POLYBROMINATED DIPHENYL ETHERS IN SEDIMENTS FROM THE RIVER ELBE, GERMANY

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Introduction

In August 2002, due to continuous heavy rainfall during several days the biggest flood ever seen at the river Elbe and its tributaries happened. Water levels rose several meters. Residential, industrial as well as agricultural areas were flooded and sewage treatment plants flew over. Together with the water huge amounts of solid material possibly also nutrients, fuels, heavy metals, and other contaminants were transported into flooded areas and the rivers. For this reason the working group for the protection of the river Elbe (ARGE Elbe) initiated a special measuring programme including nutrients, heavy metals, pesticides, pharmaceutical, endocrine disrupting chemicals, PCBs, PCDD/PCDFs and PBDEs to assess the impact of the flood on the ecosystem of the river Elbe. We report here the results of an extensive survey conducted on the River Elbe for a total of 14 PBDEs determined in sediment samples using a fully optimised and validated GC-ECNI-MS method.

Materials and Methods

Surficial sediment samples (0-2 cm) were taken at 29 sites, mainly from breakwaters, abandoned channels and harbours, along the course of the River Elbe from Obriství (Czech Republic) to Hamburg using Van Veen grab sampler or sediment scraper. Samples sites were selected in such a way that inputs of PBDEs from tributaries could be detected. All sediment samples were freeze-dried, sieved (<2 mm) and then grinded in a mortar. A modified analytical procedure described previously was employed[1]. In brief, 5 g of freeze-dried sediment were extracted with toluene four times using a ASE-system (Dionex Corporation, Sunnyvale, CA, U.S.A.) operated at 125°C and 14 MPa. The obtained extract was cleaned-up by multi-layer column chromatography (silica gel, alkaline- and acid-impregnated silica gel, silica gel impregnated with silver nitrate) and gel permeation chromatography. Quantification of BDEs 28, 47, 66, 71, 75, 85, 99, 100, 138, 153, 154, 183, 190 and 209 was performed by capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC-ECNI-MS) in the selected ion monitoring mode under the following conditions: GC 6890+ / MSD 5973 (Agilent, Palo Alto, CA, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Switzerland) and PTV injector KAS 4 plus (Gerstel, Mülheim/Ruhr,Germany); capillary column: Rtx-CLPesticides (Restek, Bellefonte, PA, U.S.A.), 30 m x 0.25 mm, film thickness: 0.25 µm; pressure-pulse injection, injection volume: 2µl; carrier gas: helium; CI ion source, reagent gas: methane; ion source temperature: 210°C. BDEs elute from the column under these conditions between 11 and 35 minutes. For congeners with three to seven bromine atoms

the most prominent ions due to bromine at m/z = 79 and m/z = 81 were recorded, while for the decabromodiphenyl ether (BDE209) the highly specific ions at m/z = 484.7 and m/z = 486.7 were monitored. BDE77, 116, 140, 181 (never found in environmental samples), ^{13}C-labelled BDE209 and BB209 were used as internal standards and syringe standard, respectively. All standards were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, U.S.A.) and Wellington Laboratories Inc. (Guelph, Ontario, Canada.), respectively.

