Joint Danube Survey 3

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

Chapter (full report) on: General physico-chemical determinands and nutrients

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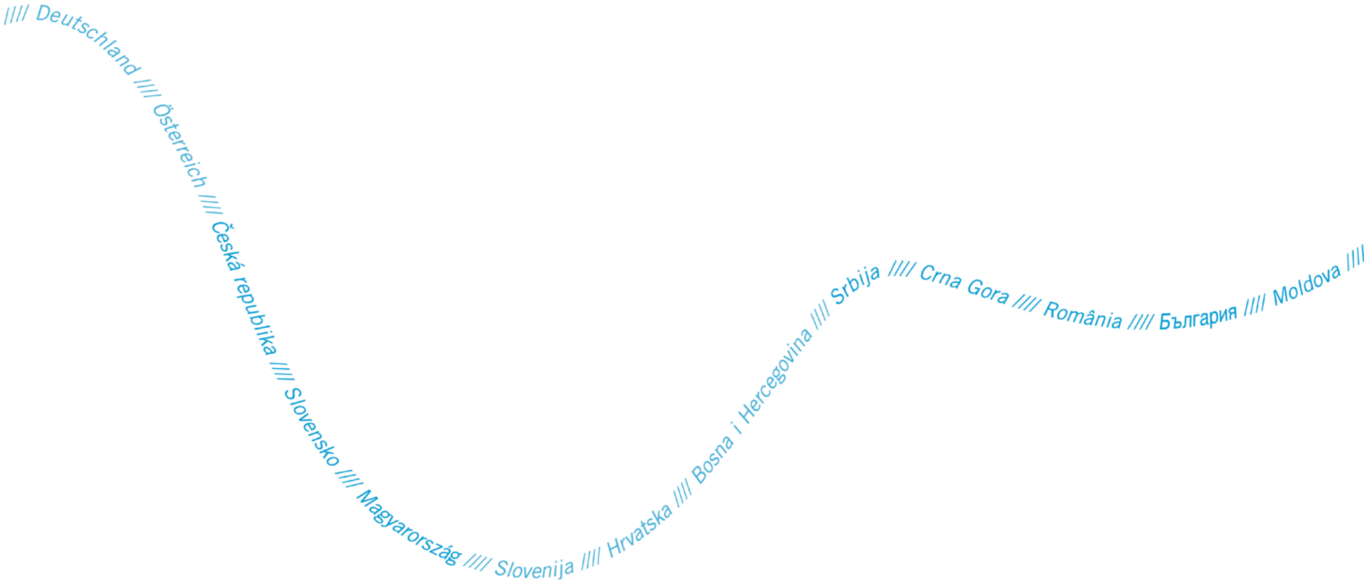

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1 Introduction

Natural background content of nutrients, especially Nitrogen (N) and Phosphorous (P) are essential to ecosystem biota, for balanced plant and microbial growth. However, excessive nutrients enrichment caused by anthropogenic activities negatively impacts the ecosystem, often resulting in eutrophication which impairs both the physical and biological health of an aquatic system. In the Danube Basin, the nutrients issue has a long history in the monitoring activity, starting from the Bucharest Declaration (1985) up to the on-going Trans-National Monitoring Network (TNMN) operated under the ICPDR monitoring strategy. In addition, nutrients loads from the Danube Basin have a major role in protection of the Western Black Sea shelf from eutrophication, therefore several international projects at the basin wide level addressed the management of the nutrients in the Danube River Basin (daNUbs 2005; Kroiss et al. 2005; Schreiber et al. 2005). Starting with the entry into force of the Water Framework Directive (WFD) in 2000, Annex V of the WFD, in Section 1.1.1 (Rivers), requires three groups of quality elements to be used in the ecological status 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 mentioned: thermal conditions, oxygenation conditions, salinity, acidification status and nutrient conditions; consequently, the following parameters were measured: water temperature, dissolved oxygen content, electrical conductivity, pH, Total Nitrogen and Total Phosphorous (as regards nutrients group, it was considered that the total forms are commonly used to represent the amount of Nitrogen and Phosphorous in the system and their relationship to primary production).

This chapter aims to present the longitudinal distribution of the selected physico-chemical parameters measured in the Danube River and major tributaries during JDS3 and to compare the obtained results with previous outcomes from both investigative and surveillance monitoring. Preliminary ecological indication given by these supportive elements is also assessed based on the ranges (minimum – maximum) of the environmental quality standards/guiding values reported by the Danube countries (where available) for *high/good* and *good/moderate* classes respectively; however, due to the lack of harmonisation of the class boundaries for these elements at the basin wide level, ecological indication obtained has a limited applicability.

2 Methods

2.1 General parameters

Water samples were collected directly from the river with the help of the motor-boat used for the collection of biological samples. *In-situ* measurements (temperature, dissolved oxygen, pH and conductivity) were carried out by portable multiple-probe YSI – EXO2 instrument with dedicated probes, in three profiles of the river (left, middle and right), based on international standardised methods. This chapter takes into account the data recorded in the middle, since the differences among the three profiles are negligible (details in Figures 4 – 8). Nutrients forms and basic ions were analysed in water samples by selected laboratories according to EN ISO standardised methods based on molecular spectrophotometry (total forms of N and P) and ion chromatography (dissolved forms of N and P and major ions). The dissolved nutrients forms and major ions (sulphates, chlorides, sodium, potassium, calcium and magnesium) were analysed in 71 sites (apart from the 68 sites from the JDS3

Cruise Manual, three additional sampling sites were sampled: two on the Danube River – upstream *Olt* and upstream *Prut* and one tributary – *Olt*) by the *JRC – Water Research Unit* as in-kind contribution for this group of quality elements.

2.2 Nutrients and major ions

According to the Cruise Manual of the JDS3, total forms of nutrients (Nitrogen and Phosphorous) were analysed in water samples in a selected laboratory, by EN ISO standardised methods based on molecular spectrophotometry.

The dissolved nutrients forms (ammonium, nitrites, nitrates and ortho-phosphates) as well as major ions (sulphates, chlorides, sodium, potassium, calcium and magnesium) were analysed in 71 sites (apart from the 68 sites from the Cruise Manual, three additional sampling sites were sampled: two on the Danube River – upstream *Olt* and upstream *Prut* and one tributary – *Olt*) by the *JRC – Water Research Unit* as in-kind contribution for this group of quality elements.

Water samples for dissolved nutrients analysis were taken in 100 ml Nalgene bottles, previously treated for sample preservation. Each sample was taken in duplicate and accompanied with a blank. Samples were filtered using a50 ml plastic syringe through Millipore HA 0.45µm pore size and 33 mm diameter filter unit.

2.2.1 Sample collection and pre-treatment (samples designated to the analysis of dissolved nutrients forms and major ions)

The following instructions were applied for the sample collection and *in situ* treatment.

- Processing of the water samples was done within 6 hours under subdued light.
- The syringe was rinsed 2-3 times with the sampling water.
- The syringe was filled with about 30-40 ml of sample.
- A Millipore HA 0.45µm pore size and 33 mm diameter filter unit was placed on the syringe.
- The filtered water was collected into a Nalgene bottle; the bottle was rinsed with the filtrate.
- The syringe was filled in again with about 50 ml sample.
- 40 ml of filtered sample was transferred into the Nalgene bottle. This time the filtered sample was preserved for the analysis.
- The 100 ml Nalgene bottle was closed, labelled adequately and kept at 4° C.

Collected samples were packed in frozen boxes, delivered to *JRC Ispra* and kept at 4°C until analysis.

A small volume of sample, typically 3-5 ml, was introduced into an ion chromatograph. The anions of interest were separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

All measurements were performed in the Ion Chromatography Laboratory of the Water Resource Unit, JRC-IES, Ispra using standard procedures of the laboratory. A brief outline is described hereafter.

2.2.2 Determination of anions

Ion chromatography is a convenient method for the determination of common inorganic anions in inland water, including nitrite and nitrate.

In ion chromatography of anions, carbonate-based eluent systems have long been the mainstay; using chemically suppressed i.c., trace nitrite, nitrate and phosphate have been accurately and rapidly determined, together with major ions.

The equipment used for the analysis was a Dionex I.C. Dx 500 with a conductivity detector (Figure 1), working with the following conditions:

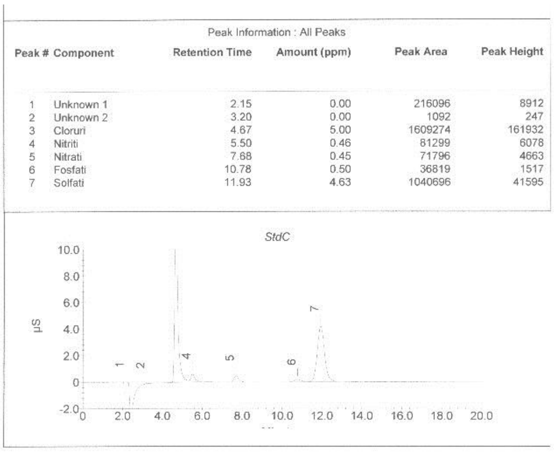
Column:	Analytical Ion-Pac AS9 , with Guard column Ion-Pac AG9
Eluent:	9 mM Sodium carbonate
Flow rate:	0.3 ml/min
Suppressor:	ASRS Ultra (2 mm), 50 mA current

- Column temperature: 25° C
- Detection: Suppressed conductivity, 10µS full scale
- Injection volume: 10 µl
- Run Time: 20 min

Figure 1: Ion Chromatograph

Calibration curves have been determined using Fluka Primary Standards, certified for ion chromatography.

Figure 2 shows a typical chromatogram for anions.



Peak Information : All Peaks

Peak #	Component	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	Unknown 1	2.15	0.00	216096	8912
2	Unknown 2	3.20	0.00	1092	247
3	Cloruri	4.67	5.00	1609274	161932
4	Nitriti	5.50	0.46	81299	6078
5	Nitrati	7.68	0.45	71796	4663
6	Fosfati	10.78	0.50	36819	1517
7	Solfati	11.93	4.63	1040696	41595

Figure 2: I.C. chromatogram for anion analysis

EPA method 300, describes the basic information for the analysis of anions by Ion Chromatography.

2.2.3 Determination of cations

The common alkali and alkaline earth cations are not considered primary nutrients; however together with ammonia they are monitored and thus analysed by I.C.

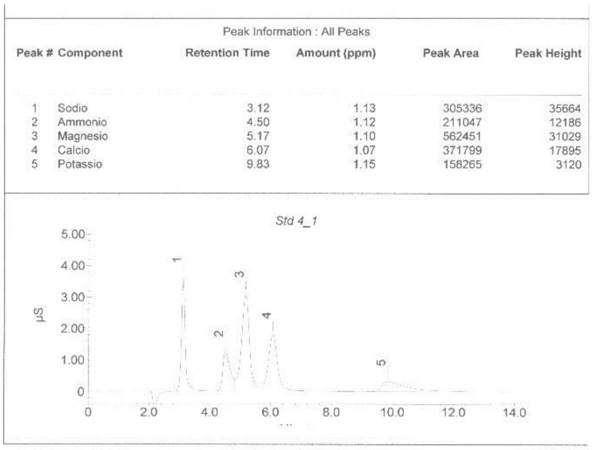
I.C. in a single run can determine ammonium plus all the important inorganic cations, including sodium, potassium, magnesium and calcium.

The equipment used for the analysis was a Dionex I.C. Dx 1500 with a conductivity detector, working with the following conditions:

- Column: Analytical Ion-Pac CS15 , with Guard column Ion-Pac CG15
- Eluent: 20 mM Acid Methane sulfonic
- Flow rate: 0.3 ml/min
- Suppressor: CSRS Ultra (2 mm), 18 mA current

- Column temperature: 45° C
- Detection: Suppressed conductivity, 5µS full scale
- Injection volume: 5 µl
- Run Time: 15 min.

Figure 3 shows a typical chromatogram for cations.



Peak Information : All Peaks

Peak #	Component	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	Sodio	3.12	1.13	305336	35664
2	Ammonio	4.50	1.12	211047	12186
3	Magnesio	5.17	1.10	562451	31029
4	Calcio	6.07	1.07	371799	17895
5	Potassio	9.83	1.15	158265	3120

Figure 3: I.C. chromatogram for cation analysis

APAT method 3030, or Dionex AN 141, describes the basic information for the analysis of cations by Ion Chromatography.

2.2.4 Interferences

- Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.
- Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.
- Filtration to prevent damage to instrument columns and flow systems is required in samples (0.45 microns) and reagent solutions (0.20 microns).
- Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

2.2.5 Reagents and Standards

- Sample bottles: Glass or polyethylene of sufficient volume (i.e. 50 mL) to allow replicate analyses of anions of interest.
- Reagent water: Deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.
- Eluent solutions:
    - sodium carbonate (CASRN 497-19-8) 9 mM. Dissolve 1.9078 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 l.
    - acid Methanesulfonic 20 mM. Dilute 2.62 ml of Acid Methanesulfonic (Fluka 64200) in 2 l of water.
- Regeneration solution (micro membrane suppressor): Sulfuric acid (CASRN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 L with reagent water.
- Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions as listed below.

1. Chloride (Cl^-) l000 mg/L: CertiPUR Merck (1.19897.0500)
2. Nitrate (NO_3^-) 1000 mg/L: CertiPUR Merck (1.19899.0500)
3. Nitrite (NO_2^-) 1000 mg/L: CertiPUR Merck (1.19811.0500)
4. Phosphate (PO_4^{---}) 1000 mg/L: CertiPUR Merck (1.19898.0500)
5. Sulfate (SO_4^{--}) 1000 mg/L: CertiPUR Merck (1.19813.0500)
6. Sodium (Na^+) l000 mg/L: CertiPUR Merck (1.19507.0500)
7. Ammonium (NH_4^+) l000 mg/L: CertiPUR Merck (1.19812.0500)
8. Calcium (Ca^{++}) l000 mg/L: CertiPUR Merck (1.19778.0500)
9. Magnesium (Mg^{++}) l000 mg/L: CertiPUR Merck (1.19788.0500)
10. Potassium (K^+) l000 mg/L: CertiPUR Merck (1.70230.0500).

Note: Stability of standards: Stock standards are stable for at least six months when stored at 4°C.

Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

2.2.6 Quality Control

In the laboratory, the minimum requirements of formal quality control (QC) of the method consist of periodic analysis of laboratory reagent blanks and other laboratory solutions as a continuing check on performance. The laboratory is maintaining performance records that define the quality of the data that are generated.

Initial demonstration of performance - The initial demonstration of performance was used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

Linear Calibration Range (LCR) - The LCR has been determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity used sufficient standards (n=7) to insure that the resulting curve is linear. The verification of linearity use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards are used to clearly define the nonlinear portion.

Quality Control Sample (QCS) – For every run of analysis or calibration, is verified the calibration standards and acceptable instrument performance with the preparation and analyses of at least a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

Method Detection Limit (MDL) - MDLs is established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, seven replicate aliquots of the fortified reagent water are processed and analyzed. Concentration values are reported in the appropriate units. The MDL is calculated as follows:

$$\boldsymbol{MDL = (t) * (S)}$$

where:

t = Student’s t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t= 3.14 for seven replicates]

S = standard deviation of the replicate analyses

MDLs is determined every six months or whenever there is a significant change in the background or instrument response.

