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# Joint Danube Survey 2

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der Donau



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Full report on:

## Polar water-soluble contaminants in the liquid water phase by SPE-LC-MS2 analysis

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# 1 Introduction

Polar water-soluble organic contaminants were analysed in the dissolved (liquid) water phase by solid-phase extraction (SPE) followed by triple-quadrupole LC-MS<sup>2</sup> analysis. The extraction volume for the River Danube and tributary samples was 400 mL. In total, 34 different compounds were analysed. The analysis included 6 priority compounds of the WFD (atrazine, simazine, isoproturon, diuron, nonylphenol, and octylphenol).

All tributary water samples (23 close to the Danube and 28 more upstream in the individual Member States) and 53 River Danube water samples along the river were analysed by the JRC-IES.

Focus was given on pharmaceutical compounds (such as ibuprofen, diclofenac, sulfamethoxazole, carbamazepine), pesticides and their degradation products (e.g. bentazone, 2,4-D, mecoprop, atrazine, terbutylazine, desethylterbutylazine), perfluorinated acids (PFOS; PFOA), and endocrine disrupting compounds (such as nonylphenol, NPE<sub>1</sub>C, bisphenol A, estrone).

# 2 Methods

## 2.1 Solid-phase extraction

The water samples were extracted by solid-phase extraction (SPE). The water was not filtered. Some samples contained particles which settled to the bottom of the plastic (PP) bottles. The water (500 mL) was decanted into a 500 mL glass bottle. Then, before extraction, the samples (500 mL) were spiked with 50 µL of the internal standard, and then they were mixed by shaking. Table 1 shows the composition of the internal standard.

**Table 1: Internal standard**

Labelled compounds	Concentration [mg/L]
PFOA <sup>13</sup> C <sub>4</sub> - Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid	0.1
PFOS <sup>13</sup> C <sub>4</sub> - Perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octansulfonate	0.1
Carbamazepine d10	1
Simazine <sup>13</sup> C <sub>3</sub>	1
Atrazine <sup>13</sup> C <sub>3</sub>	1
Ibuprofen <sup>13</sup> C <sub>3</sub>	1
4n-Nonylphenol d8	1

This procedure results in an internal standard concentration in the water of 10 ng/L for PFOA <sup>13</sup>C<sub>4</sub> and PFOS <sup>13</sup>C<sub>4</sub> and 100 ng/L for the other labelled compounds.

The SPE procedure for the clean-up and concentration of water samples was performed automatically using an AutoTrace<sup>®</sup> SPE workstation (Caliper Life Sciences). 200 mg (6 mL) Oasis<sup>®</sup> HLB columns (Waters, Milford, MA, USA) were used. The cartridges were activated and conditioned with 5 mL

methanol and 5 mL water at a flow-rate of 5 mL min<sup>-1</sup>. The water samples (400 mL) were passed through the wet cartridges at a flow-rate of 5 mL min<sup>-1</sup>, the columns rinsed with 2 mL water (flow 3 mL min<sup>-1</sup>), and the cartridges dried for 30 min using nitrogen at 0.6 bars. Elution was performed with 6 mL methanol. Evaporation of the extracts with nitrogen to 500 µL was performed at a temperature of 35°C in a water bath using a TurboVap® II Concentration Workstation (Caliper Life Sciences).

## 2.2 Liquid Chromatography Tandem Mass Spectrometry (LC-MS<sup>2</sup>)

Analyses were performed by reversed-phase liquid chromatography (RP-LC) followed by electrospray ionization (ESI) mass spectrometry (MS) detection using atmospheric-pressure ionization (API) in the negative and positive ionization mode with a triple-quadrupole MS-MS system. LC was performed with an Agilent 1100 Series LC system consisting of a binary pump, vacuum degasser, autosampler and a thermostated column compartment. LC separations were performed using a Hypersil Gold column (Thermo Electron Corp., 100 × 2.1 mm, 3µm particles). The alkylphenolic compounds and steroid estrogens were analysed with an Ultra Aqueous C18 column (Restek, 100 × 2.1 mm, 3µm). Tandem mass spectrometry was performed on a bench-top triple-quadrupole *Quattro micro* MS from Waters-Micromass (Manchester, UK) equipped with an electrospray probe and a Z-spray interface.

The compounds were analysed in three separate analytical runs (methods) because the compounds amenable to negative and positive ionization have to be analysed in separate LC-MS runs. In addition, the alkylphenolic compounds and steroid estrogens need to be analysed with an aqueous phase without the addition of acetic acid. This improves the detection sensitivity for these phenolic compounds and ensures the separation of nonylphenol from its carboxylates (Loos et al., 2007b).

The eluants used for the separations of the target analytes were water and acetonitrile. The water phase used was acidified with 0.1 % acetic acid (pH 3.5). The flow-rate was 0.25 mL min<sup>-1</sup>. The gradient started with 90 % water and proceeded to 90 % acetonitrile over 25 min, conditions hold for 5 min, returned back to the starting conditions over 5 min, and followed by 5 min equilibration. The injection volume was 5 µL; injection was performed by the autosampler.

Quantitative LC-MS<sup>2</sup> analysis was performed in the multiple reaction monitoring (MRM) mode. Collision-induced dissociation (CID) was carried out using argon at approx.  $3.5 \times 10^{-3}$  mbar as collision gas at collision energies of 7 - 60 eV. The optimized characteristic MRM precursor → product ion pairs monitored for the quantification of the compounds together with the cone voltage and collision energy are given in Table 2.

The compound-dependent method detection limits (MDLs) or LODs for the SPE-LC-MS<sup>2</sup> procedure were determined from real water samples, at a signal-to-noise ratio of 3; 400 mL water was extracted and concentrated to 500 µL (enrichment factor 800). The injection volume was 5 µL (Loos et al., 2007a).

The compounds were identified by retention time match and their specific MRM transitions. The compounds were quantified using labelled internal standards (see above). The recoveries were determined with spike experiments in the concentration range of 10 and 100 ng L<sup>-1</sup> using Milli-Q water (replication n = 6); they were in the range of 50 –90 % (see Table 2 and (Loos et al., 2007a; 2008a)).

## 2.3 Quality assurance

The JRC laboratory participated within the NORMAN project (URL2) in the 1<sup>st</sup> and 2<sup>nd</sup> interlaboratory study for the analysis of non-steroidal anti-inflammatory drugs (NSAIDs), organized by CSIC (Environmental Institute; Barcelona) and the Josef Stefan Institute (Ljubljana) (Farre et al.,

2008), and in the third international interlaboratory study on perfluorinated compounds, organized within the PERFORCE II project (van Leeuwen et al.).

## 2.4 Comments to individual compounds

It must be noted that not all compounds reported could be analysed with the same precision, because the analyses of some compounds is easier in comparison to others. Moreover, internal standards were not available for all compounds.

The analysis of 2,4-D, ketoprofen, naproxen, diclofenac, and bisphenol A is difficult due to their polar and relatively non-stable character in water.

Nonylphenol shows elevated blank values. The blank problematic for nonylphenol has been described elsewhere (Loos et al., 2007b). The blank was in the range of 50-100 ng/L. Only concentrations > 100 ng/L were reported, and a blank subtraction of 100 ng/L was applied. For NPE<sub>1</sub>C no blank was observed, and for caffeine a blank of ~ 1 ng/L. The LODs are given in Table.

