

PBDES IN WATER, SEDIMENTS AND BIOTA OF THE RIVER DANUBE FROM GERMANY TO THE BLACK SEA

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Abstract

PBDEs were analysed in a transect along the Danube River from Germany to the Black Sea. A zone of higher PBDE concentrations in water, sediment and SPM appeared in a stretch of about 1000 km downstream of Budapest, with a tendency of stronger releases from the right-hand side of the catchment along that section. Sediment and SPM were dominated by BDE-209, which dominated also the congener pattern of the PBDE content in the whole water column. The dissolved phase water phase was instead dominated by BDE-47, BDE-99 and BDE-209, and among the BDEs of the cPenta-BDE mixture analysed in mussels, BDE-47 and BDE-99 were the dominant congeners.

Introduction

On August 14, 2007 the International Committee for the Protection of the Danube River (ICPDR) launched the second Joint Danube Survey (JDS 2). Starting from Kehlheim, Germany, three research vessels travelled 2600 km downstream through 10 countries and arrived at the Danube Delta in late September 2007. The objective of this mission was to assess water pollution in relation to the obligations laid down in the Danube River Protection Convention and with view to the EU Water Framework Directive (WFD). During this survey an international research team acquired a comprehensive data set on nutrients, organic and inorganic pollution and biodiversity, for assessing the current status and that shall act as a sound basis for decision making in the adjacent countries.

Among more than 100 sampling sites in the Danube and its tributaries, 23 sites were selected where water, sediment and biota samples were taken simultaneously.

In this paper we present a summary on the data obtained for Polybrominated Diphenylethers (PBDEs), a compound class within the family of Persistent Organic Pollutants (POPs) that deserves particular interest due to rising concentrations both in the environment and human tissue, in contrast to the "classical POPs" subject to the Stockholm Convention that display decreasing trends since many years. A detailed description on the experimental approach and results on the PBDES and other POPs is given by Umlauf et al. (2008).

Materials and Methods

On 23 sites, Sediments were samples from the right- and left-hand side of the River in order to derive a first idea of the geographical origin of contamination. Surface sediment samples (ca. 5-10 cm in depth) were taken with a Kick & Sweep sampler and wet sieved <63µm on board of the Argus. The samples were stored in dark at 4°C and then transported to the laboratory of Umweltbundesamt GmbH Vienna for freeze drying. At part of these sites mussel samples were taken.

SPM samples were collected in the vicinity of the 23 sediment sampling sites with a continuous-flow centrifuge mostly during cruising. Centrifugation, preservation and storage were performed on board of the Argus. The centrifuge was a Z61H from Carl Padberg Zentrifugenbau GmbH, (Germany) operating at a cylinder speed of 17000 rpm. SPM samples were kept in the dark and in between 2°C and 5°C (ISO 5667-15). After shipping to UBA Vienna, the SPM samples were lyophilized and shipped to the JRC. In parallel to the SMP sampling the corresponding dissolved phase water sample (between 10 and 49.5L) was pumped at a rate of 200mL/min with a LIQUIPORT® KNF NF 1.100 FT.18 S PTFE-coated diaphragm pump (KNF FLODOS AG, Switzerland) through 8 mm i.d. Teflon tubing directly from the Danube River over a 293 mm (diameter) glass fibre filter (GFF) and the filtrate was passed online by a modified ASE cartridge containing 50g XAD 2. A detailed description of the sampling approach is given by Olivella (2006).

Mussels *Anadonta anatina*, *Sinodonta waodina*, *Unio pictorum*, and *Unio tumidus* were taken on 24 sites that were only partially identical with the 23 sites selected for the inter-matrix comparison.

The quantification was done with GC/HRMS, using isotope labeled surrogate standards for all analytes presented in this paper.

Solid samples were Soxhlet extracted with hexane/acetone (220:30) after spiking with the surrogates. After the removal of sulfur with elemental Cu, the extracts were subjected to a more intensive clean up (Acidic Silica, Basic Alumina and Active Carbon) using a Power Prep P6 instrument from Fluid Management Systems (FMS) Inc., Watertown, MA, USA. For the analyses in the dissolved phase, extraction of the XAD was done with Accelerated Solvent Extraction (ASE® 300, Dionex Cooperation, USA) directly from the 100 ml cells that had been used for the sampling. First methanol, then n-hexane was used. After adding the internal standards water was added to the combined extracts and the analytes were liquid/liquid-extracted by n-hexane. Dissolved phase PBDEs were analyzed using GC/HRMS without further clean-up.