In addition, Table 15 from the Annex 1 shows the Quality Control results for Primary Standard solutions and for the Certified Reference Materials.

3 Results

The results obtained for the *in-situ* measurements carried out in the left, middle and right profile of the Danube River and four tributaries (*Drava*, *Tisa*, *Sava and Siret*) are shown in Figures 4 – 8, from which it can be noticed that no significant differences were detected among the three transversal profiles, therefore the values measured in the middle of the river were taken into account.
The longitudinal profiles of the measured concentrations of selected parameters are shown in Figures 9 – 14.

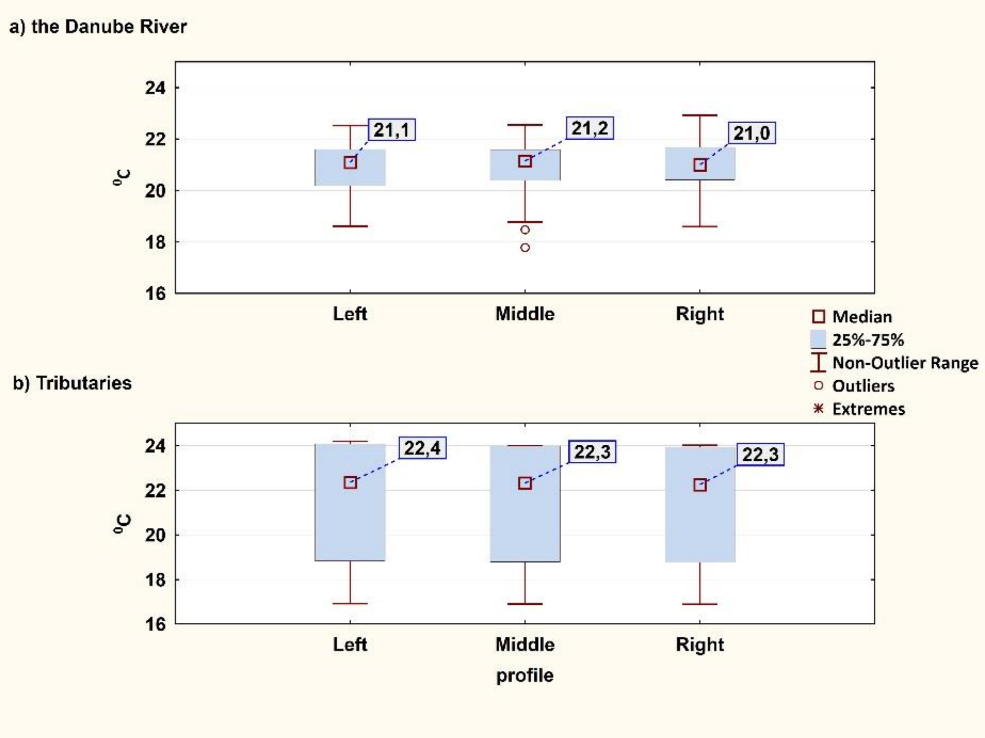


Figure 4: Box-plots of temperature values measured in the left, middle and right profiles of the Danube River and four tributaries

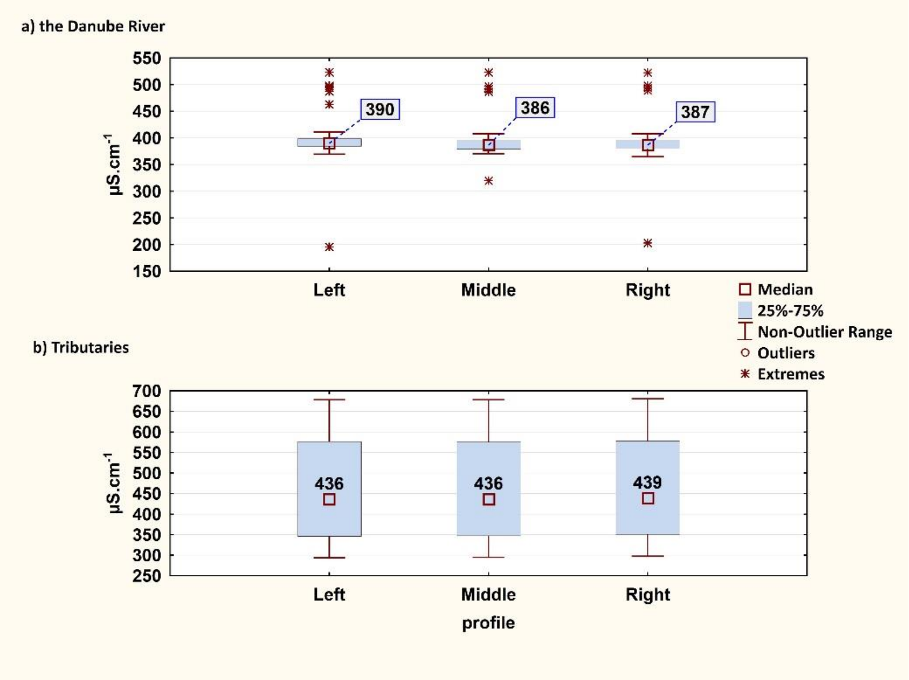


Figure 5: Box-plots of conductivity values measured in the left, middle and right profiles of the Danube River and four tributaries

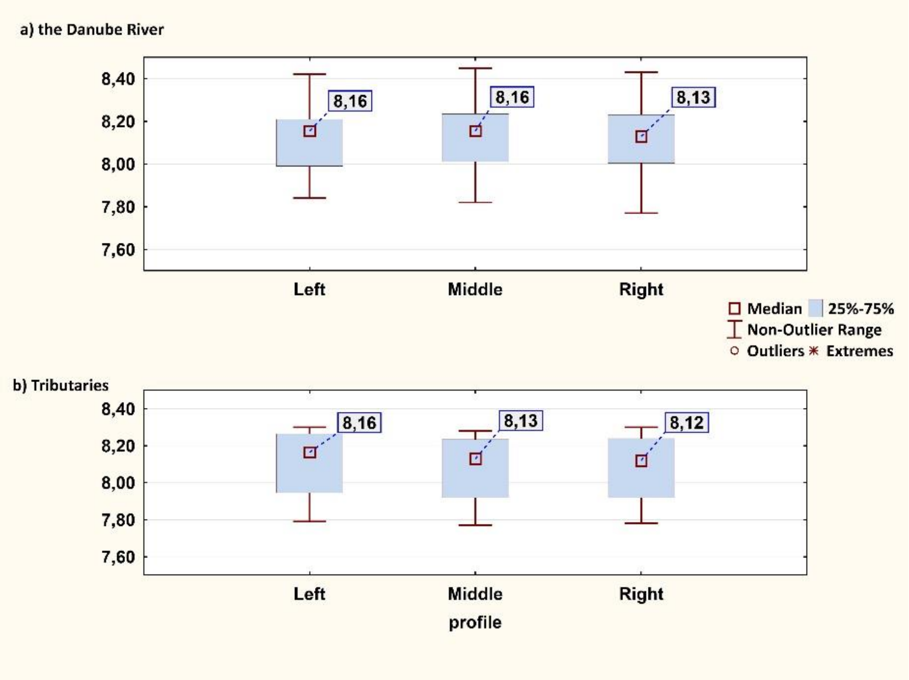


Figure 6: Box-plots of pH values measured in the left, middle and right profiles of the Danube River and four tributaries

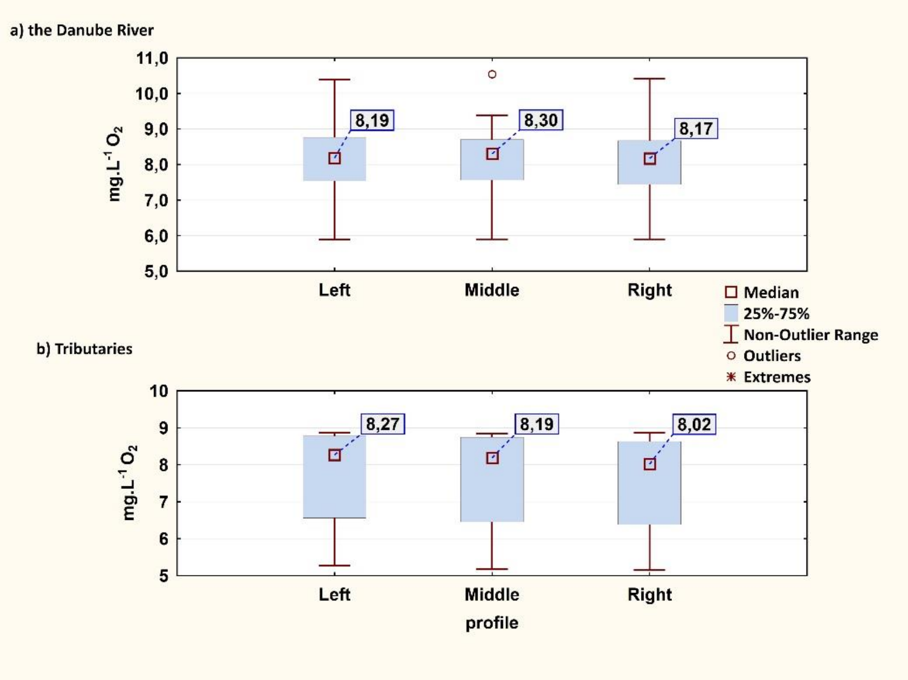


Figure 7: Box-plots of dissolved oxygen concentrations values measured in the left, middle and right profiles of the Danube River and four tributaries

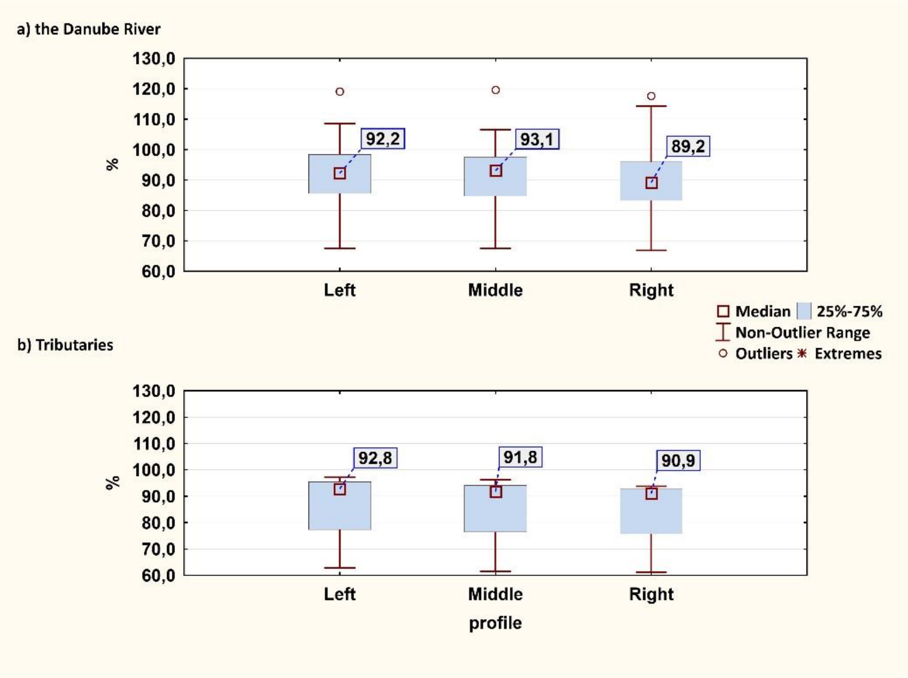


Figure 8: Box-plots of dissolved oxygen saturation values measured in the left, middle and right profiles of the Danube River and four tributaries

Similarly to the previous surveys (JDS1 and JDS2), the interpretation of the results was made according to the splitting of the Danube main course into three major sections (Joint Danube Survey, Final Report of the ICPDR, 2002; Joint Danube Survey 2, Final Scientific Report 2008): *the Upper Danube* – from river km 2600 to river km 1880 (stations JDS1 – JDS12), the *Middle Danube* – from river km 1868 to river km 1095 (stations JDS13 – JDS42) and the *Lower Danube*: from river km 1077 to river km 0 (stations JDS43 to JDS68). One biological indicator (chlorophyll – a) and two physical parameters (suspended solids – SS) and measured water discharge (Q) have also been considered in order to investigate the possible relationship among variables.

Descriptive statistics of the general physico-chemical parameters, nutrients forms and basic ions are given in Tables 1 and 2, for the main course of the Danube River and for selected tributaries respectively.

Table 1: Descriptive statistics of the general physico-chemical determinands, total nutrients forms and basic ions measured in the water samples during JDS3 in the Danube River; marked values (*) represent half of the Limit of Quantification reported by the laboratory, according to the provisions of the Directive 2009/90/EC. Additional parameters: chlorophyll - a, suspended solids and measured water discharge

parameter	*unit*	*N*	*Mean*	*Median*	*Minimum*	*Maximum*	*Range*	*Std.Dev.*
Water temperature (w.t.)	^{0} C	55	20.9	21.1	17.8	23.3	5.6	1.1
pH	-	55	8.12	8.14	7.82	8.45	0.63	0.14
Conductivity (Cond.)	µS.cm^{-1}	55	397	386	320	566	246	41.0
Dissolved Oxygen Saturation (DO sat.)	%	55	90.8	93.1	50.6	119.6	69.0	11.3
Dissolved Oxygen Concentration (DO conc.)	mg.L^{-1}	55	8.1	8.2	4.3	10.5	6.2	1.0
Total Nitrogen (TN)	mg.L^{-1} N	55	1.65	1.64	0.75	3.37	2.62	0.51
Total Phosphorous (TP)	mg.L^{-1} P	55	0.07	0.07	0.03	0.11	0.08	0.02
Ammonium (NNH_4)	mg.L^{-1} N	57	0.03	0.02	0.02 *	0.23	0.21	0.03
Nitrite (NNO_2)	mg.L^{-1} N	57	0.004	0.003	0.003 *	0.024	0.021	0.004
Nitrate (NNO_3)	mg.L^{-1} N	57	1.40	1.39	0.038	3.29	3.25	0.526
Ortho-Phosphates (PPO_4)	mg.L^{-1} P	57	0.044	0.046	0.0008 *	0.108	0.107	0.020
Sodium (Na)	mg.L^{-1}	57	15.0	14.3	10.8	21.8	11.0	2.86
Potassium (K)	mg.L^{-1}	57	3.4	3.3	2.9	4.3	1.4	0.25
Calcium (Ca)	mg.L^{-1}	57	42.0	42.4	32.8	51.2	18.4	3.76
Magnesium (Mg)	mg.L^{-1}	57	14.0	13.8	12.5	16.8	4.3	0.91
Chlorides (Cl)	mg.L^{-1}	57	21.9	20.8	16.7	32.6	15.9	4.21
Sulphates (SO_4)	mg.L^{-1}	57	31.0	31.4	18.3	42.5	24.3	3.93
Chlorophyll - a (Chll. - a)	µg.L^{-1}	55	10.69	9.14	1.16	31.63	30.47	7.19
Suspended Solids (SS)	mg.L^{-1}	55	14.9	12.0	2.7	47.0	44.3	10.9
Water discharge (Q)	m^3.s^{-1}	50	1936.3	1950.3	49.3	3298.8	3249.5	901.6

