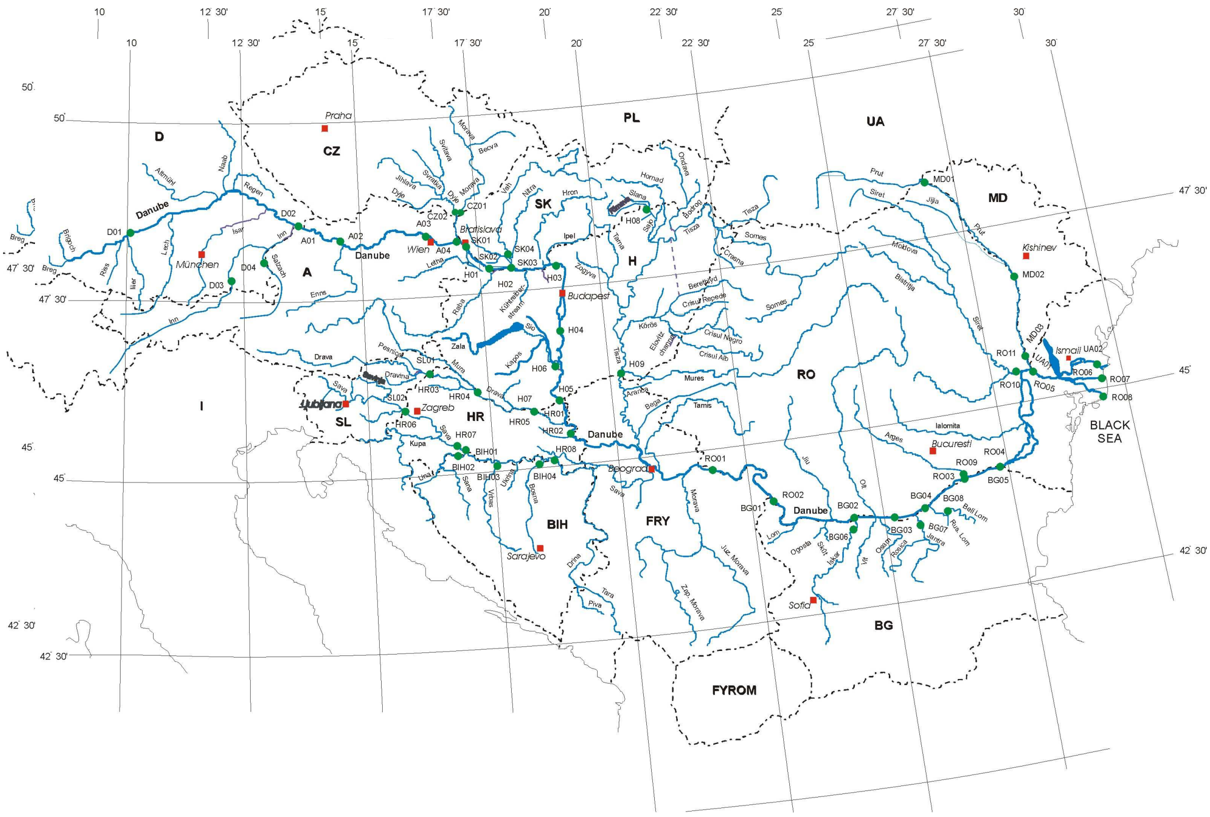
ENVIRONMENTAL PROGRAMME

FOR THE DANUBE RIVER BASIN

in support of

DANUBE RIVER PROTECTION CONVENTION

WATER QUALITY IN THE DANUBE RIVER BASIN 1996 (TNMN – Yearbook)



1999

Austria – Bosnia and Herzegovina – Bulgaria – Croatia – Czech Republic – Germany – Hungary – Moldova – Romania – Slovakia – Slovenia - Ukraine

Acknowledgement

With the occasion of elaboration and launching of the first Yearbook of the TransNational Monitoring Network (TNMN) for the Danube River Basin, I like to express, on behalf of experts involved in the former Monitoring Laboratory and Information Sub Group & Working Groups, also personally, our gratitude and appreciation to the European Commission - and personally to Mr. Bernardus Griepink, Head of Section, European Commission Services (SCR.A1), who helped so much in securing financial support through EU Phare Multi-Beneficiary Environmental Programme and Tacis Programme for our countries. This support has allowed all these countries in transition to establish acceptable water quality monitoring in the region. Moreover, I would like to mention the effort of the Programme Coordination Unit of the Environmental Programme for the Danube River Basin (EPDRB). Finally, I express my appreciation to the work of the Bucharest Expert Group because the TNMN in fact carries on the monitoring activities of the Bucharest Declaration in so far as most of the transboundary sampling locations from this are integrated into the TNMN.

I would like to mention that Austria, Croatia and Germany co-operated and actively participated in the Sub Group and Working Groups in the frame of EPDRB, in line with the agreements, and in spite of the fact that these countries were not supported by the PHARE or TACIS Project.

I would like to expand my gratitude and appreciation to the Hungarian government for financial support and in particular to Water Resources Research Centre, VITUKI Plc Budapest –for initiation and implementation of the QUALCO Danube proficiency testing scheme for quality assurance within the laboratories involved in the TNMN monitoring programme.

The same appreciation goes to Croatia for supporting the establishing of a basin wide TNMN data base and particularly to the Rudjer Boskovic Institute in Zagreb for acting as the Central Information Point for data collection, merging and standard data processing.

I would like to thank the consultants for their efforts and creative work in designing and implementing the TNMN monitoring programme, and in producing and supporting the application of special software for data collection and data processing, e.g. the Data Exchange File Format (DEFF), AARDVARK, etc.

At last, but not least, my special appreciation goes to the experts in the MLIM Sub-Group and Working Groups - since end of October 1998 MLIM Expert Group and MLIM Expert Sub-Groups - for their efforts during all the years since the EPDRB has started. They and a large number of additional colleagues made the arriving at the data possible - be it by work in the field and or in the laboratories. Only this enabled to come up with this Yearbook. It will be hopefully be followed by others, more and more complete over time.

Special acknowledgements go also to the Slovak Government and the Slovak experts for preparing this yearbook.

On behalf of the MLIM/EG, L. N. Popescu, Chairman

Preface

Experts from the Danube countries have been working together to develop a TransNational Monitoring Network (TNMN). This is aimed at establishing a system for water quality monitoring enabling comparisons to be made on water quality issues within the Danube River Basin in agreed formats. This water quality data is the basis for the information used by decision makers in the region and to enhance public awareness of the major issues and, in time, to observe improvements in the environmental quality of the River Basin.

Many years there has been a strong wish within the Danube River Basin to implement such a system, but this has been delayed due to political situation in the past. This initiative, to create an international monitoring programme, began with the signing of the Bucharest Declaration in 1985. Data has been collected since 1988 under this Declaration from key cross-border stations.

In September 1991, the Danubian countries, international and financing institutions, G-24 countries and NGO´s met in Sofia and decided to launch the Environmental Programme for the Danube River Basin (EPDRB). At this meeting a Task Force was created and a Programme Co-ordination Unit (PCU) was established to implement the EPDRB. The objective was to strengthen the operational basis for environmental management in the Danube River Basin. To secure the legal basis for the protection of water resources, the 'Convention on Co-operation for the Protection and Sustainable Use of the Danube River' (Danube River Protection Convention – DRPC) was signed by most of the Danube States and the European Union in 1994. This convention entered into force on 22 October 1998.

A common understanding on producing comparable water quality data has been achieved between the twelve countries involved, although the equipment and methods used for sampling, laboratory analysis and data processing was very different at the start of the EPDRB. Although there is still a lot of work to do for the future to improve the reliability and comparability of data it has been an exceptional example of co-operation between so many countries with the common objective of ensuring the environmental quality of the Danube River Basin.

International Commission for the Protection of the Danube River (ICPDR)

Former Task Force of the Environmental Programme for the Danube River Basin (EPDRB)

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1. Introduction

This is the first Yearbook based on the TNMN (TransNational Monitoring Network) for the Danube River and selected tributaries. The TNMN is 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 is stated that the monitoring network for the Danube shall:

- 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
- assist in the identification of major pollution sources
- include sediment monitoring and bioindicators
- include quality control

Furthermore, it is defined that:

- The monitoring network shall provide outputs compatible with those in other major international river basins in Europe.
- In the future the monitoring network will comply with standards used in the western part of Europe.
- The design shall split into immediate and longer term needs - starting with practical and routine functions already performed.

Finally the Environmental Programme for the Danube River Basin (EPDRB) is intended to substantially contribute to the implementation of the Danube River Protection Convention (DRPC). Therefore the TNMN objectives and definitions also comply with this intention, as these are oriented towards the relevant provisions of the DRPC (in particular Article 9, para (1), (2) and (4) DRPC). With this understanding the Yearbook for 1996 is intended to form the starting point for a continuous series of yearbooks compiled and published by the "International Commission for the Protection of the Danube River (ICPDR)".

In order to comply with these provisions, objectives and definitions, it was decided to split the design, implementation and operation of the network into two phases. The first phase is seen as a period with:

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

The second phase will build upon experience gained through operation of the first phase and the organisational structures formed for discussion, planning, management procedures (QA, AQC, etc.), training and applied research. Also the second phase shall revise the number of stations, the sampling frequencies, the determinands and the procedures for information exchange.

The history of the decisions taken, the agreements made and the organisational structures formed between the riparian countries leading to an operational TransNational Monitoring Network for the

Danube and its tributaries is briefly described in chapter 2 of this first yearbook. The design and the results obtained are described in the following chapters.

A consultant team produced the first design of the TNMN for the first phase based on inputs from 8 riparian countries. The design principles are briefly described in section 3.1. The implementation was agreed by the MLIM-Subgroup, but the design has been further simplified resulting in the monitoring, laboratory and information management aspects and designs described in sections 3.1 to 3.4. These designs now comprise the first phase starting with 1996 as a trial year. The future plans for evaluation and upgrading of the first phase are already now under preparation.

2. Development of the Institutional Framework supporting the TNMN

The first steps towards the TNMN were taken in Bucharest in December 1985 by the Governments of the Danube riparian countries who signed the Bucharest Declaration. The Declaration has 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 based on agreed methods in order to obtain comparable data was established. The monitoring network used according to the Bucharest Declaration consists of eleven cross sections of the Danube with 1 to 3 sampling locations. All cross sections are placed on the Danube itself where the river forms or crosses the border between the countries.

In 1991 the Danubian countries decided to take further actions in order to protect the environment of the Danube River Basin and started the preparation of the Danube River Protection Convention (DRPC), which was signed in Sofia in June 1994.

