INTERNATIONAL COMMISSION FOR THE PROTECTION OF THE DANUBE RIVER

INTERNATIONALE KOMMISSION ZUM SCHUTZ DER DONAU

WATER QUALITY

IN THE DANUBE RIVER BASIN

TNMN Yearbook 2005

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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 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 2004.

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 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 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 2005 danubian countries provided data from 77 monitoring locations, including 107 sampling sites. 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	Abwinden-Asten	48 15 21	14 25 19	2120	251	83992	L2200	R
A03	Danube	Wien-Nussdorf	48 15 45	16 22 15	1935	159	101700	L2180	R
A04	Danube	Wolfsthal	48 8 30	17 3 13	1874	140	131411	L2170	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
SCG01	Danube	Bezdan	45 51 15	18 51 51	1427	83,15	210250	L2350	L
SCG02	Danube	Bogojevo	45 31 49	19 5 2	1367	80,41	251253	L2360	L
SCG03	Danube	Novi Sad	40 15 3	19 51 40	1258	74,52	254085	L2370	R
SCG04	Danube	Zemun	44 50 56	20 25 2	1174	70,76	412762	L2380	R
SCG05	Danube	Pancevo	44 51 25	20 36 28	1154,8	70,14	525009	L2390	L
SCG06	Danube	Banatska	44 49 6	21 20 4	1076,6	68,58	568648	L2400	M
SCG07	Danube	Tekija	44 41 56	22 25 24	954,6		574307	L2410	R
SCG08	Danube	Radujevac	44 15 50	22 41 9	851	32,45	577085	L2420	R
SCG09	Danube	Backa Pal	45 15 13	19 31 35	1287		253737	L2430	L
SCG10	/Tisza	Martonos	46 5 59	20 3 50	152	75,54	140130	L2440	R
SCG11	/Tisza	Novi Becej	45 35 9	20 8 23	66	74,03	145415	L2450	L
SCG12	/Tisza	Titel	45 11 52	20 19 9	8,9	72,55	157147	L2460	M
SCG13	/Sava	Jamena	44 52 40	19 5 21	195	77,67	64073	L2470	L
SCG14	/Sava	Sremska	44 58 1	19 36 26	136,4	75,24	87996	L2480	L
SCG15	/Sava	Sabac	44 46 12	19 42 17	103,6	74,22	89490	L2490	R
SCG16	/Sava	Ostruznica	44 43 17	20 18 51	17		37320	L2500	R
SCG17	/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	22 47	834	35	580100	L0730	LMR

			50,58,66	36,47,58					
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	Sampling location in profile:
Altitude:	The mean surface water level in meters above sea level	L: Left bank
Catchment:	The area in square km, from which water is drains through the station	M: Middle of river
ds.	Downstream of	R: Right bank
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.	

In year 2005 monitoring point Drava - Varazdin was moved two km to monitoring point is Drava - Ormoz (L1300) this is a transnational Slovenian - Croatian point.

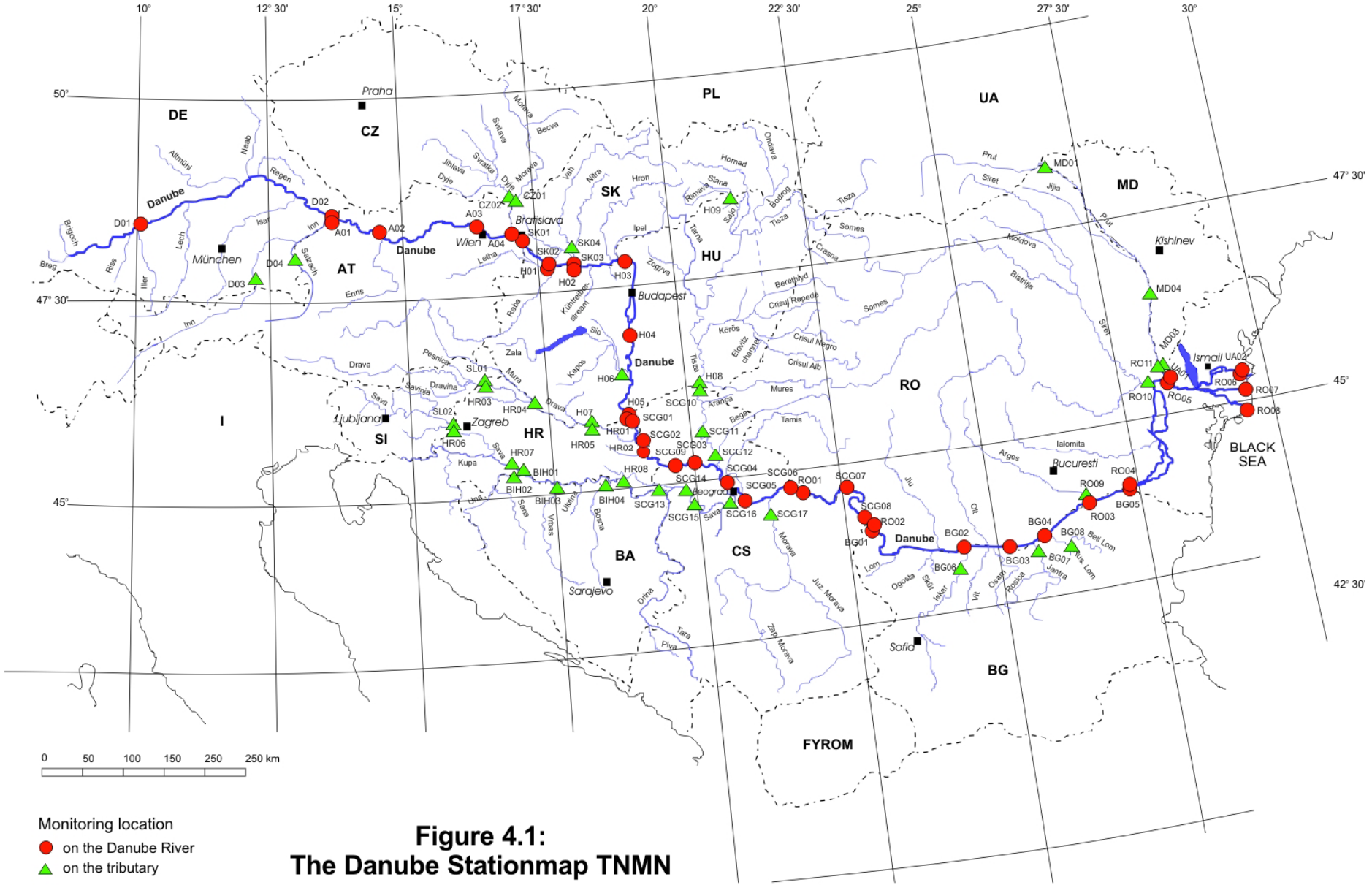


Figure 4.1:
The Danube Stationmap TNMN

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 2005

The organisation of interlaboratory comparison studies in the transboundary water quality monitoring in the Danube river basin was first agreed in 1992; in the frame 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 of QualcoDanube.
After the first randomly organized distributions (in 1993), regular distribution programme, i.e. quarterly distribution of synthetic concentrates, real water and sediment samples for analyzing determinands of the TNMN determinand lists, started in 1996.

Because of the observed discrepancies among the analytical results obtained in the different Danubian laboratories, the parameters and the concentration levels were adjusted according to the requirements, helping the laboratories to make connective parameters and improving the quality of the analytical results. After several distributions, particularly for analysing nutrients, significant improvements were observed.
During the EU-PHARE programme supported enhancement and strengthening of the Danube basin monitoring programme including upgrading the analytical quality control (AQC) schemes. Accordingly, new elements, e.g., preparation of Danube reference materials were introduced in the QualcoDanube AQC, interlaboratory comparison programme. This was further supported in the frame of the UNDP/GEF Danube Regional Project.
Based on the past interlaboratory comparison studies as well as on the new requirements of the EU Water Framework Directive (WFD), analyses of micropollutants, particularly those listed in priority list.
As the latest MLIM-Expert Group Meeting (14-15 April, 2005) the AQC programme were revised. It was suggested that all determinands could be covered during three quarterly distributions and the fourth distribution could be reserved for those matrix/determinands which showed more than 30 % flagged results.

In the QualcoDanube performance testing scheme the Youden-pair evaluation technique was usually applied. The results of the four distributions and their evaluation have been published in the evaluation report (QualcoDanube, AQC for Water Labs in the Danube River Basin, Summary Report 2005, VITUKI, Budapest).

The interlaboratory comparative results are discussed separately for the different determinands.

It was a success that 37 laboratories reported results. The interlaboratory comparative results are discussed below separately for the different determinands. The results were provided by total 37 laboratories.

4.3.1.1 Results of performance testing of water samples

General parameters

Real-world samples were distributed for analyses of these compounds. In general the results were good, but influenced by slight systematic error. In the case of calcium and total hardness the analytical results were excellent, all the data were inside of limit of error.
The performances on potassium, sodium and magnesium were also good with one-one rejected data. The results of chloride and sulphate were relatively good with a few outliers.

Nutrients

Real-world samples were also distributed for nutrients.The results were influenced by significant systematic error in the case of ammonium and Kjeldahl-N. These analysis were repeated in the fourth quarter and the results showed influence of systematic error again.
The performance on nitrate was characterized by significant systematic error, while nitrite was excellent without outliers. The results of phosphate and total phosphorus were quite good.

Organic pollutants

Real-world samples were also distributed for chemical-, biological oxygen demand as well as for MBAS and DOC.
The performances on these parameters were characterized by significant systematic error. The results of AOX (synthetic samples were analysed by 13 laboratories) were good with one rejected value. Concentrates were also analysed in the case of phenol index. The determination was relatively good with a few extreme low and high results.
Results reported by 21 laboratories for petroleum hydrocarbons showed significant systematic error but all the data were inside of limit of error and most of the reported results were near the assigned values.
The performance on atrazine systematic error was dominated at the both analyses.
In the case of lindane, the analytical data reported by 20 laboratories showed significant discrepancies. Although the analysis had to be repeated during the 4th quarter, results were influenced by significant systematic error and random error. The determination for DDT was rather poor in both cases. Although the numbers of rejected data decreased, more analytical results fell into warning limit than previously.

Metals, heavy metals

In the case of the seven heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, Hg), the analytical results were influenced by significant systematic error in general. The analysis of cadmium, copper and nickel were repeated due to poor results. The repeated analyses were relatively good.
The performances on chromium, lead, zinc and mercury were quite good with a few outliers.
The analytical results of iron, manganese as well as aluminum and arsenic were influenced by systematic error. In the case of aluminum and arsenic the analyses were repeated, the results of repeated determinations were better than previous analyses.

4.3.1.2 Results of performance testing of sediment samples

Nutrients

The results reported by laboratories for total N and total P quite good with slight systematic error.

Organic determinands

In the case of petroleum hydrocarbons as well as TOC the results were influenced by significant systematic error. Inspite of the systematic error, all the data of TOC were inside of limit of error.
The determinations for organic micropollutants had to be repeated due to poor results. At atrazine the results were characterized mainly systematic error. The reported data for lindane demonstrated high discrepancies, unfortunately results of the repeated analysis brought about similar results.
The analytical data reported by 12 laboratories were rather different, most of them were rejected.
In the case of PAHs (Borneff PAH) results showed significant systematic error, nearly half of all the results were rejected.
The performances on PCBs were somehow better than PAHs. Inspite of the significant systematic error which characterized the analytical data, the acceptable results were more than rejected data.

Metals, heavy metals

The analytical results of iron, manganese, calcium and magnesium were quite good with slight systematic error.
The performance on aluminum was rather poor, nearly half of all the values were acceptable only. The results of arsenic determination were similar to aluminum.
Systematic error characterized the results of heavy metals. In the case of chromium, copper there were no rejected data.
The performances on cadmium, nickel, lead, zinc were quite good, while at mercury there were some rather low data due to significant systematic error.

4.3.1.3 Conclusion

In accordance with the new principle (34th MLIM Expert Group Meeting) the previous distribution programme was slightly modified, so during the 1st, 2nd and 3rd quarter of the year real-world samples and/or synthetic concentrates were distributed, two concentration levels for each determinand, covering all determinands listed in the TNMN.
Based on the results obtained during the first three quarters, some determinands, mainly trace organics were redistributed during the last quarter in 2005.

The participants obviously had no serious problems determining the general parameters and reasonable quality improvement could be observed during the years in the case of nutrients and metals except a few parameters, e.g., Kjeldahl-N, aluminum, where the performances were unsatisfactory.
As regards organic micropollutants, based on the results, it is obvious that the laboratories, in general, have serious problems determining these compounds/parameters.
In total 20 laboratories provided data for TPH and nine to ten laboratories reported results for the other organic micropollutants.
In general, the results were poor and there are no significant differences between results of water and sediment samples.

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 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 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 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 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 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
** for dissolved metals only guideline values are indicated
bg background values
TV target value

5. Results of basic statistical processing

In 2005, 77 monitoring locations had been monitored in the frame of TNMN in 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 2005
Mean	arithmetical mean of the measurements done in the year 2005
Max	maximum value of the measurements done in the year 2005
C50	50 percentile of the measurements done in the year 2005
C90	90 percentile of the measurements done in the year 2005
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 (4 times per year 2005) and Ukraine (UA01) (8 times per year 2004). 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 Danube River and its tributaries in 2005. 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 also in Danube river and tributaries.

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in Danube River and its tributaries in 2005.

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	0.2	**30.0**	**9.2**	**17.2**	37/39	0.1	28.0	5.8	14.7
Suspended Solids	mg/l	38/60	< 0.5	**1413.0**	**6.1**	**171.5**	37/39	< 1	242.9	8.3	2110.0
Dissolved Oxygen	mg/l	40/68	**2.3**	**15.1**	**5.7**	**11.4**	37/39	4.1	16.4	7.1	12.2
BOD_5	mg/l	40/68	0.1	13.7	1.3	6.3	37/39	< 0.2	16.4	1.2	8.8
COD_{Mn}	mg/l	40/68	< 0.2	27.8	1.9	12.1	30/32	0.7	30.3	0.7	11.9
COD_{Cr}	mg/l	37/65	2.9	203.0	7.1	31.3	35/37	< 1	73.6	5.0	44.7
TOC	mg/l	14/16	0.7	9.8	2.1	4.8	13/13	0.9	11.0	1.4	7.2
DOC	mg/l	5/5	0.5	4.0	1.8	2.2	7/7	0.8	9.5	1.5	6.7
pH		40/68	6.2	8.8	7.4	8.3	37/39	6.8	8.8	6.8	8.2
Alkalinity	mmol/l	36/64	< 0.1	9.4	2.7	5.4	30/32	0.8	9.4	1.9	8.0
Ammonium-N	mg/l	40/68	< 0.004	3.900	0.015	0.519	37/39	< 0.004	2.400	0.010	1.211
Nitrite-N	mg/l	40/68	< 0.002	0.225	0.012	0.039	36/38	0.001	0.570	0.003	0.069
Nitrate-N	mg/l	40/68	< 0.1	4.700	0.600	3.400	38/40	0.02	8.59	0.59	6.95
Total Nitrogen	mg/l	22/34	0.60	4.90	1.40	2.90	24/24	0.40	10.60	0.80	9.10
Organic Nitrogen	mg/l	22/27	< 0.01	2.30	0.05	1.20	24/26	0.01	4.55	0.25	2.00
Ortho-Phosphate-P	mg/l	40/68	0.001	0.820	0.025	0.177	36/38	< 0.002	0.440	0.008	0.309
Total Phosphorus	mg/l	40/68	0.01	0.14	0.03	0.05	34/36	0.01	1.60	0.04	0.59
Total Phosphorus - Dissolved	mg/l	9/9	0.01	0.14	0.03	0.05	10/10	0.01	0.19	0.01	0.12
Chlorophyll-a	µg/l	30/51	< 0.1	7400.0	0.4	3081.8	15/17	< 1	214.0	1.8	66.4
Conductivity @ 20°C	µS/cm	38/66	222	790	339	622	37/39	< 20	1110	233	905
Calcium	mg/l	40/68	27.4	135.0	48.7	86.7	36/38	< 1	116.0	35.7	103.8
Sulphates	mg/l	38/66	4.5	108.0	17.3	86.7	33/35	5	187	14	152
Magnesium	mg/l	40/68	4.9	84.0	10.0	29.6	37/39	4.0	69.0	9.1	62.8
Potassium	mg/l	37/65	0.6	24.0	1.5	4.6	31/33	0.3	10.0	1.2	8.1
Sodium	mg/l	39/67	3.5	52.2	10.3	31.0	31/33	1.1	80.2	4.7	61.6
Manganese	mg/l	24/46	< 0.001	0.997	0.005	0.157	25/25	< 0.001	1.990	0.002	0.382
Iron	mg/l	26/50	< 0.010	12.800	0.048	1.368	20/20	0.004	61.000	0.004	3.170
Chlorides	mg/l	38/66	5.3	53.0	17.2	33.8	33/35	2.0	117.0	5.8	75.0
Macrozoobenthos- saprobic index		12/12	2.0	2.6	2.0	2.4	6/6	1.0	37.0	2.0	37.0
Macrozoobenthos - no.of taxa		4/4	15	42	15	42	13/13	2	3	2	3

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in Danube River and its tributaries in 2005. (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	26/29	< 0.8	124.0	1.7	36.0	16/16	< 1.6	68.0	2.8	33.3
Copper - Dissolved	µg/l	34/38	< 0.05	82.00	1.10	27.10	25/25	< 0.046	53.00	0.70	26.40
Chromium - Dissolved	µg/l	31/39	< 0.05	42.00	0.20	7.10	25/25	< 0.056	48.00	0.20	9.20
Lead - Dissolved	µg/l	32/40	< 0.05	6.60	0.20	2.10	25/25	0.05	21.00	0.20	< 3
Cadmium - Dissolved	µg/l	29/38	< 0.02	8.20	0.02	1.49	25/25	< 0.02	1.00	< 0.02	< 0.5
Mercury - Dissolved	µg/l	23/23	< 0,050	0.325	0.078	1.800	18/18	< 0.030	1.200	0.032	0.625
Nickel - Dissolved	µg/l	31/39	0.05	30.00	0.70	4.70	25/25	< 0.045	60.00	1.00	6.13
Arsenic - Dissolved	µg/l	23/23	0.41	11.10	0.70	2.10	19/19	< 0.05	6.40	0.43	3.10
Aluminium - Dissolved	µg/l	12/12	2.7	223.0	15.3	63.5	9/9	< 0,8	1660.0	5.5	188.5
Zinc	µg/l	29/51	< 1	374.0	6.4	80.0	19/19	< 1	271.0	3.5	78.2
Copper	µg/l	29/51	0.37	70.00	1.00	17.50	23/23	< 0.046	69.00	0.88	18.70
Chromium - total	µg/l	26/48	0.09	52.50	0.33	< 10	22/22	< 0.004	48.70	< 0.004	< 10
Lead	µg/l	27/49	< 0.05	29.60	0.94	5.33	19/19	< 0.05	26.30	0.69	6.71
Cadmium	µg/l	27/50	< 0.02	148.30	0.04	9.73	19/19	< 0.01	18.20	0.02	2.60
Mercury	µg/l	22/39	< 0.025	21.000	0.200	1.300	18/18	< 0.030	1.100	< 0.030	0.218
Nickel	µg/l	27/49	0.16	37.42	1.00	8.18	23/23	< 0.004	70.00	< 0.004	11.58
Arsenic	µg/l	17/21	0.45	9.00	0.90	2.69	12/12	0.30	25.30	0.57	0.44
Aluminium	µg/l	14/18	< 20,0	4640.0	67.7	1278.8	10/10	3.7	36500.0	85.9	4731.0
Phenol index	mg/l	38/66	< 0.001	0.117	< 0.001	< 0.020	30/32	< 0.001	0.400	< 0.001	0.049
Anionic active surfactants	mg/l	38/66	< 0.006	0.875	< 0.010	0.127	28/30	< 0.006	0.315	< 0.010	0.133
AOX	µg/l	9/11	5.4	58.0	8.8	26.5	7/7	3.0	130.0	8.5	78.8
Petroleum hydrocarbons	mg/l	34/54	< 0.002	24.700	< 0,005	5.490	27/27	< 0.002	11.760	< 0.005	2.989
PAH (sum of 6)	µg/l	3/3	< 0.1	< 0.1	< 0.1	< 0.1	2/2	< 0.005	0.174	< 0.005	0.174
PCB (sum of 7)	µg/l	0/0					2/2	< 0.002	< 0.002	< 0.002	< 0.002
Lindane	µg/l	28/46	< 0.001	0.113	< 0.001	< 0.1	25/25	< 0.001	0.064	< 0.002	< 0.1
pp´DDT	µg/l	29/49	< 0.001	0.190	< 0.001	< 0.1	24/24	< 0.0001	0.106	< 0.002	0.078
Atrazine	µg/l	29/47	< 0.001	0.524	0.009	0.093	20/20	< 0.001	0.532	0.009	0.175
Chloroform	µg/l	18/20	< 0.01	9.30	0.01	5.55	12/12	< 0.01	13.20	< 0.01	7.50
Carbon tetrachloride	µg/l	16/19	< 0.01	1.20	0.01	0.01	12/12	< 0.01	1.20	< 0.01	1.20
Trichloroethylene	µg/l	17/19	< 0.01	3.20	< 0.02	1.70	11/11	< 0.01	5.10	< 0.01	1.70
Tetrachloroethylene	µg/l	17/19	< 0.01	2.10	< 0.02	2.10	12/12	< 0.01	2.20	< 0.02	< 2.1
Total Coliforms (37°C)	10^3 CFU/ 100 ml	30/53	0.01	2250.00	0.68	538.40	18/20	0.02	7200.00	1.96	1304.80
Faecal Coliforms (44°C)	10^3 CFU/ 100 ml	20/42	0.004	70.00	0.19	36.10	14/16	0.04	4500.00	0.14	912.20
Faecal Streptococci	10^3 CFU/ 100 ml	22/48	0.003	80.00	0.006	15.20	12/14	0.01	180.00	0.12	47.23

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in Danube River and its tributaries in 2005 (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	26/29	< 0.8	124.0	1.7	36.0	16/16	< 1.6	68.0	2.8	33.3
Copper - Dissolved	µg/l	34/38	< 0.05	82.00	1.10	27.10	25/25	< 0.046	53.00	0.70	26.40
Chromium - Dissolved	µg/l	31/39	< 0.05	42.00	0.20	7.10	25/25	< 0.056	48.00	0.20	9.20
Lead - Dissolved	µg/l	32/40	< 0.05	6.60	0.20	2.10	25/25	0.05	21.00	0.20	< 3
Cadmium - Dissolved	µg/l	29/38	< 0.02	8.20	0.02	1.49	25/25	< 0.02	1.00	< 0.02	< 0.5
Mercury - Dissolved	µg/l	23/23	< 0,050	0.325	0.078	1.800	18/18	< 0.030	1.200	0.032	0.625
Nickel - Dissolved	µg/l	31/39	0.05	30.00	0.70	4.70	25/25	< 0.045	60.00	1.00	6.13
Arsenic - Dissolved	µg/l	23/23	0.41	11.10	0.70	2.10	19/19	< 0.05	6.40	0.43	3.10
Aluminium - Dissolved	µg/l	12/12	2.7	223.0	15.3	63.5	9/9	< 0,8	1660.0	5.5	188.5
Zinc	µg/l	29/51	< 1	374.0	6.4	80.0	19/19	< 1	271.0	3.5	78.2
Copper	µg/l	29/51	0.37	70.00	1.00	17.50	23/23	< 0.046	69.00	0.88	18.70
Chromium - total	µg/l	26/48	0.09	52.50	0.33	< 10	22/22	< 0.004	48.70	< 0.004	< 10
Lead	µg/l	27/49	< 0.05	29.60	0.94	5.33	19/19	< 0.05	26.30	0.69	6.71
Cadmium	µg/l	27/50	< 0.02	148.30	0.04	9.73	19/19	< 0.01	18.20	0.02	2.60
Mercury	µg/l	22/39	< 0.025	21.000	0.200	1.300	18/18	< 0.030	1.100	< 0.030	0.218
Nickel	µg/l	27/49	0.16	37.42	1.00	8.18	23/23	< 0.004	70.00	< 0.004	11.58
Arsenic	µg/l	17/21	0.45	9.00	0.90	2.69	12/12	0.30	25.30	0.57	0.44
Aluminium	µg/l	14/18	< 20,0	4640.0	67.7	1278.8	10/10	3.7	36500.0	85.9	4731.0
Phenol index	mg/l	38/66	< 0.001	0.117	< 0.001	< 0.020	30/32	< 0.001	0.400	< 0.001	0.049
Anionic active surfactants	mg/l	38/66	< 0.006	0.875	< 0.010	0.127	28/30	< 0.006	0.315	< 0.010	0.133
AOX	µg/l	9/11	5.4	58.0	8.8	26.5	7/7	3.0	130.0	8.5	78.8
Petroleum hydrocarbons	mg/l	34/54	< 0.002	24.700	< 0,005	5.490	27/27	< 0.002	11.760	< 0.005	2.989
PAH (sum of 6)	µg/l	3/3	< 0.1	< 0.1	< 0.1	< 0.1	2/2	< 0.005	0.174	< 0.005	0.174
PCB (sum of 7)	µg/l	0/0					2/2	< 0.002	< 0.002	< 0.002	< 0.002
Lindane	µg/l	28/46	< 0.001	0.113	< 0.001	< 0.1	25/25	< 0.001	0.064	< 0.002	< 0.1
pp´DDT	µg/l	29/49	< 0.001	0.190	< 0.001	< 0.1	24/24	< 0.0001	0.106	< 0.002	0.078
Atrazine	µg/l	29/47	< 0.001	0.524	0.009	0.093	20/20	< 0.001	0.532	0.009	0.175
Chloroform	µg/l	18/20	< 0.01	9.30	0.01	5.55	12/12	< 0.01	13.20	< 0.01	7.50
Carbon tetrachloride	µg/l	16/19	< 0.01	1.20	0.01	0.01	12/12	< 0.01	1.20	< 0.01	1.20
Trichloroethylene	µg/l	17/19	< 0.01	3.20	< 0.02	1.70	11/11	< 0.01	5.10	< 0.01	1.70
Tetrachloroethylene	µg/l	17/19	< 0.01	2.10	< 0.02	2.10	12/12	< 0.01	2.20	< 0.02	< 2.1
Total Coliforms (37°C)	10^3 CFU/ 100 ml	30/53	0.01	2250.00	0.68	538.40	18/20	0.02	7200.00	1.96	1304.80
Faecal Coliforms (44°C)	10^3 CFU/ 100 ml	20/42	0.004	70.00	0.19	36.10	14/16	0.04	4500.00	0.14	912.20
Faecal Streptococci	10^3 CFU/ 100 ml	22/48	0.003	80.00	0.006	15.20	12/14	0.01	180.00	0.12	47.23

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 for the presentation to be shown by maps and charts 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) or – in case of group of heavy metals and organic micropollutants – to illustrate only a few selected determinands from these groups.

