

POLYBROMINATED FLAME RETARDANTS

COMPARISON OF BROMINATED DIPHENYL ETHER FIRE RETARDANT AND ORGANOCHLORINE BURDENS IN FISH FROM VIRGINIA RIVERS (USA)

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Introduction

Brominated diphenyl ethers (BDEs) are widely used as additive fire retardants in polymers and textiles. These materials find their way into a variety of products, notably electronics, vehicles and furniture. BDEs serve a critical function in this fire retarding role. They are commercially produced as mixtures, containing congeners of varying degrees of bromination. Some BDE congeners are highly persistent and bioaccumulative. Toxicology studies suggest they may compromise endocrine and hepatic system function. These effects typically are greater for the less brominated components¹. Research, done mainly in Europe, suggests BDEs have become widely distributed in the environment¹. Consumption of fish may be an important route of exposure for humans. Unlike many of the "historical" organochlorines, BDEs are "current-use" chemicals and their concentrations in some compartments appear to be increasing, e.g. in human breast milk in Sweden². For these reasons restrictions on use are being considered in Europe. In the U.S, in contrast, BDEs have not been closely scrutinized by regulatory agencies and few studies have examined their environmental distribution. The current project focused on the distribution of BDEs in edible tissues of Virginia freshwater fish and compared levels to those of the widely recognized chlorinated pollutants (particularly PCBs and DDE).

Methods and Materials

Edible (muscle) tissues were taken from fish collected at 50 freshwater sites in Virginia. A total of 253 samples were examined for a suite of halogenated contaminants (BDEs, PCBs and chlorinated pesticides). The collection included 30 different species. Emphasis was placed on those species eaten by humans. Samples analyzed consisted of both individual fish and composites of single species taken at a given location. Parts of the study area, the Roanoke and Dan River (south central Va., US Middle Atlantic) are under a fish consumption advisory due to elevated PCB concentrations (Fig. 1). The Roanoke River is dammed in several locations, restricting the movement of fish.

Tissues were lyophilized and a surrogate standard added (containing PCB30, 65, 121 and 204; IUPAC naming conventions were used for PCB and BDE congeners). Samples were subjected to enhanced solvent extraction (Dionex ASE 200, 2 cycles with CH₂Cl₂, 100^o C, 1000 psi). Lipids were estimated by evaporation of a fraction of the resulting extract. The remainder of each extract was purified by size exclusion (Envirosep[®] column) and silica gel (2 g SPE) chromatography. Purified components in the extracts were separated by gas chromatography (60 m, DB5 column, 0.25 μm film, 0.32 ID, helium carrier gas, splitless injection). Detection was by either a halogen specific electrolytic conductivity (ELCD; 253 samples) or mass spectrometric (MS) detector (EI-full scan; subset of 86 samples).

Three major ions for BDEs of each degree of bromination were chosen and the sum of these used for MS quantitation versus PCB204. Surrogate recoveries were estimated by ELCD relative to

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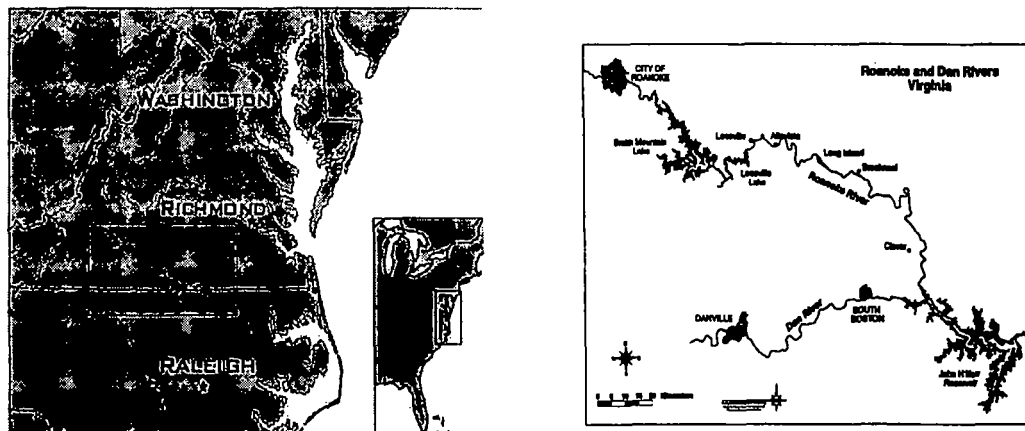


