Semivolatile Organic Compounds in Water, Suspended Particulate Matter, Sediments and Biota in the Danube

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Abstract During the second joint Danube survey (JDS 2) in autumn 2007, water, sediment, suspended particulate matter and mussel samples were collected from 23 sites covering the River Danube and important tributaries from Germany until the Black Sea. The compound classes investigated were polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs) and polyaromatic hydrocarbons (PAHs).

The results revealed no exceeding of the environmental quality standards (EQS) according to the Directive 2008/105/EC for all investigated compounds except the $\sum$benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, where the concentrations at most sites were close to the EQS of 2 ng/L. In five sites the EQS were slightly exceeded, with a maximum concentration 3.1 ng/L close to Bratislava.

OCP concentrations in water were orders of magnitude below the EQS except for HCH that reached levels up to 25% of the EQS in the lower Danube. Maximum PBDE concentration in water was at 20% of the EQS.

The longitudinal concentration profiles in water and sediment suggest DDT, HCH and to a lower extent chlordane and heptachlor releases into the lower Danube originating from left bank sources and tributaries especially Arges, Siret and Prut. PBDEs showed a maximum in the middle Danube stretch impacted from releases from the right bank tributaries such as Drava, Sava and Velika Morava.

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Concentrations in the investigated compartments were generally at the lower end of the concentration ranges typically found in European freshwaters.

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Abbreviations

AA-EQS	EQS based on the average concentration of the substance concerned calculated over a 1-year period
ASE	Accelerated solvent extraction
B(ghi)P	Benzo(g,h,i)perylene
BDE	Brominated diphenyl ether
cDeca-BDE	Commercial decabromodiphenyl ether
cOcta-BDE	Commercial octabromodiphenyl ether

cPenta-BDE	Commercial pentachlorodiphenylether
CTRTAP	Convention on long-range transboundary air pollution
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DL-PCBs	Dioxin-like PCBs
EC6-PCBs	Sum of PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180
EI mode	Electron ionisation, electron impact
EPA	Environmental protection agency
EQS	Environmental quality standard
GC	Gas chromatography
GFF	Glass fibre filter
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HRMS	High-resolution mass spectrometry
ICPDR	International commission for the protection of the Danube River
I-TEQ	International toxicity equivalent
JDS	Joint Danube survey
JRC	Joint Research Centre of the European Commission
Ko/w	Octanol/water partition coefficient
LRMS	Low-resolution mass spectrometry
MAC-EQS	EQS based on the maximum allowable concentration
Milli-Q	Trademark by Millipore Corporation to describe 'ultrapure' water of 'Type 1', as defined by various authorities (e.g. ISO 3696)
NOEC	No observed effect concentration
OCPs	Organochlorine pesticides
PAHs	Polyaromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and -dibenzofurans
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PTV	Programmed temperature vaporisation
SIM	Single ion monitoring
SOCs	Semivolatile organic compounds
SPM	Suspended particulate matter
UBA	Umweltbundesamt/federal environment agency
WFD	Water Framework Directive
WHO	World health organisation
WHO-TEQ	Toxicity equivalent acc. to WHO
XAD2	Nonpolar resin generally used for adsorption of organic substances from aqueous systems

1   Introduction

The target compounds of the cross-matrix screening programme were polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs), organochlorine pesticides (OCPs) and polyaromatic hydrocarbons (PAHs), all of them semivolatile organic compounds (SOCs) with high octanol/water partition coefficients (Ko/w) and low vapour pressures. As a result of their lipophilicity, persistence and low-volatility SOCs tend to accumulate in the sediments and biota of aquatic environments.

In the aqueous phase, SOCs distribute between dissolved phase and suspended particulate matter (SPM), depending on their Ko/w and the amount and adsorptive properties of the SPM. The transport of the nonpolar SOCs in the river is mainly associated with the hydraulic remobilisation of sediments into the water column and the subsequent transport and re-sedimentation of the SPM.

An important objective of the second joint Danube survey (JDS 2) was to check the compliance with the environmental quality standards (EQS) according to the Directive 2008/105/EC [31].

Beyond the scope of the compliance checking spatially overlapping data from sediment, SPM, water and biota were generated, which would allow an insight into the interactions between the aquatic compartments relevant for storage, remobilisation, transport and bioaccumulation of SOCs.

2   Experimental

2.1   Overview on the Sampling Sites

Samples were collected from 23 sites on the Danube and its key tributaries over a distance of 2,600 km from Germany until the Black Sea. The selection of sites was based on the Transnational Monitoring Network of the International Commission for the Protection of the Danube River (ICPDR) and took into account transboundary aspects and major pollution sources. A geographical overview on the '23 super sites' is given in Fig. 1.

At the end of the upper stretch (km 1,800), the river Danube reaches approximately one third of its final discharge into the Black Sea, with the tributary Inn (km 2,225) contributing about 50% of the discharge volume at km 1,800.

At the end of the middle stretch (Iron Gate at km 933), approx. 90% of the final discharge into the Black Sea appears. The most important tributaries are the Rivers Drava (km 1,379), Tisa (km 1,215), Sava (km 1,170) and to a smaller extent Velika Morava (1,103); they all contribute around 60% to the discharge of the Danube at the Iron Gate.

Fig. 1 Location of the 23 sampling stations for cross-matrix screening of SOCs

In the lower Danube, between the Iron Gate and the Black Sea, only a small increase of the discharge appears, mainly caused by the Rivers Siret (km 154) and Prut (km 135), contributing with about 5% to the discharge into the Black Sea.

More detailed information about the sampling sites can be found in the JDS 2 logbook under http://www.icpdr.org/jds/diary_sites.

2.2 Investigated Compound Classes

2.2.1 Polycyclic Aromatic Hydrocarbons

In aquatic systems PAHs tend to associate with SPM and accumulate in sediments but – compared to other SOC compound classes – only to some extent in biota, since they can be more easily metabolised than the halogenated aromatic SOC classes discussed below. Their transport within rivers is mainly driven by the hydraulic dynamics between with sediments and SPM. 16 EPA priority PAH plus benzo(e)pyrene and benzo(j)fluoranthene were analysed in water, SPM and sediments. The individual PAHs analysed were acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene and pyrene.

2.2.2 Organochlorine Pesticides

In aquatic systems OCPs tend to associate more (DDT) or less (HCH) with SPM and to accumulate in sediments and biota. Their transport within rivers is mainly driven by the hydraulic dynamics between with sediments and SPM. OCPs are toxic (including endocrine disruption) to aquatic organisms and mammals.

The individual OCPs and related metabolites analysed were α-HCH, aldrin, β-HCH, *cis*-chlordane, *cis*-nonachlor, dieldrin, endosulfan-α, endosulfan-β, endosulfan sulphate, endrin, γ-HCH (Lindane), hexachlorobenzene (HCB), heptachlor, heptachlor-*endo*-epoxide, heptachlor-*exo*-epoxide, Mirex, *o,p*-DDD, *o,p*-DDE, *o,p*-DDT, oxychlordane, *p,p'*-DDD, *p,p*-DDE, *p,p*-DDT, *trans*-chlordane, *trans*-nonachlor, δ-HCH, ε-HCH, isodrin and methoxychlor.

2.2.3 Indicator Polychlorinated Biphenyls

In aquatic systems PCBs tend to associate with SPM and accumulate in sediments and biota. Their transport within rivers is mainly driven by the hydraulic dynamics between with sediments and SPM.

Among the 209 isomers present in technical PCB mixtures, 6 Indicator PCBs (EC6-PCBs) have been selected for the characterisation of the presence of PCBs (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180). The sum of their concentration is commonly reported as 'Sum of Indicator PCBs'.

2.2.4 Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans and Dioxin-Like Polychlorinated Biphenyls (DL-PCBs)

In aquatic systems PCDD/Fs and DL-PCBs tend to associate with SPM and accumulate in sediments and biota. Their transport within rivers is mainly driven by the hydraulic dynamics between with sediments and SPM.

Due to the risk for wildlife and humans arising from PCDD/Fs in sediments, quality objectives for PCDDs and PCDFs have been set. Out of eight approaches available [1], the tissue residue-based (TRB) method is the most commonly used. This method defines a safe chemical concentration in sediment, which results in an acceptable tissue concentration in biota. A no observed effect concentration (NOEC) of 200 pg of international toxicity equivalent (I-TEQ)/g dry weight (d.w.) in sediment was derived, but since only few chronic toxicity data were available, a safety factor of 10 was applied, which resulted in the proposal of a 'safe sediment value' of 20 pg I-TEQ/g d.w. [2].

The PCDD/F and DL-PCBs analysed were the 29 2,3,7,8 chlorine-substituted congeners included in the WHO-TEQ scheme.

2.2.5   Polybrominated Diphenyl Ethers

In aquatic systems PBDEs tend to associate with SPM and accumulate in sediments and biota. Their transport within rives occurs to a large extent associated with SPM and is driven by the hydrodynamics between water and sediments.

PBDEs were produced mainly in three commercial formulations, the so-called Deca-, Octa- and Penta-mixtures.

Commercial decabromodiphenyl ether (cDeca-BDE) consists mainly of BDE 207, BDE-208 and BDE-209.

Commercial octabromodiphenyl ether (cOcta-BDE) consists mainly of BDE 183, 196, 197 and 203. cOcta-BDE has recently been proposed to be added to the list of POPs under the UNECE convention on long-range transboundary air pollution (CTRTAP).

The commercial pentachlorodiphenylether (cPenta-BDE) mixture is included in the priority substance list of the WFD. The related AA-EQS for inland waters is 0.5 ng/L for the $\sum$ of BDE 28, 47, 99, 100, 153 and 154. In Europe the use of cPenta-BDE and cOcta-BDE is prohibited since 2003 [3].

The PBDEs analysed in this study were BDE-17 (Tri), BDE-28 (Tri), BDE-47 (Tetra), BDE-49 (Tetra), BDE-66 (Tetra), BDE-85 (Penta), BDE-99 (Penta), BDE-100 (Penta), BDE-153 (Hexa), BDE-154 (Hexa), BDE-183 (Hepta), BDE-196 (Octa), BDE-197 (Octa), BDE-203 (Nona), BDE-206 (Nona), BDE-207 (Nona), BDE-208 (Nona) and BDE-209 (Deca).

2.3   Materials and Methods

The Danube and its tributaries show low contamination levels with SOCs when compared to other European Rivers. During JDS 1 it had appeared that classic standard methods for water analyses based on liquid/liquid extraction of sample volumes of around one litre fail in the quantification of a series of compounds and often do not fit even the requirements for the compliance checking of existing EQS. Moreover the intention of the JDSs is not only compliance checking but also the creation of an overview of the baseline contamination, which, supplemented later on trough subsequent surveys, shall allow to look into time trends also for compounds that do not yet pose a risk. Also for the estimation of the pollutant loads into the Black Sea, sound data are needed, since flux estimates cannot be based on 'less than' concentration values.

In order to increase the sensitivity of quantification and with regard to the EQS set in the WFD, we used large volume sampling techniques both for SPM and the dissolved phase and quantified where necessary with HRMS, thus increasing the sensitivity by approximately an order of magnitude when compared to LRMS.

2.3.1 Sampling

Sediment

Sediments were obtained from 23 sites, among them 14 sites where both sides of the river were sampled. Sediments were sampled by sampling net, taking upper layer (ca. 5–10 cm) of the sediment at the places of the Kick & Sweep sampling for macro-zoobenthos and phyto-benthos. Ca. 10 kg sample was transported to the ship in PP buckets. This was followed by on-board grain size fractioning with wet sieving in order to separate the <63 μm fraction for analyses. The samples were stored in dark at 4°C and sent to the laboratory of Umweltbundesamt GmbH Vienna for freeze-drying.

Water: Dissolved Phase

Dissolved phase water samples were collected in situ on 50 g XAD-2 contained in modified extraction cartridges of the ASE extraction system. The methodology allowed to sample between 10 and 49.5 L of water, depending on the residence time at the sampling sites.

Water was pumped at a rate of 200 mL/min with a LIQUIPORT KNF NF 1.100 FT.18S 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 extracted online by a modified ASE cartridge containing 50 g XAD 2 [4]. In some cases two cartridges were connected in series to check for eventual breakthrough. The GFF was transferred for transport and storage in a 500 mL Schott Duran borosilicate bottle and frozen until further processing, whereas the XAD containing cartridges were put in a fridge and transported back to the laboratory (arrived in blocks approximately one week after sampling at the lab), stored again at 4°C and processed in February 2008 by pressurised liquid extraction using a Dionex accelerated solvent extractor (ASE 300, Dionex Corporation, USA).

Two breakthrough experiments were executed (JDS 22 and JDS 92). For most PAHs breakthrough on the 2nd cartridge was <4% except for fluorene and phenanthrene which ranged up to 11% and 13%, respectively, in site JDS 22. The breakthrough for OCPs varied from a minimum of 2% for HCHs to the maximum of 15% for oxychlordane and from a minimum of 7% for PCB-28 to the maximum of 34% for PCB-189.

Suspended Particulate Matter

Twenty-three SPM samples were collected with a continuous-flow centrifuge mostly during cruising, while contemporarily the dissolved-phase water samples

were collected through the Filter/XAD system described above. Centrifugation, preservation and storage were performed on board of Argus. The centrifuge was a Z61H from Carl Padberg Zentrifugenbau GmbH (Germany), operating at a cylinder speed of 17,000 rpm. Sampling typically took from 30 min to several hours, depending on the concentration of suspended solids in water. Preservation was attained through keeping the samples in the dark and refrigerated (or on ice during transportation) at between −20 and −50°C (ISO 5667-15). After shipping to UBA Vienna, the SPM samples were lyophilised and shipped to the JRC.

Mussel

Mussel samples were *Anodonta anatina*, *Sinanodonta woodiana*, *Unio pictorum* and *Unio tumidus* taken on 24 sites that were only partially identical with the 23 sites selected for the inter-matrix comparison. The samples were kept in the dark and refrigerated (or on ice during transportation) at between −20 and −50°C (ISO 5667-15). After shipping to UBA Vienna, the mussel samples were lyophilised and shipped to the JRC.

2.3.2 Analytical Methodology

A sample preparation method for determination of PCDD/Fs, EC-6 PCBs and DL-PCBs was adopted to include PBDEs in the analysis [5–7]. The analysis of all compounds was done using isotope dilution and GC/MS techniques, starting from one extract, where isotope-labelled standards were added for each analyte prior to extraction.

Ten percent of the extract was separated to analyse PAHs and OCPs (except for the dissolved phase where PCBs, PBDEs and PAH were analysed in the raw extract before splitting the sample). In the remaining 90% of the extract, PCDD/F, PCBs and PBDEs were analysed.

Materials

68-CVS and 68-LCS were native and 13C-labelled internal standards for 12 congeners' DL-PCBs (Wellington Laboratories Guelph, Ontario, Canada). EC-4058 was native for Indicator PCBs (CIL, Andover, Massachusetts, USA). 13C-labelled PCB-111 and PCB-170 were used as recovery standards (Wellington Laboratories Guelph, Ontario, Canada). EPA-1613CVS, EPA1613LCS and EPA-1613ISS were native, 13C-labelled internal and recovery standards, respectively, for 17 PCDD/Fs. The standards were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Ten 13C-labelled PBDE congeners were used as internal standards (in accordance with IUPAC nomenclature: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207 and BDE-209), nine were

present in MBDE-MXE-STK solution (in accordance with IUPAC nomenclature: BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207 and BDE-209) and one BDE-100 was added from the solution MBDE-100. 13C-labelled BDE-126 and BDE-206 were used as recovery standards. BDE-MXE was native solution. All PBDE standards were obtained from Wellington Laboratories (Guelph, Ontario, Canada).

Ten deuterated PAH isomers, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, benzo(b)fluoranthene, dibenz(a,h)anthracene, fluoranthene, fluorene and indeno(1,2,3-c,d)pyrene, were used as internal standards; deuterated acenaphthene, benzo(e)pyrene, benzo(k)fluoranthene and pyrene were used as recovery standards. All PAH standards were obtained from Dr. Ehrenstorfer GmbH, Augsburg, GER.

OCP internal standards were 13C labelled except for d8 *p,p*-DDD. Isotope-labelled aldrin, α-HCH, γ-HCH, *cis*-nonachlor, dieldrin, α-endosulfan, β-endosulfan, endrin, heptachlor, heptachlor-*endo*-epoxide (*trans*, isomer A), HCB, Mirex, *o,p*-DDD, *o,p*-DDT, Oxy-chlordane (gamma), *p,p'*-DDE, *p,p'*-DDT, *trans*-chlordane (gamma) and *trans*-nonachlor were used as internal standards.

13C-labelled β-HCH, *o,p*-DDE and *p,p'*-DDD were used as recovery standards. All OCP standards were obtained from Cambridge Isotope Laboratories.

All organic solvents used were Dioxin analysis grade (Sigma-Aldrich, Buchs SG, Switzerland). Sulphuric acid was 98% extra pure (VWR International s.r.l., Milan, Italy). Clean-up of PCDD/Fs, PCBs and PBDEs was conducted on ready to use multilayer (acidic silica, basic alumina and carbon) columns (Fluid Management Systems (FMS) Inc., Watertown, MA, USA).

Treatment of Solid Samples

The freeze-dried solid samples were extracted with a mixture of *n*-hexane/acetone (220/30) by Soxhlet for 48 h after spiking with isotope-labelled surrogate standards. For bottom sediments and SPM, copper powder was added to the solvent during the extraction to remove sulphur. For the further analysis of SPM, sediments and biota, 10% of the Soxhlet extract was separated to execute the combined clean-up of PAHs and OCPs. The remaining 90% of the extract was subjected to an automated clean-up for the purification and separation of the fractions containing PCDD/Fs, PCBs and PBDEs.

PCDD/Fs, PCBs and PBDEs

After treatment of the raw extract with conc. H_2SO_4 extract purification was executed with an automated clean-up system (Power-Prep P6, Fluid Management Systems (FMS) Inc., Watertown, MA, USA). This system was previously described [8] and uses a multilayer silica column (acid/neutral), basic alumina and carbon column combination. Two fractions were collected: one containing mono-*ortho* PCBs, Indicator PCBs and PBDEs and one for non-*ortho* PCBs and PCDD/Fs.

OCPs and PAHs

The n-hexane extracts from solid samples were submitted to a clean-up using 2 g of deactivated (10% H_2O) Alumina-B (Supelco) over a SPE cartridge containing 5 g of Florisil (Waters, WAT043370). The samples were eluted with 40 mL of CH_2Cl_2/ *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.

Treatment of Dissolved-Phase Water Samples

Dissolved-phase water samples were collected on 50 g XAD-2 contained in modified extraction cartridges of the ASE extraction system [4]. The cartridges were extracted using the Dionex ASE 300 applying in a first extraction methanol (3 cycles each with a static time of 5 min at 75°C, heat-up time of 5 min, a flush volume of 100%, a purging time of 60 s and a pressure of 1,500 psi) and in a second extraction *n*-hexane (same parameters as for methanol), respectively.

Surrogate standards were added to the hexane phase of the ASE after extraction. The methanol and hexane phases were combined in a separator funnel, and ca. 60–80 mL (1/3 of the volume of the methanol phase) Milli-Q water was added for improved phase separation.

After phase separation the methanol phase was collected in the ASE bottles and the hexane phase transferred into vials for concentration.

The methanol phase was extracted three times with 20 mL *n*-hexane and the hexane phases combined with the first extract from the ASE.

The combined extract was evaporated to 0.5 mL under purified N_2 using a TURBOVAP workstation (Zymak) and transferred into a 2 mL conic vial.

Labelled syringe standard (internal standard recovery check) was added before the final evaporation to 50 μL under a gentle stream of purified N_2.

PCBs, PBDEs and PAHs were analysed in the raw extract before splitting the sample. Subsequently 10% of the raw extract was separated for clean-up for OCPs (as described above for solid matrices). Extract purification of the remaining 90% was executed with an automated clean-up system (Power-Prep P6, Fluid Management Systems (FMS) Inc., Watertown, MA, USA) described above to obtain the fraction containing PCDD/Fs and coplanar PCBs.