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.

With purpose to illustrate the share of locations fulfilling requirements on target value (corresponding to class I and II) and of those on the non-complying site, Figures 6.10 – 6.20 show percentage of monitoring locations in water quality classes. 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 activites 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 2005 was 85 % of locations in the Danube River in class I and II. This is less than in 2004, when 95 % of locations in the Danube was in class I and II. From locations in tributaries 79 % could be classified by class I and II and the worst class III were represented by 18 % of locations (see also Figure 6.10). This situation in 2005 is better than in 2004, were 8 % classes IV and V were classified. But in 2004 84 % locations in tributaries was classified by class I and II, this is a little bit more than in year 2005.

BOD_5 is used as an indicator of biodegradable organic pollution in waters. The share of locations satisfying target value for BOD_5 in 2005 is 83 % of locations in the Danube River corresponded to class I and II. This is less than in 2004, when 100 % of locations in the Danube was in class I and II. From locations in tributaries 84 % could be classified by class I and II and the class III by 11 % of locations (see also Figure 6.11). This situation is better than in year 2004, when 65 % was in I and II class and 18 % in III class. But in 2005 there was observed also 3 % in IV class in tributaries and in 2004 there not observed IV class.

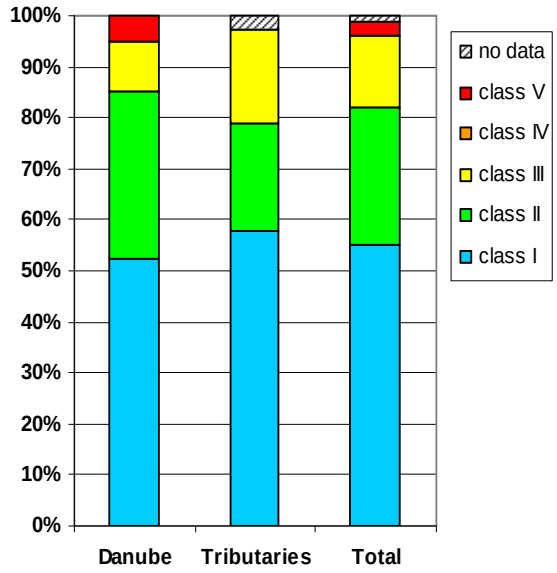


Figure 6.10: Distribution of water quality classes for dissolved oxygen.

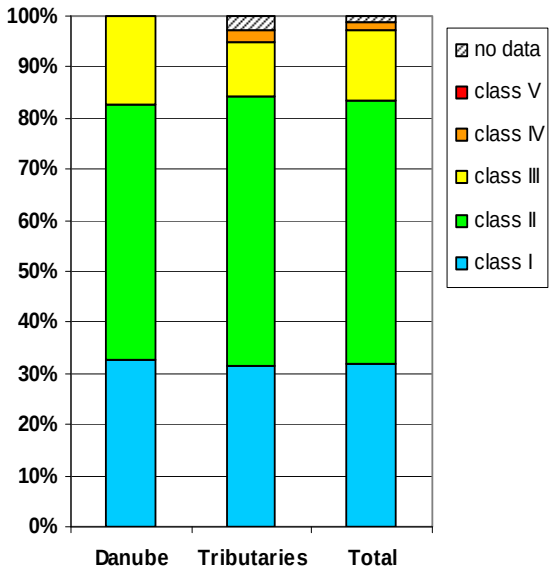


Figure 6.11: Distribution of water quality classes for BOD_5.

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 15 % of all monitoring locations. In 2005, 73 % of locations in Danube River and 58 % of locations in tributaries in class I and II the results of classification are similar to situation in year 2004. In class IV are not any of locations in Danube River and 5.3 % of locations in tributaries. In year 2004 there were one location in class IV in the Danube River and 2 in tributaries like in year 2005 (see Figure 6.12).

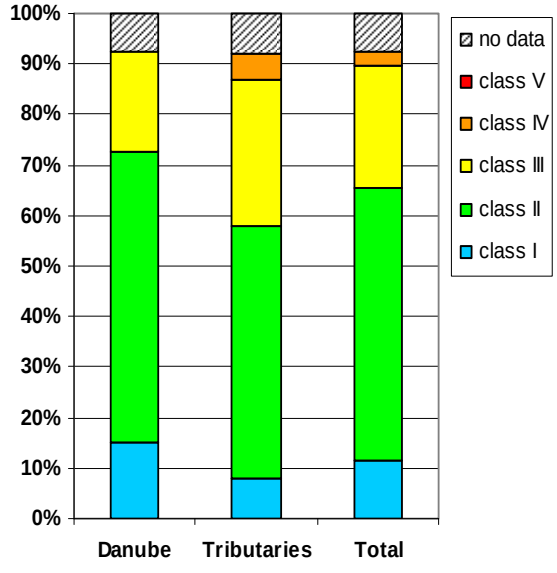


Figure 6.12: Distribution of water quality classes for$COD_{Cr.}$

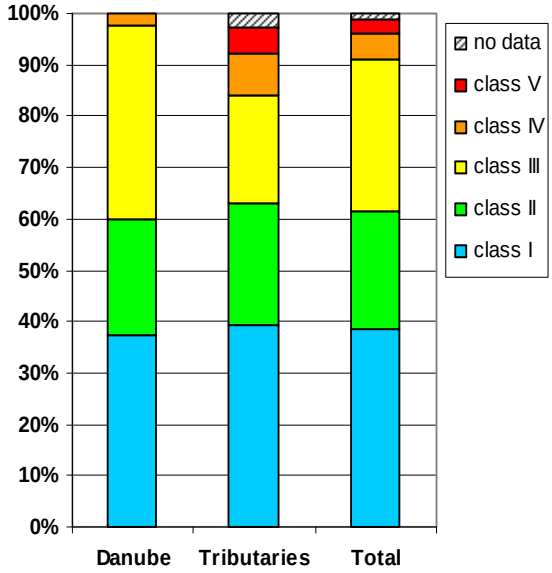


Figure 6.13: Distribution of water quality classes forAmmonium-N.

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 2005 concentrations of ammonium-N corresponded to class I and II in 68 % of locations in Danube River and 63 % of locations in tributaries. This is comparable with classification in 2004. In Danube River, 38 % of locations corresponded to class III and 3 % to class IV. In tributaries all five classes were represented, with 8 % in class III, 6 % in class IV and 3 % in the class V.

Figure 6.14 shows the distribution of water quality classes for nitrate-N in Danube River and tributaries. In 2005 there was not any of Danube locations representing class I from those included in TNMN, class II was observed in 73 % of locations. An exceeding of the target value was observed in 28 % of locations, corresponding to class III.
From locations on tributaries, 87 % of them satisfied target value with vast majority in class II (79 %) and only 8 % in class I, situation is similar as in 2004. The rest of locations belonged to either class III (11 %) or class IV (3 %).

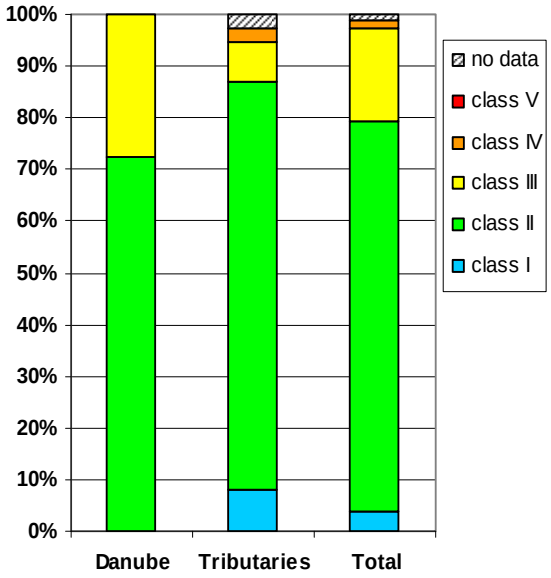


Figure 6.14: Distribution of water quality classes for Nitrate-N.

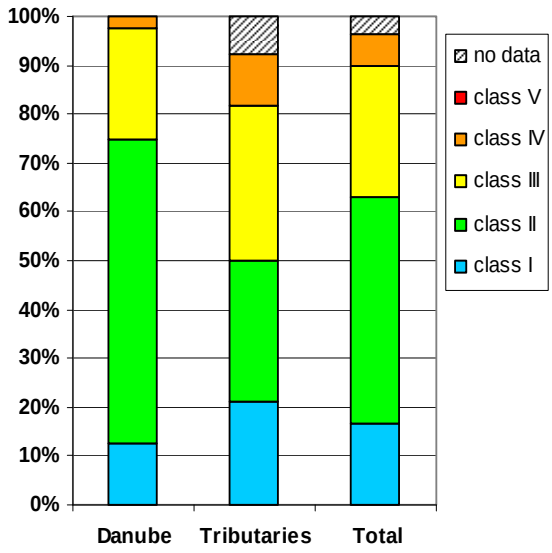


Figure 6.15: Distribution of water quality classes for Ortho-phosphate-P.

Regarding ortho-phosphate-P, from the Figure 6.15 can be seen that in the Danube River classes I-IV and in tributaries classes I-IV were represented. A situation in the Danube River is comparable in years 2004 and 2005 75 % of locations satisfying target value (in 2004 it was 68 %). The situations of ortho-phosphate-P in tributaries in year 2005 are better than in 2004, 50 % of locations corresponding to class I and II, 32 % to class III, and 11 % in classes IV. In 2005 there were no locations representing class V.

In 2005, 68 % of locations in Danube River deteminad Ptotal corresponded to class I and II, whilst class III had been represented by 28 %. In 2005 there were 5 % of Danube River locations representing class IV. These situation is a litle bit worse than results observed in Danube River in 2004.
Tributaries indicate worse quality, with only 37 % of locations satisfying the target value. The rest of locations corresponded to class III (37 %), class IV (16 %). (see Figure 6.16). These results are comparable with those observed in Danube River in 2004.

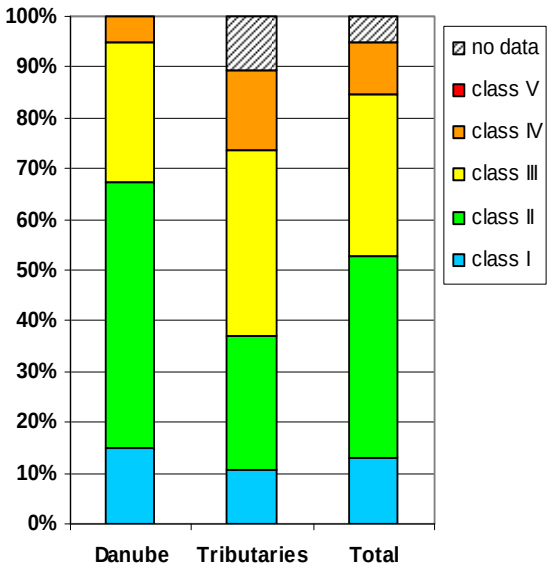


Figure 6.16: Distribution of water quality classes for $P_{total.}$

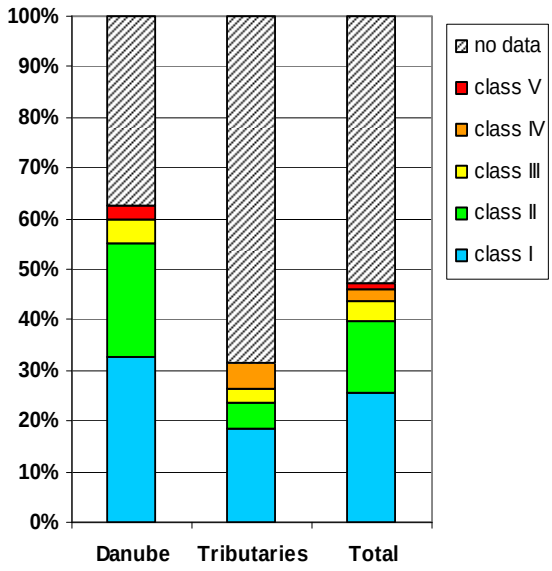


Figure 6.17: Distribution of water quality classes for Chlorophyll-a.

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 not even half of the locations from TNMN possesses this information. Therefore it can not be expected that classification results shown in figure 6.17 could give representative picture. Anyhow, class I and II were observed in 55 % of locations in Danube River and 24 % of locations in tributaries. In Danube river 5 % in tributaries 3 % was classified in class III, but in tributaries was 5 % of locations in class IV.

Classification of heavy metals was also affected by high proportion of locations without their measurements. In Danube River, data on cadmium, chromium, copper, zinc, nickel and lead content are missing in 28-33 % of locations, concentration of mercury and arsenic were missing in 48 % and 58 % of locations, respectively.
Similar picture is in tributaries, with 40- 66 % of locations without data on cadmium, chromium, copper, zinc, nickel and lead and 53 % of locations without mercury and 68 % without arsenic analysis.
In the Danube River, class II was achieved in the following percentage of locations: 55 % for cadmium, 58 % for copper, 70 % for zinc, 35 % for mercury, 43 % for arsenic, 43 % for lead, 65 % for chromium and 68 % for nickel.
Regarding tributaries, the percentage satisfying target value represented by class II is the following: 40 % for cadmium, 32 % for mercury, 58 % for chromium, 50 % for copper, 42 % for zinc, 61 % for nickel, 29 % for arsenic and 37 % for lead.
These situation is similar than results observed in Danube River and tributaries 2004. In whole TNMN locations for chromium, nickel and arsenic were observed only class II, for copper, cadmium, zinc, lead and mercury class III and IV were observed.

From the group of heavy metals cadmium has been selected for presentation and is shown in Figure 6.18.

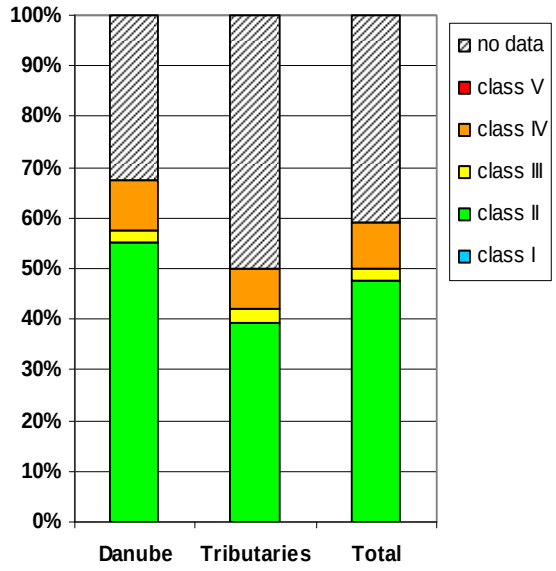


Figure 6.18: Distribution of water quality classes for Cadmium.

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 and 42 % of location in tributaries. The rest of locations in the Danube River are in class IV and V (20 %) and in tributaries 8 % are in class III and 3 % in IV. These results are similar than in year 2004. In 2005 42 % of TNMN locations are without p,p-DDT data. 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 55 % of locations corresponded to class I – II, 5 % to class III and 18 % to class IV in the Danube River, 23 % of locations are without data. The non-completeness of data is even more significant in tributaries, with 45 % corresponded to class I and II, and 8 % to classes III-IV. In 2005 the percentage of TNMN locations without atrazine data was 35 %.

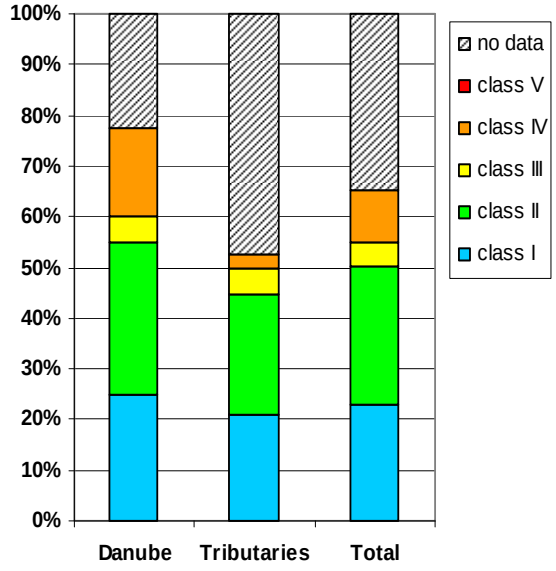


Figure 6.20: Distribution of water quality classes for Atrazine.

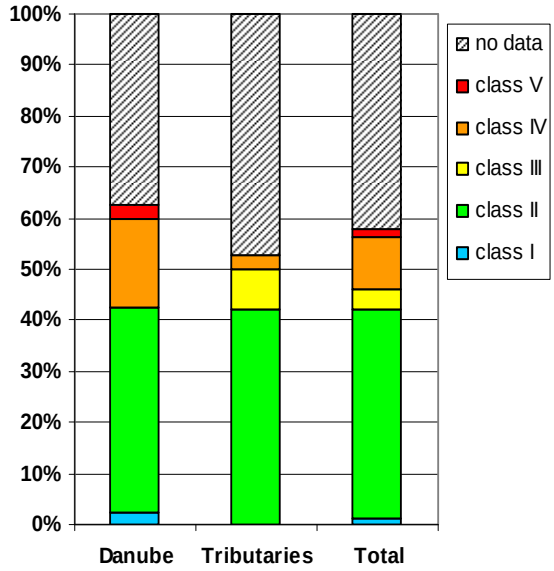


Figure 6.19: Distribution of water quality classes for p,p-DDT.

