European HBCD Industry Working Group

Environmental Monitoring of Hexabromocyclodecane in Europe

Project Description

Project Sponsor:

The industry working group for Hexabromocyclododecane (HBCD) – a sector group of the European Chemical Industry Council (CEFIC)

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1. Introduction

The industry working group for Hexabromocyclododecane (HBCD) is a sector group of the European Chemical Industry Council (CEFIC). The Environmental Advisory Group (EAG) for HBCD is a subgroup of the Industry working group with technical experts from HBCD producers, polystyrene foam producers and from the Bromine Science and Environmental Forum (BSEF). The EAG recommends and coordinates research related to environmental effects and fate of HBCD.

In recent years emissions from HBCD production and formulation have continuously been reduced and further reduction is attempted. The following project is intended to monitor concentrations of HBCD in relevant environmental compartments over a prolonged period of time (10 years) and to reveal the impact and relevance of the emission control program on the HBCD levels found in the environment.

Hexabromocyclododecane is used as a flame retardant in building insulation composed of extruded or expanded polystyrene foam. Another use is in flame retardant back-coats for instance for upholstery textiles. Sales in Europe are estimated to be 9000 t/yr (1).

The commercial product of hexabromocyclododecane (HBCD) consists mainly of the 3 diasteroemers α, ß, and γ; with fractions of 8, 15 and 75%, respectively (2). HBCD has a low water solubility (65.6 µg/L, sum of the individual solubilities of the three diastereomers (3)), a low vapour pressure (6.3 x 10^{-5} Pa (2)) and is very hydrophobic (Log Kow=5.62 (2)). Based on these properties, a moderate potential for long range transport HBCD has been estimated1 (4). In line with the high hydrophobicity, considerable bioconcentration has been reported for HBCD (log BCF=4) (2,5). Biotransformation occurs predominantly under anaerobic conditions with half-lives ranging from approximately two days to two months (6). Complete debromination by dehaloelimination has been confirmed for all diasteroemers of the technical product (7). Complete mineralisation of the transformation intermediate cyclododecatriene has been proven in a recent study (manuscript in preparation).

Results from monitoring studies performed until 2003, reveal detectable levels of HBCD in environmental samples (river and estuarine sediments) predominantly in areas with known point sources or in river basins (8-10). In wildlife, detectable levels are more dispersive (8,11) and low levels of HBCD have also been reported in fat tissues of top predators in the arctic (12,13). Unlike the technical product, the prevalent diastereomer in biota is α-HBCD (14), and in top predators α–HBCD has been detected exclusively (13,15). In microsomal preparations of liver from rats and harbour seals selective metabolism by cytochrome P450 systems *in vitro* has been reported for the β- and γ-HBCD while the α-HBCD did not appear to be metabolized (15). An extensive review of published monitoring data has recently been published by Covaci et al. (16).

2. Objective of the Project

The overarching objective of the planned work is to provide data that allow following the temporal trend of HBCD concentrations in the European environment and to reveal the impact and relevance of the emission control program. The data should enable conclusions on the longer-term trend of the entry of HBCD into the environment. The study focuses on compartments which are expected to be sinks for the product based

1 Note, that for Log Kow a value of 7.6 and for the water solubility a value of 3.4 µg/l was used in the assessment of long rang transport potential. For details see (4).

on its physico-chemical properties and based on information on the lifecycle of the product. Data and conclusions will be reported in appropriate regular intervals to the sponsor.

3. Project outline

Before the start of the experimental work a literature review on HBCD monitoring programs and concentrations in environmental compartments will be performed. This review might lead to refinements of the project as outlined in the following.

3.1 Choice of sampling types

3.1.1 General considerations

Based on the physico-chemical properties, sampling of biota and suspended particulate matter are considered the most relevant matrices for the HBCD monitoring program.

Sampling of fish will provide a biomarker of exposure for limnetic ecosystems. The uptake of substances by aquatic organisms depends mostly on the concentration in the surrounding medium. In the ideal case, equilibrium between the organism and this medium is reached (continuous exposure assumed). Food chain effects in the water phase are considered of minor importance.

As additional biota specimens, eggs from birds will be used as a sample type for terrestrial ecosystems. Environmental monitoring with birds (as well as fish) has the advantage that the substance of interest is stored in the organisms over a certain period of time (time integrative). Nevertheless, eggs are a fast reacting matrix. Particularly for lipophilic compounds they indicate the burden of females that take them up in the period before breeding in order to build up additional fat deposits. In the energy intensive breeding period these fat reserves are diminished and the accumulated lipophilic materials are excreted via the eggs. Therefore the eggs reflect mainly the fraction of a compound that was accumulated by female birds immediately before the breeding period. For comparison of different regions it is essential that the organisms are non-migrating (17).

