Water Quality in the Danube River Basin - 2015

TNMN – Yearbook 2015

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1. Introduction

1.1 History of the TNMN

In June 1994, the Convention on Cooperation for the Protection and Sustainable Use of the Danube River (DRPC) was signed in Sofia, coming into force in October 1998 with the main objectives of achieving sustainable and equitable water management, including the conservation, improvement and the rational use of surface and ground waters in the Danube catchment area. The DRPC also emphasizes that the Contracting Parties shall cooperate in the field of monitoring and assessment. In this respect, the operation of the Trans National Monitoring Network (TNMN) in the Danube River Basin aims to contribute to the implementation of the DRPC. This Yearbook reports on results of the basin-wide monitoring programme and presents TNMN evaluated data for 2010.

The TNMN has been in operation since 1996, although the first steps towards its creation were taken about ten years earlier. In December 1985 the governments of the Danube riparian countries signed the Bucharest Declaration. The Declaration had as one of its objectives to observe the development of the water quality of the Danube, and in order to comply with this objective, a monitoring programme containing 11 cross-sections of the Danube River was established.

1.2 Revision of the TNMN to meet the objectives of EU WFD

The original objective of the TNMN was to strengthen the existing network set up by the Bucharest Declaration, to enable a reliable and consistent trend analysis for concentrations and loads of priority pollutants, to support the assessment of water quality for water use and to assist in the identification of major pollution sources.

In 2000, having the experience of the TNMN operation, the main objective of the TNMN was reformulated: to provide a structured and well-balanced overall view of the status and long-term development of quality and loads in terms of relevant constituents in the major rivers of the Danube Basin in an international context.

Implementation of the EU Water Framework Directive (2000/60/EC, short WFD) after 2000 necessitated the revision of the TNMN in the Danube River Basin District. In line with the WFD implementation timeline, the revision process has been completed in 2007.

The major objective of the revised TNMN is to provide an overview of the overall status and long-term changes of surface water and – where necessary – groundwater status in a basin-wide context with a particular attention paid to the transboundary pollution load. In view of the link between the nutrient loads of the Danube and the eutrophication of the Black Sea, it is necessary to monitor the sources and pathways of nutrients in the Danube River Basin District and the effects of measures taken to reduce the nutrient loads into the Black Sea.

To meet the requirements of both EU WFD and the Danube River Protection Convention the revised TNMN for surface waters consists of following elements:

- Surveillance monitoring I: Monitoring of surface water status

- Surveillance monitoring II: Monitoring of specific pressures
- Operational monitoring
- Investigative monitoring

Surveillance monitoring II is a joint monitoring activity of all ICPDR Contracting Parties that produces annual data on concentrations and loads of selected parameters in the Danube and major tributaries.

Surveillance monitoring I and the operational monitoring is based on collection of the data on the status of surface water and groundwater bodies in the DRB District to be published in the DRBM Plan once in six years.

Investigative monitoring is primarily a national task but at the basin-wide level the concept of Joint Danube Surveys was developed to carry out investigative monitoring as needed, e.g. for harmonization of the existing monitoring methodologies, filling the information gaps in the monitoring networks operating in the DRB, testing new methods or checking the impact of "new" chemical substances in different matrices. Joint Danube Surveys are carried out every 6 years.

A new element of the revised TNMN is monitoring of groundwater bodies of basin-wide importance. More information on this issue is provided in the respective chapter in this Yearbook.

This Yearbook presents the results of the Surveillance monitoring II: Monitoring of specific pressures.

2. Description of the TNMN Surveillance Monitoring II: Monitoring of specific pressures

2.1 Objectives

Surveillance Monitoring II aims at long-term monitoring of specific pressures of basin-wide importance. Selected quality elements are monitored annually. Such denser monitoring programme is needed to identify the specific pressures in the Danube River Basin District in order to allow a sound and reliable long-term trend assessment of specific quality elements and to achieve a sound estimation of pollutant loads being transferred across states of Contracting Parties and into the Black Sea.

Surveillance Monitoring II is based on the set-up of the original TNMN and is fitted to respond to pressures of basin-wide importance. The monitoring network is based on the national monitoring networks and the operating conditions are harmonized between the national and basin-wide levels to minimise the efforts and maximise the benefits.

2.2 Selection of monitoring sites

The selection of monitoring sites is based on the following criteria:

- Monitoring sites that have been monitored in the past and are therefore suitable for long-term trend analysis; these include sites
    - located just upstream/downstream of an international border,

- located upstream of confluences between Danube and main tributaries or main tributaries and larger sub-tributaries (to enable estimation of mass balances),
- located downstream of the major point sources,
- located to control important water uses.

- Sites required to estimate pollutant loads (e.g. of nutrients or priority pollutants) which are transferred across boundaries of Contracting Parties, and which are transferred into the marine environment.

The sites are located in particular on the Danube and its major primary or secondary tributaries near crossing boundaries of the Contracting Parties. List of monitoring sites is in the Table 1.

Table 1: List of monitoring sites

No.	Country code	TNMN code	River	Name of site	Loca-tions	x-coord	y-coord	River-km	Alti-tude	Catch-ment
1	DE	DE2	Danube	Jochenstein	M	13.703	48.520	2 204	290	77 086
2	DE	DE5	Danube	Dillingen	L	10.499	48.568	2 538	420	11 315
3	DE	DE3	/Inn	Kirchdorf	M	12.126	47.782	195	452	9 905
4	DE	DE4	/Inn/Salzach	Laufen	L	12.933	47.940	47	390	6 113
5	AT	AT1	Danube	Jochenstein	M	13.703	48.521	2 204	290	77 086
6	AT	AT5	Danube	Enghagen	R	14.512	48.240	2 113	241	84 869
7	AT	AT3	Danube	Wien-Nussdorf	R	16.371	48.262	1 935	159	101 700
8	AT	AT6	Danube	Hainburg	R	16.993	48.164	1 879	136	130 759
9	CZ	CZ1	/Morava	Lanzhot	M	16.989	48.687	79	150	9 725
10	CZ	CZ2	/Morava/Dyje	Pohansko	M	16.885	48.723	17	155	12 540
11	SK	SK1	Danube	Bratislava	LMR	17.107	48.138	1 869	128	131 329
12	SK	SK2	Danube	Medveďov	M	17.652	47.794	1 806	108	132 168
13	SK	SK4	/Váh	Komárno	M	18.142	47.761	1.5	106	19 661
14	SK	SK5	Danube	Szob	LMR	18.890	47.805	1 707	100	183 350
15	SK	SK6	/Morava	Devín	M	16.976	48.188	1	145	26 575
16	SK	SK7	/Hron	Kamenica	M	18.723	47.826	1.7	114	5 417
17	SK	SK8	/Ipeľ	Salka	M	18.763	47.886	12	110	5 060
18	HU	HU1	Danube	Medvedov	M	17.652	47.792	1 806	108	131 605
19	HU	HU2	Danube	Komarom	LMR	18.121	47.751	1 768	101	150 820
20	HU	HU3	Danube	Szob	LMR	18.860	47.811	1 708	100	183 350
21	HU	HU4	Danube	Dunafoldvar	LMR	18.934	46.811	1 560	89	188 700
22	HU	HU5	Danube	Hercegszanto	LMR	18.814	45.909	1 435	79	211 503
23	HU	HU6	/Sio	Szekszard-Palank	M	18.720	46.380	13	85	14 693
24	HU	HU7	/Drava	Dravaszabolcs	M	18.200	45.784	78	92	35 764
25	HU	HU8	/Tisza/Sajo	Sajopuspoki	M	20.340	48.283	124	148	3 224
26	HU	HU9	/Tisza	Tiszasziget	LMR	20.105	46.186	163	74	138 498
27	HU	HU10	/Tisza	Tiszabecs	M	22.831	48.104	757	114	9707
28	HU	HU11	/Tisza/Szamos	Csenger	M	22.693	47.841	45	113	15283
29	HU	HU12	/Tisza/Hármas-Körös/Sebes-Körös	Korosszakal	M	21.657	47.020	59	92	2489
30	HU	HU13	/Tisza/Hármas-Körös/Kettõs-Körös/Fekete-Körös	Sarkad	M	21.431	46.694	16	85	4302
31	HU	HU14	/Tisza/Hármas-Körös/Kettõs-Körös/Fehér-Körös	Gyulavari	M	21.336	46.629	9	85	4251
32	HU	HU15	/Tisza/Maros	Nagylak	R	20.703	46.161	51	80	30149
33	SI	SI1	/Drava	Ormož most	LM	16.155	46.403	300	192	15 356
34	SI	SI2	/Sava	Jesenice na Dolenjskem	R	15.692	45.861	729	135	10 878
35	HR	HR1	Danube	Batina	MR	18.829	45.875	1 429	86	210 250
36	HR	HR2	Danube	Borovo	R	18.967	45.381	1 337	89	243 147

No.	Country code	TNMN code	River	Name of site	Loca-tions	x-coord	y-coord	River-km	Alti-tude	Catch-ment
37	HR	HR9	/Drava	Ormoz	LM	16.155	46.403	300	192	15356
38	HR	HR4	/Drava	Botovo	MR	16.938	46.241	227	123	31 038
39	HR	HR5	/Drava	Donji Miholjac	MR	18.201	45.783	78	92	37 142
40	HR	HR6	/Sava	Jesenice	LR	15.692	45.861	729	135	10 834
41	HR	HR7	/Sava	Upstream Una Jasenovac	L	16.915	45.269	525	87	30 953
42	HR	HR8	/Sava	Zupanja	LMR	18.696	45.040	254	85	62 890
43	RS	RS1	Danube	Bezdan	L	18.860	45.854	1 426	83	210 250
44	RS	RS2	Danube	Bogojevo	L	19.079	45.530	1 367	80	251 593
45	RS	RS3	Danube	Novi Sad	R	19.855	45.255	1 255	74	254 085
46	RS	RS4	Danube	Zemun	R	20.412	44.849	1 173	71	412 762
47	RS	RS5	Danube	Pancevo	L	20.637	44.854	1 155	71	525 009
48	RS	RS6	Danube	Banatska Palanka	M	21.339	44.826	1 077	70	568 648
49	RS	RS7	Danube	Tekija	R	22.419	44.700	954	68	574 307
50	RS	RS8	Danube	Radujevac	R	22.680	44.263	851	32	577 085
51	RS	RS9	Danube	Backa Palanka	L	19.382	45.234	1 299	77	253 737
52	RS	RS10	/Tisza (Tisa)	Martonos	R	20.081	46.114	152	76	140 130
53	RS	RS11	/Tisza (Tisa)	Novi Becej	L	20.135	45.586	65	75	145 415
54	RS	RS12	/Tisza (Tisa)	Titel	M	20.312	45.198	9	73	157 174
55	RS	RS13	/Sava	Jamena	L	19.084	44.878	205	77	64 073
56	RS	RS14	/Sava	Sremska Mitrovica	L	19.602	44.967	139	75	87 996
57	RS	RS15	/Sava	Sabac	R	19.699	44.770	106	74	89 490
58	RS	RS16	/Sava	Ostruznica	R	20.312	44.732	17	72	95 430
59	RS	RS17	/Velika Morava	Ljubicevski Most	R	21.132	44.586	22	71	37 320
60	BA	BA5	/Sava	Gradiska	M	17.255	45.141	457	86	39 150
61	BA	BA6	/Sava/Una	Kozarska Dubica	M	16.836	45.188	16	94	9 130
62	BA	BA7	/Sava/Vrbas	Razboj	M	17.458	45.050	12	100	6 023
63	BA	BA8	/Sava/Bosna	Modrica	M	18.313	44.961	24	114	10 500
64	BA	BA9	/Sava/Drina	Foca	M	18.833	43.344	234	442	3 884
65	BA	BA10	/Sava/Drina	Badovinci	M	19.344	44.779	16	90	19 226
66	BA	BA11	/Sava	Raca	M	19.335	44.891	190	80	64 125
67	BA	BA12	/Sava/Una	Novi Grad	M	16.295	44.988	70	137	4 573
68	BA	BA13	/Sava/Bosna	Usora	M	18.074	44.664	78	148	7 313
69	BG	BG1	Danube	Novo Selo harbour	LMR	22.785	44.165	834	35	580 100
70	BG	BG9	Danube	Lom	R	23.270	43.846	741	24	588 860
71	BG	BG10	Danube	Orjahovo	R	23.963	43.741	679	22	607 260
72	BG	BG2	Danube	Bajkal	R	24.400	43.711	641	20	608 820
73	BG	BG11	Danube	Nikopol	R	24.891	43.706	598	21	648 620
74	BG	BG3	Danube	Svishtov	R	25.345	43.623	554	16	650 340
75	BG	BG4	Danube	Upstream Russe	R	25.907	43.793	503	12	669 900
76	BG	BG5	Danube	Silistra	LMR	27.268	44.125	375	7	698 600
77	BG	BG12	/Iskar	mouth	M	24.456	43.706	4	27	8 646
78	BG	BG13	/Vit	Guljantzi	M	24.728	43.644	7	29	3 225
79	BG	BG14	/Jantra	mouth	M	25.579	43.609	4	25	7 869
80	BG	BG15	/Russenski Lom	mouth	M	25.936	43.813	1	17	2 974
81	RO	RO1	Danube	Bazias	LMR	21.384	44.816	1 071	70	570 896
82	RO	RO18	Danube	Gruia/Radujevac	LMR	22.684	44.270	851	32	577 085
83	RO	RO2	Danube	Pristol/Novo Selo	LMR	22.676	44.214	834	31	580 100
84	RO	RO3	Danube	Dunare - upstream Arges (Oltenita)	LMR	26.619	44.056	432	16	676 150
85	RO	RO4	Danube	Chiciu/Silistra	LMR	27.268	44.128	375	13	698 600
86	RO	RO5	Danube	Reni	LMR	28.232	45.463	132	4	805 700
87	RO	RO6	Danube	Vilkova-Chilia arm/Kilia arm	LMR	29.553	45.406	18	1	817 000
88	RO	RO7	Danube	Sulina - Sulina arm	LMR	29.530	45.183	0	1	817 000
89	RO	RO8	Danube	Sf. Gheorghe-Ghorghe arm	LMR	29.609	44.885	0	1	817 000

No.	Country code	TNMN code	River	Name of site	Loca-tions	x-coord	y-coord	River-km	Alti-tude	Catch-ment
90	RO	RO9	/Arges	Conf. Danube (Clatesti)	M	26.599	44.145	0	14	12 550
91	RO	RO10	/Siret	Conf. Danube (Sendreni)	M	28.009	45.415	0	4	42 890
92	RO	RO11	/Prut	Conf. Danube (Giurgiulesti)	M	28.203	45.469	0	5	27 480
93	RO	RO12	/Tisza/Somes	Dara (frontiera)	M	22.720	47.815	3	118	15 780
94	RO	RO13	/Tisza/Hármas-Körös/Sebes-Körös/Crisul Repede	Cheresig	M	21.692	47.030	3	116	2 413
95	RO	RO14	/Tisza/Hármas-Körös/Kettõs-Körös/Crisul Negru	Zerind	M	21.517	46.627	13	86.4	3 750
96	RO	RO15	/Tisza/Hármas-Körös/Kettõs-Körös/Crisul Alb	Varsand	M	21.339	46.626	0.2	88.9	4 240
97	RO	RO16	/Tisza/Mures	Nadlac	M	20.727	46.145	21	85.6	27 818
98	RO	RO17	/Tisza/Bega	Otelec	M	20.847	45.620	7	46	2 632
99	RO	RO19	/Jiu	Zaval	M	23.845	43.842	9	30.9	10 046
100	RO	RO20	/Olt	Islaz	M	24.797	43.744	3	32	24 050
101	RO	RO21	/Ialomita	Downstream Tandarei	M	27.665	44.635	24	8.5	10 309
102	MD	MD1	/Prut	Lipcani	L	26.483	48.152	658	100	8 750
103	MD	MD3	/Prut	Conf. Danube-Giurgiulesti	LMR	28.124	45.285	0	5	27 480
104	MD	MD5	/Prut	Costesti Reservoir	L	27.145	47.513	557	91	11 800
105	MD	MD6	/Prut	Braniste	L	27.145	47.475	546	63	12 000
106	MD	MD7	/Prut	Valea Mare	L	27.515	47.075	387	55	15 200
107	UA	UA1	Danube	Reni	M	28.288	45.437	132	4	805 700
108	UA	UA2	Danube	Vylkove	M	29.592	45.394	18	1	817 000
109	UA	UA4	/Tisza	Chop	M	22.184	48.416	342	92	33000
110	UA	UA5	/Tisza/Bodrog/ Latoritsa	Strazh	M	22.212	48.454	144	96	4418
111	UA	UA6	/Prut	Tarasivtsi	M	26.336	48.183	262	122	9836
112	UA	UA7	/Siret	Porubne	M	26.030	47.981	100	303	2070
113	UA	UA8	/Uzh	Storozhnica	R	22.200	48.617	106	112	1582
114	ME	ME1	/Lim	Dobrakovo	L	19.773	43.121	112	609	2875
115	ME	ME2	/Cehotina	Gradac	L	19.154	43.396	55.5	55	809.8

Distance: The distance in km from the mouth of the mentioned river
Altitude: The mean surface water level in meters above sea level
Catchment: The area in square km, from which water drains through the station
ds. Downstream of
us. Upstream of
Conf. Confluence tributary/main river
/ Indicates tributary to river in front of the slash. No name in front of the slash means Danube

Sampling location in profile:
L: Left bank
M: Middle of river
R: Right bank

Figure 2.1: The Danube Station map TNMN

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* Surveillance Monitoring 2 provides an assessment of long-term trends of specific pollutants and of loads of substances transferred downstream the Danube.

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2.3 Quality elements

2.3.1 Parameters indicative of selected biological quality elements

To cover pressures of basin-wide importance as organic pollution, nutrient pollution and general degradation of the river, following biological quality elements have been agreed for SM2:

- Phytoplankton (chlorophyll-a)
- Benthic invertebrates (mandatory parameters: Saprobic index and number of families once yearly, both Pantle&Buck and Zelinka&Marvan SI are acceptable; optional parameters: ASPT and EPT taxa)
- Phytobenthos (benthic diatoms – an optional parameter)

2.3.2 Priority pollutants and parameters indicative of general physico-chemical quality elements

The list of parameters for assessment of trends and loads and their monitoring frequencies are given in Table 2

Table 2: Determinand list for water for TNMN

	Surveillance Monitoring II	
	Water	**Water**
	concentrations	**load assessment**
Parameter		
Flow	anually / 12 x per year	Daily
Temperature	anually / 12 x per year	
Transparency (1)	anually / 12 x per year	
Suspended Solids (5)	anually / 12 x per year	anually / 26 x per year
Dissolved Oxygen	anually / 12 x per year	
pH (5)	anually / 12 x per year	
Conductivity @ 20 °C (5)	anually / 12 x per year	
Alkalinity (5)	anually / 12 x per year	
Ammonium (NH_4^+ -N) (5)	anually / 12 x per year	anually / 26 x per year
Nitrite (NO_2^- -N)	anually / 12 x per year	anually / 26 x per year
Nitrate (NO_3^- -N)	anually / 12 x per year	anually / 26 x per year
Organic Nitrogen	anually / 12 x per year	anually / 26 x per year
Total Nitrogen	anually / 12 x per year	anually / 26 x per year
Ortho-Phosphate (PO_4^{3-} -P) (2)	anually / 12 x per year	anually / 26 x per year
Total Phosphorus	anually / 12 x per year	anually / 26 x per year
Calcium (Ca^{2+}) (3, 4, 5)	anually / 12 x per year	
Magnesium (Mg^{2+}) (4, 5)	anually / 12 x per year	
Chloride (Cl^-)	anually / 12 x per year	
Atrazine	anually / 12 x per year	
Cadmium (6)	anually / 12 x per year	
Lindane (7)	anually / 12 x per year	
Lead (6)	anually / 12 x per year	

	Surveillance Monitoring II	
	Water	**Water**
	concentrations	**load assessment**
Parameter		
Mercury (6)	anually / 12 x per year	
Nickel (6)	anually / 12 x per year	
Arsenic (6)	anually / 12 x per year	
Copper (6)	anually / 12 x per year	
Chromium (6)	anually / 12 x per year	
Zinc (6)	anually / 12 x per year	
p,p´-DDT and its derivatives (7)	see below	
COD_{Cr} (5)	anually / 12 x per year	
COD_{Mn} (5)	anually / 12 x per year	
Dissolved Silica		anually / 26 x per year
BOD_5	anually / 12 x per year	

(1) Only in coastal waters
(2) Soluble reactive phosphorus SRP
(3) Mentioned in the tables of the CIS Guidance document but not in the related mind map
(4) Supporting parameter for hardness-dependent eqs of PS metals
(5) Not for coastal waters
(6) Measured in a dissolved form. Measurement of total concentration is optional
(7) In areas with no risk of failure to meet the environmental objectives for DDT and lindane the monitoring frequency is 12 x per a RBMP period; in case of risk the frequency is 12 x year

2.4 Analytical Quality Control (AQC)

Parameters covered and samples distributed in the 2015 QUALCODanube programme were as follows:

- real surface water samples for nutrient analysis: preserved natural surface water, spiked if necessary and adequately homogenised. Sample codes were SW-N-1 and SW-N-2. 500 cm^3 plastic bottles were provided for $NH4^+$, NO_3^-, organic N, total N, PO_4^{3-} and total P analysis. Measurement results were asked to be reported as mg N/dm^3 and mg P/dm^3, respectively.

- spike solutions together with matrix water for NO_2^- analysis: due to stability concerns during transport, it was decided that participants should compose the proficiency testing samples themselves in situ by mixing prescribed amounts of the spike solutions (synthetic concentrates preserved by addition of $Hg(II)Cl_2$) of the measurand with the matrix water provided (simulated surface water pretreated by bringing to boiling point) according to instructions. Spike solutions were put in 20 cm^3 plastic containers with sample codes SW-N/M-1 and SW-N/M-2, whereas matrix water was provided in 500 cm^3 plastic bottles labelled "SW-N/M-1, SW-N/M-2 WATER FOR DILUTION". Measurement results were asked to be reported as mg N/dm^3 .

- spike solutions for organic micropollutant analysis: methanolic spike solutions were distributed. Participants had to compose the proficiency testing samples themselves in situ by mixing prescribed amounts of the spike solutions (synthetic concentrates) of the measurand with pesticides-free laboratory water (e.g. high purity water) according to instructions. Spike solutions were put in 5 cm^3 amber capillary bottles with sample codes SW-Org-1 and SW-Org-2. Measurement results were asked to be reported as $\mu g/dm^3$.

Evaluation was performed according to ISO 13528:2015 and ISO/IEC 17043:2010. Reported results were first inspected for obviously erroneous results or blunders, which were excluded from the dataset in accordance with section B.2.5. of ISO/IEC 17043:2010. Then the assigned value of the parameter [$\dot{X}$], the standard uncertainty of the assigned value [u(x)] and the standard deviation for proficiency assessment (SDPA) was determined. Finally, performance statistics was calculated including z-scores, z'- scores and En numbers (section 9.4. and 9.6. of ISO 13528:2015) and assessment was given based on the performance statistics.

Assigned value was determined as a consensus value from all participants. For this end, robust average of all laboratories was calculated according to algorithm "A" (for details see Annex C of ISO 13528:2015). The same algorithm was used to calculate the standard uncertainty of the assigned value, i.e. the robust average of all laboratories. Assigned values were tested against analytical measurements by WESSLING Hungary Ltd. The standard deviation for proficiency assessment was chosen as a fit-for-purpose value, pre-set as percentage of the assigned value. Regulatory requirements, previous experience with the proficiency testing scheme, and expert judgement were taken into consideration when defining SDPA. Robust standard deviations calculated from the current datasets (using algorithm "A") were given special emphasis.

Number of participants in 2015 was 48. Most of the new entries were experienced laboratories who had formerly participated in and were familiar with the scheme. Despite repeated requests, laboratory coded nr. 409 did not return results, thus the actual number of participants was 47. The 2015 proficiency testing scheme was performed with good results overall: evaluation could be performed for all parameters, number and ratio of unsatisfactory results remained low, despite the marked increase in number of participants. Almost all participants reported their expanded uncertainties together with measurement results, allowing for calculation of En numbers, thus assessment of the validity of the underlying uncertainty estimation. En numbers were visualized on graphs as extended uncertainty bars around reported results. Graphs clearly show which participants have precision reserves, i.e. margin for the extended uncertainty range between upper and lower unsatisfactory limits. Number and ratio of unsatisfactory En numbers shows a decreasing trend overall, reflecting improvements in estimation of measurement uncertainty by participants.

Ammonium and nitrite measurements were notably better as compared to previous years: uncertainty of assigned values decreased significantly, allowing for z-score assessment instead of z'-score assessment in all samples. Additionally, none of the results were unsatisfactory for ammonium and only one unsatisfactory result can be found for nitrite. Improvements in nitrite results is partially attributable to new sample type (i.e. simulated instead of natural surface water as matrix). As previously, phosphorus measurements were highly successful, none of the results were unsatisfactory for phosphate and only one unsatisfactory result can be found for total phosphorus. Organic nitrogen, which debuted in the scheme in 2013, was measured by 18 participants (increasing from 14 last year), but agreement among results improved further. Uncertainty of the assigned value compared to the standard deviation of proficiency assessment decreased slightly for both samples, but it is still higher than in case of any other parameter in the scheme. Z'-scores were used for performance assessment. Organic micropollutants were measured by 21-22 laboratories. Despite the relatively small number of participants, results cluster well around assigned values, number and ratio of unsatisfactory results is low. Higher uncertainties of assigned values necessitated the use of z'-scores for assessment in case of lindane and the lower concentration sample of 4,4'-DDT.

In summary, the 2015 QualcoDanube proficiency testing scheme was successful, the scheme remains a useful and relevant tool in the quality framework of the Danube region.

2.5 TNMN Data Management

The procedure of TNMN data collection is organized at a national level. The National Data Managers (NDMs) are responsible for data acquisition from TNMN laboratories as well as for data checking, conversion into an agreed data exchange file format (DEFF) and sending it to the TNMN data management centre in the Slovak Hydrometeorological Institute in Bratislava. This centre performs a secondary check of the data and uploads them into the central TNMN database. In cooperation with the ICPDR Secretariat, the TNMN data are uploaded into the ICPDR website (www.icpdr.org).

3. Results of basic statistical processing

156 sites at 110 TNMN monitoring stations were monitored in the Danube River Basin in 2015 (some monitoring stations contain two or three sampling sites - left, middle and/or right side of the river). The data was collected from 74 sampling sites at 39 stations on the Danube River and from 82 sampling sites at 71 stations at the tributaries.

The basic processing of the TNMN data includes the calculation of selected statistical characteristics for each determinand/monitoring site. Results are presented in tables in the Annex I using the following format:

Term used	Explanation
Determinand name	name of the determinand measured according to the agreed method
Unit	unit of the determinand measured
N	number of measurements
Min	minimum value of the measurements done in the year 2015
Mean	arithmetical mean of the measurements done in the year 2015
Max	maximum value of the measurements done in the year 2015
C50	50 percentile of the measurements done in the year 2015
C90	90 percentile of the measurements done in the year 2015

When processing the TNMN data and presenting them in the tables of the Annex, the following rules have been applied:

- *If "less than the quantification limit" values were present in the dataset for a given determinand, then the ½ value of the limit of quantification was used in statistical processing of the data.*
- *If the number of measurements for a particular determinand was lower than four, then only the minimum, maximum and mean are reported in the tables of the Annex.*
- *The statistic value "C90" is equal to 90 percentile (10 percentile for dissolved oxygen and lower limit of pH value) if the number of measurements in a year was at least eleven. If the number of measurements in a year was lower than eleven, then the "C90" value is represented by a maximum value from a data set (a minimum value for dissolved oxygen and lower limit of pH value).*

In year 2009 the analytical data method according to Directive 2009/90/EC with limit of quantification (LOQ) has been applied. In this case if values were less than limit of quantification in statistic processing of data was used ½ limit of quantification (LOQ).

The problem is the reduced monitoring frequency for certain determinands such as dissolved phosphorus, biological determinands, heavy metals and specific organic micropollutants, primarily in the lower part of the Danube River Basin.

Table 3, created on the basis of data in tables in the Annex I, shows in an aggregated way the concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2015. These include indicators of the oxygen regime, nutrients, heavy metals, biological determinands and organic micropollutants.

Table 3 also includes information about the number of monitoring locations and sampling sites providing measurements of the determinands.

In the table there are minimal, maximal values for all determinands calculated from all Danube or tributaries station and minimal and maximal values for all determinands calculated from mean (average) values from all Danube or tributaries.

