Joint Danube Survey 2

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International Commission for the Protection of the Danube River

Internationale Kommission zum Schutz der Donau

Full report on General Physico-Chemical Quality Elements (Nutrients)

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1 Introduction

This chapter refers to the nutrients forms analysed during JDS2, both by on-board and reference laboratories analyses.

1.1 Relevancy of nutrients in the Water Framework Directive

The EU Water Framework Directive (WFD) significantly changed the water management by shifting the view of water quality from chemical targets to ones based on ecological assessment of natural systems (Pollard and Huxham, 1998). Nevertheless, WFD requires surface water classification by means of the assessment of ecological status (or ecological potential) and surface water chemical status, imposing to achieve good ecological status in all water bodies by 2015 (Council Directive 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy, 2000). In Annex V, Section 1.1.1 (Rivers), WFD lists three groups of quality elements to be used in this assessment, among which the third group refers to the "**chemical and physico-chemical elements supporting the biological elements**". Within this group, under the "General" category, the following quality elements are listed: thermal conditions, oxygenation conditions, salinity, acidification status and nutrient conditions. Beside Annex V, WFD explicitly refers to nutrients (Annex VIII. 12) as "substances which contribute to eutrophication (in particular nitrates and phosphates)."

1.2 Relevancy of nutrients in the Danube River Basin

The nutrients loads and their consequences have been recognised as one of the most striking issues in the Danube catchment area, the Danube Delta and the Black Sea. In the recent decades comprehensive studies and projects were dedicated to the nutrients problem (Environmental Programme for the Danube River Basin: Danube integrated environmental study, Final report, Haskoning, Nijmegen, The Netherlands, 1994), (Nutrient Balances for the Danube Countries, Project EU/AR/102A/91, Final Report, 1997), Water Quality Targets and Objectives for Surface Water in the Danube Basin, Progress Report Phase 2, Delft Hydraulics, 1997), daNUbs Project, 2005). In addition, nutrients data from the Danube Basin were subject for modelling tools that quantified the Danube in-stream loads of Nitrogen and Phosphorous - Danube Water Quality Model (UNDP/GEF) and estimated the nutrient emissions -MONERIS Model. According to the results obtained by the latter model, nutrient emissions by point and diffuse sources into the Danube River Basin in the period 1998-2000 were 758 kt of Nitrogen and 68 kt of Phosphorus, figures that are much above the background conditions - (background: 8 % for N and 10 % for P, Schreiber et al., 2004).

Nutrients issue was also subject of analysis in the first main output of the joint implementation process of the WFD in the Danube River Basin, Roof Report 2004. Within this analysis an assessment of risk of failure to reach the environmental objectives was carried out; according to these results, across the basin a high proportion of water bodies will be at risk of failing to meet the WFD's "good ecological status" objectives due to the impact of four major causes among the second one is "nutrient pollution". Based on the risk assessment approach used and based on the available data (especially in case of tributaries), in total 55% of the Danube River length and 49% of the Danube tributaries are "at risk" or "possibly at risk" due to nutrient pollution (Roof Report, 2004).

2 Methods

2.1 Sampling and storage

Water samples

Water samples designated to nutrients analysis were collected directly from the river using the motor-boat used for the collection of biological samples. Water samples were stored in amber glasses and polypropylene (PP) containers. Original water samples and filtered samples were preserved and properly stored for analysis (in selected laboratories) of organic nitrogen, total phosphorous and dissolved silicate. Samples from the longitudinal surveys on major tributaries were sampled by national experts from the riparian countries of a given tributary and transported to the laboratory ship within the required period of time in order to perform immediately the analytical determination.

Suspended solids and sediment samples

Suspended solids and sediment samples addressed to be analysed for organic nitrogen and total phosphorous were stored in glass or PP containers and properly kept for later delivery to the selected laboratories.

2.2 Determination

Table 1 presents the overall summary of the chemical quality elements that were determined both on board and in laboratory. The Standard Operational Procedures (SOPs) based on international standardised methods were used for on-board analyses. Water samples intended to be analysed for dissolved nutrients forms were filtered by 0.45µm pore size membranes prior to analysis.

2.3 Analytical Quality Control

Calibration curves for the nutrients dissolved forms were carried out according to the specific SOPs. Technical specifications of the on-board analysis of nutrients (correlation coefficient, standard deviation, limit of detection – LOD and limit of quantification – LOQ) are presented in Table 2.

Depending on the number of sampling stations per each sampling day, the samples from one day were analysed in one or more analysis batches. Consequently, batch of analysis is the term referred to in the quality control activity described below:

- ***Duplicate sample***: for every batch of analysis, a Precision Control (duplicate) sample was included. Two sub-samples from the same sample bottle were removed and run each through the analysis.
- ***Spiked sample***: for every two batches of analysis, an Accuracy Control (spiked) sample was included.
- ***Calibration check sample***: for every batch of analysis a Calibration Check (standard) sample was included.

Stock standard solutions used for the preparation of the Quality Control Samples were prepared and delivered every two weeks during the survey by a reference laboratory (VITUKI Budapest).

Table 1: General chemical quality elements analysed on-board and in laboratory

Sample type	Sampling profile	Quality element	Unit	Determination	Analytical method - principle
Water	Middle	Ammonium (NH_4^+ -N)	mg/l	On-board analysis	ISO 7150/1-1984 (sodium dichloroisocyanurate)
Water	Middle	Nitrite (NO_2^- -N)	mg/l	On-board analysis	SMEWW 419 – VIS spectrophotometry (sulphanilic acid and NED)
Water	Middle	Nitrate (NO_3^- -N)	mg/l	On-board analysis	ISO 7890-3:1988 VIS spectrophotometry

					(sulfosalicylic acid)
Water	Middle	Ortho-phosphate (PO_4^{3-} -P)	mg/l	On-board analysis	SMEWW 424 – VIS spectrophotometry (ascorbic acid)
Water	Middle	Organic Nitrogen	mg/l	Laboratory analysis	MSZ EN 25663:1988
Water	Middle	Total Phosphorus	mg/l	Laboratory analysis	MSZ 1484-3:2006
Water	Middle	Dissolved silicate (SiO_2)	mg/l	Laboratory analysis	EPA Method 370.1
SPM	Middle	Organic Nitrogen	mg/kg	Laboratory analysis	MSZ 318-18:1981
SPM	Middle	Total Phosphorus	mg/kg	Laboratory analysis	MSZ 1484-3:2006
Sediments	Left and Right	Organic Nitrogen	mg/kg	Laboratory analysis	SPM MSZ 318-18:1981
Sediments	Left and Right	Total phosphorus	mg/kg	Laboratory analysis	MSZ 1484-3:2006

Table 2: Technical specifications for nutrients dissolved forms

Nutrient form	Correlation coefficient	Standard deviation	LOD	LOQ
		mg/l	mg/l	mg/l
Ammonium (NH_4^+ -N)	0.9991	0.006	0.020	0.060
Nitrite (NO_2^- -N)	0.9997	0.0013	0.005	0.012
Nitrate (NO_3^- -N)	0.9984	0.0331	0.100	0.300
Ortho-phosphate (PO_4^{3-} -P)	0.9992	0.0016	0.005	0.015
Dissolved silicates (SiO_2)	1.0000	0.0180	0.057	0.114

3 Results and discussion

The analytical data and results obtained by on-board and laboratory analysis of the water, sediment and suspended solids samples are presented by type of samples and groups of determinands. In order to have a better view of the spatial distribution of values, the interpretation of the results will be made according to a previous splitting of the Danube Basin into three major sections (Joint Danube Survey, Technical Report of the ICPDR, 2002)

- *Upper Danube: from river km 2600 to river km 1880 (sampling stations JDS1 – JDS15).*
- *Middle Danube: from river km 1869 to river km 1077 (sampling stations JDS16 – JDS58).*
- *Lower Danube: from river km 1077 to river km 0 (sampling stations JDS59 to JDS0).*

3.1 Water

The primary limiting macro-nutrients in freshwaters are nitrogen (N) and phosphorous (P). If in certain amounts they are essential for living organisms, the nutrients' enrichment has adverse ecological effect, leading to a reduction in dissolved oxygen content and appearance of harmful algal blooms, process known as eutrophication.

Variation intervals and average values for nutrient forms analysed in water samples during JDS2 are presented in Table 3.

Table 3: Variation ranges and statistical data for the *nutrients forms* analysed in water samples - Danube River and tributaries

Quality element	Unit	Danube River			Tributaries		Longitudinal surveys on major tributaries	
		Minimum value	Maximum value	Mean value	Minimum value	Maximum value	Minimum value	Maximum value
Ammonium (NH_4^+-N)	mg/l	< 0.020[1]	0.379	0.041	< 0.020	7.2	< 0.020	7.38
Nitrite (NO_2^--N)	mg/l	< 0.005[2]	0.072	0.020	< 0.005	0.129	< 0.005	0.236
Nitrate (NO_3^--N)	mg/l	0.78	3.12	1.66	0.39	8.02	0.38	9.37
Organic Nitrogen	mg/l	0	0.365	0.035	0	0.131	0	0.51
Ortho-phosphate (PO_4^{3-}-P)	mg/l	0.010	0.093	0.036	< 0.005[3]	1.000	< 0.005	1.000
Total Phosphorous	mg/l	0.06	0.91	0.11	0.07	0.80	0.06	0.78
Dissolved silicates (SiO_2)	mg/l	1.43	9.26	5.20	2.88	23.64	1.88	22.25

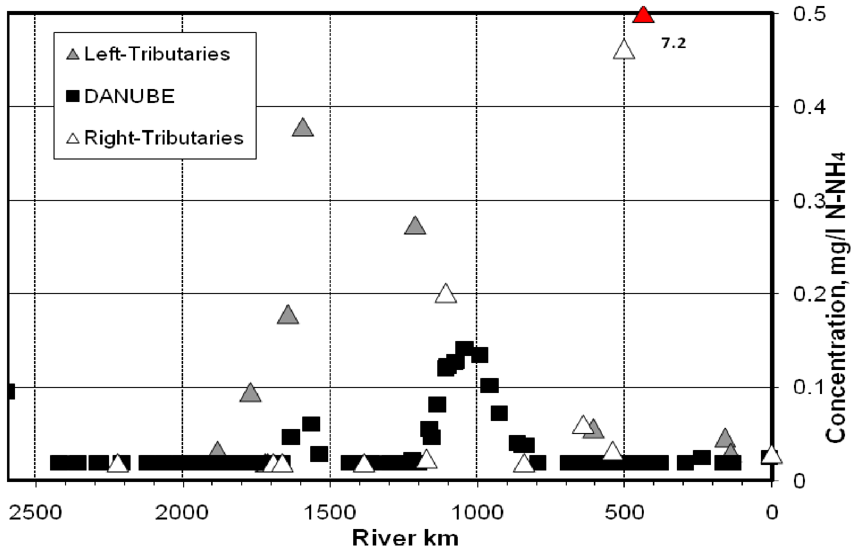
3.1.1 Nitrogen Forms

The overall spatial variation of the nitrogen forms in the water samples is shown in Figure 9 for the Danube River and in Figure 10 for mouth of the selected tributaries.

3.1.1.1 Ammonium

In water samples collected during JDS2, N-ammonium ranged between less than the limit of detection (0.02 mg/l N) and 0.379 mg/l, but the spatial pattern had few specific peaks (Figure 1).

Figure 1: Variation in *N-ammonium* concentrations for the Danube River and selected tributaries during JDS2



In the upper course, a strong decreasing profile from 0.095 mg/l N-NH_4^+ at river km 2600 (*Upstream Iller*) to an undetectable level along the Danube stretch comprised between river km 2415 (*Kelheim*) and 1658 (*/Budapest (old Danube end of S. Arm)*) was found. The first detectable N-ammonium value in the middle stretch (except of the dammed side *Rackeve-Soroskar Danube Arm*) was at river km 1632 (*Budapest downstream*). The increasing profile between upstream and downstream *Budapest* indicated the presence of organic pollution stemming from emission of insufficiently treated municipal wastewaters. As regards the *Rackeve-Soroskar* side arm, high N-ammonium concentrations were found at the start (0.178 mg/l) and at the end of the arm respectively (0.379 mg/l). Correlated with the

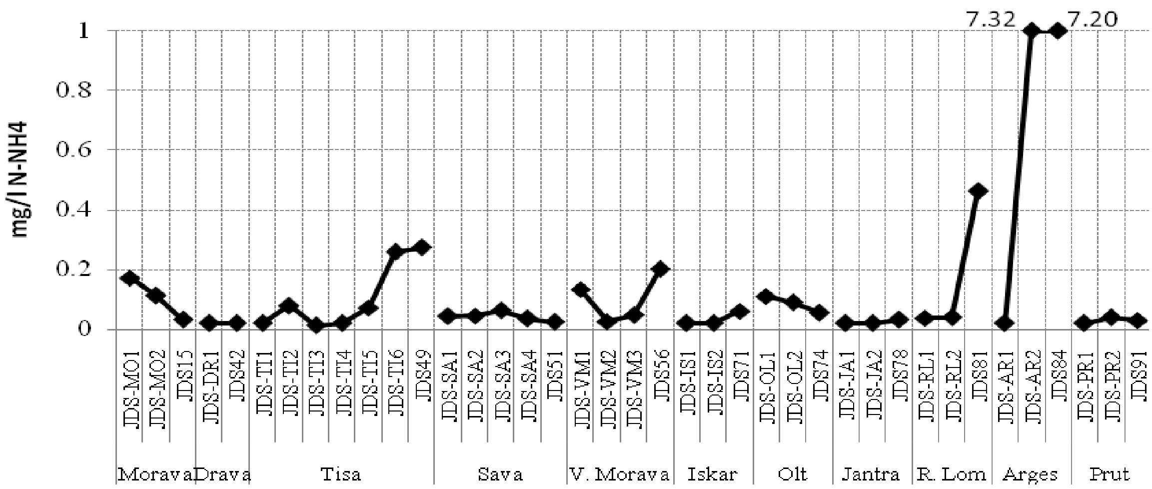
[1] Limit of Detection for N-NH_4^+ determination by ISO-7150/1-1984
[2] Limit of Detection for N-NO_2^- determination by SMEWW 419
[3] Limit of Detection for P-PO_4^{3-} determination by ISO SMEWW 424

pH values and the dissolved oxygen depletion along this arm (54.7% saturation at the end), these values indicated a high organic pollution combined with secondary pollution from decomposition of organic matter. The increasing line continued down to km 1560 (*Dunafoldvar*) followed by a decreasing profile to an undetectable level of N-ammonium approximately down to river km 1200 (*Downstream Tisa*) (it is worth to mention that even if in the *Tisa* tributary 0.274 mg/l –$N\text{-}NH_4^+$ was measured, no influence was noticed downstream the confluence). A significant increasing peak was present between river km 1151 (*Downstream Pancevo*) and river km 1040 (*Iron Gates reservoir*), from 0.047 mg/l to 0.142 mg/l $N\text{-}NH_4^+$ respectively. Correlated with other relevant variations in this area (pH, dissolved oxygen and nitrates decreasing), this pattern might be caused by a synergistic situation: point sources emissions by wastewater effluents, diffuse sources by runoff (given the heavy rain condition during that period), ammonification (decomposition of organic nitrogen to produce ammonium) and denitrification (reduction of nitrates in low oxygen condition). Following the downstream stretch, N-ammonium profile decreased down to river km 834 (*Pristol/Novo Selo Harbour*). Along the rest of the Danube down to the three Delta arms, N-ammonium remained undetectable, mainly due to the dilution effect given by the high water flow in the second part of the lower Danube (see Figure 6).

