5.2.1 General Characteristics

The determinands reviewed and discussed under the general characteristics included the following:

(a) In the water column:
- water temperature,
- conductivity,
- alkalinity,
- pH values,
- dissolved oxygen,
- suspended solids.

(b) In the bottom sediment:
- grain-size distribution,
- calcium, magnesium.

Water temperature

Because of the timing of JDS, the air and water temperature represented the typical European summer conditions that could be considered favourable for a number of chemical characteristics such as nutrients, faster degradation of organic pollutants, etc. Figure C2.1.-1. shows the measured water temperature values.

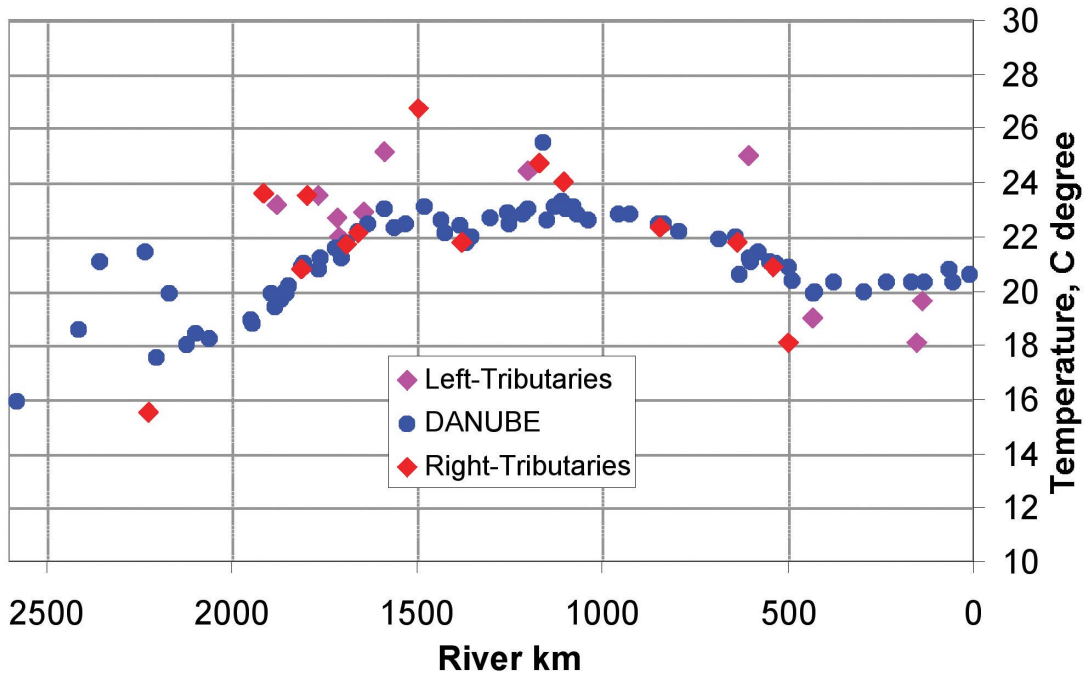

FIGURE C2.1.-1: Variation in water temperature during JDS.

Conductivity and alkalinity

The conductivity and alkalinity values measured during the Survey are shown in Figures C2.1.-2. and C2.1.-3. respectively.

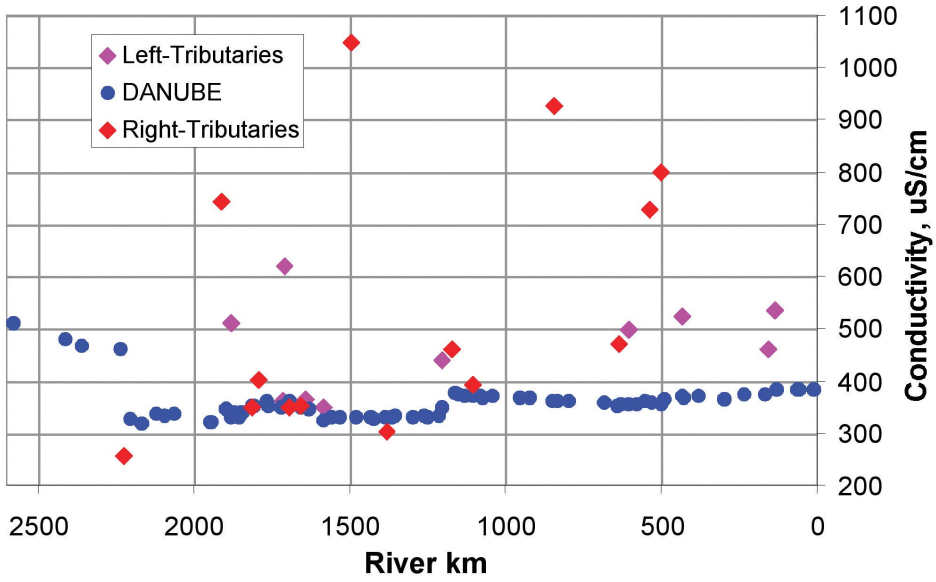

FIGURE C2.1.-2: Variation in conductivity in the Danube and its tributaries during the JDS

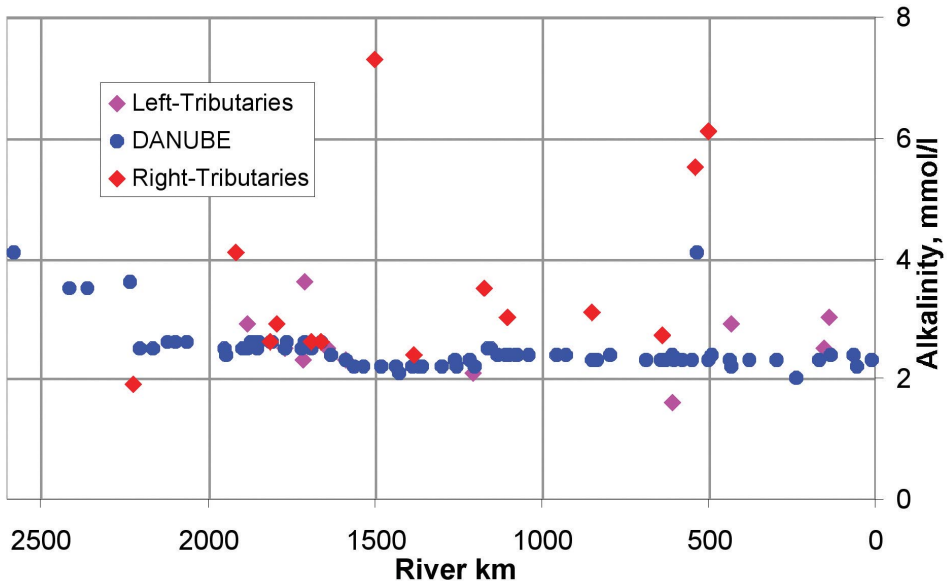

FIGURE C2.1.-3: Variation in alkalinity in the Danube and its tributaries during JDS

Conductivity, which reflects the total dissolved salts in the water, was in the upper Danube Reach significantly influenced by the low salt content of the Inn, which had a discharge of 755 m^3/s compared to the 455 m^3/s in the Danube upstream of the confluence with the Inn.

In the tributaries, conductivity was usually higher than in the Danube, which resulted in a slight increase downstream towards the confluence with the Tisza. As a result of the significant discharge rate in both the Tisza and the Sava and their higher salt content, conductivity of the Danube significantly increased downstream of these tributaries.

Despite the higher conductivity in the tributaries along the lower Danube Reach, there was a very slight increase in the Danube's conductivity downstream towards the Delta.

Alkalinity values showed nearly the same variations and trends as in the case of conductivity, and for the same reasons.

pH Value

pH values measured during the Survey are shown in Figure C2.1.-4.

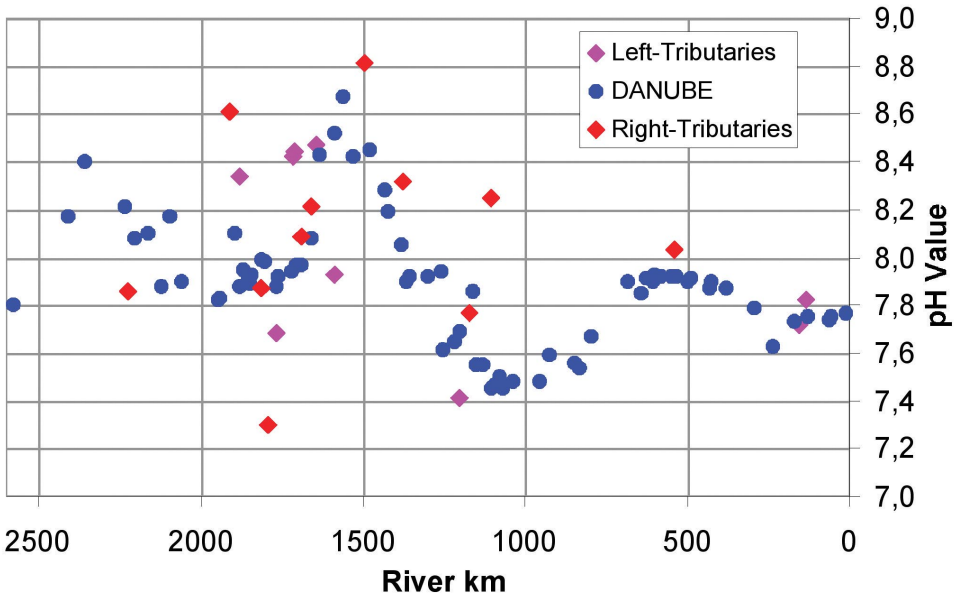

FIGURE C2.1.-4: Variation in pH values in the Danube and its tributaries found during JDS

The pH values showed some significant trends along the Danube during the Survey. In the upper and lower part of the lower Danube Reaches, the pH values demonstrated a good balance between primary production and decomposition of organic matter. In the middle and upper part of the lower Danube Reaches, a significant increase was followed with a significant decrease as a result of increased primary production and later increased organic matter decomposition producing carbon-dioxide, consequently decreasing the pH value.

Dissolved oxygen

Dissolved oxygen concentrations measured during the Survey are shown in Figure C2.1.-5.

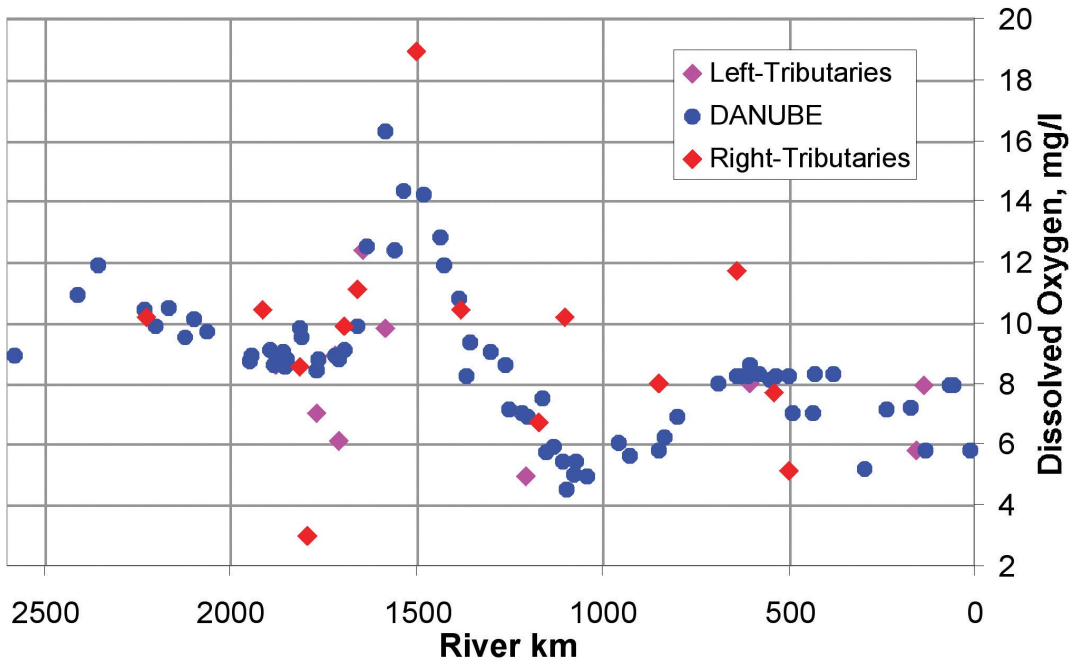

FIGURE C2.1.-5: Variation in the dissolved oxygen content of the Danube and its tributaries found during JDS

The dissolved oxygen content of the Danube and the tributaries showed a similar trend as in the case of pH values.

The over-saturation of the middle Danube Reach with dissolved oxygen was due to the observed intensive primary production, supported with the algal blooms, very high algal biomass and chlorophyll content. The relation between oxygen saturation and chlorophyll-a content of the water samples, shown in Figure C2.1.-6., clearly shows that the cause of the high dissolved oxygen content in the water lies in accelerated primary production.

Although determinands characterizing oxygen-consuming compounds, e.g., BOD, COD or TOC were not determined in the water samples during the Survey, the decrease in dissolved oxygen significantly below saturation, together with the decrease in pH values, definitely demonstrate the presence of oxygen- consuming pollutants (NB. These may include primarily produced organic matter).

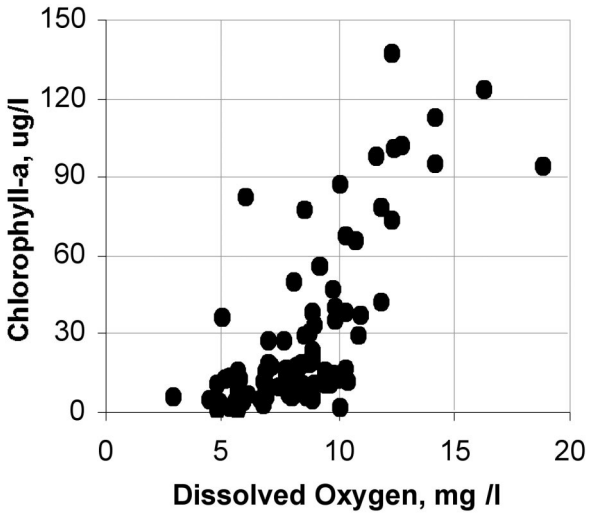

FIGURE C2.1.-6: The relationship between dissolved oxygen and chlorophyll-a content of the water samples collected during JDS

Suspended solids

Variations in the concentration of suspended solids measured during the Survey are shown in Figure C2.1.-7.

