WATER QUALITY

in the Danube River Basin 1999

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, 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: p_matter@hotmail.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 co-operate 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 concerned as well as the typical emissions of pollutants discharged within the respective catchment area. In addition, the Parties shall periodically assess the quality conditions of the Danube River and the progress 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 fourth one in a planned continuous series of yearbooks compiled by the ICPDR. Its main objective is to present the monitoring programme and the data obtained from the operation of TNMN in 1999.

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 1999 provides only a chronology of events in the development of TNMN and its supporting bodies. Chapter 3 describes TNMN's objectives are described in Chapter 3 and a description of TNMN is given in Chapter 4. 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

2. History of TNMN

In spite of the fact that TNMN has been in operation only since 1996, the first steps towards creating it had been taken many years ago. 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 Danubian countries. Monitoring, laboratories and information management became the highlight of the Programme in December 1992 when the Monitoring, Laboratory and Information Management Sub-Group (MLIM-SG) 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 (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 funding 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. The Task Force of the EPDRB was invited to co-operate with the Interim ICPDR and its Secretariat to contribute to the effective implementation of the DRPC.

As a Technical Sub-Group of the 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 by the first ICPDR Plenary Meeting.

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 reliable and consistent trend analysis for 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 split into 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 according to defined objectives;
- a determinand lists reflecting the Bucharest Declaration and EU-Directives;
- information management based on a simple data exchange file format between the riparian countries.

The second phase will build upon 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 with 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 which 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 a 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 confluence 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 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 - 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 to meet 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 led to a full definition of each station.

However, the 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.

4. Description of TNMN

Sampling and analyses are carried out on a 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 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. 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 Chapter 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 TNMN;
- the principal level of interest is the concentration at which the bulk of monitoring is expected to be carried out;
- the required limit of detection is the target limit of detection (LOD) which laboratories are asked to achieve. This has been set, wherever practicable, at one third of the minimum level of interest. This is intended to ensure that the 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;
- 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 Detection	Tolerance
Flow	m^3/s	-	-	-	-
Temperature	^0C	-	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 ^0C	µS/cm	30	300	5	5 or 10%
Alkalinity	mmol/l	1	10	0.1	0.1
Ammonium (NH_4^+ -N)	mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO_2^- -N)	mg/l	0.005	0.02	*0.005*	*0.005 or 20%*
Nitrate (NO_3^- -N)	mg/l	0.2	1	0.1	0.1 or 20%
Organic Nitrogen	mg/l	0.2	2	0.1	0.1 or 20%
Ortho- Phosphate (PO_4^{3-} -P)	mg/l	0.02	0.2	0.005	0.005 or 20%
Total Phosphorus	mg/l	0.05	0.5	0.01	0.01 or 20%
Sodium (Na^+)	mg/l	1	10	0.1	0.1 or 10%
Potassium (K^+)	mg/l	0.5	5	0.1	0.1 or 10%
Calcium (Ca^{2+})	mg/l	2	20	0.2	0.1 or 10%
Magnesium (Mg^{2+})	mg/l	0.5	5	0.1	0.2 or 10%
Chloride (Cl^-)	mg/l	5	50	1	1 or 10%
Sulphate (SO_4^{2-})	mg/l	5	50	5	5 or 20%
Iron (Fe)	mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese (Mn)	mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc (Zn)	µg/l	10	100	3	3 or 20%
Copper (Cu)	µg/l	10	100	3	3 or 20%
Chromium (Cr) – total	µg/l	10	100	3	3 or 20%
Lead (Pb)	µg/l	10	100	3	3 or 20%
Cadmium (Cd)	µg/l	1	10	*0.5*	*0.5 or 20%*
Mercury (Hg)	µg/l	1	10	0.3	0.3 or 20%
Nickel (Ni)	µg/l	10	100	3	3 or 20%
Arsenic (As)	µg/l	10	100	3	3 or 20%
Aluminium (Al)	µg/l	10	100	*10*	10 or 20%
BOD_5	mg/l	0.5	5	*0.5*	*0.5 or 20%*
COD_{Cr}	mg/l	10	50	*10*	*10 or 20%*
COD_{Mn}	mg/l	1	10	0.3	0.3 or 20%
DOC	mg/l	0.3	1	*0.3*	*0.3 or 20%*
Phenol index	mg/l	0.005	0.05	*0.005*	*0.005 or 20%*
Anionic active surfactants	mg/l	0.1	1	0.03	0.03 or 20%
Petroleum hydrocarbons	mg/l	0.02	0.2	*0.05*	*0.05 or 20%*
AOX	µg/l	10	100	10	10 or 20%
Lindane	µg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	µg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine	µg/l	0.1	1	0.02	0.02 or 30%
Chloroform	µg/l	0.1	1	0.02	0.02 or 30%
Carbon tetrachloride	µg/l	0.1	1	0.02	0.02 or 30%
Trichloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Tetrachloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Total Coliforms (37 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Coliforms (44 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Streptococci	10^3 CFU/100 ml	-	-	-	-
Salmonella sp.	in 1 litre	-	-	-	-
Macrozoobenthos	no. of taxa	-	-	-	-
Macrozoobenthos	Sapr. index	-	-	-	-
Chlorophyll – a	µg/l	-	-	-	-

4. Description of TNMN

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

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

4.3 Analytical Quality Control (AQC)

The analytical methods 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 require each laboratory to use the same method, provided the laboratory could demonstrate that the method in use (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 were using would be acceptable.

It is good practice that targets for analytical accuracy define the standard of accuracy necessary for the task in hand. Therefore, two key concentration levels - the minimum level of interest and the principal level of interest – were defined for each determinand. These levels define the aims of the monitoring programme and can be used to establish the performance needed from analytical systems used in the laboratories involved in TNMN, assuming that the aims of the programme will be satisfied provided that

- relatively few results are reported as ”less than” the minimum level;
- the accuracy achieved at the principal level is not worse than ± 20% of the principal level.

4. Description of TNMN

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 done 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 the laboratory performance of the National Reference Laboratories and 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.

4.3.1. Performance testing in the Danube laboratories

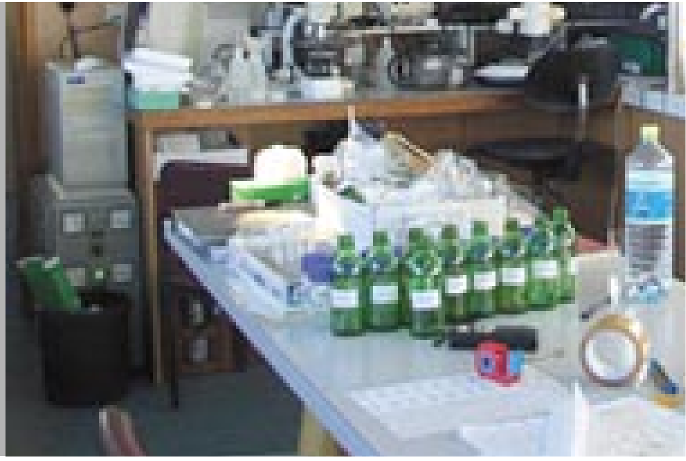
The organisation of inter-laboratory comparison in the monitoring of the Danube under the Bucharest Declaration Danube was agreed in 1992. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered and took the responsibility for organising the first study under the name of QualcoDanube. 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, orthophosphates and total-P) as well as different metals, including Fe, Mn, Ca, Mg, Cd, Cu, Hg, Pb, Ni and Zn. In 1996 the QualcoDanube proficiency testing scheme was extended to the National Reference Laboratories (NRL) established for Trans-National Monitoring Network (TNMN) and the 1996/2 distribution already included all Danubian laboratories - 11 NRLs and 18 national laboratories - participating in the implementation of TNMN. This distribution was further extended to six laboratories responsible for pollution monitoring in the area of the Black Sea.

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

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 sediments in addition to the artificial concentrates, and the analysis were extended to anionic active surfactants.

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

In 1998, four distributions had been taken with selected determinands and types of samples similar to those of the previous years.



4. Description of TNMN

In 1999, water and sediment samples were distributed four times.

The results and their evaluation during the four distributions have been published in the summary report (QualcoDanube, AQC for Water Labs in the Danube River Basin, Summary Report 1999, VITUKI Plc., Budapest).

In the QualcoDanube performance testing scheme, the Youden-pair evaluation technique was usually followed.

The inter-laboratory comparative results are discussed separately for the different determinands. It was quite an achievement that results were reported by 31 out of 33 laboratories. Most of the laboratories reported the results of the analysis of nutrients and general determinands. Only eight laboratories provided results of lindane, DDT and six laboratories reported results of AOX.

Results of heavy metal analysis were reported by 14-22 laboratories.

General determinands of water samples

Chlorides, sulphate and total hardness were analysed in real surface water samples.

Results provided by laboratories were relatively good in the case of total hardness, but a relatively large number of data was rejected for chlorides and sulphates. It is worth mentioning that the rejected results had been generated by the same four laboratories and that they were due to systematic errors, especially in the case of chloride.

Organic pollutants in water samples

Besides chemical oxygen demand (with permanganate and dichromate method), biological oxygen demand, anionic active surfactants and petroleum hydrocarbons, AOX, lindane and DDT were analysed.