The analysis of the estradiol hormones is difficult due to their low LC-MS<sup>2</sup> sensitivity and the low concentration levels in the water samples.

Quantification of the individual compounds was performed with similar internal standards (IS). For instance, the first compounds (pesticides, pharmaceuticals) in Table 2 were all quantified with the internal standard ibuprofen <sup>13</sup>C<sub>3</sub>. All perfluorinated carboxylates were quantified with PFOA <sup>13</sup>C<sub>4</sub>. Sulfamethoxazole, carbamazepine, and caffeine were quantified with the IS carbamazepine d10. The pesticides and metabolites were quantified with atrazine <sup>13</sup>C<sub>3</sub> and simazine <sup>13</sup>C<sub>3</sub>. All compounds in the alkylphenolic compounds group (including the estradiol hormones) were quantified with the IS 4-n-nonylphenol d8. The relative response factors of the compounds in relation to the IS were calculated in all cases. Thus, the reported concentrations are corrected with the recoveries of the compounds, since the IS have similar recovery values.

A comparative check of internal quantification was always performed with external quantification. By internal quantification, usually higher concentration values were obtained due to the incomplete recovery of the polar analytes studied.

### **Benzotriazoles**

Analytical standards for the two benzotriazoles were not available at the beginning of the study. Therefore, only a few samples were analysed afterwards for these compounds. The analytical method was adopted from (Weiss and Reemtsma, 2005).

Interest in benzotriazoles is emerging (Richardson, 2007). Benzotriazoles are complexing agents that are widely used as anticorrosives in industrial and household applications (e.g., in engine coolants, aircraft deicers, or antifreezing liquids; silver protection in dish washing liquids). Benzotriazoles are weakly basic compounds of high polarity.

The two common forms, benzotriazole and tolyltriazole (methyl-benzotriazole), are soluble in water, resistant to biodegradation, and are only partially removed in wastewater treatment. They are ubiquitous environmental contaminants, but have a limited biological activity; for example, acute toxicity to aquatic organisms is in the low to moderate mg/L range (Weiss and Reemtsma, 2005, Weiss et al., 2006).

**Table 2: LC-MS<sup>2</sup> parameters, retention times, LODs.**

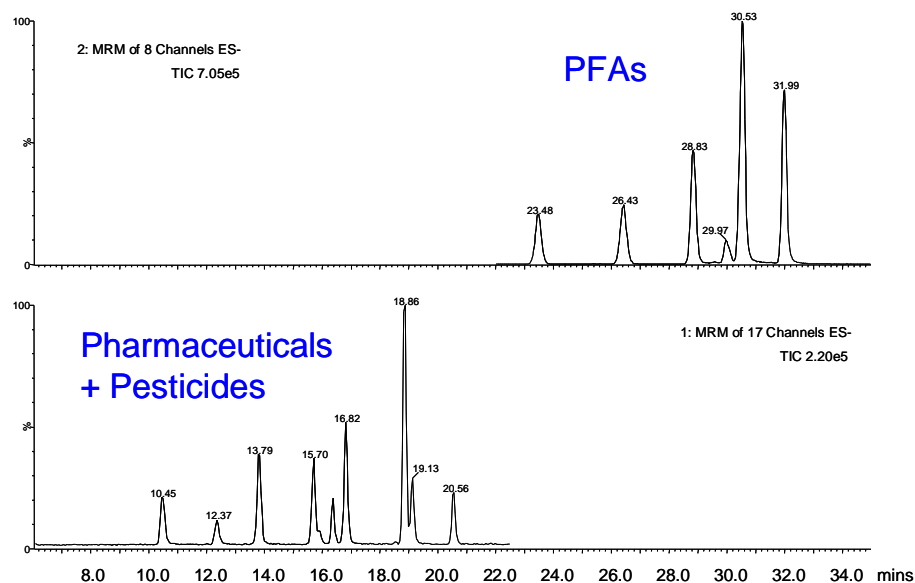
Compound	MRM	Cone [V]	Coll.	Ret. Time [min]	Recovery [%]	LOD [ng/L]
<b>Negative mode</b>						
Bentazone	239 > 132	42	27	13.8	62 ± 8	1
2,4-D	219 > 161	20	13	15.7	56 ± 8	1
Ketoprofen	253 > 209	28	10	15.9	71 ± 8	1
Naproxen	229 > 169	26	10	16.1	65 ± 8	1
Bezafibrate	360 > 274	32	17	16.4	66 ± 12	1
Mecoprop	213 > 141	25	14	16.8	62 ± 8	1
Ibuprofen	205 > 161	25	8	19.1	62 ± 12	1
Ibuprofen <sup>13</sup> C <sub>3</sub>	208 > 163.4	12	8	19.1	62 ± 9	
Diclofenac	294 > 250	25	13	18.9	65 ± 6	1
Gemfibrozil	249 > 121	27	15	20.6	62 ± 9	1
<b>Perfluorinated acids</b>						
PFHpA; perfluoroheptanoate	363 > 319	14	10	23.5	81 ± 14	1
PFOA; perfluorooctanoate	413 > 369	14	10	26.4	85 ± 11	1
PFNA; perfluorononanoate	463 > 419	14	10	28.8	85 ± 9	1
PFOA <sup>13</sup> C <sub>4</sub>	417 > 372	14	10	26.4	82 ± 9	
PFOS; perfluorooctansulfonate	499 > 80 (99)	60	47	30.2	65 ± 10	1
PFOS <sup>13</sup> C <sub>4</sub>	503 > 80 (99)	60	47	30.2	66 ± 12	
PFDA; perfluorodecanoate	513 > 469	14	11	30.5	76 ± 8	1
PFUnA; perfluoroundecanoate	563 > 519	14	11	32.0	78 ± 13	1
<b>Positive mode</b>						
1H-Benzotriazole	120.1 > 64.6 (91.7)	35	20	5.2	56 ± 9	1
1-Methyl-1H-benzotriazole	134.1 > 78.6 (76.7)	40	19	8.9	47 ± 8	1
Caffeine (stimulant)	195 > 138	25	19	3.4	75 ± 8	2*
Atrazine-desethyl	188 > 146	35	16	8.4	71 ± 10	1
Sulfamethoxazole	254 > 156	30	17	9.6	64 ± 9	1
Terbutylazine-desethyl	202 > 146	20	15	11.6	70 ± 8	1
Simazine	202 > 132	40	18	11.6	70 ± 11	1
Simazine <sup>13</sup> C <sub>3</sub>	205 > 134	26	18	11.6	72 ± 9	
Carbamazepine	237 > 194	35	18	13.1	68 ± 11	1
Carbamazepine d10	247 > 204	32	20	13.1	68 ± 8	
Atrazine	216 > 174	35	17	13.9	72 ± 13	1
Atrazine <sup>13</sup> C <sub>3</sub>	219 > 177	25	18	13.9	73 ± 8	
Isoproturon	207 > 72	30	17	14.7	72 ± 13	1
Diuron	233 > 72	30	17	14.8	72 ± 12	1
Terbutylazine	230 > 174	35	17	16.6	69 ± 8	1
<b>Alkylphenolic compounds</b>						
Bisphenol A	227 > 212 (133)	45	30	8.5	89 ± 3	1
Nonylphenol	219 > 133 (147)	45	32	20.6	72 ± 5	50*
4n-Nonylphenol d8	227 > 112	45	23		65 ± 8	
tert-Octylphenol	205 > 106	45	20	21.2	52 ± 5	1
Nonylphenoxyacetic acid NPE <sub>1</sub> C	277 > 219 (133)	35	18	15.4	68 ± 12	2
<b>Steroid estrogens</b>						
Estradiol	271 > 145 (183)	50	45	8.8	72 ± 12	5
Estrone	269 > 145 (143)	50	45	10.6	54 ± 13	2
17α-Ethinylestradiol	295 > 145 (159)	50	40	10.2	63 ± 1	5

MRM = multiple reaction monitoring; IS = internal standard; coll. = collision energy; SPE recovery rates from 400 mL water spiked at 10 ng/L using 200 mg Oasis HLB cartridges; LOD = method detection limits; n.a. = not applicable; \* blank value determined LODs.