N-ammonium in mouth of the selected tributaries presented a highly scattered profile: 5 out of 18 tributaries (*Inn*, *Hron*, *Ipoly*, *Drava* and *Timok*) had undetectable concentrations, while in *Morava*, *Vah*, *Sava*, *Jantra*, *Iskar*, *Olt*, *Siret* and *Prut* tributaries concentrations below 0.100 mg/l $N\text{-}NH_4^+$ were measured. Rather high values were found in *Sió*, *Velika Morava* and *Tisa* (values between 0.186 and 0.274 mg/l $N\text{-}NH_4^+$), as a consequence of organic pollution influence in low flow water course (the *Sió* tributary with a mean annual discharge of 39 m^3/s) and, probably, both organic pollution from waste water effluents and runoff (for *Tisa* and *Velika Morava*). An elevated N-ammonium concentration (0.462 mg/l) was measured in the *Russenski Lom* tributary, also due to the waste water discharge, but the most critical situation occurred in the *Arges*, where 7.2 mg/l was found. This latter concentration, correlated with the severe dissolved oxygen saturation (17.4%) is a clear indication that this tributary acts as receptor of totally untreated municipal wastewater from the sewage system of a major city (Bucharest), even if the *Arges* tributary is the secondary receptor after the *Dambovita* River.

In samples from the longitudinal surveys on the major tributaries, N-ammonium was undetectable in 11 sampling sites (JDS-DR1, JDS42/Drava, JDS-TI1, JDS-TI3, JDS-TI4, JDS-IS1, JDS-IS2, JDS-JA1, JDS-JA2, JDS-AR1 and JDS-PR1) while the maximum concentration was found in JDS-AR2, located downstream the municipal wastewater discharge from Bucharest city. Relatively constant profiles were noticed on *Sava* (from JDS-SA1 to JDS-SA2), *Jantra* and *Prut* rivers and decreasing trends from the upper part to the confluence with the Danube River on *Morava*, *Sava* (from JDS-SA3 to JDS51/Sava) and *Olt*. Increasing concentrations from upstream to downstream were present along *Tisa* River (from JDS-TI4 to JDS-TI6), *Velika Morava* (from JDS-VM2 to JDS56/Velika Morava) and *Iskar*. Very pronounced N-ammonium concentration leaps from upper sampling sites to the confluence with the Danube were recorded on both *Russenski Lom* and *Arges* tributaries – see Figure 2.

Figure 2: Variation in *N-ammonium* concentrations for the longitudinal surveys on major tributaries



3.1.1.2 Nitrites

In Danube water samples, N-nitrite ranged between less than the limit of detection (0.005 mg/l N) at 16 sampling sites and 0.072 mg/l at river km 926 (*Vrbica/Simijan*) - see Figure 3. The spatial pattern had a decreasing line in the upper course of the Danube and higher values in the middle stretch, in the *Rackeve-Soroksar Danube arm* (0.040 mg/l N-NO_2^- at the end of the arm). The rest of the middle reach was characterised by a uniform profile, followed by a peak in the *Iron Gates* reservoir, similar with the N-ammonium, but slightly shifted to the headwater of the reservoir and downstream the dam (since nitrites are the intermediary product in the oxidation/reduction process of nitrogen forms, its variation pattern in this area reflected the specific behaviour of the nitrogen species in a big reservoir). In the lower Danube, downstream of river km 685 (*Downstream Kozlodui*), N-nitrite decreased to an approximate concentration level of 0.020 mg/l, probably due to the dilution effect.

In mouth of the tributaries, N-nitrite concentrations ranged between less than the limit of detection (*Inn*, *Drava* and *Arges*) and 0.129 mg/l in *Russenski Lom;* also a high N-nitrite concentration – 0.120 mg/l – was measured in *Sió* tributary. The rest of the selected tributaries at the confluence were characterised by N-nitrite values lower than 0.050 mg/l.

Along the major studied tributaries, N-nitrites were found undetectable in seven sampling sites (JDS42/Drava, JDS-TI1, JDS-TI5, JDS-JA2 and all the three sampling sites along the *Arges* tributary). The most elevated concentrations were measured along the *Russenski Lom* tributary – Figure 4.

Figure 3: Variation in *N-nitrite* concentrations for the Danube River and selected tributaries during JDS2

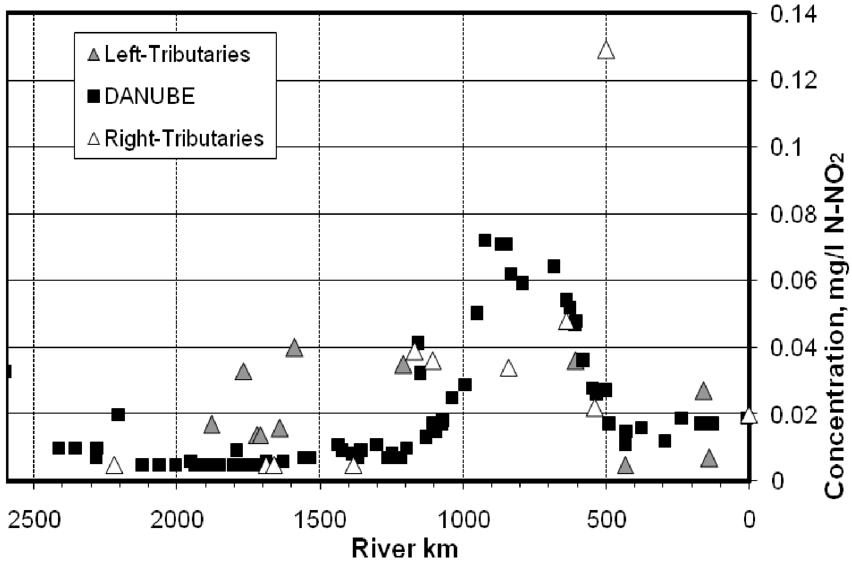
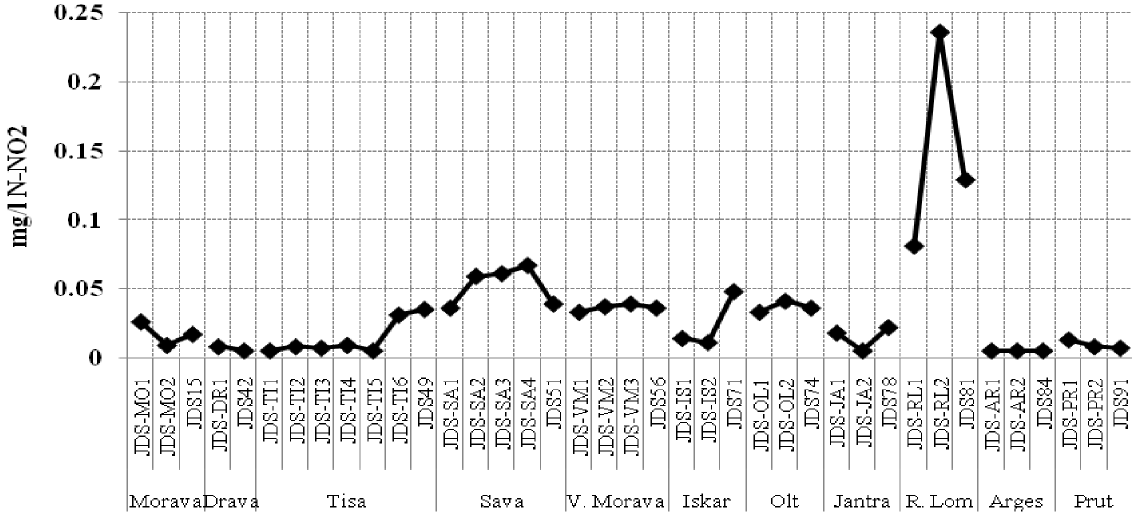


Figure 4: Variation in *N-nitrite* concentrations for the longitudinal surveys on major tributaries



3.1.1.3 Nitrates

The spatial variation of N-nitrate concentrations in the Danube River and tributaries is illustrated in Figure 5. A significant decreasing profile was visible from 3.12 mg/l N-NO_3^- at the first sampling site – river km 2600 (*Upstream Iller*) to 1.91 mg/l at river km 2204 (*Jochenstein*). The decreasing trend was present also along the middle Danube and at the beginning of the lower course, down to 1.32 mg/l N-NO_3^- at river km 991 (*Donji Milanovac*) caused by a possible denitrification process in the reservoir area. In the middle stretch of the Danube, slightly lower values (1.28 and 0.78 mg/l) were found in the side arms *Moson Danube arm-end* and *Rackeve Soroskar Danube arm–end* (river km 1794 and river km 1586 respectively), most likely due to a specific summer pattern in shallow waters: uptake by the biological activity in the former arm (chlorophyll "a" of 44.4 µg/l) and to an increased organic pollution in the latter arm (high N-ammonium and N-nitrite content, low dissolved oxygen saturation). Downstream the *Iron Gates* dam, an increasing profile of N-NO_3^- was present, from 1.32 mg/l at river km 926 (*Vrbica/Simijan*) to 1.67 mg/l at river km130 (*Reni*), except for the value measured (0.88 mg/l) at river km 532 (*Downstream Jantra*).

In mouth of the tributaries N-nitrate concentrations had a highly scatter profile, with a variation range of 0.39 mg/l N-NO_3^- in the *Arges* and 8.02 mg/l in the *Russenski Lom*. It is worth to mention that although the two tributaries had indications of high pollution, the ratio of the nitrogen forms is opposite – see Figure 10: while in the *Arges* tributary most of the nitrogen content was found as N-ammonium (caused, as it was already mentioned, by totally untreated municipal waste waters) and the extreme low dissolved oxygen capital made impossible further oxidation (N-nitrite was undetectable and N-nitrate was the lowest measured value in tributaries), in the *Russenski Lom* tributary, the highest proportion of nitrogen content belonged to N-nitrate.

Figure 5: Variation in *N-nitrate* concentrations for the Danube River and selected tributaries during JDS2

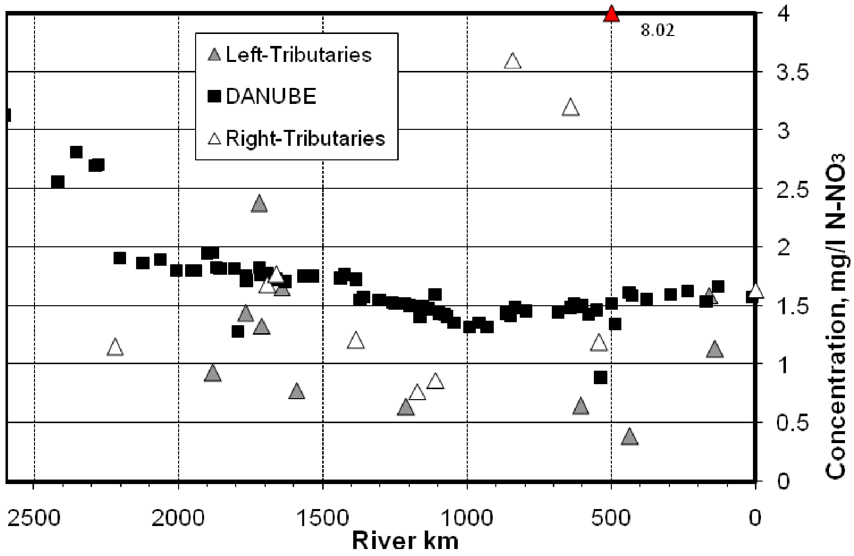
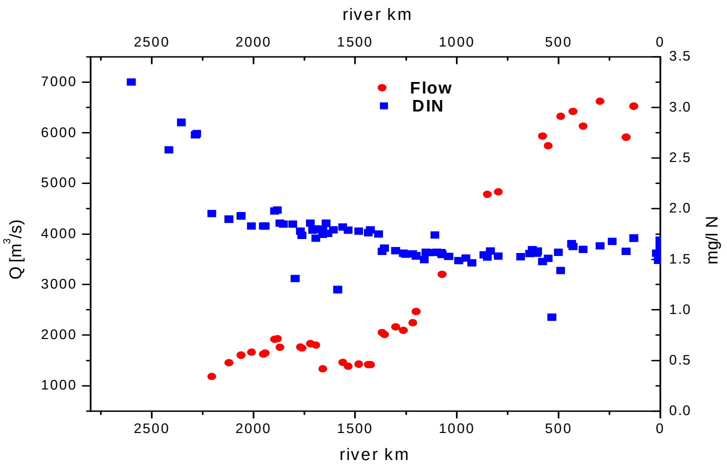
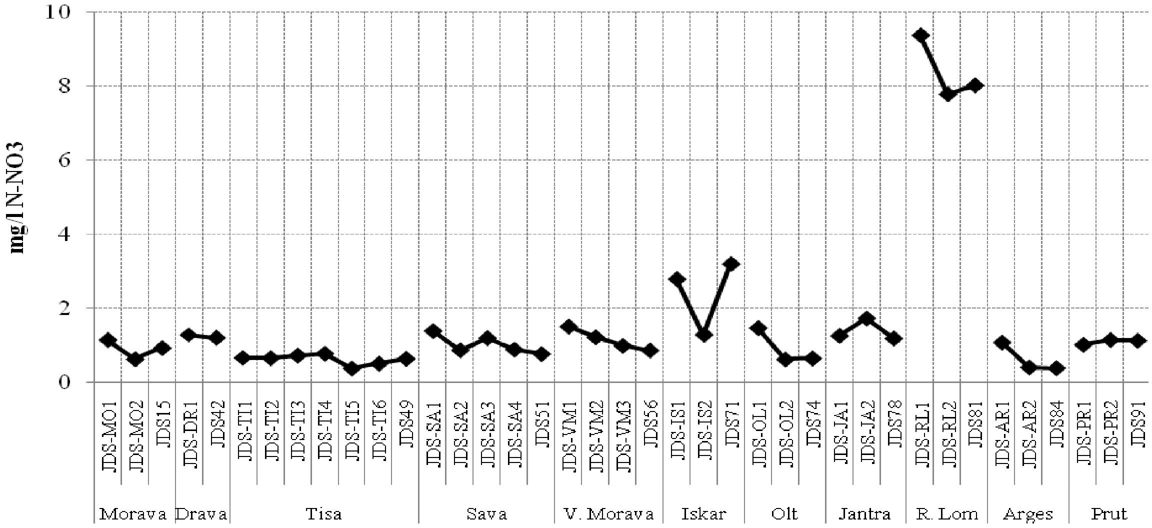


Figure 6: Variation in Dissolved Inorganic Nitrogen (DIN) against instantaneous flow data (where available)



Along the most of the major tributaries, N-nitrates had "V" profile from upper down to the confluence with the Danube River; the highest concentrations were recorded along the *Russenski Lom* tributary – Figure 7.