Table 2: Descriptive statistics of the general physico-chemical determinands and total nutrients forms measured in the water samples during JDS 3 in tributaries; additional parameters: chllorophyll "a", suspended solids and measured water discharge. Marked values (*) represent half of the Limit of Quantification reported by the laboratory, according to the provisions of the Directive 2009/90/EC

parameter	*unit*	*N*	*Mean*	*Median*	*Minimum*	*Maximum*	*Range*	*Std.Dev.*
Water temperature (w.t.)	^{0} C	13	20.6	20.9	16.9	24.0	7.1	10.9
pH	-	13	7.96	8.10	6.73	8.35	1.62	5.47
Conductivity (Cond.)	µS.cm^{-1}	13	551	476	295	1122	827	40
Dissolved Oxygen Saturation (DO sat)	%	13	83.4	87.6	48.4	100.7	52.3	18.1
Dissolved Oxygen Concentration (DO conc.)	mg.L^{-1}	13	7.5	7.8	4.3	8.9	4.6	19.0
Total Nitrogen (TN)	mg.L^{-1} N	13	2.21	1.49	0.69	5.77	5.08	78.33
Total Phosphorous (TP)	mg.L^{-1} P	13	0.17	0.11	0.015*	0.55	0.54	92.97
Ammonium (NNH_4)	mg.L^{-1} N	14	0.33	0.02	0.02 *	3.71	3.69	1.25
Nitrite (NNO_2)	mg.L^{-1} N	14	0.033	0.003	0.003 *	0.348	0.345	0.12
Nitrate (NNO_3)	mg.L^{-1} N	14	1.40	1.02	0.02	5.21	5.18	1.64
Ortho-Phosphates (PPO_4)	mg.L^{-1} P	14	0.116	0.060	0.0008 *	0.502	0.501	0.173
Sodium (Na)	mg.L^{-1}	14	32.5	33.1	8.3	71.3	63.0	20.00
Potassium (K)	mg.L^{-1}	14	5.4	5.1	2.1	8.9	6.8	2.23
Calcium (Ca)	mg.L^{-1}	14	55.6	46.6	37.4	190.7	153.4	50.2

parameter	unit	N	Mean	Median	Minimum	Maximum	Range	Std.Dev.
Magnesium (Mg)	mg.L-1	14	16.0	13.8	6.0	38.7	32.7	10.0
Chlorides (Cl)	mg.L-1	14	40.1	32.8	1.1	139.0	137.9	42.6
Sulphates (SO_4)	mg.L-1	14	83.4	46.3	19.7	533.4	513.7	168.1
Chllorophyll - a (Chll. - a)	µg.L-1	13	13.98	8.28	2.88	53.49	50.61	15.85
Suspended Solids (SS)	mg.L-1	12	43.5	28.0	4.0	118.0	114.0	43.4
Water discharge (Q)	$m^3.s^{-1}$	9	162.4	80.2	13.7	493.1	479.4	173.5

3.1 General physico-chemical determinands

3.1.1 Water temperature

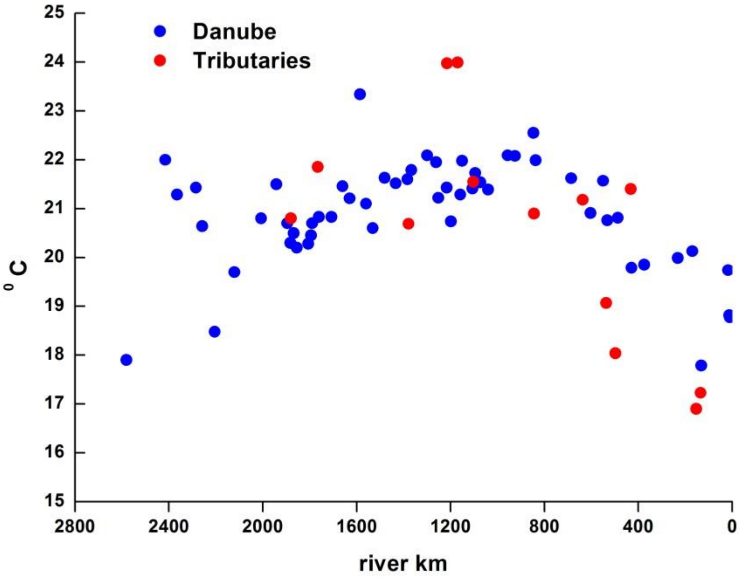


Figure 9: Longitudinal variation of conductivity in water samples during JDS3 in the Danube River and selected tributaries

Water temperature in the Danube River ranged between 17.8 ^{0}C at river km 132 (*Reni*) and 23.3 ^{0}C at river km 1586 (*Rackeve-Soroksar Danube Arm).* In tributaries, the range was slightly larger, between 16.9 ^{0}C in the *Siret* and 24.0 ^{0}C in *Tisa* and *Sava* tributaries. Generally, the variation pattern followed the typical behaviour of this variable during the survey period (August – September) and the daily sampling time.

3.1.2 Conductivity

Figure 10 shows the conductivity values for the Danube River and tributaries during JDS3. In the Upper Danube stretch, conductivity significantly decreased from 566 µS.cm^{-1} at river km 2581 (*Böfinger Halde*) to 320 µS.cm^{-1} at river km 2007 (*Oberloiben*); the rapid change (from 497 to 377 µS.cm^{-1}) occurred at river km 2205 (*Jochenstein*), due to the increased water discharge (from 353.3 m^3.s^{-1} to 886 m^3.s^{-1}); this profile is determined by the influence of the *Inn* tributary, with low salt content and similar flow discharge (Laszlo 2002; Hamchevici and Craciun 2008). In the Middle and Lower Danube stretches, the conductivity remained relatively constant – around 400 µS.cm^{-1} – except for the values recorded in two side arms: *Moson Danube Arm end* – 456 µS.cm^{-1} and *Rackeve - Soroksar Danube Arm* – 358 µS.cm^{-1}. Four tributaries – *Sava, Velika Morava, Iskar* and *Jantra* had conductivity level very similar to the Danube River's, while eight tributaries recorded higher values than the main course, but no influence for the downstream stretch of the Danube was noticed. The maximum level (1122 µS.cm^{-1}) was measured in the *Timok* tributary and the minimum (295 µS.cm^{-1}) was measured in the *Drava*.

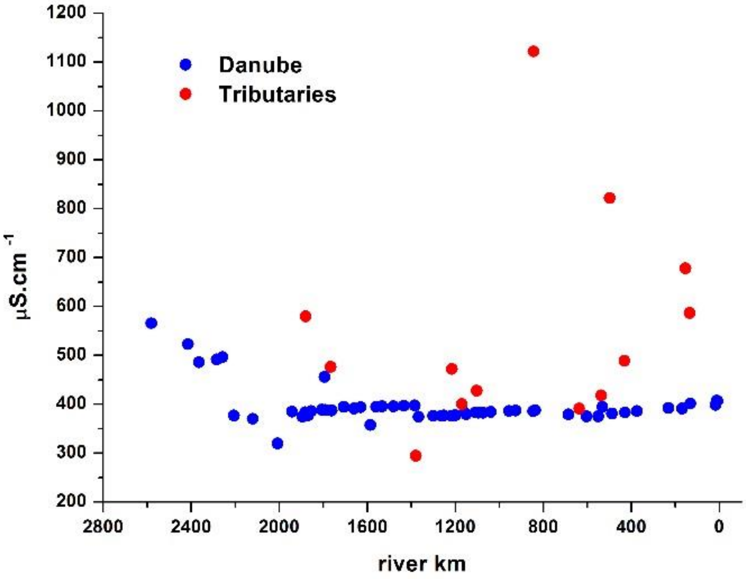


Figure 10: Longitudinal variation of conductivity in water samples during JDS3 in the Danube River and selected tributaries

3.1.3 pH

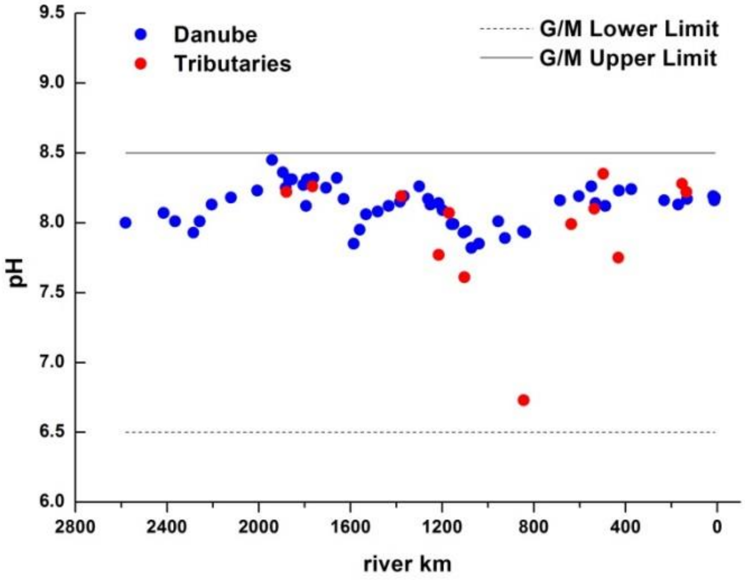


Figure 11: pH variation in water samples during JDS3 in the Danube River and selected tributaries

The pH variation range was rather low in the Danube River (0.63 units), showing a good buffer capacity of the water. Nevertheless, the longitudinal profile showed several fluctuations (Figure 11): in the Upper Danube, pH value increased from 7.93 at river km 2285 (*Deggendorf*) to 8.45 at river km

1942 (*Klostemeuburg*); in the Middle Danube, values slightly below 8.00 (7.85 and 7.95) were measured at river km 1586 (*Rackeve-Soroksar Danube Arm*) and downstream, at river km 1560 (*Dunafoldvar*). A significant decreasing profile appeared in the *Iron Gates reservoir area*, down to 7.82 at river km 1073 (*Banatska Palanka /Bazias*), due to the decomposition of organic matter in slow flowing water stretches and consequently lowering the pH by the produced carbon dioxide. In the Lower Danube, most of the pH values were above 8.00. In tributaries, the variation range was higher than in the Danube itself (1.62 units), with the maximum value (8.35) recorded in the *Russenski Lom*; the minimum value (6.73) was measured in the *Timok* tributary, probably due to the effect of local mining activity.

3.1.4 Dissolved oxygen

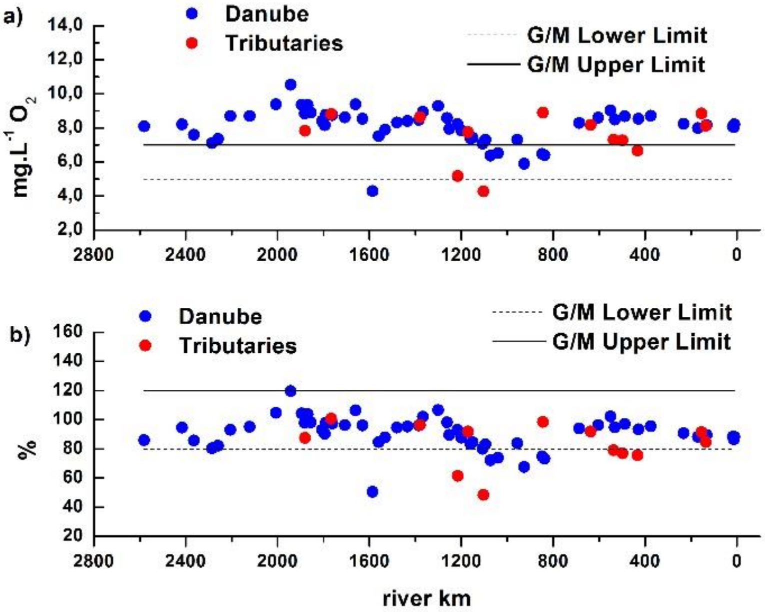


Figure 12: Dissolved Oxygen content - a) concentration and b) saturation – during JDS3 in the Danube River and selected tributaries

The longitudinal profile of the dissolved oxygen content, concentration and saturation respectively (Figure 12 – a,b) is highly similar with that observed for pH, showing a relative good equilibrium between oxygen-consuming processes (decomposition of organic matter and respiration) and oxygen-releasing processes (production and physical transfer from the atmosphere), with most of the saturation levels situated between 80 % and 110 %. In the Danube River, except for two values, all sampling sites were characterised by concentrations above 6.0 mg.L^{-1} with 80% saturation. Oxygen depletion situation (4.3 mg.L^{-1} with 50.6%) appeared at river km 1586 (*Rackeve-Soroksar*), likely due to the high organic pollution in this dammed side arm. Particularly in the *Iron Gates* area, dissolved oxygen saturation fell below 80%, reaching 67.6% downstream the dam, at river km 926 (*Vrbica/Simijan*), this local fluctuation being caused by the increased biodegradation process of organic matter in low-velocity stream. Two tributaries – *Tisa* and *Velika Morava* presented low dissolved oxygen content (5.2 mg.L^{-1} with 61.5% and 4.3 mg.L^{-1} with 48.4% respectively), but the rest of the tributaries showed a similar level compared to the main course of the Danube.

3.2 Nutrients

3.2.1 Total Nitrogen

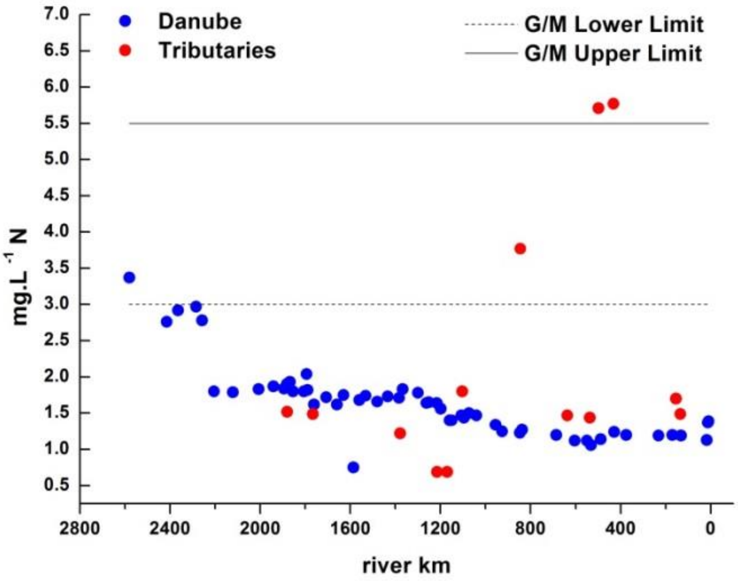


Figure 13: Total Nitrogen concentrations in water samples during JDS3 (the Danube River and selected tributaries)

Figure 13 shows the spatial pattern of the Total Nitrogen concentration in water samples, with a variation range of 2.62 mg.L^{-1} N in the Danube River and 5.08 mg.L^{-1} N in tributaries. A significant decreasing line from Upper towards Middle and Lower Danube is noticed (N=55, $r^2 = 0.6278$, $p<0.0001$). The highest concentrations from the Danube (above 2.50 mg.L^{-1} N) were measured in the first five sampling sites, followed by a pronounced dropping after the river km 2285 (*Mühlau*). Along the middle stretch of the river, Total Nitrogen ranged between 1.40 and 2.04 mg.L^{-1} N, except for the low value (0.75 mg.L^{-1} N) recorded in the *Rackeve-Soroksar Danube Arm*, caused either by strong uptake during biological activity or by denitrification process in this slow-flow area. In the Lower Danube, the Total Nitrogen concentrations fell from 1.50 mg.L^{-1} N at river km 1073 (*Banatska Palanka/Bazias*) to 1.06 mg.L^{-1} N at river km 532 (*downstream Jantra*), the decreasing profile (mainly visible in the *Iron Gates reservoir* stretch) being a direct consequence of the denitrification process in this region. A slight increasing profile was present in the second part of the Lower Danube, up to 1.39 mg.L^{-1} N in the *Sf. Gheorghe arm*, which shows that the Danube Delta itself has no influence in nitrogen retention or loss. All the tributaries sampled in the upper and in the middle stretch of the Danube had concentrations lower than in the Danube, except for the *Velika Morava*, with higher value. Very low concentrations (0.69 mg.L^{-1} N) were found in the *Tisa* and *Sava* tributaries. In the lower stretch, in four tributaries – *Iskar*, *Jantra*, *Siret* and *Prut* – Total Nitrogen concentrations were slightly higher than in the Danube, but in *Timok*, *Russenski Lom* and *Arges* rather elevated levels were measured: 3.77, 5.71 and 5.77 mg.L^{-1} N respectively, most likely caused by the insufficiently treated waste water discharge in these recipients.

