Revised
Danube WQ Model:
Analysis of available data

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Contents

List of Figures

List of Tables

List of Figures

List of Tables

1 Introduction

1.1 The *daNUbs* project

The acronym "*daNUbs*" represents the research project "Nutrient Management in the Danube Basin and its Impact on the Black Sea", which is a part of the EU's 5th framework programme (EVK1-2000-0603). The project deals with the Programme Environment and Sustainable Development (1.1.4), and covers the thematic priority of Strategic Planning and integrated management, methodologies and tools on the catchment scale (1.1.1).

daNUbs aims at providing scientifically sound and sustainable solutions to the problem of mismanagement of nutrients in the Danube Basin. To this end, different research activities are foreseen:

I. Improvement of process understanding:
This research, including literature and data review in combination with additional field work, will address
(a) the nutrient balance in the catchment with main emphasis on diffuse pollution (e.g. agriculture, air pollution) and the transport, retention and losses of nutrients in the catchment (nutrient balances in case study regions),
(b) the transport, retention and losses of nutrients and silica along the Danube River and
(c) the functioning of the Western Black Sea ecosystem concerning the direct influence of riverine nutrient and silica discharges.

II. Mathematical models:
Based on an improved process understanding, mathematical models will be improved, combined, and applied to quantitatively assess nutrient fluxes from the Danube Basin along the Danube and the Delta to the Western Black Sea and to quantify the impact of these fluxes on the mixing zone of Danube River in the Western Black Sea. This part will use
(a) the MONERIS-emission model based on a GIS data base,
(b) the Danube Water Quality Model (DWQM) for the description of the transport and transformation processes in the river system,
(c) the Danube Delta Model (DDM) for the quantification of nutrient transport in the Danube Delta and
(d) the Shelf Model for modelling the impact of the Danube load on the Western Black Sea.
Based on these models the whole system can be considered as a complex unit and scenarios can be developed as a basis for scenario evaluation.

III. Strategic planning:
Consequently the project will be oriented towards elaboration of advice for future strategic planning on the catchment scale. This part will include
(a) a method to establish comparable, basin-wide, periodic nutrient balances considering the national data availability and
(b) the evaluation of different solutions for future nutrient management strategies considering socio-economic developments in the Danube Basin.

For further details we refer to the Description of Work of the *daNUbs* project (*daNUbs*, 2000).

1.2 The present report

The *daNUbs* project is organised in different Work Packages. The modelling work is divided in the modelling of the Danube catchment area and the modelling of the Black Sea shelf. The work on the Danube catchment is situated in Work Package 5: "Danube Water Quality Model (incl. Delta)/ MONERIS)".

In this work package 3 models play a key role:

I. the model MONERIS (MOdeling Nutrient Emissions in RIver Systems);
II. the DWQM (Danube Water Quality Model);
III. the DDM (Danube Delta Model).

The difference between MONERIS on one hand and DWQM/DDM on the other hand is a conceptual one: the former focuses on the whole catchment (both land and water) and the emissions of nutrients stemming from human activities, while the latter focuses on the river system and the fate of the nutrients once they reach the surface waters. The difference between the DWQM and the DDM is a geographical one: the DWQM runs up to the upstream end of the Danube Delta, where the DDM takes over.

The current report constitutes a part of deliverable D5.9 ("Revised Danube WQ Model”). It is drafted by WL | Delft Hydraulics, Delft, The Netherlands. Data have been incorporated from several other partners within *daNUbs*, in particular:

- Vienna University of Technology, Institute for Water Quality and Waste Management (IWA), Austria;
- Forschungsverbund Berlin e.V., Institute for Freshwater Ecology and Inland Fisheries (FVB.IGB), Berlin, Germany;
- Danube Delta National Institute for Research and Development (DDNI), Tulcea, Romania;
- National Institute for Marine Research and Development (NIMRD), Constanta, Romania;
- Water Resource Research Centre Plc., Vituki Plc., Institute for Water Pollution Control (VITUKI), Budapest, Hungary.