Instrumental Analyses

All instrumental analyses of PCDD/Fs, PCBs and PBDEs were based on isotope dilution using HRGC-HRMS (high-resolution gas chromatography-high-resolution mass spectrometry) for quantification on the basis of EPA 1613 [32], EPA 1668 [33] and EPA 1614 [34] methods. OCPs were analysed using isotope dilution with HRGC-HRMS for quantification on the basis of an in-house method applying the QA/QC criteria laid down in the methods above for PCDD/Fs, PCBs and PBDEs.

Non-*ortho* PCBs, PCDD/Fs, PBDEs and OCPs were analysed on double HRGC (Thermo Trace GC Ultra, Thermo Electron, Bremen, Germany) and were coupled with a DFS high-resolution mass spectrometer (HRMS) (Thermo Electron, Bremen, Germany) operating in the EI mode at 45 eV with a resolution of >10,000. For non-*ortho* PCBs, PCDD/Fs, the two most abundant ions of the isotopic molecular cluster were recorded for both native and labelled congeners.

For tri- to octa-brominated congeners, two ions of the isotopic molecular cluster were recorded; for nona- and deca-brominated congeners, two isotopic ions of the cluster $M \pm 2Br$ were recorded for both native and labelled congeners. The quantified isomers were identified through comparison of retention times of the corresponding standard and the isotopic ratio of the two ions recorded.

Non-*ortho* PCBs, PCDD/Fs and OCPs were separated on a BP-DXN 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 μm films (SGE, Victoria, Australia). The following gas-chromatographic conditions were applied for non-*ortho* PCBs, PCDD/Fs: split/splitless injector at 280°C, constant flow at 1.0 mL min^{-1} of He, GC-MS interface at 300°C and a GC programme rate starting at 160°C with a 1 min hold, then 2.5°C min^{-1} to 300°C and a final hold at 300°C for 8 min.

Gas chromatographic conditions for OCPs were split/splitless injector at 250°C, constant flow at 1.0 mL min^{-1} of He, GC-MS interface at 270°C and a GC programme rate: 100°C with a 1 min hold, then 10°C min^{-1} to 300°C and a final hold at 300°C for 9 min.

PBDEs were analysed on a Sol-gel-1 ms, 15 m with 0.25 mm i.d. and 0.1 μm film GC column (SGE, Victoria, Australia). The following gas-chromatographic conditions were applied: PTV injector with temperature programme from 110 to 300°C at 14.5°C s^{-1}, constant flow at 1.0 mL min^{-1} of He, GC-MS interface at 300°C and a GC programme rate (110°C with a 1 min hold, then 20°C min^{-1} to 300°C and a final hold at 300°C for 6 min). The selection of the chromatographic conditions was optimised following the literature indications [5,9–11].

Mono-*ortho* PCBs and Indicator PCBs were analysed on a GC (HP-6890, Hewlett Packard, Waldbronn, Germany) coupled with a VG Autospec Ultima high-resolution mass spectrometer (Micromass, Manchester, UK) operating in EI mode at 34 eV with a resolution of >10,000.

Mono-*ortho* PCBs were separated on a HT-8 capillary column, 60 m long with 0.25 mm i.d. and 0.25 μm film (SGE, Victoria, Australia).

Gas chromatographic conditions for mono-*ortho* PCBs were split/splitless injector at 280°C, constant flow at 1.5 mL min^{-1} of He, GC-MS interface at 280°C and a

GC programme rate starting from 120°C with 20°C min^{-1} to 180°C, 2°C min^{-1} to 260°C and 5°C min^{-1} to 300°C isotherm for 4 min.

PAHs were analysed by GC/LRMS consisting of a GC (6,890 N Agilent Technologies) coupled to a low-resolution mass selective detector (5,973 Agilent Technologies), an autosampler and a PTV injector (CIS 4 Gerstel). The GC-MS was operated in single ion mode (SIM), and quantification was performed by using ten deuterated internal standards and four syringe standards. The GC separation was performed on a J&W DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm).

Gas chromatographic conditions for PAHs were split/splitless PTV injection (temperature ramp 80–300°C at 12°C s^{-1}, constant flow at 1 mL min^{-1} of He, GC-MS interface at 300°C and a GC programme rate: starting from 100°C for 1 min isotherm with 7°C min^{-1} to 280°C for 12 min isotherm, with 12°C min^{-1} to 310°C for 28 min isotherm.

QA/QC

The quantified isomers were identified through retention time comparison of the corresponding standard, and the isotopic ratios between two ions were recorded for all halogenated compounds analysed.

Reference materials were analysed in parallel with sediments and SPM samples for PCDD/Fs, DL-PCBs and PBDEs. The concentrations detected were in accordance with the reference values.

Levels of analytical blanks obtained during the clean-up process were at least 5–10 times lower of the reported concentrations for all compounds studied. The blank level was not subtracted. The reported detection limits were calculated on the basis of a signal to noise ratio of 3/1.

Several duplicate samples were performed in order to keep under control the QA/QC and the method reproducibility for the compounds where reference materials were not available. During the analysis of OCPs, a p,p'-DDT standard was injected every tenth sample in order to check for DDT degradation inside the injector system. If degradation occurred the liner was replaced and the GC column cut or replaced.

3   Results and Discussion

In the following an overview on the average abundance of the pollutants in sediments, SPM, dissolved phase and mussels will be given and EQS values will be discussed as far as applicable. In addition Danube downstream concentration profiles will be discussed. PCDD/Fs and DL-PCBs are reported as 2,3,7,8 TCDD toxicity equivalents applying the WHO 1998-TEFs [12].

Sediment can be considered as long- to mid-term memory of pollutant discharges into the Danube River. Changes in pollutant loads in sediments occur in

the range of decades. Therefore the concentrations in the sediments from different sampling stations can be compared even though not collected contemporarily.

By looking at the concentration changes in sediments downstream the Danube, it is possible to locate sources or the influence from incoming 'clean tributaries'. The occurrence of a source is furthermore indicated through differences in concentrations between left- and right-hand sediment samples, since inlets from one side of the river need many kilometres to mix homogeneously along the medial profile of the river.

The downstream concentration profile in SPM and water is more a snapshot and depends very much on the momentary hydraulic conditions (sedimentation/ remobilisation) in the watershed, as a significant fraction of SOCs is transported associated with SPM. Due to the 'short memory' of the water column, the samples taken during JDS 2 cannot be regarded as taken contemporarily. Therefore, the water data are less suitable for the indication of spatial patterns of contamination and should not be over-interpreted with that respect. To localise current sources of contamination, annual concentration averages of the water column obtained with a considerably dense temporal resolution would be needed.

Mussels were analysed only for PCBs and PCDD/Fs and cPenta-BDE.

All concentration data reported for solids are given on a dry weight basis.

The results presented for all SPM-associated concentrations in the water column were calculated from the concentrations measured by the JRC in the SPM samples generated with a centrifuge along the transects and the suspended solid concentrations in water measured gravimetrically by the 'Institute for Limnology' in Mondsee, Austria, from filtration samples taken contemporaneously during JDS 2.

3.1 Compliance with EQS Set by the Directive 2008/105/EC

For all priority substances, EQS in inland surface waters were set as the annual average concentration (AA-EQS) and for some of them also as maximum allowable concentration (MAC-EQS). In Table 1 the results obtained during JDS 2 are compared with the corresponding EQS.

3.1.1 OCPs and cPenta-BDE

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 1,000. Average cPenta-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.

Table 1 Overview on concentrations in the water subject to WFD EQS

$n = 23$	Av (ng/L)	Med (ng/L)	Range (ng/L)	AA-EQS (ng/L)	MAC-EQS (ng/L)
Anthracene	0.47	0.39	0.13–1.5	100	400
Fluoranthene	3.1	2.9	1.8–6.8	100	1,000
Benzo(a)pyrene	0.72	0.73	0.4–1.2	50	100
$\sum$Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene	1.5	1.3	0.43–3.2	2	–
$\sum$Benzo(b)-, benzo(k)fluoranthene	1.4	1.3	0.42–3.8	30	–
Naphthalene			<250[*]	2,400	–
HCHs ($\sum\alpha$-, β-,γ-,δ-, ε-HCH)	2.7	0.79	0.17–11.4	20	40
HCB	0.059	0.050	0.02–0.11	10	50
p,p'-DDT	0.047	0.028	0.006–0.26	10	–
Total DDT ($\sum p,p'$-DDT, p,p'-DDE, p,p'-DDD, o,p-DDT)	0.21	0.13	0.038–1.2	25	–
Cyclodiene pesticides ($\sum$aldrin, dieldrin, endrin, isodrin)	0.023	0.025	0.002–0.046	10	–
Endosulfan ($\sum\alpha$-, β)	0.012	0.010	0.004–0.017	5	10
cPenta-BDE, $\sum$BDE-28, 47, 99, 100, 153,154)	0.057	0.051	0.025–0.12	0.5	–

AA-EQS is the EU quality standard for the annual average concentration in inland surface waters; MAC-EQS is the maximum allowable concentration

3.1.2 PAHs

The concentration of most of the PAHs in water was at least one order of magnitude below the AA-EQS except for the $\sum$benzo(g,h,i)perylene and indeno(1,2,3-cd) pyrene, where the limit was exceeded in 5 sites out of 23 (Fig. 2). The stations were JDS 02 (2,4 ng/L), JDS 16 (3.1 ng/L), JDS 39 (2.2 ng/L), JDS 92 (2.5 ng/L) and JDS 95 (2.3 ng/L). 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 $\sum$benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, it remains unclear whether or not the Danube is within the EQS for these compounds.

Naphthalene data reported in Table 1 have been analysed by Literathy et al. [13] during the JDS 2 survey. All samples were below the LOQ of 0.25 µg/L of the ISO 17993 method applied, thus clearly below the AA-EQS of 2 ng/L.
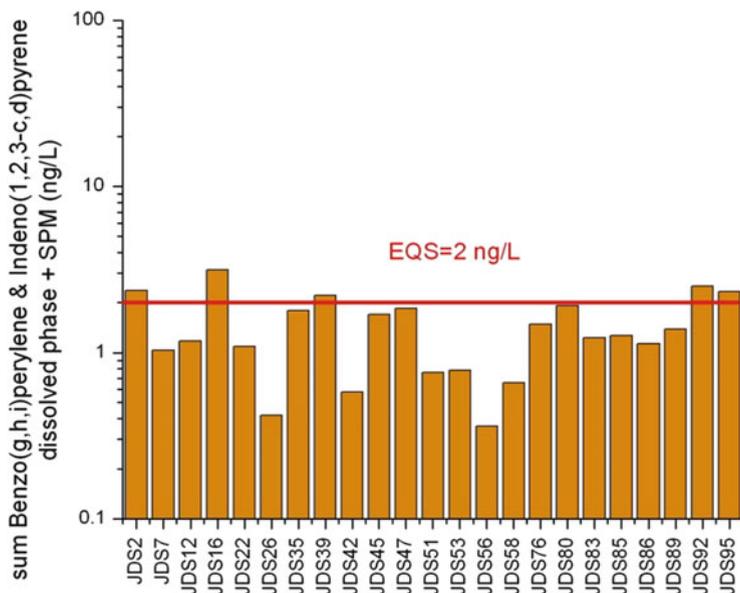
Fig. 2 Concentration of ∑benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene in water

3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

3.2.1 Overview on All Matrices

PAHs were determined in sediments, SPM and the dissolved phase.

The reported ∑PAH data refer to the ∑16 EPA priority PAH plus benzo(e) pyrene and benzo(j)fluoranthene in water, SPM and sediments (Fig. 3, Table 2).

Among the ∑16 EPA PAH, no explicit quantitative data could be obtained for naphthalene, acenaphthylene and acenaphthene, since the extraction conditions, optimised for PCDD/Fs and PBDEs, lead to low recoveries for the volatile PAHs. However, the semi-quantitative results obtained for the naphthalene, acenaphthylene and acenaphthene in SPM and sediments suggest a minor contribution to the ∑EPA PAH between 7% and 4% at average. We assume therefore that the ∑PAH data reported here can be compared with literature data referring to ∑EPA PAH.

Most sediment and SPM samples display moderate ∑PAH concentrations in a range of 250–750 μg/kg with extreme values of up to 2,600 μg/kg for SPM. For comparison in the German stretch of the River Elbe, typical values for ∑16 EPA PAHs in SPM and SPM-derived sediments are one order of magnitude higher and maximum levels range up to 50 mg/kg [14]. From the River Seine estuary, PAH data from SPM are available. The ∑11 PAH determined there overlaps with the ∑PAH from the JDS 2 except for fluorene, anthracene and dibenz(a,h)anthracene, which play only a minor role in the sediment pattern. For sediments a median of
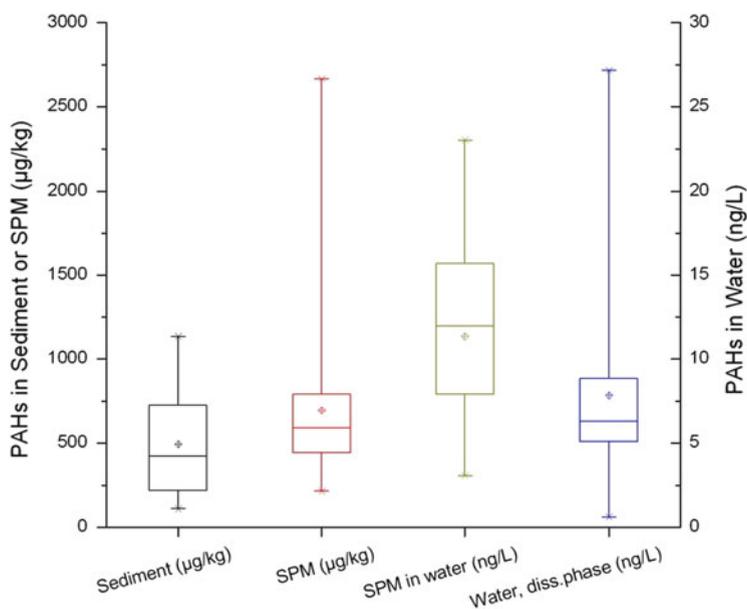
Fig. 3 $\sum$PAH concentrations in all abiotic compartments, box-whiskers diagram, *boxes* represent the 25/75 percentiles with median (——) and average ($\oplus$), and the whiskers represent minimum and maximum values

Table 2 $\sum$PAH concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (ng/L)	Water dissolved (ng/L)
Average	493	696	11	7.8
Median	407	590	12	6.3
Min	111	216	3.1	0.62
Max	1,135	2,665	23	27
25-Percentile	220	436	6.9	5.0
75-Percentile	712	787	15	8.8

2.65 mg/kg is reported [15], which corresponds to the extreme value in SPM measured during JDS 2. In ten sediment samples taken in 2002 along the German stretch of the Danube, $\sum$16 EPA PAH concentrations of 0.24–5.3 mg/kg were reported [16].

Among all sediment sites sampled during JDS 1, the $\sum$16 EPA PAH ranged between 2 and 16 mg/kg at 16 sites, which is considerably higher than the maximum level of 1.3 mg/kg detected during JDS 2. This suggests a decrease in PAH

content in the Danube sediments since 2001. However, before concluding, the techniques applied for the sediment sampling during both campaigns should be carefully evaluated for their inter-comparability. Among the PAHs that were quantified in sediments and SPM, the most abundant were fluoranthene and pyrene.

In the water column, significant amounts of PAHs are associated with SPM, in particular the higher boiling compounds. Average (dissolved plus SPM) concentrations of $\sum$PAH around 17 ng/L and a maximum of 35 ng/L were detected in water, which is at the lower end of typical findings in the River Elbe [14]. The comparably low contamination level with PAHs in Danube water is further illustrated by comparing with data from the Seine estuary where an average/median concentration of 187/172 ng/L has been reported for the $\sum$11 PAH [15].

3.2.2   Downstream Concentration Profile

Sediments (Fig. 4)

The sediments at site JDS 02_L display comparably high PAH concentrations, which indicate an input from the tributary Altmuehl/Rhein-Main-Donau Channel, supported by the comparably high PAH content of the SPM (not reported here) at this site.
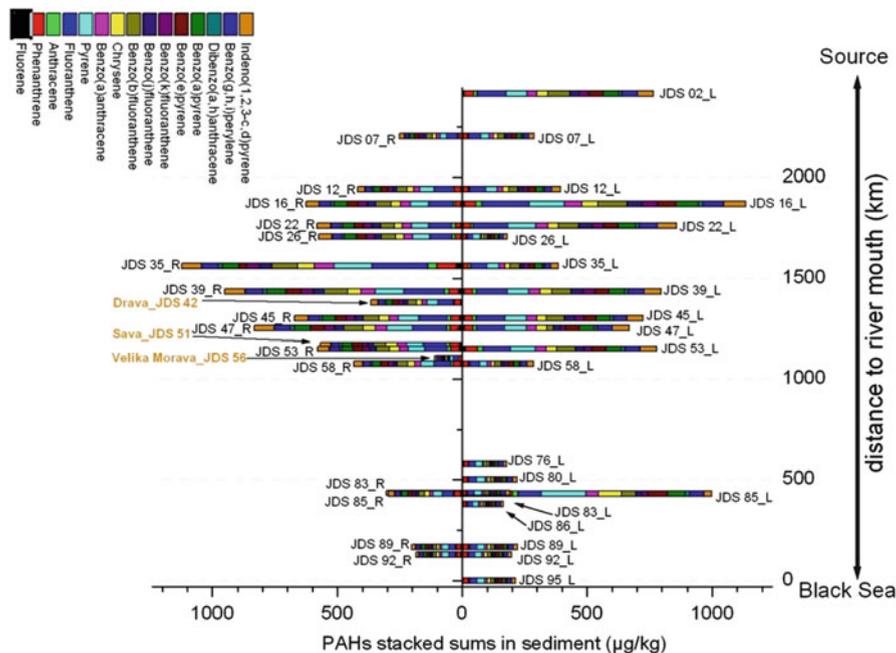
Fig. 4 Downstream concentration profile of PAHs in sediments

Site JDS 07 (AT) after the inlet of the tributary Inn shows lower concentrations similar on both sides of the Danube, which suggests a diluting effect of the River Inn for PAHs in the Danube.

Site JDS 16 shows an increase in concentration, in particular on the left-hand side downstream of the inlet of the tributary Morava, indicating an input from the tributary Morava.

Site JDS 22 shows a similar asymmetry in concentrations with a higher concentration on the left-hand side downstream of the inlet of the tributary Vah, which indicates a moderate input from the tributary Vah.

Site JDS 26 shows a concentration drop on the right bank downstream the mouth of the tributaries Hron and Ipoly, which indicates a dilution due to low PAH levels of the rivers Hron and Ipoly.

Site JDS 35 shows a strong asymmetry in the sediments with high concentrations on the left-hand side. This might be still due to the dilution influence of the rivers Hron and Ipoly entering left bank upstream. Another possibility is an unknown source (since no tributary enters in this section) on the right-hand side.

At site JDS 42 the sediment sample was taken inside the tributary Drava entering the Danube from the left bank. The sediments in the River Drava contain considerably less PAH than the Danube itself, and also the PAH content in the SPM is low, which indicates a dilution due to low PAH levels in the tributary Drava.

The sediments at site JDS 51 taken in the tributary Sava displayed about two times lower PAH levels in the sediments, when compared to the samples from the corresponding Danube stretch. Site JDS 56 inside the tributary Velika Morava displayed even five times lower PAH concentrations in sediments and SPM. This indicates a diluting effect of both tributaries as regards PAHs.

The sampling sites downstream the Iron Gate reservoir mostly display comparable low PAH concentrations in the sediments and SPM, indicating a sink for SPM-associated PAHs in the reservoir.

PAH inputs downstream the Iron Gate seem to be low, except at the inlet of the tributary Arges entering from the left-hand side between the sampling sites JDS 83 and JDS 85. A significant rise of PAHs in sediments after the inlet is visible in between sampling stations JDS 83 and JDS 85_L, indicating the tributary Arges being a source of PAHs into the lower stretch of the Danube. However, in this case, there was no confirmation through the SPM data, which points to historic inputs rather than recent ones.

