Fate studies on selected brominated flame retardants in indoor-mesocosm ponds

Feibicke, M.[(1)], Meinecke, S.[(1)], Mailahn, W.[(1)], Lepom, P.[(1)], Sawal, G.[(1)], Opitz, S.[(1)], Müller, J.[(2)], Nowak, J.[(2)]

[(1)] Federal Environment Agency (UBA), Schichauweg 58, D-12307 Berlin
Corresponding author: michael.feibicke@uba.de

[(2)] Fraunhofer Institute Molecularbiology and Applied Ecology (IME)
Corresponding co-author: josef.mueller@ime.fraunhofer.de

Fließ- und Stillgewässer-Simulationsanlage

Introduction

In 2008, mesocosm studies were conducted in indoor-ponds of the Artificial Stream and Pond System (FSA) of the Federal Environment Agency in order to investigate the environmental fate of four high production volume brominated flame retardants (BFR), which are still in use namely decabromodiphenyl ether (BDE-209), decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and hexabromocyclododecane (HBCD).
HBCD, DBDPE as well as BDE-209 are widely distributed in various environmental compartments. There are still limited data about BTBPE which is marketed as a substitute for the Octa-BDE mixture in the last few years. Little is known about the fate of DBDPE, which was provided as a replacement for Deca-BDE since the early 1990s. HBCD is considered to be a PBT candidate with a high potential for long-range environmental transport.
Up to now, no fate data for these compounds from aquatic mesocosm studies have been published. Reasons for this are their physical-chemical properties, which makes it challenging with regard to application, sampling and analysis as well as their widespread environmental presence which may lead to contamination before or during large scale experimental testing and in the laboratory.

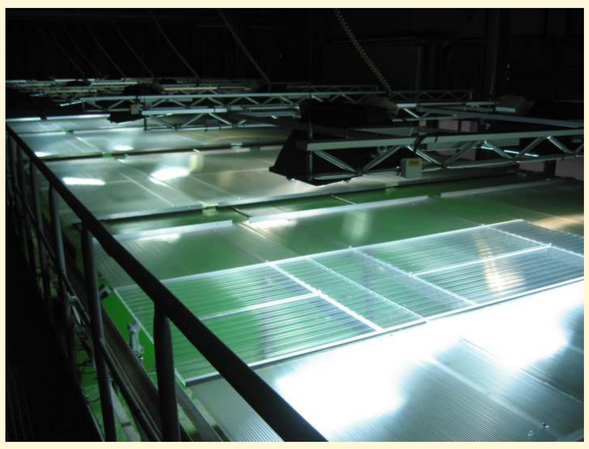


Fig. 1: Indoor pond systems (FSA) of the UBA with BFR-free plastics covers to prevent dust immission into the mesocosm system

Materials & Methods

Pond design

Size: L 6.9 x W 3.3 x H 1.0-1.1 m, Vol 22-25 m^3
Material: Gel-coated fibre-reinforced composite material
Light: HQI-lamps (all ponds), UV-A/B-tubes (only BDE-209)
Ground: Sand, natural fine particular lake sediment
Biofilm: Gel coated fibre flags exposed in 10 cm depth
Water circulation: Bubbling of cleaned compressed air
Pond cover: BFR-free cover to prevent dust immission

Experimental design

Initial analyte concentrations in fortified ponds systems:
HBCD (24 µg/L): 1 pond (HT3) dosed + 1 control pond,
Start 10-06-2008, duration: 120 d, only HQI-Lamps
BDE-209, DBDPE (100 ng/L each) + BTBPE (1000 ng/L):
2 ponds dosed (HT4, HT7) + 1 control pond (HT5),
Start 08-07-2008, duration: 191 d, additional UV-tubes

