Joint Danube Survey 2

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Summary report on:
Methods used for the analysis of priority substances and additional organic compounds

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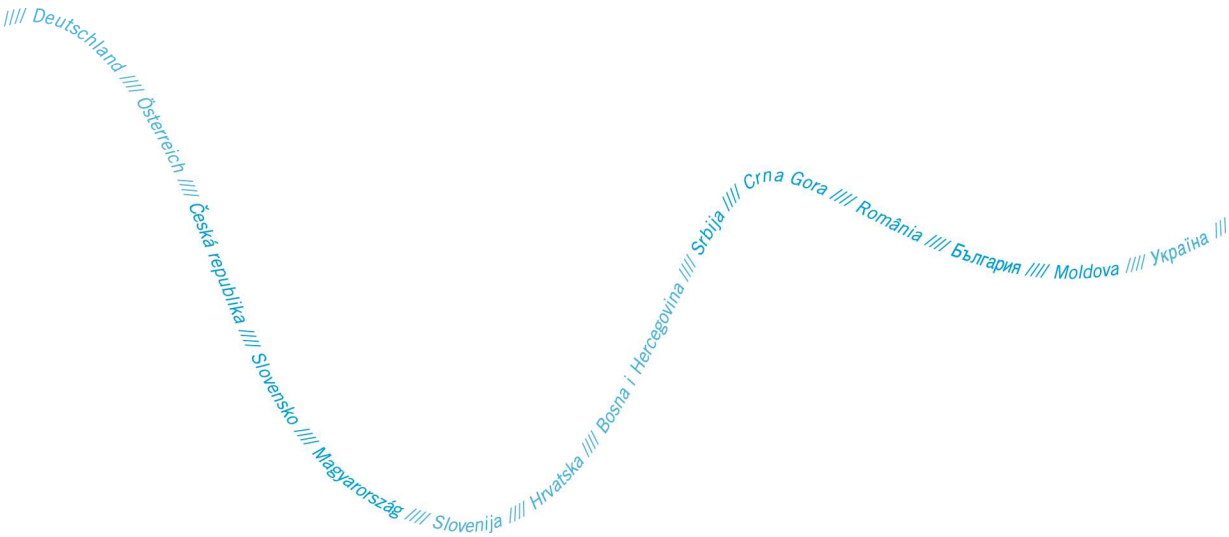
Author:
Dr. Manfred Sengl
Bavarian Environment Agency



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Contact
ICPDR Secretariat
Vienna International Centre / D0412
P.O. Box 500 / 1400 Vienna / Austria
T: +43 (1) 26060-5738 / F: +43 (1) 26060-5895
icpdr@unvienna.org / www.icpdr.org

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1 Introduction

This part of the report deals with the analytical methods applied for priority substances by the different laboratories are listed.

The following laboratories were involved:

Table 1 Laboratories, methods and limits of quantification for organic compounds

laboratory	determinand	matrix	method	unit	limit of quantification (LOQ)
WRI Prague	4-iso-nonylphenol	water	CSN EN ISO 18857-2	µg/l	0,02
WRI Prague	p-octylphenol	water	CSN EN ISO 18857-2	µg/l	0,005
TZW Karlsruhe	4-iso-nonylphenol	sed	ultrasonic extr. GC-MS	mg/kg	0,01
TZW Karlsruhe	p-octylphenol	sed	ultrasonic extr. GC-MS	mg/kg	0,005
Univ. Vienna	4-iso-nonylphenol	spm/sed	ASE, deriv., GC-MS	mg/kg	0,02
Univ. Vienna	p-octylphenol	spm/sed	ASE, deriv., GC-MS	mg/kg	0,0015
LfU Munich	4-iso-nonylphenol	spm	soxhlet, deriv., GC-MS	mg/kg	0,01
LfU Munich	p-octylphenol	spm	soxhlet, deriv., GC-MS	mg/kg	0,005
Univ. Vienna	NP1EO	spm/sed	ASE, deriv., GC-MS	mg/kg	0,02
Univ. Vienna	NP2EO	spm/sed	ASE, deriv., GC-MS	mg/kg	0,02
Univ. Vienna	OP1EO	spm/sed	ASE, deriv., GC-MS	mg/kg	0,0025
Univ. Vienna	OP2EO	spm/sed	ASE, deriv., GC-MS	mg/kg	0,003
WRI Bratislava	DEHP	water	LC-DAD	µg/l	0,2
TZW Karlsruhe	DEHP	sed	ultrasonic extr. GC-MS	mg/kg	0,01
LfU Munich	DEHP	spm	soxhlet, GC-MS	mg/kg	0,3
TZW Karlsruhe	BDE-28	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-47	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-66	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-85	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-99	sed	ASE, GC-MS	mg/kg	0,0001
TZW	BDE-100	sed	ASE, GC-MS	mg/kg	0,0001