Site JDS 89, which according to the cruise protocol is suspected to be impacted by an oil refinery, shows no abnormalities regarding PAHs in sediments, SPM and water.
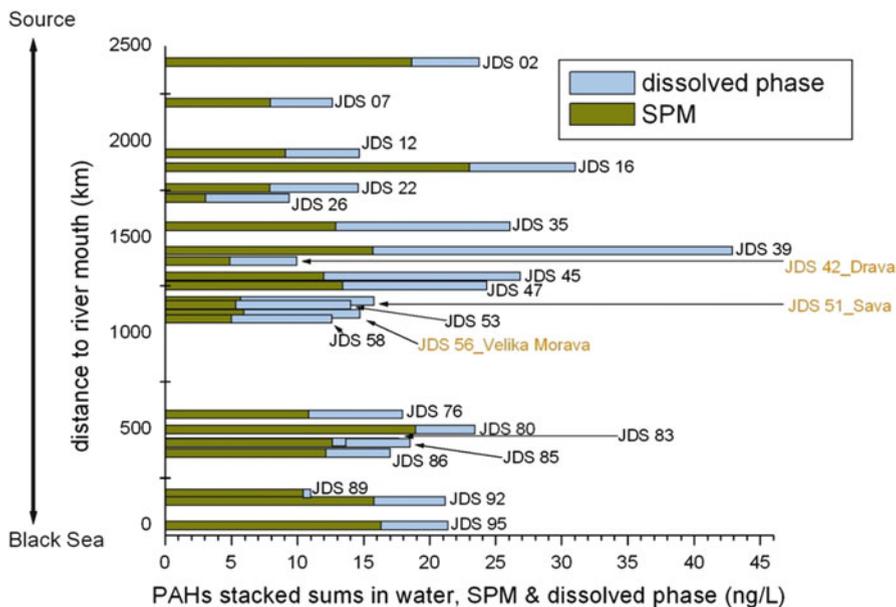
Fig. 5 Downstream concentration profile of PAHs in water

Water (Fig. 5)

Looking at the whole water column, the ∑PAHs show a more equilibrated situation with low concentrations in the tributaries Drava (JDS 42), Sava (JDS 51) and Velika Morava (JDS 56) as observed in the sediments above. The maximum concentration of ∑PAH in the water was 42 ng/L found at JDS 39 (border station HU/HR), with a comparably high contribution from the dissolved phase.

3.3 Hexachlorocyclohexane (HCH, ∑α-, β-, γ-, δ-HCH)

3.3.1 Overview on All Matrices

The group of HCHs includes eight isomers. The EQS for HCH refers to α-, β-, γ- and δ-HCH, the four major isomers present in the technical mixture. According to the Draft Technical Guidance CMA, the sum of α-, β-, γ- and δ-HCH has to be reported (Fig. 6, Table 3).

Sediments and SPM display similar concentrations with average values below 1 µg/kg. For comparison: In the River Elbe, average values in the sediments of the CZ stretch were around 15 µg/kg (0.69–104 µg/kg), followed by levels up to 224 µg/kg after the confluence of the contaminated tributary Mulde in Germany [17]. In the water column, HCHs were detected almost exclusively in the dissolved phase.
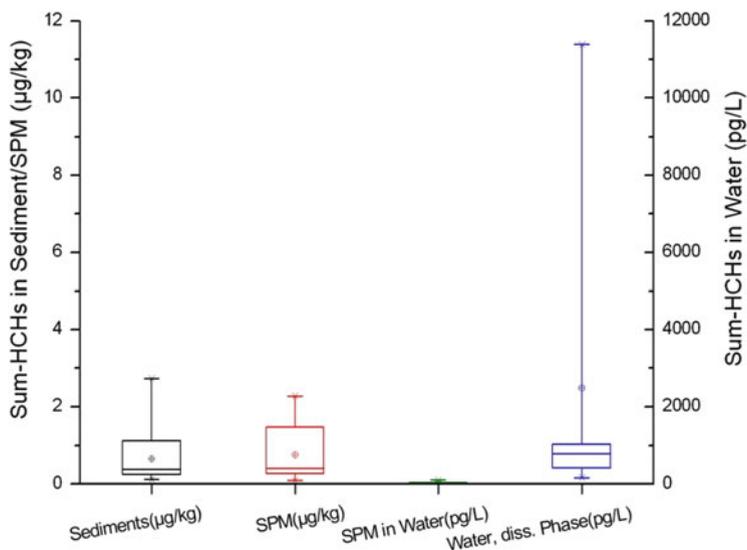
Fig. 6 $\sum$HCH concentrations in all abiotic compartments

Table 3 $\sum$HCH concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	SPM in water (pg/L)	Water dissolved (pg/L)
Average	0.66	0.77	23	2,489
Median	0.35	0.42	5.1	752
Min	0.12	0.091	1.2	164
Max	2.7	2.3	105	11,386
25-Percentile	0.25	0.26	2.4	414
75-Percentile	1.1	1.5	42	2,431

For HCHs in water, the AA-EQS is 0.02 µg/L and the MAC-EQS is 0.04 µg/L; both of them were not exceeded. The maximum of $\sum$HCHs in the water column was 0.011 µg/L at site JDS 85 downstream of Arges (RO/BG).

3.3.2 Downstream Concentration Profile

Sediment (Fig. 7)

In the sediments HCH concentrations display a higher abundance in the samples taken on the left-hand side.
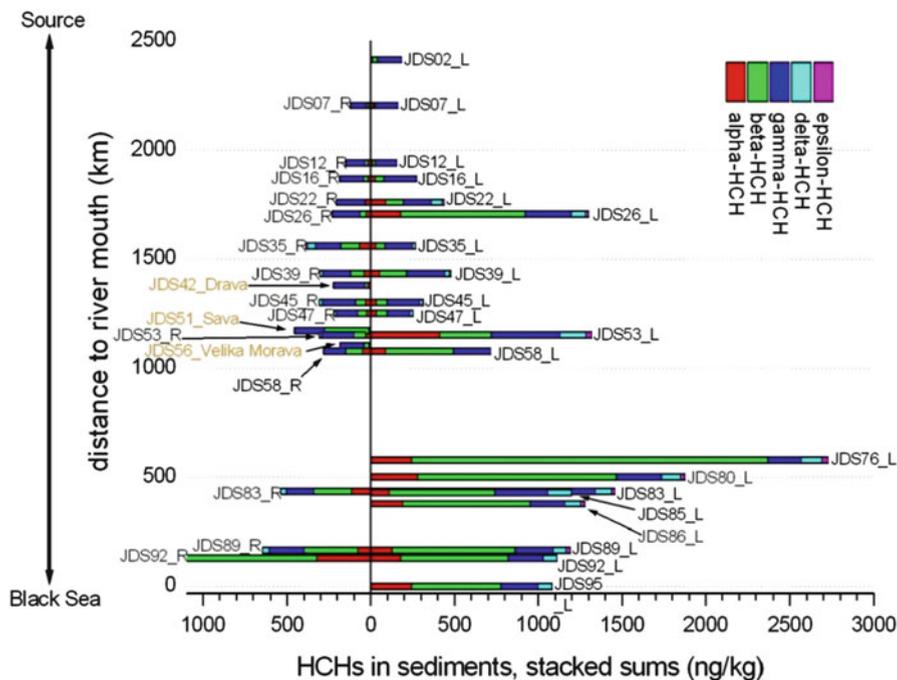
Fig. 7 Downstream concentration profile of HCHs in sediments

The sediments on the left-hand side of the middle stretch display the two distinct maxima: first at JDS 26 (HU), indicating a historic influence of the Hron (km 1,716) and Ipoly (km 1,708) tributaries entering only a few kilometres upstream on the left-hand side (in the tributary Hron high Lindane concentrations were detected during JDS 1), and second at JDS 53 (RS), downstream Pancevo situated on the left-hand side of the Danube, where high Lindane concentrations were detected also during JDS 1. Sediments taken in the tributaries Drava (JDS 42), Sava (JDS 51) and Velika Morava (JDS 56) display low concentration levels similar to those in the Danube sediments taken on the right-hand side.

In the lower Danube stretch from JDS 76 (RO/BG) downstream, a general tendency towards higher concentrations was observed. JDS 76 is located only 26 km downstream of the Olt Tributary entering from the left-hand side, where high Lindane concentrations were found also during JDS 1. The increase in HCH concentrations in the dissolved phase downstream the Olt Tributary goes along with a change of the HCH concentration pattern.

Water (Fig. 8)

Similar to the sediments, the downstream profile in the dissolved phase displays low HCH concentrations in the upper and middle stretch. A sharp increase was observed

starting from site JDS 76 (RO/BG) downstream the Olt Tributary that had shown high Lindane concentrations during JDS 1 as well.

Most sites downstream the Olt Tributary remain at a high HCH level in the dissolved phase. The historic signals observed more upstream in the sediments at JDS 26 and JDS 53 are no longer visible in the dissolved phase.

The samples from the tributaries Drava (JDS 42) and Sava (JDS 51) display slightly lower concentrations than the Danube itself. The Velika Morava Tributary (JDS 56) shows, as for SPM, slightly higher concentrations in the dissolved phase as well.

The sharp increase in HCH concentrations in the dissolved phase of the lower stretch goes along with a significant change of the HCH concentration pattern: In the upper stretch of the Danube (JDS 02 to JDS 16), the sum of HCHs consists almost exclusively of γ-HCH. In the section between JDS 22 and JDS 58, the abundance of α-, β-HCH equals that of γ-HCH, and from site JDS 76 all sites showing high HCH concentrations in the dissolved phase are dominated by α- and β-HCH. A similar tendency can be seen in the sediment and to a lower extent in SPM (not reported here).

We got no explanation for the low HCH values observed at the sites JDS 80 and JDS 89. In the whole section of the lower Danube downstream the Iron Gate, no important tributaries come in, which might have caused a dilution effect explaining
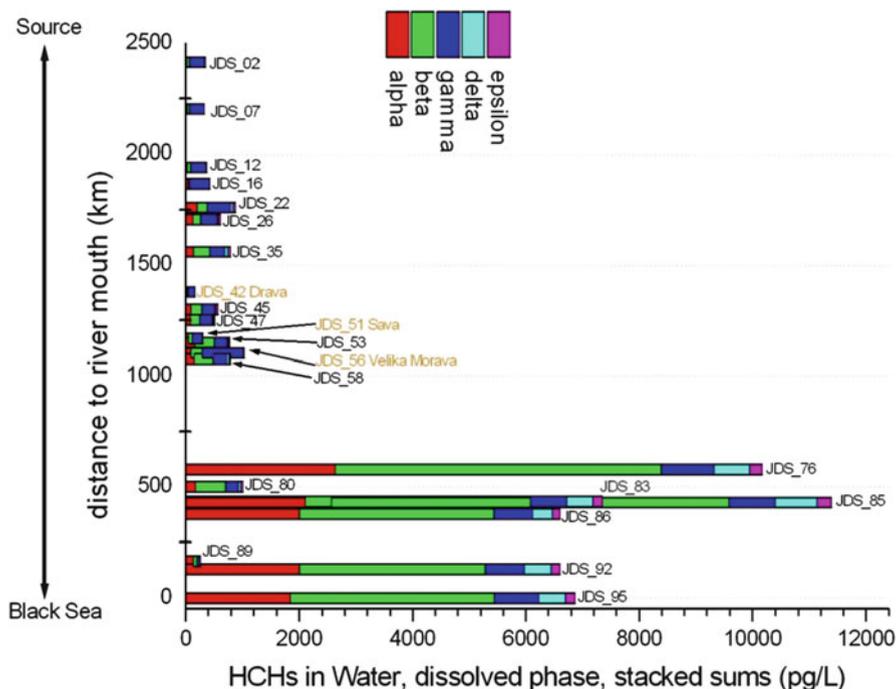

Fig. 8 Downstream concentration profile of HCHs in water, dissolved phase. HCHs associated with SPM are negligible

the locally low HCH findings on these two sites. A sampling error seems unlikely, since the concentration of other compounds as PCBs, PBDEs and OCPs in the dissolved phase do not show comparable spatial variations in that stretch.

3.4 Hexachlorobenzene

3.4.1 Overview on All Matrices

Average concentrations in sediments and SPM were around 1 and 0.65 µg/kg, respectively.

In the water column HCB was detected both in SPM and the dissolved phase, with a tendency towards the dissolved phase in the upper stretch and a stronger association with SPM in the lower stretch. The maximum value for HCB at site JDS 92 (RO) was 0.11 ng/L, which is around two orders of magnitude below the respective AA-EQS of 10 ng/l and the MAC-EQS of 50 ng/l (Fig. 9, Table 4).

3.4.2 Downstream Concentration Profile

Sediment (Fig. 10)

In the sediments a tendency of enhanced HCB concentrations in the samples taken on the left-hand side can be seen; however, it is less pronounced as above for the
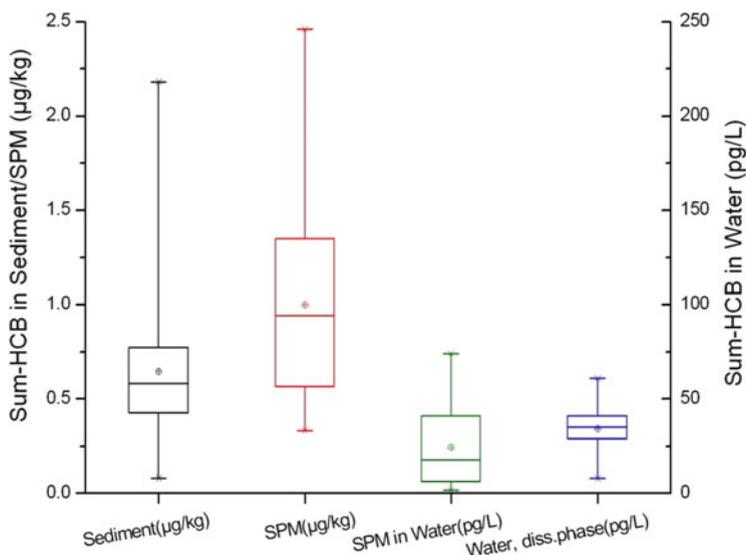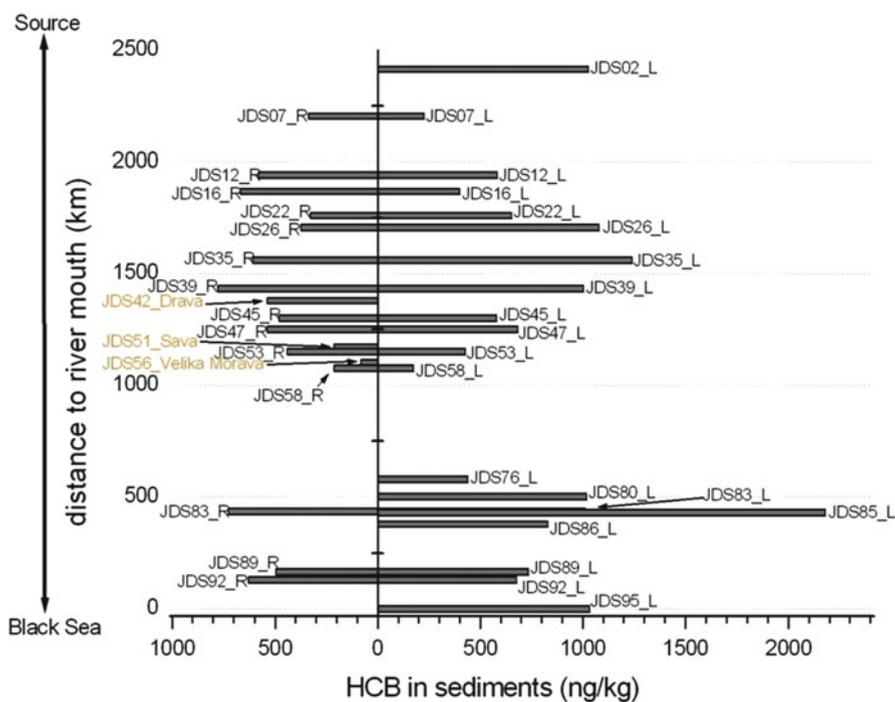

Fig. 9 HCB concentrations in all abiotic compartments

Table 4 HCB concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	0.65	1.0	25	34
Median	0.58	0.94	18	35
Min	0.081	0.33	1.8	7.9
Max	2.2	2.5	74	61
25-Percentile	0.42	0.51	6.1	28
75-Percentile	0.79	1.3	38	41

Fig. 10 Downstream concentration profile of HCB in sediments

HCHs. An influence of the tributary Altmuehl appears in the sediments at JDS 2 (DE), and comparably high levels at JDS 85 (RO) suggest a historic impact from the tributary Arges.

Water (Fig. 11)

In the water column, HCB does not show particular gradients in the downstream profile, except for slightly higher concentrations in the lower stretch, together with a higher abundance of SPM-associated HCB.

The SPM associate portion of HCB increases in the lower stretch.

The water samples from the tributaries Drava (JDS 42, HR/RS) and Velika Morava (JDS 56, RS) show comparable concentrations as in the Danube itself, whereas the sample from the tributary Sava (JDS 51, RS) displays lower concentrations.

3.5 DDT and Metabolites (p,p′-DDT, p,p′-DDE, p,p′-DDD, o,p-DDT)

3.5.1 Overview on All Matrices

Average concentrations of $\sum p,p'$-DDT, p,p'-DDE, p,p'-DDD, o,p-DDT in sediments were 6.6 µg/kg and slightly lower in SPM with 4.4 µg/kg.
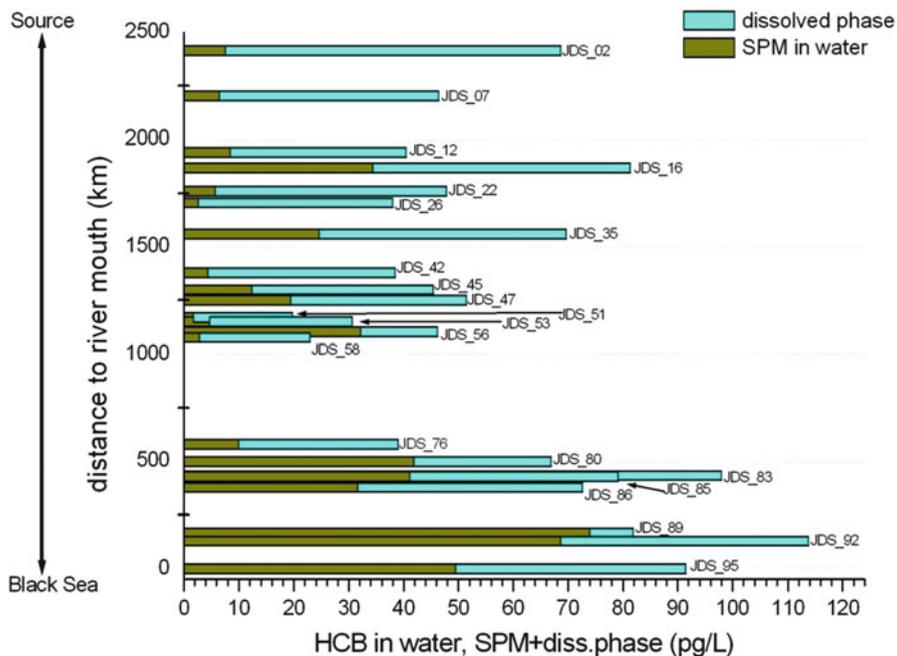

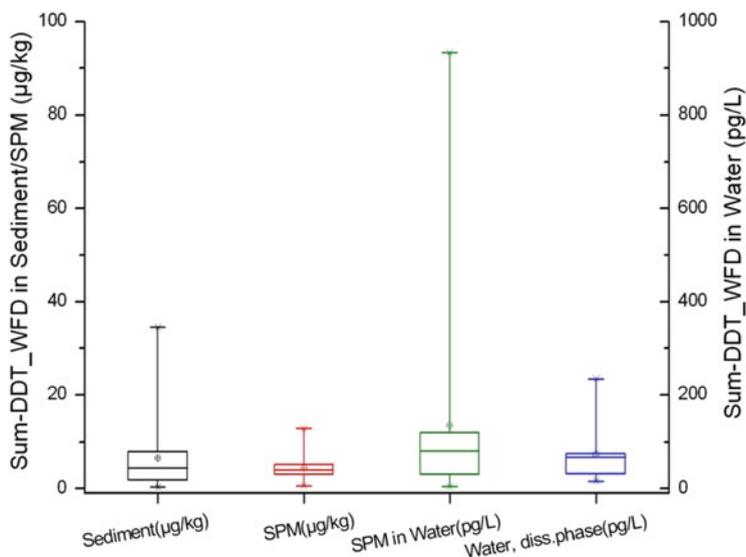**Fig. 11** Downstream concentration profile of HCB in water

Fig. 12 ∑DDT and metabolite concentrations in all abiotic compartments

Table 5 ∑DDT and metabolite concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	SPM in water (pg/L)	Water dissolved (pg/L)
Average	6.6	4.4	135	74
Median	4.5	4.0	81	66
Min	0.36	0.63	4.6	16
Max	35	13	933	234
25-Percentile	1.9	3.0	27	37
75-Percentile	7.8	5.0	111	75

In the water column, DDT and its metabolites were detected to a larger extent associated with SPM. The maximum concentration of $\sum p,p'$-DDT, p,p'-DDE, p,p'-DDD, o,p-DDT in the water column was around 1.2 ng/L at sites JDS 92, 95 (RO), which is more than one order of magnitude below the AA-EQS of 25 ng/L.

