6 FINDINGS, CONCLUSIONS

The Joint Danube Survey conducted in August-September 2001 achieved all its main objectives, i.e.:

- It generated comparable biological and chemical characteristic data for the main river bed of the Danube and its major tributaries. In addition to producing comparable data sets, JDS was the most comprehensive survey covering a wide range of chemical pollutants, aquatic flora and fauna and bacteriological indicators. It was also intended to provide appropriate data and information for testing the EU Water Framework Directive (EU-WFD) for both the ecological and chemical status characterization;
- The cohesive team-work of the core scientists and their effective collaboration with national scientists provided a framework for the harmonization of sampling, sample preparation and partly analytical methods among the different Danubian countries, which is important prerequisite for producing reliable and comparable results in the transnational monitoring program;
- The jointly collected samples, divided and analyzed in both JDS and national laboratories provided an opportunity for the scientists to compare the respective results and – if needed - to take the necessary action to improve the quality of their analytical work and the monitoring results in the future;
- The meetings held during the Survey with country representatives, the media, the experts and the general public created a forum for public awareness raising, which is expected to have a positive influence on pollution reduction in every country.

It was agreed at the planning stage that the Survey should be conducted as much as possible during a low-water period. Judging by the actual flow-rates, the Survey satisfied this requirement almost all along the Danube. This allowed the concentration of chemical pollutants to represent – as far as possible - the worst-case scenario. However, the warm summer period also meant that there was accelerated biological activity and degradation of some pollutants, particularly in the water column.

The Survey targeted both the water column and the bottom sediment as the two major compartments of an aquatic environment. Taking into account the dynamic character of flowing waters it was foreseen that both biological and chemical characteristics of the water column would significantly depend on the seasonal conditions. Therefore, it was agreed that these conditions would be taken into account in the interpretation of the measurement results, particularly in the case of the water column.

Both biological and chemical results of the Survey provided a basis for characterizing the ecological and chemical status of the Danube River and its major tributaries. In addition, comparing the results of JDS with those of earlier surveys and with the relevant results of the Danube Transnational Monitoring Programs, i.e. the Bucharest Declaration and TNMN, were used to make a preliminary trend assessment. Results of JDS also made it possible to compare the quality/pollution characteristics of the Danube River Basin with other major river basins in Europe or elsewhere.

JDS yielded results for the characterization of the biological and chemical quality of the Danube River from Neu Ulm (2581 river km) to the Danube Delta, and of its major tributaries at their confluences. According to the EU-WFD, both the ecological and chemical status of a river depends on the biogeochemistry of its catchment area as well as the free flow of the river and its modifications. Accordingly, the Danube River can be divided into different Reaches.

6.1 Characteristic Danube Reaches

Geo-morphological landscape features strongly impact the chemical and biological condition of rivers. Features such as discharge, slope, depth-width-variations, substrate composition or sediment transport are crucial to the development of hydraulic and morphological elements. These elements determine the variety and quality of riverine habitats for aquatic organisms. The Danube River integrates in its catchment a wide diversity of different morphological patterns and reflects this variation in a broad spectrum of chemical and ecological variation from its source to its mouth in the Black Sea.

To enable a better understanding of the chemical and ecological data obtained during JDS, the Danube was divided into three major Reaches: (1) the Upper Danube Reach from the source of the River to the Gabcikovo Dam (1816 river km), nearly 1000 km characterised by frequent damming and very limited free-flow sections, (2) the Middle Danube Reach from the Gabcikovo Dam to the Iron Gate Dam (943 river km), a completely free-flow section, and (3) the Lower Danube Reach from the Iron Gate Dam to the Danube Delta another free-flow section. Each of these three major Danube Reaches can be further subdivided into three sub-Reaches, forming altogether nine geo-morphological Reaches characterised by specific geo-morphological landscape features within the Danube Basin and by anthropogenic impacts. These geo-morphological Reaches are as follows:

Reach 1: *Neu Ulm - Confluence with the Inn River (river km 2581-2255)*
Alpine river character; anthropogenic impact by hydroelectric power plants

Reach 2: *River Inn - Confluence with the Morava River (river km 2225-1880)*
Alpine river character; anthropogenic impact by hydroelectric power plants

Reach 3: *Morava River – Gabcikovo Dam (river km 1880-1816)*
Anthropogenic impact by the construction of Gabcikovo Dam

Reach 4: *Gabcikovo Dam – Budapest (upstream, river km 1816-1659)*
Turning from an Alpine into a lowland river, the Danube flows through the Hungarian Highlands

Reach 5: *Budapest (upstream) – confluence with the Sava River (river km 1659-1202)*
As a lowland river, the Danube flows across the Hungarian Lowlands; anthropogenic impact by significant emissions of untreated wastewater in Budapest