In most samples, the concentration of suspended solids was low, mainly due to the favourable flow conditions, i.e. low discharge rates. The increasing-decreasing tendency along the middle Danube Reach was similar to the trend reported for some other determinands that might be related to suspended solids, e.g., algal biomass, correlated to chlorophyll-a and dissolved oxygen.

It is interesting to note that the suspended solids content of the Sio River (JDS-42) was 28.2 mg/l, out of which 18.3 % was total organic carbon; consequently, the major part of the suspended solid in this sample was algal biomass (N.B: Chlorophyll-a content was also high, i.e. 94,1 µg/l).

Slightly higher suspended solid concentrations were found in the upper and lower sections of the Danube, and in particular in two tributaries, the Siret and the Prut.

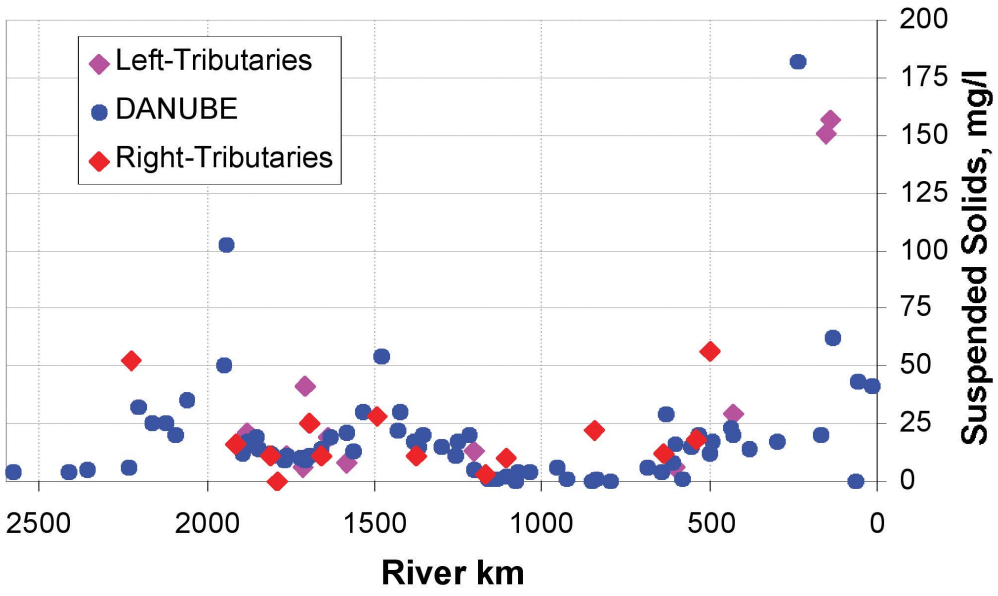

FIGURE C2.1.-7: Variations in the suspended solids content of the Danube and its tributaries reported during JDS

Bottom sediment

Variations reported during JDS in the less-than-63 µm grain-size fraction of the bottom sediment samples analysed for various pollutants are shown in Figure C2.1.-8.

The percentage of the less-than-63-µm grain-size fraction varied very significantly in the different bottom sediment samples, without showing any trends or relation to any other characteristics. It was also important that most samples, with the exception of one, contained more than 10 % fine fraction in the sediment, making the analysis reliable as far as the samples' representativeness.

It is also important that the analysis of this particular grain-size fraction provides a normalization scheme for comparing the analytical results. If we had analysed bulk sediment samples, the significantly variable course sediment would have produced dilution effects and made data interpretation difficult.

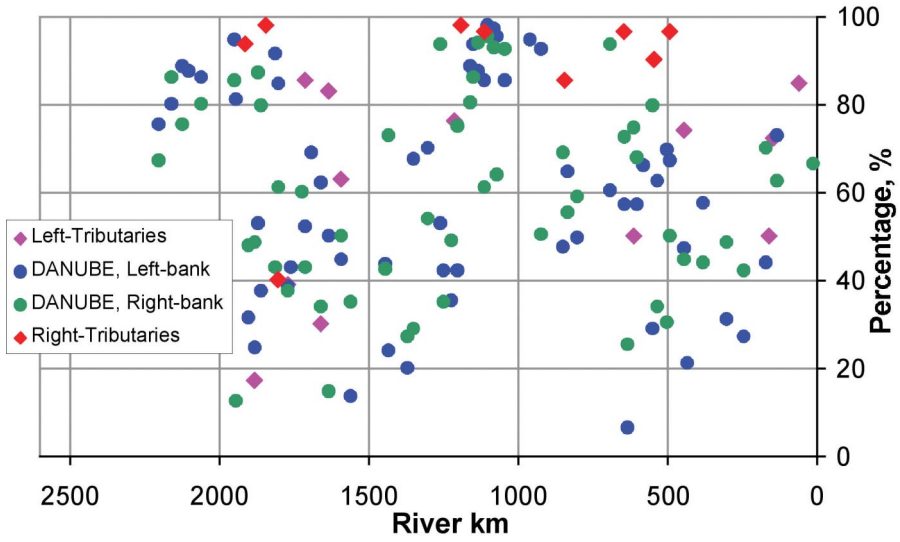

FIGURE C2.1.-8: Percentage of the less-than-63-μm fraction of the bottom sediment in the Danube and its tributaries.

5.2.2 Nutrients

Nitrogen Forms

Ammoniacal-N (NH4-N), Nitrite-N (NO2-N), Nitrate-N (NO3-N) and Organic nitrogen (Org-N) were measured in the water samples, while suspended solids and sediment samples were analysed for organic nitrogen.

The MLIM proposal for water quality classification includes the following reference (class I) and target (class II) values for nitrogen forms:

Nutrient	Unit	Class I Reference value	Class II Target value
Ammonium-N	mg/l	0.2	0.3
Nitrite-N	mg/l	0.01	0.06
Nitrate-N	mg/l	1	3
Total nitrogen	mg/l	1.5	4

All nitrogen forms measured in the Danube water showed a characteristic concentration distribution profile along the Danube.

NH4-N concentrations varied in the River between < 0,01-0,2 mg/l, Fig. C2.2.-1. In the upper Danube, NH4-N concentrations were between 0,07-0,09 mg/l. The concentration decreased downstream along the 2200-1500 rkm section. A characteristic peak evolved at around the confluence with the Tisza (concentration of NH4-N near 0,2 mg/l). In the lower part of the Danube, NH4-N concentrations varied in the range of 0,01-0,1 mg/l.

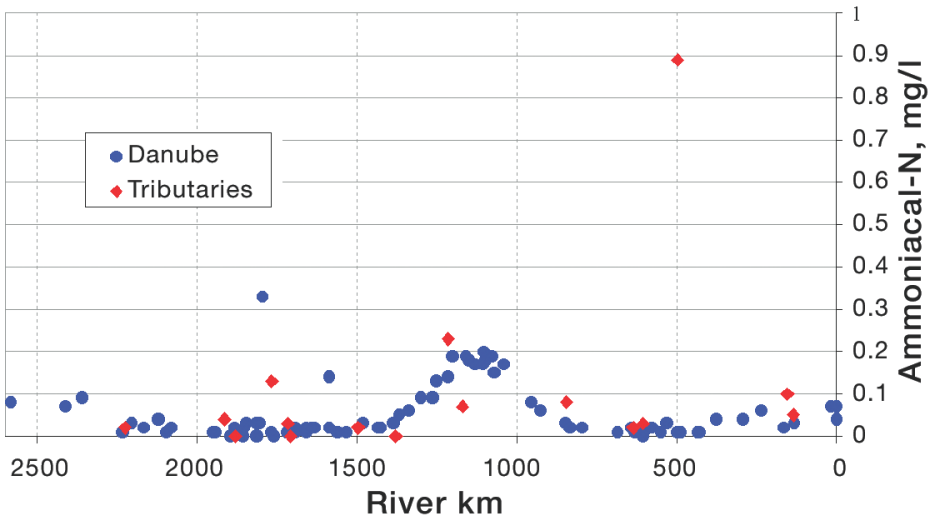

FIGURE C2.2.-1: Longitudinal variation in the concentration of NH4-N in the Danube River and its tributaries reported during JDS.

Compared to the concentrations in the Danube, NH4-N concentrations in the tributaries varied within a wider range (Fig. C2.2.-1.). Record concentration (3,2 mg/l) was measured in the Arges tributary. Presumably, inefficiently treated wastewater discharge caused the high ammonium content.

NO2-N is a transient nitrogen form in the reduction/oxidation process of the nitrogen species. Its concentration varied in the Danube between 0,006-0,069 mg/l (Fig. C2.2.-2.). Nitrite-nitrogen concentrations were around 0,01 mg/l along the upper and partially along the middle section of the Danube. The maximum values of nitrite were found in the Iron Gate Reservoir, which can be a suitable place for oxidation changes of nitrogen species.

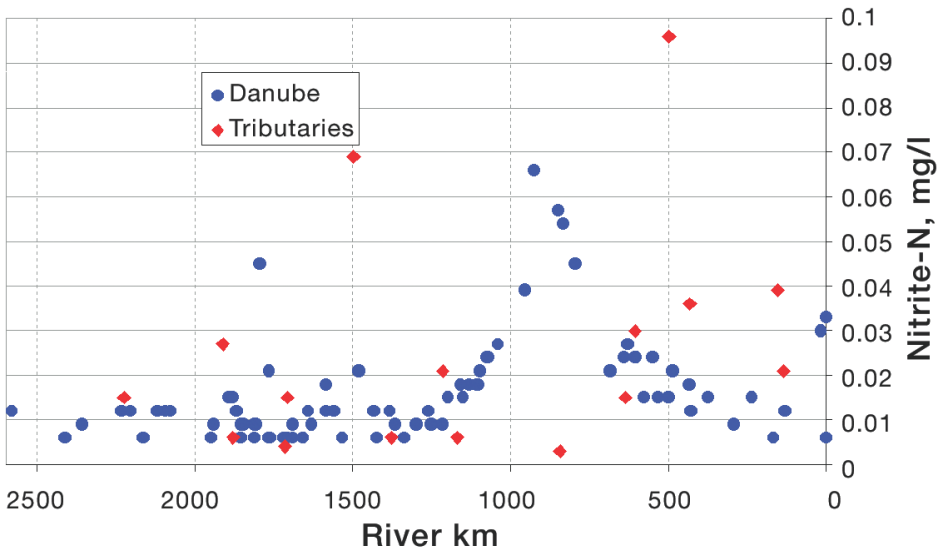

FIGURE C2.2.-2: Longitudinal variations in the concentration of NO2-N in the Danube River and its tributaries reported during JDS.

NO2-N concentrations in the tributaries varied within a wider range than in the Danube, but extremely high values did not occur (Fig. C2.2.-2.). The highest (0,096 mg/l) NO2-N concentration was found in the Russenski-Lom tributary.

The most oxidized nitrogen form, NO3-N had the maximum values in the Danube in the upper section of the River, where NO3-N concentrations were around 2 mg/l (Fig. C2.2.-3.).

NO3-N concentrations decreased gradually downstream along the river and in the middle section NO3-N was below 1 mg/l. Downstream of the Iron Gate Reservoir, NO3-N concentrations increased again due to the loads from point and non-point sources. NO3-N concentration values were approximately 1-1,2 mg/l in the last 500-km section of the Danube.

In the tributaries (shown in Fig. C2.2.-3.), the highest NO3-N concentration (3,8 mg/l) was measured in the Russenski Lom.

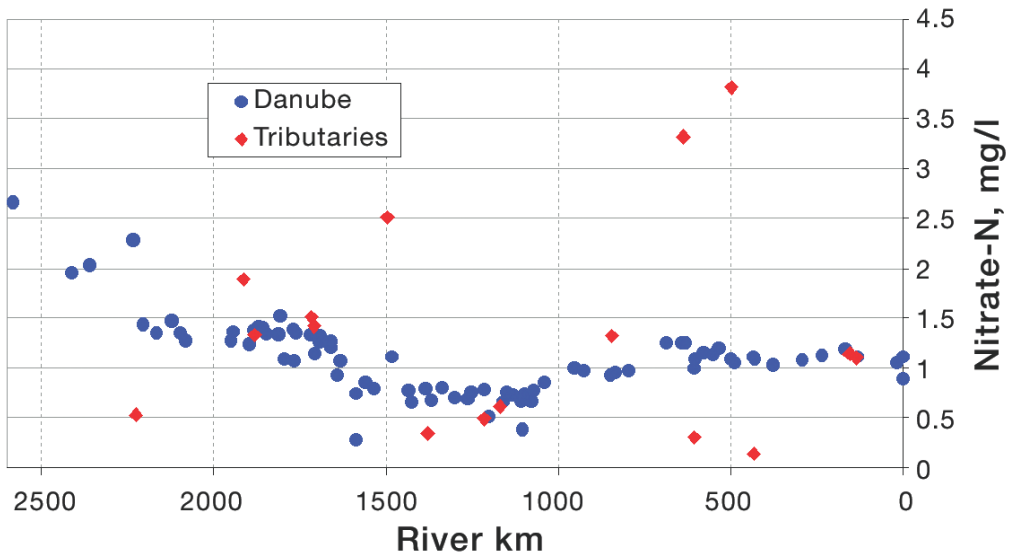

FIGURE C2.2.-3: Longitudinal variation in the concentration of NO3-N in the Danube river and its tributaries during the JDS.

Organic-N concentrations in the Danube and in the tributaries are shown in Fig. C2.2.-4. The mean Org-N concentration of the Danube water samples was 0,76 mg/l in the measured concentration range of < 0,3-5,1 mg/l.

