

WATER QUALITY

in the Danube River Basin 2000

TNMN-Yearbook

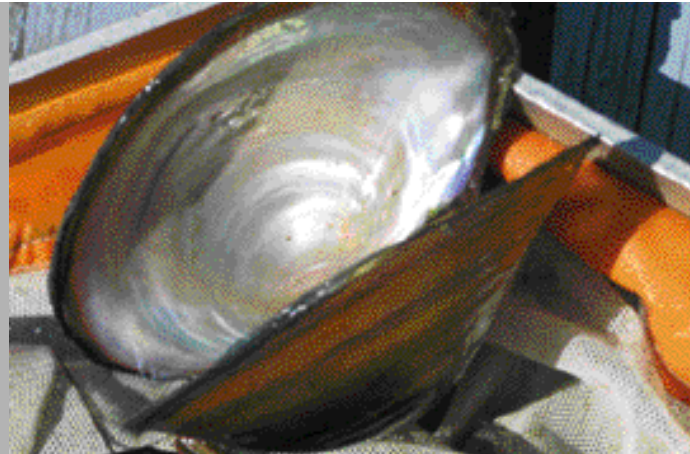
Information

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1. Introduction



In June 1994, the Convention on Cooperation for the Protection and Sustainable Use of the Danube River (Danube River Protection Convention) was signed in Sofia and came into force in October 1998. Its main objectives are to achieve 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 builds on the Convention on the Protection and Use of Transboundary Watercourses and International Lakes of March 1992.

Regarding monitoring programmes, the Danube Convention stipulates that the Contracting Parties shall cooperate in the field of monitoring and assessment, i.e. that they shall:

- 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 to set up monitoring points on the Danube and to regularly and frequently enough evaluate river quality characteristics and pollution parameters taking into account the ecological and hydrological character of the watercourse and the typical emissions of pollutants discharged within the respective catchment area. In addition, the Parties shall periodically assess the quality conditions of the Danube River and the progress made through the measures taken in order to prevent, control and reduce transboundary impacts.

The operation of the TransNational Monitoring Network (TNMN) is designed to contribute to the implementation of the Danube River Protection Convention, particularly of its above-mentioned provisions. This yearbook is the fifth in a planned continuous series of yearbooks to be compiled by the ICPDR and its main objective is to present the monitoring programme and the data obtained from the operation of TNMN in 2000. For the first time, results of pollution load assessment are presented in this Yearbook.

Since a detailed description of the development of the institutional framework supporting TNMN was provided in the first TNMN yearbook (1996), Chapter 2 of the present yearbook provides only a chronology of events in the development of TNMN and its supporting bodies. Chapter 3 then describes TNMN's objectives and Chapter 4 provides a description of TNMN. Chapters 5, 6 and 7 comprise tables with basic statistical figures for the entire TNMN – station data, maps of selected determinands and profiles of selected determinands along the Danube River. Chapter 8 is dedicated to the assessment of pollution loads.

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2. History of TNMN



In spite of the fact that TNMN has been in operation since 1996, the first steps towards creating the Network were taken many years earlier. In December 1985, the governments of the Danube riparian countries signed the Bucharest Declaration. One of the objectives of the Declaration was to ensure that the development of the water quality of the Danube is monitored. In order to meet this objective, a monitoring programme was established based on agreed methods designed to obtain comparable data. The monitoring network used under the Bucharest Declaration consisted of eleven cross sections of the Danube with 1 to 3 sampling locations. All cross sections were placed on the Danube itself where the River forms the border between countries or crosses it.

The drafting of the Danube River Protection Convention (DRPC) started in 1991 and the Convention was signed in Sofia in June 1994.

The Environmental Programme for the Danube River Basin (EPDRB) led by a Task Force also started in 1991; it was implemented to support and reinforce national actions geared towards the restoration and protection of the Danube River and to supplement the future work of International Commission for the Protection of the Danube River.

In 1992, the Task Force agreed a three-year (1992-95) Work Plan. The emphasis was placed on creating consensus, sharing information and promoting joint decision-making between the Danubian countries. Monitoring, laboratories and information management became the highlight of the Programme in December 1992 when the Monitoring, Laboratory and Information

Management Sub-Group (MLIM-SG) dedicated to this topic met for the first time in Bucharest.

The main outcome of the three-year Work Plan was the Strategic Action Plan (SAP). It was approved by the Task Force and supported by a Ministerial Declaration of the Danubian countries in December 1994. Once approved, the Strategic Action Plan marked the end of the first phase (Phase I, 1992-95) of the EPDRB, and implementation was scheduled to start in the next phase (Phase II, 1996-2000). One of the major undertakings during 1996 was the initiation and approval by the Task Force of the Strategic Action Plan Implementation Programme (SIP), also designed to support the implementation of the Convention.

The 1996 and 1997 budgets of Phare Multi-Country Environmental Programme (MCEP) allocated substantial funds to all EPDRB projects to support further development of the monitoring and assessment programme and the launch of TNMN into operation.

The responsibility for TNMN was assigned to MLIM-SG. The three Working Groups set up under MLIM-SG

- addressed the development of a Danubian water quality monitoring network (Monitoring Working Group, MWG),
- introduced harmonised sampling procedures and enhanced laboratory analysis capabilities (Laboratory Management Working Group, LMWG),
- formed the core of a Danube Information Management System on the status of in-stream

2. History of TNMN

(immissions) water quality (Information Management Working Group, IMWG).

The Working Groups worked in accordance with the TNMN Implementation Plan approved by the Task Force and MLIM-SG.

At the same time that the Danube River Protection Convention was signed, the International Commission for the Protection of the Danube River (ICPDR) was established on an interim basis, allowing for the implementation of the Convention pending its entry into force. The Task Force of the EPDRB was invited to co-operate with the Interim ICPDR and its Secretariat to contribute to a successful implementation of the DRPC.

As a Technical Sub-Group of EPDRB, MLIM-EG was incorporated in the ICPDR organisational

structure as an Expert Group. Since October 29, 1998, the MLIM Expert Group - including its three Expert Sub-Groups - has been working on the basis of TORs agreed upon by the first ICPDR Plenary Meeting.

The EU Water Framework Directive (Directive 2000/60/EC) that came into force on December 22, 2000, established a framework for Community action in the field of water policy. Its implementation represents the highest priority for the ICPDR which will provide a platform for coordination of the activities leading to the development of a River Basin Management Plan for the Danube River Basin. The implementation of the Directive will have a considerably impact on TNMN in the near future as the Network adjusts its water status monitoring programme to meet the requirements of the Directive.

3. Objectives of TNMN



TNMN is a result of the work done towards meeting the objectives defined in the Environmental Programme for the Danube River Basin - Programme Work Plan, which states that the monitoring network for the Danube shall:

- strengthen the existing network set up under the Bucharest Declaration;
- be capable of supporting reliable and consistent trend analysis of the concentrations and loads for priority pollutants;
- support the assessment of water quality for water use;
- assist in the identification of major pollution sources;
- include sediment monitoring and bioindicators;
- include quality control.

Furthermore, the Programme Work Plan provides that:

- the monitoring network shall provide outputs compatible with those in other major international river basins in Europe;
- the monitoring network shall in future comply with standards used in the western part of Europe;
- it shall be designed in a way to reflect immediate and long-term needs - starting with practical and routine functions already performed.

The design, implementation and operation of the network are divided in two phases. The first

phase is marked by:

- the operation of a limited number of stations with defined objectives already included in national monitoring networks in keeping with the defined objectives;
- a determinand lists reflecting the Bucharest Declaration and EU-Directives;
- information management based on a simple data exchange file format between the riparian countries.

The second phase will build on the experience gained through the operation of the first phase and the organisational structures formed for discussion, planning, management procedures (QA, AQC, etc.), training and applied research. In addition, the number of stations, the sampling frequencies, the determinands and the procedures for information exchange shall also be reviewed in the second phase.

4. Description of TNMN

TNMN was originally designed in 1993 during the "Monitoring, Laboratory Analysis and Information Management for the Danube River Basin" project conducted by the WTV Consortium. The implementation was agreed by MLIM-SG, but the design was further simplified resulting in the monitoring, laboratory and information management aspects and designs described in Sub-Chapters 4.1 to 4.4. These designs comprise the first phase starting in 1996. The evaluation and upgrading of the first phase is now under way.

4.1 Principles of TNMN design

Since the new transboundary network should build on national surface water monitoring networks in the Danube Basin and seen that the number of stations in these countries can be counted in thousands, it was decided to establish a simple procedure for the selection of existing monitoring stations that would qualify for the new TransNational Monitoring Network - a procedure which would also comply with the objectives listed in Chapter 3.

It was agreed that in order to qualify under the selection criteria, a station had to meet at least one of the following requirements:

- be located just upstream/downstream of an international border;
- be located upstream of confluences between the Danube and its main tributaries or the main tributaries and larger sub-tributaries (mass balances);
- be located downstream of the biggest point sources;
- be located upstream of drinking water abstraction points.

The information obtained from Danubian countries included descriptions of nearly 200 monitoring sites out of which 61 were selected to be included in TNMN - Phase 1 (See List of Monitoring Sites in Table 4.1).

Sampling and analyses are undertaken on a national level and carried out as far as possible according to the resulting determinand lists (on the total sample) presented in more detail in Sub-Chapters 4.2 and 4.3. All results are reported and distributed in a common data exchange file format (DEFF). The structure and use of DEFF, which was also included in the first design and further developed during implementation, is described in more detail in Chapter 4.4.

Key to Table 4.1.

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

4. Description of TNMN



Table 4.1: List of monitoring sites

Station list									
COuntry code	River	Town/location	Latitude d. m. s.	Longitude d. m. s.	Distance km	Altitude m	Catchment sq.km	DEFF code	Loc. profile
D01	Danube	Neu-Ulm	48 25 31	10 1 39	2581	460	8107	L2140	L
D02	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2130	M
D03	/Inn	Kirchdorf	47 46 58	12 7 39	195	452	9905	L2150	M
D04	/Inn/Salzach	Laufen	47 56 26	12 56 4	47	390	6113	L2160	L
A01	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2220	M
A02	Danube	Abwinden-Asten	48 15 21	14 25 19	2120	251	83992	L2200	R
A03	Danube	Wien-Nussdorf	48 15 45	16 22 15	1935	159	101700	L2180	R
A04	Danube	Wolfsthal	48 8 30	17 3 13	1874	140	131411	L2170	R
CZ01	/Morava	Lanzhot	48 41 12	16 59 20	79	150	9725	L2100	R
CZ02	/Morava/Dyje	Breclav	48 48 12	16 51 20	17	155	12540	L2120	R
SK01	Danube	Bratislava	48 8 10	17 7 40	1869	128	131329	L1840	M
SK02	Danube	Medvedov/Medve	47 47 31	17 39 6	1806	108	132168	L1860	M
SK03	Danube	Komarno/Komarom	47 45 17	18 7 40	1768	103	151961	L1870	M
SK04	/Váh	Komarno	47 46 41	18 8 20	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov	47 47 31	17 39 6	1806	108	131605	L1470	M
H02	Danube	Komarom/Komarno	47 45 17	18 7 40	1768	101	150820	L1475	M
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	Dravasabolcs	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/Sajó	Sajopuspoki	48 16 55	20 20 27	124	148	3224	L1770	M
SI01	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1390	L
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	135	10878	L1330	R
HR01	Danube	Batina	45 52 27	18 50 03	1429	86	210250	L1315	M
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M
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	R
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	M
BIH01	/Sava	Jasenovac	45 16 0	16 54 36	500	87	38953	L2280	M
BIH02	/Sava/Una	Kozarska Dubica	45 11 6	16 48 42	16	94	9130	L2290	M
BIH03	/Sava/Vrbas	Razboj	45 3 36	17 27 30	12	100	6023	L2300	M
BIH04	/Sava/Bosna	Modrica	44 58 17	18 17 40	24	99	10308	L2310	M
R001	Danube	Bazias	44 47	21 23	1071	70	570896	L0020	LMR
			55,57,58	24,40,54					
R002	Danube	Pristol/Novo Selo Harbour	44 11	22 45	834	31	580100	L0090	LMR
			18,23,29	57,64,69					
R003	Danube	us. Arges	44 4 25	26 36 35	432	16	676150	L0240	LMR
R004	Danube	Chiciu/Silistra	44 7 18	27 14 38	375	13	698600	L0280	LMR
R005	Danube	Reni-Chilia/Kilia arm	45 28 50	28 13 34	132	4	805700	L0430	LMR
R006	Danube	Vilkova-Chilia arm/Kilia arm	45 24 42	29 36 31	18	1	817000	L0450	LMR
R007	Danube	Sulina - Sulina arm	45 9 41	29 40 25	0	1	817000	L0480	LMR
R008	Danube	Sf.Gheorghe-Ghorghe arm	44 53 10	29 37 5	0	1	817000	L0490	LMR
R009	/Arges	Conf. Danube	44 4 35	26 37 4	0	14	12550	L0250	M
R010	/Siret	Conf. Danube Sendreni	45 24 10	28 1 32	0	4	42890	L0380	M
R011	/Prut	Conf.Danube Giurgiulesti	45 28 10	28 12 36	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	44 09	22 47	834	35	580100	L0730	LMR
			50,58,66	36,47,58					
BG02	Danube	us. Iskar - Bajkal	43 42 58	24 24 45	641	20	608820	L0780	M
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
MD02	/Prut	Leuseni	46 48 0	28 9 0	292	19	21890	L2250	M
MD03	/Prut	Conf. Danube-Giurgiulesti	45 28 10	28 12 36	0	5	27480	L2270	LMR
UA01	Danube	Reni - Kilia arm/Chilia arm	45 28 50	28 13 34	132	4	805700	L0630	M
UA02	Danube	Vilkova-Kilia arm/Chilia arm	45 24 42	29 36 31	18	1	817000	L0690	M

4. Description of TNMN

4.2 Determinands

The determinand list was originally based on that proposed by the Bucharest Declaration and was subsequently extended or reduced in light of the the EU directives and the riparian countries' own demands. The list was divided into 10 groups and each group was given a sampling frequency according to location. Furthermore, it was specified how many sampling points (left, middle, right) each site should include. This, together with the allocation of determinand groups and sampling frequencies according to the location of each site led to a full definition of each of the sites.

However, discussions held in the working groups during the implementation phase showed that there was a need for a simpler approach and a somewhat reduced determinand list. As a result, all sites were given the same minimum sampling frequency of 12 per year for determinands in water and two per year for bio-monitoring and for determinands in sediment.

The resulting lists of determinands for water and sediments as agreed for TNMN Phase 1 are presented in Tables 4.2.1 and 4.2.2 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 TNMN;
- the principal level of interest is the concentration at which most monitoring is expected to 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 highest possible precision is achieved at the principal level of interest and that relatively few "less than results" are 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 the best practice. In these cases, the targets are marked by italics;

- 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 to 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;

- analytical accuracy targets for sediments are defined for <63 mm size fraction.

Sediments comprise suspended solids and bottom sediments.