laboratory	determinand	matrix	method	unit	limit of quantification (LOQ)
Karlsruhe					
TZW Karlsruhe	BDE-138	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-153	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-154	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-183	sed	ASE, GC-MS	mg/kg	0,0001
TZW Karlsruhe	BDE-209	sed	ASE, GC-MS	mg/kg	0,00025
WRI Bratislava	pentachlorophenol	water	SBSE, GC-MS	µg/l	0,1
TZW Karlsruhe	pentachlorophenol	sed	ultrasonic extr. GC-MS	mg/kg	0,005
WRI Prague	BDE-47	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-99	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-100	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-153	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-154	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-183	water	LLE, GC-NCI-MS	µg/l	0,002
WRI Prague	BDE-203	water	LLE, GC-NCI-MS	µg/l	0,005
WRI Prague	BDE-205	water	LLE, GC-NCI-MS	µg/l	0,005
LfU Munich	HHCB	spm	soxhlet, GC-MS	mg/kg	0,005
LfU Munich	triclosan	spm	soxhlet, GC-MS	mg/kg	0,001
LfU Munich	triclosan-methyl	spm	soxhlet, GC-MS	mg/kg	0,001
WRI Bratislava	trichloroethylene	water	ISO 10301 (HS, GC-ECD)	µg/l	1,7
WRI Bratislava	1,2-dichloroethan	water	ISO 10301 (HS, GC-ECD)	µg/l	0,7
WRI Bratislava	1,2,4-trichlorobenzene	water	ISO 10301 (HS, GC-ECD)	µg/l	0,5
WRI Bratislava	benzene	water	ISO 10301 (HS, GC-FID)	µg/l	0,3
WRI Bratislava	dichloromethane	water	ISO 10301 (HS, GC-ECD)	µg/l	0,5
WRI Bratislava	hexachlorobutadiene	water	ISO 10301 (HS, GC-ECD)	µg/l	0,1
WRI Bratislava	tetrachloroethylene	water	ISO 10301 (HS, GC-ECD)	µg/l	0,5
WRI Bratislava	tetrachloromethane	water	ISO 10301 (HS, GC-ECD)	µg/l	1,2
WRI Bratislava	trichloromethan	water	ISO 10301 (HS, GC-ECD)	µg/l	1,8
WRI Bratislava	trifluralin	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	pentachlorobenzene	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,018
WRI Bratislava	hexachlorobenzene	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,02
WRI Bratislava	p-p´-DDT	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,007
WRI	o,p-DDT	water	ISO 6486 (LLE, GC-	µg/l	0,007

laboratory	determinand	matrix	method	unit	limit of quantification (LOQ)
Bratislava			ECD)		
WRI Bratislava	p-p´-DDE	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,007
WRI Bratislava	o,p-DDE	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,007
WRI Bratislava	p-p´-DDD	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,007
WRI Bratislava	lindan	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,02
WRI Bratislava	isodrin	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	endrin	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,023
WRI Bratislava	dieldrin	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,021
WRI Bratislava	aldrin	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,01
WRI Bratislava	alpha-endosulfan	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	chlorphenvinfos	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	chlorpyriphos	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	anthracene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
WRI Bratislava	benzo(a)pyrene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002
WRI Bratislava	benzo(b)fluoranthene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
WRI Bratislava	benzo(k)fluoranthene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
WRI Bratislava	benzo(ghi)perylene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002
WRI Bratislava	indenopyrene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002
WRI Bratislava	naphthalene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,25
WRI Bratislava	PCB-8	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-28	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-52	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-101	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,003
WRI Bratislava	PCB-118	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,005
WRI Bratislava	PCB-138	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-153	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-180	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,004
WRI Bratislava	PCB-203	water	ISO 6486 (LLE, GC-ECD)	µg/l	0,003