## 3 Results

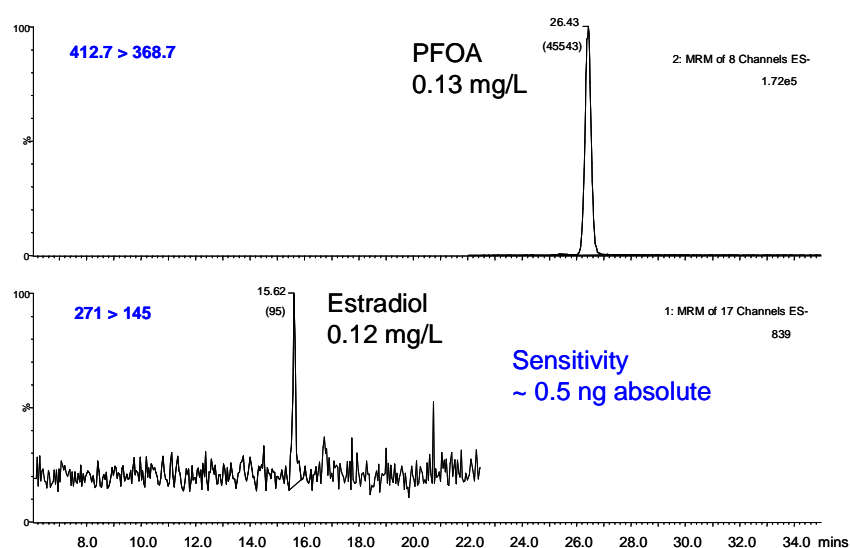
### 3.1 LC-MS<sup>2</sup> analysis of polar organic contaminants

Figure 1 shows a total ion current LC-MS<sup>2</sup> chromatogram of a standard mixture at 0.1 mg/L in the negative ionization mode, using a Hypersil Gold column (100 × 2.1 mm); the water-acetonitrile gradient starts with 90 % water. Two time-scheduled detection windows were used. Polar pesticides and pharmaceuticals are detected in the first, and PFAs in the second window.



**Figure 1: LC-MS<sup>2</sup> chromatogram of a standard mix in negative mode**

Figure 2 depicts the compound dependent LC-MS<sup>2</sup> sensitivity for two selected compounds. Phenolic substances such as estradiol have a low detection sensitivity.

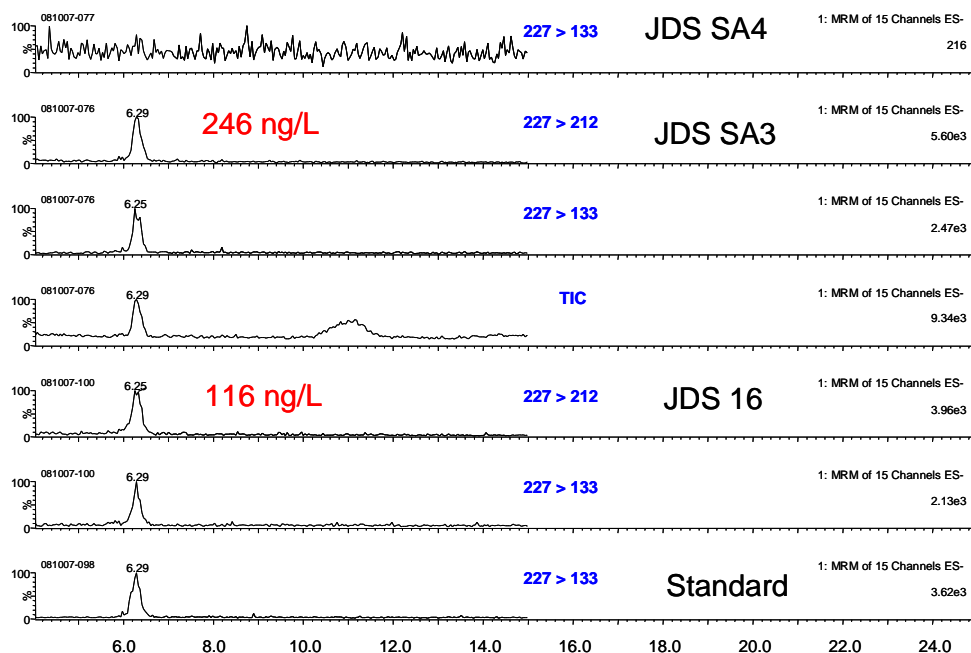


**Figure 2: Compound dependent sensitivity of LC-MS<sup>2</sup>**



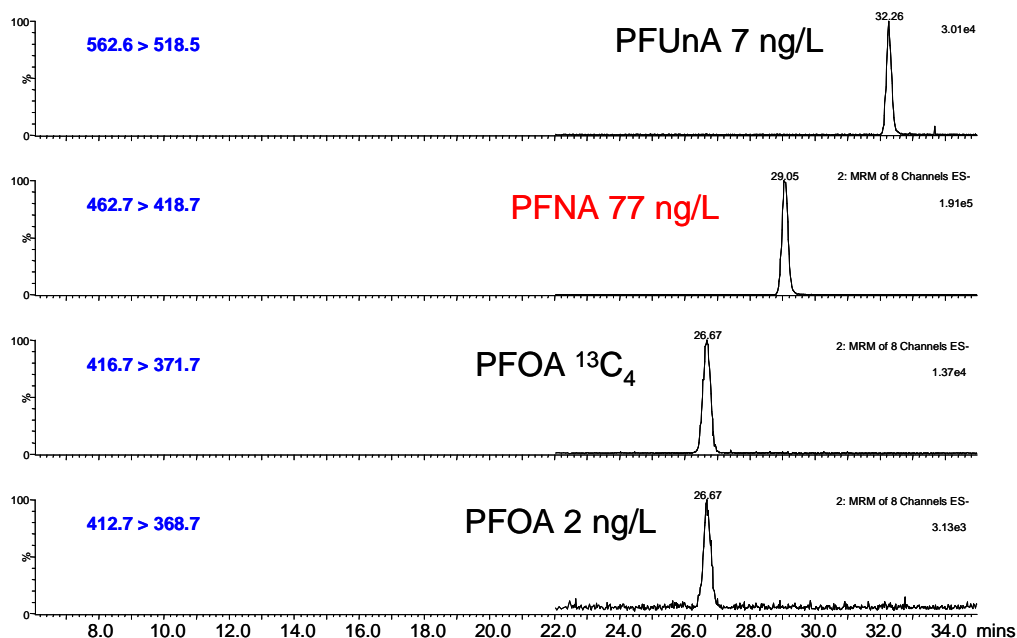
The following figures give some exemplary LC-MS<sup>2</sup> chromatograms.

