

WATER QUALITY IN THE DANUBE RIVER BASIN

TNMN Yearbook 2003

(long version)

IMPRINT

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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 Inatitute, 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 2003.

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 instream 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 2003, data from monitoring locations in Bosnia and Herzegovina had been provided to the joint TNMN database for the first time, although these locations had been included in the TNMN list of monitoring sites from the very beginning. Therefore it can be summarised that in 2003 danubian countries provided data from 76 monitoring locations, including 105 sampling sites. Samples were taken from 38 monitoring stations (65 sampling sites) located in the Danube River itself and from 38 monitoring station (40 sampling sites) in tributaries.

Table 4.1.1: List of monitoring sites.

	1	monitoring sites.				1		•	
Country	River	Town/Location	Latitude	Longitude	Distance	Altitude	Catch-	DEFF	Loc.in
Code	Name	Name	d. m. s.	d. m. s.	[Km]	[m]	ment	Code	profile
					' '	' '	[km ²]		· ·
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	М
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	М
SK03	Danube	Komarno/Komarom	47 45 17	18 7 40	1768	103	151961	L1870	М
SK04	/Váh	Komarno	47 46 41	18 8 20	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov			1806	108	131605		M
			47 47 31	17 39 6				L1470	
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	М
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R
									1
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M
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	М
BIH02	/Sava/Una		45 11 6	16 48 42		94	9130	L2290	M
		Kozarska Dubica			16	-			
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				20 36 28			525009		
	Danube	Pancevo	44 51 25		1154,8	70,14		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	
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		Titel	45 11 52	20 19 9	8,9	74,03	157147	L2450	
	/Tisza					,			M
SCG13	/Sava	Jamena	44 52 40	19 5 21	195	77,67	64073	L2470	l Ŀ
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	Ljubicevska	44 35 6	21 8 15	34,8	75,09	37320	L2510	R
	Morava	,			,-	-,,,,,		5.5	1
RO01	Danube	Bazias	44 47	21 23	1071	70	570896	L0020	LMR
NO01	Danube	Dazias			10/1	10	210090	L0020	LIVIT
	l	B	55,57,58	24,40,54	١	١.,			
B 0 0 -	1.1.1	Pristol/Novo Selo Harbour	44 11	22 45	834	31	580100	L0090	LMR
RO02	Danube		1 10 22 20	57,64,69					
	Danube		18,23,29		1 400	16	676150	1 00 40	LMR
RO02 RO03	Danube	us. Arges	44 4 25	26 36 35	432	10	070130	L0240	
RO03	Danube		44 4 25						
RO03 RO04	Danube Danube	Chiciu/Silistra	44 4 25 44 7 18	27 14 38	375	13	698600	L0280	LMR
RO03 RO04 RO05	Danube Danube Danube	Chiciu/Silistra Reni	44 4 25 44 7 18 45 28 50	27 14 38 28 13 34	375 132	13 4	698600 805700	L0280 L0430	LMR LMR
RO03 RO04 RO05 RO06	Danube Danube Danube Danube	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm	44 4 25 44 7 18 45 28 50 45 24 42	27 14 38 28 13 34 29 36 31	375 132 18	13 4 1	698600 805700 817000	L0280 L0430 L0450	LMR LMR LMR
RO03 RO04 RO05 RO06 RO07	Danube Danube Danube Danube Danube	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41	27 14 38 28 13 34 29 36 31 29 40 25	375 132 18 0	13 4 1 1	698600 805700 817000 817000	L0280 L0430 L0450 L0480	LMR LMR LMR LMR
RO03 RO04 RO05 RO06 RO07 RO08	Danube Danube Danube Danube Danube Danube Danube	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm Sf.Gheorghe-Ghorghe arm	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41 44 53 10	27 14 38 28 13 34 29 36 31 29 40 25 29 37 5	375 132 18 0	13 4 1 1	698600 805700 817000 817000 817000	L0280 L0430 L0450 L0480 L0490	LMR LMR LMR LMR LMR
RO03 RO04 RO05 RO06 RO07	Danube Danube Danube Danube Danube	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41	27 14 38 28 13 34 29 36 31 29 40 25	375 132 18 0	13 4 1 1	698600 805700 817000 817000	L0280 L0430 L0450 L0480	LMR LMR LMR LMR
RO03 RO04 RO05 RO06 RO07 RO08	Danube Danube Danube Danube Danube Danube Danube	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm Sf.Gheorghe-Ghorghe arm Conf. Danube	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41 44 53 10 44 4 35	27 14 38 28 13 34 29 36 31 29 40 25 29 37 5	375 132 18 0	13 4 1 1	698600 805700 817000 817000 817000 12550	L0280 L0430 L0450 L0480 L0490 L0250	LMR LMR LMR LMR LMR
RO03 RO04 RO05 RO06 RO07 RO08 RO09 RO10	Danube Danube Danube Danube Danube Danube Janube /Arges /Siret	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm Sf.Gheorghe-Ghorghe arm Conf. Danube Conf. Danube Sendreni	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41 44 53 10 44 4 35 45 24 10	27 14 38 28 13 34 29 36 31 29 40 25 29 37 5 26 37 4 28 1 32	375 132 18 0 0 0	13 4 1 1 1 14 4	698600 805700 817000 817000 817000 12550 42890	L0280 L0430 L0450 L0480 L0490 L0250 L0380	LMR LMR LMR LMR LMR M
RO03 RO04 RO05 RO06 RO07 RO08 RO09	Danube Danube Danube Danube Danube Danube Danube /Arges	Chiciu/Silistra Reni Vilkova-Chilia arm/Kilia arm Sulina - Sulina arm Sf.Gheorghe-Ghorghe arm Conf. Danube	44 4 25 44 7 18 45 28 50 45 24 42 45 9 41 44 53 10 44 4 35	27 14 38 28 13 34 29 36 31 29 40 25 29 37 5 26 37 4	375 132 18 0 0	13 4 1 1 1 14	698600 805700 817000 817000 817000 12550	L0280 L0430 L0450 L0480 L0490 L0250	LMR LMR LMR LMR LMR M

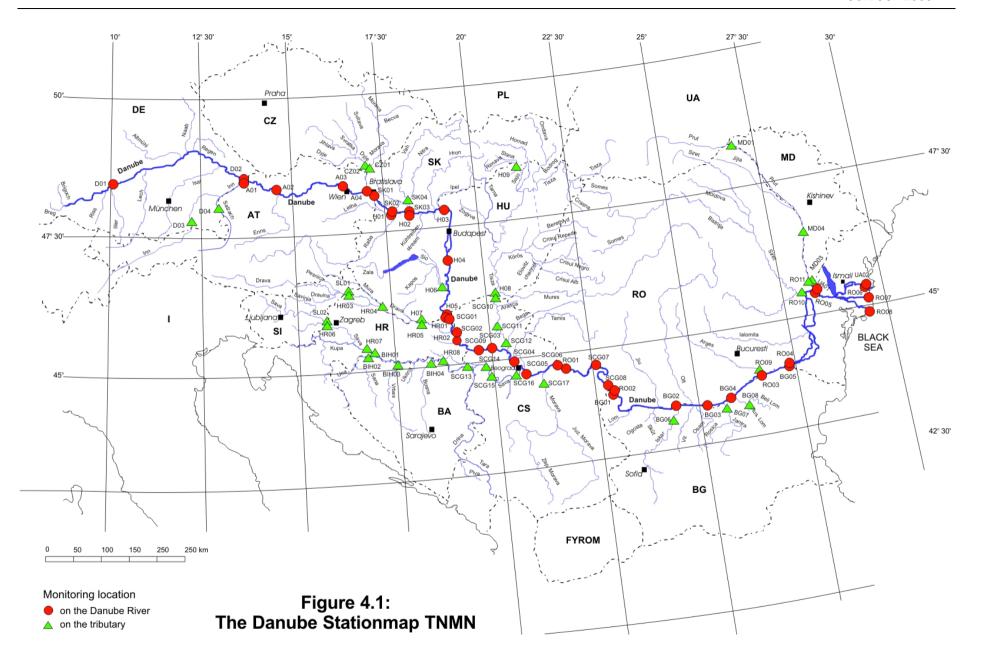
			50,58,66	36,47,58					
BG02	Danube	us. Iskar - Bajkal	43 42 58	24 24 45	641	20	608820	L0780	R
BG03	Danube	Downstream Svishtov	43 37 50	25 21 11	554	16	650340	L0810	MR
BG04	Danube	us. Russe	43 48 06	25 54 45	503	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	44 7 02	27 15 45	375	7	698600	L0850	LMR
BG06	/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	45 28 50	28 13 34	132	4	805700	L0630	М
UA02	Danube	Vilkova-Kilia arm/Chilia arm	45 24 42	29 36 31	18	1	817000	L0690	M

Sampling location in profile: Distance: The distance in km from the mouth of the mentioned river

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

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.



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%
pН	-	-	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 μg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	μg/l μg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine		0.03	1	0.01	0.01 of 30% 0.02 or 30%
Chloroform	μg/l	0.1	1	0.02	0.02 or 30% 0.02 or 30%
Carbon tetrachloride	μg/l	0.1	1	0.02	0.02 or 30%
	μg/l /l		1	0.02	
Trichloroethylene	μg/l	0.1	1		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 $\pm 20\%$ 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 2003

The organisation of interlaboratory comparison in the Danubian laboratories started in 1992 to support monitoring activities under Bucharest Declaration. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, took the responsibility for organising the testing. Since the first distribution in 1993 both the range of tested determinands and the number of participating laboratories increased significantly. At present time, National Reference Laboratories (NRL) and other national laboratories taking part in the monitoring activities of the TNMN, as well as laboratories responsible for pollution monitoring in the Black Sea area, participate in the QualcoDanube proficiency testing.

In 2003 four distributions had been made. The number of participating laboratories was 36 with an additional laboratory (from Constanta) in the third distribution.

In the process of assessment, the Youden-pair evaluation technique was usually followed. The results and an evaluation have been published in the separate report.

4.3.1.1 Results of performance testing of water samples

General determinands

Chloride, potassium, sodium were analysed in real water sample from Danube River. The results were characterized by systematic error.

For sulphate, calcium, magnesium and total hardness determinations synthetic samples were distributed. The performance of calcium was excellent with every analytical result within the range \pm 10%, the results of total hardness were also satisfactory except results of three laboratories.

Results of analysis of magnesium were influenced not only by systematic but random error too.

Determinands characterising organic pollution

Real surface water samples were analysed for testing of COD_{Mn} , TOC and AOX performance, while synthetic samples were distributed for COD_{Cr} , BOD_5 , TOC (at wastewater level), phenol index and MBAS (methylene blue anion active surfactants). Samples for petroleum hydrocarbons were as extracts.

Results of COD_{Mn} were not good, with only two thirds of data acceptable, the rest of results fell into the warning limit or out of the limit. The performance of TOC was relatively good, determination of AOX was very good. Eleven laboratories reported results without any rejected data.

 ${
m COD_{Cr}}$ at wastewater level showed quite good results except of three laboratories. The results of ${
m BOD_5}$ demonstrate very strong systematic error. Altogether 38% of the results fell into warning limit. Results of TOC at wastewater level were relatively good except three laboratories again.

The results of MBAS indicated significant systematic error. Among the reported data there had been extremely low and high values, some of them were given by the same laboratories as in a previous year.

Relatively small number of laboratories reported results of petroleum hydrocarbons. These showed high systematic error and altogether 62-64% were within acceptable limit. Unacceptable results were reported by the same laboratories as in previous years.

Results of phenol index were influenced by strong systematic error both at surface water and waste water concentration level. In waste water samples the analytical results showed significant discrepancies in both positive and negative direction.

Nutrients

Determinands from the group of nutrients had been analysed in real surface water.

Results of ammonium and total P were relatively satisfactory but influenced by significant systematic error. In case of nitrates 70 % of analytical results were within acceptable limit (+15%). Results of phosphate showed both systematic and random error.

Non-specific determinand

Cyanides were analysed in synthetic samples at concentration level of both surface water and waste water. The reported data showed significant systematic error in both cases with only two thirds of data acceptable.

Heavy metals

Real surface water samples had been distributed for iron, manganese, cadmium, chromium and copper analysis.

The results of iron and manganese analysis were quite satisfactory with slight systematic error. Analysis of cadmium, chromium and copper cadmium were relatively good. The best results were achieved in case of copper, while the results of cadmium, chromium were characterized by significant systematic error.

Synthetic samples were distributed for cadmium, chromium, copper as well as lead, nickel, zinc and arsenic at waste water concentration level. The performance of lead was rather good, while data of nickel and zinc were influenced by systematic error.

Samples for mercury analysis as synthetics were distributed three times during 2003. The performance of mercury at surface water concentration level was good with 81% acceptable results, at waste water concentration level was rather weak.

The analyses of arsenic were quite good except one laboratory; the others were inside of limit of error.

There were few laboratories which reported biased data in most cases and these were the same as in a previous year.

Micropollutants

In case of micropollutants (atrazine, lindane, DDT) the results were rather various. The samples for analysis of these determinands had been distributed three times (except DDT) as extracts. Results of atrazine analysis were rather scattered at surface water concentration level while at higher concentration level the results were better but still showing very strong systematic error.

The results of lindane and DDT analysis were similar but influenced by random error also.

4.3.1.2 Results of performance testing of sediment samples

During 2003 determinands representing nutrients (total N, total P), heavy metals (cadmium, chromium, copper, lead, nickel, zinc) and synthetic pollutants (lindane, atrazine, DDT) had been measured in sediment samples as a part of interlaboratory comparison.

Nutrients

The results of total N were relatively good and the results of total P show surprisingly good agreement.

Heavy metals

The results of cadmium, chromium, lead and nickel were quite good but influenced by systematic error. In case of zinc a good performance was achieved with only slight systematic error.