Reach 6: *The Sava River/Belgrade – Iron Gate Dam (river km 1202-943)*
As a lowland River, the Danube breaks through the Carpatian and Balkan mountains; anthropogenic impact by damming effects of Iron Gate hydroelectric power plant and significant emission input of untreated wastewater in Belgrade

Reach 7: *Iron Gate Dam – Confluence with the Jantra River (river km 943-537)*
As a lowland river, the Danube flows through the Walachian Lowlands (Aeolian sediments and loess); steep sediment walls of up to 150m characterise the River bank on the Bulgarian side

Reach 8: *The Jantra River – Reni (river km 537-132)*
Lowland river; alluvial islands between two Danube arms

Reach 9: *Reni – the Black Sea / Danube Delta arms (river km 132 – 12)*
The Danube splits into three Delta arms; characteristic wetland and estuary ecosystem; slopes decrease to 0,01

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6.2 Characterization of the Ecological Status of the Danube River

The aquatic community in rivers integrates all impacts - the effects of pollution as well changes in hydro-morphology. The appearance and distribution of aquatic organisms in rivers is significantly influenced by flow conditions, temperature, transparency of the water, habitat/substrate conditions and variation as well as the chemical status of the aquatic environment. The planktonic and benthic communities, their species composition and frequency of the individuals are used as the basis for the assessment of the ecological status of rivers included in the EU-WFD.

All biological elements mentioned in the EU-WFD for the assessment of the ecological status (benthic invertebrates, phytobenthos, macrophytes and phyto-, and zooplankton) were investigated during JDS except for fish because this group of organisms would have required a different methodological approach in terms of sampling. Special emphasis was placed on the evaluation of organic pollution (saprobity) and eutrophication. In addition to to the aquatic communities already mentioned above, microbiological parameters (total coliforms, faecal coliforms, feacal streptococci as well as heterotrophic bacteria) were also analysed in the water.

Altogether more than 1000 aquatic taxa (macrozoobenthos, phytobenthos, macrophytes, phyto- and zooplankton) were identified in the Danube and its tributaries. Based on the results obtained during JDS, the ecological status of the Danube is characterized by these biological groups.

Macrozoobenthos

In evaluating the biological results of JDS in terms of the benthic invertebrate fauna one should bear in mind that the Survey took place in August/September 2001 when a large number of aquatic insects had already emerged.

268 taxa were detected in the benthic samples collected during JDS with the polyp grab of "Argus". When all the species from accessory light trap catches and from manual collections with a sweep net are added to this, the number increases to somewhat less than 300 taxa. It may also increase considerably in case of multiple collections at JDS stations and differentiated determination of taxonomically difficult groups such as oligochaetes and chironomids.

The largest number of taxa was found in the Upper Danube Reach where it averaged 40 species. In the middle and lower Reaches, the figures range from 30 to 10. The different grain size of the substrate and flow velocities in the Danube considerably influence the number of taxa. The number of taxa for both banks matched only up to 60 %, and the biggest differences between the left and the right riverbank could be observed in the middle and lower Reaches of the Danube. The number of taxa in the tributaries differs very slightly from that found in the Danube.

The dominant groups of invertebrate show a varying distribution along the Danube. While in crustaceans the same species colonizes the whole of the Danube, insects show the greatest decrease in the number of taxa downstream. Molluscs and detritivores dominate the middle and lower Reaches.

Biological water quality classes

Macroinvertrebrates (macrozoobenthos) in particular have for many years been widely used in Europe in assessing the organic pollution of rivers. In the Danubian area this assessment is mainly based on the saprobic system which leads to a classification of water quality into seven biological water quality classes (four main and three in-between classes). Water quality class II (moderately polluted) indicates the general water quality objective.

The saprobity of the Danube varied between water quality class II (moderately polluted) or II/III (critically polluted). Taking into account that the saprobic index is also influenced by the habitat structure (for example comparison of free-flowing stretches to impounded areas), the Upper Danube Reach showed good water quality (class II). The same is true of the stretch downstream to Budapest.

Downstream of Budapest, where the Danube passes through the Hungarian Lowlands, water quality often decreased to class II-III indicating significant organic pollution. Taking into account the high chlorophyll-a values as well as the extreme over-saturation with oxygen in this Reach, secondary pollution caused by an elevated phytoplankton biomass becomes clearly recognizable, which usually leads to increased saprobity.

Downstream of Belgrade to the Iron Gate Reservoir, water quality varied between class II and II-III. A pollution trend began to appear; the saprobity of the samples collected from the left and right riverbank at a sampling site on the Danube showed significant differences, which seemed to be due to the pollution effects of the discharging tributaries. Only the impounded Reach upstream of the Iron Gate Dam showed saprobity values below the water quality class II limit.

