UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation in the
Danube River Basin

Final Report
Support for TNMN and EMIS Inventory Harmonization

Project Component 2.2: Development of operational tools for
monitoring, laboratory and information management with
particular attention to nutrients and toxic substances

December 2003

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Table of Content

Executive Summary

This project assisted DRB countries to develop, upgrade and reinforce capacities of tools for emission control and monitoring of water quality. Both water quality assessment and emission control (assessment of pressures/programme of measures) are key issues in implementation of the EU WFD. The implementation process has a high priority in the work of the ICPDR. Therefore, current activities of those ICPDR expert groups responsible for water quality (MLIM EG) and emission control (EMIS EG) reflect the needs of the EU WFD implementation. In line with the Work Programmes of MLIM and EMIS Expert Groups, following major issues were addressed by the project:

- Development of water quality objectives for nutrients and water quality standards for toxic substances;

- Development of application for pressure /stress (emissions) and impact (water quality/change in ecosystems) analysis, based on MLIM and EMIS databases (TNMN, JDS, EMIS Inventory) including analysis and comparison of data in these databases;

- Improvement of the scope of the Trans-National Monitoring Network and Emission Inventory, including harmonization of their databases, considering EU and DRPC Priority Substances. TNMN related activities included analysis and assessment of TNMN results, development of SOPs and upgrade of web-based databases.

Major deliverables from particular project components are summarized below:

1. Development of a proposal on water quality objectives for nutrients in line with requirements of EU WFD and development of a proposal on water quality standards for toxic substances from DRPC list of priority substances in line with requirements of EU WFD

The study aimed at formulating Environmental Quality Standards (EQSs) for those Danube specific substances that are not included in the list of priority substances of the EU Water Framework Directive. The Danube specific priority substances comprise: total nitrogen (Ntot), total phosphorous (Ptot), ammonium (NH4+), chemical oxygen demand (COD), and the metals As, Cr, Cu and Zn.

For the nutrients (Ntot, Ptot) the study used the following working definition in order to make the WFD's 'good status' description for physico-chemical parameters more operational: "nutrient concentrations such that chances on the occurrence of eutrophication are minimised, or (preferably) avoided". The query into existing systems for water quality assessment and standards resulted in the following preliminary recommendations for EQSs to be used as representing 'good status' thresholds for nutrients: Ntot: 1.0 - 1.5 mg N/l; Ptot: 0.02 – 0.08 mg P/l. Compared to estimated natural background levels for the Danube river (Ntot ˜ 0.8 mg N/l; Ptot ˜ 0.03 mg P/l) the proposed EQSs seem rather steep. The major comment during the presentation of the previous values was that they do not meet with the requirements of the type specific approach (which was acknowledged by the study). Following the type specific approach, the conditions (including natural background) and requirements of the specific water body should be assessed and taken into account when setting its corresponding EQS. Therefore, the figures for both the EQS as well as for natural background mentioned in the report are considered merely indicative.

For ammonium (NH4+) a separate EQS has been proposed, since ammonium can have toxic effects under certain conditions and concentration levels. The proposed threshold value representing the physico-chemical 'good status' of NH4+ is =0.2 mg N/l.

The proposed threshold value representing the physico-chemical 'good status' of chemical oxygen demand is CODMn =10 mg O2/l.

For the metals As, Cr, Cu and Zn it was not possible to extract common denominators from the existing systems of water quality standards. Firstly, existing systems can differ for the matrices included in the defined standards (total, dissolved, suspended solids and/or sediment). Secondly, differences in an order of magnitude of 10 can be observed between comparable water quality standards, like the 'No Observed Effect Level' for zinc applying in the Netherlands (total= 12 µg/l) versus the one used by the US-EPA (dissolved= 120 µg/l). Since comparing existing systems is not expected to provide a common ground for reaching consensus, for possible follow-up it has been proposed to a) 'pragmatically' adopt of one existing system of EQSs, or b) to infer EQSs for the Danube specific metals applying the methodology used by the Fraunhofer Institute for setting the EQSs for the WFD priority pollutants. As it turned out, Austria already has implemented option b) for dissolved concentrations of As, Cr, Cu and Zn. The final report is expected to be made public around the end of the year 2003.

2. Preparation of a proposal for connection/operational link of the data collected during the Joint Danube Survey into ICPDR Information System, with particular attention to biological database

Primary objective of this project component was to develop a proposal for an operational link between the JDS and TNMN databases. The project team with a help of selected MLIM experts and UNDP/GEF Information Specialist, who participated at the development of the original JDS Database, undertook an approach of on-line introduction of suggested changes/recommendations into the web-based ICPDR Information System. This gave an instant feedback on the practicality and usefulness of the JDS database upgrades and improvements. Prior to the final interlinking of databases, numerous efforts were made consisting of completion of the database for missing parameters and thorough check on the quality of stored data.

As a result recommendations for a link between the JDS and TNMN databases and harmonisation of their query templates were made and incorporated into their New Draft Versions. A proposal of the new central page on the ICPDR website comprising of all ICPDR databases (TNMN, EMIS, Bucharest Declaration Database, JDS, JDS – Investigation of the Tisa River) was drafted. During the project, the JDS Database was gradually improved and developed into the stage, that it is ready for the public use (for latest version, see www.icpdr.org [Databases/New Draft Versions]).

Several suggestions, which go beyond the scope of this project component, were made by the project team and MLIM experts to improve the ease-of-use of the JDS and TNMN databases. A principal upgrade and Europe-wide harmonisation of the coding system and systematic tracking of taxonomical changes in the biological part of the database was proposed in order to assure its sustainability. Also, further upgrade of the GC-MS screening part of the database was suggested to allow proper evaluation of the screening data on emerging, unknown and Danube River Basin specific pollutants as required by the WFD. A specific recommendation was made to perform similar upgrade at the JDS – Investigation of the Tisa River database, containing valuable data from survey conducted in October 2001, however, not being ready for public use in its present form.

Final goal of all the above efforts is to create a fully interlinked ICPDR Information System. This would require future harmonization of the coding system between the TNMN and EMIS databases and further development of the link between the two databases. The knowledge obtained at the development and upgrade of the JDS Database created a solid base for extension of the TNMN Database for new chemical parameters, parameters measured in other matrices than water, GC-MS screening and biological data.

3. Analysis of the results of the EMIS Inventory and their comparison with TNMN and JDS results, with particular attentions to EU Priority List of Pollutants

The main objective of this activity was to prepare a background material for future harmonization of the ICPDR databases (EMIS, TNMN). Therefore, a comparative analysis of determinands (i) included in the EMIS inventories/database, (ii) routinely measured in the TNMN and (iii) analyzed within the Joint Danube Survey (JDS) was made. A particular attention was given to a comparison with the determinands from the EU Water Framework Directive (WFD) List of Priority Substances. The analysis made also a comparison with the recently agreed provisional Danube List of Priority Substances.

At present, for water matrix 26 determinands from EU & Danube Priority Lists are not in the analytical programme of TNMN and 29 are not in the EMIS inventories. In the JDS, 17 out of these 26 determinands were included in the analytical programme for the water matrix. Eight JDS determinands that are listed in the Decision No. 2455/2001/EC showed results below detection limit (n.d.). Mercury was below detection limit in the JDS datasets (due to relatively high LOD of the analytical method applied), however, it is reported in the TNMN list. For 14 determinands (all organic micropollutants) listed in the Decision No. 2455/2001/EC no data in water exists in the ICPDR databases (TNMN and JDS; data from PHARE Applied Research Programme for DRB exist for PAHs).

For sediment / suspended solids altogether 20 determinands of the EU WFD Priority Substances Lists are not in the analytical programme of TNMN while 22 are not in the EMIS inventories. Ten, out of these 20 non-TNMN determinands, were included in the analytical programme of the JDS for sediments/suspended solids. For ten determinands present in the EU WFD Priority Substances list no data are available in suspended solids/sediments analysed within the TNMN and JDS.

In the technical report results are discussed in detail for each (group of) determinand(s). Considerations are presented for each determinand whether to include it or not in either the EMIS inventories or the analytical programme of TNMN. Comments on possible emission sources were made as well, based on current versions of respective EC documents (source screening). The considerations were used as a basis for the recommendations. Recommendations referred also to monitoring matrices agreed until now by EAF PS.

4. Development of the Danube List of Priority Substances and SOPs for newly included determinands

The main objective of this activity was to develop the Danube List of Priority Substances, based on the EU List of Priority Substances, determinands of TNMN and JDS; and taking into account the results of Phare project ZZ-97-25 Component VI in line with work of EMIS EG on this topic. However, the activities concerning developing the Danube List of Priority Substances had started long time before the Danube Regional Project began and the list was finalized by the ICPDR during course of the project. Therefore, a summary is provided of the activities performed and milestones achieved. Moreover, general recommendations are given for the follow-up actions.

In line with the Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, and taking into account determinands analysed within TNMN and JDS as well as the results of Phare project ZZ-97-25 Component VI, the EMIS EG prepared the draft Danube List of Priority Substances. At the 1st Meeting of the Joint MLIM/EMIS Working Group in February 2003 this draft was discussed and it was suggested to keep the Annex A as prepared by the EMIS EG (identical with the EU WFD list). The Annex B was proposed to be divided into two groups – General Parameters (COD, NH4, N, P) and Danube Specific Priority Substances (As, Co, Zn, Cr). The ICPDR at its 1st Standing Working Group meeting in June 2003 agreed with the proposed Danube List of Priority Substances but considered it only as provisional. To arrive at a final list the national targeted screenings for EU WFD Priority Substances will have to be performed to prove their relevance for the specific area/region.

For the determinands, which newly appeared in the proposed Danube List of Priority Substances it was necessary to make available the respective standard operational procedures (SOPs). The overview of SOPs provided in the technical report takes into account the results of the review on possibilities to analyze the EU WFD priority substances in the Danube countries, which was performed by the MLIM EG in 2002. An attention was also paid to the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the "EU Expert Advisory Forum on Priority Substances and Pollution Control". The recommended standard operational procedures are divided into two groups - priority substances from the DECISION No. 2455/2001/EC and geneneral parameters and priority substances specific for the Danube River Basin.

5. Proposal (recommendations for) an upgrade of the TNMN by including the Danube List of Priority Substances, taking into account the 5 years data of TNMN

The objective of this report was to assess water quality in Danube River basin, including classification and identification of spatial and temporal changes. The basis for assessment is data on physico-chemical and biological determinands collected in the frame of TNMN in five-years period 1996 – 2000. The main assessment objectives were as follows:

- Checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;

- Identification of water quality changes along the Danube River;

- Detection of trends in water quality;

- Assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

In general, following facts concerning classification and trend evaluation of the processed TNMN data should be highlighted:

Nutrients

Ammonium-N and nitrite-N concentrations increase from upper to lower Danube. In the Danube River, 53.3 % of ammonium-N and 37.2 % nitrite-N values were found to be above the target limits for these determinands. A special concern should be paid to the ammonium-N content recorded on the Arges river, where all five yearly values of C90 in time period 1996-2000 were above the limit for Class V; these extremely high values, correlated with BOD5 values, show the impact of untreated or insufficiently treated waste waters from municipalities. In the Danube River, occurrence of ammonium-N shows a decreasing tendency from 1996 to 2000 in the upper part and in the middle section in Slovak monitoring sites.

The spatial distribution of nitrate-N concentrations shows a decrease from upper/middle to lower Danube. Tributaries with the highest content of nitrate-N are Morava, Dyje, Sio in the upper/middle part, and Iskar, Russenski Lom, Arges and Prut in the lower part of river basin. For nitrate-N concentrations the fluctuations in time profile are low for the Danube River, but rather high for the tributaries.

Orthophosphate-P shows a spatial pattern similar to that of total phosphorous characterized by a slight increasing profile from upper to lower Danube. In the upper/middle part of the Danube a decreasing tendency in P concentration is seen in the section from Danube-Bratislava (km 1869) down to Danube-Szob (km 1708) with an exception at Danube-Medvedov/Medve (km 1806). In general, the time variance of total P concentrations is much higher than that of ortho-phosphates.

Heavy metals

Except of manganese, for which a maximum of the spatial profile is present in the middle Danube reach, for most of the discussed heavy metals the general pattern is an increase from the upper and middle to the lower Danube. Furthermore, the heavy metals content in some tributaries – mainly those located in the lower Danube - is higher than the content in the Danube River itself.

The contamination of the Danube River by lead and copper was found rather high. A slightly better was the situation for cadmium and mercury with 47.4% of values exceeding cadmium target level and 36.6% of values exceeding mercury target level. In general, relatively high fluctuations of heavy metal concentrations were observed along the Danube. Despite these uncertainties the development of heavy metal content in some tributaries was found positive – a decrease is indicated in Drava river (cadmium, chromium, copper, lead, nickel and zinc), in Arges (cadmium, chromium, copper, lead), Prut (cadmium, chromium, lead) and in Siret (chromium, copper, lead).

In general, five years trends of heavy metal pollution can hardly been evaluated because a relatively high deviation of results occurred. High values of heavy metals often result from high loads of suspended solids caused by flood events. The statistical parameter used in this report (90% percentile) – was certainly influenced by such hydrological processes. For this five-years evaluation report the data on total concentration of heavy metals in water samples had been used because data related to dissolved fraction was not available in sufficient amount. Therefore, it must be stressed that such a rather scattered pattern of the heavy metal pollution data for the water matrix clearly supports future orientation of TNMN activities on the solid phase, i.e., in TNMN planning activities the analysis of suspended solids and sediments should be preferred.

Oxygen regime

Dissolved oxygen concentrations show positive results, with only 7.4% of values being below the quality target in the Danube River and 8.6% being below the quality target in monitored tributaries. Oxygen concentration decreases from upper to lower part of the Danube River, lowest values being in the section from Danube-Bazias to Danube-Novo Selo/Pristol. As for the tributaries, rather low oxygen content was identified in those located in the lower part of the river basin.

As for BOD values 13.3% of them are above the target value in the Danube River (mainly in the middle and in the lower sections) and 35.9% exceed the target value in tributaries. Organic pollution expressed by BOD increases along the Danube, reaching its maximum in the secion from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm 834, RO02). The tributaries most polluted by degradable organic matter are Morava, Dyje and Sio in the upper/middle part of the Danube mainstream and Russenski Lom and Arges in the lower part.

For CODCr, 22.4% of all values for the Danube mainstream and 39.7% for tributaries were found above the quality target; the situation is more positive in case of CODMn - no value above this limit for the Danube River and 18.2% for tributaries. In principle, the results obtained for CODCr and CODMn show the highest values in the lower part of the Danube River.

Organic micropollutants

The organochlorine compounds (Lindan and p,p'-DDT) showed similar spatial profile, with an increasing pattern from upper/middle to lower Danube. The polar pesticide Atrazine was undetectable at most of the monitoring sites along the Danube River, only 12.5% of the data were found above the target limit. In tributaries, 30% of Atrazine values were above the quality target, the maximum values were found in rivers Sio and the Sajo.

For the volatile organic compounds, data is available for upper and middle Danube only. Chloroform and tetrachloroethylene show values above the target limits in a following pattern: 29.0% of the Danube samples and 39.5% of the samples taken from tributaries exceeded the target values for chloroform, for tetrachloroethylene the respective numbers were 13.6% for the Danube and 7% for tributaries. The situation was found to be better for tetrachloromethane and trichloroethylene - in the Danube River mainstream no value was detected above the target limit for these compounds, while in tributaries only a small percentage of all data (2.3%) was above the target limits for both these determinands.

Biological determinands

Evaluation of saprobic index of macrozoobenthos using Austrian standard ÖNORM M6232 showed that the Danube River and most of its tributaries correspond to classes II – II-III. Only Sava River was characterized by a worse quality class (III – III-IV), however, within the years the situation improved.

In 1996 – 2000 the microbiological water quality corresponded to classes I – IV in the Danube River mainstream. Some tributaries, as e.g., Vah, Tisza and Siret can be characterized as extensively polluted, however, data from many other relevant tributaries is missing. It was observed that sedimentation had positive effects to number of total coliforms below Gabcíkovo Reservoir, Iron Gates and in Danube Delta as well.

For biological determinands a slightly positive time trend appeared in case of saprobic index of macrozoobenthos, but no significant trend in microbiological determinands was observed.

6. Development of a methodological concept for assessment of environment stress and impacts as a basis for preparation of a computer-based application for stress-impact analysis

In this activity a concept for a computer based application was developed assessing the relation between a pressure (the emission of a pollutant by a point source) and the downstream increase of the concentration of a pollutant ("state"). For this concept the use of existing databases (EMIS, TNMN) and existing models or modules from these models (MONERIS, DBAM, DWQM) was considered. Assessing different conceptual choices using the above mentioned models/modules three different functionalities were defined:

Detection of pressure based on observed concentration increase (accidental pollution pressures)

This application would consist of an "inverse DBAM" model. In its simplest form, the application could be based on a large database of computed pollutant clouds C(t) by DBAM, for different spill and observation positions, under different hydrological conditions. By comparing the observed cloud of pollutants with the database of clouds, given the actual hydrologic conditions, potential spill sites can be observed. Under the assumption that the removal rate of the pollutant is known, the spill mass can be back-computed.

Detection of pressure based on observed concentration increase (regular pollution pressures)

The application would start from an observed trend-wise increase of the concentration of a given substance at a given location from one year to another. Upstream point sources which show a corresponding increase of their emissions could be detected and listed. The decay rate of the substance in question could be taken into account to eliminate pollution sources too far away for their emitted pollutants to reach the observation point.

Effects of pollution reduction measures (only regular pollution pressures)

This application could consist of an application like the present DBAM, with some modifications: a continuous spill should be modelled instead of an accidental spill, average hydrological conditions should be used rather than actual conditions. To keep things simple, the application should include only one particular point source for which reduction measures need to be analysed. The background pollution from the other point sources and from diffuse sources needs to be back-computed for any selected observation location. The computed concentration from the point source in question before the reduction is subtracted from the present concentration at the observation point: the difference is the background concentration. The total concentration after reduction is obtained by adding the computed concentration from the point source in question after the reduction to the background concentration.

From assessment of practical implications of the three proposed functionalities it was clear, that the development of the computer based application for stress-impact analysis, which can calculate a quantitative relation between a point source and downstream changes in concentration levels or vice versa, will require a major investment in model/software development.

Therefore, a simpler practical concept was proposed as an alternative solution. In this case, the data of the TNMN would be the starting point for further analysis. If for a pollutant a significant concentration increase is observed during, e.g., 23 months, analysis of more upstream stations should indicate between which two stations the increase has started. In that stretch of the river the discharge should occur. At that point, a link with the EMIS database should be made to identify the point source.

Such a solution would require a proper coverage by the TNMN, in particular at the discharge of major tributaries and small tributaries with relevant point sources. A direct link with the EMIS database can be made through the geographical codes in both databases. Results should be presented in GIS. This concept would require adjustments in the TNMN as well as the development of a link between TNMN and EMIS based on GIS.

UNDP/GEF Danube Regional Project

Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation
in the Danube River Basin

Orientation on environmental quality standards for nutrients and other Danube specific priority substances

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

October 22, 2003

Prepared by: Rodeco Consulting GmbH
Author: Paul H.L. Buijs

Preface

In its original settings, the activities under the project tasks 2.1 and 2.2 envisaged to develop (2.1) a proposal on water quality objectives for nutrients in line with requirements of EU WFD, and (2.2) a proposal on water quality standards for toxic substances from the Danube River Protection Convention list of priority substances.

In total two person-weeks of input were allocated for these tasks. With such limited time, it is not feasible to cover the subjects in-depth and to be exhaustive for all different regions within the Danube basin. Therefore, while aiming at formulating preliminary recommendations for Environmental Quality Standards, it was considered equally important to provide background material and arguments to the MLIM and EMIS expert groups for supporting their further activities. Besides the amount of information included in this report, the references contain many links to WebPages in Internet from where more (background) information easily can be retrieved.

The Draft Final report of August 2003 was discussed during the Second Joint MLIM/EMIS meeting in Bratislava (September 17th, 2003) and the 31st MLIM meeting on September 19th, 2003 (in Bratislava). A number of questions and comments were raised during the meetings and the author received e-mails afterwards summarising the comments. Some of the remarks critically commented parts of the report, like not having followed the typespecific approach in line with the Water Framework Directive.

The author decided to add the several questions and comments, together with responses by the author, in the separate 'Epilogue' chapter 7. The remaining contents are similar to the draft final report. By doing so, it remains more clear on which specific grounds the various comments were based, and why certain items were raised as discussion points. In this way, it also remains more transparent how to use (and not to use) the report during further discussions and studies.

Paul Buijs

22 October 2003

Amersfoort, the Netherlands

Table of contents

Abbreviations, Acronyms, and Definitions

CCC	The Criterion Continuous Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect
CMC	The Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.
COD	Chemical Oxygen Demand
DIN	dissolved inorganic nitrogen (NH_4, NO_2, NO_3)
DRPC	Danube River Protection Convention
Eutrophication	The enrichment of water by nitrogen compounds, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the water balance of organisms present in the water and to the quality of the water concerned (91/676/EEC, Article 2).
EQO	Environmental Quality Objective. Policy or management goal to achieve within a certain period of time. This may be a specific use/function of the water system or any goal, e.g. 50% reduction in nutrient load within 10 years. An EQO also can be expressed as a set of numerical standards for each designated use of the water, which specify the maximum permissible level of pollutants, which must not be exceeded in the shorter and longer term. The timeframe for achieving an EQO is directly dependent on analysis of the technical, financial and other implications associated with the desired improvement in water or sediment quality (Reynolds, 2001).
EQS	Environmental Quality Standard. The concentration of a parameter that should not be exceeded in the receiving water in order to protect the use of the water. The EQS for the protection of aquatic life is derived to protect all aquatic species (Reynolds, 2001).
IRC	International Rhine Commission
ISQG	Interim sediment quality guideline
Kd	partition coefficient
N	nitrogen
NH_4	NH_4^+, ammonium
NL	The Netherlands
NO_2	NO_2^-, nitrite
NO_3	NO_3^-, nitrate
NOEL	No Observed Effect Level
N_{tot}	total nitrogen
P	phosphorous
PEL	Probable effect level
PO_4	PO_4^{3-}, ortho-phosphate
P_{tot}	total phosphorous
RAP	Rhine Action Programme
SS	suspended solids
TNMN	Transnational Monitoring Network
US-EPA	United States Environmental Protection Agency

Executive summary

The underlying study aimed at formulating Environmental Quality Standards (EQSs) for those Danube specific substances that are not included in the list of priority substances of the EU Water Framework Directive. The Danube specific priority substances comprise: total nitrogen (N_{tot}), total phosphorous (P_{tot}), ammonium (NH_4^+), chemical oxygen demand (COD), and the metals As, Cr, Cu and Zn.

Given the resources and the time available for the study, it was merely feasible to collect and assess already existing systems of EQSs. Further, it was feasible to prepare preliminary recommendations for EQSs at a rather generic and broad scope. The typespecific approach as required by the WFD could not be implemented.

For the nutrients (N_{tot}, P_{tot}) the study used the following working definition in order to make the WFD's 'good status' description for physico-chemical parameters more operational: "nutrient concentrations such that chances on the occurrence of eutrophication are minimised, or (preferably) avoided". The query into existing systems for water quality assessment and –standards resulted in the following preliminary recommendations for EQSs to be used as representing 'good status' thresholds for nutrients: N_{tot}: 1.0 - 1.5 mg N/l; P_{tot}: 0.02 – 0.08 mg P/l. Compared to estimated natural background levels for the Danube river (N_{tot} ˜ 0.8 mg N/l; P_{tot} ˜ 0.03 mg P/l) the proposed EQSs seem rather steep. The major comment during the presentation of the previous values was that they do not meet with the requirements of the typespecific approach (which was acknowledged by the study). Following the typespecific approach, the conditions (including natural background) and requirements of the specific water body should be assessed and taken into account when setting its corresponding EQS. Therefore, the figures for both the EQS as well as for natural background mentioned in the report are considered merely indicative.

For ammonium (NH_4^+) a separate EQS has been proposed, since ammonium can have toxic effects under certain conditions and concentration levels. The proposed threshold value representing the physico-chemical 'good status' of NH_4^+ is =0.2 mg N/l.

The proposed threshold value representing the physico-chemical 'good status' of chemical oxygen demand is COD_{Mn} =10 mg O_2/l.

For the metals As, Cr, Cu and Zn it was not possible to extract common denominators from the existing systems of water quality standards. Firstly, existing systems can differ for the matrices included in the defined standards (total, dissolved, suspended solids and/or sediment). Secondly, differences in an order of magnitude of 10 can be observed between comparable water quality standards, like the 'No Observed Effect Level' for zinc applying in the Netherlands (total= 12 µg/l) versus the one used by the US-EPA (dissolved= 120 µg/l). Since comparing existing systems is not expected to provide a common ground for reaching consensus, for possible follow-up it has been proposed to a) 'pragmatically' adopt of one existing system of EQSs, or b) to infer EQSs for the Danube specific metals applying the methodology used by the Fraunhofer Institute for setting the EQSs for the WFD priority pollutants. As it turned out, Austria already has implemented option b) for dissolved concentrations of As, Cr, Cu and Zn. The final report is expected to be made public around the end of the year 2003.

1   Introduction

1.1   Scope

In its original settings, the activities under the tasks 2.1 and 2.2 envisaged to develop (2.1) a proposal on water quality objectives for nutrients in line with requirements of EU WFD, and (2.2) a proposal on water quality standards for toxic substances from the DRPC (Danube River Protection Convention) list of priority substances.

During the 30th MLIM-EG Meeting, it was decided that the present project should focus on parameters, specific for the DRPC (general parameters: COD, NH_4, N, P, and Danube Specific Priority Substances: As, Cr, Cu, Zn). The remaining Danube priority substances are similar to the WFD priority substances. The recommendations on water quality standards to be formulated by the Expert Advisory Forum on Priority Substances are expected to be implemented for the Danube basin as well and therefore does not require further elaboration here.

During the first Joint MLIM/EMIS Working Group meeting in Vienna (3 February 2003) it was agreed that the focus of the work would be on the main course of the Danube River. If possible, recommendations for major trans-boundary tributaries, such as Morava, Tisza, Sava, and Drava, should be drawn.

1.2   General departure points

With the time and resources available under this project, only existing systems of EQO/EQS could be taken into consideration as references for formulating recommendations for water quality objectives and –standards for the Danube. Preference was given to systems that were formulated to apply at regional (international) scales. At least the following EQO/EQS systems are taken into consideration for the assessments:

- EU-guidelines, notably: 76/464/EEC: on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (incl. daughter directives); 78/659/EC: on the quality of fresh waters needing protection or improvement in order to support fish life; 75/440/EC: concerning the quality required of surface water intended for the abstraction of drinking water in the Member States;)

- Rhine Action Programme;

- UN "ECE Standards Statistical Classification of Surface Water Quality for the Maintenance of Aquatic Life;

- other systems where appropriate.

It is presumed, that the approach for deriving the water quality standards in the systems mentioned above have followed the core features of the procedures as outlined in the WFD (Annex V, 1.2.6 Procedure for the setting of chemical water quality standards by Member States).

1.3   Comments to draft report

The main comments made to the draft final report of August 2003 report are included in chapter 7, together with brief responses by the author. For proper understanding and perception of the previous chapters, readers should take the remarks from chapter 7 into account.

2   Nutrients (N_{tot}, P_{tot})

2.1   Nutrients and the WFD

Nutrients are not included in the final list of WFD priority substances as such (decision No 2455/2001/EC). They are mentioned in Annex VIII: Indicative list of the main pollutants, "11. Substances which contribute to eutrophication (in particular, nitrates and phosphates)". Further, nutrients are addressed in the definitions of ecological status (Annex V, table 1.2, physico-chemical quality status):

- **High status**: nutrient concentrations remain within range normally associated with undisturbed conditions.

- **Good status**: nutrient concentrations do not exceed the levels established as to ensure the functioning of the ecosystem and the achievement of the values specified above (*author: this is a reference to table 1.1 in Annex V*) for the biological quality elements.

The WFD puts nutrients dominantly in the perspective of eutrophication. For nitrite (N02), ammonia (NH3), and ammonium (NH_4) also toxic effects on aquatic life forms can apply (without the occurrence of eutrophication).

Although WFD Annex VIII specifically mentions *nitrates*, it is common to consider total nitrogen when dealing with nitrogen-based eutrophication parameters (refer also to textbox 2.1). The priority substances specific for the Danube include total-nitrogen and ammonium. Therefore, this document will mainly focus on these two parameters.

Textbox 2.1   Appearances of N and P in riverine systems

Nitrogen compounds occur both dissolved in the water phase, as well as in particulate matter. Generally, following subdivisions are made:
- Dissolved inorganic nitrogen: nitrite (NO_2), nitrate (NO_3), ammonia (NH_3), and ammonium (NH_4). NO_2 and NH_3 are quite instable, and only occur in more extreme conditions (like: low oxygen levels). Dominating are NO_3 and NH_4.
- Dissolved organic nitrogen, like amino-acids, peptides, proteins, etc...
- Particulate inorganic nitrogen: mainly adsorbed NH_4.
- Particulate organic nitrogen: all kinds of occurrences of N, like in decaying organic plant and animal material etc...
- *Dissolved gas: N_2 or N_2O, which can be neglected in the present context.*

Total nitrogen (N_{tot}) in principle encompasses the sum of all the above mentioned occurrences. (Especially in the former Soviet region it was a practice to label the sum of NO_2, NO_3, and NH_4 as total nitrogen, which is not correct. Analysing organic/particulate nitrogen was not a tradition at all).
What is available as data partially depends on the methods of analysis applies. When for instance determining nitrogen with the Kjeldahl method, the results comprises both the organic particulate nitrogen + ammoniacal nitrogen (NH_4/NH_3). The sum of Kjeldahl-nitrogen+NO_2+NO_3 then is normally considered as being total nitrogen.
Phosphorous also occurs in both dissolved and particulate forms. In water quality monitoring, normally samples are determined for ortho-phosphate and total phosphorous.
- orthophosphate (PO_4) is the major dissolved inorganic form of phosphorous
- total phosphorous (P_{tot}) includes all occurrences of phosphorous, also PO_4, of course assuming that samples were not filtered prior to analysis.

2.2 Considerations for formulating EQO and EQS for nutrients in the Danube

The final aim of the WFD can be considered as one overall Environmental Quality Objective: reaching (at least) good ecological status before the end of the year 2015.

With regard to the physico-chemical quality elements (including nutrients), conditions are implied such as they can enable at least good ecological status. The nutrients can be combined with biological quality elements in terms of phytoplankton, being one of the phenomena that can be related to eutrophication (like algae blooms). High respectively good status for Phytoplankton are defined as (Annex V, table 1.2.1):

- **High status** : The taxonomic composition of phytoplankton corresponds totally or nearly totally to undisturbed conditions.
  The average phytoplankton abundance is wholly consistent with the type-specific physico-chemical conditions and is not such as to significantly alter the type-specific transparency conditions.
  Planktonic blooms occur at a frequency and intensity, which is consistent with the type-specific physicochemical conditions.

- **Good status** : There are slight changes in the composition and abundance of planktonic taxa compared to the type-specific communities. Such changes do not indicate any accelerated growth of algae resulting in undesirable disturbances to the balance of organisms present in the water body or to the physico-chemical quality of the water or sediment.
  A slight increase in the frequency and intensity of the type-specific planktonic blooms may occur.

As for macrophytes and phytobenthos (also using nutrients as 'fertilisers') the differences between high and good status contain similar wordings (good status: "there are slight changes in the composition and abundance of macrophyte and phytobentic taxa compared to type-specific communities. Such changes do not indicate any accelerated growth …").

A more precise definition and quantification of 'slight changes, slight increase, and accelerated growth' are not considered part of this specific project component (expected to be addressed in the activities dealing with the issues typology, reference conditions, and ecological classification). Nevertheless, the above can be translated to formulating an EQO for nutrients as the situation where nutrient concentrations are such that chances for the occurrence of eutrophication are minimised, or (preferably) avoided. Two (complementary, but slightly different) angles were followed in this study to formulate nutrient EQSs.

1. The interpretation of 'high status' is a situation with no or only minor anthropogenic impacts. An inventory of natural background concentrations for nutrients has been made in order to provide with such perspective when defining the water quality standards for nutrients.

2. Another part of the inventory aimed at collecting data about nutrient concentrations that are considered safe in relation to the occurrence of eutrophication.

The value-added of this combined approach is that the discrepancy/similarity between both sets of results (high and good status approximations) provide additional arguments when defining the EQSs for nutrients.

As mentioned in the introduction, the main scope of present study is the major course of the Danube River itself. This can be amended as following.

- Standing waters are more prone to eutrophication compared to running waters. In many tributaries to the Danube (more-or-less) 'standing waters' occur in the form of reservoirs (for irrigation, drinking water supply or hydropower purposes). Further, the Danube delta comprises many sections with standing waters (incl. lakes) that are fed by the Danube. In the queries for data about nutrient levels considered safe in relation to eutrophication, information on standing freshwaters was included. Applying (basically: more stringent) standing waters' criteria also to the running parts of the Danube will better safeguard the good status situation.

- The water quality of the northwestern part of the Black Sea is heavily influenced by the inflow of the Danube. Since the Black Sea is not part of this assignment, it has not been taken into account yet as additional criterion when formulating the recommended EQSs for nutrients. Unless mentioned otherwise, figures for water quality standards apply to freshwater. A narrative in section 2.6 briefly puts the findings of underlying study in the perspective of the Black Sea.

- Eutrophication in freshwaters is often related to phosphorous being the decisive (limiting) factor, while for marine waters nitrogen would be more determining. Nevertheless, sufficient situations exist where the situation is opposite (N being the limiting factor in freshwaters and P in marine/tidal waters). The queries for EQSs included both nitrogen and phosphorous, to anticipate different environments, and to keep the perspective on the Black Sea. The search has been limited to straightforward concentrations. In reality, not only the absolute concentrations, but also N/P-ratios can be determinative in the actual occurrence of eutrophication.

2.3   Natural background concentrations of nutrients

As applying to virtually all parameters that originate from natural sources, also for nutrients not one single natural background concentration in freshwaters exists. Natural background nutrient concentrations for the Danube are available from calculations with the MONERIS model [Schreiber et. al., 1993; Behrendt, 2003]. Additional data for other basins were added for the sake of completeness.

2.3.1   Nitrogen

Table 2.1   Estimates for natural background concentrations of total nitrogen (in [mg N/l])

Average	Min	Max	water(s)	reference
0.8	-	-	Danube	*Schreiber, 2003 see text below*
0.75	0.55	1.2	main Danube tributaries	*Behrendt, 2003*
1.5	-	-	Danube (TNMN, class I)	*Adamková et. al., 2003*
0.64	0.27	1.00	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*
0.6	-	-	Dutch rivers	*Breukel, 1993*
$0.60+(0.0024*SS)^X$	-	-	rivers in temperate zones	*Riet, 1998*
1.0	-	-	national (undeveloped areas) USA	*US Dept., 2002*
<1.5	-	-	background rivers in Estonia	*EEIC, 2000*

X   contents of particulate N estimated as 2400 µg/g; multiplying the suspended solids (SS) contents (in mg/l) with a factor 0.0024 provides the particulate N fraction as mg N/l

The average concentration of 0.8 mg N/l for the Danube was calculated as follows. The total natural background emissions of total nitrogen into the Danube basin estimated by MONERIS is 163 kt/a [Schreiber, 2003]. Dividing this load by the long-term average downstream flow of the Danube -6500 m^3/s- results in 0.8 mg N/l. Since the load of 163 kt/a represents <u>emissions</u> over the whole basin, the actual load in the Danube downstream near the delta could be lower, e.g. due to retention.

Most of the other estimates, ranging between 0.6 – 1.0 mg N/l, are in line with the value calculated for the Danube. The interim water quality class I of the Danube TNMN is with 1.5 mg N/l the highest estimate. TNMN class I is to represent reference conditions or background concentrations

There is seasonality in nutrients concentrations in water systems. Concentrations tend to be lower in summer period, when for instance assimilation of nutrients by phytoplankton is relatively high. Therefore, an (annual) average concentration might not properly represent the specific features of nutrients like nitrogen. This issue will be further elaborated in section 2.5.

Results for other occurrences of nitrogen are summarised in the tables below.

Table 2.2   **Estimates for natural background concentrations of dissolved nitrate (in [mg NO$_3$_N/l])**

Average	Min	Max	water(s)	*reference*
1	-	-	Danube (TNMN, class I)	*Adamková et. al., 2003*
0.13	0.05	0.20	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*
-	0.1	1.0	rivers and lakes	*Meybeck, 1989*
0.3	-	-	most European rivers	*EEA, 2001*
0.6	-	-	national (undeveloped areas) USA	*US Dept., 2002*

Table 2.3   **Estimates for natural background concentrations of dissolved ammonium (in [mg NH$_4$_N/l])**

Average	Min	Max	water(s)	*reference*
0.2	-	-	Danube (TNMN, class I)	*Adamková et. al., 2003*
0.07	0.03	0.10	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*
0.015	-	-	most European rivers	*EEA, 2001*
0.1	-	-	national (undeveloped areas) USA	*US Dept., 2002*

Table 2.4   **Estimates for natural background concentrations of dissolved organic nitrogen (in [mg N/l])**

Average	Min	Max	water(s)	*reference*
0.01	-	-	Danube (TNMN, class I)	*Adamková et. al., 2003*
0.30	0.12	0.50	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*

Table 2.5   **Estimates for natural background concentrations of particulate organic nitrogen (in [mg N/l])**

Average	Min	Max	water(s)	reference
0.14[*]	0.07	0.20	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*

[*] based on suspended solids concentration of 30 mg/l, with 10% organic matter

2.3.2   Phosphorous

Table 2.6   **Estimates for natural background concentrations of total phosphorous (in [mg P/l])**

Average	Min	Max	water(s)	reference
0.028	-	-	Danube	*Schreiber, 2003 see text below*
0.027	0.021	0.037	main Danube tributaries	*Behrendt, 2003*
0.1	-	-	Danube (TNMN class I)	*Adamková, 2003*
0.11	0.023	0.19	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*
0.06	-	-	Dutch rivers	*Breukel, 1993*
$0.011+(0.00115*SS)^{X}$	-	-	rivers in temperate zones	*Riet, 1998*
-	0.0	0.05	various catchments	*EEA, 2001*
0.10	-	-	national mean of streams in USA	*Pope, 2002*
0.10	-	-	national (undeveloped areas) USA	*US Dept., 2002*
0.05	-	-	natural rivers in Estonia	*EEIC, 2000*

[X] contents of particulate P estimated as 1150 µg/g; multiplying the suspended solids (SS) contents (in mg/l) with a factor 0.00115 provides the particulate P fraction as mg P/l

The average Danube concentration of 0.028 mg P/l was derived from a natural background of 5.8 kt/a as calculated by MONERIS, divided by a flow of 6500 m^3/s.

The natural background concentrations of P$_{tot}$ calculated for the Danube based on MONERIS are the lowest compared to the estimates for other rivers: 0.03 mg P/l. The remaining data in table 2.6 range between 0.05 - 0.10 mg P/l, except for the river Rhine with an estimated maximum of 0.19 mg P/l.

Data about other appearances of phosphorous are included in the following two tables.

Table 2.7   Estimates for natural background concentrations of ortho-phosphate (in [mg PO$_4$_P/l])

Average	Min	Max	water(s)	*reference*
0.05	-	-	Danube (TNMN, Class I)	*Adamková, 2003*
0.05	0.003	0.10	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*

Table 2.8   Estimates for natural background concentrations particulate bound phosphorous (in [mg P/l])

Average	Min	Max	water(s)	*reference*
0.06[*]	0.02	0.09	river Rhine at Lobith (Dutch-German border)	*Veldstra, 1989*

[*] based on suspended solids concentration of 30 mg/l, with 10% organic matter

2.3.3   Historic data on nutrients in the Danube

According to Kroiss "… in 1961 the nutrient discharge was close to 'natural' conditions as there were no adverse effects reported from Black Sea" [Kroiss, 2002]. This implies that, measurement data around the year 1960 could serve as an adequate reference for (more or less) natural background concentrations.

Loads discharged into the Black Sea in 1961 are estimated as 140 kiloton DIN (dissolved inorganic nitrogen) and 12 kt PO$_4$-P [Kroiss, 2002]. Following the method used above (dividing the load by a flow of 6500 m^3/s), these loads would imply the following average concentrations:

- DIN: 0.68 mg N/l
- PO$_4$_P: 0.063 mg PO$_4$_P/l

In 1960, the DIN load at Sulina was estimated to 140 kton [NIMRD]. The P$_{tot}$ load at Reni was in 1960 13 kt [VITUKI, 1997]. These loads would result in the following average concentrations:

- DIN: 0.68 mg N/l
- P$_{tot}$: 0.063 mg P/l

The loads mentioned above are higher than the natural background emissions calculated by MONERIS.

According to MONERIS the natural background loading for N$_{tot}$ is 163 kt/a. Since the above DIN loads (140 kton) do not include organic nitrogen, the accompanying total nitrogen loads can be assumed to be higher than the MONERIS estimate.

The 1961 phosphorous load (12 kton) comprises PO$_4$ only, hence the P$_{tot}$ load will be higher. The 1960 P$_{tot}$ load at Reni (13 kt) is two times higher than the total natural P-emissions calculated by MONERIS.

The notice of Kroiss ("close to 'natural' conditions as there were no adverse effects reported from Black Sea") can be considered a working definition of a WFD 'good status'. As within the WFD itself, it is still arbitrary how large 'close' would be.

Collecting and analysing individual measurement data around the 1960-ies could provide additional support in defining the nutrient EQSs for the Danube. One advantage of collecting measurement data is that seasonality phenomena better can be estimated, and data themselves are actual concentrations

(and not approximates from loads). Main disadvantages of this approach are that it could be an elaborate process to retrieve the data from paper archives, there will be missing data (notably organic nitrogen), and the comparability of analyses/analytical results needs to be crosschecked.

2.4   Nutrients levels avoiding risks for eutrophication ('good status')

In section 2.3 it is proposed to use as (limits for) natural background concentrations of nutrients in the Danube basin: N_{tot}: =1.0 mg N/l, and P_{tot}: =0.10 mg P/l. Concentrations at background levels are regarded to represent a 'high status'. The WFD does not impose high status, but allows for at least 'good status'. Under good status, nutrient concentrations may deviate from an undisturbed situation, as long as the functioning of the ecosystem is ensured and the values specified for the biological quality elements can be achieved. As argued in section 2.2, eutrophication is considered the major phenomenon occurring when nutrient levels are too high. From this, it can be postulated that nutrient concentrations not exceeding levels associated with causing eutrophication can be regarded as good status levels. The tables below contain the results of literature and Internet queries on this topic.

2.4.1   Nitrogen

2.4.1.1   United Nations

The UN "ECE Standards Statistical Classification of Surface Water Quality for the Maintenance of Aquatic Life" defines five classes in relation to eutrophication (for the parameters N_{tot}, P_{tot} and chlorophyll) [UN/ECE, 1992]. As major criteria apply "Trophic state and best available expert judgement regarding the impact of trophic state on aquatic life, maintaining consistency between the three variables".

The concentrations for N_{tot} are shown below.

UN-ECE N_{tot}	class I[1] Oligotrophic	class II Mesotrophic	class III moderately Eutrophic	class IV strongly Eutrophic	class V extensively polluted
[mg N/l]	<0.3	0.30 - 0.75	0.75 - 1.50	1.50 – 2.50	>2.50

2.4.1.2   United States

Quoting part of the opening EPA page at   http://www.epa.gov/ost/standards/nutrient.html   "The United States Environmental Protection Agency (EPA) is publishing recommended water quality criteria to reduce problems associated with excess nutrients in waterbodies in specific areas of the country. EPA will work with states and tribes to adopt regional-specific and locally appropriate water quality criteria for nutrients in lakes, reservoirs, rivers, streams, and wetlands in seventeen ecoregions." Interesting in their approach is the use of "Ecoregional Nutrient Criteria". In total seventeen ecoregions are recognised within the United States. Different water quality criteria can

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[1]   UN/ECE eutrophication classes:

I   Clear, oligotrophic water with, at most, a very slight, occasional anthropogenic pollution with organic matter. Low nutrient content, providing spawning ground for salmonoids

II   Slightly polluted, mesotrophic water receiving small discharges of organic matter. The loadings may lead to slightly increased primary productivity.

III   Moderately euthrophic water receiving considerable amounts of discharges of organic matter and nutrients. The level of primary production is considerable, and some changes in the community structure, including fish species, can be observed

IV   Strongly eutrophic, polluted water, receiving discharges of organic matter, nutrients and harmful substances. Algal blooms are common. Increased decomposition of organic matter together with stratification of water bodies may entail anaerobic conditions and fish kills. Mass occurrences of more tolerant species; population of fish and benthic organisms are affected.

V   Extensively polluted, hyperthropic water. Decomposers dominate over producers. Fish or benthic species do not occur permanently.

apply to different regions. This approach/philosophy resembles the approach of the WFD that also acknowledges ecoregions. (No attempt has been made to identify similarities in the ecoregions defined by the EPA, and the Danube basin, going beyond the scope of this project, and the present state of information concerning the typology setting for the Danube.) The overall strategy "to reduce overenrichment in surface waters" and the accompanying water quality criteria can be considered equivalent to "avoiding eutrophication".

The following boundaries for trophic classification are suggested:
(http://www.epa.gov/waterscience/criteria/nutrient/guidance/rivers/chapter_2.pdf)

US EPA N_{tot}	Oligotrophic-mesotrophic boundary	Mesotrophic-eutrophic boundary
[mg N/l]	0.7	1.5

The recommended nutrient criteria for the different ecoregions range between the following values (http://www.epa.gov/waterscience/criteria/nutrient/ecoregions/sumtable.pdf)

US EPA N_{tot} [mg N/l]	nutrient criteria Lakes and reservoirs (12 ecoregions)	nutrient criteria Rivers and Streams (13 ecoregions)
minimum	0.10	0.12
maximum	1.27	2.18
average	0.51	0.67
median	0.45	0.56

2.4.1.3 Sweden

The Swedish EPA uses the following criteria for assessment of the trophic state in lakes [SEPA, 2002]:

Sweden N_{tot} [mg N/l]	Oligotrophic (level Low)	Mesotrophic (level Moderately high)	Eutrophic (level High)	Eutrophic (level Very High)	Hypertrophic (level Extremely high)
average May-Oct	<0.300	0.300 - 0.625	0.625– 1.25	1.25 – 5	>5

2.4.1.4 The Netherlands

The Dutch system of water quality standards generally distinguishes two concentration levels:
- A "landelijke streefwaarde" (national target value), which can be considered equivalent to a No Observed Effect Level (NOEL). Water quality meeting these NOELs are objectives of the medium to long-term policy strategy.
- A "Maximaal Toelaatbaar Risico" (maximum allowable risk), equivalent to MAC values. These standards are mandatory for current water policy and -management; exceeding requires immediate remedial actions.

The Netherlands N_{tot}	NOEL [mg N/l]	MAC [mg N/l]
standing waters: average of concentrations during summer (Apr-Sep)	1.0	2.2
running waters: annual mean concentration	1.0	2.2

2.4.1.5 TNMN

An interim water quality classification scheme had been approved by the Monitoring, Laboratory and Information Management Sub-Group in 2001. The interim class II represents the target values.

Danube, TNMN N_{tot}	[mg N/l]
Class II (interim target value)	4.0

The Class II value of 4 mg N/l is considerably higher than the values mentioned in the previous sections.

2.4.1.6 Synthesis of eutrophication thresholds for N_{tot}

Refining the descriptions in the section 2.2 and the introduction of 2.4, it is suggested that the approximation of a 'good status' situation in the context of the eutrophication issue could be set equal to "Mesotrophic level or better". The concentrations associated with the boundary Mesotrophic – Eutrophic in the data above range from 0.6 (0.625 Sweden) through 0.8 (UN/ECE) to 1.5 (US EPA) mg N/l. The recommended US EPA nutrient criteria for N_{ot} (average 0.6 mg N/l for lakes and reservoirs, and 0.7 mg N/l for rivers and streams) imply that the (US EPA) Oligotrophic-Mesotrophic boundary prevails. (It is not immediately clear whether the US-EPA nutrient criteria could be considered more equivalent to a 'high' status situation.) Nevertheless, setting 1.5 mg N/l as the ultimate limit for the 'good status' total nitrogen concentration seems reasonable with the above data. The UN-ECE and Swedish trophic level boundaries indicate that 1.0 mg N/l can be considered a safer threshold.

Combining these various findings, for total nitrogen in the (freshwater part of the) Danube basin an EQS in the range 1.0 – 1.5 mg N/l is recommended. Input from other tasks, Danubian experts, and additional activities will be needed to fine-tune the recommended value (beyond the lifetime of this project) towards just one concentration. Part of the fine-tuning is also to comprise defining additional criteria, like whether the EQS should be an annual, or a summer average concentration (see also section 2.5 below).

Taking the Dutch 2.2 mg N/l as MAC into consideration, then it seems prudent to qualify N_{ot} concentrations =2 mg N/l as 'moderate' (or worse) physico-chemical status.

The TNMN Class II target value (4 mg N/l) is an outlier in the series. Systems like those from the UN/ECE, US EPA, or Sweden would associate such a concentration with eutrophic waters. This does not imply that the Class II value not would be appropriate. It merely shows that during the follow-up activities (beyond the lifetime of the underlying project) the arguments and findings of earlier discussions are to be considered as well.

2.4.2 Phosphorous

2.4.2.1 Overview of different water quality/eutrophication criteria for phosphorous

For background information about the various water quality standards/criteria mentioned in the tables below, refer the previous subsection, except for the following.

- The OECD has defined boundary value criteria for trophic categories. They apply to temperate region lakes and reservoirs. The figures shown further below were quoted from [Meybeck, 1989].

- The UK Environment Agency has defined interim targets for phosphorous in fresh waters [UK/EA, 2001].

- EU. The Council Directive 78/659/EEC "on the quality of fresh waters needing protection or improvement in order to support fish life" mentions no concentration figures for P_{tot}. But, the table in Annex I of this directive mentions under the header Observations "In other cases limit values of 0.2 mg PO_4/l (*author: corresponding to 0.065 mg PO_4_P/l*) in salmonid waters and of 0.4 mg PO_4/l (*author: corresponding to 0.13 mg PO_4_P/l*) in cyprinid waters may be regarded as indicative in order to reduce eutrophication."

- The Rhine Action Programme has defined 0.15 mg P/l as the target-value for P_{tot} [IKSR, 1992]. This target value aims at reduction of algae growths.

UN/ECE, 1992 P_{tot} [mg P/l]	class I Oligotrophic	class II Mesotrophic	class III moderately eutrophic	class IV strongly eutrophic	class V extensively polluted
standing water	<0.01	0.010 – 0.025	0.025 – 0.050	0.050 – 0.125	>0.125
running water	<0.015	0.015 – 0.040	0.040 – 0.075	0.075 – 0.190	>0.190

US EPA P_{tot}	Oligotrophic-mesotrophic boundary	Mesotrophic-eutrophic boundary
[mg P/l]	0.025	0.075

US EPA P_{tot} [mg P/l]	nutrient criteria Lakes and Reservoirs (12 ecoregions)	nutrient criteria Rivers and Streams (13 ecoregions)
minimum	0.008	0.010
maximum	0.038	0.128
average	0.017	0.041
median	0.016	0.033

OECD P_{tot}	Ultra-logographic	Oligotrophic	Mesotrophic	Eutrophic	Hypertrophic
[mg P/l]	0.004	0.01	0.01-0.035	0.035-0.1	0.1

Rhine P_{tot}	IRC target-value ('Zielvorgabe')
[mg P/l] - average	0.15

Sweden P_{tot} [mg P/l]	Oligotrophic (level Low)	Mesotrophic (level Moderately high)	Eutrophic (level High)	Eutrophic (level Very High)	Hypertrophic (level Extremely high)
average May-Oct	<0.0125	0.0125 – 0.0250	0.025-0.050	0.050-0.100	>0.100

The Netherlands P_{tot}	NOEL [mg P/l]	MAC [mg P/l]
standing waters: average of concentrations during summer (Apr-Sep)	0.05	0.15
running waters: annual mean concentration	0.05	0.15

Danube, TNMN P_{tot}	[mg P/l]
Class II (interim target value)	0.1

United Kingdom P_{tot} [mg P/l]	Oligotrophic	Mesotrophic	Meso-Eutrophic	Eutrophic
standing waters (annual geometric mean)	0.008	0.025	-	0.085
running waters (annual mean)	0.020	0.060	0.100	0.200

EU 78/659/EEC PO_4	salmonid waters	cyprinid waters
[mg P/l]	0.065	0.13

2.4.2.2   Synthesis of eutrophication thresholds for P_{tot}

Following the approach for N_{tot}, the boundary Mesotrophic-Eutrophic –for standing waters- for P_{tot} ranges from 0.025 (UN-ECE, Sweden) through 0.035 (OECD) to 0.075 (US-EPA) mg P/l. As was the case with N_{tot}, also the US-EPA nutrient criteria for P_{tot} are lower than this boundary (average 0.02 mg P/l for lakes and reservoirs, and 0.04 mg P/l for rivers and streams).

The findings suggest recommending the EQS for P_{tot} in the Danube to 0.02-0.08 mg P/l. Excluding the US-EPA, the data gear towards a range of 0.02 – 0.05 mg P/l. Both ranges completely fit within the range of natural background concentrations as suggested in subsection 2.3.2!

A shared feature in most of the above systems is that P_{tot} concentrations =0.1 mg P/l are associated with strongly eutrophic and worse states. Implying that a freshwater water quality with concentrations of 0.1 mg P/l or more anyway cannot qualify as 'good status' waters. The major exception is the target-value defined for the Rhine Action Programme (0.15 mg P/l). The TNMN Class II target value (0.1 mg P/l) is also relatively high.

2.5 Comparison of proposed EQSs with actual concentrations

The above-recommended EQSs are put into perspective by comparing them with actual measurements in the Danube. The results of the Joint Danube Survey (JDS) are elaborated in this report. Another output of the underlying project consists of an assessment of 5 years of TNMN data in the report entitled "Five-years Report on Water Quality in Danube River Basin Based on TransNational Monitoring Network - 1996-2000" [Adamková, 2003]. Readers are referred to this report for more details.

2.5.1 Seasonality

Before going into further details it is considered appropriate first to outline some features that are rather typical for nutrients. Generally, during summer period nutrient concentrations, notably nitrogen compounds, tend to be lower because of the assimilation and fixation by phytoplankton. An example is shown in the graph below.

Figure 2.1   Nitrate concentrations at Reni (left bank) 1996-2000 [mg NO3_N/l]
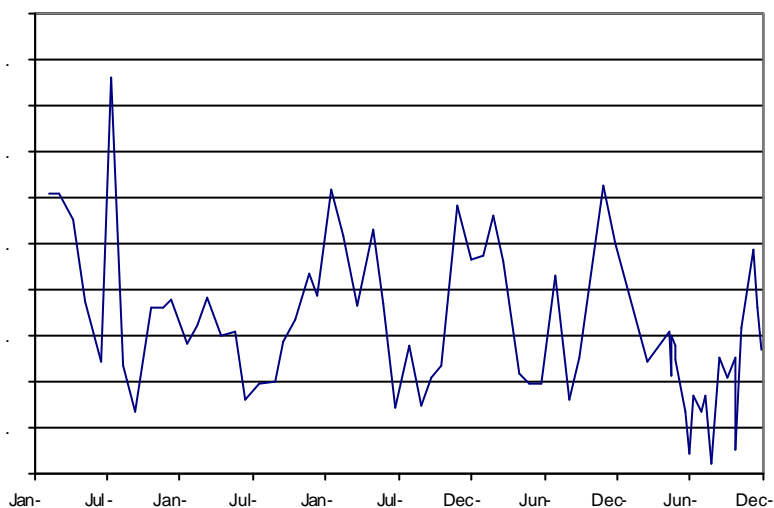
The implications of such seasonal variations are following:

- Eutrophication normally occurs in warmer periods, tentatively in the period May – September. If the EQSs are formulated in relation to (avoiding) eutrophication, then basically it would be important to set the standards for the period most prone to eutrophication. In the case of nitrogen this actually implies that one could allow for lower concentrations for the EQS. Eutrophication is less likely to occur during the colder season (November – March) during which N-concentrations tend to be higher!

- Status assessments comprising annual mean concentrations basically are not sufficient. Season (averaged) concentrations would prevail.

2.5.2 Joint Danube Survey

The results of the JDS are exhaustively elaborated and discussed in the technical report [ICPDR, 2002]. Readers are referred to this report for more details. This section mainly contains some highlights, together with a few additional assessments.

2.5.2.1 Total nitrogen

Many of the JDS data are unprecedented, including the systematic sampling and analysis for organic nitrogen along the whole stretch of the Danube river. Data for organic and total nitrogen in the Danube

basin are still scant, also in the 1996-2000 TNMN database. The JDS took place in the warmer summer-autumn period. Hence, the nutrient/nitrogen concentrations presumably are reflecting the lower ranges over the year 2002.

The JDS Technical report does not contain an assessment of total nitrogen. These figures (based upon data retrieved from the ICPDR Danubis website) have been generated for this reported in the following way. The water samples were analysed for organic nitrogen with application of Kjeldahl method ammonium analysis by spectrophotometric method [ICPDR, 2002, subsection 5.1.3]. The Kjeldahl method results in the sum of organic plus (the inorganic) ammonium, NH_4, nitrogen. Hence, the total nitrogen concentrations were calculated as the sum of organic nitrogen + NO_2 + NO_3. The 'pure' organic nitrogen concentrations were calculated by subtracting the (separately reported) NH_4-concentrations from the organic-N concentrations for each sampling site.

Since the JDS took place in an 'eutrophication-sensitive' period, the concentrations can be considered to be 'low-year values'.

The total nitrogen figures for the main part of the river are shown in the graph below.

Figure 2.2   Total nitrogen concentrations in the Danube's main course, JDS survey [mg N/l]

River km (distance to Black Sea)
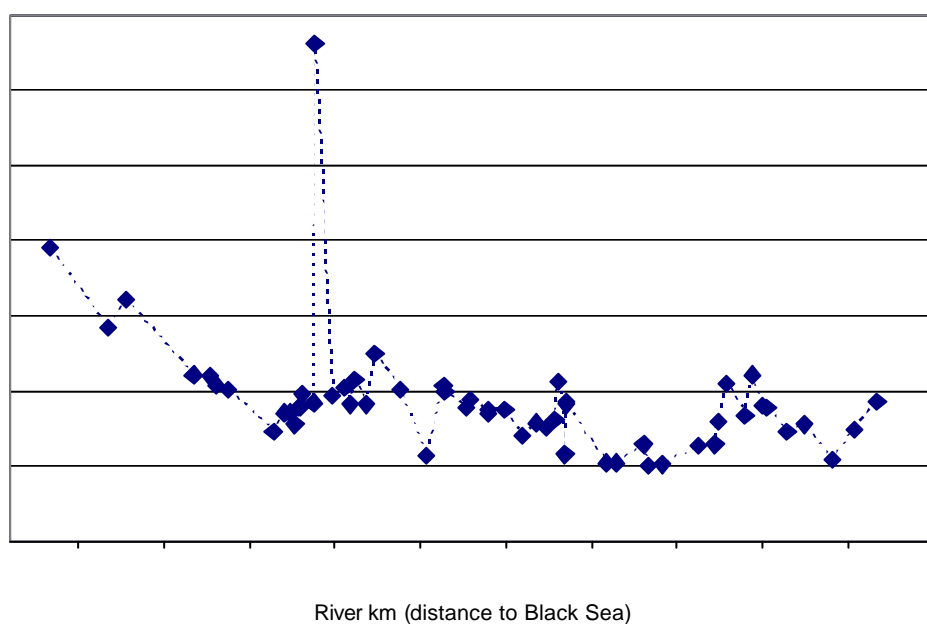
The average concentration along the main course of the Danube was 1.9 mg N/l. The maximum of the recommended EQS range (1.0 - =1.5 mg N/l) was exceeded in 75% of the occasions (43 out of 57 sampling locations marked as 'Danube'). The total nitrogen concentrations of the samples taken at (near the mouth of) the tributaries and/or Danube arms (code 'Tributary/arm') exceed the proposed maximum of the EQSs range in 19 out of 25 (76%) of the cases. Not surprisingly, the concentrations in the tributaries tend to be (slightly) higher than in the main course of the Danube River.

Table 2.9   Summary statistics of N_{tot} in Joint Danube Survey [mg N/l]

	Main Danube course	Tributaries/arms
average	1.9	2.4
median	1.9	2.1
5-percentile	1.0	1.1
95-percentile	2.9	4.5
minimum	1.0	0.9
maximum	6.6	7.0

2.5.2.2   Organic nitrogen

When subtracting the NH4 concentrations from the (Kjeldahl determined) organic nitrogen contents, the results are as follows.

Figure 2.3   'Plain' organic nitrogen concentrations in the Danube's main course, JDS survey [mg N/l]

River km (distance to Black Sea)
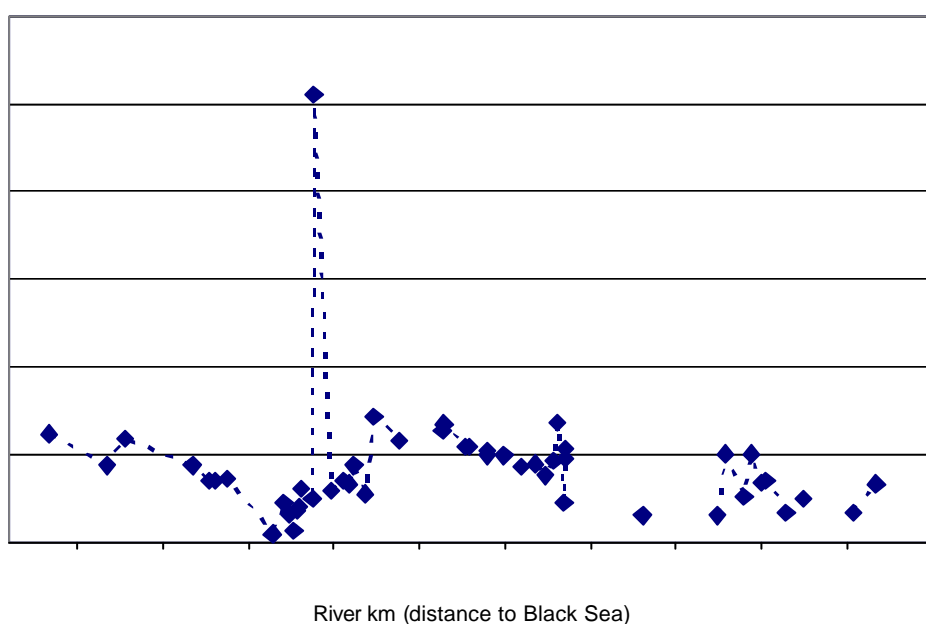
Table 2.10   Summary statistics of 'plain' organic N in Joint Danube Survey [mg N/l]

	Main Danube course	Tributaries/arms
average	0.85	0.98
median	1.28	0.90
5-percentile	0.30	0.49
95-percentile	1.36	1.66
minimum	0.10	0.44
maximum	5.10	2.21

On average, the organic_N concentrations comprise about 40% of the total_N concentrations.

2.5.2.3   Total phosphorous

Since P_{tot} was directly analysed in the water samples, no intermediate calculations were required. The graph below shows the P_{tot} concentrations along the main course of the river. The table includes the summary statistics for the main course of the Danube River and for the tributaries.

Figure 2.4 P_{tot} concentrations in the Danube's main course, JDS survey [mg P/l]

River km (distance to Black Sea)
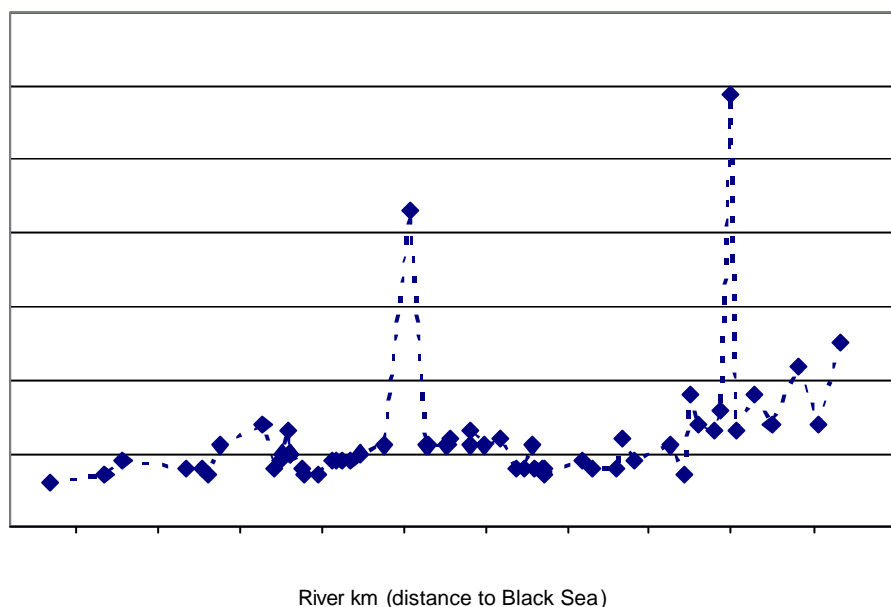
Table 2.11   Summary statistics of P_{tot} in Joint Danube Survey [mg P/l]

	Main Danube course	Tributaries/arms
average	0.12	0.23
median	0.10	0.16
5-percentile	0.07	0.08
95-percentile	0.23	0.67
minimum	0.06	0.08
maximum	0.59	0.92

Compared to the proposed EQS-range (0.02 – 0.08 mg P/l), most of the JDS samples would exceed the maximum of 0.08 mg P/l.

The graph below contains the annual mean P_{tot} concentrations of the TNMN stations along the main course of the Danube for the year 2000.

Figure 2.5   **Annual mean P$_{tot}$ concentrations in the Danube, TNMN data 2000 [mg P/l]**

River km (distance to Black Sea)
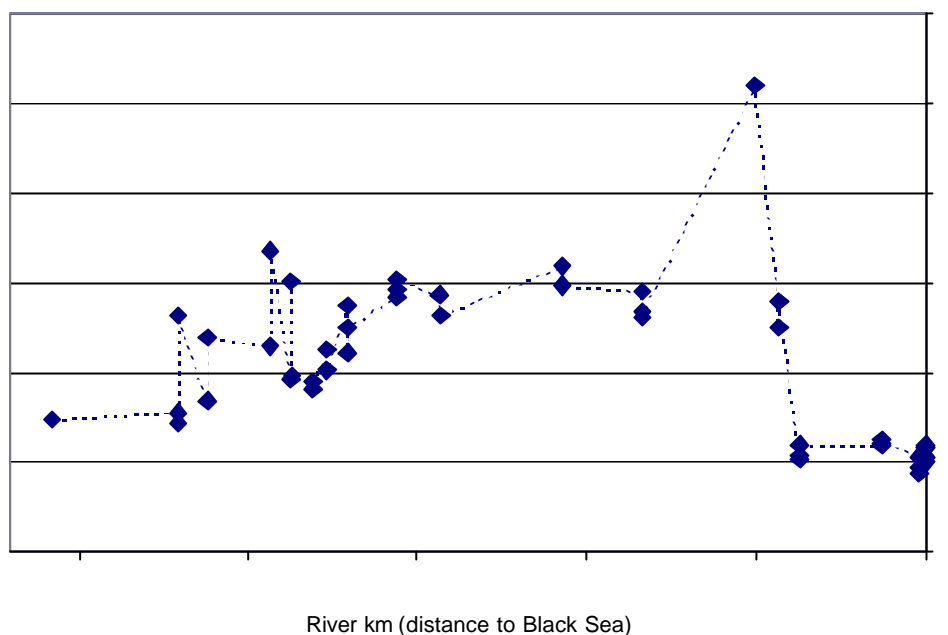
The annual mean concentrations tend to be slightly higher than the JDS results. More details on the results of the TNMN can be found in [Adamková, 2003].

2.5.2.4 'Eutrophication'

One should keep in mind that the suggested N$_{tot}$ and P$_{tot}$ thresholds are merely physico-chemical approximates for the occurrence of eutrophication. Finally, the occurrence of the more distinctive features of eutrophication, like algae blooms, chlorophyll-a concentrations, very low/either oversaturated oxygen levels, etcetera, are better indicators.

Section 4.5: Phytoplankton of the JDS technical report indeed mentions the occurrences of eutrophication and/or eutrophic states in various instances [ICPDR, 2002]. Linking these observations with the measured nutrient concentrations in the main course of the Danube (5/95-percentile concentrations were: N$_{tot}$: 0.3 – 1.9 mg N/l; P$_{tot}$: 0.07 - 0.23 mg P/l), one can infer that the proposed 'good status' EQS for N$_{tot}$ (1.0 – 1.5 mg N/l) is supported, while the proposed EQS for P$_{tot}$ (0.02 – 0.08 mg P/l) may be considered too stringent.

2.6 Synthesis and discussion of previous findings

While trying to formulate recommendations for EQSs for nutrients in the Danube River basin, the underlying study at the same time aimed at providing with (background) material to support the MLIM and other expert groups in the completion of their tasks.

The recommended EQSs are:
- 1.0 – 1.5 mg N/l for N$_{tot}$
- 0.02 – 0.08 mg P/l for P$_{tot}$

The proposed values first of all are suggested to become the focus of future discussions. Among others, further agreements finally should be reached on:

- the proposed ranges as such;
- the upper/lower/medium of the ranges (if agreed as such);
- setting the EQSs as 'season variable' values (e.g. just summer-average means);
- checking and testing the physico-chemical values against ecological/biological criteria and empirical findings.

The proposed EQSs seem rather stringent. Nevertheless, they were formulated from a common denominator that can be recognised in the 'best-available-knowledge' contained in a representative series of references.

When applying them for instance to the results of the JDS, then the conclusion would be that the physico-chemical situation would not comply with "good status" for nutrients. The EQSs could partially be supported by yet other sets of data more specific for the Danube, notably the Joint Danube Survey findings. The biological results of the JDS indicate occurrences of eutrophication, with nutrient concentrations not that much exceeding the recommended EQSs.

The Black Sea has not could be taken into account in the assessments of the underlying study. Acknowledging the fact that the discharge of the Danube has an significant impact on the status of the Black Sea (at least in the north-western part), implies that, while formulating water quality criteria for the freshwater part of the Danube basin, the final resulting water quality of the Black Sea should be taken into consideration as well. Additional considerations, when taking the Black Sea into account as well, include:

- Discharged loads as a criterion; this not necessarily conflicts with the approach of formulating EQSs, but may result in yet other viewpoints. The concept of "critical loads" is still under development.
- Seasonality criteria: for loading of the Black Sea with nutrients it finally may not matter whether they are discharged in summer of wintertime, since they will be retained in the sea anyway. This could conflict with the option to 'optimise' EQSs in the freshwater Danube basin for the summer period.

3   Ammonium (NH₄)

3.1   Introduction

Ammonium[2] is one of the nutrients that can contribute to eutrophication. However, NH_4 is also related with toxic impacts, notably the toxicity of (ammonia) NH_3. Ammonia is instable, and in freshwaters only will occur in larger concentrations under more extreme conditions (relevant parameters are water temperature and pH; low oxygen levels also can be relevant). Because of its potential toxicity, it has been decided to deal separately with NH_4 in this chapter.

In this context, ammonium can be regarded as a 'specific non-synthetic pollutant'. The WFD defines the status of these specific non-synthetic pollutants as follows (annex V, table 1.2)

- **High status** : Concentrations remain within the range normally associated with undisturbed conditions (background levels = bgl).
- **Good status** : Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 (2) without prejudice to Directive 91/414/EC and Directive 98/8/EC. (<EQS).[3]

3.2   Inventory of EQSs for NH₄

Compared to the nutrients (chapter 2) and the metals (chapter 5), the available information for EQS for ammonium will be presented rather straightforward. The major information is included in table 3.1.

Table 3.1   Overview of EQSs for ammonium

Water quality criteria system	Concentration (lower range) [mg NH₄_N/l]	Concentration (higher range) [mg NH₄_N/l]	Remarks	*Reference*
Rhine	0.2		Target value (Zielvorgabe)	*IKSR, 1992*
United States	3.8	20 (salmonids present) 30 (salmonids absent)	see note (1) below	*EPA, 1999*
EU	=0.04 salmonid =0.2 cyprinid	=1 salmonid waters =1 cyprinid waters	low= G(uide) value higher= I(mperative)	*Directive 78/559/EEC*
UN-ECE	n.a.		The document just mentions NH3 without any values	*UN-ECE, 1992*
TNMN	0.2 Class I 0.3 Class II	0.6 - >1.5 (Class III – V)		*Adamková, 2003*
Czech Republic	0.2 Class I	0.4 Class II 5 Class IV >5 Class V	I: very clean II: clean IV: intensely polluted V: very polluted	*Haskoning, 1994*
Hungary	0.8 Class I	1.9 Class II	I: high quality, clean waters	*Haskoning,*

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[2] This report will use the name ammonium for NH_4. Sometimes, NH_4 is called "total ammonia", where NH_3 then is called "un-ionised" ammonia.

[3] Section 1.2.6 of WFD Annex V outlines the procedure for the setting of chemical quality standards by Member States. Directive 91/414/EC is the COUNCIL DIRECTIVE of 15 July 1991 concerning the placing of plant protection products on the market. 98/8/EC refers to the Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market.

Water quality criteria system	Concentration (lower range) [mg NH$_4$_N/l]	Concentration (higher range) [mg NH$_4$_N/l]	Remarks	*Reference*
		>1.9 Class III	II: polluted; no detrimental impact on aquatic ecosystem III: polluted, detrimental to aquatic ecosystem	*1994*
Romania	0.1 Class I	0.2 class II 0.4 class III	I: drinking water II: recreation and fishing III: irrigation and industry	*Haskoning, 1994*
The Netherlands	-	0.02 mg **NH$_3$**_N/l (MAC)	no values for ammonium	*V&W, 2000*

(1)   The US-EPA actually mentions formulas as criteria for total ammonia, where the result depends on the water temperature and pH. In the above table as 'low range' concentration the CCC (chronic criterion, see also chapter 5) for pH=7.2 and T= 20 ^{o}C is mentioned [EPA, 1999, page 87]. As high range, the CMC (acute criterion) for pH= 7.2 is mentioned [EPA, 1999, page 86].

3.3 Synthesis of findings for 'good status' of NH$_4$

A natural background concentration of ammonium will be less than 0.1 mg NH$_4$_N/l (compare Table 2.3). Hence, as EQS for 'high' status of ammonium, a concentration of 0.1 mg NH$_4$_N/l is suggested.

The US-EPA concentrations are exceptionally high compared to the other criteria. The lowest CMC (Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect) concentration in [EPA, 1999, table page 86] is 0.9 mg N/l, applying to water with pH=9 and salmonids present.

The remaining concentrations mentioned in the 'lower range' column tend towards 0.2 mg NH$_4$_N/l or less (except Hungary Class I). Based upon this overview it is proposed to use =0.2 mg NH$_4$_N/l as the 'good status' EQS for ammonium.

3.4 Comparison of proposed EQS with actual concentrations

3.4.1 Joint Danube Survey

Figure 3.1   NH$_4$ concentrations in the Danube's main course, JDS survey [mg N/l]

River km (distance to Black Sea)
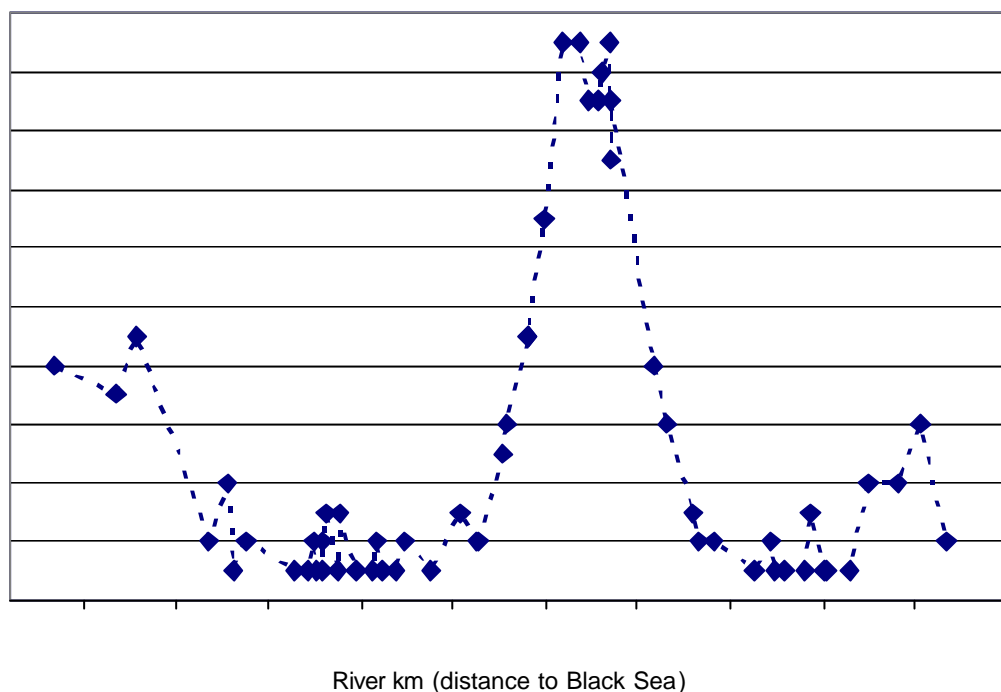
Table 3.2   Summary statistics of NH$_4$ in Joint Danube Survey [mg N/l]

	Main Danube course	Tributaries/arms
average	0.05	*0.23*
median	0.02	0.03
5-percentile	0.01	0.01
95-percentile	0.18	0.78
minimum	0.01	0.01
maximum	0.19	3.24

The JDS findings would comply with 0.2 mg NH$_4$_N/l as "good status" EQS for ammonium. (Because of one extreme outlier, the average tributaries/arms concentration is higher than the median concentration; also the 95%-concentration seems relatively high).

3.4.2 TNMN

Since the JDS was conducted during the warm August-October period, one may expect relatively low concentrations. The graph below contains the annual mean concentrations of the TNMN stations along the main course of the river for the year 2000[4].

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[4] Please refer for details to the separately reported TNMN 1995-2000 results in [Adamková, 2003].

Figure 3.2   NH$_4$ concentrations in the Danube, TNMN stations, annual mean 2000 [mg N/l]

River km (distance to Black Sea)
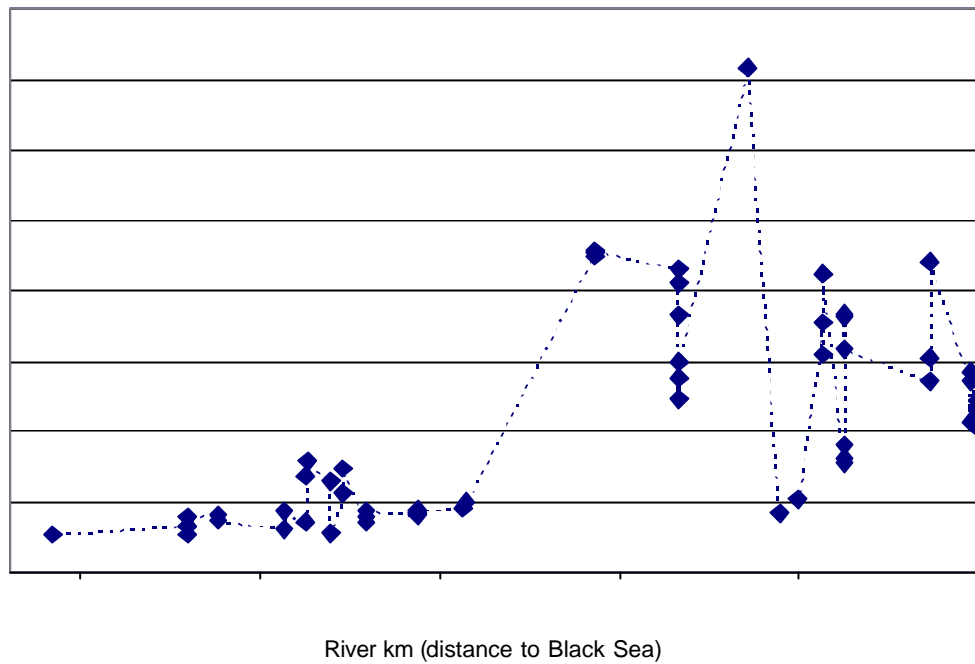
Indeed this shows quite a different picture compared to the JDS results. Similar patterns (concentrations levels and higher concentrations in the downstream half of the river) can be recognised for the years 1996-1999. There are many locations where the annual mean concentration exceeds the proposed EQS of 0.2 mg N/l (and higher concentrations can be expected during the winter period).

3.4.3   Seasonality

The argument that could be applied to eutrophication (an EQS could refer to a summer, low concentration, period only) is not valid from a <u>toxicity</u> point of view. It is the actual concentration that might be harmful to organisms. In fact, one should apply the potential winter maximum conditions when formulating the EQS for NH$_4$.

4   Chemical oxygen demand (COD)

4.1   Introduction

COD is a bit of an exception in the parameters dealt with in this report. The other parameters are distinct compounds, whereas COD is merely an indicative 'sum' parameter. COD can be defined as:

- (1) A measure of the chemically oxidizable material in the water, which provides an approximation of the amount of organic and reducing material present. The determined value may correlate with Biochemical Oxygen Demand (BOD) or with carbonaceous organic pollution from sewage or industrial wastes; (2) A chemical measure of the amount of organic substances in water or wastewater. A strong oxidizing agent together with acid and heat are used to oxidize all carbon compounds in a water sample. Nonbiodegradable and recalcitrant (slowly degrading) compounds, which are not detected by the test for BOD, are included in the analysis. The actual measurement involves a determination of the amount of oxidizing agent (typically, potassium dichromate) that is reduced during the reaction [NDWR, 1999].

- The mass concentration of oxygen consumed by the chemical breakdown of organic and inorganic matter [UN/ECE, 1992].

The following quote shows how COD can be used and interpreted in an environmental context (note: the situation described in the quotation applies to Japan).

> "Chemical Oxygen Demand: COD_{Mn} is used as an organic pollution index including phytoplankton growth. A COD of less than 1 mg/l is assumed not to be caused by anthropogenic influence. Waters under this condition are suitable for conservation of the natural environment. According to the drinking water law, the standard value for $KmnO_4$ consumption is 10 mg/l, which is equivalent to 2.5 mg/l of COD. A survey, conducted by the Ministry of Health and Welfare, found that most lakes being used for drinking water supply have a COD of less than 3 mg/ l. Water quality for fisheries were classified as either oligotrophic or eutrophic. In oligotrophic lakes, having very clear water, COD should be less than 1 mg/l that is required for oligosaprobic species such as rainbow trout. In general, the COD of oligotrophic and eutrophic lakes containing oligosaprobic fish such as smelt, should be less than 3 mg/l. In eutrophic lakes containing carp, the COD should be less than 5 mg/l (Water Quality Standards for Fisheries, 1965). Less than 8 mg/l COD is desirable for waters used for swimming. High COD interferes with oxygen transfer to the soil, resulting death of rice plants. Experimental results show that a COD of less than 6 mg/l are desirable for agriculture use. In general 8 mg/l of COD is acceptable for most industrial uses and for conservation of environment" [EMECS, 2003].

There are two methods for analysing COD, using the dichromate method (results then should be indicated as COD_{Cr}), or the permanganate method (COD_{Mn}). Analysis of the same water sample with COD_{Cr} results in higher (factor 2 to 3) concentrations than with COD_{Mn}.

4.2   Inventory of EQSs for COD

Compared to the other parameters, relatively few information on EQS systems could be identified. From the major used reference systems (EU, UN, Rhine, US-EPA) only the UN-ECE presents EQSs for COD. The only EU Directive mentioning a distinct value for COD is the Council Directive 75/440/EEC (30 mg O2/l as Guide value for the A3 drinking water treatment category).

4.2.1   United Nations

The UN-ECE groups COD under the Oxygen regime category. Major criteria for this category are oxygen content, together with presence of oxygen-demanding substances, and the impact of oxygen content levels on aquatic life.

UN-ECE	class I[5]	class II	class III	class IV	class V
COD_{Mn} (mg O_2/l]	<3	3 – 10	10 – 20	20 -30	>30

4.2.2   Danube basin

Table 4.1   Overview of COD_{Mn} criteria in various Danube countries

Water quality criteria system	Concentration (lower range) [mg O_2/l]	Concentration (higher range) [mg O_2/l]	Remarks	Information source
TNMN	5 Class I 10 Class II	20 - >50 (Class III – V)		*Adamková, 2003*
Czech Republic	5 Class I	10 Class II 25 Class IV >25 Class V	I: very clean II: clean IV: intensely polluted V: very polluted	*Haskoning, 1994*
Hungary	8 Class I	15 Class II >15 Class III	I: high quality, clean waters II: polluted; no detrimental impact on aquatic ecosystem III: polluted, detrimental to aquatic ecosystem	*Haskoning, 1994*
Romania	10 Class I	15 class II 25 class III	I: drinking water II: recreation and fishing III: irrigation and industry	*Haskoning, 1994*

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[5] UN/ECE oxygen regime classes:

I   Constant near-saturation of oxygen content. Insignificant presence of oxygen demanding substances from the point of view of aquatic life.

II   The oxygen saturation of water is good. Oxygen demanding substances do not normally disturb oxygen saturation

III   Oxygen deficiencies may occur in the hypolimnion. The presence of oxygen demanding substances risks having sometimes considerable negative impact s on aquatic life through the reduction of oxygen contents.

IV   Oversaturation of oxygen or oxygen deficiency occurs in the epilimnion and oxygen deficiencies are frequent in the hypolimnion, possibly owing to chronic problems with the presence of oxygen demanding substances.

V   Acute problems occur in oxygen regime, i.e. oversaturation or oxygen deficiency in the epilimnion, and oxygen deficiency leading to anaerobic conditions in the hypolimnion. The high level of presence of oxygen demanding substances may equally cause acute oxygen deficiencies.

4.2.3   Japan (lakes)

The information mentioned in the introduction of this chapter is summarised in the table below [EMECS, 2003].

Table 4.2   Overview of COD$_{Mn}$ criteria in Japan (lakes)

COD$_{Mn}$ [mg O$_2$/l]	Description
=1	not to be caused by anthropogenic influence
=3	oligotrophic and eutrophic lakes containing oligosaprobic fish such as smelt
=5	eutrophic lakes containing carp (Water Quality Standards for Fisheries, 1965)
=6	for agriculture use
=8	desirable for waters used for swimming; acceptable for most industrial uses and for conservation of environment

4.3   Synthesis of findings for 'good status' of COD$_{Mn}$

The EQSs in the previous section are rather well comparable. The UN-ECE class II range (3 – 10 mg O2/l) encompasses the lower ranges of the other EQS criteria. The class II description ("The oxygen saturation of water is good. Oxygen demanding substances do not normally disturb oxygen saturation") is an appropriate approximation of the 'good' status of the oxygen regime. Hence, the recommended EQS for 'good status' for CODMn is set to =10 mg O$_2$/l.

4.4   Comparison of proposed EQS with actual concentrations

COD was not analysed during the JDS. Using the annual average data (as can be retrieved from Danubis), the average COD$_{Mn}$ concentration of the TNMN data over the period 1996-2000 was 4.7 mg O$_2$/l. This easily fits within the recommended EQS of =10 mg O$_2$/l. Maximum concentrations though could go as high as 49 mg O$_2$/l. More details on the results of the TNMN can be found in [Adamková, 2003].

5   Metals (As, Cr, Cu, Zn)

5.1   Introduction

Metals can be present in rivers originating from natural (geogenic) sources. The WFD defines the status of these specific non-synthetic pollutants as follows (annex V, table 1.2)

- **High status** :   Concentrations remain within the range normally associated with undisturbed conditions (background levels = bgl).

- **Good status** :   Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 (2) without prejudice to Directive 91/414/EC and Directive 98/8/EC. (<EQS).[6]

At low concentration levels many (heavy) metals as natural trace elements can be essential for most living organisms. However, at higher concentrations, metals can become toxic.

The general purpose one can derive from the text of WFD Annex V, 1.2.6 is the need for defining a No Observed Effect Concentration. The differences between the description of 'high' and 'good' status of the specific non-synthetic pollutants like metals in the WFD in principle allow for environmental conditions influenced by anthropogenic activities (read: polluted beyond the natural background loading).

5.2   Total, dissolved, adsorbed?

A discussion about monitoring and setting EQSs for heavy metals often concerns which occurrence(s) should be taken into account: only the dissolved part (more readily bioavailable), or the total concentration (adsorbed + dissolved)?

In this context, it is interesting to notice that the target-values (in German: "Zielvorgaben") for heavy metals in the Rhine Action Programme are formulated for suspended solids only. These 'Zielvorgaben' for suspended solids/sediment take into account: disposal of dredged sediment on land and sea, plus protection of organisms living in the sediment.

As far as the queries could identify, actually few existing water quality criteria systems for heavy metals in aquatic environments comprise EQSs for suspended solids/sediment. The Netherlands has elaborated quite an extensive set of EQSs for heavy metals. This includes water quality standards for total, dissolved, and sediment concentrations.

With the majority of water quality systems having defined standards for total (and/or dissolved) concentrations, the focus of this project will be on total concentrations. Nevertheless, relevant data concerning suspended solids and sediments will be incorporated as well.

5.2.1   Short primer on some key features of total, dissolved, and adsorbed metals

Heavy metals in aquatic environments normally are present in both the water phase (dissolved) and adsorbed to particles (suspended solids, sediment). The ratio dissolved/adsorbed varies among the metals. The table below shows the percentage dissolved in the total concentration for some metals for average conditions that apply to the river Rhine (refer also to textbox 5.1 for details).

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[6] Section 1.2.6 of WFD Annex V outlines the procedure for the setting of chemical quality standards by Member States. Directive 91/414/EC is the COUNCIL DIRECTIVE of 15 July 1991 concerning the placing of plant protection products on the market. 98/8/EC refers to the Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market.

Textbox 5.1   **Partitioncoefficient Kd and formulas for (re-)calculation of metal concentrations**

The partitioncoefficient Kd represents for metals in aquatic systems the 'equilibrium' between the amount of the metal dissolved in the water phase versus the amount adsorbed to the suspended solids (adsorbed; solid phase).

$$K\mathrm{d} = \frac{Ctot - Cdis}{SS * Cdis} \qquad (1)$$

The Kd values mentioned in table 5.1 were calculated from three years of field data collected in various Dutch waterways [RIZA, 1989].

In case only dissolved concentrations are known (measured), then the total metal concentration can be calculated using formula (2a), either (2b)

$$Ctot = Kd*SS*Cdis + Cdis \qquad (2a)$$

$$Ctot = Cdis * (1 + Kd*SS) \qquad (2b)$$

The metal concentration adsorbed to the suspended solids could be calculated directly from the field data (in this case, the total and dissolved metal concentration plus the suspended solids concentration are measured) using formula (3),

$$Cads = \frac{Ctot - Cdis}{SS} \qquad (3)$$

or approximated with formula (4) (following from *(1)* and *(3)*), when only the dissolved concentration is known

$$Cads = Kd * Cdis \qquad (4)$$

either through formula (5), when the total metal concentration plus the suspended solids concentration are known

$$Cads = \frac{Ctot}{SS + (1/Kd)} \qquad (5)$$

with: Kd: partitioncoefficient water/solid phase [l/g]

Ctot: total heavy metal concentration [µg/l]

Cdis: dissolved heavy metal concentration [µg/l]

Css: concentration heavy metals in suspended solids fraction [mg/kg]

SS: suspended solids concentration in [g/l]

Formulas quoted from [RIZA, 1989].

Please refer to subsection 5.3 for examples of the limitations and pitfalls of the formulas above.

Table 5.1   Percentages dissolved metals of total concentration

	Kd [l/g]	Dissolved fraction (with SS= 30 mg/l)
Ni	*8*	*81%*
As	**10**	**77%**
Cu	**50**	**40%**
Zn	**110**	**23%**
Cd	*130*	*20%*
Hg	*170*	*16%*
Cr	**290**	**10%**
Pb	*640*	*5%*

SS= suspended solids

The table illustrates that in an <u>unfiltered</u> (freshwater) water sample for instance arsenic is dissolved in the water phase for 77%, while in the case of chromium 90% is adsorbed to the suspended solids.

For particulate (adsorbed) concentrations of micropollutants further the composition of the suspended solids and sediment are relevant. Micropollutants tend to adsorb to the smaller suspended solids fraction (e.g. clay) and to the organic matter. The Dutch EQSs therefore apply to 'standard suspended solids', consisting of 20% organic matter and 40% 'lutum' (clay <2 µm fraction). 'Standard sediment' consists of 10% organic matter and 25% lutum [V&W, 2000].

For a proper comparison of sample concentrations with the Dutch EQSs, the results are first to be (re-)calculated to the standard conditions[7]. This, in order to remove the bias that would result from differences in the amount of organic matter and/or small solids fractions. (A more sandy sediment sample might seem to be less polluted than a sample taken at the same location containing finer particles. If no sieving prior to analysis, or standardisation like above on the analysis results has been carried out, such would be the interpretation.)

An alternative approach for standardising sediment (and suspended solids, given a sufficient amount of material) prior to analysis is sieving; common are 63 or 20 µm pores.

5.3   Natural background levels

Data on natural background levels of heavy metals for the purposes of this study could be identified for: the Danube, the Rhine basin, and the Netherlands. The International Rhine Commission (IRC) has defined natural background for sediment/suspended solids for the Rhine River basin. The Netherlands has defined natural background concentrations of metals in sediment and in water (total concentration). Data related to the Danube basin are included in section 5.2.3 of the JDS Technical report [ICPDR, 2002]. The various values are included in the tables below.

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[7] The actual (re-)calculations are a bit more complicated than mentioned here. Additional coefficients are used in the calculations, which differ among the various metals.

Table 5.2   Natural background concentrations of metals in sediment [mg/kg]

	Rhine [IKSR, 1993a,b] (< 20 µm fraction) AVERAGE	Rhine [IKSR, 1993a] (< 20 µm fraction) RANGE	The Netherlands [V&W, 2000] (sediment with 10% organic matter and 25% <2 µm)	Danube baseline [ICPDR, 2002] (< 63 µm)
As	*20*[&]	*not defined*	29	10
Cr	80	40 – 160	100	10 - 50 (?)
Cu	20	10 – 40	36	35
Zn	100	50 – 200	140	130

[&] The Rhine target value for As has been defined as 2 x natural background, hence 20 mg/kg can be deferred.

Table 5.3   Natural background concentrations of metals in water [µg/l]

	Rhine [IKSR]	The Netherlands [V&W, 2000] total	The Netherlands [V&W, 2000] dissolved	'Danube' [ICPDR, 2002] total
As	*not defined*	1.0	0.8	-
Cr	*not defined*	1.6	0.2	1.3 – 5.0
Cu	*not defined*	1.1	0.4	0.5 – 2.0
Zn	*not defined*	12	2.8	1.8 – 7

Table 5.2 implies that the IRC has defined lower background concentrations for Cr, Cu, and Zn in sediment than the Netherlands[8]. These are not necessarily 'real' differences (both the IRC and the Dutch values are estimated 'best-expert' approximations). The IRC for instance applies the same natural background levels for the metals in both sediment and in suspended solids [IKSR, 1993a, 1993b]. The explanation of the IRC is that sieving suspended solids either sediment over 20 µm more or less will equalise possible differences in the composition of the original material (like unsieved sediment samples containing more sand). No data were immediately available showing whether or not sieving sediment over 20 µm would result in 'standard sediment' complying with the Dutch definitions.

'Indirectly' one can infer that the IKSR and the Dutch systems actually share similarities that could explain the apparent differences in the background concentrations. Being a bit ahead of the EQSs presented later on, this can be illustrated as follows. The 'Zielvorgaben' for metals of the Rhine Action Programme (RAP) are defined for suspended solids [IKSR, 1992]. The table with the EQSs for the Netherlands contains numeric values for sediment [V&W, 2000]. As mentioned in this document, the EQSs for metals in suspended solids are a factor 1.5 higher than the sediment concentrations (assuming both 'standard sediment' and 'standard suspended solids'. Refer also to [RIZA, 1989]). The various values are included in the table below. (As mentioned in subsection 2.4.1.4, in the Netherlands actually two sets of EQSs are defined, a No Effect Level and a MAC value. The Rhine target-values are considered to be equivalent to NOELs).

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[8] Arsenic is not a priority substance in the Rhine Action Programme, hence no 'Zielwert' or background concentration have been formulated.

Table 5.4   **Target values for particulate metal contents in the RAP and in NL [mg/kg]**

	The Netherlands sediment, NOEL	The Netherlands SS, NOEL (=sediment * 1.5)	Rhine [IKSR] SS, Zielvorgabe
As	**29**	**44**	*not defined*
Cr	**100**	**150**	**100**
Cu	**36**	**54**	**50**
Zn	**140**	**210**	**200**
Cd	*0.8*	*1.2*	*1.0*
Hg	*0.3*	*0.45*	*0.5*
Ni	*35*	*52*	*50*
Pb	*85*	*128*	*100*

The Dutch 'calculated' suspended solids target values are comparable to the RAP target values[9], except for chromium. From this, one can infer that the associated sediment quality (also of the natural background) actually can supposed to be similar as well.

5.3.1   Examples of limitations for using the formulas in textbox 5.1

The Rhine Action Programme has formulated target-values for suspended solids only. Of course this triggers the question how these will relate to dissolved or total metal concentrations. This, in order to be able to compare with other sets of EQS that for instance only contain total or dissolved concentrations.

The formulas presented in textbox 5.1 imply this should be feasible, and only requires rather basic mathematics. Unfortunately, it turns out that the Dutch EQSs for total, dissolved, and sediment mutually do not comply with the results as would be expected when applying these formulas. The Dutch NOEL water quality standards for the metals of present study are summarised in the table below [V&W, 2000].

	dissolved [µg/l]	total [µg/l]	sediment [mg/kg]	*suspended solids (= sediment * 1.5) [mg/kg]*
As	1.0	1.3	29	*44*
Cr	0.3	2.4	100	*150*
Cu	0.5	1.1	36	*52*
Zn	2.9	12.0	140	*210*

Applying the formulas in textbox 5.1, together with the Kd values mentioned in Table 5.1, and 30 mg/l as the 'standard suspended solids concentration', following results are obtained.

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[9] Of course, this is not just a coincidence. The major part of the Netherlands is part of the Rhine basin. There are many cross-references and overlaps between the national Dutch and international Rhine policy settings and strategies.

Total ⇔ Dissolved

The calculated results match quite well with the defined values, maybe except for the total-Cr concentration calculated from the dissolved chromium concentration (see table below)

	dissolved *defined* [µg/l]	dissolved *calculated from total* [µg/l]	total *defined* [µg/l]	total *calculated from dissolved* [µg/l]
As	1.0	1.00	1.3	*1.3*
Cr	0.3	0.25	2.4	*2.9*
Cu	0.5	0.44	1.1	*1.25*
Zn	2.9	2.79	12.0	*12.5*

Adsorbed ⇔ Total and Dissolved

The results of using the total and dissolved concentrations for calculating the suspended solids significantly differ from the actual ones!

	Suspended solids *defined* [mg/kg]	Suspended solids *calculated from total* [mg/kg]	Suspended solids *calculated from dissolved* [mg/kg]
As	44	10	10
Cr	150	72	87
Cu	52	22	25
Zn	210	307	319

The above findings indicate that one should be quite careful when applying formulas like the ones presented in textbox 5.1. More considerations then merely equilibrium coefficients can apply when establishing EQSs, for instance depending the specific feature of the media (like organisms living in the water phase, versus those mainly living in bottom sediments).

5.4 Inventory of water quality criteria for metals resembling 'good status'

5.4.1 United Nations

The UN "ECE Standards Statistical Classification of Surface Water Quality for the Maintenance of Aquatic Life" defines five classes of metal concentrations [UN/ECE, 1992]. Major criterion underlying the metal section is "Toxicological impact on aquatic life as established in US-EPA practices." Although not explicitly mentioned in the document, metal concentrations can be inferred to apply to *total concentration* in water.

UN-ECE [µg/l]	class I[10]	class II	class III	class IV	class V
As[c]	<10	10 - 100	100 -190	190 – 360	>360
Cr[c]	<1	1 – 6	6 – 11	11 – 16	>16
Cu[d]	<2	2 – 7	7 – 12	12 – 18	>18
Zn[d]	<45	45 – 77	77 – 110	110 -120	>120

[c] Applicable for hardness from about 0.5 meq/l to 8 meq/l. Arsenic V (chromium III) to be converted to arsenic III (chromium VI).

[d] Applicable for hardness from about 0.5 meq/l to 8 meq/l.

5.4.2 European Union

EU Directives, explicitly mentioning EQSs for As, Cr, Cu, and/or Zn are:

- 75/440/EEC, concerning the quality required of surface water intended for the abstraction of drinking water in the Member States;
- 78/659/EC: on the quality of fresh waters needing protection or improvement in order to support fish life.

The standards of the 75/440/EEC Directive are merely mentioned for the sake of completeness. The Guide respectively Imperative values for total concentrations of the most stringent A1 category are:

75/440/EEC [µg/l]	A1 Guide	A1 Imperative
As	10	50
Cr (VI)	-	50
Cu	20	50
Zn	500	3000

The basic aims of the 78/659/EEC directive are close to the context of the WFD. This 'fish directive' contains EQSs for Cu and Zn. For *copper* only Guidance (non-binding) concentrations are formulated for the *dissolved fraction*. For **zinc** only Imperative (mandatory) EQSs for the ***total concentrations*** are defined. The main values as mentioned in Annex I of the directive apply to a hardness corresponding with 100 mg/l CaCO3. Annex II of the Directive shows the concentrations associated with other hardness values. Further, two different kinds of waters are further discriminated: Salmonid and Cyprinid. The various criteria are included in the table below.

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[10] UN/ECE metal classes:

I   No anthropogenic pollution with inorganic matter.

II   Concentrations are below midpoint between natural and chronically toxic levels.

III   Concentrations are above midpoint between natural and chronically toxic levels.

IV   Excursions beyond chronic criteria concentrations occur, but do not establish chronically toxic conditions in terms of concentration levels, duration or frequency.

V   Excursions beyond chronic criteria concentrations allow acutely toxic conditions in terms of concentration levels, duration or frequency.

78/669/EEC	hardness [mg/l CaCO3]	Cu dissolved Salmonid waters (Guide value) [µg/l]	Cu dissolved Cyprinid waters (Guide value) [µg/l]	Zn total Salmonid waters (Imperative value) [µg/l]	Zn total Cyprinid waters (Imperative value) [µg/l]
	10	-	5	30	300
	50	-	22	200	700
	100	**400**	**40**	**300**	**1000**
	500	-	112	500	2000

For dissolved copper, the most stringent value applies to Salmonid waters, while for Zn the most stringent values apply to Cyprinid waters. Hence, assigning one of both water categories (Salmonid or Cyprinid) would not suffice when trying to be on the safe side of both metals. Secondly, the directive explicitly discriminates different concentration criteria for different levels of water hardness. This is different from the UN criteria that encompass one single concentration for quite a wide hardness range.

While keeping the constraints of calculations in mind: a dissolved copper concentration of 400 µg/l would imply a total concentration of 1000 µg/l; 40 µg/l dissolved Cu implies 100 µg/l.

5.4.3   United States

The National Recommended Water Quality Criteria as defined by the US-EPA comprise two sets of concentrations of the four metals: CMC and CCC levels [EPA, 2002]. Quoting [EPA, 2002]: "The Criteria Maximum Concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. The Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect."

The description of the (lower, more stringent) CCC can be considered as an approximation of 'good status'. Nevertheless, both classes of concentrations are shown in the table below.

Following footnote D in [EPA, 2002]: "Freshwater and saltwater criteria for metals are expressed in terms of the dissolved metal in the water column", the water quality criteria refer to ***dissolved concentrations***. The total concentrations were calculated for this report purposes only; the limitations of such calculations should be kept in mind.

	CMC [µg/l]	CCC [µg/l]	*calculated total CCC [µg/l]*
As	340	150	*195*
Cr (III)	2.0	0.25	-
Cr (VI)	570	74	*718*
Cu	13	9.0	*22*
Zn	120	120	*516*

5.4.4   The Netherlands; Rhine

Also referring to the discussion in section 5.3, it has been decided to mention the Dutch EQSs only. The calculation exercises, that inferring concentrations/EQSs for total and dissolved concentrations

from suspended solids concentrations only, can be very tricky. In addition, may lead to inconsistent results. As far as the suspended solids are concerned, the EQSs defined for the Rhine basin and for the Netherlands compare quite well (except for chromium). It is assumed that the major principles underlying the EQSs for the RAP and for NL are comparable.

Basically, four times two sets of EQSs can be discriminated in the Dutch system of EQSs. For respectively total, dissolved, sediment, and suspended solids metal concentrations both NOEL and MAC values are defined.

The NOELs of the *total concentrations* of Cu and Zn are similar to the natural background. For As and Cr, the NOELs are higher.

NL Total	natural background [µg/l]	NOEL [µg/l]	MAC [µg/l]
As	1.0	1.3	32
Cr	1.6	2.4	84
Cu	1.1	1.1	3.8
Zn	12.0	12	40

The NOELs of the *dissolved concentrations* for all four metals are (slightly) higher than the natural background.

NL Dissolved	natural background [µg/l]	NOEL [µg/l]	MAC [µg/l]
As	0.8	1.0	25
Cr	0.2	0.3	8.7
Cu	0.4	0.5	1.5
Zn	2.8	2.9	9.4

The NOELs for sediment for all four metals are equal to the natural background.

NL Adsorbed	Sediment natural background [mg/kg]	Sediment NOEL [mg/kg]	Sediment MAC [mg/kg]	Suspended solids NOEL [mg/kg]	Suspended solids MAC [mg/kg]
As	29	29	55	44	83
Cr	100	100	380	150	570
Cu	36	36	73	54	110
Zn	140	140	620	210	930

Generally, the Dutch NOELs are quite close to the defined natural background concentrations. Therefore, it seems reasonable to interpret them as 'high status' criteria. The MAC values could be qualified as setting the boundaries for 'moderate' (or worse) status.

5.4.5   Canada

The Canadian systems of water quality standards comprises water as well as sediment [Environment Canada, 2002]. For water, different sets of standards are formulated: community, recreation and aesthetics, and aquatic life. In the table below, the freshwater standards for aquatic life are mentioned. The values refer to the total concentration in an unfiltered sample [Environment Canada, 1999a]. For sediment in freshwaters, two categories are discriminated: ISQG: Interim sediment quality guideline, and PEL: Probable effect level. The ISQG is more stringent than the PEL. There is no explicit mentioning of sieving prior to analysis or to a certain composition of the sediment [Environment Canada, 1999b].

Canada	Water (aquatic life) [µg/l]	Sediment ISQG [mg/kg]	Sediment PEL [mg/kg]
As	5.0	5.9	17
Cr	&	37.3	90
Cu	2 – 4	35.7	197
Zn	30	123	315

& For water, no value is contained for chromium as such. Values are include for trivalent chromium Cr(III): 8.9 µg/l, and hexavalant chromium Cr(VI): 1.0 µg/l.

5.4.6   Joint Danube Survey

The heavy metal section 5.2.3 of the JDS Technical Report contains a series of quality targets [ICPDR, 2002]. They are compiled from various sets of standards, and from different data sources. For the sake of completeness, the quality targets are included in the table below.

JDS	Water (total) [µg/l]	Suspended solids [mg/kg]	Sediment [mg/kg]
As	-	20	20
Cr	3.1	100	100
Cu	3	60	60
Zn	7	200	200

The quality targets are the same for sediment and suspended solids. In most cases the suspended solids/sediment targets are similar, either quite close to the of the IRC.

5.4.7   Synthesis of findings for 'good status' of metals

First of all it can be concluded that there can be big differences between the various sets of EQSs. Compare for instance the UN/ECE and Dutch EQSs on the one hand, versus those from the EU and US on the other hand.

The dissolved US-EPA CCC concentration of Cr is higher than the UN/ECE Class V (total) concentration, while the dissolved CCC concentration of Zn is equal to the boundary between Class IV and V (120 µg/l). The dissolved Cu CCC concentration would qualify as UN-ECE Class III. The calculated total CCC concentrations surpass the UN-ECE class V substantially.

The US-EPA arsenic criteria would qualify as UN-ECE Class III (dissolved) to IV (calculated total).

The guide concentrations of dissolved Cu in the EU are higher than US-EPA CMC criteria.

The mandatory Zn total concentration for Salmonid waters (300 µg/l) is higher than the dissolved CMC/CCC (same values) concentration of 120 µg/l, but lower than the calculated total (516 µg/l). The mandatory Zn concentration is almost three times larger than the concentration marking UN-ECE class V (>120 µg/l).

The Dutch EQSs were not yet mentioned, but it should be sufficient to mention that the MAC values for Zn would fit in Class I of the UN-ECE, and for As and Cu in class II. The MAC for Cr (84 µg/l) is significantly higher than the Class V boundary (16 µg/l), but quite close to the dissolved CCC concentrations of the US-EPA (74 µg/l).

For the sake of completeness, the descriptions of the CMC, CCC and of Class V are quoted again:

- CMC   The Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

- CCC   The Criterion Continuous Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

- Class V Excursions beyond chronic criteria concentrations allow acutely toxic conditions in terms of concentration levels, duration or frequency.

What is considered as a critical (MAC, acute toxic) concentration in one system (UN, NL) can be a recommended (acceptable) concentration in the other system (EU, US). Or, an approximate 'high'/'good status' in one set of criteria would qualify as 'moderate' (and worse) in another.

This observation leads to a 'stalemate' also as far as the aims of present project are concerned. The different water quality criteria systems were developed by well-known and respectable bodies. For all four systems it is mentioned, or can it be inferred, that the concentrations were defined based upon eco-toxicological risk assessments. It would be imprudent to 'choose' one of the EQS systems (either to compile some averages) without having additional knowledge, arguments, and criteria. Latter implies a more in-depth screening by a qualified ecotoxicologist, which definitely goes beyond the settings of this project. It is therefore proposed to be taken into consideration as a follow-up activity.

5.4.7.1   Total, dissolved, adsorbed?

Taking into account the approach of the RAP, where target-values for metals were set for suspended solids only on the one hand, and e.g. the US-EPA approach (where criteria for metals apply to the dissolved concentrations only) on the other hand, it generally can be advised for the Danube to define metal EQSs for both the total, dissolved, and adsorbed (suspended solids) concentrations. In this way one anticipates all possible environmental situations and compartments. A system of EQSs for metal encompassing both water and solid phases is definitely more watertight, and is not expected to demand too much extra efforts (compared to defining EQSs for e.g. dissolved concentrations only).

Section 5.3 outlines points of attention for continuation of such activities, like the (im-)possibility for establishing mathematical relationships between total, dissolved, and adsorbed concentrations. Since analysing the metals concentrations in suspended solids will become more a common practice in the Danube basin, information can be gathered which allows for defining factors more specific for condition in the Danube basin (e.g. Kd, average suspended solids concentration, composition of suspended solids and sediment).

5.5   Comparison with actual metal concentrations

Because of the stalemate in recommending EQSs for the metals, a proper comparison with measured data cannot be made. Readers are referred to section 5.2.3 of the JDS Technical report [ICPDR, 2002]. This contains an exhaustive assessment of the heavy metal findings in the JDS.

6   Conclusions and recommendations

Readers are forwarded to chapter 7 for proper apprehension of the conclusions and recommendations contained in this chapter.

While aiming at formulating recommendations for EQO/EQSs, it has been considered equally important to provide background material and arguments to the MLIM and EMIS expert groups for supporting their further activities. The findings of the underlying study can be summarised as follows.

6.1   Nutrients: N_{tot} and P_{tot}

For nutrients the following EQSs are suggested as "good status" values, in line with the WFD. The related EQO is to avoid eutrophication in the Danube basin.

> ➢ N_{tot}:   1.0 – 1.5 mg N/l
> ➢ P_{tot}:   0.02 – 0.08 mg N/l

The above values are presented as ranges. The present study could not provide additional criteria to decide which single value to select from within these ranges. Follow-up activities can include:

- consultations with biological experts;
- investigations on the actual occurrences of eutrophication in the Danube basin, combining the findings with the physico-chemical data available;
- developments in other European river basins during implementation of the WFD.

The proposed EQSs have not taken the Black Sea into account. Ultimately, the EQSs to be set should both enable a "good status" situation within the Danube Basin itself, as well as in the Black Sea regions influenced by the discharge of the Danube.

6.2 NH_4

From a potential toxicity point of view, a separate EQS has been established for the "good physico-chemical status" of ammonium:

> ➢   NH4:   =0.2 mg N/l

6.3 COD_{Mn}

For the chemical oxygen demand, the following EQS is suggested:

> ➢ COD_{Mn}: =10 mg O_2/l

6.4   Metals: As, Cr, Cu, Zn

It has not been feasible to prepare recommendations for EQSs for the metals As, Cr, Cu, and Zn. The major problem is that there can be huge differences between the values of different sets of water quality standards. In principle, ecotoxicological research and –criteria have been underlying the sets of standards included in the inventory of this study. It will require further, more in-depth investigations to find out how such differences can be explained, despite sharing 'ecotoxicology' as a shared basis. In addition, it is useful to keep track in the development in other European river basins, as far as they also will include these metals in addition to the list of WFD priority pollutants.

7   Epilogue: comments to the draft final report

The draft final report of August 2003 was discussed on 17 and 19 September 2003 during respectively the 2nd Joint MLIM/EMIS Working Groups meeting and the 31st MLIM meeting. The German and Austrian representatives afterwards sent their comments and suggestions by e-mail, which contains the majority of the issues raised during the meetings in September. The comments sent by e-mail are included in the first section, followed by brief responses by the author.

7.1   Remarks to draft report submitted by e-mail

7.1.1   Germany

The draft report deals with quality standards for nutrients. This is a very complex issue which has been discussed within the ICPDR-MLIM working group for several years. It should be made clear that aspects mentioned in this report shall not be interpreted as final solution but can be used as a contribution to this discussion.

The following items should be added / considered, at least by a few remarks:

- background of the EQS or reference values mentioned in the report (context in which they were developed, purpose, water types, legal restrictions)
- differentiation between surface water types
- relation between nutrient concentration and eutrophic conditions
- availability of nutrients / heavy metals to organisms (discussion on dissolved fractions by MLIM)
- relation between concentrations and loads

Concerning seasonality of concentration and time specific EQS this approach is not considered as very helpful because for example phosphate concentrations may be decrease to detection limit when this nutrient is assimilated in spring. In this case no EQS could be defined for this season. Usually seasonality is considered by using 90 percentiles of an annual data set which reflects periods of higher concentrations.

7.1.2   Austria

In general, the current report can serve as an interesting discussion basis for developing quality objectives for nutrients in the Danube basin. Specific issues within the report need reconsideration. Therefore and in addition to the comments made during the referring discussion in Bratislava, we would like to state the following input comments:

- The typespecific approach – required by the EU Water Framework Directive – is not considered within the report.
  - One single concentration value for N and P parameters concerning high status, reference/background conditions, good status and thresholds (in general and such thresholds demanding immediate action, EQS values) for the entire extent of the Danube and its tributaries does not follow the typespecific approach. The mentioned values will for sure differ within the Danube Basin depending on the typological region. Hence, set concentration values for high status, reference/background conditions, good status and thresholds (in general and such thresholds demanding immediate action, EQS values) will vary over the extent of the Danube and in its tributaries.
  - If thresholds/EQSs are suggested they have to follow the typespecific approach and therefore need value adaptation to the relating condition of the Danube or its tributaries.
  - The recommended EQS values need reconsideration.
- MONERIS is definitely an interesting and useful model for the calculation of diffuse inputs and origins in river basins. However, MONERIS cannot be used for setting any concentration values for High Status or other management thresholds.
- Concerning several mentioned N and P concentrations it is unclear what kind of in-stream values are addressed (e.g. guideline values or threshold values etc.).

- All values which go back to specifications by MLIM expert group are not average but 90% values (e.g. see table 2.2-2.5.).
- A correlation between chemical values and their effect on biological coenoses is missing in general. E.g. concerning historical data.
- Concerning eutrophication, nutrient values related for lakes are regarded. Lake values should not be used for river related considerations and management due to the different typespecific characterisation of these two systems. Even in the dammed sections of the Danube such values do not seem appropriate.
- Values for oligotrophic conditions are considered relevant for indicating High Status and concentrations of mesotrophic conditions for Good Status. This approach should be reconsidered as it does not include the typespecific approach.

7.2   Heavy metals

During the presentation of the results on 17 September 2003, it was suggested that one of the options to proceed with formulating EQSs for the Danube specific priority metals (As, Cr, Cu, and Zn) could be to apply the methodology of the Expert Advisory Forum on WFD Priority Substances.

As it turned out, this actually already has been done in Austria. The approach for the derivation of EQSs follows strictly the procedure given in Annex V, 1.2.6 of the Water Framework Directive and the methodical proposals of the EQS-study commissioned by the EC to the Fraunhofer Institute (FHI) for Molecular Biology and Applied Ecology. It follows the "added-risk" approach (see also the section on Typespecific approach below) and focuses on the dissolved phase as the first step in setting out EQS for metals as applied by FHI.

The report also touches upon the discussion still ongoing in Europe, concerning the issue whether the added-risk approach refers to the dissolved (i.e. filtered at 0.45 µm) or to the total metal fraction or suspended matter fraction.

The final document is still being subjected to a national review; hence, the final details will be made public after completion of the review. It is expected that this document will be useful for the Danube community concerning the formulation of EQSs for As, Cr, Cu and Zn.

7.3   Typespecific approach

Several of the remarks comment upon the report not having followed the typespecific approach. The author acknowledges this notice. The present study not having followed the typespecific approach had two major reasons. One reason has been that several Danube countries still are working on the typology and reference conditions for surface water bodies. The other and most limiting factor was simply time constraints (two person-weeks were allocated for both underlying tasks). As was agreed during the 1st Joint MLIM/EMIS meeting in February 2003, this assignment was first of all to focus on the main course of the Danube River. (In the MLIM-Working paper on Typology and reference conditions for surface water bodies of 13 May 2003 it has been recommended to consider the Danube river itself as a water body of its own.)

 The report already included several subsections where limitations in the approach and in the results were addressed, but a brief review is added here as well.

Generally, taking into account the typespecific approach when formulating environmental quality standards for physico-chemical parameters implies that at least following issues are taken into account:

- Natural background conditions. This applies to both nutrients and heavy metals. Differences in the (geogenic) conditions of a certain (sub)basin already can result in different loading of the water system by natural sources. There are examples where concentrations in the water already could exceed existing water quality standards due to natural background loading only!

  Partially in this context, the Austrian colleagues pointed-out to the so-called added-risk approach when formulating EQSs for heavy metals, as recommended by the Fraunhofer

Institute (who is working on establishing water quality standards for the WFD priority substances). The environmental quality standard is derived from the sum of the background concentration and a maximum permissible additional concentration derived from ecotoxicological test data.

With respect to nutrients it further can be argued that specific and unique biological characteristics of certain water bodies can only exist with relatively high nutrient concentrations (from natural sources). Vice versa, examples exist of ecosystems with a delicate balance that easily could be disturbed even by minor increases in a nutrient concentration.

- Typespecific conditions. This applies especially to the nutrients (for potentially harmful substances like heavy metals the –added- risks for organisms are considered to be more applicable more generally, although conditions like salinity or hardness are relevant as well). One example is for instance the difference between freshwaters and marine waters. Generally, it is understood that for occurrence of eutrophication phenomena in freshwaters the P-concentrations are most relevant (P-limited), while for marine waters nitrogen is the most decisive ingredient (N-limited). This is merely a fist of rule, since there are also examples of eutrophication occurring in freshwater due to enrichment with nitrogen. The EU-nitrates directive 91/676/EEC for instance deals with this issue. Further, instead of absolute concentrations, it can be the ratio between N and P concentrations, which is most relevant. Unfortunately, there is no strict (mathematical) relationship between absolute concentrations of nutrients and the actual occurrence of eutrophication. Finding out such peculiarities is a good example of features of the typespecific approach,

  Another already rather generic difference is whether one is dealing with a running freshwater or a standing freshwater (as annotated by the Austrian colleagues, one also cannot put lakes and reservoirs together by them sharing to be -rather- standing waters).

  More specifically, the composition of the aquatic community in a certain water body will be relevant when evaluated in the context of its sensitivity in relation to elevated concentration of nutrients. Here quite sophisticated biological knowledge and expertise needs to be included in the assessment and the setting of water quality standards.

The present study first of all made an attempt to make operational the WFD 'good status' definition for physico-chemical parameters. Also under the typespecific approach there still will be the need for a translation key to convert a description like "nutrient concentrations do not exceed the levels established as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements" into actual concentrations. As a bridging factor 'eutrophication' was used in the present study. The searches aimed at identifying concentrations of N and P that can be related to the (risk of) occurrence of eutrophication. Consequently, in existing systems the concentrations related to oligotrophic and mesotrophic conditions were discriminated (not implying that to meet good status the whole Danube basin should be considered (to become) a mesotrophic water).

In order to avoid possible misunderstanding: the recommended EQSs for N_{tot} and P_{tot} in section 2.6 were not suggested to apply to the whole Danube basin[11], as already indicated by the points of attention mentioned in section 2.6. To these points, the typespecific approach and other additional remarks can be added. As complications already experienced in the present study, following can be mentioned.

- Defining natural background conditions. Even though meeting 'good status' is the major final WFD requirement, it can be very helpful to be able to formulate also the conditions where there is undisturbed with virtually no anthropogenic impact ('high status'). It was not so easy to find references that were dealing with defining natural background concentrations, let alone that such information could be acquired for specific subbasins in the Danube. Maybe in national or scientific libraries reports exist to such extent, but these sources were out of reach

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[11] During the discussions in September 2003 for instance it was mentioned that apples and pears were compared and combined since for instance lake values seem to be implied for river related situations …

of present study. If such data are not explicitly available, then there can be some fallback options. 1) Historic data sets, where monitoring results are available going back until the 1950/60-ies, or preferably earlier. For reliable assessment of heavy metals such historic datasets presumably are not suitable (because of analytical constraints). For nutrients, there may exist significant data, but then again one can expect few or no data at all for organic nitrogen. 2) Models like MONERIS are capable of calculating natural loads into (subbasins of) the Danube, which can be used as a basis for estimating natural background concentrations. 3) Reference areas, for which data about natural background concentrations exist, and which then are assumed for the corresponding water body in the Danube basin.

- Additional criteria for setting the EQS. The nutrient concentrations presented in section 2.6 are ranges. As mentioned there, more criteria are required to decide whether the range fits to the specific water body at all, and if so, in which part of the range to seek the corresponding EQS. Depending on the outcome of the (national and international) typology of the Danube basin one might consider the development of set of uniform criteria to be applied. Further, it has been suggested to find out whether there are more datasets available that combine biological and chemical assessments, as was the case in the Joint Danube Survey. Using the actual occurrence of eutrophication phenomena as criterion, they than can be associated with the measured nutrient concentrations.

- The recommended EQS for nutrients seem too stringent. This at least would be the conclusion when one compares the suggested natural background concentrations (range) with the suggested EQS-ranges. Whether or not they are too stringent finally will depend on the features and water quality requirements of the specific water bodies. The author agrees that it would become quite a difficult a task to realise good status, assuming that the proposed EQSs indeed would turn out to be applicable for the Danube river itself.

7.4   Background of the values mentioned in the report

Some of the remarks asked for clarification of the status of the values mentioned in the various report sections. Most of suchlike information is included in most sections when it was available (readers could consult the various –Internet- references for further information).

The status of the various sets of water quality standards can differ. For example, the Dutch MAC-standards are already used as binding limits under the present water quality management (hence appropriate action is required when water quality does not comply), while the NOEL-levels are considered to provide a medium-range perspective of the desired situation. The 'Zielvorgaben' of the Rhine represent agreed water quality targets to which the riparian committed themselves to reach such quality in the river Rhine. The values proposed by the UN/ECE are first of all suggested as values for assessment of the water quality, hence in itself they are not EQSs (by e.g. adopting the Class II values, the same values can become EQSs).

Generally, for the nutrients in chapter 2 in many cases status assessment values are mentioned. These assessment values were then transferred by present study to setting the provisional range of the proposed 'good status' EQS for N_{tot} and P_{tot}. The heavy metals chapter contains more examples of values which are already existing as EQSs in various countries.

In several cases, it is sometimes a matter of interpretation whether or not one a certain value could be set equivalent to 'high' status, or 'good status', 'moderate status', etcetera.

In the case of the heavy metals, it is obvious that the differences between values are not a matter of for instance comparing MAC with NOEL levels. From the descriptions provided in the text of the report, the intention of the different sets can be interpreted rather straightforward.

In the synthesis of the EQSs for P_{tot}, N_{tot}, NH_4 and COD_{Mn}, it was aimed at proposing values to be considered as threshold values for 'good status' (non-compliance means moderate status or worse).

For P_{tot} and N_{tot}, the EQSs are suggested to apply to total concentrations. For the occurrence of eutrophication, both the dissolved and adsorbed nutrients are relevant (the issue of eutrophication is a different from the discussion on bioavailablity of dissolved fractions of heavy metals).

7.5   Compliance testing

Several remarks can be summarised as addressing the issue of compliance testing[12]. As mentioned just above, the EQSs suggested for the nutrients and for chemical oxygen demand are considered to represent threshold values for a WFD 'good status'. The author did not elaborate on how to use the values in the perspective of compliance testing.

- Percentiles. It is quite common to use the 90-percentile (or other peak-shaving methods) of the –annual– monitoring results when comparing the actual water quality with the standards. Using a statistical method as the 90-percentile implies that one has a sufficient number of data available, often mentioned to be from 6 to 10 samples as a minimum. In this perspective, it is interesting to notice that the WFD mentions in Annex V, 1.3.4 a sampling frequency of 3 months (implying four samples a year) for nutrient status.

- Average concentrations/seasonality. The author suggested taking into consideration some general season-specific features of nutrients that might be used as an advantage for compliance testing. The reasoning is following. Notably nitrogen concentrations are normally lower in the period late spring – early autumn. This is more or less the same period during which one could expect eutrophication phenomena actually to happen. The suggestion would be to apply the nutrient EQSs only for that period during which eutrophication actually can happen. This implies that compliance then would be checked during the period with overall lower concentrations in the water body (compared to the winter period). It can be noticed that such a principle is implemented two of the systems mentioned in chapter 2. The SEPA has defined an EQS for the May-October average concentration for N_{tot} and P_{tot} in lakes. The Netherlands applies the EQS to the April-September average concentrations of N_{tot} and P_{tot} in standing waters.
  This approach seems not to be compatible when putting the Black Sea into the perspective (compare section 2.6).
  Such an approach further cannot apply to NH_4 anyway, since for ammonium the potential toxicity is relevant and therewith the higher (90-percentile) values.

7.6   Concentration and loads

Relationships between concentrations, flows, and loads actually can be rather complicated, and go beyond the scope of the present study.

The mentioning of loads in the report has merely been made in order to relate the discussion of formulating EQSs for nutrients in the freshwater part of the Danube to the Black Sea. It is expected that the EQSs formulated for the Danube itself somehow are to be consistent with reaching the quality objectives for the (north-western part of the) Black Sea. Assuming the Danube itself as one of the water bodies, and having formulated EQSs for phosphorous (plus possibly nitrogen) for his water body, then it is not automatically obvious how this water quality status will affect the water quality in the (north-western part of the) Black Sea. In order to conduct such assessments, one needs to work with Danube pollution loads discharged into the Black Sea (and with computer models).

Maybe such an exercise is not necessary. Discussions in the Black Sea community seem to gear towards agreeing that if the pollution of the Danube would be comparable the situation in the early 1960-ies this would be satisfactory with respect to no eutrophication in the Black Sea. Of course, this implies that one there are historic data for the nutrient concentrations in the Danube in the early 1960-ies one can use to agree upon.

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[12] Part of the confusion may arise from the comparisons in this report with annual averaged TNMN 1995-2000 results. Comparing with annual average TNMN data in the underlying report merely has been done because of illustration purposes; details of the TNMN results are included in other reports.

7.7   Closing remarks

From the previous sections one can conclude that there is still quite some work to be done in order to formulate EQSs for the Danube specific priority substances; also discussions definitely are not yet completed. Nevertheless, the author expects that the information and the experiences gathered during this study indeed will facilitate the expert groups in continuing and structuring their activities concerning this topic.

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UNDP/GEF Danube Regional Project

Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation
in the Danube River Basin

Preparation of a proposal for connection/operational link of the data collected during the Joint Danube Survey into ICPDR Information System, with particular attention to biological database

Project Component 2.2: Development of operational tools for
monitoring, laboratory and information management with
particular attention to nutrients and toxic substances

October 31, 2003

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Preface

The Joint Danube Survey (JDS) was carried out in August and September 2001 and provided complex information on the chemical and microbiological water quality as well as on the biodiversity in the main course of the Danube River and its major tributaries. The JDS was the most comprehensive survey ever performed in the Danube River Basin yielding information on a wide range of chemical pollutants in water, sediments, suspended solids and mussels matrices, aquatic flora and fauna and biological indicators. The survey generated data and information necessary for the ecological and chemical surface water status characterization in line with the requirements of the EU Water Framework Directive (WFD). A geo-morphological division of the Danube River Basin (DRB) was proposed and evaluated using the obtained data. The scientific outputs of the JDS were used for development of the Danube List of Priority Substances and also for the upgrade of the TNMN. Next to the printed and electronic version of the JDS Technical Report, the results were also summarized in a web-based database designed for the use by water management experts. Biological and GC-MS screening databases were established in the Danube River Basin for the first time.

The main goal of the presented part of the project was to develop a proposal for connection/operational link of the JDS data into the ICPDR Information System (DANUBIS) in order to fully utilize potential of the obtained data. A particular attention was given to the biological part of the database, with the final goal to set up a basis for regular collection of biological data for the TNMN Database in the near future. Successful implementation of the WFD requires availability of both hydrobiological and chemical data organized in a systematic way allowing experts to draw conclusions in a basin-wide scale. Having this in mind, many new ideas and inputs came either from the project team or MLIM experts during the implementation phase of this project component. Many of them were immediately used to upgrade the existing ICPDR Information System and, therefore, to see the latest version of the JDS and TNMN databases one is advised to look directly at the www.icpdr.org [Databases/New Draft Versions].

Given by the importance of the new biological and chemical parameters, which were not yet monitored within the TNMN, it is expected that the JDS and TNMN databases will be further developed in line with recommendations of the MLIM EG and this report. The results of this project component will also be provided to the DRP project outputs 1.1.6 and 1.1.7.

Table of contents

Preface
Abbreviations
Executive summary

Abbreviations

JDS   Joint Danube Survey
WFD   Water Framework Directive
DRB   Danube River Basin
TNMN   Trans-National Monitoring Network
ICPDR   International Commission for the Protection of the Danube River
MLIM   Monitoring and Laboratory Information Management
EG   Expert Group
DRP   UNDP/GEF Danube Regional Project
GC-MS   Gas chromatography – mass spectrometry
LC-MS   Liquid chromatography – mass spectrometry
MS-MS   Mass spectrometry – mass spectrometry
HTG   Higher Taxonomic Group

Executive summary

Primary objective of this project component was to develop a proposal for an operational link between the JDS and TNMN databases. The project team with a help of selected MLIM experts and UNDP/GEF Information Specialist, who participated at the development of the original JDS Database, undertook an approach of on-line introduction of suggested changes/recommendations into the web-based ICPDR Information System. This gave an instant feedback on the practicality and usefulness of the JDS database upgrades and improvements. Prior to the final interlinking of databases, numerous efforts were made consisting of completion of the database for missing parameters and thorough check on the quality of stored data.

As a result recommendations for a link between the JDS and TNMN databases and harmonisation of their query templates were made and incorporated into their New Draft Versions. A proposal of the new central page on the ICPDR website comprising of all ICPDR databases (TNMN, EMIS, Bucharest Declaration Database, JDS, JDS – Investigation of the Tisa River) was drafted. During the project, the JDS Database was gradually improved and developed into the stage, that it is ready for the public use (for latest version, see www.icpdr.org [Databases/New Draft Versions]).

Several suggestions, which go beyond the scope of this project component, were made by the project team and MLIM experts to improve the ease-of-use of the JDS and TNMN databases. A principal upgrade and Europe-wide harmonisation of the coding system and systematic tracking of taxonomical changes in the biological part of the database was proposed in order to assure its sustainability. Also, further upgrade of the GC-MS screening part of the database was suggested to allow proper evaluation of the screening data on emerging, unknown and Danube River Basin specific pollutants as required by the WFD. A specific recommendation was made to perform similar upgrade at the JDS – Investigation of the Tisa River database, containing valuable data from survey conducted in October 2001, however, not being ready for public use in its present form.

Final goal of all the above efforts is to create a fully interlinked ICPDR Information System. This would require future harmonization of the coding system between the TNMN and EMIS databases and further development of the link between the two databases. The knowledge obtained at the development and upgrade of the JDS Database created a solid base for extension of the TNMN Database for new chemical parameters, parameters measured in other matrices than water, GC-MS screening and biological data.

1. Introduction

Joint Danube Survey (JDS) was organized by the ICPDR and took place from 13 August till 20 September 2001. The major goal was to obtain comparable, accredited information on the quality of the Danube river in its entire length. Two ships collected samples from 98 sampling sites, 74 of them on the Danube and 24 major tributaries. Among the investigated matrices were water, sediments, suspended solids and mussels. Next to chemical and microbiological determinands a wide range of biological parameters, including macrozoobenthos, phytobenthos, phytoplankton, zooplankton and macrophytes were investigated. In total, over 140 different parameters were analysed in the studied matrices by a team of international experts on the board of the ships and in seven reference laboratories. The survey generated over 40.000 results, which were stored in the web-based JDS Database. Biological and GC-MS screening databases were developed for the first time in the Danube Basin.

The results of the survey gave an overview on the ecological and chemical status of the Danube. Over 1000 biological species were found to inhabit the Danube basin and microbiological pollution profiles were constructed. Analyses of numerous chemical parameters, including EU WFD determinands, pharmaceuticals, pesticides and the screening of unknown substances were carried out for the first time. Obtained sediments, suspended solids and biological samples were stored for several years in selected institutes (VITUKI, CBC Frankfurt) to allow for follow up analyses.

The use of the obtained data was intended primarily for an upgrade of the TNMN and development of the Danube List of Priority Substances.

Among the major goals of this project component were:

- Completion of the database for missing parameters (in cooperation with the ICPDR);
- Check on the quality of data;
- Preparation of the public version of the JDS Database;
- Recommendations for a link between the JDS and TNMN databases;
- Selection of relevant database parameters and upgrade of the existing version of the JDS Database.

A close cooperation with MLIM experts was foreseen in order to achieve the project goals.

2. Description of activities and methodology used

In the course of the project, the JDS and TNMN databases were thoroughly reviewed in order to assess needs for their interlinking, future development and upgrade. Prior to the further development of the biological database its completion was proposed by the project team and ensured by the ICPDR.

Next to the project team, five MLIM experts, actively participating at the collection and storage of the JDS data in 2001 and 2002, were invited to comment on the current structure of the JDS Database. Their expertise covered all major components of the databases: (i) chemical and microbiological data, (ii) macrozoobenthos, (iii) phytobenthos, (iv) phytoplankton and zooplankton and (v) macrophytes data. Among specific tasks of the MLIM experts were:

- Thorough examination of the current version of the JDS Database and provision of comments/suggestions, whose implementation will make the database fully operational and ready to be accessible by the general public;
- Check of all data (chemical and microbiological data, macrozoobenthos, phytobenthos, phytoplankton and zooplankton and macrophytes) for correctness;
- Proposal for handling of data, which are not correct;

- Preparation of an introduction to the Chapters: "Chemical and microbiological parameters, Biological parameters – macrozoobenthos, phytobenthos, phytoplankton and zooplankton and macrophytes", which will be placed in the explanatory text of "About the database". The text should introduce in a brief and comprehensive way following:

  i. Background information on selection of measured parameters, units;

  ii. Mathematical models and calculations (if used for any of the parameters, e.g. Saprobic indeces);

  iii. Coding system;

  iv. Way of handling the data and generating reports;

- Proposal for the selection and layout of the database search parameters (if different from the current version);

- Proposal for the new coding system (if not acceptable in the current version);

- Proposal for the future direct interlinking of the biological databases of the TNMN and JDS;

- Proposal for the layout/parameters of TNMN Biologic al Database (if different from the current version of the JDS Database).

A close cooperation was established between the project team and the Information Specialist of the UNDP/GEF Danube Regional Project at the development of the final version of the JDS Database. Majority of the proposed changes/upgrades of the JDS Database were implemented in the course of the project duration (for details, see www.icpdr.org [Databases/New Draft Versions]).

The necessity of direct interlinking of the chemical databases of the TNMN and JDS were consulted with the chemical experts from the MLIM EG.

The goals and interim results of the activities were discussed and approved at the 1st and 2nd Joint MLIM-EMIS Meetings in Vienna (3 February 2003) and Bratislava (17 September 2003), respectively. The information was also presented and approved at the MLIM EG meetings in Vienna (27 - 28 March 2003) and Bratislava (18 – 19 September 2003).

3. Results

The JDS Database consists of five major components: chemical and microbiological data, macrozoobenthos, phytobenthos, phytoplankton and zooplankton and macrophytes. Comments on the current version of the JDS Database and recommendations of individual MLIM experts are included separately below:

3.1 Biological database

3.1.1 Macrozoobenthos

General introduction

Regarding the WFD, biota is the most important component for the evaluation of the ecological quality of running water bodies. The communities investigated in rivers should include: algae, macrophytes, macrozoobenthos and fish. To describe the biological elements the following attributes have to be considered: taxa composition, abundance, and the ratio of disturbance sensitive taxa to insensitive taxa. With respect to most of the methods used to evaluate the river quality in European countries the WFD enforces a re-orientation of the monitoring procedures towards an integrative approach. Future assessment of the ecological status of water bodies considers the relationships between biota and the hydro-morphological and chemical components, instead of only documenting the biological water quality with respect to organic pollution. The current JDS database therefore serves as a valuable base for future activities in the Danube catchment area.

The evaluated part of the database focuses on benthic macro-invertebrates. Benthic invertebrates have a high indicative value, and are the most widely used indicators for water quality assessment (Rosenberg & Resh, 1993).

Aim and content of this report is to comment on the current version of the database. Main scope is turned to the structure and the handling of data for external users. For several parts suggestions for improvements are given.

Macro-invertebrate data and coding system

The coding system for benthic invertebrates is based on the Austrian Software ECOPROF (www. ecoprof.at), that was developed by the Department of Hydrobiology (BOKU, University of Natural Resources and Applied Life Sciences, Vienna; http://www.boku.ac.at/hfa). The coding system was extended for taxa that did not occur within the Austrian Taxa List (Fauna Aquatica Austriaca, Moog (ed.), 1995 and 2002). As a consequence not all taxa-codes correspond to the original ECOPROF list or any other coding system currently in use. Parallel to the ECOPROF coding system a pan-European coding system already exists, developed within the EU funded projects AQEM (www.aqem.de) and STAR (www.eu-star.at) and it is recommended to change the identity numbers to this system before going on-line with the database for the public. In order to comply only with one European taxalist it would also be useful to use taxonomy, synonymy and systematics from the AQEM and STAR taxalists, as they were already checked by taxonomical experts.

The database currently contains double entries that have to be removed.

Mathematical models and calculations

Currently available calculation parameters are:

- Abundance value per taxon;

- Number of taxa per sampling site;

- Saprobic Index per sampling site.

The Saprobic Index is based on the calculation method of Zelinka & Marvan (1961) according to the following formula:

$$SI = \frac{\sum\limits_{i=1}^{n} s_i \cdot A_i \cdot G_i}{\sum\limits_{i=1}^{n} A_i \cdot G_i}$$

SI   Saprobic Index of the benthic community
A_i Abundance of taxon i
s_i Saprobic Value of taxon i
G_i Indication weight of taxon i
n   Number of taxa

Saprobic values as compiled in the Fauna Aquatica Austriaca (Moog (ed.), 1995 and 2002) were used. The latest version of the Fauna Aquatica Austriaca is available at: www.lebensministerium.at/wasser/, sub-item "Wassergüte".

Dominance of Higher Taxonomic Groups (HTG) is currently only calculated for macrophytes and would also make sense for benthic invertebrates (and also phytobenthos).

Data handling and reports

Regarding the selection of datasets a second selection list within the benthic invertebrates is recommended. In this selection list it should additionally be possible to choose the HTG, because taxonomical specialists are mostly interested in only one taxa-group.

Default sorting of the species according to their taxagroup, family and (within the family) species alphabetically.

Concerning the output options, it would improve readability, if identical columns could be skipped and written instead in the caption of the displayed table.

The additional display of the AQEM/STAR 8 letter shortcode within the result output would be of a value, because such a code might often be used for further analysis.

In the current version of the database JDS and ITR data are presented together: in case of entering overlapping river km values on the Danube and the Tisa (i.e. 0-500), JDS and subsequently ITR data will appear on the screen – databases should be separated.

All biological databases (macrozoobenthos, phytobenthos, phytoplankton, zooplankton, macrophytes) should use the same structure and queries.

Proposal for the layout/parameters of TNMN Biological Database

Concerning the report generation page it could be considered to choose more than only one parameter within "determinand". For practical use it would be comfortable to have related calculations displayed together, e.g. number of taxa AND Saprobic Index. Further, it would make sense to extend the calculated parameters by the dominance of higher taxonomic groups (HTG).

Regarding the output, the sampling site could be complemented by the river kilometre. It is recommended to add the previously defined query elements in the caption text of the displayed table.

General conclusions

The available databases are already well established and publishable for further public use. Generally a common design and layout for all different databases within the ICPDR web-page should be considered.

3.1.2 Phytobenthos

General introduction

The JDS phytobenthos data consists of the groups of Cyanophyceae, Bacillariophyceae (Diatomophyceae), Chrysophyceae, Bangiophyceae, Chlorophyceae, Charophyceae, Xanthophyceae, Zygnematophyceae. Organisms of the group of Bryophyta were not identified. Quantitative data are in the form of estimation of the relative abundance (scale 1 -5).

Background database for phytobenthic organisms was based on the list compiled within the "Development of a Preliminary Set of Danube River Basin Ecosystem Indicators, Preparation of a Concept for Monitoring Ecological Status of Significant Impact Areas and Wetlands" in "Review of the Bioindicators Study in Yugoslavia" (ICPDR, 2000) and (ii) software ECOPROF that was developed by the Department of Hydrobiology (BOKU, University of Natural Resources and Applied Life Sciences, Vienna, Austria).

Phytobenthos data and coding system

Basically, the problem of synonyms and new taxa names should be solved. This relates mainly to the diatoms, where new taxa and new combinations of the taxa are published frequently in connection to the new development in this field, e.g., techniques using electron microscopy.

New taxa can be added to the database easily (using new code). Renamed taxa should be connected to the previous ones to keep continuity with old and new data.

From time to time (e.g. every five years) the database should be revised by the experts for the individual group of organisms to provide about mentioned changes.

The use of certain determination keys for individual groups of organisms would be useful (e.g. Susswasserflora von Mitteleuropa, Gustav Fischer Verlag). This is important mainly from the point of view of future upgrade of the TNMN Database for biological parameters.

Sorting the species could be arranged first according to their taxa-group, then according to the family and finally the species alphabetically including synonyms.

In connection to the proposal of EN standard for the benthic diatoms (pr 13946: Rutin sampling and pre-treatment of benthic diatoms from rivers; pr 14407: Identification and enumeration of benthic

diatoms from rivers) also relative abundance should be included (instead of estimation the scale 1-5) and/or some transfer between this different quantitative data should be done.

Mathematical models and calculations

Currently available calculation parameters are:

- Abundance value per taxa;

- Number of taxa per sampling site;

- Saprobic Index per sampling site.

The Saprobic Index is based on the calculation method of Zelinka & Marvan (1961) according to the following formula:

$$SI = \frac{\sum\limits_{i=1}^{n} s_i \cdot A_i \cdot G_i}{\sum\limits_{i=1}^{n} A_i \cdot G_i}$$

SI	Saprobic Index of the benthic community
A_i	Abundance of taxon i
s_i	Saprobic Value of taxa i
G_i	Indication weight of taxa i
n	Number of taxa

3.1.3 Macrophytes

After a thorough examination of the database concerning the biological parameter macrophytes the following should be further integrated:

General suggestions

The macrophyte database still demands some improvements/corrections concerning species terminology. Related changes were suggested. The following categories for changes were created:

a) Corrections concerning terminology mistakes;

b) Species, which were not collected during JDS but were collected in general in the Danube River. It should be mentioned within the database where these data stem from (probably from Pall & Janauer (1998) Macrophyte Inventory of the Danube River);

c) Species which do not exist – need to be deleted;

d) Species, which were initially missing in database - to be added.

- Abbreviation P. within the column GENUS should always be changed to POTAMOGETON.

- The Higher Taxonomic Group CHLOROPHYTA/CHAROPHYCEAE shows a mismatched Group Code. Therefore, the current Group Code should be changed from H (phytobenthos) to F (macrophytes). If the biological parameter group Phytobenthos also includes the Higher Taxonomic Group CHLOROPHYTA/CHAROPHYCEAE both Group Codes H and F need to be included in the database.

Coding system

The used coding system is reasonable (consecutive numbering) and can therefore stay unchanged. Therefore, no further suggestion concerning a new coding system is made.

Proposal for selection and layout of database search parameters

The database is well structured and intuitive to use. Generating reports is easy. Following suggestions are made:

- So far the database enables a report generation using SPECIES or SPECIES CODES. It would be very useful to additionally enable an inquiry using the FAMILY/HIGHER TAXONOMIC GROUP level. This option would be reasonable for all biological parameter groups;

- After a report was generated and when clicking the option BACK TO FORM it would be useful if the content of the last used inquiry were not erased out of the database mask.

Proposal of layout/parameters of TNMN biological database / interlinking

Possible combination of determinants would be useful and reasonable in order to achieve complex reports.

Introductory text for macrophyte chapter

The objective of the Joint Danube Survey concerning the collection and evaluation of macrophytes was to gain comparable and reliable information by applying uniform, standardised methodologies. JDS provided a unique, first time opportunity to gain an overview of aquatic plant growth for the entire course of the Danube River.

Within the frame of the Joint Danube Survey macrophytes (aquatic plants) were collected on both banks of the Danube River. Although the tributaries were searched for macrophytes on both banks, the collection results were integrated into one single sample due to the smaller size of tributaries providing very consistent abiotic habitat conditions for the whole river transect. Adding seven further investigation sites to the original JDS sampling programme, a total of 180 sites (both banks of Danube and tributaries) were investigated for macrophytes. At each site a longitudinal stretch between 0.2 and 5 river km was sampled for aquatic plants.

Each collected species was associated to one of six species groups: 1) Bryophyta, 2) Chlorophyta, 3) Spermatophyta (higher plants) - submerged Rhizophytes, 4) Spermatophyta - free floating and floating leafed plants, 5) Spermatophyta - amphibious plants and 6) Spermatophyta – Helophytes. These species groups and their relevant species are included in the present JDS Database. Reports providing information on macrophytes can be generated via species names or species codes. To investigate on a species code number a separate list with all collected species plus their corresponding code is provided in the database. The coding is based on consecutive numbering of species.

Further, the available database includes Relative Plant Mass (RPM, Pall & Janauer 1995) calculations, which were based on plant mass estimations (Kohler 1978) on a five–level scale (Equation 1). The Relative Plant Mass, weighted for the mass of each species or group of species and the stretches of species occurrence, indicates dominant and sub dominant species within each sampled reach in relation to the overall plant mass in the relevant reach. Additionally, the database contains the calculated dominance of each Higher Taxonomic Group (Equation 2).

$$RPM(\%) = \frac{\sum_{i=1}^{n}(M_1^3 * L_i) * 100}{\sum_{j=1}^{k}\left[\sum_{i=1}^{n}(M_{ji}^3 * L_i)\right]}$$

Equation 1: Relative Plant Mass (RPM), Li=length of reach i; Mi=estimated plant mass of a species for a reach; j=different plant species.

$$Do\min anceHTGx = \frac{NumberTaxaHTGx * 100}{TotalTaxaNumber}$$

Equation 2: Dominance of each Higher Taxonomic Group (HTG)

References

Pal, K. & Janauer G.A. (1995): Die Makrophytenvegetation von Flussstauen am Beispiel der Donau zwischen Fluss-km 2552 und 2511,8 in der Bundesrepublik Deutschland. Arch.Hydrobiol.Suppl. 101, Large Rivers 9/2, 91-109

Kohler, A. (1978): Methoden der Kartierung von Flora und Vegetation von Süßwasserbiotopen. Landschaft und Stadt, 10:23-85

3.1.4 Phytoplankton and zooplankton

General

Regarding the WFD, aquatic biota is the most important component for the evaluation of the ecological status of running water bodies. Although zooplankton does not occur among the biological elements investigated in rivers (such as algae, macrophytes, benthic invertebrates, and fish) the involvement of this group of organisms is inevitably important, especially on the middle and lower Danube sections and on the large Danube tributaries, as well.

The JDS Database contains also quantitative data on phytoplankton and zooplankton. Phytoplankton abundance is given in individual number/l, zooplankton abundance is given in individual number/100 l.

Use of the database

The user first has to select or determine one of the "Location" items in any particular combination, country, river stretch or sampling site(s) could be selected. Second step is to select "Biological data" from the "Determinand" dropdown list, and, either Phytoplankton or Zooplankton from the "Group" dropdown list. The possibility to search for particular species is provided by the database, as well.

The data can be sorted out or grouped for further analysis according to the following parameters:

Higher Taxonomic Group	Family	Genus Species	Author	Sampling Site	Determinand Name	Value	Unit	River km	Species Code

General comments

Phytoplankton and zooplankton data of the JDS Database were tested and controlled in order to reveal possible and/or evident mistakes. As a result, it can be generally stated that there is no evident mistake among the data on phytoplankton and zooplankton. The database is well established and ready to be used by general public.

Specific comments

The search results on the screen are limited to 50 rows – should be adjusted to higher (unlimited) number.

Sorting out data according to "Value" should be enabled.

If a data set consisting of several hundreds of rows is created, there is no option to go back directly to the original query panel – should be added.

Concerning the "Determinand" name it could be advised that instead of "*Zooplankton - Total Number of Individuals*" only "*Zooplankton - Number of Individuals*" should be used because the total number includes all individual numbers of zooplankton at a given sampling site, whereas this particular values mean only the number of the given species. The same is true for phytoplankton.

A default view on the result of the database search should be given: the most important columns being "Sampling site", "River km", "Genus species" and "Value". Other columns could be selectable as "Additional information".

Names of the sampling sites in a given country should be written also in the national language.

The query options as selected by the user should be maintained when searching the database (not set to default).

3.2 Chemical and microbiological data

General comments

JDS microbiological data in surface water and chemical data in surface waters, sediments and suspended solids have been reviewed from the point of view of (i) logical relations between couples or groups of the measured determinands, (ii) theoretically *allowed* ranges of values that can occur in water samples and (iii) limits of detection. Found errors are reported among the *Specific comments*. It can be generally stated that, taken into account the number of measurements done within the JDS, the extent of erroneous data is low. Majority of inconsistencies were found in surface water samples.

There is a need for the central page at the ICPDR Information System for accessing of all (public and expert) databases.

An idea of "expandable" database, which can store data from all future surveys and investigations in the major tributaries is welcome. This should not be limited only to „major tributaries", but to all survey activities done within the ICPDR countries in the future, even if it would be concerned only to limited stretches of the Danube River.

Missing possibility of selection of several (choice of the database user) locations at the same time.

Missing possibility of selection of several (choice of the database user) determinands at the same time.

Recommendations for a link between the JDS and TNMN databases

The JDS data should be linked to TNMN data from the same (or closest sampling site) via button "SHOW TNMN Database" – using river km.

It is recommended that in the first step the nearest TNMN locations would appear – closest station up the JDS site and the closest station below the JDS site, with basic information such as the TNMN code of the station and river km. However, a possibility to show more than two stations on the screen should be given due to the following:

- Some stations are included in TNMN by both neighbouring countries, therefore at one river km data from two stations are reported;

- Some stations have three sites in one profile (at one location) – left, middle and right.

Having a choice of TNMN stations, the user could then select the sampling site of interest for further data search/export.

As regards the linking of all databases (including EMIS database, especially when data on the priority and other relevant substances will be collected by both TNMN and EMIS) – the coding of determinands in EMIS and TNMN databases should be harmonized.

Specific comments

In the current TNMN Database (DANUBIS) - if statistical characteristics are calculated, the "zero" values represent actual value of "below limit of detection" (LOD) and should be included in calculations (not to calculate with the "zero" value). This method of data processing is used in the current ICPDR publications. The proposal is to include in the JDS Database also the option "CALCULATIONS USING VALUES BELOW LOD" with three possibilities:

1. Calculation with value of LOD;

2. Calculation with half of the LOD value;

3. Calculation with "zero" value.

This would give a possibility to select appropriate type of data processing according to specific needs of the report.

The option of selecting data from the TNMN database on the basis of analytical methods might be deleted.

List of discovered inconsistencies in the results of analyses of surface water:

- Ptotal $<$ P-PO4 at the JDS stations No. 67, 73, 74, 82, 84 and 87;
- Measured value of concentration of N_{org} is lower than indicated limit of detection for this determinand at the JDS stations No. 12 and 17;
- Limits of detection are not listed for ammonium-N, nitrate-N, nitrite-N and orthophosphate-P;
- pH 0 is reported at the JDS stations No. 58, 69, 74, 84 and 87;
- conductivity is reported as „zero" value at the JDS station No. 58;
- Concentrations of several "total" concentrations of metals is lower than "dissolved" concentrations in the same sample: Al (stations 29, 37, 70), As (35 samples, probably in the range of uncertainty of the analysis, larger differences at stations No. 43), Cd (six samples, probably in the range of uncertainty of the analysis), Co (stations No. 24 and 42), Pb (station No. 2), Zn (31 samples, large differences at stations No. 01, 02).

List of discovered inconsistencies in the results of analyses of organic micropollutants:

- Measured value of 4-para-nonylophenol was lower than its limit of detection at the JDS station No. 05.

It is proposed that all erroneous data should be flagged with an explanatory note describing the problem (special section as in the TNMN database).

3.3 GC-MS screening database

Experience from building GC-MS databases in the Netherlands and the Slovak Republic was used at the development of the current version of the GC-MS component of the JDS Database. In order to improve the current structure, the search query template consisting of (at least) following parameters was proposed:

- Characteristic ions: BP, P1, P2, P3, P4 [BP - base peak m/z, P – ion m/z]
- Match factor [Given by the library search]
- CAS Number [Identification number of the compound in the CAS registry]
- MW [Molecular weight]
- Chemical formula
- Compound name

The query using "Characteristic ions" should allow for searching all ions in all fields (BP, P1-4) if typed in the field P1-4. If typed in "BP" field, only base peaks should be searched. "Match factor" should give hits for all values "equal" and "higher than" the typed in number (0-100).

Databases using mass spectral information (obtained mostly by the GC-MS or LC-MS(MS) techniques) are at present the major source of information on unknown, emerging and river basin specific pollutants. Therefore inclusion of the GC-MS screening data into the ICPDR Information System is highly recommended.

Further development of the GC-MS database should focus on the following:

- Availability of the raw GC-MS spectra of both tentatively identified and unknown substances in order to allow for their future identification;
- Organisation of the raw GC-MS spectra in the Danube Basin Spectral Library;
- Harmonisation of methodologies using at the (GC-MS) screening projects in the ICPDR countries and related trainings of experts responsible for data processing;
- Harmonisation of methodologies used for semi-quantitative evaluation of GC-MS data.

The structure of the database should allow for future extensions using LC-MS and LC-MS-MS data on substances, which are not amenable to GC analysis.

3.4 Hydro-morphology

The JDS resulted also in a proposal of the hydro-morphological division of the Danube basin, which are essential at evaluation of the ecological status of the river. The database was upgraded to be able to sort out data automatically within the individual hydro-morphological reaches as proposed by Vogel et al.

4. Recommendations and assessment of needs

The work of the project team and MLIM experts resulted in a significant improvement of the existing version of the JDS Database. Still, several recommendations were made to improve the current version of the ICPDR Information System, which go beyond the scope of this project component. A summary of major suggestions is given below:

ICPDR Information System
- Development of a central page for all ICPDR databases;
- Subdivision of the databases into:
  - Emission sources – EMIS Database;
  - Water quality – TNMN Database, Bucharest Declaration Database, Surveys – JDS, JDS-Investigation of the Tisa River;
  - Water quality/Surveys - expandable for data from similar (to be organised) surveys on all major tributaries/stretches of the Danube;
  - Water quality/Surveys – expandable for data from national surveys.
- ALL DATABASES TO BE ACCESSIBLE BY GENERAL PUBLIC
  - Each of the database users to be identified by providing basic information on his/her name, organisation, coordinates and intended use of the database;
- Improvement/upgrade of the JDS – Investigation of the Tisa River Database in the same way as the JDS Database.

Welcome page of the JDS and TNMN databases
Should allow selection of options "Search the database" and "About the database" (to be developed: information on sampling sites, parameters, matrices, laboratories, how to work with the data, assumptions and calculation models used).

Interlinking of the JDS and TNMN Databases
- TNMN Database should use the same structure (layout/coding) as the JDS Database;
- Currently, only a link from the JDS Database to the TNMN database was established, the TNMN Database should have the same option.

Biological databases
- Using the JDS Database structure and coding for establishment of the TNMN Biological Database;
- Coding:
  - Change/upgrade of the JDS codes taking into account work of expert groups at the EU level (e.g., AQEM project);
  - Incorporation of taxonomical changes according to AQEM;
  - Introduction of a shortcode for species (8 letter code) and different national codes and a table of current synonyms;
- Using special (non-Excel) data collection sheets (e.g., adjusted AQEM-DIP programme);
- Dominance of Higher Taxonomic Groups (HTG) should be calculated for macrozoobenthos, phytobenthos and macrophytes;

- A selection tree "HTG – Families – Species" should be a query option in biological databases;
- Upgrades and introduction of data into each part of the biological database (macrozoobenthos, phytobenthos, macrophytes, zooplankton, phytoplankton) should be taken care of by several institutions /team of experts.

GC-MS screening databases
- Using the JDS Database structure for establishment of the TNMN GC-MS Screening Database;
- Upgrade of the existing database structure to facilitate storage of the raw GC-MS spectra of both tentatively identified and unknown substances in order to allow for their future identification;
- Systematic evaluation of data by a separate institution/team of experts in order to gain information on unknown, emerging and Danube River Basin specific pollutants.

5. Conclusions

The JDS Database was completed for the missing parameters and quality of all stored data was thoroughly checked. During the project, the database was gradually improved and developed into the stage, that it is ready for the public use. Recommendations for a link between the JDS and TNMN databases and harmonisation of their query templates were made and incorporated into the New Draft Versions of both databases. A proposal of the new central page on the ICPDR website comprising of all ICPDR databases was made.

Despite the current version of the JDS Database (www.icpdr.org [Databases/New Draft Versions] is fully usable by both experts and general public, several suggestions, which go beyond the scope of this project component, were made by the project team and MLIM experts to improve its ease-of-use. A principal upgrade and Europe-wide harmonisation of the coding system and systematic tracking of taxonomical changes in the biological part of the database was proposed in order to assure its sustainability. Also, further upgrade of the GC-MS screening part of the database was suggested to allow proper evaluation of the screening data on emerging, unknown and Danube River Basin specific pollutants as required by the WFD. A need has arisen to perform similar upgrade at the JDS – Investigation of the Tisa River database, which is not ready for public use in its present form.

Final goal of all the above efforts is to create a fully interlinked ICPDR Information System. This would require future harmonization of the coding system between the TNMN and EMIS databases and further development of the link between the two databases. The knowledge obtained at the development and upgrade of the JDS Database created a solid base for extension of the TNMN Database for new chemical parameters, parameters measured in other matrices than water, GC-MS screening and biological data. Here, it should be seriously considered that systematic feeding of databases with data, check on their correctness and upgrade of parameters in line with scientific developments and experience gained at the implementation of the WFD can be accomplished only by a dedicated team of experts.

6. References

Referred web-pages:
- www.aqem.de
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UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient Reduction and Transboundary Cooperation in the Danube River Basin

Analysis of the results of the EMIS inventory and their comparison with TNMN and JDS results with particular attention to the EU Priority List of Pollutants

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

August 31, 2003

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Table of contents

Abbreviations, Acronyms, and Definitions
Executive summary

Abbreviations

TNMN   Trans-National Monitoring Network
EMIS   Emission Sources Expert Group
JDS   Joint Danube Survey
WFD   Water Framework Directive
ICPDR   International Commission for the Protection of the Danube River
DRPS   Danube River Priority Substances
DRB   Danube River Basin
MLIM   Monitoring and Laboratory Information Management
EG   Expert Group
DRP   UNDP/GEF Danube Regional Project
EAF   Expert Advisory Forum
PS   Priority Substances

Analysis of the results of the EMIS inventory and their comparison with TNMN and JDS results
with particular attention to the EU Priority List of Pollutants

III – 7

Executive Summary

The main objective of this activity was to prepare a background material for future harmonization of the ICPDR databases (EMIS, TNMN). Therefore, a comparative analysis of determinands (i) included in the EMIS inventories/database, (ii) routinely measured in the TNMN and (iii) analysed within the Joint Danube Survey (JDS) was made. A particular attention was given to a comparison with the determinands from the EU Water Framework Directive (WFD) List of Priority Substances. The analysis made also a comparison with the recently agreed provisional Danube List of Priority Substances.

At present, for water matrix 26 determinands from EU & Danube Priority Lists are not in the analytical programme of TNMN and 29 are not in the EMIS inventories. In the JDS, 17 out of these 26 determinands were included in the analytical programme for the water matrix. Eight JDS determinands that are listed in the Decision No. 2455/2001/EC showed results below detection limit (n.d.). Mercury was below detection limit in the JDS datasets (due to relatively high LOD of the analytical method applied), however, it is reported in the TNMN list. For 14 determinands (all organic micropollutants) listed in the Decision No. 2455/2001/EC no data in water exists in the ICPDR databases (TNMN and JDS; data from PHARE Applied Research Programme for DRB exist for PAHs).