Organic micropollutants

Results reported by laboratories could not be evaluated and represented on figures. Both systematic error and significant discrepancies in positive and negative directions were observed. The results reported by laboratories differed from each other in order of magnitude.

4.3.1.3 Conclusion

Four distributions in 2003 provided information on the performance of the laboratories participating in the monitoring process in the frame of TransNational Monitoring Network. As regards general determinands, good performance was observed, as well as for nutrients. These determinands have been analysed since the beginning of QualcoDanube intercalibration programme, but some analyses still require improvement, e.g. ammonium-N and also cyanides as non-specific determinand.

The performance of determinands characterizing organic pollution (e.g., COD, BOD₅, MBAS, TOC, AOX) were relatively good. Analyses of BOD₅ have improved significantly and AOX was also excellent this time.

In the field of organic micropollutants analysis, an improvement is required. While the results of extracts could be evaluated, they had been influenced by strong systematic and random error. Results from sediment samples analysis, reported by laboratories for the same micropollutants, could not be evaluated. It is supposed that sample pre-treatment for analyses is rather poor and causes troubles contributing to bad analytical results.

Performance of metals analysis was moderate; the results were influenced mainly by systematic error. Analyses of arsenic and mercury have improved significantly in comparison with results of previous years.

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 BOD₅, PO₄³-P and NO₃-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 for TNMN purposes.

Determinand	Unit		· · · · · · · · · · · · · · · · · · ·	Class		
		I	II	III	IV	V
			TV			
			Cl	ass limit val	ues	
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			
	. 1		< 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	μg.l ⁻¹	25	50	100	250	> 250
Metals (dissolved) ***	*-1		1,5			
Zinc	μg.l ⁻¹	-	5	-	-	-
Copper	μg.l ⁻¹	-	2	-	-	-
Chromium (Cr-III+VI)	μg.l ⁻¹	-	2	-	-	-
Lead	μg.l ⁻¹	-	1	-	-	-
Cadmium	μg.l ⁻¹	-	0.1	-	-	-
Mercury	μg.l ⁻¹	-	0.1	-	-	-
Nickel	μg.l ⁻¹	-	1	-	-	-
Arsenic	μg.l ⁻¹	-	1	-	-	-
Metals (total)						
Zinc	μg.l ⁻¹	bg	100	200	500	> 500
Copper	μg.l ⁻¹	bg	20	40	100	> 100
Chromium (Cr-III+VI)	μg.l ⁻¹	bg	50	100	250	> 250
Lead	μg.l ⁻¹	bg	5	10	25	> 25
Cadmium	μg.l ⁻¹	bg	1	2	5	> 5
Mercury	μg.l ⁻¹	bg	0.1	0.2	0.5	> 0.5
Nickel	μg.l ⁻¹	bg	50	100	250	> 250
Arsenic	μg.l ⁻¹	bg	5	10	25	> 25
Toxic substances						
AOX	μg.l ⁻¹	10	50	100	250	> 250
Lindane	μg.l ⁻¹	0.05	0.1	0.2	0.5	> 0.5
p,p'-DDT	μg.l ⁻¹	0.001	0.01	0.02	0.05	> 0.05
Atrazine	μg.l ⁻¹	0.02	0.1	0.2	0.5	> 0.5
Trichloromethane	μg.l ⁻¹	0.02	0.6	1.2	1.8	> 1.8
Tetrachloromethane	μg.l ⁻¹	0.02	1	2	5	> 5
Trichloroethene	μg.l ⁻¹	0.02	1	2	5	> 5
Tetrachloroethene	μg.l ⁻¹	0.02	1	2	5	> 5
Biology						
	f -	≤ 1.8	1.81 - 2.3	2.31 - 2.7	2.71 - 3.2	> 3.2
macrozoobenthos						

^{*} values concern 10-percentile value

bg background values TV target value

^{**} for dissolved metals only guideline values are indicated

5. Results of basic statistical processing

In 2003, 76 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 105 sampling sites, out of which 65 are located on the Danube River itself and 40 on the tributaries. Comparing the list of monitoring locations presented in Table 4.1.1 with the list of locations from which data had been sent to the Central Point it can be concluded that the only missing are data from two Ukrainian monitoring locations.

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 of the determinand measured according to the agreed method
name	
Unit	unit of the determinand measured
N	number of measurements
Min	minimum value of the measurements done in the year 2003
Mean	arithmetical mean of the measurements done in the year 2003
Max	maximum value of the measurements done in the year 2003
C50	50 percentile of the measurements done in the year 2003
C90	90 percentile of the measurements done in the year 2003
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 corresponding class was assigned to 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 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 only statistics was 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 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 in 2003 (4 times per year). 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 2003. 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 itself except several heavy metals, in case of which higher concentrations were measured in the Danube River.

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in Danube River and its tributaries in 2003.

Determinand name	Unit	Danube					Tributaries					
		No.of monitoring	Range o	Range of values Mean			No.of monitoring	of monitoring Range of values		Mean		
		locations / No. of	Min	Max	Min _{avg}	Max _{avg}	locations / No. of	Min	Max	Min _{avg}	Max _{avg}	
		monitoring sites with					monitoring sites with					
		measurements					measurements					
Temperature	°C	37/64	0,0	29,2	11,0	16,7	38/40	0,0	32,4	8,1	24,3	
Suspended Solids	mg/l	37/64	< 1	143	5	100	38/40	< 1	400		147	
Dissolved Oxygen	mg/l	37/64	2,9	17,1	8,0	11,9		3,3		7,4	12,0	
BOD₅	mg/l	37/64	< 0,5	8,7	1,2	4,1	34/36	0,5			7,5	
COD _{Mn}	mg/l	35/62	0,6	7,5	1,7	5,3	31/33	1,0				
COD _{Cr}	mg/l	30/48	< 1,0	36,0	5,5	32,0	30/32	3,0	76,0	6,5	33,4	
TOC	mg/l	14/20	1,1	7,9	1,8	4,7	11/13	1,0	22,0	1,5	11,7	
DOC	mg/l	6/8	< 0,1	3,4	0,3	1,8	7/7	1,2	9,6	1,9	7,7	
pH		37/64	6,5	9,0	7,4	8,4	38/40	6,2	9,3			
Alkalinity	mmol/l	36/63	0,9	6,5	1,5	3,6	38/40	0,8	8,9	1,3	7,7	
Ammonium-N	mg/l	37/64	< 0,004	1,280	0,021	0,387	38/40	< 0,010	5,560	0,027	3,515	
Nitrite-N	mg/l	37/64	< 0,003	0,407	0,014	0,090	38/40	0,001	0,193	0,004	0,113	
Nitrate-N	mg/l	37/64	0,07	4,40	0,66	3,17	38/40	< 0,05	11,20	0,30		
Total Nitrogen	mg/l	19/33	0,60	6,94	1,79	3,42	29/31	0,50	11,00	0,65		
Organic Nitrogen	mg/l	17/25	0,01	6,07	0,04	1,93	24/26	0,03	5,45	0,21	2,19	
Ortho-Phosphate-P	mg/l	37/64	0,003	4,401	0,025	0,215	36/38	< 0,002	1,888	0,006	0,424	
Total Phosphorus	mg/l	37/64	0,01	5,10	0,05	0,36	35/37	0,01	3,63	0,04	1,00	
Total Phosphorus - Dissolved	mg/l	10/12	0,01	0,25	0,04	0,14		0,01	0,56			
Chlorophyll-a	μg/l	17/26	< 0,1	143,0	5,7	31,6	14/16	< 0,1	381,8	1,5	107,7	
Conductivity @ 20°C	μS/cm	37/64	237	1353	369	634	38/40	131	1320		993	
Calcium	mg/l	36/63	12,2	164,0	45,2	66,7	38/40	12,0	172,0	33,7	96,3	
Sulphates	mg/l	35/62	4	112	20	82	34/36	4	220	15	142	
Magnesium	mg/l	36/63	4,9	102,0	12,1	27,9	38/40	2,6			56,6	
Potassium	mg/l	35/60	0,7	9,9	1,9	5,3	31/33	0,3	14,8		10,0	
Sodium	mg/l	35/60	1,3	76,9	9,0	74,7	31/33	2,0	89,0			
Manganese	mg/l	23/46	< 0,001	1,135	0,009	0,200	13/13	0,002	0,550	0,017	0,244	
Iron	mg/l	23/46	< 0,010	4,482	0,078	0,985		< 0,002	9,400	0,005		
Chlorides	mg/l	36/63	9	387	16	77	34/36	2	197	4	97	
Macrozoobenthos- saprobic index		14/14	1,93	3,23	2,02	2,66	15/15	1,20				
Macrozoobenthos - no.of taxa		9/9	3	82	5	82	8/8	2	49	3	49	

Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in Danube River and its tributaries in 2003 (cont.).

Determinand name	Unit		Danı		tea acte		is in Bundoe Tave		Tributaries			
		No.of monitoring	Range o	f values	Me	an	No.of monitoring	Range o	of values	Me	an	
		locations / No. of	Min	Max	Min _{avg}	Max _{avg}	locations / No. of	Min	Max	Min _{avg}	Max _{avg}	
		monitoring sites with			3	9	monitoring sites with			9	9	
		measurements					measurements					
Zinc - Dissolved	μg/l	22/22	< 0,8	154,0	3,3	37,9	14/14	< 2,1	824,0	< 3,0	131,6	
Copper - Dissolved	μg/l	22/22	0,05	182,90	1,00			< 0,06	5,42	0,47	< 3,00	
Chromium - Dissolved	μg/l	23/23	0,05	16,81	0,24	< 3,00	11/11	< 0,07	6,50	0,28	2,57	
Lead - Dissolved	μg/l	23/23	0,05	14,10	< 0,20	2,53	14/14	< 0,04	< 3,00	0,17	< 3,00	
Cadmium - Dissolved	μg/l	22/22	< 0,02	15,06	0,02	2,10	14/14	< 0,02	< 0,50	< 0,02	< 0,50	
Mercury - Dissolved	μg/l	31/32	< 0,050	< 0,300	0,058	< 0,300	20/20	< 0,030	< 0,300	< 0,030	< 0,300	
Nickel - Dissolved	μg/l	22/22	0,05	9,11	0,92	2,23	14/14	0,60	15,20	1,16	3,83	
Arsenic - Dissolved	μg/l	14/14	< 0,20	5,67	0,67	1,38	11/11	0,10	10,90	0,54	2,93	
Aluminium - Dissolved	μg/l	12/12	< 1,0	227,0	12,0	38,2	9/9	< 0,8	345,0	7,4	41,6	
Zinc	μg/l	26/47	< 0,8	400,0		62,4	20/20	< 1	1600,0	5,9	288,9	
Copper	μg/l	26/47	0,05	283,60		27,95	24/24	< 0,06	177,30	0,60	33,44	
Chromium - total	μg/l	26/47	0,05	83,17	0,60	< 10		< 0,07	29,60	0,57	< 10	
Lead	μg/l	26/47	0,05	152,20	0,66	11,99	20/20	< 0,04	51,00	0,71	13,58	
Cadmium	μg/l	26/47	< 0,02	68,39		6,79		< 0,01	7,21	0,03	2,31	
Mercury	μg/l	22/38	< 0,050	6,270	0,092	0,673	14/14	< 0,030	0,380	0,030	< 0,300	
Nickel	μg/l	26/47	0,05	41,37	1,00	8,15		0,05	50,14	1,50	16,14	
Arsenic	μg/l	17/22	0,32	10,00		3,35		0,14	12,50	0,60	5,73	
Aluminium	μg/l	14/16	< 20,0	3140,0	25,0	533,3	10/10	12,4	3990,0	56,2	1445,6	
Phenol index	mg/l	36/62	< 0,001	0,100	0,001	< 0,020	31/33	< 0,001	0,024	< 0,001	< 0,020	
Anionic active surfactants	mg/l	36/62	< 0,006	1,210		0,296	31/33	< 0,010	0,192	< 0,010	0,102	
AOX	μg/l	14/14	3,1	119,0	6,9	24,7	11/11	9,0	162,0	< 10,0	122,0	
Petroleum hydrocarbons	mg/l	27/45	0,002	7,410		2,007		< 0,005	4,900	< 0,005	1,370	
PAH (sum of 6)	μg/l	8/10	< 0,001	< 0,100	0,002	< 0,100		< 0,004	< 0,100	< 0,004	< 0,100	
PCB (sum of 7)	μg/l	5/7	< 0,005	0,030		0,018	5/5	< 0,002	0,085	< 0,002	0,032	
Lindane	μg/l	31/52	< 0,001	0,990	< 0,001	0,192		< 0,001	0,426	< 0,001	0,114	
pp′DDT	μg/l	31/52	0,001	0,110	0,001	0,021	26/26	< 0,002	< 0,050	< 0,002	< 0,050	
Atrazine	μg/l	25/45	< 0,001	0,430	0,009	0,181	13/13	0,001	0,585	0,008	0,123	
Chloroform	μg/l	17/19	< 0,01	1,10	0,01	0,55	11/11	< 0,01	26,10	< 0,01	13,65	
Carbon tetrachloride	μg/l	17/19	< 0,01	0,10	< 0,01	0,10	10/10	< 0,01	0,30	< 0,01	0,14	
Trichloroethylene	μg/l	16/18	< 0,01	0,10		0,10	10/10	< 0,01	2,50	< 0,01	0,52	
Tetrachloroethylene	μg/l	16/18	< 0,01	0,20	< 0,02	0,11	11/11	< 0,01	0,20	0,01	0,12	
	10 ³ CFU/											
Total Coliforms (37°C)	100 ml	24/51	0,00	160,00	0,01	44,58	23/25	0,00	1800,00	0,29	154,58	
	10 ³ CFU/											
Faecal Coliforms (44°C)	100 ml 10° CFU/	20/41	0,00	16,00	0,04	3,56	18/20	0,00	350,00	0,09	56,67	
Faecal Streptococci	100 ml	21/46	0,00	3,20	0,00	0,99	15/17	0,00	11,00	0,00	4,29	

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6. Presentation of classification results

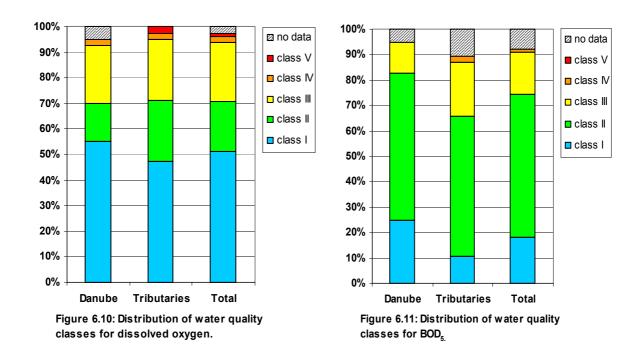
The classification results given in tables of Annex 1 are presented in this chapter in aggregated way in the form of maps and charts. The selection of determinands for the presentation to be shown by maps and charts has been conducted by intention to present either characteristic basic determinands of 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.