Fig. 1. Map of Virginia and the Roanoke/Dan River basin. Most intensive sampling was conducted on the Roanoke and Dan Rivers (area enclosed by box) due to concerns over PCB burdens in indigenous fish.

pentachlorobenzene (PCB204 mean recovery 82.6%). Standards used included DE-71 (a commercial "penta" mixture) and individual BDE congeners and mixtures (Cambridge Isotope Laboratories). Some unidentified BDEs could only be characterized by their degree of bromination. For these, response factors were estimated based on congener standards possessing the same degree of bromination.

Results and Discussion

Commercial "deca-" and "octa-" BDE mixtures were reported to constitute 90% of the world production of 40,000 tons/year in 1992.³ The "penta" formulations supposedly only contributed 10%. Unfortunately, recent U.S. production figures are not publicly available. In contrast to these figures, GC/MS analyses suggested that the BDEs in Va. fish were dominated by tetra- thru hexa- brominated congeners (Fig 2), in general agreement with most published reports on fish burdens. BDE47 dominated the total BDEs detected in fish. This pattern may be indicative of the source, preferential uptake of the less brominated or degradation of more highly brominated components⁴. A number of other congeners were detected in addition to the six indicated below. BDE153 and BDE154 were chromatographically resolved, but concentrations were combined to simplify the figure. Commercial "penta-" mixtures (e.g. DE-71) typically contain three major congeners. These are 2,2',4,4'-tetrabromodiphenylether (BDE47); 2,2',4,4',5-pentabromodiphenylether (BDE99) and 2,2',4,4',6-pentabromodiphenylether (BDE100).

BDEs have seldom been reported in the environment. This is likely due to the fact that most monitoring programs focus on organochlorine pollutants. While BDEs occur as complex mixtures in fish, determination of BDE47 with a halogen-selective detector, such as the ELCD, may provide a cost-effective screening approach. The 60 m GC column used here permitted complete resolution of PCB180 and BDE47. GC/ELCD and GC/MS provided similar results for BDE47, suggesting that this congener contributed about 70% of the total BDEs in the fish

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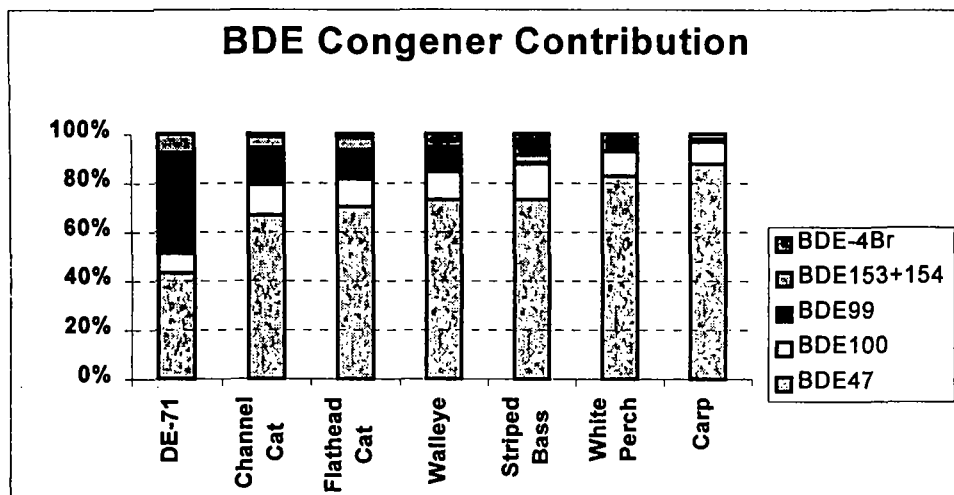


Fig. 2. Contributions of major BDE congeners in DE-71 and different fish species.

samples examined. However, GC/MS or enhanced chromatographic separations were still required to distinguish the remaining BDEs from other co-eluting halogenated components.