For sediment / suspended solids altogether 20 determinands of the EU WFD Priority Substances Lists are not in the analytical programme of TNMN while 22 are not in the EMIS inventories. Ten, out of these 20 non-TNMN determinands, were included in the analytical programme of the JDS for sediments/suspended solids. For ten determinands present in the EU WFD Priority Substances list no data are available in suspended solids/sediments analysed within the TNMN and JDS.

In the technical report results are discussed in detail for each (group of) determinand(s). Considerations are presented for each determinand whether to include it or not in either the EMIS inventories or the analytical programme of TNMN. Comments on possible emission sources were made as well, based on current versions of respective EC documents (source screening). The considerations were used as a basis for the recommendations. Recommendations referred also to monitoring matrices agreed until now by EAF PS.

1. Introduction

A comparative analysis of determinands (i) included in the EMIS inventories/database, (ii) routinely measured in the TNMN and (iii) analyzed within the Joint Danube Survey (JDS) was made. A particular attention was given to a comparison with the determinands from the EU Water Framework Directive (WFD) List of Priority Substances. The analysis includes also a comparison with the recently agreed provisional Danube List of Priority Substances.

The main objective of this activity was to prepare a background material for future harmonization of the ICPDR databases (EMIS, TNMN). Recommendations for the harmonization of the databases are therefore presented, taking into account findings of the JDS as well as the Danube List of Priority Substances.

2. Methodology

A matrix was produced for five sets of parameters (EU WFD List of Priority Substances, Danube List of Priority Substances, EMIS, TNMN and JDS), displaying also units associated with each of the determinands. Both water and suspended solids/sediments (two matrices) were taken into account. The matrix provided a basis for the comparative analysis. The EU WFD and the Danube lists of Priority Substances have been included without changes. For the TNMN determinands in both matrices, the lists presented in the TNMN Yearbook 2000 were used. However, six determinands (Na, K, Ca, BOD5, COD-Mn and DOC) were excluded in the water matrix; these parameters were considered as not relevant for the study. Similarly, seven determinands (Ca, Mg, Mn, Fe, Al, TOC and Total extractable matter) were excluded from the TNMN list for the suspended solids/sediments matrix. For the JDS list of determinands, the lists in Chapter 2 of the JDS Technical Report were used in both matrices. For the water matrix, the list stayed unchanged; for suspended solids/sediment, similarly as for TNMN data set, seven determinands were excluded.

Determinands, that are not compatible with EMIS were excluded from the TNMN and JDS lists in both matrices. These parameters relate to: general physical conditions (e.g., temperature), hydrology (e.g., flow), biology (e.g., chlorophyll-A), microbiology (e.g., Salmonella) and general chemical determinands (e.g., alkalinity). A specific group of compounds excluded from the comparison were pharmaceuticals. The reason was current unavailability of sufficient information on their occurrence in surface waters in the Danube River Basin as well as their absence in the Decision No. 2455/2001/EC. However, owing to the increasingly frequent detection of pharmaceuticals in surface waters (mainly due to upgrade of analytical capabilities of water laboratories) it is advisable to focus on their occurrence in the future.

The matrices clearly indicate differences among the five investigated data sets. These differences are discussed for each (group of) determinand(s) and considerations are given on consequences for the set up of the EMIS database and the analytical programme of TNMN. Based on the above, recommendations have been developed for harmonization of EMIS and TNMN with the EU WFD and Danube Priority Substances lists. The EU list is a legal document, approved and adopted by the EU Member States and may be revised/amended in the future at the EU level. The Danube list of Priority Substances has recently been agreed by the ICPDR at its 1st Standing Working Group meeting, however, still being considered only as provisional National screenings for EU WFD Priority Substances will have to be performed in order to draft the final list of the Danube Priority Substances. The current Danube list is based on the determinands contained in the Decision No. 2455/2001/EC. In total eight parameters have been added (COD, NH4-N, Ntot, Ptot, and four heavy metals). The JDS was a single, specific survey and provided additional information for recommendations to harmonize EMIS and TNMN.

3. Results

The discussed determinands in the five data sets are presented for water and suspended solids/sediments matrices in Annex 1 and 2, respectively.

3.1 Water (Annex 1)

The columns for the EU and the Danube Lists of Priority Substances show 33, resp. 41 substances, (44, resp. 52 considering all individual determinands). At present, 26 determinands of these Priority Lists are not in the analytical programme of TNMN and 29 are not in the EMIS inventories. In the JDS, 17 out of these 26 determinands were included in the analytical programme for the water matrix. Eight JDS determinands that are listed in the Decision No. 2455/2001/EC showed results below detection limit (n.d.). Mercury was below detection limit in the JDS datasets (due to relatively high LOD of the analytical method applied), however, it is reported in the TNMN list. For 14 determinands (all organic micropollutants) listed in the Decision No. 2455/2001/EC no data in water exists in the ICPDR databases (TNMN and JDS; data from PHARE Applied Research Programme for DRB exist for PAHs).

3.2 Suspended solids/sediments (Annex 2)

The columns for the EU and the Danube Lists of Priority Substances comprise of 25 and 31 substances, respectively. Here, it must be stressed that the selection of parameters relevant for the solid phase matrices was based on the current status in elaboration of quality standards by the Expert Advisory Forum of Priority Substances (EAF PS; as of summer 2003). As this issue is not concluded yet, some amendments in the solid phase matrices may be expected in near future. At present, 20 determinands of the EU WFD Priority Substances Lists are not in the analytical programme of TNMN while 22 are not in the EMIS inventories. Ten, out of these 20 non-TNMN determinands, were included in the analytical programme of the JDS for sediments/suspended solids. For ten determinands present in the EU WFD Priority Substances list no data are available in suspended solids/sediments analysed within the TNMN and JDS.

3.3 Discussion of the results with recommendations

The results are discussed for each (group of) determinand(s). Considerations are presented for each determinand whether to include it or not in either the EMIS inventories or the analytical programme of TNMN. Comments on possible emission sources were made as well, based on current versions of respective EC documents (source screening). The considerations were used as a basis for the recommendations. Recommendations will refer also to monitoring matrices agreed until now by EAF PS.

It is expected that the considerations will be discussed with the MLIM/EMIS expert groups and this discussion may result to adjustments of the recommendations. Moreover, the evaluation of 5-Years TNMN will most likely provide additional considerations/recommendations. Therefore, the discussion presented here can be considered only as a first step in the process and certainly cannot lead to final conclusions.

Alachlor

This polar pesticide is EU WFD priority substance and is suspected to affect endocrine regulation. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). AMPS agreed on recommendation to monitor alachlor in water. Alachlor is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of the samples.

It is recommended to check whether alachlor is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities,

Analysis of the results of the EMIS inventory and their comparison with TNMN and JDS results
with particular attention to the EU Priority List of Pollutants

III – 11

further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include alachlor in the TNMN programme as a separate determinand in water.

Anthracene

This polycyclic aromatic hydrocarbon is a EU WFD priority substance under review. Anthracene has several major sources/pathways in quantitative terms of total releases. Its major point sources are run off from buildings and constructions in paved urban area (creosote treated timber) and large industrial sites (mainly production of creosote). The main non-point source is release from materials and constructions in non-urban area (creosote treated timber). Its emissions to atmosphere predominantly origin from traffic and infrastructure, households and other consumer use, and from industry. AMPS has not agreed on recommendation on monitoring matrices, yet. Anthracene is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and detected in all but two sediment samples at concentration levels of 0.0008 – 1.648 mg/kg and in all but one suspended solid samples at concentration levels of 0.0012 – 0.212 mg/kg.

It is recommended to check whether anthracene is produced/used in industrial technologies in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of municipal and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include anthracene in the TNMN programme for water and solid phase (suspended solids).

Atrazine

This polar pesticide is EU WFD priority substance under review and it is a substance with evidence on endocrine disrupting potential. Atrazine metabolites are considered significantly less toxic than atrazine itself. In terms of exposure, in surface water atrazine itself is the only environmentally significant residue where contamination results from spray drift.

Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). An important role is attributed also to atmospheric deposition of atrazine on the water surface. AMPS agreed on recommendation to monitor atrazine in water. Atrazine was detected within both TNMN and JDS in water samples. During JDS it was detected in majority of water samples at concentration levels of 0.02 – 0.78 µg/l.

It is recommended to check where atrazine is manufactured in the Danube River Basin (e.g., JDS Technical Report refers to manufacturing site in Sisak in Croatia) and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. It is recommended to keep atrazine among TNMN determinands to be analyzed in water. It seems to be not relevant to analyze atrazine in solid phase, due to its polarity.

Benzene

This aromatic hydrocarbon is EU WFD priority substance. Its major point source is emission from atmosphere from traffic and infrastructure. Direct non-point and point emission sources to surface waters are of minor importance. AMPS agreed on recommendation to monitor benzene in water. Benzene is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, and detected only in seven from 99 water samples at concentration levels of 0.1 – 0.5 µg/l.

It is recommended to check whether benzene is produced/used in industrial technologies in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of municipal and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed.

This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include benzene in the TNMN programme for water.

Brominated diphenylethers

There are 209 theoretical congeners of polybrominated diphenylethers (PBDE), out of which only few are present in technical mixtures. The individual congeners are numbered according to the IUPAC system used for the numbering of PCBs. The most frequent congeners are penta-, octa- and deca-brominated diphenylethers. Pentabromodiphenylether is EU WFD priority hazardous substance, octabromodiphenyl ether is considered as priority substance. Major sources/pathways in quantitative terms of total releases of PBDEs are (i) point sources to surface water caused by households and consumer use of flexible polyurethane foam (furniture/upholstery), resins, polyesters, textiles, ABS plastics in castings and covers for electric and electronic equipment, synthetic carpets; and (ii) large industrial point sources (either production/formulation of PBDEs or industrial use of PBDEs as flame retardants in the production of flexible polyurethane foam, resins, polyesters, textiles, etc.). AMPS agreed on recommendation to monitor bis(pentabromophenyl)ether, pentabromodiphenylether and octabromodiphenyl ether in suspended particulate matter (SPM), settled sediment and biota. Polybrominated diphenylethers are not included in the EMIS inventory or TNMN programme. They were analyzed in the JDS in suspended solids and sediment, but not detected in any of the samples.

It is recommended to check whether PBDEs are produced/used in industrial technologies in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of municipal and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for their presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include PBDEs in the TNMN programme for solid phase (and biota).

Cadmium and its compounds

This heavy metal is EU WFD priority hazardous substance. Cadmium has a wide range of major sources/pathways in quantitative terms of total releases – (i) diffuse sources (atmospheric deposition on the water surface, agricultural activities, transport and infrastructure without connection to canalisation), (ii) point sources (households, consumer use, industrial activities such as zinc mining, lead and zinc refining, manufacture of cadmium compounds, primary and secondary batteries, pigments, stabilisers, phosphoric acid and/or phosphatic fertiliser from phosphatic rock, etc.), as well as (iii) emissions to atmosphere from industry. AMPS has not agreed on recommendation on monitoring matrices, yet. Cadmium is included in all reviewed data sets and detected in all matrices.

For a proper assessment of occurrence of cadmium of anthropogenic origin in the Danube River Basin the estimation of natural background concentrations of cadmium in water, suspended particulate matter (and sediments) should be done (including issues related to the spatial and temporal variability of these background concentrations). Nevertheless, it is recommended to keep cadmium in all ICPDR programmes (emission inventories of municipal and industrial point sources, TNMN monitoring in water and suspended solids).

C_{10-13}- *Chloroalkanes*

C_{10-13}-Chloroalkanes (short-chain chlorinated paraffins, SCCPs) are polychlorinated n-alkanes with chlorine content ranging from 49 to 70% by weight. The theoretical maximum number of positional isomers calculated for $C_nH_{2n+2-z}Cl_z$, assuming no more than one bound chlorine atom on an carbon atom, for SCCPs is 7820. However, the complexity of mixture of C_{10-13}- Chloroalkanes is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers are generated. Furthermore, although the source hydrocarbon skeletons are primarily n-alkanes, they can contain branched alkanes and also other hydrocarbons, which increase the complexity of mixtures. Hence, it can be expected that commercial mixtures of C10-13- chloroalkanes contain several thousands of compounds.

C_{10-13}-Chloroalkanes are categorised as EU WFD priority hazardous substances. Major sources/pathways in quantitative terms of total releases of C_{10-13}-chloroalkanes are industrial point sources to surface water (manufacture of metal working fluids, leather applications). AMPS has not agreed on recommendation on monitoring matrices, yet. C_{10-13}- Chloroalkanes are not included in the EMIS inventory or TNMN programme.

It is recommended to check whether C_{10-13}-chloroalkanes are produced/used in industrial technologies in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of industrial point sources. Based on the emission data, further targeted investigations/surveys to check for their presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include C_{10-13}-chloroalkanes in the TNMN programme for water and solid phase.

Chlorfenvinphos

This polar pesticide is EU WFD priority substance. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere including following atmospheric deposition on the water surface). AMPS agreed on recommendation to monitor chlorfenvinphos in water. Chlorfenvinphos is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of the samples.

It is recommended to check whether chlorfenvinphos is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include chlorfenvinphos in the TNMN programme as a separate determinand in water.

Chlorpyrifos

This polar pesticide is categorised as EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). AMPS agreed on recommendation to monitor chlorpyrifos in water. Chlorpyrifos is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of the samples.

It is recommended to check whether chlorpyrifos is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include chlorpyrifos in the TNMN programme as a separate determinand in water.

1,2-Dichloroethane

This volatile chlorohydrocarbon is categorised as EU WFD priority substance. 1,2-Dichloroethane is primarily released into atmosphere by industrial point sources (production of 1,2-dichloroethane and its processing into, e.g., ethylene diamine, ethylene polyamine, 1,1,1-trichloroethane, trichloroethylene and perchloroethylene; degreasing of metals). AMPS agreed on recommendation to monitor 1,2-dichloroethane in water. 1,2-Dichloroethane is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS and it was detected in 18 from 99 the samples at concentration levels of 0.1 – 10 µg/l.

It is recommended to check whether 1,2-dichloroethane is manufactured in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of industrial point

sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include 1,2-dichloroethane in the TNMN programme as a separate determinand in water.

Dichloromethane

This volatile chlorohydrocarbon is categorised as EU WFD priority substance. Dichloromethane is primarily released into atmosphere by industrial point sources (pharmaceutical industry). Direct industrial point sources to surface waters are of minor importance. AMPS agreed on recommendation to monitor dichloromethane in water. Dichloromethane is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of water samples.

It is recommended to check whether dichloromethane is manufactured in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include dichloromethane in the TNMN programme as a separate determinand in water.

Di(2-ethylhexyl)phthalate (DEHP)

This alkyl derivative of phthalic acid is categorised as EU WFD priority substance under review. Major sources/pathways in quantitative terms of total releases of di(2-ethylhexyl)phthalate are industrial and municipal point sources to surface water (run off from buildings and constructions in paved urban area, e.g. from roofs containing PVC with DEHP; households & consumer use of PVC with DEHP as stabiliser; production of DEHP and of PVC with DEHP as stabiliser). AMPS has not agreed on recommendation on monitoring matrices, yet. Di(2-ethylhexyl)phthalate is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and it was detected in almost all sediment samples at concentration levels of 0.032 – 170 mg/kg and in all suspended solids at concentration levels of 0.021 – 3 mg/kg.

It is recommended to check whether di(2-ethylhexyl)phthalate is manufactured in the Danube River Basin. In reference to its potential major pathways (especially a frequent consumer use) it should be included into EMIS inventory of industrial and municipal point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include di(2-ethylhexyl)phthalate in the TNMN programme as a separate determinand in water and solid phase.

Diuron

This polar pesticide is a EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). AMPS agreed on recommendation to monitor diuron in water. Diuron is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of water samples.

It is recommended to check whether diuron is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to the regions where it is produced/used. This should be taken into account during

national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include diuron in the TNMN programme as a separate determinand in water.

Endosulfan (alpha-endosulphan)

This polar pesticide is a EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters). AMPS has not agreed on recommendation on monitoring matrices, yet. Alpha-endosulphan is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of water samples.

It is recommended to check whether alpha-endosulphan is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include alpha-endosulphan in the TNMN programme as a separate determinand in water.

Fluoranthene

This polycyclic aromatic hydrocarbon is a EU WFD priority substance. Fluoranthene has several major sources/pathways in quantitative terms of total releases. Its major point sources are run off from buildings and constructions in paved urban area (creosote treated timber) and large industrial sites (power generation; primary aluminium production; iron and steel industry; production of creosote and creosote treated timber; waste incineration; industrial combustion). The main non-point sources are releases from materials and constructions in non-urban area (creosote treated timber), accidental oil spills, transport and infrastructure without connection to canalisation and atmospheric deposition on the water surface. Its emissions to atmosphere predominantly origin from traffic and infrastructure, households and other consumer use, and from industry. AMPS has not agreed on recommendation on monitoring matrices, yet. Fluoranthene is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and detected in all sediment samples at concentration levels of 0.001 – 0.876 mg/kg and in all suspended solid samples at concentration levels of 0.0046 – 0.467 mg/kg.

It is recommended to check whether fluoranthene is produced/used in industrial technologies in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of municipal and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include Fluoranthene in the TNMN programme for water and solid phase (suspended solids).

Hexachlorobenzene

This chlorinated aromatic hydrocarbon is categorised as EU WFD priority hazardous substance. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters) and losses from historically contaminated (aquatic) soils. AMPS has not agreed on recommendation on monitoring matrices, yet. Hexachlorobenzene is not included in the EMIS inventory or TNMN programme. It was measured both in water and in suspended solids/sediments during the JDS. During this survey hexachlorobenzene was not found in water and it was detected in most of the sediment samples at concentration levels of 0.0001 – 2.6 mg/kg and in most of the suspended solid samples at concentration levels of 0.002 – 0.0069 mg/kg.

It is recommended to check whether hexachlorobenzene is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural and industrial point sources. Based on the emission data, further targeted

investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include hexachlorobenzene in the TNMN programme for solid phase (suspended solids).

Hexachlorobutadiene

Hexachlorobutadiene is categorised as EU WFD priority hazardous substance. There were identified no major sources/pathways of total releases of hexachlorobutadiene. The industrial point-sources (production of trichloroethylene and perchloroethylene; solid waste treatment) and losses from historically contaminated (aquatic) soils are considered to have only a minor importance. AMPS has not agreed on recommendation on monitoring matrices, yet. Hexachlorobutadiene is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and its concentrations were below the detection limit in all analyzed samples.

It is recommended to check whether hexachlorobutadiene is manufactured in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include hexachlorobutadiene in the TNMN programme for solid phase (suspended solids).

Hexachlorocyclohexane (Lindane)

This chlorinated hydrocarbon is categorised as EU WFD priority hazardous substance. There is evidence suggesting that lindane caused hormonal disruption. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters, emission to atmosphere including following atmospheric deposition on the water surface). Losses from historically contaminated (aquatic) soils are considered to be of a minor importance. AMPS agreed on recommendation to monitor lindane in water. Lindane is not included in the EMIS inventory. Within TNMN programme it is monitored in sediments and water. Lindane was also measured in water and in suspended solids/sediments during the JDS. During this survey Lindane was not found in water and it was detected in 60% of the sediment samples at concentration levels of 0.0001 – 2.4 mg/kg and in 50% of the suspended solid samples at concentration levels of 0.0001 – 0.0058 mg/kg.

It is recommended to check whether Lindane is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural and industrial point sources. It is recommended to keep lindane among TNMN determinands to be analyzed in water and in solid phase.

Isoproturon

This polar pesticide is a EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). AMPS agreed on recommendation to monitor isoproturon in water. Isoproturon is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of water samples.

It is recommended to check whether isoproturon is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include isoproturon in the TNMN programme as a separate determinand in water.

Lead and its compounds

This heavy metal is categorised as EU WFD priority substance under review. Lead has a wide range of major sources/pathways in quantitative terms of total releases – diffuse sources (atmospheric deposition on the water surface), industrial point sources (zinc production; calcium carbide production; mining), as well as emissions to atmosphere from industry, traffic and infrastructure. AMPS has not agreed on recommendation on monitoring matrices, yet. Lead is included in all reviewed data sets and detected in all matrices.

For a sound assessment of occurrence of lead of anthropogenic origin in the Danube River Basin, an estimation of natural background concentrations of lead in water, suspended particulate matter (and sediments) should be done (including issues related to the spatial and temporal variability of these background concentrations). Nevertheless, it is recommended to keep lead in all ICPDR programmes (emission inventories of municipal and industrial point sources, TNMN monitoring in water and suspended solids).

Mercury and its compounds

This heavy metal is categorised as EU WFD priority hazardous substance. Mercury has a wide range of major sources/pathways in quantitative terms of total releases – diffuse sources (atmospheric deposition on the water surface), industrial point sources (chemical industry using mercury catalysts; processes involving the manufacture of organic and non-organic mercury compounds; mercury recovery plants and extraction and refining of non-ferrous metals; plants for the treatment of toxic waste containing mercury; production of steel; dental technologies), as well as emissions to atmosphere from industry. AMPS has not agreed on recommendation on monitoring matrices, yet. Mercury is included in all reviewed data sets and detected in all matrices. In JDS water samples mercury was not detected due to high LOD of the applied analytical method.

For a proper assessment of occurrence of mercury of anthropogenic origin in the Danube River Basin an estimation of natural background concentrations of mercury in water, suspended particulate matter (and sediments) should be done (including issues related to the spatial and temporal variability of these background concentrations). Nevertheless, it is recommended to keep mercury in all ICPDR programmes (emission inventories of municipal and industrial point sources, TNMN monitoring in water and suspended solids).

Naphthalene

This polycyclic aromatic hydrocarbon is categorised as EU WFD priority substance under review. The major source in quantitative terms of total release of naphthalene is its emission to atmosphere. Direct emissions from point and non-point sources into surface waters are considered to have only minor importance. AMPS has not agreed on recommendation on monitoring matrices, yet. Naphthalene is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and detected in most of the sediment samples at concentration levels of 0.0001 – 0.02 mg/kg and in approx. 60% of suspended solid samples at concentration levels of 0.001 – 0.039 mg/kg.

It is recommended to check whether naphthalene is produced/used in industrial technologies in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of municipal and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include naphthalene in the TNMN programme for water and solid phase (suspended solids).

Nickel and its compounds

This heavy metal is categorised as EU WFD priority substance. Nickel is primarily released by emissions to atmosphere from industry, traffic and infrastructure with following deposition to surface

waters. AMPS has not agreed on recommendation on monitoring matrices, yet. Nickel is included in all reviewed data sets and detected in all matrices.

For a proper assessment of occurrence of nickel of anthropogenic origin in the Danube River Basin an estimation of natural background concentrations of nickel in water, suspended particulate matter (and sediments) should be done (including issues related to the spatial and temporal variability of these background concentrations). Nevertheless, it is recommended to keep nickel in all ICPDR programmes (emission inventories of municipal and industrial point sources, TNMN monitoring in water and suspended solids).

Nonylphenols

4-Nonylphenol (branched) and nonylphenol are categorised as EU WFD priority hazardous substances. Nonylphenol and nonylphenol ethoxylates do exhibit estrogenic activity. For nonylphenol ethoxylates the activity was found to increase with decreasing chain length, with nonylphenol showing the greatest activity. Most of the tests indicate that estrogenic effects may start to occur at around 10-20 µg/l. Commercially produced nonylphenols contain predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. Nonylphenols found in the environment do not originate directly from a production process and from their direct use but they are usually degradation products of the nonylphenol polyethoxylates (non-ionic surfactants).

Major sources/pathways in quantitative terms of total releases of nonylphenols are industrial and municipal point sources to surface water (domestic cleaning; use of water-based paints; use as detergent / cleaning agent in industry; use in emulsion polymerisation and as auxiliaries by industrial sectors for production of polymers, pulp- and paper, textiles, leather, paints, adhesives and plastics; nonylphenols are absorbed by sewage sludge in treatment plants). AMPS has not agreed on recommendation on monitoring matrices, yet. Nonylphenols are not included in the EMIS inventory or TNMN programme. 4-iso-Nonylphenol was measured in suspended solids/sediments during the JDS and it was detected in almost all sediment samples at concentration levels of 0.006 – 160 mg/kg and in almost all suspended solids at concentration levels of 0.015 – 1.4 mg/kg.

It is recommended to check whether nonylphenols are manufactured and/or used at manufacturing of non-ionic surfactants in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of industrial and municipal point sources. If they are used in considerable quantities, further targeted investigations/surveys are necessary to check for their presence in specific stretches in the basin, close to these regions where they are produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include nonylphenols in the TNMN programme as a separate determinand in a solid phase.

Octylphenols

Octylphenols (para-tert-octylphenol) are categorised as EU WFD priority substances under review. Para-tert-octylphenol is a substance with evidence of endocrine disrupting potential. Octylphenols found in the environment do not originate directly from a production process and from their direct use but they are usually degradation products of the octylphenol polyethoxylates (non-ionic surfactants).

Major sources/pathways in quantitative terms of total releases of octylphenols are industrial and municipal point sources to surface water (domestic cleaning; use of water-based paints; use as detergent / cleaning agent in industry; use in emulsion polymerisation and as auxiliaries by industrial sectors for production of polymers, pulp- and paper, textiles, leather, paints, printing inks and pesticides). AMPS has not agreed on recommendation on monitoring matrices, yet. Octylphenols are not included in the EMIS inventory or TNMN programme. Para-tert-octylphenol was measured in suspended solids/sediment during the JDS and it was detected in ca. half of the sediment samples at concentration levels of 0.005 – 1.7 mg/kg. It was not detected in suspended solids.

It is recommended to check whether octylphenols are manufactured and/or used in manufacturing of non-ionic surfactants in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of industrial and municipal point sources. If they are used in

considerable quantities, further targeted investigations/surveys are necessary to check for their presence in specific stretches in the basin, close to these regions where they are produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include octylphenols in the TNMN programme as a separate determinand in a solid phase.

Pentachlorobenzene

This chlorinated aromatic hydrocarbon is categorised as EU WFD priority hazardous substance. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emissions to atmosphere). AMPS has not agreed on recommendation on monitoring matrices, yet. Pentachlorobenzene is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS. During this survey pentachlorobenzene was detected in almost all sediment samples at concentration levels of 0.0001 – 3.5 mg/kg and in most of the suspended solid samples at concentration levels of 0.001 – 0.028 mg/kg.

It is recommended to check whether pentachlorobenzene is manufactured in the Danube River Basin and/or used as a pesticide (also to check its possible occurrence as impurity in pesticide quintozene). In reference to its potential major pathways it should be included into EMIS inventory of agricultural and industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include pentachlorobenzene in the TNMN programme for monitoring of a solid phase.

Pentachlorophenol

Pentachlorophenol is categorised as EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are industrial activities (point source emission to surface waters from production of wood and heavy textile). AMPS agreed on recommendation to monitor pentachlorophenol in water. Pentachlorophenol is not included in the EMIS inventory or TNMN programme. It was measured in suspended solids/sediments during the JDS and its concentrations were below the detection limit in all analyzed samples.

It is recommended to check whether pentachlorophenol is manufactured in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include pentachlorophenol in the TNMN programme for monitoring of a solid phase.

Polyaromatic hydrocarbons

The polycyclic aromatic hydrocarbons are EU WFD priority hazardous substances. They have several major sources/pathways in quantitative terms of total releases. Their major point sources are run off from buildings and constructions in paved urban area and large industrial sites (power generation; production of creosote and creosote treated timber; waste incineration; industrial combustion). The main non-point sources are releases from materials and constructions in non-urban area (creosote treated timber), accidental oil spills, transport and infrastructure without connection to canalisation and atmospheric deposition on the water surface. Their emissions to atmosphere predominantly origin from traffic and infrastructure, households and other consumer use, as well as from industry. AMPS has not agreed on recommendation on monitoring matrices, yet. PAHs are not included in the EMIS inventory. They are included TNMN programme (analysis in sediments). They were measured in suspended solids/sediments during the JDS and detected in all sediment / suspended solid samples. Their summary concentrations in sediments were mostly below 2 mg/kg, none of the samples had PAH contamination higher than 20 mg/kg.

It is recommended to assess the use of PAHs in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of municipal and industrial point sources. It is recommended to keep PAHs among TNMN determinands to be analyzed in a solid phase.

Simazine

This polar pesticide is a EU WFD priority substance under review and it is a substance with evidence on endocrine disrupting potential. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere). AMPS agreed on recommendation to monitor simazine in water. Simazine is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of water samples.

It is recommended to check where simazine is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include simazine in the TNMN programme as a separate determinand in water. It seems to be not relevant to analyze simazine in solid phase, due to its polarity.

Tributyltin compounds (tributyltin cation)

Tributyltin compounds (tributyltin cation) are categorised as EU WFD priority hazardous substances. Major sources/pathways in quantitative terms of total releases of tributyltin compounds are diffuse sources to surface water from transport and infrastructure without connection to canalisation (leaching antifouling on ship hulls). AMPS has not agreed on recommendation on monitoring matrices, yet. Tributyltin compounds are not included in the EMIS inventory or TNMN programme. They were measured in suspended solids/sediments during the JDS and it was detected in approx. half of sediment samples at concentration levels of 0.002 – 0.04 mg/kg and in approx. half of suspended solids at concentration levels of 0.002 – 0.02 mg/kg.

It is recommended to check whether tributyltin compounds are manufactured in the Danube River Basin (even though their manufacturing plants are considered to have negligible importance as emission sources). In reference to their potential major pathways they should be included into EMIS inventory of industrial point sources. Their inclusion into inventory of diffuse sources is also recommended. Regardless to results of emission inventories further targeted investigations/surveys are necessary to check for the presence of tributyltin compounds in specific stretches in the basin. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include tributyltin compounds in the TNMN programme as a separate determinand in a solid phase.

Trichlorobenzenes (1,2,3-TCB; 1,2,4-TCB; 1,3,5-TCB)

These chlorinated aromatic hydrocarbons are categorised as EU WFD priority substances under review. Their major sources/pathways in quantitative terms of total releases are industrial activities (large industrial point sources - production and or processing of chlorobenzenes via chlorination and/or using TCB as chemical intermediate). AMPS agreed on recommendation to monitor trichlorobenzenes in water. Trichlorobenzenes are not included in the EMIS inventory or TNMN programme. They were measured in water during the JDS and detected only in three samples at concentration levels of 0.1 – 0.6 µg/l (summary concentration) and 0.1 – 0.5 µg/l (1,2,4-TCB).

It is recommended to check whether trichlorobenzenes are manufactured in the Danube River Basin. In reference to their potential major pathways they should be included into EMIS inventory of industrial point sources. Based on the emission data, further targeted investigations/surveys to check for its presence in specific stretches in the basin should be performed. This should be taken into

account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include trichlorobenzenes in the TNMN programme for water.

Trichloromethane

This volatile chlorohydrocarbon is categorised as EU WFD priority substance. Trichloromethane is primarily released by point sources to surface waters (industrial sources - production of chloroform; plants using chloroform as solvent or in which cooling water or effluents are chlorinated) and it is also released into atmosphere by industrial point sources with following atmospheric deposition on the water surface. Emissions from households and consumer use are of minor importance. AMPS agreed on recommendation to monitor trichloromethane in water. Trichloromethane is not included in the EMIS inventory. It is monitored within TNMN programme in water. It was measured in water during the JDS and detected in ca. 40% of samples at concentration levels of 0.1 – 1.3 µg/l.

It is recommended to check whether trichloromethane is manufactured in the Danube River Basin. In reference to its potential major pathways it should be included into EMIS inventory of industrial point sources. It is recommended to keep trichloromethane among TNMN determinands to be analyzed in water.

Trifluralin

This polar pesticide is categorised as EU WFD priority substance under review. Its major sources/pathways in quantitative terms of total releases are agricultural activities (diffuse emission to surface waters and emission to atmosphere with following atmospheric deposition on the water surface). AMPS has not agreed on recommendation on monitoring matrices, yet. Trifluralin is not included in the EMIS inventory or TNMN programme. It was measured in water during the JDS, but not detected in any of the samples.

It is recommended to check whether trifluralin is manufactured in the Danube River Basin and/or used as a pesticide. In reference to its potential major pathways it should be included into EMIS inventory of agricultural diffuse sources and of industrial point sources. If it is used in considerable quantities, further targeted investigations/surveys are necessary to check for its presence in specific stretches in the basin, close to these regions where it is produced/used. This should be taken into account during national EU WFD monitoring surveys. Based on these findings it can be decided whether or not to include trifluralin in the TNMN programme as a separate determinand in water.

Danube Specific Priority Substances (As, Co, Zn, Cr)

These heavy metals are not EU WFD priority substances but were agreed upon as specific for the Danube River Basin. They are included in all reviewed data sets and were detected in all matrices.

For a sound assessment of occurrence of As, Co, Zn, Cr of anthropogenic origin in the Danube River Basin an estimation of natural background concentrations of these heavy metals in water, suspended particulate matter (and sediments) should be performed (including issues related to the spatial and temporal variability of these background concentrations). Nevertheless, it is recommended to keep As, Co, Zn, Cr in all ICPDR programmes (emission inventories of municipal and industrial point sources, TNMN monitoring in water and suspended solids).

General Parameters (COD, NH$_4$, N, P)

These determinands are included as a special category in the Danube List of Priority Substances. They are included in all reviewed data sets and detected in all investigated matrices (with the exception of COD within the JDS). Nitrogen is in EMIS inventories reported to as total N, in the TNMN data it is expressed in terms of organic N and its inorganic forms (NH4, NO3, NO2).

It is recommended to keep COD, NH4, N and P in the ICPDR programmes under current structure. In case of nitrogen it is worth of consideration to provide information on total N from TNMN / load programme (Yearbooks) so that a better comparison with EMIS data could be done.

Analysis of the results of the EMIS inventory and their comparison with TNMN and JDS results
with particular attention to the EU Priority List of Pollutants

III – 23

Annexes

Annexes

Annex 1

Table 1 – Comparison of data in the ICPDR Information System – water.

	EU WFD priority substances	Danube priority substances	TNMN	JDS	Emission inventories
Alachlor	µg/l	µg/l		n.d.	
Anthracene	µg/l	µg/l			
Atrazine	µg/l	µg/l	µg/l	µg/l	
Benzene	µg/l	µg/l		µg/l	
Brominated diphenylethers	µg/l	µg/l			
Cadmium and its compounds	µg/l	µg/l	µg/l	µg/l	t/a
C_{10-13}-chloroalkanes	µg/l	µg/l			
Chlorfenvinphos	µg/l	µg/l		n.d.	
Chlorpyrifos	µg/l	µg/l		n.d.	
1,2-Dichloroethane	µg/l	µg/l		µg/l	
Dichloromethane	µg/l	µg/l		n.d.	
Di(2-ethylhexyl)phthalate (DEHP)	µg/l	µg/l			
Diuron	µg/l	µg/l		n.d.	
Endosulfan	µg/l	µg/l		n.d.	
(alpha-endosulfan)	µg/l	µg/l		n.d.	
Fluoranthene	µg/l	µg/l			
Hexachlorobenzene	µg/l	µg/l		n.d.	
Hexachlorobutadiene	µg/l	µg/l			
Hexachlorocyclohexane	µg/l	µg/l			
(gamma-isomer, Lindane)	µg/l	µg/l	µg/l	n.d.	
Isoproturon	µg/l	µg/l		n.d.	
Lead and its compounds	µg/l	µg/l	µg/l	µg/l	t/a
Mercury and its compounds	µg/l	µg/l	µg/l	n.d.	t/a
Naphthalene	µg/l	µg/l		n.d.	
Nickel and its compounds	µg/l	µg/l	µg/l	µg/l	t/a
Nonylphenols	µg/l	µg/l			
(4-(para)-nonylphenol)	µg/l	µg/l			
Octylphenols	µg/l	µg/l			
(para-tert-octylphenol)	µg/l	µg/l			
Pentachlorobenzene	µg/l	µg/l			
Pentachlorophenol	µg/l	µg/l			
Polyaromatic hydrocarbons	µg/l	µg/l			
(Benzo(a)pyrene)	µg/l	µg/l			
(Benzo(b)fluoranthene)	µg/l	µg/l			
(Benzo(g,h,i)perylene)	µg/l	µg/l			
(Benzo(k)fluoranthene)	µg/l	µg/l			
(Indeno(1,2,3-cd)pyrene)	µg/l	µg/l			
Simazine	µg/l	µg/l		n.d.	
Tributyltin compounds	µg/l	µg/l			
(Tributyltin-cation)	µg/l	µg/l			
Trichlorobenzenes	µg/l	µg/l		µg/l	
(1,2,4-Trichlorobenzene)	µg/l	µg/l		µg/l	
Trichloromethane (Chloroform)	µg/l	µg/l	µg/l	µg/l	
Trifluralin	µg/l	µg/l		n.d.	
Chemical Oxygen Demand (COD)		mg/l	mg/l		t/a
Ammoniacal Nitrogen (NH$_4$-N)		mg/l	mg/l	mg/l	t/a
Organic Nitrogen			mg/l	mg/l	
Total Nitrogen (tot N)		mg/l			t/a
Total Phosphorus (tot P)		mg/l	mg/l	mg/l	t/a
Arsenic and its compounds		µg/l	µg/l	µg/l	t/a
Copper and its compounds		µg/l	µg/l	µg/l	t/a
Zinc and its compounds		µg/l	µg/l	µg/l	t/a
Chromium and its compounds		µg/l	µg/l	µg/l	t/a
p,p'DDT			µg/l		
Carbon tetrachloride			µg/l	µg/l	
Trichloroethylene			µg/l	µg/l	
Tetrachloroethylene			µg/l	µg/l	
Iron			mg/l		t/a
Manganese			mg/l		t/a
Magnesium			mg/l		t/a
Aluminium			µg/l	µg/l	t/a
Sulphates			mg/l		t/a
Phenols			mg/l		t/a
Fluorides					t/a

Table 1 – cont.

Petroleum Hydrocarbons			mg/l		t/a
Chlorides			mg/l		t/a
Detergents			mg/l		t/a
Sulfide					t/a
Formaldehyde					t/a
Methanol					t/a
AOX			µg/l		t/a
Nonpolar extractables					t/a
Dissolved inorganic substances					t/a
Chlorinated hydrocarbons					t/a
Suspended solids			mg/l	mg/l	t/a
Nitrate (NO3-N)			mg/l	mg/l	t/a
Nitrite (NO2-N)			mg/l	mg/l	t/a
Ortho-phosphate (PO4-P)			mg/l	mg/l	t/a
Active chlorine					t/a
Dissolved silicate				mg/l	t/a

Analysis of the results of the EMIS inventory and their comparison with TNMN and JDS results
with particular attention to the EU Priority List of Pollutants

III – 27

Annex 2

Table 2 - Comparison of data in the ICPDR Information System – suspended solids and sediments.

	EU WFD priority substances	Danube priority substances	TNMN	JDS	Emission inventories
Anthracene	µg/kg	µg/kg		mg/kg	
Atrazine	µg/kg	µg/kg			
Brominated diphenylethers	mg/kg	mg/kg		n.d.	
Cadmium and its compounds	mg/kg	mg/kg	mg/kg	mg/kg	t/a
C$_{10-13}$-chloroalkanes	µg/kg	µg/kg		n.a.	
Chlorpyrifos	µg/kg	µg/kg			
Di(2-ethylhexyl)phthalate (DEHP)	mg/kg	mg/kg		mg/kg	
Endosulfan	µg/kg	µg/kg			
(alpha-endosulfan)	µg/kg	µg/kg			
Fluoranthene	µg/kg	µg/kg		mg/kg	
Hexachlorobenzene	µg/kg	µg/kg		mg/kg	
Hexachlorobutadiene	µg/kg	µg/kg		mg/kg	
Lindane (gamma HCH)	µg/kg	µg/kg	mg/kg	mg/kg	
Lead and its compounds	mg/kg	mg/kg	mg/kg	mg/kg	t/a
Mercury and its compounds	mg/kg	mg/kg	mg/kg	mg/kg	t/a
Naphthalene	µg/kg	µg/kg		mg/kg	
Nickel and its compounds	mg/kg	mg/kg	mg/kg	mg/kg	t/a
Nonylphenols	µg/kg	µg/kg		mg/kg	
(4-(para)-nonylphenol)	µg/kg	µg/kg		mg/kg	
Octylphenols	µg/kg	µg/kg		mg/kg	
(para-tert-octylphenol)	µg/kg	µg/kg		mg/kg	
Pentachlorobenzene	µg/kg	µg/kg		mg/kg	
Pentachlorophenol	µg/kg	µg/kg		n.d.	
Polyaromatic hydrocarbons	µg/kg	µg/kg	mg/kg	mg/kg	
(Benzo(a)pyrene)	µg/kg	µg/kg	mg/kg	mg/kg	
(Benzo(b)fluoranthene)	µg/kg	µg/kg	mg/kg	mg/kg	
(Benzo(g,h,i)perylene)	µg/kg	µg/kg	mg/kg	mg/kg	
(Benzo(k)fluoranthene)	µg/kg	µg/kg	mg/kg	mg/kg	
(Indeno(1,2,3-cd)pyrene)	µg/kg	µg/kg	mg/kg	mg/kg	
Simazine	µg/kg	µg/kg			
Tributyltin compounds	µg/kg	µg/kg		mg/kg	
(Tributyltin-cation)	µg/kg	µg/kg		mg/kg	
Trichlorobenzenes	µg/kg	µg/kg			
(1,2,4-Trichlorobenzene)	µg/kg	µg/kg			
Trichloromethane (Chloroform)	µg/kg	µg/kg			
Trifluralin	µg/kg	µg/kg			
Organic Nitrogen			mg/kg	mg/kg	
Total Nitrogen (tot N)		mg/kg			t/a
Total Phosphorus (tot P)		mg/kg	mg/kg	mg/kg	t/a
Arsenic and its compounds		mg/kg	mg/kg	mg/kg	t/a
Copper and its compounds		mg/kg	mg/kg	mg/kg	t/a
Zinc and its compounds		mg/kg	mg/kg	mg/kg	t/a
Chromium and its compounds		mg/kg	mg/kg	mg/kg	t/a
p,p'DDT			mg/kg	mg/kg	
PCB			mg/kg	mg/kg	
Petroleum Hydrocarbons			mg/kg	mg/kg	t/a

Development of the Danube List of Priority Substances and SOPs for newly included determinands

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

August 28, 2003

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Table of contents

Abbreviations

DRPS   Danube River Priority Substances
TNMN   Trans-National Monitoring Network
JDS   Joint Danube Survey
EMIS   Emission Sources Expert Group
MLIM   Monitoring and Laboratory Information Management
ICPDR   International Commission for the Protection of the Danube River
WFD   Water Framework Directive
DRB   Danube River Basin
EG   Expert Group
AMPS   Expert Group on Analysis and Monitoring of Priority Substances

Executive Summary

The main objective of this activity was to develop the Danube List of Priority Substances, based on the EU List of Priority Substances, determinands of TNMN and JDS; and taking into account the results of Phare project ZZ-97-25 Component VI in line with work of EMIS EG on this topic. However, the activities concerning developing the Danube List of Priority Substances had started long time before the Danube Regional Project began and the list was finalized by the ICPDR during course of the project. Therefore, a summary is provided of the activities performed and milestones achieved. Moreover, general recommendations are given for the follow-up actions.

In line with the Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, and taking into account determinands analysed within TNMN and JDS as well as the results of Phare project ZZ-97-25 Component VI, the EMIS EG prepared the draft Danube List of Priority Substances. At the 1st Meeting of the Joint MLIM/EMIS Working Group in February 2003 this draft was discussed and it was suggested to keep the Annex A as prepared by the EMIS EG (identical with the EU WFD list). The Annex B was proposed to be divided into two groups – General Parameters (COD, NH4, N, P) and Danube Specific Priority Substances (As, Co, Zn, Cr). The ICPDR at its 1st Standing Working Group meeting in June 2003 agreed with the proposed Danube List of Priority Substances but considered it only as provisional. To arrive at a final list the national targeted screenings for EU WFD Priority Substances will have to be performed to prove their relevance for the specific area/region.

For the determinands, which newly appeared in the proposed Danube List of Priority Substances it was necessary to make available the respective standard operational procedures (SOPs). The overview of SOPs provided in the technical report takes into account the results of the review on possibilities to analyze the EU WFD priority substances in the Danube countries, which was performed by the MLIM EG in 2002. An attention was also paid to the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the "EU Expert Advisory Forum on Priority Substances and Pollution Control". The recommended standard operational procedures are divided into two groups - priority substances from the DECISION No. 2455/2001/EC and geneneral parameters and priority substances specific for the Danube River Basin.

1. Development of the Danube List of Priority Substances

1.1   Introduction

The main objective of this activity was to develop the Danube List of Priority Substances, based on the EU List of Priority Substances, determinands of TNMN and JDS; and taking into account the results of Phare project ZZ-97-25 Component VI in line with work of EMIS EG on this topic. However, the activities concerning developing the Danube List of Priority Substances had started long time before the Danube Regional Project began and the list was finalized by the ICPDR during course of the project. Therefore, the authors could only provide a summary of the activities performed, milestones achieved and a general recommendation for the follow-up actions.

1.2   Summary of activities and recommendations

In line with the Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, and taking into account determinands analysed within TNMN and JDS as well as the results of Phare project ZZ-97-25 Component VI, the EMIS EG prepared the draft Danube List of Priority Substances. They recommended to the Contracting Parties that the substances and groups of substances they had put on the list should be Priority Substances for the Danube River Basin and should be subject for the following measures:

- Introduce subsequently these substances into the monitoring programmes for discharges wherever the possibility exists that those substances might occur.

- Introduce subsequently these substances into the monitoring programmes for the in-stream chemical status. Parameter No. 34 (Chemical Oxygen Demand) might be substituted by the parameter BOD (Biological Oxygen Demand).

- Introduce subsequently these substances into permits for discharge of waste waters, which contain those substances regulate or their use via other relevant national legislation.

They also recommended that this list should be reviewed in 2004 considering further development of the EU List of Priority Substances, especially, concerning the identification of priority hazardous substances of which emissions, discharges and losses will have to be finished within a time frame of 20 years.

With respect to the substances in the Annex IA of the proposed Danube list the MLIM EG at its 29th meeting had reservations about the automatic inclusion of all EU WFD priority substances into the Danube list. MLIM EG recommended that further investigation in this area should be performed from the emission and in-stream standpoint. The MLIM EG decided to proceed with the evaluation of the in-stream measurements and the EMIS EG was asked to provide information on estimated emissions of the substances on the WFD list. With respect to the substances in the Annex IB of the proposed Danube list the MLIM EG discussed the parameters 34 – 41 and because of the lack of clarity in the used terminology doubts were expressed if the parameters 34 – 37 may be looked upon as the priority substances, especially, in the view of in-stream water quality. It was stated that for priority substances the quality objectives were necessary to be set. At the ICPDR Chairpersons meeting in October 2002 it was agreed that a Joint MLIM/EMIS Working Group should further deal with finalization of the Danube List of Priority Substances. At the 1st Meeting of the Joint MLIM/EMIS Working Group in February 2003 it was suggested to keep the Annex A as prepared by the EMIS EG (identical with the EU WFD list). The Annex B was proposed to be divided into two groups – General Parameters (COD, NH4, N, P) and Danube Specific Priority Substances (As, Co, Zn, Cr). The MLIM EG and the EMIS EG accepted this amendment to the first version of the Danube List of Priority Pollutants and agreed that this version should be revised after the national surveys on priority substances as well as an update of the industrial discharges inventory would be carried out.

The ICPDR at its 1st Standing Working Group meeting in June 2003 agreed with the proposed Danube List of Priority Substances but considered it only as provisional. To arrive at a final list the national targeted screenings for EU WFD Priority Substances will have to be performed to prove their relevance for the specific area/region.

Therefore, it is recommended to summarize within the MLIM EG time plans for the national screenings for priority substances and based on this data to agree the deadline for reporting on results of these screenings and for preparation of amendment to the Danube List of Priority Substances. The national screenings should be focused on the in-stream quality as well as on the emission sources (the latter part should be carried out under supervision of the EMIS EG).

2. Development of SOPs for newly included determinands

2.1   Introduction

The objective of this activity was to make available SOPs for newly included determinands. It was planned that after reaching an agreement on the final version of the Danube List of Priority Substances the standard operational procedures in form of a brief description of recommended analytical methods would be developed for all relevant substances. This precondition, however, could not be met as the final version of the Danube List was not available in the course of this assignment. Therefore a brief method description refers to the provisional list.

The overview of SOPs takes into account the results of the review on possibilities to analyze the EU WFD priority substances in the Danube countries, which was performed by the MLIM EG in 2002. As stated in the Inception Report an attention was paid also to the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the "Expert Advisory Forum on Priority Substances and Pollution Control".

The term newly included determinands is understood in this report as those substances, which are new to the current analytical practice within the TNMN activities. For this purpose the provisional Danube List of Priority Substances will be discussed in two separate chapters – one dedicated to general parameters and priority substances specific for the Danube River Basin (Annex B of the Danube List) and the second referring to the substances from the Decision No 2455/2001/EC (Annex A of the Danube List).

2.2   Results and assessment of needs

2.2.1   General parameters and priority substances specific for the Danube River Basin

COD, NH_4, N and P are considered as general parameters while As, Co, Zn and Cr has been identified as substances specific for the Danube. They are all included in the TNMN (nitrogen is expressed in terms of organic N and its inorganic forms - NH_4, NO_3, NO_2). For all these parameters appropriate analytical methods were agreed upon for the Phase I of the TNMN as follows:

Determinand	Agreed method
Ammonium (NH_4^+ -N)	**ISO 7150-1:1984** Water quality. Determination of ammonium. Part 1: Manual spectrometric method.
Nitrite (NO_2^- -N)	**ISO 6777:1984** Water quality. Determination of nitrite. Molecular absorption spectrometric method.
Nitrate (NO_3^- -N)	**ISO 7890-3:1988** Water quality. Determination of nitrate. Part 3: Spectrometric method using sulfosalicylic acid.
Organic Nitrogen	Kjeldahl-N, or instrumental Total-N (minus inorganic -N)
Total Nitrogen	**EN ISO 11905-1:1998** "Water quality – Determination of nitrogen – Part 1: Method using oxidative digestion with peroxodisulfate", and, **ISO 11261:1995** Soil quality – Determination of total nitrogen – Modified Kjeldahl method (Total N in the sediment)
Orthophosphate (PO_4^{3-} -P)	**ISO 1189:1996** Water quality. Determination of phosphorus. Ammonium molybdate spectrometric methods.
Total Phosphorus	**ISO 1189:1996** Water quality. Determination of phosphorus. Ammonium molybdate spectrometric methods.
COD_{Cr}	**ISO 6060:1989** Water quality. Determination of chemical oxygen demand. This ISO method was replaced by the DIN low level COD method.
Arsenic (As)	**ISO 11969:1996** Determination of arsenic. Atomic absorption spectrometric method (hydride technique).
Copper (Cu)	Atomic absorption spectrophotometric method
Zinc (Zn)	Atomic absorption spectrophotometric method
Chromium (Cr) – total	**ISO 9174:1990** Water quality. Determination of total chromium. Atomic absorption spectrometric method.

More detailed description of these methods can be found in the Guidance Notes for MLIM that were prepared within the EU Phare project "Strengthening Sustainability of Water Quality Management in the Danube River Basin" in 2000.

2.2.2   Priority substances from the DECISION No. 2455/2001/EC

The recommendations for the standard operational procedures provided in this chapter will primarily reflect current opinions and developments in the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the Expert Advisory Forum on Priority Substances (EAF PS).

In principle the authors of this chapter share the opinion of those AMPS experts stating that it is better not to set a predetermined specific methodology to analyze the priority substances since a flexibility in choosing the appropriate analytical method is necessary. As it was pointed out during AMPS discussions, usually the development of analytical chemistry is faster than the promulgation of a Directive. Thus, it may happen that the proposed methodology is not the best technique for all the laboratories. Therefore, the methods indicated in this paper should be considered as recommended procedures and the use of an alternative technique should not be excluded.

An excellent tabled overview of the current status of availability of SOPs for the analysis of the priority substances from the Decision No. 2455/2001/EC (Table of existing standard methods and proposed quality standards for priority substances in water) was prepared by EU JRC and is available in Annex 1. This overview served as a basis for the methods recommended for the application within the TNMN activities. Additional sources for these recommendations were the remarks done by the CEN TC 230 and the inquiry on availability of standard methods for EU WFD priority substances in the Danube countries done by the ICPDR Secretariat in 2002. Even though the data for this ICPDR

questionnaire came only from Germany, Austria, Czech Republic, Slovakia, Slovenia and Romania, it represents a good overview of the situation in the ICPDR countries.

At this point it must be emphasized that the following overview covers all substances from the Decision No. 2455/2001/EC. However, in future, an attention will be given at the ICPDR level (i.e., adding parameters to the TNMN list) only to those determinands, which will be selected for the final version of the Danube List of Priority Substances after carrying out national screenings. This means that some of the methods discussed below may not be necessary for application at the ICPDR level in the future.

Alachlor

EN ISO 6468 (Determination of certain organochlorine insecticides, polychlorine biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction) is a recommended technique. This method is applicable for drinking, ground, surface and wastewater; detection limit: 1 ng/l to 10 ng/l.

It prevails the ISO 11 370 because of the lower LOD. The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Anthracene

ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass concentrations > 0,01 µg/l. The ICPDR questionnaire indicates that there are applicable methods for anthracene in the Danube countries.

Atrazine

Atrazine belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of atrazine in the Danube countries. Guidance Notes for MLIM recommended the ISO 6468:1996 "Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction" as a method of choice.

However, in line with the AMPS and CEN TC 230, the EN ISO 11369 and the EN ISO 10695 are recommended for the use in the Danube countries in the future. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) is based on high performance liquid chromatography with UV detection after solid-liquid extraction and is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l. EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and wastewater and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimisation of analysis): 0,05 µg/l.

Benzene

ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption) is the preferred method owing to the high sensitivity. This method for drinking, ground, surface, sea and (diluted) wastewater has a detection limit of 10 ng/l and a working range: up to 100 µg/l.

The head-space technique (ISO 11 423), which is also considered by AMPS, does not have sufficiently low LOD to cope with the quality standards.

The ICPDR questionnaire indicates that there are applicable methods for analysis of benzene in several Danube countries, however, some countries still require methodological support.

Brominated diphenylethers

There are 209 theoretical congeners of polybrominated diphenylethers (PBDE), out of which only few are present in technical mixtures. In this respect the analysis of PBDE resembles that of PCBs and requires a widely agreed approach based on the consensus. The agreement on the analysis of groups of substances is probably the major obstacle to be coped with during selection of suitable SOPs for the EU WFD priority substances. According to the ICPDR questionnaire in 2002 only Germany, Slovakia and Austria (expected in 2003) reported availability of SOP for PBDE, the other Danube countries still required methodological support. In this respect PBDE belong to problematic substances for the TNMN as far as their analysis is concerned.

AMPS recommends for analysis of PBDE in sludge and sediment the ISO WD 22032 method employing gas chromatography with mass spectrometric detection.

Recently, a background paper on Indicator Substances and Analytical Methods for the determination of groups of substances was elaborated by Peter LEPOM, Robert LOOS and Alfred RAUCHBÜCHL to support the AMPS activities. This document provides very good review of the present possibilities in analysis of polybrominated diphenylethers, alkylphenols and short-chain chlorinated paraffins and is attached to this report as Annex 2. We recommend to use this background paper at the ICPDR level.

Cadmium and its compounds

Cadmium belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of cadmium in the Danube countries. Guidance Notes for MLIM recommend the ISO 5861 "Water quality. Determination of cadmium by atomic absorption spectrometry" as a method of choice. The same method is recommended by AMPS.

C_{10-13}- Chloroalkanes

C_{10-13}- Chloroalkanes (short-chain chlorinated paraffins, SCCPs) are polychlorinated n-alkanes with chlorine content ranging from 49 to 70% by weight. The theoretical maximum number of positional isomers calculated for $n\text{-}C_nH_{2n+2-z}Cl_z$, assuming no more than one bound chlorine atom on an carbon atom, for SCCPs is 7820. However, the complexity of mixture of C_{10-13}- chloroalkanes is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers are generated. Furthermore, although the source hydrocarbon skeletons are primarily *n*-alkanes, they can contain branched alkanes and also other hydrocarbons, which increase the complexity of mixtures. Hence, it can be expected that commercial mixtures of C_{10-13}- chloroalkanes contain several thousands of compounds. According to the ICPDR questionnaire in 2002 only Czech Republic and Austria (expected in 2004) reported availability of SOP for SCCPs, the other Danube countries still require methodological support. SCCPs are the only substances, for which AMPS reports no standard method available. In this respect SCCPs can probably be considered as the most problematic substances to be included into TNMN from the methodological point of view.

Therefore, similarly to PBDE, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 is recommended as the best reference for considerations on analysis of C_{10-13}- chloroalkanes.

Chlorfenvinphos, Chlorpyrifos

EN 12918 (Water quality – Determination of parathion, parathion-methyl and some other organophosphorus compounds in water by dichlormethane extraction and gas chromatographic analysis) is recommended by AMPS for both pesticides. This method for drinking, surface and waste water has reported LOD of about >0,05 µg/l for drinking water.

According to the ICPDR questionnaire most of the countries do not report any method available. Thus, the analysis of chlorfenvinphos and chlorpyrifos will require methodological support in the ICPDR countries provided these pesticides will be found relevant for the Danube River Basin.

1,2-Dichloroethane, Dichloromethane

ISO 15680 using gas chromatography after purge & trap preconcentration with thermal desorption is the preferred method owing to the high sensitivity. The head-space technique, which is also considered by AMPS does not have sufficiently low LOD to cope with the quality standards. The ICPDR questionnaire indicates that there are applicable methods for analysis of benzene in the Danube countries; however, some may still require methodological support.

Di(2-ethylhexyl)phthalate (DEHP)

According to the ICPDR questionnaire in 2002 only Germany reported availability of a method for analysis of DEHP, Slovakia and Austria expected to have it developed by the end of 2002 and in 2003, respectively.

AMPS recommends an ISO DIS 18856 (Water quality – Determination of selected phthalates by gas chromatography/mass spectrometry), which is suitable for drinking, ground, surface and waste water having an application range between 0,02 µg/l to 0,15 µg/l, depending on the individual substance.

Diuron

EN ISO 11369 (Water quality – Determination of selected plant treatment agents - Method using high performance liquid chromatography with UV detection after solid-liquid extraction) is a recommended method. It is applicable for drinking and ground water for concentrations >0,05 - 0,1 µg/l.

The ICPDR questionnaire indicates that there are applicable methods only in some Danube countries.

Endosulfan (alpha-endosulphan)

EN 6468 (Water quality – Determination of certain organochlorine insecticides, polychlorine biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction) is a recommended technique. It is applicable for drinking, ground, surface and waste water having detection limit of 1 ng/l to 10 ng/l.

The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Fluoranthene

ISO 17993: (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection) is a recommended method. It is suitable for drinking and ground water for mass concentrations > 0,005 µg/l and for surface water for mass concentrations > 0,01 µg/l.

The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Hexachlorobenzene

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods in most of the responding Danube countries. For those reporting no method for HCB but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane) the verification of this procedure for HCB is recommended.

Hexachlorobutadiene

EN ISO 10301 (Water quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods) is a recommended technique. There are two optional procedures available:

a) liquid-liquid extraction; method for drinking, ground, bathing, surface and waste water; typical "quantification" limits between 0,01 µg/l and 50 µg/l, depending on the compound,

b) head-space method; method for drinking, ground and surface, typical "quantification" limits between 0,1 µg/l and 200 µg/l, depending on the compound.

The ICPDR questionnaire indicates that there are applicable methods only in some Danube countries.

Hexachlorocyclohexane (Lindane)

Lindane belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of lindane in the Danube countries. Guidance Notes for MLIM recommend the ISO 6468:1996 "Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction" as a method of choice. This method is also recommended by AMPS.

Isoproturon

The ICPDR questionnaire indicates that there are applicable methods for analysis of isoproturon in Danube countries, however, some countries still require methodological support. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) that is based on high performance liquid chromatography with UV detection after solid-liquid extraction is recommended for the use in the Danube countries. This method is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l.

Lead and its compounds

Lead belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of lead in all reporting countries. Guidance Notes for MLIM recommend atomic absorption spectrometric method as a method of choice. In line with CEN TC 230 and AMPS it is recommended to use EN ISO 11 885 (Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy) that is applicable for raw, drinking and waste water having detection limit between 0,0005 mg/l to 2mg/l, depending on sample and matrix; (for lead: 0,07/0,2 mg/l). In case of absence of an ICP AES unit the laboratories can apply ISO 15 586 (Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace), which is applicable for fresh waters (e.g,. lake and river water, precipitation, ground water, drinking water, waste water) and sediments with detection limit between 0,1 µg/l to 2 µg/l, depending on the element (1 µg/l for lead).

Mercury and its compounds

Mercury belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of mercury in the Danube countries. Guidance Notes for MLIM recommend the ISO 1483 "Water quality – Determination of mercury) as a method of choice. This method is suitable for analysis of ground, waste and surface water having a working range of 0,1 µg/l - 10 µg/l. The same method is recommended by AMPS.

Naphthalene

ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection) is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass

concentrations > 0,01 µg/l. The ICPDR questionnaire indicates that there are applicable methods for naphthalene in the Danube countries.

Nickel and its compounds

Nickel belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of nickel in all reporting countries. Guidance Notes for MLIM recommend atomic absorption spectrometric method as a method of choice. In line with CEN TC 230 and AMPS it is recommended to use EN ISO 11 885 (Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy) that is applicable for raw, drinking and waste water having detection limit between 0,0005 mg/l to 2 mg/l, depending on sample and matrix. In case of absence of an ICP AES unit the laboratories can apply ISO 15 586 (Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace), which is applicable for fresh waters (e.g., lake and river water, precipitation, ground water, drinking water, waste water) and sediments with detection limit between 0,1 µg/l to 2 µg/l, depending on the element (1 µg/l for nickel).

Nonylphenols

Commercially produced nonylphenols contain predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. According to product data sheets of some nonylphenol manufacturers the two most important impurities in commercial 4-nonylphenol are 2-nonylphenol (up to 10 % w) and 2,4-dinonylphenols (up to 1 % w).

According to the ICPDR questionnaire in 2002 only Germany, Czech Republic Slovakia (expected by the end of 2002) and Austria (expected in 2003) reported availability of SOP for nonylphenols, the other Danube countries still require methodological support. AMPS recommends for analysis of nonylphenols ISO 18 857 (Water quality – Determination of selected alkylphenols – Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection). This method is applicable for selected alkylphenols (octyl- and nonylphenols) in non-filtered samples from drinking, ground, and surface water in a concentration range from 0,005 µg/l to 0,2 µg/l.

For considerations on analysis of nonylphenols, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 can serve as an excellent reference.

Octylphenols

The case for octylphenols is analogous to that for nonylphenols. According to the ICPDR questionnaire in 2002 only Germany, Czech Republic, Slovakia (expected by the end of 2002) and Austria (expected in 2003) reported availability of SOP for octylphenols; the other Danube countries still require methodological support. AMPS recommends for analysis of octylphenols ISO 18 857 (Water quality – Determination of selected alkylphenols – Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection). This method is applicable for selected alkylphenols (octyl- and nonylphenols) in non-filtered samples from drinking, ground, and surface water in a concentration range from 0,005 µg/l to 0,2 µg/l.

For considerations on analysis of octylphenols, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 can serve as an excellent reference.

Pentachlorobenzene

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods in most of the responding Danube countries. For those reporting no method for pentachlorobenzene but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane), a verification of this procedure for pentachlorobenzene is recommended.

Pentachlorophenol

EN 12 673 (Water quality – Gas chromatographic determination of some selected chlorophenols in water) is a recommended SOP. It is applicable method for drinking, ground, rain, waste, sea and surface water having a working range of 0,1 µg/l - 1 mg/l. The ICPDR questionnaire indicates that there are appropriate methods in most of the responding Danube countries, methodological support will be necessary in certain national laboratories.

Polyaromatic hydrocarbons

PAHs belong to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of PAHs in the Danube countries. ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass concentrations > 0,01 µg/l.

Simazine

Simazine belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of simazine in the Danube countries.

In line with the AMPS and CEN TC 230 the EN ISO 11369 and the EN ISO 10695 are recommended for the use in the Danube countries. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) is based on high performance liquid chromatography with UV detection after solid-liquid extraction and is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l. EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and waste water and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimization of analysis): 0,05 µg/l.

Tributyltin compounds (Tributyltin cation)

According to the ICPDR questionnaire in 2002 only Germany and Austria reported availability of a method for analysis of DEHP, Slovakia expected to have it developed by the end of 2002.

AMPS recommends an ISO DIS 17 353 (Water quality – Determination of selected organotin compounds – Gas-chromatographic method). This method is suitable for drinking, surface and wastewater with a maximum of 2 g/l of suspended material; Method working range is between 10 ng/l to 1000 ng/l, depending on the individual substance.

Trichlorobenzenes (1,2,3-TCB; 1,2,4-TCB; 1,3,5-TCB)

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods for trichlorobenzenes only in Germany, Czech Republic and Slovakia; Austria should have a method available in 2003. For those reporting no method for trichlorobenzenes but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane) the verification of this procedure for trichlorobenzenes is recommended.

An optional SOP is ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption). This method is applicable for drinking, ground, surface, sea and (diluted) waste water having detection limit of 10 ng/l and working range up to 100 μg/l.

Trichloromethane

Trichloromethane belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of trichloromethane in most of the Danube countries, however, some countries report no method available (possibly caused by missing equipment). This also causes a data gap in the TNMN database.

Guidance Notes for MLIM recommend for the analysis of chloroform EN ISO 10301 (Water quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods). There are two optional procedures available:

liquid-liquid extraction; method for drinking, ground, bathing, surface and wastewater; typical "quantification" limits between 0,01 µg/l and 50 µg/l, depending on the compound.

head-space method; method for drinking, ground and surface, typical "quantification" limits between 0,1 µg/l and 200 µg/l, depending on the compound.

EN ISO 10301 is also one of the methods recommended by AMPS, the other option is ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption). This method is applicable for drinking, ground, surface, sea and (diluted) waste water having detection limit of 10 ng/l and working range up to 100 µg/l. In case of chloroform there is no apparent prevalence of the purge & trap method over the head-space procedure regarding the LODs. Presence of three chlorine atoms enables sensitive detection by the ECD detector even in the case of the low-recovery head-space.

Trifluralin

EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and waste water and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimization of analysis): 0,05 µg/l.

The ICPDR questionnaire indicates that there are applicable methods for analysis of Trifluralin in several Danube countries, however, some countries still require methodological support.

2.3   Conclusions

To summarize visually all the above-mentioned methodological recommendations for the Danube-specific substances as well as for the EU WFD priority substances, a summary table, derived from the original AMPS table, was drafted and is presented in Annex 3. It must be stressed that this table reflects the current situation (i.e., the provisional Danube List of Priority Substances). In future, methodological demands will be influenced by final changes of the Danube List.

Annexes

Annex 1
Table of existing standard methods and proposed QS for PS in water (as of 14 January 2003)

Priority Substance	Available standard method (Ref.)			Specific ring trial data for surface water			Method-Applicability	Proposals for Quality standards for PS of the WFD			76/464/EEC
	Standard	Year	Principle	Lowest conc. [3]	S$_R$ [3]	Application range [2]	Applicability in routine labs - (yes/no) or remarks	AA-QS[7] for inland (In) & transitional (Tr) waters	AA-QS[7] for coastal (Co) & territorial (Te) waters	MAC -QS[7]	Quality objective
Alachlor	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (2), yes (2)	0.035 µg/l	n.a.	1.15 µg/l	
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Anthracene	ISO 17993: 2002 or see PAH´s						yes (2)	0.063 µg/l	0.0063 µg/l	0.01 µg/l	
	US EPA 8100		GC/FID				yes (1)				
Atrazine	EN ISO 11369	Nov-97	HPLC/UV				no (1), yes (1)	0.34 µg/l	0.34 µg/l	2 µg/l	
	EN ISO 10695: 2000	Nov-00	GC/NPD (MS for conf.)				no (1), yes (2)				
	ISO 11370 2000	Jan-95	TLC, AMD-Technique	0,13 µg/l	38%	³ 0.13 µg/l	no (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Benzene	DIN 38407-9	May-91	Headspace-GC/FID	ca. 5,9 µg/l	16-29%	³ 5,9 µg/l	no (1), yes (1)	16 µg/l*	1.6 µg/l*	49 µg/l	
	Draft ISO 15680	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	15%	³ 0.2 µg/l	no (1), yes (1)				
	ISO 11423-1	Sep-97	Headspace-GC/FID	6 µg/L	16%	³ 6 µg/l	yes (1)				
Brominated diphenylethers	ISO WD 22032	Mar-02	GC/MS				no (3), yes (1)				
Bis(pentabromophenyl)ether	*ISO WD 22032*	Mar-02	GC/MS				--	n.a.	n.a.	not required	
Diphenyl ether, octabromo derivate	*ISO WD 22032*	Mar-02	GC/MS				--	33.8 µg/l (1217 µg/kg seafood, 1513 mg/kg SPM)	not required		
Diphenyl ether, pentabromo derivate	*ISO WD 22032*	Mar-02	GC/MS				--	0.0005 µg/l	0.00018 µg/l	1.4 µg/l	
Cadmium and its compounds	EN ISO 5961	May-95	ET-AAS				yes (4)	0.08 µg/l	n.a.		5 µg/l (2.5-0.5 µg/l)
	DIN 38406-16	Mar-90	Voltametry	0,81 µg/l	29%	³ 0,81 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	5,75 µg/l	8.5%	³ 5,75 µg/l	yes (1)				
	EN ISO 11885	Apr-98	ICP-AES				yes (1)				
	ISO DIS 15586 ⁵	May 01	ET-AAS				--				
C10-13-chloroalkanes	**no Standard available**	--	--				no (3)	0.41 µg/l	0.1 µg/l	1.4 µg/l	

| Priority Substance | Available standard method (Ref.) | | | Specific ring trial data for surface water | | | Method-Applicability | Proposals for Quality standards for PS of the WFD | | | 76/464/EEC |
	Standard	Year	Principle	Lowest conc. [3]	S_R [3]	Application range [2]	Applicability in routine labs - (yes/no) or remarks	AA-QS[7] for inland (In) & transitional (Tr) waters	AA-QS[7] for coastal (Co) & territorial (Te) waters	MAC-QS[7]	Quality objective
Chlorfenvinphos	DIN EN 12918	Nov-99	GC	0,081 µg/l	13%	[3] 0,081 µg/l	no (3), yes (1)	0.01 µg/l	0.01 µg/l	0.01 µg/l	
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				
Chlorpyrifos *(-ethyl, -methyl)*	DIN EN 12918	Nov-99	GC				no (3), yes (1)	0.00046 µg/l	0.00046 µg/l	0.001 µg/l	
1,2-Dichloroethane	EN ISO 10301	Aug-97	GC or Headspace-GC				yes (4)	1060 µg/l*	1060 µg/l*	1080 µg/l	**10 µg/l**
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	[3] 0.2 µg/l	--				
Dichloromethane	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				no (1), yes (3)	8.2 µg/l	8.2 µg/l	162 µg/l	
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	[3] 0.2 µg/l	--				
Di(2-ethylhexyl)phthalate (DEHP)	ISO DIS 18856	Mar-02	GC/MS				no (2), yes (2)	0.33 µg/l	0.17 µg/l	not required	
Diuron	EN ISO 11369	Nov-97	HPLC/UV				no (2), yes (2)	0.046 µg/l	0.046 µg/l	1.1 µg/l	
Endosulfan	EN ISO 6468	Feb-97	GC/ECD	0.194 µg/l	68% (10% recovery!)	[3] 0.194 µg/l	no (2), yes (1)	0.004 µg/l	0.004 µg/l	0.004 µg/l	
	US EPA 8081		GC/ECD				yes (1)				
Fluoranthene	ISO 17993: 2002 or see PAH´s						no (1), yes (1)	0.12 µg/l	0.12 µg/l	0.9 µg/l	
	US EPA 8270		GC/MS				yes (1)				
Hexachlorobenzene	EN ISO 6468	Feb-97	GC/ECD	0.058 µg/l	34%	[3] 0.058 µg/l	yes (3)	0.008 µg/l*	0.008 µg/l*	0.05 µg/l	0.03 µg/l
	US EPA 8081		GC/ECD				yes (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Hexachlorobutadiene	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				no (2), yes (2)	= 0.003 µg/l	= 0.003 µg/l	0.59 µg/l	0.1 µg/l
Hexachlorocyclohexane	EN ISO 6468	Feb-97	GC/ECD	0.039 µg/l	38%	[3] 0.039 µg/l	yes (4)	0.042 µg/l	0.01 µg/l	0.9 µg/l	
gamma-HCH (Lindane)	*EN ISO 6468*	Feb-97	GC/ECD	0.039 µg/l	38%	[3] 0.039 µg/l	--	0.02 µg/l	0.002 µg/l	0.03 µg/l	
Isoproturon	EN ISO 11369	Nov-97	HPLC/UV				no (2), yes (2)	0.32 µg/l	0.32 µg/l	1.3 µg/l	
Lead and its compounds	DIN 38406-6	Jul-98	ET-AAS	29,5 µg/l	11-16%	[3] 29,5 µg/l	yes (3)	1 µg/l	1 µg/l	2 µg/l	
	ISO 8288		flame AAS				yes (1)				
	US EPA 7421		ET-AAS				yes (1)				
	DIN 38406-16	Mar-90	Voltametry	2,9 µg/l	53%	[3] 2,9 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	13,6 µg/l	8.3%	[3] 13,6 µg/l	yes (2)				

Priority Substance	Available standard method (Ref.)			Specific ring trial data for surface water			Method-Applicability	Proposals for Quality standards for PS of the WFD			76/464/EEC
	Standard	Year	Principle	Lowest conc. [3]	S_R [3]	Application range [2]	Applicability in routine labs - (yes/no) or remarks	AA-QS[7] for inland (In) & transitional (Tr) waters	AA-QS[7] for coastal (Co) & territorial (Te) waters	MAC-QS[7]	Quality objective
	EN ISO 11885	Apr-98	ICP-AES				yes (2)				
	ISO DIS 15586 [5]	May 01	ET-AAS				--				
Mercury and its compounds	EN 1483	Aug-97	Cold Vapour-AAS	1,474 µg/l	27%	[3] 1,474 µg/l	no (1), yes (3)	0.036 µg/l*	0.036 µg/l*	0.07 µg/l	1 µg/l (0.3 µg/l)
	EN 12338	Oct-98	CV-AAS with Amalgamation	0,283 µg/l	19%	[3] 0,283 µg/l	yes (2)				
	EN 13506	Nov-01	Atomic fluor. spectrometry	0,05 µg/l	11.6% (25.9% ?)	[3] 0,05 µg/l [4]	--				
Naphthalene	ISO 17993: 2002 or see PAH´s						yes (2)	2.4 µg/l	1.2 µg/l	80 µg/l	
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	32%	[3] 0.2 µg/l	--				
	US EPA 8270		GC/MS				yes (1)				
Nickel and its compounds	DIN 38406-11	Sep-91	ET-AAS				yes (3)	0.6 µg/l	0.6 µg/l	1.3 µg/l	
	ISO 8288		flame AAS				yes (1)				
	US EPA 7521		ET-AAS				yes (1)				
	DIN 38406-16	Mar-90	Voltametry	3.2 µg/l	30%	[3] 3,2 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	5,44 µg/l	14.5%	[3] 5,44 µg/l	yes (2)				
	EN ISO 11885	Apr-98	ICP-AES				yes (2)				
	ISO DIS 15586 [5]	May 01	ET-AAS				--				
Nonylphenols	ISO CD 18857-1	Jul-01	GC/MS	0,023 µg/l	57.20%	[3] 0,023 µg/l	no (1), yes (2)	0.33 µg/l	0.033 µg/l	2.1 µg/l	
	Sweedish EPA Raport 3829-1990		GC/ECD				yes (1)				
Octylphenols	ISO CD 18857-1	Jul-01	GC/MS	0,019 µg/l	25.10%	[3] 0,019 µg/l	no (3), yes (1)	0.1 µg/l	0.01 µg/l	0.133 µg/l	
Pentachlorobenzene	EN ISO 6468	Feb-97	GC/ECD				yes (3)	< 0.05 µg/l	< 0.05 µg/l	1 µg/l	
	US EPA 8081		GC/ECD				yes (1)				
Pentachlorophenol	EN 12673	May-99	GC/ECD/MS after Deriv.	0,25 µg/l	37%	[3] 0,25 µg/l	yes (4)	0.1 µg/l	0.1 µg/l	1 µg/l	2 µg/l
	ISO 8165-2	Jul-99	GC/ECD after Deriv.				no (1), yes (1)				
Polyaromatic Hydrocarbons (PAH´s)	ISO 17993: 2002		HPLC/Fluo				yes (1)				
	US EPA 8270		GC/MS				yes (3)				
	DIN 38414-23	Feb-02	HPLC/Fluo				no (1), yes (1)				

| Priority Substance | Available standard method (Ref.) | | | Specific ring trial data for surface water | | | Method-Applicability | Proposals for Quality standards for PS of the WFD | | | 76/464/EEC |
	Standard	Year	Principle	Lowest conc. [3]	S$_R$ [3]	Application range [2]	Applicability in routine labs - (yes/no) or remarks	AA-QS[7] for inland (In) & transitional (Tr) waters	AA-QS[7] for coastal (Co) & territorial (Te) waters	MAC-QS[7]	Quality objective
	XP X33-012	Mar-00	HPLC/UV or GC/MS				--				
Benzo(a)pyrene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	0.05 µg/l*	0.005 µg/l*	0.05 µg/l	
Benzo(b)fluoroanthene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Benzo(g,h,i)perylene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Benzo(k)fluoroanthene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	0.0054 µg/l*	0.00054 µg/l*	n.a.	
Indeno(1,2,3-cd)-pyrene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Simazine	EN ISO 11369	Nov-97	HPLC/UV				no (1), yes (1)	< 1 µg/l (In)	1.1 µg/l (Tr, Co, Te)	4.2 µg/l	
	EN ISO 10695: 2000	Nov-00	GC/MS or GC/NPD				no (1), yes (1)				
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Tributyltin compounds	ISO/DIS 17353		GC/MS - FPD - AES	0.39 µg/l	24%	[3] 0.39 µg/l	no (1), yes (3)	0.0001 µg/l	0.0001 µg/l	0.0015 µg/l	
	WD DIN 38414-XX	??					no (1), yes (1)				
	NF T 90-250	Jul-01	GC				--				
	ISO/AWI 23161	Apr-02	GC/MS				--				
Trichlorobenzenes	EN ISO 6468	Feb-97	GC/ECD	0.182 µg/l	35%	[3] 0.182 µg/l	no (1), yes (3)	1.8 µg/l	0.4 µg/l	50 µg/l	**0.4 µg/l**
	US EPA 8081		GC/ECD				yes (1)				
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	[3] 0.2 µg/l	--				
Trichloromethane	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				yes (4)	3.85 µg/l	3.85 µg/l	38.5 µg/l	12 µg/l
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	[3] 0.2 µg/l	--				
Trifluralin	EN ISO 10695: 2000	Nov-00	GC/MS or GC/ECD or GC/NPD				no (2), yes (2)	0.03 µg/l	0.03 µg/l	0.42 µg/l	
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				

Priority Substance	Available standard method (Ref.)			Specific ring trial data for surface water			Method-Applicability	Proposals for Quality standards for PS of the WFD			76/464/EEC
	Standard	Year	Principle	Lowest conc. [3]	S_R [3]	Application range [2]	Applicability in routine labs - (yes/no) or remarks	AA-QS [7] for inland (In) & transitional (Tr) waters	AA-QS [7] for coastal (Co) & territorial (Te) waters	MAC-QS [7]	Quality objective
DDT	*EN ISO 6468*		GC/ECD	0.015 µg/l	37%	[3] 0.015 µg/l	--	n.a. (proposal at a later date)			10 µg/l (25 µg/l total)
Aldrin	*EN ISO 6468*		GC/ECD				--	n.a. (proposal at a later date)			**10 µg/l**
Endrin	*EN ISO 6468*		GC/ECD	0.051 µg/l	22%	[3] 0.051 µg/l	--	n.a. (proposal at a later date)			**5 µg/l**
Isodrin	--	--					--	n.a. (proposal at a later date)			**5 µg/l**
Dieldrin	*EN ISO 6468*		GC/ECD	0.031 µg/l	52%	[3] 0.031 µg/l	--	n.a. (proposal at a later date)			**10 µg/l**
Tetrachloroethene	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	10 µg/l	5.1 µg/l	36 µg/l	10 µg/l
Tetrachloromethane	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	7.2 µg/l	7.2 µg/l	24.6 µg/l	12 µg/l
Trichloroethene	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	10 µg/l	10 µg/l	210 µg/l	10 µg/l

EN = European Standard
ISO = International Standard
DIN = German Standard
DIN V = German Pre-standard
WD = Working Draft

Format code :
black = conc. ≤ AA-QS
red (normal) = conc. ≤ AA-QS for In & Tr
but > AA-QS for Co & Te
red bold = conc. > both AA-QS

[1] The proposed application range derives from chapter "Scope of the method"
[2] The application range for surface water corresponds to the lowest concentrations for which tests of precision and bias have been carried out, according to the definition in ISO/TR 13530, 1997-09
[3] Concentrations of the analyte(s) in the intercomparison samples used for the determination of repeatability and reproducibility; S_R = relative reproducibility standard deviation
[4] Performance data according to ISO 5725
[5] Standard is part of CEN working programm (2001-11)
[6] ≥ 0,01 µg/l for surface water, ≥ 0,005 µg/l for drinking water
[7] Two kinds of quality standards are proposed, referring to (1) annual average concentration **AA-QS** and (2) short term concentration peaks, maximum admissible concentration **MAC-QS**

Format code:
Priority Substance normal format = WFD priority substance
Priority Substance italic format = 76/464/EEC priority substance or quality standard proposed
Priority substance in black = at least one method with application range $\leq$ AA-QS or 76/464/EEC quality objective
Priority Substance red (normal) = available methods with application range $\leq$ AA-QS for In & Tr but > AA-QS for Co & Te
Priority Substance red & bold = no standard method available at all or no available method with application range £ AA-QS for In & Tr nor for Co & Te

 values in red are lower than propsed QS
- "specific QS"

[D] = Drinking water
[G] = Ground water
[S] = Surface water
[W] = Waste water
[Std.] = standard solution
[Dist.] = distilled water

Annex 2

Water Framework Directive / Priority Substances

Analytical determination of groups of substances
New analytical methods

- Proposal for Indicator Substances and Analytical Methods –

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Introduction and problem identification

Article 16 of the Water Framework Directive (2000/60/EC) sets out the Community strategy against pollution of water by dangerous substances. According to the provisions of this article, a list of priority substances was established which represent a significant risk to or via the aquatic environment at Community level. Following the proposals of the European Commission in February 2000 and January 2001 and the first Parliament's reading, Council and European Parliament agreed to a list of 33 substances on 7 June 2001. The list of priority substances was finally published in December 2001 (Decision No 2455/2001/EC).

Four priority substances, namely polybrominated diphenyl ethers (PBDEs), C_{10}-C_{13}-chloroalkanes (short-chain chlorinated paraffins, SCCPs), nonylphenols and octylphenols (the last two summarized as alkylphenols in this paper) comprise groups of chemicals consisting of a few to several thousands of positional isomers. For the time being, only an ISO committee draft for the determination of alkylphenols in surface water (ISO/CD18857-1) and a first working draft for the determination of polybrominated diphenyl ethers in sludge and sediments (ISO/WD 22032) are available. For SCCPs, there is neither an agreed analytical reference method nor does a well-defined set of „indicator substances" exist as for other pollutants e.g. PAH or PCB. For this reason, monitoring data, which are available for SCCPs often, relate to different quantification methods and calibration substances (e.g. different technical mixtures). This makes the comparison and assessment of published data difficult if not impossible.

Comparability of analytical data clearly is a prerequisite for the assessment of monitoring results as well as for the establishment of harmonised environmental quality standards at Community level. Therefore, it is suggested, that the expert advisory forum EAF may attempt to make strong efforts to identify indicator substances for each of the three groups to be analysed obligatory or to define reference methods for the determination of the total content of the priority chemicals as sum parameter.

At present, a variety of different high-sophisticated analytical methods for the determination of the three groups of substances are available on research level often lacking proper validation by interlaboratory studies. At the moment, it seems to be difficult to recommend one or the other of the published analytical procedures. The identification of single reference methods would probably exclude a number of methods with similar performance characteristics and therefore, not be approved on Community level. Hence, it is proposed to favour the identification of indicator substances which shall be analysed obligatory associated with proper calibration standards and the definition of minimum performance criteria for analytical methods rather than to focus on single reference methods for each of the three priority chemicals.

In order to inspire the discussion at European level, this paper sets out in the annex a number of concrete proposals based on background information, found in the literature as well as on recent experience in the analysis of the priority substances under discussion gained during pilot studies which have been carried out by the German and Austrian Federal Environmental Agencies, respectively. It is organised as follows.

„Information on composition and production volume of technical mixtures "
„Indicator substances"
„Standard material"
„Analytical method"

Under section „Information on composition and production volume of technical mixtures" some information is provided regarding the individual compounds of each group of substances under discussion contained in technical products. On the basis of data on toxicity, production volumes and occurrence in environmental samples, most important representatives for each group of substances are identified.

In section „Indicator substances" a concrete proposal for individual substances to be analysed is provided.

Section „Standard material" contains some details regarding the availability of analytical standards for identification and quantification purposes with emphasis on the compounds proposed for analysis in the previous section as well as information on certified reference materials (CRMs) as far as available.

In section „Analytical method" the literature on analytical methods is summarised, advantages and limitations of the different procedures will be discussed and proposals for analysis and quantification of the three priority chemicals will be given.

Finally, in section "Need for Action" problems are identified which need further consideration and/or research work to end up with analytical procedures which are capable to provide accurate and comparable results.

Short-chain chlorinated paraffins (C_{10}-C_{13})

Information on composition of technical mixtures and production volume

Short-chain chlorinated paraffins (SCCPs) are polychlorinated n-alkanes (C_{10}-C_{13}) with chlorine content ranging from 49 to 70% by weight. They are used mainly in metal working fluids for a variety of engineering and metal working operations such as drilling, machining/cutting, drawing and stamping. SCCPs are also used in sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings [1]. Production figures for SCCPs are hard to find in the literature. Based on EURO-Chlor information, the total EU production volume was 15,000 t/year or less in 1994 and about 4,000 t/year in 1998 [2]. It is thought that the current level is probably lower than this, particularly due to reduction in uses of SCCPs, especially in the metalworking industry. SCCPs are manufactured by chlorination of liquid n-paraffin. In Western Europe, major producers are INEOS CHLOR and CAFFARO.

Risk assessment for short chain chlorinated paraffins has been completed under Regulation 793/1993/EEC [1]. SCCPs are classified as dangerous to the environment, being very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. The Commission has adopted a recommendation to take measures to restrict the use of SCCPs, in particular in metal working fluids and leather finishing products in order to protect the aquatic environment [3].

Indicator substances

It seems not possible to identify indicator compounds for routine quantitative analysis of SCCPs.

Standard material

Until recently technical mixtures with known chlorine content have been used for calibration purposes. An international interlaboratory study [4] indicated that some of the observed variability in the analytical results may be introduced when different commercial formulations are used as external standards. These results were confirmed by [5] who investigated the influence of carbon chain length and chlorine content of the external standard used for quantification on the analytical results. In this study, SCCP concentrations of fish samples were quantified using several individual polychlorinated alkane standards and a commercial formulation. Results varied widely (by a factor of ten) depending on chlorine content of the standard used. These findings emphasise the importance of the choice of suitable standards for quantitative analysis. The authors showed that technical SCCP mixtures should not be used as standards in many cases because the SCCP carbon chain pattern in various fish species varied considerably and did not resemble that of the technical formulation.

Recently, numerous synthetic individual SCCPs of particular carbon chain length and different degree of chlorination have become available from Dr. Ehrenstorfer GmbH, Augsburg, Germany. These are:

Chloroparaffin C10, chlorine content 44.82%, 50.18%, 55.00%, 60.09% and 65.02%, respectively.

Chloroparaffin C11, chlorine content 45.50%, 50.21%,55.20%,60.53% and 65.25%, respectively.

Chloroparaffin C12, chlorine content 45.32%, 50.18%, 55.00%, 65.08% and 69.98%, respectively

Chloroparaffin C13, chlorine content 44.90%, 50.23%, 55.03%, 59.98% and 65.18%, respectively.

A final recommendation what standard to be used for quantification of SCCPs in environmental samples can not be given at the moment.

Analytical method

Extraction and clean-up techniques for the analysis of SCCPs in biological samples and sediments are quite similar to those developed for the analysis of other halogenated compounds such as PCBs and chlorinated pesticides. Most procedures are based on batch or Soxhlet extraction with organic solvents, clean-up of the extracts by adsorption and gel permeation chromatography and determination by gas chromatography electron capture [6] or mass spectrometric detection [7-11]. Another approach is carbon skeleton analysis by gas chromatography with flame ionisation detection after simultaneous dechlorination and hydrogenation [12,13]

An accurate chemical analysis of SCCPs in environmental samples is difficult to achieve due to the highly complex nature of commercial formulations, the impact of numerous physical, chemical and biological processes after use, and the lack of certified chemical standards. SCCPs are very complex mixtures containing many congener groups chlorinated to various degrees and positions on the carbon backbone. The theoretical maximum number of positional isomers calculated for $n\text{-}C_nH_{2n+2-z}Cl_z$, assuming no more than one bound chlorine atom on an carbon atom, for SCCPs is 7820 [14]. However, the complexity of SCCP mixture is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers will be generated. Furthermore, although the hydrocarbon feedstocks used to prepare SCCPs are primarily *n*-alkanes, they do contain branched alkanes and probably other hydrocarbons which would also add to the complexity of the mixtures. Even if only a small percentage of the theoretically possible number of chloroalkanes are readily formed, it can be assumed that commercial SCCP formulations contain many thousand compounds.

There are three different approaches to analyse SCCPs in environmental samples, these are:

Carbon skeleton analysis after simultaneous catalytic dechlorination and hydrogenation by gas chromatography [12,13], gas chromatography with electron capture detection [6] and gas chromatography-mass spectrometry in the negative chemical ionisation mode [see e.g. 7-11].

Due to the lack in sensitivity and selectivity – no information on the degree of chlorination of the SCCPs can be achieved - the first approach will not be considered further. GC-ECD analysis of SCCPs is quite unspecific. Since the compounds of interest elute over a wide retention time range, an unequivocal identification is not possible due to interferences from other halogenated compounds, even when applying lengthy and expansive clean-up procedures and using several stationary phases of different polarity.

Therefore, electron capture negative ionisation mass spectrometry (ECNI-MS) at low or high resolution is generally favoured.

To obtain reliable results, the variability of the mass spectra of SCCPs in dependence on degree of chlorination and ion source temperature and to a lesser extent on chain length of the carbon skeleton has to be taken into consideration [15, 16]. At 250°C, mass spectra of higher chlorinated SCCPs are characterised by a peak cluster representing the [M-Cl]$^-$ fragment ion for all chlorination degrees with an relative intensity ranging from some 50 to 65%. The relative intensities of the [M]$^-$, [M-HCl]$^-$, [M-2HCl]$^-$ and [M-HCl$_2$]$^-$, are around or below 10%. At low ion source temperature (100°C), [M-Cl]$^-$ and [M-HCl]$^-$are most prominent ion clusters with higher intensity of the latter for lower chlorinated SCCPs. Fragmentation is shifted to [M-Cl]$^-$ with increasing degree of chlorination. The relative response factors of SCCP mixtures vary by one order of magnitude depending on the degree of chlorination with lowest response factors for the low chlorinated mixtures (chlorine content 45 to 50%). Compared to the influence of chlorination degree on the fragmentation, that of carbon skeleton chain length is less important [15].

[M+Cl]$^-$ as well as [M-Cl]$^-$ ions were reported in the ECNI mass spectra of synthesised lower chlorinated SCCPs [16]. Their abundances decreased with increasing ion source temperature, while the abundances of the structurally non-characteristic ions, [Cl$_2$]$^-$ and [HCl$_2$]$^-$, increased.

Jansson et al. [7, 8] analysed environmental samples using GC-ECNI-MS in the selected ion monitoring mode after selective clean-up. Structurally non-characteristic [Cl$_2$]$^-$ and [HCl$_2$]$^-$ ions at m/z = 70 to 73 that predominate in the mass spectra of SCCPs at high ion source temperatures were recorded. A similar approach was used by Nicholls et al. [11]. They analysed SCCPs and MCCPs in water, sediment, sewage sludge and biota samples from selected industrial areas in England and Wales. SCCPs were determined in sample extracts using GC-ion trap mass spectrometry operated in the negative chemical ionisation mode.

Three technical products were chosen for reference calibration purposes. The analysis and quantification of formulations identified in sample extracts was undertaken by a two-step GC-MS process:

1. qualitative identification of formulation type
2. quantitative analysis based on the response characteristics summed across the mass region m/z = 70 to 75 corresponding to [Cl$_2$]$^-$ (70, 72, 74) and [HCl$_2$]$^-$ (71,73,75) for most appropriate calibration standard

Average recoveries of SCCPs from spiked sediments (1-2 mg/kg, n=8) were 84%. The limit of determination was equivalent to a SCCP formulation containing 1 ng/µl in solution. Within batch repeatability for the GC-MS measurement using the internal standard method was in the range 6-10% RSD (n=10) for SCCP.

Procedures based on monitoring structurally non-characteristic fragment ions corresponding to [Cl$_2$]$^-$ and [HCl$_2$]$^-$ present the problem that many other halogenated compounds fragment to yield such ions, e.g. p,p'-DDT, p,p'-DDE, lindane, dieldrin, aldrin and endrin. Thus, if these contaminants are not completely removed from the sample matrix during extraction and clean-up, they ultimately contribute to the response of the quantification ions [Cl$_2$]$^-$ (m/z = 70, 72, 74) and [HCl$_2$]$^-$ (m/z = 71, 73, 75) and lead to an overestimation of SCCPs.

Recently, Tomy et al. [9] published a method for quantifying SCCPs in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry in the selected ion monitoring mode at an ion source temperature of 120°C. The molecular compositions of commercial SCCPs and of SCCP-containing extracts were determined by monitoring the two most intensive ions in the [M-Cl]$^-$ cluster, one for quantification and the other for confirmation for the following formula groups: C$_{10}$ (Cl$_5$ to Cl$_{10}$), C$_{11}$ (Cl$_5$ to Cl$_{10}$), C$_{12}$ (Cl$_6$ to Cl$_{10}$), and C$_{13}$ (Cl$_7$ to Cl$_9$), and assuming that integrated signals are proportional to molar concentrations weighted by the number of chlorine atoms in the formula group. Quantification was achieved by selecting the biggest peak corresponding to [M-Cl]$^-$ ion in the most abundant formula group present in the sample and

correcting for variations in the formula group abundances between standard and sample. It has been shown that high-resolution mass spectrometry eliminates self-interferences between SCCPs and potential interferences from chlordanes, toxaphenes, PCBs and other organochlorine pesticides. Recoveries of SCCPs from fish averaged >80%. The analytical detection limit was 60 pg of injected SCCP at a signal-to-noise ratio of 4:1, while method detection limit was 23 ng/g.

Although the proposed method seems to be a suitable approach to analyse SCCPs in environmental samples on the research level, its application for routine analysis is questionable due to the use of a high-resolution mass spectrometer for detection that is not available in most environmental laboratories responsible for routine monitoring, its complexity and the observed variability in results as shown in a recent interlaboratory study [4].

Coelhan [10] proposed a short-column GC-ECNI-MS method for the determination of SCCPs in fish samples that dispenses with chromatographic separation. Only a short capillary column of 62 cm length (thereof 42 cm in the interface) is coupled to a low resolution mass spectrometer operated in the negative ionisation mode at an ion source temperature of 100°C using methane as reagent gas. SCCPs in fish samples were identified by comparison of mass spectra of sample extracts with those of synthesised polychlorinated alkanes and of CERECLOR 63L. The quantification was performed by reintegration of selected ions from full-scan spectra. Without chromatographic separation, all SCCPs elute from the column as only one peak. Consequently, this leads to an enormous increase in sensitivity and makes it more easy to survey the mass spectra. If the SIM mode is used, an additional enhancement in sensitivity is possible. Detection limits in the full-scan mode ranged from 10 to 100 pg depending on carbon chain length of the n-alkane and on the degree of chlorination. Recoveries of SCCPs from spiked herring oil averaged to 112% for the low spiking level (200 ng/g) and to 102% for the high dose (800 ng/g). Since no chromatographic separation has to be achieved, time of analysis is only one minute. Due to dispensing with chromatographic separation complete removal of all other halogenated compounds, which might interfere with the determination of SCCPs is a fundamental requirement.

Methods that monitor ions at nominal mass present the primary problem that interferences from higher chlorinated PCBs, toxaphenes and chlordane-related compounds, all of which elute in the retention time range of SCCPs and have similar molecular masses to SCCPs, can not be excluded of a certainty.

Although some work has been conducted on development of selective and sensitive methods for SCCP analysis in recent years no validated procedure is available at present that meets the specific requirements of WFD and which could be recommended for routine monitoring of SCCPs in environmental samples. Taking into account all information available GC-ECNI-MS seems to be the most appropriate technique for quantitative analysis of SCCPs at the required low concentration levels.

Need for Action

Preparation of certified reference materials (standard solutions, sediment and biota samples)

Methods for the analysis of SCCPs require the use of surrogate standards (usually ^{13}C-labelled) and certified or standard reference materials (CRMs or SRMs). For the time being, there are neither standard reference materials for calibration purposes nor isotopically labelled reference standards, and no reference materials have yet been certified for SCCP content. However, SCCPs were found in two SRMs from the National Institute for Standards and Technology (NIST). SRM 1588, a cod liver oil extract and SRM 1945 a whale blubber extract contained 49 and 172 ng/g of ΣSCCPs, respectively [14]. These SRMs are, therefore, possible candidates for future certification.

Development of analytical methodologies for the determination of SCCPs in environmental samples

As outlined in section "Analytical method" there is no validated analytical procedure available for routine monitoring of SCCPs in environmental samples. Method development should focus on appropriate calibration protocols, improvement in clean-up methods and optimisation of mass spectrometric detection preferably using electron capture negative ionisation low resolution mass spectrometry. Furthermore, in- house validation studies comparing the most promising approaches GC-ECNI-LRMS, GC-ECNI-HRMS and short-column GC-ECNI-LRMS are highly recommended.

Development of an European standard for the determination of SCCPs in sediments

The responsible ISO/TC 147 "Water quality" has not started any standardisation work on this issue yet, mainly due to the lack of validated analytical protocols from research laboratories which might be used as basis for standardisation work.

Establishment of Laboratory Performance Studies on the determination of SCCPs in sediments and biota in the near future.

Polybrominated Diphenyl Ethers

<u>Information on composition of technical mixtures and production volume</u>

There are 209 theoretical congeners of which only a few are present in technical formulations. The individual congeners are numbered according to the IUPAC system used for the numbering of PCBs based on the position of the halogen atoms on the rings. The major technical products are Penta-, Octa- and DecaBDE. The consumption of PBDEs for 1999 within the European Community was estimated to be 210, 450 and 7,500 tons, respectively [17]. Each product is a mixture of diphenyl ethers of varying degree of bromination. Although there is no guarantee that the composition of products from different manufacturers is the same, the proportion of the main components seems to be of the same order. According to information of BSEF the technical Penta-mix consists of 33.7 % tetraBDE, 54.6% pentaBDE and 11.7% hexaBDE whilst the Octa-Mix contains 35.5% hexaBDE, 42% heptaBDE, 36% octaBDE 13.9% nonaBDE and 2.1% decaBDE. Technical DecaBDE contains 3% nonaBDE and 97% decaBDE. For a typical commercial PentaBDE (Bromkal 70-5DE) Sjödin et al. [18] reported the following main constituents: 35% BDE-47, 37% BDE-99, 6.8% BDE-100, 3.9% BDE-153, 2,5% BDE-154, and 1.6% BDE-85. From this follows that five congeners contribute more than 80% to the technical mixture and should be considered when analysing for PentaBDE classified as priority hazardous chemicals. The main PBDEs reported in environmental samples are 2,2',4,4'-TetraBDE (BDE-47), 2,2',4,4',5-PentaBDE (BDE-99), 2,2',4,4',6-PentaBDE (BDE-100), 2,2',4,4',5,5'-HexaBDE (BDE-153), 2,2',4,4',5,6'-HexaBDE (BDE-154) and 2,2',3,3',4,4',5,5',6,6'-DecaBDE (BDE 209) [18]. 2,2',3,4,4',5',6-HeptaBDE (BDE183) may also be of importance as this is one of the main constituents of the technical OctaBDE formulation, but up to now only a limited number of data are available for this congener. A small number of other BDE congeners have been found in environmental samples occasionally including BDE-28, BDE-85, BDE-66, BDE-138, BDE-71, BDE-75 but only at low concentrations. Tetra- to hexabrominated congeners dominate in biota samples with highest concentrations for BDE 47 whilst DecaBDE is the most important BDE in sediment and solid particulate matter (SPM) with regard to frequency of occurrence and concentration level [17].

For pentabromodiphenyl ethers risk assessment under Regulation EEC No. 793/93 has been completed and identified unacceptable risks from use in polyurethane foams [19]. For octa- and decabromodiphenyl ether risk assessment is in progress.

Indicator substances

Technical Pentabromodiphenyl ether

2,2´,4,4´-Tetrabromodiphenyl ether (BDE-47)
2,2´,4,4´,5-Pentabromodiphenyl ether (BDE-99)
2,2´,4,4´,6-Pentabromodiphenyl ether (BDE-100)
2,2´,4,4´,5,5´-Hexabromodiphenyl ether (BDE-153)
2,2´,4,4´,5,6´-Hexabromodiphenyl ether (BDE-154)

Technical Octabromodiphenyl ether

2,2´,3,4,4´,5´,6-Heptabromodiphenyl ether (PDBE 183)

Technical Decabromodiphenyl ether

2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)

Standard material

According to the increasing awareness of flame retardants as possible sources of environmental pollution two standard manufacturers (Cambridge Isotope Laboratories and Wellington Laboratories, Inc.) have reacted and offer now a wide range of unlabelled and ^{13}C-labelled polybrominated diphenyl ether standard solutions and standard mixtures as well as samples of technical products. The offered standard solutions include the proposed indicator substances. The most important suppliers for polybrominated diphenyl ethers are:

- Cambridge Isotope Laboratories, Andover. MA, U.S.A.
- Wellington Laboratories, Inc., Guelph, Ontario, Canada
- Dr. Ehrenstorfer GmbH, Augsburg, Germany
- Greyhound chromatography, Birkenhead, U.K.
- LGC Promochem GmbH, Wesel, Germany
- Accustandard, Inc., New Haven, CT, U.S.A.

Analytical method

Extraction and clean-up techniques for the analysis of PBDE residues in biological samples and sediments are quite similar to those developed for the analysis of other halogenated compounds such as PCBs and chlorinated pesticides. Most procedures are based on batch or Soxhlet extraction with organic solvents, purification of the extracts by adsorption and/or gel permeation chromatography and determination by gas chromatography with electron capture, atomic emission or mass spectrometric detection [see 20-24].

Both GC-MS with electron impact or electron capture negative ionisation may be used for final analysis of PBDEs. Another variety of GC-MS method is gas chromatography with high resolution mass spectrometric detection. Due to the fact that some of the individual compounds are very similar in their chemical and physical behaviour, a separation method with high resolution power is necessary. In a recent study retention times of 34 (Br$_2$-Br$_7$) BDE congeners on a 30 m 5% diphenyl-95%-dimethylsiloxane type column were compared to those of 131 commonly observed PCB congeners and 26 organochlorine pesticides. Results from this study indicate that there is a potential for co-elution of 10 PBDE, PCB's and organochlorine pesticides. Of particular concern is the interference of BDE-47 the predominant congener in biota samples with CB-180 [25]. The brominated biphenyl

congener 153 and Tetrabromobisphenol A can co-elute with BDE-154 and BDE-153, respectively, when using non-polar capillary columns [20]. Therefore, mass spectrometric detection should be preferred. Since the ECD responds also to other halogenated compounds its use seems possible only for BDE-209. This congener has a very long retention time and no of the other environmental relevant halogenated compounds elute in this area of the chromatogram. The analysis of BDE-209 is considerably more complicated than that of most lower brominated diphenyl ethers. BDE-209 is subject to degradation when exposed to daylight in the laboratory, and at higher temperatures. Therefore, the use of amber glassware is recommended for analysis of DecaBDE. In addition it should not be exposed to high temperatures for long time periods. This implies that the final temperature of the oven programme should not exceed 320°C for more than a few minutes. Consequently, short GC columns should be used for the analysis of this compound. By separate instrumental analysis of BDE-209 on a short column and of all other congeners using e.g. a 50 m column, thermal degradation of BDE-209 is prevented while adequate resolution of the other BDEs is ensured. However, a recent intercomparison exercise between three laboratories showed that combined analysis of all BDEs on a single 25 m capillary columns resulted in reliable results for BDE 209 as well as the lower brominated congeners [26]. That approach offers the advantage of considerable reduction in time for gas chromatographic analysis.

Both high resolution (HRMS) and low resolution (LRMS) instruments are used for GC-MS analysis of PBDEs in environmental samples. In principle, HRMS is preferred because of its higher selectivity, however, it has not been demonstrated that in practice GC-HRMS is superior to GC-LRMS [23, 26]. Most often used LRMS technique is based on electron capture negative ionisation (ECNI) with methane or ammonia as reagent gas that offers a considerable higher sensitivity than electron impact ionisation (EI). A drawback of the ECNI technique is that for most BDE congeners only ions due to bromine can be monitored (m/z=79/81). BDE-209 is the only conger which forms intensive mass fragments in the higher mass range, such as m/z = 484.7; 486.7 and 488.7. These ions can be used for quantification. EI-MS offers more selectivity and the possibility to confirm identity of compounds from their full scan mass spectra, but with considerable lower sensitivity. A recent study indicated that by combining GC/EI-MS with large volume injection and narrow bore columns (I.D. 0.1mm) a sensitivity can be obtained which is comparable to that of ECNI-MS [27].

Unlabelled and ^{13}C-labelled analytical standards are now available for many congeners but the selection of appropriate internal standards is still problematic. When applying EI mass spectrometry ^{13}C-labelleld BDEs can be generally used but in case of ECNI technique labelled compounds are of little value as only bromine ions are usually being monitored. The only exception is BDE-209 where the labelled congener can be used successfully as internal standard.
The following compounds were used as internal standards for PBDE analysis:

[13]C-labelled BDEs, BDEs not occurring in technical mixtures and never being found in environmental samples such as BDE-15, BDE-77, BDE-181, BDE-190, decabromobiphenyl, chlorinated biphenyls, ^{13}C-labelled chlorinated biphenyls, ^{13}C-labelled chlorinated diphenyl ethers, dechlorane and tetrachloro-p-terphenyl [22]

From reported environmental concentrations of PBDEs [17] it can be concluded that due to its low sensitivity GC-LRMS in the electron impact mode is not appropriate to monitor the concentrations of BDE congeners in sediments, suspended particulate matter and biota to be expected in European river systems in most cases. Therefore, GC-ECNI-LRMS and GC-HRMS seem to be the methods of choice for the analysis of PBDE in environmental samples. This is reflected in recent publications on analytical methodologies for the determination of PBDEs (19, 21-24) and in methods used by the participants of the first world-wide interlaboratory study on polybrominated diphenyl ethers [26]. Instrumentation for HRMS is much less common in routine environmental laboratories and more expensive than that for GC-ECNI-MS.

Taking into account all information available at the moment GC-ECNI-MS seems to be the most appropriate technique for quantitative analysis of PBDEs in environmental samples at the required low concentration levels.

In May 2002 a first working draft "Water quality - Determination of polybrominated diphenyl ethers in sediments and sewage sludge" (ISO/WD 22032) has been presented for discussion by ISO/TC 147 on its meeting at Orlando, Florida. Both GC-LRMS and GC-ECNI-MS are included but many of the technical details have not been agreed upon yet. Approval as committee draft can be expected in 2003 at the earliest.

Need for Action

Preparation of CRMs (biota and sediment)

No Certified reference materials for PBDEs are available at present. However, some analyses have been carried out on fish reference materials with certified concentrations for other organic contaminants, which indicated the presence of PBDEs in those materials [22]. These materials might be useful for QA/QC and method validation. Netherlands Institute for Fisheries Research (RIVO) is working on a feasibility study on the preparation of CRMs for PBDS in biological samples and sediments.

Further improvement of analytical methodologies for the determination of PBDEs with emphasis on the analysis of BDE-209

The first world wide inter-laboratory study on PBDEs was performed in 2000. It involved five biological samples, two sediments and two standard solutions. Results reported were acceptable for BDE-47 with a range of relative standard deviations (Rsd) of 17 to 40%, Results for BDE-99 (Rsd 25-77%), BDE-100 (Rsd 19-48%), BDE-153 (Rsd 30-48%) and BDE-154 (25-43%) showed a need for further improvement of the analysis of these congeners. The analysis of BDE-209 was not under control by the participating laboratories [26]. Results of the second international interlaboratory study on brominated flame retardants were reported, recently [28]. Progress was made with regard to reproducibility of analytical results for some BDE congeners, e.g. BDE-99, but analysis of BDE-209 is still not under control by the majority of laboratories. A coefficient of variation (CV) of 65% (n=13) was obtained for the analysis of a sediment sample.

Establishment of regular Laboratory Performance Studies on the determination of PBDE in biota and sediments

The QUASIMEME Laboratory Performance Studies (Aberdeen, UK) has organised a development exercise for brominated flame retardants in biota, sediment and milk in 2002 [28]. A new developing exercise is planned in 2003.

Alkylphenols (Nonylphenols/Octylphenols)

Information on composition of technical mixtures and production volume

Commercially produced nonylphenols contain predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. According to product data sheets of some nonylphenol manufacturers the two most important impurities in commercial 4-nonylphenol are 2-nonylphenol (up to 10 % w) and 2,4-dinonylphenols (up to 1 % w). Due to the manufacturing process no 4-n-nonylphenol is present in commercial products. Therfore this isomer seems to be suitable as internal standard for analysis.

The most comprehensive source for production and usage data yet available seems to be the report of the risk assessment conducted under Regulation EEC No 793/93 [29]. According to this report 73500 t of production capacity within the EU, 3500 t exports and 8500 t of imports give 78500 t of nonylphenol used in 1997. Nonylphenol is a raw material for the manufacture of i.a. nonylphenol ethoxylates, modified phenolic resins, plastics, stabilisers and phenolic oximes. More than half of the nonylphenol production (some 60% in 1997) is used for manufacturing nonylphenol ethoxylates.

Production data for octylphenol are even scarcer. Although theoretically several isomers in the alkyl part are possible, only the 4(1,1,3,3-tetramethylbutyl)-phenol (4-tert-Octylphenol) seems to be of relevance due to the manufacturing process, that is the reaction of 2,2,4-trimethylpentane with phenol. Production in the EU is reported to be 6800 t in 1998, thereof 5000 t are estimated to be used for the production of octylphenoxy ethoxylates [30]. The use pattern seems to differ to some extent from nonylphenol.

Besides their high aquatic toxicity nonylphenols show endocrine disrupting effects but only alkylphenols with the alkylgroup in para-position have been identified as estrogenic active compounds. Octylphenols show a higher endocrine disrupting potential than nonylphenols [31].

Risk assessment for nonylphenol and 4-nonylphenol (branched) has been completed under Regulation 793/1993/EEC [29]. A need for limiting the risks to due to the toxicity and estrogen activity of nonylphenol has been idientified. The risks from other degradation products of alkylphenolethoxylates (see below) has not been adressed in this study.

Nonylphenols (NPs) and octylphenol (OP) found in the environment do not stem from the production process and use of NP and OP itself but are mainly degradation products of the non-ionic surfactants nonylphenol polyethoxylates (NPEOs) and octylphenol polyethoxylates (OPEOs).

Alkylphenol polyethoxylate (APEO) surfactants are used worldwide in various industry, agricultural, and household applications. Industrial uses include the manufacture of plastics, textiles, paper, and agricultural chemical products. Commercial blends of APEOs are polydisperse mixtures of isomers (alkyl chain branching) and oligomers (2 to 20 ethoxy units). The biodegradation pathway of APEOs to short-chain ethoxylate ($APE_{1-3}O$), and ethoxy carboxylate metabolites ($APE_{1-3}C$) is well established. The polyethoxylate chain of 1 to 20 ethoxy units is shortened during aerobic and anaerobic wastewater treatment processes, or in river waters if discharged directly (Figure 1). APECs are relatively water soluble, so that the concentrations of APECs in river water are typically higher than that of the short-chain ethoxylated APEOs or APs, which have lower water solubilities [33-37].
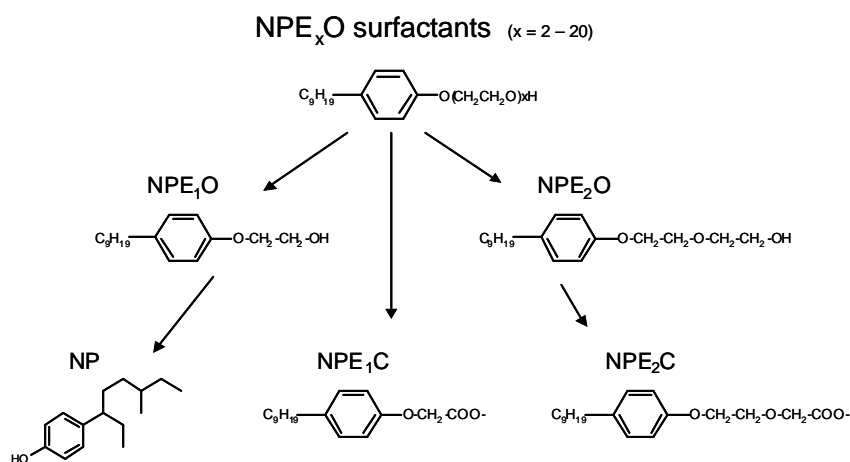
Figure 1: Endocrine disrupting metabolites of NPEO surfactants.

NP is lipophilic with reported octanol-water partition coefficients in a range of log Kow = 3.01 – 4.48. Thus, moderate to high adsorption potential to the soil matrix can be expected. NP behaves as a weak acid with a p_{ka} of 10.7. Ionisation under neutral to alkaline conditions influences its solubility and sorption to solid matrices; it accumulates in anaerobically digested sewage sludge [38].

APEOs are biodegradable materials that are effectively removed in well-functioning biological WWTPs. Biodegradation of APEOs occurs via ether cleavage which leads to the formation of short-chain APEOs, mostly mono- (APE_1O), di- (APE_2O), and triethoxylates (APE_3O). Under aerobic conditions carboxylation of the terminal alcoholic group with production of more persistent nonylphenol polyethoxycarboxylates (APECs) occurs. These APEO metabolites formed are more toxic than their parent compounds, and more bioaccumulative in aquatic organisms. APEOs with short ethoxy chains (1-3) are lipophilic, while those with long chains are hydrophilic [35,38].

Indicator substances

4-Nonylphenol
4-Nonylphenol mono-ethoxylate, NPE_1O
4-Nonylphenol di-ethoxylate, NPE_2O
4-Nonylphenoxy acetic acid, NPE_1C
4-Nonylphenoxyethoxy acetic acid, NPE_2C

4-Octylphenol
4-Octylphenol mono-ethoxylate, OPE_1O
4-Octylphenol di-ethoxylate, OPE_2O
4-Octylphenoxy acetic acid, OPE_1C
4-Octylphenoxyethoxy acetic acid, OPE_2C

Standard material	Supplier
4-Nonylphenol, technical mixture of isomers	Aldrich
4-Octylphenol	Aldrich
4-n-Nonylphenol	Dr. Ehrenstorfer
4-n-Nonylphenol, d8	Dr. Ehrenstorfer
4-Nonylphenol mono-ethoxylate, NPE_1O	Dr. Ehrenstorfer
4-Nonylphenol di-ethoxylate, NPE_2O	Dr. Ehrenstorfer
4-Nonylphenol mono-ethoxylate, d2, NPE_2O	Dr. Ehrenstorfer
4-Octylphenol mono-ethoxylate, OPE_1O	Dr. Ehrenstorfer
4-Octylphenol di-ethoxylate, OPE_2O	Dr. Ehrenstorfer
4-Nonylphenoxy acetic acid, NPE_1C	Dr. Ehrenstorfer
4-Nonylphenoxy acetic acid, d2, NPE_1C	Dr. Ehrenstorfer
4-Octylphenoxy acetic acid, OPE_1C	Dr. Ehrenstorfer

Analytical Methods

The substance example alkylphenols (APs) shows the difficulty in the establishment of a common agreed analytical method for their determination in environmental matrices.
A literature review on existing methods for the determination of nonyl-, and octylphenol was conducted, which points out that many different analytical methods are existing. Nearly every laboratory uses in general it's own procedure.

The analytical determination of alkylphenolic compounds is dominated by chromatographic methods. The collected literature data (Tables 1-2) show that gas chromatographic (GC) and liquid chromatographic (LC) separation techniques for the analysis of APs are used more or less in the same

extent. However, in the last 10 years LC-MS gained in popularity and partially substituted GC-MS methodologies [39].

Also included in the review and the tables are shorter APEO surfactant metabolites (APE$_{1-3}$O), and carboxylated APE$_{1-3}$C compounds because they are often analysed together with the APs and also have an endocrine disrupting potential.

The list of priority substances of the WFD will be constantly revised. Also additional substances which are relevant for individual water basins have to be measured by the Member States. Due to the endocrine disrupting potential of the APEO metabolites APE$_{1-3}$O and APE$_{1-3}$C and the often higher concentration values found for these compounds compared to NP itself, they might in the future become priority substances.

The main difference in the separation efficiency of GC- and LC-methods is that GC reveals the presence of the different isomers of the alkyl chain – NP is detected as an isomer cluster peak consisting of approx. 10 peaks which spans a retention time window of 1-2 minutes – whereas in LC NP elutes in 1-4 peaks (Figure #). Thus, both separation principles have their pros and cons.

A very good and comprehensive review article on APEOs and their metabolites was published by Thiele et al. [34] in the year 1997, and recently a review on endocrine disrupting compounds (EDCs) by Petrovic et al. [39].

Liquid Chromatography

LC is predominantly performed by reversed-phase (RP)-LC, but also in the normal-phase mode (Table 1). In normal-phase HPLC, the APEOs are separated according to the increasing number of ethylene oxide units, RP-HPLC separates the oligomers only slightly. RP-LC allows the separation of different alkyl-chain isomers. Detection is mostly conducted by electrospray ionization (ESI) mass spectrometry (MS), but also by fluorescence and UV. Another problematic fact for the comparison of the methods is that usually different LC eluants with diverse modifiers are used (Table 1).

Figure # shows the RP-HPLC separation of technical NP and 4n-NP. The isomers of the technical NP can be slightly separated, but it is normally more convenient to integrate and quantify only the first big peak. 4n-NP instead elutes as a single peak.
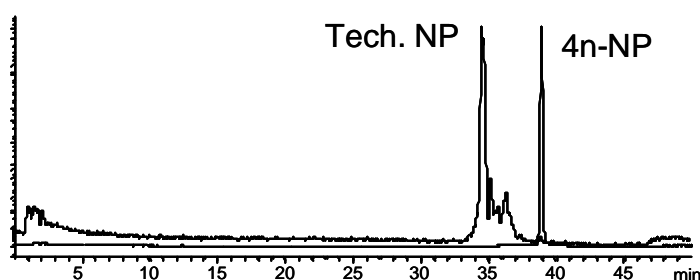
Figure: HPLC separation of technical NP and 4n-NP. Superspher 100 RP-18 column (250 x 2 mm, 4 µm particles), linear gradient from 20 to 90 % acetonitrile (water with 5 mM acetic acid) in 40 min and back to 20 % in 5 min at a flow rate of 0.4 ml/min. One results of the IES-JRC-Ispra (R. Loos).

Gas Chromatography

The main problem of the comparison of the GC methods is that APs are either analysed after derivatization of the hydroxy-group or without derivatization. The OH-group can be derivatized to e.g. acetyl-, methyl-, heptafluorobutyl-, pentafluorobenzoyl-, or trimethylsilyl ethers.

ISO-CEN [40] proposed a method for the determination of APs in water samples based on liquid extraction and GC analysis of the underivatized phenols. The water samples are acidified to pH 2 and are during 4 h extracted in a shaking device using toluene. Clean-up is performed with silica gel using

n-hexane and toluene elution. NP is analysed by GC-MS in the SIM mode detecting the mass fragments m/z 135 and 107. These ions are formed during electron impact fragmentation of the alkyl-chain.

However, it has been reported that several problems are usually encountered with trace level analysis of phenolic compounds without derivatization. E.g., analyte losses due to adsorption in the GC inlet may occur. Moreover, peak tailing due to interaction of the analytes with active sites in the analytical column can be observed. With derivatization instead sharper peaks are obtained. Consequently, lower detection limits can be obtained. Another beneficial effect of derivatization is that much higher m/z values are formed, which increases analytical precision [41,42]. Meesters et al. [43] report that the application of a derivatization step – acetylation by acetic anhydride – led to a tremendous improvement in the SIM trace.

Problematic of the NP detection in its underivatized form is the detection of the small m/z fragment ions 107, 121, 135, and 149 (Table 2). This increases the probability of false positive responses due to interfering matrix constituents.

A problematic fact of the good separation efficiency of GC is that the NP isomer cluster of usually 12 peaks might complicate detection and quantification of "total NP" [42,43].

Extraction methods

Water extraction is mostly performed by liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Also steam distillation, solvent sublation, and solid-phase microextraction (SPME) are used. SPE and SPME methodologies are gaining popularity due to simpler handling operations [38]. SPE is performed with C18, polymeric sorbents, or graphitized carbon blacks using different elution solvents (Table 3).

Solid samples like sediment, sewage sludge, fish, tissue, etc. are extracted by soxhlet, pressurized liquid extraction (PLE) also known as accelerated solvent extraction (ASE), steam distillation, supercritical hot-water extraction, supercritical fluid extraction (SFE), ultrasonic irradiation (sonication), microwave extraction, or SPE (Table 4).

All these extraction procedures yield different extraction efficiencies, also depending on the solvents and conditions used. Some scientists have compared different extraction methods. E.g., Meesters and Schroeder [43] performed a comparison of Soxhlet, steam distillation, supercritical fluid (SFE), and ASE extraction for the extraction of NP from sewage sludge and obtained the best results with ASE using ethylacetate-formic acid (9:1).

Pryor et al. [32] performed an analytical reference check of a soxhlet extraction procedure for sewage sludge samples with a SFE method and found apparent discrepancies in the NP concentration data using these 2 different extraction methods.

Thus, it can be concluded that the recoveries and resulting concentrations depend on the extraction procedure.

Some laboratories perform the extraction of NP at acidic pH which increases extraction efficiency due to reduced water-solubility. However, disadvantageous is that also interfering matrix substances such as humic acids are co-extracted at acidic pH and can complicate the analysis.

Clean-up

Another problem of the analysis of alkylphenolic compounds is that usually a clean-up step is necessary for a correct determination. It has been reported that without column clean-up, matrix compounds from sludge, sediment or polluted water samples interfere with the analytes and prevent a correct determination [39,43,45]. Table 4 shows that most of the extraction methods for solid samples are followed by a clean-up step. However, also solid sample extraction methods without clean-up are reported [32]. The conventional clean-up procedures are either based on solid-liquid adsorption chromatography in open columns using different adsorbents (silica, Florisil, Alumina, or carbon), or on SPE with C_{18}, NH_2, or CN modified silica [39].

Also contradictory clean-up results are reported in the literature. E.g., Meesters and Schroeder [43] report that methanol and acetone are not well suited for the ASE extraction of NP. Their optimized

extraction conditions are ethylacetate-formic acid (9:1) at 170°C. Petrovic et al. [33] in contrast use acetone-methanol (1:1) at 50°C.

Need for action

Preparation of certified reference materials (standard solutions, sediment samples)

No certified reference material seems to be available for the time being. To improve comparability of monitoring data the production of reference material should be initated.

Establishment of Laboratory Performance Studies on the determination of NP/OP and further degradation products of APEOs

In conclusion of the analytical method section, monitoring data often relate to different extraction, sample clean-up, and quantification methods. This makes the comparison and assessment of published data difficult, if not impossible. Therefore there is a need for validation of different analytical methods by interlaboratory studies.

Further Studies on degradation of APEOs

To elucidate the environmental fate of NP/OP, also the differing behaviour of its various isomers should be respected in the future.

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Annex 3

Reduced summary table of the standard methods

Priority Substance	Danube TNMN	Available standard method (Ref.)			Scope of method		Method Applicability
	agreed method	Standard	Year	Principle	Proposed Range of Application [1]	Matrix	Applicability in routine labs - (yes/no) or remarks
Alachlor		ISO 11370 2000	Jan-95	TLC, AMD-Technique	**? 50 ng/l**	Water	no (2), yes (2)
		EN 6468		GC, LLE	detection limit: 1 ng/l to 10 ng/l		
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**0,5-40 µg/L**	Water (D,G,S)	--
Anthracene		ISO 17993: 2002 or see PAH´s		HPLC/fluorescence	? 0,01 µg/l [6]		yes (2)
		US EPA 8100		GC/FID	? 0.1 or 0,01 µg/l	Water	yes (1)
Atrazine		EN ISO 11369	Nov-97	HPLC/UV	? ca. 0,1 µg/l	Water [D,G]	no (1), yes (1)
		EN ISO 10695: 2000	Nov-00	GC/NPD (MS for conf.)	? 50 ng/l	Water [D,G,S,W]	no (1), yes (2)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	? 50 ng/l	Water	no (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**3-50 µg/L**	Water [D,G,S]	--
Benzene		DIN 38407-9	May-91	Headspace-GC/FID	? 5 µg/l	Water [D,G,S,W]	no (1), yes (1)
		Draft ISO 15680	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	no (1), yes (1)
		ISO 11423-1	Sep-97	Headspace-GC/FID	? 2 µg/l	Water [D,G,S,W]	yes (1)
Brominated diphenylethers		ISO WD 22032	Mar-02	GC/MS	0.005 - 100 µg/kg	Sludge, Sediment	no (3), yes (1)
Bis(pentabromophenyl)ether		*ISO WD 22032*	Mar-02	GC/MS	0.03 - 100 µg/kg	Sludge, Sediment	--
Diphenyl ether, octabromo derivate		*ISO WD 22032*	Mar-02	GC/MS	0.005 - 25 µg/kg	Sludge, Sediment	--
Diphenyl ether, pentabromo derivate		*ISO WD 22032*	Mar-02	GC/MS	**0.005 - 25 µg/kg**	Sludge, Sediment	--
Cadmium and its compounds	ISO 5961	EN ISO 5961	May-95	ET-AAS	**0,3 - 3 µg/l**	Water	yes (4)
		DIN 38406-16	Mar-90	Voltametry	**0,1 µg/l - 50 mg/l**	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS	**? 0,5 µg/l**	Water [D,G,S,W]	yes (1)
		EN ISO 11885	Apr-98	ICP-AES	**? 0,01 mg/l**	Water [D,G,S,W]	yes (1)
		ISO DIS 15586 [5]	May 01	ET-AAS	**0,4 - 4 µg/l**	Water [D,G,S,W] ,Sediment	--
C10-13-chloroalkanes		**no Standard available**	--	--	--	--	no (3)
Chlorfenvinphos		DIN EN 12918	Nov-99	GC	0,01 - 1 µg/l	Water [D,G,S,W]	no (3), yes (1)

Priority Substance	Danube TNMN	Available standard method (Ref.)				Scope of method		Method-Applicability
	agreed method	Standard	Year	Principle		Proposed Range of Application [1]	Matrix	Applicability in routine labs - (yes/no) or remarks
		ISO 11370 2000	Jan-95	TLC, AMD-Technique		**? 50 ng/l**	Water	no (1)
Chlorpyrifos (*-ethyl, -methyl*)		DIN EN 12918	Nov-99	GC		**0,01 - 1 µg/l**	Water [D,G,S,W]	no (3), yes (1)
1,2-Dichloroethane		EN ISO 10301	Aug-97	GC or Headspace-GC		? 5 or ? 100 µg/l	Water [D,G,S,W]	yes (4)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.		10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Dichloromethane		EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other		**? 50 µg/l**	Water [D,G,S,W]	no (1), yes (3)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.		10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Di(2-ethylhexyl)phthalate (DEHP)		ISO DIS 18856	Mar-02	GC/MS		0,02 - 0,15 µg/l	Water [D,G,S,W]	no (2), yes (2)
Diuron		EN ISO 11369	Nov-97	HPLC/UV		**? ca. 0,1 µg/l**	Water [D,G]	no (2), yes (2)
Endosulfan		EN ISO 6468	Feb-97	GC/ECD		**? ca. 10 ng/l**	Water [D,G,S,W]	no (2), yes (1)
		US EPA 8081		GC/ECD		**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
Fluoranthene		ISO 17993: 2002 or see PAH´s				? 0,01 µg/l [6]		no (1), yes (1)
		US EPA 8270		GC/MS		? 0,01 µg/l	Water, Soil, Sludge	yes (1)
Hexachlorobenzene		EN ISO 6468	Feb-97	GC/ECD		**? ca. 10 ng/l**	Water [D,G,S,W]	yes (3)
		US EPA 8081		GC/ECD		**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)		**0,01-0,4 µg/L**	Water [D,G,S]	--
Hexachlorobutadiene		EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other		**? 0,01 µg/l**	Water [D,G,S,W]	no (2), yes (2)
Hexachlorocyclohexane		EN ISO 6468	Feb-97	GC/ECD		? ca. 10 ng/l	Water [D,G,S,W]	yes (4)
gamma-HCH (Lindane)	ISO 6468:1996	*EN ISO 6468*	Feb-97	GC/ECD		? ca. 10 ng/l	Water [D,G,S,W]	--
Isoproturon		EN ISO 11369	Nov-97	HPLC/UV		? ca. 0,1 µg/l	Water [D,G]	no (2), yes (2)
Lead and its compounds	ET AAS (EN ISO 11885)	DIN 38406-6	Jul-98	ET-AAS		**5 - 50 µg/l**	Water	yes (3)
		ISO 8288		flame AAS		**n.a.**		yes (1)
		US EPA 7421		ET-AAS		5-100 µg/L	Water, Soil, Sludge	yes (1)
		DIN 38406-16	Mar-90	Voltametry		0,1 µg/l - 50 mg/l	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS		? 0,1 µg/l	Water [D,G,S,W]	yes (2)
		EN ISO 11885	Apr-98	ICP-AES		**? 0,07 mg/l**	Water [D,G,S,W]	yes (2)

Priority Substance	Danube TNMN	Available standard method (Ref.)			Scope of method		Method Applicability
	agreed method	Standard	Year	Principle	Proposed Range of Application[1]	Matrix	Applicability in routine labs - (yes/no) or remarks
		ISO DIS 15586[5]	May 01	ET-AAS	**10 - 100 µg/l**	Water [D,G,S,W] ,Sediment	--
Mercury and its compounds	ISO 1483	EN 1483	Aug-97	Cold Vapour-AAS	**0,1 - 10 µg/l**	Water [D,G,S,W]	no (1), yes (3)
		EN 12338	Oct-98	CV-AAS with Amalgamation	0,01 - 1 µg/l	Water [D,G,S,W]	yes (2)
		EN 13506	Nov-01	Atomic fluor. spectrometry	0,01 - 10 µg/l	Water	--
Naphthalene		ISO 17993: 2002 or see PAH´s			? 0,01 µg/l [6]		yes (2)
		Draft ISO 15680[5]	Sep-01	Purge/Trap + Therm. Desorp.	0,01 - 100 µg/l	Water [D,G,S,W]	--
		US EPA 8270		GC/MS	? 0,01 µg/l	Water, Soil, Sludge	yes (1)
Nickel and its compounds	ET AAS (EN ISO 11885)	DIN 38406-11	Sep-91	ET-AAS	**5 - 100 µg/l**	Water	yes (3)
		ISO 8288		flame AAS	**n.a.**		yes (1)
		US EPA 7521		ET-AAS	**5-50 µg/L**	Water, Soil, Sludge	yes (1)
		DIN 38406-16	Mar-90	Voltametry	0,1 - 10 µg/l	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS	**? 1 µg/l**	Water [D,G,S,W]	yes (2)
		EN ISO 11885	Apr-98	ICP-AES	**?**	Water [D,G,S,W]	yes (2)
		ISO DIS 15586[5]	May 01	ET-AAS	**7 - 70 µg/l**	Water [D,G,S,W] ,Sediment	--
Nonylphenols		ISO CD 18857-1	Jul-01	GC/MS	0,005 - 0,2 µg/l (0.1-50 [W])	Water [D,G,S,W]	no (1), yes (2)
		Sweedish EPA Raport 3829-1990		GC/ECD	**n.a.**		yes (1)
Octylphenols		ISO CD 18857-1	Jul-01	GC/MS	0,005 - 0,2 µg/l (0.1-50 [W])	Water [D,G,S,W]	no (3), yes (1)
Pentachlorobenzene		EN ISO 6468	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	yes (3)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
Pentachlorophenol		EN 12673	May-99	GC/ECD/MS after Deriv.	0,1 - 1000 µg/l	Water [D,G,S,W]	yes (4)
		ISO 8165-2	Jul-99	GC/ECD after Deriv.	? 0,1 µg/l	Water	no (1), yes (1)
Polyaromatic Hydrocarbons (PAH´s)		ISO 17993: 2002		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	yes (1)
		US EPA 8270		GC/MS	? 0,01 µg/l	Water, Soil, Sludge	yes (3)

Priority Substance	Danube TNMN	Available standard method (Ref.)			Scope of method		Method-Applicability
	agreed method	Standard	Year	Principle	Proposed Range of Application[1]	Matrix	Applicability in routine labs - (yes/no) or remarks
		DIN 38414-23	Feb-02	HPLC/Fluo	? 0,05 mg/kg	Sludge, Sediment	no (1), yes (1)
		XP X33-012	Mar-00	HPLC/UV or GC/MS	n.a.	Sludge	--
Benzo(a)pyrene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	--
Benzo(b)fluoroanthene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	--
Benzo(g,h,i)perylene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	--
Benzo(k)fluoroanthene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	--
Indeno(1,2,3-cd)-pyrene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l [6]	Water [D,G,S]	--
Simazine		EN ISO 11369	Nov-97	HPLC/UV	? ca. 0,1 µg/l	Water [D,G]	no (1), yes (1)
		EN ISO 10695: 2000	Nov-00	GC/MS or GC/NPD	? 50 ng/l	Water [D,G,S,W]	no (1), yes (1)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	? 50 ng/l	Water	no (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**12-50 µg/L**	Water [D,G,S]	--
Tributyltin compounds		ISO/DIS 17353		GC/MS - FPD - AES	**10 - 1000 ng/l**	Water (D,G,S,W)	no (1), yes (3)
		WD DIN 38414-XX	??		**n.a.**	Sludge, Sediment	no (1), yes (1)
		NF T 90-250	Jul-01	GC	20 - 2000 µg Sn/kg dry matter	Sediment	--
		ISO/AWI 23161	Apr-02	GC/MS	**???**	Soil	--
Trichlorobenzenes		EN ISO 6468	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	no (1), yes (3)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Trichloromethane	ISO 10301:1997	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other	? 0,05 or ? 0,3 µg/l	Water [D,G,S,W]	yes (4)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Trifluralin		EN ISO 10695: 2000	Nov-00	GC/MS or GC/ECD or GC/NPD	**? 50 ng/l**	Water [D,G,S,W]	no (2), yes (2)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	**? 50 ng/l**	Water	no (1)
COD	ISO 6060:1989						

Priority Substance	Danube TNMN	Available standard method (Ref.)			Scope of method		Method-Applicability
	agreed method	Standard	Year	Principle	Proposed Range of Application[1]	Matrix	Applicability in routine labs - (yes/no) or remarks
Ammoniacal nitrogen	ISO 7150-1:1984						
total N	EN ISO 11905-1:1998						
	ISO 11261:1995						
Total P	ISO 1189:1996						
Arsenic	ISO 11969:1996						
Copper	ET-AAS (EN ISO 11885)						
Zinc	ET-AAS (EN ISO 11885)						
Chromium	ISO 9174:1990						

EN = European Standard
ISO = International Standard
DIN = German Standard
DIN V = German Pre-standard
WD = Working Draft

Format code:
black = conc. ≤ AA-QS
red (normal) = conc. ≤ AA-QS for In & Tr
but > AA-QS for Co & Te
red bold = conc. > both AA-QS

[1] The proposed application range derives from chapter "Scope of the method"
[2] The application range for surface water corresponds to the lowest concentrations for which tests of precision and bias have been carried out, according to the definition in ISO/TR 13530, 1997-09
[3] Concentrations of the analyte(s) in the intercomparison samples used for the determination of repeatability and reproducibility; S_R = relative reproducibility standard deviation
[4] Performance data according to ISO 5725
[5] Standard is part of CEN working programm (2001-11)
[6] ≥ 0,01 µg/l for surface water, ≥ 0,005 µg/l for drinking water
[7] Two kinds of quality standards are proposed, referring to (1) annual average concentration **AA-QS** and (2) short term concentration peaks, maximum admissible concentration **MAC-QS**

Format code:
Priority Substance normal format = WFD priority substance
Priority Substance italic format = 76/464/EEC priority substance or quality standard proposed
Priority substance in black = at least one method with application range ≤ AA-QS or 76/464/EEC quality objective
Priority Substance red (normal) = available methods with application range ≤ AA-QS for In & Tr but > AA-QS for Co & Te
Priority Substance red & bold = no standard method available at all or no available method with application range £ AA-QS for In & Tr nor for Co & Te

UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation
in the Danube River Basin

Five-years Report on Water Quality in the Danube River Basin Based on Trans-National Monitoring Network

1996-2000

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

October 31, 2003

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Table of contents

Annex 1: Classification Tables

Executive summary

The objective of this report was to assess water quality in Danube River basin, including classification and identification of spatial and temporal changes. The basis for assessment is data on physico-chemical and biological determinands collected in the frame of TNMN in five-years period 1996 – 2000. The main assessment objectives were as follows:

- Checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;

- Identification of water quality changes along the Danube River;

- Detection of trends in water quality;

- Assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

In general, following facts concerning classification and trend evaluation of the processed TNMN data should be highlighted:

Nutrients

Ammonium-N and nitrite-N concentrations increase from upper to lower Danube. In the Danube River, 53.3 % of ammonium-N and 37.2 % nitrite-N values were found to be above the target limits for these determinands. A special concern should be paid to the ammonium-N content recorded on the Arges river, where all five yearly values of C90 in time period 1996-2000 were above the limit for Class V; these extremely high values, correlated with BOD5 values, show the impact of untreated or insufficiently treated waste waters from municipalities. In the Danube River, occurrence of ammonium-N shows a decreasing tendency from 1996 to 2000 in the upper part and in the middle section in Slovak monitoring sites.

The spatial distribution of nitrate-N concentrations shows a decrease from upper/middle to lower Danube. Tributaries with the highest content of nitrate-N are Morava, Dyje, Sio in the upper/middle part, and Iskar, Russenski Lom, Arges and Prut in the lower part of river basin. For nitrate-N concentrations the fluctuations in time profile are low for the Danube River, but rather high for the tributaries.

Orthophosphate-P shows a spatial pattern similar to that of total phosphorous characterized by a slight increasing profile from upper to lower Danube. In the upper/middle part of the Danube a decreasing tendency in P concentration is seen in the section from Danube-Bratislava (km 1869) down to Danube-Szob (km 1708) with an exception at Danube-Medvedov/Medve (km 1806). In general, the time variance of total P concentrations is much higher than that of ortho-phosphates.

Heavy metals

Except of manganese, for which a maximum of the spatial profile is present in the middle Danube reach, for most of the discussed heavy metals the general pattern is an increase from the upper and middle to the lower Danube. Furthermore, the heavy metals content in some tributaries – mainly those located in the lower Danube - is higher than the content in the Danube River itself.

The contamination of the Danube River by lead and copper was found rather high. A slightly better was the situation for cadmium and mercury with 47.4% of values exceeding cadmium target level and 36.6% of values exceeding mercury target level. In general, relatively high fluctuations of heavy metal concentrations were observed along the Danube. Despite these uncertainties the development of heavy metal content in some tributaries was found positive – a decrease is indicated in Drava river (cadmium, chromium, copper, lead, nickel and zinc), in Arges (cadmium, chromium, copper, lead), Prut (cadmium, chromium, lead) and in Siret (chromium, copper, lead).

In general, five years trends of heavy metal pollution can hardly been evaluated because a relatively high deviation of results occurred. High values of heavy metals often result from high loads of suspended solids caused by flood events. The statistical parameter used in this report (90% percentile)

– was certainly influenced by such hydrological processes. For this five-years evaluation report the data on total concentration of heavy metals in water samples had been used because data related to dissolved fraction was not available in sufficient amount. Therefore, it must be stressed that such a rather scattered pattern of the heavy metal pollution data for the water matrix clearly supports future orientation of TNMN activities on the solid phase, i.e., in TNMN planning activities the analysis of suspended solids and sediments should be preferred.

Oxygen regime

Dissolved oxygen concentrations show positive results, with only 7.4% of values being below the quality target in the Danube River and 8.6% being below the quality target in monitored tributaries. Oxygen concentration decreases from upper to lower part of the Danube River, lowest values being in the section from Danube-Bazias to Danube-Novo Selo/Pristol. As for the tributaries, rather low oxygen content was identified in those located in the lower part of the river basin.

As for BOD values 13.3% of them are above the target value in the Danube River (mainly in the middle and in the lower sections) and 35.9% exceed the target value in tributaries. Organic pollution expressed by BOD increases along the Danube, reaching its maximum in the secion from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm 834, RO02). The tributaries most polluted by degradable organic matter are Morava, Dyje and Sio in the upper/middle part of the Danube mainstream and Russenski Lom and Arges in the lower part.

For CODCr, 22.4% of all values for the Danube mainstream and 39.7% for tributaries were found above the quality target; the situation is more positive in case of CODMn - no value above this limit for the Danube River and 18.2% for tributaries. In principle, the results obtained for CODCr and CODMn show the highest values in the lower part of the Danube River.

Organic micropollutants

The organochlorine compounds (Lindan and p,p'-DDT) showed similar spatial profile, with an increasing pattern from upper/middle to lower Danube. The polar pesticide Atrazine was undetectable at most of the monitoring sites along the Danube River, only 12.5% of the data were found above the target limit. In tributaries, 30% of Atrazine values were above the quality target, the maximum values were found in rivers Sio and the Sajo.

For the volatile organic compounds, data is available for upper and middle Danube only. Chloroform and tetrachloroethylene show values above the target limits in a following pattern: 29.0% of the Danube samples and 39.5% of the samples taken from tributaries exceeded the target values for chloroform, for tetrachloroethylene the respective numbers were 13.6% for the Danube and 7% for tributaries. The situation was found to be better for tetrachloromethane and trichloroethylene - in the Danube River mainstream no value was detected above the target limit for these compounds, while in tributaries only a small percentage of all data (2.3%) was above the target limits for both these determinands.

Biological determinands

Evaluation of saprobic index of macrozoobenthos using Austrian standard ÖNORM M6232 showed that the Danube River and most of its tributaries correspond to classes II – II-III. Only Sava River was characterized by a worse quality class (III – III-IV), however, within the years the situation improved.

In 1996 – 2000 the microbiological water quality corresponded to classes I – IV in the Danube River mainstream. Some tributaries, as e.g., Vah, Tisza and Siret can be characterized as extensively polluted, however, data from many other relevant tributaries is missing. It was observed that sedimentation had positive effects to number of total coliforms below Gabčíkovo Reservoir, Iron Gates and in Danube Delta as well.

For biological determinands a slightly positive time trend appeared in case of saprobic index of macrozoobenthos, but no significant trend in microbiological determinands was observed.

1.   Introduction

The Danube River flows through ten countries, and its large river basin of 817 000 km^2 is shared between 17 countries. The waters in Danube River Basin serve people for many purposes – drinking water preparation, use for industrial and agricultural activities, recreation, hydropower generation, and navigation. Very important function of the rivers in Danube River Basin is ecological function, to which attention is growing also due to the latest development of EU legislation. On the other hand human activities result in discharging of waste waters, release of pollutants from diffuse sources, change of natural habitats for aquatic biota and risk of accidental pollution. To protect waters in the Danube River Basin and to ensure their functions and sustainable human uses, cooperation of Danubian states is inevitable.

The Danube River Protection Convention (DRPC), signed in 1994 and entering into force in 1998, creates the basis for such cooperation. Its main objective is to achieve sustainable and equitable water management, including conservation, improvement and the rational use of surface and ground waters. Danubian countries shall take all appropriate legal, administrative and technical measures to at least maintain and improve environmental and water quality conditions of the Danube River and of waters in its catchment area.

To be able to assess the progress in improvement of environmental conditions of waters in Danube River basin, and to assess effectiveness of measures set up, the role of information from water quality monitoring is crucial. The Danube River Protection Convention says that the Contracting Parties shall cooperate in the field of monitoring and assessment. For this aim they shall harmonise or make comparable their monitoring and assessment methods and shall periodically assess the quality conditions of Danube River and the progress made by taken measures.

As one of the tools for implementation of DRPC, Joint Action Programme for the Danube River Basin (JAP) had been prepared defining the integrated measures for improvement of the environment related to the waters in the Danube River Basin. Danubian States and Permanent Secretariat of ICPDR had developed JAP for period of years 2001-2005. In relation to basin-wide cooperation in the field of monitoring JAP stresses necessity to prepare the data in such a way that allows using them in comparative way and serving as a reliable basis for making decisions throughout the Basin.

Presented report would like to contribute to fulfil the above-mentioned requirements on information related to the quality of waters in Danube River Basin. It contains assessment of the data, collected by Danubian countries in the period of years 1996-2000 in the frame of joint Trans-national monitoring network (TNMN).

2.   Objectives of the report

The process of assessing of water quality in this report is an evaluation of the physico-chemical and biological status of waters based on the results collected in the frame of TNMN in five-years period 1996 – 2000, with the following main assessment objectives:

- checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;
- identification of water quality changes along the Danube River;
- detection of trends in water quality;
- assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

Load assessment generally belongs to main assessment objectives and is of concern also in Danube River Basin. As the load assessment programme started in year 2000, it is not included in the 5-years summarising report.

This is the first time, when complete data sets from 5-years operation of TNMN will be processed. For the first time these data will be used for classification of water quality in accordance to joint classification system prepared for the Danube river basin; and for assessment of temporal and spatial changes in water.

The results of this activity should have not been seen as a self-standing activity, but should be seen in a broader context to recognise the needs for TNMN improvements. On one hand, in the report TNMN data from the first phase of its operation are evaluated, which can be used in identification of possible weak points in the monitoring programme and the following suggestions for future TNMN improvement. On the other hand it has to be mentioned that improvement of TNMN has to be strongly connected to continuous implementation of Water Framework Directive, which entered in force in EU in 2000 and Danube countries agreed on its joint implementation in the river basin.

3.   History of TNMN

The first steps towards joint water quality monitoring network in Danube River basin were taken when governments of the Danube countries signed the Bucharest Declaration. The monitoring network used for the purposes of the Declaration consisted of eleven monitoring locations and were located on the Danube River itself where the river formed or crossed the border between the countries.

In 1991 the Danubian countries started preparation of the Convention on cooperation for the protection and sustainable use of the Danube River (DRPC), which was signed in 1994.
The Environmental Programme for the Danube River Basin, lead by a Task Force, also started in 1991 with the main objective to strengthen the operational basis for environmental management in the Danube River Basin and to support the Danubian countries to implement the DRPC.

In 1992, the Task Force agreed a three-year Work Plan (1992-95) with monitoring, laboratories and information management having between the main Programme actions. In 1992 the Monitoring, Laboratory and Information Management Sub-Group (MLIM-SG) was established to deal with this topic.
The main outcome of the three-year Work Plan was the Strategic Action Plan (SAP). Its approval marked the end of the first phase of the EPDRB (1992-95) and implementation was scheduled to start in the next phase (1996-2000).

The TNMN was originally designed in 1993 during the project "Monitoring, Laboratory Analysis and Information Management for the Danube River Basin", conducted by the WTV Consortium in close cooperation with MLIM-SG.
The responsibility for TNMN was assigned to MLIM-SG, which consisted of three Working Groups – Monitoring WG, Laboratory Management WG and Information Management Working Group. MLIM-SG should address the development of water quality monitoring network in Danube River Basin; introduce harmonised sampling procedures and enhanced laboratory analysis capabilities; and form the core of a Danube information system on the status of in-stream water quality. The 1996 and 1997 budgets of Phare Multi-Country Environmental Programme allocated substantial funds to EPDRB projects to support further development of the monitoring and assessment programme and the launch of TNMN into operation.

After entry of the DRPC into force in October 1998, MLIM-Expert Group was incorporated in the organisational structure of International Commission for the Protection of the Danube River (ICPDR) and has been working on the basis of TORs agreed by the ICPDR Plenary Meeting. In accordance with the TORs, the overall objective of the MLIM-EG is to create a strengthened and more strategic approach to monitoring, laboratory and information management for surface waters. The key role of the Group is to address the organisational and operational aspects related to the monitoring of water riverine conditions in the Danube River Basin and to provide basic data as an input to the ICPDR information system.

4.   Description of TNMN

4.1.   Objectives of TNMN

TNMN has been designed with purpose to meet the main objectives defined for monitoring network in Danube River basin by the Work Plan of EPDRB. The Work Plan states that the monitoring network shall:
- strengthen the existing network set up by the Bucharest Declaration;
- be capable of supporting reliable and consistent trend analysis for concentrations and loads for priority pollutants;
- support the assessment of water quality for water use;
- assist in the identification of major pollution sources;
- include sediment monitoring and bioindicators;
- include quality control.

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

As was already mentioned, the TNMN was originally designed in 1993 during the project conducted by WTV Consortium. The implementation was agreed by MLIM-SG, but the design was further simplified for operation in the first phase, starting in 1996. The first phase is seen as a period with:

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

4.2.   Network of monitoring locations

The monitoring network in the frame of TNMN builds on national surface water monitoring networks. To select monitoring locations for the purposes of international network in Danube River Basin, respecting also the above-mentioned TNMN objectives, the following concrete selection criteria had been set up:

- located just upstream/downstream of an international border
- located upstream of confluences between Danube and main tributaries or main tributaries and larger sub-tributaries (mass balances)
- located downstream of the biggest point sources
- located according to control of water use for drinking water supply

Monitoring location included in TNMN should meet at least one of the selection criteria.

The selection procedure has lead to preparation of a final list of 61 monitoring locations. These are given in Map.1. and Table 4.2.1 with basic information characterising the location. The monitoring locations in the Table 4.2.1 are grouped in accordance to countries and not as they are ordered along the Danube River.

Map 1:
The Danube Stationmap TNMN
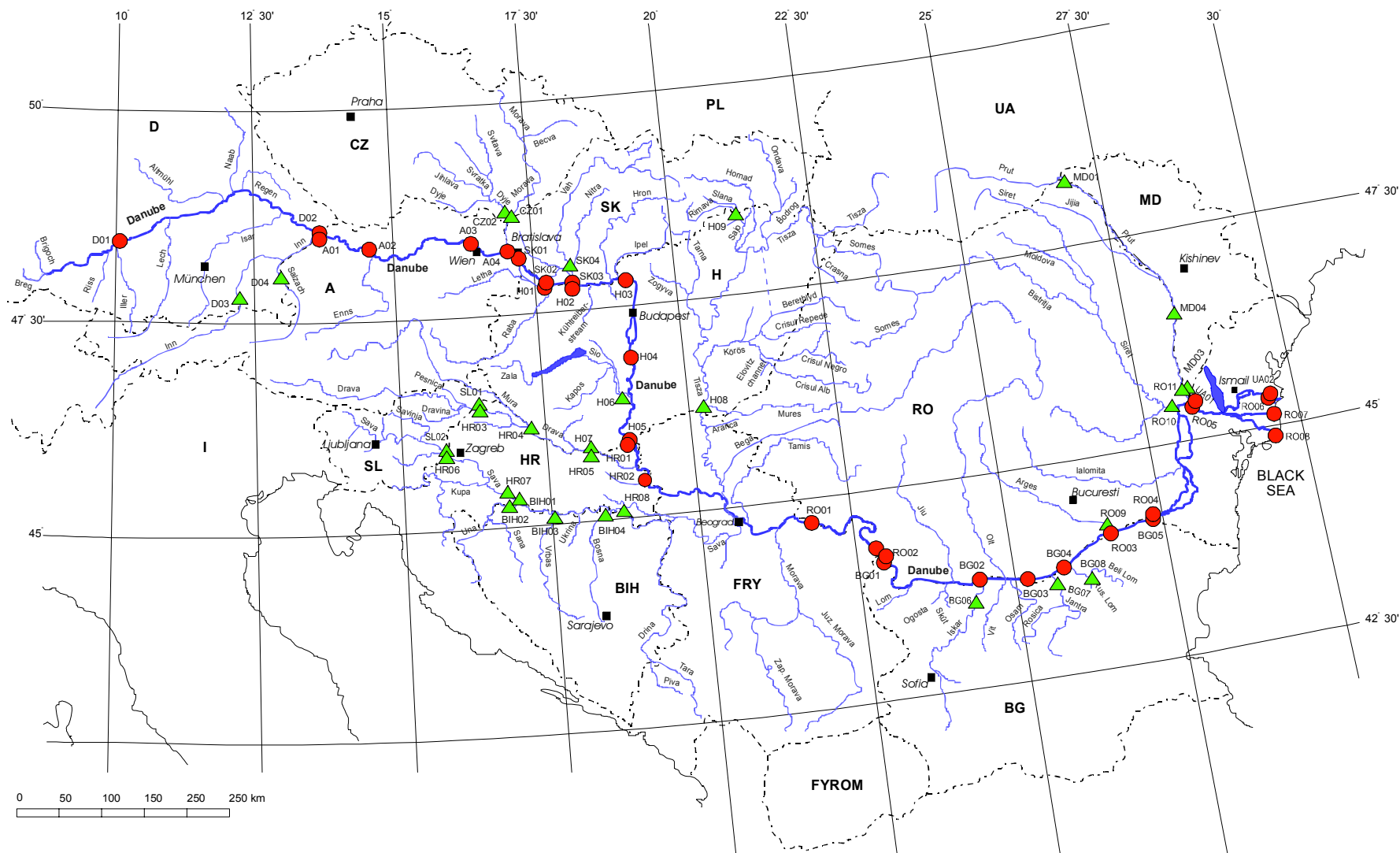
Monitoring location
● on the Danube River
▲ on the tributary

Each monitoring location can have up to three sampling points, located on the left side, right side or in the middle of a river. More than one sampling point was proposed for selected monitoring locations in the middle and lower part of the Danube River and for large tributaries like Tisza and Prut Rivers are. In spite of the fact, that monitoring locations from Bosnia and Herzegovina create a part of the network, no data had been provided from them in evaluated period 1996-2000.

Table 4.2.1: List of monitoring sites.

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance [Km]	Altitude [m]	Catchment [km²]	DEFF Code	Loc.in 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	Pohansko	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	MR
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
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	R
BG03	Danube	Downstream Svishtov	43 37 50	25 21 11	554	16	650340	L0810	MR
BG04	Danube	us. Russe	43 48 06	25 54 45	503	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	44 7 02	27 15 45	375	7	698600	L0850	LMR
BG06	/Iskar	Orechovitza	43 35 57	24 21 56	28	31	8370	L0930	M
BG07	/Jantra	Karantzi	43 22 42	25 40 08	12	32	6860	L0990	M
BG08	/Russ.Lom	Basarbovo	43 46 13	25 57 34	13	22	2800	L1010	M
MD01	/Prut	Lipcani	48 16 0	26 50 0	658	100	8750	L2230	L

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance [Km]	Altitude [m]	Catch-ment [km²]	DEFF Code	Loc.in profile
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 drains through the station	M: Middle of river	
ds.	Downstream of	R: Right bank	
us.	Upstream of		
Conf.	Confluence tributary/main River		
/	Indicates tributary to river in front of the slash. No name in front of the slash means Danube.		

4.3.   Determinands

To be able to fulfil TNMN objectives listed in chapter 4.1, determinands to be measured in monitoring network of Danube River basin should be indicative to human uses, functions of the rivers and problems identified in the river basin. On the other hand, the scope of determinands was limited by available and affordable methods of measurements.

The original determinand list for the first phase of TNMN prepared to reflect also existing EU directives and the riparian countries´ own demands had to be reduced after discussions held in MLIM-SG. The resulting list is given in Tables 5.2.1.1 and 5.2.1.2 for water and sediment phase, respectively. The agreed frequency of measurements for determinands in water was 12 per year and 2 per year for biomonitoring and determinands analysed in sediments.

Sampling and analysis were carried out on the national level, respecting agreed quality system, which is described in more details in the chapter 5.

4.4.   TNMN data management

The primary purpose of data management is to transform raw data to needed information, coming from monitoring objective. The basic assumption for this process is to have got standard procedure for collection, validation, merging, storage, and processing of the data.

The importance of TNMN data management was recognised in very early stage of TNMN operation and well-defined structure for data storage had been prepared. The data are organised in a system of joined tables, containing information related to monitoring locations, determinands, methods of sampling, methods of analysis, remarks and information on taken samples and results of analysis. From 1996, several parts of the database had been modified to adjust the system to the new needs, or to increase efficiency of the system.

The procedure of TNMN data collection starts on a national level of each country. Nominated National Information Managers (NIMs) are responsible for collection of the data from National Reference Laboratories and other national laboratories involved in TNMN, where the data from sampling and analysis are generated. In the next step the NIMs are responsible for data checking, preparation in agreed data exchange file format (DEFF) and sending to the Central Point. Here the data are checked again and suspicious data are consulted with NIMs. After the consultation process the data from TNMN are merged and stored in one relational database for further use.

Collection of TNMN data started in 1996, TNMN data have been regularly collected from Germany, Austria, the Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Bulgaria and Romania. Data from Ukraine and Moldova have been available since 1998.

Basic processing and presentation of the TNMN data is done on a yearly basis in the form of Danube Yearbook, first of which was prepared from 1996 data.

5.   Quality System

5.1.   Introduction

Before 1985, water quality monitoring in the Danube river basin had been carried out independently in the different countries, in several cases as part of bilateral agreements. In 1985, the Bucharest Declaration was the first sign of a basin-wide international cooperation. The gaps in existing knowledge and the problems of the comparability of the monitoring results have been recognized. The Environmental Programme for the Danube River Basin (EPDRB), started in 1991, provided a framework to extend and upgrade the monitoring program. One of the major tasks of the EPDRB was to establish the Trans-National Monitoring Network (TNMN) using accepted methodologies and appropriate quality control. The mission of the established Monitoring, Laboratory and Information Management Expert Group (MLIM-EG), and particularly of its Laboratory Management Working Group (LMWG), included the harmonization of the sampling and analytical methods for use in the TNMN and establishment of an appropriate, effective quality assurance system. In the late 90s, after ratification of the International Convention for the Protection of the Danube River Basin (ICPDR) the water quality/pollution monitoring became one of the important activities, and the monitoring and laboratory experts further improved the operational elements of the TNMN.

The most difficult issue in the monitoring of international rivers is to obtain reliable information, comparable data on the different pollutants. Therefore, implementation of monitoring programmes in international river basins requires harmonization and coordination. Harmonization should be first of all during the design period when target determinands and matrices for monitoring are identified, sampling locations and frequencies, sampling and analytical methodologies, the quality control measures particularly for the analytical quality control (AQC) are selected and agreed.

Evaluation of the quality of the river system, the realistic description of the concentrations and trends of pollution the analytical results should be of the same high quality, irrespective of the laboratory that provided the results. The appropriate operation of the TNMN was an important part of the monitoring strategy ensured throughout harmonization sampling and analytical methodologies, establishment of quality targets and appropriate quality assurance scheme. This was a prerequisite to the proper operation of the monitoring network which includes selected monitoring sites along the Danube and its tributaries. In each country, a National Reference Laboratory (NRL) was nominated and additional national laboratories were involved in the implementation of the TNMN. The LMWG took the responsibility to harmonize the monitoring methodologies and coordinate the AQC among the 11 NRLs and the additional 18 national laboratories.

In addition to the preparation of Standard Operational Procedures (SOPs) to be followed during sample collection and analysis, the quality assurance program in the Danube river basin laboratories included: (a) recommendations for similar laboratory facilities, (b) provision of necessary analytical instrumentation in the laboratories, (c) implementation of integrated training programs, and (d) proficiency testing carried out in interlaboratory comparison studies.

The implementation plan for the TNMN was prepared and agreed. This included provision of sampling equipment and analytical instruments for the eligible countries from the EU PHARE programme. As far as the laboratory work is concerned, harmonization of the related activities, coordinated by the LMWG of MLIM-EG, included:

- Selection of determinands and matrices for the TNMN in the Danube river basin;
- Selection of appropriate sampling and sample handling procedures for water, sediment and biota;
- Selection of reference and optional analytical methods for determination of the identified physical, chemical, radiochemical, biological and microbiological determinands;
- Establishment of the AQC, performance testing system;
- Regular revision of the methodologies;

- Harmonization of laboratory facilities, instrumentation;
- Identification of training needs and implementation; and
- Co-ordination of the laboratory work through regular meetings of the National Reference Laboratories.

During 1998-2000, in the frame of the EU supported projects on "Water Quality Enhancement in the Danube River Basin" and "Strengthening Capabilities in the Danube River Basin" significant efforts were devoted to the development of the quality assurance elements of the Danube TNMN. In the second project, the Volume 2 of the Guidance Notes dealt with all quality assurance issues pertaining to the sampling, sample preparation and analysis of TNMN determinands.