The Environmental Programme for the Danube River Basin (EPDRB) lead by a Task Force was also started in 1991; it was implemented to support and reinforce national actions for the restoration and protection of the Danube River , but also to supplement the future ICPDR's work with developed applications.

• Austria	• Romania	• EU-Commission	• Danube Environmental Forum
• Bulgaria	• Slovakia	• European Investment Bank	• Global Environment Facility
• Croatia	• Slovenia	• World Bank	• GEF Black Sea Programme
• Czech Republic	• Ukraine	• UN Development Programme	• Equipe Cousteau
• Germany	• The Netherlands	• UN Economic Comm. for Europe	• Barbara Gauntlett Foundation
• Hungary	• U.S.A.	• UN Environment Programme	• World Conservation Union
• Moldova	• European Bank for Reconstruction and Development	• Regional Environment Centre for Central and Eastern Europe	• World Wild Fund for Nature

Table 2.1: The Danube Task Force

The Task Force members are listed in table 2.1. The Task Force agreed on organisational structure to implement the EPDRB (figure 2.1). The Programme Co-ordination Unit (PCU), which has been based in Vienna since August 1994, was responsible for the daily co-ordination and monitoring of the Programme on behalf of the Task Force. The staff and further management costs of the PCU was and still are financed by the EU Phare programme and the Global Environment Facility. The Country Programme Coordinators (CPC) are nominated officials from each of the Danube countries and are responsible for the management of the Programme within their own country. The National Focal Points are nominated Danube institutes serving as technical and scientific back-up for the CPCs.

The Task Force agreed in 1992 a three-year (1992-95) Work Plan. Emphasis is laid on creating consensus, sharing information and promoting joint decision-making between the Danubian countries. Monitoring, Laboratories and Information Management (MLIM) has been a main Programme action since December 1992 when the MLIM Sub-Group dedicated to this topic met for the first time in Bucharest.

A main outcome of the three-year programme of work is 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. The Strategic Action Plan, once approved, marked the end of the first phase (1992-95) of the EPDRB, and in the next Phase II (1996-2000), implementation had to start. One of the major undertakings during 1996 was the initiation and approval by the Task Force of the Strategic Action Plan Implementation Programme (SIP), dedicated also to support the implementation of the Convention.

By that time the first stage of designing and development of TNMN, as it was planned in the EPDRB Work Plan, was almost finished and further activities for its second stage of development were identified by the MLIM Sub-Group and proposed for support by Phare.

The EU Phare Multi-Country Environmental Programme agreed to provide funding, in the framework of EPDRB, for the implementation of the demonstration projects identified in SIP, as well as continued funding for basin-wide activities, such as: the MLIM activities directed at TNMN development, the Accident Emergency Alarm System (AEWS) and EMIS Expert Group´s emission inventories and programmes preparation.

The 1996 and 1997 budgets of Phare Multi-Country Environmental Programme (MCEP) allocated substantial funding throughout out the EPDRB projects to support the further development of the monitoring and assessment programme (MLIM) and the start of operation of TNMN. The support for the completion of this stage of the TNMN is under way. Further funding for the integration of Bosnia and Herzegovina is planned.

Moldova and Ukraine are joining now in MLIM projects. The Tacis 1996 Cross-Border Environmental Cooperation allocated funds to support the MLIM activities in Moldova and Ukraine. The implementation of these projects will significantly strengthen the work of the MLIM Expert Group of the ICPDR.

The Technical Sub-Groups of the Task Force were responsible for dedicated technical tasks and had as members an appointed representative from each of the Danubian Countries. Two Sub-Groups have been active since 1992 - the Monitoring, Laboratory Management and Information Management (MLIM) Sub-Group and the Accident Emergency Warning System (AEWS) Sub-Group. The MLIM Sub-Group also had the responsibility for the TNMN. This was designed in 1993 during the first MLIM project lead by the WTV-Consortium, and in cooperation with the Working Groups of the MLIM-SG. These working groups address 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), and formed the core of a Danubian information management system on the status of in-stream (immissions) water quality (Information Management Working Group, IMWG).

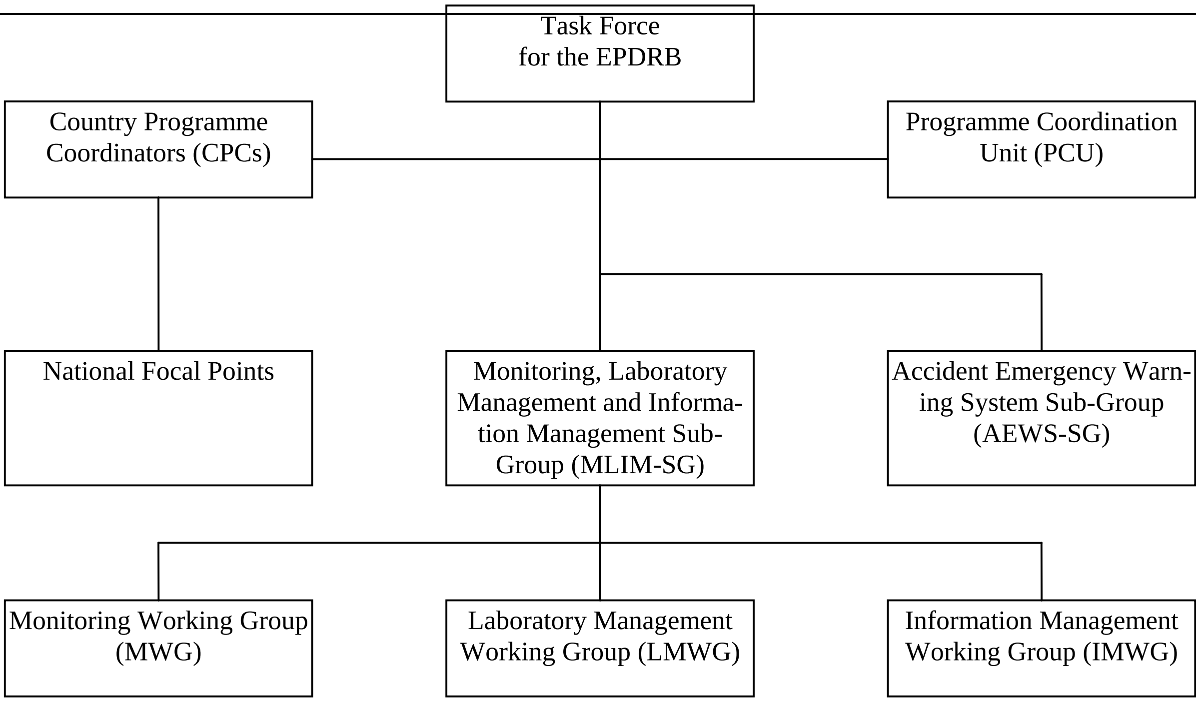


Figure 2.1: Organisational Structure of the Environmental Programme for the Danube River Basin (EPDRB) until 22 October 1998

The three Working Groups were chaired by members of the MLIM-SG, who are specialists in these topics, and the WG members are national experts from the Danube countries. The WGs have since 1994 - as one of their most important activities - worked with the implementation of the TNMN according to an implementation plan approved by the Task Force and the MLIM-SG. The arriving at the first TNMN Yearbook is a major milestone in this work.

In order to achieve this milestone the implementation plan included a major procurement programme and establishment of networks of National Reference Laboratories (NRL) and National Information Centres (NIC). Furthermore, the staffs of the NRLs, NICs and others who are doing the operational work of the TNMN have participated in training programmes on all the aspects of operating the TNMN.

At the same time as the Danube River Protection Convention was signed, the Signatories agreed in a Ministerial Declaration to establish the International Commission for the Protection of the Danube River (ICPDR) on an interim basis, allowing for implementation pending the Convention's entry into force. The Signatories agreed in this Ministerial Declaration also on a mandate in which i.a. the former Task Force of the EPDRB was invited to co-operate with the Interim ICPDR and its Secretariat and to contribute to the effective implementation of the DRPC.

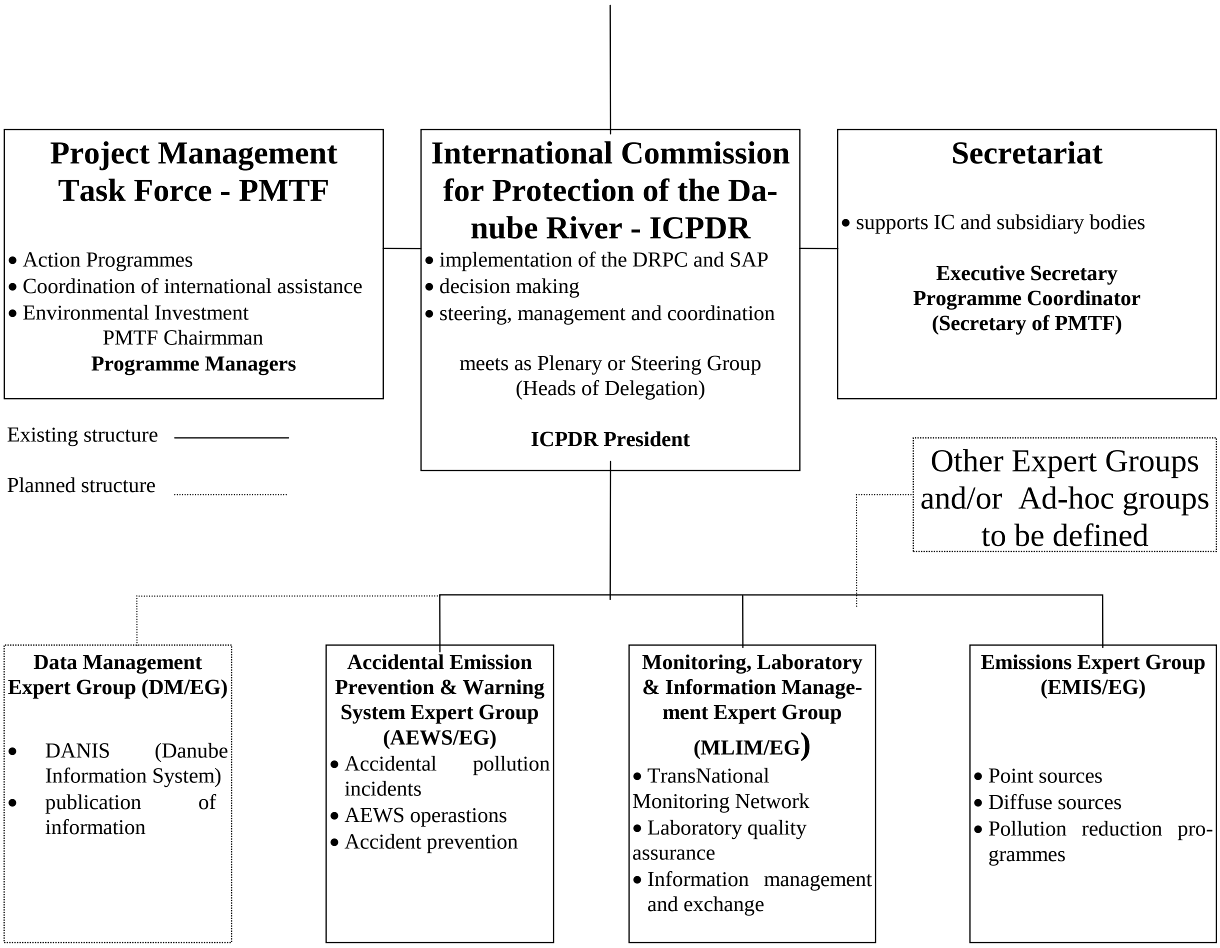


Figure 2.2: Organisational Structure of the International Commission for the Protection of the Danube River (ICPDR) according to the decisions of the ICPDR Plenary of 29 October 1998