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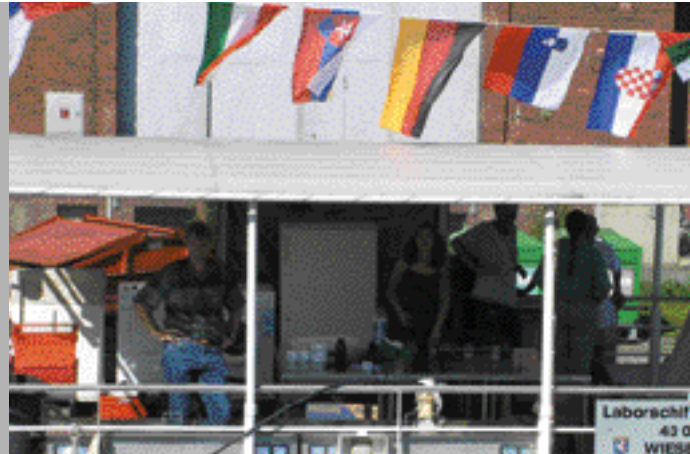


Table 4.2.1: Determinand list for water for Phase 1 of TNMN

Determinands in water	Unit	Minimum likely level of interest	Principal level of interest	Target limit of detection	Tolerance
Flow	m ³ /s	-	-	-	-
Temperature	°C	-	0-25	-	0.1
Suspended solids	mg/l	1	10	1	1 or 20%
Dissolved oxygen	mg/l	0.5	5	0.2	0.2 or 10%
PH	-	-	7.5	-	0.1
Conductivity @ 20 °C	µS/cm	30	300	5	5 or 10%
Alkalinity	mmol/l	1	10	0.1	0.1
Ammonium (NH ₄ ⁺ -N)	mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO ₂ ⁻ -N)	mg/l	0.005	0.02	0.005	0.005 or 20%
Nitrate (NO ₃ ⁻ -N)	mg/l	0.2	1	0.1	0.1 or 20%
Organic nitrogen	mg/l	0.2	2	0.1	0.1 or 20%
Ortho-phosphate (PO ₄ ³⁻ -P)	mg/l	0.02	0.2	0.005	0.005 or 20%
Total phosphorus	mg/l	0.05	0.5	0.01	0.01 or 20%
Sodium (Na ⁺)	mg/l	1	10	0.1	0.1 or 10%
Potassium (K ⁺)	mg/l	0.5	5	0.1	0.1 or 10%
Calcium (Ca ²⁺)	mg/l	2	20	0.2	0.1 or 10%
Magnesium (Mg ²⁺)	mg/l	0.5	5	0.1	0.2 or 10%
Chloride (Cl ⁻)	mg/l	5	50	1	1 or 10%
Sulphate (SO ₄ ²⁻)	mg/l	5	50	5	5 or 20%
Iron (Fe)	mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese (Mn)	mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc (Zn)	µg/l	10	100	3	3 or 20%
Copper (Cu)	µg/l	10	100	3	3 or 20%
Chromium (Cr) - total	µg/l	10	100	3	3 or 20%
Lead (Pb)	µg/l	10	100	3	3 or 20%
Cadmium (Cd)	µg/l	1	10	0.5	0.5 or 20%
Mercury (Hg)	µg/l	1	10	0.3	0.3 or 20%
Nickel (Ni)	µg/l	10	100	3	3 or 20%
Arsenic (As)	µg/l	10	100	3	3 or 20%
Aluminium (Al)	µg/l	10	100	10	10 or 20%
BOD ₅	mg/l	0.5	5	0.5	0.5 or 20%
COD _{Cr}	mg/l	10	50	10	10 or 20%
COD _{Mn}	mg/l	1	10	0.3	0.3 or 20%
DOC	mg/l	0.3	1	0.3	0.3 or 20%
Phenol index	mg/l	0.005	0.05	0.005	0.005 or 20%
Anionic active surfactants	mg/l	0.1	1	0.03	0.03 or 20%
Petroleum hydrocarbons	mg/l	0.02	0.2	0.05	0.05 or 20%
AOX	µg/l	10	100	10	10 or 20%
Lindane	µg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	µg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine	µg/l	0.1	1	0.02	0.02 or 30%
Chloroform	µg/l	0.1	1	0.02	0.02 or 30%
Carbon tetrachloride	µg/l	0.1	1	0.02	0.02 or 30%
Trichloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Tetrachloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Total coliforms (37 C)	10 ³ CFU/100 ml	-	-	-	-
Faecal coliforms (44 C)	10 ³ CFU/100 ml	-	-	-	-
Faecal streptococci	10 ³ CFU/100 ml	-	-	-	-
Salmonella sp.	in 1 litre	-	-	-	-
Macrozoobenthos	no. of taxa	-	-	-	-
Macrozoobenthos	Sapr. index	-	-	-	-
Chlorophyll - a	µg/l	-	-	-	-

4. Description of TNMN

Table 4.2.2: Determinand list for sediments for Phase 1 of TNMN

Determinands in sediments (dry matter)	Unit	Minimum likely level of interest	Principal level of interest	Target limit of detection	Tolerance
Organic nitrogen	mg/kg	50	500	10	10 or 20%
Total phosphorus	mg/kg	50	500	10	10 or 20%
Calcium (Ca ²⁺)	mg/kg	1000	10000	300	300 or 20%
Magnesium (Mg ²⁺)	mg/kg	1000	10000	300	300 or 20%
Iron (Fe)	mg/kg	50	500	20	20 or 20%
Manganese (Mn)	mg/kg	50	500	20	20 or 20%
Zinc (Zn)	mg/kg	250	500	50	50 or 20%
Copper (Cu)	mg/kg	2	20	1	1 or 20%
Chromium (Cr) – total	mg/kg	2	20	1	1 or 20%
Lead (Pb)	mg/kg	2	20	1	1 or 20%
Cadmium (Cd)	mg/kg	0.05	0.5	0.05	0.05 or 20%
Mercury (Hg)	mg/kg	0.05	0.5	0.01	0.01 or 20%
Nickel (Ni)	mg/kg	2	20	1	1 or 20%
Arsenic (As)	mg/kg	2	20	1	1 or 20%
Aluminium (Al)	mg/kg	50	500	50	50 or 20%
TOC	mg/kg	500	5000	100	100 or 20%
Petroleum hydrocarbons	mg/kg	10	100	1	1 or 20 %
Total extractable matter	mg/kg	100	1000	10	10 or 20 %
PAH – 6 (each)	mg/kg	0.01	0.1	0.003	0.003 or 30%
Lindane	mg/kg	0.01	0.1	0.003	0.003 or 30%
pp'DDT	mg/kg	0.01	0.1	0.003	0.003 or 30%
PCB – 7 (each)	mg/kg	0.01	0.1	0.003	0.003 or 30%

4.3 Analytical quality control (AQC)

The analytical methods for determinands used in TNMN are based on a list containing reference and optional 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 can demonstrate that its method (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 Tables 4.2.1 and 4.2.2), in order to enable laboratories to determine whether the analytical methods they are using are acceptable.

It is good practice that targets for analytical accuracy define the standard of accuracy 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. These levels define the aims of the monitoring programme and can be used to establish the required performance of analytical systems used in the laboratories involved in TNMN, assuming that the aims of the programme will be satisfied provided that:

4. Description of TNMN



- 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 harmonisation of TNMN-related analytical activities within the Danube Basin as well as the implementation and operation of an Analytical Quality Control (AQC) Programme. It was therefore used in identifying the needs for staff training that was necessary to improve the performance of the National Reference Laboratories and other laboratories involved in the implementation of the TNMN. As a result, the managers and personnel of the involved laboratories were provided with practical training for analytical instrumentation and on-site sampling and were introduced to the theoretical aspects of AQC.

4.3.1. Performance testing in the Danube laboratories

The organisation of interlaboratory comparison in the monitoring of the Danube under the Bucharest Declaration was agreed in 1992. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered to take and was given the responsibility to organise the first study under the name of QualcoDanube. Since the first distribution in 1993

when only a few determinands were analysed - pH, conductivity and total hardness - the range of determinands has grown and so has the number of participating laboratories.

In addition to QualcoDanube, another interlaboratory comparison, the AQUACHECK performance testing scheme, organised by WRC (UK), was conducted for NRLs, mainly focusing on the analysis of specific micropollutants.

In 2000, four distributions were carried out analysing synthetic and real water samples. For the first time reference materials (one water sample and three sediment samples) were distributed to be analysed and used as reference materials in the future.

In water samples, general determinands such as chlorides, sulphates and total hardness, nutrients and heavy metals were analysed and in those characterising organic pollution - both general and specific determinands. In the wake of the January 2000 cyanide spill in the Tisza River, additional samples were distributed in April to be screened for cyanide and selected heavy metals (Pb, Zn and Cu).

Nutrients, heavy metals and petroleum hydrocarbons were analysed in sediment samples.

In the QualcoDanube performance testing scheme, the Youden-pair evaluation technique was usually applied. The results of the four distributions and their evaluation have been published in the evaluation report (QualcoDanube, AQC for Water Labs in the Danube River Basin, Summary Report 2000, VITUKI Plc., Budapest).

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The interlaboratory comparative results are discussed below separately for the different determinands. The results were provided by 31 out of 33 laboratories. Most of the laboratories reported results for cyanide, nutrients and general determinands, but only ten provided results of lindane and DDT. Six laboratories reported results of AOX. Results of heavy metals analysis in sediment were provided by 15–21 laboratories and nine laboratories reported results of total P.

4.3.1.1 Results of performance testing of water samples

General determinands

Chlorides, sulphates and total hardness were analysed in real surface water samples. In general, in the case of chloride and total hardness the results were relatively good but the results of sulphates testing were influenced by systematic and random errors.

Nutrients in water samples

Ammonium-nitrogen and ortho-phosphate samples were distributed four times and nitrate-N samples were distributed three times, partly as real surface water and partly as synthetic samples. The reported values were quite satisfactory in the synthetic samples with a slight systematic error, while the results obtained from real surface water were affected by a significant systematic error and a slight random error. The results of total phosphorus were not so good although synthetic samples were analysed.

Cyanides

The results of cyanides analysis, reported by 31 laboratories, showed a relatively high variation, owing to a systematic error and a significant random error. Almost one third of the results were rejected. There were some extremely low values owing to a loss of determinand through distillation.

Determinands characterising organic pollution

COD_{Mn} and COD_{Cr} results were affected mainly by systematic error.

Results of BOD₅ were slightly better than in the previous years but still showed a significant systematic error in both positive and negative directions (see Figure 4.3.1.1.1).

The results of anionic active surfactants showed a significant systematic error (see Figure 4.3.1.1.1).

Only six laboratories (four NRLs and two others) reported analytical results of AOX (Adsorbable Organic Halogens) which fell into two groups. Since few analytical results were available it was not possible to get sufficient information on the performance of the laboratories (see Figure 4.3.1.1.2).

A few laboratories, mainly NRLs, analysed lindane in water samples and the results were rather scattered and below the theoretical values. Some results were biased either by erroneous calculation and/or misreported expression unit (theoretical value from the preparation of the solutions was used for evaluation). (See Figure 4.3.1.1.2.)

4. Description of TNMN



Samples of DDT were analysed by the same laboratories that analysed lindane samples. The results were scattered similarly as in the case of lindane. Usually the laboratories reported values less than the assigned value (theoretical value from the preparation of the solutions was used for evaluation). (See Figure 4.3.1.1.2).

Results of petroleum hydrocarbons (distributed as extract) were reported by 21 laboratories. They showed a slight systematic error, but were relatively satisfactory. Except for five results that were rejected, most results were relatively close to the assigned value.

Heavy metals

Five metals were analysed - Cd, Cr, Cu, Pb, Zn, out of which the results of cadmium, chromium, copper and lead were quite satisfactory, but were influenced by a slight systematic error.

4.3.1.2 Results of performance testing of sediment samples

Organic determinands

One half of the reported results of petroleum hydrocarbons showed relatively good coincidence and the other half were outside the error limit, mainly in the positive direction.

Nutrients

Few laboratories reported the results for total P and total N (9 and 12 respectively) in sediment samples. The measured values were influenced by a slight systematic error.

Heavy metals

Six metals (Cd, Cr, Cu, Ni, Pb, Zn) were analysed in sediment samples. The best results were observed in the case of cadmium, copper, nickel and lead, while chromium showed a significant systematic error and the results of zinc were irregularly scattered.

Conclusion

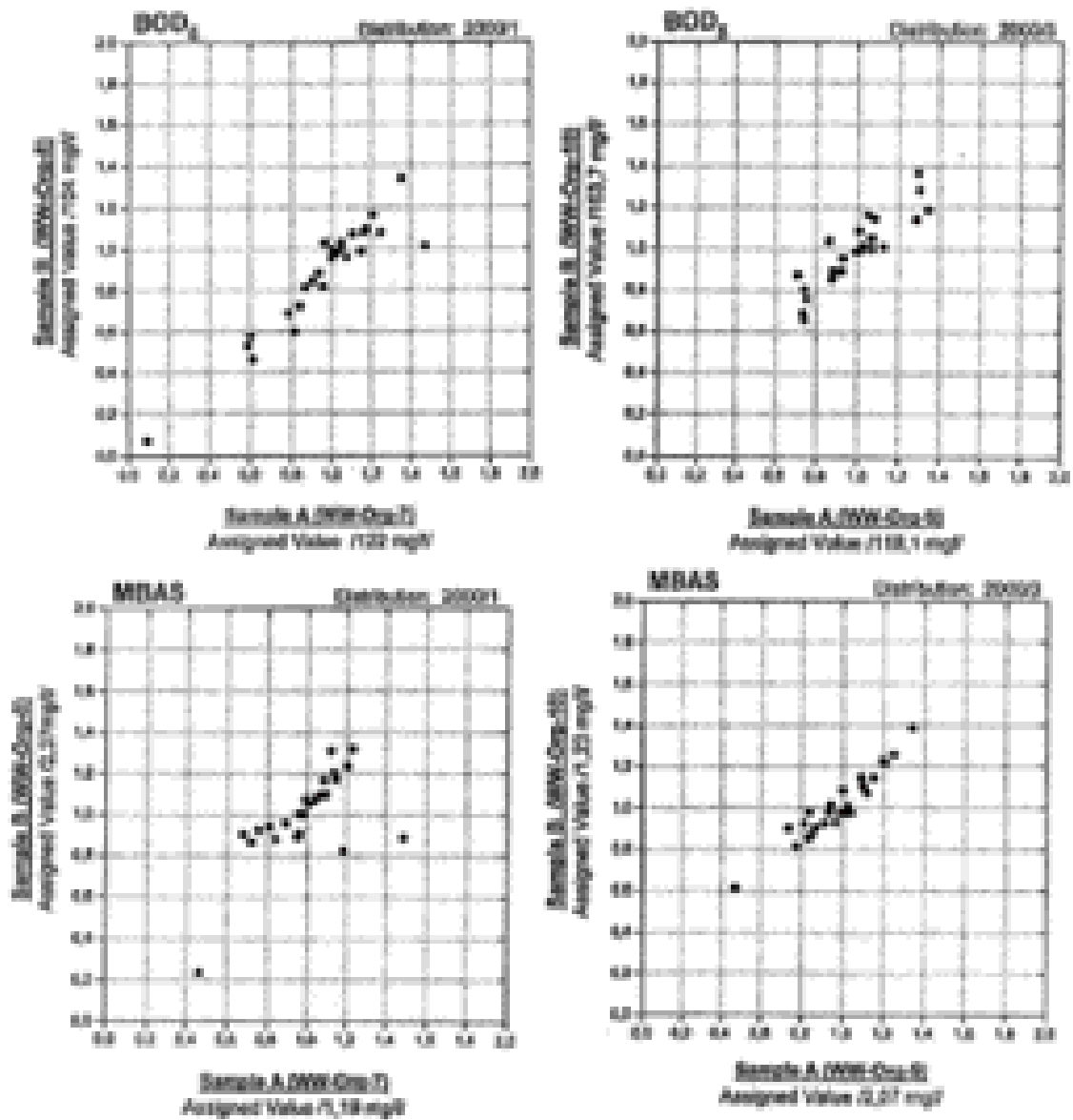
The four QualcoDanube distributions in 2000 provided information on the performance of the laboratories participating in the process of water and sediment analysis in the Danube River Basin. The results demonstrated the comparability of the analytical data on the tested determinands and revealed some methodological problems that may arise during the analysis.