laboratory	determinand	matrix	method	unit	limit of quantification (LOQ)
UBA Vienna	dibutyltin	water	ISO CD 17353	µg/l	0,0002
UBA Vienna	tributyltin	water	ISO CD 17353	µg/l	0,0002
UBA Vienna	tetrabutyltin	water	ISO CD 17353	µg/l	0,0002
UBA Vienna	diphenyltin	water	ISO CD 17353	µg/l	0,0002
UBA Vienna	triphenyltin	water	ISO CD 17353	µg/l	0,0002
UBA Vienna	monobutyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
UBA Vienna	dibutyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
UBA Vienna	tributyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
UBA Vienna	tetrabutyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
UBA Vienna	diphenyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
UBA Vienna	triphenyltin	sed	extr. EtOH, deriv., GC-MS	mg/kg	0,005
WRI Prague	anthracene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	benzo(a)pyrene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	benzo(b)fluoranthene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	benzo(k)fluoranthene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	benzo(ghi)perylene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	indenopyrene	sed	ASE, LC-FLD	mg/kg	0,02
WRI Prague	naphthalene	sed	ASE, LC-FLD	mg/kg	0,02
WRI Prague	fluoren	sed	ASE, LC-FLD	mg/kg	0,02
WRI Prague	pyren	sed	ASE, LC-FLD	mg/kg	0,02
WRI Prague	fluoranthene	sed	ASE, LC-FLD	mg/kg	0,04
WRI Prague	dibenzo(ah)anthracene	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	chrysen	sed	ASE, LC-FLD	mg/kg	0,01
WRI Prague	phenanthrene	sed	ASE, LC-FLD	mg/kg	0,03
WRI Prague	benzo(a)anthracene	sed	ASE, LC-FLD	mg/kg	0,01
VITUKI	alachlor	water	EN ISO 11369	µg/l	0,05
VITUKI	atrazine	water	EN ISO 11369	µg/l	0,005
VITUKI	simazine	water	EN ISO 11369	µg/l	0,01
JRC	diuron	water	SPE, LC-MS/MS	µg/l	0,001
JRC	isoproturon	water	SPE, LC-MS/MS	µg/l	0,001
JRC	terbuthylazine	water	SPE, LC-MS/MS	µg/l	0,001
JRC	desethylterbutylazine	water	SPE, LC-MS/MS	µg/l	0,001
JRC	desethylatrazine	water	SPE, LC-MS/MS	µg/l	0,001
JRC	bentazone	water	SPE, LC-MS/MS	µg/l	0,001
JRC	mecoprop	water	SPE, LC-MS/MS	µg/l	0,001
JRC	2,4-D	water	SPE, LC-MS/MS	µg/l	0,001

2 Methods

2.1 Alkylphenols and alkylphenolethoxylates

2.1.1 Alkylphenols in water (WRI Prague)

Table 2.1-1 Methods and parameters used for the determination of alkylphenols in water

Determinand	CAS No.	Unit	Method Used	Method	Limit of Quantification (LOQ)
Octylphenol	140-66-9	ng/l	GC-MS	CSN EN ISO 18857-1	5
Nonylphenol	84852-15-3	ng/l	GC-MS	CSN EN ISO 18857-1	20

The alkylphenols were extracted from water by liquid/liquid extraction with toluene as a solvent. Concentrated extracts were analysed by gas chromatography with mass selective detection in SIM mode.

To control quality of the alkylphenol determination, every batch of 20 samples included a blank extraction sample and quality control sample. The relative uncertainty of measurement is about 20 %.

Duplicate samples were analysed for comparison. The analytical results obtained for these water samples were as follows:

Table 2.1-2 Results of the alkylphenols duplicate samples

JDS 2 Code	Determinand	Sample 1	Sample 2
JDS 14	OP	< 5.0 ng/l	< 5.0 ng/l
	NP	110 ng/l	92.8 ng/l
JDS 50	OP	< 5.0 ng/l	< 5.0 ng/l
	NP	103 ng/l	133 ng/l

2.1.2 Alkylphenols and alkylphenolethoxylates in suspended particulate matter and sediments (University of Vienna, Department of Environmental Geosciences)