Application

Substances: sprayed on water surface with a spray gun by injection of organic solvent into the spray waterflow.
HBCD: diluted in acetonitrile + ethanol (v/v: 71/171)
BDE-209, DBDPE + BTBPE: diluted in tetrahydrofurane + toluene + i-propanol (v/v/v: 30/30/140)
LiBr + Uranine: solved in water tank, tracers (check homogeneity, calibration of pond water volume)

Sampling

Water: mixed duplicate samples (incl. various water depths), directly filled in submersed glass bottles
Sediment: duplicate core sampling with modified Berggren sampler, upper 2.5 cm layer was analyzed
Biofilm: scratching samples from exposed gel coated resin flags with a stainless steel scraper
Biota: manual sampling of macrophytes (*Myriophyllum spicatum*, filamentous algae) and snails (*Lymnaea stagnalis*)

Analysis

BTBPE, BDE-209, DBDPE (UBA: Lepom, Sawal, Opitz)
Sample preparation:
Water + biofilm: Liquid/liquid extraction (water), Soxhlet extraction (biofilm) with toluene, cleanup with multi-layer column with neutral silica gel and acidified silica gel, GC-ECNI-MS after extract concentration
Sediment: Pressurized liquid extraction (PLE) with toluene and *in-situ* elemental sulfur removal with activated copper granules, cleanup with gel permeation chromatography (GPC) and multi-layer column with neutral silica gel and acidified silica gel

Quantification by short column GC-ECNI-MS in SIM mode using internal standardization with F-PBDE-201, 13C-BDE-209

HBCD (Fh IME: Müller, Nowak & co-workers)
Sample preparation:
Water + biofilm: Extraction with n-pentane, LC-MS-MS after extract concentration
Sediment: Freeze drying, grinding to <200 µm, extraction with acetone + dichloromethane (50+50, v/v), silica gel cleanup, LC-MS-MS
Biota: Homogenization, extraction with acetone, GPC cleanup, LC-MS-MS

Quantification by HPLC-MS-MS in electrospray negative mode using internal standardization with a-, b- and g-13C-HBCD

Results & Discussion

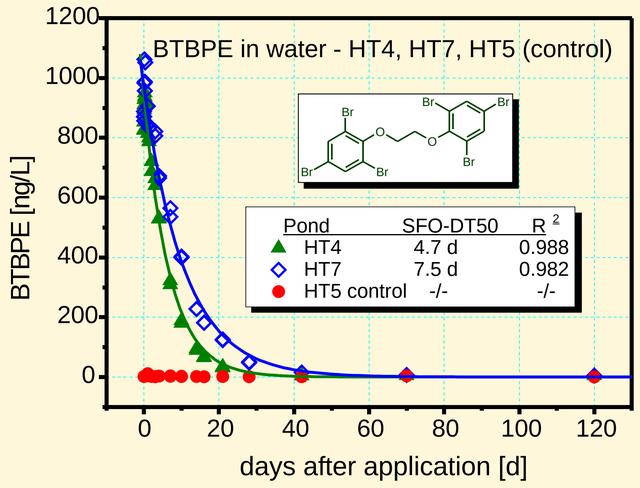


Fig. 2: BTBPE - water concentration and DT50 in the spiked ponds (HT4, HT7) and in the control pond (HT5)

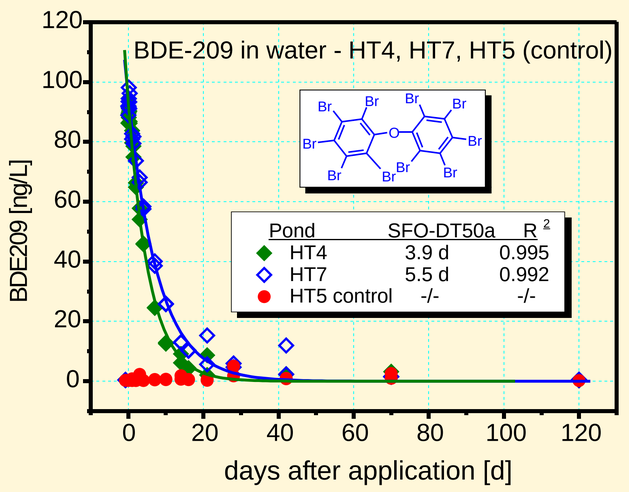


Fig. 3: BDE-209 - water concentration and DT50 in the spiked ponds (HT4, HT7) and in the control pond (HT5)