Table 3: Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2015

Determinand name	Unit	Danube					Tributaries				
		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean	
			Min	Max	Min_{avg}	Max_{avg}		Min	Max	Min_{avg}	Max_{avg}
Temperature	°C	69/39	1.0	30.9	11.3	16.4	73/71	0.0	29.2	7.7	16.2
Suspended solids	mg/l	69/39	< 0	260	< 1	71	73/71	< 1	4064	< 1	541
Dissolved oxygen	mg/l	69/39	5.1	14.2	7.7	11.0	73/71	4.0	15.3	8.0	12.3
BOD (5)	mg/l	69/39	< 0.20	6.2	0.9	4.8	73/71	< 0.25	77.0	< 0.25	8.9
COD (Mn)	mg/l	61/31	0.8	14.7	1.8	5.8	39/39	0.8	21.9	1.9	9.3
COD (Cr)	mg/l	61/31	< 2.50	37.1	6.2	31.8	66/64	< 2.50	164.1	3.4	62.7
TOC	mg/l	45/25	1.4	23.5	2.3	5.5	25/23	< 0.25	17.0	1.3	12.7
DOC	mg/l	30/14	1.3	8.0	2.0	3.4	9/9	0.6	8.1	1.0	6.3
pH	-	69/39	7.1	9.2	7.9	8.4	69/69	6.4	9.6	7.4	8.3
Alkalinity - total	mmol/l	69/39	1.3	8.1	1.6	4.6	65/63	0.9	276.0	1.2	217.5
Ammonium (NH4-N)	mg/l	67/37	< 0.002	1.05	0.02	0.23	73/71	< 0.002	2.88	0.01	1.20
Nitrite (NO2-N)	mg/l	69/39	< 0.0005	0.140	0.009	0.028	73/71	< 0.0005	0.6	0.0036	0.13
Nitrate (NO3-N)	mg/l	69/39	< 0.035	4.14	0.66	3.05	73/71	0.017	10.20	0.545	8.192
Total nitrogen	mg/l	61/31	< 0.500	4.7	1.5	2.8	65/63	0.2	13.3	0.6	9.5
Organic nitrogen	mg/l	31/21	< 0.025	2.41	0.03	1.20	34/32	< 0.000	4.45	0.17	1.11
Orthophosphate (PO4-P)	mg/l	66/38	< 0.0025	0.589	0.026	0.126	73/71	< 0.0015	0.604	0.006	0.246
Total phosphorus	mg/l	63/35	0.0123	0.789	0.052	0.310	69/67	0.007	1.600	0.022	0.509
Total phosphorus, dissolved	mg/l	40/18	0.0097	0.260	0.048	0.094	16/16	0.007	0.499	0.017	0.241
Phytoplankton (biomass - chlorophyll-a)	µg/l	55/26	< 0.0015	112.14	1.59	33.94	43/41	< 0.0015	354.20	0.70	80.11
Conductivity	µS/cm	65/35	29	707	37	513	67/67	14.8	1979	24	1176
Calcium (Ca++)	mg/l	69/39	28.6	104.0	44.1	84.8	71/69	4.4	192	21.44	93.5
Sulphate (SO4--)	mg/l	53/29	11.2	94.1	16.8	54.4	47/45	7.01	182.0	12.22	123.23
Magnesium (Mg++)	mg/l	69/39	5.4	34.0	12.0	20.3	71/69	0.7	75	4.83	59.33
Potassium (K+)	mg/l	36/22	1.2	8.4	1.7	3.3	40/38	0.59	15.0	1.23	9.73
Sodium (Na+)	mg/l	36/22	7.50	38.00	11.78	22.53	40/38	2.1	278	4.92	58.22
Manganese (Mn)	mg/l	17/11	< 0.0005	0.23	0.0050	0.07	19/19	< 0.0025	0.47	0.0065	0.306
Iron (Fe)	mg/l	18/10	< 0.005	2.59	0.012	0.966	25/25	< 0.005	3.06	0.016	0.937
Chloride (Cl-)	mg/l	69/39	6.9	108.4	16.2	47.2	73/71	0.34	496	2.2	183.97
Silicates (SiO2)	mg/l	13/7	1.4	9.1	2.7	6.9	9/7	0.5	25.8	1.8333	21.3
Silicates(SiO2), dissolved	mg/l	15/11	1	12.1	1.2	6.9	16/16	< 0.125	14.9	2.881	11.1
Macrozoobenthos- saprobic index		27/18	1.9	2.33	1.9	2.307	42/41	1.64	3.15	1.75	3.00

Table 3: Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2015 (cont.)

Determinand name	Unit	Danube					Tributaries				
		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean	
			Min	Max	Min_{avg}	Max_{avg}		Min	Max	Min_{avg}	Max_{avg}
Zinc - Dissolved *	µg/l	68/39	< 0.150	91.40	1.76	35.75	69/67	< 0.150	161.60	< 1.500	36.01
Copper - Dissolved	µg/l	69/39	< 0.100	35.40	< 0.750	9.93	71/69	< 0.100	28.20	< 0.500	7.80
Chromium - Dissolved	µg/l	60/34	0.07	6	< 0.11	3	56/54	< 0.02	24.40	0.15	6.80
Lead - Dissolved	µg/l	62/34	< 0.040	6.6	0.079	1.468	61/59	0.04	15.07	< 0.092	4.46
Cadmium - Dissolved	µg/l	62/34	< 0.003	0.77	< 0.006	0.25	61/59	< 0.003	1.02	< 0.007	0.28
Mercury - Dissolved	µg/l	62/34	< 0.0010	0.17	0.00	< 0.0500	56/54	< 0.0010	0.20	0.003	0.07
Nickel - Dissolved	µg/l	62/34	< 0.025	8.20	0.47	3.47	61/59	< 0.250	21.40	0.44	6.47
Arsenic - Dissolved	µg/l	66/37	< 0.250	5.68	0.36	2.37	53/51	< 0.050	10.60	< 0.370	6.48
Aluminium - Dissolved	µg/l	16/10	0.94	36.40	3.31	15.92	19/17	< 0.25	705.00	< 1.50	76.60
Zinc *	µg/l	33/21	< 0.50	142.00	3.68	75.75	29/29	< 1.50	236.00	3.65	140.00
Copper	µg/l	28/18	1	39.40	2.16	14.80	26/26	< 0.100	120.00	1.29	31.52
Chromium - total	µg/l	42/26	< 0.0250	13.59	0.24	3.79	31/31	< 0.0500	46.90	0.16	5.61
Lead	µg/l	31/19	< 0.0500	10.06	0.46	2.17	32/32	< 0.0500	37.15	< 0.5000	7.53
Cadmium	µg/l	31/19	< 0.00250	1.34	0.02	0.26	31/31	< 0.00250	2.21	0.03	0.99
Mercury	µg/l	31/19	< 0.0075	0.20	0.01	0.11	33/33	< 0.0050	0.30	< 0.0075	0.20
Nickel	µg/l	31/19	< 0.500	60.80	0.81	9.25	30/30	< 0.500	68.90	< 0.500	14.31
Arsenic	µg/l	27/17	< 0.250	3.30	0.99	2.33	21/21	< 0.250	10.00	< 0.500	5.00
Aluminium	µg/l	4/4	33.00	604.00	136.25	195.00	7/7	32	1050.00	32.00	232.84
Phenol index	mg/l	43/17	< 0.0025	< 0.0250	< 0.0025	< 0.0250	30/30	< 0.0004	0.02	< 0.0004	0.02
Anionic active surfactants	mg/l	45/19	< 0.0025	0.65	< 0.0045	0.36	29/27	< 0.0050	300.00	0.01	46.67
AOX	µg/l	12/6	< 1.0000	21.90	< 5.0000	12.88	8/8	< 5.0000	94.20	8.12	55.36
Petroleum hydrocarbons	mg/l	36/14	< 0.0025	13.60	0.00	4.67	32/32	0.01	33.50	0.02	22.30
Lindane	µg/l	54/28	< 0.0003	< 0.0250	< 0.0004	< 0.0250	52/50	< 0.0003	< 0.0250	< 0.0004	< 0.0250
pp´DDT	µg/l	59/31	< 0.0003	< 0.0250	< 0.0004	< 0.0250	55/53	< 0.0003	< 0.0250	< 0.0004	< 0.0250
Atrazine	µg/l	56/28	< 0.0005	< 0.0900	0.0025	< 0.0900	43/41	< 0.0005	< 0.0900	< 0.0008	< 0.0900
Chloroform	µg/l	18/10	< 0.005	0.8	< 0.005	0.266	21/21	< 0.050	< 5.000	< 0.050	< 5.000
Carbon tetrachloride	µg/l	15/9	< 0.020	1.1	< 0.020	< 0.200	18/18	< 0.020	< 0.250	< 0.050	< 0.250
Trichloroethylene	µg/l	6/4	< 0.050	< 0.250	< 0.050	< 0.250	14/14	< 0.050	< 10.000	< 0.050	< 10.000
Tetrachloroethylene	µg/l	9/5	< 0.025	< 0.250	< 0.025	< 0.250	14/14	< 0.050	< 5.000	< 0.050	< 5.000

4. Profiles and trend assessment of selected determinands

The 90 percentiles (C90) of selected determinands (dissolved oxygen, $BOD_{5,}$ COD_{Cr}, N-$NH_{4,}$ N-NO_3, P-PO_4, Ptotal and Cd) measured in last ten years are displayed in the Figures 4.1-4.16. Due to revision of the TNMN in 2006 following monitoring points on the Danube were replaced: AT2 rkm 2120 to AT5 rkm 2113, AT4 rkm 1874 to AT6 rkm 1879, DE1 rkm 2581 to DE5 rkm 2538. Among tributaries the site HR3 rkm 288 was replaced by HR9 rkm 300 BG8 rkm 54 to BG14 rkm 4 and BG8 rkm 13 to BG15 rkm 1. In 2009 SK3 was replaced with SK5, this monitoring point is also in graphs illustrated as Hungarian point HU3. For trend graphs was used illustration of SK5 and HU3.

To indicate the long-term trends in the upper, middle and lower Danube a more detailed analysis for selected parameters ($BOD_{5,}$ N-NO_3, P_{total}) is provided for the sites SK1 Bratislava, HU5 Hercegszanto and RO5 Reni (Figures 4.17-4.25).

As regards a general spatial distribution of key water quality parameters along the Danube River in 2015 the highest concentrations of biodegradable organic matter were observed in the lower parts of the river. The concentration of nutrients and cadmium reached their highest concentration values in the lower part of the Danube.

The highest pollution by the biodegradable organic matter in 2015 was measured in Sio, Arges Russenski Lom.

The highest values of dissolved oxygen were observed in the upper part of the Danube, in the lower Danube dissolved oxygen levels decrease (Figure 4.1). The lowest dissolved oxygen value was at the monitoring point HU3. Low values of dissolved oxygen were in 2015 measured in tributaries Sio, Sava , Tisza.

Decreasing tendencies of biodegradable organic matter have been observed in the upper Danube. In 2015 BOD significantly decreased at the monitoring site BG2 (see Figure 4.3) a decrease was also observed at SK2 and RO6. An increase of BOD level was observed at HU2 and HU5.

A decreasing tendency of BOD concentrations was found in the tributaries Sio, Siret and Sava (Figure 4.4). In 2015 concentration of BOD slightly increased in Inn, Russenski Lom, Jantra.

The decreasing or stable level of concentration of ammonium-N was recorded in the whole Danube River. In 2014 and 2015 concentration of ammonium-N decreased in BG2. During the last ten years of TNMN operation, concentration of ammonium was decreasing in the Morava, Dyje, Vah, Sava and Tisza rivers. In 2015 decreased concentration of ammonium-N was observed in tributaries Russenski Lom and Arges (see Figure 4.8).

The level of nitrate-N concentrations is rather stable during recent years. A decrease was observed at several stations along the whole Danube and especially in its lower part (e.g., RO3, RO5, RO6, RO8 see Figure 4.9). At the selected monitoring sites (SK1, HU5 and RO5) nitrate-N concentrations in 2015 increased slightly at SK1 and HU5 and decreased at RO5 (Figure 4.20-4.22).

The nitrate-N has an increasing in 2015 in the tributaries Russenski Lom (Figure 4.10).

In the last decade a decreasing tendency of ortho-phosphate-P concentrations is mostly seen in the upper part of the Danube, but a concentration decrease can be observed at some of the lower Danube stations (BG1, BG3, RO4, RO7 and RO8; see Figure 4.11). Decreasing tendency of ortho-phosphate-P was observed in the tributaries Russenski Lom, Arges and Siret (Figure 4.12). In 2015 concentration slightly increased in the tributary Jantra.

P-total concentration has decreasing tendency in the last decade in the upper and middle Danube (Figure 4.13). In 2015 increased concentration in monitoring sites BG3 and HR1. In 2015 the P-total concentration has decreased in the tributaries Inn, Sio, Russenski Lom, Jantra and Siret (see Figure 4.14).

The trends of COD_{Cr} in the Danube River was rather stable during last ten years, the highest concentrations were found in the lower part of the Danube River. The highest COD_{Cr} concentrations in 2015 were observed in the tributaries Russenski Lom, Arges, Sio.

The cadmium concentration is constant or slightly decreasing along the whole Danube River as well as in its tributaries (Figures 4.15 and 4.16). In 2015 concentration of cadmium was decreased in the tributaries Morava and Prut (MD3).

The 90 and 10 percentiles of selected determinands (N-NH_4, P-PO_4, COD_{Cr}, BOD_5) measured in 2015 are displayed in the Figures 4.26-4.33. Pictures indicate the margins of a usual annual concentration range for a given parameter and site. In graphs for tributaries there are rkm of Danube, where tributary discharge to the Danube River.

The annual differences between C90 and C10 have an insignificant variation for COD_{Cr} and BOD_5 in the in upper and middle Danube. The visible differences were observed P-PO_4 and N-NH_4 in the middle and lower part of Danube.

Insignificant differences were observed for COD_{Cr} and BOD_5 in the upper and middle Danube tributaries.

Large variation for N-NH_4 was observed in the lower Danube tributaries Bega, Bosna and Arges. Differences between 10 and 90 percentiles for P-PO_4 were observed in the upper and lower Danube tributaries Dyje, Sio and Sava.

Significant differences are between 10 and 90 percentiles for COD_{Cr} and BOD_5 in many of the lower Danube tributaries. Significant differences were observed in Ialomita for COD_{Cr} and BOD_5.

Figure 4.1.: Temporal changes of dissolved oxygen (c10) in the Danube River.

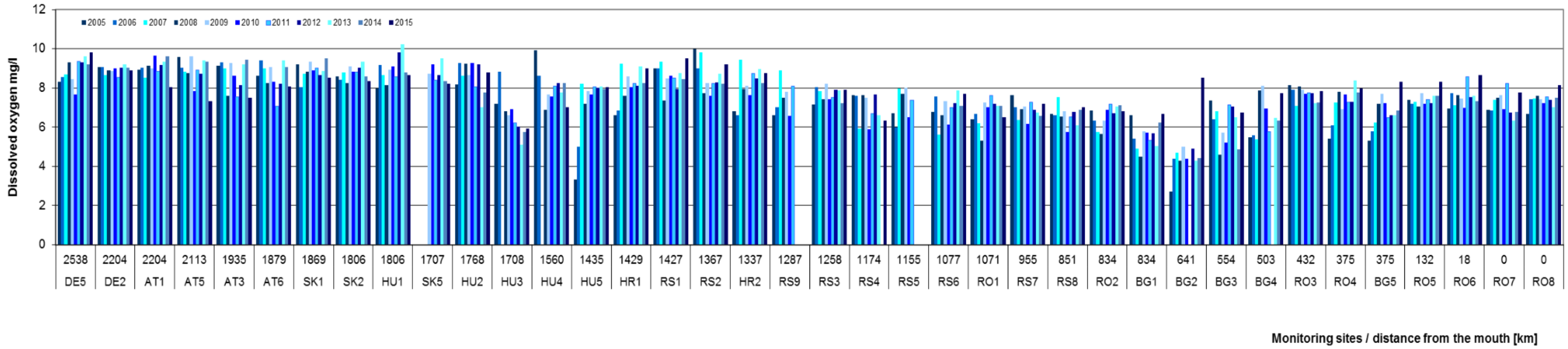


Figure 4.2.: Temporal changes of dissolved oxygen (c10) in tributaries.

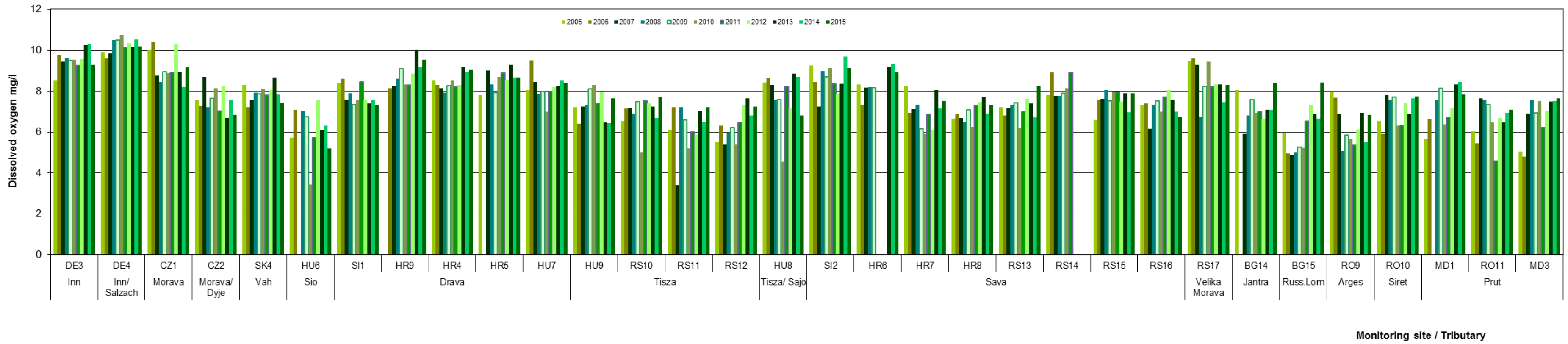


Figure 4.3.: Temporal changes of BOD_5 (c90) in the Danube River.

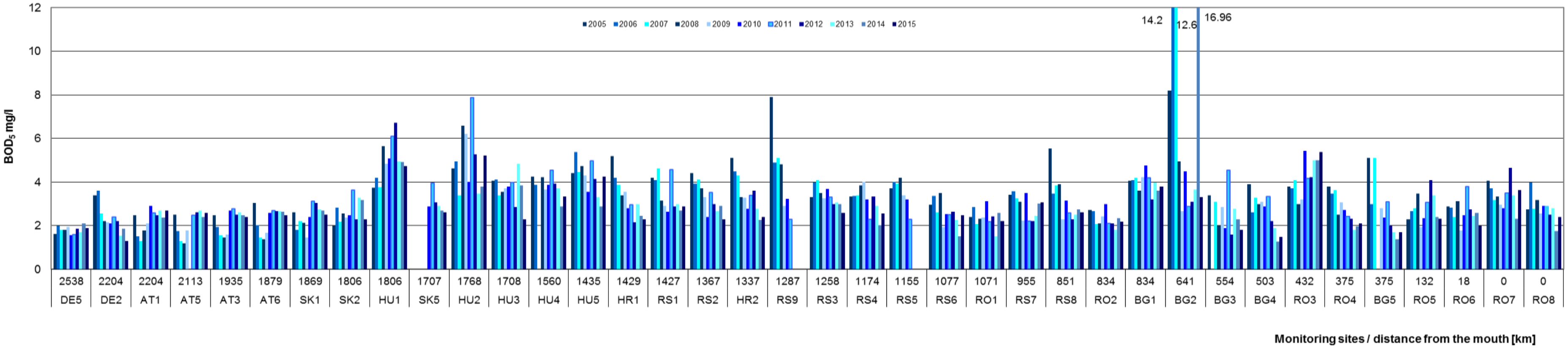


Figure 4.4.: Temporal changes of BOD_5 (c90) in tributaries.

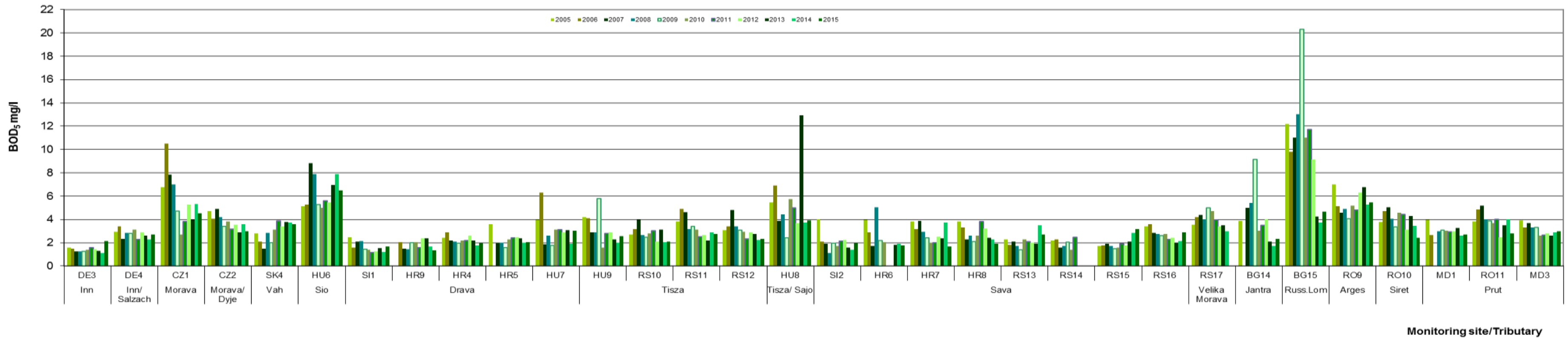


Figure 4.5.: Temporal changes of COD_{Cr} (c90) in the Danube River.

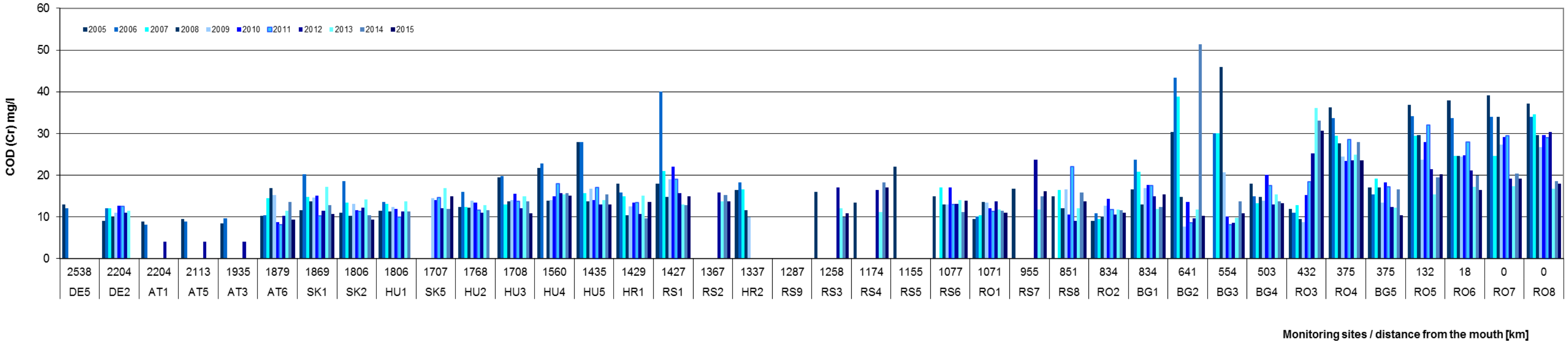


Figure 4.6.: Temporal changes of COD_{Cr} (c90) in tributaries.

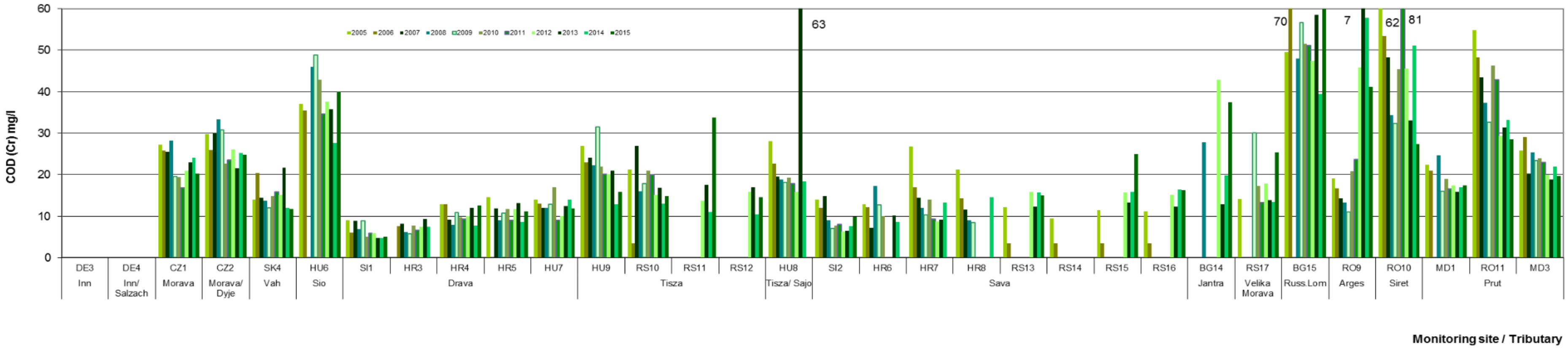


Figure 4.7.: Temporal changes of N-NH₄ (c90) in the Danube River.

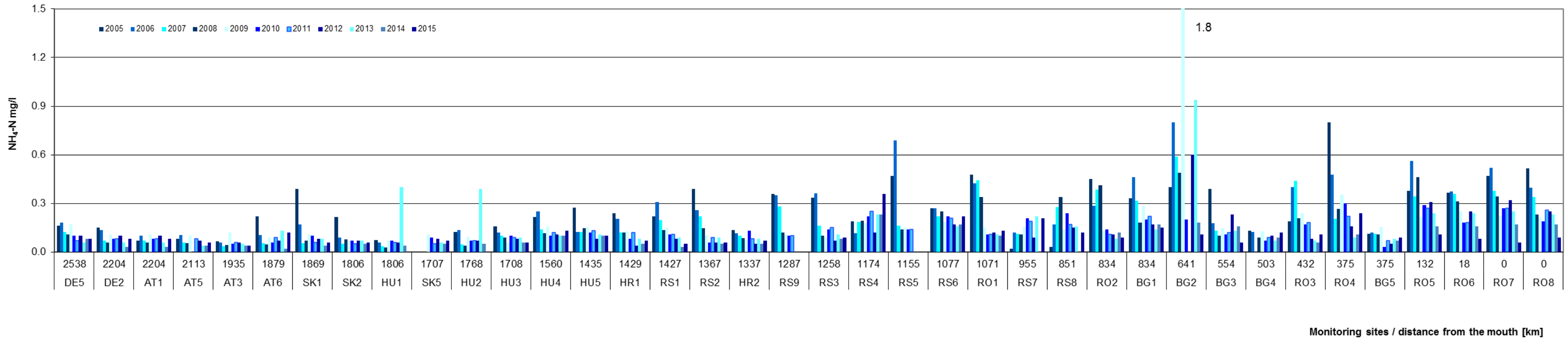


Figure 4.8.: Temporal changes of N-NH₄ (c90) in tributaries.

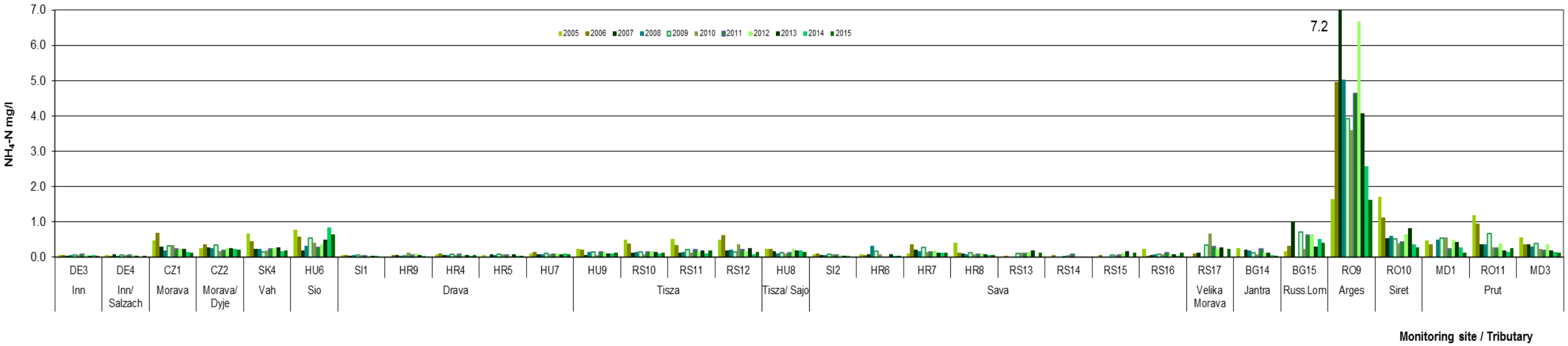


Figure 4.9.: Temporal changes of N-NO₃ (c90) in the Danube River.