The results of COD (chemical oxygen demand with permanganate method and dichromate method) showed a significant systematic error in the case of real surface water. The reported values of BOD demonstrated mainly systematic error. The results of anionic active surfactants were slightly better than earlier. It is worth mentioning that the same three laboratories supplied quite bad results during both distributions.

AOX (Adsorbable Organic Halogens): this determinand was analysed for the first time in the frame of QualcoDanube inter-calibration programme. Altogether eight laboratories reported results that – except for one - were quite good.

Lindane: relatively few laboratories (12), mainly NRLs, reported analytical results, which were rather scattered. There were some results biased either by erroneous calculation and/or misreported expression unit (maybe µg/l instead of mg/l). In the case of lindane, the assigned value was identical to the lindane concentration of the prepared solution. Laboratories usually reported values below that assigned.

DDT: samples for DDT determination were analysed by 12 laboratories. The results were scattered similarly as in the case of lindane. The reason could again lie in the faulty expression of units.

4. Description of TNMN

The laboratories in the scale of the graph fell into two groups: one group reported higher values than the assigned value (three laboratories) and the other group reported lower concentrations (four laboratories), most likely due to wrong calculation. Theoretical value from the preparation of the solutions was used for evaluation.

Petroleum hydrocarbons (distributed as an extract): petroleum hydrocarbons extracts were analysed during the first distribution in 1999. The results were more acceptable than the year before, but they showed a systematic error.

Organic pollutants in sediment samples

The results of petroleum hydrocarbons were scattered in two different groups. The first group showed deviation in the negative direction while the data of the second group showed higher values (Figure 4.3.1.1).

Nutrients in water samples

In the case of ammonium-N, results from real surface water showed relatively high variation and a significant systematic error, while analytical data were quite good in the case of synthetic samples (none of thirty results was rejected). The results of nitrate-N of the second distribution showed that some laboratories most probably had not corrected the pH of real surface water samples before analysis.

The results of ortho-phosphates (three distributions) showed good conformity, but were influenced by a slight systematic error. Slight systematic error was observed also in case of total phosphorus.

Nutrients in sediment samples

Relatively few laboratories analysed total phosphorus and total nitrogen in sediment samples.

Total-N: in case of this determinand about half of the reported values was rejected. The remainders showed both systematic and random errors. The most likely the reason for these discrepancies was incorrect analyses and not the mineralisation, because the same sediment had to be investigated for both total-P and total-N.

Total-P: the results supplied by 14 laboratories were good and none were rejected.

Heavy metals in water

Cadmium, chromium and copper were analysed in water samples. The results of cadmium and copper were satisfactory (except the last cadmium distribution), but the results of chromium were strongly influenced by systematic error.

Heavy metals in sediment

Eight heavy metals were analysed in sediment samples. The best results were achieved in the case of copper - there was no rejected value. The analytical results of nickel were relatively good, whilst the results of lead were strongly influenced by systematic error and so were those of zinc, cadmium and chromium.

In the case of mercury, the analytical performance was slightly better than in the previous year. Eleven laboratories reported results for

arsenic, which showed either extremely high or extremely low values. The most likely reason for these discrepancies was the different way of mineralisation and/or incorrect analysis (Figure 4.3.1.2).

Conclusions

The four QualcoDanube distributions in 1999 provided information on the performance of laboratories participating in the implementation of Trans-National Monitoring Network (TNMN) in the Danube River Basin.

In addition to regularly analysed determinands, distributions in 1999 provided specific organic determinands in waters for quantitative determinations as being involved in the TNMN for the River Danube, (e.g. lindane, DDT). The results of these determinands are not satisfactory and nor are the results of petroleum hydrocarbons in both water and sediment. In the case of water samples, the analyses extracts were distributed so that the discrepancies of results most likely originated from incorrect analyses and/or unsuitable analytical methods.

The distributed samples were generally preserved (regularly by acid and/or by sterilisation depending on determinands), so before analyses pH checking and adjustment should have been done. This simple but important step might have been left out of consideration, e.g., at NO_3^--N determination. The results of some laboratories could be out of range due to this reason.

In the case of analyses of metals, particularly in sediment, the reason for discrepancies could lie in the different way of mineralisation, or in systematic errors during analyses.

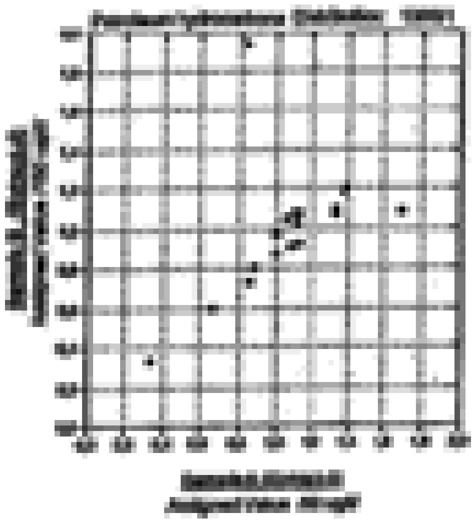
Overall, most determinations were influenced by systematic error.

Some laboratories regularly reported outlying results for certain determinands. They had to pay attention to the whole process of analysis of these determinands (analytical method, standard materials, etc.).

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

It is expected that the performance of laboratories analysing samples in the frame of TNMN will further improve and that the comparability of water quality monitoring results in the River Basin and related regions will be ensured.

Figure 4.3.1.1: Variation in the reported/assigned value of petrolueum hydrocarbons in sediment samples.



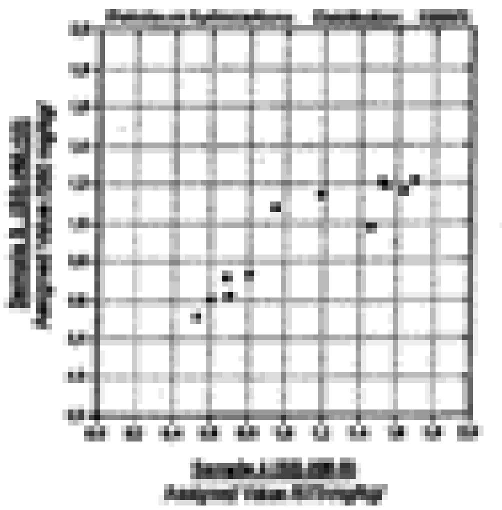
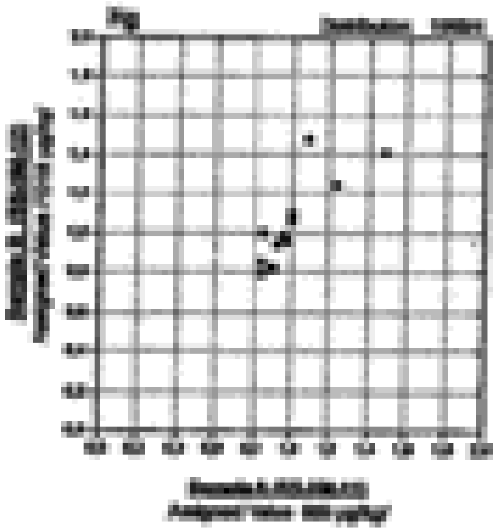
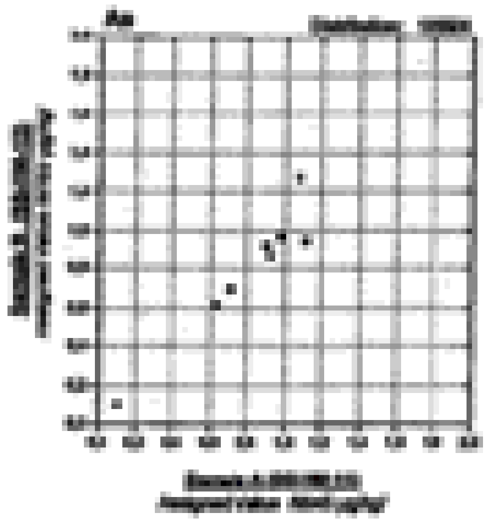


Figure 4.3.1.2: Variation in the reported values of mercury and arsenic in sediment samples.





4.4 TNMN Data Management

Data storage, exchange, retrieval and analysis have been dealt with in the frame of TNMN data management and so have other types of data processing activities involved in information management. On the basis of a relational database, in-stream water quality data of TNMN are organised in a well-defined structure using rules of reference integrity. This yielded a system of joined tables with information about TNMN. Data exchange is organised quarterly according to a standard operational procedure. A special data exchange file format (DEFF) is used for this purpose.

The above summary briefly describes the current activities guided by the following principles and needs:

- to concentrate on the quality of obtained data;
- to introduce a process of transferring data from the national information systems to a Central Information Point (CIP);
- to build on the existing experience in individual countries rather than try to force all participating countries to adapt their national information systems and procedures;
- to promote and increase the use and processing of data into information by introducing dedicated 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) that - after a training course in 1996 – all countries 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.

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

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 description of monitoring stations was included in TNMN database

4. Description of TNMN

The standard operational procedure (SOP) for the exchange of DEFF data starts with data generation (sampling and analysis) and their input in the system. This 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 processing (e.g. the Yearbook).

During 1996 and 1997, TNMN data were regularly collected from Germany, Austria, the Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Bulgaria and Romania. Data from Ukraine and Moldavia have been regularly provided since 1998.