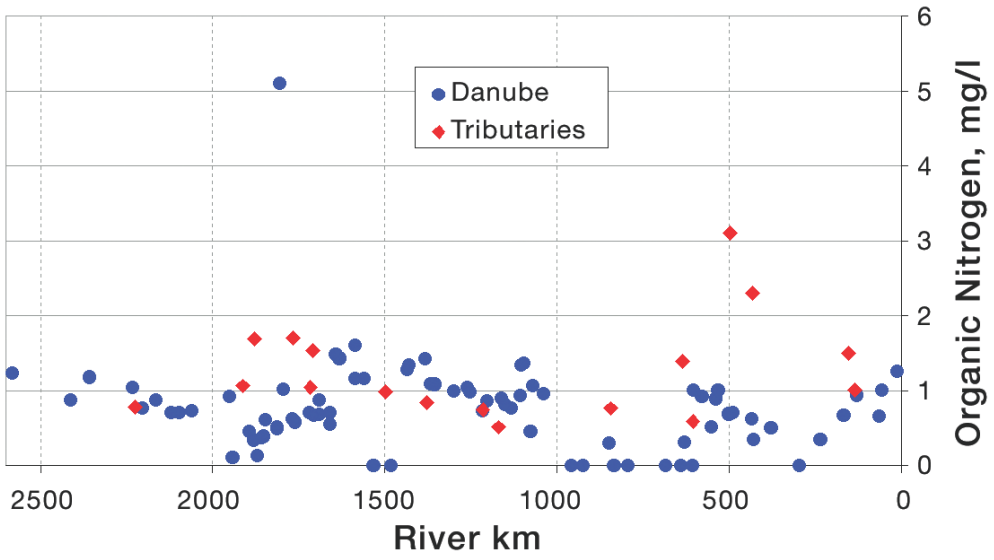

FIGURE C2.2.-4: Longitudinal variations in the concentration of organic nitrogen in the Danube River and its tributaries reported during JDS.

The highest value was in the water sample taken at Medvedov/Medve at rkm 1806, downstream of the Gabcikovo Reservoir. Except for this maximum value, Org-N content of the Danube did not exceed 2 mg/l. In the tributaries, Org-N level was also below 2 mg/l but in the Russenski-Lom and the Arges this concentration was slightly higher, i.e., 3.1 and 2.3 mg/l respectively.
The ratio of the different nitrogen forms in the water very much depends on the temperature because of the temperature-depending oxidation/reduction reaction rates of nitrogen transition. JDS was carried out in the summer-autumn season, and the results are, therefore, typical for this warm season. In low-temperature seasons, ammonium concentrations are characteristically higher than in warm-water periods.

Org-N in particulate matter was measured in ***suspended solids*** and ***bottom sediments***, and its concentrations are shown in Figures C2.2.-5. and C2.2.-6. respectively.

In several sites, suspended solid samples had significantly higher organic nitrogen levels than did bottom sediment (Fig. C2.2.-5.). The highest concentrations exceeded 20,000 mg/kg. In the lower section of the Danube – downstream of 400 rkm – the organic nitrogen content of suspended solids and sediments was similar at a relatively low level - below 5,000 mg/kg.

Concentrations in the bottom sediment samples ranged between 1,000-5,000 mg/kg. High concentrations were characteristic of the upstreammost and middle part (1500-1100 rkm) of the Danube.

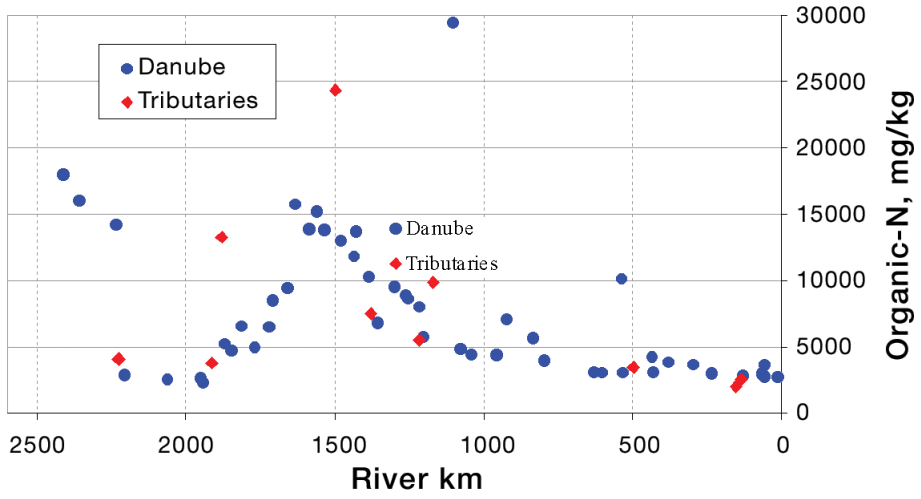

FIGURE C2.2.-5: Longitudinal variation in the concentration of organic nitrogen in suspended solids collected from the Danube River and its tributaries during JDS.

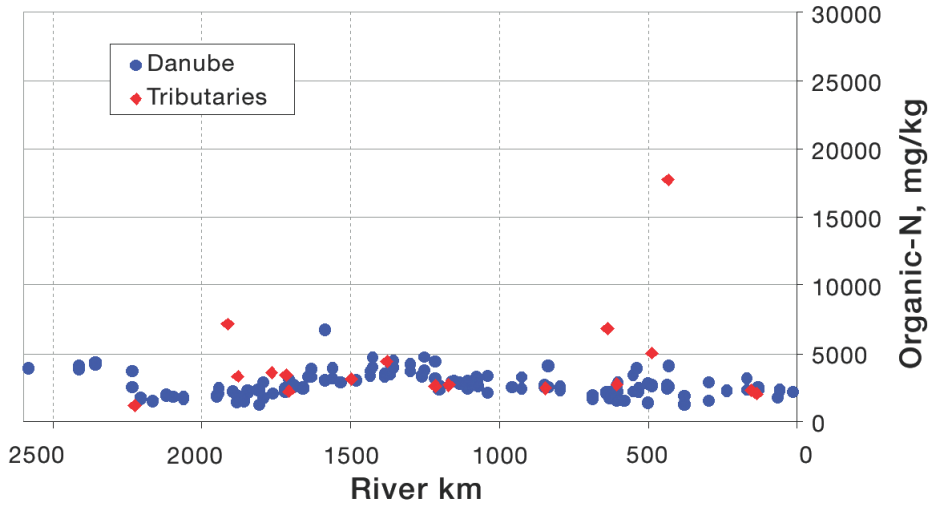

FIGURE C2.2.-6: Longitudinal variation in the concentration of organic nitrogen in the bottom sediment collected from the Danube River and its tributaries during JDS.

Phosphorus forms

The MLIM proposal for water quality classification includes the following reference (class I) and target (class II) values for phosphorus forms:

Determinand	Unit	Class I Reference value	Class II Target value
Ortho-phosphate P	mg/l	0.05	0.1
Total P	mg/l	0.1	0.2

Ortho-phosphate (PO_4-P) and total phosphorus (Total-P) concentrations were measured in

water samples. In the Danube River, PO4-P levels were below 0.05 mg/l in the upper 500-600 km section, and typically above 0.05 mg/l in the lower 1,000 km stretch of the river (Fig. C2.2.-7.). Total-P concentrations are shown in Fig. C2.2.-8.

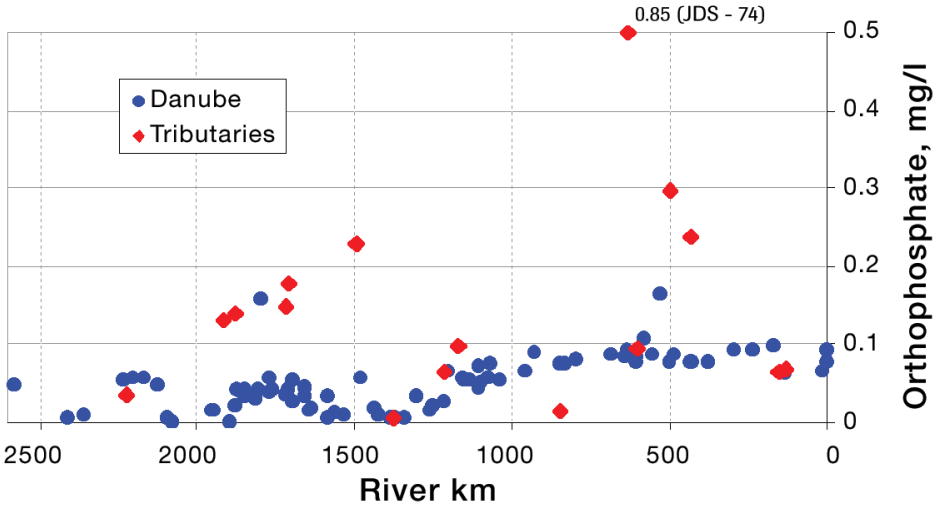

FIGURE C2.2.-7: Longitudinal variation in the concentration of PO_4-P in the Danube River and its tributaries during JDS.

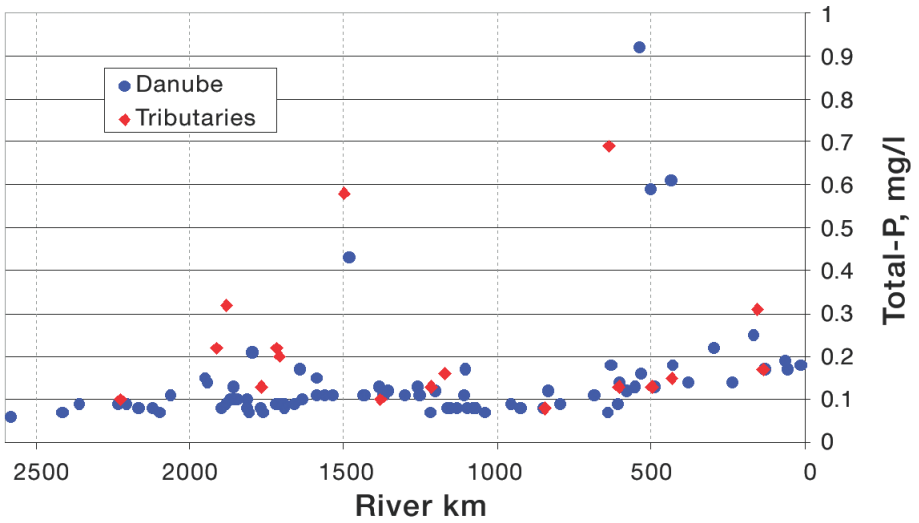

FIGURE C2.2.-8: Longitudinal variation in the concentration of Total-P in the Danube River and its tributaries during JDS.

In some tributaries, PO4-P concentration was much higher than in the Danube; the maximum value (0,85 mg/l) was measured in the Iskar River.

In suspended solids, Total-P content varied between 300 to 6,600 mg/kg while bottom sediments had lower concentration ranging between 500-2,000 mg/kg, as shown in Figures C2.2.-9 and C2.2.-10 respectively. Similarly to the organic nitrogen distribution in suspended solids and bottom sediment, higher concentrations of Total-P were measured in the suspended solids samples.

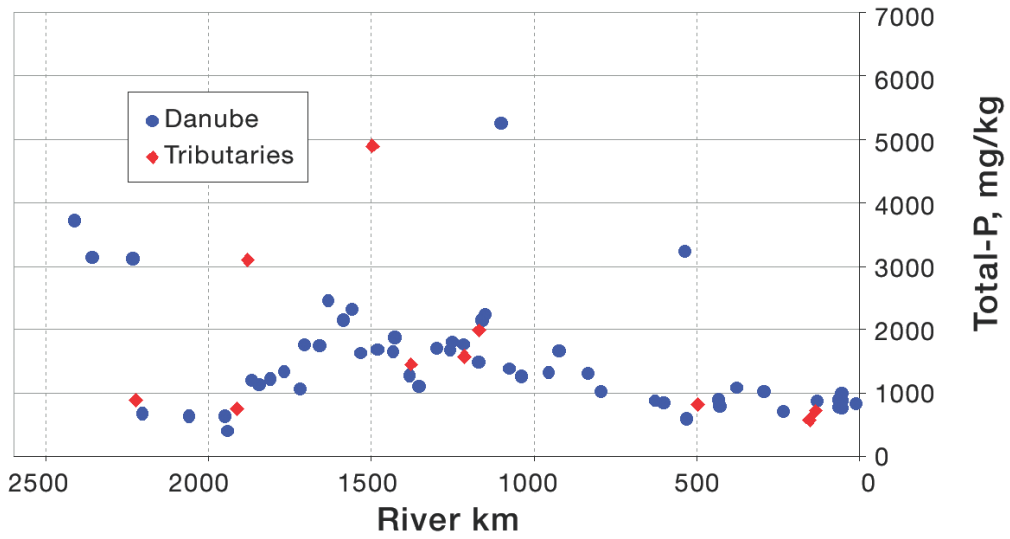

FIGURE C2.2.-9: Longitudinal variation in the concentration of Total-P in suspended solids collected from the Danube River and its tributaries during JDS.

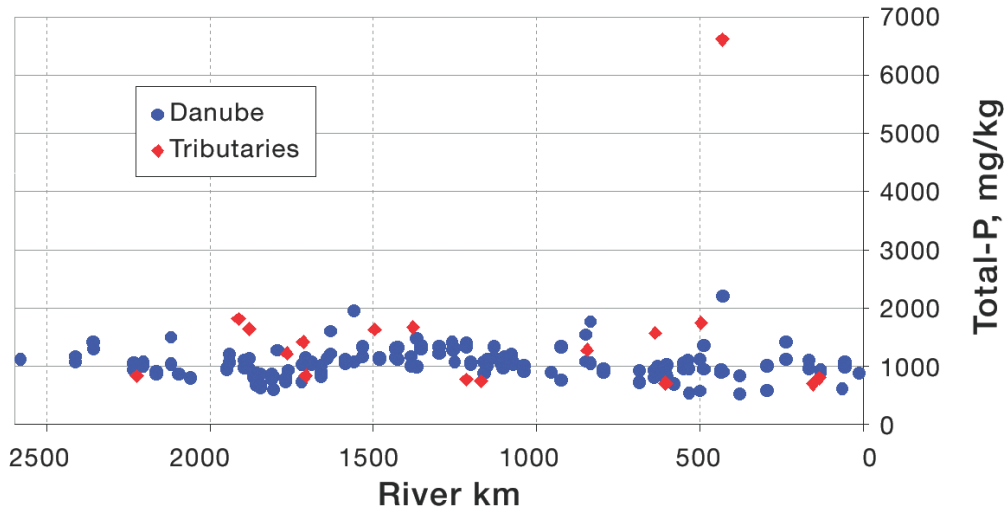

FIGURE C2.2.-10: Longitudinal variation in the concentration of Total-P in the bottom sediment collected from the Danube River and its tributaries during JDS.

Silica

The dissolved silicate concentration was rather constant (around 4 mg/l) along the upper section of the Danube. The silicate concentration had its highest values in the middle stretch of the Danube. In the downstream section, the concentrations varied between 2-6 mg/l. Fig. C2.2-11. shows the longitudinal variation in dissolved silica, together with total phosphorus and organic nitrogen, in the Danube River.

