Brominated diphenyl ethers in the sediments, porewater, and biota of the Chesapeake Bay, USA

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Introduction. Levels of brominated diphenyl ethers (BDEs) are rapidly increasing in the environment, and in a short time these chemicals have evolved from 'emerging contaminants' to globally-distributed organic pollutants[1]. Recent research demonstrates BDEs are sufficiently stable to be transported long distances in the environment and to accumulate in higher trophic levels[2]. Photolysis and metabolism appear to be dominant loss processes for the parent compounds, generating a variety of lower brominated diphenyl ethers, hydroxylated metabolites, and other products[3-7]. BDEs are hydrophobic, and therefore their transport in aquatic systems is likely controlled by sorption to sediments and perhaps exchange across the air-water interface. To date, few studies have examined the geochemistry of BDEs in natural waters. In this paper, we review our recent measurements of BDEs in the Chesapeake Bay, a shallow, productive estuary in eastern North America. We focus on the distribution of BDE congeners sediment, porewater, and in faunal benthos along a contamination gradient downstream from a wastewater treatment plant and on the spatial distribution of BDEs in bottom-feeding and pelagic fish species.

Methods and Materials. Various fish species, including white perch (*Morone americana*), channel catfish (*Ictalurus punctatus*), and striped bass (*Morone saxitalis*) and the blue crab *(Callinectes sapidus*) were sampled throughout the northern Chesapeake Bay in 2002 and 2003. Sampling was conducted as part of the Maryland Fish Tissue Monitoring Program, a comprehensive analysis of contaminant levels in finfish and shell fish used to set consumption advisories by the State of Maryland. Fish were collected by trawling and processed according to U.S. Environmental Protection Agency protocols. Fillets from 5 individual fish from each species at each site were composited prior to analysis. Blue crabs were collected by baited traps and muscle and hepatopancreas tissues were extracted

from several individual crabs from each site for analysis. Blue crabs are opportunistic feeders, consuming a wide range of prey, including live small bivalves and fish as well as dead tissue. All samples were frozen in glass jars prior to analysis.

To determine the geochemical partitioning of BDEs in estuarine sediments, samples were collected along a transect in the Back River, a small, urbanized tributary to the Chesapeake Bay that receives treated wastewater effluent from a tertiary treatment plant. Samples of surficial sediment (ca. top 2 cm) were collected at four location using a Ponar sampler. Bulk sediment was sieved in the field to isolate benthic organisms, and separate whole sediment samples were returned to the laboratory for solid phase and porewater analysis. Benthic organisms were returned to the laboratory, separated by crude taxonomy, and allowed to depurate in clean water. Porewater was isolated as follows. To minimize possible oxidation of reduced iron and manganese (and subsequent precipitation of metal oxides which may alter the speciation of organic analytes), all processing was done in a nitrogen atmosphere in glove bags. Fresh sediment was mixed well and transferred into several 250 mL Teflon bottles. Each bottle was tared to 0.01 g, completely filled with fresh sediment and reweighed to 0.01 g. The sediment was then centrifuged at 3000 rpm for 30 minutes at 4 C. The supernatant from each bottle was carefully poured into a filter funnel containing a 47 mm GF/F glass fiber filter (0.4 m nominal pore size). The porewater was filtered under gentle vacuum and transferred to a tared glass bottle. After addition of analytical surrogate compounds, BDEs and other organochlorine analytes were extracted from the porewater by sequential liquid-liquid extractions with hexane. Bulk sediment was dried by grinding with anhydrous sodium sulfate and extracted with dichloromethane. Both the porewater and bulk sediment extracts were concentrated, treated with activated copper to remove elemental sulfur, and purified using alumina and Florisil liquid-solid chromatography. Concentrated, purified extracts were analyzed for PCB congeners using GC with electron capture detection and then analyzed for BDE congeners using GC-NCI-MS.

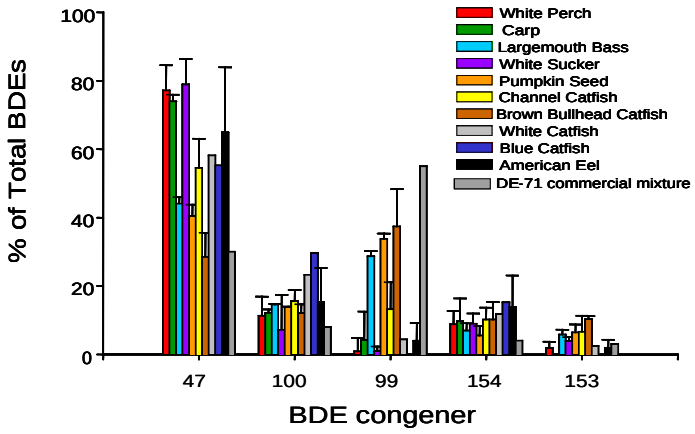
Fish Tissue Analysis: Six BDE congeners were quantified in the samples from the fish tissue monitoring program: 2,2',4,4'-tetrabromodiphenyl ether (BDE 47), 2,2',4,4',5-pentabromodiphenyl ether (BDE 99), 2,2',4,4',6-pentabromodiphenyl ether (BDE 100), 2,2',4,4',5,5'- hexabromodiphenyl ether (BDE 153), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE 154) and 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE 183). All BDE congeners were purchased from Cambridge Isotope

Laboratories, Inc., Andover, MA. BDEs were quantified using a Hewlett Packard 5890/5972A GC/MSD operated in the selected ion monitoring mode. Chromatographic conditions were as follows: injection port temperature was maintained at 260 C; detector temperature was maintained at 320 C and oven temperature ramp was initially held for two minutes at 80 C followed by a 30 C/min ramp to 200 C and then a ramp of 5 C/min to 300 C which was held for an additional 5 min. Helium was used as the carrier gas through the GC and the flow was maintained at 1.40 ml/min through a 30 m DB-5 column. Quantification and confirmation ions respectively for the six BDE congeners were 486 and 326 (BDE 47); 404 and 565 (BDE 99 and 100); 484 and 644 (BDE 153 and 154) and 562 and 563 for BDE 183. PCB 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) was used as the internal standard. Detection limits ranged from 0.4 ng/g-wet weight up to 3.0 ng/g-wet weight for BDE 47 and BDE 183, respectively, in a typical biota sample.

