

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

Final Report
Support for TNMN and EMIS Inventory
Harmonization

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

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Executive Summary

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

- Development of water quality objectives for nutrients and water quality standards for toxic substances;
- Development of application for pressure /stress (emissions) and impact (water quality/change in ecosystems) analysis, based on MLIM and EMIS databases (TNMN, JDS, EMIS Inventory) including analysis and comparison of data in these databases;
- Improvement of the scope of the Trans-National Monitoring Network and Emission Inventory, including harmonization of their databases, considering EU and DRPC Priority Substances. TNMN related activities included analysis and assessment of TNMN results, development of SOPs and upgrade of web-based databases.

Major deliverables from particular project components are summarized below:

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

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

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 type specific approach (which was acknowledged by the study). Following the type specific approach, the conditions (including natural background) and requirements of the specific water body should be assessed and taken into account when setting its corresponding EQS. Therefore, the figures for both the EQS as well as for natural background mentioned in the report are considered merely indicative.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- Checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;
- Identification of water quality changes along the Danube River;
- Detection of trends in water quality;
- Assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

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

Nutrients

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

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

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

Heavy metals

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

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

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

Oxygen regime

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

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

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

Organic micropollutants

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

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

Biological determinands

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

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

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

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

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

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

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

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

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

Effects of pollution reduction measures (only regular pollution pressures)

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

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

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

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