The structural organisation of the International Commission for the Protection of the Danube River, with its supporting bodies and the special supporting body PMTF (Figure 2.2) allows for incorporation of the Technical Sub-Groups of the EPDRB as ICPDR Expert Groups in its structure. Preparatory steps have been taken during the interim implementation phase by the decision of the Interim ICPDR to avoid the duplication of activities, due to the transfer of tasks and responsibilities from the EPDRB to the ICPDR, pending the DRPC's entry into force.

The Programme Management Task Force (PMTF) is a special supporting body which assists the ICPDR in its work, especially regarding project identification and financing and technical assistance to promote the implementation of the DRPC through environmental investments. The transition of the tasks from the Task Force of the EPDRB formally took place during the first meeting of the PMTF on October 30, 1998. Thereafter the EPDRB Task Force ceded to exist.

Transition plans valid till 1998 concerning the transfer of tasks and responsibilities of the MLIM-SG and the AEWS-SG to the ICPDR Expert Groups were agreed by the EPDRB-Task Force and the ICPDR in March 1996. The plans distinguished between the initial development undertaken by the technical Sub-Groups under the EPDRB and the following operation by the Expert Groups (EG) under the ICPDR. The transfer is considered to be fully valid with the Convention's entry into force.

This inter alia applies to the TNMN and the MLIM/EG under the ICPDR. Since October 29th, 1998 the MLIM Expert Group - including its three Expert Sub-Groups are working on the basis of TORs agreed upon by the first ICPDR Plenary Meeting.

3. Description of the TNMN

One of the items in the Work Plan agreed by the Task Force in 1992 was "Water Quality Monitoring", which has over time developed into the TNMN. 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 MLIM-SG was set up in order to secure the implementation of the TNMN and to meet the needs of the Task Force Work Plan, and under the MLIM-SG three working groups were set up to:

- address the development of an international water quality monitoring network (MWG)
- introduce harmonised sampling procedures and enhance laboratory analysis capabilities (LMWG)
- form the core of an international data management system (IMWG)

3.1 Principles of the network design

As the new transboundary network should build on national surface water monitoring networks in the Danube basin and as the number of stations in these countries can be counted in thousands, it was decided to establish a simple procedure for selection of existing monitoring stations which could be the "candidates" for the new TransNational Monitoring Network - a procedure which also would respect the objectives as listed in chapter 1.

The criteria for selection of stations required these to be:

- 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

The information obtained from Romania, Ukraine, Bulgaria, Croatia, Slovenia, Hungary, Slovakia and the Czech Republic, which were the countries included in the first design round, included detailed description of nearly 200 monitoring stations on the Danube and its tributaries located according to the above criteria. Originally 44 of these were selected to be included in the TNMN. Further discussion lead to an increased number of 61 stations in Phase 1. The station list is shown in chapter 4.

The determinand list was based on the list from the Bucharest Declaration extended/reduced with determinands recommended according to EC-directives and the riparian countries own demands. The list was divided into 10 groups, each group given a sampling frequency according to the different locations mentioned above. Furthermore, it was specified how many sampling points (Left, Middle, Right) each station should include, and this together with allocation of determinand groups and sampling frequencies according to the location of each station gave a full definition of each of the stations.

However, the discussions in the Working Groups during the implementation phase showed the need for a more simple approach and somewhat reduced determinand lists. The result of this was that all stations were given the same minimum sampling frequency of 12 per year for determinands in water and 2 per year for biomonitoring and for determinands in sediment.

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), which are presented in more detail in section 3.2 and 3.3. However, it has been agreed that sediment samples would not be included in 1996, which is the first Phase 1 year of the TNMN. All results are reported and distributed quarterly via e-mail (originally on diskettes) in a common data exchange file format (DEFF) also including station information and methods of analysis used, as these still can differ from country to country. The structure and use of DEFF, which was also included in the first design and further developed during implementation, is described in more details in section 3.4.

3.2 Determinands

The resulting lists of determinands for water and sediments as agreed for TNMN Phase 1 are presented in table 3.1 and 3.2 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 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.
- Analytical accuracy targets for sediments are defined for <63 µm size fraction.

Sediments comprise suspended solids and bottom sediments.

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	-	-	-	-

Table 3.1: Determinand list for water for phase 1 of the 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%

Table 3.2: Determinand list for sediments for phase 1 of the TNMN

3.3 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 3.1 and 3.2), in order to enable laboratories to determine whether the analytical methods currently in use are acceptable.

It is 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 have been defined for each determinand:

- the lowest level likely to be encountered in the waters / sediments of interest (the minimum level of interest)
- the concentration which represents the likely level at which most monitoring (for example, for the assessment of trends or compliance with water quality standards) will be carried out (the principal level of interest)

These levels define the aims of the monitoring programme and can now 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 (This will assist in load calculations and will ensure that real data are reported for the majority of sampling sites)
- that the accuracy achieved at the principal level is not worse than ± 20% of the principal level. This assumption has been tested in a wide range of environmental monitoring laboratories. Experience suggests that it is usually appropriate to set a required limit of detection which is at least one tenth of the principal level of interest. A subsidiary aim is that the limit of detection should be at least one third of the minimum level of interest. It is obvious that the whole philosophy depends on the initial estimates of minimum and principal concentrations of interest. However, this approach to defining accuracy targets (or something closely similar) is the only logical strategy by which to establish the real analytical needs of a monitoring programme.

The above reflects that 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 has 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 have been provided with practical training for analytical instrumentation and on-site sampling as well as with theoretical aspects of AQC.

The practical and quality related approach has also resulted in the preparation of a Position Paper on sampling and analysis of sediment-associated pollutants dealing with:

- Guidelines on objectives of sediment associated pollutant monitoring
- Sampling and sample preparation guidelines
- Analysis of heavy metals
- Analysis of organic micropollutants
- Assessment and interpretation problems

and support to the problem of oil pollution analysis including

- organisation of the Workshop on Sampling and Analysis Methods for Oil Pollution Monitoring in the Aquatic Environment
- adoption/development of the UV and fluorescence method for analysis of petroleum hydrocarbons (oil products) in water and sediment
- organisation of special intercalibration exercises for oil analysis in the frame of QualcoDanube proficiency testing scheme.

3.3.1. *Performance testing in the Danubian laboratories*

The organisation of interlaboratory comparison in the Bucharest Declaration Danube monitoring was agreed in 1992. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered and took the responsibility for organising the first study under the name of QualcoDanube. The first distribution in 1993 included samples for the analysis of three determinands: pH, conductivity and total hardness. By the end of 1995, four more distributions had been made for the analysis of the following determinands: chlorides, COD, nutrients (ammonium, nitrate, Kjeldahl-nitrogen, orthophosphate and total-P) as well as different metals, including Fe, Mn, Ca, Mg, Cd, Cu, Hg, Pb, Ni, Zn. In 1996 the QualcoDanube proficiency testing scheme was extended to the National Reference Laboratories (NRL) in the TransNational Monitoring Network (TNMN) and the 1996/2 distribution already included all Danubian laboratories - 11 NRLs and 18 national laboratories - implementing the TNMN. This distribution was further extended to 6 Black Sea laboratories responsible for pollution monitoring in their area.

In addition to the QualcoDanube, another interlaboratory comparison, the AQUACHECK performance testing scheme, organized by WRc (UK), was conducted for the NRLs, mainly aiming at the analysis of specific micropollutants.

QualcoDanube distributions in 1996

In 1996 the distribution of the samples was slightly different from the previous distributions when only concentrates were distributed. These samples included real surface waters, spikes and also sediments in addition to the artificial concentrates.

The results and their evaluation during the four distributions have been published in the relevant report (QualcoDanube, AQC for Water Labs in the Danube River Basin. Summary of Results 1996, VITUKI Plc., Budapest). Major findings are summarised in the following:

In the QualcoDanube performance testing scheme the Youden-pair evaluation technique is usually followed. Exception was during the 1996/2 distribution in the case of the river sediment because of distribution of a single sample.

The interlaboratory comparative results are discussed separately for the different determinands. It was a success that 27 laboratories reported results out of the 29, and most of the laboratories reported results for ammonium-N, nitrate-N, orthophosphate-P and total-P, but 14 laboratories reported results for Kjeldahl-N. Heavy metals in the sediment were reported from 19 laboratories and only six laboratories reported for the optional Kjeldahl-N and total-P.

Nutrients in water samples

Ammonium-N: The results demonstrated relatively high variation during the first distribution among the NRLs. After a reasonable quality improvement among the laboratories during the second and third distribution there was more significant systematic errors in the analysis.

Nitrate-N: The results in Figure 3.4.1 are self explanatory showing the highest rate of quality improvement during the four distributions. It was unfortunate that one laboratory reported always extremely higher values, around 10-20 times more than the assigned value.

Kjeldahl-N: The results showed slight improvement by the fourth distribution, however, the reported values - usually with negative error - were scattered within the range of the plot. It is interesting to note that the performance on sample B were usually better than in sample A. In the case of this determinand about half of the laboratories reported the results.

Orthophosphate-P and Total-P: The results showed similar trends than in the case of ammonium-N.

