

CONCENTRATIONS OF HEXABROMOCYCLODOCANES AND TETRABROMOBISPHENOL-A IN WATER, SEDIMENT, AND FISH FROM ENGLISH LAKES

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Introduction

There is increasing evidence of environmental contamination with brominated flame retardants (BFRs) like hexabromocyclododecanes (HBCDs), and tetrabromobisphenol-A (TBBP-A) (Covaci et al, 2006; 2009). However, notwithstanding reports of HBCDs in sediments and eels from riverine and estuarine environments (Morris et al, 2004) and in marine sediments and biota (Janák et al, 2005), there is little known worldwide about HBCDs and TBBP-A in freshwater environments. We reported previously that despite its greater production, concentrations of TBBP-A in UK indoor dust, indoor and outdoor air are lower than those of HBCDs (Abdallah et al, 2008a). We attributed this to TBBP-A being used primarily as a reactive flame retardant. However it is not known currently to what extent this less facile release and subsequent environmental transport of TBBP-A is reflected in freshwater aquatic environments. An important recent finding is that sediment microcosms under both aerobic and anaerobic conditions suggest HBCDs are debrominated sequentially via dihaloelimination to tetrabromocyclododecene (TBCDe), dibromocyclododecadiene, and cyclodecatriene (Davis et al, 2006). To our knowledge, these findings have not been verified in field studies. This may be important, as we have observed an alternative debromination mechanism in indoor dust, viz photolytically-mediated loss of HBr to pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) (Abdallah et al, 2008b). Also of interest are recent reports of the possible presence (unconfirmed) in fish (Janák et al, 2005) and piscivorous birds (Janák et al, 2008) of the δ -HBCD *meso* form found at very low levels (0.5% Σ HBCDs) in a commercial HBCD formulation (Heeb et al, 2005). Within the Open Air Laboratories (OPAL) project, concentrations of HBCDs, TBBP-A, and other pollutants are being monitored in nine English freshwater lakes between 2008 and 2012. The principal matrix monitored is water, alongside surficial sediments and fish. This abstract reports concentrations of HBCDs and TBBP-A in water samples taken during three quarters of the 1st year of the project. Concentrations are also reported in surficial sediments and in fish, alongside concentrations of dehalogenated HBCD degradation products in sediment. Our specific objectives were to:

- Compare the relative abundance of HBCDs and TBBP-A in English lakes with that in other matrices;
- Identify and quantify degradation products of HBCDs in sediments; and
- Monitor samples for the δ -HBCD *meso* form

Materials and Methods

Sampling Sites and Methodology

Water Water was sampled from nine English freshwater lakes. At each location, a grab sample of 40 L of water was collected from 50 cm below the surface in 2 x 20 L precleaned HDPE containers. Samples were taken from the profundal point of each lake. Exact sampling dates varied; however, the 1st sample batch was taken between 31st July-17th August 2008 (summer); the 2nd between 6th-16th November 2008 (autumn); and the 3rd between 19th-25th January 2009 (winter).

Sediments Surface sediments were taken at the same location as water samples using a gravity corer with a polycarbonate tube of internal diameter 8.5 cm. The top 5 cm from each of seven cores were taken from the profundal area of each lake, amalgamated and homogenized. Sub-samples were freeze-dried prior to analysis.

Fish Fish (n=30) were collected in summer 2008, either dissected in the field, or where not possible, were frozen immediately upon retrieval and dissected in the laboratory. After dissection and removal of skin, the muscle tissue was freeze-dried, and an aliquot provided for analysis.

Analysis Samples were analyzed for concentrations of HBCDs, PBCDs, TBCDs and TBBP-A using LC-ESI-MS/MS as reported elsewhere (Abdallah et al, 2008a, b).

Results and Discussion

Seasonal and Spatial Variability of Concentrations in Water Concentrations (sum of particulate and dissolved phases) of Σ HBCDs and TBBP-A in water samples are summarized in Table 1. To our knowledge this is the first report worldwide of concentrations of HBCDs or TBBP-A in freshwater; hence these data represent a valuable benchmark for future studies. Very striking are the low standard deviations for the three samples from each site, indicating no obvious seasonal variability in contamination. The inter-site spatial variability for Σ HBCDs is low (Table 1) as the ratio of maximum:minimum concentrations is 3.4. This contrasts with TBBP-A, for which the maximum:minimum concentration ratio is 23. We hypothesize the greater inter-site variability of TBBP-A indicates a shorter environmental half-life.