Figure 3 shows the detection of bisphenol A in selected samples. Analysis of bisphenol A is in general difficult due to its polar character and resulting little column retention.

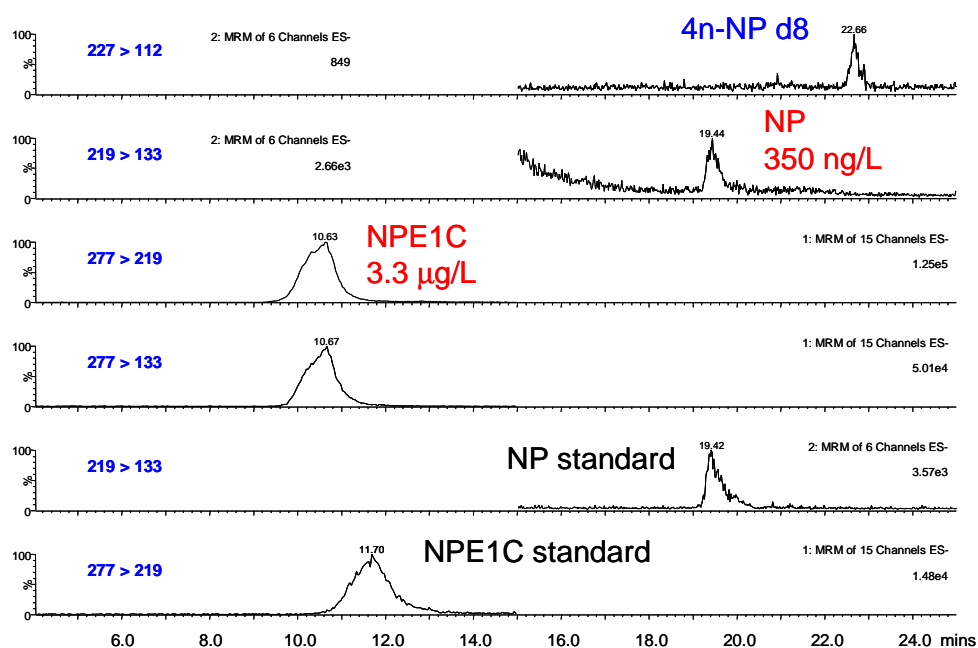


**Figure 3: Bisphenol A in JDS 16 and JDS SA3**

The sample JDS TI4 is the only sample in which PFNA and PFUnA were detected in “higher” concentrations; therefore, a chromatogram is shown in figure 4.



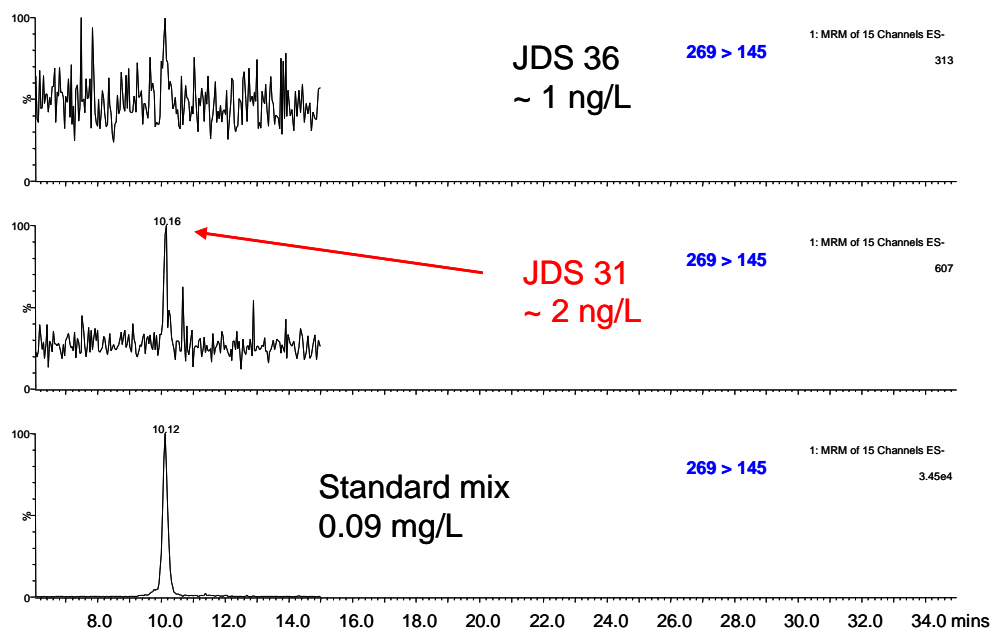
**Figure 4: PFNA in JDS TI4 sample**



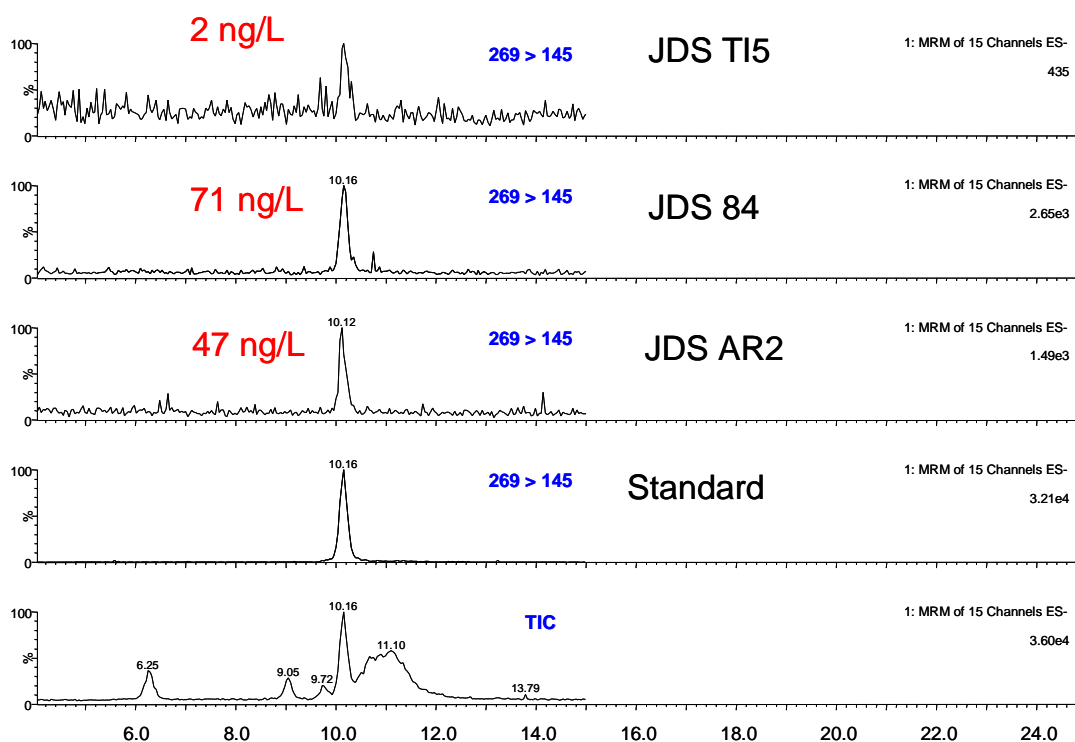
**Figure 5: Nonylphenol and NPE1C in JDS 66**

Figure 5 shows the analysis of nonylphenol and NPE1C. 4n-NP d8 is the internal standard used. The retention time for NPE1C is not constant under these chromatographic conditions (water without acetic acid).

