

# WATER QUALITY

## in the Danube River Basin 1998 TNMN-Yearbook



### Information

ICPDR – International Commission for the Protection  
of the Danube River / Permanent Secretariat  
Vienna International Centre, D0412  
P. O. Box 500, 1400 Vienna / Austria  
Tel: 0043-1-260 60-5738, Fax: 0043-1-260 60-5895  
e-mail: [icpdr@unvienna.org](mailto:icpdr@unvienna.org), [www.icpdr.org](http://www.icpdr.org)

## **Imprint**

**Owner:** ICPDR– International Commission for the Protection of the Danube River / Permanent Secretariat, **Design and Production:** p:matter Vienna, e-mail: h\_warmuth@yahoo.com; **Photos:** Warmuth/Krobath; **Editing/Proofreading:** Parole Language Services, Croatia; **Print:** Print Tech Ltd., Hungary

# 1. Introduction



In June 1994, the Convention on Cooperation for the Protection and Sustainable Use of the Danube River (The Danube River Protection Convention) was signed in Sofia and it came into force in October 1998. Its main objectives are to achieve sustainable and equitable water management including the conservation, improvement and 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 quality conditions of the Danube River and the progress achieved through the measures taken in order to prevent, control and reduce the transboundary impacts.

The operation of the Trans-National 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 third 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 1998.

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 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.

# Contents

1. INTRODUCTION	3
2. HISTORY OF TNMN	5
3. OBJECTIVES OF TNMN	7
4. DESCRIPTION OF TNMN	8
4.1 PRINCIPLES OF NETWORK DESIGN	8
4.2 DETERMINANDS	9
4.3 ANALYTICAL QUALITY CONTROL (AQC)	11
4.3.1. Performance Testing in the Danube Laboratories	13
4.4 INFORMATION MANAGEMENT	18
5. TABLES OF STATISTICAL DATA FROM TNMN STATIONS	20
6. MAPS OF SELECTED DETERMINANDS	26
7. PROFILES OF SELECTED DETERMINANDS	35
8. ABBREVIATIONS	40
9. ANNEX 1	41

## 2. History of TNMN



In spite of the fact that TNMN has been in operation only since 1996, the first steps towards creating the Network had been taken many years earlier. In December 1985, the Governments of the Danube countries signed the Bucharest Declaration. One of the objectives of the Declaration was to ensure that the development of the Danube water quality 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 one to three sampling locations. All cross sections were placed along 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 was also launched in 1991. It was designed to support and reinforce national efforts geared towards the restoration and protection of the Danube River and to supplement the future work of the 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 reaching a consensus, sharing information and promoting joint decision making between the Danube 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) charged with these responsibilities 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 Danube countries in December 1994. The Strategic Action Plan, once approved, marked the end of the first phase (Phase I - 1992-95) of 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 the Phare Multi-Country Environmental Programme (MCEP) allocated substantial funds to all EPDRB projects to support further development of the monitoring and assessment programme as well as the launching of TNMN into operation.

## 2. History of TNMN

*The responsibility for TNMN was assigned to MLIM/SG. The three Working Groups set up under MLIM/SG did the following:*

- they addressed the development of the Danube water quality monitoring network (Monitoring Working Group, MWG)
- they introduced harmonised sampling procedures and enhanced laboratory analysis capabilities (Laboratory Management Working Group, LMWG)
- they formed the core of the Danube information management system on the status of in-stream (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 pending the Convention's entry into force. EPDRB Task Force was invited to cooperate with the Interim ICPDR and its Secretariat to contribute to a successful implementation of DRPC.

As a Technical Sub-Group of EPDRB, MLIM/SG 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 at the first ICPDR Plenary Session.

### 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 by the Bucharest Declaration;
- be capable of supporting a reliable and consistent trend analysis of the concentrations and loads of 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 the future comply with the standards used in the western part of Europe;
- the design shall split into immediate and longer-term needs - starting with the practical and routine functions already performed.

*The design, implementation and operation of the network were divided in two phases. The first phase was 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 list 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 during 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 project "Monitoring, Laboratory Analysis and Information Management for the Danube River Basin" conducted by 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 are now under preparation.

### 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 could qualify for the new Trans-National Monitoring Network - a procedure which would also comply with the objectives listed in Chapter 3.

In order to qualify under the selection criteria, it was agreed that the station had to meet at least one of the following criteria:

- be located just upstream/downstream of an international border;
- be located upstream of the 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 Romania, Ukraine, Bulgaria, Croatia, Slovenia, Hungary, Slovakia and the Czech Republic - countries included in the first design round - included a detailed description of nearly 200 monitoring stations along the Danube and its tributaries located in a way that meets the above criteria. 44 of these were originally selected to be included in TNMN. Following further discussion, the number of stations was increased to 61 in Phase 1. The station list is shown in Chapter 5.

The determinand list was based on the list from the Bucharest Declaration extended/reduced with determinands recommended according to 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 the different locations mentioned above. Furthermore, it was specified how many sampling points (Left, Middle, Right) each station should include, which together with the allocation of determinand groups and sampling frequencies according to the location of each station lead to a full definition of each station.

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

Sampling and analyses are carried out on a



## 4. Description of TNMN



national level following as closely as possible the resulting determinand lists (on the total sample), which are presented in more detail in sub-chapters 4.2 and 4.3. All results together with station information and methods of analysis used are reported and distributed quarterly via e-mail (originally on diskettes) 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 section 4.4.

### 4.2 Determinands

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 the TNMN;
- the principal level of interest is the concentration at which most monitoring is anticipated 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" 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 the best practice. In these cases, the targets are entered in italics;

- tolerance indicates the largest allowable analytical error which is consistent with the correct interpretation of the data and with the 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.

## 4. Description of TNMN

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 Tolerance Detection	
Flow	m <sup>3</sup> /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	mS/cm	30	300	5	5 or 10%
Alkalinity	mmol/l	1	10	0.1	0.1
Ammonium (NH <sub>4</sub> <sup>+</sup> -N)	mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO <sub>2</sub> <sup>-</sup> -N)	mg/l	0.005	0.02	0.005	0.005 or 20%
Nitrate (NO <sub>3</sub> <sup>-</sup> -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 <sub>4</sub> <sup>3-</sup> -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 <sup>+</sup> )	mg/l	1	10	0.1	0.1 or 10%
Potassium (K <sup>+</sup> )	mg/l	0.5	5	0.1	0.1 or 10%
Calcium (Ca <sup>2+</sup> )	mg/l	2	20	0.2	0.1 or 10%
Magnesium (Mg <sup>2+</sup> )	mg/l	0.5	5	0.1	0.2 or 10%
Chloride (Cl <sup>-</sup> )	mg/l	5	50	1	1 or 10%
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	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)	mg/l	10	100	3	3 or 20%
Copper (Cu)	mg/l	10	100	3	3 or 20%
Chromium (Cr) – total	mg/l	10	100	3	3 or 20%
Lead (Pb)	mg/l	10	100	3	3 or 20%
Cadmium (Cd)	mg/l	1	10	0.5	0.5 or 20%
Mercury (Hg)	mg/l	1	10	0.3	0.3 or 20%
Nickel (Ni)	mg/l	10	100	3	3 or 20%
Arsenic (As)	mg/l	10	100	3	3 or 20%
Aluminium (Al)	mg/l	10	100	10	10 or 20%
BOD <sub>5</sub>	mg/l	0.5	5	0.5	0.5 or 20%
COD <sub>Cr</sub>	mg/l	10	50	10	10 or 20%
COD <sub>Mn</sub>	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	mg/l	10	100	10	10 or 20%
Lindane	mg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	mg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine	mg/l	0.1	1	0.02	0.02 or 30%
Chloroform	mg/l	0.1	1	0.02	0.02 or 30%
Carbon tetrachloride	mg/l	0.1	1	0.02	0.02 or 30%
Trichloroethylene	mg/l	0.1	1	0.02	0.02 or 30%
Tetrachloroethylene	mg/l	0.1	1	0.02	0.02 or 30%
Total Coliforms (37 C)	103 CFU/100 ml	-	-	-	-
Faecal Coliforms (44 C)	103 CFU/100 ml	-	-	-	-
Faecal Streptococci	103 CFU/100 ml	-	-	-	-
Salmonella sp.	in 1 litre	-	-	-	-
Macrozoobenthos	no. of taxa	-	-	-	-
Macrozoobenthos	Sapr. index	-	-	-	-
Chlorophyll – a	mg/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 Tolerance Detection	
Organic Nitrogen	mg/kg	50	500	10	10 or 20%
Total Phosphorus	mg/kg	50	500	10	10 or 20%
Calcium (Ca <sup>2+</sup> )	mg/kg	1000	10000	300	300 or 20%
Magnesium (Mg <sup>2+</sup> )	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 methodologies applied to determinands in TNMN are based on a list containing reference and optional analytical methods. The National Reference Laboratories (NRLs) were provided with a set of ISO standards (reference methods) reflecting the determinand lists, but also taking into account the current practice in environmental analytical methodology in the EU. It was decided not to ask each laboratory to use the same method, providing the laboratory could demonstrate that the method it used (optional method) met the required performance criteria. Therefore, the minimum concentrations expected and the tolerance required of actual measurements were defined for each determinand (as reported in Tables 4.2.1 and 4.2.2), in order to enable the laboratories to determine whether the

analytical methods they are currently 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 were 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)

## 4. Description of TNMN

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 TNMN, assuming that the aims of the programme will be satisfied provided that

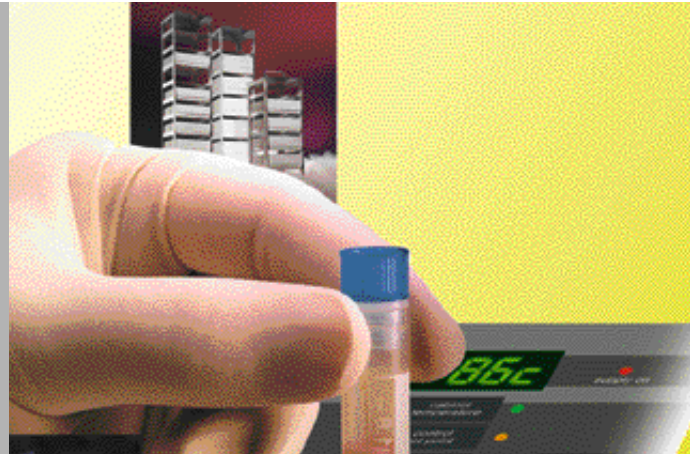
- relatively few results are reported as "less than" the minimum level (This will assist in load calculations and will ensure that real data are reported for the majority of sampling sites.)

