PARTITIONING OF POLYBROMINATED DIPHENYL ETHERS BETWEEN AIR, WATER, SEDIMENT AND FISH IN LAKE THUN (SWITZERLAND)

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Abstract
Concentrations and congener patterns of polybrominated diphenyl ethers (PBDE), including deca-BDE, were determined in the most important environmental compartments of a lake ecosystem (Lake Thun, Switzerland). An overview of the partitioning and the preferential transport pathways of these compounds is provided. Several recent studies have shown that deca-BDE may be debrominated to lower brominated, potentially critical congeners. Therefore it is important to investigate whether or not deca-BDE may be considered as a safe alternative to penta-BDE and octa-BDE products (banned in the EU in 2004) by looking more closely into occurrence and origin of lower brominated BDE congeners in the environment. Deca-BDE is the most prominent PBDE congener in atmospheric deposition, suspended particulate matter and surface sediment, while tri- to hepta-BDE dominate in the water phase and in fish. The ratio of BDE-47 / BDE-99 in the various compartments was investigated to distinguish among possible processes leading to an altered pattern observed in the environment compared to the technical PBDE formulations. The identification of octa-BDE and nona-BDE congeners in atmospheric deposition and in sediment indicates that debromination of deca-BDE into lower brominated congeners occurs in the environment.

Introduction
PBDE are widely used as flame retardants in plastics and textiles[1]. Emissions of PBDE occur during production, use and disposal of flame-proofed materials and PBDE have become ubiquitous environmental contaminants. PBDE are persistent as well as subject to bioaccumulation and long-range transport[2]. Some of the lower-brominated PBDE congeners are known to induce adverse health effects[3], including endocrine disruption, while deca-BDE has less toxic properties[3]. With regard to the recent ban of penta-BDE and octa-BDE formulations in various countries, deca-BDE will probably become more important on the market. Since several studies have recently shown that deca-BDE can be debrominated to lower brominated congeners[4,5,6], it is important to investigate whether or not deca-BDE may be considered as a safe alternative to the already banned penta- and octa-BDE products. Here, first results on a study to assess the fate of PBDE in the ecosystem of Lake Thun (LT), a prealpine lake in the centre of Switzerland, are presented.

Materials and Methods
LT is an oligo-mesotrophic lake situated in the alpine region of the Canton of Bern in the centre of Switzerland. LT has a surface area of 47.69 km^2, a mean depth of 136 m, a volume of 6.42 km^3 and a hydraulic residence time of 684 days. The catchment area is 2451 km^2 with mean and maximum altitudes of 1748 and 4272 m, respectively. Concentrations of PBDE have been measured in the following media. **Sediment**: PBDE were measured in a sediment core taken from the deepest point (217 m) in July 2005. **Fish**: PBDE were analysed in fat from muscle tissue of whitefish (*Coregonus sp.*) sampled in September 2005. **Water**: A large volume filtration method was developed for the determination of PBDE in lake water. The method was based on a pumping system followed by a glass fibre filter and three subsequent polyurethane foam plugs. Thus, this method allowed to differentiate between particle bound (filter pore size 0.7 μm) and dissolved PBDE in water samples taken in March 2007 from the same position as the sediment core. **Atmospheric deposition**: PBDE were measured in bulk atmospheric deposition on the southern shore of LT using Bergerhoff jars exposed for 6 weeks in July and August 2006.

For all samples, soxhlet extraction was used (apart for fish tissue and deposition samples, where liquid-liquid extraction was employed). Clean-up included gel permeation chromatography followed by chromatography over

acidic silica. Quantification was performed by gas chromatography / electron impact high resolution mass spectrometry (GC/EI-HRMS) based on the isotope dilution method (^{13}C-labelled internal standards were used for all analytes, except for octa-BDE and nona-BDE where ^{13}C$_{12}$-BDE-183 was used as internal standard).

Quality control included analysis of field blank samples, repeated analyses of identical fish samples (4 % RSD), checking for recovery of isotope labelled internal standards ($\geq$ 50 %) and checking for recovery of native analytes in spiked sediments (mean recovery 89 %). For the discussion of the results, blank corrected concentrations were considered (see Table 1).

Results and Discussion

Concentrations and congener patterns. The concentrations of deca-BDE (BDE-209), Σ octa-nona BDE (BDE-194+196/200+197/204+198/203+201+202+206+207+208) and Σ tri-hepta BDE (BDE-28+47+99+100+153+ 183) in LT samples are given in Table 1. The distribution of Σ tri-hepta BDE and deca-BDE in various environmental compartments of LT (data on plankton, river-input and river-output are not available, yet) is summarized in Figure 2. For sediment only results from the top layer representing sediment deposited in 2004-2005 are presented here.

