Environmental monitoring of HBCD in Europe

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Hexabromocyclododecane (HBCD) is a brominated flame retardant applied mainly in extruded (XPS) and expanded (EPS) polystyrene foams. These are used as thermal insulation in the building industry. In 2001, the estimated annual HBCD demand in Europe was 9500 tons. During recent years, emissions control programs (VECAP and SECURE) have been implemented by the HBCD industry in order to reduce potential environmental burdens. To assess the impact and relevance of the implemented emission reduction measures, an environmental monitoring project for HBCD was initiated in 2007 by the 'Industry working group for HBCD', a sector group of the European Chemical Industry Council (CEFIC). The project was commissioned to a team of monitoring experts from Fraunhofer IME, Schmallenberg (project coordination, HBCD analyses), University of Trier (biota sampling), and Free University of Berlin (SPM sampling).

By temporal and spatial comparisons of monitoring data over a period of up to ten years, conclusions on how environmental concentrations of HBCD change with time could be elaborated. The study focuses on relevant environmental compartments which are expected to be sinks for HBCD based on its physico-chemical properties and on information on the lifecycle of the products. Samplings cover fish (every year) and suspended particulate matter (SPM; every second year) at four different locations in Europe.
Monitoring data for fish are now available for the period 2007 to 2009. Freshwater fish were collected from the rivers Tees/UK, Western Scheldt/Netherlands, and Rhone/France as well as from Lake Belau/Germany, which represents a pristine site. At all selected sites bream (*Abramis brama*), an accumulation bio-indicator also used for the German Environmental Specimen Bank, was caught. In the brackish Scheldt area, sole (*Solea solea*) was collected in addition. After sampling and dissecting the fish, muscle tissue samples were frozen immediately. Samples of usually 15 fish from one site were grinded and homogenized by cryomilling. HBCD analyses are performed under ISO 17025 accreditation by a validated LC/MS-MS method that allows quantification of the major HBCD diastereomers (alpha-, beta- and gamma-HBCD).

After the first three years, initial data on fish show decreasing concentrations of HBCD at some locations. A decrease of HBCD levels was obvious for Rhone bream (about –60 %: from 1417 µg/kg lipid weight, lw, in 2007 to 531 µg/kg lw HBCD in 2009) and the bream from the Western Scheldt (about –45 %: from 93 µg/kg lw in 2007 to 51 µg/kg lw

in 2009). For the Scheldt, additionally sole was analyzed. Here, too, a decrease of HBCD levels was observed from about 600 µg/kg lw in 2007 to about 180 - 200 µg/kg lw for 2008/2009.
The average HBCD concentrations measured in 2009 for Lake Belau fish were notably lower than in the two previous years (about –98 % from 2008 to 2009; based on lipid weight data). In 2009, the HBCD values detected in the pooled bream from Lake Belau were the lowest of all sites investigated (sum of three HBCD isomers; 11 µg/kg lw). High HBCD levels with extensive variations between the individual years were found in bream from the Tees river sampled downstream a former production site (range: 9480 - 14500 µg/kg lw). This high level is in line with published data for fish originating from regions close to point sources. In fish samples, alpha-HBCD was the dominant isomer, except for Lake Belau bream during the first two years and Scheldt sole, where gamma-HBCD was dominant.

It is important to note that the observed concentration changes of HBCD in fish tissue are only based on data from three years. Before arriving at a more final conclusion whether the apparent trends are statistically significant, data from a larger number of years is required. For such an analysis, the variability of the data will also have to be considered. Thus, the present data only allow preliminary conclusion. However, taken together, there is some evidence that at the investigated sites with diffuse contamination characteristics the environmental burdens of HBCD are decreasing. This may be regarded as a result of the implemented emission control measures. However, at the site which was impacted by a former point source (i.e., Tees) no decreasing concentrations in fish could be observed so far over the indicated observed period.

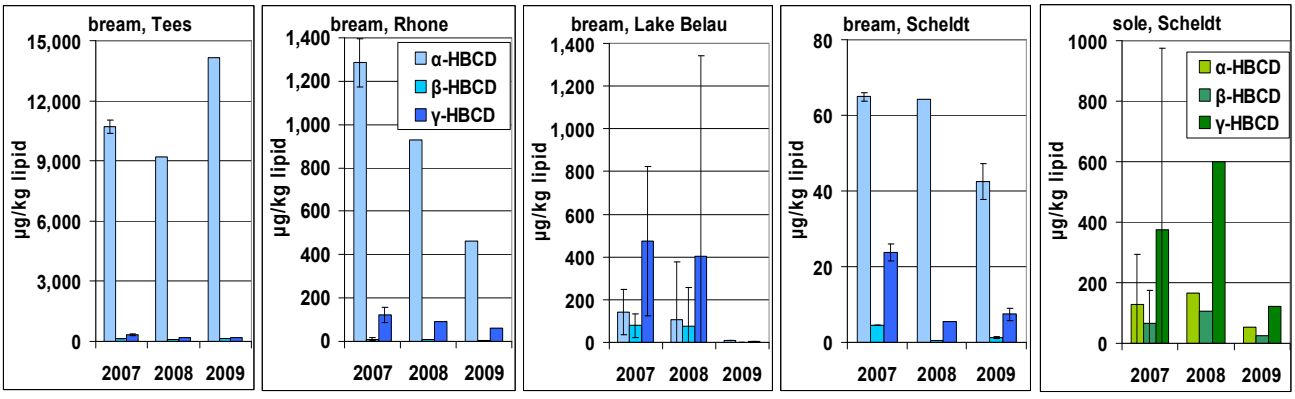

Figure 1: Comparison of monitoring data for alpha-, beta-, and gamma-HBCD for bream and sole muscle tissue (lipid weight data). Standard deviations are from replicate analysis or individual fish analysis (Lake Belau, 2008 and sole, 2007).