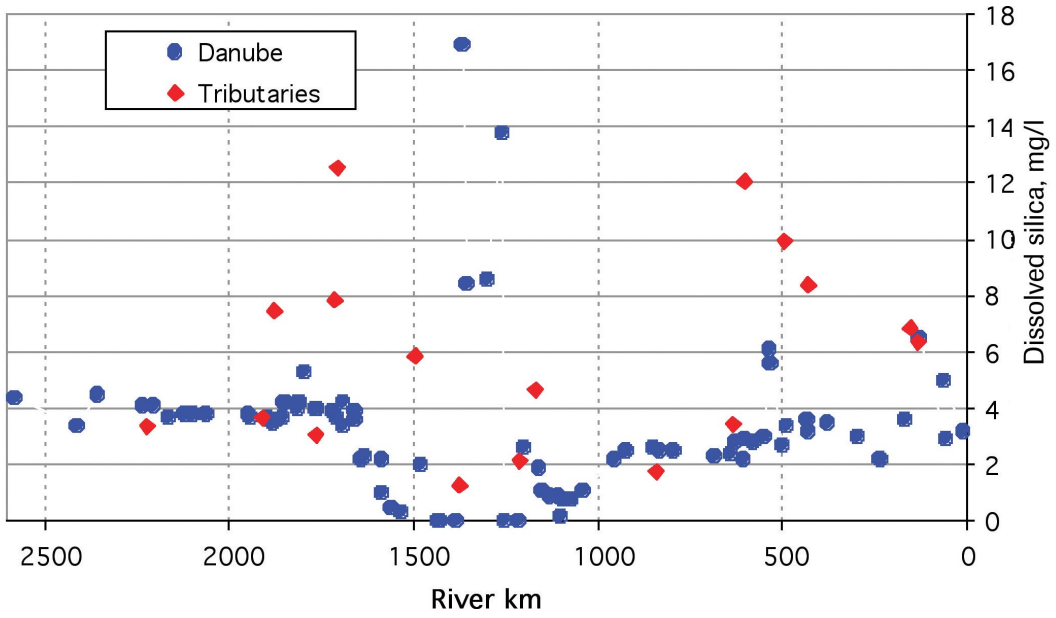

FIGURE C2.2.-11: Longitudinal variation in the concentration of dissolved silica in the Danube River and its tributaries during JDS.

In the tributaries, silicate concentrations were between 1-13 mg/l; high and low concentrations occurred in the tributaries of the upper and lower part of the Danube Basin.

The silicate concentration pattern is related to algae distribution, because the diatoms build in the silicate in their cells.

5.2.3 Heavy Metals

Concentrations of aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in water

Heavy metals in the water of the Danube River and its main tributaries were analysed in filtered ("dissolved") and unfiltered ("total") samples. Table C2.3.-1 shows the range of concentrations determined in the Danube and its main tributaries in comparison with published data on river water background concentrations [1], quality targets of various river monitoring networks [2] and TNMN data 2000 [3].

TABLE C2.3.-1: Range of element concentrations (minimum - maximum) in water samples of the Danube River and its tributaries and comparison with background concentrations, TNMN data of 2000 and quality targets ("<" – values below the method detection limit)

	"Dissolved" Concentration [µg/l]		"Total" Concentration [µg/l]		Background Values [µg/l]	TNMN 2000 [µg/l]	Quality Target [µg/l]
	Danube	Tributaries	Danube	Tributaries			
Al	< 5 - 40.5	7.21 - 122	< 10 - 2045	< 10 - 1690	-	0- 10559	?
As	< 1 - 4.55	1.05 - 44.8	< 1 - 6.42	< 1 - 73.6	-	0 - 91.8	?
Cd	< 0.2 - 0.5	< 0.2	< 0.2 - 0.8	< 0.2 - 0.7	0.009 – 0.036	0 - 9.43	0.072
Cr	< 1 – 1	< 1 - 1	< 1 - 7	< 1 - 31	1.3 – 5.0	0 - 61.1	3.1
Cu	2 – 6	2 - 16	2 - 13	2 - 163	0.5 - 2.0	0 - 136	3
Pb	< 1 - 1.38	< 1 - 1.2	< 1 - 8	< 1 - 10	0.4 – 1.7	0 - 260	3.4
Hg	< 0.2	< 0.2	< 0.2	< 0.2	0.005 – 0.02	0 - 3.9	0.04
Ni	< 1 – 3	< 1 - 6	< 1 - 13	< 1 - 11	0.6 – 2.2	0 - 34	1.8
Zn	< 1 – 291	3.27 - 66.3	< 10 - 333	< 10 - 164	1.8 - 7	0 - 324	7

Figure C2.3.-1. shows the number of sampling stations (in %) at which the determined total element concentrations exceeded the quality targets of Table C2.3.-1. The results indicate that the Danube can be regarded as unpolluted in terms of heavy metals cadmium, chromium, lead and zinc. This is supported by the fact that element concentrations were found to be below the method detection limit at a lot of sampling stations. Higher concentrations of these metals were detected in several tributaries. Particularly, the concentration of zinc was above the quality target of 7.0 µg/l in nearly 50% of all investigated tributaries. However, it should be taken into account that JDS water samples characterise only the contaminant level at the time of the Survey. Recent TNMN data (Table C2.3.-1) show at least for aluminium, cadmium, lead and mercury significantly higher maximum concentrations. Therefore, data on suspended solids, sediment and biota may provide a better insight into heavy metal pollution of rivers.

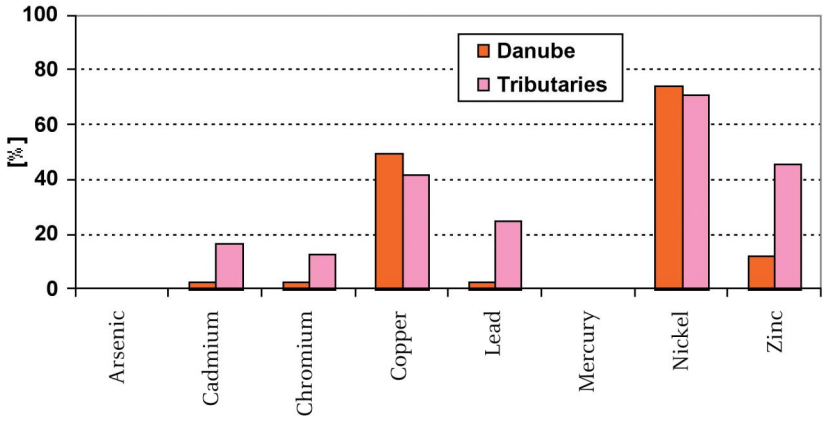

FIGURE C2.3.-1: Number of JDS water samples (in %) with heavy metal concentrations exceeding the quality targets listed in Table C2.3.-1.

A serious heavy metal contamination of the Danube water and several of its tributaries can be discussed for copper and nickel (Figure C2.3.-1). The concentrations of arsenic exceed the quality target at almost all investigated sampling stations. Taken the recent TNMN data [3], about 60% of all reported values are above the quality target for copper and nickel as well as for cadmium and zinc.

Based on the measured concentrations, some JDS sampling stations can be regarded as specific pollution points (Table C2.3.-2). Three of them are characterised by the highest concentrations of several elements: the Russenski Lom tributary (JDS84 - Cr, Pb, Ni, Zn), the Olt (upstream, JDS76 – Cd, Pb, Zn) and the Giurgeni (JDS91 - Cr, Ni).

Since the element concentrations were below the method detection limit for a lot of JDS water samples, a significant correlation between dissolved and total heavy metals could only be found for arsenic. However, a graphical presentation of arsenic concentrations along the entire course of the Danube (without tributaries) reveals spatial differences in the distribution of this element between dissolved and particulate phase (Figure C2.3.-2). The upper and lower sections of the River contain only dissolved arsenic, whereas a significant amount of this element is transported in the particulate fraction between km 1103 and km 632. The cause for the different behavior of arsenic may lie in the change in the geochemistry of the Danube's solid material. The longitudinal variation in the concentration of heavy metals - particularly aluminium and chromium – observed in JDS sediment samples indicates such a change behind km 1300.

Element	JDS-Position		Concentration [µg/l]	Quality Target [µg/l]
Arsenic	JDS74	Iskar (Trib.)	73.6	-
Cadmium	JDS76	Upstream Olt	0.8	0.072
	JDS87	Arges (Trib.)	0.7	0.072
Chromium	JDS84	Russenski Lom (T)	31	3.1
	JDS91	Giurgeni	7	3.1
Copper	JDS69	Timok (Trib.)	163	3
Lead	JDS76	Upstream Olt	8	3.4
	JDS84	Russenski Lom (T)	10	3.4
Nickel	JDS84	Russenski Lom (T)	11	1.8
	JDS91	Giurgeni	13	1.8
	JDS93	Siret (Trib.)	11	1.8
	JDS94	Prut (Trib.)	10	1.8
Zinc	JDS76	Upstream Olt	333	7
	JDS84	Russenski Lom (T)	164	7

TABLE C2.3.-2: Highest element concentrations determined in JDS water samples

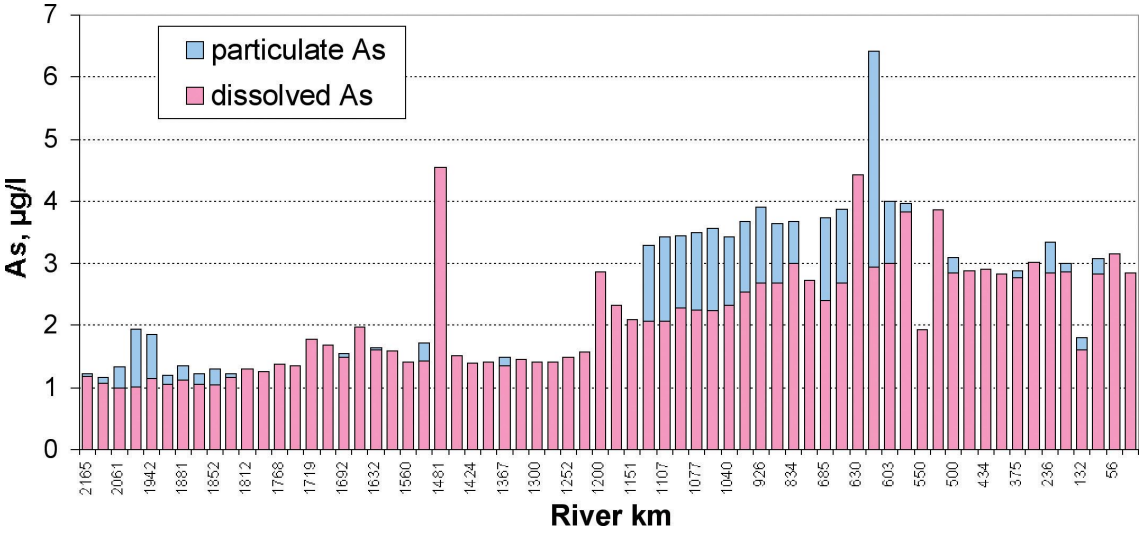

FIGURE C2.3.-2: Distribution of dissolved and particulate arsenic along the Danube river determined in JDS water samples (particulate As is calculated as the difference between total and dissolved As concentration).

Concentrations of aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc in suspended solids

Since heavy metals tend to adsorb on particulate matter, suspended solids should be a better pollution indicator than water samples. In contrast to water concentrations, which showed a huge variation along the Danube River, the heavy metal content in suspended solids was found to be much more evenly distributed.

Looking only at the samples taken from the Danube River, without its tributaries, the concentrations of aluminium and iron showed slight and comparable variations along the River (Figure C2.3.-3). After higher concentrations between river km 2100 and 1800 (geo-morphological Reach 2 after confluence with the Inn River), the values decreased (minimum around river km 1500, geo-morphological Reach 5, the great Hungarian Lowlands). Beginning at river km 1300 (Novi Sad), an increase in the concentrations of aluminium and iron was followed by more or less constant values in the Danube Delta and on the way to it. The highest concentrations were detected in the Iron Gate Reservoir (km 1040 – 943) and behind Russe (km 493).

Interestingly, the concentrations of arsenic, chromium and nickel showed the same spatial distribution along the Danube (Figure C2.3.-3). Provided that aluminium and iron reflect the geochemical background in the composition of particulate matter, the similar trend in Figure C2.3.-3. indicates that the Danube can be regarded as unpolluted at least in terms of arsenic, chromium and nickel.

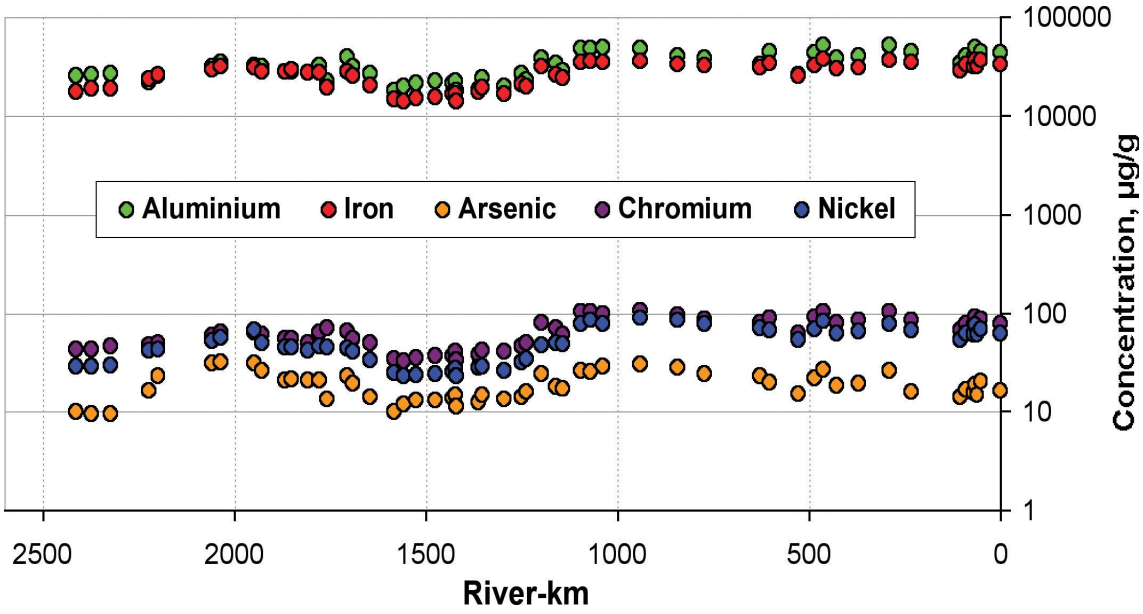

FIGURE C2.3.-3: Spatial distribution of selected elements (logarithmic scale) in suspended solids samples of the Danube River (without tributaries).

