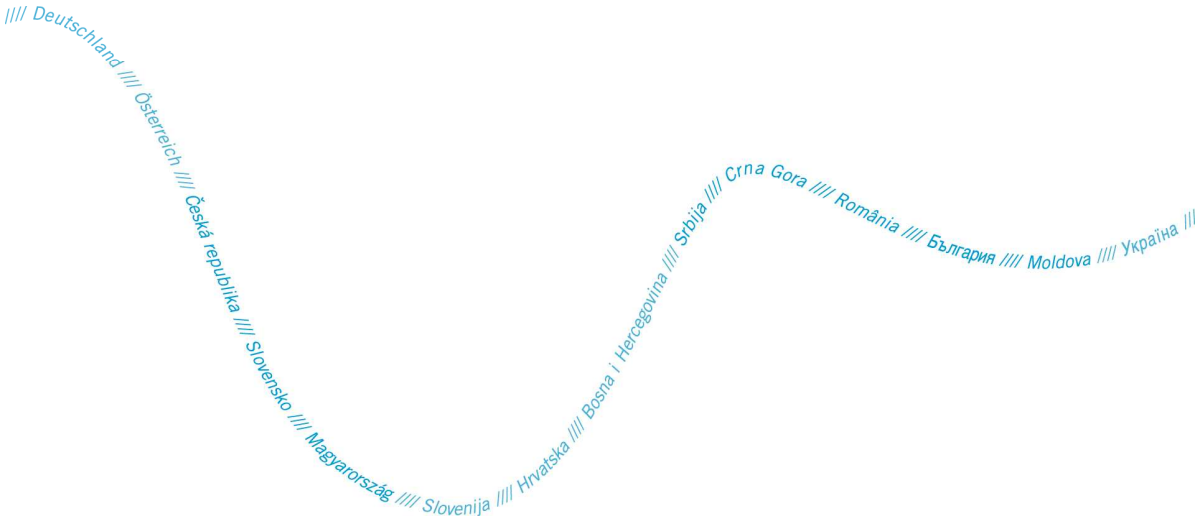
Joint Danube Survey 2

icpdr International Commission for the Protection of the Danube River
iksd Internationale Kommission zum Schutz der Donau

Final Report on
Heavy metals and Arsenic in water, suspended particulate matter, sediments and biota

Peter Literathy, Ioana Enache, Michal Pavonic, Vera Ocenaskova and Jürgen Diemer



Imprint

Published by:
ICPDR – International Commission for the Protection of the Danube River

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

Table of content

1 Introduction

Heavy metals and Arsenic can be present in industrial, municipal, and urban runoff, causing adverse effects in the aquatic ecosystem when the concentration in the water as well as in the sediment exceeds the tolerance limits. Furthermore, heavy metals and Arsenic in water can limit drinking water supplies, affect aquatic organisms, livestock and wildlife, and after bioaccumulation it may enter to the food chain causing environmental and public health risks.

The water solubility of most of these elements concerned is limited in natural water, and most of them are readily associated with the solid phase (particulate matter) either in suspension or after settling in the bottom sediment. Depending on turbulence, flow velocity in the surface waters, the sedimentation and re-suspension is in a dynamic equilibrium. Changing redox conditions, particularly in the case of anaerobic media (likely in the bottom sediment), mobilization and increasing bioavailability may increase the adverse effects. Since several major cities and towns uses the river water or bank-filtered water for drinking water supply, therefore, increased metal concentration in the sediment is usually a major concern.

During JDS 2, selected heavy metals and Arsenic were analysed in water, suspended particulate matter and bottom sediments as well as in mussels and fish. The investigated elements were categorised in three groups that are as follows:

- Group 1: Heavy metals included in the Priority List of the WFD
  - Cadmium;
  - Lead;
  - Mercury; and
  - Nickel.
- Group 2: Other heavy metals and Arsenic:
  - Arsenic;
  - Chromium;
  - Copper;
  - Zinc;
  - Bismuth, Cobalt, Molybdenum (in SPM only); and
  - Cobalt, Titanium, Vanadium (in bottom sediment only).
- Group 3: Other heavy metals (important for overall assessment):
  - Aluminium, Iron and Manganese.

Table 1-1 gives an overview on the limits of quantification (LOQ), the corresponding EQS for the relevant heavy metals dissolved in the water and the laboratory involved. For yellow labelled substances the LOQ was not sufficient for compliance checking. The international standards for these elements in the sediments and biota as well as other heavy metals for each matrix must be further developed, improved to meet the requirements.

Table 1-1 LOQs of analytical methods for WFD target compounds in water samples in comparison to the environmental quality standards (EQS), including the tentative Austrian EQSs (for Cu and Zn)

Determinand	Unit	LOQ	AA-EQS	Laboratory
Cadmium	µg/l	0,2		WRI T.G.M., Prague
if Total Hardness is:				
Class 1: <40 mg/l $CaCO_3$	µg/l		**≤ 0.08**	
Class 2: 40 to <50 mg/l $CaCO_3$	µg/l		**0.08**	
Class 3: 50 to <100 mg/l $CaCO_3$	µg/l		**0.09**	
Class 4: 100 to <200 mg/l $CaCO_3$	µg/l		**0.15**	
Class 5: ≥200 mg/l $CaCO_3$	µg/l		**0.25**	
Lead	µg/l	0,004	**7.2**	WRI T.G.M., Prague
Mercury	µg/l	0.05	**0.05**	WRI T.G.M., Prague
Nickel	µg/l	0,5	**20**	WRI T.G.M., Prague
Copper,	µg/l	2.0		WRI T.G.M., Prague
if Total Hardness is:				
<50 mg/l $CaCO_3$			**1.1**	
50 to 100 mg/l $CaCO_3$			**4.8**	
>100 mg/l $CaCO_3$			**8.8**	
Zinc,	µg/l	5.0		WRI T.G.M., Prague
if Total Hardness is:				
<50 mg/l $CaCO_3$			**7.8**	
50 to 100 mg/l $CaCO_3$			**35.1**	
>100 mg/l $CaCO_3$			**52**	

LOQ > EQS LOQ = EQS

In addition to the EQS for priority heavy metals dissolved in the water, according to paragraph 3. under *Article 2.* Environmental quality standards, in the proposed directive on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, the Member States shall ensure that the methyl-mercury concentration of 20 µg/kg in prey tissue (wet weight) for biota (fish, molluscs, crustaceans and others) is not exceeded.

Table 1-2 shows the involvement of different laboratories performing element analysis of different matrices, including overlaping in several cases.

Table 1-2 Laboratories performing heavy metals and Arsenic analysis in different matrices

Environmental Matrix	Element Analysed	Laboratory
Water, dissolved	Cd, Pb, Hg, Ni As, Cr, Cu. Zn	Water Research Institute T.G.M. Prague, Czech Republic
Suspended Particulate Matter	Cd,Pb,Hg, Ni As, Bi, Co, Cr Cu, Mo, Zn Mn	Bavarian Environment Agency Augsburg, Germany
	Al, Fe, Mn	VITUKI, Budapest, Hungary
Bottom Sediment	Cd, Pb, Hg, Ni As, Cr, Cu. Zn, Al, Fe, Mn	ICIM, Bucharest, Romania
	Cd, Pb, Hg, Ni As, Co, Cr, Cu.Ti, V, Zn Al, Fe, Mn, Si, Ca, Mg, Na, K	EC-JRC/IES, Ispra, Italy
Biota (mussel, fish)	Cd, Pb, Hg, Ni As, Cr, Cu. Zn	Water Research Institute T.G.M. Brno, Czech Republic

2 Methods

2.1 Determination of heavy metals and As in water

Surface water samples were filtered through 0.45 µm pore-size membranes on board the ship, and preserved with addition of nitric acid to <2 pH. The samples were stored in plastic bottle, except for mercury which were stored in glass container. The analysis was performed according to the procedures summarized in Table 2-1. Accordingly, the results represent the dissolved form of the elements.

Table 2-1: Methods for the determination of heavy metals and As in water

Determinand	Unit	Limit of Quantification (LOQ)	Method Used	Method
Cadmium (Cd)	µg/l	0.2	AAS – GF*	Equivalent to CSN EN ISO 5961
Lead (Pb)	µg/l	2	AAS - GF	Internal procedure
Mercury (Hg)	µg/l	0.05	AAS – CV**	Internal procedure
Nickel (Ni)	µg/l	0.5	AAS - GF	Internal procedure
Arsenic (As)	µg/l	0.8	hydride AAS	Equivalent to CSN EN ISO 11969
Chromium (Cr)	µg/l	0.5	AAS - GF	Equivalent to CSN EN 1233
Copper (Cu)	µg/l	2	AAS - GF	Internal procedure
Zinc (Zn)	µg/l	5	ICP-OES***	Equivalent to CSN EN ISO 11888

* AAS – GF – Atomic Absorbtion Spectrometry with Graphite Furnace
** AAS – CV – Atomic Absorption with Cold Vapor
*** ICP - OES – Inductively Coupled Plasma Optical Emission Spectrometry

2.2 Determination of heavy metals and As in suspended particulate matter (SPM)

Homogenized and freeze dried samples of suspended particulate matter were provided in amber glass bottles by Umweltbundesamt Wien.

2.2.1 Analysis of SPM samples in the laboratories of Bavarian Environment Agency, Augsburg, Germany

Approximately 1 g of the freeze-dried samples, weighted on analytical balance, was extracted with aqua regia (21 ml HCl / 7 ml HNO3 of suprapure quality) for 3 hours under reflux (DIN EN 13346, method A). It is noteable that during JDS 1 extraction was carried out using concentrated Nitric Acid/ H_2O_2 (3:2 v/v), which may cause different extraction yields for some elements (e.g. Cr). Analysis was performed by inductively coupled plasma – mass spectrometry (ICP-MS, DIN EN ISO 17294-1) using Rh and Lu as internal standards.

Mercury was directly analysed from the dried SPM using an "automated mercury analyzer"(LECO AMA 254). Analytical results obtained with this method are comparable to the classic aqua regia extraction followed by AAS determination using cold vapour technique.

The analytical procedures used for determination of the heavy metals and As are summarized in Table 2-2, together with the relevant Limit of Quantification.

Table 2-2: Methods for the determination of heavy metals and As in SPM

Determinand	Unit	Limit of Quantification (LOQ)	Sample Digestion	Analytical Method Used	Analytical Method
Cadmium (Cd)	mg/kg	0.02	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Lead (Pb)	mg/kg	0.1	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Mercury (Hg)	mg/kg	0.02	-	AMA	EPA Method 7473
Nickel (Ni)	mg/kg	0.3	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Arsenic (As)	mg/kg	0.1	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Bismuth (Bi)	mg/kg	0.01	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Cobalt (Co)	mg/kg	0.02	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Chromium (Cr)	mg/kg	1	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Copper (Cu)	mg/kg	0.2	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Molybdenum(Mo)	mg/kg	0.02	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Zinc (Zn)	mg/kg	1	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*
Manganese (Mn)	mg/kg	0.3	DIN EN 13346	ICP-MS	*DIN EN ISO 17294*

2.2.2 Analytical Quality Control

To check the accuracy of the mercury determination using the LECO AMA 254 analyzer, with every set of samples the BCR-142 certified reference material was measured the same way as the samples. Results, presented in Table 2-3, show a good agreement between the measured and the certified mercury concentration.

Table 2-3: Measurements of the certified reference material BCR-142 as a QC sample for mercury determinations in SPM

Element	CRM BCR 142		Results using AMA 254			
	Certified value	Uncertainty*	Number of measurements	Average	SD**	RSD
	mg/kg	mg/kg		mg/kg	mg/kg	%
Hg	0.104	0.012	22	0.112	0.006	5.5

*uncertainty quoted by CRM certificate
**standard deviation of the single measurement

2.2.3 Analysis of Al, Fe and Mn in SPM samples in the laboratories of VITUKI, Hungary.

The freeze-dried SPM samples were digested in microwave oven with a mixture of concentrated Nitric Acid/H_2O_2 (3:2 v/v), and the filtered solution analysed by ICP-AES (Perkin Elmer 3200DV).

2.3 Determination of heavy metals and As in bottom sediment

2.3.1 Analysis of bottom sediment samples in the laboratories of ICIM, Romania.

Homogenised and freeze-dried samples of sediments (grain-size fraction <63 µm) were provide in polypropylene bottles (by UBA, Vienna, Austria). The samples were stored at room temperature before they were analysed.

Regarding the sample pre-treatment, the heavy metals were extracted from the sediment according to the EPA 3051 method using Aqua Regia as acid mixture and microwave digestion.
Analysis of the heavy metals in the bottom sediment was carried out by using the methods summarized in Table 2-4.

