INTERNATIONAL COMMISSION FOR THE PROTECTION OF THE DANUBE RIVER

INTERNATIONALE KOMMISSION ZUM SCHUTZ DER DONAU

WATER QUALITY

IN THE DANUBE RIVER BASIN

TNMN Yearbook 2006

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1. Introduction

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. The main objective of the Conventions is 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 Convention refers also to the *Convention on the protection and use of transboundary watercourses and international lakes* of March 1992.

Regarding the monitoring programmes, it is stated in the DRPC that the Contracting Parties shall cooperate in the field of monitoring and assessment. For this aim they shall, e.g.:

- harmonise or make comparable their monitoring and assessment methods, in particular in the field of river quality
- develop concerted or joint monitoring systems applying stationary or mobile measurement devices, communication and data processing facilities
- elaborate and implement joint programmes for monitoring the riverine conditions in the Danube catchment area concerning both water quantity and quality, sediments and riverine ecosystems, as a basis for the assessment of transboundary impacts

The Parties shall agree upon monitoring points, river quality characteristics and pollution parameters regularly to be evaluated for the Danube River with sufficient frequency taking into account the ecological and hydrological character of the watercourse concerned as well as typical emissions of pollutants discharged within the respective catchment area. In addition, the Parties shall periodically assess the quality conditions of the Danube River and the progress made by their measures taken aiming at the prevention, control and reduction of transboundary impacts.

The operation of the TransNational Monitoring Network (TNMN) is aimed to contribute to implementation of the DRPC and is in operation since 1996. Water quality data from the monitoring programme are regularly gathered by Danubian countries, merged at Central Point at Slovak Hydrometeorological Institute, processed by using agreed procedures and provided to ICPDR information system. The yearbooks belong to the main outputs of activities under the monitoring programme and this one presents data from TNMN operation in year 2006.

2. History of the TNMN

The first steps towards TNMN were taken many years ago. 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 eleven cross sections of the Danube was established.
In 1991 the Danubian countries started preparation of the *Convention on cooperation for the protection and sustainable use of the Danube River*, which was signed in 1994.

The Environmental Programme for the Danube River Basin, lead by a Task Force, also started in 1991 with the main objective to strengthen the operational basis for environmental management in the Danube River Basin and to support the Danubian countries to implement the DRPC.

The TNMN was originally designed in 1993 during the project “Monitoring, Laboratory Analysis and Information Management for the Danube River Basin”, conducted by the WTV Consortium. The project was realized in close cooperation with Monitoring, Laboratory and Information Management Sub-group (MLIM-SG) to which the responsibility for TNMN was assigned. MLIM-SG should address the development of water quality monitoring network in the Danube River Basin; introduce harmonised sampling procedures and enhanced laboratory analysis capabilities; and form the core of a Danube information system on the status of in-stream water quality.

After entry of the DRPC into force in October 1998, MLIM-Expert Group was incorporated in the organisational structure of International Commission for the Protection of the Danube River (ICPDR) and has been working on the basis of TORs agreed by the ICPDR Plenary Meeting. In accordance with the TORs, the overall objective of the MLIM-EG is to create a strengthened and more strategic approach to monitoring, laboratory and information management for surface waters. The key role of the Group is to address the organisational and operational aspects related to the monitoring of water riverine conditions in the Danube River Basin and to provide basic data as an input to the ICPDR information system.

3. Objectives of the TNMN

The TNMN started as a result of the work done according to the objectives defined in the "Environmental Programme for the Danube River Basin - Programme Work Plan", where it was stated that the monitoring network for the Danube should strengthen the existing network set up by the Bucharest Declaration, be capable of supporting reliable and consistent trend analysis for concentrations and loads for priority pollutants, support the assessment of water quality for water use and assist in the identification of major pollution sources.

In 2000, after several years of TNMN operation, discussion was held on improvement of TNMN based on experience gained. It was agreed that the main objective of the TNMN should be a structured and well balanced overall view of the situation and long-term development of quality and loads in terms of relevant constituents for the greater rivers in the Danube Basin from an international line and range of vision.

The discussion on improvements of TNMN was influenced also by the fact that in 2000 the EU Water Framework Directive (Directive 2000/60/EC) came into force establishing a framework for Community action in the field of water policy. Its implementation represents the highest priority for the ICPDR, which provides a platform for coordination of the activities leading into the development of a River Basin Management Plan for the Danube River Basin. Danubian countries have intensively started activities that should lead to implementation of specific requirements of the Directive on monitoring and assessment of surface water status and the TNMN will also have to be adjusted to these new needs in the near future.

4. Description of the TNMN

4.1 Monitoring stations network

The TNMN builds on national surface water monitoring networks. To select monitoring locations for the purposes of international monitoring network in the Danube River Basin, the following selection criteria for monitoring location had been set up:

- located just upstream/downstream of an international border
- located upstream of confluences between Danube and main tributaries or main tributaries and larger sub-tributaries (mass balances)
- located downstream of the biggest point sources
- located according to control of water use for drinking water supply

Monitoring location included in TNMN should meet at least one of the selection criteria.

The selection procedure lead to preparation of an original list of 61 monitoring locations. In 2001 monitoring stations from Serbia and Montenegro (at that time Yugoslavia) have extended the monitoring network filling the gap in water quality data in the middle part of the Danube River and related tributaries. With some other minor changes the final list contains 78 monitoring locations.
Monitoring locations can have up to three sampling points, located on the left side, right side or in the middle of a river. More than one sampling point had been proposed for selected monitoring locations in the middle and lower part of the Danube River and for large tributaries like Tisza and Prut Rivers are.

Updated list of monitoring locations is shown in the Table 4.1.1 and Figure 4.1. Table 4.1.1 contains basic information characterising the locations provided by the countries including latitude, longitude, distance from the mouth, altitude and catchment area. Some characteristics given for monitoring locations, which are included in the list by two neighbouring countries, are still not harmonised.

In year 2006 Danubian countries provided data from 77 monitoring locations, including 107 sampling sites. In year 2006 are missing complete data set from monitoring point L0930 (BG06 –Iskar) and for monitoring point L0990 was measured only few determinands. Samples were taken from 40 monitoring stations (68 sampling sites) located in the Danube River itself and from 37 monitoring station in tributaries.

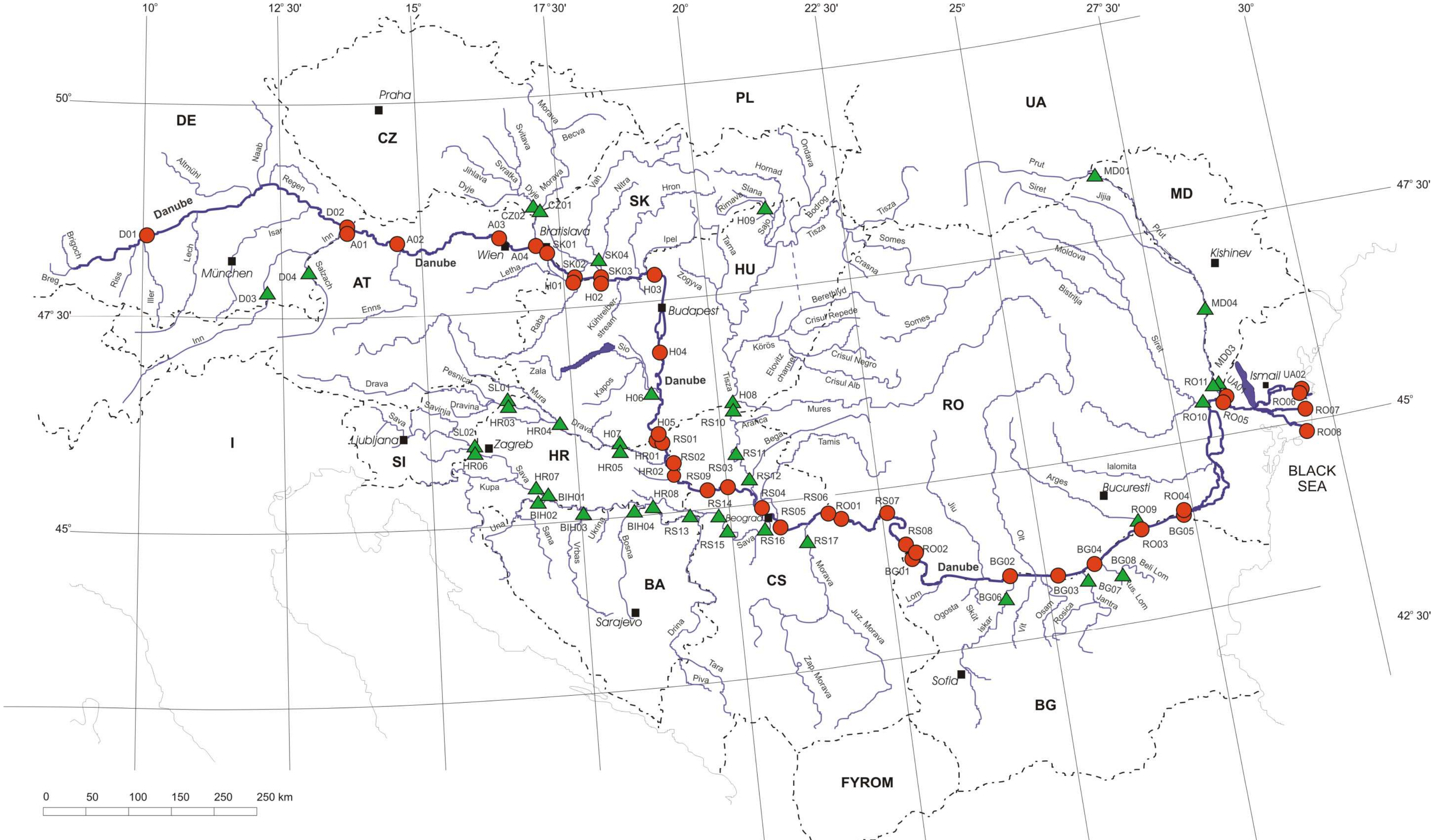
4.1.1: List of monitoring sites.

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance [Km]	Altitude [m]	Catch-ment [km^2]	DEFF Code	Loc.in profile
D01	Danube	Neu-Ulm	48 25 31	10 1 39	2581	460	8107	L2140	L
D02	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2130	M
D03	/Inn	Kirchdorf	47 46 58	12 7 39	195	452	9905	L2150	M
D04	/Inn/Salzach	Laufen	47 56 26	12 56 4	47	390	6113	L2160	L
A01	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2220	M
A02	Danube	Enghagen	48 24 04	14 51 20	2113	241	84869	L2201	R
A03	Danube	Wien-Nussdorf	48 15 45	16 22 15	1935	159	101700	L2180	R
A04	Danube	Hainburg	48 16 44	16 99 26	1879	136	130759	L2171	R
CZ01	/Morava	Lanzhot	48 41 12	16 59 20	79	150	9725	L2100	M
CZ02	/Morava/Dyje	Pohansko	48 48 12	16 51 20	17	155	12540	L2120	M
SK01	Danube	Bratislava	48 8 10	17 7 40	1869	128	131329	L1840	M
SK02	Danube	Medvedov/Medve	47 47 31	17 39 6	1806	108	132168	L1860	M
SK03	Danube	Komarno/Komarom	47 45 17	18 7 40	1768	103	151961	L1870	M
SK04	/Váh	Komarno	47 46 41	18 8 20	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov	47 47 31	17 39 6	1806	108	131605	L1470	M
H02	Danube	Komarom/Komarno	47 45 17	18 7 40	1768	101	150820	L1475	LMR
H03	Danube	Szob	47 48 44	18 51 42	1708	100	183350	L1490	LMR
H04	Danube	Dunafoldvar	46 48 34	18 56 2	1560	89	188700	L1520	LMR
H05	Danube	Hercegszanto	45 55 14	18 47 45	1435	79	211503	L1540	LMR
H06	/Sio	Szekszard-Palank	46 22 42	18 43 19	13	85	14693	L1604	M
H07	/Drava	Dravaszabolcs	45 47 00	18 12 22	78	92	35764	L1610	M
H08	/Tisza	Tiszasziget	46 9 51	20 5 4	163	74	138498	L1700	LMR
H09	/Tisza/Sajo	Sajopuspoki	48 16 55	20 20 27	124	148	3224	L1770	M
SI01	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1390	L
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	135	10878	L1330	R
HR01	Danube	Batina	45 52 27	18 50 03	1429	86	210250	L1315	M
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M
HR03**	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1300	L
HR04	/Drava	Botovo	46 14 27	16 56 37	227	123	31038	L1240	M
HR05	/Drava	D.Miholjac	45 46 58	18 12 20	78	92	37142	L1250	R
HR06	/Sava	Jesenice	45 51 40	15 41 48	729	135	10834	L1220	L
HR07	/Sava	us. Una Jasenovac	45 16 02	16 54 52	525	87	30953	L1150	L
HR08	/Sava	ds. Zupanja	45 02 17	18 42 29	254	85	62890	L1060	MR
BIH01	/Sava	Jasenovac	45 16 0	16 54 36	500	87	38953	L2280	M
BIH02	/Sava/Una	Kozarska Dubica	45 11 6	16 48 42	16	94	9130	L2290	M
BIH03	/Sava/Vrbas	Razboj	45 3 36	17 27 30	12	100	6023	L2300	M
BIH04	/Sava/Bosna	Modrica	44 58 17	18 17 40	24	99	10308	L2310	M
RS01	Danube	Bezdan	45 51 15	18 51 51	1427	83,15	210250	L2350	L
RS02	Danube	Bogojevo	45 31 49	19 5 2	1367	80,41	251253	L2360	L
RS03	Danube	Novi Sad	40 15 3	19 51 40	1258	74,52	254085	L2370	R
RS04	Danube	Zemun	44 50 56	20 25 2	1174	70,76	412762	L2380	R
RS05	Danube	Pancevo	44 51 25	20 36 28	1154,8	70,14	525009	L2390	L
RS06	Danube	Banatska	44 49 6	21 20 4	1076,6	68,58	568648	L2400	M
RS07	Danube	Tekija	44 41 56	22 25 24	954,6		574307	L2410	R
RS08	Danube	Radujevac	44 15 50	22 41 9	851	32,45	577085	L2420	R
RS09	Danube	Backa Pal	45 15 13	19 31 35	1287		253737	L2430	L
RS10	/Tisza	Martonos	46 5 59	20 3 50	152	75,54	140130	L2440	R
RS11	/Tisza	Novi Becej	45 35 9	20 8 23	66	74,03	145415	L2450	L
RS12	/Tisza	Titel	45 11 52	20 19 9	8,9	72,55	157147	L2460	M
RS13	/Sava	Jamena	44 52 40	19 5 21	195	77,67	64073	L2470	L
RS14	/Sava	Sremska	44 58 1	19 36 26	136,4	75,24	87996	L2480	L
RS15	/Sava	Sabac	44 46 12	19 42 17	103,6	74,22	89490	L2490	R
RS16	/Sava	Ostruznica	44 43 17	20 18 51	17		37320	L2500	R
RS17	/Velika Morava	Ljubicevska	44 35 6	21 8 15	34,8	75,09	37320	L2510	R
RO01	Danube	Bazias	44 47 55,57,58	21 23 24,40,54	1071	70	570896	L0020	LMR
RO02	Danube	Pristol/Novo Selo Harbour	44 11 18,23,29	22 45 57,64,69	834	31	580100	L0090	LMR
RO03	Danube	us. Arges	44 4 25	26 36 35	432	16	676150	L0240	LMR
RO04	Danube	Chiciu/Silistra	44 7 18	27 14 38	375	13	698600	L0280	LMR
RO05	Danube	Reni-Chilia/Kilia arm	45 28 50	28 13 34	132	4	805700	L0430	LMR
RO06	Danube	Vilkova-Chilia arm/Kilia arm	45 24 42	29 36 31	18	1	817000	L0450	LMR
RO07	Danube	Sulina - Sulina arm	45 9 41	29 40 25	0	1	817000	L0480	LMR
RO08	Danube	Sf.Gheorghe-Ghorghe arm	44 53 10	29 37 5	0	1	817000	L0490	LMR

RO09	/Arges	Conf. Danube	44 4 35	26 37 4	0	14	12550	L0250	M
RO10	/Siret	Conf. Danube Sendreni	45 24 10	28 1 32	0	4	42890	L0380	M
RO11	/Prut	Conf.Danube Giurgiulesti	45 28 10	28 12 36	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	44 09 50,58,66	22 47 36,47,58	834	35	580100	L0730	LMR
BG02	Danube	us. Iskar - Bajkal	43 42 58	24 24 45	641	20	608820	L0780	R
BG03	Danube	Downstream Svishtov	43 37 50	25 21 11	554	16	650340	L0810	MR
BG04	Danube	us. Russe	43 48 06	25 54 45	503	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	44 7 02	27 15 45	375	7	698600	L0850	LMR
BG06	/Iskar	Orechovitza	43 35 57	24 21 56	28	31	8370	L0930	M
BG07	/Jantra	Karantzi	43 22 42	25 40 08	12	32	6860	L0990	M
BG08	/Russ.Lom	Basarbovo	43 46 13	25 57 34	13	22	2800	L1010	M
MD01	/Prut	Lipcani	48 16 0	26 50 0	658	100	8750	L2230	L
MD03	/Prut	Conf. Danube-Giurgiulesti	45 28 10	28 12 36	0	5	27480	L2270	LMR
MD04*	/Prut	Leova	46 20 0	28 10 0	216	14	23400	L2240	L
UA01	Danube	Reni - Kilia arm/Chilia arm	45 28 50	28 13 34	132	4	805700	L0630	M
UA02	Danube	Vilkova-Kilia arm/Chilia arm	45 24 42	29 36 31	18	1	817000	L0690	M

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 is 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
*	Monitoring site MD04 replaces the site MD02 that was originally selected for TNMN.
**	From year 2005 is used monitoring point Drava - Ormoz (L1300) this is a transnational Slovenian - Croatian point.

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



Monitoring location
- on the Danube River
- on the tributary

Figure 4.1:
The Danube Stationmap TNMN

4.2 Determinands

The determinand list was originally based on the list from the Bucharest Declaration, which was extended/reduced with determinands recommended according to existing EC-directives and the riparian countries own demands. However, the discussions in the MLIM-SG during the implementation phase showed the need for reduced determinand lists. The minimum sampling frequency of 12 per year in water and 2 per year for biomonitoring and for determinands in sediment was agreed.

The resulting lists of determinands for water as agreed for TNMN are presented in tables 4.2.1 together with the levels of interest and analytical accuracy targets, which are defined as follows:

- The minimum likely level of interest is the lowest concentration considered likely to be encountered or important in the TNMN.
- The principal level of interest is the concentration at which it is anticipated that most monitoring will be carried out.
- The required limit of detection is the target limit of detection (LOD) which laboratories are asked to achieve. This has been set, wherever practicable, at one third of the minimum level of interest. This is intended to ensure that the best possible precision is achieved at the principal level of interest and that relatively few "less than results" will be reported for samples at or near the lowest level of interest. Where the performance of current analyses is not likely to meet the criterion of a LOD of one third of the lowest level of interest, the LOD has been revised to reflect best practice. In these cases, the targets have been entered in *italics*.
- The tolerance indicates the largest allowable analytical error which is consistent with the correct interpretation of the data and with current analytical practice. The target is expressed as ”x concentration units or P%”. The larger of the two values applies for any given concentration. For example, if the target is 5 mg/l or 20% - at a concentration of 20 mg/l the maximum tolerable error is 5 mg/l (20% is 4 mg/l); at a concentration of 100 mg/l, the tolerable error is 20 mg/l (i.e. 20%) because this value exceeds the fixed target of 5 mg/l.

Table 4.2.1: Determinand list for water for TNMN

Determinands in Water	**Unit**	**Minimum likely level of interest**	**Principal level of interest**	**Target Limit of Detection**	**Tolerance**
Flow	m^3/s	-	-	-	-
Temperature	°C	-	0-25	-	0.1
Suspended Solids	mg/l	1	10	*1*	*1 or 20%*
Dissolved Oxygen	mg/l	0.5	5	0.2	0.2 or 10%
pH	-	-	7.5	-	0.1
Conductivity @ 20 °C	µS/cm	30	300	5	5 or 10%
Alkalinity	mmol/l	1	10	0.1	0.1
Ammonium (NH_4^+ -N)	mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO_2^- -N)	mg/l	0.005	0.02	*0.005*	*0.005 or 20%*
Nitrate (NO_3^- -N)	mg/l	0.2	1	0.1	0.1 or 20%
Organic Nitrogen	mg/l	0.2	2	0.1	0.1 or 20%
Ortho- Phosphate (PO_4^{3-} -P)	mg/l	0.02	0.2	0.005	0.005 or 20%
Total Phosphorus	mg/l	0.05	0.5	0.01	0.01 or 20%
Sodium (Na^+)	mg/l	1	10	0.1	0.1 or 10%
Potassium (K^+)	mg/l	0.5	5	0.1	0.1 or 10%
Calcium (Ca^{2+})	mg/l	2	20	0.2	0.1 or 10%
Magnesium (Mg^{2+})	mg/l	0.5	5	0.1	0.2 or 10%
Chloride (Cl^-)	mg/l	5	50	1	1 or 10%
Sulphate (SO_4^{2-})	mg/l	5	50	5	5 or 20%
Iron (Fe)	mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese (Mn)	mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc (Zn)	µg/l	10	100	3	3 or 20%
Copper (Cu)	µg/l	10	100	3	3 or 20%
Chromium (Cr) - total	µg/l	10	100	3	3 or 20%
Lead (Pb)	µg/l	10	100	3	3 or 20%
Cadmium (Cd)	µg/l	1	10	*0.5*	*0.5 or 20%*
Mercury (Hg)	µg/l	1	10	0.3	0.3 or 20%
Nickel (Ni)	µg/l	10	100	3	3 or 20%
Arsenic (As)	µg/l	10	100	3	3 or 20%
Aluminium (Al)	µg/l	10	100	*10*	*10 or 20%*
BOD_5	mg/l	0.5	5	*0.5*	*0.5 or 20%*
COD_{Cr}	mg/l	10	50	*10*	*10 or 20%*
COD_{Mn}	mg/l	1	10	0.3	0.3 or 20%
DOC	mg/l	0.3	1	*0.3*	*0.3 or 20%*
Phenol index	mg/l	0.005	0.05	*0.005*	*0.005 or 20%*
Anionic active surfactants	mg/l	0.1	1	0.03	0.03 or 20%
Petroleum hydrocarbons	mg/l	0.02	0.2	*0.05*	*0.05 or 20%*
AOX	µg/l	10	100	10	10 or 20%
Lindane	µg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	µg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine	µg/l	0.1	1	0.02	0.02 or 30%
Chloroform	µg/l	0.1	1	0.02	0.02 or 30%
Carbon tetrachloride	µg/l	0.1	1	0.02	0.02 or 30%
Trichloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Tetrachloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Total Coliforms (37 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Coliforms (44 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Streptococci	10^3 CFU/100 ml	-	-	-	-
Salmonella sp.	in 1 litre	-	-	-	-
Macrozoobenthos - no. of taxa	-	-	-	-	-
Macrozoobenthos - Saprobic index	-	-	-	-	-
Chlorophyll - a	µg/l	-	-	-	-

4.3 Analytical Quality Control (AQC)

The analytical methodologies for the determinands applied in TNMN are based on a list containing reference and optional analytical methods. The National Reference Laboratories (NRLs) have been provided with a set of ISO standards (reference methods) reflecting the determinand lists, but taking into account the current practice in environmental analytical methodology in the EU. It has been decided not to require each laboratory to use the same method, providing the laboratory would be able to demonstrate that the method in use (optional method) meets the required performance criteria. Therefore, the minimum concentrations expected and the tolerance required of actual measurements have been defined for each determinand (as reported in table 4.2.1), in order to enable laboratories to determine whether the analytical methods currently in use are acceptable.
It is a good practice that targets for analytical accuracy define the standard of the accuracy, which is necessary for the task in hand. Therefore, two key concentration levels - the minimum level of interest and the principal level of interest - have been defined for each determinand as described in chapter 4.2. These levels define the aims of the monitoring programme and can be used to establish the performance needed from analytical systems used in the laboratories involved in the TNMN, assuming that the aims of the programme will be satisfied provided that

- relatively few results are reported as ”less than” the minimum level
- the accuracy achieved at the principal level is not worse than ± 20% of the principal level.

Any practical approach to monitoring must take into account the current capabilities of analytical science. This means that if some targets are recognised as very difficult to achieve, it may be necessary to set more relaxed, interim targets and to review performance and data use in the course of the monitoring programme.

The described approach supports the work of harmonising the analytical activities within the Danube Basin related to the TNMN as well as the implementation and operation of an Analytical Quality Control (AQC) programme. Therefore, it had been used in development of the training needs required to improve the laboratory performance of the National Reference Laboratories as well as the other laboratories involved in the implementation of the TNMN. The result is that managers and personnel of the involved laboratories had been provided with practical training for analytical instrumentation and on-site sampling as well as with theoretical aspects of AQC.

4.3.1 Performance testing in the Danubian laboratories in 2006

Organisation of interlaboratory comparison studies in the transboundary water quality monitoring in the Danube river basin was first agreed in 1992, within the framework of the Bucharest Declaration monitoring programme. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered and took responsibility for organising the performance testing exercises under the name QualcoDanube.
After the first, randomly organized distributions in 1993, a regular distribution programme started in 1996, which involved quarterly distribution of synthetic concentrates, real water and sediment samples for analyzing determinands from the TNMN (TransNational Monitoring Network) determinand lists.

Observed discrepancies among the analytical results obtained in different Danubian laboratories determined the parameters and the concentration levels involved in the scheme, aiming to help the laboratories make connective parameters and to improve the quality of analytical results. Significant improvements were observed after several distributions, particularly in case of nutrient analysis.

The EU-PHARE programme supported the enhancement and strengthening of the Danube basin monitoring programme, which led to the upgrading of the analytical quality control (AQC) schemes. New elements were introduced into the QualcoDanube AQC interlaboratory comparison programme accordingly, e.g. preparation of Danube reference materials. This activity was further supported by the UNDP/GEF Danube Regional Project.

Based on experiences of the previous interlaboratory comparison studies as well as on the new requirements of the EU Water Framework Directive (WFD), micropollutants became the focus of attention in 2005. At the 2005 MLIM-Expert Group Meeting the AQC programme was revised as well: all determinands are covered during the first three quarterly distributions and the fourth distribution is reserved for repeating the analysis for those matrix/determinands where more than 15 % of the laboratories reported rejected (i.e. double-flagged) results.

The number of participating laboratories increased by one to 38 in 2006. The QualcoDanube analytical quality control scheme traditionally uses the Youden-pair experimental design and evaluation technique. Detailed results of the four distributions and their evaluation have been published elsewhere (QualcoDanube, AQC in Water Analytical Laboratories in the Danube River Basin, Summary Report 2006, VITUKI, Budapest). A brief summary is presented hereafter, with the separate discussion of results for different determinands.

4.3.1.1 Results of performance testing of water samples

General parameters

Real surface water samples were distributed for the analysis of these compounds. In general, results are very good: no measurement values were rejected in case of chloride, calcium and total hardness, while only slight systematic errors can be observed for other determinands (sulphate, potassium, sodium and magnesium), where one or two results were double-flagged.

Nutrients

Nutrients were analysed in real surface water samples (with the exception of nitrite which was a synthetic solution). Performance was found to be rather good for these determinands as well, though slightly worse than in case of general parameters.

Kjeldahl-N measurement results were influenced by significant systematic error, thus samples for this determinand were redistributed in the fourth quarter. The performance in case of ammonium and nitrate was somewhat better, but equally characterized by significant systematic error, while nitrite showed excellent results with only one outlier per sample. The results of phosphate and total phosphorus were rather good, influence of systematic error is small.

Organic pollutants
Samples were either of natural (chemical/biological oxygen demand, petroleum hydrocarbons and DOC) or synthetic (MBAS, AOX, phenol index, atrazine, lindane, 4,4'-DDT) origin.
With the exception of phenol index and AOX which show good results, performance on organic micropollutants was rather poor in general, which is demonstrated by the fact that six of the eleven parameters (COD_{Cr}, BOD_5, MBAS, and atrazine, lindane, 4,4'-DDT) had to be redistributed in the fourth and final round due to the pronounced presence of systematic error.

Metals, heavy metals
Determination was highly successful for certain components, such as iron, cadmium, arsenic, nickel and zinc, while systematic error markedly influences measurement of manganese, chromium, copper, lead, mercury and aluminium.
Only aluminium analysis had to be repeated due to poor results. The Youden-plot reveals that measured values tend to concentrate in two groups, nevertheless this fact cannot be attributed to differences in analytical methods used (i.e. values measured by different methods appear in both groups).

4.3.1.2 Results of performance testing of sediment samples

Nutrients
The results reported by laboratories for total N and total P in real sediment samples were quite good with only minor influence of systematic error.

Organic determinands
Real Danube sediment samples (spiked if necessary) were distributed to the participants. It should be noted that the low number of laboratories reporting (6-16) made evaluation difficult. Performance in this determinand group is rather poor, with the exception of TOC. This marks an improvement compared to previous years. Improvement was observed in case of PAHs as well, that - first the first time in the history of the AQC - did not have to be repeated at the end of the year.
Presence of systematic error is evident for petroleum hydrocarbons, lindane, atrazine, 4,4'-DDT and PCBs (in case of the latter, the first round could not be evaluated due to high discrepancies in data, thus result were sent to laboratories as indicative only). With the exception of petroleum hydrocarbons, these compounds were redistributed in the fourth round. Some improvement could be observed in the repeated rounds, but performance remained rather poor.

Metals, heavy metals
Test samples were natural sediment samples from the Danube in case of all determinands. Determination of metals and heavy metals is highly successful in general. No repetition was necessary for any of the determinands in this group.
Excellent results were obtained for iron and magnesium where none of the measured values were rejected. Performance in case of manganese, calcium, copper, cadmium, chromium, lead and zinc was equally very good, while effect of systematic error could be observed in case of aluminium, arsenic, nickel and mercury.

4.3.1.3 Conclusion

Surface water

In accordance with previous years, general parameters were measured with negligible problems in 2006; moreover, performance even improved in case of certain parameters (chloride, sulphate, potassium) as compared to 2005. A slight positive change can be observed with nutrients as well (especially nitrate and nitrite); however this group of parameters in general is somewhat more affected by systematic error.
As regards to metals/heavy metals, determination definitely improved for most parameters (examples could be iron, manganese, mercury or arsenic), but in many case stagnation or even slight deterioration (chromium) is observable in comparison with previous years. In addition, effect of systematic or random error is still pronounced in case of several elements (e.g. aluminium, lead, copper).
Determination of organic pollutant is the most problematic analysis. Positive change is shown for two determinands (AOX and phenol index), but performance in case of other parameters remains poor (especially 4,4'-DDT, BOI_5 and MBAS) and stagnated at best in comparison with previous years' data.