- the accuracy achieved at the principal level is not worse than  $\pm 20\%$  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.

This means that any practical approach to monitoring must take into account the current capabilities of analytical science. This in its turn 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 the performance and data use in the course of the monitoring programme.

The described approach supports the work towards harmonising the analytical activities within the Danube Basin related to TNMN as well as the implementation and operation of the Analytical Quality Control (AQC) Programme. Therefore, the approach was used in identifying the needs for training required for improving laboratory performance of the National Reference Laboratories as well as the other laboratories involved in the implementation of 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 also introduced to the theoretical aspects of AQC.

## 4. Description of TNMN



### 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 and took the responsibility to organise 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 were 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 Trans-National Monitoring Network (TNMN) and the 1996/2 distribution already included all Danube laboratories - 11 NRLs and 18 national laboratories - implementing TNMN. This distribution was further extended to include six Black Sea laboratories responsible for pollution monitoring in their respective area.

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

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

sediments in addition to the artificial concentrates, and the analysis were extended to MBAS.

By the end of 1997, four distributions had been made. The analysed samples included synthetics (concentrates), real surface water, spikes as well as sediments. For the first time petroleum hydrocarbon extracts were also distributed.

In 1998, four distributions were taken and determinands and samples were similar to the earlier ones.

The results and their evaluation during the four distributions have been published in the relevant reports (QualcoDanube, AQC for Water Labs in the Danube River Basin, Summary Report 1998, VITUKI Plc., Budapest).

In the QualcoDanube performance testing scheme, the Youden-pair evaluation technique is usually applied. The interlaboratory comparative results for different determinands are discussed separately. It is seen as an achievement that 28 out of 29 laboratories reported results. Most laboratories reported results for ammonium-N, nitrate-N, orthophosphate-P and total-P, but only 15 laboratories reported results for Kjeldahl-N. Heavy metals in sediment were not analysed by all the laboratories. Some metals, such as cadmium and copper, were measured by 21 laboratories and mercury was measured by 16 laboratories.



## 4. Description of TNMN

### General determinands of water samples

Conductivity, pH-value, total dissolved solids (TDS), total hardness, chloride and sulphate were analysed from real surface water and synthetic samples. In general, the results were good but were influenced by a slight systematic error except sulphate and chloride, where random error characterized mainly the results in the case of real surface water sample.

### *Nutrients in water samples*

- Ammonium-N: The results demonstrated relatively high systematic errors in the analysis.

- Nitrate-N: The results were quite good, but it was unfortunate that a few laboratories always reported extremely low values.

- Kjeldahl-N: In the case of this determinand about half of the laboratories reported results. The reported values were rather scattered within the range of the plot. The most likely reason for this discrepancies is the different way of mineralization.

- Orto-phosphate-P and Total-P: The results showed mainly systematic error. After a reasonable quality improvement among the laboratories during the second and third distribution, the results were surprisingly good.

### *Organics determinands of water samples*

- Chemical oxygen demand (COD) (with permanganate and dichromate method): Showed systematic error. In spite of this fact, results are quite good.

- Biochemical oxygen demand (BOD): the results demonstrated strong systematic error in both directions.

- Methylene blue anionic surfactants (MBAS): among the results were extremely low and high values. Most of outliers results were reported by the same laboratories in both distributions.

### *Heavy metals in water*

Four metals were analysed. The results of cadmium were influenced by systematic error more than were those of chromium. In the case of copper analysis, results were satisfactory with a few outliers. 16 laboratories reported mercury results only, which were not satisfactory. Nearly one third of the results were unacceptably influenced by - mainly systematic - error.

### *Heavy metals in sediments*

Real Danube sediment samples collected at Budapest were analysed. No assigned value was available and the results were statistically evaluated.

- The results of zinc show surprisingly good agreement with one outlier.

- In the case of nickel there are a few outliers only. The results are not so good as of zinc or lead because they are influenced by systematic and random error respectively.

The same heavy metals were analysed in sediment as well as in water at the fourth distribution.

## 4. Description of TNMN



- The results of cadmium are scattered and influenced mostly by random error.
- In the case of chromium systematic error can be observed.
- The results of copper show a good agreement, but are influenced by a slight systematic error.
- Relatively few laboratories analysed mercury in the sediment. The figure shows unsatisfactory performance.

### *Conclusion*

The four QUALCODanube distributions in 1998 provided information on the performance of the participating water laboratories in the Danube River Basin. The overall output of the results demonstrates the comparability of the analytical data on the studied determinands as well as the possible methodological problems during the analysis.

The analytical results of synthetic samples are better than the results of real water samples. In the latter case, due to matrix effect the results are influenced by systematic and random error, while the results of synthetic samples were mainly influenced by systematic error.

Among the nutrients Kjeldahl-N-nitrogen (1998/2) and among organic pollutants chemical oxygen demand were analysed once with dichromate method (1998/1) according to the agreement reached in Ljubljana in May 1998.

In general, the results of metals are satisfactory, especially of zinc; only those of mercury are scattered.

In sediment in particular, the results are influenced by random and systematic error.

### *Need for continuation of interlaboratory comparison studies*

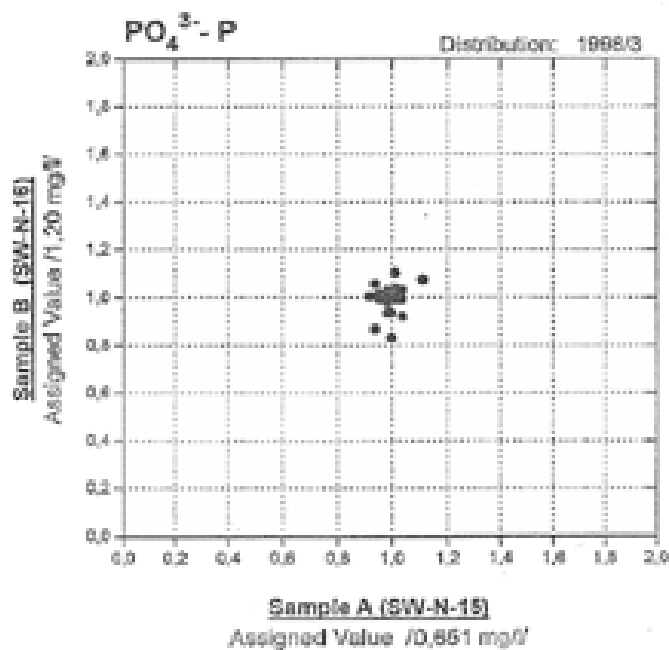
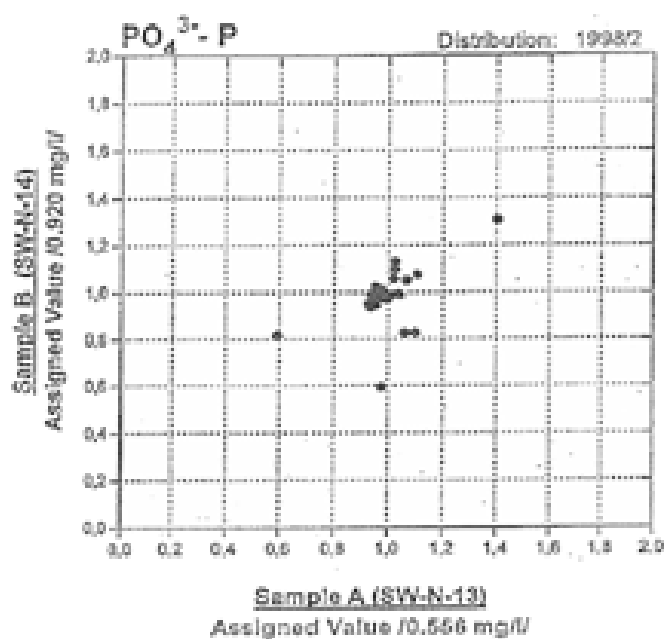
Regularly organised interlaboratory studies are an important part of QA/QC system. They help to improve analytical performances by allowing the participants to review their own performance concerning the accuracy of the analytical results and - where necessary - investigate the sources of error and take corrective actions.

It is therefore expected that the performance of the Danube Basin laboratories will further improve and the comparability of the water quality monitoring results in the river basin and related regions will be ensured.