Figure 7: Variation in *N-nitrate* concentrations for the longitudinal surveys on major tributaries



3.1.1.4 Organic Nitrogen

Organic Nitrogen concentrations ranged between 0 (or less than limit of detection) and 0.37 mg/l N and between 0 (or less than limit of detection) and 0.13 mg/l in tributaries; the maximum values were measured at river km 1719 (*Sturovo/Esztergom*) and in the *Sió* tributary respectively – Figure 8. The values distribution showed that, in the case of the Danube itself, most of the concentrations (74.4%) were below 0.05 mg/l, which indicated very low content of organic nitrogen in water samples. For tributaries at the confluence, four of them (the *Inn*, *Hron*, *Ipoly* and *Arges*) were characterised by zero values, whereas the rest of them had organic nitrogen content comparable with the Danube River.

Figure 8: Variation in *Organic Nitrogen* concentrations in water samples for the Danube River and selected tributaries during JDS2

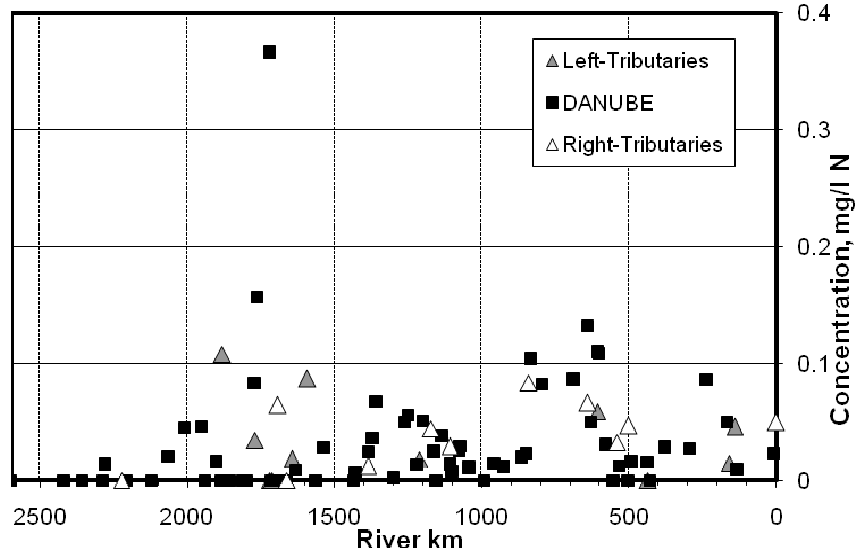


Figure 9: Variation in *Nitrogen forms* in water samples during JDS2 – the Danube River

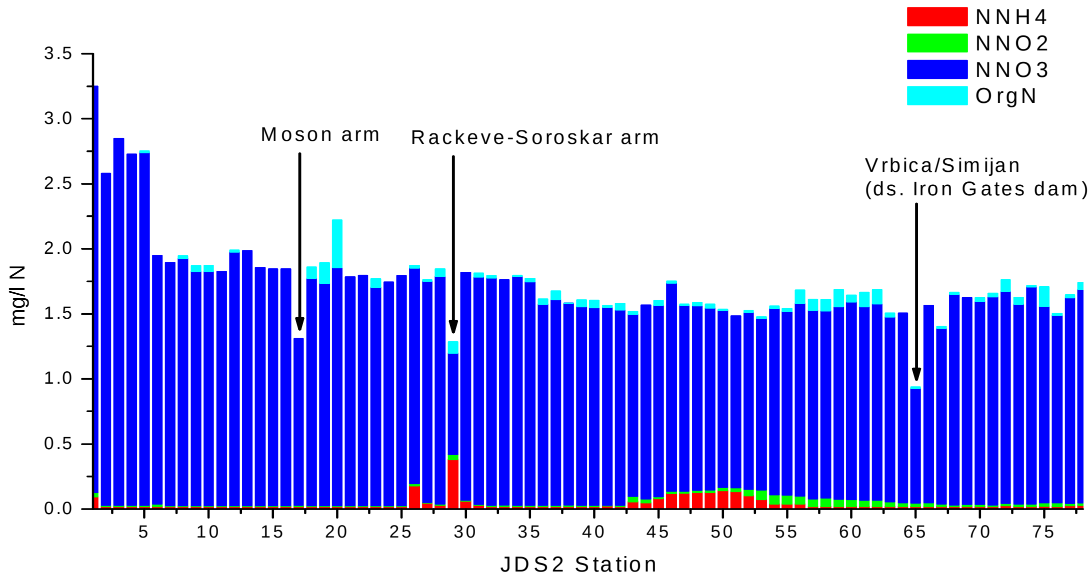
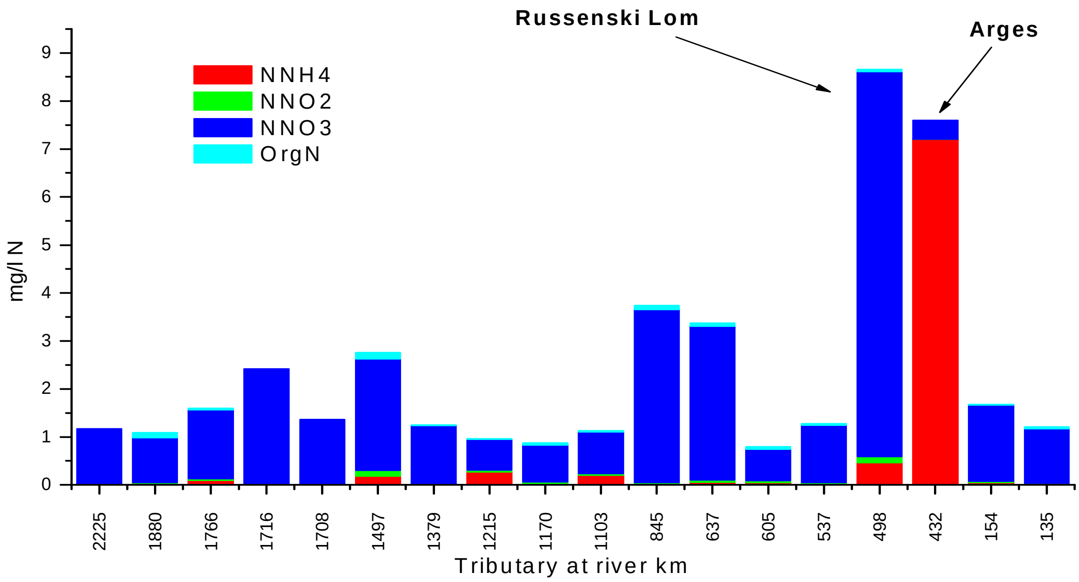


Figure 10: Variation in *Nitrogen forms* in water samples during JDS2 – Tributaries



3.1.2 Phosphorous Forms

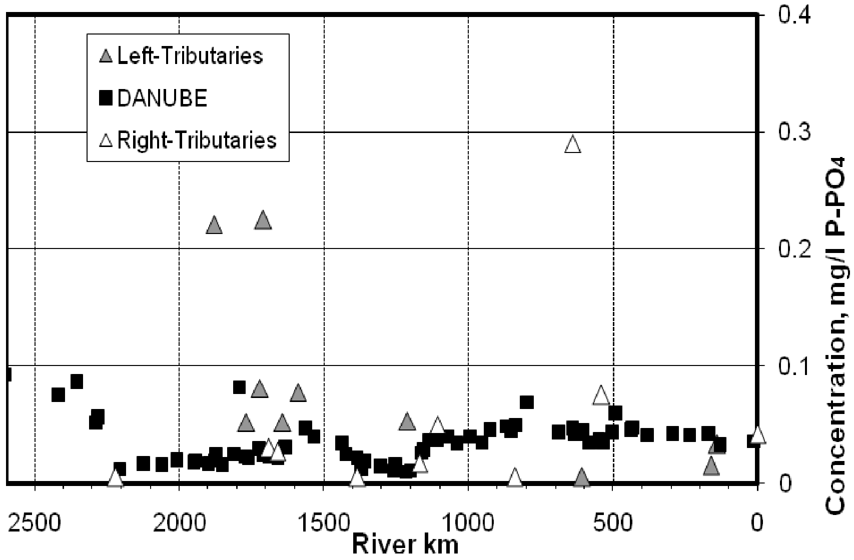
The overall spatial variation of the phosphorous forms in the water samples is shown in Figure 14 for the Danube River and in Figure 15 for mouth of the selected tributaries.

3.1.2.1 Ortho-phosphates

The biologically available form of inorganic P in water is orthophosphate. The longitudinal variation of orthophosphates in the Danube water samples ranged within 0.010 mg/l P-PO_4^{3-} and 0.093 mg/l P-PO_4^{3-}, with an average concentration of 0.036 mg/l. A marked decreasing line was noticed in the upper stretch, from the maximum concentration at river km 2600 (*Upstream Iller*) to 0.056 mg/l at river km 2278 (*Niederalteich*) – Figure 11. Downstream the *Inn* confluence, more pronounced decreasing trend was visible. In the middle stretch, a slight increasing line was noticed down to river km 1560 (*Dunafoldvar*) and rather higher values were measured in the side arms *Moson Danube-end* (0.082 mg/l), *Rackeve-Soroksar Danube start* (0.052 mg/l) and *end* respectively (0.078 mg/l). In the backwaters of the *Iron Gates reservoir* an increasing orthophosphates concentrations level was measured,, while in the *reservoir itself*, slightly lower concentrations were found (less than 0.040 mg/l), but no relevant phosphorous retention could be observed. In the lower stretch, a slight increasing profile was noticed, mainly caused by discharges of municipal waste waters containing non-free P detergents.

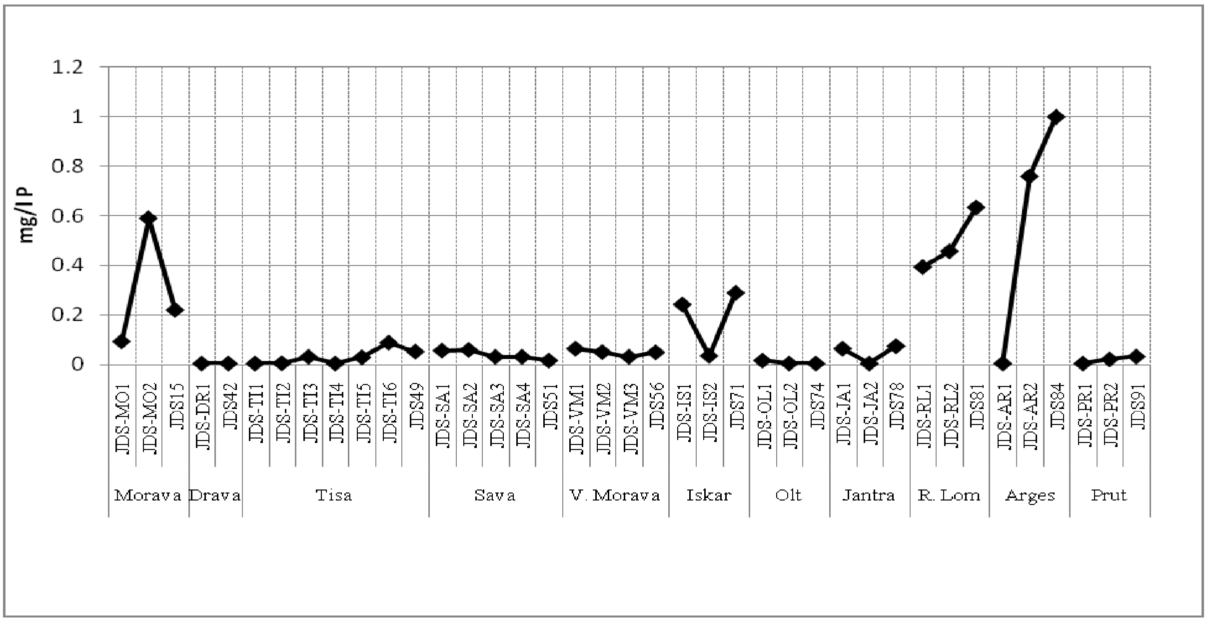
In the case of mouth of the tributaries, a large variation interval of orthophosphate concentrations was noticed, between less than the limit of detection (0.005 mg/l) in *Inn*, *Drava*, *Timok* and *Olt* and 1.000 mg/l in *Arges* tributary. Comparable values with the Danube River level were measured in most of the tributaries at the confluence, with few exceptions: the *Morava* (0.221 mg/l, due to the runoff effect induced by storming conditions prior to sampling), *Ipoly* (0.225 mg/l), *Sió* (0.256 mg/l caused by low dilution effect) and *Iskar* (0.290 mg/l). Very high orthophosphate concentrations were measured in the *Russenski Lom* (0.635 mg/l) and *Arges* (1.000 mg/l), both values being determined mainly by the discharge of totally untreated wastewater.

Figure 11: Variation in *P-orthophosphate* concentrations in water samples for the Danube River and selected tributaries during JDS2



As regards the longitudinal survey of the major tributaries, no significant variations could be emphasized, except for the pronounced increasing profile along the *Morava*, *Russenski Lom* and *Arges* tributaries – see Figure 12.