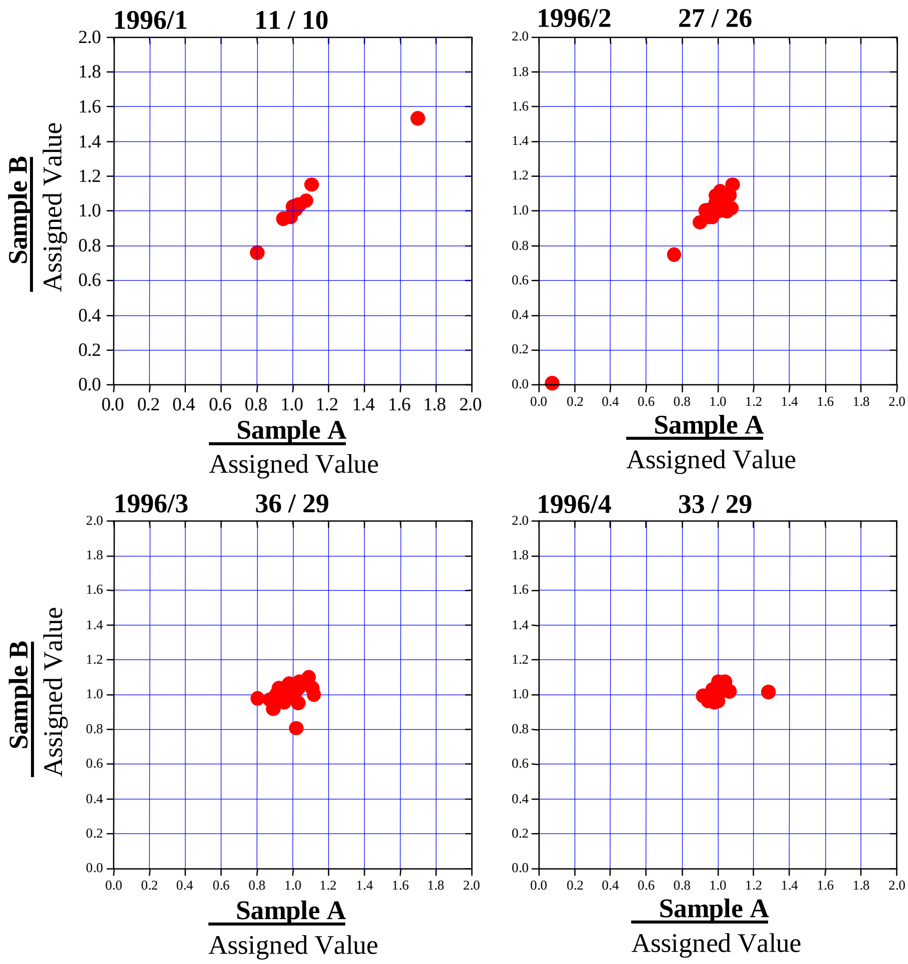


Figure 3.3.1: Variation in the reported and assigned values of Nitrate-N during the four distributions in 1996.
(On the top of the plots:
Distribution number and number of laboratories: reported results / plotted results)

Other parameters in water samples

During the 1996/1 distribution pH and conductivity was studied and the Youden-pair evaluation proved that the NRLs laboratories had no problems with these determinations.

During the 1996/3 distribution the most comprehensive exercise in 1996 was completed. In addition to the nutrients different organic characteristics, general parameters and heavy metals were evaluated.

- The chemical oxygen demand (COD) with permanganate and dichromate method showed characteristic variation. Systematic negative error occurred with the permanganate method, whereas in the case of the dichromate method the variation was significantly higher in sample B than in sample A. This could be explained with the lower concentration in sample B, and it was supported by the fact that this method is not reliable around and below 50 mg/l. The results demonstrated very high systematic error in the case of BOD determination. In that case, however, the higher variation was observed in the higher concentration sample.

- The anionactive surfactants measured as MBAS, calibrated for Na-lauryl-sulphate, showed significant systematic error among the laboratories. Because similar observation was made during the Hungarian performance testing of this determinand the most likely reason for the discrepancies is the calibration standard which may change activity during storage. It was planned for the future studies to provide laboratories with the calibration standard to ensure that the same substance would be used for the quantitative measurement.

- Among the major ions in the water, chloride, sulphate and total hardness was determined. Relatively high variation was observed in the low concentration of chloride most likely due to overtitration with the titrimetric method. Sulphate showed slight systematic error and total hardness showed significant discrepancies in both positive and negative direction.

- Among the heavy metals the variation was significant in the case of mercury, showing systematic errors. In the case of the other heavy metals, lead, cadmium, chromium and copper good agreement was observed with a few outliers. This was most likely due to the high concentrations for each metal.

Heavy metals - Hg, Cd, Cr, Cu, Pb and Zn - in sediment

In the case of the sediment sample, i.e., a real Danube sediment collected at Budapest, no assigned value was available and the results were statistically evaluated. 21 laboratories which reported results analysed Cd, Cu, Pb and Zn, 20 reported Cr and 15 reported Hg. The results showed that the best performance was in the case of Pb and Zn, and the performance decreased to Cu, Cr, Cd and Hg.

Conclusions

The four QualcoDanube distributions in 1996 provided information on the performance of the participating water laboratories in the Danube river basin. The overall output of the results is the demonstration of the comparability of the analytical data on the studied determinands as well as the possible methodological problems during the analysis.

Since the start of the QualcoDanube AQC programme nutrients were included in several distributions and therefore it is possible to assess the quality improvement in the analytical work by comparing the performance during the different distributions. The results in 1996 showed the quality improvement in most of the determinands. Although the number of laboratories during the first distributions was almost one third of the other distributions the performance significantly improved during the study period, particularly in the case of Nitrate-N. Variation in the Orthophosphate-P and the Total-P was significant, therefore significant improvement is needed before the monitoring data of these determinands could be considered reliable in the entire Danube basin. The results of the heavy metal analysis are promising because with very few exceptions they were within an acceptable range.

It was expected that the performance of the Danube basin laboratories as well as of the additional laboratories from the Black Sea region would further improve which would ensure the comparability of the water quality monitoring results in the river basin and related regions.

3.4 Information Management

In the frame of Information Management is dealt with data storage, data analysis and data exchange. On the basis of a relational data base water quality data of TNMN is organised in a well-defined structure using rules of reference integrity. This results in a system of joined tables, covering information about TNMN. For data analysis values can be exported to various statistical software packages e.g. AARDVARK. Data exchange is organised quarterly according to a standard operational procedure. A special data exchange file format (DEFF) serves for this purpose.

The above summary briefly describes the current activities, which have been established by using the following approach:

- to concentrate on the quality of data obtained
- to introduce a process of exchanging data from the national information systems to a Central Information Point (CIP)
- to build on the existing experience in the individual countries and not to try to force all participating countries to adapt their national information system and procedures
- to promote and increase the use and processing of data into information by introducing dedicated software for time series analysis (AARDVARK)

It was resulting in the important decision of leaving the responsibility of the national information systems to the countries themselves and to concentrate on an agreed protocol and data exchange format (DEFF), which all countries after a training course in 1996 can 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 anticipate future changes and therefore the data of interest had to be normalised. This resulted in nine tables of which seven are filled with static data and two with dynamic data. The tables with static data are agreed by the MLIM-SG and contain the stations, determinands, analytical methods, remarks, participating countries and sampling methods. These tables are maintained by the CIP on the basis of the agreements in the MLIM-SG. The tables with dynamic data contain the samples and analytical results. These tables are also maintained at CIP level by merging data received from all countries on a three monthly basis.

The standard operational procedure (SOP) for the exchange of DEFF data starts at the data generation (sampling and analysis) and input of data to the system followed by a description of all the activities carried out by the 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 information processing (e.g. the Yearbook).

4. Tables of statistical data from the TNMN stations

The determinands measured in 1996, which is the first year of operating the TNMN - Phase 1, cover the main physical, chemical and biological water quality characteristics including the major anions and cations, nutrients, oxygen regime determinands, organic pollutants, heavy metals and characteristic biological and bacteriological determinands.

Sampling and analyses have - if possible - been performed according to the specifications in section 3.1 and 3.2. However, the number of determinands measured at the different stations as well as the frequencies have not been uniform - at some stations no measurements were performed at all due to the lack of proper equipment or restricted access for political reasons. Furthermore, relatively few data were available for organic micropollutants.

The 61 stations included in the TNMN - Phase 1 are characterised on the following station list and station map. In the station list official national data are specified, which are not harmonized in all cases. Inconsistencies concerning catchment area and altitude may be due to different national calculation procedures. It is recommended to solve this problems within the transboundary commissions.

Each station can have up to 3 sampling points named L, M and R (Left, Middle, Right). Counted by sampling points the TNMN - Phase 1 consists of 95 sampling points.

In 1996 data are available from 50 stations including in total 75 sampling points. Lack of availability of data for some stations was for example in Croatia and Bosnia and Herzegovina due to the fact that sampling was not possible because of the war.
Data available from the 75 sampling points mentioned above are presented in 75 tables (Annex 1) according to the following legend. Tables for those stations where no data were available are excluded from this yearbook.

Term used	**Explanation**
Determinand	The name of the determinand measured according to the agreed method
Unit	The unit of the determinand measured
N	The number of measurements
Min	The minimum value of the measurements done in the year 1996
Mean	The arithmetical mean of the measurements done in the year 1996
Max	The maximum value of the measurements done in the year 1996
C50	The 50 percentile of the measurements done in the year 1996
C90	The 90 percentile of the measurements done in the year 1996
Q1	The arithmetical mean of the measurements done in the first quarter of the year 1996
Q2	The arithmetical mean of the measurements done in the second quarter of the year 1996
Q3	The arithmetical mean of the measurements done in the third quarter of the year 1996
Q4	The arithmetical mean of the measurements done in the fourth quarter of the year 1996

If values less than the detection limit are present in the dataset for a given determinand, the calculations use half of the value of the detection limit. In case of all measurements in the year being below the detection limit, only minimum, mean and maximum were put in the table without any other statistical data.