Table 2-4: Methods for the determination of heavy metals and As in bottom sediment

Determinand	Unit	Limit of Quantification (LOQ)	Method Used	Method
Cadmium (Cd)	mg/kg	0.08	AAS – GF*	EPA 3051
Lead (Pb)	mg/kg	0.2	AAS - GF	EPA 3051
Mercury (Hg)	mg/kg	0.008	FIMS**	EPA 3051
Nickel (Ni)	mg/kg	0.24	AAS – GF	EPA 3051
Arsenic (As)	mg/kg	0.01	AAS – GF	EPA 3051
Chromium (Cr)	mg/kg	0.39	AAS - GF	EPA 3051
Copper (Cu)	mg/kg	0.4	AAS – GF	EPA 3051
Zinc (Zn)	mg/kg	4	AAS – F***	EPA 3051
Aluminium (Al)	mg/kg	3.32	AAS - F	EPA 3051
Iron (Fe)	mg/kg	10	AAS - F	EPA 3051
Manganese (Mn)	mg/kg	8	AAS - F	EPA 3051

* AAS – GF – Atomic Absorbtion Spectrometry with Graphite Furnace
** FIMS – Flow Injection Mercury System
*** AAS – F – Atomic Absorbtion Spectrometry with Flame

2.3.2 Analytical Quality Control

For AQC, with every 5 samples a certified reference material – CRM - (river sediment LGC 6187 from monitoring station lagoon on the river Elbe close to the Czech – German border) was analyzed.
The extraction of heavy metals from sediment CRM followed the same procedure as for the samples with the difference that for the certified reference materials approximate 0.2-0.5 g of dry sediment were weighted into PTFE.
The results of the quality control samples are summarized in Table 2-5.

Table 2-5: Concentration of heavy metals (overall mean ± uncertainty*) in certified reference material (CRM)

Metals	CRM LGC 6187		ICIM Results	
	mg/kg	Uncertainty*	mg/kg	Uncertainty**
Cd	2.7	0.3	1.79	0.3
Pb	77.2	4.5	86.6	16.6
Hg	1.4	0.1	1.27	0.31
Ni	34.7	1.7	38.9	8.91
Cr	84.0	9.4	86.1	9.94
Cu	83.6	4.1	85.5	11.9
Zn	439	26	480	27.1
Fe	23600	1500	23500	1910
Mn	1240	60	1220	145

* the uncertainty quoted is an expanded uncertainty with a coverage factor of 2, and approximates to the half width of the 95% confidence interval
** the uncertainty was calculated based on the ICIM results as twice the standard deviation of the overall mean.

The results indicated no significance difference between certified concentration results and the results obtained by ICIM laboratory, with two exceptions: one for Cd were the lower results can be explain by partial extraction procedure and the second for Pb were the results are higher than the certified concentration results caused may be by some contamination of the sample.

2.3.3 Analysis of bottom sediment samples in the laboratories of EC-JRC/IES, Ispra.

Upon arrival, the samples were dried for 24 hours in an oven at a temperature not exceeding 40°C. Upon completion, each sample was ground using an planetary mill equipped with agate-zirconia milling vessels. Each sample was ground for about five minutes. The resulting powder was then transferred to pre-cleaned HDPE sample containers until further processing:

- For WDXRF measurements, samples were pelletised using a hydraulic press (Herzog). For this purpose, appr. 2 g of samples were placed in special XRF sample containers. A pressure of 20 t/cm^2 was applied for 20 sec, resulting into a solidified pellet ready for analyses by means of WDXRF.
- For Hg analysis, no further treatment was necessary.

The WDXRF measurements were carried out on a Bruker-AXS® SRS-3400 X-ray fluorescence spectrometer equipped with four analysing crystals, a Rh-anode end-window X-ray tube (75 lm Be window) and 4 kW maximum power. The spectrometer is controlled by an external PC using the 241 manufacturer's software SPECTRAplus®. The calibration was built using the following certified reference materials of soils and sediments: BCR-141, BCR-141R, BCR-142, BCR-142R, BCR-143, BCR-143R, BCR-144, BCR-144R, BCR-145, BCR-145-R, BCR-146, BCR-146R, BCR-277, BCR-280, BCR-320, CANMET- SO1, CANMET-SO2, CANMET-SO3, CANMET-SO4, NIST-SRM-2704, NIST-SRM-2709, NIST-SRM-2710, NIST-SRM-2711, IAEA-SOIL-7.

All measurements were run under repeatability conditions, i.e. in one analytical run. Given the significant size and mass of test portion in relationship to the grain size after milling, only one test portion was analysed per laboratory sample.

Analysis of the heavy metals in the bottom sediment was carried out according to Table 2-6.

Table 2-6: Performance characteristics of the determination of heavy metals (except mercury) and As in bottom sediment

Determinand	Unit	Limit of Quantification (LOQ)	Uncertainty (%) at LOQ	Method
Cadmium (Cd)	mg/kg	24	50	WDXRF
Lead (Pb)	mg/kg	15	10	WDXRF
Nickel (Ni)	mg/kg	15	10	WDXRF
Arsenic (As)	mg/kg	15	10	WDXRF
Chromium (Cr)	mg/kg	9	10	WDXRF
Cobalt (Co)	mg/kg	6	10	WDXRF
Copper (Cu)	mg/kg	15	10	WDXRF
Titanium (Ti)	mg/kg	12	5	WDXRF
Vanadium (V)	mg/kg	6	5	WDXRF
Zinc (Zn)	mg/kg	15	10	WDXRF
Aluminium (Al)	mg/kg	90	5	WDXRF
Iron (Fe)	mg/kg	30	5	WDXRF
Manganese (Mn)	mg/kg	210	5	WDXRF

For the mercury analysis an Advanced Mercury Analyser (AMA-254, made by ALTEC and distributed by LECO) was used. This technique uses a direct atomic absorption cold-vapour method with gold amalgamation. The analysis was performed in solid samples without any further sample preparation. Calibration standard solutions were made by stepwise dilution of these stock solutions. Final acid concentration was 10 ml/l sulphuric acid (Merck, ‘‘Suprapur’’). The concentrations of calibration solutions in dosing of 100 µl are as follows: 5, 10, 20, 50, 100, 200 and 500 ng/100 µl solutions. Pure O_2 was used as carrier gas. Calibration curves were verified using the following certified reference materials: BCR-141R (0.25 ± 0.02 mg/kg Hg), BCR-143R (1.10 ± 0.07 mg/kg Hg), RTH-953 (1.84 ± 0.22 mg/kg Hg).

2.4 Determination of heavy metals and As in biota (mussels and fish)

2.4.1 Sample preparation

2.4.1.1 Mussels

The freeze-dried mussel samples were provided in 50 ml PE bottles. Samples were stored at room temperature until they were analyzed.

Dry mussel sample (around 0.3 g) was precisely weighed into Teflon vessel and heavy metals were extracted by digestion in microwave oven (MLS 1200), using 3 ml of concentrated Nitric Acid (ANALPUR SD) and 1 ml hydrogen peroxide (30%). After cooling to room temperature the sample extract was transferred into 50 ml volumetric flask, filled up to sign, ready for the analytical measurement.

2.4.1.2 Fish

Frozen samples of fish were provided in aluminum foil. Samples were stored in a freezer.
Fish sample (around 2 g) was precisely weighed into Petri dish and freeze-dried. Freeze-dried sample was mineralized in microwave (MLS 1200) by 6 ml of concentrated Nitric Acid (ANALPUR SD) and 1 ml hydrogen peroxide (30%). After cooling to room temperature the sample extract was transferred into 50 ml volumetric flask, filled up to sign, ready for the analytical measurement.

2.4.2 Analytical procedures

Determination of arsenic, cadmium, chromium, lead and nickel in the extracts from mussels and fish was carried out by flameless AAS (Perkin Elmer ANALYST 600), copper and zinc by flame AAS (Perkin Elmer ANALYST 400) and mercury by AAS (AMA 254). **NB.: Methyl-mercury has not been analyzed in biota.**

An overview on the analytical procedures used for determination of heavy metals and As in the biota samples is given in Table 2-7.

Table 2-7: Methods for the determination of heavy metals and As in mussels and fish

Determinand	Unit	Limit of Quantification (LOQ)		Method Used	Method
		Mussels	Fish		
Cadmium (Cd)	mg/kg	0.001	0.001	ETA-AAS	National standard
Lead (Pb)	µg/kg	0.6	0.6	ETA-AAS	National standard
Mercury (Hg)	µg/kg	0.05	0.05	AMA	National standard
Nickel (Ni)	mg/kg	0.002	0.002	ETA-AAS	National standard
Arsenic (As)	mg/kg	0.001	0.001	ETA-AAS	National standard
Chromium (Cr)	mg/kg	0.001	0.001	ETA-AAS	National standard
Copper (Cu)	mg/kg	0.01	0.002	ETA-AAS	National standard
Zinc (Zn)	mg/kg	0.001	0.001	F-AAS	National standard

2.4.3 Analytical Quality Control

Each batch of 15 samples included a quality control sample and blank samples were analysed as well. As the values of blank samples for all measured metals (except As) were low no blank correction was carried out for heavy metals determination (only As correction 0.04 mg/kg for fish was performed).

Standard additions of heavy metals to the samples were carried out as well, in order to take into consideration the sample preparation and matrix influence. As the results of the recovery were near 100 %, no recovery rate was used for the results of samples.

3 Results

3.1 Heavy metals and As in water

Results of the determination of the dissolved heavy metals in the surface water samples are summarized in Tables 3-1 and 3-2.

Table 3-1 Minimum and maximum concentration of dissolved heavy metals and As in water

Elements	Concentration, µg/l			
	Danube		Tributaries	
	min	max	min	max
Cadmium (**Cd**)	<0.2	<0.2	<0.2	<0.2
Lead (**Pb**)	<2.0	<2.0	<2.0	5.07
Mercury (**Hg**)	<0.05	0.071	<0.05	<0.05
Nickel (**Ni**)	<2.0	12.2	<2.0	33.3
Arsenic (**As**)	<0.8	4.31	<0.8	13.2
Chromium (**Cr**)	<0.5	1.26	<0.5	1.73
Copper (**Cu**)	<2.0	4.59	<2.0	34.5
Zinc (**Zn**)	<5.0	16.1	<5.0	67.9

Table 3-2 The highest concentration of heavy metals and As in water

Element	JDS 2 code	Sampling station	Concen-tration [µg/l]	AA-EQS* [µg/l]	AA-EQS** [µg/l]
Pb	JDS-IS2	before Reservoir Iskar	5.07	7,2	-
Hg	JDS32	Budapest downstream	0.071	0,05	-
	JDS33	Adony/Lórév	0.063	0,05	-
Ni	JDS66	/Timok (rkm 0.2)	33.3	20	-
	JDS32	Budapest downstream	12.2	20	-
	JDS15	/Morava (rkm 0.08)	7.63	20	-
As	JDS24	/Hron (rkm 0.5)	13.2	-	-
	JDS-MO2	Dyje - Pohansko	7.53	-	-
	JDS37	Sio (rkm 1.0)	7.44	-	-
Cr	JDS-RL2	Beli Lom, Pisanetz	1.73	-	-
	JDS-IS2	before Reservoir Iskar	1.67	-	-
	JDS81	/Russenski Lom	1.26	-	-
Cu	JDS66	/Timok (rkm 0.2)	34.5	-	8.8
	JDS85	Downstream Ruse/Giurgiu	14.6	-	8.8
	JDS81	/Russenski Lom	11.2	-	8.8
Zn	JDS-IS2	before Reservoir Iskar	67.9	-	35.1
	JDS83	Upstream Arges	16.1	-	35.1
	JDS66	/Timok (rkm 0.2)	9.3	-	52

****Proposal for amending Directive 2000/60/EC*** ****Austrian proposal, hardness dependent***

Table 1-1 demonstrated the problem of evaluation of the Cd results pertaining to the AA-EQS because the LOQ of the method used is higher than the relevant total hardness dependent EQS values. Although the total hardness in most of the water samples is in the range of 100 to 200 mg/l $CaCO_3$, but the Table 3-1 shows that the Cd has not been quantified in any of the water samples; therefore, the exceedance of the EQS for Cd can not be evaluated.

Concerning the other heavy metals on the list of Priority Substances, the Pb has not reached the EQS at any sampling sites. The concentration of Hg slightly (by 30-40%) exceeded the EQS at two sites downstream of Budapest, measuring 0.071 and 0.063 µg/l at JDS32 and JDS33, respectively. The concentration of Ni exceeded the EQS by 67% in the Timok river at its confluence with the Danube.

Two more heavy metals, Cu and Zn, require further attention. Austria and Slovakia are preparing tentative EQS for these two metals depending on the total hardness of the water, and the JDS2 results for these two metals revealed the following:

- In the case of Cu, the exceedance of the proposed EQS was observed in three water samples, as demonstrated in Figure 3-1, in the Danube downstream of Ruse/Giurgiu (JDS85) and in two tributaries, the Timok (JDS66) and the Russenski Lom (JDS81). The total hardness in these water samples were 101, 311 and 226 mg/l $CaCO_3$, respectively, and accordingly the EQS for Cu was 8.8 µg/l for each sample. The results showed that the Cu concentration in the Timok river exceeded the EQS around four times. Relatively higher concentrations were characteristic downstream of the *Irongate*.

- In the case of Zn, relatively high concentration was measure in three samples but only one sample, in the upstream section of the tributary Iskar (at station JDS-IS2) exceeded the hardness dependant EQS. (NB.: The total hardness of JDS66-Timok, JDS83-Danube upstream Arges, and JDS-IS2 were 311, 99 and 100 mg/l $CaCO_3$, respectively).