This maximum corresponds to high DDT concentrations in SPM detected during JDS 1 (Fig. 12, Table 5).

3.5.2 Downstream Concentration Profile

Sediments (Fig. 13)

In sediments, DDT and metabolites show tendentially higher concentrations in the samples taken on the left-hand side, except at site JDS 92 (RO/UA) after the inlet of
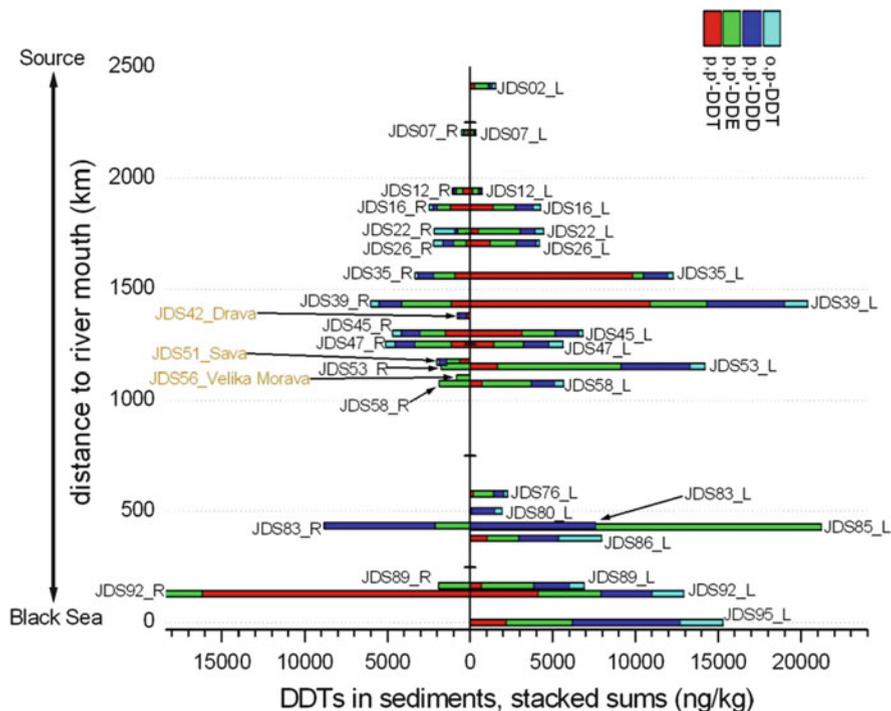
Fig. 13 Downstream concentration profile of p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p-DDT in sediments

the tributaries Siret and Prut entering from the right-hand side. This site displayed also the maximum abundance in SPM-associated DDT (not reported here) and in the water column, thus confirming the high p,p'-DDT concentrations reported from this site in SPM during the JDS 1 cruise. In contrast, the other tributaries entering from the right-hand side (Drava, Sava and Velika Morava) displayed low concentrations in their sediments. Historic (since not visible in the water column) intakes from the left-hand side are indicated at sites JDS 35, JDS 39, JDS 53 and JDS 85. However, none of these left-hand sites showed a significant signal in the water column,

Water (Fig. 14)

In water only JDS 92 and JDS 95 appear as sites of considerably enhanced concentrations. The sites in the middle stretch that had displayed higher DDT concentrations in the sediments do not result in high concentrations in water. This suggests that for DDT and metabolites the only significant current sources are in
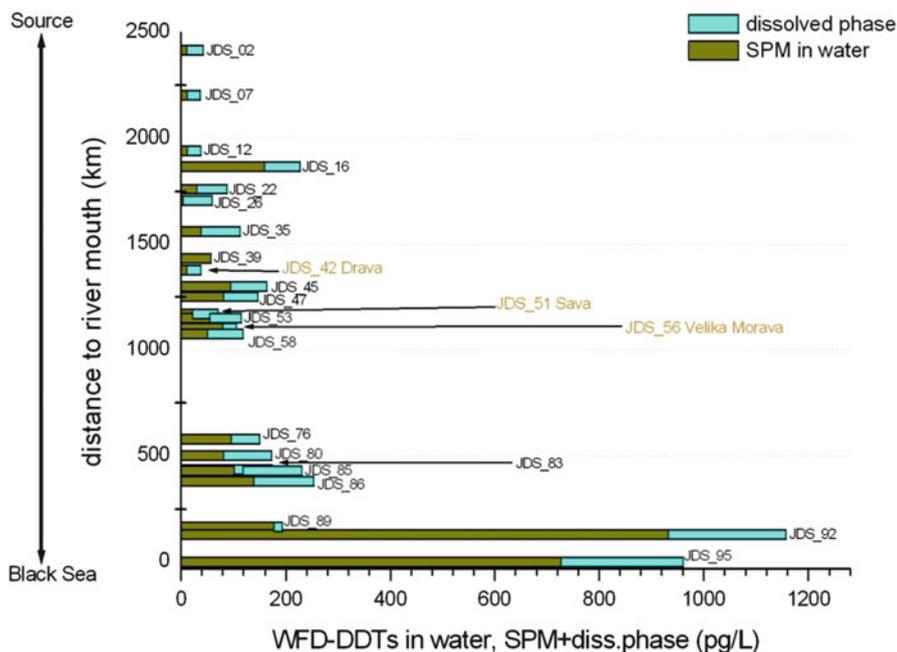
Fig. 14 Downstream concentration profile of $\sum p,p'$-DDT, p,p'-DDE, p,p'-DDD, o,p-DDT in water

between JDS 89 (upstream tributaries Siret and Prut) and JDS 92 (downstream tributaries Siret and Prut).

In the water column, the share of SPM-associated DDT and metabolites in general rises towards the Black Sea.

3.6 Cyclodiene ($\sum$Aldrin, Dieldrin, Endrin, Isodrin)

3.6.1 Overview on All Matrices

Average concentrations in sediments were 0.046 μg/kg, while SPM displayed higher average concentrations of 0.090 μg/kg. In sediments isodrin and endrin were < LOD in all samples. In SPM isodrin was < LOD in all samples.

In the water column, $\sum$aldrin, dieldrin, endrin, isodrin were detected almost exclusively in the dissolved phase. Endrin could be quantified in all dissolved-phase samples. For aldrin 14 sites were below the dissolved-phase LOD of 1.1 pg/L. For endrin 6 sites were below the LOD of 3.4 pg/L and isodrin was detected in none of the sites (LOD of 6.1 pg/L). Within the sites with quantifiable amounts of the $\sum$cyclodiene, endrin concentrations were always dominant. In the statistics and the figure below, only quantified concentration data are included.
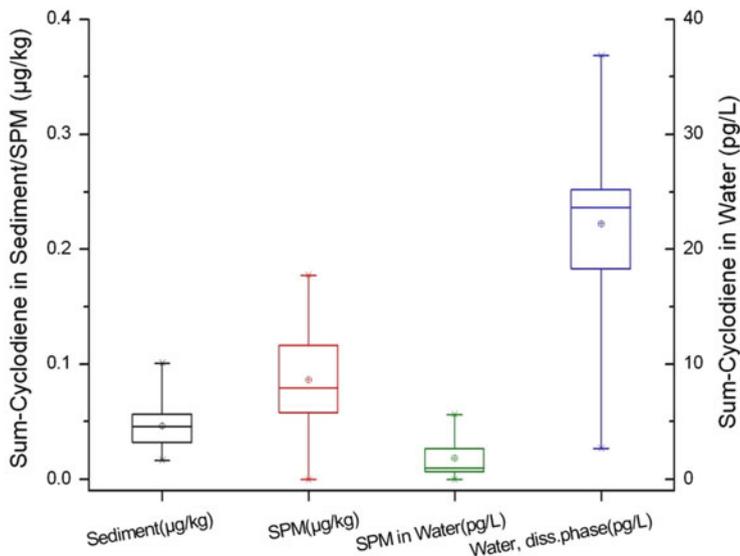
Fig. 15 ∑Aldrin, dieldrin, endrin, isodrin concentrations in all abiotic compartments

Table 6 ∑Aldrin, dieldrin, endrin, isodrin concentrations in all abiotic compartments, dissolved phase upper bound in brackets

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	0.046	0.090	1.9	22 (29)
Median	0.046	0.080	0.98	24 (28)
Min	0.017	0	0	2.7 (15)
Max	0.10	0.18	5.6	37 (61)
25-Percentile	0.032	0.062	0.64	19 (22)
75-Percentile	0.055	0.12	2.7	25 (33)

Even when calculating upper bound concentrations in water, the ∑aldrin, dieldrin, endrin, isodrin remain more than two orders of magnitude below the respective AA-EQS of 10 ng/L (Fig. 15, Table 6).

3.6.2 Downstream Concentration Profile

Sediment (Fig. 16)

The downstream profile in sediments displays an influence of the tributary Altmuehl visible in the sediments of site JDS 02 (DE). Concentrations decrease then downstream JDS 02, suggesting a dilution from the tributary Inn confluence at
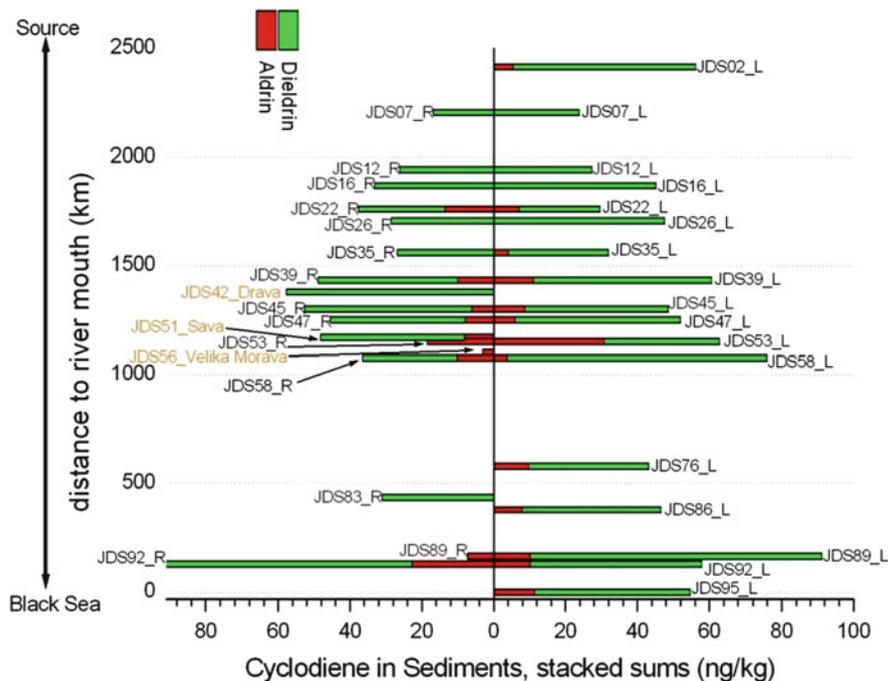
Fig. 16 Downstream concentration profile of ∑cyclodiene in sediments

km 2,225. A slight rise in concentration becomes visible along the middle stretch of the Danube. After the Iron Gate concentrations are somewhat lower except at JDS 89 and JDS 92 in Romania.

In SPM (not displayed here) the gradient is similar, however, with concentration maxima more upstream around JDS 85 (RO/BG).

In all sediment samples, the values for endrin and isodrin were < LOD.

Water (Fig. 17)

The downstream profile in the dissolved-phase water displays a slight trend of higher concentrations towards the Black Sea. As in the sediments, mainly Dieldrin was detected. The dissolved-phase water samples from the tributaries Drava (JDS 42, HR), Sava (JDS 51, RS) and Velika Morava (JDS 56, RS) display lower concentrations than the Danube itself.
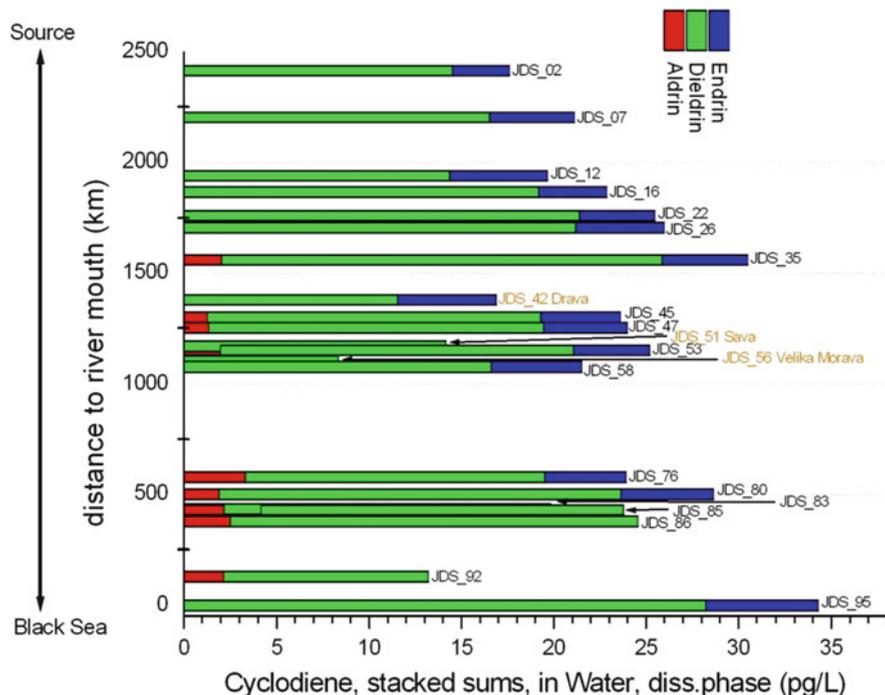
Note: all samples < LOD are set to 0 in the figures.

Fig. 17 Downstream concentration profile of ∑cyclodiene in dissolved phase

3.7 Endosulfan (∑α,β-Endosulfan)

3.7.1 Overview on All Matrices

Due to very low concentration levels, a series of sites displayed non-detectable concentrations.

In sediments only at site JDS 12_R, one value above LOD was detected for α-endosulfan, with 0.20 µg/kg.

In SPM only site JDS 56 in the Velika Morava Tributary (RS) was positive, with levels of 0.53 µg/kg for α-endosulfan and 0.11 µg/kg for β-endosulfan.

In the water column, ∑α,β-endosulfan was detected only in the dissolved phase except at site JDS 56 (Velika Morava Tributary, RS), with concentrations typically below 0.02 ng/L, more than two orders of magnitude below EQS (Table 7).

3.7.2 Downstream Concentration Profile

α- and β-Endosulfan were not detected in sediments besides site JDS 12_R where a value for α-endosulfan was detected above the LOD with 0.20 µg/kg, and in SPM

Table 7 Sum-endosulfans in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	SPM in water (pg/L)	Water dissolved (pg/L)
Average	0.20	0.64	16	10
Median	0.20	0.64	16	8.1
Min	0.20	0.64	16	3.2
Max	0.20	0.64	16	39
25-Percentile				6.4
75-Percentile				11
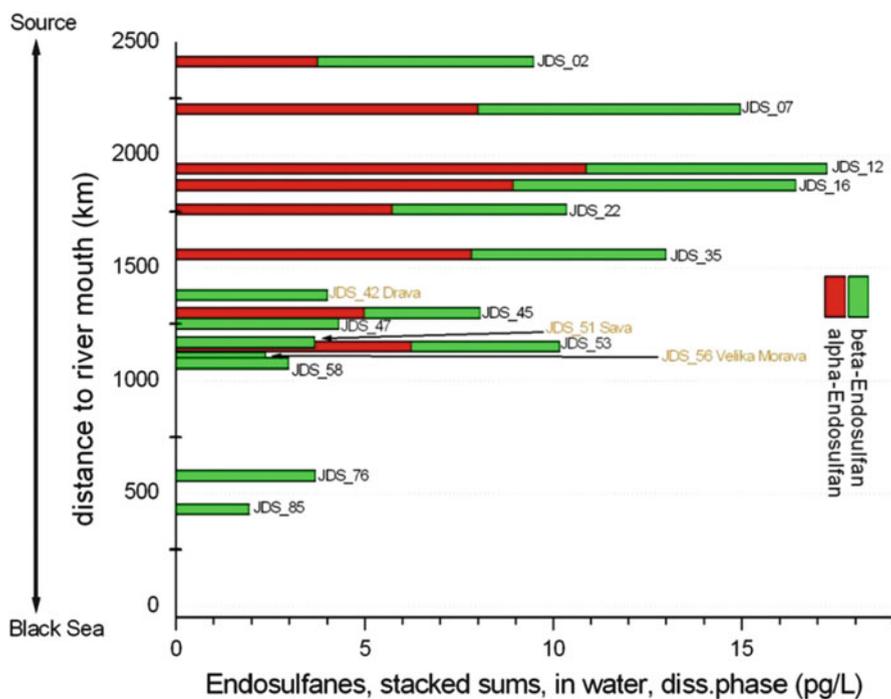
Fig. 18 Downstream concentration profile of $\sum\alpha,\beta$-endosulfan, dissolved

only site JDS 56 (Velika Morava Tributary, RS) was positive at a level of 0.53 µg/kg for α-endosulfan and 0.11 µg/kg for β-endosulfan.

The downstream profile in the dissolved phase displays a decreasing trend downstream JDS 12 (AT) towards the Black Sea (Fig. 18).

3.8   Cis- *and* Trans-*Chlordanes*

3.8.1   Overview on All Matrices

Sediments displayed average values around 0.033 µg/kg. In SPM, due to some isolated maxima, the average concentration was around 0.084 µg/kg. In the water column, the chlordanes were detected both in the dissolved phase and associated with SPM with average level of around 2.3 pg/L each (Fig. 19, Table 8).
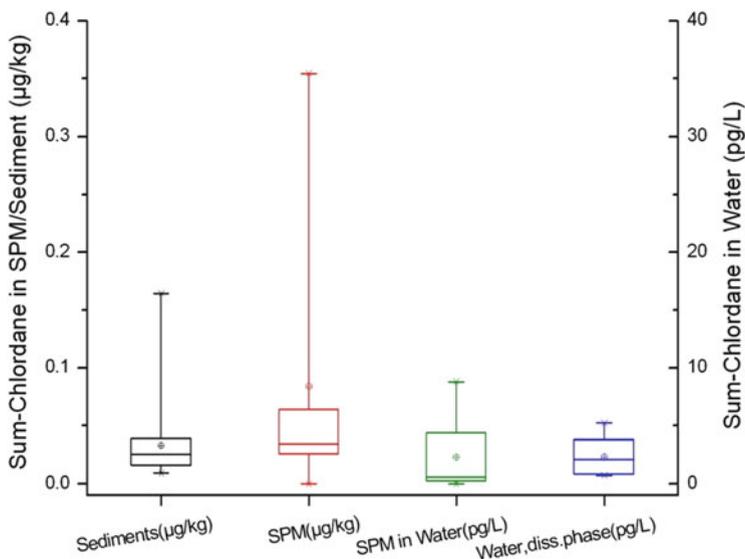

Fig. 19 *Cis-* and *trans*-chlordane concentrations in all abiotic compartments

Table 8 *Cis-* and *trans*-chlordane concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (ng/L)	Water dissolved (ng/L)
Average	0.033	0.084	2.3	2.3
Median	0.026	0.035	0.58	1.9
Min	0	0	0	0.74
Max	0.16	0.35	8.8	5.2
25-Percentile	0.016	0.025	0.26	0.90
75-Percentile	0.039	0.062	4.2	3.8

3.8.2 Downstream Concentration Profile

Sediment (Fig. 20)

In the sediments the downstream profile displays a marginal trend of rising concentrations towards the Black Sea with no clear differentiation between left- and right-hand side samples. One distinct higher level was found in the sediments around the site JDS 85 (RO/BG), in particular on the left-hand side downstream the Arges Tributary entering from left. The share of *trans*-chlordane in sediments rises slightly towards the Black Sea.