3.2.2 Total Phosphorous

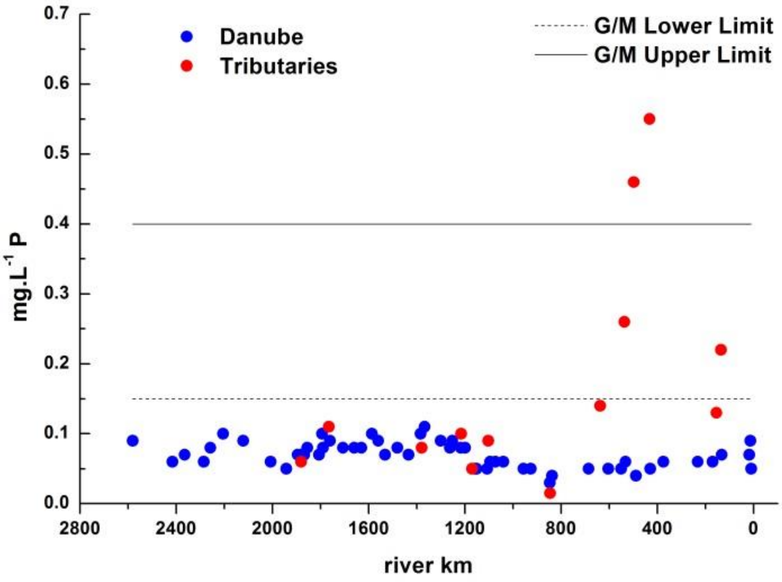


Figure 14: Total Phosphorous concentrations in water samples during JDS3 in the Danube River and selected tributaries

The variation ranges of Total Phosphorous were 0.08 mg.L^{-1} P in the Danube River and 0.54 mg.L^{-1} P in tributaries (Figure 14). Unlike the Total Nitrogen, no systematic spatial trend was recorded along the Danube, but several local fluctuations were present: in the upper stretch, a decreasing line from 0.10 mg.L^{-1} P at river 2205 (*Jochenstein*) to 0.05 mg.L^{-1} P at river km 1942 (*Klostemeuburg*). The concentration level of 0.10 mg.L^{-1} P was reached in the middle stretch in the side arms *Moson Danube* and *Rackeve-Soroksar* and at river km 1384 (*upstream Drava*). The maximum value from the Danube River (0,11 mg.L^{-1} P) was measured at river km 1367 (*downstream Drava (Erdut/Bogojevo)*), but not caused by the confluence with the *Drava* tributary, in which little content of Total Phosphorous was found (0.08 mg.L^{-1} P). In the lower stretch, a strong decreasing profile was noticed after the confluence with the *Tisa* tributary, from 0.08 mg.L^{-1} P at river km 1199 (*downstream Tisa/Upstream Sava (Belegis)*) to 0.05 mg.L^{-1} P at river km 1159 (*upstream Pancevo/downstream Sava*). The minimum concentration (0.03 mg.L^{-1} P) was measured at river km 847 (*upstream Timok (Rudujevac / Gruia)*). This significant declining profile in concentrations comes in good agreement with previous results according to which the *Iron Gates reservoir* and backwaters – as a net sedimentation area – act as a major retention sink for Total Phosphorous (van Gils 2004). Along the rest of the lower stretch, Total Phosphorous concentrations gradually increased up to 0.09 mg.L^{-1} P in the *Sulina arm*, profile which is confirmed by similar previous findings which shows that the delta does not play a major role in Phosphorous retention (van Gils 2004; daNUbs 2005). The selected tributaries from the upper and middle stretches showed similar levels as the main course of the river. In the tributaries from the lower stretch concentrations varied from undetectable level (less than 0.03 mg.L^{-1} P) in *Timok* to the maximum level (0.55 mg.L^{-1} P) in *Arges*. Elevated concentrations were also measured in *Siret, Iskar, Prut, Jantra* and *Russenski Lom*.

3.2.3 Dissolved nutrients forms: ammonium, nitrites, nitrates and ortophosphates

Tables 3 – 6 give the visual quantification along the Danube River and selected tributaries for each measured ion.

Detailed results for dissolved nutrients forms and major ions are given in Tables 16 – 17 from Annex 1 of the Full Report.

Table 3: Visual quantification for ammonium measured in the Danube River and selected tributaries during JDS3 (results in mg.L^{-1} NH_4)

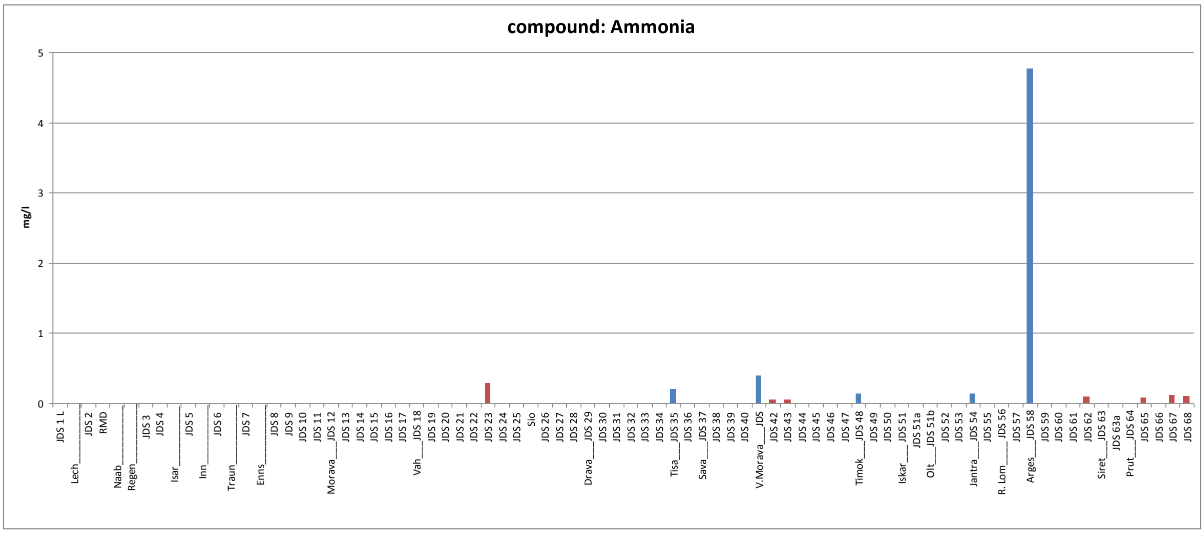


Table 4: Visual quantification for nitrites measured in the Danube River and selected tributaries during JDS3 (results in mg.L^{-1} NO_2)

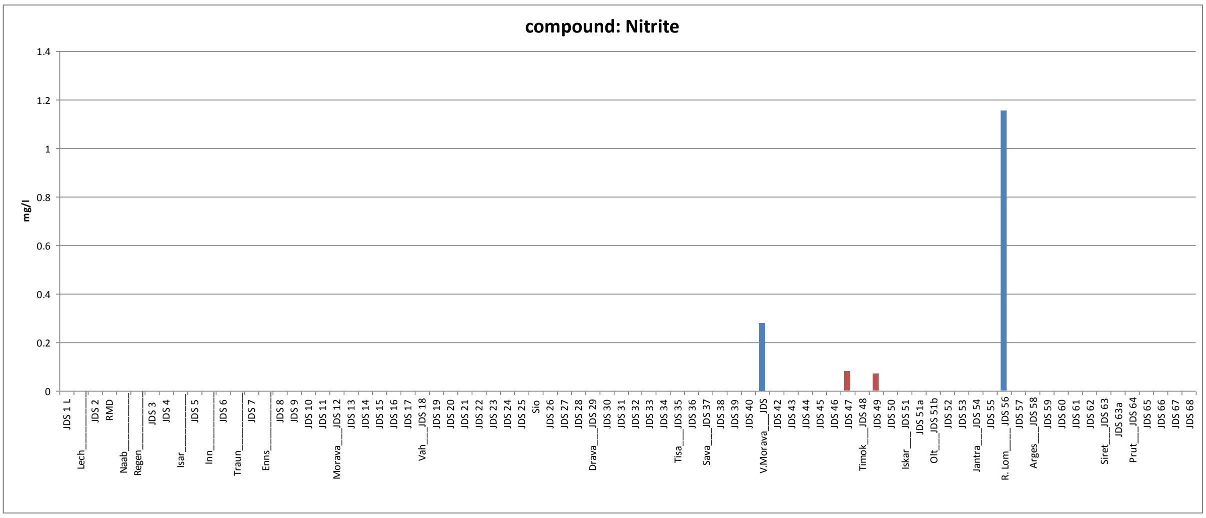


Table 5: Visual quantification for nitrates measured in the Danube River and selected tributaries during JDS3 (results in mg.L^{-1} NO_3)

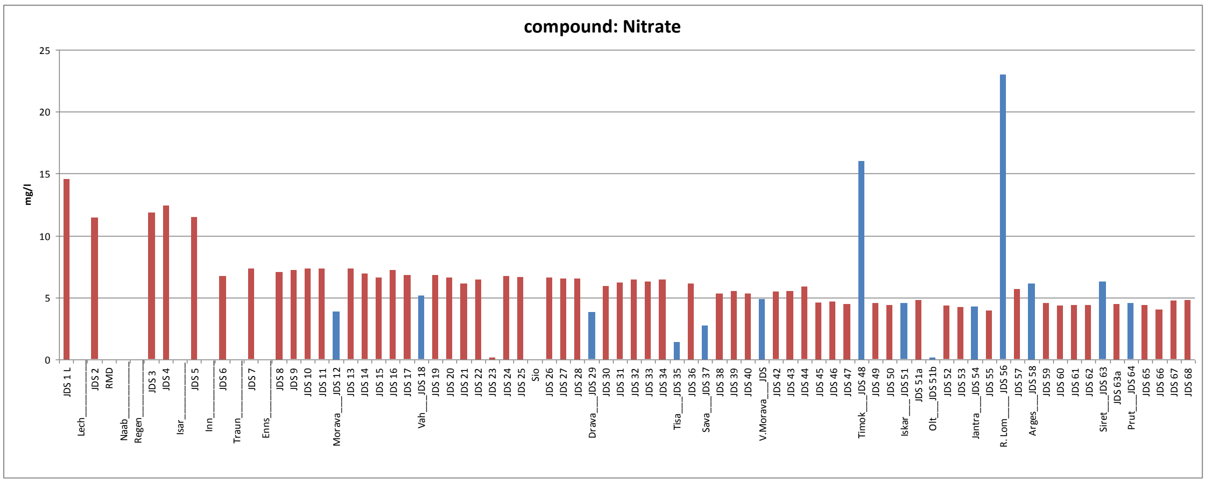
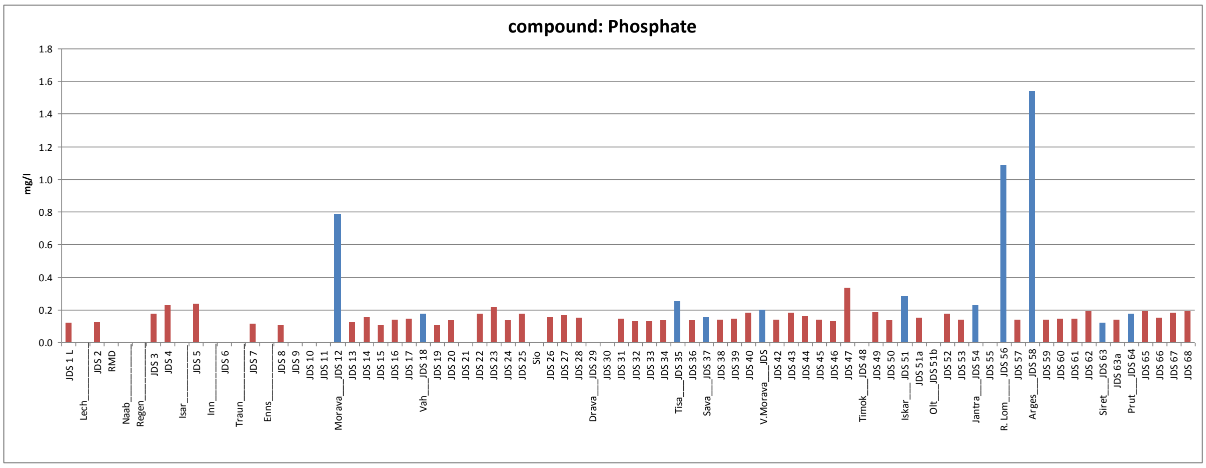


Table 6: Visual quantification for ortho-phosphates measured in the Danube River and selected tributaries during JDS3 (results in mg.L^{-1} PO_4)



The general view of the spatial distribution shows that:

- Most of the sampling sites from the main course of the Danube River (50 out of 57) and nine tributaries presented N-ammonium concentrations below the limit of quantification (0.04 mg.L^{-1} N-NH_4); the maximum values (0.23 mg.L^{-1} N-NH_4 in the Danube and 3.71 mg.L^{-1} N-NH_4 in tributaries) were recorded at river km 1586 (*Rackeve-Soroksar*) and in *Arges* tributary respectively, caused by the high organic pollution in these sites (Table 3).
- All N-nitrites concentrations were below the limit of quantification (0.006 mg.L^{-1} N-NO_2) except for two values measured downstream the *Iron Gates reservoirs* area – 0.024 and 0.021 mg.L^{-1} N-NO_2 at river km 847 (*Upstream Timok (Rudujevac/Gruia)*) and at river km 837 (*Pristol/Novo Selo Harbour*) and two measured in tributaries – 0.08 mg.L^{-1} N-NO2 in *Velika Morava* and 0.35 mg.L^{-1} N-NO_2 in *Jantra* (Table 4).
- N-nitrates concentrations showed a decreasing longitudinal profiles from Upper to Middle and Lower Danube, starting from the maximum value of 3.20 mg.L^{-1} N-NO_3 at river km 2581 (*Böfinger Halde*) to the level of 0.90 mg.L^{-1} N-NO_3 in the Lower Danube. In tributaries, the highest concentrations (3.62 mg.L^{-1} N-NO_3 and 5.21 mg.L^{-1} N-NO_3) were found in *Timok* and *Russenski Lom* respectively (Table 5).
- Ortho-phosphates concentrations presented a scattered spatial profile along the Danube, with a variation range of 0.107 mg.L^{-1} P-PO_4; in tributaries, values below the limit of quantification (0.0008 mg.L^{-1} P-PO_4) were measured in *Drava*, *Timok* and *Olt*, while the most elevated concentrations (0.258, 0.355 and 0.502 mg.L^{-1} P-PO_4) were found in *Morava*, *Russesnki Lom* and *Arges* (Table 6).