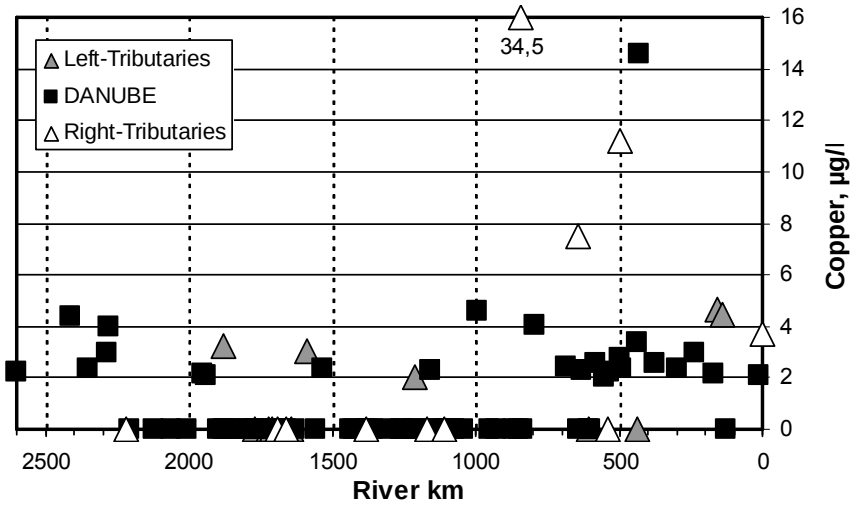


Figure 3-1 Variation in the concentration of Copper dissolved in the water during JDS2

Most of the other heavy metals and the As were present in concentration below the LOQ or slightly above this limit. Cr were present in concentrations little higher at few stations, these were mostly in tributaries, e.g., Russenski Lom, Iskar, at the lower Danube. Figure 3-2 demonstrate the variations in the dissolved As content in the samples collected during JDS2, showing the significantly higher concentrations in the tributaries and the relatively higher concentrations in the Danube downstream of the *Tisa-Sava* confluences.

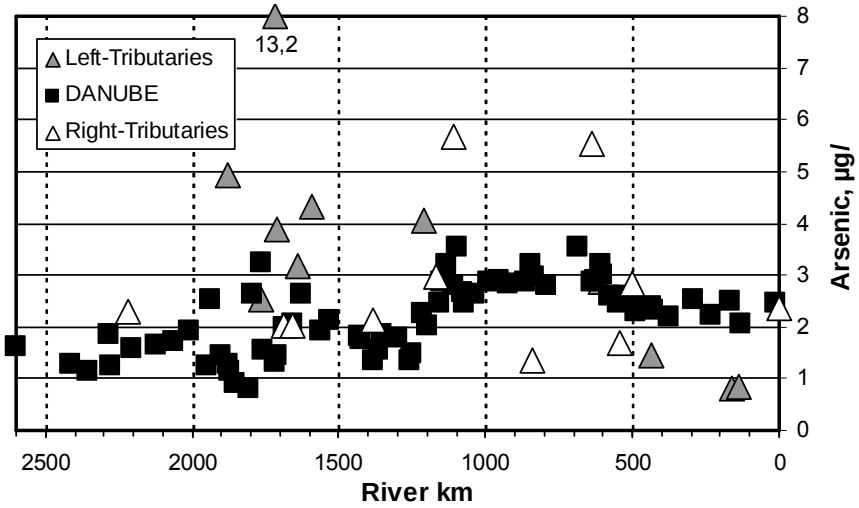


Figure 3-2 Variation in the concentration of Arsenic dissolved in the water during JDS2

It should be taken into account that these results obtained by analyzing the JDS water samples to characterise the dissolved contaminant level, which is dependent on the ionic environment in the river, the pH and redox conditions, the presence of chelating agents, etc., at the time of the survey; however, this dissolved form is the most bioavailable form which is ready for bioaccumulation in the food chain. Furthermore, it is also known that the major transportation route of the heavy metals are in the solid phase, i.e., suspended particulate matter, which may accumulate in the bottom sediment; therefore, characterization of the heavy metals contamination in the SPM and the bottom sediment is equally important.

3.2 3.2 Heavy metals and As in the suspended particulate matter (SPM)

3.2.1 Quality standards

For the evaluation of heavy metals in suspended particulate matter and sediments there are different sources for environmental quality standards (see Table 3-3):

- Quality target used for the evaluation of JDS 1 data;
- Sediment standards derived from the WFD Priority Substances data sheets (the values are under discussion and to be confirmed);
- Dutch quality standards – target values according to “Staatscourant, The Netherlands, June 2000;” and
- Target values from the International Commission for the River Rhine.

Table 3-3 Quality targets for heavy metals and As in sediments (including both SPM and bottom sediment)

Element	Sediment Quality Target during JDS1 (mg/kg)	Dutch Target Value* (mg/kg)	Rhine Target Value (mg/kg)
Cadmium	1.2	0.8	1
Lead	100	85	100
Mercury	0.8	0.3	0.5
Nickel	50	35	50
Arsenic	20	29	40
Chromium	100	100	100
Copper	60	36	50
Zinc	200	140	200
Molybdenum	-	3	-

* The Dutch Target Values are given for normalized sediment [10% TOC and 25% lutum (clay)]

At the time of preparation of this report WFD Priority Substances data sheets included proposed limit values for the benthic community, sediments, which are a little confusing and should be confirmed. Therefore, the evaluation of the sediments the quality targets used during JDS1 is primarly used during interpretation of the JDS2 results. It is notable; however, that these target values are very similar to those used in the Rhine river basin, and they are also close to the Dutch tagret values particularly if we consider the normalization requirements in the latter case.

3.2.2 Longitudinal profile of the Group 1 heavy metals (Cd, Pb, Hg and Ni)

Cadmium, Lead, Mercury and Nickel are listed among the Priority Substances of the WFD, therefore, particular attention was made to these heavy metals during the data interpretation. The following four figures (Figs. 3-3 through 3-6) show the longitudinal variation of these heavy metals in the suspended particulate matter in the Danube and its tributaries.

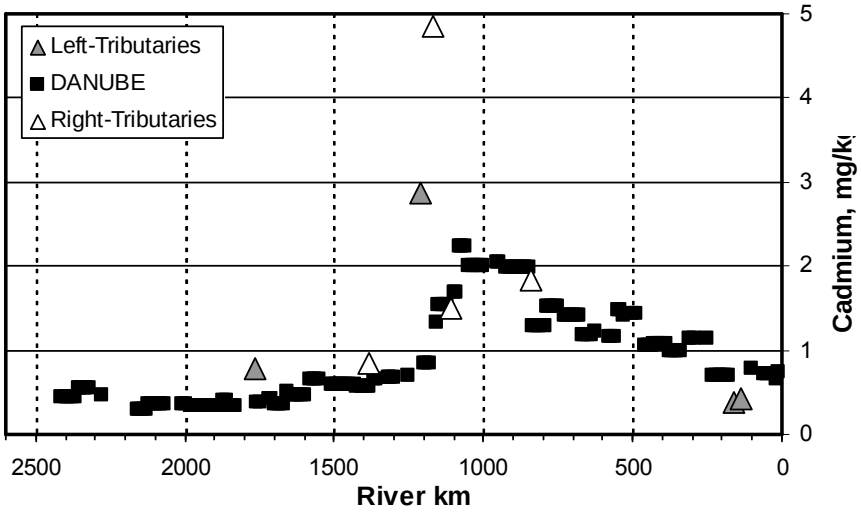


Figure 3-3 Distribution of Cadmium in the SPM along the Danube river during JDS2

Figure 3-3 clearly demonstrate the significant impact of two major tributaries, the Tisa and Sava, by the increasing concentration of Cadmium in the suspended solids along the lower Danube reach. The 1.2 mg/kg sediment standard was significantly exceeded in these two rivers and as a result of the transport of these metals to the Danube, their affect (the exceedance of the sediment standard) on the Danube SPM was obvious along a 1,000 km Danube reach downstream of confluence of the Sava river.

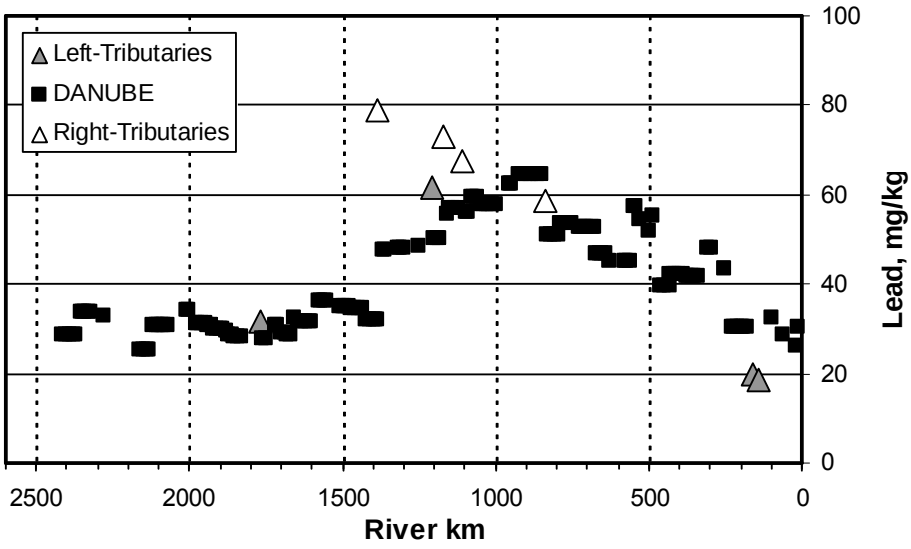


Figure 3-4 Distribution of Lead in the SPM along the Danube river during JDS2

As shown in Figure 3-4 the Lead concentration in the SPM has not reached the 100 mg/kg sediment standard but the polluting affect of the tributaries, i.e., Drava, Tisa, Sava and the Velika Morava, was clearly demonstrated by the variation in the Pb concentration in the Danube SPM downwards to the Danube Delta.

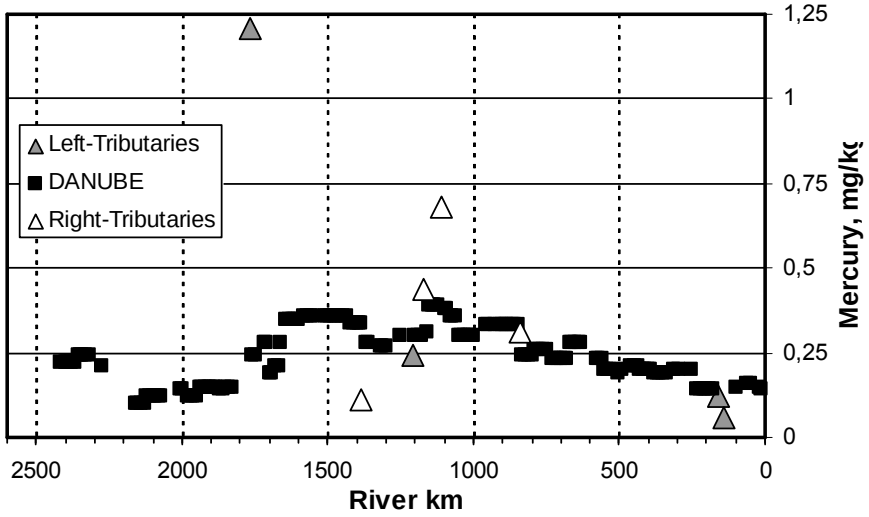


Figure 3-5 Distribution of Mercury in the SPM along the Danube river during JDS2

The Mercury concentration in the SPM (see Figure 3-5) exceeded sediment standard (0.8 mg/kg) in the tributary Vah river only. Increased concentration was also in the Velika Morava; however, this was slightly below the sediment standard. The Vah (JDS21), caused impact was particularly significant because it more than doubled the Mercury concentration in the SPM along the downstream Danube reach compared to the upstream Danube reach. The Mercury concentration in the SPM slightly exceeded even the strict Dutch target value of 0,3 mg/kg along the Danube from the confluence of Vah downwards to the Irongate.

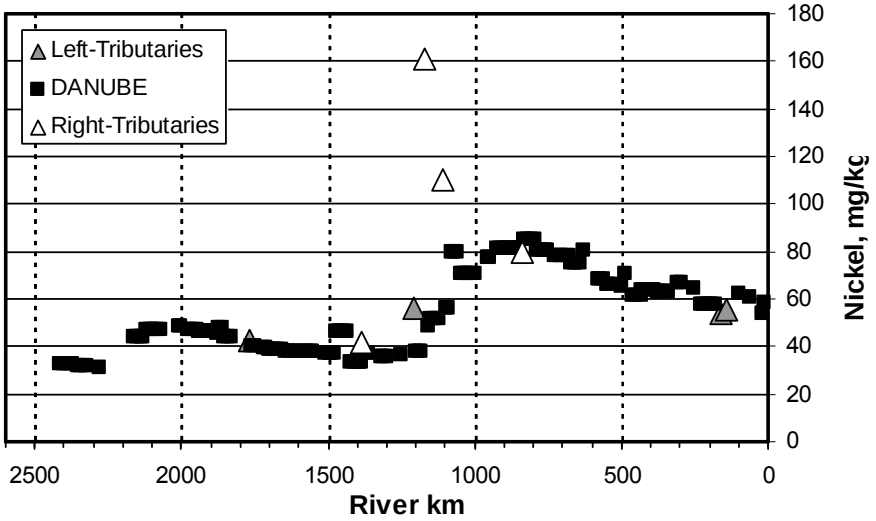


Figure 3-6 Distribution of Nickel in the SPM along the Danube river during JDS2

The Nickel contamination profile in the SPM (see Figure 3-6) clearly demonstrate the significant affect of the SPM transported through the Sava (161 mg Ni/kg) and Velika Morava (110 mg Ni/kg).to the Danube resulting exceedance of the 50 mg/kg sediment standard from the confluence of these tributaries downwards to the Danube Delta.