Sediment

General parameters and metals/heavy metals were measured with success from solid samples. This is in accordance with experience from previous years, even positive change could be observed with some elements (lead, copper, magnesium).
Organic pollutants, as in case of liquid samples, are the most problematic of analyses in sediment samples as well. Pesticides and macropollutants (i.e. petroleum hydrocarbons and TOC) show poor performance, and no change can be observed when compared to previous years (it should be noted though that the number of reporting laboratories increased, e.g. TOC). On the other hand, results of PAHs were good or at least satisfactory, which is a remarkable improvement compared to 2005 and 2006. PCBs show a less favourable picture, this determination remained rather problematic.

4.4 TNMN Data Management

The importance of TNMN data management was recognised in very early stage of TNMN operation and well-defined structure for data storage in relational database had been prepared. The data are organised in a system of joined tables, containing information related to monitoring locations, determinands, methods of sampling, methods of analysis, remarks, information on taken samples and results of analysis. From 1996, several parts of the database had been modified with purpose to either adjust the system to the new needs, or to increase an efficiency of the system.
The procedure of TNMN data collection starts on a national level of each country. Nominated National Information Managers (NIMs) are responsible for collection of the data from National Reference Laboratories and other national laboratories involved in TNMN, where the data from sampling and analysis are generated. In the subsequent step the NIMs are responsible for data checking, preparation in agreed data exchange file format (DEFF) and sending to the Central Point in Slovak Hydrometeorological Institute in Bratislava.

Here the data are checked again and suspicious ones consulted with NIMs. After the consultation process the data from TNMN are merged and stored in one relational database for further use and are also included in the information system of ICPDR - DANUBIS.

4.5 Water Quality Classification

The first attempt to come up with proposal of joint water quality classification for the Danube river basin had been done in 1997 by PHARE Applied Research Project EU/AR/203/90 “Water Quality Targets and Objectives for Surface Waters in the Danube basin” (WRRC Vituki, 1997). The classification proposed by the project has not been applied for evaluation of results from TNMN, it was only partly used by means of using its limit values for illustration of BOD_5, PO_4^{3-}-P and NO_3^--N concentrations on the maps in the first TNMN-Yearbooks (1996-2000).

In 1999 the EU PHARE Programme contributed to the EPDRB by initiating the project “Danube River Basin Water Quality Enhancement”. One of the objectives was to make a proposal for a unified water quality classification for the entire the Danube River basin region based on

- review of existing water quality and sediment quality classification methods in Danubian countries
- review of EU legislation
- experience within the different countries

The activity was realised by *IWACO BV Consultants for water and environment* in Rotterdam. Although the attention was given to WFD, it was concluded that to come to ecologically based and regionally differentiated water quality criteria according to WFD in the Danube River Basin will take considerable effort and time. In the meantime interim water quality classification scheme had been proposed. This proposal was further discussed, adjusted by Monitoring, Laboratory and Information Management Sub-Group and finally approved in 2001.

The classification scheme as presented in Table 4.5.1 is meant to serve international purposes for the presentation of current status and improvements of water quality in the Danube river and its main tributaries and is not to be a tool for implementation of national water policy. It covers 37 determinands. Five classes are used for assessment, with target value being the limit value of class II. The class I should represent reference conditions or background concentrations. For number of determinands it was not possible to establish real reference values due to existence of many types of water bodies in the Danube river basin differing in physico-chemical characteristics naturally. For synthetic substances the detection limit or minimal likely level of interest was chosen as limit value for class I.
The classes III – V are on the “non-complying“ side of the classification scheme and their limit values are usually 2-5-times the target values. They should indicate the seriousness of the exceedence of the target value and help to recognise the positive tendency in water quality development.
For compliance testing 90-percentile value of at least 11 measurements in a particular year should be used in the classification system.

Table 4.5.1: Water Quality Classification used for TNMN purposes.

Determinand	Unit	Class				
		I	II TV	III	IV	V
		Class limit values				
Oxygen/Nutrient regime						
Dissolved oxygen *	$mg.l^{-1}$	7	6	5	4	< 4
BOD_5	$mg.l^{-1}$	3	5	10	25	> 25
COD_{Mn}	$mg.l^{-1}$	5	10	20	50	> 50
COD_{Cr}	$mg.l^{-1}$	10	25	50	125	> 125
pH	-		> 6.5* and < 8.5			
Ammonium-N	$mg.l^{-1}$	0.2	0.3	0.6	1.5	> 1.5
Nitrite-N	$mg.l^{-1}$	0.01	0.06	0.12	0.3	> 0.3
Nitrate-N	$mg.l^{-1}$	1	3	6	15	> 15
Total-N	$mg.l^{-1}$	1.5	4	8	20	> 20
Ortho-phosphate-P	$mg.l^{-1}$	0.05	0.1	0.2	0.5	> 0.5
Total-P	$mg.l^{-1}$	0.1	0.2	0.4	1	> 1
Chlorophyll-a	$\mu g.l^{-1}$	25	50	100	250	> 250
Metals (dissolved) **						
Zinc	$\mu g.l^{-1}$	-	5	-	-	-
Copper	$\mu g.l^{-1}$	-	2	-	-	-
Chromium (Cr-III+VI)	$\mu g.l^{-1}$	-	2	-	-	-
Lead	$\mu g.l^{-1}$	-	1	-	-	-
Cadmium	$\mu g.l^{-1}$	-	0.1	-	-	-
Mercury	$\mu g.l^{-1}$	-	0.1	-	-	-
Nickel	$\mu g.l^{-1}$	-	1	-	-	-
Arsenic	$\mu g.l^{-1}$	-	1	-	-	-
Metals (total)						
Zinc	$\mu g.l^{-1}$	Bg	100	200	500	> 500
Copper	$\mu g.l^{-1}$	Bg	20	40	100	> 100
Chromium (Cr-III+VI)	$\mu g.l^{-1}$	Bg	50	100	250	> 250
Lead	$\mu g.l^{-1}$	Bg	5	10	25	> 25
Cadmium	$\mu g.l^{-1}$	Bg	1	2	5	> 5
Mercury	$\mu g.l^{-1}$	Bg	0.1	0.2	0.5	> 0.5
Nickel	$\mu g.l^{-1}$	Bg	50	100	250	> 250
Arsenic	$\mu g.l^{-1}$	Bg	5	10	25	> 25
Toxic substances						
AOX	$\mu g.l^{-1}$	10	50	100	250	> 250
Lindane	$\mu g.l^{-1}$	0.05	0.1	0.2	0.5	> 0.5
P,p´-DDT	$\mu g.l^{-1}$	0.001	0.01	0.02	0.05	> 0.05
Atrazine	$\mu g.l^{-1}$	0.02	0.1	0.2	0.5	> 0.5
Trichloromethane	$\mu g.l^{-1}$	0.02	0.6	1.2	1.8	> 1.8
Tetrachloromethane	$\mu g.l^{-1}$	0.02	1	2	5	> 5
Trichloroethene	$\mu g.l^{-1}$	0.02	1	2	5	> 5
Tetrachloroethene	$\mu g.l^{-1}$	0.02	1	2	5	> 5
Biology						
Saprobic index of macrozoobenthos	-	≤ 1.8	1.81 – 2.3	2.31 – 2.7	2.71 – 3.2	> 3.2

* values concern 10-percentile value — bg background values
** for dissolved metals only guideline values are indicated — TV target value

5. Results of basic statistical processing

In 2006, 77 monitoring locations had been monitored in the frame of TNMN in the Danube River Basin. As some locations consist of more sampling sites in the profile (usually left, middle and right side of the river), data had been collected from altogether 107 sampling sites, out of which 68 are located on the Danube River itself and 39 on the tributaries.
The basic processing of the TNMN data consisted of calculation of selected statistical characteristics and classification of water quality determinands in each monitoring site.
Results of the processing are presented in tables in Annex 1, separately for each sampling site and according to the following legend.

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 2006
Mean	arithmetical mean of the measurements done in the year 2006
Max	maximum value of the measurements done in the year 2006
C50	50 percentile of the measurements done in the year 2006
C90	90 percentile of the measurements done in the year 2006
Class	result of classification of the determinand

When processing the TNMN data and presenting them in the tables of Annex 1, the following rules have been applied:

- If "less than the detection limit" values were present in the dataset for a given determinand, the value of detection limit was used in statistical processing of the data.
- If number of measurements for determinand was lower than four, from the set of statistical characteristics only minimum, maximum and mean were presented in the tables of Annex 1.
- For the purposes of classification, *testing value* has been calculated for each determinand, which was further compared to limit values for water quality classes given in Chapter 4.5 and the corresponding class was assigned to the determinand. The testing value is equal to 90 percentile (10 percentile for dissolved oxygen and lower limit of pH value) if number of measurements in a year was at least eleven. If the number of measurements in a year was lower than eleven, the testing value is represented by a maximum value from a data set (a minimum value for dissolved oxygen and lower limit of pH value).
- It happened in some cases that limit of detection used by a country was higher than limit value for class II, representing the target value. In these cases the statistics were calculated and presented in a table, but classification has not been done.

- An indication of water quality class for each determinand in the tables of Annex I is presented by the respective class number and highlighted by using colouring of the respective field of the table, using the colours given below:

blue colour	class I
green colour	class II
yellow colour	class III
orange colour	class IV
red colour	class V

- If number of measurements for a classified water quality determinand was lower than four in sampling site, the result of classification was presented in tables by light blue colour to indicate lower reliability of such results (with an exception of saprobic index).

The frequencies of measurements in sampling sites and completeness of datasets regarding the determinands were being gradually improved since the start of TNMN operation in 1996. The required sampling frequency 12 times per year had been significantly lower only in monitoring locations of Bosnia and Herzegovina (8 times per year 2006) and Ukraine (UA01) (11 times per year 2006). But there are still differences in frequency of measurement of individual determinands, with generally lower number of measurements of dissolved phosphorus, biological determinands, heavy metals and specific organic micropollutants, especially in the lower part of the Danube River Basin.

Table 5.1, created on the basis of data in tables in Annex 1, shows in aggregated way the concentration ranges and mean annual concentrations of selected determinands representing group of oxygen regime, nutrient status, heavy metals, group of biological determinands and organic micropollutants in the Danube River and its tributaries in 2006. Information on number of monitoring locations and sampling sites with measurements of the determinands is also given there.

The statistical results indicate that in general the concentration ranges of measured determinands were larger in the tributaries than in the Danube. In concentration of heavy metals was significant range of values in the Danube river and tributaries.

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2006.

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	40/68	0.1	28.4	9.6	18.0	36/38	0.1	29.7	5.8	20.5
Suspended Solids	mg/l	40/68	< 0.5	332.0	9.2	138.2	37/39	< 1	2260.0	5.0	344.2
Dissolved Oxygen	mg/l	40/68	3.1	16.2	6.6	11.3	37/39	3.8	16.9	7.2	12.7
BOD_5	mg/l	39/67	< 0.2	16.6	1.1	10.4	35/37	< 0.2	35.5	1.2	8.3
COD_{Mn}	mg/l	40/68	1.0	34.9	2.0	19.7	27/29	3.1	108.0	3.5	41.9
COD_{Cr}	mg/l	34/62	1.0	53.0	3.5	31.3	22/24	0.5	36.0	1.7	12.7
TOC	mg/l	23/35	0.5	11.4	2.0	6.3	17/17	0.5	91.0	1.5	10.0
DOC	mg/l	12/25	1.0	7.9	2.1	7.9	14/14	0.6	14.1	1.3	8.1
pH		40/68	6.8	8.7	7.5	8.3	37/39	6.5	9.0	7.0	8.3
Alkalinity	mmol/l	36/64	2.0	5.7	3.0	4.2	30/32	1.0	9.7	1.8	7.5
Ammonium-N	mg/l	40/68	< 0.004	1.470	0.027	0.339	35/37	0.005	6.418	0.017	3.402
Nitrite-N	mg/l	40/68	< 0.002	0.273	0.010	0.068	37/39	0.001	0.405	0.003	0.069
Nitrate-N	mg/l	40/68	< 0.1	7.320	0.740	3.350	37/39	0.070	11.400	0.436	9.531
Total Nitrogen	mg/l	16/27	0.73	7.63	1.60	3.37	22/22	0.56	858.00	1.03	688.00
Organic Nitrogen	mg/l	15/23	< 0.01	2.13	0.07	1.00	24/26	< 0.01	2.63	0.10	1.41
Ortho-Phosphate-P	mg/l	39/67	< 0.003	1.480	0.029	0.197	30/32	< 0.003	0.488	0.007	0.236
Total Phosphorus	mg/l	40/68	0.010	2.080	0.046	0.486	33/35	0.013	764	0.036708	747
Total Phosphorus - Dissolved	mg/l	9/9	<0.005	0.107	0.038	0.065	10/10	< 0.005	0.288	0.011846	0.12
Chlorophyll-a	µg/l	32/60	0.02	104.0	0.7	24.8	11/13	1.2	152.0	2.2	43.6
Conductivity @ 20°C	µS/cm	38/66	219	678	368	511	35/37	148	1999	251	965
Calcium	mg/l	40/68	27.1	87.0	47.1	79.8	35/37	25.6	130.0	38.7	98.1
Sulphates	mg/l	38/66	5.4	98.8	18.3	59.1	31/33	1.1	252.0	11.6	160.0
Magnesium	mg/l	40/68	1.4	70.9	11.3	36.4	37/39	5.4	86.0	9.3	70.8
Potassium	mg/l	37/65	0.8	11.4	1.6	4.0	31/33	0.4	14	0.9125	10.1167
Sodium	mg/l	39/67	1.9	177.5	11.2	45.3	30/32	2.4	83.0	5.9	72.1
Manganese	mg/l	22/38	< 0.00001	0.585	0.009	0.082	21/21	< 0.001	8.000	0.012	1.094
Iron	mg/l	23/39	< 0.010	7.340	0.087	0.953	20/20	0.010	17.000	0.288	3.374
Chlorides	mg/l	39/67	4.7	83.9	18.4	39.9	31/33	0.5	100.9	6.2	62.5
Macrozoobenthos- saprobic index		6/6	2.0	4.9	2.0	4.8	5/5	1.2	2.6	1.5	2.4
Macrozoobenthos - no.of taxa		4/4	26	44	26	44	11/11	2.0	68.0	2.3	62.5

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2006. (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	31/53	< 0.8	600.0	1.3	144.2	29/31	< 1.0	90.0	2.0	34.0
Copper - Dissolved	µg/l	29/52	< 0.5	200.00	0.96	29.00	29/31	< 0.046	58.00	0.873	29.00
Chromium - Dissolved	µg/l	29/52	< 0.2	< 20	< 0.2	< 20	29/31	0.19	14.56	0.23	5.70
Lead - Dissolved	µg/l	31/53	0.10	7.50	0.67	7.50	24/26	0.17	25.00	0.50	6.40
Cadmium - Dissolved	µg/l	30/52	< 0.036	5.00	< 0.05	5.00	17/19	< 0.03	10	0.05	0.95
Mercury - Dissolved	µg/l	30/52	< 0.025	1.100	0.039	0.233	21/23	< 0.005	3.1	0.0627	0.36382
Nickel - Dissolved	µg/l	31/53	0.45	64.00	0.72	9.63	24/26	< 0.4	87	1	6.95
Arsenic - Dissolved	µg/l	31/53	0.23	9.00	0.23	2.61	21/23	0.16	9.00	0.16	5.38
Aluminium - Dissolved	µg/l	12/20	< 5	96.0	11.4	63.4	11/13	< 3.0	88.0	5.0	78.8
Zinc *	µg/l	24/46	< 0.8	118.0	3.5	33.5	22/24	< 1.0	152.0	10.2	59.8
Copper	µg/l	27/46	< 0.7	103.00	1.00	23.50	26/28	< 0.5	66.60	1.23	31.92
Chromium - total	µg/l	24/44	< 0.001	40.00	0.27	10.00	22/24	0.20	36.50	0.23	10.00
Lead	µg/l	23/44	< 0.05	107.00	0.14	9.60	17/19	< 0.5	19.00	0.98	6.40
Cadmium	µg/l	20/42	< 0.036	7.50	< 0.05	1.50	24/26	< 0.03	3.40	0.05	1.56
Mercury	µg/l	18/35	< 0.01	1.700	0.040	0.358	23/25	< 0.01	7.000	0.022	2.200
Nickel	µg/l	33/44	< 0.1	43.00	0.60	9.00	27/29	< 0.004	83.240	0.052	29.438
Arsenic	µg/l	21/48	0.04	5.00	0.26	2.90	14/16	0.10	9.00	0.52	6.71
Aluminium	µg/l	14/32	< 20	1792.0	26.0	406.3	12/14	8.5	3900.0	35.4	1835.0
Phenol index	mg/l	36/62	< 0.001	0.084	< 0.001	< 0.020	27/29	< 0.0008	0.013	0.001	0.0065
Anionic active surfactants	mg/l	38/66	< 0.006	0.126	< 0.010	0.058	27/29	< 0.006	0.236	0.01	0.12433
AOX	µg/l	17/33	4.9	69.0	9.9	22.4	7/7	<10	137	10	63.1
Petroleum hydrocarbons	mg/l	36/64	< 0.002	0.800	< 0.005	0.317	27/29	< 0.002	20.080	0.005	19.525
PAH (sum of 6)	µg/l	0/0					2/2	0.008	0.103	0.016	0.034
PCB (sum of 7)	µg/l	0/0					2/2	< 0.002	0.004	< 0.002	0.002
Lindane	µg/l	29/56	< 0.001	4.520	< 0.001	0.378	29/29	< 0.0005	< 0.1	< 0.0005	< 0.1
pp´DDT	µg/l	27/59	< 0.001	1.300	< 0.001	0.110	28/28	< 0.00005	0.08	< 0.00005	0.05
Atrazine	µg/l	33/58	< 0.001	0.500	0.006	0.500	20/20	0.007	0.5	0.009	0.5
Chloroform	µg/l	25/49	< 0.01	542.14	0.02	42.51	11/13	< 0.01	4.00	0.02	2.90
Carbon tetrachloride	µg/l	22/51	< 0.01	< 1.2	< 0.01	< 1.2	12/12	< 0.01	1.20	0.01	1.20
Trichloroethylene	µg/l	22/50	< 0.01	< 1.7	< 0.02	< 1.7	12/12	< 0.01	< 1.7	< 0.01	< 1.7
Tetrachloroethylene	µg/l	22/50	< 0.01	< 2.1	< 0.02	< 2.1	12/12	< 0.01	< 2.1	< 0.02	< 2.1
Total Coliforms (37℃)	10^3 CFU/ 100 ml	26/54	0.02	750.00	0.36	287.50	15/17	0.40	3800.00	2.05	747.91
Faecal Coliforms (44℃)	10^3 CFU/ 100 ml	18/40	0.009	240.00	0.07	41.77	14/16	0.07	400.00	0.82	137.04
Faecal Streptococci	10^3 CFU/ 100 ml	23/51	0.001	35.00	0.009	7.14	15/17	0.02	325.00	0.13	52.95

6. Presentation of classification results

The classification results given in tables of Annex 1 are presented in this chapter in aggregated way in the form of maps and charts. The selection of determinands has been conducted by intention to present either characteristic basic determinands of the main groups of water quality determinands (dissolved oxygen, BOD_5 and COD_{Cr} representing pollution by organic substances; ammonium-nitrogen, nitrate-nitrogen, ortho-phosphate phosphorus and total phosphorus characterising nutrient content; chlorophyll-a as an indicator of eutrophication). In case of group of heavy metals and organic micropollutants, only a few selected determinands from these groups are illustrated.

The maps presented on Figures 6.1 – 6.9 show water quality classes in TNMN monitoring locations. The locations in the Danube River itself and those located in tributaries are differentiated by different marks. The spot indicating water quality class on a map is of a smaller size in case the classification result in location is based on lower number of measurements than eleven. If there were data from more sampling sites (left, middle, right) at one monitoring location, only the data from the middle of a river are presented in the maps.

The figures 6.10 – 6.20 show percentage of monitoring locations in water quality classes. They illustrate the share of locations fulfilling requirements on target value (corresponding to class I and class II) and of those on the non-complying site. The percentages were calculated on the basis of the whole set of TNMN locations given in Table 4.1.1, respecting above mentioned criteria that in case of more sites in the profile only data from the middle of a river were taken into account.

Dissolved oxygen content in water can be affected by human activities in both directions – decrease is a result of pollution by degradable organic matter, an increase from normal level can be associated with eutrophication processes. In 2006 was 90 % of locations in the Danube River in class I and class II. This is more than in 2005, when 85 % of locations in the Danube was in classes I and II. From locations in tributaries 76 % could be classified by classes I and II and the worst class III were represented by 8 % of locations (see also Figure 6.10). This situation is similar as in 2005, when in classes IV and V were not classified any monitoring points in tributaries.

BOD_5 is used as an indicator of biodegradable organic pollution in waters. The share of locations satisfying target value for BOD_5 in 2006 is 95 % of locations in the Danube River corresponded to classes I and II. This is more than in 2005, when 83 % of locations in the Danube was in classes I and II. From locations in tributaries 71 % could be classified by classes I and II and the class III by 18 % of locations (see also Figure 6.11). This situation is worse than in year 2005, when 84 % was in I class and in II class, in III class was 11 %. In 2006 there was observed also 3 % in IV class in tributaries as well as year in 2005.

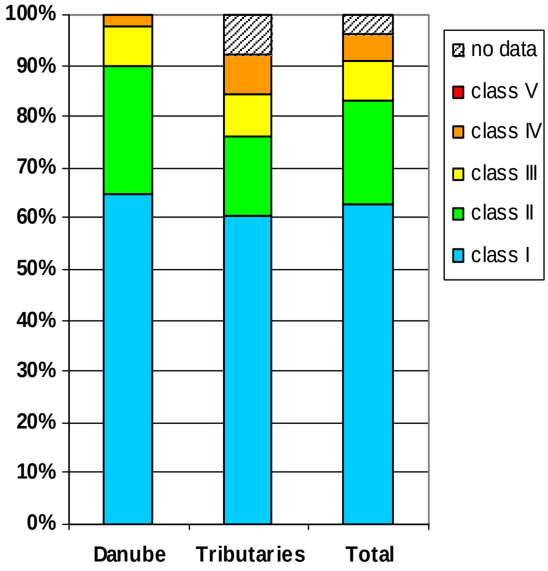


Figure 6.10: Distribution of water quality classes for Dissolved oxygen.

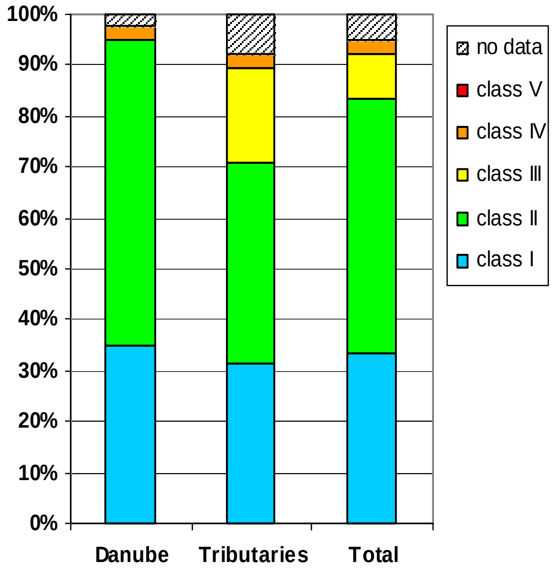


Figure 6.11: Distribution of water quality classes for $BOD_{5.}$

COD_{Cr} belongs among basic determinands characterising presence of oxidizable organic compounds in waters. It can be seen from Figure 6.12 that COD_{Cr} is still not measured in 19 % of all monitoring locations. In 2006, 68 % of locations in the Danube River and 50 % of locations in tributaries were in classes I and II. The results of classification are similar to situation in year 2005. In year 2006 there were not location in class IV in the Danube River and two locations in tributaries were in class IV (see Figure 6.12).

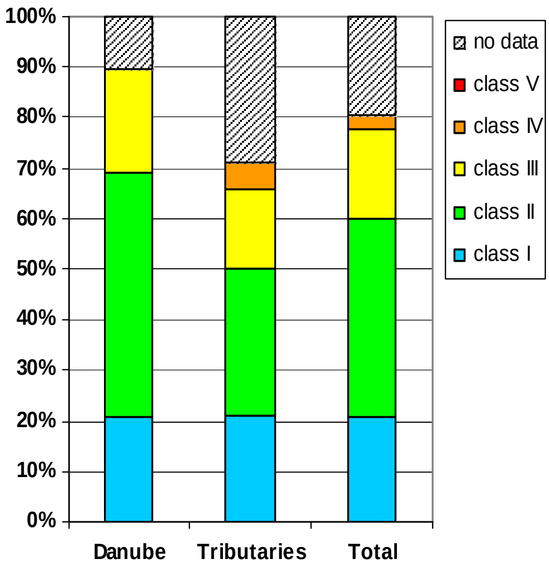


Figure 6.12: Distribution of water quality classes for $COD_{Cr.}$

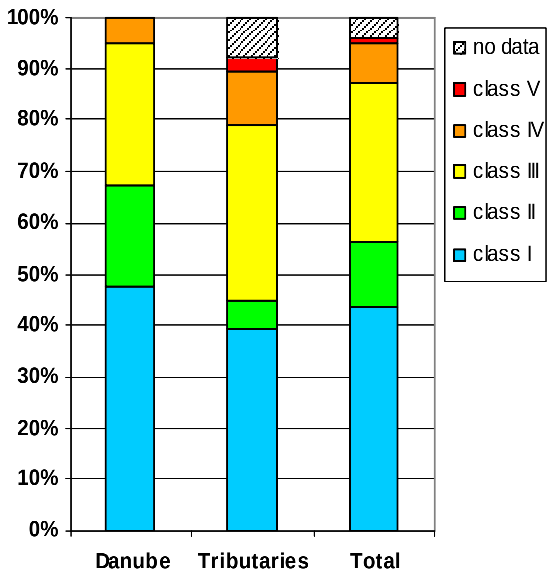


Figure 6.13: Distribution of water quality classes for Ammonium-N.

From the group of nutrients, ammonium-N, nitrate-N, ortho-phospate P and total P have been selected for presentation of classification results.
From the Figure 6.13 can be seen that in 2006 concentrations of ammonium-N corresponded to classes I and II in 68 % of locations in the Danube River and 45 % of locations in tributaries. It the same situation is for the Danube as in year 2005, but for tributaries it is worse than in 2005.

In the Danube River, 28 % of locations corresponded to class III and 5 % to class IV. In tributaries all five classes were represented, 11 % were in class IV and 3 % in the class V.

Figure 6.14 shows the distribution of water quality classes for nitrate-N in the Danube River and tributaries. In 2006 there was one of the Danube locations classified in to class I from those included in TNMN, class II was observed in 65 % of locations. An exceeding of the target value was observed in 35 % of locations, corresponding to class III.
From locations on tributaries, 76 % of them satisfied target value with vast majority in class II (66 %) and only 11 % in class I. The rest of locations belonged to either class III (11 %) or class IV (5 %).

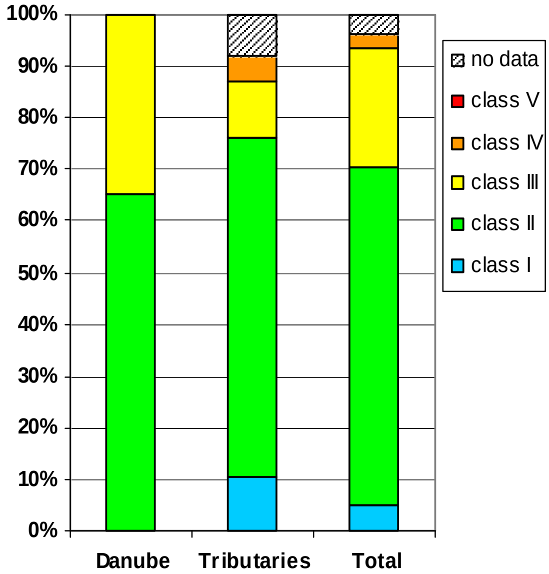


Figure 6.14: Distribution of water quality classes for Nitrate-N.

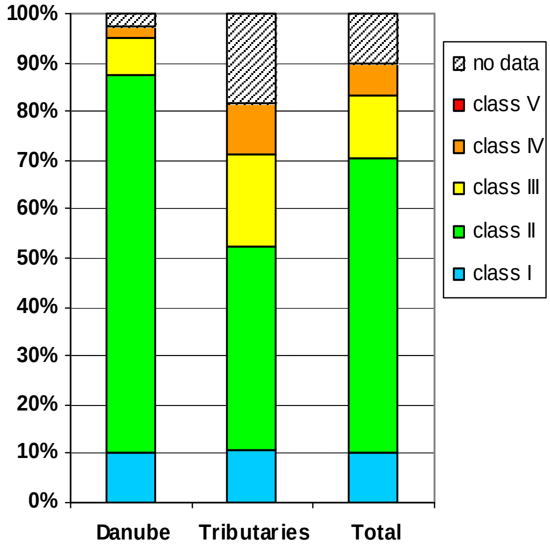


Figure 6.15: Distribution of water quality classes for Ortho-phosphate-P.

Regarding ortho-phosphate-P, from the Figure 6.15 can be seen that in the Danube River classes I-IV and also in tributaries classes I-IV were represented. A situation in the Danube River is comparable in years 2005 and 2006, 88 % of locations satisfying target value (in 2005 it was 75 %). The situations of ortho-phosphate-P in tributaries in year 2006 are a little bit better than in 2005, 53 % i.e. of locations corresponding to classes I and II, 18 % to class III, and 11 % in class IV.

In 2006, 60 % of locations in the Danube River in deteminand P_{total} corresponded to classes I and II, whilst class III had been represented by 38 % (see in Fig. 6.16) . The class IV represented in 2006 3 % of the Danube River locations.
Tributaries indicate worse quality. The target value was satisfied only 37 % of locations.
The rest of locations corresponded to class III (32 %), class IV (13 %). (see Figure 6.16). These results are comparable with those observed in the Danube River in 2005.

Content of chlorophyll-a as an indicator of primary production is closely connected to nutrient content. This determinand, which is important especially in slow-flowing lowland rivers, still does not possess this information in 37 % of the locations from TNMN. Therefore it can not be expected that classification results shown in figure 6.17 could give representative picture.

Anyhow, classes I and II were observed in 80 % of locations in the Danube River and 34 % of locations in tributaries. In the Danube river were observed in 2006 only classes I and II. In tributaries 8 % was classified in class III and 3 % of locations were in class IV.