Station List:

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance Km	Altitude m	Catch-ment Sqr.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 13	16 59 29	79	150	9883	L2100	M
CZ02	/Morava/Dyje	Breclav	48 15 57	16 53 19	17	155	12352	L2120	L
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	Dravaszabolcs	45 46 57	18 12 8	68	87	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	200	15356	L1390	L
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	133	10878	L1330	R
HR01	Danube	Batina	45 51 53	18 51 37	1424	83	210250	L1315	R
HR02	Danube	Borovo	45 23 0	18 58 8	1337	79	243147	L1320	LMR
HR03	/Drava	Varzdin	46 19 24	16 21 28	288	167	15616	L1290	M
HR04	/Drava	Botovo	46 14 31	16 56 36	226	123	31038	L1240	M
HR05	/Drava	D.Miholjac	45 47 0	18 12 19	78	89	37142	L1250	R
HR06	/Sava	Jesenice	45 51 41	15 41 47	729	132	10834	L1220	R
HR07	/Sava	us. Una Jasenovac	45 16 9	16 42 42	525	89	29585	L1150	L
HR08	/Sava	ds. Zupanja	45 3 49	18 42 42	254	79	62890	L1060	R
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
RO01	Danube	Bazias	44 48 5	21 23 46	1071	58	570896	L0020	LMR
RO02	Danube	Pristol/Novo Selo Harbour	44 11 25	22 45 20	834	31	580100	L0090	LMR
RO03	Danube	us. Arges	44 4 25	26 36 35	432	16	676150	L0240	LMR
RO04	Danube	Chiciu/Silistra	44 7 47	27 15 59	375	13	698600	L0280	LMR
RO05	Danube	Reni-Chilia/Kilia arm	45 28 50	28 13 34	132	4	805700	L0430	LMR
RO06	Danube	Vilkova-Chilia arm/Kilia arm	45 24 42	29 36 31	18	1	817000	L0450	LMR
RO07	Danube	Sulina - Sulina arm	45 9 41	29 40 25	0	1	817000	L0480	LMR
RO08	Danube	Sf.Gheorghe-Ghorghe arm	44 53 10	29 37 5	0	1	817000	L0490	LMR
RO09	/Arges	Conf. Danube	44 4 35	26 37 4	0	14	12550	L0250	M
RO10	/Siret	Conf. Danube Sendreni	45 24 10	28 1 32	0	4	42890	L0380	M
RO11	/Prut	Conf.Danube Giurgiulesti	45 28 10	28 12 36	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	44 11 25	22 45 20	834	27	580100	L0730	LMR
BG02	Danube	us. Iskar - Bajkal	43 45	24 20	641	20	608820	L0780	M
BG03	Danube	Downstream Svishtov	43 36	25 23	554	16	650340	L0810	MR
BG04	Danube	us. Russe	43 48	25 59	496	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	44 7 47	27 15 59	375	7	698600	L0850	LMR
BG06	/Iskar	Orechovitza	43 35 20	24 41 40	28	31	8370	L0930	M
BG07	/Jantra	Karantzi	43 35	25 44	12	32	6860	L0990	M
BG08	/Russ.Lom	Basarbovo	43 46 30	25 57 10	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

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

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

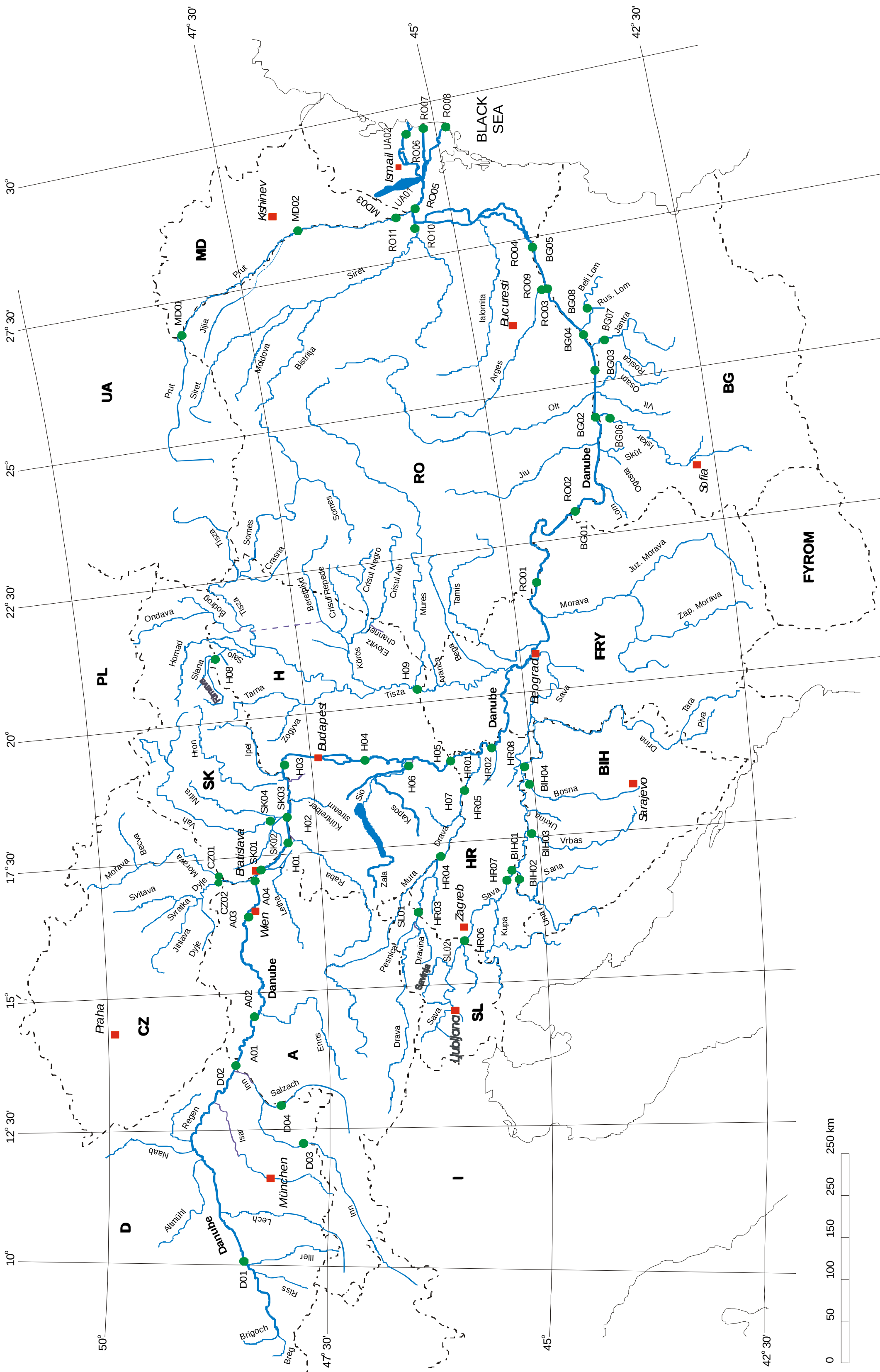


Figure 4.1: The Danube Stationmap TNMN-Phase 1

As already mentioned above this yearbook contains the results of the first trial year of the TNMN. Interpretation can only be done by looking at the data very carefully.

It has to be emphasized that natural characteristics (e.g. flow regime, flow velocity, substrate composition, mean water temperature, natural state of saprobity and trophy, etc.) change from the source to the mouth of the Danube. This is the reason why it is useful to take into account the specific characteristics of the upper part and the lower part of the Danube as being crucial for the interpretation of data in principle. It also has to be mentioned that effect of the Iron Gate-reservoirs on the water quality of the Danube is not fully clarified at all.

Validity and full comparability of data is also a prerequisite for data interpretation which is not yet reached in all cases. On the one hand this was due to the fact that the agreed sampling frequency for physico-chemical determinands of at least 12 times per year was not kept at all monitoring sites. This is very essential especially for those determinands which vary seasonally or are highly correlated to the discharge. On the other hand results from QualcoDanube and AQUACHECK have shown that a number of determinands are considered to be problems (especially Kjeldahl-N, BOD_5, trace organics), and that there is still a need for improving the quality of data and comparability although considerable progress was already made.

Concerning the organic pollution and the oxygen regime the determinand „biological oxygen demand within 5 days“ (BOD_5) is one of the major indicators. But as already pointed out above some analytical problems which have still to be solved for this determinand to ensure comparability. It also has to be mentioned that BOD_5 can be decreased by toxic effects. Therefore interpretation of results may be misleading as the occurring of toxic effects can not be ruled out.

In addition to BOD_5 biological determinands like the saprobic index of the macroinvertebrate community could be very helpful for assessing the organic pollution. As there are only few results for the trial year of 1996 efforts have to be made to ensure the proper application of this biological determinand in the future.

Interpreting the nutrient status of the Danube it has to be taken into account, that for phosphorus it is crucial to clarify the share of the bioavailable fraction and the role of the Iron Gate-reservoir.
Nitrogen is also blamed to be essential causing eutrophication effects in the Danube delta and the Black Sea. Up to now figures can only be given for the inorganic nitrogen as $(NH_4 + NO_3)$-N but – due to analytical problems – not for the concentration of total nitrogen as the organic fraction is not measured routinely and the share of organic nitrogen seems to be increasing considerably along the Danube on its way to the Black Sea.

The statistical results presented in the tables in Annex 1 indicate that in general the ranges of the measured determinands were larger in the tributaries than in the Danube itself. The highest pollutant levels (see maximum and C90) were typical for some tributaries. Seasonal variation of some determinands were also typical: e.g. high NH_4-N concentrations were dominant in the first quarter of the year when the water temperature was at its minimum.

5. Maps of selected determinands

The organic pollution and the concentrations of selected nutrient-fractions in the Danube River Basin based on the available data from 1996 from the TNMN - Phase 1 are presented on the following three maps. The maps show the average concentration of BOD_5 , ortho-Phosphate-Phosphorus (PO_4^{3-}-P) and (NH_4^++ NO_3^-)-N respectively.

If there were data of three sampling sites (left, middle, right) of a monitoring station only the data of the "middle" is presented in the following maps.

Table 5.1: Preliminary set of surface water quality standards for the Danube riparian countries (Water Quality Targets and Objectives for Surface Waters in the Danube Basin – Project EU/AR/203/90; Final Report (1997)

Determinand	**Unit**	**Quality class**				
		I Blue	**II green**	**III yellow**	**IV red**	**V black**
Biological oxygen demand (BOD_5)	mg/l	<3	5	9	15	>15
Ortho-Phosphate-Phosphorus (PO_4^{3-}-P)	mg/l	0.05	0.1	0.2	0.5	>0.5
Nitrate-Nitrogen (NO_3^--N)	mg/l	1	5	10	25	>25

The colour coding 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). Although this classification is not yet agreed it was decided to use the proposed classification for BOD_5 and PO_4^{3-}-P only for the presentation in this yearbook. As there was no classification proposed for inorganic nitrogen as (NH_4^+ + NO_3^-)-N, it was agreed that the classification should be done according to the WQTO-proposal for NO_3^--N (see Table 5.1).