2 Problem description and objectives

2.1 Problem description

The project *daNUbs* investigates in-depth the pathways of nutrients from their sources to their sinks in the sea. Thus, important aspects of the *daNUbs* project are the transport, retention and losses of nutrients in the water courses. Floodplains, dams and impounded river reaches play an important role in nutrient retention and /or release (mobilisation). In this respect models like the Danube Water Quality Model (DWQM) and the Danube Delta Model (DDM) play a key role. Only this type of modelling allows the characterisation of the nutrient transport in floodplains, reservoirs and in impounded sections in the Danube river basin.

The project *daNUbs* also aims at analysing the effect of the nutrient (mis-)management on the ecology of the Black Sea shelf. To this end, mathematical models are prepared which need to be driven by data regarding the Danube outflow (discharge and concentration). These data need to be available on a day-by-day basis. Again, models like the DWQM and the DDM are suited for such analyses.

The present report is intended to support the development of the “revised Danube Water Quality Model” (deliverable D5.9 of the *daNUbs* project). This revised model is in many respects similar to the first version of the DWQM (van Gils, 1999). The application of this first version however, revealed some significant knowledge gaps. The *daNUbs* project aims at closing these gaps, thus making the DWQM a more reliable tool for policy making.

One big improvement is the development of better emission data, especially for diffuse sources of pollution. To this end, the project *daNUbs* provides the coupling of the GIS-based emission model MONERIS and the DWQM. The set-up as well as the implementation of this coupling is discussed by van Gils (2001) and Constantinescu ea. (2001).

2.2 Objectives

The present report provides and discusses the data for the further refinement and calibration of the DWQM. Specific questions to be answered are:

1. What are the Danube loads of nitrogen, phosphorus and silica in the recent years, and is there a trend in these loads?
2. Are there specific areas along the Danube river and its main tributaries where the retention of nitrogen, phosphorus or silica is exceptionally strong?
3. To what extent does the organic fraction of nitrogen influence the nitrogen mass balance of the Danube river and its main tributaries?
4. To what extent does the frequency of sampling influence the computed river loads of especially phosphorus?

5. To what extent does the fact that sampling is usually done at the water surface affect the computed river loads of especially phosphorus?

Questions 1 and 2 can be translated as the set-up of a basin-wide mass balance of the nutrients nitrogen, phosphorus and silica. Apparently, these questions need to be answered if a suitable DWQM is to be developed.

Question 3 is especially related to the fate of nitrogen. The different species of inorganic nitrogen are sampled more frequently at more locations than the organic fraction of nitrogen. For this reason it is often assumed that total N is accurately represented by total *inorganic* N. Consequently, there is a possible source or sink in the observed mass balance of (inorganic) nitrogen: there could be a net flux from or towards the organic pool. This needs to be clarified.

Questions 4 and 5 are related to the fate of phosphorus. Due to the fact that a substantial fraction of the total phosphorus in surface water is present in the suspended solids (adsorbed, mineral or organic), it is important that the loads of suspended solids are computed accurately. It is known that floods carry a more than proportional part of the annual suspended solids load. By sampling 12 times per year, the chance exists that a relevant flood is not “captured” and the annual load of suspended solids is underestimated. It is also known that there usually is a vertical gradient in the suspended solids concentration: the concentrations increase going from the water surface towards the bottom. By sampling at the water surface only, the chance exists that the profile averaged concentration and consequently the river load of suspended solids is underestimated. These two factors were in the past suspected to cause an underestimation of the computed river loads of phosphorus of a factor of 2. This needs to be verified.

2.3 Overview of information sources

Data have been collected from various sources. Each data set has its own characteristics with respect to spatial and temporal coverage and the analysed parameters. Table 2-1 provides a brief overview. More details are given in the following chapters.

Table 2-1: Overview of sources of information.