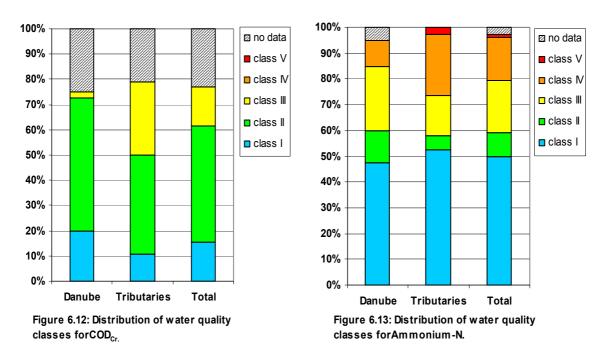
With purpose to illustrate the share of locations fulfilling requirements on target value (corresponding to class I and II) and of those on the non-complying site, Figures 6.10 - 6.20 show percentage of monitoring locations in water quality classes. The percentages were calculated on the basis of the 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 2003, 70 % of locations in the Danube River satisfied the target value. This is less than in 2002, when 85 % of locations corresponded to class I and II. From locations in tributaries 71 % could be classified by class I and II and the worst classes IV and V were represented by 5 % of locations (see also Figure 6.10).

 BOD_5 is used as an indicator of biodegradable organic pollution in waters. The share of locations satisfying target value for BOD_5 in 2003 is similar to situation in 2002 - 83 % of locations in Danube River and 66 % in tributaries. Slightly different was a distribution of locations between class I and II, with lesser amount of locations in class I in 2003. The rest of locations in the Danube River corresponded to class III (13 %), in case of tributaries to class III and IV (24 %) (see also Figure 6.11).



 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 23 % of all monitoring locations. In 2003, the results of classification were more favourable than in 2002, with 73 % of locations in Danube River and 50% of locations in tributaries in class I and II (in comparison to 58 % and 39 % in Danube River and tributaries, respectively, in 2002). There were no locations in class IV and V in the Danube River or tributaries.

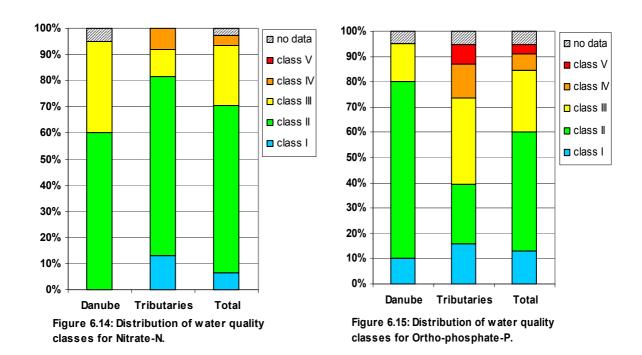


From the group of nutrients, ammonium-N, nitrate-N, ortho-phospate P and total P have been selected for presentation of classification results.

From the Figure 6.13 can be seen that in 2003 concentrations of ammonium-N corresponded to class I and II in 60 % of locations in both Danube River and 58% of locations in tributaries. This is comparable with classification in 2002. In Danube River, 25% of locations corresponded to class III and 10 % to class IV. In tributaries all five classes were represented, with 16 % in class III, 24 % 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 Danube River, the results of nitrate-N classification are rather balanced over the years. In 2003 there were no locations representing class I from those included in TNMN, class II was observed in 60% of locations. An exceeding of the target value was observed in 35 % of locations, corresponding to class III.

From locations on tributaries, 82 % of them satisfied target value with vast majority in class II (68%) and only 13 % in class I, which is slightly better situation than in 2002. The rest of locations belonged to either class III (11%) or class IV (8%).

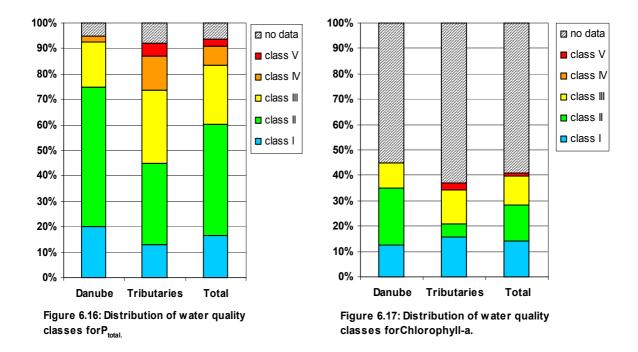


Regarding ortho-phosphate-P, from the Figure 6.15 can be seen that while in the Danube River itself classes I-III were represented, all 5 classes of the classification scheme occured in tributaries. A situation in the Danube River is practically without changes in comparison with 2002, with 80% of locations satisfying target value. The content of ortho-phosphate-P is significantly higher in tributaries included in TNMN, with 40 % of locations corresponding to class I and II, 34% to class III, and 21% in classes IV and V. The results of ortho-phosphate P classification in tributaries in 2003 indicate worse conditions than in 2002.

The number of locations with available results on total P had increased in 2003, especially in tributaries, in case of which 24% of locations were without total P data in 2002.

In 2003, 75% of locations in Danube River corresponded to class I and II, whilst class III had been represented by 18%. Class IV also occurred (2,5%). These results are comparable with those observed in Danube River in 2002.

Similarly to ortho-phosphate P, tributaries indicate worse quality, with only 45% of locations satisfying the target value. The rest of locations corresponded to class III (29%), class IV (13%) and class V (5%) (see Figure 6.16).



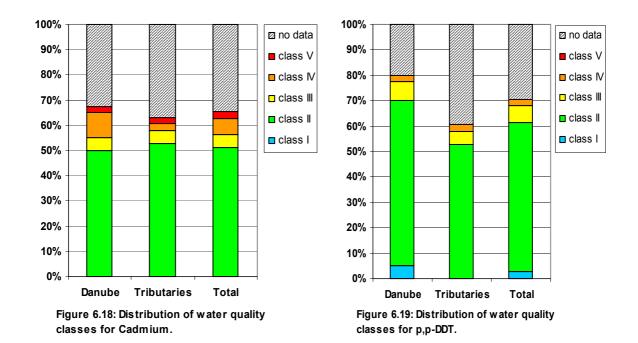
Content of chlorophyll-a as an indicator of primary production is closely connected to nutrient content. Inspite of its importance especially in slow-flowing lowland rivers, still not even half of the locations from TNMN possesses this information. Therefore it can not be expected that classification results shown in figure 6.17 could give representative picture. Anyhow, class I and II were observed in 35 % of locations in Danube River and 21 % of locations in tributaries.

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 33% of locations, concentration of mercury and arsenic were missing in 45% and 55% of locations, respectively.

Similar picture is in tributaries, with 37-47 % of locations without data on cadmium, chromium, copper, zinc and lead and 63% of locations without mercury and arsenic analysis. In the Danube River, class II was achieved in the following percentage of locations: 50 % for cadmium, 53% for copper, 50% for zinc, 20% for mercury, 45% for arsenic, 48% for lead, 68% for chromium and 68% for nickel. In case of chromium and nickel all locations with measurements were on a complying site.

Regarding tributaries, the percentage satisfying target value represented by class II is the following: 53% for cadmium, 11% for mercury, 55% for chromium, 53% for copper, 40% for zinc, 61% for nickel, 32% for arsenic and 29% for lead.

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



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 70 % of locations in the Danube River and 53 % of location in tributaries. Non-compliance is observed in 10 % and 8 % of locations in the Danube River and tributaries, respectively. The rest of locations are without measurements.

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 38 % of locations corresponded to class I – II and 23 % to class III in the Danube River, 38 % of locations are without data. The non-completeness of data is even more significant in tributaries, with only 34 % of locations possible to classify - 24 % corresponded to class I and II, and 11% to classes III-IV. On the other hand it should be noted that the percentage of TNMN locations without atrazine data had decreased from 63% in 2002 to 51 % in 2003.

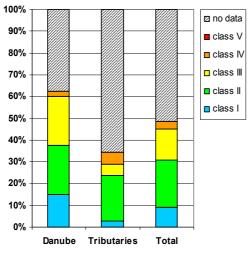
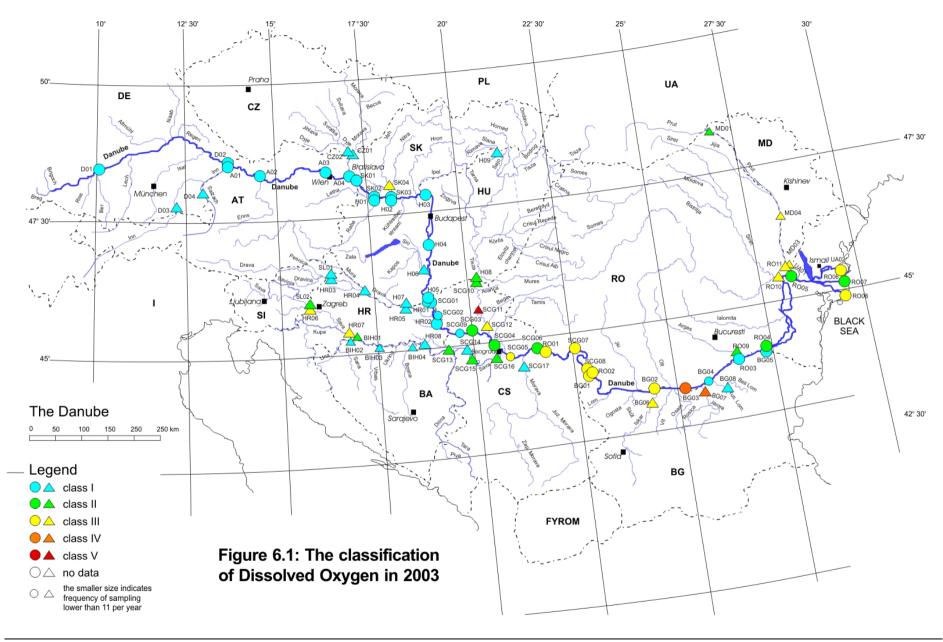
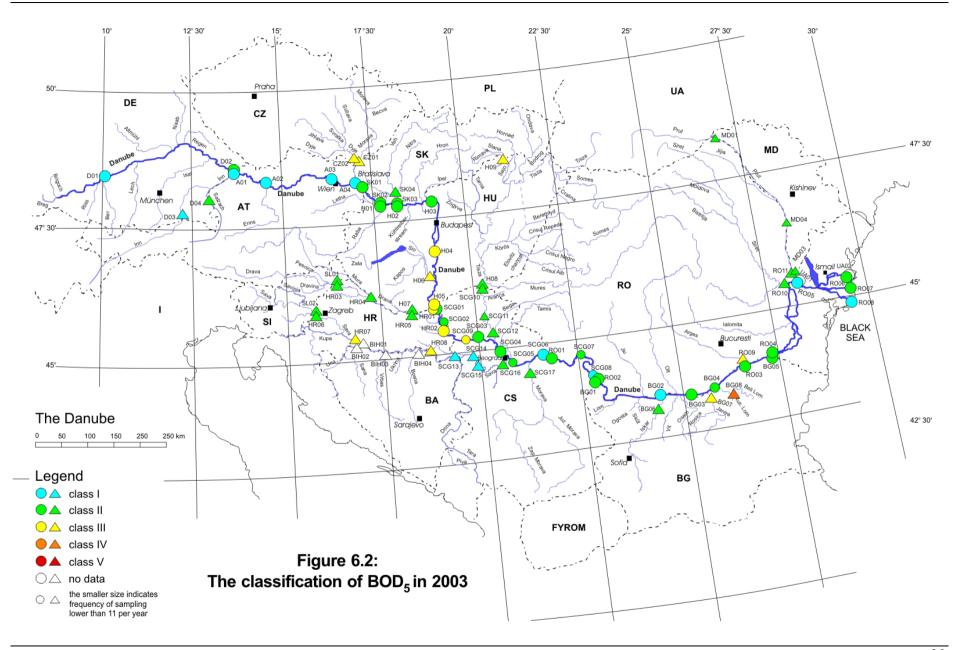
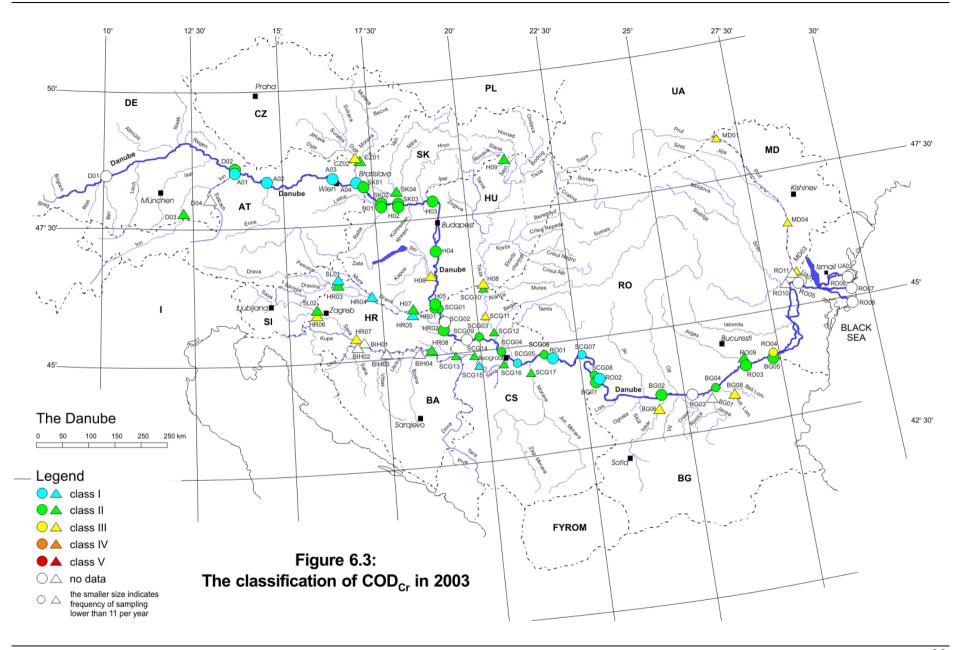
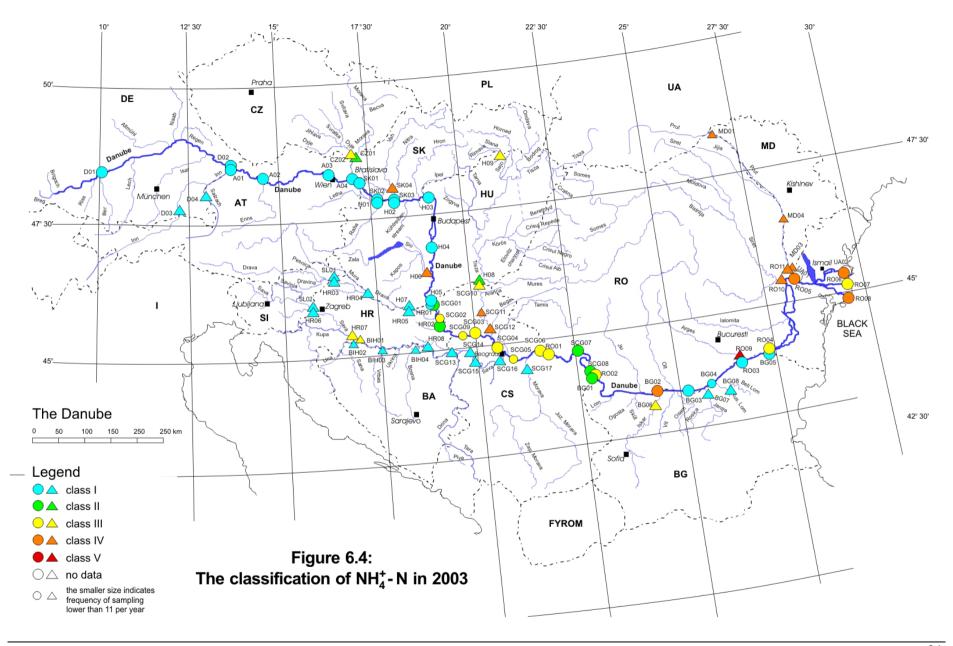