Figure 12: Variation in *P-orthophosphates* concentrations in water samples for the longitudinal surveys on major tributaries



3.1.2.2 Total Phosphorous

Total Phosphorous consists of inorganic orthophosphate and organic phosphorus-containing compounds. In the Danube water samples, TP ranged between 0.06 mg/l and 0.91 mg/l, with an average concentration of 0.11 mg/l – Figure 13. A relative constant profile was present in the upper reach of the Danube River and slightly higher concentrations were measured in the middle reach. A specific situation was noticed in the *Iron Gates backwaters* and *reservoir* area: TP concentration decreased from 0.12 mg/l P at river km 1151 (*Downstream Pancevo*) to 0.06 mg /l P at river km 954 (*Iron Gates reservoir, Tekija/Orsova*), due to a probable effect of sedimentation of particles on which phosphorus was adsorbed. The same decreasing profile in this stretch was noticed also in the case of TP in suspended solids matrix, but this pattern could not be well correlated with the variation of TP in solid matrices (see Figure 21 and Figure 24). This decreasing profile of TP in the *Iron Gates reservoir* water is confirmed by other projects and studies: according to the Danube Water Quality Model (DWQM) used in the daNUbs Project, 7.6 kt/year (11% of emissions) phosphorous are retained in the *Iron Gates reservoir* given the low water velocity and under low flow conditions (daNUbs Final Report, 2005). Along the rest of the lower Danube reach, a decreasing trend caused mainly by the increasing Danube flow during the sampling period was noticed, except of two elevated TP values (0.91 mg/l P and 0.41 mg/l P) measured at river km 488 (*Downstream Ruse/Giurgiu*) and river km 434 (*Upstream Arges*) respectively

Tributaries at the confluence presented a similar variation range of TP concentrations with the Danube: 0.07 – 0.80 mg/l P, most of them having comparable concentration levels with the main course of the river. The maximum concentration was found in the *Timok* tributary.

Total Phosphorous concentrations along the major tributaries significantly increased from upper down to the confluence with the Danube River in the case of *Iskar* and *Olt* tributaries. A marked “V” profile was present for *Russenski Lom* while an inverted “V” profile occurred along the *Morava*, *Sava*, *Velika Morava*, *Jantra* and *Arges* tributaries - see Figure 16.

Figure 13: Variation in *Total Phosphorous* concentrations for the Danube River and selected tributaries during JDS2

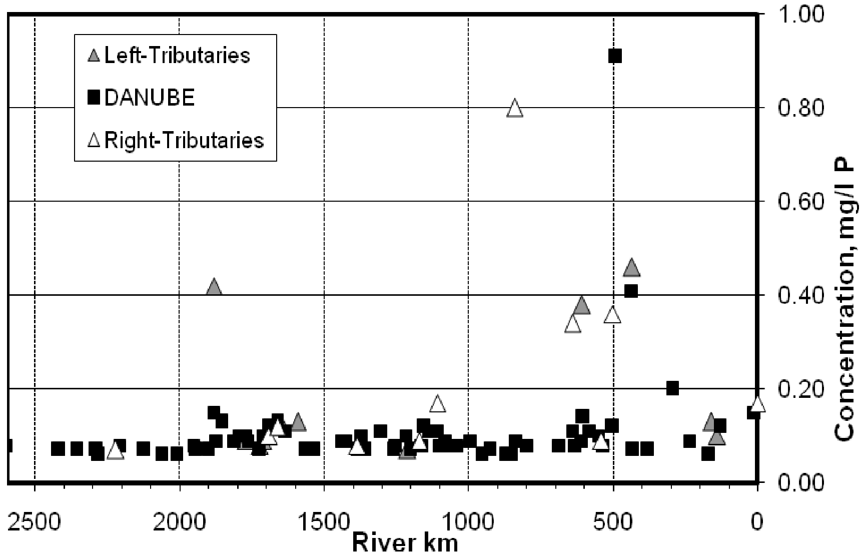


Figure 14: Variation in *Phosphorous forms* in water samples during JDS2 – the Danube River

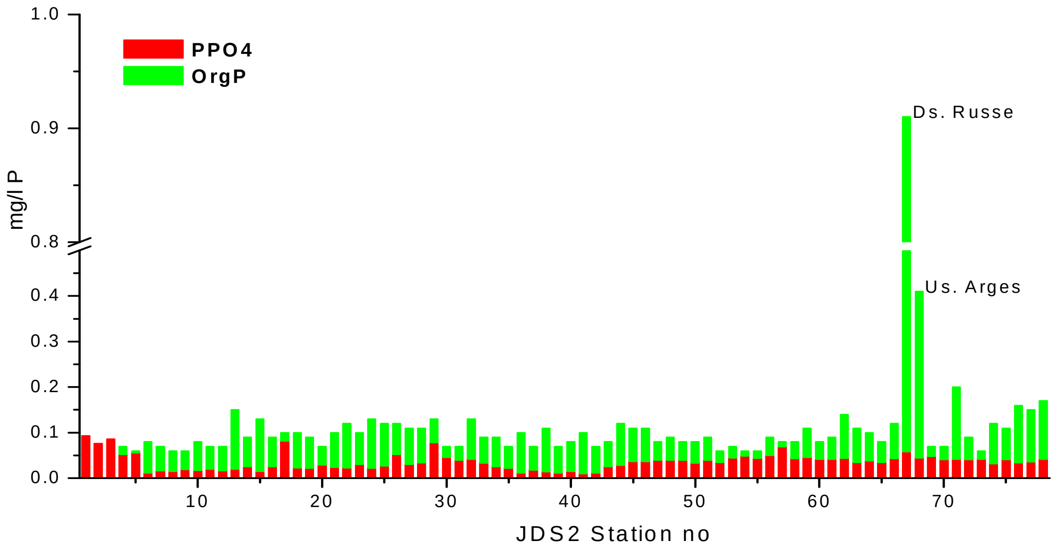


Figure 15: Variation in *Phosphorous forms* in water samples during JDS2 – Tributaries

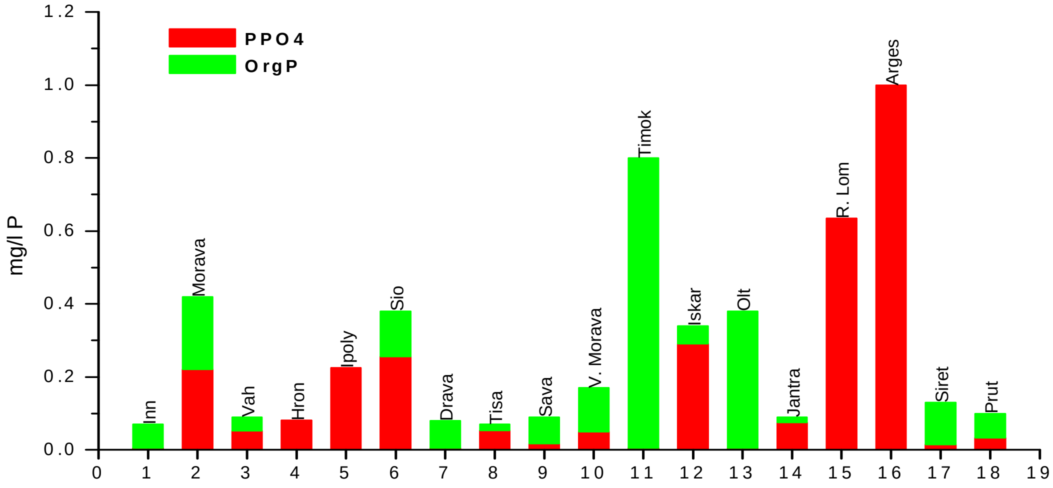
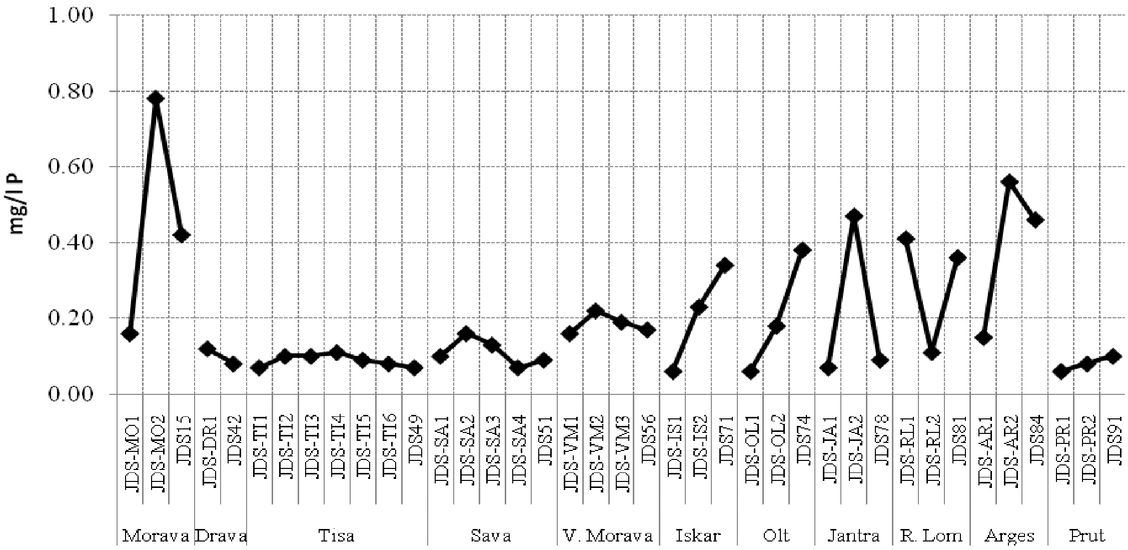


Figure 16: Variation in *Total Phosphorous* in water samples from the longitudinal surveys on major tributaries



3.1.2.3 Dissolved silicates

Dissolved silicates ranged between 1.43 mg/l and 9.26 mg/l in the Danube River and between 2.88 mg/l and 23.64 mg/l in tributaries, values characteristic to usual water surface pattern for this parameter (Chapman and Kimstach, 1996). The longitudinal profile is illustrated in Figure 17, where general decreasing pattern from upper to lower Danube is noticed. Even if a slightly marked lower profile was present in the *Iron Gates* area, no significant difference between entering the reservoir (5.17 mg/l at river km 1071) and downstream the dam (4.18 mg /l at river km 926) could be seen, which is also confirmed by other studies in this area (Friedl et al, 2004).

At confluence of the tributaries, dissolved silicates measurements were unevenly distributed: while in several water courses, concentrations were lower than the Danube River level, higher values were measured in *Morava*, *Hron*, *Ipoly* (in the middle stretch) and at mouth of the all tributaries from the lower stretch, except of *Jantra*.

As regards the concentrations present along the major tributaries, the general view showed a decreasing trend from upper down to the confluence with the Danube River – see Figure 18.

Figure 17: Variation in *dissolved silicates* concentrations for the Danube River and selected tributaries during JDS2

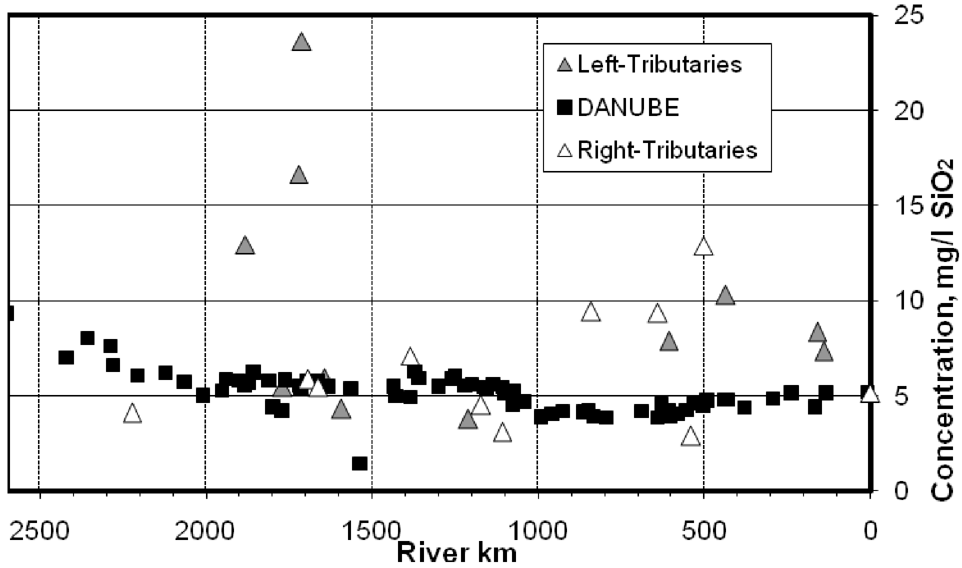
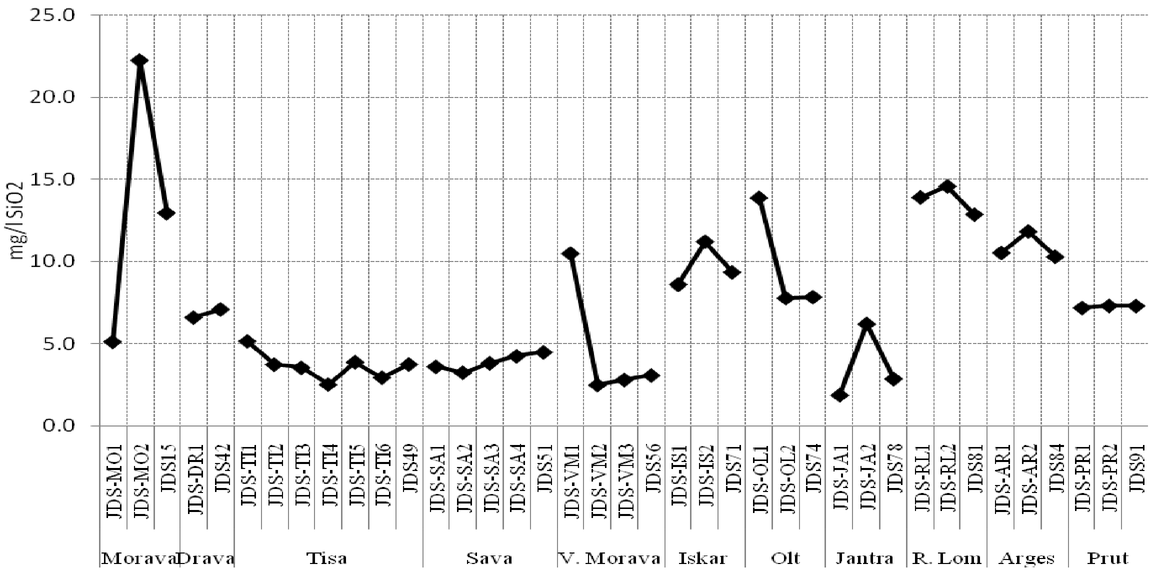


Figure 18: Variation in *Dissolved silicates* in water samples from the longitudinal surveys on major tributaries



3.2 Sediment

In solid matrices (sediment and suspended solids) organic nitrogen and total phosphorous were analysed. In Table 4 statistical data for these results are presented.