In the Lower Danube Reach, especially downstream of big cities, their discharges seemed to result in a turnover mainly on the level of destruents, bacteria- and detritus feeders; even toxic effects seemed to exist. On the left bank of the Danube at Vrbica/Smiijan, for example, no invertebrates were present on rocks and pebbles, and the very fine-grained, reduced sediment was predominantly inhabited by a few oligochaetes and chironomids. Comparing the sum of abundances, a significant decrease in biodiversity in the lower section of the Danube became obvious.

The Danube arms and tributaries were more polluted than the Danube and even reached water quality class III (strongly polluted) or higher. The Moson-Danube arm and the dammed Rackeve-Soroksar arm were critically polluted (water quality class II-III). The Schwechat, the Drava and theTisza could be classified between class II and II-III. The mouth of the Vah, Velika Morava, Jantra, Siret and Prut tributaries proved to be critically polluted (water quality class II-III). The Sio even reached water quality class III. No macroinvertebrates were found in the Iskar, Olt and Arges tributaries. This might be due to toxic effects – representing the worst quality conditions (exceeding the limit of water quality class III) during JDS.

Alien species

The building of the Main-Danube Canal and its opening in 1992 removed a natural biogeographical barrier which had existed for millennia between the Rhine and the Danube. Since that time mutual fauna transfer has occured. The competition between local and foreign aquatic animals (neozoa) for food and habitat has resulted in changes in the diversity of macrozoobenthos. Shipping facilitates a fast dispersal of neozoans, for example in the case of the mussel Corbicula. This mussel was transported by ship from Europe and Egypt (the Nile) as far as North America and then returned to Europe around 1980. It migrated into the Danube in 1997 starting in the Rhine River, reached the Hungarian region by 1998/99 and was found in the Delta during JDS in 2001.

Phytobenthos

Phytobenthos is defined as the totality of algae living on the surface of substrata in the river bed, thus being mainly autotrophic organisms. The ecological niche of phytobenthos algae can be characterised by a long list of environmental variables (hydrology, substratum, light, water chemistry, temperature and other biota) showing river-type-specific variation ranges. On a long-term scale, phytobenthos communities respond to environmental stress (e.g. abrasion, siltation, instability of substratum, seasonal and horizontal shade pattern, turbidity, hardness, nutrient content, diurnal and seasonal variations, grazing by zoobenthos, fish, shading by riparian vegetation) primarily with changes in species composition.

Altogether 340 taxa of phytobenthos were identified in the Danube, its side arms and tributaries during JDS.

The richest group was Bacillariophyceae with 264 taxa. This algal group also called diatoms is well known for having a species-specific silicate structure. JDS samples were dominated by pennate-species of diatoms mainly the genera of Navicula, Nitzschia, Achnanthes, Amphora, Cocconeis, Cymbella, Diatoma, Fragillaria, Gomphonema, Gyrosigma, Pinnularia and Surirella.

The number of species identified at individual sampling sites varied in the range of 20-96 in the Danube and between 16 -109 in the tributaries. Downstream of Koszloduy (river km 685), the number of phytobenthic species significantly decreased. This seemed to be due to the type of substratum (mud and sand). An extremely low number of species was found in the Danube Delta (20-39 taxa).

Macrophytes

The Danube River offers a broad diversity of abiotic habitat parameters such as different substrate types, flow types and transparency as a sound basis for the development of a manifold macrophyte vegetation.

Altogether 49 different aquatic plant species were collected and determined during JDS, consisting of

- 14 moss species,
- 16 Spermatophyta (higher plants) - submerged rhizophyte species,
- 9 floating leafed and free-floating plants,
- 6 species representing Amphiphytes,
- 3 Helophyte species,
- 1 species belonging to the group of Characeae (Phycophyta).

Within JDS macrophyte evaluations, the impact of flow conditions became very clear because mosses, submerged rhizophyte species, floating leafed and free-floating plants can serve as good indicators of flow conditions. Mosses preferably grow on hard substrates (e.g. boulders) which dominantly characterised the Upper Danube Reach (Austria, Germany); they represented a considerable share of plant mass in Reaches 1, 2 and 4.

Concerning plant mass, a clear dominance of higher plants (Spermatophyta) – free-floating and floating leafed plants was observed in the Danube. In general, submerged macrophyte species prefer higher flow velocities than do floating leafed or even free-floating species. The final dominance of these two plant groups is decided upon the factor of light availability which in turn is determined by the transparency of the river water. Submerged species prefer high transparency values as habitat conditions. A dominant occurrence of submerged Rhizophytes due to high transparency values was found along Reach 3 (Gabcikovo Reservoir) and Reach 7.

If transparency values are low, macrophyte species which grow very close to or on the water surface become dominant key species. Therefore in the last two Reaches (8 and 9) where lower transparency values could be recorded, floating leafed and free floating aquatic plant species dominated the macrophytes.