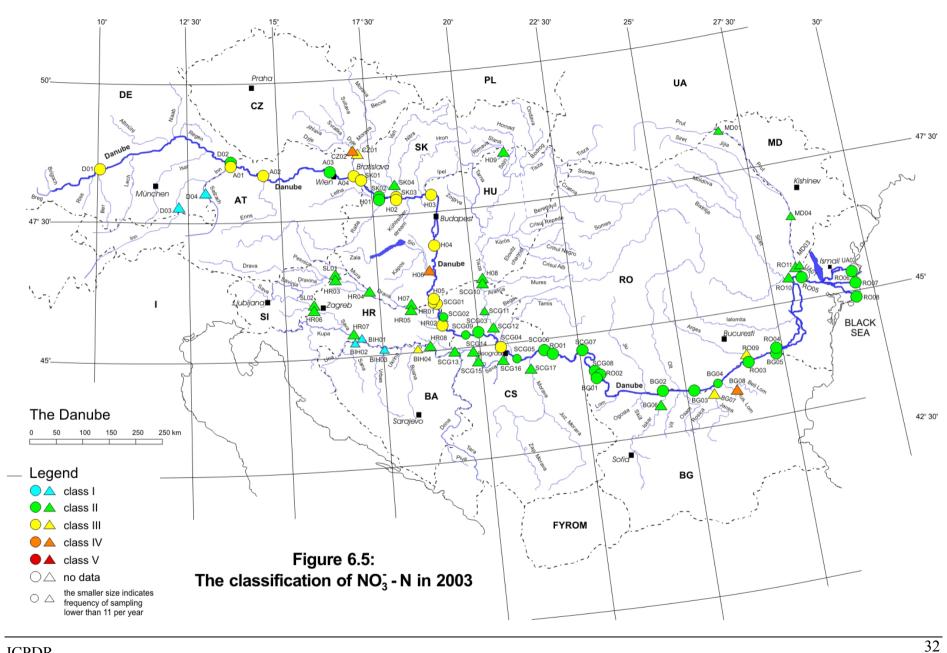
Figure 6.20: Distribution of water quality classes for Atrazine.

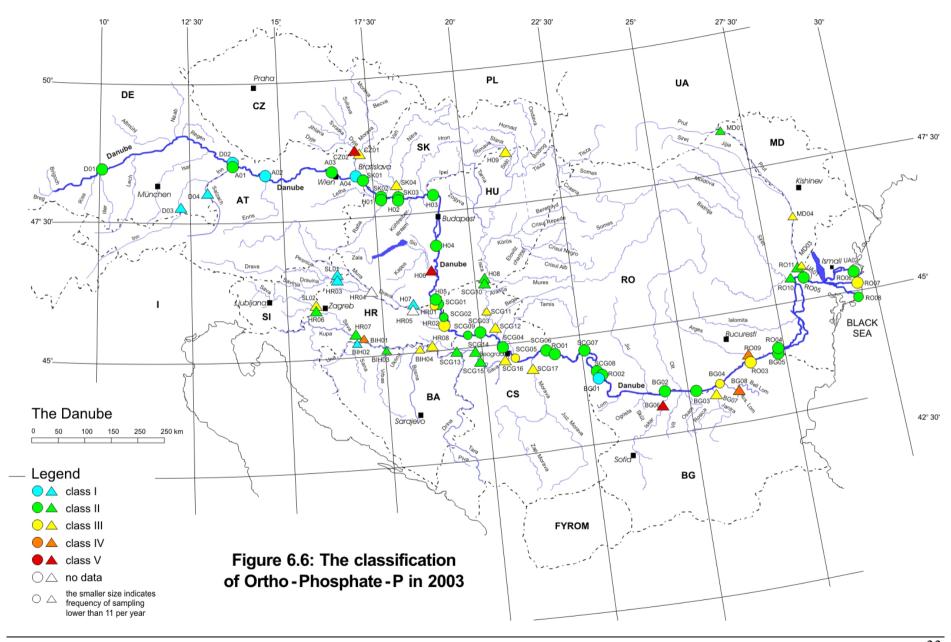


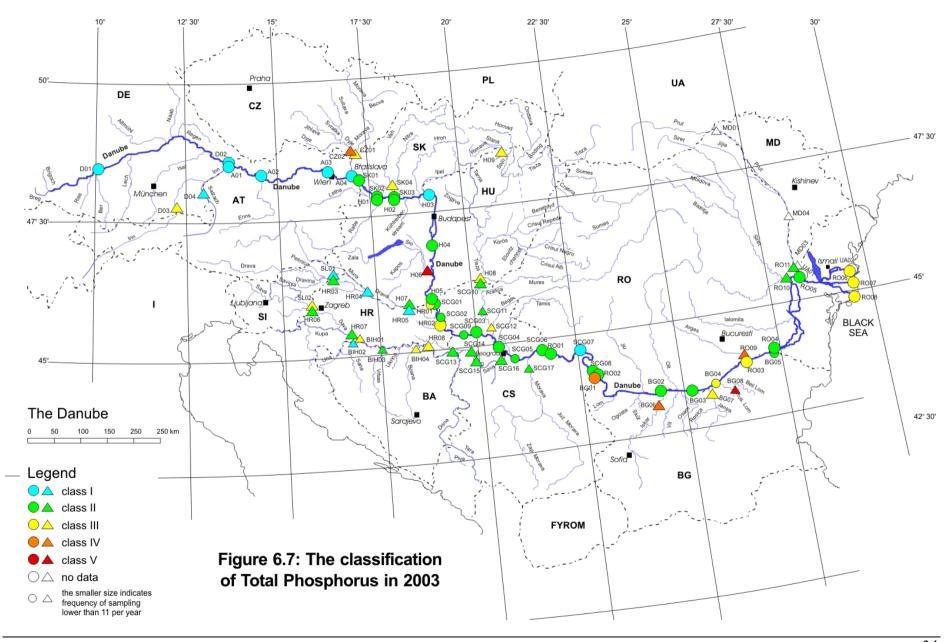


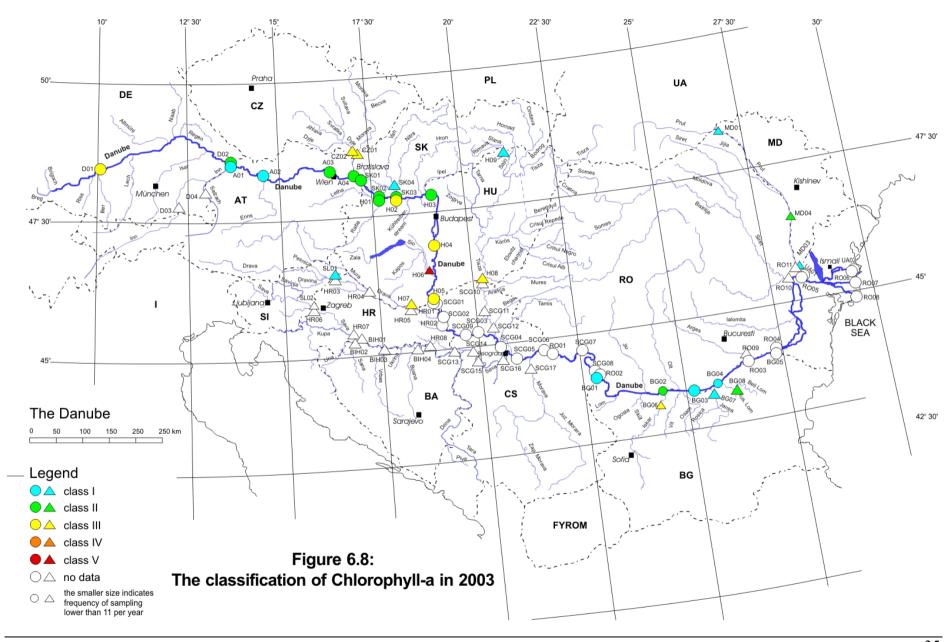


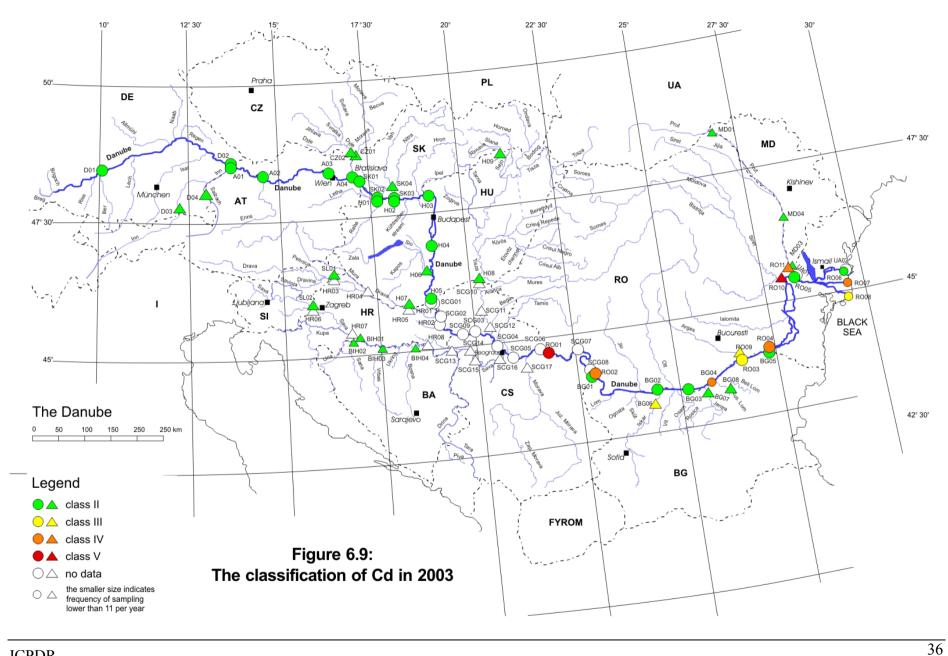












7. Profiles and trend assessment of selected determinands

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, BOD₅, COD_{Cr}, NH₄⁺-N, NO₃⁻-N, PO₄³--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 2003, the highest content of degradable 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 degradable organic matter in 2003 were Russenski Lom, Sio, Jantra. In case of nutrients there were more tributaries considered rather polluted in 2003 – Prut, Arges, Russenski Lom, Iskar, Sio, Dyje and Sava at Una Jasenovac.