Table C2.3.-3. contains information on the range of element concentrations in suspended solids samples of the Danube River and some of its tributaries (unfortunately, the water level during the Survey did not allow the sampling of particulate matter in all main tributaries).

Figure C2.3.-4. shows the number of JDS suspended solids samples with element concentrations exceeding the quality targets listed in Table C2.3.-3. The Danube and its tributaries can be described as being polluted with arsenic, cadmium, nickel and zinc, because more than one-third of the investigated samples were found to have higher concentrations of these elements than the quality target. As stated above, at least the elements arsenic, nickel and chromium show the same spatial distribution as aluminium and iron. Therefore, an adjustment of the quality targets to reflect the specific geochemical conditions of the Danube River may be needed.

TABLE C2.3.-3: Range of element concentrations (minimum - maximum) in suspended solids samples of the Danube River and some of its tributaries, and comparison with data of the Burgund Survey [9], background concentrations and quality targets [1] ("<" – values below the method quantitation limit)

	Concentration [µg/g]		MS Burgund Survey	Background Values	Quality Target
	Danube	Tributaries	[µg/g]	[µg/g]	[µg/g]
Al	17900 – 52800	15300 – 54100	-	-	-
As	9.4 – 32.1	10.4 – 29	4 - 26	-	20
Cd	< 1.1 – 7.6	< 1.1 – 25.6	0.4 - 1.1	0.15 – 0.60	1.2
Cr	32.9 – 107.5	55.0 – 148.9	20 - 100	40 – 160	100
Cu	28.3 – 193.7	26.9 – 95.5	20 - 105	10 – 40	60
Fe	14300 – 38300	21300 – 37200	-	-	-
Hg	< 0.10 – 0.55	< 0.10 – 0.79	0.2 - 0.5	0.1 – 0.4	0.8
Mn	565 – 4028	963 – 3340	800 - 3300	-	-
Ni	23.2 – 89.8	32.6 – 170.9	9 - 62	15 – 60	50
Pb	18.2 – 85.0	17.3 – 214.9	20 - 70	12.5 – 50	100
Zn	99 – 398	87 – 2224	150 - 370	50 - 200	200

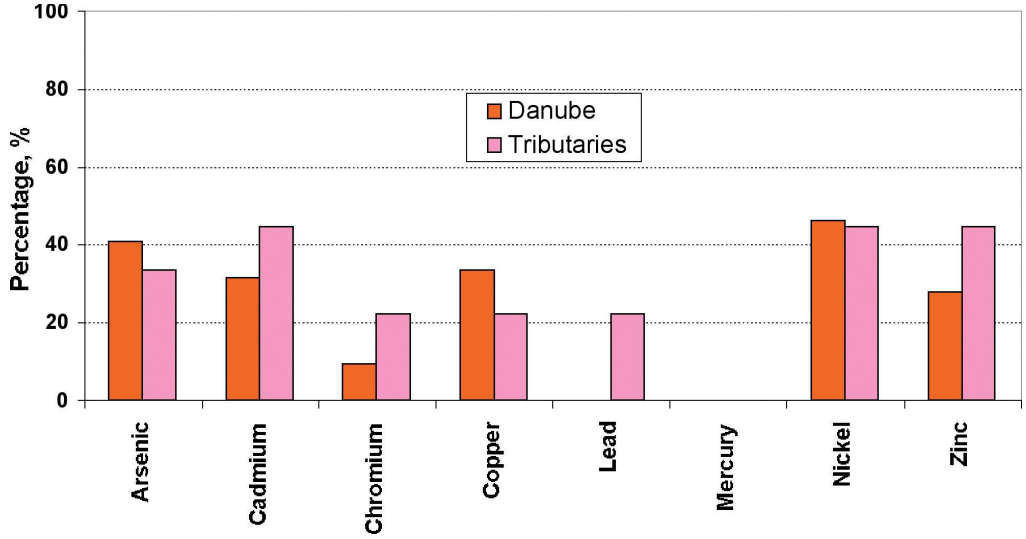

FIGURE C2.3.-4: Number of JDS suspended solids samples (in %) with heavy metal concentrations exceeding the quality targets listed in Table C2.3.-3.

The determination of total and dissolved heavy metal concentrations in JDS water samples allows the calculation of particle-bound element concentrations. On the other hand, the concentration of particle-bound elements can be estimated from the suspended solids data by using technical specifications of the centrifuge and JDS sampling protocols (to calculate the concentration of suspended solids in the water phase).

However, a significant correlation could only be found for aluminium (Figure C2.3.-5). Additionally, aluminium concentration in the water phase (measured as the difference between dissolved and total aluminium) was found to be far too low compared to its concentration in suspended solids. This difference and the non-correlation of all other investigated elements can be attributed to the analytical difficulties in measuring the very low concentrations in water samples. To get a reliable picture on the pollution of the River, the determination of heavy metals in suspended solids is suggested.

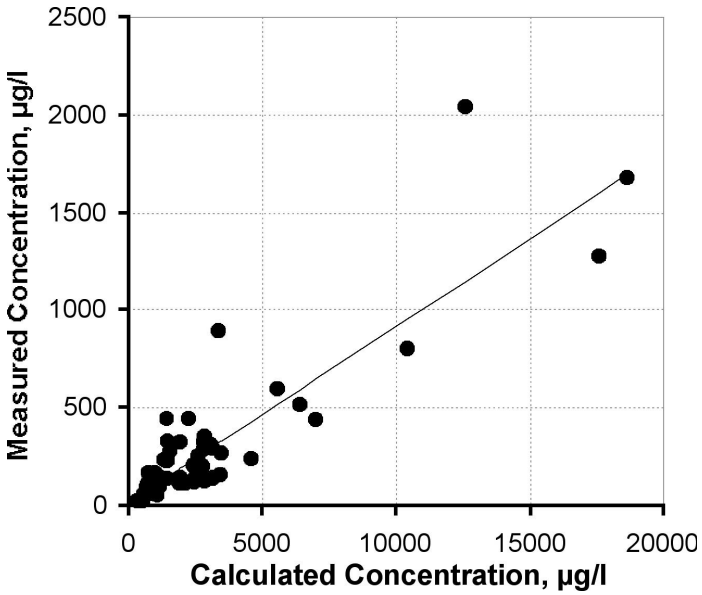

FIGURE C2.3.-5: Comparison between calculated (suspended solids data) and measured particle-bound aluminium (water data, difference between dissolved and total aluminium)

Concentrations of aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc in sediments

Analysis of heavy metals in sediments of the Danube River and its tributaries was carried out in the wet sieved-below-63-μm fraction to minimize the "dilution" effect of larger particles with low element concentrations.

Figure C2.3.-6. shows the number of sampling stations (in %) at which the determined element concentrations exceed quality targets (Table C2.3.-3). It can be suggested that the sediments of the Danube River can be regarded as unpolluted in terms of chromium, mercury and lead. The concentrations of arsenic, cadmium, copper, nickel, zinc and lead (in tributaries only) were above the quality targets at more than one-third of the sampling points. This is confirmed by the data of the TNMN 2000 [3]. Although only a small amount of sediment analysis results is available, the highest concentrations found are well above the quality targets for each of the elements (Table C2.3.-4).

A comparison of Figure C2.3.-4. and Figure C2.3.-6. shows a similar pollution pattern of sediments and suspended solids indicating arsenic, cadmium, copper, nickel and zinc as the elements of highest concern. The variation in the concentrations of elements along the entire course of the River reveals that a contamination of sediments by these elements is particularly serious in the lower section of the River. Figure C2.3.-7. demonstrates the obvious effects of the two right-bank tributaries (the Sava and the Velika Morava) in terms of nickel, effects that are also reflected in the right-bank Danube sediment downstream of these tributaries. The highest metal-concentrations were found in some of the tributaries, indicating the main pollution sources of the Danube (Table C2.3.-4).

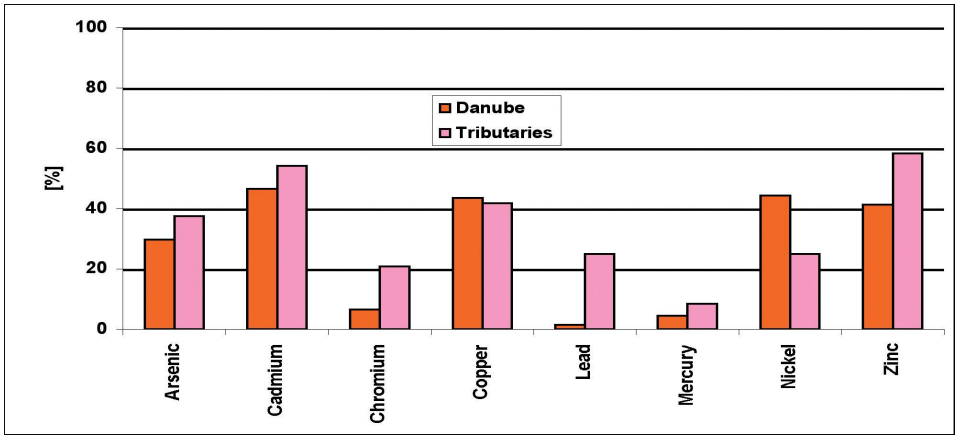

FIGURE C2.3.-6: Number of JDS sediment samples (in %) with heavy metal concentrations exceeding the quality targets listed in Table C2.3.-4.

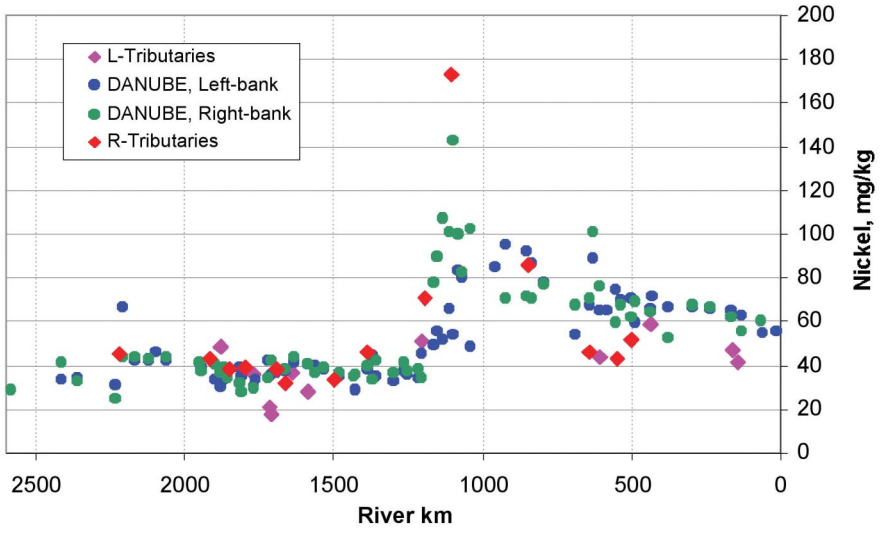

FIGURE C2.3.-7: Longitudinal variation in the concentration of nickel in the bottom sediment collected from the Danube River and its tributaries during JDS.

Element	JDS-Position		Concentration [µg/g]	Background [µg/g]	TNMN 2000 [µg/g]	Quality Target [µg/g]
As	JDS69	Timok	388	-	8.7 – 34.7	20
Cd	JDS74	Iskar	32.9	0.15 – 0.60	0.2 – 3.1	1.2
Cr	JDS84	Russ. Lom	556	40 – 160	1 – 193.6	100
Cu	JDS69	Timok	8088	10 – 40	6.7 – 345	60
Hg	JDS26	Vah	2.56	0.1 – 0.4	0.045 – 2.1	0.8
Ni	JDS61	Vel. Morava	173	15 – 60	10 – 69.8	50
Pb	JDS74	Iskar	542	12.5 – 50	13 – 230	100
Zn	JDS74	Iskar	2010	50 - 200	71 – 552	200

TABLE C2.3.-4: The highest element concentrations determined in JDS sediment samples in comparison with background concentrations [1], TNMN data of 2000 [3] and quality targets of various river monitoring networks [2]

Based on element concentrations that exceed background concentrations more than by a factor of 10, the Iskar and the Timok tributaries may be regarded as specific contamination sources for cadmium, lead and zinc (the Iskar) or arsenic and copper (the Timok). This is supported by total element concentrations found in JDS water samples which, likewise, showed higher concentrations of these elements.

As suggested in the case of suspended solids, the concentration of aluminium and iron may reflect a geochemical variation in sediments along the Danube. Relatively comparable concentrations up to river km 1300 (Novi Sad) were followed by a slight increase up to the Iron Gate Reservoir (around river km 1000). Behind the Iron Gate Reservoir, relatively constant concentrations were found in the Danube Delta and on the way to it. This is supported by a strong correlation of both element concentrations for all investigated samples. Similarly, the variation of chromium, lead, mercury and manganese along the Danube can be attributed to the geochemistry as indicated by the strong correlation to aluminium with only some exceptions, mostly concerning the tributaries (Figure C2.3.-8). Therefore, higher values of chromium and lead in the lower section of the Danube do not appear to be a manifestation of anthropogenic contamination of the River sediments. Polluted sediments possess a different regres-

sion pattern as shown in Figure C2.3.-8. for arsenic, copper, nickel, cadmium and zinc; many more sediment samples are characterised by a high element/aluminium ratio as indicated by points well above the geochemical regression line. The regression line was calculated without sediment samples having significantly higher element/Al ratios (Arsenic/Al > 0.75 ng/µg, Cadmium/Al > 0.1 ng/µg, Chromium/Al > 2.5 ng/µg, Copper/Al > 2.5 ng/µg, Iron/Al > 1.4 µg/µg, Lead/Al > 3.0 ng/µg, Manganese/Al > 36 ng/µg, Mercury/Al > 0.015 ng/µg, Nickel/Al > 2.0 ng/µg, Zinc/Al > 9.5 ng/µg).