Table 5.2: TNMN 1996 - average concentrations of BOD_5: distribution of monitoring sites according to the classification listed in table 5.1.

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	21	*78*	9	*39*	30	*60*
II	6	*22*	8	*35*	14	*28*
III	0	*0*	4	*17*	4	*8*
IV	0	*0*	1	*4*	1	*2*
V	0	*0*	1	*4*	1	*2*

BOD_5 is a commonly used indicator for organic pollution, which effects the oxygen regime in water. Nevertheless the interpretation of results has some difficulties concerning possible toxic effects as already pointed out in chapter 3.3.1. Intercalibration tests within the Danubian laboratories have proved that comparability and quality of data is still not really satisfactory.

Considering all TNMN monitoring sites the BOD_5 average concentrations varied from 1.5 up 28.0 mg/l. The results presented in Figure 5.1 show that at most of the monitored sites (60%) the average concentrations measured are below 3 mg/l (class I). All monitoring sites along the Danube are within the ranges of class I and II respectively. More highly polluted sites could only be found in the tributaries (see also table 5.2).

Nutrients are very important as they are responsible for eutrophication in lakes, rivers and the receiving sea. The concentrations of PO_4^{3-}-P and Inorganic Nitrogen as $(NH_4^+ + NO_3^-)$-N were selected from the different nutrient fractions, which are analysed within the TNMN-programme, to be presented in the following maps and graphs.

Table 5.3: TNMN 1996 - average concentrations of PO_4^{3-}-P: distribution of monitoring sites according to the classification listed in table 5.1.

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	9	*33*	6	*26*	15	*30*
II	15	*56*	6	*26*	21	*42*
III	0	*0*	3	*13*	3	*6*
IV	2	*7*	6	*26*	8	*16*
V	1	*4*	2	9	3	*6*

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.

Average concentrations of PO_4^{3-}-P varied from 0.009 up to 1.068 mg/l. Considering all monitoring sites again most of them (72%) show concentrations within the range of class I and II. As for the tributaries at 35% of the monitoring sites the average concentration for PO_4^{3-}-P is above 0.2 mg/l indicating higher nutrient levels than in the river Danube (see also table 5.3).

Table 5.4: TNMN 1996 - average concentrations of $(NH_4^+ + NO_3^-)$-N: distribution of monitoring sites according to the classification listed in table 5.1.

Water	**Monitoring sites**	**Monitoring sites**	**Monitoring sites**

Quality class	(Danube)		(tributaries)		(Danube + tributaries)	
	number within class	**%** *of total*	**number** within class	**%** *of total*	**number** within class	**%** *of total*
I	0	*0*	2	*10*	2	*4*
II	25	*100*	16	*80*	41	*91*
III	0	*0*	2	*10*	2	*4*
IV	0	*0*	0	*0*	0	0
V	0	*0*	0	*0*	0	0

In Figure 5.3 the average concentrations of (NH_4^+ + NO_3^-)-N are presented which varied from 0.73 up to 5.81 mg/l. At most of the monitoring sites (91 %) the average concentrations measured in 1996 indicate class II. All monitoring sites in the Danube were within the range of water quality class II (see table 5.4)

The inorganic nitrogen can not be equated with the total amount of nitrogen in the river, because the total nitrogen also includes the organic fraction. Unfortunately the organic nitrogen was analysed only in very few stations, but the results seem to indicate that the organic nitrogen may play a more important role in the lower parts of the Danube than in the upper parts.