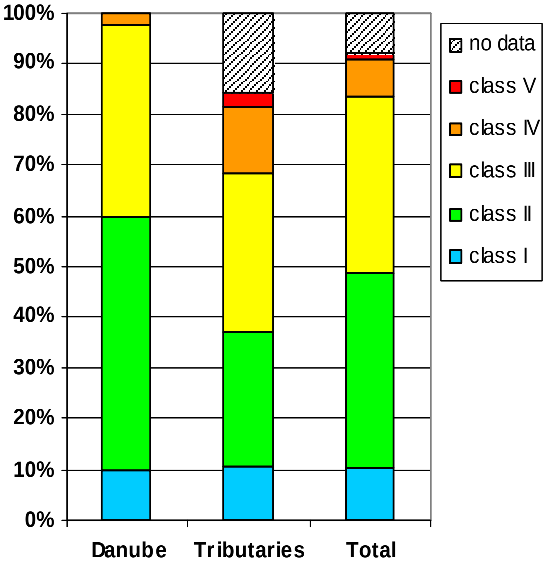


Figure 6.16: Distribution of water quality classes for P_{total}.

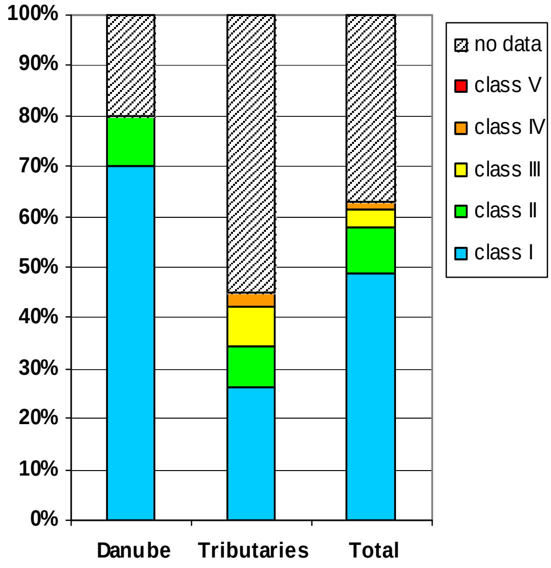


Figure 6.17: Distribution of water quality classes for Chlorophyll-a.

Classification of heavy metals was also affected by high proportion of locations without their measurements. In the Danube River, data on cadmium, chromium, copper, zinc, nickel and lead content are missing in 26-45 % of locations, concentrations of mercury and arsenic were missing in 53 % and 40 % of locations, respectively.

Similar picture is in tributaries, with 26-55 % of locations without data on cadmium, chromium, copper, zinc, nickel and lead concentration of mercury is missing in 40 % of locations, without arsenic analysis were 58 % of locations.

In the Danube River, class II was achieved in the following percentage of locations: 43 % for cadmium, 55 % for copper, 63 % for zinc, 33 % for mercury, 60 % for arsenic, 40 % for lead, 70 % for chromium and 60 % for nickel.

Regarding tributaries, the percentage satisfying target value represented by class II is the following: 40 % for cadmium, 42 % for mercury, 58 % for chromium, 55 % for copper, 60 % for zinc, 66 % for nickel, 34 % for arsenic and 55 % for lead.

The situation is similar to results observed in the Danube River and tributaries in 2005. In the Danube locations for chromium, nickel, zinc and arsenic were observed only class II, for copper, cadmium, lead classes III and IV were observed. For tributaries only for chromium were all locations in class II, for nickel, zinc and arsenic were observed also class III and copper, cadmium, lead were in class IV. Mercury was classified in class V in the Danube river locations and also in tributaries locations.

Cadmium has been selected from the group of heavy metals for presentation and it is shown on Figure 6.18.

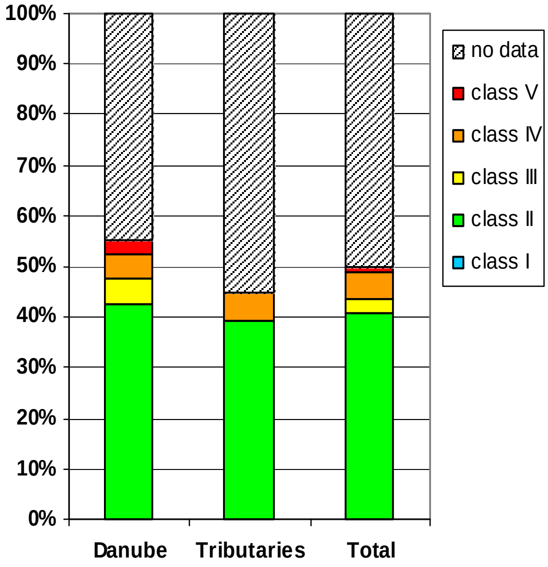


Figure 6.18: Distribution of water quality classes for Cadmium.

The group of micropollutants is represented there by p,p-DDT (Figure 6.19) and atrazine (Figure 6.20). The target value set up for p,p-DDT was achieved by 43 % of locations in the Danube river and 50 % of location in tributaries. The rest of locations in the Danube River are in classes III, IV and V (33 %) locations and in tributaries 3 % are in classes III and 16 % in IV. In 2006 42 % of TNMN locations are without p,p-DDT data. Situation was similar as in year 2005.

Distribution of water quality classes for atrazine is shown on Figure 6.20. On the basis of available information it can be concluded that in case of atrazine 60 % of locations corresponded to classes I – II, not any was in class III and 23 % was in class IV in the Danube River. Without data were 18 % of Danube locations. The non-completeness of data is even more significant in tributaries, with 42 % corresponded to classes I and II, and 8 % to class IV. In 2006, the percentage of tributaries locations without atrazine measurements was 50 %.

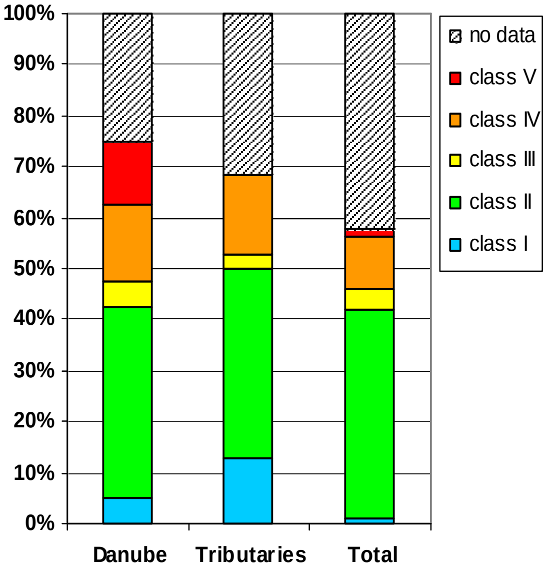


Figure 6.19: Distribution of water quality classes for p,p-DDT.

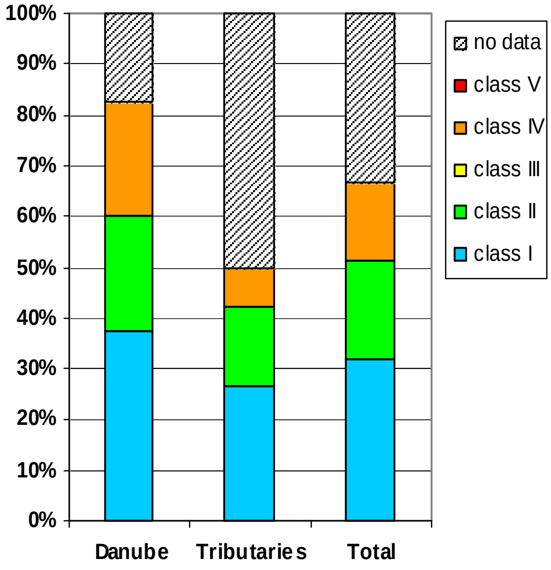


Figure 6.20: Distribution of water quality classes for Atrazine.

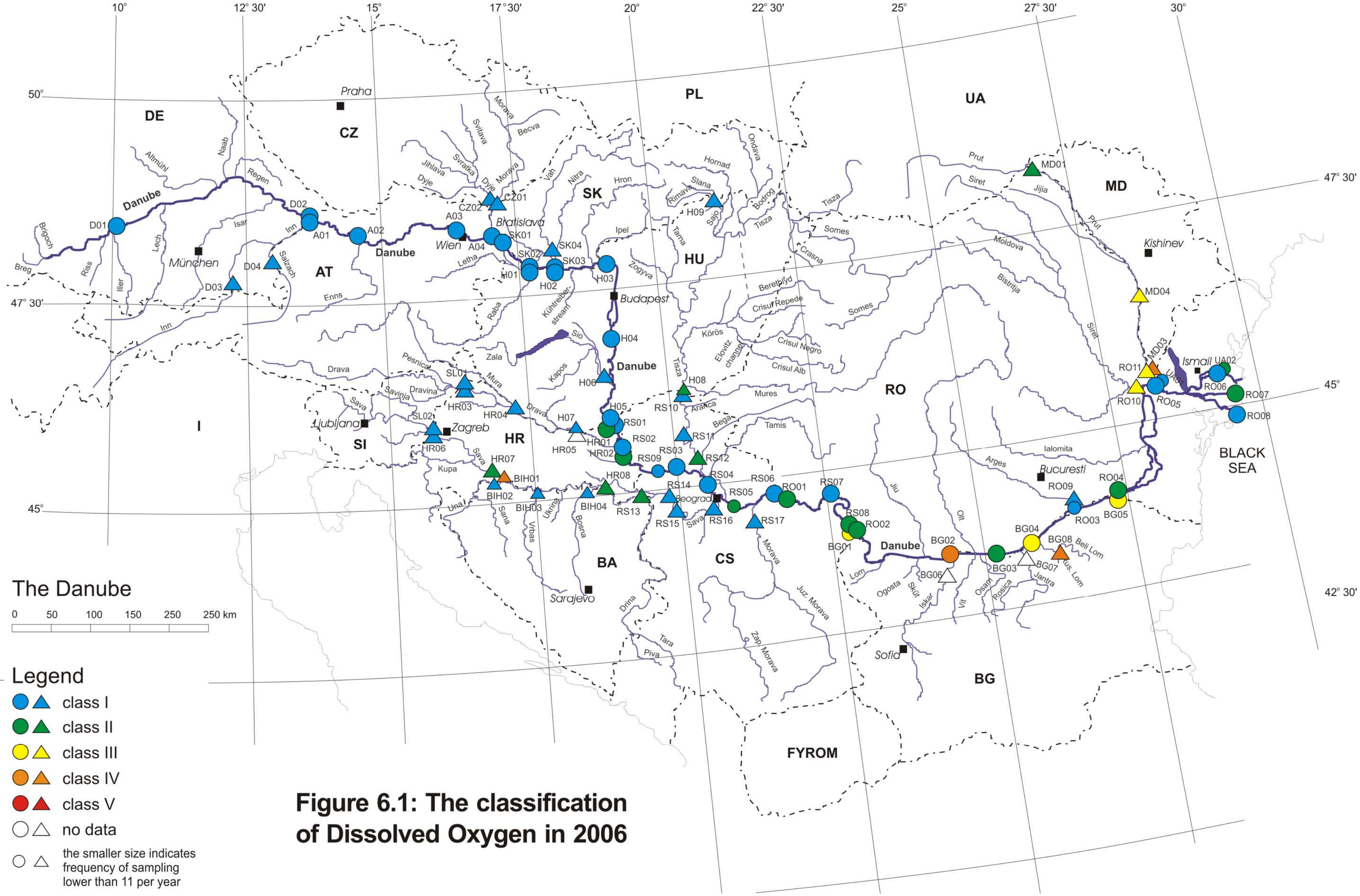


Figure 6.1: The classification of Dissolved Oxygen in 2006

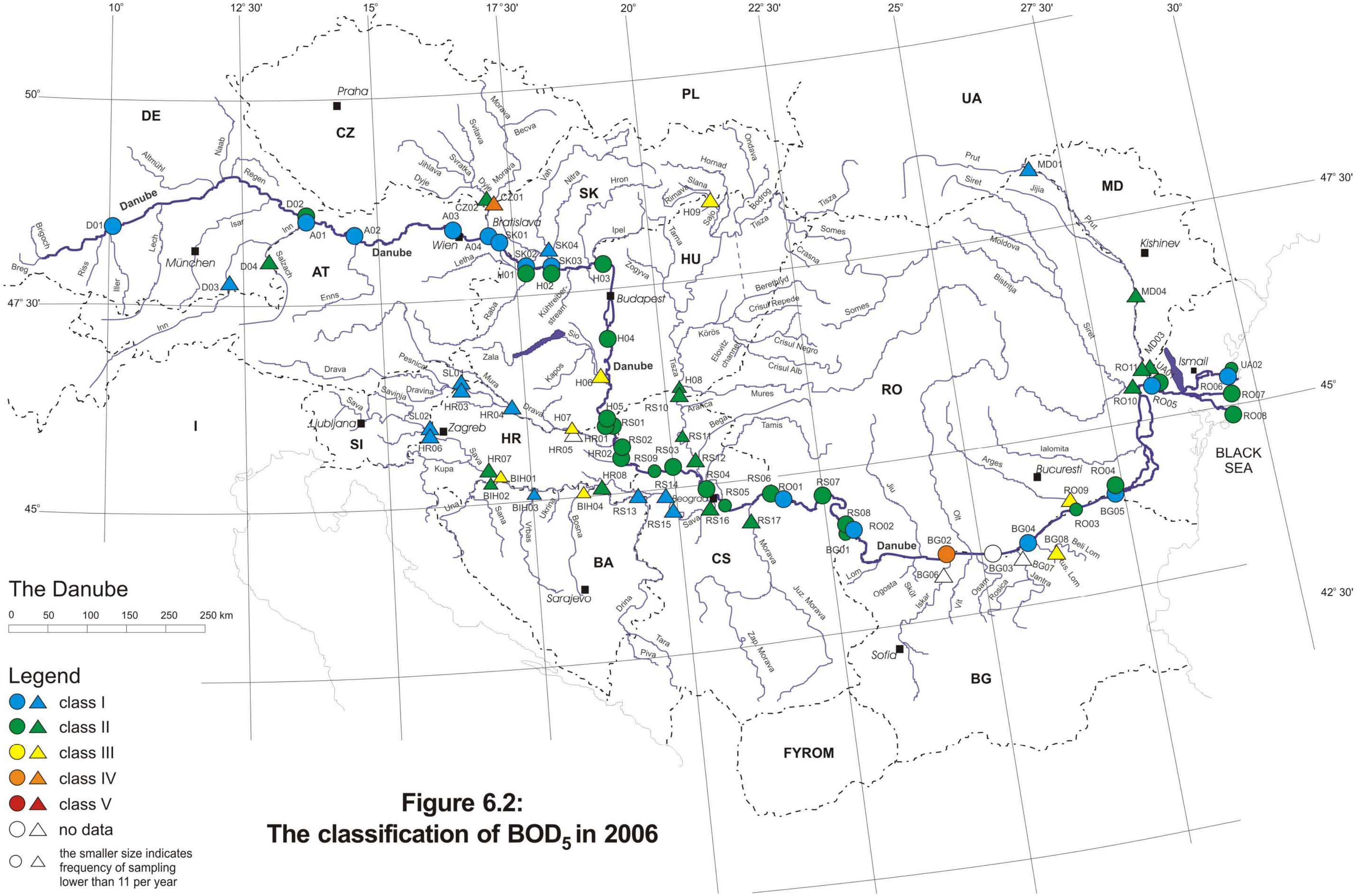


Figure 6.2:
The classification of BOD_5 in 2006

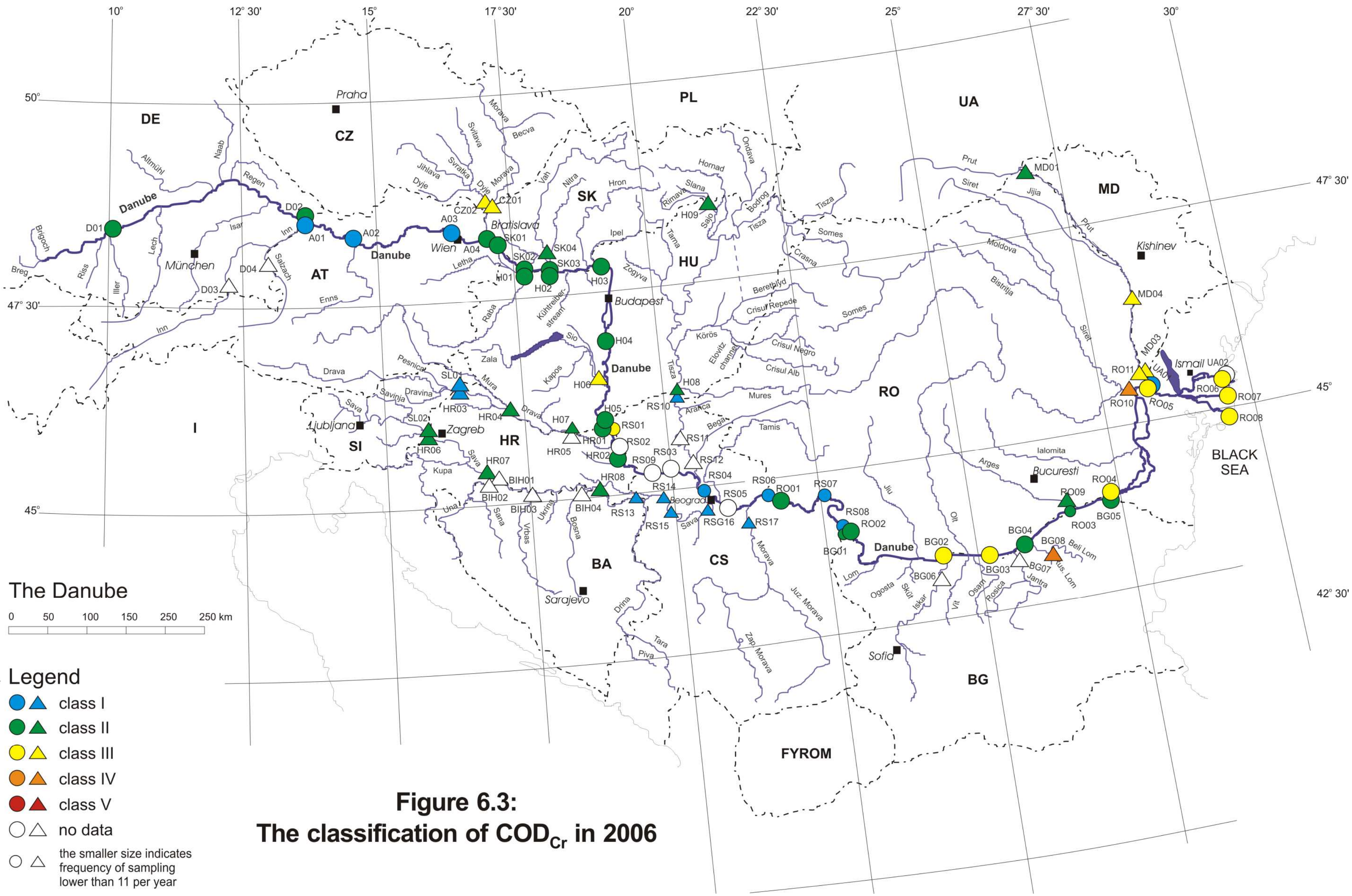


Figure 6.3:
The classification of COD_{Cr} in 2006

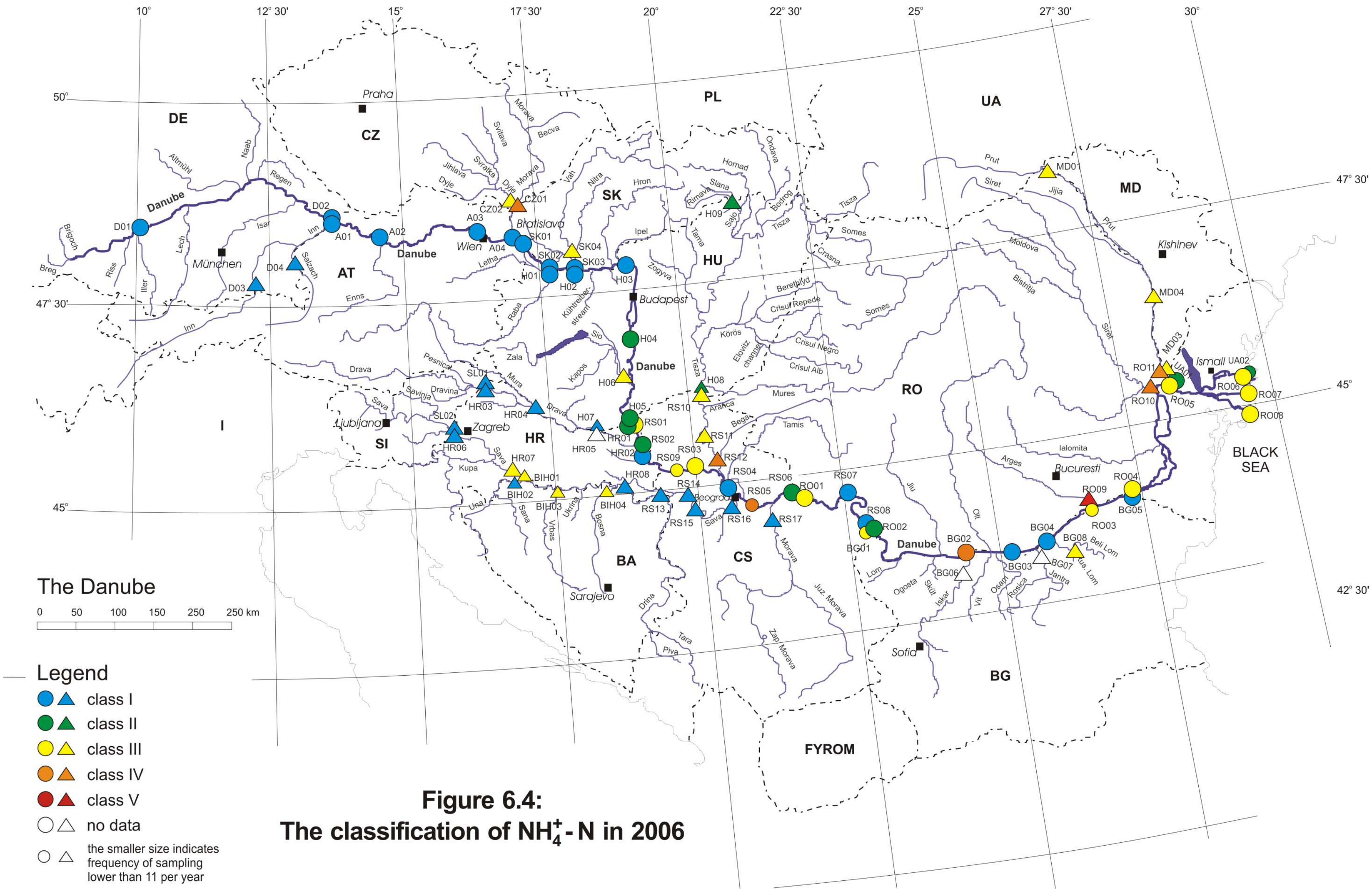
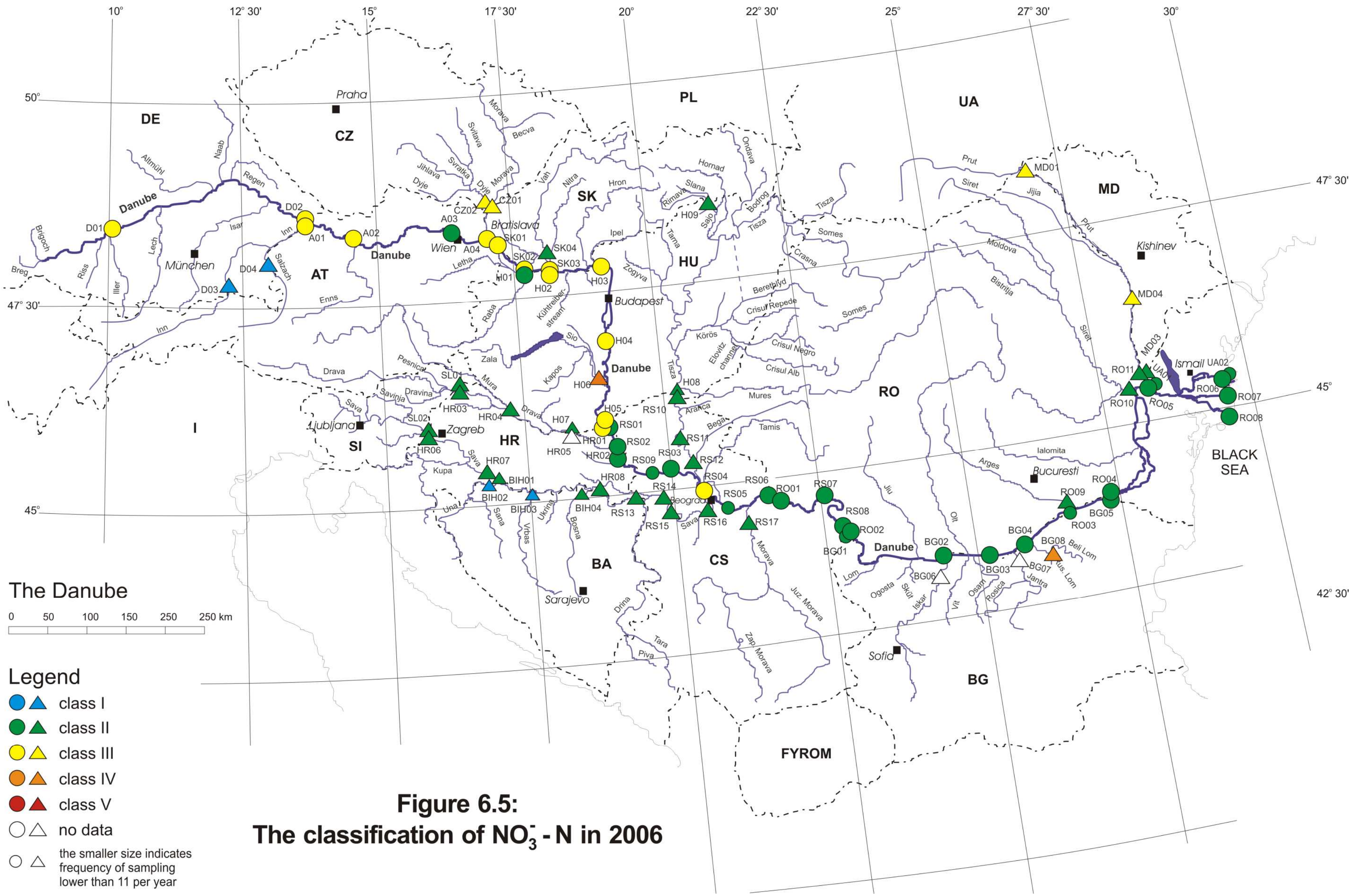


Figure 6.4:
The classification of NH_4^+-N in 2006



Legend

- class I
- class II
- class III
- class IV
- class V
- no data
- the smaller size indicates frequency of sampling lower than 11 per year