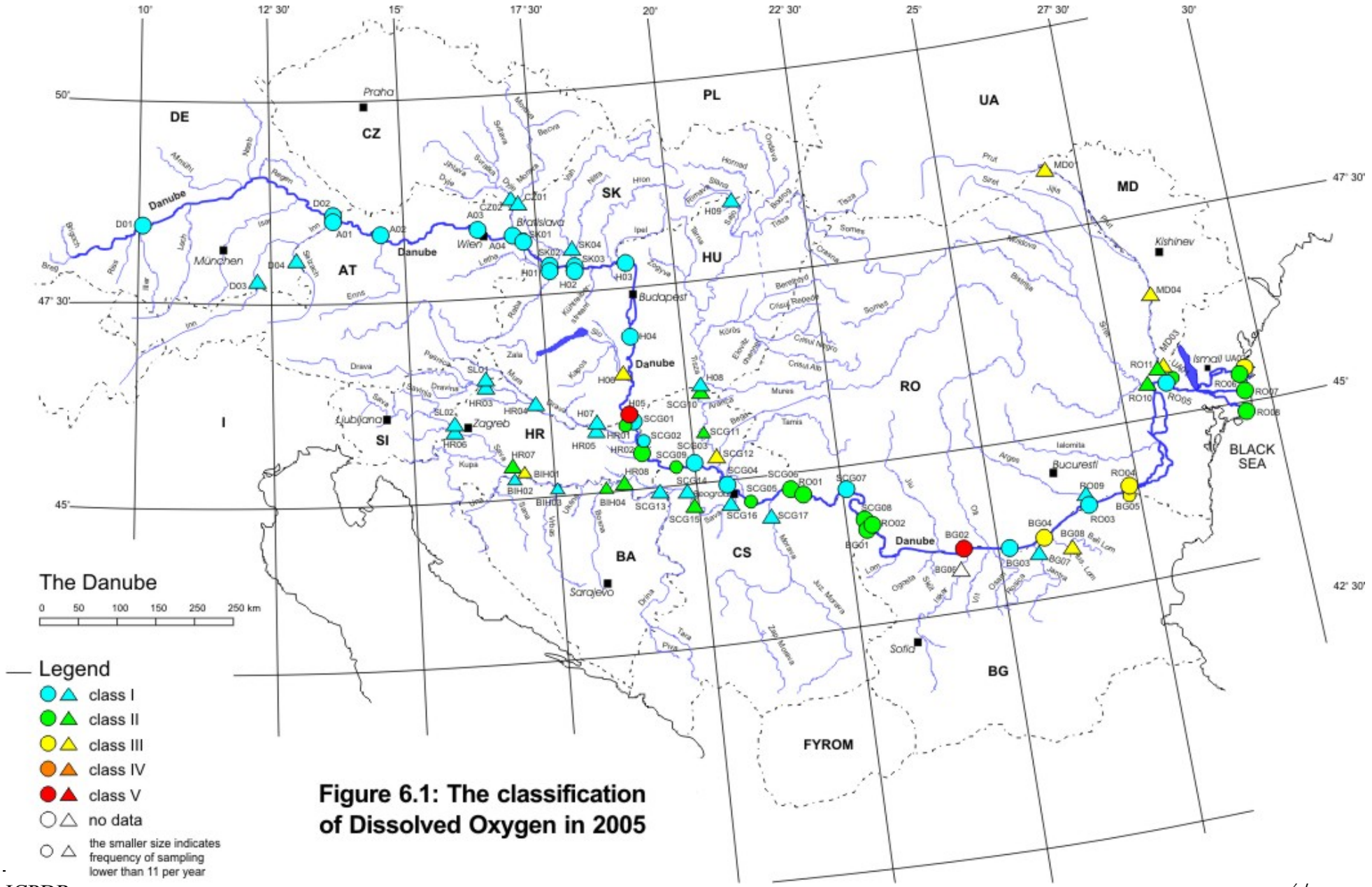


Figure 6.1: The classification of Dissolved Oxygen in 2005

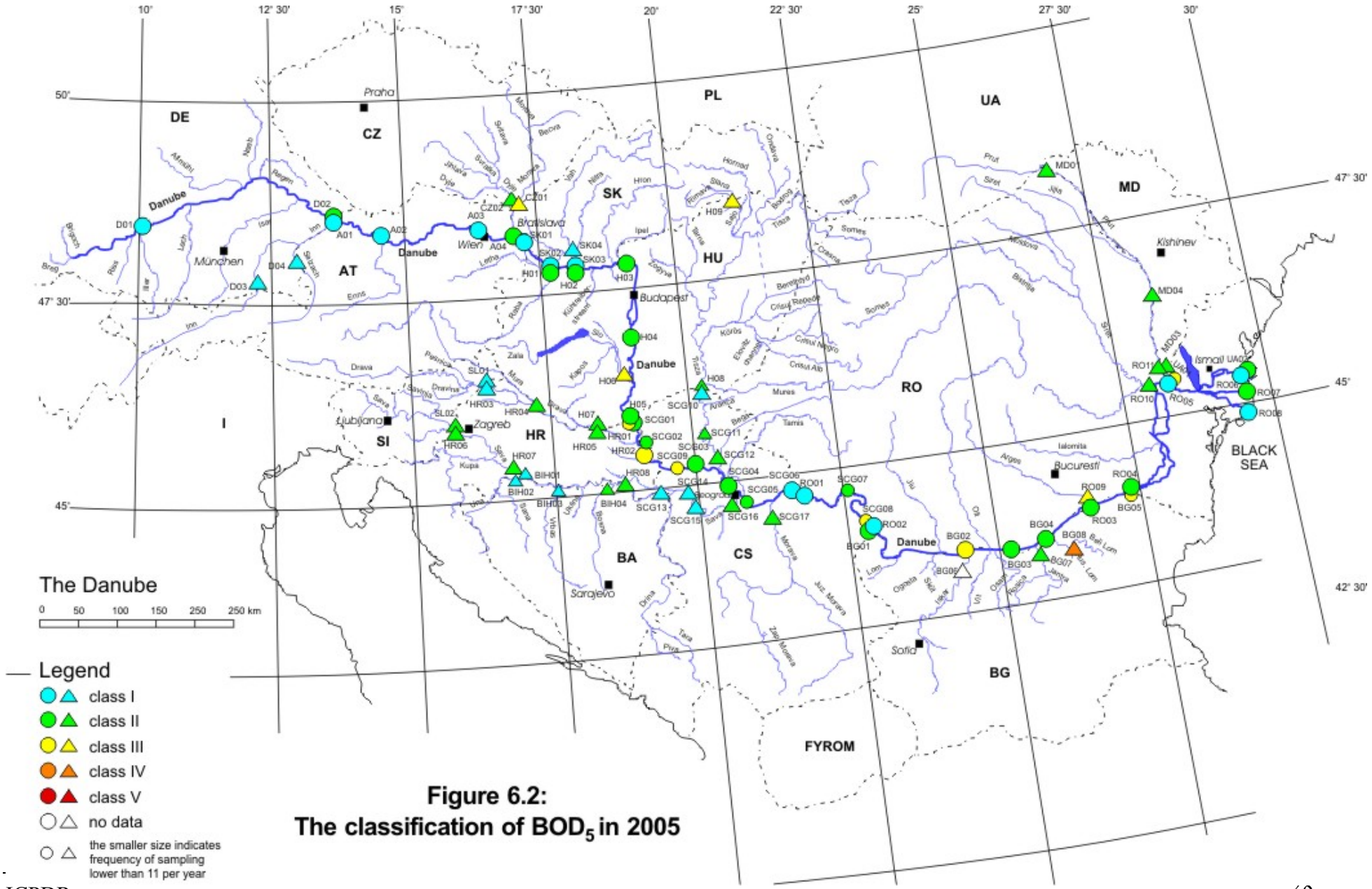


Figure 6.2:
The classification of BOD_5 in 2005

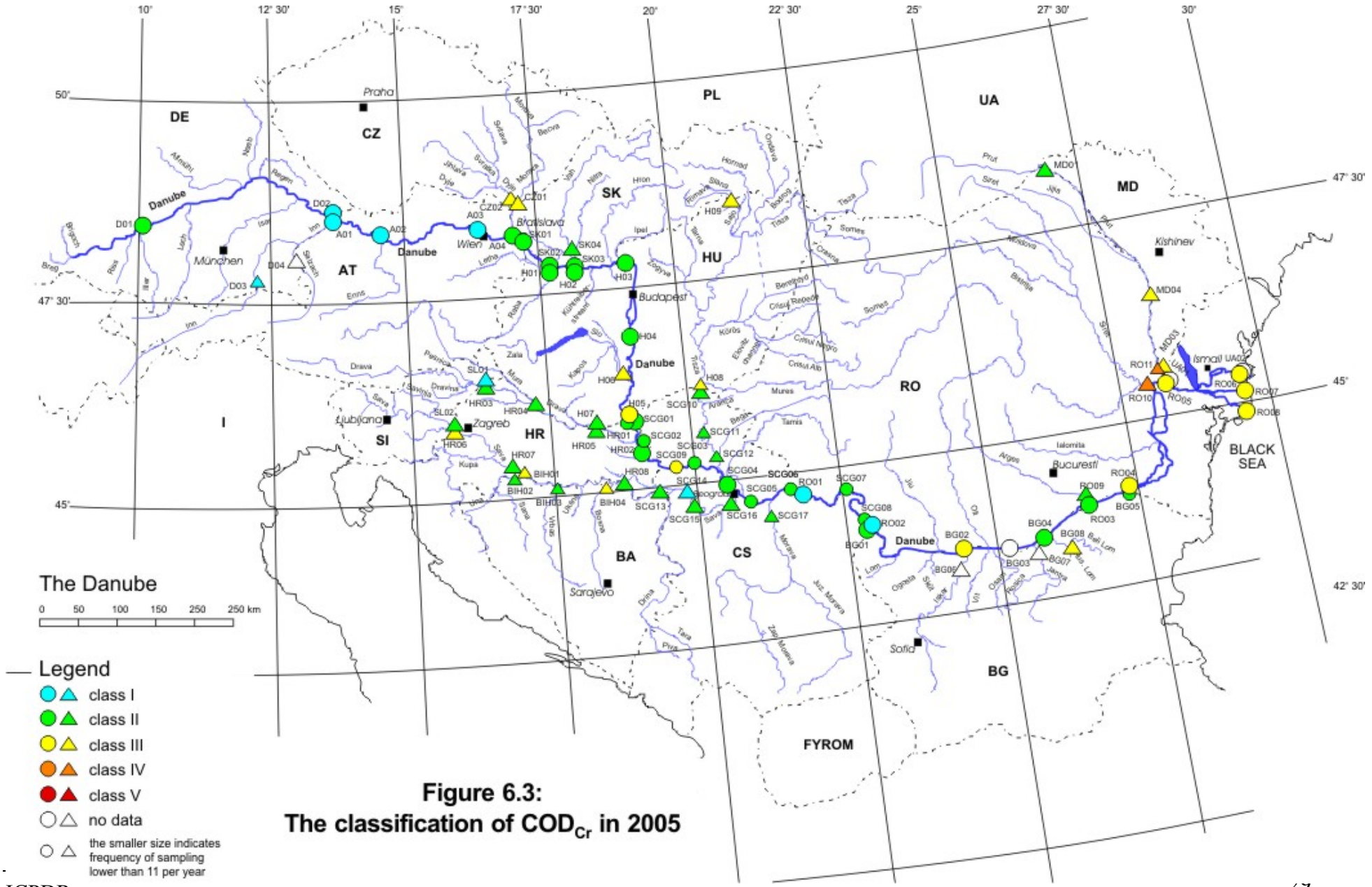


Figure 6.3:
The classification of COD_{Cr} in 2005

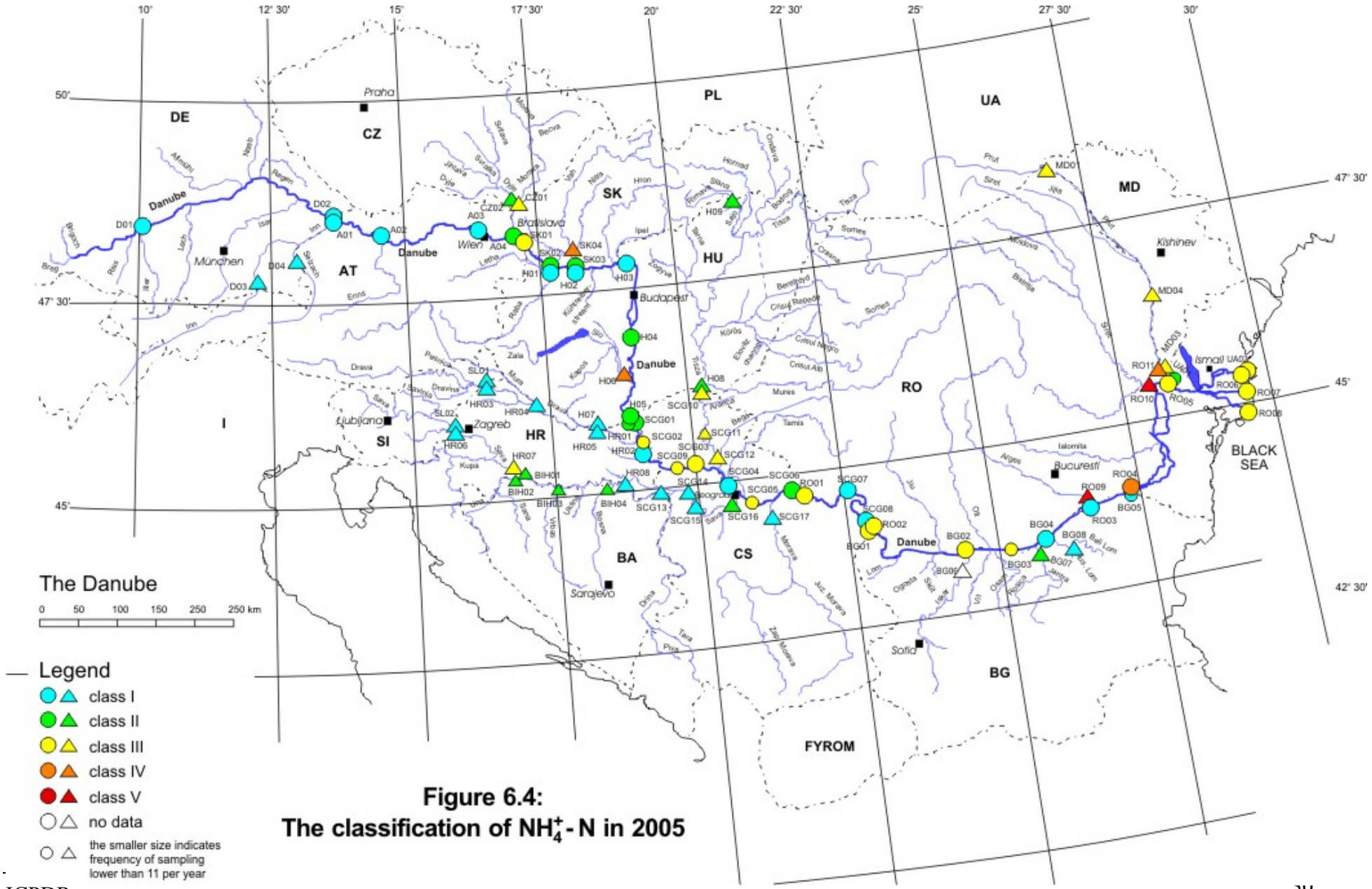


Figure 6.4:
The classification of NH_4^+-N in 2005

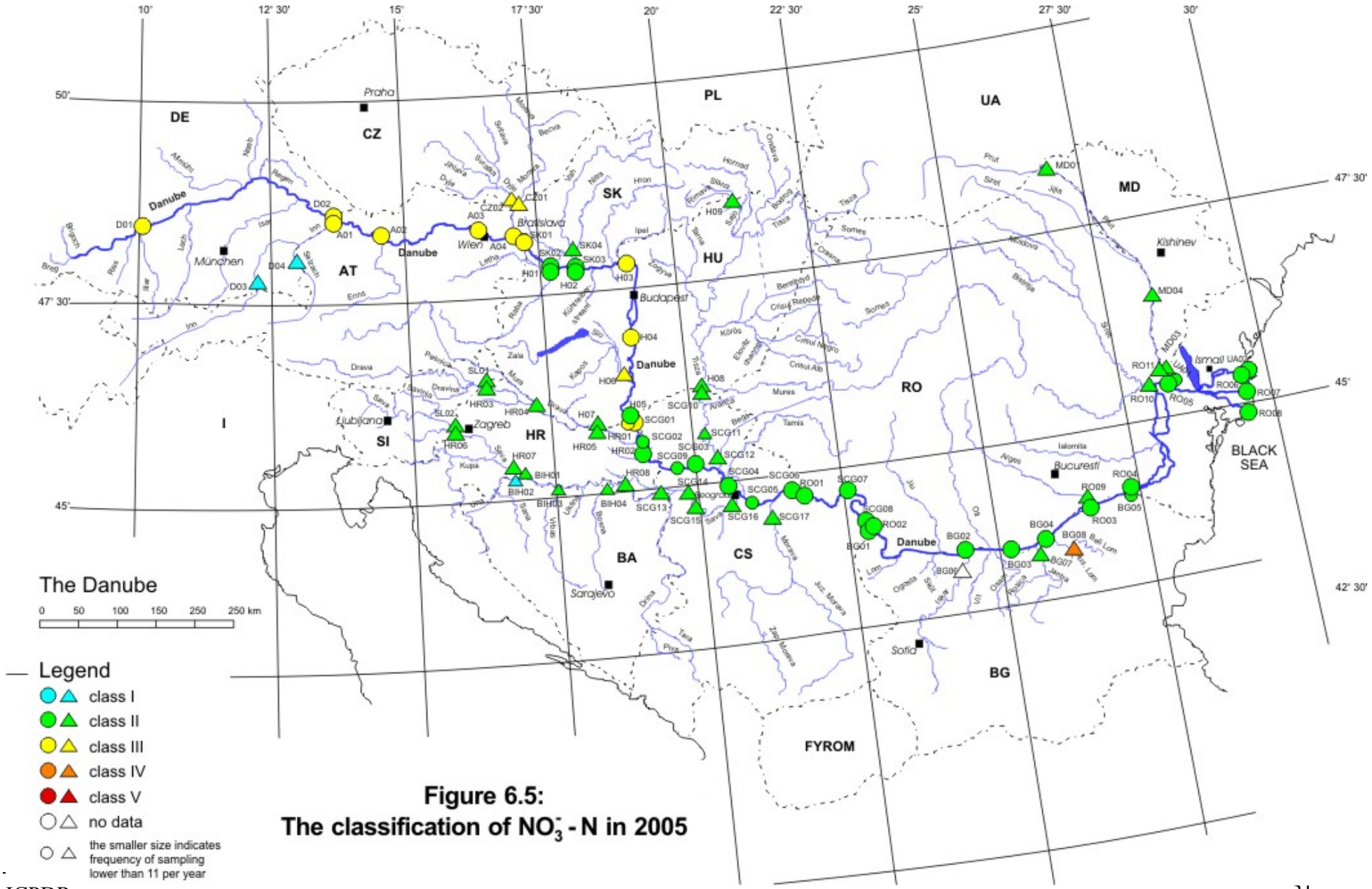


Figure 6.5:
The classification of NO_3^- - N in 2005

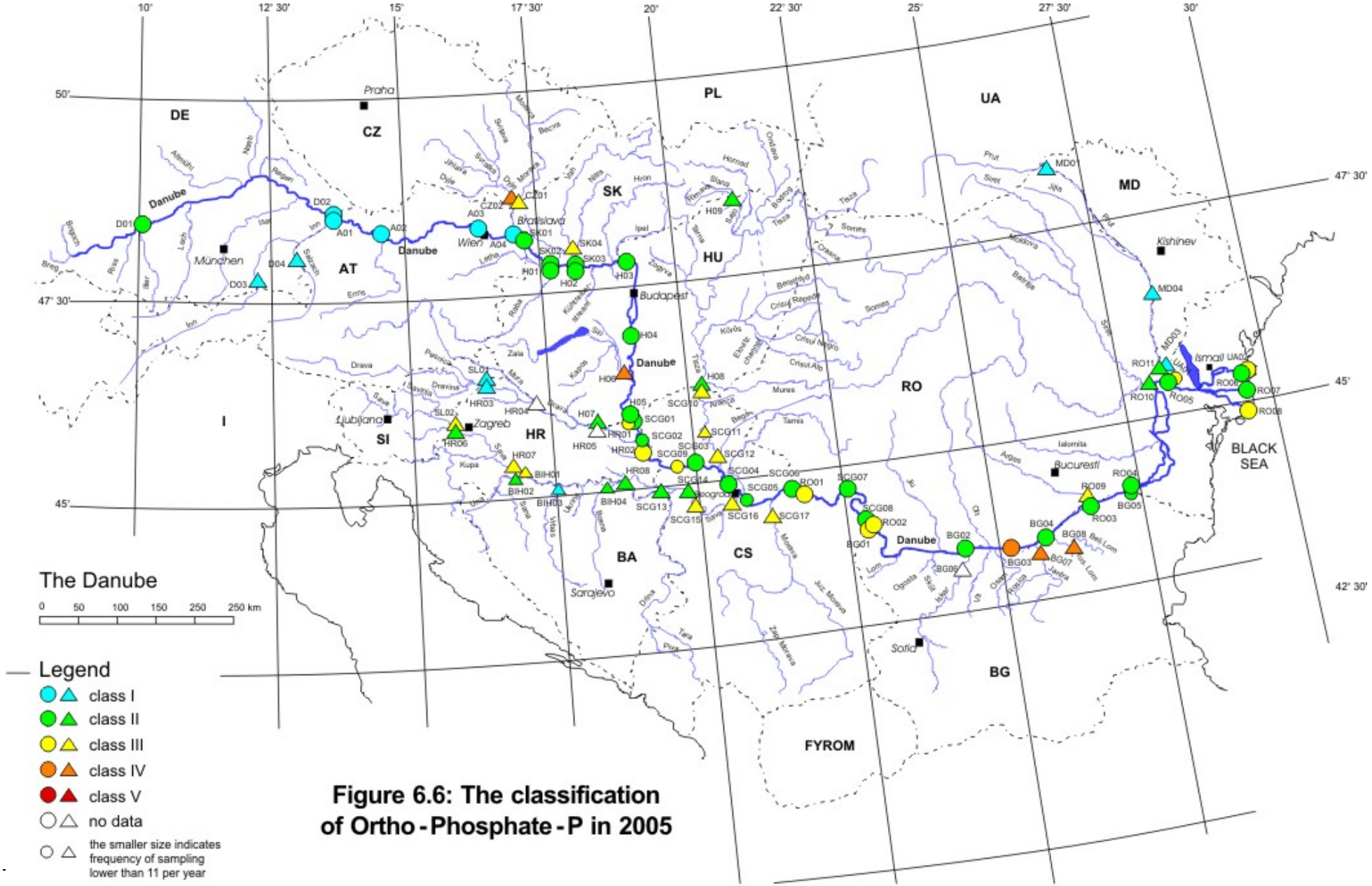


Figure 6.6: The classification of Ortho-Phosphate-P in 2005

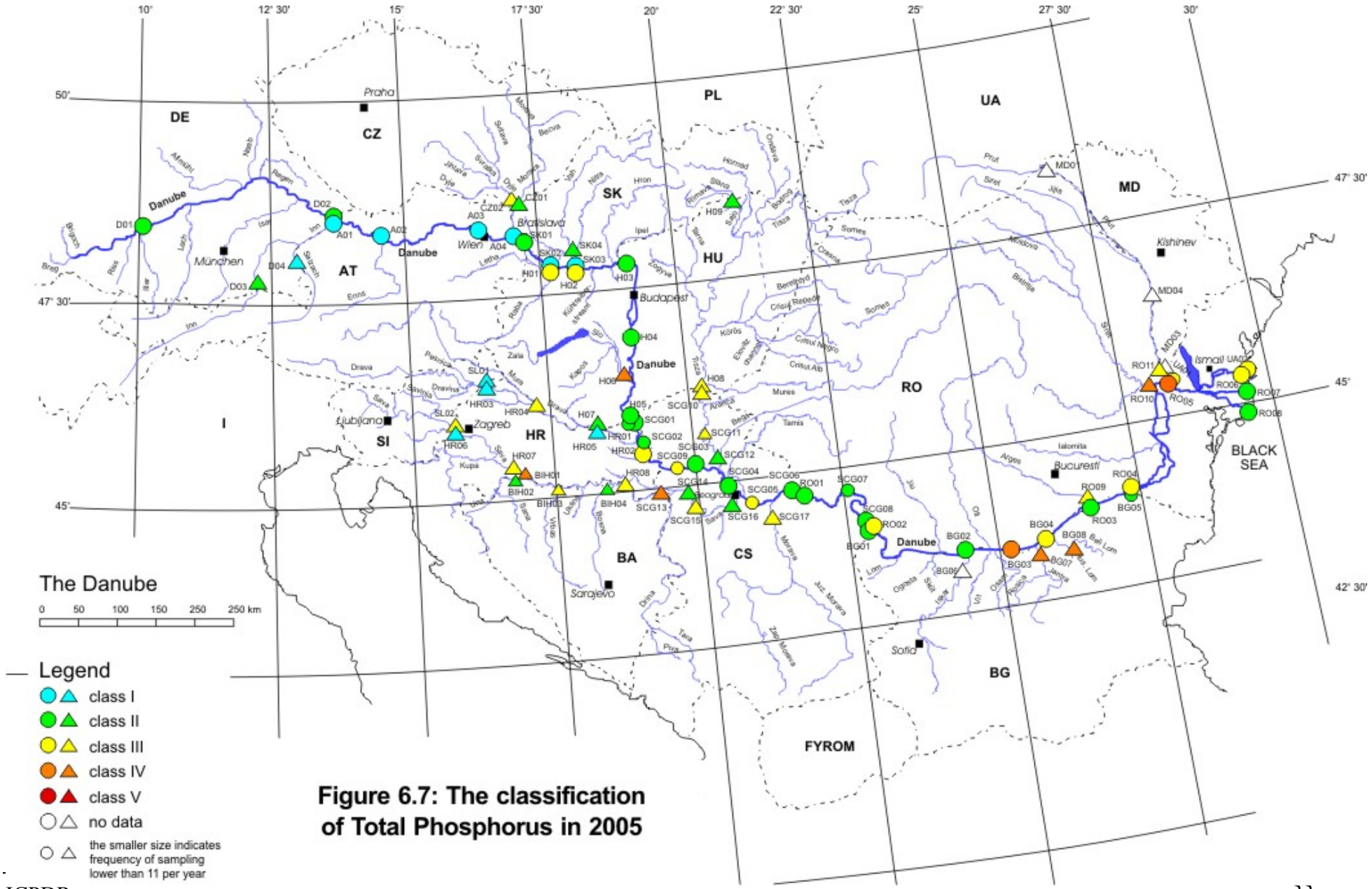


Figure 6.7: The classification of Total Phosphorus in 2005

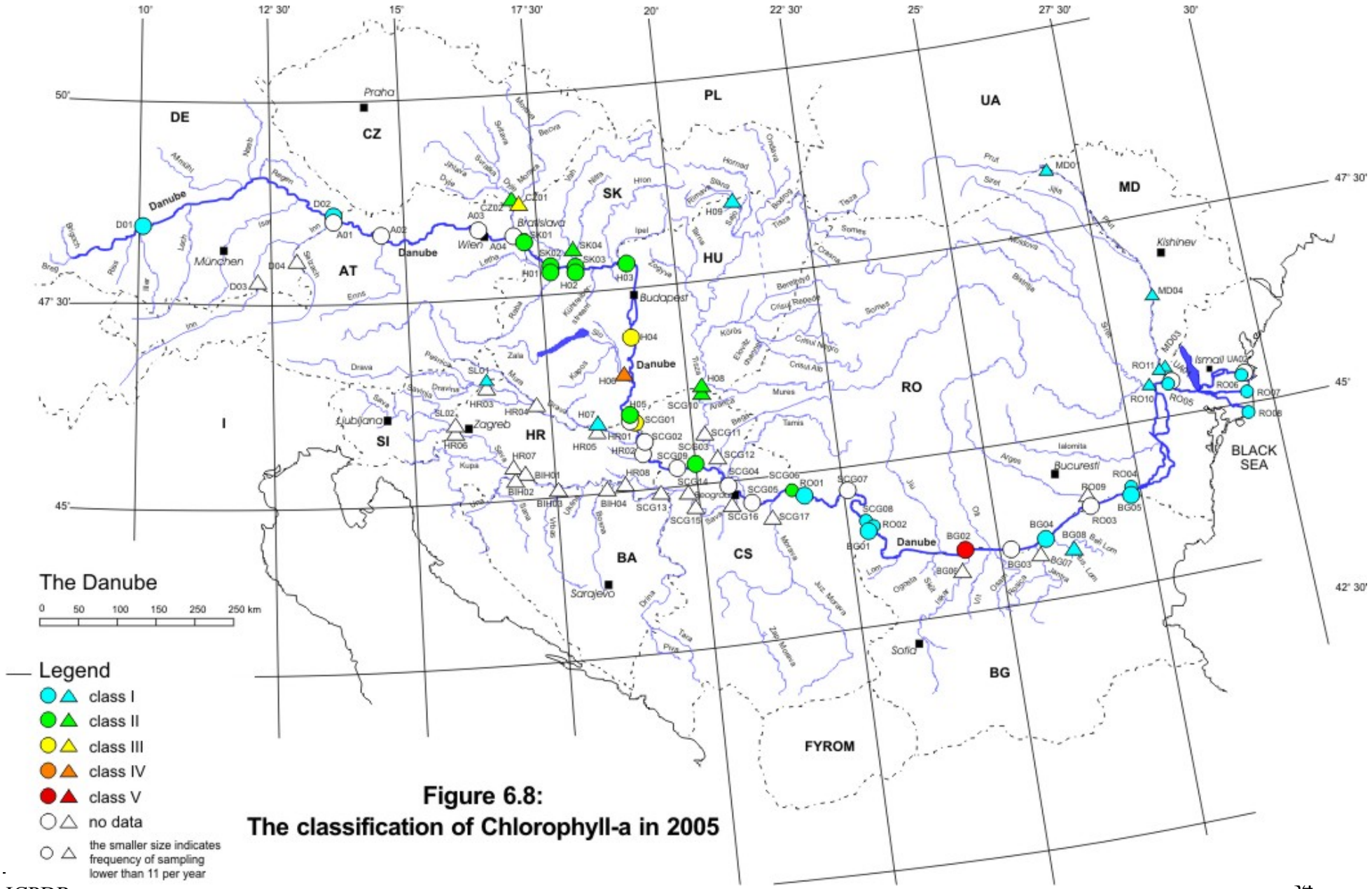


Figure 6.8:
The classification of Chlorophyll-a in 2005

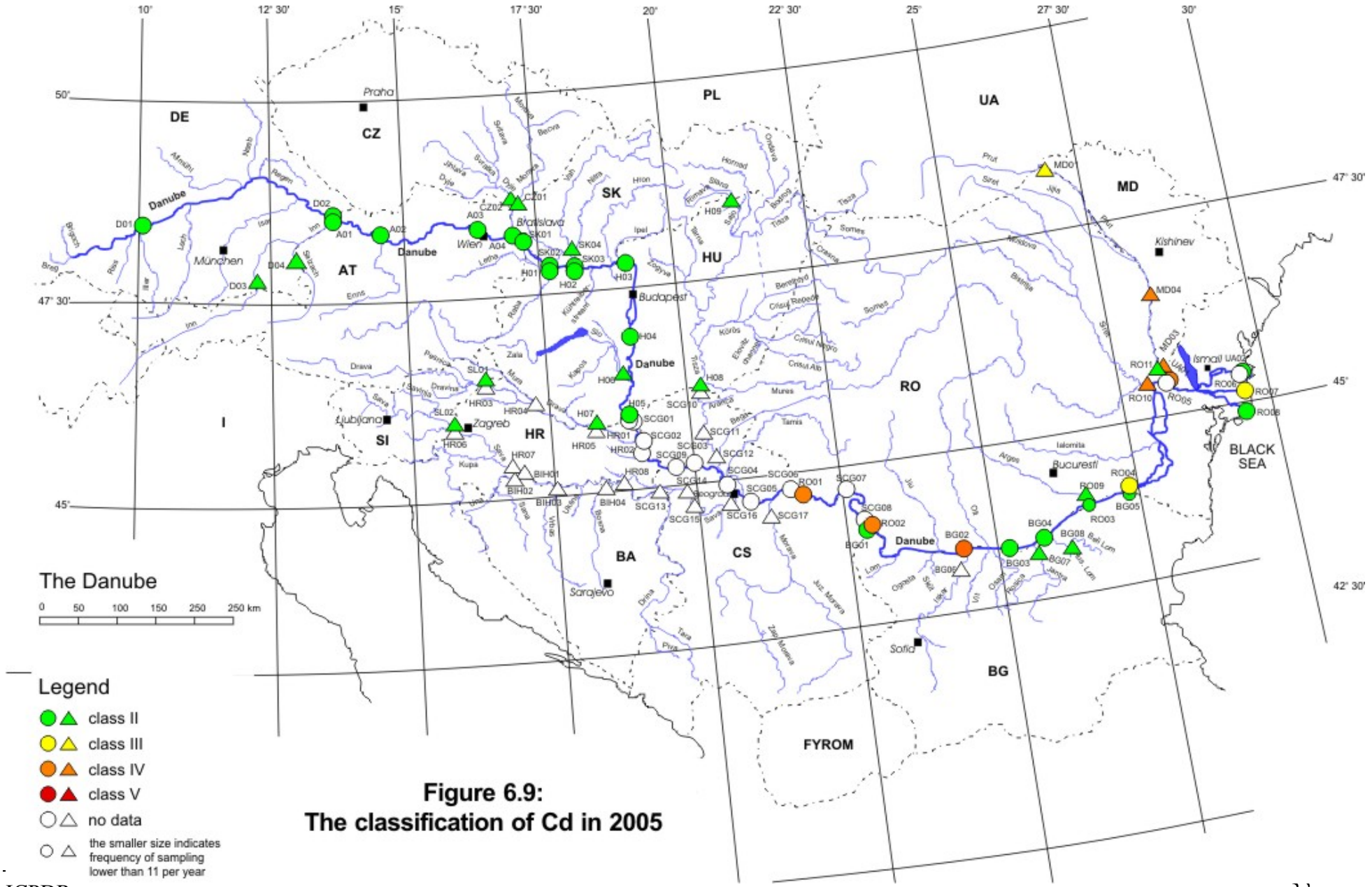


Figure 6.9:
The classification of Cd in 2005

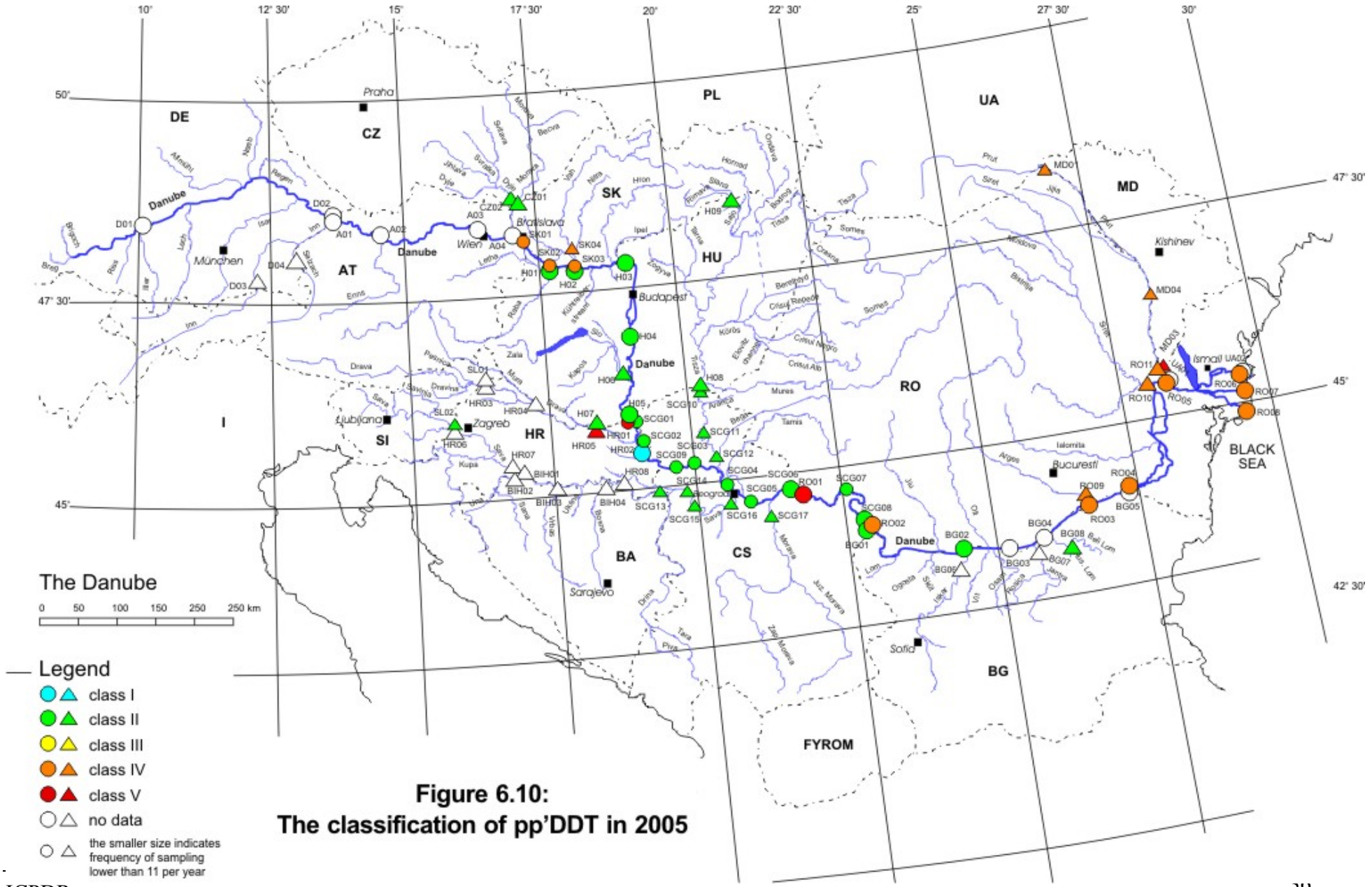


Figure 6.10:
The classification of pp'DDT in 2005

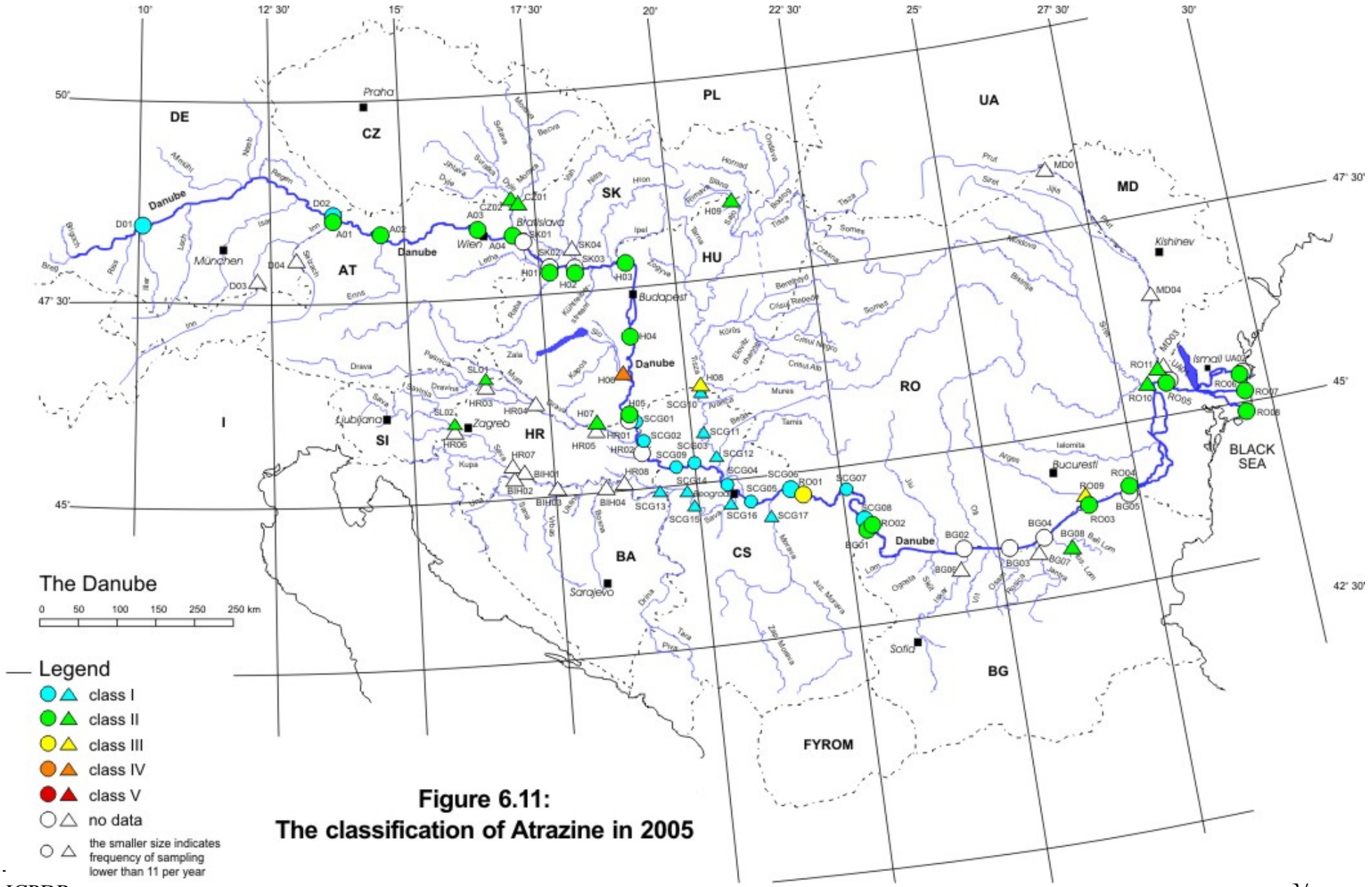


Figure 6.11:
The classification of Atrazine in 2005

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 the 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 in the respective year.

Regarding the spatial pattern of water quality along the Danube River in 2005, the highest content of biodegradable organic matter was observed in the middle part of the river, whilst 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 2005 were Russenski Lom, Sio, Arges, Jantra. In case of nutrients there were more tributaries considered rather polluted in 2005 – Prut, Arges, Russenski Lom, Sio , Morava and Dyje, Vah.

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 Austrian parts, in Slovakian section of Danube River and in some parts of lower Danube section (Bazias, Pristol, Ren-Chilia and mouth). Tributary Dyje has decreasing tendency, tribunaries of Inn, Drava and Arges show a little increasing in year 2005.