The occurrence and distribution of macrophyte species is also crucially determined by nutrients. The majority of the plant species collected during JDS are indicators of eutrophic (high amount of nutrients) conditions. Some collected species such as *Ceratophyllum demersum, Potamogeton crispus* and *Zannichellia palustris* commonly serve as indicators of significant nutrient loads. The species group of Characea (Phycophyta) usually serves as an indicator of oligotrophic (low in nutrients) habitats marked by high transparency values. Obviously, such preferred conditions occur in some parts of the Iron Gate Reservoir where this specific group could be found.

Phytoplankton - Zooplankton

Phytoplankton

The development of phytoplankton biomass depends on the concentrations and availability of nutrients, light conditions, flow velocity (residence time) and the "grazing" effect of zooplankton and benthic filter-feeding animals. Increase in nutrient concentration in the water usually results in an increase of algal (or plant) biomass. Phytoplankton biomass (mg/l) and/or chlorophyll-a concentrations are commonly used as variables to characterise the trophic status of a water body in addition to the concentration of plant nutrients (phosphor and nitrogen), oxygen saturation and transparency.

Qualitative and quantitative algological investigations were carried out during JDS to get an overview of the longitudinal variation in species composition and to characterize the eutrophication status of the River. A total of 261 phytoplankton taxa were found during JDS in the plankton of the Danube and its tributaries. Longitudinal variations in phytoplankton biomass are also related to the variation in the number of taxa.

The increase in species richness in the middle and most eutrophicated part of the Danube was caused mainly by the increasing number of coccal forms of green alge (Chlorococcales taxa) as might have been expected in an eutrophic environment. In general, high values reported for biomass/chlorophyll-a indicated eutrophic conditions in the middle Danube Reach particularly downstream of Budapest.

Concerning the tributaries, the highest concentrations of phytoplankton biomass were found in the Iskar, the Velika Morava, the Ipoly and the Sio where the high eutrophic status was usually also underlined by high nutrient concentrations and oxygen-hypersaturation. Despite the fact that the Jantra, the Russenski Lom, the Arges, the Siret and the Prut were also highly polluted with nutrients or biodegradable organic matter, their phytoplankton biomass was low probably due to the retarding or toxic effects. In contrast, a high concentration of phytoplankton biomass was observed in the Drava despite a low concentration of nutrients.

Zooplankton

Zooplankton communities can only develop in rivers exceeding the length of about 500-700 km since the growth of the species requires a certain time period such as 3-7 days for Rotatoria, one week for Cladocerans and one month for Copepods. Temperature is particularly important in the case of Rotatoria. If the river flow is high and water level fluctuations are large without the necessary depth, zooplankton will be destroyed due to frictions against the riverbank, the riverbed and plants. Suspended solids could damage zooplankton species. Qualitative and quantitative composition of zooplankton could be highly influenced by the effects of the confluence of a species-poor canal and water diversion devices (closures).

Altogether 120 species (79 Rotatoria, 27 Cladocera and 14 Copepoda taxa) forming the zooplankton community were identified in the Danube and its tributaries during JDS.

The number of zooplankton taxa found at JDS sampling sites varied between 4-26 in the Danube and between 6-30 in the tributaries. A gradual increase in the number of taxa was observed in the Danube downstream to the Delta.

The occurrence of many rare species was recorded especially in the German, Austrian, Slovakian and Hungarian part of the Danube. The highest species richness was found in the Hungarian and Yugoslavian sections of the River.

Individual abundance of zooplankton communities varied largely between 280 – 1,380,000 ind/m^3 in the Danube and 1,140 – 799,000 ind/m^3 in the tributaries. The lowest individual numbers were measured along the German, Austrian, and Romanian and Bulgarian stretches of the River. The highest individual numbers were registered downstream of Budapest and in the Yugoslavian part of the Danube near Novi-Sad, as well as between the confluence points with the Tisza and the Sava rivers. These results are not in accordance with the results of previous investigations where maximal individual numbers were observed further downstream on the Romanian, Bulgarian and Ukrainian stretches of the River and in the Danube Delta. In many cases the Danube was noticeably influenced by its tributaries which changed its species composition and caused an increase in zooplankton density in the Danube downstream of the confluence with the tributary.

Comparing the longitudinal variation in phytoplankton biomass and zooplankton density, shown in Figure ZPL-1 (see Chapter 4.6), it can be seen that the peak of phytoplankton biomass is followed by the maxima of zooplankton density in the Middle Danube Reach. That the decrease in phytoplankton was associated with an increase in zooplankton density is most probably due to the grazing effect of zooplankton.

Microbiology

Microbial communities represent a fundamental part of aquatic ecosystems. They degrade organic matter thus contributing to the self-purification of rivers. Bacteria are ideal sensors because of their fast response to changing environmental conditions.