5. Tables of statistical data from TNMN stations

The determinands measured in 1999, the fourth year of the operation of TNMN - Phase 1, covered 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.

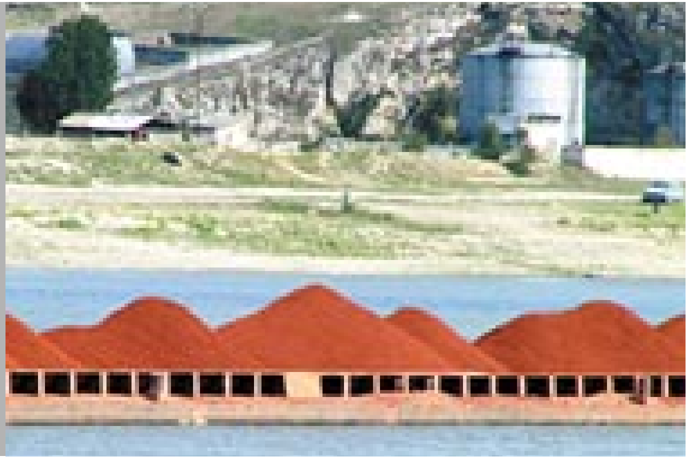
The 61 stations included in TNMN - Phase 1 are characterised on the following station list and station map (Figure 5.1). The station list specifies the official national data, which are not harmonised in all cases. There are still inconsistencies concerning catchment area and altitude related to the stations measured by both neighbouring countries, most probably due to different national calculation procedures. It was recommended that these problems should be solved and that the data should be made consistent within the transboundary commissions.
Each station can have up to three sampling points named L, M and R (Left, Middle, Right). TNMN - Phase 1 consists of 93 sampling points.

In 1999, data were available from 57 stations including a total of 81 sampling points. At some stations, no measurements were performed at all due to a lack of proper equipment or restricted access for political reasons. There are still no data from Bosnia-Herzegovina. Data from Ukraine and Moldava have been provided and presented in yearbooks since 1998.

Basic statistical characteristics based on available data from 81 sampling points mentioned above are presented in 81 tables in Annex 1 according to the following legend. 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 1999
Mean	Arithmetical mean of the measurements done in the year 1999
Max	Maximum value of the measurements done in the year 1999
C50	50 percentile of the measurements done in the year 1999
C90	90 percentile of the measurements done in the year 1999
Q1	Arithmetical mean of the measurements done in the first quarter of the year 1999
Q2	Arithmetical mean of the measurements done in the second quarter of the year 1999
Q3	Arithmetical mean of the measurements done in the third quarter of the year 1999
Q4	Arithmetical mean of the measurements done in the fourth quarter of the year 1999

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 value of detection limit was used in statistical processing of the data. In case all the measurements in the year were below the detection limit, only minimum, mean and maximum values were put in the table without any other statistical data. Similarly, in case of only four or fewer measurements of particular determinand in a year, only minimum, mean and maximum values were calculated and presented in tables in Annex 1.

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 12	16 59 20	79	150	9725	L2100	R
CZ02	/Morava/Dyje	Breclav	48 48 12	16 51 20	17	155	12540	L2120	R
SK01	Danube	Bratislava	48 8 10	17 7 40	1869	128	131329	L1840	M
SK02	Danube	Medvedov/Medve	47 47 31	17 39 6	1806	108	132168	L1860	M
SK03	Danube	Komarno/Komarom	47 45 17	18 7 40	1768	103	151961	L1870	M
SK04	/Váh	Komarno	47 46 41	18 8 20	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov	47 47 31	17 39 6	1806	108	131605	L1470	M
H02	Danube	Komarom/Komarno	47 45 17	18 7 40	1768	101	150820	L1475	M
H03	Danube	Szob	47 48 44	18 51 42	1708	100	183350	L1490	LMR
H04	Danube	Dunafoldvar	46 48 34	18 56 2	1560	89	188700	L1520	LMR
H05	Danube	Hercegszanto	45 55 14	18 47 45	1435	79	211503	L1540	LMR
H06	/Sio	Szekszard-Palank	46 22 42	18 43 19	13	85	14693	L1604	M
H07	/Drava	Dravaszabolcs	45 47 00	18 12 22	78	92	35764	L1610	M
H08	/Tisza	Tiszasziget	46 9 51	20 5 4	163	74	138498	L1700	LMR
H09	/Tisza/Sajo	Sajopuspoki	48 16 55	20 20 27	124	148	3224	L1770	M
SI01	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1390	L
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	135	10878	L1330	R
HR01	Danube	Batina	45 52 27	18 50 03	1429	86	210250	L1315	M
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M
HR04	/Drava	Botovo	46 14 27	16 56 37	227	123	31038	L1240	M
HR05	/Drava	D.Miholjac	45 46 58	18 12 20	78	92	37142	L1250	R
HR06	/Sava	Jesenice	45 51 40	15 41 48	729	135	10834	L1220	R
HR07	/Sava	us. Una Jasenovac	45 16 02	16 54 52	525	87	30953	L1150	L
HR08	/Sava	ds. Zupanja	45 02 17	18 42 29	254	85	62890	L1060	M
BIH01	/Sava	Jasenovac	45 16 0	16 54 36	500	87	38953	L2280	M
BIH02	/Sava/Una	Kozarska Dubica	45 11 6	16 48 42	16	94	9130	L2290	M
BIH03	/Sava/Vrbas	Razboj	45 3 36	17 27 30	12	100	6023	L2300	M
BIH04	/Sava/Bosna	Modrica	44 58 17	18 17 40	24	99	10308	L2310	M
RO01	Danube	Bazias	44 47 55,57,58	21 23 24,40,54	1071	70	570896	L0020	LMR
RO02	Danube	Pristol/Novo Selo Harbour	44 11 18,23,29	22 45 57,64,69	834	31	580100	L0090	LMR
RO03	Danube	us. Arges	44 4 25	26 36 35	432	16	676150	L0240	LMR
RO04	Danube	Chiciu/Silistra	44 7 18	27 14 38	375	13	698600	L0280	LMR
RO05	Danube	Reni-Chilia/Kilia arm	45 28 50	28 13 34	132	4	805700	L0430	LMR
RO06	Danube	Vilkova-Chilia arm/Kilia arm	45 24 42	29 36 31	18	1	817000	L0450	LMR

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

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

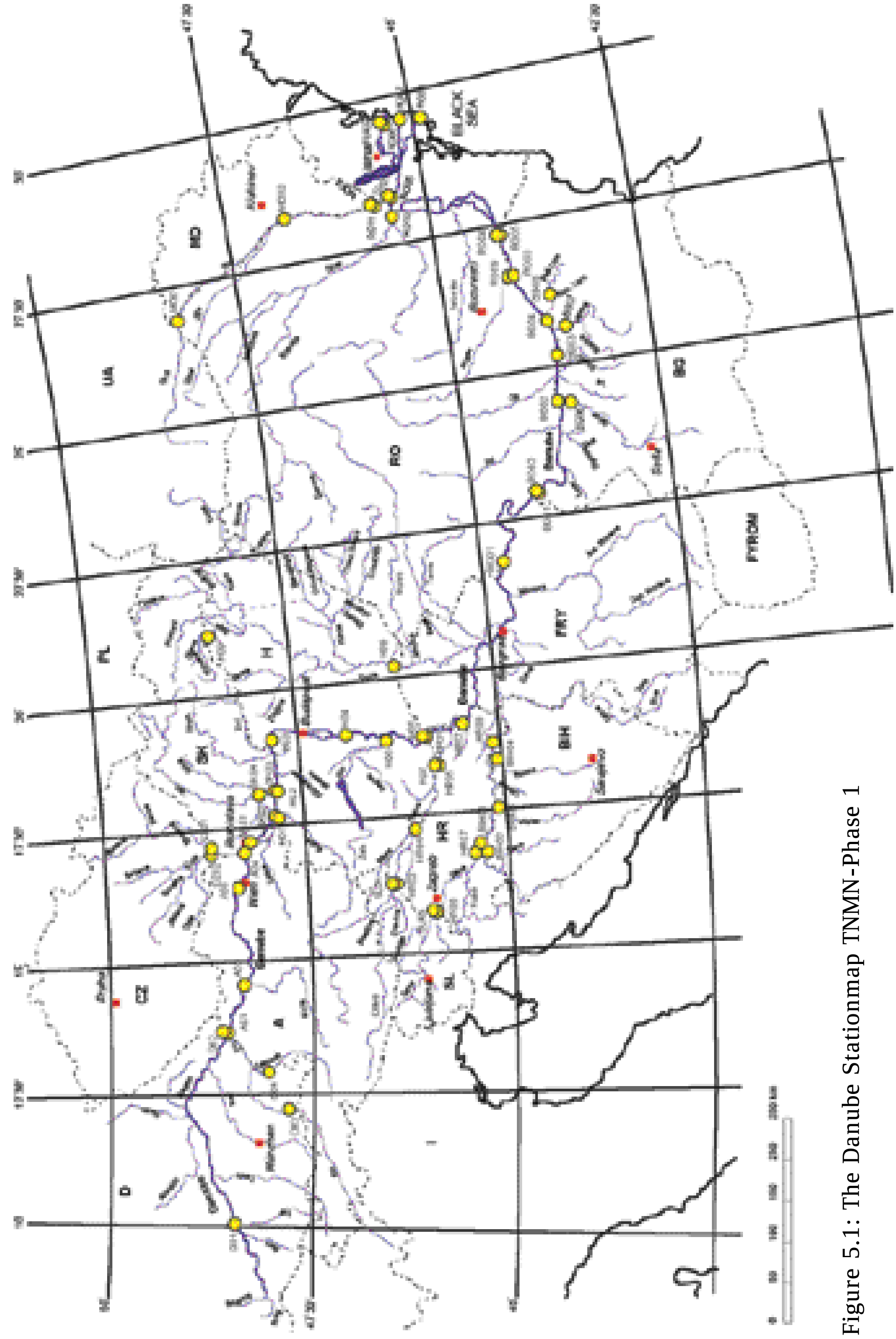


Figure 5.1: The Danube Stationmap TNMN-Phase 1

5. Tables of statistical data from TNMN stations

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

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

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

When looking at the water quality data presented in the Yearbook, one should take into account the results of QualcoDanube intercalibration studies because 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 must also be pointed out that methods for measurements of microbiological and biological determinands have not yet been fully harmonised.