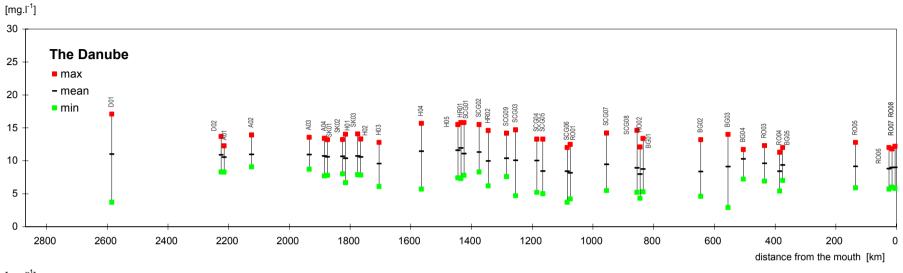
Positive changes in water quality can be seen in several TNMN locations. Taking into account the whole period of TNMN operation, decrease of biodegradable organic pollution is visible in Austrian, Slovakian section of Danube River and in some parts of lower Danube section (Bazias, Pristol, Ren-Chilia and mouth). Tributaries Inn, Dyje, Drava downstream of Botovo and Arges show the same tendency.

As for the nutrients, ammonium-N decreases in locations of the upper part of Danube River down to Hercegszanto (H05), in tributaries of 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. A tendency of development at location Danube-Silistra-Chiciu is not the same taking into account results of measurements done by Bulgaria and Romania. Nitrate-N decreases also in tributaries Morava, 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 Novo Selo Harbour/Pristol and us. Iskar. An improvement can be seen also in tributaries like Iskar, Jantra, Russensko Lom and Siret. Worth mentioning is also a very high variability between years in lower part of Danube River. This causes interpretation of temporal changes rather difficult, but could be an indication of the fact that situation regarding pollution discharge into surface waters is not under control there. Some part of this variability, especially in case of tributaries, could be attributable also to climatic and hydrological conditions.

Figure 7.1: The minimum, mean and maximum of Dissolved Oxygen in 2003



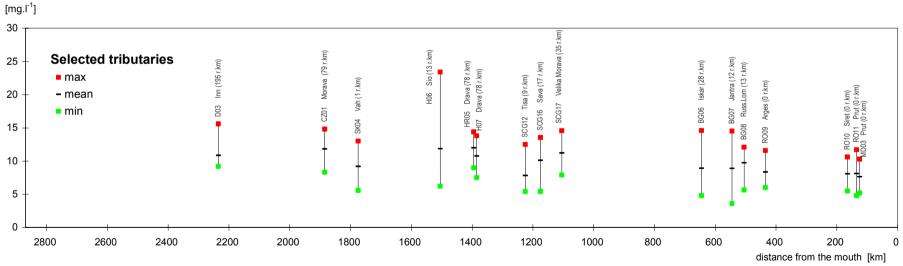
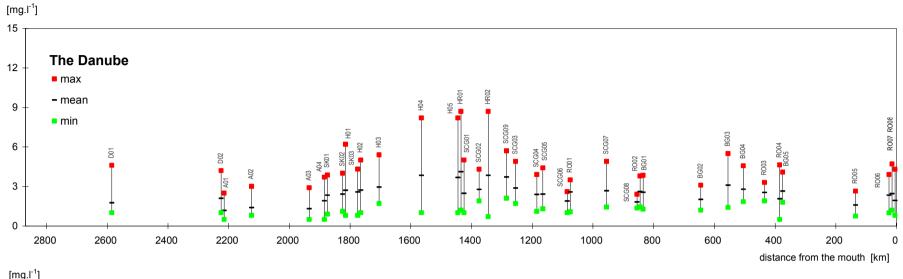
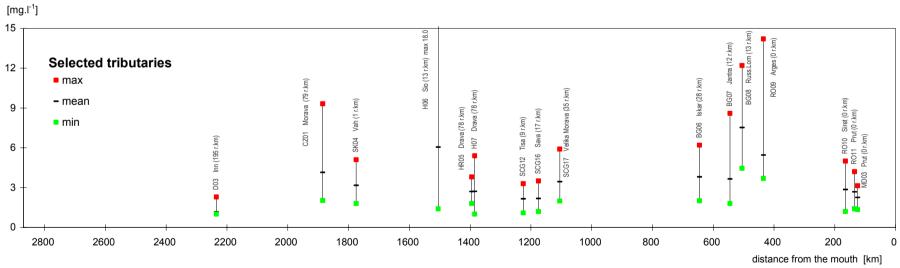


Figure 7.2: The minimum, mean and maximum of BOD₅ in 2003





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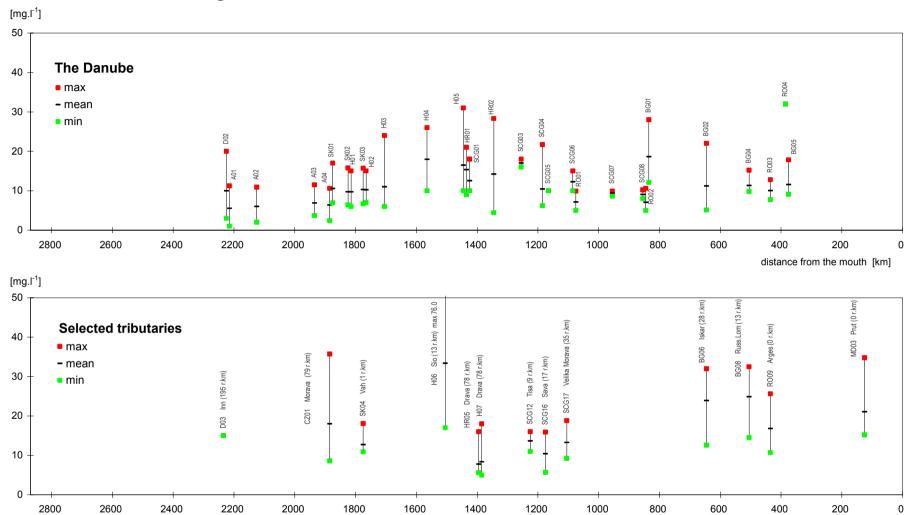
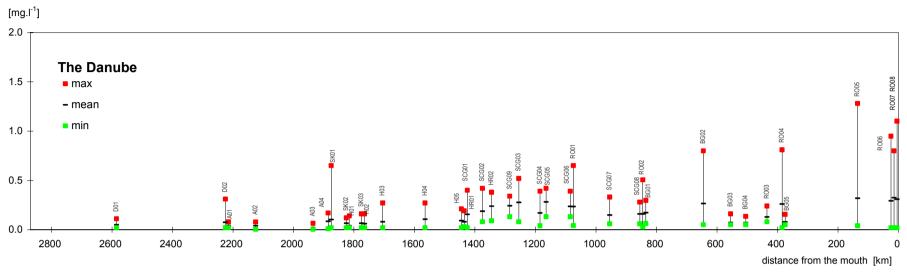


Figure 7.3: The minimum, mean and maximum of COD_{Cr} in 2003

41

distance from the mouth [km]

Figure 7.4: The minimum, mean and maximum of NH₄-N in 2003



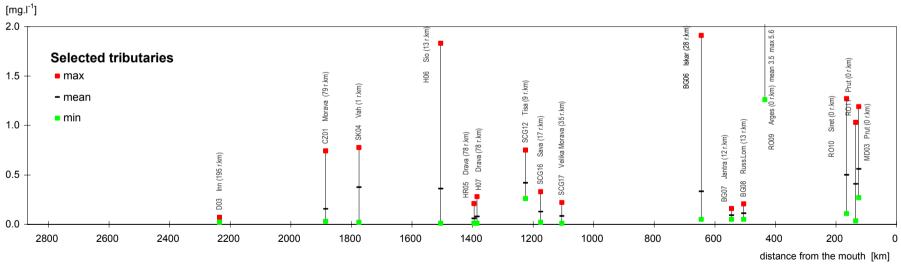
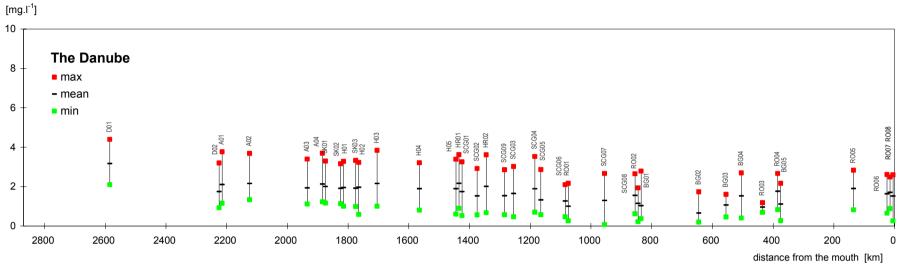
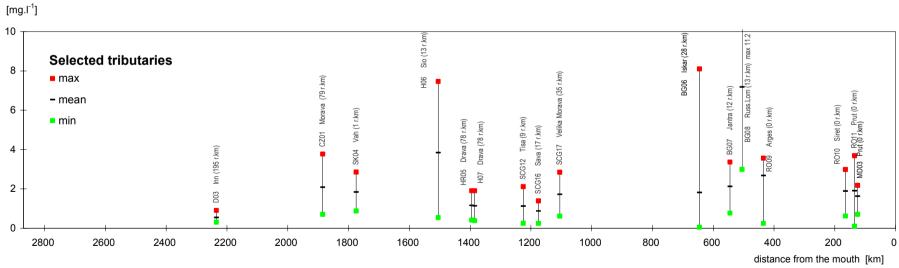
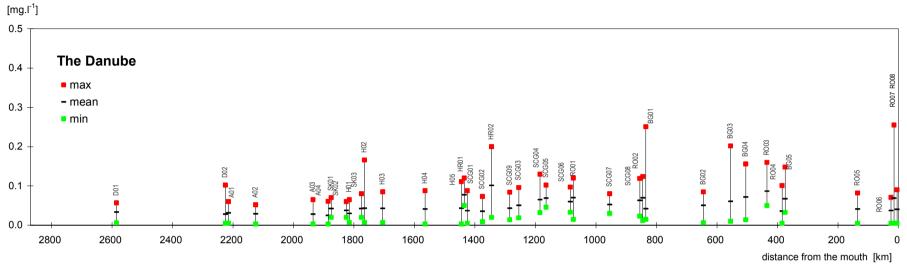


Figure 7.5: The minimum, mean and maximum of NO_3 -N in 2003









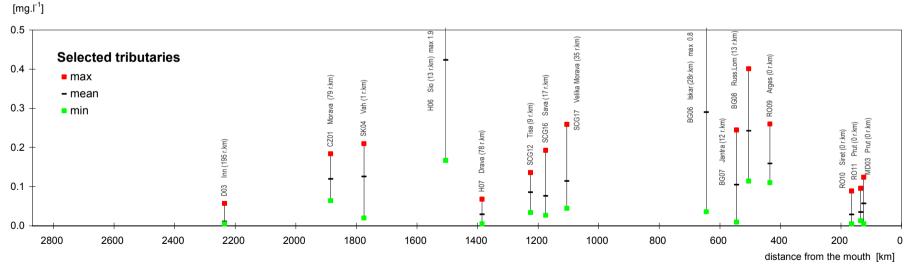
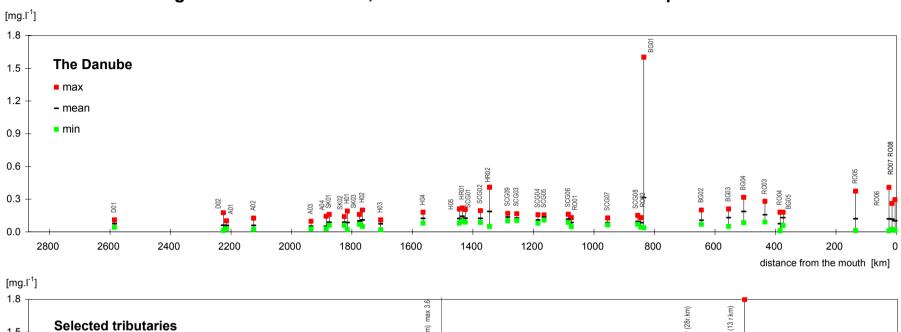
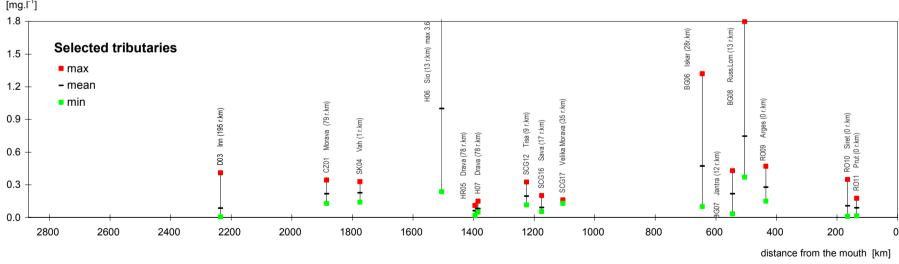
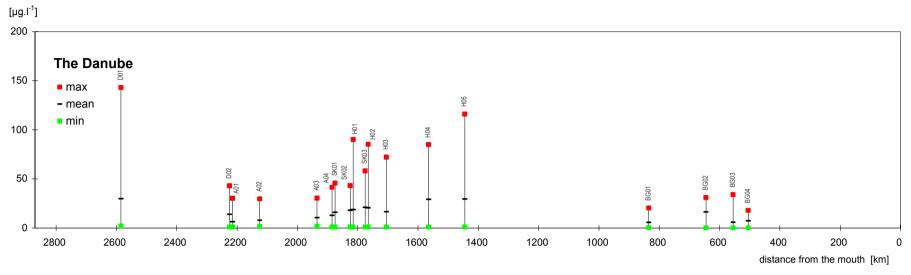