3.3 Major Ions

The major ions measured in the Danube River and tributaries ranged within the normal levels given by the local geological, climatic and geographical conditions. Tables 7 – 12 present the visual quantification for major cations and anions measured during JDS3. Rather high values of chlorides (139.0 mg.L^{-1} Cl) and sulphates (533.4 mg.L^{-1} SO_4) were measured in *Olt* and *Timok* tributaries respectively.

Table 7: Visual quantification for sodium measured in the Danube River and selected tributaries during JDS3

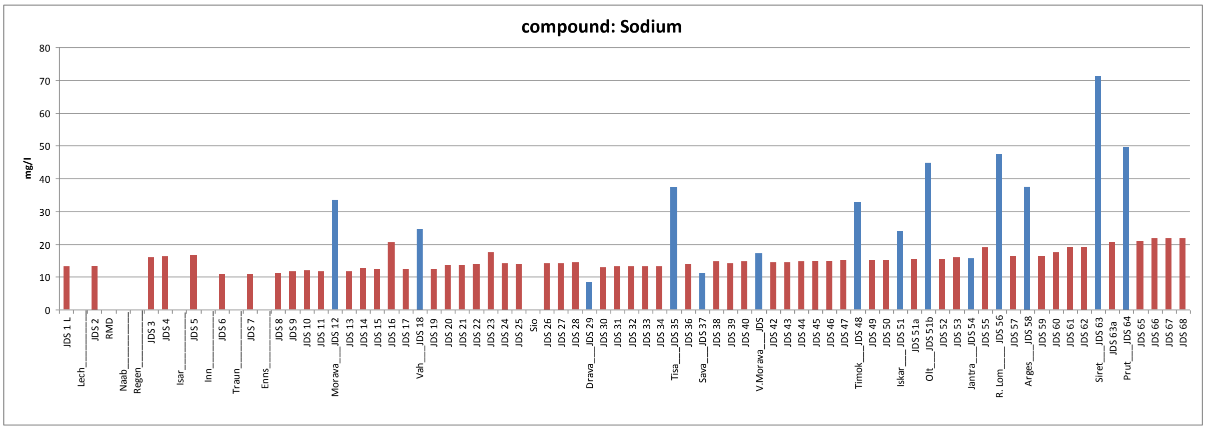


Table 8: Visual quantification for potassium measured in the Danube River and selected tributaries during JDS3

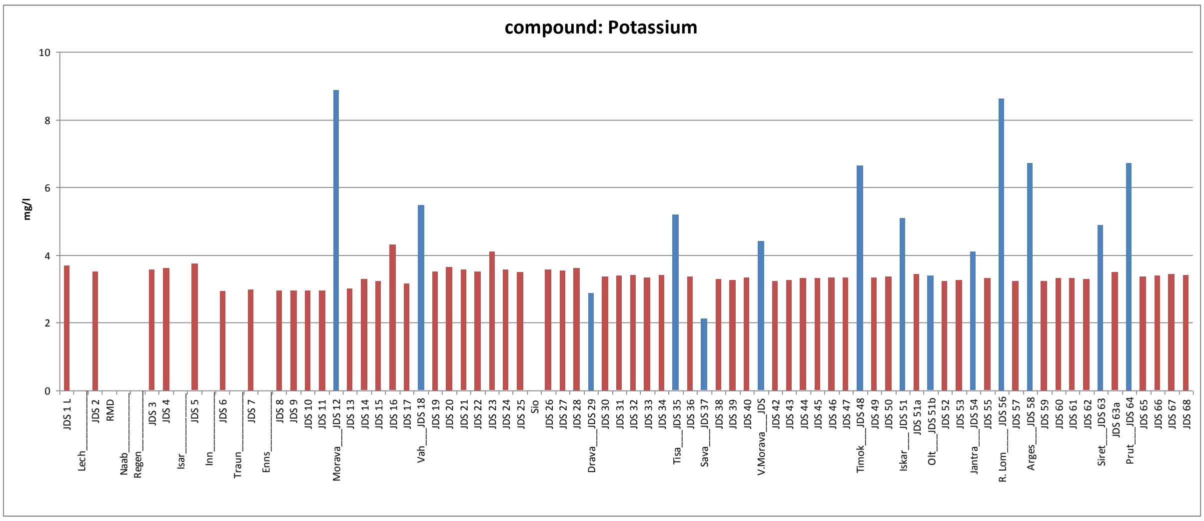


Table 9: Visual quantification for calcium measured in the Danube River and selected tributaries during JDS3

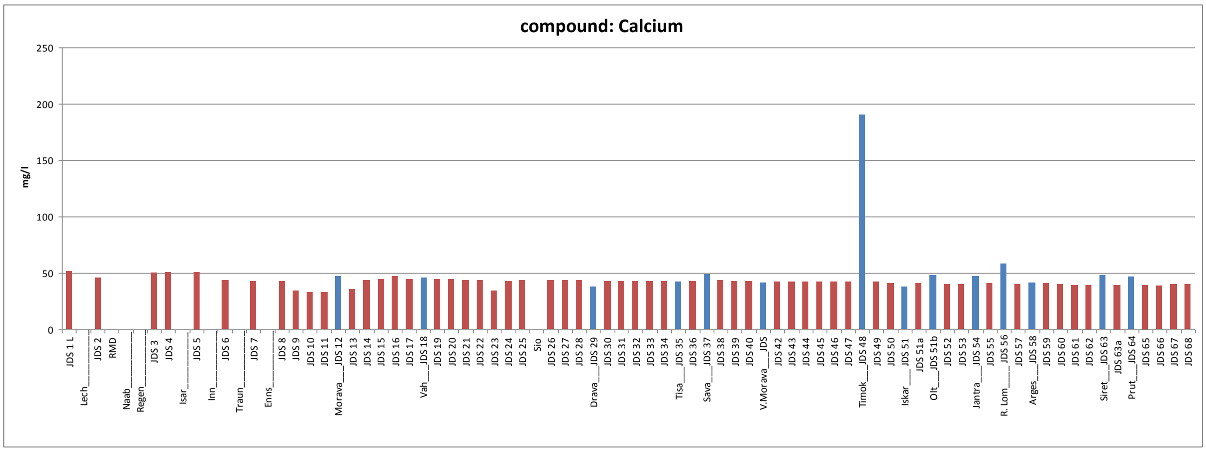


Table 10: Visual quantification for magnesium measured in the Danube River and selected tributaries during JDS3

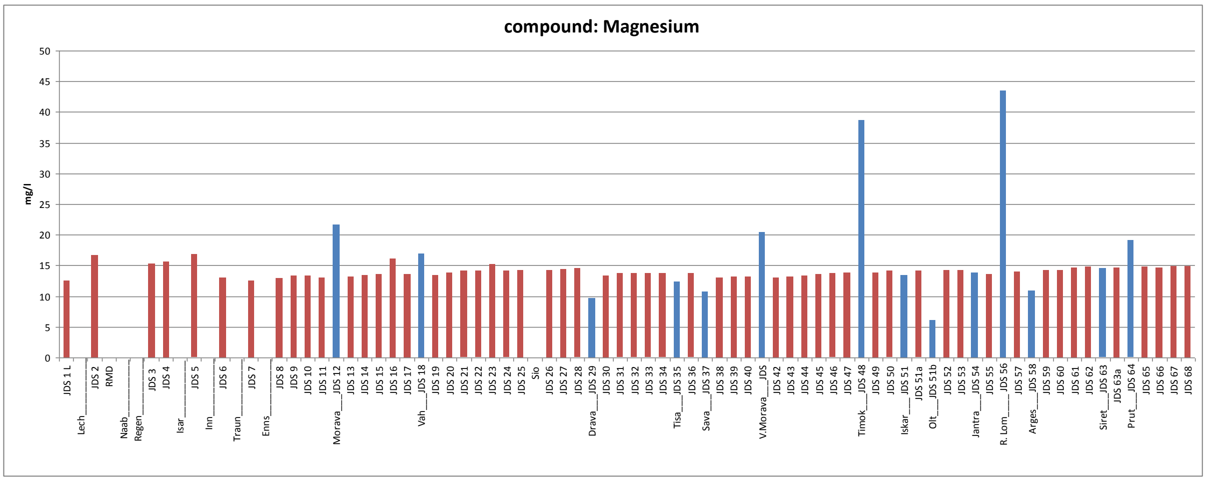


Table 11: Visual quantification for chlorides measured in the Danube River and selected tributaries during JDS3

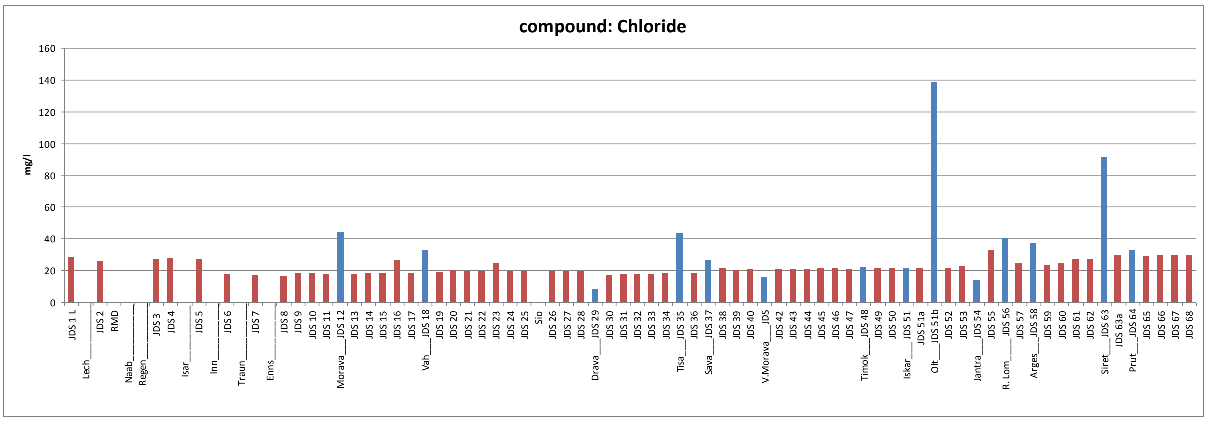
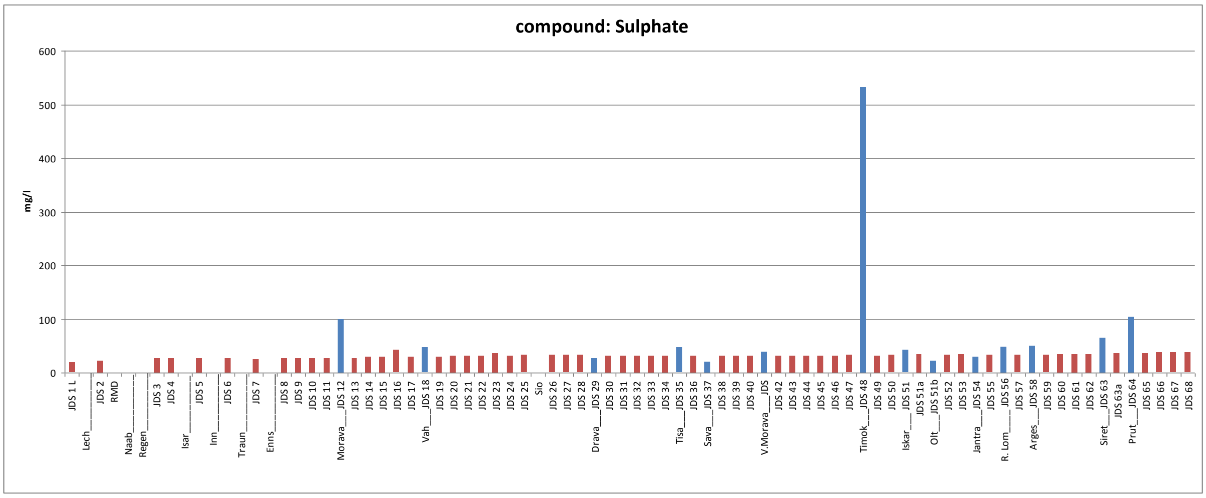


Table 12: Visual quantification for sulphates measured in the Danube River and selected tributaries during JDS3



3.4 Correlation among variables

In order to have a more illustrative view of the interrelation of the selected parameters, the correlation matrix among variables was carried out for the data corresponding to the Danube River only (Table 13). Statistically significant coefficients ($p<0.05$) were found between variables showing causes (nutrients input), biological response of the primary production process (chlorophyll – a) and secondary effects (dissolved oxygen content and pH): positive correlations were obtained between Total Phosphorous and chlorophyll – a (0.489), between chlorophyll – a and both pH and dissolved oxygen saturation (0.516 and 0.634 respectively), while the highest coefficient wad noticed between pH and dissolved oxygen saturation (0.906). Nevertheless, it turned out that the hydrological regime had a strong influence on the investigated elements: the dilution effect was highlighted by the negative significant coefficients between water discharge and conductivity (-0.585), more powerful in the case of Total Nitrogen (-0.720) than in the case of Total Phosphorous (-0.364), for the second nutrient form the adsorption on the suspended solids being demonstrated by the significant positive coefficient (0.535) between these two variables.