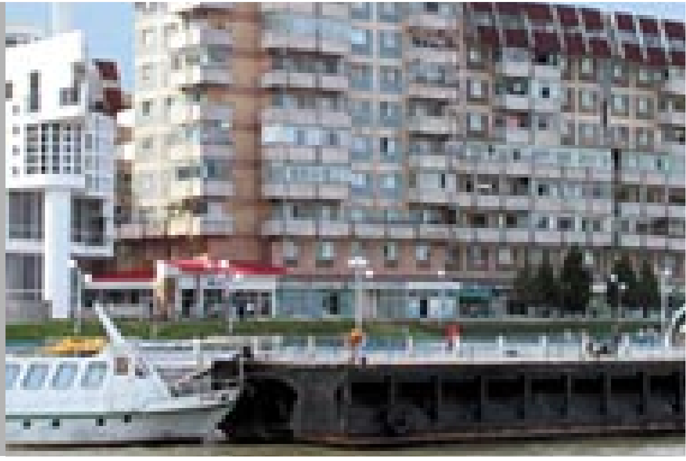
Concerning oxygen regime determinands, the major indicators include dissolved oxygen, BOD_5 and COD_{Cr}.

Dissolved oxygen content was measured at all 81 sampling points generating 1999 data. The concentration range varied from 4,5 – 15,3 mg/l (annual means 6,9 – 11,1 mg/l) in the Danube River itself, and from 2,9 - 15,3 mg/l (annual means 6,4 - 11,5 mg/l) in its tributaries.

BOD_5 characterising content of biodegradable organic substances in water was measured at all 81 sampling points, but QualcoDanube intercalibration studies showed a systematic error also discovered in the previous years. BOD_5 values were in 1999 in the range from 0,5 to 16,8 mg/l (annual means 1,3 - 4,5 mg/l) in the Danube River and from 0,5 to 10,5 mg/l (annual means 1,2 - 6,9 mg/l) at sampling points located along the tributaries.

CODCr is a determinand in which a significant systematic error was discovered in QualcoDanube intercalibration testing. It was measured at 77 sampling points, with concentrations varying from 0,4 to 61,0 mg/l (annual means 9,8 - 21,9 mg/l) in the Danube River and from 2,8 to 80,0 mg/l (annual means 5,9 - 28,6 mg/l) in the tributaries.

Nutrient status of the Danube River and its tributaries is very important because nitrogen is blamed as the major cause of eutrophication in the Danube Delta and the Black Sea. While inorganic fractions of nitrogen like ammonium-nitrogen and nitrate-nitrogen were measured at all 81 sampling points in 1999, information on organic nitrogen was available only from countries in the middle part of the Danube River Basin - from the Czech Republic down to Croatia and several stations in Bulgaria.



5. Tables of statistical data from TNMN stations

The content of ortho-phosphate phosphorus and total phosphorus was measured at 77 and 79 sampling points respectively. The results of QualcoDanube intercalibration studies of these determinands in real water samples also proved unsatisfactory.

Ammonium-N was observed in the range from 0,01 to 1,72 mg/l (annual means 0,06 – 0,45 mg/l) in the Danube itself and from 0,01 to 3,04 mg/l (annual means 0,03 - 1,82 mg/l) in the tributaries.

Nitrate-N concentration ranged from 0,09 to 5,31 mg/l (annual means 1,08 - 3,18 mg/l) in the Danube River and from 0,15 to 11,00 mg/l (annual means 0,57 – 7,51 mg/l) in the tributaries.

Concentrations of ortho-phosphate-P were in the range from 0,005 to 0,870 mg/l (annual means 0,027 – 0,241 mg/l) in the Danube River and from 0,003 to 1,400 mg/l (annual means 0,016 – 0,738 mg/l) in its tributaries.

Total phosphorus concentrations were in the range from 0,02 to 1,36 mg/l (annual means 0,07 – 0,35 mg/l) in the Danube River and from 0,005 to 2,61 mg/l (annual means 0,03 – 0,99 mg/l) in the tributaries.

The statistical results presented in the tables in Annex 1 indicate that the concentration ranges of measured determinands were overall larger in the tributaries than in the Danube itself. The highest levels of pollution were typical of 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-P were observed in the majority of cases 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 surface waters in the Danube River Basin, the assessment based on the available data of TNMN –Phase 1 from 1999 are 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_5, ortho-phosphate-phosphorus PO_4^{3-}-P, ammonium-nitrogen NH_4^+-N and nitrate-nitrogen NO_3^--N respectively.

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

The sampling sites at which the presented water quality determinand was measured less than 11 times per year are indicated on the map with a smaller circle.

As in the previous years, the colour coding used for BOD_5 and PO_4^{3-}-P presentation in the maps and tables of this chapter corresponds to the classification (5 class-system) 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).

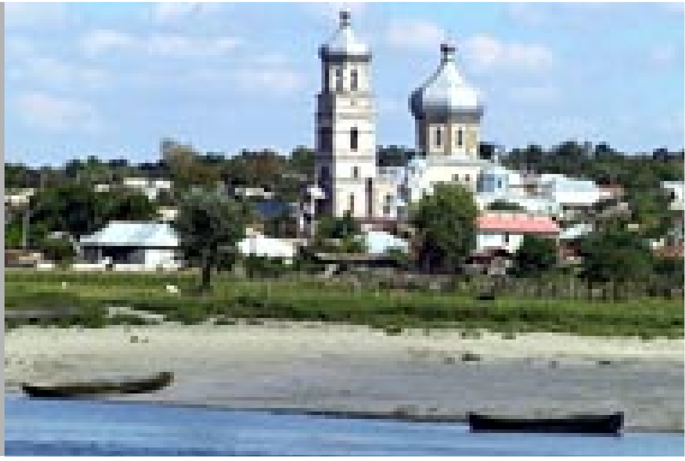
The classification of NO_3^--N is also based on water quality standards proposed by this report, but for determinand NH_4^+-N the proposed classification was considered very weak taking into account the negative effects of ammonia on aquatic ecosystem. Therefore, it was agreed to use for presentation of NH4+-N limit values from "Proposal for the Classification for TNMN Purposes", prepared by MLIM-ESG in 2001.

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

Determinand	Unit	Quality class I blue	 II green	 III yellow	 IV red	 V black
Biological oxygen demand [1] (BOD_5)	mg/l	<3	5	9	15	>15
Ortho-Phosphate-Phosphorus [1] (PO_4^{3-}-P)	mg/l	0.05	0.1	0.2	0.5	>0.5
Ammonium-Nitrogen [2] (NH_4^+-N)	mg/l	0.2	0.3	0.6	1.2	>1.2
Nitrate-Nitrogen [1] (NO_3^--N)	mg/l	1	5	10	25	>25

1) Water Quality Targets and Objectives for Surface Waters in the Danube Basin – Project EU/AR/203/90; Final Report (1997).
2) Proposal for classification for TNMN purposes, prepared by MLIM/SG in 2001.

6. Maps of selected determinands



BOD_5 is a commonly used indicator for biodegradable organic pollution, which affects the oxygen regime in water. Nevertheless the interpretation of results has some difficulties concerning possible toxic effects which can cause decreasing of BOD_5 values.

The results presented in Figure 6.1 show that at 93 % of all monitoring stations the average concentrations of BOD_5 corresponded to class I or II. It means that at those monitoring stations the average values of BOD_5 were not higher than 5 mg/l. All monitoring stations along the Danube River itself were within the ranges of class I and II. Higher average values of BOD_5 were identified in four tributaries, corresponding to class III (see also Table 6.2).

In the upper part of the Danube River itself, water indicated class I exclusively; from the middle down to the lower part of the River class I - II was observed.

Compared to the previous year 1998, the percentage of stations corresponding to class I or II did not change, but the percentage of stations along the Danube River itself within the range of class I was higher (65 % in 1999 against 56 % in 1998).