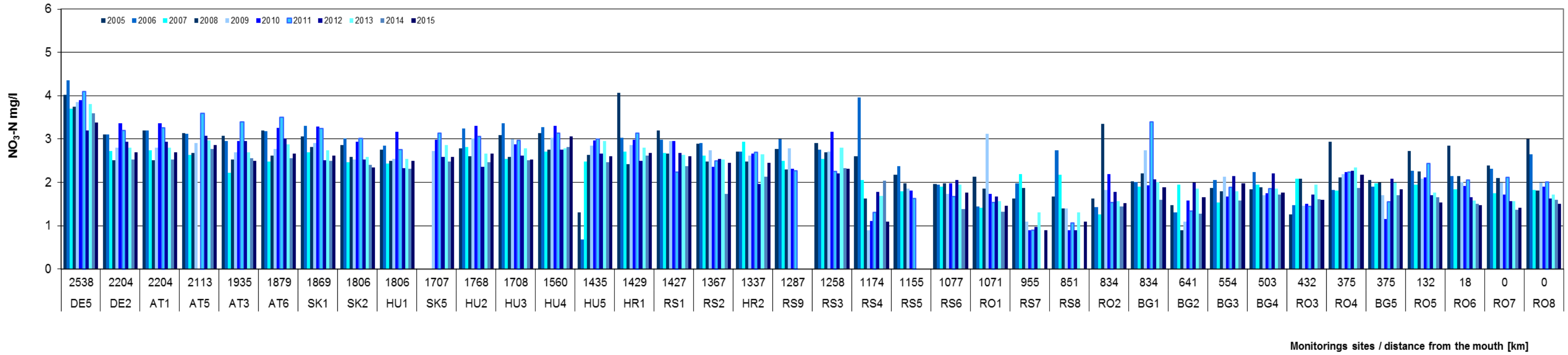


Figure 4.10.: Temporal changes of N-NO₃ (c90) in tributaries.

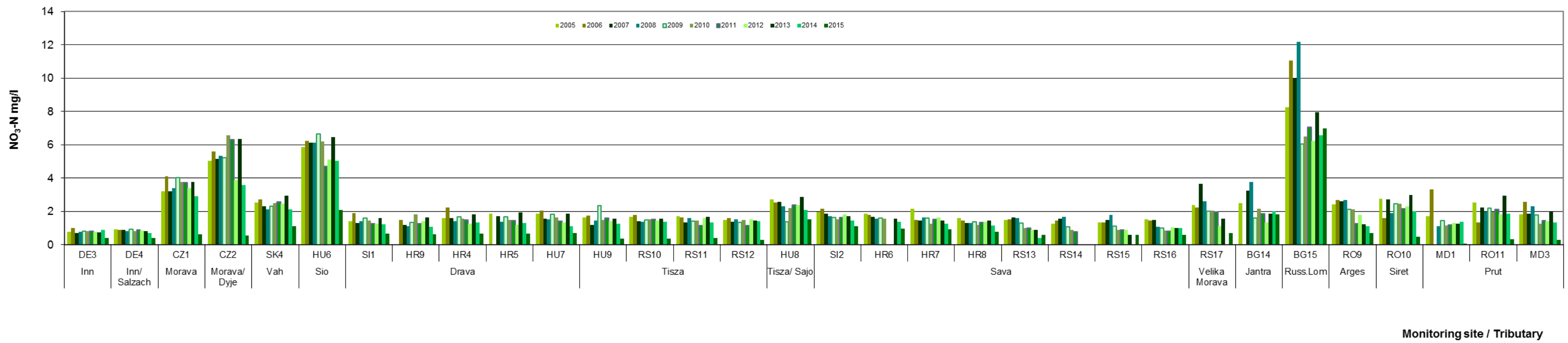


Figure 4.11: Temporal changes of P-PO₄ (c90) in the Danube River.

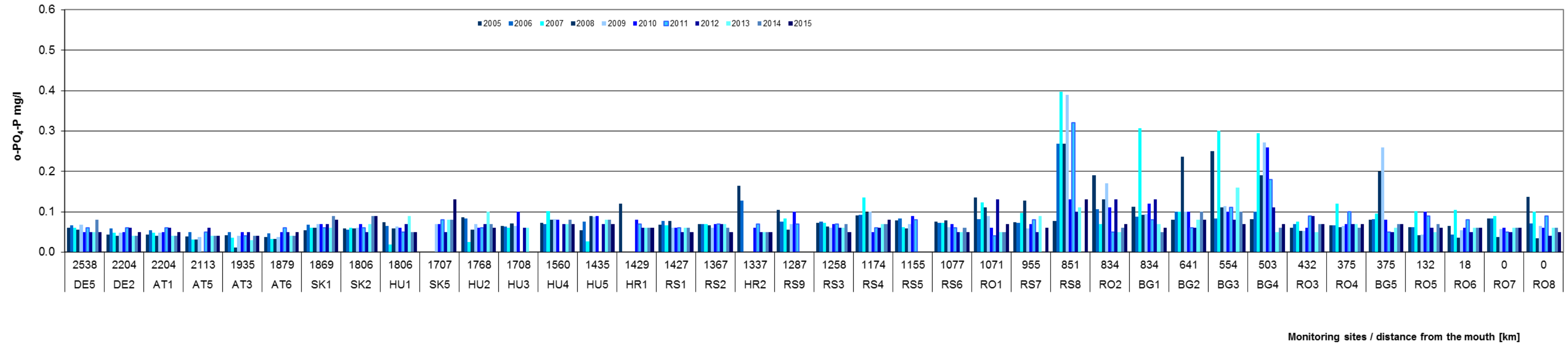


Figure 4.12: Temporal changes of P-PO₄ (c90) in tributaries

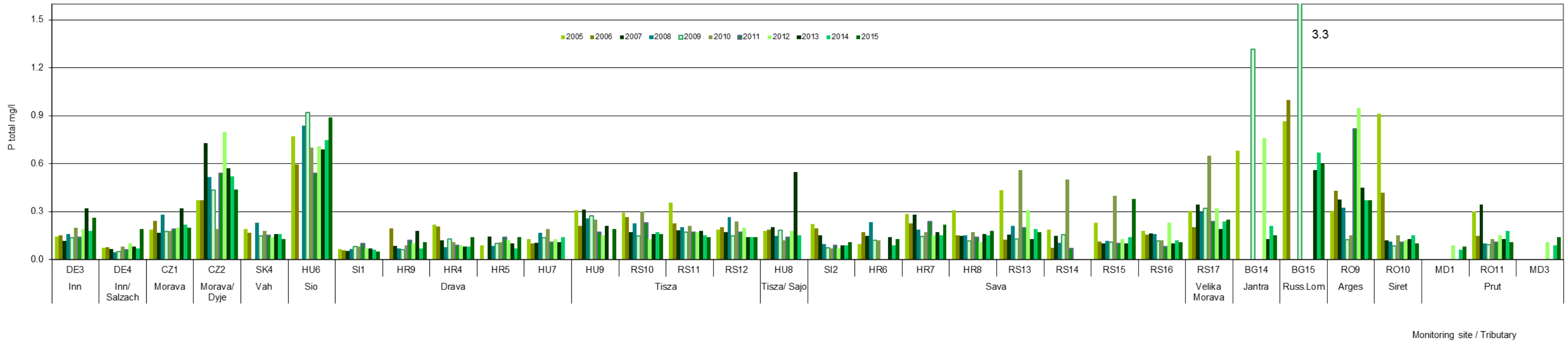


Figure 4.13: Temporal changes of total phosphorus (c90) in the Danube River.

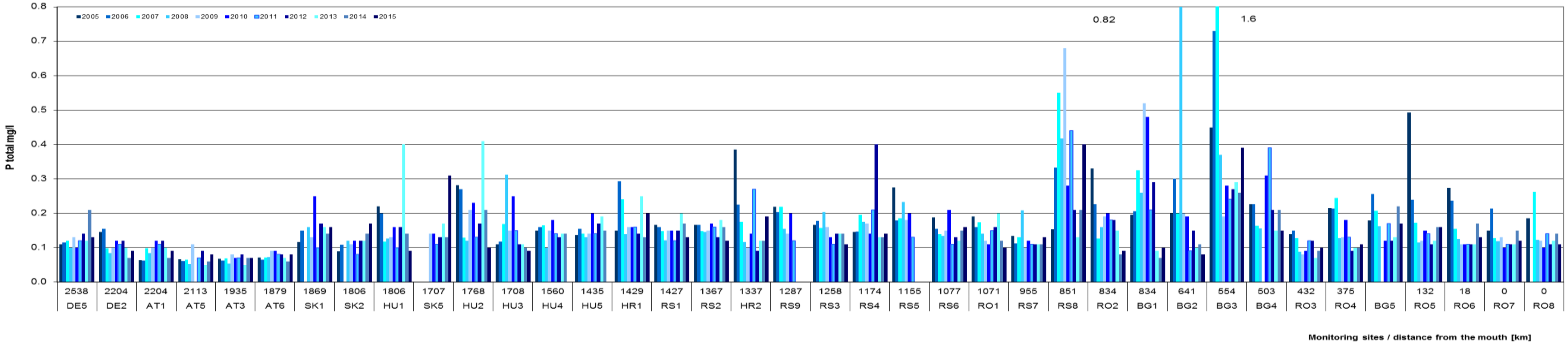


Figure 4.14: Temporal changes of total phosphorus (c90) in tributaries.

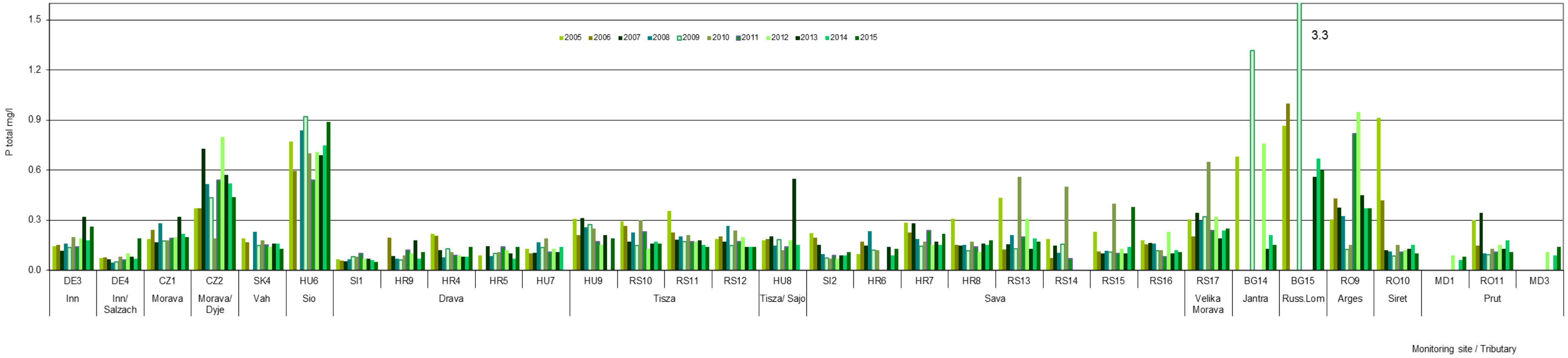


Figure 4.15: Temporal changes of cadmium (c90) in the Danube River.

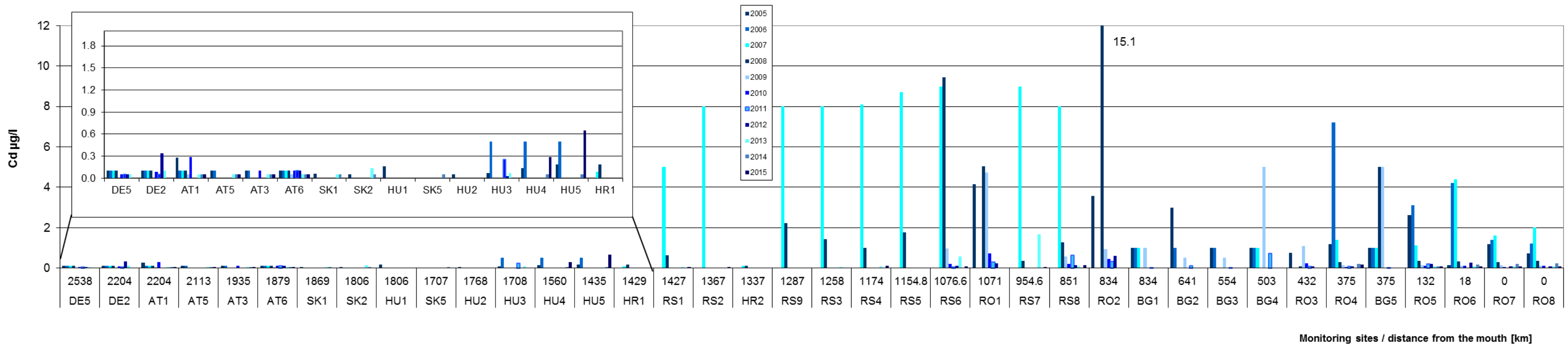


Figure 4.16: Temporal changes of cadmium (c90) in tributaries.

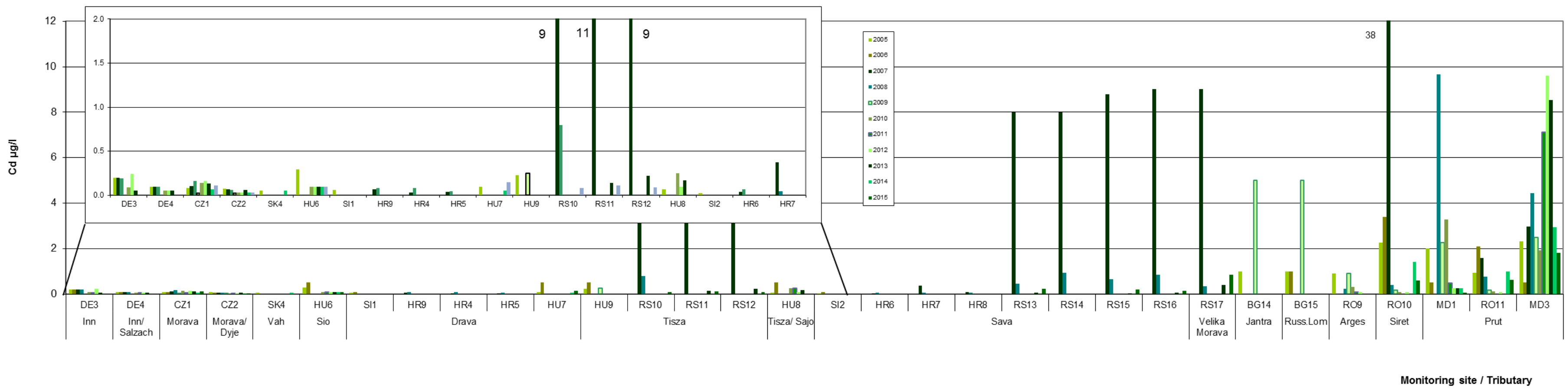


Figure 4.17: Temporal changes of BOD_5 (c90) in Bratislava

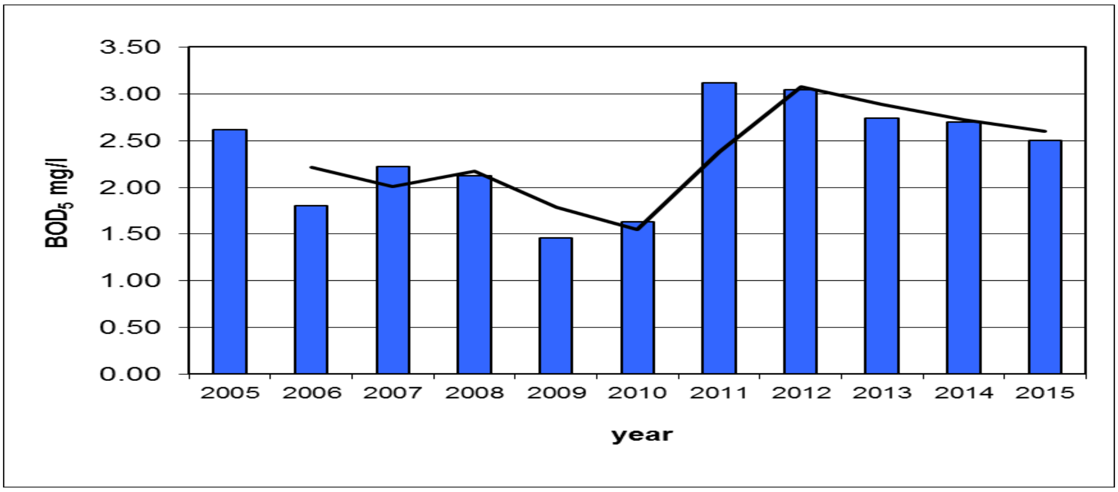


Figure 4.18: Temporal changes of BOD_5 (c90) in Hercegszanto

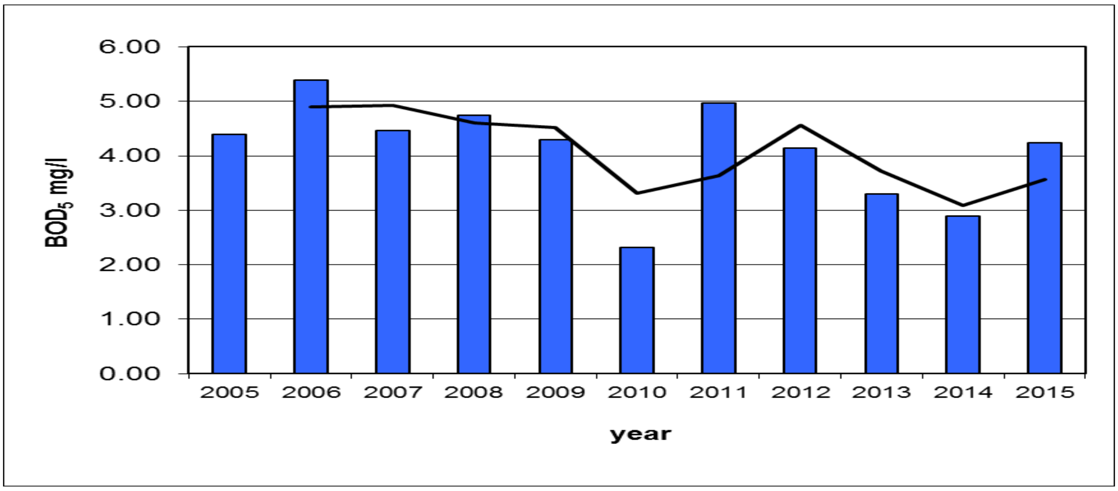


Figure 4.19: Temporal changes of BOD_5 (c90) in Reni

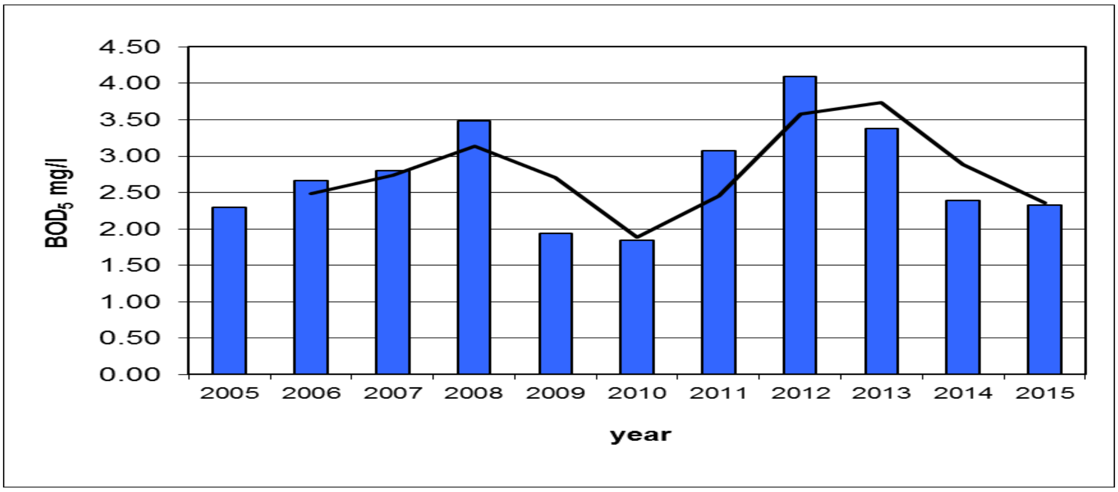


Figure 4.20: Temporal changes of N-NO_3 (c90) in Bratislava

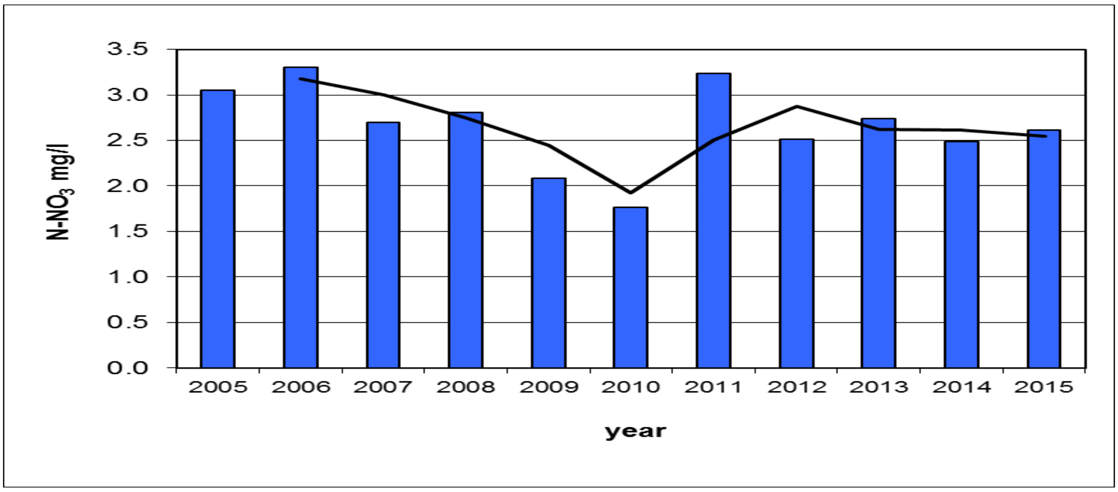


Figure 4.21: Temporal changes of N-NO_3 (c90) in Hercegszanto

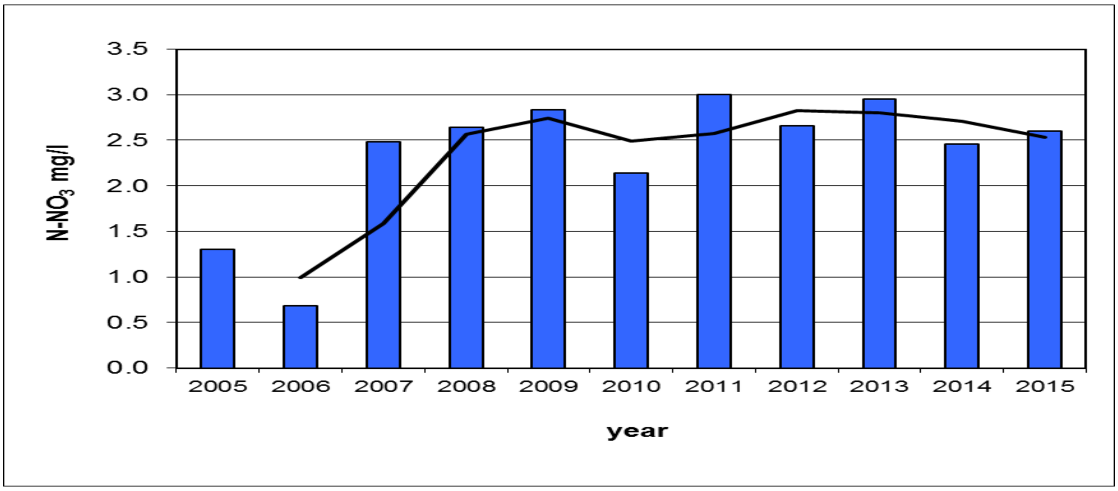


Figure 4.22: Temporal changes of N-NO_3 (c90) in Reni

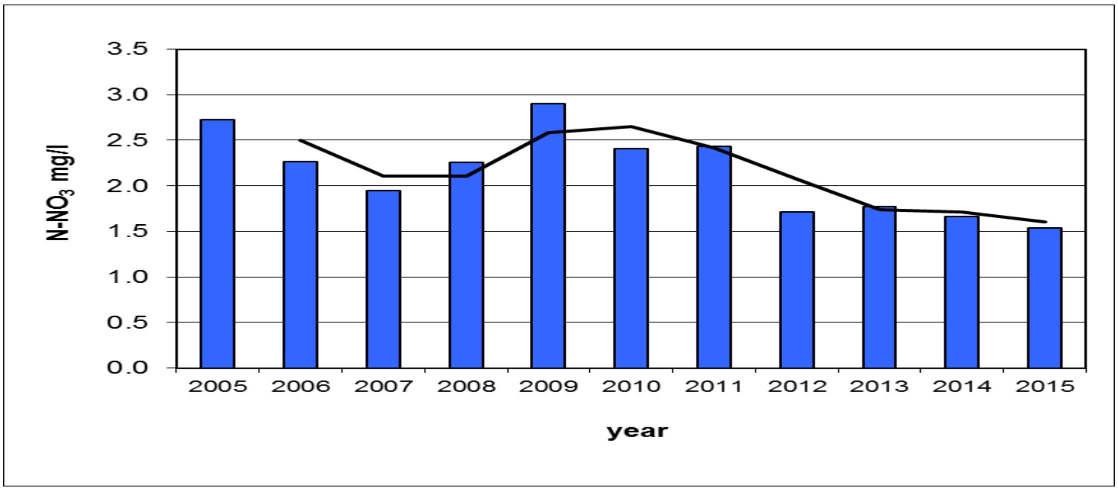


Figure 4.23: Temporal changes of total phosphorus (c90) in Bratislava

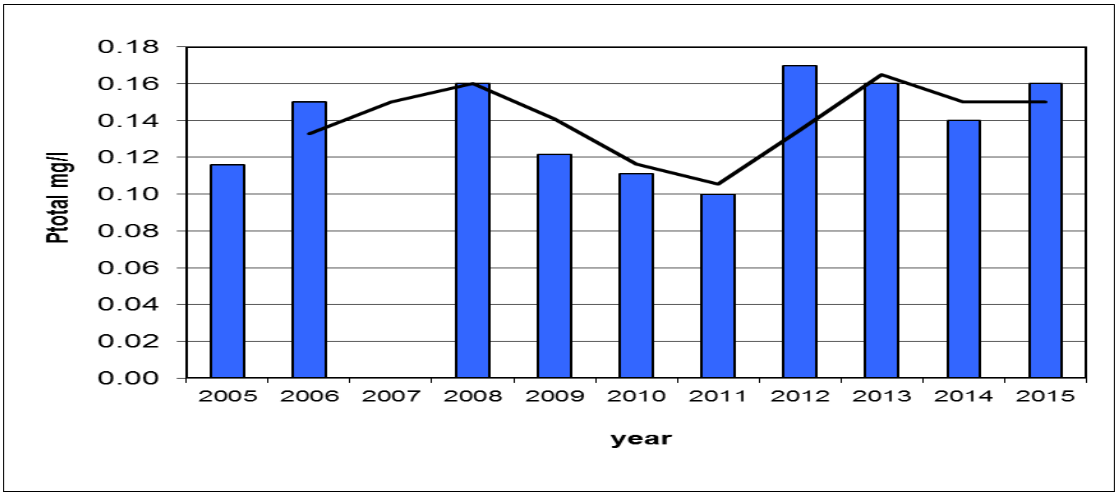


Figure 4.24: Temporal changes of total phosphorus (c90) in Hercegszanto

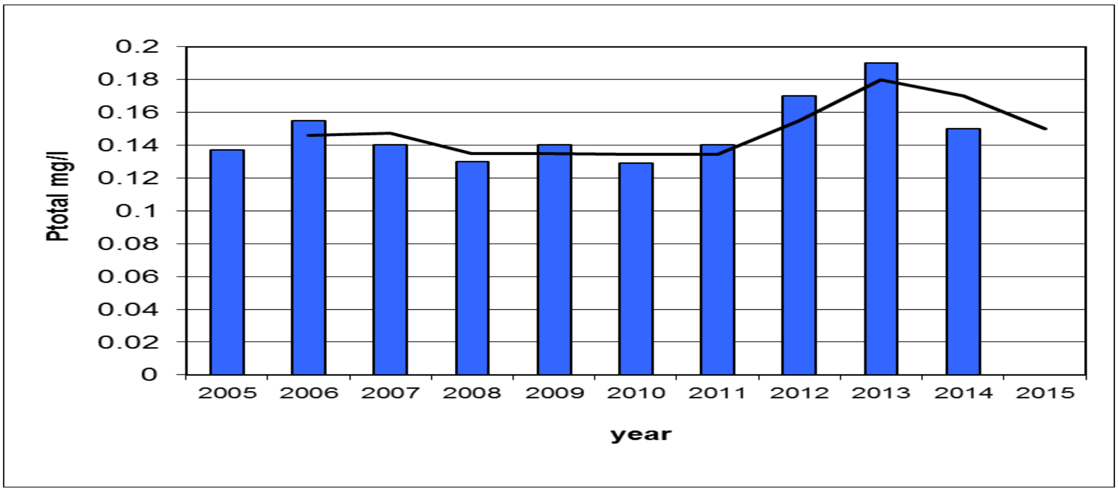


Figure 4.25: Temporal changes of total phosphorus (c90) in Reni

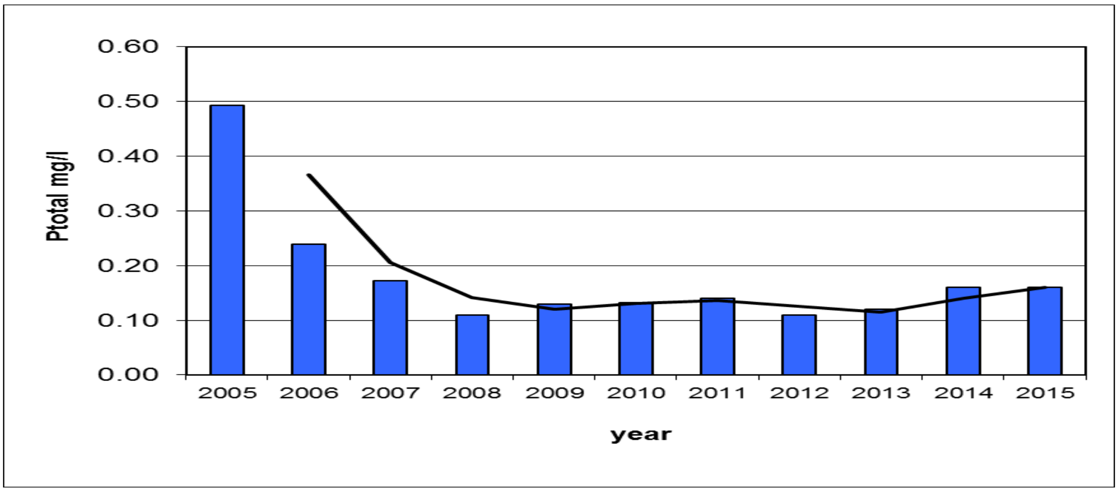


Figure 4.26: The percentile (90, 10) of N-NH$_4$ concentration along the Danube River in 2015.