Table 4: Variation ranges and statistical data for the *nutrients forms* analysed in sediments and suspended solids samples - Danube River and tributaries

Quality element	Unit	Danube River			Tributaries		Longitudinal surveys on major tributaries	
		Minimum value	Maximum value	Mean value	Minimum value	Maximum value	Minimum value	Maximum value
Sediment								
Organic Nitrogen	mg/kg	54	2528	812	144	1398	325	1400
Total Phosphorous	mg/kg	369	2033	794	393	2297	370	3158
Suspended Solids								
Organic Nitrogen	mg/kg	5	3381	1047	10	2500	-	-
Total Phosphorous	mg/kg	558	2073	1029	617	3014	-	-

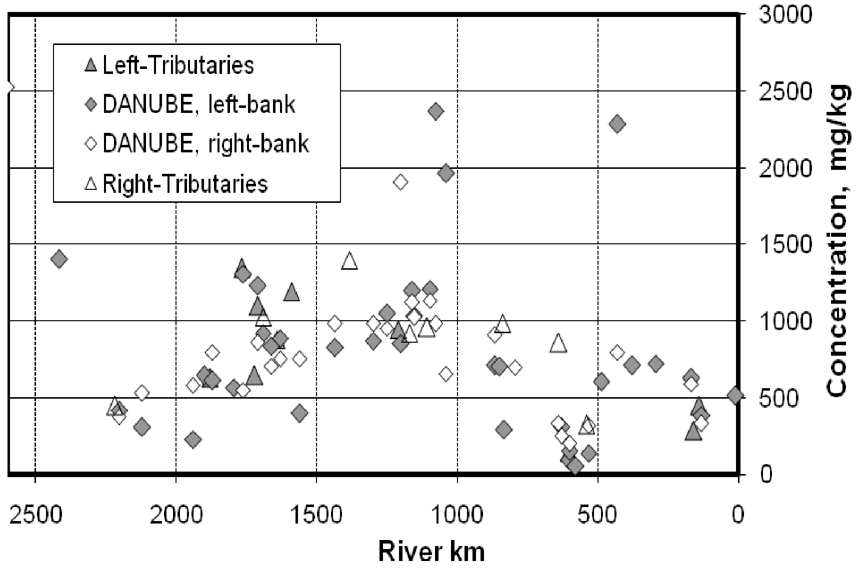
3.2.1 Organic Nitrogen

Organic Nitrogen ranged between 54 mg/kg and 2528 mg/kg for the sampling sites located on the Danube River and between 144 mg/kg and 1398 mg/kg in mouth of the tributaries. The spatial distribution of Organic Nitrogen in sediment samples is illustrated in Figure 19, in which an increasing profile can be noticed from the upper to middle and the beginning of the lower Danube stretch. The decreasing profile started from downstream of the *Iron Gates* area, as a consequence of denitrification process in the reservoir. Even if in the lower Danube stretch a marked lower pattern was present (approximately half of the sites had Organic Nitrogen less than 500 mg/kg and the other half less than 1000 mg/kg respectively), higher content (2284 mg/kg) was measured at river km 429 (*Downstream Arges - left*). Since at the confluence of the *Arges tributary* no sediment sample was collected, this elevated organic nitrogen content downstream of the confluence might be assigned to the influence of the highly pollution stemming from discharge of untreated municipal sewage waters in the *Arges* tributary.

As regards the distribution of organic nitrogen between the left and the right side samples (where available), the ratios between these values showed relatively uniform pattern, with few peaks: at river km 1761 (*Iza/Szony*) and at river km 1077 (*Starapalanka – Ram*), Organic Nitrogen from the left bank was 2.4 times higher than from the right bank; the highest ratios (2.9 and 3.0) were recorded at river km 429 (*Downstream Arges*) and river km 1040 (*Iron Gates reservoir / Golubac Koronin*) respectively, due to highly organic pollution in the former case and different retention rate in the latter.

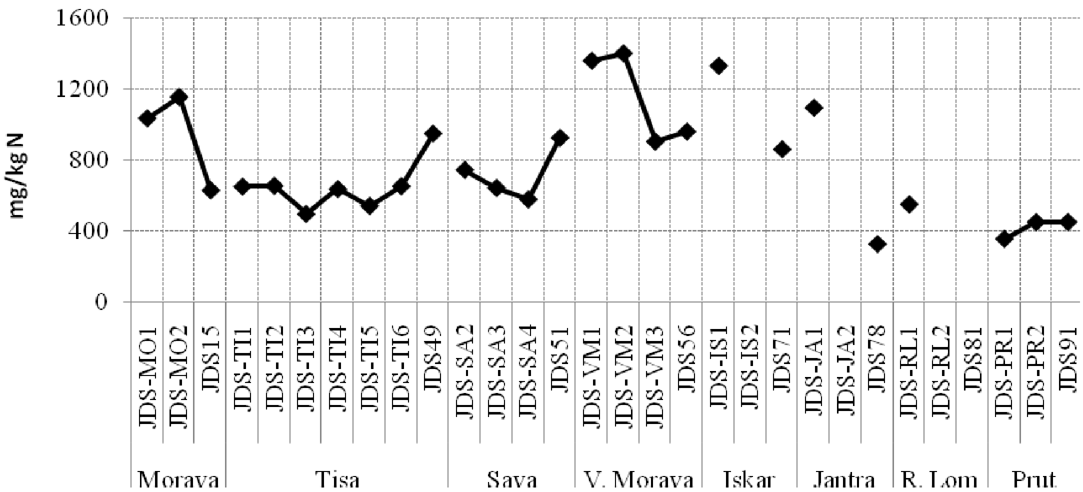
In the case of sediment samples from mouth of the selected tributaries, the organic nitrogen level was generally comparable with the Danube River, with no value exceeding 1500 mg/kg level.

Figure 19: Variation in *Organic Nitrogen* in sediment samples for the Danube River and tributaries



The Organic Nitrogen variation in sediment samples from the longitudinal surveys on major tributaries (where samples available) showed that, in the case of *Tisa*, *Sava* and *Prut* tributaries, the site located at the confluence with the Danube River had higher concentration than the upper sites. For *Morava* and *Velika Morava*, at the second sampling site the maximum concentration was measured on both tributaries – see Figure 20.

Figure 20: Variation in *Organic Nitrogen* in sediment samples for the longitudinal surveys on major tributaries



3.2.2 Total Phosphorous

Longitudinal profile of Total Phosphorous in sediment samples from the Danube River and mouth of the tributaries is shown in Figure 21. A pronounced decreasing line was noticed in the upper Danube stretch, from the maximum recorded value of 2033 mg/kg at river km 2600 (*Upstream Iller*) to 642 mg/kg at river km 2204 (*Jochenstein*). No specific trend was visible in the beginning of the middle

Danube, but the maximum peak was noticed from 557 mg/kg at river km 1659 (*Upstream Budapest*) to 1282 mg/l at river km 1262 (*Upstream Novisad*). The *Iron Gates reservoir* area was characterised by lower TP in sediment between river km 1077 (*Starapalanka Ram*) and river km 954 (*Iron Gate reservoir, Tekija/Orsova*), but downstream the dam relatively higher concentration was measured, slightly contrary to the previously specific data in this stretch according to which the *Iron Gates* sediment is a P-reserve for the future. Between river km 926 (*Vrbica/Simijan*) and river km 606 (*Upstream Olt*), a marked decreasing line was present, from 892 mg/kg to 369 mg/kg respectively, followed by an increasing TP concentration until river km 429 (*Downstream Arges- left*). Similarly to Organic Nitrogen, a high TP ratio (2.21) between the left and the right bank was recorded for the site located downstream the *Arges* tributary as a consequence of pollution from the mentioned tributary. Down to the Danube Delta, TP in sediment slightly decreased.

Along the studied major tributaries, no significant variation of TP among the sampling sites could be noticed, except for JDS-VM3, where the TP concentration in sediment sample was four times higher than the concentration from the confluence of the *Velika Morava* tributary with the Danube River – Figure 22.

Figure 21: Variation in *Total Phosphorous* in sediment samples for the Danube River and tributaries

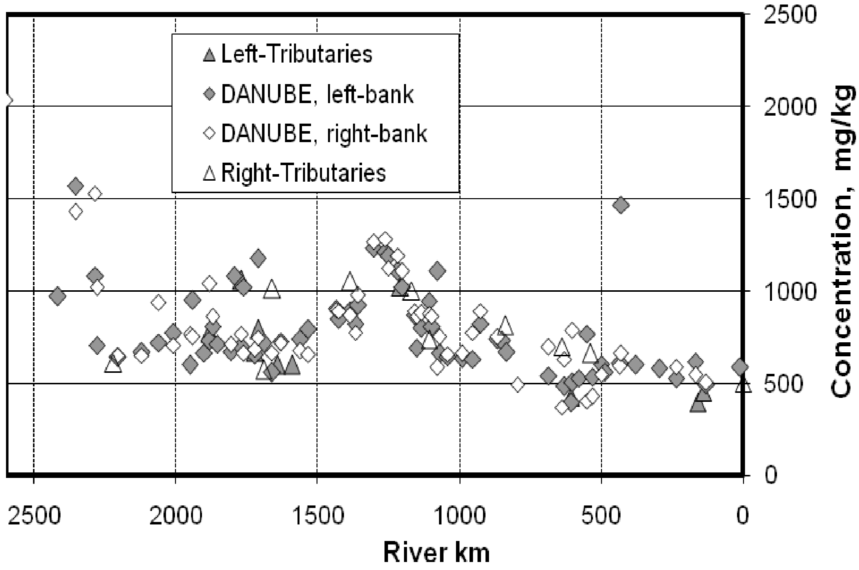
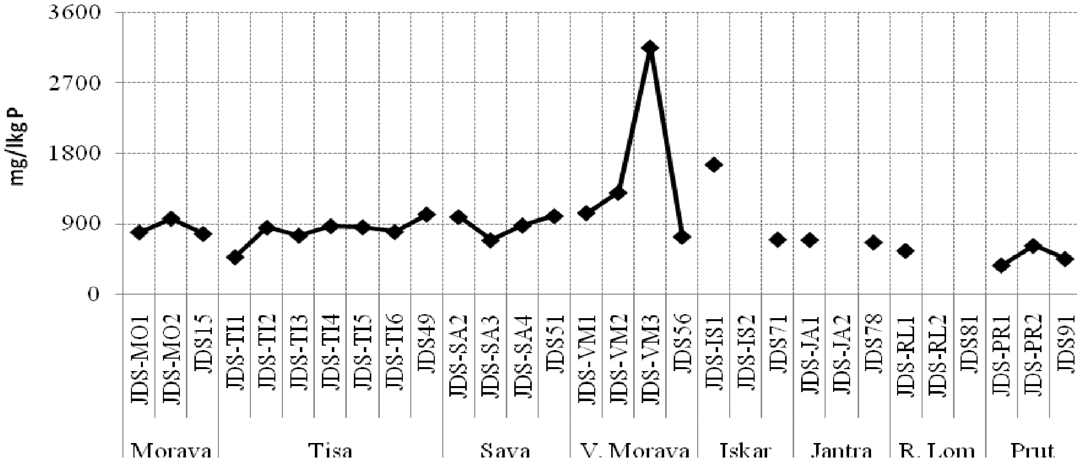


Figure 22: Variation in *Total Phosphorous* in sediment samples for the longitudinal surveys on major tributaries

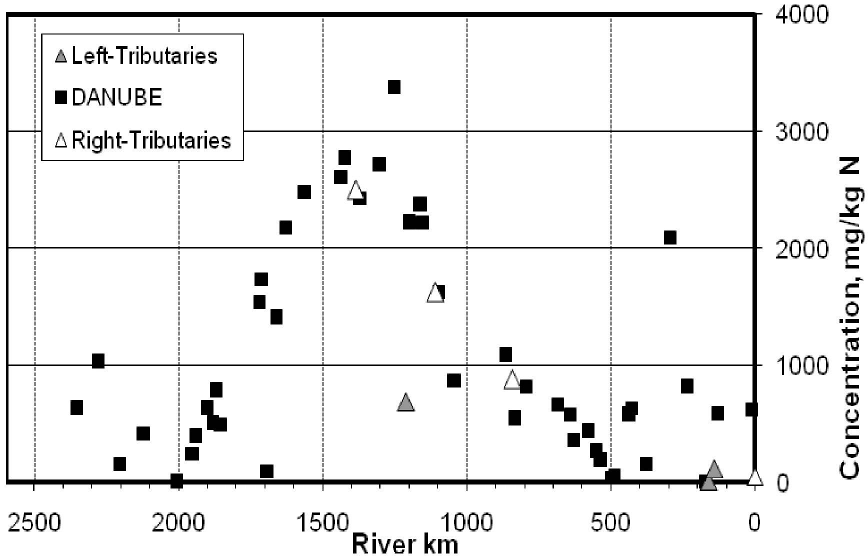


3.3 Suspended solids

3.3.1 Organic Nitrogen

Organic Nitrogen in suspended solids ranged between 5 mg/kg and 3381 mg/kg in the Danube River and between 10 mg/kg and 2500 mg/kg in tributaries. From the longitudinal variation presented in Figure 23 a relatively "symmetrical pattern" with the maximum profile located in the middle stretch of the Danube can be seen. In the upper Danube, a pronounced decreasing profile was present from 1030 mg/kg at river km 2278 (*Niederalteich*) to 5 mg/kg at river km 2008 (*Oberloiben*). A significant increasing profile was characteristic for the following Danube stretch, reaching the maximum value at river km 1252 (*Downstream Novisad*) followed by a strong decreasing trend in the backwaters of the *Iron Gates* reservoir (873 mg/kg at river km 1040), probably due to the mineralisation of the organic matter adsorbed on the solid matters. The decreasing trend continued in the lower Danube down to river km 500 (*Upstream Ruse*), followed by a slight increasingly profile. A relatively high value (2095 mg/kg) was recorded at river km 295 (*Upstream Cernavoda*). In mouth of the tributaries, Organic Nitrogen content was lower than in the Danube itself.