As a non biotic matrix, Suspended Particulate Matter (SPM) will be sampled. SPM is the material from which new sediment is formed by sedimentation. Both SPM and sediment are important structural and functional elements in aquatic ecosystems. SPM (and finally sediments) are potential sinks for chemicals which enter the water phase via direct emissions or via the atmosphere. It is assumed that sediments are a major sink for HBCD in the environment, too (18). Therefore, the concentration of HBCD in SPM seems to mirror best the actual fraction that will be deposited to the sediment.

No marine monitoring will be performed as part of this project. It can be assumed that the main input into the open sea is via the large streams. Therefore, the marine organisms will reflect the same trends as the limnetic organisms but with an unknown time delay and probably a less pronounced trend as a consequence of the lower concentration at project initiation (16).

For the choice of monitoring organisms and tissues recommendations from the 'UNEP Guidance for a Global monitoring Programme for Persistent Organic Pollutants' were observed (19). General demands for representative organisms are: widespread occurrence, site fidelity of individuals, well studied in terms of ecology and trophic level, known to be bioaccumulators and easily sampleable. Criteria for selection are further: wide geographic distribution, readily collectable, large enough to be sampled, enough individuals to be sampled.

3.1.2 Fish samples

Fish is assumed to be the most appropriate organism for monitoring of bioaccumulating compounds in aquatic systems (20). Appropriate fish species should be high in the food chain, they should have a relatively high fat content, should be non-migrating, and there should be no large population changes during the investigation period.

Considering these prerequisites, the non-migrating bream (*Abramis brama*) will be used in the project. Bream is quite common in central, south and north European countries and is widely used as a monitoring organism (17) which will allow a comparison of results between different years and between different regions. Due to its feeding from the bottom, bream is in close contact to the sediment which is a probable sink for HBCD.

For monitoring of lipophilic compounds the muscle tissue is most appropriate (fat content 1 – 10 % depending on age and nutrition state). Standard operating procedures have been developed for sampling of bream and sample treatment (dissection of muscles tissue) in the frame of the German Environmental Specimen Bank (http://www.umweltbundesamt.de/specimen/upb22.htm). A more detailed review on the use and the suitability of bream for monitoring programs is available from Klein et al. (21).

For each sampling, musculature from about 15 fish will be collected (age: > 8 years if possible). The selection of > 8 year-aged bream is primarily justified by the intended standardization of the samples. In order to yield physiologically comparable samples, a uniform age group of sexually mature individuals should be selected. The variability of physiological parameters of non-sexually mature bream (i.e., < 4 - 5 years) seems too large in order to consider such specimens in a program for the monitoring of lipophilic materials. Thus, with sexually mature individuals, changes of the HBCD levels could be monitored more reliably due to smaller variations of the sampled bream.

Sampling of bream will be performed with nets by specialists (biologists) between July and September each year after the spawning season. The fish will be dissected and the muscle tissue will be frozen directly after sampling (sample weight: at least 100 g per fish). Samples will be immediately frozen with liquid nitrogen (< -135 °C) and kept at this temperature during transport and storage until analysis. For analysis pooled samples will be prepared. However, in some cases all fish samples will be analyzed separately in order to get data on the variability of the HBCD content of individual fish (at least for two sampling sites of different HBCD levels a variability study in one year during the program will be performed).

3.1.3 Bird egg samples

Birds are also suitable monitoring organisms for compounds with lipophilic properties, e.g. (19,22). In most cases eggs are chosen as the matrix. The egg shell serves as a contamination barrier and the high lipid content is advantageous for the potential accumulation of lipophilic compounds. The determination of the concentrations of these chemicals in the egg allows an assessment of the contamination of the breeding females with the respective compounds. Egg sampling has the advantage that no organisms have to be sacrificed. Most appropriate for monitoring purposes are birds which are at a top position in the food web and accumulate chemicals from prey over time.

Considering various options the rook (*Corvus frugilegus*) was chosen for the project for the following reasons:

- *C. frugilegus* feeds predominantly on earthworms and slugs in the summer months allowing a direct relationship to the soil as potential HBCD sink.
- Due to the high nest density a sufficient large sample (> 15 eggs) can be collected. Furthermore, the population will not be endangered by the sampling since large amounts of eggs are produced.
- The West-European rook is a sedentary species. Therefore, HBCD concentrations of the eggs reflect the bioavailable fraction of the HBCD burden of the respective sampling area.

