Brominated Flame Retardants. Analysis, Sources, Environmental Levels and Fate.

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Analysis

During the last year an increasing number of papers has been published on the occurrence of brominated flame retardants (BFRs). Also, at Dioxin 2005 there is an absolute record of BFR papers presented. It is interesting to see that the increase in papers is particularly in papers on the occurrence and behaviour of BFRs, and also, as we hoped a few years ago, on the toxicology, and on human exposure. However, the number of papers on the analytical side of BFRs is relatively small. Apparently we are at a stage at which the various research groups have developed a 'basic' method for a number of BFRs which they now use for generating data. However, it will be necessary to improve those methods, as interlaboratory studies still show insufficient quality, particularly of the decaBDE analysis. Also extension to methods for other BFRs is desired. An intercalibration study in which 13 laboratories in Japan participated was initiated in April, 2003. Following the results on PBDD/DFs, MoBPCDDs/DFs and PBDEs in 'Mixed Standard Solutions' and 'Air-Dried Sediment', that were presented at Dioxin 2004, new results of a 'Waste TV Cabinet' and animal fat are reported by Takahashi et al.

Stapleton et al. present a study that provides certified values for PBDE congeners in three indoor dust SRMs and two fish tissue SRMs. Measurements were made for 30 individual PBDE congeners in the fish tissue and indoor dust SRMs. The dominant congener in all the house dust SRMs was BDE 209, the primary component of the decaBDE commercial mixture. The high levels of PBDEs measured in these house dust samples (~3500 ng/g) suggests that indoor environments may be an important route of exposure to PBDEs as was seen for lead exposure in the past. Three nona BDE's and one chloro-nonaBDE have been synthesized by Christiansson et al., which is a welcome addition to the selection of congeners for analytical and toxicological purposes.

Konstantinov et al. identified nine new BDE isomers in the technical mixture DE-71TM: the tetra-BDEs 42, 48, 51, and 91, and the penta-BDEs 102, 119, 139, 140, and 155. Quantification of the BDEs in DE-71TM by either NMR or HRGC/HRMS gave similar values. In another paper Konstantinov et al. describe structural diagrams of HBCD stereoisomers. Hanari et al. also analysed technical BDE mixtures. The occurrence of PBBs at nanogram per gram levels in BDE preparations suggests the environmental emission of PBBs from the use of PBDEs. Technical BDE preparations did not contain PBDD/DF congeners at a detection limit of 70 ng/g in this study. Further investigation using high resolution mass spectrometry regarding impurities in technical DE preparations, is necessary to understand the behaviour of BBs/BDDs/BDFs in the environment and emission inventories in the world. Zetsch et al. present preliminary data of a photolysis study of a technical mixture DE79 (mainly octaBDE).

Kuch et al. reported the presence of other BFRs in addition to the more common PBDE's. Thirty-two wastewater treatment plants in South Germany were screened for bromobenzenes and bromophenols. HexaBBz, PentaBP, 1,2,4,5-TetraBBz, and 2,4-DiBP are produced and

used as industrial bulk chemicals today and emitted in considerable quantities into the (German) environment.

Sources

Autoshredder is identified as a source of BFRs by Petreas et al. Different devices have quite different ΣPBDE content (from low ppb to *percent* levels), probably reflecting different manufacturing practices and year of manufacture. The pattern of individual PBDE congeners varies across products (computers, microwaves and VCRs). High ppm to percent levels of PBDEs (mostly PBDE 209 but also PBDE 47 and PBDE 99) were measured in autoshredder waste. Cai et al. identified elevated PBDE levels in soil from the vicinity of e-waste recycling sites.

Gevao et al. report the presence of the BDEs 47, 99, 100, 153, 154 and 183 in air and sediment from Kuwait and the Arabian Gulf. Long range air transport is supposed to be a major transportation mechanism that is reinforced by the high temperatures in this area.

Environmental Levels and Fate

Gorgy et al. presented a desorption study on various PBDE congeners. It is suggested that due to desorption some PBDE's may reach the groundwater. Two papers on anaerobic degradation of decaBDE are presented by Skoczynska et al. and Robrock et al. Both papers suggest possible degradation routes of decaBDE. De Wit et al. report that higher brominated PBDEs, including BDE-209 are bioavailable from the sewage-sludge treated soils. Thus, past and current use of sewage sludge as a fertilizer has increased concentrations of PBDEs in agricultural soils in Sweden and these will remain in the soil for a long time. This in turn leads to higher concentrations in worms, including for BDE-209. As earthworms are at the base of the terrestrial food web, the use of sewage sludge as a fertilizer leads to increased PBDE concentrations in soils and the terrestrial food web. Mariussen et al. confirm that most PBDEs, including the decaBDE, may be spread into the terrestrial environmental and that the decaBDE is the dominating compound. They had collected mosses from twelve different localities in Norway, expected to be non-contaminated areas. Eljarrat et al. report decaBDE and decabromodiphenylethane concentrations in sewage sludge from Spain. Decabromodiphenylethane is found, but normally at levels of <1-5% of decaBDE.

Trophic magnification of a number of BFRs including bis(tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) in a pelagic food web of Lake Winnipeg was studied by Law et al. Trophic magnification factor (TMF) values suggest that HBCD, certain PBDEs and DBDPE are biomagnifying within the food web. Fabrellas et al. report the occurrence of PBDE's in household dust from Italy, Spain, Belgium and Portugal. Mean total PBDE concentrations are around 0.2-0.5 mg/kg dry weight (dw), with a highest value of ca. 4 mg/kg dw from Italy. DecaBDE is always 60% of the total amount. Webster et al. suggest that both diet and indoor dust (ingestion and dermal) may be important sources of exposure to BDE 47. In comparison, inhalation appears relatively minor on average, although it may play a more important role in extreme cases.

Relatively high PBDE concentrations in Danube sediment from the high industrialised region of Schwechat, Austria are reported by Moche et al. The influence of the treated wastewater on the river sediments is shown. Sawal et al. report the results of an extensive survey conducted on the River Danube. The predominance of BDE-209 in the sediment analyzed is consistent with other studies. In general they found that side arms and tributaries of the Danube are more contaminated with PBDEs that the River Danube itself. Zeng et al. report a theoretical calculation of thermodynamic properties of Polybrominated Diphenyl Ethers and prediction of photodecomposition products of BDE-209. The results suggest that the photodecomposition of BDE-209 follows certain pathways determined by the dissociation

energies leading to BDE-47 and BDE-49. They also suggest that the photodecomposition of PBDE's is kinetically, not thermodynamically controlled. Gouteux et al. carried out a thermal stress experiment to investigate if the potential loss of brominated compounds from BFR polymers occurs. Several lower molecular weight compounds were observed after experiments with the polymer PBS-64. Nose et al. show that reactivities of bromine on *para* and *meta* substituents are similar but that of *ortho* bromine was extremely low. The debromination rates of para and meta substituents were about 7 times higher than the latter. The reactivity of the bromine substituents in hydrothermal reaction was similar to that of DeCB.

Clearly, a large of number of data has been produced and the understanding of the environmental behaviour of BFRs is continuously improving. New studies in Canada (Danon-Schaffer et al.) and Europe (Rothenbacher et al.) are presented to monitor future trends in sediments, sludges and food chains. Given the ongoing production of at least a number of BFRs, and ongoing monitoring studies taking place, it may be expected that many results will be presented at future occasions. As indicated under 'Analysis', scientist will have to ensure that the quality of those data is of a high quality.