Sediment, porewater, and benthos analysis: The BDE analyte list was extended to include decabromodiphenyl ether (BDE 209) as well as other components of commercial mixtures and possible degradation products (*e.g.*, nona- and octa-BDEs). To minimize degradation of BDE 209 in the gas chromatograph, a method was developed using a Programmed Temperature Vaporization inlet (PTV) coupled with an Agilent Technologies 6890 GC/MS equipped with a short (15 m) thin film (0.1 m) DB-1 column[8]. The PTV inlet kept cool during the injection to limit thermal decomposition of BDEs. BDEs were quantified in the sediment, porewater, and benthos samples by negative chemical ionization mass spectrometry using a chlorinated diphenyl ether as an internal standard.

Results and Discussion. Concentrations of total BDE (sum of six congeners) ranged from 1 to 61 ng/g-wet (11 to 2,600 ng/g-lipid) in Chesapeake Bay fish collected in 2002 and 2003. BDE 47 was detected in 100% of samples and BDE

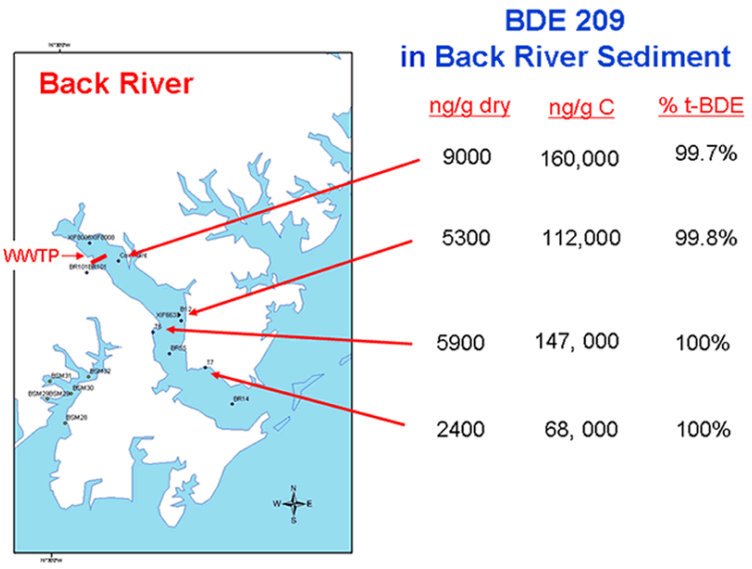
Distribution of BDE congeners in Chesapeake Bay fish species



100 was detected in 95% of samples. Of 20 white perch and 4 carp samples, only one sample of each species contained detectable levels of BDE 99. American eel and white sucker also had very low concentrations of BDE 99. BDE 183 was detected in 5% of samples (1 crab muscle and hepatopancreas, 1 brown bullhead catfish), and were < 1 ng/g wet weight. On a ng/g lipid basis, pumpkin seed, white catfish, carp, and largemouth bass had the highest BDE concentrations. Not surprisingly, fish containing the highest BDE concentrations were collected from sites adjacent to a wastewater treatment plant and near a municipal waste processing facility in the Baltimore, Maryland urban area.

Preferential accumulation of BDEs in crab hepatopancreas relative to muscle tissue was observed in all samples. An active accumulation/detoxification mechanism or enhanced passive partitioning into more lipid-rich tissues of the hepatopancreas may be responsible. BDE 47 was the most abundant congener in both crab muscle and hepatopancreas. Among the remaining congeners, 99 > 100, 154, 153 > 183. In contrast to BDE 47, higher brominated congeners (BDEs 99, 154, and perhaps 153) constituted a higher percentage of the total BDE in the hepatopancreas than in crab muscle. This may suggest that active uptake and biotransformation processes are occurring in the hepatopancreas for all congeners, while BDE 47 is the primary congener accumulating in muscle tissue.

BDE Distribution in Sediments: Greater than 95% of total BDEs measured in the Back River transect downstream from a wastewater treatment plant was decabromodiphenl yether (BDE 209). Unlike previous studies, we find very low relative concentrations of the components of the 'Penta' commercial mixtures in these



sediments. However, BDE 209 concentrations are 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. Concentrations of BDEs in porewaters ranged from 0.1 to 1 ng/L. Preliminary porewater/solid distribution coefficients for BDE 47 and 99 are 9700 and 54800 L/kg (Log K_d = 4.0 and 4.7, respectively). Initial efforts to measure BDE 209 in porewater did not find detectable levels, and improved detection limits will be required to study BDE 209 behavior in porewater and benthos.

Analysis of benthos continues with the specific goal of determining the extent to which BDE 209 may be accumulated from sediments. These sediments are enriched in BDE 209, providing a worse case for benthic trophic transfer and accumulation.

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