

## BROMINATED FLAME RETARDANTS IN SEDIMENTS FROM EUROPEAN ESTUARIES, THE BALTIC SEA AND IN SEWAGE SLUDGE

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### Introduction

Previous studies in Japan have found polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCD), polybrominated biphenyls (PBB) and tetrabromobisphenol A (TBBPA) in sediment samples (1-4). In Sweden, higher levels of Te- and PeBDE as well as TBBPA were found in sediment downstream from a plastics industry than upstream (5,6). Increasingly higher concentrations of TeBDE, PeBDE, DeBDE and HBCD were also found in sediments from a Swedish river as more textile industries were passed. Recently, PBDE were also found in sediments from a number of rivers in the UK (7). In previous analyses of sludge from sewage treatment plants in Sweden, TeBDE, PeBDE (8) and TBBPA (6) were found. In Germany, PBDE were found in sludge from several sewage treatment plants (9). In the following, sediments from the Baltic Sea were analysed for TeBDE and PeBDE within a sediment baseline study initiated by HELCOM (Helsinki Commission). Within a survey organised by the Oslo - Paris Convention for the Prevention of Marine Pollution, the DIFFCHEM study, sediments from the mouths of European rivers were analysed for TeBDE, PeBDE, DeBDE, HxBB and DeBB. Several sludge samples from municipal sewage treatment plants in Stockholm, Sweden, were analysed for TeBDE, PeBDE, DeBDE, HBCD and TBBPA.

### Materials and Methods

Surficial sediments from 20 off-shore locations in the Baltic Sea were collected within the HELCOM sediment baseline study (SBS)(10). In the DIFFCHEM survey, surficial sediments from 22 estuaries in Western Europe were analysed (11). In Figure 1, a map of the sediment sampling locations is shown. Sewage sludge samples from 3 plants in the region of Stockholm, Sweden were also analysed. The extraction method used for all samples is described elsewhere (8). The clean-up procedures used were somewhat different for different samples as different substances were to be analysed. The Baltic Sea sediments and the sewage sludge samples were treated according to (8). Some of the sewage sludge samples were also analysed for TBBPA and treated according to (6). The DIFFCHEM samples were also subject to clean-up using an HPLC amino column for the separation of HxBB from HxBDE, which would otherwise interfere in the GC-MS analysis. The GC-MS/ECNI analysis is described in detail elsewhere (12).

### Results and Discussion

## Sediment

In Figure 2, the sum of BDE47+99 and BDE209 concentrations in sediments are shown (the BDE numbers are used in analogy to the numbering system of PCB). The DIFFCHEM sediments

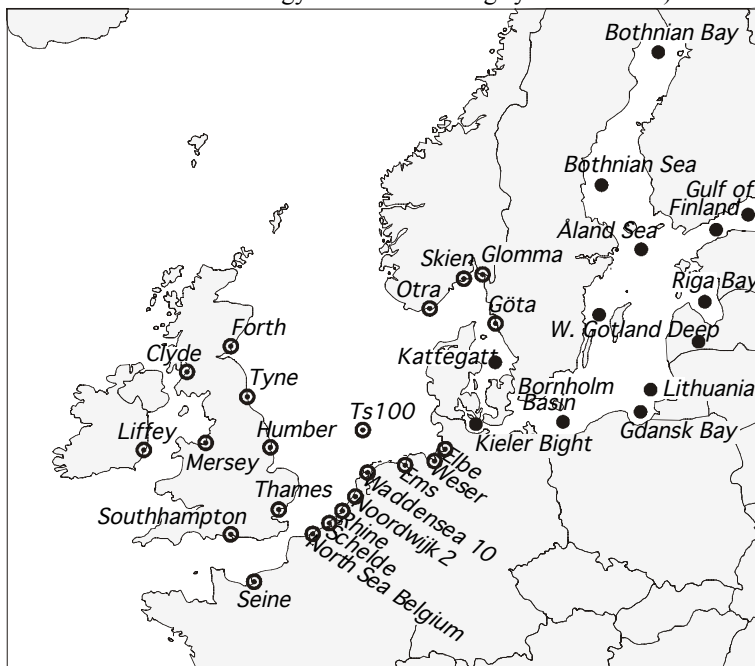


Figure 1. Sampling locations for the sediments.

showed large differences in concentrations. The highest concentration of BDE209 was found in River Mersey, UK (1700 ng/g d.w.), followed by River Schelde, Belgium (200 ng/g d.w.). In Japan, 20 ng/g d.w. of BDE209 was found in one estuary sediment from Osaka in the early 1980s (2), and concentrations between 33-390 ng/g d.w. were found in river sediments (1,2,4). In the Swedish River Viskan, where textile industries are situated, a maximum of 390 ng/g d.w. of BDE209 was found (12). High concentrations of BDE209 do not always accompany high concentrations of BDE47 and BDE99, which indicates different sources. Generally, the southern parts of the investigation area are more polluted by PBDE than the northern ones. The concentrations of BDE47 and BDE99 were below detection limits at the sampling locations Northsea Belgium and the Rivers Elbe (Germany), Götå (Sweden), Glomma, Skien and Otrå (Norway). The BDE47 and BDE99 concentrations (0.38 ng/g d.w., sum of 2 congeners) at the reference location TS100 (100 km north-west of the Oysterground coast, Holland) are about the same as in the Baltic Sea (Fig. 2). In the Swedish River Viskan the sum of BDE47 and BDE99 was between 0.56 and 8.2 ng/g d.w. (12). Downstream from a plastics industry, the sum of the two congeners was 1300 ng/g d.w. (5).