A detailed description of the analytical methodology is given in Mariani et al. (2008a)

The coding of samples in the following figures follows the official coding of the JDS2 survey. Samples can be located on the map following this link: http://www.icpdr.org/jds/files/JDS2_Overview_Map.pdf

Results and Discussion

Fingerprints

Deca BDE (209) dominated the congener profile in sediment and SPM (Figures 1 and 2), and - to some extent - also the dissolved phase (Figure 5). For this reason, and since the water solubility of BDE 209 is low, the distribution of the total PBDE content in the water column is dominated by the SPM associated share of BDE-209 (Figure 3). In contrast, the dissolved phase was dominated by BDE 47, 99 and 209, and the mussels by BDE 47 and BDE-99.

Downstream concentration profiles of PBDEs

In sediments (Figure 1) the PBDE concentrations are low along a stretch of about 1000km, apart from the station JDS 2 (GER), downstream the confluence of the Rhine-Main-Danube Canal that connects the North Sea and the Black Sea. Then the concentrations are peaking downstream of Budapest in the stretch between km 1560 (JDS 35, HU) and km 1077 (JDS 58, RS). The maximum was found in the sediments of the tributary Drava JDS 42 (HR). The concentration differences between right and left-hand side sediment samples suggest a higher abundance of releases from the right-hand side of the catchment in that stretch, thus indicating an impact from the catchments of the tributaries Drava, Sava and Velika-Morava, all entering River Danube from the right-hand side. It is noteworthy that these rivers displayed a diluting effect for PAHs, PCBs and PCDD/Fs instead (Umlauf et al. 2008; Mariani et al. 2008b). More downstream the concentrations drop again and the comparison of both river sides at JDS 89 suggests impacts now from the left hand side, possibly associated with the confluence of River Arges with the city Bucharest (RO) part of its catchment.

PBDEs in SPM (Figure 2) display a similar spatial profile with a zone of higher concentrations on a dry weight base in between river km 1500 and 1000. The highest concentrations of Σ PBDEs in SPM and water were found at site JDS 45 (HR).

In the water (dissolved phase plus SPM, Figure 3) the spatial concentration pattern shows similarity both with sediments and SPM, with higher concentrations in the middle stretch of the river around sampling station JDS 45 (HR). The major part of the Σ PBDEs is associated with SPM, especially in the zone with higher concentrations. Consequently the SPM associated concentrations in water show a similar picture (Figure 4). In the dissolved phase the maximum concentrations of Σ PBDEs were found more upstream in between JDS 12 and JDS 35, a stretch which includes Vienna and Budapest (Figure 5).

Mussel samples, only available from the middle stretch and some samples close to the Black Sea reflect to some extent (as far as they overlap with the other samples) the decrease of concentration from the middle to the lower stretch (Figure 6). For the outlier on site JDS 52, after the confluence of River Sava, no explanation can be given, since no corresponding samples of water or sediment were available there.

