Levels and trends of HBCD and BDEs in the European and Asian environments

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Introduction

Following the BFR2004 and Dioxin 2004 conferences a review of brominated flame retardants (BFRs), including brominated diphenyl ethers (BDEs), in the European environment was prepared, utilising the literature published or available via journal websites up until the end of September 2004 (Law *et al*. 2006a). Subsequently, this has been supplemented by a review by Covaci *et al*. (2006) which extended the timeline for hexabromocyclododecane (HBCD) to include literature published up until the end of 2005. In this paper, we summarise the subsequent literature for Europe until November 2006 and, in view of the data now becoming available for countries other than Japan, include data available in recent samples from Asia for comparative purposes.

Summary of literature reviewed

Indoor Air and Dust

16 studies reviewed, including samples from the UK, Greece, Sweden, Kuwait, Australia, Germany, Spain, Belgium, Portugal, Italy, Japan, Singapore and New Zealand. Main findings: concentrations are highly variable between different microenvironments; but a consistent message emerges that indoor contamination may provide an important human exposure pathway.

Outdoor Air

11 studies reviewed, including samples from the UK, Norway, Spain, China, Japan, Singapore, South Korea, the Maldive Islands, Sumatra and Kuwait. Main findings: concentrations are uniformly higher in more urbanised locations This, combined with levels being lower than those detected indoors, suggests significant emissions from indoor environments.

Sewage Sludge

4 studies reviewed, including samples from Germany and Spain. Main findings: two "novel" BFRs, hexabromobenzene and pentabromophenol, were found in sludges from municipal STPs at maximum concentrations of 2,470 and 870 $\mu g\ kg^{-1}$ wet weight, respectively. These concentrations were higher than the maximum concentrations of ΣBDE and TBBP-A in the same samples (Kuch *et al*. 2005).

Water and Suspended Particulates

1 study reviewed, with samples from Hong Kong. Main findings: as could be expected given their hydrophobic character, BDE concentrations were low in both the dissolved and particulate phases.

Sediments and Soils

19 studies reviewed, including samples from Sweden, the Netherlands, Austria, Romania, Spain, Belgium, Singapore, China, Korea, Taiwan and Hong Kong. Main findings: significant concentrations of BDEs (especially BDE209) are found in sediments from SE Asia, and can occur at similar concentrations to those observed previously in sediments from the Great Lakes area of North America (Moon *et al*. 2007).

Plants

2 studies reviewed, including samples of moss from Norway and archived grass from the UK. Main findings: in the grass samples covering the period 1903-2004, BDEs were not detected in the early samples. BDE concentrations increased during the 1970s, peaked in 1999, and have declined subsequently (Hassanin *et al*. 2005).

Biota

Terrestrial Animals

3 studies reviewed, including earthworms from Sweden, and hedgehogs and foxes from Belgium. Main findings: higher brominated BDEs, including BDE209, are bioavailable from soils and accumulate in earthworms, presenting an exposure pathway into the terrestrial foodweb (Sellström *et al.* 2005).

Birds' Tissues and Eggs

17 studies reviewed, including samples from the Faroe Islands, Norway, Sweden, Spain, Belgium, Denmark and Japan. Main findings: in samples from Spain, the higher brominated BDE congeners from BDE183 to BDE209, as well as several unidentified octa- and nona-congeners, were found in almost all samples of peregrine falcon eggs analysed (Jiménez *et al*. 2005).

Fish, Shellfish and Benthic Invertebrates

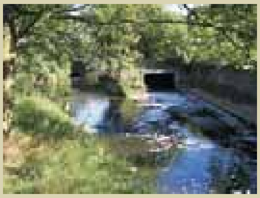
24 studies reviewed, including samples from Norway, France, Finland, Switzerland, Liechtenstein, the Netherlands, Ireland, Portugal, Spain, Italy, India, Indonesia, China, Hong Kong, Japan, Cambodia, Vietnam, the Philippines, Korea and Taiwan. Main findings: in the French Pyrénées, lake elevation was the parameter most closely correlated with ΣBDE concentrations, and this was related to the result of higher deposition and/or retention of contaminants in lakes at higher altitude (Blais *et al*. 2006).