It is worth pointing out that the analytical results of synthetic samples were better than those obtained from real water samples. In the latter case the results were influenced by both systematic and random error due to matrix effect, while the results of synthetic samples were mostly affected by systematic error.

Generally, the results of general determinands, nutrients in synthetic samples and metals were relatively good, while the results of nutrients in real water samples were influenced by a significant systematic error and a slight random error. The analysis of organic compounds needs to be further improved, especially in the case of micropollutants, in which the performance was not sufficient.

4. Description of TNMN

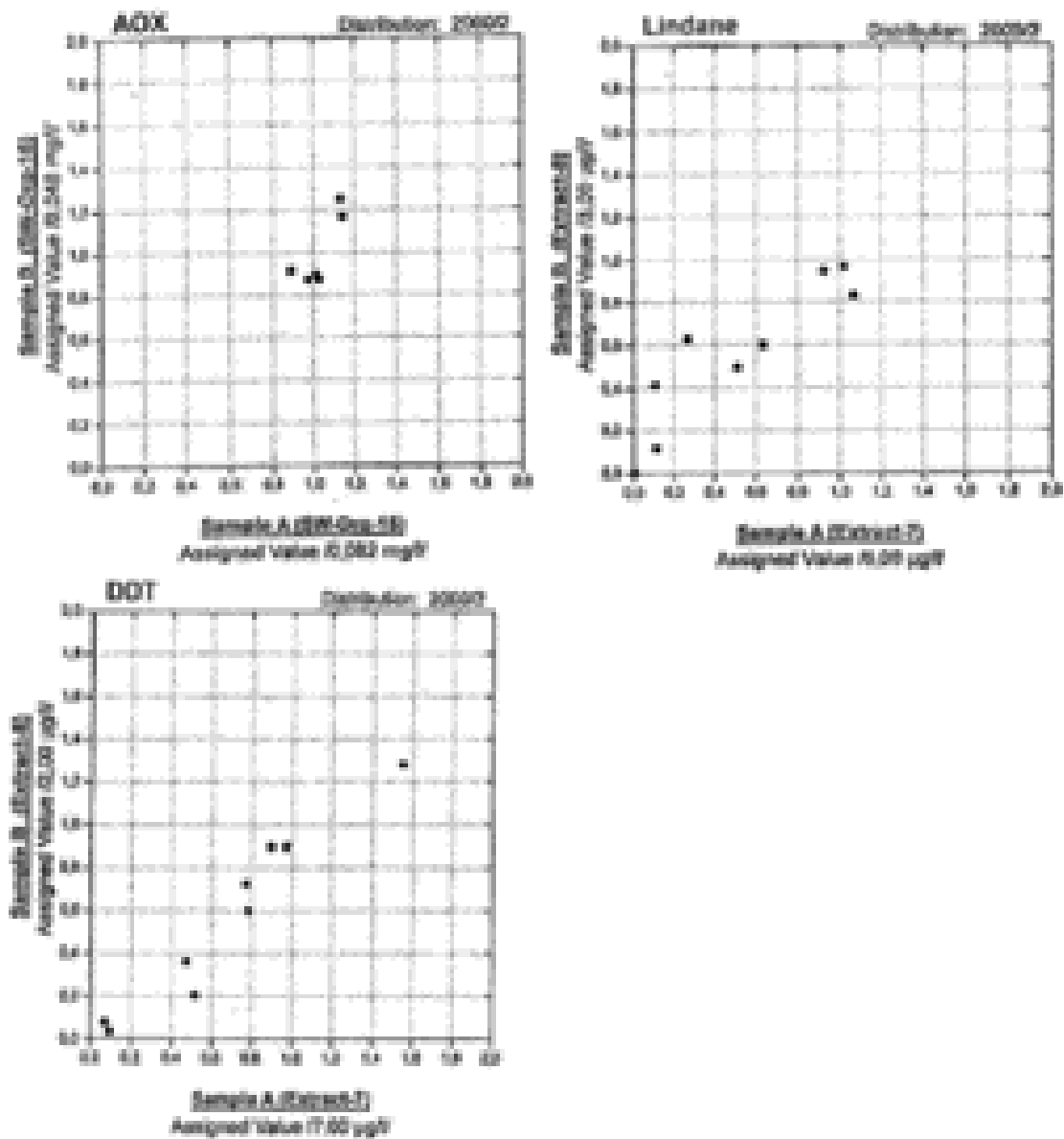
Figure 4.3.1.1.1: Variation in the reported/assigned value of BOD₅ and anionic surfactants (MBAS) in water samples



4. Description of TNMN



Figure 4.3.1.1.2: Variation in the reported/assigned value of AOX, lindane and DDT in water samples.



4. Description of TNMN

4.4 TNMN data management

Information management has involved data storage, exchange, retrieval and analysis as well as other types of data processing activities needed for successful information management. On the basis of a relational data base, TNMN in-stream water quality data are organised in a well-defined structure using rules of reference integrity. This has resulted in a system of joined tables, covering information about TNMN. Data exchange is organised quarterly according to a standard operational procedure. A special data exchange file format (DEFF) is used for this purpose.

The above summary briefly describes the current activities, which are rooted in the commitment to:

- concentrate on the quality of the obtained data;
- introduce a process of transferring data from the national information systems to a Central Information Point (CIP);
- build on the existing experience of individual countries rather than force all participating countries to adapt their national information systems and procedures;
- promote and increase the use and processing of data into information by introducing special software designed for time series analysis (AARDVARK).

This resulted in the important decision to leave the responsibility of the national information

systems to the countries themselves and to concentrate on an agreed protocol and data exchange format (DEFF) that all countries after a training course in 1996 could use to send their national data to the Central Information Point (CIP) or to load data into their national information systems for further processing.

The format of DEFF should be such as to anticipate future changes. Therefore, the data of interest had to be normalised. This resulted in nine tables of which seven are filled with more “static” data and two with dynamic ones. The tables with static data are agreed by the MLIM-SG and contain information regarding the monitoring stations, determinands, analytical methods, remarks, participating countries and sampling methods. These tables are maintained by the CIP on the basis of the agreements reached in the MLIM-SG. The tables with dynamic data contain information on taken samples and analytical results. These tables are also maintained at CIP level by merging the data received from all countries.

Based on the experience gained during the first years of TNMN data collection, storage and maintenance, it was recognized that several parts of the database needed to be adjusted or redesigned. The following steps were taken in response to that:

- a new system of coding of analytical methods was agreed for further use;
- the list of determinands was reviewed and expanded in accordance with the new requirements;

4. Description of TNMN



- units in which values of determinands are to be reported were adjusted in the case of several determinands;

- new information for the description of monitoring stations was included in TNMN database.

The standard operational procedure (SOP) for the exchange of DEFF data starts with data generation (sampling and analysis) and input of data to the system followed by a description of all the activities carried out by three key players - the National Reference Laboratory (NRL), the National Information Centre (NIC) and the

CIP - before the merged and validated final data report can be used for further processing (e.g. the Yearbook).

In the 1996-1997 period, TNMN data were regularly collected from Germany, Austria, the Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Bulgaria and Romania. Data from Ukraine and Moldova have been available since 1998 (data from Ukraine for the year 2000 are missing). Of all monitoring stations included in TNMN-Phase I, only those from Bosnia-Herzegovina are not yet part of CIP.

5. Tables of statistical data from TNMN stations

The determinands measured in 2000, the fifth year TNMN-Phase1 has been in operation, included the main physical, chemical, biological and microbiological water quality characteristics including the major anions and cations, nutrients, oxygen regime determinands, organic pollutants, heavy metals and characteristic biological and microbiological determinands.

The 61 stations participating in TNMN-Phase 1 are characterised on the station list in Table 4.1 and are illustrated in the station map (Figure 5.1). The station list shows official national data, which are not yet harmonized in all cases. Stations measured by two neighbouring countries still show inconsistencies concerning catchment area and altitude, most probably due to different national calculation procedures. It had been recommended that these problems

should be solved and that data should be made consistent within the transboundary commissions.

Each station can have up to three sampling points named L, M and R (Left, Middle, Right). TNMN-Phase 1 consists of 93 sampling points.

In 2000, data were available from 55 stations including a total of 81 sampling points. No data at all were available from Bosnia-Herzegovina and data from Ukraine for the year 2000 have not yet been provided.

Data available from 81 sampling points mentioned above are presented in 81 tables in Annex 1 according to the following key. Tables for those stations where no data were available are excluded from the Yearbook.

Term used	Explanation
Determinand	Name of the determinand measured according to the agreed method
Unit	Unit of the determinand measured
N	Number of measurements
Min	Minimum value of the measurements done in the year 2000
Mean	Arithmetical mean of the measurements done in the year 2000
Max	Maximum value of the measurements done in the year 2000
C50	50 percentile of the measurements done in the year 2000
C90	90 percentile of the measurements done in the year 2000
Q1	Arithmetical mean of the measurements done in the first quarter of the year 2000
Q2	Arithmetical mean of the measurements done in the second quarter of the year 2000
Q3	Arithmetical mean of the measurements done in the third quarter of the year 2000
Q4	Arithmetical mean of the measurements done in the fourth quarter of the year 2000

5. Tables of statistical data from TNMN stations



If values less than the detection limit were present in the dataset for a given determinand, the value of detection limit was used in the statistical processing of data. In case all measurements taken during the year were below the detection limit, only minimum, mean and maximum values were entered without any other statistical data. Similarly, in case of only four or less measurements of a particular determinand in a year, only minimum, mean and maximum values were calculated and presented in tables in Annex 1.

Water sampling and analysis should have been performed according to the specification in Chapter 4. As was already mentioned, at some stations no measurements were performed at all. Even in sampling points from which water samples were taken, the range of measured determinands are not uniform, although from 1996 the situation has been continuously improving.

It was agreed that sampling for the selected physico-chemical determinands would be carried out at least 12 times per year. However, this frequency was not observed at all monitoring sites, although there was a noticeable improvement in comparison with the first years of TNMN operation. Frequency of measurements lower than 11 times per year was very seldom, which is positive because it is very essential for determinands varying seasonally or highly correlating to the discharge. In the case of heavy metals, organic micropollutants and microbiological determinands, measurement frequency was lower.

When analysing the water quality data presented in the Yearbook, results from QualcoDanube intercalibration studies should be taken into account because the validity and full comparability of data is a prerequisite for their further use in the assessment process. On the basis of QualcoDanube studies it is evident that further improvement of analytical measurements is necessary and that the main problems are associated with determinands characterising nutrient content and pollution by organic substances. It also needs to be pointed out that methods for the measurement of microbiological and biological determinands have not yet been fully harmonised.

Table 5.1 shows the concentration ranges and mean annual concentrations of selected determinands characterising oxygen regime and nutrient status of the Danube River itself and its tributaries in 2000. The statistical results indicate that, in general, the concentration ranges of the measured determinands were larger in the tributaries than in the Danube itself. The highest pollutant levels were typical of some tributaries.

Seasonal variation in some determinands was also typical. For example, at the sites where water samples were taken and analysed at regular intervals throughout the year, maximum concentrations of ammonium-N, nitrate-N and ortho-phosphate-P were in most cases observed in the first or fourth quarter of the year.

5. Tables of statistical data from TNMN stations



Table 5.1: Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2000.

Determinand	No. of monitoring sites [mg/l]	Danube River		Tributaries		QualcoDanube
		Annual mean values [mg/l]	Concentration range [mg/l]	Annual mean values [mg/l]	Concentration range	
Dissolved Oxygen	81	7,2 - 11,3	4,3 - 15,6	7,5 - 11,5	3,7 - 15,9	systematic error systematic error
COD _{Cr}	78	9,0 - 36,7	2,0 - 120,0	4,9 - 38,0	2,6 - 120,0	
BOD ₅	81	1,2 - 4,2	0,3 - 8,1	1,3 - 10,0	0,30 - 58,2	
NH ₄ ⁺ -N	81	0,05 - 0,72	0,01 - 2,07	0,03 - 3,11	0,01 - 4,80	
NO ₃ ⁻ -N	81	1,08 - 3,20	0,06 - 6,00	0,60 - 6,90	0,05 - 11,50	
PO ₄ ³⁻ -P	69	0,021 - 0,125	0,005 - 0,260	0,014 - 0,319	0,004 - 0,872	
P _{total}	70	0,04 - 0,26	0,015 - 0,75	0,03 - 0,55	0,014 - 1,27	
N _{org} *	33	0,10 - 1,74	0,10 v 3,27	0,28 - 1,71	0,02 - 4,53	

* data on N_{org} content is available only from countries in the middle of the Danube River Basin from Czech Republic down to Croatia and several monitoring sites in Bulgaria

6. Maps of selected determinands

For the selected determinands characterising organic pollution and nutrient fractions in surface waters in the Danube River Basin the assessment based on the available data of TNMN – Phase 1 from 2000 are presented on the Map 6.1, 6.2, 6.3 and 6.4. The maps show interim water quality classes based on the average concentrations of BOD₅, ortho-phosphate-phosphorus PO₄³⁻-P, ammonium-nitrogen NH₄⁺-N and nitrate-nitrogen NO₃⁻-N, respectively.

If there were data from three sampling sites (left, middle, right) of a monitoring site only the data of the “middle” are presented in the following maps.

For indication of a sampling site, in which presented water quality determinand was measured in frequency lower than 11 times per year, the coloured circle on the map is of smaller size.

As in the previous years, the colour coding used for BOD₅ and PO₄³⁻-P presentation in the maps and tables of this chapter corresponds to the classification (5 class-system) which was proposed in the Final Report of the Applied Research Project “Water Quality Targets and Objectives for Surface Waters in the Danube Basin” WQTO (Project EU/AR/203/90).

Classification of NO₃⁻-N is also based on water quality standards proposed by this report, but for determinand NH₄⁺-N the proposed classification was considered very weak taking into account negative effects of ammonia on aquatic ecosystem. Therefore, it was agreed to use for presentation of NH₄⁺-N limit values from “Proposal for classification for TNMN purposes”, prepared by MLIM-ESG in 2001.

The set of surface water quality standards used for presentation in the yearbook is in Table 6.1.