Figure 6.5: The classification of NO_3^- - N in 2006

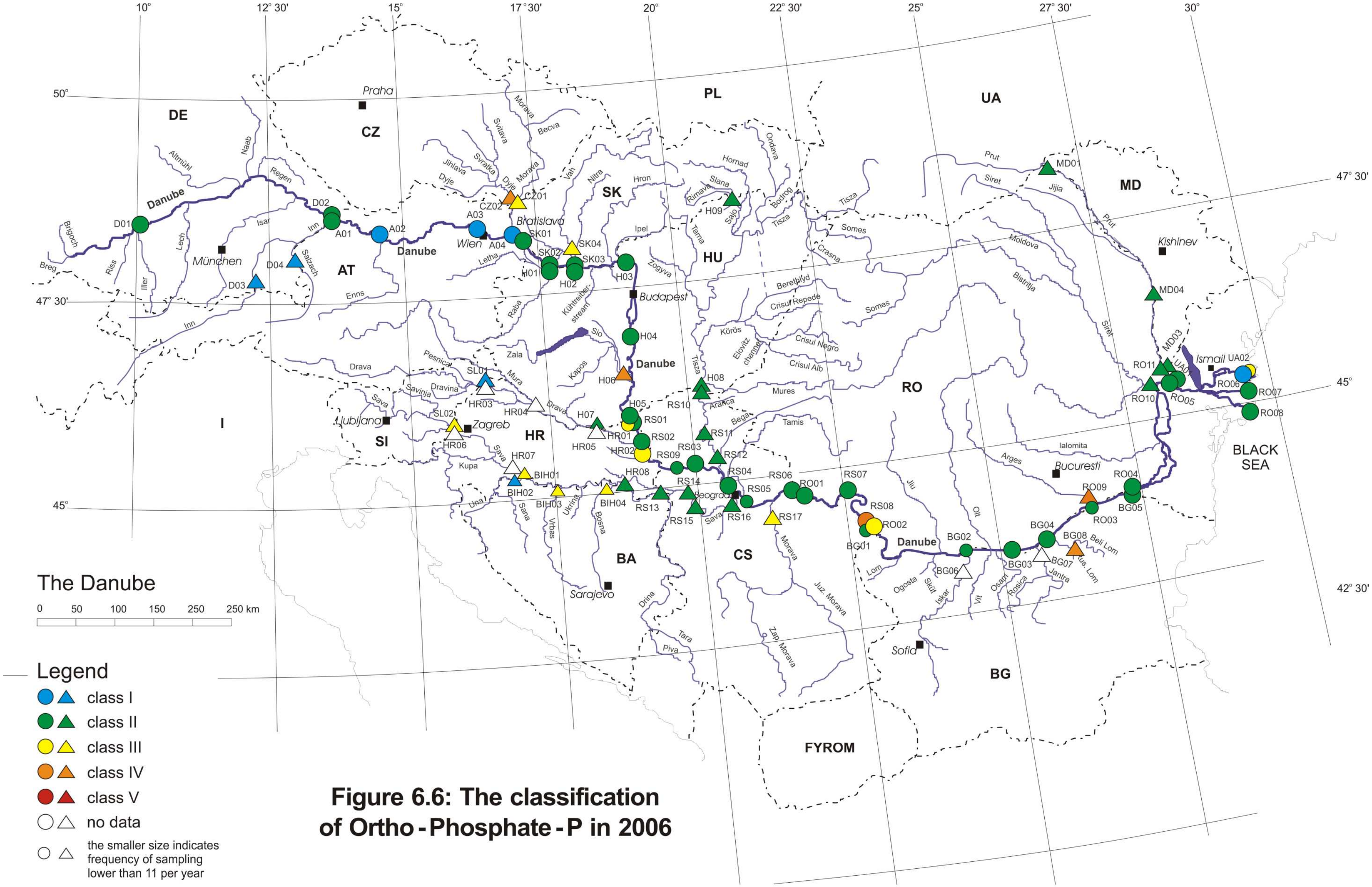


Figure 6.6: The classification of Ortho-Phosphate-P in 2006

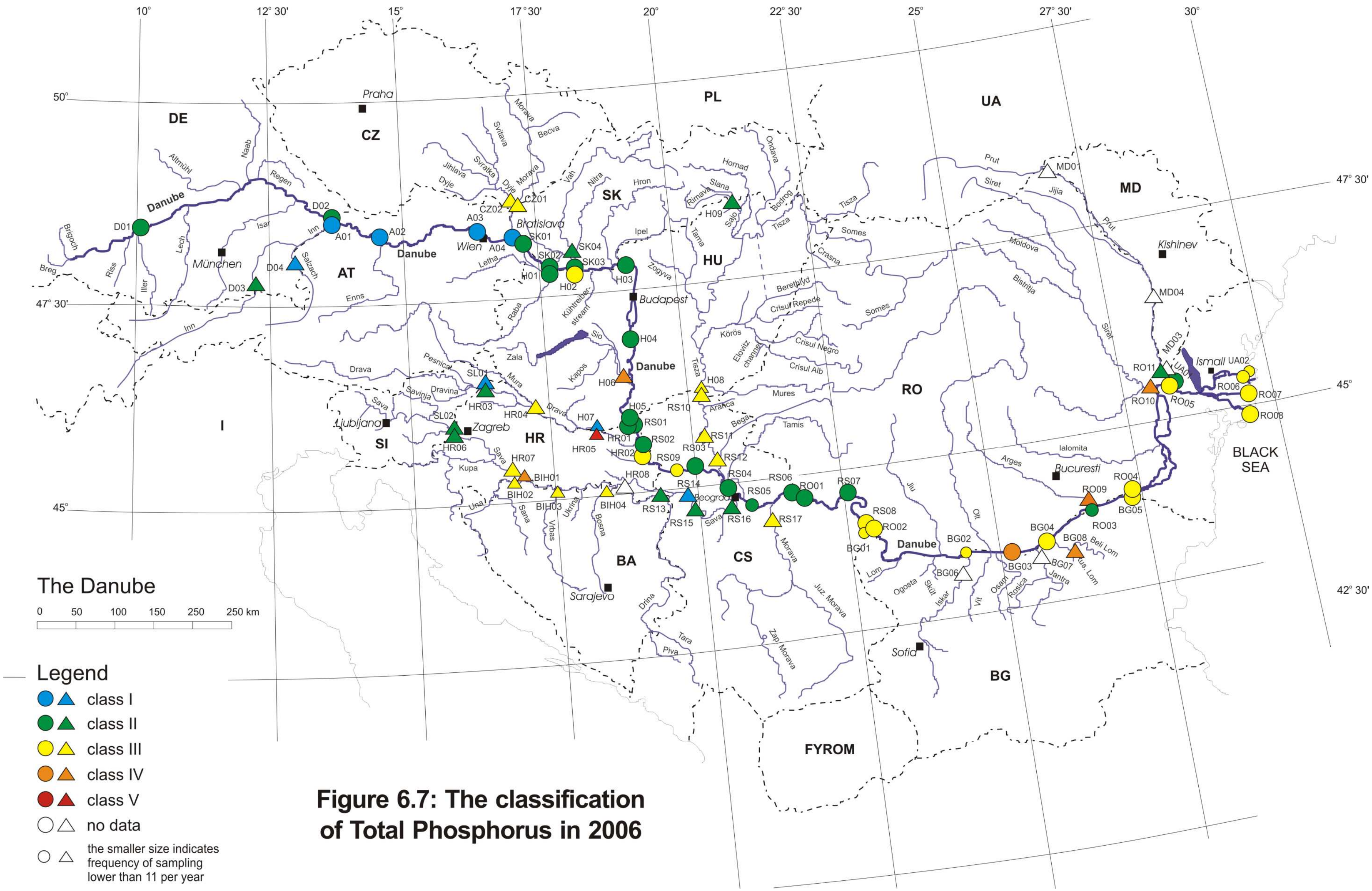


Figure 6.7: The classification of Total Phosphorus in 2006

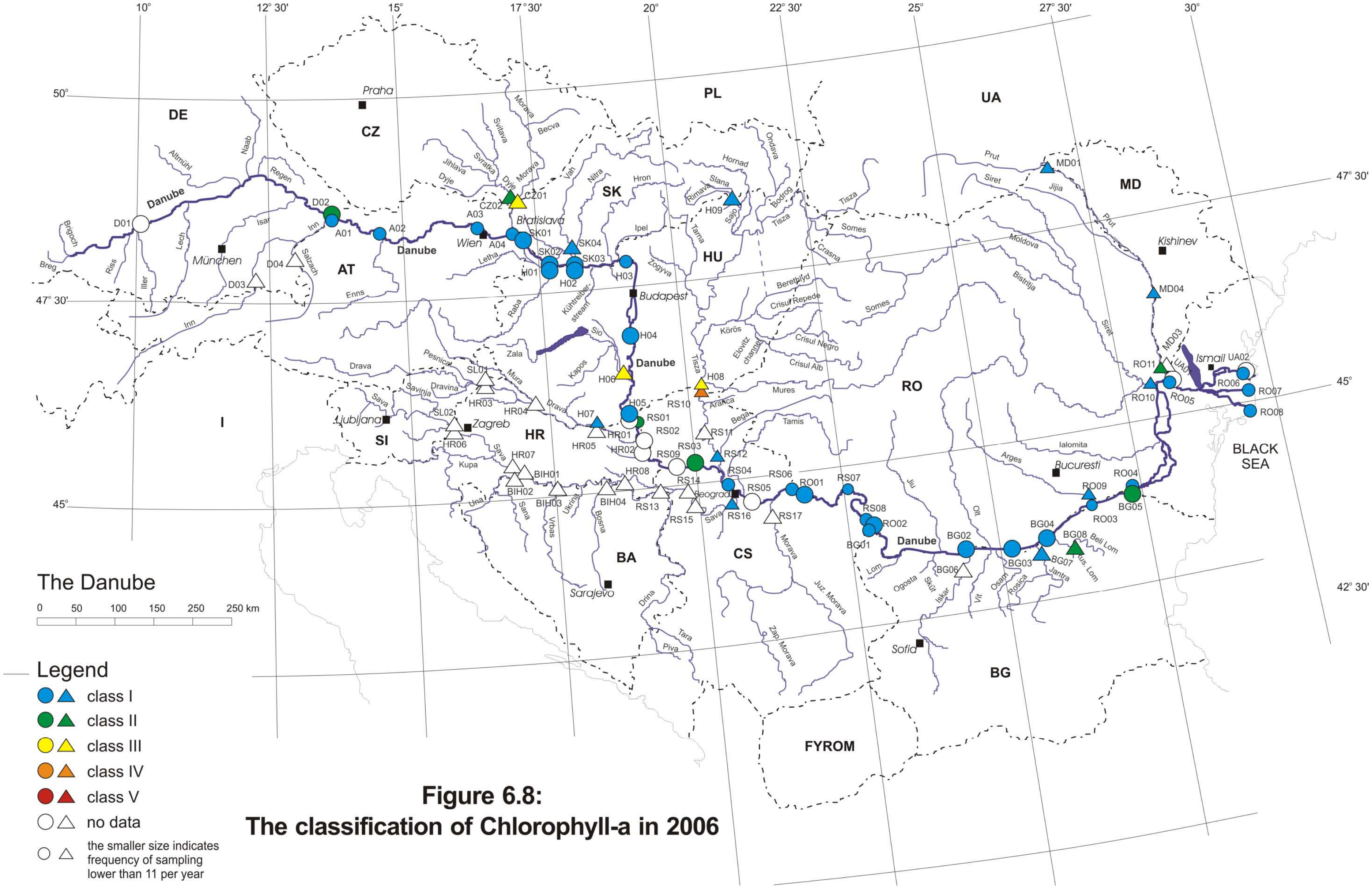


Figure 6.8:
The classification of Chlorophyll-a in 2006

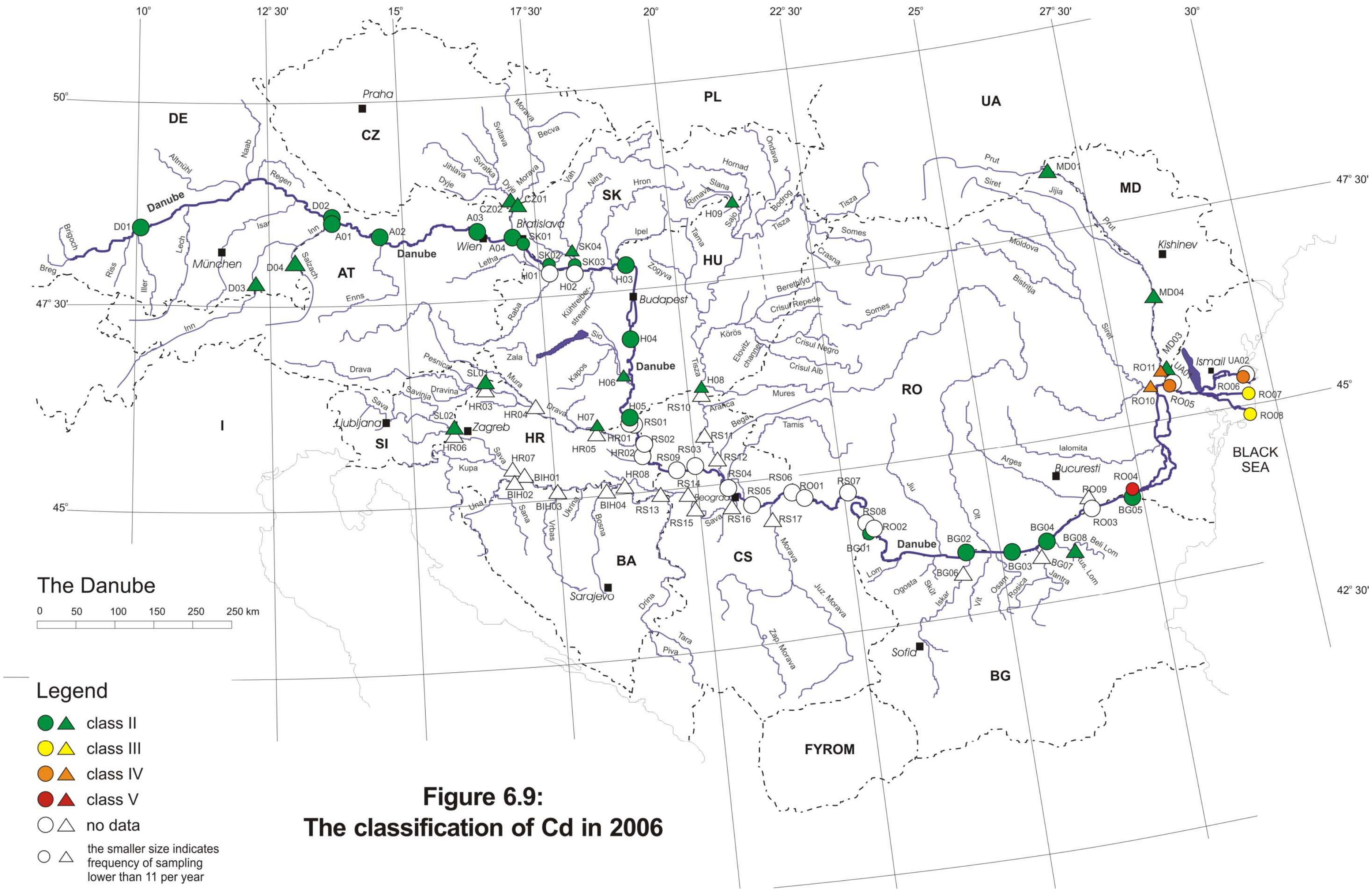


Figure 6.9:
The classification of Cd in 2006

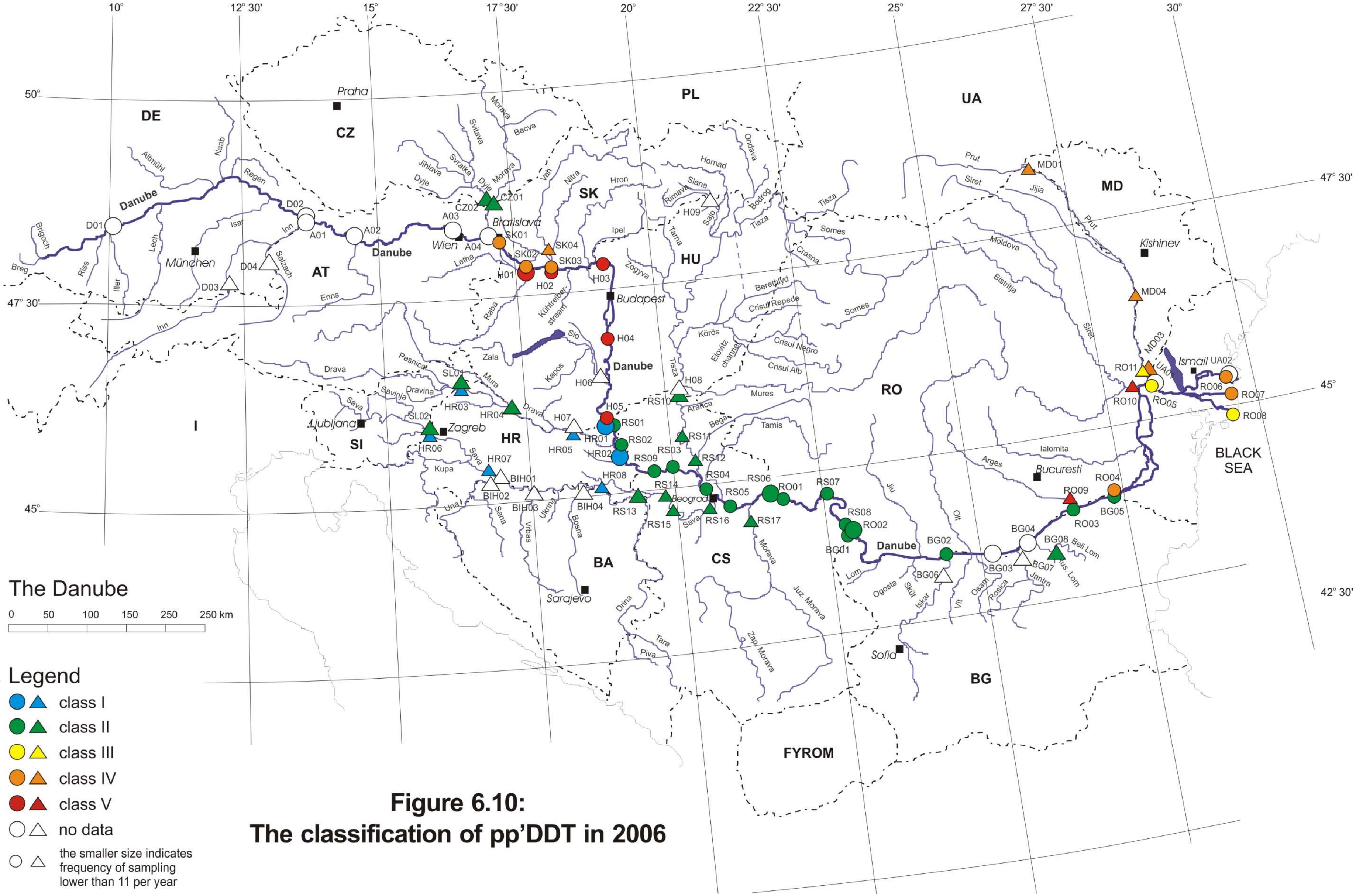


Figure 6.10: The classification of pp'DDT in 2006

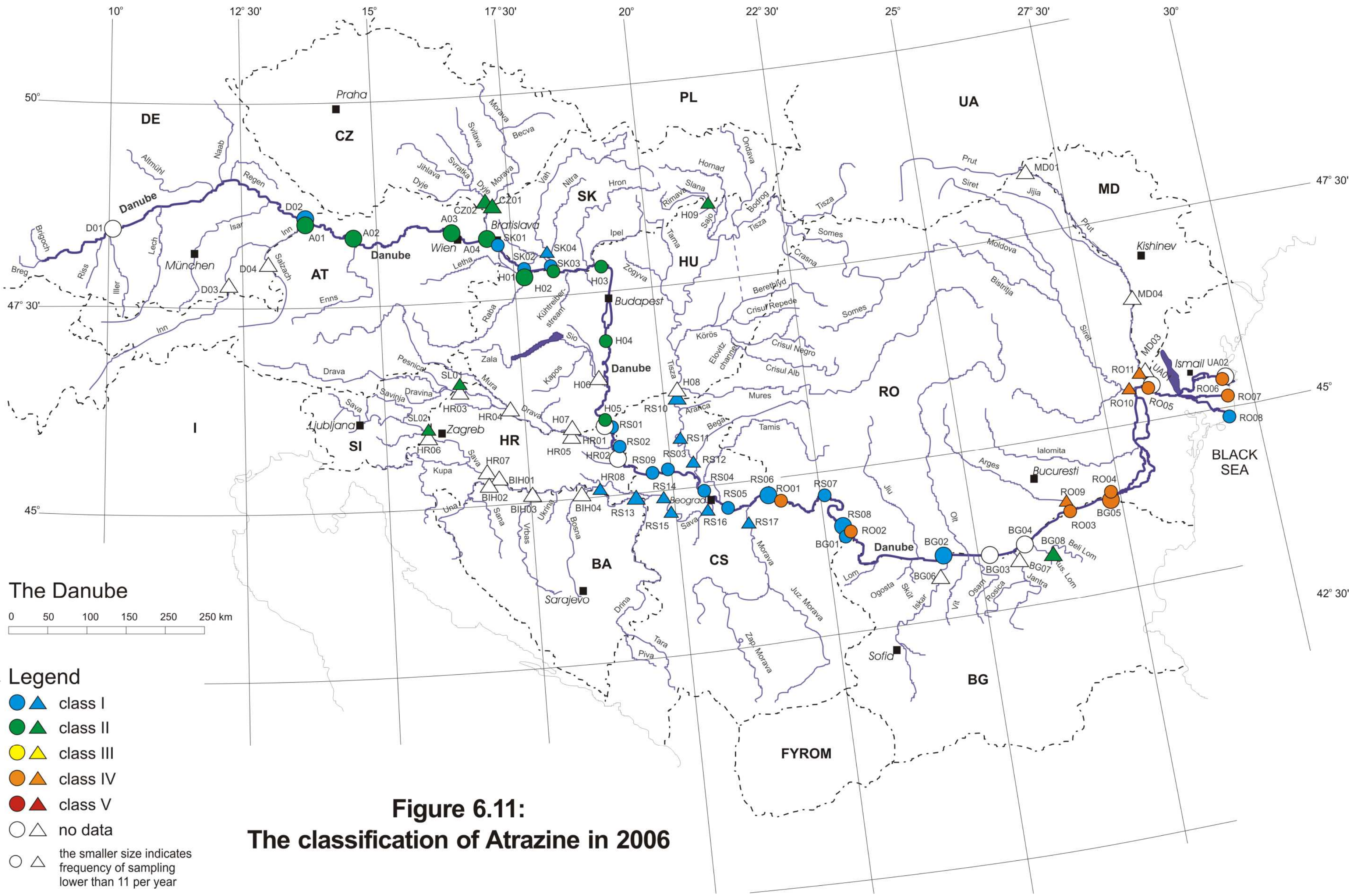


Figure 6.11:
The classification of Atrazine in 2006

7. Profiles and trend assessment of selected determinands

To present the variation of water quality along the Danube river and in the main tributaries the average, maximum and minimum concentrations are shown on Figures 7.1 – 7.11 for dissolved oxygen, BOD_5, COD_{Cr}, NH_4^+-N, NO_3^--N, PO_4^{3-}-P, total phosphorus, chlorophyll-a, cadmium, p,p´DDT and atrazine.
Each of Figures 7.1 – 7.11 consists of two plots. The upper plot shows bars indicating the average, maximum and minimum concentrations in the Danube River at the respective distance from the mouth (km). The minimum values are indicated on the plot by green colour and the maximum values by the red one. Monitoring locations close to each other or those, which are monitored by two countries (transboundary stations), had to be shifted slightly along the X-axis.
Using the same method the lower plot shows the concentration ranges at the most downstream stations on the primary tributaries. In these graphs the bars are plotted at the river-km of the confluence of the tributary with the Danube.

With purpose to illustrate the changes of water quality in TNMN monitoring stations during TNMN operation, Figures 7.12 – 7.27 show 90 percentiles (10 percentile in case of dissolved oxygen) of yearly data sets for selected determinands. The 90 percentile as a statistical characteristic used for this assessment is presented only for the monitoring stations where frequency of measurements was higher than 5-times in the respective year.

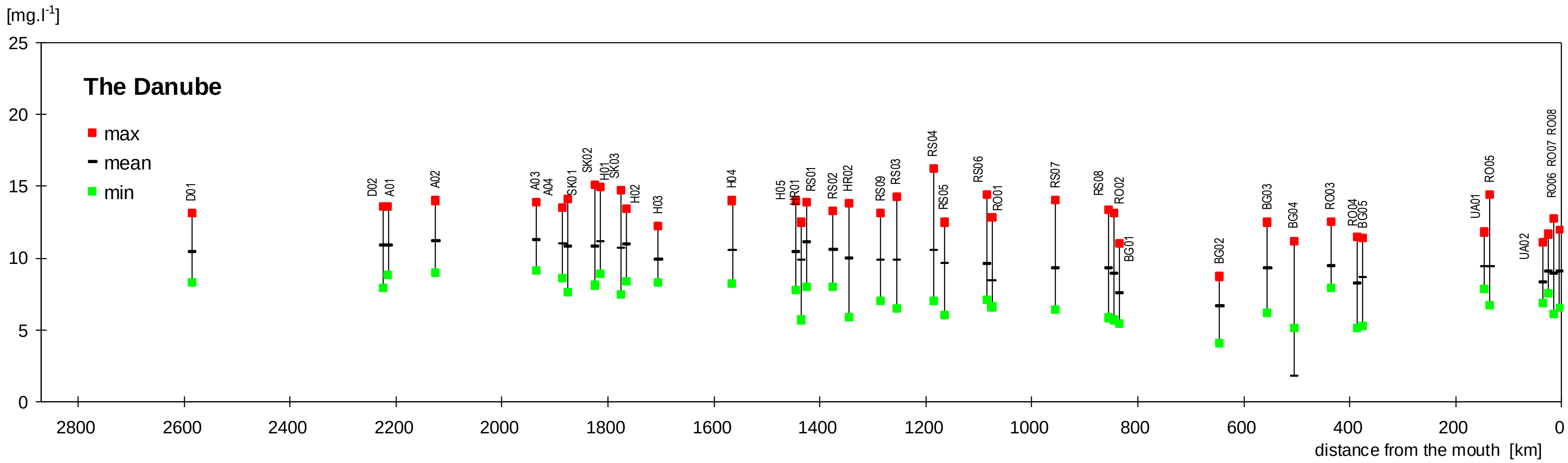
Regarding the spatial pattern of water quality along the Danube River in 2006, the highest content of biodegradable organic matter was observed in the middle and lower part of the river, also ammonium-N, ortho-phosphate P, total P and cadmium reached the highest values in the lower Danube part. Concentration of nitrate-N was higher in the upper part of the river.
The most polluted tributaries from the point of view of biodegradable organic matter in 2006 were Russenski Lom, Sio, Morava, Drava, Tizsa/Sajo. In case of nutrients there were more tributaries considered rather polluted in 2006 – Prut, Arges, Russenski Lom, Sio.

Positive changes in water quality can be seen in several TNMN locations. Taking into account the whole period of TNMN operation, decrease of biodegradable organic pollution is visible in upper parts and in some parts of lower Danube Bulgarian and Rumanian section (Bazias, Pristol, Reni and mouth). Tributaries Dyje, Inn, Sava, Arges, Siret, Sio, Vah show decreasing tendency. Tribunaries Morava and Drava (HR04, H07) showed increased values in year 2006, tributary Sajo increased trend.
COD had decreasing tendency or stable in all upstream Danube monitoring locations. On the contrary, the COD increased in us. Iskar and Bezdan (RS1, BG02) in year 2006.
COD in tributaries has decreasing tendency in Morava, Dyje, Vah, Sio, Drava, Tisza, Tizsa/Sajo, Sava, Arges, Siret.
As for the nutrients, ammonium-N decreases in locations of the upper part of the Danube River down to (H04). In the middle part of Danube was some increasing concentration of ammonium-N and also in the lower part of the Danube concerns (BG01, BG02). Further downstream decrease and situation without big changes were observed. Significant decrease is apparent also in Danube-Silistra/Chiciu (BG05). This observation is not supported by Romanian data at the same monitoring location.

In tributaries in whole period of operation ammonium decreases in the upper section down to river Vah (Inn, Salzach, Morava, Dyje) and further in Sava, Arges and Siret.
Nitrate-N content is more stable in locations during last years than the content of other determinands representing nutrient content. It decreases in several locations of upper and middle part of the Danube River. The concentration Nitrate-N in lower part decreases at Danube (Silistra, Reni, Vilkova and mouth).
Nitrate-N has decreasing tendency in tributaries Dyje, Vah, Tisza/Sajo, Sio, Sava, Arges, Siret. However a little bit increase Nitrate-N in upper Prut.

Decreasing tendency of ortho-phosphate-P is observed in the upper part, but in some monitoring point in year 2006 was a little bit increased of concentration. Decreasing tendency was observed also in lower part of Danube (in Bulgarian and Rumanian part)
An improvement can be seen also in tributaries like Morava, Dyje, Vah, Sio, Siret, also Russenski Lom. In Arges the concentration a little bit increased in year 2006.
In generally, the P-total concentration has the decreasing tendency during the last years in the upper part of the Danube River. On the other hand the P-total concentration increases in year 2006 in some locations concentration of upper and also lower part.
P-total had decreasing trends in last period in tributaries Inn, Salzach, Dyje, Morava, Vah, Drava, Tisza, Tisza/Sajo, Sio, Siret, Russensko Lom and Arges with a little bit increased concentration in year 2006.
Situation for cadmium concentration has a decreasing or stable trend in the Danube river, as well as in its tributaries. The results for cadmium are improved during the last years.