Water Quality class	Monitoring sites (Danube) number within class	% of total	Monitoring sites (tributaries) number within class	% of total	Monitoring sites (Danube + tributaries) number within class	% of total
I	20	65	16	62	36	63
II	11	35	6	23	17	30
III	0	0	4	15	4	7
IV	0	0	0	0	0	0
V	0	0	0	0	0	0

Table 6.2: TNMN 1999 - average concentrations of BOD_5: distribution of monitoring stations according to the classification listed in Table 6.1.

6. Maps of selected determinands

Nutrients are very important as they are responsible for the process of eutrophication in lakes, rivers and the receiving sea. The concentrations of PO_4^{3-}-P, NH_4^+-N and 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.

Instead of total phosphorus, ortho-phosphate-phosphorus was chosen to be presented 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.

On the basis of results presented in Figure 6.2 and Table 6.3 it can be concluded that - taking into account all monitoring stations - the average PO_4^{3-}-P concentrations were in the range of class I and II at 82 % of the sampling sites.

In the Danube itself, the average PO_4^{3-}-P concentrations corresponded to class I and II at 89 % of the sampling stations.

Concerning TNMN monitoring stations located on the tributaries, a higher variability in the concentration of PO_4^{3-}-P was observed there. Along the tributaries, the average PO_4^{3-}-P concentrations corresponded to class I and II at 72 % of the monitoring stations; at 8 % of the monitoring stations they corresponded to class III and at 20 % of the monitoring stations the averagePO_4^{3-}-P concentrations were in the range of classes IV – V.

The changes of PO_4^{3-}-P content along the Danube River itself can be seen from presentation of results in Figure 6.2. The water of the Danube River corresponds to class I in the whole upper part of river, middle part of Danube river can be characterised by classes I-II and lower part by classes I - III.

The percentage of monitoring stations that correspond to class I or II did not change in comparison with 1998, but the percentage of stations within the range of class I along the Danube River increased from 52 % in 1998 to 71 % in 1999.

Figure 6.3 shows the average concentrations of NH_4^+-N. At most monitoring stations (75 %) the average concentrations measured in 1999 indicated class I or II. In the Danube itself, 87 % of the monitoring stations were within the range of class I or II and 13 % corresponded to class III.

61% of the monitoring stations located along the tributaries corresponded to class I or II; 35% were in class III (see Table 6.4).

Compared to the previous year, the percentage of stations indicating class I or II increased slightly from 63 % in 1998 to 75 % in 1999. The percentage of stations located along the Danube River, characterised by class I, was also higher - 77 % in comparison with 59% in 1998.

Table 6.3: TNMN 1999 - average concentrations of PO_4^{3-}-P: distribution of monitoring stations according to the classification listed in Table 6.1.

Water Quality class	Monitoring sites (Danube) number within class	% of total	Monitoring sites (tributaries) number within class	% of total	Monitoring sites (Danube + tributaries) number within class	% of total
I	20	71	10	40	30	57
II	5	18	8	32	13	25
III	3	11	2	8	5	9
IV	0	0	4	16	4	8
V	0	0	1	4	1	2

Table 6.4: TNMN 1999 - average concentrations of NH_4^+-N: distribution of monitoring stations according to the classification listed in Table 6.1.

Water Quality class	Monitoring sites (Danube) number within class	% of total	Monitoring sites (tributaries) number within class	% of total	Monitoring sites (Danube + tributaries) number within class	% of total
I	24	77	12	46	36	63
II	3	10	4	15	7	12
III	4	13	9	35	13	23
IV	0	0	0	0	0	0
V	0	0	1	4	1	2

6. Maps of selected determinands

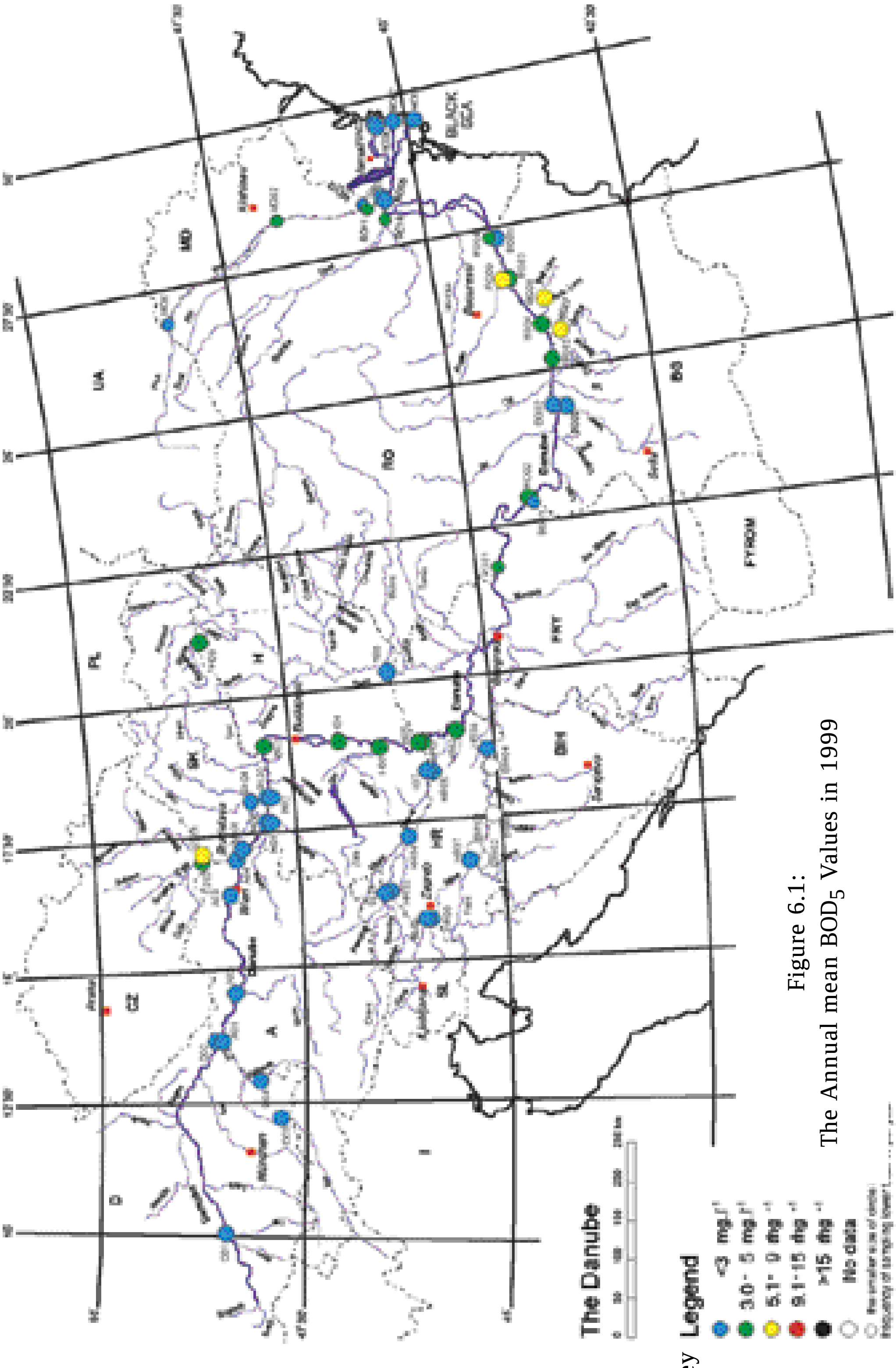
The average concentrations of NO_3^--N were in a rather narrow range, especially in the Danube River (see Figure 6.4). As a result, NO_3^--N average values corresponded to class II in all monitoring stations located along the Danube River and 97 % of the monitoring stations located along the tributaries were within the range of class I and II (see Table 6.5).

The results are comparable to those from the previous year.

Table 6.5: TNMN 1999 - average concentrations of NO_3^--N: distribution of monitoring stations according to the classification listed in Table 6.1.

Water Quality class	Monitoring sites (Danube) number within class	% of total	Monitoring sites (tributaries) number within class	% of total	Monitoring sites (Danube + tributaries) number within class	% of total
I	0	0	3	12	3	5
II	31	100	22	85	53	93
III	0	0	1	4	1	2
IV	0	0	0	0	0	0
V	0	0	0	0	0	0