2.1.2.1 Analytical Method

All solvents used were of SupraSolv grade supplied by Merck KGaA (Darmstadt, Germany). Diatomaceous Earth was supplied by Dionex (Sunnyvale, CA, USA) and anhydrous sodium sulphate by Acros Organics (Geel, Belgium). 4-*n*-NP, NP1EOs, NP2EOs, OP1EO and OP2EO were purchased from Dr. Ehrenstorfer GmbH (Augsburg , Germany), iso NP and 4-*n*-NP2EO by LGC Promochem (Wesel, Germany), OP, N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and trimethylsilane iodide (TMIS) by Sigma-Aldrich (St. Louis, USA). All the glassware was rinsed with acetone (p.a grade, Acros Organics, Geel, Belgium) and then baked in a muffle furnace for 5 h at 550°C prior to use to avoid organic contamination.

Freeze-dried sediments and SPM samples were ground in a mortar and homogenized before accelerated solvent extraction (ASE).

1 g of dry sediment or SPM was mixed with Diatomaceous Earth (previously baked at 550 °C) and anhydrous Na_2SO_4 (previously baked at 550 °C and stored in a glass desiccator before use), spiked with recovery surrogate 4-*n*-NP and 4-*n*-NP2EO, and this mixture was then packed into 11-ml stainless steel cells and extracted in an ASE (ASE 200, Dionex, Sunnyvale, CA, USA) using methanol as extraction solvent. Two 5-min cycles of extraction were performed at 100 °C and 100 atm, in static mode (flush 60 %, purge 90 s).

The extracts were reconstituted with hexane under gentle nitrogen stream and transferred into a 1.5-ml glass screw vial with a 300 µl insert. The solvents in the inserts were nitrogen-evaporated to dryness and derivatized by adding 100 µl 5% solution of MSTFA/TMIS (1000:2) in hexane, followed by 30-min reaction at 80 °C. The derivatized extracts were subjected to the GC-MS analysis.

Target compounds (NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO) were analyzed on Agilent Technologies 5975C quadrupole mass spectrometer fitted with a 7890A gas chromatograph. A DB-5 MS (J&W Scientific) fused silica capillary column (30 m, 0.25 mm i.d., and 0.25 µm film thickness) was used with helium as the carrier gas with a constant flow of 0.9 ml/min. GC-MS operating conditions were 70 eV ionization potential with the MS interface at 280°C. The injection port was maintained at 300 °C, and the sample was injected in splitless mode followed by purge 1 min after the injection. The column oven temperature was held at 100 °C for the initial 1 min, then programmed at 10 °C/min to 200 °C, held for 3 min and then programmed at 10 °C/min to 300 °C and held for 7 min. A selected ion monitoring method was employed after solvent delay of initial 7 min. Post run time was set to 30 min at 300°C.

Chromatograms of NPs, NP1EOs and NP2EOs consist of at least 5 isomer peaks with various branched structures in the nonyl substituent. Some of individual NPs, NP1EOs and NP2EOs peaks contain several isomers and do not represent pure isomers. On the other hand, OP, OP1EO and OP2EO consist of a single peak due to one specific structure.

Quantification was achieved by extracting mass chromatograms at the main mass fragments of the target compounds and the internal standards: 4-*n*-NP (for NPs, NP1EOs, OP and OP1EO) and 4-*n*-NP2EO (for NP2EOs and OP2EO). In these internal standards, the nonyl chain is linear, and therefore they have slightly longer retention time than the other, branched analytes. For the quantification of NPs and NP1EOs five isomer peaks were summed up. In contrast, for the quantification of NP2EOs, the peak area of three peaks (m/z= 309) were summed up, since the separation of other peaks was not satisfactory on the 30 m capillary column.

Diagnostic ions for target compounds and internal standards are presented in Table 1.

Table 2.1-3 Selected diagnostic ions

	Target ion (m/z)	Qualifier ion (m/z)	Qualifier ion (m/z)
NPs	207	221	193
NP1EOs	251	265	279
NP2EOs	309	295	323
OP	207	278	
OP1EO	251		
OP2EO	295		
4-*n*-NP	179		
4-*n*-NP2EO	246		

All analyses were performed in SIM mode. Relative response factors were calculated from quantification standards containing both the internal standards and the mixture of the NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO. These relative response factors used to calculate the levels in the samples are shown in Table 2. Thereby results are automatically compensated for losses during extraction and further analytical steps.