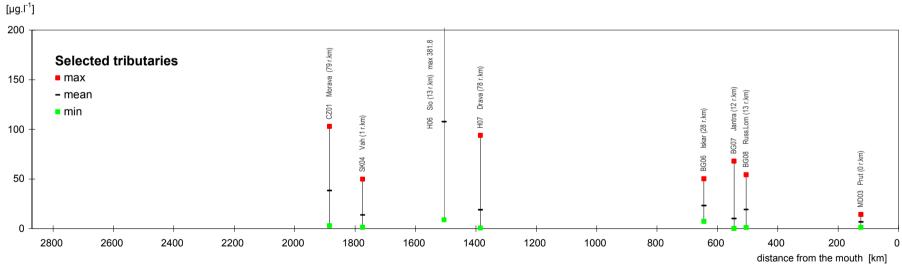
Figure 7.7: The minimum, mean and maximum of Total Phosphorus in 2003











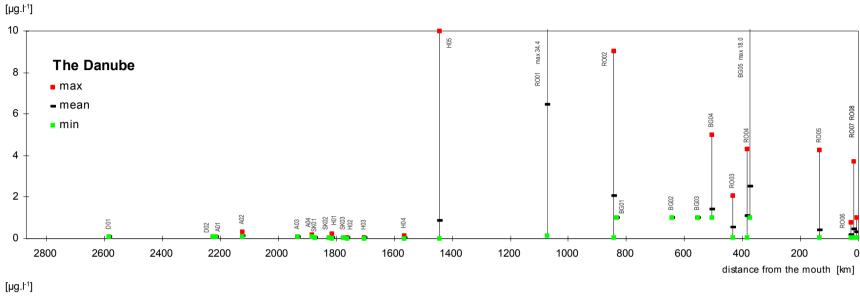


Figure 7.9: The minimum, mean and maximum of Cd in 2003

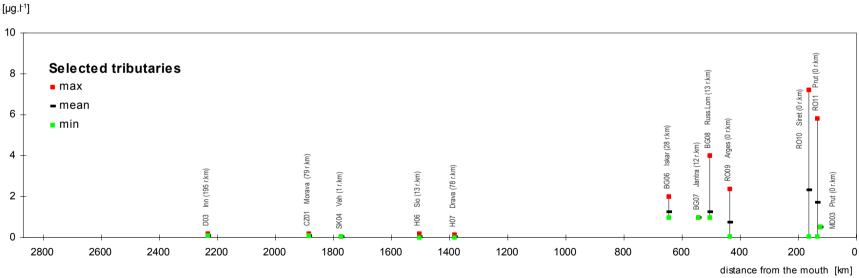
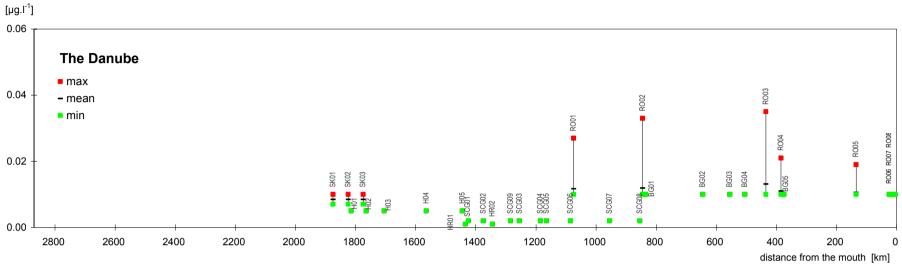
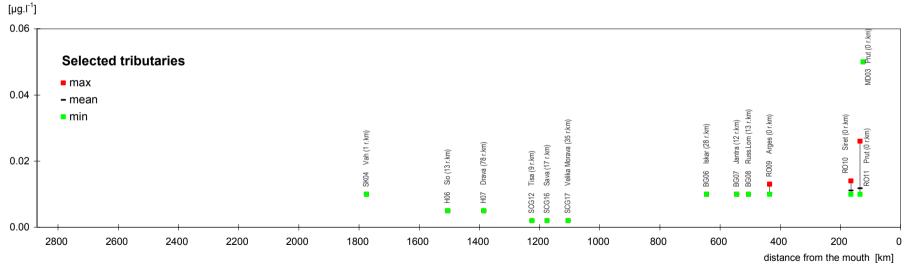
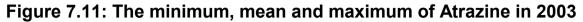


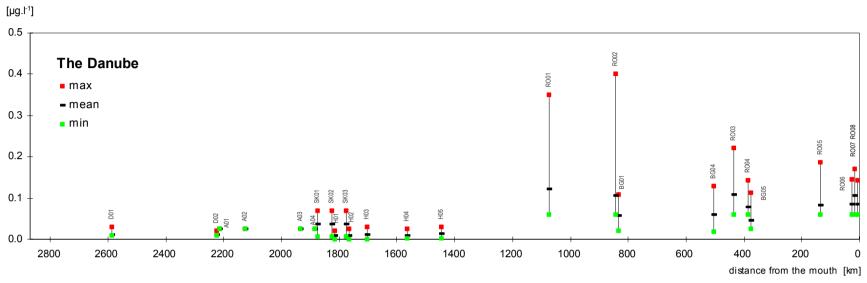
Figure 7.10: The minimum, mean and maximum of pp'DDT in 2003





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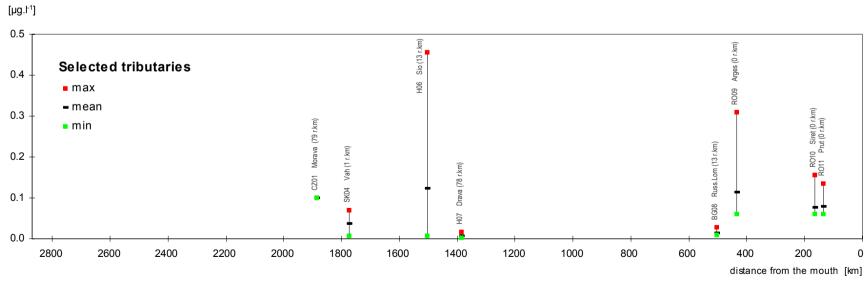
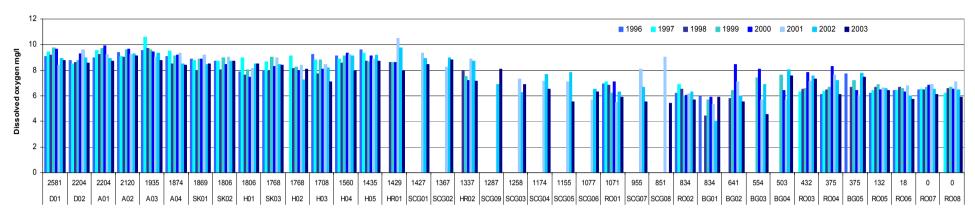


Figure 7.12: Temporal changes of dissolved oxygen in Danube River.



Monitoring sites / distance from the mouth [km]

Figure 7.13: Temporal changes of dissolved oxygen in tributaries.

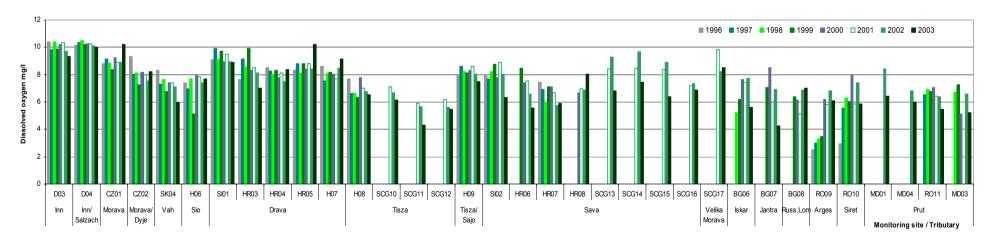


Figure 7.14: Temporal changes of BOD₅ in Danube River.

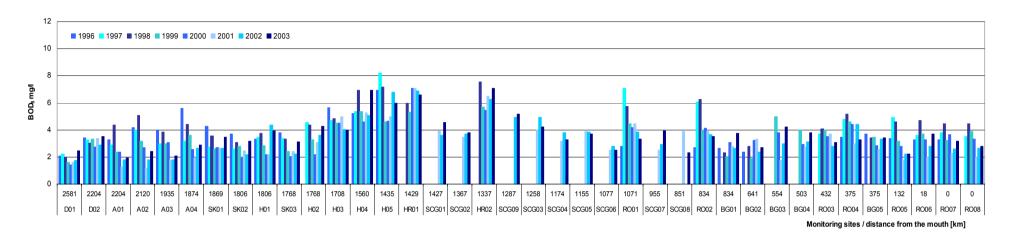


Figure 7.15: Temporal changes of BOD₅ in tributaries.

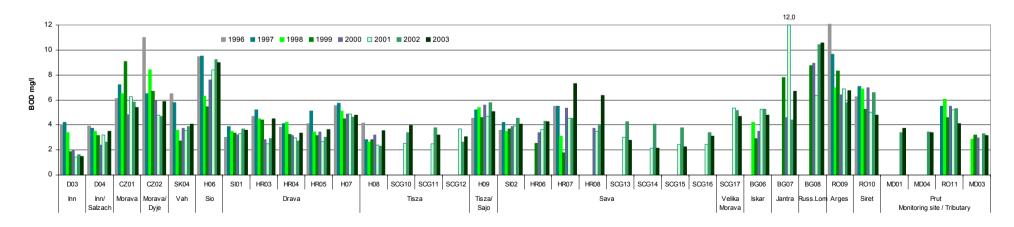


Figure 7.16: Temporal changes of COD_{Cr} in Danube River.

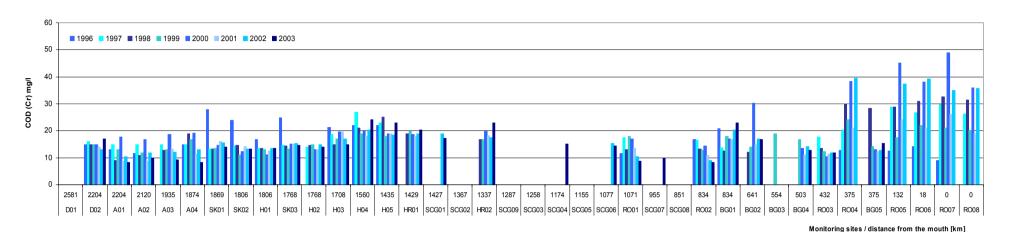


Figure 7.17: Temporal changes of COD_{Cr} in tributaries.

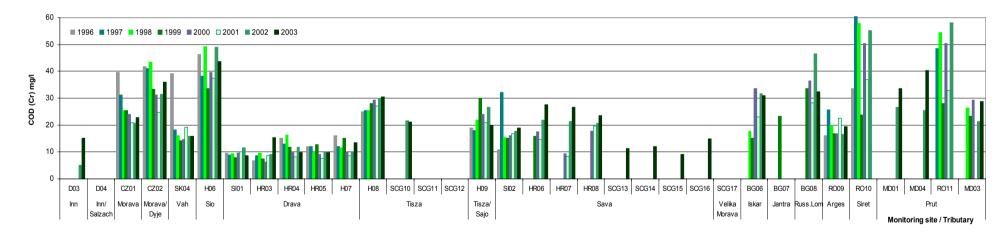


Figure 7.18: Temporal changes of ammonium-nitrogen in Danube River.

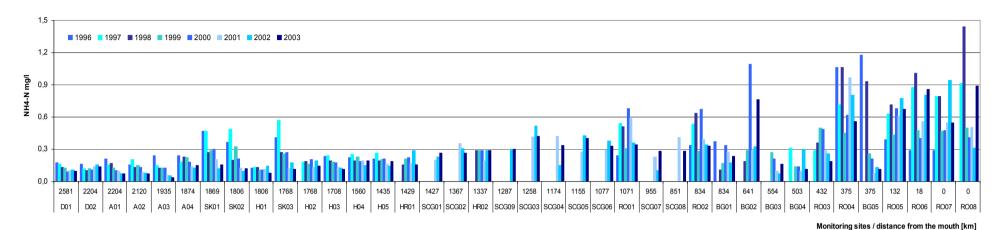


Figure 7.19: Temporal changes of ammonium-nitrogen in tributaries.

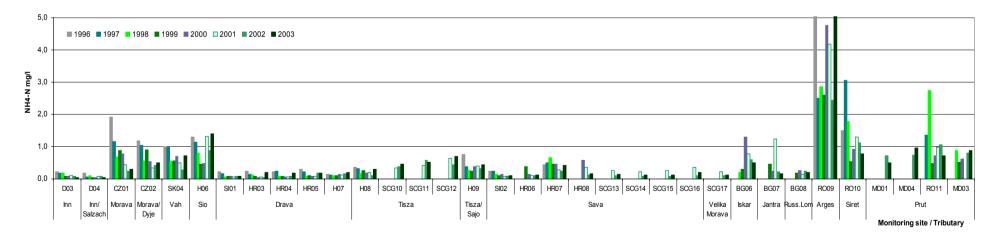
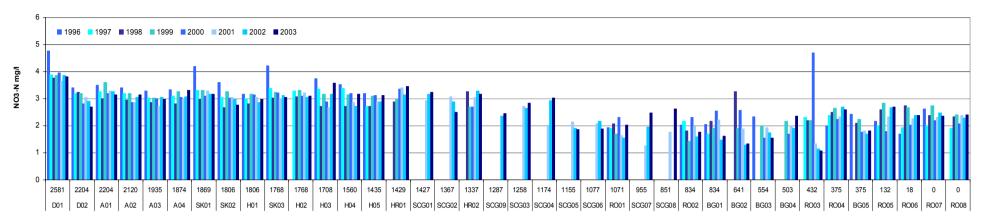


Figure 7.20: Temporal changes of nitrate-nitrogen in Danube River.