Total coliforms, faecal coliforms and faecal streptococci are very good indicators for the assessment of faecal pollution mainly caused by raw and treated sewage and diffuse impacts from farmland and pastures, also indicating the potential presence of pathogenic bacteria, viruses and parasites. The concentration of heterotrophic bacteria usually shows a correlation to organic pollution.

In monitoring the quality of river water intended for the abstraction of drinking water, irrigation and bathing, the examination of these microbiological standard parameters is obligatory (e.g. EU-Surface & Drinking Water Directive 75/440/EEC, WHO - Guidelines for the safe use of wastewater and excreta in agriculture and aquaculture, 1989; EU-Bathing Water Directive 76/160/EEC).

As Danubian countries are using different analysis methods, JDS provided a unique opportunity to obtain comparable results from Neu-Ulm (Germany) to the Black Sea. For the first time standard microbiological determinands were analysed on board by using uniform methodology for all sampling sites.

The evaluation of the microbiological results revealed that the highest pollution values occurred in the tributaries (the Russenski Lom, the Arges, the Siret and the Prut in particular) and in the side arms (the Moson arm, the Rackeve-Soroksar arm). Lower bacterial values could be observed in the upper Danube Reach as well as in and downstream of the Iron Gate Reservoir. Higher levels of faecal pollution were found in the middle part of the Danube, particularly donwstream of the major cities (Budapest, Beograd), downstream to 1100 river km and again in the lower Danube from 500 river km to the Danube Delta.

6.3 Characterization of the Chemical Status of the Danube River

JDS provided results on the quality status of the water column characteristic for the time period of the Survey, particularly in the case of the general variables and nutrients. The determination of selected pollutants, e.g. heavy metals, volatile organic hydrocarbons, polar pesticides and pharmaceuticals provided information on direct inputs and facilitated the detection of hot-spots. The latter was further supported with GC/MS screening.

Chemical pollution characteristics of the sediment and selected aquatic organisms such as mussels reflect longer-time exposure to pollution. The analysis of sediment samples was extended to include a wide range of pollutants, while mussels were analysed only for selected pollutants such as heavy metals, polyaromatic and chlorinated hydrocarbons. Some specific EU-WFD priority pollutants were analysed for the first time along the Danube. GC/MS screening also provided additional information on the pollution by detecting compounds beyond those targeted.

The characterization of the general quality characteristics and nutrients, as well as the different type of pollutants follows.

General characteristics

Conductivity measurements in the Danube and its tributaries revealed the salt content of the different water bodies. Significant effects were observed in the form of a dilution of the Danube water with the low-salinity Inn River in the Upper Danube Reach, and an increasing salt content in the Middle Danube Reach downstream of its confluence with the Tisza and the Sava rivers.

pH values and dissolved oxygen concentrations in the water varied according to the increased primary productivity and degradation of the organic pollution load; both occurred particularly in the Middle Danube Reach. Algal blooming increased both the pH values and the dissolved oxygen concentration as it was already discussed earlier under the characterization of the phytoplankton. Downstream from the high primary production section, both the pH value and the dissolved oxygen content of the water significantly decreased probably due to the biodegradable organic pollution from the major cities (Budapest and Belgrade) and from the load of the natural organic matter (plankton).

In general, the concentration of suspended solids was below 50 mg/l, which was also expected given the relatively low flow regime. The suspended solid concentration exceeded 150 mg/l in two tributaries (the Siret and the Prut) and one Danube water samples.

General characteristics of the bottom sediment included grainsize distribution. Since sediment-associated pollutants were determined in the less-than-63-µm size fraction, it was important to demonstrate its percentage in the original sediment sample. According to the measurements, the majority of the samples contained more than 20% of this fine fraction in the sediment. Therefore, this fraction can be considered a representative part of the sediment for the analysis of specific pollutants.

Nutrients

Different forms of nitrogen and phosphorus were measured in the water, suspended solids and bottom sediment samples.

In the water column, ammoniacal- and nitrite-nitrogen concentrations were slightly increased in the lower part of the Middle Danube Reach, following the decreasing trends in pH value and dissolved oxygen content. The organic nitrogen content of the suspended solids was related to the algal bloom demonstrated with the results of phytoplankton. The organic nitrogen content was relatively constant in the bottom sediment along the whole surveyed Danube and some elevated values were found in the tributaries.

Both ortho-phosphate-P and total-P showed a slight increase in the water along the Danube. In suspended solids, the total-P concentration followed the same trend as in the case of organic nitrogen. However, high concentrations were measured in the Danube samples upstream of the Inn confluence but they were significantly lower downstream as a result of the Danube water mixing with the Inn water. In the case of bottom sediment, total-P concentration showed no variation at all along the whole Danube, not even in the tributaries except for the Arges.