5.2.   Quality Assurance in Water Quality Data Collection

The measurement cycle for the implementation of the monitoring starts with the collection of samples and closes with reporting the analytical results and the reliability of the results depends on the effectiveness of the quality assurance as shown in Fig. 5.2.1.
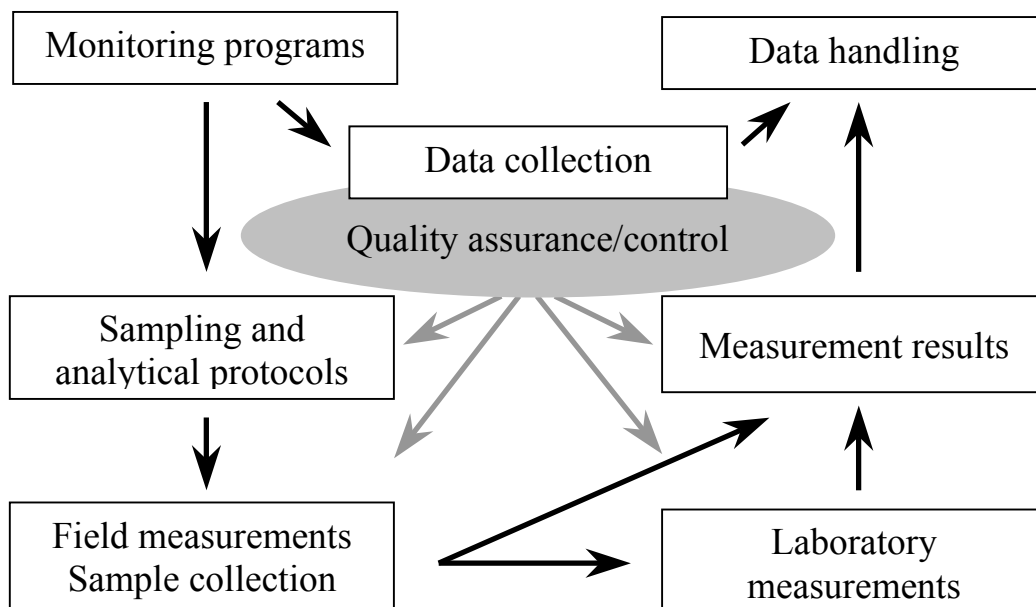
Fig. 5.2.1. Quality assurance/control in the data collection/measurement cycle

Quality assurance/control in monitoring programme design as well as in the data handling is considered in the relevant chapters of this review report. Here, major emphasise is given to the laboratory work, particularly to the analytical quality control.

5.2.1.   Quality and Accuracy Targets

Water/sediment quality targets, objectives and standards are set to evaluate the quality of the water resources, both surface and subsurface water bodies, to characterise chemical and ecological status (for surface waters) and to establish satisfactory condition for intended uses of the aquifer. The laboratory data define whether that condition is being met, and whether the water is at acceptable quality to fit for the purpose. If the laboratory results indicate a violation of the standard, action is required by the pollution control authorities. The analyst must be aware that his professional

competence, the procedures he has used, and the reported values are reliable and may be used with confidence.

The approach adopted in proposing the analytical accuracy targets for monitoring the quality of water (Table 5.2.1.1) and sediment (Table 5.2.1.2) in the Danube river basin is summarized as follows:

- Two key concentration levels have been defined for each determinand. These are: (i) the lowest level likely to be encountered in the waters / sediments of interest (**the minimum level of interest**); and (ii) the concentration which represents the likely level   at which most monitoring (for example, for the assessment of trends or compliance with water quality standards) will be carried out (**the principal level of interest**). These levels define the aims of the program; they can be used to establish the performance needed from analytical systems used in the laboratories.

- It is then assumed that the aims of the program will be satisfied provided: (i) that relatively few results are reported as "less than" the minimum level and (ii) that the accuracy achieved at the principal level is not worse than ± 20% of the principal level. This assumption has been tested in a wide range of environmental monitoring laboratories. Experience suggests that it is usually appropriate to set a required limit of detection which is at least one tenth of the principal level of interest. A subsidiary aim is that the limit of detection should be at least one third of the minimum level of interest.

- Any practical approach to monitoring must take into account the current capabilities of analytical science. This means that if some targets are recognized 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 program.

5.2.2.   Analytical Methodologies

The analytical methodologies for the determinands applied in TNMN are based on a list containing reference and optional analytical methods. The National Reference Laboratories (NRLs) have been provided with a set of ISO standards (reference methods) reflecting the determinand lists, but taking into account the current practice in environmental analytical methodology in the EU. It has been decided not to require each laboratory to use the same method, providing the laboratory would be able to demonstrate that the method in use (optional method) meets the required performance criteria. Therefore, the minimum concentrations expected and the tolerance required of actual measurements have been defined for each determinand (as reported in Tables 5.2.1.1 and 5.2.2.2), in order to enable laboratories to determine whether the analytical methods currently in use are acceptable.

Table 5.2.1.1: Accuracy targets of water quality variables selected for the TNMN

DETERMINANDS in Water	Level of Interest		Analytical Accuracy Targets	
	Minimum likely (Note 1)	Principal (Note 2)	Limit of Detection (Note 3)	Tolerance (Note 4)
Physical, Chemical Parameters				
Temperature, °C	-	0-25	-	0.1 °C
Suspended Solids, mg/l	1	10	*1*	*1mg/l or 20%*
Dissolved Oxygen, mg/l	0.5	5	0.2	0.2 or 10%
pH	-	7.5	-	0.1
Conductivity µS/cm, @ 20°C	30	300	5	5 or 10%
Alkalinity, mmol/l	1	10	0.1	0.1
Chloride, mg/l	5	50	1	1 or 10%
Sulphate, as SO_4 mg/l	5	50	5	5 or 20%
Nutrients				
Ammonium (NH_4) as N mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO_2) as N mg/l	0.005	0.02	*0.005*	*0.005 or 20%*
Nitrate (NO_3) as N mg/l	0.2	1	0.1	0.1 or 20%
Organic Nitrogen as N mg/l	0.2	2	0.1	0.1 or 20%
Total - Nitrogen as N mg/l	0.2	2	0.5	0.5

DETERMINANDS in Water	Level of Interest		Analytical Accuracy Targets	
	Minimum likely (Note 1)	Principal (Note 2)	Limit of Detection (Note 3)	Tolerance (Note 4)
Orthophosphates (PO_4) as P mg/l	0.02	0.2	0.005	0.005 or 20%
Total Phosphorus as P mg/l	0.05	0.5	0.01	0.01 or 20%
Elements (Metals)				
Sodium mg/l	1	10	0.1	0.1 or 10%
Potassium mg/l	0.5	5	0.1	0.1 or 10%
Calcium mg/l	2	20	0.2	0.1 or 10%
Magnesium mg/l	0.5	5	0.1	0.2 or 10%
Iron mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc mg/l	0.01	0.1	0.003	0.003 or 20%
Copper mg/l	0.01	0.1	0.003	0.003 or 20%
Chromium mg/l	0.01	0.1	0.003	0.003 or 20%
Lead mg/l	0.01	0.1	0.003	0.003 or 20%
Cadmium mg/l	0.001	0.01	*0.0005*	*0.0005 or 20%*
Mercury mg/l	0.001	0.01	0.0003	0.0003 or 20%
Nickel mg/l	0.01	0.1	0.003	0.003 or 20%
Arsenic mg/l	0.01	0.1	0.003	0.003 or 20%
Aluminium mg/l	0.01	0.1	*0.01*	*0.01 or 20%*
Organic Components				
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	3	*0.3*	*0.3 or 20%*
Phenol index, mg/l	0.005	0.05	*0.005*	*0.005 or 20%*
Anionic 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 or30%
pp'DDT, µg/l	0.05	0.5	0.01	0.01 or30%
Atrazine, µg/l	0.1	1	0.02	0.02 or30%
Chloroform, µg/l	0.1	1	0.02	0.02 or30%
Carbontetrachloride, µg/l	0.1	1	0.02	0.02 or30%
Trichloroethylene, µg/l	0.1	1	0.02	0.02 or30%
Tetrachloroethylene, µg/l	0.1	1	0.02	0.02 or30%

Table 5.2.1.2. Accuracy targets of sediment quality variables selected for the TNMN

DETERMINANDS in Sediment	Level of Interest		Analytical Accuracy Targets (for <63 μm size fraction)	
	Minimum likely (Note 1)	Principal (Note 2)	Limit of Detection (Note 3)	Tolerance (Note 4)
Elements				
Organic Nitrogen, mg/kg	50	500	10	10 or 20%
Total Phosphorus, mg/kg	50	500	10	10 or 20%
Calcium, mg/kg	1000	10000	300	300 or 20%
Magnesium, mg/kg	1000	10000	300	300 or 20%
Iron, mg/kg	50	500	20	20 or 20%
Manganese, mg/kg	50	500	20	20 or 20%
Zinc, mg/kg	250	500	50	50 or 20%
Copper, mg/kg	2	20	*1*	*1 or 20%*
Chromium, mg/kg	2	20	*1*	*1 or 20 %*
Lead, mg/kg	2	20	*1*	*1 or 20 %*
Cadmium, mg/kg	0.05	0.5	*0.05*	*0.05 or 20%*
Mercury, mg/kg	0.05	0.5	0.01	0.01 or 20%
Nickel, mg/kg	2	20	*1*	*1 or 20 %*
Arsenic, mg/kg	2	20	*1*	*1 or 20 %*
Aluminium, mg/kg	50	500	*50*	*50 or 20%*
Organic pollutants				
TOC, mg/kg	50000	500000	10000	10000 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%
PCBs - 7 (each), mg/kg	0.01	0.1	0.003	0.003 or 30%

Note 1 - The minimum likely level of interest is the lowest concentration considered likely to be encountered or important in the Danube monitoring program.

Note 2 - The principal level of interest is the concentration at which it is anticipated that most monitoring will be carried out.

Note 3 - The required limit of detection is the target limit of detection (LD) 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. (N.B. Where the performance of current analyses is not likely to meet the criterion of a LD of one third if the lowest level of interest, the LD has been revised to reflect best practice. In these cases, the targets have been entered in italics).

Note 4 - The tolerance indicates the largest allowable analytical error which is consistent with the correct interpretation of the data and with current analytical practice. The target is expressed as "x concentration units or P%". The larger of the two values applies for any given concentration. For example, if the target is 5 mg/l or 20% - at a concentration of 20 mg/l the maximum tolerable error is 5 mg/l (20% is 4 mg/l); at a concentration of 100 mg/l, the tolerable error is 20 mg/l (i.e. 20%) because this value exceeds the fixed target of 5 mg/l.

5.3.   Performance testing in the Danubian laboratories

As part of the AQC, a performance testing scheme under the name of *QualcoDanube* has been established and implemented as the primary inter-laboratory quality control program in the Danube basin, started in 1993 with the participation of the laboratories involved in the Danube water quality monitoring in the framework of the Bucharest Declaration. In 1995, it was extended, in the frame of the TNMN, to the 11 National Reference Laboratories and in 1996 to another 19 national laboratories within the Danube river basin implementing the TNMN. Since 1996, the *QualcoDanube* performance testing intercalibration results demonstrate significant improvement.

5.3.1.   Perspectives of Proficiency Testing

One of the most important parts of the sustainable AQC is the design of an organisational structure for proficiency testing that can ensure continuity of analytical quality control in the Danube TNMN and the following points had to be considered: (a) the determinands of interest and type of matrix, (b) the level of concentration of determinands, (c) sample preparation, (d) analysis and reporting, and (e) evaluation of the results.

The key agreed requirements for the performance testing scheme are as follows:
- The sample should be considered to be adequately representative of a real test material. Determinands and matrix depend on parameters and sample type analysed routinely by the laboratories of Danube River Basin. Care needs to be taken to ensure that no sample is lost during shipment and that the sample is well homogenised.
- Concentration level of determinands depends on parameters and sample type analysed routinely by the laboratories in the Danube river basin. In the case of real surface water, sediment samples or biota, concentration range is limited. In other cases (e.g., synthetic sample) concentrations vary depending on the target level of contamination.
- The number of samples should be sufficient to distribute sample-pairs according to the Youden-technique, to each of the 29 TNMN implementing laboratories. As it is anticipated that other laboratories in Danubian countries should have the opportunity to take advantage of the respective performance testing exercises, an additional sample set should be prepared per material.
- Sampling should ideally be at a frequency of four-times per year according to the distribution schedule. Samples should be accompanied with clear instructions on the procedures for the PT analysis and the reporting procedure.
- The results reported back from the analytical laboratories should be evaluated and fed back to the laboratories within two weeks. Laboratories are identified by code numbers.

The sample preparation, distribution and evaluation schemes of the performance testing is demonstrated in Fig. 5.3.1.1. Laboratories receive selected well homogenized environmental samples for analysis. The reported analytical results are compared with the assigned reference values.

The test materials to be distributed in the scheme must be similar to the materials that are routinely analysed (in respect of composition of the matrix and the concentration range or quality of the determinand) including the type of samples as follows:
- synthetic water samples as concentrate-pairs (according to the Youden-technique),
- real-world water and sediment samples and their spikes ensuring sample-pairs again according to the Youden-technique,

reference materials (water and sediment). Sediment references materials shall be prepared from samples collected at different representative sites in the Danube river basin in a relatively large quantity allowing to use these samples for internal quality control as in-house RM.

```
┌─────────────────────────────────────────────┐
│        Selection of Determinands and Matrix  │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│          Preparation of AQC Samples          │
└─────────────────────────────────────────────┘
      ↓                  ↓                  ↓
┌──────────────┐  ┌──────────────┐  ┌──────────────┐
│  Synthetic   │  │ Real-world   │  │  In-house RM │
│   Sample     │  │   Sample     │  │(concentrate/ │
│(concentrate) │  │(water/       │  │  sediment)   │
│              │  │ sediment)    │  │              │
└──────────────┘  └──────────────┘  └──────────────┘
      │                  ↓                  ↓
      │           ┌────────────────────────────────┐
      │           │        Homogenisation          │
      │           │    (testing homogeneity)       │
      │           └────────────────────────────────┘
      ↓                  ↓                  ↓
┌─────────────────────────────────────────────┐
│           Distribution of Samples            │
│   Sending Samples According to Schedule      │
│    Requesting Results by Strict Deadline     │
└─────────────────────────────────────────────┘
   ↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓↓
┌─────────────────────────────────────────────┐
│          Evaluation of the Results           │
│        (e.g. Youden-pairs, Z-score)          │
└─────────────────────────────────────────────┘
      ↓                  ↓                  ↓
┌──────────────┐  ┌──────────────┐  ┌──────────────┐
│   Evaluate   │  │   Evaluate   │  │  Assigned    │
│  Laboratory  │  │   Method     │  │ Values for   │
│ Performance  │  │ Performance  │  │  Reference   │
│              │  │              │  │  Material    │
└──────────────┘  └──────────────┘  └──────────────┘
┌─────────────────────────────────────────────┐
│                 Follow-up                    │
│          (actions, utilization)              │
└─────────────────────────────────────────────┘
      ↓                  ↓                  ↓
┌──────────────┐  ┌──────────────┐  ┌──────────────┐
│   Initiate   │  │   Method     │  │  In-house    │
│  Actions if  │  │ Modification │  │  Reference   │
│ Performance  │  │or Replacement│  │  Material    │
│  is Poor     │  │  if Needed   │  │ Available    │
│              │  │              │  │  for AQC     │
└──────────────┘  └──────────────┘  └──────────────┘
```

Figure 5.3.1.1: Sample preparation and evaluation scheme for AQC in the Danube river basin

5.3.2. QualcoDanube, AQC in Water Labs in the Danube River Basin

The organisation of interlaboratory comparison in the Bucharest Declaration Danube monitoring was agreed in 1992. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered and took the responsibility for organising the first study under the name of QualcoDanube. The first distribution in 1993 included samples for the analysis of three determinands: pH, conductivity and total hardness. By the end of 1995, four more distributions had been made for the analysis of the following determinands: chlorides, COD, nutrients (ammonium, nitrate, Kjeldahl-nitrogen, orthophosphate and total-P) as well as different metals, including Fe, Mn, Ca, Mg, Cd, Cu, Hg, Pb, Ni, Zn.

In 1996 the QualcoDanube proficiency testing scheme was extended to the National Reference Laboratories (NRL) in the Trans-National Monitoring Network (TNMN) and the 1996/2 distribution already included all Danubian laboratories - 11 NRLs and 18 national laboratories - implementing the

TNMN. This distribution was further extended to 6 Black Sea laboratories responsible for pollution monitoring in their area.

Since 1996 QualcoDanube check samples are distributed quarterly in each year.

5.3.3. Other Proficiency Testing Schemes

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

5.4. Main achievements

The described approach supports the work of harmonising the analytical activities within the Danube Basin related to the TNMN as well as the implementation and operation of an Analytical Quality Control (AQC) programme. Therefore, it has been used in development of the training needs required to improve the laboratory performance of the National Reference Laboratories as well as the other laboratories involved in the implementation of the TNMN. The result is that managers and personnel of the involved laboratories have been provided with practical training for analytical instrumentation and on-site sampling as well as with theoretical aspects of AQC.

Interlaboratory studies - organized regularly - help to improve analytical performances because the participants can review their own performance concerning the accuracy of the analytical results and where necessary, investigate the sources of error and take corrective actions.

5.4.1. Lessons learnd from the 5 year QA/QC Activies

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

Since the start of the QualcoDanube AQC programme nutrients were included in several distributions and therefore it was possible to assess the quality improvement in the analytical work by comparing the performance during the different distributions.

The results in **1996** showed the quality improvement in most of the determinands. Although the number of laboratories during the first distributions was almost one third of the other distributions the performance significantly improved during the study period, particularly in the case of Nitrate-N. Variation in the Orthophosphate-P and the Total-P was significant, therefore, improvement is needed before the monitoring data of these determinands could be considered reliable in the entire Danube basin. The results of the heavy metal analysis were promising because with very few exceptions they were within an acceptable range.

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

Most of the data provided by the laboratories during the **1997** QualcoDanube intercalibration study were satisfactory, when comparing to error thresholds.

While the results in 1996 showed the quality improvement in most of the determinands, further improvement could not be observed in 1997. The performance for the general parameters was

satisfactory. Some problems arose due to stability of the samples (e.g. MBAS, PO$_4$-P) and a relatively long analysis time which can influence the variation between results. In the case of metals different digestion methods were used and there were some problems for less commonly measured metals (e.g. Hg, As) and at low concentration level (e.g. Cd, Ni, Pb).

In **1998**, the analytical results of synthetic samples were better than results of real water samples. In the latter case, due to matrix effect, results were influenced by both systematic and random errors, while systematic error characterized mainly the results of the synthetic samples. Among the nutrients Kjeldahl-N (1998/2) and among the organic pollutants the Chemical Oxygen Demand with dichromate method (1998/1) were analysed. In general, the results of the metals were satisfactory, especially of zinc, and only the results of mercury were scattered. Similarly to the real water samples, the results of the sediment samples were also influenced by both random and systematic errors.

In addition to regularly analysed determinands, distributions in **1999** included specific trace 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 were poor, unsatisfactory together with the results of petroleum hydrocarbons in both water and sediment. In the case of water samples solvent extracts were distributed so the discrepancies in the results most likely originated from incorrect analyses and/or unsuitable analytical methods.

In **2000**, the analytical results of synthetic samples were again better than results obtained from real water samples. Results of general determinands, nutrients in synthetic samples and metals were relatively good, but results of nutrients in real water samples were influenced by significant systematic error and slight random error. Analysis of organic compounds proved to be a field requiring improvement, especially of micropollutants, in case of which the performance was not sufficient.

In summary, there was significant quality improvement in most of the determinands during the five years. For further improvement more attention should be paid particularly to:
- the distributed samples were preserved (regularly by acid and/or by sterilization 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 determination of metals, particularly in sediment, the reason for discrepancies could be the different way of mineralization, or systematic errors during analyses.
- Most of the measurements were influenced by systematic error which is calling for more attention in the sample preparation and calibrations.
- There were some laboratories which regularly reported outlying results for certain determinands. They should pay attention to the whole process of analysis of these determinands (analytical method, standard materials, etc.).

5.4.2. Need for continuation of interlaboratory comparison studies

Intercalibration studies organised regularly present 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 the analytical results and, where necessary, investigate the sources of error and take corrective actions.

It is expected that performance of laboratories analysing samples in the frame of TNMN will further improve and the comparability of the water quality monitoring results in the river basin and related regions will be ensured. To achieve this goal regular performance testing and the continuation of the interlaboratory comparison studies are of paramount importance.

6.   Five Years of Monitoring – a Statistical Overview

Over the five years period the number of sampling sites where data have been provided has increased from 75 (1996) to 81 (2000). Most of the sites have been maintained – only a few sites were shifted from one river side to another: BG03 from middle to right, HR08 from right to middle, HR06 from right to left.

The amount of investigations differs, not all determinands were analysed at all monitoring sites. Table 6.1 gives an overview on the number of monitoring sites where data of a specific determinand is available. Comparing the years an upward trend can be stated. At the same time the number of samples per year increased. As an example, in Fig. 6.1 the percentage of sites with the number of nitrate measurements in 1996-2000 is shown.

However, there are big differences regarding the determinands. As to basic descripters, currently many samples are taken but for specific organic pollutants the number of samples is still very low. Seasonal fluctuations and particular situations like flood events or algae blooms can not be detected and for this reason data processing and data interpretation is rather limited for several determinands.

Fig.6.1: Nitrate – percentage of sites with number of measurements per year.
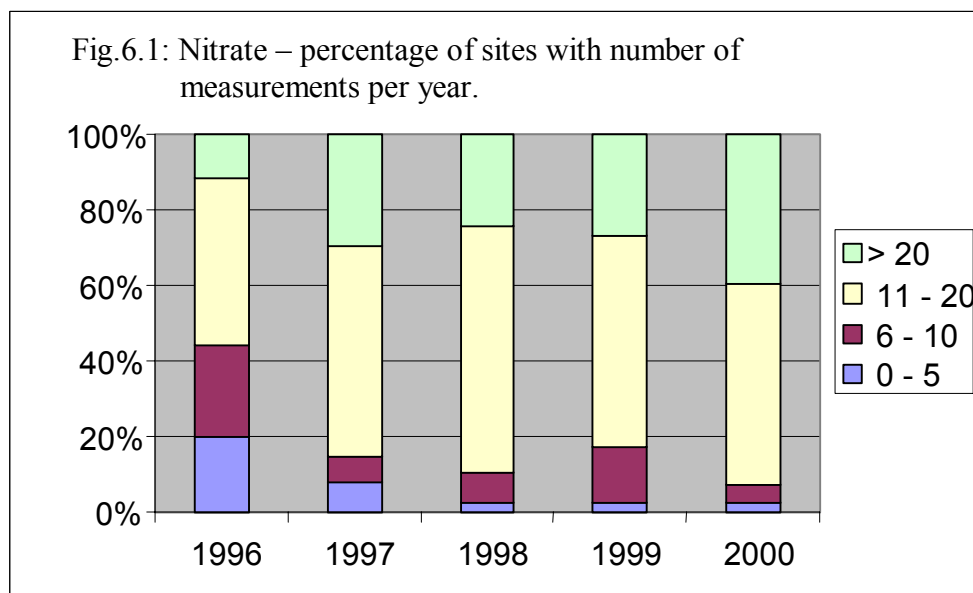
Concerning analytical methods changes over time have been reported for every data delivery. Frequently these changes have been affected the detection limit. This has to be beared in mind when processing the data of determinands, which usually occur in low concentrations. For the five-years period table 6.2 shows the overall range of detection limits reported by countries, which are stored in the TNMN database.

Table 6.1: Number of monitoring sites where data are available

Determinand	Number of monitoring sites				
	1996	1997	1998	1999	2000
Basic Descriptors					
Water temperature					
Dissolved oxygen [*]	74	75	77	81	71
Conductivity	72	74	71	75	77
Suspended solids	66	74	74	81	81
pH	74	75	77	81	81
Alkalinity	62	67	71	75	80
Nutrient regime					
Ammonium-N	70	75	77	81	81
Nitrite-N	71	76	76	79	79
Nitrate-N	75	75	77	81	81
Organic N	29	24	22	33	34
Total-N					4
Ortho-phosphate-P	72	74	75	76	69
Total-P	65	66	67	79	78
Chlorophyll-a					
Pollution indicators					
BOD_5	73	71	77	81	82
COD_{Mn}	72	74	74	78	78
COD_{Cr}	64	70	73	77	79
AOX	8	8	23	22	14
Heavy Metals (total)					
Zinc	70	70	73	73	77
Copper	70	70	73	73	77
Chromium (Cr-III+VI)	64	65	68	68	68
Lead	66	69	68	68	74
Cadmium	65	66	66	68	74
Mercury	52	34	33	29	35
Nickel	69	42	42	63	74
Arsenic	29	30	31	31	39
Manganese	67	71	71	75	68
Iron	68	73	74	80	70
Toxic substances					
Lindane	28	51	56	66	69
p,p´-DDT	28	47	59	66	69
Atrazine	37	27	28	36	62
Trichloromethane	9	15	23	28	29
Tetrachloromethane	9	15	23	28	29
Trichloroethene	9	15	23	28	27
Tetrachloroethene	9	15	23	28	27
PAL A	29	53	73	73	77
NES	28	37	44	48	51

Table 6.2: Range of detection limits in 1996-2000, reported by countries.

Determinands	Range of detection limits 1996-2000 (all monitoring sites)	Units
Basic Descriptors		
Suspended solids	0,2 - 10	mg.l^{-1}
Alkalinity	0,01 - 0,4	mmol.l^{-1}
Ca	0,003 - 10	mg.l^{-1}
Mg	0,0005 – 5	mg.l^{-1}
Na	0,005 – 1,0	mg.l^{-1}
K	0,005 – 1,0	mg.l^{-1}
Nutrient regime		
Ammonium-N	0,008 - 0,05	mg.l^{-1}
Nitrite-N	0,001 - 0,02	mg.l^{-1}
Nitrate-N	0,002 - 1	mg.l^{-1}
Organic N	0,05 - 1	mg.l^{-1}
Total-N	0,2	mg.l^{-1}
Ortho-phosphate-P	0,003 - 0,05	mg.l^{-1}
Total-P	0,005 - 0,05	mg.l^{-1}
Pollution indicators		
BOD$_5$	0,01 - 1	mg.l^{-1}
COD$_{Mn}$	0,01 - 0,8	mg.l^{-1}
COD$_{Cr}$	0,01 - 15	mg.l^{-1}
AOX	0,01 - 10	µg.l^{-1}
Heavy Metals (total)		
Zinc	0,003 - 20	µg.l^{-1}
Copper	0,003 - 3	µg.l^{-1}
Chromium (Cr-III+VI)	0,03 - 10	µg.l^{-1}
Lead	0,003 - 2	µg.l^{-1}
Cadmium	0,01 - 5	µg.l^{-1}
Mercury	0,01 - 3	µg.l^{-1}
Nickel	0,003 - 2,5	µg.l^{-1}
Arsenic	0,02 - 2	µg.l^{-1}
Manganese	0,00001 - 0,5	mg.l^{-1}
Iron	0,00002 - 0,2	mg.l^{-1}
Toxic substances		
Lindane	0,001 - 0,1	µg.l^{-1}
p,p´-DDT	0,001 - 0,05	µg.l^{-1}
Atrazine	0,001 - 1	µg.l^{-1}
Trichloromethane	0,01 - 1	µg.l^{-1}
Tetrachloromethane	0,01 - 1	µg.l^{-1}
Trichloroethene	0,01 - 1	µg.l^{-1}
Tetrachloroethene	0,01 - 1	µg.l^{-1}
PAL A	0,005 - 0,1	mg.l^{-1}
NES	0,005 - 0,2	mg.l^{-1}

7.   Description of Methodology of Assessment in the Report

Reffering to objectives of the report, there is a need to obtain information on water quality in the Danube River and its main tributaries based on data from five-years joint monitoring of Danubian states. The questions regarding the water quality, its compliance with set up target values, spatial changes along the river and questions whether and where the water quality is improving or deteriorating, are of concern for not only decision makers, but also for public.

Assessment in the report consists of several parts:

· classification of surface water quality in accordance to classification system developed for TNMN, methodology of which is described in chapter 7.1.;
· assessment of spatial changes and trend assessment of physico-chemical determinands, approach for which is described in chapter 7.2 and 7.3, respectively;
· assessment of biological determinands measured in TNMN, for which methodology described in chapter 7.4.;
· assessment of dangerous substances content in waters in accordance to Environmental Quality Standards established or proposed for use in EU, methodology of which is described in chapter 7.5.

7.1.   Water Quality Classification

The first attempt to come up with proposal of joint water quality classification for Danube river basin had been done in 1997 by PHARE Applied Research Project EU/AR/203/91 "Water Quality Targets and Objectives for Surface Waters in the Danube basin" (WRRC, Vituki, Plc., 1997).
The proposed classification has not been applied for evaluation of results from TNMN, it was only partly used by means of using its limit values for illustration of BOD_5, PO_4^{3-}-P and NO_3^--N concentrations on the maps in the TNMN-Yearbooks 1996-2000.

In 1999 the EU PHARE Programme contributed to the EPDRB by initiating the project "Danube River Basin Water Quality Enhancement". One of its objectives was to make a proposal for a unified water quality classification for the entire Danube River basin region based on
  ▪ review of existing water quality and sediment quality classification methods in Danubian countries
  ▪ review of EU legislation
  ▪ experience within the different countries

The activity was realised by IWACO BV Consultants for water and environment in Rotterdam. Although the attention was given to Water Famework Directive (WFD) (at that time still under preparation), it was concluded that to come to ecologically based and regionally differentiated water quality criteria according to WFD in Danube River Basin will take considerable effort and time. In the meantime interim water quality classification scheme had been proposed. This proposal was further discussed and adjusted by Monitoring, Laboratory and Information Management Sub-Group and approved finally in 2001.

The classification scheme as presented in Table 7.1.1 is meant to serve international purposes for the presentation of current status and improvements of water quality in Danube river and its main tributaries and is not to be a tool for implementation of a national water policy.
Five classes are used for assessment, with target value being the limit value of class II. The class I should represent reference conditions or background concentrations. For number of determinands it was not possible to establish real reference values due to existence of many types of water bodies in Danube river basin differing in its physico-chemical characteristics naturally. For synthetic substances the detection limit or minimal likely level of interest was chosen as limit value for class I.

The classes III – V are on the "non-complying" side of the classification scheme and their limit values are usually 2-5-times the target values. They should indicate the seriousness of the exceedance of the target value and help to recognise the positive tendency in water quality development.

For compliance testing 90-perentile value of at least 11 measurements in a particular year is used.

Table 7.1.1: Water Quality Classification used for for TNMN purposes.

Determinand	Unit	Class				
		I	II TV	III	IV	V
		Class limit values				
Oxygen/Nutrient regime						
Dissolved oxygen [*]	mg.l^{-1}	7	6	5	4	< 4
BOD$_5$	mg.l^{-1}	3	5	10	25	> 25
COD$_{Mn}$	mg.l^{-1}	5	10	20	50	> 50
COD$_{Cr}$	mg.l^{-1}	10	25	50	125	> 125
pH	-		> 6.5[*] and < 8.5			
Ammonium-N	mg.l^{-1}	0.2	0.3	0.6	1.5	> 1.5
Nitrite-N	mg.l^{-1}	0.01	0.06	0.12	0.3	> 0.3
Nitrate-N	mg.l^{-1}	1	3	6	15	> 15
Total-N	mg.l^{-1}	1.5	4	8	20	> 20
Ortho-phosphate-P	mg.l^{-1}	0.05	0.1	0.2	0.5	> 0.5
Total-P	mg.l^{-1}	0.1	0.2	0.4	1	> 1
Chlorophyll-a	µg.l^{-1}	25	50	100	250	> 250
Metals (dissolved) [**]						
Zinc	µg.l^{-1}	-	5	-	-	-
Copper	µg.l^{-1}	-	2	-	-	-
Chromium (Cr-III+VI)	µg.l^{-1}	-	2	-	-	-
Lead	µg.l^{-1}	-	1	-	-	-
Cadmium	µg.l^{-1}	-	0.1	-	-	-
Mercury	µg.l^{-1}	-	0.1	-	-	-
Nickel	µg.l^{-1}	-	1	-	-	-
Arsenic	µg.l^{-1}	-	1	-	-	-
Metals (total)						
Zinc	µg.l^{-1}	bg	100	200	500	> 500
Copper	µg.l^{-1}	bg	20	40	100	> 100
Chromium (Cr-III+VI)	µg.l^{-1}	bg	50	100	250	> 250
Lead	µg.l^{-1}	bg	5	10	25	> 25
Cadmium	µg.l^{-1}	bg	1	2	5	> 5
Mercury	µg.l^{-1}	bg	0.1	0.2	0.5	> 0.5
Nickel	µg.l^{-1}	bg	50	100	250	> 250
Arsenic	µg.l^{-1}	bg	5	10	25	> 25
Toxic substances						
AOX	µg.l^{-1}	10	50	100	250	> 250
Lindane	µg.l^{-1}	0.05	0.1	0.2	0.5	> 0.5
p,p´-DDT	µg.l^{-1}	0.001	0.01	0.02	0.05	> 0.05
Atrazine	µg.l^{-1}	0.02	0.1	0.2	0.5	> 0.5
Trichloromethane	µg.l^{-1}	0.02	0.6	1.2	1.8	> 1.8
Tetrachloromethane	µg.l^{-1}	0.02	1	2	5	> 5
Trichloroethene	µg.l^{-1}	0.02	1	2	5	> 5
Tetrachloroethene	µg.l^{-1}	0.02	1	2	5	> 5
Biology						
Saprobic index - macrozoobenthos	-	≤ 1.8	1.81 – 2.3	2.31 – 2.7	2.71 – 3.2	> 3.2

[*]   values concern 10-percentile value   bg   background values
[**]   for dissolved metals only guideline values are indicated   TV   target value

For the purpose of classification, the data 1996-2000 had been processed and are presented in tables of Annex 1. The classification scheme originally covers 37 determinands, out of which 29 are presented in the report. The tables showing results of each determinand are sequenced in the Annex in the same order as determinands in the classification scheme, given in Table 7.1.1. The group of metals in dissolved phase is missing because number of available data in evaluated period 1996-2000 is not sufficient to provide representative picture along the Danube River. Similarly in case of some other determinands, like are AOX and volatile hydrocarbons there are parts of Danube River basin covered rather sparsely.

The results of classification are given in tables prepared separately for each water quality determinand. The rows of tables present sampling points, ordered in a way as they occur in a reality from the most upper sampling point in Germany down to the mouth to Black Sea. *Italic letters* used for name of river and location indicate tributaries.

Results characterising each year in a period from 1996-2000 are given in columns of tables. Both calculated mean annual value and so-called "testing value" are given in a cell for each sampling site in a year. Testing value was equal to 90 %-ile (10 %-ile for dissolved oxygen and lower limit of pH value), if number of measurements in a year was at least eleven. If number of measurements in a year was lower than eleven, the testing value was represented by maximum value from a data set (a minimum value for dissolved oxygen and a lower limit of pH value).
Water quality classes in sampling points for each year were expressed by using the following colours:

blue colour	class I
green colour	class II
yellow colour	class III
orange colour	class IV
red colour	class V

It happened in some cases (Cd, Hg, p,p′ DDT, atrazine, trichloromethane) that limit of detection used by country was higher than limit value for class II, representing the target value. In these cases only statistics was calculated and presented in a table, but classification has not been done.

An agreed frequency of measurements has not always been kept in monitoring programme. Using blue colour for figures presenting the statistical haracteristics in tables of Annex 1 expresses those results of classification, which are based on very few (less than three) measurements and therefore are not sufficiently reliable. An exception is saprobic index of macrozoobenthos, in case of which agreed frequency of measurements is two times per year.

7.2.   Assessment of spatial changes of physico-chemical determinands

In each profile of the river the water quality reflects the effects of both natural and antropogenic origin. In accordance to the type and extent of these processes water is differently affected in particular sections along the river. To indicate the changes between locations or sections of the river, visualisation by using the charts for each evaluated determinand is provided in the report. Where it is relevant, the charts are also accomplished by target value indication for respective determinands, providing also visualisation of the distance of real situation from this value.

In assessment ofspatial changes in water quality 57 monitoring stations are included, out of which 31 sites are located on the main course of the Danube River and 26 on the first and second tributaries. They are illustrated in Table 7.2.1. in the order of their occurrence along the Danube River. This order was also used in graphical presentations illustrating situation along the river.

Table 7.2.1: List of Monitoring Sites located on the Danube River and its tributaries.

Country Code	River	Town/Location	Distance (km)	River km	Location in Profile	Section
D01	Danube	Neu-Ulm	2581	2581	L	UPPER
D03	/ Inn	Kirchdorf	195	/ 2225	M	
D04	/ Inn / Salzach	Laufen	47	-	M	
D02	Danube	Jochenstein	2204	2204	M	
A01	Danube	Jochenstein	2204	2204	M	
A02	Danube	Abwinden-Asten	2120	2120	R	
A03	Danube	Wien-Nussdorf	1935	1935	R	
CZ01	/ Morava	Lanzhot	79	/ 1880	R	
CZ02	/ Morava / Dyje	Breclav	17	-	R	
A04	Danube	Wolfsthal	1874	1874	R	
SK01	Danube	Bratislava	1869	1869	M	MIDDLE
SK02	Danube	Medvedov/Medve	1806	1806	M	
H01	Danube	Medve/Medvedov	1806	1806	M	
SK03	Danube	Komarno/Komarom	1768	1768	M	
H02	Danube	Komarom/Komarno	1768	1768	M	
SK04	/ Vah	Komarno	1	/ 1766	M	
H03	Danube	Szob	1708	1708	LMR	
H04	Danube	Dunafoldvar	1560	1560	LMR	
H06	/ Sio	Szekszard - Palank	13	/ 1497	M	
H05	Danube	Hercegszanto	1435	1435	LMR	
HR01	Danube	Batina	1429	1429	M	
SL01	/ Drava	Ormoz	300	-	L	
HR03	/ Drava	Varazdin	288	-	M	
HR04	/ Drava	Botovo	227	-	M	
HR05	/ Drava	D. Miholjac	78	/ 1379	R	
H07	/ Drava	Dravaszabolcs	78	/ 1379	M	
HR02	Danube	Borovo	1337	1337	R	
H08	/ Tisza	Tiszasziget	163	/ 1215	LMR	
H09	/ Tisza/ Sajo	Sajopuspoki	124	-	M	
SL02	/ Sava	Jesenice	729	-	R	
HR06	/ Sava	Jesenice	729	-	R	
HR07	/ Sava	Us. Una Jasenovac	525	-	L	
HR08	/ Sava	Ds. Zupanja	254	/ 1170	M	
RO01	Danube	Bazias	1071	1071	LMR	LOWER
RO02	Danube	Pristol/Novo Selo	834	834	LMR	
BG01	Danube	Novo Selo/Pristol	834	834	LMR	
BG02	Danube	Us. Iskar - Bajkal	641	641	M	
BG06	/ Iskar	Orechovitza	28	637	M	
BG03	Danube	Ds. Svishtov	554	554	MR	
BG07	/ Jantra	Karantzi	12	537	M	
BG04	Danube	Us. Russe	503	503	MR	
BG08	/ Russenski Lom	Basarbovo	13	498	M	
RO03	Danube	Us. Arges	432	432	LMR	
RO04	Danube	Chiciu/Silistra	375	375	LMR	
RO09	/ Arges	Conf. Danube	0	/ 432	M	
BG05		Silistra/Chiciu		375	LMR	
RO10	/ Siret	Conf. Danube - Sendreni	0	/ 154	M	
MD01	/ Prut	Lipcani	658	-	L	
MD02	/ Prut	Leuseni	292	-	M	
MD03	/ Prut	Conf. Danube - Giurgiulesti	0	/ 135	M	

Country Code	River	Town/Location	Distance (km)	River km	Location in Profile	Section
RO11	/ Prut	Conf. Danube - Giurgiulesti	0	/ 135	M	
RO05	Danube	Reni-Chilia/KiliaArm	132	132	LMR	
UA01	Danube	Reni-Kilia Arm/Chilia Arm	132	132	M	
RO06	Danube	Vilkov-Chilia Arm/Kilia Arm	18	18	LMR	
UA02	Danube	Vilkov-Kilia Arm/Chilia Arm	18	18	M	
RO07	Danube	Sulina – Sulina Arm	0	0	LMR	
RO08	Danube	Sf. Gheorghe – Sf. Gheorghe Arm	0	0	LMR	

Legend for Table 7.2.1:
- River: The water course where the sampling site is located
- Distance: The distance (km) from the mouth of the considered river
- River km (rkm): The Danube River km (from confluence with the Black Sea) where the sampling site is located
- / Tributary
- Us. – Upstream of
- Ds. – Downstream of
- Conf.: Confluence tributary / main river
- Location in profile:
    o L – left bank of the river
    o M – middle of the river
    o R – right bank of the river
- Section:
    o Upper Danube
    o Middle Danube
    o Lower Danube

According to a previous approach (*Joint Danube Survey – Technical Report, 2002*) and to a regional agreement among the Danube countries, the Danube Basin was divided into three main sections for the purpose of assessmen (Fig. 7.2.1):
- Upper Section: from Danube-Neu Ulm (km 2581, D01) to Danube-Wolfsthal (km 1874, A04), comprising of 6 monitoring sites;
- Middle Section: from Danube-Bratislava (km 1869, SK01) to Danube-Borovo (km 1337, HR02), comprising of 10 monitoring sites;
- Lower Section: from Danube-Bazias (km 1071, RO01) to Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08) comprises 15 monitoring sites. In order to make the charts more clear and due to the fact that entire lower section has more than 1000 km length, this section was further divided into two parts. Second part of the lower section starts in Danube-Us. Arges (km 432, RO03).
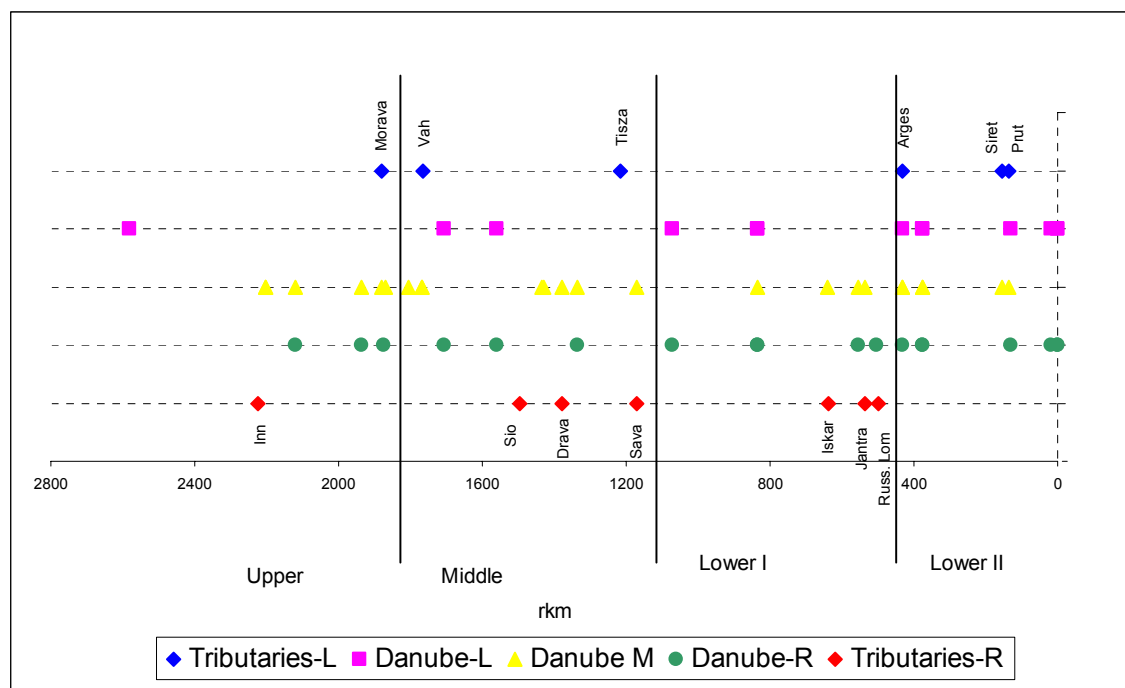
Fig. 7.2.1: Selected monitoring sites

Legend for Fig. 7.2.1:
- Danube-L: the left bank of the Danube River
- Danube-R: the right bank of the Danube River
- Tributary-L: tributary for which the confluence is located on the left side of the Danube River
- Tributary-R: tributary for which the confluence is located on the right side of the Danube River

Physico-chemical determinands selected for the assessment have been divided to five groups in accordance to Table 7.2.2.

Table 7.2.2.: List of selected physico-chemical determinands for water quality assessment

Group of determinands	Determinand	Unit
General characteristics	Suspended Solids (SS)	mg/l
	pH	-
	Conductivity	µS/cm
	Alkalinity	mmol/l
Nutrients	Ammonium-N (N-NH$_4^+$)	mg/l
	Nitrite-N (N-NO$_2^-$)	mg/l
	Nitrate-N (N-NO$_3^-$)	mg/l
	Ortho-phosphate-P (P-PO$_4^{3-}$)	mg/l
	Total Phosphorous	mg/l
Oxygen regime	Dissolved oxygen (concentration)	mg/l
	Biochemical Oxygen Demand (BOD$_5$)	mg/l
	Chemical Oxygen Demand by K$_2$Cr$_2$O$_7$ (COD$_{Cr}$)	mg/l
	Chemical oxygen demand by KMnO$_4$ (COD$_{Mn}$)	mg/l
Heavy Metals	Iron (Fe)	mg/l
	Manganese (Mn)	mg/l
	Zinc (Zn)	µg/l
	Copper (Cu)	µg/l
	Chromium – total (Cr)	µg/l
	Lead (Pb)	µg/l
	Cadmium (Cd)	µg/l
	Mercury (Hg)	µg/l

Group of determinands	Determinand	Unit
	Nickel (Ni)	µg/l
	Arsenic (As)	µg/l
Organic micropollutants	Lindan	µg/l
	pp'-DDT	µg/l
	Atrazine	µg/l
	Chloroform	µg/l
	Carbon tetrachloride	µg/l
	Trichloroethylene	µg/l
	Tetrachloroethylene	µg/l

The basis for the evaluation was 90 %-ile (c90) for each considered determinand (90 percentile method has the advantage that extreme values caused by exceptional conditions or measuring errors are not taken into account, but still represents "unfavourable" situation that occurred in monitoring site in a year). For dissolved oxygen content 10%-ile data were considered, but maximum and minimum values were also taken into account.

Here is necessary to stress that whilst for assessment of spatial and temporal changes c90 was used, in classification c90 value was used in all those cases when frequency of measurements of determinand in a year was at least 11. In case of lower frequency, testing value as a basis for classification was maximum value from a data set, as was explained in a chapter 7.1. Therefore, c90 value in charts presented in evaluation part of the report can differ from numerical value given in classification tables at a place of "testing value".

There are two main types of the charts used for illustration of determinands. The first type is a bar chart presenting 90 %-iles calculated for each year in all monitoring sites measured in TNMN (it means that in case of measurements made on right side, left side and in the middle of a profile the data from all three sites are presented). The distance between monitoring sites is proportional on the x-axis. This type of chart is made separately for Danube River and for tributaries.

The second type is x/y chart with river kilometres on x-axis. The chart is prepared separately for Danube River itself and for tributaries again. In case of presenting tributaries concentrations are plotted at the river km of the confluence of the tributary with the Danube. Therefore, in the Table 7.2.1. also river km of confluence with Danube is given for tributaries. In this type of chart a lne is added displaying the target value equal to class II limit value. By comparing the real values against the distance from target value can be seen.

7.3.   Trend Analysis

After five years of monitoring the question rises whether water quality in the Danube River Basin improves, remains stable or get worse. Many changes took place regarding the economic situation in the countries, industrial production, agricultural methods, land use and protection of environment. The human impact on rivers might differ now from that of 1996. In the meantime the physical, chemical and biological characteristics of the Danube and its tributaries have also varied because they are dependent on hydrological conditions and climate. There are the natural trends in water quality that reflect either short-term or long-term changes and cyclic repetitions like daily, seasonal or longer periodicity. Taking this in consideration five years are not very much for trend analysis.

Several methods for trend analysis are described in literature. Nearly every software used for calculation or data base has a tool for adding trend line to time-series plots. However without having any information on the behaviour of the determinands no serious evaluation can be done. To calculate trend lines as a precondition periodic cycles have to be substracted from the time-series. Afterwards the quality of the so called trend model has to be proved e.g. by checking the distribution frequency of the square deviations from the line. To apply these procedures for time-series analysis sufficient data of high quality is needed and much information on the processes, which steer the environmental

turnover of a substance, should be available. Within the TNMN network about 60 samples should be stored for every determinand, but actually there are much less particularly for specific pollutants. For some determinands few samples may be sufficient if there is no seasonal periodicity and if fluctuations of values are either random or very strong dependent on a known predicting variable. While only few determinands fulfil these preconditions it was decided to firstly use a very simple approach for trend analysis comparing to the models mentioned above.

The simple approach for trend assessment is based on the comparison of statistical parameters of yearly data sets. According to the parameter different situations can be evaluated, the choice is dependent on the target of the analysis. Critical situations can be expressed best by the 90percentile (or 10percentile for pH and dissolved oxygen) of a yearly data set. As they occur naturally or as a result of human impacts it often appears difficult to interpret the year-on-year variations. To calculate 90percentiles mathematically reliable a sufficient number of samples per year are required, too. Although all data sets, which consist of more than five samples, were considered, valid statements can only be given for some determinands where more samples are available.

The trend assessment was carried out for all monitoring sites of the TNMN. At sites where samples are taken from left, middle and right only the middle was used. In general the different riversides fit quite well together. For the year 1996 the differences are often higher than for other years and for some nutrients (ammonia, ortho-phosphate phosphorus and total phosphorus) and heavy metals greater deviations have to be observed, too. A systematic difference is monitored for Kilia-arm at Reni: values of COD_{Cr} of the left side exceed that of the right side.

7.4.   Evaluation of biological determinands

An integral part of TNMN are biological determinands and MLIM-EG exerted a big effort to harmonise methodologies of their measurements and evaluation to assure their comparability throughout the River basin and to utilise their potential of being good indicators of water quality. In TNMN Phase I chlorophyll-a, macrozoobenthos and microbiological determinands had been measured.

Phytoplankton biomass – concentration of the chlorophyll-*a*

Chlorophyll-a is the essential photosynthetic pigment present in all green plants. The chlorophyll content in surface water is an indicator of its trophic state. The determination of the chlorophyll-a concentration provides information concerning the quantity and potential photosynthetic activity of the algae in the water column. The ratio of chlorophyll to phaeopigments (important metabolites of chlorophylls) is indicative of the physiological state of the algae.

Phytoplankton together with phytobenthos and water macrophytes reflect the primary production in the watercourses. Therefore it is important community to investigate it. Increase of the phytoplankton biomass is one of the characteristics of the eutrophication in the rivers. Eutrophication of the large rivers is caused by input of the nutrients in excess in combination with other factors like suitable light, temperature, transparency. High level of eutrophication lead to negative consequences for the river itself and reservoirs in particular (Wetzel, 1983).

Development of the phytoplankton biomass can be measured also as a concentration of the chlorophyll-a. For this purpose the method of ISO 10260 (1992) was recommended. Method consists of four steps (collection of algae from water by filtration; extraction of algal pigments from the filter residue into hot ethanol; spectrometric determination of chlorophyll-a concentration in the extract and evaluation of the chlorophyll-a and phaeopigment from the difference in absorbance prior to and after acidification of the extract).

Based on the TNMN database from the period 1996-2000 the statistical processing of selected characteristic values was used for individual year. In case of less than 3 measurements existing in a year, no value was used. Up to 10 measurements a maximum was used as a characteristic value. If more data were available 90 percentile was calculated. If the chlorophyll-a was measured at cross section of the river (left, middle and right), the mean value of three sites was taken into account. Characteristic values categorized individual TNMN stations according to the classification scheme (tab. 7.4.1).

Tab.7.4.1: Classification scale of the quality class for the chlorophyll-a concentration.

CLASSIFICATION SCALE	I. High status	II. Good status	III. Moderate status	IV. Bad status	V. Very bad status
µg/l of the chlorophyll-a	≤25	≤50	≤100	≤250	>250

Saprobic index of macrozoobenthos

Macroscopic organisms – macroinvertebrates create the important part of the aquatic community. In accordance with specific autecological demands for life in the aquatic environment, individual species react in different ways to variations in its physical and chemical state like diffuse and point sources pollution, light, temperature, flow velocity, oxygen condition and the structure of the river bed.

Macrozoobenthos taxa are space and/or food competitors with different feeding habitats and they are capable to self-regulate their population size. They also depend on other biological compartments, in particular on micro-organisms, whose metabolic activity can lead to negative effect on the oxygen budget of the water body and its fauna during decomposition of great amounts of organic substances (saprobity).

Within the TNMN the standard operational procedure have been proposed to monitor macrozoobenthos in the Danube river and its tributaries. The SOP covered macroinvertebrates only and was focused on the numerical evaluation for the system of saprobity by means of the Saprobic Index. The macroinvertebrates sampling and biological assessment was a first step in the development of a more comprehensive ecological assessment of the river water quality. There were a few sampling methods, level of taxa identification and numerical evaluation suggested. For TNMN it was recommended to use the Pantle & Buck formula, modified by Zelinka & Marvan:

$$SI = \frac{\sum h_i * s_i * I_i}{\sum h_i * I_i}$$

with: h_i = quantity of species i in sample
I_i = weight of species i in sample.
s_i = saprobic index of species i.

The quantity (h) in the formula can be expressed as an estimation of the number of individuals in the sample based on 5 class scale. The Saprobic Index ranges from 1 to 4 and is in current practice divided into 4 or 7 classes covering the range from xenosaprobic to polysaprobic. SOP proposed five class scale to evaluate biological results for TNMN (see table 7.4.2).

Tab. 7.4.2: Proposal for classification of Saprobic Index in the natural rivers in Danube basin.

Class	I	II	III	IV	V
Saprobic Index	< 1.8	1.81-2.3	2.31-2.7	2.71-3.2	>3.2

Whilst the results of saprobic index classification in accordance to TNMN classification scheme are presented in Annex 1, in the special chapter dedicated to biological determinands (chapter 8.2) the seven-class scale was used based on the Saprobic Index in accordance to Austrian standard ÖNORM M6232. The reason is that this scale is more detailed, mainly in the range of the first three classes (see table 7.4.3).

Tab. 7.4.3: Classification scale based on the Saprobic Index (in accordance to Austrian standard ÖNORM M6232).

CLASSIFICATION SCALE	I. unpolluted	I.-II. low polluted	II. moderately polluted	II.-III. criticaly polluted	III. strongly polluted	III.-IV. very high polluted	IV. extensively polluted
	≤1,25	≤1,75	≤2,25	≤2,75	≤3,25	≤3,75	>3,75

Based on the TNMN database from the period 1997-2000 the statistical processing of selected characteristic values was used for individual year. Usually 3-4 measurements were done by the individual countries. Characteristic values (maximum for individual year) categorized individual TNMN stations according to the above mentioned classification scale.

Microbiological determinands

Heterotrophic bacteria play a decisive role in river ecosystem in degrading organic matter. Their contribution to self purification processes of rivers is of great interest within a scope of water quality assessment. Bacteria are ideal sensors because of their fast response to changing environmental conditions (Kavka, 2002).

Bacterial indicators such as total coliforms, faecal coliforms (thermotolerant coliforms), E.coli, faecal streptococci (enterococci) and colony counts are widely applied to the assessment of water quality. On one hand, because of their mainly allochthonous origin, these standard parameters are used as indicators of change in the natural stage of rivers. On the other hand, they indicate anthropogenic impact such as faecal pollution in the water. E.coli and faecal coliform bacteria are the best indicators for assessment of faecal pollution, mainly caused by raw and treated sewage and e.g. diffuse impact from farmlands and pastures. Faecal indicators are excreted by humans and warm-blooded animals treated to a large extent in sewage treatment plants and ultimately found in aquatic environment where they survive for a relatively long time. E.coli and faecal coliforms also indicate the potential presence of pathogenic bacteria, viruses and parasites (Kavka, 2002).

For the TNMN database Total Coliforms, Faecal Coliforms, Faecal Streptococci (enterococci) and *Salmonella* sp. were proposed for monitoring. However data on Faecal Streptococci and *Salmonella* sp. are for evaluated period (1996-2000) insufficient. Therefore only Total Coliforms and Faecal Coliforms were processed for the purpose of this report.

Total Coliforms usually contained typical coliform bacteria (*Escherichia coli*, Klebsiella sp., Citrobacter sp., Enterobacter sp.). For TNMN the proposed method was according to the ISO 9308-1:1990. Method is based on membrane filtration, cultivation (mEndo-Agar LES, Difco) and incubation of 24 hours at 37ºC.

For the Faecal Coliforms (thermotolerant coliform bacteria) the method of ISO 9308-1:1990 was recommended. Method is based on membrane filtration, cultivation (mFC medium, Difco) and incubation of 24 hours at 44ºC.

Base on the TNMN database from the period 1996-2000 the statistical processing of selected characteristic values was used for individual year. In case of less than 3 measurements exist in a year, no value was used. Up to 10 measurements a maximum was used as a characteristic value. If more

data were available 90 percentile was calculated. If the analyses of bacteria were provided at cross section of the river (left, middle and right), the mean value of three sites was taken into acount.

TNMN classification does not contain limit values for microbiological deterinands. Therefore, the classification scale given in table 7.4.4 was used to categorize water quality from the point of view of microbiological pollution in TNMN stations.

Table 7.4.4: Classification system of Kohl (1975), the EU-Bathing Water Quality Directive 76/160 EEC and new EU expert proposals (verbal information) were taken into account.

CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
POLLUTION	Low	Moderate	Critical	Strong	Extensive
Total Coliforms (CFU/100 ml)	≤500	≤10000	≤100000	≤1000000	>1000000
Faecal Coliforms (CFU/100 ml)	≤100	≤1000	≤10000	≤100 000	>100000

7.5.   Comparison of TNMN results 1996-2000 with Environmental Quality Standards of EU legislation

7.5.1.   Introduction

With the publication of the Water Framework Directive (EC 2000) in December 2000 a new legal basis for the protection of ground and surface waters within the European Union has been put into force. One of the objectives of the Water Framework Directive (WFD) is to achieve a "good surface water status" for all surface waters irrespective of their size until 2015. Regarding dangerous substances this means that all environmental quality standards (EQS) "established
- in Annex IX
- and under Article 16(7) of the WFD
- and under other relevant Community legislation setting EQS at Community level" have to be met.

Annex IX of the WFD lists the daughter directives of the Dangerous Substances Directive (EEC 1976, EEC 1982, EEC 1983, EEC 1984/1, EEC 1984/2, EEC 1986). This legislation stipulates the EQS for the seventeen so called List 1 substances (see Table 7.5.1.1).

Table 7.5.1.1   Environmental Quality Standards for List 1 substances according to the daughter directives of Council Directive 76/464/EEC (Dangerous Substances Directive, EEC 1976)

List 1 Substance	CAS number	Directive	EQS water µg/l	EQS sediment	EQS biota
Cadmium	7440-43-9	83/514	1 [a), b)]	Standstill [e)]	Standstill [c)]
DDT total		86/280	0,025 [d)]	Standstill [e)]	Standstill [f)]
1,2-Dichloroethane	107-06-2	86/280	10		
Drins		86/280	0,01 [g)]	Standstill [e)]	Standstill [f)]
Hexachlorobenzene	118-74-1	86/280	0,03	Standstill [e)]	Standstill [f)]
Hexachlorobutadiene	87-68-3	86/280	0,1		
Hexachlorocyclohexane	608-73-1	84/491	0,05 [h)]	Standstill [e)]	Standstill [f)]
Pentachlorophenol	87-86-5	86/280	2	Standstill [e)]	Standstill [f)]

List 1 Substance	CAS number	Directive	EQS water μg/l	EQS sediment	EQS biota
Mercury	7439-97-6	82/176, 84/156	1 [b]	Standstill [e]	0.3 mg/kg [i] Standstill [j]
Tetrachloroethene	127-18-4	86/280	10		
Tetrachloromethane	56-23-5	86/280	12		
Trichlorobenzene	120-82-1	86/280	0,4 [k]	Standstill [e]	Standstill [f]
Trichloroethene	79-01-6	86/280	10		
Trichloromethane	127-18-4	86/280	12		

a) Without direct impact of a discharge, otherwise 5 μg/l
b) Total metal concentration
c) Mollusks and shellfish (if possible, mytilus edulis)
d) p,p'-DDT 0,01 μg/l, DDT total comprises p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD
e) optional to standstill in biota
f) Standstill in Fish and/or mollusks and/or shellfish
g) Endrin and Isodrin 0,005 μg/l
h) Without direct impact of a discharge, otherwise 0,1 μg/l. The directive does not specify to which isomer the limit value relates
i) For Fish, wet weight
j) Mollusks and shellfish (optional to sediments)
k) Related to the sum of three isomers

Article 16 of the WFD summarizes the strategies against pollution of water. In 16(2) the European Commission is obliged to submit a list of priority substances "which present a significant risk to or via the aquatic environment". With Decision 2455/2001/EEC (EC 2001) this obligation was fullfilled and a first list of priority substances published. For the time being no binding EQS have been set for these compounds but on behalf of the European Commission the Fraunhofer-Institute (FHI) for Molecular Biology and Applied Ecology (Schmallenberg, Germany) carried out a study which aimed to derive EQS for the priority substances based on ecotoxicological data according to the procedure laid down in Annex V, 1.2.6 of the WFD (FHI 2002). This proposal is available now and the EQS will be put into force with minor modifications in 2003/2004. The priority substances and the proposed quality objectives are given in Table 7.5.1.2.

Table 7.5.1.2: List of Priority Substances according to Decision 2455/2001/EC and Overall Environmental Quality Standards for Inland and Transitional Waters proposed by FHI

Priority Substance	CAS number	EQS FHI [μg/l]
Alachlor	15972-60-8	0,035
Anthracene	120-12-7	0,063
Atrazine	1912-24-9	0,34
Benzene	71-43-2	16 [a]
Brominated diphenylethers	32534-81-9	0,0005 [b]
Cadmium and its compounds	7440-43-9	0,08 [c]
C_{10-13}-chloroalkanes	85535-84-8	0,41
Chlorfenvinphos	470-90-6	0,01
Chlorpyrifos	2921-88-2	0,00046
1,2-Dichloroethane	107-06-2	10 [d]
Dichloromethane	75-09-2	8,2
Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	0,33

Priority Substance	CAS number	EQS FHI [µg/l]
Diuron	330-54-1	0,046
Endosulfan alpha-Endosulfan	115-29-7 959-98-8	0,004
Fluoranthene	206-44-0	0,12
Hexachlorobenzene	118-74-1	e)
Hexachlorobutadiene	87-68-3	0,003
Hexachlorocyclohexane (gamma-isomer, Lindane)	608-73-1 58-89-9	0,042 0,02
Isoproturon	34123-59-6	0,32
Lead and its compounds	7439-92-1	1 c)
Mercury and its compounds	7439-97-6	0,036 c), f)
Naphthalene	91-20-3	2,4
Nickel and its compounds	7440-02-0	0,6 c)
Nonylphenols (4-(para)-nonylphenol) (4-nonylphenol, branched)	25154-52-3 104-40-5 84852-15-3	0,33
Octylphenols (para-tert-octylphenol)	1806-26-4 140-66-9	0,1
Pentachlorobenzene	608-93-5	0,05
Pentachlorophenol	87-86-5	0,1
Polyaromatic hydrocarbons (Benzo(a)pyren) (Benzo(b)fluoroanthene) (Benzo(g,h,i)perylene) (Benzo(k)fluoroanthene) (Indeno(1,2,3-cd)pyrene)	50-32-8 205-99-2 191-24-2 207-08-9 193-39-5	e)
Simazine	122-34-9	1
Tributyltin compounds (Tributyltin-cation)	688-73-3 36643-28-4	0,0001
Trichlorobenzenes (1,2,3-Trichlorobenzene) (1,2,4-Trichlorobenzene) (1,3,5-Trichlorobenzene)	12002-48-1 87-61-6 120-82-1 108-70-3	1,8
Trichloromethane (Chloroform)	67-66-3	3,85
Trifluralin	1582-09-8	0,03

a)   No proposal for an overall QS was made in the FHI study. Specific QS derived for the protection of aquatic life is given.

b)   Individual substances are very different regarding their physico-chemical properties and toxic potential. QS for the most harmful individual compound Pentabromo diphenylether is given.

c)   Maximum permissible addition (MPA) according to the "Added Risk" approach for the QS derivation of metals, for details see text.

d)   No proposal for an overall QS was made in the FHI study. EQS of CD 86/280/EEC currently in force is given (see also Table 1)

e)   No proposal for an overall QS was made in the FHI study.

f)   No proposal for an overall MPA was made in the FHI study.

The other, above-mentioned "Community legislation setting EQS at Community level" comprises application-oriented directives containing EQS for specific water uses, which are of regional and not of general significance. These EQS are not further considered within this report.

In 1996-2000 a number of List 1 and Priority Substances were analysed within TNMN in Danube River and tributaries (see Table 7.5.1.3).

Table 7.5.1.3: List 1 and Priority Substances observed within TNMN in the time period 1996- 2000 and TNMN substance code

Substance	List 1 Substance	Priority Substance	TNMN Code
Atrazine		X	4.75
Cadmium (total)	X		3.65
Cadmium (dissolved)		X	3.66
p,p'-DDT	X		4.65
Lead (dissolved)		X	3.61
Lindane (gamma-Hexachlorcyclohexane)	X	X	4.60
Mercury (total)	X		3.70
Mercury (dissolved)		X	3.71
Nickel (dissolved)		X	3.76
Tetrachloroethene	X		4.95
Tetrachloromethane (Carbon tetrachloride)	X		4.85
Trichloroethene	X		4.90
Trichloromethane (Chloroform)	X		4.80

With respect to the fact that two riparian countries of the Danube River are member states of the European Union and another four will join the community in near future and therefore are obliged to implement the WFD it seems very interesting to compare these results with already valid and future EQS.

Motivation for such an assessment is
- identification of possible problems with exceeding substance concentrations
- identification of data gaps
- recommendations for the analysis of List 1 substances and PS in future based on experiences in compliance checking of this report

7.5.2. Testing for compliance

Choice of statistical quantity

In Annex V, 1.2.6 of the WFD dealing with the derivation procedure for EQS is stated that quality objectives should be laid down by "setting of a maximum annual average concentration". No further guidance is given for compliance checking. For List 1 substances this is specified in more detail in the daughter directives of CD 76/464/EEC: the arithmetic annual mean of analytical results shall be used to check the compliance with EQS. On EC level the Expert Advisory Forum Priority Substances (EAF - an expert advisory panel supporting the European Commission in implementing the WFD) has agreed to use the arithmetic mean at least for the discussion of the proposal of EQS for Priority Substances. There are still other statistical quantities in discussion for compliance checking, namely a combination of mean and a maximum allowable concentration (MAC) and the 90 percentile, but for

the time being the annual arithmetic mean is the preferred statistical quantity. For this reason the *mean* was selected too to compare TNMN data with EQS for the purpose of this report. (Note: Due to the fact that for comparison of TNMN data with EQS of EU legislation the the mean was used, the values presented in chapter 8.1.6 are different than those presented by charts in chapters 8.1.3 and 8.1.5, where c90 was used).

Dealing with "less than" values

For the time being no information can be found in EC legislation or guidance documents how to handle data below the detection limit when calculating the mean. This is a very important detail because in certain cases (EQS close to the limit of detection of the analytical method, many less than values) the chosen convention resp. method can influence the results of the compliance check dramatically. It is common practice to use simple substitution methods for taking into account less than values. The problem associated with this methods is that they have no theoretical basis and are defined by convention. The mean is biased and deviates more or less from the real location (HELSEL 2002). In TNMN yearbooks the mean is calculated by substituting the less than values with the limit of detection (LOD) of the specific analytical method. Although this is a very pesimistic approach because the mean is definitely shifted to higher concentrations in comparison with its true location this method was used for the purpose of this report to keep comparability with the yearly evaluations (this convention is named "LOD-method"). For some substances an additional evaluation using the most optimistic approach for calculation of the mean by setting the less then values to zero has been included to show the influence of the averaging method (called "Zero-method" in the following text).

Dealing with EQS lower than LOD

Derivation of EQS on a ecotoxicological basis sometimes results in a very low concentration as limit value which is out of range of the available analytical methodologies. Although this problem is evident for a number of Priority Substances it hasn't been tackled on EU level. One proposal to be discussed is to use the LOD as substitute for the actual EQS value. Of course this approach needs a harmonisation of methods or at a least the definition of minimum requirements regarding the LOD to avoid different limit values in the respective states. Whether a data set including some less than values gives compliance or non-compliance again depends on the convention used for calculating the mean. The "LOD-method" results in a non-compliance with only one figure above LOD (see also related text in an evaluation part of the report).

8.   Assessment of Water Quality

The assessment of water quality in Danube River basin in the report is divided into two basic parts – assessment on the basis of physico-chemical determinands and assessment of biological determinands. Chapter 8 is dedicated to assessment on the basis of physico-chemical determinands. It is structured in a way, that for each evaluated determinand information on results of classification are given (on the basis of tables with results of classification in the Annex 1), followed by information on spatial changes and trend assessment in Danube River itself and tributaries. This chapter is supplemented by sub-chapter 8.1.6 dealing with comparison of available TNMN data on hazardous substances with Environmental Quality Standards of European Union legislation and with proposed EQS for priority substances.
Results of water quality assessment based on biological determinands are given in chapter 8.2.

8.1. Assessment of water quality based on physico-chemical determinands

8.1.1.   General Characteristics

Suspended solids

Suspended matter comprises the quantity of insoluble substances in water that can be separated by filtration, centrifugal action and sedimentation. Insoluble substances, composed by organic and inorganic particles, can be both rough dispersions (particles size above 0.1 mm) and fine dispersions (particle size between 0.1 mm and 0.1 μm). Depending on size and specific gravity these particles are settling, remaining in suspended form or floating on the water surface.
In assessment of river water quality, strong correlation of suspended solids content with the flow discharge conditions must be taken into account. Several determinands measured in frame of TNMN are highly dependent on suspended solids content in waters, like total P, heavy metals (if sample is not filtered before analysis) and specific organic micropollutants with affinity to solid particles.

For the Danube River itself, the spatial pattern of suspended solids variation is shown in **Fig. 8.1.1.1a** and **Fig. 8.1.1.1b**.

As it can be seen, in the upper section of the Danube River, excepting the first monitoring station, Danube-Neu Ulm (km 2581, D01), where the concentration values are below 35 mg/l, all the other values show a relative uniform profile of spatial pattern. Still, an increasing spatial line is noticeable along this stretch.

For the middle section, suspended solids concentrations decrease from Danube-Bratislava (km 1869, SK01) down to Danube-Medvedov/Medve (km 1806, SK02) due to sedimentation process in Gabcikovo dam. For the following part of this stretch, the spatial pattern remains constant down to Danube-Hercegszanto (km 1435, H05). Slight higher concentrations, exceeding 100 mg/l in 2000, are present at Danube-Batina (km1429, HR01) and Danube-Borovo (km 1337, HR02), in conditions of discharge of 4305 m^3/s and 4464 m^3/s, respectively.

In the first part of lower section, most of the suspended solids concentration values are higher than in the middle section, but a decreasing tendency from Danube-Bazias (km 1071, RO01) down to Danube-us. Russe (km 503, BG04) can be noticed.
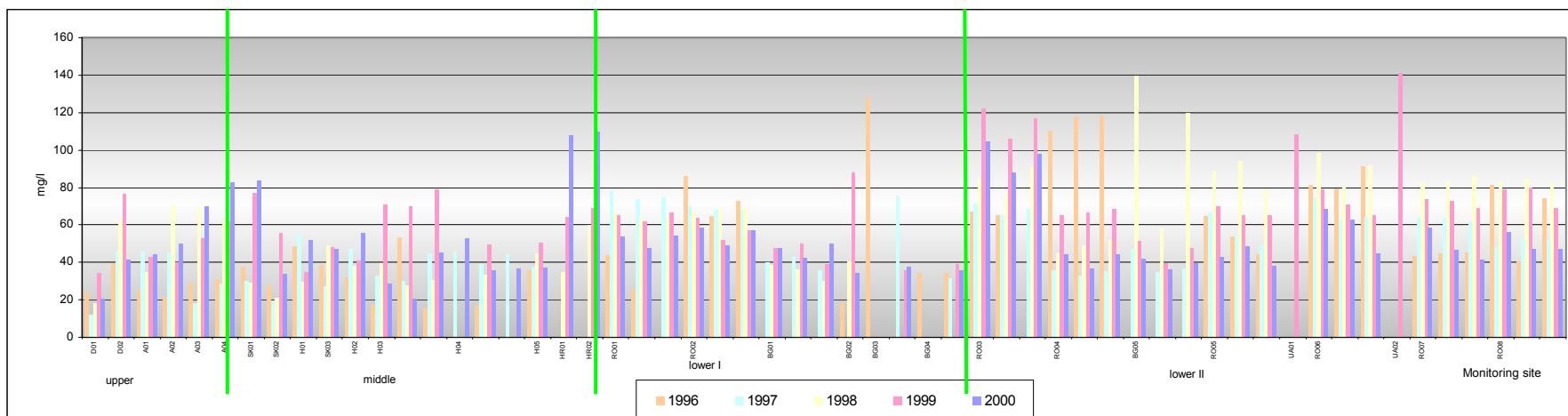
Fig. 8.1.1.1a: Spatial variation of Suspended Solids content – Danube River
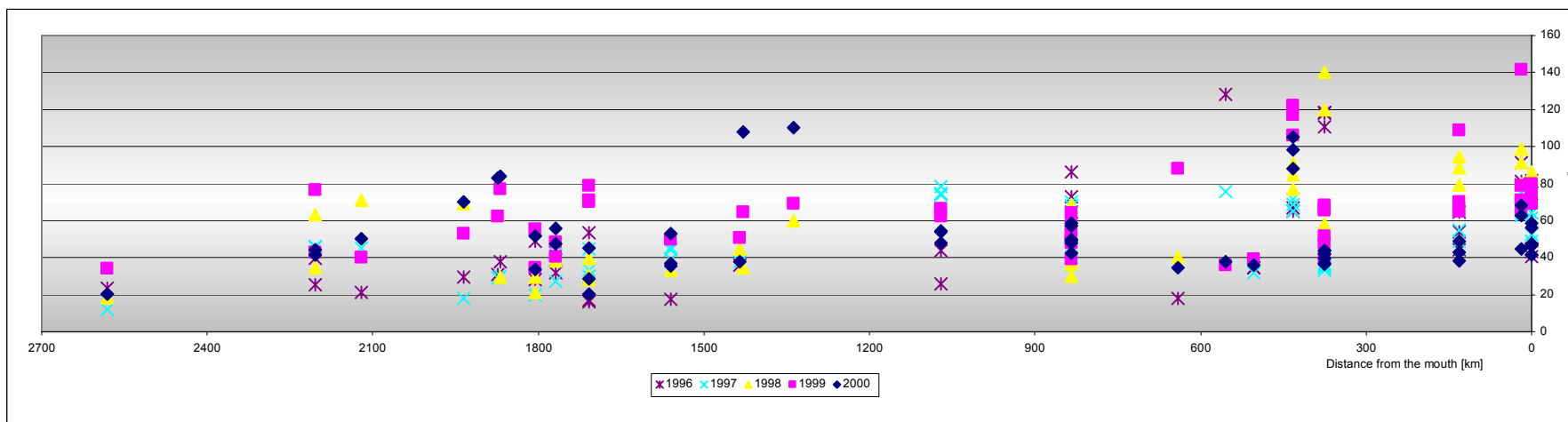
Fig. 8.1.1.1b: Spatial variation of Suspended Solids content – Danube River

The second part of the lower Danube section shows a relative constancy, but the suspended solids level is higher than in the previous part: here many values exceed 80 mg/l, while just a few of them are above this value in the first part. A few higher values are recorded at Danube-us. Arges (km 432, RO03) and at Danube-Chiciu/Silistra (km 375, RO04), but these concentration values are not very well in correlation with those reported for the same location but different site - Danube-Silistra/Chiciu (km 375, BG05).

The maximum values from this stretch belong to Danube-Silistra/Chiciu (km 375, BG05) and to Danube-Vilkov-Kilia arm/Chilia arm (km 18, UA02): 140.0 and 141.4 mg/l, respectively.

Selected tributaries generally present a higher suspended solids content than the Danube itself – **Fig. 8.1.1.2a, 8.1.1.2b and 8.1.1.3**:

- in the upper section, the Inn-Kirchdorf (D03) - 315 mg/l in 2000 and 158.4 mg/l in 1996 and the Morava-Lanzhot (CZ01) - 154.8 in 1996 versus 83.1 mg/l, represent the maximum value in the Danube River in this section;
- in the middle section, the Sio-Szekszard-Palank (H06) shows 140.8 mg/l in 1999 and 116.0 mg/l in 1998 versus approx. 50.0 mg/l for the upstream/downstream monitoring sites, Danube-Dunafoldvar (H04) and Danube-Hercegszanto (H05); but the maximum values for tributaries located in this stretch belong to the Tisza-Tiszasziget (H08) – 336.6 mg/l (L), 372.9 mg/l (M) and 414.0 mg/l (R) in 1998. The values above 100 mg/l appear also on the Sava-Jesenice (HR06) and Sava-us. Una Jasenovac (HR07), in 1998;
- from tributaries the highest suspended solids content belongs to those from the lower section, where the Russenski Lom-Basarbovo (BG08) is characterized by values ranging between 252.6 mg/l and 569.8 mg/l. Also the Siret-Conf. Danube-Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti present rather high concentrations – 308.3 mg/l in 1998 and 278.0 mg/l respectively, in 2000.

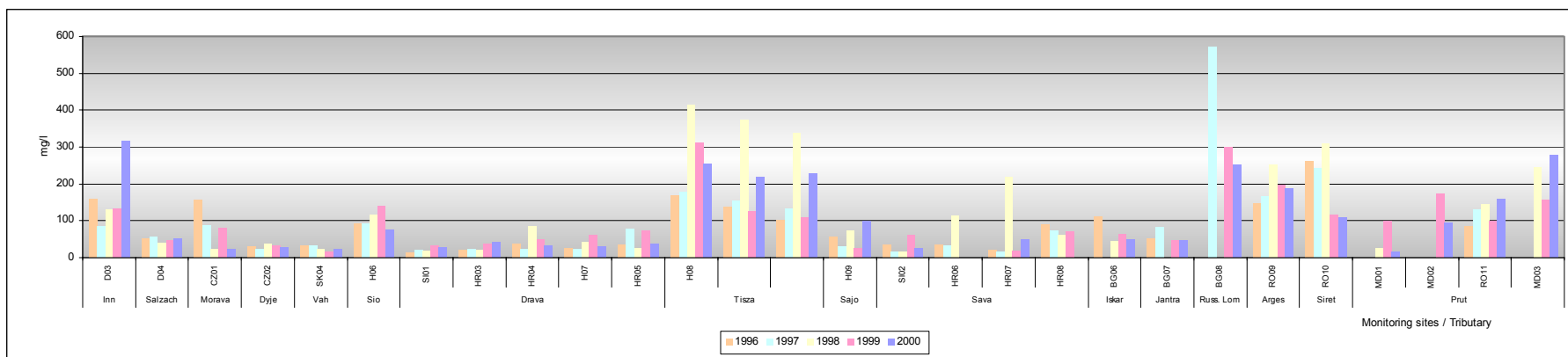Fig. 8.1.1.2a: Spatial variation of Suspended Solids content – Tributaries
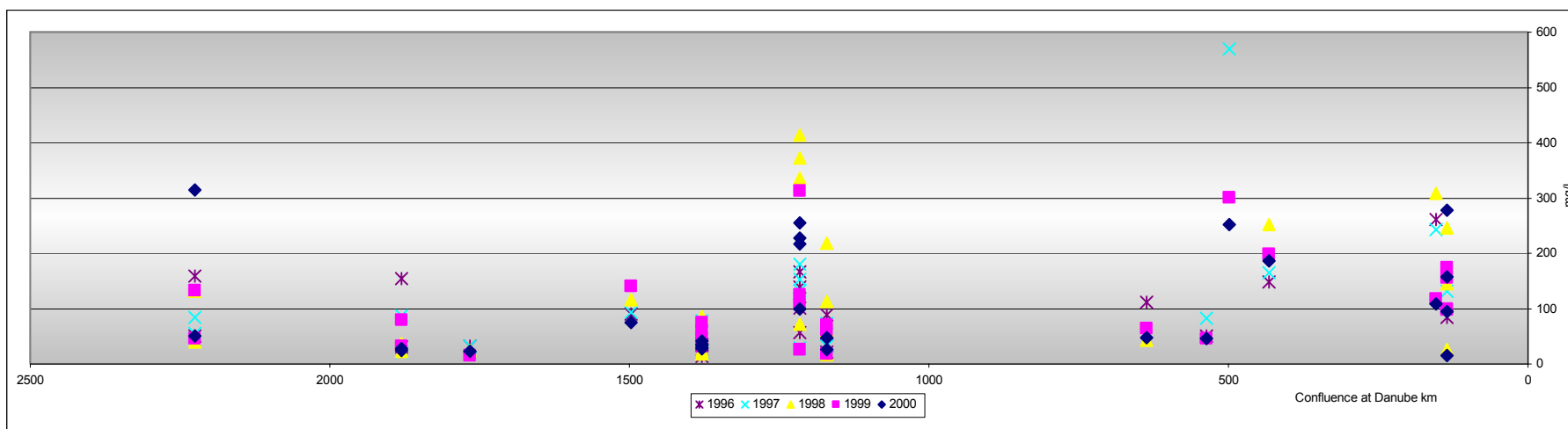

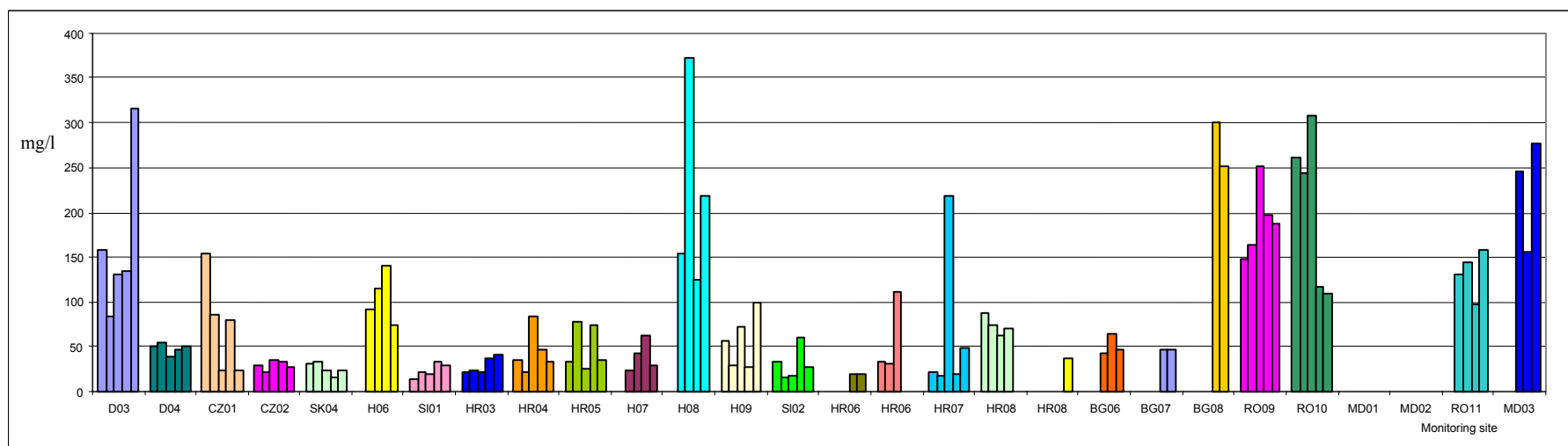Fig. 8.1.1.2b: Spatial variation of Suspended Solids content – Tributaries

Fig. 8.1.1.3:   Temporal trends of Suspended Solids content – Tributaries

pH

Hydrogen ion concentration, expressed in the form of pH value, is an important property of natural waters influenced by the substances dissolved in the water and influencing chemical reactions and the ability of water to bring other substances into solution. Beside, it represents an important factor that determines the water reactivity, its aggressiveness and its capacity of supporting life and growth of different organisms. Between the pH value and alkalinity or acidity value, no identity can be emphasized: increasing in either alkalinity or acidity is not visible in increasing or decreasing of pH value, due to the buffer capacity of natural waters, particularly. The main buffer system of natural water is composed by acid carbonates/carbonates, for a pH range of 6.50 – 8.50 (Varduca, 1997).

Concerning the Quality Classification System in the Danube River Basin applied to pH values (**Fig. 8.1.1.4**), the following remarks can be done:
-   the evaluation is based on data recorded from 87 monitoring sites (it means that out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements of pH had been done in 1996-2000);
-   more than 70 % of considered monitoring sites belong to Class II, with a maximum of 90.8 % in 1999;
-   Class III is represented in all five studied years, with a maximum of 16.1 % in 1997; excluding Danube-Bazias (RO01-middle, rkm 1071), all cases of non-compliance with class II are caused by exceedance of upper limit set up for pH value. Therefore, the figures illustrating pH are concentrated on the "upper" border of target value.
-   the percentage for monitoring sites with no reported data slowly decreases from 1996 to 2000.
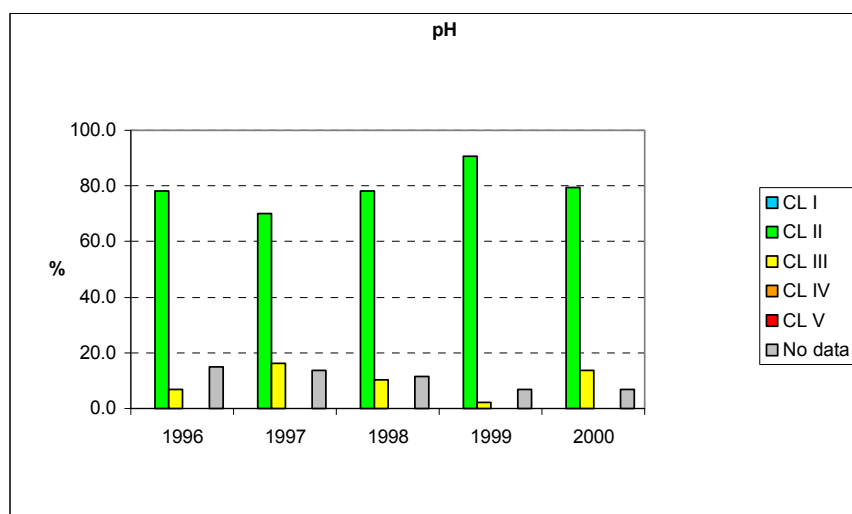
Fig. 8.1.1.4: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **pH**

The spatial variation of pH values along the Danube River, shown in **Fig. 8.1.1.5a**, has the following pattern:

In the upper section, pH values show a slight alkaline medium; with the exception of only one value - 8.14 - in 1999 at Danube-Jochenstein (km 2204, D02), all the other values are in the range 8.20 – 8.60. Spatial distribution shows also that between Danube-Jochenstein (km 2204, D02) down to Danube-Wien-Nussdorf (km 1935, A03) an increasing tendency is present.

Taking into account the spatial pattern of 90%-iles of pH along the Danube River, just in the middle section is the majority of values not-satisfying the upper limit of pH target values. Between Danube-Medve (km 1806, H01) down to Danube-Hercegszanto (km 1435, H05) a maximum values were observed - pH in the range 8.6-8.8 - followed by a decreasing tendency of pH values down to 7.80 at

Danube-Borovo (km 1337, HR02). These long-term monitoring values correlate well with previous data (*Joint Danube Survey* Technical Report, 2002), this variation being caused mainly by the balance between the increased primary production followed by the increased organic matter decomposition.

The decreasing visible in the last part of the middle stretch seems to be valid also for the first part of the lower Danube, between Danube-Bazias (km 1071, RO01) and Danube-Pristol/NovoSelo (km 834, RO02), although a few values exceed pH 8.20. (Still, differences of 0.20-0.40 pH units could be detected between the recorded values for the same cross section - km 834: RO02/BG01). For the stretch located between Danube-ds. Svishtov (km 554, BG03) and Danube-us. Russe (km 503, BG04) spatial distribution presents a scattered profile: rather different values are recorded at the same location but in different years - 7.49 in 1996 and 8.52 in 1997 at Danube-us. Russe (km 503, BG04 M and R).

In the second part of the lower Danube, between Danube-us. Arges (km 432, RO03) down to the main arms of the Danube Delta (km 0, RO07 and RO08) an increasing tendency in pH values is recorded, especially in year 2000, when most pH values are within the range 8.42 – 8.50, showing the same slightly alkaline medium.

Selected tributaries do not show significant differences among the pH values – **Fig. 8.1.1.6a**.
- Concerning the number of pH values exceeding the target value (8.50) during the five evaluated years, 21 values are above this limit in the Danube itself and 7 values in selected tributaries - **Fig. 8.1.1.5b** and **8.1.1.6b.** In the Danube River can be seen that most of the pH values that exceed the target value are recorded in 1997, 1998 and rarely in 2000. Values exceeding the target value in tributaries are recorded in 1996 and 2000, on Dyje-Pohansko (CZ02), Sio-Szekszard-Palank (H06) and Prut-Lipcani (MD01).

The temporal pattern of pH values in the Danube River is illustrated in **Fig. 8.1.1.7** and in selected tributaries in **Fig. 8.1.1.8**.
The following remarks can be done in this respect:
- the upper section is practically without any trends;
- similarly in the middle section, temporal variation is rather scattered and no systematic trend is detectable;
- in the first part of the lower Danube, a decreasing tendency from 1996 to 2000 is visible at Danube-Bazias (km 1071, RO01); an increasing, also from 1996 to 2000 is visible at Danube-ds. Svishtov (km 554, BG03),;
- in the second part of the lower Danube, no temporal changes are present at Danube-us. Arges (km 432, RO03); most of the remaining sites in this stretch shows a tendency of increasing from 1996 to 2000 , maximum values reaching mostly in 2000.

Selected tributaries present the following temporal changes:
- an increasing was observed for the Arges-Conf. Danube (RO09) and Siret-Conf. Danube-Sendreni (RO10);
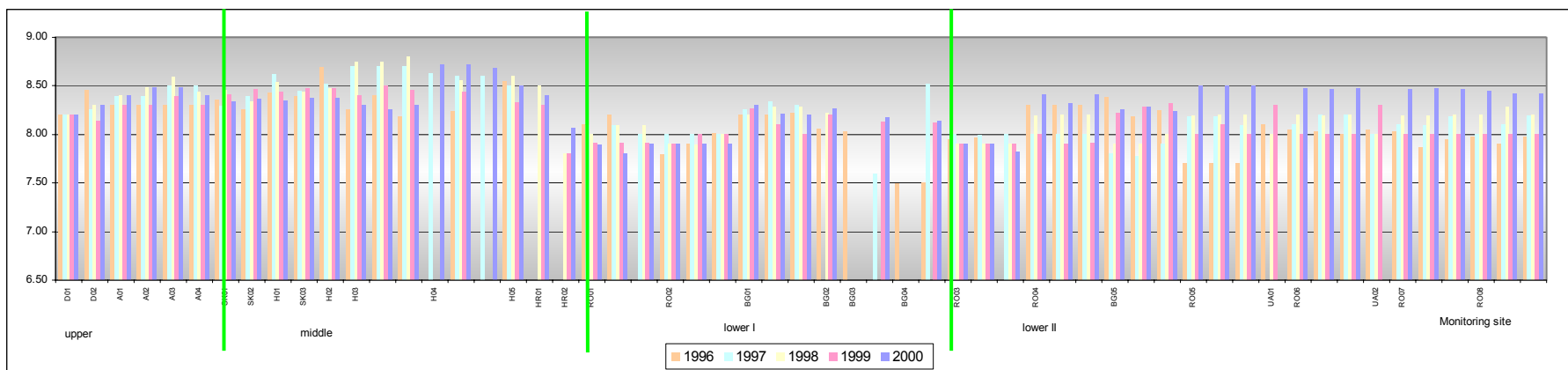- a decreasing tendency is indicated in Sava-Jesenice (SL02).

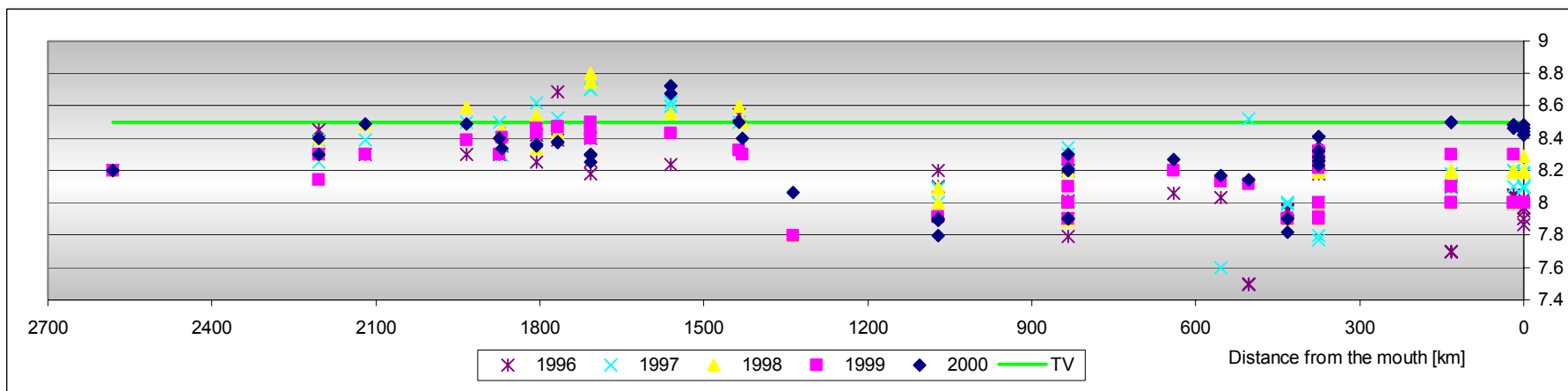Fig. 8.1.1.5a: Spatial variation of pH – Danube River

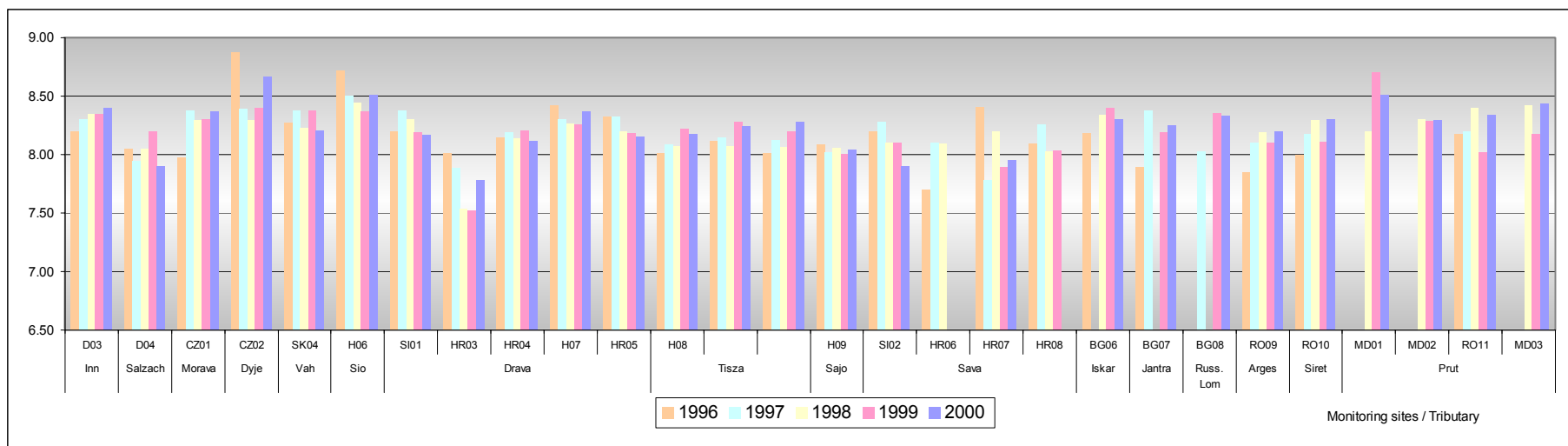Fig. 8.1.1.5b: Spatial variation of pH – Danube River

Fig. 8.1.1.6a: Spatial variation of pH – Tributaries
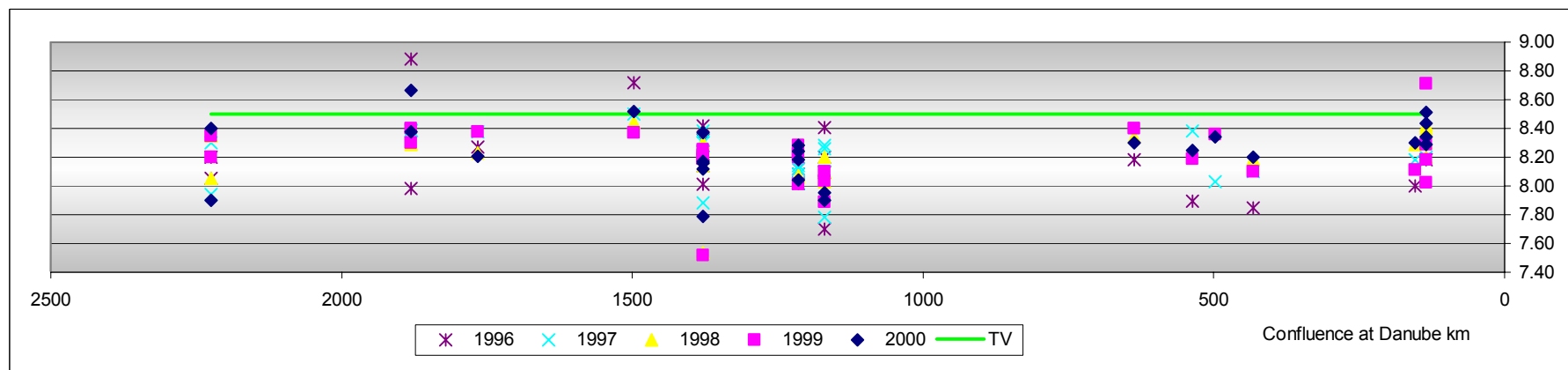
Fig. 8.1.1.6b: Spatial variation of pH – Tributaries
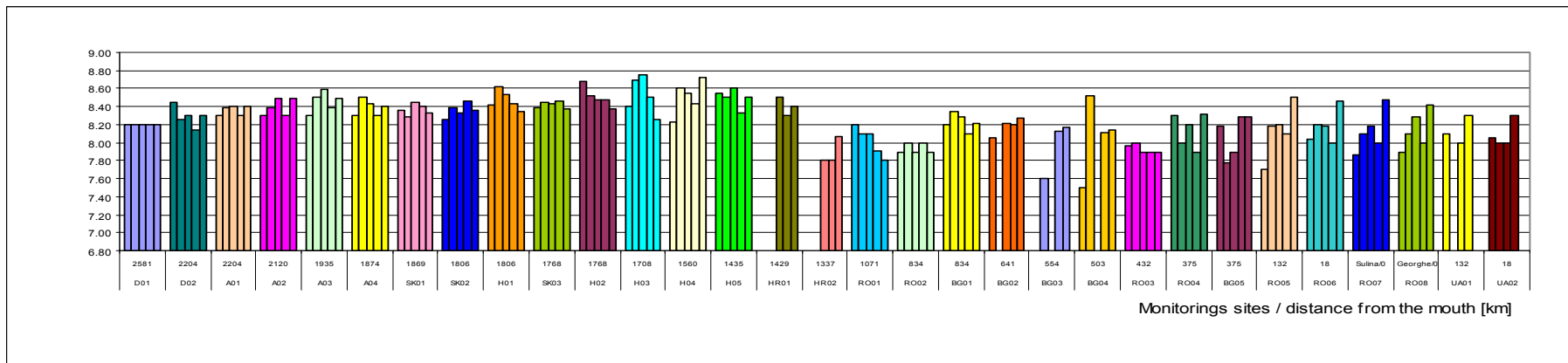
Fig. 8.1.1.7: Temporal trends of pH – Danube River
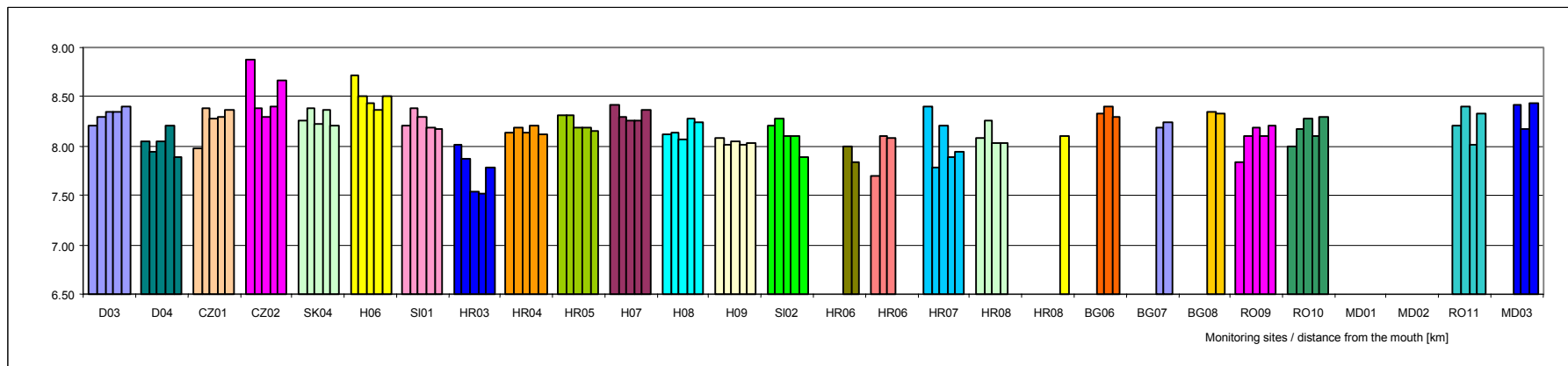
Fig. 8.1.1.8: Temporal trends of pH – Tributaries

Conductivity

Conductivity is one of the most frequently used determinands for assessing the mineralization degree of a natural watercourses as it is a measure of total dissolved salts in water column.

The spatial distribution of the conductivity values along the Danube River is shown in **Fig. 8.1.1.9a** and **8.1.1.9b.**
For the monitoring points located on the Danube in the upper section of the Danube itself, conductivity is within the range 400 – 539 µS/cm. From the above-mentioned figures can be seen the influence that the low salts content of the Inn-Kirchdorf (D03) has upon the downstream stretch.

The middle section of the river is characterized by small spatial variation. Only at Danube-Szob (km 1708, H03), a slight increasing pattern is noticeable, probably caused by an anthropogenic influence.

The first part of the lower Danube section shows no significant variation in spatial distribution between Danube-Bazias (km 1071, RO01) and Danube-us. Russe (km 503, BG04), only two values exceed the level of 500 µS/cm.
The pattern for the second part of the lower Danube is characterized by slightly higher values than in the first part; e.g. values increase from 405µS/cm in 2000 at Danube-us. Arges (km 432, RO03)up to 598µS/cm at Danube-Sulina/Sulina arm (km 0, RO07) in the same year.

Tributaries are generally characterized by higher conductivity levels than the Danube itself – **Fig. 8.1.1.10a** and **8.1.1.10b**:
- in the upper section, relatively higher values (637 µS/cm in 1996 – 784 µS/cm in 1998) were recorded on the Dyje but they are due to the low values of the flow (123.2 and 37.3 m^3/s, respectively). In 1997 there was higher conductivity than in 1996.
- the highest conductivity values belong to the Sio-Szekszard-Palank (H06), in the middle section (992 µS/cm in 1998 - 1195 µS/cm in 1997) in good correlation with flow discharges in respective years (63.9 m^3/s in 1998 and 49.0 m^3/s in 1997);
- in the lower Danube, the conductivity levels increase (e.g.: two c90 values, characterising Russenski Lom-Basarbovo (BG08), exceed 800 µS/cm - in 1997 and 1999). However, the highest values for tributaries along this stretch belong to the Prut-Conf. Danube Giurgiulesti (RO11) - 1100 µS/cm and 1110 µS/cm in 1997 and 1998, respectively.

The temporal trend for conductivity values in the Danube River is shown in **Fig. 8.1.1.11**, and in **Fig. 8.1.1.12** for selected tributaries:
- in the upper and the middle Danube, the general trend is decreasing from 1996 to 2000;
- in the first part of lower Danube, no general trend was observed; in the second part, the general tendency is increasing from 1996 to 1998 or 1999;
- selected tributaries from the upper river show a relative uniform temporal distribution of conductivity values; on the Morava-Lanzhot (CZ01) and Djye-Pohansko (CZ02) higher values are recorded in 1997 and 1998 respectively;
- the same uniform temporal pattern is valid also for the tributaries from the middle section, with few exceptions: on the Sio-Szekszard-Palank (H06), the maximum value appears in 1997 and on the Sava-us. Jesenovac (HR07) a decreasing trend from 1996 to 2000 is detectable.
- tributaries from the lower Danube present a scattered temporal profile, with no visible systematic trend.

Fig. 8.1.1.9a: Spatial variation of Conductivity – Danube River

Fig. 8.1.1.9b: Spatial variation of Conductivity – Danube River

Fig. 8.1.1.10a: Spatial variation of Conductivity – Tributaries

Fig. 8.1.1.10b: Spatial variation of Conductivity – Tributaries

Fig. 8.1.1.11: Temporal trends of Conductivity – Danube River

Fig. 8.1.1.12: Temporal trends of Conductivity – Tributaries

Alkalinity

Alkalinity is conditioned by the presence of acid carbonate, carbonate, hydroxide and only rarely by borate and silicate ions in water column. Values of "p" alkalinity (given by hydroxide and carbonate) and "m" alkalinity (given by acid carbonate) show the equilibrium status among the above-mentioned ions in water.

Spatial variation of alkalinity values along the Danube River is shown in **Fig. 8.1.1.13a** and **8.1.1.13b**.

For the upper section, unlike the first monitoring point, Danube-Neu-Ulm (km 2581, D01) where the alkalinity is in the range 4.6-4.8 mmol/l, all the other monitoring sites from this stretch are characterized by values in the range 3.5-3.9 mmol/l.

In the middle section, excepting two values, the range of alkalinity is 3.4 – 4.1 mmol/l. The exceptions are recorded at Danube-Batina (km 1429, HR01), where alkalinity values are 7.4 and 8.1 mmol/l in 1998 and 2000, respectively.

The spatial pattern of alkalinity in the first part of the lower section shows a slight increasing line from Danube-Bazias (km 1071, RO01) down to Danube-us. Iskar-Bajkal (km 641, BG02); at the following monitoring site, higher alkalinity value is recorded in 2000 (5.4 mmol/l).

In the second part of this lower stretch a slight increasing tendency of alkalinity values is present as well, with a maximum 4.9 mmol/l in 2000, at Danube-Silistra/Chiciu (km375, BG05).

The profile characteristic to selected tributaries presents maximum values on the Sio-Szekszard-Palank (H06), where the alkalinity values are within the range 6.4 – 8.5 mmol/l. Also the Jantra-Karantzi (BG07) and Russenski Lom-Basarbovo (BG08) show relatively higher values in 1999 and 2000 - between 5.6 and 7.5 mmol/l (see **Fig. 8.1.1.14a** and **8.1.1.14b)**.

From the temporal point of view, the following can be concluded based on illustration on **Fig. 8.1.1.15**, for the Danube River and in **Fig. 8.1.1.16** for selected tributaries:

-   a uniform profile for upper and middle Danube, slight variations being noticeable at Danube-Medve/Medvedov (km1806, H01) and at Danube-Komarom/Komarno (km 1768, H02);
-   in the first part of the lower Danube, a slight increasing trend from 1996 to 1999 or 2000 is present at Danube-Novo Selo/Pristol (km 834, BG01);
-   in the second part of lower Danube, the temporal view is inhomogeneous, but it can be seen that higher values are recorded in 1997, 1998 or 2000, depending on the monitoring site.
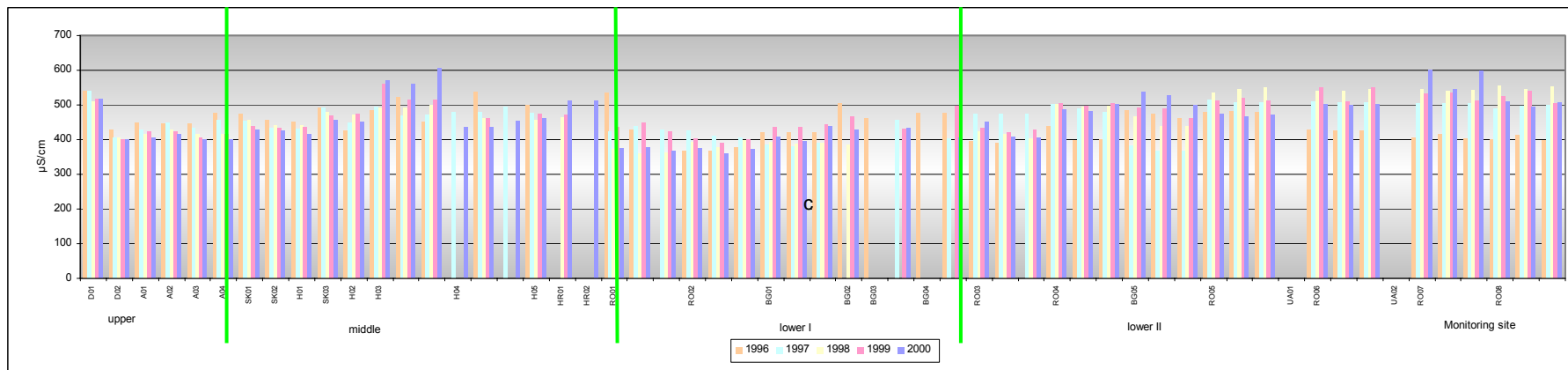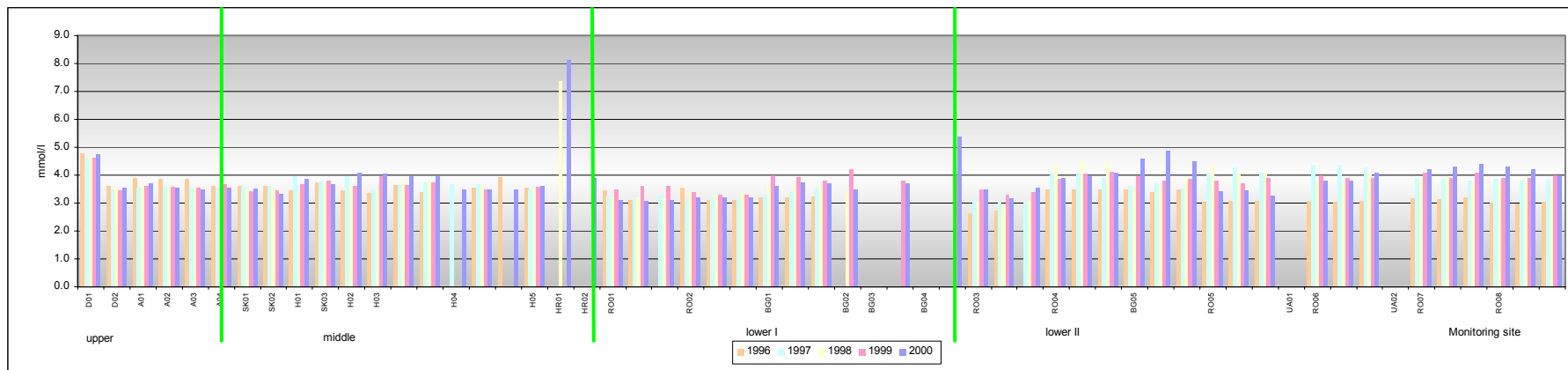
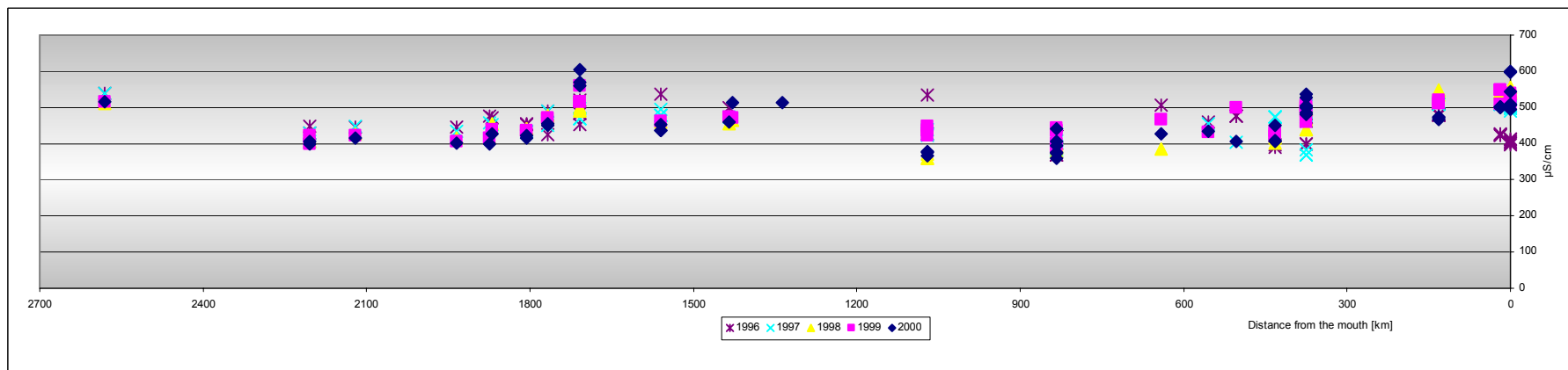Fig. 8.1.1.13a: Spatial variation of Alkalinity – Danube River
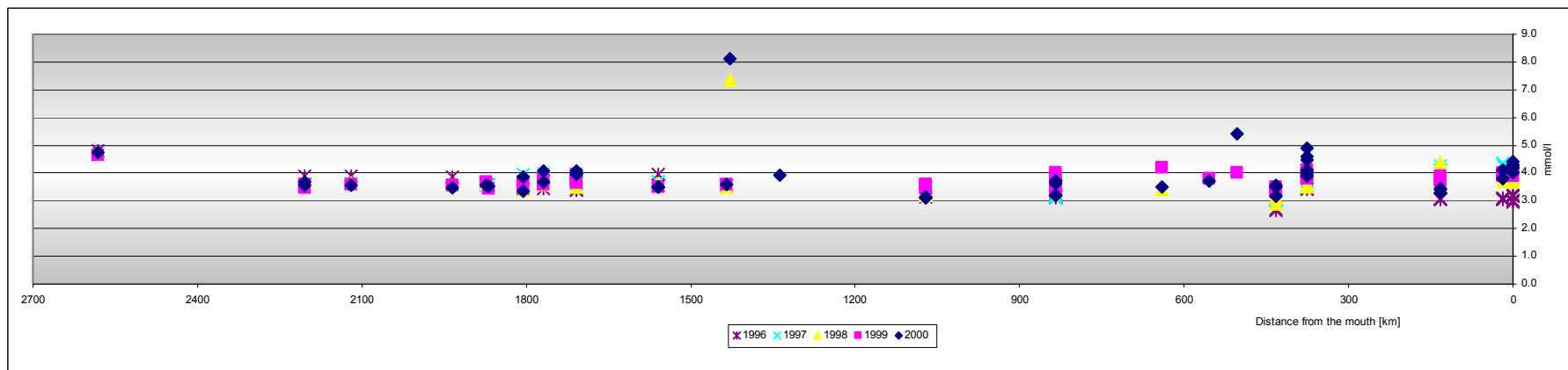
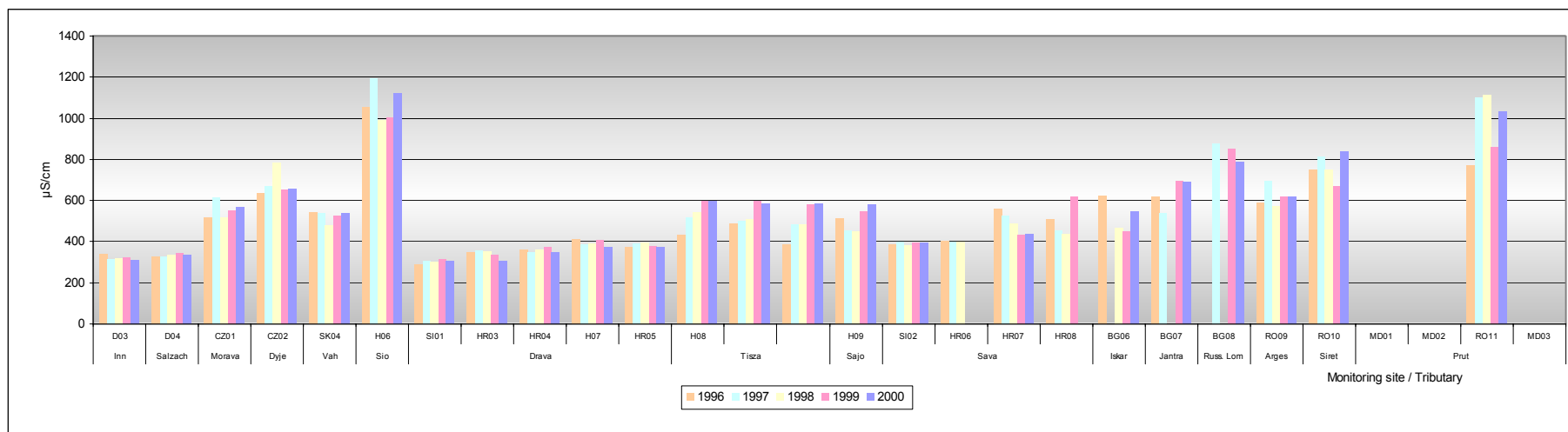Fig. 8.1.1.13b: Spatial variation of Alkalinity – Danube River
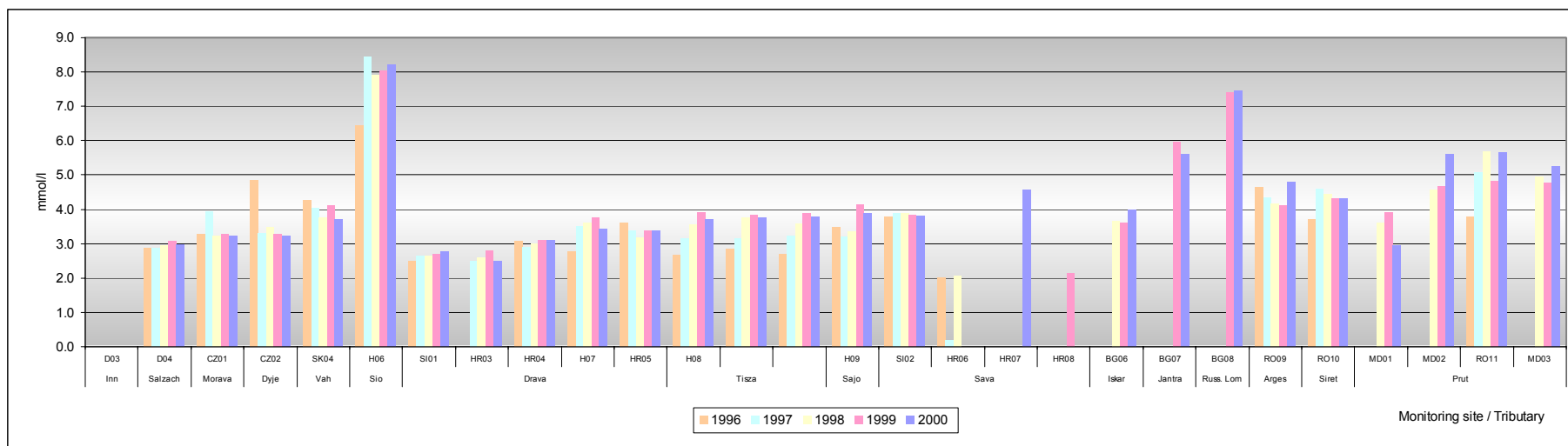
Fig. 8.1.1.14a: Spatial variation of Alkalinity – Tributaries
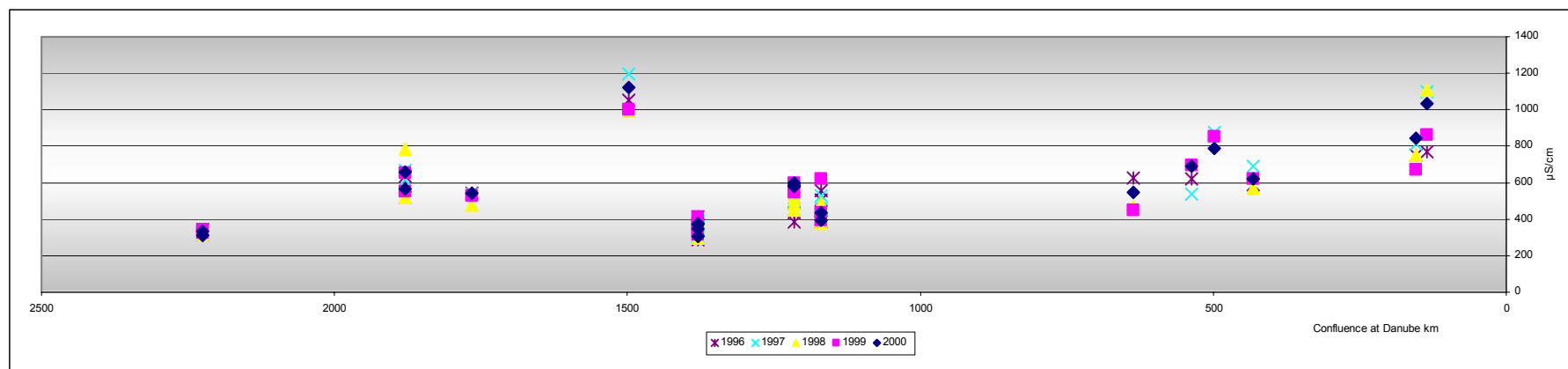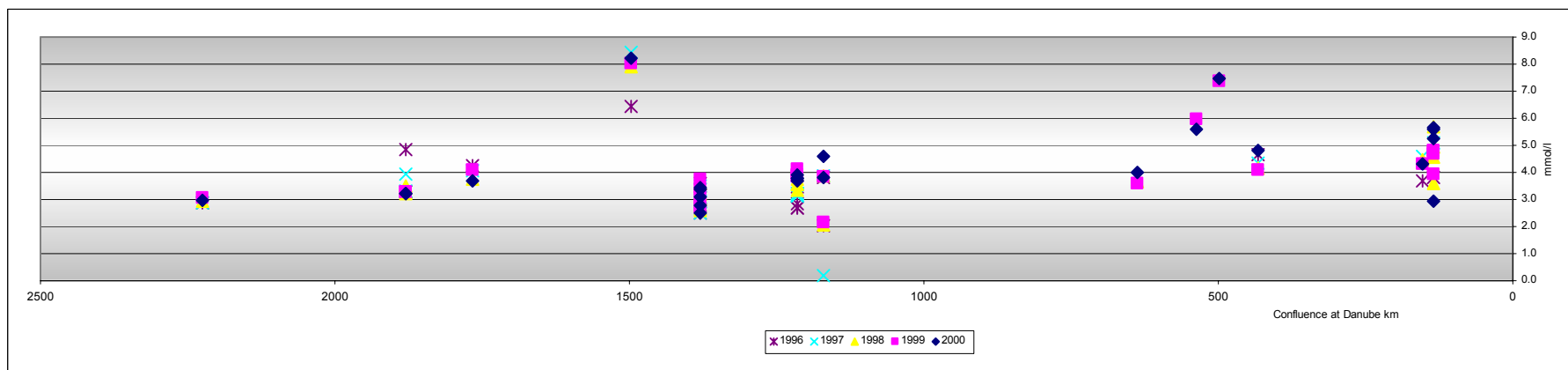

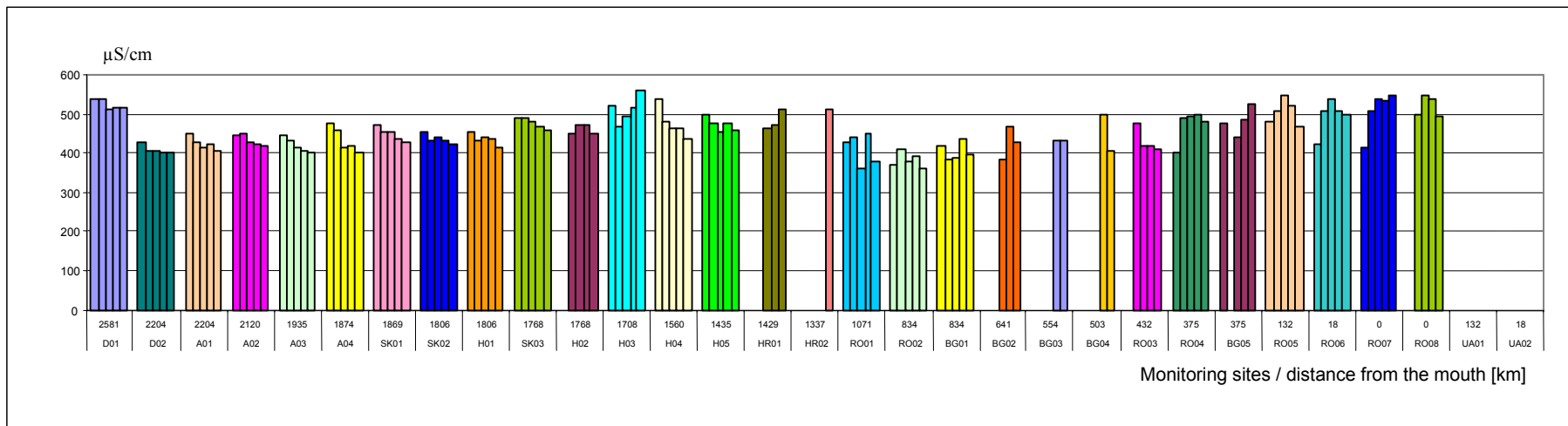Fig. 8.1.1.14b: Spatial variation of Alkalinity – Tributaries

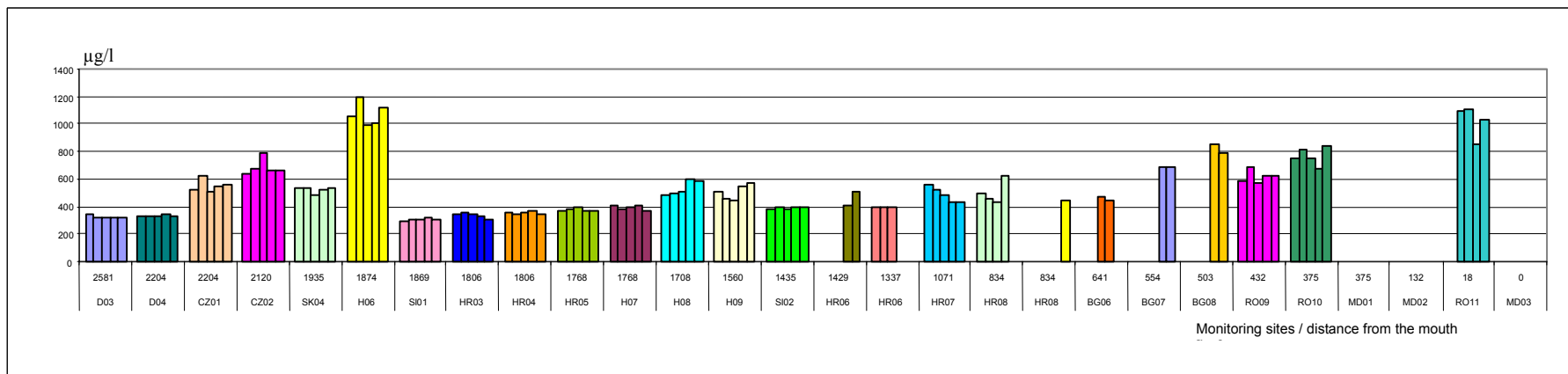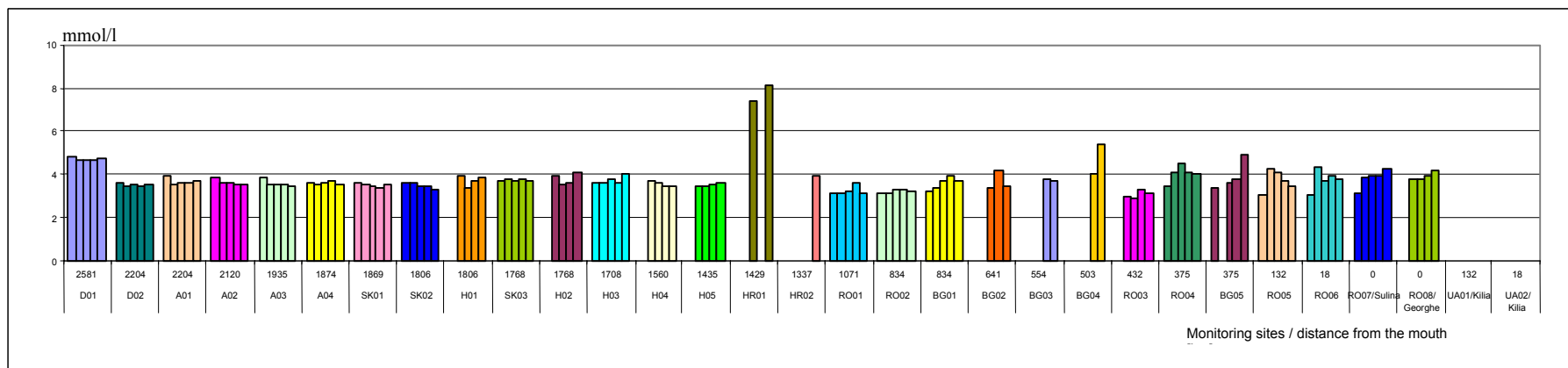Fig. 8.1.1.15: Temporal trends of Alkalinity – Danube River
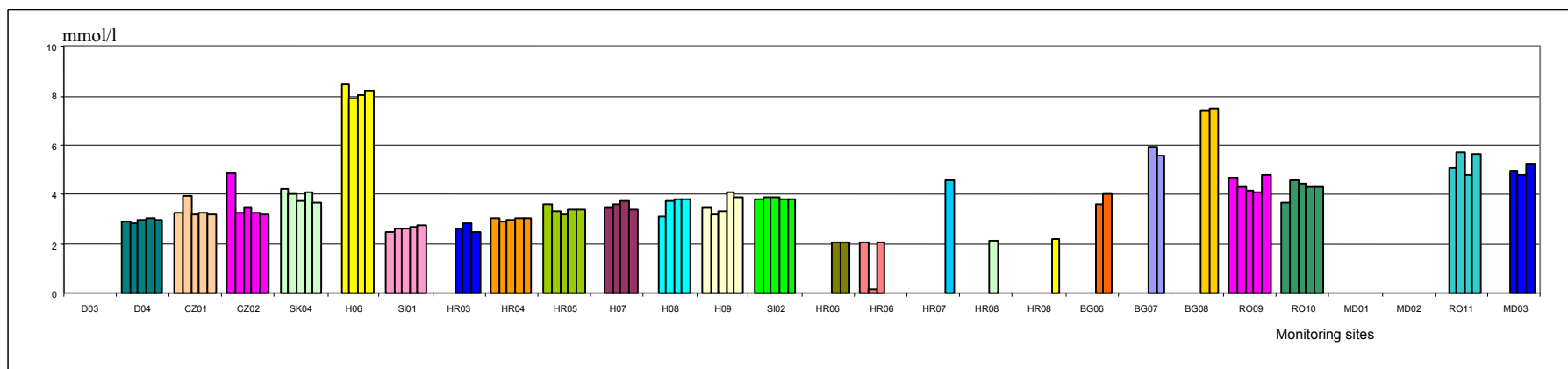
Fig. 8.1.1.16: Temporal trends of Alkalinity – Tributaries

8.1.2.   Nutrients

Assessment of nutrients levels in water column has a particulate importance due to the fact that the input of nutrients into surface waters (mainly nitrogen and phosphorous), either from natural or anthropogenic sources, leads to the process being known as eutrophication. The direct consequences of eutrophication – increased algal bloom, accelerated biological activity (metabolism and decomposition), widespread reduction in dissolved oxygen concentration, growth of higher plants, changes in aquatic food chain and, eventually, a disturbed ecosystem and a deteriorated water quality – make the assessment of nutrients level to be one of the most important issue in assessment of water quality. Although the associated effects of eutrophication are characteristic particularly to lakes, reservoirs, coastal areas and large slowly flowing rivers as well, it could also be apparent in the case of the various conditions specific to the Danube River.

From the different fractions analyzed within the TNMN Programme, ammonium-N, nitrite-N, nitrate-N, ortho-phosphate-P and total phosphorous were chosen for spatial pattern assessment and trend assessment in the report.

Nitrogen

Dissolved inorganic nitrogen, particularly ammonium and nitrate, constitutes most of the total nitrogen in river waters. They derive mainly from the decomposition of protein compounds that enter the surface water along with urban and industrial waste discharge. Among the indirect sources of various nitrogen forms, erosion/runoff from agriculture and effluents from animal farms can be mentioned.

As it will be shown, nitrogen levels have a characteristic concentration distribution along the Danube and its tributaries.

Ammonium

Ammoniacal-nitrogen occurs in two forms: ammonia (NH_3) and ammonium (NH_4^+); the first one is a dissolved gas with much higher toxicity on aquatic ecosystem than the ionized form. The equilibrium between the two species depends on pH. Mediated by microorganisms, decomposition of protein organic matter has as final result release of ammonium. It can also emerge from decomposition of mineral and vegetal matters. Dissolved ammonium is further oxidized to nitrites and nitrates.

The distribution of monitoring sites according to the Classification System in the DRB for ammonium-N is shown in **Fig. 8.1.2.1**:
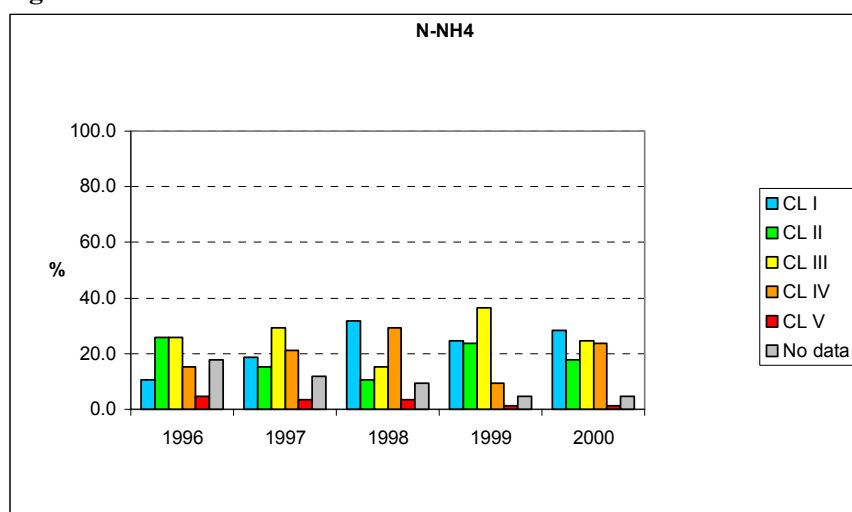
Fig. 8.1.2.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NH$_4$**

The quality assessment within the five-class system is made based on data reported from 85 monitoring sites (out of the assessment are 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000) and the following remarks can be done in this respect:
-   the temporal distribution of monitoring sites within quality classes is generally uneven during five studied years, with no percentage above 50 % in one class;
-   The percentage of sites in Class I varies between 10.6 % in 1996 and 31.8 % in 1998;
-   The percentage of sites corresponding to Class II is in the range from 7 % (1998) to 26 % (1996);
-   The maximum percentage of sites in Class III is in 1999 (36.5 %) and in Class IV in 1998 (29.4%)
-   Only few monitoring sites (1.2 – 4.7 %) correspond to Class V;
-   the number of measurements was increasing from 1996 to 2000.

The spatial variation of ammonium-N along the Danube River is shown in **Fig. 8.1.2.2a** and **8.1.2.2b**.

In the upper section of the river, ammonium-N concentrations have a homogenous level, with no value above the target value (0.30 mg/l).

In the middle section most of the concentrations are below 0.30 mg/l, too. Slightly higher values were recorded at Danube-Bratislava (km 1869, SK01), Danube-Medvedov/Medve (km 1806, SK02) and Danube-Komarno/Komarom (km 1768, SK03). It has to be mentioned that at the last two mentioned cross-sections (SK02/H01 and SK03/H02) results reported by the Hungarian part are significantly lower than results from Slovakia. Along this middle stretch, 18 c90 values are indicated as above the target value.

The ammonium-N spatial pattern changes in the first part of the lower Danube section, where the concentration level rises up to 0.75 mg/l between Danube-Bazias (km 1071, RO01) and Danube-Pristol/NovoSelo (km 834, RO02). An even higher value (1.09 mg/l) was observed at Danube-us. Iskar – Bajkal (km 641, BG02).
In the second part of lower Danube section, the general pattern shows an increasing of concentrations. Thus, the ammonium-N values recorded in 1998 in two arms of the Danube Delta (Sulina/Sulina arm and Sf. Gheorghe/Sf. Gheorghe arm) are 1.39 and 1.44 mg/l, respectively. For the entire lower Danube, 151 values were above the quality target in the period 1996-2000.

The large differences of the upper and the middle section ammonium-N levels against the ones from the lower Danube section are mainly attributable to the anthropogenic influence upon lower Danube on one hand (sewage effluent and runoff from agriculture) and to the general improvement in waste water treatment in the upper and the middle sections on the other hand.
Remarkable is high year-to-year variability in ammonium-N values in the monitoring sites of lower Danube section.

The spatial distribution of ammonium-N level for selected tributaries is illustrated in **Fig. 8.1.2.3a** and **8.1.2.3b**.

As it can be seen, for tributaries located in the upper and the middle section, rather high ammonium-N concentrations were recorded on the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02), Vah-Komarno (SK04) and Sio-Szekszard-Palank (H06); most of these ammonium-N values (above 0.60 mg/l – the limit value for Class III) are mainly attributable both to urban waste waters and agricultural inputs. on In case of Tisza and Sava tributaries, with only few exceptions the ammonium-N c90 level is below 0.60 mg/l. The water quality is totally different in tributaries located in the lower Danube: if in Iskar-Orechovitza (BG06) and Jantra-Karantzi (BG07) only one value correspond to Class IV and Class V,

respectively, in Arges-Conf. Danube (RO09), all ammonium-N concentrations - between 2.49 – 7.68 mg/l - are within Class V. These extreme high values, correlated with BOD_5 values, are mostly caused by non- or insufficiently treated waste waters from municipalities. Still very high ammonium-N concentrations (above 1.50 mg/l in 1996 – 1998) were observed on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11). In all selected tributaries, 67 concentrations are above the quality target for ammonium-N.

The temporal trends for ammonium-N concentrations along the Danube River are shown in **Fig. 8.1.2.4** and for tributaries in **Fig. 8.1.2.5**:
- for the upper Danube, a decreasing trend from 1996 to 2000 is visible;
- in the middle Danube, for monitoring sites located on left side of the river (the Slovakian part) there is a decreasing trend from 1996-1997 to 1998, followed by a stationary state until 2000; for the rest of monitoring sites located along this stretch, a relatively constant temporal profile is observed;
- in the first lower part of Danube River, temporal pattern is very scattered, with higher values recorded in 1997, 1998 and 2000. In the second part, situation is similar, with higher concentrations characteristic mainly to 1996, 1997 and 1998;
- in majority of tributaries located in the upper and middle Danube, generally ammonium –N seems to decrease, excepting Croatian sites located on the Sava River;
- for tributaries located in the lower Danube, the Arges-Conf. Danube (RO09) shows most critical ammonium-N values in 1996 and 2000; in Siret-Conf. Danube (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) values observed in 1999-2000 were significantly lower than those measured in 1997 and 1998.

Fig. 8.1.2.2a: Spatial variation of N-NH$_4$ – Danube River

Fig. 8.1.2.2b: Spatial variation of N-NH$_4$ – Danube River

Fig. 8.1.2.3a: Spatial variation of N-NH$_4$ – Tributaries

Fig. 8.1.2.3b: Spatial variation of N-NH$_4$ – Tributaries
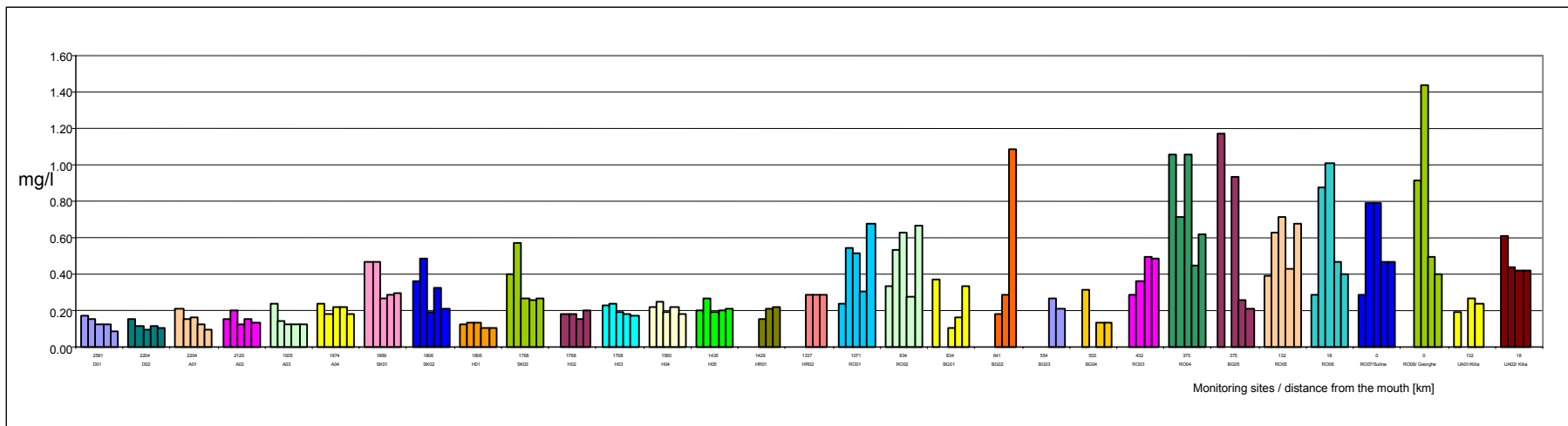
Fig. 8.1.2.4: Temporal trends of N-NH$_4$ – Danube River
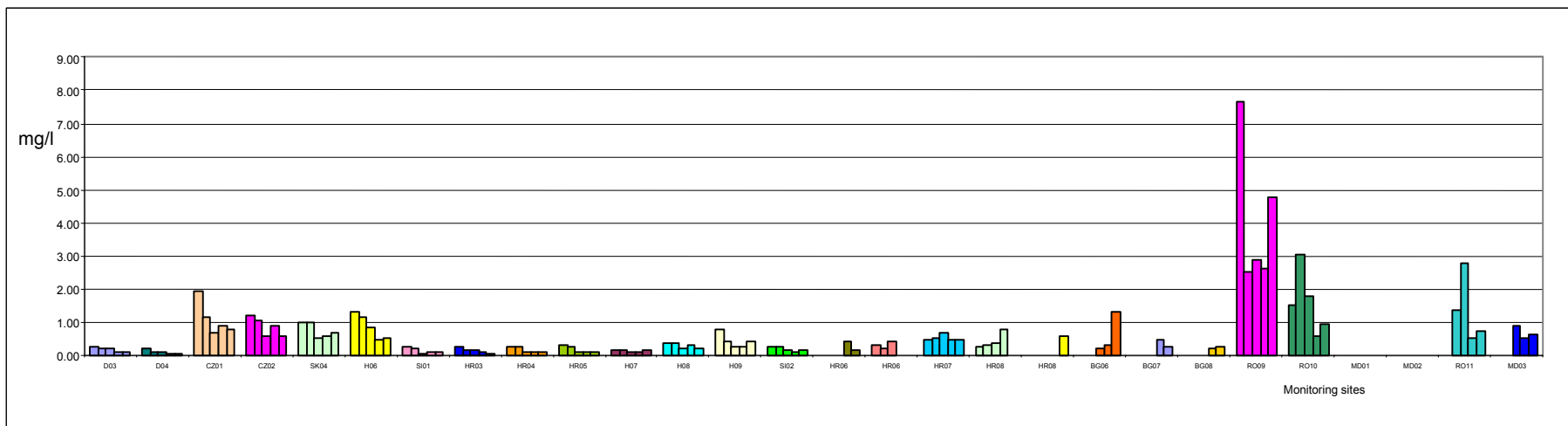
Fig. 8.1.2.5: Temporal trends of N-NH$_4$ – Tributaries

Nitrite

Nitrite is an intermediate nitrogen form in the oxidation/reduction process of the nitrogen dissolved forms.

The distribution of monitoring sites according to the Classification System in the DRB for nitrite-N is shown in **Fig. 8.1.2.6**:
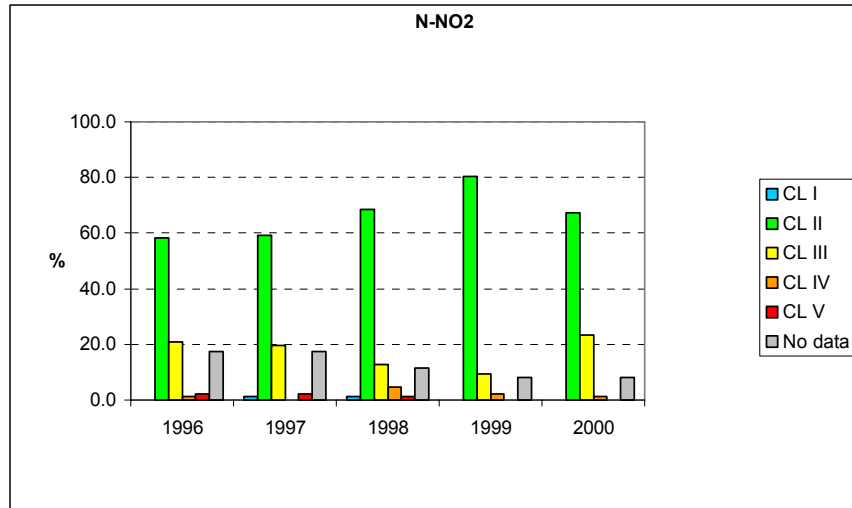
Fig. 8.1.2.6: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NO₂**

From the above-mentioned figure, based on data reported from 86 monitoring sites, (out of the assessment is 17 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be seen that:
- no site presents nitrite values corresponding to Class I
- more than 50 % of all sites are within Class II each year. The respective percentages increase from 1996 to 1999 and then decrease in 2000 in favour of Class III;
- the temporal profile corresponding to Class III is opposite to the previous one: decreases from 1996 to 1999 and increases in 2000;
- there are no sites corresponding to Class IV in 1997, the values representing other years are very low, with a maximum of 4.7 % in 1998;
- Class V is represented during 1996 – 1998 only, by a percentage of less than 3 % of all sites each year;
- number of measurements increased in evaluation period in a similar pattern as ammonium-N.

The spatial pattern for nitrite-N concentrations for the Danube River is shown in **Fig. 8.1.2.7a** and **8.1.2.7b** and it has the following features:

In the upper part of the Danube, almost no value exceeds 0.040 mg/l, which is less than the quality target (0.060 mg/l).

Approximately the same spatial pattern is present in the middle section of the river, where the nitrite-N concentrations vary within the range 0.020 – 0.051 mg/l. Apart an extreme value (0.233 mg/l) observed in 1998 at Danube-Bratislava (km 1869, SK01), along this stretch an increasing spatial variation is present; only 8 nitrite-N concentrations are above the target value.

In the first part of the lower Danube, nitrite-N concentrations are higher than in the middle stretch, reaching the 0.071 mg/l in 1996 at Danube-Pristol/Novo Selo (km 834, RO02).

In the second part of the lower Danube section, nitrite-N concentrations continue to rise up to 0.126 mg/l at Danube-Reni/Kilia arm/Chilia arm (km 132, UA01).

For the entire lower Danube, 58 values are above target value 0.060 mg/l.

For selected tributaries, (the spatial variation in **Fig. 8.1.2.8a** and **8.1.2.8b**), the concentrations vary within the range 0.009 – 0.720 mg/l. In the upper part, the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) show values exceeding 0.060 mg/l in all five studied years. In the middle Danube, the Sio-Szekszard-Palank (H06) is characterized by high nitrite-N concentrations ranging between 0.147 and 0.435 mg/l. In a smaller extent, the Vah-Komarno (SK 04), Sajo-Sajopuspoki (H09), Sava-Jesenice and Sava-us. Una Jasenovac (HR06 and HR07) present concentrations above 0.060 mg/l.
The nitrite-N levels are different for the Jantra-Karantzi (BG07), Prut-Leuseni (MD02) and particularly for the Siret-Conf. Danube Sendreni (RO10): if for the first two ones the concentration reaches 0.280 mg/l in 1997 and 0.282 mg/l in 1998 respectively, the last one is characterized by a value of 0.720 mg/l recorded in 1998.
The total number of nitrite-N c90 values exceeding the target value in selected tributaries is 45.

The temporal trend (**Fig. 8.1.2.9**) shows no significant variation during 1996 – 2000 for upper Danube. In the middle Danube, a slight decreasing trend from 1996 to 2000 is present for Slovak results (SK02 and SK03), while for Hungarian results at the same cross sections the trend is quite opposite. In the first part of the lower Danube, a zigzag profile characterizes the Danube-Bazias and Danube-us. Iskar-Bajkal monitoring sites. At the cross section from Danube-Pristol/NovoSelo/Pristol (km 834 - RO02/BG01), temporal trends are different: according to RO02 results, higher values are recorded in 1996 and 1997 and according to BG01, in 1999. In the second part of the lower Danube section, the temporal profile is unevenly distributed among the five years, most of the sites showing a decreasing line from 1996 to 1999, followed by an increasing in 2000.

For selected tributaries, the temporal variation of the nitrite-N concentrations (**Fig. 8.1.2.10**) shows that for the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02) and Vah-Komarno (SK04) a decreasing trend from 1996 to 2000 can be seen. For the Sio-Szekszard-Palank (H06) high values are recorded in 1996 and 1997, followed by decreasing values until 2000. The other tributaries from the middle section present no significant temporal variation during the studied period. In the lower Danube, the Arges-Conf. Danube (RO09) shows an increasing tendency from 1996 to 1999, while for the Siret-Conf. Danube Sendreni (RO10) the trend is opposite from 1996 to 2000.
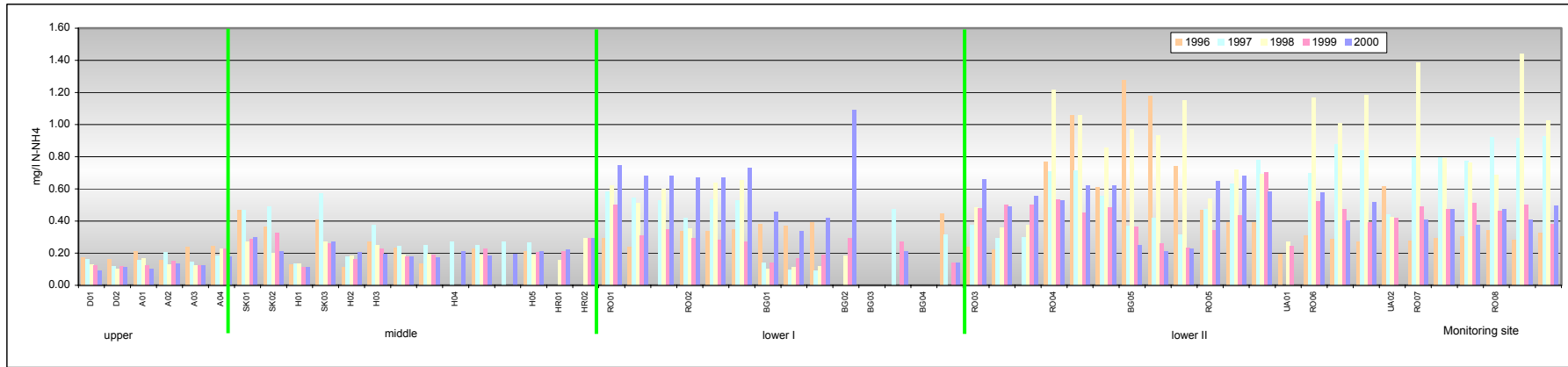
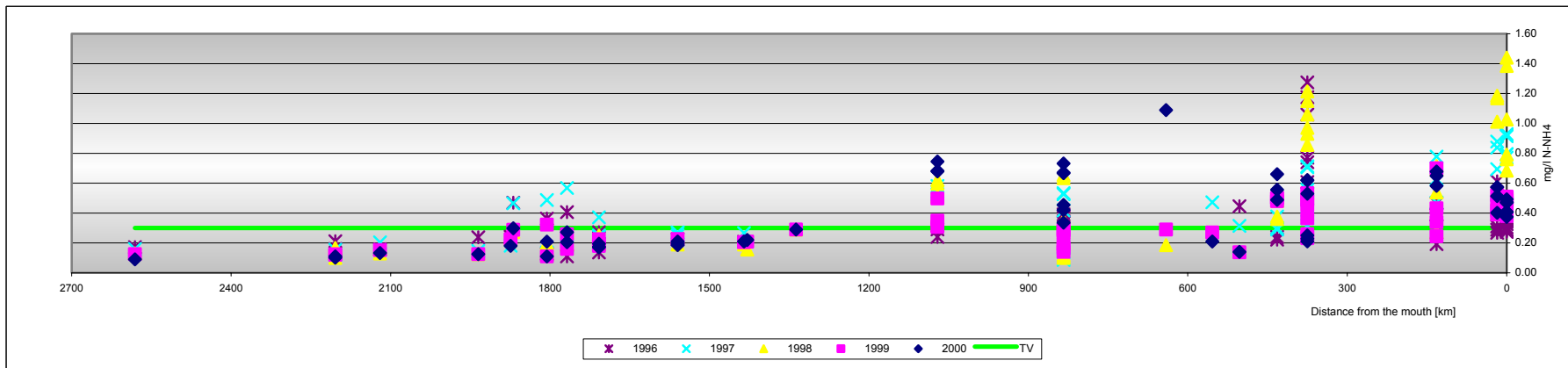Fig. 8.1.2.7a: Spatial variation of N-NO$_2$ – Danube River

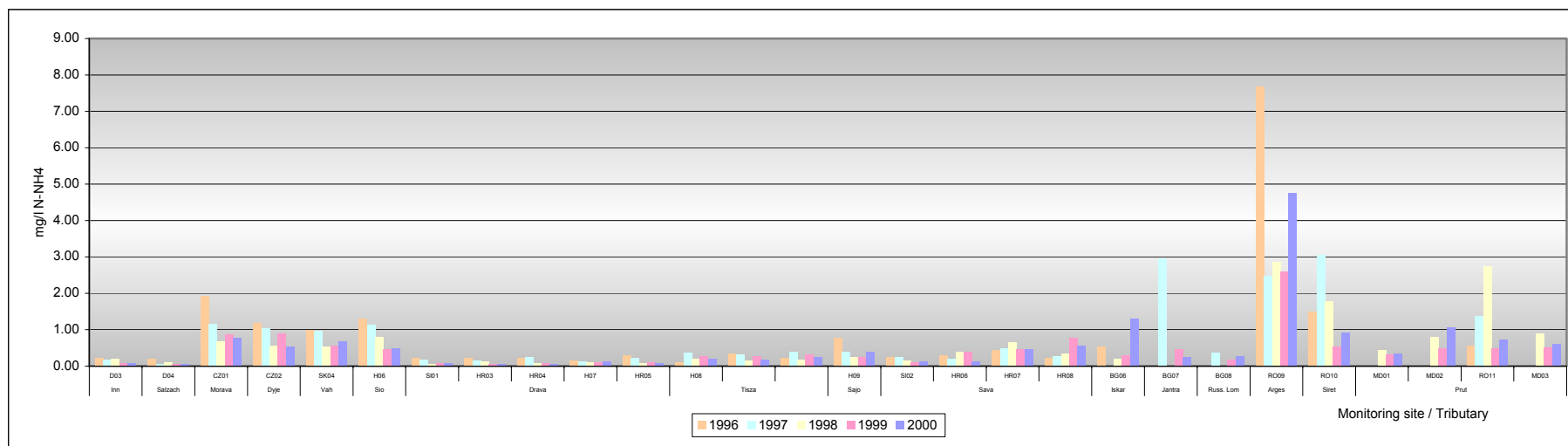Fig. 8.1.2.7b: Spatial variation of N-NO$_2$ – Danube River

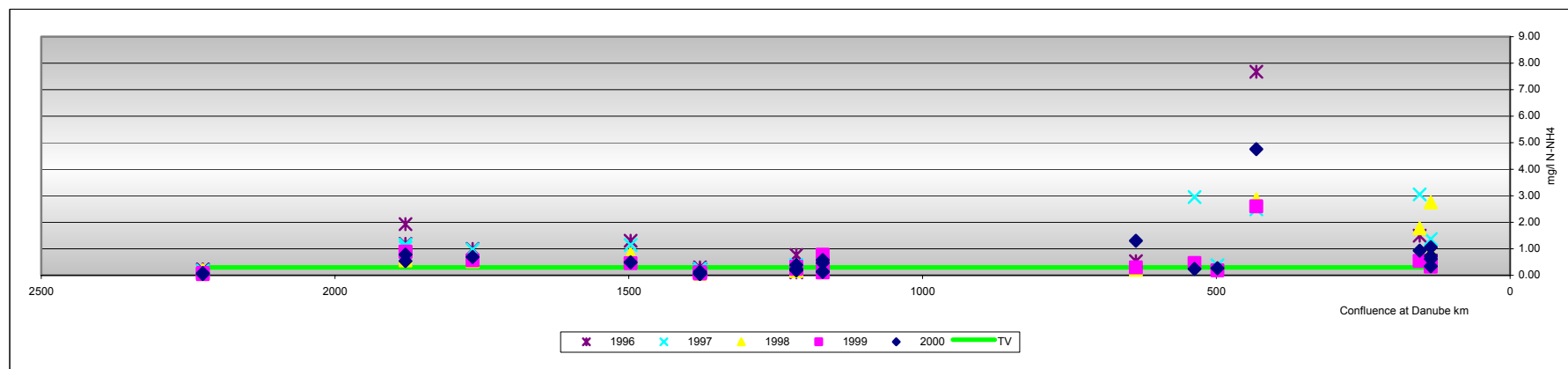Fig. 8.1.2.8a: Spatial variation of N-NO$_2$ – Tributaries

Fig. 8.1.2.8b: Spatial variation of N-NO$_2$ – Tributaries
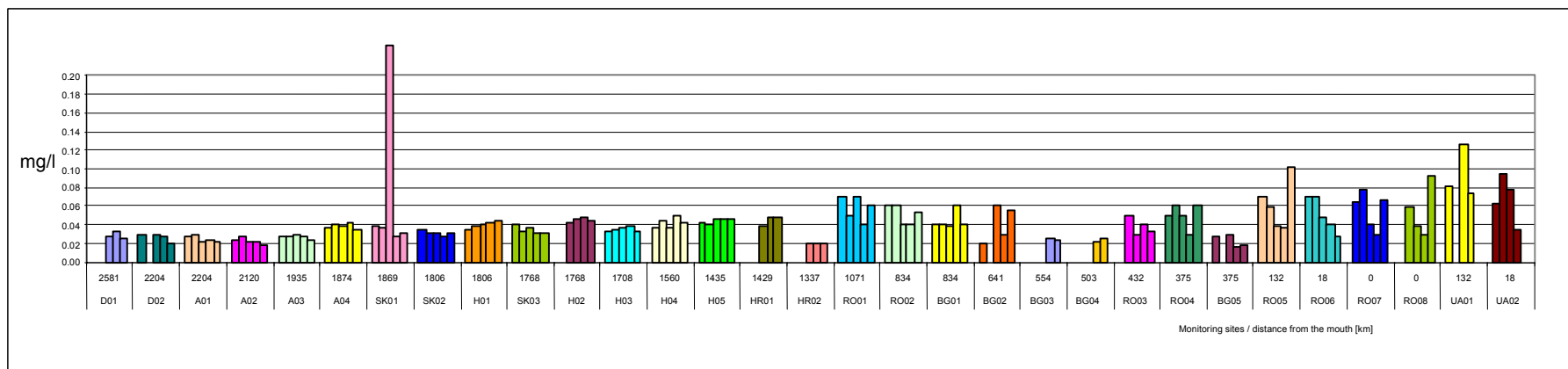
Fig. 8.1.2.9: Temporal trends of N-NO$_2$ – Danube River
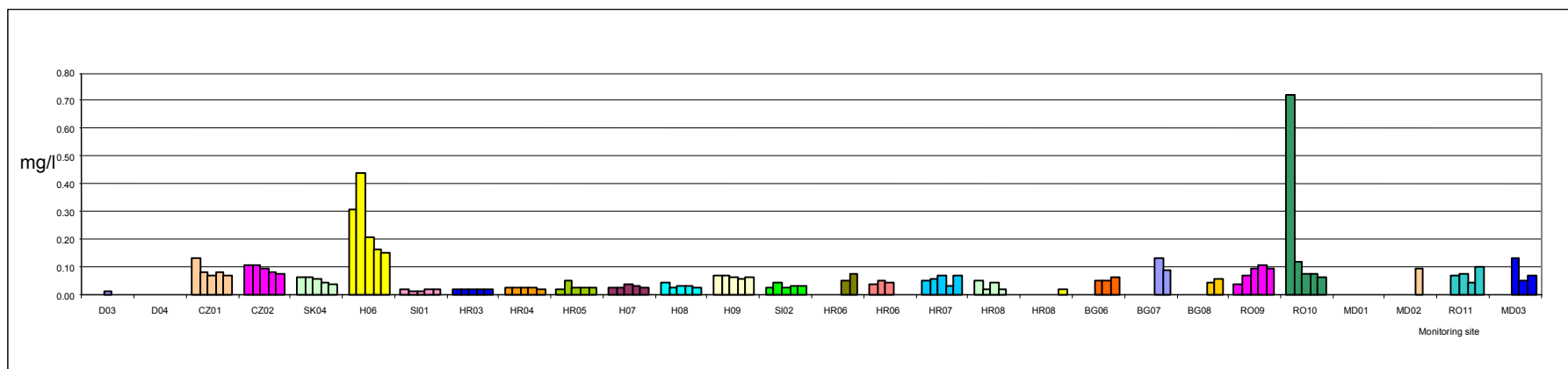
Fig. 8.1.2.10: Temporal trends of N-NO$_2$ – Tributaries

Nitrate

Nitrate is the final product of oxidation of N-components. Potential sources of nitrate include industrial wastes, animal wastes and fertilizers applied to agricultural crop land.