Monitorings sites / distance from the mouth [km]

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

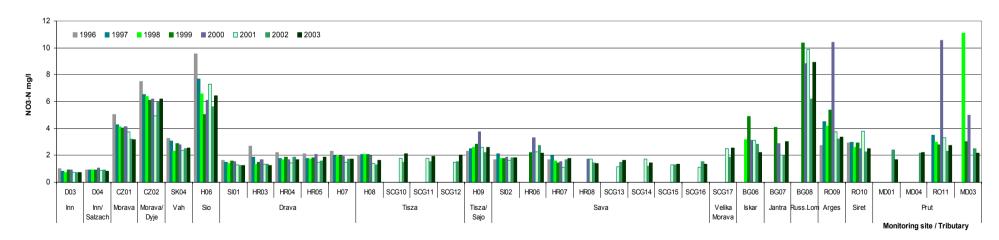
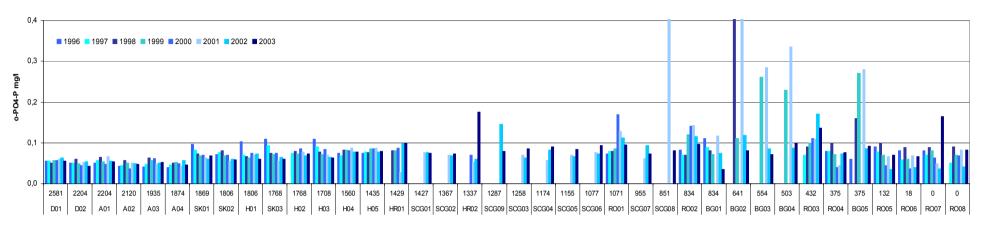


Figure 7.22: Temporal changes of ortho-phosphate-phosphorus in Danube River.



Monitoring sites / distance from the mouth [km]

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

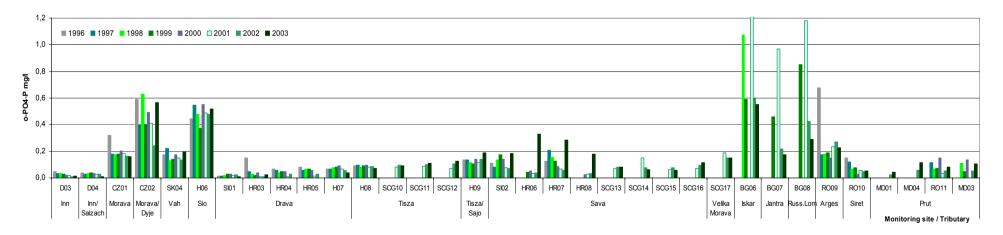


Figure 7.24: Temporal changes of total phosphorus in Danube River.

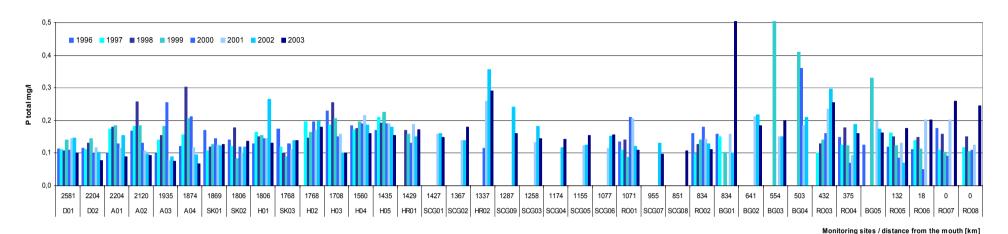


Figure 7.25: Temporal changes of total phosphorus in tributaries.

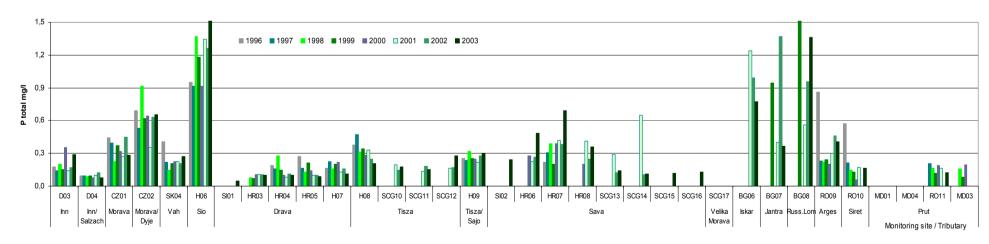


Figure 7.26: Temporal changes of cadmium in Danube River.

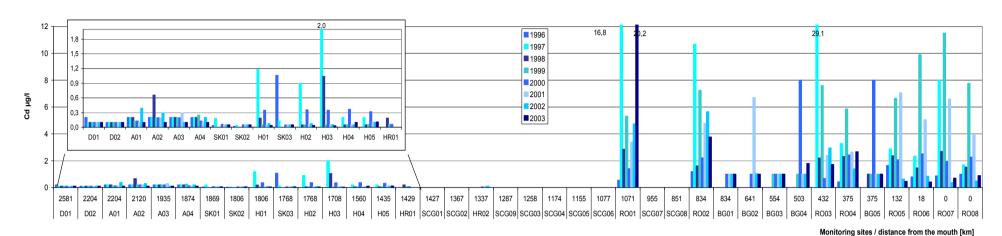
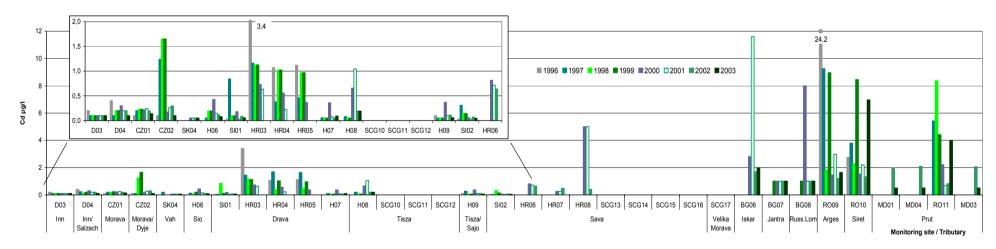


Figure 7.27: Temporal changes of cadmium in tributaries.



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 2003 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: BOD₅, inorganic nitrogen, orthophosphate-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 21 monitoring locations from 9 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 19, with 10 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 q	uality monitoring lo	Hydrolog	gical station	
		Country Code	Location	Distanc e 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/Dyj e	CZ02	Pohansko	17	Breclav-Ladná	32,3
Slovakia	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-Chilia arm	132	Isaccea	101
Ukraine	Danube	UA02	Vilkova-Kilia arm	18		

8.3 Monitoring Data in 2003

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.

There are still no data from Ukraine, flow data are missing in two Croatian monitoring locations. In majority of locations number of samples was higher than 20, the frequency 12 times per year was applied only in Morava, Dyje and Danube-Jochenstein (A01). But as the Danube Jochenstein is assessed on the basis of combined data from two countries, there is no problem with insufficient frequency there. A similar approach would be recommendable to be adopted at the two other sampling sites on the Morava (CZ/SK) and Dyje (CZ/A), which also have a transboundary character and are monitored only by Czech Republic, at present. 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 2003.

Country	River	Location	Location	River	er Number of meausrements in 2003							
Code			in profile	Km	Q	SS	N_{inorg}	P-PO ₄	P _{total}	BOD ₅	Cl	P _{diss}
D02	Danube	Jochenstein	M	2204	365	26	26	26	26	26	26	12
D03	Inn	Kirchdorf	M	195	365	24	26	26	26	25	26	0
D04	Inn/Salzach	Laufen	L	47	365	26	26	26	26	26	26	0
A01	Danube	Jochenstein	M	2204	365	12	12	12	12	12	12	12
A04	Danube	Wolfsthal	R	1874	365	24	24	24	24	24	24	24
CZ01	Morava	Lanzhot	M	79	365	11	11	11	11	11	11	0
CZ02	Morava/Dyj	Pohansko	M	17	365	12	12	12	12	12	12	0
SK01	Danube	Bratislava	M	1869	365	25	25	12	25	25	25	12
H03	Danube	Szob	L	1708		26	26	26	26	26	26	0
			M		365	26	26	26	26	26	26	0
			R			24	24	24	24	24	24	0
H05	Danube	Hercegszántó	M	1435	365	25	37	37	37	37	25	0
H08	Tisza	Tiszasziget	L	163		12	26	26	26	26	12	0
			M		365	12	26	26	26	26	12	0
			R			12	26	26	26	26	12	0
HR02	Danube	Borovo	R	1337	0	26	26	26	26	26	0	0
HR06	Sava	Jesenice/D	R	729	0	25	25	25	25	25	12	0
HR07	Sava	us Una Jesenovac	L	525	365	25	25	25	25	25	12	0
HR08	Sava	ds Zupanja	R	254	365	24	25	25	25	25	12	0
SI01	Drava	Ormoz	L	300	365	24	24	24	24	24	24	0
SI02	Sava	Jesenice	R	729	365	24	24	24	24	24	24	0
RO02	Danube	Pristol-Novo Selo	L	834		23	24	24	24	24	24	0
			M		365	23	24	24	24	24	24	0
			R			23	24	24	24	24	24	0
RO04	Danube	Chiciu-Silistra	L	375		24	24	24	22	24	20	0
			M		365	24	24	24	22	24	20	0
			R			24	24	24	22	24	20	0
RO05	Danube	Reni-Chilia arm	L	132		24	24	24	22	24	20	0
			M		365	24	24	24	22	24	20	0
			R			23	24	24	22	24	20	0
UA02	Danube	Vilkova-Kilia arm	M	18	0	0	0	0	0	0	0	0

Regarding particular determinands, there is still lack of data on dissolved phosphorus as it was measured in 4 locations only, which is even lower number than in the previous year. 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.

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:

$$C_{m}\left[mg.l^{\text{-}1}\right] = \frac{\sum\limits_{i \in m} C_{i}\left[mg.l^{\text{-}1}\right]. \ Q_{i}\left[m^{3}.s^{\text{-}1}\right]}{\sum\limits_{i \in m} Q_{i}\left[m^{3}.s^{\text{-}1}\right]}$$

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:

$$\begin{array}{ll} L_m \, [tones] \, = \, C_m \, [mg.l^{\text{-}1}] \, . \, Q_m \, [m^3.s^{\text{-}1}] \, . \, days \, (m) \, . \, 0,0864 \\ \\ where & L_m \quad monthly \, load \\ & Q_m \quad average \, monthly \, discharge \end{array}$$

- 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, BOD₅, 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
Qa	mean annual discharge in the year 2003
C _{mean}	arithmetical mean of the concentrations in the year 2003
Annual Load	annual load of given determinand in the year 2003

The mean annual discharge was significantly lower in 2003 in comparison with previous year, reaching on average 70 % of values observed in 2002 in both Danube River and tributaries. Suspended solids concentrations as sensitive to flow conditions were lower in 2003 too. Significantly higher concentrations in 2003 in comparison to 2002 had been observed in case of ortho-phosphate P in monitoring locations of Sava River and in Dyje River. In Sava River also higher content of total phosphorus was obvious.

Mainly as a result of lower discharges in 2003 load of suspended solids, nutrients and BOD₅ was generally much lower in comparison with 2002, this being most significant in case of suspended solids and total phosphorus.

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 load of inorganic nitrogen, total phosphorus and chlorides increases continuously along the river. In case of organic pollution, ortho-phosphate phosphorus and suspended solids the highest load is also observed in the lower part of the Danube River, but maximum is reached in monitoring location Danube-Pristol-Novo Selo (RO02, r.km 834) with further decrease of the values.

From tributaries the highest load of nutrients and BOD₅ is coming from Tisza and Sava rivers. Worth mentioning is also a high load of suspended solids in Inn (D03), in which variation of flow and related suspended solids content is very high.

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

Station	Profile	River Name	Location	River km	Q_a	Q _a C _{mean}						
Code						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)
D02 +A01	M	Danube	Jochenstein	2204	1153	16	1,92	0,028	0,06	1,9	16	0,040
A04	R	Danube	Wolfsthal	1874	1640	13	2,25	0,025	0,05	1,9	18	0,037
SK01	М	Danube	Bratislava	1869	1647	21	2,13	0,042	0,09	2,3	18	0,063
H03	LMR	Danube	Szob	1708	1722	11	2,27	0,053	0,08	3,3	24	
H05	М	Danube	Hercegszántó	1435	1786	19	2,02	0,043	0,12	3,7	19	
HR02	R	Danube	Borovo	1337		55	2,28	0,101	0,19	3,8		
RO02	LMR	Danube	Pristol-Novo Selo	834	3825	28	1,35	0,075	0,09	2,8	22	
RO04	LMR	Danube	Chiciu-Silistra	375	4571	13						
RO05	LMR	Danube	Reni-Chilia arm	132	5021	15	2,23	0,042	0,12	1,6	44	

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

Station	Profile	River Name	Location	River km	Q_a	C _{mean}						
Code						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	М	Inn	Kirchdorf	195	255	55	0,55	0,011	0,09	1,2	4	
D04	L	Inn/Salzacl	Laufen	47	203	29	0,67	0,006	0,04	2,0	8	
CZ01	М	Morava	Lanzhot	79	40	18	2,28	0,120	0,22	4,1	31	
CZ02	L	Morava/Dy	Pohansko	17	32	18	3,06	0,280	0,38	4,1	44	
H08	LMR	Tisza	Tiszasziget	163	604	35	1,19	0,051	0,16	2,4	49	
SI01	L	Drava	Ormoz	300	230	13	0,99	0,006	0,04	2,6	6	
SI02	R	Sava	Jesenice	729	158	7	1,52	0,094	0,14	3,0	10	
HR06	L	Sava	Jesenice	729		7	1,79	0,164	0,30	3,0	11	
HR07	Ĺ	Sava	us. Una Jasenovac	525	348	14	1,47	0,172	0,34	4,1	13	
HR08	R	Sava	ds. Zupanja	254	651	16	0,98	0,101	0,23	3,4	16	

Table 8.5.3: Annual load in selected monitoring locations on Danube River.