## 4. Description of TNMN

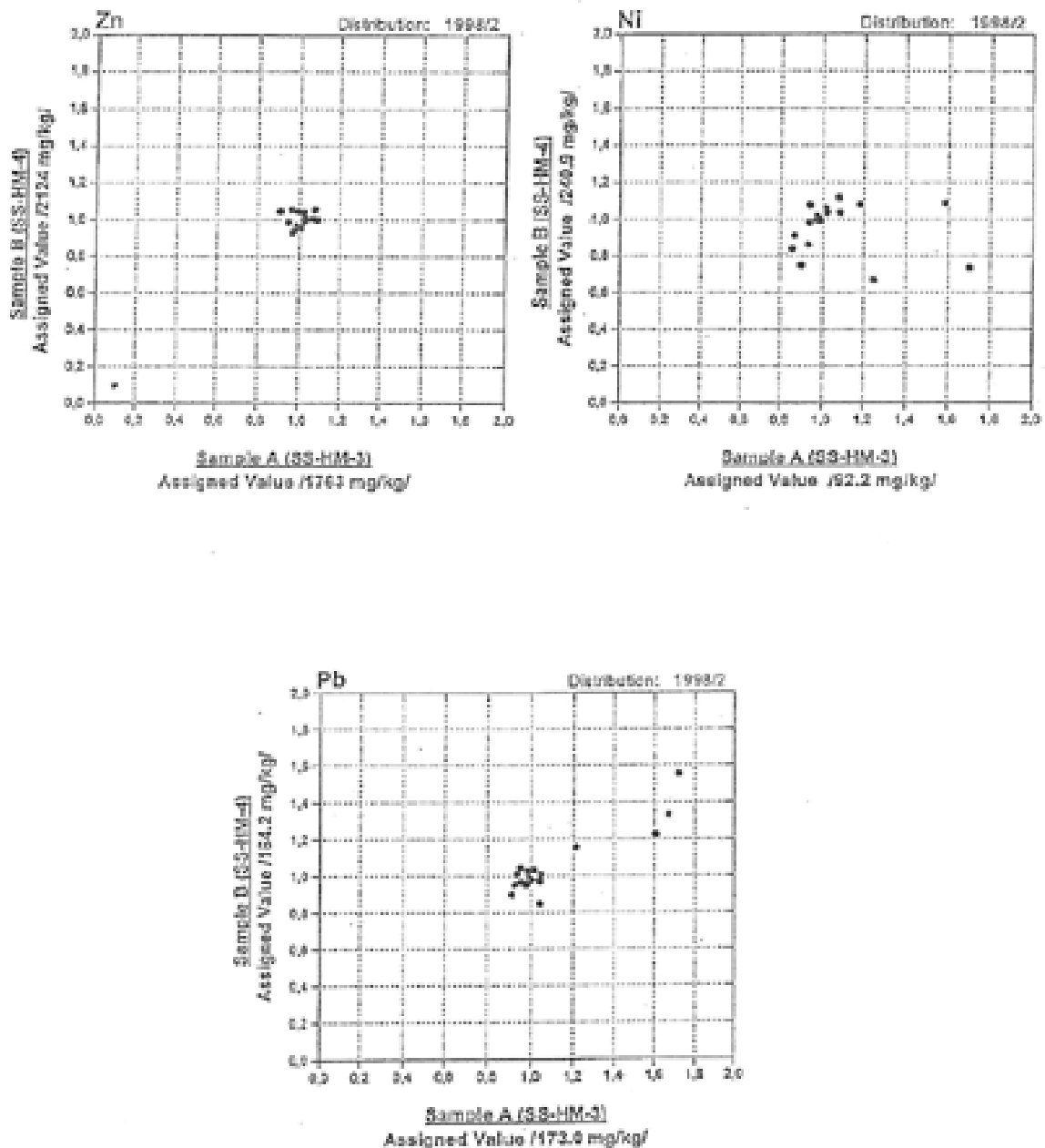
Figure 4.3.1.1: Variation in the reported/assigned values of  $\text{PO}_4^{3-}\text{-P}$  in the check samples.



## 4. Description of TNMN



Figure 4.3.1.2: Variation in the reported/assigned values of Zn, Ni, Pb in the sediment samples.



## 4. Description of TNMN

### 4.4 Information management

Data storage, exchange, retrieval and analysis have been dealt with in the frame of Information Management, and so were other types of data processing needed for information management activities. On the basis of a relational data base, TNMN's instream water quality data are organised in a well-defined structure using rules of reference integrity. This has yielded a system of joined tables, covering information about TNMN. For the purpose of data processing, 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. Data collection initiated in 1996 relied on diskettes as a medium for the exchange. At present, the use of e-mail is also accepted in accordance with a new standard operational procedure.

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

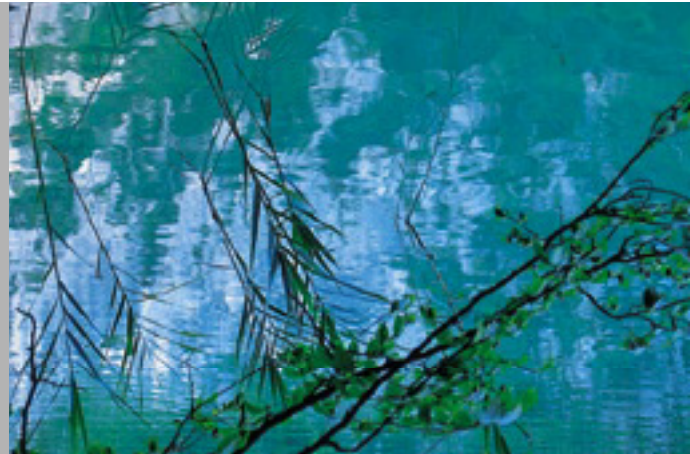
- concentrate on the quality of data obtained
- introduce a process of transferring data from the national information systems to a Central Information Point (CIP)
- build on the existing experience in the individual countries and not to try to force all the participating countries to adapt their national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

ted software for time series analysis (AARDVARK)

This approach resulted in the important decision to leave the responsibility for national information systems with 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, seven of which are filled with static data, and two with dynamic. The tables with static data are agreed by MLIM/EG and contain information regarding the monitoring stations, determinands, analytical methods, remarks, the participating countries and the sampling methods. These tables are maintained by the CIP on the basis of the agreements in the MLIM/EG. The tables with dynamic data contain information on taken samples and analytical results. These tables are also maintained at CIP level by merging data received from all countries on a quarterly basis.

## 4. Description of TNMN



*On the basis of the experience gained during the first years of TNMN data collection, storage and maintenance, it was recognised that there was a need to adjust or redesign several parts of the database. Consequently, the following steps were taken:*

- a new system for coding analytical methods was proposed and agreed for further use;
- the list of determinands was reviewed and extended in accordance with the new requirements;
- 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 the input of data in the system. It is 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). In 1996 the CIP was in Sofia at the National Center of Environment and Sustainable Development (home Institution for NRL and NIC for Bulgaria and of a former chairman of IMWG). In 1997 this CCIP was transferred to the Center for Marine and Environmental Research of the Rudjer Boskovic Institute in Zagreb (home Institution for NRL and NIC of Croatia and of a current chairman of IMWG). TNO Institute of

Applied Geoscience in Delft, The Netherlands, backed up the collected data.

TNMN data were regularly collected from Germany, Austria, the Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Bulgaria and Romania. Yearbook 1998 includes, in addition, data from Ukraine and Moldavia.

## 5. Tables of statistical data from TNMN stations

The determinands measured in 1998 - the second year of operation of TNMN Phase 1 - 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 included in TNMN Phase 1 are characterised on the following station list and station map (Figure 5.1). The station list specifies the official national data, which are not harmonised in all cases. Inconsistencies concerning catchment area and altitude of the stations measured by both neighbouring countries may be due to different national calculation procedures. It has been recommended that these problems should be solved and that data within the transboundary commissions should be made consistent.

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

In 1998, data were available from 51 stations including a total of 75 sampling points, which is more than in the previous year, 1997. Some stations performed no measurements at all due to a lack of proper equipment or to restricted access for political reasons. There are still no data at all from Bosnia-Herzegovina, but data from Ukraine and Moldova have been provided for the first time and are presented in this Yearbook. Data available from 75 sampling points mentioned above are presented in 75 tables in Annex 1 according to the key shown below. 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 1998
Mean	Arithmetical mean of the measurements done in the year 1998
Max	Maximum value of the measurements done in the year 1998
C50	50 percentile of the measurements done in the year 1998
C90	90 percentile of the measurements done in the year 1998
Q1	Arithmetical mean of the measurements done in the first quarter of the year 1998
Q2	Arithmetical mean of the measurements done in the second quarter of the year 1998
Q3	Arithmetical mean of the measurements done in the third quarter of the year 1998
Q4	Arithmetical mean of the measurements done in the fourth quarter of the year 1998

## 5. Tables of statistical data from TNMN stations



If values less than the detection limit are present in the datasheet for a given determinand, the calculations use half of the value of the detection limit. In case all the measurements in the year were below the detection limit, only minimum, mean and maximum were put in the table with-

out any other statistical data. Similarly, in case of only four or fewer measurements of a particular determinand in a year, only minimum, mean and maximum values were calculated.