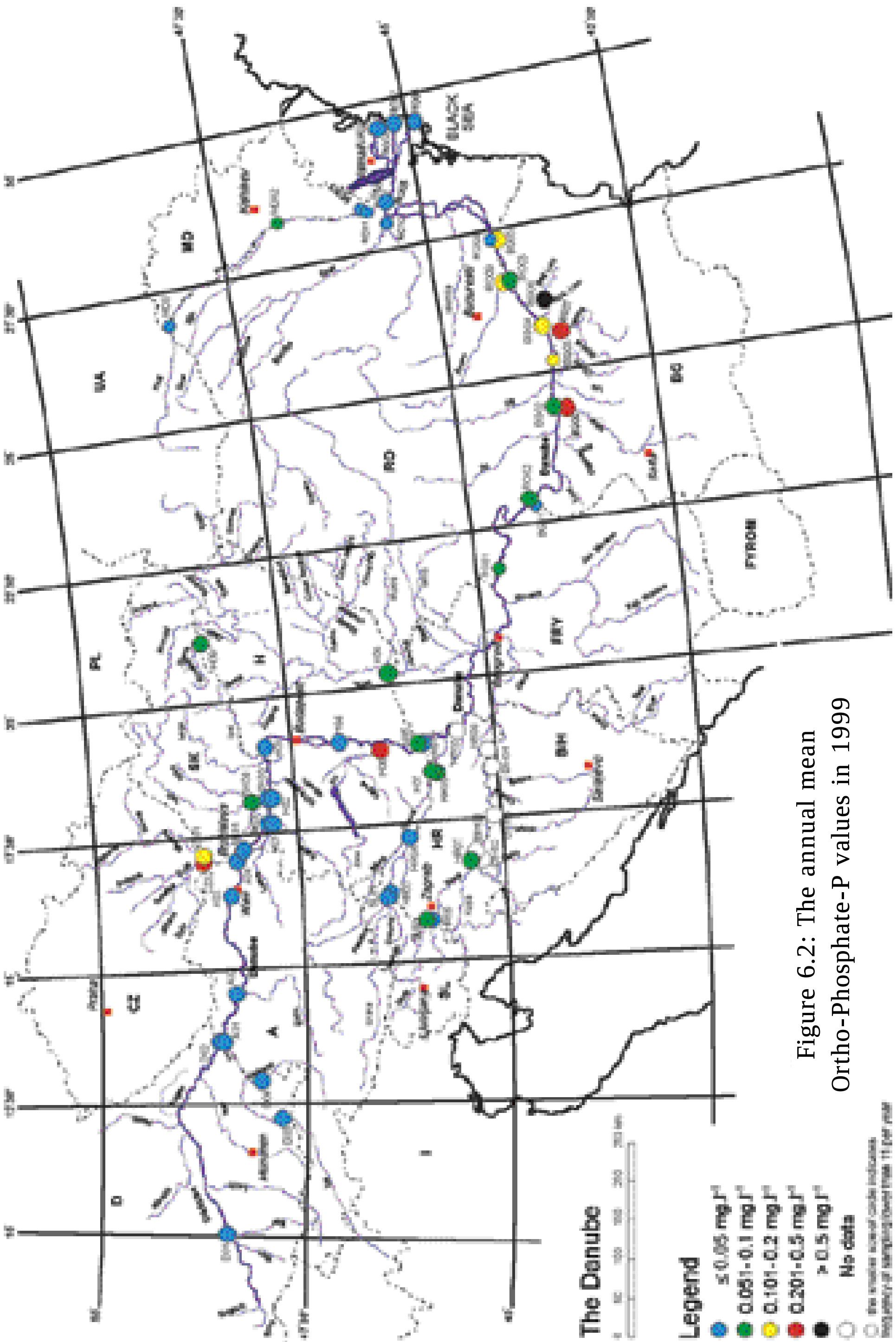
6. Maps of selected determinands



Key

Figure 6.1:
The Annual mean BOD_5 Values in 1999

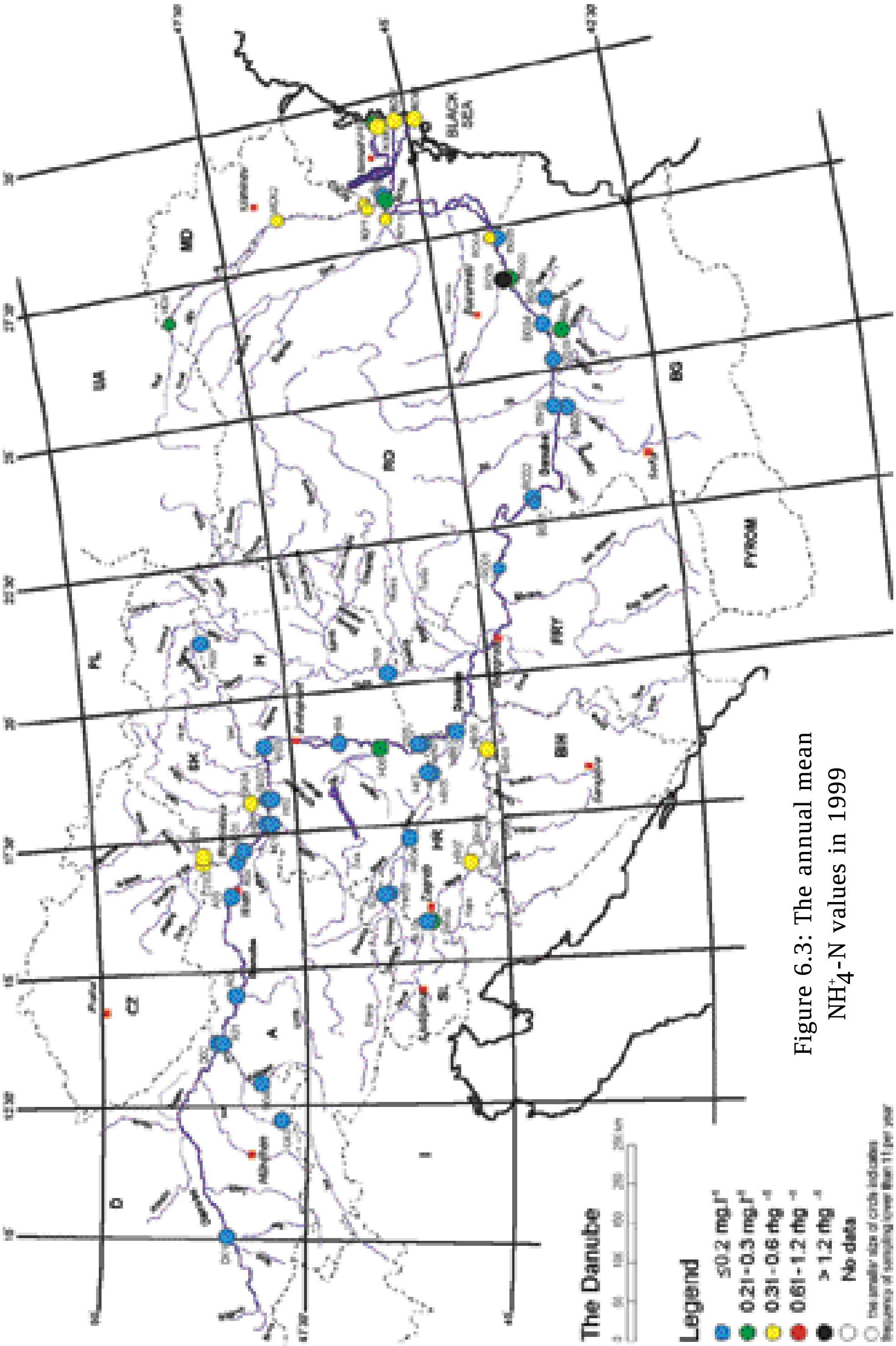
6. Maps of selected determinands



Key

Figure 6.2: The annual mean Ortho-Phosphate-P values in 1999

6. Maps of selected determinands



Key

Figure 6.3: The annual mean NH_4^+-N values in 1999

6. Maps of selected determinands

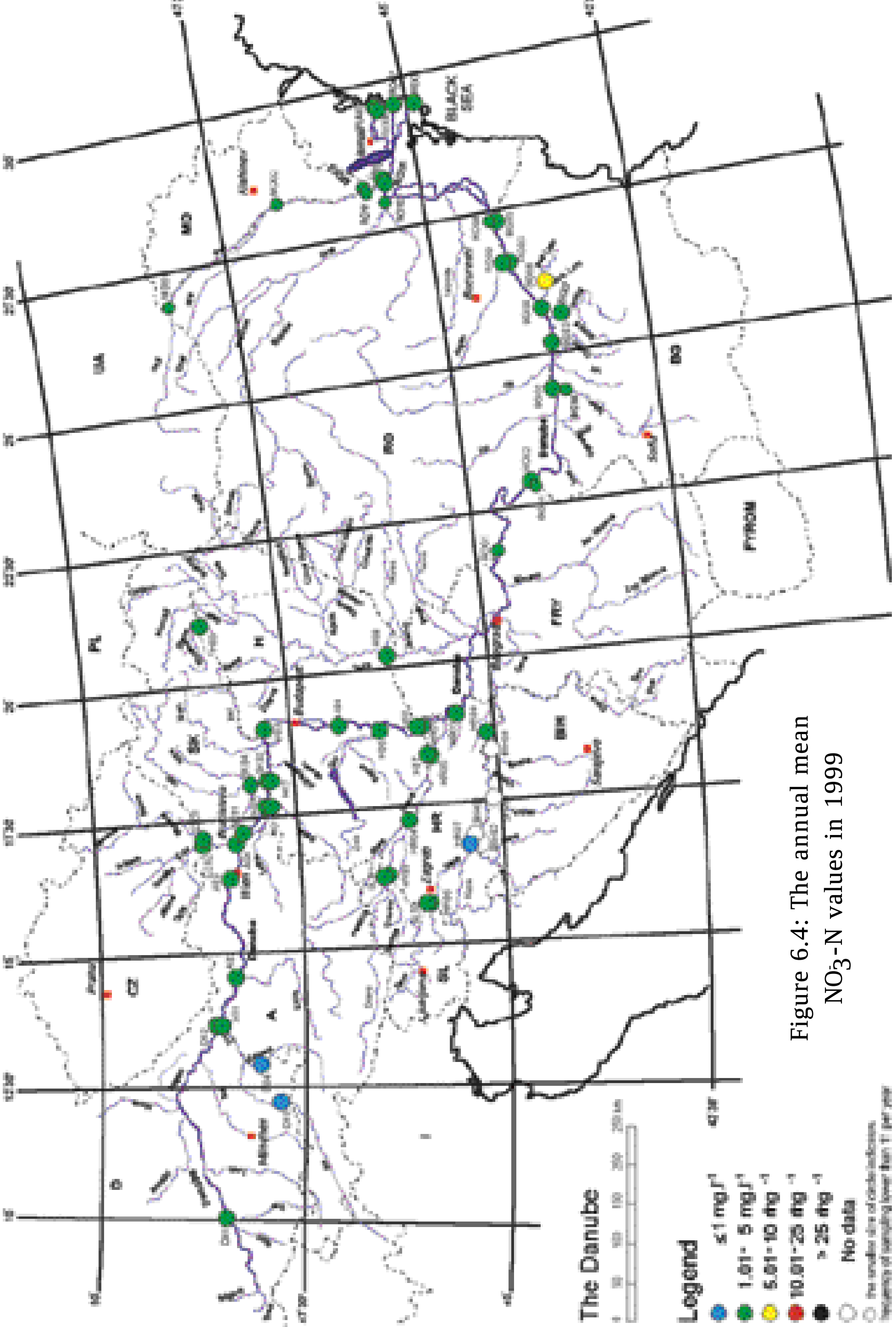


Figure 6.4: The annual mean NO_3-N values in 1999

Key

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 plots 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 the concentration ranges at the stations located at the furthermost 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 there are three sampling sites (left, middle, right) of a monitoring station, only data of the "middle" are shown in the following profiles.