The dissolved silica content of the water was significantly lower, reaching almost zero mg/l, along the Danube section were high algal blooms were observed. This was mainly due to the uptake of silica by the algae, particularly diatoms. Downwards from this section, the dissolved silica concentration increased again probably originating from the decomposition of the algal and other organic detritus.

Heavy metals

A variety of elements (aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, zinc) were determined in water samples, sediments, suspended solids and mussels of the Danube and its tributaries.

Strong correlations between the heavy metal content in suspended solids, sediments and mussels indicate the applicability of these matrices for monitoring purposes. Data evaluation was carried out by using heavy metal quality targets for sediments and suspended solids. Except some restricted areas and tributaries, the contamination of the Danube by chromium and lead proved to be rather low. However, some hot-spots were detected at the same site as during earlier surveys (Cousteau-survey, Phare AR105 research study). All other metals were found in elevated concentrations in at least one of the investigated matrices, particularly in the lower part of the Middle Danube Reach and in the Lower Danube Reach (downstream of the confluence with the Sava River). Despite a significant decrease of arsenic, chromium, mercury, lead, nickel and zinc in sediment core samples of the Iron Gate, their surface concentrations were still well above the quality targets.

Characteristic "natural background" or baseline values, or the geochemical/geographical variation of conservative elements such as aluminium, could be used as benchmarks in the interpretation of heavy metal pollution in the river basin. This could also be a good basis for the adjustment of sediment quality targets to the specific geochemical conditions of the Upper, Middle and Lower Danube Reaches.

Organic pollutants

The presence of organic compounds in the water is a direct consequence of natural processes in the environment as well as of various anthropogenic activities in the industrial, agricultural and municipal sectors. While the occurrence of organic compounds of a natural origin, which are part of nature's life cycle, usually does not pose any remarkable threat to the environment, the presence of organic micropollutants has an adverse impact on the quality of the natural world. To prevent this undesirable phenomenon, the most dangerous substances are regulated by legislation. Based on the established quality standards, a number of priority pollutants are regularly being monitored in the river basins all over Europe. Within the framework of the Transnational Monitoring Network (TNMN) in the Danube River Basin, seven organic micropollutants are analysed monthly in water in the selected profiles. Another 15 organic micropollutants are on the TNMN determinand list for sediments. This limited number of compounds is considered as an absolute minimum necessary to be monitored regularly in the Danube River Basin. To enlarge the information on organic contamination in the Danube and its tributaries, additional groups of organic micropollutants were selected as target compounds to be analysed in the Joint Danube Survey samples. The results of those analyses are discussed in the previous chapters of this report. However, besides all these listed pollutants, there are still hundreds of other organic compounds originating from anthropogenic activities, which may potentially enter the hydrosphere.

<u>Aggregate Characteristics</u>

In the water, UV absorbance at 254 nm showed a very slight variation along the Danube. However, this variable can be used for comparison with other results from other river basins to characterise overall dissolved organic matters. In addition, the determination of humic substances, showing also slight variations and low concentration values, indicates the level of organic matter from natural origin. In the case of both variables, relatively high values were measured in the tributaries. The correlation between these two variables indicated that the bulk of the dissolved organic matter was of natural origin.

Total organic carbon (TOC) in suspended solids followed the same trend as the variation in phytoplankton. High values were measured in the same samples that contained a high algal biomass. In the bottom sediment, higher concentrations were measured in the lower part of the Middle Danube Reach as well as upstream of the Inn confluence, same as in the case of total-P.

Total extractable matter (TEM) in suspended solids correlated with TOC values. In the case of the bottom sediment, TEM concentrations demonstrated an increasing trends downstream to the Danube Delta. This was probably related to the accumulation of hydrophobic organic pollutants, particularly petroleum-related compounds, in the bottom sediment.

Petroleum hydrocarbons

Results of earlier surveys and monitoring had revealed a significant level of oil pollution in the Danube River Basin. Therefore, special attention was paid to determining oil pollutants in the water, suspended solids, bottom sediment and biota samples. The interpretation of the results of the analysis of petroleum-related pollutants is difficult because there is no single analytical method, and each of the available methods has its own information content. GC/FID, UV absorption and fluorescence methods were used during JDS for general characterization of the total petroleum hydrocarbon contamination and GC/MS method was used for determining one of the most important group of petroleum hydrocarbons, i.e. polyaromatic hydrocarbons (PAHs). Because GC/FID, UV absorption and fluorescence methods use an arbitrary calibration standard, the actual concentration values are not always consistent.

In the water samples, the analysis was carried out with the single fluorescence method. By using this method it was also possible to characterise the type of the oil pollution. Most of the samples contained mainly the most water soluble light petroleum hydrocarbons (e.g. monoaromatics). However, some samples were highly contaminated with heavier petroleum products.