3.2.3 Longitudinal profile of the Group 2 heavy metals (Cr, Cu, Zn, Bi and Mo) and As

The following six figures (Figs. 3-7 through 3-12) show the longitudinal variation of the five heavy metals and As in the suspended particulate matter in the Danube and its tributaries.

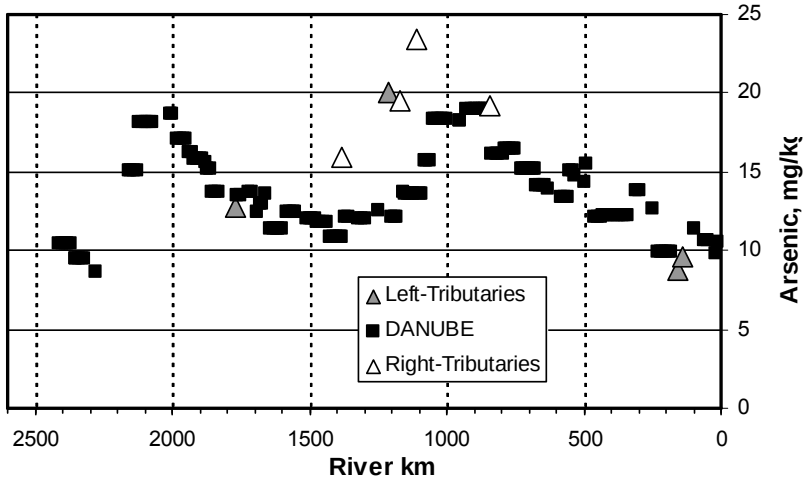


Figure 3-7 Distribution of Arsenic in the SPM along the Danube river during JDS2

With one exception, Velika Morava, the concentration of the As in the SPM were below the 20 mg As/kg sediment standard in all samples from the Danube and the other tributaries. Unfortunately there was no SPM sample from the river Inn, which very likely cause the significant increase in the As concentration downstream of the Inn confluence. From the 2,000 rkm the As concentration gradually decreased along around 1,000 km Danube reach. As a result of the input from the three tributaries (i.e., Tisa, Sava and Velika Morava) the As concentration increased again near to the concentration of the sediment standard value; however, again decreased gradually downwards to the Danube Delta.

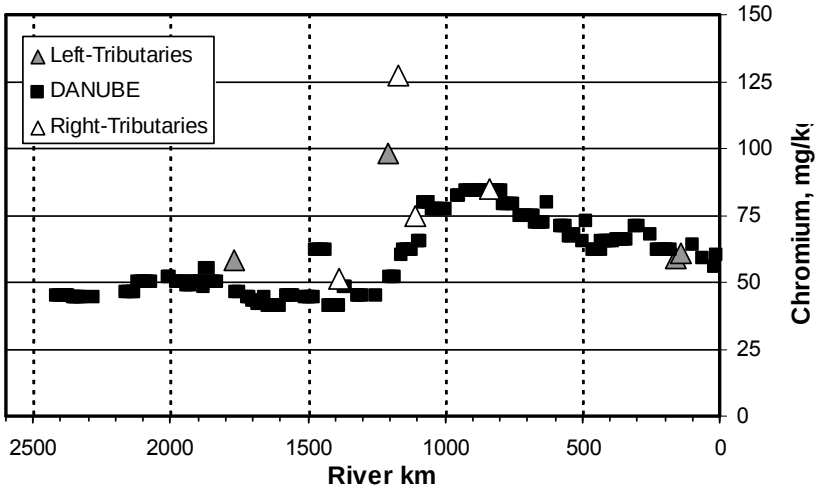


Figure 3-8 Distribution of Chromium in the SPM along the Danube river during JDS2

The longitudinal profile of the Cr concentration in the SPM (Figure 3-6), shows very strong similarity to the Ni. A characteristic „hump“ was developed downstream of the Tisa and Sava confluence, the latter one was the only in which the sediment standard for Cr was exceeded (JDS51, 127 mg Cr/kg). The concentration hump downstream the Sava confluence gradually decreased but even in the Danube Delta the concentration of Cr in the SPM was around 50% higher than along the upper Danube reach.

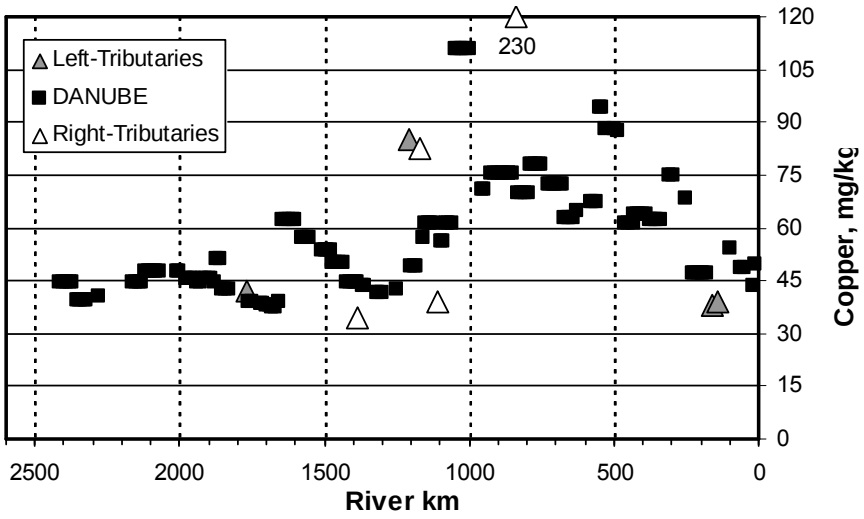


Figure 3-9 Distribution of Copper in the SPM along the Danube river during JDS2

The 60 mg/kg sediment standard was basically exceeded in all SPM samples downstream of the Tisa and Sava confluence. The highest concentration (230 mg Cu/kg) was found in the Timok river (JDS66). The overall longitudinal concentration profile was also similar to the Cd and Ni, which may indicate mainly geochemical origin of these metals in the relevant sub-basins, ie., Tisa and Sava.

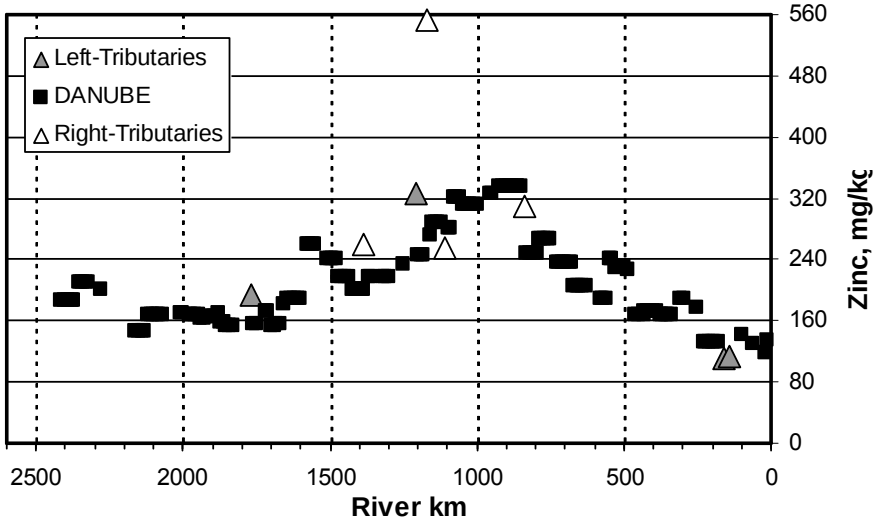


Figure 3-10 Distribution of Zinc in the SPM along the Danube river during JDS2

The Zn is the fourth heavy metal joining the group of Cd, Ni and Cu regarding the characteristic of the longitudinal profiles. The 200 mg Zn/kg sediment standard in the SPM was exceeded in the samples very similarly as in the case of Cu, and showing the major influence by the composition of the SPM in the Tisa and Sava rivers. The highest concentration was found in the Sava river (554 mg Zn/kg).

In addition to the Arsenic and the other three frequently monitored heavy metals in Group 2, Bismuth and Molybdenum were also analyzed in the SPM. Their longitudinal trends are shown in Figures 3-11 and 3-12.

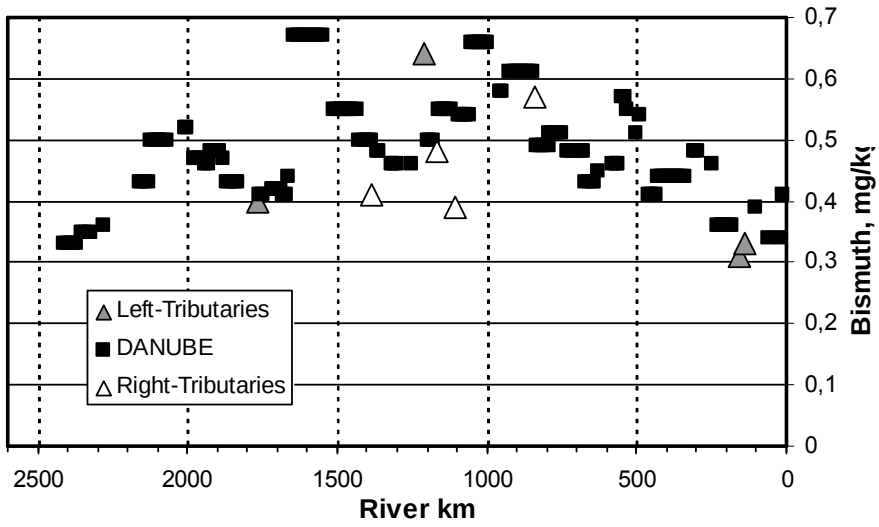


Figure 3-11 Distribution of Bismuth in the SPM along the Danube river during JDS2

The spatial distribution for Bi shows a more scattered picture in comparison to other metals but the concentrations were within a relatively narrow, 0,3 to 0,7 mg/kg range.

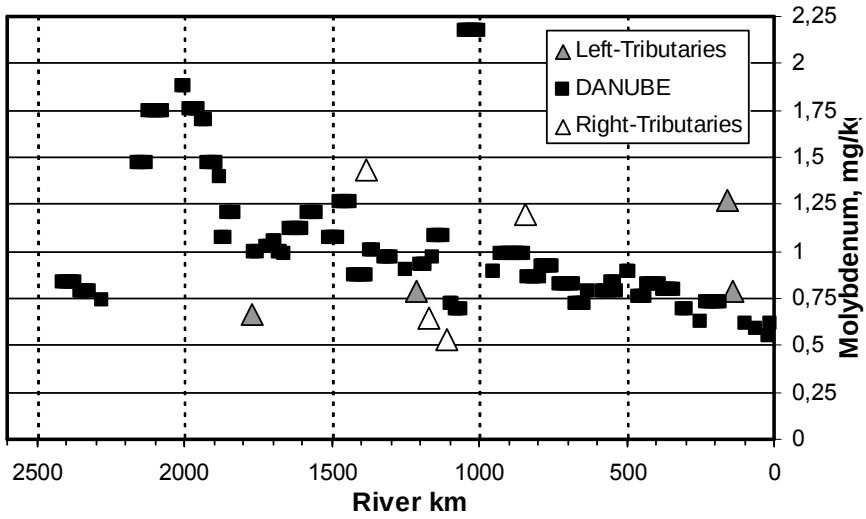


Figure 3-12 Distribution of Molybdenum in the SPM along the Danube river during JDS2

Molybdenum has a clear peak in the upper Danube, which similarly to the As, could be related to input through the Inn or to anthropogenic influences. However, the Mo concentration in the SPM were low, below the Dutch target value of 3 mg/kg at all sampling sites.

3.2.4 Longitudinal profile of the Group 3 heavy metals (Al, Fe and Mn)

The concentrations of Al and Fe in the SPM showed (see Figures 3-13 and 3-14) significantly different trends upstream and downstream of the Irongate. It is very likely because these two metals are mainly have geochemical origin and controlled by the different mineralogical composition of the SPM, that is more variable upstream of the Irongate due to the inputs from the different geochemical characteristics of the sub-basins of the tributaries. The variation in Al could be controlled by the clay content of the SPM, which could be useful for normalization of the other heavy metal results in the full report.