Table 13: Correlation matrix for selected physico-chemical indicators and additional parameters (* marked correlations are significant at $p < .05$ for N=50 and case wise deletion of missing data)

parameter	***w.t.***	***pH***	***Cond.***	***DO sat.***	***Total N***	***Total P***	***Chll. a***	***SS***	***Q***
w.t.	1.000								
pH	**-0.335 ***	1.000							
Cond.	0.026	-0.261	1.000						
DO sat.	-0.110	**0.906 ***	-0.230	1.000					
Total N	0.151	-0.026	**0.700 ***	0.119	1.000				
Total P	-0.219	**0.294 ***	0.048	**0.344 ***	**0.323 ***	1.000			
Chll. a	0.254	**0.516 ***	**-0.312 ***	**0.634 ***	0.018	**0.489 ***	1.000		
SS	-0.190	**0.308 ***	-0.275	**0.299 ***	-0.087	**0.535 ***	**0.634 ***	1.000	
Q	0.254	-0.228	**-0.585 ***	-0.232	**-0.720 ***	**-0.364 ***	0.139	0.136	1.000

3.5 Comparison with previous outcomes

One of the specific objectives of the investigative monitoring surveys is to increase the comparability between a homogenous data set produced by a single sampling procedure and laboratory analysis (JDS measurements) and data generated by long-term surveillance type of monitoring (TNMN data) carried out by the basin-wide network of National Reference Laboratories under the ICPDR Monitoring strategy. In order to have an optimal way of data comparison and given the survey timing of JDSs (August – September), the momentary results obtained during the three investigative surveys (JDS1 – 2001, JDS2 – 2007 and JDS3 – 2013) were compared with mean, median and 90-Percentiles of the TNMN data set from August – September during 2001 – 2011 (Yearbooks, 2001 – 2011). Data analysis was carried out for Total Nitrogen and Total Phosphorous, for the common sampling sites of TNMN and JDS located on the main course of the Danube and selected major tributaries (Laszlo 2002; Hamchevici and Craciun 2008). The box-plots shown in Figures 15 (a,b) – 16 (a,b) conclude the followings:

- **Total Nitrogen** (Figure 15 a, b): the general view shows high comparability of the three JDSs with TNMN data for the Danube River. A closer look indicates that the median value of concentrations measured during JDS3 (1.40 mg.L^{-1} N) was lower than the ones from JDS1 and JDS2 (1.82 and 1.67 mg.L^{-1} N) and lower than statistics of the TNMN (1.82, 1.71 and 2.29 mg.L^{-1} N), which generally demonstrates an improvement in Total Nitrogen content in the main course of the river. The median value measured during JDS3 in tributaries (1.49 mg.L^{-1} N) was lower than the one from JDS1 (2.14 mg.L^{-1} N) and the statistics TNMN (2.02, 1.96 and 2.42 mg.L^{-1} N), but slightly higher than in JDS2 (1.26 mg.L^{-1} N). It is important to mention that the Total Nitrogen concentrations in JDS3 in the *Russenski Lom* and *Arges* tributaries were lower than the ones measured during the previous two surveys.
- **Total Phosphorous** (Figure 16 a, b): the same high comparability of the three JDSs with TNMN data for the Danube River is present also in the case of Total Phosphorous. In details, the median value of concentrations measured during JDS3 is the lowest from the three surveys and the TNMN statistics for the Danube River as well as for the selected tributaries. Unlike the Total Nitrogen, Total Phosphorous concentrations measured in JDS3 in the *Russenski Lom* and *Arges* tributaries were higher than the ones measured during JDS1 and JDS2, but still within the non-outlier range given by the 90-Percentiles of the TNMN data (this is valid for

the *Arges* tributary only, for the *Russenski Lom* TNMN data compilation was not carried out because of the data inconsistency).

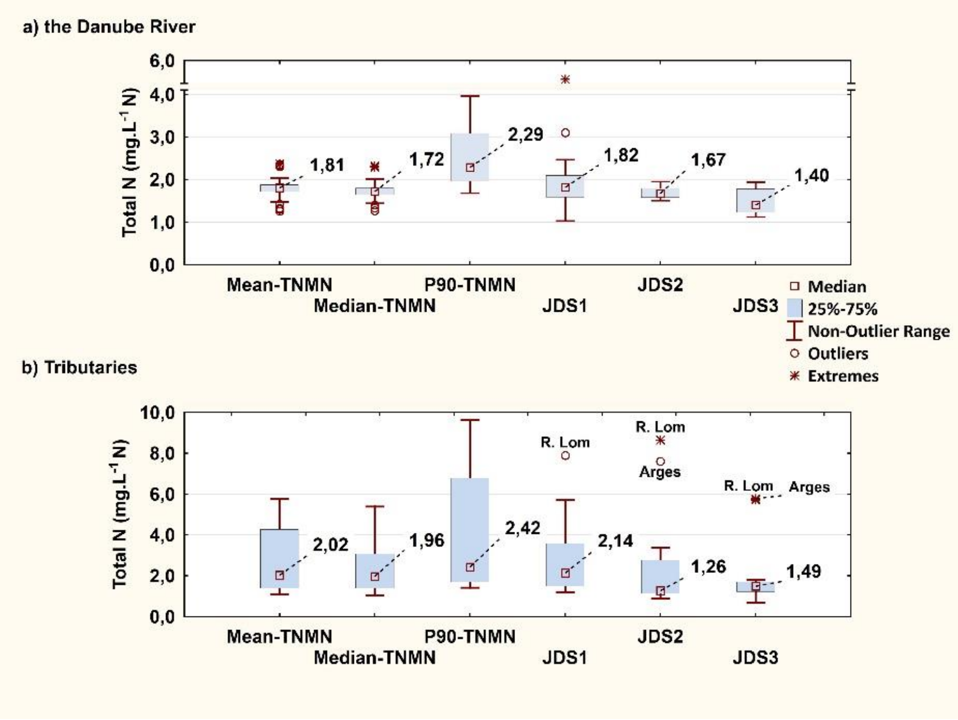


Figure 15: Comparative view of the data from Surveillance Monitoring TNMN (August – September during 2001 – 2011) and Investigative Monitoring (JDS1–2001, JDS2–2007 and JDS3–2013) for Total Nitrogen concentrations in a) the Danube River and b) selected tributaries

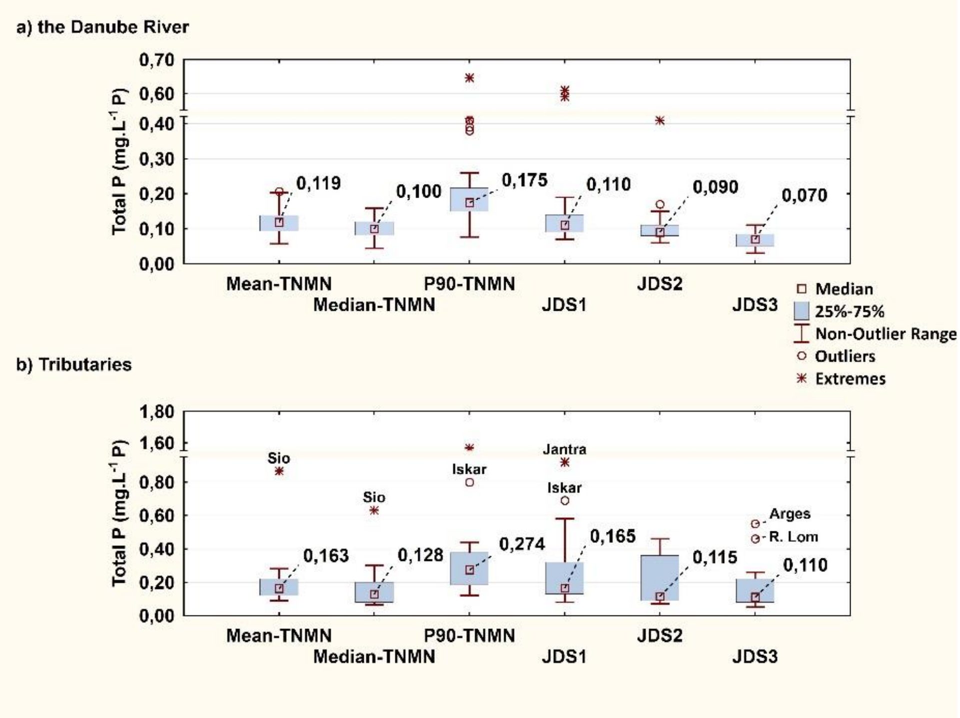


Figure 16: Comparative view of the data from Surveillance Monitoring TNMN (August – September during 2001 – 2011) and Investigative Monitoring (JDS1–2001, JDS2–2007 and JDS3–2013) for Total Phosphorous concentrations in a) the Danube River and b) selected tributaries

3.6 Compliance with Danube relevant environmental quality standards/guiding values

Despite the fact that one single measurement does not give fully reliable information on the ecological status as required by the WFD, a preliminary ecological indication described by the general physico-chemical elements is given below. Due to the lack of harmonisation of the environmental quality standards between ecological classes at the basin wide level for these quality elements, the compliance was made taking into account the ranges (lower – upper limits) of the values reported by the Danube countries (where available) for *high/good* and *good/moderate* classes respectively (Table 14).

Table 14: Compliance intervals for high/good and good/moderate ecological classes as resulted from the environmental quality standards/guiding values reported by the Danube countries

Quality Element	***Parameter***	***High / Good***	***Good / Moderate***
Oxygenation Conditions	DO – concentration (mg.L^{-1})	9.0 – 7.0	7.0 – 5.0
	DO – saturation (%)	80 – 120	
Acidification Status	pH	6.50 – 8.50	
Nutrient Conditions	Total Nitrogen (mg.L^{-1} N)	1.5 – 3.0	3.0 – 5.5
	Total Phosphorous (mg.L^{-1} P)	0.100 – 0.250	0.150 – 0.400
	N-ammonium (mg.L^{-1} N)	0.10 – 0.30	0.20 – 0.70
	N-nitrites (mg.L^{-1} N)	-	0.300
	N-nitrates (mg.L^{-1} N)	1.0 – 4.0	2.0 – 7.0
	P-orthophosphates (mg.L^{-1} P)	0.050 – 0.080	0.080 – 0.200

From Figures 11 – 14 (in which only the critical *good/moderate* boundaries are drawn), the following information is obtained:

- all pH values are within the ”*good*” class for both Danube River and tributaries;
- the compliance results for dissolved oxygen content are different, depending on the quality standard involved: based on the saturation data, five sampling sites located in the *Iron Gates reservoirs* and downstream (JDS43, JDS44, JDS46, JDS47 and JDS49) fall into the ”*moderate*” class, while based on the concentration data, these five sites are still in ”*good*” class. Similar situation is shown in case of four tributaries: *Tisa*, *Jantra*, *Russenski Lom* and *Arges*: ”*moderate*” by saturation and ”*good*” by concentration. The *Rackeve-Soroksar arm* and *Velika Morava* are in ”*moderate*” class based on both concentration and saturation results. The rest of the sites from the main course of the Danube as well as the rest of selected tributaries are in ”*good”* or *”high”* classes based on both parameters;
- all Total Nitrogen and Total Phosphorous concentrations measured in the Danube and in most of the tributaries are characteristic to ”*good*” class, while the values from *Russenski Lom* and *Arges* fall in ”*moderate*” class; similarly, the dissolved nutrients forms put the Danube River and most of the selected tributaries in ”*high*” or ”*good*” class; ”*moderate*” class appears in three tributaries: *Morava* (P-orthophosphates), *Russenski Lom* (N-nitrates and P-orthophosphates) and *Arges* (N-ammonium and P-orthophosphates).

4 Conclusions

- Water temperature measured in the Danube River and in selected major tributaries followed the typical pattern for the timing of the survey (August – September), with larger variation range in tributaries than in the Danube.
- The longitudinal distribution of conductivity in the Danube River showed a strong decreasing line in the upper stretch, followed by a constant profile towards the middle and lower stretches. The dilution effect along the Danube was showed by the significant correlation coefficient of conductivity with water discharge values.

- pH and dissolved oxygen content (high positive correlation) demonstrated a general good balance between primary production and decomposition of organic matter, with most of the oxygen saturation levels situated around equilibrium value. Several local depletions were found in specific areas (dammed *Rackeve-Soroksar* side arm, the *Iron Gates* reservoir) and two tributaries (*Tisa* and *Velika Morava*).
- Total Nitrogen presented a strong decreasing profile from upper to middle and lower stretches of the Danube, significantly negatively correlated with water discharge. The typical lower profile was noticed in the *Iron Gates reservoir*, due to the denitrification process from this area. Most of the selected tributaries presented levels similar to those in the Danube, but elevated concentrations were found in the *Timok*, *Russenski Lom* and *Arges* tributaries.
- No systematic trend in Total Phosphorous concentrations along the Danube River was found; still, a slight decreasing line appeared in the lower stretch of the river, more pronounced in the *Iron Gates reservoir* area, due to the retention of the suspended material on which this nutrient form is adsorbed. Six tributaries at their confluence to the Danube presented higher concentrations than the main course of the river, but no influence on the downstream stretch was noticed.
- The Total Nitrogen and Phosphorous levels measured in the three arms of the Danube Delta come in good agreement to previous findings which showed that the contribution by the Danube Delta in nutrients retention is negligible, because most of the Danube water passes directly to the Black Sea, almost not reaching the Delta itself.
- N-ammonium and N-nitrites showed levels below the limit of quantification in most of the sampling sites; N-nitrates showed a significant decreasing profile from upper to lower Danube, while no specific trend was noticed for P-orthophosphates; rather elevated values were detected in the mouth of *Morava* (P-orthophosphates), *Timok* (N-nitrates), *Jantra* (N-nitrites), *Russenski Lom* (N-nitrates and P-orthophosphates) and *Arges* (N-ammonium and P-orthophosphates).
- Major ions presented levels given by the local geological, climatic and geographical conditions. *Timok* and *Olt* tributaries showed elevated concentrations of sulphates and chlorides respectively.
- Compared with the JDS1 and JDS2 results, Total Nitrogen and Total Phosphorous concentrations measured in the Danube River during JDS3 were lower than in the two previous surveys. For these two nutrients forms, high comparability was found between investigative monitoring data (JDS type) and corresponding data (August – September) from long-term surveillance monitoring (TNMN during 2001 – 2011). This outcome clearly demonstrates that one set of homogenous data produced by a single sampling procedure and laboratory analysis carried out by selected laboratory soundly confirms the on-going harmonisation and improvement of operational activity of the of National Reference Laboratories network and the effectiveness of the Analytical Quality Control (AQC) programme organised by the ICPDR at the basin wide level.
- The ecological indication given by the general physico-chemical quality elements was assessed based on the intervals for *high/good* and *good/moderate* ecological classes as resulted from the environmental quality standards/guiding values reported by the Danube countries. The general view is that most of the sampling sites located on the Danube River belongs to either ”*high*” or ”*good*” class, except for the dammed side arm *Rackeve-Soroksar* and the *Iron Gates reservoir area*, which fall in ”*moderate*” class due to the oxygen depletion. ”*Moderate*” class is also determined by low oxygen saturation and dissolved nutrients forms in several tributaries (Morava, *Tisa, Velika Morava, Jantra, Russenski Lom and Arges*).

As concluding remark the authors of this report wish to thank all contributing persons involved directly and indirectly in this monitoring. The monitoring as described here is a result of a considerable commitment of all partners and laboratories participating and should be brought to the attention of a larger audience.