Figure 7.1: The minimum, mean and maximum of Dissolved Oxygen in 2006



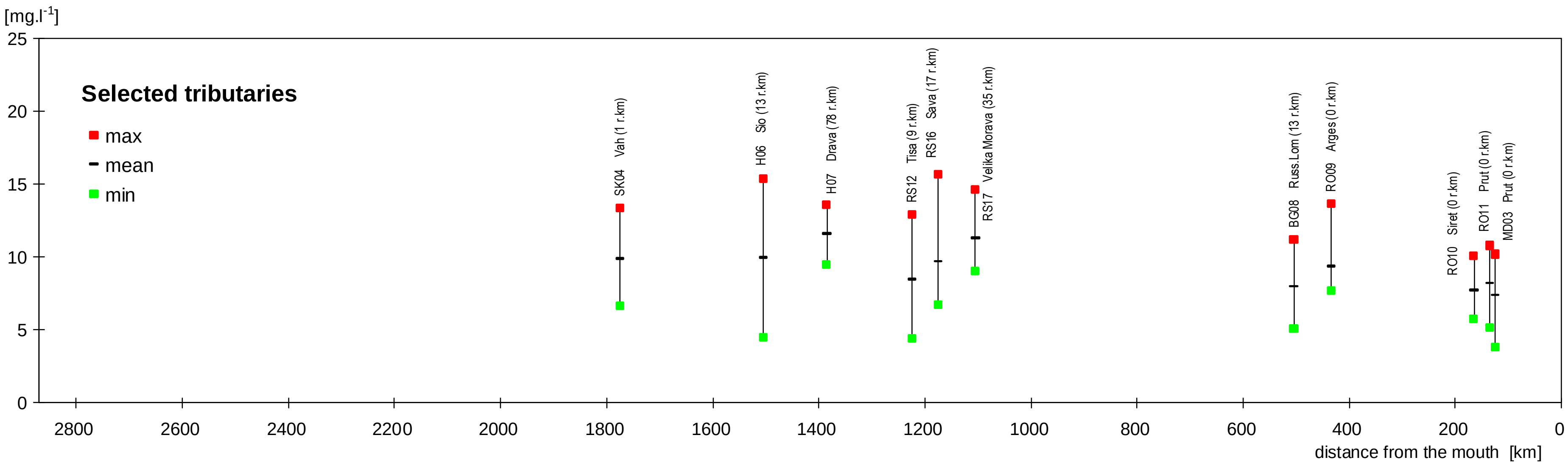


Figure 7.2: The minimum, mean and maximum of BOD_5 in 2006

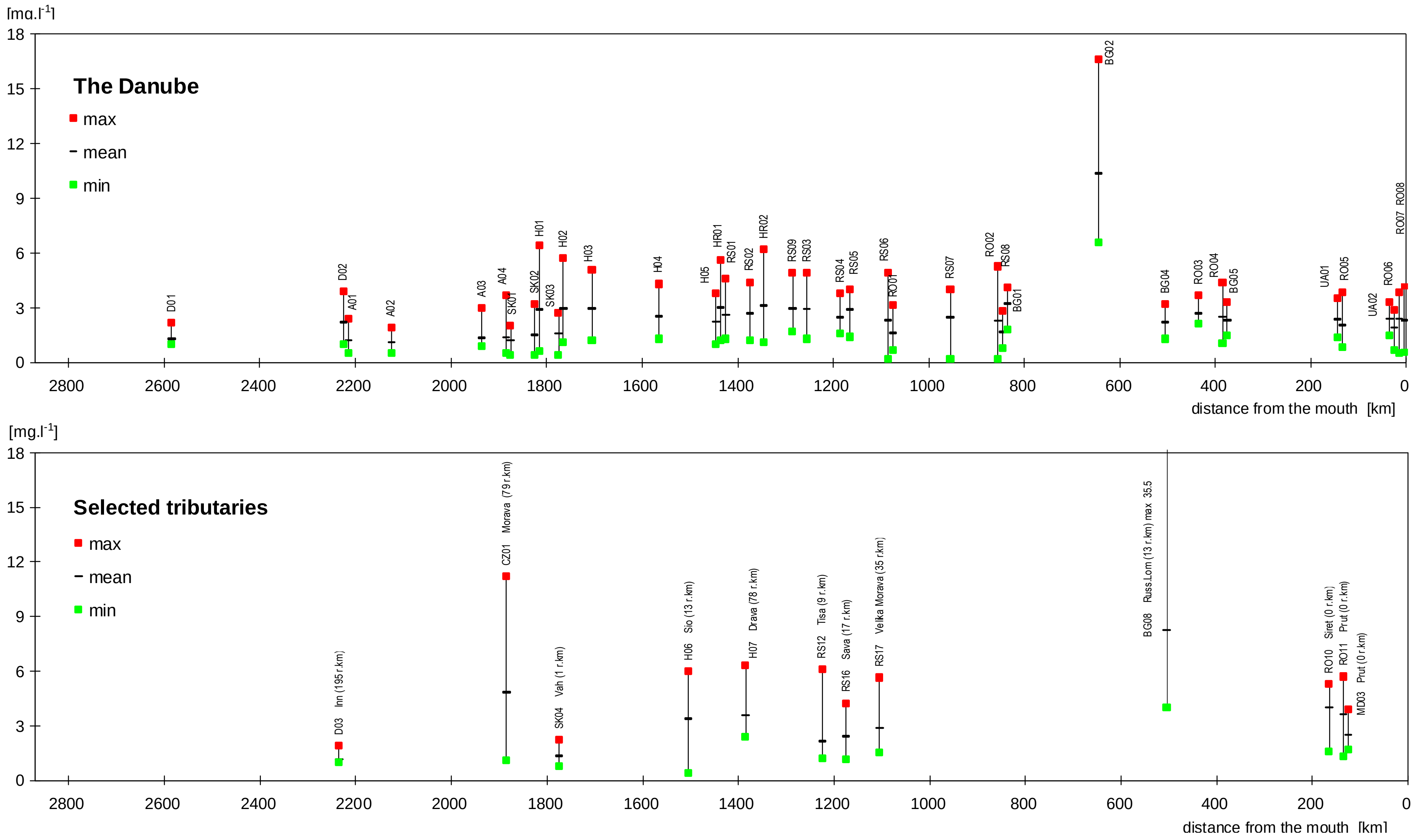
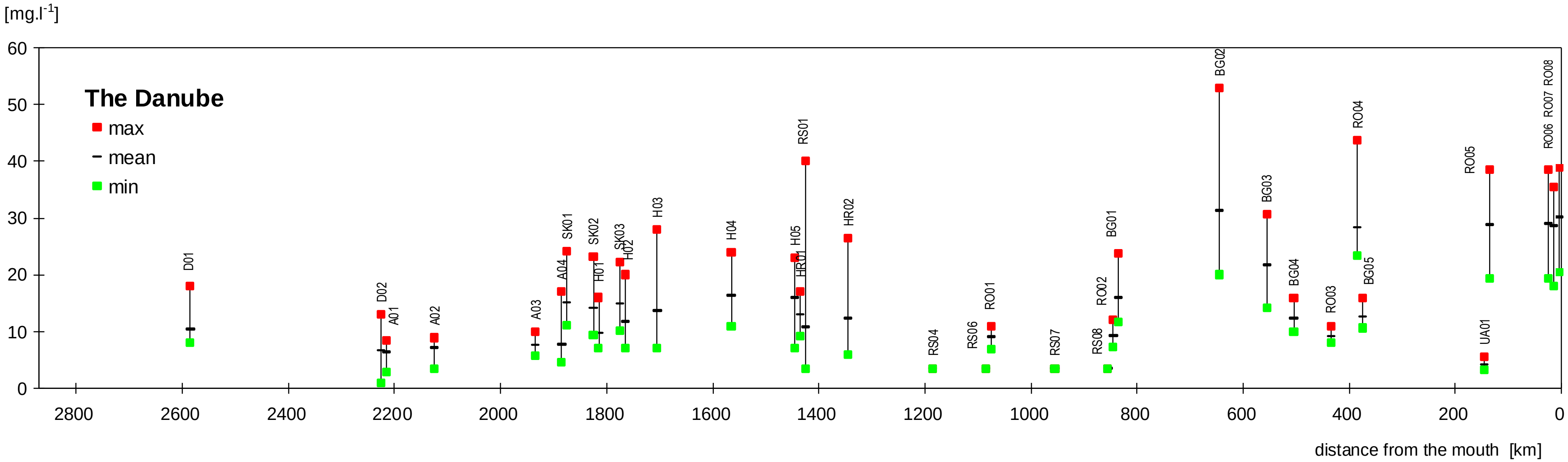


Figure 7.3: The minimum, mean and maximum of COD_{Cr} in 2006



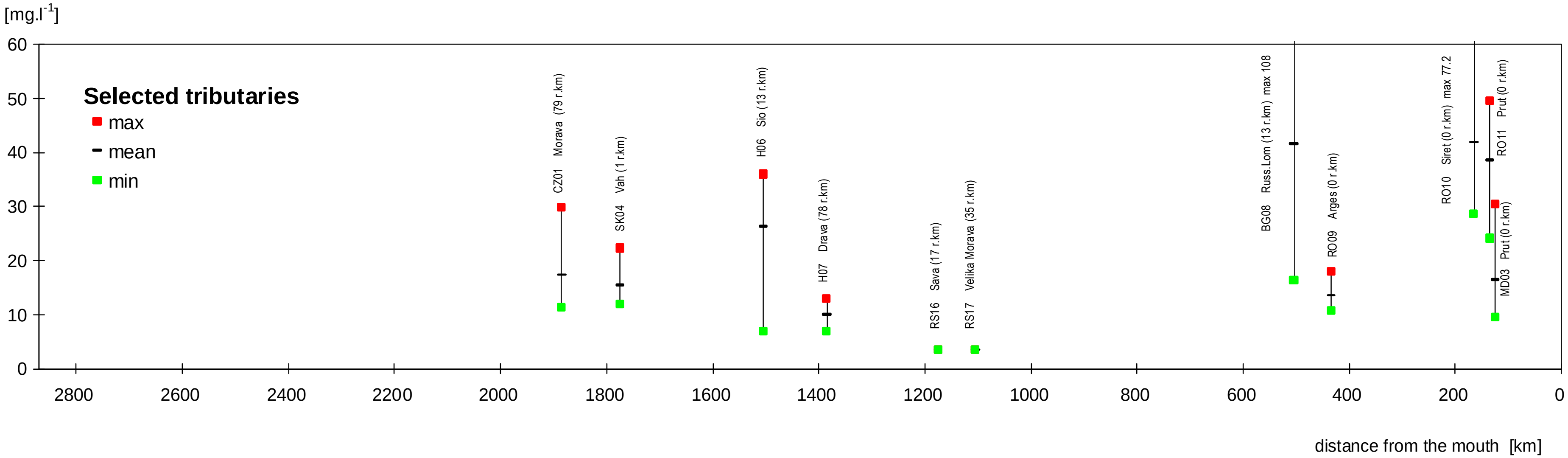


Figure 7.4: The minimum, mean and maximum of NH_4-N in 2006

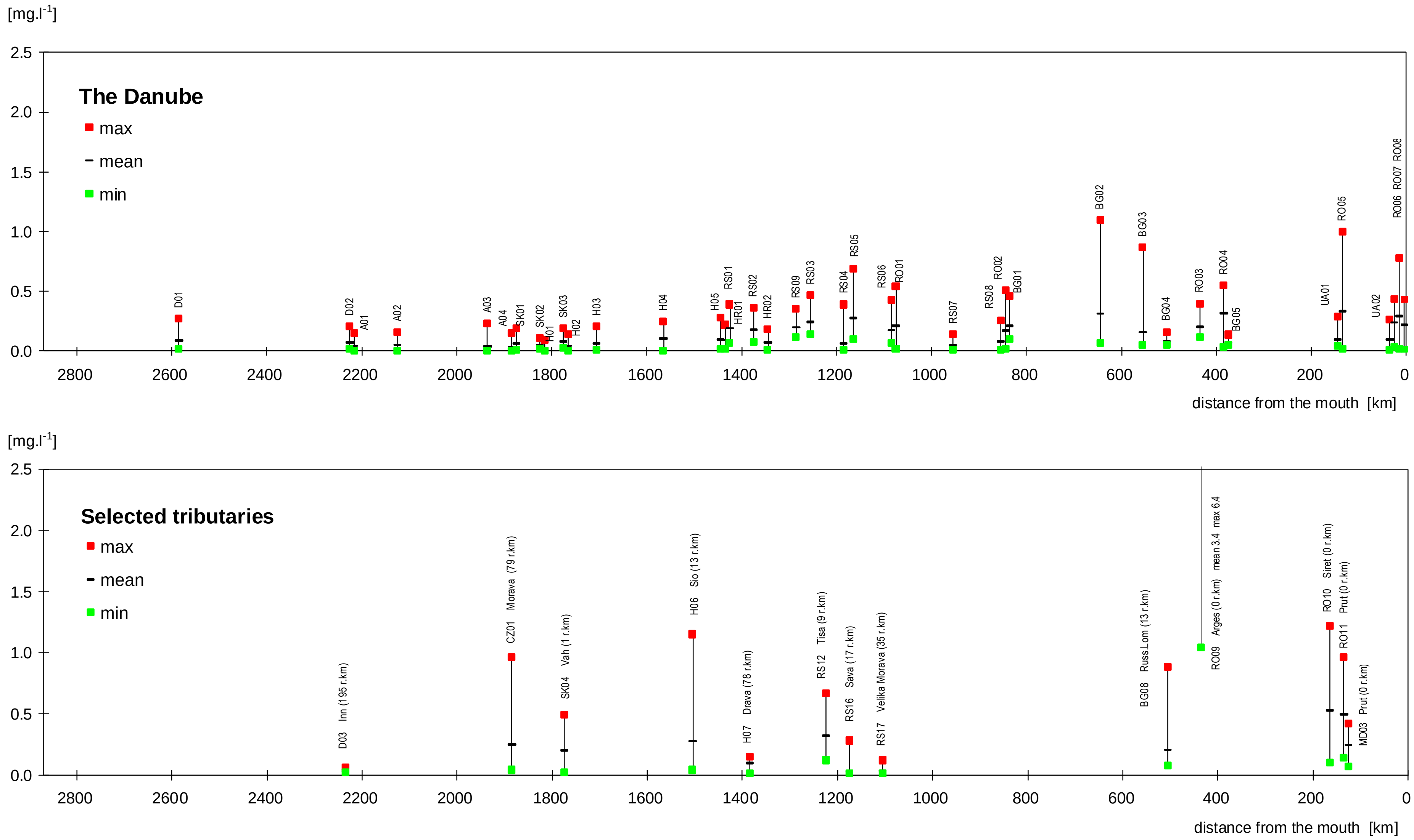
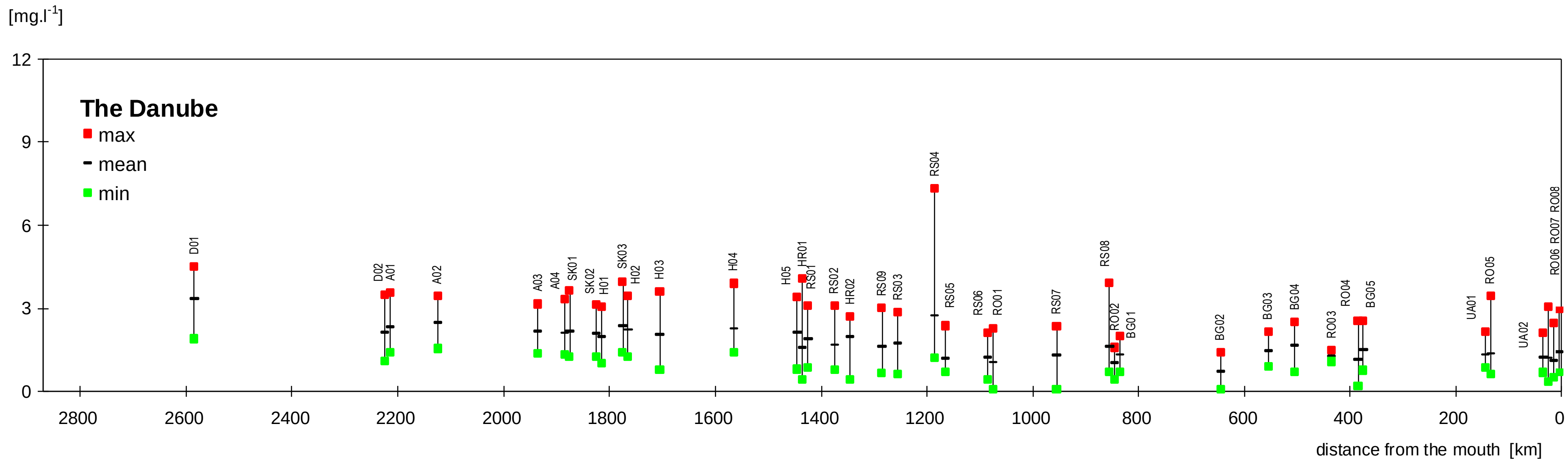


Figure 7.5: The minimum, mean and maximum of NO_3-N in 2006



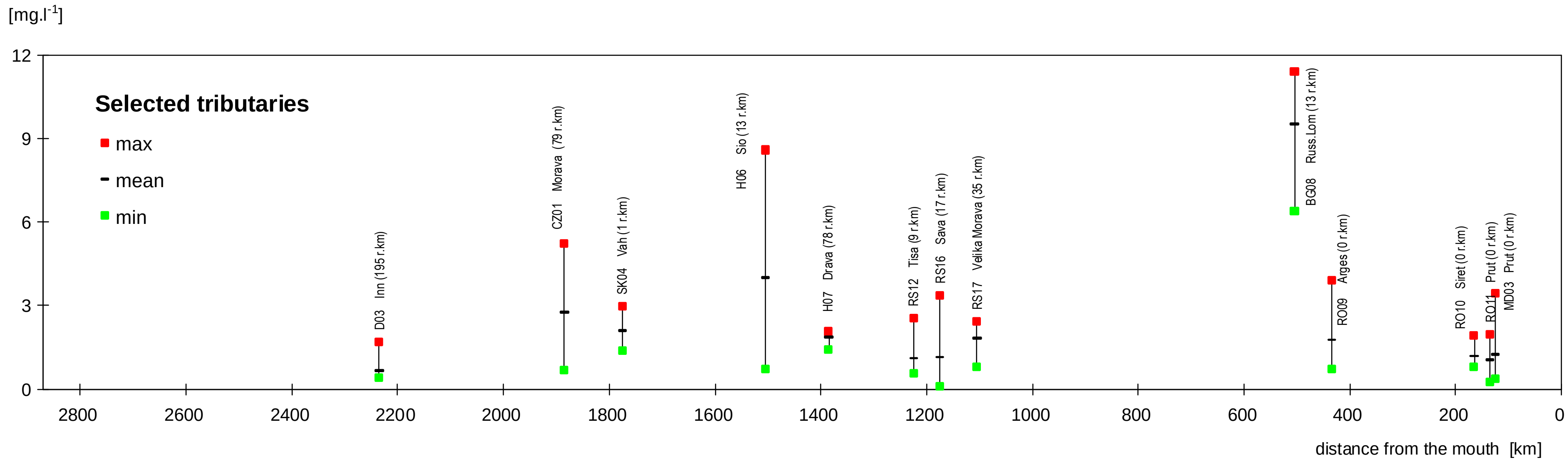


Figure 7.6: The minimum, mean and maximum of Ortho-Phosphate-P in 2006

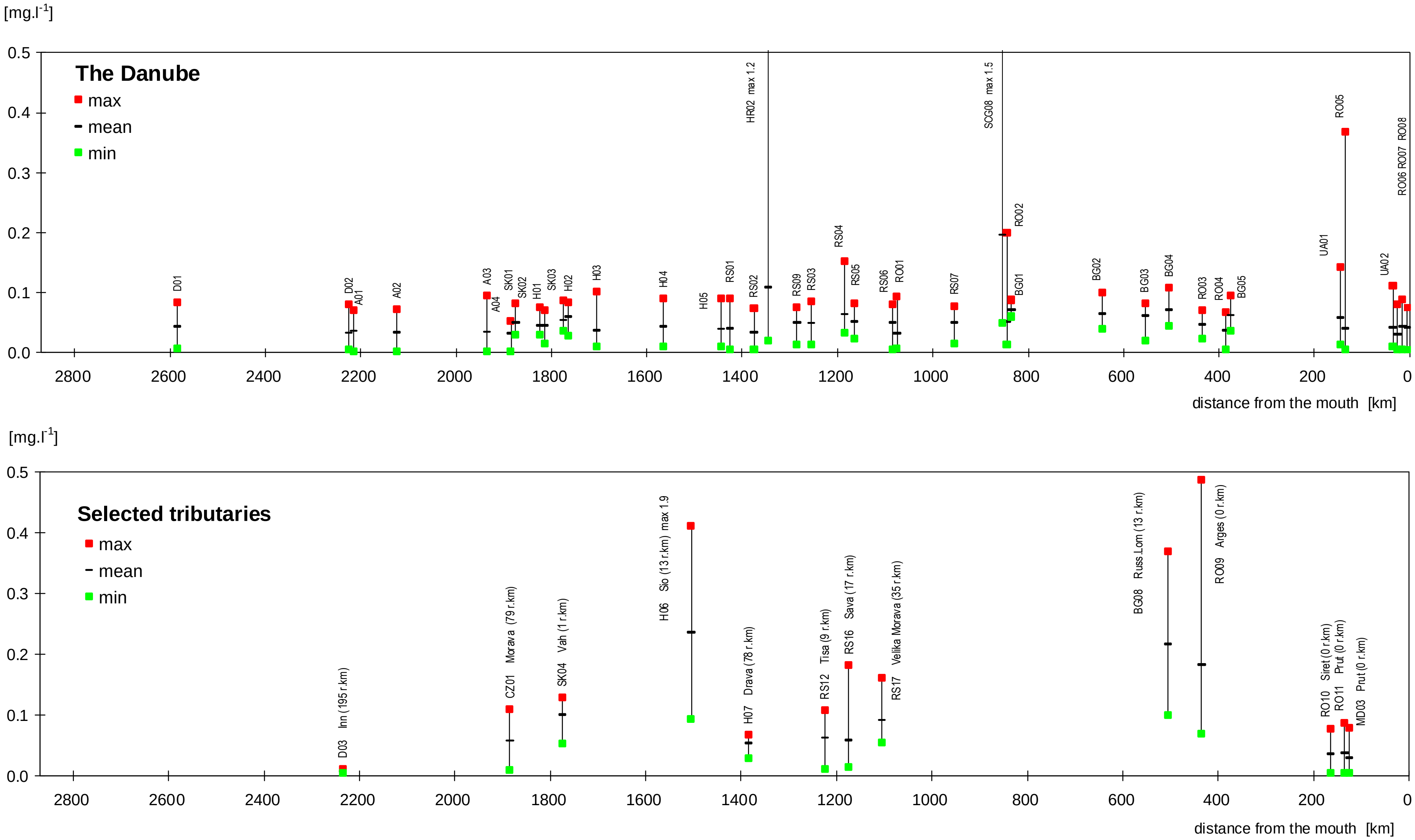
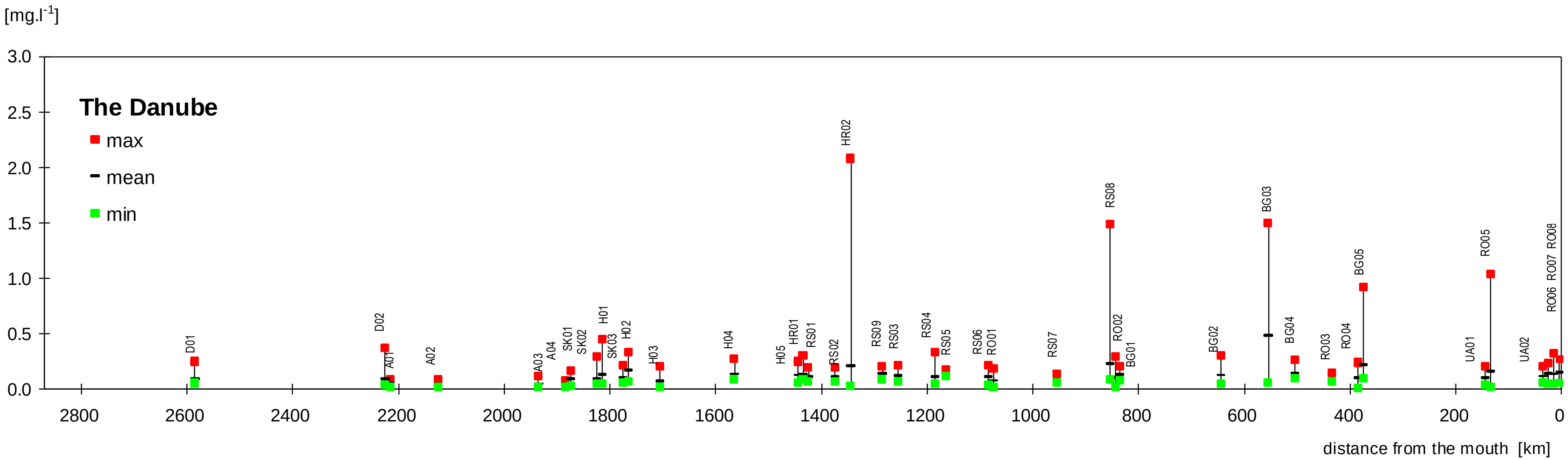


Figure 7.7: The minimum, mean and maximum of Total Phosphorus in 2006



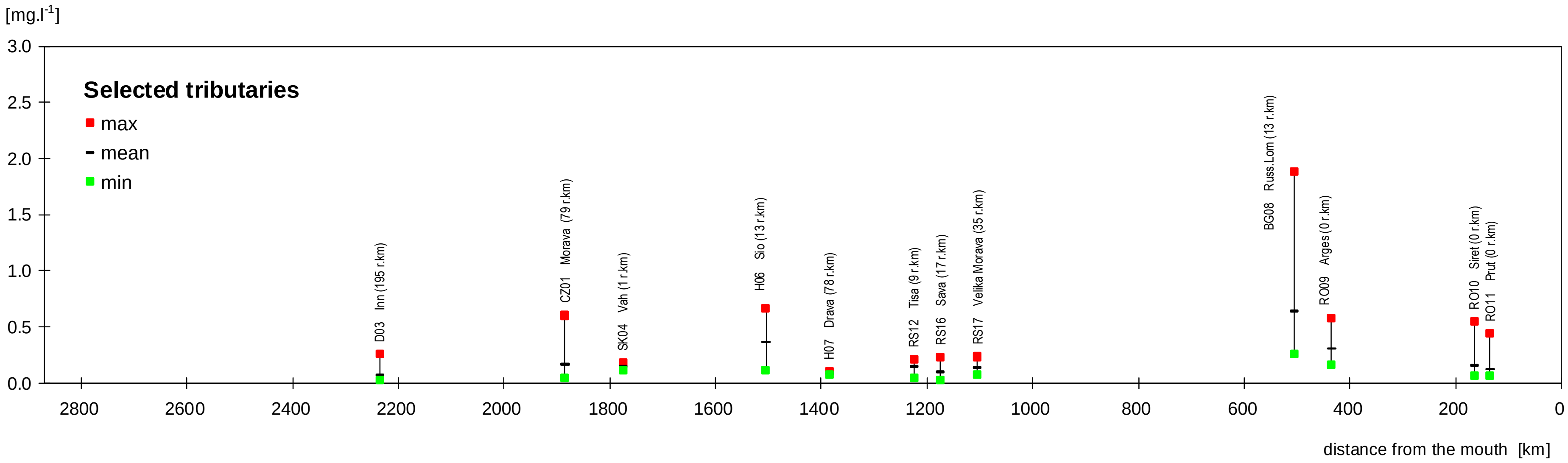
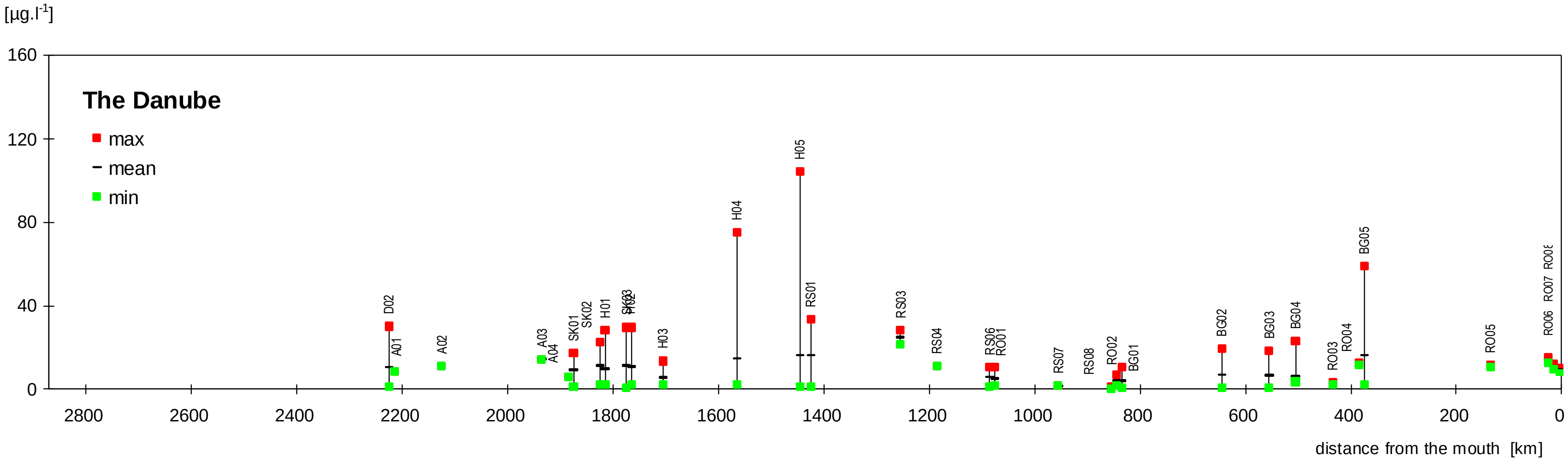


Figure 7.8: The minimum, mean and maximum of Chlorophyll-a in 2006



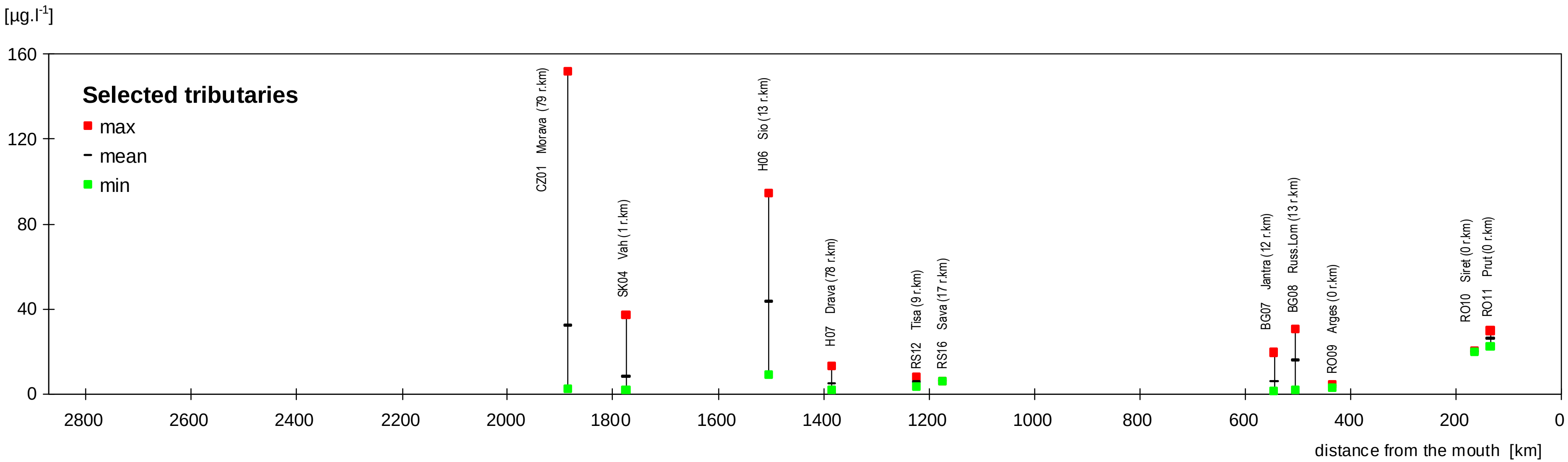
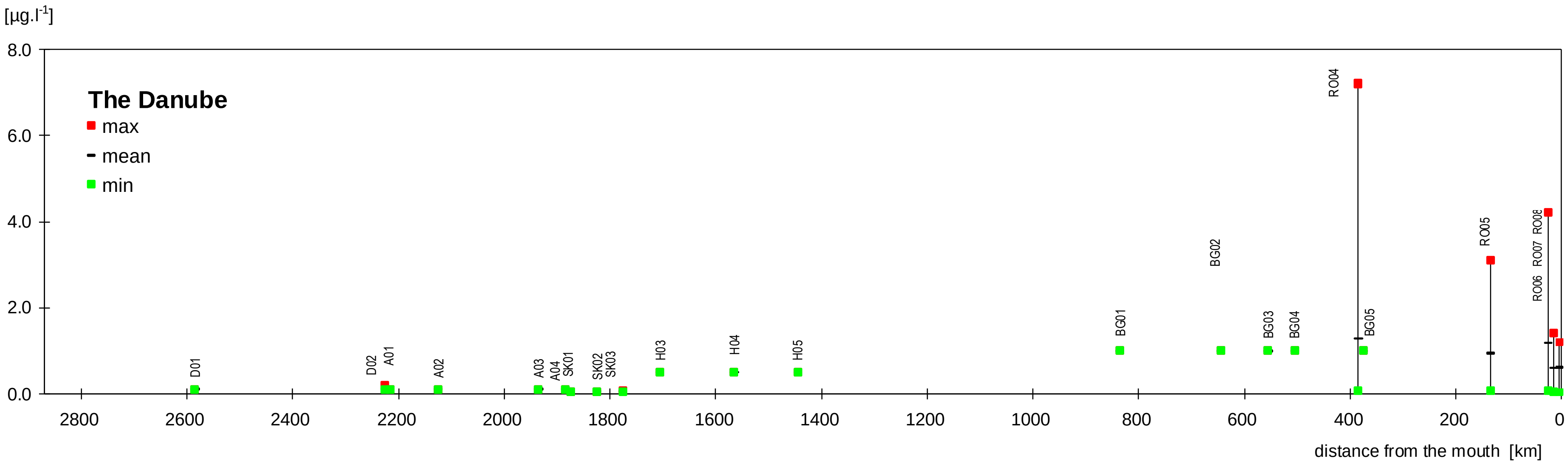