Table 2.1-4 Response factors used for the quantification of analytes

	NPs	NP1EOs	NP2EOs	OP	OP1EO	OP2EO
Response factor	0.41	0.2	0.39	1.1	0.66	6.17
RSD [%]	10	3	7	8	9	6

2.1.2.2 Analytical Precision

Reproducibility of NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO, for sediment and SPM samples was examined through one duplicate analysis of one sample at each working day. The relative standard deviation (RSD) for each analyte in sediments were 9 %, 14 %, 7 %, 9 %, 4 % 5% respectively. In suspended particulate matter RSD of NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO were 3 %, 3 %, 4 %, 12 %, 1 % and 2 % respectively.

The extraction recovery was checked through five replicate analyses of one Danube sediment spiked with NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO standard solutions. The recovery percentage and relative standard deviations are presented in Table 3. The tests showed satisfactory recoveries; therefore no recovery corrections were necessary.

Table 2.1-5 Extraction recovery of target compounds

	NPs	NP1EOs	NP2EOs	OP	OP1EO	OP2EO
Extraction recovery [%]	95.7	114.2	112.0	79.8	88.0	92.0
RSD [%]	8.5	8.6	1.4	15.8	12.8	1.1

A laboratory blank was processed on each ASE extraction run, using the same procedure as for the real samples. In average, 4 ng of NPs, NP1EOs, and NP2EOs, 0.15 ng for OP, 0.25 ng for OP1EO and 0. 3 ng for OP2EO were found. Quantification limits of NPs, NP1EOs and NP2EOs were defined as 5 times as the procedure blank value. Quantification limits of OP, OP1EO and OP2EO were defined as 10 times as the procedure blank value. For the 1g sediment and SPM samples, the limit of quantification of NPs, NP1EOs, NP2EOs, OP, OP1EO and OP2EO were 20, 20, 20, 1.5, 2.5 and 3.0 ng/g respectively.

Derivatization efficiency by 5% solution of MSTFA/TMIS (1000:2) in hexane was investigated by inspection calibration curves linearity over broad concentration range (5 – 1000 ng) for each analyte.

All calibration curves showed high linearity ($r^2 \geq 0.97$) confirming that 5% solution of MSTFA/TMIS (1000:2) in hexane was efficient for the complete derivatization of target compounds.

2.1.3 Alkylphenols in suspended particulate matter (LfU, Munich)

The analytical method used comprises of the following steps:

- Soxhlet-extraction with hexane/dichloromethane (1:1)
- Sample clean-up using a silica column
- Derivatization (silylation) with MSTFA
- Gas-chromatography/mass-spectrometry

Six isotope-labelled internal standards are used to control the overall-procedure and for quantification. Iso-nonylphenol is a mixture of various peaks representing isomers and was quantified using the 4 largest signals and external calibration.

The samples were freeze-dried at the Umweltbundesamt in Vienna. Three samples were broken (JDS 04, JDS 19 and JDS 22) during the transport to Munich and could not be replaced as there was no additional material available. For sample JDS 62 organic substances could not be determined because the material was completely used for analysis of heavy metals. In total 60 samples were analysed.

For analytical quality control 5 samples were analysed twice using the overall procedure. The variation between each of these two samples was mostly 10% and didn´t exceed 20%.

2.1.4 Alkylphenols in sediments (TZW Karlsruhe)

Analysis for OP, NP, PCP and DEHP was done by ultrasonic extraction followed by a derivatisation step and GC/MS determination. Ultrasonic extraction was done in duplicate with a solvent mixture of cyclohexane and 10% acetone. After extraction, the organic solvent was evaporated to dryness and the dry residue was reconstituted with 100 µL of a silylation reagent. After a reaction time of 35 min at 80 °C in a drying oven, analysis of the target compounds was done by GC/MS.

The quantification of the target compounds was done by an external calibration.