As for the nutrients, ammonium-N decreases in locations of the upper part of Danube River in Germen and Austrian part, in Slovak and down to (H04) concentration of ammonium was decreased. In the middle part of Danube some increasing and lower part decreasing and situation without big changes were observed. In tributaries ammonium decreases in the upper section down to river Vah (Inn, Salzach, Morava, Dyje) and further in Sava, Arges and Siret. Significant decrease is apparent also in Danube-Silistra/Chiciu (BG05), but this observation is not supported by Romanian data at the same monitoring location.

Nitrate-N content is more stable in locations during the years than the content of other determinands representing nutrient content. It decreases in several locations of German, Austrian and Slovakian part of the Danube River and at Danube-us.Arges (RO3).

Nitrate-N decreases or the same concentration level was in tributaries Morava, Dyje, Vah, Sio and some parts of Drava.
Decreasing tendency of ortho-phosphate-P is observed at Slovak-Hungarian section of the Danube River and further in Danube at Silistra/Chiciu, downstream Svishtov and us. Russe. An improvement can be seen also in tributaries like Iskar, Morava, Dyje, Jantra, Russenski Lom, Arges and Siret.
P total decreases in locations of the upper part of Danube River in Austrian part and in locations and Downstream Svishtov (BG03). In year 2005 at us Russe (BG04) concentration was increased. P total decreases also in tributaries Inn, Salzach, Morava, Arges, Russensko Lom and Jantra.
Situation for cadmium has a decreased or stable trend in Danube river also in tributaries. During the last years the results for cadmium are improved.