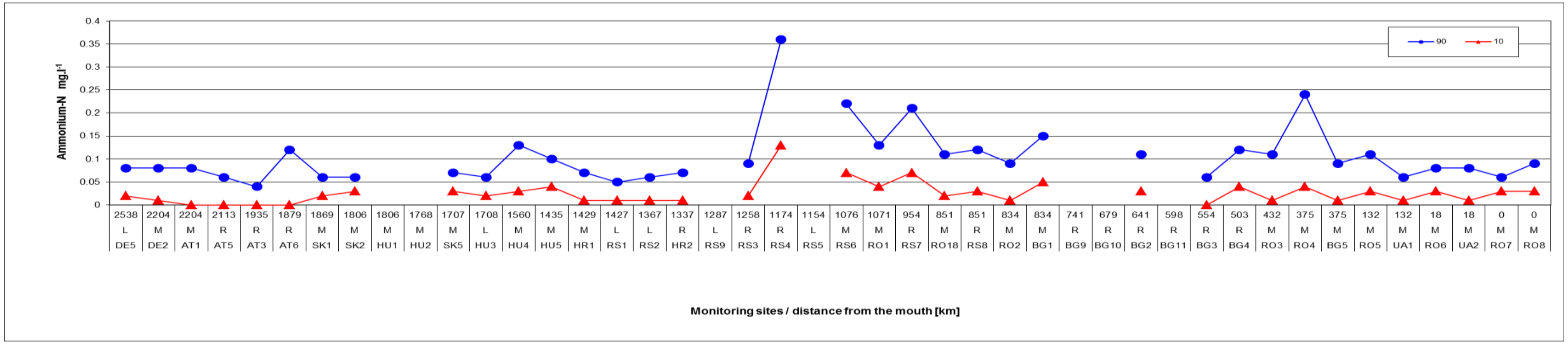


Figure 4.27: The percentile (90, 10) of N-NH$_4$ concentration in the tributaries in 2015.

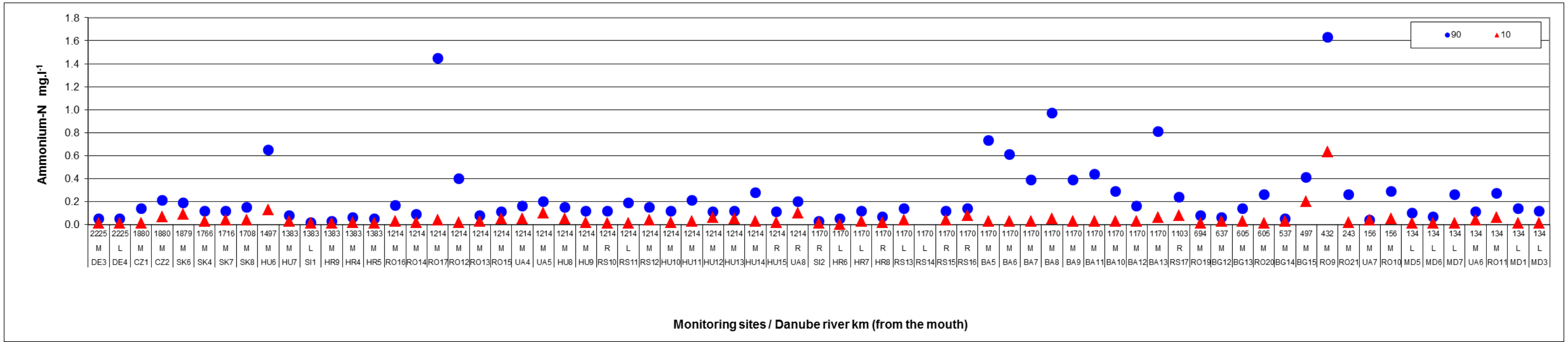


Figure 4.28: The percentile (90, 10) of P-PO_4 concentration along the Danube River in 2015.

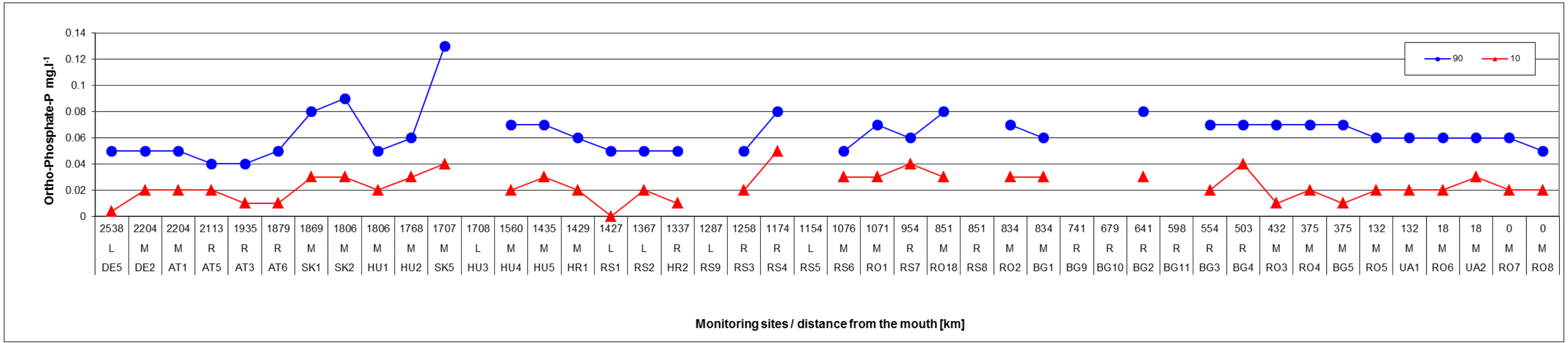


Figure 4.29: The percentile (90, 10) of P-PO_4 concentration in the tributaries in 2015.

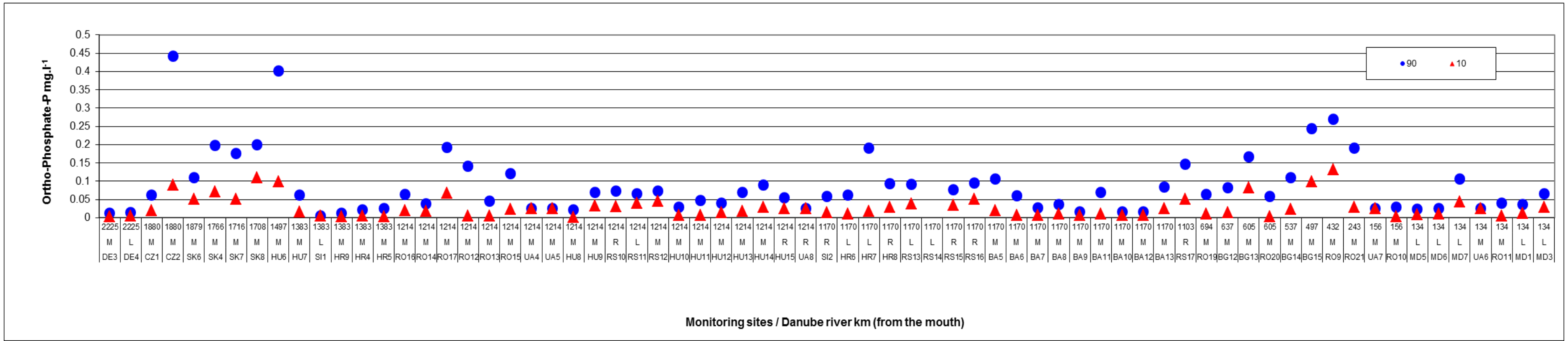


Figure 4.30: The percentile (90, 10) of COD_{Cr} concentration along the Danube River in 2015.

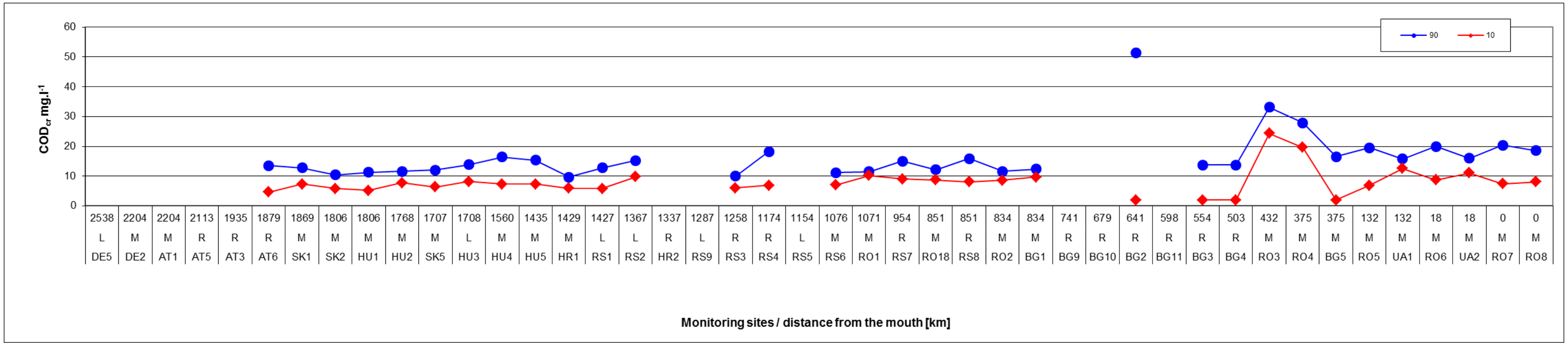


Figure 4.31: The percentile (90, 10) of COD_{Cr} concentration in the tributaries in 2015.

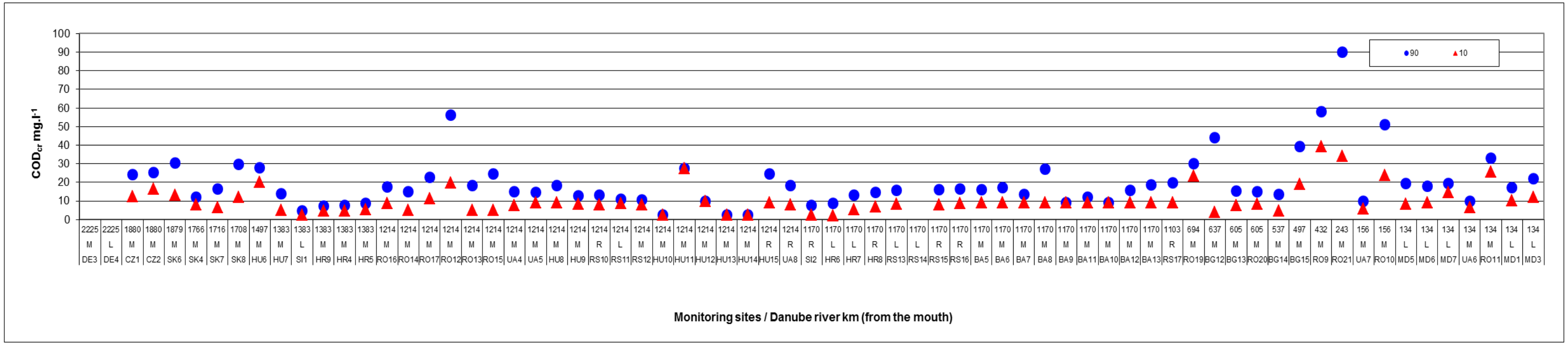


Figure 4.32: The percentile (90, 10) of BOD_5 concentration along the Danube River in 2015.

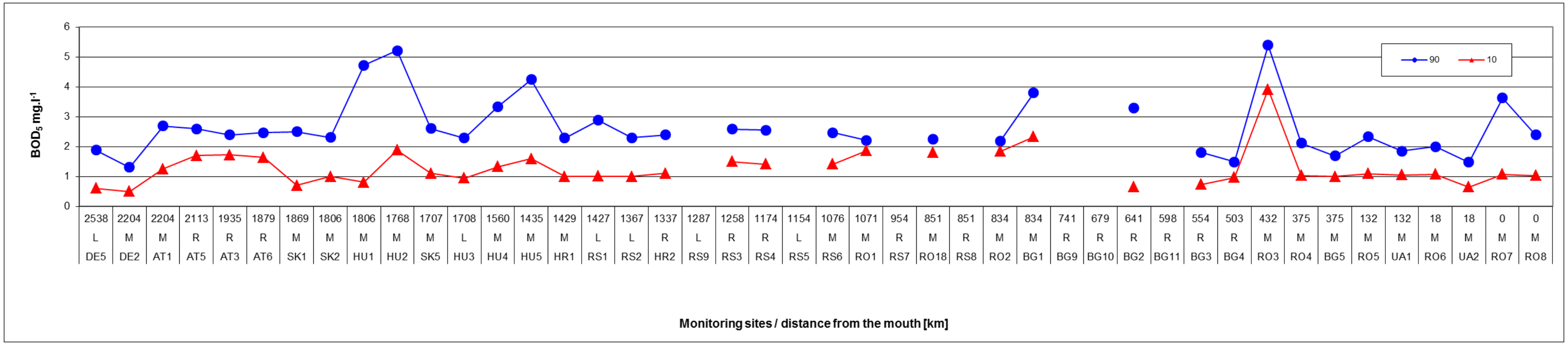


Figure 4.33: The percentile (90, 10) of BOD_5 concentration in the tributaries in 2015.

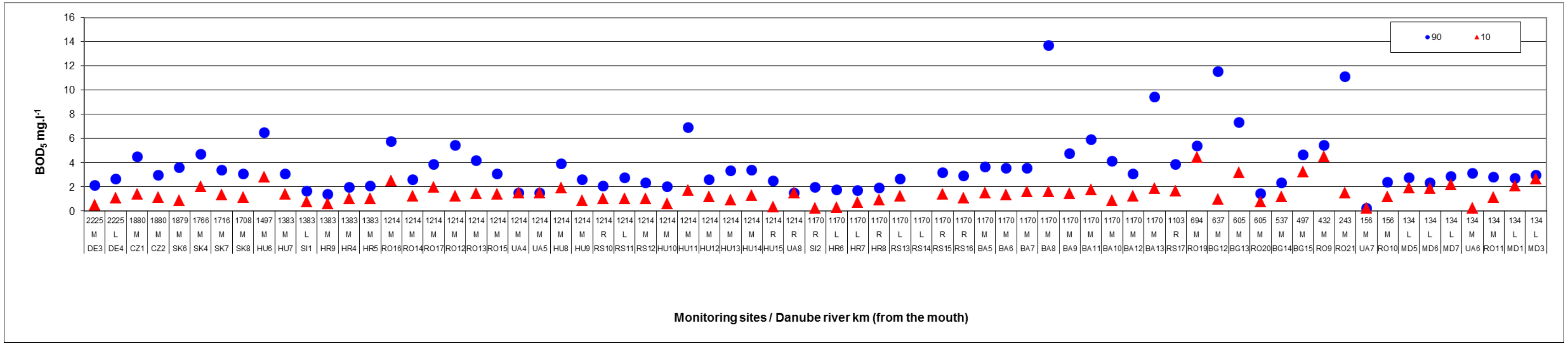


Figure 4.34: The maximum values of macrozoobenthos- saprobic index along the Danube River in 2015.

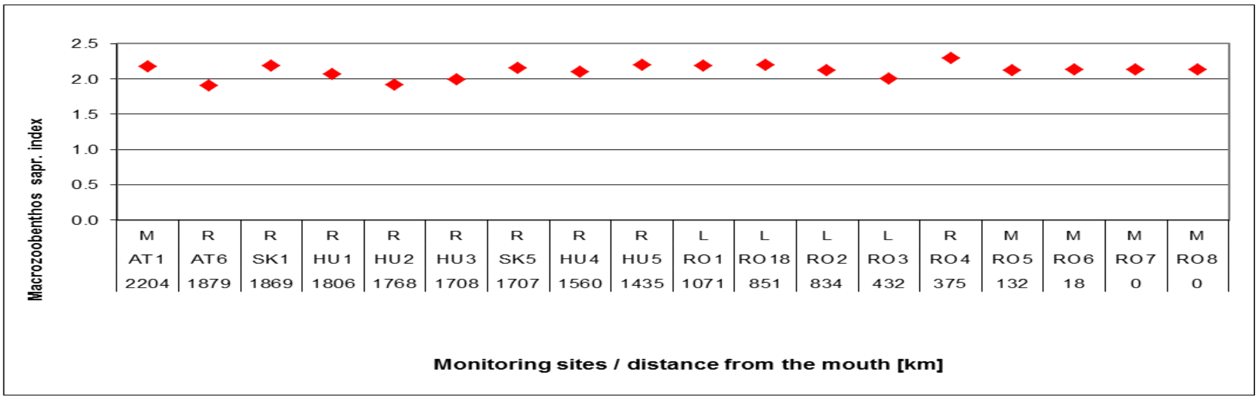
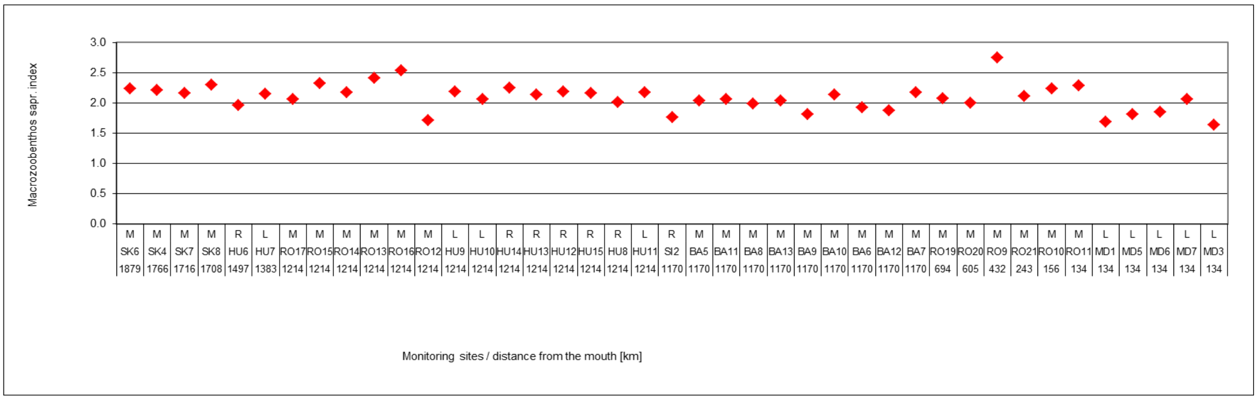
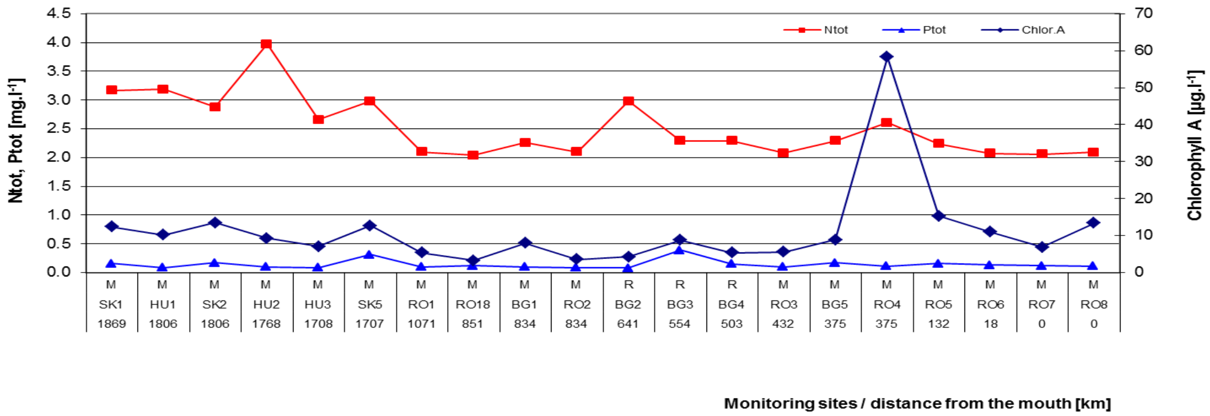


Figure 4.35: The maximum values of macrozoobenthos- saprobic index in the tributaries in 2015.



The maximum values of macrozoobenthos - saprobic index in the Danube River and its tributaries are presented in Figures 4.34 and 4.35. The data of macrozoobenthos were delivered during the year 2015 for 18 monitoring points located in the Danube River and for 41 monitoring points in the tributaries. The maximal value of saprobic index was determined in RO4 Chiciu. The highest value of macrozoobenthos - saprobic index was found in the tributary Arges (RO9).

Figure 4.36: The percentile (90) of total nitrogen, phosphorus and chlorophyll *a* concentration along the Danube River in 2015.



The concentration of nutrients and the chlorophyll *a* are presented in Figure 4.36 (this figure shows only those monitoring sites where all three determinands were measured). The maximal concentration of chlorophyll *a* was observed at RO4. The highest concentration of N_{total} was observed at HU2 and maximal concentration of P_{total} was at BG3.

Figure 4.37: The percentile (90) of $N_{tot.}$, $N\text{-}NH_4$ and $N\text{-}NO_3$ concentration along the Sava River in 2015.

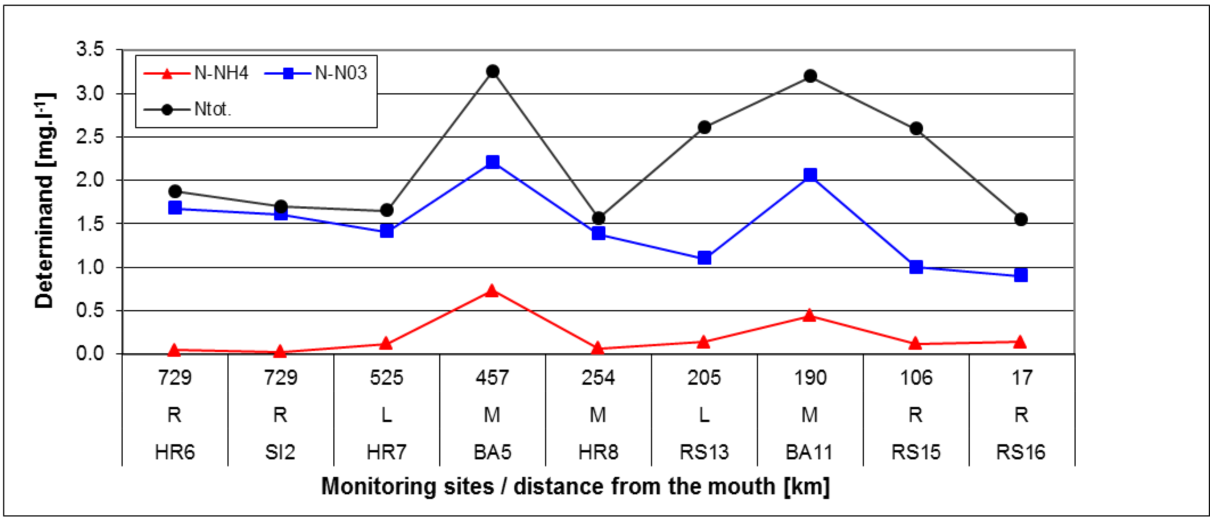
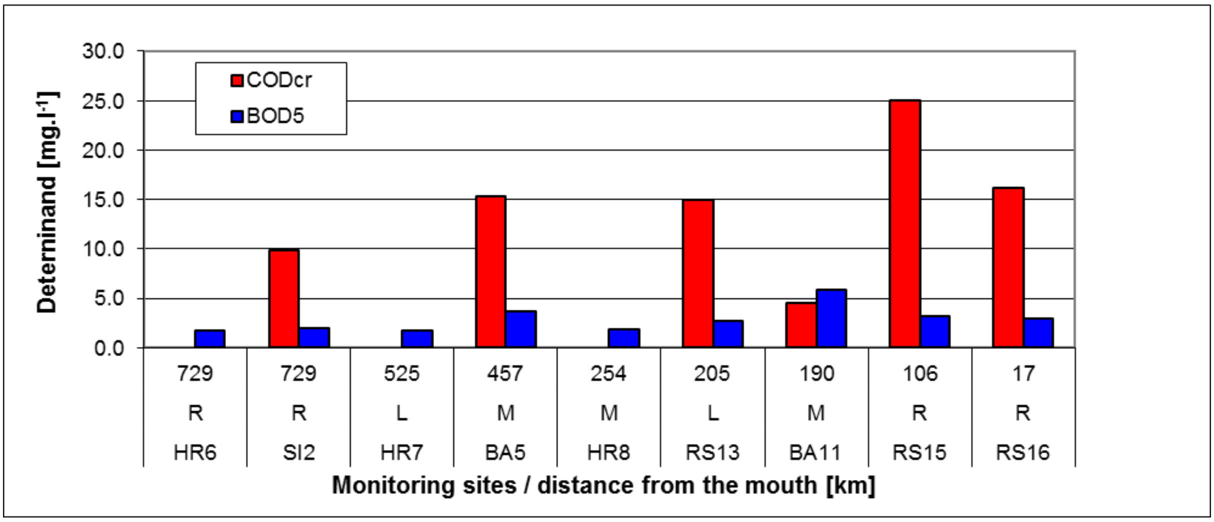


Figure 4.38: The percentile (90) of BOD_5 and COD_{Cr} concentration along the Sava River in 2015.



The percentiles 90 of nutrients COD_{Cr}, BOD_5 measured in 2015 in Sava and Tisza rivers are presented in the Figures 4.37-4.38. The highest value of $N\text{-}NH_4$ in Sava River was found at the monitoring point BA5 (rkm 457). The maximal concentration of $N\text{-}NO_3$ and N_{total} was also observed at BA5 (rkm 457, Figure 4.37). The highest values of BOD_5 in Sava River were measured at the monitoring point BA11 rkm 190 and the highest COD_{Cr} value was measured at the monitoring point RS15 (rkm 106, Figure 4.38).

Figure 4.39: The percentile (90) of total nitrogen, $N\text{-}NH_4$ and $N\text{-}NO_3$ concentration along the Tisza River in 2015.