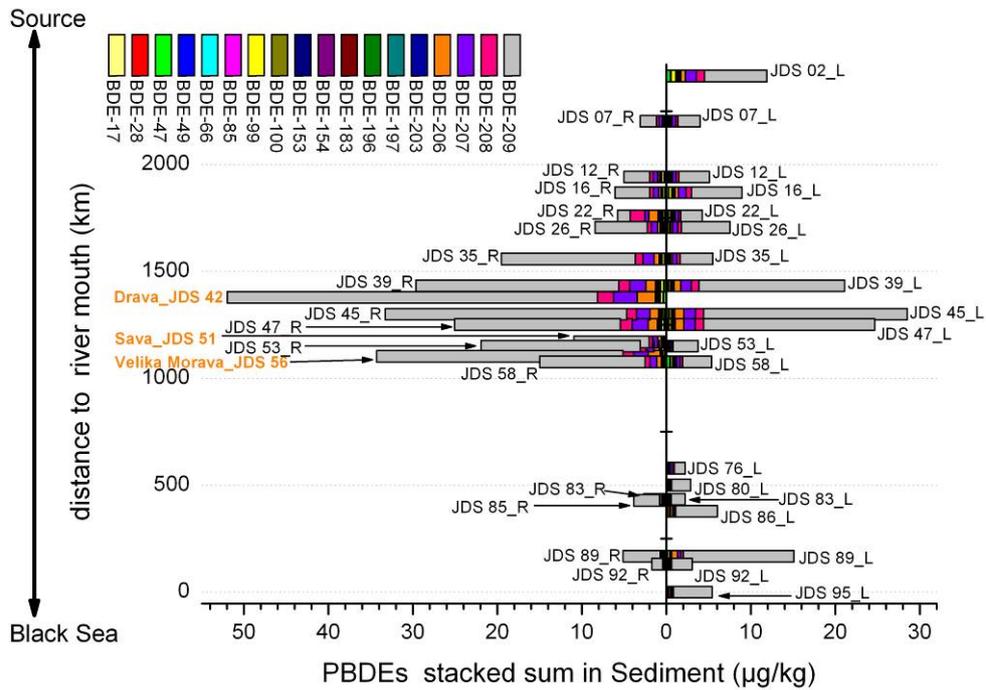


Figure 1: Downstream concentration profile of PBDEs in sediments

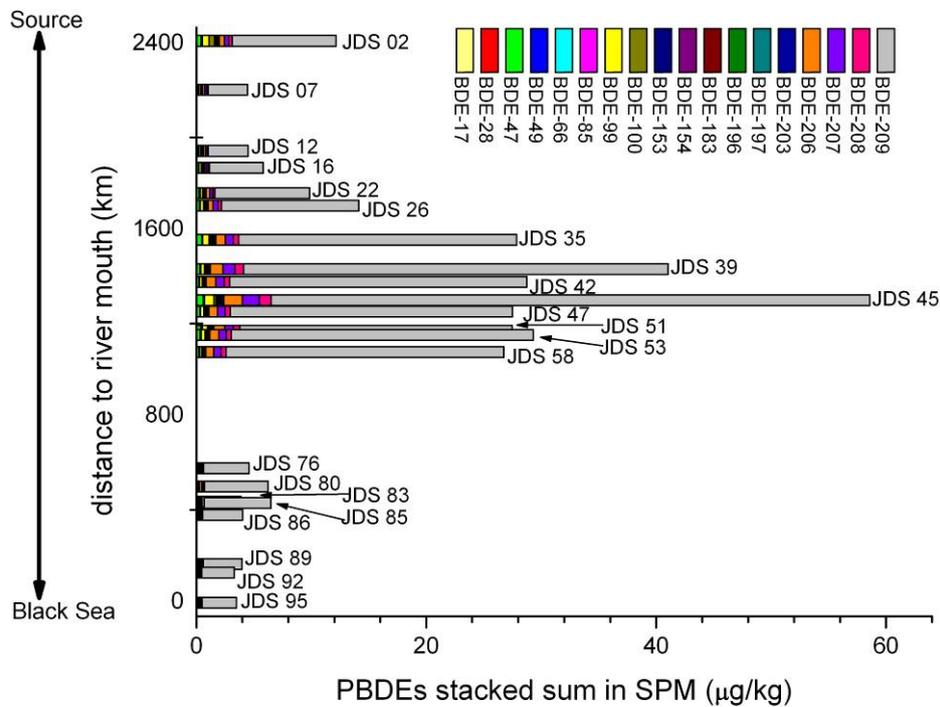


Figure 2: Downstream concentration profile of PBDEs in SPM

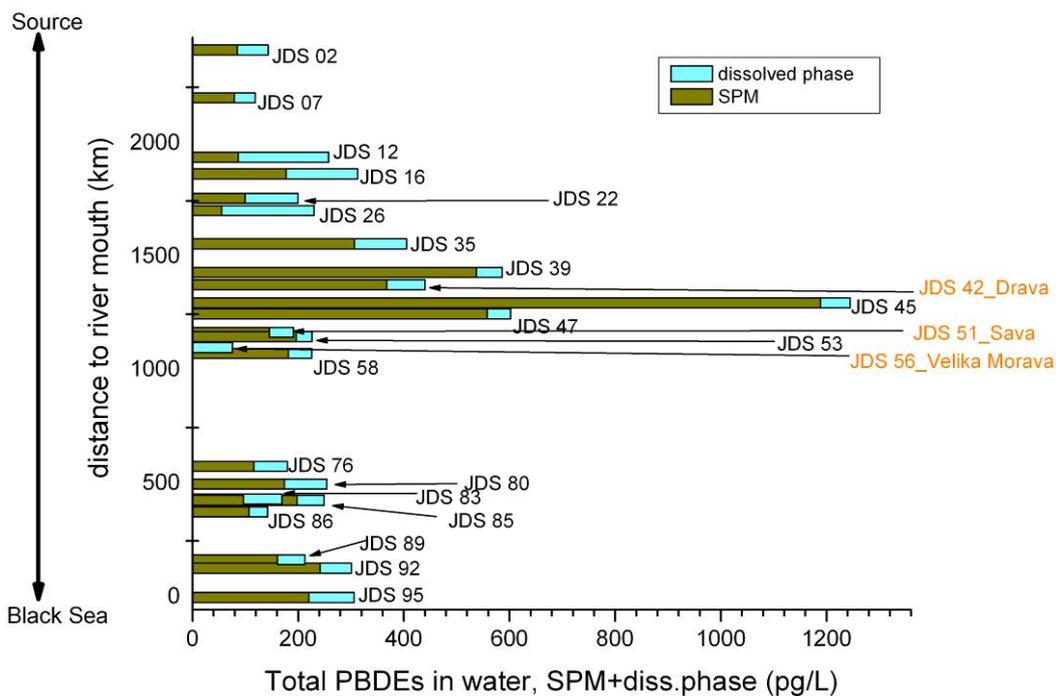


Figure 3: Total PBDEs in water (SPM + dissolved phase)

