

# SOCS IN THE RIVER DANUBE FROM GERMANY TO THE BLACK SEA: COMPLIANCE CHECKING FOR PRIORITY SUBSTANCES SUBJECT TO THE EUROPEAN WATER FRAMEWORK DIRECTIVE

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## 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) and its Environmental Quality Standards (EQS). 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. For an overview on the JDS2 Survey see ICPDR 2008a.

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 the data obtained for several Polyaromatic Hydrocarbons (PAHs), Organochlorine Pesticides (OCPs) and Polybrominated Diphenylethers (PBDEs) subject to Environmental Quality Standards (EQS) in the EU (Directive 2008/105/EC, OJ L 348/84, 16.12.2008, Annex I), partially also covered by the Stockholm Convention on POPs.

## Materials and Methods

SPM samples were collected in 23 sites with a continuous-flow centrifuge mostly during cruising; Centrifugation, preservation and storage were performed on board. 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 at between 2<sup>0</sup>C and 5<sup>0</sup>C (ISO 5667-15). After shipping to UBA Vienna, the SPM samples were lyophilized and shipped to the JRC. The SPM associated concentration in water as below reported were calculated on the basis of the Total Suspended Matter Concentrations (TSM) that were acquired gravimetrically in parallel.

In parallel to the SMP sampling the 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 through a modified ASE cartridge containing 50g XAD 2 (Olivella, 2006). Extraction was done in the ASE system by one cycle of MeOH followed by 2 cycles of n-hexane, where the surrogate standards were added. The MeOH phase was liquid/liquid extracted with n-hexane, the combined hexane extracts were evaporated and analysed without further clean-up.

The SPM was Soxhlet extracted using hexane/acetone (220:30), for the analyses in the dissolved phase, extraction of the XAD was done with Accelerated Solvent Extraction directly from the 100 ml cells that had been used for sampling. Prior to the extraction isotope labeled internal standards for had been added for the quantification of all analytes reported here except Benzo(k)Fluoranthene, β-HCH and p,p'DDD. The extracts from SPM solid samples were submitted to a clean-up using 2g of deactivated (10 % H<sub>2</sub>O) Alumina-B (Supelco) over a SPE cartridge containing 5g of Florisil (Waters, WAT043370). The samples were eluted with 40 ml of CHCl<sub>2</sub>/n-Hexane (1:2) vol/vol. After evaporation of the extract to 100 µl the syringe standards for PAHs and OCPs were added. The sample was analysed in separate runs for OCPs and PAHs. Quantification of OCPs was done using GC/HRMS, PAHs were analysed by GC/LRMS. After treatment of the raw extract with conc. H<sub>2</sub>SO<sub>4</sub> extract purification of the PBDEs was executed with an

automated clean-up system (Power-Prep P6, Fluid Management Systems (FMS) Inc., Watertown, MA, USA). PBDEs quantification was performed by HRGC-HRMS. A detailed description of the analytical methodology and the spatial distribution of the sampling sites is given by Umlauf et al. 2008.

## Results and Discussion

### *Concentrations in water in relation to the EQS values in the WFD:*

For all priority substances subject to the WFD, EQS in inland surface waters were set for the Annual Average Concentration (AA-EQS), and for some of them also Maximum Allowable Concentration (MAC-EQS). In the figures below all relevant EQS values are given.

### *OCPs and cPenta-BDE:*

The compounds analysed were HCHs ( $\Sigma$   $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\epsilon$ -HCH), HCB, p,p'-DDT, Total DDT ( $\Sigma$  p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT), Cyclodiene pesticides ( $\Sigma$  Aldrin, Dieldrin, Endrin, Isodrin), Endosulfan ( $\Sigma$   $\alpha$ -,  $\beta$ ), Chlordane (cis, trans), and commercial pentabromodiphenylether (cPenta BDE,  $\Sigma$  BDE- 28, 47, 99, 100, 153, 154).

