

BIOMAGNIFICATION OF α - AND γ -HEXABROMOCYCLODODECANE CONGENERS IN A LAKE ONTARIO FOOD WEB

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Introduction

Hexabromocyclododecane (HBCDD) belongs to the class of cycloaliphatic brominated flame retardants (BFRs) and is used primarily in the building industry as a thermal insulator additive in polystyrene foam^{1,2,3}. Secondary uses are in upholstery textiles². HBCDD is synthesized industrially by the addition of bromine to *cis-trans-trans*-1,5,9-cyclododecatriene². The resulting technical mixture contains three diastereoisomers (α , β , γ , Figure 1) existing in proportions of approximately 6, 8 and 80 %, respectively, together with other lower brominated impurities².

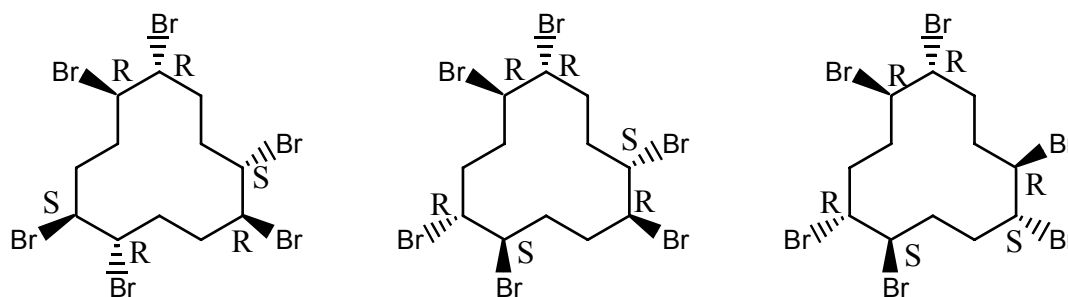


Figure 1. Structures of the α -(left), β -(middle) and γ -(right) HBCDD isomers

In 2001, the global market demand for HBCDD was 16700 tonnes⁴. The demand for HBCDD is now second to the deca-BDEs. The physical chemical properties of HBCDD are similar to those of PBDEs and other persistent organic pollutants, including polychlorinated biphenyls (PCBs), which are known to be persistent, bioaccumulative and toxic^{1,3,5,6}.

This study examines the biomagnification of α - and γ -HBCDD congeners in a Lake Ontario food web. Samples were analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

Methods and Materials

Chemicals. The γ -HBCDD congener (1R,2R,5R,6S,9S,10R) was purchased from CIL (MA, USA). The α -HBCDD (1R,2R,5S,6R,9R,10S) and β -HBCDD congeners (1S,2S,5R,6S,9R,10S) were a kind gift from Dr. Tom Harner (Meteorological Services of Canada, ON, Canada).

Samples. Lake trout, alewife, rainbow smelt, slimy sculpin, *Mysids* and *Diporeia* were collected from offshore sites in Lake Ontario. The invertebrates (*Mysids* and *Diporeia*) and forage fish (alewife, smelt and sculpin) were processed as composites of whole individuals whereas all lake trout were individual whole fish.

Analytical Method. All samples were ASE extracted and cleaned-up using GPC and Florisil^{7,8}. Sample sizes ranged from 8 to 15 grams wet weight for the various fish species and 20 grams wet weight for the zooplankton species. The detection of HBCDD was based on the method recently described by Budakowski and Tomy⁹. In brief, separations were performed on C₁₈ analytical column (5.0 cm × 2.1 mm i.d., 4 μm particle size) at a flow-rate of 300 μL/min. MS/MS detection used MRM conditions for the m/z 640.6 ([M - H]⁻) → Br⁻ reaction (both isotopes), utilizing unit resolution on the first and third quadrupoles and a 200 ms dwell time. Collision activated dissociation gas pressure was 8 a.u. and the collision energy was -50 eV.

QA/QC. Procedural blanks were analyzed for each batch of samples. Recovery of α-HBCDD was tested by adding 1.5 ng of the α-isomer to a recovery blank and processed along with the samples. All results were both blank and recovery corrected. In addition, duplicate samples from each fish species were processed to verify reproducibility of the analytical method.

Results and Discussion

α- and γ-HBCDD were detected in all trophic levels of the Lake Ontario food web. The β-isomer was below method detection limits. The ion chromatograms of α- and γ-HBCDD in biota from Lake Ontario are shown in Figure 2. The remarkable feature of the profiles is that the γ-HBCDD which is the dominant isomer in the technical standard is much abundant in the samples than the α-isomer. The ratio of the γ- to α- isomer (based on their areas) in the technical standard is ~13, whereas in the samples the γ- to α- isomer ratio ranges from 0.12 for alewife to 0.47 for *Diporeia*. These results are consistent with the γ- to α-HBCDD concentration profiles observed in sediments from the Detroit River where the α-isomer appears to be enriched in the samples relative to the technical standard.

