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

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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.

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Table of contents

Preface
Abbreviations, Acronyms, and Definitions
Executive summary

References

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 (Ptot) 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 emissions 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_{tot} (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_{tot} 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_{ot}, 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.

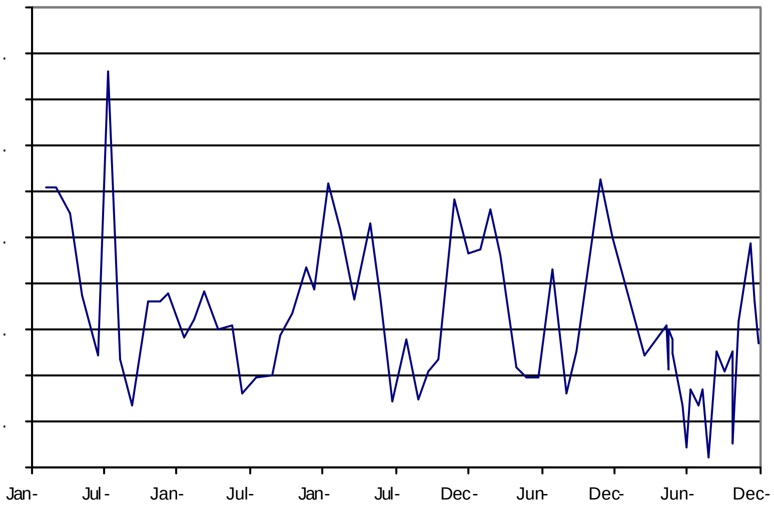
2.5 Comparison of proposed EQSs with actual concentrations

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

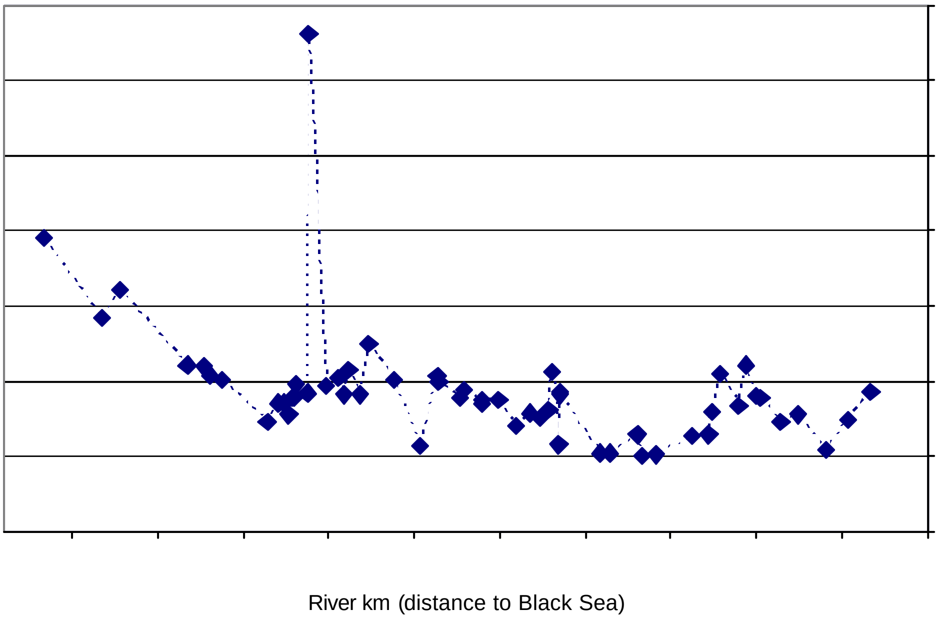
Many of the JDS data are unprecedented, including the systematic sampling and analysis for organic nitrogen along the whole stretch of the Danube river. Data for organic and total nitrogen in the Danube basin are still scant, also in the 1996-2000 TNMN database. The JDS took place in the warmer summer-autumn 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]



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]