The concentrations of OCPs and cPenta-BDE in water were all below related Annual Average (AA)-EQS, most of them by more than one or two orders of magnitude. Only HCHs reached the order of magnitude of the AA-EQS along the lower stretch of the Danube downstream river km 1000. Average c-Penta BDE concentrations in water (dissolved phase + SPM) were 57 pg/L with a maximum level of 121 pg/L, which is still fairly below the AA-EQS of 500 pg/L

### *PAHs:*

The compounds analysed were Anthracene, Fluoranthene, Benzo(a)Pyrene,  $\Sigma$  Benzo(g,h,i)perylene, Indeno(1,2,3-cd)Pyrene, and  $\Sigma$  Benzo(b)-, Benzo(k)fluoranthene. Naphtalene, which is not subject to this paper has been analysed by Literathy et al. (2008) during the JDS2 survey. All samples were below the LOQ of 0.25  $\mu$ g/L of the ISO 17993 method applied, thus clearly below the AA-EQS of 2.4  $\mu$ g/L.

The concentration of the PAHs were at least one order of magnitude below the AA-EQS except of the  $\Sigma$  Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene, where the limit was exceeded in 5 sites out of 23. However, the maximal concentration was around 1.6 times the AA-EQS during one day in summer 2007. Thus, the annual average concentration might as well be below the EQS. Therefore, and since no MAC-EQS exists for  $\Sigma$  Benzo(g,h,i)perylene and Indeno(1,2,3-cd)Pyrene, it remains unclear whether or not the Danube is within the environmental quality standards for these compounds.

### *Downstream concentration profiles*

The coding of samples in the following figures follows the official coding of the JDS2 survey. The sampling sites can be located on the map following the link given at ICPDR 2008b. At the sites where no bar appears, concentrations were < LOD, "+" means that SPM was not quantified and "\*" means that the dissolved phase was not quantified.

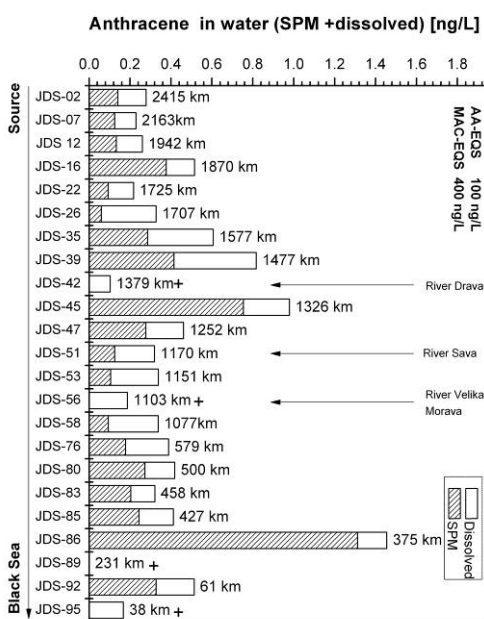
### *PAHs:*

Anthracene displays an equilibrated downstream profile with few sampling sites with higher concentrations, which, however, were not coherent with confluent tributaries except in Romania at river km 375, a site under the influence of River Arges tributaries. Fluoranthene displays slightly higher concentrations in the upper stretch between river km 2500 and 1500.

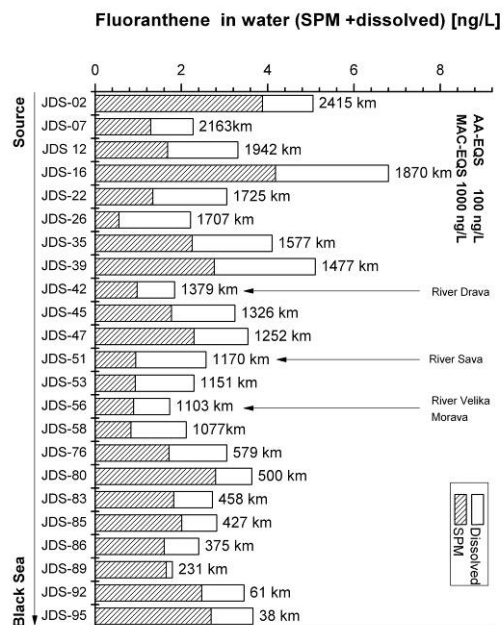
Both PAHs are distributed between SPM and the dissolved phase. Benzo(a)Pyrene, the  $\Sigma$  Benzo(g,h,i)perylene and Indeno(1,2,3-cd)Pyrene and the  $\Sigma$  Benzo(b)- and, Benzo(k)fluoranthene were detected almost entirely in SPM and do not show explicit spatial trends except of some sites of low concentrations in the middle stretch.