Figure 7.9: The minimum, mean and maximum of Cd in 2006



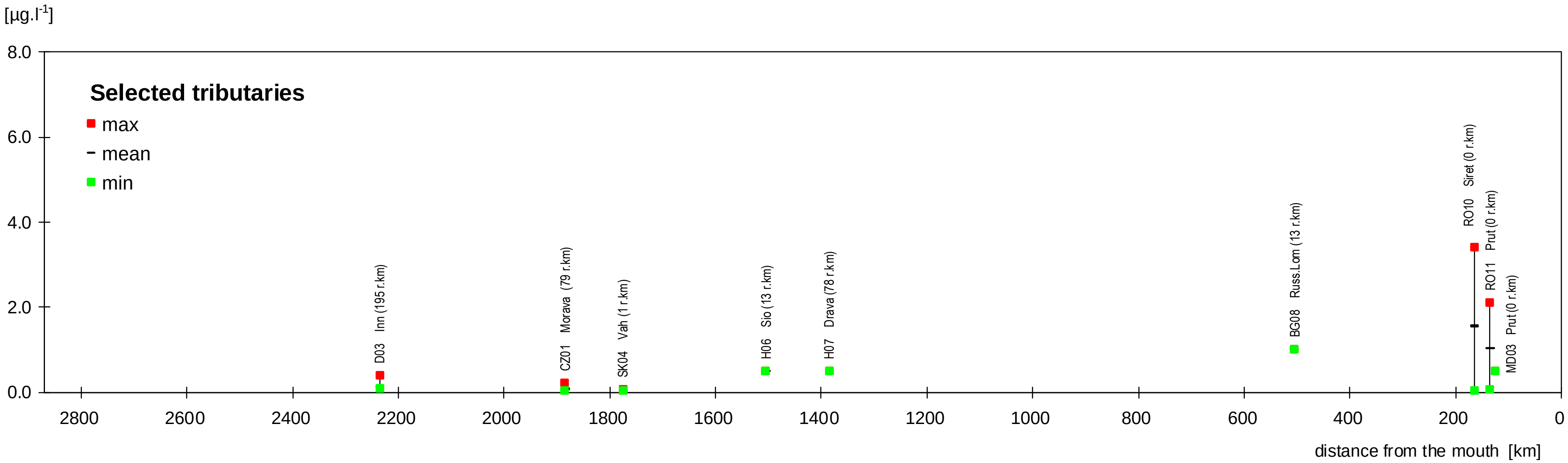
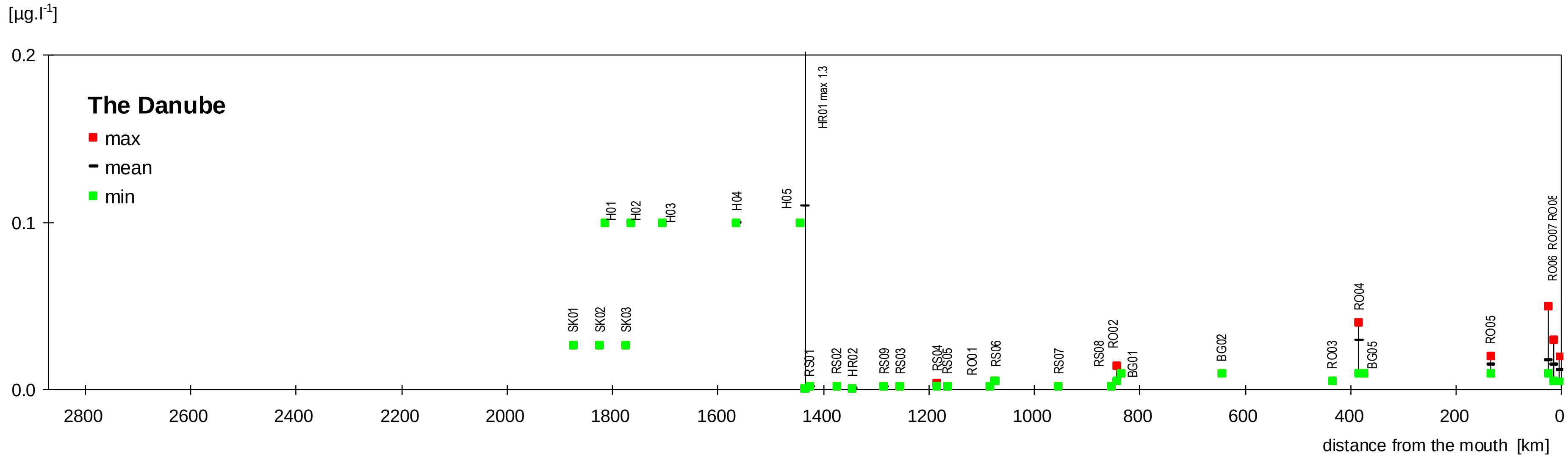


Figure 7.10: The minimum, mean and maximum of pp'DDT in 2006



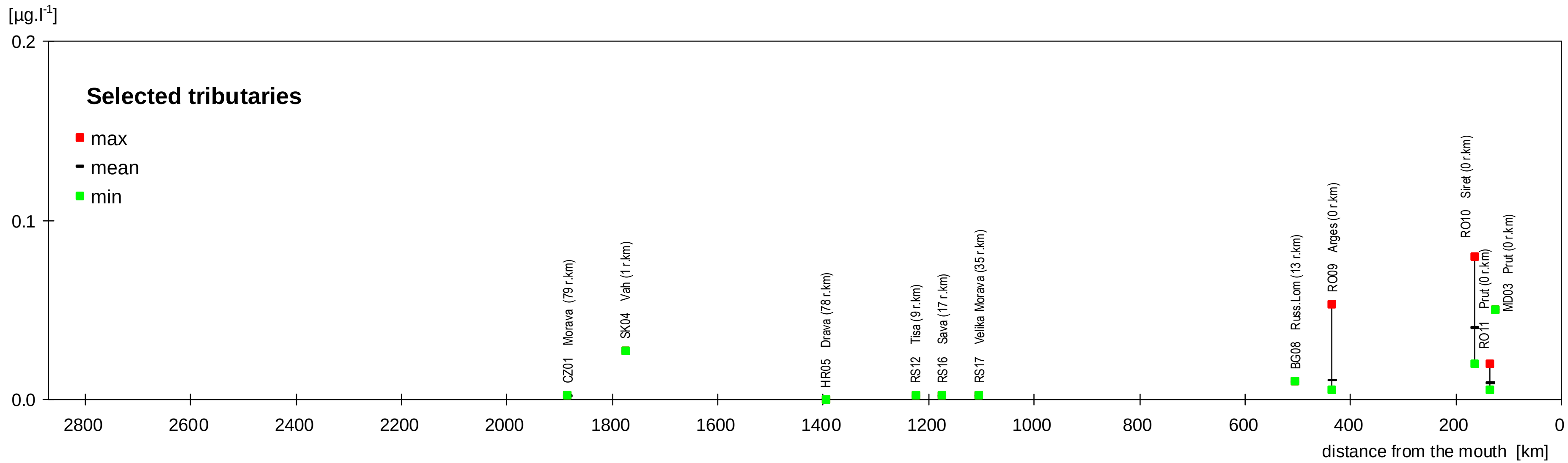
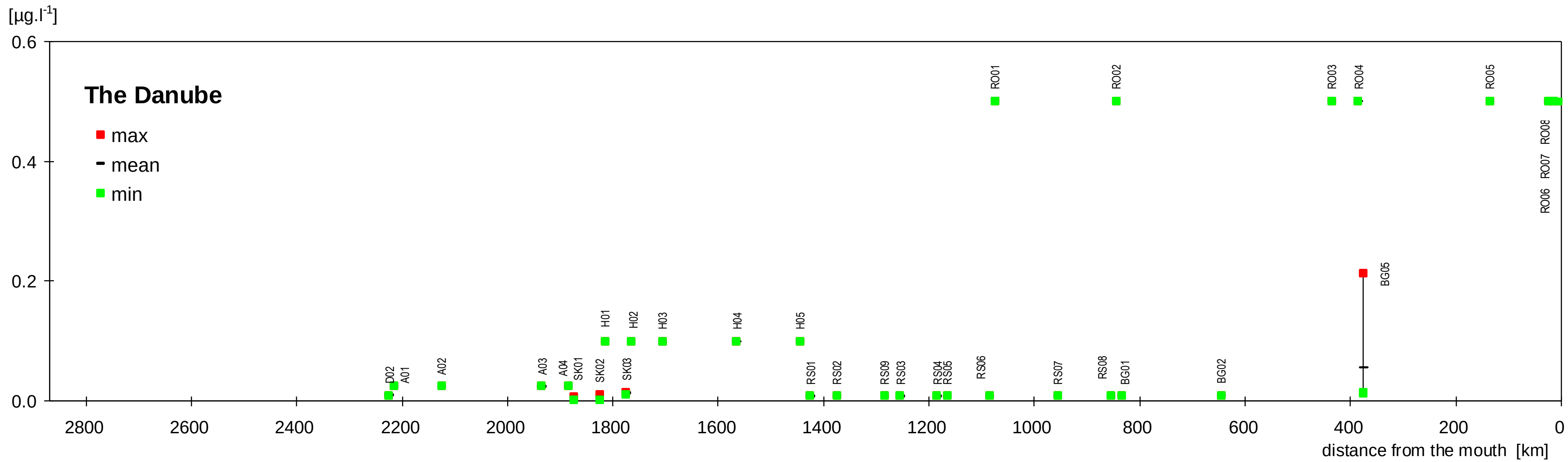


Figure 7.11: The minimum, mean and maximum of Atrazine in 2006



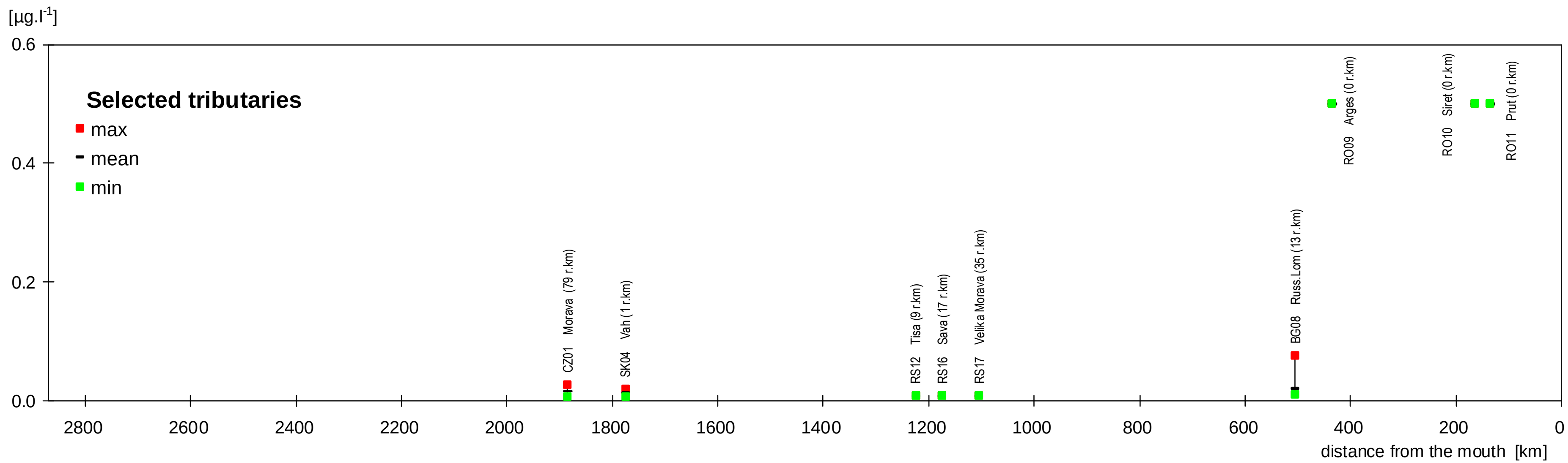


Figure 7.12: Temporal changes of dissolved oxygen in the Danube River.

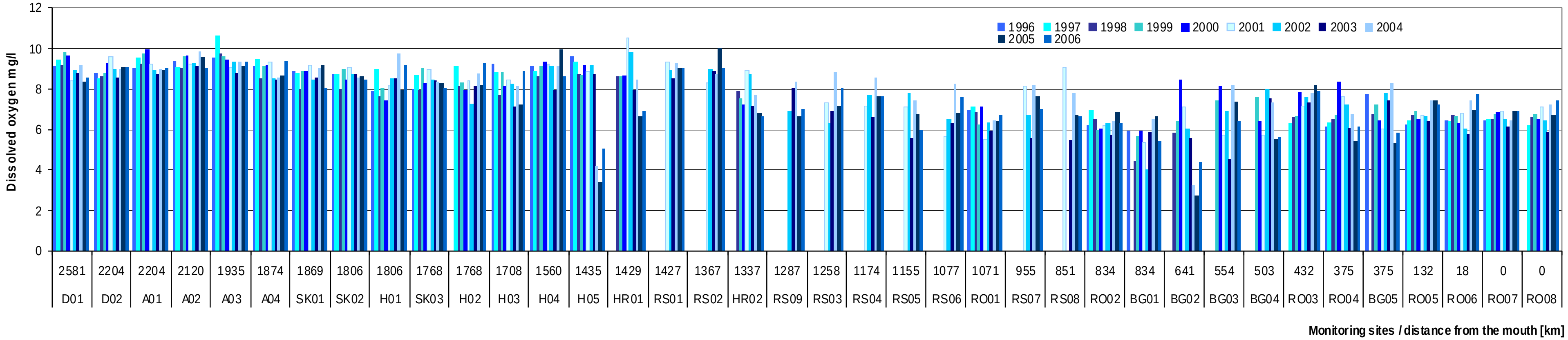


Figure 7.13: Temporal changes of dissolved oxygen in tributaries.

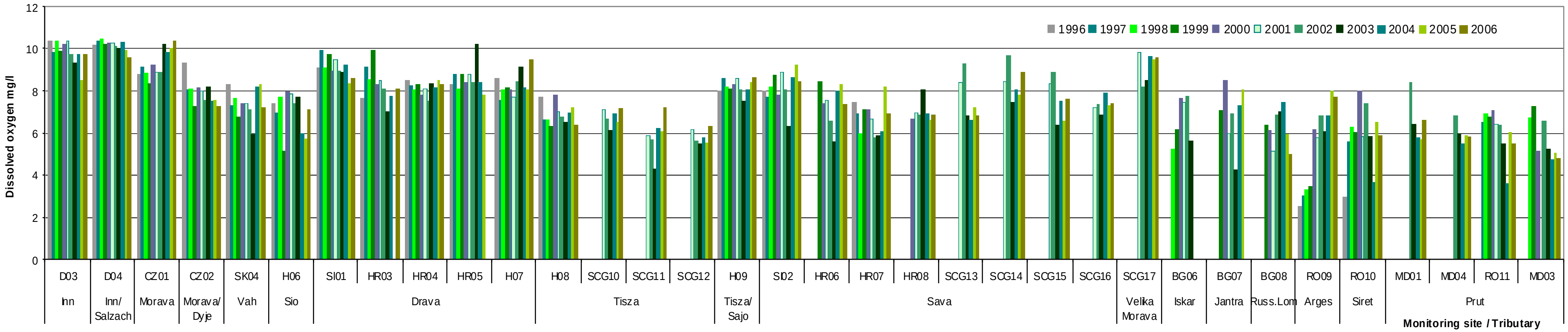


Figure 7.14: Temporal changes of BOD_5 in the Danube River.

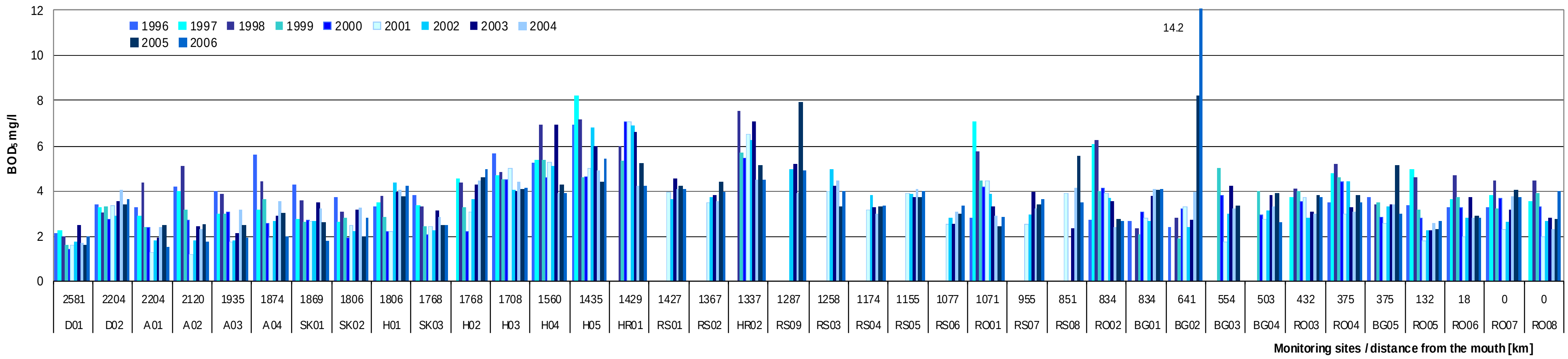


Figure 7.15: Temporal changes of BOD_5 in tributaries.

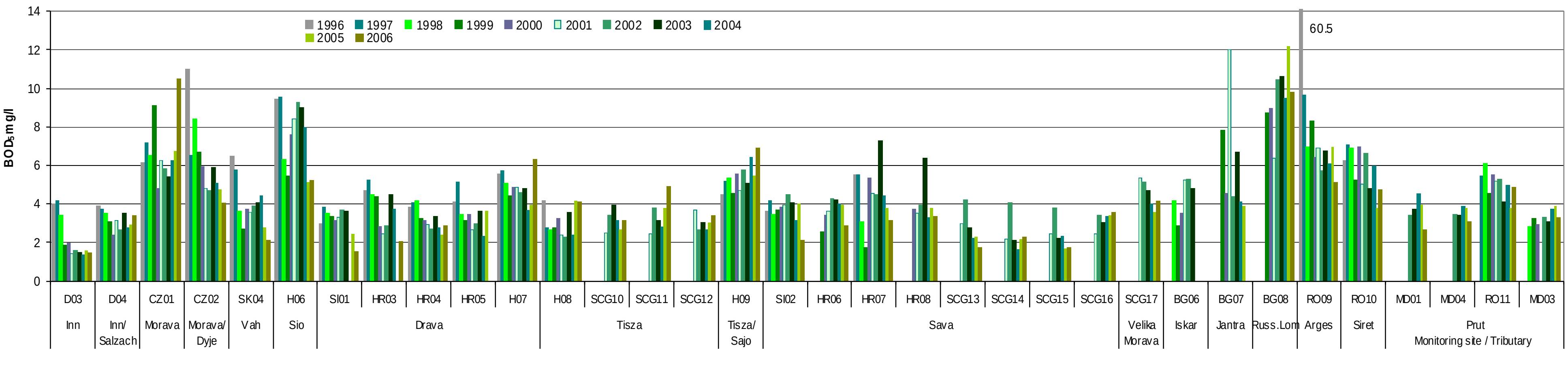


Figure 7.16: Temporal changes of COD_{Cr} in the Danube River.

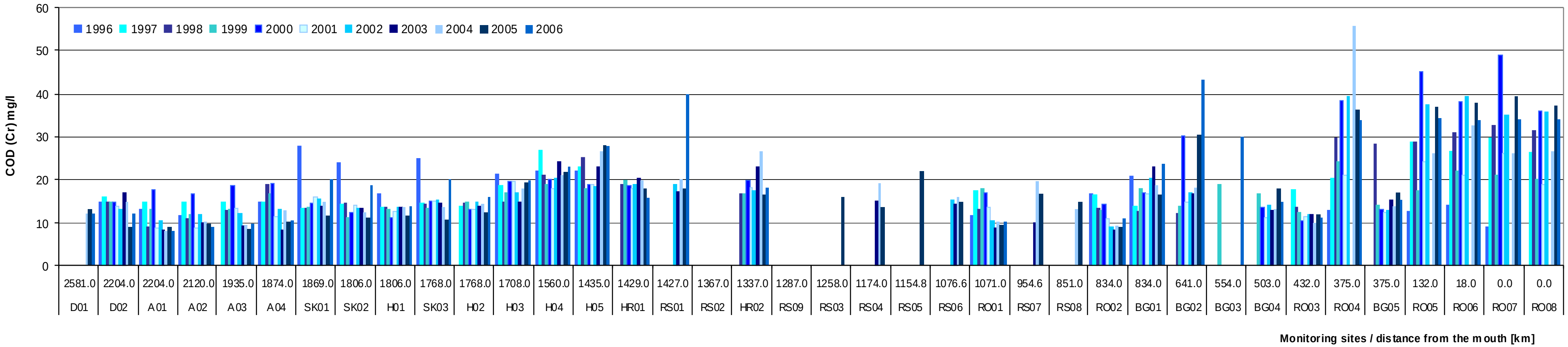


Figure 7.17: Temporal changes of COD_{Cr} in tributaries.

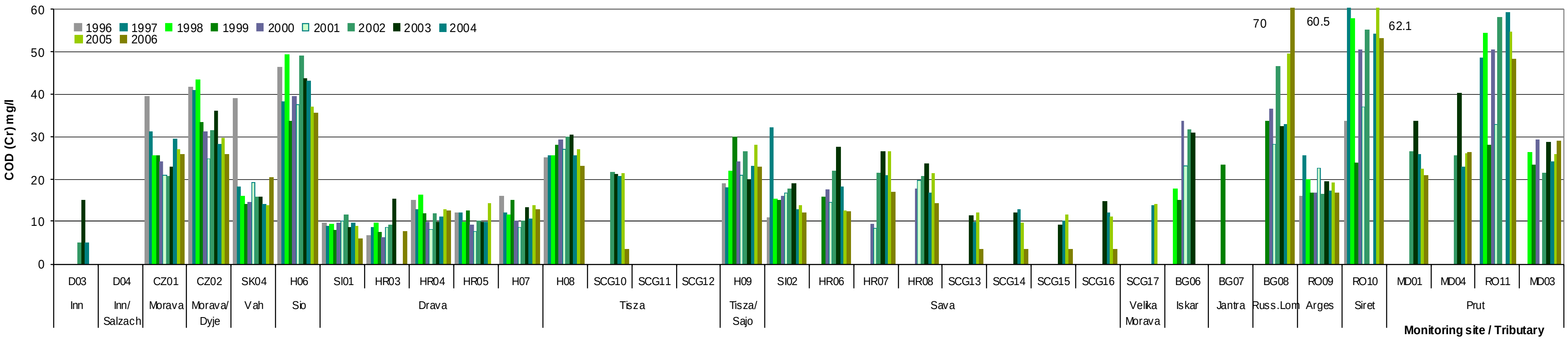


Figure 7.18: Temporal changes of ammonium-nitrogen in the Danube River.

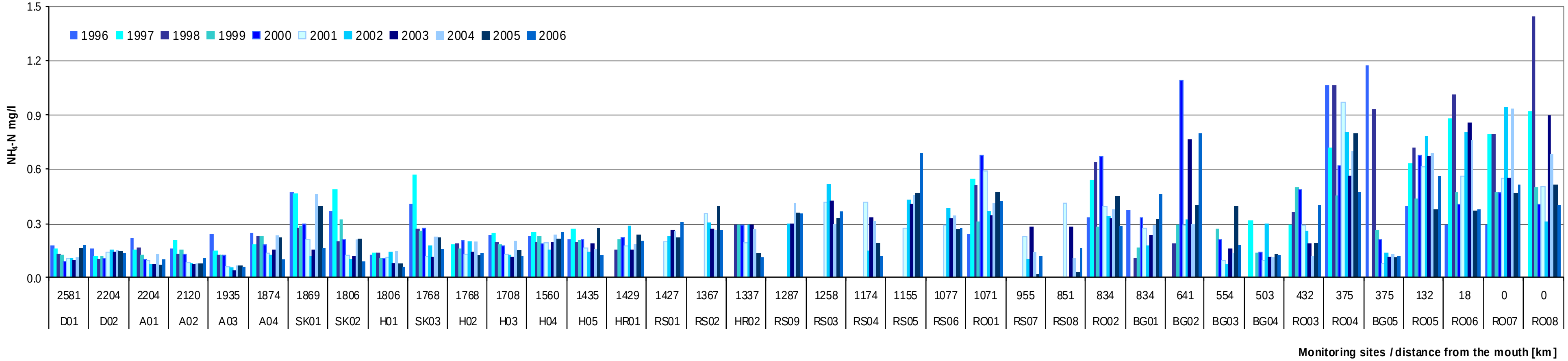


Figure 7.19: Temporal changes of ammonium-nitrogen in tributaries.

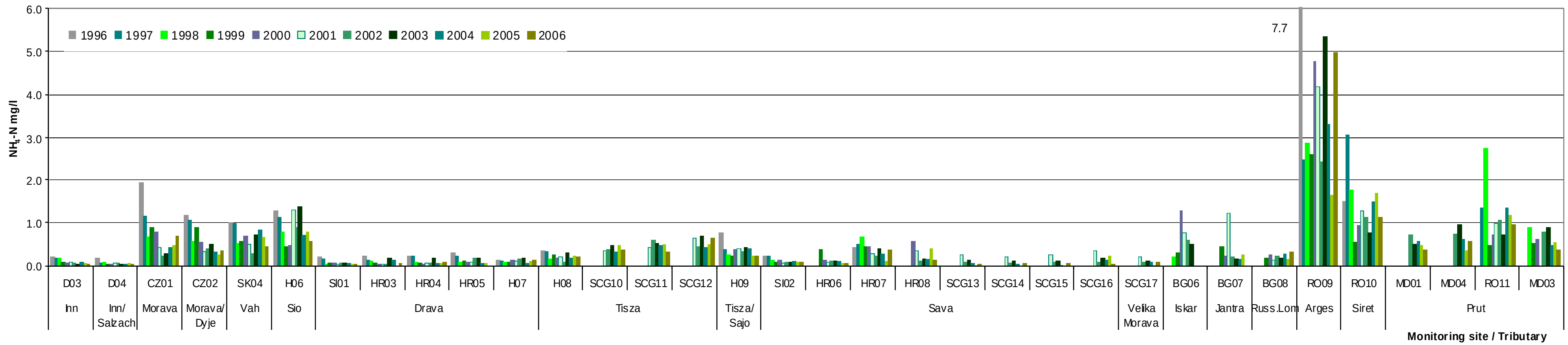


Figure 7.20: Temporal changes of nitrate-nitrogen in the Danube River.

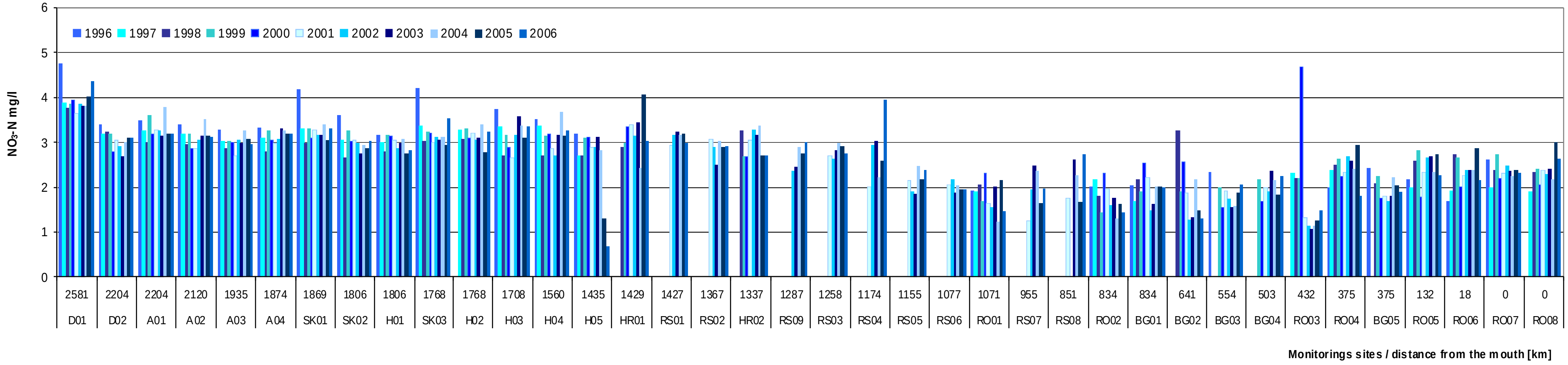


Figure 7.21: Temporal changes of nitrate-nitrogen in tributaries.

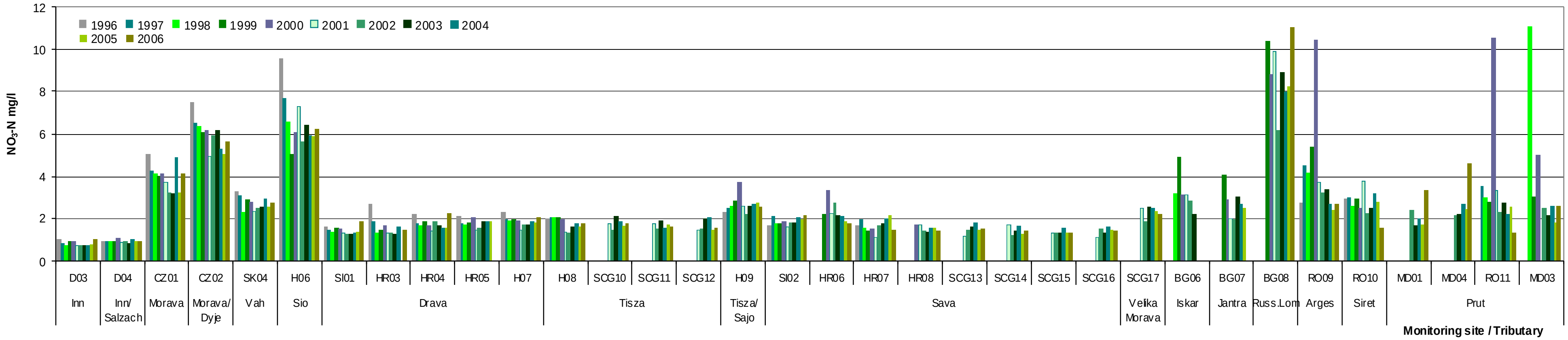


Figure 7.22: Temporal changes of ortho-phosphate-phosphorus in the Danube River.