About 85% of the samples examined (Fig. 3) contained detectable BDE47 burdens (>5 ug/kg, GC/ELCD), supporting the view that BDEs are widely distributed in the environment. Fish with levels >1000 ug/kg were observed at 9 of 50 sites, suggesting the presence of multiple, BDE point sources. Highest total BDE concentrations (up to 57,000 ug/kg lipid basis: carp composite-GC/MS determination) were observed downstream of the town of South Boston in the Dan/Hyco river area (Fig. 1). This rivals the highest level reported in fish to date. The Hyco River is a small stream that enters the Dan River downstream of South Boston and originates in North Carolina. Textile and furniture facilities are dominant industries in south-central Va. and north-central North Carolina.

Overall, BDE47 concentrations detected rivaled those of organochlorine pesticides and PCBs, contaminants commonly reported to dominate in U.S. fish⁵. For example, BDE47 surpassed the concentration of PCB153 in 58% and 4,4'-DDE in 29% of the 253 samples examined (as ascertained by GC/ELCD). BDE concentrations in Leesville Lake fish, a manmade reservoir located downstream of Smith Mountain Lake and the city of Roanoke (Fig. 1) appeared anomalously low. This may be due to the absence of significant point source discharges and restriction of the fishes' movements by dams located on both ends of this reservoir.

BDEs were also detected in some sediments taken near fish collection points. On a dry weight basis, sediment concentrations were typically in the low ug/kg range.

Acknowledgements

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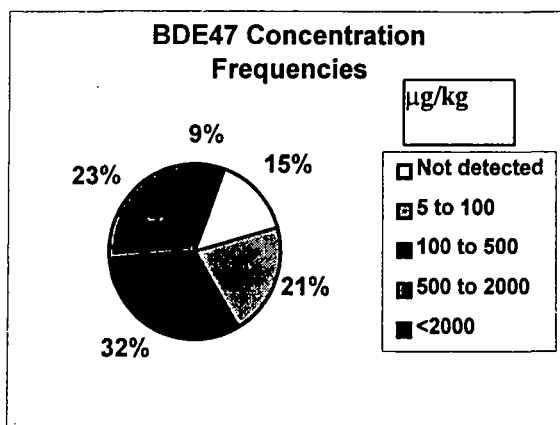


Fig. 3. Frequencies of various BDE47 concentration ranges encountered in fish (ug/kg lipid weight). BDE47 was detected in 85% of the samples examined (>5 ug/kg). This congener was observed at concentrations greater than 2000 ug/kg in 9% of the samples.

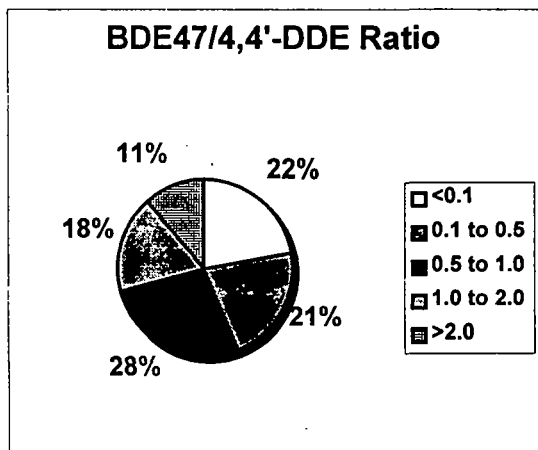
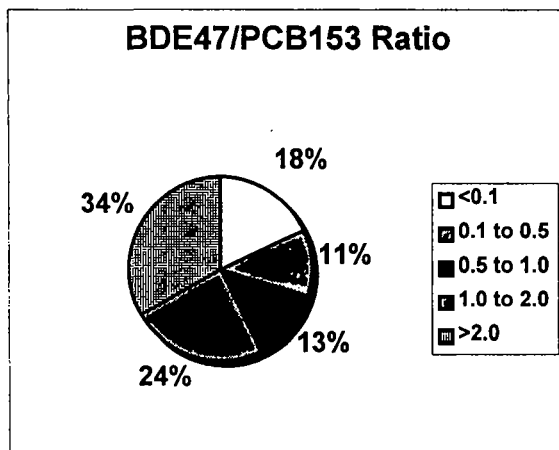


Fig. 4. Percentage of fish samples exhibiting different BDE47/PCB153 and BDE47/4,4'-DDE ratios. BDE47 surpassed the concentration of PCB153 and 4,4'-DDE in 58% and 29% of fish, respectively.

References

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