In SPM (not displayed here) concentrations were again higher around JDS 85 but also in the sample JDS 56 (RS) taken in the tributary Velika Morava.

Water (Fig. 21)

The water column displays higher concentrations in the tributary Velika Morava (RS) and again in the lower Danube from JDS 83, to a large extent caused by the presence of SPM-associated chlordane.
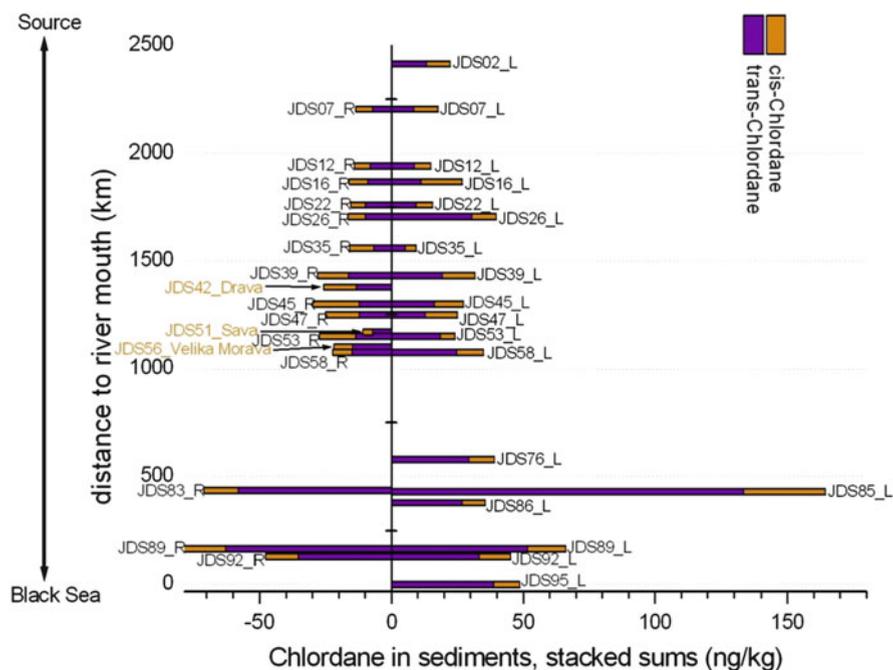

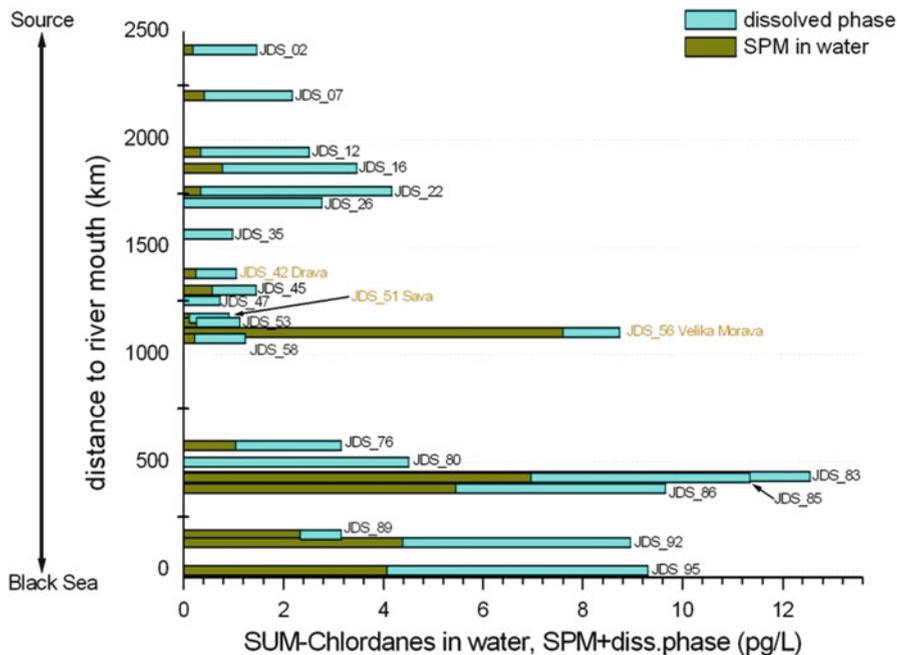**Fig. 20** Downstream concentration profile of chlordane in sediments

Fig. 21 Downstream concentration profile of chlordane in water

3.9 Mirex

In sediment, SPM and the dissolved phase, all samples were $<$ LOD, which was 3.3 pg/L for the dissolved phase, 6.7 ng/kg for SPM and 17 ng/kg for sediments.

3.10 Heptachlor

Heptachlor and its *exo-* and *endo*-epoxides were not detected in sediments apart from some isolated signals for heptachlor-*exo*-epoxide not exceeding 0.1 µg/kg.

3.10.1 Downstream Concentration Profile in Water

The detected concentrations in the dissolved phase and SPM were close to the LOD and shall only be considered as an indication. The downstream profile in SPM and in the water column displays some distinct signals at JDS 22, JDS 56 and zone of higher concentration between JDS 80 and JDS 86 (Fig. 22).
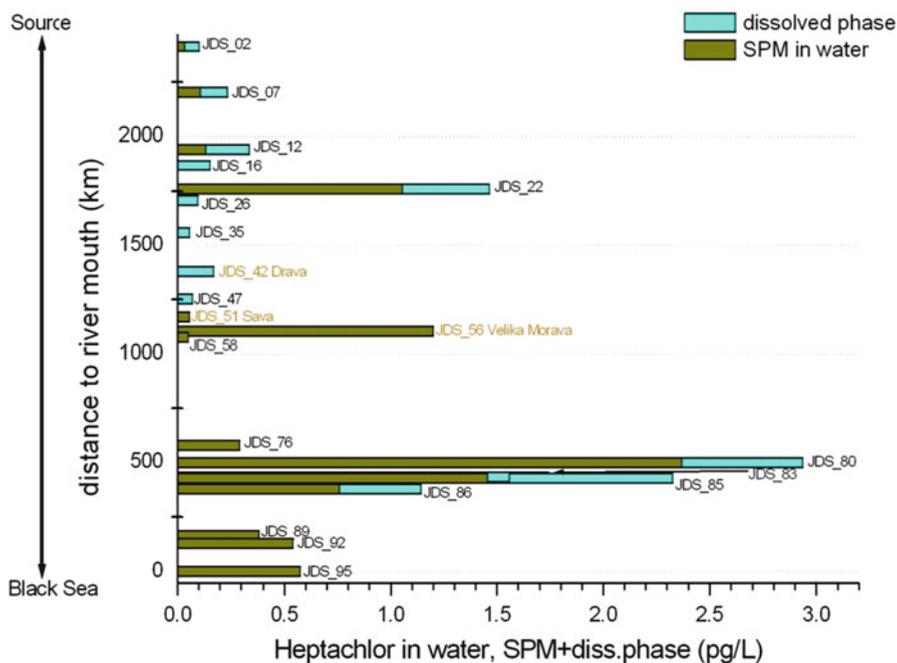
Fig. 22 Downstream concentration profile of heptachlor in water (SPM + dissolved phase)

3.11 Indicator Polychlorinated Biphenyls (EC-6 PCBs)

3.11.1 Overview on All Matrices

Indicator PCBs, also referred to as EC-6 PCBs in the Water Framework Directive, are the sum of PCB 28, 52, 101, 138, 153 and 180 and were analysed in sediment, SPM, dissolved phase and mussels (Fig. 23, Table 9).

EC-6 PCBs in sediments were at average 6.4 μg/kg with a maximum of 46 μg/kg at JDS 85 (RO/BG).

None of the individual EC-6 PCBs exceeded the chemical quality standard of 20 μg/kg for the individual EC-6 PCBs in sediments applied in Germany [14]. SPM samples display similar, somewhat lower median/average concentrations of 4.6 μg/kg also with a lower maximum of 9.1 μg/kg at JDS 92 (DE).

The observed data range fits into the lower end of the concentration ranges observed in fresh SPM from the River Elbe, where annual averages of SPM-derived fresh sediments were 2, 8 and 6.5 μg/kg in Hamburg, the highest annual average for the EC-6 PCBs of 1200μg/kg was found at Magdeburg during 2006 [14].

In the Seine estuary, typical PCB contents in SPM are one order of magnitude higher; 12 SPM samples of EC-6 PCBs without PCB 28 displayed an average of 183 μg/kg with a maximum of 380 μg/kg [15].
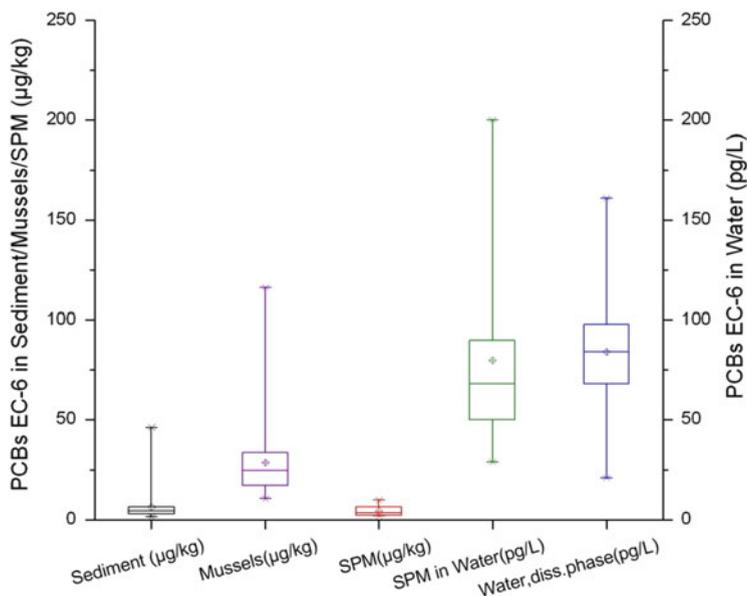
Fig. 23 EC-6 PCB concentrations in all compartments

Table 9 EC-6 PCB concentrations in all compartments

	Sediment (µg/kg)	Mussels (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	6.4	29	4.6	80	84
Median	4.3	25	3.6	68	84
Min	1.5	11	1.9	29	21
Max	46	116	9.9	200	161
25-Percentile	3.0	17	2.2	50	68
75-Percentile	6.3	34	6.4	90	98

In the water column, the average concentrations were around 150 pg/L, which is low compared to typical annual averages of the River Elbe and individual samples from the River Seine (River Elbe, 1.6 ng/L at Zehren in the stretch after Dresden [14]; River Seine estuary, 12 water samples of EC-6 PCBs without PCB 28 = 20 ng/L with a maximum of 47 ng/L [15]).

In mussels the $\sum$EC-6 PCB concentrations were about an order of magnitude higher as in the solids with an average of 29 µg/kg and a range of 11–116 µg/kg dry weight. For comparison Covaci et al. [18] report for freshwater mussel species from Flanders (BE) a range of 6.2–102 µg/kg wet weight, which corresponds approximately to 62–1,020 µg/kg dry weight.

Mussel/sediment bioconcentration would average around a factor of 5 on a dry weight base within the zones where a spatial overlap between sediment and mussel sampled could be obtained.

3.11.2 Downstream Concentration Profile

Sediment (Fig. 24)

The overall picture of the downstream concentration profile of EC-6 PCBs in sediments suggests some distinct historic (historic because the distinction is not visible in the SPM and water data) inputs form the left-hand side of the Danube.

The important tributary Inn apparently has a diluting influence as indicated by the lower concentration in the sediments on the right-hand side at JDS 07 (AT), 20 km downstream the inlet and further on lower concentrations downstream at JDS 12.

At JDS 16, downstream the tributary Morava (SK) from left, higher concentration with a high abundance of PCB 28 was observed on the left-hand side, pointing to an input from tributary Morava
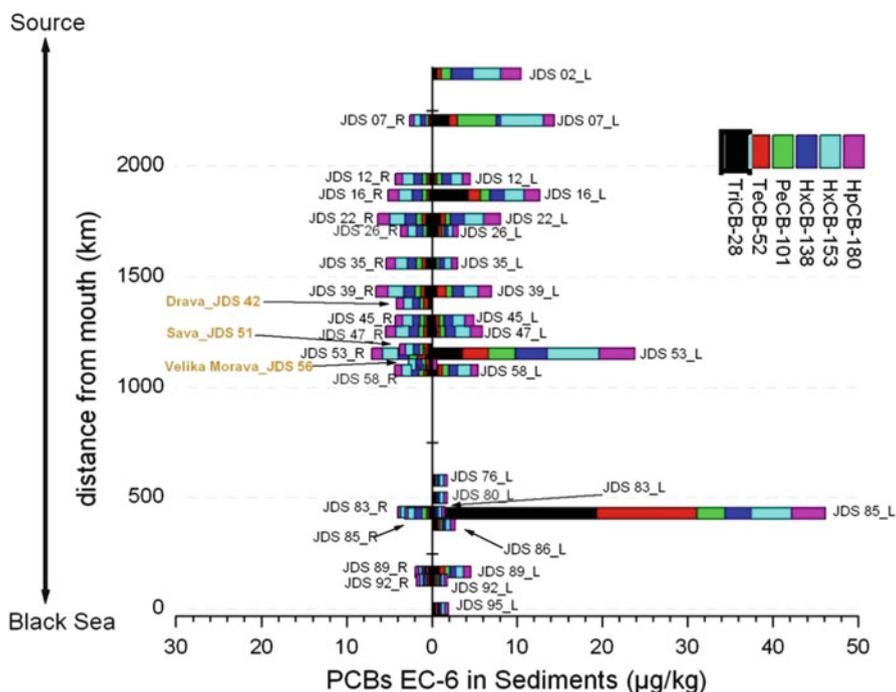

Fig. 24 Downstream concentration profile of EC-6 PCBs in sediment

The samples from the tributaries Drava, Sava and Velika Morava (JDS 42, JDS 51 and JDS 56, respectively) show low concentrations compared to Danube sediments and indicate a diluting effect from those tributaries entering the Danube from the right-hand side.

At site JDS 53, downstream the city of Pancevo[1] (RS, left-hand shore of the Danube), with tributary Tamis from entering from left, a significant concentration rise was observed (JDS 52 is also the site with the maximum concentration of PCDD/Fs in sediments).

The highest PCB concentrations in sediments were detected in the left-hand side sediments of site JDS 85 (RO/BG), again with a strong abundance of PCB 28 and also PCB 52. This suggests a strong historic influence of the tributary Arges entering 2 km upstream of site JDS 85. The impact from River Arges is supported by the comparable low concentrations detected in the sediments of site JDS 83 taken in the Danube at 3 km upstream the confluence.

SPM (Fig. 25)

The downstream profile in SPM appears more equilibrated when compared to the sediments above. The higher PCB concentrations in SPM appear in the upper stretch of the Danube. After the Iron Gate, constantly lower concentrations were observed, which suggests an efficient removal of PCB-contaminated SPM in the reservoir through sedimentation.

The high PCB levels found in the sediments downstream of the tributary Arges (JDS 53) and downstream Pancevo (JDS 85) are not visible in the SPM samples, which supports the historic character of the sediment contamination of these sites.

Differences in congener distribution in SPM are less obvious than in the sediments.

Similar to the sediments, the SPM samples taken in the tributary Drava (JDS 42) show low levels when compared to the Danube itself.

Water (Fig. 26)

In the water columns, the downstream concentration profile is more equilibrated when compared to sediments and SPM. This suggests that the Danube is currently affected rather by diffuse impacts from environmental sinks rather from distinct PCB releases from urban activities. Historic impacts, still reflected in the sediments, are no longer visible in the water column. A considerable portion of the EC-6 PCBs present in water is associated with SPM.

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[1] In 1999 the city of Pancevo (left-hand side of the Danube) was heavily bombed by NATO forces. Targets included an oil refinery, the airplane factory Lola-Utva and chemical plants.
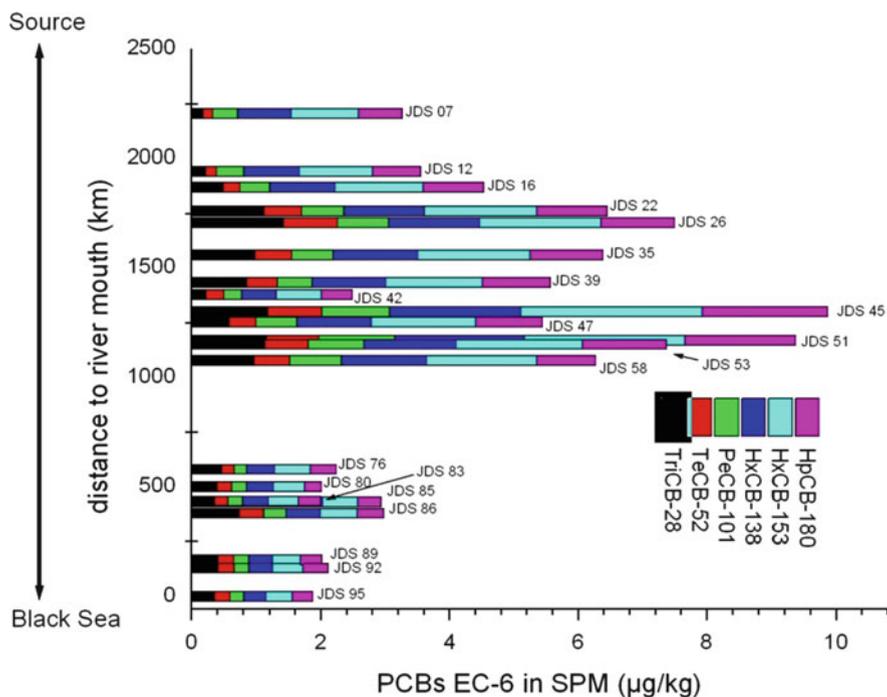
Fig. 25 Downstream concentration profile of EC-6 PCBs in SPM

EC-6 PCB Fingerprint

At average the PCB pattern in the sediments shows the typical 'aged' environmental fingerprint dominated by the higher boiling isomers of the technical mixtures. Sediments from the River Elbe [14] and the River Seine [15] show a similar distribution.

As discussed above the variability of the pattern in the sediments is much higher than in SPM. This suggests that the SPM reflects the current situation of diffuse, secondary PCB releases into the Danube, whereas the sediments reflect the historic primary inputs from different types of industrial effluents that displayed a high variability in PCB composition.

The fingerprint in mussels follows that of SPM, except for a lower abundance of PCB 28.

Mussel (Fig. 27)

For 8 sites where corresponding concentrations were available, no correlation with dissolved phase or SPM was observed for selected isomers. A slight coherence of
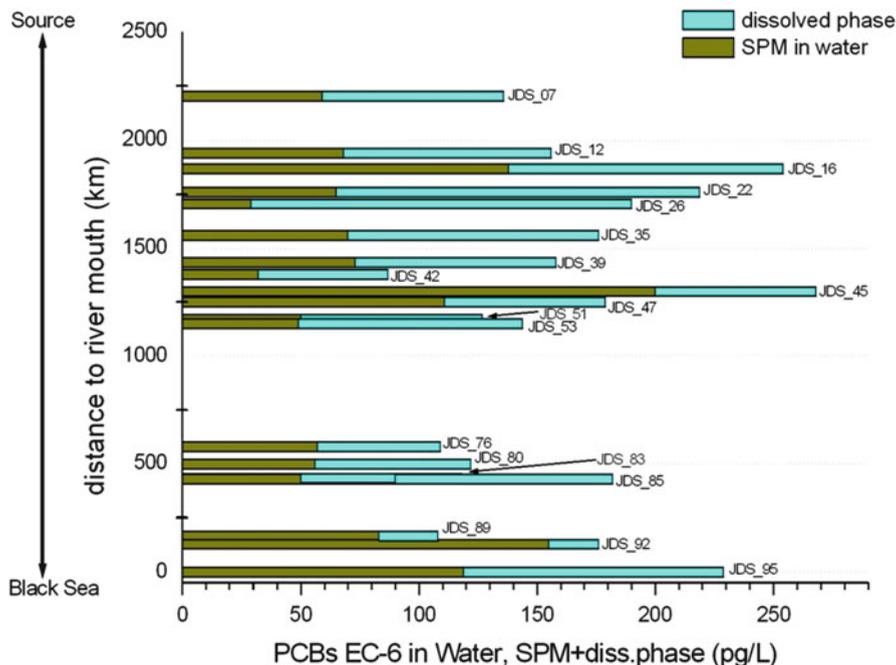
Fig. 26 Downstream concentration profile of EC-6 PCBs in water

the spatial trends was observed between *Unio tumidus* and sediment, however at a R^2 of typically below 0.2. The spatial EC-6 PCB pattern in mussels follows to some extent the concentration decrease in the sediments between the sites JDS 15 and JDS 35, as well as the subsequent concentration rise in sediment until maximum concentration at JDS 53. Subsequently the concentrations decrease both in mussels and sediment.