The distribution of monitoring sites according to the Classification System in the DRB for nitrate-N is shown in **Fig. 8.1.2.11**.
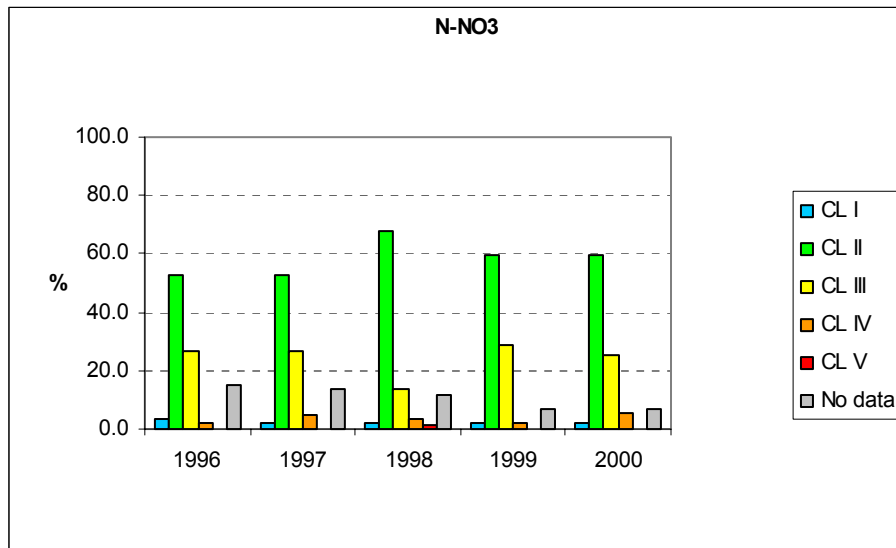
Fig. 8.1.2.11: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NO₃**

Based on data measured at 87 monitoring sites (therefore out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following pattern is valid:
- the number of sites within Class I is very low, actually between from 2.3 -3.4 %
- more than 50 % of all sites correspond to Class II each year, with a maximum of 67.8 % in 1998; almost 60 % of sites are characterised by this quality class during 1999 – 2000;
- representation of Class III has an inhomogeneous temporal variation, with a minimum percentage of 13.8 % in 1998 and a maximum of 28.7 in 1999;
- Class IV has less than 5 % of all sites during 1996 – 2000 and 5.7 % in 2000;
- Class V is present in 1998 only, with 1.1 % of sites.

The spatial variation for nitrate-N concentrations is shown in **Fig. 8.1.2.12a** and **8.1.2.12b**:

In the upper part of the Danube, 25 nitrate-N concentrations are above the quality target (3.00 mg/l), with the maximum value (4.76 mg/l) at Danube-Neu-Ulm (km 2581, D01). Probably the main cause of this profile is the base flow (*Nutrient Balances for Danube Countries* Project, 1991). Downstream this location, the concentrations level remains constant down to Danube-Wolfsthal (km 1874, A04).

In the middle section, the nitrate-N concentration level is quite homogenous, with 47 values exceeding the quality target.

In the first part of the lower Danube, nitrate-N level is lower than in the middle one, the influence of the Iron Gate reservoir being visible in this area. Rather high values appear at Danube-us. Iskar-Bajkal (km 641, BG02) and at Danube-ds. Svishtov (km 554, BG03)– 3.27 and 5.28 mg/l respectively. In the second part of the lower Danube, avoiding three high values within the range 4.70 – 5.80 mg/l, recorded at Danube-us. Arges (km 432, RO03), all the other concentrations are within the range 1.16 – 2.99 mg/l.

Tributaries are illustrated in **Fig. 8.1.2.13a** and **8.1.2.13b.** As it has already been shown also in case of previous nutrient forms, the tributaries from the upper and the middle Danube that are characterized by higher nitrate-N concentrations values are   Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02), Sio-Szekszard-Palank (H06) and in a smaller extent Vah-Komarno (SK04). Thus, on Dyje and Sio rivers, nitrates level exceeds 6 mg/l, the limit value for Class III. (7.50 and 9.54 mg/l respectively). The next tributaries from the middle Danube present a uniform level of variation - below 3.00 mg/l - with exceptions occurring on the Sajo-Sajopuspoki (H09) and Sava-Jesenice (HR06), where several values are above this limit. As far as concerns the tributaries located in the lower Danube, the nitrates-N values are the highest from those observed in tributaries in Russenski Lom-Basarbovo (BG08) - 10.39 mg/l, Arges-Conf. Danube (RO09) - 10.40 mg/l and Prut-Conf. Danube Giurgiulesti (RO11 and MD03) - 10.37 and 11.10 mg/l, respectively. In all tributaries, there are 43 values above the quality target in evaluated period.

The temporal trend for the Danube River is shown in **Fig. 8.1.2.14** and for selected tributaries in **Fig. 8.1.2.15**. Thus, the following general trends are visible:
- for the upper Danube, no significant temporal changes of nitrate-N values are observed;
- in the middle Danube the situation is the same, but can be mentioned that in majority of monitoring sites in this section nitrate-N values were highest in 1996;
- in the lower Danube, temporal variation shows that in the first part the most elevated values are recorded in 1998 and 2000, while in the second part, the general trend is increasing from 1996 to 1999;
- tributaries from the upper Danube present a relatively stable state for Inn-Kirchdorf (D03) and Salzach-Laufen (D04); in Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) the nitrate-N values decrease;
- in the middle section, a decreasing trend from 1996 to 1998 followed by an increasing until 1999 or 2000 is valid for the Vah-Komarno (SK04) and for several monitoring sites located on Drava (Ormoz-SL01, Varazdin-HR03, Botovo-HR04 and D. Miholjac-HR05). A clear decreasing trend from 1996 to 1999 is visible on the Sio-Szekszard-Palank (H06). An opposite temporal variation appears on the Sajo-Sajopuspoki (H09). For the Sava tributary, no systematic temporal trend is noticeable;
- tributaries located in the first part of the lower Danube do not indicate any trend; in the second part, in Arges-Conf. Danube (RO09) an increasing trend from 1996 to 2000 is visible. For the Siret-Conf. Danube Sendreni (RO10) a relatively stable state is characteristic, while for the Prut tributary, two different monitoring sites (RO11 and MD03) show the highest values recorded in 2000 and 1998, respectively.

Fig. 8.1.2.12a: Spatial variation of N-NO$_3$ – Danube River

Fig. 8.1.2.12b: Spatial variation of N-NO$_3$ – Danube River

Fig. 8.1.2.13a: Spatial variation of N-NO$_3$ – Tributaries
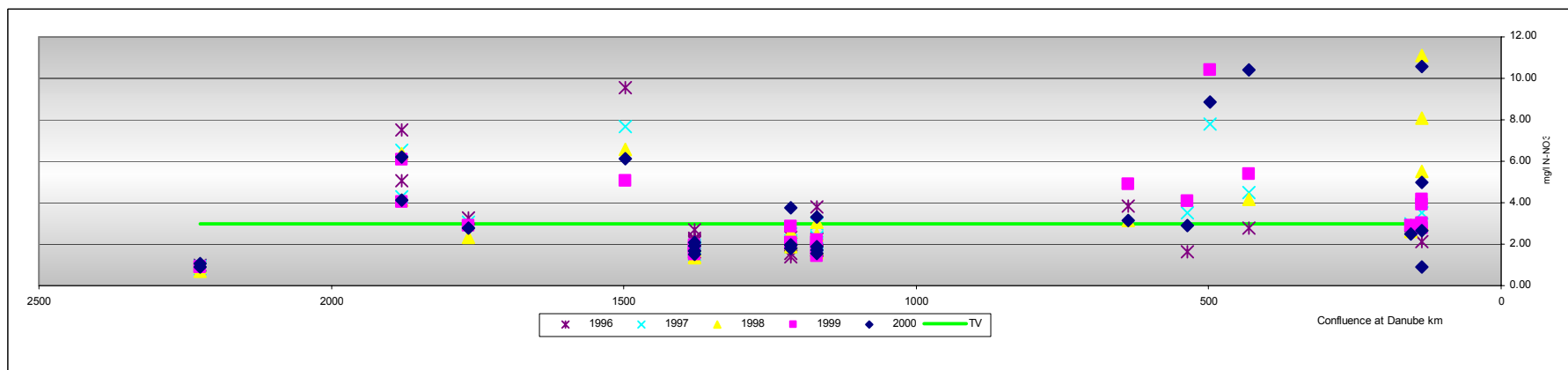
Fig. 8.1.2.13b: Spatial variation of N-NO$_3$ – Tributaries
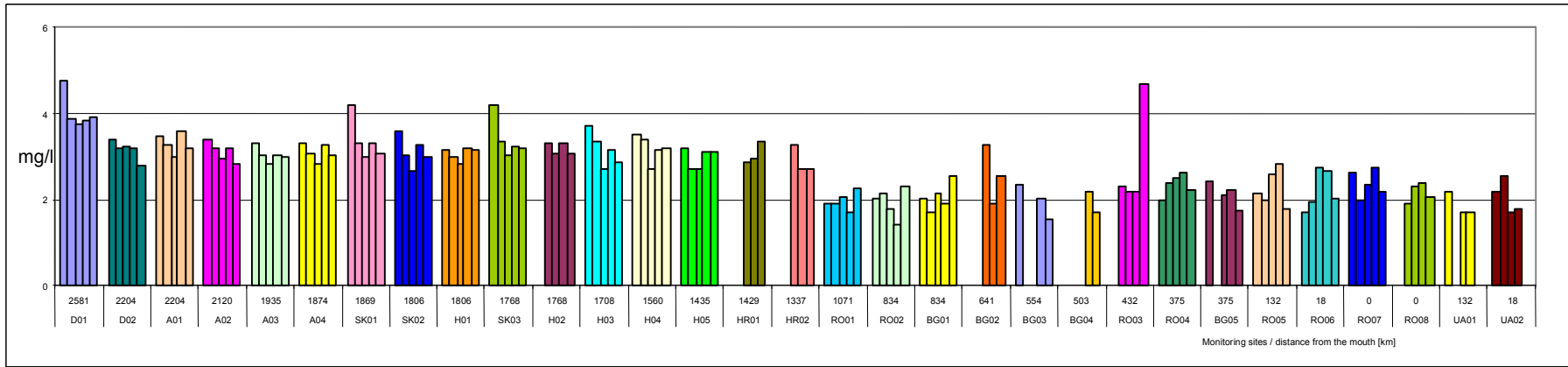
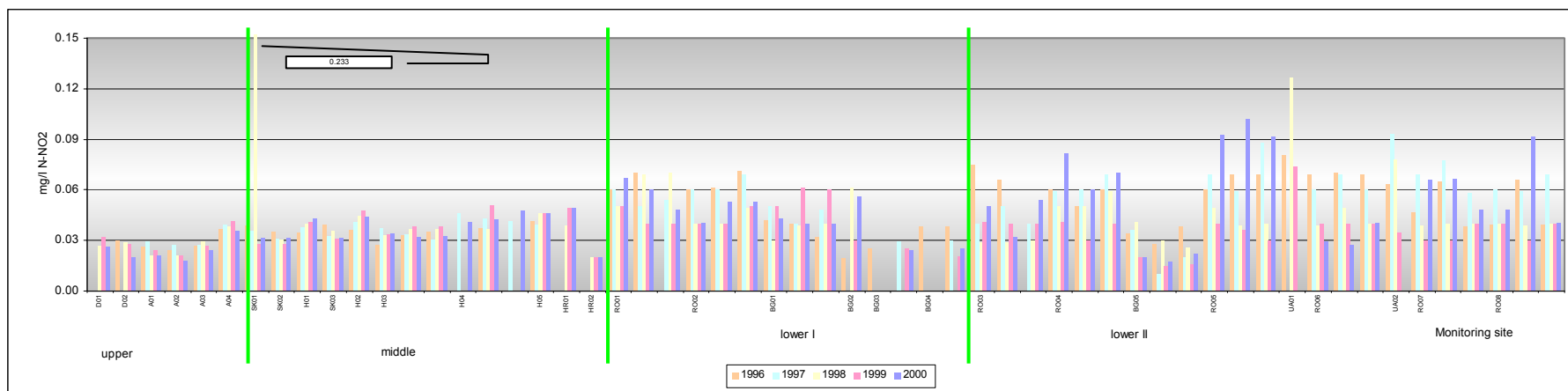Fig. 8.1.2.14: Temporal trends of N-NO$_3$ – Danube River
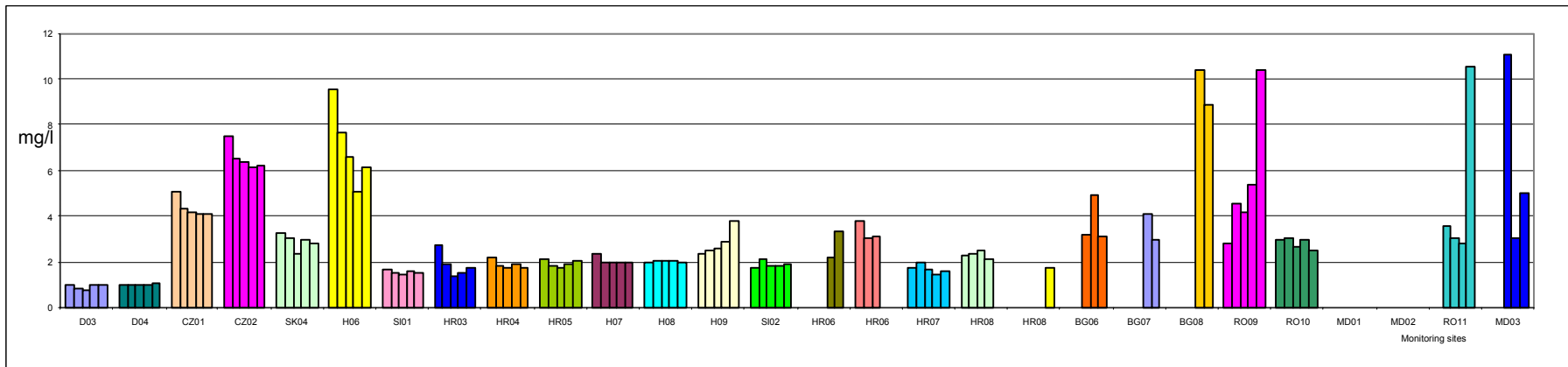
Fig. 8.1.2.15: Temporal trends of N-NO$_3$ – Tributaries

Phosphorous

Phosphorous is one of the main components in organic matter. It generally originates from mineralization from the soil and rocks (as natural sources) and from waste effluents, municipal wastewaters or drainage that contain fertilizers (as anthropogenic sources). Although phosphorous tends to be the nutrient that mostly limits plant growth in lakes in reservoirs, its presence assessment in flowing rivers is not of a less importance. If the natural background concentration of dissolved phosphorous is about 0.025 mg/l P, the polluted segment of a watercourse may contain up to 1 mg/l P or even more (*The Dobris Assessment, 1991*).

In TNMN Programme, phosphorous is measured both as total phosphorous and soluble reactive phosphate or ortho-phosphate. The latter form is the only biologicaly available form of phosphorous.

Ortho-phosphate

The distribution of monitoring sites according to the Classification System in the DRB for ortho-phosphate-P is shown in **Fig. 8.1.2.16**.
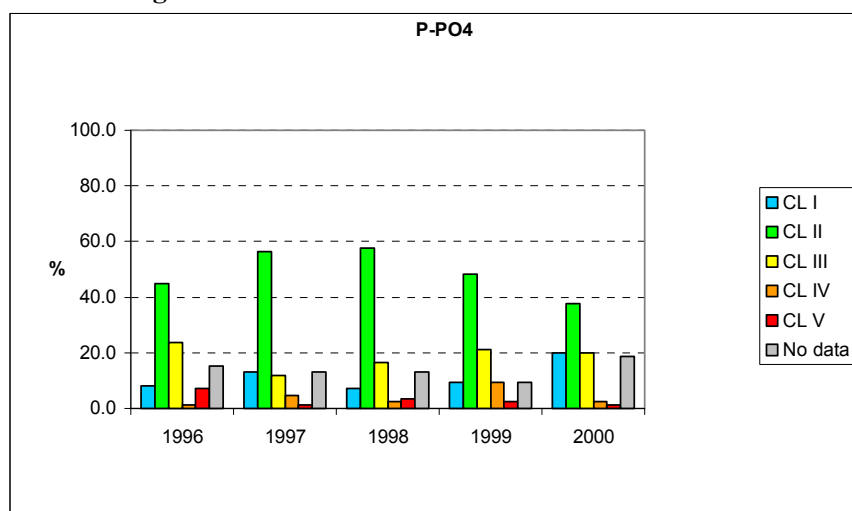
Fig. 8.1.2.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **P-oPO$_4$**

On the bases on data reported from 85 monitoring sites (out of the assessment are 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following can be concluded:
-   the number of monitoring sites within Class I shows an uneven temporal variation, with a minimum of 7.1 % in 1998 and a maximum of 20% in 2000;
-   Class II comprises the maximum percentages in each year, with an increasing line from 1996 to 1998, followed by a decreasing until 2000. Percentage of sites in Class II varies from 38% (2000) to 58% (1998);
-   the percentage of monitoring sites within Class IV is low, with maximum value of 9.4% in 1999;
-   similarly low percentage if sites correspond to Class V, with a maximum of 7.1% in 1996.

The spatial assessment of orthophosphate-P concentration along the Danube River is shown in Fig. **8.1.2.17a** and **8.1.2.17b**.

In the upper Danube, ortho-phosphate concentrations level is nearly 0.050 mg/l at all monitoring sites, so no value is above the target value for this nutrient (0.10 mg/l).

In the middle Danube, spatial profile is slightly changed, with most of the values within the range 0.060 – 0.126 mg/l. Comparing with the quality target value, there are 18 values above it.

In the first part of the lower Danube, the ortho-phosphate-P concentrations are higher than in the middle Danube, the variation range of c90 is 0.070 – 0.186 mg/l for the first 200 km of this stretch. Although high values from Danube-Bazias (km 1071, RO01) were recorded in 2000, the previous four years do not show many values above the 0.100 mg/l level. An extreme high value (0.446 mg/l) was observed at Danube-us. Russe (km 503, BG04) in 1996.

In the second part of the lower Danube, ortho-phosphate-P c90 values seldom exceed 0.100 mg/l level. However, the big difference between the recorded data at the same cross section (RO04/BG05 and RO06/UA02) gives an inhomogeneous picture of the spatial distribution. Leaving apart this incoherence, a slight decreasing spatial tendency is visible from Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta (RO06, RO07 and RO08).

Along the entire lower Danube, 51 ortho-phosphate-P concentrations are above the quality target.
The spatial pattern of ortho-phosphate-P concentrations in selected tributaries is shown in **Fig. 8.1.2.18a** and **8.1.2.18b**.
  - in the upper and middle section of the Danube, in two tributaries only ortho-phosphate values exceed 0.20 mg/l (the limit value for Class III) in evaluated period: Dyje-Pohansko (CZ02) and the Sio-Szekszard-Palank (H06). In strong correlation with other data from the group of nutrients, these values are caused mainly by anthropogenic inputs.
  - in the lower section, there are far more elevated values for ortho-phosphate, characteristic to Class V: 1.322 and 1.072 mg/l in 1996 and 1998 on the same tributary - Iskar-Orechovitza (BG06). High values were also recorded in 1996 and 1999 on the Jantra-Karantzi (BG07) – 0.460 and 0.484 mg/l, Russenski Lom-Basarbovo (BG08) – 0.850 mg/l and Arges-Conf. Danube (RO09) – 0.675 mg/l and 0.850 mg/l;
  - in TNMN tributaries, 57 values are above the target value in period 1996-2000.

Temporal trend for ortho-phosphate-P is shown in **Fig. 8.1.2.19** for the Danube River and in **Fig. 8.1.2.20** for selected tributaries. The following can be concluded:
  - for monitoring sites located in the upper Danube, no significant temporal variation is visible;
  - in the middle Danube, a decreasing trend from 1996 to 1999 is characteristic from Danube-Bratislava (km 1869, SK01) down to Danube-Szob (km 1708, H03); an exception appears at Danube-Medvedov/Medve (km 1806, SK02). For the rest of the sites in this stretch, the temporal distribution is almost stationary.
  - as regards the first part of the lower Danube section, from Danube-Bazias (km 1071, RO01) down to Danube-Pristol/Novo Selo (km 834, RO02) an increasing tendency from 1996 to 2000 is present if the Romanian results are taken into account; according to the Bulgarian data, the temporal trend for Danube-Novo Selo/ Pristol (km 834, BG01) is opposite - decreasing from 1996 to 1999;
  - in the second part of lower Danube section, in most of the monitoring points the values are reather varying. In addition, rather high differences exist between the reported data for the same cross section – Danube-Silistra/Chiciu/Silistra (RO04/BG03, km 375). At the Danube-us. Arges (km 432, RO03) an increasing line from 1997 to 2000 is noticeable;
  - selected tributaries show inhomogeneous temporal trends: the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) have high values recorded in 1996 and 1998 respectively, while the Sio-Szekszard (H06) is characterized by high values in 1997 and 2000. Except a decreasing trend observed in Drava-Varazdin (HR03) the rest of monitoring sites located on this tributary present a relatively stable state. No temoral changes were observed in Tisza tributary, even the variation between years is low. The picture shows differently for the Sava, where no systematic temporal trend is detectable, but year-to-year variation is much higher there.
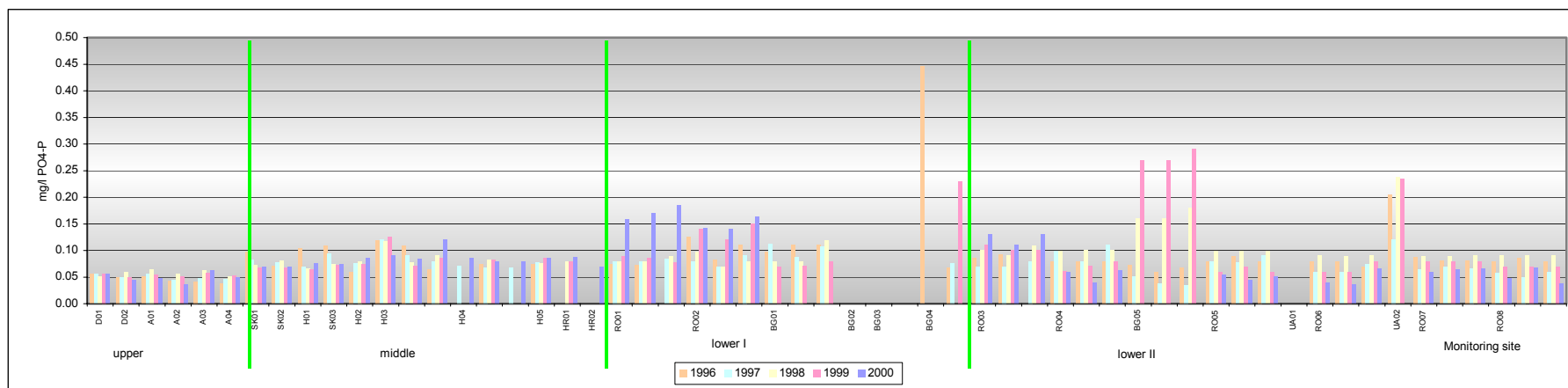
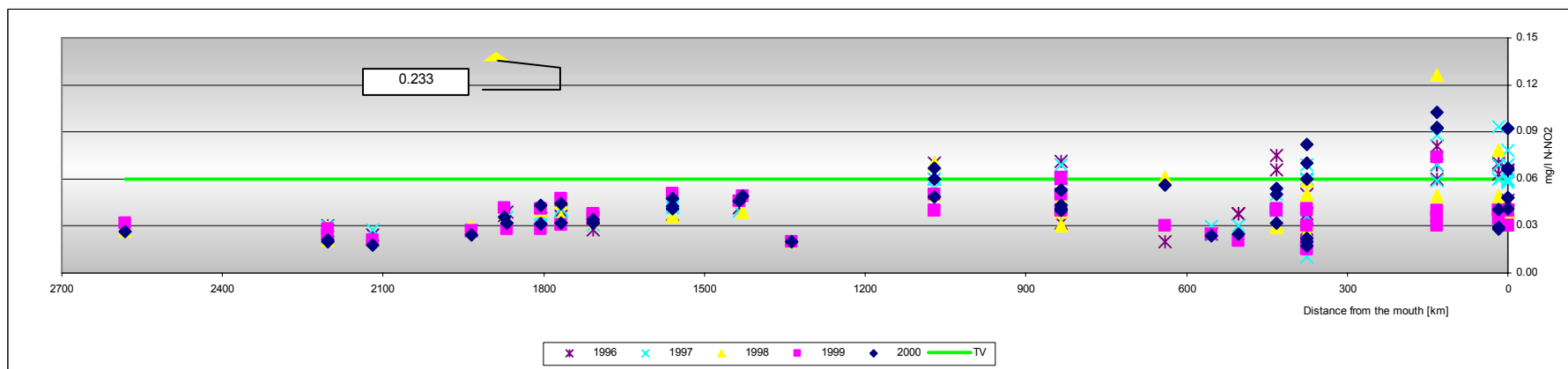Fig. 8.1.2.17a: Spatial variation of P-oPO$_4$ – Danube River
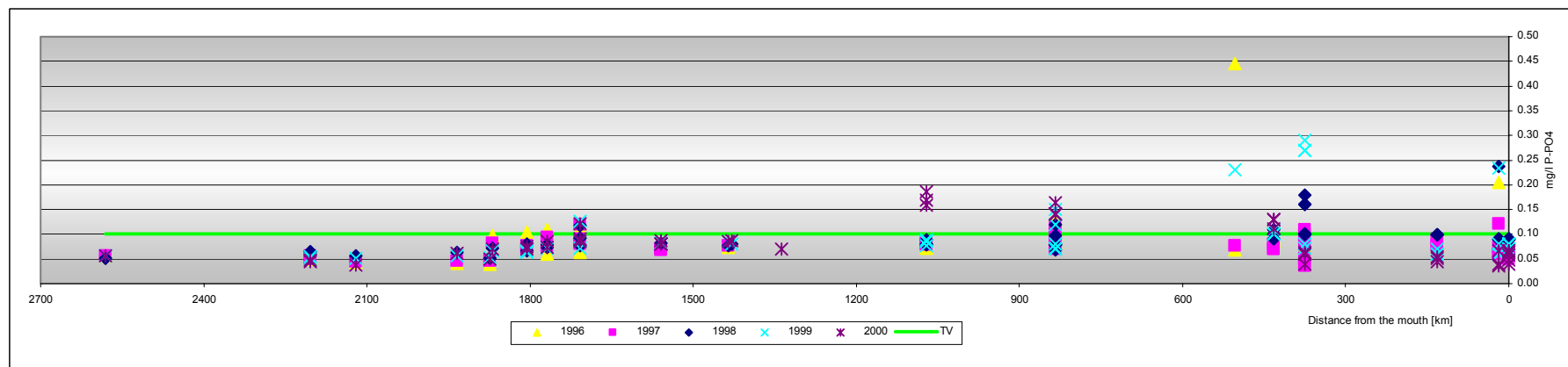
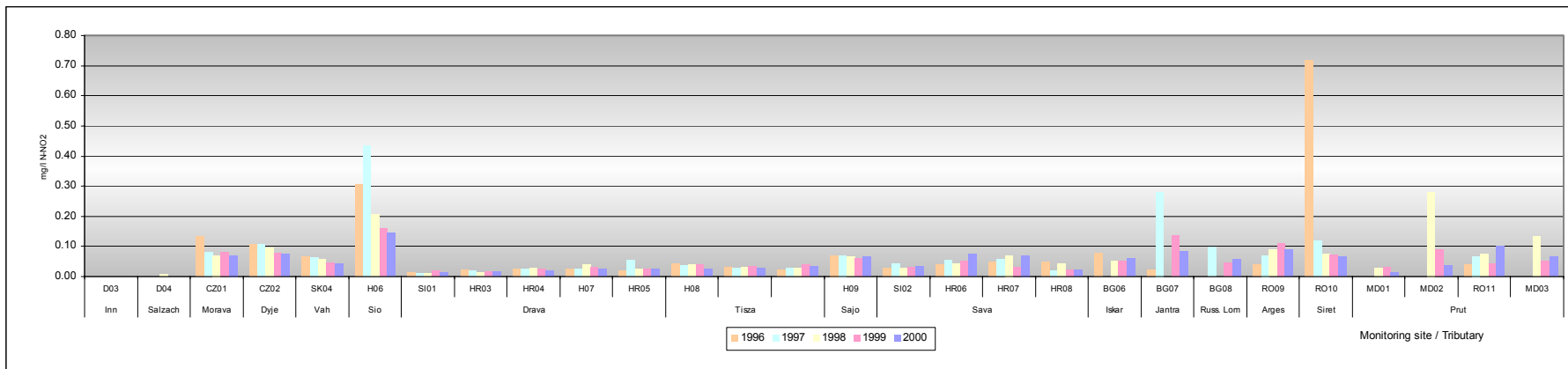Fig. 8.1.2.17b: Spatial variation of P-oPO$_4$ – Danube River
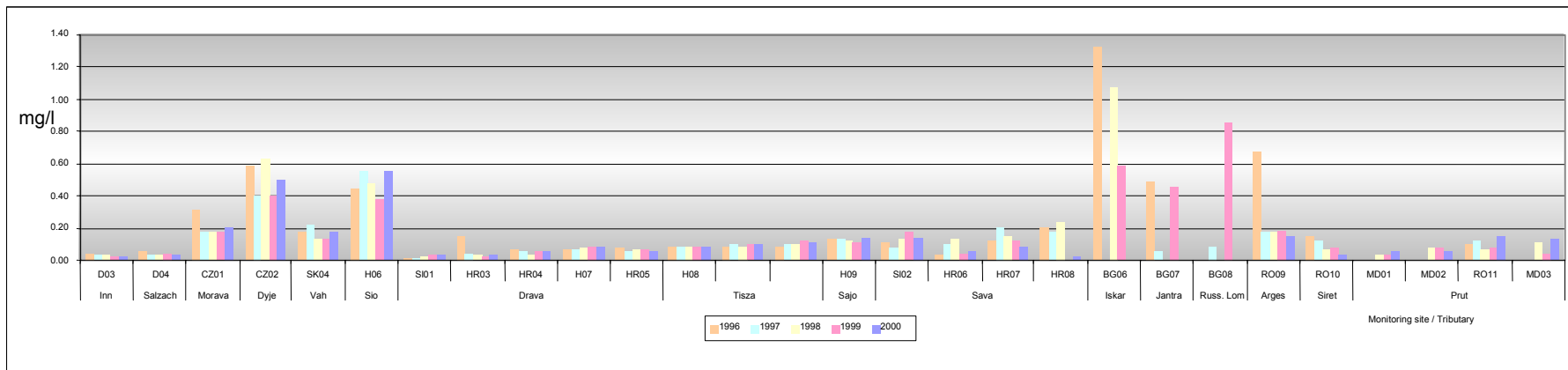
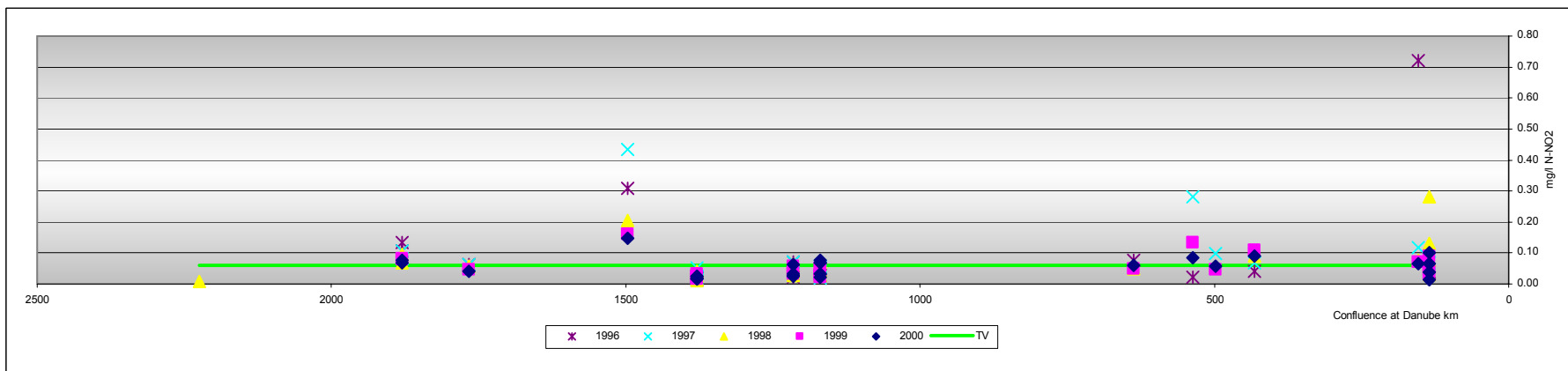Fig. 8.1.2.18a: Spatial variation of P-oPO$_4$ – Tributaries


Fig. 8.1.2.18b: Spatial variation of P-oPO$_4$ – Tributaries
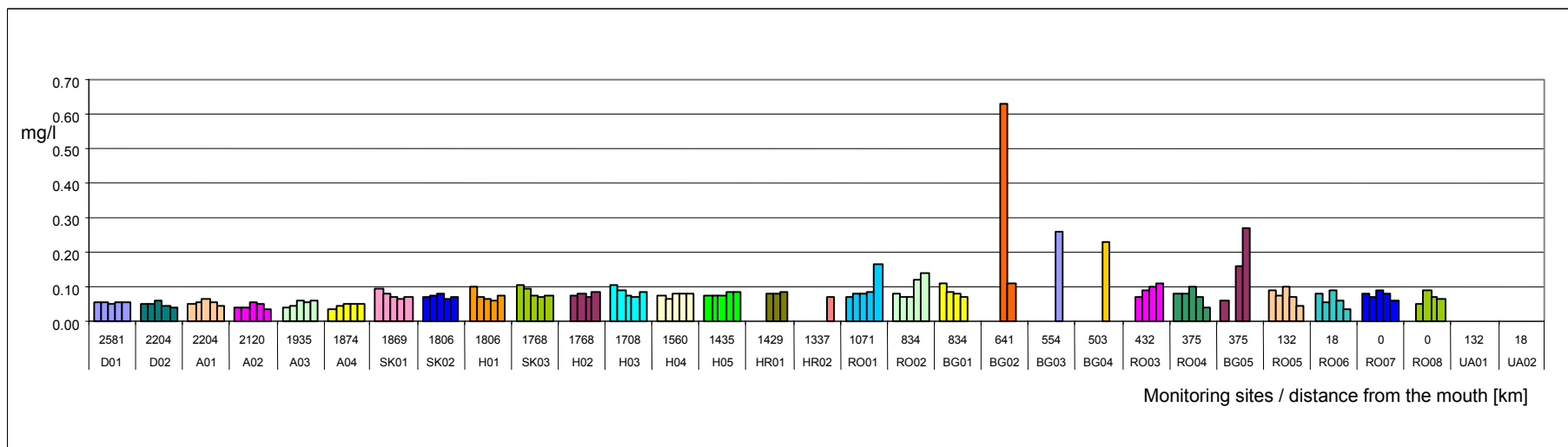
Fig. 8.1.2.19: Temporal trends of P-oPO$_4$ – Danube River
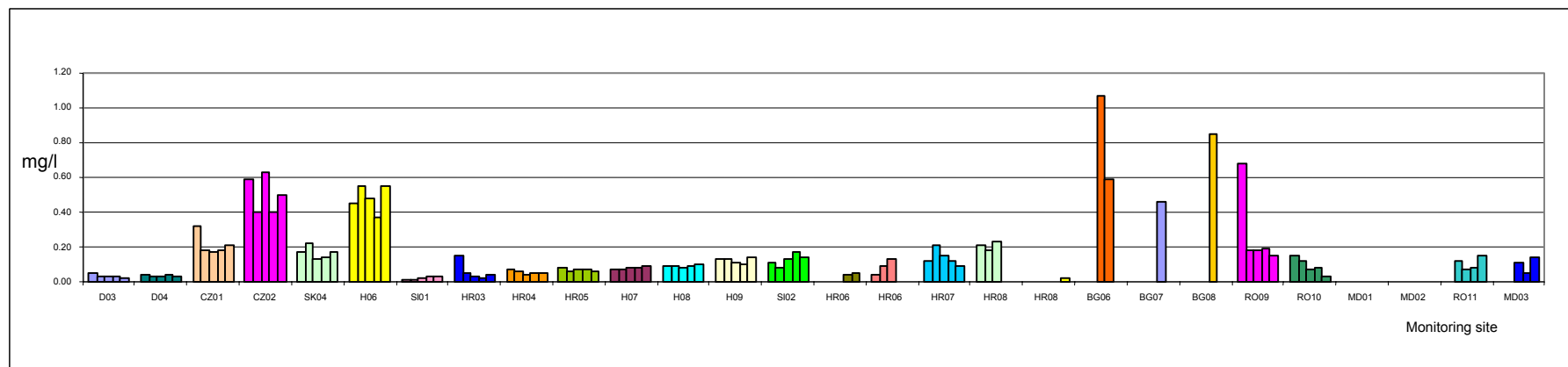
Fig. 8.1.2.20: Temporal trends of P-oPO$_4$ – Tributaries

Total Phosphorous

The distribution of monitoring sites according to the Classification System in the DRB for Total P is shown in **Fig. 8.1.2.21**.
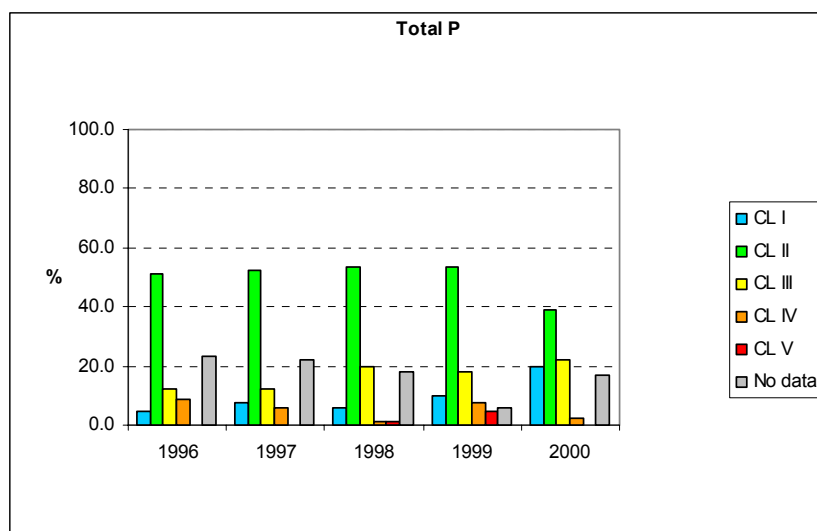
Fig. 8.1.2.21: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Total P.**

Based on data recorded at 824 monitoring sites (it means that out of the assessment is 21 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- Class I comprises less than 20 % of all monitoring sites, with a minimum of 6.0 % in 1996 and 1998;
- during 1996 – 1999, more than 40 % of all sites belong to Class II, but in 2000 the percentage decreases to 38.1 %;
- the number of sites within Class III increases from 1996 to 2000, the maximum value being 21.4 %;
- the number of sites within Class IV decreases during 1996 – 1998 and from 1999 to 2000 and increases from 1998 – 1999; the variation range is 1.2 % - 8.3 %;
- Class V is represented in 1998 and 1999 only, by 1.2 % and 4.8 % of all sites respectively;
- "no data" category" from 84 monitoring sites has a constant variation around 20 %, excepting 1999 when only 6 % of all sites are included in this category.

The spatial variation of Total P concentration along the Danube River is shown in **Fig. 8.1.2.22a** and **8.1.2.22b.**

Unlike the spatial variation for ortho-phosphate in the upper Danube, the total P concentrations increase from Danube-Neu-Ulm (km 2581, D01), where the variation range is 0.106-0.140 mg/l to Danube-Wolfsthal (km1874, A04), where the range is 0.120-0.302 mg/l. There are five c90 values of total P above the quality target (0.200 mg/l) .

In the middle section of the river the maximum value was located in Danube-Szob (km 1708, H03L) – 0.310 mg/l in 1998, being the sampling site where Danube leaves Slovakia. Along this stretch, 23 values are above the target limit.

In the first part of the lower Danube, after Danube-Bazias (km 1071, RO01) where the concentrations values reach 0.240 mg/l, a decreasing is observed down to Danube-us. Iskar-Bajkal (km 641, BG02), where the concentration is 0.144 mg/l. Although the missing data cannot provide enough information

for the next stretch, a high value (0.765 mg/l) is visible at Danube-ds. Svishtov (km 554, BG03) in 1999.

In the second part of the lower Danube, Total P values follow a relatively uniform line regarding spatial variation, only three values being outside of this profile, recorded at Danube-Silistra/Chiciu (km 375, BG05). However, a slight decreasing is noticeable below Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta.

For the entire lower Danube, 21 values are above the quality target 0,2 mg/l.

Total P in the selected tributaries has an inhomogeneous profile, mainly in accordance to extent of human influences in the river basins of these tributaries – **Fig. 8.1.2.23a** and **8.1.2.23b**. Thus, relatively high Total P values, corresponding to Class IV and V, were recorded on the following watercourses:
  - the Dyje-Pohansko (CZ02) – all values exceeding 0,5 mg/l with maximum 0.917 mg/l in 1998;
  - the Sio-Szekszard-Palank (H06) – all values exceeding 0,9 mg/l with maximum 1.370 mg/l in 1998;
  - the Jantra-Karantzi (BG07) – with c90 value of 0.942 mg/l in 1999 (only the data from this year available);
  - the Russenski Lom-Basarbovo (BG08) – with c90 value of 1.805 mg/l in 1999 (only the data from this year available);
  - the Arges-us. Arges (RO09) – with c90 value of 0.865 mg/l in 1996.
There are 63 Total P values above the quality target.

Temporal trend for Total P concentrations is illustrated in **Fig. 8.1.2.24** for the Danube River and in **Fig. 8.1.2.25** for selected tributaries. Concerning total phosphorus the variance between the years is much higher than that of orthophosphates because of its connection to short-time process. When samples are taken during high-flow period, 90 %-iles of that year are supposed to be on a higher level. In many cases the years showing high values of suspended solids have high values of total phosphorus, too. Regarding temporal assessment, the following can be concluded:
  - in the upper Danube, slight continuous increasing is visible in Danube Wien-Nussdorf (A03, rkm 1935)
  - in the middle part of the Danube, Total P temporal distribution is rather scattered, with no indication of general increasing or decreasing trend;
  - similar situation is in the first part of the lower Danube; at the cross section Danube-Pristol NovoSelo/ Pristol, the changes in time are opposite, depending on whether results provided by Romania or Bulgaria are taken into account;
  - in the second part of the lower Danube, if at Danube-us. Arges (km 432, RO03) Total P concentrations increase from 1997 to 2000 and at Danube-Reni-Chilia/kilia arm (km 132, RO05) values decrease from 1997 to 2000; for almost all remaining sites, the maximum values are recorded in 1996 and 1998;
  - there is only one tributary, in which an indication of an increase is observable - Inn – Kirchdorf (D03), but this "change" in time can be explained by suspended solids content in a water in 2000 (see also Fig. 8.1.1.4). The decrease is visible in Arges (RO09) and Siret (RO10), especially taking into account high values reached in 1996 that did not occur later in the evaluated period.
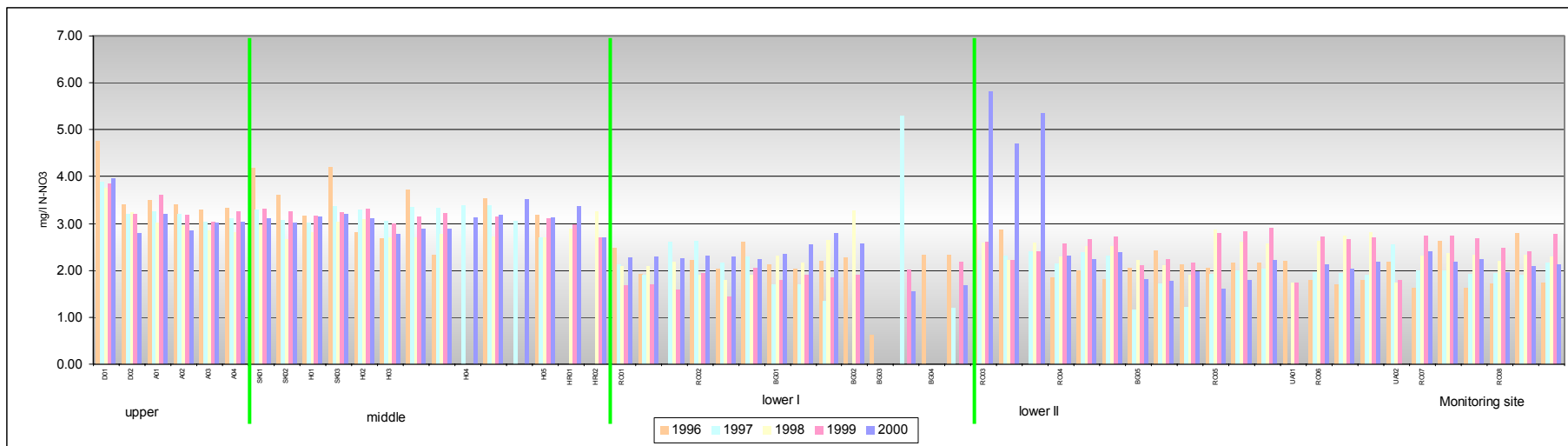
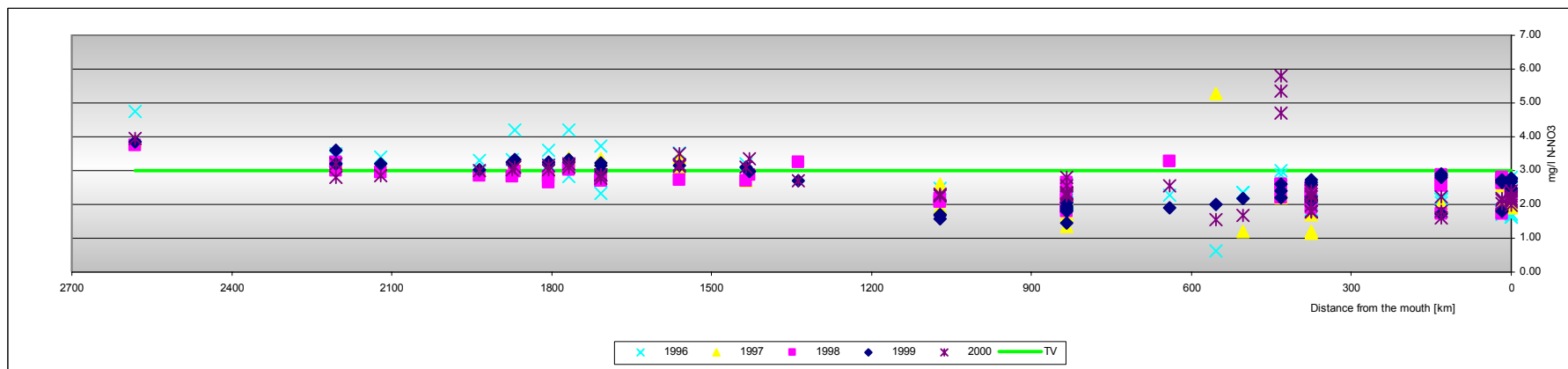Fig. 8.1.2.22a: Spatial variation of Total P – Danube River

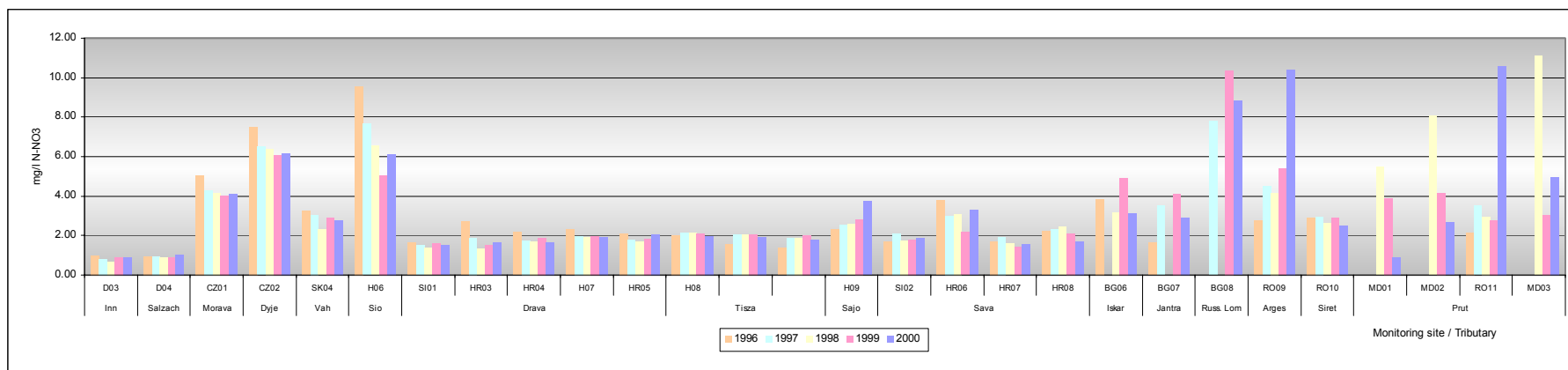Fig. 8.1.2.22b: Spatial variation of Total P – Danube River

Fig. 8.1.2.23a: Spatial variation of Total P – Tributaries

Fig. 8.1.2.23b: Spatial variation of Total P – Tributaries
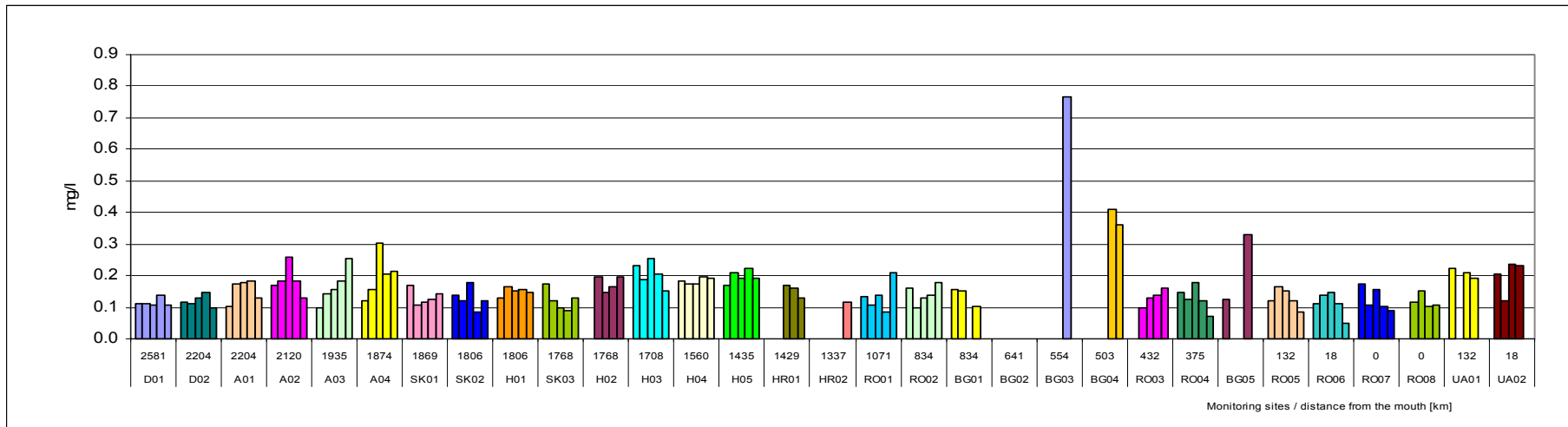
Fig. 8.1.2.24: Temporal trends of Total P – Danube River

Fig. 8.1.2.25: Temporal trends of Total P – Tributaries

Regarding exceedance of the target limit of Total-P, set up on the level of 0.2 mg/l, 18.0 % of c90 values are above this limit in the Danube River and 57.3 % in selected tributaries – **Fig. 8.1.2.22b and 8.1.2.23b**.

If the orthophosphate is a reliable indicator of bioavailability, total phosphorous concentration can be related with suspended solids content, due to the fact that phosphorous compounds tend to be adsorbed on particulate matter. In this respect, the charts illustrating the spatial distribution of suspended solids versus so-called "particulate phosphorous", approximated as the difference between total P and ortho-phosphate P (where available), was done for each studied year (see **Fig. 8.1.2.26 - 8.1.2.30)**. Results present a large variability in longitudinal profile of the Danube itself and the only conclusive data are visible for several sites, listed in **Table 8.1.2.1**.

Table 8.1.2.1: Several correlations between the particulate phosphorous (PP) and suspended solids content (SS):

Year	Monitoring site	PP (mg/l)	SS (mg/l)
1996	H08	0.247	138.4
	RO09	0.190	147.5
	RO10	0.420	261.5
1997	HO8	0.372	153.4
1998	D03	0.169	131.0
1999	H06	0.805	140.8
	H08	0.254	125.3
	BG08	0.955	300.6
	UA01	0.194	108.7
2000	D03	0.335	315.0
	H08	0.183	217.4

Fig. 8.1.2.26 - 8.1.2.30: Suspended solids content vs. particulate phosphorous
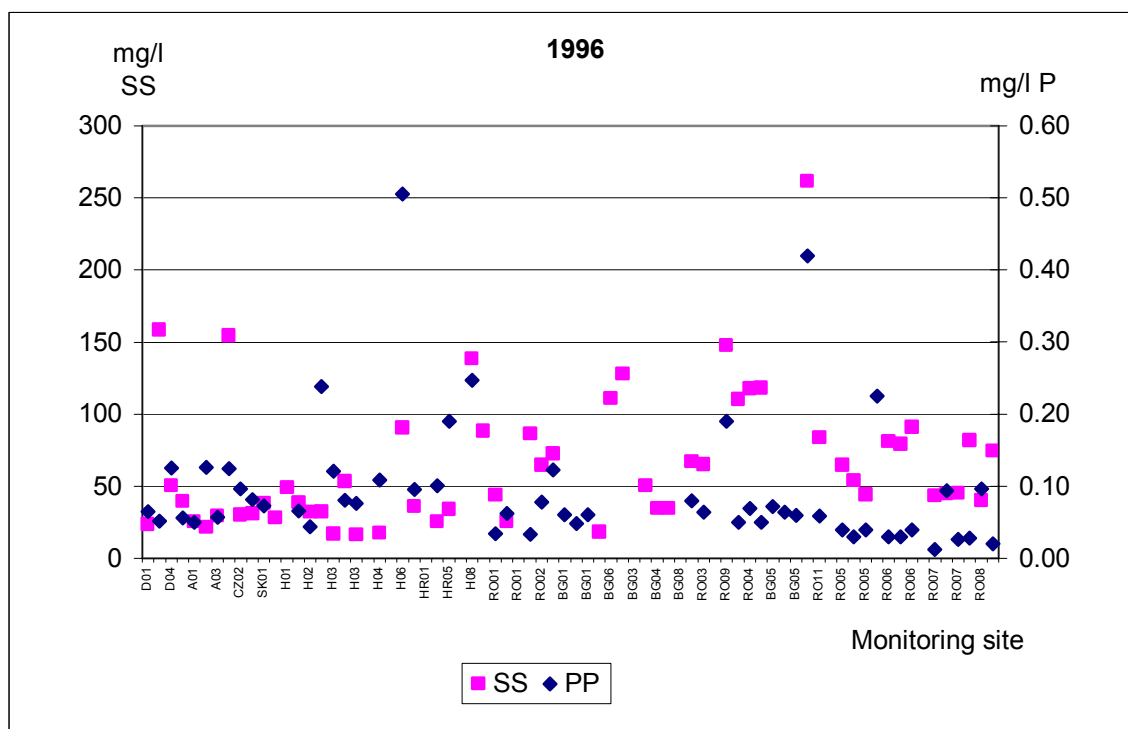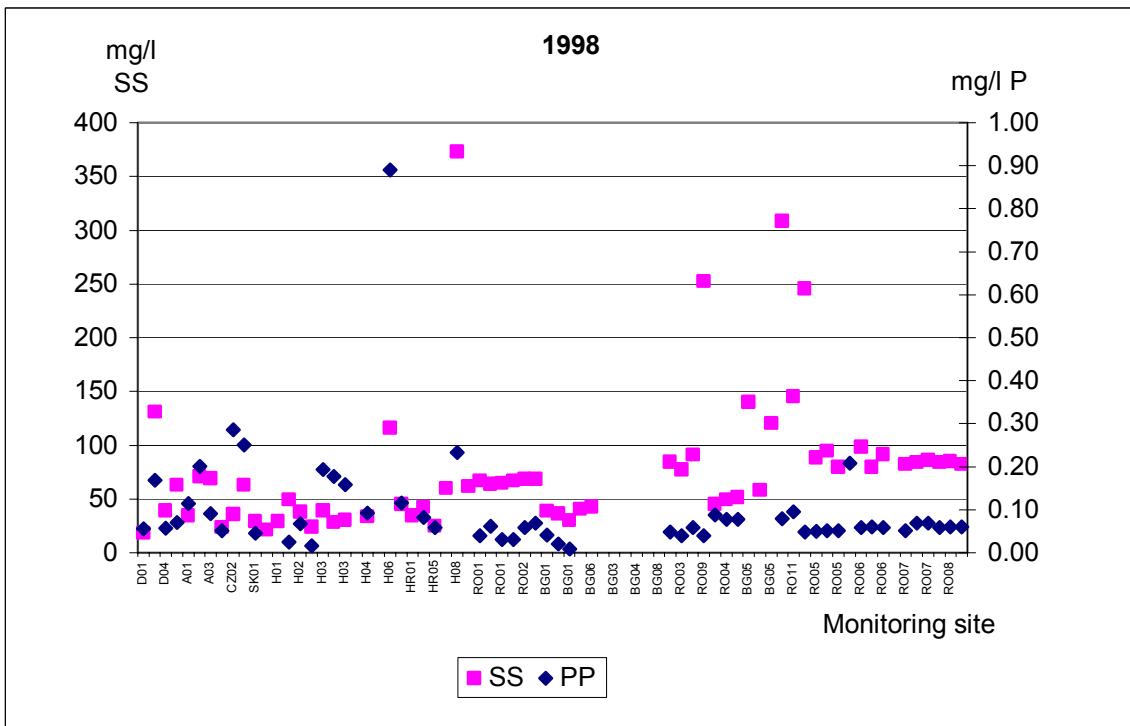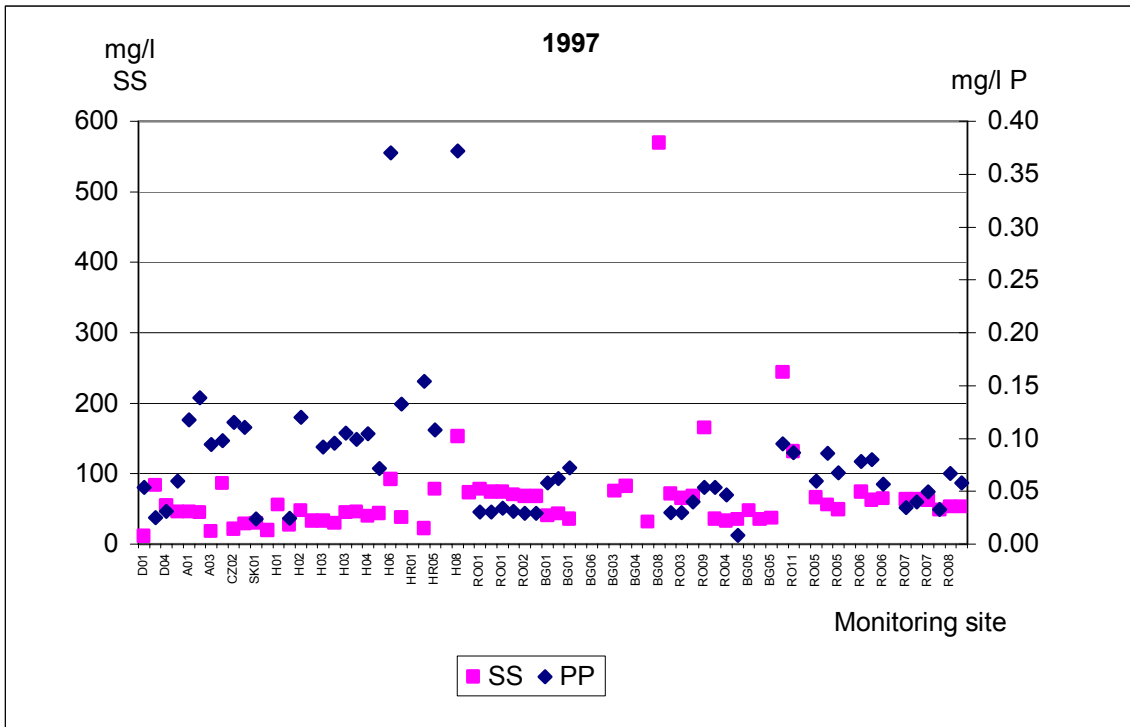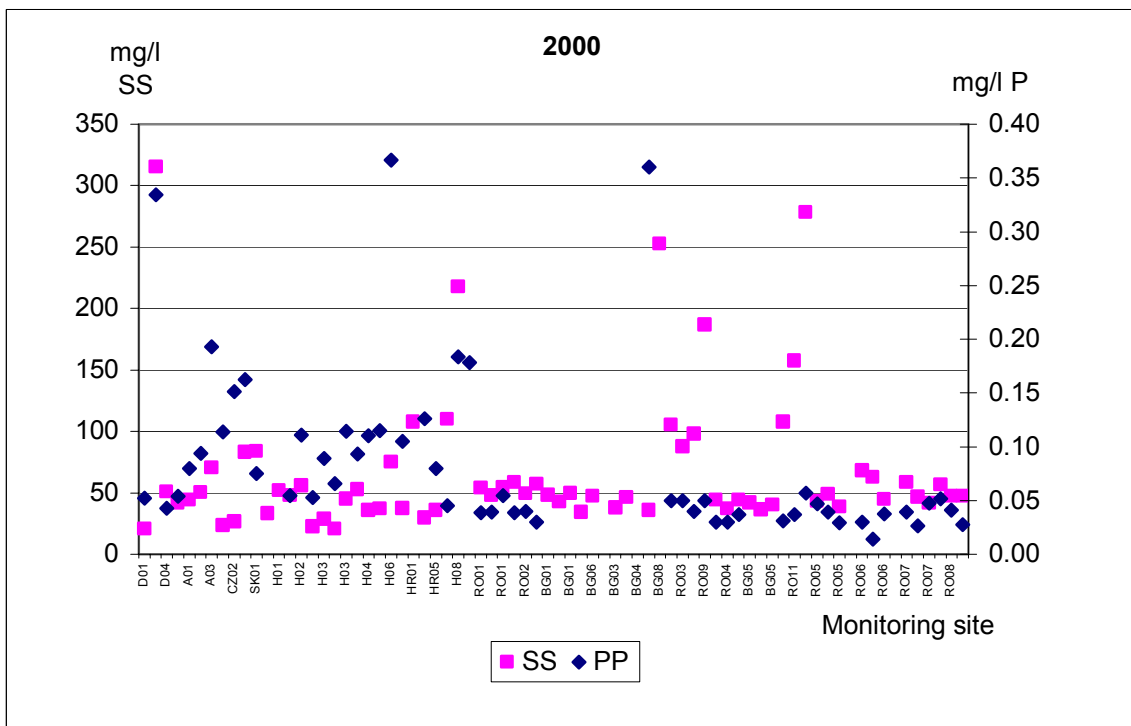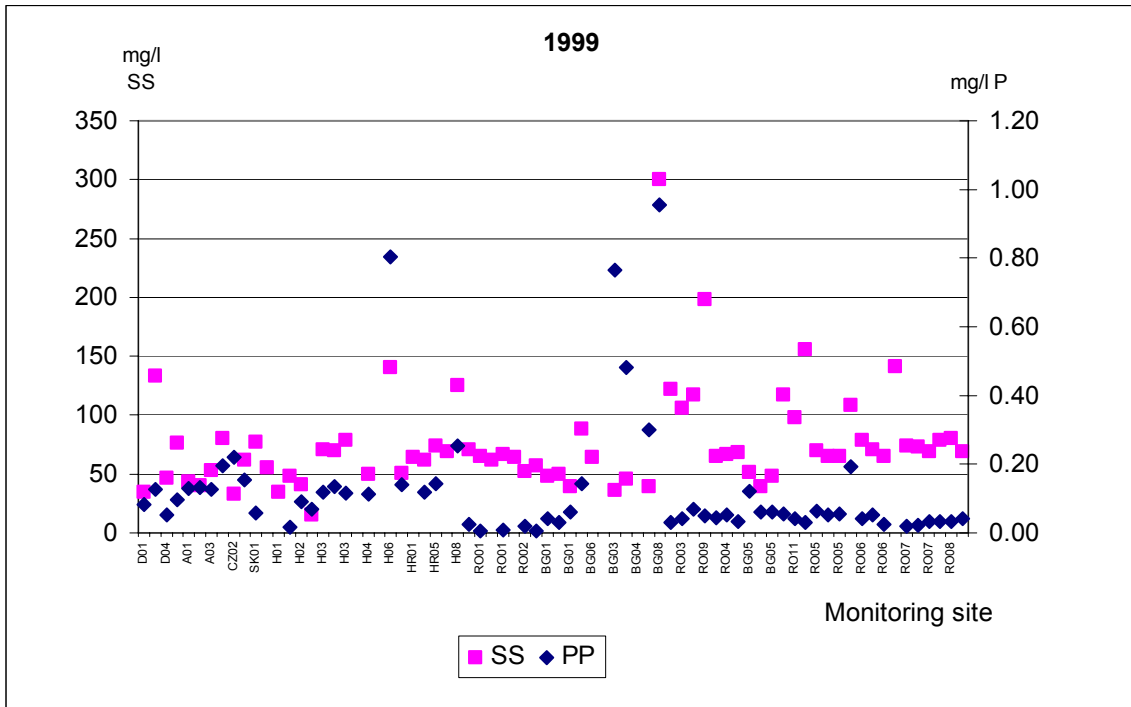
8.1.3.   Heavy Metals

All heavy metals exist in surface waters in colloidal, particulate and dissolved phases, although dissolved concentrations are generally low (*Kennish, 1992*). The colloidal and particulate metal may be found in hydroxides, oxides, silicates and sulfides or adsorbed to clay, silica or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by pH, the type and concentration of ligands on which the metal could adsorb and the oxidation state of the mineral components and redox environment of the system (*Connel et al., 1984*). The water chemistry also controls the rate of adsorption and desorption of metals to and from sediment. Thus, metals can be desorbed from the sediment if the water increases in salinity, decreases in redox potential or decreases in pH.

In surface waters system, heavy metals can be from natural and anthropogenic sources, but currently human inputs of metals exceed the natural ones. As natural sources, chemical and physical weathering of rocks and soils can be mentioned, further decomposition of plants and animal detritus, wind erosion, atmospheric deposition of airborne particles (Kennish, 1992). As antropogenic non-point sources, the most important are surface runoff from mining operations, urban storm water runoff, combustion of fossil fuels; as anthropogenic point sources, among the most important are domestic wastewater effluents, corrosion of water pipes and industrial effluents (Connel et al., 1984).

Within the TNMN Programme, a number of 11 heavy metals are routinely analyzed in water samples, both as total water concentration and as dissolved fraction. The ration of these fractions in water varies from substance to substance. The concentration of heavy metals is strongly dependent on quantity and nature of suspended solids. This is the reason of natural variations and trends which hide the effect of anthropogenic contaminations. High values often reflect situations with high loads of suspended solids and flood events – statistical parameters ike 90 %-ile, using also in the assessment in this report, are therefore influenced by these processes. To eliminate such effects it is preferred to determine heavy metals dissolved in water as well as concentrations in suspended solids.

Referring to the five-years synthesis report, the main focus is directed to the total heavy metals content in water samples during 1996 – 2000, because dissolved fraction data are available for recent years only, and collected data do not even cover the whole river basin.

Iron

The spatial distribution of Iron concentrations along the Danube River is shown in **Fig. 8.1.3.1a** and **8.1.3.1b**:

In the upper section, Iron concentrations vary within the range 0.208 – 1.190 mg/l, with a slight spatial increasing from Danube-Neu Ulm (km 2581, D01) down to Danube-Wolfsthal (km 1874, A04), reaching 1.19 mg/l.

In the middle section, the spatial profile is relatively constant down to Danube-Szob (km 1708 H03), where the highest values range between 0.82 – 0.99 mg/l. Downstream this monitoring site, a significant decreasing is visible.

In the first part of the lower section, iron concentration profile is higher than in the middle stretch. The maximum recorded value from the whole Danube River appears at Danube-Bazias (km 1071, RO01) – 4.40 mg/l.

In the second part of the lower Danube, iron concentrations generally increase. Taking into account whole Danube River, here are the highest concentration of iron, increasing frequently over 1.00 mg/l. The highest c90 values from this sub-section (2.78 mg/l) is present at Danube-Silistra/Chiciu (km 375, BG05)

Iron concentrations for selected tributaries is shown in **Fig. 8.1.3.2a** and **8.1.3.2b**:
- for those located in the upper section, the Inn-Kirchdorf (D03) and, in a smaller extent, the Salzach-Laufen (D04) and Morava-Lanzhot (CZ01) present values above 2.00 mg/l;
- most of the tributaries located in middle stretch of the Danube are characterized by low Iron concentrations, only on the Tisza-Tiszasziget (H08) and the Sava-ds. Zupanja (HR08) two values exceed 2.00 mg/l;
- there is a change in the lower section, where three tributaries show quite high concentration levels, as follows:
  - the Russenski Lom-Basarbovo (BG08) – 6.59 and 6.86 mg/l;
  - the Arges-Conf. Danube (RO09) – 8.14 mg/l;
  - the Siret-Conf. Danube Sendreni (RO10) – with the maximum recorded value for tributaries - 18.73 mg/l.

The temporal trends for the Danube River are shown in **Fig. 8.1.3.3a** and **8.1.3.3b** for the Danube River and in **Fig. 8.1.3.4** for selected tributaries:
- from sites located in Danube River, only in Danube-Szob (rkm 1708, H03) there is an indication of increase;
- from tributaries, decreasing in period 1996-2000 is observable in Morava-Lanzhot (CZ01), Drava-Varazdin (HR03), Drava-Botovo (HR04), Arges (RO09) and Siret (RO10).

Fig. 8.1.3.1a: Spatial variation of Fe – Danube River

Fig. 8.1.3.1b: Spatial variation of Fe – Danube River
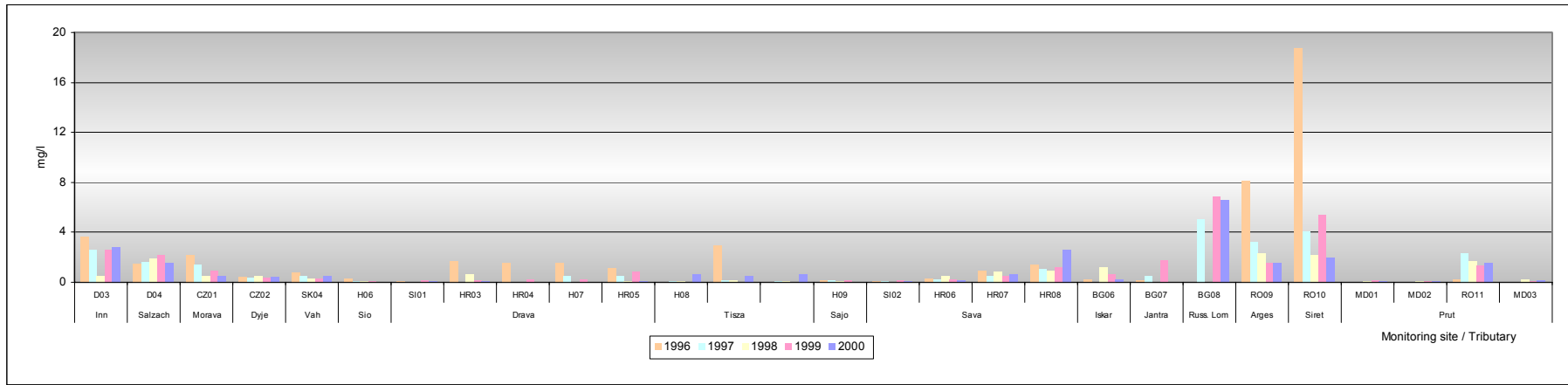
Fig. 8.1.3.2a: Spatial variation of Fe – Tributaries
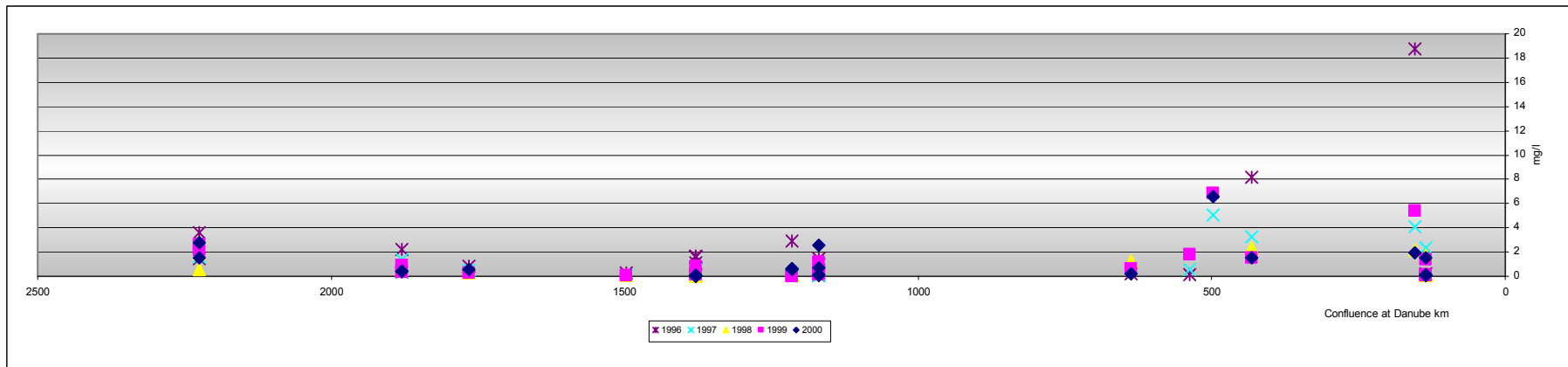
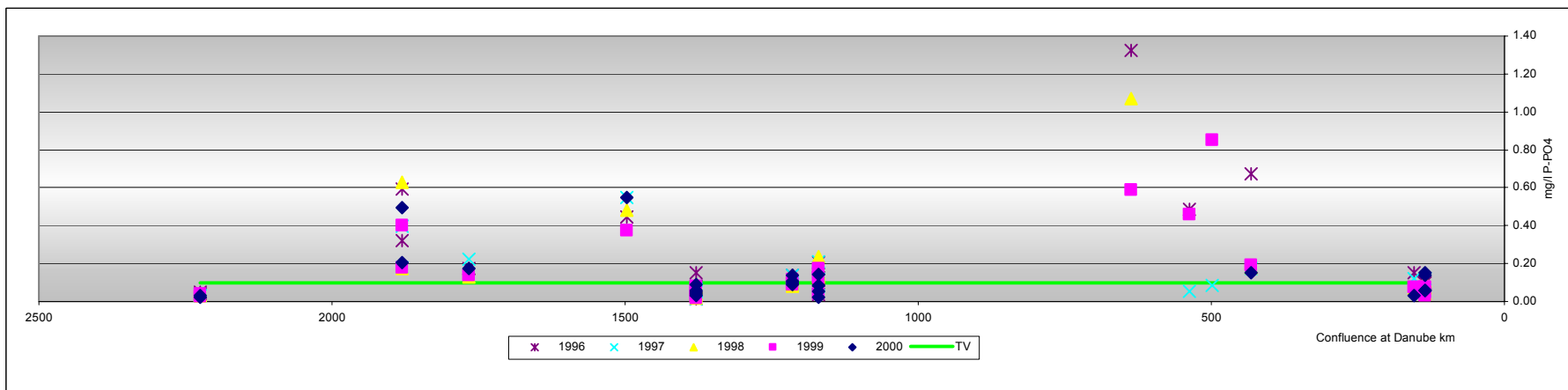Fig. 8.1.3.2b: Spatial variation of Fe – Tributaries
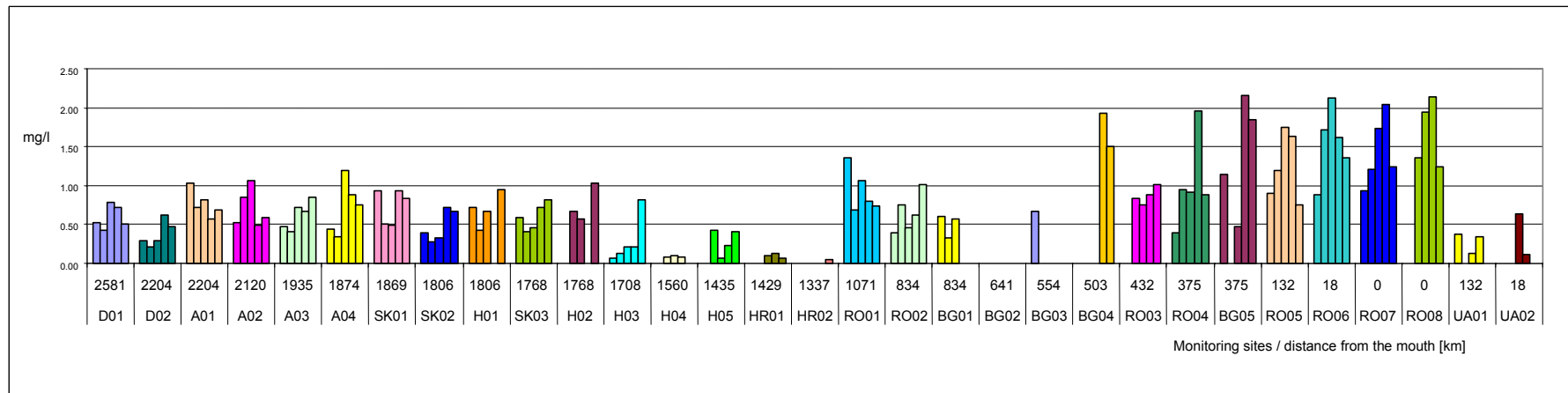
Fig. 8.1.3.3: Temporal trends of Fe – Danube River
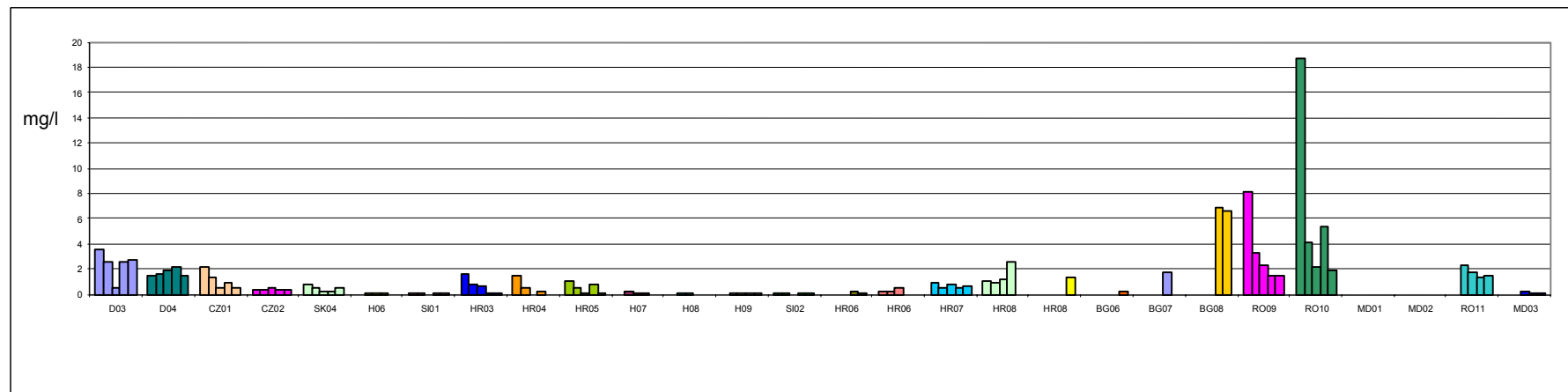
Fig. 8.1.3.4: Temporal trends of Fe – Tributaries

Manganese

For the Danube River itself, the spatial distribution of manganese concentrations is shown in **Fig. 8.1.3.5a** and **8.1.3.5b.**

In the upper section of the Danube, spatial distribution is relative uniform, with only one concentration value reaching 0.10 mg/l, at Danube-Wolfsthal (km 1874, A04).

In the middle stretch, spatial variation assessment depends on which data are taken into account: it results in a uniform spatial pattern in accordance to Slovak data (SK02 and SK03), but higher values in accordance to the Hungarian ones (H01 and H02). A significant decreasing of manganese values is visible from Danube-Szob (km 1708, H03) to Danube-Borovo (km 1337, HR02). Taking into account Hungarian data, in the section between rkm 1800 – 1700 are the highest manganase values along the Danube River.

The first part of the lower Danube shows a scattered profile of manganese concentrations: from Danube-Bazias (km 1071, RO01) to Danube-us. Iskar Bajkal (km 641, BG02), nearly half of the values are equal to or exceed the 0.10 mg/l level. The next two monitoring sites in this sub-section, Danube-ds. Svishtov (km 554, BG03) and Danube-us. Russe (km 503, BG04), indicate much lower values.

The second part of the lower Danube section is characterized by a relatively uniform distribution, with few exceptions. Thus, the maximum manganese value (0.27 mg/l in 2000) is recorded at Danube-us. Arges (km 432, RO03); also several values along this stretch exceed the 0.20 mg/l level.

The spatial distribution of manganese c90 values on selected tributaries is shown in **Fig. 8.1.3.6a** and **8.1.3.6b**. Regarding those located in the upper Danube, the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) present concentration above 0.20 mg/l. In the middle stretch, only the Tisza-Tiszasziget (H08) shows rather high values, reaching 0.87 mg/l in 1996. In the lower section, majority of tributaries is characterized by high values, but some of them exceed 1.00 mg/l: 1.02 mg/l on the Iskar-Orechovitza (BG06), 1.01 and 1.26 mg/l on the Siret-Conf. Danube Sendreni (RO10).

The temporal trends of manganese concentrations are shown in **Fig. 8.1.3.7** for the Danube River and in **Fig. 8.1.3.8** for selected tributaries:
-   in the upper Danube, temporal pattern is without significant changes, also variation between years is rather low there;
-   in the middle Danube, increase of iron in Danube-Szob (rkm 1708, H03) is in coincidence with increse of manganese;
-   in the lower Danube, an increasing is observed in Danube-Bazias (km 1071, RO01), and decrease in Danube-Novo Selo/Pristol /rkm 834, BG01);
-   for two tributaries located in the upper Danube, the Morava-Lanzhot (CZ01) and Dyje-Pohansko, the temporal trends are opposite: decreasing for the first one and increasing in the same sense for the second. Also relative decreasing trends are valid for tributaries located in the middle and lower Danube: the Vah-Komarno (SK04), Arges-Conf. Danube (RO09) and the Prut-Conf. Danube Giurgiulesti (RO11).
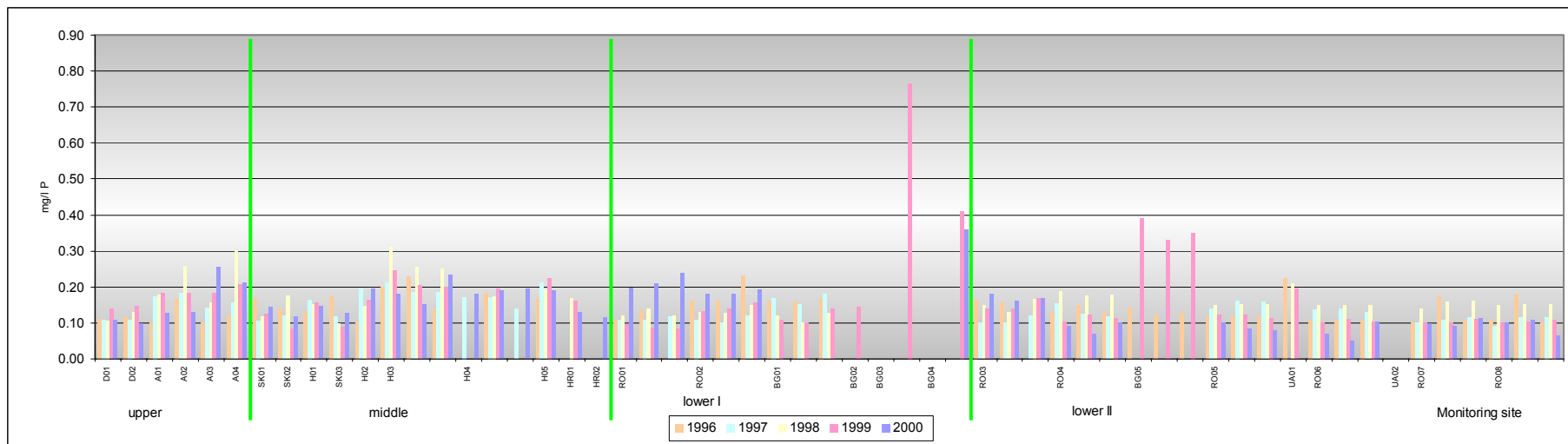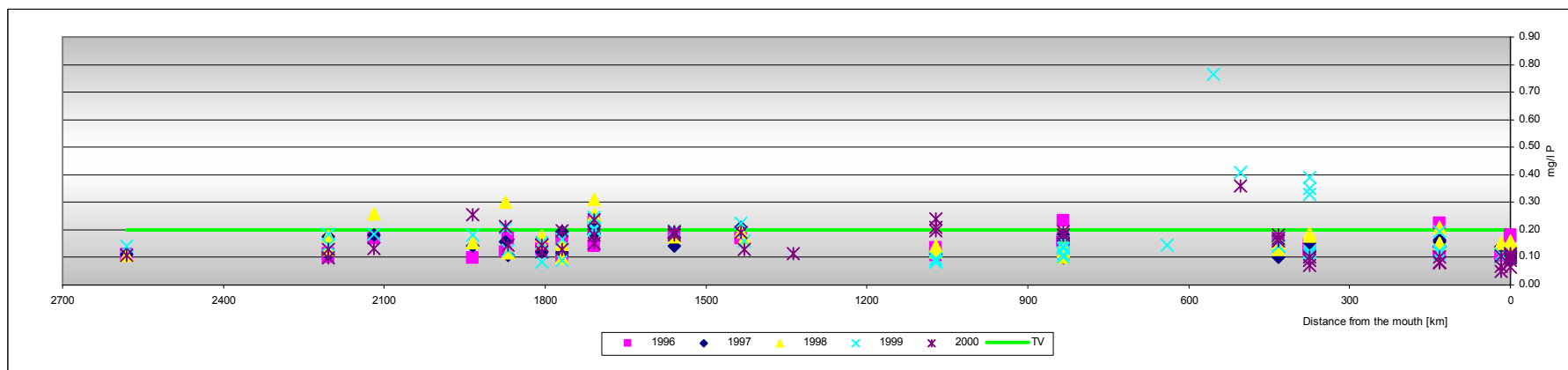
Fig. 8.1.3.5a: Spatial variation of Mn – Danube River
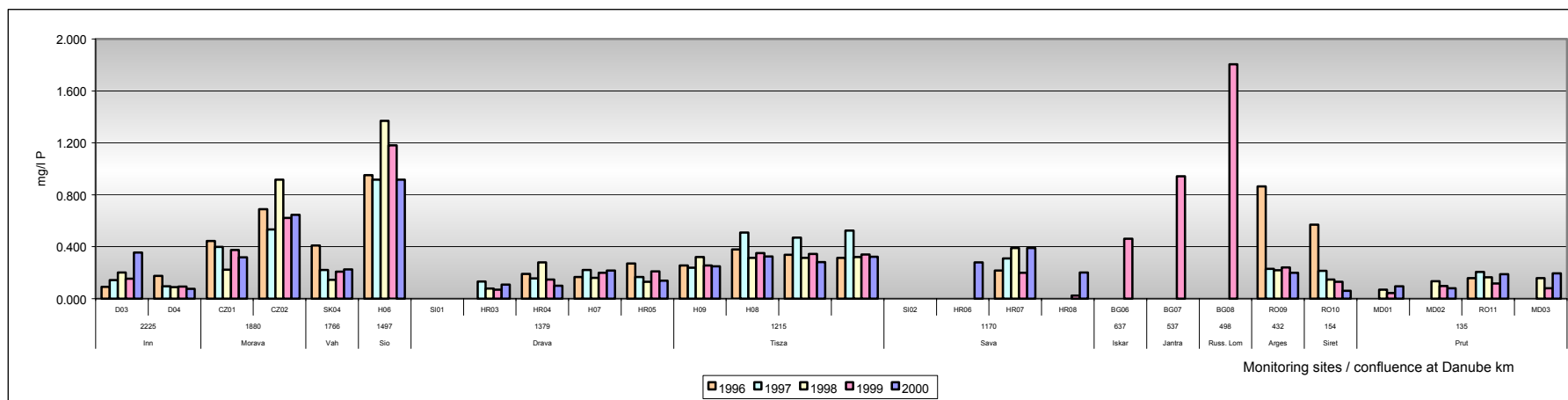

Fig. 8.1.3.5b: Spatial variation of Mn – Danube River

Fig. 8.1.3.6a: Spatial variation of Mn – Tributaries

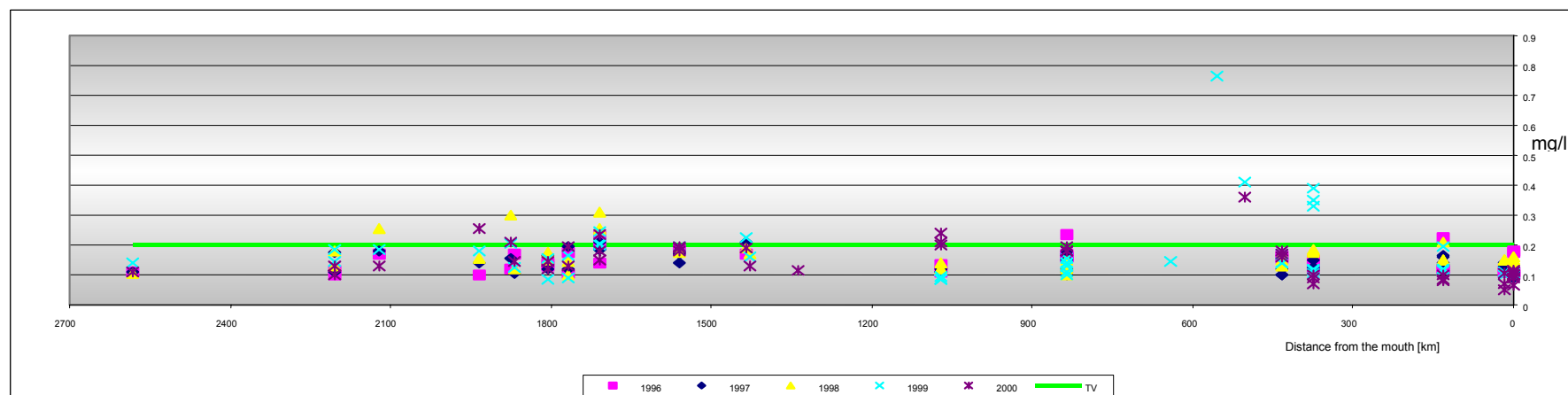Fig. 8.1.3.6b: Spatial variation of Mn – Tributaries
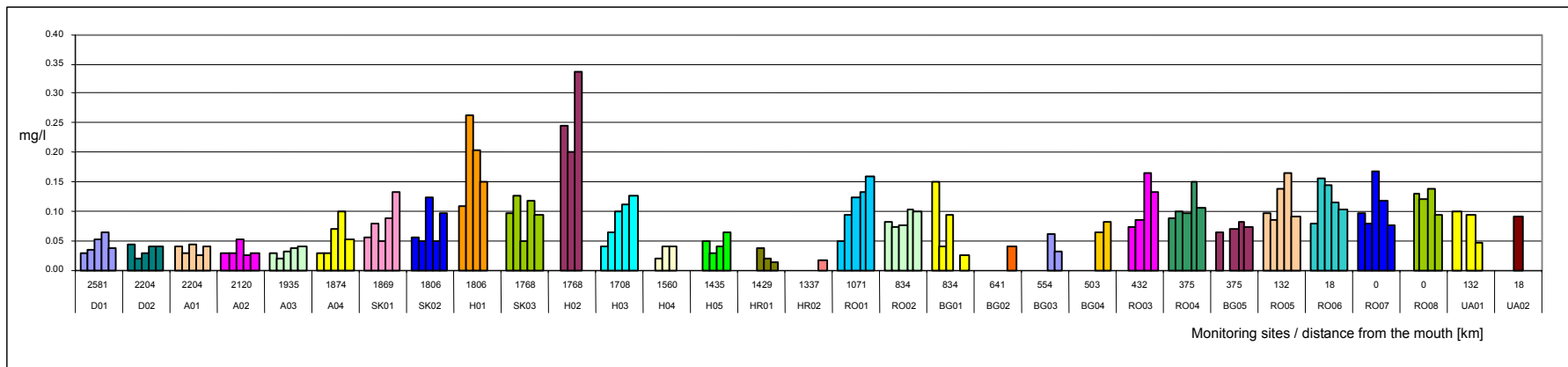
Fig. 8.1.3.7: Temporal trends of Mn – Danube River
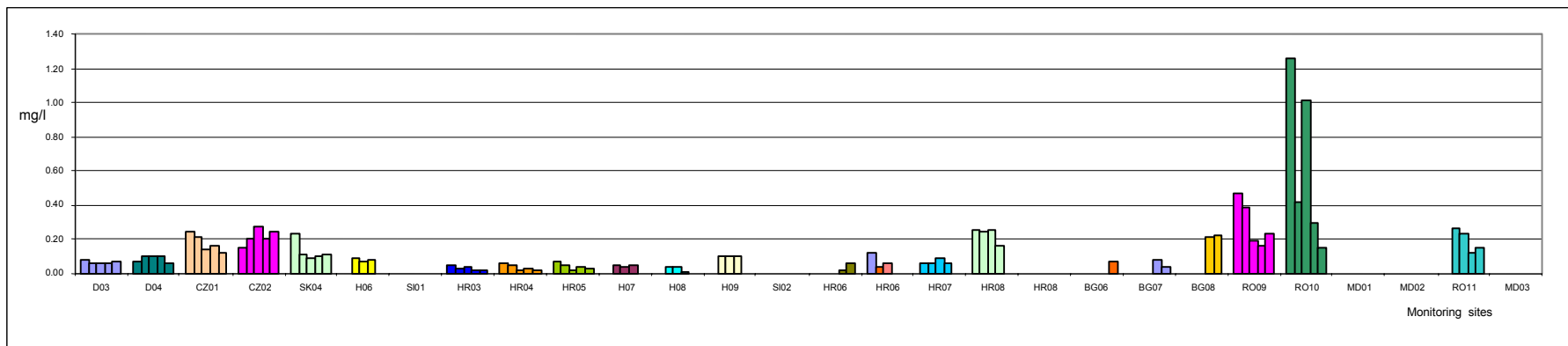
Fig. 8.1.3.8: Temporal trends of Mn – Tributaries

Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in unfiltered water samples (total forms)

The heavy metals like arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc are of a particular concern to surface water systems. The Water Quality Classification for DRB set up limit values for five classes for total forms and only guidelines values for dissolved forms at the border between class II and class III.

For heavy metals in unfiltered water samples (total forms) data are available for the entire time period 1996 – 2000 and for dissolved forms during 1998-2000 only. In addition, data on dissolved forms are available only for part of river basin.

Arsenic

Arsenic can be found naturally in small concentrations. It occurs in soil and minerals and it may enter air, water and land by wind-blown dust and water run-off. Arsenic is a component that is extremely hard to convert to water-soluble or volatile products. Because arsenic is naturally a quite mobile component, it means that large concentrations are not likely to appear on one specific site. However, the negative fact is that arsenic pollution becomes a wider issue because it easily spreads. In the aquatic systems, arsenic ends up through effluents from industrial production of copper, lead and zinc and also through insecticide applications on land. Although arsenic may be found in surface water, ground water is the main source of arsenic in water.

The distribution of monitoring sites according to the Classification System in the DRB for arsenic is shown in **Fig. 8.1.3.9**:
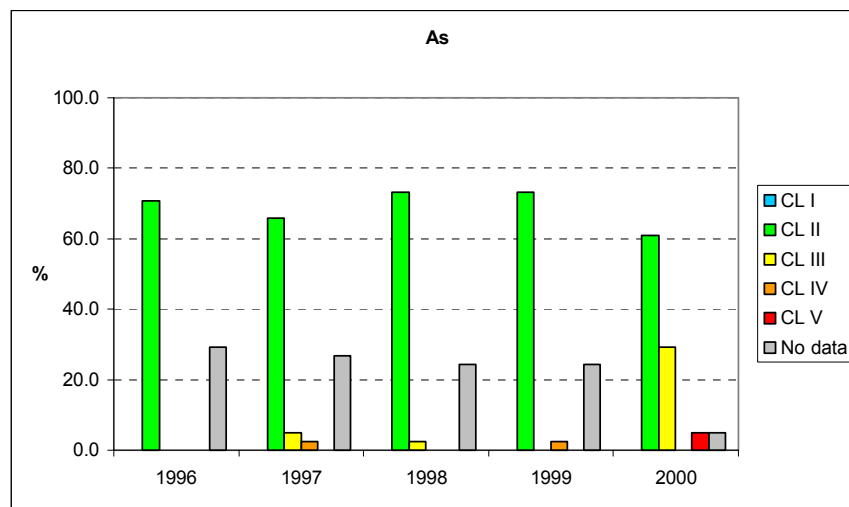
Fig. 8.1.3.9: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **As**

Based on data reported from 41 monitoring sites (out of the assessment is 62 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that most of the monitoring sites are within Class II (61.0 % – 73.2 %). Other classes are represented in very small percentages, with an exeption 30 % of sites in Class III in 2000.

The spatial pattern for arsenic concentrations along the Danube River is shown in **Fig. 8.1.3.10a** and **8.1.3.10b** and in **Fig. 8.1.3.11a** and **8.1.3.11b** for selected tributaries.

In the upper section, arsenic is detectable starting from Danube-Jochenstein (km 2204, A01), but no monitoring site from this section has arsenic concentration exceeding the target value (5 μg/l).

In the middle section, an increasing spatial pattern is present from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03), followed by a decreasing to Danube-Borovo (km 1337, HR02); along this stretch no value is above the target limit as well.

Lower section is characterized mainly by lack of reported data for arsenic. However, the existing values are higher than in previous river sections, the maximum concentration (11.02 μg/l) being recorded at Danube-us. Iskar – Bajkal (km 641, BG02). Along the entire part of lower Danube 9 values exceed the target value set up for arsenic.

Selected tributaries present 8 concentration values exceeding the target value:
-    the Salzach-Laufen (D04) – 8.00 μg/l (in 2000);
-    the Vah-komarno (SK04) – 5.17 μg/l (in 2000);
-    the Sio-Szekszard-Palank (H06)– 90 %-iles during the whole period exceeded target value and were in a range from 5.24 - 12.32 μg/l;
-    the Iskar-Orechovitza (BG06) – 79.36 μg/l (in 2000);
-    the Russenski Lom-Basarbovo (BG08) – 10.00 μg/l (in 2000).

The temporal trends for the Danube River are illustrated in **Fig. 8.1.3.12a** and **8.1.3.12b** and in **Fig. 8.1.3.13** for selected tributaries:
-    for upper Danube, Austrian sites show slight increasing tendency;
-    for middle Danube, most of the sites show a decreasing trend from 1997 to 2000;
-    for entire lower Danube, even if the missing data cannot give a complete picture, it can be seen that all the high values are specific to year 2000;
-    from tributaries, a slight increasing was in Dyje-Pohansko (CZ02) and Tisza-Tiszasziget (H08); a decreasing trend in the same sense in Inn-Kirchdorf (D01) and Sajo-Sajopuspoki (H09).

Fig. 8.1.3.10a: Spatial variation of As – Danube River

Fig. 8.1.3.10b: Spatial variation of As – Danube River

Fig. 8.1.3.11a: Spatial variation of As – Tributaries

Fig. 8.1.3.11b: Spatial variation of As – Tributaries
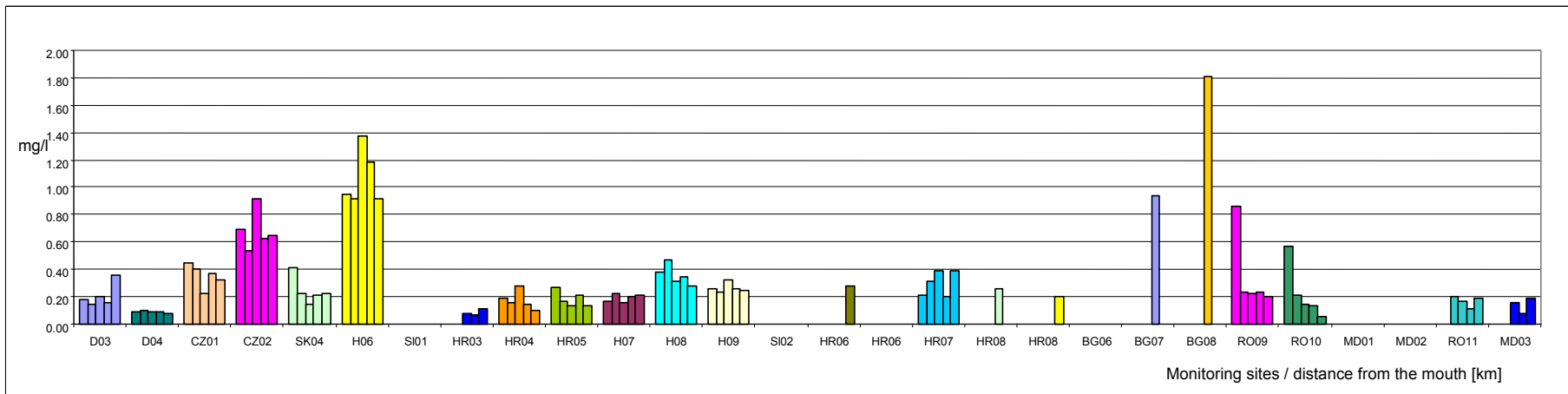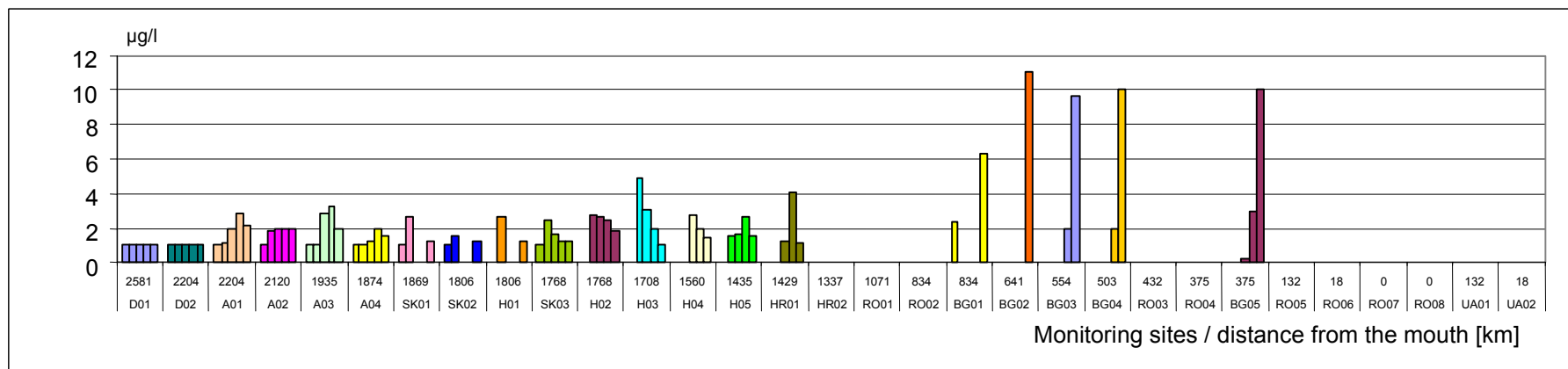
Fig. 8.1.3.12: Temporal trends of As – Danube River
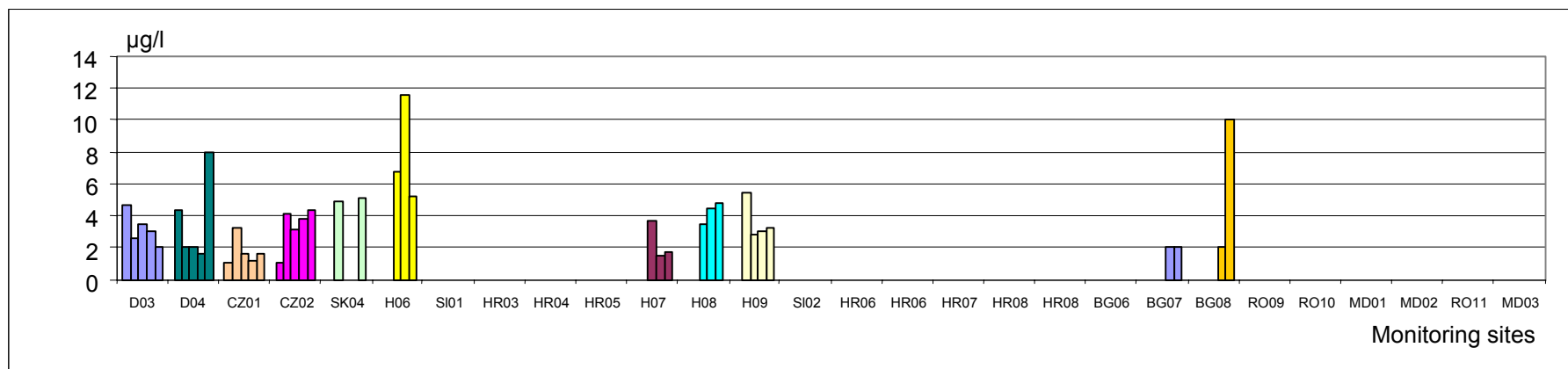
Fig. 8.1.3.13: Temporal trends of As – Tributaries

Cadmium

Cadmium is one of the most hazardous heavy metal pollutants. Naturally, it can mainly be found in the earth's crust and it always occurs in combination with zinc. Cadmium enters the environment mainly through the ground, because it is found in manure and pesticides. Cadmium is released into rivers through weathering of rocks and human activities, such as manufacturing. An important source of cadmium emission is also the production and applying of phosphate fertilizers. In natural waters, unaffected by anthropogenic impacts, the cadmium concentration is less than 1 μg/l (*The Dobris Assessment, 1991*).

The distribution of monitoring sites according to the Classification System in the DRB for cadmium is shown in **Fig. 8.1.3.14**:
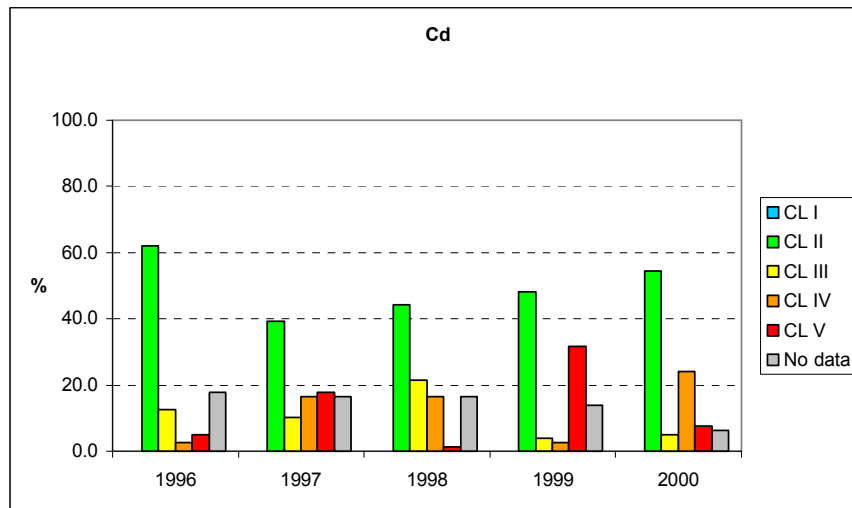
Fig. 8.1.3.14: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cd**

Based on data reported from 79 monitoring sites (out of the assessment is 24 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that:
- most of monitoring sites belongs to Class II (39.2 % - 62.0%) and this percentage increases from 1997 to 2000
- percetage of sites corresponding to Class III decreases from 1998 to 2000;
- distribution corresponding to Class IV is uneven during the five years period;
- in 1999 more than 30% of the monitoring points are within Class V, but this figure decreased in 2000.

The spatial distribution of cadmium concentrations is shown in **Fig. 8.1.3.15a** and **8.1.3.15b** for the Danube River and in for tributaries.

In the upper section, level of cadmium is low at all monitoring points; the maximum value recorded on this stretch is 0.66 μg/l at Danube-Abwinden-Asten (km 2120, A02), but no value is above the target limit for cadmium (1 μg/l).

In the middle section, between Danube-Medve/Medvedov (km 1806, H01) and Danube-Szob (km 1708, H03), 9 cadmium c90 values exceed the target value. Downstream to Danube-Szob, cadmium level is again very low.

First part of the lower section is characterized by high values from Danube-Bazias (km 1071, RO01) to Danube-Pristol/Novo Selo (km 834, RO02), but also with very high variability among the years. Cadmium c90 values reach up to 16.81 μg/l and 17.70 μg/l there according the Romanian data. On the

other hand, at the cross section from km 834, the Bulgarian data show undetectable cadmium concentrations. For the rest of the stretch, excepting one high value of 8.00 μg/l, recorded at Danube-us. Russe (km 503, BG04), cadmium presence is also undetectable. From the reported data, only three values along this stretch are below the target value.

The second part of the lower Danube section shows even higher cadmium concentrations than the first one: thus, 76 values are above the target limit. The highest c90 value for this stretch, which is also the highest value for the entire Danube - 29.10 μg/l - was recorded at Danube-us. Arges (km 432, RO03) in 1997.

The spatial variation for selected tributaries, shown in **Fig. 8.1.3.16a** and **8.1.3.16b**. It is seen that 34 values exceeded the target value. It is also visible that tributaries at the lower part of river basin are characterised by much higher cadmium values than those in the upper and middle section. Going to more details, it can be concluded that:
-   in the upper section, only on the Dyje-Pohansko (CZ02) concentrations slightly exceed the target value;
-    in the middle Danube, in Sava-ds. Zupanja (HR08) and Drava River excepting Drava-Ormoz (SL01), cadmium concentrations are above 1μg/l;
-   as was already indicated, the situation is much worse regarding the tributaries from the lower Danube, where actually all of them are characterized by very high cadmium concentrations, leading to the following c90 values:
    o   the Iskar-Orechovitza (BG06) – 10.00 μg/l in 1996;
    o   the Jantra-Karantzi (BG07) – 9.10 μg/l in 1996;
    o   the Russenski Lom-Basarbovo (BG08) – 8.00 μg/l in 2000;
    o   the Arges-Conf. Danube (RO09) – 24.18 μg/l (1996), 9.25 μg/l (1997) and 8.96 μg/l (1999);
    o   the Siret-Conf. Danube Sendreni (RO10) – 8.46 μg/l in 1999;
    o   the Prut-Conf. Danube Giurgiulesti (RO11) – 8.36 μg/l (in 1998).

The temporal trend for cadmium concentrations is shown in **Fig. 8.1.3.17** for the Danube River and in **Fig. 8.1.3.18** for selected tributaries:
-   for the upper Danube, no systematic temporal trend is visible;
-   a slight decreasing tendency from 1997 to 2000 is valid for most of the sites located in the middle Danube from Danube Medve/Medvedov (rkm 1806, H01) to Danube-Szob (rkm 1708, H03);
-   in the lower Danube, most of monitoring sites are characterized by high values recorded in 1997 and 1999, significant decrease is observed in 2000;
-   from selected tributaries, only several monitoring sites indicate temporal changes: decreasing is observed in Drava River, Jantra (BG07), Arges (RO09) and Prut-Conf. Danube-Giurgiulesti (RO11).

JDS results from analysis of cadmium (0.2 – 0.8 μg/l in total sample) indicated that Danube River can be regarded as unpolluted by this metal. However, TNMN results does not confirm this finding, great differences are especially in the lower part of the Danube River.
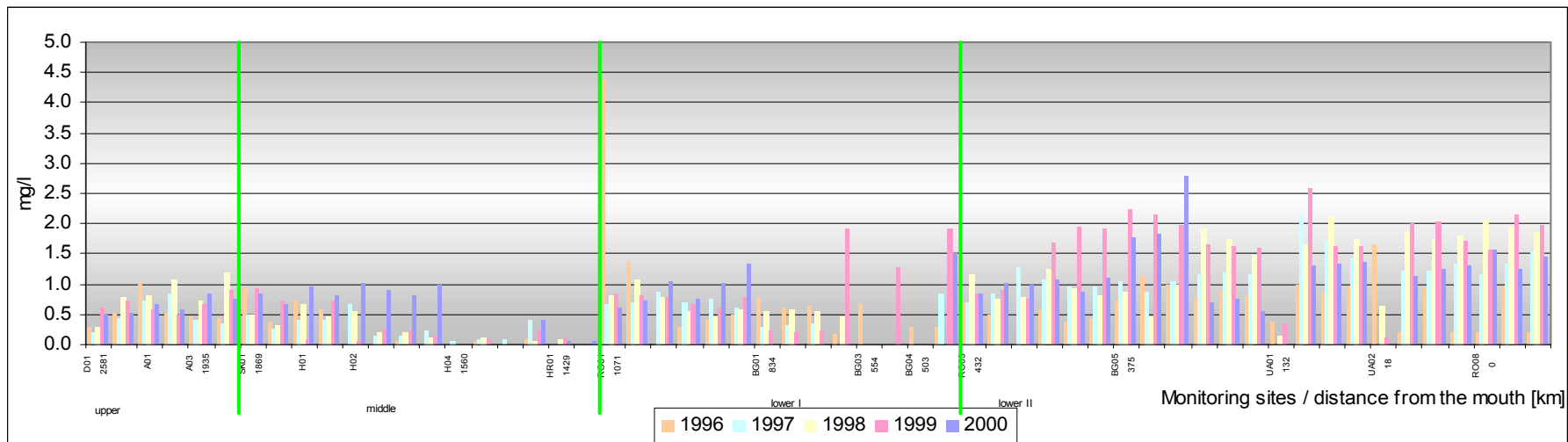
Fig. 8.1.3.15a: Spatial variation of Cd – Danube River
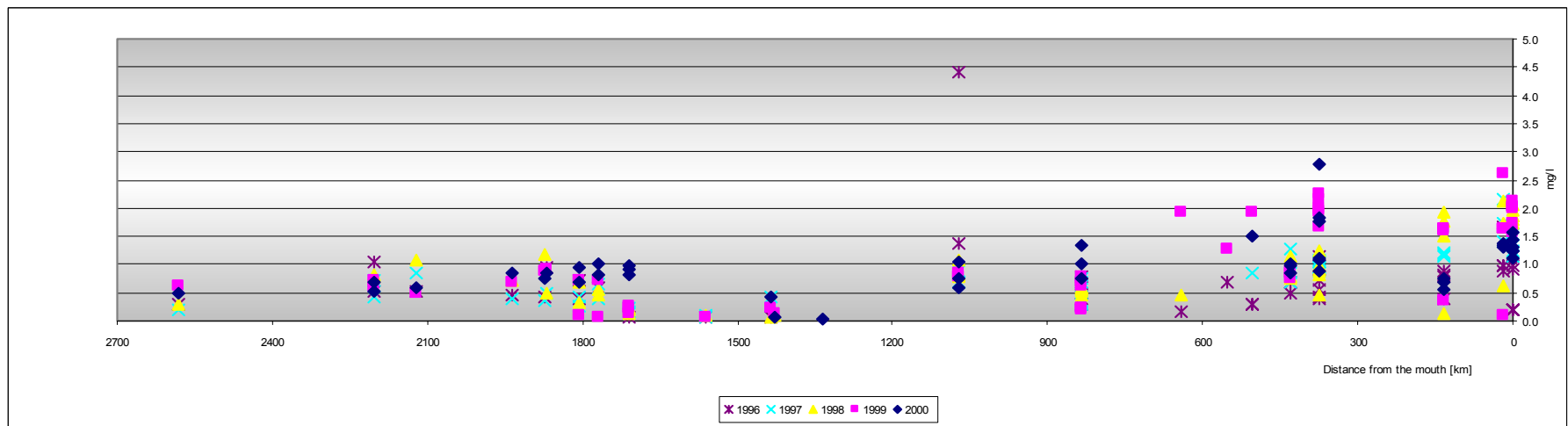

Fig. 8.1.3.15b: Spatial variation of Cd – Danube River
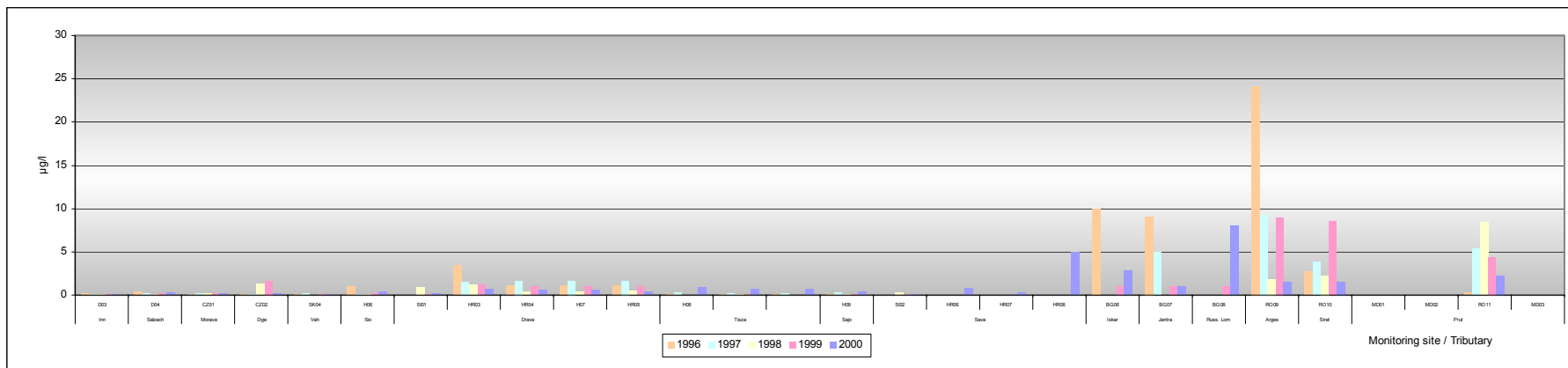
Fig. 8.1.3.16a: Spatial variation of Cd – Tributaries

Fig. 8.1.3.16b: Spatial variation of Cd – Tributaries

Note: In HR08 (2000) the value in the graph represents limit of detection that is higher than the target value.
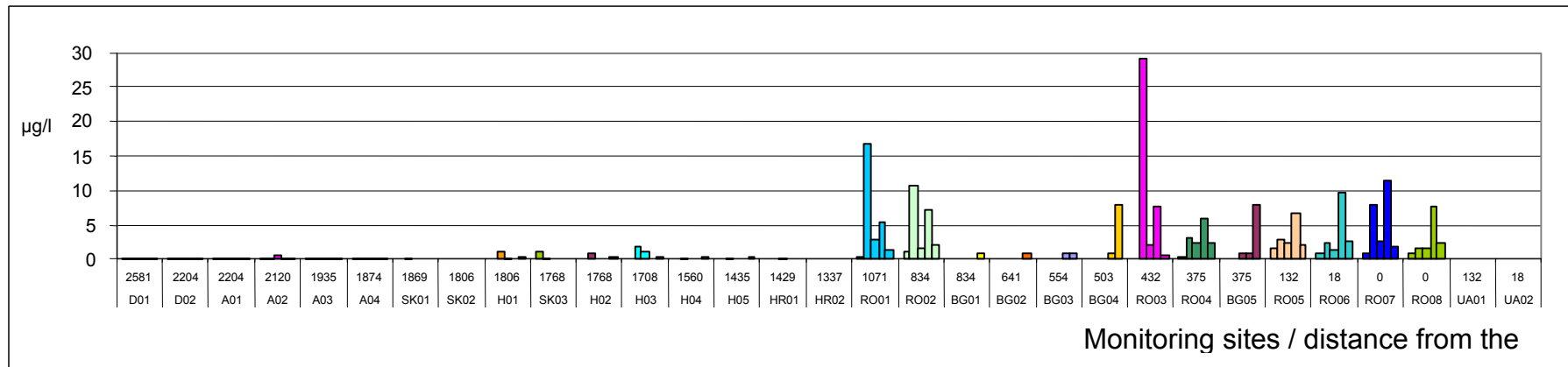
Fig. 8.1.3.17: Temporal trends of Cd – Danube River
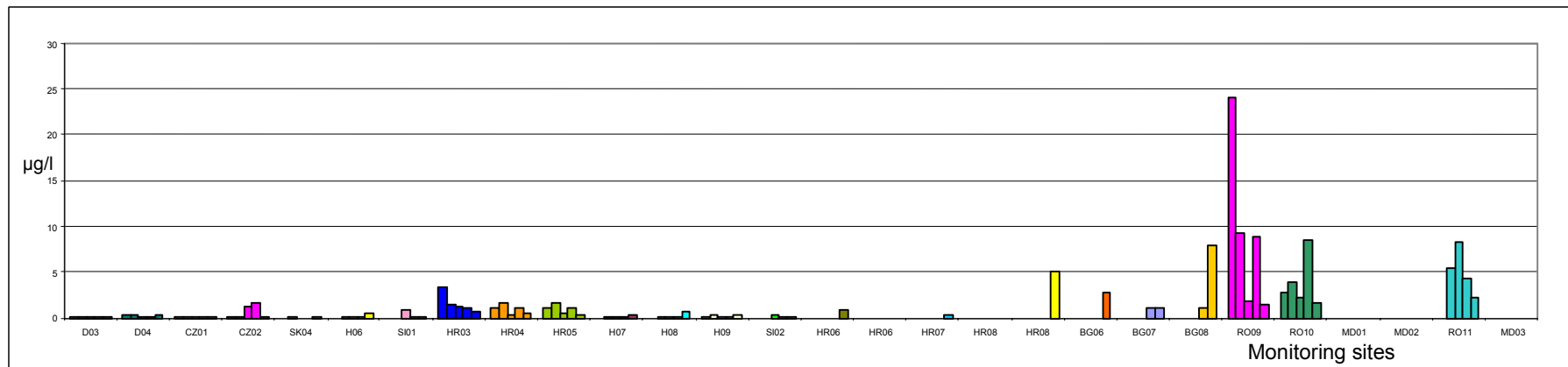
Fig. 8.1.3.18: Temporal trends of Cd – Tributaries

Chromium

There are two kinds of chromium with different effects upon environment: chromium (III) and chromium (VI). If the first one is an essential nutrient for humans, the second one is dangerous to health. Both forms can enter the environment through both natural sources and human activities. The main activities that increase the chromium (III) content are steel and leather manufacturing; for chromium (VI) chemical, textile manufacturing, electro-painting and other industrial applications of this form. In water, chromium is adsorbed on sediment and becomes immobile. That is why only a small part of chromium that ends up in water eventually dissolves.

In TNMN Programme, chromium is measured as total chromium (III + VI).

The distribution of monitoring sites according to the Classification System in the DRB for chromium is shown in **Fig. 8.1.3.19**.
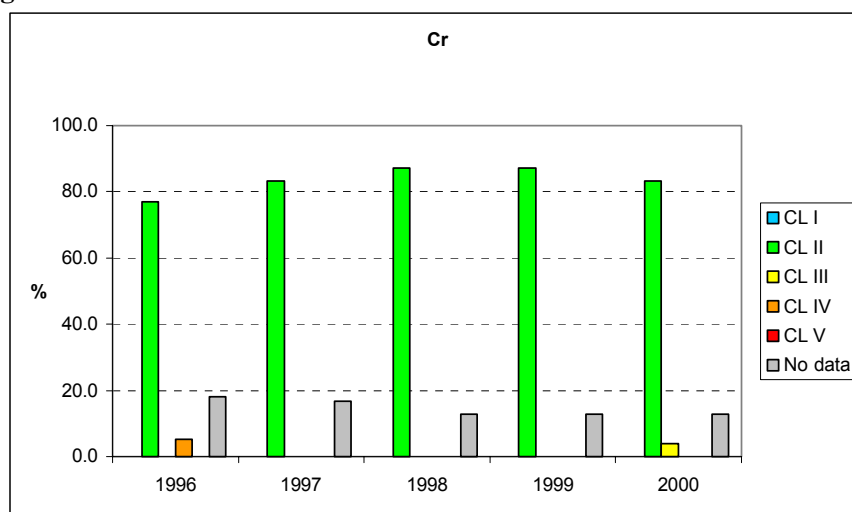
Fig. 8.1.3.19: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cr**

Based on data reported from 78 monitoring sites (out of the assessment is 25 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- during 1997 – 2000, more than 80% of the monitoring points belong to Class II;
- very few monitoring sites are within Class III and IV (less than 6 %).

The spatial pattern for chromium concentrations along the Danube River is shown in **Fig. 8.1.3.20a** and **8.1.3.20b**:

Excepting the first and the last monitoring site from the upper section - Danube-Neu-Ulm (km 2581, D01) and Danube-Wolfsthal (km 1874, A04) - where chromium is detectable in very low concentrations, all the other monitoring sites reported data below the declared detection limit.

In the middle section, even though the spatial pattern shows significantly higher values according to the Hungarian data, no value from this stretch exceeds the target value for chromium (50 μg/l). Maximum values are around 20 μg/l there.

In the first part of the lower Danube, an increasing is observed between Danube-Bazias (km 1071, RO01) and Danube-Pristol/Novo Selo (km 834, RO02), followed by a decreasing profile down to Danube-us. Russe (km 503, BG04). Along this part of the river, no value is above the target limit.

In the second part of the lower section, chromium concentrations increase from Danube-Chiciu/Silistra (km 375, RO04) down to the Danube Delta. Three values exceed the quality target there: 82.00 µg/l at Danube-us. Arges (km 432, RO03), 79.45 µg/l at Danube-Sulina/ Sulina arm (km 0, RO07) and 97.00 at Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08), all characterising year 1996.

The spatial distribution of chromium concentrations for selected tributaries is shown in **Fig. 8.1.3.21a** and **8.1.3.21b**: even if higher values appear on tributaries located in the lower section of the Danube - the Arges-Conf. Danube (RO09), the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) - no chromium concentration is above the target limit.

The temporal trend for chromium is shown in **Fig. 8.1.3.22** for the Danube River and in **Fig. 8.1.3.23** for selected tributaries:
-   in the upper and partially in the middle Danube, the general trend is a relative stationary state during the studied years; however, a slight decreasing tendency from 1996 to 2000 can be mentioned at Danube-Neu-Ulm (km 2581, D01);
-   Hungarian sites located in the middle Danube, are characterized by higher chromium concentration values in 1999 and 2000;
-   in the lower Danube, a decreasing decreasing tendency from 1998 to 2000 in Danube-Bazias (km 1071, RO01) and Danube-Sulina-Sulina arm (km 0, RO07) is observed;
-   from tributaries in the upper Danube, in Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02), a slight decreasing trend from 1996 to 2000 is present;
-   a relatively common decreasing trend is visible at three monitoring sites located on the Drava tributary: the Drava-Varazdin (HR03), Drava-Botovo (HR04) and Drava-D. Miholjac (HR05);
-   for the Arges-Conf. Danube (RO09), Siret (RO10) and Prut-Conf.Danube-Giurgiulest (RO11) also a decreasing tendency is observed.

In the frame of JDS maximum concentration   of chromium was 7 µg/l. This value was exceeded frequently inTNMN, even reaching values higher by one order.
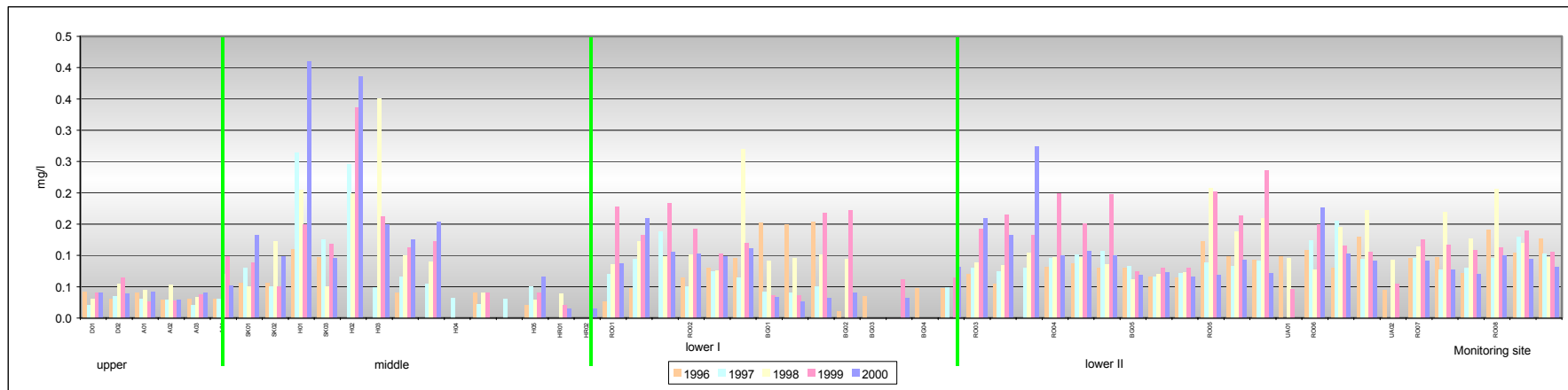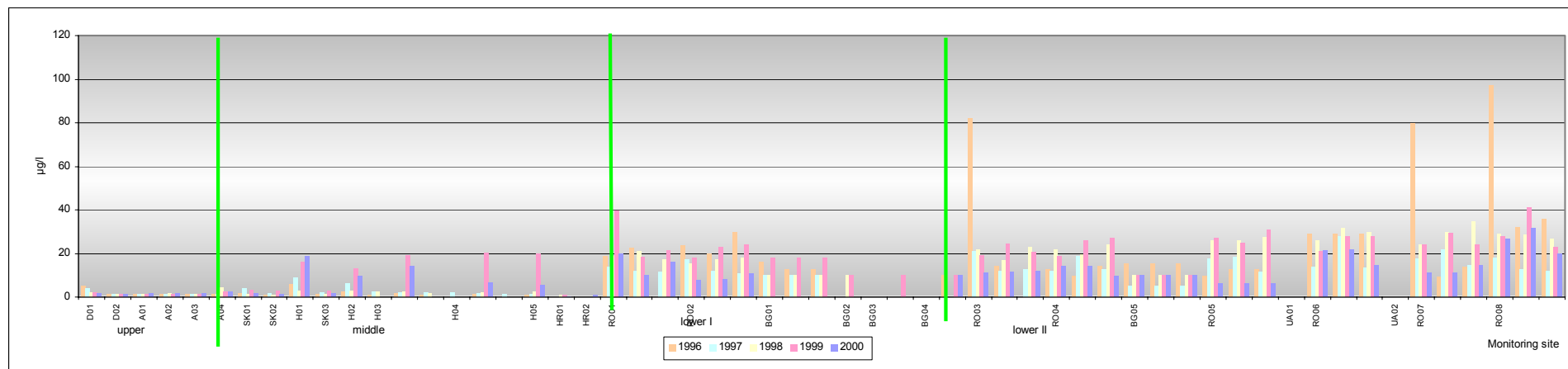
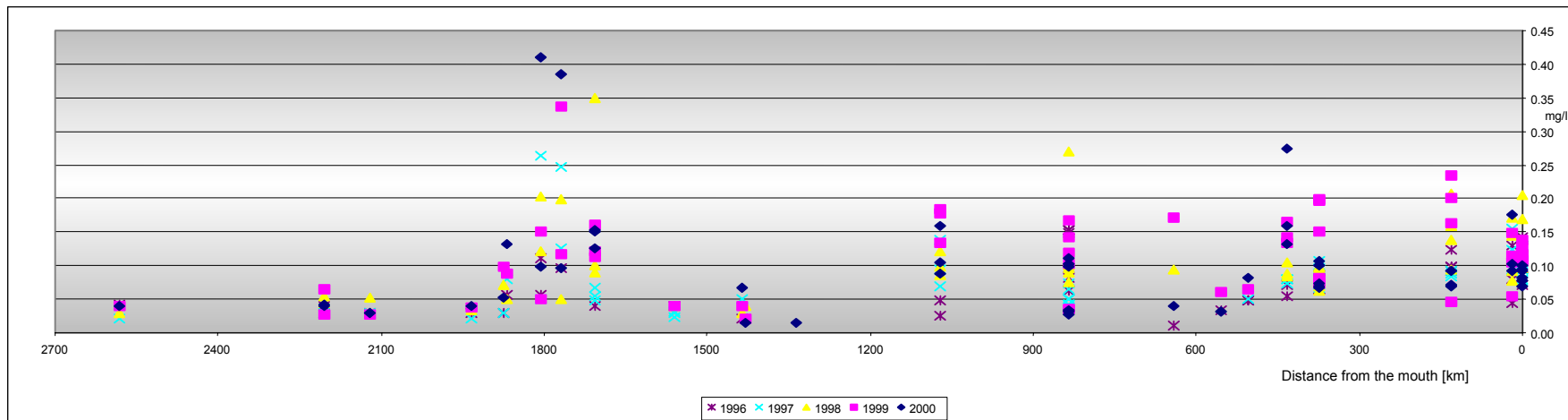Fig. 8.1.3.20a: Spatial variation of Cr – Danube River
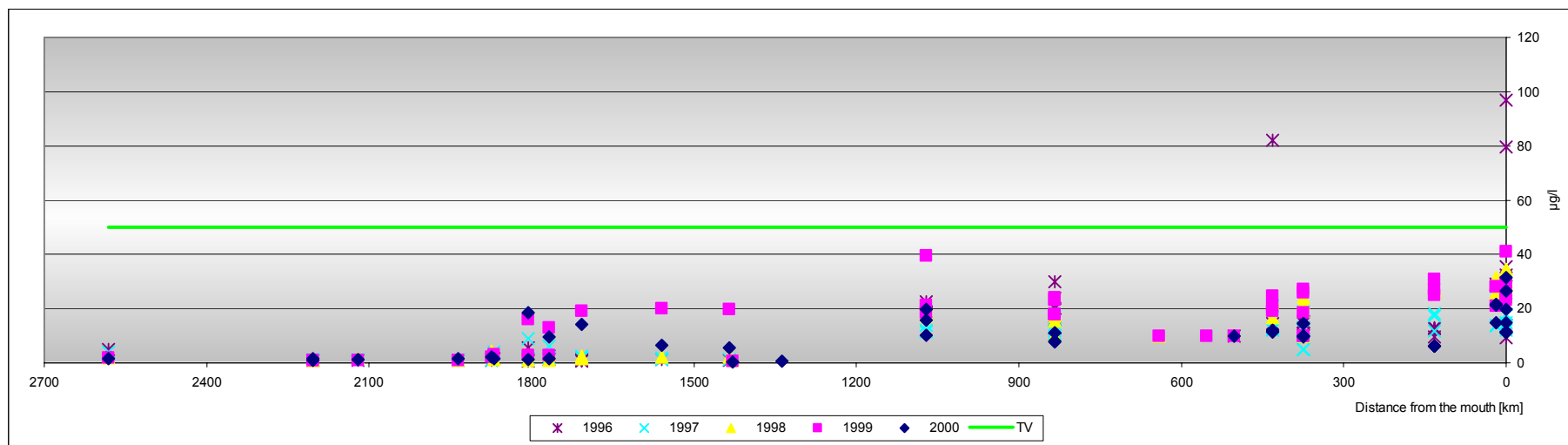
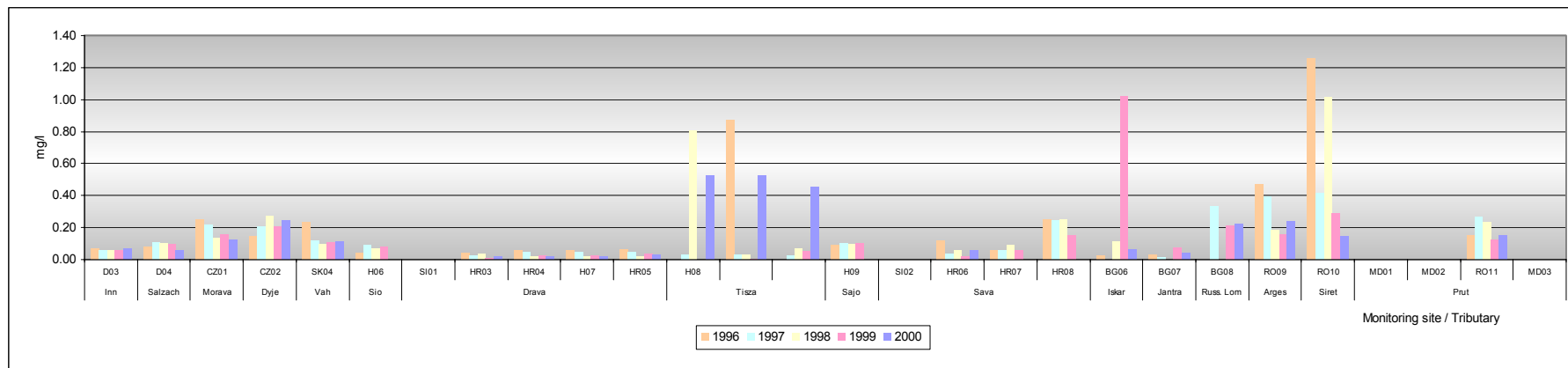Fig. 8.1.3.20b: Spatial variation of Cr – Danube River
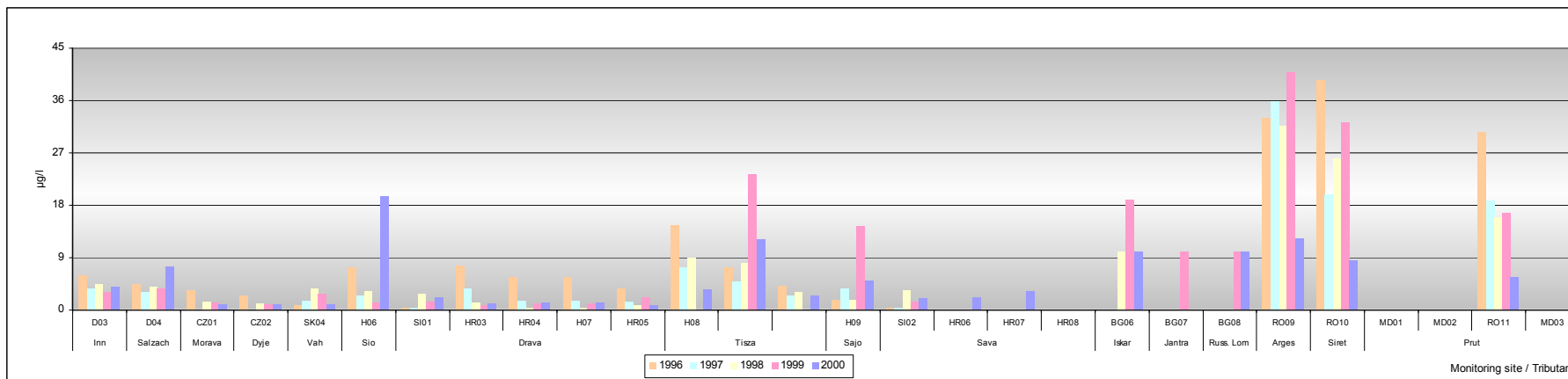
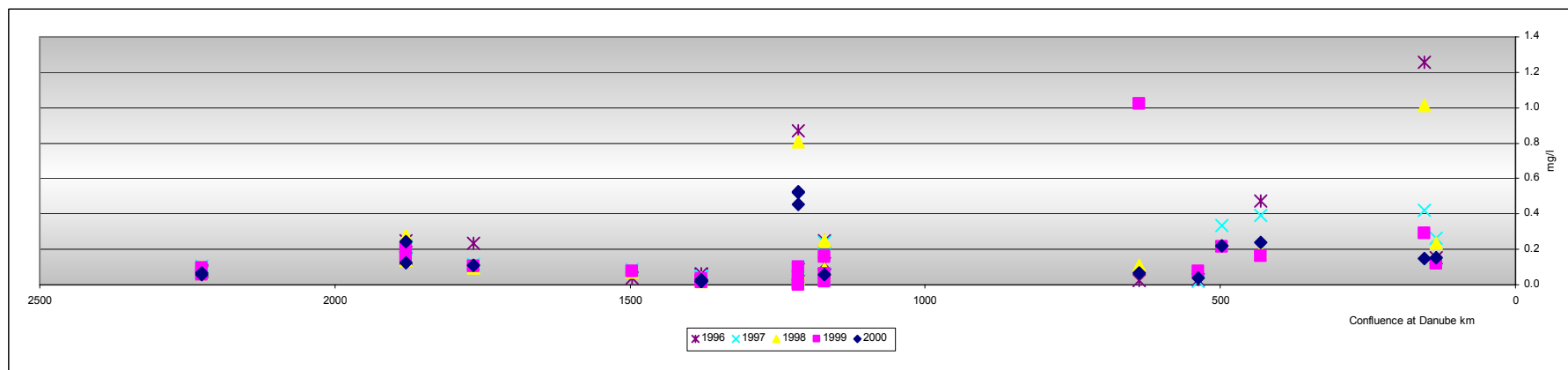Fig. 8.1.3.21a: Spatial variation of Cr – Tributaries


Fig. 8.1.3.21b: Spatial variation of Cr – Tributaries
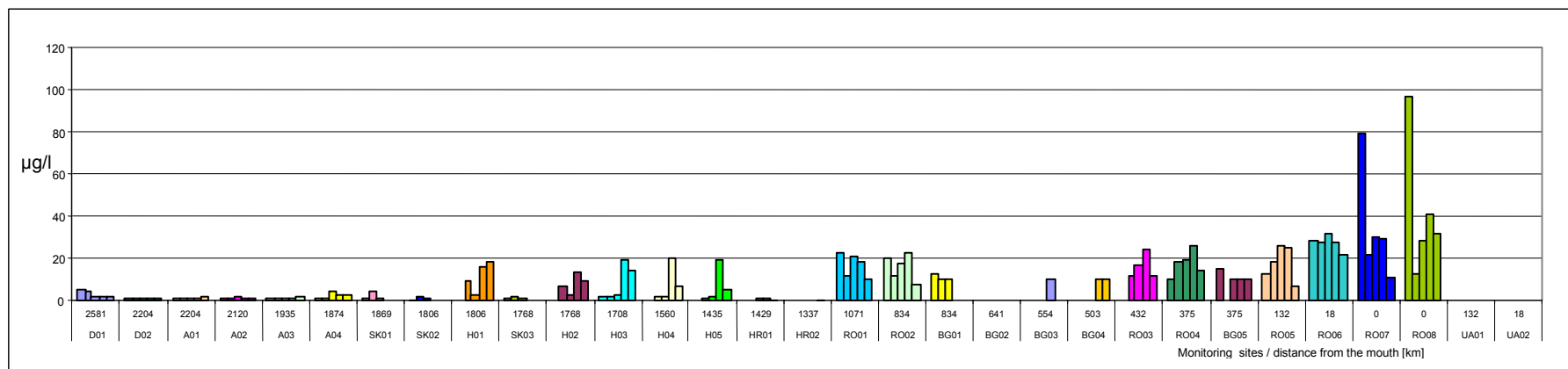
Fig. 8.1.3.22: Temporal trends of Cr – Danube River
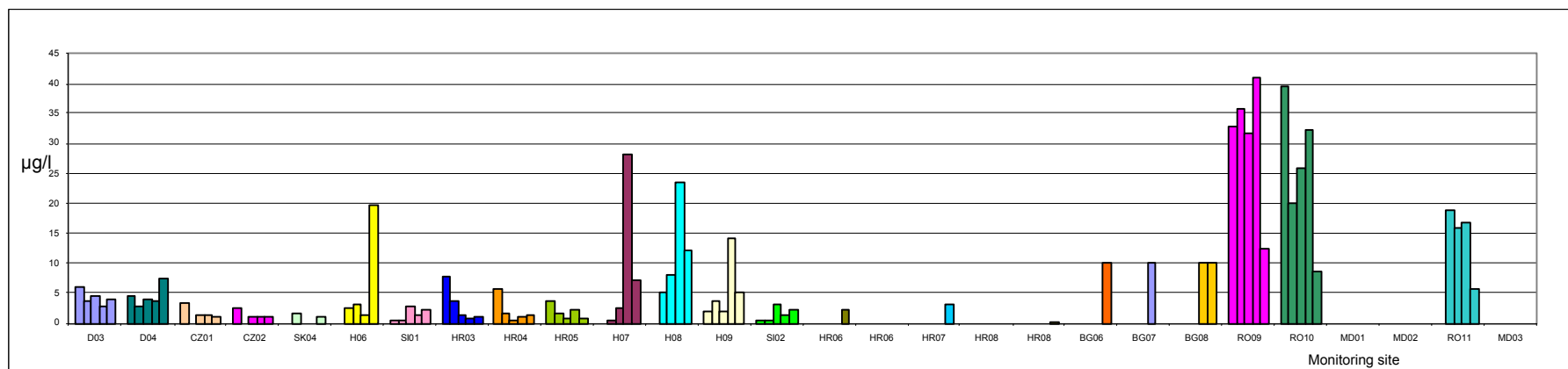
Fig. 8.1.3.23: Temporal trends of Cr – Tributaries

Copper

Copper is a very common substance that occurs naturally in the environment. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Humans widely use copper, because it is applied in industry and agriculture. That is why copper is often found near mines, industrial settings, landfills and waste disposals. In surface water, copper can be transported along great distances, either adsorbed on particles or as free ions. In catchments with no human inputs, the copper concentration is generally lower than 2 to 5 μg/l (*The Dobris Assessment, 1991*).

The distribution of monitoring sites according to the Classification System in the DRB for copper is shown in **Fig. 8.1.3.24**:
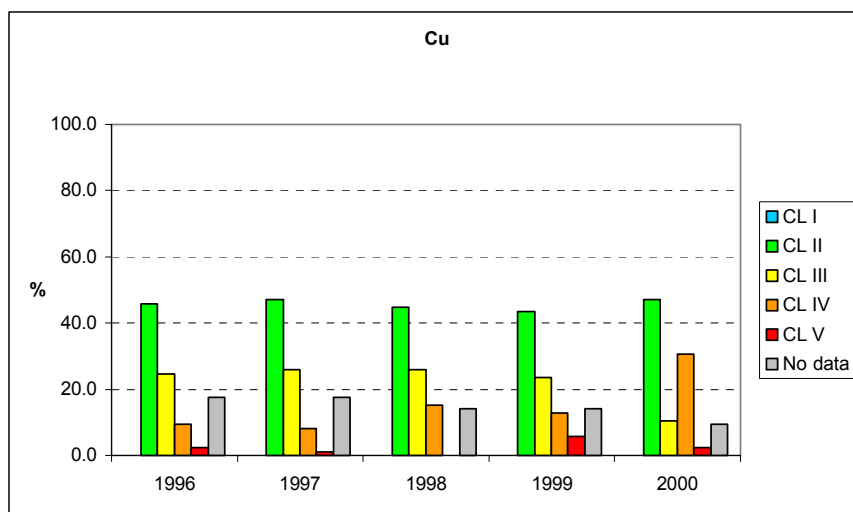
Fig. 8.1.3.24: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cu**

Based on data reported from 85 monitoring sites (out of the assessment is 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:
   -   a relative uniform temporal distribution appears for Class II (more than 40% of monitoring sites) each year;
   -   percentage of sites within Class III decreases from 1996 to 2000, but percentage within Class IV increases in the same period;
   -   a small part of sites belongs to Class V (the maximum percentage is recorded in 1999 – 5.9%);

The spatial pattern for copper concentrations along the Danube River is shown in **Fig. 8.1.3.25a** and **8.1.3.25b**:

In the upper part of the Danube River, the distribution of the copper c90 values is uniform, with the maximum value hardly reaching half of the target value for this heavy metal (20 μg/l).
In the middle stretch, excepting only one value, the same spatial pattern as in the upper section is present. Exception occurs at Danube-Medve/Medvedov (km 1806, H01), where the copper concentration exceeds more than two times the quality target in 1996.

In the lower section, the first part is characterized by an elevated profile between Danube-Bazias (km 1071, RO01) and Danube-Pristol/Novo Selo (km 834, RO02). Differences between the reported data from Romania and Bulgaria at the same cross section are still noticeable. Downstream km 834, a decreasing spatial pattern is present, even if two high values appear at Danube-ds. Svishtov (km 554, BG03) and at Danube-us. Russe (km 503, BG04): 117.0 μg/l and 138.20 μg/l, respectively, in 1997.

In the second part of the lower Danube, copper concentrations begin to increase along the entire stretch. Thus, the maximum values appear at Danube-Silistra/Chiciu (km 375, BG05), ranging between 162.10 and 213.10 μg/l. It has to be mentioned that in the lower section, during 1996 – 2000, 139 values exceed the target value.

The spatial pattern for selected tributaries is shown in **Fig. 8.1.3.26a** and **8.1.3.26b**:
- copper concentrations have a relatively uniform distribution in tributaries located in the upper and in the middle sections, with two exceptions: the Salzach-Laufen (D04) with one value exceeding the target limit and the Tisza-Tiszasziget (H08) with 4 values above this limit
- as regarding the tributaries from the lower Danube, six of them are characterized by values above 20μg/l.

The temporal distribution for copper concentrations is shown in **Fig. 8.1.3.27** for the Danube River and in **Fig. 8.1.3.28** for tributaries. The following can be concluded:
- in the upper Danube, an increasing tendency is observed in Danube-Wolfsthal (km 1874, A04), for the rest of monitoring sites a relatively steady state is present excluding Danube Neu-Ulm (D01), being the site with higher variability of copper content in comparison with other sites in this section;
- in the middle Danube, a slight decreasing trend appears from Danube-Bratislava (km 1869, SK01) down to Danube-Komarno/Komarom (km 1768, SK03). In Danube-Hercegszanto (km 1435, H05) a slight increasing in time is present;
- in the first part of the lower Danube, the temporal trends are different from one site to another: Danube-Bazias (km 1071, RO01) is characterized by an increasing tendency, similarly as Danube-Chiciu-Silistra (RO04) and Danube – Vilkov-Chilia Arm/Kilia Arm (RO06). A decrease is observed in Danube-Novo Selo/Pristol (BG01);
- in the second part of the lower section, an increasing trend from 1996 to 2000 is observed in Danube-Chiciu/Silistra (km 375, RO04) and Danube-Vilkov-Chilia arm/Kilia arm (km 18, RO06); Monitoring sites like Danube-Ds.Svishtov (km 554, BG03), Danube-Us.Russe (km 503, BG04), Danube-Silistrta/Chiciu (km 375, BG05) and Danube-Sf.Gheorghe/Sf.Gheorghe arm (km 0, RO08) show high yearly variability without indication general tendency of development in time;
- for tributaries from the upper section, excepting the Salzach-Laufen (D04), where the maximum copper value appears in 1998, a relatively constant temporal profile is valid;
- for tributaries located in the middle Danube, different trends are present: a decreasing in Drava River, an increasing in Tisza-Tiszasziget (H08) and Sajo-Sajopuspoki (H09);
- for tributaries from the lower Danube, a decreasing trend is observed in Arges-Conf. Danube (RO09) and from 1997 in Siret-Conf. Danube Sendreni (RO10) and increase in Russenski Lom (BG08). For the rest of the tributaries in this section, the existing data cannot provide a clear temporal tendency.

Similarly to other heavy metals, in accordance to JDS results copper was found in much lower concentrations in the Danube River. In the frame of TNMN, concentrations are much higher.
Generally, concentrations of copper increase significantly along the Danube. Also in case of tributaries, those located in the lower part of Danube River Basin are characteristic by higher concentrations.
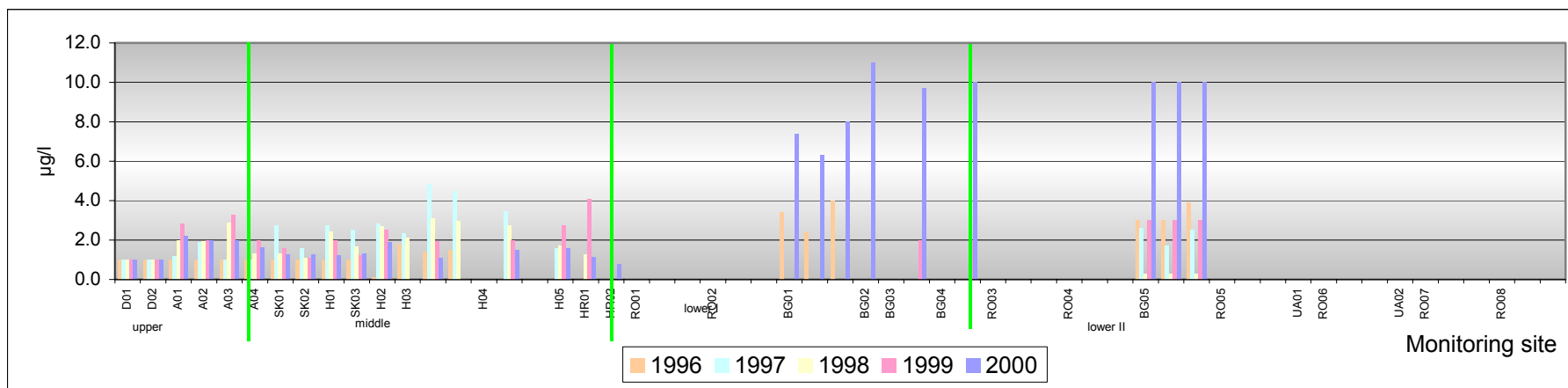
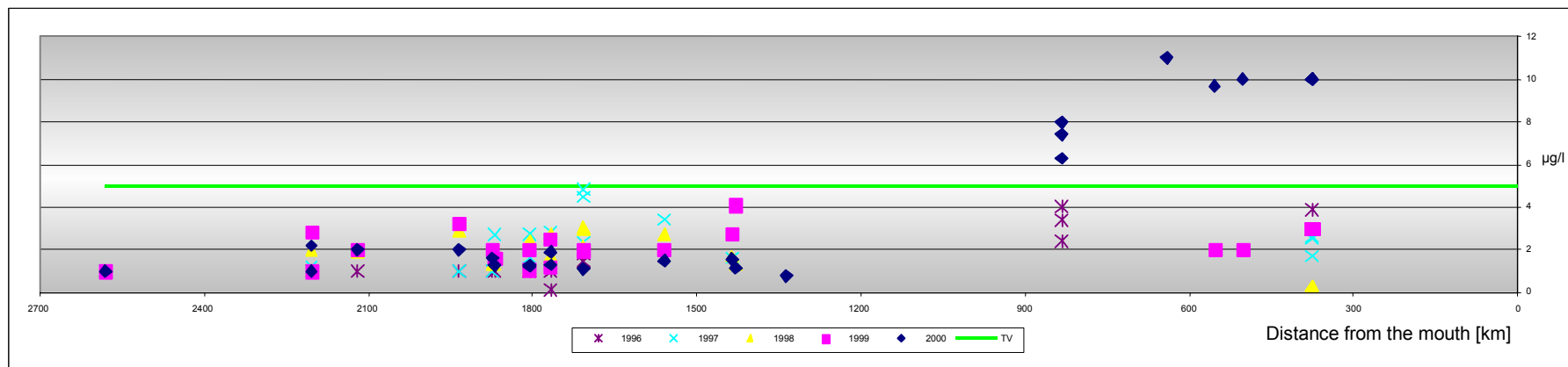Fig. 8.1.3.25a: Spatial variation of Cu – Danube River

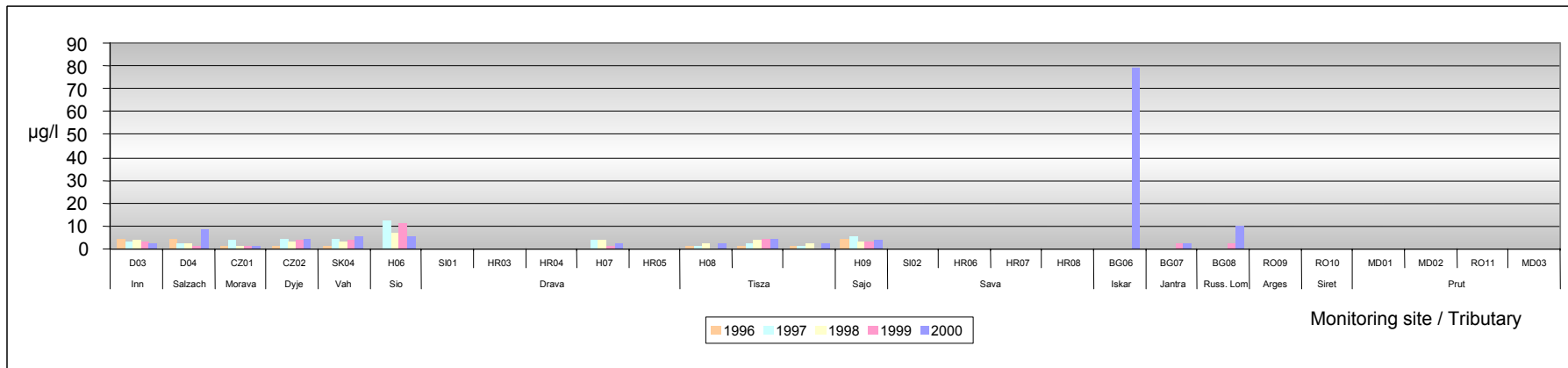Fig. 8.1.3.25b: Spatial variation of Cu – Danube River

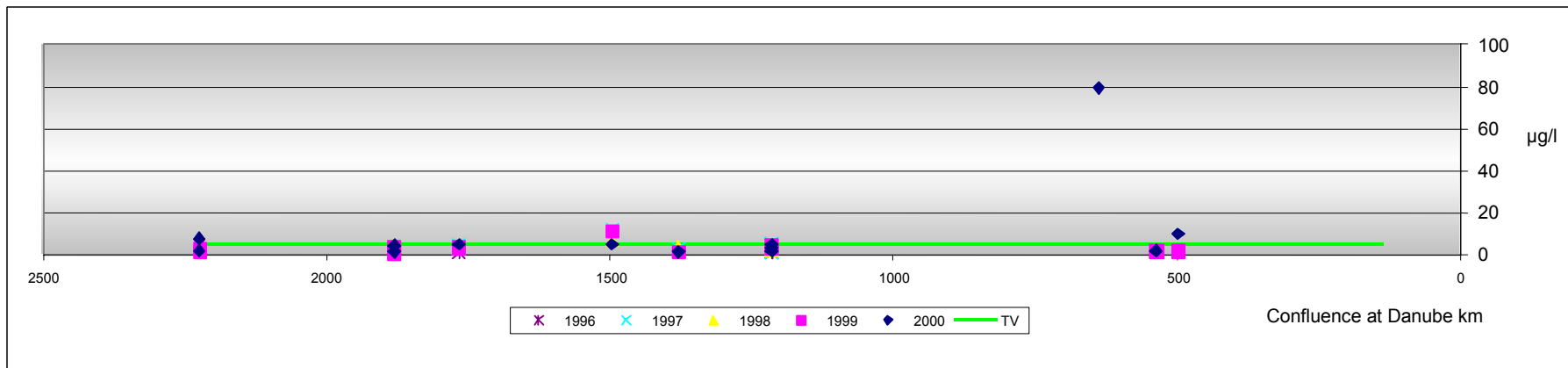Fig. 8.1.3.26a: Spatial variation of Cu – Tributaries


Fig. 8.1.3.26b: Spatial variation of Cu – Tributaries
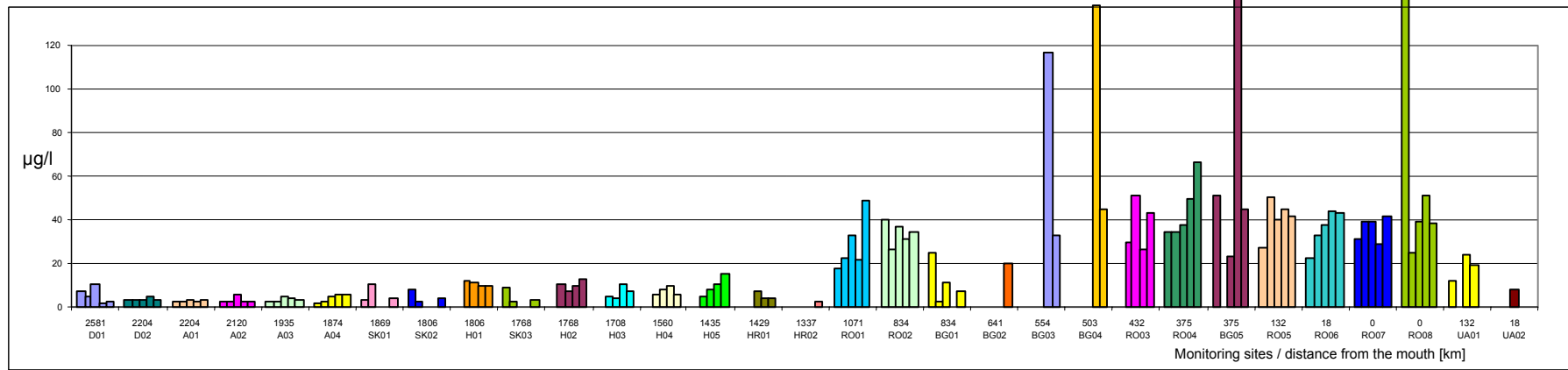
Fig. 8.1.3.27: Temporal trends of Cu – Danube River
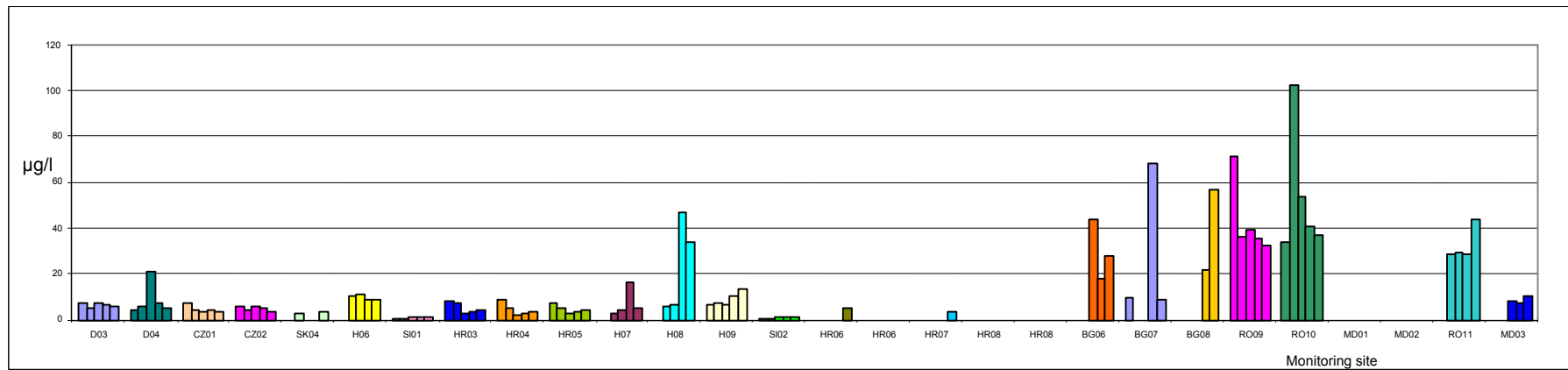
Fig. 8.1.3.28: Temporal trends of Cu – Tributaries

Lead

Lead is a particularly dangerous chemical. Most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline, through burning in car engines, lead salts (chlorine, bromines and oxides) enter the environment: the larger particles drop to ground immediately and pollute soils and surface waters, the smaller particles are transported long distances through air and fall back by raining. In water and soils lead can also end up through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints (more likely to happen when the water is slightly acidic).