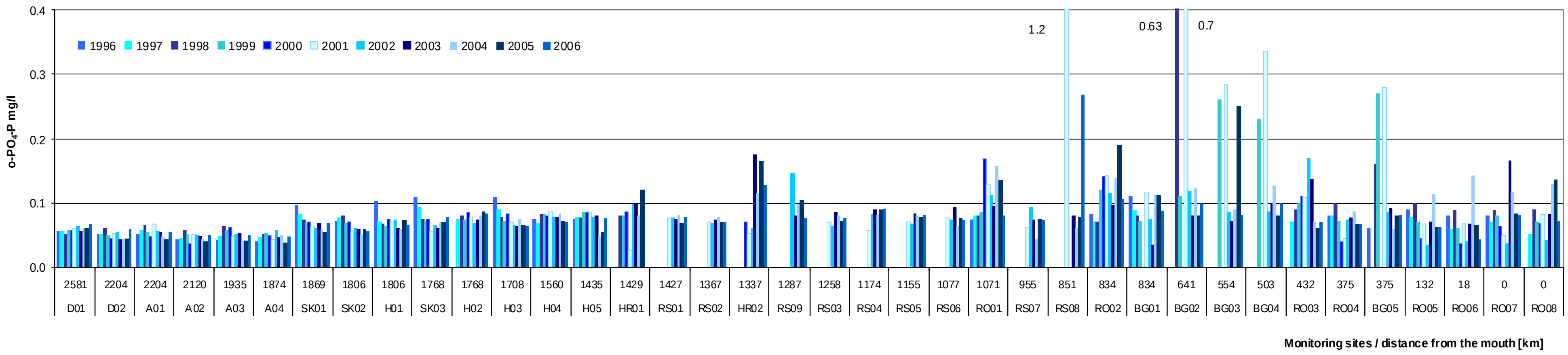


Figure 7.23: Temporal changes of ortho-phosphate-phosphorus in tributaries

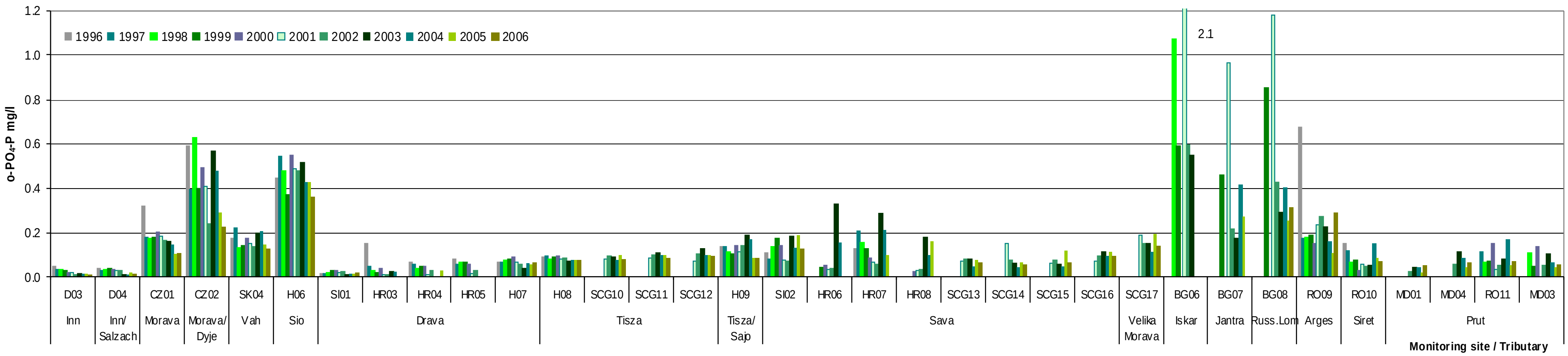


Figure 7.24: Temporal changes of total phosphorus in the Danube River.

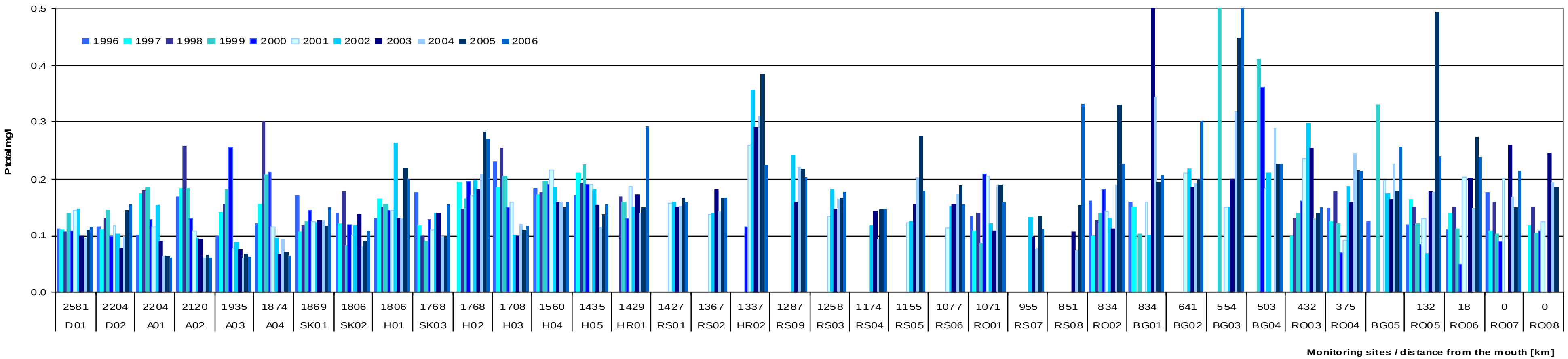


Figure 7.25: Temporal changes of total phosphorus in tributaries.

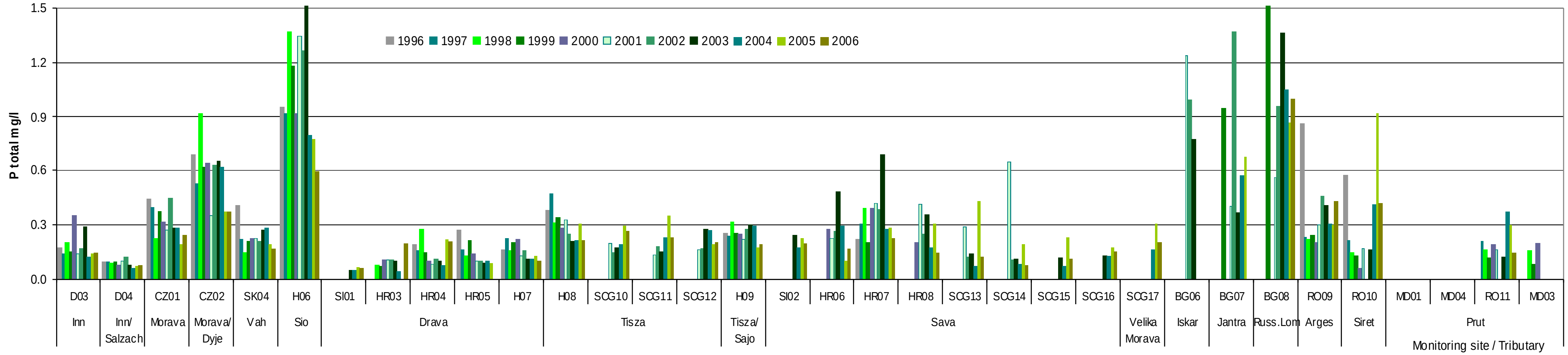


Figure 7.26: Temporal changes of cadmium in the Danube River.

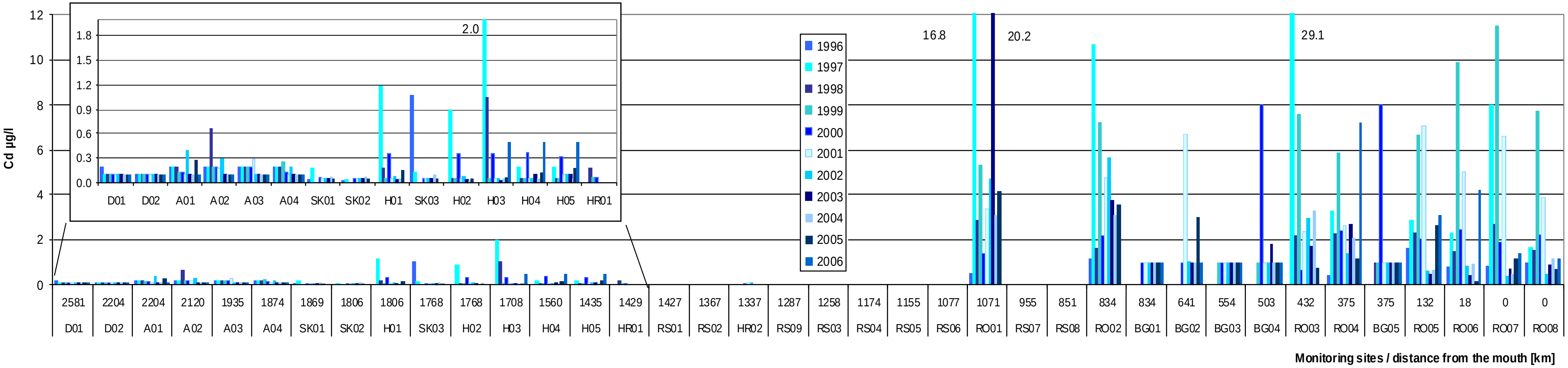
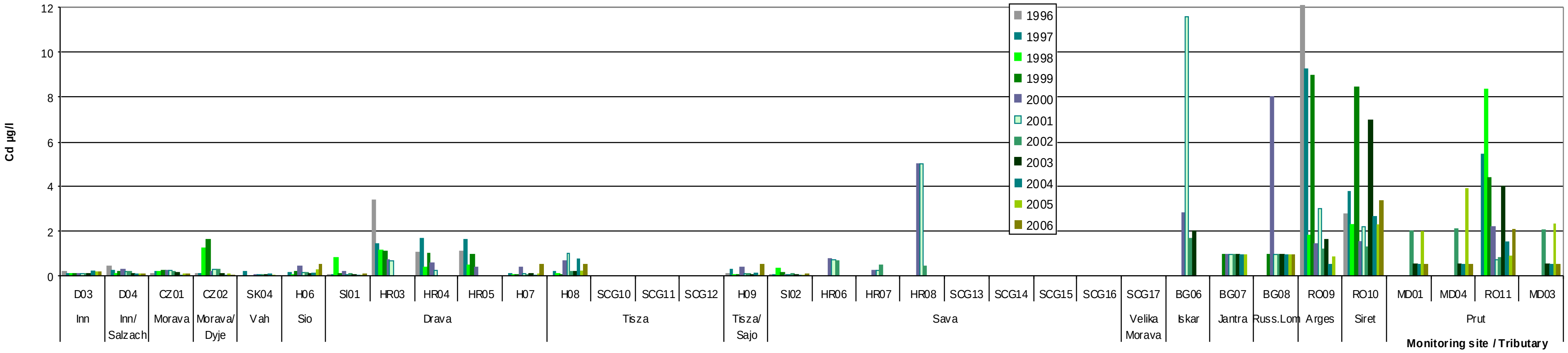


Figure 7.27: Temporal changes of cadmium in tributaries.



8. Load Assessment

8.1 Introduction

One of the main objectives of TNMN from the beginning of its operation was producing reliable and consistent trend analysis of concentrations and loads of substances diluted in water or attached to sediments. The objective was confirmed also later, in 2000, when obtaining of an overall view of the situation and long-term development of loads of relevant determinands in the important rivers of the Danube Basin was agreed as the main objective of he TNMN.

Load assessment programme started in 2000 and the countries agreed to use the Standard Operational Procedure (SOP) developed in the frame of EU Phare Project "Transboundary Assessment of Pollution Loads and Trends" (1998) for its operation in the Danube River Basin.

In the following chapters the principles and calculation procedure for the load assessment, information on the network for load assessment, available data in 2006 and results are presented.

8.2 Description of load assessment procedure

MLIM EG has agreed the following principles 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 voluntary basis – chlorides;
- minimum sampling frequency in sampling sites selected for load calculation is set at 24 per year;
- load calculation is processed according to the procedure recommended by the Project “Transboundary assessment of pollution loads and trends” and described in Chapter 8.4. 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 where valid flow data is available (see Table 8.2.1).

Table 8.2.1 shows TNMN monitoring locations selected for load assessment programme with information on hydrological stations used for obtaining flow data needed for load assessment in respective locations.
Altogether 19 monitoring locations from 8 countries are included in the list. Two locations – Danube-Jochenstein and Sava –Jesenice – have been included by two neighbouring countries, therefore actual number of locations is 17, with 8 locations on the Danube River itself and 9 locations on the tributaries.

Table 8.2.1: List of TNMN locations selected for load assessment program.

Country	River	Water quality monitoring location			Hydrological station	
		Country Code	Location	Distance from the mouth (km)	Location	Distance from the mouth (km)
Germany	Danube	D02	Jochenstein	2204	Achleiten	2223
Germany	Inn	D03	Kirchdorf	195	Oberaudorf	211
Germany	Inn/Salzach	D04	Laufen	47	Laufen	47
Austria	Danube	A01	Jochenstein	2204	Aschach	2163
Austria	Danube	A04	Hainburg	1879	Hainburg (Danube) Angern (March)	1884 32
Czech Republic	Morava	CZ01	Lanzhot	79	Lanzhot	79
Czech Republic	Morava/Dyje	CZ02	Pohansko	17	Breclav-Ladná	32.3
Slovak Republic	Danube	SK01	Bratislava	1869	Bratislava	1869
Hungary	Danube	H03	Szob	1708	Nagymaros	1695
Hungary	Danube	H05	Hercegszántó	1435	Mohács	1447
Hungary	Tisza	H08	Tiszasziget	163	Szeged	174
Croatia	Danube	HR02	Borovo	1337	Borovo	1337
Croatia	Sava	HR06	Jesenice	729	Jesenice	729
Croatia	Sava	HR07	Una Jesenovac	525	Una Jesenovac	525
Croatia	Sava	HR08	Zupanja	254	Zupanja	254
Slovenia	Drava	SI01	Ormoz	300	Borl HE Formin Pesnica-Zamusani	325 311 10.1(to the Drava)
Slovenia	Sava	SI02	Jesenice	729	Catez Sotla –Rakovec	737 8.1 (to the Sotla)
Romania	Danube	RO 02	Pristol-Novo Selo	834	Gruia	858
Romania	Danube	RO 04	Chiciu-Silistra	375	Chiciu	379
Romania	Danube	RO 05	Reni	132	Isaccea	101
Ukraine	Danube	UA02	Vilkova-Kilia arm	18		

8.3 Monitoring Data in 2006

The frequency of measurements is very important for assessment of pollution loads. Table 8.3.1 presents the number of measurements of flow and water quality determinands in TNMN locations selected for load assessment.

From Ukraine there are 7 data from measurements and for year 2006, this enabled a rough calculation of loads. Flow data are missing in two Croatian monitoring locations and one Hungarian location. In majority of locations number of samples was higher than 20, the frequency 12 times per year was applied in Morava, Dyje and Danube-Jochenstein (A01) and Hungarian Tizsa. But as the Danube Jochenstein is assessed on the basis of combined data from two countries, there is no problem with insufficient frequency there. The second location that could potentially be processed by using combined data from two countries is Sava – Jesenice, but this approach was not applied there due to the different methods of measurements used for some determinands, leading to differences in results. In addition, Croatia does not have flow data for this monitoring location.

Table 8.3.1: Number of measurements in TNMN locations selected for assessment of pollution load in 2006.

Country Code	River	Location	Location in profile	River Km	Number of meausrements in 2006								
					Q	SS	N_{inorg}	$P\text{-}PO_4$	P_{total}	BOD_5	Cl	P_{diss}	SiO_2
D02	Danube	Jochenstein	M	2204	365	26	26	26	26	26	26	11	0
D03	Inn	Kirchdorf	M	195	365	20	25	25	25	26	25	18	0
D04	Inn/Salzach	Laufen	L	47	365	26	26	26	26	26	26	26	0
A01	Danube	Jochenstein	M	2204	365	12	12	12	12	12	12	12	0
A04	Danube	Hainburg	R	1879	365	24	24	24	24	24	24	24	0
CZ01	Morava	Lanzhot	M	79	365	12	12	12	12	12	12	0	0
CZ02	Morava/Dyje	Pohansko	M	17	365	12	12	12	12	12	12	0	0
SK01	Danube	Bratislava	M	1869	365	25	25	12	25	25	25	12	0
H03	Danube	Szob	L	1708		25	25	25	25	25	24	0	0
			M	1708	365	23	23	23	23	23	22	0	0
			R	1708		25	25	25	25	25	25	0	0
H05	Danube	Hercegszántó	M	1435	0	11	12	12	12	12	12	0	0
H08	Tisza	Tiszasziget	L	163		12	12	12	12	9	11	0	0
			M	163	365	9	10	11	10	7	10	0	0
			R	163		12	12	12	12	8	12	0	0
HR02	Danube	Borovo	R	1337	0	26	26	0	26	26	0	0	0
HR06	Sava	Jesenice/D	L	729	0	25	25	0	25	25	12	0	0
HR07	Sava	us Una Jesenovac	L	525	365	25	25	0	25	25	12	0	0
HR08	Sava	ds Zupanja	R	254	365	25	25	0	25	25	12	0	0
SI01	Drava	Ormoz	L	300	365	24	24	24	24	24	24	0	0
SI02	Sava	Jesenice	R	729	365	24	24	24	24	24	24	0	0
RO02	Danube	Pristol-Novo Selo	L	834		21	21	21	21	21	21	0	19
			M	834	365	20	20	20	20	20	20	0	17
			R	834		20	20	20	20	20	20	0	16
RO04	Danube	Chiciu-Silistra	L	375		22	22	22	21	21	12	0	23
			M	375	365	22	22	22	21	21	12	0	23
			R	375		22	22	22	21	21	12	0	23
RO05	Danube	Reni	L	132		24	24	24	22	22	18	0	24
			M	132	365	24	24	24	22	22	18	0	24
			R	132		24	24	24	22	22	18	0	24
UA02	Danube	Vilkova-Kilia arm	M	18	365	7	7	7	7	7	7	0	0

Regarding particular determinands, there is still lack of data on dissolved phosphorus as it was measured in 5 locations only. Results for dissolved P are therefore given only in tables but are not presented in Figures showing the load in the context of the whole river basin. For Rumanian monitoring point load for silicates was calculated, results are only in table, not in figures.

8.4 Calculation Procedure

The loads have been calculated in accordance to the following procedure:

- In case of several sampling sites in the profile, average concentration at the location is calculated for each sampling day.

- In case of values "below limit of detection", value of limit of detection is used in the further calculation.

- The average monthly concentrations is 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, Q_m is calculated from those discharges.
  - In case of 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:

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

8.5 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 - are presented in tables 8.5.1 to 8.5.4, separately for monitoring locations on the Danube River and monitoring locations on tributaries. Explanation of terms used in the tables 8.5.1 - 8.5.4 is in the following legend.

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 2006
c_{mean}	arithmetical mean of the concentrations in the year 2006
Annual Load	annual load of given determinand in the year 2006

The mean annual discharge was similar in 2006 as in 2005. There are not significant differences in discharges measured in the Danube River and in tributaries during these two years.

Higher annual load of SS was observed in comparison with 2005 in Jochenstein, therefore the mean concentration of SS was increased from 11,0 $mg.l^{-1}$ to 35,5 $mg.l^{-1}$, because discharge increased. The rests of annual load values were similar as in 2005.

In addition to the tables, the mean annual discharge and annual loads of suspended solids, inorganic N, ortho-phosphate P, total P, BOD_5 and chlorides are presented on the plots, prepared separately for monitoring locations on the Danube River itself and locations on its primary tributaries (Figures 8.5.1 – 8.5.12).

Figures 8.5.1 – 8.5.12 show that the spatial pattern of annual load along the Danube River is similar to the previous year. In case of suspended solids, inorganic nitrogen, Ptotal and chlorides the highest load is observed in the lower part of the Danube River, maximum is reached in monitoring location Danube-Reni (RO05). The maximum of ortho-phosphate load was in Danube- Pristol-Novo Selo RO02 and maximum of BOD_5 load was Danube-Chiciu-Silistra (RO04).

In the case of tributaries, the highest load of SS, nutrients and chlorides is coming from Tisza river. Maximum of BOD_5 loading for is coming from Sava river.

Maximal loading for silicates is reached in Danube Reni – 2.3. 10^6 tones. In Table 8.5.5 are presented other annual load, mean concentration and number of measurements for additional determinands come out of the agreement between ICPDR and Black sea commission.

Table 8.5.1: Mean annual concentrations in monitoring locations selected for load assessment on the Danube River in 2006

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
					($m^3.s^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
D02 +A01	M	Danube	Jochenstein	2204	1396	35.54	2.25	0.03	0.08	1.90	19.76	0.04	
A04	R	Danube	Hainburg	1879	2183	27.01	2.17	0.03	0.05	1.38	20.01	0.04	
SK01	M	Danube	Bratislava	1869	2186	41.24	2.25	0.05	0.09	1.22	21.05	0.05	
H03	LMR	Danube	Szob	1708	2503	19.893	2.953	0.049	0.088	3.155	24.544		
H05	M	Danube	Hercegszántó	1435		7.00	0.48	0.03	0.09	3.47	24.59		
HR02	R	Danube	Borovo	1337		38.19	2.07		0.11	3.383			
RO02	LMR	Danube	Pristol-Novo Selo	834	6616	29.65	1.31	0.06	0.12	1.74	21.06		6.06
RO04	LMR	Danube	Chiciu-Silistra	375	7370	41.44	1.53	0.04	0.11	2.52	30.60		5.76
RO05	LMR	Danube	Reni	132	8428	48.01	1.67	0.03	0.15	2.13	31.72		5.77
UA02	M	Danube	Vilkova-Kilia arm	18	1034	138.17	1.37	0.04	0.12	2.44	30.94		

Table 8.5.2: Mean annual concentrations in monitoring locations selected for load assessment on tributaries in 2006

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
					($m^3.s^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
D03	M	Inn	Kirchdorf	195	335	22.00	0.70	0.01	0.07	1.16	6.17	0.02
D04	L	Inn/Salzach	Laufen	47	262	105.50	0.72	0.01	0.11	2.31	9.82	0.01
CZ01	M	Morava	Lanzhot	79	75	44.08	3.05	0.06	0.16	4.82	31.51	
CZ02	L	Morava/Dyje	Pohansko	17.00	55	17.92	3.61	0.16	0.23	2.81	41.33	
H08	LMR	Tisza	Tiszasziget	163	1224	44.89	1.30	0.05	0.16	1.79	45.53	
SI01	L	Drava	Ormoz	300	265	12.09	1.37	0.01	0.04	1.18	6.79	
SI02	R	Sava	Jesenice	729	235	8.73	1.88	0.08	0.12	1.34	9.76	
HR06	L	Sava	Jesenice	729		5.01	1.52		0.12	1.74	9.96	
HR07	L	Sava	us. Una Jasenovac	525	578	11.68	1.40		0.16	2.41	10.28	
HR08	R	Sava	ds. Zupanja	254	1068	24.48	1.14		0.12	2.34	18.88	

Table 8.5.3: Annual loads of pollutants in selected monitoring locations on the Danube River.

Station Code	Profile	River Name	Location	River km	Annual Load in 2006							
					Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved	Silicates
					($x10^6$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^6$tonns)	($x10^3$tonns)	($x10^6$tonns)
D02 +A01	M	Danube	Jochenstein	2204	2.317	94.744	1.377	4.281	87.367	1.119	2.384	
A04	R	Danube	Hainburg	1879	2.804	145.634	1.988	3.058	100.714	1.261	2.457	
SK01	M	Danube	Bratislava	1869	3.957	161.181	3.517	7.347	82.709	1.367	3.778	
H03	LMR	Danube	Szob	1708	1.942	235.674	3.446	6.065	272.324	1.760		
H05	M	Danube	Hercegszántó	1435								
HR02	R	Danube	Borovo	1337								
RO02	LMR	Danube	Pristol-Novo Selo	834	5.339	227.332	10.805	21.742	308.798	3.407		0.893
RO04	LMR	Danube	Chiciu-Silistra	375	11.151	378.743	9.540	25.480	579.436	6.766		1.410
RO05	LMR	Danube	Reni	132	13.994	484.209	8.044	35.722	481.479	8.300		1.626
UA02	M	Danube	Vilkova-Kilia arm	18	3.468	33.965	1.182	3.040	61.102	0.699		

Table 8.5.4: Annual loads of pollutants in selected monitoring locations on tributaries.

Station Code	Profile	River Name	Location	River km	Annual Load in 2006						
					Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved
					($x10^6$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^6$tonns)	($x10^3$tonns)
D03	M	Inn	Kirchdorf	195	0.295	6.560	0.072	1.009	12.739	0.065	0.153
D04	L	Inn/Salzach	Laufen	47	1.748	5.476	0.067	1.655	17.714	0.062	0.086
CZ01	M	Morava	Lanzhot	79	0.131	8.290	0.133	0.371	9.270	0.065	
CZ02	L	Morava/Dyje	Pohansko	17	0.043	8.788	0.223	0.349	5.894	0.067	
H08	LMR	Tisza	Tiszasziget	163	1.920	47.043	1.904	5.854	48.857	1.286	
SI01	L	Drava	Ormoz	300	0.111	11.050	0.089	0.323	9.474	0.054	
SI02	R	Sava	Jesenice	729	0.103	14.931	0.549	0.758	9.790	0.069	
HR06	L	Sava	Jesenice	729							
HR07	L	Sava	us. Una Jasenovac	525	0.221	24.587		2.468	38.884	0.177	
HR08	R	Sava	ds. Zupanja	254	0.697	38.823		3.961	71.130	0.445	

Table 8.5.5: Number of measurement, mean concentration and annual load in Reni for additional come out of the agreement between ICPDR and Black sea commission.

Country Code	River	Location	Location in profile	River km	Number of measurements in 2005											
					Q	$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg
RO05	Danube	Reni	LMR	132	365	24	24	24	24	8	1	8	1	8	1	8
Country Code	**River**	**Location**	**Location in profile**	**River km**	c_{mean}											
					Q_a	$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg
					$(m^3.s^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$	$(\mu g.l^{-1})$
RO05	Danube	Reni	LMR	132	8428	0.31	0.04	1.33	2.13	4.65	-	1.97	-	0.93	-	0.05
Country Code	**River**	**Location**	**Location in profile**	**River km**	Annual Load in 2006											
						$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	N_{total}	Cu	$Cu_{diss.}$	Pb	$Pb_{diss.}$	Cd	$Cd_{diss.}$	Hg
						$(x10^3 tonns)$	$(x10^3 tonns)$	$(x10^3 tonns)$	$(x10^3 tonns)$	$(x10^3 tonns)$	$(x10^3 tonns)$	(tonns)	(tonns)	(tonns)	(tonns)	(tonns)
RO05	Danube	Reni	LMR	132		82.99	12.25	389.37	612.92	-	-	-	-	-	-	-

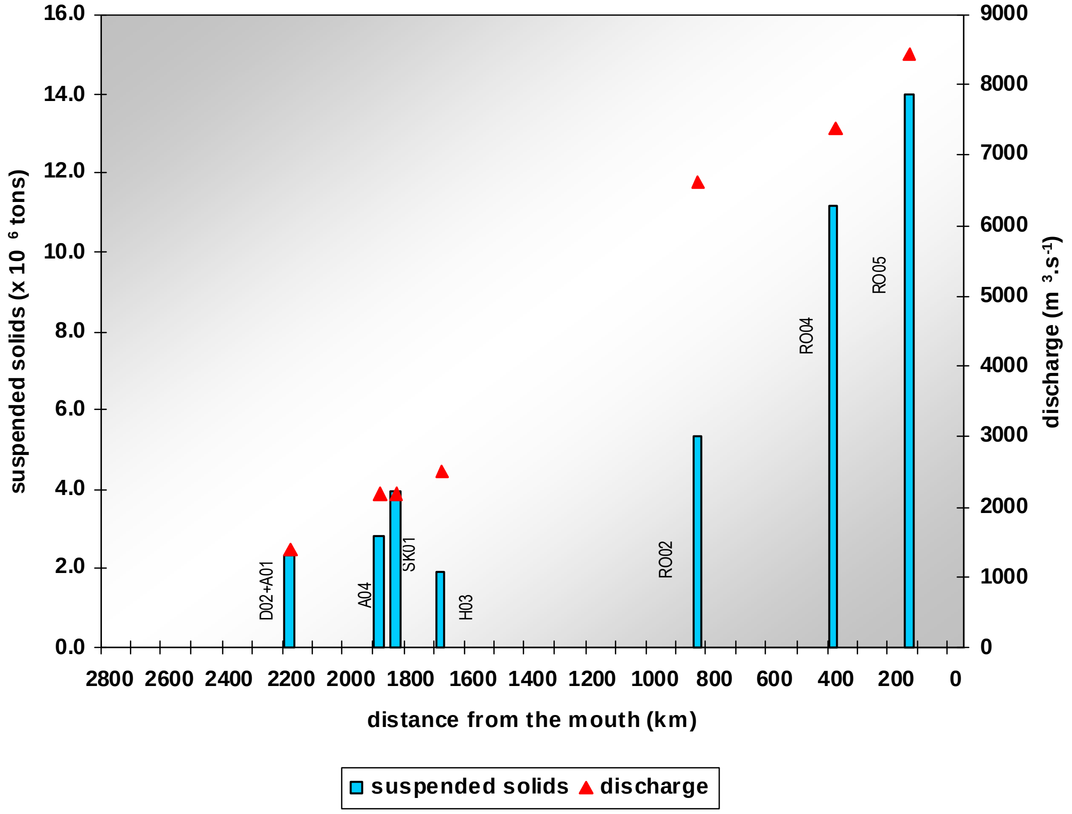


Figure 8.5.1: Annual load of suspended solids at monitoring locations along the Danube River.