Station List										
Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance Km	Altitude m	Catchment 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 15	16 59 27	79	150	9883	L2100	M	
CZ02	/Morava/Dyje	Breclav	48 43 26	16 53 12	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	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/Sajo	Sajopuspoki	48 16 55	20 20 27	124	148	3224	L1770	M	
SI01	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1390	L	
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	135	10878	L1330	R	
HR01	Danube	Batina	45 52 27	18 50 03	1429	86	210250	L1315	M	
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R	
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M	
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	508	92	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	
R002	Danube	Pristol/Novo Selo Harbour	55,57,58 44 11 18,23,29	24,40,54 22 45 57,64,69	834	31	580100	L0090	LMR	
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	



## 5. Tables of statistical data from TNMN stations

RO07	Danube	Sulina - Sulina arm	45 9 41	29 40 25	0	1	817000	L0480	LMR
RO08	Danube	Sf.Gheorghe-Ghorghe arm	44 53 10	29 37 5	0	1	817000	L0490	LMR
RO09	/Arges	Conf. Danube	44 4 35	26 37 4	0	14	12550	L0250	M
RO10	/Siret	Conf. Danube Sendreni	45 24 10	28 1 32	0	4	42890	L0380	M
RO11	/Prut	Conf.Danube Giurgiulesti	45 28 10	28 12 36	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	44 09	22 47	834	35	580100	L0730	LMR
BG02	Danube	us. Iskar - Bajkal	50,58,66	36,47,58					
BG03	Danube	Downstream Svishtov	43 42 58	24 24 45	641	20	608820	L0780	M
BG04	Danube	us. Russe	43 37 50	25 21 11	554	16	650340	L0810	MR
BG05	Danube	Silistra/Chiciu	43 48 06	25 54 45	503	12	669900	L0820	MR
BG06	/Iskar	Orechovitzza	44 7 02	27 15 45	375	7	698600	L0850	LMR
BG07	/Jantra	Karantzi	43 35 57	24 21 56	28	31	8370	L0930	M
BG08	/Russ.Lom	Basarbovo	43 22 42	25 40 08	12	32	6860	L0990	M
MD01	/Prut	Lipcani	43 46 13	25 57 34	13	22	2800	L1010	M
MD02	/Prut	Leuseni	48 16 0	26 50 0	658	100	8750	L2230	L
MD03	/Prut	Conf. Danube-Giurgiulesti	46 48 0	28 9 0	292	19	21890	L2250	M
UA01	Danube	Reni - Kilia arm/Chilia arm	45 28 10	28 12 36	0	5	27480	L2270	LMR
UA02	Danube	Vilkova-Kilia arm/Chilia arm	45 28 50	28 13 34	132	4	805700	L0630	M
			45 24 42	29 36 31	18	1	817000	L0690	M

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



## 5. Tables of statistical data from TNMN stations

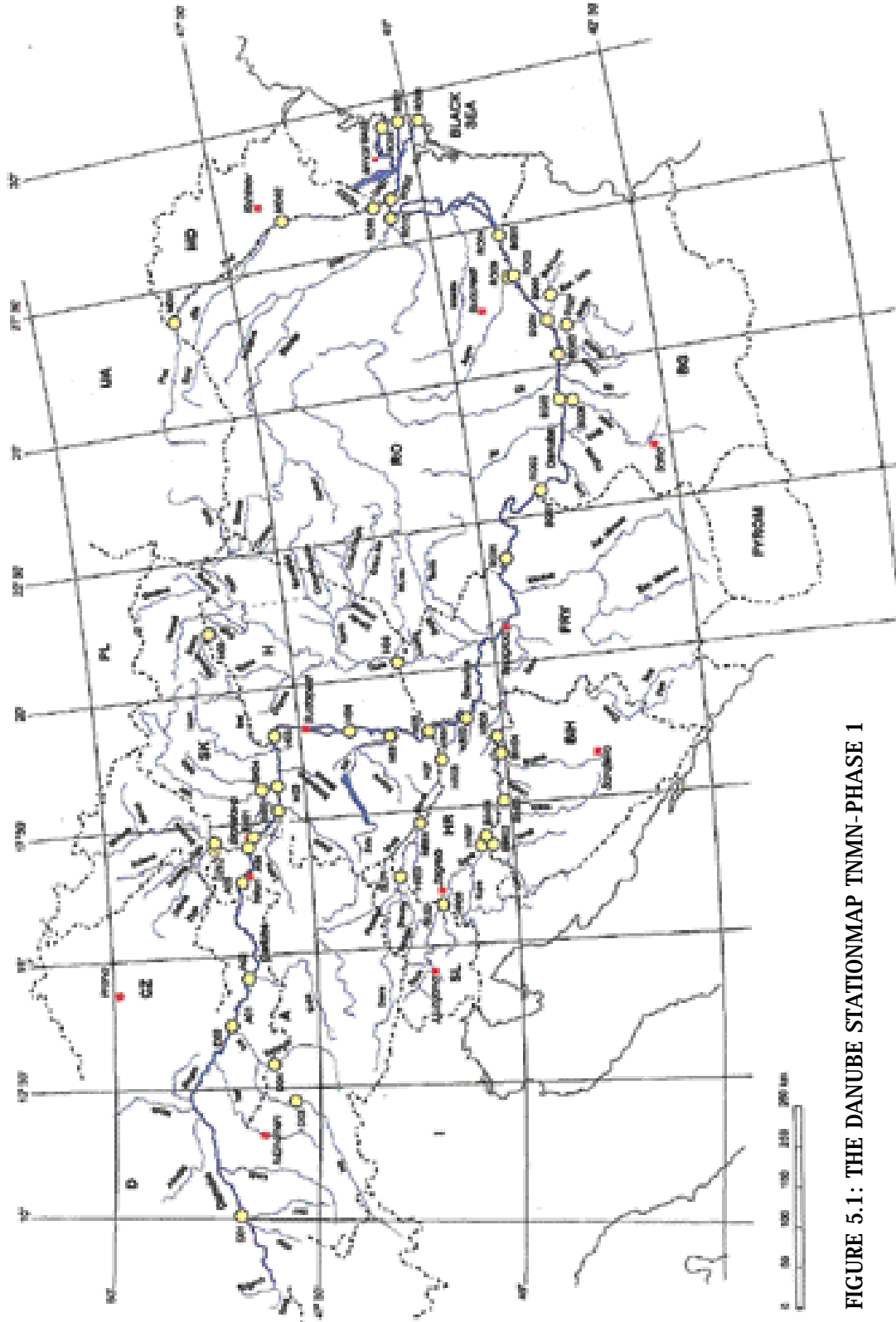


FIGURE 5.1: THE DANUBE STATIONMAP TNMN-PHASE 1

## 5. Tables of statistical data from TNMN stations

Water sampling and analysis should have been performed according to the specification in Chapter 4. However, as was already mentioned, some stations performed no measurements at all. Even in sampling points from which water samples were taken, the range of measured determinands is not uniform. Relatively few data are available for organic micropollutants and biological determinands, especially from the lower part of the Danube River Basin.

The agreed sampling frequency of at least 12 times per year for physico-chemical determinands was not observed by all monitoring sites, but the frequency increased in comparison with the previous years.

In the case of basic physico-chemical determinands, measurement frequency below 11 times per year was very seldom, which is positive because it is essential for determinands varying seasonally or highly correlating to the discharge. Measurement frequency for heavy metals and organic micropollutants was lower.

When analysing water quality data presented in the Yearbook, one should take into account the results of QualcoDanube intercalibration studies because the validity and full comparability of data is a prerequisite for their further use in the assessment process. The QualcoDanube studies clearly demonstrate that there have been some problems in the case of some determinands and that analytical measurements need to be further improved. It should also be pointed out that methods for the measurement of microbiological and biological determinands have not yet been fully harmonised.

Concerning oxygen regime determinands, the major indicators include dissolved oxygen, BOD<sub>5</sub> and COD<sub>Cr</sub>.

Dissolved oxygen content was measured at all 75 sampling points generating 1998 data. The concentration range varied from 4.30 – 15.10 mg/l (annual means 6.6 – 11.8 mg/l) in the Danube itself, and from 3.0 – 17.4 mg/l (annual means 6,7 – 11.9 mg/l) in the tributaries.

BOD<sub>5</sub> characterising content of biodegradable organic substances in water was measured at all 75 sampling points, but QualcoDanube intercalibration studies discovered, similar to previous years, a strong systematic error for this determinand. BOD<sub>5</sub> values were in the range from 0.3 – 9.0 mg/l (annual means 1.2 – 4.6 mg/l) in the Danube River and from 0.2 – 12.2 mg/l (annual means 1.6 – 6.4 mg/l) at sampling points located on the tributaries.

COD<sub>Cr</sub> was measured at 71 sampling points, with concentrations varying from 1.0 – 57.0 mg/l (annual means 5.7 – 24.3 mg/l) in the Danube River and from 1.0 – 103.0 mg/l (annual means 5.5 – 36.4 mg/l) in the tributaries.

Nutrient status of the Danube River and its tributaries is very important because nitrogen is blamed as being the major cause of eutrophication in the Danube delta and the Black Sea. While inorganic fractions of nitrogen like ammonium-N and nitrate-N were measured in all 75 sampling points in 1998, information on organic nitrogen is available only from countries in the middle part of the Danube River Basin - from the Czech Republic down to Croatia.

## 5. Tables of statistical data from TNMN stations



Content of ortho-phosphate phosphorus and total phosphorus was measured at 73 sampling stations and total phosphorus was measured at 68 sampling points only.

Ammonium-N was observed in the range from 0.01 – 2.93 mg/l (annual means 0.06 – 0.67 mg/l) in the Danube itself and from 0.01 – 4.54 mg/l (annual means 0.04 – 1.97 mg/l) on tributaries.

Nitrate-N concentration range was from 0.08 – 4.80 mg/l (annual means 1.15 – 2.73 mg/l) in the Danube River and from 0.03 – 21.90 mg/l (annual means 0.59 – 6.04 mg/l) on tributaries.

Concentrations of ortho-phosphate-phosphorus were in the range from 0.003 – 0.640 mg/l (annual means 0,027 – 0,342 mg/l) in the Danube River and from 0.002 – 1.120 mg/l (annual means 0.016 – 0.636 mg/l) in the tributaries.

The statistical results presented in the tables in Annex 1 indicate that overall the ranges of measured determinands were larger in the tributaries than in the Danube itself. The highest pollutant levels were typical for some tributaries.

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

## 6. Maps of selected determinands

For the selected determinands characterising organic pollution and nutrient fractions in the surface waters of the Danube River Basin, the assessment based on the available data of TNMN Phase 1 of 1998 is shown in Maps 6.1, 6.2, 6.3 and 6.4. The maps show interim water quality classes based on the average concentrations of BOD<sub>5</sub>, ortho-phosphate-phosphorus PO<sub>4</sub><sup>3-</sup>-P, ammonium-nitrogen NH<sub>4</sub><sup>+</sup>-N and nitrate-nitrogen NO<sub>3</sub><sup>-</sup>-N.