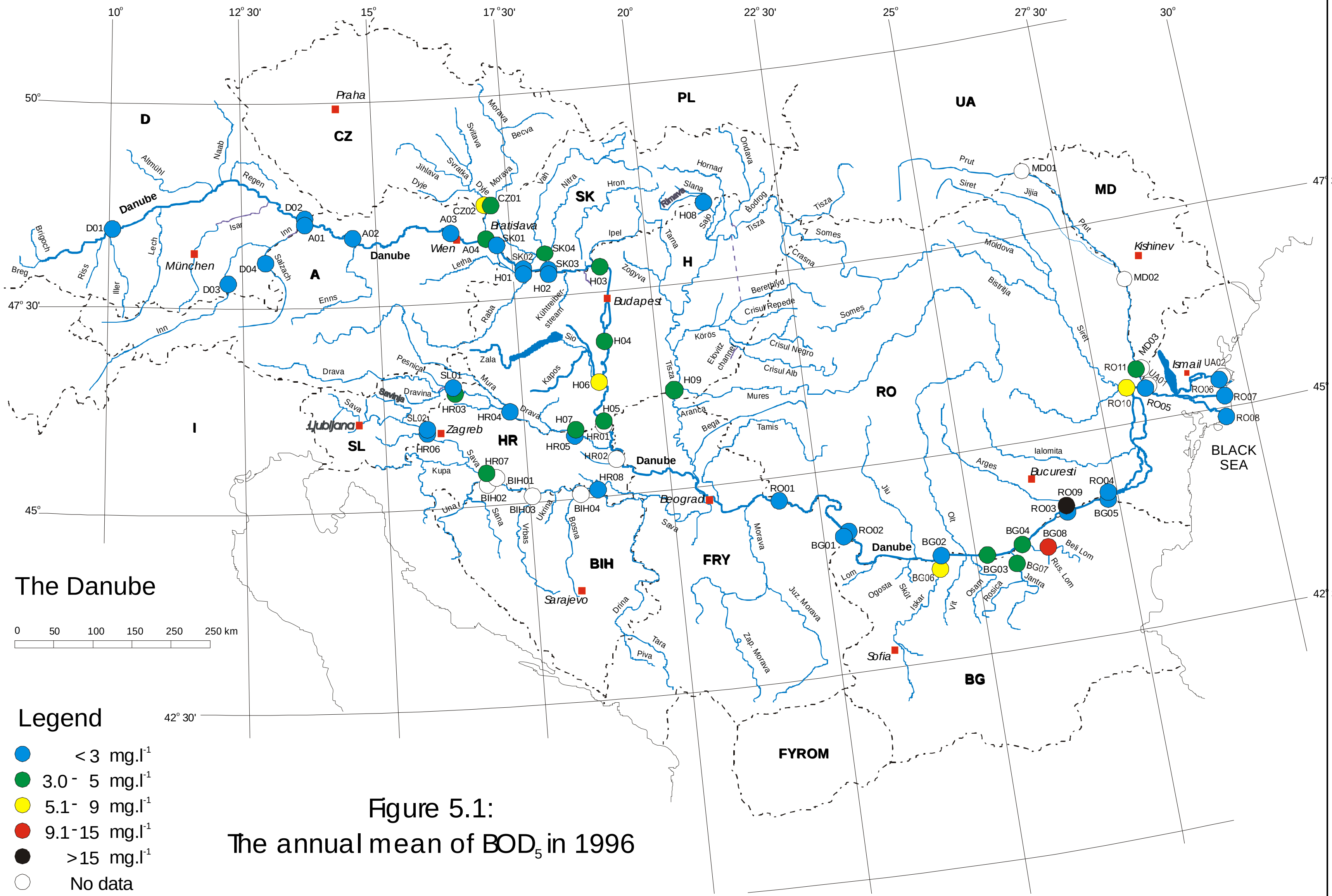


Figure 5.1:
The annual mean of BOD_5 in 1996

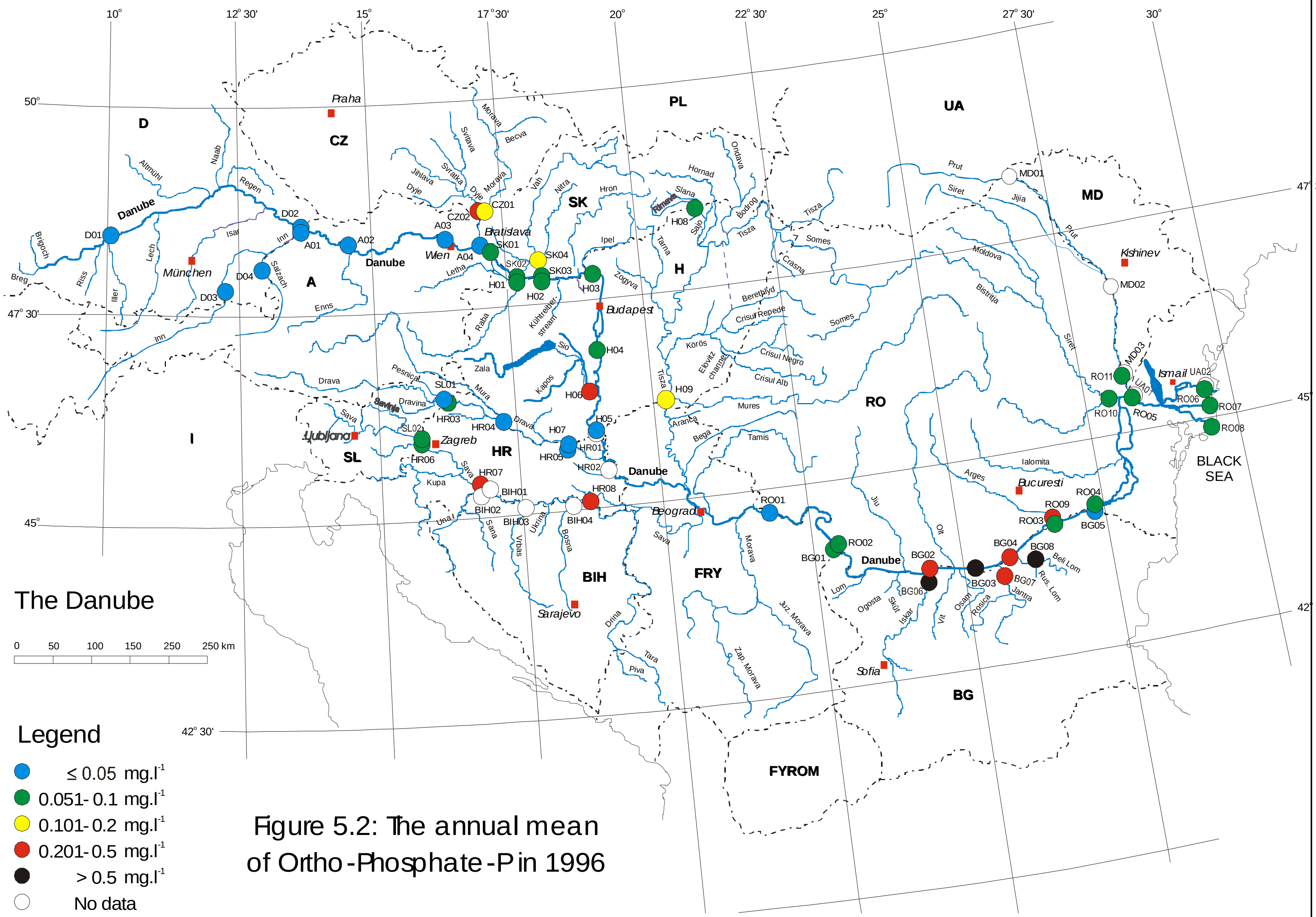


Figure 5.2: The annual mean of Ortho-Phosphate-P in 1996

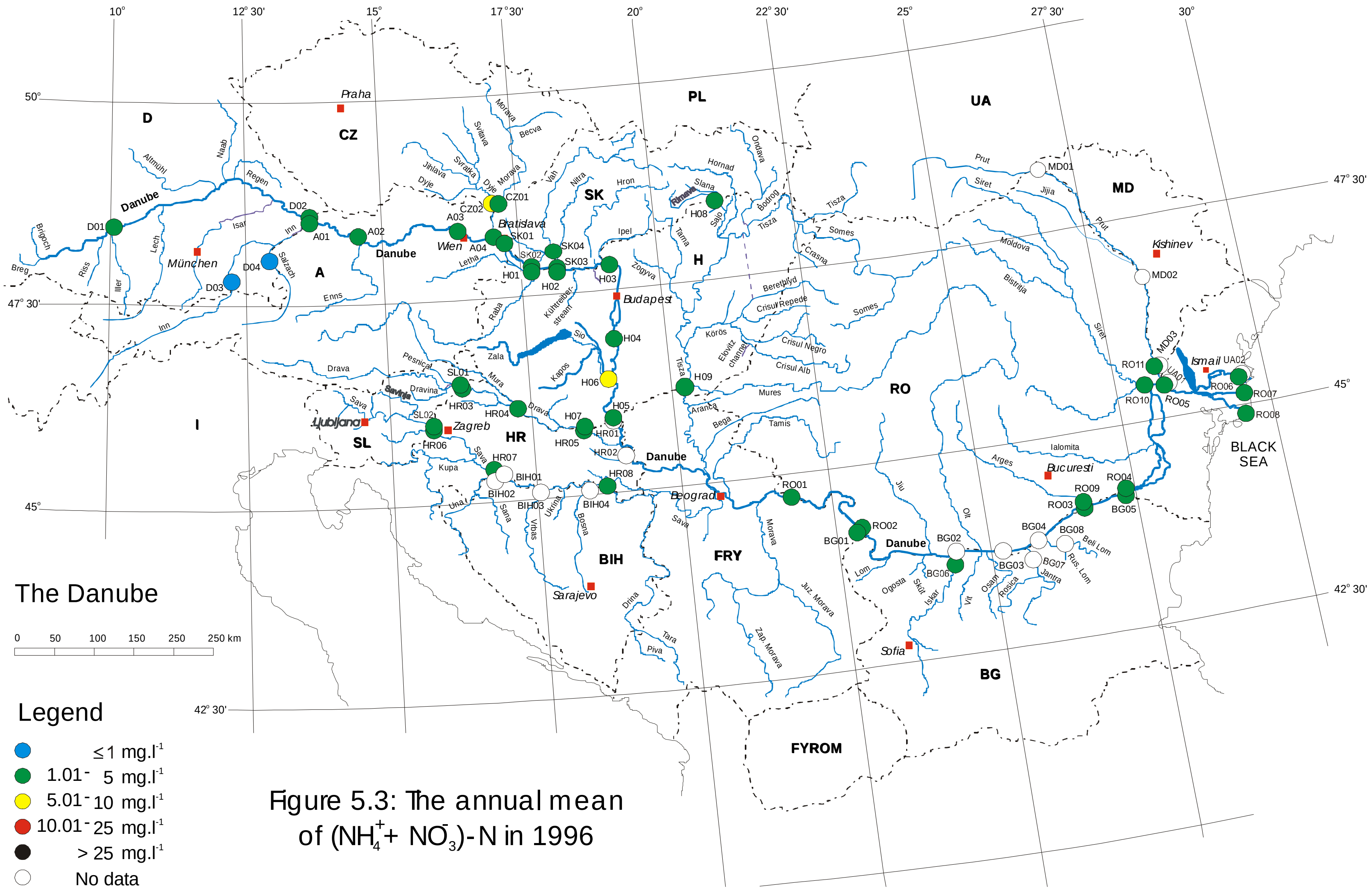


Figure 5.3: The annual mean of $(NH_4^+ + NO_3^-)$-N in 1996

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

Each of the profiles consists of two plots. The upper plot shows bars indicating the average, maximum and minimum concentrations in the Danube at the respective distance from the mouth (km). By green colour minimum values and by red colour maximum values are indicated on the plots. Stations close to each other or those which are monitored by two countries (transboundary stations) are 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.

If there are three sampling sites (left, middle, right) of a monitoring station only the data of the "middle" is presented in the following profiles.

As general comments concerning the interpretation of determinands and data are already made in chapter 4 and chapter 5 only some remarks should be given explaining the results presented in the following graphs. However some further remarks are considered worthy at this point as follows:

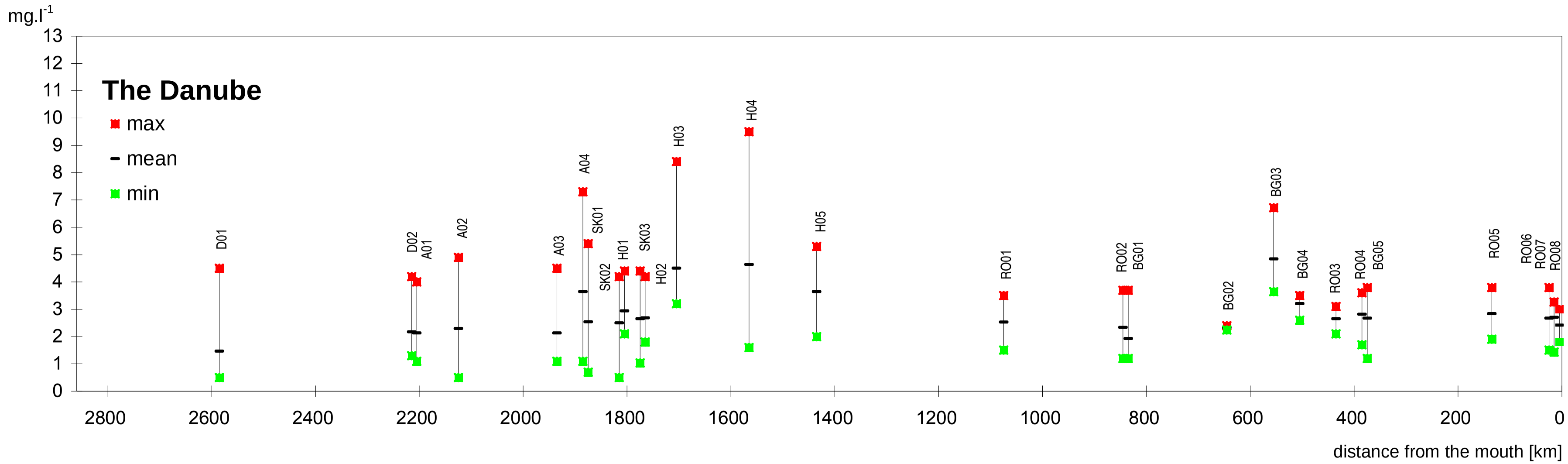
The BOD_5 concentrations characterising the content of the oxygen demanding biodegradable substances varied in the Danube between 0.5 mg/l and 9.5 mg/l, in the primary tributaries between 0.5 and 62.5 mg/l. In the Danube high values could be found downstream of polluted tributaries and downstream of hot spots.

The values of $(NH_4^+ + NO_3^-)$-N were between 0.65 and 5.61 mg/l in the Danube and between 0.43 and 17.06 mg/l in the primary tributaries.

For PO_4^{3-}-P minimum concentrations of 0.002 mg/l and maximum concentrations of 1.260 mg/l could be observed in the Danube while in the primary tributaries the variation was even higher from 0.007 to 2.000 mg/l.

Differences in results of some transboundary stations in the Danube, which are monitored by both neighbouring countries, are maybe due to differences in sampling time and sampling frequencies. Problems of larger differences may be solved by improving the sampling procedures or by improving the analytical performance.