Figure 6 shows the analysis of estrone in samples JDS31 and 36 (close to the LOD), and figure 7 in the samples JDS TI5, JDS 84, and JDS AR2.



**Figure 6: Estrone in sample JDS31**



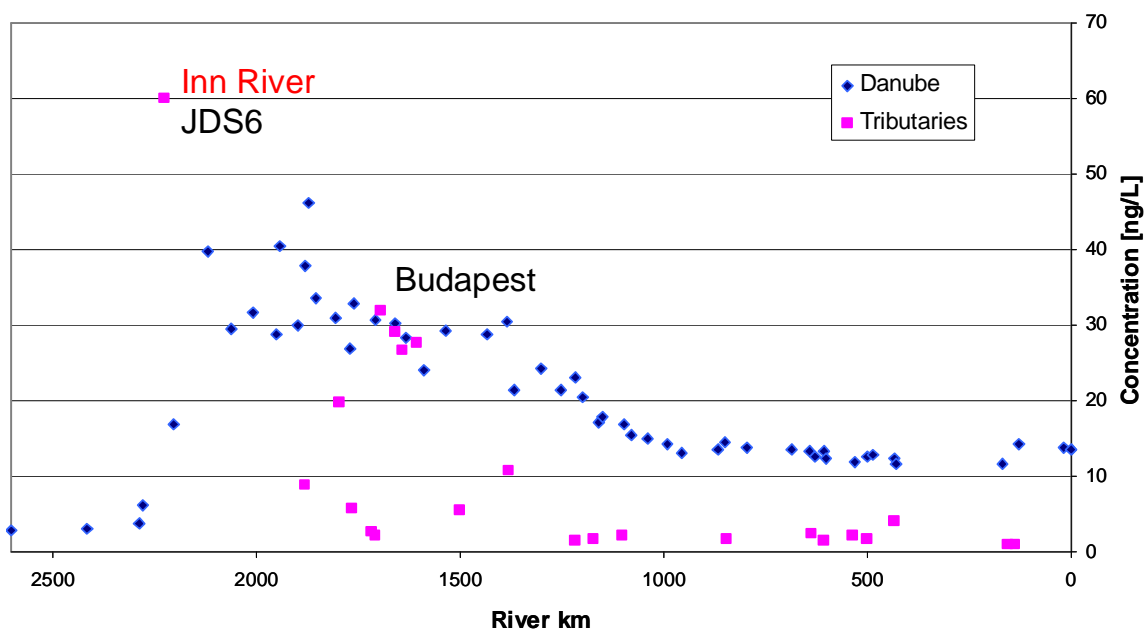
**Figure 7: Estrone in JDS TI5, JDS 84, and JDS AR2**

### 3.2 JDS 84 – Arges tributary

Sample JDS 84 was the most contaminated sample. It contained also “dissolved” green algae which rendered the SPE extraction difficult. Low recoveries were achieved for the compounds of the internal standard.

### 3.3 Perfluorinated acids (PFAs)

The highest PFOA level was detected in the River Inn (Germany); a concentration of 60 ng/L was measured. This river is the major PFOA source for the Danube. A lot of information on this issue is available on the web-page of the German “Bayerische Landesamt für Umweltschutz” ([URL1](#)). In the Danube downstream of this influent PFOA levels up to 46 ng/L were found. The dilution of PFOA along the course of the river is depicted in Figure 8.



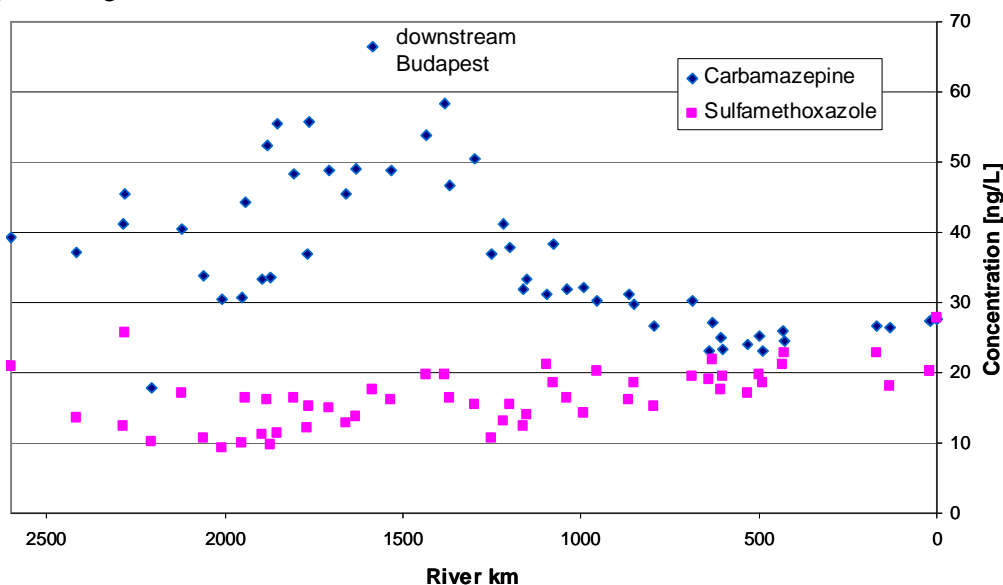
**Figure 8: PFOA in the Danube River and tributaries**

The PFOS concentration was quite constant in the upstream part of the Danube (~ 10 ng/L). At the river mouth in Romania 6 ng/L were reached. In the following tributaries higher PFOS concentration levels could be detected: Morava (20 ng/L), Jantra (57 ng/L), and Arges (101 ng/L).

Noticeable is the high concentration level of PFNA in sample JDS TI4 (108 ng/L). In this sample also some PFUnA was detected (10 ng/L), but little PFOA (3 ng/L), and PFOS (3 ng/L). This indicates that there might be an industry using PFNA instead of PFOA, which should be investigated in more detail.

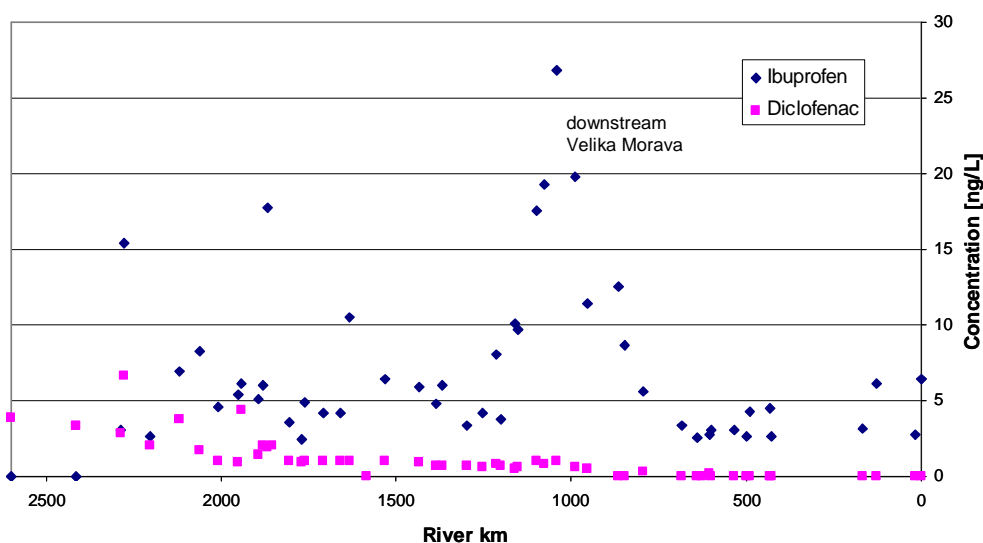
### 3.4 Pharmaceuticals

In the Danube quite low pharmaceutical concentration levels were detected. The highest levels were found for the compounds carbamazepine and sulfamethoxazole, because they are the most persistent. For carbamazepine, in the upstream part slightly higher levels were detected than more downstream (around 50-60 ng/L around Budapest, and ~30 ng/L from sample 50 onwards). For sulfamethoxazole levels ~20 ng/L were detected along the whole river (Figure 9). These anthropogenic substances are “discharged” along the whole river.