Figure 7.1: The minimum, mean and maximum of Dissolved Oxygen in 2005

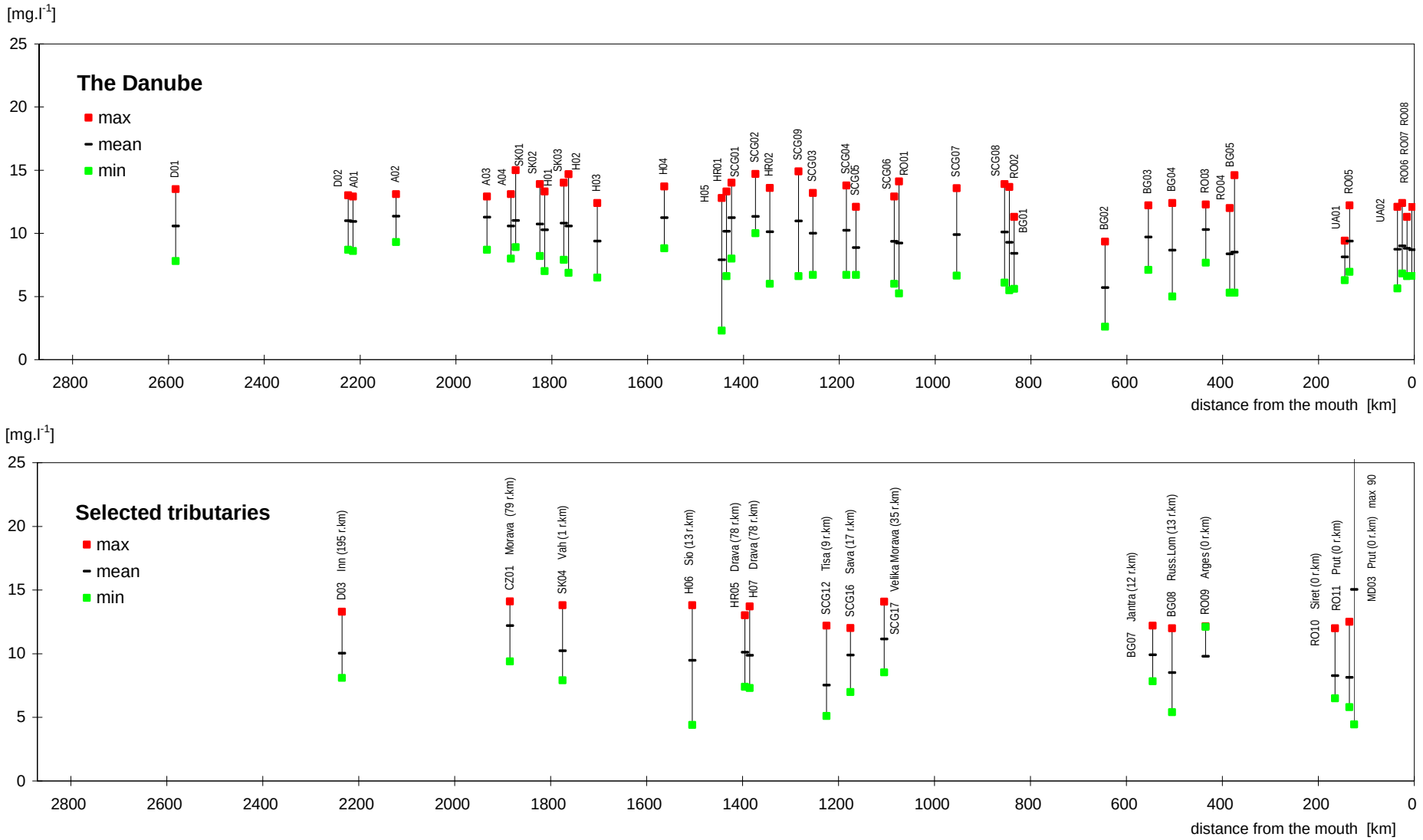


Figure 7.2: The minimum, mean and maximum of BOD_5 in 2005

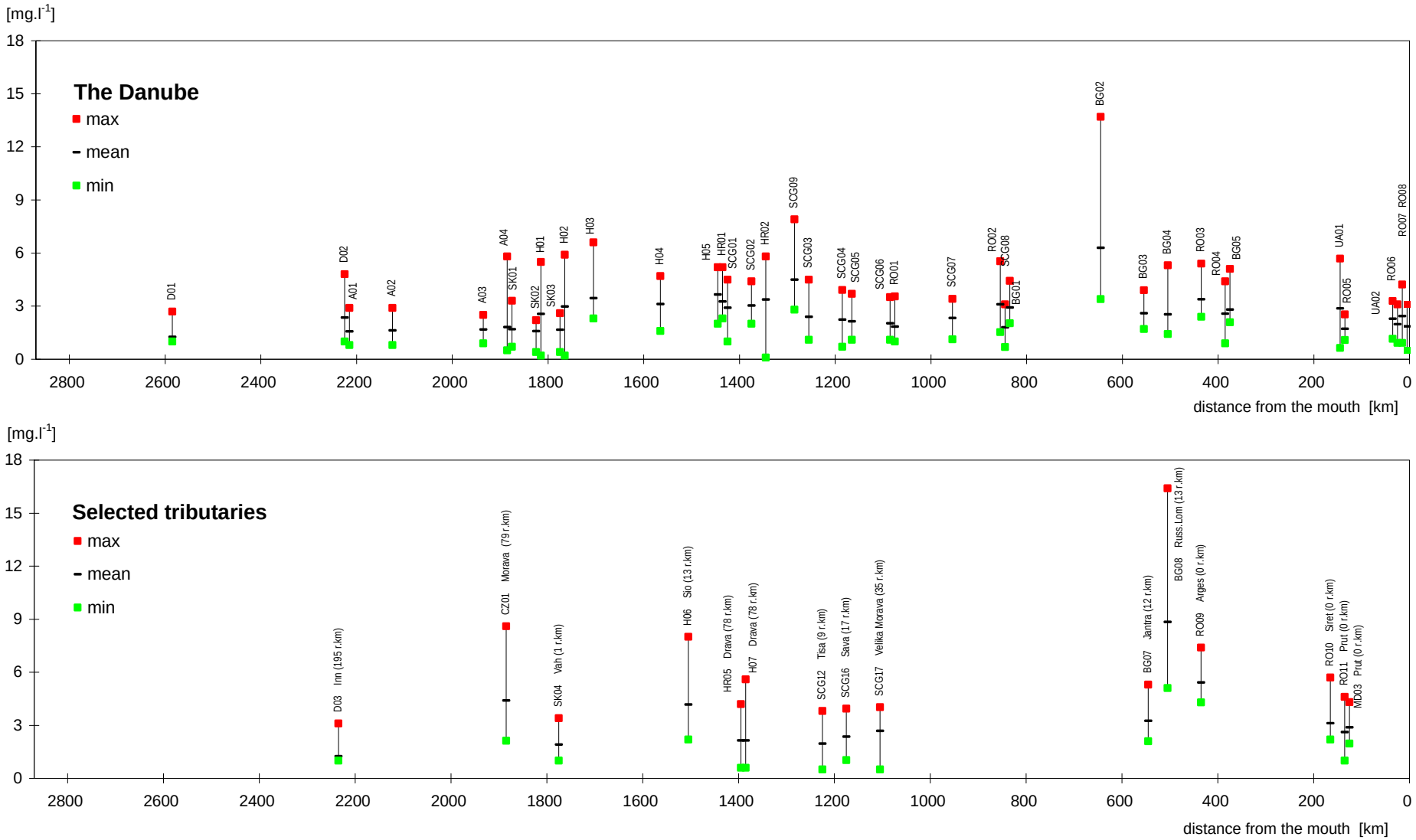


Figure 7.3: The minimum, mean and maximum of COD_{Cr} in 2005

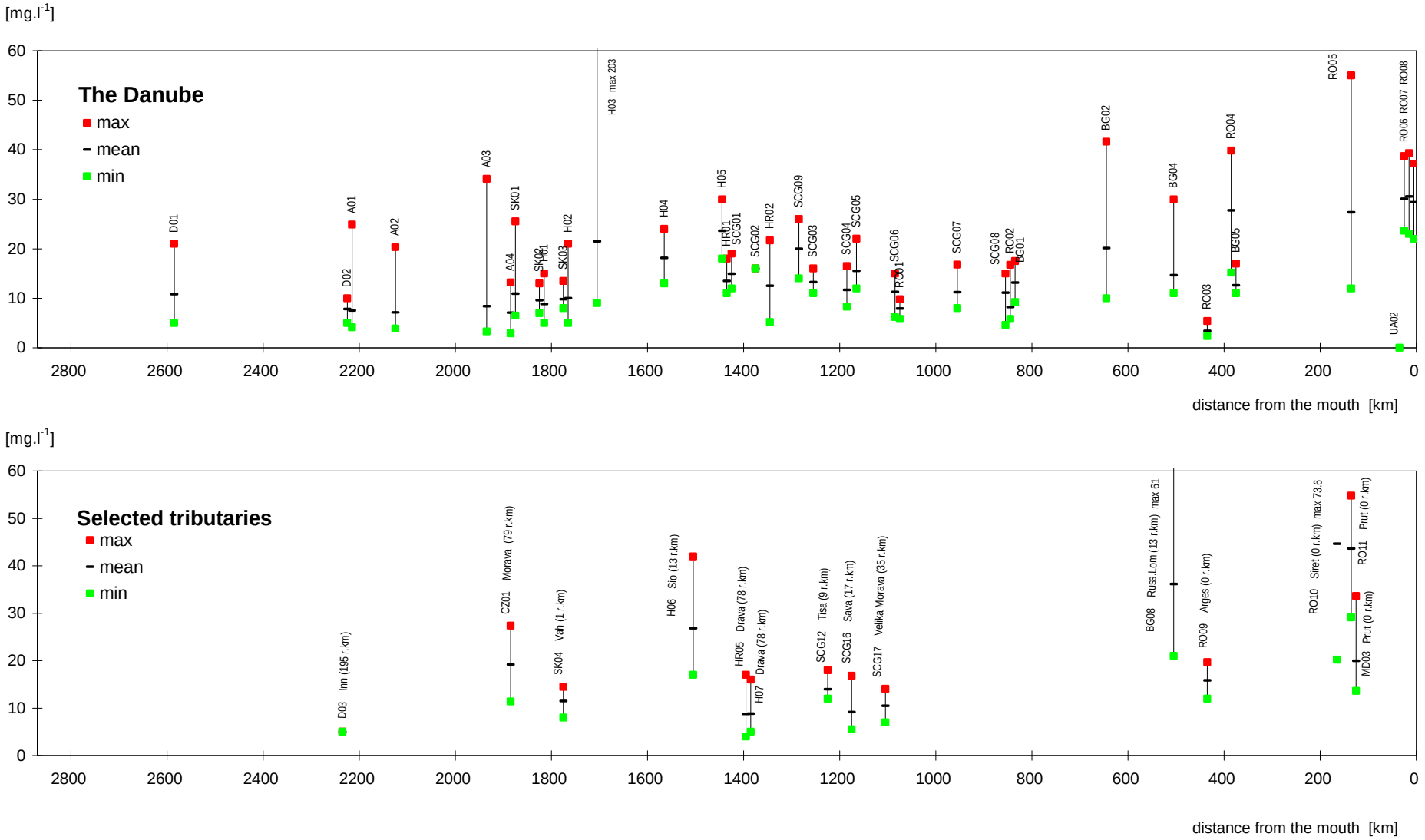


Figure 7.4: The minimum, mean and maximum of NH_4-N in 2005

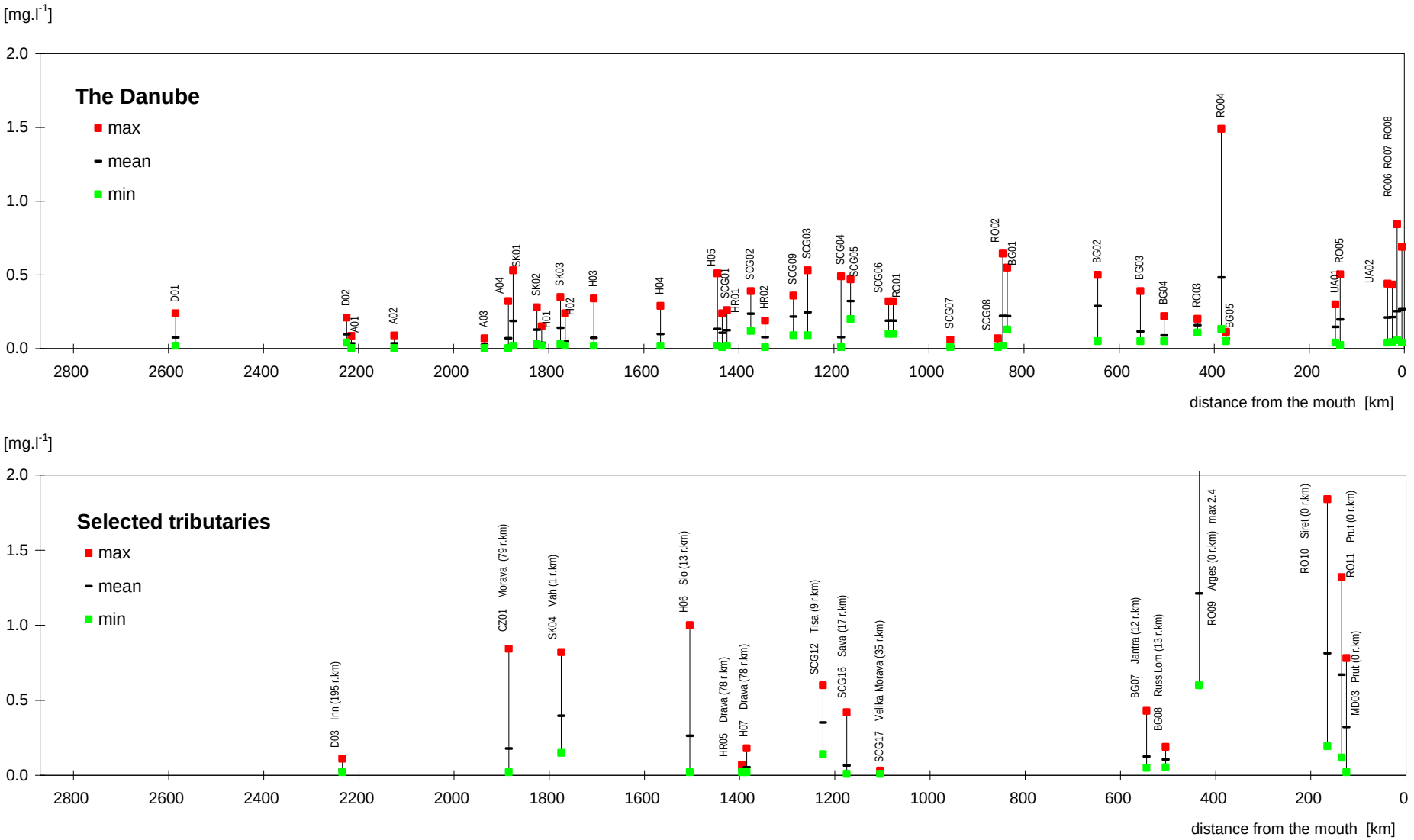


Figure 7.5: The minimum, mean and maximum of NO_3-N in 2005

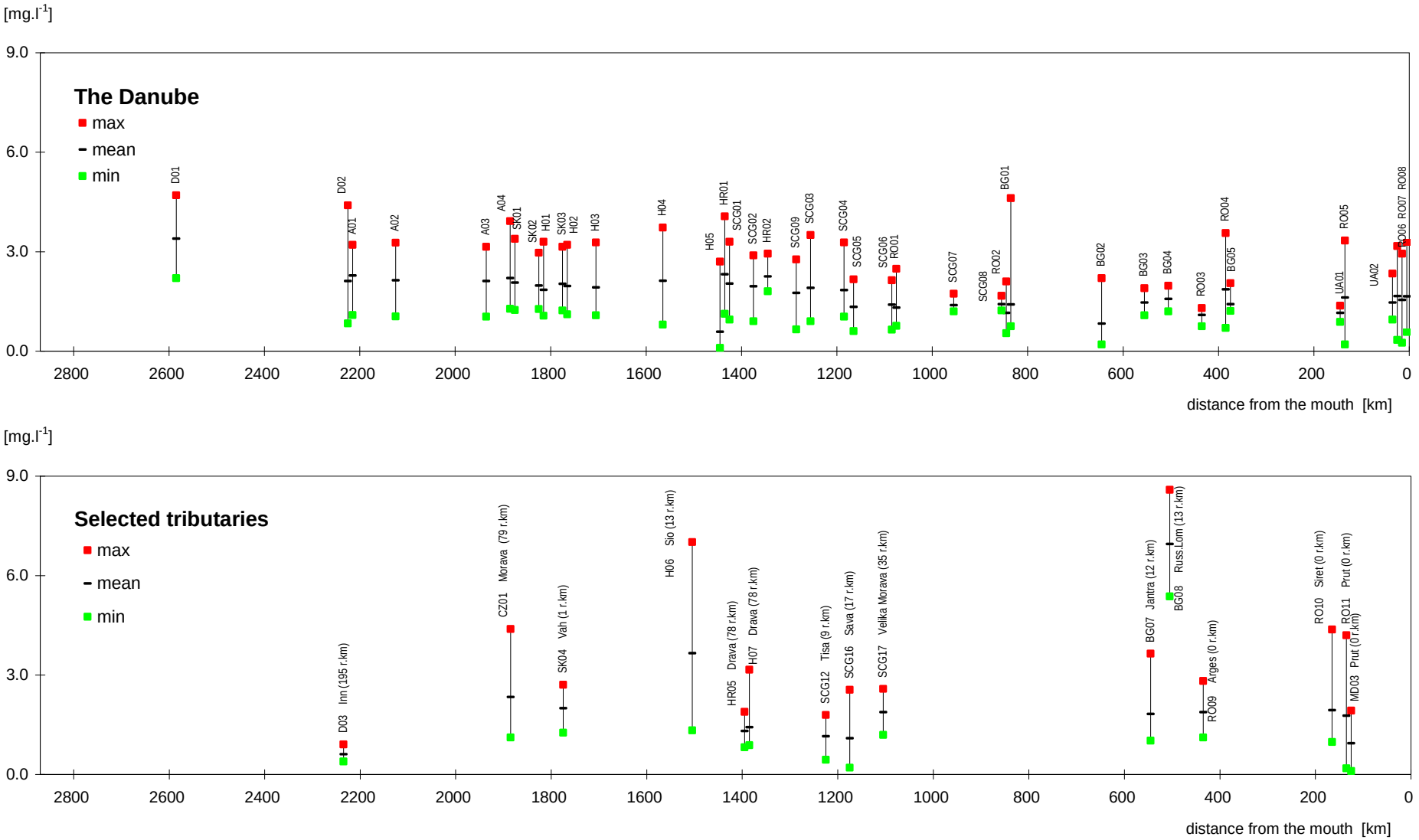


Figure 7.6: The minimum, mean and maximum of Ortho-Phosphate-P in 2005

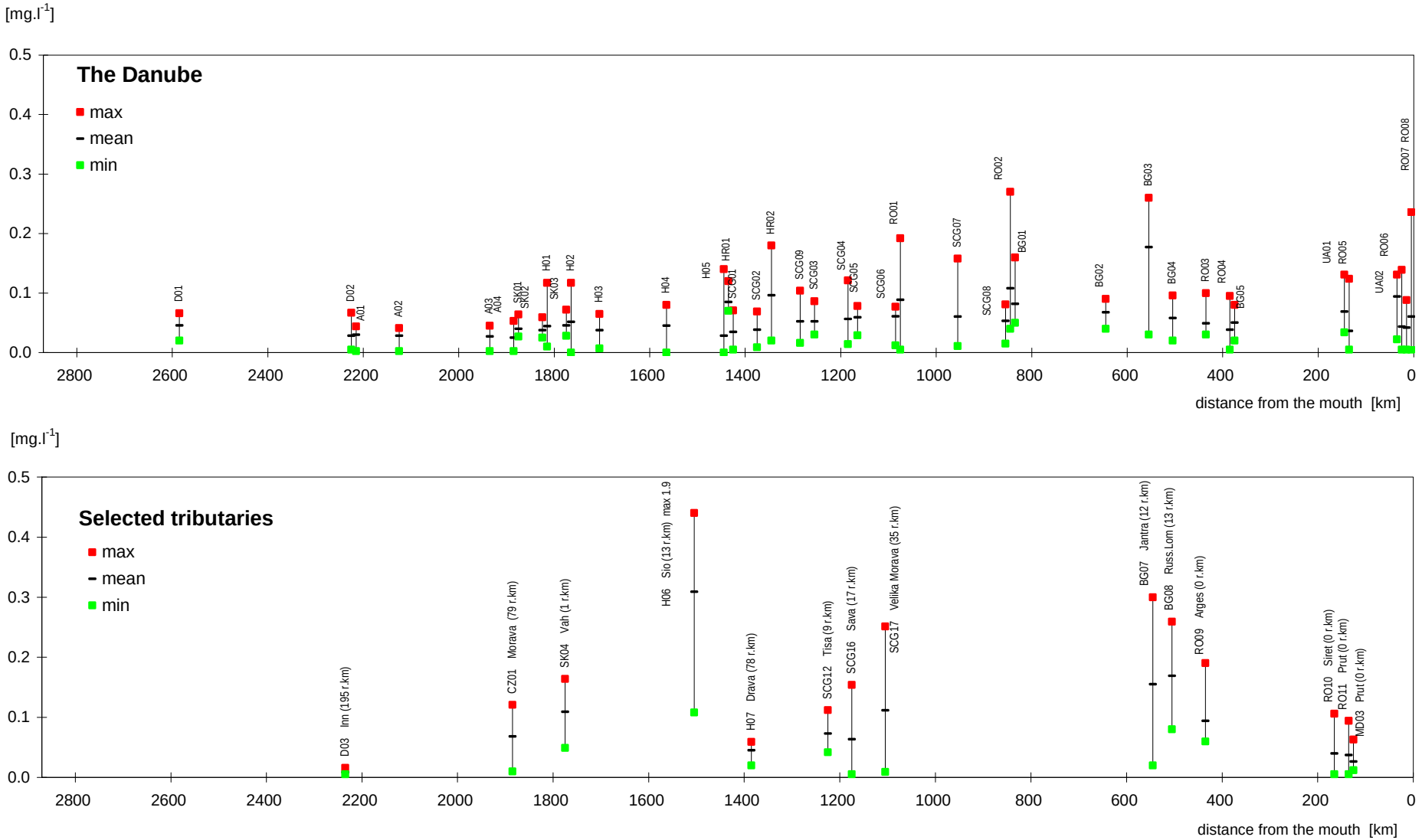


Figure 7.7: The minimum, mean and maximum of Total Phosphorus in 2005

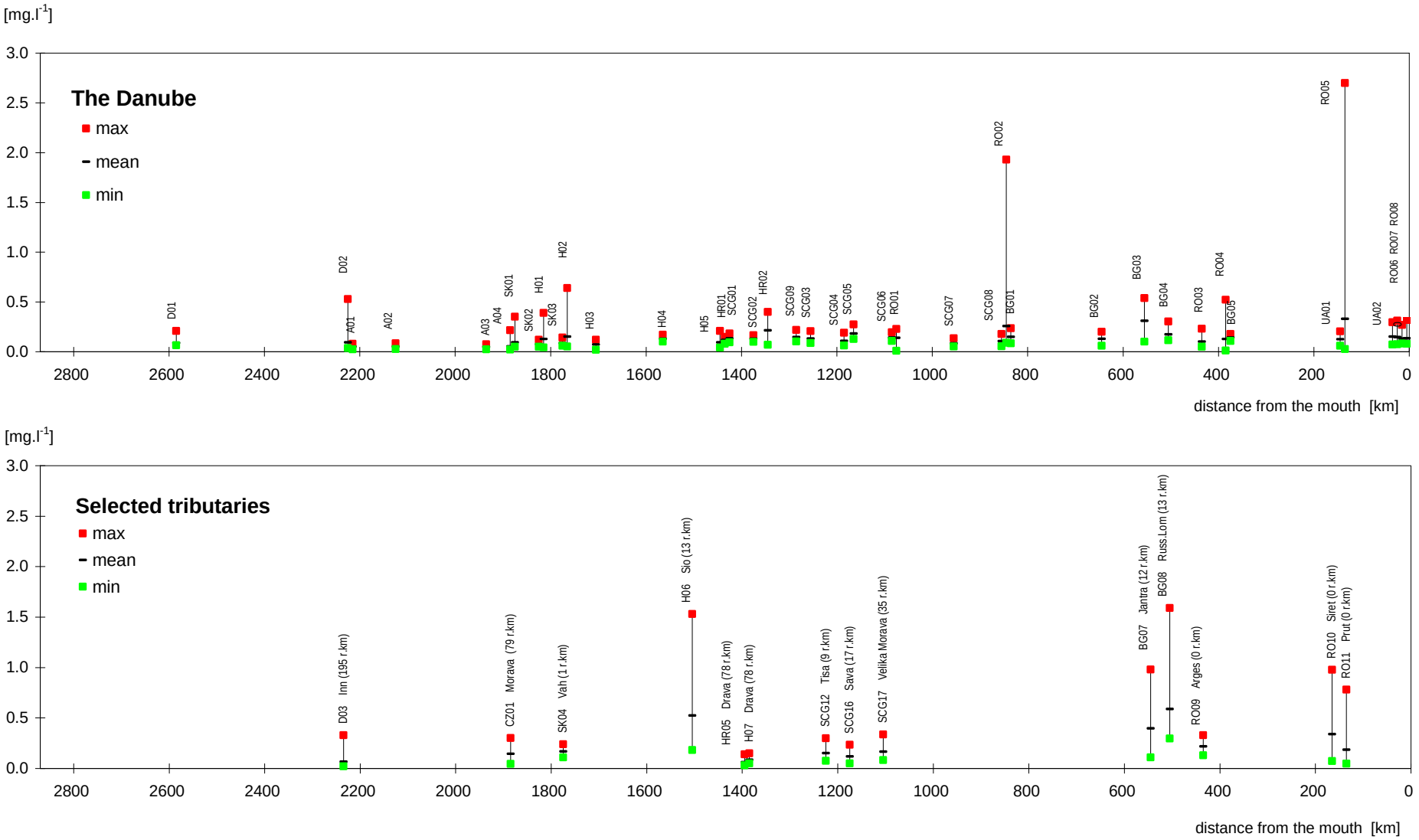


Figure 7.8: The minimum, mean and maximum of Chlorophyll-a in 2005

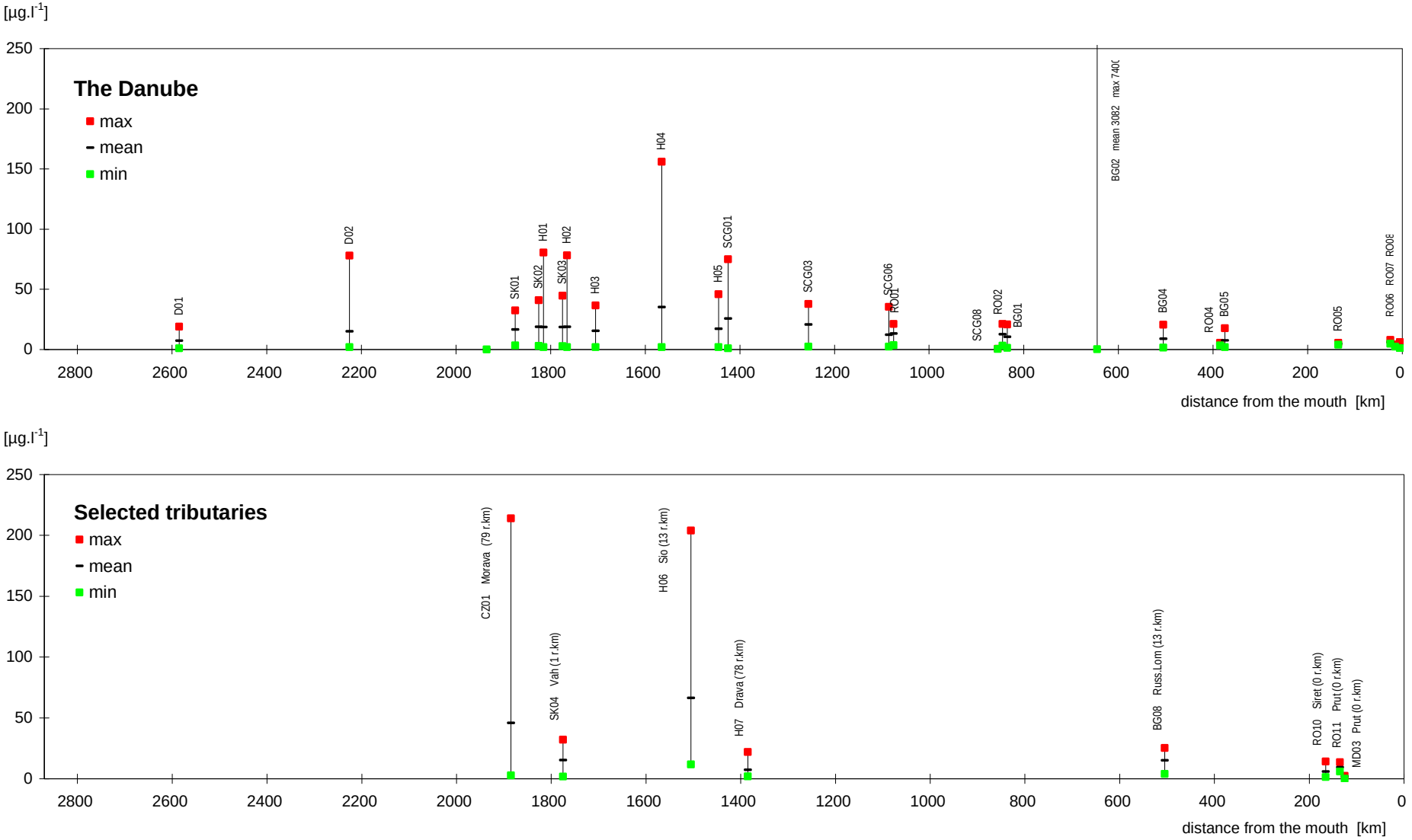


Figure 7.9: The minimum, mean and maximum of Cd in 2005

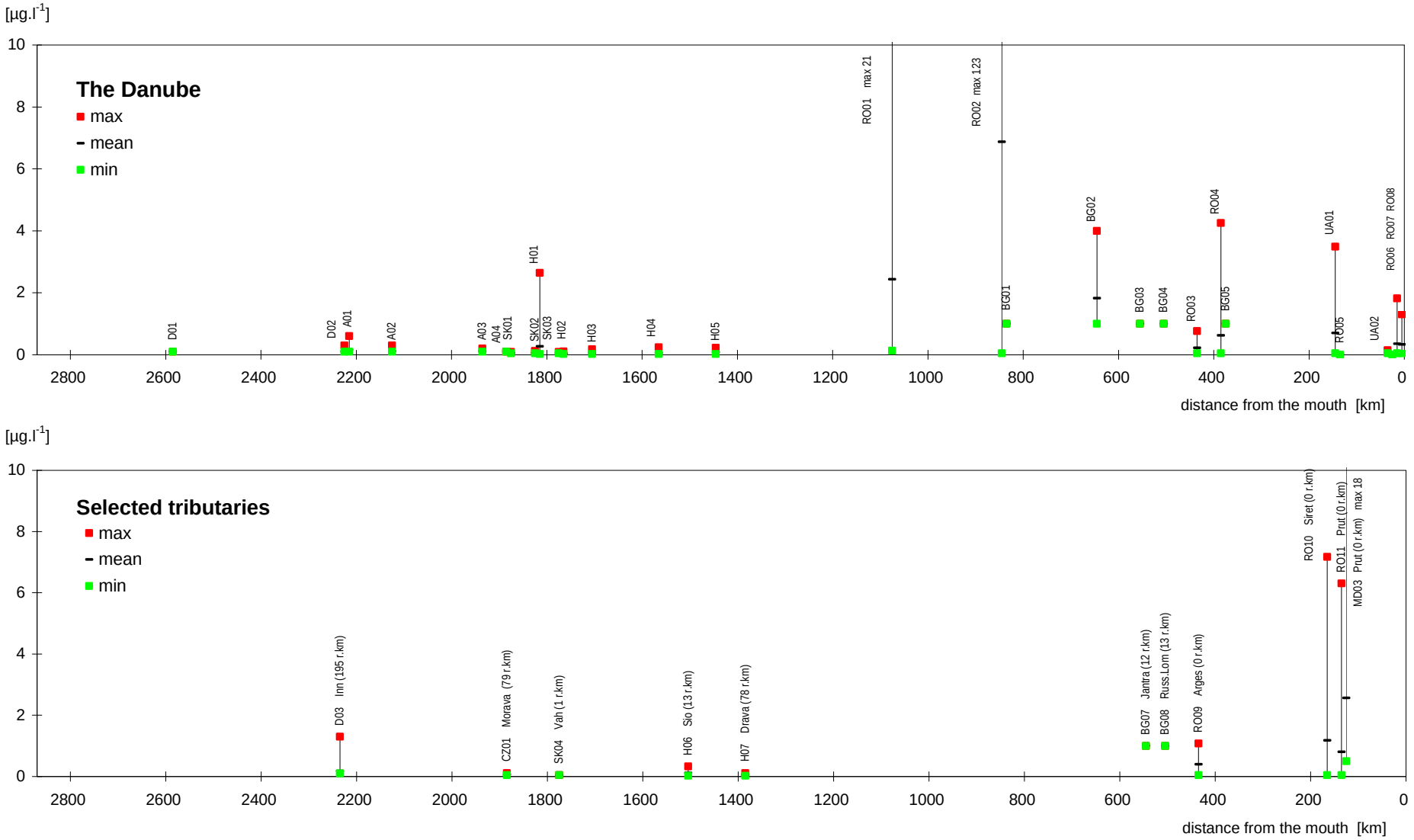


Figure 7.10: The minimum, mean and maximum of pp'DDT in 2005

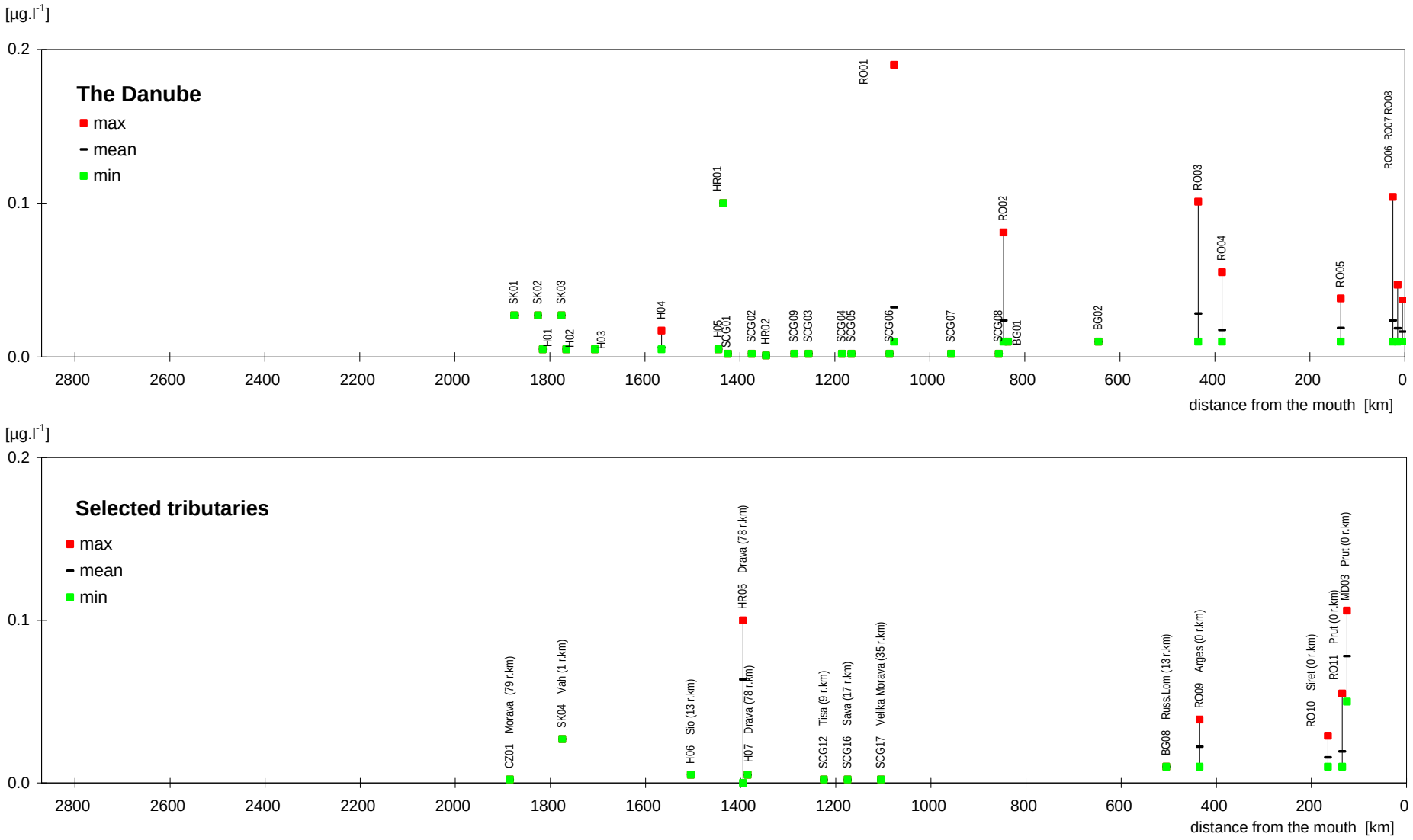


Figure 7.11: The minimum, mean and maximum of Atrazine in 2005

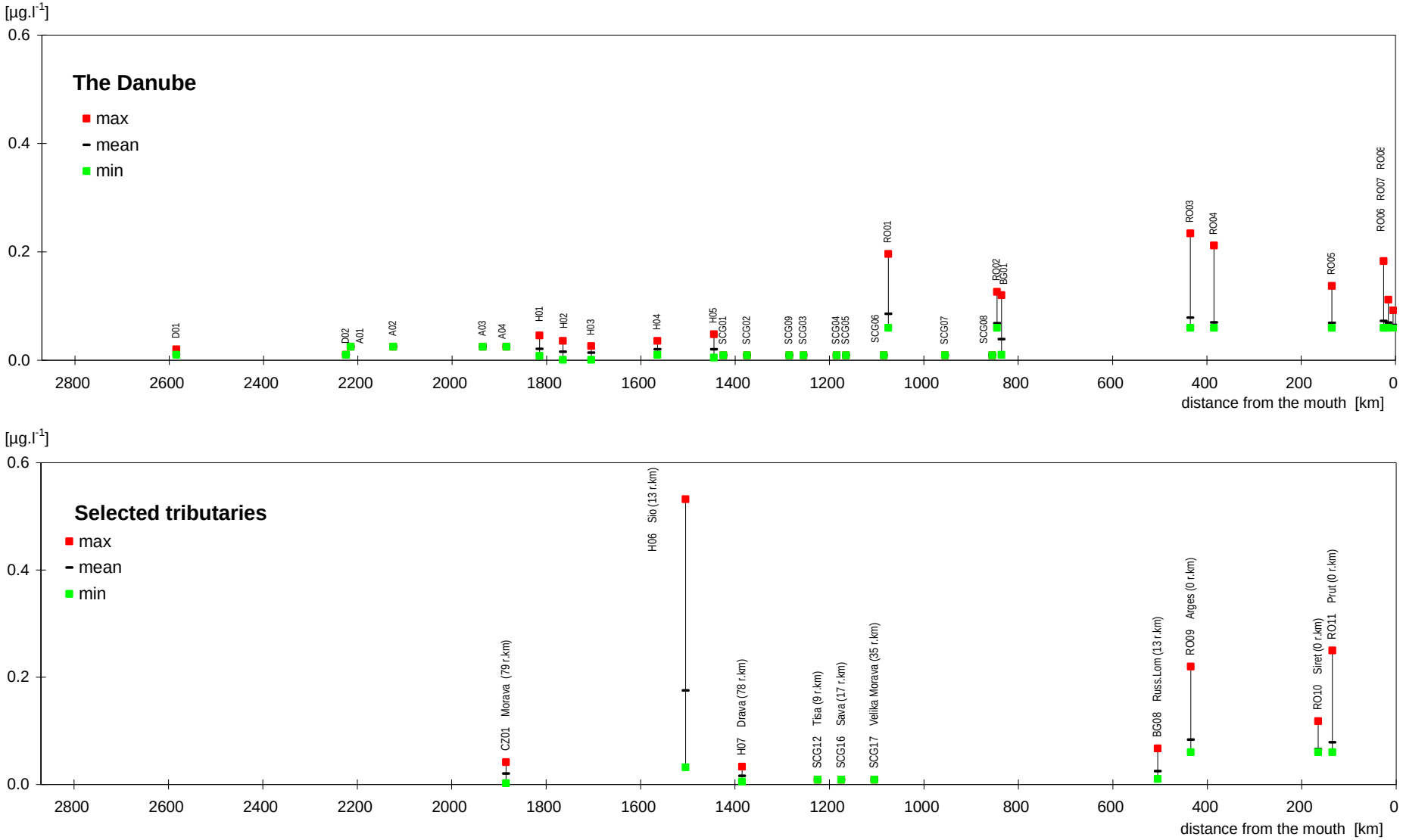


Figure 7.12: Temporal changes of dissolved oxygen in Danube River.

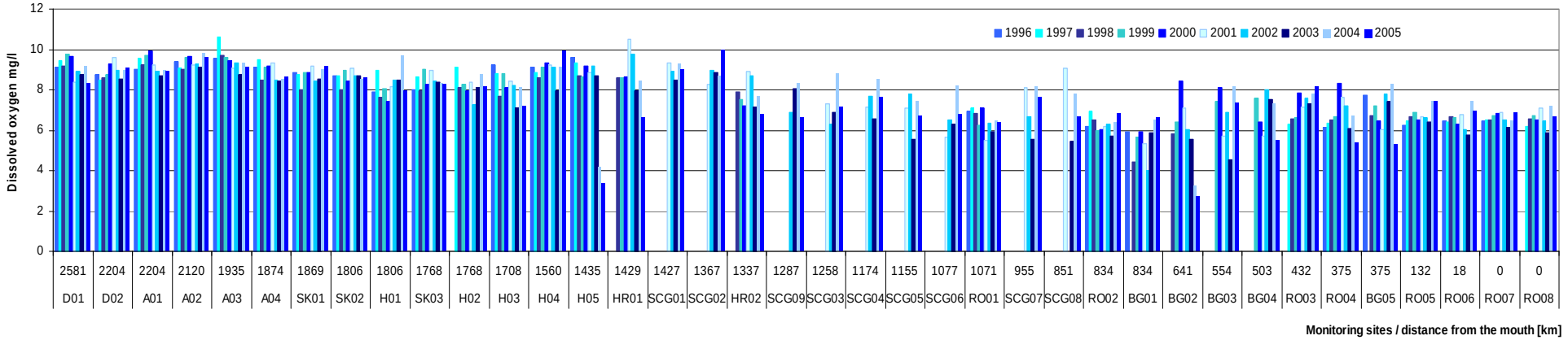