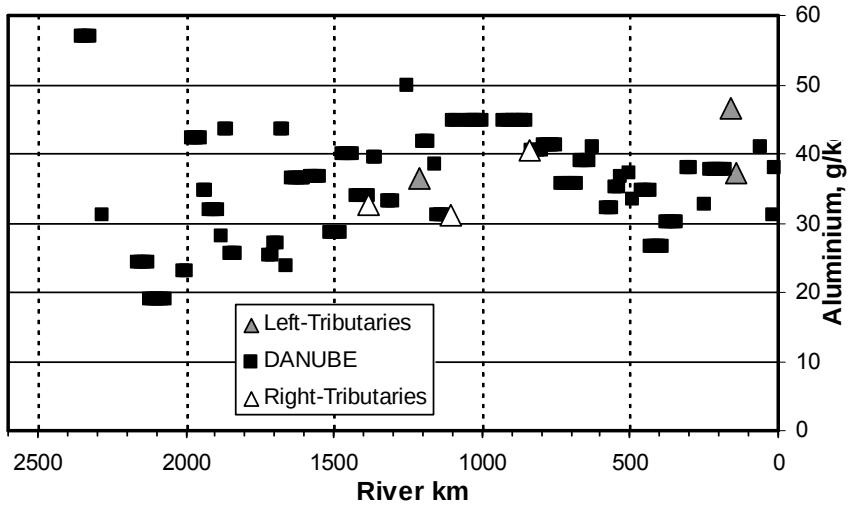


Figure 3-13 Distribution of Aluminium in the SPM along the Danube river during JDS2

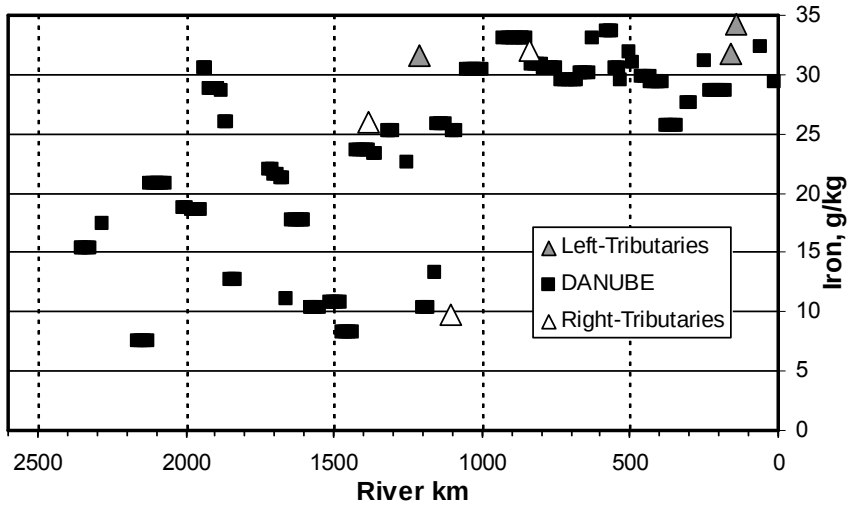


Figure 3-14 Distribution of Iron in the SPM along the Danube river during JDS2

After the lower concentrations and significant variations along the upper Danube reach the concentration of Al and Fe followed more or less constant values from the Irongate downwards to the Danube Delta.

The concentration of Mn in the SPM (see Figure 3-15) showed similar longitudional trend as in the case Cu and Zn. Significant increase was observed downstream the Velika Morava and the Irongate reservoire, which gradually decreased downwards to the Danube Delta.

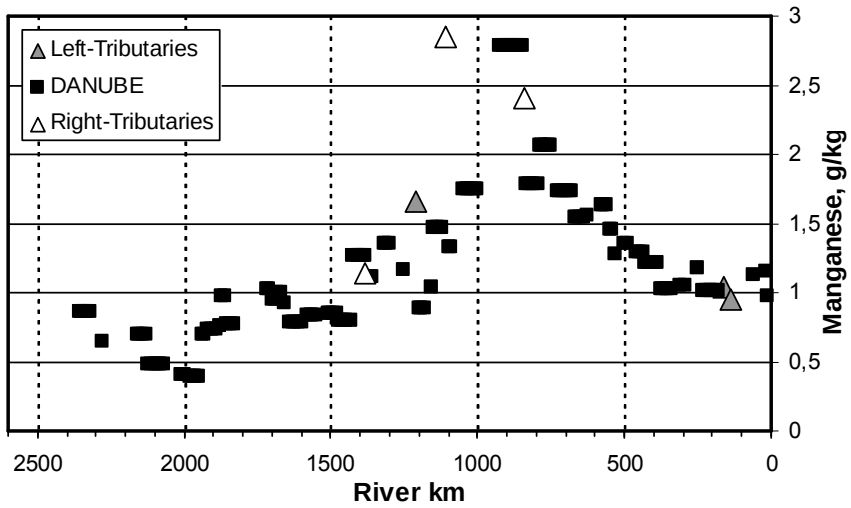


Figure 3-15 Distribution of Manganese in the SPM along the Danube river during JDS2

3.2.5 Comparison of the concentration of heavy metals and As in SPM between JDS1 and JDS2

Regarding the four heavy metals in the list of Priority Substances, the minimum and maximum concentrations in the SPM, summarized in Table 3-4, revealed the following:

- In the case of Cd, the minimum concentrations were basically the same (NB.: During JDS1 the LOQ was significantly higher; therefore, the minimum values are „less than“); however, significantly lower maximum values were measured in both the Danube and in the tributaries;
- In the case of Pb, insignificant increase in the minimum values, and in the maximum values insignificant decrease in the Danube but significant decrease in the tributaries were observed;
- In the case of Hg, The minimum values were basically the same, the maximum value decreased in the Danube but increased in the tributaries; and
- In the case of Ni, none of the values shows significant difference between the two survey results.

Table 3-4 Range of element concentrations in the SPM samples of the river Danube and some of its tributaries, during JDS1 and JDS2

Element	Concentration, mg/kg			
	Danube		Tributaries	
	JDS 1	JDS 2	JDS 1	JDS 2
Cd	< 1.1 – 7.6	0.294 – 2.23	< 1.1 – 25.6	0.394 – 4.85
Pb	18.2 – 85.0	25.3 – 64.6	17.3 – 214.9	18.5 – 79.1
Hg	< 0.10 – 0.55	0.102 – 0.388	< 0.10 – 0.79	0.060 – 1.21
Ni	23.2 – 89.8	30.9 – 85.0	32.6 – 170.9	41.4 – 161.0
As	9.4 – 32.1	8.62 – 19.0	10.4 – 29	8.83 – 23.4
Cr	32.9 – 107.5	40.8 – 94.3	55.0 – 148.9	38.0 – 127.0
Cu	28.3 – 193.7	37.7 – 111.0	26.9 – 95.5	34.4 – 230.0
Zn	99 – 398	117 - 335	87 - 2224	111 - 553
Al	17900 – 52800	19000 - 57000	15300 – 54100	31200 - 49800
Fe	14300 – 38300	7180 - 35400	21300 – 37200	9700 - 34300
Mn	565 – 4028	770 - 3150	963 – 3340	1060 - 4120

Regarding the other elements, concentration ranges are also shown in Table 3-4, the spatial distribution of Cu, Zn (similarly to the Priority Substances Cd and Ni) was very similar to the distribution of Al and Fe during JDS1 and JDS2 as well. This comparable trend was interpreted as a reflection of the geochemical background in both surveys.

It is notable that significant change can be observed in the case of the maximum values such as (a) the Copper concentration decreased in the Danube and increased in the tributaries, and (b) the Zinc concentration decrease in the tributaries.

All the other concentrations were very similar during the two surveys.

3.3 Heavy metals and As in the bottom sediment

Bottom sediment samples were collected from both left and right banks of the Danube, and one mixed sediment samples from the tributaries. The revealed significant differences between the sediments collected from the two river banks, particularly downstream of significant in put s from the tributaries, e.g., affect of the Hg input from the left-tributary Vah, on the downstream left-bank sample from the Danube, etc.

3.3.1 Longitudinal profile of the Group 1 heavy metals (Cd, Pb, Hg and Ni)

The longitudinal profile of the Group 1 heavy metals (Cd, Pb, Hg and Ni) are shown in Figures 3-16 through 3-19.

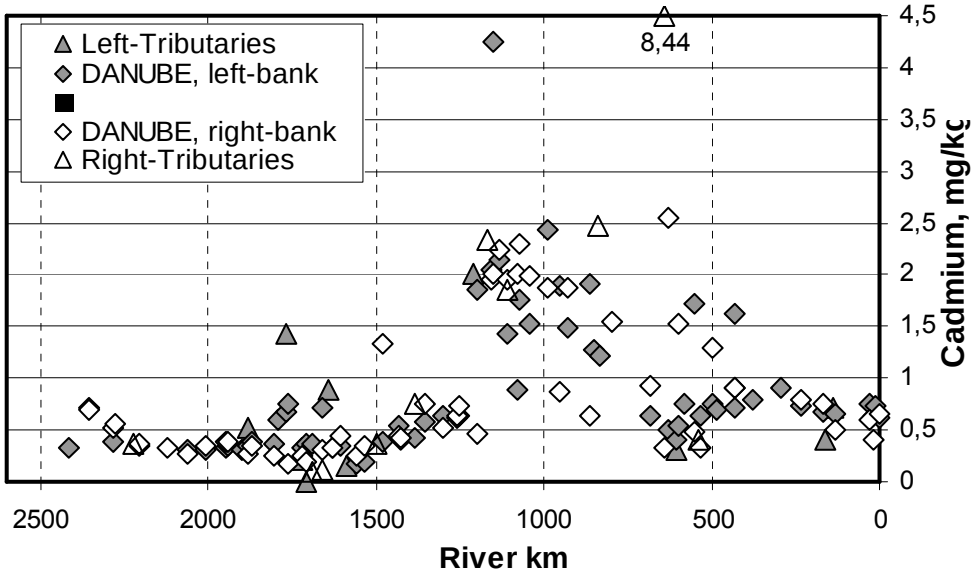


Figure 3-16 Variation in the concentration of Cadmium in the bottom sediment during JDS2

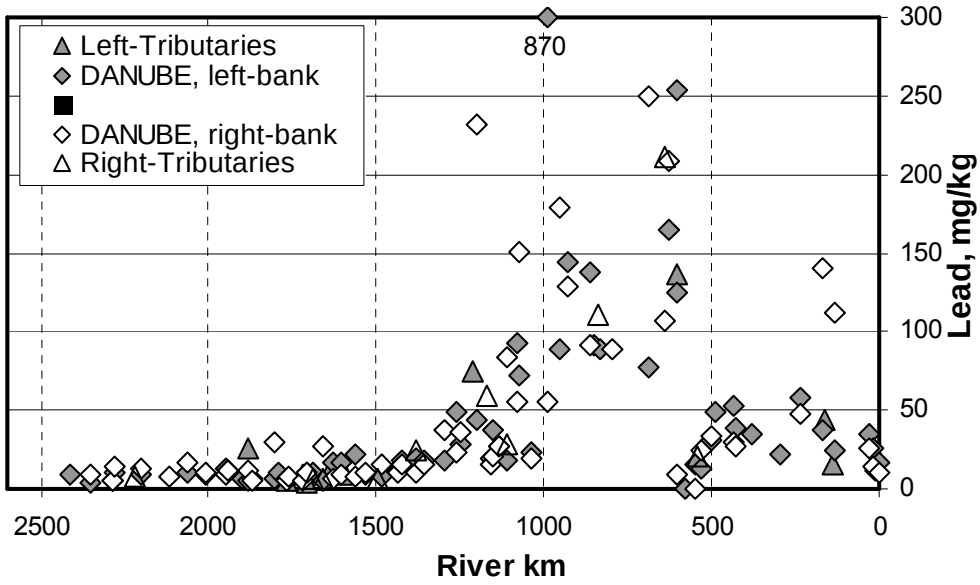


Figure 3-17 Variation in the concentration of Lead in the bottom sediment during JDS2

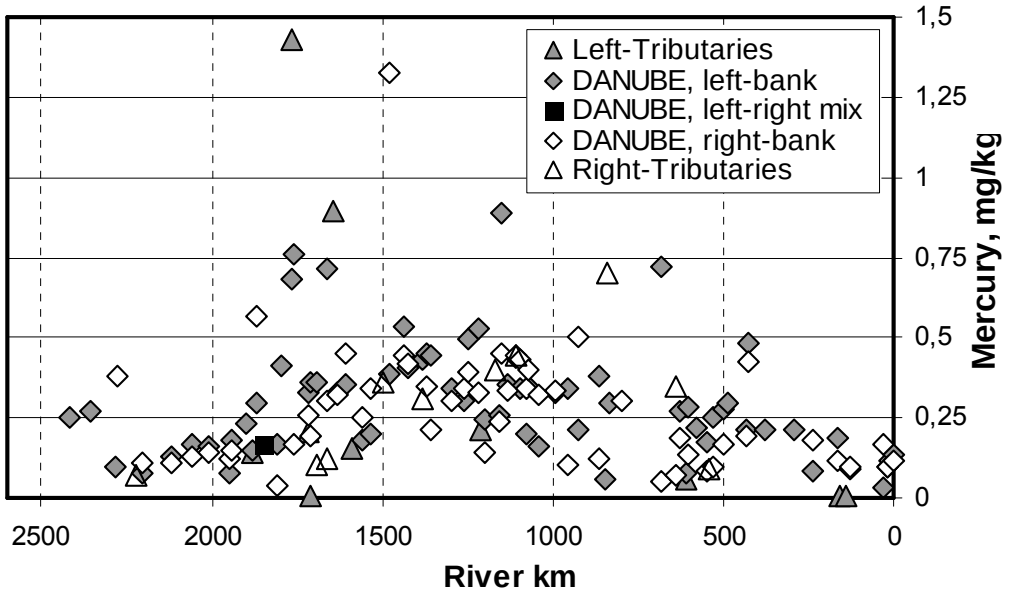


Figure 3-18 Variation in the concentration of Mercury in the bottom sediment during JDS2