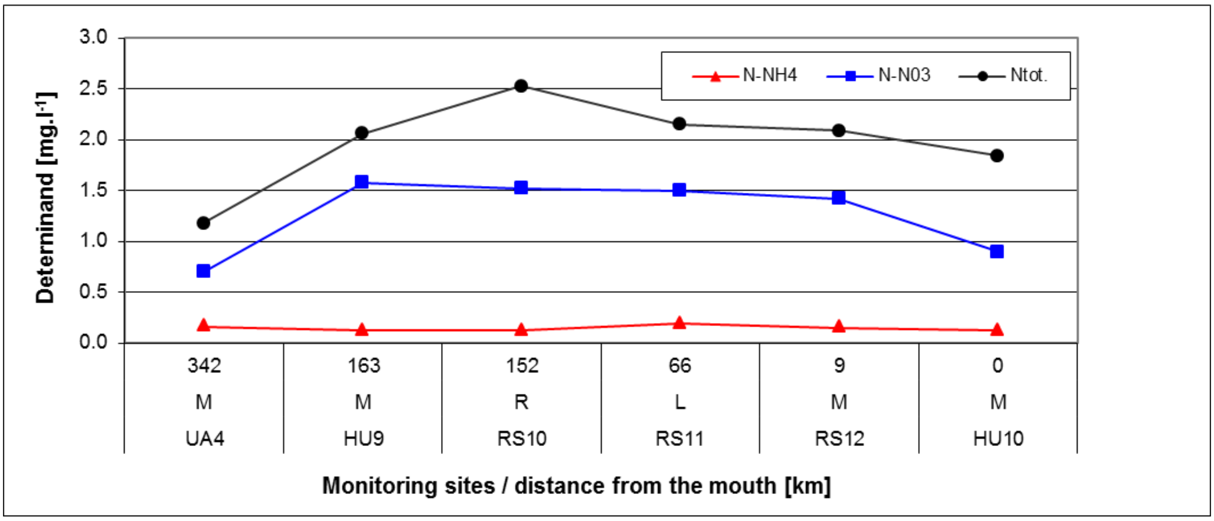
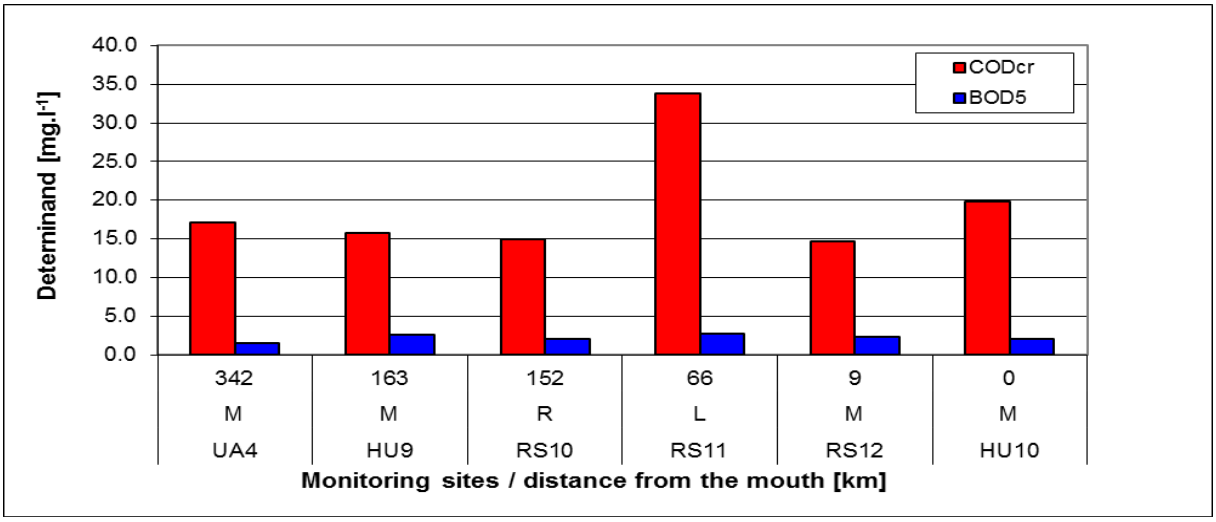


Figure 4.40: The percentile (90) of BOD_5 and COD_{Cr} concentration along the Tisza River in 2015.



The maximal value of $N\text{-}NH_4$ in the Tisza River was measured at the monitoring point RS11 rkm 66 (see Figure 4.39). The highest value of $N\text{-}NO_3$ was measured in HU9 rkm 163. In 2015 maximum of N_{total} was measured in RS10 rkm 152.

The highest value of COD_{Cr} and BOD_5 in Tisza River was found in monitoring point RS11 (rkm 66, Figure 4.40).

5. Load Assssment

5.1 Introduction

The long-term development of loads of relevant determinands in the important rivers of the Danube Basin is one of the major objectives of the TNMN. This is why the load assessment programme in the Danube River Basin started in 2000. For the calculation of loads, a commonly agreed standard operational procedure is used.

5.2 Description of load assessment procedure

The following principles have been agreed for the load assessment procedure:

- *Load is calculated for the following determinands: BOD_5, inorganic nitrogen, ortho-phosphate-phosphorus, dissolved phosphorus, total phosphorus, suspended solids and - on a voluntary basis - chlorides; based on the agreement with the Black Sea Commission, silicates are measured at the Romanian load assessment sites since 2004;*
- *The minimum sampling frequency at sampling sites selected for load calculation is set at 24 per year;*
- *The load calculation is processed according to the procedure recommended by the Project "Transboundary assessment of pollution loads and trends" and described in Chapter 6.4. Additionally, countries can calculate annual load by using their national calculation methods, results of which would be presented together with data prepared on the basis of the agreed method;*
- *Countries should select for load assessment those TNMN monitoring sites for which valid flow data is available (see Table 5).*

Table 5 shows TNMN monitoring locations selected for the load assessment program. It also provides information about hydrological stations collecting flow data for load assessment. Altogether 27 monitoring locations from nine countries are included in the list. One location – Danube-Jochenstein have been included by two neighbouring countries, therefore the actual number of locations is 26, with ten locations on the Danube River itself and 16 locations on the tributaries. Rivers Prut and Siret were added in the year 2010.

The second location that could potentially be processed by using combined data from two countries is Sava-Jesenice.

5.3 Monitoring Data in 2015

The monitoring frequency is an important factor for the assessment of pollution loads in water courses. Table 6 shows the number of measurements of flow and water quality determinands in the TNMN load assessment sites.

Data are shown in tables 7 and 8. In most of the locations, the number of samples was higher than 20, lower frequency was for chlorides. A frequency of 10-12 times per year was applied for Czech, Croatians and Ukraine monitoring stations. In 2010 load calculation for Slovakian monitoring points on tributaries Morava, Hron, Ipeľ was added, for this point's frequency of monitoring were also 12.

The loads in the Danube at Jochenstein are being assessed on the basis of combined data from Germany and Austria, there is no problem with insufficient frequency there.

Regarding particular determinands, there is still a lack of data on dissolved phosphorus as it was measured in 13 locations only. At 13 monitoring points the silicate or dissolved silicate load was calculated. This calculation of the silicate load is to respond to the agreements with the Black Sea Commission.

Table 5: List of TNMN locations selected for load assessment program

Country	River	Water quality monitoring location			Hydrological station	
		TNMN Code	Location	Distance from mouth (Km)	Location	Distance from mouth (Km)
Germany	Danube	DE2	Jochenstein	2204	Achleiten	2223
Germany	Inn	DE3	Kirchdorf	195	Oberaudorf	211
Germany	Inn/Salzach	DE4	Laufen	47	Laufen	47
Austria	Danube	AT1	Jochenstein	2204	Aschach	2163
Austria	Danube	AT6	Hainburg	1879	Hainburg (Danube) Angern (March)	1884 32
Czech Republic	Morava	CZ1	Lanzhot	79	Lanzhot	79
Czech Republic	Morava/Dyje	CZ2	Pohansko	17	Breclav-Ladná	32,3
Slovak Republic	Danube	SK1	Bratislava	1869	Bratislava	1869
Slovak Republic	Váh	SK4	Komárno		Sum of: Maly Dunaj -Trstice Vah- Sala Nitra -Nove Zamky	22,5 58,8 12,3
Slovak Republic	Morava	SK6	Devín		Zahorska Ves	32,5
Slovak Republic	Hron	SK7	Kamenica		Kanenin	10,9
Slovak Republic	Ipeľ	SK8	Salka		Salka	12,2
Hungary	Danube	HU3	Szob	1708	Nagymaros	1695
Hungary	Danube	HU5	Hercegszántó	1435	Mohács	1447
Hungary	Tisza	HU9	Tiszasziget	163	Szeged	174
Croatia	Danube	HR2	Borovo	1337	Vukovar	1337
Croatia	Sava	HR06	Jesenice	729	Jesenice	729
Croatia	Sava	HR7	Una Jesenovac	525	Una Jesenovac	525
Croatia	Sava	HR8	Zupanja	254	Zupanja	254
Slovenia	Drava	SI1	Ormoz	300	Borl HE Formin Pesnica-Zamusani	325 311 10.1(to the Drava)
Slovenia	Sava	SI2	Jesenice	729	Catez Sotla -Rakovec	737 8.1 (to the Sava)
Romania	Danube	RO2	Pristol-Novo Selo	834	Gruia	858

Country	River	Water quality monitoring location			Hydrological station	
		TNMN Code	Location	Distance from mouth (Km)	Location	Distance from mouth (Km)
Romania	Danube	RO4	Chiciu-Silistra	375	Chiciu	379
Romania	Danube	RO5	Reni	132	Isaccea	101
Romania	Siret	RO10	Sendreni	0	Sendreni	0
Romania	Prut	RO11	Giurgiulesti	0	Giurgiulesti	0
Ukraine	Danube	UA2	Vylkove	18		

5.4 Calculation Procedure

Regarding several sampling sites in the profile, the average concentration at a site is calculated for each sampling day. In case of values “below the limit of detection”, the value of the limit of detection is used in the further calculation. The average monthly concentrations are calculated according to the formula:

$$C_m\,[mg.l^{-1}] = \frac{\sum_{i \in m} C_i\,[mg.l^{-1}]\,.\,Q_i\,[m^3.s^{-1}]}{\sum_{i \in m} Q_i\,[m^3.s^{-1}]}$$

where C_m average monthly concentrations

C_i concentrations in the sampling days of each month

Q_i discharges in the sampling days of each month

The monthly load is calculated by using the formula:

$$L_m\,[tones] = C_m\,[mg.l^{-1}]\,.\,Q_m\,[m^3.s^{-1}]\,.\,days\,(m)\,.\,0{,}0864$$

where L_m monthly load

Q_m average monthly discharge

- *If discharges are available only for the sampling days, then Q_m is calculated from those discharges.*
- *For months without measured values, the average of the products $C_m.Q_m$ in the months with sampling days is used.*

The annual load is calculated as the sum of the monthly loads:

$$L_a\,[tones] = \sum_{m=1}^{12} L_m\,[tones]$$

Table 6: Number of measurements in TNMN locations selected for assessment of pollution load in 2015

Country	River	Location	Location	River	Number of meausrements in 2015								
Code			in profile	Km	Q	SS	N_{inorg}	$P\text{-}PO_4$	P_{total}	BOD_5	Cl	P_{diss}	SiO_2
DE2	Danube	Jochenstein	M	2204	365	13	25	25	25	13	13	12	
DE3	Inn	Kirchdorf	M	195	365	12	12	12	12	12	12		
DE4	Inn/Salzach	Laufen	L	47	365	13	13	13	13	13	13		
AT1	Danube	Jochenstein	M	2204	365	12	25	25	25	12	12		
AT6	Danube	Hainburg	R	1879	365	24	24	24	24	24	24	24	
CZ1	Morava	Lanzhot	M	79	365	12	12	12	12	12	12		
CZ2	Morava/Dyje	Pohansko	M	17	365	12	12	12	12	12	12		
SK1	Danube	Bratislava	M	1869	365	26	26	26	2	26	12	26	26
SK4	Váh	Komárno	M	1	365	12	12	12	1	12	12	12	8
SK6	Morava	Devín	M	1	365	12	12	12	12	12	12	12	6
SK7	Hron	Kamenica	M	2	365	12	12	12	1	12	12	12	7
SK8	Ipoly	Salka	M	12	365	12	12	12	1	12	12	12	7
HU3	Danube	Szob	L	1708		24	24		23	24	24		
			M	1708	365	23	23		22	23	23		
			R	1708		24	24		23	24	24		
HU5	Danube	Hercegszántó	M	1435	365	24	24	24		24	24		24
HU9	Tisza	Tiszasziget	L	163		26	26	26	26	12	14		26
			M	163	365	25	25	24	25	12	14		25
			R	163		26	26	26	26	12	14		26
HR2	Danube	Borovo	R	1337	365	12	12	12	12	12	12		12
HR6	Sava	Jesenice	R	729	365	12	12	12	12	12	12		12
HR7	Sava	us Una Jesenovac	L	525	365	12	12	12	12	12	12		12
HR8	Sava	ds Zupanja	ML	254	365	11	11	11	11	11	11		
SI1	Drava	Ormoz	L	300	362	25	25	25	25	25	12		
SI2	Sava	Jesenice	R	729	365	24	24	24	24	24	12		
RO2	Danube	Pristol-Novo Selo	L	834		26	26	26	26	26	12	26	26
			M	834	365	25	25	25	25	25	12	25	25
			R	834		25	25	25	25	25	12	25	25
RO4	Danube	Chiciu-Silistra	L	375		25	26	26	26	26	12	14	
			M	375		25	26	26	26	26	12	14	
			R	375		25	26	26	26	26	12	14	
RO5	Danube	Reni	L	132		25	25	25	25	25	12	12	25
			M	132	365	25	25	25	25	25	12	12	25
			R	132		25	25	25	25	25	12	12	25
RO10	M	Siret	M	0	365	26	26	26	26	26	13	14	
RO11	M	Prut	M	0	365	26	26	26	26	26	13	15	
UA2	Danube	Vylkove	M	18	365	12	12	12		12	12	12	12

5.5 Results

The mean annual concentrations and annual loads of suspended solids, inorganic nitrogen, ortho-phosphate-phosphorus, total phosphorus, BOD_5, chlorides and – where available – dissolved phosphorus and silicates - are presented in tables 7 to 10, separately for monitoring locations on the Danube River and for monitoring locations on tributaries. The explanation of terms used in the tables 7 to 10 is as follows.

Term used	Explanation
Station Code	TNMN monitoring location code
Profile	location of sampling site in profile (L-left, M-middle, R-right)
River Name	name of river
Location	name of monitoring location
River km	distance to mouth of the river
Q_a	mean annual discharge in the year 2015
c_{mean}	arithmetical mean of the concentrations in the year 2015
Annual Load	annual load of given determinand in the year 2015

Table 11 shows loads of other determinands (nitrogen forms and heavy metals) at the profile Reni, which are monitored since 2005 based on the agreement with the Black Sea Commission. Annual loads for Danube and tributaries are in figures 5.5.1 -5.5.12.

Trends for load during last 10 years in the Reni are in figures 5.5.13.-5.5. 18. In general loads has a decreasing tendency in years 2011 and 2012. Due to the high discharges in 2005 and 2010 the loads were higher in those years. In 2015 loads decreased, only for suspended solids and chlorides increased loads were observed.

The mean annual discharge was lower in whole Danube River compared to 2014. Also in the tributaries the discharges were lower than in 2014. Only in Vah and Siret the 2015 discharge was higher than in 2014.

The spatial pattern of the annual load along the Danube River is similar to the previous year. In the case of suspended solids, inorganic nitrogen, BOD_5, ortho-phosphate, total phosphorus and chlorides, the highest load is observed in the lower part of the Danube River. The highest load of suspended solids, total phosphorus, dissolved phosphorus, chlorides and silicates was measured at the monitoring location Danube-Reni (RO5). The highest load of the inorganic nitrogen and ortho-phosphates was observed at RO4 Chiciu-Silistra. The highest load for BOD_5 was found at RO2 Pristol-Novo Selo.

In the case of the tributaries, the highest load of inorganic nitrogen, BOD_5, total phosphorus and chlorides is coming from the Sava River (HR7 and HR8). The highest load of the dissolved phosphorus was observed in the Vah River. For suspended solids the maximum was measured in the Inn River and maximum of silicates was measured in the Tisza River.

Table 7: Mean annual concentrations in monitoring locations selected for load assessment on Danube River in 2015

Station Code	Profile	River Name	Location	River km	Q_a	c_{mean}							
						Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved	Silicates
					$(m^3.s^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$
DE2 +AT1	M	Danube	Jochenstein	2204	1240	18.19	1.99	0.03	0.06	1.50	18.97	0.05	
AT6	R	Danube	Hainburg	1879	1673	12.47	1.93	0.03	0.05	2.13	19.21	0.05	
SK1	M	Danube	Bratislava	1869	1629	22.56	1.97	0.05	0.13	1.48	18.54	0.06	5.29
HU3	LMR	Danube	Szob	1708	1903	14.02	1.94		0.08	1.92	20.93		
HU5	M	Danube	Hercegszántó	1435	2030	17.85	1.89	0.04		2.73	27.48		4.58
HR2	R	Danube	Borovo	1337	2676	17.75	1.69	0.03	0.12	1.66	18.20		5.16*
RO2	LMR	Danube	Pristol-Novo Selo	834	4971	34.08	1.30	0.06	0.08	2.08	21.09	0.07	1.47*
RO4	LMR	Danube	Chiciu-Silistra	375	5722	20.71	1.55	0.05	0.08	1.55	23.88	0.07	
RO5	LMR	Danube	Reni	132	6138	49.51	1.25	0.04	0.10	1.55	27.35	0.07	3.14*
UA2	M	Danube	Vylkove	18	3030	58.81	1.08	0.04		1.13	34.78	0.09	2.73

*Silicates (SiO_2) in dissolved form

Table 8: Mean annual concentrations in monitoring locations selected for load assessment on tributaries in 2015

Station Code	Profile	River Name	Location	River km	Q_a	c_{mean}							
						Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved	Silicates
					$(m^3.s^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$
DE3	M	Inn	Kirchdorf	195	298	185.42	0.81	0.01	0.16	1.16	6.07		
DE4	L	Inn/Salzach	Laufen	47	225	65.88	0.56	0.01	0.07	1.92	8.09		
CZ1	M	Morava	Lanzhot	79	40	27.13	2.32	0.05	0.11	2.88	31.58		
CZ2	L	Morava/Dyje	Pohansko	17.00	30	11.50	3.09	0.21	0.24	2.12	46.00		
SK4	M	Váh	Komárno	1	177	18.17	2.04	0.08	0.13	2.18	19.71	0.09	6.01
SK6	M	Morava	Devín	1	71	34.83	2.21	0.13	0.24	2.90	42.58	0.15	6.80
SK7	M	Hron	Kamenica	2	41	27.00	1.83	0.11	0.28	2.51	14.34	0.12	11.04
SK8	M	Ipoly	Salka	12	13	40.58	2.15	0.15	0.31	2.33	23.57	0.17	21.30
HU9	LMR	Tisza	Tiszasziget	163	525	32.85	1.06	0.05	0.14	1.93	33.12		7.51
SI1	L	Drava	Ormoz	300	270	8.46	0.97	0.01	0.04	1.11	6.82		
SI2	R	Sava	Jesenice	729	226	5.78	1.43	0.04	0.08	1.15	7.20		
HR6	R	Sava	Jesenice	729	220	9.23	1.43	0.04	0.09	1.03	8.55		2.88*
HR7	L	Sava	us. Una Jasenovac	525	731	15.72	1.31	0.10	0.17	1.28	9.17		3.74*
HR8	ML	Sava	ds. Zupanja	254	1113	13.56	1.10	0.05	0.12	1.27	28.83		
RO10	M	Siret	Conf. Danube (Sendreni)	0	176	177.69	1.29	0.01	0.13	1.75	89.27	0.06	
RO11	M	Prut	Conf. Danube (Giurgiulesti)	0	58	53.00	1.08	0.02	0.07	1.75	52.78	0.04	

*Silicates (SiO_2) in dissolved form

Table 9: Annual load in selected monitoring locations on Danube River

Station Code	Profile	River Name	Location	River km	Annual Load in 2015							
					Suspended Solids (x10^6tonns)	Inorganic Nitrogen (x10^3tonns)	Ortho-Phosphate Phosphorus (x10^3tonns)	Total Phosphorus (x10^3tonns)	BOD_5 (x10^3tonns)	Chlorides (x10^6tonns)	Phosphorus - dissolved (x10^3tonns)	Silicates (x10^6tonns)
DE2 +AT1	M	Danube	Jochenstein	2204	0.91	79.7	1.15	2.61	58.77	0.71	2.09	
AT6	R	Danube	Hainburg	1879	0.79	100.42	1.53	2.82	112.81	0.96	2.54	
SK1	M	Danube	Bratislava	1869	1.72	99.59	2.66	0.86	81.15	0.94	3.27	0.26
HU3	LMR	Danube	Szob	1708	1.02	119.65		4.43	127.14	1.22		
HU5	M	Danube	Hercegszántó	1435	1.35	126.67	2.76		175.64	1.91		0.30
HR2	R	Danube	Borovo	1337	1.59	150.77	2.49	10.17	135.12	1.53		0.44*
RO2	LMR	Danube	Pristol-Novo Selo	834	5.36	214.34	8.54	11.38	324.61	3.24	9.83	0.23*
RO4	LMR	Danube	Chiciu-Silistra	375	4.70	298.72	9.73	14.78	299.27	4.25	12.31	
RO5	LMR	Danube	Reni	132	10.20	255.60	7.86	19.65	308.28	5.41	14.82	0.65*
UA2	M	Danube	Vylkove	18	6	97.60	4.29		115.00	3.33	8.59	0.28

*Silicates (SiO_2) in dissolved form

Table 10: Annual load in selected monitoring locations on tributaries

Station Code	Profile	River Name	Location	River km	Annual Load in 2015							
					Suspended Solids (x10^6tonns)	Inorganic Nitrogen (x10^3tonns)	Ortho-Phosphate Phosphorus (x10^3tonns)	Total Phosphorus (x10^3tonns)	BOD_5 (x10^3tonns)	Chlorides (x10^6tonns)	Phosphorus - dissolved (x10^3tonns)	Silicates (x10^6tonns)
DE3	M	Inn	Kirchdorf	195	3.05	7.67	0.08	2.31	11.36	0.04		
DE4	L	Inn/Salzach	Laufen	47	0.67	3.76	0.06	0.65	13.47	0.05		
CZ1	M	Morava	Lanzhot	79	0.04	4.12	0.05	0.14	2.70	0.03		
CZ2	L	Morava/Dyje	Pohansko	17	0.01	4.00	0.13	0.16	1.52	0.04		
SK4	M	Váh	Komárno	1	0.11	11.87	0.43	0.08	13.78	0.10	0.55	0.019
SK6	M	Morava	Devín	1	0.07	6.95	0.24	0.41	6.30	0.08	0.26	0.004
SK7	M	Hron	Kamenica	2	0.04	2.62	0.14	0.04	3.25	0.02	0.16	0.006
SK8	M	Ipoly	Salka	12	0.02	0.97	0.05	0.01	1.18	0.01	0.06	0.003
HU9	LMR	Tisza	Tiszasziget	163	0.73	20.33	0.76	2.52	32.42	0.49		0.136
SI1	L	Drava	Ormoz	300	0.07	7.65	0.04	0.29	8.53	0.05		
SI2	R	Sava	Jesenice	729	0.05	9.17	0.23	0.49	6.58	0.04		
HR6	R	Sava	Jesenice	729	0.09	10.34	0.30	0.68	7.34	0.06		0.022*
HR7	L	Sava	us. Una Jasenovac	525	0.42	30.76	1.90	3.76	29.40	0.21		0.096*
HR8	ML	Sava	ds. Zupanja	254	0.49	33.14	1.44	3.39	39.54	0.77		
RO10	M	Siret	Conf. Danube (Sendreni)	0	1.83	8.10	0.11	0.37	12.03	0.49	0.32	
RO11	M	Prut	Conf. Danube (Giurgiulesti)	0	0.09	2.28	0.04	0.13	3.27	0.10	0.11	

*Silicates (SiO_2) in dissolved form

Table 11: Additional annual load data at Reni for reporting to the Black Sea Commission

Location in profile	River km	Number of measurements in 2015												
		Q	N-NH_4	N-NO_2	N-NO_3	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg	$Hg_{diss.}$
LMR	132	366	25	25	25	25	12	12	12	12	12	12	12	12
Location in profile	**River km**	c_{mean}												
		Q_a	N-NH_4	N-NO_2	N-NO_3	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg	$Hg_{diss.}$
		($m^3.s^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)	($\mu g.l^{-1}$)
LMR	132	6138	0.07	0.02	1.17	1.72	8.27	3.82	1.41	0.69	0.10	0.08	0.02	0.011
Location in profile	**River km**	Annual Load in 2015												
			N-NH_4	N-NO_2	N-NO_3	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg	$Hg_{diss.}$
			($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	(tonns)	(tonns)	(tonns)	(tonns)	(tonns)	(tonns)	(tonns)	(tonns)
LMR	132		11.62	3.63	241.81	359.28	1978.85	645.27	311.16	124.22	17.79	14.60	3.05	2.33

Figure 5.5.1: Annual load of suspended solids at monitoring locations along the Danube River.

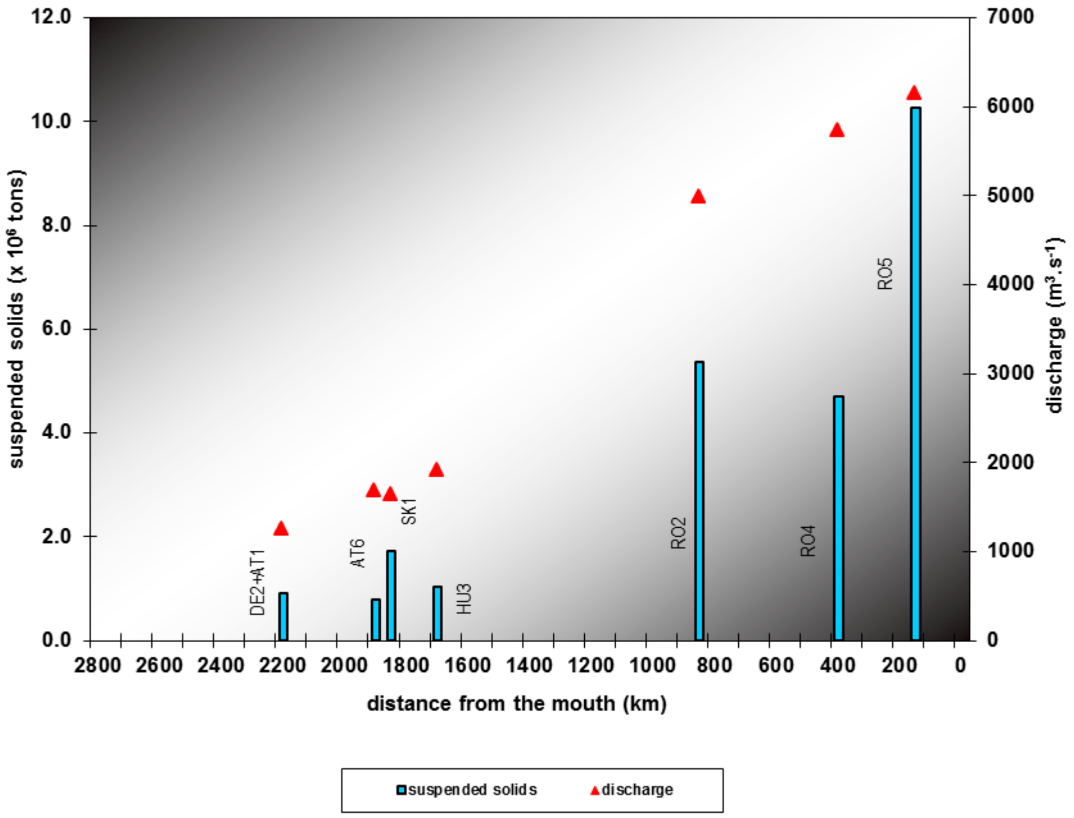


Figure 5.5.2: Annual load of suspended solids at monitoring locations on tributaries.

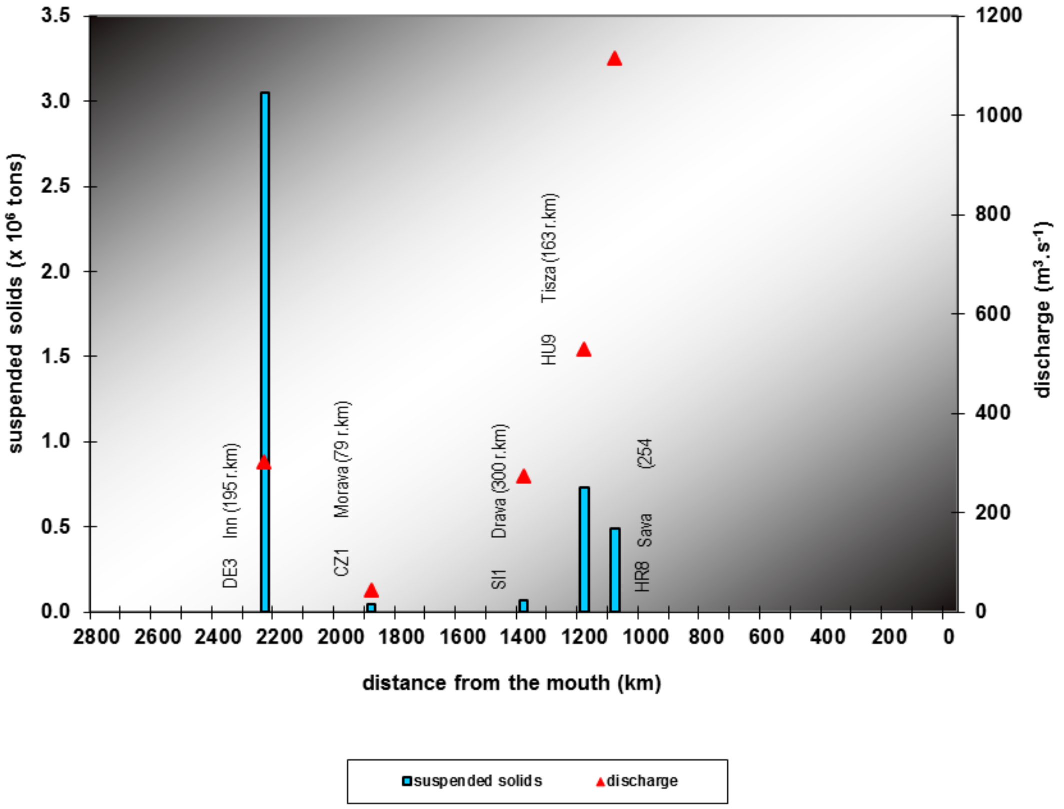


Figure 5.5.3: Annual loads of inorganic nitrogen at monitoring locations along the Danube River.