In the Baltic Sea, detectable levels of BDE47 and BDE99 were found at eight locations in the southern part (Baltic Proper) at concentrations between 0.21 and 1.1 ng/g d.w., while in the northern part, (Bothnian Bay), the concentrations were below detection limits. This geographical

pattern was similar to those for PCB and PAH which have also been analysed (10). Concentrations may represent background levels caused by diffuse sources and possibly long range transport.

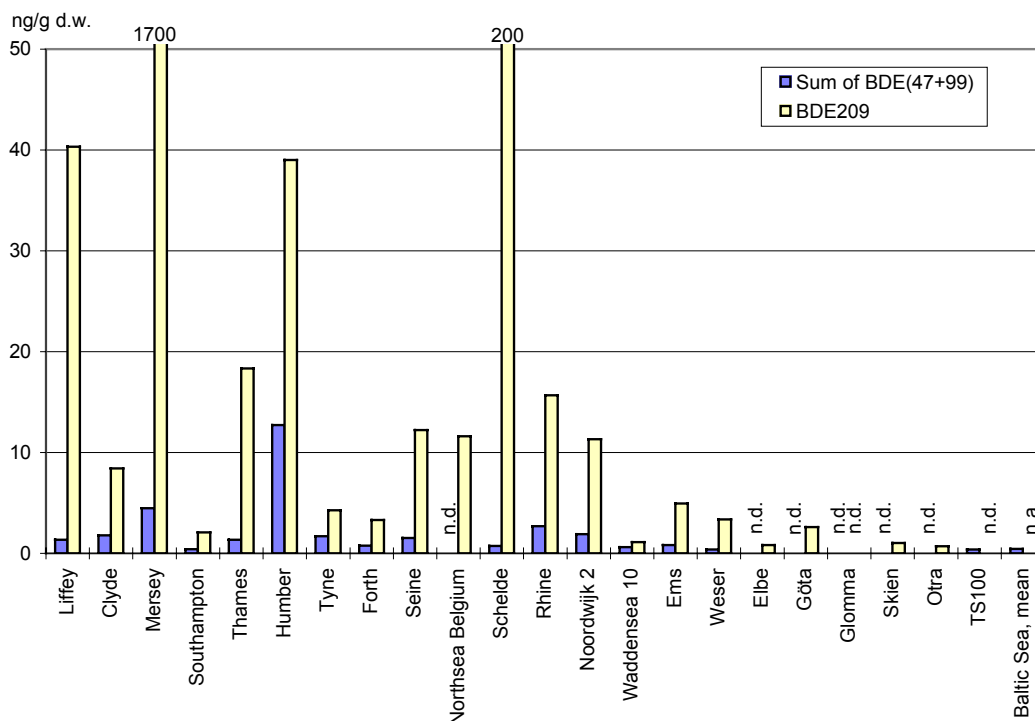


Figure 2. Concentrations of PBDE in sediments from European estuaries and the Baltic Sea.

The DIFFCHEM sediments were also analysed for two PBBs; BB153 and BB209. The concentrations of these were lower than the concentrations of PBDE, and in many cases, below the detection limits of 0.009 ng/g d.w. for BB153 and about 0.1 ng/g d.w. for BB209. The highest concentrations of both congeners were found in the River Seine, 0.050 and 3.4 ng/g d.w. of BB153 and BB209, respectively. This could be due to the production of PBBs in France.

## Sewage Sludge

The concentrations of some brominated flame retardants in sewage sludge from 3 different plants in Stockholm, Sweden, are shown in Figure 3. The concentrations of BDE47, 99 and 209 didn't differ as much between the plants as did TBBPA and HBCD. In Germany, Tr- to HpBDE were found in sewage sludge from different plants (9). The sum of TeBDE and PeBDE was between 0.39-15 ng/g in these samples. In earlier investigations of sewage sludge from Sweden, 18 ng/g d.w. of the sum of BDE47 and BDE99 (8) and 31-56 ng/g d.w. of TBBPA (6) were found. In this investigation, the sum concentrations of BDE47 and BDE99 were about ten times higher.

## Conclusions

Based on previous results, high PBDE, HBCD and TBBPA concentrations indicate releases from

sources using or producing brominated flame retardants. The results from the DIFFCHEM study indicate possible such sources at several European locations. The results from the Baltic Sea are more indicative of diffuse releases. The presence of brominated flame retardants in sewage sludge indicate leakage from households, industries, traffic and/or other diffuse sources.

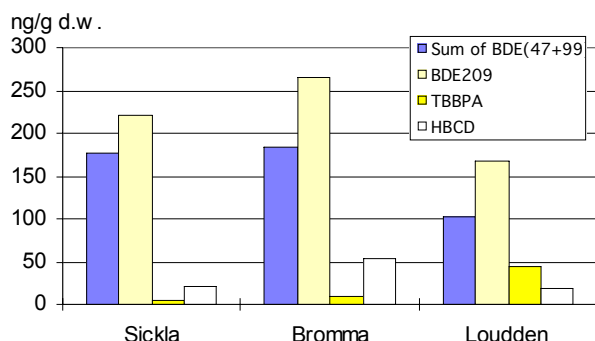


Figure 3. Mean concentrations of PBDE (n=4), TBBPA (n=2) and HBCD (n=4) in sludge from three municipal sewage treatment plants in Stockholm, Sweden.

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