If there were data from three sampling sites (left, middle, right) of a monitoring station, only the “middle” data are shown.

The smaller coloured circle on the map indicates sampling sites at which the presented water quality determinand was measured less than 11 times per year.

As in the previous two years, the colour coding used for BOD<sub>5</sub> and PO<sub>4</sub><sup>3-</sup>-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 NO<sub>3</sub><sup>-</sup>-N is also based on water quality standards proposed by this report, but for determinand NH<sub>4</sub><sup>+</sup>-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 NH<sub>4</sub><sup>+</sup>-N limit values from “Proposal for classification for TNMN purposes”, prepared by MLIM/SG in 2001.

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

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

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

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

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

## 6. Maps of selected determinands



BOD<sub>5</sub> is a commonly used indicator for biodegradable organic pollution, which affects the oxygen regime in water. Nevertheless, the interpretation of results poses some difficulty concerning the possible toxic effects, which can cause a decrease in BOD<sub>5</sub> values. In addition, intercalibration tests within the Danube laboratories have proved that the quality of data is still not fully satisfactory.

The results presented in Figure 6.1 show that at 94 % of all monitoring stations the average concentrations of BOD<sub>5</sub> corresponded to class I or II. It means that the average value of BOD<sub>5</sub> was not higher than 5 mg/l there. All monitoring stations along the Danube River itself were within the ranges of class I and II. Higher average values of BOD<sub>5</sub> were identified in case of three tributaries, corresponding to class III. On

the whole, it can be concluded that the Danube's tributaries are more polluted by biodegradable organic substances than the river itself (see also Table 6.2).

In comparison with the previous year, in spite of the fact that there are BOD<sub>5</sub> data from more monitoring stations than in the previous year, a higher percentage of monitoring stations corresponds to class I and II. Even the range of BOD<sub>5</sub> values occurring in TNMN monitoring sites in 1998 is narrower than in the year 1997.

Table 6.2: TNMN 1998 - average concentrations of BOD<sub>5</sub>: 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	15	56	14	58	29	57
II	12	44	7	29	19	37
III	0	0	3	13	3	6
IV	0	0	0	0	0	0
V	0	0	0	0	0	0

## 6. Maps of selected determinands

Nutrients are very important because they are responsible for eutrophication processes in lakes, rivers and the receiving sea. The concentrations of  $\text{PO}_4^{3-}\text{-P}$  and  $\text{NH}_4^+\text{-N}$  presented in the following maps and graphs were selected from the different nutrient fractions that are analysed within the TNMN Programme.

Ortho-phosphate-phosphorus was chosen to be presented instead of total phosphorus because 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. In addition, the content of total phosphorus was not measured at all monitoring stations in 1998.

On the basis of results shown in Figure 6.2 and Table 6.3, it can be concluded that when all monitoring stations are considered, the average  $\text{PO}_4^{3-}\text{-P}$  concentrations were in the range of class I and II at 84 % of the sampling sites.

In the Danube itself, the average  $\text{PO}_4^{3-}\text{-P}$  concentrations corresponded to class I and II at 96 % sampling stations.

As regards TNMN monitoring stations located along the tributaries, they reported higher variability in the concentrations of  $\text{PO}_4^{3-}\text{-P}$ . The average  $\text{PO}_4^{3-}\text{-P}$  concentration along the tributaries corresponded to class I and II at 71 % sampling stations; at 29 % of the sampling stations the average  $\text{PO}_4^{3-}\text{-P}$  concentrations were in the range of classes III – V.

An increase in  $\text{PO}_4^{3-}\text{-P}$  content along the Danube River itself can be seen from the presentation of

results in Figure 6.2. The Danube water corresponds to class I in the whole upper part of the river; while the middle and lower part of the Danube River can be characterised by classes I-II and II and IV respectively.

Comparing the results of classification with the previous years, the average concentrations of  $\text{PO}_4^{3-}\text{-P}$  in 1996 and 1997 corresponded to classes I and II at 72 % and 90 % sampling stations respectively.

Figure 6.3 shows the average concentrations of  $\text{NH}_4^+\text{-N}$ . Considering all monitoring stations, at most of them (63 %) the average concentrations measured in 1998 indicated class I or II. In the Danube itself, 70 % of the monitoring stations were within the range of class I or II and 30 % of the stations corresponded to class III.

54 % of the monitoring stations located along the tributaries corresponded to class I or II and 33 % to class III. Class IV or V was observed at 12 % of the monitoring stations; these stations also reported the highest average  $\text{BOD}_5$  values of all TNMN monitoring stations (see Table 6.4).

## 6. Maps of selected determinands



Table 6.3: TNMN 1998 - 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	13	52	9	38	22	45
II	11	44	8	33	19	39
III	0	0	4	17	4	8
IV	1	4	2	8	3	6
V	0	0	1	4	1	2

Table 6.4: TNMN 1998 - 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	16	59	12	50	28	55
II	3	11	1	4	4	8
III	8	30	8	33	16	31
IV	0	0	2	8	2	4
V	0	0	1	4	1	2



## 6. Maps of selected determinands

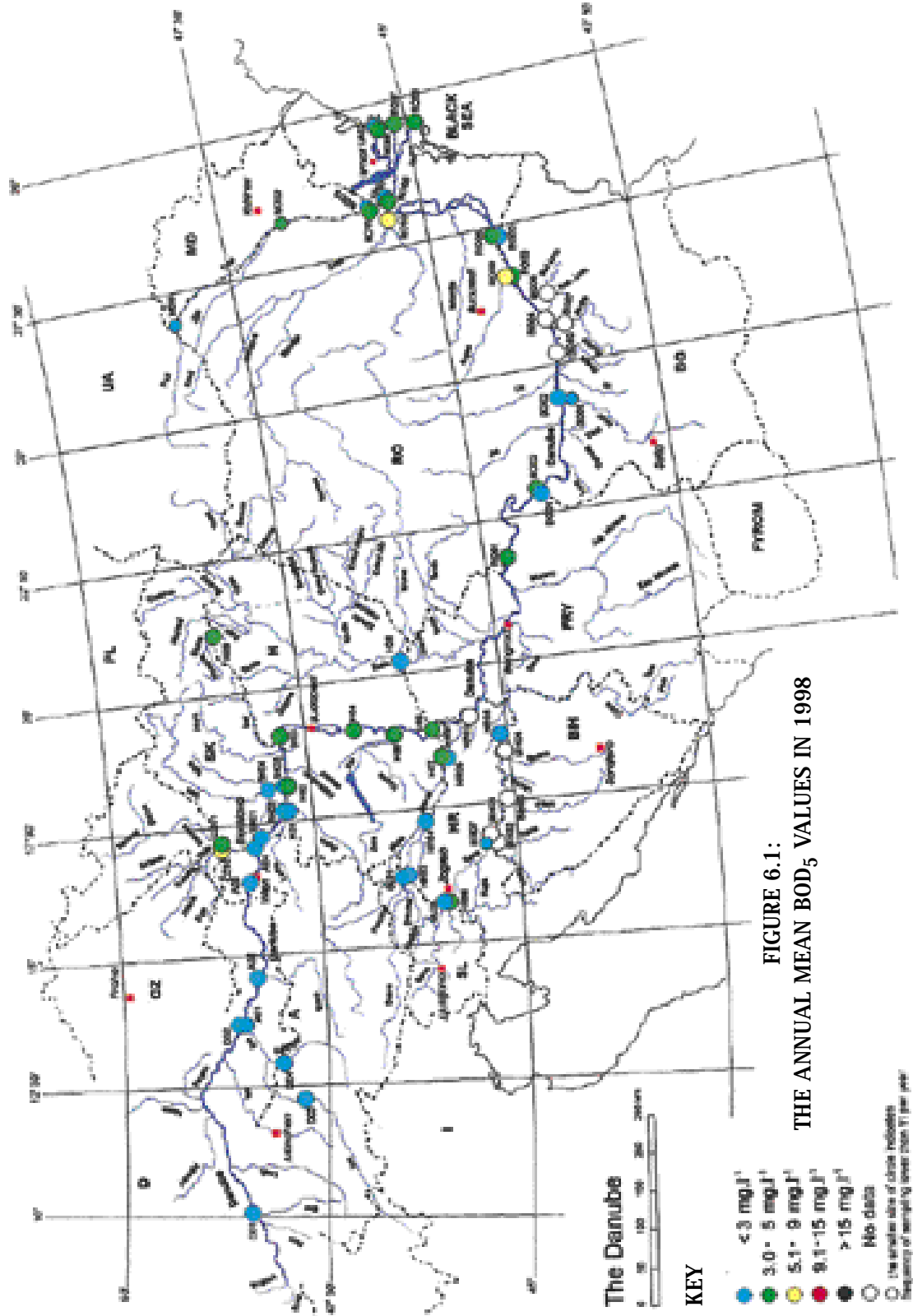
The average concentrations of NO<sub>3</sub>-N were in a rather narrow range, especially in the Danube River (see Figure 6.4). As a result, NO<sub>3</sub>-N average values at all monitoring stations located in the Danube River corresponded to class II. A higher variability in NO<sub>3</sub>-N concentrations was

observed in the case of tributaries. Although the majority of monitoring stations along the tributaries (79 %) were within the range of water quality class II, 13 % corresponded to class I and only 8 % indicated class III (see Table 6.5).