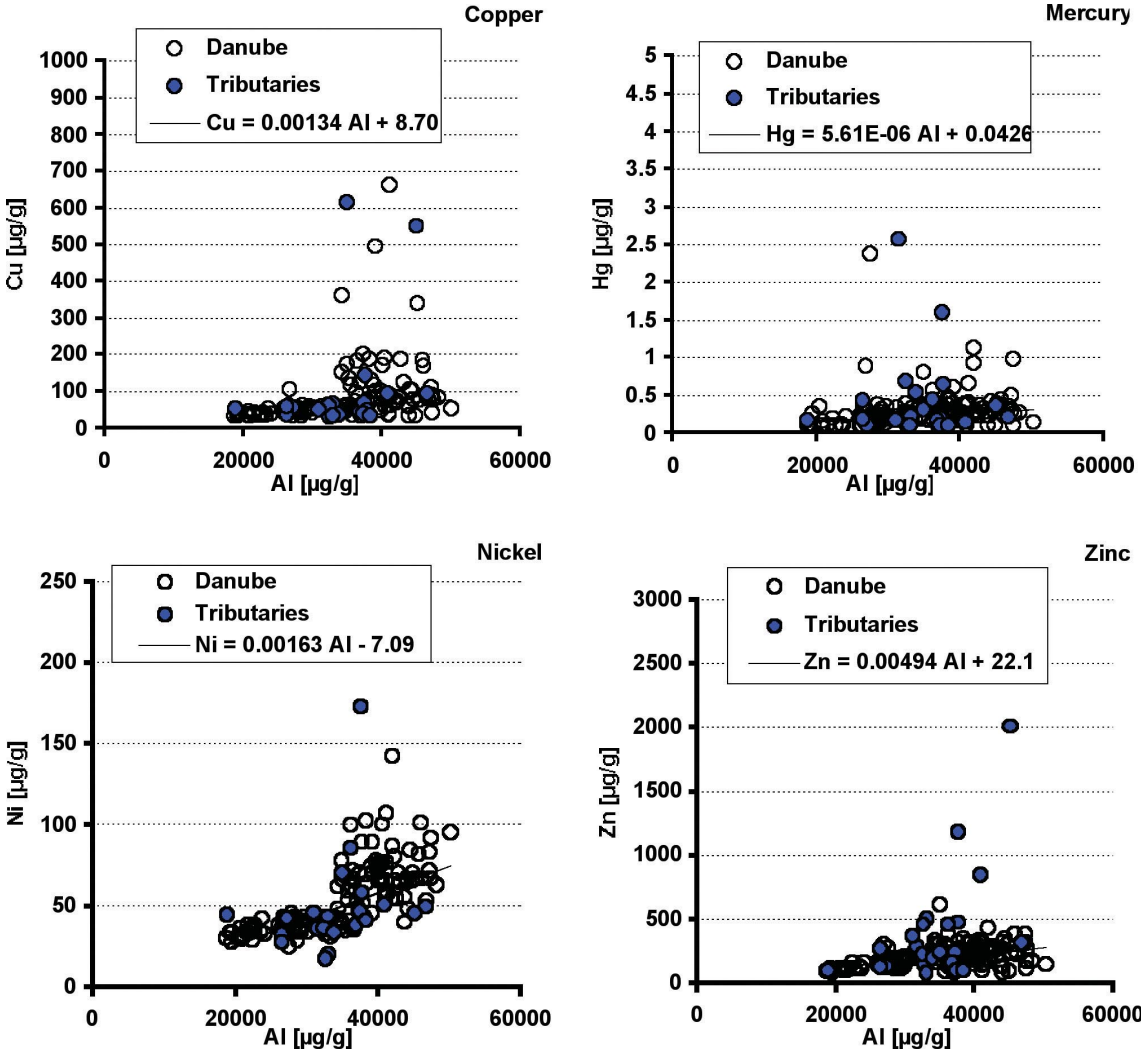

FIGURE C2.3.-8: Correlation of heavy metal concentrations with aluminium for all investigated JDS sediment samples. The black line represents " geochemical regression" (element = f(Al), calculated without outlying concentration ratios - see text)

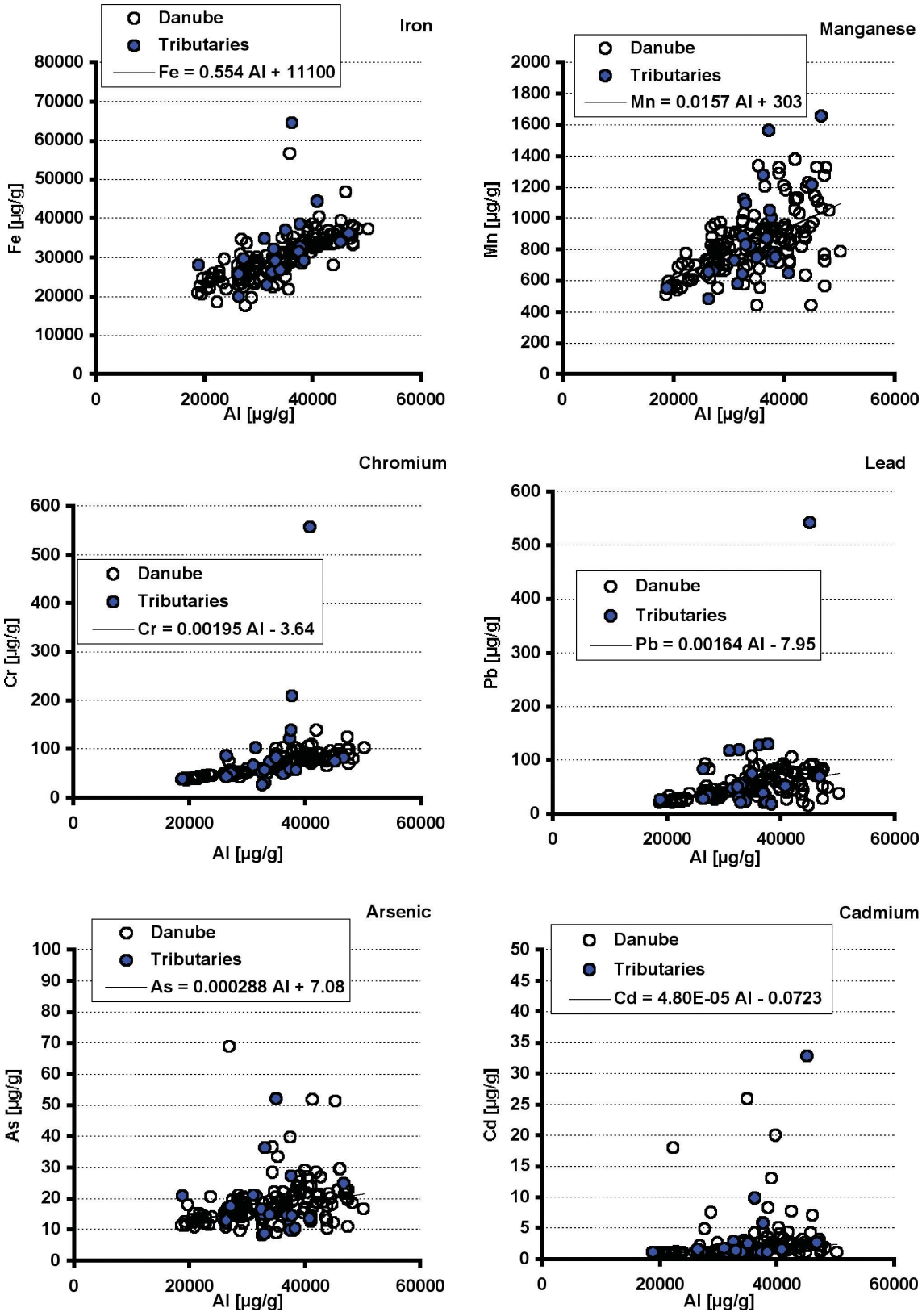

FIGURE C2.3.-8: (cont.) Correlation of heavy metal concentrations with aluminium for all investigated JDS sediment samples. The black line represents " geochemical regression" (element = f(Al), calculated without outlying concentration ratios - see text)

To make sure the investigated samples were representative, they were taken both on the right and the left bank of the Danube at every sampling station. Except for the "geochemical" normaliser, aluminium, which showed increasing concentrations in the lower Danube Reach but had comparable concentrations on both sides of the River (Figure C2.3.-9.), the other elements possess a heterogeneous distribution along the Danube. At most of the sampling stations, the concentration differences were found to be significantly higher than the uncertainty of the analytical procedure (Table C2.3.-5). Further investigations are necessary to differentiate between geochemical and anthropogenic reasons for the uneven element distribution.

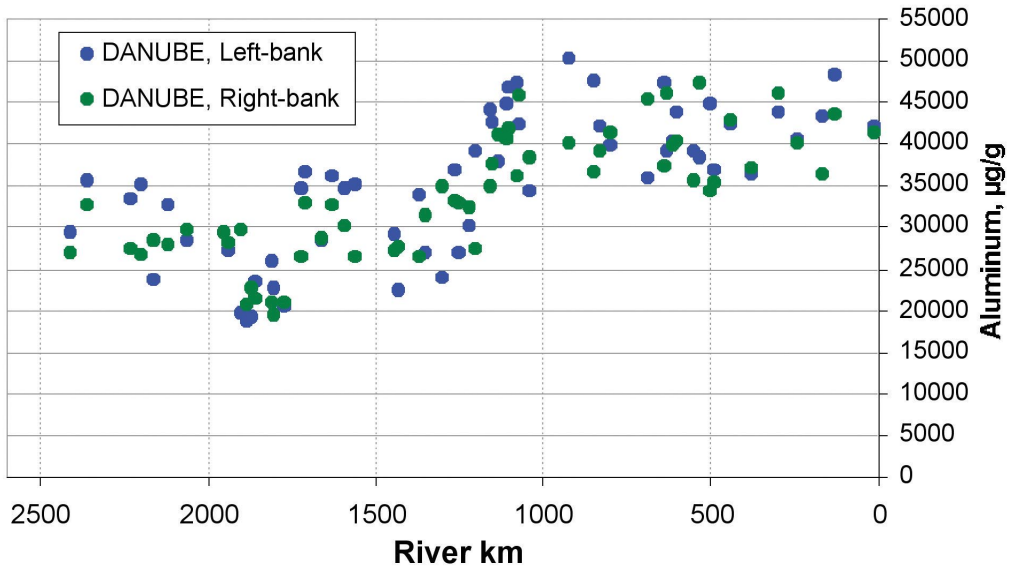

FIGURE C2.3.-9: Concentration of aluminium in sediments sampled on both sides of the Danube River

Element	As	Cr	Hg	Pb	Cu	Ni	Cd	Zn	Fe	Mn	Al
Uncertainty [%]	15	11	14	14	7	8	11	10	11	10	15
Number of Stations [%]	33	17	54	48	59	46	65	48	21	35	5

TABLE C2.3.-5: Number of JDS sampling stations (in %) where the difference in element concentrations between the left and right riverbank was higher than the uncertainty of the analytical procedure

At selected positions, sediment cores were taken during JDS (JDS20 - Gabcikovo Reservoir, JDS36 - Rackeve-Soroksar Danube Arm, JDS63 - left bank and right bank in the Iron Gate Reservoir). Generally and in agreement with the data on sediments and suspended solids, the more downstream the sediment cores were taken the higher the heavy metal concentrations were. For cadmium, for example (Figure C2.3.-10), the concentration was below the method quantitation limit (1.1 µg/g) in the sediment core of the Gabcikovo Reservoir. In the deeper sediment layers of the Rackeve-Soroksar Danube arm, the concentration of cadmium was around the quality target of 1.2 µg/g. However, a significant increase was detected from –20 cm up to the sediment surface. The highest concentrations were found in the sediment cores of the Iron Gate Reservoir. Provided that the sediment cores were taken at undisturbed sediment accumulation sites, a change in the element concentration may indicate a temporal trend

in sediment pollution. Table C2.3.-6. summarises the sediment core data using a significant difference in the heavy metal concentration between the upper and the lower sediment layer (concentration difference exceeds the uncertainty of the analytical method.

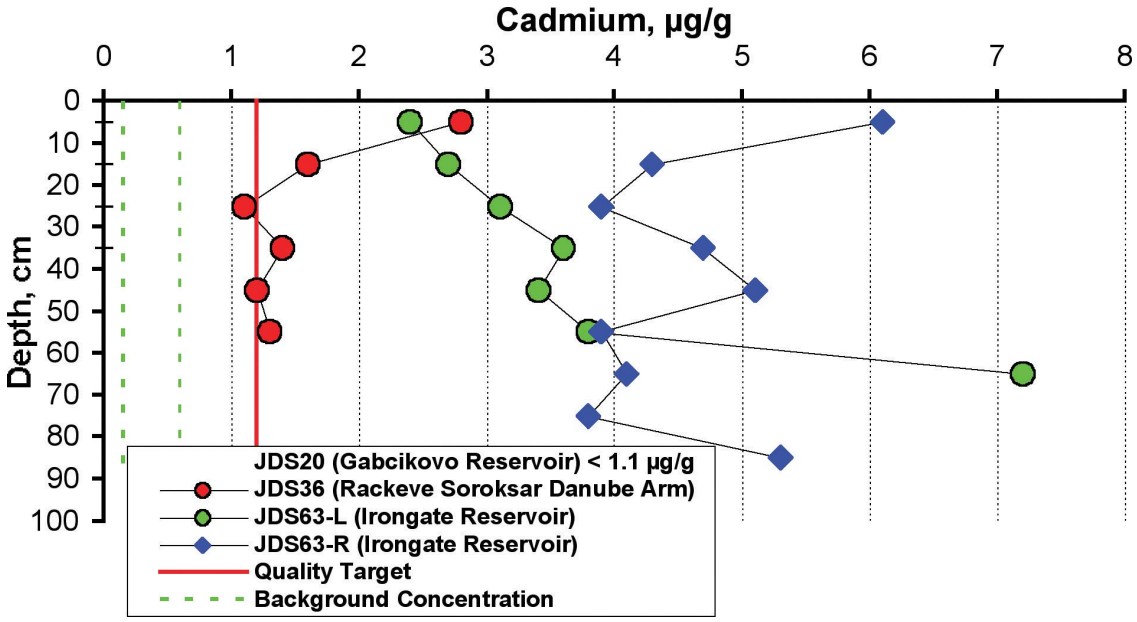

FIGURE C2.3.-10: Concentration of cadmium in the investigated sediments core samples. Sediment cores were separated into 10 cm layers. Background concentrations and quality target according to [1] and [2] (see Table C2.3.-4)

TABLE C2.3.-6: Significant change (concentration difference higher than uncertainty of the analytical procedure) in the element concentration between upper and lower layers of the sediment cores ("⇓" - decreasing temporal trend, "⇑" - increasing temporal trend, "≈" – no significant change)

Element	As	Cr	Hg	Pb	Cu	Ni	Cd	Zn	Fe	Mn	Al
Uncertainty of Analytical Method [%]	15	11	14	14	7	8	11	10	11	10	15
Gabcikovo Reservoir (JDS20)	≈	≈	⇑	≈	≈	≈	≈	≈	≈	≈	≈
Rackeve-Soroksar Danube (JDS36)	≈	≈	⇑	≈	⇑	≈	⇑	≈	≈	≈	≈
Iron Gate Reservoir (JDS63-L)	⇓	⇓	⇓	⇓	≈	⇓	⇓	⇓	≈	≈	≈
Iron Gate Reservoir (JDS63-R)	⇓	⇓	⇓	⇓	≈	⇓	≈	⇓	≈	≈	≈

Except for mercury, no significant changes in the element concentrations were found in the sediment core of the Gabcikovo Reservoir. However, the determined concentration of 0.27 µg/g mercury is well below the quality target of 0.8 µg/g. No other element exceeded its quality target, either Therefore, it is suggested that the lowest concentrations determined in the Gabcikovo sediment core should be used as background concentrations, at least for the upper Danube section up to river km 1300 (see above). The element concentrations in the upper layers of the Iron Gate Reservoir sediment cores are well in agreement with those determined in suspended solids and in other sediment samples. A significant decrease was found for arsenic, chromium, mercury, lead, nickel and zinc (Table C2.3.-6) indicating a reduction in heavy metal input in the past. Nevertheless, the concentrations of cadmium, copper and zinc still exceed the quality targets. The relatively constant concentrations of iron, manganese and aluminium in each of the investigated sediment cores point again to their use as a geochemical normaliser.

Concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in mussels

The heavy metal content of mussels sampled in the Danube River and its main tributaries was determined in five different mussel species: Anodonta anatina (49 samples), Unio tumidus (62 samples), Unio pictorum (20 samples), Pseudanodonta complanata (two samples) and Anodonta cygnea (three samples). It is well known that individual species may have a different bioaccumulation or regulation pattern for heavy metals leading to different tissue concentrations. However, Figure C2.3.-11. demonstrates for zinc as an example that the variation of heavy metal concentration is species-independent and determined by the sampling point (river km). Therefore, the following presentation of heavy metals in biota is based on pooled mussel data.

Since no data for quality targets of heavy metal concentrations in bivalves are available at this point, twice the background concentration was used according to one of the approaches of the German LAWA for sediments and suspended solids [5]. Except for mercury and copper, these quality targets are well in agreement with international legal limits for shellfish for human consumption [6] (Table C2.3-7). Table C2.3.-8. shows the range of concentrations determined in the Danube and its main tributaries in comparison with published data on background concentrations [9] and concentrations determined in mussel samples of German rivers (the Elbe, the Saar, the Rhine) [8].

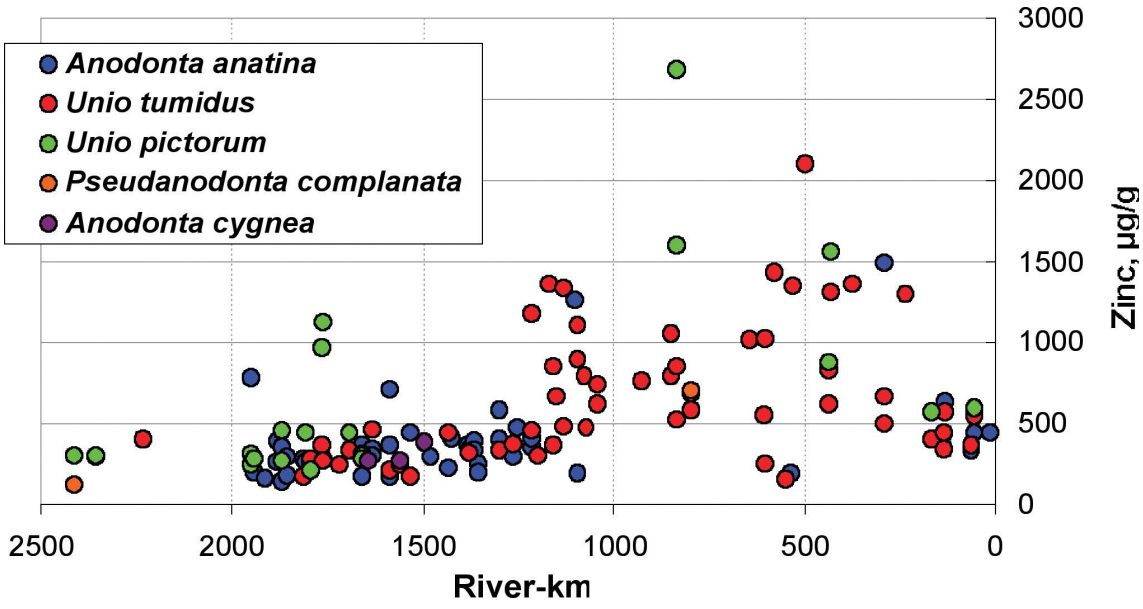

FIGURE C2.3.-11: Zinc concentration in different mussel species sampled along the Danube River and its tributaries during JDS (all values in µg/g dry weight).

TABLE C2.3.-7: International legal limits for heavy metals in mussels [6] and proposed quality targets for the heavy metal content in mussels of the Danube (all values in µg/g dry weight)

Element	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
International Legal Limits [µg/g]	9.8	7	7	140	14	3.5	?	490
Proposed Quality Target [µg/g]	20	4	6	20	10	0.4	10	400

TABLE C2.3.-8: Range of element concentrations (minimum - maximum) in mussel samples of the Danube River and its tributaries and comparison with background concentrations [9], German river data /10/ and proposed quality targets (all values in µg/g dry weight, MQL - method quantification limit)

	Danube	Tributaries	Background Values	German river data	Quality Target
	Concentration [µg/g]		[µg/g]	[µg/g]	[µg/g]
As	0.08 - 1.23	0.06 - 0.81	10	2.4 - 8.3	20
Cd	0.1 - 35.9	0.2 - 16.4	2	0.38 - 1.81	4
Cr	0.5 - 11.7	< MQL - 24.12	3	-	6
Cu	4.5 - 178.4	4.3 - 54.0	10	13.7 - 32.7	20
Pb	0.5 - 49.9	0.7 - 31.7	5	0.93 - 4.70	10
Hg	0.055 - 0.412	0.037 - 0.742	0.2	0.066 - 0.305	0.4
Ni	0.44 - 4.69	0.49 - 9.43	200	13.7 - 28.7	10
Zn	120 – 2680	160 - 1360	5	?	400

The number of JDS mussel samples whose element content was found to exceed the proposed quality targets is shown in Figure C2.3.-12.

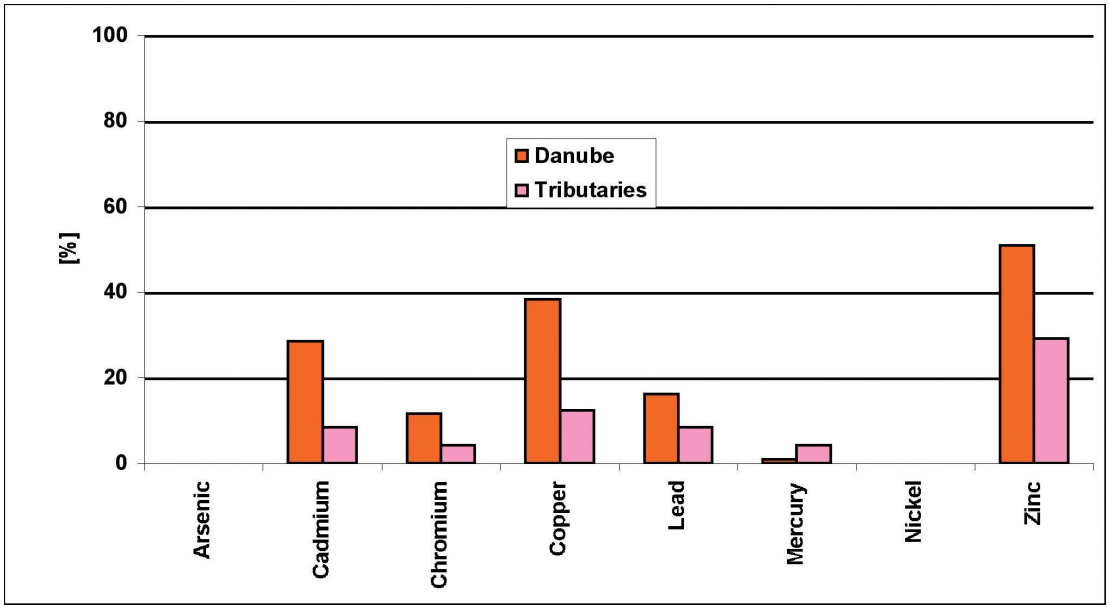

FIGURE C2.3.-12: Number of JDS mussel samples (in %) with heavy metal concentrations exceeding the quality targets listed in Table C-2.3.8

As the data on suspended solids and sediments indicate (Figure C2.3.-4 and 6), the Danube and its tributaries can be said to be polluted with cadmium, copper and zinc. However, the heavy metal load in mussels was more pronounced in the Danube than in the investigated tributaries. The arsenic pollution of the Danube system found in sediment and suspended solids samples was not confirmed by the analysis of the sampled mussels.

A similar geographical variation along the Danube was found for all heavy metals. Up to river km 1300 (Novi Sad), the concentrations were relatively constant, at least cadmium, copper, mercury, nickel, lead and zinc, with a minimum around river km 1500. A slight increase up to the Iron Gate Reservoir (around river km 1000) was then followed by slightly decreasing concentrations to the

Danube Delta. This geographical distribution of element concentrations reveals a contamination of mussels particularly in the lower section of the River. Based on the determined element concentrations, some JDS sampling stations can be regarded as polluted mussel sites (Table C2.3.-9).

TABLE C2.3.-9: Highest element concentrations determined in JDS mussel samples in comparison with background concentrations [7] and proposed quality targets (all values in µg/g dry weight)

Element	JDS-Position		Species*	Concentration [µg/g]	Background [µg/g]	Quality Target [µg/g]
Cd	JDS98	St. Gheorghe	A	35.9	2	4
Cr	JDS54	Tisza	B	24.12	3	6
Cu	JDS70	Pristol	B	178.4	10	20
Pb	JDS46	Upstream Drava	A	49.9	5	10
Hg	JDS61	Velika Morava	A	0.742	0.2	0.4
Zn	JDS70	Pristol	C	2680	5	400
* A - Anodonta anatina, B - Unio tumidus, C - Unio pictorum						

Mussels are in many freshwater and marine monitoring programmes used as indicator organisms for detecting pollution with hazardous substances such as heavy metals or several organic contaminants. The element concentrations in suspended solids, sediments and mussels sampled during JDS showed a very similar spatial variation in the Danube River thus confirming the applicability of mussels for monitoring the Danube water quality as well. As an example, Figure C2.3.-13. compares the concentration of copper determined in JDS sediment and mussel samples.

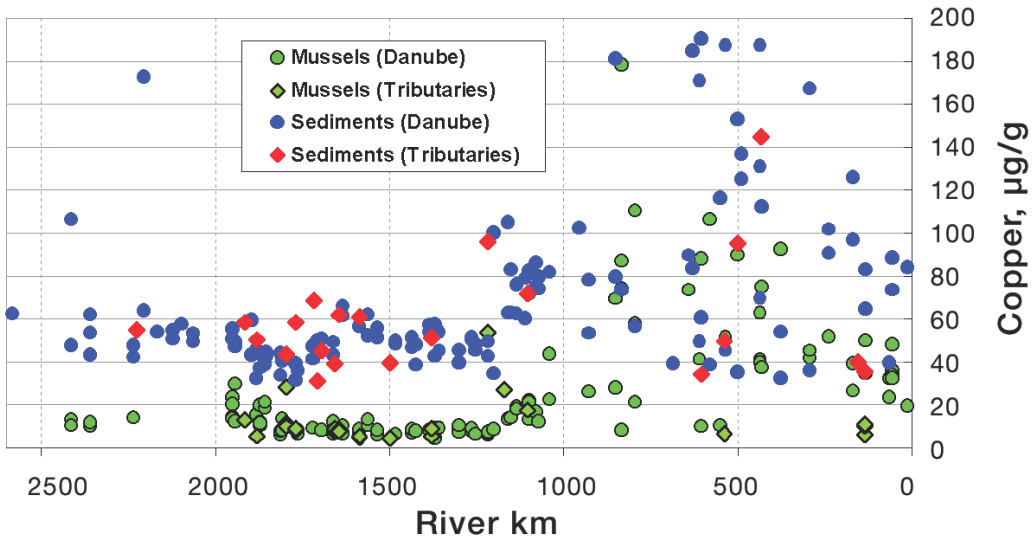

FIGURE C2.3.-13: Copper concentration in JDS sediment and mussel samples along the Danube River and its tributaries (all values in µg/g dry weight)

To investigate the presence of heavy metals in suspended solids, sediments and mussels and identify the differences between matrices and/or sampling points (river vs. tributaries), a factor analysis was carried out using the whole data set of element concentrations. Figure C2.3.-14. displays the plot of the two main factors representing nearly 60% of the overall data variance. Clearly, there is no difference in the pollution patterns of sediments and suspended

solids. A sharp distinction does, however, exist between the sediments and suspended solids on the one hand and mussels on the other, reflecting a totally different heavy metal composition of the biota samples.