The distribution of monitoring sites according to the Classification System in the DRB for lead is shown in **Fig. 8.1.3.29**:
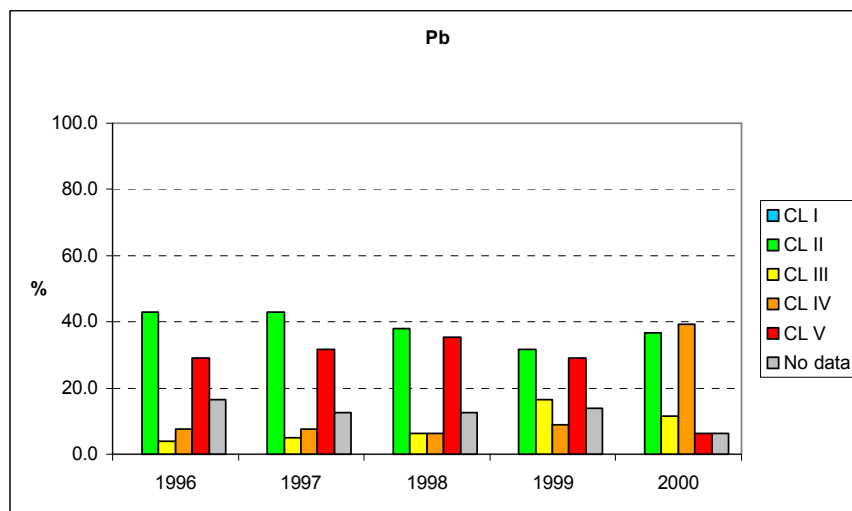
Fig. 8.1.3.29: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Pb**

Based on data reported from 79 monitoring sites (out of the assessment is 24 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:
-    the highest percentage of sites within Class II is observed in years 1996-1999;
-    year 2000 is the only one in which with percentage of sites corresponding to Class IV (39 %) exceed percentage of sites in Class II (37 %);
-    the number of sites within Class III increases from 1996 to 1999, followed by a decreasing in
-    lead is actually the only heavy metal which is represented by high percentage in Class V - even more than 30 % of the monitoring points in 1998), but this situation became better in 2000 (with 6.3 % of monitoring sites);

The spatial pattern of lead concentrations along the Danube River is illustrated in **Fig. 8.1.3.30a** and **8.1.3.30b**.

Similarly to the already discussed heavy metals, lead concentrations in the upper section present a uniform distribution, all values are below the target limit (5 μg/l).

This profile is valid also for the middle stretch; excepting one value – 17.45 μg/l at Danube-Dunafoldvar (km 1560, HO4) - all the others are below 5μg/l.

Spatial variation of lead concentration is totally different in the first part of the lower Danube. There is dramatic increase of lead concentrations from the beginning of this section and maximum is detected between Danube-Bazias (km 1071, RO01) – Danube-Pristol/Novo Selo (km 834, RO02); along this

stretch, excepting the value from 2000, all the others are above two times target value. Here are also the highest values along the Danube River, the lead c90 value reaches up to 82.00 μg/l. Downstream this location, the existing data shows a decreasing spatial pattern.

The second part of the lower Danube is also characterised by rather high lead concentrations, especially at Danube-Chiciu/Silistra (km 375, RO04), where according to Romanian data the lead c90 value reaches up to 57.30 μg/l.
Concerning the exceeding of the target value, along the entire lower stretch, 136 values are above this limit. Most of the values are actually characteristic to Quality Class V.

The spatial distribution of lead concentrations in the selected tributaries is shown in **Fig. 8.1.3.31a** and **8.1.3.31b**. It can be seen that 55 values exceed the target value. Target limit for lead is exceeded in majority of monitoring sites. The highest concentrations are observed in the tributaries of the lower part of river basin. Maximum c90 values had been observed in Arges (RO09), Siret (RO10) and Prut (RO11), reaching values 91.00 μg/l in Arges-Conf. Danube (RO09); 88.71 μg/l in Siret-Conf. Danube Sendreni (RO10) and 49.70 μg/l in Prut-Conf. Danube Giurgiulesti (RO11).

The temporal distribution of lead c90 values along the Danube River is shown in **Fig. 8.1.3.32** and in **Fig. 8.1.3.33** for selected tributaries. It can be concluded that:
- in the upper and middle Danube, a relative constant values in evaluated period are present, excepting the monitoring site located at Danube-Dunafoldvar (km1560, H04), where an increasing tendency appears from 1997 to 2000;
- in the lower Danube, decreasing from 1998 is observed in all Romanian monitoring sites from Danube-Bazias (km 1071, RO01), down to Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08). In cross section RO02/BG01 and RO04/BG05, in accordance to existing Bulgarian data, the trend is somehow opposite - increasing from 1996 to 2000;
- as far as concerns the temporal changes in selected tributaries, the following has been observed:
  o increasing from 1997 to 2000 in Salzach-Laufen (D04);
  o decreasing in Drava-Varazdin (HR03), Drava-Botovo (HR04) and Drava-D. Miholjac (HR05);
  o decreasing in Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11).

The spatial pattern of lead is the same as was in case of other heavy metals, with generally several-times higher values in lower part of river basin, which is valid for both – Danube River itself and monitored tributaries. JDS results are much lower, TNMN data indicate values characterising lead content in lower Danube part sometimes even higher by one order.
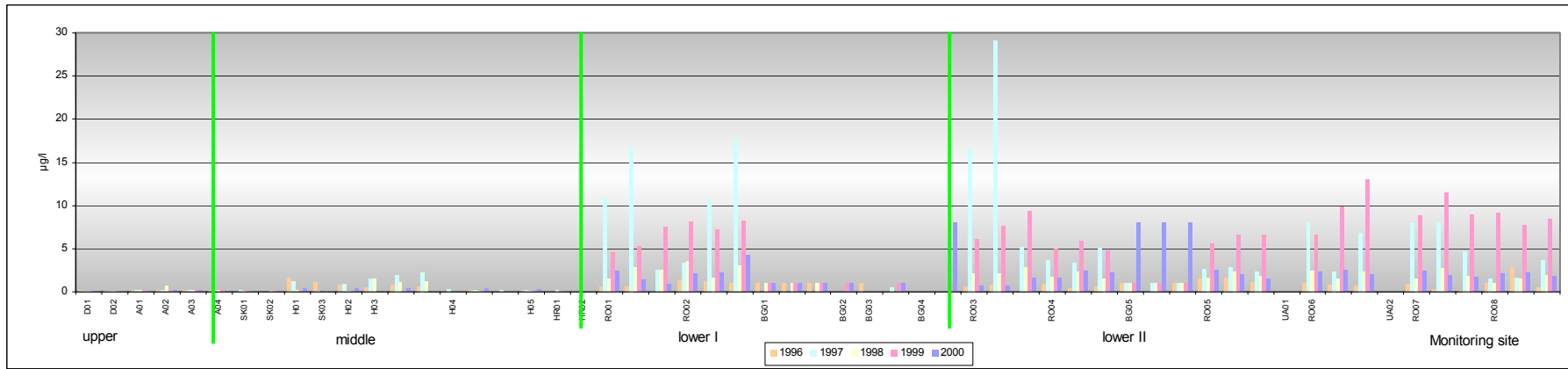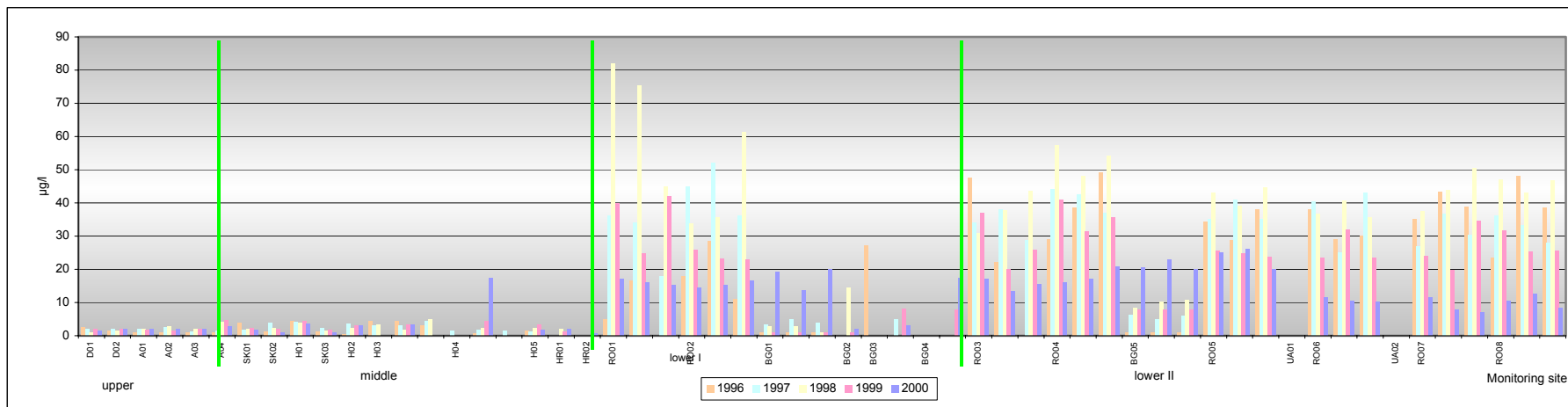
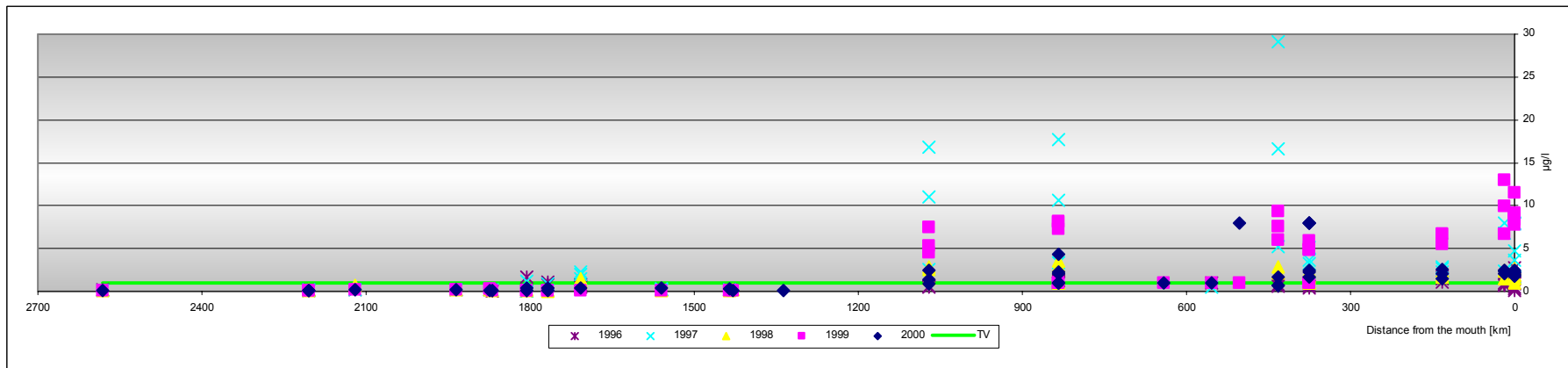Fig. 8.1.3.30a: Spatial variation of Pb – Danube River
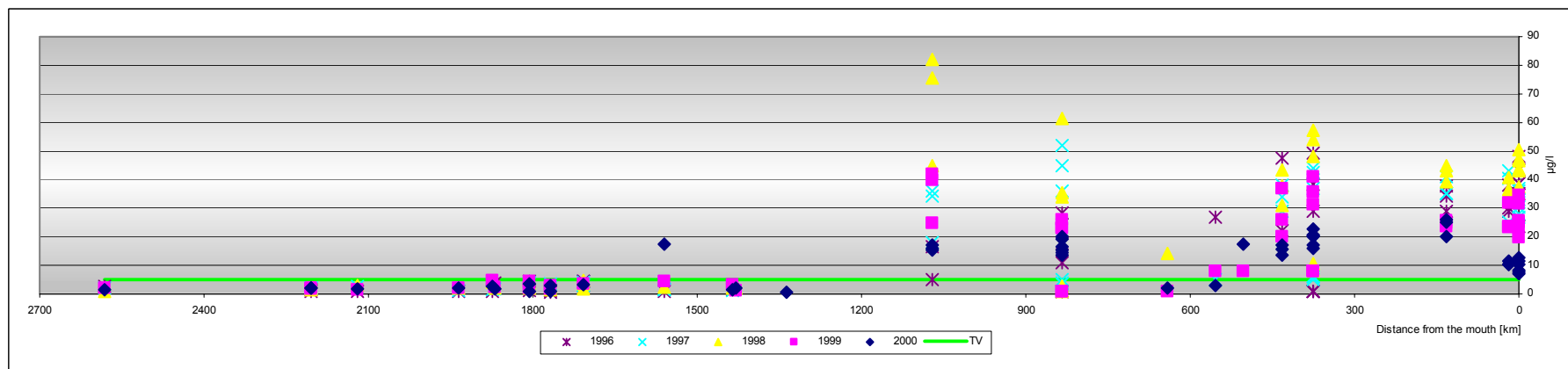
Fig. 8.1.3.30b: Spatial variation of Pb – Danube River
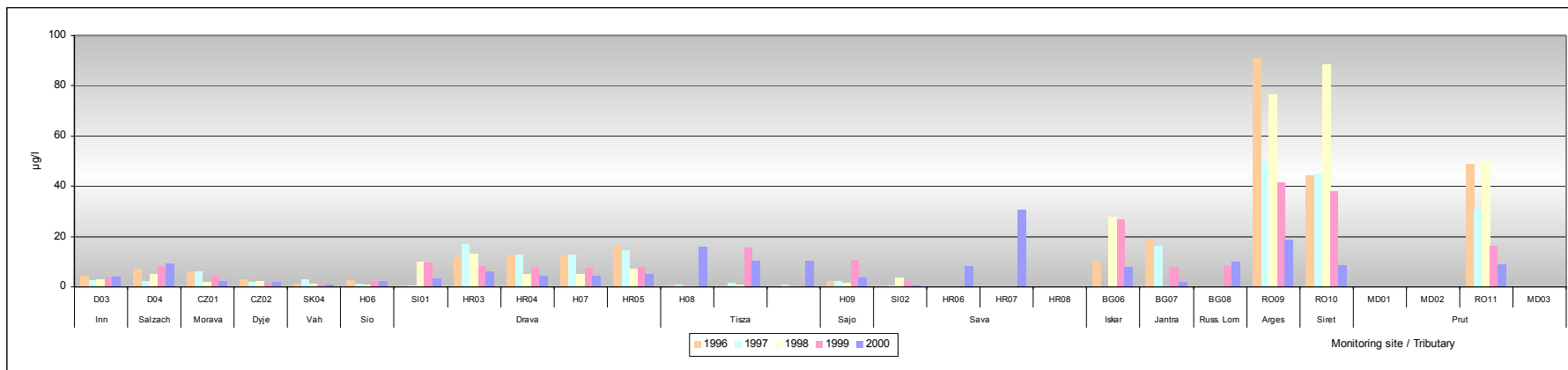
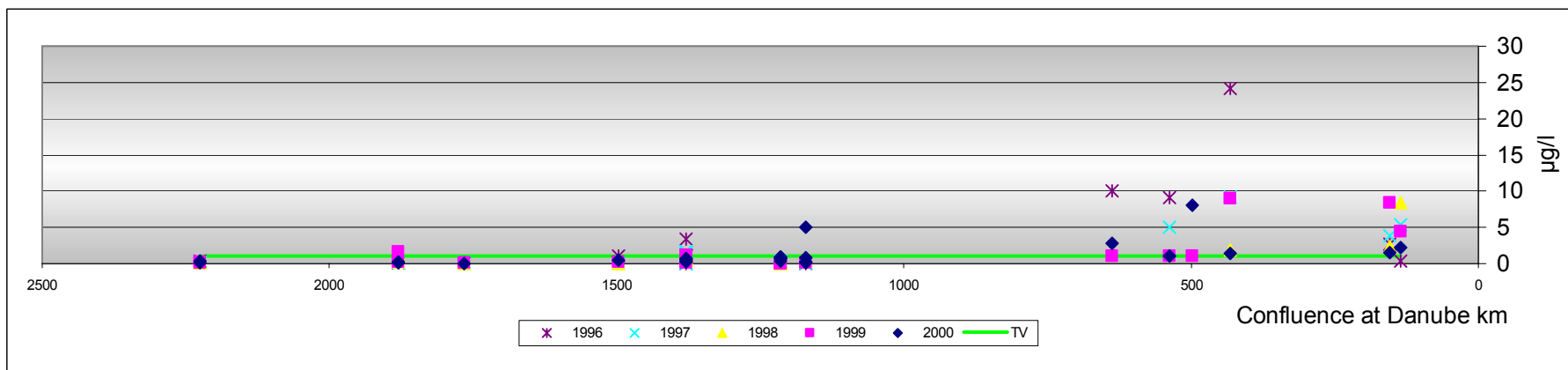Fig. 8.1.3.31a: Spatial variation of Pb – Tributaries
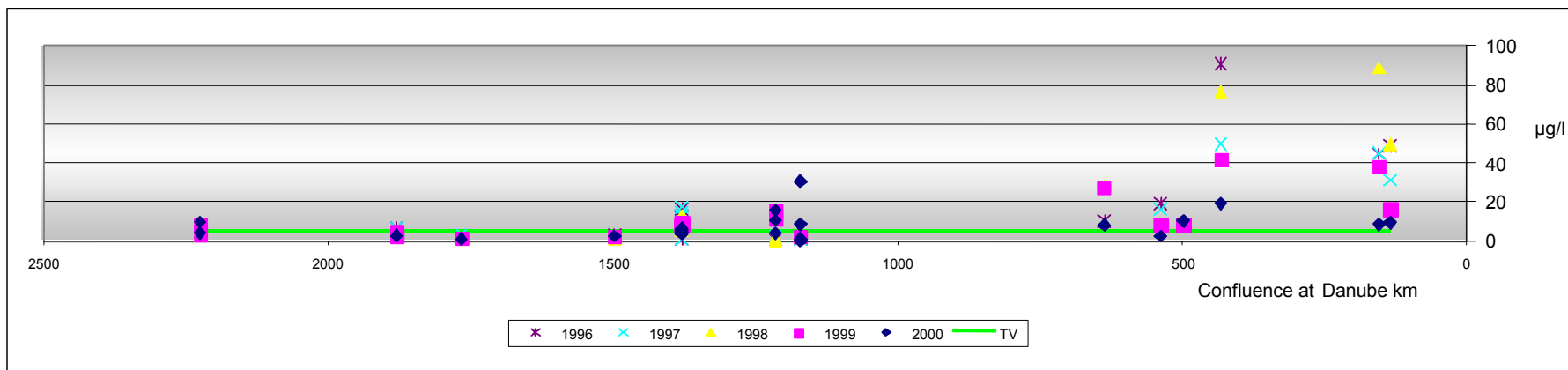
Fig. 8.1.3.31b: Spatial variation of Pb – Tributaries
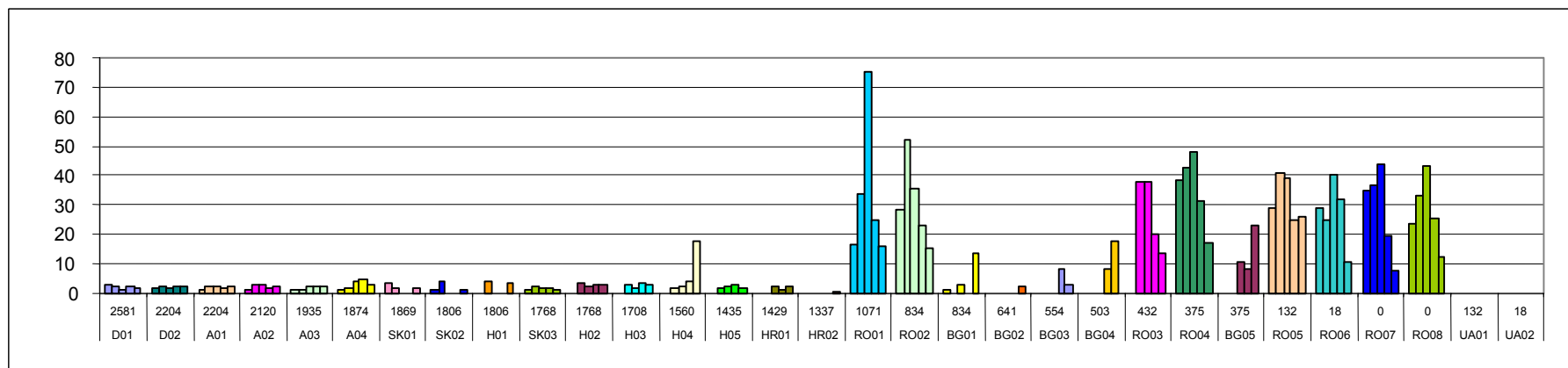
Fig. 8.1.3.32: Temporal trends of Pb – Danube River
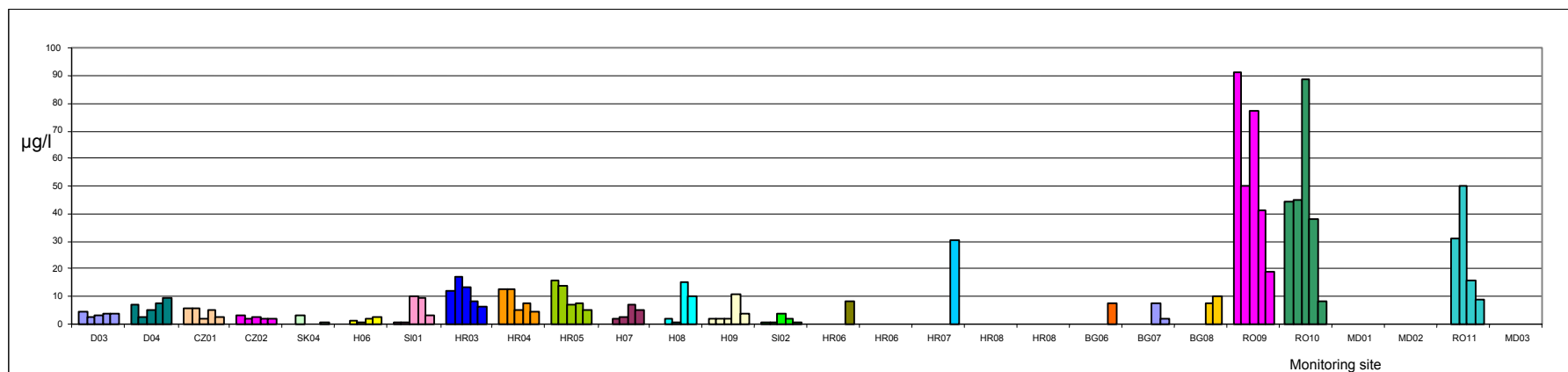
Fig. 8.1.3.33: Temporal trends of Pb – Tributaries

Mercury

Mercury is a metal that occurs naturally in the environment. It can be found as mercury salts or as organic mercury compounds. It enters the environment as a result of normal breakdown of minerals and exposure to wind and water. From human activities, mercury is released into air through fossil fuel combustion, mining, smelting and solid waste combustion. Some forms of human activities release mercury directly into soil or water, for instance the application of agricultural fertilizers and industrial waste water discharges. All mercury released into environment will eventually end up in soil and surface water. Acidic surface waters can contain significant amounts of mercury: when the pH values are between 5.00 and 7.00, the mercury concentrations in water increase due to mobilization of mercury in the ground. Once it reaches the surface water, microorganism can convert it into methyl mercury, a very dangerous organic compound.

The distribution of monitoring sites according to the Classification System in the DRB for mercury is shown in **Fig. 8.1.3.34**:
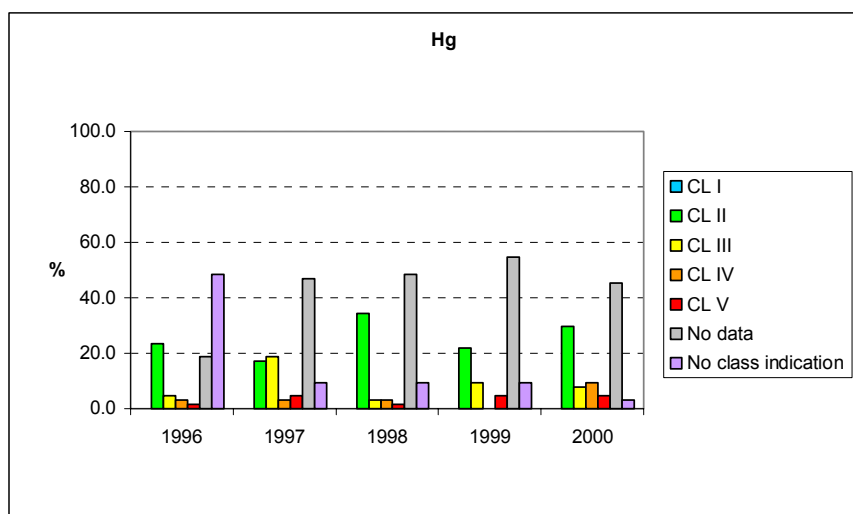
Fig. 8.1.3.34: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Hg**

Based on data reported from 64 monitoring sites (out of the assessment is 49 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:
-   almost 50 % of the monitoring sites (in 1996) have no quality class indication, because the limit of detection is higher than the limit value for Class II. In years 1997-2000 sites with "no class" indication is low because data have not been provided from majority of these sites (and therefore percentage of sites with "no data" from the basic set of 64 monitoring sites is so high in 1997-2000) (see also Annex 1)
-   in four of the five studied years, maximum percentage of sites correspond to Class II. In 1997, maximum belongs to Class III;
-   the number of sites corresponding Class IV is uniform during 1996-1998 (3.1%), absent in 1999 but increases in 2000 at 9.4 %;
-   the number of sites within Class V is below 5 % during the evaluated period;

The spatial pattern for mercury concentrations along the Danube River is shown in **Fig. 8.1.3.35a** and **8.1.3.35b**.

Mercury c90 values are between 0.100 – 0.416 μg/l in the upper section, being undetectable at Danube-Neu Ulm (km 2581, D01) and Danube-Jochentein (km 2204, D02). Mercury is the only heavy metal in case of which the upper Danube section contains 16 values above the target limit.

Although mercury was mostly undetected at monitoring sites from the middle stretch, still 14 values are above the quality target. The maximum value (0.82 μg/l) appears at Danube-Dunafoldvar (km 1560, H04).

Entire lower section of the Danube has no suitable data for assessment.[1]

The spatial pattern of mercury concentrations for selected tributaries is illustrated in Fig. **8.1.3.36a** and **8.1.3.36b**. All four tributaries from the upper section show mercury values exceeding the target value. Those from the middle stretch also show values above 0.1 μg/l. It has to be mentioned that in the case of the Drava-Ormoz (SL01) and the Sava-Jesenice (SL02) the represented values (0.5 μg/) are actually the limit of detection, so mercury is undetected at those sites. The maximum mercury concentration (1.54 μg/) appears on the Sava-ds. Zupanja (HR08). Concerning the tributaries from the lower Danube section, no mercury data are suitable for assessment[1].

The temporal distribution of mercury concentrations along the Danube River is shown in **Fig. 8.1.3.37** and in **Fig. 8.1.3.38** for selected tributaries. It can be concluded that:
- no tendency of development can be observed in the monitoring sites from the upper and middle Danube section;
- for selected tributaries, slight increase in Inn-Kirchdorf (D03) and Dyje (CZ02) and slight decrease in Morava-Lanzhot (CZ01) is observed.

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[1] the reported data for Romanian monitoring sites are excluded from assessment because all data are equal to 3.00μg/l, identical with the reported limit of detection
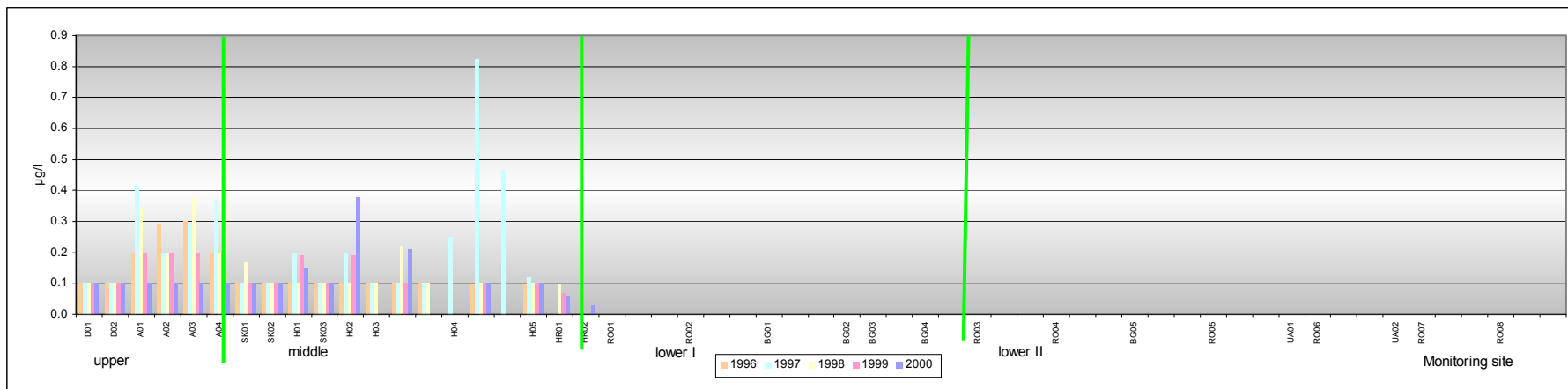
Fig. 8.1.3.35a: Spatial variation of Hg – Danube River
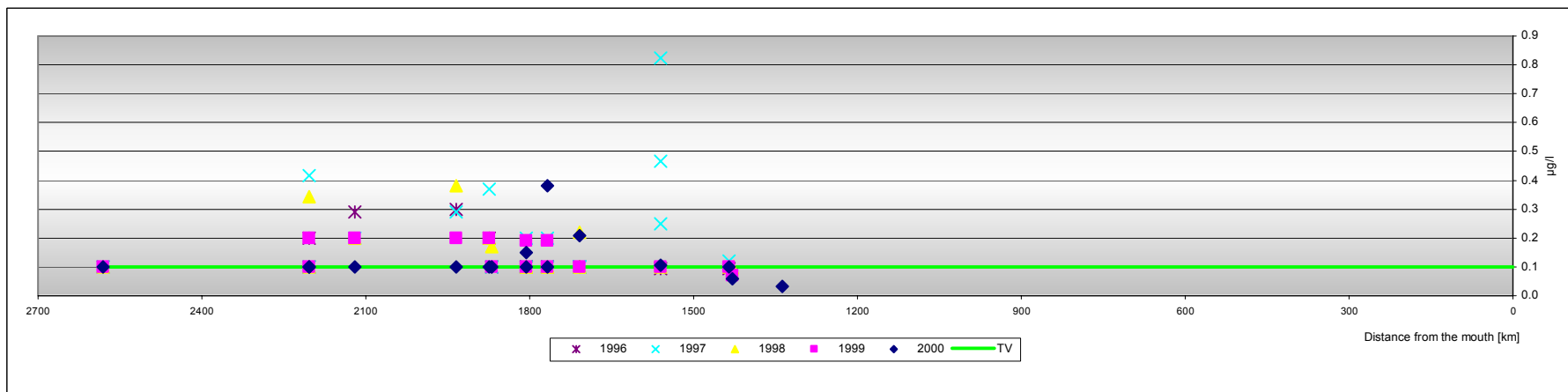
Fig. 8.1.3.35b: Spatial variation of Hg – Danube River

Note: In locations A01, A02, A03, A04 (96-99), RO01, RO02, RO03, RO04, RO05, RO06, RO07, RO08 (96) the values in the graph represent limits of detection that are higher than the target value.
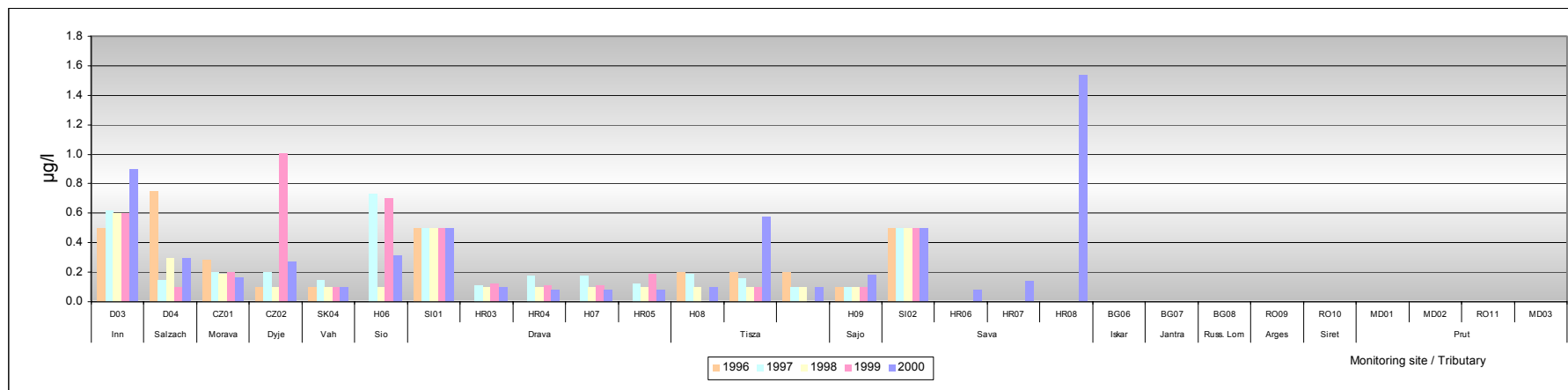
Fig. 8.1.3.36a: Spatial variation of Hg – Tributaries
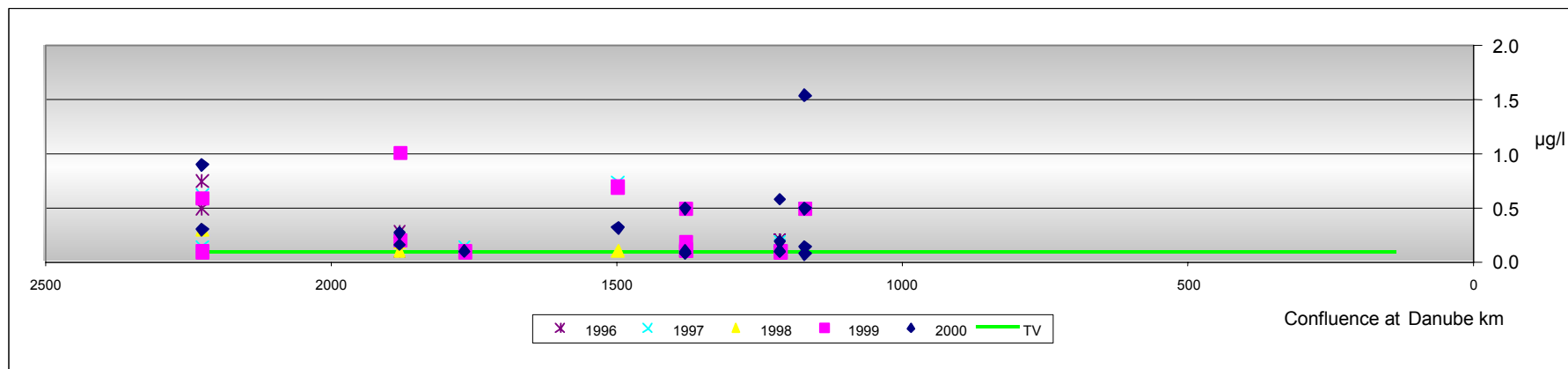
Fig. 8.1.3.36b: Spatial variation of Hg – Tributaries

Note: In locations SL01, SL02 (96-00), RO09, RO10, RO11 (96) the values in the graph represent limits of detection that are higher than the target value.
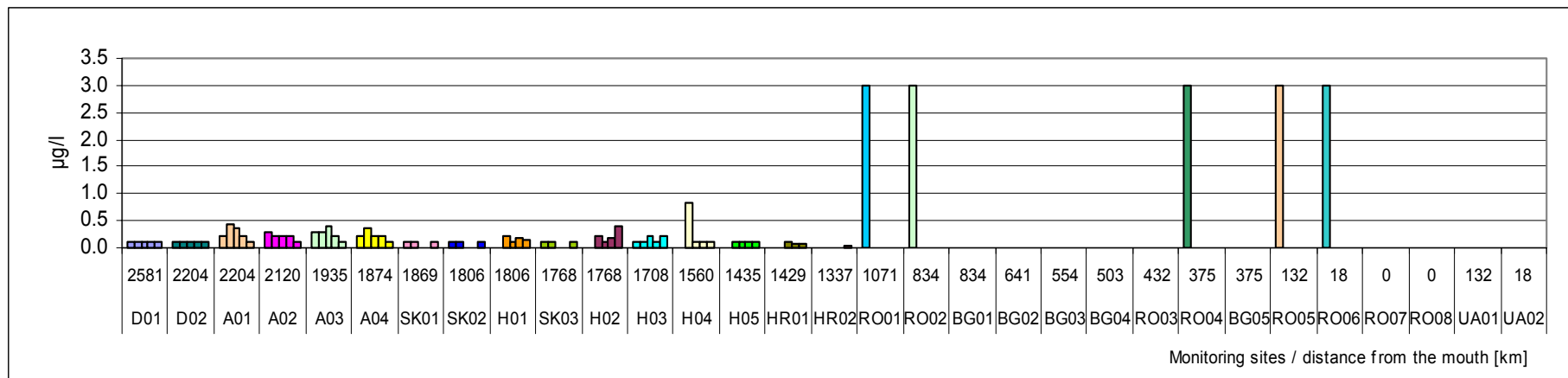
Fig. 8.1.3.37: Temporal trends of Hg – Danube River
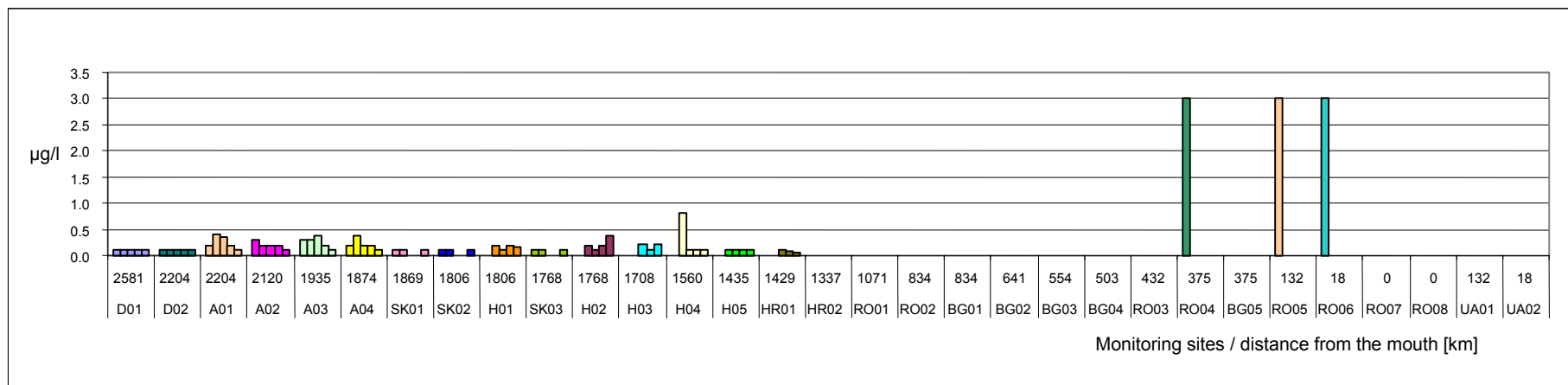
Fig. 8.1.3.38: Temporal trends of Hg – Tributaries

Nickel

The distribution of monitoring sites according to the Classification System in the DRB for nickel is shown in **Fig. 8.1.3.39**:
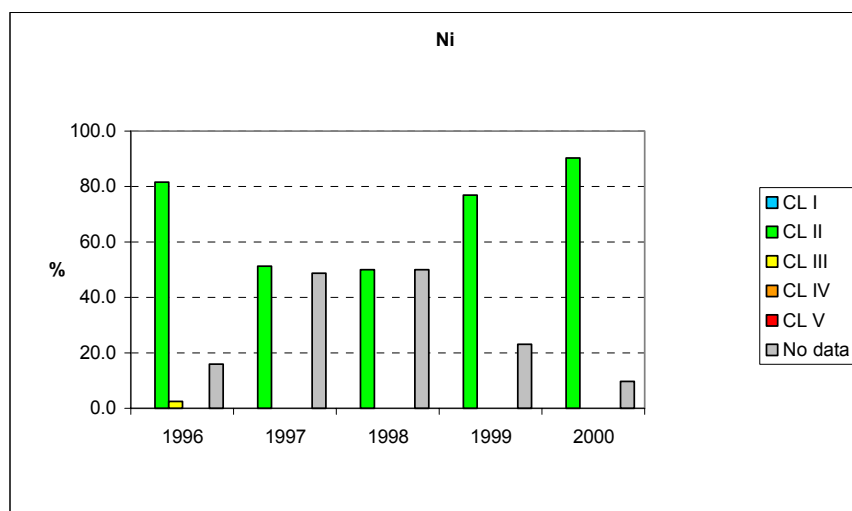
Fig. 8.1.3.39: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Ni**

Based on data reported least in one year by 82 monitoring sites (out of the assessment is 21 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that nickel seems to be the heavy metal for which the Danube River and its tributaries have "the best" quality, taking into account target value given by Class II of TNMN classification scheme. Monitoring sites correspond to Class II and Class III is represented only in 1996 by 2.4 % of monitoring sites.

The spatial distribution of nickel concentrations along the Danube River is shown in **Fig. 8.1.3.40a** and **8.1.3.40b**.

In the upper Danube, a slight increasing spatial profile is present from Danube-Jochenstein (km 2204, D02) to Danube-Wolfsthal (km 1874, A04), but no nickel concentration is above the target limit for this heavy metal (50 μg/l).

In the middle Danube, also an increasing pattern is present along Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03), followed by a decreasing down to Danube-Borovo (km 1337, HR02). Even the maximum value for this stretch (16.21 μg/l) is well below the target limit.

Along the first part of the lower Danube section, nickel concentrations are higher than in the middle stretch, reaching c90 value 28.10 μg/l at Danube-Pristol/Novo Selo (km 834, RO02). However, no value exceeds the quality target.

The second part of the lower Danube section shows several nickel concentrations higher than in the first section. Three monitoring sites - Danube-us. Arges (km 432, RO03), Danube-Chiciu/ Silistra (km 375, RO04) and Danube-Vilkov/Chilia arm/Kilia arm - present values above 30 μg/l, The target limit is not exceeded.

The spatial profile of nickel concentrations in the selected tributaries is shown in **Fig. 8.1.3.41a** and **8.1.3.41b**. It can be seen that, excepting one value recorded on the Salzach-Laufen (D04), the tributaries from the upper and middle Danube are characterized by low nickel concentrations, with no

value above the target limit. For those located in the lower Danube, 2 values are above 50µg/l: on the Arges-Conf. Danube (RO09) and Siret-Conf. Danube Sendreni (RO10).

The temporal trends for nickel concentrations are shown in **Fig. 8.1.3.42** for the Danube River and in **Fig. 8.1.3.43** for selected tributaries:

- increasing tendency is observed in Hungarian section of the Danube River, from Danube-Komarom/Komarno (km1768, H02) down to Danube-Hercegszanto (km 1435, H05);
- in the lower part of Danube River interpretation is rather difficult, because whilst in Romanian sites maximum values have been observed at the beginning of the evaluated period – in 1996, in Bulgarian ones at the end of this period – in 2000
- from selected tributaries decreasing from 1996 to 2000 in Salzach-Laufen (D04) and Drava-Varazdin (HR03) is observed;
- for interpretation of tributaries in the lower part, the data available are not sufficient.

Fig. 8.1.3.40a: Spatial variation of Ni – Danube River

Fig. 8.1.3.40b: Spatial variation of Ni – Danube River

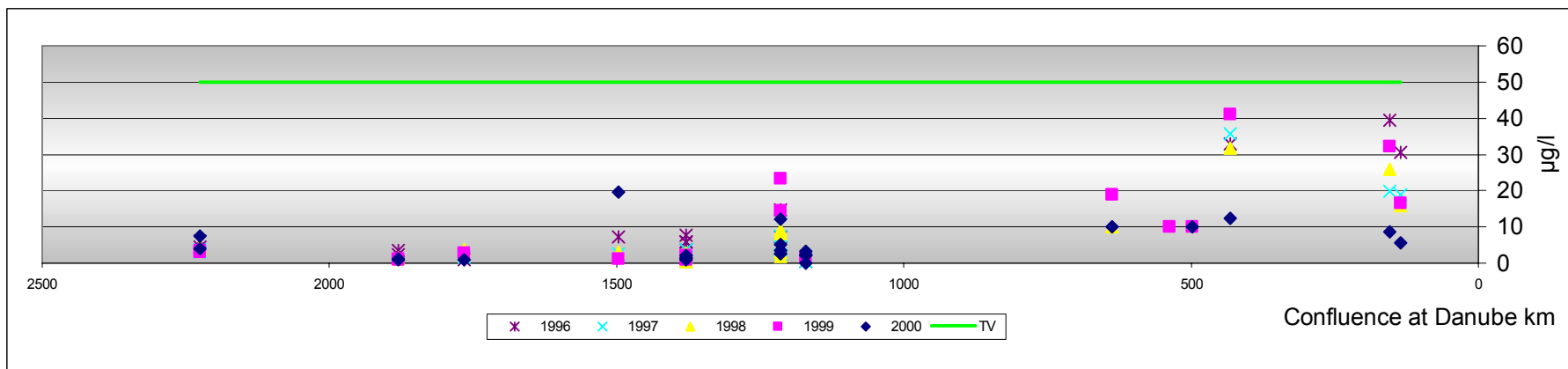Fig. 8.1.3.41a: Spatial variation of Ni – Tributaries

Fig. 8.1.3.41b: Spatial variation of Ni – Tributaries
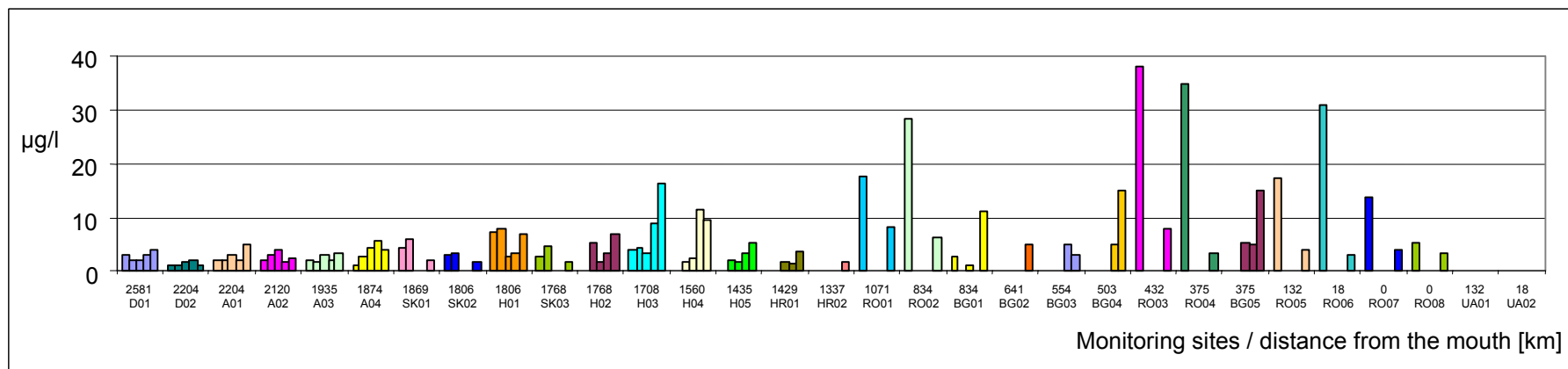
Fig. 8.1.3.42: Temporal trends of Ni – Danube River
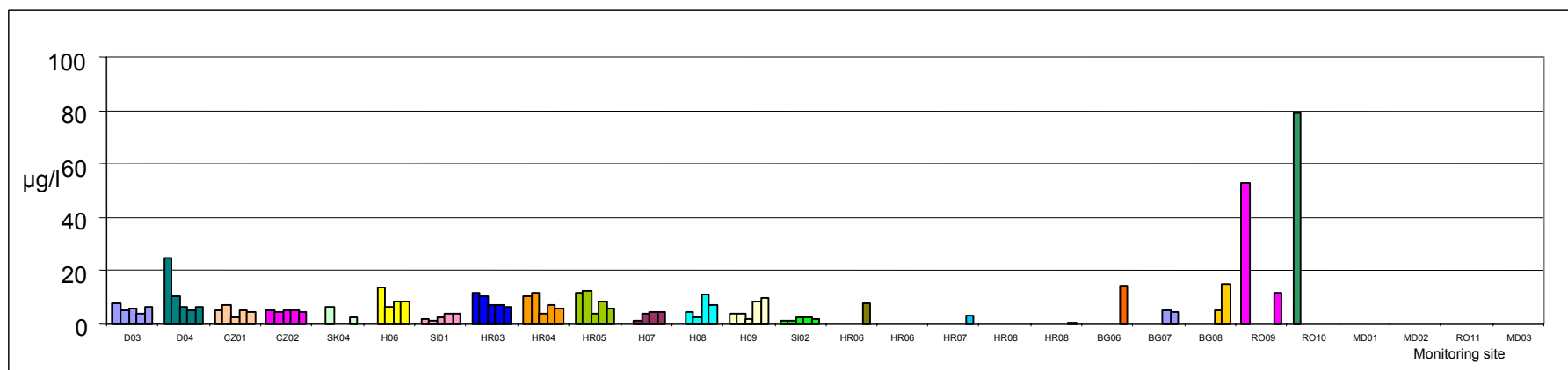
Fig. 8.1.3.43: Temporal trends of Ni – Tributaries

Zinc

Zinc occurs naturally in air, water and soil. Similar to copper, zinc is widely used in human activities. Mining of other different metals results in zinc discharging in the environment. In natural water, unaffected by anthropogenic influence, zinc concentration is usually below 5 μg/l (*The Dobris Assessment, 1991*). Due to the fact that its toxicity is generally higher in water with a low mineral content, the Council Directive 78/659/EEC concerning water standards for fish recommends that Zn levels to be below 300 μg//l in water with a hardness of 100 mg/l $CaCO_3$, but below 30 μg//l in water with a hardness of 10 mg/l $CaCO_3$. Within the Danube River Basin, Water Quality Classification System sets 100 μg/l as target value for zinc.

The distribution of monitoring sites according to the Classification System in the DRB for zinc is shown in **Fig. 8.1.3.44**:
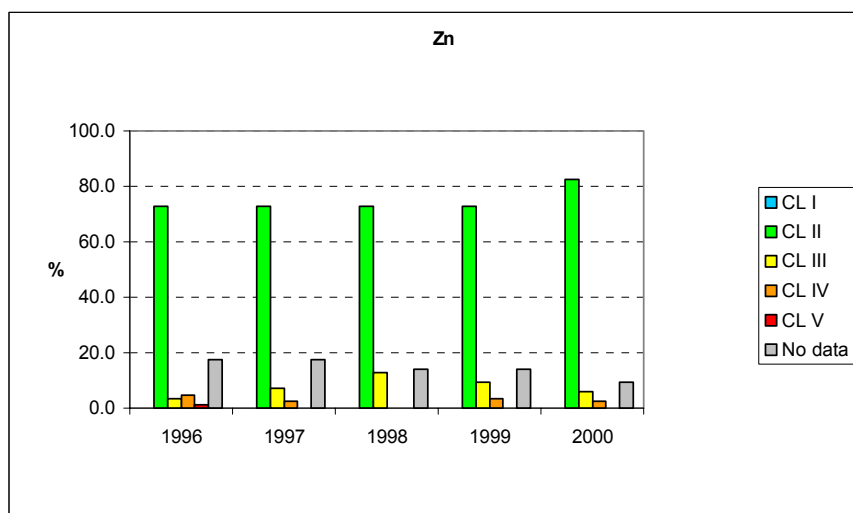
Fig. 8.1.3.44: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Zn**

Based on data reported from 85 monitoring sites (out of the assessment is 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:
-   a relatively positive distribution is present, with more than 70 % of the monitoring sites within Class II during 1996 – 1999 and more than 80 % in 2000;
-   Class III is represented by the maximum percentage in 1998 (12.9 %);
-   percentage of sites corresponding to Class IV and Class V is low, less than 10 %.

The spatial distribution of zinc concentrations along the Danube River is shown in **Fig. 8.1.3.45a** and **8.1.3.45b**.

In the upper section, zinc concentration has an uneven spatial distribution: at first two monitoring sites – Danube-Neu Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02) - excepting one value, this metal is undetectable, the limit of detection being here 10 μg/l. The rest of sites from this stretch are characterized by higher zinc concentrations, but no value is above the target limit.

In the middle stretch, the spatial distribution shows a maximum profile at Danube-Szob (km 1708 H03), where only one value exceeds the target limit. It has to be mentioned that at the cross sections from this stretch (SK02/H01 and SK03/H02), the Hungarian data shows higher concentrations. Downstream of Danube-Szob (H03) zinc content decreases, all c90 values are below 70 μg/l.

In the first part of the lower Danube, the spatial distribution presents a significantly higher values than in the middle stretch, with 11 values exceeding the target value. The maximum - 302.0 μg/l - appears at Danube-ds. Svishtov (km 554, BG03).

The second part of the lower Danube is also characterized by high zinc concentrations. At Danube-us. Arges (km 432, RO03) three values are more than two times higher than the target limit. For this part, the total number of zinc values above this limit is 14.

The spatial distribution for selected tributaries is shown in **Fig. 8.1.3.46a** and **8.1.3.46b**. Taking the target limit as a criterion for assessment the zinc concentration levels in tributaries, the following remarks can be done:
- in upper stretch, no c90 value is above the target value;
- in the middle stretch, above the target value are   concentrations characterising Tisza-Tiszasziget (H08) and Sajo-Sajopuspoki (H09);
- in the lower stretch, the Iskar-Orechovitza (BG06), Russenski Lom-Basarbovo (BG08), Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) are the tributaries with zinc content exceeding target value.

The temporal trends for zinc concentrations are shown in **Fig. 8.1.3.47** for the Danube River and in **Fig. 8.1.3.48** for selected tributaries:
- in the upper Danube, at the monitoring sites where zinc is detectable, the temporal profile shows that higher values are recorded in 1998 and/or 1999;
- in the middle Danube, an increasing is observed in Danube-Dunafoldvar (km 1560, H04) and Danube-Herceszanto (km 1435, H05); decreasing in Danube-Bratislava (km 1869, SK01), and Danube-Komarno/Komarom (km 1768, SK03);
- sites in the lower Danube are characteristic with rather high variability, but decrease can be observed in Danube-Chiciu/Silistra (km 375, RO04), Danube-Reni-Chilia/Kilia Arm (km 132, RO05) and taking into account high value in 1997, also in Danube-Sulina-Sulina Arm (km 0, RO07) temporal changes are going in a positive direction.
- tributaries from the upper Danube do not show significant temporal variations, only on Dyje-Pohansko (CZ02) a decreasing trend is visible;
- in the middle Danube, increasing tendency is observed in Sio-Szekszard-Palank (H06) and Drava-Ormoz (SL01) and decreasing tendency in the rest on monitoring sites on Drava River and in Sajo-Sajopuspoki (H09);
- for Romanian tributaries located in the lower Danube – the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) the general trend is decreasing, while for Iskar (BG06) and Russenski Lom (BG08) there is an increase in evaluated period.
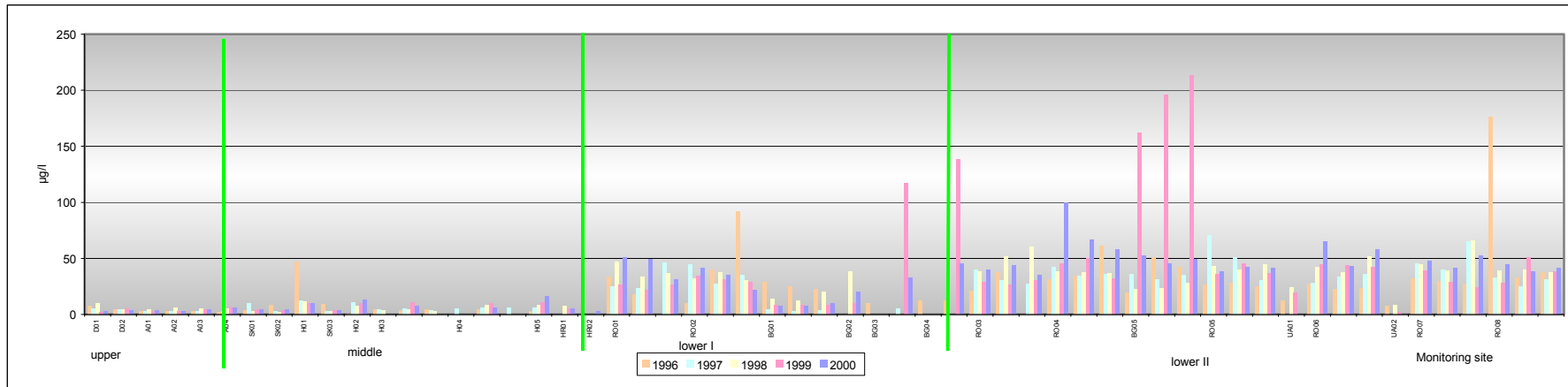
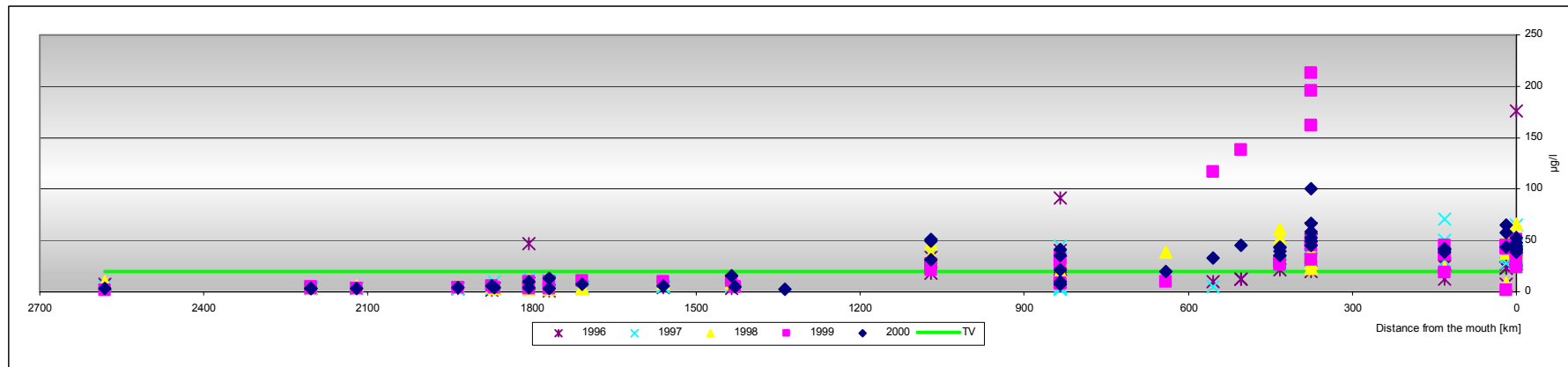Fig. 8.1.3.45a: Spatial variation of Zn – Danube River

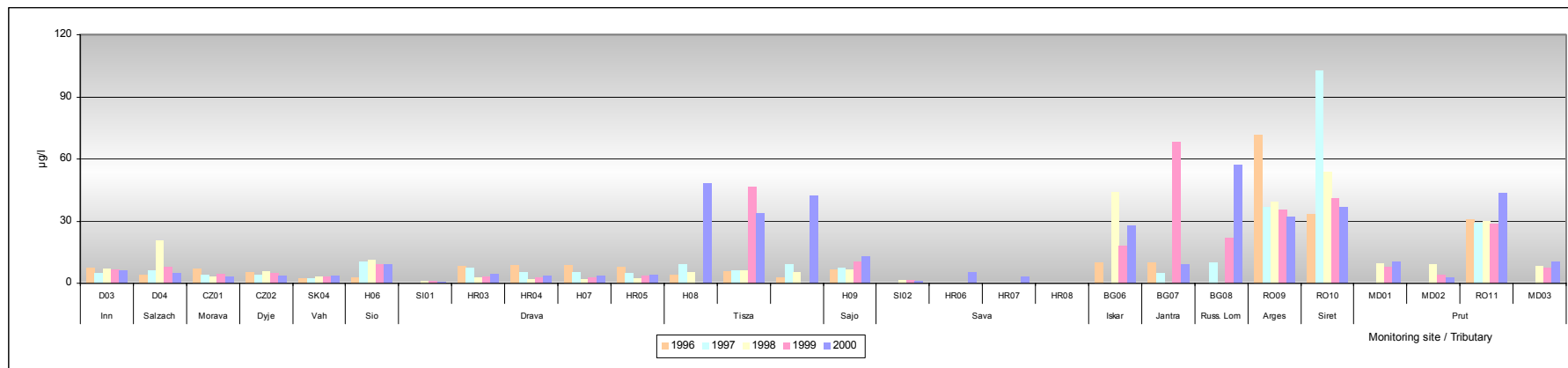Fig. 8.1.3.45b: Spatial variation of Zn – Danube River

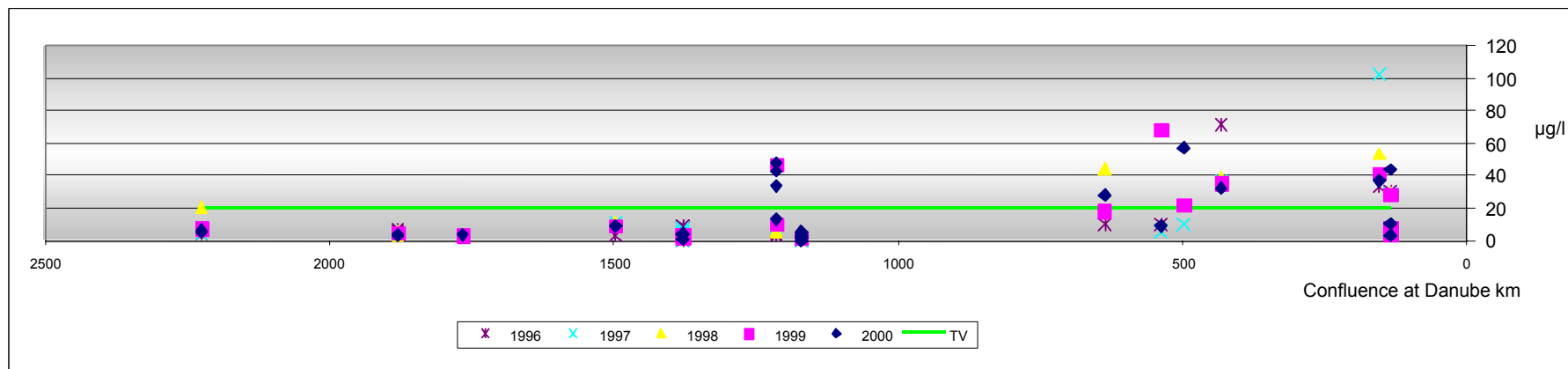Fig. 8.1.3.46a: Spatial variation of Zn – Tributaries

Fig. 8.1.3.46b: Spatial variation of Zn – Tributaries
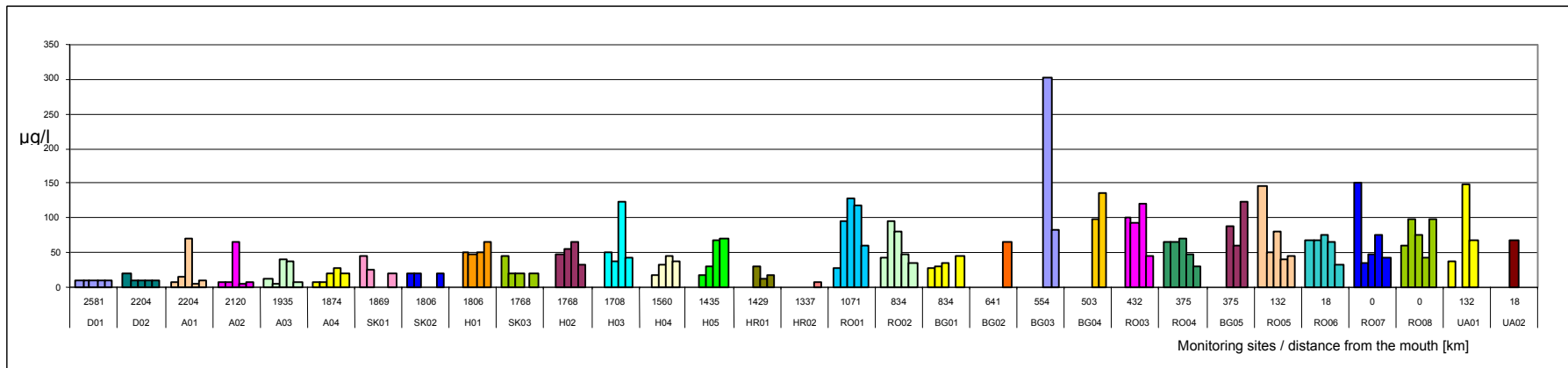
Fig. 8.1.3.47: Temporal trends of Zn – Danube River
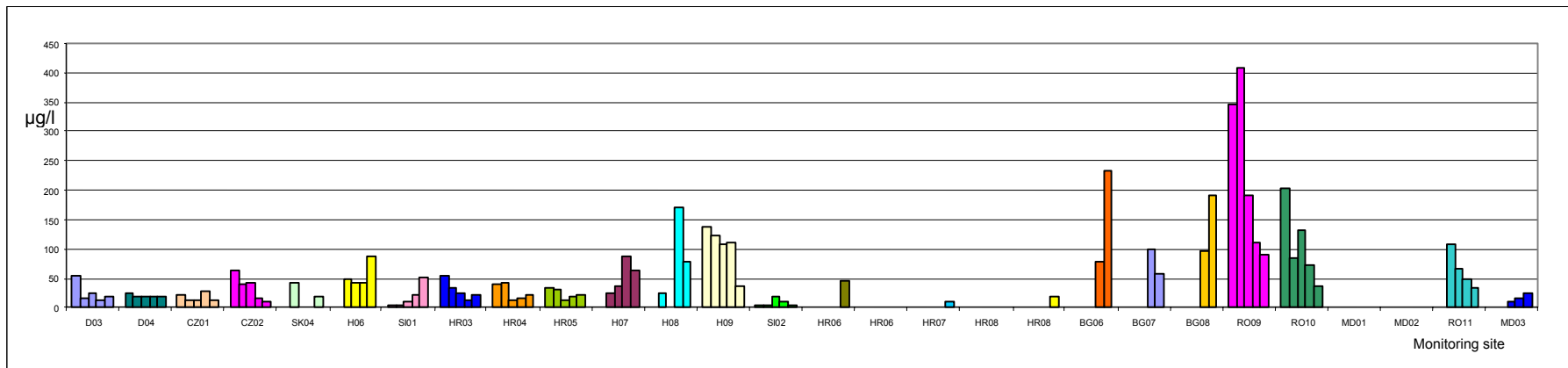
Fig. 8.1.3.48: Temporal trends of Zn – Tributaries

Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in filtered water samples (dissolved forms)

For heavy metals in the filtered water samples (dissolved forms), data are available from 1998 to 2000 only. The monitoring sites for which dissolved forms data are available are located in the upper and in the middle section of the Danube River, the same situation being valid also for the tributaries.

Based on existing data, the **Fig. 8.1.3.49** illustrates the percentage of monitoring sites, which exceed the target limits - for both dissolved and total forms, and for entire studied period (1996 – 2000).
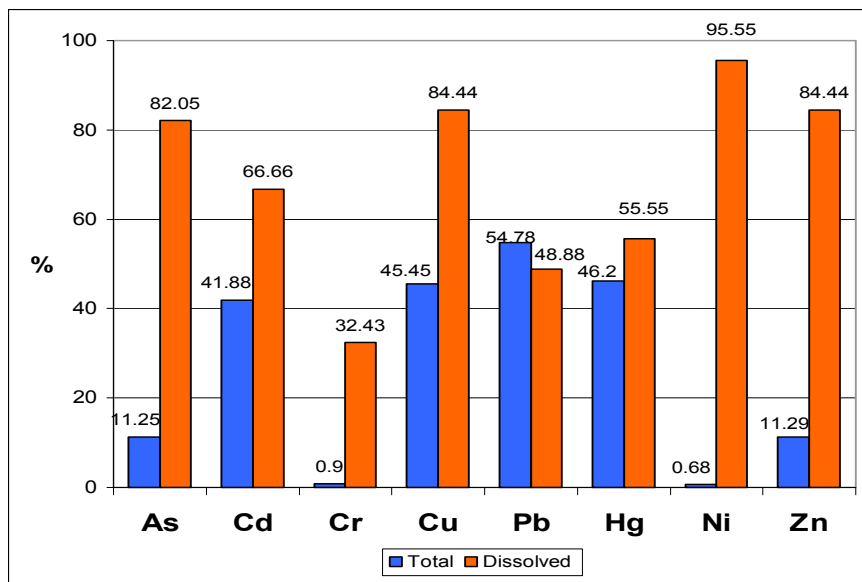
Fig. 8.1.3.49: Total percentage of monitoring sites exceeding target values in period 1996-00

As it can be seen from the figure above, the highest differences between percentages of exceedance based on analysis of total samples and dissolved fraction belong to nickel, chromium, arsenic and zinc, dissolved fractions having much higher percentage of exceedance.

As an overview on heavy metals concentration levels in the Danube River and its main tributaries, the Table 8.1.3.1 shows a comparison of TNMN data for several investigated heavy metals with literature data on river water background concentration, quality targets of other river monitoring networks and of those from water quality classification of MLIM Expert Group Proposal.

Table 8.1.3.1: Comparison of heavy metals concentration in the Danube River and its tributaries with various concentration levels (the concentration ranges are valid for total heavy metals forms)

Metal	Upper Danube	Middle Danube	Lower Danube	Tributaries	Background level [2]	Target Value [3] (diss.)	Target Value [4] (Total / diss.)
	Range concentration (min – max) µg/l				µg/l		
As	1.00 – 3.27	0.10 – 4.84	0.30 – 11.02	1.00 – 79.36	-	?	5 / 1
Cd	0.10 – 0.66	0.02 – 2.25	0.14 – 29.10	0.02 – 24.18	0.009 – 0.036	0.072	1 / 0.1
Cr	1.00 – 5.00	0.43 – 20.17	5.00 – 97.00	0.10 – 41.00	1.3 – 5.0	3.1	50 / 2

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[2] LAWA Guide
[3] Joint Danube Survey – Technical Report, 2002
[4] MLIM Expert Group Proposal on Water Quality Classification in Danube River Basin

Metal	Upper Danube	Middle Danube	Lower Danube	Tributaries	Background level [2]	Target Value [3] (diss.)	Target Value [4] (Total / diss.)
	Range concentration (min – max) µg/l				µg/l		
Cu	2.00 – 10.20	0.73 – 46.98	2.00 – 213.1	0.02 – 102.5	0.5 – 2.0	3	20 / 2
Pb	1.00 – 4.70	0.55 – 17.45	1.00 – 82.00	0.05 – 91.00	0.4 – 1.7	3.4	5 / 1
Hg	0.10 – 0.42	0.03 – 0.82	-	0.08 – 1.54	0.005 – 0.020	0.04	0.1 / 0.1
Ni	1.00 – 5.40	0.39 – 16.21	0.05 – 42.90	0.05 – 79.00	0.6 – 2.2	1.8	50 / 1
Zn	3.90 – 69.00	9.05 – 122.9	18.0 – 288.0	4.0 – 409.0	1.8 – 7.0	7	100 / 5

8.1.4.   Oxygen Regime

The natural organic matter occurring in water originates mainly from soil erosion and decomposition of dead plants and animals; it is relatively insoluble and slowly decomposed. Organic matter evolved from various human activities represent one of the most important pollutants discharged into a rivers; it is generally soluble and rapidly divided and decomposed. Since the decomposition of this matter is carried out by microorganisms and requires consumption of oxygen, the assessment of oxygen regime indicators is of a major importance. Hence, the variation of dissolved oxygen in terms of concentration (DO), biochemical oxygen demand (BOD_5) and chemical oxygen demand – both COD-Mn and COD-Cr was taken into account:

Dissolved oxygen

The actual amount of oxygen present is an important water quality parameter. As a general rule, the less of oxygen dissolved in water the worse is the water quality. Therefore, for oxygen low values, described in this report by 10 %-iles, have to be examined. In general the concentration of dissolved oxygen shows strong daily and seasonal variation. Monitoring results are therefore very much dependent on the time of sampling. In periods of high primary production and algae growth concentration may fluctuate for several milligrams per litre.

The distribution of monitoring sites according to the Classification System in the DRB for dissolved oxygen is shown in **Fig. 8.1.4.1**:
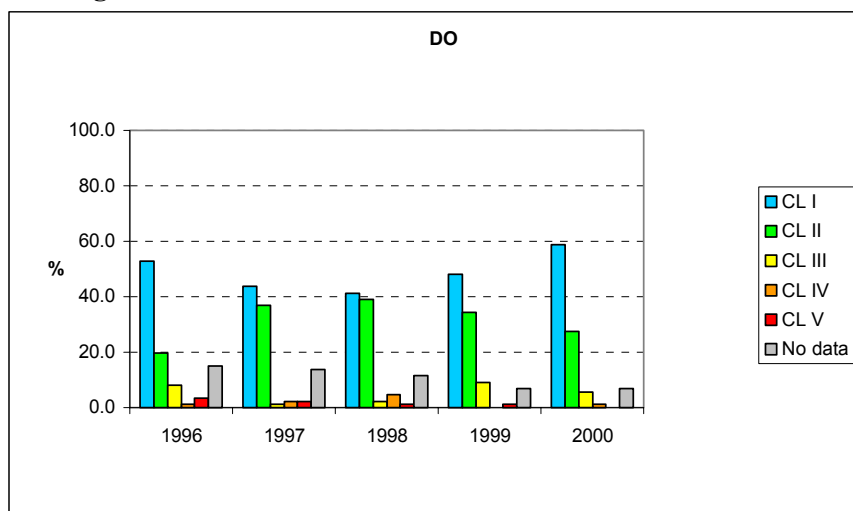
Fig. 8.1.4.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **DO**

The quality assessment within the five-class system is made on the basis of data reported from 87 monitoring sites (out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000) and the following remarks can be done in this respect:

- the number of monitoring sites within Class I decreases from 1996 to 1998 and then increases until 2000; values above 50% are present in 1996 and 2000 only;
- the monitoring sites within Class II show a maximum percentage in 1998 (when the percentage for Class I is minimum);
- the number within Class III is below 10% in all five years;
- Class IV does not appear in 1997; for the other years, all values are below 5% of the monitoring sites;
- the number of sites within Class V decreases continuously from 1996 to 1999, in 2000 being totally absent, which demonstrates the improving in water quality from the DO point of view;

The spatial pattern of dissolved oxygen concentrations for the Danube River is shown in **Fig, 8.1.4.2a** and **8.1.4.2.b**.

In the upper section, dissolved oxygen values increase from Danube-Neu Ulm (km 2581, D01) to Danube-Wien-Nussdorf (km 1935, A03). In this stretch, all concentrations are above 8.5 mg/l and no value is below the target limit for oxygen (6 mg/l).

In the middle stretch, oxygen concentrations are slightly lower then that from the upper one, but a uniform pattern is present along this stretch. The apparent "V" profile with minimum located at Danube-Medve/Medvedov (km 1806, H01) is caused by the lower Hungarian data in comparison with Slovak data in this cross section. It has to be mentioned that along this stretch no value is below the target limit.

In the first part of the lower section, oxygen c10 values clearly decrease from Danube-Bazias (km 1071, RO01) to Danube-Novo Selo/Pristol (km 834, BG01) by more than 2 mg/l, varying in the range 4.45 – 7.10 mg/l O_2; this situation can be mainly attributable to the Iron Gate Reservoir influence. From Danube- us. Iskar (km 641, BG02) to Danube-us. Russe (km 503, BG04), the dissolved oxygen regime is better, even if due to the lack of some data it is not possible to give a comprehensive picture.

The second part of the lower Danube shows a uniform spatial pattern of dissolved oxygen, the values vary within the range 5.72 – 8.80 mg/l O_2.
For the entire lower Danube, 19 values were below the target limit, with minimums in Danube-Novo Selo/Pristol (km 834, BG01); but especially in 1997-1998 there are remarkable differences in the results reported by Bulgaria and Romania in this river profile (BG01 and RO02) (see Fig. 8.1.4.2a).

The spatial distribution of dissolved oxygen concentrations in selected tributaries is illustrated in **Fig. 8.1.4.3a** and **8.1.4.3b**. It can be mentioned that oxygen content generally decreases, from those located in the upper to those from the lower part. For example, two tributaries from the upper Danube, the Inn-Kirchdorf (D03) and Salzach-Laufen (D04), have a dissolved oxygen concentration ranging between 9.9 – 10.5 mg/l O_2, while for a tributary located in the lower Danube, the Arges-Conf. Danube (RO09), this range is 2.50 – 6.20 mg/l O_2. Similarly, on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giugiulesti (RO11), rather low values are recorded (2.95 and 2.06 mg/l O_2, respectively).

As concerning the tributaries located in the middle section, the oxygen content is generally lower than in the Danube itself, the minimum values are recorded on the Sio-Szekszard-Palank (H06) and Sava-ds. Zupanja (HR08) – 5.13 and 5.52 mg/l O_2, respectively.

From selected tributaries, 11 values of dissolved oxygen are below the target limit most of them being in the lower Danube - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giugiulesti (RO11).

Regarding yearly variations of oxygen it can be concluded, that they do not exceed 1 mg/l at many monitoring sites. In particular the sites at the Danube River remain rather constant. As to the tributaries, Arges (RO09) and Siret (RO10) show the biggest differences between the years.

The temporal trends are illustrated in **Fig. 8.1.4.4** for the Danube River and in **Fig. 8.1.4.5** for selected tributaries. The following trends are visible:

- increasing tendencies were observed in Danube-Neu-Ulm (D01), Danube-Jochenstein (km 2204, D02), Danube-us. Arges (km 432, RO03), Danube-Chiciu/Silistra (km 375, RO04) and Danube-us. Iskar-Bajkal (km 641, BG02);
- slight decreasing tendencies are in Danube-Borovo (km 1337, HR02) and Danube-Pristol/Novo Selo (km 834, RO02);
- the different tendencies at the cross sections at km 834 (RO02/BG01) and km 375 (RO04/BG05) has to be mentioned, the reason of which could be a lower frequencies of measurements in Bulgaria;
- in selected tributaries increasing tendencies were observed in Iskar-Orechovitza (BG06), Arges-Conf. Danube (RO09) and Siret-Conf. Danube Sendreni (RO10).

Fig. 8.1.4.2a: Spatial variation of DO – Danube River

Fig. 8.1.4.2b: Spatial variation of DO – Danube River
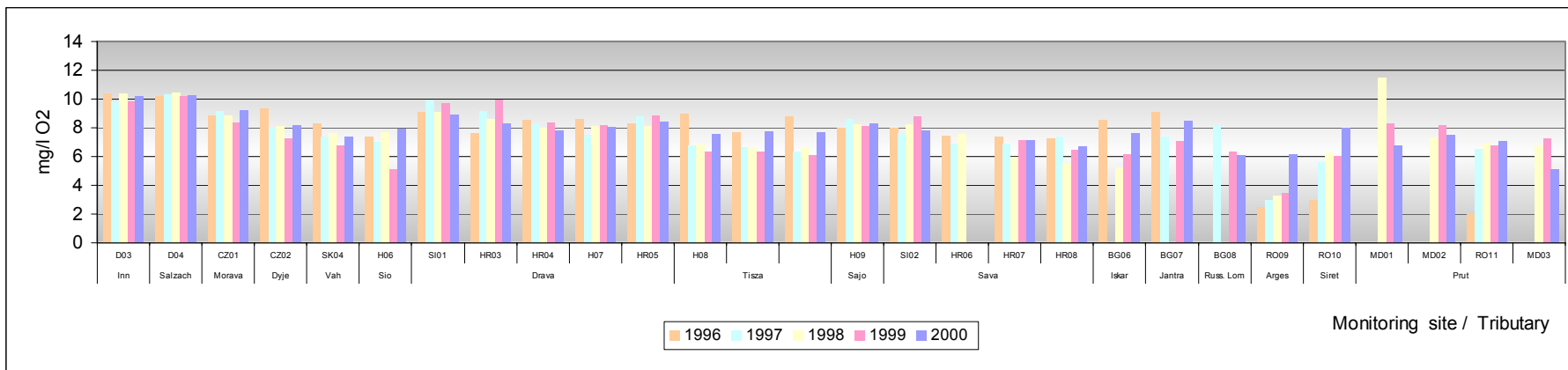
Fig. 8.1.4.3a: Spatial variation of DO – Tributaries
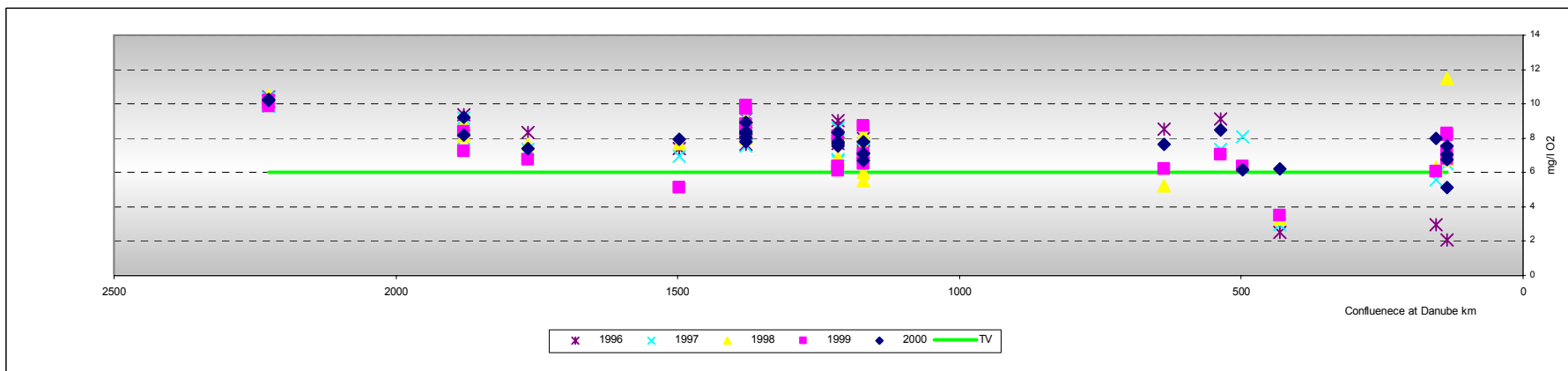
Fig. 8.1.4.3b: Spatial variation of DO – Tributaries
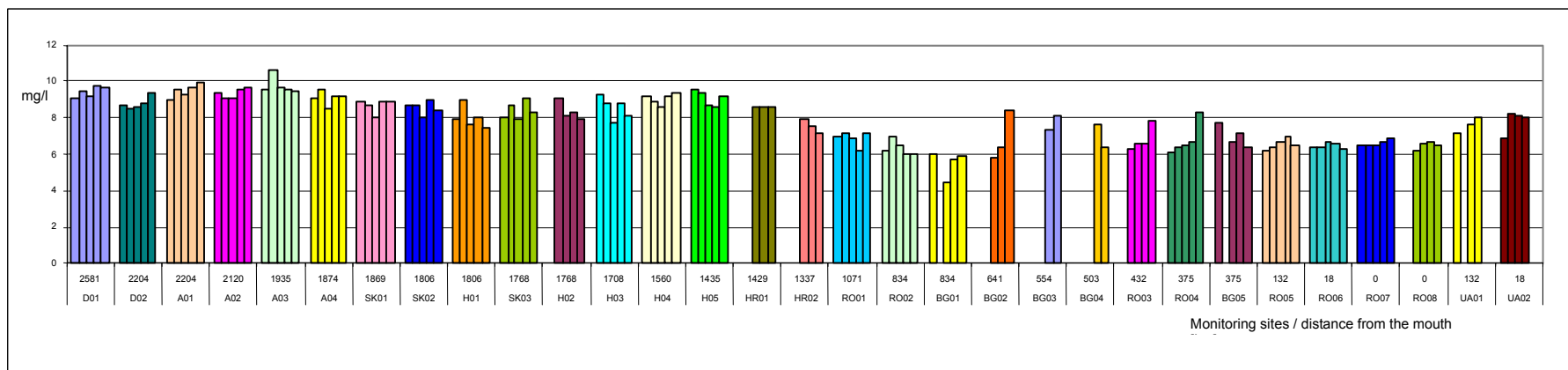
Fig. 8.1.4.4: Temporal trends of DO – Danube River
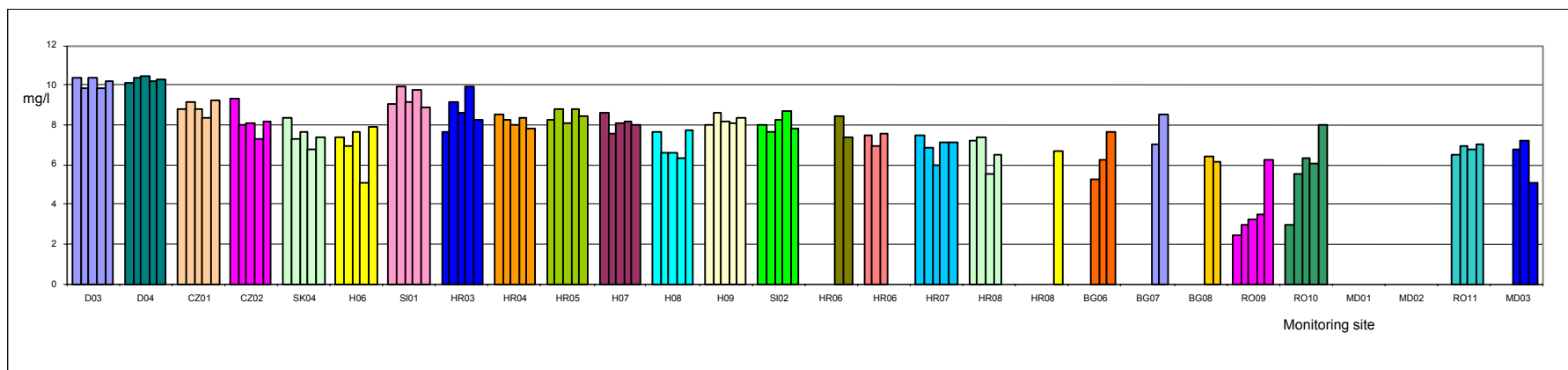
Fig. 8.1.4.5: Temporal trends of DO – Tributaries

In order to have a more comprehensive picture of the dissolved oxygen distribution along the Danube River within the five years time period (1996-2000), beside 10 percentiles both maximum and minimum concentration values were represented for each studied year, separately for the Danube River itself and selected tributaries - **Fig. 8.1.4.6 – 8.1.4.15.**

Table 8.1.4.1.summarizes some relevant data related to oxygen content distribution along the Danube and its tributaries:

Table 8.1.4.1: Ranges of maximum and minimum values for dissolved oxygen concentrations

Year	Range of maximum values (mg/l O_2)		Range of minimum values (mg/l O_2)	
	Danube	**Tributaries**	**Danube**	**Tributaries**
1996	8.6 – 16.0	9.1 – 29.5	4.8 – 9.6	2.4 – 10.4
1997	8.3 – 18.3	8.1 – 15.2	3.9 – 9.4	2.3 – 9.9
1998	10.3 – 15.6	8.5 – 17.4	4.3 – 9.2	3.0 – 11.4
1999	8.8 – 15.3	6.4 – 15.3	4.5 – 9.5	2.9 – 9.8
2000	8.5 – 15.6	6.1 – 15.9	4.3 – 9.8	3.7 – 9.9

Based on the above mentioned figures and table, the following remarks can be done:
- apart from the extreme values, a relative constancy among the studied years for both minimum and maximum dissolved oxygen ranges is illustrated;
- a closer look should be given to the "top" of the maximum recorded values as well as to the "bottom" of the minimum ones.
  - o the maximum-recorded value for the Danube River itself (18.3 mg/l O_2) appears in 1997, at Danube-Dunafoldvar (km 1560, H04);
  - o the maximum-recorded value for tributaries (29.5 mg/l O_2) is present in 1996 on the Sio-Szekszard (H06). Other related data - pH = 8.72, BOD_5 = 9.5 mg/l O_2, $N-NH_4$ = 1.30 mg/l, $N-NO_3$ = 9.54 mg/l (*TNMN Data Base 1996 - 2000*) - indicate strong pollution by nutrients, allowing excessive growth of primary producers producing an oxygen. Also data obtained in the frame of JDS (*Joint Danube Survey – 2001*) indicated a high value of oxygen content for the Sio-Szekszard (H06) tributary – 18.9 mg/l O_2;
  - o the minimum dissolved oxygen concentration on the Danube River (3.9 mg/l O_2) is present in 1997, at Danube-Novo Selo/Pristol (km 834, BG01), but is not in harmony with the observations from Romanian side at the same cross section (6.4 mg/l O_2);
  - o the minimum dissolved oxygen concentration for selected tributaries (2.3 mg/l O_2) appears in 1997 and, as well as the most of the minimum recorded values, is specific to the Arges-Conf. Danube. This critical problem is mainly caused by the fact that this tributary regularly serves as recipient of untreated and not adequately treated waste water and its low dilution regime (discharge flows ranging within the range 34.9 – 102.0 m^3/s) cannot compensate these pollution inputs;
- some differentiations can be made among the oxygen contents in the studied years:
  - o *1996,* as the first year of TNMN monitoring Programme, is characterized by a scattered profile of both minimum and maximum oxygen concentrations; apart from the above discussed value of 29.5 mg/l O_2, the maximum level of 16.0 mg/l O_2 is met at several monitoring point located on the main course of the Danube and on tributaries: Danube-Medvedov/Medve (km 1806, SK02) even if it doesn't make a good correlation with the cross reported data (12.2 mg/l O_2 at H01), further in Danube-Szob (km 1708, H03), Danube-Hercegszanto (km 1435, H05) and on the alpine tributary, Drava-Dravaszabolcs (H07);

o *1997*: as it was already mentioned, the maximum recorded value appears at Danube-Dunafoldvar (km 1560, H04); the minimum values profile of the Danube is spatially uniform;

o *1998*: the maximum value (17.4 mg/l O_2) is recorded on the Sio-Szekszard -Palank (H06), but the other maximum concentrations do not exceed 16.0 mg/l O_2. Excepting one already mentioned value, all minimum ones are above 4.0 mg/l O_2;

o *1999* and *2000* present a uniform spatial distribution of maximum and minimum concentration values, ranging between 4.0 and 16.0 mg/l O_2, only one value being outside of this interval.

Fig. 8.1.4.6 – 8.1.4.15: Minimum, maximum and 10%-iles values for Dissolved Oxygen (Danube River and Tributaries)

1997

1997
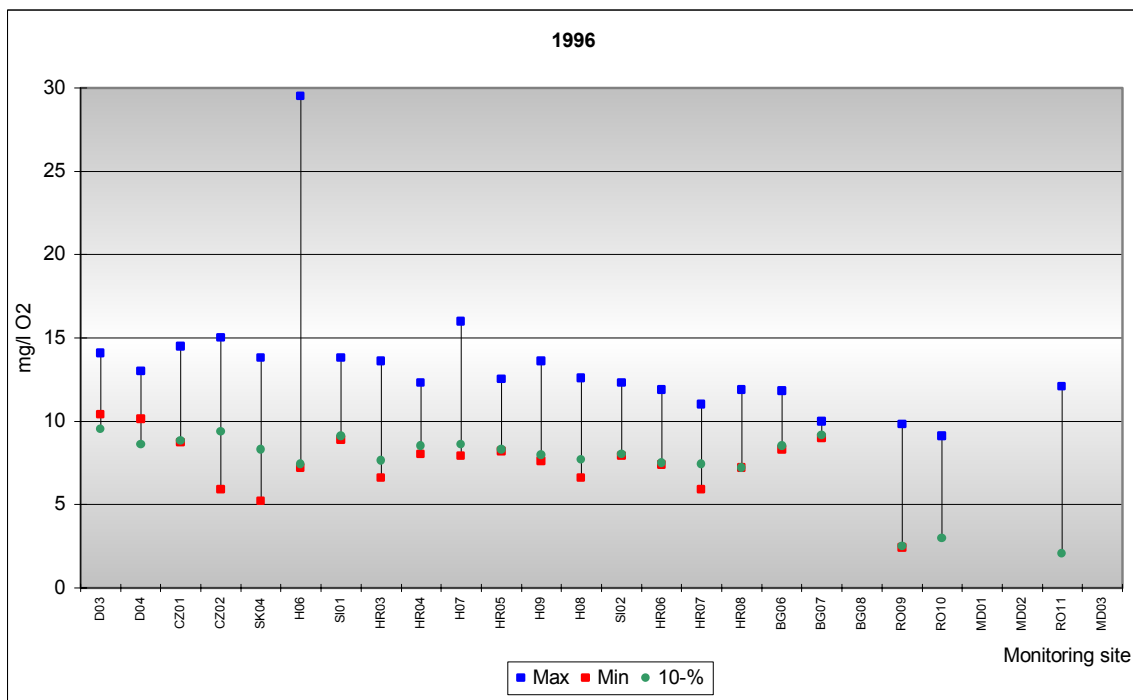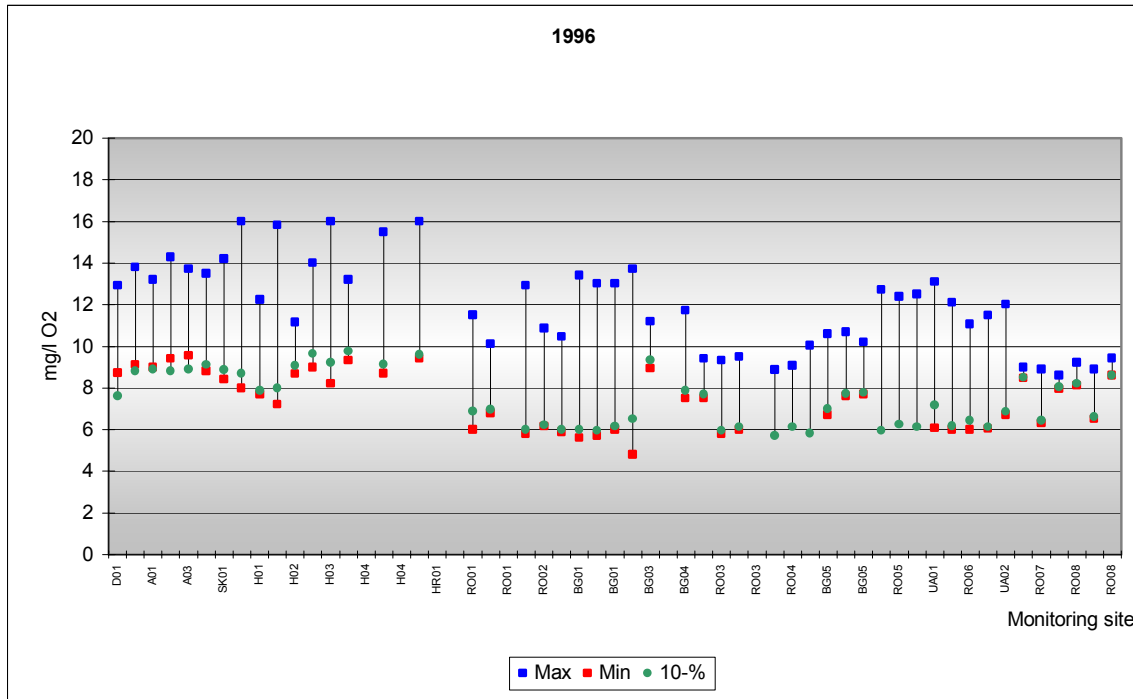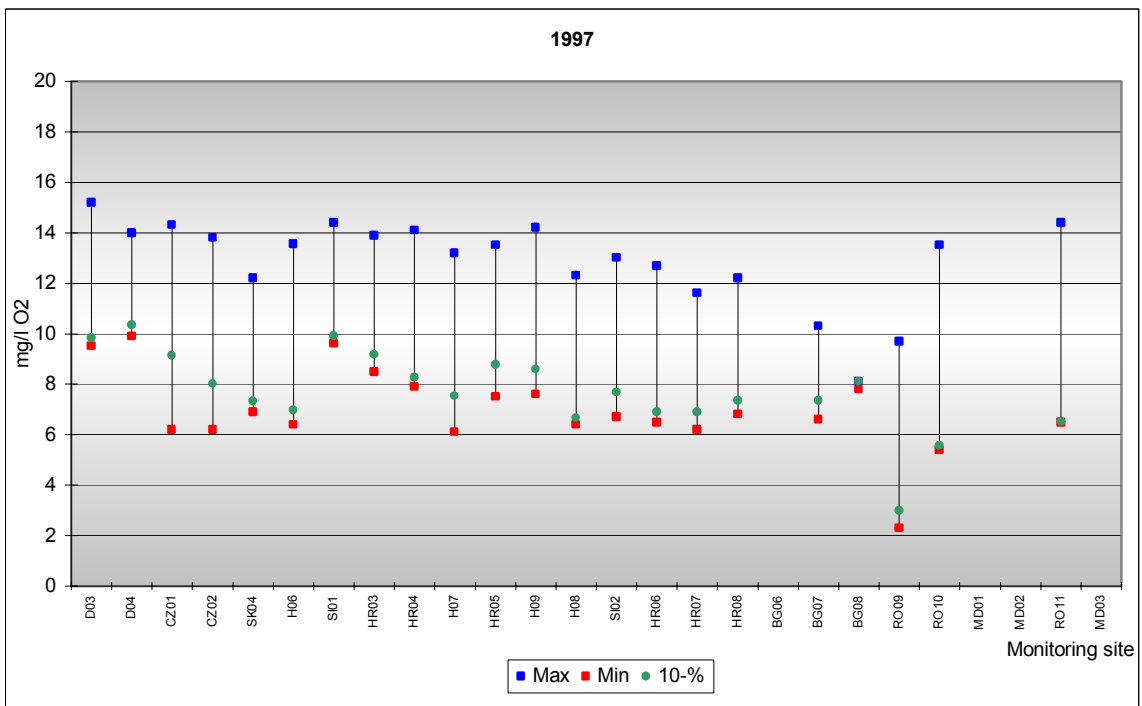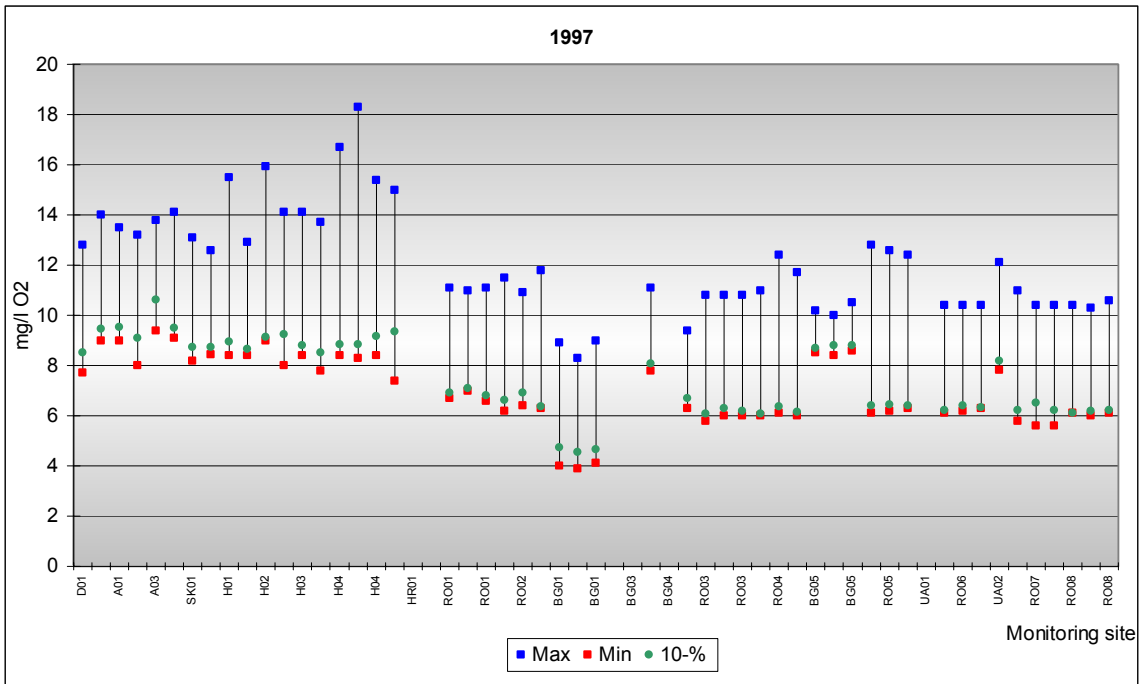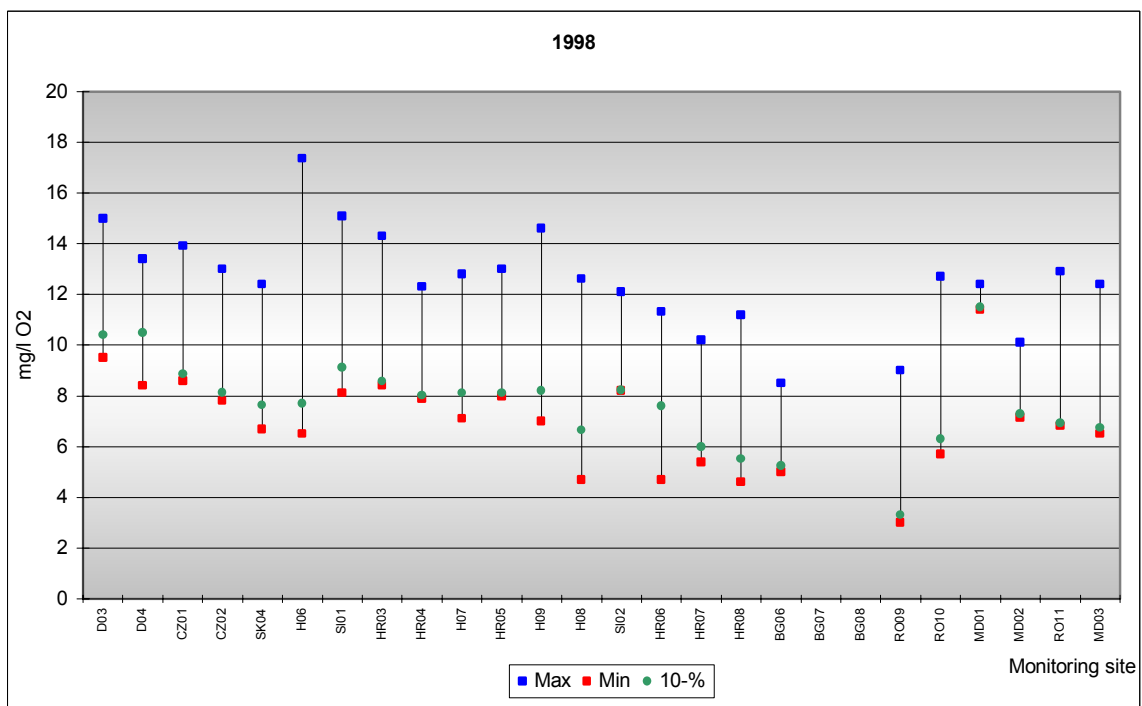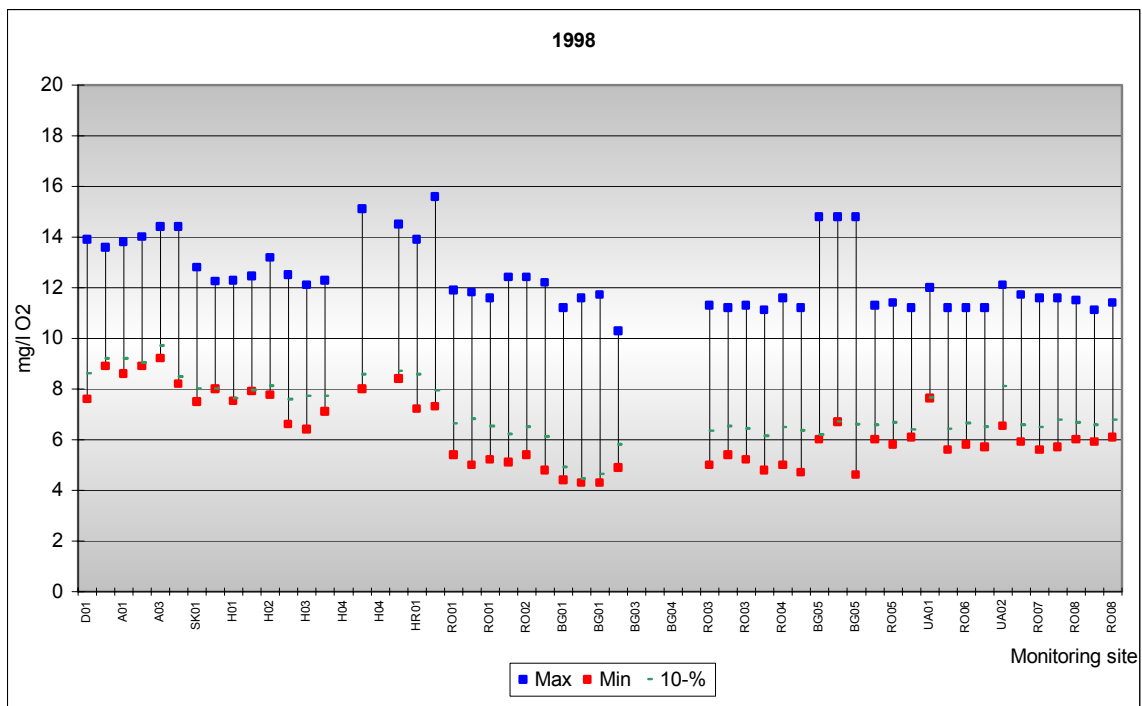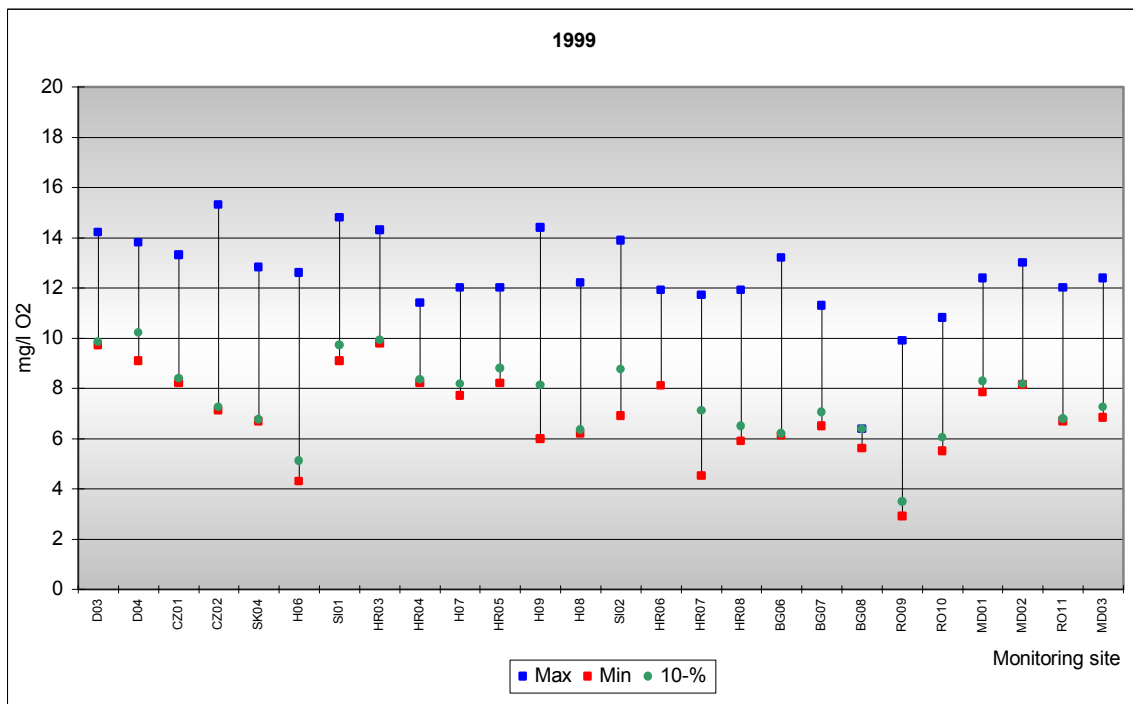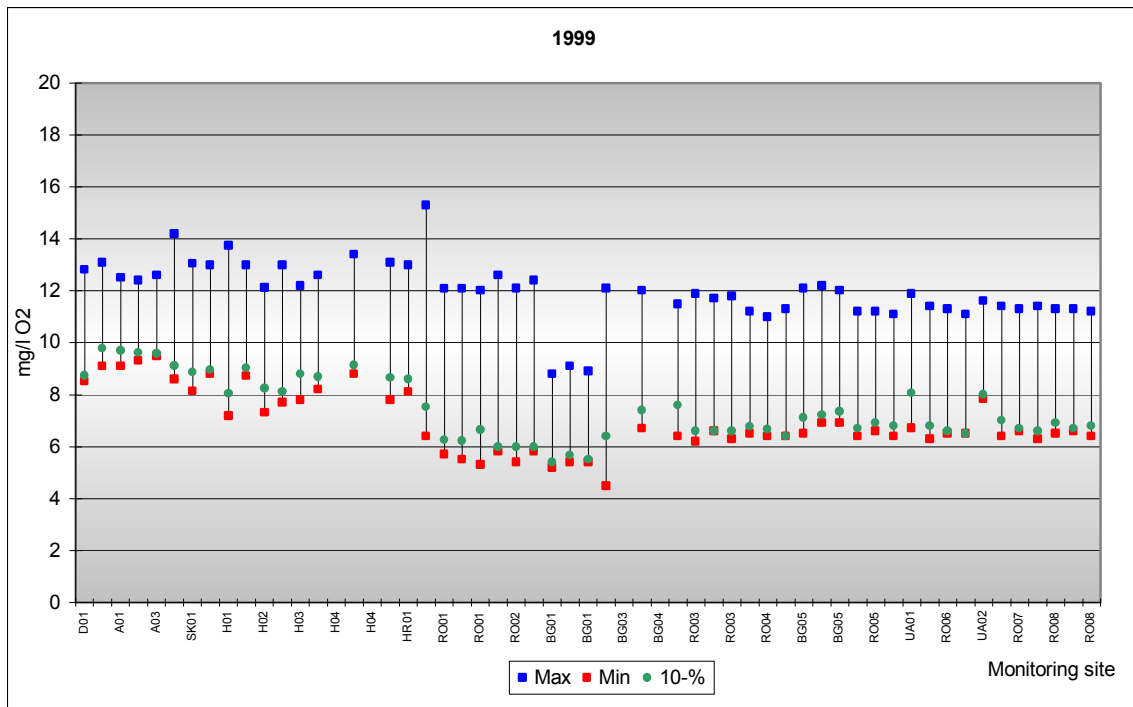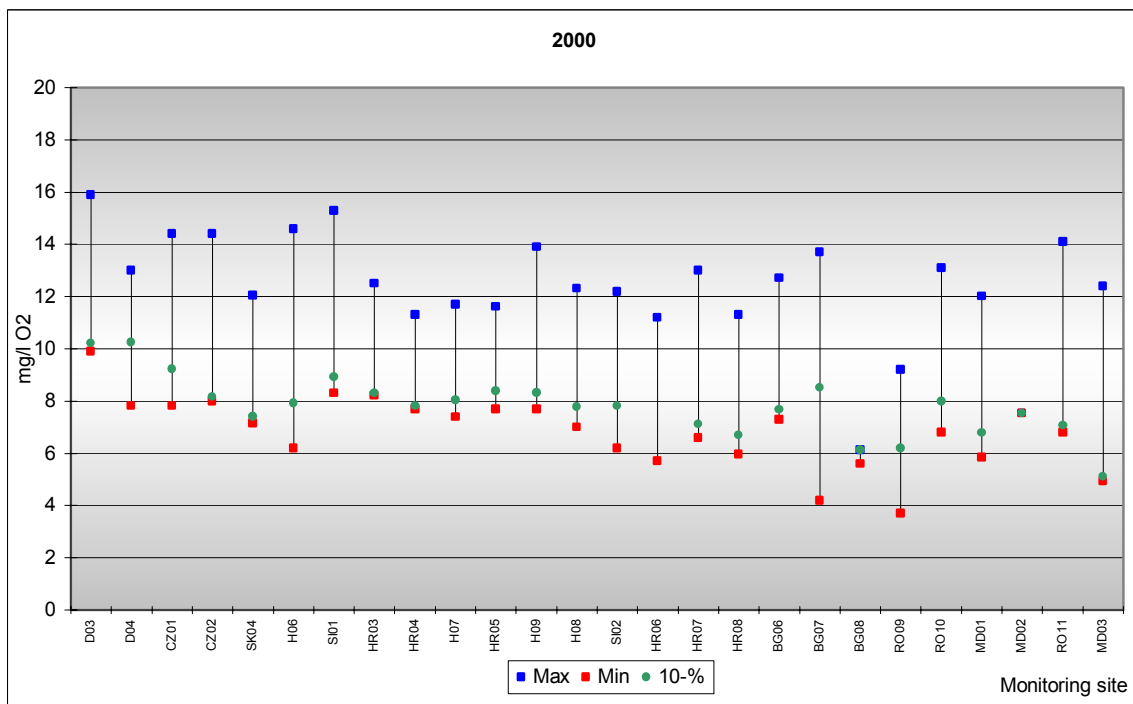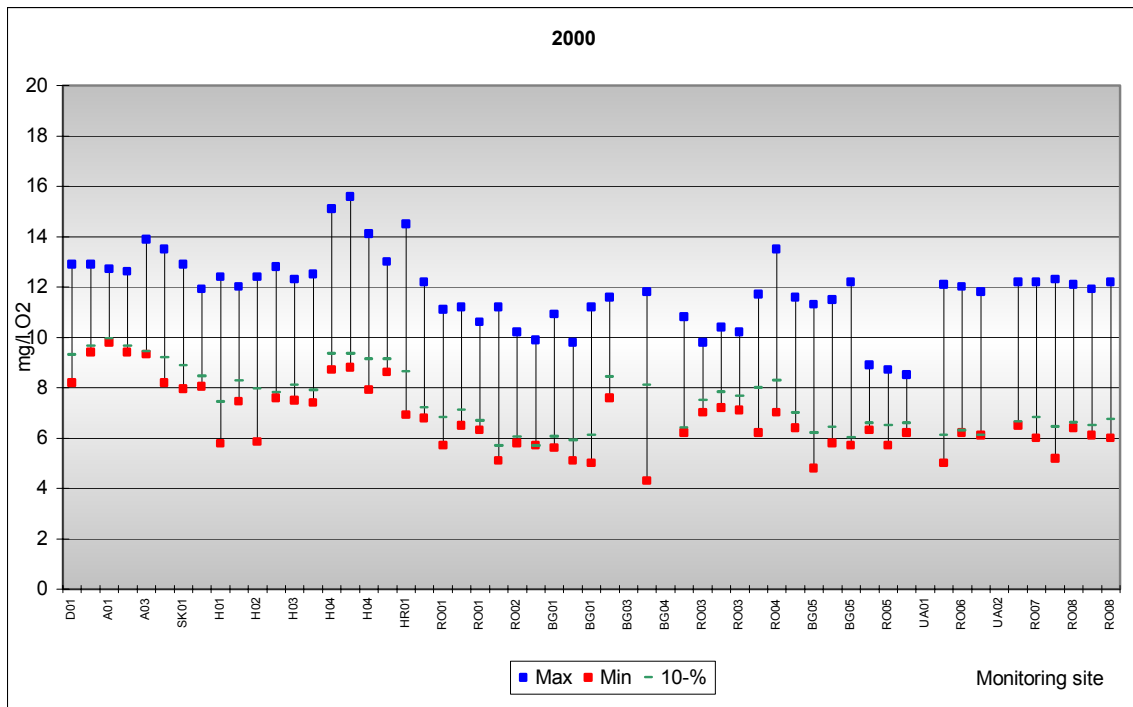
Biochemical and Chemical Oxygen Demand

Because microorganisms mediate the composition of organic matter and it is an oxygen consuming process, the amount of organic matter in a water body is measured in terms of biochemical and chemical oxygen demand. Thus, in order to evaluate the temporal variation of organic matter content in the longitudinal profile of the Danube River and in its selected tributaries, BOD_5, COD-Mn and COD-Cr are the determinands that were taken into account in this respect.

Biochemical Oxygen Demand (BOD_5)

The distribution of monitoring sites according to the Classification System in the DRB for **BOD_5** is shown in **Fig. 8.1.4.16**:
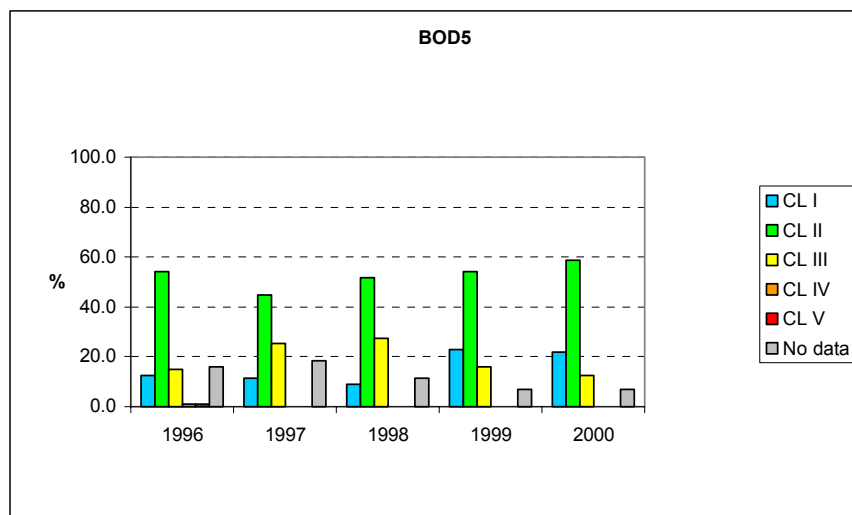
Fig. 8.1.4.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **BOD_5**

The assessment is made based on data reported from 87 monitoring sites (out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):
-   the percentage of monitoring sites within Class I is below 25% during the entire time period;
-   the maximum percentages belong to Class II and the values within this quality class increase from 44.8 % in 1997 to 58.6 % in 2000;
-   the number of sites within Class III increases from 1996 to 1998 up to 27.6 % and decrease until 2000 down to 12.6 %;
-   Class IV and V are present in 1996, at 1.1 % of all monitoring sites only.

The spatial variation of BOD_5 values for the Danube River is illustrated in **Fig. 8.1.4.17a** and **8.1.4.17b**.

In the upper section of the Danube, BOD_5 values increase from Danube- Neu-Ulm (km 2581, D01) to Danube-Wolfsthal (km 1874, A04), excepting the monitoring site located at Danube-Wien –Nussdorf (km 1935, A03). It has to be mentioned that in the upper Danube two values are below 2 mg/l O_2, indicating no human activities impact (*The Dobris Assessment, 1991),* but two values are above the target limit for BOD_5.

In the middle stretch, a relative constancy (2.0 – 4.6 mg/l O_2) is visible from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03). In this point - the confluence with the Ipoly tributary – values are within the interval 4.4 – 5.6 mg/l O_2. The spatial increasing pattern is valid also down to

Danube-Hercegszanto (km 1435, H05), where BOD_5 reaches 8.2 mg/l O_2, the maximum obtained value for the Danube River. For the middle stretch, 15 BOD_5 values are above the target limit, mainly located in the stretch from Danube-Szob (km 1708, H03) to Danube-Borovo (km 1337, HR02).

Longitudinal assessment in the first part of the lower Danube shows a different spatial variation of BOD_5 values, it depends on the cross section data at which the reference is made to: a uniform spatial profile if the Danube-Pristol/Novo Selo (km 834, RO02) data are taken into account and a spatial decreasing if the Danube- Novo Selo/Pristol (km 834, BG01) data are considered. (Actually, the differences between the data reported in 1997 are serious: from 6.1 mg/l O_2 in RO02 to 2.1 mg/l O_2 in BG01). Even if the interpretation is quite problematic, it can be estimated that a uniform level is valid for this stretch.

The second part presents a uniform spatial pattern from Danube-us. Arges (km 432, RO03) and the three arms of the delta, with BOD_5 values within the range 1.8 – 5.5 mg/l O_2.

Generally can be said that along the Danube the organic pollution expressed by BOD increases, reaching maximum values in the section from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm834, RO02). Here is also the highest frequency of exceedance of target value recorded in 5-years evaluation period. In addition, in this section there is the highest year-to-year variability of values, reaching in some cases even more than 3 mg/l.

For selected tributaries, the BOD_5 values are illustrated in **Fig. 8.1.4.18a** and **8.1.4.18b**. The following remarks can be done:
- even if in the upper and in the middle Danube, the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02) and Sio-Szekszard (H06) have values above the target limit, the general spatial pattern of BOD_5 values is decreasing down to Tisza tributary, with no big differences between the tributaries and the Danube itself;
- in the lower section, BOD_5 values are slightly higher for the right side tributaries - the Iskar-Orechovitza (BG06), Jantra-Karantzi (BG07) and Russenski Lom-Basarbovo (BG08), but the most critical problem occurs on the Arges-Conf. Danube (RO09), where an extreme value (60.5 mg/l O_2) is recorded in 1996;
- for all selected tributaries, 46 BOD_5 values exceed the target limit; most likely, the main reason for this exceeding is existence of significant point sources of pollution in some cases in combination with low flows.

The temporal trends of BOD_5 are illustrated in **Fig. 8.1.4.19** for the Danube River and in **Fig. 8.1.4.20** for tributaries. Several different trends can be noticed:
- decreasing from 1997 or 1998 to 2000 from Danube-Neu Ulm (km 2581, D01) to Danube-Abwinden-Asten (km 2120, A02), at the cross sections Danube-Medve/Medvedov/Medve (km 1806, SK02/H01) and Danube-Komarom/Komarno/Komarom (km 1768, SK03/H02), from Danube-Borovo (km 1337, HR02) to Danube-Bazias (km 1071, RO01), in Danube-Reni/Chilia arm/Kilia arm (km 132, RO05), Danube-Vilkov/Kilia arm/Chilia arm (km 18, UA02);
- increasing from 1996 to 1997 or 1998 followed by a decreasing until 2000 at Danube-Dunafoldvar (km 1560, H04), Danube-Hercegszanto (km 1435, H05) and from Danube-Chiciu/Silistra (RO04) to Danube-Sulina/Sulina arm (km 0, RO07);
- regarding tributaries, a decreasing trend for BOD_5 can be observed in Inn (D03), Salzach (D04), Dyje (CZ02), Vah (SK04) Drava (HR03, HR04,HR05, H07) and Arges (RO09), whilst the sites at Tisza River (H08) ad its tributary Sajo (H09) show a reverse behaviour.
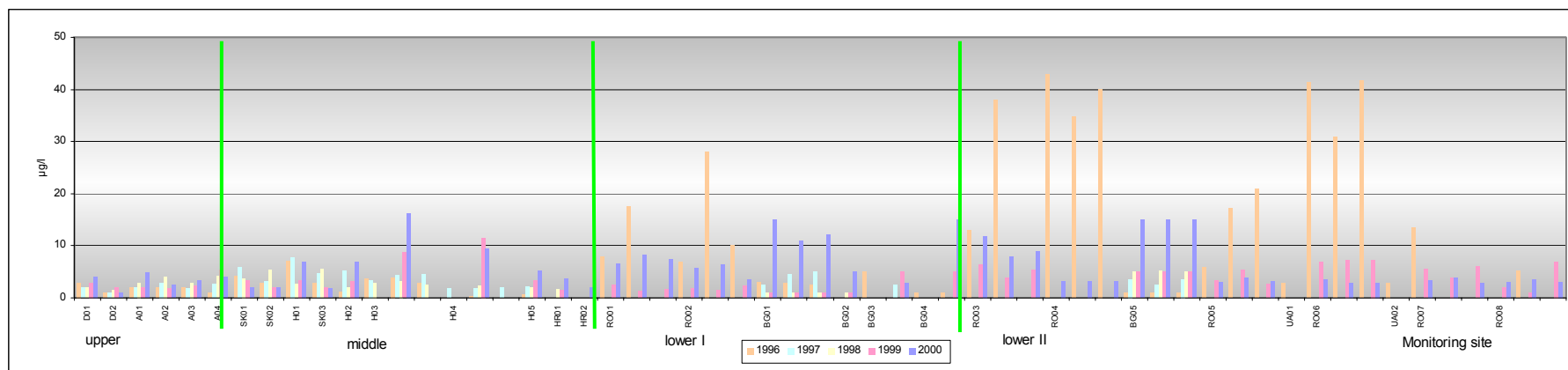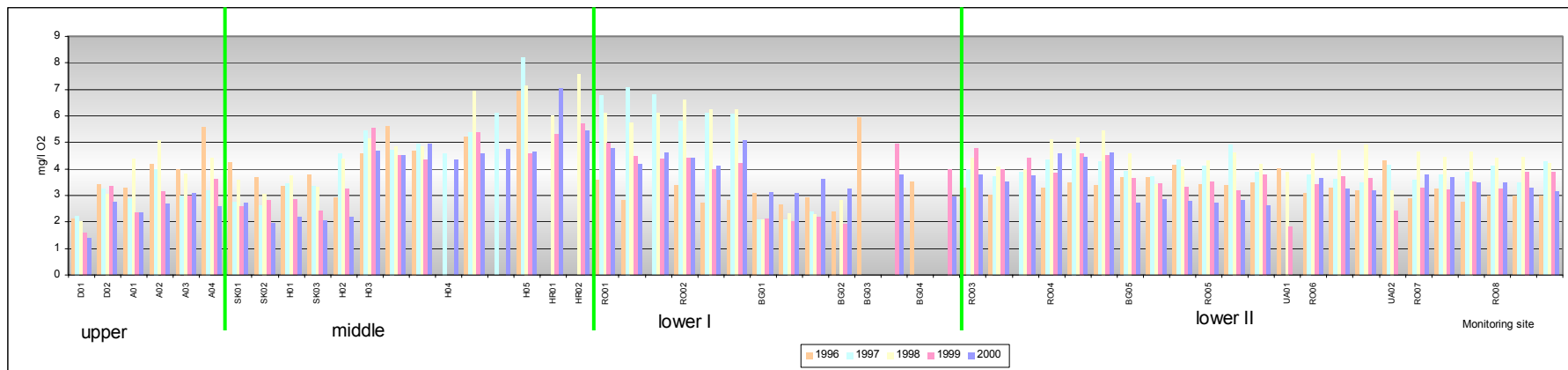
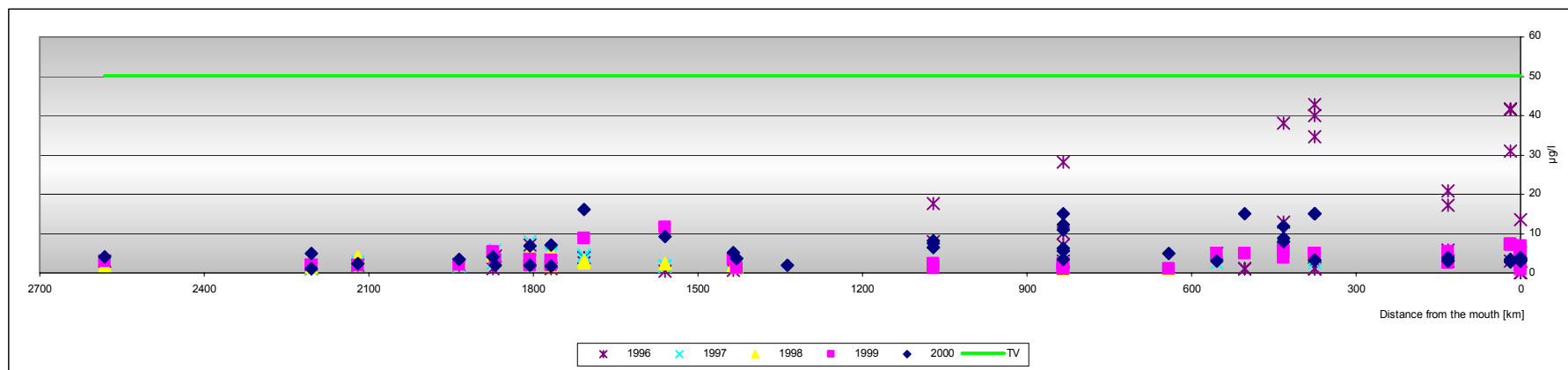Fig. 8.1.4.17a: Spatial variation of BOD$_5$ – Danube River
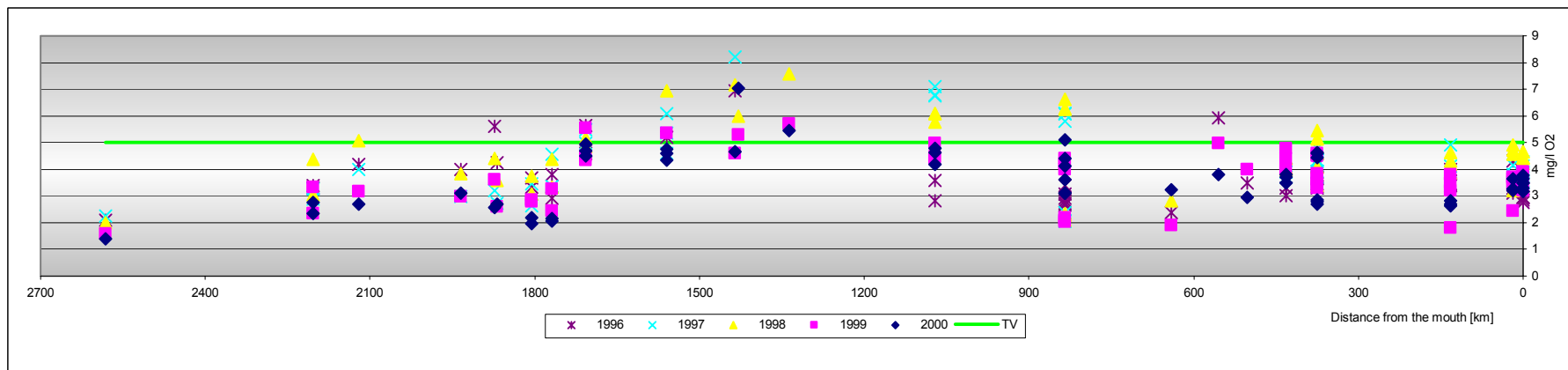
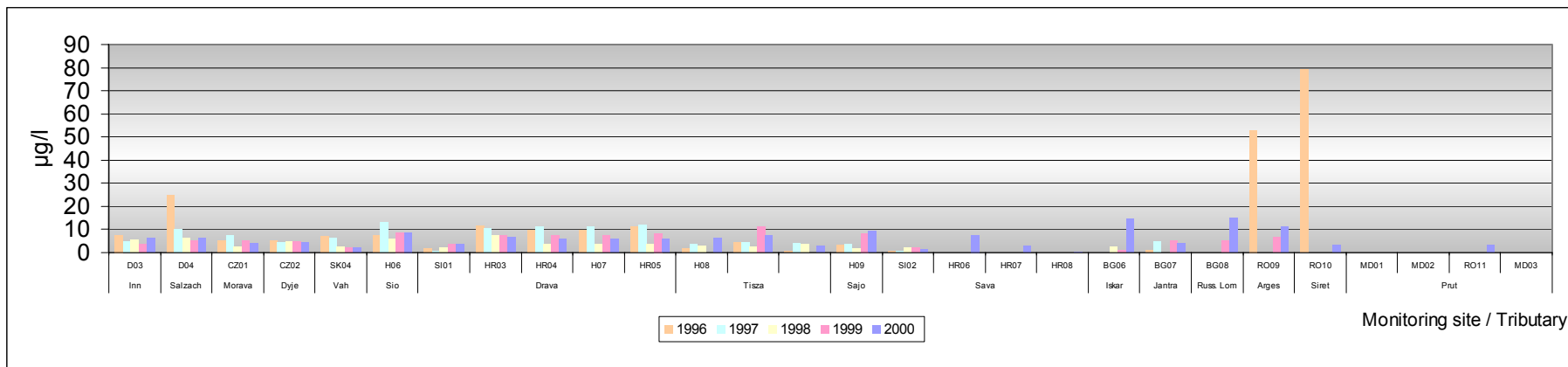Fig. 8.1.4.17b: Spatial variation of BOD5 – Danube River
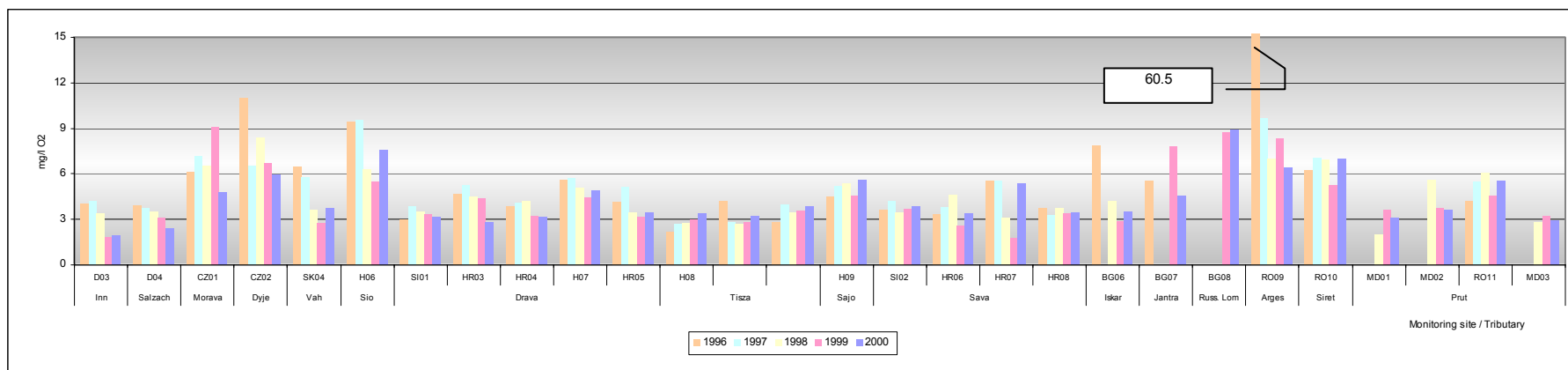
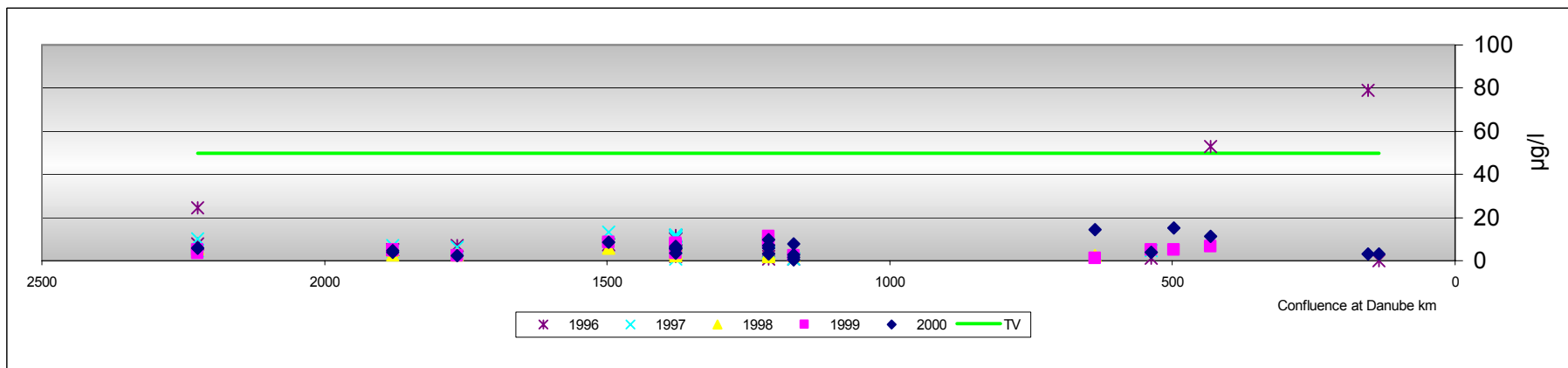Fig. 8.1.4.18a: Spatial variation of BOD5 – Tributaries
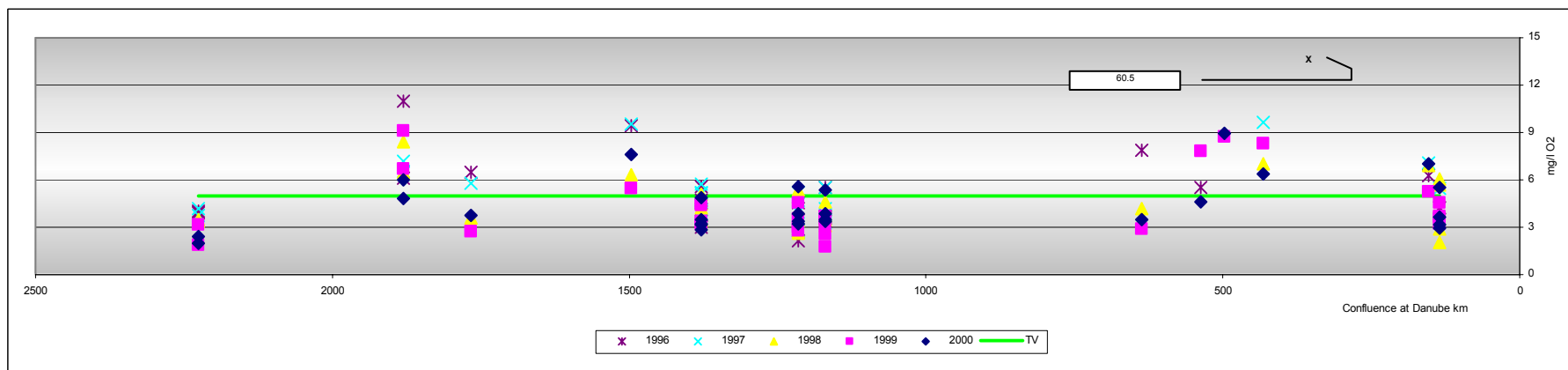


Fig. 8.1.4.18b: Spatial variation of BOD5 – Tributaries
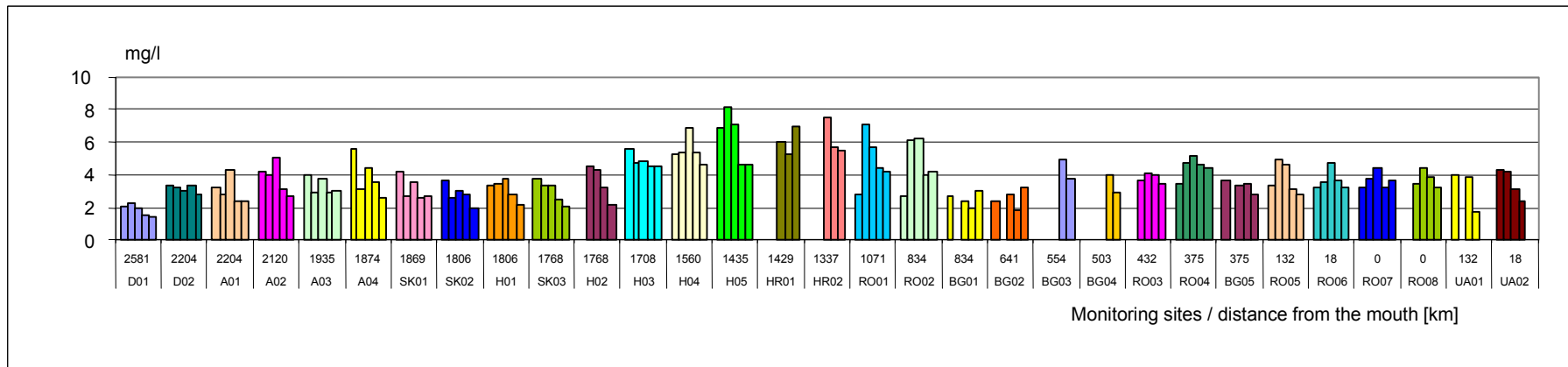
Fig. 8.1.4.19: Temporal trends of BOD5 – Danube River
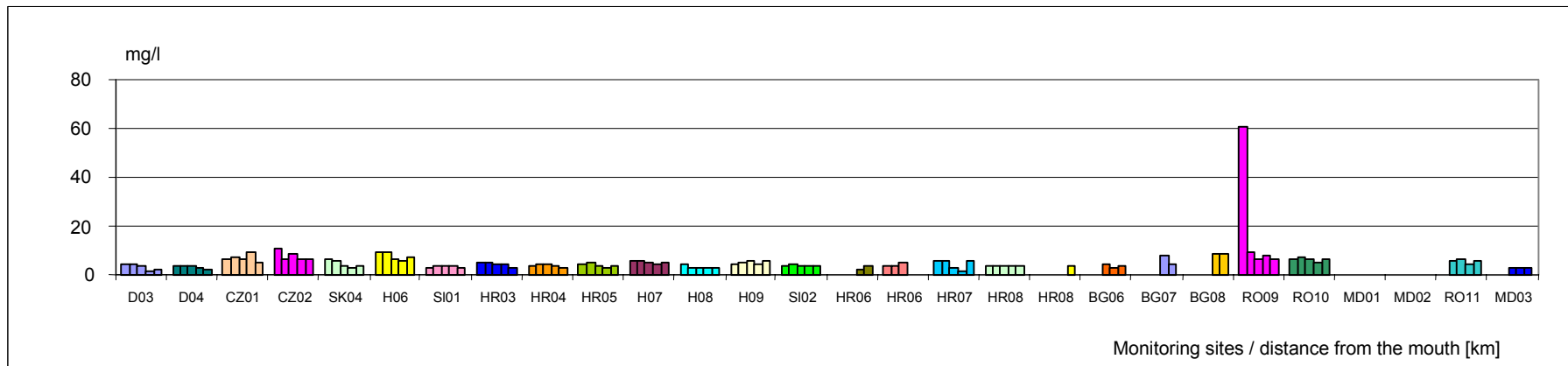
Fig. 8.1.4.20: Temporal trends of BOD5 – Tributaries

Chemical Oxygen Demand

COD-Mn and COD-Cr
The other two determinands that illustrate the presence of oxygen-consuming compounds in the water column are COD by $KMnO_4$ and $K_2Cr_2O_7$ methods.
The distribution of monitoring sites according to the Classification System in the DRB for **COD-Mn** is shown in **Fig. 8.1.4.21**:
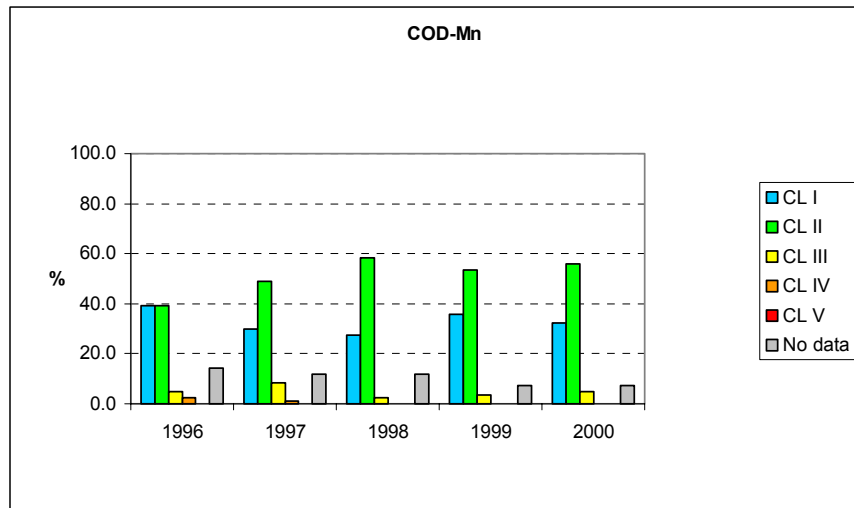
Fig. 8.1.4.21: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **COD-Mn**

For COD-Mn, the assessment is made based on data reported from 84 monitoring sites (out of the assessment is 19 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):
- Class I is represented by less than 40 % of all monitoring sites;
- excepting 1996, when the number of monitoring sites within Class I is identical to that specific to Class II (39.3%), for all the other studied years the maximum percentages belong to Class II, in the range of 48.8 % in 1997 –58.3 % in 1998;
- Class III is represented by low percentages in all five years, within the range from 2.4 % in 1998 – 8.3 % in 1997;
- Class IV appears only in 1996 and 1997 (at 2.4 % and 1.2 % of sites respectively);
- no monitoring site shows values within Class V;

The distribution of monitoring sites according to the Classification System in the DRB for **COD-Cr** is shown in **Fig. 8.1.4.26**:
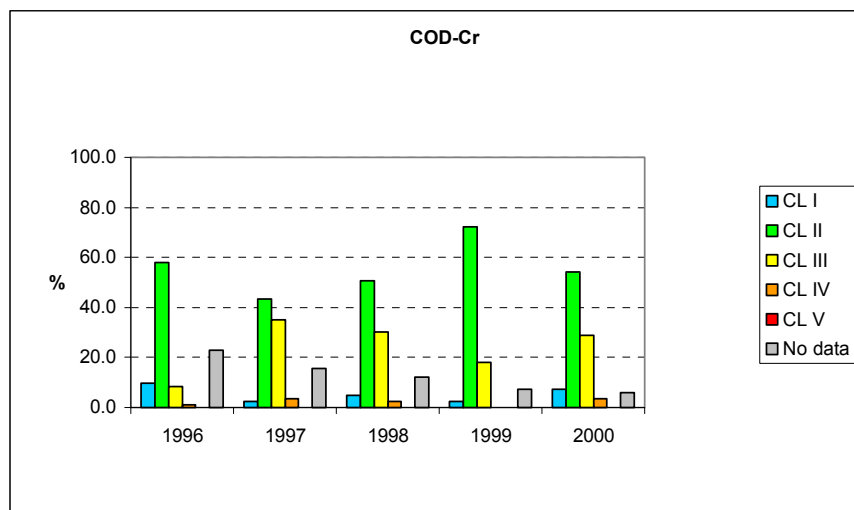
Fig. 8.1.4.26: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **COD-Cr**

For COD-Cr, the assessment is made based on data reported from 83 monitoring sites (therefore, out of the assessment is 20 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is represented by low number of sites, with a minimum of 2.4 % in 1997 and 1999 and a maximum of 9.6 % in 1996;
- the maximum percentages from all sites belong to Class II each year: in 1997 only, less than 50 % of the monitoring sites belong to this class, all the other values are above this level;
- Class III has an uneven distribution, with percentages within the range 8.4 % in 1996 up to 34.9 % in 1997;
- only few monitoring sites show values within Class IV, the maximum being 3.6 % in 1997 and 2000;
- similarly to COD-Mn, no monitoring site is described by COD-Cr values within Class V.

The spatial distributions of COD-Mn and COD-Cr values for the Danube River are shown in **Fig. 8.1.4.22a, 8.1.4.22b** and **Fig. 8.1.4.27a, 8.1.4.27b,** respectively.

In the upper section of the Danube River, both determinands present a uniform spatial pattern, with variation intervals of 1.8 – 6.1 mg/l O_2 for COD-Mn and 8.9 – 19.2 mg/l O_2 for COD-Cr. For monitoring sites located in this stretch, no value is above the target limits (10.0 mg/l O_2 for COD-Mn and 25.0 mg/l O_2 for COD-Cr).

Middle stretch is characterized by slightly higher values than the upper part for both determinands. But, unlike the COD-Mn for which no value is above the target limit in this stretch, for COD-Cr four values exceeded this limit.

For COD-Mn, the first part of the lower Danube is characterized by higher values than the middle stretch, within the range 2.8 – 9.6 mg/l O_2. A similar pattern as for BOD_5 is valid at the cross section from Danube-Pristol Novo Selo/Pristol (km 834, RO02/BG01), where again the differences between the recorded data by two countries are noticeable. For COD-Cr spatial pattern is uniform, with values within the range 11.5 – 23.9 mg/l O_2, only one value reaching 30.0 mg/l O_2 level.

The second part of the lower Danube shows a uniform line for COD-Mn. However, slightly increased values are noticed at Danube-Chiciu/Silistra (km 375, RO04), with values within the range 5.5 – 10 mg/l O_2. COD-Cr pattern is characterized by an increasing values from Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta. The maximum value (58.0 mg/l O_2) appears at Danube-Sulina/Sulina arm (km 0, RO07).

For the entire lower Danube, no COD-Mn value is above the target limit, but 51 values exceed this limit for COD-Cr – few of them in the middle section, but most of them in the lower Danube section. It also should be mentioned that yearly variation of COD-Mn and COD-Cr is much higher in the lower Danube section than in the upper and middle ones.

The spatial pattern of COD-Mn and COD-Cr values for selected tributaries are shown in **Fig.8.1.4.23a**, **8.1.4.23b** and **8.1.4.28a**, **8.1.4.28b** respectively. The following remarks can be done in this respect:
-   in the upper section Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) are characterized by rather high values, in Dyje exceeding 10.0 mg/l in COD-Mn and 40.0 mg/l in COD-Cr;
-   in the middle stretch Sio-Szekszard (H06) presents relatively higher values, with intervals of 14.7 – 16.5 mg/l O_2 for COD-Mn and 33.5 – 49.2 mg/l O_2 for COD-Cr, but still these are not extreme values for a tributary;
-   in the first part of the lower Danube, only one tributary located in this section, the Jantra-Karantzi (BG07) shows higher organic matter content with values up to 33.8 mg/l and 90.4 mg/l using COD-Mn and COD-Cr, respectively;
-   in the second part of the lower Danube stretch, concerning COD-Mn, three tributaries along this stretch – the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) - do not present extreme values for this determinand; COD-Cr values are above level 50.0 mg/l O_2 on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), but they are not much different from the values recorded on the main delta arms;
-   concerning the exceeding quality target for selected tributaries, 22 values are above this limit for COD-Mn and 46 for COD-Cr.

