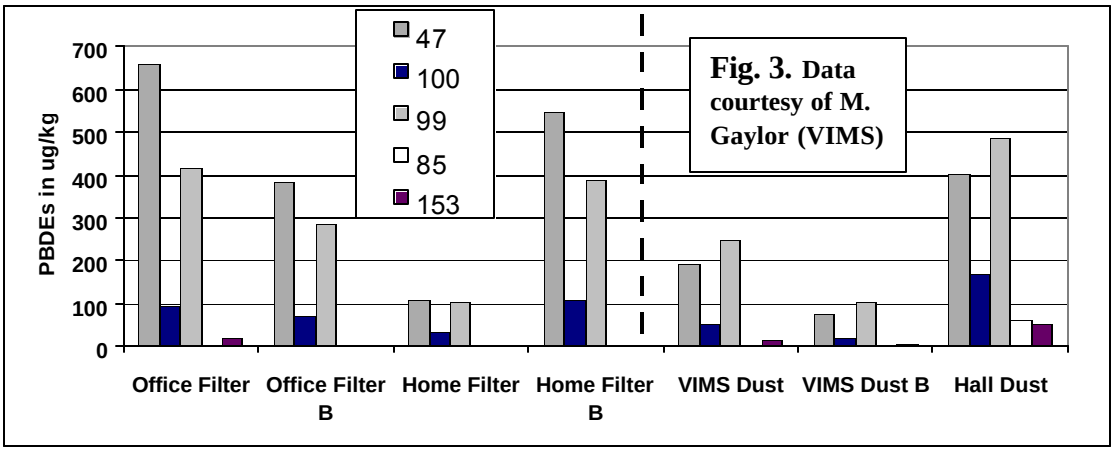


Fig. 3. **Data courtesy of M. Gaylor (VIMS)**

Monitoring sludge may serve as a rapidly responding, early-warning system for BFR releases. Based on POTW influent and sewage sludge data, it appears that ~95% of PBDEs associate with sewage sludge during treatment. PBDE burdens in U.S. sludge (typically >1 mg/kg) exceed European levels 10-fold, reflective of higher use here.[9] No data on HBCD in U.S. sludges was found, but levels in European samples range upwards of 1 mg/kg.[10] Subsequent sludge land application on agricultural and other lands redistributes the contained BFRs to the soil compartment. In most sludges worldwide, PBDE congener patterns match the Penta- mixture profile and BDE-209 now dominates. Use of Penta- has been curtailed in Europe and is slated in the U.S. for discontinuation

after 2004. However, as pre-existing foam products will remain a reservoir, releases will continue for years. Demand for Deca-BDE is likely increasing, a temporal trend reflected in Fig. 1 for the U.S. and recently reported for Swiss sludges[11].

Water

Penta-related PBDE concentrations in whole effluents from POTWs are usually in the sub-ug/L range. However, the high water volumes discharged translate into significant PBDE amounts. BDE-209 at 12 ug/L was observed in a POTW effluent serving a U.S. plastics product manufacturer.[12] Most was likely associated with the suspended solids released. Analysis of effluent particulates from The Netherlands supports this, wherein BDE-209 exceeded 100 ug/kg[13]. Hence, more effective capture of suspended solids may substantially reduce BFR releases from wastewater treatment plants. BDE-209 burdens up to 4600 ug/kg have also been reported on suspended particulates from Dutch surface waters, decreasing with distance from textile facilities.[13] This reinforces the Fig. 1 TRI impression that textile facilities merit scrutiny. PBDEs in surface waters removed from sources are dominated by the more water soluble congeners and are typically <1 ug/L.[9]

Sediments and Soils

Aquatic sediments generally contain low BFR burdens, although PBDE levels nearing 1000 ug/kg have been detected near industrial concerns and POTWs[12-14] Sediments near such sources are generally enriched in the more hydrophobic congeners compared to more distant samples. European core data suggest that Penta-BDEs have entered sediments since the early 1970's and the congener profiles are relatively unaltered, indicating minimal degradation.[15] Decabromodiphenyl ethane, tetrabromobisphenol A and HBCD have also been detected in European sediments.[10,16] BFR data for soils are limited, but levels are expected to be low, except in proximity to point sources, such as manufacturing facilities where fugitive dust emissions (see Fig. 2) may be important.

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