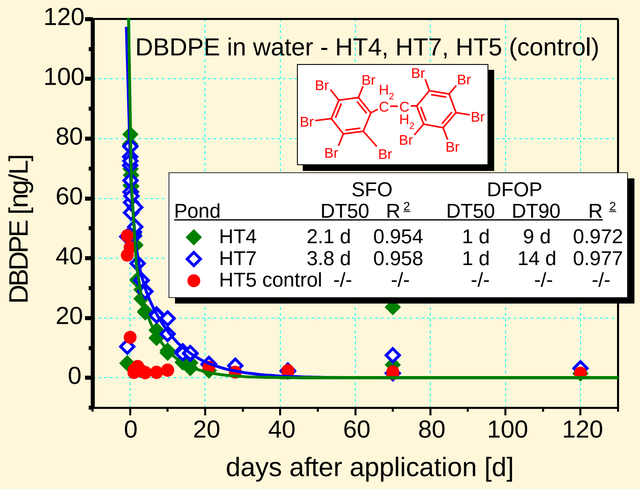


Fig. 4: DBDPE - water concentration and DT50 of in the spiked ponds (HT4, HT7) and in the control pond (HT5)

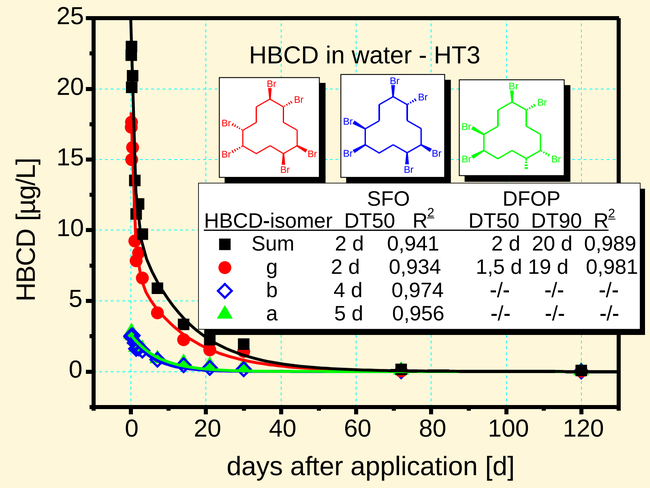


Fig. 5: HBCD (isomers + sum) - water concentration and DT50 in the spiked pond (HT3)

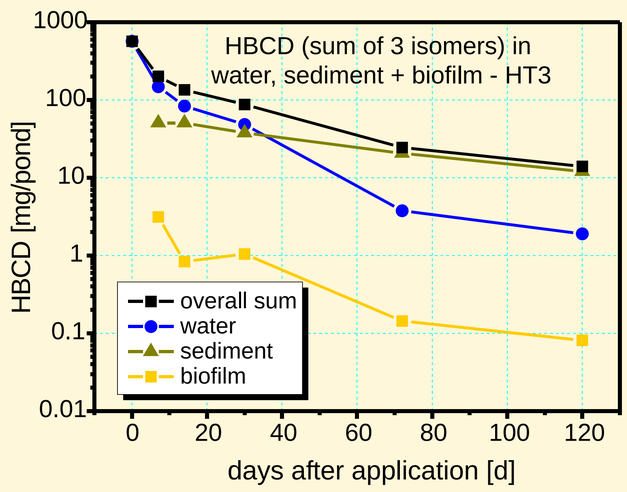


Fig. 6: HBCD (sum of isomers) - pond budget (HT3) for a 120-d-period incl. water, sediment and biofilm