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6 Annex 1

Table 15: Quality Control for ions analysis

Certified Material	Cl^- mg/l	NO_3^- mg/l	PO_4^{---} µg/l	SO_4^{--} mg/l	Na^+ mg/l	NH_4^+ mg/l	Mg^{++} mg/l	Ca^{++} mg/l	K^+ mg/l
CRM 409 - 1	4.00	4.88		5.13	1.83	1.93	0.41	0.61	0.16
CRM 409 - 2	4.00	4.89		5.23	1.83	1.91	0.40	0.61	0.13
CRM 409 - 3	4.01	4.91		5.24	1.82	1.91	0.40	0.60	0.12
CRM 409 - 4	4.03	4.94		5.18	1.85	1.93	0.38	0.65	0.17
CRM 409 - 5	4.02	4.94		5.22	1.84	1.92	0.38	0.65	0.18
CRM 409 - 6	4.01	4.96		5.21	1.85	1.92	0.38	0.65	0.15
CRM 409 - 7	4.05	4.95		5.23	1.83	1.86	0.35	0.61	0.13
CRM 409 - 8	4.05	4.96		5.22	1.85	1.88	0.34	0.64	0.17
CRM 409 - 9	4.03	4.95		5.22	1.85	1.91	0.37	0.63	0.14
CRM 409 - 10	3.91	4.85		5.69	1.85	1.88	0.37	0.63	0.17
CRM 409 - 11	3.93	4.81		5.12	1.84	1.88	0.37	0.64	0.15
CRM 409 - 12	3.90	4.81		5.04	1.86	1.89	0.38	0.66	0.18
CRM 409 - 13	3.95	4.84		5.11	1.87	1.88	0.38	0.62	0.17
CRM 409 - 14	3.95	4.87		5.11	1.86	1.88	0.38	0.64	0.16
CRM 409 - 15	3.95	4.83		5.14	1.86	1.87	0.38	0.65	0.18
CRM 409 - 16	3.88	4.86		5.13	1.83	1.84	0.39	0.62	0.17
CRM 409 - 17	3.89	4.86		5.14	1.82	1.82	0.38	0.61	0.18
CRM 409 - 18	3.90	4.94		5.18	1.82	1.82	0.38	0.61	0.16
CRM 409 - 19	3.99	4.87		5.19	1.81	1.74	0.38	0.61	0.16
CRM 409 - 20	3.97	4.89		5.10	1.82	1.73	0.38	0.61	0.16
CRM 409 - 21	3.97	4.87		5.15	1.81	1.73	0.38	0.61	0.16
CRM 409 - 22	3.96	4.89		5.14	1.84	1.74	0.38	0.60	0.17
CRM 409 - 23	3.97	4.93		5.11	1.83	1.74	0.38	0.59	0.17
CRM 409 - 24	3.97	4.86		5.15	1.82	1.74	0.38	0.60	0.19
Average	**3.97 ± 0.05**	**4.98 ±0.05**		**5.18 ± 0.12**	**1.84 ± 0.02**	**1.85 ± 0.07**	**0.38 ± 0.01**	**0.62 ± 0.02**	**0.16 ± 0.02**
Certified Value	**4.01 ± 0.07**	**4.84 ±0.06**		**5.11 ± 0.07**	**1.91 ± 0.03**	**1.91 ± 0.04**	**0.3 ± 0.01**	**0.62 ± 0.01**	**0.17 ± 0.01**

Certified Material	Cl$^-$	NO$_3^-$	PO$_4^{---}$	SO$_4^{--}$	Na$^+$	NH$_4^+$	Mg^{++}	Ca^{++}	K$^+$
CRM 617 - 1	27.76	26.27	0.25	27.66	15.99	0.06	7.89	15.28	9.83
CRM 617 - 2	27.77	26.24	0.26	27.64	15.97	0.05	7.95	15.33	9.74
CRM 617 - 3	27.73	26.25	0.26	27.58	15.96	0.04	7.92	15.23	9.34
CRM 617 - 4	27.95	26.40	0.27	27.42	16.19	0.05	7.78	15.18	9.31
CRM 617 - 5	27.95	26.32	0.23	27.37	16.18	0.06	7.86	15.39	9.36
CRM 617 - 6	27.95	26.38	0.25	27.47	16.27	0.08	7.90	15.45	9.35
Average	**27.8 ± 0.11**	**26.3 ±0.07**	**0.25 ± 0.01**	**27.5 ± 0.12**	**16.1 ± 0.14**	**0.06 ± 0.02**	**7.88 ± 0.06**	**15.3 ± 0.1**	**9.49 ± 0.23**
Certified Value	**26.4 ± 0.4**	**25.8 ± 0.5**	**(0.27)**	**26.3 ± 0.5**	**14.6 ± 0.3**	**(0.064)**	**7.32 ± 0.15**	**14.6 ± 0.4**	**9.93 ± 0.26**
ICC DX 621 - 1					193.2	221.8	250.2	490.9	460.2
ICC DX 621 - 2					194.7	221.4	250.0	487.8	457.1
ICC DX 621 - 3					194.0	220.5	251.3	491.0	456.8
ICC DX 621 - 4					207.6	256.5	277.2	523.2	494.6
ICC DX 621 - 5					208.1	255.9	278.2	524.4	487.1
ICC DX 621 - 6					208.1	254.9	278.2	524.5	486.2
ICC DX 621 - 7					205.8	249.0	270.9	517.6	450.0
ICC DX 621 - 8					205.7	250.9	272.6	525.4	466.1
ICC DX 621 - 9					205.2	243.2	269.5	515.5	445.6
ICC DX 621 - 10					209.8	249.3	276.7	526.2	485.0
ICC DX 621 - 11					209.0	247.8	277.5	526.0	481.2
ICC DX 621 - 12					209.4	247.0	277.6	526.9	479.0
ICC DX 621 - 13					209.0	244.0	278.5	519.7	489.3
ICC DX 621 - 14					209.3	242.9	279.6	521.2	491.4
ICC DX 621 - 15					209.5	241.3	279.4	521.4	489.3
Average					**205 ± 6.0**	**243 ± 12.2**	**271 ± 11.1**	**516 ± 14.0**	**475 ± 16.7**
Certified Value					**198**	**248**	**249**	**501**	**497**

Table 16: Analysis results: anions

Local code	Cl^- (Chloride) mg/l	Standard deviation mg/l (n=3)	NO_2^- (Nitrite) mg/l	Standard deviation mg/l (n=3)	NO_3^- (Nitrate) mg/l	Standard deviation mg/l (n=3)	PO_4^{---} (Phosphate) mg/l	Standard deviation mg/l (n=3)	SO_4^{--} (Sulphate) mg/l	Standard deviation mg/l (n=3)
LOD	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.002***	***mg/l***
LOQ	***0.002***	***mg/l***	***0.015***	***mg/l***	***0.004***	***mg/l***	***0.016***	***mg/l***	***0.005***	***mg/l***
JDS_3_1	28.46	± 0.03	< 0.02		14.55	± 0.07	0.11	± 0.02	18.27	± 0.07
JDS_3_2	25.62	± 0.02	< 0.02		11.45	± 0.04	0.12	± 0.01	21.93	± 0.03
JDS_3_3	26.77	± 0.03	< 0.02		11.83	± 0.04	0.17	± 0.01	26.23	± 0.05
JDS_3_4	27.90	± 0.06	< 0.02		12.43	± 0.01	0.22	± 0.01	26.77	± 0.05
JDS_3_5	27.48	± 0.10	< 0.02		11.53	± 0.05	0.23	± 0.01	26.55	± 0.04
JDS_3_6	17.34	± 0.02	< 0.02		6.73	± 0.03	<0.02		27.08	± 0.04
JDS_3_7	17.00	± 0.03	< 0.02		7.31	± 0.04	0.11	± 0.00	24.92	± 0.04
JDS_3_8	16.67	± 0.02	< 0.02		7.04	± 0.04	0.10	± 0.01	26.44	± 0.03
JDS_3_9	17.94	± 0.02	< 0.02		7.15	± 0.02	<0.02		25.91	± 0.08
JDS_3_10	18.08	± 0.04	< 0.02		7.28	± 0.02	<0.02		26.28	± 0.04
JDS_3_11	17.44	± 0.06	< 0.02		7.32	± 0.03	<0.02		25.59	± 0.07
JDS_3_12	44.45	± 0.02	< 0.02		3.89	± 0.01	0.79	± 0.02	98.61	± 0.07
JDS_3_13	17.71	± 0.04	< 0.02		7.32	± 0.03	0.12	± 0.01	26.33	± 0.01
JDS_3_14	18.57	± 0.06	< 0.02		6.94	± 0.02	0.16	± 0.01	29.65	± 0.02
JDS_3_15	18.61	± 0.03	< 0.02		6.61	± 0.03	0.10	± 0.01	28.77	± 0.05
JDS_3_16	26.05	± 0.04	< 0.02		7.18	± 0.03	0.14	± 0.01	42.53	± 0.03
JDS_3_17	18.63	± 0.01	< 0.02		6.75	± 0.03	0.14	± 0.00	28.85	± 0.03
JDS_3_18	32.50	± 0.08	< 0.02		5.15	± 0.03	0.17	± 0.01	45.94	± 0.07
JDS_3_19	18.81	± 0.01	< 0.02		6.81	± 0.03	0.10	± 0.00	29.53	± 0.03
JDS_3_20	20.07	± 0.03	< 0.02		6.56	± 0.03	0.13	± 0.01	31.48	± 0.02

Local code	**Cl$^-$ (Chloride) mg/l**	**Standard deviation mg/l (n=3)**	**NO$_2^-$ (Nitrite) mg/l**	**Standard deviation mg/l (n=3)**	**NO$_3^-$ (Nitrate) mg/l**	**Standard deviation mg/l (n=3)**	**PO$_4^{---}$ (Phosphate) mg/l**	**Standard deviation mg/l (n=3)**	**SO$_4^{--}$ (Sulphate) mg/l**	**Standard deviation mg/l (n=3)**
LOD	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.002***	***mg/l***
LOQ	***0.002***	***mg/l***	***0.015***	***mg/l***	***0.004***	***mg/l***	***0.016***	***mg/l***	***0.005***	***mg/l***
JDS_3_21	19.33	± 0.03	< 0.02		6.14	± 0.03	<0.02		31.06	± 0.04
JDS_3_22	19.70	± 0.03	< 0.02		6.47	± 0.009	0.17	± 0.01	30.56	± 0.04
JDS_3_23	24.88	± 0.03	< 0.02		0.17	± 0.002	0.21	± 0.006	35.09	± 0.02
JDS_3_24	19.66	± 0.08	< 0.02		6.68	± 0.02	0.13	± 0.01	31.34	± 0.03
JDS_3_25	19.33	± 0.03	< 0.02		6.68	± 0.05	0.17	± 0.01	32.25	± 0.02
JDS_3_26	19.52	± 0.01	< 0.02		6.61	± 0.05	0.15	± 0.005	32.50	± 0.28
JDS_3_27	19.55	± 0.03	< 0.02		6.49	± 0.03	0.16	± 0.00	32.02	± 0.08
JDS_3_28	19.63	± 0.01	< 0.02		6.51	± 0.01	0.15	± 0.009	32.39	± 0.04
JDS_3_29	8.19	± 0.01	< 0.02		3.80	± 0.03	<0.02		26.18	± 0.04
JDS_3_30	16.93	± 0.05	< 0.02		5.93	± 0.04	<0.02		30.64	± 0.04
JDS_3_31	17.48	± 0.06	< 0.02		6.17	± 0.01	0.14	± 0.01	31.57	± 0.09
JDS_3_32	17.59	± 0.02	< 0.02		6.42	± 0.01	0.13	± 0.01	31.56	± 0.19
JDS_3_33	17.59	± 0.05	< 0.02		6.23	± 0.07	0.13	± 0.01	31.63	± 0.04
JDS_3_34	17.79	± 0.11	< 0.02		6.43	± 0.02	0.13	± 0.01	31.61	± 0.03
JDS_3_35	43.81	± 0.03	< 0.02		1.41	± 0.01	0.25	± 0.00	46.58	± 0.09
JDS_3_36	18.34	± 0.03	< 0.02		6.13	± 0.02	0.13	± 0.01	31.52	± 0.03
JDS_3_37	26.49	± 0.36	< 0.02		2.73	± 0.03	0.15	± 0.00	19.71	± 0.05
JDS_3_38	20.89	± 0.03	< 0.02		5.30	± 0.04	0.14	± 0.01	30.54	± 0.06
JDS_3_39	20.07	± 0.02	< 0.02		5.55	± 0.03	0.14	± 0.01	30.58	± 0.03
JDS_3_40	20.79	± 0.01	< 0.02		5.33	± 0.05	0.18	± 0.02	31.13	± 0.02
JDS_3_41	15.73	± 0.03	0.28	± 0.01	4.88	± 0.03	0.20	± 0.00	38.16	± 0.04

Local code	**Cl^- (Chloride) mg/l**	**Standard deviation mg/l (n=3)**	**NO_2^- (Nitrite) mg/l**	**Standard deviation mg/l (n=3)**	**NO_3^- (Nitrate) mg/l**	**Standard deviation mg/l (n=3)**	**PO_4^{---} (Phosphate) mg/l**	**Standard deviation mg/l (n=3)**	**SO_4^{--} (Sulphate) mg/l**	**Standard deviation mg/l (n=3)**
LOD	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.002***	***mg/l***
LOQ	***0.002***	***mg/l***	***0.015***	***mg/l***	***0.004***	***mg/l***	***0.016***	***mg/l***	***0.005***	***mg/l***
JDS_3_42	20.69	± 0.09	< 0.02		5.46	± 0.04	0.14	± 0.02	30.61	± 0.01
JDS_3_43	20.53	± 0.02	< 0.02		5.54	± 0.04	0.18	± 0.03	31.07	± 0.01
JDS_3_44	20.80	± 0.03	< 0.02		5.84	± 0.02	0.16	± 0.01	31.31	± 0.04
JDS_3_45	21.39	± 0.03	< 0.02		4.61	± 0.02	0.14	± 0.00	31.10	± 0.02
JDS_3_46	21.50	± 0.00	< 0.02		4.66	± 0.03	0.13	± 0.02	31.11	± 0.03
JDS_3_47	20.80	± 0.03	0.08	± 0.007	4.42	± 0.03	0.33	± 0.01	32.60	± 0.55
JDS_3_48	21.92	± 0.03	< 0.02		16.02	± 0.05	<0.02		533.37	± 0.38
JDS_3_49	21.05	± 0.01	0.07	± 0.002	4.55	± 0.04	0.18	± 0.01	31.38	± 0.06
JDS_3_50	21.08	± 0.14	< 0.02		4.36	± 0.01	0.13	± 0.01	32.52	± 0.02
JDS_3_51	21.30	± 0.02	< 0.02		4.55	± 0.04	0.28	± 0.00	42.29	± 0.05
JDS_3_51a	21.41	± 0.04	< 0.02		4.80	± 0.03	0.15	± 0.02	33.86	± 0.01
JDS_3_51b	139.03	± 0.15	< 0.02		0.11	± 0.007	<0.02		21.65	± 0.05
JDS_3_52	21.03	± 0.04	< 0.02		4.30	± 0.04	0.17	± 0.00	33.29	± 0.22
JDS_3_53	22.65	± 0.04	< 0.02		4.22	± 0.02	0.14	± 0.01	33.37	± 0.06
JDS_3_54	13.99	± 0.02	< 0.02		4.23	± 0.02	0.22	± 0.02	29.09	± 0.07
JDS_3_55	32.58	± 0.02	< 0.02		3.94	± 0.02	<0.02		32.64	± 0.04
JDS_3_56	40.03	± 0.02	1.16	± 0.03	23.04	± 0.04	1.09	± 0.01	47.70	± 3.72
JDS_3_57	24.47	± 0.03	< 0.02		5.68	± 0.01	0.14	± 0.03	33.00	± 0.09
JDS_3_58	37.19	± 0.06	< 0.02		6.11	± 0.02	1.54	± 0.03	49.38	± 0.06
JDS_3_59	23.32	± 0.03	< 0.02		4.49	± 0.03	0.14	± 0.01	33.33	± 0.03
JDS_3_60	24.70	± 0.01	< 0.02		4.34	± 0.01	0.14	± 0.01	33.94	± 0.02