Figure 23: Variation in *Organic Nitrogen* in suspended solids samples for the Danube River and tributaries

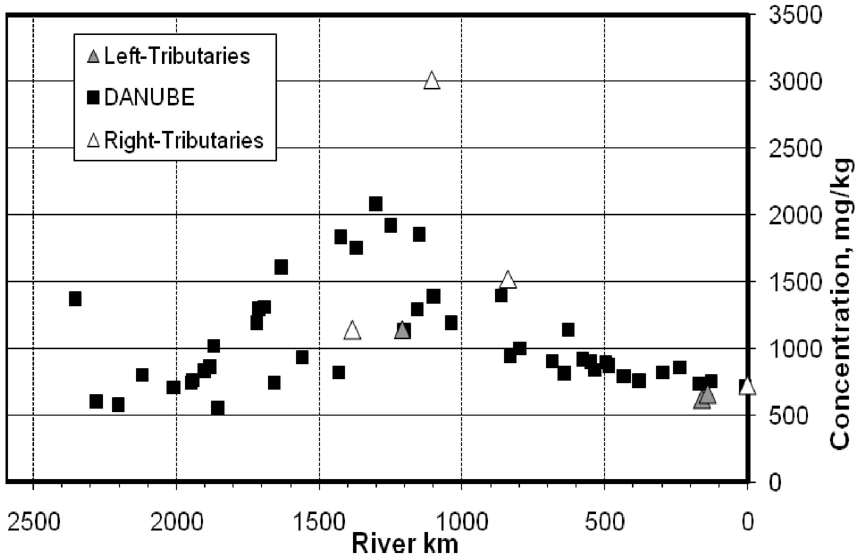


3.3.2 Total Phosphorous

Total Phosphorous in suspended solids ranged between 558 mg/kg and 2073 mg/kg in the Danube River and between 617 mg/kg and 3014 mg/kg in tributaries at the confluence. The variation of TP presented in Figure 24 shows a maximum profile located in the middle stretch of the Danube, at river km 1300 (*Ilok/Backa Palanka*) and the minimum value in the *Gabcikovo reservoir* at river km 1852. If the general pattern is relatively similar to organic nitrogen, still local variations from one sampling site to another occurred along the entire Danube stretch.

Total P in suspended solids from mouth of the tributaries (where available) showed a comparable level with the Danube itself, except for the *Velika Morava* tributary, in which TP was rather high, probably due to high runoff influence caused by a high precipitation regime during the sampling period.

Figure 24: Variation in *Total Phosphorous* in suspended solids samples for the Danube River and tributaries



3.4 Comparison with previous data

3.4.1 Comparison with Joint Danube Survey 1 (August – September 2001)

In order to fulfil one of the specific objectives of JDS2 – to compare the results with outcomes of the JDS1, the comparative view of the results obtained during JDS2 with the ones of the first similar survey shows the following:

3.4.1.1 Water

- *N-ammonium* concentrations in the Danube River had a relatively similar profile, except for few sites: the *Moson Danube Arm* (higher concentration measured in JDS1), the *Rackeve-Soroksar Danube start* and *end* respectively (much higher concentrations found in JDS2), middle reach of the river and the *Iron Gates* stretch, where the maximum peak was slightly shifted to reservoir area during the JDS2. For tributaries, concentrations were almost at the same level, except for the *Arges* tributary, in which more than two times higher N-ammonium concentration was measured during JDS2 – see Figure 25;
- *N-nitrite* pattern from JDS2 almost followed the one recorded during JDS1, but it can be seen that in the upper and the middle reaches of the Danube, the values measured in JDS1 were slightly higher (with few exceptions), while downstream the *Iron Gates* area and the lower Danube the situation is opposite. For tributaries, no specific pattern is visible, the profile being relatively scattered, but it can be noticed that in the case of the *Sió* and *Russenski Lom* rather higher concentrations were measured in JDS2 when compared with JDS1 – see Figure 26;
- except for the situation from river km 532 (*Downstream Jantra*), all *N-nitrate* concentrations measured during JDS2 were higher than the ones from JDS1 for the sampling sites located on the Danube itself. This trend is visible also for the selected tributaries, except for the *Morava*, *Ipoly*, *Sió* and *Iskar*, in which higher concentrations were found during JDS1 – see Figure 27;
- *Organic Nitrogen* concentrations were systematically much lower during JDS2 than JDS1, both for the Danube River and tributaries – Figure 28;
- *P-orthophosphate* concentrations measured during JDS2 were generally lower than the ones from JDS1, with few exceptions located in the middle Danube reach. In selected tributaries, the *Iskar*

showed a better situation in JDS2 (almost three times higher concentration measured in JDS1), but worse condition was recorded in the *Russenski Lom* and *Arges* tributaries (two and four times higher concentrations respectively were found during JDS2) – see Figure 29;

- *Total Phosphorous* profiles were relatively similar during the two joint surveys, with few exceptions: much higher TP concentrations found in JDS1at rkm 1481 (*Baja*), rkm 500 (*Upstream Ruse*) and rkm 434 (*Upstream Arges*) while a seven times higher concentration was found in JDS2 at rkm 488 (*Downstream Ruse/Giurgiu*). For 11 out of 18 selected tributaries (*Inn, Hron, Ipoly, Sió, Drava, Tisa, Sava, Iskar, Jantra, Siret* and *Prut*) TP values measured during JDS2 were lower than the ones from JDS1, for five tributaries (*Morava, Vah, Olt, Russenski Lom* and *Arges*) the situation was opposite, while for the *Veliko Morava* tributary the two values were the same. The biggest difference was recorded in the case of the *Timok* tributary, in which a ten times higher concentration was measured in JDS2 - see Figure 30;

- *Dissolved silica:* concentrations measured during JDS2 were slightly higher than ones from JDS1 in the Danube River, except for few sites located in the middle Danube reach. For tributaries, the pattern was similar except for the *Sió, Sava, Olt* and *Jantra*. The biggest difference occurred in the *Veliko Morava* tributary, in which the dissolved silica concentration measured in JDS2 was fifteen times higher than the one from JDS1 – see Figure 31.

Figure 25: Comparison between *N-ammonium* values from JDS2 and JDS1

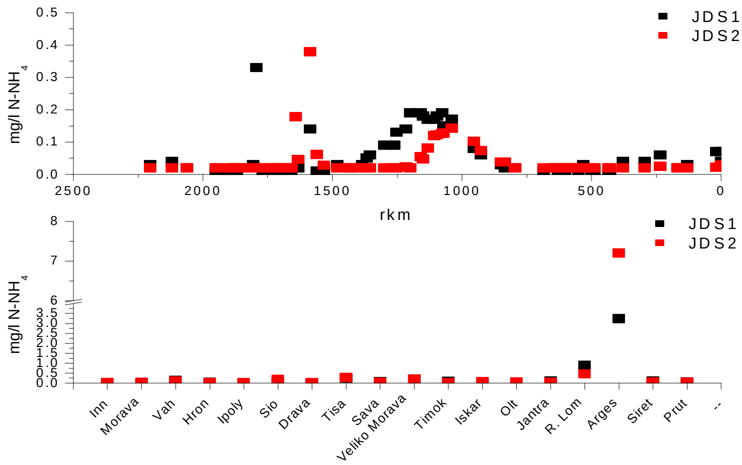


Figure 26: Comparison between *N-nitrite* values from JDS2 and JDS1

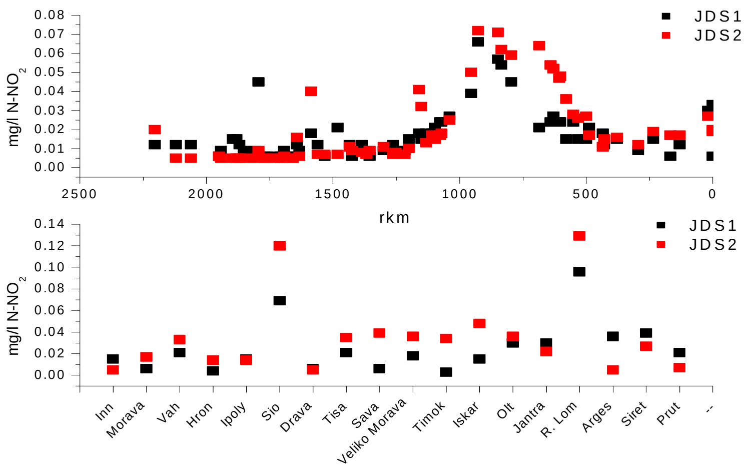


Figure 27: Comparison between *N-nitrate* values from JDS2 and JDS1

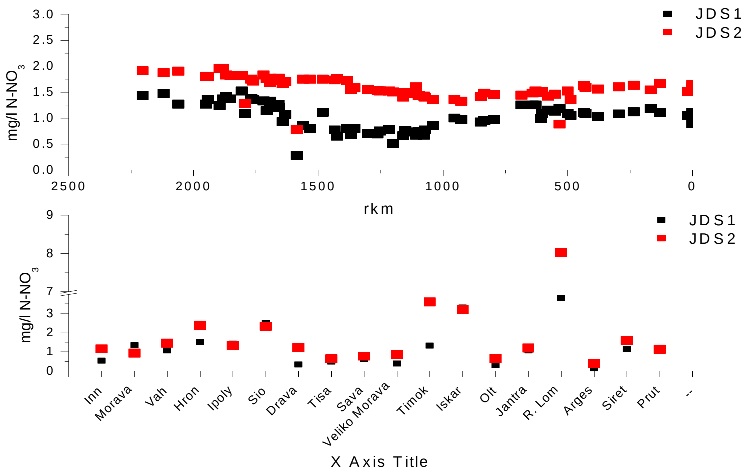


Figure 28: Comparison between *Organic Nitrogen* values from JDS2 and JDS1

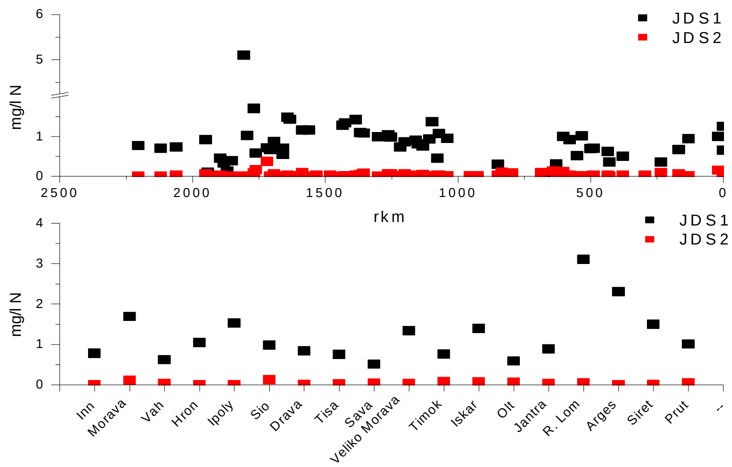


Figure 29: Comparison between *P-orthophosphate* values from JDS2 and JDS1

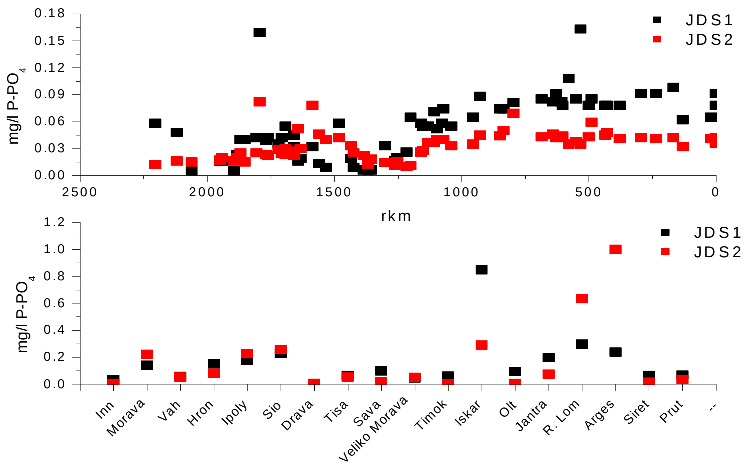


Figure 30: Comparison between *Total Phosphorous* values from JDS2 and JDS1

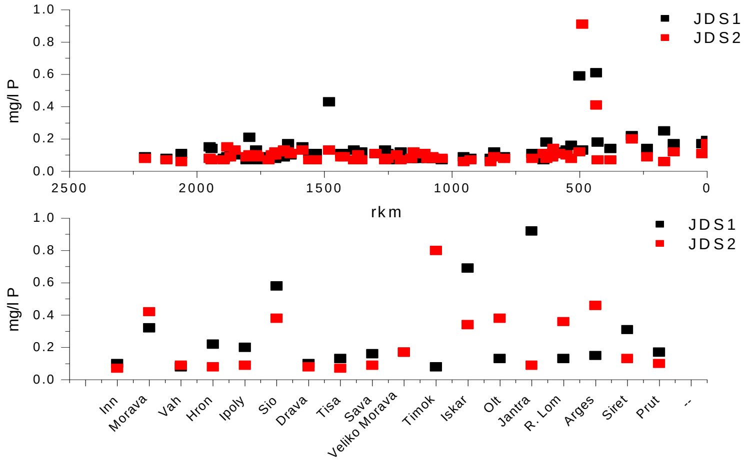
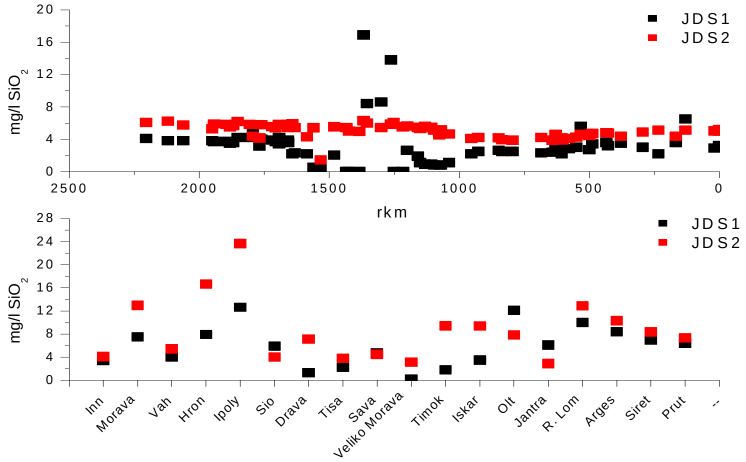


Figure 31: Comparison between *Dissolved Silica* values from JDS2 and JDS1



3.5 Water Quality Assessment

The water quality assessment for the JDS2 results was being carried out based on three different approaches: the Austrian and the Czech proposals (which are WFD compliant) and the Trans National Monitoring Network of ICPDR (TNMN) classification system (used for TNMN purposes only).