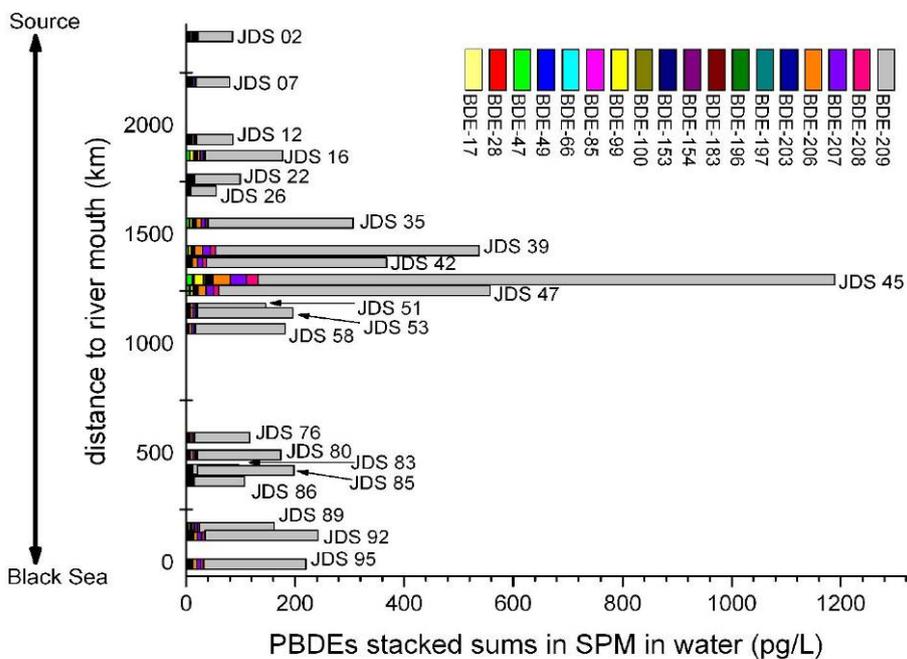


Figure 4: Concentration of SPM-associated PBDEs in water

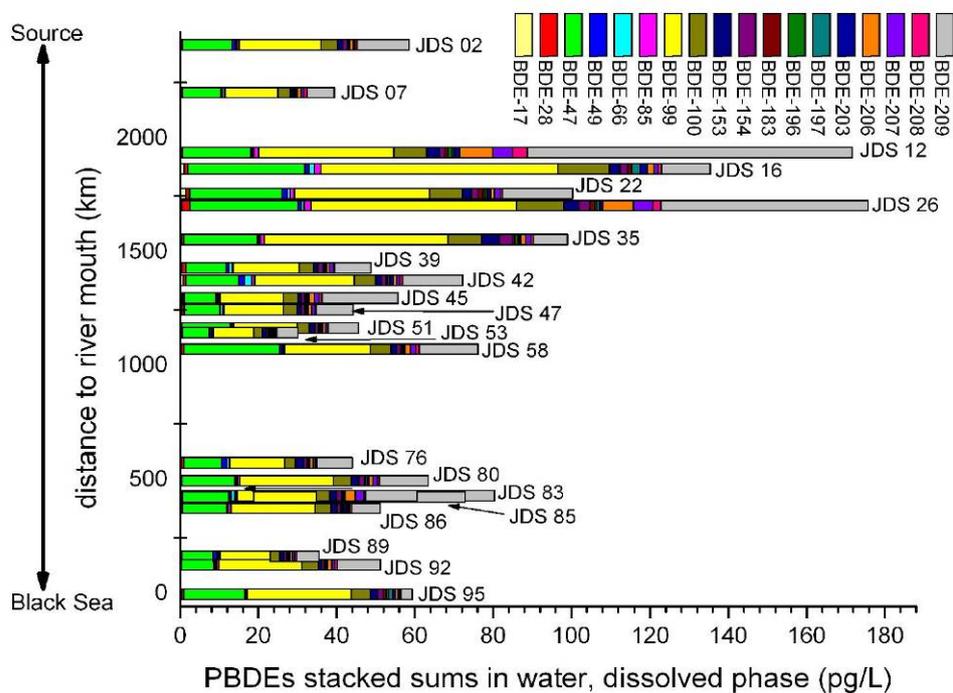


Figure 5: Concentration of dissolved PBDEs in water

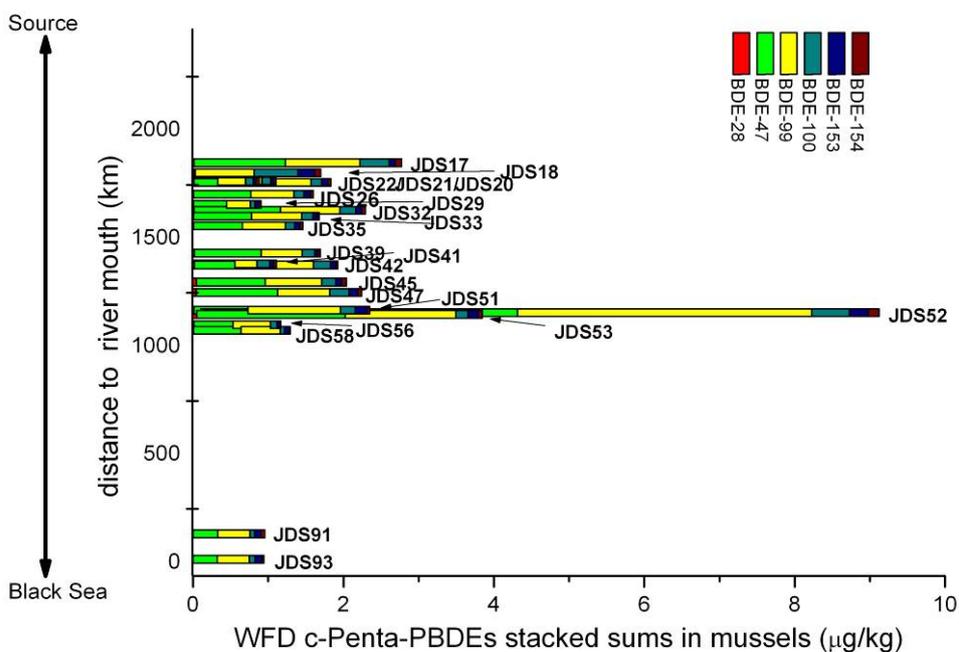


Figure 6: Commercial Penta-BDE (Σ BDE-28, -47, -99, -100, -153, 154) in mussels (all species)

Within the congeners we quantified as part of the c-Penta-BDE mixture the pattern is equally dominated by the congeners BDE-47 and BDE-99, which are the congeners that, together with BDE 209, were the most abundant c-Penta-BDE congeners in the dissolved phase water samples as well.

Conclusion

The zone of comparably high PBDE concentrations in water, sediment and SPM appeared downstream of Budapest in the stretch between km 1560 (JDS 35, HU) and km 1077 (JDS 58, RS).

It is remarkable, that the zone of maximal PBDE concentration is highly agglomerated cross all matrices we analysed. In contrast to PCBs, PAHs and PCDD/Fs analysed in these samples - the PBDEs show a strong spatial coherence in sediments (historic signal) and the water column (current signal). This suggests an overall situation of recent emissions for PBDEs into the river.

Acknowledgements

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