- There is a high probability to yield freshly laid eggs in sufficient number which excludes problems of HBCD metabolization in older eggs.
- There are standard operating procedures from the German environmental specimen bank available for sampling of eggs of gulls and domestic pigeons (23) which can be adapted to the sampling of rooks eggs.

A disadvantage of rooks is that they are not ground breeders. Rooks prefer old, high trees for breeding. For the sampling, specially trained tree climbers will be employed.

3.1.4 Suspended particulate matter (SPM)

For the sampling of suspended particulate matter, stainless steel traps that are operated from buoys in the open water will be used. Traps will be sampled every three month throughout the whole year. SPM traps that are operated only a part of a year may not yield representative results because flood events or other turbations may re-suspend older sediment layers. This may impair the value of the samples for trend analysis. In view of the expected variability and the probable slower temporal change, sampling will only be performed at an interval of two years.

4. Sampling sites

The suggested river sampling sites for fish and SPM are listed in Table 1. They cover different climate regions in Europe. Sampling sites will be located at the river end/in the estuary. The sites should be representative for industrial HBCD inputs from point sources and also for diffuse emissions from non-point sources which may enter the aqueous environment via sewage treatment plants (STP). Lake Belau is suggested as a rural area with only low anthropogenic influences. It is also used for the German environmental specimen bank program as a reference site.

Table 1: Suggested aquatic sampling sites for the HBCD monitoring program.

Region	Country	Fresh water	locations
Western Mediterranean	South France	Rhone	River end/estuary
Scandinavia	South Sweden	Gota Älv	River end/estuary
North western Europe	United Kingdom	Tees	River end/estuary
North western Europe	United Kingdom	Mersey	River end
Central Europe	The Netherlands	Western Scheldt	River end/estuary
Central Europe	Germany	Lake Belau	Rural lake

For sampling of bird eggs, countries with land application of sludge will be chosen. Locations considered for sampling of bird eggs are given in Table 2. Before starting the monitoring it will be reconfirmed with local authorities that sludge application as fertiliser is an on-going practice.

Table 2: Suggested sampling sites for the HBCD monitoring program – bird eggs.

Region	Country	Location
North western Europe	United Kingdom	near mouth of river Tees
Central Europe	Germany	near Lake Belau

5. Sampling intervals and number of samples per sampling

The number of samples should allow the generation of representative environmental data for the given matrix at the defined sampling site. The choice of the sampling interval should further allow the detection of significant changes in HBCD emissions during the applied observation period. All sampling locations will be sampled once a year for aquatic biota (fish). Suspended particulate matter will be sampled every two years. Bird eggs will be sampled at the beginning of program (year 2008) and in 2 further years (2012 and 2016).

All bird eggs will be analyzed as individual samples. For fish pooled samples consisting of 15 individuals per sampling site will be taken and analyzed. However, for two locations (with different HBCD levels) 15 individual samples will be analyzed individually at one time point to gain information on the variability of the HBCD-levels in the different organisms for each site.

For the suspended particulate matter monitoring pooled samples will be taken and analyzed (homogenates from the four sampling intervals of three months, respectively). However, an analysis of the individual four samples from the three months-intervals from one site will be performed for two sites with different HBCD levels, to identify possible differences between seasons and/or water regime.

The sampling and analysis scheme proposed is shown in table 3. This proposed scheme might be modified and adapted to the actual needs in the course of the project. For example, if it would turn out in the course of the project that some sampling sites should be sampled and analyzed more intensively than others an appropriate modification could be made in agreement with the sponsor. Furthermore, options for increasing the number of sampled sites or the sampling interval may be considered as result of the literature study and discussions with the sponsor.

Table 3: Annual sampling and analysis scheme (for fish one sampling per site and year; for bird eggs sampling in three years; for SPM sampling every other year starting mid 2007).

Years	Locations per year	Samples per location and year
Suspended particulate matter		
2007/2008, 2009/2010, 2011/2012, 2013/2014, 2015/2016	6 (5 in 2007/2008, 2009/2010)	1 pooled SPM sample (mix of 4 quarterly samples; sampling periods Q3 2007 - Q2 2008; Q3 2009 – Q2 2010 and so on)
2008, 2010	1	4 individual SPM samples (2 samples from Q3 and Q4 of previous year, 2 samples from Q1 and Q2 of actual year)
Fish		
2007 - 2016	6 (5 in 2007, 2008)	1 pooled fish sample (mix of 15)
2007, 2008	1	15 individual fishes
Bird eggs		
Sampling in 3 years: 2008, 2012, 2016	2	15 individual bird eggs from each site

6. Sample preparation and sample storage

Sampling will be performed according to the quality standards of the German Environmental Specimen Bank Program following the respective guidelines (SOPs). Dissection of biological samples is performed in a clean bench to prevent contamination. Samples will be cooled immediately after dissection with liquid nitrogen for transport and storage.