3.12 Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans

3.12.1 Overview on All Matrices

PCDD/Fs were quantified at all sites (Table 10, Fig. 28). Most sediment samples display moderate TEQs at an average of 2.8 ng/kg WHO-TEQ, with an isolated maximum level of 21 ng/kg WHO-TEQ (21 ng/kg I-TEQ) at site JDS 53 on the left-hand side downstream Pancevo (RS). This has been the only site where the safe sediment level of 20 ng/kg I-TEQ was exceeded.

Similar concentration ranges in sediments were reported for the River Po showing PCDD/F concentrations between 1.3 and 13 ng/kg WHO-TEQ [19].
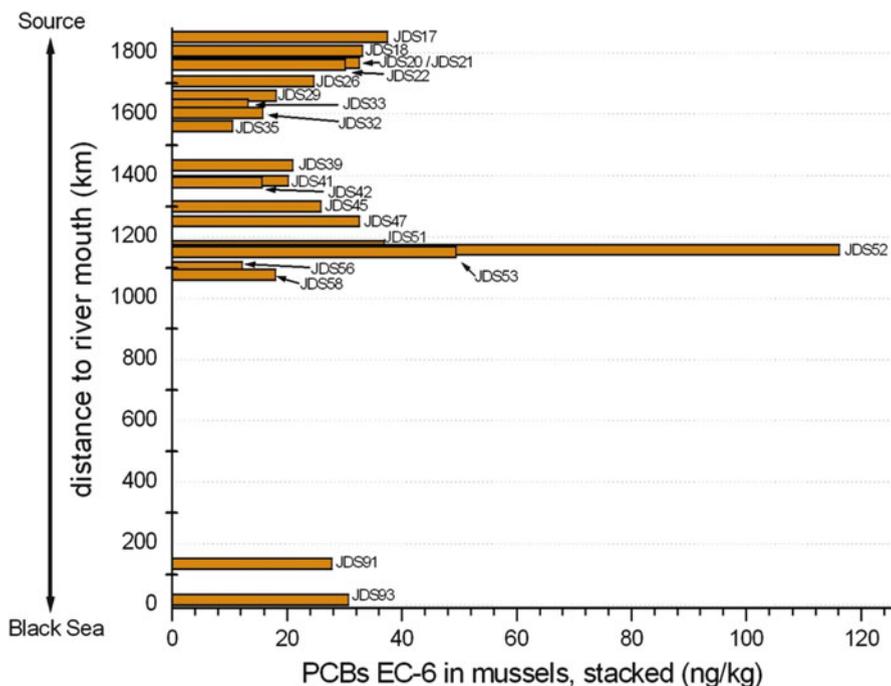
Fig. 27 Downstream concentration profile of EC-6 PCBs in mussels (all species)

Table 10 PCDD/Fs (WHO-TEQ) in all compartments

	Sediment (ng/kg)	Mussels (ng/kg)	SPM (ng/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	2.8	1.4	2.0	0.037	0.077
Median	1.9	1.3	1.6	0.032	0.072
Min	0.97	0.61	0.83	0.0094	0.049
Max	21	4.5	8.2	0.17	0.21
25-Percentile	1.4	0.94	1.1	0.021	0.061
75-Percentile	3.3	1.7	2.4	0.041	0.081

Levels in sediments of the River Elbe are typically around 40–80 ng/kg WHO-TEQ in the more industrialised stretches and around 5–10 ng/kg WHO-TEQ along stretches with diffuse inputs [20–23].

Concentrations in SPM were slightly lower than in sediments with an average of 2.0 ng/kg WHO-TEQ and a maximum of 8.2 ng/kg WHO-TEQ at site JDS 45 (HR/RS) downstream the confluence of the River Drava.

In the water column, no PCDD/Fs were detected in the dissolved phase. LOD for PCDD/Fs on a WHO-TEQ base was 0.039 pg/L in the dissolved phase, which is at the range of the average concentration in water associated with SPM. In the water
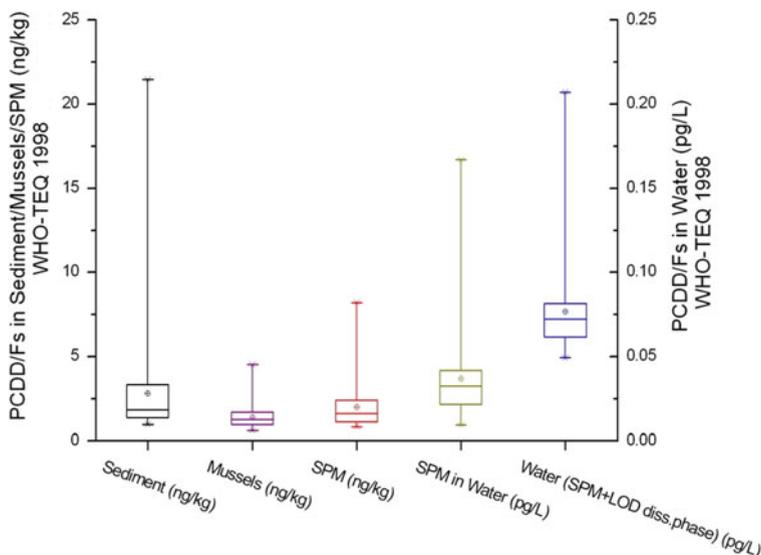
Fig. 28 PCDD/F concentrations in all compartments

phase, PCDD/Fs are predominantly associated with SPM [24], which means that the average value 0.037 pg/L WHO-TEQ derived from the quantification based on SPM should fairly reflect the total concentration in the water column.

However, a theoretical upper bound calculation for the total PCDD/F TEQ concentration in water taking into consideration the LODs in the dissolved phase is given in Fig. 28.

In the mussels the PCDD/F concentration on a TEQ base was lower compared to SPM and sediments suggesting a lower bioavailability as observed for the $\sum$EC-6 PCBs above.

3.12.2   Downstream Concentration Profile

Sediment (Fig. 29)

The downstream concentration profile of PCDD/Fs in the sediments shows only few extremes and in most cases no interpretable differences between left- and right-hand side samples, which suggest input coming from various diffuse sources.

Comparably high concentrations at Site JDS 02 point again to an input from the tributary Altmuehl as observed for PAHs above. Another site with somewhat higher PCDD/F concentrations on both sides of the Danube was at JDS 39 (HU), which had displayed highest PCP (known for containing impurities of PCDD/Fs) result during JDS 1. Maximum TEQ concentrations in sediment of 21 ng/kg were detected
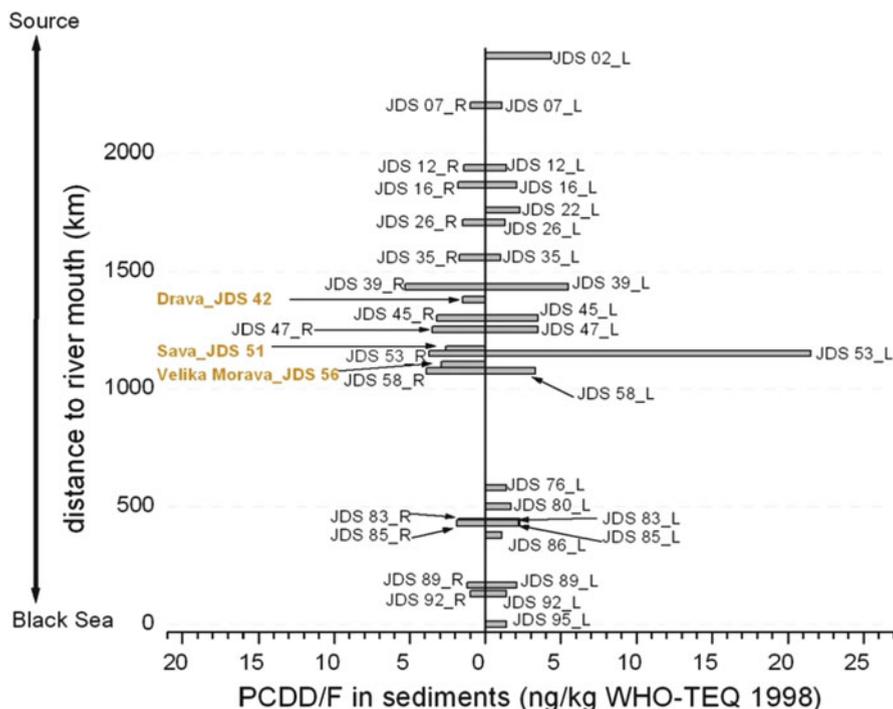
Fig. 29 Downstream TEQ profile of PCDD/Fs in sediments

at JDS 53 (RS) on the left-hand side downstream of Pancevo and River Sava. The site had shown a high abundance of EC6- and DL-PCBs as well.

As for the EC-6 PCBs, the samples taken in the 3 tributaries Drava, Sava and Velika Morava (JDS 42, JDS 51 and JDS 56, respectively) show lower levels both in sediments and SPM when compared to the Danube itself.

SPM (Fig. 30)

The downstream concentration profile in SPM shows a tendency of higher concentrations in the upper and middle stretch and lower concentrations at all sites after the Iron Gate, similar to what could be seen for PAHs and PCBs.

Noticeable is site JDS 45 (Bačka Palanka, HR/RS) where the maximum TEQ concentration of 8.2 ng/kg WHO-TEQ was detected. An influence from the tributary Drava (site JDS 42) entering 79 km upstream that site can be excluded, also due to the low PCDD/F contents in SPM measured there. The NATO air strike in 1999 was limited to The Bridge of Yough or Ilok–Bačka Palanka Bridge; therefore an impact from damaged industrial installation seems unlikely, especially since this should have left a signal in the sediment as well. The question whether the
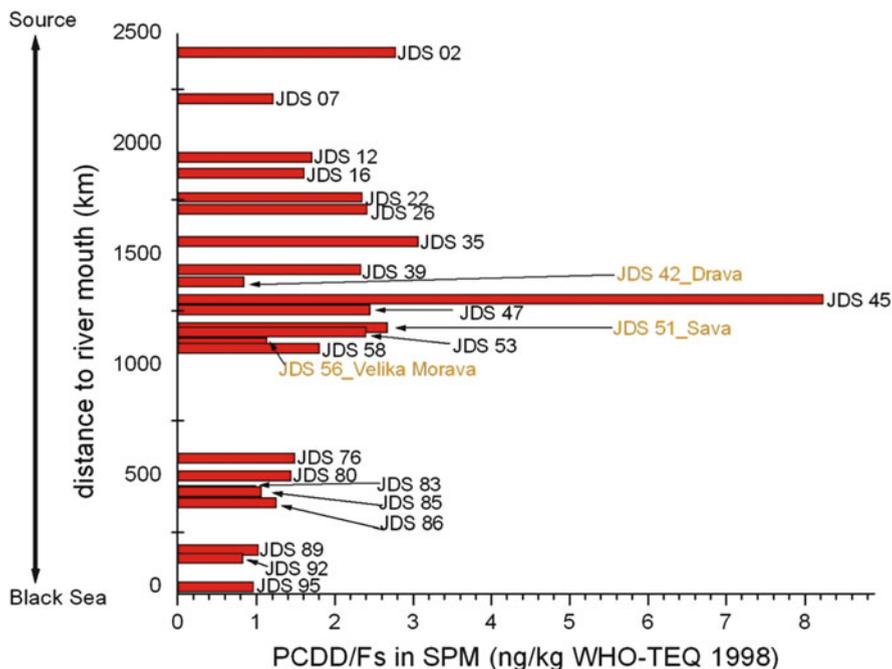
Fig. 30 Downstream TEQ profile of PCDD/Fs in SPM

local metallurgy, textiles and electronic and machine industry might release PCDD/Fs remains. Especially the metallurgic sector is known for diffuse PCDD/F emissions [25, 26].

Water (Fig. 31)

In the water column, PCDD/Fs were detected only in SPM. A slight tendency of rising concentrations towards the Black sea can be observed, as a result of higher SPM contents in the water column. However, a single maximum appears – as seen above in SPM on a dry weight base – at site JDS 45, which seems the only sampling station affected by current releases of PCDD/Fs.

Left-hand side upstream of JDS 45 is Bačka Palanka, an agricultural and industrial centre. Main industries there are food, metallurgy, textiles and electronic and machine industry.

However, the concentration at site JDS 47 only 50 km downstream of JDS 45 does not show abnormalities in PCDD/F, suggesting only a local impact of the higher PCDD/F levels around JDS 45. Also the PCDD/F contents in mussels from site JDS 45 are not peculiar (Fig. 36).
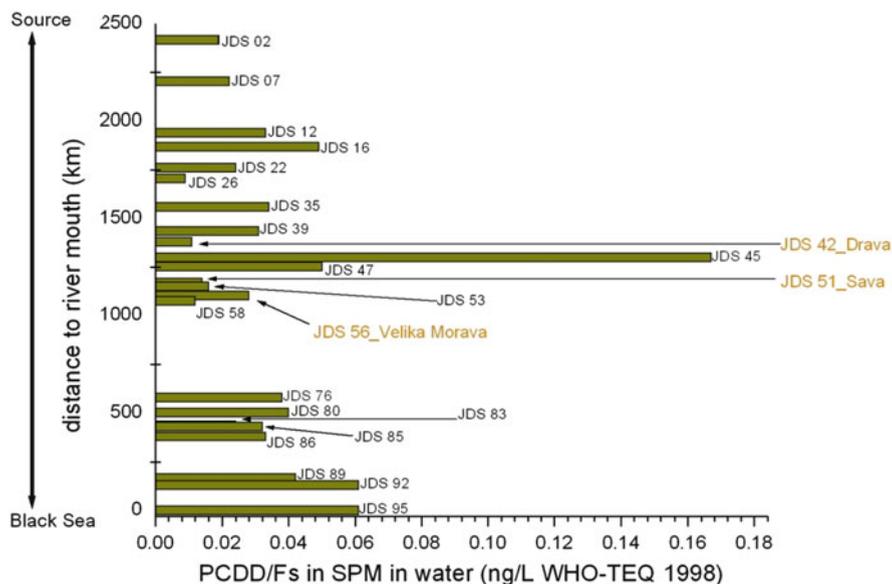
Fig. 31 Downstream TEQ profile of PCDD/Fs in water (SPM only)

PCDD/F Fingerprint

The congener pattern of 2,3,7,8-PCDD/Fs in sediments and SPM, dominated by OCDD and some minor contribution from HpCDD and OCDF, is typical for a profile altered by long-range atmospheric transport/deposition [27]. It can be found worldwide in background soils and sediments at the absence of the influence of direct emissions. Taking also into consideration the comparably low PCDD/F concentrations as discussed above, current PCDD/F emissions do not seem to affect the Danube.

3.13 Dioxin-Like Polychlorinated Biphenyls

3.13.1 Overview on All Matrices

DL-PCBs were quantified at all sites (Table 11, Fig. 32). Most sediment samples display low TEQs with an average value of 0.6 ng/kg WHO-TEQ, with maximum levels of 2.6 ng/kg at site JDS 85 on the left-hand side (downstream tributary Arges, RO) and 2 more distinctive input spots at JDS 53 (downstream tributary Tamis, RS) and JDS 02 (downstream tributary Altmuehl, DE), both on the left-hand side.

SPM samples displayed lower values with highest concentration of 1.5 ng/kg WHO-TEQ at site JDS 02 downstream tributary Altmuehl.

Table 11 DL-PCBs (WHO-TEQ) in all compartments

	Sediment (ng/kg)	Mussels (ng/kg)	SPM (ng/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	0.59	1.9	0.46	0.0091	0.0019
Median	0.49	1.5	0.42	0.0081	0.0016
Min	0.17	0.79	0.16	0.0033	0.00083
Max	2.63	8.1	1.53	0.021	0.0042
25-Percentile	0.29	1.2	0.22	0.0061	0.0012
75-Percentile	0.64	2.2	0.60	0.011	0.0024
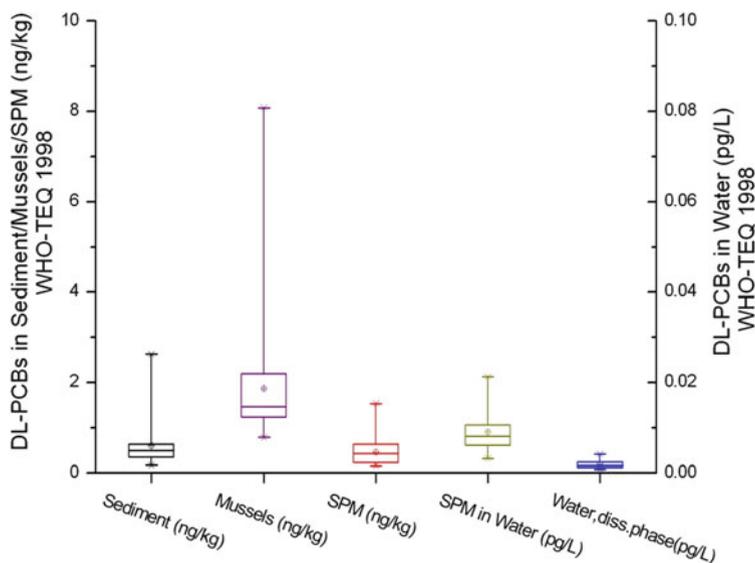
Fig. 32 DL-PCB concentration in all compartments

The low overall contribution of DL-PCBs of less than 20% to the combined PCDD/F and DL-PCB-TEQ in SPM and sediments of the Danube is typical for surface waters without significant impact of industrial discharges and reflects the situation in atmospheric deposition.

In the water column, DL-PCBs were detected predominately associated with SPM at an average TEQ level of around 10 fg/L. In the dissolved phase, the average WHO-TEQ was five times lower.

In mussels the average concentration of DL-PCBs was close to 2 ng/kg. DL-PCBs in mussel contributes a higher share to the combined TEQ of PCDD/Fs and DL-PCBs than in the sediments and SPM samples. In some cases the TEQ contribution from the DL-PCBs was even higher (compare section on PCDD/Fs).

DL-PCBs bioconcentrate in mussel (this observation is mainly based on PCB 126, which dominates the PCB-TEQ). Bioconcentration factors for sediment/mussel were typically around 4 on a dry weight basis, similar to those observed for the $\sum$EC-6 PCBs

3.13.2 Downstream Concentration Profile

Sediment (Fig. 33)

The downstream concentration profile of DL-PCBs (on a TEQ basis), dominated by inputs from the left-hand side of the catchment, is very similar to those of the EC-6 PCBs discussed above, except for a stronger signal at JDS 2 (DE) under the influence of the tributary Altmuehl. On a concentration basis, the maximum in sediments was found at site JDS 7.