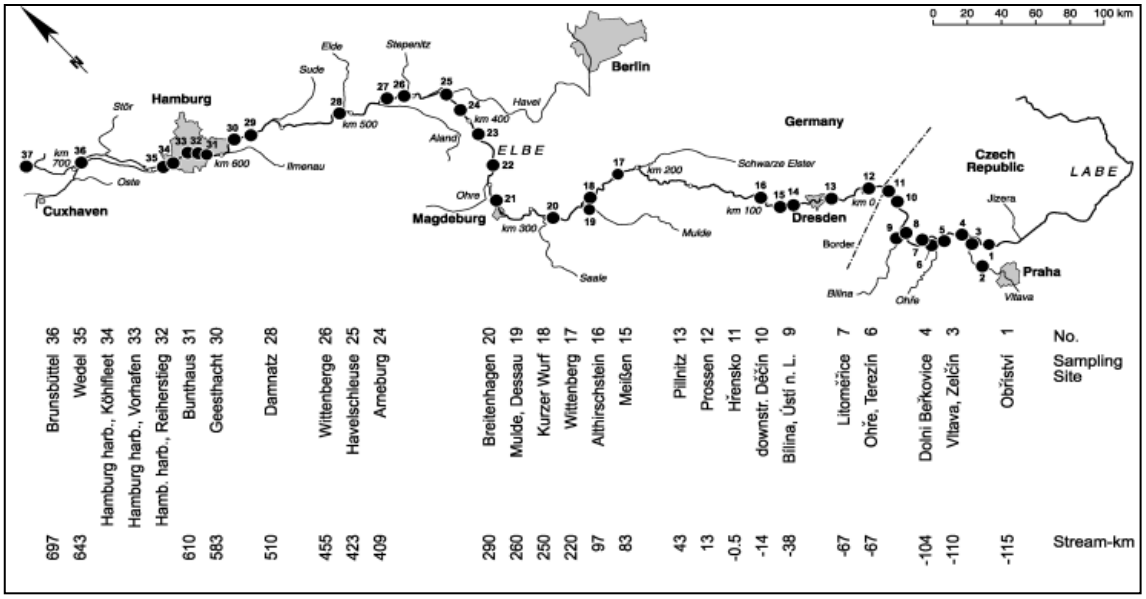

Figure 1 River Elbe and its tributaries with sampling sites at which sediment samples for BDE analysis has been taken.

Results and discussion

BDE patterns in most sediment samples were dominated by decabromodiphenyl ether (DecaBDE, BDE209), which in the German part of the River Elbe contributes on the average 78 ± 6% to the total PBDE content of the sediment samples. In the Czech Republic three samples showed the same congener pattern, whilst in the other samples higher percentages of tetra- to hexabrominated congeners (up to 70%) were seen. This indicates input of technical penta-formulation from local point sources. Besides DecaBDE BDE47, BDE85, BDE99, BDE100, BDE153, BDE154 and BDE183 (indicator of technical octa-formulation) were detected in most samples at low concentrations. BDE209 concentrations were given on dry weight (dw) basis as well as normalised to the organic carbon (OC) content (fig 2 and 3) and ranged from 0.5 to 17.4 µg/kg dw corresponding to 10 to 230 µg/kg OC. Despite of the similar carbon content of most samples (5.5 ± 2%) the observed increase in BDE209 concentrations when expressed in µg/kg dw from the German-Czech border to Hamburg (sampling site 30) was not as pronounced as expected when normalising data to organic carbon content. This indicates that differences seen in

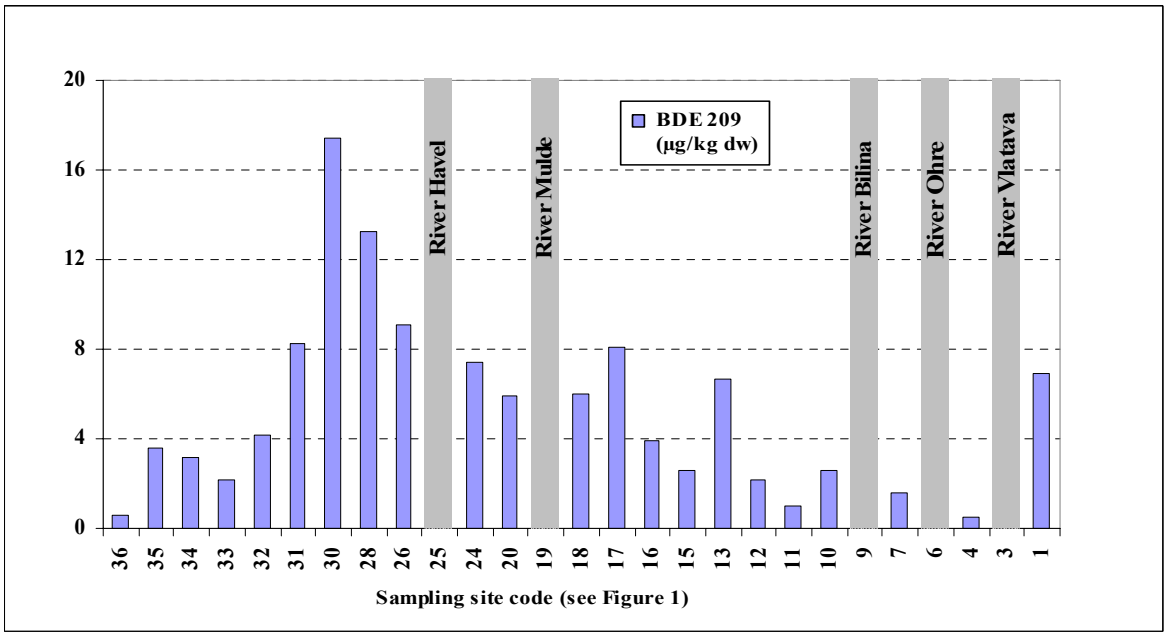

Figure 2 BDE209 concentrations in sediment samples taken along the course of the river Elbe expressed in µg/kg dry weight. Highlighted bars represent sampling sites at the mouth of tributaries.