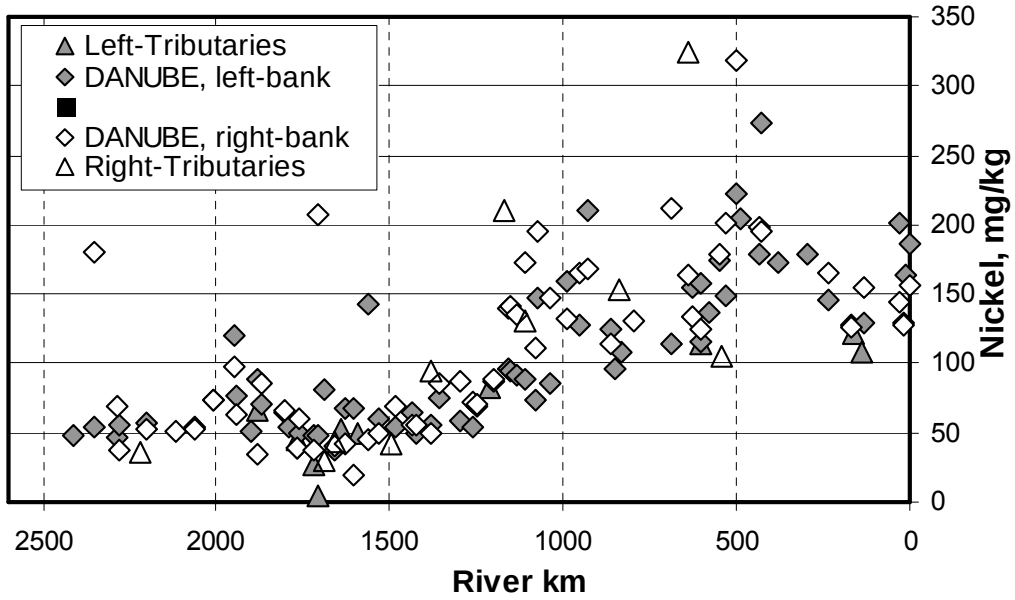


Figure 3-19 Variation in the concentration of Nickel in the bottom sediment during JDS2

In addition to the concentration ranges of priority heavy metals in Table 3-5, the exceedance of the sediment standards and the longitudinal trends could be summarized as follows:

- For Cadmium, the longitudinal trend is very similar to the SPM; however, the concentration and the number of sites where the sediments standard was exceeded were higher than in the case of SPM. Significant variation was observed downstream of the two major polluting rivers the Tisa and Sava. The distribution pattern is also similar to the one during JDS1.
- In the case of Lead, significantly higher concentrations occurred as in the SPM. The longitudinal profile is very impressively show low concentrations along the upper Danube reach and the high variation downstream the Tisa and Sava. The sediment standard was exceeded in relatively large number of samples.
- In the case of Mercury, the impact of the major pollution source from the tributary Vah and other inputs along the middle section of the Danube can be recognized in the variation of the typically anthropogenic pollutant. It is notable; however, that the sediment standard 0.8 mg/kg was exceeded at a few sampling site only.
- In the case of Nickel, contrary to the SPM, the concentration in the bottom sediment exceeded the 50 mg/kg sediment standard at most of the sampling sites. As for several other heavy metals the longitudinal trend was typical, significantly increasing downstream of the confluence of the Tisa and Sava rivers.

Table 3-5 Concentration ranges for priority heavy metals in sediments of Danube tributaries

Element	Concentration, mg/kg		
	Range (mg/kg)	Location of the lowest recorded value	Location of the highest recorded value
Cd	0.23 – 8.44	JDS RL2 Russenski Lom	JDS 71 Iskar (km 0.3)
Pb	22.8 – 2110	JDS TI 1	JDS 71 Iskar (km 0.3)
Hg	0.06 – 1.44	JDS RL2 Russenski Lom	JDS 49 Tisa (km 1.0)
Ni	5.08 – 183	JDS 25, Ipoly (km 0.7)	JDS Prut 2

3.3.2 Longitudinal profile of the Group 2 heavy metals (Cr, Cu and Zn) and As

The following Figures 3-20 through 3-23 show the variation in the concentrations of the heavy metals and As in the bottom sediment samples collected from the Danube and its tributaries during JDS2.

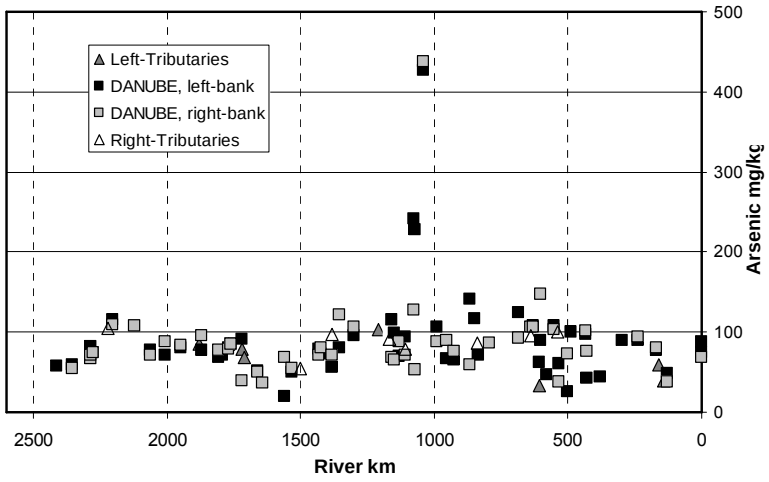


Figure 3-20 Variation in the concentration of Arsenic in the bottom sediment during JDS2

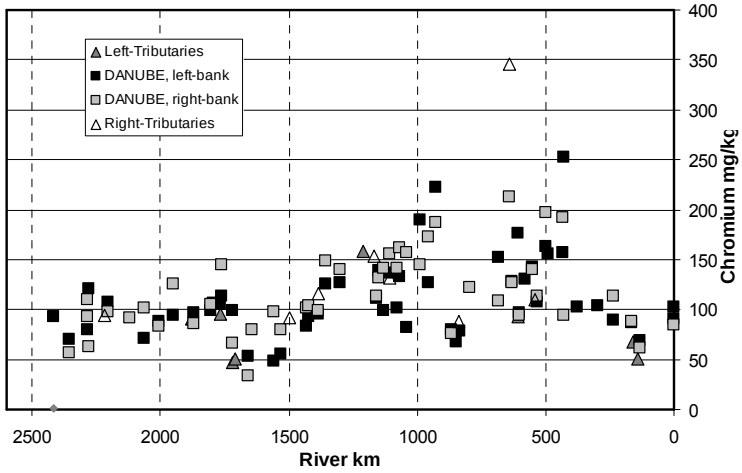


Figure 3-21 Variation in the concentration of Chromium in the bottom sediment during JDS2

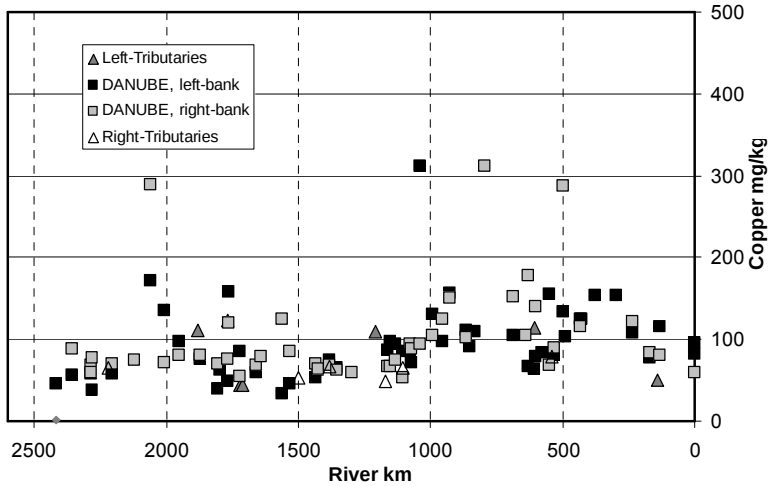


Figure 3-22 Variation in the concentration of Copper in the bottom sediment during JDS2

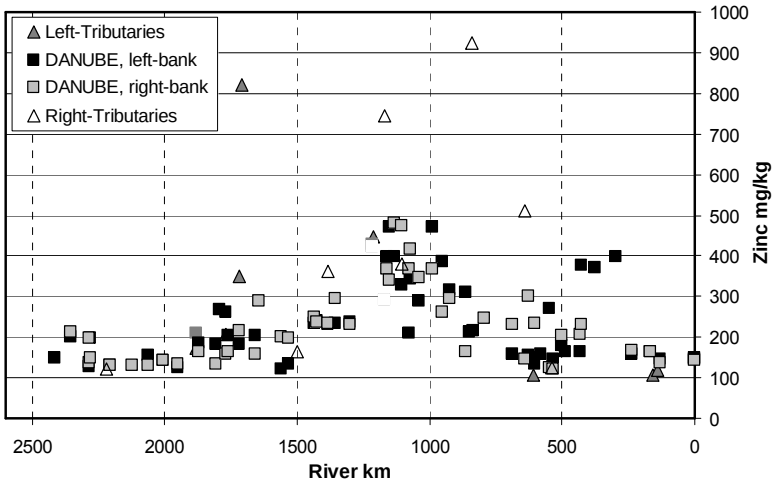


Figure 3-23 Variation in the concentration of Zinc in the bottom sediment during JDS2

Regarding the Group 2 heavy metals (Cr, Cu and Zn) and As the following observations are made:

- In the case of Arsenic, most of the results are between 50 to 100 mg/kg, however a few very high concentration were observed in the vicinity of the Velika Morava confluence;

- In the case of Copper, Chromium and Zinc, the concentration distribution pattern was similar to the Nickel without any significantly high concentrations. This may indicate that the concentration of these metals in the sediments relates to the natural background, the geochemistry of the Danube Basin. Slightly higher concentrations and fluctuation (of each of the three metals) can be observed from the Irongate reservoir downwards to the Danube Delta.

3.3.3 Longitudinal profile of the Group 3 (Al, Fe and Mn) heavy metals

The variation in the concentration of these three metals in the Danube and its tributaries' bottom sediment is demonstrated in Figures 3-24 to 3-26.
As demonstarted in the figures, in the case of the Group 3 heavy metals (Al, Fe and Mn), the distribution patterns are very similar to each other and to those mentioned earlier indicating that they are of geochemical origin.
These metals, particularly the Aluminium, can be used for normalizing the concentration values of other metals, primarily originating from pollution sources, to describe their concentration enrichment and trends in the river basin.

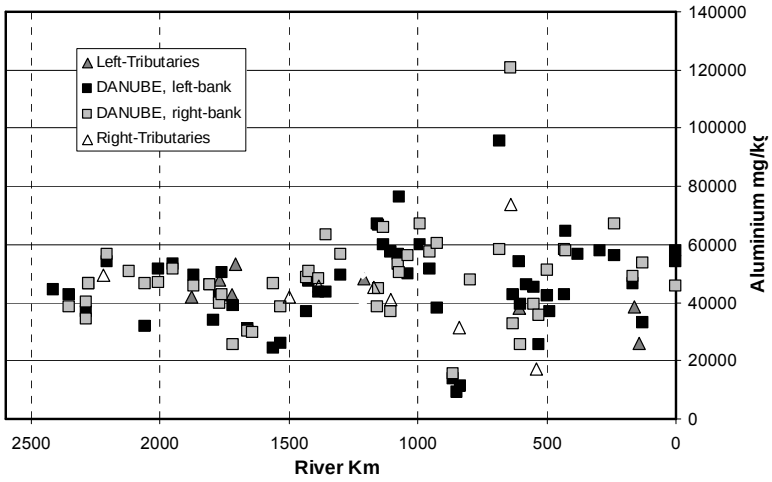


Figure 3-24 Variation in the concentration of Aluminium in the bottom sediment during JDS2

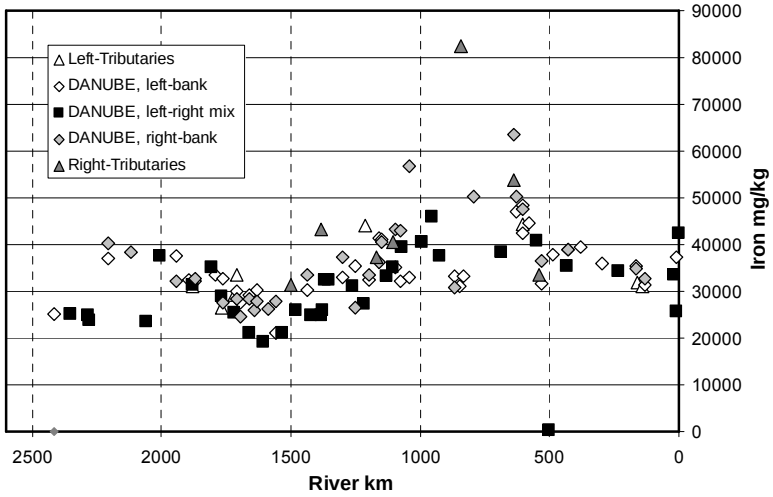


Figure 3-25 Variation in the concentration of Iron in the bottom sediment during JDS2