Determinand	Unit	Quality class				
		I blue	II green	III yellow	IV red	V black
Biological oxygen demand ¹⁾ (BOD ₅)	mg/l	<3	5	9	15	>15
Ortho-phosphate-phosphorus ¹⁾ (PO ₄ ³⁻ -P)	mg/l	0.05	0.1	0.2	0.5	>0.5
Ammonium-nitrogen ²⁾ (NH ₄ ⁺ -N)	mg/l	0.2	0.3	0.6	1.2	>1.2
Nitrate-nitrogen ¹⁾ (NO ₃ ⁻ -N)	mg/l	1	5	10	25	>25

Table 6.1: Set of surface water quality standards used for presentation in the Yearbook

¹⁾ Water Quality Targets and Objectives for Surface Waters in the Danube Basin – Project EU/AR/203/90; Final Report (1997).

²⁾ Proposal for classification for TNMN purposes, prepared by MLIM/SG in 2001.

6. Maps of selected determinands



BOD₅ is a commonly used indicator for biodegradable organic pollution which affects the oxygen regime in water. Nevertheless the interpretation of results involves some difficulties concerning the possible toxic effects that can cause a decrease in BOD₅ values.

The results presented in Figure 6.1 show that at 97 % of all monitoring sites the average concentrations of BOD₅ corresponded to class I or II. It means that at those sites the average value of BOD₅ was not higher than 5 mg/l. All monitoring sites along the Danube River itself were within the range of class I and II. Higher average values of BOD₅, corresponding to class III and IV, were identified in the case of two tributaries (see also Table 6.2).

In the upper part of the Danube River itself water belongs exclusively to class I, while class I - II is observed from the middle down to lower part of River.

Generally, no change was observed in comparison with 1999.

Water quality class	Monitoring sites (Danube)		Monitoring sites (tributaries)		Monitoring sites (Danube + tributaries)	
	number within class	% of total	number within class	% of total	number within class	% of total
I	20	69	15	58	35	64
II	9	31	9	35	18	33
III	0	0	1	4	4	2
IV	0	0	1	4	4	2
V	0	0	0	0	0	0

Table 6.2: TNMN 2000 - average concentrations of BOD₅; distribution of monitoring stations according to the classification listed in Table 6.1.

6. Maps of selected determinands

Nutrients are very important because they are responsible for the eutrophication process in lakes, rivers and receiving seas. The concentrations of $\text{PO}_4^{3-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were selected from the different nutrient fractions analysed within the TNMN-programme, to be presented in the following maps and graphs.

Ortho-phosphate-phosphorus was chosen to be presented instead of total phosphorus, as it is a more reliable indicator of bioavailability. Total phosphorus is highly correlated with the transport of suspended solids and discharges with extreme concentrations during flood events, which are monitored only rarely.

Results presented in Figure 6.2 and Table 6.3 show that 83% of all monitoring sites reported average $\text{PO}_4^{3-}\text{-P}$ concentrations in the range of class I and II. In the Danube River itself, the average $\text{PO}_4^{3-}\text{-P}$ concentrations corresponded to class I and II at 92 % of the sampling sites. As to the sites located along the tributaries, they reported a higher variability in $\text{PO}_4^{3-}\text{-P}$ concentrations. The average $\text{PO}_4^{3-}\text{-P}$ concentrations in the tributaries corresponded to class I and II at 74 % of the sampling sites; at 17 % of the sampling sites they corresponded to class III and at 9 % of the sampling sites the average $\text{PO}_4^{3-}\text{-P}$ concentrations were in the range of class IV.

Variations in $\text{PO}_4^{3-}\text{-P}$ content along the Danube River itself can be seen in Figure 6.2. In the entire upper part of the Danube River water corresponds exclusively to class I; the middle part of the River can be characterised by classes I-II and the lower part by classes I - III.

The number of monitoring sites that in 2000 reported class I or II did not change in comparison with 1999. There was, however, a noticeable change against 1999 in terms of the lower percentage of sampling sites on the tributaries that reported the worst water quality classes, i.e. IV-V (20 % in 1999 down to 9 % in 2000).

Figure 6.3 shows the average concentrations of $\text{NH}_4^+\text{-N}$. Considering all monitoring sites, at most of them (75 %) the average concentrations measured in 2000 indicated class I or II. In the Danube itself, 83 % of the monitoring sites were within the range of class I or II; 14 % corresponded to class III and 3 % to class IV.

66 % of the monitoring sites located on the tributaries corresponded to class I or II; 23 % reported class III water quality and 12 % were in the range of class IV - V (see Table 6.4).

These results are comparable with those of the year 1999.

6. Maps of selected determinands



Table 6.3: TNMN 2000 - average concentrations of $\text{PO}_4^{3-}\text{-P}$: distribution of monitoring stations according to the classification listed in Table 6.1.

Water quality class	Monitoring sites (Danube)		Monitoring sites (tributaries)		Monitoring sites (Danube + tributaries)	
	number within class	% of total	number within class	% of total	number within class	% of total
I	19	79	12	52	31	66
II	3	13	5	22	8	17
III	2	8	4	17	6	13
IV	0	0	2	9	2	4
V	0	0	0	0	0	0

Table 6.4: TNMN 2000 - average concentrations of $\text{NH}_4^+\text{-N}$: distribution of monitoring stations according to the classification listed in Table 6.1.

Water quality class	Monitoring sites (Danube)		Monitoring sites (tributaries)		Monitoring sites (Danube + tributaries)	
	number within class	% of total	number within class	% of total	number within class	% of total
I	20	69	14	54	34	62
II	4	14	3	12	7	13
III	4	14	6	23	10	18
IV	1	3	2	8	3	5
V	0	0	1	4	1	2

6. Maps of selected determinands

The average concentrations of $\text{NO}_3\text{-N}$ were in a rather narrow range, especially in the Danube River (see Figure 6.4). As a result, $\text{NO}_3\text{-N}$ average values corresponded to class II at all monitoring sites located along the Danube River and 92 % of the monitoring sites located along the

tributaries were within the range of class I and II (see Table 6.5).

These results are comparable with those from the year 1999.

Table 6.5: TNMN 2000 - average concentrations of $\text{NO}_3\text{-N}$; distribution of monitoring sites according to the classification listed in Table 6.1.

Water Quality class	Monitoring sites (Danube)		Monitoring sites (tributaries)		Monitoring sites (Danube + tributaries)	
	number within class	% of total	number within class	% of total	number within class	% of total
I	0	0	4	15	4	7
II	29	100	20	77	49	89
III	0	0	2	8	2	4
IV	0	0	0	0	0	0
V	0	0	0	0	0	0