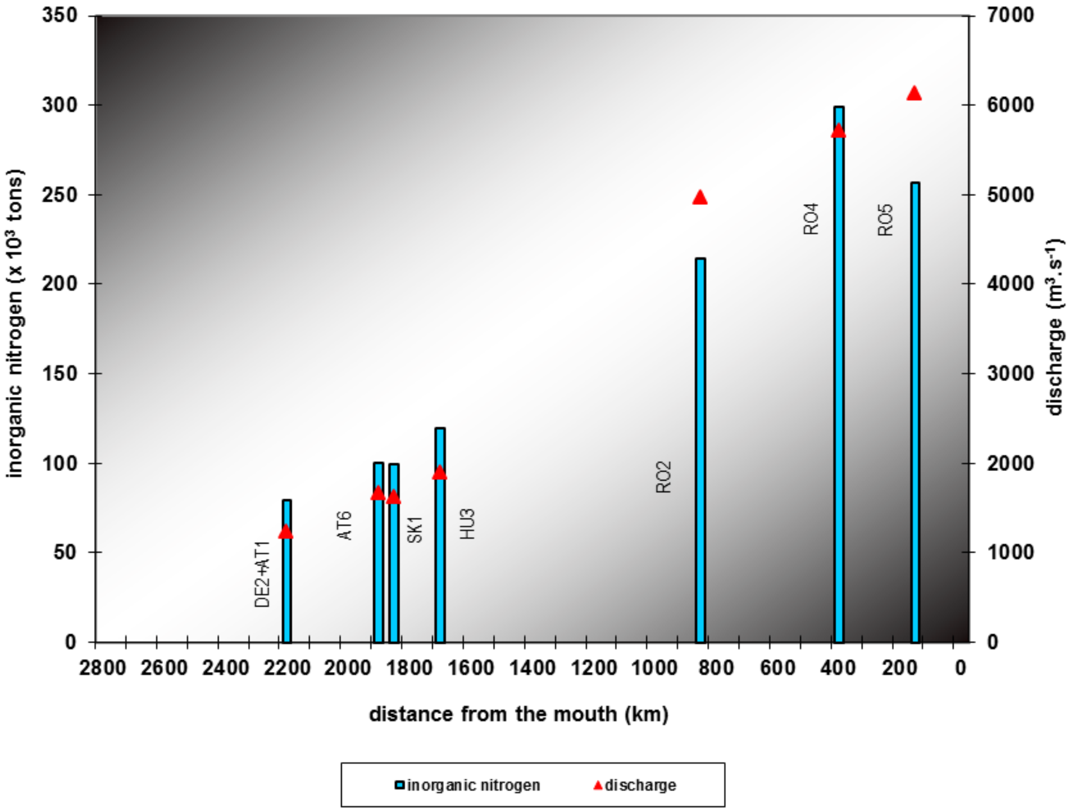


Figure 5.5.4: Annual loads of inorganic nitrogen at monitoring locations on tributaries.

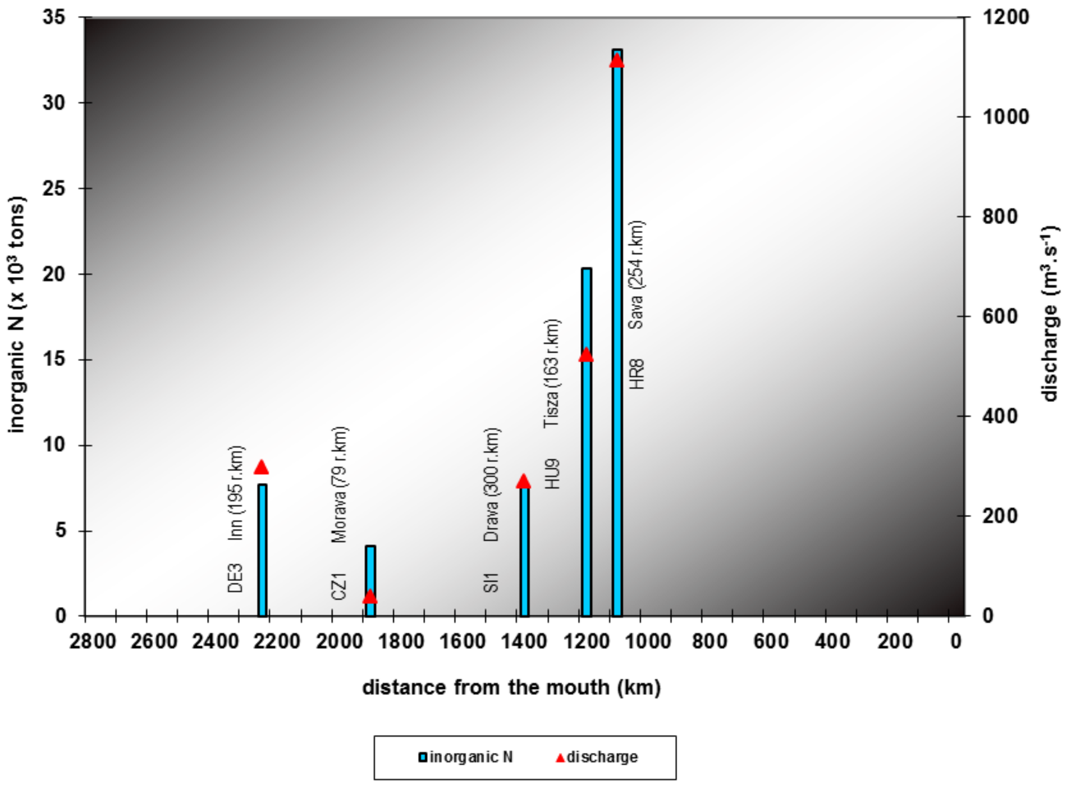


Figure 5.5.5: Annual loads of P-PO_4 at monitoring locations along the Danube River.

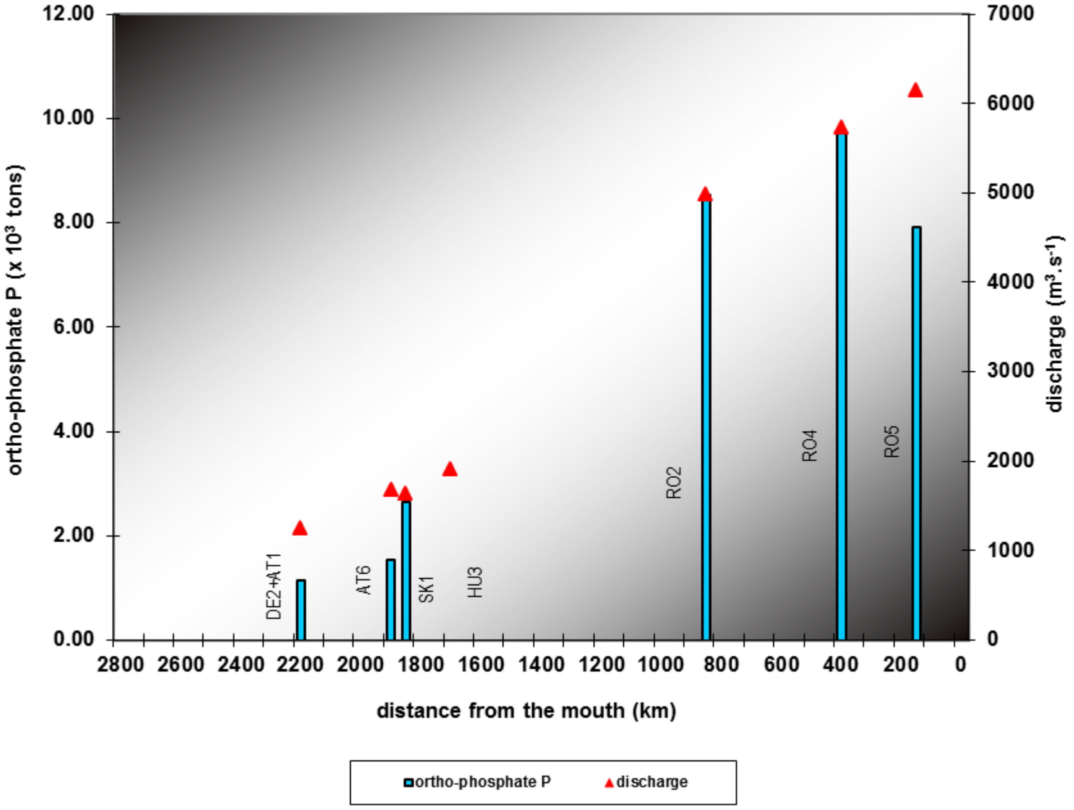


Figure 5.5.6: Annual loads of P-PO_4 at monitoring locations on tributaries.

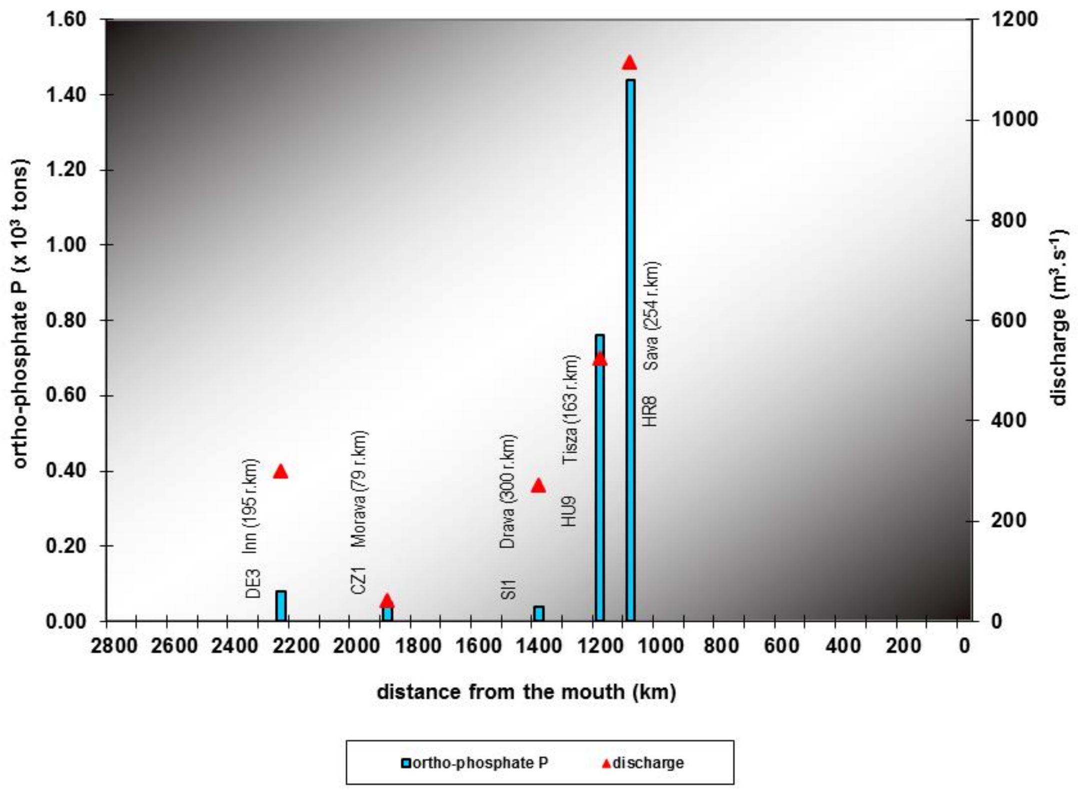


Figure 5.5.7: Annual loads of total phosphorus at monitoring locations along the Danube River.

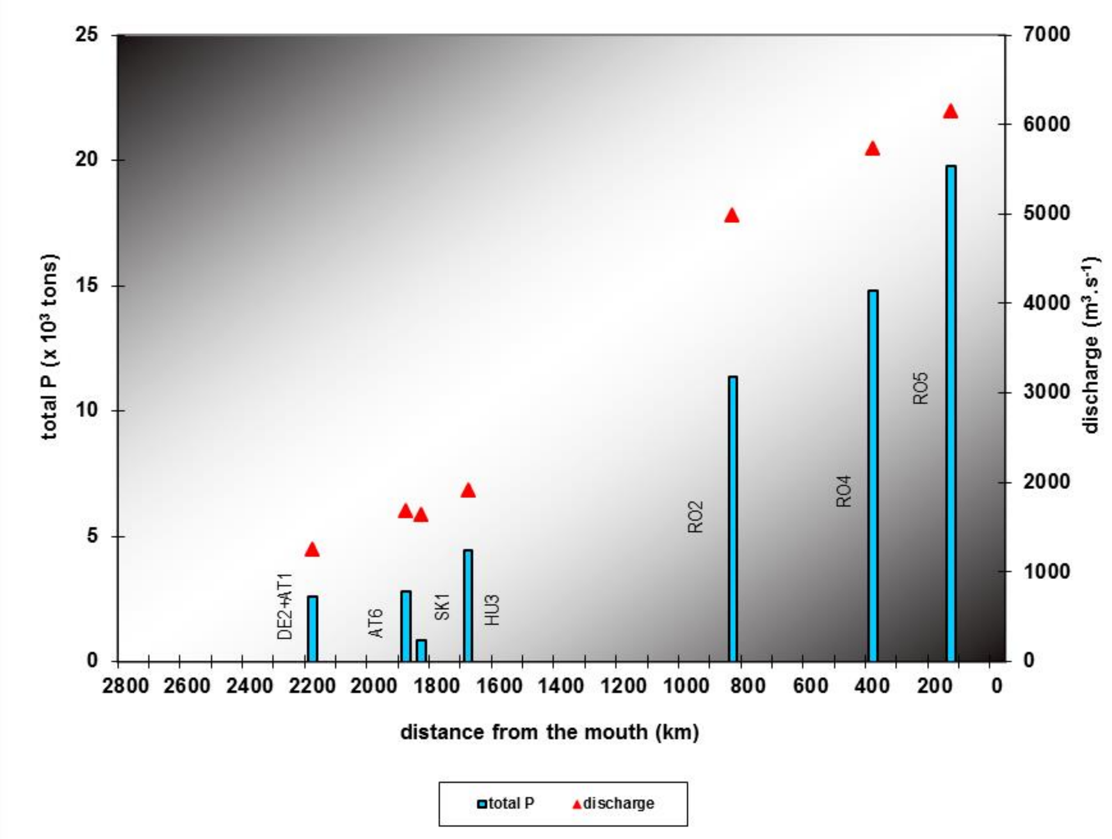


Figure 5.5.8: Annual loads of total phosphorus at monitoring locations on tributaries.

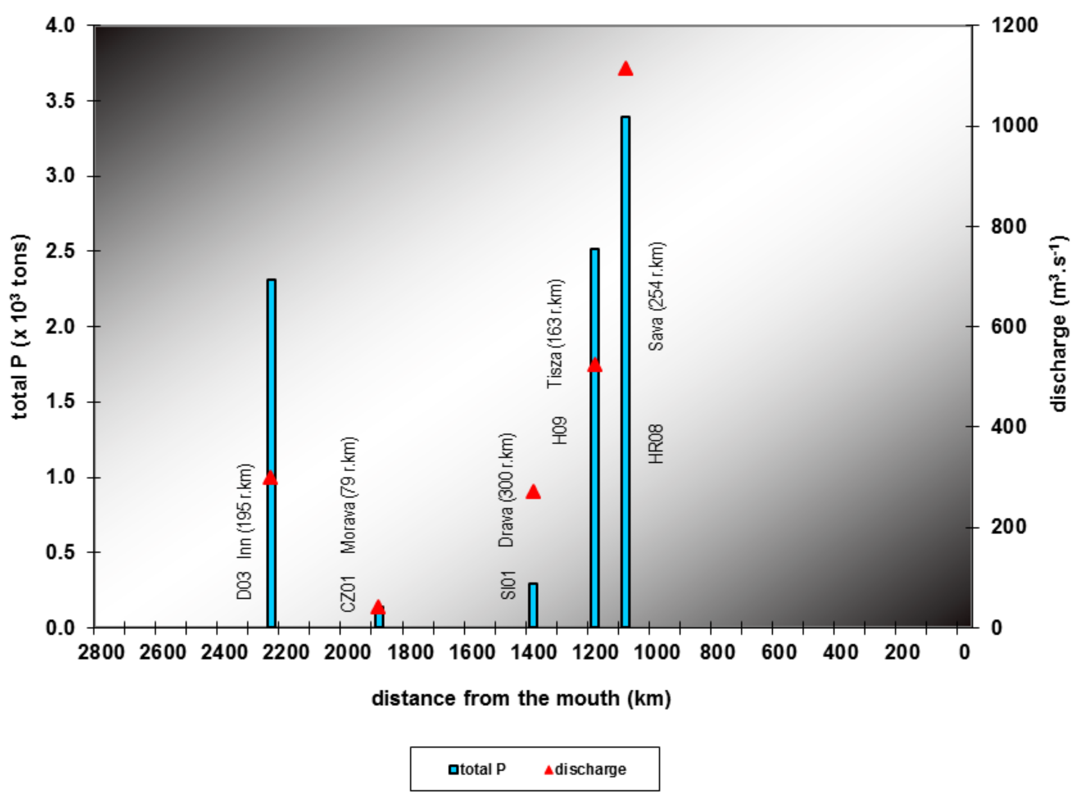


Figure 5.5.9: Annual loads of BOD_5 at monitoring locations along the Danube River.

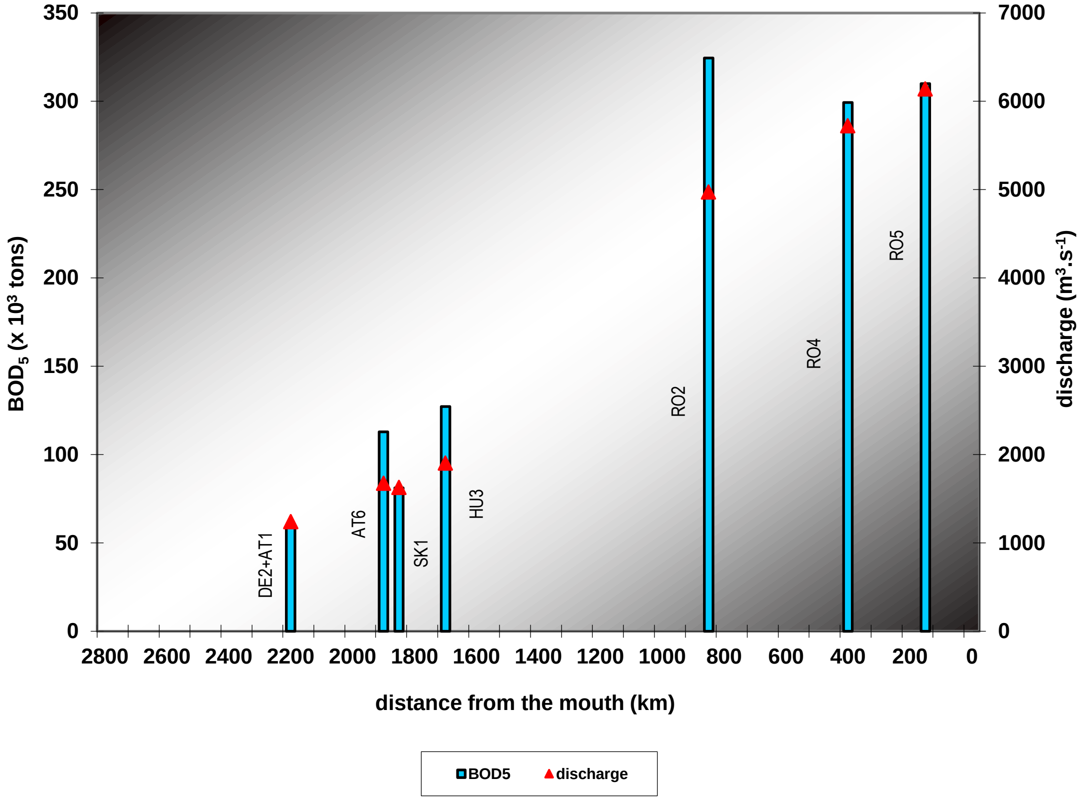


Figure 5.5.10: Annual loads of BOD_5 at monitoring locations on tributaries.

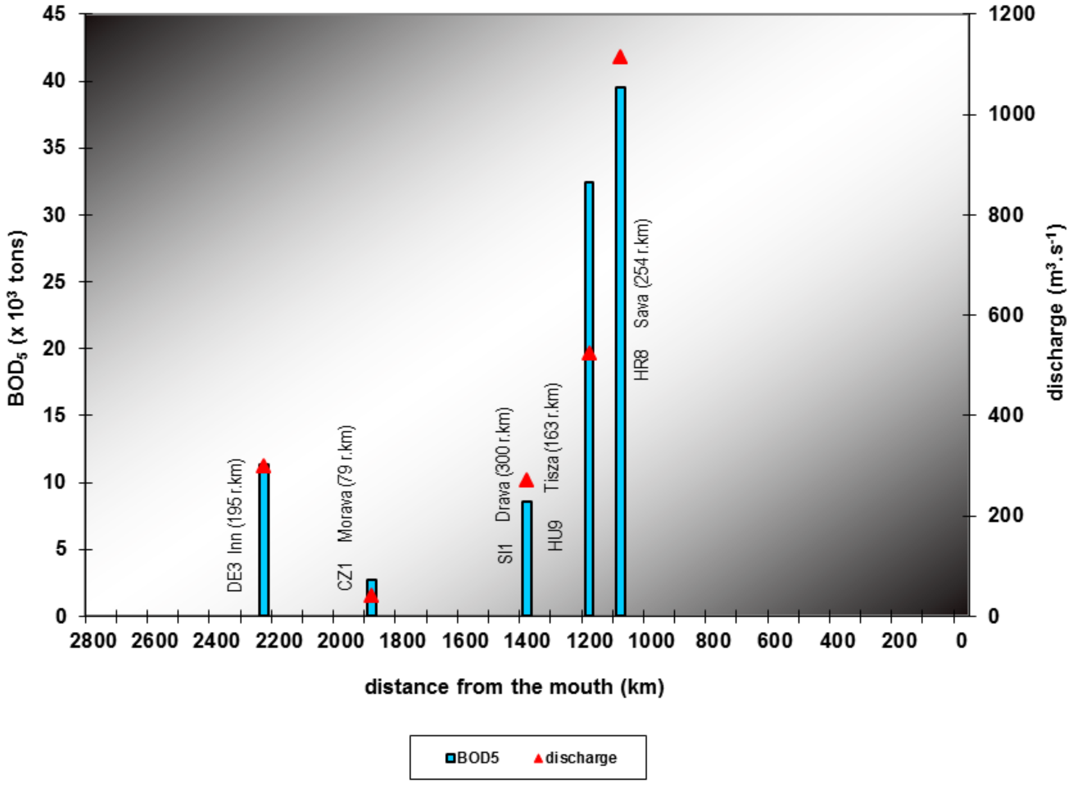


Figure 5.5.11: Annual loads of chlorides at monitoring locations along the Danube River.

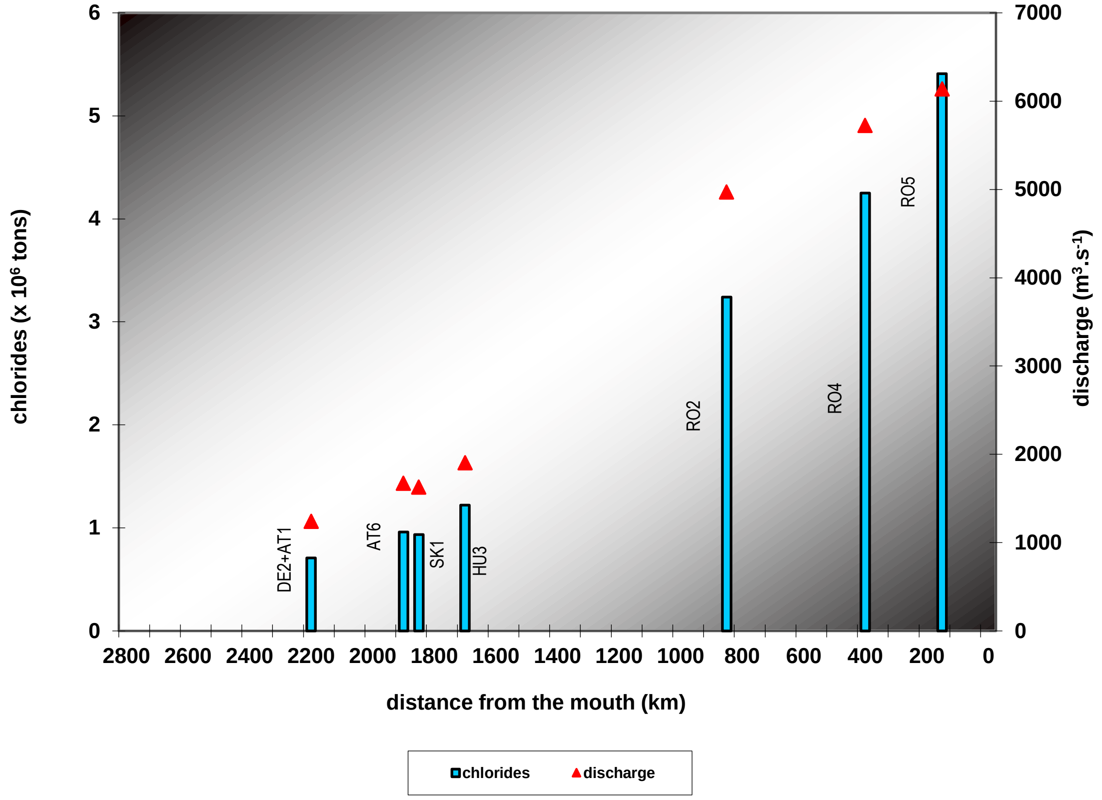


Figure 5.5.12: Annual loads of chlorides at monitoring locations on tributaries.

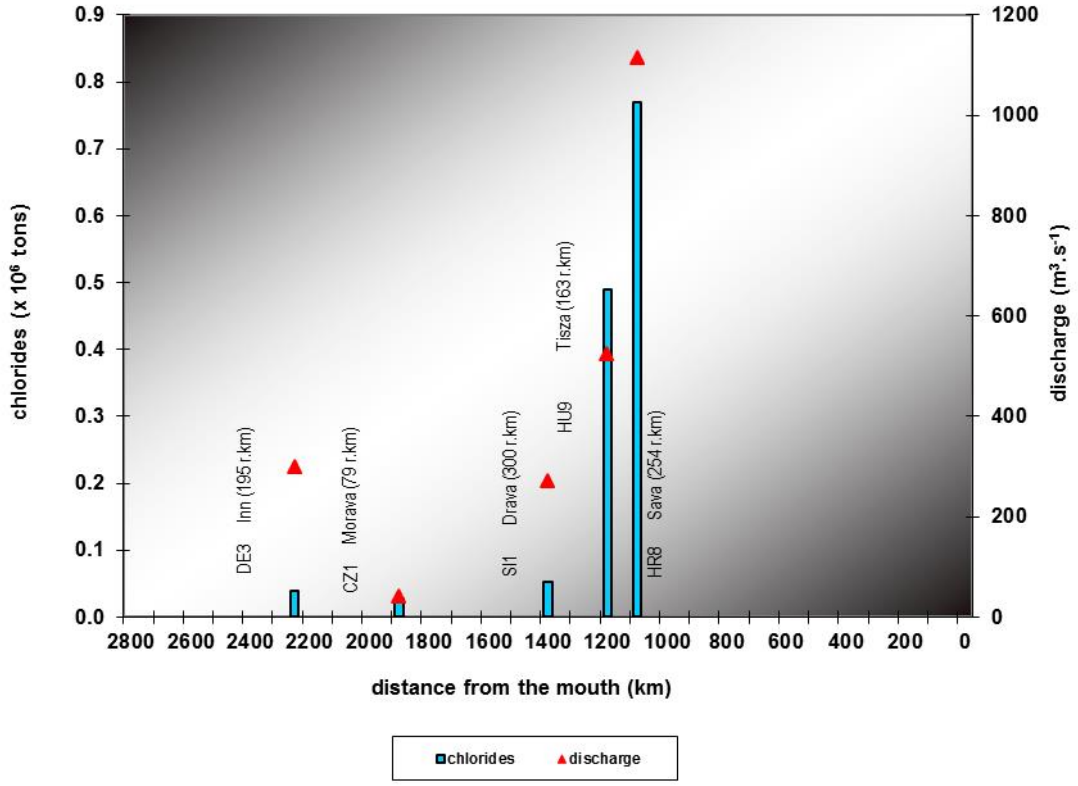


Figure 5.5.13: Trends of annual loads of suspended solids at Reni.