Local code	Cl^- (Chloride) mg/l	Standard deviation mg/l (n=3)	NO_2^- (Nitrite) mg/l	Standard deviation mg/l (n=3)	NO_3^- (Nitrate) mg/l	Standard deviation mg/l (n=3)	PO_4^{---} (Phosphate) mg/l	Standard deviation mg/l (n=3)	SO_4^{--} (Sulphate) mg/l	Standard deviation mg/l (n=3)
LOD	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.001***	***mg/l***	***0.005***	***mg/l***	***0.002***	***mg/l***
LOQ	***0.002***	***mg/l***	***0.015***	***mg/l***	***0.004***	***mg/l***	***0.016***	***mg/l***	***0.005***	***mg/l***
JDS_3_61	27.33	± 0.10	< 0.02		4.38	± 0.06	0.14	± 0.01	34.51	± 0.04
JDS_3_62	27.29	± 0.01	< 0.02		4.40	± 0.03	0.19	± 0.01	34.77	± 0.06
JDS_3_63	90.90	± 0.01	< 0.02		6.28	± 0.00	0.12	± 0.01	65.65	± 0.05
JDS_3_63a	29.09	± 0.03	< 0.02		4.43	± 0.01	0.14	± 0.02	35.77	± 0.03
JDS_3_64	33.18	± 0.04	< 0.02		4.50	± 0.02	0.17	± 0.00	103.50	± 0.08
JDS_3_65	28.90	± 0.01	< 0.02		4.42	± 0.04	0.19	± 0.02	36.08	± 0.07
JDS_3_66	29.67	± 0.01	< 0.02		4.00	± 0.05	0.15	± 0.004	36.47	± 0.04
JDS_3_67	29.93	± 0.04	< 0.02		4.70	± 0.01	0.18	± 0.02	36.71	± 0.02
JDS_3_68	29.58	± 0.03	< 0.02		4.77	± 0.01	0.19	± 0.01	36.74	± 0.06

Table 17: Analysis results: cations

Local code	Na^+ (Sodium) mg/l	Standard deviation mg/l (n=3)	NH_4^+ (Ammonia) mg/l	Standard deviation mg/l (n=3)	Mg^{++} (Magnesium) mg/l	Standard deviation mg/l (n=3)	Ca^{++} (Calcium) mg/l	Standard deviation mg/l (n=3)	K^+ (Potassium) mg/l	Standard deviation mg/l (n=3)
LOD	***0.007***	***mg/l***	***0.016***	***mg/l***	***0.001***	***mg/l***	***0.084***	***mg/l***	***0.007***	***mg/l***
LOQ	***0.020***	***mg/l***	***0.048***	***mg/l***	***0.002***	***mg/l***	***0.253***	***mg/l***	***0.021***	***mg/l***
JDS_3_1	13.21	± 0.04	< 0.05		12.54	± 0.03	51.24	± 0.07	3.69	± 0.04
JDS_3_2	13.24	± 0.02	< 0.05		16.68	± 0.00	45.58	± 0.03	3.51	± 0.04
JDS_3_3	15.77	± 0.02	< 0.05		15.30	± 0.03	50.22	± 0.01	3.56	± 0.02
JDS_3_4	16.19	± 0.05	< 0.05		15.63	± 0.01	50.42	± 0.02	3.62	± 0.04
JDS_3_5	16.70	± 0.01	< 0.05		16.78	± 0.01	50.60	± 0.03	3.74	± 0.05
JDS_3_6	10.80	± 0.04	< 0.05		13.03	± 0.03	43.20	± 0.04	2.92	± 0.03
JDS_3	10.8	± 0.02	< 0.05		12.51	± 0.00	42.41	± 0.02	2.99	± 0.01

Local code	**Na$^+$ (Sodium) mg/l**	**Standard deviation mg/l (n=3)**	**NH$_4^+$ (Ammonia) mg/l**	**Standard deviation mg/l (n=3)**	**Mg^{++} (Magnesium) mg/l**	**Standard deviation mg/l (n=3)**	**Ca^{++} (Calcium) mg/l**	**Standard deviation mg/l (n=3)**	**K$^+$ (Potassium) mg/l**	**Standard deviation mg/l (n=3)**
LOD	***0.007***	***mg/l***	***0.016***	***mg/l***	***0.001***	***mg/l***	***0.084***	***mg/l***	***0.007***	***mg/l***
LOQ	***0.020***	***mg/l***	***0.048***	***mg/l***	***0.002***	***mg/l***	***0.253***	***mg/l***	***0.021***	***mg/l***
_7	9									
JDS_3_8	11.00	± 0.02	< 0.05		12.84	± 0.02	43.07	± 0.05	2.95	± 0.01
JDS_3_9	11.61	± 0.01	< 0.05		13.36	± 0.01	34.32	± 0.05	2.94	± 0.01
JDS_3_10	11.83	± 0.02	< 0.05		13.33	± 0.01	32.93	± 0.10	2.96	± 0.01
JDS_3_11	11.48	± 0.04	< 0.05		13.03	± 0.03	32.80	± 0.04	2.96	± 0.02
JDS_3_12	33.43	± 0.03	< 0.05		21.67	± 0.01	47.22	± 0.01	8.88	± 0.02
JDS_3_13	11.63	± 0.03	< 0.05		13.19	± 0.03	35.69	± 0.04	3.00	± 0.02
JDS_3_14	12.48	± 0.03	< 0.05		13.45	± 0.01	43.75	± 0.01	3.29	± 0.01
JDS_3_15	12.30	± 0.02	< 0.05		13.58	± 0.00	44.29	± 0.02	3.24	± 0.02
JDS_3_16	20.36	± 0.03	< 0.05		16.11	± 0.02	46.77	± 0.03	4.30	± 0.03
JDS_3_17	12.34	± 0.02	< 0.05		13.63	± 0.00	44.29	± 0.01	3.17	± 0.05
JDS_3_18	24.68	± 0.03	< 0.05		16.87	± 0.05	45.72	± 0.06	5.48	± 0.07
JDS_3_19	12.32	± 0.08	< 0.05		13.40	± 0.03	44.09	± 0.05	3.51	± 0.12
JDS_3_20	13.62	± 0.05	< 0.05		13.79	± 0.01	43.97	± 0.03	3.63	± 0.02
JDS_3_21	13.58	± 0.03	< 0.05		14.08	± 0.03	43.64	± 0.06	3.57	± 0.02
JDS_3_22	13.73	± 0.003	< 0.05		14.10	± 0.02	43.20	± 0.01	3.52	± 0.06
JDS_3_23	17.48	± 0.03	0.29	± 0.01	15.18	± 0.03	33.86	± 0.05	4.09	± 0.02
JDS_3_24	13.99	± 0.02	< 0.05		14.13	± 0.03	43.09	± 0.01	3.55	± 0.03
JDS_3_25	13.92	± 0.02	< 0.05		14.19	± 0.02	43.78	± 0.04	3.49	± 0.05
JDS_3_26	14.11	± 0.03	< 0.05		14.27	± 0.03	43.52	± 0.06	3.55	± 0.01
JDS_3_27	14.21	± 0.04	< 0.05		14.39	± 0.02	43.67	± 0.11	3.54	± 0.05
JDS_3_28	14.29	± 0.01	< 0.05		14.50	± 0.02	43.68	± 0.02	3.62	± 0.03

Local code	**Na$^+$ (Sodium) mg/l**	**Standard deviation mg/l (n=3)**	**NH$_4^+$ (Ammonia) mg/l**	**Standard deviation mg/l (n=3)**	**Mg^{++} (Magnesium) mg/l**	**Standard deviation mg/l (n=3)**	**Ca^{++} (Calcium) mg/l**	**Standard deviation mg/l (n=3)**	**K$^+$ (Potassium) mg/l**	**Standard deviation mg/l (n=3)**
LOD	***0.007***	***mg/l***	***0.016***	***mg/l***	***0.001***	***mg/l***	***0.084***	***mg/l***	***0.007***	***mg/l***
LOQ	***0.020***	***mg/l***	***0.048***	***mg/l***	***0.002***	***mg/l***	***0.253***	***mg/l***	***0.021***	***mg/l***
JDS_3_29	8.25	± 0.02	< 0.05		9.63	± 0.00	37.35	± 0.05	2.87	± 0.04
JDS_3_30	12.88	± 0.02	< 0.05		13.36	± 0.04	42.43	± 0.02	3.37	± 0.04
JDS_3_31	13.12	± 0.03	< 0.05		13.65	± 0.02	42.54	± 0.03	3.40	± 0.04
JDS_3_32	13.11	± 0.00	< 0.05		13.68	± 0.01	42.57	± 0.03	3.41	± 0.03
JDS_3_33	13.08	± 0.00	< 0.05		13.69	± 0.01	42.59	± 0.02	3.34	± 0.03
JDS_3_34	13.11	± 0.04	< 0.05		13.72	± 0.02	42.50	± 0.03	3.40	± 0.00
JDS_3_35	37.29	± 0.07	0.20	± 0.00	12.31	± 0.01	41.84	± 0.02	5.19	± 0.03
JDS_3_36	13.84	± 0.04	< 0.05		13.68	± 0.01	42.54	± 0.04	3.36	± 0.03
JDS_3_37	11.07	± 0.03	< 0.05		10.74	± 0.02	48.34	± 0.02	2.12	± 0.05
JDS_3_38	14.64	± 0.01	< 0.05		13.03	± 0.01	43.13	± 0.03	3.29	± 0.02
JDS_3_39	14.11	± 0.01	< 0.05		13.16	± 0.02	42.84	± 0.04	3.25	± 0.02
JDS_3_40	14.68	± 0.02	< 0.05		13.18	± 0.03	42.84	± 0.02	3.34	± 0.02
JDS_3_41	17.16	± 0.01	0.39	± 0.01	20.43	± 0.02	41.15	± 0.02	4.40	± 0.06
JDS_3_42	14.32	± 0.02	0.05	± 0.01	12.98	± 0.02	42.10	± 0.03	3.23	± 0.03
JDS_3_43	14.31	± 0.04	0.05	± 0.004	13.17	± 0.02	41.93	± 0.01	3.26	± 0.03
JDS_3_44	14.67	± 0.01	< 0.05		13.33	± 0.01	41.94	± 0.04	3.32	± 0.01
JDS_3_45	14.89	± 0.04	< 0.05		13.61	± 0.00	42.05	± 0.02	3.31	± 0.03
JDS_3_46	14.90	± 0.03	< 0.05		13.75	± 0.02	42.04	± 0.02	3.33	± 0.01
JDS_3_47	14.98	± 0.01	< 0.05		13.86	± 0.01	41.73	± 0.04	3.34	± 0.03
JDS_3_48	32.79	± 0.04	0.14	± 0.002	38.68	± 0.07	190.74	± 0.42	6.63	± 0.06
JDS_3_49	15.03	± 0.03	< 0.05		13.81	± 0.02	41.93	± 0.03	3.32	± 0.02
JDS_3_50	15.14	± 0.02	< 0.05		14.12	± 0.01	40.67	± 0.05	3.37	± 0.02

Local code	Na$^+$ (Sodium) mg/l	Standard deviation mg/l (n=3)	NH$_4^+$ (Ammonia) mg/l	Standard deviation mg/l (n=3)	Mg^{++} (Magnesium) mg/l	Standard deviation mg/l (n=3)	Ca^{++} (Calcium) mg/l	Standard deviation mg/l (n=3)	K$^+$ (Potassium) mg/l	Standard deviation mg/l (n=3)
LOD	***0.007***	***mg/l***	***0.016***	***mg/l***	***0.001***	***mg/l***	***0.084***	***mg/l***	***0.007***	***mg/l***
LOQ	***0.020***	***mg/l***	***0.048***	***mg/l***	***0.002***	***mg/l***	***0.253***	***mg/l***	***0.021***	***mg/l***
JDS_3_51	23.80	± 0.03	< 0.05		13.40	± 0.03	37.48	± 0.04	5.08	± 0.01
JDS_3_51a	15.25	± 0.01	< 0.05		14.14	± 0.02	40.45	± 0.01	3.43	± 0.02
JDS_3_51b	44.82	± 0.05	< 0.05		6.00	± 0.02	48.04	± 0.03	3.38	± 0.09
JDS_3_52	15.44	± 0.01	< 0.05		14.29	± 0.00	39.85	± 0.01	3.22	± 0.03
JDS_3_53	15.88	± 0.03	< 0.05		14.23	± 0.03	39.60	± 0.01	3.26	± 0.00
JDS_3_54	15.70	± 0.02	0.14	± 0.002	13.78	± 0.03	46.87	± 0.02	4.10	± 0.03
JDS_3_55	18.84	± 0.02	< 0.05		13.64	± 0.01	40.29	± 0.03	3.31	± 0.01
JDS_3_56	47.19	± 0.12	< 0.05		n.a.		58.03	± 0.02	8.61	± 0.05
JDS_3_57	16.39	± 0.05	< 0.05		14.02	± 0.01	40.19	± 0.03	3.22	± 0.03
JDS_3_58	37.54	± 0.08	4.76	± 0.04	10.84	± 0.003	41.09	± 0.01	6.73	± 0.02
JDS_3_59	16.23	± 0.04	< 0.05		14.28	± 0.01	40.36	± 0.11	3.24	± 0.01
JDS_3_60	17.30	± 0.03	< 0.05		14.30	± 0.01	40.11	± 0.04	3.32	± 0.01
JDS_3_61	19.07	± 0.04	< 0.05		14.67	± 0.02	39.30	± 0.04	3.30	± 0.02
JDS_3_62	19.21	± 0.04	0.08	± 0.003	14.80	± 0.01	38.92	± 0.03	3.28	± 0.01
JDS_3_63	71.29	± 0.15	< 0.05		14.52	± 0.02	47.94	± 0.05	4.88	± 0.01
JDS_3_63a	20.54	± 0.03	< 0.05		14.60	± 0.03	39.33	± 0.03	3.49	± 0.06
JDS_3_64	49.68	± 0.20	< 0.05		19.12	± 0.02	46.26	± 0.04	6.71	± 0.02
JDS_3_65	20.80	± 0.03	0.07	± 0.001	14.82	± 0.01	39.26	± 0.03	3.37	± 0.00
JDS_3_66	21.69	± 0.03	< 0.05		14.61	± 0.02	38.62	± 0.03	3.39	± 0.01
JDS_3_67	21.76	± 0.04	0.10	± 0.000	14.92	± 0.01	39.78	± 0.01	3.43	± 0.00
JDS_3_68	21.64	± 0.04	0.10	± 0.002	14.92	± 0.01	39.88	± 0.03	3.41	± 0.00