The temporal trends for the Danube River are illustrated in **Fig. 8.1.4.24** and **8.1.4.29**. For selected tributaries, the trends are shown in **Fig. 8.1.4.25** and **8.1.4.30**:
-   for COD-Mn, the following temporal changes are observed for the Danube River and its tributaries:
    -   o   slight increasing tendency in monitoring sites from Danube-Jochenstein (km 2204, D02) to Danube-Bratislava (km 1869, SK01);
    -   o   most of the monitoring sites from the middle Danube are characterized by slight decreasing trend from 1996 to 2000;
    -   o   in the lower Danube, most of the sites do not indicate any clear trend, high values were observed mainly in 1997 and 1998;
    -   o   from tributaries, slight increasing trend is visible in Sajo-Sajopuspoki (H09); all the others are characterized either by stationary state or decreasing trends;
-   for COD-Cr, the following was observed for the Danube River and its tributaries:
    -   o   in the upper and middle Danube, most of the monitoring sites present a "V" temporal profile, with lower values in 1998 and 1999 or a decreasing trend;
    -   o   concerning the sites located in the lower Danube, in its second part – downstream Danube-Chiciu/Silistra (rkm 375, RO04) – increasing was observed especially in sites measured by Romania, which was not confirmed by Bulgarian data in the same section RO04/BG05. Bulgarian data indicate decrease in period 1998-2000 there;
    -   o   similarly to COD-Mn, slight increasing trend is observed in Sajo-Sajopuspoki (H09), but the general trend is decreasing from 1996 to 2000; it has to be mentioned that for three tributaries located in the lower Danube, the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), very high values are recorded in 1997 and 1998.
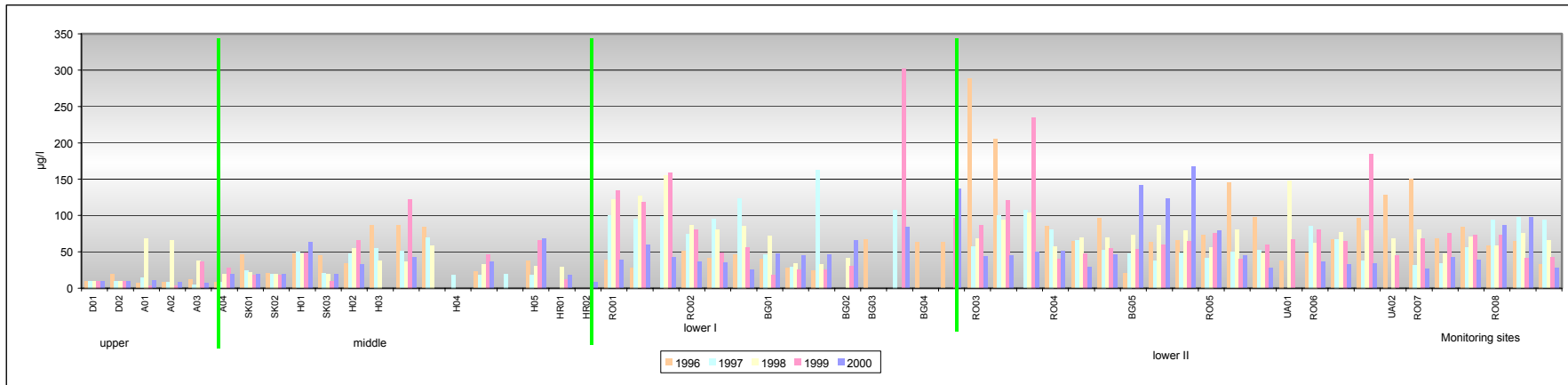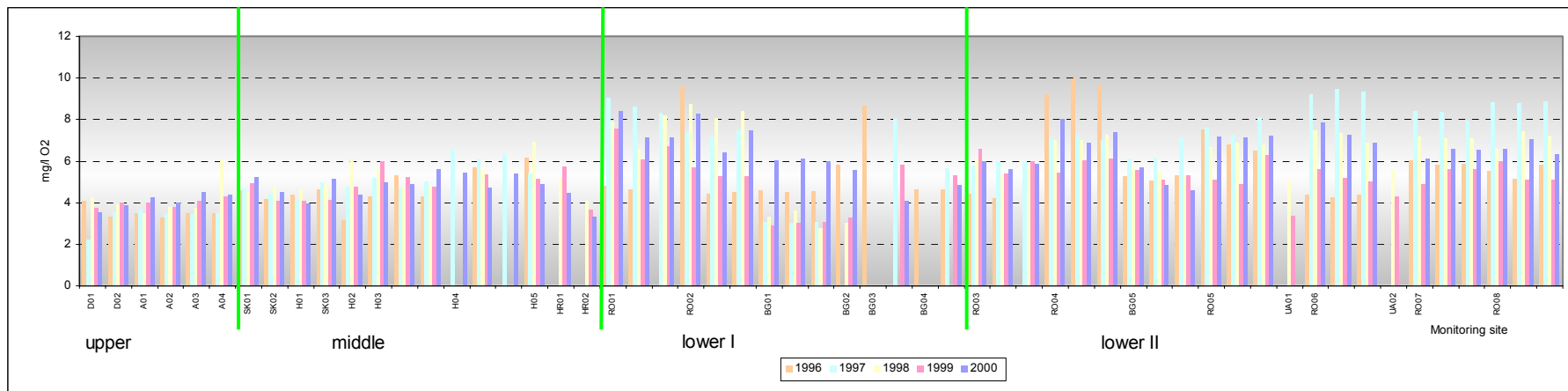
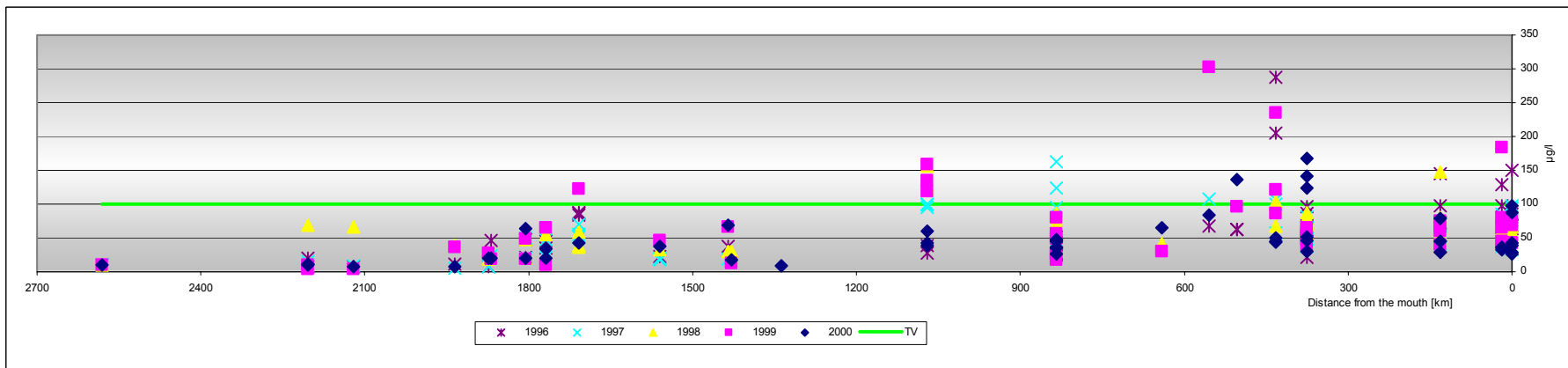Fig. 8.1.4.22a: Spatial variation of COD-Mn – Danube River
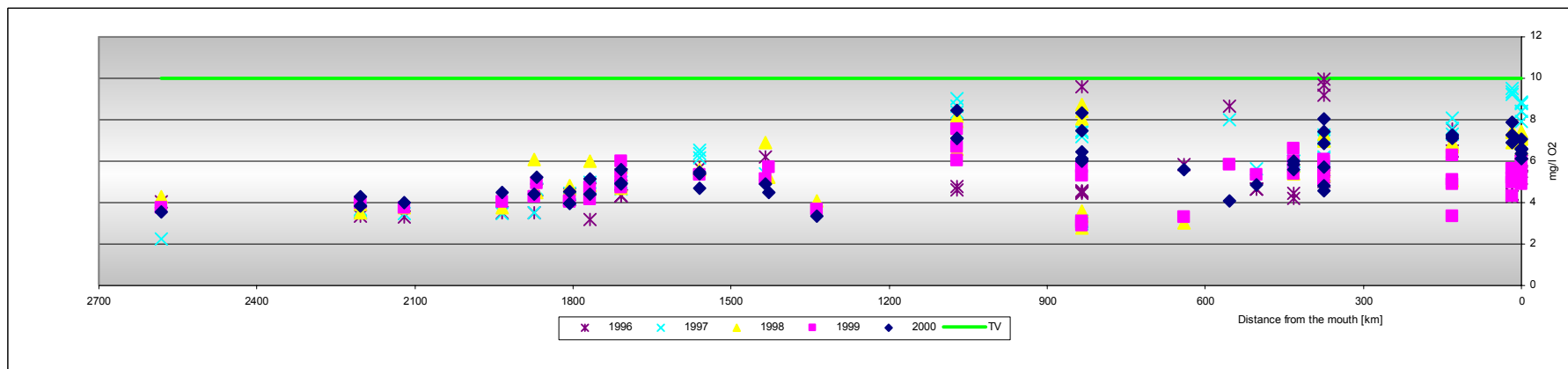
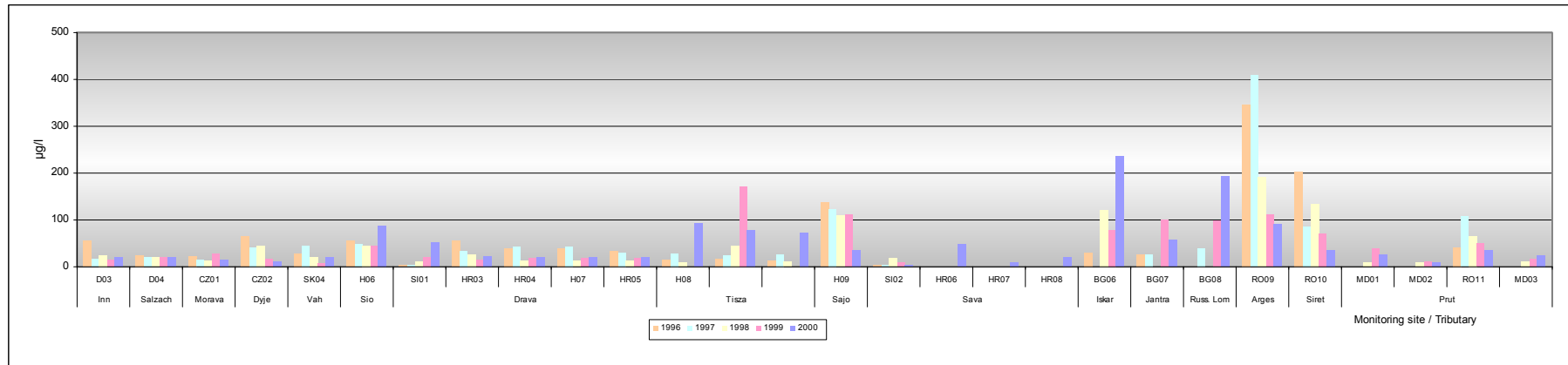Fig. 8.1.4.22b: Spatial variation of COD-Mn – Danube River
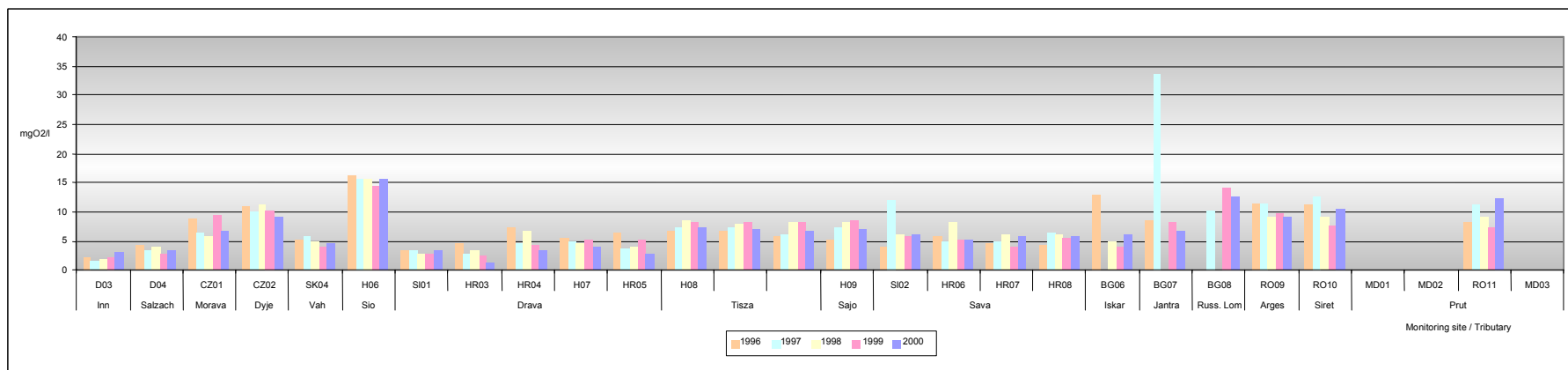
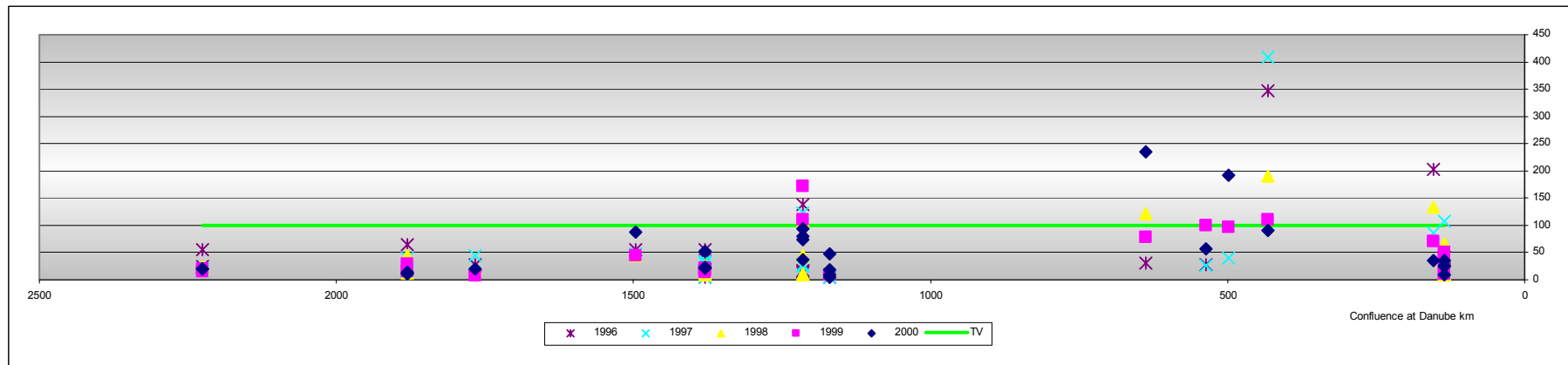Fig. 8.1.4.23a: Spatial variation of COD-Mn - Tributaries
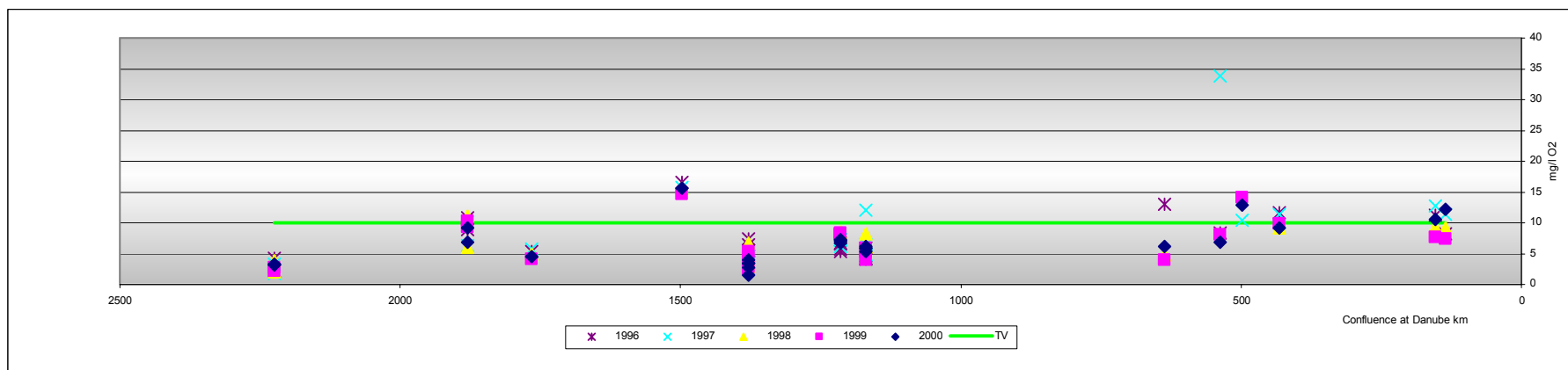
Fig. 8.1.4.23b: Spatial variation of COD-Mn - Tributaries
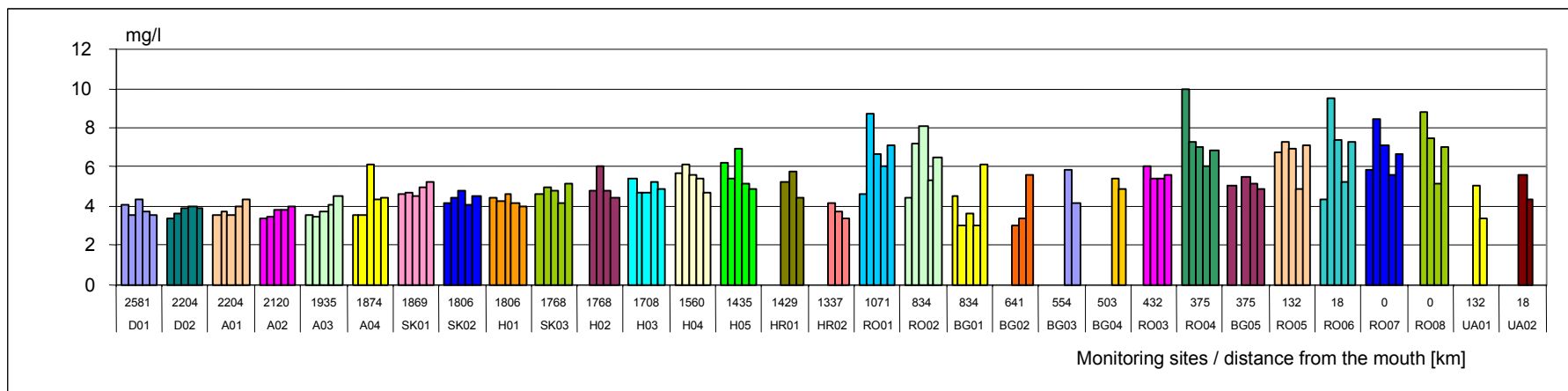
Fig. 8.1.4.24: Temporal trends of COD-Mn – Danube River
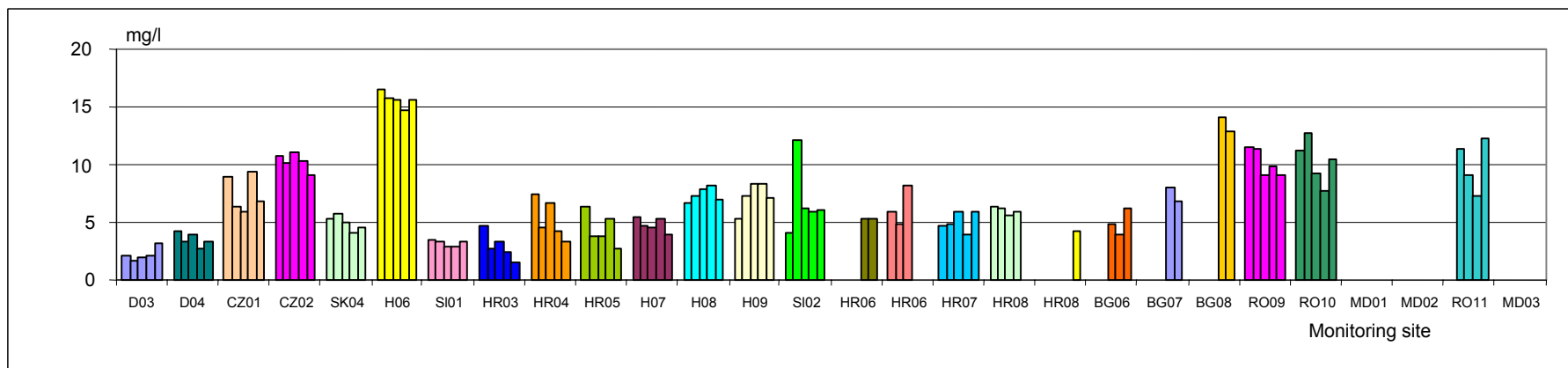
Fig. 8.1.4.25: Temporal trends of COD-Mn – Tributaries
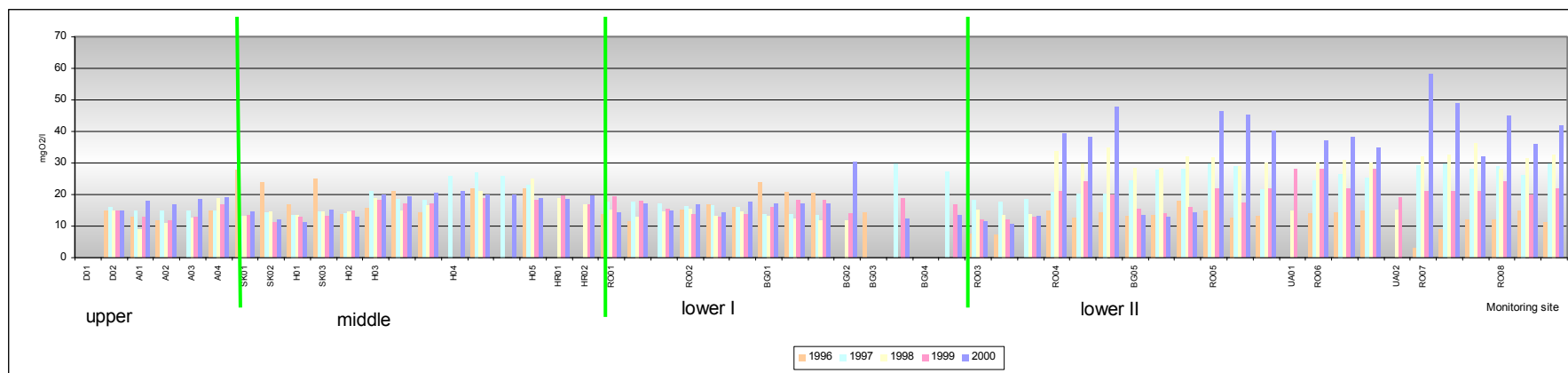
Fig. 8.1.4.27a: Spatial variation of COD-Cr – Danube River
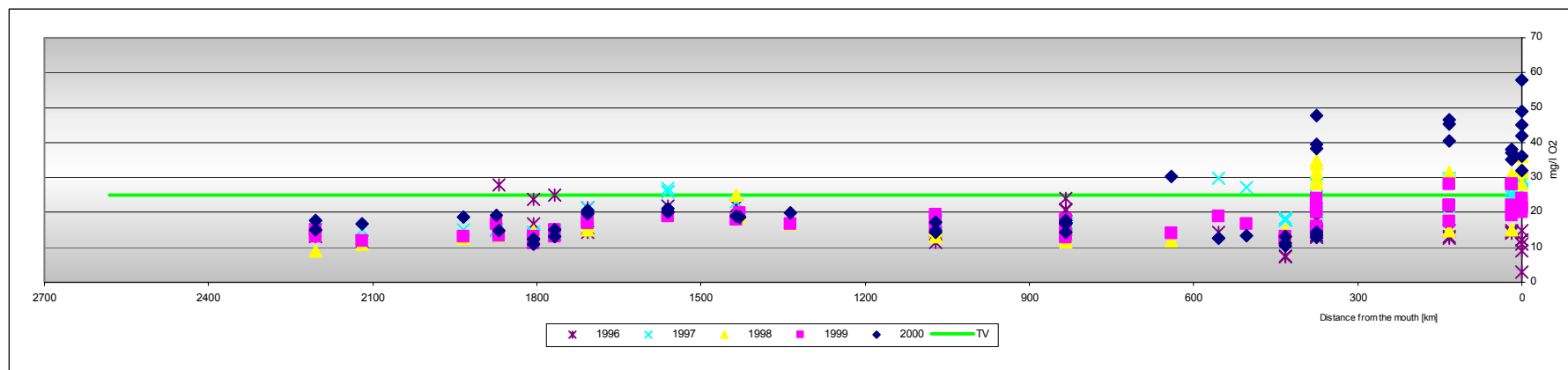
Fig. 8.1.4.27b: Spatial variation of COD-Cr – Danube River
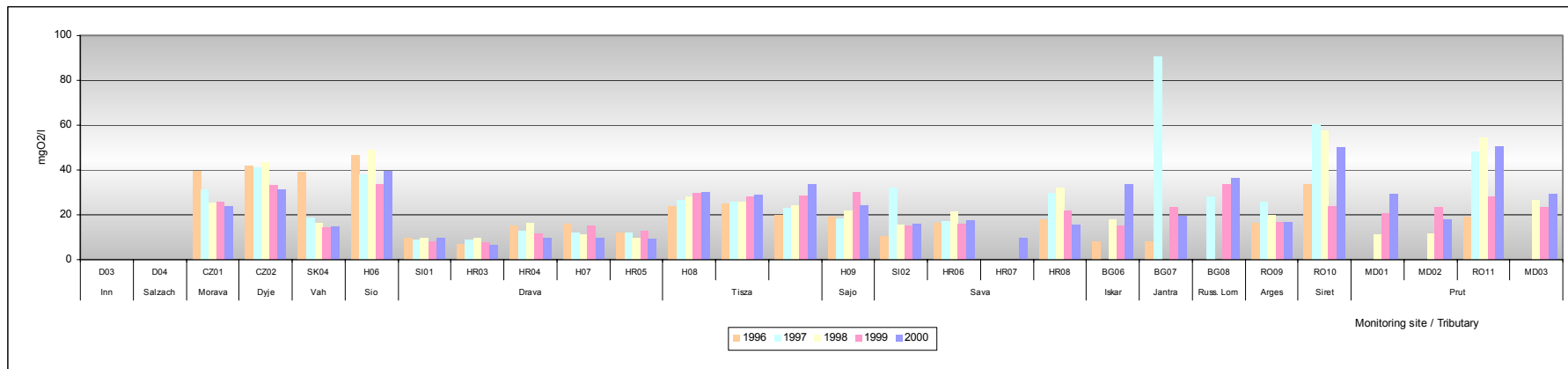
Fig. 8.1.4.28a: Spatial variation of COD-Cr – Tributaries
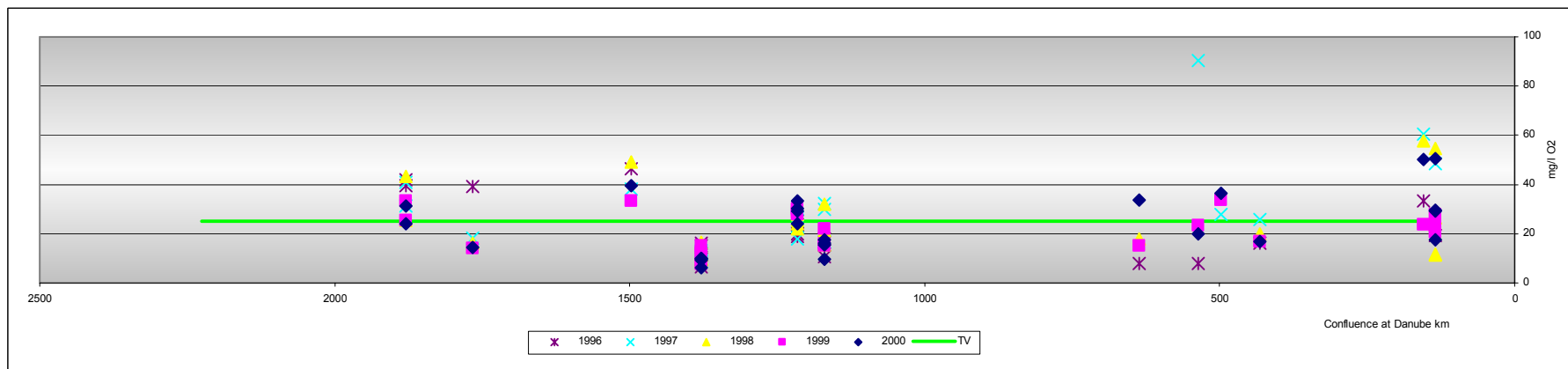
Fig. 8.1.4.28b: Spatial variation of COD-Cr – Tributaries
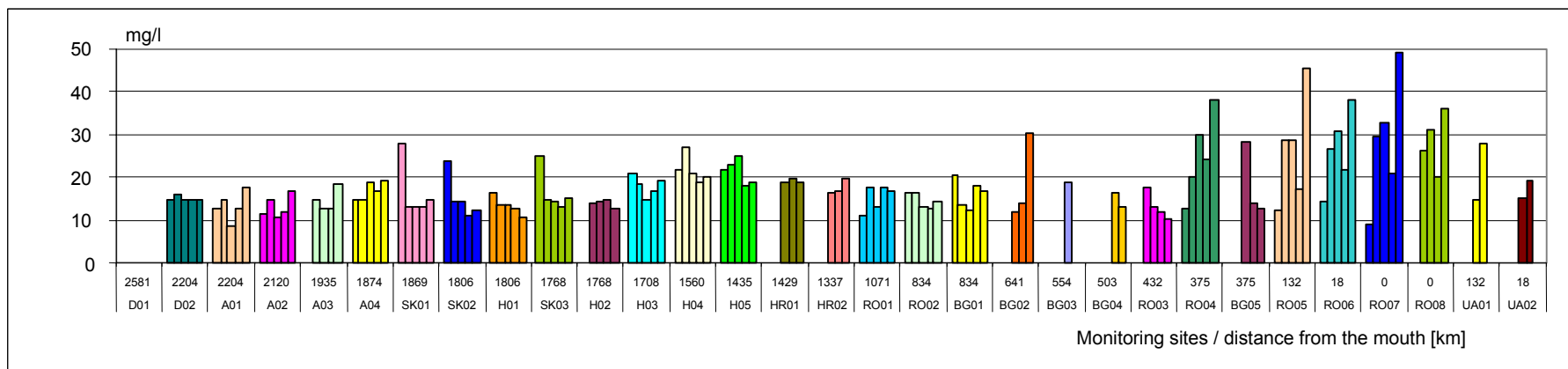
Fig. 8.1.4.29: Temporal trends of COD-Cr – Danube River
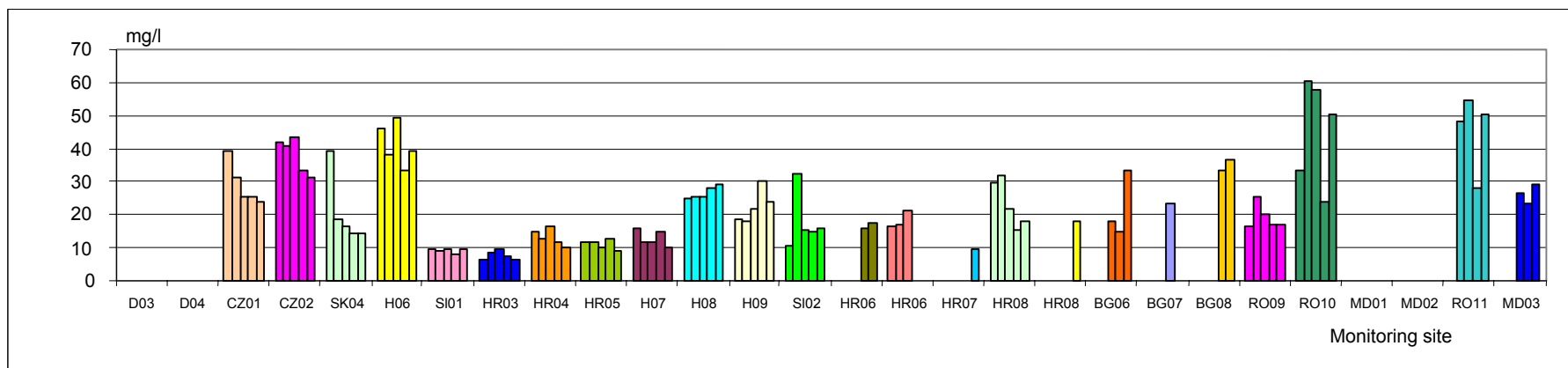
Fig. 8.1.4.30: Temporal trends of COD-Cr – Tributaries

It is well known that when a watercourse receives sewage effluent or effluent from animal farms, the levels of organic matter and ammonium rise, while the level of oxygen falls. In order to illustrate this relation in the Danube River and its tributaries, for each evaluated year a chart has been made in which both the BOD-5 values and ammonium content are represented versus the minimum dissolved oxygen values (**Fig. 8.1.4.31. – 8.1.4.35**). Significant relations between these determinands had been identified in monitoring sites listed in Table 8.1.4.2 below.

Table 8.1.4.2: Significant relations between the $N-NH_4$ and BOD_5 levels versus minimum dissolved oxygen.

Year	River	Country code	$N-NH_4$ (mg/l)	BOD_5 (mg/l O_2)	DO Min. (mg/l O_2)
1996	Dyje	CZ02	1.18	11.0	5.9
	Vah	SK04	1.00	6.5	5.2
	Sio	H06	1.30	9.5	7.2
	Arges	RO09	7.68	60.5	2.4
	Siret	RO10	1.50	6.3	0.2
1997	Morava	CZ01	1.16	7.2	6.2
	Djye	CZ02	1.05	6.5	6.2
	Sio	H06	1.14	9.5	6.4
	Jantra	BG07	2.95	-	6.6
	Arges	RO09	2.49	9.7	2.3
	Siret	RO10	3.05	7.1	5.4
1998	Dyje	CZ02	0.56	8.4	7.8
	Arges	RO09	2.86	7.0	3.0
1999	Morava	CZ01	0.88	9.1	8.2
	Dyje	CZ02	0.89	6.7	7.1
	Jantra	BG07	0.46	5.0	6.5
	Russenski Lom	BG08	0.19	8.8	5.6
	Arges	RO09	2.60	8.3	2.9
	Siret	RO10	0.54	5.3	5.5
2000	Sio	H06	0.49	7.6	6.2
	Russenski Lom	BG08	0.26	8.9	5.6
	Siret	RO10	0.93	7.0	6.8

Fig. 8.1.4.31 – 8.1.4.35: Correlation between ammonium content and biochemical oxygen demand versus minimum of dissolved oxygen
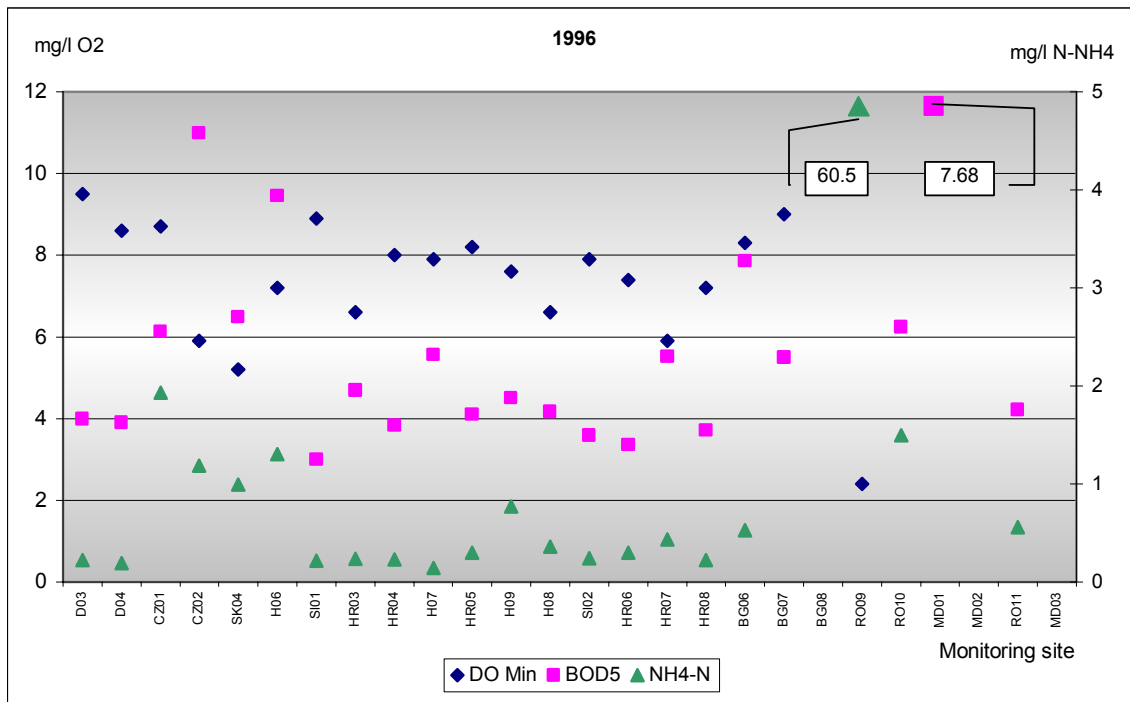
Fig. 8.1.4.31
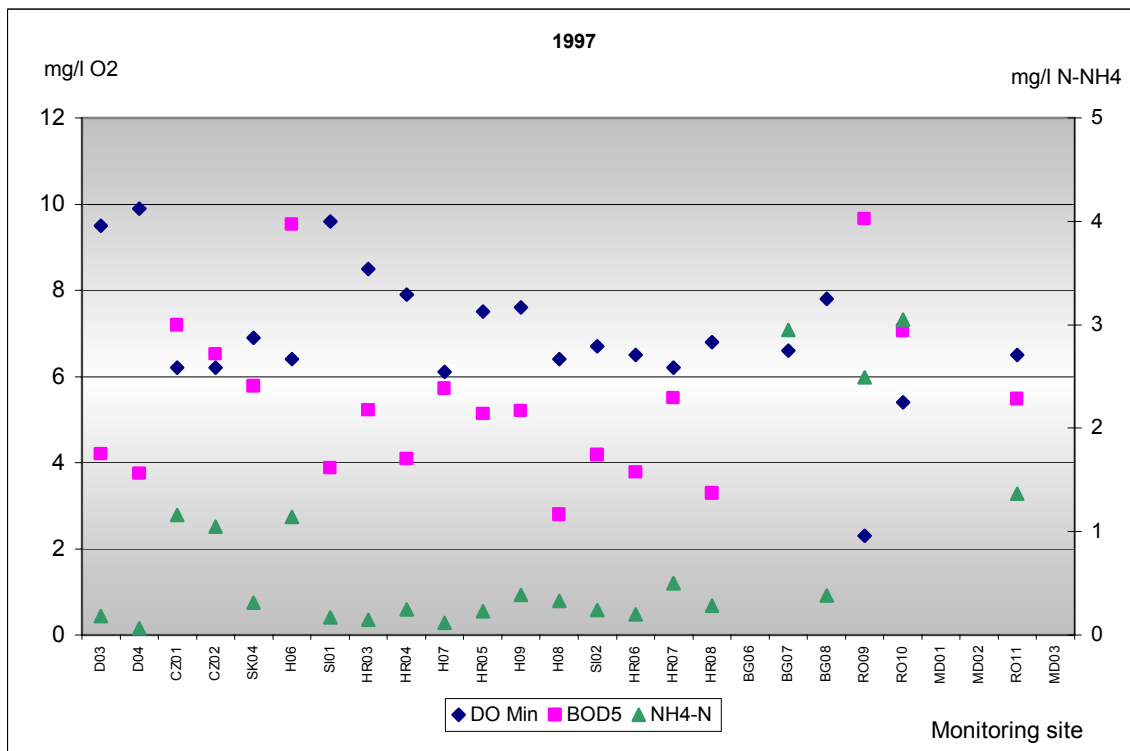
Fig. 8.1.4.32
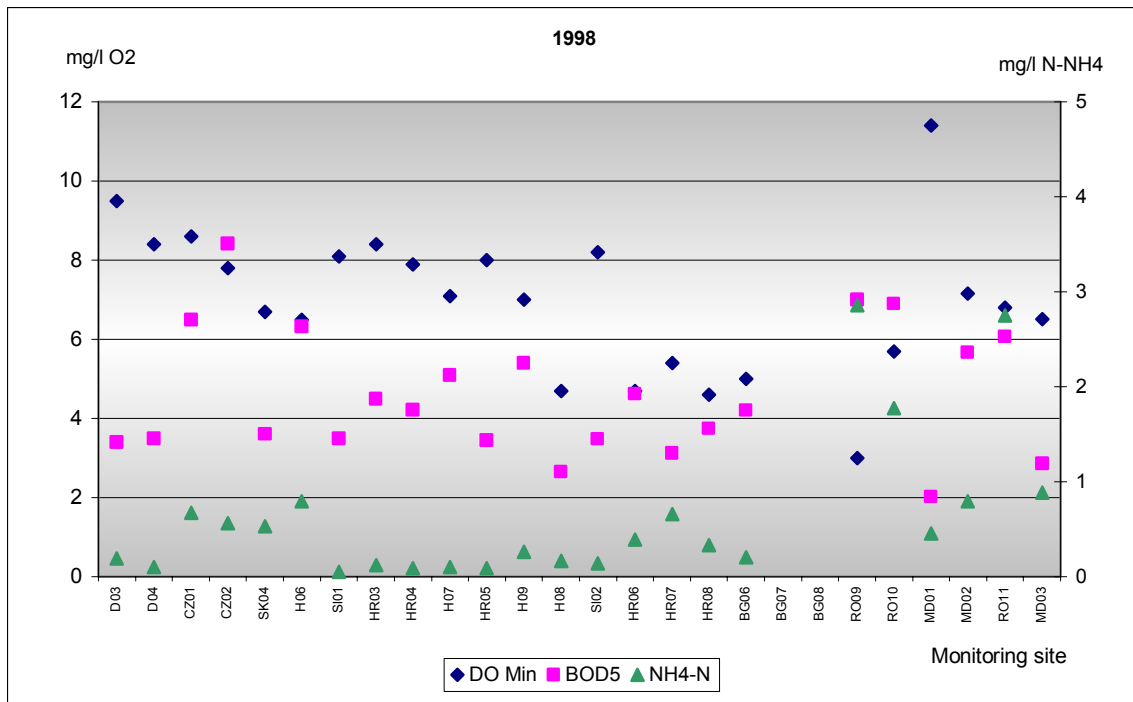
Fig. 8.1.4.33
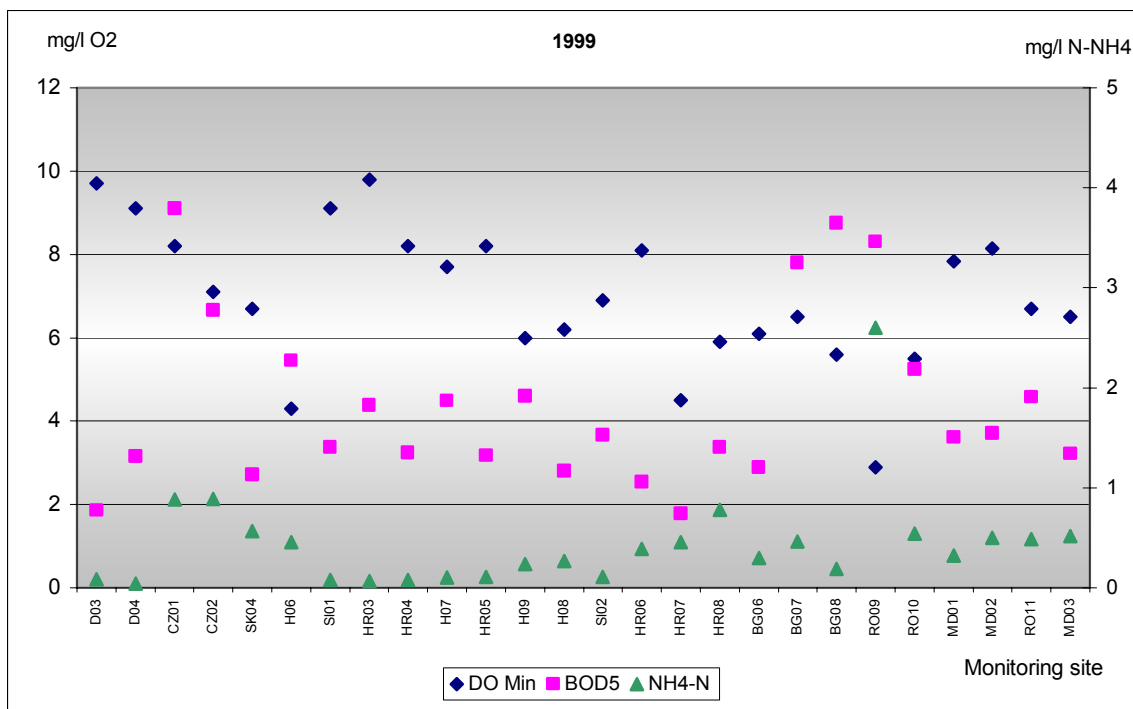
Fig. 8.1.4.34
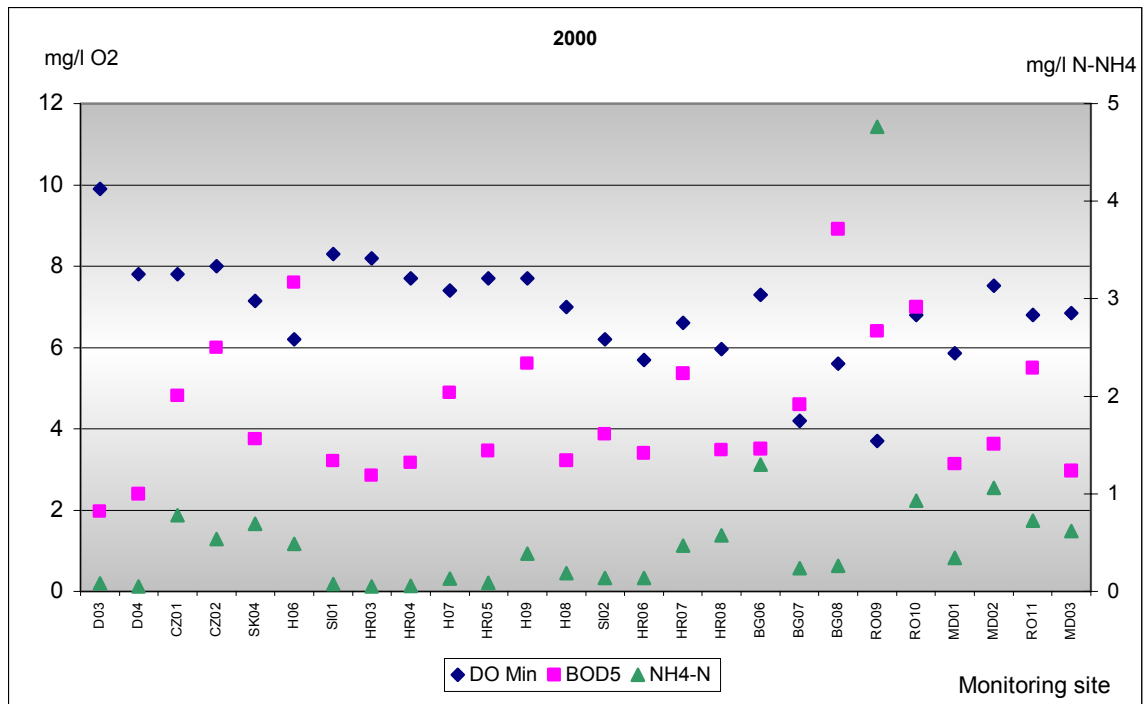
Fig. 8.1.4.35

8.1.5. Organic Micropollutants

Among the main sources of organic micropollutants in surface waters industrial, urban activities and application of pesticides in agriculture can be mentioned.

Within the TNMN Programme, organic micropollutants that are regularly monitored are Lindan, p,p'-DDT, Atrazine, chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene. Because of the low frequencies of measurements, trend analysis has not been possible to done for these determinands, so only some observations related to temporal patterns are mentioned.

When assessing organic micropollutants results of classification, percentage of monitoring sites satisfying limit values for different water quality classes is influenced very much by uneven number of measurements in particular years. As can be seen later, the number of monitoring sites without measurements has decreased significantly from 1996 to 2000, but still there is rather large group of monitoring sites without measurements of organic micropollutants.

Lindan (gamma isomer of hexachlorocyclohexane)

The distribution of monitoring sites according to the Classification System in the DRB for **Lindan** is shown in **Fig. 8.1.5.1**:
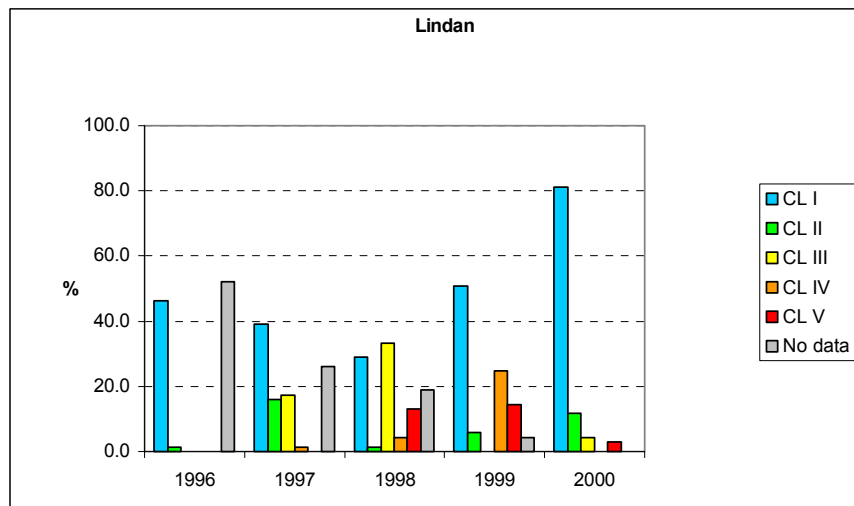
Fig. 8.1.5.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Lindan**

The assessment is made based on data reported from 69 monitoring sites (out of the assessment is 34 monitoring sites from Phase I List of Monitoring Sites, in which no measurements of Lindane had been done in 1996-2000):
- the number of monitoring sites corresponding to Class I decreases from 1996 to 1998 and then increases until 2000 up to 81.2 %;
- Class II is represented by a minimum value of 1.4 % in 1996 and 1998 and by a maximum of 15.9 % in 1997;
- no monitoring site corresponds to Class III in 1996 and 1999; in the other years Class III is represented by 4.3 % - 33.3% of sites;
- Class IV is absent in 1996 and 2000; during 1997 – 1999 perentage of sites in in this Class is in the range from 1,4 – 24,6 %;
- Class V is present during 1998 – 2000, with the minimum in 2000 (2.9 %) and the maximum in 1999 (14.5 %);

The pattern for Lindan concentrations in the Danube River is shown in **Fig. 8.1.5.2a** and **8.1.5.2b**.

In the upper Danube, Lindan is actually undetectable at the first two monitoring sites, Danube-Neu-Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02), according to German results. For the rest four sites, Lindan is also undetectable during 1997–1999 even though there are differences among years, caused by the differences in reported limits of detection. According to Austrian data, from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km1874, A04), Lindan seems to be detectable in 2000 only, at the level of 0.100 μg/l, the target value for Lindan.

In the middle section, all Lindan values are below 0.050 μg/l, the limit value for Quality Class I.

In the first part of the lower Danube, Lindan concentrations are much higher than 0.100 μg/l. From Danube-Bazias (km 1071, RO01) down to Danube-Pristol/Novo Selo (km 834, RO02), Lindan concentrations increase reaching c90 values up to 0.398 μg/l according to Romanian data. The higest values from this part are recorded mainly in 1999. It has to be mentioned that, similar to some other determinands, big differences exist between the reported data for the cross section from km 834 (RO02/BG01).

In the second part of the lower Danube Lindan c90 values are even above 0.20 μg/l, corresponding to Class IV. This is observed in all Romanian monitoring sites mainly in 1999. Again has to be mentioned that there are extremely high differences between Romanian and Bulgarian results in the same cross sections.

For the entire lower Danube, 46 Lindan c90 values exceeded the level set up as a target value.

The distribution of Lindan concentrations in selected tributaries is illustrated in **Fig. 8.1.5.3a** and **8.1.5.3b** and shows an inhomogeneous picture:
- those tributaries from the upper section, in which Lindan is detectable - the Morava-Lanzot (CZ01) and Dyje-Pohansko (CZ02), present Lindan concentrations below 0.05 μg/l;
- in the middle stretch, in Sio-Szekszard (H06), an extreme value is recorded in 2000 (5.75 μg/l); higher values that appear on Sajo-Sajopuspoki (H09) in 1996 and 1997 do not exceed the target limit;
- in the lower section, three tributaries - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), show values above 0.100 μg/l, especially in 1999, with a maximum value of 0.321 μg/l on the Arges-Conf. Danube (RO09);
- majority of values characterising Lindan content, which were above the target limit, were observed on tributaries from the lower Danube.
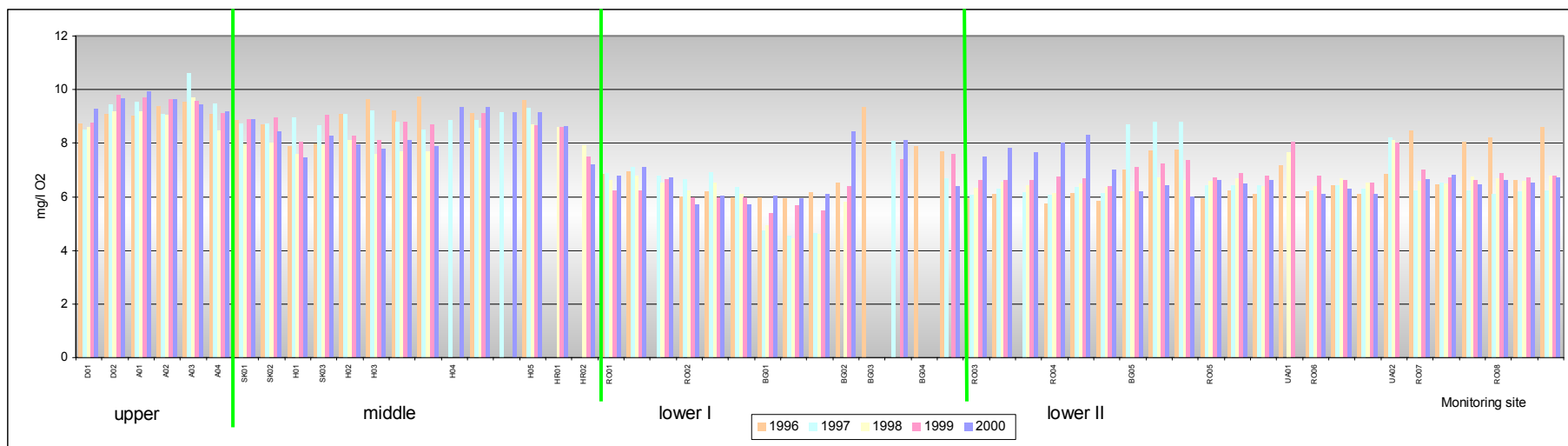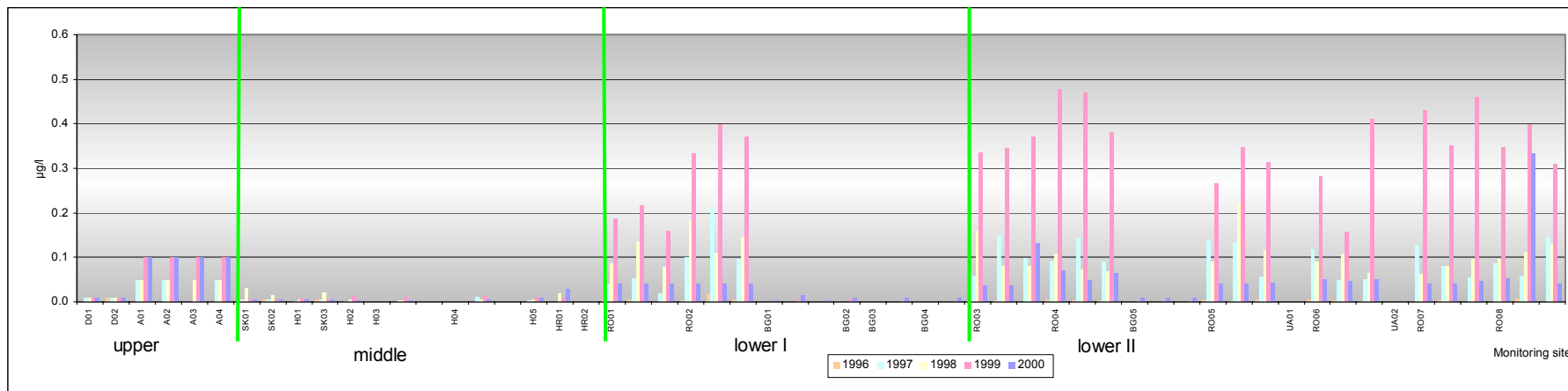
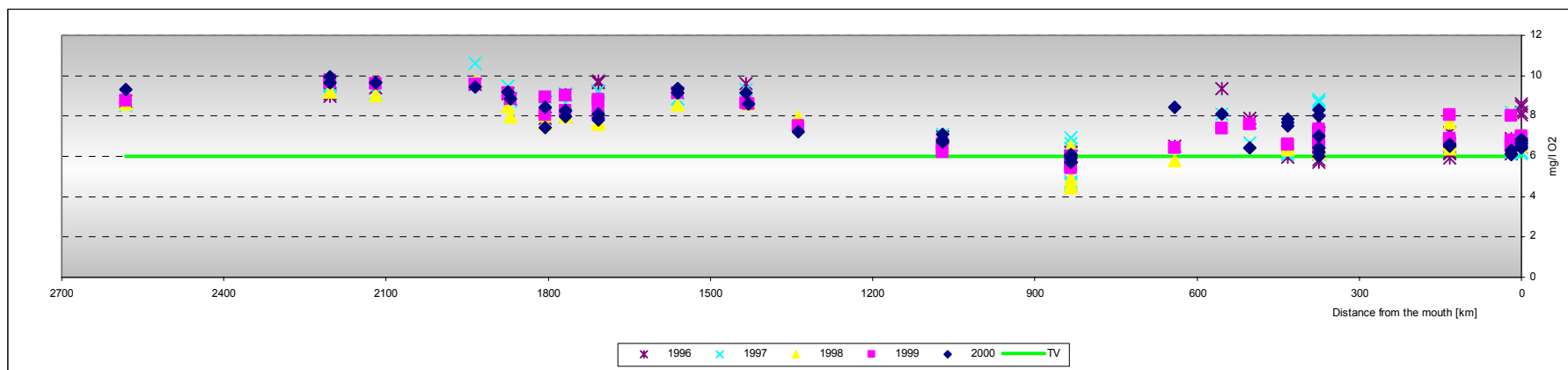Fig. 8.1.5.2a: Spatial variation of Lindan – Danube River
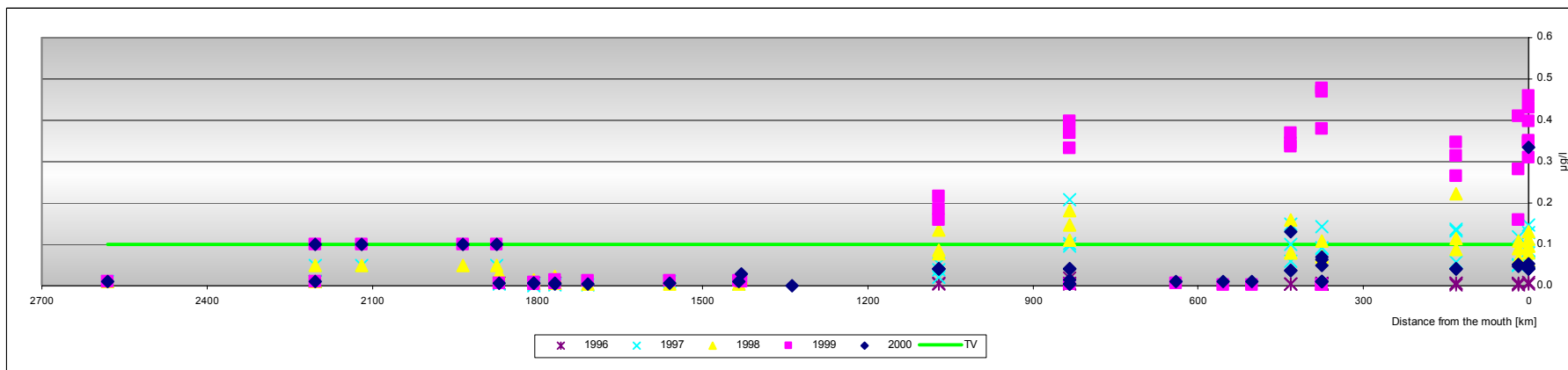
Fig. 8.1.5.2b: Spatial variation of Lindan – Danube River
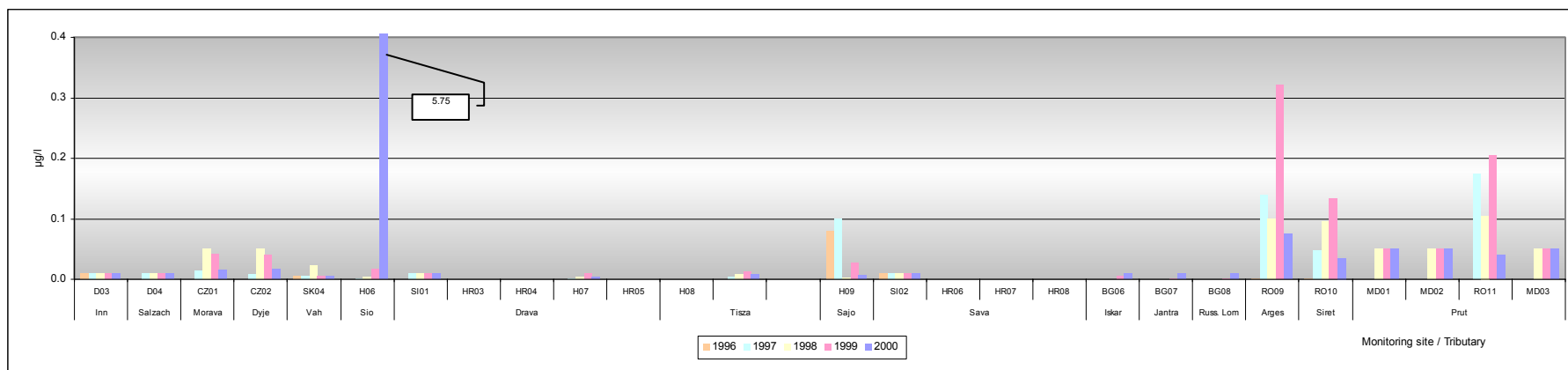
Fig. 8.1.5.3a: Spatial variation of Lindan – Tributaries
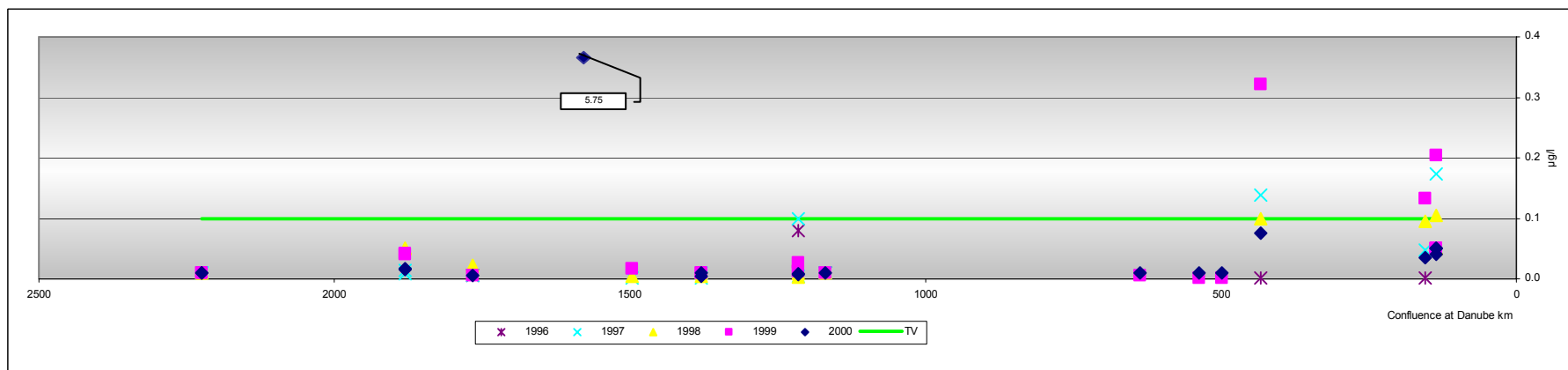

Fig. 8.1.5.3b: Spatial variation of Lindan – Tributaries

pp'-DDT (isomer of dichlorodiphenyltrichloroethane)

The distribution of monitoring sites according to the Classification System in the DRB for **pp'-DDT** is shown in **Fig. 8.1.5.4**:
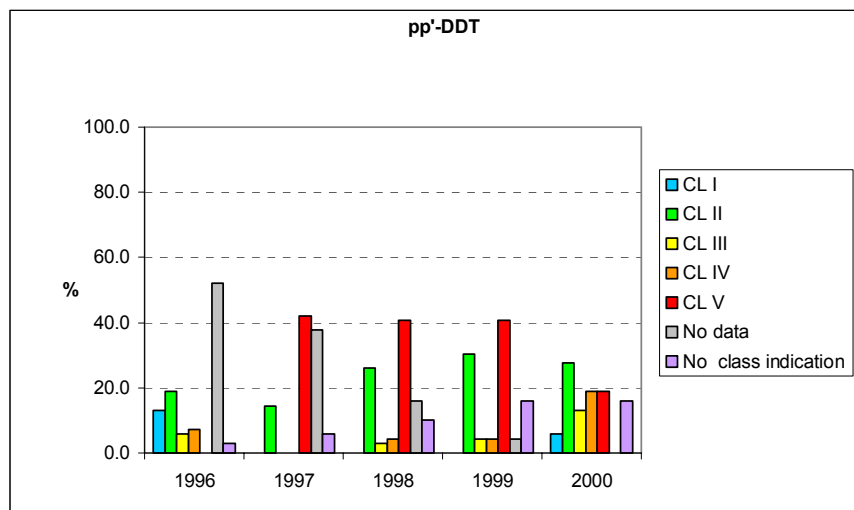
Fig. 8.1.5.4: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **pp'-DDT**

The quality assessment is made based on data reported by 69 monitoring sites (out of the assessment is 34 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is represented in 1996 and 2000 only, by 13.0 % and 5.8 % respectively;
- the percentage of monitoring sites within Class II is in the range from 14,5 – 30,4 %;
- Class III and Class IV have been represented by less than 10 % in the period from 1996-1999, in 2000 13.0 % and 18.8 % of monitoring sites corresponded to Class III and Class IV, respectively;
- Class V is absent in 1996, but the number of sites within this class is approximately 40 % during 1997 – 1999 and less than 20 % in 2000;
- the additional category of "no class indication" (sites, in which limit of detection of p,p'-DDT measurement was higher than limit value for Class II, and therefore have not been classified) is represented in all five studied years.

The spatial variation of pp'-DDT concentrations for the Danube River is illustrated in **Fig**. **8.1.5.5a** and **8.1.5.5b**.

In the upper section of the river, the pp'-DDT concentrations level shows a similar profile with that of Lindan: is undetectable at first two monitoring sites, Danube-Neu-Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02), according to German results. According to Austrian data, pp'-DDT is undetectable during 1997 – 1999; the only measurable concentrations appear in 2000, from Danube-Jochenstein (km 2204, A01) down to Danube-Wolfsthal (km 1874, A04), at the level of 0.05 µg/l.

The middle stretch is characterized by values below the limit of detection, according to Slovak results, excepting the value recorded at Danube-Komarno/Komarom (km 1768, SK03) – 0.080 µg/l in 1999. For the rest of the stretch, values below 0.050 µg/l are present.

In the first part of the lower Danube, pp'-DDT concentrations are much higher than in the middle stretch, They exceed 0.50 µg/l level in 1998 and 1999 from Danube-Bazias (km 1071, RO01) to

Danube-Pristol/Novo Selo   (km 834, RO02), if the Romanian results are taken into account. According to Bulgarian data, values are below 0.10 µg/l.

The second part of lower Danube section is characterized by higher values than the first part - above 0.60 µg/l, recorded mainly in 1997 and 1999 from Danube-us. Arges (km 432, RO03) to Danube-Chiciu/Silistra (km 375, RO04). Much higher p,p'-DDT concentrations appear in three main arms of the Danube Delta –Chilia (RO06), Sulina (RO07) and Sf. Gheorghe (RO08). The maximum c90 value (1.498 µg/l) is observed at Danube- Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08) in 1999.

Fig. **8.1.5.6a** and **8.1.5.6b** show p,p'-DDT c90 values in selected tributaries. It can be seen that high p,p'-DDT concentrations are recorded only on Romanian tributaries - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11). The maximum value for tributaries (1.142µg/l) appears on the Siret-Conf. Danube Sendreni (RO10) in 1999.
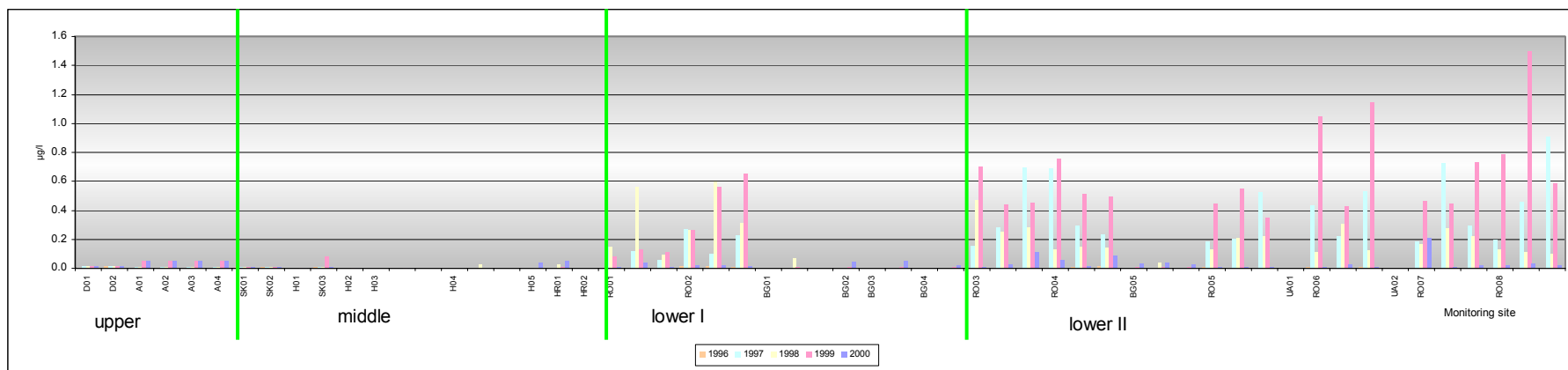
Fig. 8.1.5.5a: Spatial variation of pp'-DDT – Danube River
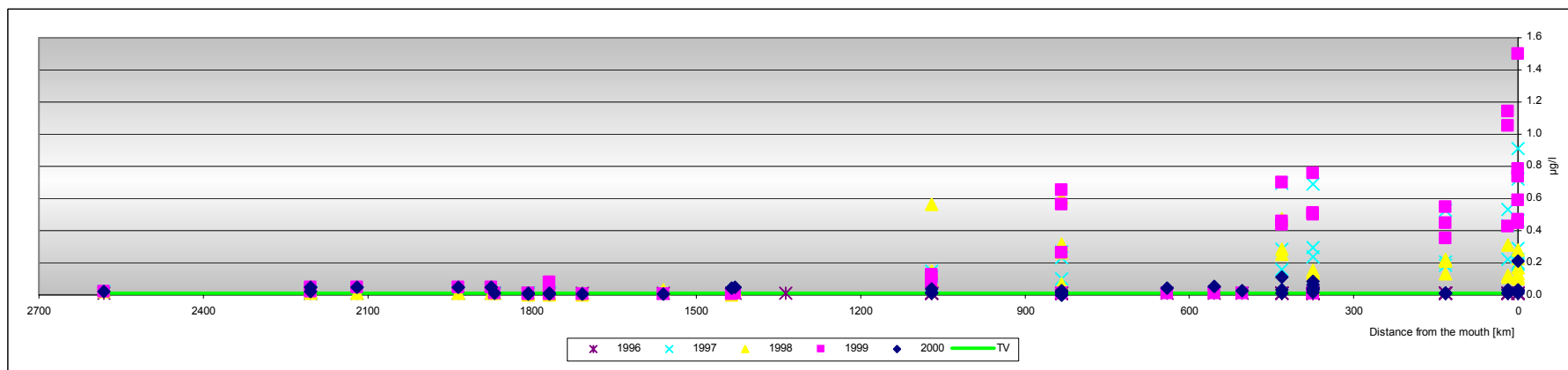
Fig. 8.1.5.5b: Spatial variation of pp'-DDT – Danube River

Note: In locations D01 (97-00), D02 (96-00), A01, A02, A03, A04 (99, 00) the values in the graph represent limits of detection that are higher than the target value.
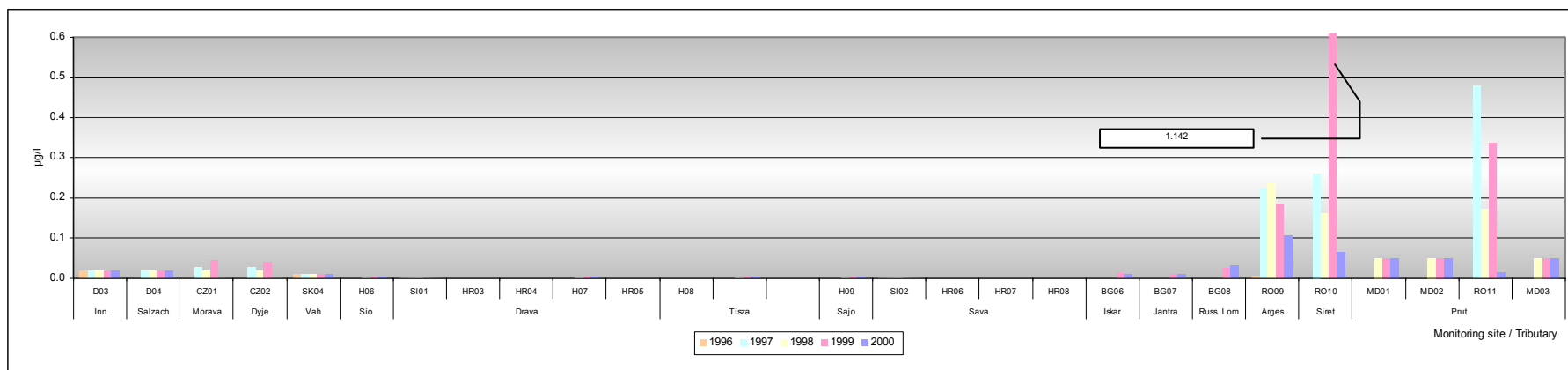
Fig. 8.1.5.6a: Spatial variation of pp'-DDT – Tributaries
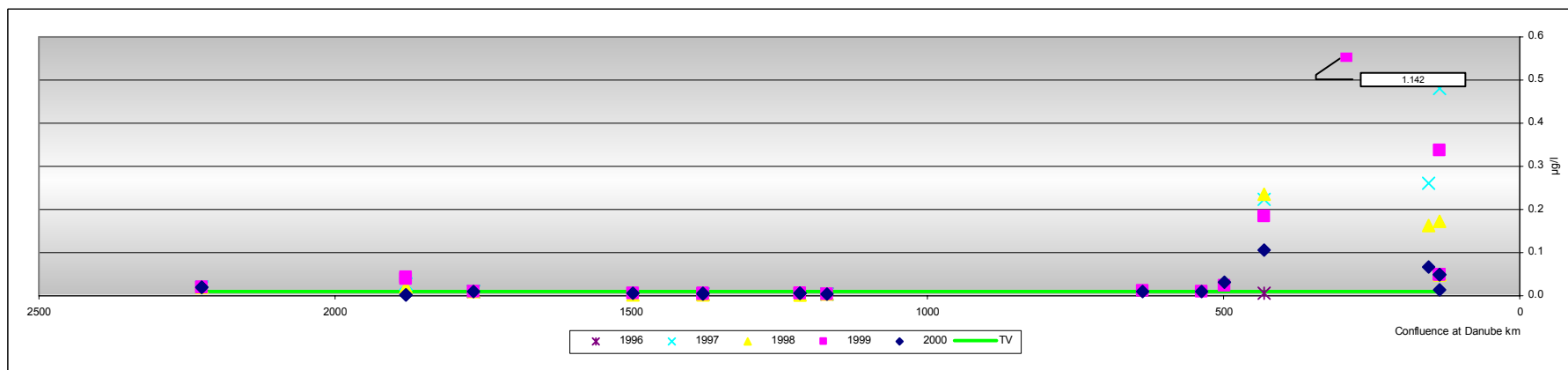
Fig. 8.1.5.6b: Spatial variation of pp'-DDT – Tributaries

Note: In locations D03 (96-00), D04 (97-00), MD01, MD02, MD03 (98-00) the values in the graph represent limits of detection that are higher than the target value

Atrazine

The distribution of monitoring sites according to the Classification System in the DRB for **Atrazine** is shown in **Fig. 8.1.5.7**:
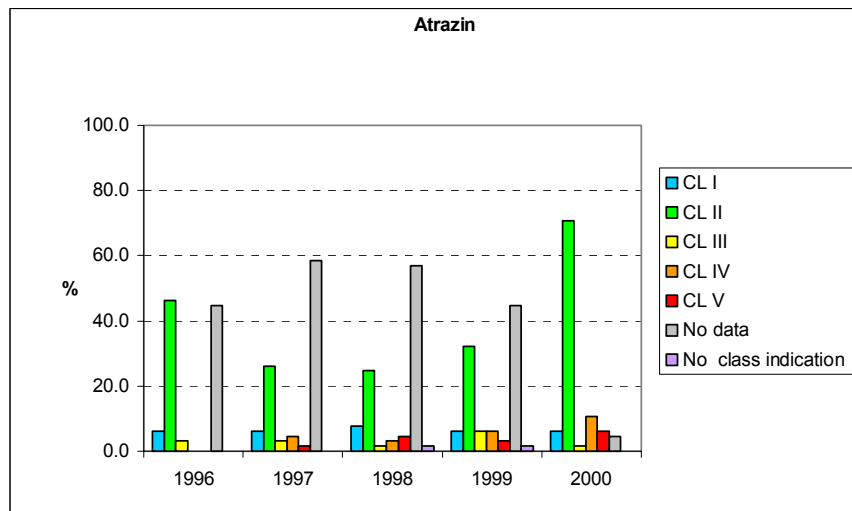
Fig. 8.1.5.7: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Atrazine**

The assessment is made based on data reported from 65 monitoring sites (therefore, out of the assessment is 38 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):
-   Class I is constantly represented by less than 8% of the considered monitoring sites;
-   percentage of sites within Class II decreases from 1996 to 1998 (reaching minimum 24,6 %) and then increases till 2000 to the level of 70.8 %;
-   the maximum percentage of sites within Class III is 6.2 % in 1999, in all other years percentage is below 4 %;
-   Class IV is represented in years 1997 – 2000, with maximum 10.8 % in 2000;
-   Class V is represented during 1997 – 2000, with the maximum value in 2000 (6.2%);
-   only 1.5 % of considered sites have "no class indication" in 1998 and 1999 (sites, in which limit of detection was higher than limit value for Class II, and therefore have not been classified).

The Atrazine concentrations in the Danube River are illustrated in **Fig. 8.1.5.8a** and **8.1.5.8b**.

In accordance to German results, Atrazine is detectable in 1999 in Danube-Neu Ulm (km 2581, D01) and excepting 1997, in all studied years in Danube-Jochenstein (km 2204, D02). According to Austrian results, in the stretch from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km 1874, A04) the only detectable values are recorded in 2000. In this stretch, no Atrazine concentration is above the target value (0.10 μg/l).

In the middle stretch from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03) Atrazine concentrations are below 0.100 μg/l, excepting one value (0.164 μg/l) at Danube-Szob in 1997. From Danube-Dunafoldvar (km 1560, H04) to Danube-Hercegszanto (km 1435, H05), Atrazine concentrations are higher, with the maximum at Danube-Hercegszanto (km 1435, H05) in 1997 (0.50 μg/l). In the middle Danube 4 values are above the target limit.

In the first part of the lower Danube, Atrazine is below reported limit of detection (0.06 μg/l), from Danube-Bazias (km 1071, RO01) to Danube-Pristol/Novo Selo (km 834, RO02) in accordance to

Romanian results. On the basis of Bulgarian results, at Danube-Novo Selo/Pristol a very high c90 value (1.316 µg/l) respresents situation in 1998.

The second part of the lower Danube shows a similar pattern to the first one. In accordance to Romanian data, Atrazine is undetectable at the respective monitoring sites - from Danube-us. Arges (km 432, RO03) to Danube-Sf. Gheorghe arm/Sf. Gheorghe arm (km 0, RO08); if the Bulgarian data are taken into account, high Atrazine values - 0.618 µg/l and 2.134 µg/l - appear in 1998 and 2000, respectively, at Danube-Silistra/Chiciu (km 375, BG05). Big differences between the reported data at cross sections make the interpretation to be rather difficult.

For the entire lower Danube, among the Atrazine values 12 of them are above the target limit of this determinand.

Atrazine c90 values for selected tributaries are illustrated in **Fig. 8.1.5.9a** and **8.1.5.9b**. It can be seen that the profile is inhomogeneous, with Atrazine values corresponding to Quality Class V on the Morava-Lanzhot (CZ02) and Tisza-Tiszasziget (H08) - 0.930 µg/l in 1998 and 0.550 µg/l in 1999, respectively. Extremely high values appear on Sio-Szekszard (H06) and Sajo-Sajopuspoki (H09) - 4.550µg/l in 1999 and 5.250 µg/l in 1997. Concerning the measured Atrazine level in selected tributaries against the target value, 18 of them are above this limit.
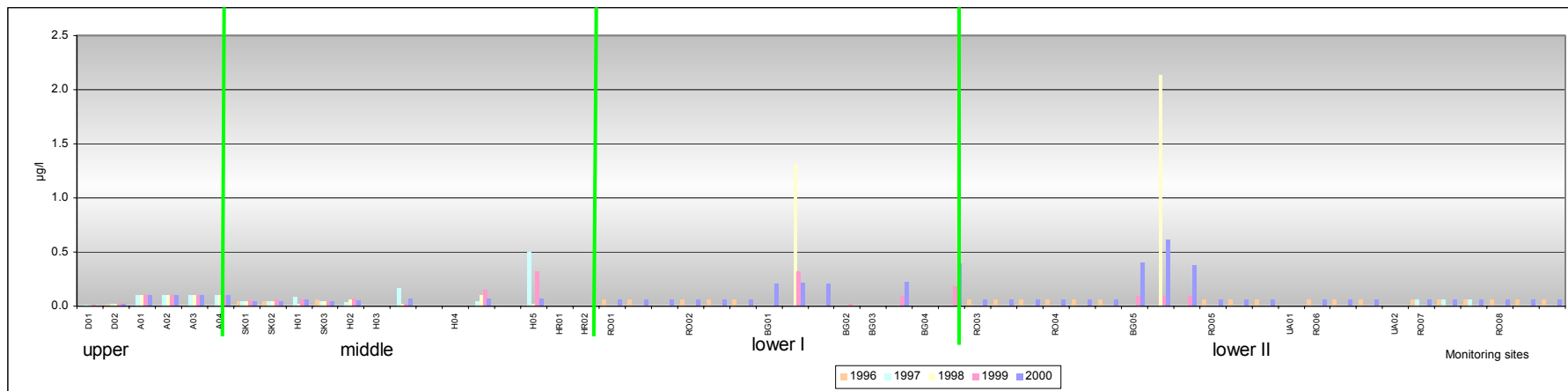
Fig. 8.1.5.8a: Spatial variation of Atrazin – Danube River
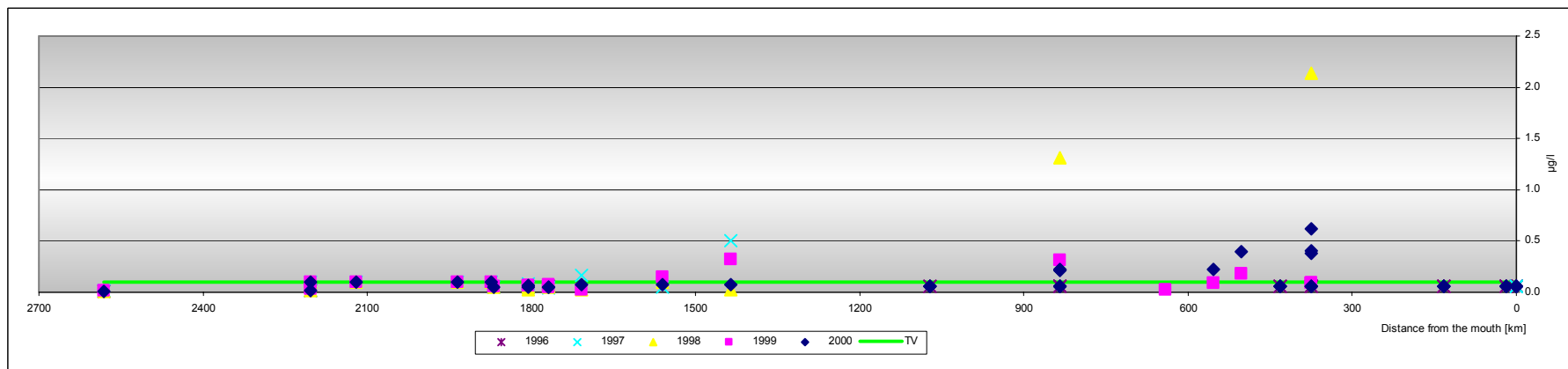
Fig. 8.1.5.8b: Spatial variation of Atrazin – Danube River
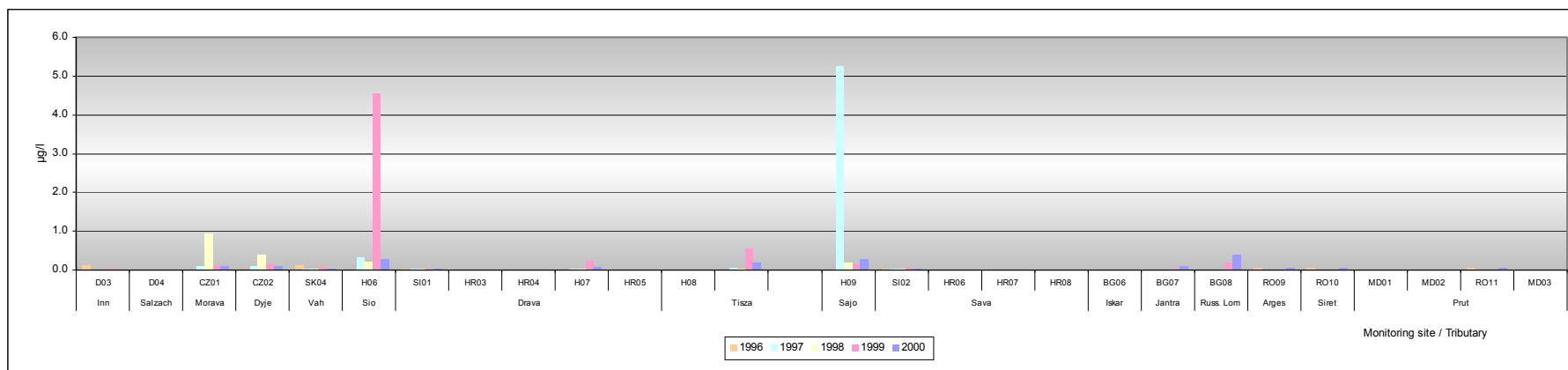
Fig. 8.1.5.9a: Spatial variation of Atrazin – Tributaries
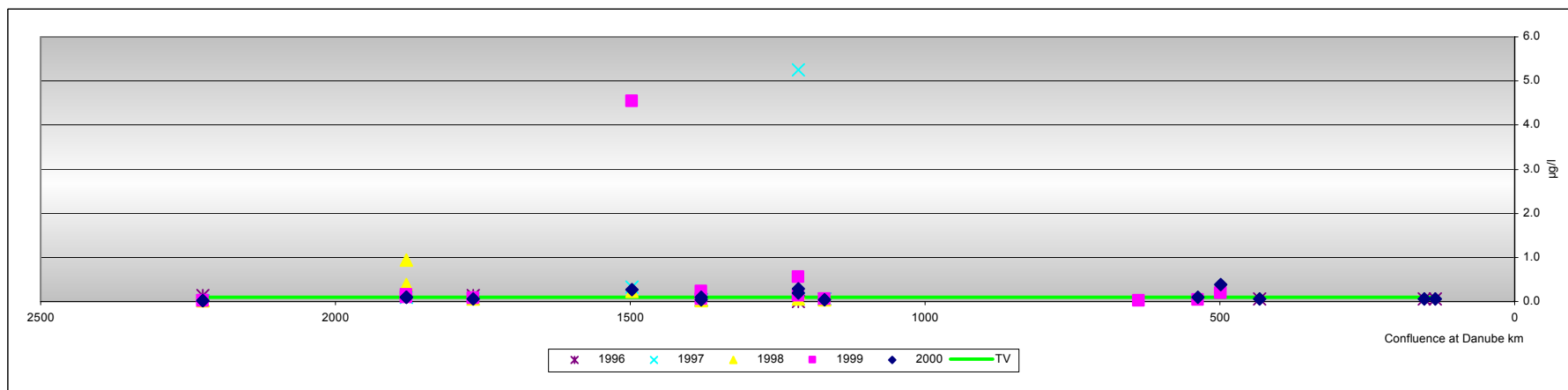
Fig. 8.1.5.9b: Spatial variation of Atrazin – Tributaries

Note: In location MD02 (98, 99) the values in the graph represent limits of detection that are higher than the target value.

Chloroform (trichloromethane)

The distribution of monitoring sites according to the Classification System in the DRB for **Chloroform** is shown in **Fig. 8.1.5.10**:
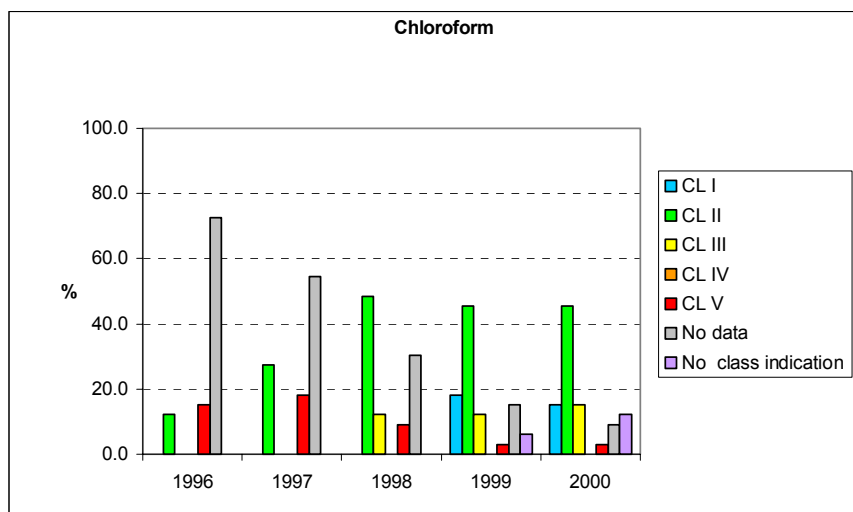
Fig. 8.1.5.10: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Chloroform**

Number of monitoring sites, in which chloroform was measured in 1996-2000, is very low - the assessment is made based on data reported from only 33 monitoring sites. Even from this low number of sites measurements were missing in more than 50 % in years 1996-97.
Completely without any measurements of chloroform during the whole period of years 1996-2000 were 70 monitoring sites.

The chloroform concentrations in the Danube River are shown in **Fig. 8.1.5.11a** and **8.1.5.11b**.

In the upper section, chloroform is undetectable during the entire studied time period. The differences in values exist because the reported limit of detection decreases from 1998 to 2000.

In the middle section, the concentration profile has very large limits of variation. A relevant example appears at Danube-Bratislava (km 1869, SK01), where chloroform is undetectable in 1999 but has a very high value in 1997 (189.1 μg/l). Downstream this monitoring site, from Danube-Medvedov/Medve (km 1806, SK02) to Danube-Komarno/Komarom (km 1768, SK03) according to Slovak data, chloroform shows concentrations values much higher than those reported by the Hungarian part at the respective cross sections. In the middle stretch, 18 concentrations are above the target limit (0.6 μg/l).

In the entire lower section, for only two monitoring sites data characterising chloroform content exist: Danube-Novo Selo/Pristol (km 834, BG01) in 2000 and Danube-Silistra/Chiciu (km 375, BG05) in 1999. All   results show that chloroform is undetectable at the reported limit of detection of 0.02 μg/l.

The values of chloroform concentrations for selected tributaries are shown in **Fig. 8.1.5.12a** and **8.1.5.12b**. The measured concentrations are quite high, with 17 values above the target limit. The most elevated values are the following:

- the Morava-Lanzot (CZ02): 3.360 μg/l in 1997;
- the Vah-Komarno (SK04): 10.310 μg/l in 1996 and 81.800 μg/l in 1997;
- the Drava-Ormoz (SL01): 3.000 μg/l in 2000;
- the Sajo-Sajopuspoki (H09): 4.060 μg/l in 1996 and 2.900 μg/l in 1997;
- the Sava-Jesenice (SL02): 3.000 μg/l in 1999.

By comparing the results with those obtained by JDS it can be concluded that in the frame of JDS were not detected such high values as in the TNMN in case of several monitoring sites. High values of chloroform sporadically found in Danube River or its tributaries can indicate that sources of pollution were still not sufficiently under control (under assumption that analysis of chloroform was correct.) As can be seen later in the text, in Slovak section of Danube River and on Vah tributary also other substances from the group of volatile organic compounds are sporadically recorded in high concentrations.
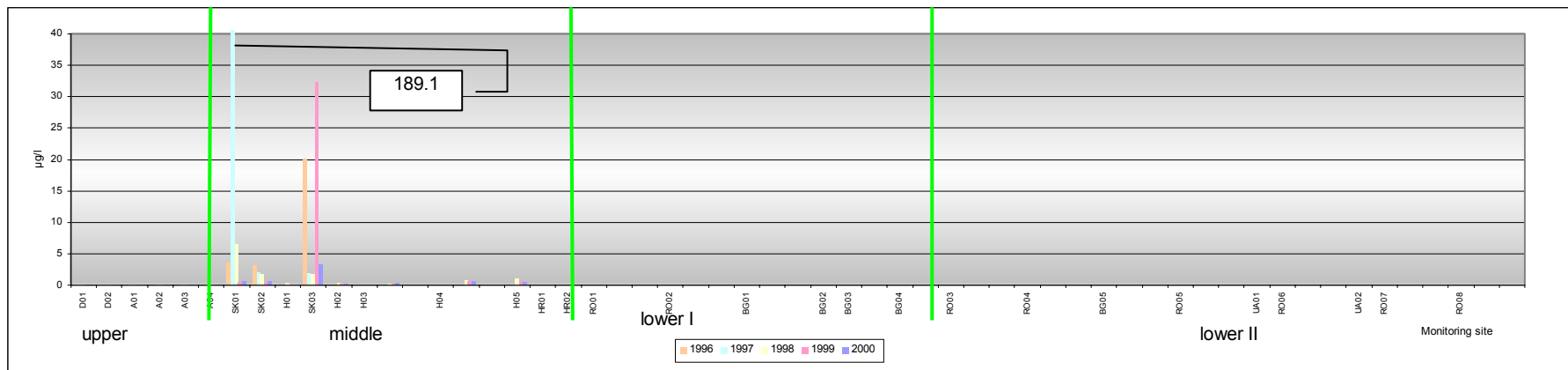
Fig. 8.1.5.11a: Spatial variation of Chloroform – Danube River
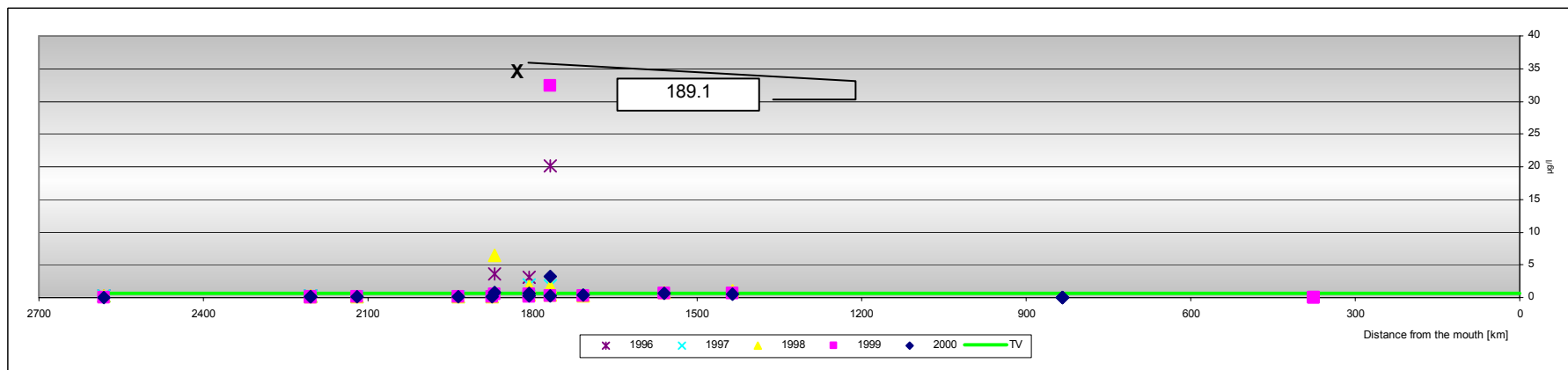
Fig. 8.1.5.11b: Spatial variation of Chloroform – Danube River
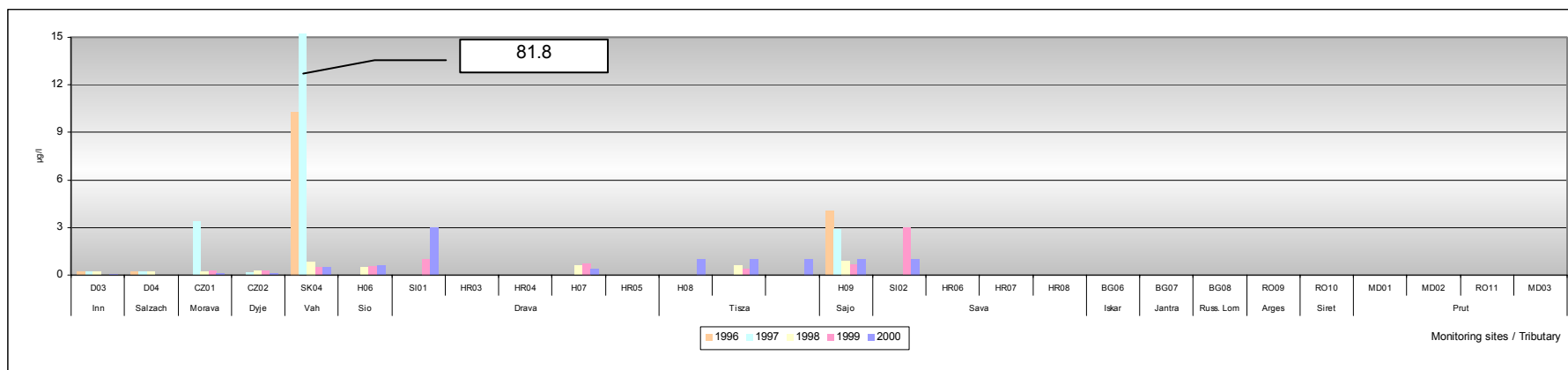
Fig. 8.1.5.12a: Spatial variation of Chloroform – Tributaries
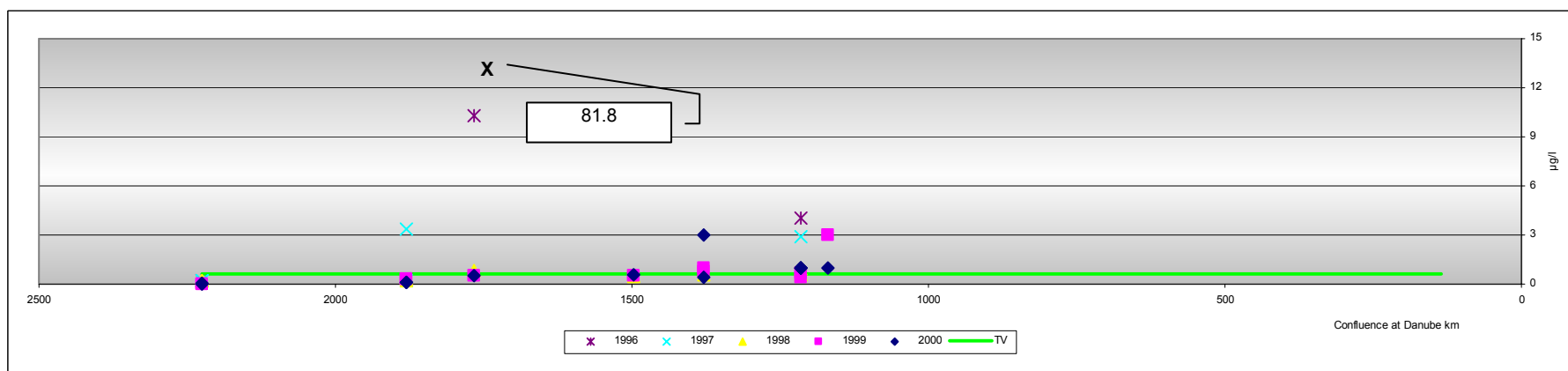
Fig. 8.1.5.12b: Spatial variation of Chloroform – Tributaries

Note: In locations SL01, SL 02 (99, 00) and H08 (00) the values in the graph represent limits of detection that are higher than the target value.

Carbon tetrachloride (tetrachloromethane)

The distribution of monitoring sites according to the Classification System in the DRB for **Carbon tetrachloride** is shown in **Fig. 8.1.5.13**:
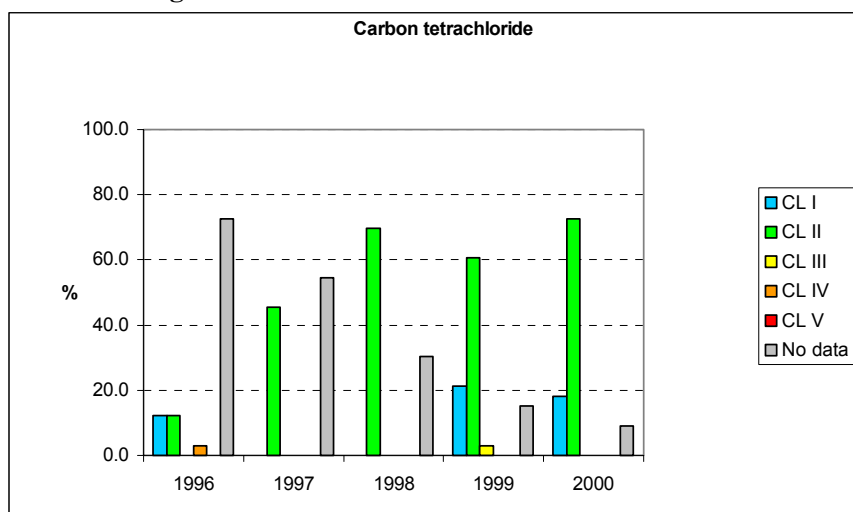
Fig. 8.1.5.13: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Carbon tetrachloride**

The situation in availability of data on tetrachloromethane is the same as in case of chloroform. The assessment is made based on data reported from only 33 monitoring sites, and absolutely no measurements had been done in 1996-2000 in 70 monitoring sites.
Class II was prevailing in monitoring sites, but due to the lack of data it is not possible to provide a satisfactory picture on the occurance of the substance in water in the whole river basin.

The spatial profile for carbon tetrachloride in the Danube River is shown in **Fig. 8.1.5.14a** and **8.1.5.14b**.

Similar to chloroform, carbon tetrachloride shows undetectable values in the upper Danube, even if the levels look different (due to differences among limits of detection).

In the middle section of the Danube, tetrachloride is detectable in 1999 only according to Slovak data and mainly during 1998-2000 according to Hungarian data. The measurable concentrations for this stretch vary within the range 0.095 - 0.600 μg/l, with maximum at Danube-Dunafoldvar (km 1560, H04).

The entire lower section of the Danube as well as the corresponding tributaries has no reported data for this organic micropollutant, with two exceptions: Danube-Novo Selo/Pristol (km 834, BG01) in 2000 and Danube-Silistra/Chiciu (km 375, BG05) in 1999. All results show that carbon tetrachloride is undetectable at the reported limit of detection of 0.02 μg/l.

It has to be mentioned that no concentration measured in the Danube River is above the target limit (1.000 μg/l).

The measurable values for carbon tetrachloride in the selected tributaries are shown in Fig. 8.1.5.15a and 8.1.5.15b. The highest value observed in Sajo/Sajopuspoki (H09) – 2.460 μg/l in 1996. The concentrations values that appear at the level of 1.00 μg/l, in Drava-Ormoz (SL01), Sava-Jesenice (SL02) and Tisza-Tiszasziget (H08) are caused by the rather high limit of detection, equal to the target value for this determinand.
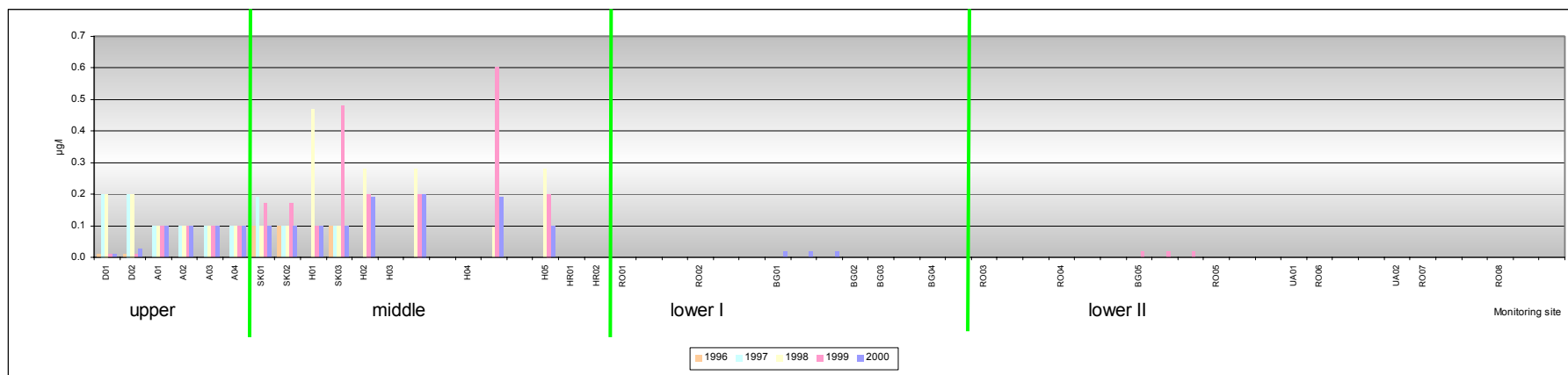
Fig. 8.1.5.14a: Spatial variation of Carbon tetrachloride – Danube River
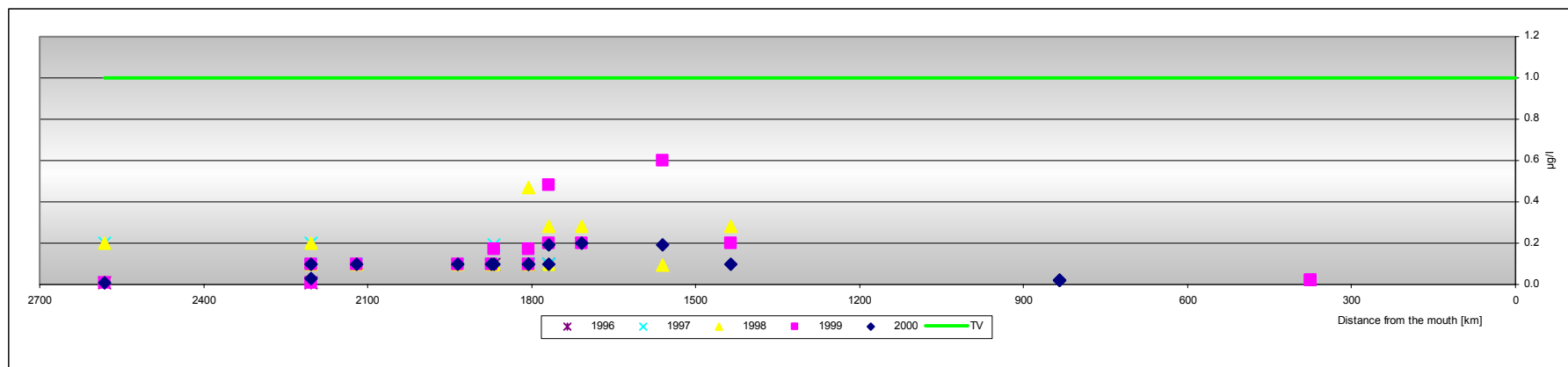
Fig. 8.1.5.14b: Spatial variation of Carbon tetrachloride – Danube River
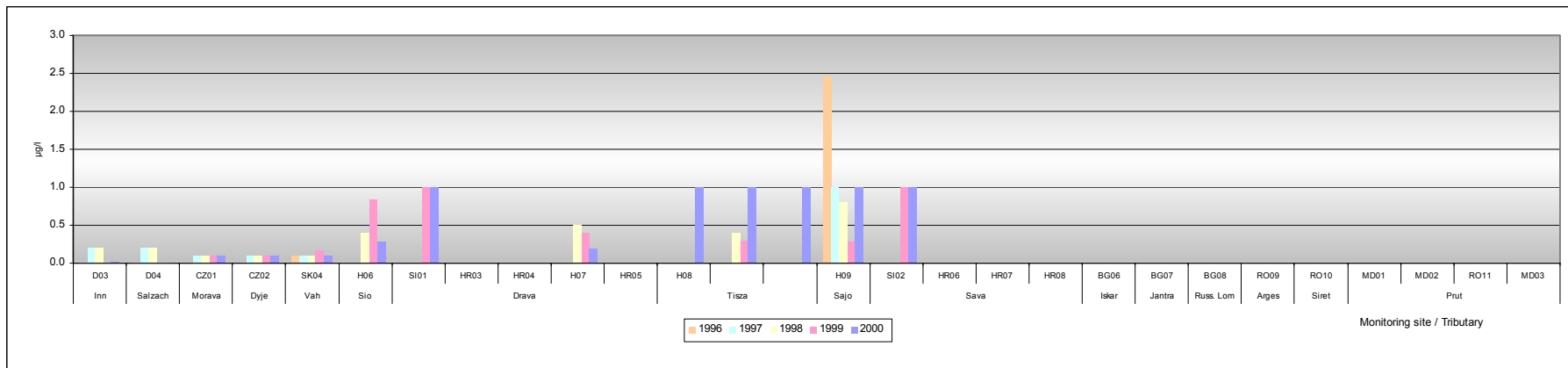
Fig. 8.1.5.15a: Spatial variation of Carbon tetrachloride – Tributaries
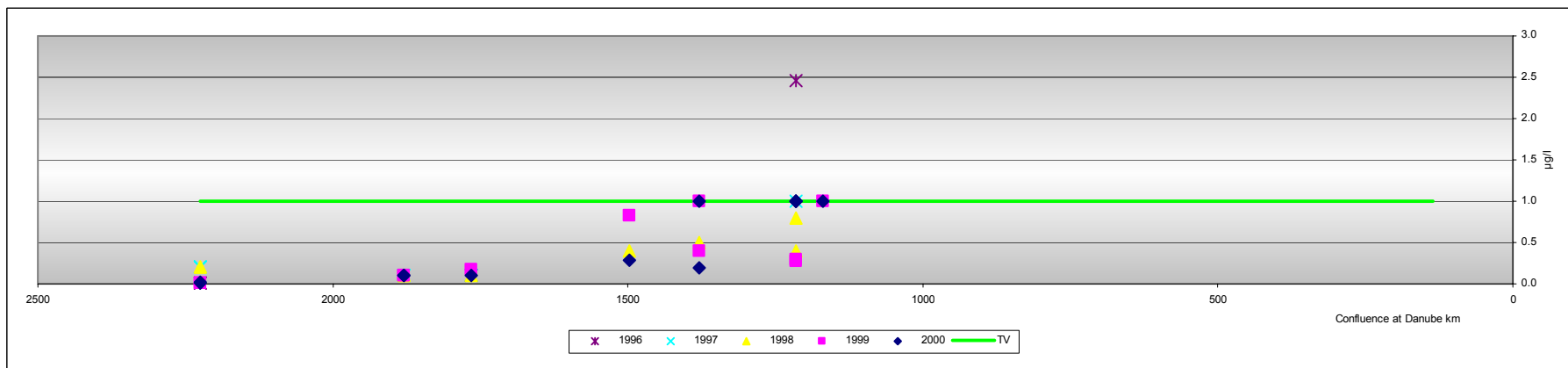
Fig. 8.1.5.15b: Spatial variation of Carbon tetrachloride – Tributaries

Trichloroethylene

The distribution of monitoring sites according to the Classification System in the DRB for **Trichloroethylene** is shown in **Fig. 8.1.5.16**:
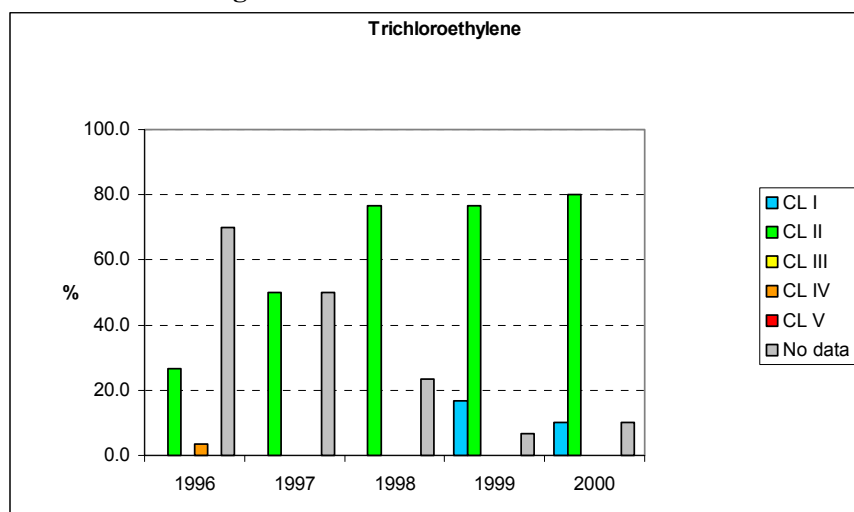
Fig. 8.1.5.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Trichloroethylene**

The assessment is made based on data reported from 30 monitoring sites, therefore without any measurement in 1996-2000 is 73 monitoring sites from Phase I List of Monitoring Sites. Number of sites with trichloroethylene is very low, but in the sites with measurements Class II is prevailing.

The spatial profile of trichloroethylene concentrations in the Danube River is illustrated in **Fig. 8.1.5.17a** and **8.1.5.17b**.

In the upper Danube, trichloroethylene is detectable in 1999 only at Danube-Neu Ulm (km 2581, D01) and Danube-Wolfsthal (km 1874, A04) and in 1999-2000 at Danube-Jochenstein (km 2204, D02), according to German data.

The middle stretch is characterized by undetectable levels of trichloroethylene, with three exceptions, all recorded in 1998, at Danube-Bratislava (km 1869, SK01), Danube-Dunafoldvar (km 1560, H04) and Danube-Herceszanto (km 1435, H05).

In the lower section, data for this determinand are reported from only one monitoring site - Danube-Silistra/Chiciu (km 375, BG05) in 1999, with undetectable values.

No concentration of trichloroethylene in the Danube River is above the target limit (1.00 μg/l).

Undetectable concentrations are observed also in almost all selected tributaries, relative to the reported limits of detection. The only measurable values appear on the Sajo-Sajopuspoki (H09); the maximum value - 2.42 μg/l in 1996 - is the only one above the target limit for trichloroethylene in tributaries – **Fig. 8.1.5.18a** and **8.1.5.18b.**
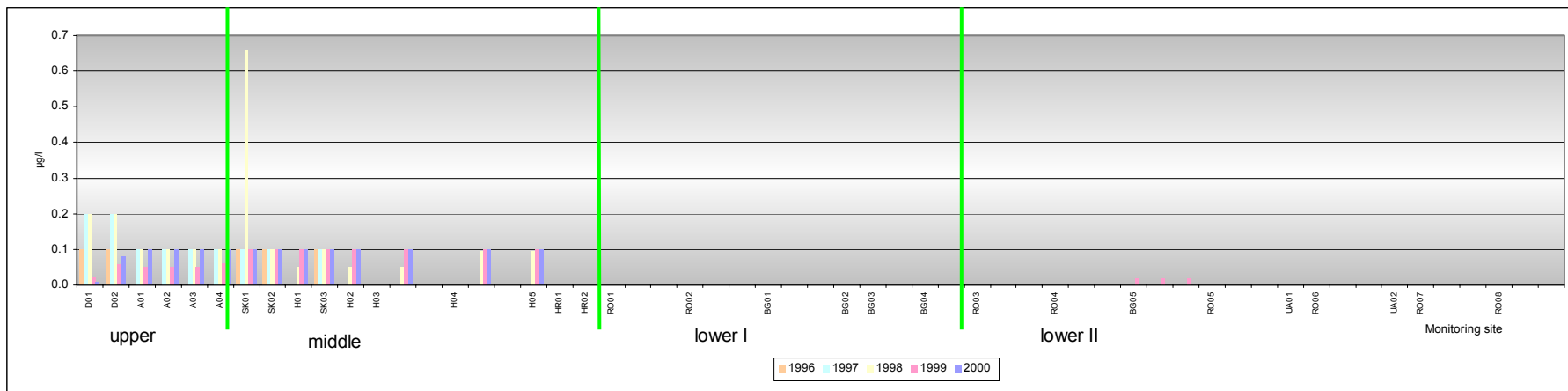
Fig. 8.1.5.17a: Spatial variation of Trichloroethylene – Danube River
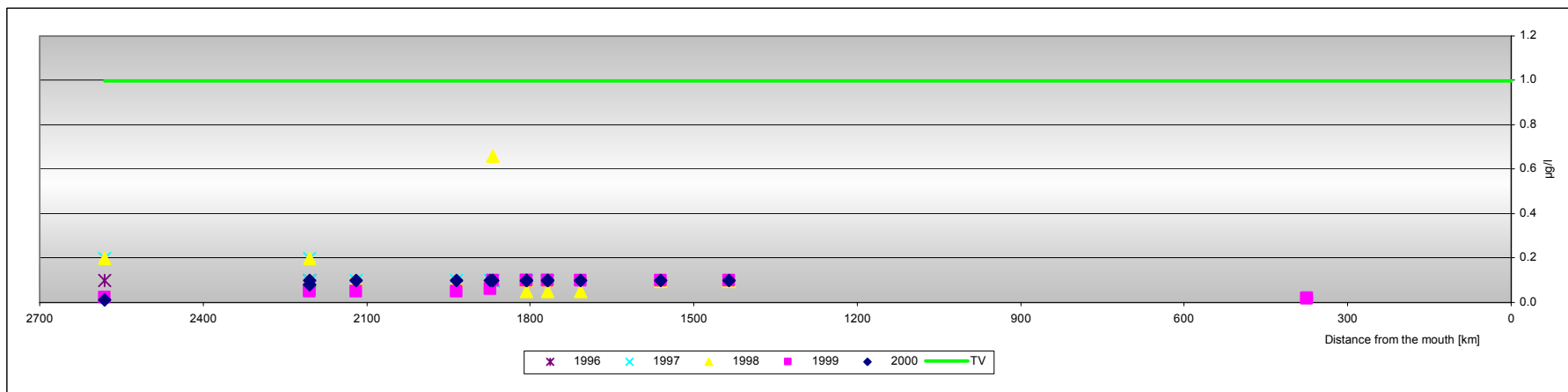
Fig. 8.1.5.17b: Spatial variation of Trichloroethylene – Danube River
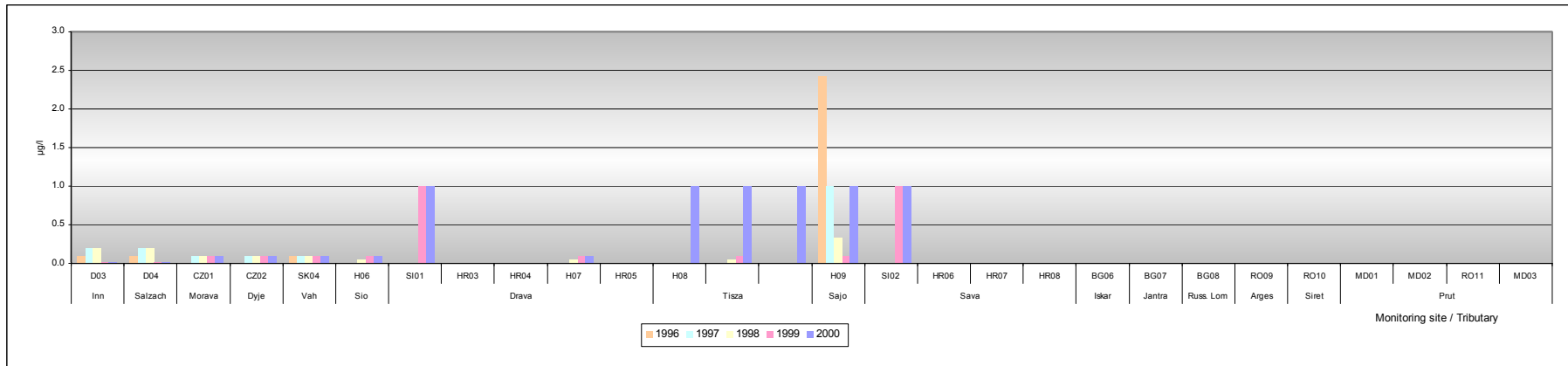
Fig. 8.1.5.18a: Spatial variation of Trichloroethylene – Tributaries
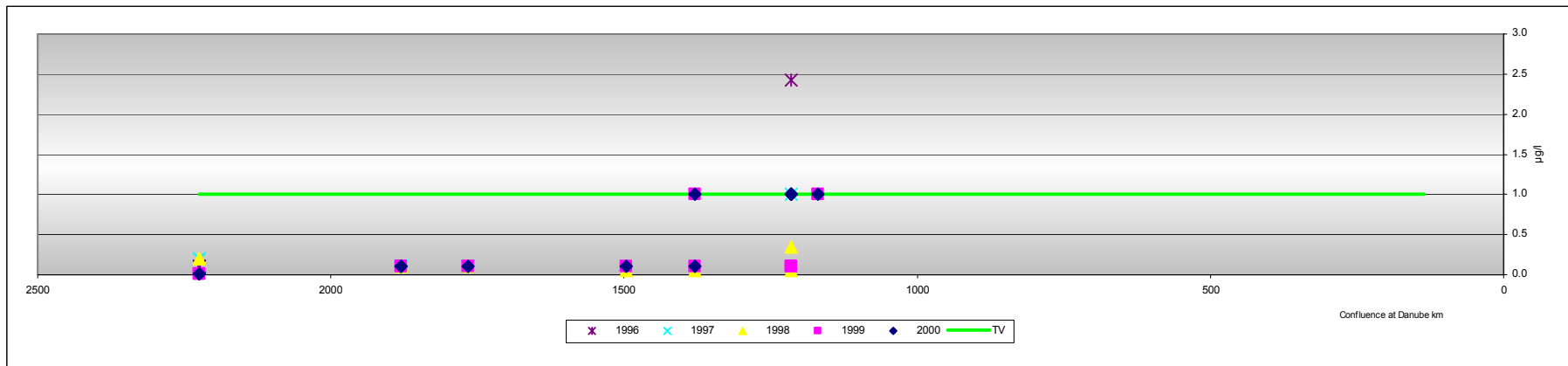
Fig. 8.1.5.18b: Spatial variation of Trichloroethylene – Tributaries

Tetrachloroethylene

The distribution of monitoring sites according to the Classification System in the Danube River basin for **Tetrachloroethylene** is shown in **Fig. 8.1.5.19**:
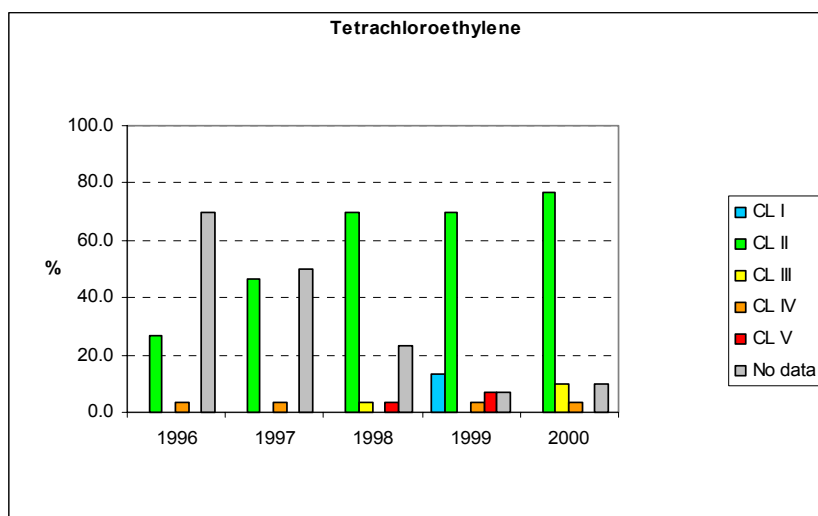
Fig. 8.1.5.19 : Distribution of monitoring sites (%) according to the Classification System in the Danube River basin for **Tetrachloroethylene**

The data on occurance of tetrachloroethylene were reported from 30 monitoring sites; out of the assessment is 73 monitoring sites, in which no measurements had been done in 1996-2000. Majority of sites with tetrachloroethylene measurement correspond to class II, but classes III – V are also represented.

The spatial profile of tetrachloroetylene concentrations in the Danube River is illustrated in **Fig. 8.1.5.19a** and **8.1.5.19b**. Unlike trichloroethylene, tetrachloroetylene is detectable at Danube-Neu Ulm (km 2581, D01) in 1998-2000 and at Danube-Jochenstein (km 2204, D02) in 1996 and 1999-2000 according to German data, but no value is above the target limit for this determinand (1.000 μg/l). If the Austrian data are taken into account, tetrachloroethylene is undetectable from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km 1874, A04).

In the middle stretch, it can be noticed that values above 2.00 μg/l from Danube-Medvedov/Medve (km 1806, SK02) to Danube-Komarno/Komarom (km 1768, SK03), according to Slovak data. According to Hungarian data at the same cross sectioned, tetrachloroetylene is undetectable. Particularly at Danube-Bratislava (km 1869, SK01), an extreme high value was observed in 1999 – 16.5 μg/l. Also according to Slovak data, in the middle Danube 8 concentrations are above the target limit.

The profile of tetrachloroethylene concentrations measured in selected tributaries, illustrated in **Fig. 8.1.5.20a** and **8.1.5.20b**, presents the following features:
- tributaries from the upper Danube show undetectable levels of tetrachloroetylene, mainly during 1996 – 1998, even though the values are different within the five years (again, different limits of detection);
- in the middle Danube, on the Vah-Komarno (SK04) higher concentrations appears in 1999 and 2000 – 1.000 μg/l and 2.26 μg/l respectively, but only the second one is above the target limit;
- two concentrations above the target limit are also recorded on Sajo-Sajopuspoki (H09) – 2.420 μg/l in 1996 and 3.100 μg/l in 1997;
- it has to be mentioned that values that appear on the Drava-Ormoz (SL01), Tisza-Tiszasziget (H08) and Sava-Jesenice (SL02) tributaries have the same explanation as in the case of trichloroethylene - the reported values are the limits of detection, hence tetrachloroethylene was undetected at the respective monitoring sites.
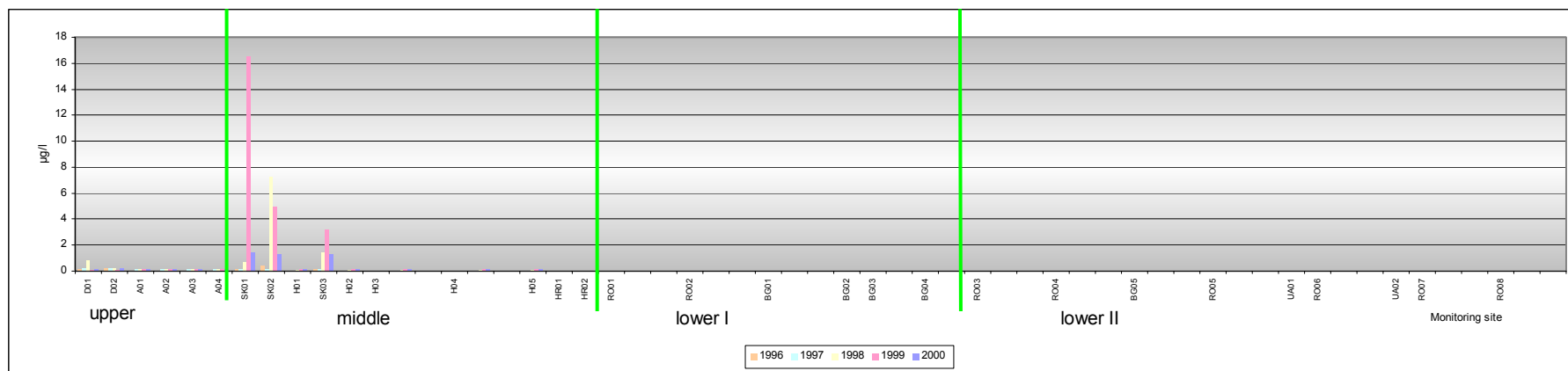
Fig. 8.1.5.19a: Spatial variation of Tetrachloroethylene – Danube River
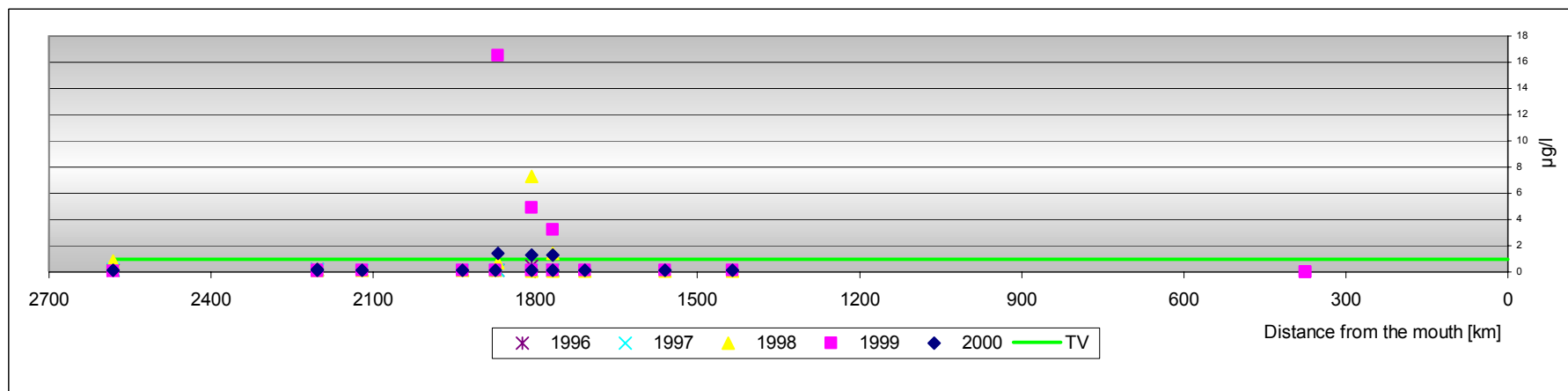
Fig. 8.1.5.19b: Spatial variation of Tetrachloroethylene – Danube River
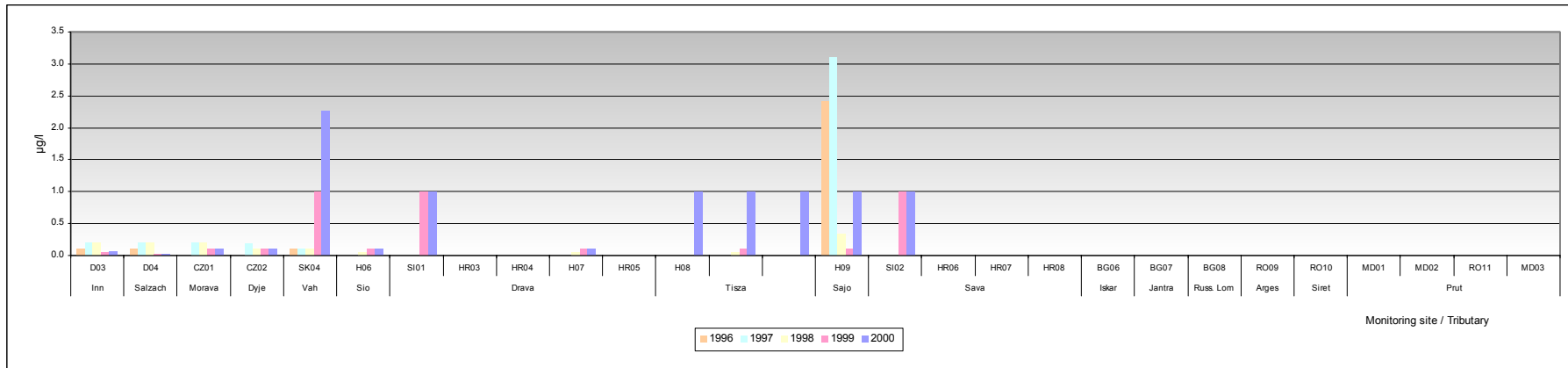
Fig. 8.1.5.20a: Spatial variation of Tetrachloroethylene – Tributaries
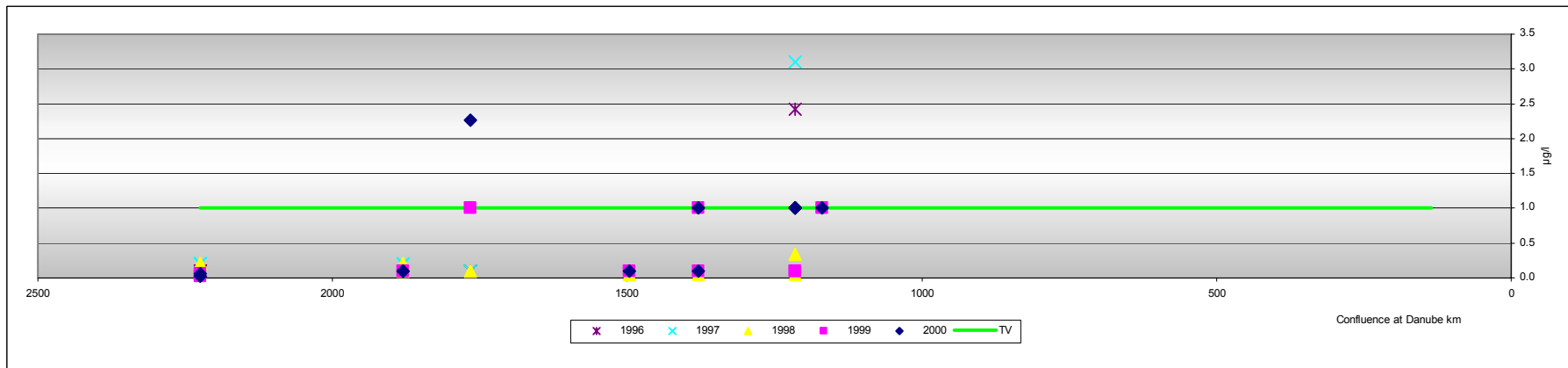
Fig. 8.1.5.20b: Spatial variation of Tetrachloroethylene – Tributaries

8.1.6.   Results of Comaprison of TNMN data with Environmental Quality Standards of EU legislation

8.1.6.1.   General comments regarding analytical data

It has to be noted that for some of the substances discussed in the following the data base shows considerable gaps, mainly in the lower stretch of the Danube River. If data are available the data set of one year sometimes consists of one or two measurements only. To avoid a further restriction of the overall picture such data have not been excluded from the evaluation.

In processing and representation of the data the following rules have been applied:
- Obviously erroneous data have been discarded
- All data sets of one year with at least one result greater than the LOD have been taken into consideration. The mean was calculated with the "LOD-method" in selected cases in addition with the "Zero-method"
- Data sets of one year where all data were below the LOD have not been included in the graph
- Mean values deviating from the reported LOD have been excluded when they obviously were produced by a LOD change within one year without any result greater than LOD (in the data base only one LOD per year and method can be stored, differing "less than" values within one year reflect a LOD change and result in a "mean of LODs" value which deviates from the stored LOD)

The mentioned limitations of the data base should be taken into account in the following assessment of the results. The focus should be better on the overall picture for a substance than on a single result.

8.1.6.2.   Atrazine

For Atrazine a nearly complete data set is available. The LOD ranges between 0,01 and 0,06 µg/l, in a few cases up to 0,1 µg/l. Atrazine was included in the list of Priority Substances. With regard to the proposed EQS of 0,34 µg/l the Atrazine concentration at all sampling sites seems to be no problem even with the used worst case calculation of the mean (see **Figure 8.1.6.2.1**). In 1998 rather high values have been measured at two sampling sites which exceed the proposed EQS, but also at this sites the mean concentration went down below 0,34 µg/l in the consecutive years.

8.1.6.3.   Cadmium (total)

The results for Cadmium (total) are characterised by high mean values in the range of 1 to 8 µg/l in lower part of Danube River (see **Figure 8.1.6.3.1**). The extreme values are caused by single data one order of magnitude higher than the rest of the data set. But even when this data are excluded the mean values lie very close to or even above the List 1 EQS of 1 µg/l for total Cadmium stipulated in CD 83/514/EEC (EEC 1983). Also an recalculation of the mean with the optimistic convention of setting values below LOD to zero does not change the situation because only few results are smaller than the method LODs (range: 0,01 - 1,0 µg/l). The results therefore indicate a severe Cadmium pollution for this Danube stretch although the concentration seems to decrease in 2000 in comparison particularly with 1997 and 1999. In the upper part of the river the mean concentrations are well below the EQS with exception of a few results in 1996/97.

8.1.6.4.   Cadmium (dissolved)

For the derivation of EQS for metals FHI proposes to use the "added risk" approach, originally introduced in the Netherlands. The reasoning behind this approach is that the adaptation of the ecosystem in a certain region with a natural metal background concentration is part of the natural biodiversity of this ecosystem. With the assumption that in different adapted ecosystems the same

amount of a metal added by human activities (maximum permissible addition - MPA) causes the same effect the EQSadd can be derived with the following equation:

EQSadd = Cbackground + MPA

where Cbackground is the natural metal background concentration of the region under concern. Cbackground estimates can be gained e.g. by evaluating monitoring data of pristine areas for the region. The MPA values are derived independently according to the procedure of Annex V, 1.2.6 of the WFD.

For Cadmium FHI proposes a MPA value of 0,08 µg/l for the dissolved fraction. Due to the fact that background concentrations may change along the Danube and may not be available for all regions, in a first approximative evaluation only the MPA was compared with TNMN results.

For Cadmium (dissolved) only few data and only for the upper part of Danube River are available in the data base. LOD ranges from 0,02 to 0,2 µg/l. With this very low EQS and the application of the LOD-method the results exceed the limit value in most cases (see Figure 8.1.6.4.1).

The situation might be improved by two measures:
- taking into account Cbackground once these vaules have been determined for the different river stretches
- using a more optimistic method for calculation of the mean

To show the influence of the second option an additional diagramm has been produced applying the "Zero-method" (see Figure 8.1.6.4.2).

8.1.6.5. p,p'-DDT

For p,p'-DDT in the upper part of the Danube practically all data are below LOD (LODs range between 0,005 and 0,05 µg/l). Downstream Hungary an increase in DDT concentration can be seen, resulting in mean values up to 0,4 µg/l. In this area the EQS of 0,01 µg/l for p,p'-DDT laid down in CD 86/280/EEC (EEC 1986) is exceeded in many cases (see **Figure 8.1.6.5.1**). Similar to Cadmium (total) change of the calculation method of the mean does not improve the situation because most of the data are above the method LODs.

8.1.6.6. Lead (dissolved)

As for the other metals data for the dissolved fraction of lead are very scarce and are only availbale for the upper stretch of the Danube (see figure **Figure 8.1.6.6.1**). The LOD ranges from 0,2 to 1 µg/l. Because of many less than values the influence of the calculation method is significant but even with the "LOD-method" most of the results are close to or below the MPA value of 1 µg/l proposed by the FHI (for explanation of MPA see Cadmium (dissolved)).

8.1.6.7. Lindane (gamma - Hexachlorocyclohexane)

Going down the Danube a sharp increase in Lindane concentration is noticable. The LOD of methods ranges from 0,001 to 0,1 µg/l. For Lindane one EQS is in force (0,05 µg/l laid down in CD 84/491/EEC (EEC 1984/2) for the sum of Hexachlorcyclohexane isomers). This value will be substituted by the FHI proposal of 0,02 µg/l in near future. While the EQS in force is only exceeded by the extreme values with new limit value the situation will get worse (see **Figure 8.1.6.7.1**). The influence of the calculation method is shown in **Figure 8.1.6.7.2**.

8.1.6.8.   Mercury (total)

For Mercury CD 82/176/EEC (EEC 1982) states an EQS of 1 µg/l. The data base provides only results for the upper part of the Danube including Hungary and Croatia. For the lower part of the Danube no data for Mercury are available at all. LODs lie mainly within 0,1 to 0,2 µg/l. The existing results show only one exceedance of the EQS caused by an extreme concentration in 1999, which can be also observed downstreams throughout Hungary (see **Figure 8.1.6.8.1**). All other mean values are well below the List 1 EQS.

8.1.6.9.   Mercury (dissolved)

Mercury is also included in the List of Priority Substances. FHI proposes an MPA of 0,036 µg/l for the dissolved metal fraction (for explanation of MPA see Cadmium (dissolved)). Again for the dissolved fraction are only very few data are available (see **Figure 8.1.6.9.1**) which in all cases exceed the limit value. The LODs (0,03 - 0,2 µg/l) lie very close or above the EQS which leads to high mean values when using the LOD-method. Switching to the Zero-method (see **Figure 8.1.6.9.2**) changes the picture dramatically. Mercury (dissolved) is one of the cases where the used convention for calculationg the mean influences the results of the compliance check to a very high degree.

8.1.6.10. Nickel (dissolved)

Nickel and its compounds is the fourth metal included in the Priority Substance list. Similar to other metals data are scarce for the dissolved fraction. Comparison with the proposed MPA of 0,6 µg/l (for explanation of MPA see Cadmium (dissolved)) shows exceedance of the EQS to a high extent for all results (see **Figure 8.1.6.10.1**). Also in this case the LODs (0,2 - 1,0 µg/l) are very close to the EQS. Therefore the influence of the calculation method was checked out (see **Figure 8.1.6.10.2**).

8.1.6.11. Chlorinated compounds
(Tetrachlorethane, Tetrachlormethane, Trichlorethene, Trichloromethane)

For these four compounds the situation is very similar in many respects. For all substances EQS are laid down in CD 86/280/EEC (EEC 1986, Tetrachloroethane, Trichlorethane: 10 µg/l, Tetrachlormethane, Trichloromethane: 12 µg/l). Data for these compounds are only available in the upper stretch of the Danube. LODs range from 0,01 to 0,5 µg/l. For Tetrachlorethane, Tetrachlormethane and Trichlorethene the results are well below the respective EQS values (see **Figure 8.1.6.11.1 – 8.1.6.11.4**). Trichloromethane exceeds the EQS of 12 µg/l in one case and shows the highest concentration in general. Its also the only one of the four compounds which has been included in the list of Priority Substances. FHI prosposes an EQS of 3,85 µg/l which increases the number of exceeding concentrations to three in the five year period.

8.1.6.12. Recommendations for future changes in TNMN regarding the needs of the EU WFD

In future TNMN investigations it should be clearly distinguished between the terms limit of detection (LOD) and limit of quantification (LOQ) should be clearly defined, following the definitions used by the EU. A review of the ANAMETH-file having in mind this definitions should be carried out and both quantities included in future data sets.

The discussions on EU level concerning the statistical quantity used for compliance checking and the calculation of this quantity in the case of less than values should be carefully followed and the results integrated in the TNMN to keep up comparability of the data and compliance with EU legislation, which is of utmost importance for at least the half of the riparian states.
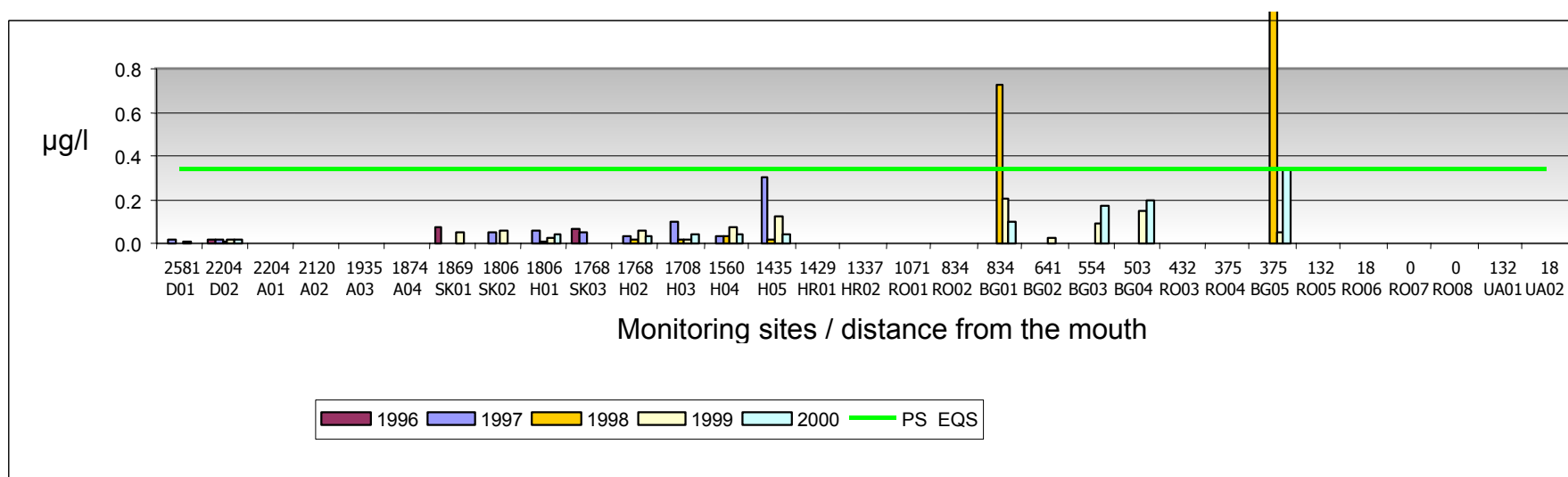
Figure 8.1.6.2.1: Atrazine
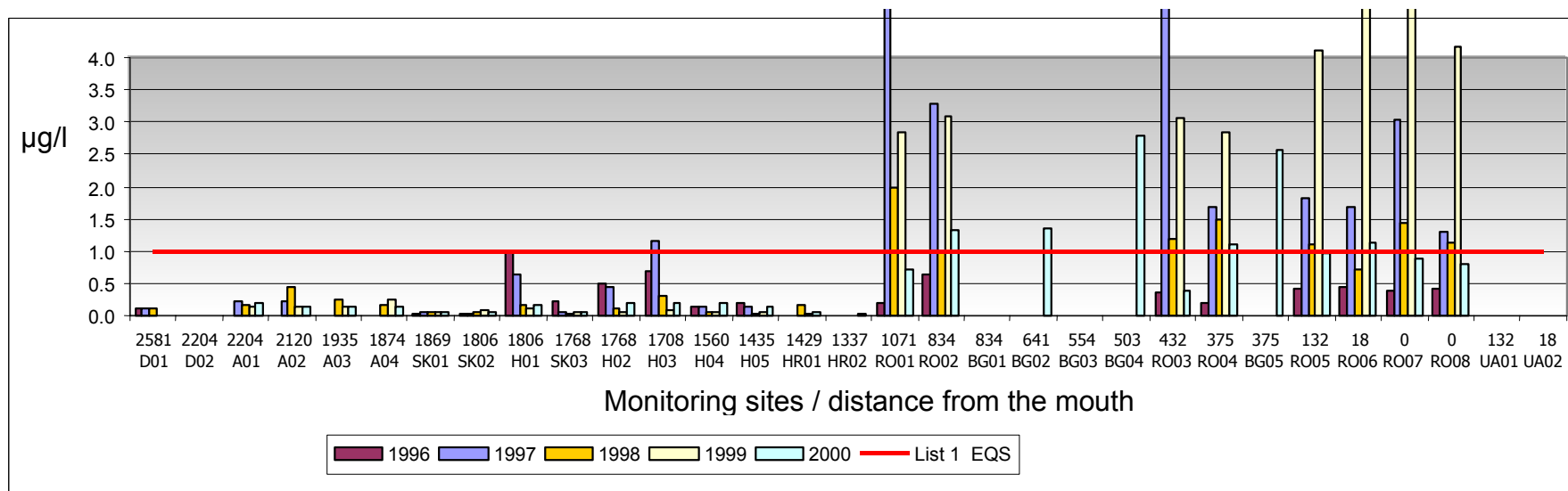
Figure 8.1.6.3.1: Cadmium (total)
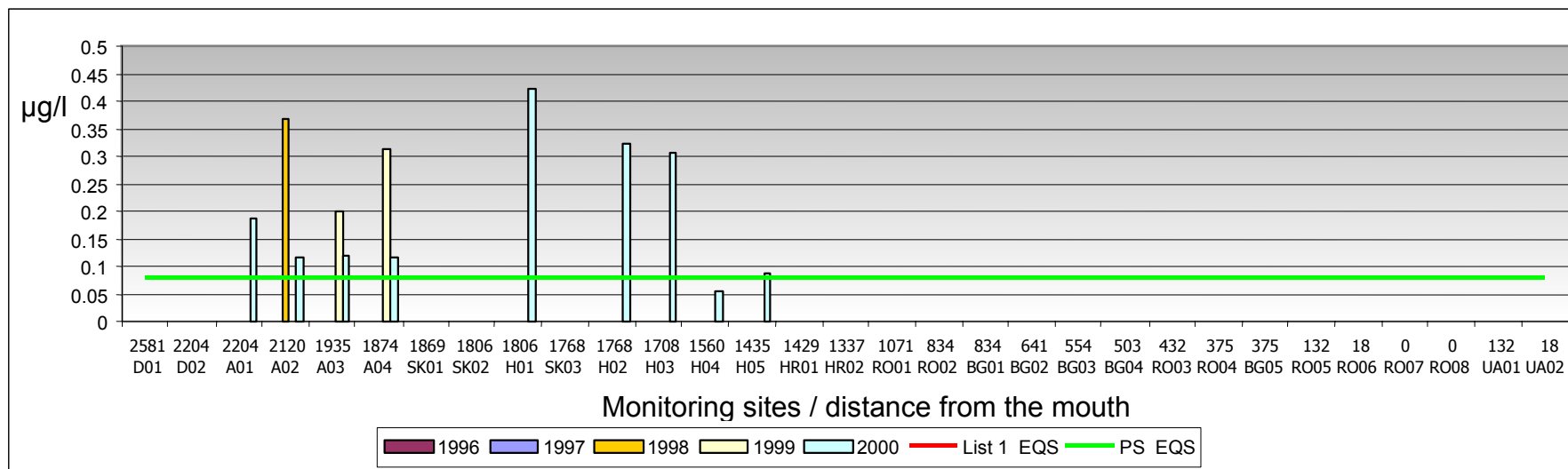
Figure 8.1.6.4.1: Cadmium (dissolved) - LOD method
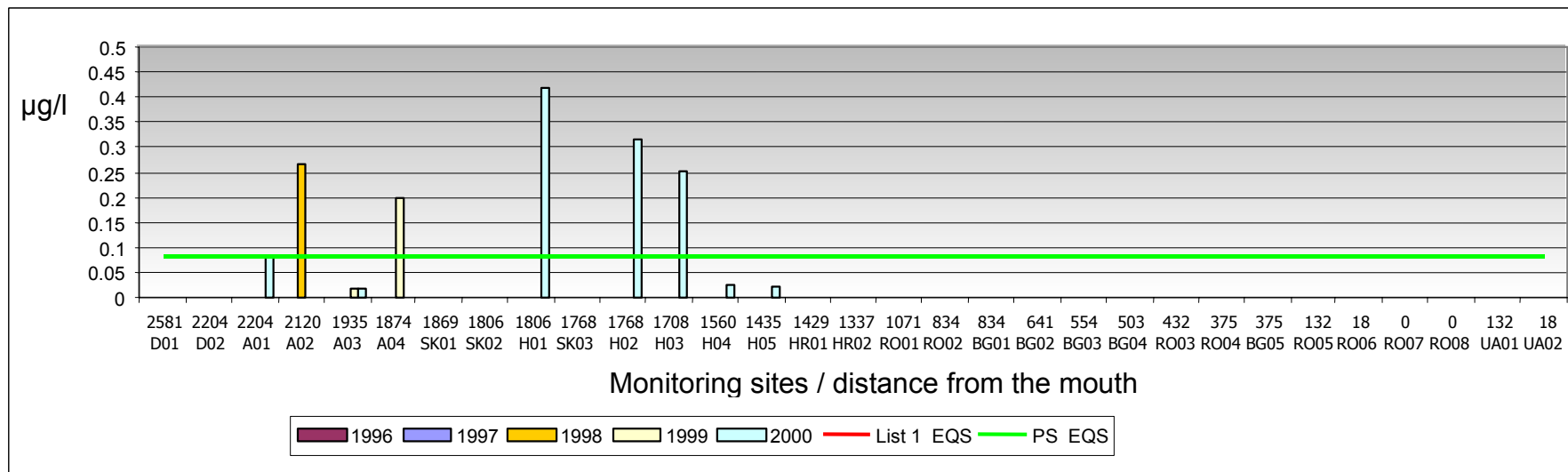
Figure 8.1.6.4.2: Cadmium (dissolved) - Zero-method
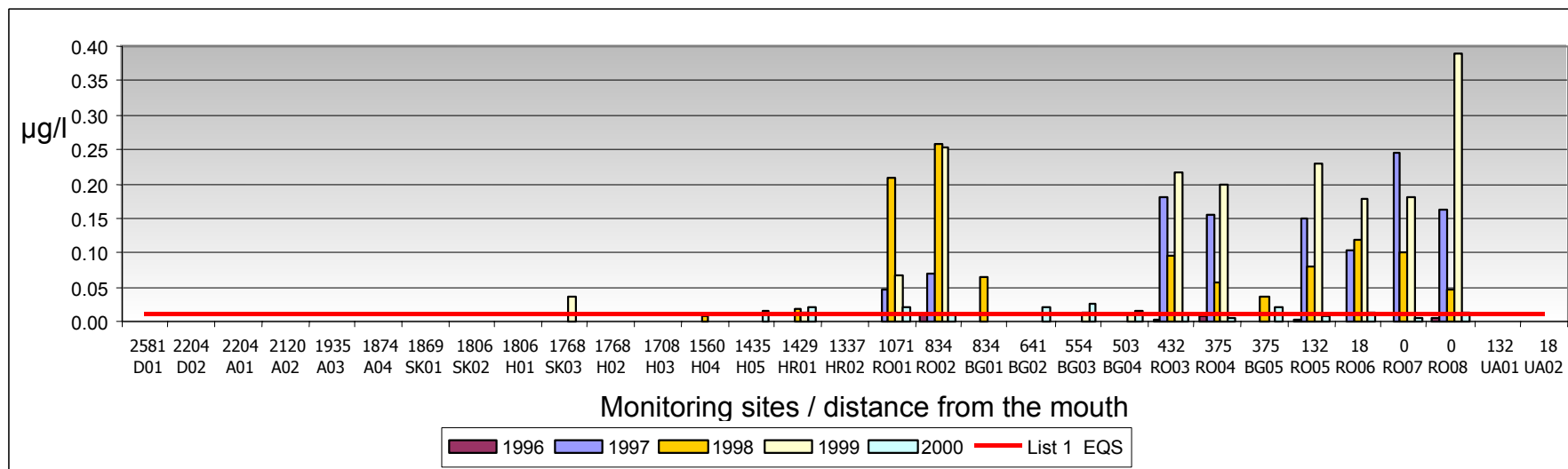
Figure 8.1.6.5.1: p,p-DDT
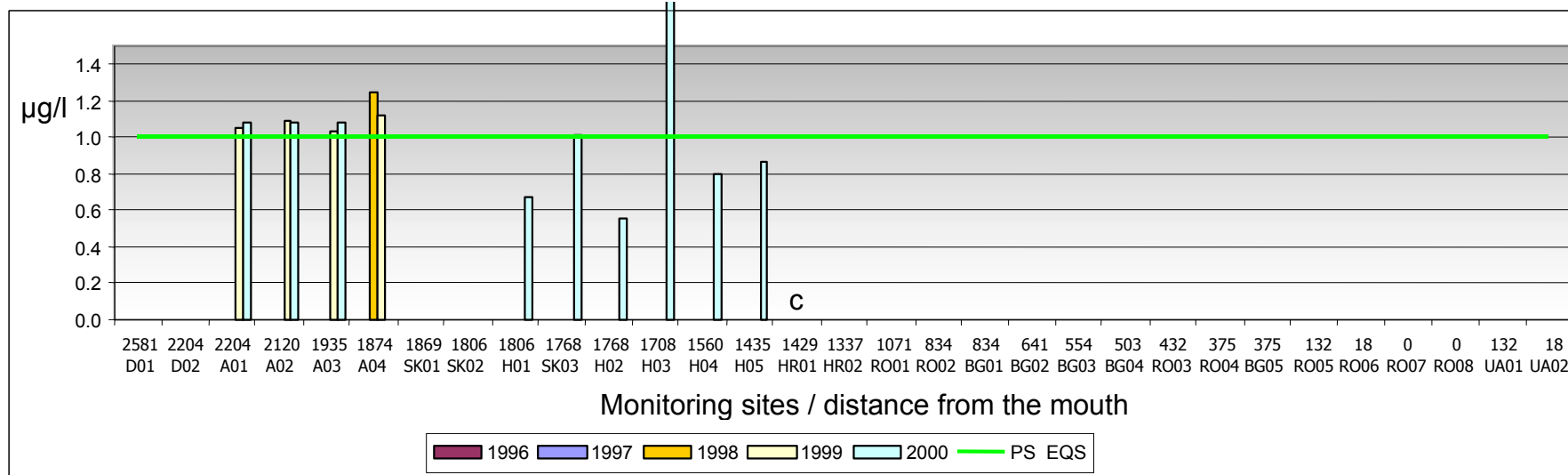
Figure 8.1.6.6.1: Lead
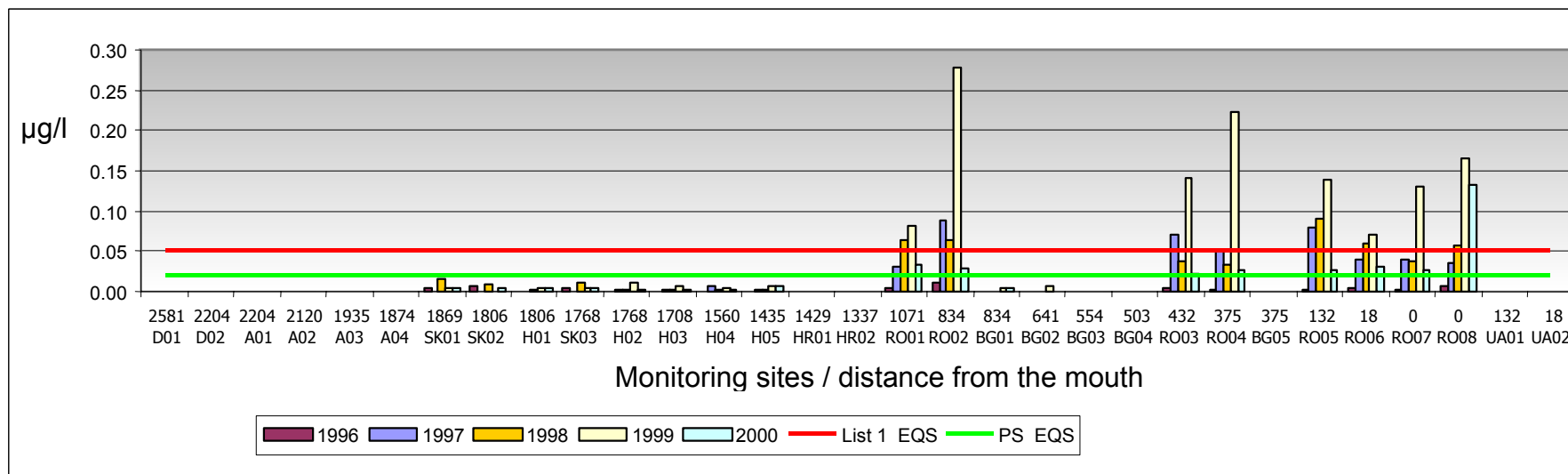
Figure 8.1.6.7.1: Lindane
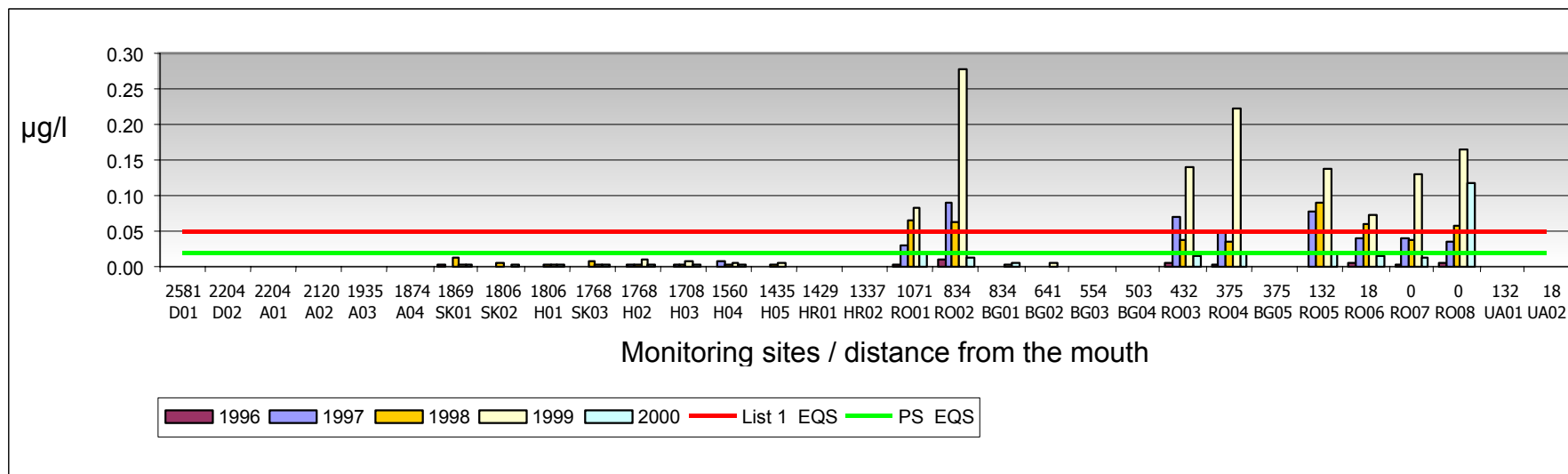
Figure 8.1.6.7.2: Lindane - Zero-method
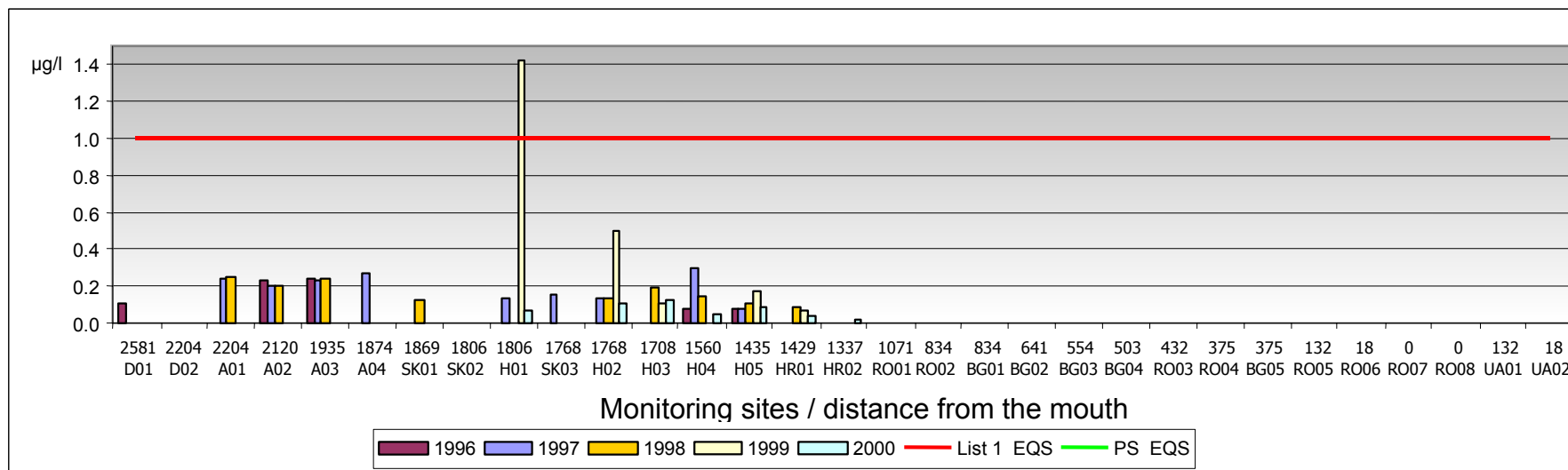
Figure 8.1.6.8.1: Mercury (total)
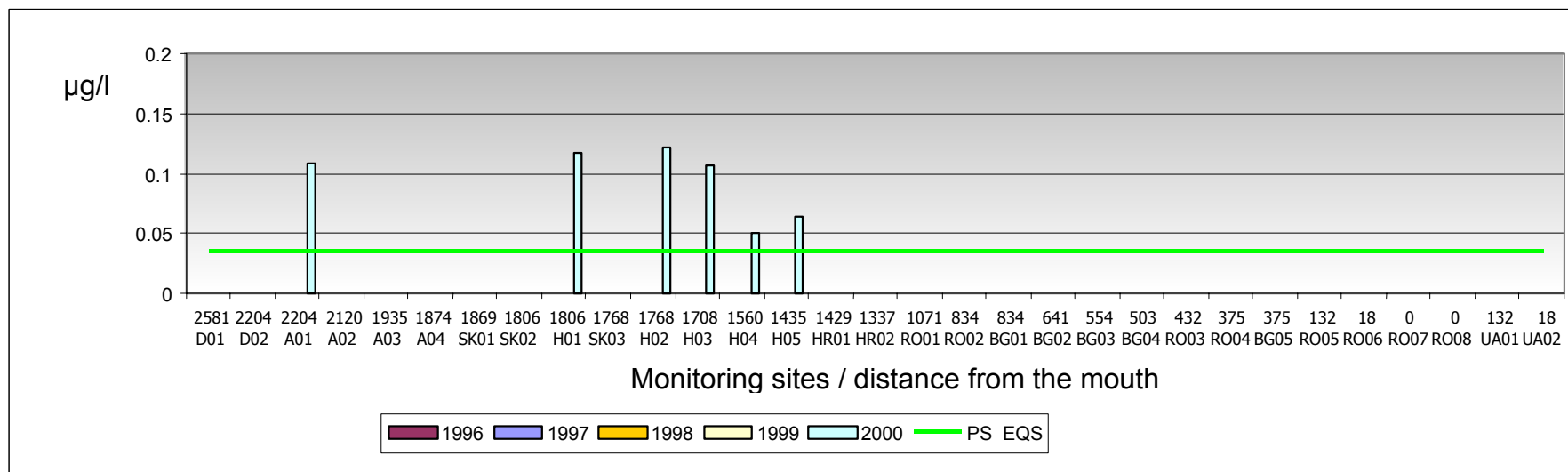
Figure 8.1.6.9.2: Mercury (dissolved) - Zero method
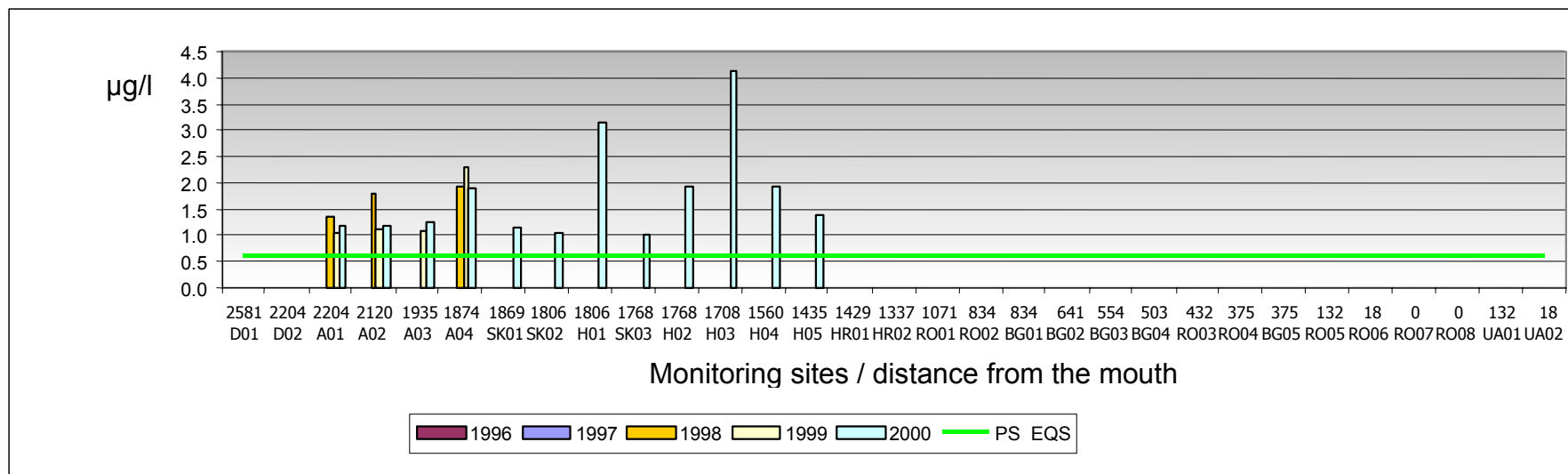
Figure 8.1.6.10.1: Nickel (dissolved)
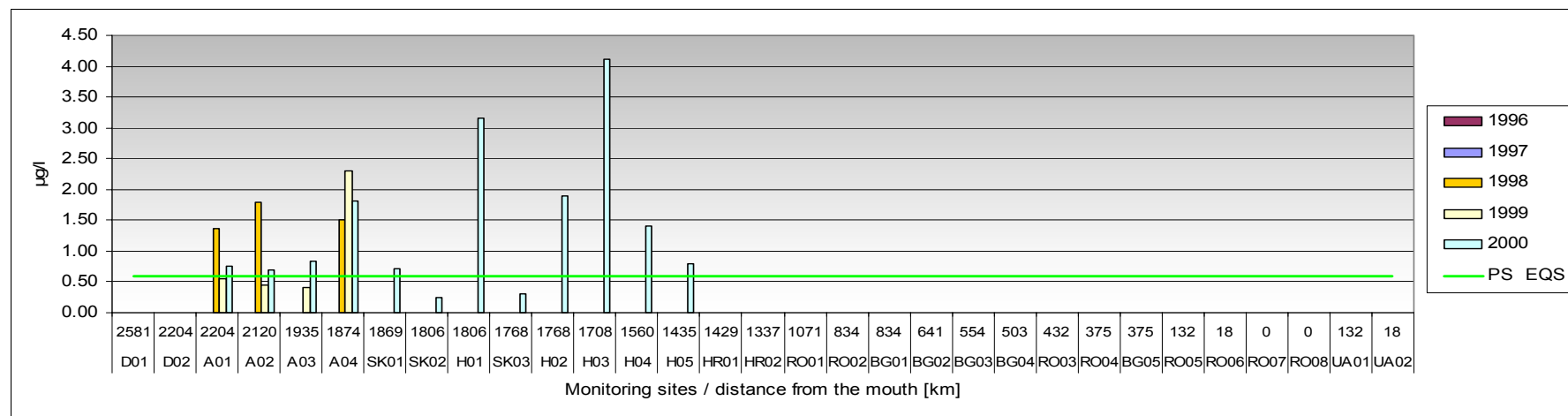
Figure 8.1.6.10.1: Nickel (dissolved) -Zero method
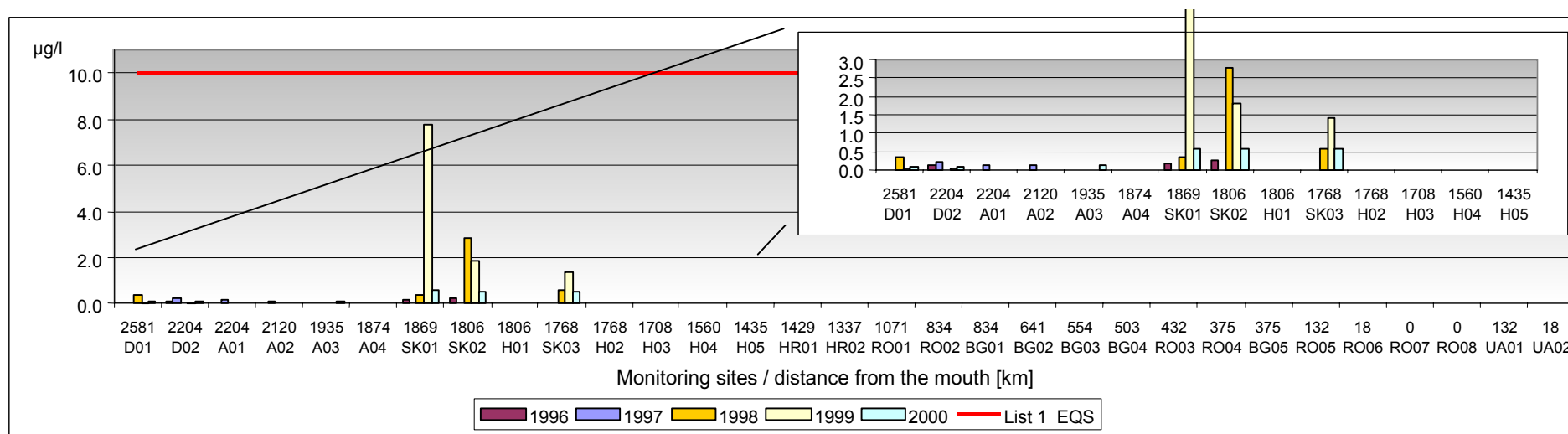
Figure 8.1.6.11.1: Tetrachloroehtene
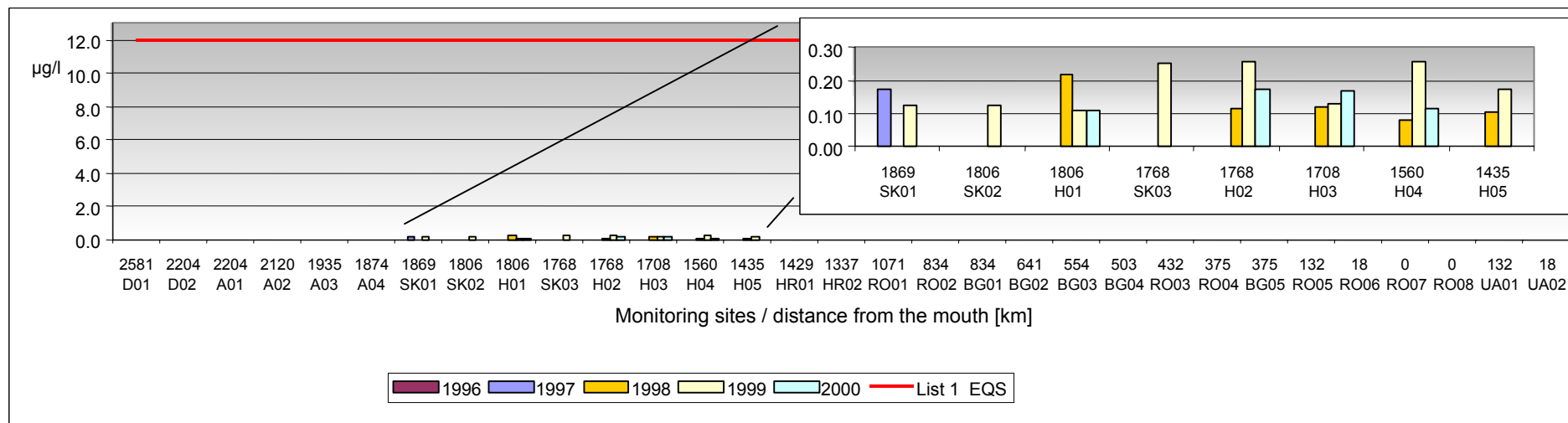
Figure 8.1.6.11.2: Tetrachloromethane
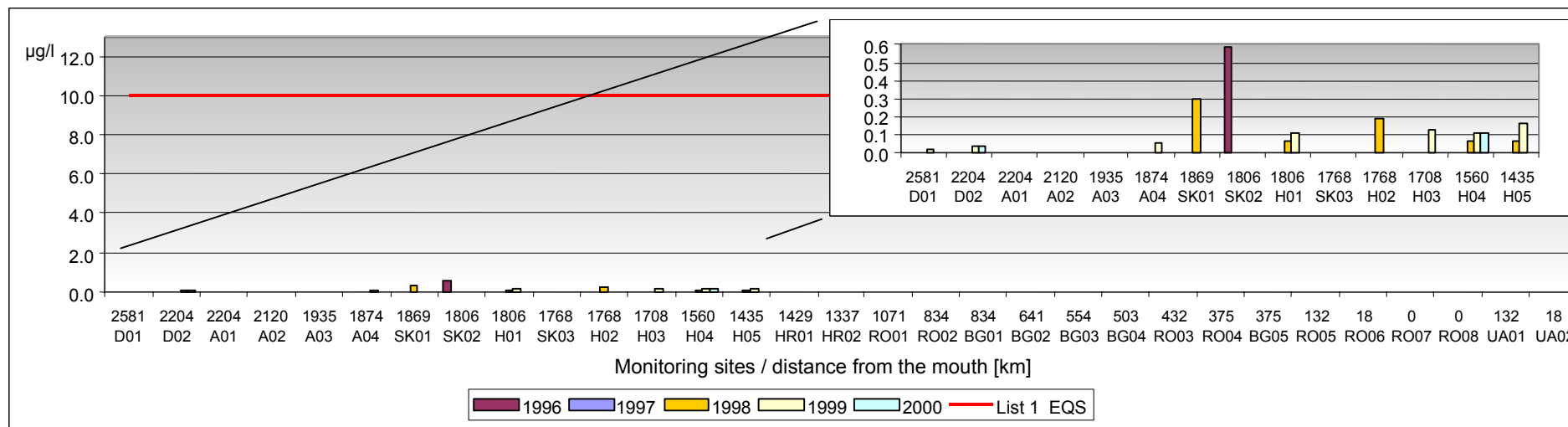
Figure 8.1.6.11.3: Trichloroethene
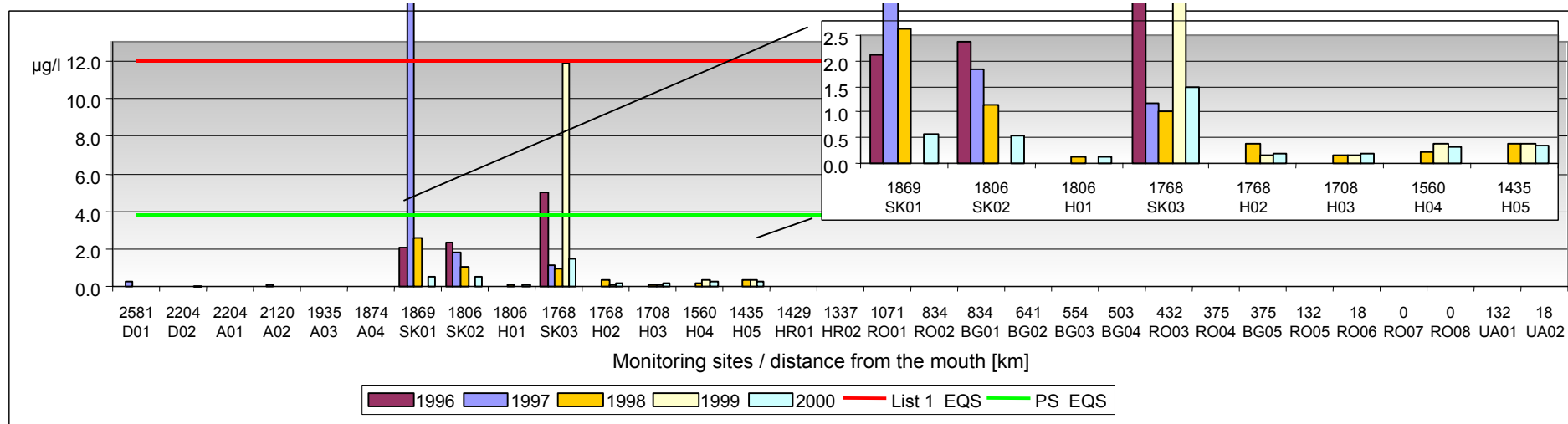
Figure 8.1.6.11.4: Trichloromethane

8.2. Evaluation of Biological Determinands

8.2.1. Phytoplankton biomass – concentration of the chlorophyll-*a*

First of all it should be stated that results of the measurements within TNMN database during period 1996 – 2000 are very heterogenious (Tab.8.2.1.1). Almost all data from the 1996 are missing (only upper two sites data are present). Upper part of the Danube and upper tributaries are covered by data (1997-2000) completely (up to 1439 r.km of the Danube). Part of the Danube from 1337 r.km was monitored very sporadicaly, only a few data from Bulgaria are present.