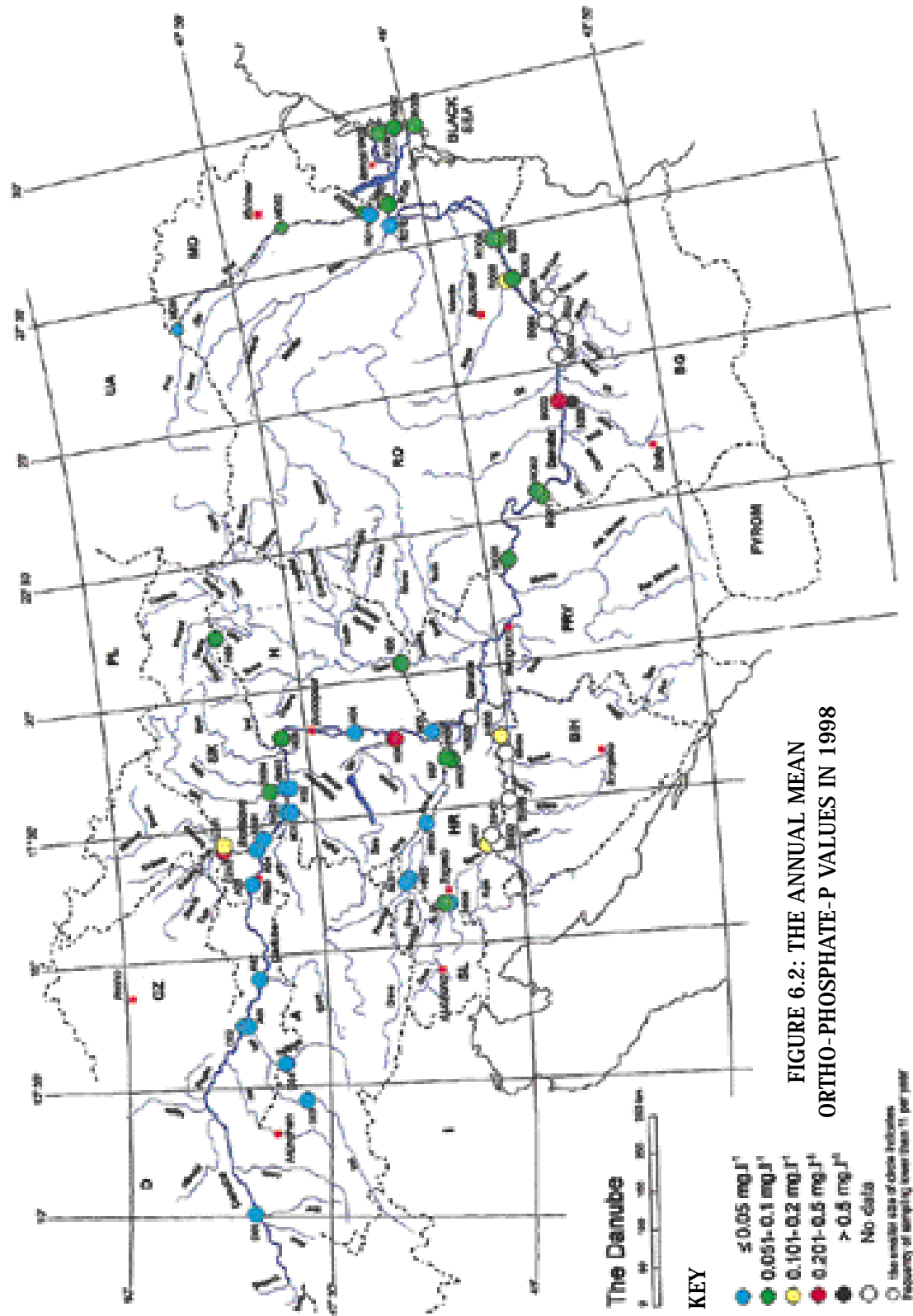
Table 6.5: TNMN 1998 - average concentrations of NO<sub>3</sub>-N: distribution of monitoring stations according to the classification listed in Table 6.1.

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	0	0	3	13	3	6
II	27	100	19	79	46	90
III	0	0	2	8	2	4
IV	0	0	0	0	0	0
V	0	0	0	0	0	0

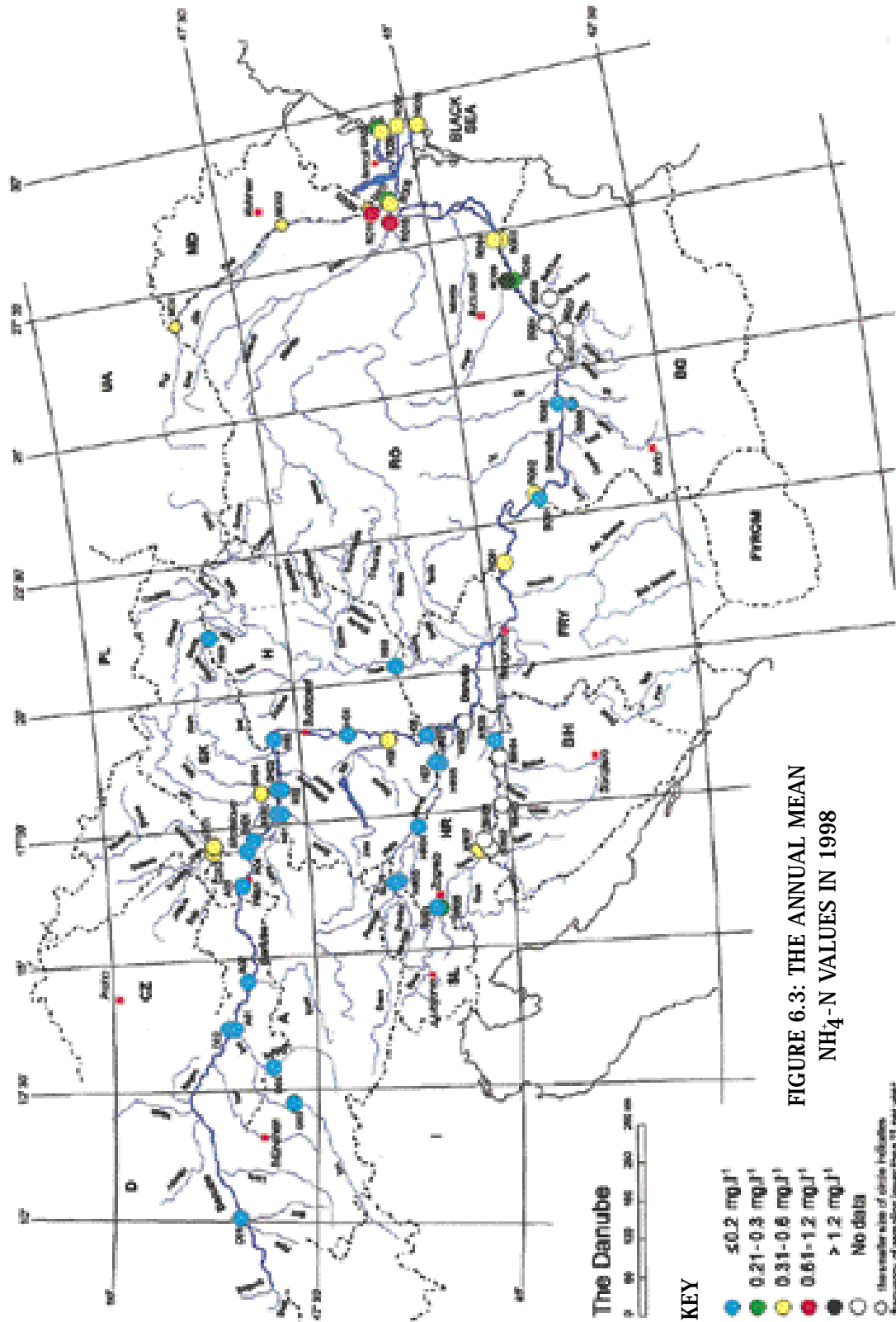
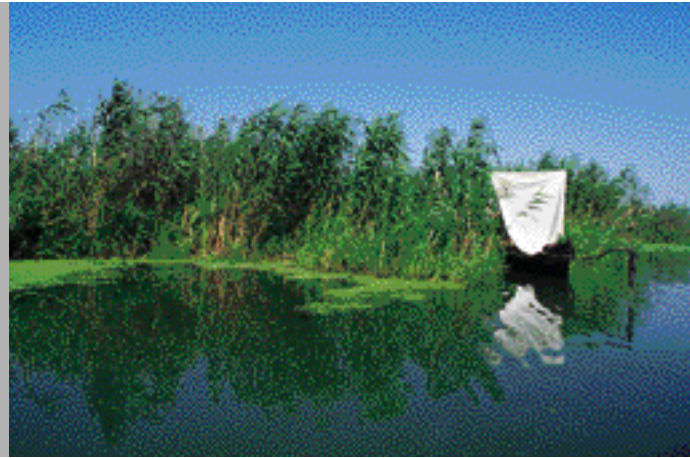
## 6. Maps of selected determinands