Two more noticeable sites with higher TEQs were the left-hand side sediments from JDS 53 (RS, downstream Pancevo) and JDS 85 (RO, downstream the confluence of the Arges tributary from the left-hand side).
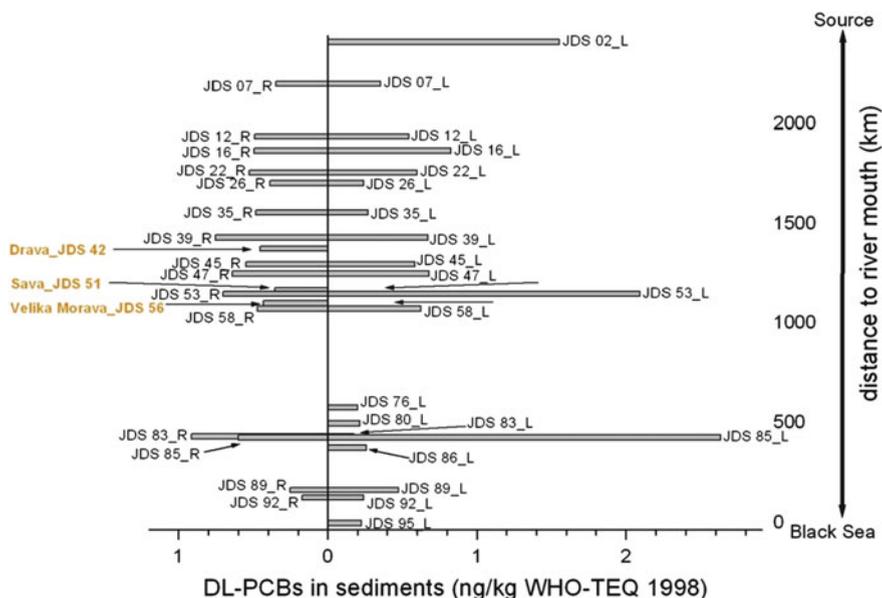

Fig. 33 Downstream TEQ profile of DL-PCBs in sediments

SPM (Fig. 34)

As seen for the PCDD/F and EC-6 PCBs, the concentration in DL-PCBs in SPM and water does not follow the spatial pattern in the sediments.

Higher concentrations up to 1.5 ng/kg WHO-TEQ appear upstream river km 1,000 while the concentrations downstream the Iron Gate are constantly below 0.25 ng/kg WHO-TEQ. The maximum concentration at JDS 02 (DE) under the influence of the tributary Altmuehl was at the concentration level of the corresponding sediment sample.

Water (Fig. 35)

In water the SPM-associated portion of the DL-PCBs dominates the TEQ. Low impacts can be seen from the tributaries Drava and Sava, while the River Velika Morava displayed higher concentrations. The high TEQ at site JDS 45 (SR) corresponds to the maxima in water observed for PCDD/Fs and EC-6 PCB. Since the upstream tributary Drava displayed low concentrations of PCDD/Fs and PCBs, the sudden rise at JDS 45 (HR/RS) suggests an influence from Bačka Palanka, an agricultural and industrial centre located on the left-hand side upstream
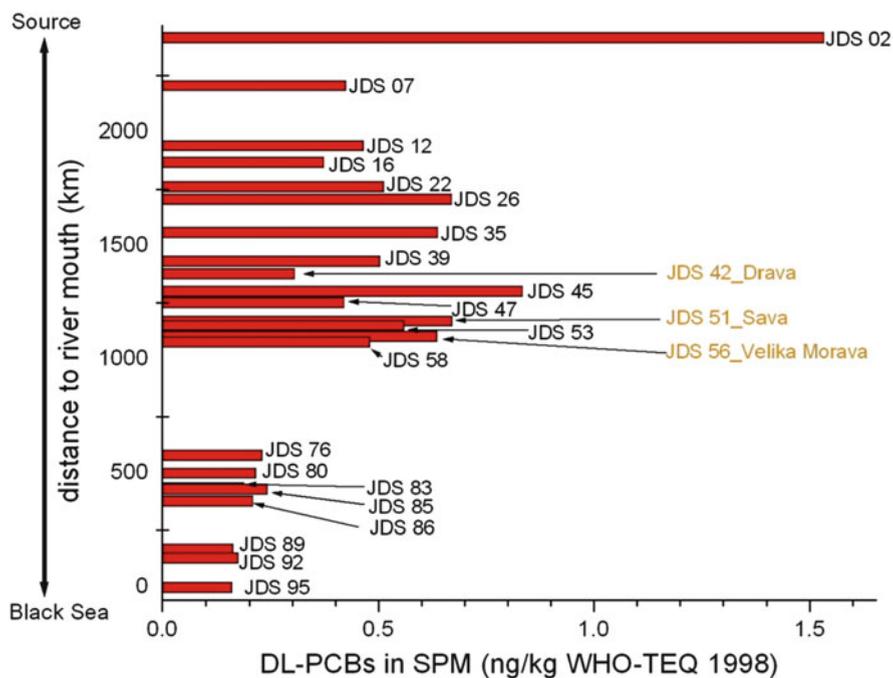

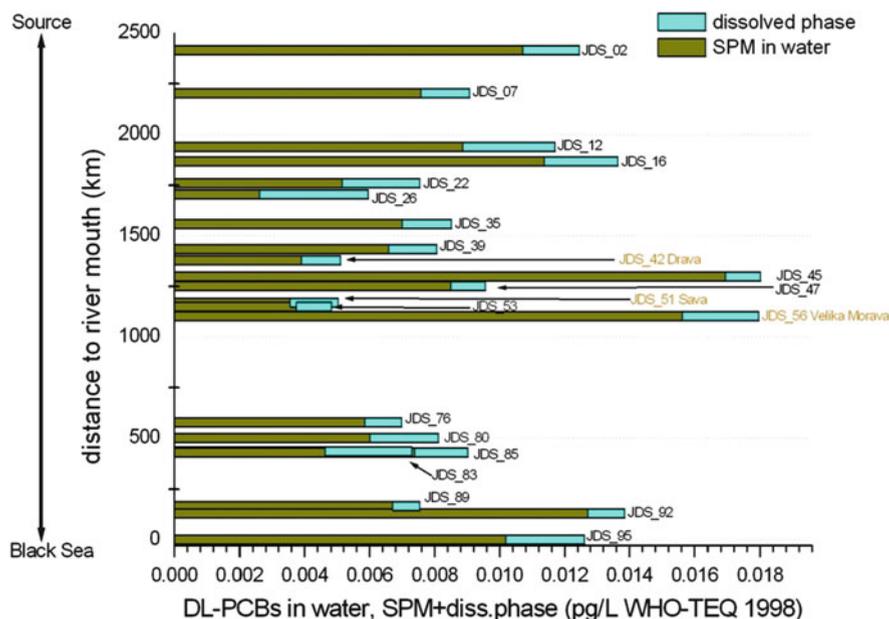**Fig. 34** Downstream TEQ profile of DL-PCBs in SPM

Fig. 35 Downstream TEQ profile of DL-PCBs in water

of JDS 45. Main industries there are food, metallurgy, textiles and electronic and machine industry.

3.13.3 Combined PCDD/Fs and DL-PCB-TEQ in Mussels

Although DL-PCBs displayed TEQs lower than PCDD/Fs in all abiotic matrices (Figs. 28 and 32), they contribute a significant portion to the combined TEQ in mussel (Fig. 36).

At sites JDS 52 and JDS 53, the sites with the highest combined TEQ, the toxicity arising from the DL-PCBs dominates.

According to our information, mussel products from the Danube are not marketed. It is noticeable, however, that at JDS 53, a stretch where higher PCDD/F and DL-PCB-TEQs were observed, the mussels exceeded the EU maximum level of 8 pg/g WHO-PCDD/F-PCB-TEQ for fish products [28].

Unfortunately it had not been possible to obtain mussel samples for most of the sites where abiotic samples were taken. For eight sites where corresponding concentrations were available, no correlation with dissolved phase or SPM was observed. A slight coherence of the spatial trends was observed between *Unio tumidus* and sediment, however at a R^2 of typically below 0.3.
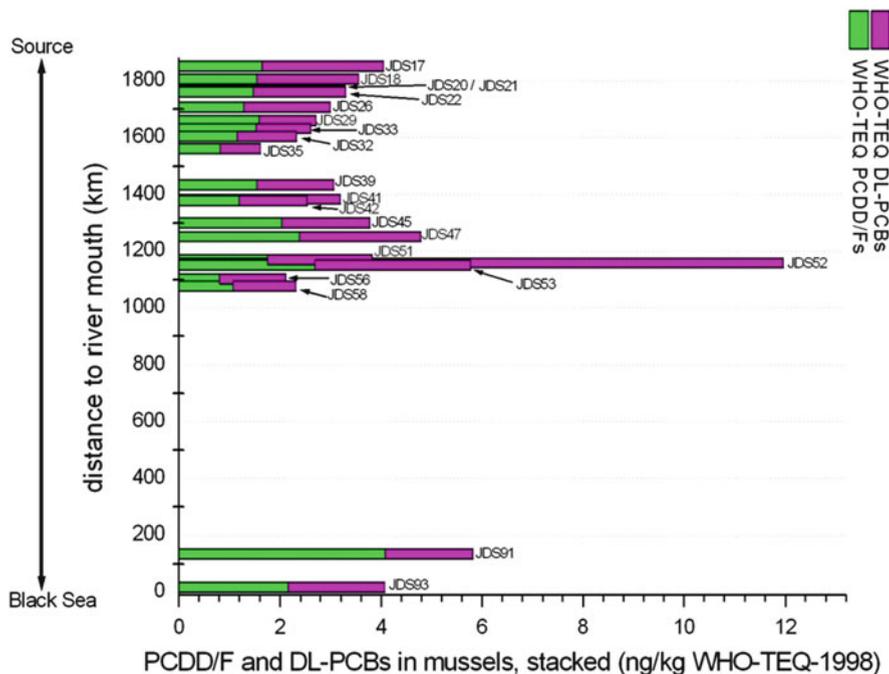
Fig. 36 Downstream TEQ profile of combined PCDD/F and PCB-TEQ in mussels (all species)

3.14 Polybrominated Diphenyl Ethers

PBDEs were quantified at all sites. Among the PBDEs measured in sediments, SPM and in the water samples, Deca-BDE dominated the pattern by far.

In the downstream profile, PBDEs in general displayed bigger and more consistent concentration gradients than PAHs and PCDD/Fs, suggesting a more recent emission history for this compound class.

3.14.1 Overview on All Matrices

Commercial Penta BDE (cPenta-BDE) (Fig. 37, Table 12)

The cPenta-BDE mixture is reported below as $\sum$BDE 28, 47, 99, 100, 153 and 154. In sediment cPenta-BDE concentrations averaged at 0.47 µg/kg. Average cPenta-BDE concentrations in SPM were somewhat higher at 0.60 µg/kg with a maximum level of 1.8 µg/kg.

In water cPenta-BDE was mainly associated with the dissolved phase. Among the PBDEs, only the cPenta mixture is regulated by the Water Framework Directive. Average cPenta-BDE concentrations in water (dissolved phase + SPM) were
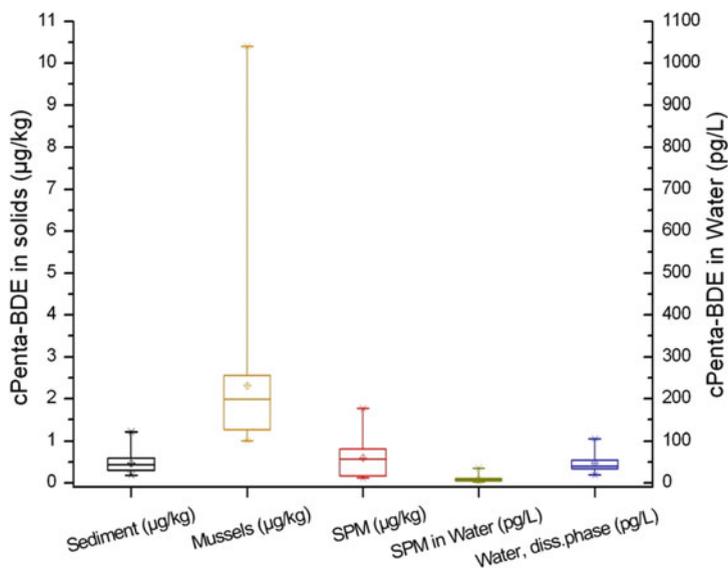
Fig. 37 cPenta-BDE concentrations in all compartments

Table 12 cPenta-BDE concentrations in all compartments

	Sediment (µg/kg)	Mussels (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	0.47	2.3	0.60	9.0	47
Median	0.43	2.0	0.54	7.5	40
Min	0.19	1.0	0.12	2.8	19
Max	1.2	10	1.77	36	105
25-Percentile	0.30	1.3	0.17	5.1	31
75-Percentile	0.59	2.5	0.80	10	54

57 pg/L with a maximum level of 121 pg/L, which is still fairly below the EQS of 500 pg/L. However, the PBDEs being among the 'emerging POPs' require future surveillance in the Danube, since future releases into the environment can be expected from many products.

cPenta-BDE in water was more associated with the dissolved phase when compared with PAHs and PCDD/Fs having similar Ko/w values, which suggests release from products and process effluents rather than from atmospheric sources where the association with carbon-containing particulates reduces the availability for redistribution in the environment.

The bioconcentration factor for mussels/solids is in the range observed for the EC-6 PCBs (Fig. 23) and DL-PCBs (Table 9).

Commercial Octa-BDE Mixture (cOcta-BDE) (Fig. 38, Table 13)

The cOcta-BDE mixture is reported below as ∑of BDE 183, 196, 197, 203.

Average concentrations of cOcta-BDE in SPM were 0.17 µg/kg with maximum levels of 0.49 µg/kg at site JDS 45 (HR/RS). Sediments displayed almost identical values.

In the water column, cOcta-BDE SPM is more strongly associated with SPM than the cPenta mixture.
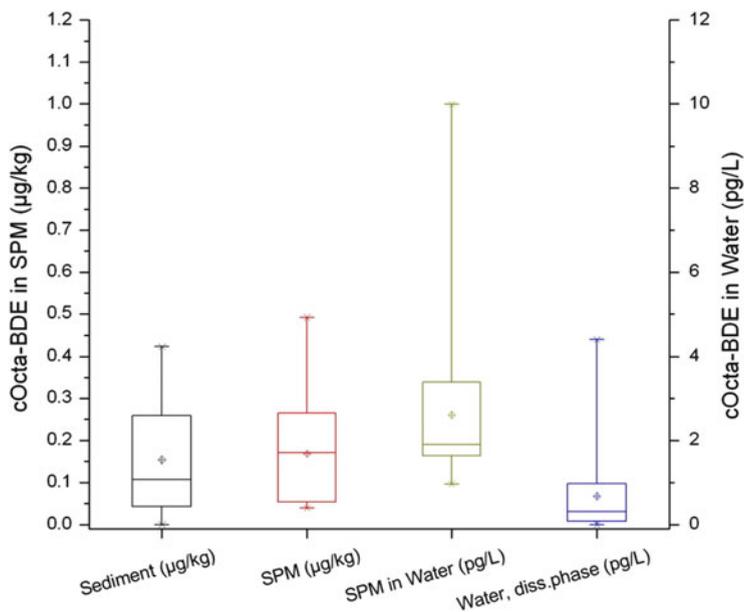

Fig. 38 cOcta-BDE concentrations in all abiotic compartments

Table 13 cOcta-BDE concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	0.15	0.17	2.6	0.68
Median	0.11	0.15	1.8	0.31
Min	0	0.04	0.97	0
Max	0.42	0.49	10	4.4
25-Percentile	0.042	0.06	1.6	0.04
75-Percentile	0.26	0.26	3.2	0.84

Commercial Deca-BDE Mixture (cDeca-BDE) (Fig. 39, Table 14)

The cDeca-BDE mixture is reported below as ∑BDE 206, 207, 208 and 209.

Average concentrations of cDeca-BDE in SPM were 15 µg/kg with maximum levels of 56 µg/kg at site JDS 45 (HR).

In the sediment samples, average and maximum concentrations were slightly lower as for SPM. The concentration levels observed in this study are around one order of magnitude lower than in SPM collected in various rivers in the Netherlands, where a median of 71 µg/kg and a range of 9–4,600 µg/kg were reported by [29].
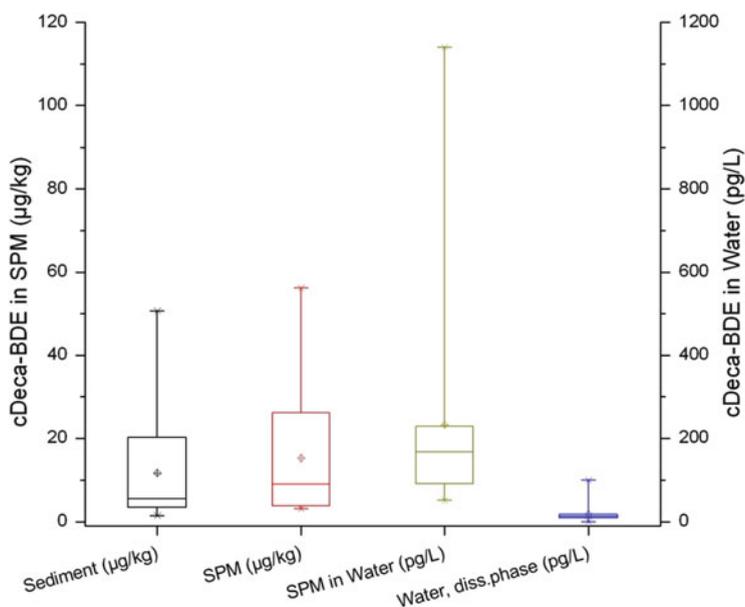

Fig. 39 cDeca-BDE concentrations in all abiotic compartments

Table 14 cDeca-BDE concentrations in all abiotic compartments

	Sediment (µg/kg)	SPM (µg/kg)	Water SPM (pg/L)	Water dissolved (pg/L)
Average	12	15.3	232	19.1
Median	5.6	7.6	162	12.5
Min	1.5	3.1	51	0.0
Max	51	56.2	1,140	100.2
25-Percentile	3.5	3.9	94	8.4
75-Percentile	18	26.1	224	17.1

In water the average concentration of cDeca-BDE was 251 pg/L, and the maximum was 1,163 pg/L at site JDS 45 (HR). In the water column cDeca-BDE was almost exclusively associated with SPM.

3.14.2 Downstream Concentration Profile

Sediment (Fig. 40)

The zone of comparably high PBDE concentrations in sediment appears on the right-hand side in the stretch between km 1,560 (JDS 35, HU) and km 1,077 (JDS 58, RS), with a maximum in the tributary Drava.

The downstream sediment data suggests PBDEs are entering from the right-hand side of the catchment, the tributaries Drava and Velika Morava being important contributors.
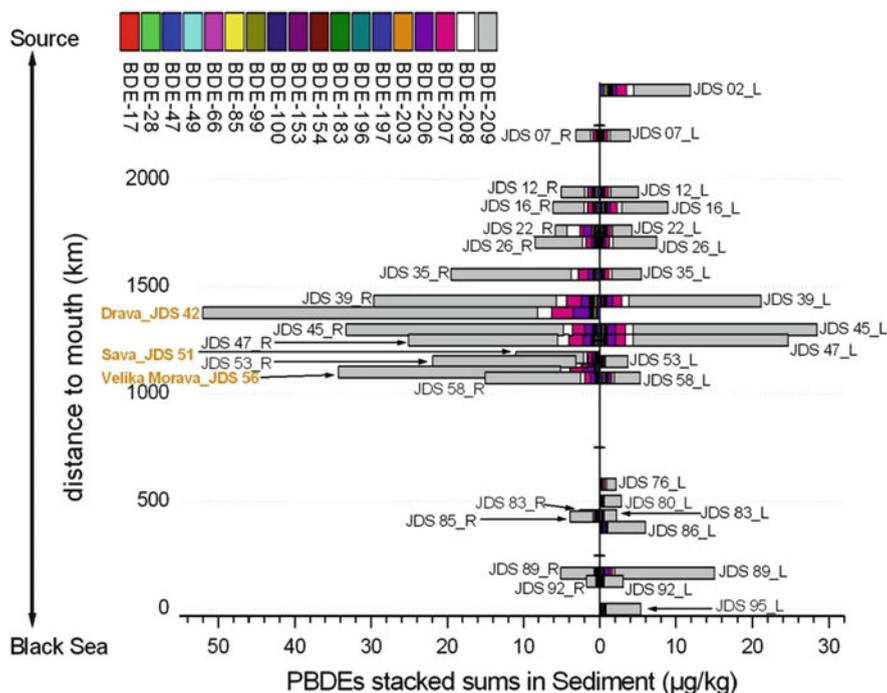

Fig. 40 Downstream concentration profile of PBDEs in sediments

SPM (Fig. 41)

In SPM the ∑PBDEs is agglomerated along the same stretch where high values in the sediment were detected. Highest concentrations were found at site JDS 45 (HR/RS) downstream Bačka Palanka and the confluence of River Drava. Compared to the sediment data, the PBDE composition in SPM displays some more contribution from lower boiling PBDEs.