Data set	**Period covered by dataset**	**Frequency of sampling**	**Spatial coverage**	**Profile coverage**	**Completeness of analysed parameters**
TNMN (ICPDR)	1996-cont.	> 12/year	Basin wide, 61 stations	LMR at surface	+
NIMRD (Constanta)	1980-cont.	daily	Station Sulina	at surface	-
DDNI (Tulcea)	1996-cont.	≈ 8/year	Station Reni	at surface (?)	0
daNUbs surveys:					
Vienna	10 days	4/day	1 station	at surface	++
Gabcikovo	3x7 days	daily	3 stations	LMR, 0-5m	+
Iron Gates	3x7 days	daily	3 stations	LMR, 0-5m	+
Delta	5x4 days	daily	1 station	LMR, 0-5m	+

Data set	**Period covered by dataset**	**Frequency of sampling**	**Spatial coverage**	**Profile coverage**	**Completeness of analysed parameters**
JDS	Aug-Sep 2001	1 sample	Basin-wide, about 100 stations	LMR at surface	++
Reschke	June 1995	1 sample	km 1072 to Black Sea	3 points in vertical	- (only SS and composition)
EAWAG	2001	weekly	Iron Gates area: several stations	3 points in vertical	+
Unesco	1956-1985	variable	20 stations along the Danube	unknown	annual SS loads only

It is obvious that the TNMN constitutes the most relevant data set in view of the objectives of the present report. This data set will therefore be discussed first. The other data sets will follow, and their results will be discussed with the TNMN data as a reference.

3 The Transnational Monitoring Network

3.1 Description of the data

The Trans-National Monitoring Network (TNMN) is the regular water quality monitoring network operated by the Danube countries under the umbrella of the International Commission for the Protection of the Danube River (ICPDR). It is operational since 1996. Details can be found in the TNMN Yearbooks (ICPDR, 1998, see also www.icpdr.org).

The available data cover the period 1996-2001. The data for 1996-2000 have been downloaded from the ICPDR web site. The data for 2001 have been obtained from the Permanent Secretariat of the ICPDR.
Preliminary as yet unverified data have been obtained for the Romanian part of the TNMN network for 2002-2003. We have made limited use of these data, and whenever we used them their status has been clearly indicated.

Up to 2000, samples were taken at 61 stations on the Danube and its larger, trans-boundary tributaries. At each of the stations up to three sampling locations are defined: on the left bank of the river (L), in the middle of the river (M) and on the right bank (R) of the river. Appendix C provides an overview. In 2001, 18 stations were added from Serbia-Montenegro. These stations are very relevant, since they are situated on the lower reaches of the two largest tributaries Tisa and Sava and on the Danube reach where these two rivers join the Danube, just upstream of the Iron Gates area.

The list of determinants consists of about 50 water quality parameters in the water samples. Out of these 50, the most relevant for the current project are: discharge, temperature, suspended solids, total nitrogen, ammonium, nitrites, nitrates, organic nitrogen, total phosphorus, phosphates, dissolved oxygen, chlorophyll-α and silicates.

The frequency of sampling and analysis is variable for the different stations and determinants. For the water quality parameters the TNMN targets a sampling and analysis frequency of at least 12/year.

Since 2000 the TNMN Yearbook includes a river loads analysis, for a limited number of stations and determinants. For load calculation purposes, the target frequency of sampling and analysis is 24/year.

For the computation of the river loads, it is at least necessary to have simultaneous measurements of the river discharge and the water quality parameters. To allow the use of accurate load calculation methods, daily observations of the river discharge are required. Since 1998, these are collected in the TNMN for the main stations.

3.2 Presentation of the data

The data from TNMN have been elaborated before presentation:

- At some occasions the discharge was given for more than one location in the profile (L, M and R), and the numbers were not identical. Sometimes, there were clear typing errors. These were corrected (See Appendix A for details).
- For the variable total phosphorus, sometimes unrealistically high values were encountered, while sometimes the unit was mentioned as mg/kg rather than mg/l. These were corrected (See Appendix A for details).
- For the variable ortho-phosphates, sometimes unrealistically high values were encountered. These were corrected (See Appendix A for details).
- For the variable nitrites, sometimes unrealistically high values were encountered. These were corrected (See Appendix A for details).