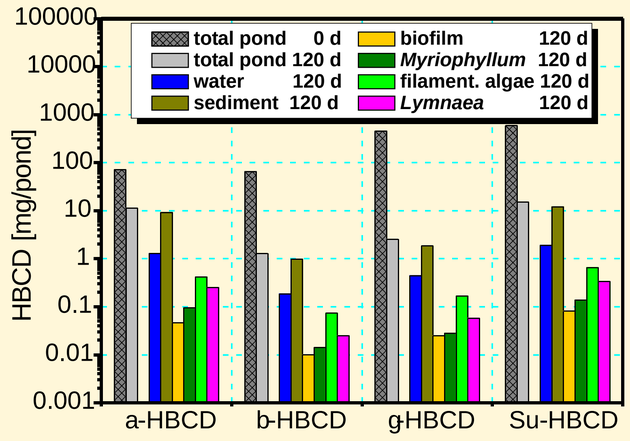
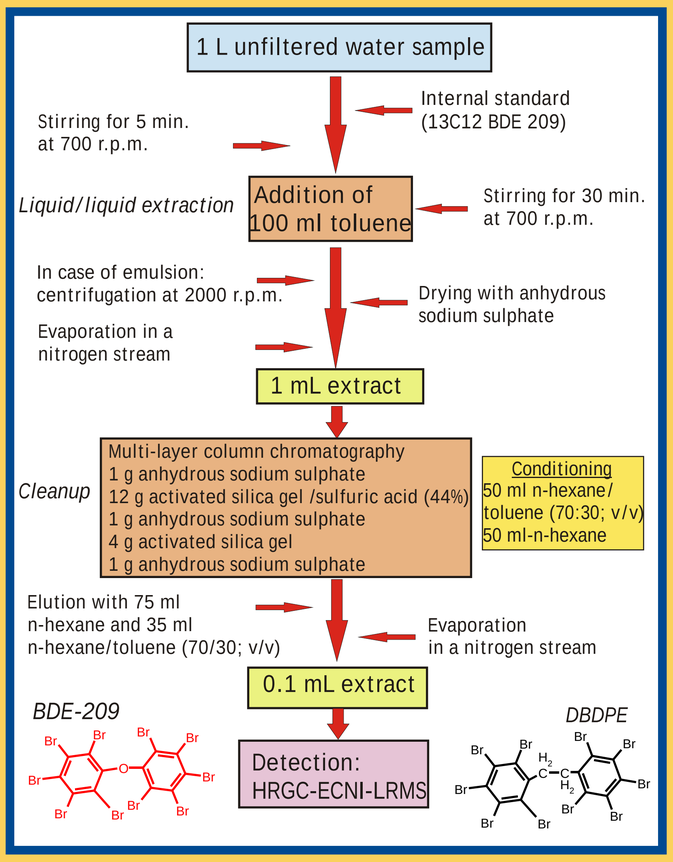
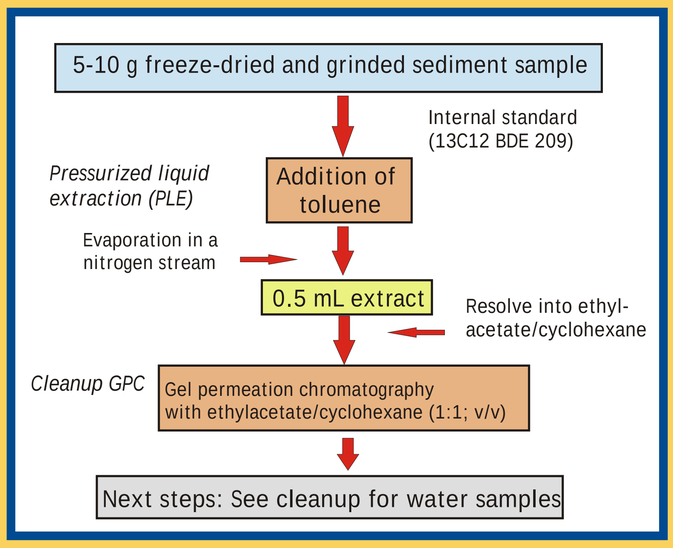