6.1 Preparation of pooled samples

For preparation of pooled biota samples the methodology will be used which is also applied for samples within the German environmental specimen program. Fish muscle and egg content samples are homogenized at temperatures below -130°C using a cryo mill. Afterwards, the samples are homogeneous fine powders which are ideal for extraction and analysis.

SPM samples will be freeze-dried with low-temperature cooling during the process. Afterwards, a pooled sample from the samples from each site will be prepared by thorough manual homogenization.

6.2 Storage of sampling material

Remainders of all pooled samples will be stored in the Fraunhofer IME cryo storage at temperatures below -135°C until an interim report with the analytical data from the respective samples has been reviewed by the sponsor.

7. Analytical strategy and methods

7.1 Analytical parameters and methods

Theoretically, hexabromocyclododecane (HBCD) consists of 16 different stereoisomers. 8 of them are known (24). 6 stereoisomers identified as 3 diastereomeric pairs of enantiomers called α-, β- and γ-HBCD have a practical environmental relevance. As their environmental fate and thus their environmental impact is different, they will be analysed separately.

For the analysis of hexabromocyclododecane in environmental samples two main analytical procedures are applied: analysis by GC-MS or by LC-MS-MS. As only the LC-MS-MS procedure is capable to differentiate between α-, β- and γ-HBCD stereoisomers, it will be applied in this program.

Analytical methods for the determination of the total HBCD content and the determination of the α-, β- and γ-HBCD stereoisomers will be adapted and/or developed and validated. The work will be based on the results of the literature review and on experiences of Fraunhofer IME. In brief, the determination of α-, β- and γ-HBCD stereoisomers will be performed by LC-MS-MS using a reversed phase HPLC column. The analytes will be extracted from the samples preferably by ASE (accelerated solvent extraction) after addition of recovery internal standards (^{13}C-labelled α-, β- and γ-HBCD). Clean up of the extract will be performed by GPC to remove lipids followed by column chromatography on Florisil or silica gel. After addition of further internal standards (deuterated α-, β- and γ-HBCD) to count for instrumental performance the solutions will be measured by LC-MS-MS. The instrumental and personnel requirements for LC-MS-MS analyses are met. Standard operating procedures will be developed and applied.

7.2 Validation of analytical methods

The analytical methods developed will be validated for every matrix to approve their suitability. Validation includes the determination of the accuracy (determination of the recovery rates of spiked samples, two spike levels), the precision (repeatability of the recovery on 2 spike levels) and the limits of detection and quantification. In addition, the measuring uncertainty will be estimated.

7.3 Quality assurance

Sampling as well as analyses will be performed according to standard operating procedures. Fraunhofer IME is accredited according to DIN EN ISO/IEC 17025. The accreditation of Fraunhofer IME comprises not only the confirmation of the professional use of standardized analytical methods but includes the expertise for the development and validation of analytical methods. All analytical work will be performed in compliance with the requirements of this accreditation. All sample treatments and analyses will be performed according to accredited standard operating procedures.

8. Responsible Scientists

The project will be coordinated by Dr. Heinz Ruedel who has broad experience with monitoring studies. He is also responsible for the tasks of Fraunhofer IME in the framework of the German environmental specimen program which is contracted by the German Environmental Agency (Umweltbundesamt). For the analytical part Dr. Josef Mueller will be responsible who has a broad experience with analyses of biological and environmental media samples with GC/MS and LC/MS methods.

The sampling at different locations will be performed by the same sub-contractor for all sampling sites. The sampling of fish and bird eggs will be performed by members of the Institute of Biogeography of the University of Trier, Germany (coordination: Prof. Dr. Roland Klein). The Institute of Biography has been involved in the German environmental specimen bank program for over 20 years and is within the program responsible for sampling of all biological specimens.

The sampling of suspended particulate matter (SPM) will be performed by members of the Institute for Hydrogeology and Environmental Geochemistry of the Free University of Berlin, Germany (coordination: Mathias Ricking). This group is involved in the German environmental specimen bank program since 2002 and is contracted to perform the annual routine sampling of SPM in German rivers within the ESB program since 2005.

9. Literature

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