Figure 7.13: Temporal changes of dissolved oxygen in tributaries.

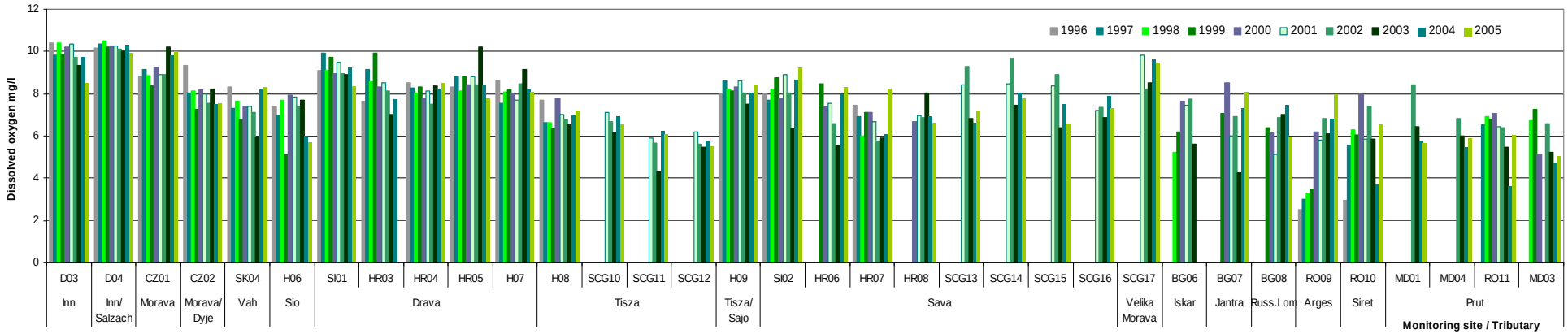


Figure 7.14: Temporal changes of BOD_5 in Danube River.

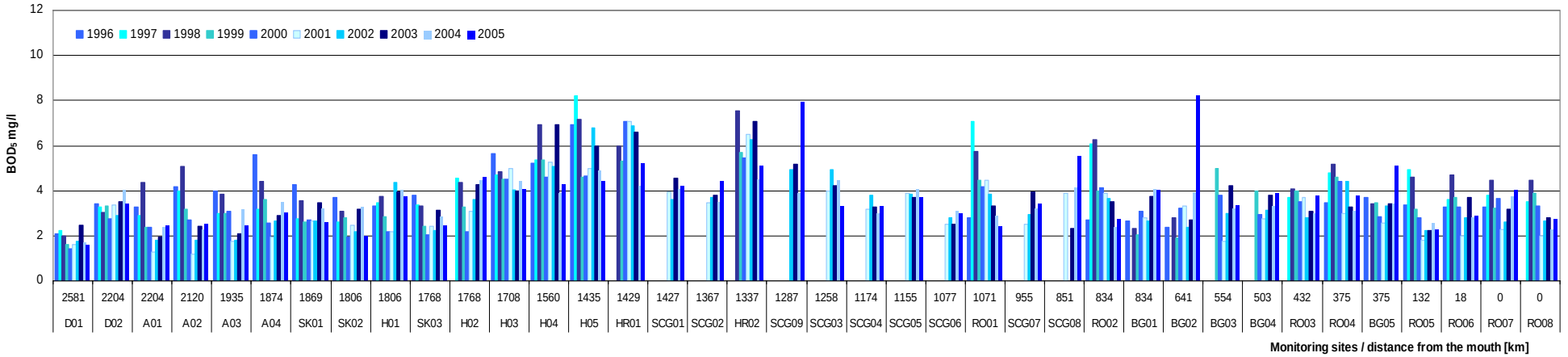


Figure 7.15: Temporal changes of BOD_5 in tributaries.

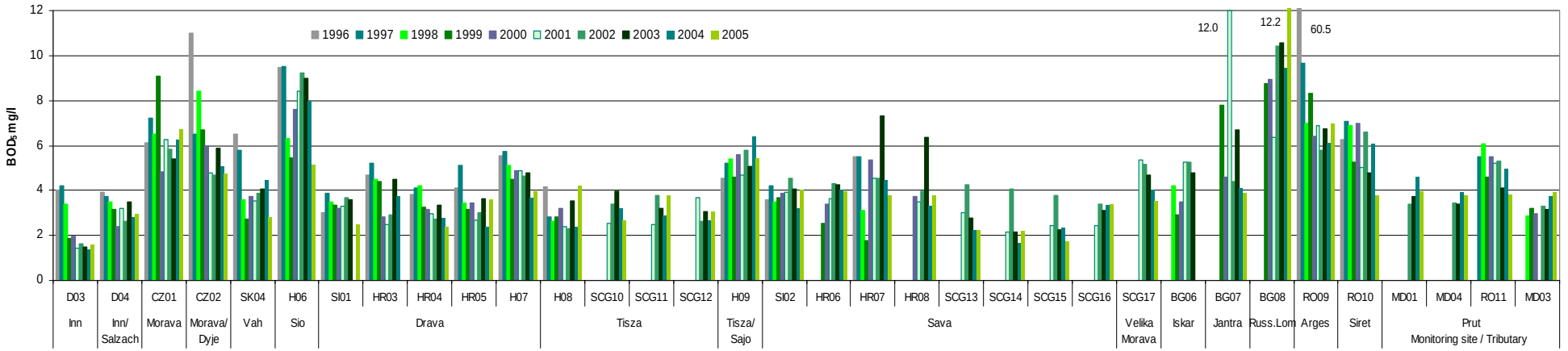


Figure 7.16: Temporal changes of COD_{Cr} in Danube River.

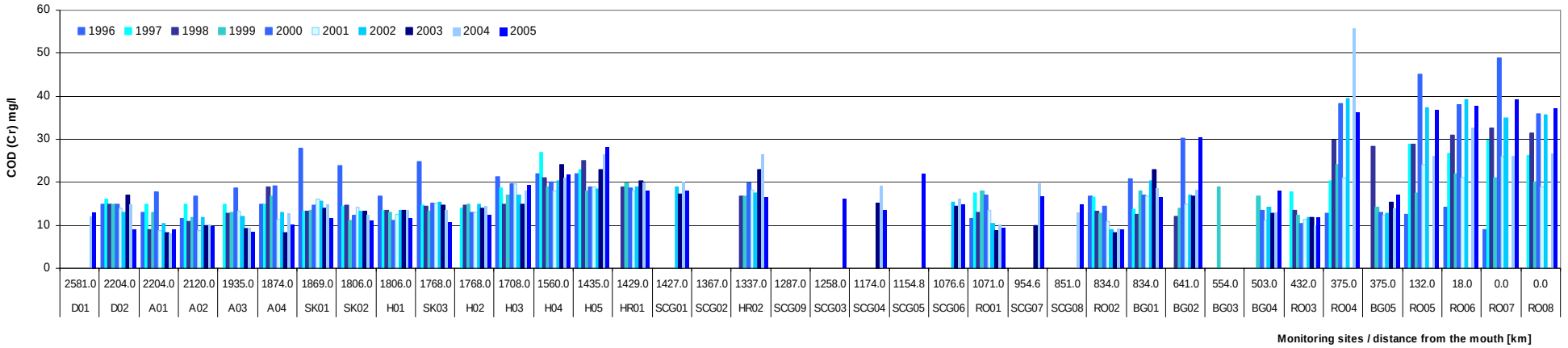


Figure 7.17: Temporal changes of COD_{Cr} in tributaries.

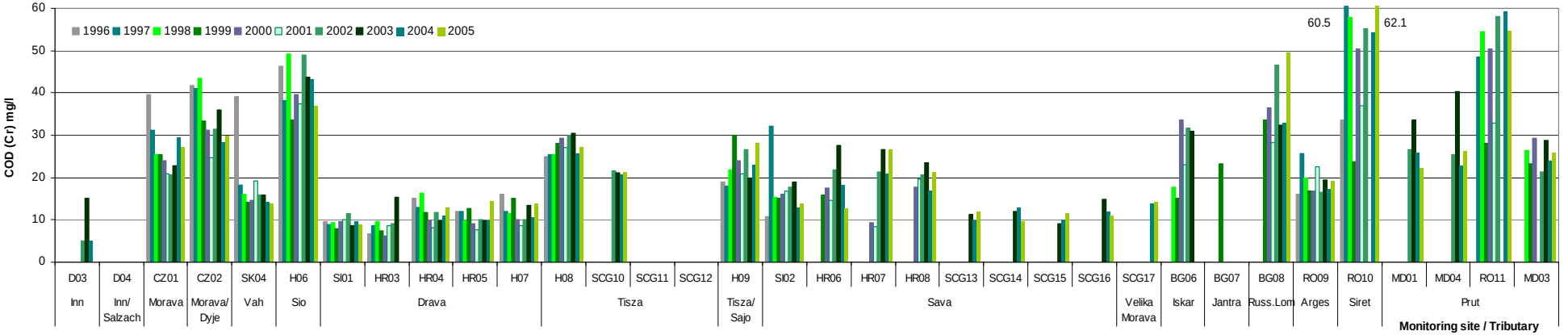


Figure 7.18: Temporal changes of ammonium-nitrogen in Danube River.

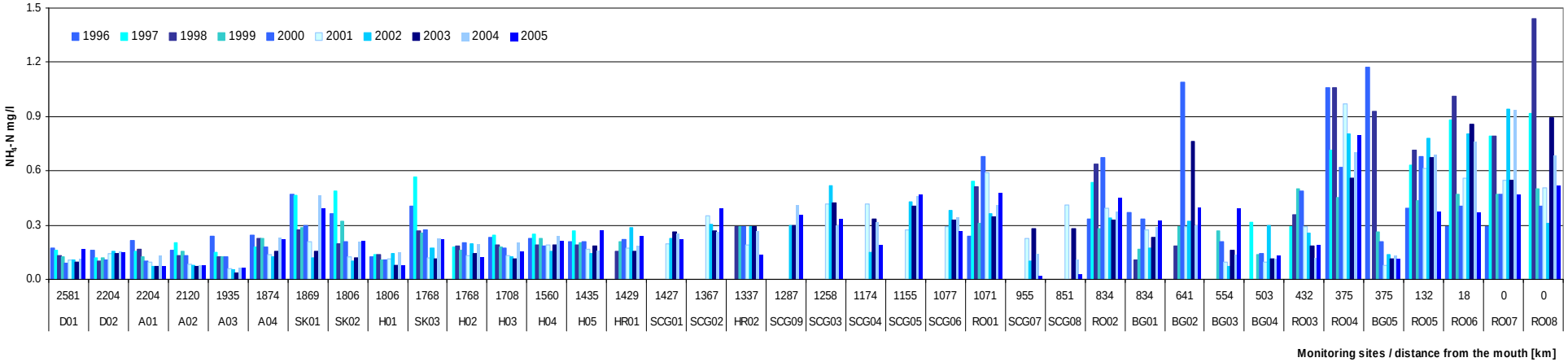


Figure 7.19: Temporal changes of ammonium-nitrogen in tributaries.

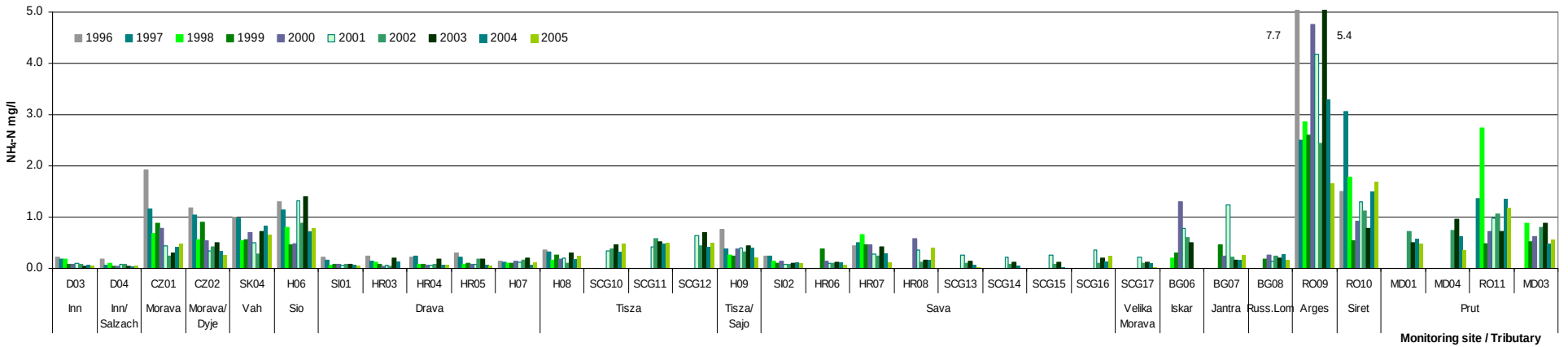


Figure 7.20: Temporal changes of nitrate-nitrogen in Danube River.

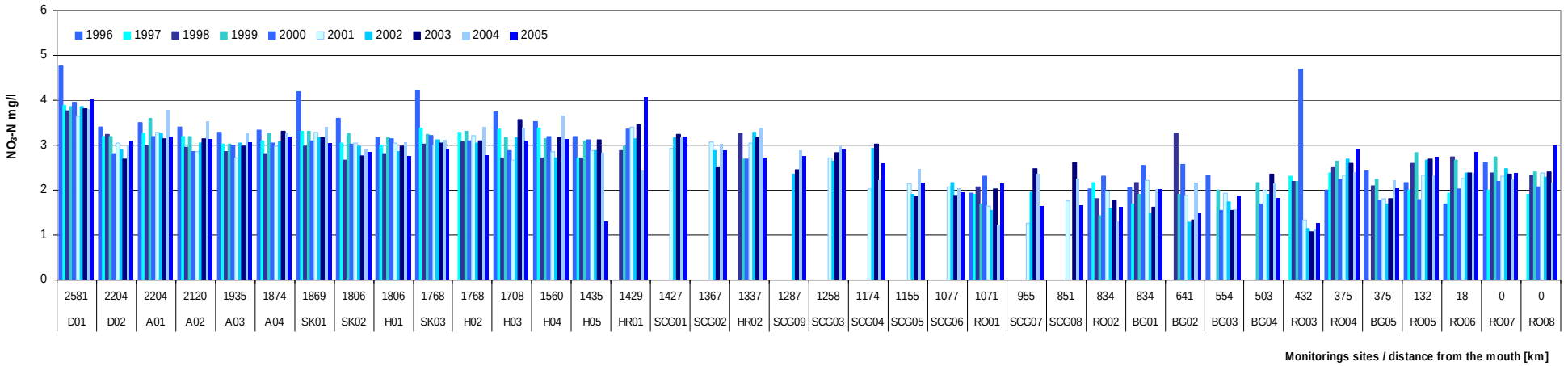


Figure 7.21: Temporal changes of nitrate-nitrogen in tributaries.

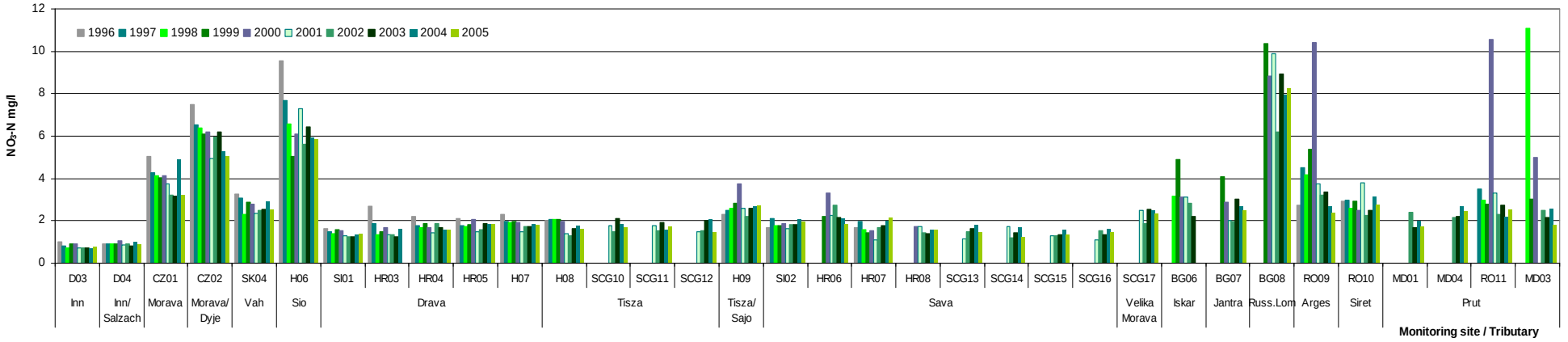


Figure 7.22: Temporal changes of ortho-phosphate-phosphorus in Danube River.

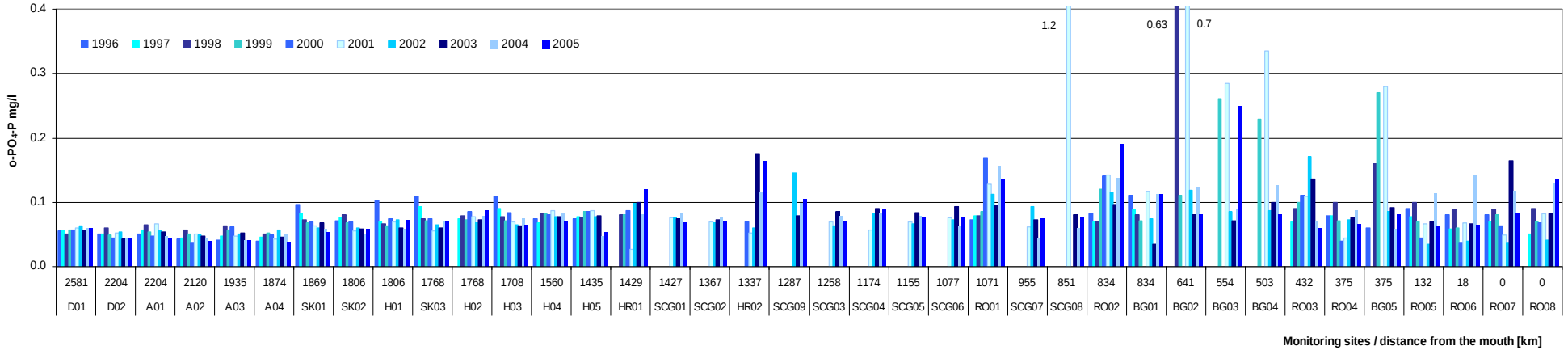


Figure 7.23: Temporal changes of ortho-phosphate-phosphorus in tributaries

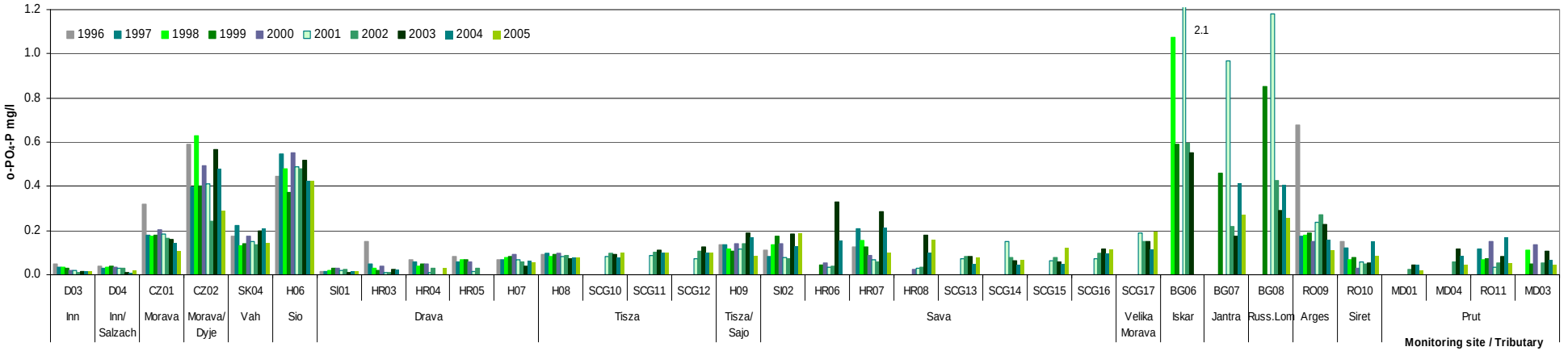


Figure 7.24: Temporal changes of total phosphorus in Danube River.