Food Chain Studies

6 studies reviewed, involving both experimental studies and modelling, and in both aquatic and terrestrial environments. Main findings: low concentrations of BDEs in red fox relative to birds of prey utilising similar food items are likely due to its high metabolic capacity, as for PCBs (Voorspoels *et al*. 2005).

Marine Mammals

12 studies reviewed, including samples from the Mediterranean Sea, UK, Norway, Spain, France, Hong Kong, Japan, the Philippines, India and China. Main finding: HBCD concentrations in harbour porpoises from the UK showed a sharp increase in concentrations from about 2001 onwards, which was not confounded by age (length), sex, nutritional status or location (Law *et al*. 2006b).



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Conclusions

There has been a marked growth in the number of studies reporting contamination of indoor environments with PBDEs. These studies provide evidence of the importance as sources of human exposure of the ingestion of indoor dust and inhalation of indoor air. In view of the potentially vast reservoir of BFR-treated goods remaining in indoor use for the foreseeable future, continued characterisation of BFRs in indoor environments with respect to sources, concentrations, and implications for human exposure is likely.

Amongst the BDEs, BDE209 retains particular difficulties due to its physico-chemical properties. Analysis of this congener is more difficult than the others routinely determined, due to its thermal instability, photosensitivity and its ability to bind strongly to surfaces, including laboratory glassware. Protocols suitable to the determination of BDE209 have been developed (de Boer *et al*. 2001) and need to be applied stringently if good interlaboratory agreement is to be achieved. This must not cause analysis of BDE209 to be neglected, as it is a high-production volume compound and widely distributed in the environment, but the best available methods should be used in all studies.

In order to establish source trends it may be advisable to conduct some studies in settled, preferably anoxic, sediments from a number of selected sites in Asia, after Zegers *et al*. (2003). Determinands should include BDE congeners selected so as to include those from all three PBDE formulations. HBCD should be analysed on a diastereoisomer-specific basis using LC-MS. TBBP-A should also be determined although it is a reactive flame retardant and so less likely to be leached from products, on the grounds that Asia is where most of the electronic items using circuit boards are produced and so the area of likely greatest direct use before it becomes reactively-bound. In contrast, most TBBP-A probably comes to Europe and the USA in completed products. Levels of TBBP-A in porpoises from the UK have been shown to be low or undetectable (Law *et al*. 2006b). There also seems to have been little or no work undertaken to date on BFRs in birds from Asia, and this is identified as a data gap.

Given the rising trend observed in HBCD concentrations in porpoises from the UK in recent years, which was not confounded by small sample size or other factors, additional studies on fish (especially fatty fish) which form part of their diet is indicated. It should also be borne in mind that some of these species are likely to form part of the human diet. Covaci *et al.* (2006) also recommended that more emphasis be placed upon the terrestrial environment, for which very limited data for HBCD are available. Also, they indicated that more detailed information concerning the kinetics, toxicology, pathways of exposure and bioavailability of HBCD is needed, as well as the study of possible metabolites.

In 2004, Martin *et al*. highlighted the paucity of environmental data available for BFRs in Asian regions. They noted that inventories of PBDE sources had not been made, noting plastics and electronics production and recycling as potential major sources in the region. Research was needed to better identify such sources, to quantify emissions and to study the environmental fate of BFRs. Of particular concern was the fact that BDEs accumulate in fish, and the per capita consumption of fish in Asian countries is high relative to other parts of the world. In Hong Kong (as an example), fish or shellfish are consumed more than four times a week by most of the population, and the annual average consumption of marine products is approximately 60 kg per person (Dickman and Leung, 1998). Although this review has noted work underway in a number of Asian countries, there is a long way to go before the environmental fate of BFRs in Asia is as well known as for Europe, North America or even the Arctic region. Other areas with little or no data regarding BFRs in environmental samples include South America, Africa (especially South Africa), Australia and New Zealand.

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