**Figure 9: Carbamazepine and Sulfamethoxazole in the Danube River**

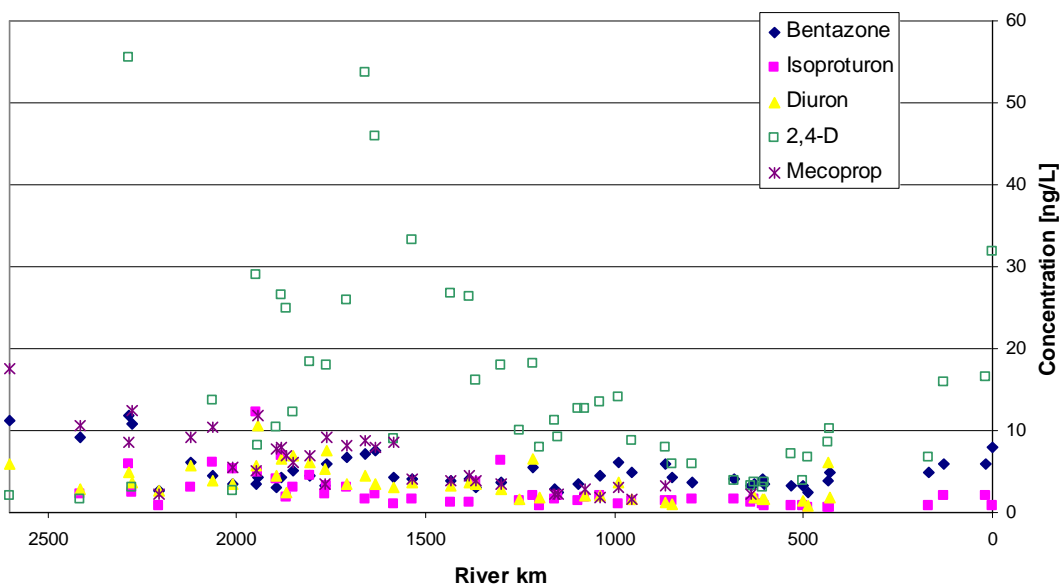
In Austria, for bezafibrate and ibuprofen levels between 5-10 ng/L were detected in the Danube, for diclofenac the levels were below 5 ng/L. More downstream in Romania, diclofenac and bezafibrate were not detected anymore, which could be explained by the biodegradability of these compounds. Ibuprofen was found after the Velika Morava tributary (JDS56) in concentration levels between 9-27 ng/L, and at the Danube river mouth ~5 ng/L (Figure 10).



**Figure 10: Ibuprofen and Diclofenac in the Danube River**

### 3.5 Pesticides

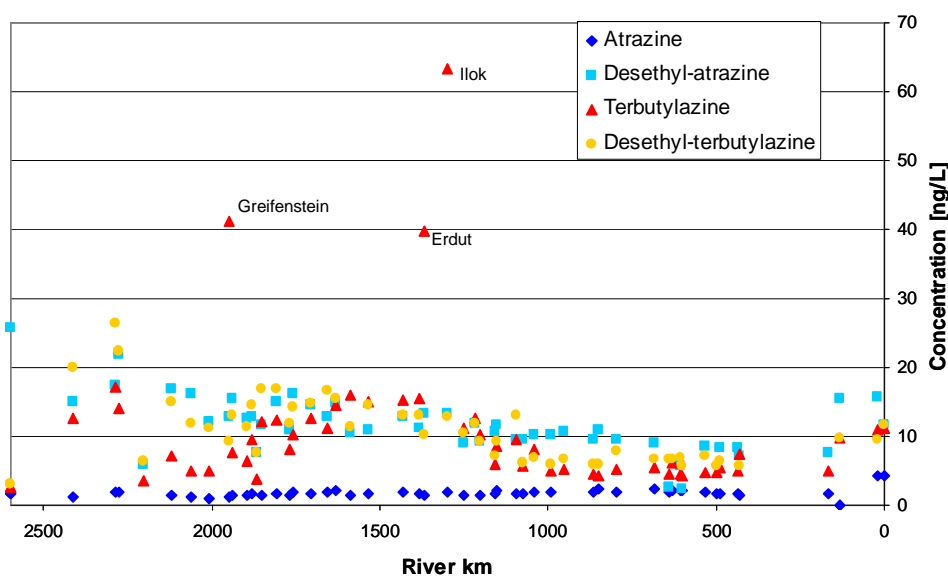
The highest concentrations for 2,4-D, one of the most widely used herbicide in the world, were found in the area around Budapest (~ 50 ng/L). In the Austrian part of the Danube ~ 20 ng/L, and in the downstream part ~ 10 ng/L were found. Bentazone levels were ~ 5-10 ng/L in the whole Danube (figure 11).



**Figure 11: Pesticides in the Danube River**

Simazine, Atrazine, Isoproturon, and Diuron levels were low (< 10 ng/L) at all parts. Terbutylazine levels were slightly higher, between 10-20 ng/L around Budapest, and between 5-10 ng/L in the downstream region of the Danube.

The concentrations for the metabolites desethylatrazine and desethylterbutylazine were in the range of 5-20 ng/L with maximum levels around Budapest (figure 12).



**Figure 12: Triazine herbicides and metabolites in the Danube River**

### 3.6 Estradiol hormones

In the River Danube the concentration levels for estradiol, and ethinylestradiol were in all cases below the LOD (5 ng/L). Estrone could be detected in some samples in the area of Budapest and downstream the Velika Morava influent. Moreover, 2 ng/L estrone were detected in the Russenski Lom, and by far the most in the Arges tributary (71 ng/L). Chromatograms for estrone are depicted in figure 6+7.

High concentration of estrone (E1) is consistent with the fact that estrone is an oxidation product of estradiol and may be formed in sewage treatment plants.

### 3.7 Nonylphenol

Nonylphenol (NP) concentrations are only reported for levels > 50 ng/L (due to the blank problematic; see experimental part). As can be seen from Table 3, NP was only detected in a small number of samples. The highest NP levels were found in the Arges (1300 ng/L), Timok (500 ng/L), and Velika Morava (260 ng/L) tributaries. In sample AR2 (Arges tributary) 1400 ng/L NP were found, correspondingly (Table 4) In the Danube River, in Donji Milanovac (JDS61) 240 ng/L, and in Vilkoovo (JDS93) 180 ng/L were detected. These two findings in the downstream part of the Danube are probably caused by a blank contamination (of the bottles).

### 3.8 Benzotriazoles

Only some selected samples were analysed for benzotriazoles because no analytical standards were available at the beginning of the measurements. The results in Table 3 show that benzotriazole was the organic compound with the highest concentration levels (130-300 ng/L) found in the Danube, followed by tolyltriazole and caffeine.