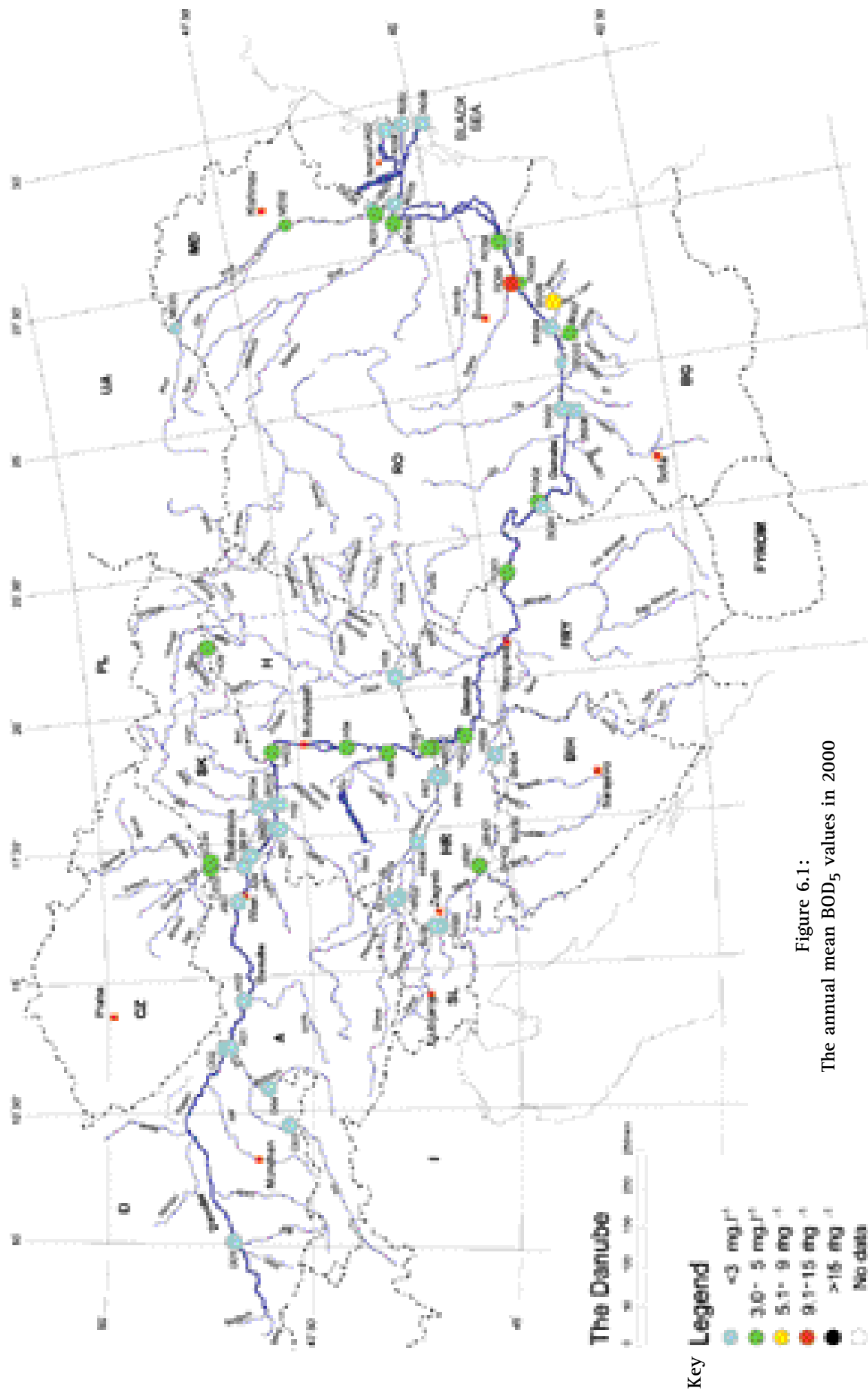


Figure 6.1:
The annual mean BOD₅ values in 2000

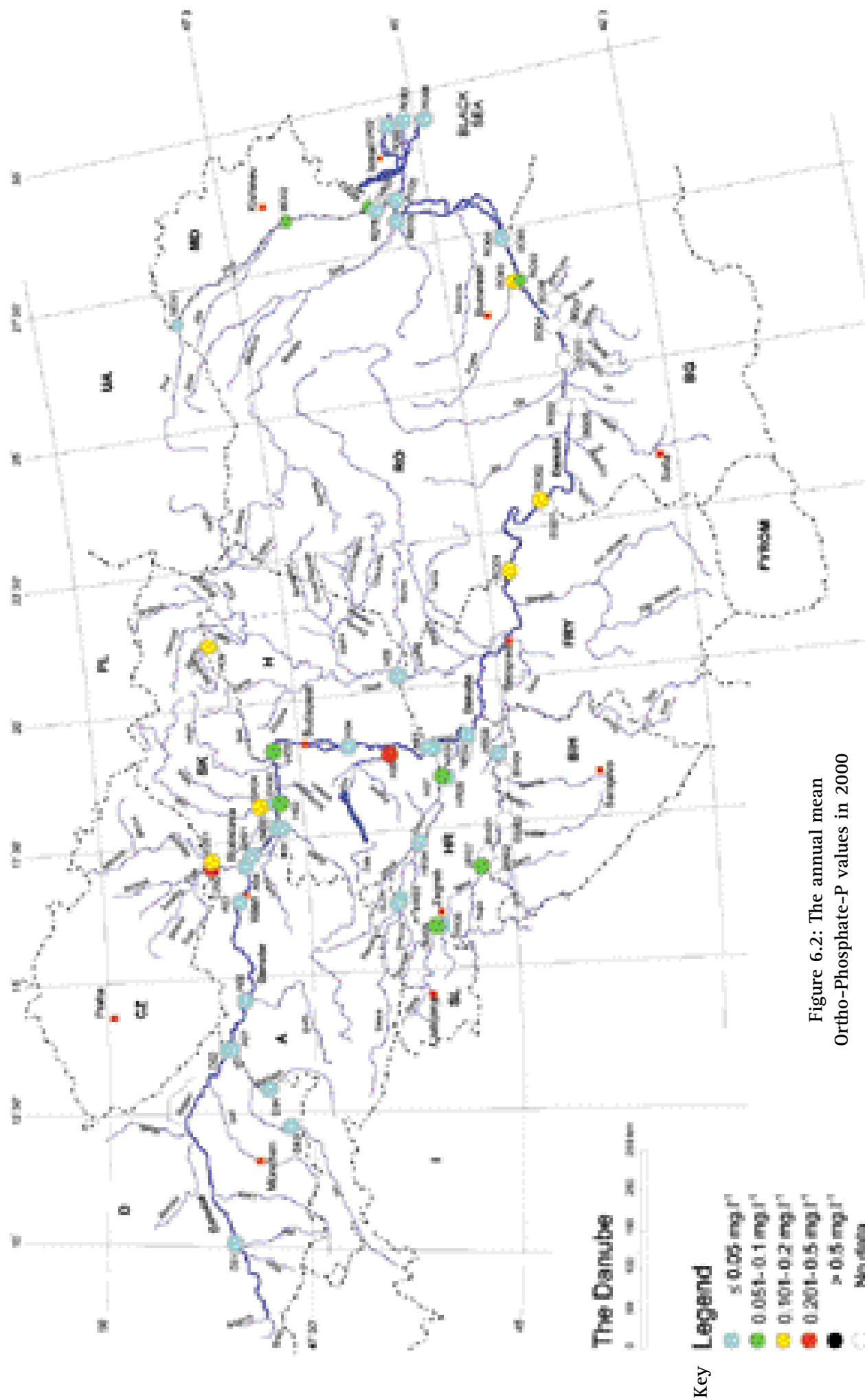


Figure 6.2: The annual mean Ortho-Phosphate-P values in 2000

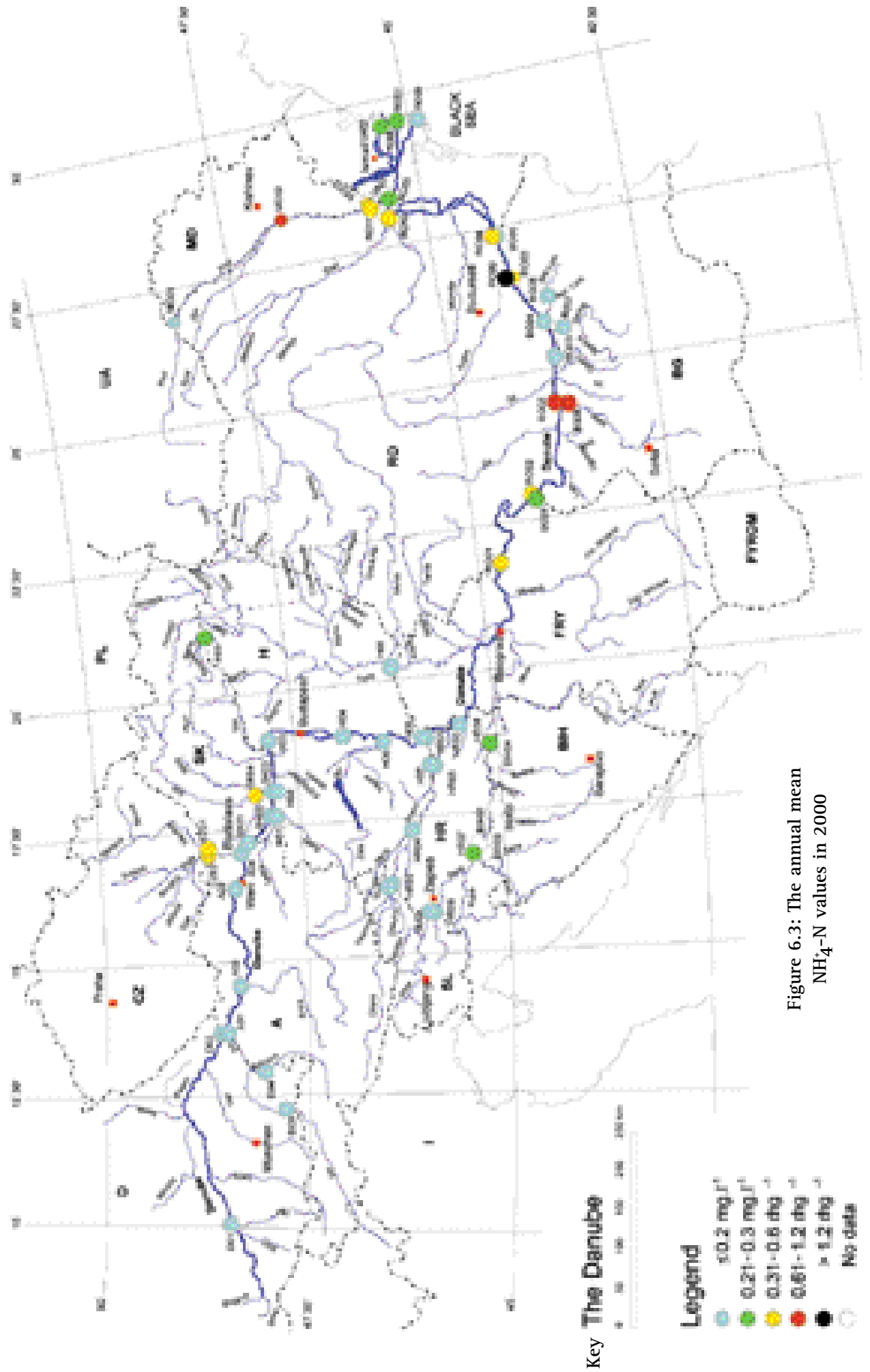


Figure 6.3: The annual mean $\text{NH}_4\text{-N}$ values in 2000

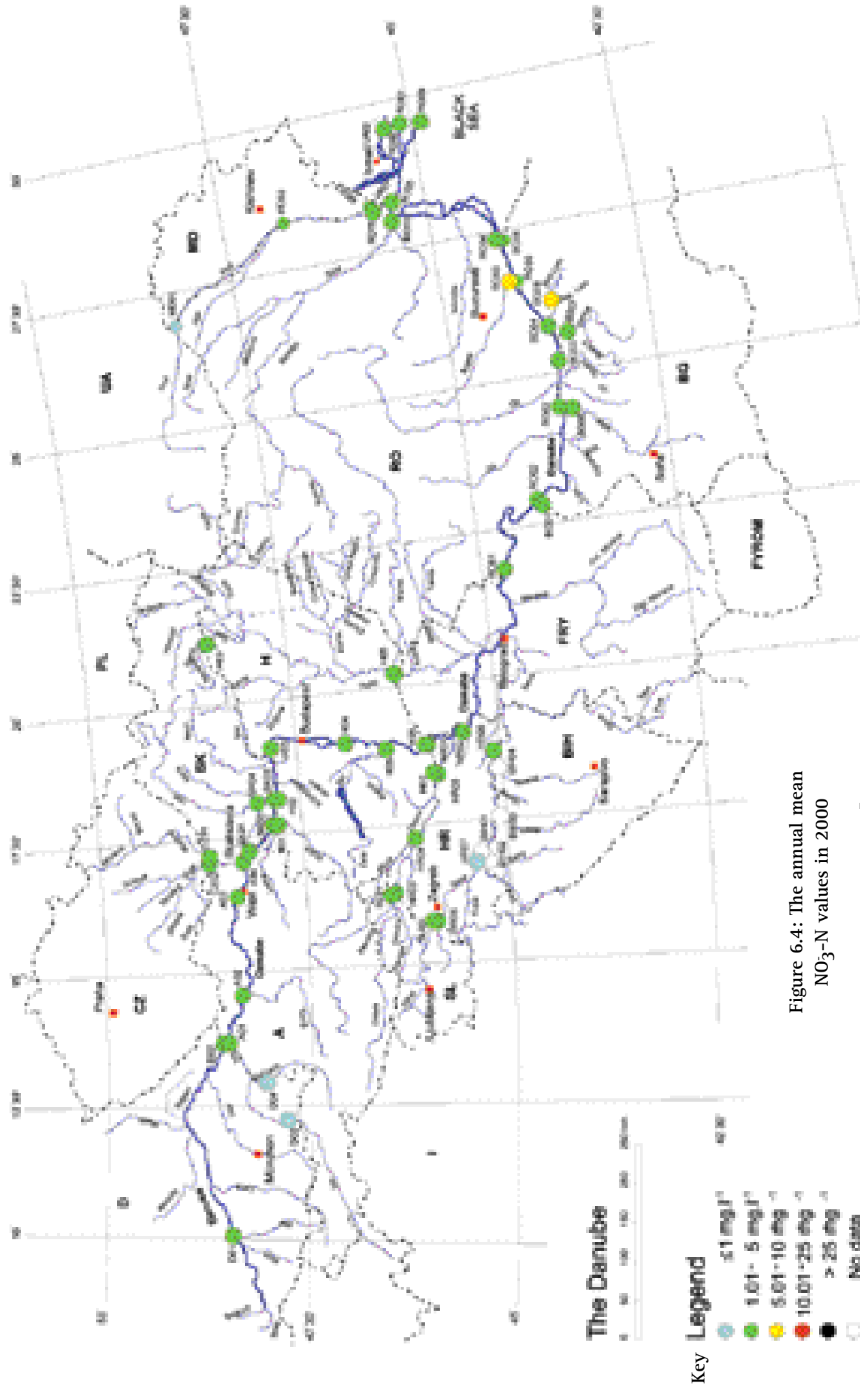


Figure 6.4: The annual mean $\text{NO}_3\text{-N}$ values in 2000

7. Profiles of selected determinands



In addition to the maps presented in the previous chapter, the average, maximum and minimum concentration profiles along the Danube of determinands BOD_5 , $PO_4^{3-}-P$, NH_4^+-N and $NO_3^- -N$ are presented on special profile plots, one profile for each of the determinands (Figures 7.1, 7.2, 7.3 and 7.4).

Each profile 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 and maximum values are indicated on the plots with green and red colour respectively. Stations close to each

other or those monitored by two countries (transboundary stations) are shifted slightly along the X-axis.

By the same method, the lower plot shows the concentration ranges at the most downstream stations on the primary tributaries. In those graphs, the bars are plotted at the river-km of the confluence of the tributary with the Danube.

If the monitoring station had three sampling sites (left, middle, right), only data produced by the middle one are presented in the following profiles.

7. Profiles of selected determinands

Figure 7.1: The minimum, mean and maximum of BOD₅ in 2000



7. Profiles of selected determinands

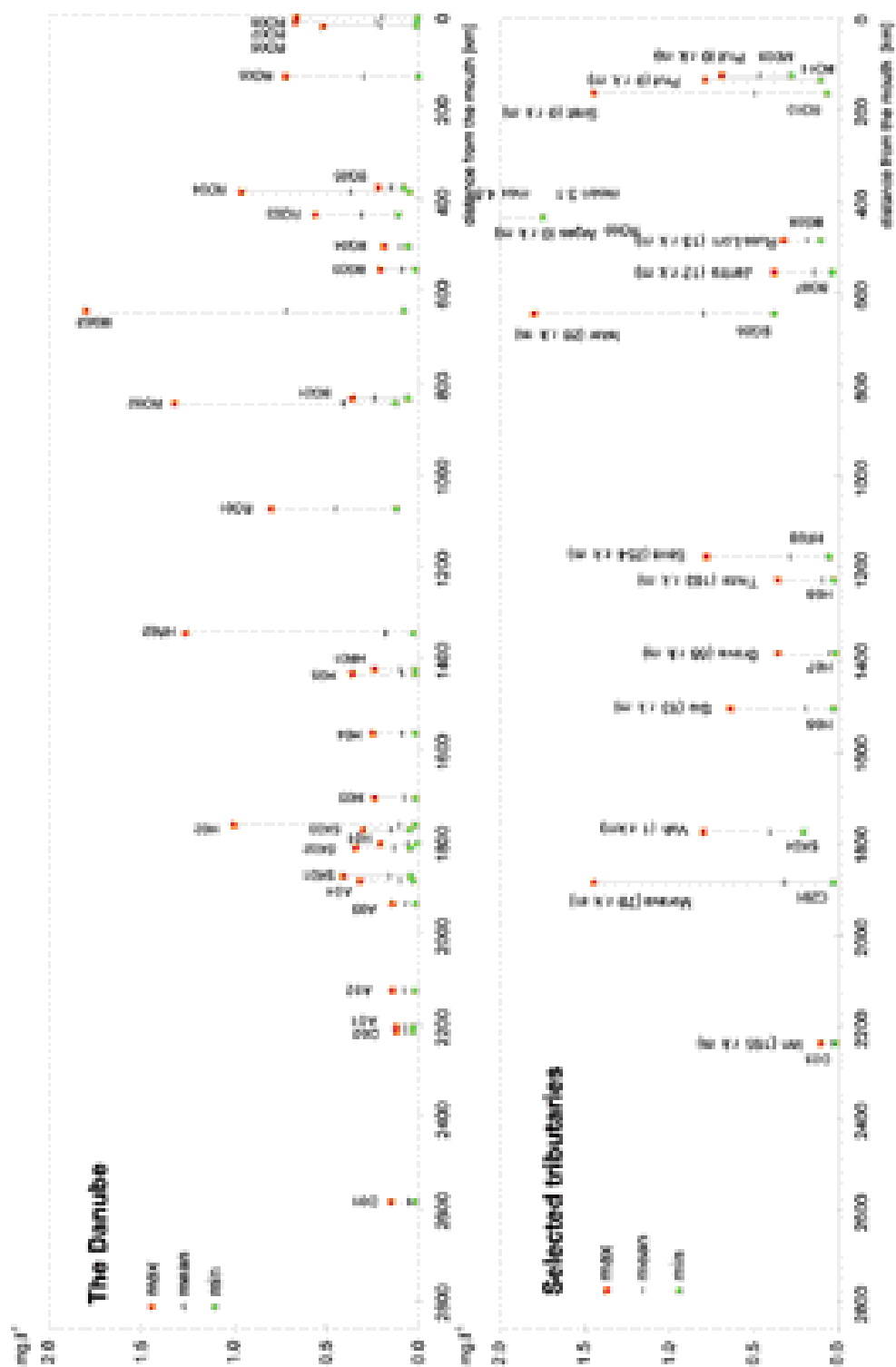


Figure 7.2: The minimum, mean and maximum Ortho-Phosphate-P in 2000



7. Profiles of selected determinands

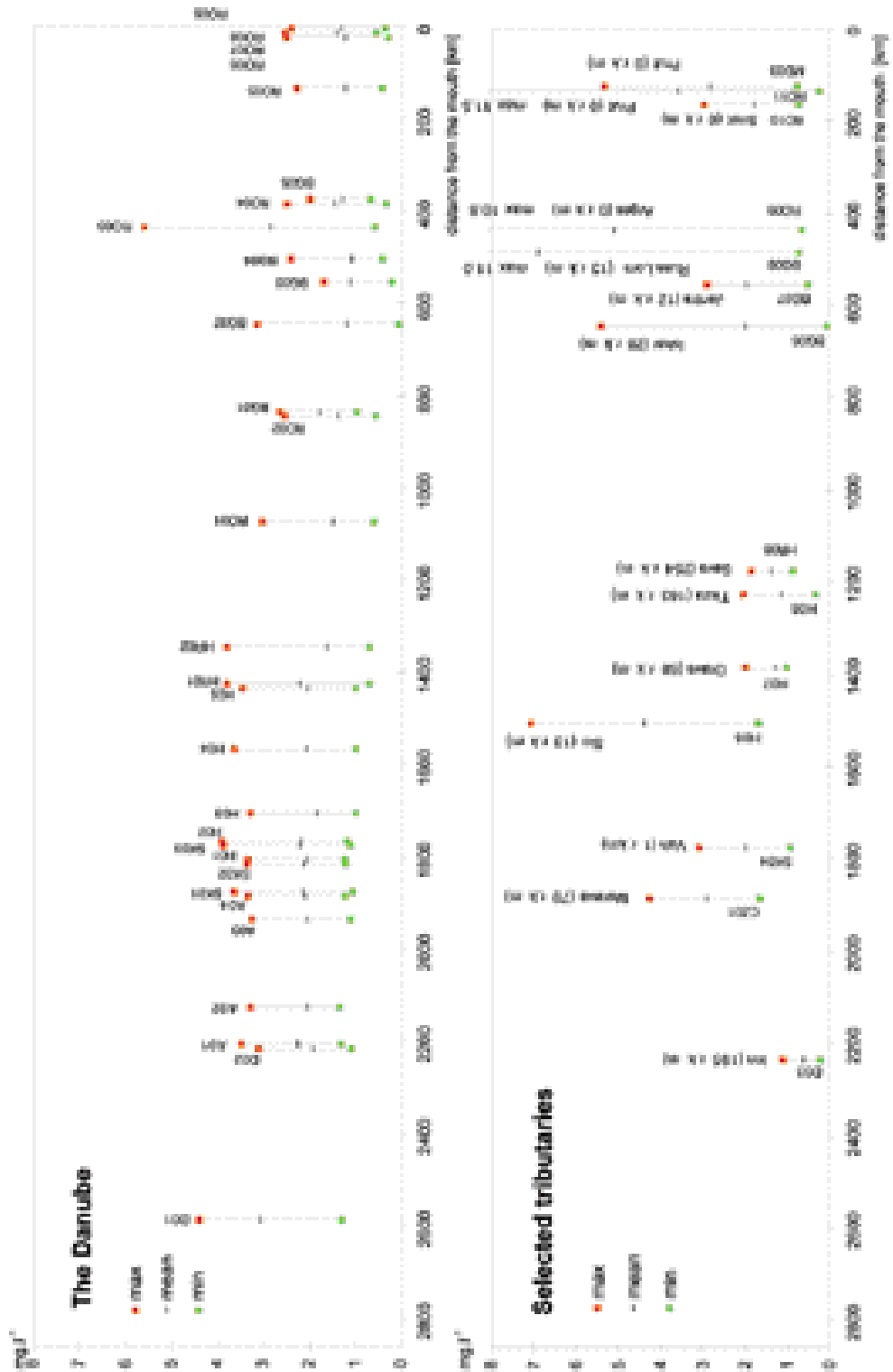
Figure 7.3: The minimum, mean and maximum $\text{NH}_4^+\text{-N}$ values in 2000



7. Profiles of selected determinands



Figure 7.4: The minimum, mean and maximum $\text{NO}_3\text{-N}$ values in 2000



8. Load assessment

8.1 Introduction

One of the main objectives of TNMN is producing reliable and consistent trend analysis of concentrations and loads of substances diluted in water or attached to sediments. Load assessment in the Danube River is necessary for estimating the input of polluting substances into the Black Sea and as an information basis for policy development and assessment.

