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Bro1, Brominated Compounds: Analysis, Levels, and Trends

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Interest in the levels and fate of brominated flame retardants (BFRs) is growing exponentially. Dioxin symposia have been a major venue for the discussion and exchange of information in this field. Over the past few years, many interesting papers on BFRs have been presented during the Dioxin conferences in Venice, Monterey, Gyongju, Barcelona and Boston. Recently, a large number of laboratories have developed analytical methods for the determination of polybrominated diphenylethers (PBDEs), Tetrabromobisphenol A (TBBPA) and isomer specific hexabromocyclododecanes (HBCDs). BFRs have been detected in various biota and sediments from the aquatic environment, air, human milk, blood and adipose tissue, bird eggs, various foodstuffs and other matrices. Some abiotic sources information has also emerged in waste electric and electronic equipment and house dust.

This year at Dioxin 2004, a substantial number of papers dealing with brominated flame retardants have been presented. As a result, the BFR sessions were split into two, a) Analysis, Levels, and Trends and b) Biota, Levels, and Trend Effects. This report focuses on the former session. A total of 17 papers were presented at this session which provided new information on the analysis, the sources and the environmental behaviour of BFRs. Below is a synopsis of these presentations.

Stapleton *et al.* reported that they will be conducting a national Standard Reference Material (SRM) program for measurement of PBDEs. This study will be undertaken by the National Institute of Standards and Technology (NIST) and will include SRM matrices such as marine mammal blubber, lake trout tissue, mussel tissue, sediment, house dust and human serum.

Arsenault *et al.* reported the full ^{1}H- and ^{13}C-NMR spectral characterization of alpha (α-) and gamma (γ-) HBCD. The structures of α- and γ-HBCD are visually quite different. These distinctions in structure will almost certainly lead to differences in properties such as polarity, dipole moment, solubility and rates of biological uptake or metabolism. There have been interesting observations that the gamma (γ-) HBCD isomer is the predominant isomer in sediments and the alpha (α-) isomer is the predominant isomer in fish.

In addition to papers on analytical methods, a number of other papers focus on BFR levels in environmental samples. de Wit *et al.* reported the review based on a recent assessment of POPs in the Arctic combined with newer data not available for that assessment. PBDEs (Br_2-Br_7) were detectable in all environmental samples from the Arctic and there is evidence for the presence of decabromodiphenlyether (BDE 209) and HBCD. While the tetra- and pentabrominated BDEs are ubiquitous in the Arctic, the presence of BDE209 in remote Arctic lake sediments indicates that even this congener is subject to long range transport. Very little data is presently available for HBCD and TBBPA however, in principle, they too could be transported by the same pathways as the Br_2-Br_{10}-PBDEs.

Baker *et al.* reviewed their recent measurements of PBDEs in Chesapeake Bay, a shallow, productive estuary in eastern North America. More than 95% of total PBDEs measured in the Back River transect downstream from a wastewater treatment plant was BDE-209. Unlike previous studies, they found very low relative concentrations of the components of the 'Penta' commercial mixtures in these sediments. However, BDE-209 concentrations were quite elevated, ranging from 9 000 ng/g-dry near the plant discharge to 2 400 ng/g-dry 6 kilometers downstream. These are among the highest reported concentrations world-wide for BDE-209.

Raff *et al.* investigated the occurrence of PBDEs (15 congeners including BDE-209) in an attempt to identify possible sources within the Mississippi River Basin. They found PBDEs to be widespread throughout the region, rivaling PCBs in their extent and magnitude of contamination. Concentrations along the main stem of the river ranged from 37–1 053 ng/g in suspended solids. The average distribution of the six most commonly measured BDE congeners in all (N = 31) samples was 1.16, 1.26, 0.26, 0.12, 0.11, and 96.8 % for BDE-47, 99, 100, 153, 154, and 209, respectively.

Schlabach *et al.* focused on the pollution of PBDEs in Lake Mjøsa, Norway, where unusually high concentrations have been found in fish. The concentrations of PBDEs in sediments from Lake Mjøsa were in the range 0.6–27 ng/g d.w. The concentrations of sum PBDEs in pooled fish samples from Lake Mjøsa were in the range 50–90 ng/g wet-weight or 1 200–22 000 ng/g lipid. The high concentrations of PBDEs in sediments close to Lillehammer, together with the high percentage of tri- to hexa-BDEs, strongly indicate that the technical product "penta-PBDE" has been discharged to the lake.