### *OCPs and C-Penta-BDE:*

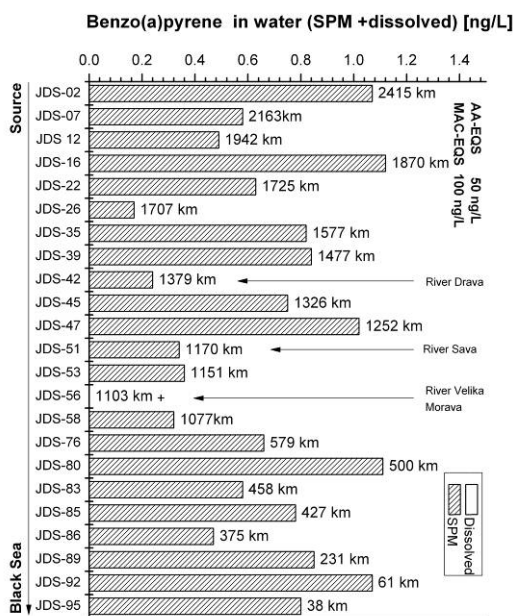
Among the OCPs DDT and metabolites, HCHs, Chlordane and to some extent HCB display a tendency of rising concentrations downstream, with DDT and metabolites, mainly SPM associated, peaking along the last 100 river kms before the Black Sea. In contrast Endosulfan shows decreasing concentrations downstream and almost disappears along the last 200 river kms before the Black Sea. The Cyclodiene group, in most of the sites dominated by Dieldrin, displays no clear spatial trend. C-Penta-BDE, mainly present in the dissolved phase and dominated by the congeners 47 and 99, displays higher concentrations in the upper stretch between river kms 2000 and 1500.



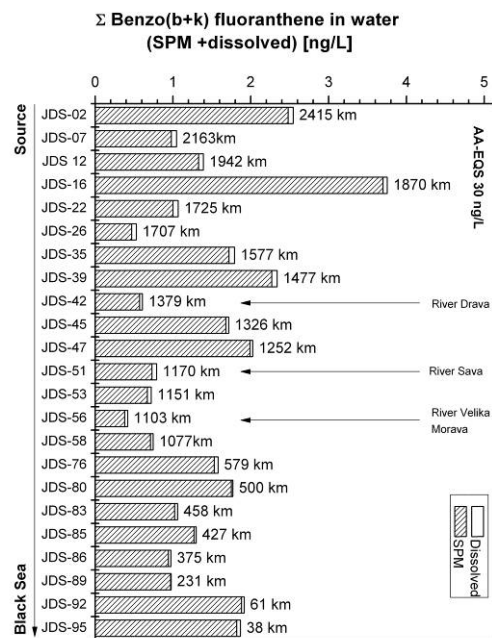
SPM LOD= 0.9 µg/kg or 0.004-0.066 ng/L for different TSM concentrations  
dissolved phase LOD= 0.01 ng/L