In the frame of EU Phare Project “Transboundary Assessment of Pollution Loads and Trends”, a Standard Operational Procedure (SOP) was developed for load assessment. The countries agreed to use this SOP as a common and cost-effective approach for load assessment in the Danube River and its tributaries.

8.2 Description of the 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, ortho-phosphate-phosphorus, dissolved phosphorus, total phosphorus, suspended solids and - on voluntary basis - chlorides;

- minimum sampling frequency in sampling sites selected for load calculation is set at 24 per year;

- load calculation is processed according to the procedure recommended by the Project “Transboundary Assessment of Pollution Loads and Trends” (1998). Additionally, countries can

calculate the 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);

- results of load calculation should be presented for the first time in the Yearbook 2000.

8. Load assessment



Table 8.2.1: List of TNMN stations selected for load assessment programme

Country	River	Water quality monitoring station			Hydrological station	
		Country code	Location	Distance from the mouth (km)	Location	Distance from the mouth (km)
Germany	Danube	D02	Jochenstein	2204	Achleiten	2223
Germany	Inn	D03	Kirchdorf	195	Oberaudorf	211
Germany	Inn/Salzach	D04	Laufen	47	Laufen	47
Austria	Danube	A01	Jochenstein	2204	Aschach	2163
Austria	Danube	A04	Wolfsthal	1874	Hainburg (Danube)	1884
					Angern (March)	32
Czech. Republic	Morava	CZ01	Lanzhot	79	Lanzhot	79
Czech. Republic	Morava/Dyje	CZ02	Pohansko	17	Breclav-Ladná	32,3
Slovak. Republic	Danube	SK01	Bratislava	1869	Bratislava	1869
Hungary	Danube	H03	Szob	1708	Nagymaros	1695
Hungary	Danube	H05	Hercegszántó	1435	Mohács	1447
Hungary	Tisza	H08	Tiszasziget	163	Szeged	174
Croatia	Danube	HR02	Borovo	1337	Borovo	1337
Croatia	Sava	HR06	Jesenice	729	Jesenice	729
Croatia	Sava	HR07	Una Jesenovac	525	Una Jesenovac	525
Croatia	Sava	HR08	Zupanja	254	Zupanja	254
Slovenia	Drava	SI01	Ormoz	300	Borl	325
					HE Formin	311
Slovenia	Sava	SI02	Jesenice	729	Pesnica-Zamusani	10.1 (to the Drava)
					Catez	737
					Sotla -Rakovec	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 2000

Not all requirements set for load assessment programme were met in the year 2000. As only a few countries provided data on dissolved phosphorus and since stations with available data on dissolved phosphorus concentrations were not evenly distributed across the Danube River Basin, they are not presented in this Yearbook.

In addition, not all selected determinands were

measured with recommended frequency. For some TNMN stations mean daily discharges were not available. Since measurement frequency is crucial for the assessment of pollution loads, Table 8.2.2 shows the number of available data of both discharge and selected determinands. The table shows that Danube-Jochenstein and Sava-Jesenice stations were included in the list by two neighbouring countries. Data from these stations were combined in the process of load calculation.

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Table 8.3.1: Number of measurements at TNMN stations selected for assessment of pollution load in 2000.

Country Code	River	Location	River Km	Number of measurements						
				Q	SS	N _{inorg}	P-PO ₄	P _{tot}	BOD ₅	Cl
D02	Danube	Jochenstein	2204	365	26	26	26	26	26	26
D03	Inn	Kirchdorf	195	366	26	26	26	26	24	26
D04	Inn/Salzach	Laufen	47	366	26	26	26	26	26	26
A01	Danube	Jochenstein	2204	366	12	12	12	12	12	12
A04	Danube	Wolfsthal	1874	366	24	24	24	24	24	24
CZ01	Morava	Lanzhot	79	366	12	12	12	12	12	12
CZ02	Morava/Dyje	Pohansko	17	366	12	12	12	12	12	12
SK01	Danube	Bratislava	1869	366	25	25	25	25	24	25
H03	Danube	Szob	1708	364	26	26	26	26	26	26
H05	Danube	Hercegszántó	1435	364	23	36	36	36	36	23
H08	Tisza	Tiszasziget	163	352	19	29	29	29	29	13
HR02	Danube	Borovo	1337	26	26	26	26	26	26	0
HR06	Sava	Jesenice/D	729	26	26	26	26	26	26	12
HR07	Sava	Una Jesenovac	525	0						
HR08	Sava	Zupanja	254	0						
SI01	Drava	Ormoz	300	366	24	24	24	24	24	24
SI02	Sava	Jesenice	729	366	24	24	24	24	24	24
RO 02	Danube	Pristol-Novo Selo	834	366	20	20	20	20	20	20
RO 04	Danube	Chiciu-Silistra	375	366	21	21	21	21	20	21
RO 05	Danube	Reni-Chilia arm	132	366	21	20	20	20	21	21
UA02	Danube	Vilkova-Kilia arm	18	0						

8.4 Calculation procedure

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

- in case of several sampling sites in the profile, the average concentration at the station is calculated for each sampling day;
- in case of values “below the limit of detection”, the value of limit of detection is used in further calculation;
- the average monthly concentration is calculated according to the formula:

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

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

m The monthly load is calculated by using the formula:

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

where

- L_m monthly load
- Q_m average monthly discharge

- If discharges are available only for the sampling days, Q_m is calculated from those discharges.
- In case of months without measured values

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the average of the products $C_m \cdot Q_m$ in the months with sampling days is used.

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

$$La \text{ [tones]} = \sum_{m=1}^{12} L_m \text{ [tones]}$$

8.5 Results

The mean annual concentrations and annual loads of suspended solids, inorganic nitrogen, ortho-phosphate-phosphorus, total phosphorus, BOD_5 and chlorides are presented in Tables 8.5.1 to 8.5.4, separately for monitoring stations located on the Danube River and those located along its tributaries. The terms used in Tables 8.5.1 - 8.5.4 are explained in the key at the bottom of the page.

The mean annual discharge and annual loads of suspended solids, inorganic N, PO_4^{3-} -P, total P, BOD_5 and chlorides are presented on the plots, prepared separately for monitoring stations located on the Danube River and stations located on its primary tributaries (Figures 8.5.3 - 8.5.14). Concerning the Figures that show the calculated values of annual load it is necessary to stress

once again that in accordance with the results of QualcoDanube proficiency testing comparability of data analysed by laboratories included in TNMN is still not satisfactory. There is a need to improve the analyses of nutrients and BOD_5 , which are included in the load assessment programme.

Figures 8.5.5 - 8.5.14 show that, in general, load increases along the Danube River. An exception was observed for suspended solids, which decrease in the middle part of the Danube due to the reduced flow velocity through damming. For determinands that depend significantly on flow regime, e.g. total phosphorus, variations in load might be caused by different monitoring timetables. Some of the high annual load values seem unrealistic and MLIM-EG recommended to respective countries to examine possible sources of errors. Among the tributaries, the highest contribution to the load of the Danube River comes from the Tisza River, its biggest tributary.

Annex II contains Figures that show the measured concentration of determinands selected for load assessment with mean daily discharges in 2000. The Figures are prepared for all monitoring stations included in load assessment programme.

Term used	Explanation
Station Code	TNMN monitoring station code
Profile	location of sampling site in profile (L-left, M-middle, R-right)
River Name	name of river
Location	name of monitoring site
River km	distance to mouth of the river
Qa	mean annual discharge in the year 2000
cmean	arithmetical mean of the concentrations in the year 2000
Annual Load	annual load of given determinand in the year 2000

8. Load assessment

Table 8.5.1: Mean annual concentrations at monitoring stations selected for load assessment on the Danube River

Station Code	Profile	River Name	Location	River km	Q ₅	Concn						
						Suspended Solids	Inorganic Nitrogen	Ortho-Phosphorus	Total Phosphorus	BOD ₅	Chlorides	
												(mg/L)
D02	+A02	M	Danube	Neckenstein	2204	1667.7	2.5	2.02	0.028	0.02	2.0	1.5
A04	R	Danube	Necksthal	1874	2327.6	8.9	2.23	0.030	0.12	1.6	1.9	
S001	M	Danube	Budapest	1845	2327.6	3.1	3.31	0.047	0.15	2.0	1.5	
H03	UPR	Danube	Szob	1793	2627.3	1.8	1.97	0.038	0.13	3.7	2.1	
H05	M	Danube	Hernyospolc	1433	2609.4	2.2	2.16	0.048	0.14	3.4	2.0	
HR02	R	Danube	Barany	1337		7.9	1.81	0.048	0.02	3.4		
RC00	UPR	Danube	Pradol-Mova Szob	834	5585.6	5.2	1.85	0.104	0.14	3.9	2.2	
RC04	UPR	Danube	Cherov-Szilva	373	6198	2.6	1.82	0.038	0.04	3.5	3.2	
RC05	UPR	Danube	Hern-Chova arm.	132	6560.4	2.8	1.02	0.033	0.02	2.2	3.8	

*, low data available only for sampling days

Table 8.5.2: Mean annual concentrations at monitoring stations selected for load assessment on tributaries

Station Code	Profile	River Name	Location	River km	Annual Load					
					Suspended Solids	Inorganic Nitrogen	Ortho-Phosphorus	Total Phosphorus	BOD ₅	Chlorides
D03	M	Isar	Reichenart	183	1.93	6.8	0.13	2.01	14.0	0.02
D04	L	Inn-Glabach	Laufen	47	0.22	0.1	0.12	0.20	12.1	0.02
C001	M	Mozart	Leimbach	70	0.02	7.0	0.21	0.43	7.1	0.02
C002	L	Mozart/Cyff	Pyhrnbach	17	0.02	6.4	0.22	0.33	6.0	0.02
H04	UPR	Trava	Travatschlag	162	3.24	42.1	2.74	6.97	67.1	1.01
S001	L	Drava	Ormozy	300	0.40	11.1	0.21	0.31	24.0	0.02
S002	UPR	Sava	Jasenice	722	0.15	12.4	0.20	0.60	18.4	0.02

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Station Code	Profile	River Name	Location	River km	O ₂	Concn					
						Suspended Solids (mg/L)	Inorganic Nitrogen (mg/L)	Ortho-Phosphorus (mg/L)	Total Phosphorus (mg/L)	BOD ₅ (mg/L)	Chlorides (mg/L)
D03	M	Don	Kirchdorf	183	201	1.0	0.65	0.014	0.19	1.9	4
D04	L	Imbsbüsch	Laufen	47	283.8	2.0	0.32	0.017	0.03	1.8	7
G201	M	Moara	Landsol	79	80	2.3	3.27	0.199	0.25	3.4	29
G202	L	Morava/Drau	Pohorac	17	38.6	1.8	3.45	0.278	0.45	4.2	42
H08	L/H	Taza	Tuzsuzd	1.7	93.3	8.0	1.25	0.078	0.25	2.4	42
S01	L	Orava	Ormar	305	350.8	2.0	1.61	0.028	0.03	2.3	4
S02	L/H	Sava	Jasenovac	725	249.4	1.1	1.74	0.035	0.11	2.5	8

Table 8.5.3: Annual load at selected monitoring stations on the Danube River

Station Code	Profile	River Name	Location	River km	Annual Load					
					Suspended Solids (x10 ⁶ tons)	Inorganic Nitrogen (x10 ⁶ tons)	Ortho-Phosphorus (x10 ⁶ tons)	Total Phosphorus (x10 ⁶ tons)	BOD ₅ (x10 ⁶ tons)	Chlorides (x10 ⁶ tons)
D02	M	Danube	Jochenstein	2204	1.6	1.04	1.4	4.7	10.7	0.7
A04	R	Danube	Wollathal	1873	4.8	1.6	2.2	10.4	1.24	1.1
S021	M	Danube	Bratislava	1852	2.6	1.7	3.0	8.2	14.5	1.2
H03	L/H	Danube	Sabo	1702	1.2	1.6	4.9	10.4	31.4	1.2
H05	M	Danube	Hennegauand	1433	2.1	1.9	4.1	12.2	28.6	1.2
H002	R	Danube	Borovo	1337	7.0	1.6	4.8	7.8	33.1	1.2
R002	L/R	Danube	Prigod-Sreb. Selo	834	10.4	3.4	17.2	24.1	69.1	4.1
R004	L/H	Danube	Schoo-Straza	273	7.8	3.8	4.2	9.2	68.3	6.2
R005	L/R	Danube	Rant-Čikla arm.	132	5.1	2.9	6.1	10.3	39.1	5.2

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

8. Load assessment

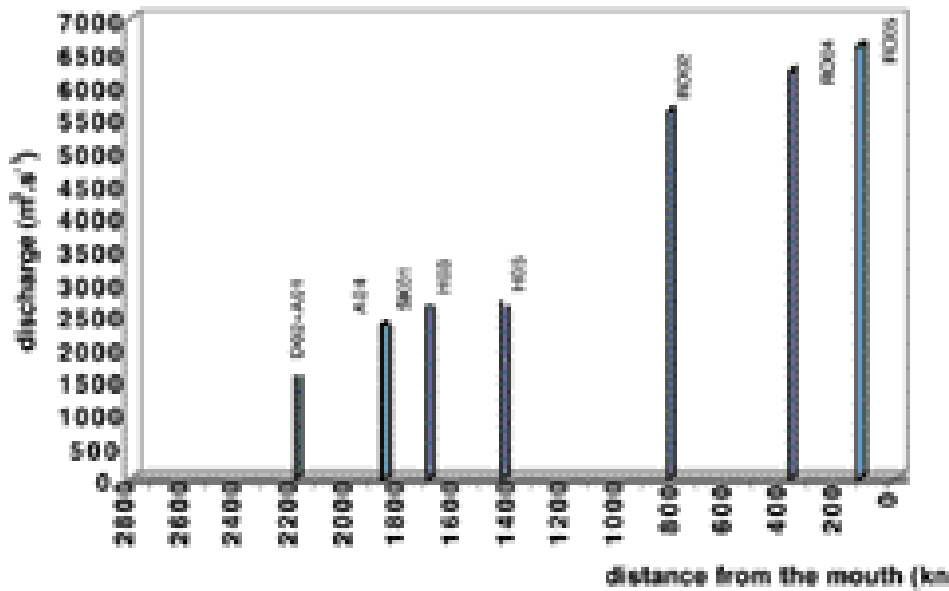


Figure 8.5.3: Mean annual discharge at monitoring stations along the Danube River.