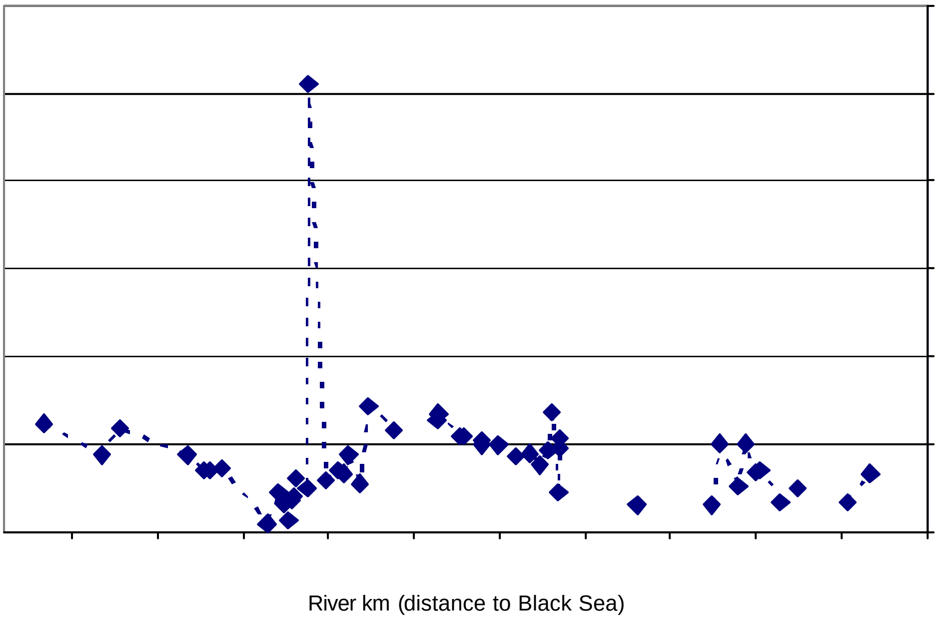


Table 2.10 Summary statistics of 'plain' organic N in Joint Danube Survey [mg N/l]

	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]

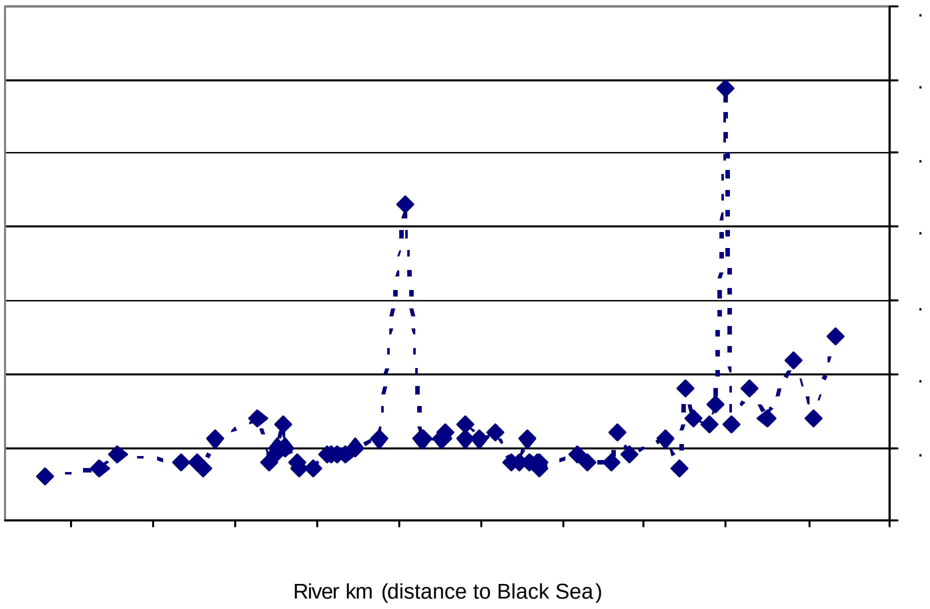


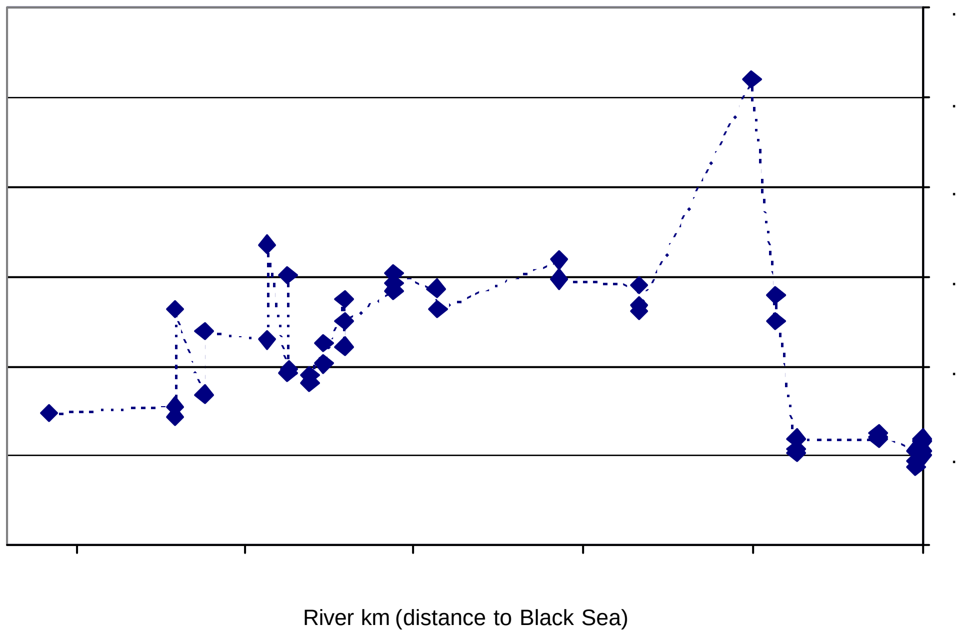
Table 2.11 Summary statistics of P_{tot} in Joint Danube Survey [mg P/l]

	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]



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 (NH_4)

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 NH_4

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 NH_4_N/l]	Concentration (higher range) [mg NH_4_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 °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]**