Concentrations of TBBP-A, HBCDs, and HBCD degradation products in Sediments Concentrations of HBCDs and TBBP-A in surficial sediment (Table 1) are at the low end of those in estuarine and river sediments in Belgium, England, and the Netherlands (Morris et al, 2004). We hypothesize that this is because the lakes in this study are not impacted directly by point emissions of HBCDs and TBBP-A. Unlike in water, concentrations of Σ HBCDs exceed those of TBBP-A in all but two samples. In four samples we detected peaks corresponding to the PBCD isomers and in seven samples peaks corresponding to the TBCD isomers reported in indoor dust (Abdallah et al, 2008b). This suggests degradation of HBCD via loss of HBr occurs in our sediments.

Concentrations of BFRs and HBCD Diastereomer Patterns in Fish

Concentrations of HBCD diastereomers and TBBP-A in selected fish (n=13 out of the 30 analysed) are reported in Table 2. While TBBP-A was rarely detectable (above LOQ in only four samples out of the 30 analysed), HBCDs were detectable in all. This marked predominance of HBCDs over TBBP-A

in fish concurs with eels from Netherlands rivers (Morris et al, 2004). We hypothesize this reflects a low persistence of TBBP-A in fish, similar to the short human half-life of 2.2 days. An alternative hypothesis is that there is minimal uptake by fish of TBBP-A. Concentrations reported here for both HBCDs and TBBP-A are consistent with those in Netherlands eels. Particularly noteworthy is the presence of the δ -HBCD *meso* form in all 13 of the fish samples reported in Table 2 – it was undetectable in the other 17 samples analysed (data not shown). This is the first confirmed report of its presence in the environment. Its relative abundance (1.0-11 % Σ HBCDs where detected) exceeds substantially its abundance in a commercial HBCD formulation (0.5 % Σ HBCDs, Janák et al, 2008). Furthermore, it was not detected in water and sediment samples. We therefore hypothesize that δ -HBCD in fish arises via biotransformation.

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Table 1: Average (σ_n) Concentrations (sum of both phases, pg L^{-1}) of HBCDs and TBBP-A in English Lake Water ($n = 3$ at each site) and Concentrations (pg g^{-1} dry weight) of HBCDs, PeBCDs, TBCDs and TBBP-A in surficial sediments from same locations

Location/Compound	Concentrations in sediment				Concentrations in water	
	Σ HBCDs	TBCDs	PeBCDs	TBBP-A	Σ HBCDs	TBBP-A
Wake Valley Pond	880	810	< LOQ	390	100 (10)	140 (9.0)
Holt Hall Lake	1100	320	220	460	120 (16)	170 (5.6)
Chapman's Pond	1700	770	42	2300	150 (32)	1100 (150)
Crag Lough	1200	240	< LOQ	330	110 (15)	170 (13)
Marton Mere	3000	72	< LOQ	1200	190 (21)	450 (26)
Slapton Ley	4000	570	100	3800	270 (18)	3200 (200)
Fleet Pond	2300	120	37	550	120 (49)	310 (16)
Edgbaston Pool	4800	270	< LOQ	3400	270 (31)	1900 (33)
Thoresby Lake	910	140	< LOQ	2900	80 (7.3)	1200 (81)

Table 2: Concentrations of HBCDs and TBBP-A in Selected Individual Fish (ng g^{-1} lipid weight) from English Lakes

Location	Species	α -HBCD	δ -HBCD	β -HBCD	γ -HBCD	TBBP-A
Crag Lough	<i>Oncorhynchus mykiss</i>	110	7.3	22	43	< LOQ
Crag Lough	<i>Perca fluviatilis</i>	28	3.3	8.0	30	< LOQ
Crag Lough	<i>Perca fluviatilis</i>	65	9.8	6.3	12	1.3
Holt Hall Lake	<i>Carassius carassius</i>	89	3.9	10	24	< LOQ
Holt Hall Lake	<i>Carassius carassius</i>	76	2.5	10	32	< LOQ
Holt Hall Lake	<i>Carassius carassius</i>	53	0.79	3.1	18	< LOQ
Chapman's Pond	<i>Carassius carassius</i>	51	1.2	3.1	11	< LOQ
Slapton Ley	<i>Rutilus rutilus</i>	120	10	30	51	< LOQ
Slapton Ley	<i>Scardinius erythrophthalmus</i>	37	3.9	17	37	< LOQ
Fleet Pond	<i>Perca fluviatilis</i>	11	1.0	3.8	4.8	< LOQ
Fleet Pond	<i>Rutilus rutilus</i>	47	7.4	14	15	< LOQ
Fleet Pond	<i>Rutilus rutilus</i>	160	17	4.6	22	< LOQ
Marton Mere	<i>Esox lucius</i>	57	8.0	6.4	19	< LOQ

<LOQ = below limit of quantitation; LOQ is 0.29 ng g^{-1} (lipid weight) for TBBP-A