Interpretation of the results can be only based on data which are at disposal from the TNMN database. Therefore the only upper part of the Danube and selected tributaries can be evaluated (r.km 2581 – 1435).

The Danube stretch between Neu-Ulm and Wolfsthall belongs to the class I - II, the characteristic values ranged from 2,0 to 43,4 µg/l. Last station of the Austrian part of the Danube (Wolfsthal) belongs to class III (50,8 µg/l) in the year 1998. Other investigated years (1999 – 2000) show class I.

Left side tributary Morava brings to the Danube waters with higher concentrations of chlorophyll-a, probably due to the higher algae growth in the reservoirs (e.g. Nové Mlýny).

Chlorophyll-a in the Danube section between Bratislava and Szob increased in 1998, in following years situation improved (class II and I). Leftside tributary Váh contained more algae in the plankton (class III - II). In the lower parts of this section (1560 – 1435 r.km) phytoplankton biomass increased (class III), characteristic values ranged between 56 and 88 µg/l. Based on the results it can be stated, that Sio is the most eutrophicated tributary in this part of the Danube (class III - IV). Better situation is in Drava and Sajó (class I), while Tisza in Tiszasziget shows increase of the eutrophication during the period 1997-2000.

Lower part of the Danube is represented only by some sporadic results from the Bulgarians section. Characteristic values were between 6,8 and 54,4 µg/l, which results to the class I - III.

Tab.8.2.1.1: Characteristic values of the concentration of the chlorophyll-a of the TNMN stations during period 1996-2000.

D - Danube site (rkm) / T, T/T Tributaries (site)		Chlorophyll-a (µg/l)				
		1996	1997	1998	1999	2000
	D D01-Neu-Ulm (2581)	5,2	2,0	28,8	8,4	8,9
T/T	D04-Salzach (Laufen)					
T	D03-Inn (Kirchdorf)					
	D D02-Jochenstein (2204)	27,8	3,6	30,0	21,4	21,5
	D A01-Jochenstein (2204)	18,0	20,2	28,6	13,1	14,1
	D A02-Abwinden-Asten (2120)			35,8	15,6	13,8
	D A03-Wien-Nussdorf (1935)			42,8	19,7	12,3
	D A04-Wolfsthal (1874)	18,0	43,4	50,8	18,7	11,7
T/T	CZ02-Dyije (Břeclav)		6,5	37,4	58,8	63,3
T	CZ01-Morava (Lanžhot)		3,8	38,3	98,9	53,5
	D SK01-Bratislava (1869)		7,1	45,9	27,9	21,3
	D SK02-Medveďov/Medve (1806)		8,2	54,6	33,8	18,4
	D H01-Medveďov/Medve (1806)		37,4	55,7	32,0	24,3
	D SK03-Komárno/Komárom (1768)		10,0	55,5	39,7	24,6
	D H02-Komárno/Komárom (1768)		49,7	83,1	52,7	26,8
T	SK04-Váh (Komárno)		10,7	75,5	27,7	33,6
	D H03-Szob (1708)		59,3	44,6	29,9	27,7
	D H04-Dunafoldvar (1560)		72,5	88,0	58,4	56,0
T	Sio (Szekszard-Palanka)		136,3	68,1	74,3	236,0
	D H05-Hercegszanto (1435)		71,9	87,0	49,0	76,0
T	H07-Drava (Dravaszabolcs)		19,0	15,5	14,4	12,3
	D HR01-Batina (1429)					
	D HR02-Borovo (1337)					

D - Danube site (rkm)	Chlorophyll-a (µg/l)				
T, T/T Tributaries (site)	1996	1997	1998	1999	2000
T HR03-Drava (Varazdin)					
H09-Sajo (Sajopuspeki) T/T		16,7	9,7	5,0	11,1
H08-Tisza (Tiszasziget) T		14,9	29,5	48,7	84,0
T SL01-Drava (Ormoz)					
T HR04-Drava (Botovo)					
T HR05-Drava (D.Miholjac)					
T SL02-Sava (Jesenice)					
T HR06-Sava (Jasenice)					
T HR07-Sava (us.Una Jasenovac)					
T BIH01-Sava (Jasenovac)					
T/T BIH02-Una (Kozarska Dubica)					
T/T BIH03-Vrbas (Razboj)					
T/T BIH04-Bosna (Modrica)					
T HR08-Sava (ds.Zupanja)					
D RO01-Bazias (1071)					
D RO02-Pristol/Novo Selo Harbour (834)					
D BG01-Novo Selo/Pristol (834)			6,5	20,5	23,8
D BG02-us.Iskar-Bajkal (641)					
T BG06-Iskar (Orechovitza)					
D BG03-ds.Svishtov (554)					54,4
T BG07-Jantra (Karantzi)					46,0
D BG04 - us.Ruse (503)					15,4
T BG08-Russenski Lom (Basarbovo)					16,6
D RO03-us.Arges (432)					
RO09-Arges T					
D RO04-Chiciu/Silistra (375)					
D BG05-Silistra/Chiciu (375)			17,7		13,8
RO10-Siret T					
MD01-Prut (Lipcani) T					
MD02-Prut (Leuseni) T					
MD03-Prut (Giurgiulesti) T					
RO11-Prut (Giurgiulesti) T					
D RO05-Reni-Chilia/Kilia arm					
D UA01-Reni-Chilia/Kilia arm					
D RO06-Vilkova-Chilia arm/Kilia arm					
D UA02-Vilkova-Chilia arm/Kilia arm					
D RO07-Sulina-Sulina arm					
D RO08-Sf.Gheorghe arm-Gheorghe arm					

CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
µg/l	≤25	≤50	≤100	≤250	>250

Conclusion

1. Spatial coverage of Danube River basin by data on chlorophyll-a in TNMN is not complete. Only the upper part of the Danube and the main tributaries were monitored during period 1997-2000 in a way as it was proposed within TNMN. Only a few data were obtained from Bulgarian section.

2. Statistical values correspond to class I - III according to the above mentioned classification scale.

3. Only the Sio river (left side tributary) was in class IV during 1997 and 2000.

4. Results from the lower part of the Danube were in the class I – III as well.

Recommendation

1. It is stated that the Danube is eutrophicated river. More attention should be focused to the monitoring of determinands characterizing eutrophication mainly in the lower part of the river. This will enable to obtain coherent database along the River Danube and its main tributaries.

2. The measurements of the chlorophyll-a content should by monitored at least 10-12 times per year to obtain sufficient database for evaluation trends and changes.

8.2.2.   Saprobic index of macrozoobenthos

Interpretation of the results can be only based on data which are at disposal from the TNMN database. Therefore only some parts of the Danube River and selected tributaries can be evaluated.

It should be said that database of the results of the measurements within TNMN is very heterogenious during period 1997 – 2000 (Tab. 8.2.2.1). Data from 1996 were missing. As it was mentioned in case of chlorophyll-a, data from the Danube River and its tributaries for mentioned period were very rare. Upper part of the Danube up to Borovo was investigated from the point of macroinvertebtares only. As for the tributaries, some of them were monitored up to Romanian stretch of the Danube.

Based on the results can be stated that the Danube and tributaries of the monitored TNMN station belong to the class II – II-III. Maximum values of Saprobic Indices ranged from 1,77 to the 2,7. This means β – α mesosaprobity. Only the Sava river (downstream Zupanja and Jasenice) belong to the worse classes in the first two years (III – III-IV) which means strong or very high pollution (up to polysaprobity). However within next two years the situation improoved (II-III; β– α mesosaprobity).

The differences show slight positive trend of pollution reduction within the investigated years. Generaly, based on this results can be said that Danube and its some tributaries were moderatelly or criticaly polluted.

Table 8.2.2.1: Saprobic Indices of macrozoobenthos of TNMN stations in the years 1997-2000.

	D - Danube site (rkm)		Saprobic index of macrozoobenthos			
	T, T/T Tributaries (site)		1997	1998	1999	2000
D	D01-Neu-Ulm (2581)					
T/T	D04-Salzach (Laufen)			2,12	2,03	2,25
T	D03-Inn (Kirchdorf)			1,86	1,77	1,85
D	D02-Jochenstein (2204)			2,26	2,27	2,19
D	A01-Jochenstein (2204)		2,11	2,09	2,00	2,19
D	A02-Abwinden-Asten (2120)		2,08		2,00	2,00
D	A03-Wien-Nussdorf (1935)		1,93	2,19	2,00	2,20
D	A04-Wolfsthal (1874)		2,14	2,15	2,10	2,20
	CZ02-Dyje (Břeclav)	T/T	2,40	2,20	2,13	2,16
	CZ01-Morava (Lanžhot)	T	2,71	2,30	2,23	2,15
D	SK01-Bratislava (1869)		2,08	2,04	2,54	1,98
D	SK02-Medveďov/Medve (1806)		2,12	2,09	2,18	1,99
D	H01-Medveďov/Medve (1806)			2,20	2,18	2,00
D	SK03-Komárno/Komárom (1768)		2,11	2,12	2,27	2,11
D	H02-Komárno/Komárom (1768)			2,25	2,27	2,10
	SK04-Váh (Komárno)	T	2,70	2,45	2,42	2,26
D	H03-Szob (1708)			2,11	2,24	2,26
D	H04-Dunafoldvar (1560)					
	H06-Sio (Szekszard-Palank)	T				2,38
D	H05-Hercegszanto (1435)					
T	H07-Drava (Dravaszabolcs)					
D	HR01-Batina (1429)					
D	HR02-Borovo (1337)					2,24
T	HR03-Drava (Varazdin)					
	H09-Sajo (Sajopuspeki)	T/T				
	H08-Tisza (Tiszasziget)	T				

D - Danube site (rkm)		Saprobic index of macrozoobenthos			
T, T/T Tributaries (site)		**1997**	**1998**	**1999**	**2000**
T	SL01-Drava (Ormoz)		2,34	2,35	2,52
T	HR04-Drava (Botovo)				
T	HR05-Drava (D.Miholjac)				
T	SL02-Sava (Jesenice)		2,57	2,32	2,36
T	HR06-Sava (Jasenice)	2,60	2,80	2,50	2,24
T	HR07-Sava (us.Una Jasenovac)	2,70	2,40	2,50	2,03
T	BIH01-Sava (Jasenovac)				
T/T	BIH02-Una (Kozarska Dubica)				
T/T	BIH03-Vrbas (Razboj)				
T/T	BIH04-Bosna (Modrica)				
T	HR08-Sava (ds.Zupanja)	3,70	2,90	2,60	2,34
D	RO01-Bazias (1071)				
D	RO02-Pristol/Novo Selo Harbour (834)				
D	BG01-Novo Selo/Pristol (834)				
D	BG02-us.Iskar-Bajkal (641)				
T	BG06-Iskar (Orechovitza)				
D	BG03-ds.Svishtov (554)				
T	BG07-Jantra (Karantzi)				
D	BG04 - us.Ruse (503)				
T	BG08-Russenski Lom (Basarbovo)				
D	RO03-us.Arges (432)				
	RO09-Arges T				
D	RO04-Chiciu/Silistra (375)				
D	BG05-Silistra/Chiciu (375)				
	RO10-Siret T				
	MD01-Prut (Lipcani) T				
	MD02-Prut (Leuseni) T				
	MD03-Prut (Giurgiulesti) T				
	RO11-Prut (Giurgiulesti) T				
D	RO05-Reni-Chilia/Kilia arm				
D	UA01-Reni-Chilia/Kilia arm				
D	RO06-Vilkova-Chilia arm/Kilia arm				
D	UA02-Vilkova-Chilia arm/Kilia arm				
D	RO07-Sulina-Sulina arm				
D	RO08-Sf.Gheorghe arm-Gheorghe arm				

	I.	I.-II.	II.	II.-III.	III.	III.-IV.	IV.
CLASSIFICATION SCALE	unpolluted	low polluted	moderately polluted	criticaly polluted	strongly polluted	very high polluted	extensively polluted
	≤1,25	≤1,75	≤2,25	≤2,75	≤3,25	≤3,75	>3,75

Conclusion

1. The TNMN data of the Saprobic Index of macrozoobenthos are not complete, only the upper part of the Danube (up to 1337 r.km) and some tributaries were monitored during period 1997-2000.
2. It is evident that some countries included saprobic index of bioseston into the database instead of saprobic index of macrozoobenthos. Such results were excluded from the evaluation.
3. In the Danube and some tributaries the statistical characteristics correspond to the class II – II-III in accordance with used seven-class classification scale.
4. Only the Sava River (stations downstream Zupanja and Jesenice) belongs to the worse classes in the first two years (III – III-IV), however within next two years the situation improved (II-III).
5. Based on the results can be said that the Danube and its some tributaries were moderately or criticaly polluted, the slight positive trend appeared within the years.
6. Saprobic Indices in the Danube and its some tributaries were in the range of β – α mesosaprobity.

Recommendation

1. In the future more characteristics of the macrozoobenthos is needed (e.g. number of taxa, diversity or other indices, list of species) for the evaluation development and changes of the invertebrates in the Danube.

2. The investigation of the macrozoobenthos should be monitored at least 2-3 times per year and on the whole stretch of the Danube to obtain sufficient database for evaluation trends and changes.

3. Connecting to the Water Framework Directive (2000/60/EC) more communities should be monitored (e.g. phytobenthos).

8.2.3.   Microbiological determinands

Based on the obtained results (see Tab.8.2.3.1) it can be stated that some data from upper part of the Danube, some data from lower part of the Danube and data from tributaries of the middle and lower part of the Danube (Dava, Una, Vrbas, Bosna, Iskar, Jantra, Arges, Prut) are missing.

In the period 1996-2000 the faecal pollution represented by the **Total Coliforms** range predominantly within class II-IV in the Danube and its tributaries. The worse situation was in Tisza (class V) in the year 1998. Class I was obtained at some Danubian stations on the Romanian-Bulgarian stretch of the river in the year 1996 only. In the next years there classes II-IV were observed. This evoke idea to check the method used for investigation of the Total Coliforms in the laboratory.

Beside Tisza (Tiszasiget), there are other tributaries bringing faecal pollution to the Danube (Váh, Siret). However, data of the tributary (Rusenski Lom and Arges), that were classified during Joint Danube Survey as the worst ones, are almost missing.

Water quality of the Danube is influenced not only by the mentioned tributaies, but predominantly by direct antropogenic impacts caused by the raw or treated sewages and diffuse impact from the agriculture.

Looking to the TNMN border stations it is shown that the measurements between countries were not harmonized. In some cases (Medve/Medveďov, Komárno/Komárom, Novo Selo/Bristol, Chiciu/Silistra, Sava) the differences are within two or three classes at the same stations in particular year.

Below Čunovo (Gabčíkovo) Reservoir and Iron gate Reservoir the number of the Total Coliforms decreased that in some years it resulted to the II (I) class. The reason is that due to the sedimentation processes bacteria that are attached to solids particles are stored in the sediments of the reservoir.

Sedimentation can be also reason for the relatively possitive situation in the Danube Delta (I-II class).

Data of the Total Coliforms from the Danube shows that pollution ranged almost between moderate and critical, in some cases strong pollution appeared. There is no trend in faecal pollution in the longitudinal profile of the Danube river. Similarly, there are no significant changes comparing individual years.

Based on the data of **Faecal Coliforms** faecal pollution of the Danube belong to the class I - IV during period 1996-2000. The Danube in Komárom (1998) was in the class V only. The extensive pollution was observed in Váh (2000), Tisza (1998) and Siret (1998).

In 1996 the low pollution is shown in the lower part of the Danube even though data from this stretch are very rare. First class was also in Bazias (1997, 1999) and Pristol/Novo Selo (1999).

Decrease of the number of Faecal coliforms due to the sedimentation can be seen in Medveďov/Medve but not downstream of Iron Gates.

In the 1999 the Danube from Jochenstein (r.km 2204) to Hercegszanto (r.km 1435) was critically polluted except Wolfsthal (r.km 1874) where was class IV.

Faecal pollution of the Danube Delta characterized by the Faecal Coliforms was slightly higher (I.- III.class) than indicated by the Total Coliforms (class I-II).

Similarly as Total Coliforms, results on Faecal Coliform bacteria did not pointed out any significant change or trend in the longitudinal profile of the
The methods of analyses were probably not fully harmonized between countries at TNMN border stations as it was in case of Total Coloforms. In Medve/Medveďov and Komárno/Komárom the differences were in two classes. Big differences within numbers of Faecal Coliform bacteria were in Siret in the individual years (64 – 920 000 CFU per 100 ml).

Tab. 8.2.3.1.: Statistical values of microbiological analyses of Total Coliforms and Faecal Coliforms in TNMN stations in the period 1996-2000.

Total coliforms (CFU per 100ml)					D - Danube site (rkm) T, T/T Tributaries (site)	Faecal coliforms (CFU per 100ml)				
1996	1997	1998	1999	2000		1996	1997	1998	1999	2000
					D D01-Neu-Ulm (2581)					
					T/T D04-Salzach (Laufen)					
					T D03-Inn (Kirchdorf)					
19200	1920	16900	10760	22380	D D02-Jochenstein (2204)	1280	332	1325	1460	2230
12600	1460	11760	14900	18720	D A01-Jochenstein (2204)	1460	116	1430	1290	2840
					D A02-Abwinden-Asten (2120)					
4530	1750	17300	10900	10820	D A03-Wien-Nussdorf (1935)	721	316	1258	1820	2520
31000	11000	204000	127000	56600	D A04-Wolfsthal (1874)	12000	3070	14000	22000	6360
1056	8260	8200	10860	7160	CZ02-Dyje (Pohansko) T/T	552	2100	3560	3200	3280
578	1260	5500	4600	10800	CZ01-Morava (Lanžhot) T	220	430	2200	1390	3100
27600	4400	10630	13600	19000	D SK01-Bratislava (1869)	9600	1520	4210	5000	3680
7220	920	3420	3020	3950	D SK02-Medveďov/Medve (1806)	2200	300	880	1100	500
		160000	5400	4200	D H01-Medveďov/Medve (1806)			17000	2400	1300
260000	24200	38100	21700	118000	D SK03-Komárno/Komárom (1768)	44800	4360	7520	6170	7900
		540000	46400	92000	D H02-Komárno/Komárom (1768)			220000	3500	16000
214000	63000	135800	205000	390000	SK04-Váh (Komárno) T	72600	18900	34400	53500	158300
		172000	13226	13510	D H03-Szob (1708)			36667	5100	5367
		295000	24700	23800	D H04-Dunafoldvar (1560)			70000	6000	11667
		50000	31000	20000	H06-Sio (Szekszard-Palank) T					
		662000	18000	28500	D H05-Hercegzanto (1435)			80000	1500	8000
		170000	25500	24700	T H07-Drava (Dravaszabolcs)			22000	1300	2730
		35500	22610	8890	D HR01-Batina (1429)					
		2290	7600	2230	D HR02-Borovo (1337)					350
13900	7500	23900	11000	11000	T HR03-Drava (Varazdin)					
		488000	50000	30000	H09-Sajo (Sajopuspeki) T/T			40000	6000	5600
		1921000	251083	255167	H08-Tisza (Tiszasziget) T			145634	18974	23527
14000	27600		8630	15170	T SL01-Drava (Ormoz)				4450	4050
5470	7910	17700	12200	6520	T HR04-Drava (Botovo)					
20980	49800	36010	9810	3060	T HR05-Drava (D.Miholjac)					
22000	27800		29000	52200	T SL02-Sava (Jesenice)				7000	3520
43800	9300	39630	43800	35000	T HR06-Sava (Jasenice)					1800
24000	24000	24000	24000	24000	T HR07-Sava (us.Una Jasenovac)					4960
					T BIH01-Sava (Jasenovac)					
					T/T BIH02-Una (Kozarska Dubica)					
					T/T BIH03-Vrbas (Razboj)					
					T/T BIH04-Bosna (Modrica)					
23100	45700	42600	15000	19500	T HR08-Sava (ds.Zupanja)					2350
1178	8270	10634	5700	7667	D RO01-Bazias (1071)		96	677	47	922
303	4300	6667	777	7467	D RO02-Pristol/Novo Selo Harbour (834)	16	1334	250	45	1357
		490334	146500	2504	D BG01-Novo Selo/Pristol (834)					
					D BG02-us.Iskar-Bajkal (641)					
					T BG06-Iskar (Orechovitza)					
					D BG03-ds.Svishtov (554)					
					T BG07-Jantra (Karantzi)					

Total coliforms (CFU per 100ml)					D - Danube site (rkm)		Faecal coliforms (CFU per 100ml)				
1996	1997	1998	1999	2000	T, T/T Tributaries (site)		1996	1997	1998	1999	2000
				140000	D BG04 - us.Ruse (503)						
				40000	T BG08-Russenski Lom (Basarbovo)						
	4845	2452	2567	16000	D RO03-us.Arges (432)			310	190	758	6830
					RO09-Arges	T					
204	13733	92133	19067		D RO04-Chiciu/Silistra (375)		10	8067	24100	1280	
		163334		32667	D BG05-Silistra/Chiciu (375)						
350	16000	24000	920000		RO10-Siret	T	64	810	920000	1300	
					MD01-Prut (Lipcani)	T					
	35000	16000	16000	16000	MD02-Prut (Leuseni)	T		16000	3600	2100	430
					MD03-Prut (Giurgiulesti)	T					
	9200	16000	9200		RO11-Prut (Giurgiulesti)	T		2200	16000	220	
193	7367	2867	7640		D RO05-Reni-Chilia/Kilia arm		16	3167	1527	1630	
					D UA01-Reni-Chilia/Kilia arm						
63	6934	2434	3864		D RO06-Vilkova-Chilia arm/Kilia arm		11	2500	1664	4467	
					D UA02-Vilkova-Chilia arm/Kilia arm						
110	7467	2300	6757		D RO07-Sulina-Sulina arm		7	2400	1860	490	
	9834	1811	3474		D RO08-Sf.Gheorghe arm-Gheorghe arm			507	1727	2700	

I.	II.	III.	IV.	V.	CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
≤500	≤10000	≤100000	≤1000000	>1000000	(CFU/100 ml)	≤100	≤1000	≤10000	≤100 000	>100000

Conclusion

1. Data on presence of bacteria (Total Coliforms and Faecal Coliforms) in TNMN databases are not complete for the river basin.

2. Data from the upper part of the Danube (up to Borovo) and the main tributaries monitored during period 1998-2000 are more homogenous than lower part of the Danube.

3. Characteristic values of the Total Coliforms result to the class I - IV in the Danube and the tributaries except for Tisza in the year 1998 (class V).

4. Statistical values of the Faecal coliforms show similar situation to the Total Coliform bacteria. The data ranged from class I to IV in the Danube and the tributaries except for Tisza (1998), Váh (2000) and Danube in Komárno (1998) where the extensive pollution was observed.

Recomendation

The results from the Danube and its tributaries were evaluated according to the about mentioned classification scheme. The EU Bathing Water Quality Directive (76/160/EEC) is now in the period of the revision.

It is recomended to wait for the new version of the mentioned EU Directive and re-valuate data from five years period (1996-2000).

For the TNMN the additional determinands should be included into the programme.

9.   Conclusions and recommendations

The objective of this report was to assess water quality in Danube River basin, including classification and identification of spatial and temporal changes. The basis for assessment are data on physico-chemical and biological determinands collected in the frame of TNMN in five-years period 1996 – 2000.

The basis for assessment of spatial and temporal changes were 90 %-iles of yearly data sets, which is able to express also unfavourable situations that occurred in particular year in the monitoring site. The 90 %-iles create also the basis for classification of water quality, but in case of frequency of measurements lower than eleven the maximum value was used for comparison with limit values for different water quality classes.

Results of classification are given in Annex I, assessment of water quality on the basis of physico-chemical determinands is in chapter 8.1 and assessment based on biological determinands in chapter 8.2.

To supplement interpretation of heavy metals and micropollutants content in water of Danube River basin, comparison of TNMN data had been done with Environmental Quality Standards (EQS) of EU legislation. Existing EQS for List I substances together with proposed EQS for Priority Substances had been used for the comparison. For this purpose, not 90 %-iles, but mean values calculated with „LOD-method" and in selected cases also with „Zero-method" were used.

General characteristics

Suspended solids content increases slightly from upper to lower Danube section; as concerning its tributaries, some of them show significantly higher concentrations of suspended solids than the Danube River itself – Tisza, Russenski Lom, Arges, Siret and Prut.

Values of pH show a slight alkaline medium; values exceeding 8.50 are present mainly in the middle Danube, where, correlated with dissolved oxygen concentrations, show the influence of primary productivity and organic matter load. This pH distribution along the Danube River is in accordance also with results obtained from Joint Danube Survey.

Conductivity values do not present significant variations along the main course of the river. However, after an intermediate decrease after confluence with Sava River, a slight increase is observed in the lower Danube. From tributaries, Sio and Prut present relatively higher salts content.
Excluding only few values (at Danube-Batina, rkm 1429), alkalinity shows a constant spatial pattern in the upper and in the middle Danube; slightly increasing values appear in the second part of the lower Danube. As concerning the tributaries, higher alkalinity values are present on Sio and Russenski Lom.

Nutrients

From the different fractions analyzed within the TNMN Programme, ammonium-N, nitrite-N, nitrate-N, ortho-phosphate-P and total phosphorous were chosen for assessment of nutrient content in waters. Information on organic and total nitrogen are sparce and can not provide a good picture on situation in the river basin.

Ammonium-N and nitrite-N present an increasing profile from upper to lower Danube, which is much more significant in case of ammonium-N. From existing data along the Danube itself, 53.3 % of ammonium-N and 37.2 % nitrite-N values are above the target limit for these determinands. For tributaries, rather high values appear on the Morava, Dyje, Vah and Sio in the upper and middle Danube and on Jantra, Arges, Siret and Prut in the lower Danube section. A special concern should be

paid to the ammonium-N content recorded on the Arges tributary, where all five values of C90 characterising situation in different years in period from 1996-2000, are above the limit for Class V; these extremely high values, correlated with BOD_5 values, show the impact of untreated or insufficiently treated waste waters from municipalities.

Unlike the ammonium-N and nitrites-N, the spatial distribution of nitrate-N concentrations show a decrease from upper and middle to lower Danube. From data for the Danube itself, 27.1% are above the target value, whereas 33.1% are above this limit in monitored tributaries. Tributaries with the highest content of nitrates-N are Morava, Dyje, Sio in the upper/middle part, and Iskar, Russenski Lom, Arges and Prut in the lower part of river basin.

Orthophosphate-P shows a similar spatial pattern with total phosphorous, both characterized by a slight increasing profile from upper to lower Danube; concerning the exceeding of the target value, 17.6% of orthophosphate-P and 11.3% of total P values are above this limit along the Danube River, while 45.2% of orthophosphate-P and 57.3% of total P values are above this limit in tributaries.

Heavy metals

Within the framework of TNMN in the Danube River Basin eleven heavy metals are regularly analyzed in water both as total and dissolved forms (for dissolved forms data are available only from 1998 to 2000, and even not for the whole river basin). Excepting the conservative element aluminium, ten of them were chosen to be discussed in the quality assessment of the Danube River water and its tributaries; out of these, eight heavy metals are of a particular importance due to the fact that they are considered as priority substances for the Danube River Basin - four of them are listed in the list of Priority Substances included in Annex X of the Water Framework Directive (cadmium, lead, mercury and nickel) and the other four belong between priority substances specific to the Danube River Basin (arsenic, copper, chromium and zinc).

Except manganese, where a maximum spatial profile is present in the middle Danube, for most of the discussed heavy metals the general pattern is increasing from upper and middle to the lower Danube. Further, the heavy metals content in some tributaries – mainly those located in the lower Danube - is higher than the content in the Danube River itself.

According to the classification for the Danube River Basin and regarding the exceeding of the target values, the assessed data for the total heavy metals forms led to the following conclusions:

- the contamination of the Danube River water is rather high in case of lead and copper, with 57.3% of values for lead and 56.7% values for copper above the target limit; in tributaries, these percentages are 52.8% for lead and 21.6% for copper.
- the contamination pattern of the Danube itself for cadmium and mercury can be characterized with 47.4% of values exceeding cadmium target level and 36.6% of values exceeding mercury target level; however, it has to be mentioned the lack of data for mercury in the lower Danube cannot provide a comprehensive picture in this respect. In tributaries, the situation is better for cadmium, with 32.4% above the quality target but worse for mercury with 63.2% above this limit.
- as regarding the contamination of the Danube river and its tributaries by arsenic, chromium, nickel and zinc, it can be roughly said these watercourses are unpolluted from this point of view; the percentages of exceeding the target values in the Danube and in selected tributaries are the following: arsenic – 8.7% in Danube River and 16.1% in tributaries, chromium – 1.3% in Danube River and 0% in tributaries, nickel – 0% in Danube River and 2.1% in tributaries and zinc – 10.5% in Danube River and 12.9% in tributaries. However, the lack of data for these heavy metals in the lower Danube section has to be mentioned again.

Because the analysis of heavy metals in water column only cannot provide a very good picture of this kind of pollution, the assessment of the heavy metals content in both sediment and suspended solids may be a better approach in this respect.

Oxygen regime

In order to assess the water quality of the Danube River and its tributaries from the point of view of oxygen regime, four determinands were used - dissolved oxygen in terms of concentration, biochemical oxygen demand (BOD) and chemical oxygen demand by $KMnO_4$ and $K_2Cr_2O_7$ (COD_{Mn} and COD_{Cr}).

Dissolved oxygen concentrations generally show positive results, with only 7.4% of values below the quality target in the Danube River and 8.6% in selected tributaries. Oxygen concentration decreases from upper to lower part of the Danube River, lowest values reaching in the section from Danube-Bazias to Danube-Novo Selo/Pristol. From tributaries, low oxygen content was also identified in those located in the lower part of the river basin.

BOD values indicate that 13.3% of values are above the target value in the Danube River (mainly in the middle and in the lower sections) and 35.9% in tributaries. Organic pollution expressed by BOD increases along the Danube, reaching its maximum in the secion from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm 834, RO02). Tributaries most polluted by degradable organic matter are Morava, Dyje and Sio in the upper/middle part and Russenski Lom and Arges in the lower part.

For COD_{Cr}, from all values 22.4% for the Danube itself and 39.7% for tributaries are above the quality target; the picture is more positive in case of COD_{Mn} - no value above this limit for the Danube River and 18.2% for tributaries. Measurements of COD_{Cr} and COD_{Mn} show the highest values in the lower part of the Danube River.

In order to obtain a more complete pattern of oxygen regime, beside the 10 percentiles for dissolved oxygen, both the minimum and maximum values were used in assessment, the results being in good correlation with previous data (*Joint Danube Survey - 2001*). Also, the results confirm the critical problems that occur in the tributaries which regularly serve as recipient of untreated or not adequately treated waste water from industry and municipalities (the Arges tributary).

Organic micropollutants

Within the TNMN Programme, organic micropollutants that are regularly monitored are Lindan, pp'-DDT, Atrazine, chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene. During the five studied years, the content of these organic compounds presents very large limits of variation due to the fact that there are big differences among the reported limits of detection.

The organochlorine compounds (Lindan and pp'-DDT) show almost the same spatial profile, with an increasing pattern from upper and middle to lower Danube; concerning the exceeding of the target value for Lindan, 23.8% from all values are above this limit in the Danube River water and 9.1% in tributaries. These percentages are higher in case of pp'-DDT: 70.5% for the Danube itself and 54.2% for tributaries.

The polar pesticide Atrazine is undetectable at most of the monitoring sites along the Danube River, but 12.5% of the data are above the target limit (as far as the data are available). In tributaries, 30% of values are above the quality target; the maximum values of Atrazine were found in rivers Sio and the Sajo.

For the volatile organic compounds, data are available for upper and middle Danube only. Chloroform and tetrachloroethylene present values above the target limits as it follows: 29.0% in the Danube and

39.5% in tributaries for chloroform and 13.6% in the Danube and 7% in tributaries for tetrachloroethylene. The situation is better in the case of tetrachloromethane and trichloroethylene - in the Danube River water, no value is above the target limit for these compounds, while in tributaries the same percentage of all data (2.3%) is above this value for both those determinands.

Biological determinands

In the group of biological determinands generally there were problems with unsufficient spatial coverage of Danube River Basin, needed for meaningful interpretation of these data. From existing results can be concluded that chlorophyll-a corresponds to class I – III, only Sio River to class IV in 1997 and 2000.

Regarding saprobic index of macrozoobenthos, by using Austrian standard ÖNORM M6232 the values in Danube River basin and some tributaries correspond to classes II – II-III. Only Sava River was characterized by worse quality class (III – III-IV), however, within the years the situation had been improved. Based on the results it can be concluded that Danube River and tributaries were moderately or critically polluted.

Water quality from microbiological point of view corresponded to classes I – IV in the Danube River. Tributaries Vah, Tisza, Siret can be characterized as extensively polluted, however, data from many important tributaries are missing. Sedimentation has positive effects to number of total coliforms below Gabčíkovo Reservoir, Iron Gates and in Danube Delta as well.

An important part of the report is the evaluation of the water quality changes in time period from 1996 to 2000, main question being whether the water quality is improving or deteriorating. Water quality changes in time depend on both natural characteristics like occurance of flood events, events of low flows, periods of sunny warm weather and antropogenic activities like discharges of waste waters, agricultural practises, accidental events. Taking into account great heterogeneity of the countries in Danube River basin, their water management practices, and in majority of them their transforming economics, both trends can be expected and should be detected.

Regarding indicators of **organic pollution** BOD, COD_{Mn} and COD_{Cr}, there is not their common trend observed. The year-to-year fluctuation rises from COD_{Mn} to BOD and to $COD_{Cr.}$
Decreasing tendency of BOD from 1997/98 to 2000 was observed in section from Danube-Neu Ulm (km 2581) to Danube-Abwindedn-Asten (km 2120), at the cross section Danube-Medvedov/Medve (km 1806) and Danube Komarno/Komarom (km 1768); further from Danube-Borovo (km 1337) to Danube-Bazias (km 1071), in Danube-Reni/Chilia arm/Kilia arm (km 132) and Danube –Vilkov/Kilia arm/Chilia arm (km 18). In evaluated period 1996-2000, BOD values in 2000 belonged to the lowest in majority of monitoring sites located in Danube River. From tributaries, a decreasing trend of BOD can be observed in Inn, Salzach, Dyje, Vah, Drava and Arges, whilst the sites at Tisza River and its tributary Sajo show a reverse behaviour.

Comparing the 90%-iles of different years of determinands characterizing content of **nitrogen** in waters, it appears that in general nitrate-N shows the less changes whereas ammonium –N and nitrite-N fluctuate to a great extent.

For nitrate-N concentrations the ratio of changes from year to year is apart from some exceptions low for the Danube itself, but higher for tributaries. At River Arges (RO09) and Prut (RO11, MD03) it amounts one to three. Despite the implications of seasonal affects this fluctuation seems to be very high. For ammonium-N annual variations exceed 100 % at quite a number of monitoring sites and even amount 300 %. This picture can be a result of natural variations but might be also an indicator for accidentally detected impacts, e.g. when a specific yearly data set contains samples that were taken just after an incident like flood event, effluence of manure or breakdown of a water treatment plant.

In the Danube River, ammonium-N shows a decreasing tendency from 1996 to 2000 in the upper part and in the middle section in Slovakian monitoring sites. In majority of tributaries located in the upper and middle Danube, generally ammonium-N seems to decrease, excepting Croatian sites located on Sava River.

Looking at nitrate-N, its content decreases in Morava and Dyje. A clear decreasing trend from 1996 to 1999 is visible on the Sio. An opposite temporal variation appears on the Sajo and Arges.

Phosphorus content was measured as a total P and ortho-phosphate P. From upper/middle part, decreasing tendency is seen in the section from Danube-Bratislava (km 1869) down to Danube-Szob (km 1708), an exception appears at Danube-Medvedov/Medve (km 1806). Further downstream, variance between the years increases and specific problem arises with comparability of data in cross sections measured by two neighbouring countries. From tributaries, decreasing tendency was observed in Drava-Varazdin (HR03), but the rest of monitoring sites located on this tributary present a relative stable state. No temporal changes were observed in Tisza River, even the variation is low there.

Concerning total P, the variance between years is much higher than that of ortho-phosphates. Generally, total P temporal distribution in monitoring sites located on Danube River is rather scattered, or tendency of development is opposite if data for the same cross section, but provided by two countries, are taken into account (Danube-Novo Selo/Pristol). From tributaries the decrease of total P is visible in Arges and Siret, especially taken into account high values reached in 1996 that did not occur in the next period.

The **heavy metals** content is strongly dependent on quantity and nature of suspended solids, which is the reason of natural variations and trends that might hide the effect of anthropogenic contaminations. High values of heavy metals often reflect situations with high loads of suspended solids and flood events and statistical parameter used also in this report (90%-ile) – could be influenced by these processes. For this five-years evaluation, data on total concentration of heavy metals in water samples had been used, because data related to dissolved fraction are not available in sufficient extent. Anyway, some restrictions related to the trend analysis of heavy metals has to be mentioned again – sparse data sets and detection limits, that had changed rapidly over the years. Besides it seems that there are differences in analytical methods or extraction methods because in many cases data from monitoring sites, which are shared by two countries, do not fit together.

As a result of above mentioned factors, rather big yearly variations were observed - up to three times at most of the monitoring sites. Further, can be concluded, that there was practically no coincidence between the developments of the different heavy metals along the Danube. In spite of these uncertainties, it seems that development of heavy metals content in some tributaries is positive – decrease is indicated in Drava river (cadmium, chromium, copper, lead, nickel and zinc), in Arges (cadmium, chromium, copper, lead), Prut (cadmium, chromium, lead), in Siret (chromium, copper, lead).

From **biological determinands**, slight positive trend appeared within the evaluated years in case of saprobic index of macrozoobenthos, but no significant trend in microbiological determinands has been observed.

From comparison of TNMN data with EQS of EU legislation it can be concluded that:
·   atrazine concentrations at sampling sites seem to be no problem in comparison with proposed EQS, even if the mean was calculated by using the worst case calculation
·   mean values of total cadmium in lower part of Danube lie very close or even above the List I EQS stipulated by Directive 83/514/EEC. In the upper part of the river mean concentrations are below the EQS with exceptions of few results in 1996/97.
·   for p,p-DDT in the upper part of the Danube practically all data are below LOD; downstream Hungary the EQS laid down by Directive 86/280/EEC is exceeded in many cases. Change of calculation method did not improve this situation.

- in case of lindane two EQS could be used – existing EQS laid down by Direcitve 84/491/EEC and proposed new EQS. Whilst the existing EQS is exceeded only by extreme values, with new limit the situation will be worse.
- for total mercury very limited data are available, and these existing results show only one exceedance of the EQS. For Tetrachloroethane, Tetrachloromethane and Trichloroethylene the results are below existing EQS. Trichloromethane exceeds the EQS in one case. This is the only one of the four compounds which has been included in the list of Priority Substances. New proposed EQS causes an increase the number of exceeding values to three in the five-year period.

Recommendations

Assessment of water quality is very much dependent on availability and comparability of data provided from countries in the river basin, if the purpose is to provide reliable information to decision makers and public. This report used data from the first five years of joint monitoring programme of Danubian countries in the River basin that have not yet fulfil all requirements on frequency and data quality and comparability, although the situation is improving in the years. The gaps were discovered during the process of data interpretation, mainly regarding data comparability – it was revealed in several cases that data from the same cross sections provided by two countries would result in different final information, for example in trend assessment. Great problems were identified in case of availability of data on biological determinands, data on heavy metals and organic micropollutants. Even frequencies of measurements were such low in case of some determinands that prevent reliable interpretation.

The main recommendations related to TNMN are the following:

- Enhance TNMN in terms of keeping agreed set of physico-chemical and biological determinands and their frequencies by countries participating in TNMN. Specifically relevant in this respect is the group of organic micropollutants, biological determinands and some heavy metals. In addition, "newly" recommended determinands like dissolved phosphorus and heavy metals in dissolved phase should be improved in this way.

- Exert an effort to further improvement of quality of data and to harmonize the methods to an extent that will ensure data comparability between the countries. In addition, after finding out of not satisfactory results repeatedly from proficiency testing organised for laboratories involved in TNMN, the laboratories should analyse the reasons of this, propose and implement the measures for improvement, which would be reported and discussed in the MLIM-EG.

- Laboratories involved in the TNMN should try to keep limits of detection agreed for selected determinands for TNMN. It should be ensured that limits of detection of determinands are at least on sufficiently low level enabling comparing the results of analysis with target values set for the determinands.

- In near future it should be clearly distinguished between the terms limit of detection (LOD) and limit of quantification (LOQ) taking into account definitions used by the EU. TNMN database should be adjusted in this sense, including both characteristics.

- More attention should be paid in the future to determinands characterising eutrophication, mainly in the lower part of the river basin. If the Danube River is generally considered as eutrophicated river, on the basis of international monitoring it should be allowed to evaluate this process, together with identification of the most critical areas.

▪ Much more attention should be paid to the microbiological analyses. As in the present time would be rather difficult to ensure proficiency testing for microbiological determinands in Danube River basin, it is recommended to focus mainly to methodological problems and to enhance at least cooperation of neighbouring countries in DRB in this field.

▪ In connection to the WFD, more biological communities should be monitored in the Danube River basin, e.g. phytobenthos. In addition, discussion on inclusion of additional indices should start.

▪ It is recommended to report the dissolved oxygen in terms of both concentration and saturation, the latter being more relevant in this respect.

▪ Only very small fraction of specific organic micropollutants has been able to assess on the basis of TNMN data. Taking into account new needs in the field of monitoring of priority substances Tand other substances discharged in significant quantities in waters in Danube River Basin, inclusion of new specific substances relevant for Danube River basin is necessary. This process is recommended to do by utilisation of information from both JDS and from national surveys performed.

Abbreviations

c90	90 percentile
c10	10 percentile
DRB	Danube River Basin
DRPC	Danube River Protection Convention
EAF	Expert Advisory Forum Priority Substances
EC	European Commission
EQS	Environmental Quality Standard
FHI	Fraunhofer-Institute
JAP	Joint Action Plan for the Danube River Basin
LOD	Limit of Detection
MAC	Maximum allowable concentration
PS	Priority Substances
SOP	Standard Operational Procedure
TNMN	TransNational Monitoring Network
WFD	Water Framework Direcive

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Annex 1

Classification tables

Dissolved oxygen

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	10.4 / 8.7	10.2 / 8.6	10.5 / 8.6	10.6 / 8.8	10.4 / 9.3
/Inn/Salzach	Laufen	L2160	L	11.4 / 10.2	11.7 / 10.4	11.3 / 10.5	11.4 / 10.2	11.3 / 10.3
/Inn	Kirchdorf	L2150	M	11.9 / 10.4	11.4 / 9.8	11.7 / 10.4	11.3 / 9.9	11.4 / 10.2
Danube	Jochenstein	L2130	M	11.1 / 9.1	11.1 / 9.5	10.9 / 9.2	11.1 / 9.8	11.0 / 9.7
Danube	Jochenstein	L2220	M	11.1 / 9.0	11.2 / 9.5	10.8 / 9.2	10.7 / 9.7	11.2 / 9.9
Danube	Abwinden-Asten	L2200	R	11.2 / 9.4	11.2 / 9.1	11.1 / 9.0	10.8 / 9.6	11.1 / 9.6
Danube	Wien-Nussdorf	L2180	R	11.4 / 9.6	11.8 / 10.6	11.8 / 9.7	10.9 / 9.6	11.3 / 9.4
/Morava/Dyje	Pohansko	L2120	L	11.3 / 9.4	10.4 / 8.0	10.5 / 8.1	11.2 / 7.3	10.8 / 8.2
/Morava	Lanzhot	L2100	M	11.2 / 8.8	11.0 / 9.2	11.0 / 8.9	10.9 / 8.4	11.1 / 9.2
Danube	Wolfsthal	L2170	R	11.0 / 9.1	11.5 / 9.5	10.9 / 8.5	10.6 / 9.1	10.7 / 9.2
Danube	Bratislava	L1840	M	10.9 / 8.9	10.5 / 8.7	10.3 / 8.0	10.4 / 8.9	10.3 / 8.9
Danube	Medvedov/Medve	L1860	M	11.0 / 8.7	10.3 / 8.7	10.2 / 8.0	10.4 / 9.0	10.0 / 8.5
Danube	Medve/Medvedov	L1470	M	9.7 / 7.9	10.9 / 9.0	9.3 / 7.6	10.0 / 8.0	9.3 / 7.4
Danube	Komarno/Komarom	L1870	M	10.4 / 8.0	10.3 / 8.7	10.3 / 8.0	10.4 / 9.0	10.0 / 8.3
Danube	Komarom/Komarno	L1475	M	10.2 / 8.7	11.0 / 9.1	10.0 / 8.1	9.6 / 8.3	9.6 / 8.0
/Vah	Komarno	L1960	M	10.1 / 8.3	9.6 / 7.3	9.9 / 7.6	9.3 / 6.8	9.9 / 7.4
Danube	Szob	L1490	L	11.7 / 9.0	11.0 / 9.2	9.8 / 7.6	10.2 / 8.1	9.5 / 7.8
Danube	Szob	L1490	M	11.4 / 9.2	11.2 / 8.8	9.9 / 7.7	10.3 / 8.8	9.5 / 8.1
Danube	Szob	L1490	R	11.3 / 9.3	10.9 / 8.5	10.0 / 7.7	10.2 / 8.7	9.3 / 7.9
Danube	Dunafoldvar	L1520	L		11.4 / 8.9			10.9 / 9.4
Danube	Dunafoldvar	L1520	M	11.0 / 9.1	11.3 / 8.9	11.1 / 8.6	10.9 / 9.1	10.8 / 9.4
Danube	Dunafoldvar	L1520	R		11.3 / 9.2			10.8 / 9.2
/Sio	Szekszard-Palank	L1604	M	11.6 / 7.4	10.3 / 7.0	10.2 / 7.7	8.7 / 5.1	10.8 / 7.9
Danube	Hercegszanto	L1540	M	11.4 / 9.6	11.4 / 9.3	11.2 / 8.7	10.5 / 8.7	10.7 / 9.2
Danube	Batina	L1315	M			11.6 / 8.6	10.7 / 8.6	10.4 / 8.6
/Drava	Ormoz	L1390	L	11.0 / 9.1	11.7 / 9.9	11.4 / 9.1	11.2 / 9.7	11.5 / 8.9
/Drava	Varazdin	L1290	M	9.9 / 7.6	10.7 / 9.2	10.6 / 8.6	11.5 / 9.9	9.8 / 8.3
/Drava	Botovo	L1240	M	10.1 / 8.5	10.3 / 8.3	9.5 / 8.0	9.7 / 8.3	9.3 / 7.8
/Drava	D.Miholjac	L1250	R	10.2 / 8.3	10.8 / 8.8	9.7 / 8.1	9.9 / 8.8	9.6 / 8.4
/Drava	Dravaszabolcs	L1610	M	10.9 / 8.6	10.1 / 7.5	9.8 / 8.1	9.8 / 8.2	9.5 / 8.0
Danube	Borovo	L1320	R			10.7 / 7.9	9.7 / 7.5	9.3 / 7.2
/Tisza/Sajo	Sajopuspoki	L1770	M	10.8 / 8.0	10.8 / 8.6	10.7 / 8.2	10.5 / 8.1	10.6 / 8.3
/Tisza	Tiszasziget	L1700	L	9.5 / 8.9	9.3 / 6.8	9.1 / 6.9	9.0 / 6.4	9.6 / 7.6
/Tisza	Tiszasziget	L1700	M	9.3 / 7.7	9.3 / 6.7	9.0 / 6.7	9.0 / 6.4	9.7 / 7.8
/Tisza	Tiszasziget	L1700	R	9.4 / 8.6	9.2 / 6.4	8.8 / 6.6	8.8 / 6.1	9.5 / 7.7
/Sava	Jesenice	L1330	R	10.5 / 8.0	10.1 / 7.7	10.0 / 8.2	10.1 / 8.8	9.7 / 7.8
/Sava	Jesenice	L1220	L				9.8 / 8.5	9.0 / 7.4
/Sava	Jesenice	L1220	R	9.6 / 7.5	9.0 / 6.9	9.1 / 7.6		
/Sava	us.Una Jasenovac	L1150	L	8.9 / 7.4	8.5 / 6.9	8.5 / 6.0	8.5 / 7.1	9.0 / 7.1
/Sava	ds.Zupanja	L1060	M	9.0 / 7.2	9.2 / 7.4	8.5 / 5.5	8.6 / 6.5	
/Sava	ds.Zupanja	L1060	R					8.6 / 6.7
Danube	Bazias	L0020	L	8.7 / 6.9	9.0 / 6.9	9.3 / 6.6	8.6 / 5.7	8.4 / 6.8
Danube	Bazias	L0020	M	8.4 / 6.8	8.9 / 7.1	9.2 / 6.8	8.4 / 5.5	8.6 / 7.1
Danube	Bazias	L0020	R		8.9 / 6.8	9.1 / 6.5	8.6 / 5.3	7.9 / 6.7
Danube	Pristol/Novo Selo Harbour	L0090	L	8.6 / 6.0	8.6 / 6.6	8.7 / 6.2	8.5 / 6.0	7.6 / 5.7
Danube	Pristol/Novo Selo Harbour	L0090	M	8.0 / 6.2	8.6 / 6.9	8.8 / 6.5	8.7 / 6.0	7.7 / 6.0
Danube	Pristol/Novo Selo Harbour	L0090	R	7.7 / 5.9	8.7 / 6.4	8.6 / 6.1	8.6 / 6.0	7.4 / 5.7
Danube	Novo Selo Harbour/Pristol	L0730	L	7.6 / 5.6	6.9 / 4.0	6.9 / 4.9	6.9 / 5.4	7.8 / 6.1

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	M	7.6 / 5.7	6.5 / 3.9	6.6 / 4.5	7.1 / 5.4	7.4 / 5.9
Danube	Novo Selo Harbour/Pristol	L0730	R	7.7 / 6.0	6.6 / 4.1	6.6 / 4.6	6.9 / 5.5	7.9 / 6.1
Danube	us.Iskar-Bajkal	L0780	R	10.6 / 4.8		6.9 / 4.9	7.5 / 6.4	9.5 / 8.4
/Iskar	Orechovitza	L0930	M	9.6 / 8.3		6.8 / 5.0	7.9 / 6.2	9.5 / 7.3
Danube	Downstream Svishstov	L0810	M	10.2 / 8.9				
Danube	Downstream Svishstov	L0810	R		9.4 / 7.8		9.2 / 7.4	9.7 / 8.1
/Jantra	Karantzi	L0990	M	9.6 / 9.0	8.5 / 6.6		9.1 / 7.1	9.9 / 8.5
Danube	us.Russe	L0820	M	9.5 / 7.5				
Danube	us.Russe	L0820	R	8.5 / 7.5	8.0 / 6.3		9.4 / 7.6	8.2 / 6.4
/Russ.Lom	Basarbovo	L1010	M		9.3 / 7.8		8.4 / 6.4	8.5 / 6.1
Danube	us. Arges	L0240	L	7.8 / 5.8	8.6 / 6.1	8.7 / 6.3	9.1 / 6.6	8.5 / 7.5
Danube	us. Arges	L0240	M	7.7 / 6.0	8.9 / 6.3	8.8 / 6.5	9.1 / 6.6	8.8 / 7.2
Danube	us. Arges	L0240	R		8.8 / 6.2	8.8 / 6.4	9.1 / 6.6	8.6 / 7.1
/Arges	Conf.Danube	L0250	M	6.0 / 2.4	5.7 / 3.0	6.7 / 3.3	6.4 / 3.5	7.5 / 6.2
Danube	Chiciu/Silistra	L0280	L	6.8 / 5.7	8.4 / 6.1	8.5 / 6.1	8.4 / 6.5	9.2 / 8.0
Danube	Chiciu/Silistra	L0280	M	7.1 / 6.1	8.9 / 6.4	8.6 / 6.5	8.3 / 6.4	9.4 / 8.3
Danube	Chiciu/Silistra	L0280	R	7.0 / 5.8	8.9 / 6.2	8.6 / 6.4	8.3 / 6.4	8.9 / 7.0
Danube	Silistra/Chiciu	L0850	L	8.3 / 6.7	9.3 / 8.5	8.6 / 6.2	9.1 / 7.1	8.0 / 6.2
Danube	Silistra/Chiciu	L0850	M	8.5 / 7.6	9.5 / 8.4	9.1 / 6.7	9.2 / 7.2	8.5 / 5.8
Danube	Silistra/Chiciu	L0850	R	8.6 / 7.7	9.6 / 8.6	8.3 / 6.6	9.2 / 7.4	8.3 / 6.0
/Siret	Conf.Danube Sendreni	L0380	M	5.9 / 0.2	8.2 / 5.6	7.8 / 6.3	8.4 / 5.5	10.4 / 8.0
/Prut	Lipcani	L2230	L			11.9 / 11.4	10.1 / 7.8	9.1 / 5.9
/Prut	Leuseni	L2250	M			8.4 / 7.2	10.0 / 8.1	7.5 / 7.5
/Prut	Conf.Danube-Giurgiulesti	L2270	L			9.1 / 6.5	8.7 / 6.8	7.8 / 4.9
/Prut	Conf.Danube Giurgiulesti	L0420	M	7.3 / 0.2	8.3 / 6.5	8.4 / 6.9	8.9 / 6.7	9.0 / 6.8
Danube	Reni-Chilia/Kilia arm	L0430	L	7.9 / 5.9	8.7 / 6.4	8.8 / 6.6	8.7 / 6.7	7.3 / 6.6
Danube	Reni-Chilia/Kilia arm	L0430	M	8.3 / 6.2	8.9 / 6.4	8.8 / 6.7	8.8 / 6.9	7.2 / 6.5
Danube	Reni-Chilia/Kilia arm	L0430	R	7.9 / 6.1	9.0 / 6.4	8.9 / 6.4	8.8 / 6.8	7.2 / 6.6
Danube	Reni-Kilia arm/Chilia arm	L0630	M	9.2 / 6.1		9.2 / 7.7	8.9 / 8.1	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	8.3 / 6.2	8.1 / 6.2	8.7 / 6.4	8.7 / 6.8	7.7 / 6.1
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	8.4 / 6.4	8.1 / 6.4	8.8 / 6.7	8.7 / 6.6	8.0 / 6.3
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	8.3 / 6.1	8.0 / 6.3	8.8 / 6.5	8.7 / 6.5	7.9 / 6.1
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	9.1 / 6.7	9.6 / 8.2	9.4 / 8.1	9.1 / 8.0	
Danube	Sulina - Sulina arm	L0480	L	8.7 / 8.5	8.3 / 6.2	8.8 / 6.6	8.8 / 7.0	8.1 / 6.6
Danube	Sulina - Sulina arm	L0480	M	7.6 / 6.3	8.2 / 6.5	8.8 / 6.5	8.8 / 6.7	8.0 / 6.8
Danube	Sulina - Sulina arm	L0480	R	8.3 / 7.9	7.8 / 6.2	8.8 / 6.8	8.7 / 6.6	7.9 / 6.4
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	8.6 / 8.1	8.2 / 6.1	8.8 / 6.7	8.7 / 6.9	8.1 / 6.6
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	7.6 / 6.5	8.2 / 6.2	8.8 / 6.6	8.8 / 6.7	8.0 / 6.5
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	8.9 / 8.6	8.1 / 6.2	8.9 / 6.8	8.7 / 6.8	8.1 / 6.7

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:

[1] mean annual value
[2] testing value, which represents:

- 10 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a year

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

BOD$_5$

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	1.5 / 2.1	1.4 / 2.2	1.4 / 2.0	1.3 / 1.6	1.2 / 1.4
/Inn/Salzach	Laufen	L2160	L	2.7 / 3.9	2.8 / 3.7	2.6 / 3.5	1.9 / 3.2	1.8 / 2.4
/Inn	Kirchdorf	L2150	M	2.8 / 4.0	2.3 / 4.2	1.9 / 3.4	1.2 / 1.9	1.3 / 2.0
Danube	Jochenstein	L2130	M	2.2 / 3.4	2.4 / 3.3	2.2 / 3.1	2.2 / 3.3	2.1 / 2.8
Danube	Jochenstein	L2220	M	2.1 / 3.3	2.0 / 2.9	2.4 / 4.4	1.8 / 2.4	1.4 / 2.4
Danube	Abwinden-Asten	L2200	R	2.3 / 4.2	2.5 / 4.0	2.6 / 5.1	2.2 / 3.2	1.7 / 2.7
Danube	Wien-Nussdorf	L2180	R	2.1 / 4.0	2.1 / 3.0	2.5 / 3.8	2.3 / 3.0	1.7 / 3.1
/Morava/Dyje	Pohansko	L2120	L	6.0 / 11.0	5.1 / 6.5	6.4 / 8.4	4.5 / 6.7	4.1 / 6.0
/Morava	Lanzhot	L2100	M	5.0 / 6.1	5.4 / 7.2	4.4 / 6.5	5.5 / 9.1	3.6 / 4.8
Danube	Wolfsthal	L2170	R	3.6 / 5.6	2.5 / 3.2	2.9 / 4.4	2.4 / 3.6	1.6 / 2.6
Danube	Bratislava	L1840	M	2.5 / 4.3	2.0 / 2.7	2.0 / 3.6	1.8 / 2.6	2.0 / 2.7
Danube	Medvedov/Medve	L1860	M	2.5 / 3.7	1.9 / 2.6	2.0 / 3.1	1.7 / 2.8	1.5 / 2.0
Danube	Medve/Medvedov	L1470	M	2.7 / 3.3	2.5 / 3.5	2.7 / 3.8	2.0 / 2.9	1.8 / 2.2
Danube	Komarno/Komarom	L1870	M	2.7 / 3.8	2.1 / 3.4	2.2 / 3.3	1.8 / 2.4	1.7 / 2.1
Danube	Komarom/Komarno	L1475	M	2.5 / 3.0	3.3 / 4.6	3.3 / 4.4	2.2 / 3.3	1.6 / 2.2
/Vah	Komarno	L1960	M	4.4 / 6.5	3.9 / 5.8	2.6 / 3.6	2.1 / 2.7	2.8 / 3.8
Danube	Szob	L1490	L	4.1 / 4.6	4.4 / 5.5	4.1 / 5.2	4.5 / 5.6	3.8 / 4.7
Danube	Szob	L1490	M	4.5 / 5.6	3.7 / 4.7	3.7 / 4.9	3.7 / 4.5	3.6 / 4.5
Danube	Szob	L1490	R	3.9 / 4.8	3.9 / 5.0	3.8 / 4.9	3.8 / 4.4	3.7 / 5.0
Danube	Dunafoldvar	L1520	L		3.5 / 4.6			3.4 / 4.4
Danube	Dunafoldvar	L1520	M	3.2 / 5.2	3.9 / 5.4	4.3 / 6.9	3.5 / 5.4	3.5 / 4.6
Danube	Dunafoldvar	L1520	R		4.1 / 6.1			3.7 / 4.8
/Sio	Szekszard-Palank	L1604	M	6.2 / 9.5	5.7 / 9.5	3.9 / 6.3	3.8 / 5.5	5.0 / 7.6
Danube	Hercegszanto	L1540	M	3.8 / 6.9	4.4 / 8.2	4.3 / 7.2	3.2 / 4.6	3.4 / 4.7
Danube	Batina	L1315	M			4.5 / 6.0	4.2 / 5.3	4.1 / 7.1
/Drava	Ormoz	L1390	L	2.3 / 3.0	3.3 / 3.9	2.2 / 3.5	2.2 / 3.4	2.3 / 3.2
/Drava	Varazdin	L1290	M	3.0 / 4.7	3.5 / 5.2	2.8 / 4.5	2.6 / 4.4	1.8 / 2.8
/Drava	Botovo	L1240	M	2.8 / 3.8	2.9 / 4.1	2.5 / 4.2	2.3 / 3.3	2.1 / 3.2
/Drava	D.Miholjac	L1250	R	2.7 / 4.1	3.2 / 5.1	2.4 / 3.5	2.4 / 3.2	2.2 / 3.5
/Drava	Dravaszabolcs	L1610	M	3.2 / 5.6	3.3 / 5.7	3.0 / 5.1	2.9 / 4.5	2.9 / 4.9
Danube	Borovo	L1320	R			4.4 / 7.6	4.1 / 5.7	3.6 / 5.5
/Tisza/Sajo	Sajopuspoki	L1770	M	3.7 / 4.5	3.8 / 5.2	3.5 / 5.4	3.2 / 4.6	3.8 / 5.6
/Tisza	Tiszasziget	L1700	L	1.8 / 2.3	2.0 / 2.7	1.9 / 2.8	2.1 / 3.0	2.1 / 3.4
/Tisza	Tiszasziget	L1700	M	2.5 / 4.2	1.9 / 2.8	1.8 / 2.7	2.0 / 2.8	2.3 / 3.2
/Tisza	Tiszasziget	L1700	R	2.4 / 2.8	2.3 / 4.0	2.1 / 3.5	2.6 / 3.6	2.9 / 3.8
/Sava	Jesenice	L1330	R	2.5 / 3.6	3.2 / 4.2	2.5 / 3.5	2.7 / 3.7	2.8 / 3.9
/Sava	Jesenice	L1220	L				1.7 / 2.6	2.1 / 3.4
/Sava	Jesenice	L1220	R	2.6 / 3.4	2.9 / 3.8	3.4 / 4.6		
/Sava	us.Una Jasenovac	L1150	L	3.1 / 5.5	3.7 / 5.5	1.7 / 3.2	1.4 / 1.8	3.2 / 5.4
/Sava	ds.Zupanja	L1060	M	2.4 / 3.3	2.8 / 3.7	2.7 / 3.4	2.7 / 3.5	
/Sava	ds.Zupanja	L1060	R					3.0 / 3.7
Danube	Bazias	L0020	L	2.6 / 3.6	4.4 / 6.8	4.6 / 6.1	3.5 / 5.8	4.2 / 4.8
Danube	Bazias	L0020	M	2.3 / 2.9	4.5 / 7.1	4.4 / 5.8	3.2 / 5.1	3.6 / 4.2
Danube	Bazias	L0020	R		4.5 / 7.1	4.6 / 6.1	3.2 / 5.0	3.9 / 4.6
Danube	Pristol/Novo Selo Harbour	L0090	L	2.5 / 3.4	4.5 / 5.8	4.5 / 6.6	3.4 / 4.4	4.1 / 4.4
Danube	Pristol/Novo Selo Harbour	L0090	M	2.1 / 2.9	4.4 / 6.1	4.2 / 6.3	3.0 / 4.0	3.5 / 4.1
Danube	Pristol/Novo Selo Harbour	L0090	R	2.2 / 3.0	4.5 / 6.1	4.5 / 6.2	3.5 / 4.2	4.0 / 5.1
Danube	Novo Selo Harbour/Pristol	L0730	L	2.0 / 3.4	1.8 / 2.1	1.6 / 2.1	1.5 / 2.1	2.4 / 3.1

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	M	1.9 / 3.7	1.9 / 2.1	1.6 / 2.3	1.4 / 2.2	2.3 / 3.1
Danube	Novo Selo Harbour/Pristol	L0730	R	2.0 / 3.8	2.0 / 2.8	1.6 / 2.3	1.6 / 2.2	2.6 / 3.6
Danube	us.Iskar-Bajkal	L0780	R	2.3 / 2.4		2.2 / 4.7	1.5 / 1.9	2.3 / 3.2
/Iskar	Orechovitza	L0930	M	6.6 / 8.3		2.6 / 4.6	2.0 / 2.9	2.6 / 3.5
Danube	Downstream Svishstov	L0810	M	4.8 / 6.7				
Danube	Downstream Svishstov	L0810	R				3.5 / 5.0	2.1 / 3.8
/Jantra	Karantzi	L0990	M	4.6 / 5.6			5.2 / 7.8	3.3 / 4.6
Danube	us.Russe	L0820	M	3.2 / 3.5				
Danube	us.Russe	L0820	R				3.1 / 4.0	2.5 / 2.9
/Russ.Lom	Basarbovo	L1010	M				6.9 / 8.8	6.9 / 8.9
Danube	us. Arges	L0240	L	2.8 / 3.4	3.4 / 4.0	3.7 / 4.4	3.9 / 4.8	3.4 / 3.8
Danube	us. Arges	L0240	M	2.6 / 3.1	3.3 / 3.7	3.4 / 4.1	3.4 / 4.0	3.1 / 3.5
Danube	us. Arges	L0240	R		3.5 / 3.9	3.6 / 4.0	3.7 / 4.4	3.4 / 3.8
/Arges	Conf.Danube	L0250	M	28.0 / 62.5	6.8 / 9.7	5.9 / 7.0	6.5 / 8.3	9.9 / 6.4
Danube	Chiciu/Silistra	L0280	L	2.7 / 3.3	3.4 / 4.3	4.2 / 5.1	3.2 / 4.3	3.6 / 4.6
Danube	Chiciu/Silistra	L0280	M	2.8 / 3.5	3.4 / 4.8	4.1 / 5.2	3.4 / 4.6	3.5 / 4.4
Danube	Chiciu/Silistra	L0280	R	2.8 / 3.4	3.4 / 4.3	4.4 / 5.5	3.5 / 4.5	3.4 / 4.6
Danube	Silistra/Chiciu	L0850	L	2.7 / 4.2	3.2 / 4.0	3.2 / 4.6	2.8 / 3.6	2.2 / 2.7
Danube	Silistra/Chiciu	L0850	M	2.7 / 3.8	3.1 / 3.7	2.7 / 3.4	2.8 / 3.4	2.3 / 3.2
Danube	Silistra/Chiciu	L0850	R	2.6 / 4.4	3.4 / 4.9	2.9 / 4.1	2.9 / 3.3	2.2 / 2.8
/Siret	Conf.Danube Sendreni	L0380	M	5.6 / 6.5	5.6 / 7.1	5.9 / 6.9	4.5 / 5.7	4.8 / 7.0
/Prut	Lipcani	L2230	L			1.6 / 2.1	2.7 / 3.9	2.4 / 3.5
/Prut	Leuseni	L2250	M			3.8 / 6.4	3.1 / 4.1	3.6 / 3.6
/Prut	Conf.Danube-Giurgiulesti	L2270	L			2.4 / 3.0	2.5 / 3.6	2.3 / 3.2
/Prut	Conf.Danube Giurgiulesti	L0420	M	2.9 / 4.3	4.3 / 5.5	5.0 / 6.1	3.9 / 5.8	4.2 / 5.5
Danube	Reni-Chilia/Kilia arm	L0430	L	2.8 / 3.4	3.5 / 4.1	3.7 / 4.3	2.9 / 3.5	2.2 / 2.7
Danube	Reni-Chilia/Kilia arm	L0430	M	2.8 / 3.4	3.6 / 4.9	3.7 / 4.6	2.8 / 3.2	2.2 / 2.8
Danube	Reni-Chilia/Kilia arm	L0430	R	2.8 / 3.5	3.5 / 3.9	3.6 / 4.2	3.0 / 3.8	2.1 / 2.6
Danube	Reni-Kilia arm/Chilia arm	L0630	M	3.0 / 4.2		2.5 / 3.9	1.3 / 1.8	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	2.6 / 3.1	2.9 / 3.8	3.8 / 4.6	3.0 / 3.4	2.5 / 3.6
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	2.8 / 3.3	3.0 / 3.6	3.7 / 4.7	2.9 / 3.7	2.6 / 3.3
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	2.5 / 3.2	2.8 / 3.5	3.7 / 4.9	3.0 / 3.7	2.4 / 3.2
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	3.3 / 4.9	3.4 / 4.2	2.3 / 3.2	1.5 / 2.4	
Danube	Sulina - Sulina arm	L0480	L	2.3 / 3.0	3.0 / 3.6	3.9 / 4.7	2.9 / 3.3	2.8 / 3.8
Danube	Sulina - Sulina arm	L0480	M	2.7 / 3.3	3.0 / 3.8	3.8 / 4.5	2.8 / 3.2	2.8 / 3.7
Danube	Sulina - Sulina arm	L0480	R	1.9 / 3.1	3.1 / 3.9	3.9 / 4.7	2.8 / 3.5	2.7 / 3.5
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	2.1 / 3.3	3.0 / 4.1	3.6 / 4.4	2.8 / 3.2	2.8 / 3.5
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	2.5 / 3.0	2.9 / 3.5	3.6 / 4.5	2.9 / 3.9	2.7 / 3.3
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	2.2 / 3.2	3.2 / 4.3	3.5 / 4.2	3.0 / 3.9	2.7 / 3.2

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:

[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a year

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

COD-Mn

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	2.7 4.1	2.6 3.5	2.9 4.3	2.6 3.8	2.4 3.6
/Inn/Salzach	Laufen	L2160	L	2.8 4.3	2.1 3.3	2.3 3.9	2.1 2.8	2.6 3.4
/Inn	Kirchdorf	L2150	M	1.7 2.2	1.5 1.8	1.4 2.0	1.5 2.2	1.7 3.2
Danube	Jochenstein	L2130	M	3.0 3.4	2.7 3.6	3.1 3.9	2.9 4.0	2.8 3.9
Danube	Jochenstein	L2220	M	3.1 3.5	2.7 3.7	3.1 3.5	3.1 4.0	3.0 4.3
Danube	Abwinden-Asten	L2200	R	2.9 3.3	2.7 3.5	3.2 3.8	3.1 3.8	2.9 4.0
Danube	Wien-Nussdorf	L2180	R	3.1 3.5	2.8 3.5	3.5 3.7	3.4 4.0	3.3 4.5
/Morava/Dyje	Pohansko	L2120	L	9.1 10.8	8.3 10.2	9.0 11.1	11.3 10.3	8.2 9.2
/Morava	Lanzhot	L2100	M	6.2 8.9	5.1 6.4	4.7 6.0	6.4 9.4	5.3 6.8
Danube	Wolfsthal	L2170	R	3.2 3.5	3.0 3.5	3.8 6.1	3.5 4.3	3.1 4.4
Danube	Bratislava	L1840	M	3.5 4.6	4.1 4.7	3.7 4.5	4.1 4.9	3.8 5.2
Danube	Medvedov/Medve	L1860	M	3.4 4.2	3.7 4.4	3.8 4.8	3.5 4.1	3.4 4.5
Danube	Medve/Medvedov	L1470	M	3.3 4.4	3.2 4.2	3.3 4.7	3.1 4.1	3.0 4.0
Danube	Komarno/Komarom	L1870	M	3.7 4.6	4.0 5.0	3.9 4.8	3.6 4.1	3.8 5.1
Danube	Komarom/Komarno	L1475	M	3.0 3.2	3.7 4.8	4.2 6.0	3.4 4.8	3.3 4.4
/Vah	Komarno	L1960	M	5.6 5.4	4.9 5.7	4.1 5.0	3.8 4.1	4.0 4.5
Danube	Szob	L1490	L	3.8 4.5	4.5 5.2	4.4 5.7	5.1 6.0	4.1 5.0
Danube	Szob	L1490	M	4.4 5.3	3.9 4.7	3.9 4.7	5.3 5.3	3.8 4.9
Danube	Szob	L1490	R	3.5 4.6	4.0 5.0	4.0 4.8	4.1 4.8	4.1 5.6
Danube	Dunafoldvar	L1520	L		4.7 6.6			4.3 5.5
Danube	Dunafoldvar	L1520	M	4.5 5.7	4.6 6.2	4.4 5.6	3.9 5.4	4.0 4.7
Danube	Dunafoldvar	L1520	R		4.7 6.4			4.1 5.4
/Sio	Szekszard-Palank	L1604	M	11.7 16.5	11.2 15.7	10.5 15.6	10.6 14.7	11.0 15.7
Danube	Hercegszanto	L1540	M	4.7 6.2	4.4 5.4	4.5 6.9	3.9 5.2	3.9 4.9
Danube	Batina	L1315	M			4.1 5.2	4.2 5.7	3.6 4.5
/Drava	Ormoz	L1390	L	3.0 3.5	3.1 3.4	2.3 2.9	2.3 2.9	2.1 3.4
/Drava	Varazdin	L1290	M	3.2 4.7	2.2 2.8	2.2 3.4	2.2 2.5	1.2 1.5
/Drava	Botovo	L1240	M	4.4 7.4	3.1 4.5	3.5 6.7	3.4 4.3	2.5 3.4
/Drava	D.Miholjac	L1250	R	4.2 6.4	3.4 3.8	3.2 3.9	3.6 5.2	2.4 2.8
/Drava	Dravaszabolcs	L1610	M	4.1 5.4	3.3 4.7	3.7 4.5	3.8 5.4	3.0 3.9
Danube	Borovo	L1320	R			2.9 4.1	2.9 3.7	2.8 3.4
/Tisza/Sajo	Sajopuspoki	L1770	M	4.2 5.4	4.5 7.3	5.3 8.3	4.6 8.4	5.0 7.1
/Tisza	Tiszasziget	L1700	L	4.8 7.4	5.1 7.3	5.8 8.5	5.8 8.3	5.3 7.3
/Tisza	Tiszasziget	L1700	M	4.8 6.7	4.8 7.3	5.6 7.9	5.7 8.2	5.1 7.0
/Tisza	Tiszasziget	L1700	R	4.5 6.2	4.8 6.1	5.6 8.1	5.7 8.1	5.3 6.7
/Sava	Jesenice	L1330	R	3.5 4.1	6.9 12.1	4.9 6.2	4.4 5.9	4.4 6.1
/Sava	Jesenice	L1220	L				3.7 5.2	4.0 5.3
/Sava	Jesenice	L1220	R	3.8 5.9	4.1 4.9	6.2 8.2		
/Sava	us.Una Jasenovac	L1150	L	3.9 4.7	3.9 4.9	4.7 6.0	3.3 4.0	4.3 5.9
/Sava	ds.Zupanja	L1060	M	4.7 6.4	4.7 6.2	4.5 5.6	4.4 5.9	
/Sava	ds.Zupanja	L1060	R					3.7 4.3
Danube	Bazias	L0020	L	4.1 4.8	6.0 9.0	6.0 7.9	5.4 8.2	5.8 8.4
Danube	Bazias	L0020	M	3.7 4.7	5.8 8.6	5.3 6.6	5.0 7.4	5.0 7.1
Danube	Bazias	L0020	R		6.1 8.7	6.0 8.2	5.1 7.5	5.5 7.1
Danube	Pristol/Novo Selo Harbour	L0090	L	6.6 9.6	5.8 7.4	6.0 8.8	4.4 5.7	5.5 8.3
Danube	Pristol/Novo Selo Harbour	L0090	M	3.7 4.9	5.5 7.2	5.5 8.1	4.0 5.3	4.8 6.4
Danube	Pristol/Novo Selo Harbour	L0090	R	3.8 4.7	5.8 7.5	5.9 8.4	4.5 5.3	5.3 7.5
Danube	Novo Selo Harbour/Pristol	L0730	L	3.2 4.9	2.7 3.2	2.6 3.4	2.5 2.9	4.3 6.0
Danube	Novo Selo Harbour/Pristol	L0730	M	3.2 4.9	2.7 3.0	2.5 3.6	2.5 3.2	4.3 6.1

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	R	3.3 / 4.7	2.7 / 3.1	2.4 / 2.8	2.6 / 3.1	4.5 / 6.0
Danube	us.Iskar-Bajkal	L0780	R	5.3 / 5.9		2.4 / 3.2	2.4 / 3.3	4.4 / 5.6
/Iskar	Orechovitza	L0930	M	9.6 / 14.8		3.5 / 5.1	3.1 / 4.0	5.3 / 6.2
Danube	Downstream Svishstov	L0810	M	6.2 / 9.4				
Danube	Downstream Svishstov	L0810	R		6.2 / 8.6		4.9 / 5.8	3.4 / 4.1
/Jantra	Karantzi	L0990	M	7.2 / 8.8	17.0 / 48.0		6.6 / 8.1	4.8 / 6.8
Danube	us.Russe	L0820	M	4.3 / 4.8				
Danube	us.Russe	L0820	R	4.3 / 4.8	4.8 / 5.9		4.4 / 5.3	4.1 / 4.9
/Russ.Lom	Basarbovo	L1010	M		9.8 / 10.5		10.5 / 14.1	11.0 / 12.9
Danube	us. Arges	L0240	L	4.0 / 4.7	4.7 / 5.8	4.9 / 6.1	4.9 / 6.6	5.2 / 6.0
Danube	us. Arges	L0240	M	3.8 / 4.3	4.5 / 6.0	4.4 / 5.4	4.4 / 5.4	4.7 / 5.6
Danube	us. Arges	L0240	R		4.5 / 6.0	4.7 / 5.7	4.6 / 6.0	5.2 / 6.0
/Arges	Conf.Danube	L0250	M	9.9 / 12.0	9.1 / 11.4	7.3 / 9.1	8.2 / 9.8	7.9 / 9.2
Danube	Chiciu/Silistra	L0280	L	5.3 / 9.2	5.9 / 7.1	6.0 / 7.0	4.4 / 6.0	5.9 / 8.0
Danube	Chiciu/Silistra	L0280	M	5.3 / 10.0	5.9 / 7.3	6.0 / 7.0	4.7 / 6.2	5.6 / 6.9
Danube	Chiciu/Silistra	L0280	R	5.5 / 9.7	5.7 / 7.0	6.4 / 7.3	4.9 / 7.9	5.7 / 7.4
Danube	Silistra/Chiciu	L0850	L	4.1 / 5.4	5.2 / 6.8	4.6 / 5.7	4.7 / 5.6	4.4 / 5.7
Danube	Silistra/Chiciu	L0850	M	3.9 / 5.1	5.0 / 6.8	4.5 / 5.5	4.3 / 5.1	4.1 / 5.1
Danube	Silistra/Chiciu	L0850	R	4.0 / 5.4	5.7 / 7.8	4.7 / 5.3	4.6 / 5.3	4.2 / 4.6
/Siret	Conf.Danube Sendreni	L0380	M	7.6 / 15.1	9.2 / 12.7	8.3 / 9.3	6.1 / 8.5	8.3 / 10.5
/Prut	Conf.Danube Giurgiulesti	L0420	M	6.5 / 9.0	8.1 / 11.3	7.5 / 9.2	5.7 / 7.9	7.4 / 12.2
Danube	Reni-Chilia/Kilia arm	L0430	L	4.4 / 7.5	6.1 / 7.6	5.8 / 6.7	4.4 / 5.1	5.1 / 7.2
Danube	Reni-Chilia/Kilia arm	L0430	M	4.3 / 6.8	5.8 / 7.3	6.3 / 6.9	4.1 / 4.9	5.0 / 7.1
Danube	Reni-Chilia/Kilia arm	L0430	R	4.3 / 6.5	5.9 / 8.1	6.1 / 6.8	4.3 / 6.3	4.9 / 7.3
Danube	Reni-Kilia arm/Chilia arm	L0630	M			3.8 / 5.0	2.5 / 3.4	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	4.0 / 4.4	6.4 / 9.2	6.3 / 7.5	4.2 / 5.6	6.4 / 7.9
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	3.9 / 4.3	6.5 / 9.5	6.4 / 7.4	4.1 / 5.2	6.1 / 7.3
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	4.1 / 4.4	6.5 / 9.4	5.9 / 6.9	4.3 / 5.0	5.8 / 6.9
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M			3.9 / 5.6	3.1 / 4.3	
Danube	Sulina - Sulina arm	L0480	L	5.4 / 6.1	6.1 / 8.4	6.4 / 7.2	4.1 / 4.9	4.8 / 6.1
Danube	Sulina - Sulina arm	L0480	M	4.6 / 5.9	6.1 / 8.4	6.2 / 7.1	4.1 / 5.6	5.5 / 6.6
Danube	Sulina - Sulina arm	L0480	R	5.2 / 5.9	6.2 / 7.9	5.9 / 7.1	4.1 / 5.6	5.0 / 6.6
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	4.9 / 5.6	6.4 / 8.8	5.9 / 6.6	4.4 / 6.0	5.3 / 6.6
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	4.4 / 5.8	6.4 / 8.8	5.9 / 7.4	4.4 / 5.1	5.4 / 7.1
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	5.0 / 5.9	6.5 / 8.9	6.2 / 7.3	4.2 / 5.1	4.9 / 6.4

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a year

blank fields mean that no measurements were done in the year

values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

COD_{cr}

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Jochenstein	L2130	M	15.0 / 15.0	15.0 / 16.0	15.1 / 15.0	15.0 / 15.0	15.0 / 15.0
Danube	Jochenstein	L2220	M	10.5 / 13.0	11.4 / 15.0	7.5 / 8.9	10.2 / 13.0	13.4 / 17.8
Danube	Abwinden-Asten	L2200	R	8.6 / 11.5	10.9 / 15.0	8.4 / 10.9	9.8 / 11.9	12.8 / 16.8
Danube	Wien-Nussdorf	L2180	R		11.3 / 15.0	9.2 / 12.7	10.7 / 13.0	13.9 / 18.6
/Morava/Dyje	Pohansko	L2120	L	37.1 / 41.8	35.1 / 41.0	36.4 / 43.4	28.6 / 33.3	24.0 / 31.2
/Morava	Lanzhot	L2100	M	28.9 / 39.6	24.0 / 31.2	18.8 / 25.4	18.0 / 25.6	16.1 / 23.9
Danube	Wolfsthal	L2170	R	9.5 / 15.0	12.8 / 15.0	11.8 / 18.9	11.9 / 16.8	14.0 / 19.2
Danube	Bratislava	L1840	M	15.5 / 27.8	11.7 / 13.1	10.6 / 13.3	11.7 / 13.4	10.9 / 14.7
Danube	Medvedov/Medve	L1860	M	13.1 / 23.8	10.0 / 14.4	10.9 / 14.6	10.1 / 11.2	10.0 / 12.3
Danube	Medve/Medvedov	L1470	M	12.3 / 16.7	9.4 / 13.5	10.9 / 13.5	11.0 / 13.0	9.0 / 11.0
Danube	Komarno/Komarom	L1870	M	15.7 / 24.9	11.8 / 14.7	11.9 / 14.5	10.4 / 13.1	10.9 / 15.0
Danube	Komarom/Komarno	L1475	M	13.0 / 14.0	10.7 / 14.0	11.3 / 14.6	11.7 / 15.0	9.8 / 13.0
/Vah	Komarno	L1960	M	19.6 / 39.2	15.0 / 18.3	13.3 / 16.2	11.8 / 14.2	12.5 / 14.6
Danube	Szob	L1490	L	14.0 / 16.0	16.1 / 21.2	14.3 / 19.0	16.7 / 18.0	15.5 / 20.0
Danube	Szob	L1490	M	15.7 / 21.2	13.9 / 18.6	12.7 / 15.0	13.3 / 17.0	15.0 / 19.5
Danube	Szob	L1490	R	12.0 / 15.0	14.2 / 18.0	12.5 / 16.5	13.1 / 17.0	15.7 / 20.5
Danube	Dunafoldvar	L1520	L		19.0 / 26.0			16.5 / 21.0
Danube	Dunafoldvar	L1520	M	17.4 / 21.9	18.9 / 27.0	17.4 / 21.1	15.2 / 19.0	16.3 / 20.0
Danube	Dunafoldvar	L1520	R		18.7 / 26.0			16.2 / 20.0
/Sio	Szekszard-Palank	L1604	M	32.7 / 46.3	30.2 / 38.2	29.0 / 49.2	27.1 / 33.5	29.7 / 39.5
Danube	Hercegszanto	L1540	M	18.5 / 21.9	17.5 / 23.0	18.4 / 25.0	15.1 / 18.0	15.1 / 19.0
Danube	Batina	L1315	M			16.6 / 19.0	14.5 / 19.8	14.7 / 18.8
/Drava	Ormoz	L1390	L	6.5 / 9.7	7.0 / 8.9	7.2 / 9.4	6.0 / 7.9	7.1 / 9.7
/Drava	Varazdin	L1290	M	4.6 / 6.7	4.4 / 8.6	5.8 / 9.7	5.9 / 7.5	4.9 / 6.3
/Drava	Botovo	L1240	M	10.1 / 15.0	8.0 / 12.9	8.8 / 16.4	8.1 / 11.8	7.1 / 9.9
/Drava	D.Miholjac	L1250	R	9.9 / 12.0	9.1 / 11.9	7.9 / 10.0	9.7 / 12.8	7.4 / 9.2
/Drava	Dravaszabolcs	L1610	M	11.6 / 16.0	8.7 / 12.0	10.3 / 11.5	11.6 / 15.0	8.0 / 10.0
Danube	Borovo	L1320	R			10.8 / 16.7	10.7 / 16.8	12.8 / 19.9
/Tisza/Sajo	Sajopuspoki	L1770	M	15.3 / 18.9	13.5 / 18.0	16.8 / 21.9	15.9 / 30.1	17.3 / 24.0
/Tisza	Tiszasziget	L1700	L	21.0 / 25.0	21.6 / 26.5	23.3 / 28.0	25.3 / 30.0	24.0 / 30.2
/Tisza	Tiszasziget	L1700	M	21.1 / 25.0	20.4 / 25.5	21.3 / 25.5	23.5 / 28.0	23.4 / 29.2
/Tisza	Tiszasziget	L1700	R	16.3 / 21.0	19.4 / 23.0	20.2 / 24.0	23.7 / 28.5	24.1 / 33.4
/Sava	Jesenice	L1330	R	7.6 / 10.7	15.8 / 32.3	12.5 / 15.3	11.0 / 15.0	11.9 / 16.0
/Sava	Jesenice	L1220	L				11.3 / 15.7	11.0 / 17.5
/Sava	Jesenice	L1220	R	12.2 / 16.4	12.4 / 16.9	18.4 / 21.5		
/Sava	us.Una Jasenovac	L1150	L					6.6 / 9.5
/Sava	ds.Zupanja	L1060	M	25.3 / 29.8	26.3 / 32.0	17.2 / 21.9	13.9 / 15.6	
/Sava	ds.Zupanja	L1060	R					13.5 / 17.8
Danube	Bazias	L0020	L	9.0 / 13.8	13.5 / 19.8	12.3 / 15.2	13.3 / 25.0	13.0 / 14.3
Danube	Bazias	L0020	M	7.1 / 12.5	13.3 / 18.4	10.8 / 13.1	12.2 / 22.0	11.2 / 17.1
Danube	Bazias	L0020	R		14.9 / 17.9	12.1 / 14.7	12.1 / 18.0	12.1 / 14.8
Danube	Pristol/Novo Selo Harbour	L0090	L	13.2 / 15.3	14.0 / 17.8	11.9 / 15.5	11.7 / 15.8	13.0 / 16.7
Danube	Pristol/Novo Selo Harbour	L0090	M	13.4 / 25.4	13.3 / 16.6	11.0 / 13.1	10.6 / 14.7	11.1 / 14.4
Danube	Pristol/Novo Selo Harbour	L0090	R	12.1 / 16.8	14.0 / 16.9	11.8 / 14.6	11.8 / 15.6	13.2 / 17.7
Danube	Novo Selo Harbour/Pristol	L0730	L	15.3 / 25.4	11.0 / 14.1	10.5 / 13.3	11.8 / 16.0	13.9 / 17.0
Danube	Novo Selo Harbour/Pristol	L0730	M	15.1 / 25.4	11.4 / 13.9	10.1 / 12.5	11.5 / 18.0	14.4 / 17.0
Danube	Novo Selo Harbour/Pristol	L0730	R	13.2 / 21.3	11.1 / 13.6	10.1 / 11.7	11.7 / 18.0	13.7 / 17.0
Danube	us.Iskar-Bajkal	L0780	R			9.4 / 13.7	10.2 / 18.0	16.4 / 32.0
/Iskar	Orechovitza	L0930	M	8.0 / 8.0		12.9 / 25.5	10.2 / 19.0	20.8 / 40.0

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Downstream Svishstov	L0810	M	11.0 15.0				
Danube	Downstream Svishstov	L0810	R		21.3 31.0		14.7 18.8	10.7 12.8
/Jantra	Karantzi	L0990	M	8.0 8.0	50.2 120.0		17.9 23.4	16.9 20.0
Danube	us.Russe	L0820	R		20.1 29.0		12.6 16.7	11.2 13.4
/Russ.Lom	Basarbovo	L1010	M		28.0 28.0		26.9 33.6	25.3 36.4
Danube	us. Arges	L0240	L	5.8 9.8	13.9 18.5	10.8 15.1	11.6 12.5	9.8 11.4
Danube	us. Arges	L0240	M	5.7 8.7	13.3 18.9	10.2 13.4	11.0 14.5	9.1 10.6
Danube	us. Arges	L0240	R		13.6 18.8	11.0 13.9	11.4 14.0	11.2 18.8
/Arges	Conf.Danube	L0250	M	10.3 17.6	19.3 25.8	16.4 20.0	14.6 17.1	14.1 17.5
Danube	Chiciu/Silistra	L0280	L	11.2 14.9	17.1 29.0	19.5 33.9	16.9 23.0	29.7 39.4
Danube	Chiciu/Silistra	L0280	M	10.6 12.8	16.4 22.0	20.4 29.8	16.9 25.0	30.6 38.2
Danube	Chiciu/Silistra	L0280	R	10.7 14.4	16.7 22.0	19.7 34.8	17.0 21.0	36.7 47.8
Danube	Silistra/Chiciu	L0850	L	11.8 13.9	18.8 25.0	16.3 28.3	12.7 15.5	11.3 13.6
Danube	Silistra/Chiciu	L0850	M	12.6 13.9	21.9 30.0	16.2 28.4	11.9 14.1	11.6 13.4
Danube	Silistra/Chiciu	L0850	R	15.7 18.2	19.0 33.0	17.4 31.8	13.1 16.1	12.0 14.4
/Siret	Conf.Danube Sendreni	L0380	M	14.5 62.0	38.4 65.0	32.3 57.8	19.1 31.0	38.0 62.0
/Prut	Lipcani	L2230	L			11.3 11.5	18.4 21.3	23.3 32.0
/Prut	Leuseni	L2250	M			11.3 11.7	17.3 25.1	17.6 17.6
/Prut	Conf.Danube-Giurgiulesti	L2270	L			22.3 27.8	18.8 26.9	23.8 34.0
/Prut	Conf.Danube Giurgiulesti	L0420	M	11.0 23.0	32.4 52.0	29.5 54.5	18.3 28.0	35.9 55.0
Danube	Reni-Chilia/Kilia arm	L0430	L	10.0 14.9	19.2 36.0	20.8 31.6	15.3 22.0	28.2 46.5
Danube	Reni-Chilia/Kilia arm	L0430	M	9.7 12.6	18.6 36.0	21.0 28.9	15.6 17.4	33.7 45.2
Danube	Reni-Chilia/Kilia arm	L0430	R	9.6 13.2	17.2 26.0	20.9 30.0	17.6 22.0	27.2 40.4
Danube	Reni-Kilia arm/Chilia arm	L0630	M			11.4 14.7	15.3 28.0	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	12.4 14.1	18.2 28.0	23.0 30.0	21.9 28.0	28.1 37.0
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	11.5 14.3	18.6 32.0	22.3 30.9	18.6 22.0	27.8 38.0
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	12.9 14.8	17.9 30.0	23.6 29.9	19.1 28.0	26.5 35.0
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M			10.3 15.1	12.9 19.1	
Danube	Sulina - Sulina arm	L0480	L	2.3 3.0	20.1 32.0	24.3 32.0	18.0 21.2	32.3 58.0
Danube	Sulina - Sulina arm	L0480	M	6.3 13.0	20.0 36.0	23.1 32.7	17.7 21.0	31.4 49.0
Danube	Sulina - Sulina arm	L0480	R	8.0 14.0	20.4 28.0	23.7 36.2	17.6 21.2	32.5 32.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	8.0 14.0	19.1 36.0	20.1 28.0	19.0 24.0	28.5 45.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	8.6 18.0	19.3 37.0	20.8 31.4	16.6 20.0	25.1 36.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	7.5 12.5	19.3 35.0	22.2 32.7	17.7 22.0	28.5 42.0

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was≥ 11 in a year
- maximum value, if number of measurements was < 11 in a yea

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

pH

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	8.1	8.1	8.1	8.2	8.2
Danube	Neu-Ulm			7.7	8.1	8.1	8.1	8.1
Danube	Neu-Ulm			8.2	8.2	8.2	8.2	8.2
/Inn/Salzach	Laufen	L2160	L	7.9	7.8	7.8	8.1	7.8
/Inn/Salzach	Laufen			7.8	7.7	7.7	8.0	7.6
/Inn/Salzach	Laufen			8.1	7.9	8.1	8.2	7.9
/Inn	Kirchdorf	L2150	M	8.1	8.1	8.2	8.1	8.2
/Inn	Kirchdorf			8.0	7.9	8.1	7.9	8.0
/Inn	Kirchdorf			8.2	8.3	8.4	8.4	8.4
Danube	Jochenstein	L2130	M	8.2	8.1	8.1	8.0	8.1
Danube	Jochenstein			8.0	7.9	7.9	7.9	8.0
Danube	Jochenstein			8.5	8.3	8.3	8.1	8.3
Danube	Jochenstein	L2220	M	8.2	8.3	8.2	8.2	8.3
Danube	Jochenstein			8.0	8.2	8.1	8.1	8.1
Danube	Jochenstein			8.3	8.4	8.4	8.3	8.4
Danube	Abwinden-Asten	L2200	R	8.2	8.3	8.3	8.2	8.3
Danube	Abwinden-Asten			8.0	8.2	8.1	8.1	8.2
Danube	Abwinden-Asten			8.3	8.4	8.5	8.3	8.5
Danube	Wien-Nussdorf	L2180	R	8.2	8.4	8.3	8.2	8.3
Danube	Wien-Nussdorf			8.0	8.2	8.1	8.1	8.2
Danube	Wien-Nussdorf			8.3	8.5	8.6	8.4	8.5
/Morava/Dyje	Pohansko	L2120	L	8.4	8.2	8.2	8.2	8.1
/Morava/Dyje	Pohansko			8.1	8.0	8.0	8.0	8.0
/Morava/Dyje	Pohansko			8.9	8.4	8.3	8.4	8.7
/Morava	Lanzhot	L2100	M	7.8	8.1	8.2	8.1	8.1
/Morava	Lanzhot			7.5	7.9	7.9	7.9	7.8
/Morava	Lanzhot			8.0	8.4	8.3	8.3	8.4
Danube	Wolfsthal	L2170	R	8.1	8.3	8.2	8.2	8.3
Danube	Wolfsthal			7.9	8.2	8.0	8.0	8.0
Danube	Wolfsthal			8.3	8.5	8.4	8.3	8.4
Danube	Bratislava	L1840	M	8.1	8.0	8.2	8.2	8.2
Danube	Bratislava			7.8	7.9	8.0	8.0	8.1
Danube	Bratislava			8.4	8.3	8.5	8.4	8.3
Danube	Medvedov/Medve	L1860	M	8.1	8.1	8.2	8.3	8.2
Danube	Medvedov/Medve			8.0	8.0	7.9	8.1	8.1
Danube	Medvedov/Medve			8.3	8.4	8.3	8.5	8.4
Danube	Medve/Medvedov	L1470	M	8.3	8.3	8.2	8.1	8.1
Danube	Medve/Medvedov			8.0	7.9	7.9	7.9	7.7
Danube	Medve/Medvedov			8.4	8.6	8.5	8.4	8.4
Danube	Komarno/Komarom	L1870	M	8.2	8.2	8.2	8.3	8.2
Danube	Komarno/Komarom			7.9	8.0	7.9	8.1	8.1
Danube	Komarno/Komarom			8.4	8.4	8.4	8.5	8.4
Danube	Komarom/Komarno	L1475	M	8.3	8.1	8.2	8.2	8.2
Danube	Komarom/Komarno			8.0	8.0	8.0	8.0	8.0
Danube	Komarom/Komarno			8.8	8.5	8.5	8.5	8.4
/Vah	Komarno	L1960	M	8.0	8.1	8.1	8.2	8.1
/Vah	Komarno			7.8	7.8	7.8	7.9	8.0
/Vah	Komarno			8.3	8.4	8.2	8.4	8.2
Danube	Szob	L1490	L	8.2	8.3	8.3	8.1	7.9
Danube	Szob			8.1	8.1	8.0	7.8	7.4
Danube	Szob			8.3	8.7	8.8	8.4	8.3
Danube	Szob	L1490	M	8.1	8.3	8.4	8.1	7.8
Danube	Szob			8.0	7.8	8.0	7.9	7.4
Danube	Szob			8.4	8.7	8.8	8.5	8.3
Danube	Szob	L1490	R	8.1	8.3	8.3	8.1	7.8
Danube	Szob			8.0	8.0	7.9	7.7	7.4
Danube	Szob			8.2	8.7	8.8	8.5	8.3
Danube	Dunafoldvar	L1520	L		8.3			8.3
Danube	Dunafoldvar				8.1			8.0
Danube	Dunafoldvar				8.6			8.7
Danube	Dunafoldvar	L1520	M	8.1	8.3	8.3	8.2	8.3
Danube	Dunafoldvar			8.0	8.0	8.0	8.0	8.0
Danube	Dunafoldvar			8.2	8.6	8.6	8.4	8.7
Danube	Dunafoldvar	L1520	R		8.3			8.2
Danube	Dunafoldvar				8.1			8.0
Danube	Dunafoldvar				8.6			8.7
/Sio	Szekszard-Palank	L1604	M.	8.3	8.3	8.3	8.2	8.3
/Sio	Szekszard-Palank			8.2	8.1	8.2	8.1	8.2
/Sio	Szekszard-Palank			8.7	8.5	8.4	8.4	8.5
Danube	Hercegszanto	L1540	M	8.2	8.3	8.3	8.1	8.2
Danube	Hercegszanto			8.0	8.0	8.0	8.0	8.0
Danube	Hercegszanto			8.5	8.5	8.6	8.3	8.5
Danube	Batina	L1315	M			8.3	8.1	8.1
Danube	Batina					8.0	8.0	7.8
Danube	Batina					8.5	8.3	8.4
/Drava	Ormoz	L1390	L	8.1	8.2	8.1	8.0	7.9
/Drava	Ormoz			8.0	7.9	7.9	7.8	7.6
/Drava	Ormoz			8.2	8.4	8.3	8.2	8.2
/Drava	Varazdin	L1290	M	7.9	7.6	7.4	7.4	7.6
/Drava	Varazdin			7.7	7.4	7.3	7.3	7.5
/Drava	Varazdin			8.0	7.9	7.5	7.5	7.8
/Drava	Botovo	L1240	M	7.9	7.8	7.7	7.8	7.8
/Drava	Botovo			7.6	7.3	7.4	7.4	7.4
/Drava	Botovo			8.1	8.2	8.1	8.2	8.1
/Drava	D.Miholjac	L1250	R	8.0	8.0	7.8	7.8	7.8
/Drava	D.Miholjac			7.4	7.7	7.5	7.5	7.5
/Drava	D.Miholjac			8.3	8.3	8.2	8.2	8.2
/Drava	Dravaszabolcs	L1610	M	8.2	8.2	8.1	8.1	8.2
/Drava	Dravaszabolcs			8.0	8.0	8.1	8.0	8.0
/Drava	Dravaszabolcs			8.4	8.3	8.3	8.3	8.4
Danube	Borovo	L1320	R			7.6	7.6	7.8
Danube	Borovo					7.3	7.4	7.5
Danube	Borovo					7.8	7.8	8.1
/Tisza/Sajo	Sajopuspoki	L1770	M	7.9	7.9	7.9	7.9	7.9
/Tisza/Sajo	Sajopuspoki			7.8	7.8	7.8	7.7	7.8
/Tisza/Sajo	Sajopuspoki			8.1	8.0	8.1	8.0	8.0

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Tisza	Tiszasziget	L1700	L	8.0	8.0	7.9	8.0	8.0
/Tisza	Tiszasziget			7.9	7.9	7.7	7.9	7.9
/Tisza	Tiszasziget			8.0	8.1	8.1	8.2	8.2
/Tisza	Tiszasziget	L1700	M	7.9	8.0	7.9	8.0	8.0
/Tisza	Tiszasziget			7.9	7.6	7.8	7.9	7.9
/Tisza	Tiszasziget			8.1	8.1	8.1	8.3	8.2
/Tisza	Tiszasziget	L1700	R	8.0	8.0	7.9	8.0	8.0
/Tisza	Tiszasziget			8.0	8.0	7.7	7.8	7.9
/Tisza	Tiszasziget			8.0	8.1	8.1	8.2	8.3
/Sava	Jesenice	L1330	R	8.1	8.0	7.9	7.9	7.7
/Sava	Jesenice			8.0	7.7	7.7	7.8	7.4
/Sava	Jesenice			8.2	8.3	8.1	8.1	7.9
/Sava	Jesenice	L1220	L				7.9	7.6
/Sava	Jesenice						7.8	7.2
/Sava	Jesenice						8.0	7.8
/Sava	Jesenice	L1220	R	7.5	7.9	7.9		
/Sava	Jesenice			7.3	7.5	7.7		
/Sava	Jesenice			7.7	8.1	8.1		
/Sava	us.Una Jasenovac	L1150	L	8.2	7.4	7.9	7.4	7.5
/Sava	us.Una Jasenovac			8.0	7.2	7.3	6.8	7.1
/Sava	us.Una Jasenovac			8.4	7.8	8.2	7.9	8.0
/Sava	ds.Zupanja	L1060	M	7.9	8.0	7.9	7.9	
/Sava	ds.Zupanja			7.5	7.8	7.7	7.8	
/Sava	ds.Zupanja			8.1	8.3	8.0	8.0	
/Sava	ds.Zupanja	L1060	R					8.0
/Sava	ds.Zupanja							7.8
/Sava	ds.Zupanja							8.1
Danube	Bazias	L0020	L	7.7	7.9	7.8	7.8	7.7
Danube	Bazias			7.5	7.7	7.6	7.7	7.4
Danube	Bazias			8.1	8.1	8.0	8.0	7.9
Danube	Bazias	L0020	M	7.7	8.0	7.8	7.8	7.6
Danube	Bazias			6.2	7.8	7.5	7.0	7.4
Danube	Bazias			8.2	8.1	8.1	8.0	7.8
Danube	Bazias	L0020	R		7.9	7.7	7.9	7.7
Danube	Bazias				7.8	7.5	7.7	7.5
Danube	Bazias				8.0	8.1	8.0	7.9
Danube	Pristol/Novo Selo Harbour	L0090	L	7.6	7.8	7.8	7.9	7.6
Danube	Pristol/Novo Selo Harbour			7.3	7.6	7.6	7.8	7.4
Danube	Pristol/Novo Selo Harbour			7.8	8.0	7.9	7.9	7.9
Danube	Pristol/Novo Selo Harbour	L0090	M	7.6	7.8	7.7	7.9	7.7
Danube	Pristol/Novo Selo Harbour			7.4	7.6	7.6	7.8	7.5
Danube	Pristol/Novo Selo Harbour			7.9	8.0	7.9	8.0	7.9
Danube	Pristol/Novo Selo Harbour	L0090	R	7.5	7.8	7.8	7.9	7.7
Danube	Pristol/Novo Selo Harbour			7.0	7.7	7.6	7.8	7.4
Danube	Pristol/Novo Selo Harbour			8.1	8.0	8.0	8.0	7.9
Danube	Novo Selo Harbour/Pristol	L0730	L	8.0	7.8	8.0	8.0	8.0
Danube	Novo Selo Harbour/Pristol			7.8	7.0	7.6	7.7	7.8
Danube	Novo Selo Harbour/Pristol			8.2	8.4	8.2	8.3	8.3
Danube	Novo Selo Harbour/Pristol	L0730	M	8.0	7.9	7.9	7.9	8.0
Danube	Novo Selo Harbour/Pristol			7.8	7.0	7.6	7.6	7.8
Danube	Novo Selo Harbour/Pristol			8.2	8.4	8.3	8.1	8.2
Danube	Novo Selo Harbour/Pristol	L0730	R	8.0	7.9	8.0	7.9	8.0
Danube	Novo Selo Harbour/Pristol			7.8	7.3	7.6	7.6	7.8
Danube	Novo Selo Harbour/Pristol			8.3	8.3	8.3	8.0	8.2
Danube	us.Iskar-Bajkal	L0780	R	7.9		8.0	8.0	8.0
Danube	us.Iskar-Bajkal			7.7		7.7	7.8	7.7
Danube	us.Iskar-Bajkal			8.1		8.4	8.2	8.3
/Iskar	Orechovitza	L0930	M	7.9		8.1	8.2	8.1
/Iskar	Orechovitza			7.6		7.8	8.0	7.8
/Iskar	Orechovitza			8.2		8.5	8.4	8.3
Danube	Downstream Svishstov	L0810	M	7.5				
Danube	Downstream Svishstov			7.1				
Danube	Downstream Svishstov			8.2				
Danube	Downstream Svishstov	L0810	R		7.3		7.9	8.0
Danube	Downstream Svishstov				7.0		7.7	7.8
Danube	Downstream Svishstov				7.7		8.1	8.2
/Jantra	Karantzi	L0990	M	7.6	7.6		8.0	8.1
/Jantra	Karantzi			7.0	6.0		7.8	7.9
/Jantra	Karantzi			7.9	8.5		8.2	8.3
Danube	us.Russe	L0820	M	7.4				
Danube	us.Russe			7.2				
Danube	us.Russe			7.5				
Danube	us.Russe	L0820	R	7.4	8.2		7.9	7.8
Danube	us.Russe			7.2	7.7		7.6	7.2
Danube	us.Russe			7.5	8.6		8.1	8.1
/Russ.Lom	Basarbovo	L1010	M		7.8		8.0	8.2
/Russ.Lom	Basarbovo				7.4		7.7	7.9
/Russ.Lom	Basarbovo				8.1		8.4	8.3
Danube	us. Arges	L0240	L	7.7	7.9	7.8	7.9	7.8
Danube	us. Arges			7.3	7.8	7.7	7.8	7.8
Danube	us. Arges			8.0	8.0	7.9	7.9	7.9
Danube	us. Arges	L0240	M	7.7	7.9	7.8	7.8	7.8
Danube	us. Arges			7.5	7.8	7.7	7.8	7.7
Danube	us. Arges			8.0	8.0	7.9	7.9	7.9
Danube	us. Arges	L0240	R		7.9	7.8	7.9	7.8
Danube	us. Arges				7.8	7.7	7.7	7.7
Danube	us. Arges				8.0	7.9	7.9	7.9
/Arges	Conf.Danube	L0250	M	7.6	7.9	8.0	7.9	8.0
/Arges	Conf.Danube			7.1	7.6	7.7	7.7	7.9
/Arges	Conf.Danube			7.9	8.1	8.2	8.1	8.2
Danube	Chiciu/Silistra	L0280	L	7.9	7.8	8.0	7.8	7.7
Danube	Chiciu/Silistra			7.6	7.6	7.8	7.7	7.3
Danube	Chiciu/Silistra			8.3	8.0	8.2	8.0	8.4
Danube	Chiciu/Silistra	L0280	M	7.9	7.8	8.0	7.8	7.7
Danube	Chiciu/Silistra			7.6	7.6	7.8	7.7	7.4
Danube	Chiciu/Silistra			8.3	8.0	8.2	7.9	8.3
Danube	Chiciu/Silistra	L0280	R	7.9	7.8	8.0	7.8	7.7
Danube	Chiciu/Silistra			7.7	7.6	7.8	7.8	7.3
Danube	Chiciu/Silistra			8.3	8.0	8.2	8.0	8.4

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Silistra/Chiciu	L0850	L	8.1	7.7	7.6	7.9	7.9
Danube	Silistra/Chiciu			7.9	7.6	7.3	7.7	7.5
Danube	Silistra/Chiciu			8.5	7.8	7.9	8.2	8.3
Danube	Silistra/Chiciu	L0850	M	8.1	7.7	7.6	8.0	7.9
Danube	Silistra/Chiciu			7.8	7.7	7.1	7.8	7.3
Danube	Silistra/Chiciu			8.3	7.8	7.9	8.3	8.6
Danube	Silistra/Chiciu	L0850	R	8.1	7.8	7.6	8.0	7.9
Danube	Silistra/Chiciu			7.9	7.6	7.3	7.8	7.6
Danube	Silistra/Chiciu			8.3	8.0	8.0	8.3	8.2
/Siret	Conf.Danube Sendreni	L0380	M	7.6	7.9	8.0	7.9	7.8
/Siret	Conf.Danube Sendreni			7.2	7.6	7.8	7.7	7.3
/Siret	Conf.Danube Sendreni			8.2	8.2	8.3	8.2	8.3
/Prut	Lipcani	L2230	L			8.2	8.4	8.3
/Prut	Lipcani					8.2	7.9	7.9
/Prut	Lipcani					8.2	8.8	8.5
/Prut	Leuseni	L2250	M			8.2	8.1	8.3
/Prut	Leuseni					8.1	7.9	8.3
/Prut	Leuseni					8.3	8.3	8.3
/Prut	Conf.Danube-Giurgiulesti	L2270	L			8.2	8.1	8.2
/Prut	Conf.Danube-Giurgiulesti					7.9	8.0	7.9
/Prut	Conf.Danube-Giurgiulesti					8.5	8.2	8.5
/Prut	Conf.Danube Giurgiulesti	L0420	M	7.9	8.0	8.1	7.9	7.9
/Prut	Conf.Danube Giurgiulesti			7.5	7.8	7.8	7.8	7.5
/Prut	Conf.Danube Giurgiulesti			8.2	8.2	8.4	8.2	8.3
Danube	Reni-Chilia/Kilia arm	L0430	L	7.5	7.9	8.1	7.9	7.7
Danube	Reni-Chilia/Kilia arm			7.3	7.6	7.9	7.8	7.3
Danube	Reni-Chilia/Kilia arm			7.7	8.2	8.2	8.0	8.5
Danube	Reni-Chilia/Kilia arm	L0430	M	7.5	7.9	8.0	7.9	7.8
Danube	Reni-Chilia/Kilia arm			7.3	7.7	7.8	7.8	7.3
Danube	Reni-Chilia/Kilia arm			7.7	8.2	8.2	8.1	8.5
Danube	Reni-Chilia/Kilia arm	L0430	R	7.5	7.9	8.1	7.9	7.8
Danube	Reni-Chilia/Kilia arm			7.4	7.7	7.9	7.8	7.3
Danube	Reni-Chilia/Kilia arm			7.7	8.1	8.2	8.0	8.5
Danube	Reni-Kilia arm/Chilia arm	L0630	M	8.0		8.0	8.2	
Danube	Reni-Kilia arm/Chilia arm			7.9		7.9	8.0	
Danube	Reni-Kilia arm/Chilia arm			8.1		8.0	8.3	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	7.7	7.9	8.1	7.9	7.9
Danube	Vilkova-Chilia arm/Kilia arm			7.5	7.6	7.9	7.8	7.3
Danube	Vilkova-Chilia arm/Kilia arm			8.1	8.1	8.2	8.0	8.5
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	7.7	7.9	8.0	7.9	7.7
Danube	Vilkova-Chilia arm/Kilia arm			7.5	7.6	7.8	7.8	7.1
Danube	Vilkova-Chilia arm/Kilia arm			8.0	8.2	8.2	8.0	8.5
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	7.7	7.9	8.1	7.9	7.8
Danube	Vilkova-Chilia arm/Kilia arm			7.5	7.6	7.9	7.8	7.1
Danube	Vilkova-Chilia arm/Kilia arm			8.0	8.2	8.2	8.0	8.5
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	8.0	8.0	8.0	8.1	
Danube	Vilkova-Kilia arm/Chilia arm			7.9	8.0	7.9	8.0	
Danube	Vilkova-Kilia arm/Chilia arm			8.1	8.0	8.0	8.3	
Danube	Sulina - Sulina arm	L0480	L	7.8	7.9	8.0	7.9	7.7
Danube	Sulina - Sulina arm			7.6	7.6	7.8	7.8	7.2
Danube	Sulina - Sulina arm			8.1	8.1	8.2	8.0	8.5
Danube	Sulina - Sulina arm	L0480	M	7.6	7.9	8.0	7.9	7.7
Danube	Sulina - Sulina arm			7.5	7.6	7.8	7.8	7.3
Danube	Sulina - Sulina arm			8.0	8.1	8.2	8.0	8.5
Danube	Sulina - Sulina arm	L0480	R	7.8	7.9	8.1	7.9	7.7
Danube	Sulina - Sulina arm			7.6	7.6	7.8	7.8	7.2
Danube	Sulina - Sulina arm			8.0	8.2	8.2	8.0	8.5
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	7.8	7.8	8.0	7.9	7.7
Danube	Sf.Gheorghe-Gheorghe arm			7.7	7.5	7.8	7.8	7.2
Danube	Sf.Gheorghe-Gheorghe arm			8.0	8.0	8.2	8.0	8.4
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	7.7	7.8	8.0	7.9	7.6
Danube	Sf.Gheorghe-Gheorghe arm			7.6	7.5	7.7	7.8	7.2
Danube	Sf.Gheorghe-Gheorghe arm			8.1	8.1	8.3	8.0	8.4
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	7.8	7.9	8.0	7.9	7.7
Danube	Sf.Gheorghe-Gheorghe arm			7.6	7.5	7.9	7.7	7.2
Danube	Sf.Gheorghe-Gheorghe arm			8.0	8.2	8.2	8.0	8.4

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

Note:

average[1]
testing value 1
testing value 2

[1] mean annual value

Testing value 1 represents lower limit of pH and is calculated as:
- *10 %-ile if number of measurement was≥ 11 in a year*
- *minimum value, if number of measurements was < 11 in a yea*

Testing value 2 represents upper limit of pH and is calculated as:
- *90 %-ile if number of measurement was≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a yea*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

N-NH$_4$

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.086 / 0.172	0.091 / 0.160	0.064 / 0.130	0.072 / 0.125	0.053 / 0.090
/Inn/Salzach	Laufen	L2160	L	0.077 / 0.190	0.037 / 0.064	0.053 / 0.105	0.028 / 0.045	0.028 / 0.050
/Inn	Kirchdorf	L2150	M	0.129 / 0.225	0.114 / 0.180	0.097 / 0.190	0.050 / 0.085	0.045 / 0.080
Danube	Jochenstein	L2130	M	0.082 / 0.160	0.067 / 0.120	0.069 / 0.100	0.078 / 0.120	0.066 / 0.110
Danube	Jochenstein	L2220	M	0.124 / 0.211	0.109 / 0.155	0.109 / 0.166	0.099 / 0.124	0.067 / 0.102
Danube	Abwinden-Asten	L2200	R	0.104 / 0.158	0.122 / 0.204	0.103 / 0.130	0.103 / 0.152	0.077 / 0.133
Danube	Wien-Nussdorf	L2180	R	0.130 / 0.238	0.110 / 0.147	0.114 / 0.125	0.135 / 0.125	0.073 / 0.125
/Morava/Dyje	Pohansko	L2120	L	0.470 / 1.184	0.476 / 1.047	0.340 / 0.564	0.387 / 0.891	0.388 / 0.539
/Morava	Lanzhot	L2100	M	0.693 / 1.930	0.661 / 1.160	0.391 / 0.673	0.444 / 0.882	0.320 / 0.780
Danube	Wolfsthal	L2170	R	0.160 / 0.242	0.124 / 0.181	0.152 / 0.227	0.121 / 0.225	0.104 / 0.180
Danube	Bratislava	L1840	M	0.293 / 0.469	0.229 / 0.466	0.141 / 0.273	0.145 / 0.288	0.158 / 0.298
Danube	Medvedov/Medve	L1860	M	0.226 / 0.363	0.200 / 0.488	0.137 / 0.198	0.147 / 0.323	0.130 / 0.209
Danube	Medve/Medvedov	L1470	M	0.071 / 0.127	0.062 / 0.135	0.062 / 0.135	0.057 / 0.110	0.057 / 0.110
Danube	Komarno/Komarom	L1870	M	0.230 / 0.406	0.240 / 0.568	0.143 / 0.270	0.161 / 0.259	0.147 / 0.272
Danube	Komarom/Komarno	L1475	M	0.087 / 0.120	0.073 / 0.180	0.080 / 0.184	0.072 / 0.160	0.111 / 0.205
/Vah	Komarno	L1960	M	0.627 / 0.996	0.539 / 0.971	0.371 / 0.530	0.378 / 0.563	0.408 / 0.691
Danube	Szob	L1490	L	0.137 / 0.330	0.149 / 0.372	0.115 / 0.250	0.113 / 0.225	0.088 / 0.195
Danube	Szob	L1490	M	0.127 / 0.234	0.115 / 0.242	0.108 / 0.190	0.086 / 0.180	0.078 / 0.175
Danube	Szob	L1490	R	0.093 / 0.150	0.130 / 0.250	0.100 / 0.195	0.089 / 0.190	0.071 / 0.170
Danube	Dunafoldvar	L1520	L		0.094 / 0.270			0.092 / 0.210
Danube	Dunafoldvar	L1520	M	0.116 / 0.225	0.093 / 0.250	0.074 / 0.190	0.092 / 0.226	0.088 / 0.185
Danube	Dunafoldvar	L1520	R		0.093 / 0.270			0.081 / 0.195
/Sio	Szekszard-Palank	L1604	M	0.524 / 1.302	0.573 / 1.144	0.330 / 0.794	0.229 / 0.455	0.196 / 0.490
Danube	Hercegszanto	L1540	M	0.106 / 0.208	0.094 / 0.266	0.072 / 0.190	0.092 / 0.205	0.090 / 0.210
Danube	Batina	L1315	M			0.091 / 0.156	0.105 / 0.209	0.100 / 0.220
/Drava	Ormoz	L1390	L	0.166 / 0.218	0.133 / 0.170	0.042 / 0.054	0.053 / 0.080	0.049 / 0.078
/Drava	Varazdin	L1290	M	0.138 / 0.235	0.099 / 0.147	0.059 / 0.120	0.041 / 0.070	0.028 / 0.050
/Drava	Botovo	L1240	M	0.170 / 0.228	0.150 / 0.270	0.042 / 0.088	0.038 / 0.080	0.034 / 0.059
/Drava	D.Miholjac	L1250	R	0.188 / 0.300	0.147 / 0.230	0.039 / 0.089	0.043 / 0.109	0.033 / 0.086
/Drava	Dravaszabolcs	L1610	M	0.048 / 0.141	0.068 / 0.120	0.056 / 0.105	0.049 / 0.104	0.060 / 0.132
Danube	Borovo	L1320	R			0.115 / 0.290	0.148 / 0.290	0.183 / 0.290
/Tisza/Sajo	Sajopuspoki	L1770	M	0.357 / 0.768	0.257 / 0.389	0.178 / 0.260	0.154 / 0.239	0.232 / 0.388
/Tisza	Tiszasziget	L1700	L	0.070 / 0.120	0.130 / 0.360	0.076 / 0.195	0.118 / 0.285	0.107 / 0.200
/Tisza	Tiszasziget	L1700	M	0.169 / 0.358	0.123 / 0.330	0.073 / 0.165	0.111 / 0.270	0.101 / 0.188
/Tisza	Tiszasziget	L1700	R	0.153 / 0.240	0.171 / 0.385	0.091 / 0.170	0.147 / 0.325	0.121 / 0.238
/Sava	Jesenice	L1330	R	0.212 / 0.241	0.167 / 0.240	0.055 / 0.140	0.055 / 0.107	0.071 / 0.135
/Sava	Jesenice	L1220	L				0.221 / 0.390	0.077 / 0.140
/Sava	Jesenice	L1220	R	0.225 / 0.300	0.200 / 0.200	0.233 / 0.390		
/Sava	us.Una Jasenovac	L1150	L	0.233 / 0.436	0.393 / 0.500	0.321 / 0.660	0.340 / 0.458	0.289 / 0.466
/Sava	ds.Zupanja	L1060	M	0.142 / 0.225	0.141 / 0.284	0.176 / 0.335	0.511 / 0.778	
/Sava	ds.Zupanja	L1060	R					0.288 / 0.573
Danube	Bazias	L0020	L	0.182 / 0.291	0.288 / 0.581	0.458 / 0.620	0.271 / 0.660	0.455 / 0.745
Danube	Bazias	L0020	M	0.157 / 0.280	0.282 / 0.543	0.333 / 0.513	0.201 / 0.380	0.447 / 0.679
Danube	Bazias	L0020	R		0.336 / 0.582	0.389 / 0.596	0.212 / 0.430	0.453 / 0.682
Danube	Pristol/Novo Selo Harbour	L0090	L	0.232 / 0.337	0.263 / 0.418	0.290 / 0.350	0.197 / 0.290	0.364 / 0.667
Danube	Pristol/Novo Selo Harbour	L0090	M	0.187 / 0.380	0.294 / 0.533	0.343 / 0.634	0.182 / 0.280	0.410 / 0.671
Danube	Pristol/Novo Selo Harbour	L0090	R	0.216 / 0.400	0.343 / 0.526	0.375 / 0.654	0.195 / 0.270	0.429 / 0.732
Danube	Novo Selo Harbour/Pristol	L0730	L	0.164 / 0.820	0.102 / 0.150	0.084 / 0.100	0.120 / 0.140	0.298 / 0.454
Danube	Novo Selo Harbour/Pristol	L0730	M	0.169 / 0.860	0.070 / 0.110	0.077 / 0.109	0.111 / 0.400	0.245 / 0.336

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	R	0.174 / 0.930	0.068 / 0.090	0.083 / 0.119	0.143 / 0.190	0.277 / 0.420
Danube	us.Iskar-Bajkal	L0780	R			0.122 / 0.230	0.165 / 0.290	0.717 / 1.089
/Iskar	Orechovitza	L0930	M	0.530 / 0.530		0.129 / 0.270	0.195 / 0.300	0.801 / 1.300
Danube	Downstream Svishstov	L0810	R		0.403 / 0.500		0.115 / 0.270	0.094 / 0.210
/Jantra	Karantzi	L0990	M		1.228 / 4.400		0.244 / 0.460	0.147 / 0.240
Danube	us.Russe	L0820	R	0.397 / 0.450	0.203 / 0.350		0.095 / 0.137	0.104 / 0.140
/Russ.Lom	Basarbovo	L1010	M		0.300 / 0.400		0.126 / 0.188	0.186 / 0.264
Danube	us. Arges	L0240	L	0.215 / 0.250	0.275 / 0.377	0.264 / 0.482	0.329 / 0.480	0.424 / 0.660
Danube	us. Arges	L0240	M	0.190 / 0.230	0.214 / 0.290	0.250 / 0.360	0.277 / 0.500	0.310 / 0.560
Danube	us. Arges	L0240	R		0.227 / 0.300	0.258 / 0.376	0.301 / 0.500	0.353 / 0.620
/Arges	Conf.Danube	L0250	M	2.963 / 14.200	1.595 / 2.490	1.966 / 2.860	1.824 / 2.600	3.107 / 4.760
Danube	Chiciu/Silistra	L0280	L	0.488 / 0.770	0.372 / 0.707	0.492 / 1.214	0.318 / 0.550	0.315 / 0.530
Danube	Chiciu/Silistra	L0280	M	0.440 / 1.059	0.337 / 0.714	0.425 / 1.059	0.306 / 0.480	0.366 / 0.620
Danube	Chiciu/Silistra	L0280	R	0.348 / 0.608	0.315 / 0.556	0.398 / 0.856	0.294 / 0.710	0.363 / 0.620
Danube	Silistra/Chiciu	L0850	L	0.728 / 1.780	0.240 / 0.430	0.532 / 0.970	0.163 / 0.365	0.181 / 0.250
Danube	Silistra/Chiciu	L0850	M	0.617 / 1.240	0.245 / 0.480	0.485 / 0.930	0.132 / 0.259	0.154 / 0.220
Danube	Silistra/Chiciu	L0850	R	0.423 / 0.850	0.252 / 0.330	0.508 / 1.150	0.123 / 0.231	0.161 / 0.229
/Siret	Conf.Danube Sendreni	L0380	M	1.117 / 1.520	1.391 / 3.052	1.155 / 1.775	0.366 / 0.660	0.498 / 0.930
/Prut	Lipcani	L2230	L			**0.385 / 0.470**	**0.300 / 0.330**	0.204 / 0.370
/Prut	Leuseni	L2250	M			0.597 / 0.850	0.310 / 0.600	**1.060 / 1.060**
/Prut	Conf.Danube-Giurgiulesti	L2270	L			0.435 / 1.020	0.363 / 0.600	0.474 / 0.690
/Prut	Conf.Danube Giurgiulesti	L0420	M	0.512 / 0.575	0.705 / 1.368	1.146 / 2.750	0.357 / 0.690	0.460 / 0.724
Danube	Reni-Chilia/Kilia arm	L0430	L	0.316 / 0.465	0.339 / 0.470	0.398 / 0.538	0.289 / 0.340	0.440 / 0.649
Danube	Reni-Chilia/Kilia arm	L0430	M	0.268 / 0.390	0.345 / 0.629	0.411 / 0.716	0.298 / 0.432	0.303 / 0.678
Danube	Reni-Chilia/Kilia arm	L0430	R	0.286 / 0.390	0.374 / 0.778	0.409 / 0.692	0.395 / 0.700	0.272 / 0.582
Danube	Reni-Kilia arm/Chilia arm	L0630	M	0.075 / 0.240		0.293 / 0.272	0.173 / 0.245	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.226 / 0.310	0.407 / 0.695	0.495 / 1.168	0.451 / 0.520	0.284 / 0.574
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.233 / 0.289	0.426 / 0.879	0.539 / 1.011	0.330 / 0.473	0.214 / 0.402
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.213 / 0.268	0.423 / 0.838	0.544 / 1.185	0.312 / 0.390	0.272 / 0.514
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	0.214 / 0.640	0.258 / 0.442	0.213 / 0.425	0.296 / 0.417	
Danube	Sulina - Sulina arm	L0480	L	0.183 / 0.310	0.450 / 0.795	0.670 / 1.385	0.330 / 0.490	0.243 / 0.408
Danube	Sulina - Sulina arm	L0480	M	0.195 / 0.370	0.403 / 0.794	0.373 / 0.791	0.309 / 0.470	0.231 / 0.472
Danube	Sulina - Sulina arm	L0480	R	0.191 / 0.350	0.436 / 0.771	0.433 / 0.760	0.317 / 0.510	0.230 / 0.374
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.228 / 0.390	0.397 / 0.919	0.402 / 0.684	0.308 / 0.460	0.244 / 0.470
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.192 / 0.350	0.438 / 0.914	0.533 / 1.440	0.311 / 0.500	0.205 / 0.406
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.218 / 0.370	0.412 / 0.928	0.480 / 1.026	0.285 / 0.380	0.271 / 0.492

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

N-NO$_2$

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L			0.020 0.027	0.023 0.032	0.020 0.027
/Inn/Salzach	Laufen	L2160	L			0.008 0.009		
Danube	Jochenstein	L2130	M	0.018 0.030		0.017 0.029	0.014 0.028	0.015 0.020
Danube	Jochenstein	L2220	M	0.018 0.027	0.016 0.029	0.015 0.021	0.015 0.024	0.014 0.021
Danube	Abwinden-Asten	L2200	R	0.017 0.024	0.016 0.027	0.014 0.021	0.013 0.021	0.012 0.018
Danube	Wien-Nussdorf	L2180	R	0.017 0.027	0.015 0.027	0.017 0.029	0.016 0.027	0.016 0.024
/Morava/Dyje	Pohansko	L2120	L	0.077 0.107	0.073 0.107	0.060 0.095	0.056 0.078	0.058 0.077
/Morava	Lanzhot	L2100	M	0.060 0.133	0.055 0.081	0.049 0.069	0.051 0.082	0.052 0.069
Danube	Wolfsthal	L2170	R	0.026 0.036	0.028 0.040	0.026 0.038	0.028 0.042	0.023 0.036
Danube	Bratislava	L1840	M	0.023 0.039	0.023 0.036	0.074 0.233	0.019 0.028	0.020 0.032
Danube	Medvedov/Medve	L1860	M	0.023 0.035	0.019 0.031	0.022 0.031	0.021 0.028	0.019 0.031
Danube	Medve/Medvedov	L1470	M	0.024 0.035	0.028 0.038	0.024 0.040	0.024 0.041	0.024 0.043
Danube	Komarno/Komarom	L1870	M	0.027 0.040	0.021 0.033	0.021 0.036	0.022 0.031	0.021 0.032
Danube	Komarom/Komarno	L1475	M	0.028 0.038	0.030 0.041	0.027 0.045	0.027 0.048	0.026 0.044
/Vah	Komarno	L1960	M	0.046 0.064	0.044 0.062	0.035 0.056	0.030 0.046	0.030 0.041
Danube	Szob	L1490	L	0.024 0.028	0.025 0.037	0.024 0.033	0.023 0.034	0.020 0.034
Danube	Szob	L1490	M	0.023 0.033	0.021 0.034	0.021 0.037	0.024 0.038	0.019 0.032
Danube	Szob	L1490	R	0.031 0.037	0.021 0.031	0.021 0.037	0.023 0.038	0.018 0.033
Danube	Dunafoldvar	L1520	L		0.025 0.046			0.026 0.041
Danube	Dunafoldvar	L1520	M	0.026 0.037	0.023 0.043	0.022 0.036	0.026 0.051	0.024 0.043
Danube	Dunafoldvar	L1520	R		0.023 0.042			0.026 0.048
/Sio	Szekszard-Palank	L1604	M	0.111 0.307	0.205 0.435	0.103 0.206	0.078 0.161	0.081 0.147
Danube	Hercegszanto	L1540	M	0.024 0.041	0.021 0.040	0.025 0.046	0.024 0.046	0.025 0.046
Danube	Batina	L1315	M			0.023 0.039	0.026 0.049	0.031 0.049
/Drava	Ormoz	L1390	L	0.012 0.015	0.010 0.012	0.009 0.012	0.012 0.020	0.011 0.015
/Drava	Varazdin	L1290	M	0.017 0.022	0.014 0.020	0.013 0.015	0.013 0.016	0.012 0.016
/Drava	Botovo	L1240	M	0.019 0.025	0.018 0.026	0.021 0.028	0.019 0.025	0.017 0.020
/Drava	D.Miholjac	L1250	R	0.015 0.020	0.025 0.052	0.020 0.026	0.017 0.024	0.014 0.025
/Drava	Dravaszabolcs	L1610	M	0.018 0.026	0.017 0.024	0.030 0.041	0.021 0.031	0.016 0.024
Danube	Borovo	L1320	R			0.014 0.020	0.014 0.020	0.014 0.020
/Tisza/Sajo	Sajopuspoki	L1770	M	0.048 0.070	0.043 0.070	0.039 0.064	0.039 0.058	0.043 0.064
/Tisza	Tiszasziget	L1700	L	0.024 0.033	0.023 0.037	0.027 0.038	0.033 0.038	0.017 0.025
/Tisza	Tiszasziget	L1700	M	0.028 0.042	0.018 0.027	0.020 0.030	0.022 0.033	0.020 0.027
/Tisza	Tiszasziget	L1700	R	0.018 0.024	0.018 0.027	0.018 0.027	0.030 0.038	0.022 0.033
/Sava	Jesenice	L1330	R	0.023 0.027	0.023 0.042	0.020 0.027	0.020 0.030	0.021 0.034
/Sava	Jesenice	L1220	L				0.030 0.051	0.047 0.077
/Sava	Jesenice	L1220	R	0.034 0.040	0.035 0.053	0.034 0.044		
/Sava	us.Una Jasenovac	L1150	L	0.035 0.049	0.033 0.056	0.037 0.070	0.029 0.031	0.042 0.069
/Sava	ds.Zupanja	L1060	M	0.028 0.048	0.018 0.019	0.023 0.042	0.017 0.022	
/Sava	ds.Zupanja	L1060	R					0.016 0.023
Danube	Bazias	L0020	L	0.043 0.060	0.038 0.060	0.036 0.050	0.034 0.050	0.034 0.067
Danube	Bazias	L0020	M	0.047 0.070	0.037 0.050	0.075 0.069	0.029 0.040	0.042 0.060
Danube	Bazias	L0020	R		0.040 0.060	0.062 0.070	0.029 0.040	0.030 0.048
Danube	Pristol/Novo Selo Harbour	L0090	L	0.038 0.060	0.040 0.060	0.035 0.040	0.033 0.040	0.036 0.041
Danube	Pristol/Novo Selo Harbour	L0090	M	0.039 0.070	0.039 0.060	0.034 0.040	0.029 0.040	0.036 0.053
Danube	Pristol/Novo Selo Harbour	L0090	R	0.040 0.080	0.042 0.069	0.035 0.049	0.035 0.050	0.037 0.053
Danube	Novo Selo Harbour/Pristol	L0730	L	0.031 0.050	0.030 0.060	0.028 0.030	0.028 0.050	0.033 0.043
Danube	Novo Selo Harbour/Pristol	L0730	M	0.028 0.040	0.027 0.050	0.028 0.039	0.032 0.070	0.031 0.040
Danube	Novo Selo Harbour/Pristol	L0730	R	0.027 0.040	0.027 0.060	0.032 0.040	0.033 0.060	0.033 0.040

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	us.Iskar-Bajkal	L0780	R	0.017 / 0.020		0.032 / 0.070	0.025 / 0.030	0.032 / 0.056
/Iskar	*Orechovitza*	L0930	M	0.043 / 0.091		0.036 / 0.050	0.030 / 0.050	0.044 / 0.060
Danube	Downstream Svishstov	L0810	M	0.011 / 0.029				
Danube	Downstream Svishstov	L0810	R		0.026 / 0.030		0.014 / 0.025	0.019 / 0.024
/Jantra	*Karantzi*	L0990	M	0.016 / 0.023	0.142 / 0.340		0.063 / 0.135	0.045 / 0.084
Danube	us.Russe	L0820	M	0.027 / 0.040				
Danube	us.Russe	L0820	R	0.027 / 0.040	0.023 / 0.030		0.013 / 0.020	0.017 / 0.025
/Russ.Lom	*Basarbovo*	L1010	M		**0.085 / 0.100**		0.028 / 0.046	0.034 / 0.057
Danube	us. Arges	L0240	L	0.040 / 0.080	0.028 / 0.040	0.018 / 0.029	0.031 / 0.041	0.036 / 0.050
Danube	us. Arges	L0240	M	0.044 / 0.070	0.026 / 0.050	0.019 / 0.029	0.028 / 0.040	0.024 / 0.050
Danube	us. Arges	L0240	R		0.029 / 0.040	0.021 / 0.030	0.026 / 0.040	0.032 / 0.070
/Arges	*Conf.Danube*	L0250	M	0.028 / 0.050	0.049 / 0.069	0.061 / 0.090	0.060 / 0.110	0.076 / 0.090
Danube	Chiciu/Silistra	L0280	L	0.037 / 0.060	0.033 / 0.059	0.030 / 0.050	0.025 / 0.050	0.038 / 0.082
Danube	Chiciu/Silistra	L0280	M	0.029 / 0.050	0.033 / 0.060	0.030 / 0.050	0.019 / 0.030	0.025 / 0.060
Danube	Chiciu/Silistra	L0280	R	0.036 / 0.060	0.037 / 0.069	0.031 / 0.059	0.022 / 0.040	0.033 / 0.070
Danube	Silistra/Chiciu	L0850	L	0.021 / 0.040	0.022 / 0.040	0.020 / 0.041	0.014 / 0.020	0.013 / 0.020
Danube	Silistra/Chiciu	L0850	M	0.016 / 0.040	0.010 / 0.010	0.017 / 0.030	0.010 / 0.015	0.013 / 0.022
Danube	Silistra/Chiciu	L0850	R	0.023 / 0.050	0.013 / 0.020	0.016 / 0.026	0.010 / 0.016	0.014 / 0.022
/Siret	*Conf.Danube Sendreni*	L0380	M	0.294 / 1.200	0.050 / 0.117	0.039 / 0.077	0.039 / 0.090	0.042 / 0.065
/Prut	*Lipcani*	L2230	L			**0.025 / 0.030**	**0.029 / 0.030**	0.012 / 0.015
/Prut	*Leuseni*	L2250	M			0.143 / 0.340	0.056 / 0.118	**0.037 / 0.037**
/Prut	*Conf.Danube-Giurgiulesti*	L2270	L			0.066 / 0.300	0.034 / 0.065	0.044 / 0.081
/Prut	*Conf.Danube Giurgiulesti*	L0420	M	0.034 / 0.040	0.040 / 0.068	0.032 / 0.076	0.026 / 0.050	0.057 / 0.100
Danube	Reni-Chilia/Kilia arm	L0430	L	0.043 / 0.060	0.037 / 0.069	0.030 / 0.049	0.025 / 0.040	0.037 / 0.093
Danube	Reni-Chilia/Kilia arm	L0430	M	0.046 / 0.069	0.035 / 0.059	0.026 / 0.039	0.024 / 0.036	0.045 / 0.102
Danube	Reni-Chilia/Kilia arm	L0430	R	0.047 / 0.069	0.046 / 0.088	0.028 / 0.040	0.020 / 0.030	0.044 / 0.092
Danube	Reni-Kilia arm/Chilia arm	L0630	M	0.039 / 0.084		0.049 / 0.126	0.038 / 0.074	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.046 / 0.069	0.038 / 0.060	0.026 / 0.039	0.039 / 0.040	0.014 / 0.029
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.048 / 0.070	0.042 / 0.069	0.028 / 0.049	0.026 / 0.040	0.013 / 0.028
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.048 / 0.069	0.041 / 0.060	0.025 / 0.040	0.025 / 0.040	0.013 / 0.040
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	0.036 / 0.096	0.057 / 0.094	0.040 / 0.079	0.024 / 0.035	
Danube	Sulina - Sulina arm	L0480	L	0.038 / 0.050	0.039 / 0.069	0.024 / 0.039	0.022 / 0.030	0.031 / 0.066
Danube	Sulina - Sulina arm	L0480	M	0.048 / 0.070	0.042 / 0.078	0.029 / 0.040	0.021 / 0.030	0.025 / 0.067
Danube	Sulina - Sulina arm	L0480	R	0.035 / 0.040	0.038 / 0.058	0.028 / 0.040	0.022 / 0.040	0.022 / 0.048
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.035 / 0.040	0.039 / 0.060	0.032 / 0.040	0.026 / 0.040	0.026 / 0.048
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.052 / 0.070	0.038 / 0.059	0.025 / 0.039	0.023 / 0.030	0.075 / 0.092
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.035 / 0.040	0.040 / 0.069	0.030 / 0.040	0.024 / 0.040	0.025 / 0.041

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was ≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

N-NO$_3$

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	3.44 4.76	3.19 3.88	2.73 3.76	3.18 3.85	3.08 3.95
/Inn/Salzach	*Laufen*	L2160	L	0.72 0.93	0.71 0.93	0.67 0.91	0.64 0.91	0.67 1.05
/Inn	*Kirchdorf*	L2150	M	0.85 1.00	0.60 0.80	0.59 0.70	0.57 0.90	0.60 0.90
Danube	Jochenstein	L2130	M	2.34 3.40	2.22 3.20	2.07 3.25	2.10 3.20	1.93 2.80
Danube	Jochenstein	L2220	M	2.45 3.50	2.17 3.26	2.14 3.01	2.38 3.60	2.26 3.20
Danube	Abwinden-Asten	L2200	R	2.35 3.41	2.13 3.20	2.18 2.95	2.22 3.20	2.05 2.86
Danube	Wien-Nussdorf	L2180	R	2.31 3.30	2.03 3.02	1.96 2.85	2.16 3.03	2.05 3.01
/Morava/Dyje	*Pohansko*	L2120	L	5.34 7.50	4.44 6.52	3.63 6.39	3.55 6.09	3.01 6.19
/Morava	*Lanzhot*	L2100	M	3.98 5.05	3.26 4.28	3.28 4.14	3.46 4.03	2.90 4.12
Danube	Wolfsthal	L2170	R	2.30 3.32	2.21 3.09	1.97 2.82	2.21 3.26	2.10 3.04
Danube	Bratislava	L1840	M	2.78 4.19	2.22 3.30	1.99 2.98	2.31 3.32	2.13 3.09
Danube	Medvedov/Medve	L1860	M	2.47 3.60	2.03 3.06	1.90 2.66	2.17 3.26	2.12 3.01
Danube	Medve/Medvedov	L1470	M	2.41 3.17	2.07 3.01	1.90 2.82	2.14 3.18	2.05 3.15
Danube	Komarno/Komarom	L1870	M	2.75 4.21	2.16 3.37	1.99 3.02	2.17 3.24	2.23 3.21
Danube	Komarom/Komarno	L1475	M	2.47 2.89	2.20 3.30	2.08 3.08	2.28 3.32	2.17 3.10
/Vah	*Komarno*	L1960	M	2.41 3.27	2.12 3.06	1.71 2.31	2.06 2.90	1.97 2.78
Danube	Szob	L1490	L	2.56 2.71	2.18 3.05	1.90 2.71	2.04 3.00	1.84 2.77
Danube	Szob	L1490	M	2.69 3.73	2.22 3.35	1.92 2.71	2.06 3.16	1.84 2.89
Danube	Szob	L1490	R	2.07 2.37	2.16 3.34	1.93 2.77	2.06 3.22	1.93 2.89
Danube	Dunafoldvar	L1520	L		2.03 3.39			2.02 3.12
Danube	Dunafoldvar	L1520	M	2.29 3.52	2.00 3.39	1.80 2.72	2.07 3.15	2.06 3.19
Danube	Dunafoldvar	L1520	R		1.96 3.05			2.09 3.51
/Sio	*Szekszard-Palank*	L1604	M	4.18 9.54	5.38 7.66	3.95 6.57	3.23 5.06	4.38 6.12
Danube	Hercegszanto	L1540	M	2.29 3.19	1.83 2.71	1.84 2.71	2.01 3.11	2.04 3.11
Danube	Batina	L1315	M			1.93 2.88	2.18 2.97	2.23 3.36
/Drava	*Ormoz*	L1390	L	1.24 1.65	1.15 1.50	1.08 1.38	1.13 1.58	1.03 1.51
/Drava	*Varazdin*	L1290	M	2.05 2.70	1.27 1.88	0.94 1.35	1.02 1.51	1.05 1.67
/Drava	*Botovo*	L1240	M	1.69 2.19	1.22 1.77	1.32 1.70	1.31 1.89	1.12 1.69
/Drava	*D.Miholjac*	L1250	R	1.56 2.10	1.24 1.79	1.31 1.72	1.41 1.85	1.29 2.06
/Drava	*Dravaszabolcs*	L1610	M	1.58 2.31	1.37 1.98	1.43 1.91	1.48 1.98	1.28 1.91
Danube	Borovo	L1320	R			2.14 3.26	1.85 2.70	1.62 2.70
/Tisza/Sajo	*Sajopuspoki*	L1770	M	1.97 2.33	2.01 2.51	2.02 2.58	2.34 2.85	2.47 3.75
/Tisza	*Tiszasziget*	L1700	L	1.45 1.58	1.64 2.15	1.57 2.13	1.48 2.09	1.16 1.96
/Tisza	*Tiszasziget*	L1700	M	1.40 2.00	1.54 2.07	1.52 2.05	1.45 2.05	1.13 1.95
/Tisza	*Tiszasziget*	L1700	R	1.29 1.40	1.44 1.88	1.44 1.88	1.39 2.04	1.09 1.81
/Sava	*Jesenice*	L1330	R	1.58 1.70	1.68 2.09	1.52 1.78	1.51 1.79	1.41 1.88
/Sava	*Jesenice*	L1220	L				1.98 2.20	1.84 3.30
/Sava	*Jesenice*	L1220	R	2.71 3.78	1.98 2.98	2.47 3.08		
/Sava	*us.Una Jasenovac*	L1150	L	1.43 1.70	1.54 1.95	1.19 1.60	0.95 1.42	0.96 1.56
/Sava	*ds.Zupanja*	L1060	M	1.77 2.25	1.60 2.33	1.98 2.46	1.64 2.09	
/Sava	*ds.Zupanja*	L1060	R					1.37 1.71
Danube	Bazias	L0020	L	1.63 2.48	1.56 2.13	1.44 2.09	1.30 2.20	1.44 2.27
Danube	Bazias	L0020	M	1.52 2.54	1.55 1.90	1.39 2.08	1.08 2.12	1.50 2.30
Danube	Bazias	L0020	R		1.52 3.12	1.31 2.17	1.16 1.65	1.43 2.26
Danube	Pristol/Novo Selo Harbour	L0090	L	1.44 2.21	1.90 2.61	1.53 1.90	1.34 1.95	1.41 2.32
Danube	Pristol/Novo Selo Harbour	L0090	M	1.60 2.65	1.77 2.16	1.37 1.80	1.21 1.44	1.37 2.30
Danube	Pristol/Novo Selo Harbour	L0090	R	1.75 2.94	1.84 2.30	1.42 1.91	1.29 2.04	1.47 2.24
Danube	Novo Selo Harbour/Pristol	L0730	L	1.69 2.20	1.47 1.83	1.69 2.40	1.53 1.80	1.78 2.35
Danube	Novo Selo Harbour/Pristol	L0730	M	1.75 2.19	1.45 1.90	1.72 2.70	1.54 1.94	1.79 2.54

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	R	1.73 / 2.20	1.23 / 1.44	1.90 / 3.00	1.62 / 1.86	1.93 / 2.79
Danube	us.Iskar-Bajkal	L0780	R	2.03 / 2.32		2.30 / 4.80	1.67 / 1.93	1.19 / 2.56
/Iskar	Orechovitza	L0930	M	2.77 / 4.13		2.11 / 3.30	2.94 / 5.00	1.99 / 3.13
Danube	Downstream Svishstov	L0810	M	0.38 / 0.63				
Danube	Downstream Svishstov	L0810	R		3.02 / 6.20		1.59 / 2.01	1.12 / 1.55
/Jantra	Karantzi	L0990	M	0.94 / 1.84	2.37 / 3.80		3.02 / 4.09	1.96 / 2.90
Danube	us.Russe	L0820	M	2.00 / 2.40				
Danube	us.Russe	L0820	R	2.00 / 2.40	1.04 / 1.21		1.72 / 2.18	1.08 / 1.68
/Russ.Lom	Basarbovo	L1010	M		7.40 / 7.90		7.51 / 10.39	6.90 / 8.85
Danube	us. Arges	L0240	L	1.83 / 3.80	1.84 / 2.21	1.82 / 2.58	1.66 / 2.60	3.12 / 5.80
Danube	us. Arges	L0240	M	1.76 / 3.59	1.74 / 2.31	1.66 / 2.20	1.64 / 2.20	2.84 / 5.60
Danube	us. Arges	L0240	R		1.81 / 2.40	1.83 / 2.59	1.81 / 2.40	3.20 / 5.90
/Arges	Conf.Danube	L0250	M	1.61 / 2.86	2.38 / 4.50	2.57 / 4.16	2.76 / 5.40	5.10 / 10.40
Danube	Chiciu/Silistra	L0280	L	1.52 / 1.86	1.65 / 2.13	1.70 / 2.30	1.79 / 2.68	1.48 / 2.31
Danube	Chiciu/Silistra	L0280	M	1.58 / 2.00	1.74 / 2.38	1.67 / 2.50	1.84 / 2.73	1.44 / 2.23
Danube	Chiciu/Silistra	L0280	R	1.57 / 1.82	1.66 / 2.31	1.69 / 2.51	1.89 / 2.73	1.46 / 2.39
Danube	Silistra/Chiciu	L0850	L	1.59 / 2.30	1.07 / 1.20	1.45 / 2.20	1.58 / 2.10	1.21 / 1.81
Danube	Silistra/Chiciu	L0850	M	1.60 / 3.02	1.32 / 1.90	1.41 / 2.10	1.48 / 2.23	1.28 / 2.00
Danube	Silistra/Chiciu	L0850	R	1.57 / 2.72	1.03 / 1.22	1.48 / 1.90	1.52 / 2.15	1.29 / 1.98
/Siret	Conf.Danube Sendreni	L0380	M	2.18 / 3.41	1.92 / 2.96	2.11 / 2.60	1.89 / 3.08	1.76 / 2.50
/Prut	Lipcani	L2230	L			**4.80 / 5.67**	**3.25 / 4.07**	0.73 / 0.91
/Prut	Leuseni	L2250	M			5.80 / 8.76	2.64 / 4.16	**2.64 / 2.64**
/Prut	Conf.Danube-Giurgiulesti	L2270	L			6.04 / 21.90	1.86 / 3.72	2.83 / 5.32
/Prut	Conf.Danube Giurgiulesti	L0420	M	1.86 / 2.16	1.94 / 3.52	1.93 / 2.97	1.88 / 3.17	3.55 / 10.57
Danube	Reni-Chilia/Kilia arm	L0430	L	1.76 / 2.04	1.50 / 1.93	1.86 / 2.87	1.85 / 2.79	1.11 / 1.61
Danube	Reni-Chilia/Kilia arm	L0430	M	1.79 / 2.16	1.50 / 2.00	1.79 / 2.60	2.02 / 2.84	1.22 / 1.80
Danube	Reni-Chilia/Kilia arm	L0430	R	1.75 / 2.15	1.54 / 2.03	1.79 / 2.56	2.04 / 2.90	1.29 / 2.21
Danube	Reni-Kilia arm/Chilia arm	L0630	M	1.64 / 2.30		1.15 / 1.73	1.43 / 1.72	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	1.43 / 1.80	1.40 / 1.96	1.91 / 2.61	1.76 / 2.73	1.21 / 2.13
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	1.41 / 1.70	1.37 / 1.94	1.82 / 2.75	1.77 / 2.66	1.22 / 2.03
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	1.45 / 1.79	1.39 / 1.91	1.93 / 2.81	1.90 / 2.70	1.22 / 2.17
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	1.75 / 2.30	2.32 / 2.54	1.21 / 1.74	1.37 / 1.79	
Danube	Sulina - Sulina arm	L0480	L	1.53 / 1.65	1.52 / 1.99	1.84 / 2.32	1.82 / 2.74	1.38 / 2.41
Danube	Sulina - Sulina arm	L0480	M	1.68 / 3.59	1.48 / 2.00	1.77 / 2.37	1.90 / 2.74	1.42 / 2.18
Danube	Sulina - Sulina arm	L0480	R	1.58 / 1.63	1.48 / 1.92	1.82 / 2.34	1.85 / 2.67	1.37 / 2.25
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	1.58 / 1.73	1.44 / 1.95	1.52 / 2.20	1.48 / 2.47	1.18 / 1.97
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	1.74 / 3.48	1.43 / 1.91	1.68 / 2.33	1.55 / 2.40	1.29 / 2.08
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	1.61 / 1.73	1.44 / 2.16	1.61 / 2.30	1.67 / 2.78	1.22 / 2.13

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

Note:

average[1]
testing value[2]