## 6. Maps of selected determinands



## 6. Maps of selected determinands



## 6. Maps of selected determinands

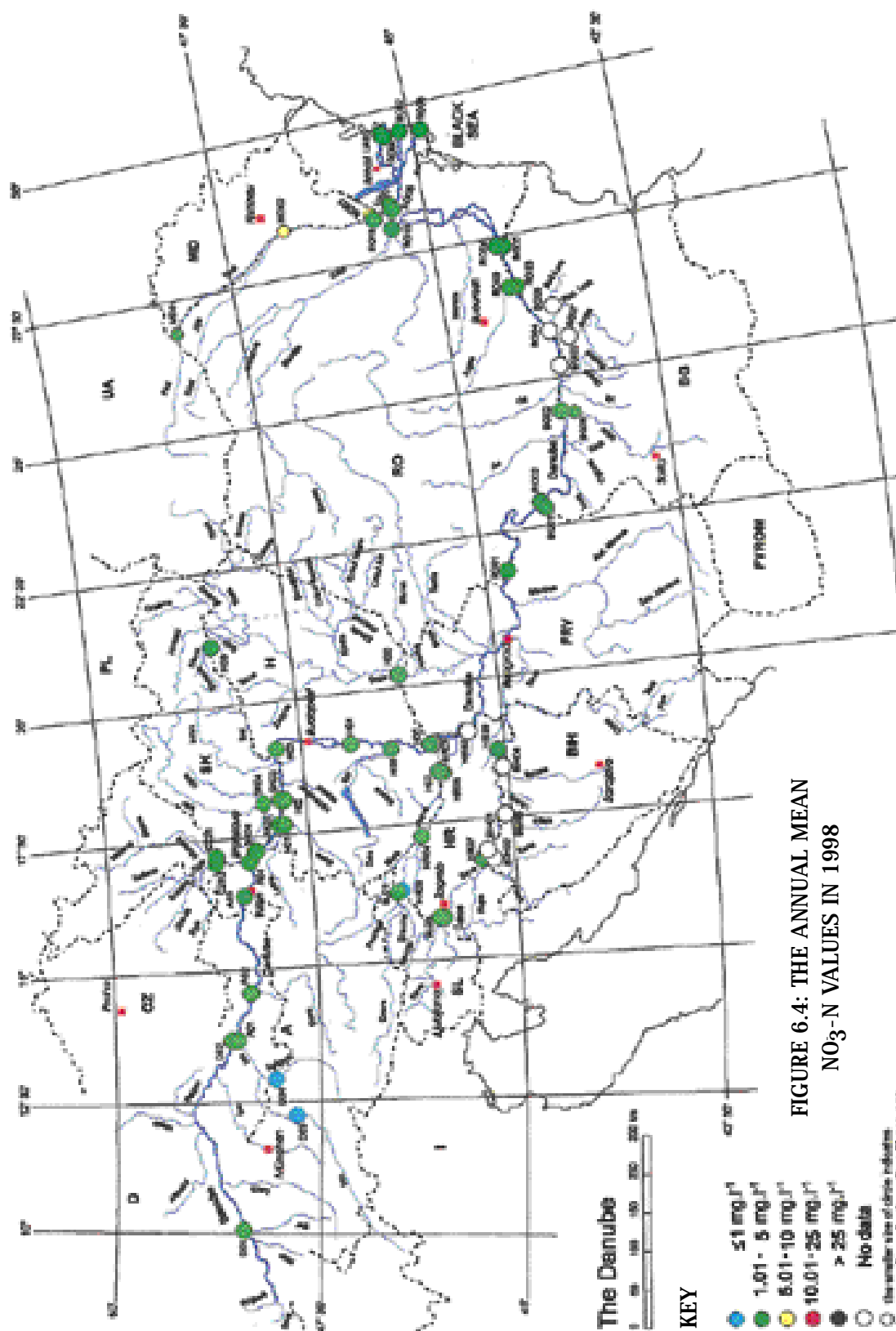


FIGURE 6.4: THE ANNUAL MEAN NO<sub>3</sub>-N VALUES IN 1998

## 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 determinand (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 its mouth (km). The minimum and maximum values are indicated on the plot in green and red colour respectively. Stations close to each

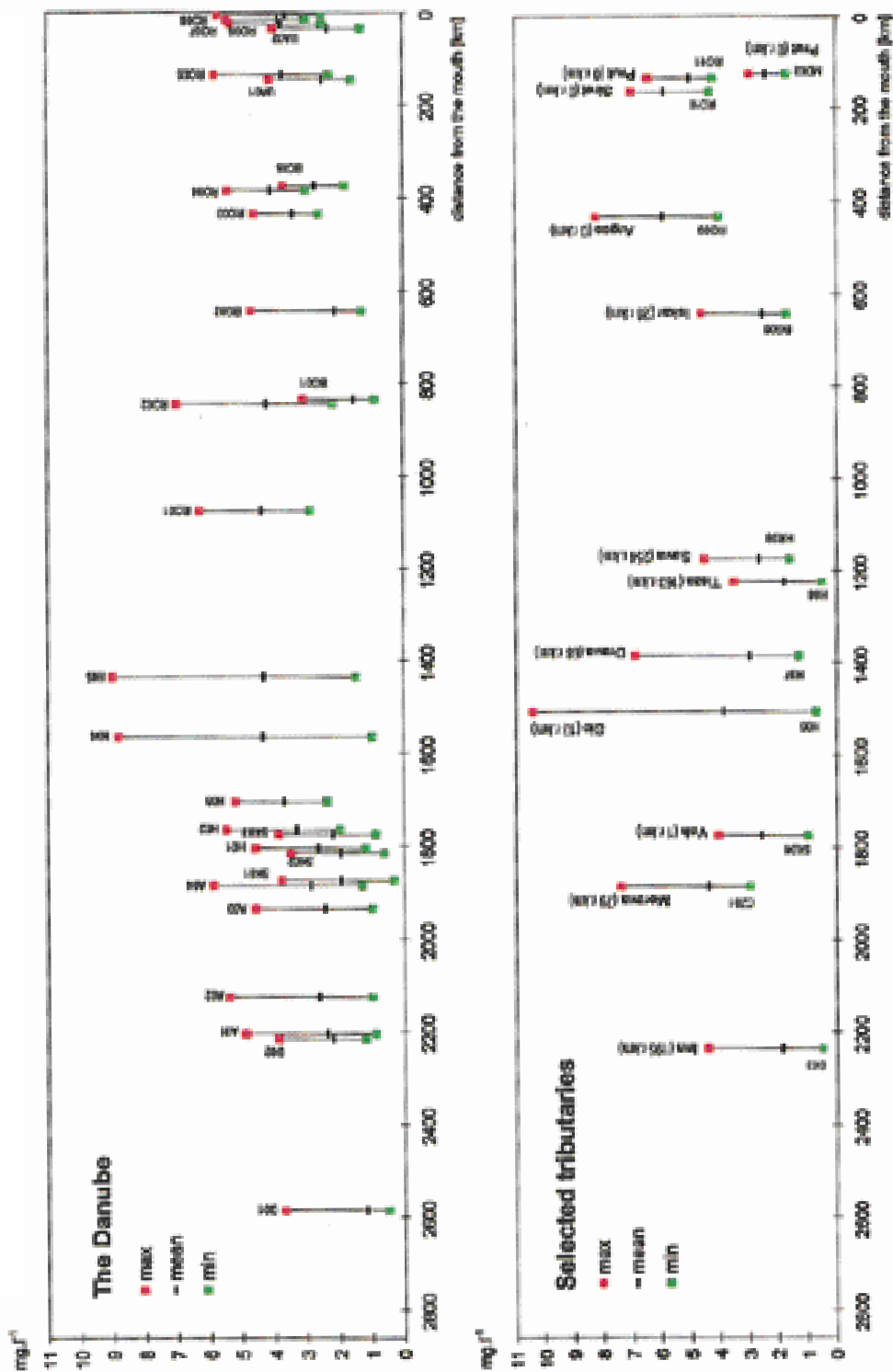
other or those monitored by two countries (transboundary stations) are shifted slightly along the X-axis.

When the same method is used, the lower plot shows concentration ranges at the stations located at the furthest downstream point along the primary tributaries. In these graphs, the bars are plotted at the river-km of the confluence of the tributary with the Danube.

If a monitoring station has three sampling sites (left, middle, right), only data from the "middle" are shown in the following profiles.