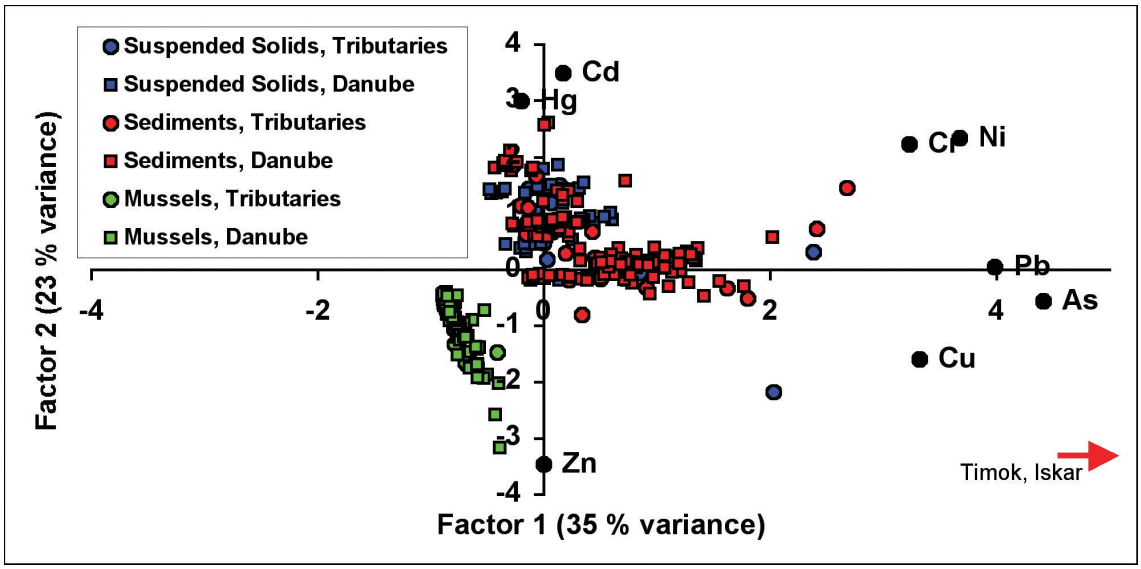

FIGURE C2.3.-14: Factor analysis (Varimax rotation, 2 factor plot) of heavy metal concentrations (As, Cd, Cr, Cu, Hg, Ni, Zn) in suspendend solids, sediments and mussels sampled during JDS. Data points of heavy metals (parameters) are scaled up by a factor of 5 for clarity.

Using the parameter points in the factor plot, this difference can be attributed to significantly lower chromium/zinc or nickel/zinc ratios in mussels compared to sediments/suspended solids. Additionally, the factor plot reveals a similar pollution pattern in the Danube and the investigated tributaries for all matrices. However, the outlying data points of the Timok (JDS69) and the Iskar (JDS74) tributaries confirm their status as heavily polluted sites.

Comparison of JDS and National Survey Data

One of the main objectives of JDS was to obtain a homogeneous set of data on a variety of contaminants for the entire Danube system that would allow a comparison with the data of national Danube monitoring programmes. Since a lot of data on heavy metals in JDS water samples are below the detection limit of the method and the majority of the national reports contain no data on mussels or suspended solids, the following comparison is carried out for heavy metals in sediments only, for which data from laboratories in Slovakia, Hungary, Croatia, Yugoslavia, Bulgaria and Romania are available.

Common interlaboratory exercises distribute dried and homogenised sediment samples to the participants. Therefore, the obtained overall reproducibility includes only heavy metal extraction and analyses. The national laboratories investigated the same sediment samples but using their own routine procedure including sub-sampling, drying and separation of the fraction below 63 µm. Differences in element concentrations must be attributed to sample preparation steps as well leading to higher between laboratory reproducibility. However, both sets of data are in sufficient agreement (see Figure C2.3.-15. for Nickel as an example) indicating the reliability of the element concentrations determined in JDS sediment samples.

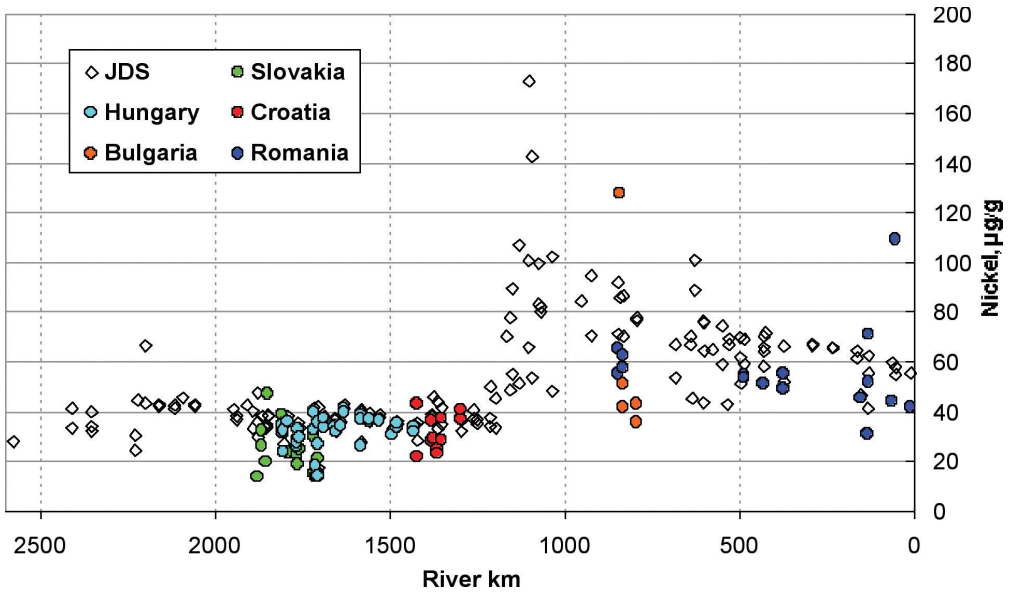

FIGURE C2.3.-15: Comparison of nickel concentrations in sediment samples along the Danube River and its tributaries, determined at JDS laboratory and several national laboratories

Comparison of JDS with earlier surveys

Several international research surveys that took place in the past investigated the Danube water/sediment quality, e.g., the field study of Equipe Cousteau (1993) [8], the Applied Research Program "Quality of Sediment and Biomonitoring" (1996) [9] or the monitoring trip of the MS "Burgund" (1998) [7]. Among a lot of other investigations, heavy metals were determined in sediments during the Cousteau survey and in suspended solids during the Burgund trip.

The main conclusion of the Burgund survey concerning the investigation of heavy metal concentrations in suspended solids was that the pollution was rather low in the Austrian and Hungarian parts of the Danube with only some results exceeding the set quality targets [7]. Comparable results were found in JDS suspended solids samples. The data in Table C 2.3.3 show a higher maximum of element concentrations in JDS suspended solids. However, these higher values were found in the lower stretch of the Danube, which was not monitored by MS "Burgund".

The assessment of element concentrations in sediments determined by Equipe Cousteau showed their levels in the lower half of the River to be generally about 50% higher than those in the upper Reaches [8]. Similar results were found for JDS sediment samples including the concentration increase between river km 1300 and 1000. Table C2.3.-10. shows the obtained concentrations ranges of both surveys indicating no improvement of the sediment quality status over the years. However, a detailed evaluation of JDS sediment data using established quality targets points to arsenic, cadmium, copper, nickel and zinc as the elements of special concern. Serious contamination with lead was detected in the tributaries only, whereas significantly higher concentrations of chromium and mercury were found in two or three samples.

TABLE C2.3.-10: Range of element concentrations (minimum - maximum) in sediment samples of the Danube River and some of its tributaries and comparison with data of the Cousteau survey [8]

	Concentration [µg/g]		Equipe Cousteau [µg/g]	Quality Target [µg/g]
	Danube	Tributaries		
As	9 - 68.9	8.1 - 388	9 – 48	20
Cd	< 1.1 - 25.9	< 1.1 - 32.9	0.35 – 4.7	1.2
Cr	35.3 - 139	26.5 - 556	35 – 310	100
Cu	31.3 - 663	31.1 - 8088	19 – 290	60
Hg	< 0.1 - 2.37	< 0.1 - 2.56	0.11 – 5.55	0.8
Ni	24.6 - 143	17.5 - 173.3	17 – 70	50
Pb	14.7 - 108	18.1 - 541.8	23 – 420	100
Zn	83 - 622	78 - 2010	73 – 2000	200

In 1995, a detailed sediment survey was carried out at almost the same sampling sites as during JDS between Greifenstein and Budapest [9]. A summary of the findings, and recommendation for the heavy metal baseline level ("background") in sediment is given in Table C2.3.-11.

TABLE C2.3.-11: Baseline levels and enrichment of the different heavy metals in the less-than-63-µm grain-size fraction in bottom sediment in the Danube Reach relevant to JDS-11 to JDS-37, during 1995 [9]

Heavy Metal	Baseline Level, mg/kg	Highest Enrichment Values, Concentration/Baseline (mg/kg)		Site above severe effect
		Danube	Tributaries	
Hg	0.2	4.8 (0.96)	14.5 (2.90)	Vah (JDS26)
Cd	0.25	6.0 (1.50)	15.0 (3.74)	
Pb	25	3.1 (0.77)	4.2 (105)	
Cu	35	2.0 (70)	3.6 (125)	Schwechat (JDS13)
Cr	10-50 (?)	up to 2.0	up to 3.5	
Zn	130	3.0 (390)	7.5 (970)	Hron (JDS29)
As	10	2.4 (24)	5.5 (55)	
Ni	10	4.5 (45)	5.0 (50)	

Most of the results of the two surveys are very similar. Concerning the maximum values, observed above the severe effect limits in some of the tributaries, mercury in the sediment of the Vah River measured 2.9 mg/kg during the 1995 survey and 2.56 mg/kg during JDS. In the case of copper and zinc measured in the Schwechat and the Hron, the relevant values were slightly lower during JDS; copper measured 125 mg/kg in 1995 and 58 mg/kg during JDS, while zinc measured 970 mg/kg during 1995 and 500 mg/kg during JDS. It is worth-mentioning, however, that both values measured during JDS were the maximum values observed in this Danube Reach.

Special attention should be paid to the cadmium. As shown in Table C2.3.-4, the quality target (1.2 mg/kg) is very close to the quantification limit (1.1 mg/kg), and the results during JDS were generally higher than during both earlier surveys, i.e., Equipe Cousteau survey (1991/2) and the 1995 survey. The national surveys carried out during JDS also revealed results similar to the ear-

lier surveys. Therefore, further discussion might be required, one that would consider the semi-quantitative results (between detection and quantification limits) in the overall assessment.

During a survey carried out by the UNEP/UNCHS Balkans Task Force for complementary measures to assess environmental impacts [10], core samples were taken in the Iron Gate Reservoir to determine, among other parameters, the distribution of mercury in the sediment. Figure C2.3.-16. indicates decreasing mercury content from deeper layers up to the surface reported in 1999 and in 2001. The difference in concentration may be attributed to the spatial non-homogeneity of sediments or variations in the analytical procedure used.

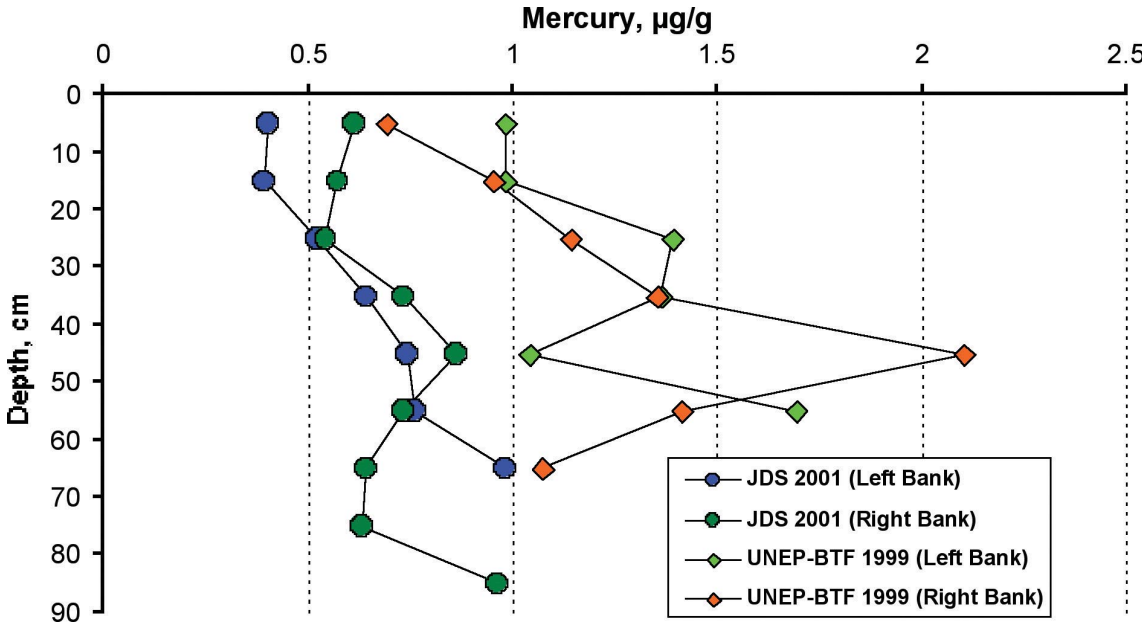

FIGURE C2.3.-16: Comparison of mercury concentrations determined in 10 cm layers of sediment cores sampled on the left and the right banks of river km 1077 (Iron Gate Reservoir)

In 2000, a survey was carried out investigating inorganic and organic contaminants in selected bioindicatororganisms [11]. One of the main objectives of that study was to determine the heavy metal content of various mussel species. Table C2.3.-12. compares the heavy metal concentrations found in mussels during that survey with those found in JDS mussel samples along the appropriate stretch between river km 1534 (Paks, Hungary) and river km 849 (confluence with the Timok River). Besides a comparable concentration range of heavy metals found in mussels in that particular stretch of the Danube, JDS data confirm the results of the 2000 survey indicating a significant increase in the heavy metal content in mussels and sediments from river km 1300 up to the Iron Gate (around river km 1000).

TABLE C2.3.-12: Range of element concentrations (minimum - maximum) in JDS mussel samples between river km 1534 and 849 compared to the data of the ICPDR 2000 survey (estimated from graphics in [11])

	Concentration [µg/g] JDS		Concentration [µg/g] Survey 2000		Quality Target
	Danube	Tributaries	Danube	Tributaries	[µg/g]
As	0.08 - 1.23	0.22 - 0.56	-	-	20
Cd	0.2 - 7.0	0.2 – 16.4	0.5 - 10	0.2 - 23	1.2
Cr	0.49 - 8.68	< 0.2 - 24.1	50 - 130	50 - 440	100
Cu	4.5 - 68.9	4.3 - 54.0	30 - 120	40 - 220	60
Hg	0.055 - 0.373	0.060 - 0.742	0.1 - 0.6	0.1 - 1.5	0.8
Ni	0.44 - 4.69	0.70 - 9.43	30 - 120	40 - 140	50
Pb	1.4 - 449.9	2.1 - 31.7	30 - 115	30 - 170	100
Zn	170 - 1340	320 – 1360	-	-	200

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