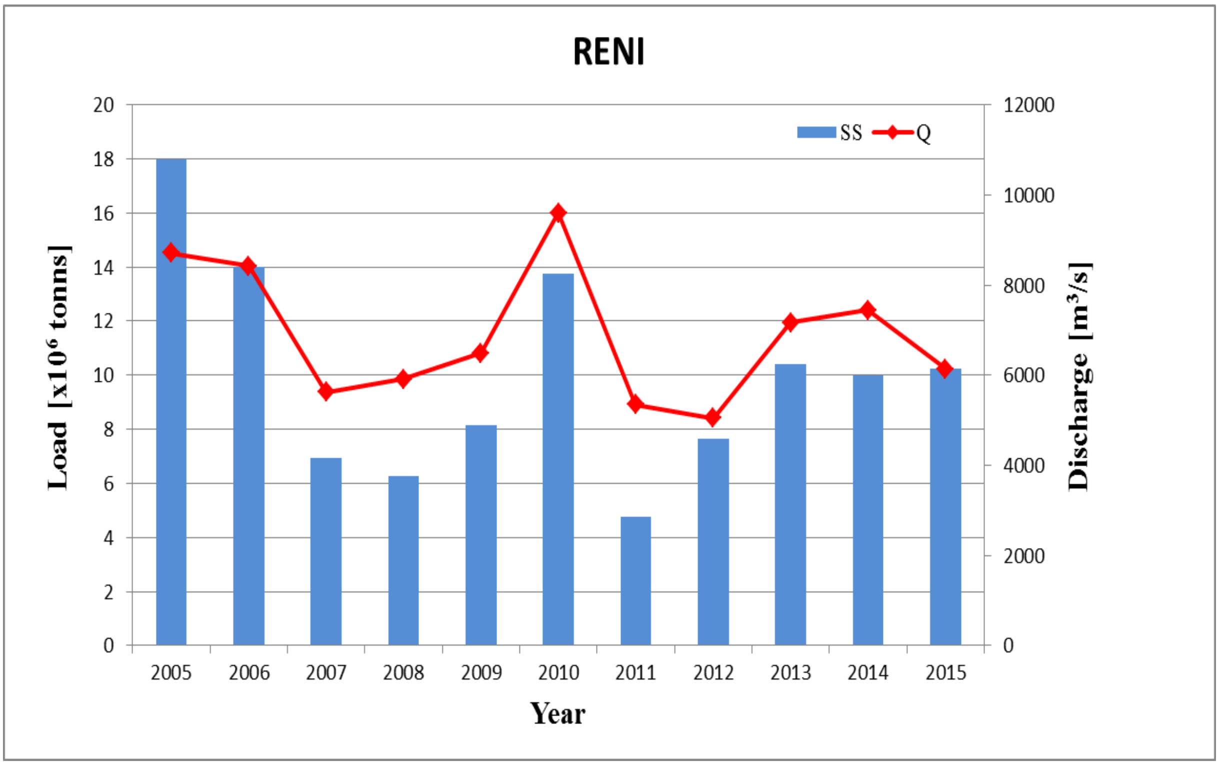


Figure 5.5.14: Trends of annual loads of inorganic nitrogen at Reni.

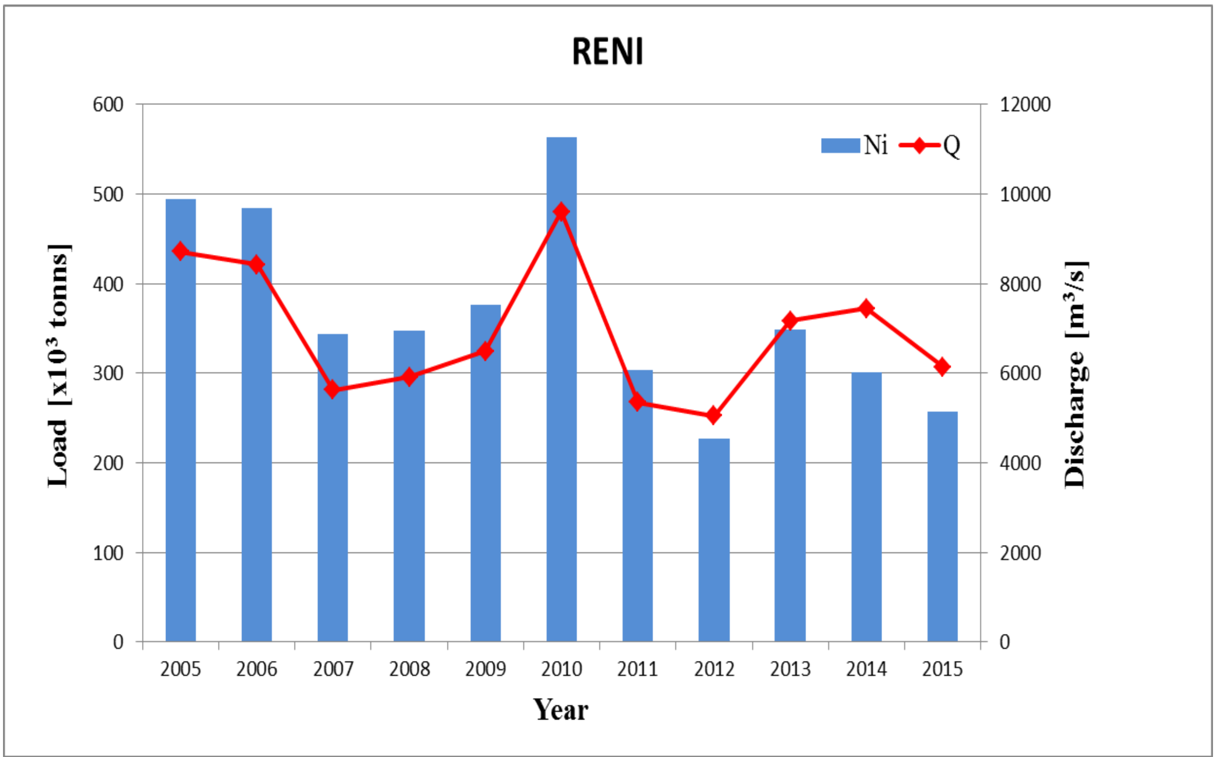


Figure 5.5.15: Trends of annual loads of P-PO_4 and total phosphorus and dissolved phosphorus at Reni.

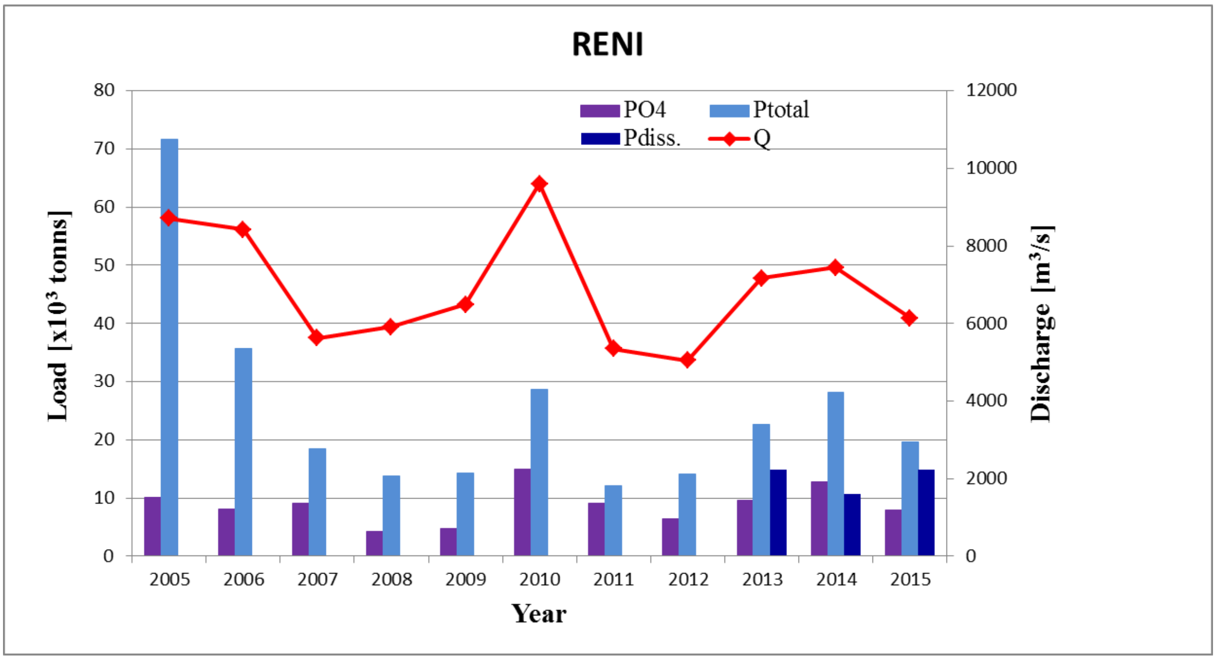


Figure 5.5.16: Trends of annual loads of BOD_5 at Reni.

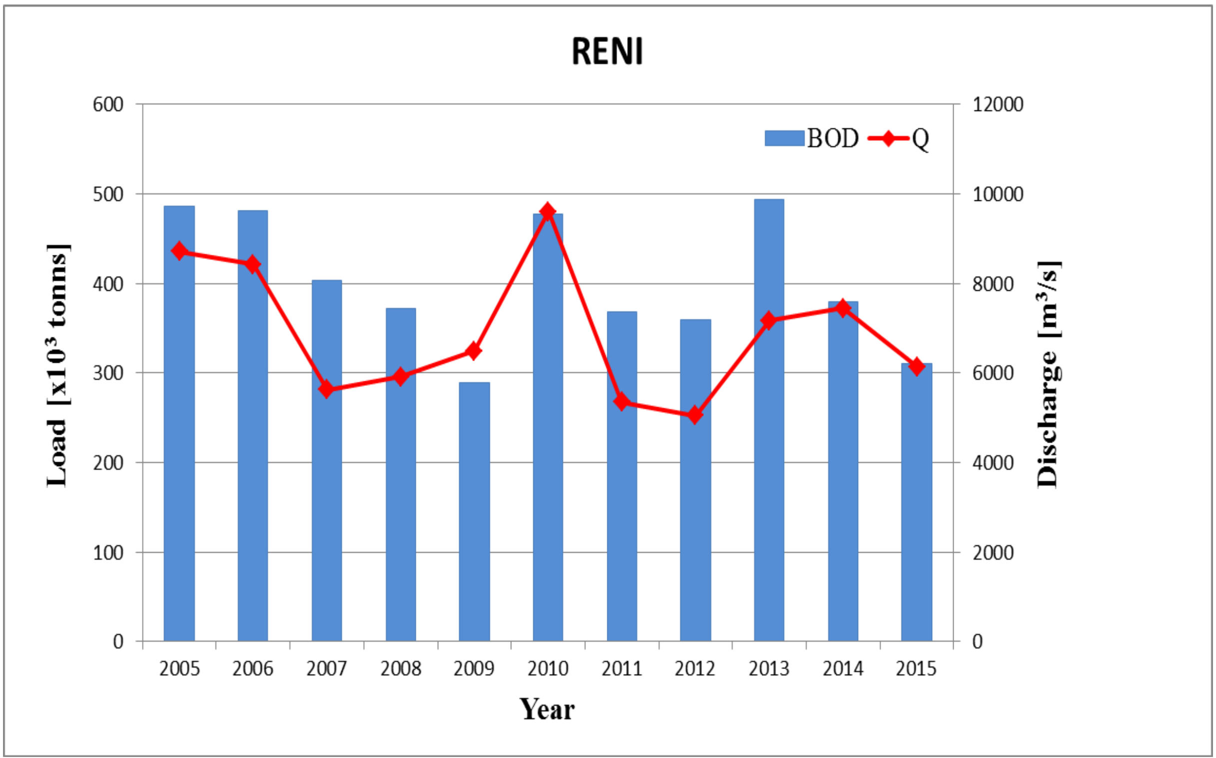


Figure 5.5.17: Trends of annual loads of chlorides at Reni.

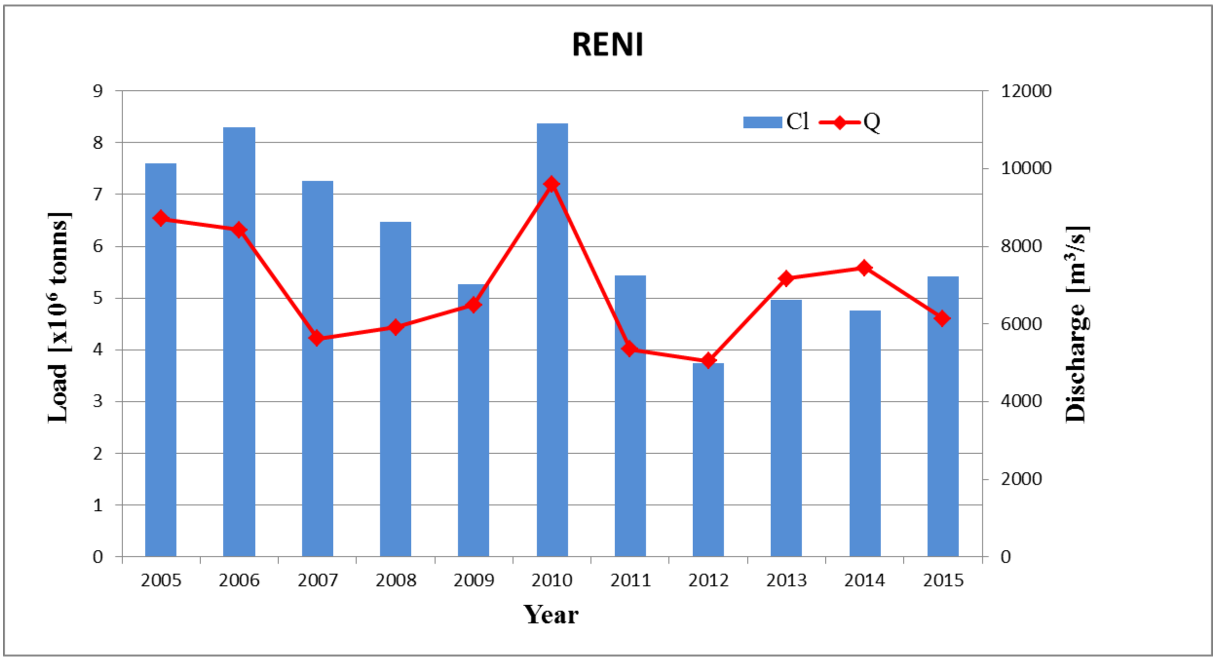
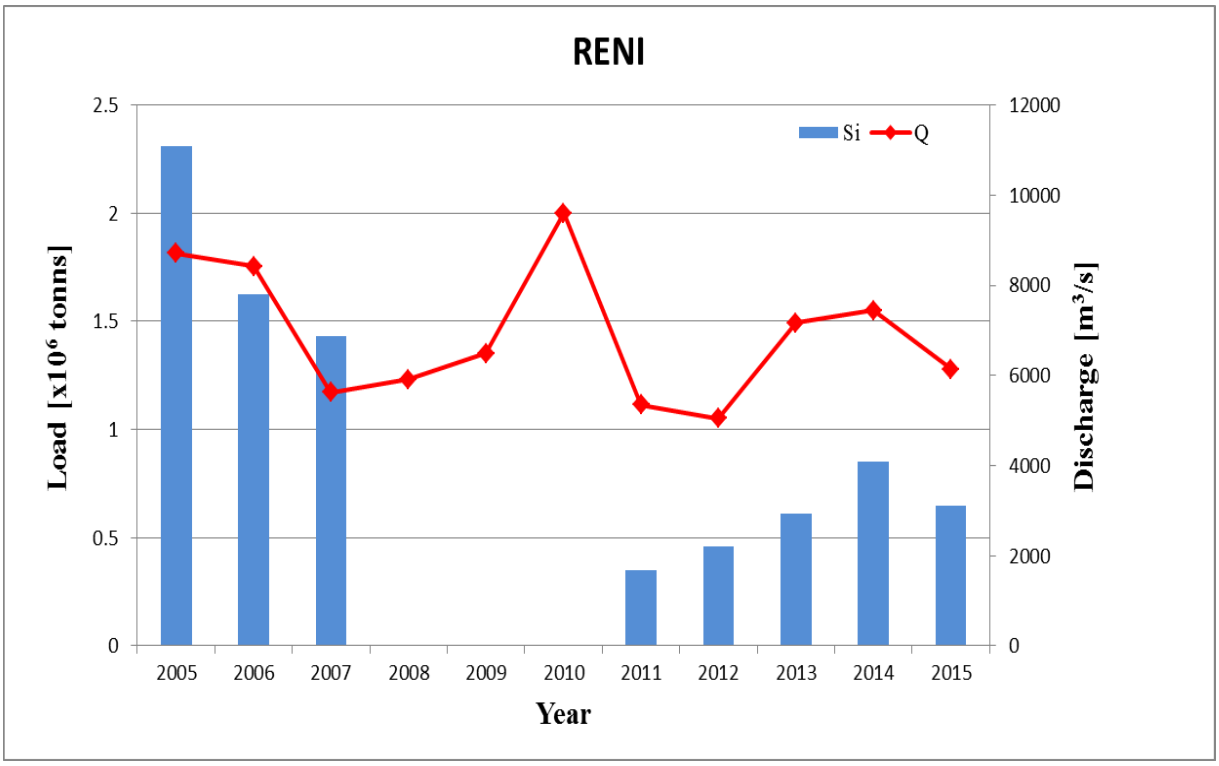


Figure 5.5.18: Trends of annual loads of silicates at Reni.



6. Groundwater monitoring

5.6 Groundwater bodies of basin-wide importance

The first analysis and review of the groundwater bodies (GW-bodies) in the Danube River Basin (DRB) as required under Article 5 and Annex II of the WFD (Danube Basin Analysis, DBA) was performed in 2004 and updated in 2013 and it reconfirmed 11 transboundary GW-bodies or groups of GW-bodies of basin-wide importance (ICPDR GW-bodies).

ICPDR GW-bodies of basin-wide importance were defined as:

- transboundary; and
- important due to the size of the GW-body which means an area larger than 4,000 km²; or
- important due to various criteria e.g. socio-economic importance, uses, impacts, pressures interaction with aquatic eco-system. The criteria and the nomination need to be agreed bilaterally.

This means that other GW-bodies even those with an area larger than 4,000 km², which are fully situated within one country of the Danube River Basin are dealt with at the national level.

5.7 Groundwater status assessment

The groundwater chemical and quantitative status was the first time assessed in 2009 by EU Member States within the preparation of the first River Basin Management Plans (RBMP) which were due under Article 13 of the WFD. The update of the RBMPs had to be finalized by the End of 2015 and reported to the European Commission until March 2016.

According to the stratified approach of three level reports which supplement each other (Part A – Roof Report, Part B – National level and/or Sub-basin level, Part C – National level and submission to EC on request), the content of the recent RBMP for the Danube of 2015 (DRBM Plan, Danube River Basin Management Plan) is focusing on the ICPDR GW-bodies only and give relevant summary information on the status of these GW-bodies, on the description of the methodologies applied for the assessment of status, on the related impacts on these GW-bodies, on the significant pressures causing poor status and on the measures implemented in order to reach good status by 2021. Detailed information is to be found in the Part B (national level) reports. A link between the content of the DRBM Plan and the national RBMPs is established by the national codes of the GW-bodies.

The ICPDR Groundwater Task Group (GW TG) acts as a platform for facilitating and promoting transnational coordination and harmonization of the implementation of EU legislation by the ICPDR Contracting Parties. It is not the aim of the GW TG to duplicate any assessments carried out by the Contracting Parties at the national level but to compile the available results as far as they are relevant on a Danube basin-wide scale.

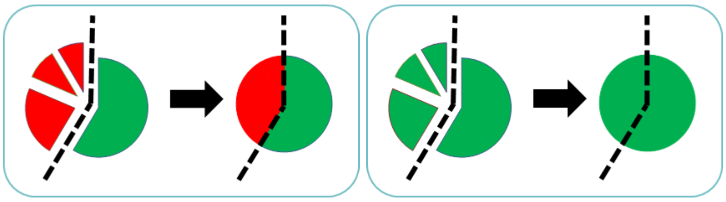
As decided by the GW TG, the result of the status assessment is illustrated for the whole national part of an ICPDR GW-body. As the WFD only foresees status indication (green and red color) for individual GW-bodies or groups of GW-bodies, criteria have been developed for the uniform presentation of status results at the basin-wide level, even if national GW-bodies are not forming a group of GW-bodies according to the definition of the WFD. If a national part of an ICPDR GW-body consists of several individual national-level GW-bodies then the poor status of only one national-level GW-body is decisive for characterizing the whole national part of an ICPDR GW-body in poor status.

To indicate the (in)homogeneity of the status within a national part of an ICPDR GW-body the concept of confidence in status assessment was introduced (illustrated in Figure 6.1). High confidence expresses that all national-level GW-bodies forming a national part of an ICPDR GW-body show the same status (either all good or all poor). Medium confidence is assigned when national-level GW-bodies show different status results within one national part of an ICPDR GW-body. Low confidence indicates that the status assessment is based on risk assessment data.

Figure 6.1: Aggregation confidence levels in groundwater status assessment

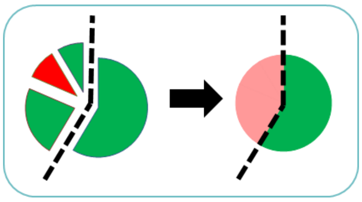
High confidence
Good or poor status

- Status assessment is based on WFD compliant monitoring data.
- If the national part of an ICPDR GW-body is formed by more than one GW-body or groups of GW-bodies, **all** have the same status.



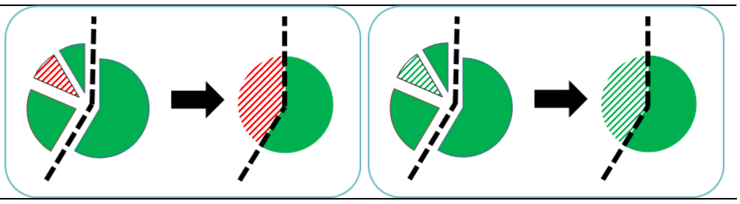
Medium confidence
Poor status

- Status assessment is based on WFD compliant monitoring data.
- If the national part of an ICPDR GW-body is formed by more than one GW-body or groups of GW-bodies, **not all** have the same status.



Low confidence
Good or poor status

- The status assessment of at least one individual GW-body is based on risk assessment data.



Poor Status   Good Status   Poor/Good Status based on Risk Assessment

The level of confidence is color coded together with the groundwater status and illustrated in the maps on groundwater quantitative (Figure 6.2) and chemical status (Figure 6.3).

5.8 Groundwater quantitative status

As reported in the DRBM Plan Update 2015, *good quantitative status* was assigned to 18 (out of 23) national parts of ICPDR GW-bodies. Three national parts of an ICPDR GW-body (HU-5, HU-7 and HU-8) are of *poor quantitative status*. One national part (RS-7) is at risk – which means poor status with low confidence – and for one (SK-11) the status is unknown.

In 7 out of 11 ICPDR GW-bodies all national parts are of *good quantitative status*. In ICPDR GW-bodies GWB-5, GWB-7 and GWB-8 *poor quantitative status* was observed in at least one national part. In GWB-11 *unknown quantitative status* was reported for one national part (SK-11).

The *poor quantitative status* is caused in two national parts (HU-7 and RS-7) by groundwater abstractions exceeding the available groundwater resources. In three national parts (HU-5, HU-7 and HU-8) significant damage of groundwater dependent terrestrial ecosystems was reported. In RS-7 the effects of groundwater abstraction on associated or dependent ecosystems or on legitimated uses or regarding saline intrusion are unknown. For SK-11 the quantitative status is unknown.

All 4 national shares now failing good quantitative status are also at risk of failing good quantitative status by 2021. For three of these national shares the date of achievement of good quantitative status is only expected by 2027 based on the application for exemption. For one national share (RS-7) this issue is not yet discussed.

Compared to the status assessment in 2009, HU-7, HU-8 and RS-7, which were in poor status, have still the same status. HU-5 which was in good status in 2009 now failed to reach good status, and HU-11 which was in poor status in 2009 has now reached good quantitative status.

The results of the quantitative status assessment are illustrated in Figure 6.2. The summary overview (Table 6.1) gives details on the achievement of the individual good quantitative status objectives which had to be considered within the status assessment according to the WFD.

Figure 6.2: ICPDR Groundwater Bodies – Groundwater Quantitative Status (Source: DRBM Plan Update 2015).

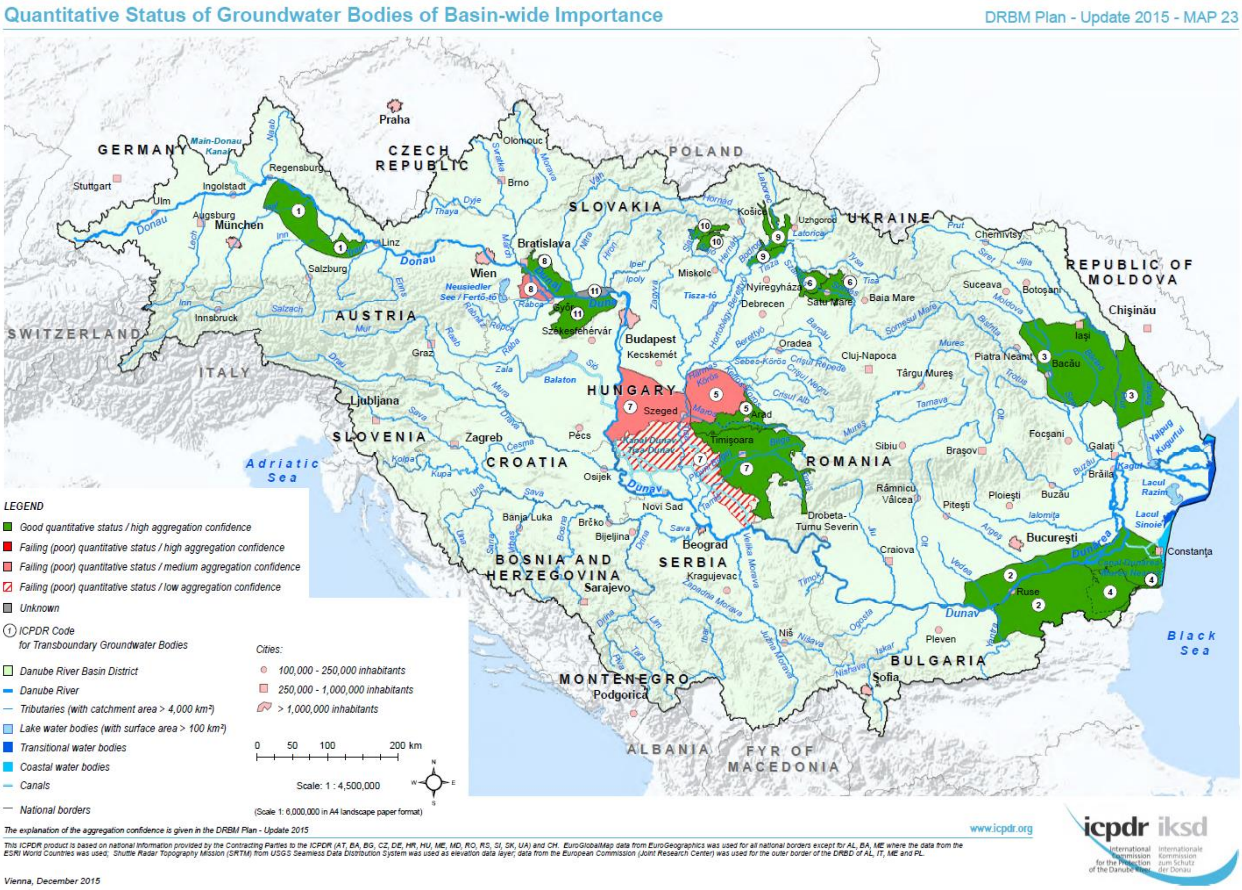


Table 6.1: ICPDR Groundwater Bodies – Groundwater Quantitative Status and achievement of Good Status Objectives (Source: DRBM Plan Update 2015)

Reasons for failing good groundwater QUANTITATIVE status in 2015 for the ICPDR GW-bodies *TABLE 19*

GWB	Name	National part	Year of status assess-ment	Quantitative status	Exceedance of available GW resource	Failed achievement of WFD Article 4 objectives for associated surface waters	Significant damage to GW dependent terrestrial ecosystem	Uses affected (drinking water use, irrigation etc.)	Intrusions detected or likely to happen due to alterations of flow directions resulting from level changes
				good / poor	Yes / No / Unknown	Yes / No / Unknown	Yes / No / Unknown	Yes / No / Unknown If yes, which?	Yes / No / Unknown
GWB-1	Deep GWB – Thermal Water	AT-1	2014	Good	–	–	–	–	–
		DE-1	2014	Good	–	–	–	–	–
GWB-2	Upper Jurassic – Lower Cretaceous GWB	BG-2	2014	Good	–	–	–	–	–
		RO-2	2014	Good	–	–	–	–	–
GWB-3	Middle Sarmatian – Pontian GWB	MD-3	2014	Good	–	–	–	–	–
		RO-3	2014	Good	–	–	–	–	–
GWB-4	Sarmatian GWB	BG-4	2014	Good	–	–	–	–	–
		RO-4	2014	Good	–	–	–	–	–
GWB-5	Mures / Maros	HU-5	2014	Poor	–	–	Yes	–	–
		RO-5	2014	Good	–	–	–	–	–
GWB-6	Somes / Szamos	HU-6	2014	Good	–	–	–	–	–
		RO-6	2014	Good	–	–	–	–	–
GWB-7	Upper Pannonian – Lower Pleistocene / Vojvodina / Duna-Tisza köze deli r.	HU-7	2014	Poor	Yes	–	Yes	–	–
		RO-7	2014	Good	–	–	–	–	–
		RS-7	2013	Poor*	Yes	Unknown	Unknown	Unknown	Unknown
GWB-8	Podunajska Basin, Zitny Ostrov / Szigetköz, Hanság-Rábca	HU-8	2014	Poor	–	–	Yes	–	–
		SK-8	2014	Good	–	–	–	–	–
GWB-9	Bodrog	HU-9	2014	Good	–	–	–	–	–
		SK-9	2014	Good	–	–	–	–	–
GWB-10	Slovensky kras / Aggtelek-hgs.	HU-10	2014	Good	–	–	–	–	–
		SK-10	2014	Good	–	–	–	–	–
GWB-11	Komarnanska Vysoka Kryha / Dunántúli-khgs. északi r.	HU-11	2014	Good	–	–	–	–	–
		SK-11	2014	Unknown	–	–	–	–	–

- means 'No'; * The status information is of low confidence as it is based on risk assessment

5.9 Groundwater chemical status

As reported in the DRBM Plan 2015, *good chemical status* was assigned to 19 (out of 23) national parts of ICPDR GW-bodies. Three national parts of an ICPDR GW-body (HU-5, RO-5 and HU-7) are of *poor chemical status* and for one national part (RS-11) the chemical status is unknown.