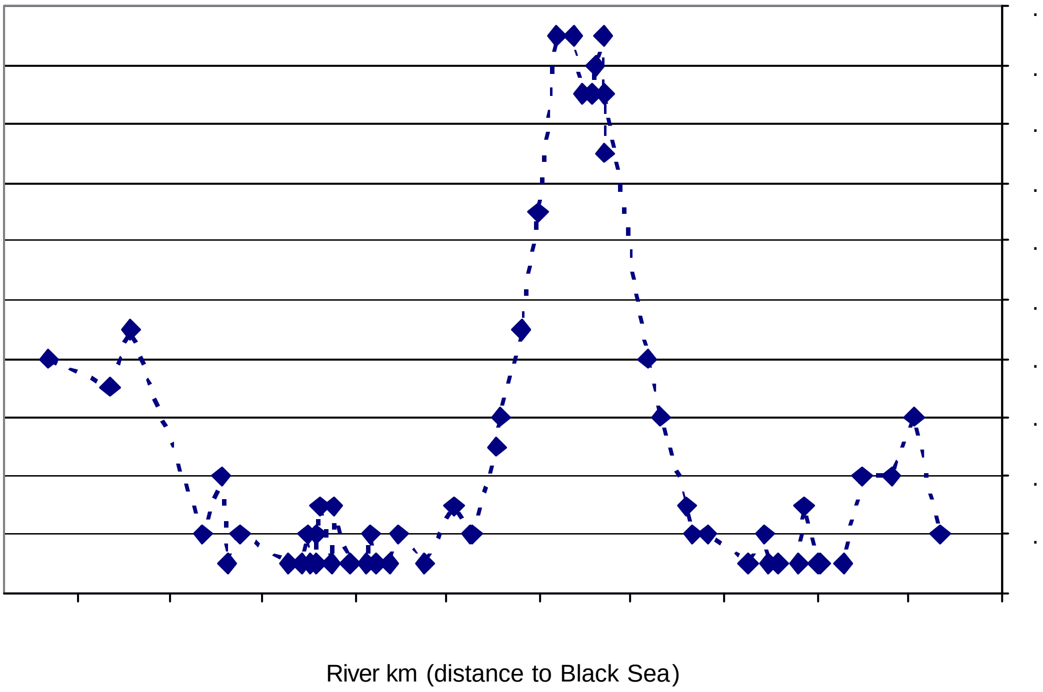

Table 3.2 **Summary statistics of NH_4 in Joint Danube Survey [mg N/l]**

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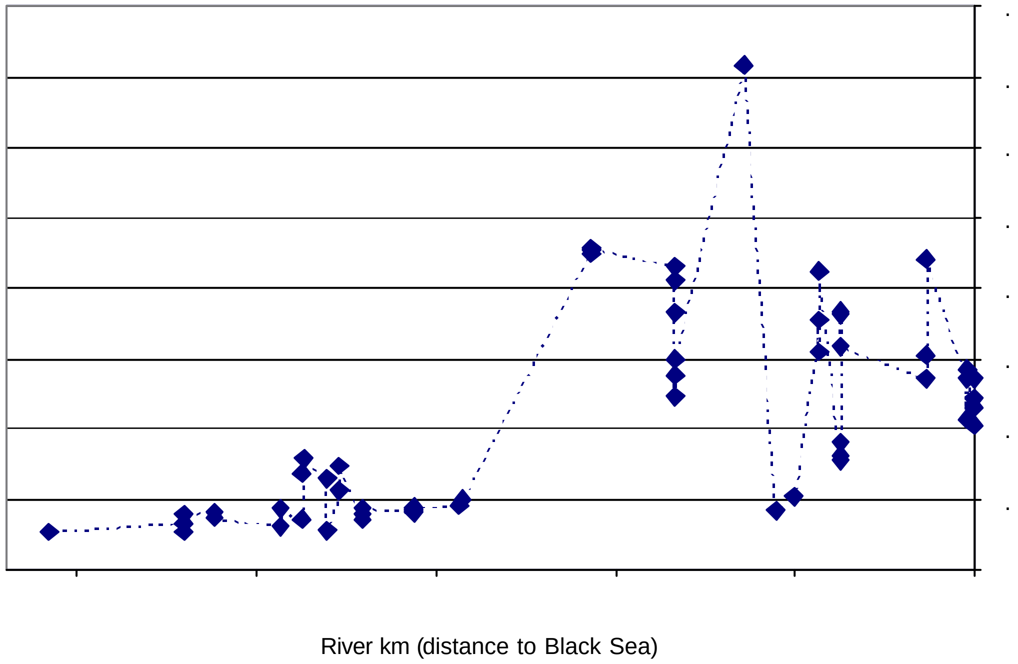
[4] Please refer for details to the separately reported TNMN 1995-2000 results in [Adamková, 2003].

Figure 3.2 NH_4 concentrations in the Danube, TNMN stations, annual mean 2000 [mg N/l]



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 toxicity 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 impacts 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).

$$Kd = \frac{Ctot - Cdis}{SS * Cdis} \qquad (1)$$

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)

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

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

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

$$Cads = \mathrm{Kd} * \mathrm{Cdis} \qquad (4)$$

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 unfiltered (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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