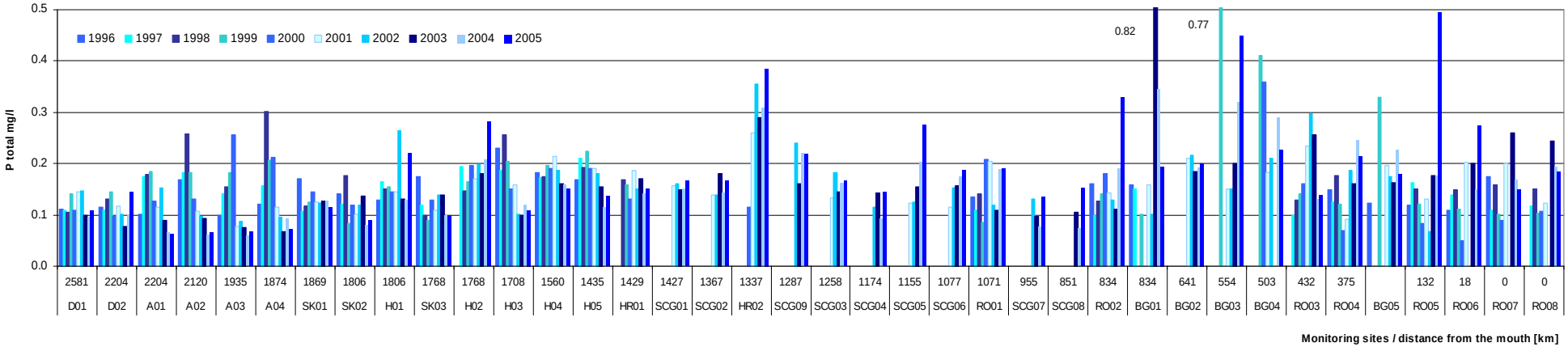


Figure 7.25: Temporal changes of total phosphorus in tributaries.

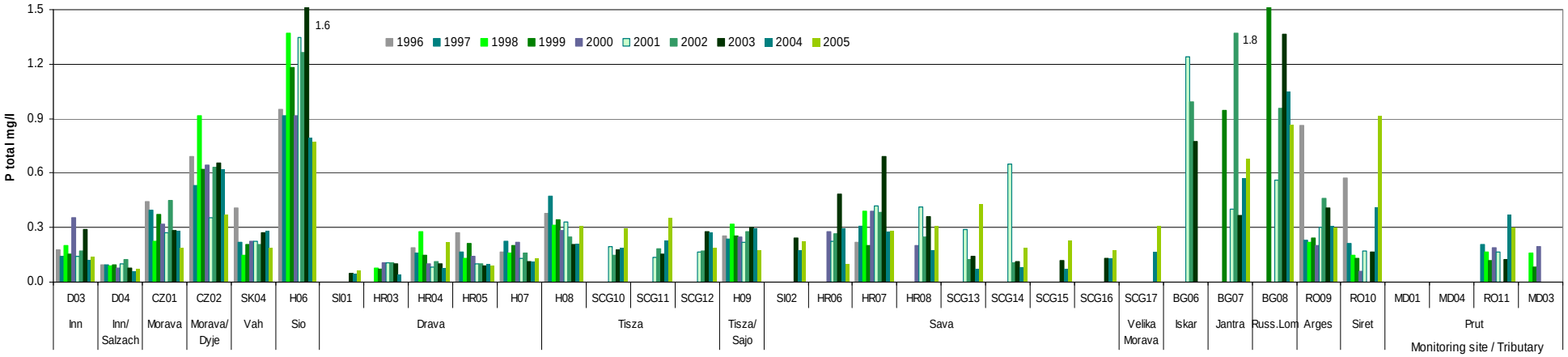


Figure 7.26: Temporal changes of cadmium in Danube River.

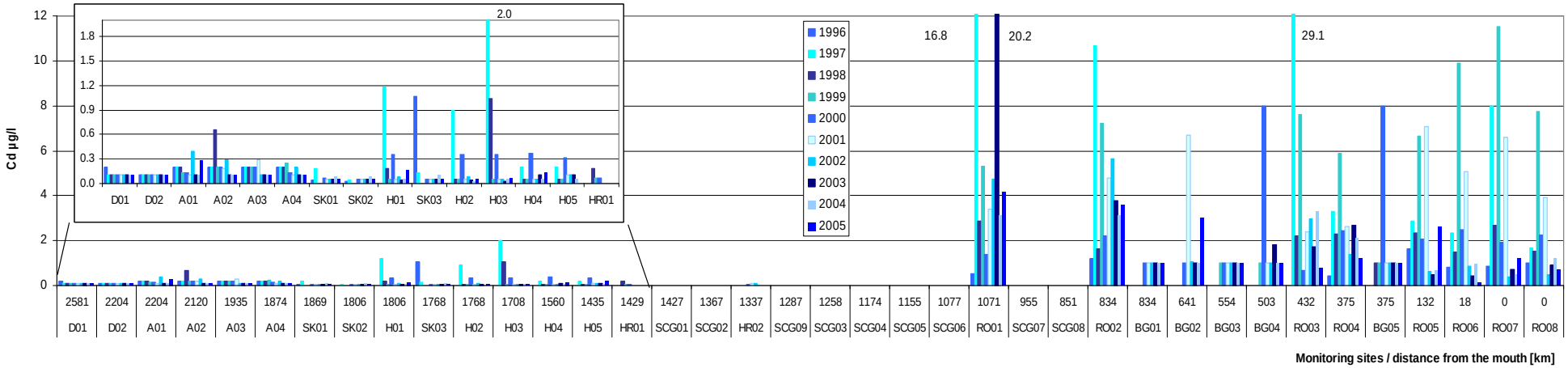
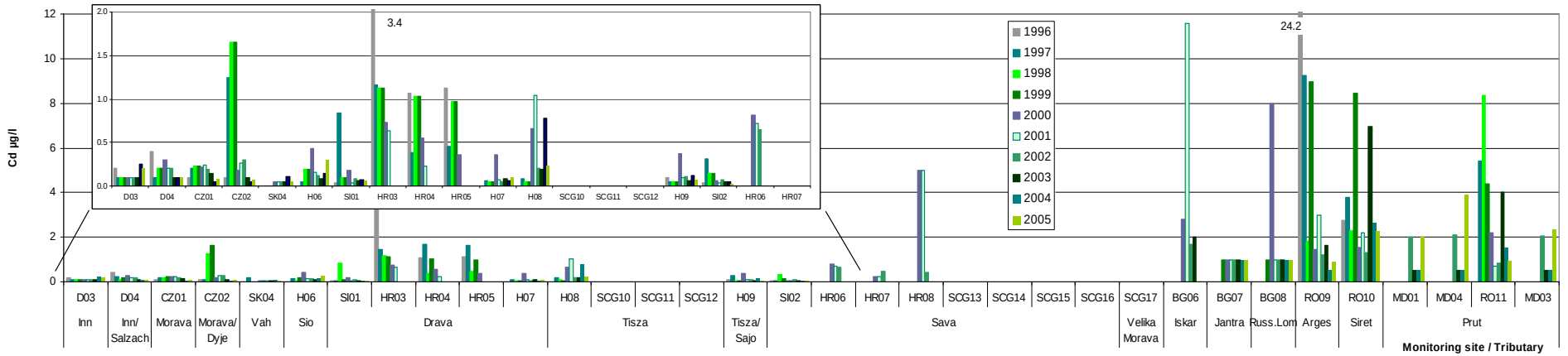


Figure 7.27: Temporal changes of cadmium in tributaries.



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 2005 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	Wolfsthal	1874	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 2005

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 18 data from measurements and for year 2005 there are not flow data therefore this loading can't be calculated. 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 2005.

Country Code	River	Location	Location in profile	River Km	Number of meausrements in 2005								
					Q	SS	N_{inorg}	$P\text{-}PO_4$	P_{total}	BOD_5	Cl	P_{diss}	SiO_2
D02	Danube	Jochenstein	M	2204	304	26	26	26	26	24	26	11	0
D03	Inn	Kirchdorf	M	195	365	23	24	23	25	24	24	11	0
D04	Inn/Salzach	Laufen	L	47	365	24	25	25	25	25	25	25	0
A01	Danube	Jochenstein	M	2204	365	12	12	12	12	12	12	12	0
A04	Danube	Wolfsthal	R	1874	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		24	24	24	24	24	24	0	0
			M	1708	365	18	18	18	16	18	18	0	0
			R	1708		24	24	24	24	24	24	0	0
H05	Danube	Hercegszántó	M	1435	0	12	14	14	14	14	12	0	0
H08	Tisza	Tiszasziget	L	163		11	15	15	14	11	12	0	0
			M	163	365	10	13	12	12	10	11	0	0
			R	163		11	15	15	14	12	12	0	0
HR02	Danube	Borovo	R	1337	0	26	26	26	26	26	0	0	0
HR06	Sava	Jesenice/D	L	729	0	26	26	26	26	26	12	0	0
HR07	Sava	us Una Jesenovac	L	525	365	26	26	26	26	26	12	0	0
HR08	Sava	ds Zupanja	R	254	365	24	24	24	24	24	11	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	0	23	23	23	23	14	23	0	24
			M	834	0	21	21	21	21	14	21	0	21
			R	834	0	20	20	20	20	14	20	0	20
RO04	Danube	Chiciu-Silistra	L	375		22	23	23	21	12	18	0	21
			M	375	365	22	23	23	22	24	22	0	21
			R	375		24	24	24	22	12	18	0	21
RO05	Danube	Reni	L	132		20	22	22	20	22	17	0	21
			M	132	365	20	22	22	20	22	17	0	21
			R	132		20	22	22	20	22	17	0	21
UA02	Danube	Vilkova-Kilia arm	M	18	0	11	11	11	11	11	11	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:

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

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:

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

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 2005
c_{mean}	arithmetical mean of the concentrations in the year 2005
Annual Load	annual load of given determinand in the year 2005

The mean annual discharge was higher in 2005 in comparison with previous year, the average value of flow is about 30 % more then in 2004 in Danube River and 32 % more in tributaries. Suspended solids concentrations as sensitive to flow conditions were higher in 2005 too.
Not all loading values was higher than values in year 2004, some of values are similar or lower than in year 2004.
Significantly higher concentrations of SS and inorganic nitrogen and in 2005 in comparison to 2004 had been observed in Reni-RO05 and Chiciu RO04. In tributary locations significant increase was in river Sava-SI02 in SS, $P\text{-}PO_4$, inorganic nitrogen and BOD_5.

In addition to 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 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. The maximum of load of ortho-phosphate phosphorus, total was in Danube- Pristol-Novo Selo RO02.
In case of suspended solids, inorganic nitrogen, BOD_5 and chlorides the highest load is observed in the lower part of the Danube River, maximum is reached in monitoring location Danube-Chiciu-Silistra (RO04).

From tributaries the highest load of SS, nutrients and BOD_5 is coming from Sava river, maximum is reached in monitoring location us. Una Jasenovac. Maximum of loading for chlorides is coming from Tisza river.
Maximal loading for silicates is reached in Danube Reni – 475. 10^3 tonnes. In table 8.5.5. are 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 Danube River in 2005.

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	1359	11.01	2.17	0.03	0.10	2.28	18.50	0.03	
A04	R	Danube	Wolfsthal	1874	2069	31.28	2.29	0.02	0.05	1.81	19.80	0.04	
SK01	M	Danube	Bratislava	1869	2115	53.68	2.26	0.04	0.09	1.69	19.09	0.05	
H03	LMR	Danube	Szob	1708	2329	24.40	2.02	0.05	0.08	3.47	24.27		
H05	M	Danube	Hercegszántó	1435		6.08	1.24	0.03	0.09	3.66	20.00		
HR02	R	Danube	Borovo	1337		42.73	2.35	0.10	0.22	3.36			
RO02	LMR	Danube	Pristol-Novo Selo	834	6396	24.55	1.02	0.11	0.23	1.87	19.81		7.59
RO04	LMR	Danube	Chiciu-Silistra	375	7659	86.55	2.32	0.04	0.14	2.61	29.77		8.55
RO05	LMR	Danube	Reni	132	8711	68.65	1.83	0.04	0.31	1.75	28.36		9.42
UA02	M	Danube	Vilkova-Kilia arm	18		158.636	1.697	0.094	0.152	2.285	32.173		

Table 8.5.2: Mean annual concentrations in monitoring locations selected for load assessment on tributaries in 2005.

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	333	36.48	0.64	0.01	0.07	1.25	5.77	0.01
D04	L	Inn/Salzach	Laufen	47	265	38.75	0.73	0.01	0.04	2.13	9.18	0.01
CZ01	M	Morava	Lanzhot	79	54	45.89	2.53	0.07	0.14	4.40	30.80	
CZ02	L	Morava/Dy	Pohansko	17.00	39	49.15	2.77	0.19	0.25	3.68	41.28	
H08	LMR	Tisza	Tiszasziget	163	1099	87.42	1.48	0.06	0.20	2.55	43.87	
SI01	L	Drava	Ormoz	300	283	16.99	1.18	0.01	0.04	2.15	6.36	
SI02	R	Sava	Jesenice	729	265	18.42	1.76	0.09	0.13	2.58	8.90	
HR06	L	Sava	Jesenice	729		25.62	1.84	0.07	0.17	2.58	9.24	
HR07	L	Sava	us. Una Jasenovac	525	637	21.85	1.61	0.09	0.19	2.76	8.38	
HR08	R	Sava	ds. Zupanja	254	1190	22.63	1.31	0.05	0.17	2.61	12.35	

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

Station Code	Profile	River Name	Location	River km	Annual Load in 2005							
					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	0.499	91.819	1.224	4.803	102.927	1.032	1.794	
A04	R	Danube	Wolfsthal	1874	3.370	147.014	1.610	3.607	138.340	1.234	2.510	
SK01	M	Danube	Bratislava	1869	5.401	147.427	2.593	7.292	113.612	1.475	3.977	
H03	LMR	Danube	Szob	1708	1.628	122.061	3.016	4.831	218.152	1.498		
H05	M	Danube	Hercegszántó	1435								
HR02	R	Danube	Borovo	1337								
RO02	LMR	Danube	Pristol-Novo Selo	834	5.073	198.966	23.603	46.499	383.312	3.821		1.509
RO04	LMR	Danube	Chiciu-Silistra	375	20.094	537.173	9.515	31.982	589.736	7.000		1.882
RO05	LMR	Danube	Reni	132	17.985	493.928	10.184	71.611	486.580	7.605		2.309
UA02	M	Danube	Vilkova-Kilia arm	18								

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 2005						
					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	0.523	6.622	0.084	0.754	12.468	0.054	0.111
D04	L	Inn/Salzach	Laufen	47	0.588	5.486	0.074	0.369	17.470	0.058	0.090
CZ01	M	Morava	Lanzhot	79	0.049	4.460	0.117	0.273	6.445	0.049	
CZ02	L	Morava/Dyje	Pohansko	17	0.050	4.485	0.193	0.282	4.467	0.052	
H08	LMR	Tisza	Tiszasziget	163	3.118	39.641	1.944	6.633	53.086	1.102	
SI01	L	Drava	Ormoz	300	0.240	10.032	0.094	0.450	18.194	0.051	
SI02	R	Sava	Jesenice	729	0.189	14.232	0.571	0.896	20.018	0.066	
HR06	L	Sava	Jesenice	729							
HR07	L	Sava	us. Una Jasenovac	525	0.445	29.485	1.345	3.549	52.126	0.151	
HR08	R	Sava	ds. Zupanja	254	0.838	49.149	1.704	6.237	91.080	0.373	

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	21	21	21	20	23	23	23	23	23	23	21
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	8711	0.21	0.04	1.62	2.32	13.002	4.129	3.509	0.982	0.736	0.113	0.032
Country Code	**River**	**Location**	**Location in profile**	**River km**	**Annual Load in 2005**											
						$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	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		49.79	9.10	407.67	610.80	3.50	1.10	943.28	215.83	167.72	26.22	7.63

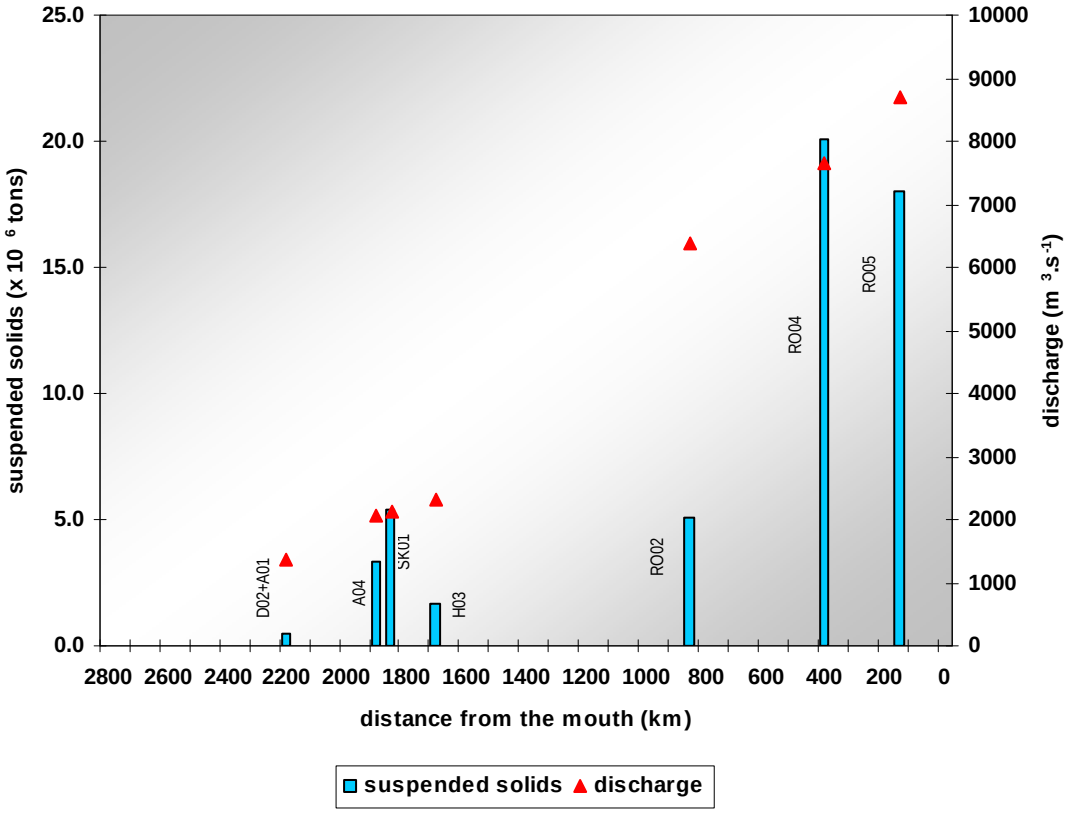


Figure 8.5.1: Annual load of suspended solids at monitoring locations along the Danube River.

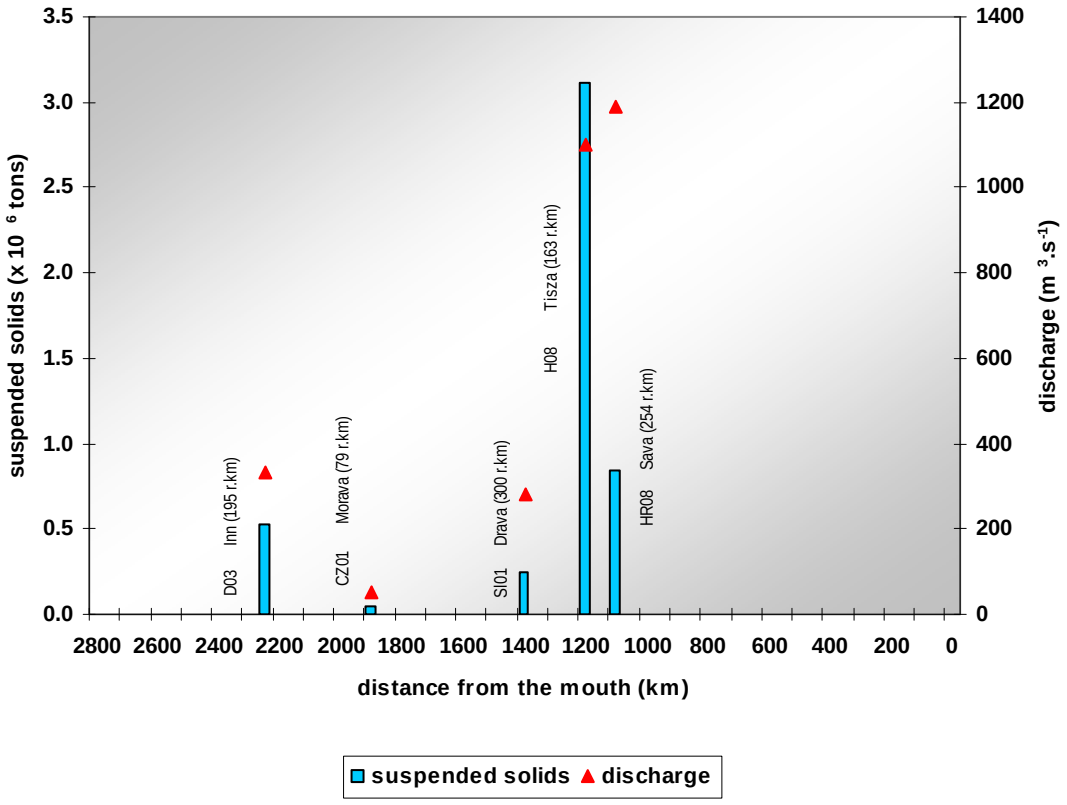


Figure 8.5.2: Annual load of suspended solids at monitoring locations on tributaries.

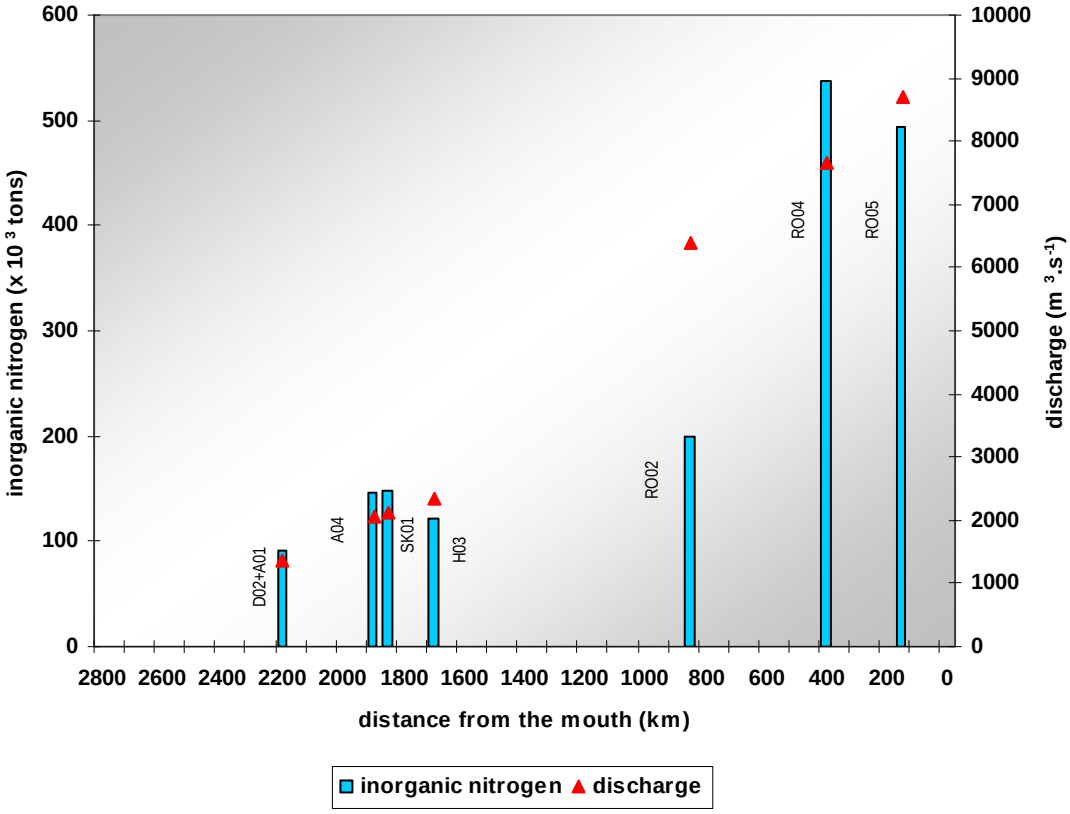


Figure 8.5.3: Annual loads of inorganic nitrogen at monitoring locations along the Danube River.