3.5.1 Water Quality Assessment according to WFD compliant criteria

The water quality assessment given by the nutrients quality elements was carried out taking into account the WFD compliant criteria set in the Austrian and the Czech proposals. Based on the JDS2 data compilation according to the numeric criteria (shown in Tables 5, 6, and 7) a preliminary and partial attend for the evaluation of the ecological quality class of the Danube and mouth of the selected tributaries given by the nutrients quality elements is presented in Tables 8, 9 and 10.

Nevertheless, the preliminary final assessment of ecological quality class has to be put in close link with the ecological assessment given by the biological elements supported by the physico-chemical elements. Also, it has to be clearly mentioned that the following data assessment has been made *based on JDS2 sampling sites only and not based on water bodies assigned for the Danube River and tributaries.*

Table 5: Numeric criteria used for the nutrients conditions according to the *Austrian* proposal

Quality Element	Parameter to be assessed	Type of criteria	The most relevant biological element			
Nutrient conditions	**N-Nitrate (N-NO₃)**	90 Percentile	Saprobic ground state (SI MZB)			
			1.75[4]		2.00[5]	
			High Class	Good Class	High Class	Good Class
			3.0	**5.5**	**4.0**	**7.0**
	P-Orthophosphate (P-PO₄)	90 Percentile	Trophic ground state (Phytobenthos)			
			me2 (meso-eutroph2)			
			High Class		Good Class	
			0.070		**0.200**	

Table 6: Numeric criteria (Environmental Quality Standards - EQS) used for the nutrients conditions according to the *Austrian* proposal

Quality Element	Parameter to be assessed	The most relevant biological element	EQS (µg/l)
Nutrient conditions	**N-Ammonium (N-NH₄)** (Calculated according to Relation (1) from Annex 1	Toxicity	**196 – 1053**[6]
	N-Nitrite (N-NO₂) (depending on the chloride content)	Toxicity	**300**[7]

Table 7: Numeric criteria (Environmental Quality Standards - EQS) used for the nutrients conditions according to the *Czech* proposal

Quality Element	Parameter to be assessed	Type of criteria	EQS (mg/l)	Type of criteria	EQS (mg/l)
Nutrient conditions	N-Ammonium (N-NH₄)	90 Percentile	0.50	Annual Average (AA)	0.23
	N-Nitrite (N-NO₂)		-		-
	N-Nitrate (N-NO₃)		7.0		4.5
	Total Nitrogen (TN)		8		5
	Total Phosphorous (TP)		0.20		0.15

In attending to obtain a preliminary view of the indicative information on ecological quality class given by the nutrients levels from JDS2, the following constraints have been taken into account in this respect:

- *the JDS2 data are only momentary data and when compared with sets of criteria referring to C90 statistics, the information yielded has an rough guide character;*
- *for the time being <u>no reference conditions for nutrients</u> are established at the level of the Danube Basin;*
- *based on the Czech proposal, "the worst case" approach has been used, therefore the compliance with EQS as annual average (AA) has been tested.*

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[4] In JDS2 data compilation, the Danube stretch comprised between river km 2600 and river km 2008 was considered as being characterised by a SI of MZB of 1.75

[5] In JDS2 data compilation, the Danube stretch comprised between river km 1950 and river km 0 was considered as being characterised by a SI of MZB of 2.00.

[6] See Table 11A from Annex 1.

[7] Since chloride concentration was not determined during JDS2, in order to assess the EQS for N-Nitrite "the principal level of interest" of 50 mg/l of Cl^- (according to TNMN Yearbooks) was chosen in this respect. Therefore, based on Table A4 from Annex 1, 300 µg/l $N\text{-}NO_2$ yielded as EQS for the Danube River Water.

The information presented in Tables 8, 9 and 10 respectively has to be further analysed and tested only after getting the complete picture given by the biological elements “supported” by the physico-chemical elements.

Table 8: *Preliminary* ecological quality class evaluation for the nutrients conditions based on the *Austrian* proposal (assessed by the most relevant biological element)

Parameter to be assessed	Indicationon ecological quality class (number of JDS2 sampling sites)							
	Danube River			Tributaries				
	High class	Good class	Non-complying “good class”	High class	Good class	Non-complying “good class”		
						Number of sites	JDS2 position	
N-Nitrates (N-NO_3)	77	1	0	17	0	1	rkm 498	Russenski Lom
P-Phosphates (P-PO_4)	73	5	0	10	2	6	rkm 1880	Morava
							rkm 1708	Ipoly
							rkm 1497	Sió
							rkm 637	Iskar
							rkm 498	Russenski Lom
							rkm 432	Arges

Table 9: *Preliminary* ecological class evaluation for the nutrients conditions based on the *Austrian* proposal (assessed by the toxicity on aquatic community)

Parameter to be assessed	Indicationon ecological quality class (number of JDS2 sampling sites)					
	Danube River		Tributaries			
	Meet the EQS		Meet the EQS			
	Yes (Good Class)	No (Moderate Class)	Yes (Good Class)	No (Moderate Class)		
				Number of sites	JDS2 position	
N-Ammonium (N-NH_4)	78	0	17	1	rkm 432	Arges
N-Nitrite (N-NO_2)	78	0	18			0

Table 10: *Preliminary* ecological class evaluation for the nutrients conditions based on the *Czech* proposal (EQS as Annual Average)

Parameter to be assessed	Indicationon ecological quality class (Number of JDS2 sampling sites)							
	Danube River				Tributaries			
	Meet the EQS (AA)				Meet the EQS (AA)			
	Yes (Good Class)	No (Moderate Class)			Yes (Good Class	No (Moderate Class)		
		Number of sites	JDS2 position			Number of sites	JDS2 position	
N-Ammonium (N-NH_4)	77	1	rkm 1586	Rackeve-Soroskar arm	15	3	rkm 1215	Tisa
							rkm 498	Russenski Lom
							rkm 432	Arges
N-Nitrate (N-NO_3)	78	0		-	17	1	rkm 498	Russenski Lom
Total Nitrogen (TN)	78	0		-	16	2	rkm 498	Russenski Lom
							rkm 432	Arges
Total Phosphorous (TP)	73	5	rkm 488	Downstream Ruse/Giurgiu	11	7	rkm 1880	Morava
			rkm 434	Us. Arges			rkm 1497	Sió
			rkm 295	Upstream Cernavoda			rkm 1103	Velika Morava
			rkm 8	Bystroe canal			rkm 845	Timok
			rkm 0	Sf. Gheorghe			rkm 637	Iskar
							rkm 605	Olt
							rkm 498	Russenski Lom
							rkm 432	Arges

According to Tables 8-10, a preliminary estimation on the possible ecological quality class given by the nutrients conditions can be made:

- *based on the Austrian proposal:*
    a. *Danube River:*
        i. *levels of nutrients that are mainly responsible for the eutrophication effect (nitrates and orthophosphates) offer a very good situation, with almost all sampling sites (98.7% and 93.6% respectively) described by "high" ecological class;*
        ii. *only one N-nitrate concentration exceeds the limit between the "high" and "good" class; the image is not that good in the case of P-orthophosphates, with five sampling sites "falling" in the "good class";*
        iii. *the nutrients with toxicity on aquatic community (ammonium and nitrites) have very good presence levels, since no value exceeds the EQSs for these quality elements.*
    b. *Tributaries at the confluence*
        i. *94.4% of tributaries are found with N-nitrate levels characteristic to the "high" class and only one tributary (*Russenski Lom*) has N-nitrate concentration exceeding the limit set for "good" class;*
        ii. *slightly more than half of selected tributaries are in the "high" class, while two tributaries are placed in the "good class" by the P-orthophosphates concentration"; six P-orthophosphate concentrations do not comply with the limit set for "good" class, in* Morava, Ipoly, Sió, Iskar, Russenski Lom and Arges;
        iii. *only one N-ammonium concentration exceeds the limit set for good status (*Arges*) and all N-nitrite concentrations are below the EQS for this parameter.*

The general overview on the indicative ecological class given by the nutrients conditions based on the Austrian proposal is presented in Table 11. The estimation of the ecological class has been made taking into account the situation given by the nutrients responsible for the eutrophication process - nitrates and orthophosphates. If the nutrients having toxic relevance had been also considered in this evaluation (ammonium and nitrites), 95 out of 96 JDS2 sampling sites would have been assessed as being in "good" class and one sampling site (*Arges* tributary) as being in "moderate" class, but these findings should be closely linked with the biological quality elements assessment.

Table 11: General overview on the indicative ecological class given by the nutrients conditions – JDS2 sampling sites for water (based on the Austrian classification)

JDS2 Code	Country	Station	Danube type	rkm	Quality Class
JDS1	DE	Upstream Iller	1	2600	2
JDS2	DE	Kelheim – gauging station	2	2415	2
JDS3	DE	Geisling power plant	2	2354	2
JDS4	DE	Deggendorf	2	2285	1
JDS5	DE	Niederalteich	2	2278	1
JDS6	DE, AT	/Inn, rkm 4.2		2225	1
JDS7	DE, AT	Jochenstein	3	2204	1
JDS8	AT	Upstream dam Abwinden-Asten	3	2120	1
JDS9	AT	Upstream dam Ybbs-Persenbeug	3	2061	1
JDS10	AT	Oberloiben	3	2008	1

JDS11	AT	Upstream dam Greifenstein	4	1950	1
JDS12	AT	Klosterneuburg	4	1942	1
JDS13	AT	Wildungsmauer	4	1895	1
JDS14	AT	Upstream Morava (Hainburg)	4	1881	1
JDS15	AT, SK	/Morava (rkm 0.08)		1880	>2
JDS16	SK	Bratislava	4	1869	1
JDS17	SK, HU	Gabcikovo reservoir	4	1852	1
JDS18	SK, HU	Medvedov/Medve	4	1806	1
JDS19	HU	/Moson Danube Arm – end (rkm 0.1)	4	1794	2
JDS20	SK, HU	Komarno/Komarom	5	1768	1
JDS21	SK	/Vah (rkm 0.8)		1766	1
JDS22	SK, HU	Iza/Szony	5	1761	1
JDS23	SK, HU	Sturovo/Esztergom	5	1719	1
JDS24	SK	/Hron (rkm 0.5)		1716	2
JDS25	SK, HU	/Ipoly (rkm 0.7)		1708	>2
JDS26	HU	Szob	5	1707	1
JDS27	HU	Upstream end of Szentendre Island	5	1692	1
JDS28	HU	/Upstream end of Szentendre Island (arm)	5	1692	1
JDS29	HU	Budapest upstream	5	1659	1
JDS30	HU	/Budapest (old Danube) end of S.arm	5	1658	1
JDS31	HU	/Rackeve-Soroksar Danube Arm - start	5	1642	1
JDS32	HU	Budapest downstream	5	1632	1
JDS33	HU	Adony/Lórév	5	1605	1
JDS34	HU	/Rackeve-Soroksar Danube Arm - end		1586	2
JDS35	HU	Dunafoldvar	5	1560	1
JDS36	HU	Paks	5	1533	1
JDS37	HU	/Sio (rkm 1.0)		1497	>2
JDS38	HU	Baja	6	1481	1
JDS39	HU	Hercegszanto	6	1434	1
JDS40	HR, RS	Batina	6	1424	1
JDS41	HR, RS	Upstream Drava	6	1384	1
JDS42	HR	/Drava (rkm 1.4)		1379	1
JDS43	HR, RS	Downstream Drava (Erdut/Bogojevo)	6	1367	1
JDS44	HR, RS	Dalj	6	1355	1
JDS45	HR, RS	Ilok/Backa Palanka	6	1300	1
JDS46	RS	Upstream Novi-Sad	6	1262	1
JDS47	RS	Downstream Novi-Sad	6	1252	1
JDS48	RS	Upstream Tisa (Stari Slankamen)	6	1216	1
JDS49	RS	/Tisa (rkm 1.0)		1215	1
JDS50	RS	Downstream Tisa/Upstream Sava (Belegis)	6	1200	1
JDS51	RS	/Sava (rkm 7.0)		1170	1
JDS52	RS	Upstream Pancevo/Downstream Sava	6	1159	1
JDS53	RS	Downstream Pancevo	6	1151	1
JDS54	RS	Grocka	6	1132	1
JDS55	RS	Upstream Velika Morava	6	1107	1

JDS56	RS	/Velika Morava		1103	1
JDS57	RS	Downstream Velika Morava	6	1097	1
JDS58	RS	Starapalanka – Ram	6	1077	1
JDS59	RS, RO	Banatska Palanka/Bazias	7	1071	1
JDS60	RS, RO	Irongate reservoir (Golubac/Koronin)	7	1040	1
JDS61	RS, RO	Donji Milanovac	7	991	1
JDS62	RS, RO	Irongate reservoir (Tekija/Orsova)	7	954	1
JDS63	RS, RO	Vrbica/Simijan	8	926	1
JDS64	RS, RO	Iron Gate II	8	865	1
JDS65	RS, RO	Upstream Timok (Rudujevac/Gruia)	8	849	1
JDS66	RS, BG	/Timok (rkm 0.2)		845	1
JDS67	RO, BG	Pristol/Novo Selo Harbour	8	834	1
JDS68	RO, BG	Calafat	8	795	1
JDS69	BG, RO	Downstream Kozloduy	8	685	1
JDS70	BG, RO	Upstream Iskar (Bajkal)	8	640	1
JDS71	BG	/Iskar (rkm 0.3)		637	>2
JDS72	BG, RO	Downstream Iskar	8	629	1
JDS73	RO, BG	Upstream Olt	8	606	1
JDS74	RO	/Olt (rkm 0.4)		605	1
JDS75	RO, BG	Downstream Olt	8	602	1
JDS76	RO, BG	Downstream Turnu-Magurele/Nikopol	8	579	1
JDS77	RO, BG	Downstream Zimnicea/Svishtov	8	550	1
JDS78	BG	/Jantra (rkm 1.0)		537	2
JDS79	RO, BG	Downstream Jantra	8	532	1
JDS80	BG, RO	Upstream Ruse	8	500	1
JDS81	BG	/Russenski Lom		498	>2
JDS82	BG, RO	Downstream Ruse/Giurgiu	8	488	1
JDS83	RO, BG	Upstream Arges	8	434	1
JDS84	RO	/Arges		432	>2
JDS85	RO, BG	Downstream Arges, Oltenita	8	429	1
JDS86	RO, BG	Chiciu/Silistra	8	378	1
JDS87	RO	Upstream Cernavoda	9	295	1
JDS88	RO	Giurgeni	9	235	1
JDS89	RO	Braila	9	167	1
JDS90	RO	/Siret (rkm 1.0)		154	1
JDS91	RO, MD	/Prut (rkm 1.0)		135	1
JDS92	RO, UA	Reni	9	130	1
JDS93	RO, UA	Vilkova - Chilia arm/Kilia arm	10	18	1
JDS94	UA	/Bystroe canal (to be confirmed)	10	8	1
JDS95	RO	Sulina - Sulina arm	10	0	1
JDS96	RO	Sf.Gheorghe - Sf.Gheorghe arm	10	0	1
		Proposal for ecological quality class	Assessment class		
		High Class	1		
		Good Class	2		
		Non-complying with good class	>2		

According to Table 11 it can be concluded that all the sampling sites located on the Danube River itself are either in the high or good ecological class while six tributaries do not comply with the “good” class criteria (*Morava, Ipoly, Sió, Iskar, Russenski Lom* and *Arges*).