2.2 Polybrominated diphenylethers (WRI Prague)

2.2.1 Polybrominated diphenylethers in water (WRI Prague)

The list of PBDEs analysed in JDS 2 is shown in the following table:

Table 2.2-1 Methods and parameters used for the determination of PBDE in water

Determinand	CAS	Unit	Method Used	Method	Limit of Quantification (LOQ)
BDE-47	40088-47-9	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5
BDE-100	189084-64-8	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5
BDE-99	32534-81-9	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5
BDE-153	68631-49-2	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5

BDE-154	207122-15-4	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5
BDE-183	207122-16-5	ng/l	GC-NCI-MS	Equivalent to ISO 22032	0.5
BDE-203	337513-72-1	ng/l	GC-NCI-MS	Equivalent to ISO 22032	1
BDE-205	446255-56-7	ng/l	GC-NCI-MS	Equivalent to ISO 22032	1

PBDE were extracted from water by liquid/liquid extraction with hexane as a solvent. Extracts were concentrated and analyse by gas chromatography with mass selected detector in negative ionisation mode.

Before GC-MS analysis the organic compounds were extracted from the samples. In the extraction procedure 1 l of the water sample was shaken for 2 hours with hexane directly in sampling bottles. After separation using special separation extender the extract was dried by anhydrous sodium sulphate, concentrated in a TurboVap II concentrator and after concentration to a final volume of 800 µl was analysed by GC-NCI- MS.

The analyses were performed using an Agilent Technologies 6890 N Network GC System gas chromatograph equipped with an autosampler Agilent Technologies 7683B Series Injector and an Agilent 5973 Network mass-selective detector. A fused-silica DB-1 capillary column 30 m of length, 0.32 mm I.D. with a film thickness of 0.1 µm connected with a 3 m HP deactivated retention gap (0.53 I.D.) was used for the separation of analytes. Helium was used as a carrier gas at a constant flow of 2.5 ml/min.

Extract aliquots of 1 µl were injected into the column by means of an autosampler using a pulsed splitless injection mode. The mass-selective detector was working in the SIM mode.

To control quality of the PBDE determination, every batch of 20 samples included a blank extraction sample and a quality control sample. The relative uncertainty of measurement is about 20 %.

2.2.2 Polybrominated diphenylethers in sediments (TZW Karlsruhe)

For analysis of PBDE, accelerated solvent extraction (ASE) followed by GC/MS determination was used. The ASE extraction process consisted of four extraction cycles with toluene. After extraction, the organic solvent was evaporated to 0.5 mL and a clean-up step on a multi-layer silica gel column took place. After reducing the solvent volume to 200 µL, analysis of the PBDEs was done by GC/MS with chemical ionisation.

Quantification of the target compounds was done by an external calibration.

2.3 Phthalates

DEHP and di(iso-nonyl)phthalate were analysed in suspended particulate matter according to the method given for alkylphenoles (LfU Munich).

DEHP in water was measured after liquid-liquid-extraction by LC-DAD (WRI Bratislava).

For DEHP-analysis in sediments (TZW Karlsruhe) see chapter 2.1.4.

2.4 VOCs

The analysis of volatile chlorinated hydrocarbons in water samples was performed using liquid-gas extraction (static headspace) followed by gas chromatography (GC) using a method derived from

STN EN ISO 10301[1]. Analytes are extracted from the water sample (15 ml) in a 20 ml headspace vial in headspace autosampler (Agilent 7694E). Headspace phase (3 mL) is injected to the GC HP 5890 series II . The separation of the analytes was performed on a Zebron ZB-624 (60 m × 32 mm × 1.8µm) column(Phenomenex). Detection was performed using electron-capture detector. Quantification of analytes was made using external standard calibration curves.

The analysis of benzene in water samples was performed using liquid-gas extraction (static headspace) followed by gas chromatography (GC) using a method derived from STN EN ISO 11423-1[2]. Benzene was extracted from 100 ml water sample in 200 ml volumetric flask by static headspace, 20 ml headspace phase was trapped on solid phase(TENAX) in a microcolumn, followed by a thermal desorption to GC HP 5890 series II inlet space. The separation of the benzene was performed on a VOCOL TM (60 m × 0.53 mm × 0.3 µm) SUPELCO column. Detection was performed using flame ionization detector. Quantification of benzene was made using external standard calibration curves.