[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a yea

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

P-PO$_4$

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.041 / 0.056	0.039 / 0.056	0.036 / 0.051	0.040 / 0.057	0.039 / 0.056
/Inn/Salzach	Laufen	L2160	L	0.027 / 0.051	0.020 / 0.031	0.020 / 0.033	0.024 / 0.040	0.017 / 0.033
/Inn	Kirchdorf	L2150	M	0.023 / 0.040	0.022 / 0.033	0.020 / 0.032	0.016 / 0.028	0.014 / 0.021
Danube	Jochenstein	L2130	M	0.037 / 0.050	0.032 / 0.050	0.033 / 0.060	0.027 / 0.049	0.028 / 0.044
Danube	Jochenstein	L2220	M	0.033 / 0.051	0.033 / 0.056	0.033 / 0.064	0.034 / 0.054	0.027 / 0.048
Danube	Abwinden-Asten	L2200	R	0.029 / 0.043	0.029 / 0.044	0.027 / 0.056	0.028 / 0.051	0.024 / 0.037
Danube	Wien-Nussdorf	L2180	R	0.031 / 0.042	0.028 / 0.047	0.032 / 0.063	0.033 / 0.057	0.031 / 0.062
/Morava/Dyje	Pohansko	L2120	L	0.364 / 0.592	0.262 / 0.397	0.342 / 0.630	0.278 / 0.401	0.278 / 0.494
/Morava	Lanzhot	L2100	M	0.214 / 0.320	0.138 / 0.178	0.142 / 0.172	0.126 / 0.179	0.150 / 0.206
Danube	Wolfsthal	L2170	R	0.032 / 0.039	0.030 / 0.046	0.032 / 0.051	0.028 / 0.052	0.030 / 0.049
Danube	Bratislava	L1840	M	0.063 / 0.097	0.046 / 0.083	0.046 / 0.072	0.043 / 0.067	0.047 / 0.070
Danube	Medvedov/Medve	L1860	M	0.051 / 0.071	0.042 / 0.077	0.046 / 0.081	0.038 / 0.067	0.046 / 0.070
Danube	Medve/Medvedov	L1470	M	0.068 / 0.103	0.045 / 0.070	0.050 / 0.067	0.042 / 0.064	0.047 / 0.075
Danube	Komarno/Komarom	L1870	M	0.068 / 0.109	0.045 / 0.094	0.041 / 0.074	0.043 / 0.072	0.046 / 0.074
Danube	Komarom/Komarno	L1475	M	0.054 / 0.062	0.047 / 0.075	0.049 / 0.079	0.045 / 0.074	0.051 / 0.085
/Vah	Komarno	L1960	M	0.139 / 0.172	0.128 / 0.222	0.100 / 0.129	0.087 / 0.138	0.114 / 0.173
Danube	Szob	L1490	L	0.106 / 0.121	0.078 / 0.120	0.079 / 0.117	0.085 / 0.126	0.062 / 0.091
Danube	Szob	L1490	M	0.065 / 0.109	0.057 / 0.091	0.058 / 0.078	0.049 / 0.072	0.052 / 0.085
Danube	Szob	L1490	R	0.058 / 0.065	0.053 / 0.080	0.060 / 0.092	0.057 / 0.085	0.059 / 0.121
Danube	Dunafoldvar	L1520	L		0.035 / 0.072			0.047 / 0.087
Danube	Dunafoldvar	L1520	M	0.056 / 0.075	0.031 / 0.069	0.041 / 0.082	0.048 / 0.082	0.046 / 0.080
Danube	Dunafoldvar	L1520	R			0.032 / 0.069		0.043 / 0.080
/Sio	Szekszard-Palank	L1604	M	0.263 / 0.446	0.360 / 0.547	0.303 / 0.480	0.252 / 0.375	0.319 / 0.550
Danube	Hercegszanto	L1540	M	0.049 / 0.074	0.039 / 0.077	0.040 / 0.076	0.053 / 0.085	0.048 / 0.085
Danube	Batina	L1315	M			0.051 / 0.080	0.048 / 0.080	0.048 / 0.087
/Drava	Ormoz	L1390	L	0.009 / 0.013	0.007 / 0.013	0.016 / 0.020	0.018 / 0.030	0.020 / 0.029
/Drava	Varazdin	L1290	M	0.115 / 0.150	0.029 / 0.049	0.018 / 0.029	0.016 / 0.020	0.021 / 0.039
/Drava	Botovo	L1240	M	0.038 / 0.068	0.034 / 0.058	0.035 / 0.039	0.034 / 0.050	0.035 / 0.050
/Drava	D.Miholjac	L1250	R	0.048 / 0.080	0.045 / 0.059	0.053 / 0.070	0.052 / 0.069	0.036 / 0.059
/Drava	Dravaszabolcs	L1610	M	0.044 / 0.066	0.046 / 0.068	0.060 / 0.078	0.059 / 0.082	0.061 / 0.090
Danube	Borovo	L1320	R					0.048 / 0.070
/Tisza/Sajo	Sajopuspoki	L1770	M	0.101 / 0.136	0.089 / 0.137	0.079 / 0.114	0.073 / 0.108	0.101 / 0.140
/Tisza	Tiszasziget	L1700	L	0.066 / 0.101	0.064 / 0.090	0.053 / 0.084	0.061 / 0.090	0.043 / 0.089
/Tisza	Tiszasziget	L1700	M	0.071 / 0.091	0.068 / 0.098	0.056 / 0.082	0.065 / 0.092	0.046 / 0.099
/Tisza	Tiszasziget	L1700	R	0.080 / 0.091	0.080 / 0.097	0.065 / 0.096	0.075 / 0.114	0.049 / 0.106
/Sava	Jesenice	L1330	R	0.063 / 0.111	0.056 / 0.081	0.090 / 0.136	0.090 / 0.174	0.084 / 0.142
/Sava	Jesenice	L1220	L				0.023 / 0.041	0.029 / 0.054
/Sava	Jesenice	L1220	R	0.020 / 0.038	0.054 / 0.093	0.047 / 0.130		
/Sava	us.Una Jasenovac	L1150	L	0.107 / 0.127	0.151 / 0.209	0.136 / 0.153	0.076 / 0.125	0.050 / 0.085
/Sava	ds.Zupanja	L1060	M	0.153 / 0.206	0.092 / 0.176	0.133 / 0.235		
/Sava	ds.Zupanja	L1060	R					0.016 / 0.024
Danube	Bazias	L0020	L	0.048 / 0.074	0.055 / 0.080	0.060 / 0.080	0.057 / 0.170	0.115 / 0.159
Danube	Bazias	L0020	M	0.047 / 0.080	0.056 / 0.079	0.061 / 0.079	0.054 / 0.140	0.120 / 0.170
Danube	Bazias	L0020	R		0.063 / 0.090	0.063 / 0.089	0.054 / 0.140	0.125 / 0.186
Danube	Pristol/Novo Selo Harbour	L0090	L	0.106 / 0.126	0.055 / 0.079	0.063 / 0.098	0.080 / 0.140	0.096 / 0.142
Danube	Pristol/Novo Selo Harbour	L0090	M	0.059 / 0.110	0.051 / 0.070	0.051 / 0.069	0.070 / 0.120	0.101 / 0.140
Danube	Pristol/Novo Selo Harbour	L0090	R	0.064 / 0.110	0.066 / 0.091	0.058 / 0.079	0.087 / 0.150	0.119 / 0.163
Danube	Novo Selo Harbour/Pristol	L0730	L	0.073 / 0.130	0.064 / 0.130	0.052 / 0.079	0.045 / 0.070	
Danube	Novo Selo Harbour/Pristol	L0730	M	0.073 / 0.110	0.063 / 0.100	0.063 / 0.080	0.048 / 0.080	

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Novo Selo Harbour/Pristol	L0730	R	0.078 0.110	0.071 0.150	0.084 0.119	0.060 0.080	
Danube	us.Iskar-Bajkal	L0780	R	0.440 0.530		0.342 0.640	0.075 0.110	
/Iskar	Orechovitza	L0930	M	0.633 1.550		0.636 1.120	0.385 0.590	
Danube	Downstream Svishstov	L0810	M	0.552 1.260				
Danube	Downstream Svishstov	L0810	R		0.247 0.360		0.191 0.360	
/Jantra	Karantzi	L0990	M	0.360 0.530	0.031 0.070		0.281 0.460	
Danube	us.Russe	L0820	M	0.397 0.450				
Danube	us.Russe	L0820	R	0.060 0.070	0.067 0.080		0.172 0.230	
/Russ.Lom	Basarbovo	L1010	M		**0.055 0.090**		0.738 0.850	
Danube	us. Arges	L0240	L	0.062 0.100	0.053 0.070	0.082 0.100	0.073 0.110	0.100 0.130
Danube	us. Arges	L0240	M	0.074 0.100	0.053 0.070	0.078 0.090	0.069 0.100	0.084 0.120
Danube	us. Arges	L0240	R		0.056 0.080	0.083 0.109	0.074 0.100	0.100 0.130
/Arges	Conf.Danube	L0250	M	0.328 0.700	0.102 0.176	0.153 0.179	0.140 0.190	0.162 0.150
Danube	Chiciu/Silistra	L0280	L	0.063 0.080	0.065 0.099	0.058 0.099	0.037 0.070	0.028 0.060
Danube	Chiciu/Silistra	L0280	M	0.060 0.079	0.058 0.079	0.058 0.100	0.042 0.080	0.025 0.040
Danube	Chiciu/Silistra	L0280	R	0.060 0.080	0.071 0.110	0.056 0.100	0.043 0.080	0.026 0.063
Danube	Silistra/Chiciu	L0850	L	0.056 0.090	0.034 0.060	0.089 0.160	0.192 0.270	
Danube	Silistra/Chiciu	L0850	M	0.049 0.060	0.033 0.040	0.078 0.160	0.175 0.270	
Danube	Silistra/Chiciu	L0850	R	0.051 0.080	0.025 0.040	0.106 0.180	0.241 0.290	
/Siret	Conf.Danube Sendreni	L0380	M	0.085 0.190	0.071 0.119	0.044 0.069	0.050 0.130	0.019 0.029
/Prut	Lipcani	L2230	L			**0.035 0.040**	**0.021 0.036**	0.028 0.078
/Prut	Leuseni	L2250	M			0.060 0.080	0.051 0.078	**0.057 0.057**
/Prut	Conf.Danube-Giurgiulesti	L2270	L			0.069 0.130	0.031 0.058	0.081 0.158
/Prut	Conf.Danube Giurgiulesti	L0420	M	0.093 0.100	0.075 0.118	0.048 0.070	0.047 0.120	0.048 0.152
Danube	Reni-Chilia/Kilia arm	L0430	L	0.068 0.080	0.060 0.079	0.057 0.099	0.045 0.060	0.038 0.055
Danube	Reni-Chilia/Kilia arm	L0430	M	0.074 0.090	0.053 0.077	0.061 0.099	0.044 0.070	0.029 0.045
Danube	Reni-Chilia/Kilia arm	L0430	R	0.072 0.080	0.054 0.091	0.063 0.099	0.049 0.060	0.031 0.051
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.058 0.079	0.053 0.060	0.052 0.090	0.044 0.060	0.021 0.039
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.061 0.080	0.050 0.059	0.053 0.089	0.042 0.060	0.021 0.036
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.056 0.070	0.055 0.074	0.057 0.090	0.049 0.080	0.032 0.067
Danube	Sulina - Sulina arm	L0480	L	0.083 0.090	0.049 0.065	0.058 0.089	0.055 0.080	0.034 0.059
Danube	Sulina - Sulina arm	L0480	M	0.065 0.082	0.047 0.069	0.057 0.089	0.050 0.080	0.035 0.064
Danube	Sulina - Sulina arm	L0480	R	0.081 0.082	0.047 0.066	0.058 0.090	0.051 0.080	0.030 0.067
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.057 0.080	0.039 0.057	0.053 0.090	0.045 0.070	0.030 0.048
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.066 0.090	0.042 0.050	0.058 0.090	0.048 0.070	0.035 0.067
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.057 0.080	0.043 0.059	0.059 0.090	0.045 0.070	0.028 0.039

class I
class II
class III
class IV
class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was ≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

P-total

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.080 0.112	0.072 0.110	0.074 0.106	0.083 0.140	0.074 0.109
/Inn/Salzach	Laufen	L2160	L	0.064 0.092	0.059 0.096	0.052 0.089	0.064 0.094	0.051 0.076
/Inn	Kirchdorf	L2150	M	0.099 0.176	0.098 0.143	0.077 0.201	0.081 0.154	0.124 0.356
Danube	Jochenstein	L2130	M	0.088 0.115	0.079 0.110	0.078 0.130	0.083 0.145	0.078 0.098
Danube	Jochenstein	L2220	M	0.078 0.101	0.121 0.174	0.104 0.179	0.143 0.184	0.102 0.128
Danube	Abwinden-Asten	L2200	R	0.093 0.168	0.122 0.182	0.114 0.257	0.130 0.183	0.102 0.131
Danube	Wien-Nussdorf	L2180	R	0.070 0.099	0.106 0.141	0.128 0.154	0.146 0.182	0.144 0.255
/Morava/Dyje	Pohansko	L2120	L	0.448 0.689	0.380 0.533	0.508 0.917	0.373 0.621	0.418 0.646
/Morava	Lanzhot	L2100	M	0.309 0.444	0.250 0.398	0.201 0.224	0.275 0.374	0.261 0.320
Danube	Wolfsthal	L2170	R	0.088 0.120	0.111 0.156	0.163 0.302	0.140 0.206	0.124 0.212
Danube	Bratislava	L1840	M	0.120 0.170	0.072 0.106	0.075 0.118	0.084 0.126	0.100 0.145
Danube	Medvedov/Medve	L1860	M	0.108 0.140	0.070 0.121	0.087 0.177	0.069 0.084	0.095 0.118
Danube	Medve/Medvedov	L1470	M	0.093 0.129	0.108 0.165	0.105 0.150	0.107 0.155	0.095 0.145
Danube	Komarno/Komarom	L1870	M	0.112 0.175	0.071 0.118	0.074 0.098	0.071 0.089	0.102 0.128
Danube	Komarom/Komarno	L1475	M	0.087 0.110	0.118 0.195	0.113 0.146	0.116 0.165	0.112 0.196
/Vah	Komarno	L1960	M	0.242 0.410	0.148 0.220	0.118 0.145	0.154 0.207	0.174 0.225
Danube	Szob	L1490	L	0.173 0.210	0.160 0.212	0.207 0.310	0.173 0.245	0.125 0.180
Danube	Szob	L1490	M	0.157 0.230	0.138 0.186	0.169 0.255	0.134 0.205	0.111 0.150
Danube	Szob	L1490	R	0.133 0.140	0.137 0.185	0.168 0.250	0.138 0.200	0.138 0.235
Danube	Dunafoldvar	L1520	L		0.146 0.171			0.152 0.180
Danube	Dunafoldvar	L1520	M	0.123 0.184	0.138 0.173	0.141 0.175	0.151 0.196	0.146 0.190
Danube	Dunafoldvar	L1520	R			0.122 0.140		0.143 0.195
/Sio	Szekszard-Palank	L1604	M	0.655 0.951	0.557 0.917	0.762 1.370	0.592 1.180	0.548 0.917
Danube	Hercegszanto	L1540	M	0.118 0.170	0.142 0.210	0.148 0.192	0.167 0.225	0.144 0.190
Danube	Batina	L1315	M			0.133 0.169	0.135 0.159	0.132 0.130
/Drava	Ormoz	L1390	L	0.034 0.033	0.015 0.022		0.048 0.110	
/Drava	Varazdin	L1290	M		0.076 0.140	0.048 0.077	0.043 0.070	0.075 0.108
/Drava	Botovo	L1240	M	0.133 0.190	0.088 0.157	0.098 0.279	0.090 0.148	0.075 0.100
/Drava	D.Miholjac	L1250	R	0.157 0.270	0.118 0.167	0.098 0.129	0.129 0.211	0.117 0.139
/Drava	Dravaszabolcs	L1610	M	0.120 0.167	0.135 0.222	0.120 0.160	0.143 0.200	0.119 0.216
Danube	Borovo	L1320	R					0.082 0.115
/Tisza/Sajo	Sajopuspoki	L1770	M	0.183 0.256	0.157 0.239	0.180 0.320	0.154 0.256	0.187 0.250
/Tisza	Tiszasziget	L1700	L	0.233 0.370	0.249 0.510	0.207 0.315	0.213 0.350	0.207 0.324
/Tisza	Tiszasziget	L1700	M	0.236 0.380	0.240 0.470	0.193 0.315	0.207 0.345	0.189 0.282
/Tisza	Tiszasziget	L1700	R	0.230 0.340	0.292 0.525	0.202 0.320	0.228 0.340	0.209 0.322
/Sava	Jesenice	L1330	R	0.095 0.153	0.065 0.088		0.117 0.202	
/Sava	Jesenice	L1220	L					0.157 0.280
/Sava	us.Una Jasenovac	L1150	L	0.165 0.217	0.195 0.310	0.236 0.390	0.163 0.199	0.252 0.390
/Sava	ds.Zupanja	L1060	M				0.178 0.254	
/Sava	ds.Zupanja	L1060	R					0.119 0.203
Danube	Bazias	L0020	L	0.083 0.108	0.087 0.110	0.102 0.120	0.068 0.110	0.148 0.198
Danube	Bazias	L0020	M	0.091 0.150	0.089 0.109	0.108 0.140	0.069 0.110	0.149 0.209
Danube	Bazias	L0020	R		0.097 0.130	0.109 0.120	0.072 0.100	0.159 0.240
Danube	Pristol/Novo Selo Harbour	L0090	L	0.114 0.159	0.088 0.110	0.104 0.129	0.102 0.150	0.134 0.181
Danube	Pristol/Novo Selo Harbour	L0090	M	0.113 0.170	0.079 0.099	0.094 0.127	0.091 0.140	0.131 0.180
Danube	Pristol/Novo Selo Harbour	L0090	R	0.188 0.800	0.098 0.120	0.108 0.148	0.106 0.210	0.146 0.193
Danube	Novo Selo Harbour/Pristol	L0730	L	0.127 0.170	0.128 0.190	0.120 0.120	0.077 0.110	
Danube	Novo Selo Harbour/Pristol	L0730	M	0.126 0.170	0.118 0.180	0.100 0.100	0.080 0.120	
Danube	Novo Selo Harbour/Pristol	L0730	R	0.140 0.170	0.127 0.200	0.120 0.130	0.105 0.140	

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	us.Iskar-Bajkal	L0780	R				**0.120** **0.150**	
/Iskar	*Orechovitza*	L0930	M				**0.430** **0.470**	
Danube	Downstream Svishstov	L0810	R				0.353 1.360	
/Jantra	*Karantzi*	L0990	M				0.486 1.470	
Danube	us.Russe	L0820	R				0.252 0.430	0.260 0.360
/Russ.Lom	*Basarbovo*	L1010	M				0.985 2.610	
Danube	us. Arges	L0240	L	0.120 0.190	0.084 0.100	0.121 0.149	0.115 0.140	0.139 0.180
Danube	us. Arges	L0240	M	0.134 0.160	0.085 0.100	0.116 0.129	0.108 0.140	0.125 0.170
Danube	us. Arges	L0240	R		0.091 0.120	0.126 0.168	0.114 0.170	0.140 0.170
/Arges	*Conf.Danube*	L0250	M	0.488 0.960	0.170 0.230	0.203 0.219	0.220 0.240	0.230 0.200
Danube	Chiciu/Silistra	L0280	L	0.116 0.130	0.096 0.152	0.102 0.187	0.072 0.120	0.060 0.090
Danube	Chiciu/Silistra	L0280	M	0.117 0.148	0.109 0.125	0.098 0.177	0.078 0.130	0.052 0.070
Danube	Chiciu/Silistra	L0280	R	0.113 0.130	0.097 0.118	0.098 0.178	0.076 0.130	0.054 0.100
Danube	Silistra/Chiciu	L0850	L	0.127 0.150			0.267 0.520	
Danube	Silistra/Chiciu	L0850	M	0.110 0.130			0.238 0.410	
Danube	Silistra/Chiciu	L0850	R	0.120 0.130			0.258 0.420	
/Siret	*Conf.Danube Sendreni*	L0380	M	0.285 0.600	0.132 0.214	0.076 0.148	0.093 0.170	0.047 0.060
/Prut	*Lipcani*	L2230	L			**0.070** **0.070**	**0.027** **0.048**	0.067 0.106
/Prut	*Leuseni*	L2250	M			0.107 0.140	0.071 0.106	**0.080** **0.080**
/Prut	*Conf.Danube-Giurgiulesti*	L2270	L			0.115 0.200	0.060 0.080	0.128 0.216
/Prut	*Conf.Danube Giurgiulesti*	L0420	M	0.132 0.166	0.124 0.205	0.083 0.165	0.082 0.140	0.076 0.189
Danube	Reni-Chilia/Kilia arm	L0430	L	0.096 0.119	0.084 0.139	0.093 0.149	0.082 0.130	0.063 0.102
Danube	Reni-Chilia/Kilia arm	L0430	M	0.103 0.119	0.102 0.163	0.100 0.150	0.079 0.130	0.061 0.084
Danube	Reni-Chilia/Kilia arm	L0430	R	0.100 0.119	0.095 0.158	0.103 0.150	0.081 0.130	0.059 0.080
Danube	Reni-Kilia arm/Chilia arm	L0630	M	0.160 0.244		0.120 0.209	0.159 0.194	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.093 0.109	0.084 0.138	0.086 0.149	0.078 0.110	0.048 0.069
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.097 0.110	0.080 0.139	0.090 0.149	0.078 0.120	0.043 0.050
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.095 0.109	0.084 0.130	0.096 0.149	0.079 0.120	0.053 0.104
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	0.151 0.228	0.102 0.121	0.140 0.238	0.141 0.234	
Danube	Sulina - Sulina arm	L0480	L	**0.100** **0.100**	0.071 0.099	0.093 0.140	0.078 0.100	0.059 0.098
Danube	Sulina - Sulina arm	L0480	M	0.120 0.190	0.074 0.109	0.098 0.158	0.078 0.110	0.058 0.090
Danube	Sulina - Sulina arm	L0480	R	0.103 0.110	0.073 0.116	0.098 0.159	0.083 0.120	0.053 0.114
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.103 0.110	0.062 0.090	0.088 0.149	0.077 0.110	0.053 0.100
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.132 0.190	0.068 0.117	0.098 0.150	0.081 0.120	0.060 0.108
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.100 0.100	0.068 0.117	0.100 0.150	0.080 0.110	0.050 0.066

Final class in accordance to Water Quality Classification for TNMN purposes

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xx blue bold letters used if no. of measurements in location was lower than three

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Note:
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Chlorophyll-a

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	2.72 / 5.20	4.09 / 7.80	10.32 / 28.80	4.70 / 8.40	5.41 / 8.90
Danube	Jochenstein	L2130	M	11.88 / 27.80	13.19 / 35.40	15.19 / 30.00	8.59 / 21.40	10.23 / 21.50
Danube	Jochenstein	L2220	M		10.03 / 16.49	14.30 / 29.00	7.09 / 13.09	7.35 / 14.12
Danube	Abwinden-Asten	L2200	R		10.33 / 16.87	15.61 / 38.20	8.41 / 15.60	7.20 / 13.77
Danube	Wien-Nussdorf	L2180	R		10.53 / 17.81	19.90 / 40.80	10.27 / 19.71	6.89 / 12.31
/Morava/Dyje	Pohansko	L2120	L		25.44 / 64.70	19.95 / 37.42	30.67 / 58.78	30.36 / 63.26
/Morava	Lanzhot	L2100	M		19.23 / 32.99	15.16 / 38.30	32.63 / 98.80	33.54 / 53.51
Danube	Wolfsthal	L2170	R		10.54 / 16.89	22.58 / 50.83	10.84 / 18.70	6.51 / 11.69
Danube	Bratislava	L1840	M		19.62 / 49.71	22.72 / 45.94	13.34 / 27.87	10.34 / 21.26
Danube	Medvedov/Medve	L1860	M		20.82 / 52.32	22.50 / 54.61	15.77 / 33.76	10.20 / 18.36
Danube	Medve/Medvedov	L1470	M	18.60 / 33.20	16.43 / 37.42	24.09 / 55.70	13.96 / 31.95	8.75 / 24.30
Danube	Komarno/Komarom	L1870	M	23.83 / 84.10	24.19 / 61.96	25.98 / 55.48	17.19 / 39.70	11.66 / 24.60
Danube	Komarom/Komarno	L1475	M	4.00 / 6.00	18.25 / 49.70	25.08 / 83.12	18.65 / 52.70	9.82 / 26.76
/Vah	Komarno	L1960	M		34.39 / 85.90	27.03 / 75.49	13.65 / 27.72	25.74 / 33.57
Danube	Szob	L1490	L	13.00 / 27.00	26.04 / 65.46	16.59 / 42.50	12.36 / 26.95	15.57 / 31.95
Danube	Szob	L1490	M	25.47 / 56.33	22.69 / 55.34	15.12 / 42.80	12.65 / 30.75	10.01 / 24.24
Danube	Szob	L1490	R	3.33 / 4.00	23.48 / 57.10	14.61 / 48.55	12.07 / 32.10	11.55 / 26.98
Danube	Dunafoldvar	L1520	L		37.46 / 78.50			21.22 / 61.50
Danube	Dunafoldvar	L1520	M	38.63 / 91.10	35.08 / 72.50	35.53 / 88.00	22.12 / 58.40	21.17 / 56.00
Danube	Dunafoldvar	L1520	R		34.12 / 66.00			22.29 / 61.50
/Sio	Szekszard-Palank	L1604	M	8.95 / 22.00	78.34 / 250.90	42.93 / 68.10	39.29 / 74.26	93.61 / 236.00
Danube	Hercegszanto	L1540	M	41.00 / 108.30	39.69 / 71.90	36.36 / 87.00	20.20 / 49.00	27.30 / 76.00
/Drava	Dravaszabolcs	L1610	M	13.65 / 31.10	9.23 / 19.00	5.42 / 15.50	5.05 / 14.40	6.18 / 12.32
/Tisza/Sajo	Sajopuspoki	L1770	M	1.79 / 3.25	6.87 / 16.67	4.41 / 9.71	1.91 / 5.00	6.43 / 11.10
/Tisza	Tiszasziget	L1700	L	4.00 / 5.00	8.33 / 14.02	10.70 / 30.70	18.74 / 50.20	32.46 / 78.42
/Tisza	Tiszasziget	L1700	M	10.20 / 19.00	7.85 / 14.56	11.43 / 42.08	18.32 / 46.84	33.74 / 81.20
/Tisza	Tiszasziget	L1700	R	3.67 / 5.00	7.64 / 16.16	9.28 / 15.62	24.77 / 49.16	38.04 / 92.38
Danube	Novo Selo Harbour/Pristol	L0730	L	**1.80** / **2.40**		2.75 / 7.10	6.15 / 14.21	9.08 / 16.68
Danube	Novo Selo Harbour/Pristol	L0730	M	**2.10** / **2.40**		3.31 / 8.29	6.75 / 17.76	8.05 / 25.52
Danube	Novo Selo Harbour/Pristol	L0730	R	**4.70** / **5.90**		2.37 / 4.14	13.02 / 29.60	11.50 / 29.12
Danube	us.Iskar-Bajkal	L0780	R				**6.52** / **8.29**	
/Iskar	Orechovitza	L0930	M				**15.40** / **21.32**	
Danube	Downstream Svishstov	L0810	R				2.37 / 2.37	18.05 / 54.40
/Jantra	Karantzi	L0990	M				**3.55** / **3.55**	15.92 / 46.00
Danube	us.Russe	L0820	R				**7.10** / **7.10**	3.88 / 15.39
/Russ.Lom	Basarbovo	L1010	M				26.63 / 42.60	6.95 / 16.58
Danube	Silistra/Chiciu	L0850	L	**3.85** / **5.90**		5.99 / 11.84	3.15 / 7.10	5.39 / 16.58
Danube	Silistra/Chiciu	L0850	M	**4.15** / **7.10**		5.25 / 21.31	7.11 / 8.30	5.08 / 14.21
Danube	Silistra/Chiciu	L0850	R	**1.80** / **2.40**		6.44 / 18.94	6.68 / 11.80	4.95 / 10.66

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Zn

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	10.6 10.0	10.2 10.0	10.0 10.0	10.0 10.0	10.2 10.0
/Inn/Salzach	Laufen	L2160	L	13.8 25.0	11.5 20.0	13.5 20.0	16.4 20.0	16.2 20.0
/Inn	Kirchdorf	L2150	M	25.0 55.0	13.2 16.0	14.6 25.0	11.9 15.0	12.7 20.0
Danube	Jochenstein	L2130	M	12.7 20.0	10.8 10.0	11.2 10.0	11.1 10.0	10.4 10.0
Danube	Jochenstein	L2220	M	5.1 7.0	7.7 14.5	31.1 69.0	2.1 3.9	6.3 10.9
Danube	Abwinden-Asten	L2200	R	5.6 8.0	4.7 8.6	28.6 66.0	2.4 4.0	5.0 7.8
Danube	Wien-Nussdorf	L2180	R	7.6 11.8	2.9 4.9	14.9 38.3	17.4 35.9	6.2 7.3
/Morava/Dyje	Pohansko	L2120	L	30.5 64.4	26.0 40.4	23.8 44.7	11.4 15.9	6.5 10.6
/Morava	Lanzhot	L2100	M	13.8 23.2	10.3 15.0	8.9 12.9	14.1 29.2	8.7 13.8
Danube	Wolfsthal	L2170	R	5.0 8.0	4.9 8.0	7.2 19.1	13.7 27.2	11.1 19.9
Danube	Bratislava	L1840	M	26.2 46.0	39.5 23.9	20.5 22.0	10.3 22.0	21.0 20.0
Danube	Medvedov/Medve	L1860	M	21.9 21.0	20.6 20.0	20.0 20.0	9.9 23.0	20.0 20.0
Danube	Medve/Medvedov	L1470	M	32.6 52.0	27.8 49.8	28.4 47.4	40.4 49.4	35.8 63.8
Danube	Komarno/Komarom	L1870	M	27.5 44.4	22.0 21.0	20.0 20.0	4.6 11.4	20.0 20.0
Danube	Komarom/Komarno	L1475	M	32.5 35.0	48.4 47.0	32.4 54.8	39.9 65.2	30.5 33.2
/Vah	Komarno	L1960	M	23.0 30.0	28.0 68.0	20.0 20.0	4.0 8.6	20.5 20.0
Danube	Szob	L1490	L	50.0 100.0	35.8 60.0	31.3 40.0		
Danube	Szob	L1490	M	51.7 100.0	33.6 60.0	24.4 35.8	89.6 122.9	27.0 42.1
Danube	Szob	L1490	R	46.7 100.0	53.3 80.0	50.0 60.0		
Danube	Dunafoldvar	L1520	L		10.8 18.8			
Danube	Dunafoldvar	L1520	M	17.5 24.0	9.7 17.8	18.3 32.5	28.0 46.5	24.6 36.9
Danube	Dunafoldvar	L1520	R		10.9 19.6			
/Sio	Szekszard-Palank	L1604	M	50.8 58.0	31.9 120.0	28.1 43.9	35.5 44.5	39.4 88.2
Danube	Hercegszanto	L1540	M	26.5 41.0	11.1 18.2	16.9 30.3	35.6 66.1	34.6 68.5
Danube	Batina	L1315	M			14.4 29.5	7.2 12.5	11.3 17.9
/Drava	Ormoz	L1390	L	4.0 4.0	4.8 9.9	6.9 21.9	10.7 52.2	17.7 52.2
/Drava	Varazdin	L1290	M	37.4 100.0	20.6 47.0	8.8 26.0	10.1 13.7	17.1 22.9
/Drava	Botovo	L1240	M	25.0 39.7	23.7 42.9	5.5 12.8	10.7 17.4	13.7 20.9
/Drava	D.Miholjac	L1250	R	23.6 40.0	24.6 30.9	5.3 12.7	11.3 18.0	13.4 21.9
/Drava	Dravaszabolcs	L1610	M	11.6 19.0	17.2 25.6	23.0 35.6	46.0 87.6	32.9 64.0
Danube	Borovo	L1320	R					6.0 9.5
/Tisza/Sajo	Sajopuspoki	L1770	M	106.0 162.0	92.6 122.9	61.8 109.2	58.1 111.2	29.4 36.2
/Tisza	Tiszasziget	L1700	L	11.3 16.0	13.7 28.4	7.2 9.4		54.7 93.2
/Tisza	Tiszasziget	L1700	M	12.5 17.0	14.7 25.2	19.7 44.0	68.7 172.1	47.4 79.3
/Tisza	Tiszasziget	L1700	R	10.3 14.0	14.1 26.6	7.1 10.8		49.5 74.0
/Sava	Jesenice	L1330	R	4.0 4.0	7.7 4.0	7.7 18.2	6.0 9.8	4.8 4.0
/Sava	Jesenice	L1220	L					32.8 47.7
/Sava	us.Una Jasenovac	L1150	L					5.6 19.0
/Sava	ds.Zupanja	L1060	R					6.3 19.0
Danube	Bazias	L0020	L	27.2 39.3	102.1 100.0	55.8 122.0	79.1 210.0	17.8 38.8
Danube	Bazias	L0020	M	18.8 48.0	57.0 95.3	66.8 127.2	54.9 187.0	22.1 59.7
Danube	Bazias	L0020	R		49.7 100.0	68.4 155.8	65.2 162.0	19.8 42.6
Danube	Pristol/Novo Selo Harbour	L0090	L	28.8 50.8	38.4 74.1	47.0 85.9	58.3 80.4	20.6 35.9
Danube	Pristol/Novo Selo Harbour	L0090	M	27.7 59.0	43.7 95.0	38.3 80.6	53.4 49.0	18.9 35.0
Danube	Pristol/Novo Selo Harbour	L0090	R	32.0 100.0	58.9 124.0	47.8 85.7	31.8 56.0	12.5 26.0
Danube	Novo Selo Harbour/Pristol	L0730	L	25.1 53.0	28.0 58.0	33.8 80.0	11.7 20.0	25.5 47.4
Danube	Novo Selo Harbour/Pristol	L0730	M	17.8 35.0	16.8 32.0	21.9 51.0	15.0 30.0	25.2 45.3
Danube	Novo Selo Harbour/Pristol	L0730	R	17.1 26.0	63.6 250.0	20.7 46.0	15.0 30.0	26.1 46.4
Danube	us.Iskar-Bajkal	L0780	R			25.5 50.0	30.0 30.0	47.0 89.0

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M	**30.0** **30.0**		80.0 140.0	**70.0** **80.0**	122.7 274.0
Danube	Downstream Svishstov	L0810	M	42.8 70.0				
Danube	Downstream Svishstov	L0810	R		53.3 130.0		159.8 302.0	58.1 84.0
/Jantra	Karantzi	L0990	M	**15.5** **30.0**	18.0 30.0		71.3 99.8	42.9 57.0
Danube	us.Russe	L0820	M	**63.0** **63.0**				
Danube	us.Russe	L0820	R	**63.0** **63.0**			65.3 96.6	89.9 140.0
/Russ.Lom	Basarbovo	L1010	M		**40.0** **40.0**		84.3 97.4	140.7 192.0
Danube	us. Arges	L0240	L	101.2 523.0	36.9 57.0	41.2 67.9	57.3 86.0	29.2 44.0
Danube	us. Arges	L0240	M	73.4 332.0	48.6 100.0	50.6 93.6	66.0 121.0	28.0 59.0
Danube	us. Arges	L0240	R		48.4 168.0	54.3 104.0	82.2 235.0	29.1 65.0
/Arges	Conf.Danube	L0250	M	179.2 356.0	167.9 409.0	86.7 190.3	75.6 111.0	58.4 91.0
Danube	Chiciu/Silistra	L0280	L	52.6 85.7	37.0 80.9	34.6 56.7	28.1 54.0	26.8 51.5
Danube	Chiciu/Silistra	L0280	M	61.8 64.4	31.8 65.2	39.8 69.8	34.5 89.0	17.9 29.9
Danube	Chiciu/Silistra	L0280	R	48.6 96.5	33.3 52.6	37.1 69.5	39.9 77.0	26.7 46.3
Danube	Silistra/Chiciu	L0850	L	8.3 30.0	40.0 51.0	51.4 112.0	42.5 53.8	91.9 155.0
Danube	Silistra/Chiciu	L0850	M	34.5 77.0	33.5 38.0	49.6 117.0	57.4 59.9	65.8 135.0
Danube	Silistra/Chiciu	L0850	R	39.5 77.0	36.2 49.0	47.4 83.0	47.3 64.7	80.5 167.0
/Siret	Conf.Danube Sendreni	L0380	M	115.2 285.0	46.3 86.3	81.6 133.5	44.8 92.0	23.0 43.0
/Prut	Lipcani	L2230	L			**6.5** **10.0**	**24.5** **42.0**	18.4 27.0
/Prut	Leuseni	L2250	M			5.7 10.0	6.4 13.0	**9.0** **9.0**
/Prut	Conf.Danube-Giurgiulesti	L2270	L			7.1 13.0	9.0 17.0	13.4 27.0
/Prut	Conf.Danube Giurgiulesti	L0420	M	28.0 43.0	67.9 107.2	43.3 65.8	33.8 71.0	21.8 35.0
Danube	Reni-Chilia/Kilia arm	L0430	L	44.5 73.1	25.9 41.8	41.1 56.5	43.9 75.0	26.1 79.1
Danube	Reni-Chilia/Kilia arm	L0430	M	53.3 145.3	28.3 50.0	33.0 80.0	26.9 40.0	25.2 45.0
Danube	Reni-Chilia/Kilia arm	L0430	R	50.4 97.5	25.3 51.9	33.9 48.6	37.0 60.0	15.8 28.6
Danube	Reni-Kilia arm/Chilia arm	L0630	M	19.7 57.0		56.4 148.0	37.6 81.0	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	42.5 49.0	36.0 85.5	41.1 62.4	39.6 80.0	21.2 73.0
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	35.7 66.8	37.3 67.3	42.6 76.8	42.9 65.0	23.2 86.0
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	36.6 97.0	29.3 37.8	40.2 79.0	69.8 184.0	20.3 83.0
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	60.6 135.0		30.4 75.0	**42.0** **45.0**	
Danube	Sulina - Sulina arm	L0480	L	36.7 79.0	23.9 31.9	57.3 80.0	38.4 69.0	18.1 27.0
Danube	Sulina - Sulina arm	L0480	M	65.5 251.0	21.4 33.7	31.7 48.1	43.7 75.0	18.8 46.0
Danube	Sulina - Sulina arm	L0480	R	58.0 94.0	31.5 56.2	35.7 70.2	39.3 73.0	23.4 46.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	36.7 76.0	48.6 94.2	35.0 58.4	46.4 73.0	34.8 92.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	32.6 78.0	40.8 97.6	40.1 75.3	39.0 42.0	52.3 324.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	21.0 38.0	38.1 93.8	32.8 65.7	30.4 43.0	17.0 38.0

Final class in accordance to Water Quality Classification for TNMN purposes

☐ class I
☐ class II
☐ class III
☐ class IV
☐ class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was ≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Cu

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	4.36 7.60	2.70 5.00	4.92 10.20	1.81 2.00	2.08 3.00
/Inn/Salzach	Laufen	L2160	L	5.77 4.00	2.93 6.00	10.48 20.80	4.25 7.70	3.88 5.00
/Inn	Kirchdorf	L2150	M	3.81 7.50	3.38 4.70	3.27 7.00	3.54 6.50	5.42 6.00
Danube	Jochenstein	L2130	M	3.27 4.00	2.73 4.00	2.96 4.00	3.07 4.80	2.50 3.50
Danube	Jochenstein	L2220	M	2.42 3.00	2.33 3.00	2.33 3.94	2.21 2.97	2.75 3.59
Danube	Abwinden-Asten	L2200	R	1.75 2.90	2.07 3.00	2.88 5.92	2.20 2.95	2.29 3.00
Danube	Wien-Nussdorf	L2180	R	2.08 3.00	1.89 2.72	2.58 4.90	2.61 4.20	2.99 4.02
/Morava/Dyje	Pohansko	L2120	L	4.26 5.36	3.39 4.08	4.05 5.85	3.69 4.90	3.01 3.70
/Morava	Lanzhot	L2100	M	3.79 6.80	2.80 4.28	2.36 3.16	3.30 4.54	2.55 3.31
Danube	Wolfsthal	L2170	R	2.00 2.00	2.35 3.09	2.58 5.00	3.00 5.80	3.16 5.90
Danube	Bratislava	L1840	M	2.91 3.60	5.05 10.16	2.63 3.00	3.55 4.10	3.03 4.40
Danube	Medvedov/Medve	L1860	M	4.32 8.50	2.00 2.60	1.93 2.50	2.85 3.60	2.74 4.20
Danube	Medve/Medvedov	L1470	M	23.10 53.10	9.35 12.20	5.63 11.60	5.90 9.56	6.32 9.53
Danube	Komarno/Komarom	L1870	M	5.30 9.19	2.09 2.80	2.25 3.00	2.78 3.30	2.22 3.50
Danube	Komarom/Komarno	L1475	M	0.45 0.80	7.15 10.84	4.26 7.30	5.72 9.86	5.33 13.00
/Vah	Komarno	L1960	M	2.10 2.50	1.73 2.70	2.33 3.40	2.68 3.40	2.33 3.50
Danube	Szob	L1490	L	3.33 4.20	3.82 4.70	2.75 4.00		
Danube	Szob	L1490	M	2.82 4.50	3.47 7.10	2.65 4.04	9.34 10.79	4.29 7.21
Danube	Szob	L1490	R	3.37 4.00	2.82 3.70	2.48 3.00		
Danube	Dunafoldvar	L1520	L		3.52 4.82			
Danube	Dunafoldvar	L1520	M	3.55 4.40	3.19 5.58	5.35 8.02	5.84 10.07	3.93 5.83
Danube	Dunafoldvar	L1520	R		3.92 5.86			
/Sio	Szekszard-Palank	L1604	M	1.70 3.00	6.46 17.20	5.30 11.27	7.74 9.07	4.52 8.86
Danube	Hercegszanto	L1540	M	2.95 3.00	3.15 5.53	4.84 8.27	5.67 10.50	6.05 15.80
Danube	Batina	L1315	M			4.87 7.78	3.01 4.77	2.26 4.79
/Drava	Ormoz	L1390	L	0.20 0.20	0.20 0.20	0.81 1.09	0.76 1.39	0.78 0.94
/Drava	Varazdin	L1290	M	5.79 12.10	4.11 7.60	1.29 2.94	2.52 3.29	3.56 4.38
/Drava	Botovo	L1240	M	4.40 8.64	3.21 5.11	0.79 2.06	2.31 3.06	2.23 3.55
/Drava	D.Miholjac	L1250	R	4.26 7.70	2.96 4.93	0.93 2.38	2.73 3.48	2.39 3.89
/Drava	Dravaszabolcs	L1610	M	1.30 3.00	1.76 3.00	2.47 4.09	6.14 16.75	2.73 4.93
Danube	Borovo	L1320	R					1.88 3.60
/Tisza/Sajo	Sajopuspoki	L1770	M	5.91 6.90	5.51 7.38	3.72 6.40	10.09 10.61	4.92 13.00
/Tisza	Tiszasziget	L1700	L	3.33 4.50	6.04 8.95	4.13 5.50		29.27 48.00
/Tisza	Tiszasziget	L1700	M	4.00 6.50	5.26 6.00	4.80 6.11	17.92 46.65	17.85 34.00
/Tisza	Tiszasziget	L1700	R	2.50 3.00	6.00 8.95	4.17 5.45		28.00 42.60
/Sava	Jesenice	L1330	R	0.20 0.20	0.20 0.20	0.74 1.45	0.90 1.57	0.81 1.30
/Sava	Jesenice	L1220	L					4.32 5.19
/Sava	us.Una Jasenovac	L1150	L					2.43 4.85
/Sava	ds.Zupanja	L1060	R					0.02 0.02
Danube	Bazias	L0020	L	13.67 33.70	16.55 25.00	22.09 46.76	17.41 27.00	23.72 50.68
Danube	Bazias	L0020	M	12.67 34.00	16.17 23.00	20.99 33.40	17.07 21.50	19.26 49.05
Danube	Bazias	L0020	R		26.00 60.00	20.61 36.40	16.33 30.70	19.79 31.20
Danube	Pristol/Novo Selo Harbour	L0090	L	6.10 10.00	23.75 44.20	17.23 31.72	17.87 34.35	18.29 41.13
Danube	Pristol/Novo Selo Harbour	L0090	M	22.40 40.00	20.27 27.00	20.50 37.06	17.08 31.07	13.24 40.26
Danube	Pristol/Novo Selo Harbour	L0090	R	33.00 97.00	22.09 35.00	18.88 30.28	17.15 28.45	15.64 63.81
Danube	Novo Selo Harbour/Pristol	L0730	L	10.13 46.00	2.60 5.00	10.67 30.00	4.00 10.00	5.32 7.40
Danube	Novo Selo Harbour/Pristol	L0730	M	8.75 41.00	1.67 3.00	9.44 20.00	4.00 10.00	4.67 7.30
Danube	Novo Selo Harbour/Pristol	L0730	R	8.38 30.00	2.33 4.00	11.44 20.00	4.00 10.00	6.35 10.00
Danube	us.Iskar-Bajkal	L0780	R			19.00 51.00	7.50 10.00	10.82 20.00

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M	10.00 / 10.00		26.67 / 50.00	10.50 / 20.00	15.75 / 39.00
Danube	Downstream Svishstov	L0810	M	7.75 / 10.00				
Danube	Downstream Svishstov	L0810	R		5.00 / 5.00		43.18 / 117.00	12.73 / 33.00
/Jantra	Karantzi	L0990	M	10.00 / 10.00	5.00 / 5.00		36.58 / 68.20	6.64 / 9.00
Danube	us.Russe	L0820	M	12.00 / 12.00				
Danube	us.Russe	L0820	R	12.00 / 12.00			33.08 / 138.20	30.70 / 56.00
/Russ.Lom	Basarbovo	L1010	M		10.00 / 10.00		30.17 / 21.90	33.73 / 57.00
Danube	us. Arges	L0240	L	8.69 / 30.00	22.64 / 40.00	22.78 / 37.75	19.94 / 28.86	21.25 / 43.30
Danube	us. Arges	L0240	M	15.22 / 55.00	20.18 / 30.00	23.79 / 51.74	18.47 / 26.51	23.00 / 43.53
Danube	us. Arges	L0240	R		20.00 / 31.00	25.60 / 60.63	19.51 / 30.00	21.78 / 35.50
/Arges	Conf.Danube	L0250	M	34.68 / 108.00	24.92 / 36.70	22.94 / 39.16	20.97 / 35.48	14.93 / 36.30
Danube	Chiciu/Silistra	L0280	L	11.03 / 31.10	24.50 / 42.20	21.64 / 38.28	27.29 / 49.00	29.38 / 100.01
Danube	Chiciu/Silistra	L0280	M	11.61 / 34.40	22.42 / 34.50	23.36 / 37.64	27.96 / 57.00	25.83 / 66.61
Danube	Chiciu/Silistra	L0280	R	19.36 / 61.40	21.67 / 35.90	20.30 / 36.80	23.47 / 37.10	23.30 / 58.33
Danube	Silistra/Chiciu	L0850	L	8.00 / 25.00	27.20 / 37.00	16.89 / 26.00	47.42 / 162.10	41.70 / 130.00
Danube	Silistra/Chiciu	L0850	M	23.67 / 63.00	21.50 / 35.00	14.22 / 24.00	49.58 / 195.40	33.67 / 46.00
Danube	Silistra/Chiciu	L0850	R	19.67 / 62.00	24.33 / 36.00	17.33 / 31.00	59.42 / 213.10	31.91 / 49.00
/Siret	Conf.Danube Sendreni	L0380	M	18.33 / 34.00	49.25 / 102.50	28.78 / 53.70	26.34 / 76.70	19.83 / 37.30
/Prut	Lipcani	L2230	L			6.50 / 10.00	6.00 / 8.00	5.80 / 14.00
/Prut	Leuseni	L2250	M			5.67 / 10.00	3.40 / 4.00	3.00 / 3.00
/Prut	Conf.Danube-Giurgiulesti	L2270	L			5.13 / 9.00	4.50 / 11.00	6.43 / 11.00
/Prut	Conf.Danube Giurgiulesti	L0420	M	24.33 / 33.00	21.75 / 28.90	19.65 / 29.60	20.04 / 35.32	16.90 / 43.71
Danube	Reni-Chilia/Kilia arm	L0430	L	8.94 / 26.20	32.33 / 70.70	25.24 / 43.16	22.17 / 36.00	21.64 / 38.45
Danube	Reni-Chilia/Kilia arm	L0430	M	12.94 / 27.70	29.00 / 50.40	23.87 / 40.02	23.60 / 45.40	20.21 / 41.94
Danube	Reni-Chilia/Kilia arm	L0430	R	8.94 / 25.00	22.42 / 30.60	24.62 / 44.17	26.67 / 36.31	18.16 / 41.18
Danube	Reni-Kilia arm/Chilia arm	L0630	M	4.96 / 16.40		8.98 / 24.00	10.82 / 64.00	
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	17.01 / 26.90	20.83 / 27.90	22.28 / 42.15	31.46 / 45.00	26.69 / 65.00
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	12.09 / 22.80	22.17 / 33.50	24.51 / 37.60	23.69 / 44.00	18.97 / 43.67
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	12.34 / 23.00	23.75 / 35.90	29.20 / 51.93	22.06 / 42.12	19.05 / 57.89
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	3.92 / 9.20		3.43 / 8.00	2.00 / 2.00	
Danube	Sulina - Sulina arm	L0480	L	25.00 / 31.00	23.84 / 45.07	26.82 / 45.02	30.51 / 39.00	16.11 / 47.90
Danube	Sulina - Sulina arm	L0480	M	25.00 / 34.00	27.80 / 39.57	26.15 / 39.37	19.27 / 29.00	18.45 / 49.64
Danube	Sulina - Sulina arm	L0480	R	23.67 / 28.00	29.74 / 64.94	29.80 / 65.67	20.05 / 24.00	23.66 / 60.29
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	27.33 / 34.00	20.75 / 32.80	25.12 / 38.85	20.04 / 28.00	15.54 / 44.31
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	71.80 / 270.00	18.75 / 24.90	24.32 / 39.53	27.28 / 51.00	16.99 / 38.45
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	31.33 / 38.00	20.92 / 30.80	21.95 / 37.01	22.75 / 38.00	16.51 / 41.42

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]	[1] mean annual value
testing value[2]	[2] testing value, which represents:

Note:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a year

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Cr

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	2.80 5.00	2.63 4.00	1.28 2.00	1.19 2.00	1.31 1.50
/Inn/Salzach	Laufen	L2160	L	2.31 4.50	1.74 3.00	2.04 4.00	2.12 3.60	2.92 7.50
/Inn	Kirchdorf	L2150	M	2.27 6.00	2.00 3.70	1.96 4.50	1.58 3.00	1.92 4.00
Danube	Jochenstein	L2130	M	1.04 1.00	1.00 1.00	1.00 1.00	1.00 1.00	1.00 1.00
Danube	Jochenstein	L2220	M	1.08 1.00	1.06 1.20	1.00 1.00	1.00 1.00	1.09 1.60
Danube	Abwinden-Asten	L2200	R	1.00 1.00	1.10 1.28	1.30 1.54	1.00 1.00	1.03 1.39
Danube	Wien-Nussdorf	L2180	R	1.00 1.00	1.00 1.00	1.00 1.00	1.00 1.00	1.36 1.64
/Morava/Dyje	Pohansko	L2120	L	1.66 2.45		1.13 1.19	1.00 1.00	1.01 1.00
/Morava	Lanzhot	L2100	M	1.91 3.40		1.43 1.47	1.08 1.28	1.10 1.05
Danube	Wolfsthal	L2170	R	1.00 1.00	1.00 1.00	1.86 4.25	1.49 2.31	1.40 2.26
Danube	Bratislava	L1840	M	0.61 1.40	1.67 4.00	0.73 1.40	1.74 3.60	0.95 1.40
Danube	Medvedov/Medve	L1860	M	0.32 0.60	0.91 1.60	0.43 1.10	1.81 3.10	0.67 1.30
Danube	Medve/Medvedov	L1470	M	2.34 6.50	4.89 9.06	1.56 2.66	5.65 15.90	7.73 18.51
Danube	Komarno/Komarom	L1870	M	0.71 1.22	0.90 1.80	0.63 1.10	1.67 2.90	0.68 1.40
Danube	Komarom/Komarno	L1475	M	**1.70** **2.70**	2.98 6.22	1.35 2.70	6.36 13.07	5.46 9.59
/Vah	Komarno	L1960	M	0.60 1.00	1.02 2.00	1.63 4.80	1.53 3.00	0.65 1.00
Danube	Szob	L1490	L	0.6 0.7	2.0 2.5	1.8 2.2		
Danube	Szob	L1490	M	0.9 1.9	1.3 2.1	1.3 2.5	10.3 19.1	7.8 14.2
Danube	Szob	L1490	R	0.7 0.8	1.2 2.0	1.0 1.6		
Danube	Dunafoldvar	L1520	L		0.9 1.8			
Danube	Dunafoldvar	L1520	M	**0.9** **1.3**	0.8 1.5	1.0 2.1	10.5 20.2	4.9 6.5
Danube	Dunafoldvar	L1520	R		0.5 1.1			
/Sio	Szekszard-Palank	L1604	M	3.3 9.0	1.7 7.0	1.5 3.1	4.5 1.3	8.0 19.6
Danube	Hercegszanto	L1540	M	**0.8** **1.0**	0.5 1.3	1.2 2.2	8.5 19.7	4.6 5.4
Danube	Batina	L1315	M			0.6 0.8	0.4 0.8	0.4 0.4
/Drava	Ormoz	L1390	L	0.4 0.4	0.4 0.4	1.3 2.8	0.6 1.5	1.1 2.1
/Drava	Varazdin	L1290	M	3.6 8.3	1.7 4.8	0.5 1.3	0.6 0.9	0.7 1.2
/Drava	Botovo	L1240	M	2.8 5.7	1.1 1.6	0.2 0.5	0.7 1.1	0.7 1.4
/Drava	D.Miholjac	L1250	R	1.8 3.8	1.0 1.5	0.4 0.9	1.0 2.1	0.6 0.9
/Drava	Dravaszabolcs	L1610	M	0.4 0.7	0.5 0.6	1.0 2.6	13.3 28.1	4.2 7.1
Danube	Borovo	L1320	R					0.4 2.6
/Tisza/Sajo	Sajopuspoki	L1770	M	0.8 2.2	2.2 3.8	0.9 1.8	13.3 14.4	3.7 5.1
/Tisza	Tiszasziget	L1700	L	7.8 17.0	4.0 7.5	4.2 9.0		**3.5** **3.5**
/Tisza	Tiszasziget	L1700	M	4.3 8.0	3.1 5.0	3.6 8.1	15.5 23.4	5.1 12.2
/Tisza	Tiszasziget	L1700	R	2.2 5.0	1.5 2.5	1.4 3.0		**2.5** **2.5**
/Sava	Jesenice	L1330	R	0.4 0.4	0.6 0.4	1.8 3.3	0.8 1.4	0.9 2.0
/Sava	Jesenice	L1220	L					1.6 2.3
/Sava	us.Una Jasenovac	L1150	L					2.1 4.1
/Sava	ds.Zupanja	L1060	R					0.1 0.1
Danube	Bazias	L0020	L	10.4 18.8	9.4 14.0	11.6 18.5	19.5 40.7	6.1 19.6
Danube	Bazias	L0020	M	11.1 28.0	8.7 12.0	12.8 20.9	11.3 25.1	4.9 10.2
Danube	Bazias	L0020	R		8.0 14.0	8.6 17.3	11.6 31.9	6.9 15.8
Danube	Pristol/Novo Selo Harbour	L0090	L	11.6 23.7	12.3 16.9	8.3 15.5	11.1 17.8	3.8 7.8
Danube	Pristol/Novo Selo Harbour	L0090	M	12.5 20.0	8.2 12.0	8.1 17.2	11.4 23.0	3.9 12.1
Danube	Pristol/Novo Selo Harbour	L0090	R	22.0 120.0	7.7 11.0	11.3 18.0	15.8 24.0	6.6 25.3
Danube	Novo Selo Harbour/Pristol	L0730	L	12.5 30.0	10.0 10.0	10.0 10.0	13.3 20.0	
Danube	Novo Selo Harbour/Pristol	L0730	M	11.3 20.0	7.5 10.0	10.0 10.0	13.3 20.0	
Danube	Novo Selo Harbour/Pristol	L0730	R	11.3 20.0	10.0 10.0	10.0 10.0	13.3 20.0	
Danube	us.Iskar-Bajkal	L0780	R			10.0 10.0	**10.0** **10.0**	

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M			10.0 10.0	**15.0** **20.0**	10.0 10.0
Danube	Downstream Svishstov	L0810	R				10.0 10.0	
/Jantra	Karantzi	L0990	M				10.0 10.0	
Danube	us.Russe	L0820	R	**10.0** **10.0**			10.0 10.0	10.0 10.0
/Russ.Lom	Basarbovo	L1010	M				10.0 10.0	10.0 10.0
Danube	us. Arges	L0240	L	28.9 150.0	9.8 21.0	11.8 21.9	11.1 19.0	6.9 22.0
Danube	us. Arges	L0240	M	6.8 16.0	8.3 12.0	10.6 16.5	13.7 24.6	5.8 12.6
Danube	us. Arges	L0240	R		7.5 19.0	13.9 22.7	13.2 20.6	5.4 12.6
/Arges	Conf.Danube	L0250	M	15.8 39.0	19.1 35.8	19.2 31.7	25.0 41.0	6.9 15.3
Danube	Chiciu/Silistra	L0280	L	5.1 13.0	8.1 11.9	14.9 21.8	11.9 33.0	7.6 14.4
Danube	Chiciu/Silistra	L0280	M	4.7 9.9	11.9 18.8	12.6 19.3	15.7 35.0	6.6 14.5
Danube	Chiciu/Silistra	L0280	R	6.4 14.5	8.5 12.9	14.3 24.1	15.4 28.0	4.9 9.6
Danube	Silistra/Chiciu	L0850	L	11.7 20.0	**5.0** **5.0**	10.0 10.0	10.0 10.0	10.0 10.0
Danube	Silistra/Chiciu	L0850	M	11.7 20.0	**5.0** **5.0**	10.0 10.0	10.0 10.0	10.0 10.0
Danube	Silistra/Chiciu	L0850	R	11.7 20.0	**5.0** **5.0**	10.0 10.0	10.0 10.0	10.0 10.0
/Siret	Conf.Danube Sendreni	L0380	M	21.3 42.0	14.0 19.9	17.3 25.9	16.9 37.0	6.2 8.8
/Prut	Conf.Danube Giurgiulesti	L0420	M	16.7 36.0	11.9 18.9	11.3 15.9	11.2 22.9	3.4 6.3
Danube	Reni-Chilia/Kilia arm	L0430	L	3.8 9.7	12.4 17.3	14.5 26.1	17.3 27.0	5.9 6.1
Danube	Reni-Chilia/Kilia arm	L0430	M	5.5 12.7	9.6 18.3	15.1 25.8	14.0 25.0	3.0 6.3
Danube	Reni-Chilia/Kilia arm	L0430	R	11.4 13.0	8.1 11.7	17.4 27.7	15.9 31.0	2.9 6.3
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	15.4 29.0	10.1 13.8	15.4 26.0	20.9 21.0	11.4 61.1
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	13.3 29.0	12.7 28.0	16.4 31.6	17.3 28.0	11.3 55.1
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	15.7 29.0	9.0 13.7	18.5 29.7	15.0 28.0	7.2 25.9
Danube	Sulina - Sulina arm	L0480	L	7.7 10.0	10.0 17.6	15.1 24.2	14.6 24.0	4.7 12.7
Danube	Sulina - Sulina arm	L0480	M	32.3 147.0	12.9 21.6	16.3 30.0	15.7 29.5	5.0 11.4
Danube	Sulina - Sulina arm	L0480	R	9.0 16.0	9.5 14.8	18.1 34.4	17.8 24.0	6.5 17.4
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	19.0 38.0	11.4 17.8	16.0 29.0	17.1 28.0	11.4 52.0
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	39.4 153.0	9.0 13.0	15.2 28.7	18.3 41.0	10.7 37.8
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	20.0 42.0	10.7 12.0	14.9 26.8	17.8 23.0	7.7 20.1

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

Note:

average[1]
testing value[2]

[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a year

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Pb								
River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	1.60 2.60	1.19 2.00	1.08 1.00	1.23 2.00	1.58 1.50
/Inn/Salzach	Laufen	L2160	L	3.38 7.00	1.81 2.40	2.15 5.00	3.12 8.00	5.81 9.50
/Inn	Kirchdorf	L2150	M	2.62 4.50	2.92 2.60	1.81 3.00	1.80 3.60	1.88 4.00
Danube	Jochenstein	L2130	M	1.42 1.50	1.23 2.00	1.19 1.50	1.63 2.00	1.19 2.00
Danube	Jochenstein	L2220	M	1.08 1.00	1.94 1.97	1.28 2.00	1.22 1.80	1.34 2.00
Danube	Abwinden-Asten	L2200	R	1.00 1.00	1.96 2.52	1.69 2.90	1.18 1.56	1.26 1.90
Danube	Wien-Nussdorf	L2180	R	1.08 1.00	1.07 1.18	1.51 2.00	1.31 1.98	1.91 2.00
/Morava/Dyje	Pohansko	L2120	L	1.91 2.95	1.53 2.00	2.03 2.40	1.40 1.80	1.48 2.08
/Morava	Lanzhot	L2100	M	2.69 5.90	2.50 5.91	1.39 1.96	2.31 4.79	1.72 2.47
Danube	Wolfsthal	L2170	R	1.09 1.00	1.13 1.54	1.72 4.00	1.88 4.70	1.72 2.70
Danube	Bratislava	L1840	M	1.58 3.80	2.28 1.81	1.20 2.30	1.72 2.70	1.18 1.80
Danube	Medvedov/Medve	L1860	M	0.73 1.20	1.31 3.90	0.95 2.60	1.20 2.40	1.02 1.00
Danube	Medve/Medvedov	L1470	M	3.10 4.70	2.19 3.96	1.50 3.75	1.73 4.48	1.92 3.64
Danube	Komarno/Komarom	L1870	M	0.88 1.24	0.88 2.30	0.73 1.70	1.06 2.00	1.00 1.00
Danube	Komarom/Komarno	L1475	M	0.35 0.60	1.36 3.68	1.09 2.36	1.72 3.09	2.04 3.00
/Vah	Komarno	L1960	M	0.68 1.40	1.15 5.40	0.88 1.60	0.62 0.88	1.00 1.00
Danube	Szob	L1490	L	3.13 5.00	2.30 3.50	2.93 3.50		
Danube	Szob	L1490	M	3.33 4.50	2.14 4.00	0.76 1.74	1.81 3.41	1.93 3.24
Danube	Szob	L1490	R	2.30 3.00	3.17 5.00	4.35 5.00		
Danube	Dunafoldvar	L1520	L		0.81 1.37			
Danube	Dunafoldvar	L1520	M	0.50 0.80	1.04 1.78	1.36 2.28	2.11 4.35	5.03 17.45
Danube	Dunafoldvar	L1520	R		0.77 1.39			
/Sio	Szekszard-Palank	L1604	M	1.58 3.00	0.74 3.00	0.53 1.00	1.76 2.08	1.51 2.29
Danube	Hercegszanto	L1540	M	1.40 1.50	0.79 1.30	0.99 2.16	1.82 3.20	1.25 1.60
Danube	Batina	L1315	M			1.04 2.05	0.85 1.28	0.82 2.02
/Drava	Ormoz	L1390	L	0.80 0.80	1.23 0.80	6.17 10.22	3.03 9.65	3.67 3.38
/Drava	Varazdin	L1290	M	10.23 12.00	12.92 19.60	5.25 13.13	5.90 8.11	4.67 6.22
/Drava	Botovo	L1240	M	7.01 12.54	6.88 12.84	1.34 5.15	3.75 7.47	2.75 4.50
/Drava	D.Miholjac	L1250	R	8.08 16.00	7.17 14.42	2.10 6.91	3.62 7.86	2.83 5.02
/Drava	Dravaszabolcs	L1610	M	1.66 2.10	1.32 1.76	1.20 2.46	2.70 7.03	2.61 4.95
Danube	Borovo	L1320	R					0.34 1.45
/Tisza/Sajo	Sajopuspoki	L1770	M	1.63 2.20	1.54 2.24	1.07 1.74	4.19 10.70	2.13 3.74
/Tisza	Tiszasziget	L1700	L	0.67 1.00	0.79 0.95	0.27 0.20		7.17 15.80
/Tisza	Tiszasziget	L1700	M	0.50 0.50	0.96 1.85	0.59 1.00	8.75 15.50	5.08 10.30
/Tisza	Tiszasziget	L1700	R	0.50 0.50	0.83 0.95	0.27 0.20		5.67 10.60
/Sava	Jesenice	L1330	R	0.80 0.80	0.80 0.80	1.85 3.72	1.16 1.93	1.00 0.80
/Sava	Jesenice	L1220	L					6.15 8.08
/Sava	us.Una Jasenovac	L1150	L					28.10 260.00
/Sava	ds.Zupanja	L1060	R					0.05 0.05
Danube	Bazias	L0020	L	2.53 4.90	20.55 36.00	37.34 82.00	24.10 63.56	10.88 24.60
Danube	Bazias	L0020	M	6.03 35.00	21.83 34.10	38.81 75.46	14.56 26.43	9.60 16.24
Danube	Bazias	L0020	R		12.00 18.00	27.73 44.92	25.82 81.24	9.60 18.33
Danube	Pristol/Novo Selo Harbour	L0090	L	7.10 17.80	24.64 45.00	22.03 33.82	12.83 25.82	10.06 26.33
Danube	Pristol/Novo Selo Harbour	L0090	M	14.90 32.00	28.82 52.00	23.66 35.51	12.42 23.09	8.69 22.60
Danube	Pristol/Novo Selo Harbour	L0090	R	6.91 20.00	26.09 36.00	29.41 61.30	11.70 23.00	10.31 28.43
Danube	Novo Selo Harbour/Pristol	L0730	L	1.00 1.00	1.80 5.00	2.00 10.00	1.00 1.00	10.84 19.20
Danube	Novo Selo Harbour/Pristol	L0730	M	1.00 1.00	3.00 5.00	2.00 10.00	1.00 1.00	6.61 13.60
Danube	Novo Selo Harbour/Pristol	L0730	R	1.00 1.00	2.00 5.00	1.00 1.00	1.00 1.00	9.55 20.10
Danube	us.Iskar-Bajkal	L0780	R			5.75 20.00	1.00 1.00	1.36 2.00

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M	10.00 / 10.00		20.00 / 30.00	15.50 / 30.00	3.75 / 14.00
Danube	Downstream Svishstov	L0810	M	15.25 / 30.00				
Danube	Downstream Svishstov	L0810	R		5.00 / 5.00		3.55 / 8.00	1.64 / 3.00
/Jantra	Karantzi	L0990	M	15.00 / 20.00	10.00 / 20.00		3.33 / 7.90	1.45 / 2.00
Danube	us.Russe	L0820	R				3.33 / 7.90	6.00 / 20.00
/Russ.Lom	Basarbovo	L1010	M				3.58 / 8.00	4.36 / 10.00
Danube	us. Arges	L0240	L	16.53 / 54.00	22.73 / 34.00	23.87 / 30.94	15.43 / 37.00	7.71 / 18.18
Danube	us. Arges	L0240	M	10.42 / 27.00	23.45 / 38.00	23.18 / 37.80	13.05 / 20.00	6.99 / 16.28
Danube	us. Arges	L0240	R		23.00 / 45.00	31.47 / 43.50	13.25 / 25.91	7.46 / 19.42
/Arges	Conf.Danube	L0250	M	51.34 / 92.00	30.33 / 49.70	41.44 / 76.76	16.08 / 41.48	8.03 / 23.64
Danube	Chiciu/Silistra	L0280	L	9.86 / 29.00	25.42 / 44.10	32.25 / 57.30	15.88 / 53.02	8.58 / 16.05
Danube	Chiciu/Silistra	L0280	M	12.11 / 38.50	25.92 / 42.50	28.79 / 48.10	15.93 / 56.25	8.35 / 17.17
Danube	Chiciu/Silistra	L0280	R	11.11 / 49.20	24.83 / 36.90	35.61 / 54.13	16.63 / 61.00	9.64 / 20.71
Danube	Silistra/Chiciu	L0850	L	1.00 / 1.00	4.60 / 7.00	7.00 / 10.00	3.33 / 7.90	7.10 / 24.00
Danube	Silistra/Chiciu	L0850	M	1.00 / 1.00	4.25 / 5.00	7.33 / 11.00	3.33 / 7.90	8.33 / 26.00
Danube	Silistra/Chiciu	L0850	R	1.00 / 1.00	4.33 / 7.00	7.56 / 13.00	3.33 / 7.90	6.64 / 20.00
/Siret	Conf.Danube Sendreni	L0380	M	23.00 / 48.00	28.82 / 45.00	48.00 / 88.71	19.39 / 38.38	4.55 / 9.45
/Prut	Conf.Danube Giurgiulesti	L0420	M	32.67 / 49.00	22.36 / 31.00	27.88 / 49.70	9.21 / 21.03	4.42 / 10.03
Danube	Reni-Chilia/Kilia arm	L0430	L	20.19 / 34.30	23.82 / 35.00	25.65 / 43.17	13.80 / 30.00	12.59 / 24.97
Danube	Reni-Chilia/Kilia arm	L0430	M	10.94 / 28.80	24.00 / 41.00	22.34 / 39.16	11.12 / 31.33	12.95 / 26.02
Danube	Reni-Chilia/Kilia arm	L0430	R	11.44 / 37.90	22.36 / 35.00	25.23 / 44.73	14.60 / 37.56	10.89 / 20.02
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	16.94 / 38.00	26.58 / 40.50	22.94 / 36.70	13.24 / 32.00	6.62 / 16.46
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	11.10 / 29.00	18.92 / 25.00	24.36 / 40.60	13.71 / 35.13	6.46 / 19.27
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	11.69 / 30.00	27.55 / 43.00	21.95 / 35.71	12.25 / 39.70	5.93 / 12.60
Danube	Sulina - Sulina arm	L0480	L	22.67 / 50.00	22.20 / 26.90	24.98 / 37.54	12.64 / 31.55	6.91 / 18.36
Danube	Sulina - Sulina arm	L0480	M	18.83 / 52.00	21.88 / 36.80	25.14 / 43.80	10.50 / 22.74	5.47 / 8.48
Danube	Sulina - Sulina arm	L0480	R	22.33 / 45.00	21.91 / 30.44	28.92 / 50.52	15.59 / 48.36	5.10 / 8.43
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	24.33 / 57.00	22.08 / 35.99	25.34 / 47.13	12.53 / 33.68	6.32 / 13.11
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	16.20 / 26.00	22.63 / 33.14	22.44 / 43.10	14.20 / 33.90	7.69 / 16.70
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	25.33 / 40.00	20.88 / 27.96	22.73 / 46.60	14.77 / 40.41	5.35 / 9.18

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
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- 90 %-ile if number of measurement was ≥ 11 in a year
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blank fields mean that no measurements were done in the year
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Cd

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.12 0.20	0.11 0.10	0.10 0.10	0.10 0.10	0.10 0.10
/Inn/Salzach	Laufen	L2160	L	0.28 0.40	0.13 0.24	0.12 0.10	0.13 0.20	0.19 0.30
/Inn	Kirchdorf	L2150	M	0.13 0.20	0.10 0.10	0.11 0.10	0.10 0.10	0.10 0.10
Danube	Jochenstein	L2130	M	0.10 0.10	0.10 0.10	0.10 0.10	0.10 0.10	0.10 0.10
Danube	Jochenstein	L2220	M	0.20 0.20	0.22 0.20	0.17 0.20	0.14 0.13	0.19 0.13
Danube	Abwinden-Asten	L2200	R	0.20 0.20	0.22 0.20	0.43 0.66	0.14 0.19	0.14 0.19
Danube	Wien-Nussdorf	L2180	R	0.20 0.20	0.20 0.20	0.24 0.20	0.14 0.19	0.13 0.19
/Morava/Dyje	Pohansko	L2120	L	0.10 0.10	0.11 0.10	0.73 1.24	0.53 1.65	0.21 0.17
/Morava	Lanzhot	L2100	M	0.10 0.10	0.13 0.20	0.16 0.20	0.16 0.23	0.17 0.22
Danube	Wolfsthal	L2170	R	0.19 0.20	0.20 0.20	0.16 0.20	0.24 0.25	0.13 0.13
Danube	Bratislava	L1840	M	0.03 0.04	0.07 0.18	0.05 0.07	0.05 0.08	0.05 0.06
Danube	Medvedov/Medve	L1860	M	0.01 0.02	0.03 0.04	0.04 0.12	0.08 0.11	0.05 0.05
Danube	Medve/Medvedov	L1470	M	1.00 1.90	0.63 1.18	0.15 0.19	0.12 0.05	0.18 0.35
Danube	Komarno/Komarom	L1870	M	0.22 1.06	0.05 0.13	0.03 0.05	0.07 0.11	0.05 0.05
Danube	Komarom/Komarno	L1475	M	0.50 0.90	0.43 0.90	0.11 0.05	0.05 0.05	0.18 0.36
/Vah	Komarno	L1960	M	0.05 0.17	0.09 0.22	0.01 0.02	0.05 0.12	0.06 0.05
Danube	Szob	L1490	L	0.33 0.50	1.05 1.60	1.03 1.60		
Danube	Szob	L1490	M	0.70 0.80	1.17 2.00	0.29 1.04	0.09 0.05	0.18 0.35
Danube	Szob	L1490	R	0.50 0.60	1.45 2.50	0.81 1.20		
Danube	Dunafoldvar	L1520	L		0.16 0.29			
Danube	Dunafoldvar	L1520	M	0.15 0.20	0.14 0.20	0.07 0.05	0.05 0.05	0.20 0.37
Danube	Dunafoldvar	L1520	R		0.16 0.20			
/Sio	Szekszard-Palank	L1604	M	0.76 1.00	0.13 0.40	0.03 0.05	0.11 0.20	0.20 0.43
Danube	Hercegszanto	L1540	M	0.20 0.20	0.13 0.20	0.04 0.05	0.05 0.06	0.15 0.32
Danube	Batina	L1315	M			0.18 0.19	0.04 0.06	0.05 0.06
/Drava	Ormoz	L1390	L	0.03 0.03	0.03 0.03	0.47 0.84	0.05 0.10	0.07 0.18
/Drava	Varazdin	L1290	M	1.82 8.50	1.21 1.70	0.50 1.16	0.79 1.13	0.44 0.73
/Drava	Botovo	L1240	M	0.61 1.07	1.65 1.69	0.11 0.38	0.42 1.02	0.20 0.56
/Drava	D.Miholjac	L1250	R	0.67 1.12	0.75 1.63	0.13 0.46	0.41 0.97	0.17 0.37
/Drava	Dravaszabolcs	L1610	M	0.10 0.10	0.07 0.10	0.04 0.06	0.05 0.05	0.19 0.36
Danube	Borovo	L1320	R					0.03 0.06
/Tisza/Sajo	Sajopuspoki	L1770	M	0.05 0.10	0.16 0.27	0.04 0.05	0.17 0.05	0.22 0.37
/Tisza	Tiszasziget	L1700	L	0.10 0.10	0.17 0.30	0.02 0.02		0.59 0.92
/Tisza	Tiszasziget	L1700	M	0.06 0.10	0.13 0.20	0.04 0.08	0.05 0.05	0.37 0.66
/Tisza	Tiszasziget	L1700	R	0.10 0.10	0.13 0.20	0.02 0.02		0.45 0.72
/Sava	Jesenice	L1330	R	0.03 0.03	0.03 0.03	0.14 0.31	0.05 0.14	0.06 0.06
/Sava	Jesenice	L1220	L					0.63 0.82
/Sava	us.Una Jasenovac	L1150	L					0.25 0.25
/Sava	ds.Zupanja	L1060	R					5.00 5.00
Danube	Bazias	L0020	L	0.20 0.61	6.37 10.97	1.09 1.45	2.62 6.31	1.06 2.47
Danube	Bazias	L0020	M	0.20 0.58	5.16 16.81	1.98 2.87	2.84 7.22	0.73 1.40
Danube	Bazias	L0020	R		1.55 2.62	1.20 2.56	3.11 10.00	0.56 0.93
Danube	Pristol/Novo Selo Harbour	L0090	L	0.34 1.32	4.78 3.32	1.48 3.49	3.35 8.10	1.26 2.11
Danube	Pristol/Novo Selo Harbour	L0090	M	0.65 1.30	3.28 10.67	0.99 1.62	3.09 8.43	1.33 4.79
Danube	Pristol/Novo Selo Harbour	L0090	R	0.39 1.00	7.53 17.70	1.88 2.99	2.88 9.23	1.76 4.73
Danube	Novo Selo Harbour/Pristol	L0730	L	1.00 1.00		1.00 1.00	1.00 1.00	1.05 1.00
Danube	Novo Selo Harbour/Pristol	L0730	M	1.00 1.00		1.00 1.00	1.00 1.00	1.00 1.00
Danube	Novo Selo Harbour/Pristol	L0730	R	1.00 1.00		1.00 1.00	1.00 1.00	1.00 1.00
Danube	us.Iskar-Bajkal	L0780	R				1.00 1.00	1.36 1.00

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M	**10.00** **10.00**			**1.00** **1.00**	1.75 7.00
Danube	Downstream Svishstov	L0810	M	1.00 1.00				
Danube	Downstream Svishstov	L0810	R		**0.50** **0.50**		1.00 1.00	1.00 1.00
/Jantra	Karantzi	L0990	M	**5.50** **10.00**	2.75 5.00		1.00 1.00	1.00 1.00
Danube	us.Russe	L0820	R				1.00 1.00	2.80 8.00
/Russ.Lom	Basarbovo	L1010	M				1.00 1.00	2.64 8.00
Danube	us. Arges	L0240	L	0.30 0.72	6.38 16.66	1.06 2.12	2.58 8.11	0.43 0.89
Danube	us. Arges	L0240	M	0.35 1.00	8.16 29.10	1.18 2.20	3.06 10.14	0.37 0.70
Danube	us. Arges	L0240	R		4.80 40.28	1.47 2.88	4.67 14.07	0.88 4.04
/Arges	Conf.Danube	L0250	M	8.76 45.60	4.18 9.25	1.88 1.82	4.57 17.17	0.84 1.83
Danube	Chiciu/Silistra	L0280	L	0.35 0.86	1.62 3.63	1.30 1.76	2.42 5.40	0.83 1.65
Danube	Chiciu/Silistra	L0280	M	0.20 0.42	1.68 3.29	1.49 2.31	2.83 6.06	1.11 2.43
Danube	Chiciu/Silistra	L0280	R	0.29 0.58	1.77 5.07	1.16 1.57	2.38 5.00	0.92 2.22
Danube	Silistra/Chiciu	L0850	L	1.00 1.00	0.70 1.00	1.00 1.00	1.00 1.00	2.40 8.00
Danube	Silistra/Chiciu	L0850	M		0.75 1.00	1.00 1.00	1.00 1.00	2.56 8.00
Danube	Silistra/Chiciu	L0850	R	1.00 1.00	0.67 1.00	1.00 1.00	1.00 1.00	2.27 8.00
/Siret	Conf.Danube Sendreni	L0380	M	1.26 3.59	2.00 3.80	1.61 2.28	3.77 9.20	0.89 2.25
/Prut	Conf.Danube Giurgiulesti	L0420	M	0.29 0.32	3.92 5.42	5.43 8.36	2.16 5.00	1.19 3.89
Danube	Reni-Chilia/Kilia arm	L0430	L	0.62 1.48	1.64 2.62	1.18 1.70	3.24 8.15	1.49 2.54
Danube	Reni-Chilia/Kilia arm	L0430	M	0.41 1.64	1.81 2.88	1.11 2.36	4.11 9.20	0.97 2.07
Danube	Reni-Chilia/Kilia arm	L0430	R	0.35 1.05	1.64 2.30	1.13 1.90	3.35 7.74	1.31 1.45
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.38 1.00	2.46 8.01	1.29 2.49	3.76 11.20	1.03 2.50
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.45 0.79	1.67 2.33	0.72 1.47	5.01 25.81	1.13 2.55
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.32 0.66	2.89 6.81	1.33 2.33	5.67 25.50	0.94 2.54
Danube	Sulina - Sulina arm	L0480	L	0.14 0.29	3.81 7.90	1.10 1.61	4.41 22.50	1.18 2.70
Danube	Sulina - Sulina arm	L0480	M	0.40 1.12	3.04 7.98	1.43 2.69	5.33 21.40	0.88 2.22
Danube	Sulina - Sulina arm	L0480	R	0.07 0.16	3.31 4.70	0.91 1.83	4.70 24.30	0.84 2.40
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	1.22 3.44	1.22 1.59	0.75 0.98	4.82 22.40	0.77 2.52
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.40 1.00	1.29 1.69	1.12 1.52	4.16 15.20	0.81 2.39
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.24 0.63	1.57 3.61	1.11 1.91	4.30 18.20	0.79 2.25

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testing value[2]

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Hg

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.104 0.100	0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
/Inn/Salzach	Laufen	L2160	L	0.304 0.750	0.123 0.150	0.143 0.300	0.122 0.100	0.131 0.300
/Inn	Kirchdorf	L2150	M	0.381 0.500	0.332 0.620	0.531 0.600	0.419 0.600	0.655 0.900
Danube	Jochenstein	L2130	M	0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Jochenstein	L2220	M	0.200 0.200	0.243 0.416	0.251 0.344	0.200 0.200	0.100 0.100
Danube	Abwinden-Asten	L2200	R	0.233 0.290	0.205 0.200	0.206 0.200	0.200 0.200	0.100 0.100
Danube	Wien-Nussdorf	L2180	R	0.242 0.300	0.235 0.289	0.243 0.380	0.200 0.200	0.100 0.100
/Morava/Dyje	Pohansko	L2120	L	0.100 0.100	0.150 0.200	0.100 0.100	0.298 1.010	0.223 0.272
/Morava	Lanzhot	L2100	M	0.225 0.280	0.142 0.200	0.117 0.190	0.142 0.200	0.120 0.166
Danube	Wolfsthal	L2170	R	0.200 0.200	0.271 0.368	0.200 0.200	0.200 0.200	0.100 0.100
Danube	Bratislava	L1840	M	0.100 0.100	0.100 0.100	0.125 0.200	0.100 0.100	0.100 0.100
Danube	Medvedov/Medve	L1860	M	0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Medve/Medvedov	L1470	M	0.100 0.100	0.138 0.200	0.100 0.100	1.425 0.190	0.070 0.150
Danube	Komarno/Komarom	L1870	M	0.100 0.100	0.155 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Komarom/Komarno	L1475	M	0.100 0.100	0.138 0.200	0.139 0.100	0.500 0.190	0.105 0.380
/Vah	Komarno	L1960	M	0.100 0.100	0.117 0.200	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Szob	L1490	L	0.100 0.100	0.100 0.100	0.100 0.100		
Danube	Szob	L1490	M	0.100 0.100	0.100 0.100	0.188 0.220	0.108 0.100	0.126 0.209
Danube	Szob	L1490	R	0.100 0.100	0.100 0.100	0.100 0.100		
Danube	Dunafoldvar	L1520	L		0.125 0.250			
Danube	Dunafoldvar	L1520	M	0.075 0.100	0.295 0.824	0.141 0.100	0.100 0.100	0.051 0.105
Danube	Dunafoldvar	L1520	R		0.183 0.466			
/Sio	Szekszard-Palank	L1604	M		0.514 0.760	0.152 0.100	0.549 0.700	0.142 0.316
Danube	Hercegszanto	L1540	M	0.075 0.100	0.073 0.120	0.105 0.100	0.169 0.100	0.085 0.100
Danube	Batina	L1315	M			0.083 0.096	0.070 0.069	0.043 0.060
/Drava	Ormoz	L1390	L	0.500 0.500	0.500 0.500	0.500 0.500	0.500 0.500	0.500 0.500
/Drava	Varazdin	L1290	M		0.080 0.150	0.085 0.100	0.108 0.118	0.100 0.100
/Drava	Botovo	L1240	M		0.114 0.180	0.070 0.100	0.102 0.109	0.024 0.082
/Drava	D.Miholjac	L1250	R		0.105 0.120	0.082 0.100	0.113 0.190	0.024 0.082
/Drava	Dravaszabolcs	L1610	M		0.067 0.100	0.100 0.100	0.100 0.100	0.083 0.144
Danube	Borovo	L1320	R					0.017 0.060
/Tisza/Sajo	Sajopuspoki	L1770	M	0.100 0.100	0.055 0.100	0.100 0.100	0.100 0.100	0.238 0.185
/Tisza	Tiszasziget	L1700	L	0.200 0.200	0.117 0.190	0.100 0.100		0.100 0.100
/Tisza	Tiszasziget	L1700	M	0.175 0.200	0.133 0.160	0.104 0.100	0.100 0.100	0.455 0.580
/Tisza	Tiszasziget	L1700	R	0.200 0.200	0.108 0.100	0.100 0.100		0.100 0.100
/Sava	Jesenice	L1330	R	0.500 0.500	0.500 0.500	0.500 0.500	0.500 0.500	0.500 0.500
/Sava	Jesenice	L1220	L					0.035 0.078
/Sava	us.Una Jasenovac	L1150	L					0.058 0.213
/Sava	ds.Zupanja	L1060	R					0.563 1.539
Danube	Bazias	L0020	L	3.000 3.000				
Danube	Bazias	L0020	M	3.000 3.000				
Danube	Pristol/Novo Selo Harbour	L0090	L	3.000 3.000				
Danube	Pristol/Novo Selo Harbour	L0090	M	3.000 3.000				
Danube	Pristol/Novo Selo Harbour	L0090	R	3.000 3.000				
Danube	us. Arges	L0240	L	3.000 3.000				
Danube	us. Arges	L0240	M	3.000 3.000				
/Arges	Conf.Danube	L0250	M	3.000 3.000				
Danube	Chiciu/Silistra	L0280	L	3.000 3.000				
Danube	Chiciu/Silistra	L0280	M	3.000 3.000				

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Chiciu/Silistra	L0280	R	3.000 3.000				
/Siret	*Conf.Danube Sendreni*	L0380	M	3.000 3.000				
/Prut	*Conf.Danube Giurgiulesti*	L0420	M	3.000 3.000				
Danube	Reni-Chilia/Kilia arm	L0430	L	3.000 3.000				
Danube	Reni-Chilia/Kilia arm	L0430	M	3.000 3.000				
Danube	Reni-Chilia/Kilia arm	L0430	R	3.000 3.000				
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	3.000 3.000				
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	3.000 3.000				
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	3.000 3.000				
Danube	Sulina - Sulina arm	L0480	L	3.000 3.000				
Danube	Sulina - Sulina arm	L0480	M	3.000 3.000				
Danube	Sulina - Sulina arm	L0480	R	3.000 3.000				
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	3.000 3.000				
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	3.000 3.000				
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	3.000 3.000				

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Ni

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	1.720 3.000	1.296 2.000	1.360 2.000	1.654 3.000	2.192 4.000
/Inn/Salzach	Laufen	L2160	L	7.615 24.500	4.630 10.200	3.077 6.000	2.458 5.000	3.154 6.000
/Inn	Kirchdorf	L2150	M	2.920 7.600	2.160 4.600	2.731 5.500	2.038 3.500	2.962 6.000
Danube	Jochenstein	L2130	M	1.192 1.000	1.154 1.000	1.115 1.500	1.222 2.000	1.115 1.000
Danube	Jochenstein	L2220	M	1.500 2.000	1.375 2.000	1.817 2.930	1.467 1.970	2.160 4.855
Danube	Abwinden-Asten	L2200	R	1.250 2.000	1.650 2.900	2.267 4.000	1.308 1.860	1.659 2.437
Danube	Wien-Nussdorf	L2180	R	1.250 2.000	1.158 1.730	1.625 3.000	1.725 2.200	2.278 3.337
/Morava/Dyje	Pohansko	L2120	L	3.475 4.960	3.267 4.380	3.592 4.860	3.904 4.770	3.628 4.509
/Morava	Lanzhot	L2100	M	3.483 5.000	3.183 7.180	1.708 2.570	3.256 4.910	3.087 4.036
Danube	Wolfsthal	L2170	R	1.182 1.000	1.492 2.630	2.206 4.300	3.167 5.400	2.859 4.000
Danube	Bratislava	L1840	M	2.600 4.200	3.583 5.850	2.550 4.300	2.275 3.900	1.645 2.000
Danube	Medvedov/Medve	L1860	M	2.345 3.000	2.082 3.300	3.250 6.200	1.625 2.000	1.355 1.900
Danube	Medve/Medvedov	L1470	M	3.120 7.400	3.585 7.860	1.704 2.570	2.433 3.390	4.975 6.980
Danube	Komarno/Komarom	L1870	M	1.600 2.700	2.718 4.700	3.000 6.200	1.825 2.000	1.355 1.800
Danube	Komarom/Komarno	L1475	M	**0.650** **1.200**	2.562 5.120	1.126 1.900	2.900 3.290	4.692 7.000
/Vah	Komarno	L1960	M	3.780 7.800	3.867 8.700	1.975 2.600	1.875 2.300	1.464 2.200
Danube	Szob	L1490	L	3.233 4.000	2.950 3.500	2.375 3.100		
Danube	Szob	L1490	M	3.200 4.000	3.329 4.400	1.782 3.240	10.433 8.820	6.967 16.210
Danube	Szob	L1490	R	2.367 2.700	3.350 5.000	2.250 2.600		
Danube	Dunafoldvar	L1520	L		1.083 1.780			
Danube	Dunafoldvar	L1520	M	**0.350** **0.400**	1.077 1.760	1.550 2.350	4.600 11.530	5.983 9.340
Danube	Dunafoldvar	L1520	R		1.125 1.890			
/Sio	Szekszard-Palank	L1604	M	4.250 8.000	7.410 33.000	3.818 5.900	5.233 8.620	5.218 8.629
Danube	Hercegszanto	L1540	M	**0.450** **0.600**	1.022 2.160	1.109 1.900	2.462 3.480	3.191 5.200
Danube	Batina	L1315	M			1.017 1.580	1.142 1.390	2.250 3.710
/Drava	Ormoz	L1390	L	1.810 10.000	0.900 0.900	1.567 2.270	1.864 3.690	1.733 3.500
/Drava	Varazdin	L1290	M	8.350 12.800	8.733 11.900	3.362 7.210	5.975 7.080	5.350 6.600
/Drava	Botovo	L1240	M	6.125 9.940	6.000 11.210	1.252 3.450	3.658 7.380	3.625 5.670
/Drava	D.Miholjac	L1250	R	6.600 11.200	5.900 11.920	1.302 3.520	3.867 8.360	3.175 5.640
/Drava	Dravaszabolcs	L1610	M	1.100 1.900	1.008 1.400	1.728 3.400	3.075 4.340	3.165 4.468
Danube	Borovo	L1320	R					1.510 8.400
/Tisza/Sajo	Sajopuspoki	L1770	M	1.843 4.100	2.093 3.610	1.443 1.900	4.033 8.280	6.180 9.544
/Tisza	Tiszasziget	L1700	L	1.167 2.000	2.000 3.450	1.889 3.000		**6.000** **6.000**
/Tisza	Tiszasziget	L1700	M	2.000 6.000	2.307 4.200	1.878 2.460	6.475 11.150	5.457 7.164
/Tisza	Tiszasziget	L1700	R	0.667 1.000	2.417 3.900	1.727 3.500		**3.000** **3.000**
/Sava	Jesenice	L1330	R	0.900 0.900	0.900 0.900	1.308 2.220	1.595 2.270	2.125 1.480
/Sava	Jesenice	L1220	L					6.792 7.590
/Sava	us.Una Jasenovac	L1150	L					2.750 5.000
/Sava	ds.Zupanja	L1060	R					0.500 0.500
Danube	Bazias	L0020	L	5.083 7.900			**2.460** **2.460**	3.239 10.020
Danube	Bazias	L0020	M	8.889 32.000			**1.330** **1.330**	3.696 8.460
Danube	Bazias	L0020	R				**1.650** **1.650**	3.087 9.460
Danube	Pristol/Novo Selo Harbour	L0090	L	3.525 7.000			**1.840** **1.840**	2.967 6.900
Danube	Pristol/Novo Selo Harbour	L0090	M	12.510 38.000			**1.410** **1.410**	3.143 9.030
Danube	Pristol/Novo Selo Harbour	L0090	R	6.810 11.000			**2.280** **2.280**	2.142 4.100
Danube	Novo Selo Harbour/Pristol	L0730	L	1.875 8.000	1.750 2.500	1.000 1.000	1.000 1.000	7.579 15.000
Danube	Novo Selo Harbour/Pristol	L0730	M	1.750 7.000	3.333 5.000	1.000 1.000	1.000 1.000	6.389 11.000
Danube	Novo Selo Harbour/Pristol	L0730	R	1.625 6.000	3.200 5.000	1.000 1.000	1.000 1.000	6.700 12.200
Danube	us.Iskar-Bajkal	L0780	R			1.000 1.000	**1.000** **1.000**	3.182 5.000

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Iskar	Orechovitza	L0930	M			2.500 2.500	1.000 1.000	6.750 34.000
Danube	Downstream Svishstov	L0810	M	3.667 5.000				
Danube	Downstream Svishstov	L0810	R		2.500 2.500		3.000 5.000	2.091 3.000
/Jantra	Karantzi	L0990	M	1.000 1.000	3.200 6.000		2.833 5.000	2.364 4.000
Danube	us.Russe	L0820	M	1.000 1.000				
Danube	us.Russe	L0820	R	1.000 1.000			2.833 5.000	4.200 15.000
/Russ.Lom	Basarbovo	L1010	M				2.917 5.000	3.909 15.000
Danube	us. Arges	L0240	L	5.358 13.000			6.260 6.260	5.130 19.950
Danube	us. Arges	L0240	M	15.620 40.000			3.900 3.900	3.718 11.040
Danube	us. Arges	L0240	R				5.340 5.340	3.950 13.120
/Arges	Conf.Danube	L0250	M	21.858 63.000			6.580 6.580	5.150 14.700
Danube	Chiciu/Silistra	L0280	L	13.021 42.900				2.595 3.326
Danube	Chiciu/Silistra	L0280	M	11.117 34.700				1.926 3.288
Danube	Chiciu/Silistra	L0280	R	10.367 40.100				1.954 3.222
Danube	Silistra/Chiciu	L0850	L	1.000 1.000	2.900 4.000	3.222 5.000	2.833 5.000	5.200 15.000
Danube	Silistra/Chiciu	L0850	M	1.000 1.000	2.250 2.500	3.333 6.000	2.833 5.000	5.667 15.000
Danube	Silistra/Chiciu	L0850	R	1.000 1.000	2.833 4.000	2.778 5.000	2.833 5.000	4.818 15.000
/Siret	Conf.Danube Sendreni	L0380	M	28.025 80.000				2.006 3.480
/Prut	Conf.Danube Giurgiulesti	L0420	M	0.050 0.050				2.034 3.780
Danube	Reni-Chilia/Kilia arm	L0430	L	3.704 5.800			3.390 3.390	1.847 3.180
Danube	Reni-Chilia/Kilia arm	L0430	M	5.371 17.200			5.380 5.380	2.117 5.300
Danube	Reni-Chilia/Kilia arm	L0430	R	5.371 20.900			2.670 2.670	1.868 3.640
Danube	Reni-Kilia arm/Chilia arm	L0630	M	3.000 3.000				
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	20.767 41.400			7.020 7.020	1.812 4.350
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	13.767 30.900			7.270 7.270	1.836 3.050
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	18.017 41.800			7.380 7.380	1.542 3.770
Danube	Vilkova-Kilia arm/Chilia arm	L0690	M	3.000 3.000				
Danube	Sulina - Sulina arm	L0480	L	0.050 0.050			5.590 5.590	1.896 3.690
Danube	Sulina - Sulina arm	L0480	M	5.025 18.000			3.900 3.900	1.912 4.510
Danube	Sulina - Sulina arm	L0480	R	0.050 0.050			5.930 5.930	1.744 3.710
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.050 0.050			1.870 1.870	1.920 3.650
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	1.830 8.000			0.940 0.940	1.970 4.510
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.050 0.050			6.940 6.940	1.954 3.280

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As

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	1.0 / 1.0	1.0 / 1.0	1.0 / 1.0	1.0 / 1.0	1.0 / 1.0
/Inn/Salzach	Laufen	L2160	L	1.9 / 4.4	1.3 / 2.0	1.5 / 2.0	1.7 / 1.6	2.7 / 8.0
/Inn	Kirchdorf	L2150	M	2.5 / 4.7	2.0 / 2.6	2.3 / 3.5	1.8 / 3.0	1.8 / 2.0
Danube	Jochenstein	L2130	M	1.1 / 1.0	1.0 / 1.0	1.0 / 1.0	1.1 / 1.0	1.0 / 1.0
Danube	Jochenstein	L2220	M	1.1 / 1.0	1.1 / 1.2	1.4 / 2.0	1.8 / 2.9	1.9 / 2.2
Danube	Abwinden-Asten	L2200	R	1.0 / 1.0	1.2 / 1.9	1.3 / 1.9	1.6 / 2.0	1.5 / 2.0
Danube	Wien-Nussdorf	L2180	R	1.0 / 1.0	1.0 / 1.0	1.5 / 2.9	2.1 / 3.3	1.7 / 2.0
/Morava/Dyje	Pohansko	L2120	L	1.0 / 1.0	2.7 / 4.1	2.2 / 3.1	2.2 / 3.8	2.3 / 4.4
/Morava	Lanzhot	L2100	M	1.0 / 1.0	2.0 / 3.3	1.1 / 1.6	1.1 / 1.2	1.2 / 1.6
Danube	Wolfsthal	L2170	R	1.0 / 1.0	1.0 / 1.0	1.1 / 1.3	1.3 / 2.0	1.2 / 1.6
Danube	Bratislava	L1840	M	1.0 / 1.0	1.6 / 2.7	1.1 / 1.4	1.2 / 1.8	1.1 / 1.3
Danube	Medvedov/Medve	L1860	M	1.0 / 1.0	1.2 / 1.6	1.0 / 1.2	1.0 / 1.1	1.1 / 1.3
Danube	Medve/Medvedov	L1470	M	1.0 / 1.0	1.0 / 3.9	1.5 / 2.4	1.3 / 2.0	1.0 / 1.2
Danube	Komarno/Komarom	L1870	M	1.0 / 1.0	1.5 / 2.5	1.3 / 1.9	1.1 / 1.3	1.3 / 1.3
Danube	Komarom/Komarno	L1475	M	0.1 / 0.1	1.1 / 4.1	1.5 / 2.7	1.4 / 2.5	1.1 / 1.9
/Vah	Komarno	L1960	M	1.2 / 1.4	2.8 / 4.9	2.3 / 2.8	2.9 / 4.0	4.1 / 5.2
Danube	Szob	L1490	L	1.3 / 2.0	1.9 / 2.4	1.9 / 2.2		
Danube	Szob	L1490	M	1.2 / 1.5	3.5 / 6.1	2.0 / 3.1	1.3 / 2.0	0.9 / 1.1
Danube	Szob	L1490	R	1.4 / 1.5	3.2 / 5.0	2.8 / 3.0		
Danube	Dunafoldvar	L1520	M		2.4 / 3.7	1.5 / 2.8	1.3 / 2.0	1.1 / 1.5
/Sio	Szekszard-Palank	L1604	M		5.6 / 15.0	3.2 / 6.8	5.8 / 18.5	4.8 / 5.2
Danube	Hercegszanto	L1540	M		1.2 / 1.6	1.3 / 1.7	1.4 / 2.7	1.3 / 1.8
Danube	Batina	L1315	M			0.9 / 1.3	1.8 / 4.1	1.0 / 1.2
/Drava	Dravaszabolcs	L1610	M		2.4 / 3.6	1.7 / 3.6	1.3 / 1.5	1.4 / 1.7
Danube	Borovo	L1320	R					0.8 / 0.8
/Tisza/Sajo	Sajopuspoki	L1770	M	3.5 / 4.9	3.5 / 6.8	1.7 / 2.8	1.6 / 3.0	2.1 / 3.2
/Tisza	Tiszasziget	L1700	L	1.0 / 1.0	1.0 / 1.0	2.0 / 2.0		2.0 / 2.0
/Tisza	Tiszasziget	L1700	M	1.0 / 1.0	1.3 / 2.5	2.5 / 3.4	2.4 / 4.5	3.2 / 4.7
/Tisza	Tiszasziget	L1700	R	1.0 / 1.0	1.0 / 1.0	2.0 / 2.0		2.0 / 2.0
Danube	Novo Selo Harbour/Pristol	L0730	L	1.7 / 4.0				4.8 / 7.4
Danube	Novo Selo Harbour/Pristol	L0730	M	1.4 / 3.0				3.9 / 6.3
Danube	Novo Selo Harbour/Pristol	L0730	R	2.0 / 4.0				4.9 / 8.0
Danube	us.Iskar-Bajkal	L0780	R					6.2 / 26.0
/Iskar	Orechovitza	L0930	M					42.2 / 91.8
Danube	Downstream Svishtov	L0810	R				2.1 / 2.0	5.5 / 9.9
/Jantra	Karantzi	L0990	M				2.0 / 2.0	1.6 / 2.0
Danube	us.Russe	L0820	R				2.1 / 2.0	3.5 / 10.0
/Russ.Lom	Basarbovo	L1010	M				2.1 / 2.0	3.3 / 10.0
Danube	Silistra/Chiciu	L0850	L	3.0 / 3.0	1.6 / 3.0	0.3 / 0.3	2.3 / 3.0	3.6 / 10.0
Danube	Silistra/Chiciu	L0850	M	3.0 / 3.0	1.3 / 2.0	0.3 / 0.3	2.3 / 3.0	3.9 / 10.0
Danube	Silistra/Chiciu	L0850	R	3.5 / 4.0	1.5 / 3.0	0.3 / 0.3	2.3 / 3.0	3.4 / 10.0

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

Note:

average[1]
testing value[2]

[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
- maximum value, if number of measurements was < 11 in a yea

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

AOX

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Inn/Salzach	Laufen	L2160	L	10.0 / 10.0	10.0 / 10.0	10.0 / 10.0	10.0 / 10.0	10.0 / 10.0
Danube	Jochenstein	L2130	M	8.3 / 10.0	10.8 / 10.0	10.9 / 10.0	10.0 / 10.0	10.0 / 10.0
Danube	Jochenstein	L2220	M	8.0 / 10.0	7.8 / 11.3	8.7 / 13.7	6.5 / 8.7	6.6 / 11.2
Danube	Abwinden-Asten	L2200	R	8.1 / 9.9	7.5 / 11.3	8.4 / 12.8	7.2 / 9.7	5.3 / 9.7
Danube	Wien-Nussdorf	L2180	R	8.7 / 13.1	7.6 / 10.8	8.6 / 9.6	7.2 / 9.4	5.3 / 9.8
/Morava/Dyje	Pohansko	L2120	L		24.9 / 30.9	23.0 / 29.7	23.9 / 31.1	27.6 / 43.4
/Morava	Lanzhot	L2100	M		17.3 / 23.2	15.5 / 23.6	17.5 / 25.3	16.4 / 22.9
Danube	Wolfsthal	L2170	R	9.2 / 14.3	8.5 / 12.3	9.2 / 11.8	8.2 / 9.8	5.9 / 10.1
Danube	Bratislava	L1840	M			52.5 / 87.4	52.3 / 76.9	41.0 / 75.7
Danube	Medvedov/Medve	L1860	M			52.3 / 129.0	39.7 / 60.8	22.3 / 29.3
Danube	Medve/Medvedov	L1470	M			16.4 / 55.0	7.6 / 17.0	
Danube	Komarno/Komarom	L1870	M			50.9 / 130.0	40.9 / 63.2	29.4 / 59.4
Danube	Komarom/Komarno	L1475	M			20.3 / 57.0	7.0 / 14.0	
/Vah	Komarno	L1960	M			101.5 / 183.0		
Danube	Szob	L1962	M				16.8 / 39.0	10.5 / 24.0
Danube	Dunafoldvar	L1520	M			27.7 / 36.0	7.7 / 23.0	
/Sio	Szekszard-Palank	L1604	M			34.9 / 59.2	58.2 / 140.0	125.0 / 229.0
Danube	Hercegszanto	L1540	M			34.8 / 89.6	6.5 / 19.0	
/Drava	Ormoz	L1390	L	0.5 / 0.5		3.0 / 3.0	1.3 / 2.0	3.5 / 5.0
/Drava	Dravaszabolcs	L1610	M			24.6 / 49.5	5.7 / 17.7	
/Tisza/Sajo	Sajopuspoki	L1770	M			11.2 / 28.1	15.0 / 20.0	
/Tisza	Tiszasziget	L1700	M			12.5 / 36.8	8.7 / 37.0	
/Sava	Jesenice	L1330	R	57.0 / 57.0		130.0 / 130.0	89.0 / 120.0	145.0 / 160.0

Final class in accordance to Water Quality Classification for TNMN purposes

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- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
[1] mean annual value
[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
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Lindane

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L		0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
/Inn/Salzach	Laufen	L2160	L		0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
/Inn	Kirchdorf	L2150	M	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Jochenstein	L2130	M	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Jochenstein	L2220	M		0.050 0.050	0.050 0.050	0.100 0.100	0.059 0.100
Danube	Abwinden-Asten	L2200	R		0.050 0.050	0.050 0.050	0.100 0.100	0.059 0.100
Danube	Wien-Nussdorf	L2180	R			0.050 0.050	0.100 0.100	0.059 0.100
/Morava/Dyje	Pohansko	L2120	L		0.014 0.030	0.059 0.050	0.022 0.041	0.006 0.017
/Morava	Lanzhot	L2100	M		0.013 0.017	0.032 0.050	0.024 0.042	0.005 0.016
Danube	Wolfsthal	L2170	R		0.050 0.050	0.050 0.050	0.100 0.100	0.067 0.100
Danube	Bratislava	L1840	M	0.005 0.007	0.005 0.005	0.015 0.037	0.006 0.007	0.005 0.006
Danube	Medvedov/Medve	L1860	M	0.006 0.010	0.005 0.005	0.009 0.018	0.005 0.005	0.005 0.006
Danube	Medve/Medvedov	L1470	M		0.001 0.001	2.334 5.660	0.004 0.009	0.004 0.007
Danube	Komarno/Komarom	L1870	M	0.006 0.010	0.005 0.005	0.011 0.029	0.006 0.007	0.006 0.007
Danube	Komarom/Komarno	L1475	M		0.002 0.002	3.108 5.560	0.011 0.014	0.002 0.003
/Vah	Komarno	L1960	M	0.005 0.005	0.005 0.005	0.011 0.029	0.005 0.005	0.005 0.005
Danube	Szob	L1490	M		0.003 0.003	1.925 3.920	0.006 0.012	0.002 0.005
Danube	Dunafoldvar	L1520	M		0.007 0.012	2.376 4.750	0.005 0.013	0.003 0.006
/Sio	Szekszard-Palank	L1604	M		0.002 0.002	3.775 4.650	0.009 0.018	2.240 5.750
Danube	Hercegszanto	L1540	M		0.002 0.005	3.150 4.780	0.006 0.012	0.007 0.010
Danube	Batina	L1315	M			0.010 0.019	0.013 0.010	0.010 0.029
/Drava	Ormoz	L1390	L		0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
/Drava	Dravaszabolcs	L1610	M		0.002 0.002	2.475 4.350	0.005 0.010	0.002 0.004
Danube	Borovo	L1320	R					0.001 0.001
/Tisza/Sajo	Sajopuspoki	L1770	M	0.034 0.100	0.081 0.100	2.167 3.480	0.008 0.027	0.003 0.008
/Tisza	Tiszasziget	L1700	M		0.004 0.005	5.745 8.800	0.007 0.013	0.006 0.009
/Sava	Jesenice	L1330	R	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Bazias	L0020	L	0.003 0.004	0.024 0.039	0.040 0.126	0.076 0.320	0.029 0.040
Danube	Bazias	L0020	M	0.004 0.006	0.031 0.054	0.065 0.143	0.082 0.389	0.033 0.040
Danube	Bazias	L0020	R		0.013 0.023	0.037 0.126	0.067 0.272	0.028 0.040
Danube	Pristol/Novo Selo Harbour	L0090	L	0.004 0.004	0.037 0.102	0.077 0.242	0.111 0.362	0.032 0.040
Danube	Pristol/Novo Selo Harbour	L0090	M	0.011 0.020	0.089 0.209	0.064 0.120	0.277 0.404	0.029 0.046
Danube	Pristol/Novo Selo Harbour	L0090	R	0.005 0.006	0.051 0.146	0.071 0.179	0.151 0.444	0.028 0.040
Danube	Novo Selo Harbour/Pristol	L0730	L					0.002 0.003
Danube	Novo Selo Harbour/Pristol	L0730	M				0.004 0.005	0.005 0.015
Danube	Novo Selo Harbour/Pristol	L0730	R					0.002 0.004
Danube	us.Iskar-Bajkal	L0780	R				0.006 0.006	0.010 0.010
/Iskar	Orechovitza	L0930	M				0.006 0.006	0.010 0.010
Danube	Downstream Svishstov	L0810	R				0.002 0.002	0.010 0.010
/Jantra	Karantzi	L0990	M				0.002 0.002	0.010 0.010
Danube	us.Russe	L0820	R				0.002 0.002	0.010 0.010
/Russ.Lom	Basarbovo	L1010	M				0.002 0.002	0.010 0.010
Danube	us. Arges	L0240	L	0.004 0.004	0.033 0.068	0.067 0.202	0.131 0.442	0.023 0.040
Danube	us. Arges	L0240	M	0.004 0.004	0.071 0.164	0.037 0.118	0.140 0.522	0.022 0.040
Danube	us. Arges	L0240	R		0.037 0.103	0.037 0.121	0.190 0.532	0.056 0.176
/Arges	Conf.Danube	L0250	M	0.002 0.002	0.051 0.138	0.055 0.127	0.125 0.450	0.036 0.157
Danube	Chiciu/Silistra	L0280	L	0.004 0.006	0.064 0.092	0.048 0.122	0.223 0.702	0.044 0.164
Danube	Chiciu/Silistra	L0280	M	0.003 0.004	0.050 0.143	0.034 0.115	0.223 0.482	0.027 0.048
Danube	Chiciu/Silistra	L0280	R	0.003 0.004	0.048 0.090	0.032 0.118	0.148 0.389	0.033 0.064

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Silistra/Chiciu	L0850	L				0.002 / 0.002	0.010 / 0.010
Danube	Silistra/Chiciu	L0850	M				0.002 / 0.002	0.010 / 0.010
Danube	Silistra/Chiciu	L0850	R				0.002 / 0.002	0.010 / 0.010
/Siret	Conf.Danube Sendreni	L0380	M	0.002 / 0.002	0.119 / 0.047	0.054 / 0.133	0.063 / 0.315	0.020 / 0.040
/Prut	Lipcani	L2230	L			0.050 / 0.050	0.050 / 0.050	0.050 / 0.050
/Prut	Leuseni	L2250	M			0.050 / 0.050	0.050 / 0.050	0.050 / 0.050
/Prut	Conf.Danube-Giurgiulesti	L2270	L			0.050 / 0.050	0.050 / 0.050	0.050 / 0.050
/Prut	Conf.Danube Giurgiulesti	L0420	M		0.080 / 0.173	0.049 / 0.129	0.095 / 0.438	0.022 / 0.040
Danube	Reni-Chilia/Kilia arm	L0430	L	0.005 / 0.006	0.051 / 0.137	0.050 / 0.117	0.119 / 0.567	0.023 / 0.040
Danube	Reni-Chilia/Kilia arm	L0430	M	0.002 / 0.002	0.078 / 0.132	0.091 / 0.341	0.138 / 0.507	0.027 / 0.040
Danube	Reni-Chilia/Kilia arm	L0430	R	0.004 / 0.006	0.031 / 0.057	0.057 / 0.140	0.133 / 0.541	0.030 / 0.041
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.004 / 0.006	0.051 / 0.118	0.050 / 0.100	0.116 / 0.368	0.034 / 0.060
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.004 / 0.004	0.041 / 0.049	0.060 / 0.113	0.072 / 0.210	0.030 / 0.050
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.002 / 0.002	0.025 / 0.052	0.033 / 0.107	0.185 / 0.505	0.033 / 0.060
Danube	Sulina - Sulina arm	L0480	L		0.048 / 0.128	0.029 / 0.109	0.153 / 0.525	0.026 / 0.040
Danube	Sulina - Sulina arm	L0480	M	0.003 / 0.004	0.040 / 0.079	0.037 / 0.125	0.130 / 0.520	0.027 / 0.040
Danube	Sulina - Sulina arm	L0480	R		0.057 / 0.055	0.054 / 0.121	0.231 / 0.590	0.035 / 0.050
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L		0.042 / 0.085	0.053 / 0.136	0.144 / 0.380	0.038 / 0.066
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.006 / 0.008	0.035 / 0.058	0.056 / 0.146	0.166 / 0.446	0.133 / 0.531
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R		0.054 / 0.147	0.071 / 0.179	0.142 / 0.324	0.034 / 0.041

Final class in accordance to Water Quality Classification for TNMN purposes

class I
class II
class III
class IV
class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:
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- 90 %-ile if number of measurement was ≥ 11 in a year
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DDT

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L		0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020
/Inn/Salzach	Laufen	L2160	L		0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020
/Inn	Kirchdorf	L2150	M	0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020
Danube	Jochenstein	L2130	M	0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020	0.020 0.020
Danube	Jochenstein	L2220	M		0.010 0.010	0.010 0.010	0.050 0.050	0.036 0.050
Danube	Abwinden-Asten	L2200	R		0.010 0.010	0.010 0.010	0.050 0.050	0.036 0.050
Danube	Wien-Nussdorf	L2180	R		0.010 0.010	0.010 0.010	0.050 0.050	0.036 0.050
/Morava/Dyje	Pohansko	L2120	L		0.046 0.099	0.013 0.020	0.018 0.040	0.002 0.002
/Morava	Lanzhot	L2100	M		0.046 0.128	0.007 0.020	0.026 0.044	0.002 0.002
Danube	Wolfsthal	L2170	R		0.010 0.010	0.010 0.010	0.050 0.050	0.039 0.050
Danube	Bratislava	L1840	M	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Medvedov/Medve	L1860	M	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Medve/Medvedov	L1470	M			0.002 0.002	0.005 0.005	0.005 0.005
Danube	Komarno/Komarom	L1870	M	0.010 0.010	0.010 0.010	0.010 0.010	0.035 0.110	0.010 0.010
Danube	Komarom/Komarno	L1475	M			0.002 0.002	0.005 0.005	0.005 0.005
/Vah	Komarno	L1960	M	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
Danube	Szob	L1490	M			0.002 0.002	0.005 0.005	0.005 0.005
Danube	Dunafoldvar	L1520	M			0.008 0.030	0.005 0.005	0.006 0.005
/Sio	Szekszard-Palank	L1604	M			0.003 0.002	0.005 0.005	0.005 0.005
Danube	Hercegszanto	L1540	M			0.002 0.002	0.005 0.005	0.015 0.040
Danube	Batina	L1315	M			0.017 0.029	0.013 0.010	0.020 0.050
/Drava	Ormoz	L1390	L	0.003 0.003	0.003 0.003	0.003 0.003	0.003 0.003	0.003 0.003
/Drava	Dravaszabolcs	L1610	M			0.002 0.002	0.005 0.005	0.005 0.005
Danube	Borovo	L1320	R					0.001 0.001
/Tisza/Sajo	Sajopuspoki	L1770	M			0.002 0.002	0.005 0.005	0.005 0.005
/Tisza	Tiszasziget	L1700	M			0.003 0.002	0.005 0.005	0.005 0.005
/Sava	Jesenice	L1330	R	0.003 0.003	0.003 0.003	0.003 0.003	0.003 0.003	0.003 0.003
Danube	Bazias	L0020	L	0.002 0.002	0.066 0.149	0.070 0.186	0.039 0.122	0.004 0.010
Danube	Bazias	L0020	M	0.001 0.001	0.047 0.116	0.208 0.885	0.068 0.180	0.020 0.114
Danube	Bazias	L0020	R		0.032 0.085	0.054 0.102	0.062 0.172	0.008 0.040
Danube	Pristol/Novo Selo Harbour	L0090	L	0.010 0.018	0.103 0.269	0.136 0.295	0.111 0.408	0.008 0.030
Danube	Pristol/Novo Selo Harbour	L0090	M	0.012 0.022	0.069 0.101	0.258 0.775	0.253 0.740	0.010 0.040
Danube	Pristol/Novo Selo Harbour	L0090	R	0.009 0.016	0.107 0.229	0.140 0.464	0.249 0.982	0.006 0.024
Danube	Novo Selo Harbour/Pristol	L0730	L					0.001 0.001
Danube	Novo Selo Harbour/Pristol	L0730	M			0.063 0.071	0.010 0.010	0.001 0.001
Danube	Novo Selo Harbour/Pristol	L0730	R					0.001 0.001
Danube	us.Iskar-Bajkal	L0780	R				0.010 0.010	0.021 0.050
/Iskar	Orechovitza	L0930	M				0.011 0.012	0.010 0.010
Danube	Downstream Svishstov	L0810	R				0.012 0.012	0.025 0.100
/Jantra	Karantzi	L0990	M				0.010 0.010	0.010 0.010
Danube	us.Russe	L0820	R				0.011 0.012	0.014 0.030
/Russ.Lom	Basarbovo	L1010	M				0.018 0.026	0.019 0.070
Danube	us. Arges	L0240	L	0.003 0.004	0.081 0.160	0.196 0.516	0.280 1.652	0.005 0.013
Danube	us. Arges	L0240	M	0.002 0.002	0.180 1.119	0.094 0.403	0.217 0.899	0.011 0.052
Danube	us. Arges	L0240	R		0.206 0.938	0.107 0.486	0.201 0.822	0.038 0.205
/Arges	Conf.Danube	L0250	M	0.004 0.006	0.111 0.224	0.094 0.382	0.105 0.186	0.036 0.184
Danube	Chiciu/Silistra	L0280	L	0.005 0.008	0.236 0.687	0.052 0.242	0.267 0.915	0.030 0.230
Danube	Chiciu/Silistra	L0280	M	0.007 0.012	0.154 0.295	0.058 0.284	0.199 0.859	0.006 0.019
Danube	Chiciu/Silistra	L0280	R	0.010 0.018	0.102 0.236	0.057 0.261	0.192 0.740	0.029 0.086

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Silistra/Chiciu	L0850	L				0.010 0.010	0.018 0.060
Danube	Silistra/Chiciu	L0850	M			0.035 0.041	0.010 0.010	0.020 0.060
Danube	Silistra/Chiciu	L0850	R				0.010 0.010	0.018 0.070
/Siret	Conf.Danube Sendreni	L0380	M		0.158 0.852	0.067 0.291	0.416 1.322	0.024 0.100
/Prut	Lipcani	L2230	L			0.050 0.050	0.050 0.050	0.050 0.050
/Prut	Leuseni	L2250	M			0.050 0.050	0.050 0.050	0.050 0.050
/Prut	Conf.Danube-Giurgiulesti	L2270	L			0.050 0.050	0.050 0.050	0.050 0.050
/Prut	Conf.Danube Giurgiulesti	L0420	M		0.321 0.481	0.069 0.302	0.183 0.352	0.007 0.015
Danube	Reni-Chilia/Kilia arm	L0430	L	0.006 0.010	0.154 0.185	0.052 0.212	0.194 0.886	0.007 0.014
Danube	Reni-Chilia/Kilia arm	L0430	M	0.004 0.006	0.149 0.732	0.081 0.235	0.228 1.203	0.007 0.014
Danube	Reni-Chilia/Kilia arm	L0430	R	0.002 0.002	0.205 0.524	0.083 0.269	0.166 0.426	0.006 0.014
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.012 0.012	0.215 0.431	0.046 0.182	0.453 2.671	0.005 0.013
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.001 0.001	0.104 0.412	0.119 0.317	0.178 0.584	0.012 0.038
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.014 0.014	0.277 0.530	0.054 0.202	0.465 2.580	0.005 0.012
Danube	Sulina - Sulina arm	L0480	L		0.107 0.189	0.065 0.298	0.166 0.638	0.073 0.291
Danube	Sulina - Sulina arm	L0480	M	0.001 0.001	0.245 0.723	0.102 0.523	0.181 0.893	0.005 0.011
Danube	Sulina - Sulina arm	L0480	R		0.134 0.291	0.085 0.408	0.261 0.889	0.011 0.040
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L		0.229 0.201	0.053 0.228	0.272 1.178	0.009 0.031
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.004 0.004	0.161 0.462	0.048 0.182	0.389 1.556	0.014 0.033
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R		0.236 0.909	0.042 0.181	0.191 0.818	0.010 0.033

Final class in accordance to Water Quality Classification for TNMN purposes

(cyan)	class I
(green)	class II
(yellow)	class III
(orange)	class IV
(red)	class V

xx blue bold letters used if no. of measurements in location was lower than three

Note:

average[1]
testing value[2]

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[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
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Atrazine

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.010 0.010	0.013 0.020	0.010 0.010	0.012 0.020	0.010 0.010
/Inn/Salzach	Laufen	L2160	L	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010	0.010 0.010
/Inn	Kirchdorf	L2150	M	0.053 0.180		0.010 0.010	0.012 0.020	0.010 0.010
Danube	Jochenstein	L2130	M	0.015 0.020	0.014 0.020	0.012 0.020	0.018 0.029	0.013 0.020
Danube	Jochenstein	L2220	M		0.100 0.100	0.100 0.100	0.100 0.100	0.060 0.100
Danube	Abwinden-Asten	L2200	R		0.100 0.100	0.100 0.100	0.100 0.100	0.060 0.100
Danube	Wien-Nussdorf	L2180	R		0.100 0.100	0.100 0.100	0.100 0.100	0.060 0.100
/Morava/Dyje	Pohansko	L2120	L		0.133 0.300	0.200 0.390	0.129 0.145	0.100 0.100
/Morava	Lanzhot	L2100	M		0.116 0.195	0.275 0.930	0.104 0.100	0.100 0.100
Danube	Wolfsthal	L2170	R		0.100 0.100	0.100 0.100	0.100 0.100	0.060 0.100
Danube	Bratislava	L1840	M	0.073 0.050	0.050 0.050	0.050 0.060	0.053 0.050	0.050 0.050
Danube	Medvedov/Medve	L1860	M	0.050 0.050	0.051 0.050	0.050 0.050	0.055 0.070	0.050 0.050
Danube	Medve/Medvedov	L1470	M		0.055 0.090	0.008 0.023	0.025 0.064	0.041 0.066
Danube	Komarno/Komarom	L1870	M	0.065 0.060	0.053 0.050	0.050 0.050	0.050 0.050	0.050 0.050
Danube	Komarom/Komarno	L1475	M		0.030 0.040	0.018 0.061	0.059 0.074	0.035 0.051
/Vah	Komarno	L1960	M	0.080 0.160	0.050 0.050	0.050 0.050	0.063 0.100	0.050 0.050
Danube	Szob	L1490	M		0.100 0.180	0.018 0.023	0.013 0.026	0.041 0.071
Danube	Dunafoldvar	L1520	M		0.035 0.050	0.034 0.100	0.073 0.150	0.044 0.070
/Sio	Szekszard-Palank	L1604	M		0.310 0.320	0.137 0.224	2.000 5.600	0.186 0.274
Danube	Hercegszanto	L1540	M		0.298 0.500	0.017 0.022	0.122 0.320	0.041 0.071
/Drava	Ormoz	L1390	L	0.030 0.030	0.030 0.030	0.030 0.030	0.040 0.050	0.030 0.030
/Drava	Dravaszabolcs	L1610	M		0.020 0.020	0.008 0.018	0.233 0.234	0.049 0.094
/Tisza/Sajo	Sajopuspoki	L1770	M	0.00 0.00	1.87 10.00	0.07 0.20	0.05 0.14	0.14 0.29
/Tisza	Tiszasziget	L1700	M		0.054 0.055	0.020 0.048	0.412 0.550	0.103 0.189
/Sava	Jesenice	L1330	R	0.05 0.05	0.05 0.05	0.03 0.03	0.05 0.07	0.03 0.03
Danube	Bazias	L0020	L	0.060 0.060				0.060 0.060
Danube	Bazias	L0020	M	0.06 0.06				0.06 0.06
Danube	Bazias	L0020	R					0.060 0.060
Danube	Pristol/Novo Selo Harbour	L0090	L	0.06 0.06				0.06 0.06
Danube	Pristol/Novo Selo Harbour	L0090	M	0.060 0.060				0.060 0.060
Danube	Pristol/Novo Selo Harbour	L0090	R	0.06 0.06				0.06 0.06
Danube	Novo Selo Harbour/Pristol	L0730	L					0.102 0.210
Danube	Novo Selo Harbour/Pristol	L0730	M			0.73 1.55	0.21 0.33	0.10 0.22
Danube	Novo Selo Harbour/Pristol	L0730	R					0.106 0.215
Danube	us.Iskar-Bajkal	L0780	R				0.03 0.03	
/Iskar	Orechovitza	L0930	M				0.010 0.010	
Danube	Downstream Svishtov	L0810	R				0.09 0.09	0.17 0.24
/Jantra	Karantzi	L0990	M				0.035 0.040	0.100 0.100
Danube	us.Russe	L0820	R				0.15 0.19	0.20 0.42
/Russ.Lom	Basarbovo	L1010	M				0.146 0.210	0.188 0.580
Danube	us. Arges	L0240	L	0.060 0.060				0.060 0.060
Danube	us. Arges	L0240	M	0.060 0.060				0.060 0.060
Danube	us. Arges	L0240	R					0.060 0.060
/Arges	Conf.Danube	L0250	M	0.060 0.060				0.060 0.060
Danube	Chiciu/Silistra	L0280	L	0.060 0.060				0.060 0.060
Danube	Chiciu/Silistra	L0280	M	0.060 0.060				0.060 0.060
Danube	Chiciu/Silistra	L0280	R	0.060 0.060				0.060 0.060
Danube	Silistra/Chiciu	L0850	L				0.051 0.092	0.258 0.850
Danube	Silistra/Chiciu	L0850	M			1.207 2.500	0.051 0.096	0.336 0.810

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Silistra/Chiciu	L0850	R				0.051 0.098	0.248 0.760
/Siret	*Conf.Danube Sendreni*	L0380	M	0.060 0.060				0.060 0.060
/Prut	*Leuseni*	L2250	M			1.000 1.000	1.000 1.000	
/Prut	*Conf.Danube Giurgiulesti*	L0420	M	0.060 0.060				0.060 0.060
Danube	Reni-Chilia/Kilia arm	L0430	L	0.060 0.060				0.060 0.060
Danube	Reni-Chilia/Kilia arm	L0430	M	0.060 0.060				0.060 0.060
Danube	Reni-Chilia/Kilia arm	L0430	R	0.060 0.060				0.060 0.060
Danube	Vilkova-Chilia arm/Kilia arm	L0450	L	0.060 0.060				0.060 0.060
Danube	Vilkova-Chilia arm/Kilia arm	L0450	M	0.060 0.060				0.060 0.060
Danube	Vilkova-Chilia arm/Kilia arm	L0450	R	0.060 0.060				0.060 0.060
Danube	Sulina - Sulina arm	L0480	L	0.060 0.060	**0.060** **0.060**			0.060 0.060
Danube	Sulina - Sulina arm	L0480	M	0.060 0.060	**0.048** **0.048**			0.060 0.060
Danube	Sulina - Sulina arm	L0480	R	0.060 0.060	**0.036** **0.036**			0.060 0.060
Danube	Sf.Gheorghe-Gheorghe arm	L0490	L	0.060 0.060				0.060 0.060
Danube	Sf.Gheorghe-Gheorghe arm	L0490	M	0.060 0.060				0.060 0.060
Danube	Sf.Gheorghe-Gheorghe arm	L0490	R	0.060 0.060				0.060 0.060

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
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- class IV
- class V

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Note:

average[1]
testing value[2]

[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Trichloromethane

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.200 / 0.200	0.338 / 0.200	0.200 / 0.200	0.011 / 0.020	0.012 / 0.020
/Inn/Salzach	Laufen	L2160	L	0.200 / 0.200	0.200 / 0.200	0.200 / 0.200	0.013 / 0.010	0.010 / 0.010
/Inn	Kirchdorf	L2150	M	0.200 / 0.200	0.200 / 0.200	0.208 / 0.200	0.014 / 0.022	0.018 / 0.029
Danube	Jochenstein	L2130	M	0.200 / 0.200	0.200 / 0.200	0.200 / 0.200	0.014 / 0.018	0.032 / 0.100
Danube	Jochenstein	L2220	M		0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Abwinden-Asten	L2200	R		0.108 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Wien-Nussdorf	L2180	R		0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
/Morava/Dyje	Pohansko	L2120	L		0.067 / 0.183	0.114 / 0.290	0.151 / 0.290	0.085 / 0.100
/Morava	Lanzhot	L2100	M		0.907 / 3.360	0.562 / 0.200	0.151 / 0.290	0.079 / 0.100
Danube	Wolfsthal	L2170	R		0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Bratislava	L1840	M	2.125 / 3.630	70.417 / 189.100	2.625 / 9.000	0.500 / 0.500	0.575 / 0.800
Danube	Medvedov/Medve	L1860	M	2.383 / 3.160	1.833 / 2.000	1.125 / 2.000	0.500 / 0.500	0.550 / 0.700
Danube	Medve/Medvedov	L1470	M			0.138 / 0.380	0.100 / 0.100	0.133 / 0.200
Danube	Komarno/Komarom	L1870	M	5.033 / 20.110	1.167 / 1.850	1.000 / 2.000	11.875 / 46.000	1.475 / 4.400
Danube	Komarom/Komarno	L1475	M			0.359 / 0.400	0.160 / 0.500	0.192 / 0.290
/Vah	Komarno	L1960	M	5.275 / 10.700	30.750 / 113.000	0.625 / 1.000	0.500 / 0.500	0.500 / 0.500
Danube	Szob	L1490	M			0.171 / 0.300	0.145 / 0.300	0.200 / 0.400
Danube	Dunafoldvar	L1520	M			0.233 / 0.760	0.391 / 0.700	0.325 / 0.670
/Sio	Szekszard-Palank	L1604	M			0.308 / 0.490	0.275 / 0.600	0.367 / 0.590
Danube	Hercegszanto	L1540	M			0.383 / 1.070	0.364 / 0.700	0.342 / 0.480
/Drava	Ormoz	L1390	L				**1.000 / 1.000**	3.000 / 3.000
/Drava	Dravaszabolcs	L1610	M			0.246 / 0.580	0.317 / 0.760	0.192 / 0.400
/Tisza/Sajo	Sajopuspoki	L1770	M	1.800 / 5.000	1.520 / 3.500	0.413 / 0.920	1.067 / 0.650	0.431 / 1.000
/Tisza	Tiszasziget	L1700	L					1.000 / 1.000
/Tisza	Tiszasziget	L1700	M			0.288 / 0.590	0.345 / 0.400	0.488 / 1.000
/Tisza	Tiszasziget	L1700	R					1.000 / 1.000
/Sava	Jesenice	L1330	R				**3.000 / 3.000**	1.000 / 1.000
Danube	Novo Selo Harbour/Pristol	L0730	L					0.020 / 0.020
Danube	Novo Selo Harbour/Pristol	L0730	M					0.020 / 0.020
Danube	Novo Selo Harbour/Pristol	L0730	R					0.020 / 0.020
Danube	Silistra/Chiciu	L0850	L				0.020 / 0.020	
Danube	Silistra/Chiciu	L0850	M				0.020 / 0.020	
Danube	Silistra/Chiciu	L0850	R				0.020 / 0.020	

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- class IV
- class V

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average[1]
testing value[2]

Note:
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[2] testing value, which represents:

- 90 %-ile if number of measurement was ≥ 11 in a year
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Tetrachloromethane

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.011 0.010	0.200 0.200	0.200 0.200	0.010 0.010	0.010 0.010
/Inn/Salzach	Laufen	L2160	L	0.010 0.010	0.200 0.200	0.200 0.200	0.010 0.010	0.010 0.010
/Inn	Kirchdorf	L2150	M	0.010 0.010	0.200 0.200	0.200 0.200	0.010 0.010	0.013 0.020
Danube	Jochenstein	L2130	M	0.010 0.010	0.200 0.200	0.200 0.200	0.010 0.010	0.020 0.100
Danube	Jochenstein	L2220	M			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Abwinden-Asten	L2200	R			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Wien-Nussdorf	L2180	R			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
/Morava/Dyje	Pohansko	L2120	L			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
/Morava	Lanzhot	L2100	M			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Wolfsthal	L2170	R			0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Bratislava	L1840	M	0.100 0.100	0.175 0.190	0.100 0.100	0.125 0.200	0.100 0.100
Danube	Medvedov/Medve	L1860	M	0.100 0.100	0.100 0.100	0.100 0.100	0.125 0.200	0.100 0.100
Danube	Medve/Medvedov	L1470	M			0.221 0.470	0.109 0.100	0.108 0.100
Danube	Komarno/Komarom	L1870	M	0.100 0.100	0.100 0.100	0.100 0.100	0.250 0.600	0.100 0.100
Danube	Komarom/Komarno	L1475	M			0.117 0.280	0.255 0.200	0.175 0.190
/Vah	Komarno	L1960	M	0.100 0.100	0.100 0.100	0.100 0.100	0.125 0.200	0.100 0.100
Danube	Szob	L1490	M			0.121 0.280	0.127 0.200	0.167 0.200
Danube	Dunafoldvar	L1520	M			0.083 0.095	0.255 0.600	0.117 0.190
/Sio	Szekszard-Palank	L1604	M			0.271 0.400	0.375 1.100	1.633 0.290
Danube	Hercegszanto	L1540	M			0.104 0.280	0.173 0.200	0.100 0.100
/Drava	Ormoz	L1390	L				1.000 1.000	1.000 1.000
/Drava	Dravaszabolcs	L1610	M			0.208 0.500	0.183 0.400	0.117 0.190
/Tisza/Sajo	Sajopuspoki	L1770	M	1.433 2.700	0.775 1.000	0.383 0.800	0.142 0.280	0.363 1.000
/Tisza	Tiszasziget	L1700	L					1.000 1.000
/Tisza	Tiszasziget	L1700	M			0.150 0.400	0.173 0.300	0.413 1.000
/Tisza	Tiszasziget	L1700	R					1.000 1.000
/Sava	Jesenice	L1330	R				1.000 1.000	1.000 1.000
Danube	Novo Selo Harbour/Pristol	L0730	L					0.020 0.020
Danube	Novo Selo Harbour/Pristol	L0730	M					0.020 0.020
Danube	Novo Selo Harbour/Pristol	L0730	R					0.020 0.020
Danube	Silistra/Chiciu	L0850	L				0.020 0.020	
Danube	Silistra/Chiciu	L0850	M				0.020 0.020	
Danube	Silistra/Chiciu	L0850	R				0.020 0.020	

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testing value[2]

Note:
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Trichloroethylene

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.100 / 0.100	0.200 / 0.200	0.200 / 0.200	0.016 / 0.060	0.010 / 0.010
/Inn/Salzach	*Laufen*	L2160	L	0.100 / 0.100	0.200 / 0.200	0.200 / 0.200	0.010 / 0.010	0.010 / 0.010
/Inn	*Kirchdorf*	L2150	M	0.100 / 0.100	0.200 / 0.200	0.200 / 0.200	0.011 / 0.010	0.010 / 0.010
Danube	Jochenstein	L2130	M	0.100 / 0.100	0.200 / 0.200	0.200 / 0.200	0.028 / 0.058	0.029 / 0.080
Danube	Jochenstein	L2220	M			0.100 / 0.100	0.050 / 0.050	0.100 / 0.100
Danube	Abwinden-Asten	L2200	R			0.100 / 0.100	0.050 / 0.050	0.100 / 0.100
Danube	Wien-Nussdorf	L2180	R			0.100 / 0.100	0.050 / 0.050	0.100 / 0.100
/Morava/Dyje	*Pohansko*	L2120	L			0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
/Morava	*Lanzhot*	L2100	M			0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Wolfsthal	L2170	R			0.100 / 0.100	0.053 / 0.060	0.100 / 0.100
Danube	Bratislava	L1840	M	0.100 / 0.100	0.100 / 0.100	0.300 / 0.900	0.100 / 0.100	0.100 / 0.100
Danube	Medvedov/Medve	L1860	M	0.583 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Medve/Medvedov	L1470	M			0.063 / 0.050	0.109 / 0.100	0.100 / 0.100
Danube	Komarno/Komarom	L1870	M	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Komarom/Komarno	L1475	M			0.188 / 0.050	0.100 / 0.100	0.100 / 0.100
/Vah	*Komarno*	L1960	M	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100	0.100 / 0.100
Danube	Szob	L1490	M			0.050 / 0.050	0.127 / 0.100	0.100 / 0.100
Danube	Dunafoldvar	L1520	M			0.067 / 0.095	0.109 / 0.100	0.108 / 0.100
/Sio	*Szekszard-Palank*	L1604	M			0.050 / 0.050	0.100 / 0.100	0.125 / 0.100
Danube	Hercegszanto	L1540	M			0.067 / 0.095	0.164 / 0.100	0.100 / 0.100
/Drava	*Ormoz*	L1390	L				**1.000 / 1.000**	**1.000 / 1.000**
/Drava	*Dravaszabolcs*	L1610	M			0.071 / 0.050	0.100 / 0.100	0.100 / 0.100
/Tisza/Sajo	*Sajopuspoki*	L1770	M	1.067 / 3.000	1.000 / 1.000	0.147 / 0.340	0.100 / 0.100	0.406 / 1.000
/Tisza	*Tiszasziget*	L1700	L					1.000 / 1.000
/Tisza	*Tiszasziget*	L1700	M			0.050 / 0.050	0.100 / 0.100	0.350 / 1.000
/Tisza	*Tiszasziget*	L1700	R					1.000 / 1.000
/Sava	*Jesenice*	L1330	R				**1.000 / 1.000**	**1.000 / 1.000**
Danube	Silistra/Chiciu	L0850	L				**0.020 / 0.020**	
Danube	Silistra/Chiciu	L0850	M				**0.020 / 0.020**	
Danube	Silistra/Chiciu	L0850	R				**0.020 / 0.020**	

Final class in accordance to Water Quality Classification for TNMN purposes

- class I
- class II
- class III
- class IV
- class V

xx blue bold letters used if no. of measurements in location was lower than three

average[1]
testing value[2]

Note:

[1] mean annual value
[2] testing value, which represents:

- *90 %-ile if number of measurement was ≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Tetrachloroethylene

River	Location	Code	Loc.	1996	1997	1998	1999	2000
Danube	Neu-Ulm	L2140	L	0.100 0.100	0.200 0.200	0.342 0.830	0.046 0.090	0.070 0.108
/Inn/Salzach	Laufen	L2160	L	0.100 0.100	0.214 0.200	0.200 0.200	0.018 0.020	0.014 0.030
/Inn	Kirchdorf	L2150	M	0.100 0.100	0.200 0.200	0.200 0.200	0.030 0.056	0.035 0.060
Danube	Jochenstein	L2130	M	0.118 0.200	0.207 0.200	0.200 0.200	0.050 0.090	0.092 0.200
Danube	Jochenstein	L2220	M		0.125 0.200	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Abwinden-Asten	L2200	R		0.117 0.190	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Wien-Nussdorf	L2180	R		0.100 0.100	0.100 0.100	0.100 0.100	0.108 0.100
/Morava/Dyje	Pohansko	L2120	L		0.117 0.190	0.100 0.100	0.100 0.100	0.108 0.100
/Morava	Lanzhot	L2100	M		0.142 0.200	0.133 0.200	0.117 0.100	0.108 0.100
Danube	Wolfsthal	L2170	R		0.100 0.100	0.100 0.100	0.100 0.100	0.100 0.100
Danube	Bratislava	L1840	M	0.150 0.100	0.100 0.100	0.325 1.000	7.800 18.000	0.575 2.000
Danube	Medvedov/Medve	L1860	M	0.233 0.460	0.100 0.100	2.800 10.000	1.825 7.000	0.550 1.700
Danube	Medve/Medvedov	L1470	M			0.050 0.050	0.100 0.100	0.100 0.100
Danube	Komarno/Komarom	L1870	M	0.100 0.100	0.100 0.100	0.575 2.000	1.393 4.000	0.550 1.800
Danube	Komarom/Komarno	L1475	M			0.050 0.050	0.100 0.100	0.100 0.100
/Vah	Komarno	L1960	M	0.100 0.100	0.100 0.100	0.100 0.100	0.775 1.000	0.900 3.100
Danube	Szob	L1490	M			0.050 0.050	0.100 0.100	0.100 0.100
Danube	Dunafoldvar	L1520	M			0.054 0.050	0.100 0.100	0.100 0.100
/Sio	Szekszard-Palank	L1604	M			0.054 0.050	0.100 0.100	0.100 0.100
Danube	Hercegszanto	L1540	M			0.054 0.050	0.100 0.100	0.100 0.100
/Drava	Ormoz	L1390	L				1.000 1.000	1.000 1.000
/Drava	Dravaszabolcs	L1610	M			0.050 0.050	0.100 0.100	0.100 0.100
/Tisza/Sajo	Sajopuspoki	L1770	M	1.034 3.000	1.750 4.000	0.160 0.340	0.100 0.100	0.325 1.000
/Tisza	Tiszasziget	L1700	L					1.000 1.000
/Tisza	Tiszasziget	L1700	M			0.050 0.050	0.100 0.100	0.325 1.000
/Tisza	Tiszasziget	L1700	R					1.000 1.000
/Sava	Jesenice	L1330	R				1.000 1.000	1.000 1.000
Danube	Silistra/Chiciu	L0850	L				0.020 0.020	
Danube	Silistra/Chiciu	L0850	M				0.020 0.020	
Danube	Silistra/Chiciu	L0850	R				0.020 0.020	

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average[1]
testing value[2]

Note:
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- *90 %-ile if number of measurement was≥ 11 in a year*
- *maximum value, if number of measurements was < 11 in a year*

blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

Saprobic index of macrozoobenthos

River	Location	Code	Loc.	1996	1997	1998	1999	2000
/Inn/Salzach	Laufen	L2160	L			2.12 / 2.12	2.03 / 2.03	2.23 / 2.25
/Inn	Kirchdorf	L2150	M			1.86 / 1.86	**1.77 / 1.77**	1.85 / 1.85
Danube	Jochenstein	L2130	M			2.23 / 2.26	2.24 / 2.27	2.18 / 2.19
/Morava/Dyje	Pohansko	L2120	L		2.30 / 2.40	2.10 / 2.20	2.05 / 2.13	2.09 / 2.16
/Morava	Lanzhot	L2100	M		2.28 / 2.71	2.24 / 2.30	2.18 / 2.23	2.13 / 2.15
Danube	Bratislava	L1840	M		2.03 / 2.08	2.04 / 2.09	2.29 / 2.58	1.90 / 1.98
Danube	Medvedov/Medve	L1860	M		2.10 / 2.12	2.09 / 2.12	2.13 / 2.18	1.96 / 1.99
Danube	Medve/Medvedov	L1470	M			2.19 / 2.20		2.10 / 2.10
Danube	Komarno/Komarom	L1870	M		2.11 / 2.11	2.12 / 2.14	2.18 / 2.44	2.03 / 2.11
Danube	Komarom/Komarno	L1475	M			2.25 / 2.25		2.10 / 2.10
/Vah	Komarno	L1960	M		2.53 / 2.70	2.45 / 2.70	2.39 / 2.42	2.19 / 2.26
Danube	Szob	L1490	L			2.25 / 2.25		
Danube	Szob	L1490	M					2.15 / 2.20
Danube	Dunafoldvar	L1520	M					2.15 / 2.20
/Sio	Szekszard-Palank	L1604	M					2.25 / 2.30
Danube	Hercegszanto	L1540	M					2.20 / 2.20
/Drava	Ormoz	L1390	L			2.30 / 2.34	2.29 / 2.35	2.44 / 2.52
/Drava	Dravaszabolcs	L1610	M					2.20 / 2.20
/Tisza/Sajo	Sajopuspoki	L1770	M					2.15 / 2.20
/Tisza	Tiszasziget	L1700	M					2.10 / 2.10
/Sava	Jesenice	L1330	R			2.40 / 2.57	2.20 / 2.32	2.23 / 2.36
/Sava	Jesenice	L1220	L				2.48 / 2.50	2.22 / 2.24
/Sava	Jesenice	L1220	R		2.55 / 2.60	2.70 / 2.80		
/Sava	us.Una Jasenovac	L1150	L		2.63 / 2.70	2.40 / 2.40	2.50 / 2.50	2.03 / 2.03
/Sava	ds.Zupanja	L1060	M		3.10 / 3.70	2.90 / 2.90	2.60 / 2.60	
/Sava	ds.Zupanja	L1060	R					2.34 / 2.34

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average[1]
testing value[2]

Note:
[1] mean annual value
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- *90 %-ile if number of measurement was≥ 11 in a year*
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blank fields mean that no measurements were done in the year
values without indication of water quality class are given if limit of detection of measurement was higher than limit value for class II

UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation
in the Danube River Basin

Development of a methodological concept for assessment of environment stress and impacts as a basis for preparation of a computer-based application for stress-impact analysis

Project Component 2.2: Development of operational tools for
monitoring, laboratory and information management with
particular attention to nutrients and toxic substances

October 31, 2003

Prepared by: Rodeco Consulting GmbH

Author: Jan Dogterom

Table of contents

Abbreviations
Executive summary

Abbreviations

TNMN   Trans-National Monitoring Network
EMIS   Emission Sources Expert Group
ICPDR   International Commission for the Protection of the Danube River
DBAM   Danube Basin Alarm Model
DWQM Danube Water Quality Model

Development of a methodological concept for assessment of environment stress and impacts as a basis
for preparation of a computer-based application for stress-impact analysis

VI – 3

Executive Summary

In this activity a concept for a computer based application was developed assessing the relation between a pressure (the emission of a pollutant by a point source) and the downstream increase of the concentration of a pollutant ("state"). For this concept the use of existing databases (EMIS, TNMN) and existing models or modules from these models (MONERIS, DBAM, DWQM) was considered. Assessing different conceptual choices using the abovementioned models/modules three different functionalities were defined:

Detection of pressure based on observed concentration increase (accidental pollution pressures)

This application would consist of an "inverse DBAM" model. In its simplest form, the application could be based on a large database of computed pollutant clouds C(t) by DBAM, for different spill and observation positions, under different hydrological conditions. By comparing the observed cloud of pollutants with the database of clouds, given the actual hydrologic conditions, potential spill sites can be observed. Under the assumption that the removal rate of the pollutant is known, the spill mass can be back-computed.

Detection of pressure based on observed concentration increase (regular pollution pressures)

The application would start from an observed trend-wise increase of the concentration of a given substance at a given location from one year to another. Upstream point sources which show a corresponding increase of their emissions could be detected and listed. The decay rate of the substance in question could be taken into account to eliminate pollution sources too far away for their emitted pollutants to reach the observation point.

Effects of pollution reduction measures (only regular pollution pressures)

This application could consist of an application like the present DBAM, with some modifications: a continuous spill should be modelled instead of an accidental spill, average hydrological conditions should be used rather than actual conditions. To keep things simple, the application should include only one particular point source for which reduction measures need to be analysed. The background pollution from the other point sources and from diffuse sources needs to be back-computed for any selected observation location. The computed concentration from the point source in question before the reduction is subtracted from the present concentration at the observation point: the difference is the background concentration. The total concentration after reduction is obtained by adding the computed concentration from the point source in question after the reduction to the background concentration.

From assessment of practical implications of the three proposed functionalities it was clear, that the development of the computer based application for stress-impact analysis, which can calculate a quantitative relation between a point source and downstream changes in concentration levels or vice versa, will require a major investment in model/software development.

Therefore, a simpler practical concept was proposed as an alternative solution. In this case, the data of the TNMN would be the starting point for further analysis. If for a pollutant a significant concentration increase is observed during, e.g., 23 months, analysis of more upstream stations should indicate between which two stations the increase has started. In that stretch of the river the discharge should occur. At that point, a link with the EMIS database should be made to identify the point source.

Such a solution would require a proper coverage by the TNMN, in particular at the discharge of major tributaries and small tributaries with relevant point sources. A direct link with the EMIS database can be made through the geographical codes in both databases. Results should be presented in GIS. This concept would require adjustments in the TNMN as well as the development of a link between TNMN and EMIS based on GIS.

Development of a methodological concept for assessment of environment stress and impacts as a basis
for preparation of a computer-based application for stress-impact analysis

VI – 5

1. The problem

The initial idea of this activity was to develop a concept for a computer based application to analyse the relation between upstream pressures (emissions) and downstream impacts, based on the EMIS and TNMN databases. In the initial approach, impacts were defined as changes in the water quality or ecosystems. At the start of this activity, the consultant has defined the problem more precise in consultation with the experts of the combined MLIM and EMIS working groups (see Inception Report, 12 December 2002, and minutes of the MLIM/EMIS working group meeting on 3 February).

Change of instream water quality is usually defined as change in "state"; ecosystem change is usually defined as "impact", the loss of a function (UNECE: Guidelines on Monitoring and Assessment of Transboundary Waters, pp 22-23). The analysis of a relation between pressures and impacts, in casu ecosystem change, is very complicated. Many variables are included: water quality, water flow, wetland management, river continuity, reduction of flood plains, shipping, fisherie s etc).

Based on this clarification, it was agreed, that in this activity a concept for a computer based application will be developed to assess the relation between a pressure: the emission of a pollutant (nutrients and toxic compounds) by a point source and the downstream increase of the concentration of a pollutant ("state").

The application should enable to calculate and visualise the quantitative relation between the location (river kilometre, GIS/map based) of a point source, the discharge load of a pollutant from this source ("pressure") and the distance over which a significant effect on concentration of the pollutant ("state") can still be expected. The application likewise should enable to trace back a point source based on the elevated pollutant concentrations measured downstream, in particular in transboundary river stretches. The concept should include the possibility of assessing the effects of pollution reduction measures. The use of existing databases (EMIS, TNMN) and existing models or modules from these models (MONERIS, DBAM, DWQM) is highly preferred.

2. The options

The basic idea for the application is to combine a data base of pressures/point sources/discharge loads (EMIS) with a model: (1) to calculate downstream changes in pollutant concentrations ("state") and (2) vice versa: to locate a point source upstream, based on real time measurements of increased pollutant concentrations (TNMN) downstream. The output of the application should be GIS based and visualise on a map the relation between locations of point sources of nutrients and toxic compounds and concentration levels downstream. It should be possible also to calculate the effects of pollution reduction measures.

The options of using the existing database on pressures (EMIS) or a model to calculate pressures (MONERIS), and to combine this with (modules of) existing models to calculate concentrations (MONERIS, DBAM, DWQM), were analysed. The features of these instruments are therefore briefly summarised and a conceptual choice is motivated subsequently.

2.1 EMIS

EMIS is a database (Excel spreadsheet) of point sources in the Danube Basin. It contains the data on discharge loads of COD, NH4-N, NO2-N, NO3-N, total-N, PO4-P and total-P from about 500 municipal and 220 industrial point sources in tonnes per year. The database is still under construction. Data on other compounds of the Danube list of priority substances need to be included. Some countries have to submit the data yet. Data on agricultural point sources is being collected. The database is in a continuous process of updating. Discharge points are indicated with a unique AVcode, the name of the point source and the geographical coordinates. The database can be easily used in combination with any model.

2.2 MONERIS

MONERIS is developed as a model to calculate nutrient emissions from point and non-point sources and to estimate nutrient loads at specific monitoring stations, based on the sum of all inputs from diffuse and point sources, taking retention in different spheres into account.

The application targets questions in which diffuse and distributed pollution sources play a crucial role. Geographically, the Danube catchment is subdivided in about 380 sub-catchments (see Figure 1). These form the basis of the calculations. It should be noted that information about individual point sources is not used directly: they are lumped per sub-catchment. The time scale of the computations is large: the solution represents the average conditions during a period of about 5 years. The application is set up in ArcView and Excell, and is intended for expert users.
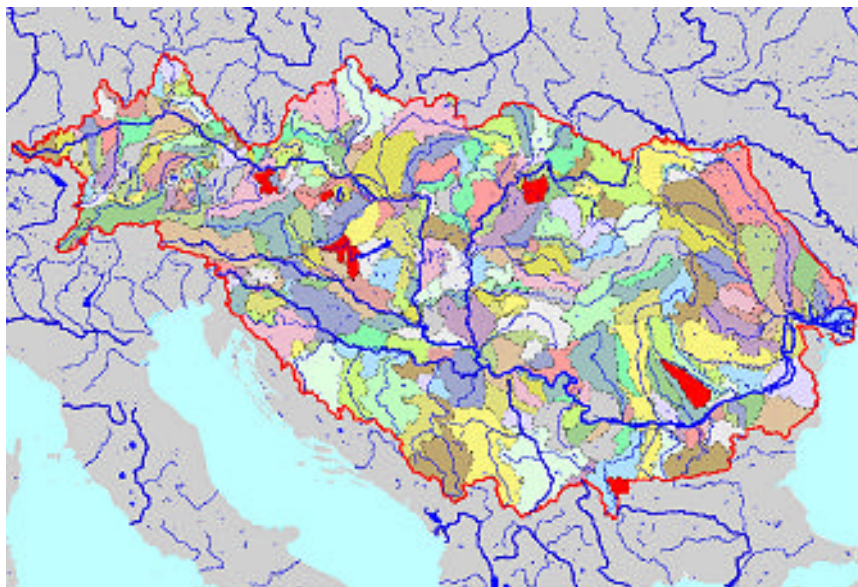

Figure 1: Subcatchments in Moneris

2.3 DBAM

The Danube Basin Alarm Model (DBAM) was designed to support decision-making in relation to accidental spills with a probable trans-boundary impact (like the January 2000 Baia Mare spill). The model provides forecasts of the travel time and the expected peak concentrations in the cloud of pollutants during its travel down the river. The DBAM was designed for use in operational conditions, to provide a fast and first order assessment of the effects of a spill. It uses limited and readily available input data. For reasons of computational speed and accuracy, the model uses an analytical technique to solve the governing mathematical advection- diffusion equation. The DBAM model is operational in 11 Danube countries. An evaluation of its accuracy has been carried out on the basis of data collected during the Baia Mare Spill. At present, the ICPDR is considering a full-scale calibration of the model. The model operates on short time scales (from hours to several weeks). The schematisation includes the Danube itself and a significant number of trans-boundary tributaries (see Figure 2).
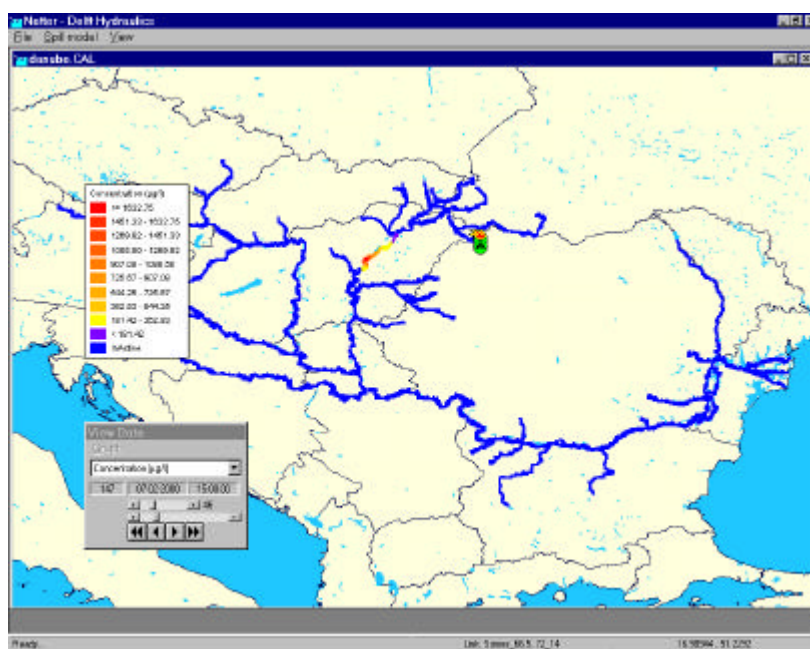
Figure 2: DBAM-schematisation

2.4   DWQM

DWQM is developed as a model to calculate the transport and transformation and retention processes of nutrients in the Danube river and its main tributaries.

The first version of the model was developed in 1998-1999 in the framework of the first Danube GEF project. The gaps in knowledge and data identified in this project are presently being addressed by the daNUbs project (EU 5th Framework Programme). This will lead to a new DWQM (to be finished in June 2003), which operates in conjunction with MONERIS. The specific tasks of the DWQM are: (a) to allow the modelling of nutrient concentrations on time scales of days over periods of several years, (b) to allow a distinction of the different nutrient species, and (c) to allow the analysis of retention processes at river anomalies (Iron Gates, Gabcikovo). Like the DBAM, the DWQM is mathematically based on the advection-diffusion equation. This time however, the solution technique is numerical, and the representation of transformation and retention processes is much more elaborate. The schematisation includes the Danube itself and its major tributaries (see Figure 3). The DWQM is consists of an application of the generic river modelling software package SOBEK, combined with a dedicated pre-processing programme written in Fortran. The application is intended for expert users.

Figure 3: DWQM-schematisation

The selection of the most suitable database(s) and model(s) to be a starting point for the development of the application, will be discussed below.

3. The conceptual choice

The selection of the appropriate concepts and the databases and models to be used as a starting point is based on a further analysis of the questions to be answered.

First, we observe that the focus is on individual point sources. This immediately leads to the conclusion that the use of MONERIS is not very logical, since individual point sources are not represented within MONERIS. The concept of DBAM and DWQM does allow the analysis of individual point sources, as long as they are situated on the river branches included in their respective schematisations.

A second observation is that both accidental and continuous pollution sources are within the scope of the application to be defined. Therefore, both DBAM and DWQM could form a basis.

A third observation is that the application to be defined is intended for operational use. This makes the DBAM a much more suitable starting point than the DWQM. The latter requires too much and too complex input data.

Detection of pressures based on observed concentration increase (both regular and accidental pollution pressures)

For both regular and accidental pollution, this functionality is possible, but not yet a functionality of DBAM or DWQM. The technique presumes the accurate detection of the C(t) profile in the field. A kind of "inverse DBAM" application could be set up based on the existing input data and concepts of the DBAM. Such an application can indicate potential spill sites and spill masses, as long as these are situated on the modelled river network. The data needs in regard to the emissions database (EMIS) are very strict, and may determine the feasibility.

Development of a methodological concept for assessment of environment stress and impacts as a basis
for preparation of a computer-based application for stress-impact analysis

VI – 9

Effects of pollution reduction measures (only regular pollution pressures)

This question can best be addressed by a very much simplified DWQM application, which looks a lot like DBAM. The application will preferably only include one particular point source for which reduction measures need to be analysed. The background pollution (from the other point sources and from diffuse sources) should not be explicitly computed (like MONERIS-DWQM), nor be neglected (like DBAM) but should be back-computed from the existing situation.

Summarising, the following choice is recommended:

The computer based application should combine the EMIS database with a model, which could basically be a variant and an extension of the DBAM. EMIS should be completed and contain the emission loads of all substances on the Danube Priority List. Point sources in EMIS are already indicated by river kilometre. Adjustment/extension of DBAM should result in the possibility to calculate the relation between the location of a discharge and elevated concentrations downstream, both in case of accidental spills and structural upward trends.

4. Technical approach

In line with the conceptual choices discussed above, three different functionalities are defined.

Detection of pressure based on observed concentration increase (accidental pollution pressures)

This application would consist of an "inverse DBAM" model. In its simplest form, the application could be based on a large database of computed pollutant clouds C(t) by DBAM, for different spill and observation positions, under different hydrological conditions. By comparing the observed cloud of pollutants with the database of clouds, given the actual hydrologic conditions, potential spill sites can be observed. Under the assumption that the removal rate of the pollutant is known, the spill mass can be back-computed.

There are probably more sophisticated techniques than the one described above. These should be identified at a later stage.

It should be pointed out that this application is conceptually complex. At this point it is not known if experience exists with a similar application elsewhere in the world.

Detection of pressure based on observed concentration increase (regular pollution pressures)

The application would start from an observed trend-wise increase of the concentration of a given substance at a given location from one year to another. Upstream point sources which show a corresponding increase of their emissions could be detected and listed. The decay rate of the substance in question could be taken into account to eliminate pollution sources too far away for their emitted pollutants to reach the observation point. Please note that this functionality presumes the existence of very accurate emissions data.

Effects of pollution reduction measures (only regular pollution pressures)

This application could consist of an application like the present DBAM, with some modifications: a continuous spill should be modelled in stead of an accidental spill, average hydrological conditions should be used rather than actual conditions. To keep things simple, the application should include only one particular point source for which reduction measures need to be analysed (although the concept allows for multiple sources). The background pollution from the other point sources and from

diffuse sources needs to be back-computed for any selected observation location. The computed concentration from the point source in question before the reduction is subtracted from the present concentration at the observation point: the difference is the background concentration. The total concentration after reduction is obtained by adding the computed concentration from the point source in question after the reduction to the background concentration.

4.1   Data requirements

EMIS: the database should be complete (river kilometre indication, loads per point source, all compounds of Danube Priority List included) and up to date (each year updated). The recently completed inventories of sites of high risk for accidental pollution should somehow be included.

For regular pollution issues, sufficient information should be available about the average concentrations of target substances at target stations as well as about the related trends. This information is supposed to come from TNMN. The coverage of TNMN (locations, substances, frequency) is therefore a decisive factor.

For accidental pollution issues measurements should be frequent enough to "capture" the shape of a clouds of pollutants. Otherwise, the possibility to trace back the pollution source is compromised.

For the detection of regular pollution pressures responsible for an upward concentration trend downstream, detailed EMIS data should be available. To support this functionality, yearly versions of EMIS should be issued on a similar time scale as TNMN (1-2 years time lag), with sufficient accuracy to detect emission changes on a yearly time scale. This may not be feasible.

5. The limits of the application

The application will not be able to:

- Assess impacts on the river system; impact is defined as loss of function (ecosystem, drinking water supply etc);

- Address pressures located on other river branches than those explicitly included in the model application.

6. Alternative solution

From the above analysis it is clear, that the development of the computer based application for stress-impact analysis, which can calculate a quantitative relation between a point source and downstream changes in concentration levels or vice versa, will require a major investment in model/soft ware development. It is not known whether such an application exists in any other river basin.

It should be considered, whether a more simple solution can provide the information needed. The basic question is to locate an increased discharge upstream, based on observed concentration increases downstream. A more simple solution would be possible if it is acceptable, that the relation is established only in a qualitative way.

In this case, the data of the TNMN is the starting point for further analysis. If for a pollutant a significant concentration increase is observed during for example 2-3 months, analysis of more upstream stations should indicate between which 2 stations the increase has started. In that stretch of the river the discharge should occur. This could be the point source or a tributary. In the latter case, the analysis should be repeated at the tributary etc. At that point, a link with the EMIS database should be made to identify the point source.

Such a solution would require a proper coverage by the TNMN, in particular at the discharge of major tributaries and small tributaries with relevant point sources. A direct link with the EMIS database can be made through the geographical codes (river kilometer !!) in both databases.. Results should be presented in GIS.

There is no doubt, that this solution is feasible. It may require adjustments in the TNMN. It will require the development of a link between TNMN and EMIS based on GIS.