- *based on the Czech proposal:*
    - a. *Danube River:*
        - i. *very good situation for nitrogen nutrients forms, with only one sampling site (*Rackeve-Soroksar-end*) with N-ammonium concentration exceeding EQS;*
        - ii. *in the case of TP, five sampling sites have concentrations exceeding the EQS (*downstream Ruse/Giurgiu, upstream Arges, upstream Cernavoda, Bystroe canal *and* Sf. Gheorghe arm*).*
    - b. *Tributaries at the confluence:*
        - i. *for the nitrogen nutrients forms, one tributary (*Tisa*) “falls” into “moderate class”because of the N-ammonium concentration,* Arges *tributary exceeds the EQS for N-ammonium and Total Nitrogen, while* Russenski Lom *exceeds the EQSs for all the nitrogen forms taken into account;*
        - ii. *in the case of TP, seven tributaries exceed the EQS for this parameter (*Morava, Sió, Velika Morava, Timok, Iskar, Olt, Russenski Lom *and* Arges).

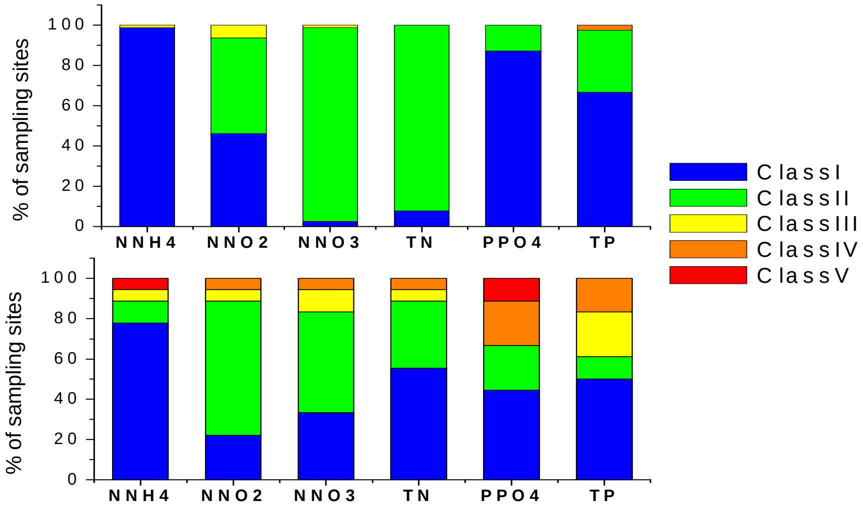
The general overview of the ecological quality information given by the two WFD compliant proposals showed a relative similarity: based on the Austrian scheme, the sampling sites from the Danube River itself are either in the “high” or “good” ecological class while six sampling sites from the mouth of tributaries do not comply with the “good” class criteria. The more restrictive Czech scheme showed that six sampling sites on the Danube and nine sampling sites located at the mouth of tributaries do not comply with “good” class criteria.

3.5.2 Water Quality Assessment according to the ICPDR Five Quality Classes (non-WFD compliant)

In the ICPDR Water Quality Scheme, five classes are used for assessment with target value being the limit value of class II. In Figure 32 the distribution (in percentages) of sampling sites into the five quality classes for the Danube River and selected tributaries is shown, based on which the following issues are summarised:

- *Danube River:*
    - a. *relatively entire course of the Danube River is mainly characterised by the nutrient levels located in Class I (reference) and Class II (Target Value) respectively, which complies with the general situation given by the TNMN Yearbooks information;*
    - b. *only one sampling site appears in Class III for N-ammonium and N-nitrate respectively and five sampling sites in the case of N-nitrites;*
    - c. *only one parameter (Total Phosphorous) determines Class IV for two sampling sites;*
    - d. *no sampling site is characterised by nutrient levels in Class V.*

Figure 32: Percentages of sampling sites into five water quality classes for the Danube River and tributaries



- *Tributaries at the confluence:*

  a. *the whole picture is not as good as in the case of the Danube River, but more 80% of the tributaries are characterised by Class I and Class II in the case of nitrogen nutrients forms;*

  b. *in the case of phosphorous forms, more than 60% of the tributaries are within the reference conditions and complying with the Target Value;*

  c. *Class III is represented by one sampling site for N-ammonium, N-nitrite and TN and by two sampling sites for N-nitrate; no sampling site in Class III for orthophosphates but four sampling sites in this Class for TP;*

  d. *one sampling site for N-nitrite, N-nitrate and TN in Class IV, but four and three sampling sites in this class in the case of orthophosphates and TP respectively;*

  e. *Class V appears for one sampling site in the case of N-ammonium and for two sites in the case of orthophosphates.*

4 Conclusions

- A quasi-constant profile of N-ammonium concentration in the upper, middle and the last stretch of the lower Danube was noticed, except for the local situation occurring in the dammed arm *Rackeve-Soroskar*. The maximum concentration peak was located in the *Iron Gates* reservoir backwaters, induced by point and diffuse emission sources and by denitrification process in low oxygen conditions. A highly uneven profile was measured at the mouth of the tributaries, from undetectable levels to extreme elevated concentration in the *Arges*, caused by secondary discharge of totally untreated municipal wastewater from the sewage system of a major city (Bucharest).

- The N-nitrite spatial pattern had a decreasing line in the upper course of the Danube. The middle reach was by a uniform profile, followed by an N-nitrite peak in the *Iron Gates* reservoir, similar with the N-ammonium, but slightly shifted to the headwater of the reservoir and downstream the dam (since nitrites are the intermediary product in the oxidation/reduction process of nitrogen forms, its variation profile in this area reflected the specific behaviour of the nitrogen species in a big reservoir). Except for two sites at the mouth of tributaries (*Sió* and *Russenski Lom*), no elevated concentrations were measured.

- A significant decreasing profile of N-nitrates concentrations from upper to middle and lower Danube reaches was noticed. Local variations took place in side arms of the Danube River, caused by the specific summer pattern in shallow waters (uptake by the biological activity and increased organic pollution). Tributaries at the confluence presented a scattered concentrations profile, with a large variation interval.

- The Danube River was characterised by very low content of organic nitrogen in water samples. For mouth of the tributaries, four of them (*Inn*, *Hron*, *Ipoly* and *Arges*) were characterised by zero values, whereas the rest of tributaries had organic nitrogen content comparable with the Danube River.

- A strong decreasing line of P-orthophosphates concentrations was present in the upper reach of the Danube and a slight increasing profile in the lower one, mainly caused by discharges of municipal wastewater containing non-free P detergents. Except for two very high concentrations (0.635 and 1.000 mg/l in the mouth of *Russenski Lom* and *Arges* respectively), the rest of the confluence of tributaries were characterised by concentration level similar with the Danube River.

- A relative constant profile of TP concentrations was present in the upper reach of the Danube River and slightly higher concentrations were measured in the middle reach. A decreasing line was noticed in the *Iron Gates* backwaters and *reservoir* area, most likely caused by the effect of sedimentation of particles on which phosphorus was adsorbed. In the lower reach, two rather elevated TP concentrations were measured at river km 488 (*Downstream Ruse/Giurgiu*) and river km 434 *(Upstream Arges) respe*ctively. Most of the tributaries at the confluence had comparable concentrations level with the main course of the river; the maximum concentration was measured in the *Timok* tributary.

- The spatial variation of dissolved silicates showed a general decreasing trend from upper to middle and lower reaches of the Danube. A slightly marked lower profile was present in the *Iron Gates* area, but no significant difference between entering the reservoir and downstream the dam could be noticed. For several mouths of tributaries, concentrations were lower than the level from the Danube River but higher values were measured in the *Morava*, *Hron*, *Ipoly* (in the middle stretch) and in all tributaries from the lower stretch, except of *Jantra.*

- The spatial distribution of Organic Nitrogen in sediment samples showed an increasing profile from the upper to middle and the beginning of the lower Danube stretch (the decreasing profile started from downstream of the *Iron Gates* area, as a consequence of denitrification process in the reservoir). In the lower reach of the Danube, highly elevated concentration was found at river km 429 (*Downstream Arges - left*); since at the mouth of the *Arges* tributary no sediment sample was collected, this organic nitrogen concentration might be assigned to the influence of the highly pollution stemming from discharge of untreated municipal sewage waters in the *Arges* tributary.

- Total Phosphorous in sediment samples presented a pronounced decreasing line in the upper Danube stretch. A maximum profile was present in the middle reach of the Danube, followed by a decreasing trend in the *Iron Gates* area, slightly contrary to the previously specific data according to which the *Iron Gates* sediment acts as phosphorous reserve.

- Organic Nitrogen in suspended matters presented a relatively "symmetrical pattern" with the maximum profile located in the middle stretch of the Danube. Samples from mouth of the tributaries showed a lower content than the Danube itself.

- The variation of TP in suspended matters showed the maximum profile located in the middle reach of the Danube and the minimum value in the *Gabcikovo* reservoir. If the general pattern is relatively similar as in the case of organic nitrogen, still local variations from one sampling site to another occurred along the entire Danube. Total P in suspended solids from mouth of the tributaries (where available) presented a comparable level with the Danube itself, except for the *Velika Morava*, in which high TP was rather high (probably due to the runoff influence caused by high precipitation regime during the sampling period).

- The longitudinal surveys on major tributaries showed (for water samples) increasing profiles from upper sites down to the confluence with the Danube River in the case of *Tisa* (from JDS-TI4 to JDS-TI6) for N-ammonium, *Iskar* and *Olt* for TP. Significantly increasing values from upstream to downstream were recorded on *Morava* (JDS-MO2) for P-othophosphates, *Russenski Lom* and *Arges* tributaries for N-ammonium and P-orthophosphates. Decreasing trends from the upper part to the confluence with the Danube River were noticed on *Morava*, *Sava* (from JDS-SA3 to JDS51/Sava), *Olt* for N-Ammonium and *Velika Morava* for N-nitrates. Organic Nitrogen variation in sediment samples showed higher concentration at the site located at the confluence with the Danube River in the case of *Tisa*, *Sav*a and *Prut* tributaries. For *Morava* and *Velika Morava*, the second sampling site on each tributary had the maximum concentration. No significant variation of TP among the sampling sites could be noticed, except for JDS-VM3, where the TP concentration in sediment sample was four times higher than the concentration from the confluence with the Danube River.

- When compared with the JDS1 results in the Danube water samples, it can be noticed that relatively similar profiles were present in the case of N-ammonium, N-nitrites and TP. N-nitrates and dissolved silica concentrations from JDS2 were almost systematically higher than the ones from JDS1, while in the case of Organic Nitrogen the situation was opposite. A distinctive variation occurred in the case of P-orthophosphates for which the JDS2 data showed lower values in the upper and lower Danube reaches and higher concentrations in the middle stretch. For the selected tributaries, the JDS2 situation looked worse for:

    - *Jantra* (N-nitrates);
    - *Inn, Siret* and *Prut* (N-nitrate and dissolved silicate);
    - *Sava* (N-nitrite and N-nitrate);
    - *Hron* (N-nitrite, N-nitrate and dissolved silicate);
    - *Ipoly* (N-ammonium, P-orthophosphates and dissolved silicate);
    - *Sio* (N-ammonium, N-nitrite and P-orthophosphates);
    - *Drava* (N-ammonium, N-nitrate and dissolved silicate);
    - *Iskar* (N-ammonium, N-nitrite and dissolved silicate);
    - *Vah* and *Timok* (N-nitrite, N-nitrate, TP and dissolved silicate);
    - *Tisa* (Inorganic Nitrogen forms and dissolved silicate);
    - *Olt* (Inorganic Nitrogen forms and TP);

  - *Morava* (N-nitrite, N-nitrate, P-orthophosphates, TP and dissolved silicate);
  - *Veliko Morava* (Inorganic Nitrogen forms, P-orthophosphates and dissolved silicate);
  - *Russenski Lom* (N-nitrite, N-nitrate, P-orthophosphates, TP and dissolved silicate);
  - *Arges* (N-ammonium, N-nitrate, P-orthophosphates, TP and dissolved silicate).

- The water quality assessment for the JDS2 results was being carried out based on three different approaches: the Austrian and the Czech proposals (which are WFD compliant) and the Trans National Monitoring Network of ICPDR (TNMN) classification system (used for TNMN purposes only).
  - Based on the Austrian proposal, it can be concluded that all the sampling sites located on the Danube River itself are either in the "high" or "good" ecological class while six tributaries do not comply with the "good" class criteria (*Morava*, *Ipoly*, *Sió*, *Iskar*, *Russenski Lom* and *Arges*).The more restrictive Czech scheme showed that six sampling sites on the Danube and nine sampling sites located at the mouth of tributaries do not comply with "good" class criteria.
  - Based on the TNMN five class classification scheme, relatively entire course of the Danube River was mainly characterised by the nutrient levels located in Class I (reference) and Class II (target value) respectively, which complies with the general situation given by the TNMN Yearbooks information. As regards the selected tributaries, more than 80% are characterised by Class I and Class II in the case of nitrogen nutrients forms and more than 60% are within the Class I and comply with the Class II in the case of phosphorous forms.

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