Station Code	Profile	River Name	Location	River km							
					Suspended Solids	Inorganic Nitrogen	Ortho- Phosphate Phosphorus	Total Phosphorus	BOD₅	Chlorides	Phosphorus - dissolved
					(x10 ⁶ tonns)	(x10³tonns)	(x10³tonns)	(x10³tonns)	(x10³tonns)	(x10 ⁶ tonns)	(x10 ³ tonns)
D02 +A01	M	Danube	Jochenstein	2204	0,590	72,473	1,130	2,351	70,542	0,564	1,545
A04	R	Danube	Wolfsthal	1874	0,722	119,015	1,268	2,669	107,503	0,918	1,850
SK01	М	Danube	Bratislava	1869	1,325	114,504	2,230	4,927	131,133	0,922	3,182
H03	LMR	Danube	Szob	1708	0,664	131,538	2,966	4,465	190,768	1,333	
H05	М	Danube	Hercegszántó	1435	1,236	123,518	2,543	7,327	211,045	1,072	
HR02	R	Danube	Borovo	1337							
RO02	LMR	Danube	Pristol-Novo Selo	834	3,470	187,884	9,187	11,102	346,548	2,638	·
RO04	LMR	Danube	Chiciu-Silistra	375	2,112	332,136	5,358	11,658	285,933	5,705	
RO05	LMR	Danube	Reni-Chilia arm	132	2,615	392,537	7,051	18,990	256,831	6,519	

Table 8.5.4: Annual load in selected monitoring locations on tributaries.

Station Code	Profile	River Name	Location	River km	River km Annual Load in 2003						
oode					Suspended Solids	Inorganic Nitrogen	Ortho- Phosphate Phosphorus	Total Phosphorus	BOD₅	Chlorides	Phosphorus - dissolved
					(x10 ⁶ tonns)	(x10 ³ tonns)	(x10³tonns)	(x10³tonns)	(x10³tonns)	(x10 ⁶ tonns)	(x10³tonns)
D03	М	Inn	Kirchdorf	195	0,727	3,945	0,104	0,975	8,937	0,028	
D04	L	Inn/Salzach	Laufen	47	0,189	4,032	0,039	0,269	12,051	0,042	
CZ01	M	Morava	Lanzhot	79	0,019	2,980	0,116	0,204	3,592	0,026	
CZ02	L	Morava/Dyje	Pohansko	17	0,016	4,799	0,206	0,296	3,788	0,040	
H08	LMR	Tisza	Tiszasziget	163	0,995	27,216	1,010	3,312	45,303	0,717	
SI01	L	Drava	Ormoz	300	0,102	7,013	0,046	0,273	17,526	0,041	
SI02	R	Sava	Jesenice	729	0,035	8,313	0,396	0,612	13,776	0,046	•
HR06	L	Sava	Jesenice	729							
HR07	L	Sava	us. Una Jasenovac	525	0,173	18,098	1,418	3,233	37,318	0,135	
HR08	R	Sava	ds. Zupanja	254	0,345	24,146	2,058	4,309	60,605	0,284	•

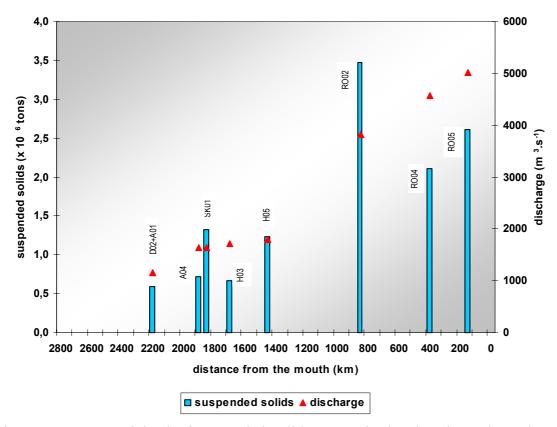


Figure 8.5.1: Annual load of suspended solids at monitoring locations along the Danube River.

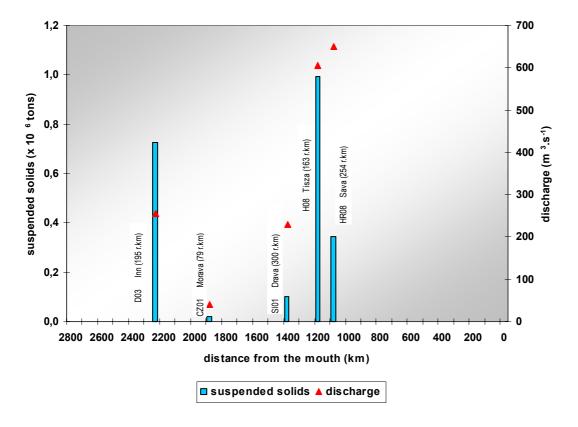


Figure 8.5.2: Annual load of suspended solids at monitoring locations on tributaries.

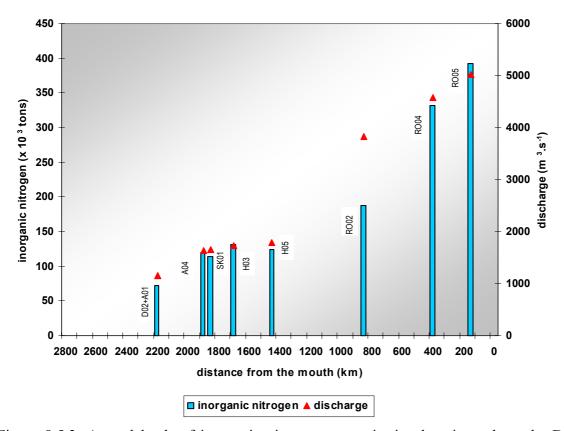


Figure 8.5.3: Annual loads of inorganic nitrogen at monitoring locations along the Danube River.

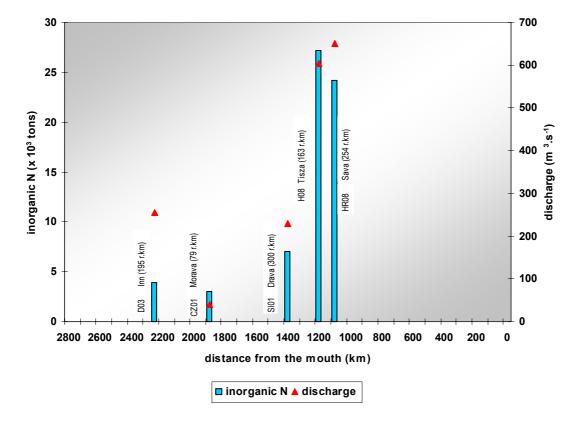


Figure 8.5.4: Annual loads of inorganic nitrogen at monitoring locations on tributaries.

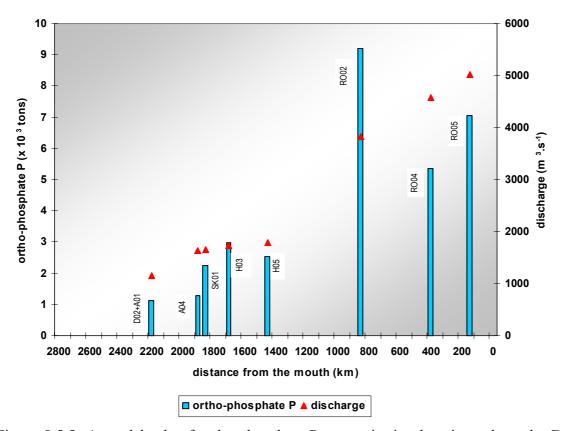


Figure 8.5.5: Annual loads of ortho-phosphate-P at monitoring locations along the Danube River.

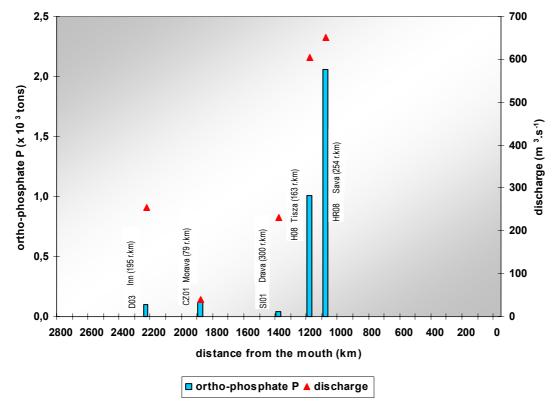


Figure 8.5.6: Annual loads of ortho-phosphate-P at monitoring locations on tributaries.

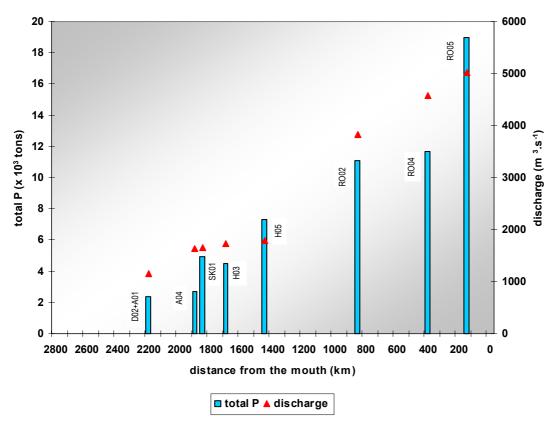


Figure 8.5.7: Annual loads of total phosphorus at monitoring locations along the Danube River.

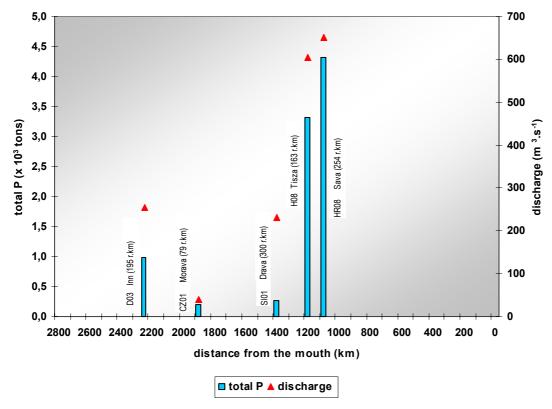


Figure 8.5.8: Annual loads of total phosphorus at monitoring locations on tributaries.

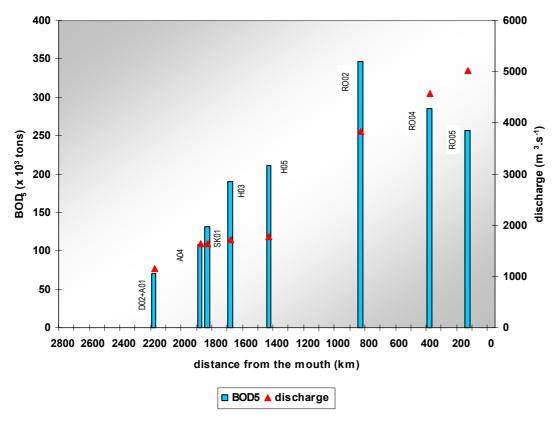


Figure 8.5.9: Annual loads of BOD₅ at monitoring locations along the Danube River.

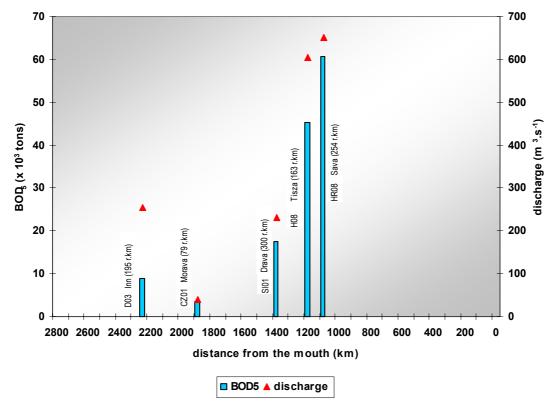


Figure 8.5.10: Annual loads of BOD₅ at monitoring locations on tributaries.

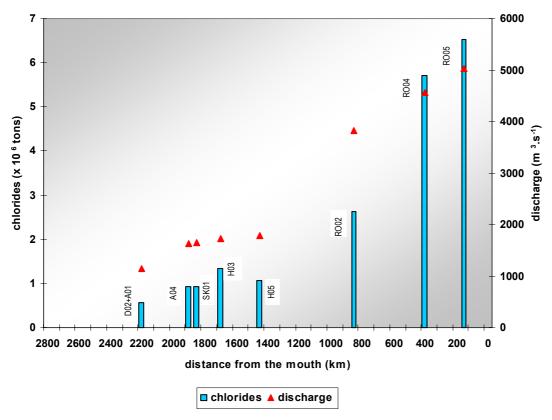


Figure 8.5.11: Annual loads of chlorides at monitoring locations along the Danube River.

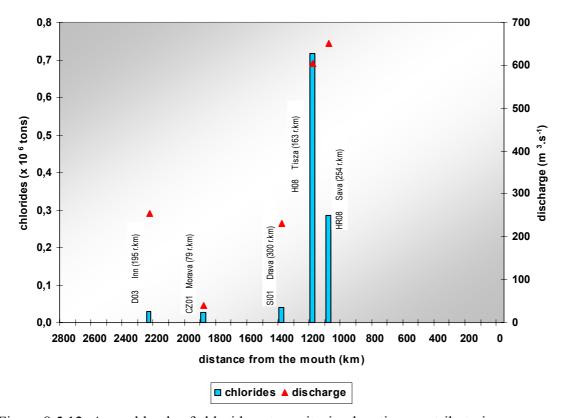


Figure 8.5.12: Annual loads of chlorides at monitoring locations on tributaries.

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)