# 7. Profiles of selected determinands

FIGURE 7.1: THE MINIMUM, MEAN AND MAXIMUM BOD<sub>5</sub> VALUES IN 1998

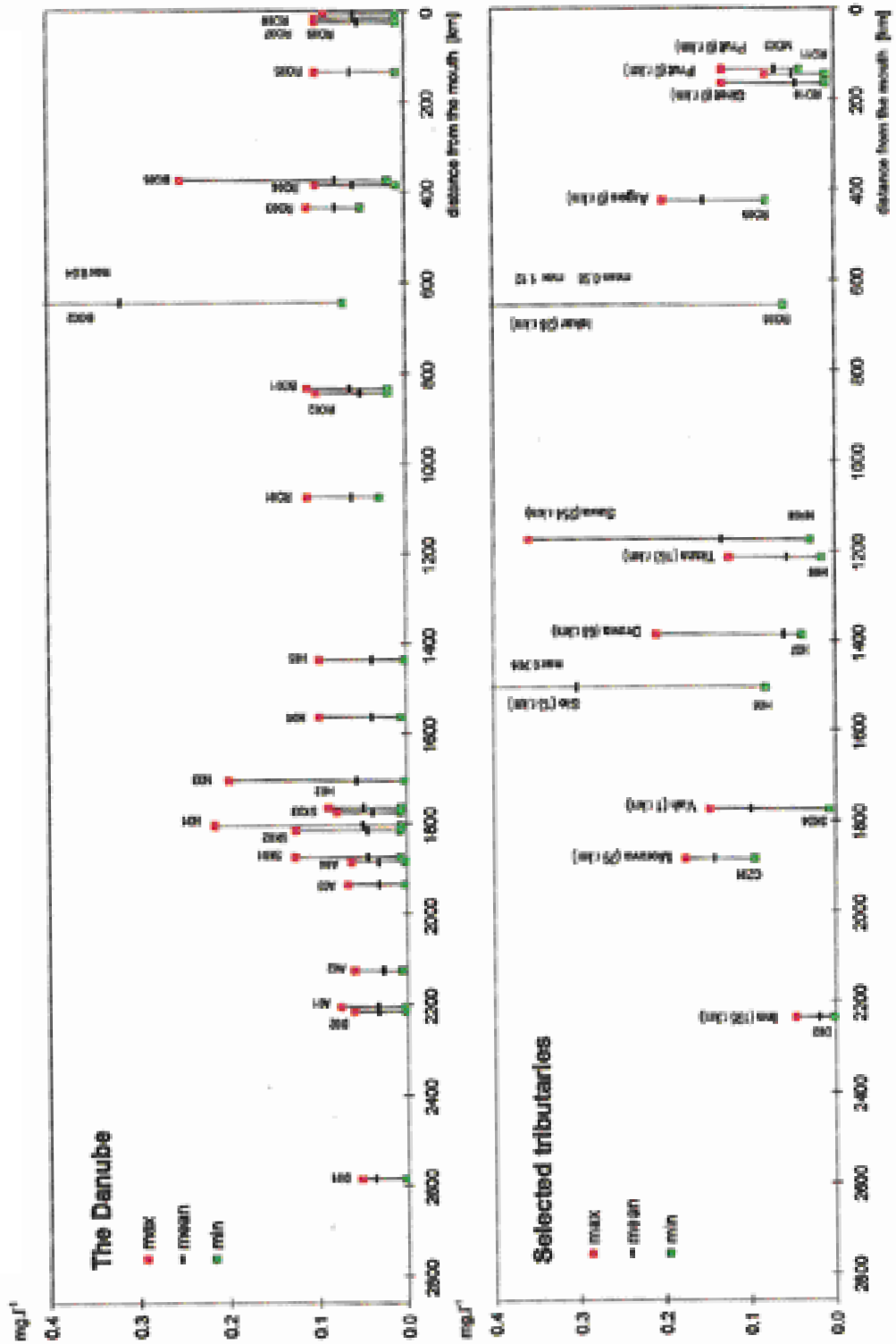




# 7. Profiles of selected determinands

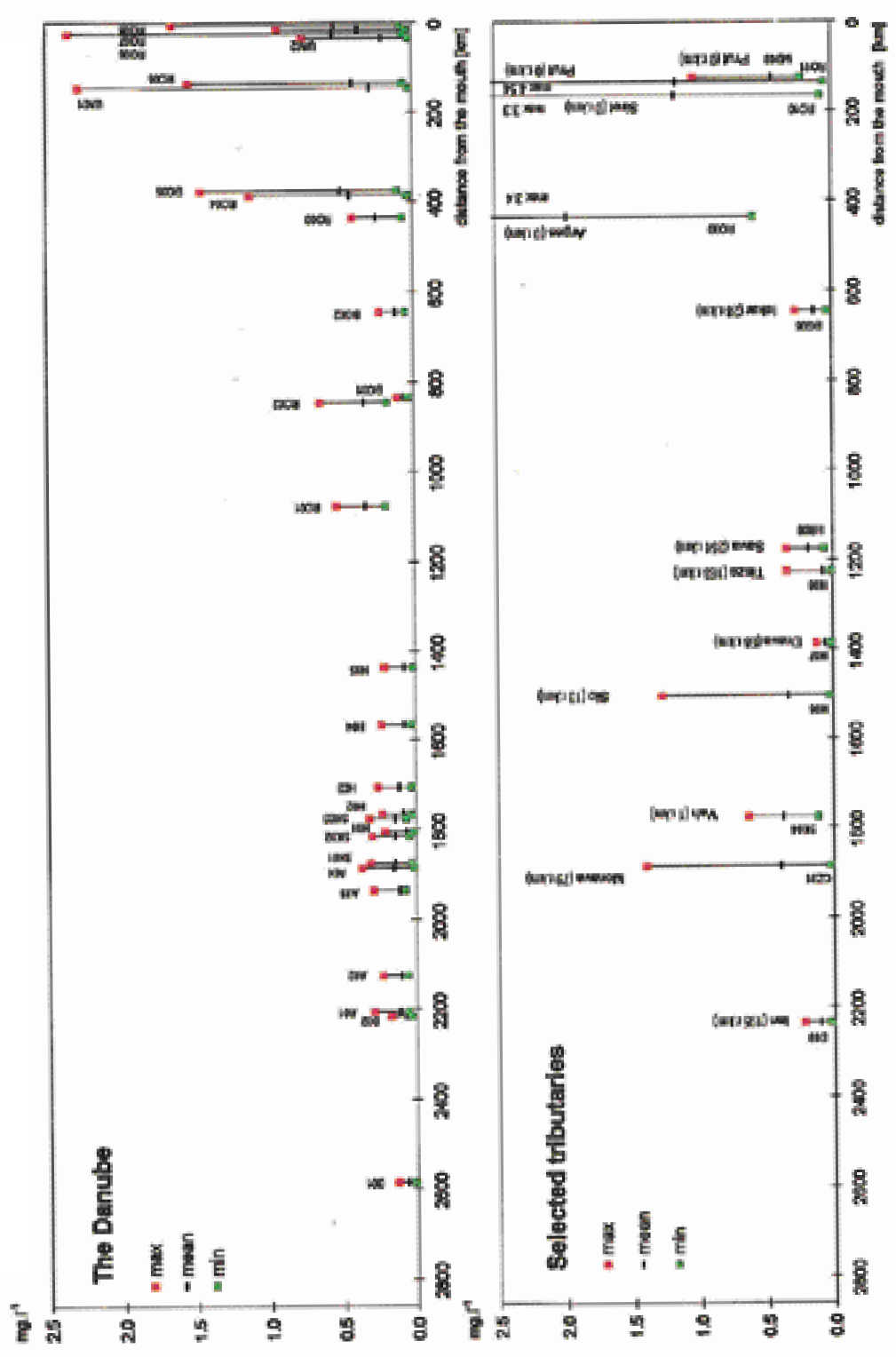


FIGURE 7.2: THE MINIMUM, MEAN AND MAXIMUM ORTHO-PHOSPHATE-P VALUES IN 1998



# 7. Profiles of selected determinands

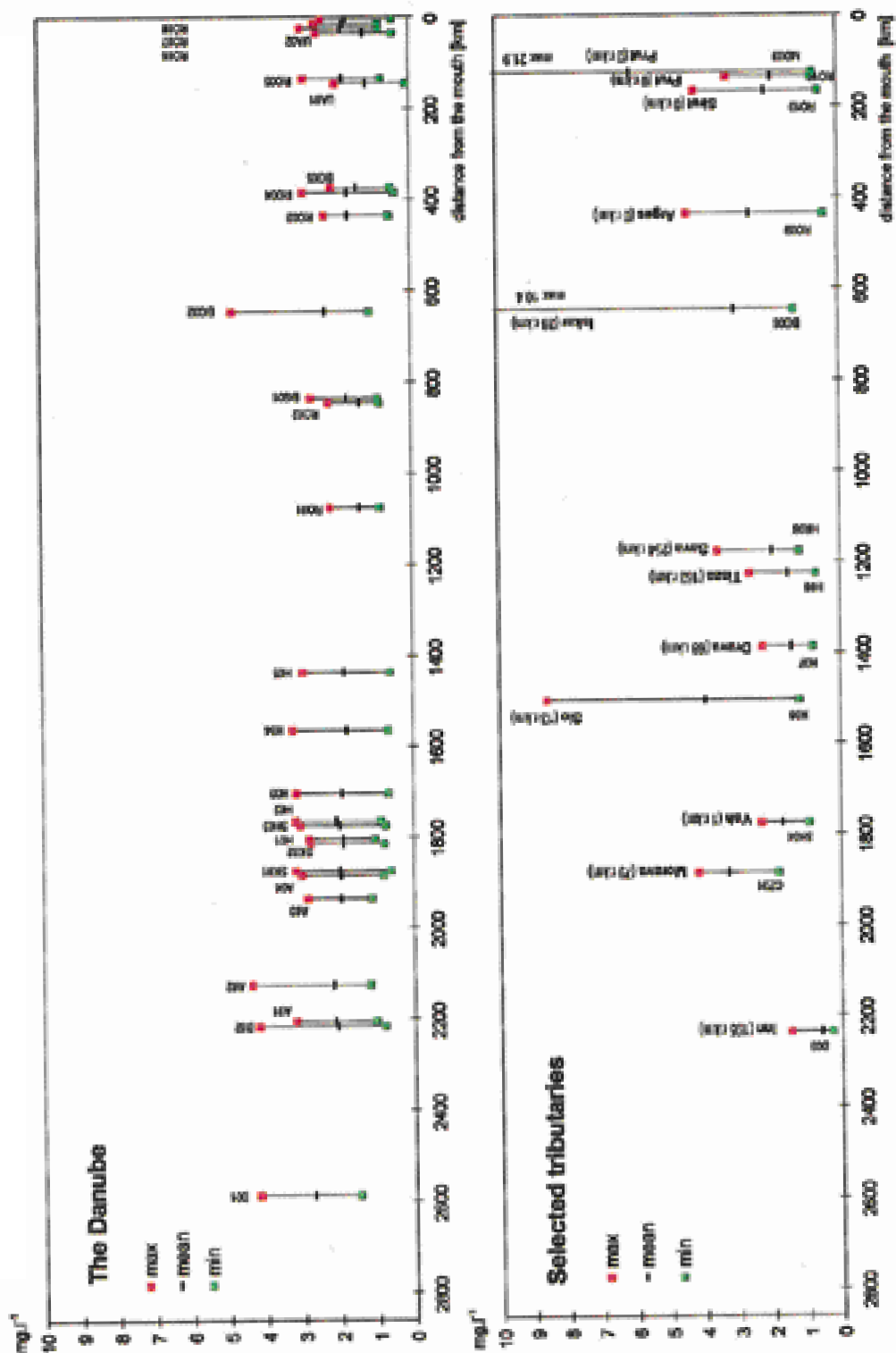
FIGURE 7.3: THE MINIMUM, MEAN AND MAXIMUM NH<sub>4</sub>-N VALUES IN 1998



## 7. Profiles of selected determinands



FIGURE 7.4: THE MINIMUM, MEAN AND MAXIMUM  $\text{NO}_3\text{-N}$  VALUES IN 1998



## 8. 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)