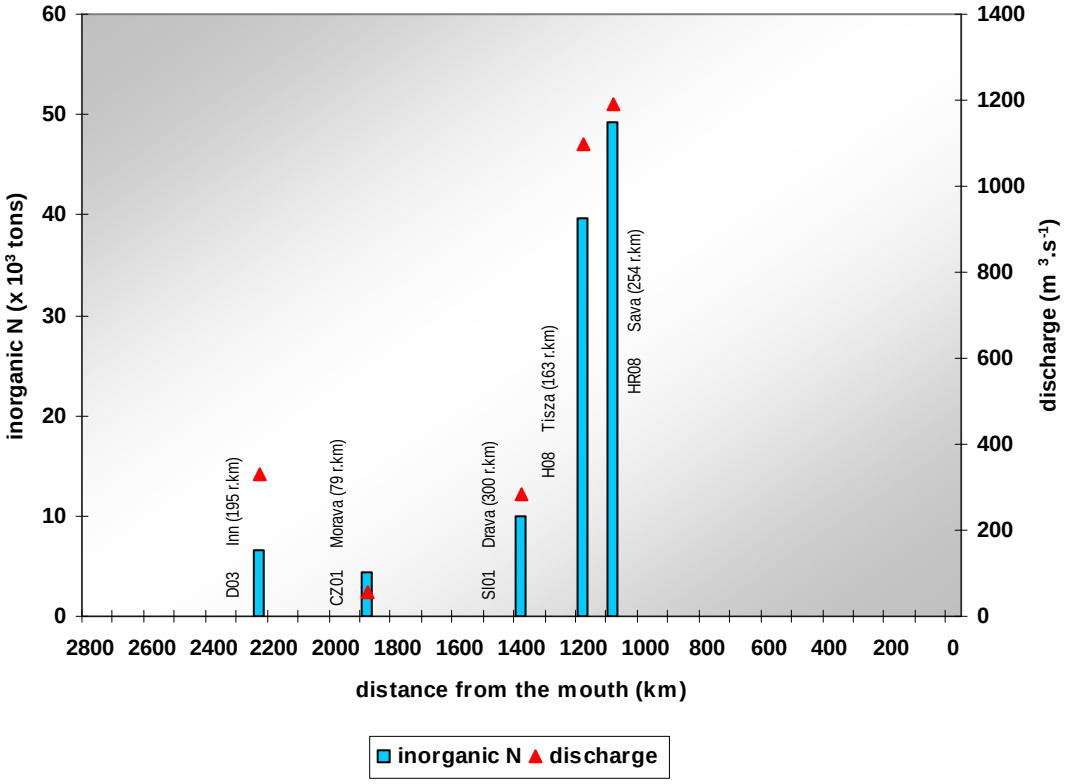


Figure 8.5.4: Annual loads of inorganic nitrogen at monitoring locations on tributaries.

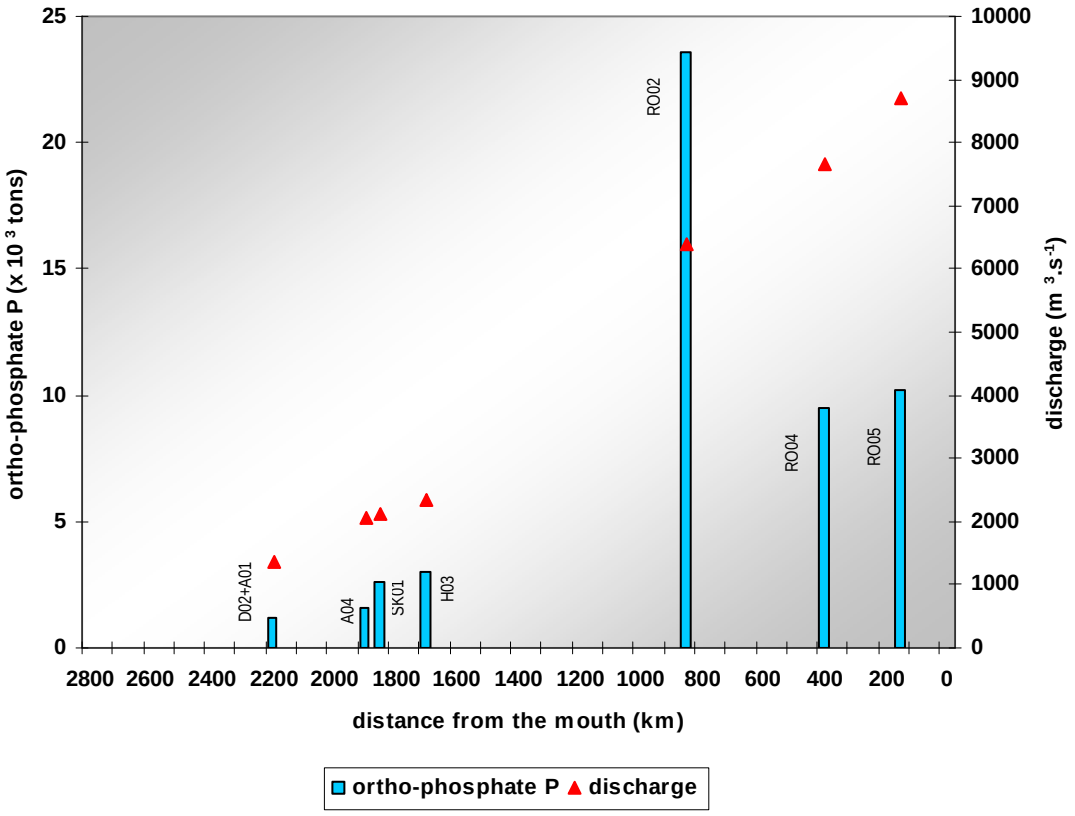


Figure 8.5.5: Annual loads of ortho-phosphate-P at monitoring locations along the Danube River.

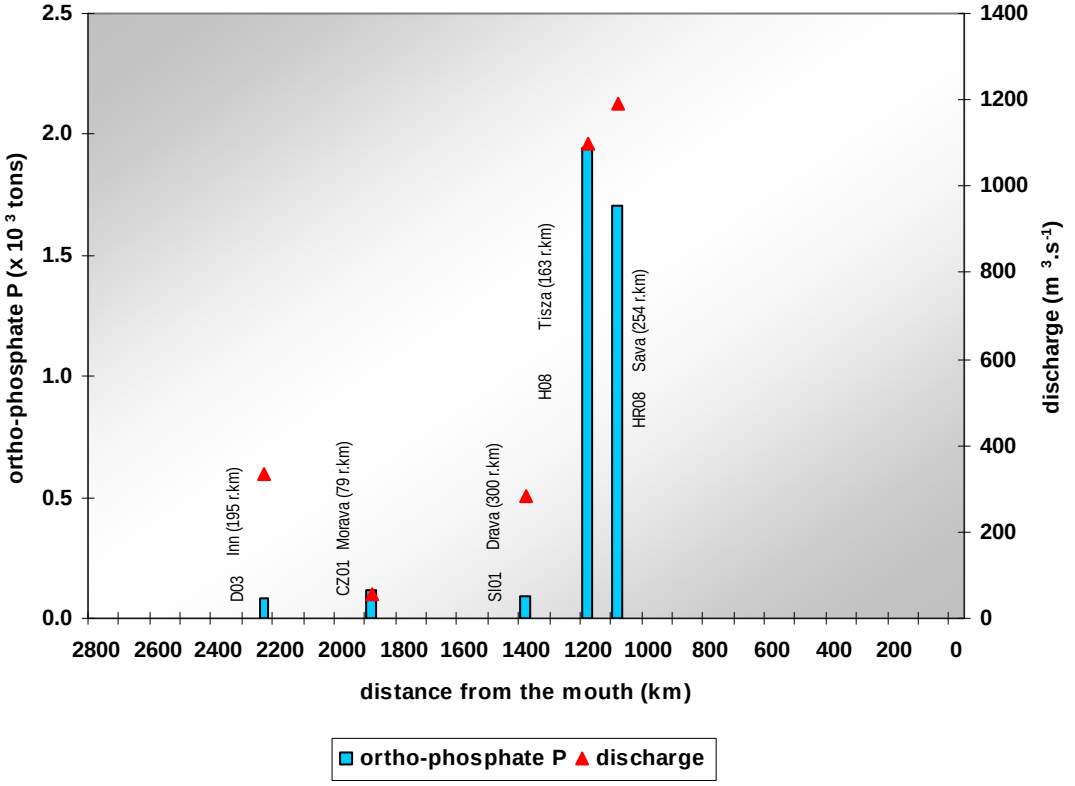


Figure 8.5.6: Annual loads of ortho-phosphate-P at monitoring locations on tributaries.

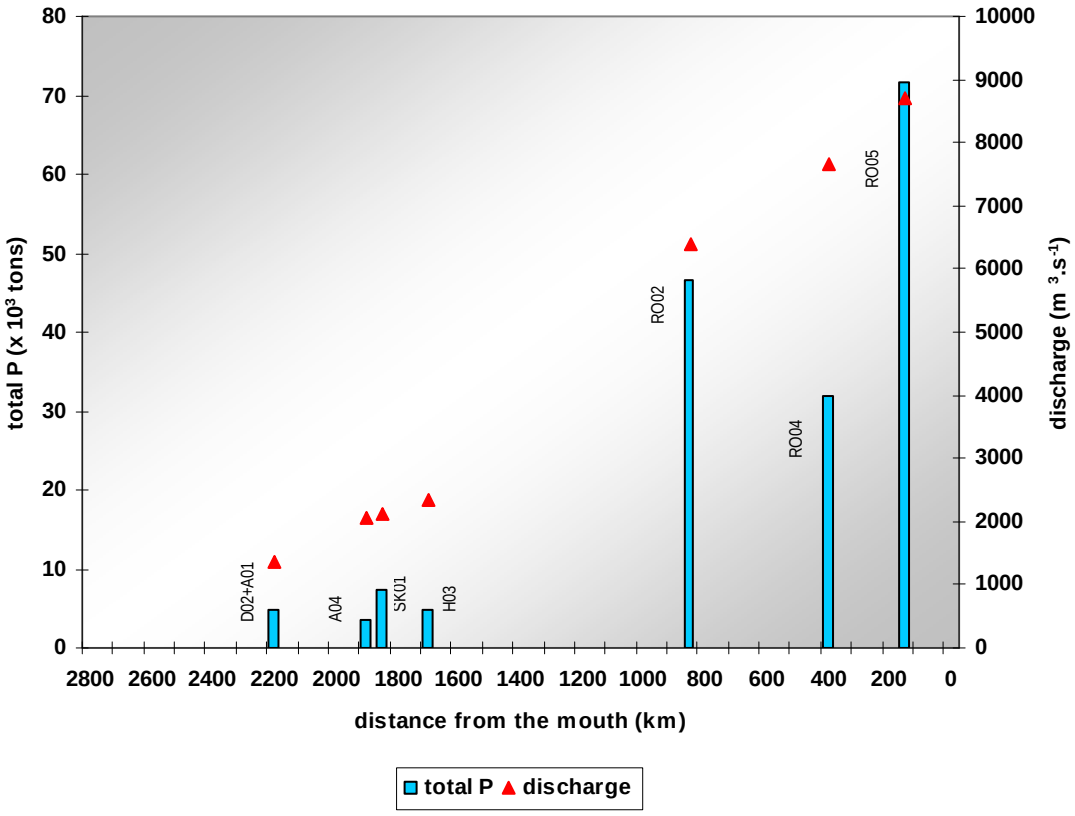


Figure 8.5.7: Annual loads of total phosphorus at monitoring locations along the Danube River.

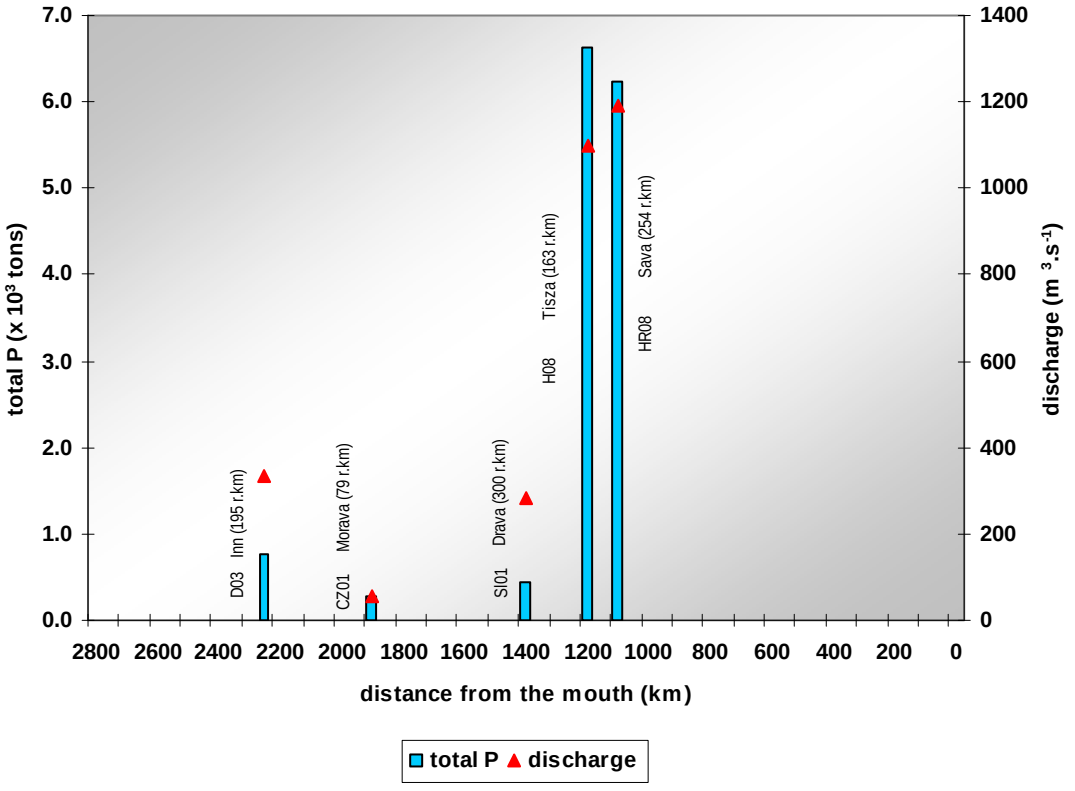


Figure 8.5.8: Annual loads of total phosphorus at monitoring locations on tributaries.

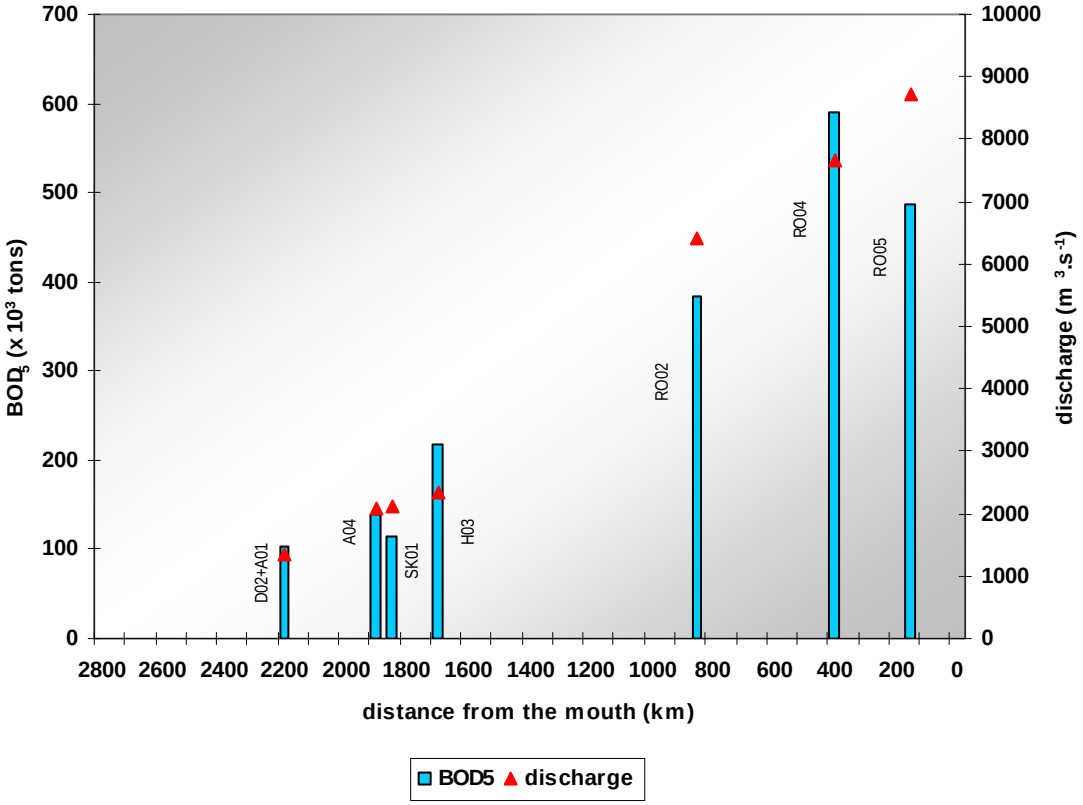


Figure 8.5.9: Annual loads of BOD_5 at monitoring locations along the Danube River.

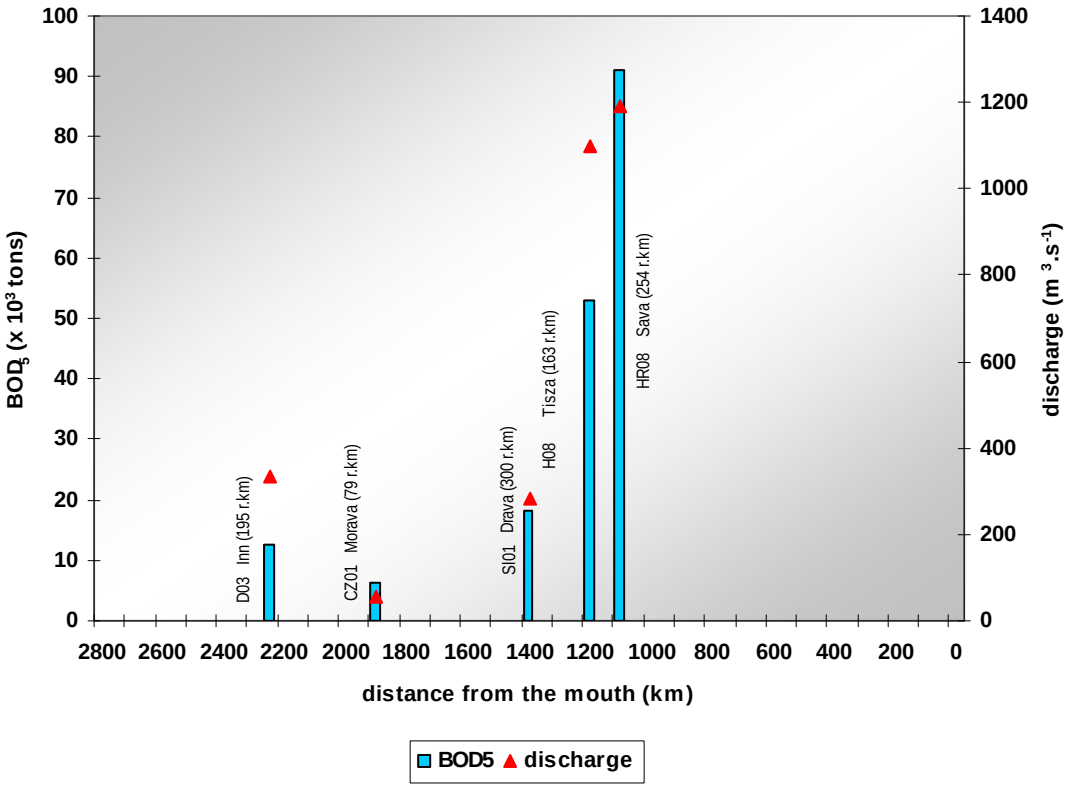


Figure 8.5.10: Annual loads of BOD_5 at monitoring locations on tributaries.

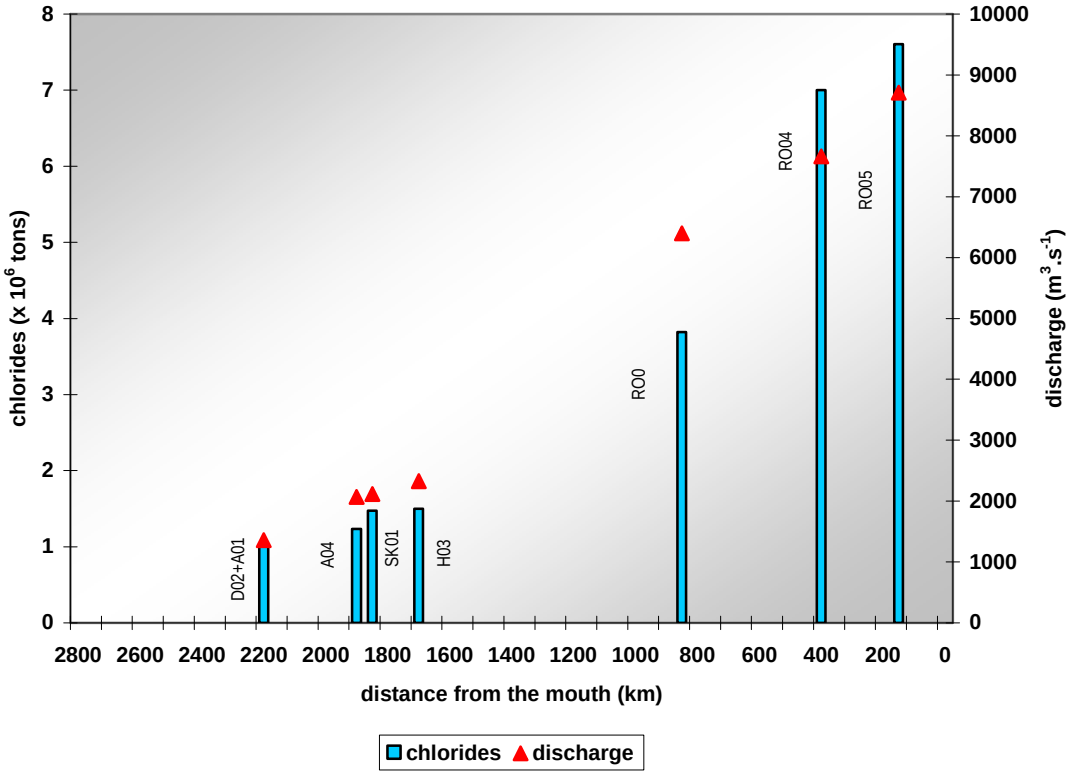


Figure 8.5.11: Annual loads of chlorides at monitoring locations along the Danube River.

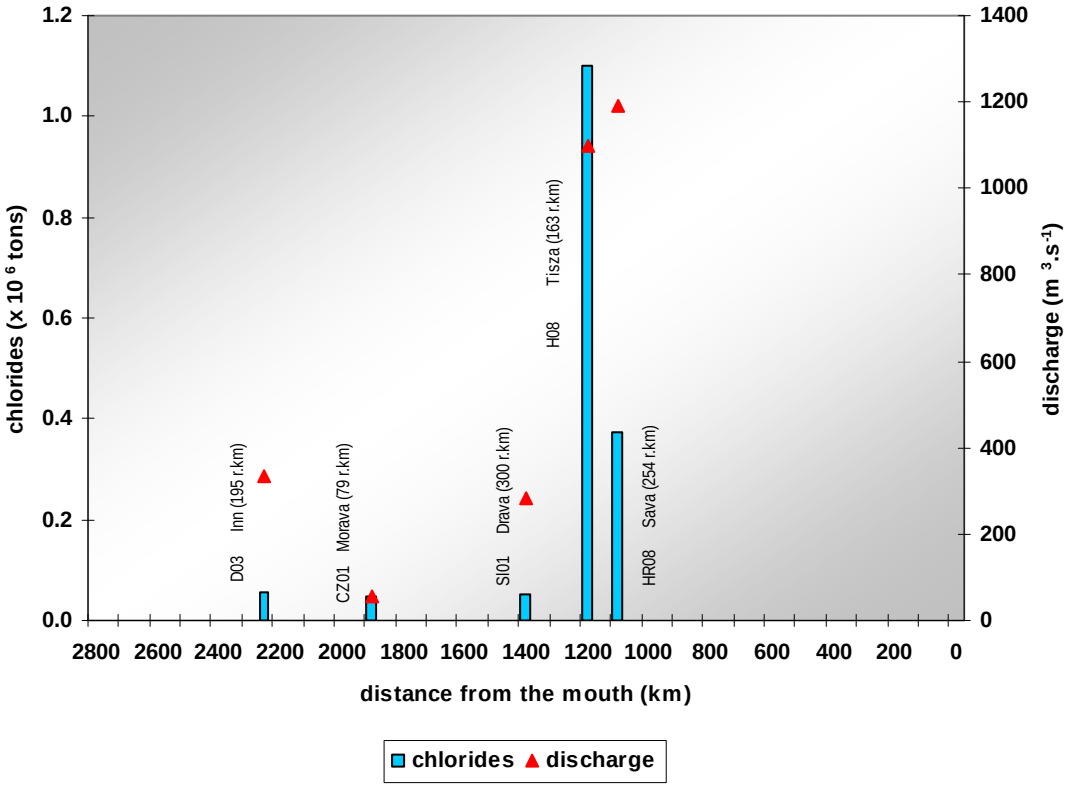


Figure 8.5.12: Annual loads of chlorides at monitoring locations on tributaries.

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 DATA