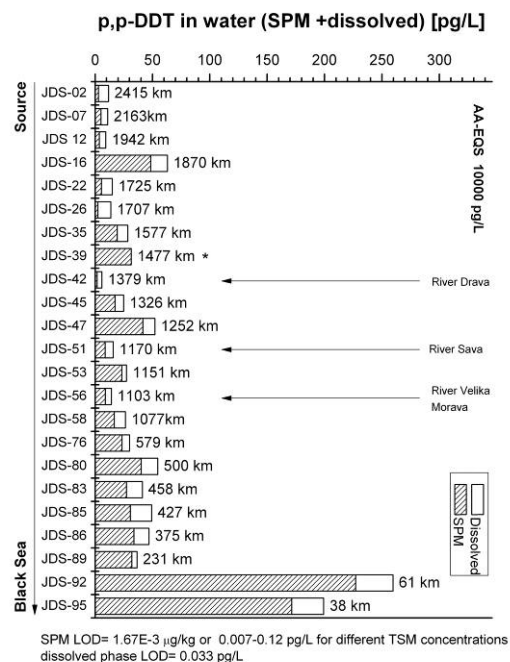
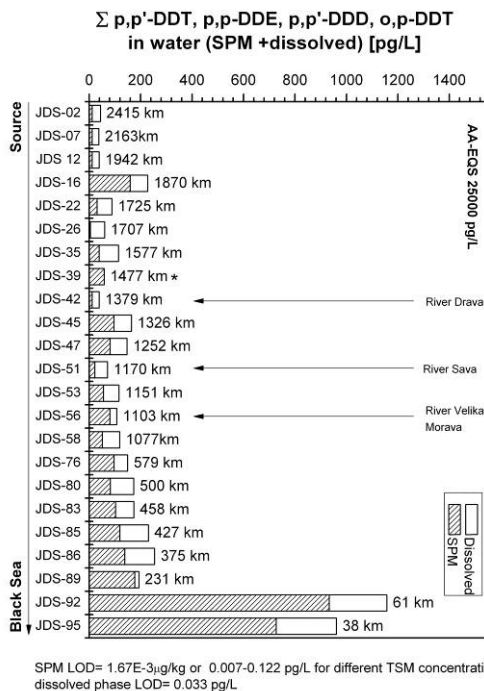
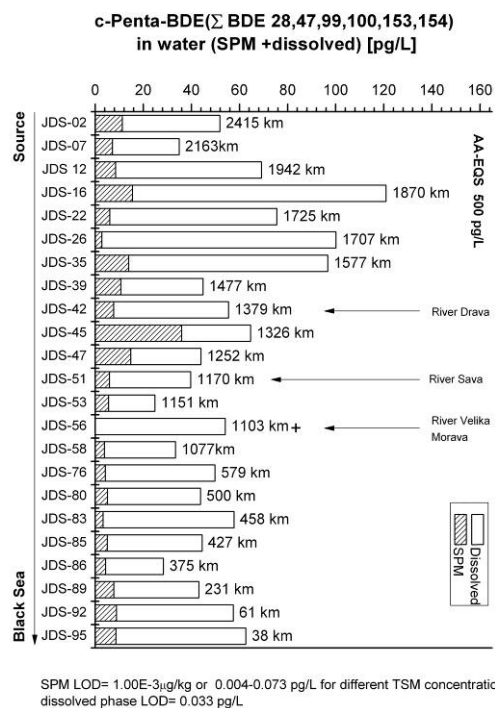
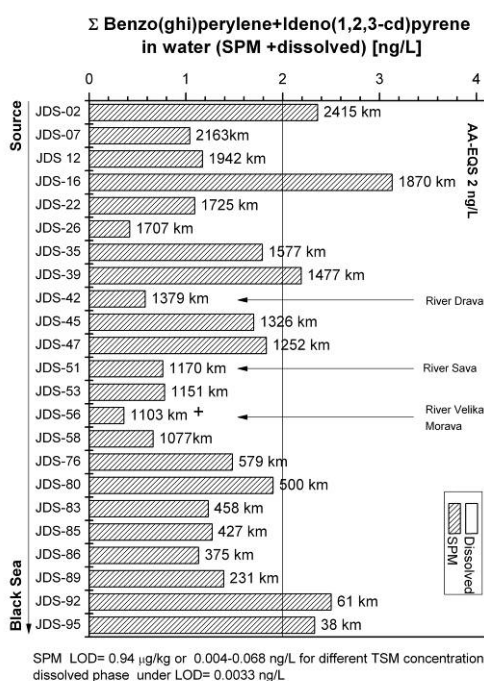
SPM LOD= 1.1 µg/kg or 0.004-0.08 ng/L for different TSM concentrations  
dissolved phase LOD= 0.01 ng/L