Fig. 7: HBCD (sum + isomers) - pond budget of HT3 at day 0 and day 120 incl. water, sediment, biofilm, macrophytes (*Myriophyllum spicatum*, filamentous algae) and snails (*Lymnaea stagnalis*) at day 120

- Recovery rates ranged from 90 - 97 % for HBCD, BTBPE, BDE-209). Only for DBDPE rates were smaller (74 - 78 %).
- Water concentrations of all BFRs declined rapidly resulting in $DT50_{water}$-values between 2 - 8 d (Fig. 2 - 5). BTBPE, BDE-209, as well as a- and b-HBCD followed simple SFO-kinetics, whereas clearly improved fitting was reached for DBDPE and g-HBCD by use of a DFOP-kinetic (Fig. 2 - 5).
- In the sediment, BDE-209, DBDPE as well as BTBPE showed no relevant degradation during a 191 d period. Analysis of biota and detailed studies on sediment on theses BFRs are not yet finished.
- Preliminary results indicate no formation of lower brominated degradation products of BDE-209 - neither in water (additional UV-A + UV-B tubes) nor in sediment (anaerobic conditions).
- a-HBCD was also persistent in the sediment in a 120-d-period, whereas b- and g-HBCD declined with DT50s of 51 and 33 d, resp. (SFO-Kinetic).
- Although a-HBCD is only present by a 12 % fraction in the technical mixture, its relative amount increased in all matrices (incl. macrophytes and snails) during the 120-d-pond study and became the most relevant isomer (Fig. 6 - 7).





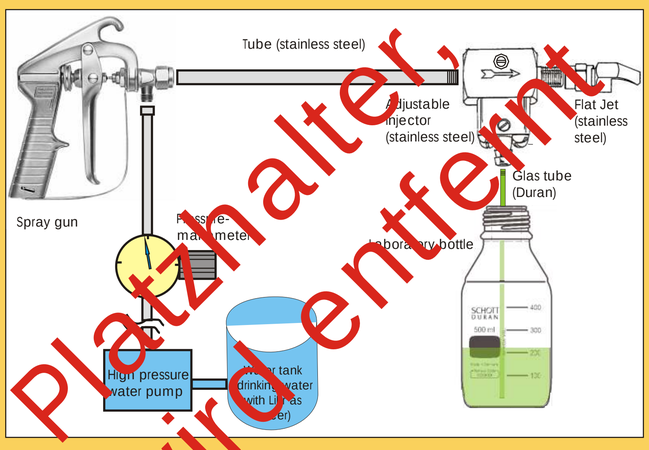


Fig. 4: Scheme of the water injection system: The test substance/acetone solution was aspirated by low pressure, pre-admixed in the water jet and sprayed through a flat nozzle in the water body

- Measured Li-tracer concentrations indicated a homogenous distribution one hour after application (Fig. 8, 9).
- The concentrations of BDE-209 and DBDPE in water decreased with time. The decline in DBDPE levels was faster than that in BDE-209 according to its higher logPow.
- Concentrations of DBDPE and BDE-209 decreased fastest in the pond with sediment. The elimination of the both compounds was described in all cases by double first order kinetic (Fig. 8, 9).
- At the end of the study 0.27 ± 0.14 µg/kg DBDPE were detected in the sediment. There was no detectable increase in BDE-209 levels in the sediment due to high background BDE-209 concentrations.
- BDE-209 and DBDPE levels in biofilms were 1.8 µg/m^2 and 3.2 µg/m^2, respectively.

Fig. 8: Water concentrations of BDE-209 and DBDPE in the pond without sediment at different times after application