Table 1: Concentrations of deca-BDE, Σ octa-nona BDE and Σ tri-hepta BDE in Lake Thun. Ranges are given in brackets (), n = number of analysed samples; dw = dry weight; lw = lipid weight.

compartment	n	deca-BDE mean concentration	blank	Σ octa-nona BDE mean concentration	blank	Σ tri-hepta BDE mean concentration	blank	unit
surface sediment	1	0.9	0.05	0.06	<0.01	0.3	0.05	ng/g dw
fish	57	7.2 (3-10)	1.9	<0.1	<0.1	123 (110-140)	0.8	ng/g lw
water (suspended particulate)	1	1.00	<0.1	<0.01	<0.01	2.7	1.3	pg/l
water (dissolved phase)	1	<0.1	<0.1	<0.01	<0.01	21.9	1.9	pg/l
atmospheric deposition	1	6.1	1.1	0.2	0.02	4.7	1.1	ng/m^2/d

Analysis of the PBDE congener distribution shows that deca-BDE is the major PBDE in sediment and bulk atmospheric deposition. Deca-BDE is also present in suspended particulates. The predominance of deca-BDE in deposition and sediment may be rationalized by the ongoing usage of deca-BDE as a flame retardant and the related emissions and/or by a high stability of deca-BDE towards biotic and abiotic environmental degradation processes.

In recent surface sediment from LT, maximum concentrations of Σ tri-hepta BDE and deca-BDE of 0.3 ng/g dw and 0.9 ng/g dw respectively, have been determined. These values represent low concentrations, compared to sites with direct input of PBDE from industrial sites (in the Western Scheldt Estuary in Belgium, concentrations of Σ tri hepta BDE and deca-BDE up to 19 ng/g dw and 1200 ng/g dw, respectively, have been reported)[7].

The bulk deposition measurement indicates that atmospheric deposition represents a relevant input pathway for deca-BDE in LT. This finding can be supported by comparing the data from bulk atmospheric deposition with sediment concentration. Considering the surface sediment concentration and the sedimentation rate, the flux of deca-BDE amounts to 1.7 µg/m^2/y. The blank-corrected atmospheric deposition measurement is 5.0 ng/m^2/d or 1.8 µg/m^2/y. The latter comparison indicates that the sedimentation flux of deca-BDE can be largely explained by atmospheric deposition. This preliminary comparison does not yet include deca-BDE input by the rivers Aare and Kander, feeding LT. Since all waste water input to LT passes through sewage treatment plants (STP have been reported to eliminate deca-BDE efficiently)[8], only lower contributions from this pathway are expected.

As PBDE are lipophilic (logK$_{OW}$ 5.9 to 8.3 for BDE-47 to BDE-183)[9] and have low vapour pressures (particularly deca-BDE; i.e. logP$^\circ_{L,25^\circ}$ -3.7 to -6.3 for BDE-47 to BDE-183)[10], they bind easily to airborne and waterborne particles that are subsequently buried in the sediment. The high proportion of deca-BDE found in the

water particulate phase and in sediment confirms that deca-BDE preferentially uses the particle-bound route to enter the sediment compartment, representing an important final sink.

Although sediments are a major sink for deca-BDE, some questions on the environmental compatibility of deca-BDE are still open. Deca-BDE could be debrominated into lower brominated congeners, and resuspension of deposited sediment might occur, leading to remobilisation of buried pollutants. Debromination of deca-BDE has recently been shown for sewage sludge[4], bacteria cultures[5] and also *in vivo* in fish[11]. The present study provides further indications for debromination of deca-BDE. Nona- and octa-BDE congeners with distinctively different congener patterns compared to the octa- and nona-BDE congener patterns present in technical products[12] were identified in sediments and deposition samples. Occurrence of environmental debromination of deca-BDE was further supported by the fact that also BDE-202 was identified in sediments and deposition samples (based on comparison of GC/HRMS chromatograms of samples and native PBDE standards), although BDE-202 is a congener that is not present in technical products.