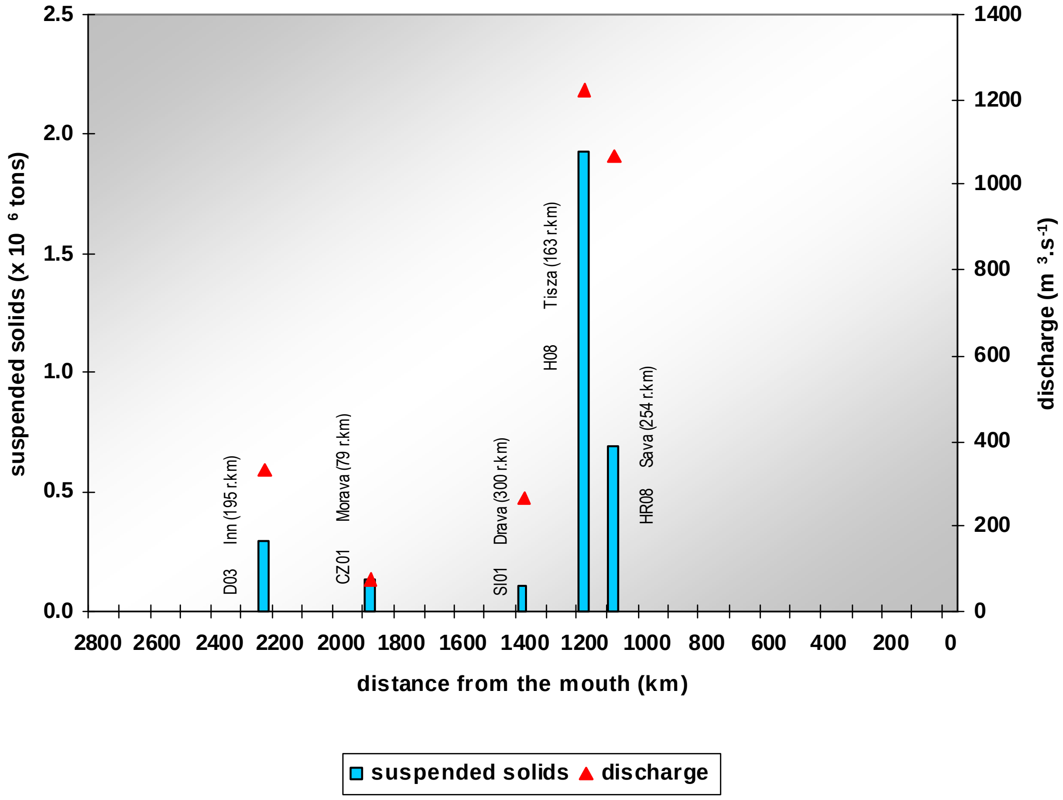


Figure 8.5.2: Annual load of suspended solids at monitoring locations on tributaries.

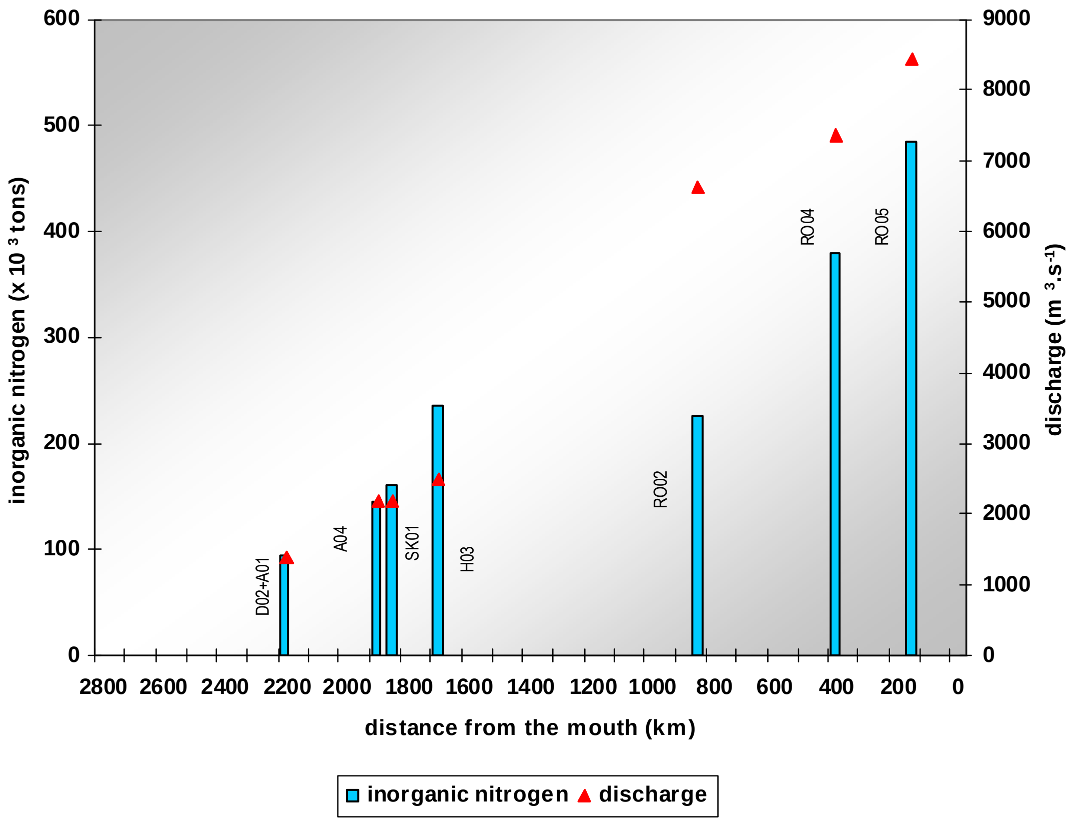


Figure 8.5.3: Annual loads of inorganic nitrogen at monitoring locations along the Danube River.

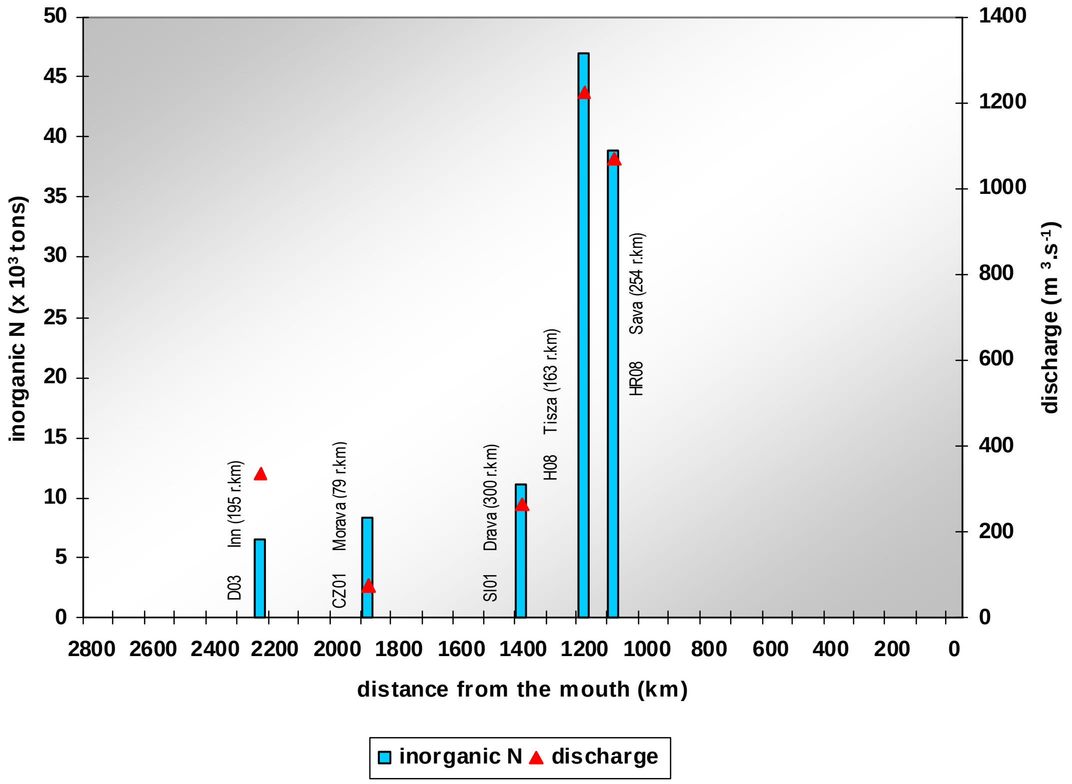


Figure 8.5.4: Annual loads of inorganic nitrogen at monitoring locations on tributaries.

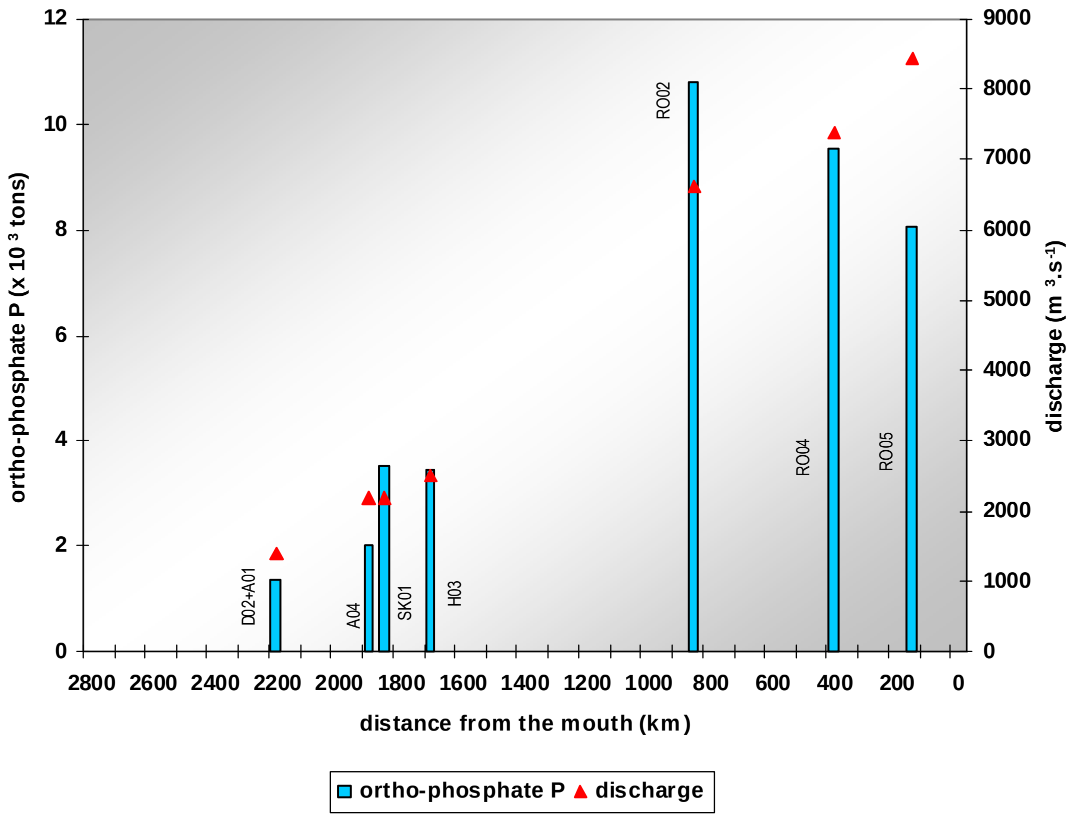


Figure 8.5.5: Annual loads of ortho-phosphate-P at monitoring locations along the Danube River.

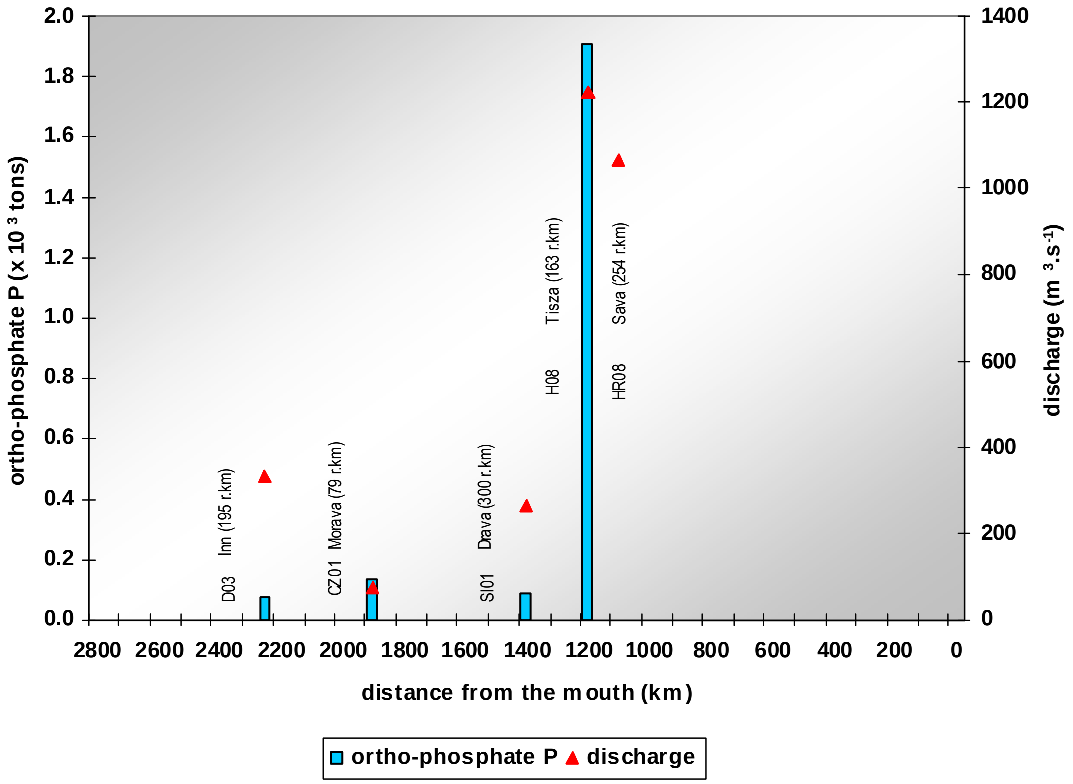


Figure 8.5.6: Annual loads of ortho-phosphate-P at monitoring locations on tributaries.

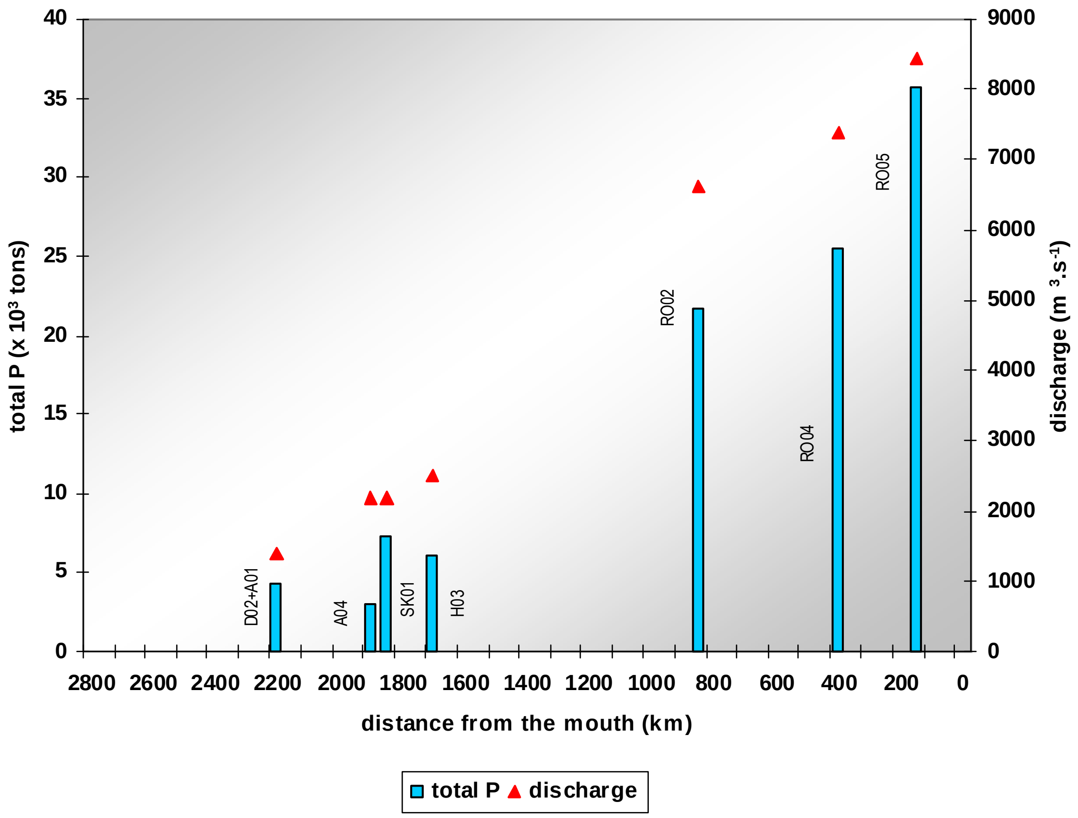


Figure 8.5.7: Annual loads of total phosphorus at monitoring locations along the Danube River.

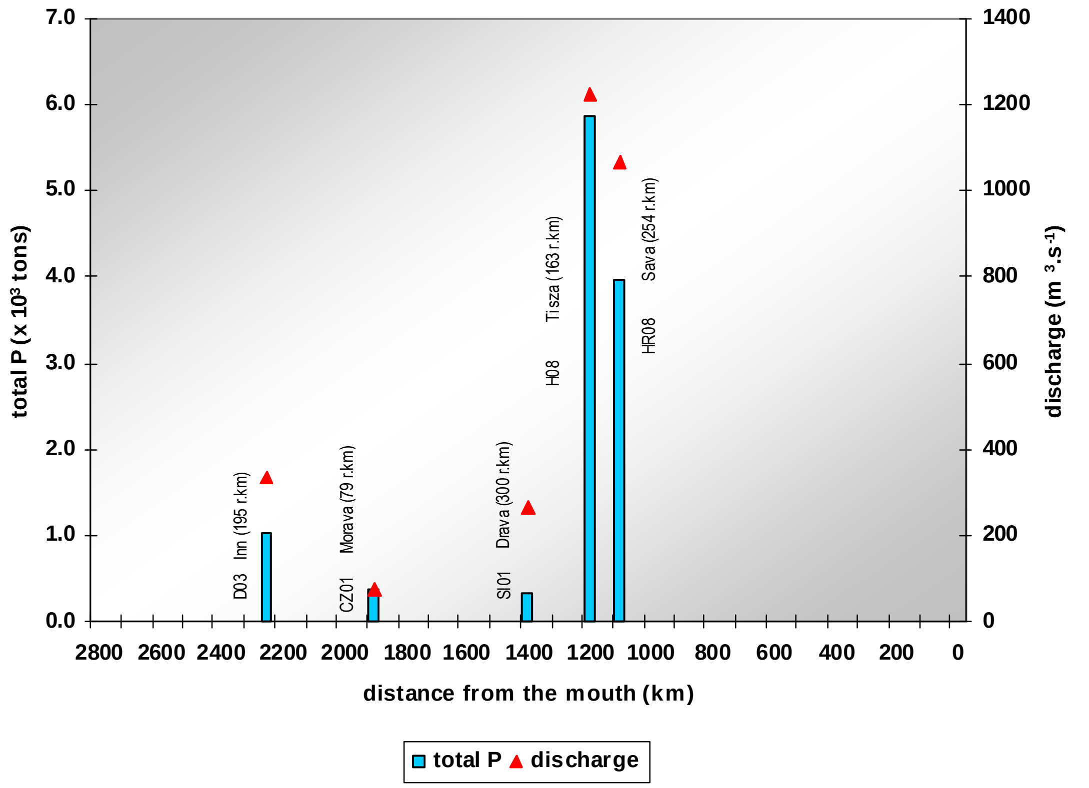


Figure 8.5.8: Annual loads of total phosphorus at monitoring locations on tributaries.

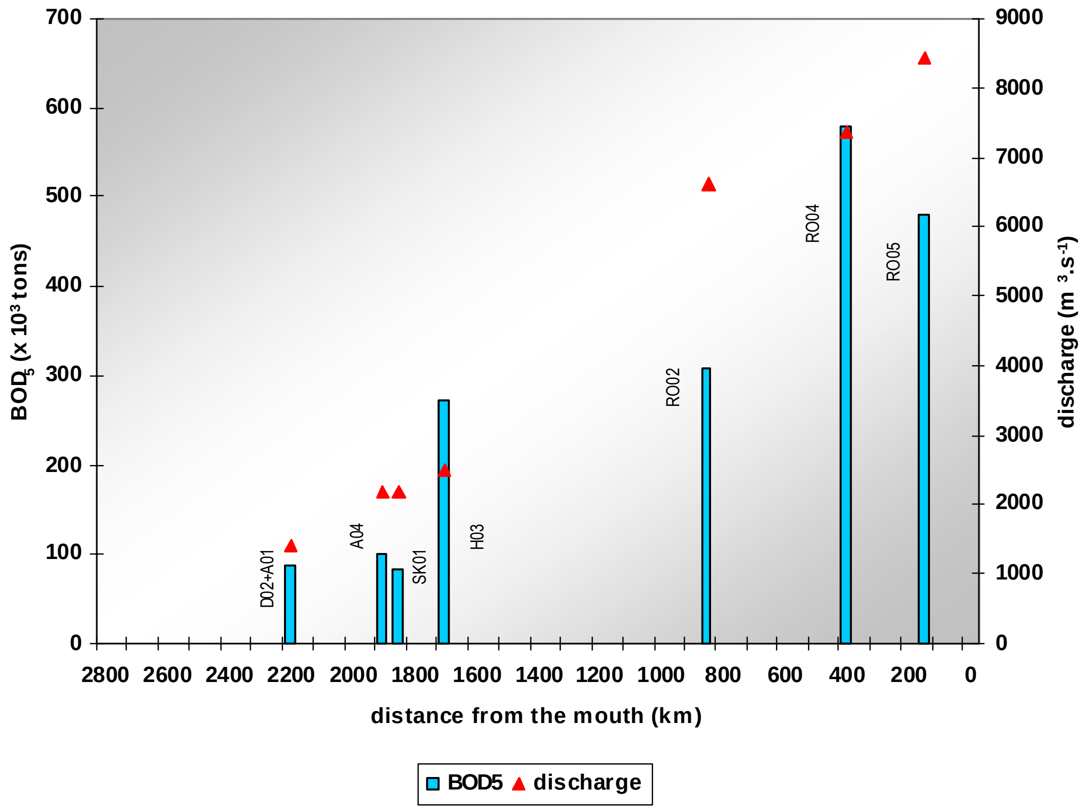


Figure 8.5.9: Annual loads of BOD_5 at monitoring locations along the Danube River.

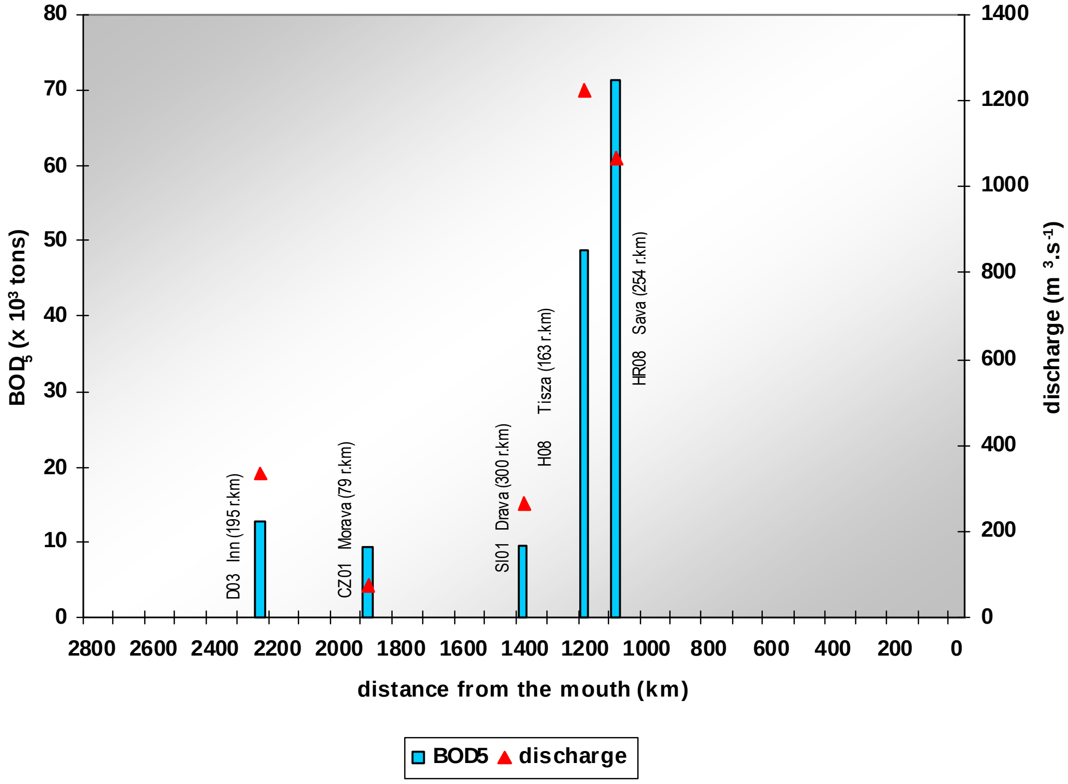


Figure 8.5.10: Annual loads of BOD_5 at monitoring locations on tributaries.

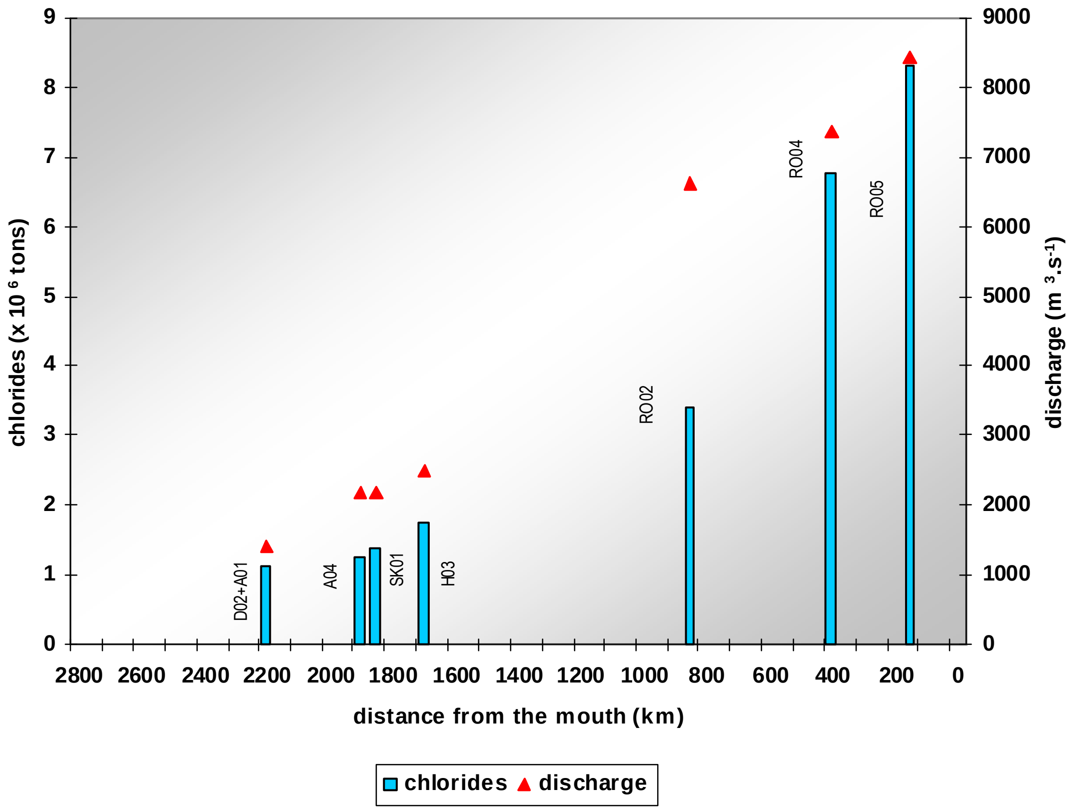


Figure 8.5.11: Annual loads of chlorides at monitoring locations along the Danube River.

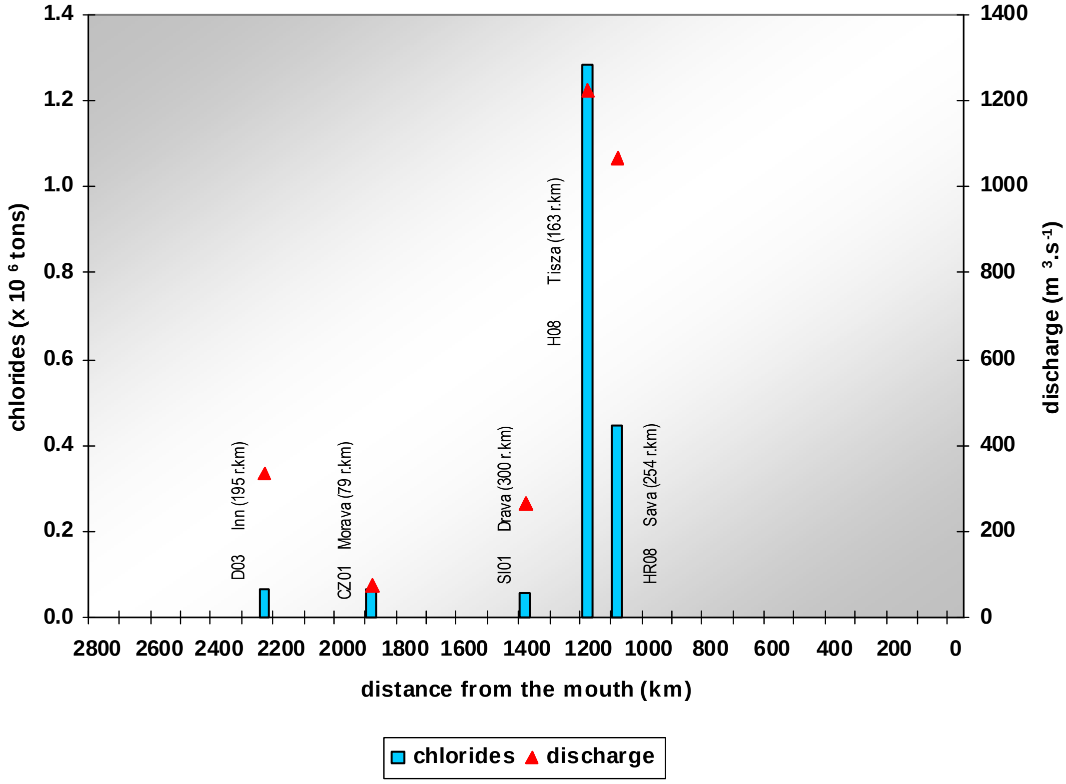


Figure 8.5.12: Annual loads of chlorides at monitoring locations on tributaries.

9. Abbreviations

Abbreviation	Explanation
AQC	Analytical Quality Control
DEFF	Data Exchange File Format
DRPC	Danube River Protection Convention
EPDRB	Environmental Programme for the Danube River Basin
ICPDR	International Commission for the Protection of the Danube River
LOD	Limit of Detection
MLIM/EG	Monitoring, Laboratory and Information Management Expert Group
MLIM-SG	Monitoring, Laboratory and Information Management Sub-Group
NRL	National Reference Laboratory
SOP	Standard Operational Procedure
TNMN	Trans National Monitoring Network
TOR	Terms of Reference
WTV	Consortium that carried out the first MLIM-study (WRc, TNO, VKI/DHI)

ANNEX 1