In 8 out of 11 ICPDR GW-bodies all national parts are of *good chemical status*. In ICPDR GW-body GWB-5, *poor chemical status* was observed in both national parts (HU-5 and RO-5). In GWB-7 one national part (HU-7) is of *poor chemical status one*, RO-7 is of good status and RS-7 of good status with low confidence (assessment based on risk assessment). In GWK-11 for the national share of SK-11 the status is unknown.

Considering the general status assessment of GWBs as a whole, nitrates were the cause of the *poor chemical status* classification in 2 national shares and ammonium in one (HU-5). In addition, increasing trends for sulphates, nitrates, ammonium, chlorides, arsenic and TOC already exceeded the starting points of trend reversal in 3 national shares. For the national shares SK-8, SK-9 and SK-10 the effects of groundwater quality on associated aquatic and dependent terrestrial ecosystems is unknown.

The three national shares now failing good chemical status are also at risk of failing good chemical status by 2021. For them the date of achievement of good chemical status is prolonged until 2027 based on the application for exemption. For one national share (MD-3) which is currently of good chemical status risk of failing good status in 2021 was reported.

Compared to the status assessment in 2009, HU-5, RO-5 and HU-7 which were in poor status have still the same status. HU-8 which was in poor status in 2009 has now reached good chemical status.

The results of the chemical status assessment (considering the confidence in the assessment) reflect the information status of 2014 and they are illustrated in Figure 6.3. The summary overview (Table 6.2) gives details on the achievement of the single groundwater quality objectives which had to be considered within the chemical status assessment according to the WFD.

Figure 6.3: ICPDR Groundwater Bodies – Groundwater Chemical Status (Source: DRBM Plan Update 2015).

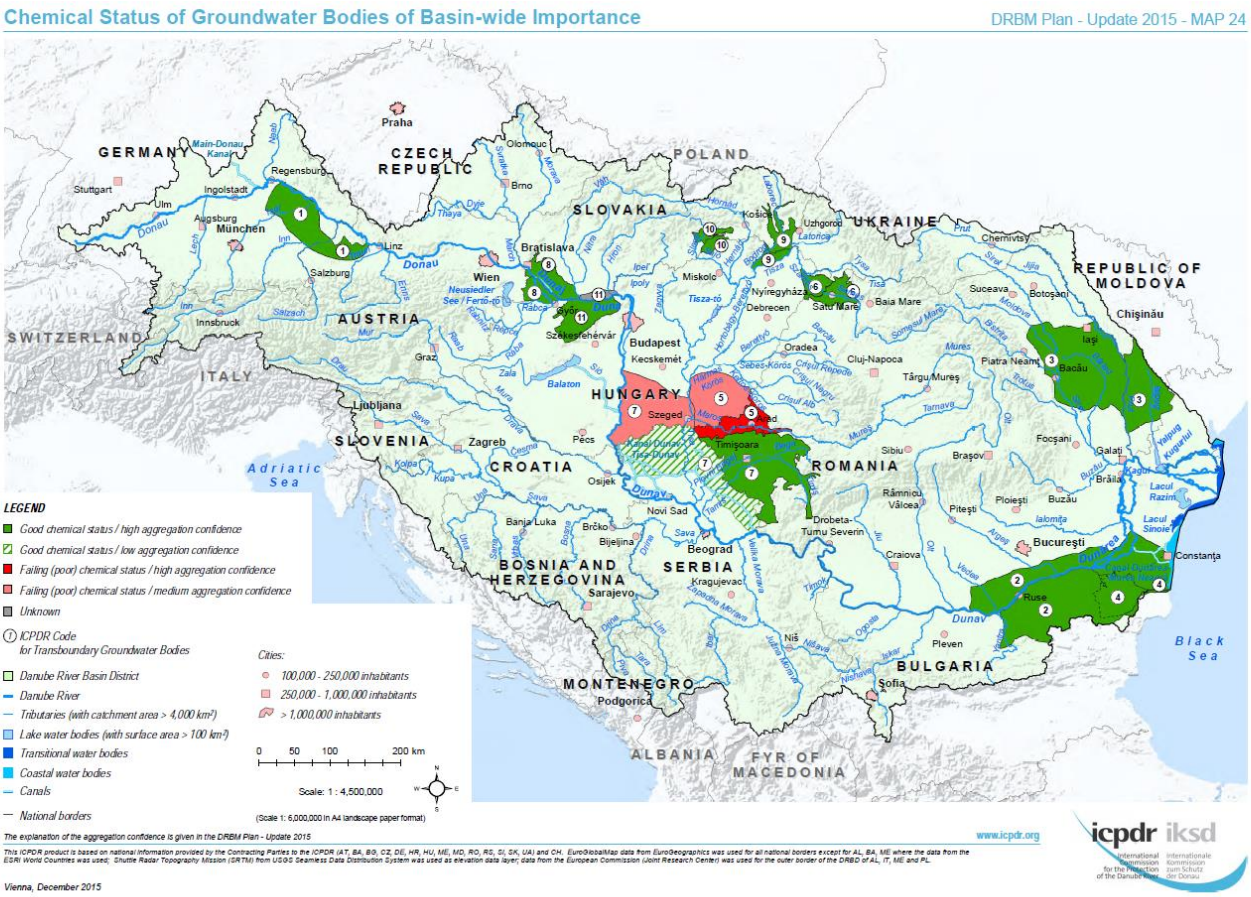


Table 6.2: ICPDR Groundwater Bodies – Groundwater Chemical Status and achievement of Good Status Objectives (Source: DRBM Plan Update 2015)

Reasons for failing good groundwater CHEMICAL status in 2015 for the ICPDR GW-bodies *TABLE 18*

GWB	Name	National part	Year of status assess-ment	Chemical Status	Which parameters cause poor status	Failed general assess-ment of GWB as a whole	Saline or other intrusions	Failed achievement of WFD Article 4 objectives for associated surface waters	Significant damage to GW dependent terrestrial ecosystem	WFD Art 7 drinking water protected area affected	Increasing trend exceeding starting points of trend reversal
				good / poor	parameter	Yes / No / Unknown (parameter)	Yes / No / Unknown (parameter)	Yes / No / Unknown (parameter)	Yes / No / Unknown (parameter)	Yes / No / Unknown (parameter)	Yes / No / Unknown (parameter)
GWB-1	Deep GWB – Thermal Water	AT-1	2014	Good	–	–	–	–	–	–	–
		DE-1	2014	Good	–	–	–	–	–	–	–
GWB-2	Upper Jurassic – Lower Cretaceous GWB	BG-2	2014	Good	–	–	–	–	–	–	–
		RO-2	2014	Good	–	–	–	–	–	–	–
GWB-3	Middle Sarmatian–Pontian GWB	MD-3	2014	Good	–	–	–	–	–	–	–
		RO-3	2014	Good	–	–	–	–	–	–	–
GWB-4	Sarmatian GWB	BG-4	2014	Good	–	–	–	–	–	–	–
		RO-4	2014	Good	–	–	–	–	–	–	–
GWB-5	Mures / Maros	HU-5	2014	Poor	ammonium	Yes	–	–	–	–	sulphates
		RO-5	2014	Poor	nitrates	Yes	–	–	–	–	–
GWB-6	Somes / Szamos	HU-6	2014	Good	–	–	–	–	–	–	–
		RO-6	2014	Good	–	–	–	–	–	–	–
GWB-7	Upper Pannonian – Lower Pleistocene / Vojvodina / Duna-Tisza köze deli r.	HU-7	2014	Poor	nitrates	Yes	–	–	–	–	nitrates
		RO-7	2014	Good	–	–	–	–	–	–	–
		RS-7	2013	Good*	–	–	–	–	–	–	–
GWB-8	Podunajska Basin, Zitny Ostrov / Szigetköz, Hanság-Rábca	HU-8	2014	Good	–	–	–	–	–	–	–
		SK-8	2014	Good	–	–	–	Unknown	Unknown	–	(NH_4,NO_3 – agri) (Cl, As, SO_4, TOC – industry)
GWB-9	Bodrog	HU-9	2014	Good	–	–	–	–	–	–	–
		SK-9	2014	Good	–	–	–	Unknown	Unknown	–	–
GWB-10	Slovensky kras / Aggtelek-hgs.	HU-10	2014	Good	–	–	–	–	–	–	–
		SK-10	2014	Good	–	–	–	Unknown	Unknown	–	–
GWB-11	Komarnanska Vysoka Kryha / Dunántúli-khgs. északi r.	HU-11	2014	Good	–	–	–	–	–	–	–
		SK-11	2014	Unknown	–	–	–	–	–	–	Unknown

'-' means 'No'; * The status information is of low confidence as it is based on risk assessment

5.10 Reporting on groundwater quality within the TNMN

The transnational groundwater management activities in the Danube River Basin District (DRBD) were initiated in 2002 and were triggered by the implementation of the WFD. Monitoring of the 11 transboundary GWBs of basin-wide importance has been integrated into the TNMN of the ICPDR. For groundwater monitoring under the TNMN (GW TNMN) a 6-year reporting cycle has been set, which is in line with reporting requirements under the WFD and which will sufficiently allow for making any relevant statement on significant changes of groundwater status for these GW-bodies.

Now groundwater quality data have been collected the second time reflecting the situation in 2015.

The core set of parameters which were agreed to be reported are: electrical conductivity, nitrates, ammonium, all parameters posing risk or causing poor status and all parameters which are characterizing groundwater chemistry. As it can be seen in Table 6.2, nitrates and ammonium are causing poor chemical status in the DRBM Plan Update 2015.

For each national part of an ICPDR GW-body the following aggregated data (statistical key values) are presented for the reference year of 2015: minimum, mean and maximum value and the 10-, 25-, 50-, 75- and 90-percentiles. The statistical values are based on annual arithmetic mean values (for the reference year) for each monitoring point. The number of sampling sites and the groundwater threshold values complement the data collection.

5.11 Groundwater chemical monitoring results

All countries sharing ICPDR GW-bodies provided groundwater quality data, except Moldova (MD-3). In addition to the 23 national parts of ICPDR GW-bodies, Hungary decided to distinguish the data for HU-5, HU-6, HU-7, HU-8 and HU-9 between a shallow and a porous part due to the striking differences in groundwater chemistry. For this data assessment, the reference year of the data is in general 2015.

The most commonly reported parameters were the core parameters electrical conductivity, nitrates and ammonium. Five countries also provided data on chloride and sulphate for in total 11 respectively 12 national parts of ICPDR GW-bodies.

To give a broader picture on the current situation by the distribution of the measured data the data are presented in a Box-and-Whisker-Plot where the 10- and 90-percentiles represent the Whiskers.

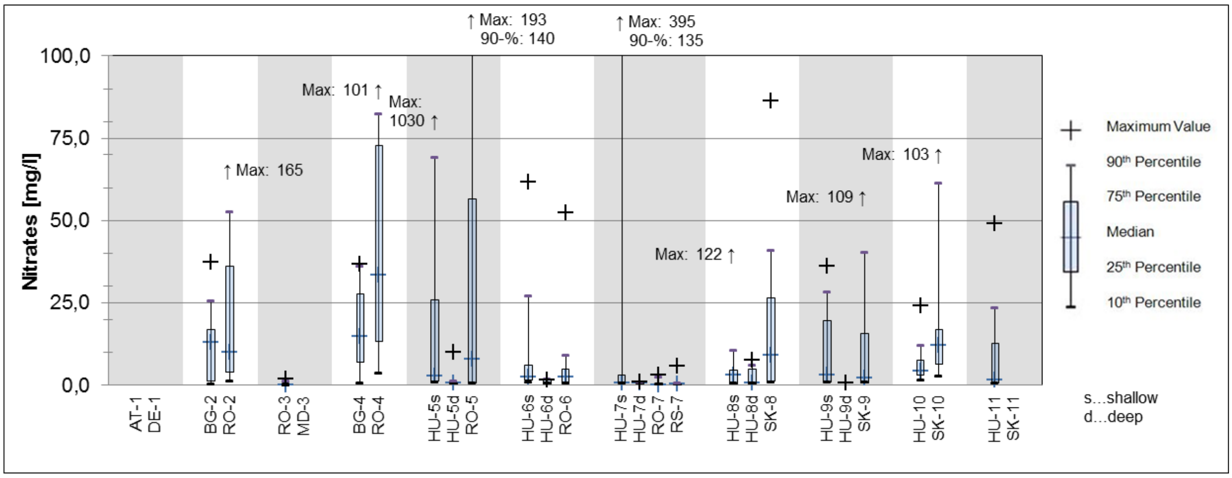
5.11.1 Nitrates in groundwater

Nitrate in groundwater is a main indicator for pollution by agricultural fertilizers and urban waste water. The EU Groundwater Directive established a groundwater quality standard of 50 gm/l to be considered within the groundwater chemical status assessment. If this standard could still lead to a failure of achieving the WFD objectives, more stringent threshold values have to be established by the EU Member States. Reported groundwater threshold values (TVs) for nitrates vary between 28.3 and 50 mg/l. Hungary, Romania and Serbia reported groundwater threshold values (TVs) for nitrates of 50 mg/l, Bulgaria established values between 38.1 and 39.9 mg/l and Slovakia between 28.3 and 33.4 mg/l. Austria and Germany did not yet establish threshold values for the common deep thermal groundwater body GWB-1.

Figure 6.4 illustrates the distribution of nitrates in groundwater. There are no data available for MD-3 and for the ICPDR GW-body GWB-1 (AT-1 and DE-1) where nitrate is not relevant as this deep thermal groundwater body is free of oxygen and therefore free of nitrates. The distribution of measured nitrate concentrations shows that within each ICPDR GW-body the concentration ranges in the single national parts are often similar. RO-5 and HU-7 are failing good status in 2015 due to nitrates.

The majority of the measured nitrate concentrations are far below 50 mg/l. The reported arithmetic mean values are between 0.3 and 42.4 mg/l and the highest reported median value is about 33 mg/l. Only in 6 of 19 national parts of ICPDR GW-bodies (where data are available) the 90-percentile exceeds 50 mg/l. In 11 of the 19 national parts with data, the maximum values exceed 50 mg/l with the highest nitrate concentration of 1,030 mg/l in HU-5 (shallow porous GWB).

Figure 6.4: ICPDR GW-bodies – Nitrate concentrations in groundwater



5.11.2 Ammonium in groundwater

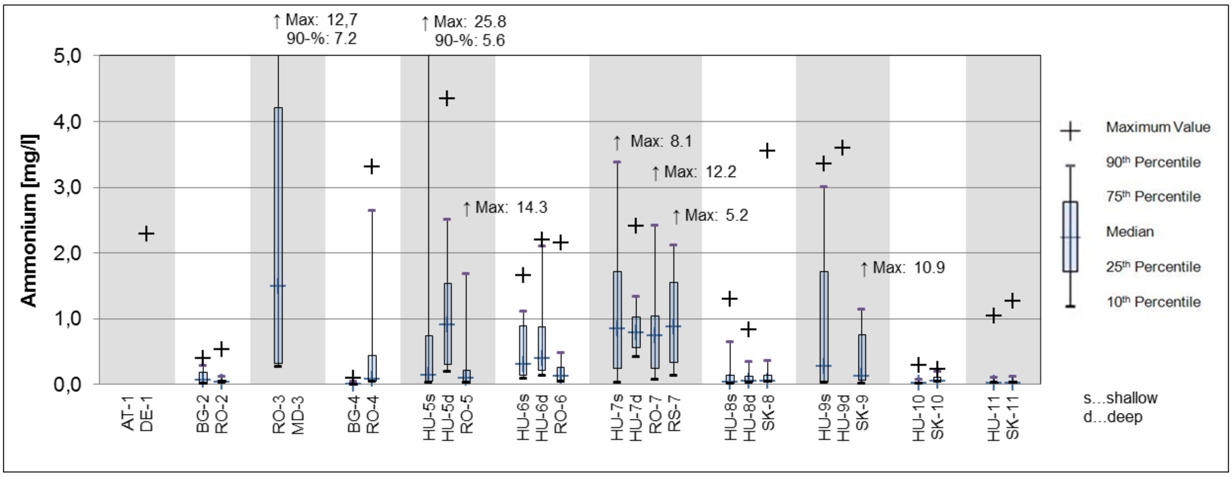
Ammonium in groundwater is a good indicator of pollution by agricultural fertilizers, waste water and leachates from landfills. Naturally occurring ammonium concentrations in groundwater are generally around 0.1 mg/l and caused by bacteriological processes in the soil.

The parametric value of the EU Drinking Water Directive (98/83/EC, DWD) is established at 0.5 mg/l. Five countries reported groundwater TVs in a range between 0.26 and 6.4 mg/l. Slovakia reported TVs in a range of 0.26 to 0.295 mg/l, Hungary reported a range of 0.26 and 4.54 mg/l, Romania reported a range of 0.5 to 6.4 mg/l, Bulgaria established values between 0.38 and 0.45 mg/l and Serbia reported a national drinking water standard of 0.1 mg/l.

Figure 6.5 illustrates the distribution of ammonium in groundwater. There are no data available for MD-3 and in AT-1 ammonium is not monitored as it is not relevant for the status assessment of this deep thermal groundwater body. Also for ammonium the distributions of concentrations in the single national parts of an ICPDR GW-body are quite similar. HU-5 is failing good status in 2015 due to ammonium.

The majority of the measured ammonium concentrations are below 1 mg/l. The reported arithmetic mean values are between 0.01 and 2.99 mg/l and the median values range between 0.0 and close to 1.5 mg/l where 11 of the 21 reported median values do not exceed 0.1 mg/l. In 12 national parts of ICPDR GW-bodies the 90-percentile exceeds 1 mg/l. In 7 of the 21 national parts with data, the maximum values exceed 5 mg/l with the highest ammonium concentration of 25.8 mg/l in HU-5.

Figure 6.5: ICPDR GW-bodies – Ammonium concentrations in groundwater



5.11.3 Electrical conductivity of groundwater

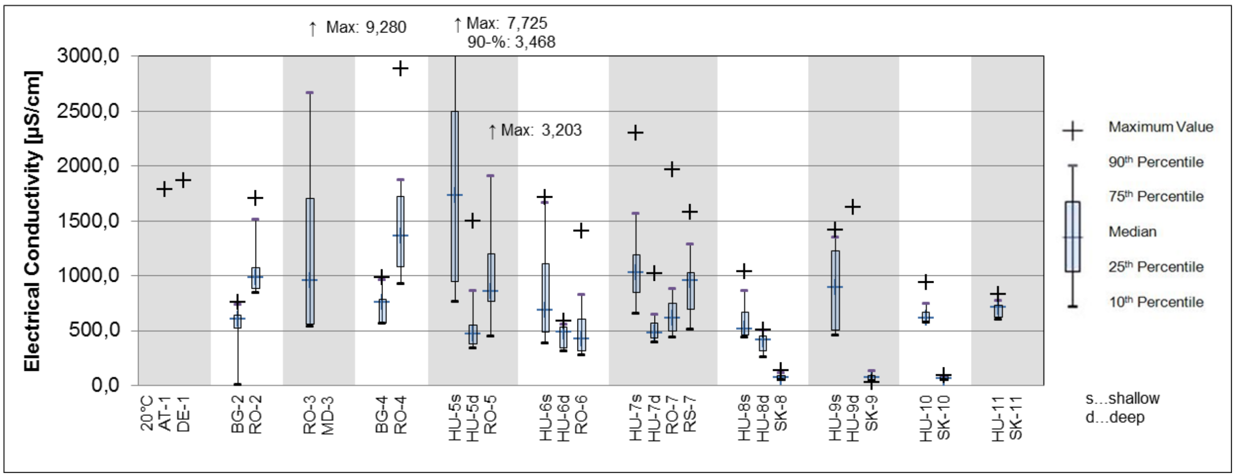
Electrical conductivity is an indicator of the degree of mineralization of groundwater which is determined by natural geological conditions and anthropogenic pollution. It is an indirect measure of salinity and often used as a general indicator for characterizing groundwater chemistry.

The parametric value of the EU Drinking Water Directive (98/83/EC, DWD) is established at 2,500 µS/cm. Three countries reported groundwater TVs in a range between 565 and 2,500 µS/cm. Hungary reported groundwater TVs between 565 and 2,500 µS/cm, Serbia reported a national drinking water standard of 896 µS/cm (the originally reported TV of 1,000 µS/cm at 25°C was re-calculated to 20°C) and Bulgaria established values between 1,470 and 1,536 µS/cm (1,640 and 1,714 µS/cm re-calculated to 20°).

Figure 6.6 illustrates the distribution of electrical conductivity of groundwater at 20°C. Data which referred to the reference temperature of 25°C were re-calculated to 20°C in order to guarantee overall comparability of the data. There are no data available for MD-3 and SK-11.

The reported arithmetic mean values of electrical conductivity are in a range of 417–3,710 µS/cm and the median values between 65 and 1,968 µS/cm where 17 of 19 reported median values are below 1,000 and 9 are below 700 µS/cm. In 8 of 19 national parts of ICPDR GW-bodies, where respective percentile data were available, the 90-percentile exceeds 1,300 µS/cm. In 3 of the 21 national parts with maximum values, the maximum values exceed 3,000 µS/cm with the highest electrical conductivity of 9,280 µS/cm in RO-3.

Figure 6.6: ICPDR GW-bodies – Electrical conductivity of groundwater



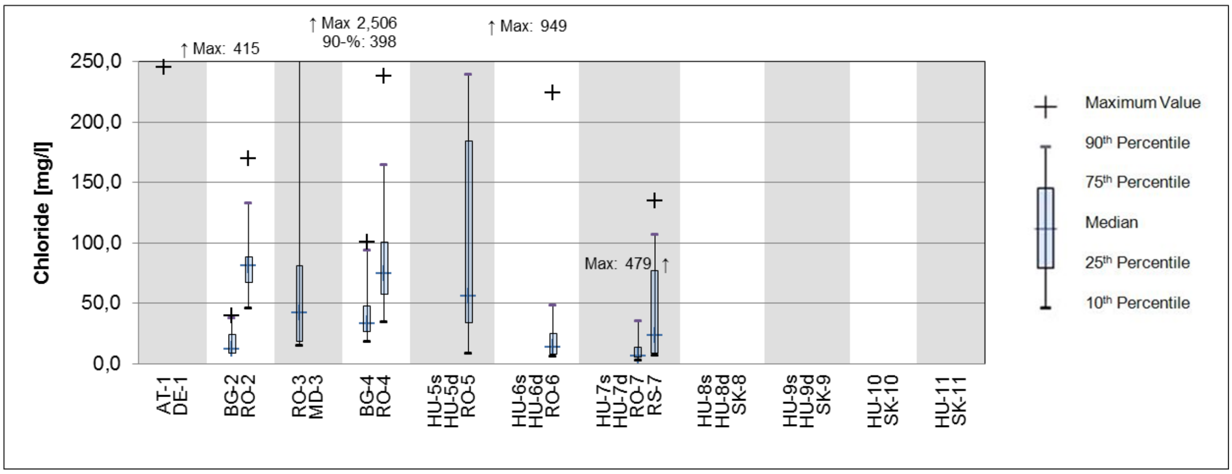
5.11.4 Chloride

Chloride background concentrations in groundwater usually range from 10–40 mg/l and originate naturally from weathering and leaching of sedimentary rocks and the dissolution of salt deposits. Other sources are saltwater intrusion, leachates from landfills, sewage, Cl-containing fertilizers and de-icing of roads. Chloride concentrations hardly change with physico-chemical and biochemical processes and remain very stable in the groundwater.

The EU Drinking Water Directive (98/83/EC) lays down a parametric value of 250 mg/l. Three countries reported groundwater TVs in a range between 189 and 250 mg/l. Romania reported a TV of 250 mg/l, Bulgaria established a range around 189 mg/l and Serbia reported a national drinking water standard of 200 mg/l.

Figure 6.7 compares the chloride concentrations for the 11 national parts of GW-bodies where data were provided. Most of the values are found below 100 mg/l (all median values are below 82 mg/l). The highest salinisation (up to 2,506 mg/l) was found in RO-5.

Figure 6.7: ICPDR GW-bodies – Chloride in groundwater



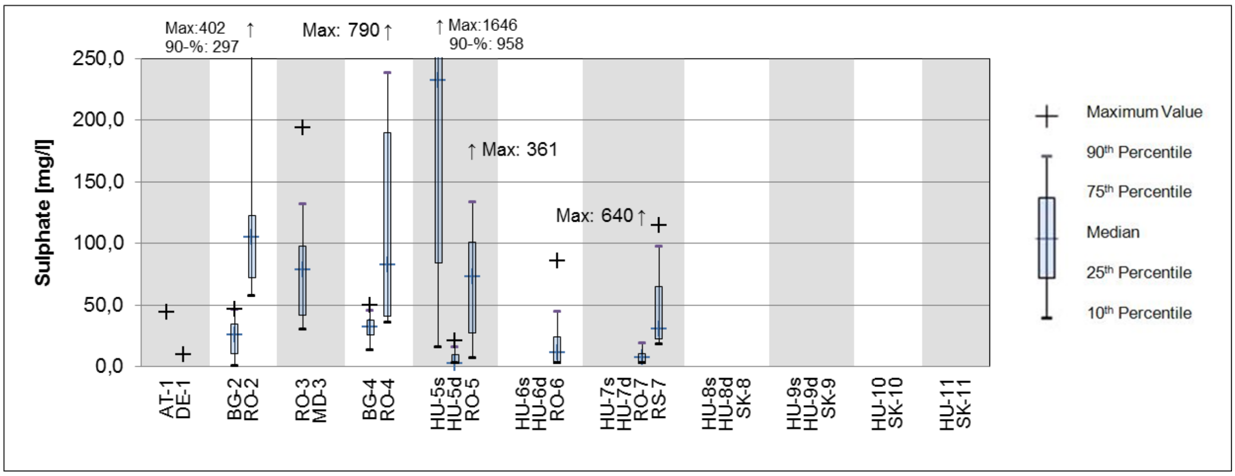
5.11.5 Sulphate

Natural origin of most sulfate compounds in groundwater is the oxidation of pyrite (ferrous sulphide) which is widely present in sedimentary rocks. Natural concentrations in groundwater range between 10 and 30 mg/l. Higher sulphate concentrations can be caused by anthropogenic inputs like leachates from landfills, industrial effluents, fertilizers and emissions from traffic (input via rain).

The EU Drinking Water Directive (98/83/EC) lays down a parametric value of 250 mg/l. Four countries reported groundwater TVs in a range between 20 and 481 mg/l. Romania and Serbia reported a TV of 250 mg/l, Bulgaria established a range between 189 and 192 mg/l and Hungary between 20 and 481 mg/l.

Figure 6.8 compares the sulphate concentrations for the 12 national parts of GW-bodies where data were provided. In 7 national shares the median values are below 50 mg/l. HU-5 shows a significant difference between the shallow (HU-5s) and the deeper porous horizon (HU-5d).

Figure 6.8: ICPDR GW-bodies – Sulphate in groundwater



7. Abbreviations

Abbreviation	Explanation
AQC	Analytical Quality Control
BSC	Black Sea Commission
DEFF	Data Exchange File Format
DRPC	Convention on Cooperation for the Protection and Sustainable Use of the Danube River (short: Danube River Protection Convention)
ICPDR	International Commission for the Protection of the Danube River
LOD	Limit of Detection
MA EG	Monitoring and Assessment Expert Group (former MLIM EG)
MLIM EG	Monitoring, Laboratory and Information Management Expert Group
NRL	National Reference Laboratory
SOP	Standard Operational Procedure
TNMN	Trans National Monitoring Network
WFD	EU Water Framework Directive
DRB	Danube River Basin
DRBMP	Danube River Basin Management Plan
GW	Groundwater
BOD_5	Biochemical oxygen demand (5 days)
COD_{Mn}	Chemical oxygen demand (Potassium permanganate)
COD_{Cr}	Chemical oxygen demand (Potassium dichromate)
TOC	Total organic carbon
DOC	Dissolved organic carbon
AOX	Adsorbable organic halogens
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls

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