**Table 3: Benzotriazoles and Caffeine in the Danube**

			<b>Benzotriazole</b>	<b>Tolyltriazole</b>	<b>Caffeine</b>
<b>Code</b>	<b>River km</b>	<b>Location</b>	<b>ng/L</b>	<b>ng/L</b>	<b>ng/L</b>
JDS4	2285	Deggendorf	130	62	59
JDS10	2008	Oberloiben	180	63	49
JDS17	1852	Gabcikovo	214	72	47
JDS26	1707	Szob	222	73	38
JDS36	1533	Paks	380	130	84
JDS47	1252	Novi-Sad	300	100	82
JDS61	991	Donji Milanovac	184	73	164
JDS64	865	Iron Gate II	186	85	212
JDS79	532	Jantra	167	84	382
JDS95	0	Sulina	170	71	64

## 4 Conclusions

The analytical results for the polar compounds analysed (pharmaceuticals, pesticides, perfluorinated acids (PFOS/A), and phenolic endocrine disrupting compounds) are in good agreement to other big European rivers such as the Rivers Rhine, Elbe or Po.

The levels for the priority compounds of the WFD (atrazine, simazine, isoproturon, diuron) were in the Danube and the tributaries in all cases, except for nonylphenol, below the EQS values. The nonylphenol EQS of 0.3 µg/L was exceeded in the Timok (JDS66), and in the Arges Rivers (JDS84).

For the other “emerging” compounds analysed no limit values in surface waters exist.

The most relevant polar compounds identified in the Danube river basin in terms of frequency of detection, persistency, and concentrations were benzotriazoles, 2,4-D, PFOA, and carbamazepine.

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## 6 Tables / Annex

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**Table 3: River Danube water concentrations in [ng/L], tributaries are grey. No value means < LOD. Red color means: “high”**

No.	Location / River	Naproxen	Bentazone	2,4-D	Ketoprofen	Mecoprop	Bezafibrate	Ibuprofen	Diclofenac	Gemfibrozil	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA	Caffeine	Desethylazine	Carbamazepine	Sulfamethoxazole	Simazine	Atrazine	Isoproturon	Duron	Terbutylazine	Desethylterbutylazine	NPEIC	Nonylphenol	Bisphenol A	Estrone	Tert-OP
JDS1	Upstream Iller		11	2		17	5		4		1	3	2	10			51	26	39	21		2		6	3	3	102				
JDS2	Kehlheim		9	2		11	6		3		1	3	1	9			42	15	37	14		1	2	3	13	20	103				
JDS4	Deggendorf	5	12	55		9	8	3	3		2	4	1	7			59	17	41	12		2	6	5	17	27	307		19		
JDS5	Niederalteich		11	3		12	10	15	7		2	6	2	19	1	1	59	22	45	26		2	2	4	14	22	131				
JDS6	Inn		1			2	2		5	1	3	60	1	2			19	5	16	3			1		1	6	71				
JDS7	Jochenstein		3			2	2	3	2		1	17		4			40	6	18	10			1	3	4	6	22				
JDS8	Abwinden Asten		6			9	6	7	4		2	40	1	10			51	17	41	17		1	3	6	7	15	46				
JDS9	Ybbs-Persenbeug	4	5	14		10	6	8	2		2	30	1	7			52	16	34	11		1	6	4	5	12	137	80	9		
JDS10	Oberloiben		3	3	3		5	4	5	1	1	2	32	1	6			49	12	31	9		1	5	3	5	11	62			
JDS11	Greifenstein		3	3	29		5	5	5	1	2	29	1	7			43	13	31	10		1	12	6	41	9	85				
JDS12	Klosterneuburg		4	8		12	5	6	4	1	3	40	2	15			57	15	44	16		1	5	11	8	13	131		15		
JDS13		4	3	11		8	8	5	1		2	30	1	7			77	13	33	11		1	4	5	6	11	68				
JDS14	Hainburg		4	26		8	11	6	2		2	38	2	15	1		71	13	52	16		2	7	6	10	15	59		8		
JDS15	Morava		20	3		22	9	11	1		2	9	2	16	1	2	53	18	149	47		4	7	16	50	50	241	55			
JDS16	Bratislava			25		7	7	18	2	3	3	46	1	6		3	161	8	34	10			2	2	4	8	22		116		
JDS17	Gabcikovo		5	12		6	10		2	1	2	33	1	10		2	47	12	55	11		1	3	7	12	17	31				
JDS18	Medvedov		5	18		7	8	4	1	1	2	31	1	10		2	58	15	48	16		2	4	6	12	17	26				
JDS19	Moson	5	5			5	2	5	1	3	2	20	1	11	1	1	65	16	118	18		4	2	7	12	14	56	60			
JDS20	Komarno	3	3			4	5	2	1		2	27	1	7			70	11	37	12		1	2	5	8	12	126				
JDS21	Vah		3			15	2	11			1	6	1	4			25	6	46	15		1	1		7	6	38	60			
JDS22	Iza		6	18		9	8	5	1		2	33	1	9			30	16	56	15		2	3	7	10	14	36	115			
JDS24	Hron		6			3		15	2		1	3	1	6			34	9	88	22		2		5	11	8	76				
JDS25	Ipoly		13								1	2	1	4			20	20	303	49		25	1	3	15	14	31				
JDS2	Szob		7	26		8	7	4	1		2	31	1	9			38	14	49	15		2	3	3	13	15	28	50	10		

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JDS5 1	Sava		4				8				2		5			1188	8	16	38		2		1	1	2	29		8		
JDS5 2	Pancevo	5	3	11		2	1	10	1	2	1	17	1	8		104	11	32	12		2	2		6	7	42		13		
JDS5 3		4	2	9		2	1	10	1	2	2	18	1	9		125	12	33	14		2	2		9	9	67		16		
JDS5 6	Velika Morava	37	14	6				34	2	11		2		5		210	0	40	85		4	3				426	260			
JDS5 7	Starapalanka	8	3	13			1	18	1	3	1	17	1	7		1467	9	31	21		2	1		9	13	58			2	
JDS5 8		9		13		3		19	0.8	3	2	16	1	7		241	10	38	19		2	2	2	6	6	49			2	
JDS6 0	Golubac		4	13		2		27	1.0	3	1	15	1	8		162	10	32	16		2	2	2	8	7	48		10	1	
JDS6 1	Donji Milanovac		6	14		3		20	0.6	2	1	14		6		164	10	32	14		2	1	4	5	6	45	240			
JDS6 2	Tekija/Orsova	4	5	9		2		11	0.6	2	1	13		6		239	11	30	20			1	2	5	7	36				
JDS6 4	Iron Gate II		6	6		3		13		1	1	14	1	6		212	10	31	16		2	1	1	4	6	56				
JDS6 5	Rudujevac/Gruia		4	6				9		1	1	14		7		195	11	30	19		2	1	1	4	6	106	60			
JDS6 6	Timok	34		3		2	1	60	0.8		2	2	1	7		83	7	29	62		2					3352	500			
JDS6 8	Calafat	3	4	6				6	0.3	1	1	14	1	6		86	9	27	15		2	2		5	8	92	70			
JDS6 9	Kozloduy	2	4	4				3		1	1	13	1	7		127	9	30	20		2	2		6	7	64				
JDS7 0	Bajkal	2	3	3		2		3		1	1	13		6		274	3	23	19		2	1		4	7	39				
JDS7 1	Iskar	1	13	6				10	2.6			2		3		54	9	44	77		1					556				
JDS7 2		1	4	4						1	1	13		6		131		27	22		2	2	2	6	7	36				
JDS7 3		3	4	3				3	0.2	1	1	13		6		145	6	25	18		2	1	2	5	7	32				
JDS7 4	Olt		2	40								1	1	12		60	8	6	8	4	3			7	5	21				
JDS7 5		2	3	4				3		1	1	12	0	6		115	2	23	19	2	2	1	2	4	6	24				
JDS7 8	Jantra		11	4				2				2		53		383	8	8	14							95				
JDS7 9		1	3	7				3		1	1	12		6		382	9	24	17		2	1		5	7	23				
JDS8 0	Ruse	2	3	4				3		1	1	13		5		135		25	20		2	1	1	5	6	29				
JDS8 1	Russenski Lom	2	101	6				16	3			2		2		1628	9	27	69	3	1	2	2	1	7	144	250	5	2	