Figure 2: Distribution of Σ tri-hepta BDE and deca-BDE in individual environmental compartments from LT. The percentages of Σ tri-hepta BDE and deca-BDE are calculated based on blank corrected concentrations.
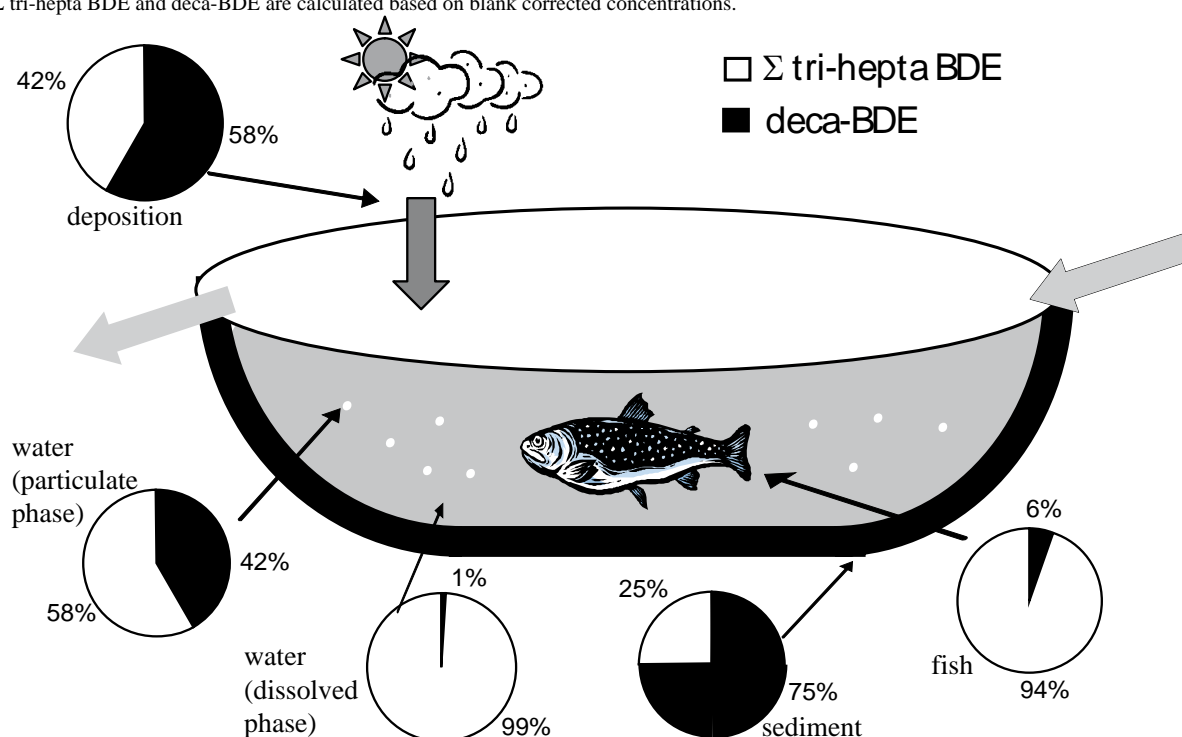
A low contribution of deca-BDE compared to Σ tri-hepta BDE was found for fish tissue and the dissolved water phase. The mean concentration of deca-BDE in fish was only 7 ng/g lw and close to the blank concentration (1.9 ng/g lw), while the mean concentration of Σ tri-hepta BDE was 123 ng/g lw. Thus, the present study shows that levels of deca-BDE in fish are low and that deca-BDE is barely taken up and/or bioaccumulated in fish from LT. On one hand, the considerably higher levels of Σ tri-hepta BDE in fish tissue are certainly due to a high bioaccumulation potential of these congeners. On the other hand, the presence of deca-BDE in sediment and in water particles and its virtual absence in fish tissue lead to the consideration of a low uptake, a rapid metabolism of deca-BDE into lower brominated congeners in fish (input of PBDE via plankton consumed by the fish are not considered, yet) or an enhanced elimination of deca-BDE. Earlier studies provided evidence for a significant uptake and biotransformation of deca-BDE in juvenile lake trout[11]. It was observed that among PBDE, deca-BDE had the shortest half-life ($t_{1/2}$ 346 d for BDE-47 and 26 d for BDE-209)[11] and the lowest biomagnification factor (BMF 37 for BDE-47 and 0.3 for BDE-209)[11].

Ratios of BDE-47 / BDE-99: Ratios of BDE-47 / BDE-99 (denoted by *R*) in the different samples from LT and in a technical penta-BDE formulation[12] (Bromkal 70-5DE) are shown in Figure 3.

Figure 3: Ratio of BDE-47 to BDE-99 in different compartments from Lake Thun and in technical penta-BDE formulation[12].

Ratio BDE-47 / BDE-99
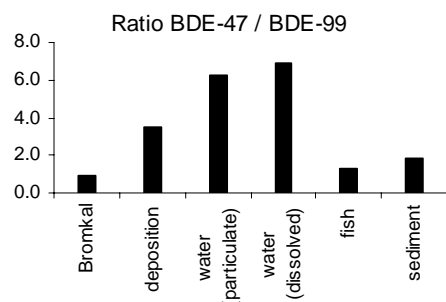
Various biotic and abiotic processes may cause a shift of *R* away from 1, which is the typical ratio observed in the technical penta-BDE product. *R* is 3.5 in deposition and above 6 in water. The enrichment of BDE-47 in deposition may be rationalized by enhanced emissions of BDE-47 from flame retarded consumer goods (higher vapour pressure), and/or may be due to transformation of higher brominated into lower brominated congeners in the atmosphere before deposition takes place. The enrichment of BDE-47 in the dissolved water phase most likely reflects the better water solubility of the lower brominated BDE-47 congener ($S_{w,25°}$ 15.0 µg/l to 1.5 µg/l for BDE-47 to BDE-183)[10]. *R* of 1.3 in fish is close to the technical penta-BDE formulation (here, preferential metabolism of BDE-99 is very likely to be the cause) and is in contrast to *R* above 6 in lake water. *R* for sediment is 1.8, which is close to the fish *R* of 1.3.

This comparison may indicate that fish uptake could also occur directly from sediment. The lower *R* of sediment compared to settling particulate matter may be due to degradation of PBDE in sediment. This process should be further studied, as anaerobic degradation in sewage sludge for instance is known to be slow[4].

A more detailed investigation of the shift of PBDE patterns between the different compartments will be performed on the basis of additional sample analyses. Further, a multicompartmental model describing the partitioning of PBDE in LT is currently set up and is expected to provide additional insight into the environmental behaviour of these compounds.

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