2.5 Organochlorine compounds

2.5.1 Determination of organochlorine compounds and polychlorine biphenyles in water (WRI Bratislava)

The analysis of organochlorine pesticides (OCP) and polychlorine biphenyles (PCB) in water samples was performed using liquid-liquid extraction (LLE) followed by gas chromatography (GC) and electron-capture detection using a method derived from STN EN ISO 6468[3]. Analytes are extracted from the water sample (1 L) using n-hexane (10 mL) in an Erlenmeyer flask with a magnetic stirrer. Following a 2h extraction, the organic phase is separated using a microseparator device that also provides drying of the extract by its filtration through a layer of anhydrous sodium sulphate. The dried extract is evaporated with a stream of an inert gas to 1 mL. 1 µL of the hexane extract are injected to the GC HP5890 series II. The separation of the analytes was performed on a HP-5 (25 m × 0,32 mm × 0,52µm) column. Detection was performed using electron-capture detector. Quantification of analytes was made using external standard calibration curves

2.5.2 Determination of organochlorine compounds in sediments, suspended particulate matter and mussels (UBA Vienna)

After addition of 9 isotope labelled internal standards the samples were extracted in a Soxhlet apparatus with n-pentane as extraction solvent. The extracts were concentrated by a rotary evaporator. Florisil columns were applied for the clean-up. Afterwards, aliquots of the extract were injected into a GC-MS system.

[1] ISO 10301: 1997. Water quality-Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic method

[2] ISO 11423-1:1997. Water quality-Determination of benzene and same derivatives – Part 1: Head-space gas chromatographic method

[3] ISO 6468: 1996. Water quality-Determination of certain organochlorine insecticides, polychlorine biphenyls and chlorbenzenes-Gas-chromatographic method after liquid-liquid extraction

2.6 Organotin compounds

2.6.1 Organotin compounds in water (UBA Vienna)

After addition of an internal standard according to Standard ISO/CD 17353 and a sodium acetate puffer, derivatization of the analytes was performed with sodium tetraethylborate. The analytes were extracted with n-hexane and after clean-up with silica gel aliquots of the extracts were injected into a GC-MS system.

2.6.2 Organotin compounds in solid matrix (UBA Vienna)

After addition of an internal standard according to Standard ISO/CD 17353 the solid samples were extracted with ethanol. After filtration sodium acetate puffer was added for the subsequently derivatization with sodium tetraethylborate. Then, the analytes were extracted with n-hexane. The same clean-up procedure was performed as described above and aliquots of the extracts were measured with GC-MS.

2.7 Polar pesticides (VITUKI and JRC)

Alachor, Atrazine, Simazine in water (EN ISO 11369:1999): Determinand separated with SPE, analyzis by GC-MS. S.r. and i. standards applied.
Alachor, Atrazine, Simazine in sediment and SPM (MSZ 21470-5:1994): Aceton/CH_2Cl_2 extraction enhanced by sonication, extract purified with SPE, solution analyzed by GC-MS. S.r. and i. standards applied. (VITUKI)

Diuron, Isoproturon and Desethylatrazine were analysed by LC-MS/MS after solid phase-extraction. A very low limit of quantification of 0,001 µg/l was achieved. (JRC)

2.8 Organochlorine compounds in fish (LfU/Munich)

For JDS 2 the species “bream” (abramis brama) was chosen for sampling. Breams predominantly live on biota from the bottom sediment of rivers.

The JDS fish team took breams from 12 sampling sites. From 6 sampling sites material from three individuals were pooled, from 6 sampling sites material of two single fish and from 4 sampling sites material of one individual fish was provided.

Fish were killed on board and the upper filet from the right and the left side of each fish was taken. From each fish also the liver was taken. The material was packed in alumina foil and frozen immediately. Frozen samples were delivered by courier service from Slovakia.

Ca. 2 g from each sample or sample pool was spiked with isotope-labelled standards and homogenized and chemically dried by grinding after addition of sodium sulphate and sea-sand. Accelerated solvent extraction was done with n-hexane. For online clean-up the extractions cells were also filled with aluminia oxide. No additional extract clean-up was needed.

Analysis was done with GC-MS (SIM-mode).

In order to reduce uncertainty coming from possible inhomogeneous distribution of analytes in the tissue samples each sample was analysed twice using the overall procedure and the mean values are reported.

Analytical quality control was done using an reference material (muscle tissue of a carp) which was produced in our laboratory and checked in an interlaboratory study some years ago.

Results are reported in µg/kg fresh weight. Lipid content of the samples was not analysed, as breams are low-fat fish. Dry weight was not analysed.