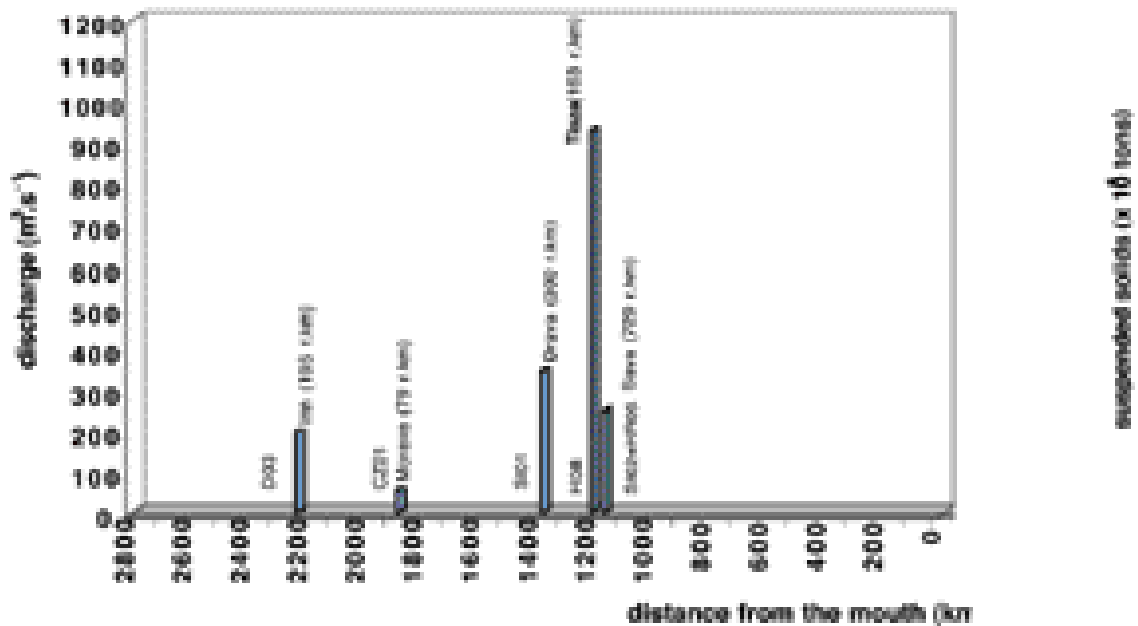


Figure 8.5.4: Mean annual discharge at monitoring stations of Danube tributaries.

8. Load assessment

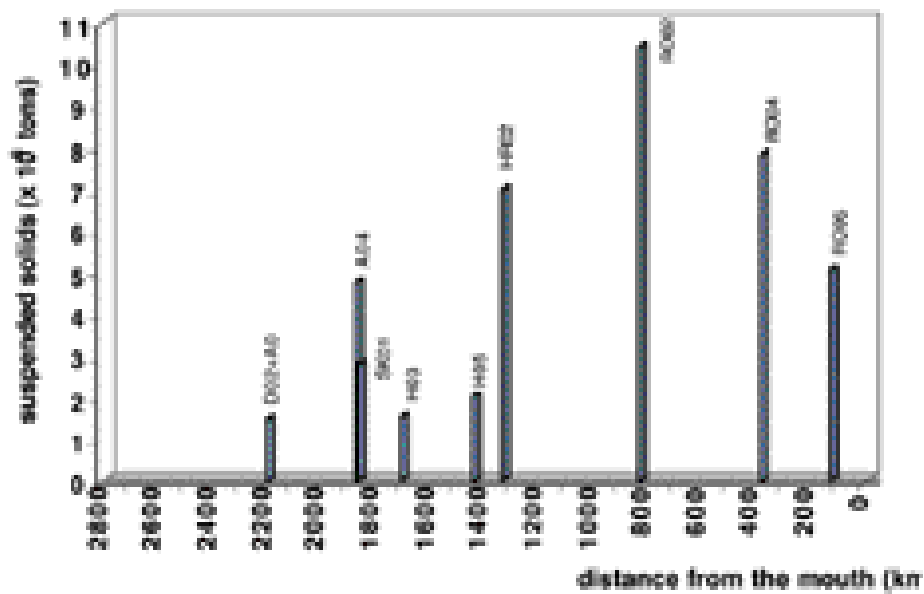


Figure 8.5.5: Annual loads of suspended solids at monitoring stations along the Danube River

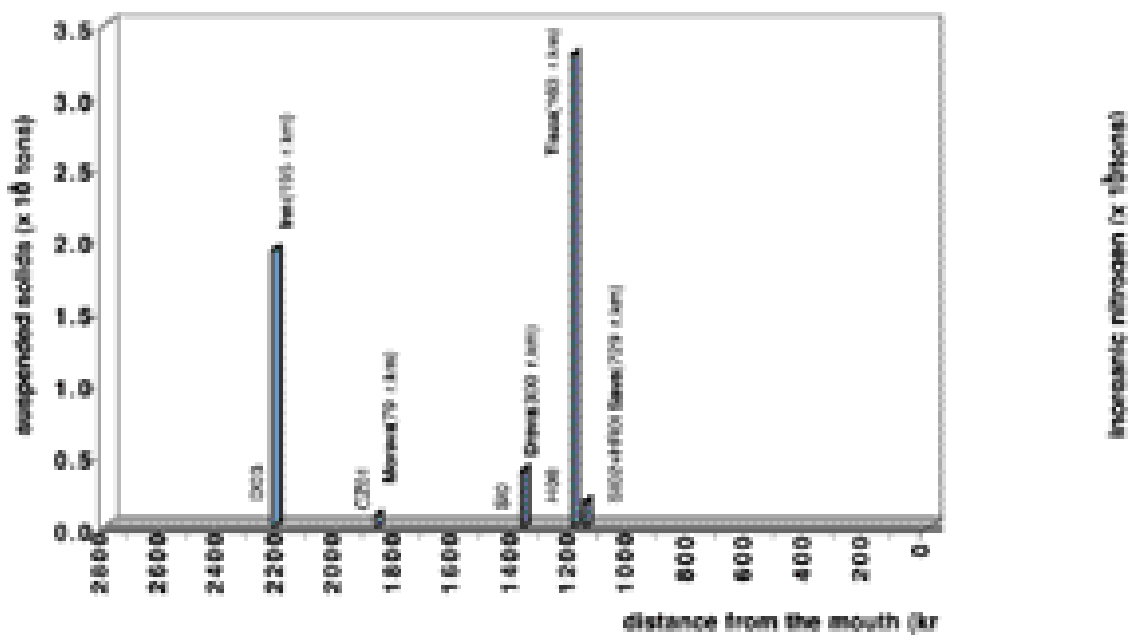


Figure 8.5.6: Annual loads of suspended solids at monitoring stations on tributaries.

8. Load assessment

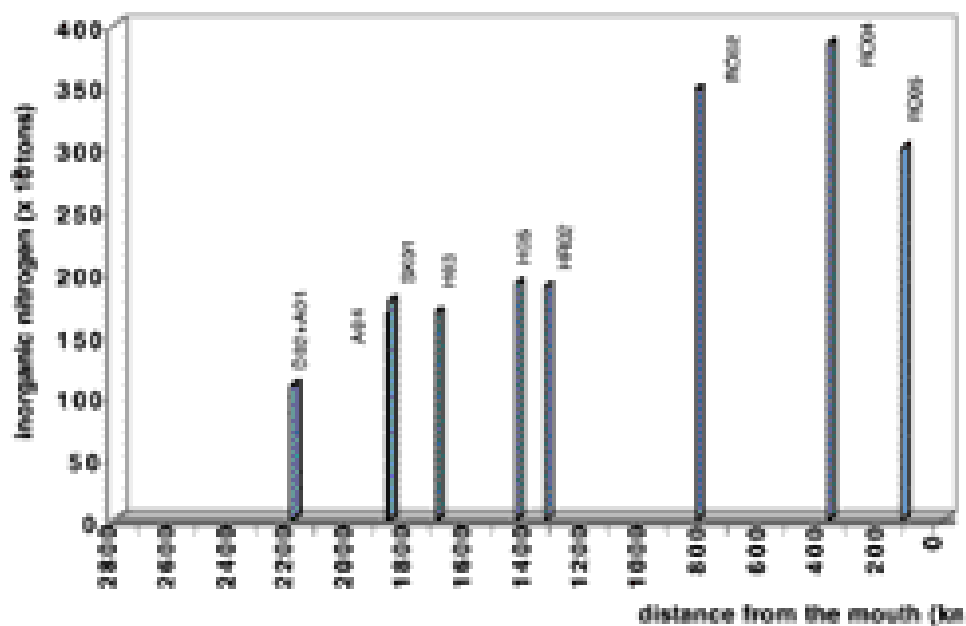


Figure 8.5.7: Annual loads of inorganic nitrogen at monitoring stations along the Danube River.

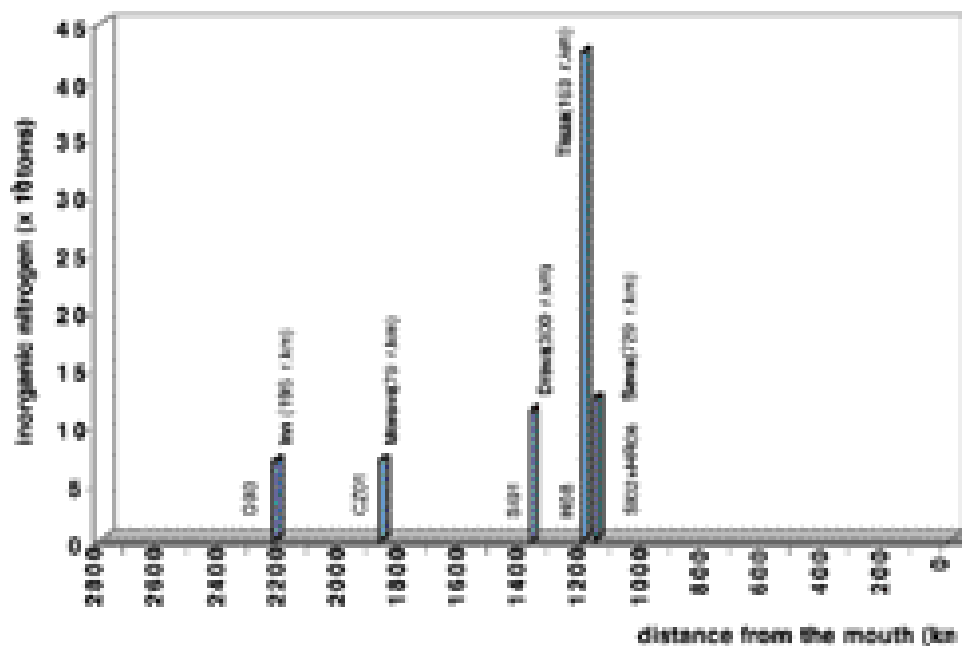


Figure 8.5.8: Annual loads of inorganic nitrogen at monitoring stations on tributaries.

8. Load assessment

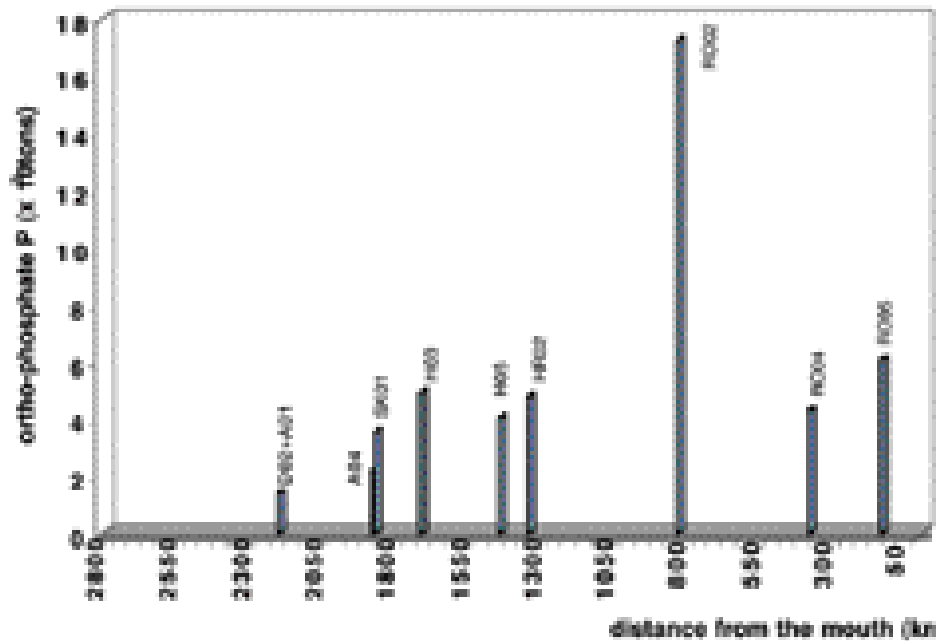


Figure 8.5.9: Annual loads of ortho-phosphate phosphorus at monitoring stations along the Danube River.

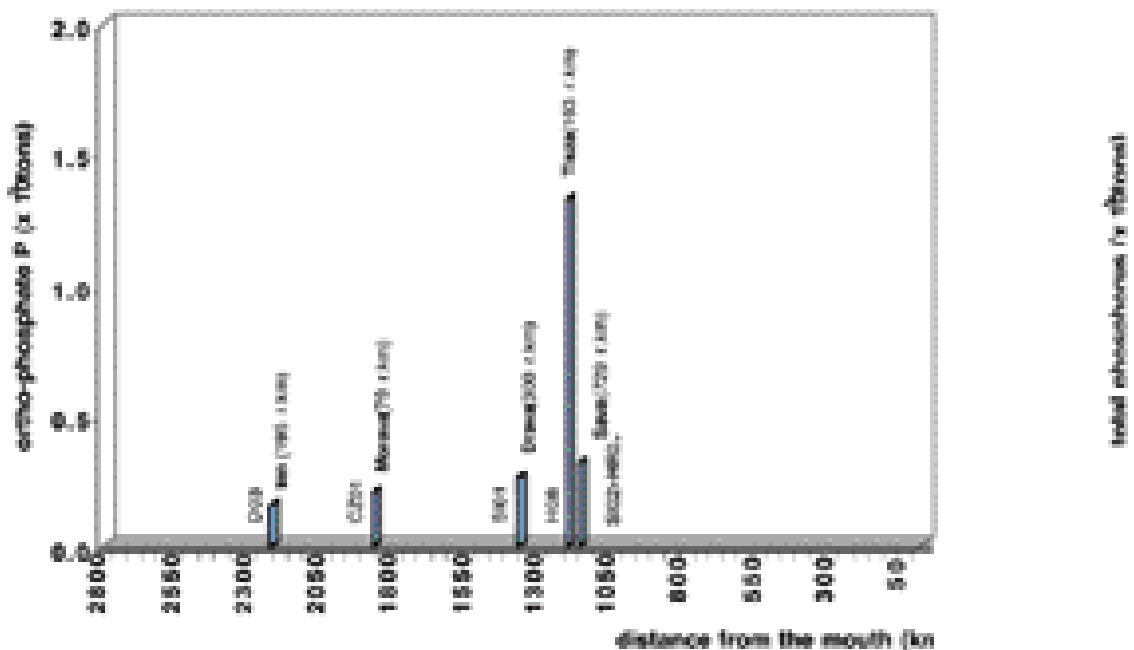


Figure 8.5.10: Annual loads of ortho-phosphate phosphorus at monitoring stations on tributaries.