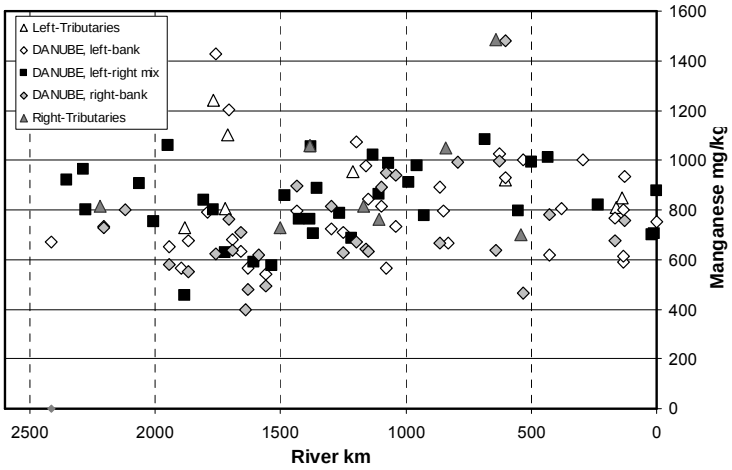


Figure 3-26 Variation in the concentration of Manganese in the bottom sediment during JDS2

3.4 Heavy metals and As in mussels and fish

3.4.1 Mussels

Mussels are used frequently for pollution monitoring, i.e., the “mussel-watch” program is one of the major monitoring program particularly for detecting heavy metals. The only difficulty can be the abundance of identical species at different sites along the surveyed river. As plankton is retaining up to 98% of heavy metals from water, *Unionida* molluscs, plankton consumers, are good indicators of heavy metal pollution.

When comparing the concentration of heavy metals in mussels with the concentrations in fish, it should be taken into account that the results in mussels are expressed in dry weight, whereby in the fish they are in mg/kg wet weight. If we consider that mussels have around 80-85% water in their tissue, the concentration in dry weight could be divided by around 6 to refer to wet weight.

During JDS2, mussel samples, depending on abundance at a given site, were collected from 20 Danube sites and from two tributaries, i.e., Vah (JDS-21), and Prut (JDS-91), significantly less than during JDS1 as demonstrated in Table 3-6.

Table 3-6 Mussel species and number of mussel samples collected during JDS1 and JDS2

Mussel species	Number of samples collected during	
	JDS 1	JDS 2
Anodonta anatina	49	9
Unio tumidus	62	19
Unio pictorum	20	3
Pseudanodonta complanata	2	-
Anodonta cygnea	3	-
Sinodonta waodiana	-	2

Mussels were identified and analysed in 22 localities covering the Danube River stretch from Gabcikovo reservoir (km 1852) to Kilia arm on Ukraine/Romanian border in km 18 and tributaries. As far as species concerns, there were identified four different species: *Anodonta anatina*, *Sinodonta waodiana*, *Unio pictorum* and *Unio tumidus*. As the most frequent species it can be designated *Unio tumidus* which was found in 17 out from mentioned 22 localities. The second most frequent species was *Anodonta anatina*. Detailed analysis of the trends in longitudinal profile of the Danube has been therefore focused on these two species occurrence following the maximum utility of available information as well as species uniformity.

Concentrations of total Hg, and the other heavy metals and As in selected mussel species (*Unio tumidus* and *Anadonta anatina*) collected during JDS2 are shown in the Figures 3-27 and 3-28, respectively.

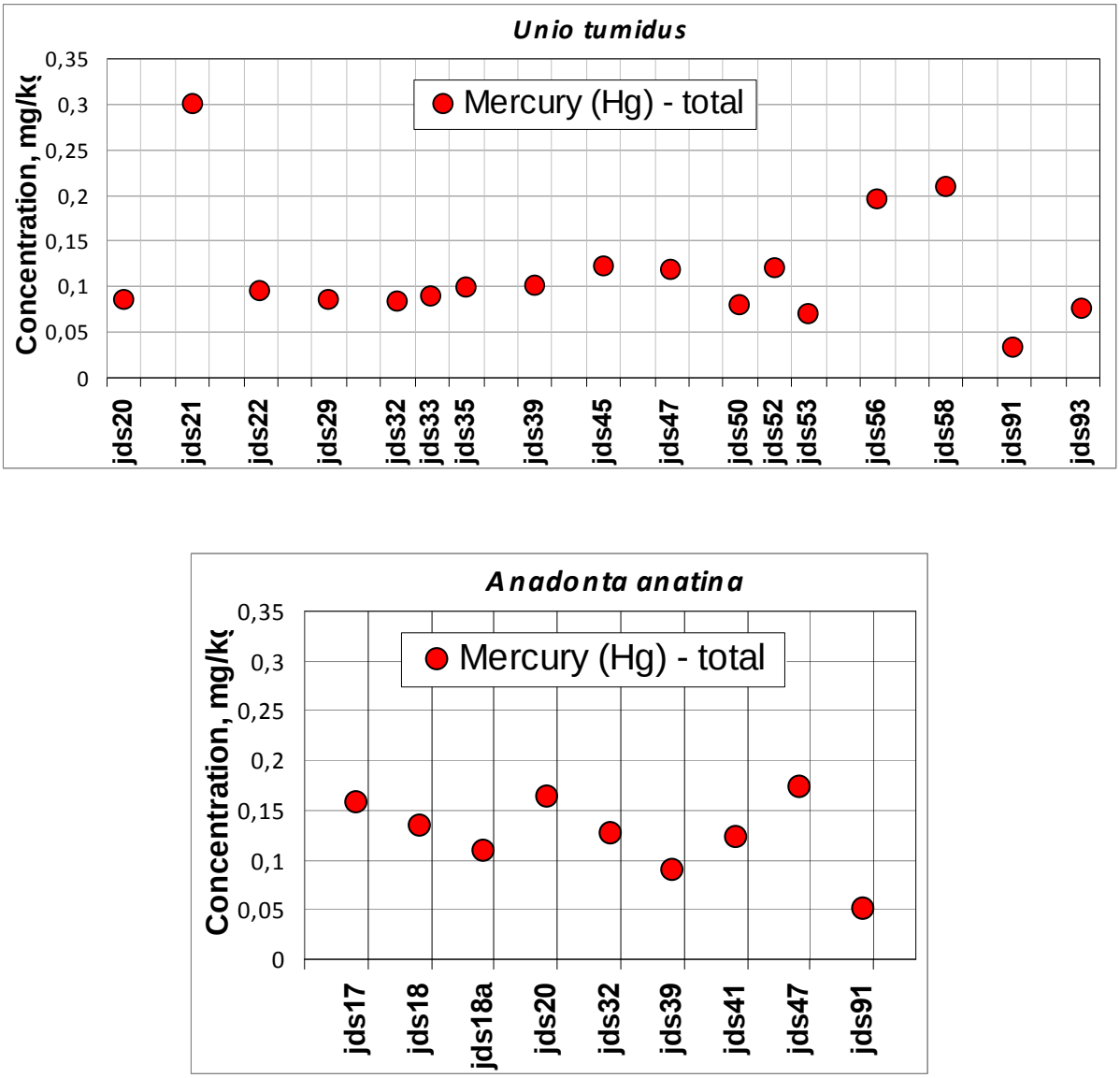


Figure 3-27 Concentration of mercury in the mussel *Unio tumidus* and *Anadonta anatina* collected according to abundance at selected sites along the Danube during JDS2

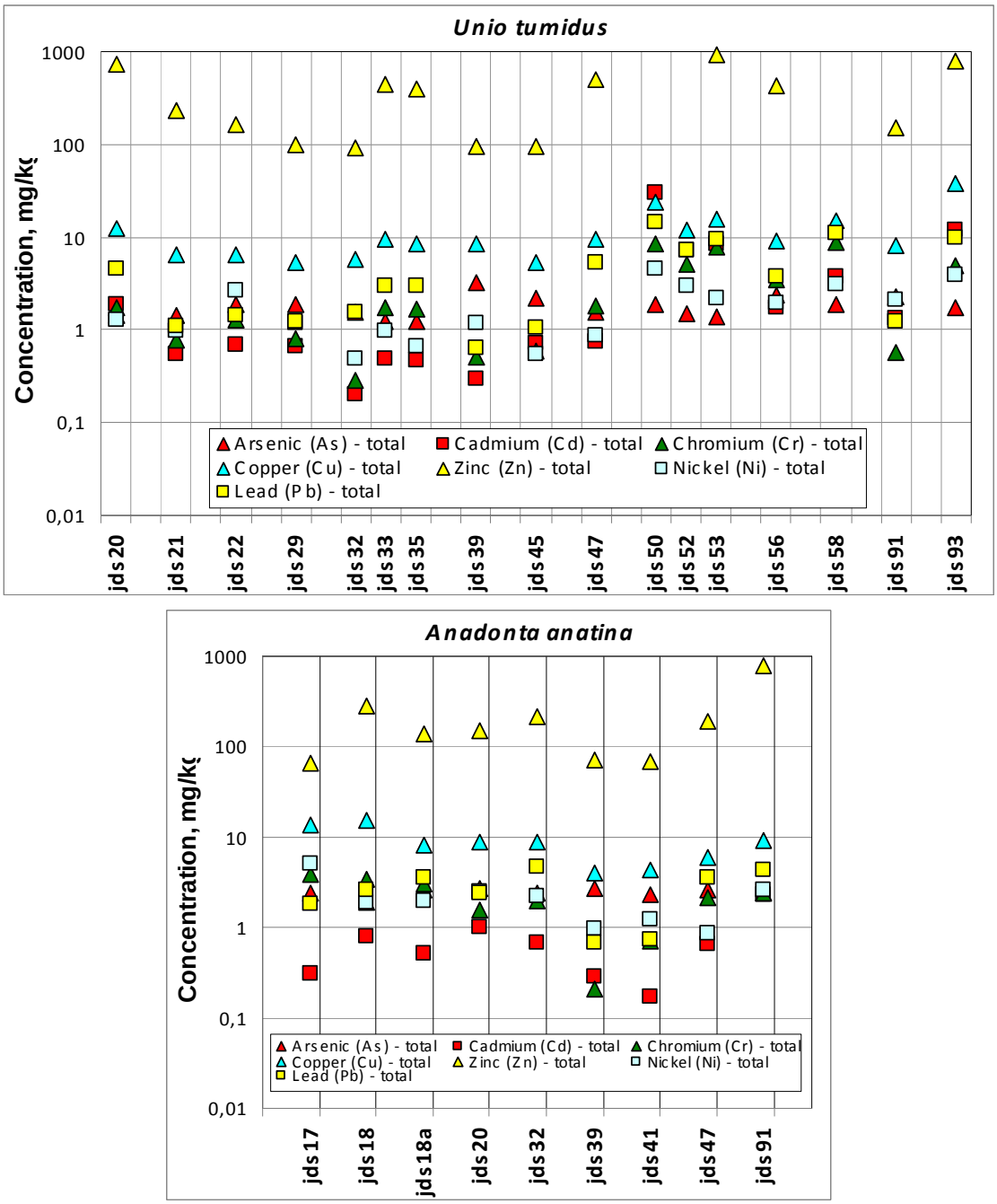


Figure 3-28 Concentration of heavy metals and As in the mussel *Unio tumidus* and *Anadonta anatina* collected according to abundance at selected sites along the Danube during JDS2

The results indicated decreasing trends in the case of the priority heavy metals Pb, Hg and Ni, as well as in the case of Cr, Cu and Zn, however, increasing concentration were found in the case of the priority heavy metal Cd and the As. Particular attention has to be paid to the concentration of Hg (even the total form) in the samples because of the specified strict limit values in the proposed EC Directive, indicated earlier. Unfortunately the specified methyl-mercury was not analysed during the survey but according to several scientific references the aquatic biota,

particularly fish and mussels, may contain over 60 to 80% of the total mercury in the alkylated form. Therefore, even the total Hg concentrations in the biota samples require special attention.

Four heavy metals (nickel, lead, cadmium and chromium) demonstrated slight decrease in both species in the upper surveyed part of the river, followed by increase in the lower stretch, starting downstream Novi Sad. Increase was evident in the case of cadmium, chromium and lead in the *Unio* group. Specifically:

- Cadmium values in the Danube itself fluctuated from 0.17 to 11.8 mg/kg; however, the highest concentration was measured in the Sava (29.6 mg/kg),
- Lead showed differences in the Danube mussels from 0.63 to 10.9 mg/kg, with the highest value again in Sava (14.6 mg/kg).
- Nickel demonstrated a bit smaller fluctuation in values ranging from 0.49 to 5.16 mg/kg.
- Concentration of chromium varied from 0.21 to 8.63 mg/kg in the Danube, with nearly the same concentration in its tributary Sava (8.47 mg/kg).
- Copper content showed greatest differences, starting with high values in the upper part sampling site, a certain decrease in the middle part of the Danube followed by second increase culminating in the Kilia arm (37.5 mg/l in the sample of *Unio tumidus*).