7. Profiles of selected determinands

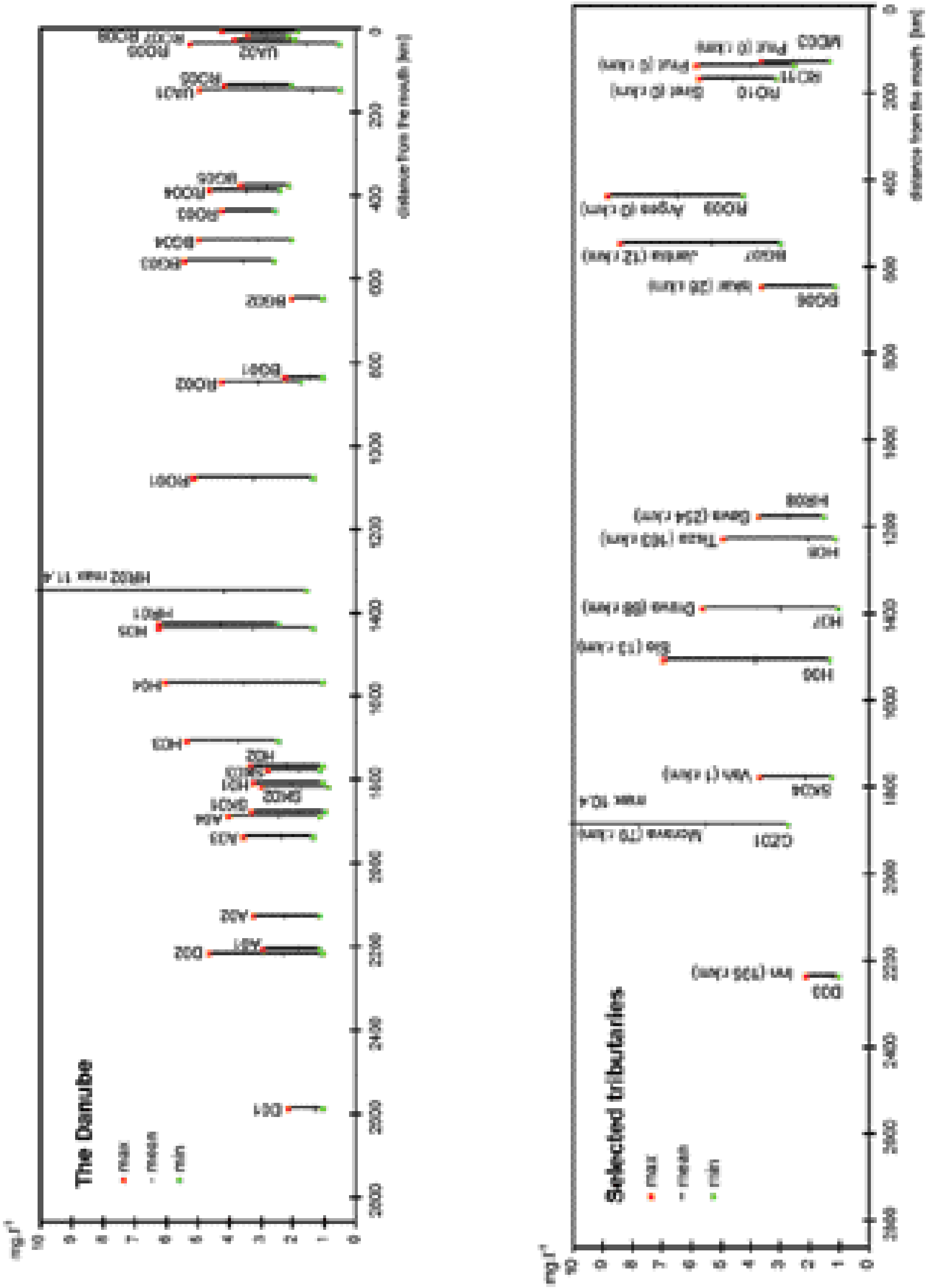


Figure 7.1: The minimum, mean and maximum of BOD_5 in 1999

7. Profiles of selected determinands

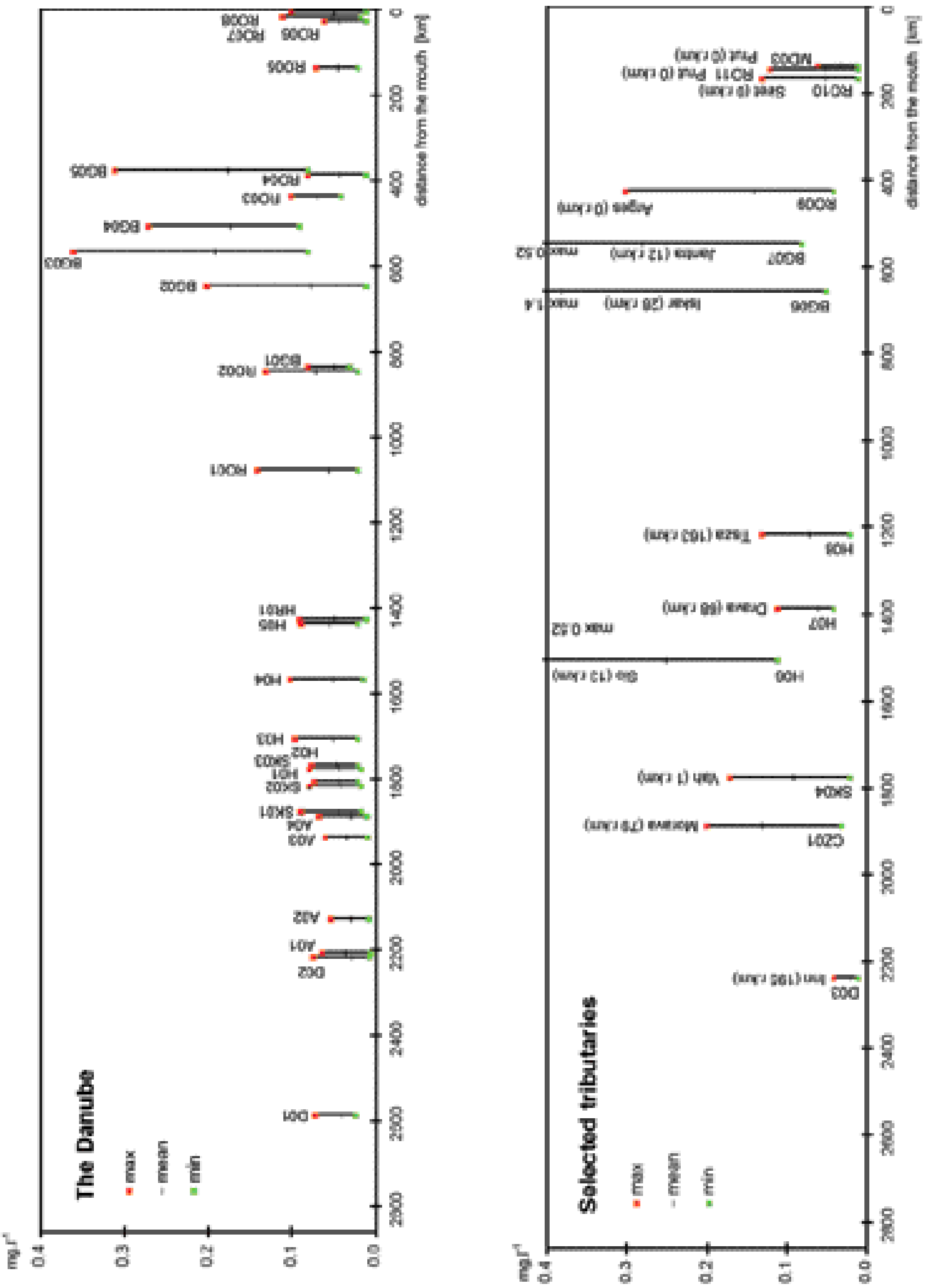


Figure 7.2: The minimum, mean and maximum Ortho-Phosphate-P in 1999

7. Profiles of selected determinands