8. Load assessment

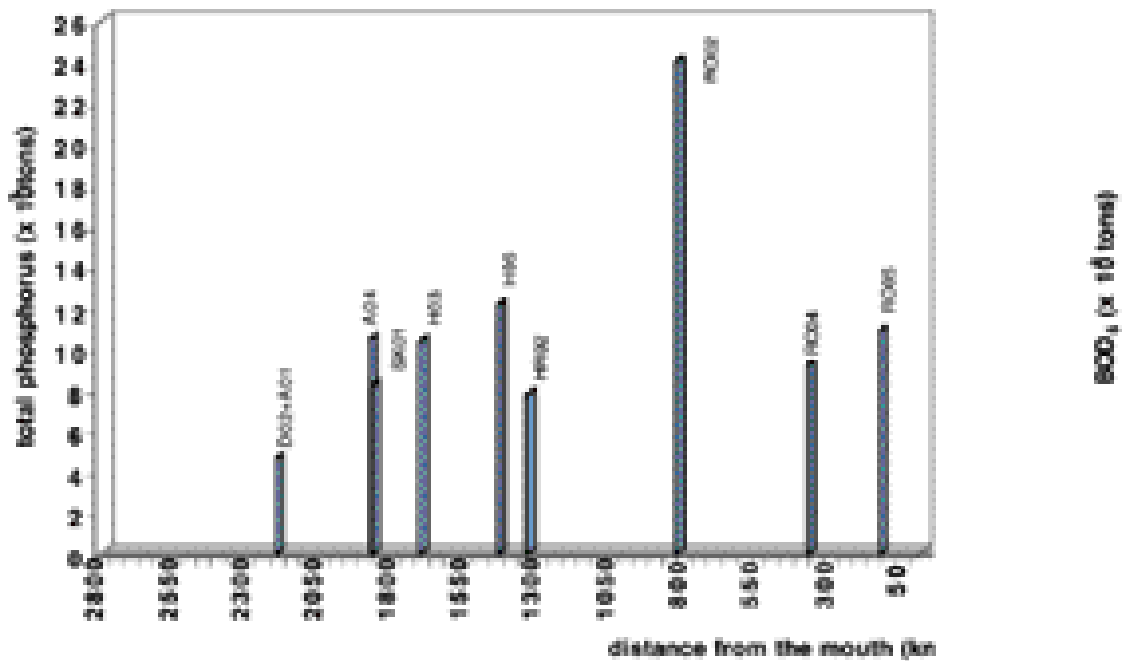


Figure 8.5.11: Annual loads of total phosphorus at monitoring stations along the Danube River

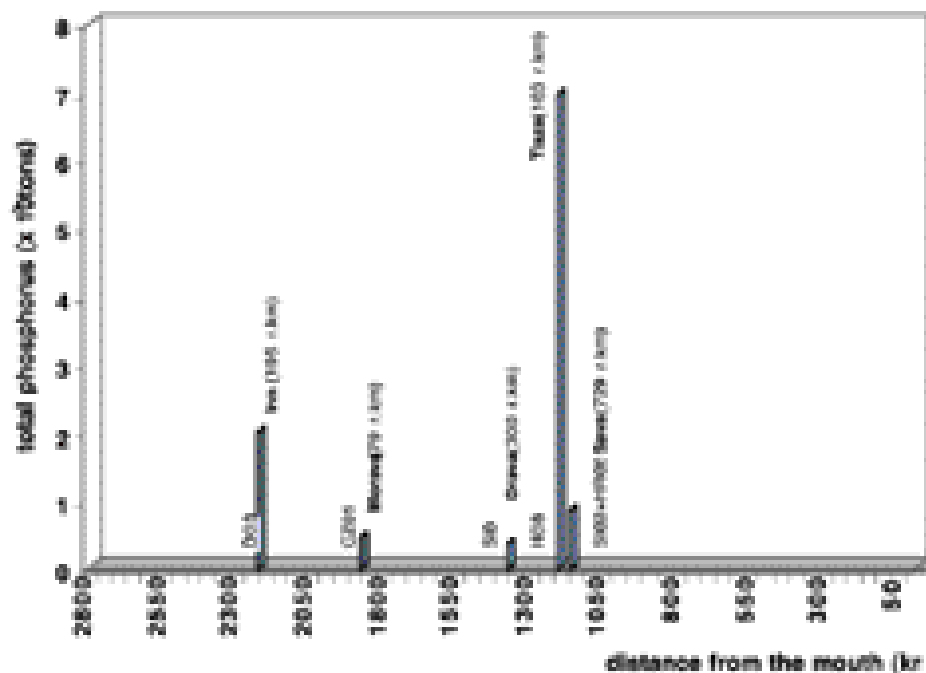


Figure 8.5.12: Annual loads of total phosphorus at monitoring stations on tributaries.

8. Load assessment

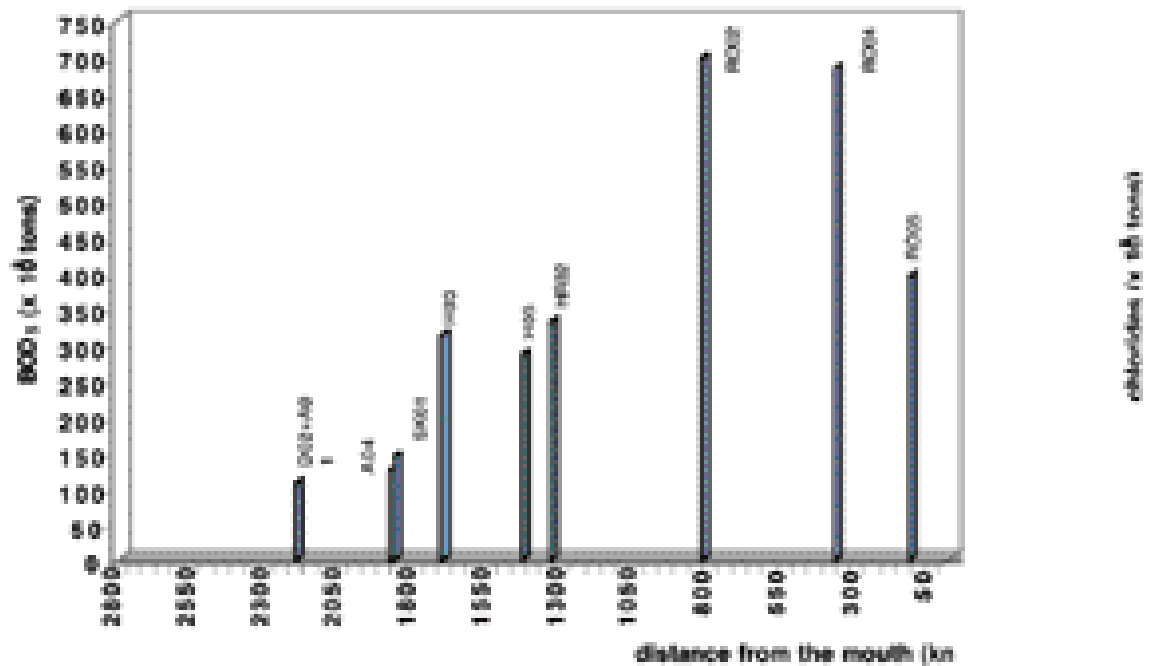


Figure 8.5.13: Annual loads of BOD₅ at monitoring stations along the Danube River.

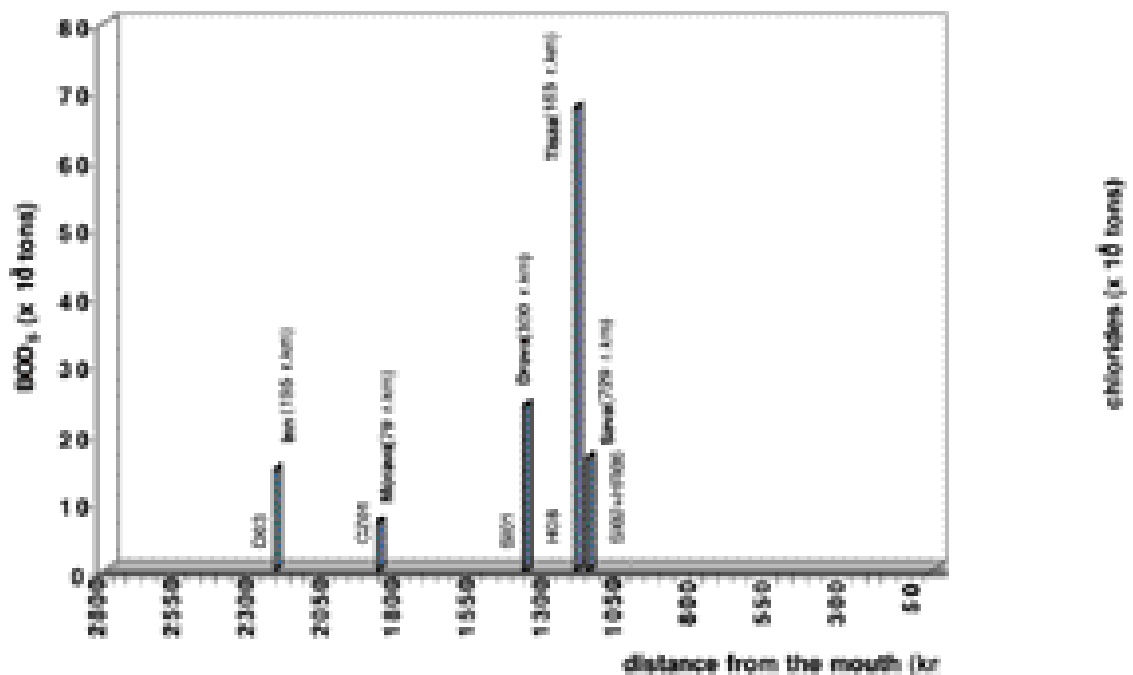


Figure 8.5.14: Annual loads of BOD₅ at monitoring stations on tributaries.

8. Load assessment

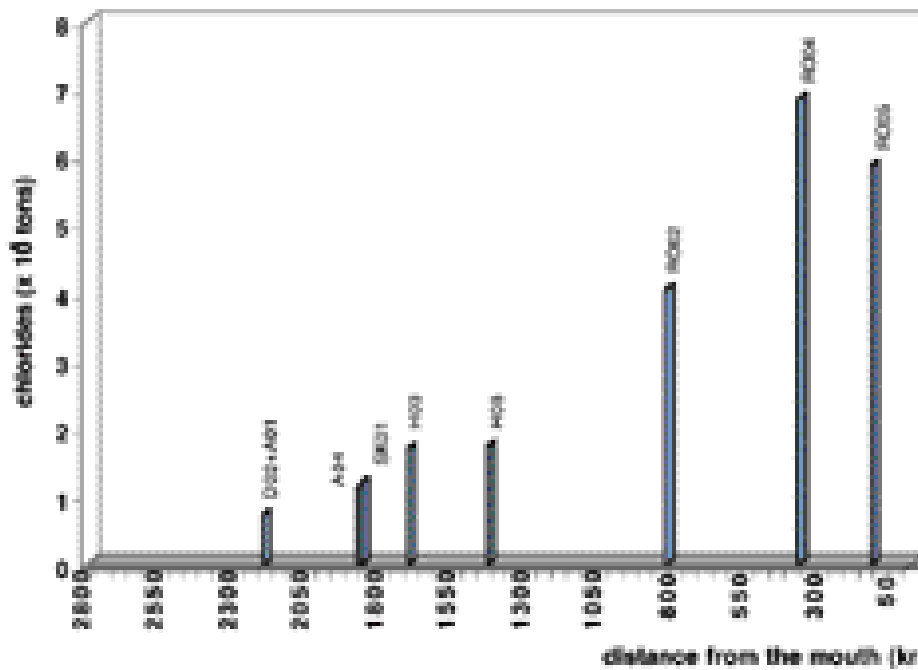
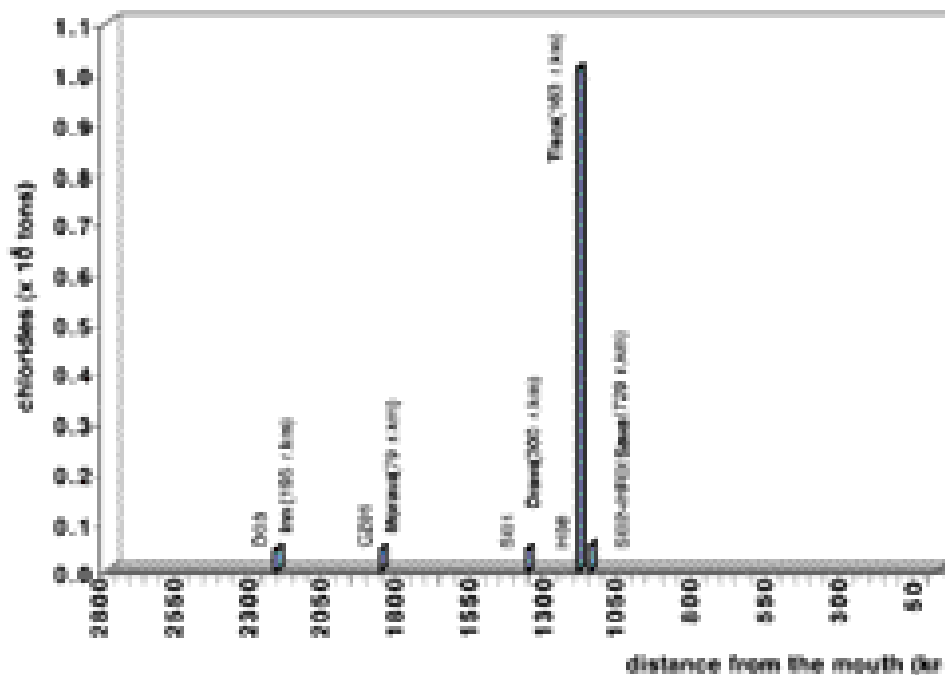


Figure 8.5.15: Annual loads of chlorides at monitoring stations along the Danube River.



9. Abbreviations



Abbreviation	Explanation
AQC	Analytical Quality Control
ARP	Applied Research Programme
BD	Bucharest Declaration
CIP	Central Information Point (for information management)
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
IM/ESG	Information Management Expert Sub-Group
IMWG	Information Management Working Group
LM/ESG	Laboratory Management Expert Sub-Group
LMWG	Laboratory Management Working Group
LOD	Limit of Detection
M/ESG	Monitoring Expert Sub-Group
MCEP	Multi-Country Environmental Programme
MLIM/EG	Monitoring, Laboratory and Information Management Expert Group
MLIM-SG	Monitoring, Laboratory and Information Management Sub-Group
MWG	Monitoring Working Group
NIC	National Information Centre
NRL	National Reference Laboratory
PCU	Programme Coordination Unit
QA	Quality Assurance
QC	Quality Control
SAP	Strategic Action Plan
SIP	Strategic Action Plan Implementation Programme
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)