Sewage sludge is an interesting medium which transports and accumulates BFRs from various sources. Some countries have promoted strategies to enlarge the knowledge of PBDE, in particular their occurrence and levels on sewage sludge. Previous observations have identified domestic washing of garment/clothes and industrial discharges from plastic and textile manufacture industry as major sources of contamination. Fabrellas *et al.* reported a preliminary assessment of selected PBDE congener levels in sewage sludge samples from different waste-water treatment plants in Spain. A characteristic trend is noticed in all cases, with a major contribution of BDE-209 (93-99 %), and minor contents of BDE-47, -99, -100, -153 and -154. Knoth *et al.* presented additional information about the levels and temporal trends of PBDE in sewage sludge in Germany and speculated on the possibility of degradation of BDE-209 by photolytic or reductive debromination during waste water treatment process.

It is important to assess the gas-phase concentrations in our atmosphere, since this is a significant route of long range transportation of PBDEs in the environment, especially the lighter congeners. Harrad *et al.* reported on a 1 year sampling campaign designed to elucidate the seasonal and spatial variation in PBDE and PCB concentrations across a large (population c. 2.5 million) conurbation in the generally densely populated UK. PBDE levels obtained through passive air sampling were presented for the month of

October 2003, and showed a clear increase and subsequent decrease in PBDE levels as the sampling sites proceed northeast through the city and back to rural locations. Congener profiles and estimated atmospheric concentrations agree well with data published from other studies conducted in the UK and Canada. Okazawa *et al.* presented preliminary data of the analytical method developed enabling the simultaneous separation of several PBDE and PBDD/DF congeners as well as the applicability of pine needles as a passive indicator of source emission related troposphere pollution with PBDEs in Tokyo Bay area in Japan.

End-of-life plastic is one of the targets containing BFRs. Senthilkumar *et al.* developed an analytical methodology for determination of PBDEs and PBBs in Waste Electrical and Electronic Equipment (WEEE) plastics; standard operating procedure was evaluated and discussed briefly, they emphasised their simple cleanup procedure and use of a single analytical method based on high-resolution gas chromatography-high-resolution mass spectrometry. Drohmann *et al.* summarised available studies and presents the latest results regarding potential formation of brominated dioxins and furans (PBDDs/DFs) in end-of-life management of plastics containing brominated flame retardants.

BFRs are liberally applied to many common household items such as furniture, mattresses, computers and TVs to retard or hinder the outbreak of fire. Household dust can be an exposure route for BFRs commonly detected in blood serum and breast milk. Stapleton *et al.* presented preliminary data on 22 BDE congeners measured in the 17 house dust samples, total BDE concentrations ranged from 780 ng/g dry mass to 29,700 ng/g dry mass. The contribution of penta PBDE (percentage of BDE -47, -99 and -100 to the total concentration) ranged from 7 % to 88% of the total PBDE burden among the homes tested while the contribution of the decaBDE product (percentage of BDE 209 to the total concentration) ranged from 10 % to 86 % among the house dust samples.

Few studies have examined the inventories of PBDEs by comparing the observed concentrations with estimated values. Sakai *et al.* measured PBDE emissions from flame retardant plastics processing plants and home appliance recycling facilities to evaluate the PBDE releases. They estimated emission factors and inventories for each phase of the life cycle in these plants. Hirai *et al.* estimated the emission inventory of BDE-209 in Japan and compared the predicted concentrations with the observed levels in the environment. They suggested that the emission factor for the use of the final product by European assessment was overestimated. On the other hand, the emission estimate for the sources based on field measurements (application to plastics, recycling, and incineration) is not sufficient to explain the current environmental levels in Japan. Further studies in the field measurements and emission factors of PBDE are necessary to fill the gap between the environmental levels and the primary sources of this compound.

Decabromodiphenylethane (DBDPE) is a relatively new brominated flame retardant for use in polystyrene and polyolefin-based thermoplastic formulations. McCrindle *et al.* characterized mass-labelled DBDPE and assessed its effectiveness in determining DBDPE levels in environmental samples. Hays *et al.* reported on the child-specific risk assessment followed the Voluntary Children’s Chemical Evaluation Program (VCCEP) guidance for a Tier I assessment, and all applicable USEPA guidance.

In this session, "Brominated Compounds: Analysis, Levels, Trends," the new information on the environmental behaviours of BFRs detected in various media was presented. However there is a need to combine the field measurements with results obtained from toxicological and exposure studies to assess the risk of BFRs.

A major gap in this field is lack of physical models which can describe the fate and transport of BFRs. These models can not only be used to forecast the outcome of control method and its effects; but they also can be used to estimate and evaluate the outcome of banning the production; and they can also be a useful mean to provide valuable information to the policy makers.

Another important gap in this area is the environmental behavior of BFRs, such as the transformation mechanism of BDE-209. It is important to make an effort to establish accreditated methods of analysis for BDE-209 and HBCD, in the meanwhile one has to be careful to assess the comparability of the analytical data.