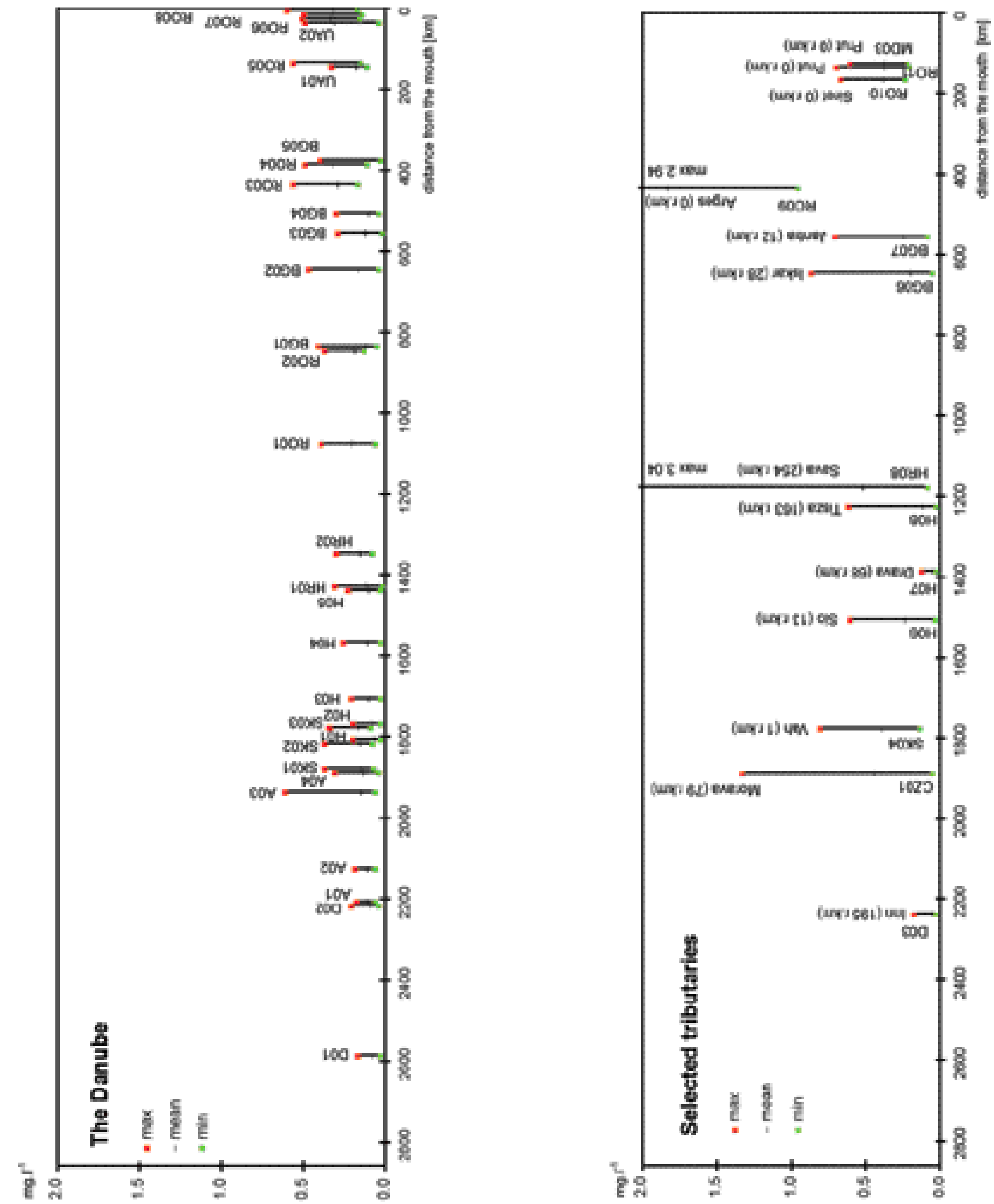


Figure 7.3: The minimum, mean and maximum NH_4^+-N Values in 1999

7. Profiles of selected determinands

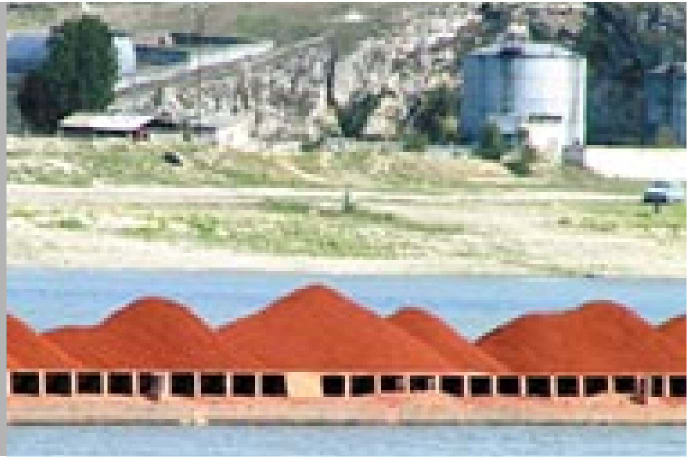
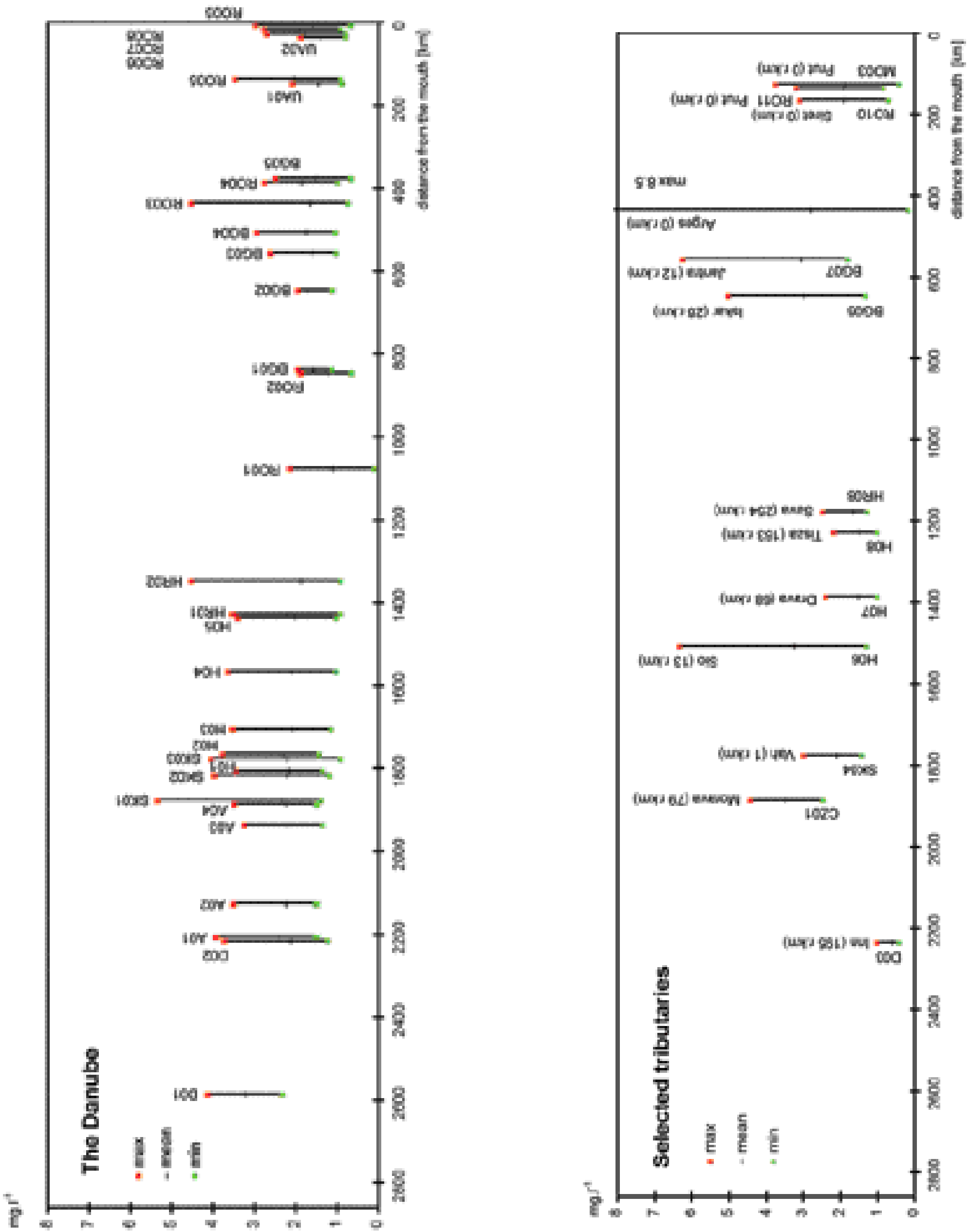


Figure 7.4: The minimum, mean and maximum NO_3-N Values in 1999



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)