GC/FID and UV absorption measurements in the suspended solid and bottom sediment samples resulted in nearly similar concentration values whereas the concentration values obtained with the fluorescence measurement were lower. The pollution trend was the same with all three methods. Like in previous studies, the highest values were reported in the Middle Danube Reach. The Lower Danube Reach was generally more contaminated than the Upper Danube Reach.

Concerning PAHs, their concentration levels in the sediment were usually lower than the sediment quality target; 2 mg/kg concentrations were exceeded in 17 samples only and none of the samples reached 20 mg/kg. The sediment core samples varied in terms of the 16 PAH compounds, but again remained below 2 mg/kg in most of the core samples. The concentration of PAHs in mussels showed increasing trends downstream on the way to the Danube Delta. The highest concentrations were measured in mussels collected from tributaries in the Middle Danube Reach.

Volatile organic compounds (VOCs)

In general the contamination of the Danube and its main tributaries with VOCs is very low. This is important for the water-works along the Danube because VOC´s are toxicologically relevant. The low VOC concentrations can also be explained by the fact that the sampling period was in summer. The water quality target values are only exceeded by 1,2-dichloroethane in a defined section of the Danube.

Polar pesticides

Of all the 23 pesticides under investigation, only Atrazine and Desethylatrazine could be found along the Danube in average concentrations of around 0,05 µg/l. Only in few samples was the quality target of 0,1 µg/l set by the Rhine Commission exceeded.

Pesticide application is not common in the summer season. The few increased-Atrazine results originated mainly from the tributaries. The maximum value for Atrazine found in the Sava River (0,78 µg/l) might be explained by emissions from a nearby Atrazine-producing factory.

Other WFD priority pollutants

63 suspended matter samples and 187 sediment samples (including 26 core samples) from the Danube River and its major tributaries and arms were analysed for the WFD compounds para-tert-octylphenol, 4-iso-nonylphenol, di[2-ethylhexyl]phthalate, pentachlorophenol, pentabromodiphenyl ether and tributyltin. C10-C13-chloroalkanes were not investigated because no indicative parameter is defined. Pentabromodiphenyl ether and penta-chloro-phenol were not found in the samples under investigation, while tributhyltin was present only in low concentrations. Para-tert.-octylphenole was found only in bottom sediments; 4-iso-nonylphenole and di[2-ethyl-hexyl]phthalate] were found in both bottom sediments and suspended solids in significant concentrations (from a few µg/kg up to more than 100 mg/kg), indicating the relevance of these compounds as indicators of industrial pollution of solid materials in the Danube River. Sediment core samples usually show decreasing concentrations of WFD compounds between old and new sediment layers.

Pharmaceuticals

The samples that originated in the Danube itself all showed relatively low concentrations of the investigated pharmaceuticals. Three tributaries showed significantly higher amounts that can presumably be assigned to wastewater discharges. The influence of contaminant loads in the tributaries on concentrations in the Danube River cannot be assessed directly because no samples were taken for the analysis of pharmaceuticals immediately upstream and downstream of the tributaries. A comparison of the flow data of the tributaries (the Iskar: 13.50 m^3/s, the Jantra: 9.50 m^3/s, the Arges: 9.99 m^3/s) and those of the Danube river (4170 – 4490 m^3/s in that region) shows that - because of dissolution of the tributaries' load - no significant effect on the concentrations in the Danube can be expected.

GC/MS screening

Both water and sediment samples were analyzed with GC/MS in scan mode to detect organic compounds not included in the targeted analysis discussed above. The results of GC/MS screening confirmed several results of the target analysis. Additionally detected compounds included: (a) pollutants characteristic of municipal wastes such as faecal sterols, carboxylic acids, (b) petroleum-related n-alkanes, alkyl-benzenes (also probably originating from surfactants), sulphur-containing compounds, and (c) other chemicals such as phthalates, etc.

7 RECOMMENDATIONS, CONSIDERATIONS FOR THE FUTURE

The Joint Danube Survey fully achieved its original objectives as summarized in the chapter on Findings, Conclusions and provided a framework for the utilization of the results and experience gained during the Survey for improving the monitoring of water quality in the Danube river basin and for setting up quality targets and a classification system particularly for the sediment. Lessons learned during JDS allowed us to formulate recommendations as detailed in the following.