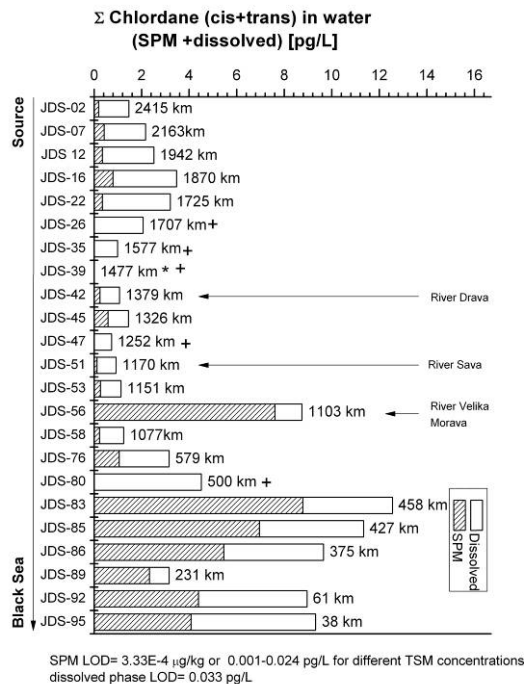
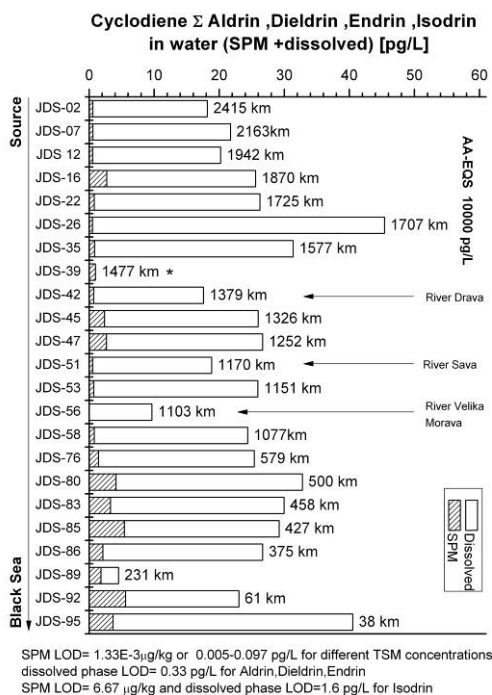
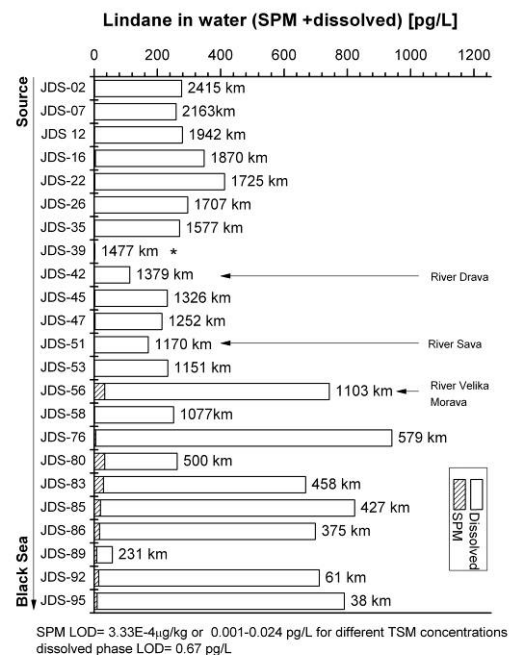
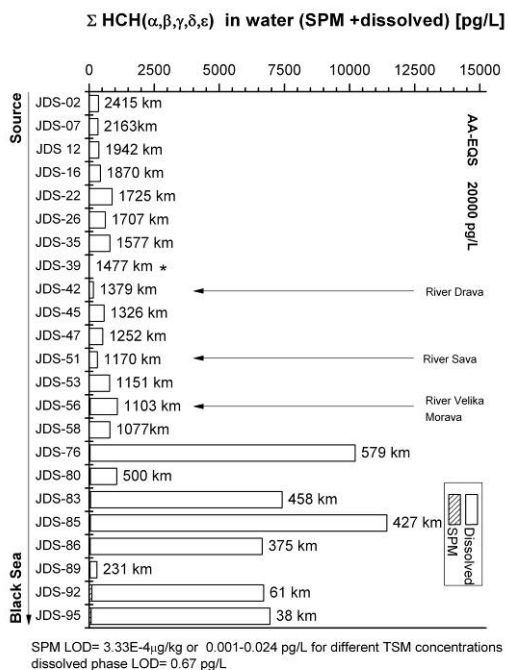