Figure 6.1: The minimum, mean and maximum of BOD_5 in 1996



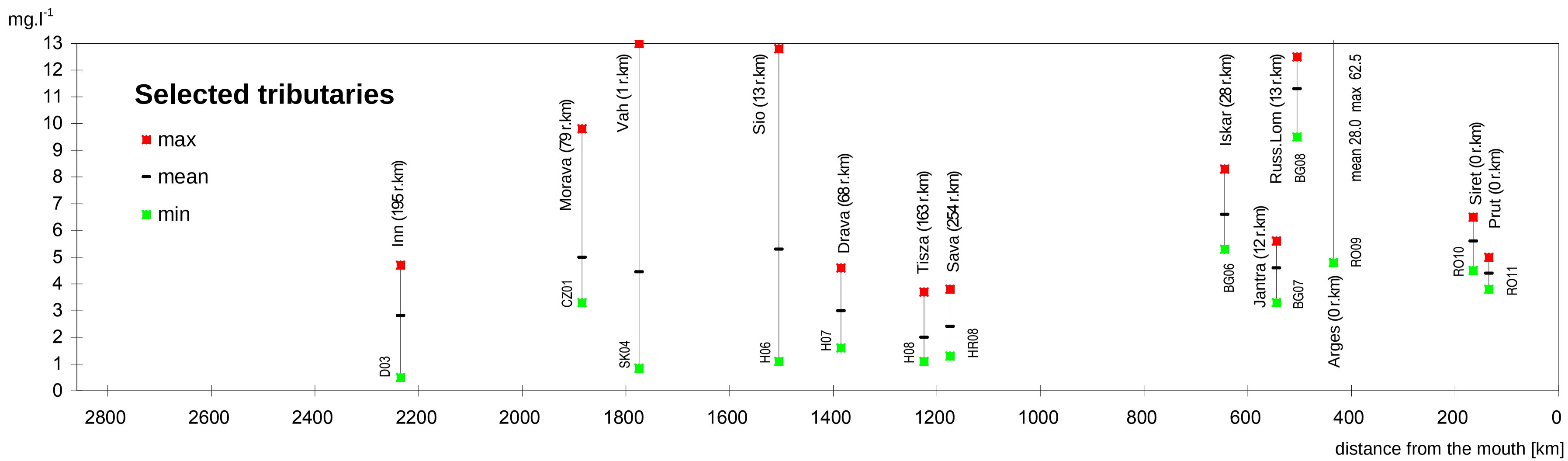


Figure 6.2: The minimum, mean and maximum of Ortho-Phosphate-P in 1996

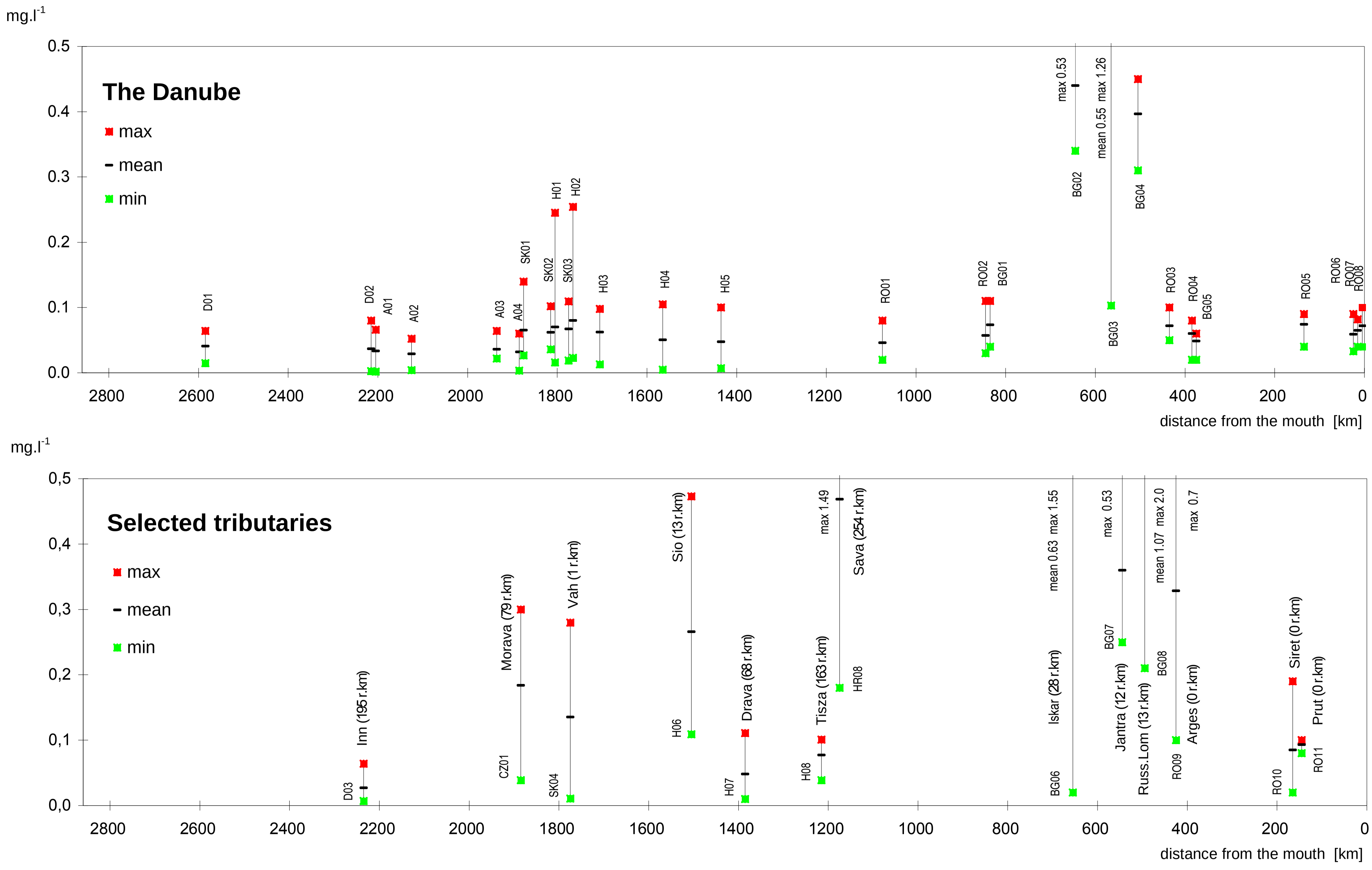
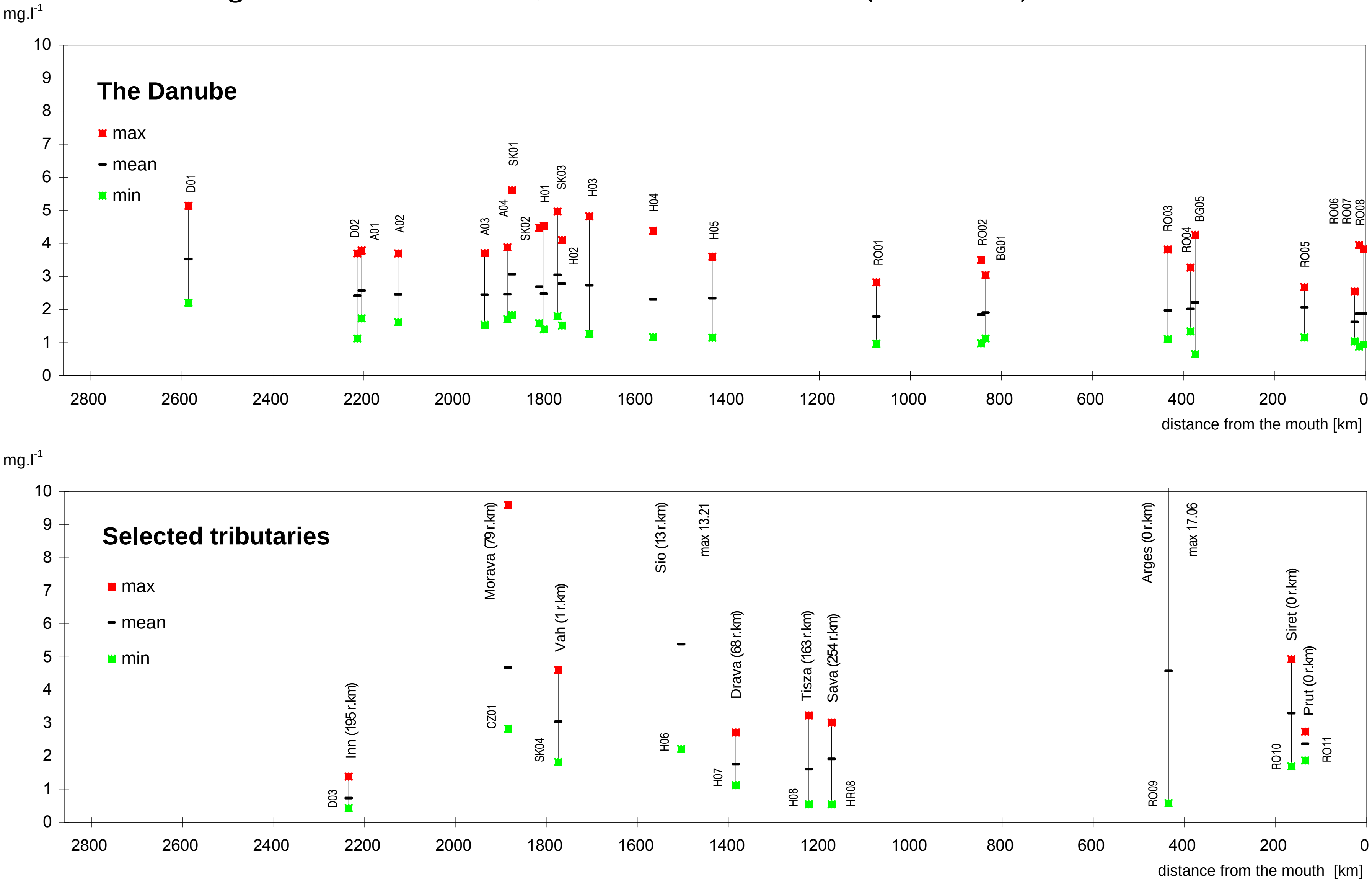


Figure 6.3: The minimum, mean and maximum of $(NH_4^{+}+NO_3^{-})$-N in 1996



7. Abbreviations

Abbreviation	Explanation
AEWS/EG	Accidental and Emergency Warning System/Expert Group
AEWS-SG	Accidental and Emergency Warning System/Sub-Group
AQC	Analytical Quality Control
ARP	Applied Research Programme
AWQAS	Automatic Water Quality Alarm Station
AWQM	Automatic Water Quality Monitoring
BD	Bucharest Declaration
CIP	Central Information Point (for information management)
CPC	Country Programme Coordinator
DBMS	Data Base Management System
DEFF	Data Exchange File Format
DEMDESS	Danube Emissions Management Decision Support System
DM/EG	Data Management Expert Group (establishment not agreed upon)
DRPC	Danube River Protection Convention
EBRD	European Bank for Reconstruction and Development
EIB	European Investment Bank
EMIS/EG	Emissions Expert Group
EPDRB	Environmental Programme for the Danube River Basin
EQS	Environmental Quality Standards
ESN	European Service Network (Travel arrangements, etc.)
GEF	Global Environment Facility
GIS	Geographical Information System
ICPDR	International Commission for the Protection of the Danube River
IM/ESG	Information Management Expert Sub-Group
IMWG	Information Management Working Group
INFODANUBE	An Ecological Information System for the Danube River Basin
LM/ESG	Laboratory Management Expert Sub-Group
LMWG	Laboratory Management Working Group
LOD	Limit of Detection
M/ESG	Monitoring Expert Sub-Group
MLIM/EG	Monitoring, Laboratory and Information Management Expert Group
MLIM-SG	Monitoring, Laboratory and Information Management Sub-Group
MWG	Monitoring Working Group
NGO	Non-Governmental Organisation
NIC	National Information Centre
NRL	National Reference Laboratory
PCU	Programme Coordination Unit
PEC	Phare Environmental Consortium (Lead Partner: Carl Bro AS)
PIAC	Principal International Alert Center
PMTF	Programme Management Task Force
RDBMS	Relational Data Base Management System
SAP	Strategic Action Plan
SIP	Strategic Action Plan Implementation Programme
SOP	Standard Operational Procedure
TNMN	Trans National Monitoring Network
TOR	Terms of Reference
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
WB	World Bank
WTV	Consortium that carried out the first MLIM-study (WRc, TNO, VKI/DHI)