JDS8 2	Ruse/Giurgiu	1	3	7			4		1	13	6			267	8	23	19		2	1	1	6	6	32				
JDS8 3			4	9			4	1	1	12	5			114	8	26	21		2	1	6	5		32				
JDS8 4	Arges	14	148	4	199		54	718	36		1	4	100		5361	92	945	204	19	17	1	2	1	6	1212	1300	490	71
JDS8 5	Oltenita	4	5	10			3		1	1	12	6		152	7	25	23		2	1	2	7	6	60	100			
JDS8 9	Braila	2	5	7			3		1	1	12	1	6	172	8	27	23		2	1		5		35		7		
JDS9 0	Siret		3	188			2				1		2	47	5	3	8		1			1	1	36		6		
JDS9 1	Prut		9	4					1		1		1	5	4	7	21		1			2	2	40	87			
JDS9 2	Reni		6	16	13		6			1	14	1	6	81	15	26	18		0	2		10	10	82		12		
JDS9 3	Vilkovo		6	16			3			1	14	1	6	77	16	27	20		4	2		11	9	91	180	13		
JDS9 5	Sulina		8	32			6		2	1	13	1	7	64	12	28	28		4	1		11	12	83		68		

Table 4: Danube tributaries; water concentrations in [ng/L]; No value means &lt; LOD.

No.	River, Location	Nap-roxen	Bent-azone	2,4-D	Keto-profen	Meco-prop	Beza-fibrate	Ibu-profen	Diclo-fenac	Gem-fibrozil	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA
MO1	Morava, Lanzhot		53	12		13		58	3		2	8	2	20		
MO2	Dyje, Pohansko		27	22		25		43	2		3	10	3	11	1	
DR1	Drava, D. Miholjac	4	1	2			3		1.0			2		5		
TI1	Tisa, Tiszabecs		0											1		
TI2	Szolnok		5	2					0.4	1	1	2	1	5		
TI3	Szeged	4	7	3					0.4	2		2		4		
TI4	Tisa, Martonoš	3	8	1					1	1	1	3	108	3		10
TI5	Tisa, Novi Bečej		9	3					1			2		3		
TI6	Tisa, Titel		7	3						1		2		4		
SA1	Sava, Zupanja	2	6			2		5		3		2		7		
SA2	Sava, Jamena	2	4			2		5		3	1	2		7		
SA3	Sava, Sremska Mitrov.		2		31			5		1		1		5		
SA4	Sava, Ušće	4	5					10		2		2		5		
VM1	V. Morava, Bagrdan	46	24	5				64	3	11				3		
VM2	V. Morava, Varvarin	38	9	4				87	3	11	1	2	1	5		
VM3	V. M., Ljubičevski Most	34	9	8				50	2	12		2		3		
OL1	Olt, Valcea		1	1				2	1			1	2	8		

OL2	Olt, Slatina		2	22								1	1	11		
AR1	Arges, Pitesti							2								
AR2	Arges, Bucharest		239	5	214		83	517	52			5	1	101		
JA1	Karantzi															
JA2	Yabalka-Gabrovo		8	3								1		57		
IS1	Orechovitza													1		
IS2	Iskar		3	6		4			1					2		
RL1	Basarbovo		174	2					4			1				
RL2	Beli Lom, Pisanetz		72	4					1			1				
PR1	Prut, Ungheni			3	1	13			1	3						
PR2	Prut, Bumbata-Leova			4	2	14			2	1			1			

MO = Morava, DR = Drava, TI = Tisza, SA = Sava, VM = Velika Morava, OL = Olt, AR = Arges, JA = Jantra, IS = Iskar, RL = Russenski Lom, PR = Prut

**Table 4: Continued.**

No.	River, Location	Caff- eine	Des- etyhl- atrazine	Carba- mazepin e	Sulfa- methox- azole	Sim- azine	Atra- zine	Isoprot- uron	Diuron	Ter- butyl- azine	Desetyh lterbuty lazine	NPE1C	Nonyl- phenol	Bis- phenol A	Estrone	Tert-OP
MO1	Morava, Lanzhot	84	14	206	86	6	5	4	12	245	97	217	53	16		
MO2	Dyje, Pohansko	61	26	140	40		3	5	22	128	117	153		23		
DR1	Drava, D. Miholjac	73	6	25	5		1	1	2	3	5	18		38		
TI1	Tisa, Tiszabecs	54	8	3	4	2		5		36	2	16				
TI2	Szolnok	48	7	40	26	3	2	3	5	26	4	21				
TI3	Szeged	188	8	72	30		2	4	7	38	5	30		6		
TI4	Tisa, Martonoš	65	9	42	18		1			2	3	33	200	24		
TI5	Tisa, Novi Bečej	30	9	35	13		2			7	5	20			2	
TI6	Tisa, Titel	36	7	36	16		2			2	3	18				
SA1	Sava, Zupanja	139	10	28	35		3			2	4	47		24		
SA2	Sava, Jamena	176	11	27	46		3			4	3	46		18		
SA3	Sava, Sremska Mitrov.	146	9	15	25		2			2	1	46	110	246		
SA4	Sava, Ušće	141	10	18	37		2				3	55	100			
VM1	V. Morava, Bagrdan	661	2	25	77		1					344				
VM2	V. Morava, Varvarin	708		34	78		1	2				332				
VM3	V. M., Ljubičevski Most	456		37	83		2	2				259		12		

OL1	Olt, Valcea	210	8	6	16		3					104		46		
OL2	Olt, Slatina	55	6	6	5		4			5	4	20				
AR1	Arges, Pitesti	57			3							6		4		
AR2	Arges, Bucharest	6798	67	316	192	21	19	2		1		567	1400	335	47	
JA1	Karantzi	5										3		33		
JA2	Yabalka-Gabrovo	28		5	7							97				
IS1	Orechovitza	50		4	6							25				
IS2	Iskar	42		26	32							428				
RL1	Basarbovo	126		17	55		1			1		62	150			
RL2	Beli Lom, Pisanetz	113	7	8	23		1			1		54	250			
PR1	Prut, Ungheni	308		1	2						1	9		15		
PR2	Prut, Bumbata-Leova	178		4	10						1	18		58		

MO = Morava, DR = Drava, TI = Tisza, SA = Sava, VM = Velika Morava, OL = Olt, AR = Arges, JA = Jantra, IS = Iskar, RL = Russenski Lom, PR = Prut