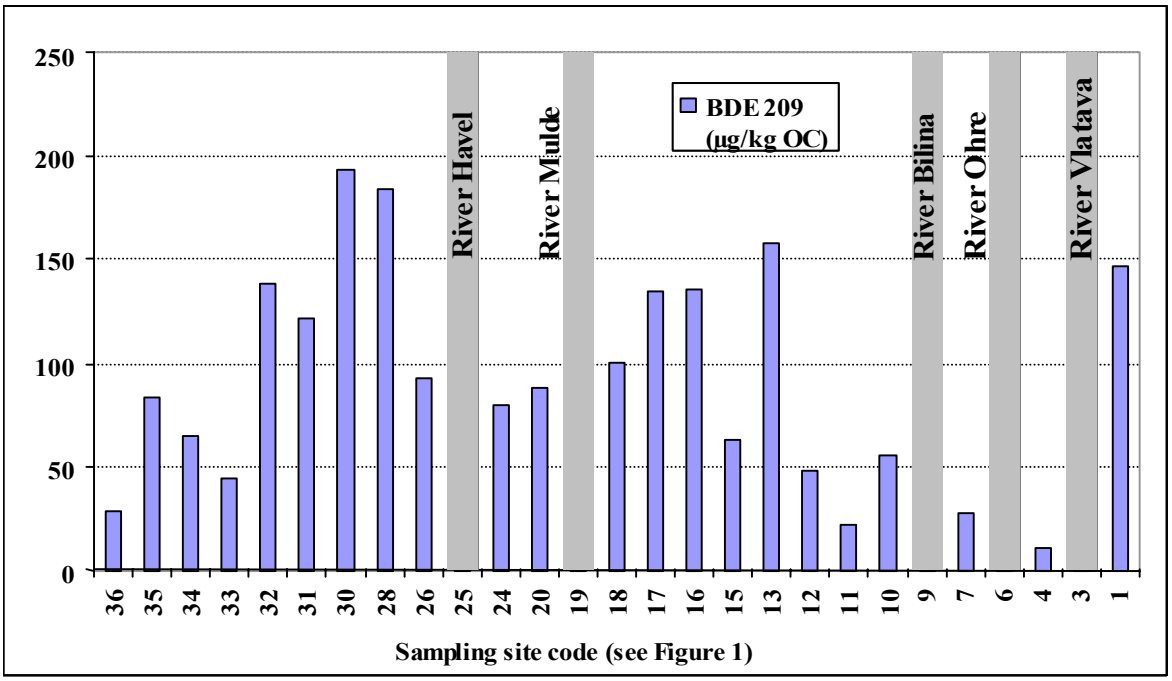

Figure 3 BDE209 concentrations in sediment samples taken along the course of the river Elbe expressed in µg/kg organic carbon. Highlighted bars represent sampling sites at the mouth of tributaries.

dry weight concentrations were partly due to differences in organic carbon content of the sediment samples. In general, concentrations in the German section of the river Elbe were higher than those in Czech Republic and increased up to the sampling sites near Hamburg (site 30). Downstream of this stations a decline of DecaBDE concentrations was seen. Probably, tidal influence causes mixing of contaminated particles from the river Elbe and non-contaminated material from the North Sea resulting in decreasing BDE concentration towards the mouth of the river Elbe. Moreover, in the river section in front of the barrage of Geesthacht (site 30) the flow velocity of the river is low and hence, sedimentation of suspended particles might increase. A study on the occurrence of DecaBDE in sediments from the Hamburg harbour area (11 sampling sites) showed also relative low DecaBDE levels with median concentrations of 4.2 µg/kg dw (Lepom et al., unpublished data). Fig 3 indicates particular input of DecaBDE from the river Mulde (site 19) running through industrialised regions of Saxony and Saxony-Anhalt into the river Elbe. Highest DecaBDE levels in the Czech section of the river Elbe were found in two of its tributaries (sampling site 3 and 6) and at Obristvi two kilometre downstream a chemical enterprise near Prague. Much higher BDE209 levels than seen in this study were reported from the Western Scheldt (up to 510 µg/kg dw)[2], the river Rhine at Lobith near the German-Dutch (84 µg/kg dw)[2] border, river Tees, U.K., (up to 1400 µg/kg dw)[3] and from Dutch (470 to 990 µg/kg OC), Irish and British rivers (up to 104,700 µg/kg OC)[4]. Low DecaBDE concentrations were found in Danish freshwater sediments[5] and sediments from the river Danube[6], which corresponds with the reported results.

Conclusion

This is the first report on PBDE levels in sediments from the river Elbe, Germany and Czech Republic. BDE209 was by far the dominant congener and contributed nearly to 80% of the total PBDE content. This is consistent with other studies on freshwater sediments and reflects high tendency of DecaBDE to adsorb to particles. BDE levels seen in this study were much lower than those reported from western European rivers and indicate low level of contamination in Germany.

Acknowledgements

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