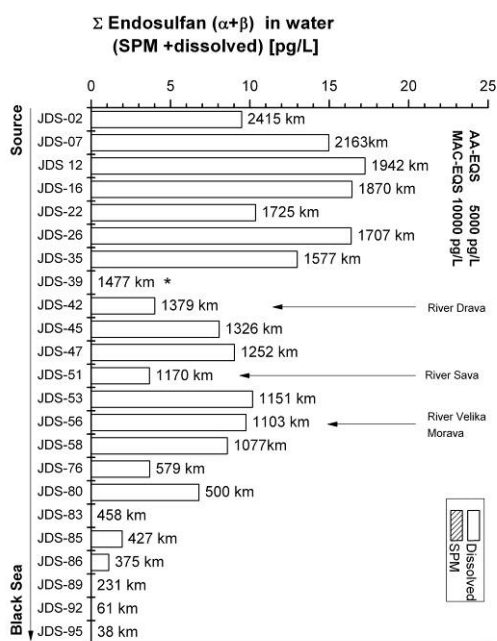
SPM LOD= 9.0E-11 µg/kg or 0.004-0.066 ng/L for different TSM concentrations  
dissolved phase under LOD= 0.0067 ng/L



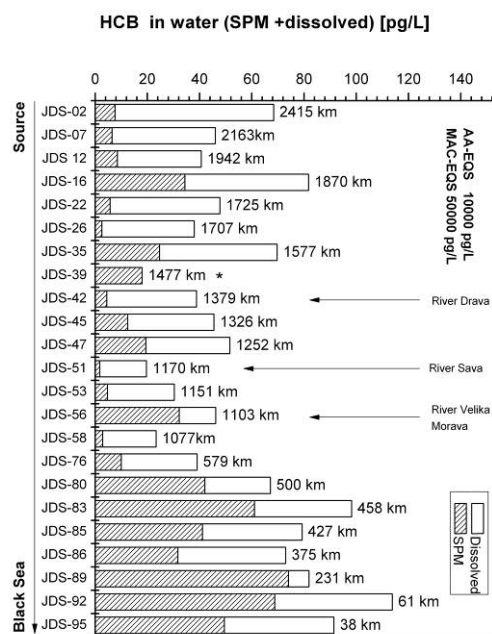
SPM LOD= 1.2 µg/kg or 0.005-0.088 ng/L for different TSM concentrations  
dissolved phase LOD= 0.0033 ng/L







SPM data under LOD= 8.3E-3 µg/kg or 0.03-0.64 pg/L for different TSM concentrations  
dissolved phase LOD= 0.33 pg/L



SPM LOD= 6.67E-3 µg/kg or 0.026-0.49 pg/L for different TSM concentrations  
dissolved phase LOD= 0.33 pg/L

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