Water (Fig. 42)

Similar as seen for SPM and sediment, the zone of maximal PBDE concentration in water is agglomerated in the middle stretch between km 1,252 (JDS 47, downstream Novi Sad, RS) and km 1,077 (JDS 58, RS). No particular impact from the River Drava (JDS 42) occurred during the sampling of the water, most probably due to the overall low water levels (and consequently low SPM mobilisation) during the sampling campaign.

The PBDE analysed in water is dominated by BDE 209, and consequently the major share of the ∑PBDE is associated with SPM, except in the stretch between JDS 35 and JDS 07 where the dissolved phase dominates the total concentration in water and where the highest absolute concentrations in the dissolved phase were detected (Fig. 43).
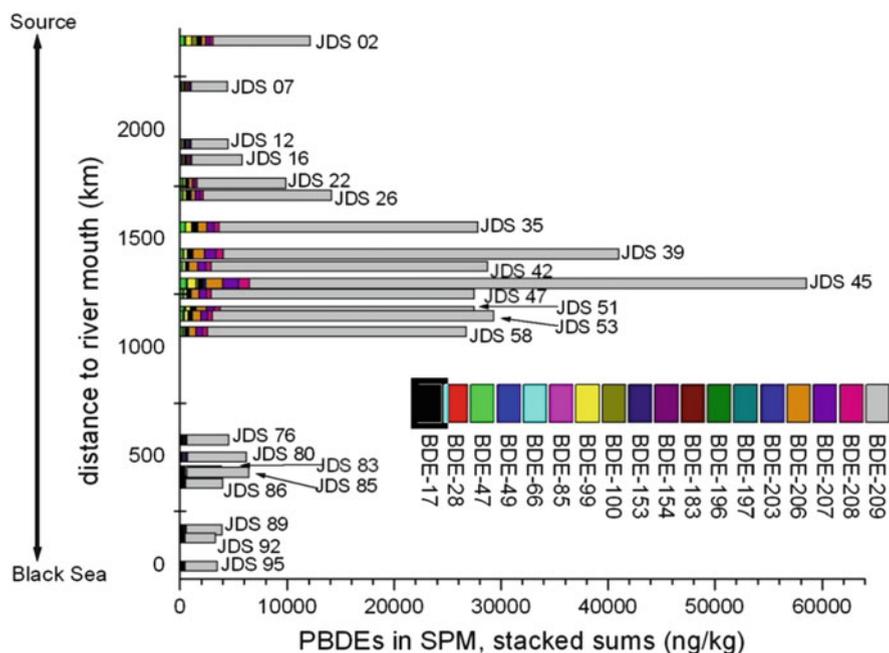

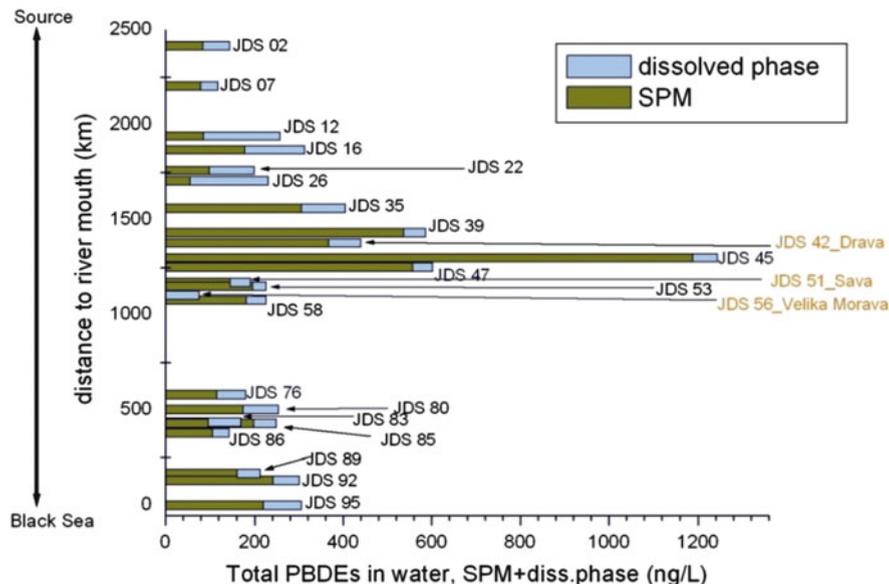Fig. 41 Downstream concentration profile of PBDEs in SPM

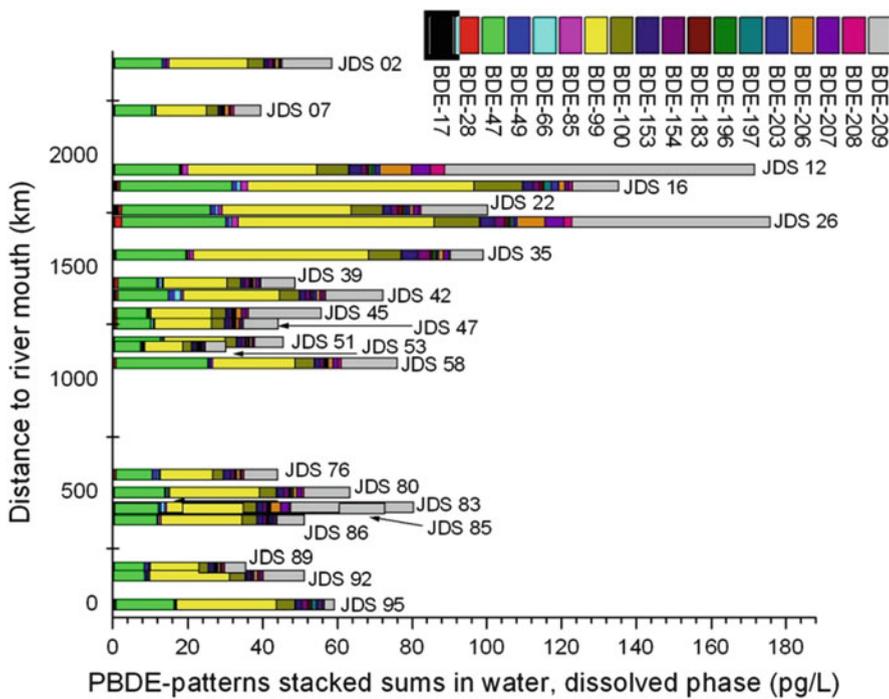**Fig. 42** Downstream concentration profile of PBDEs in water

Fig. 43 Downstream concentration profile of PBDEs in dissolved phase

The dissolved-phase isomer pattern is dominated by BDE 47, BDE 99 and BDE 209. The high Ko/w of the Deca-BDE suggests that its presence in the apparent dissolved-phase fraction is not a truly dissolved fraction but adsorbed to colloidal organic matter [30].

The PBDE concentrations detected in sediments, SPM and in the water column suggest an important impact from the catchments of the tributaries Drava, Sava and Velika Morava all entering River Danube from the right-hand side. These tributaries displayed a diluting effect instead for PAHs, PCBs and PCDD/Fs. The zone of maximal PBDE concentration is agglomerated around a 500 km stretch. In contrast to PCBs, PAHs and PCDD/Fs, we got a clear spatial signal for PBDE and a good spatial overlap between sediments (historic signal) and the water column (current signal). This suggests recent and ongoing emissions for PBDEs in this region.

Mussel (Fig. 44)

The downstream concentration pattern of the cPenta-BDE mixture in the mussel samples does not reflect the situation in the sediments, SPM and water except for a general trend of lower concentrations in the lower Danube.
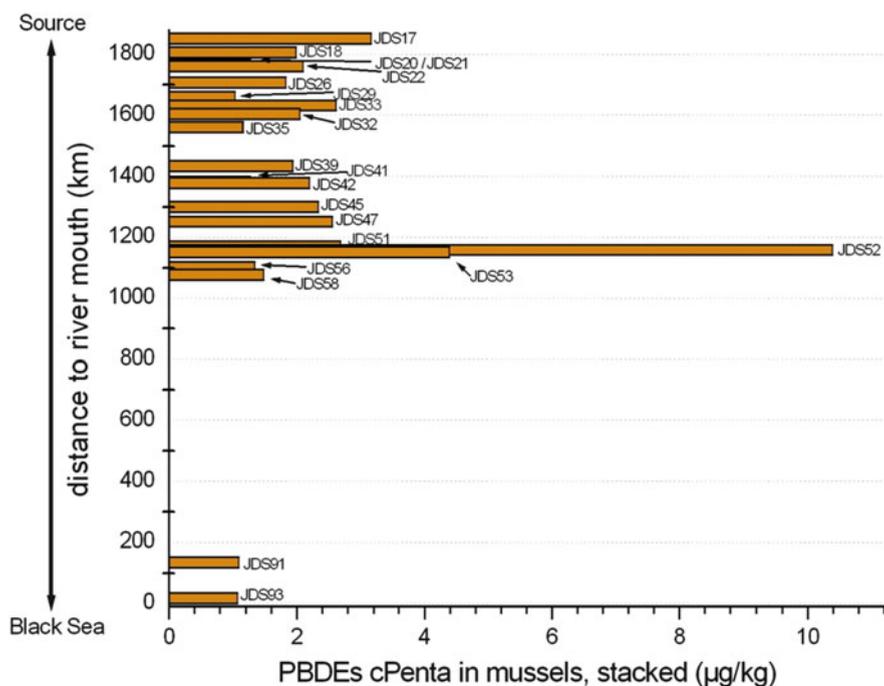

Fig. 44 Downstream concentration profile of cPenta-BDE in mussels (various species)

The isolated concentration maximum in mussel at site JDS 52, followed by the second highest concentration further downstream at JDS 53, lies within the zone where high PBDE levels were detected also in the sediments. But mussel samples taken more upstream do not reflect the high PBDE releases in this zone.

For eight sites where corresponding concentrations were available, no correlation with dissolved phase, SPM or sediment was observed except for BDE 47 in the sediments that correlated with the *Unio tumidus* at R^2 of 0.47.

4 Summary

4.1 Indication of the Chemical Status of the Water Column During the JDS 2 Cruise

From the available data of the 23 sites analysed, EQS set by the Directive 2008/105/EC were not exceeded for most of the following compound classes:

PAHs, where most of the PAHs in water samples of all 23 sites were far below the WFD-AA-EQS values and values in sediments, were about one order of magnitude lower than typically found in the River Elbe. Only for the $\sum$benzo(g,h,i) perylene and indeno(1,2,3-cd)pyrene concentrations at most sites were close to the EQS of 2 ng/L. In five sites the EQS was exceeded, namely, at sampling stations JDS 02, 16, 39, 92 and 95.

OCPs, where most compounds in the water column were orders of magnitude below the EQS and only HCH displayed some isolated maxima in the lower stretch, which however were still a factor of 4 below the MAC-EQS.

PCDD/Fs and dioxin-like PCBs, which were more than one order of magnitude lower in all compartments compared to River Elbe and in which only one site exceeded slightly the 'safe sediment value' for PCDD/Fs.

EC-6 PCBs, which were not exceeding the related German quality standards in sediment.

PBDEs, where concentrations in SPM were an order of magnitude lower than in Dutch rivers for c-Deca-BDE and where cPenta-BDE was around a factor of 5 below the EQS value in all water samples.

4.2 Spatial Distribution: Downstream Concentration Profiles

The concentration profiles in the sediments downstream the Danube suggest that PAHs and PCDD/Fs arise from diffuse sources, whereas PBDEs (currently) and PCBs (historically) display distinct zones of contamination. This fits into the picture of PAHs and PCDD/Fs as combustion by-products being dispersed mainly into the atmosphere, whereas 'intentionally produced industrial chemicals' such as PCBs and PBDEs arise from punctual emissions through industrial and urban effluents.

Among the OCPs in water, DDT and metabolites as well as HCHs displayed rising concentrations towards the Black Sea. HCB and the cyclodiene pesticides displayed no expressed spatial trend, and endosulfan concentrations decreased downstream the Danube.

The comparison of left and right bank sediment data suggests a diffuse emission from both sides of the catchment for PAHs. PCDD/Fs and PCBs and OCPs (except DDT and metabolites) show some distinct signals from the left bank while the PBDEs are emitted from the right bank of the catchment.

Only PBDEs show a clear impact from the tributaries Drava, Sava and Velika Morava all entering River Danube from the right bank, whereas for the other compound classes reported here, these tributaries displayed a diluting effect.

For most compounds, the memory contained in the sediments is scarcely reflected by the data in the water column, where the spatial gradients are less pronounced and maxima appear often at different sites than in the sediments. This underlines the historic character of many of the findings in the sediments. Exceptions were PBDEs, the most recent class of chemicals investigated in this study, and DDT and metabolites.

In order to assess the current situation of pollutant releases into the River Danube and to localise their current sources, temporarily resolved water column data from the whole watershed are desirable.

4.3 Mussels

For EC-6 PCBs, dioxins, DL-PCBs and cPenta-BDE, the downstream concentration profiles in the mussels do not show particular gradients that would exceed the inner- and interspecies deviations. The only exception with higher levels that exceeds the inner- and interspecies variability was at JDS 52, where all compound classes displayed a distinct maximum. However, from this site, no samples from the other compartments were available for this study.

The lack of correlation between the concentration in mussels and the other compartments at the sites where all matrices were sampled suggests a poor suitability of mussels as an indicator for spatial trends of SOCs in the Danube.

References

1. Iannuzzi TJ, Bonnevie NL, Wenning RJ (1995) An evaluation of current methods for developing sediment quality guidelines for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Arch Environ Contam Toxicol 28:366–377

2. Evers EHG, Laane RWPM, Groeneveld GJJ, Olie K (1996) Levels, temporal trends and risk of dioxins and related compounds in the Dutch aquatic environment. Organohalogen Compd 28:117–122

3. Directive 2003/11/EC of the European parliament and of the council of February 2003 amending for 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). Official Journal L42

4. Olivella MA (2006) Isolation and analysis of polycyclic aromatic hydrocarbons from natural water using accelerated solvent extraction followed by gas chromatography-mass spectrometry. Talanta 69:267–275

5. Covaci A, Voorspoels S, de Boer J (2003) Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDE) in environmental and human samples: a review. Environ Int 29:735–756

6. Pirard C, De Pauw E, Focant JF (2003) New strategy for comprehensive analysis of polybrominated diphenyl ethers, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzo-furans and polychlorinated biphenyls by gas chromatography coupled with mass spectrometry. J Chromatogr A 998:169–181

7. Thomsen C, Nicolaysen T, Broadwell SL, Huag LS, Becher G (2004) Simultaneous extraction of PCDDs/PCDFs, PCBs and PBDE: extension of a sample preparation method for determination of PCDDs/PCDFs. Organohalogen Compd 66:145–152

8. Abad E, Saulo J, Caixach J, Rivera J (2000) Evaluation of a new automated cleanup system for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in environmental samples. J Chromatogr A 893:383–391

9. Sjödin A, Jakobsson E, Kierkegaard A, Marsh G, Sellström U (1998) Gas chromatographic identification and quantification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE. J Chromatogr A 822:83–89

10. Björklund J, Tollbäck P, Dyremark E, Hiärne C, Östman C (2004) Influence of the injection technique and the column system on fast chromatographic determination of polybrominated diphenyl ethers. J Chromatogr A 1041:201–210

11. Korytár P, Covaci A, de Boer J, Gelbin A, Brinkman UAT (2005) Retention-time database of 126 polybrominated diphenyl ether congeners and two Bromkal technical mixtures on seven capillary gas chromatographic columns. J Chromatogr A 1065:239–249

12. Van Den Berg M, Birnbaum L et al (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 106(12):775–792

13. Literathy P, Pavonic M, Ocenaskova V (2008) PAH and petroleum hydrocarbon contamination in water, suspended particulate matter, sediments and biota. In: Liska I, Wagner F, Slobodnik J (eds) Joint Danube survey 2 – final scientific report. ICPDR – International Commission for the Protection of the Danube River, Vienna, pp 147–153. http://www.icpdr.org/main/activities-projects/joint-danube-survey-2

14. Bergemann M, Gaumert T, Wasserguetestelle Elbe, Hamburg 2008. http://www.fgg-elbe.de/dokumente/gewaesserguete.html

15. Chailleaud K, Forget-Leray J, Souissi S, Hilde D, LeMenach K, Budzinski H (2007) Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species *Eurytemora affinis* (Calanoïd, copepod). Part 1: PCBs and PAHs. Chemosphere 70:270–280

16. Keiter S, Grund S, van Bavel B, Hagberg J, Engwall M, Kammann U, Klempt M, Manz W, Olsman H, Braunbeck T, Hollert H (2008) Activities and identification of aryl hydrocarbon receptor agonists in sediments from the Danube River. Anal Bioanal Chem 390:2009–2019

17. Mariani G, Skejo H, Mueller A, Stachel B, Umlauf G (2011) HCHs in solid matter from the River Elbe, its tributaries and the North Sea. Organohalogen Compd 73:1884–1887

18. Covaci A, Bervoets L, Hoff P, Voorspoels S, Voets J, Van Campenhout K, Blust R, Schepens P (2005) Polybrominated diphenyl ethers (PBDEs) in freshwater mussels and fish from Flanders, Belgium. J Environ Monit 2005(7):132–136

19. Fattore E, Vigano L, Mariani G, Guzzi A, Benfenati E, Fanelli R (2002) Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in River Po sediments. Chemosphere 71:1156–1161
20. Stachel B, Jantzen E, Knoth W, Krueger F, Lepom P, Oetken M, Reincke H, Sawal G, Schwartz S, Uhlig S (2005) The Elbe flood in August 2002—organic contaminants in sediment samples taken after the flood event. J Environ Sci Health A 40(2):265–287
21. Umlauf G, Christoph E, Bidoglio G (2004) Dioxin- und Quecksilberanalysen an ausgewaehlten Proben aus den Ueberschwemmungsgebieten. In: Geller W, Ockenfeld K, Boehme M, Knoechel A (eds) Schadstoffbelastung nach dem Elbe-Hochwasser 2002. Endbericht des Ad-hocVerbundprojekts BMBF Foerderkennzeichen PTJ 033049. ISBN:3-00-0136615-0. http://www.ufz.de/data/HWEnd1333.pdf
22. Umlauf G, Bidoglio G, Christoph E, Kampheus J, Krueger F, Landmann D, Schulz AJ, Schwartz R, Severin K, Stachel B, Stehr D (2005) The situation of PCDD/Fs and dioxin-like PCBs after the flooding of River Elbe and Mulde in 2002. Acta Hydrochim Hydrobiol 33 (5):543–554, Special Issue: Displacement of Pollutants during the River Elbe Flood in August 2002
23. Umlauf G, Mariani G, Skejo H, Mueller A, Baek L, Stachel B, Goetz R (2010) Dioxins and dioxin-like PCBs in solid material from the River Elbe, its tributaries and from the North Sea. Organohalogen Compd 72:95–99
24. Dueri S, Castro-Jimenez J, Zaldivar Comenges JM (2008) On the use of the partitioning approach to derive environmental quality standards (EQS) for persistent organic pollutants (POPs) in sediments: a review of existing data. Sci Total Environ 403:23–33
25. Buekens A, Cornelis E, Huang H, Dewettinck T (2000) Fingerprints of dioxin from thermal industrial processes. Chemosphere 40:1021–1024
26. Zhu J, Hirai Y, Yu G, Sakai S (2008) Levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in China and chemometric analysis of potential emission sources. Chemosphere 70:703–711
27. Hagenmeier H, Lindig C, She J (1994) Correlation of environmental occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans with possible sources. Chemosphere 29:2163–2174
28. Commission Regulation (EC) 1881/2006 of 19th December 2006 setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union L 364/5-24
29. de Boer J, Wester PG, van der Horst A, Leonards PEG (2003) Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands. Environ Pollut 122:63–74
30. Zarnadze A, Rodenburg LA (2008) Water-column concentrations and partitioning of polybrominated diphenyl ethers in the New York/New Jersey Harbor, USA. Environ Toxicol Chem 27(8):1552–8618
31. Common Position adopted by the Council with view to the adoption of a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directives 82/176/EEC, 83/513/EEC. 84/156/EEC, 84/491/EEC, 86/280//EEC and 2000/60/EEC.ANNEX I, Brussels. Accessed 29 Nov 2007
32. EPA (1994) Method 1613: tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS
33. EPA (1999) Method 1668, revision A: chlorinated biphenyl congeners in water, soil, sediment and tissue by HRGC/HRMS
34. EPA (2003) Method 1614: brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS, draft