As far as five surveyed tributaries, most of the highest concentrations were measured in the Sava River. The Proposed Quality Targets were significantly exceeded in the case of Cd and Zn, slightly also in Cr, Cu and Pb.

Altogether 33 mussel samples were collected during JDS2 compared to 136 during JDS1. The significant difference regarding the number of samples during the two surveys makes the comparison also difficult. Therefore, the ranges of concentrations of the different elements during JDS1 are given and compared with the maximum measured values during JDS2. These are summarized in Table 3-7, whereby the highest element concentrations during the two surveys are shown in Table 3-8. These tables also show the quality targets used during JDS1.

Table 3-7 Range of element concentrations (minimum - maximum) in mussel samples of the river Danube and its tributaries during JDS1, the highest concentrations during JDS2 and the quality targets used during JDS1 (all values in µg/g dry weight)

Element	Concentration Ranges During JDS1 [mg/kg dry weight]		Highest Concentration During JDS2 [mg/kg dry weight]	Quality Targets During JDS1 [mg/kg dry weight]
	Danube	Tributaries		
As	0.08 - 1.23	0.06 - 0.81	**2.7** (JDS39)	20
Cd	0.1 - 35.9	0.2 - 16.4	**29.6** (JDS50)	4
Cr	0.5 - 11.7	< MQL - 24.12	**4.9** (JDS93)	6
Cu	4.5 - 178.4	4.3 - 54.0	**37.5** (JDS93)	20
Pb	0.5 - 49.9	0.7 - 31.7	**9.8** (JDS93)	10
Hg	0.055 - 0.412	0.037 - 0.742	**0.3** (JDS21)	0.4
Ni	0.44 - 4.69	0.49 - 9.43	**5.16** (JDS17)	10
Zn	120 - 2680	160 - 1360	**1880** (JDS50)	400

Table 3-8 Highest element concentrations determined in JDS1 and JDS2 mussel samples in comparison with background concentrations and proposed quality targets (all values in µg/g dry weight)

Element	JDS-Position		Species*	Concentration	Background Values	Quality Target
Cd	JDS1-98	St. Gheorghe	A	35.9**	2	4
	JDS2-93	**Kilia-arm**	**B**	**11.8**		
Cr	JDS1-54	Tisa	B	24.12	3	6
	JDS2-93	**Kilia-arm**	**B**	**4.9**		
Cu	JDS1-70	Pristol	B	178.4	10	20
	JDS2-93	**Kilia-arm**	**B**	**37.5**		
Pb	JDS1-46	Upstream Drava	A	49.9	5	10
	JDS2-93	**Kilia-arm**	**B**	**9.8**		
Hg	JDS1-61	Velika Morava	A	0.742	0.2	0.4
	JDS2-21	**Vah**	**A**	**0.3**		
Zn	JDS1-70	Pristol	C	2680	5	400
	JDS2-50	**Upstream Sava**	**B**	**1880**		

* A - *Anodonta anatina*, B - *Unio tumidus*, C - *Unio pictorum*
** Values exceeding the Quality Targets

For the assessment and comparison of mussels' qualitative status since 2001 (JDS 1) it is to be emphasized that due to the high water conditions in the river basin there is a lack of data in the last stretch of the Danube from *Irongate*, e.g. in the length of more than thousand km, together with tributaries. According to JDS1 results this stretch can be considered as the most polluted part of the Danube by heavy metals. In JDS2 only arsenic and nickel showed larger variations with higher concentrations also in the other parts of the Danube, but all found values of these two parameters were markedly below natural background or proposed the target values. Concentration of cadmium, copper and chromium in mussels showed higher values than proposed targets nearly in all four sampled sites in the lower stretch of the Danube. With the exception of arsenic the average values of given parameters were comparable and have not significantly increased.

The maximum total Hg concentration – 0.3 mg/kg - was measured in a *Unio tumidus* mussel sample. Because the results of the mussel samples are expressed in dry weight, this concentration could be around 0.05 mg/kg (50 µg/kg) in wet weight, likely exceeding the proposed EQS.

3.4.2 Fish

Samples of fish tissue (*Abramis brama*) were taken from in 11 characteristic localities covering the length of 1842 km of the Danube run starting in Kelheim in Germany downstream to the Danube Delta.

Concentrations of total Hg, and the other heavy metals and As in fish (*Abramis brama*) from the Danube River are shown in the Figures 3-29 and 3-30, respectively.

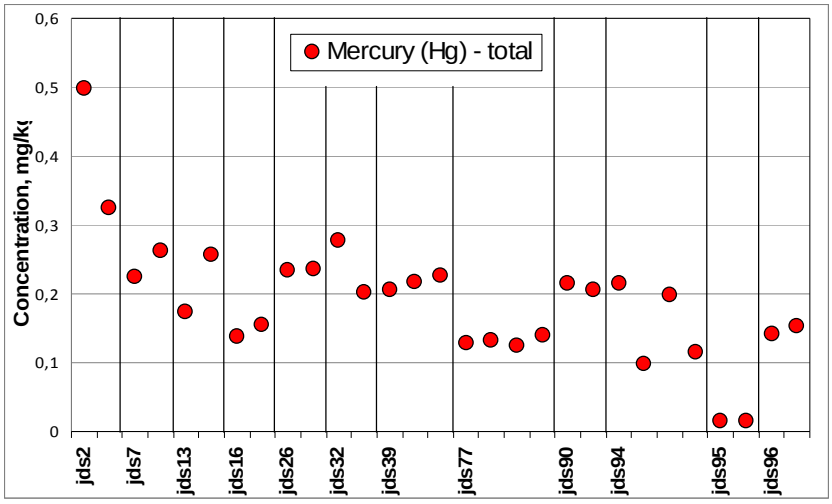


Figure 3-29 Total Mercury in *Abramis brama* along the Danube (all results are in mg/kg wet weight)

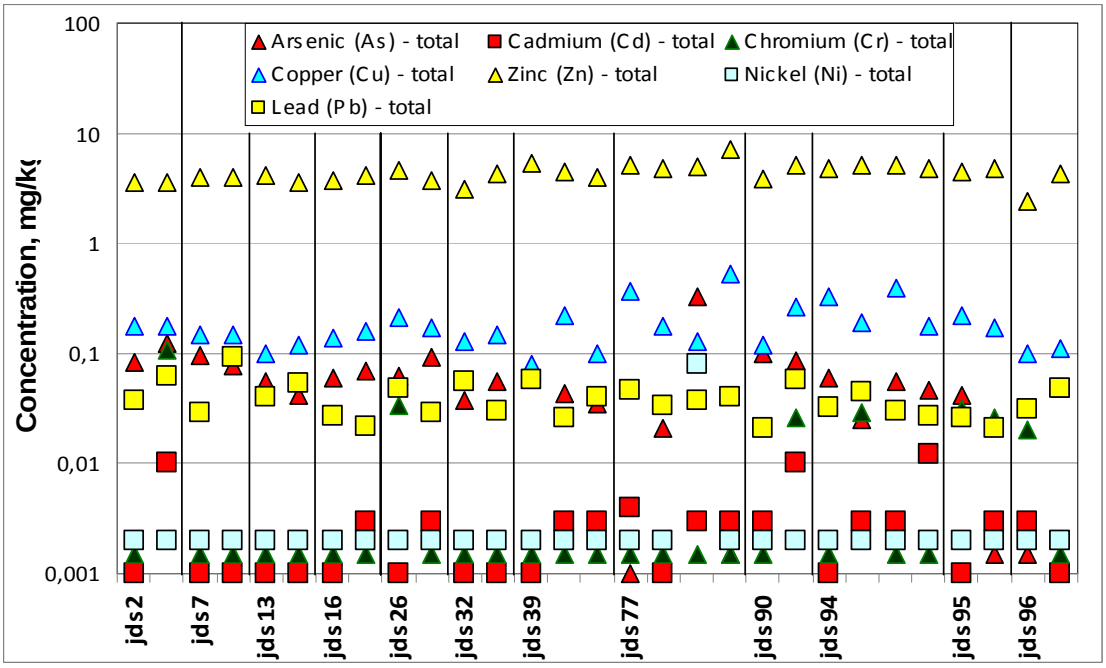


Figure 3-30 Heavy metals and As in *Abramis brama* along the Danube (all results are in mg/kg wet weight)

Out of seven heavy metals and the As analysed in the given group the most serious problem appeared to be in the case of mercury. In the 29 analysed samples Hg content varied from 0.015 to 0.499 mg/kg of tissue. The highest individual value was found in the most upper part of the measured part of the Danube (Kelheim). As far as the longitudinal variation is concerned, the Hg concentration showed decreasing trend towards Bratislava, then after minor increase it was decreasing again downstream on the Danube. The Hg concentration was significantly lower in in one of the Danube arms in the Delta.

Despite the fact that these results are below the maximum value 1.0 mg Hg/kg of wet weight given in Commission Regulation No 221/2002 amending Regulation No 446/2001 setting maximum levels for certain contaminants in foodstuffs; however, the values would significantly exceed the quality target of JDS1 (0.4 mg/kg in dry weight), because the concentrations would be around six times higher if they are expressed in dry weight.

Copper showed similar longitudinal variation, between 0.08 to 0.52 mg/kg with the increase downstream Iron Gate. The concentrations of the two other heavy metals – Cd and Pb – limited by the corresponding Commission Regulation were significantly lower in all samples than the given limit values (most of Cd values were below the LOQ and that is why the values are not recognisable in the figure). The concentration of both heavy metals varied slightly (<0.003–0.012 mg/kg for Cd and 0.021–0.092 mg/kg for Pb), without showing any trends along the Danube. The other heavy metals and As were near to the LOQ in most of the samples.

In summary, because the total Hg concentrations found in the fish samples may indicate accumulation in the fish tissue, and likely exceedance of the newly proposed EQS; therefore, it is important that the Hg contamination issue will be further investigated and considered.

4 Conclusions

The concentration ranges of the heavy metals as well as Arsenic in water, suspended and bottom sediments during the JDS2 were very similar to the concentrations ranges observed in the JDS1 samples.

Regarding the water samples, the dissolved heavy metals included in the list of priority substance, i.e., Cd, Hg, Ni. and Pb, it was unfortunate that the dissolved Cd results were all „not quantified“ because of the relatively high LOQ, which was also higher than the relevant EQS; therefore, it was not possible to make a comparison with the EQS.

4.1 Compliance checking for priority substances according to WFD

The requirements of the WFD surveillance monitoring of priority substances, according to Annex 4 of the proposed draft EC Directive, is described in more details in the summary report on Priority Substances. For Pb and Ni, and their compounds the MAC-EQS is marked as “not applicable.” Therefore, we consider the AA-EQS values all the four heavy metals as indicative for being protective against short-term pollution peaks in continuous discharges.

The draft directive also include an EQS for methyl-mercury (20 µg/kg in wet weight) in aquatic biota (fish, mollusks, etc.), but this substance was not included in the analytical parameter list of JDS2. The results of the total mercury determined in mussels and fish; however, indicate relatively high concentrations, particularly in the fish tissue, which may be a concern in future monitoring.

4.2 Assessment of the indication of the chemical status from JDS2 results

During JDS2, one single water sample was taken at each sampling site. For this reason the assessment of the chemical status cannot be done in-line with the WFD requirements.
Similarly to the assessment of other priority substances, an **indication** of the chemical status is given for each sampling site by using the proposed AA-EQS for inland waters.

Table 4-1 shows the sampling sites where AA-EQS are exceeded in the case of the corresponding heavy metals.

Table 4-1 Sampling sites and the priority heavy metals exceeding AA-EQS values for inland waters

JDS2 Code	Heavy Metal	Sampling Station	Concentration [µg/l]	AA-EQS[1] [µg/l]
JDS32	**Hg**	Budapest downstream	**0.071**	0,05
JDS33		Adony/Lórév	**0.063**	0,05
JDS66	**Ni**	/Timok (rkm 0.2)	**33.3**	20

[1] ***Proposal for amending Directive 2000/60/EC***

These results are also presented as the indication of the chemical status in the corresponding map.

4.3 Assessment of other heavy metals and As

For some of the other heavy metals only national EQS or EQS-proposals might be used for assessment. Accordingly, the tentative Austrian EQS for dissolved Cu and Zn (both depend on the total hardness) was considered and the exceedances are shown in Table 4-2. Most of the other elements present in dissolved form were at around the natural background.

Table 4-2 Sampling sites and parameters exceeding the proposed Austrian EQS values

JDS2 Code	Heavy Metal	Sampling Station	Concentration [µg/l]	EQS[2] [µg/l]
JDS66	**Cu**	/Timok (rkm 0.2)	**34.5**	8.8
JDS85		Downstr. Ruse/Giurgiu	**14.6**	8.8
JDS81		/Russenski Lom	**11.2**	8.8
JDS-IS2	**Zn**	before Reservoir Iskar	**67.9**	35.1

[2] ***Austrian proposal, hardness dependent***

Regarding the suspended particulate matter and bottom sediments the results indicated significant inputs into the Danube mainly from some tributaries such as in the case of Cadmium (Sava and Tisa), Lead (Drava, Tisa, Sava and Velika Morava), and Mercury (Vah and Velika Morava).