Revision/Improvement of the Danube TNMN

Recommendations for a revision of the TNMN on the basis of the lessons learned during JDS relate to the selection of determinands, sampling sites, timing and methods for both biological and chemical monitoring as follows:

- In the water column, heavy metals were analysed in both membrane filtered (dissolved) and original water samples. This allowed a comparison with earlier monitoring results, including those of TNMN. Based on the results, it is recommended that the monitoring of heavy metals in suspended solids only should be considered, excluding the dissolved phase.
- Some of the EU-WFD priority pollutants, which were detected in at least 50% of the samples, should be considered for inclusion in the TNMN.
- In the case of biological monitoring, the selection of sampling sites and the timing of the survey should be adjusted. It is recommended that the sampling sites, particularly for macrozoobenthos, should include additional sites downstream of dams and between JDS stations where the distance between two stations exceeds several tens of km. The addition of sampling sites will result in an extended taxa list, which should be as complete as possible, to allow sound ecological evaluations. Future monitoring should be conducted during spring or early summer when species diversity is expected to be higher than in August/September because many species of water insects are still in the aquatic phase of ontogenetic development as adult larvae. When they emerge later on they cannot be taken into account in the assessment of macrozoobenthos. It is important, however, that the flow regime should be at the low water level.
- It is recommended that microbiological sampling sites should include the river banks to increase the chance of detecting hot spots.
- There is a need to continue to compare the analytical methods used during JDS with those agreed for the TNMN. Because JDS laboratories were usually not the same as the Danube laboratories that are part of TNMN, methodological differences exist but comparability of results should be ensured. Special attention should be paid to the characterization of petroleum-related pollution, which requires a thorough review and agreement regarding analytical methods. The microbiological parameters and methods should be revised especially with reference to the updated EN ISO Standards for isolating indicator bacteria. The harmonization of microbiological assessment methods is also urgently needed starting with intensive information exchange (know-how transfer and education programs) and a step-by-step implementation.
- Since JDS provided an opportunity for each Danubian country to participate in the Survey and gain relevant experience, it is recommended that similar national surveys be launched at least twice a year as part of the national participation in the TNMN.

Sediment quality targets and classification

One of the main achievements of JDS was a characterization of the chemical composition of suspended solids and bottom sediments in the Danube and its major tributaries. Based on the results of the analysis of heavy metals and organic micropollutants, the following is recommended:

- A large body of data from JDS and earlier surveys on the concentration of heavy metals in sediments allows the establishment of baseline ("natural background") levels reflecting the geochemistry of the Danube Reaches. The available data are usually generated by the analysis of a given grainsize fraction, e.g. the less-than-63-µm fraction. However, further normalization of the results to the aluminum content of the sediment might be considered. Quality targets and limit values for classification should be established as enrichment factors relative to the baseline concentrations.
- Concerning organic pollutants, quality targets and classification should be established separately for the naturally occurring organics such as several of the petroleum-related variables and for synthetic, man-made chemicals. In the case of naturally occurring organics, the approach could be similar to the one used for heavy metals. However, more data are needed for establishing the baseline levels. Concerning synthetic organics, the baseline should be the detection limit and the target values and classification limits should follow international practices.

Coordinated surveys in the future

The achievements of JDS provide the basis for considering and recommending coordinated surveys in the future. Lessons learned from JDS could be used for improving the planning and implementation of such surveys, and the following could be recommended:

- Taking into account the revision cycle of the EU-WFD, surveys similar to JDS should be organized every five-to-six years. Consequently, JDS-II could be expected to be launched in 2006-2007.
- When planning JDS-II, the lessons learned from the completed JDS should be used pertaining to the selection of sampling sites, on-board sample preparation and analysis. Core-team members should be selected on the basis of their field experience in the different Danube Reaches.
- In addition to the "one boat, one team" surveys, the ICPDR should consider implementing coordinated surveys including a similar sampling and analytical program for both biological and chemical variables either in the framework of the TNMN, as recommended earlier, or as a separate activity in its pollution monitoring program. Such a survey would be similar to the involvement of national teams in JDS, except that each country would provide the boat and team in their territorial waters. The sampling and analytical program and the timing of the survey would be coordinated by the ICPRD, but should be agreed and supported by each country as part of their national monitoring program.

Future biological investigations could benefit from the following recommendations:

- Sample collection close to the river banks is only possible at low water levels and ice-free conditions. Sampling should never be done at a rising water before the previously dry bank strip has been re-colonized by all macrozoa. Solid substrates should always be brushed off under water as far as possible in order to identify the quantity of all sessile and attached organisms. It is not advisable to collect organisms only with a pair of tweezers because very small species (e.g. Turbellaria, Jaera) and juvenile larvae-stages are easily overlooked in this way and the assessment of species-specific abundance becomes difficult.
- In order to get a more precise picture of the potentially possible benthic organisms as well as for a better comparability of the composition of species from sampling locations with differently structured river bottom, the application of artificial substrates for the colonization with macrozoa should be considered. This method could be particularly suitable

in the lower course of the Danube.

• It is recommended that the variety of animal population in the Danube Delta should be thouroughly registered as a genetic pool for the re-colonization of the upper Reach of the River.

• Harmonisation of microbiological assessment methods is needed starting with an intensive information exchange (know how transfer/ education programmes) and a step-by-step implementation of AQC

• Phytobenthos samples should be analysed directly on-board to allow the identification of the ratio between individual groups and their dominances and to facilitate the identification of species according to their special characteristic features in the living stage.