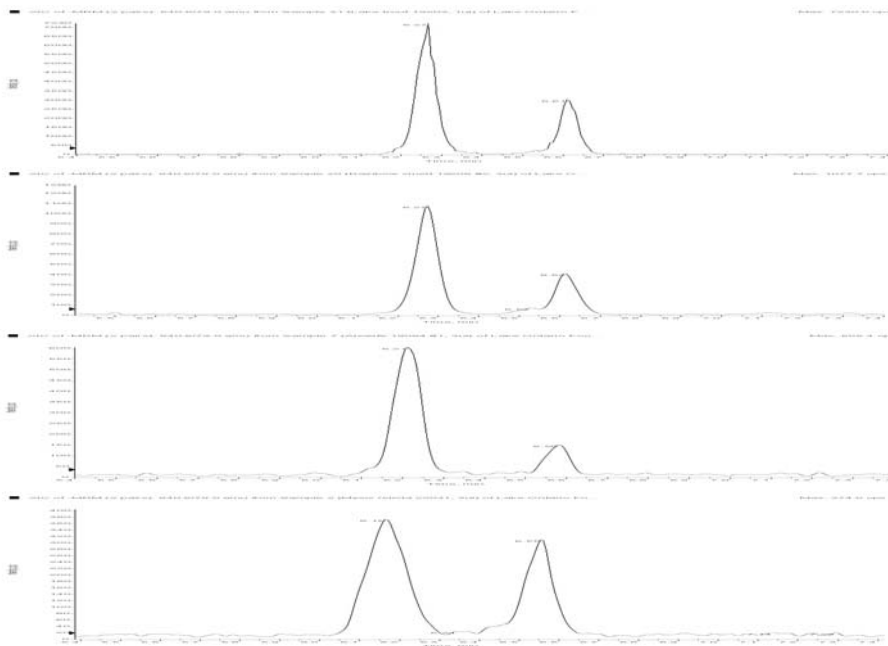


Figure 2. Elution profiles of α- and γ-HBCDD isomers in lake trout (top), smelt, alewife and *Mysis* (bottom)

Whole body concentrations (ng/g, wet wt) of α - and γ -HBCDD in biota are shown in Figure 3. α - and γ -HBCDD levels were highest in the lake trout ranging from 1.2–5.9 ng/g (wet wt) for the α - isomer and 0.2–1.2 ng/g for the γ -isomer. For the forage fish, the trends in α - and γ -HBCDD levels were slimy sculpin > smelt > alewife. Because of their benthic association and high lipid content, it is not surprising that the levels of HBCDDs are highest in the sculpin compared to the other two forage fish species. In contrast, alewife, which is a planktivore, had the lowest concentrations of HBCDD.

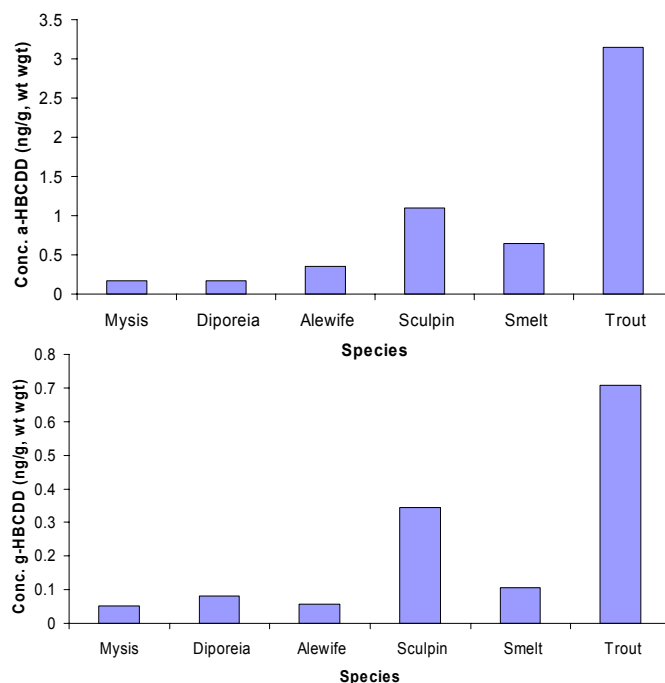


Figure 3. Concentrations (ng/g, wet wt) of α - (top) and γ -HBCDD (bottom) in a Lake Ontario food web

Biomagnification. The biomagnification factors (BMFs = wet wt concentration in predator/wet wt concentration in prey) are shown in Table 1. The highest BMF was seen between lake trout and alewife for both isomers. No real differences in BMFs were observed between the δ - and α - isomers. This suggests that either (a) uptake is non-selective or (b) biotransformation (or lack of) occurs in a similar manner for the two isomers.

Table 1. BMFs for α - and γ -HBCDD in a lake Ontario food web

	α -	γ -
Trout:Alewife	8.9	12.4
Trout:Smelt	4.9	6.6
Trout:Sculpin	2.8	2.0
Sculpin:Diporeia	6.6	4.2

Smelt:Diporeia	3.9	1.3
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Further research is ongoing to elucidate the cause of the drastic change in congener profiles of the Lake Ontario samples and the technical standard. Perhaps like the isomers of hexachlorocyclohexane (HCH), there are differences in the physical-chemical properties of HBCDD congeners.

Acknowledgements

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