- The parameters Total Inorganic Nitrogen (TIN) and Total Oxidised Nitrogen (NOx) have been calculated for those locations and dates where all components of these sum parameters were actually analysed.
- For those locations and dates where the ortho-phosphates concentration exceeds the total phosphorus concentration, the latter has been made equal to the former.
- For stations with multiple sampling locations (L, M and R), the average concentrations have been calculated. The results for sampling days on which not all locations in the profile were actually sampled have been omitted from the analysis.

The results are presented for a number of characteristic locations (see Table 3-1).

Table 3-1: TNMN stations used for data presentation

Station	Locations in profile	River	Distance from mouth (km)	Comments
Jochenstein (D) / Jochenstein (A)	M M	Danube	2204	ds Inn, more data for Austrian station
Wolfsthal (A) / Bratislava (SK)	R M	Danube	1874 1869	ds Morava
Medve (H) / Medvedov (SK)	M M	Danube	1806	inside Gabcikovo area
Komarom (H) / Komarno (SK)	M M	Danube	1768	ds Gabcikovo area
Szob (H)	LMR	Danube	1708	ds Vah, Nitra, Ipel, Hron
Dunafoldvar (H)	LMR	Danube	1560	ds Budapest, only data for M allow analysis for whole period

Station	Locations in profile	River	Distance from mouth (km)	Comments
Hercegszanto (H) /	LMR	Danube	1435	us Drava, Tisa, Sava,
Batina (HR)	M		1429	more data for Hercegszanto
Bezdan (SM)	L		1427	
Dravaszabolcs (H) /	M	/Drava	78	Important tributary,
D.Miholjac (HR)	M			More data for Dravaszabolcs
Bogojevo (SM)	L	Danube	1367	ds Drava
Borovo (HR)	R		1337	
Novi Sad (SM)	L	Danube	1258	
Tiszasziget (H)	LMR	/Tisa	163	Important tributary
Martonos (SM)	R	/Tisa	152	
Novi Becej (SM)	L		66	
Titel (SM)	M		9	
Zemun (SM)	R	Danube	1174	ds Tisa (from discharge data: also ds Sava!)
Zupanja (HR)	MR	/Sava	254	Important tributary, limited information available, station is situated us of the Drina tributary
Jamena (SM)	L	/Sava	195	ds Drina
S.Mitrovica (SM)	L		135	
Sabac (SM)	R		104	
Pancevo (SM)	L	Danube	1155	ds Sava
Banatska Palanka (SM)	L	Danube	1077	us Iron Gates backwater area
Bazias (RO)	LMR		1071	
Tekija (SM)	R	Danube	955	inside Iron Gates backwater area
Radujevac (SM)	R	Danube	851	ds Iron Gates,
Novo Selo (BG) /	LMR		834	more data for Pristol
Pristol (RO)	LMR		834	
Silistra (BG) /	LMR	Danube	375	ds joint BG/RO Danube stretch,
Chiciu (RO)	LMR			more data for Chiciu
Reni	LMR	Danube	132	ds Prut, Siret, us Delta

ds = downstream
us = upstream

3.2.1 River discharges

The TNMN database contains a lot of information regarding the river discharges. For 1996-1997 the discharge data are usually available at the sampling days only. From 1998 onwards, the database contains daily discharge records for a significant number of stations.

These data have been used to produce annual discharges for selected stations over the period 1996-2001.

Figure 3-1 and Figure 3-2 present the results. Since the discharge data for 1996-1997 are not collected on a daily basis, the numbers presented for 1996-1997 are not really yearly averages. The size of the error is small, see Appendix B.

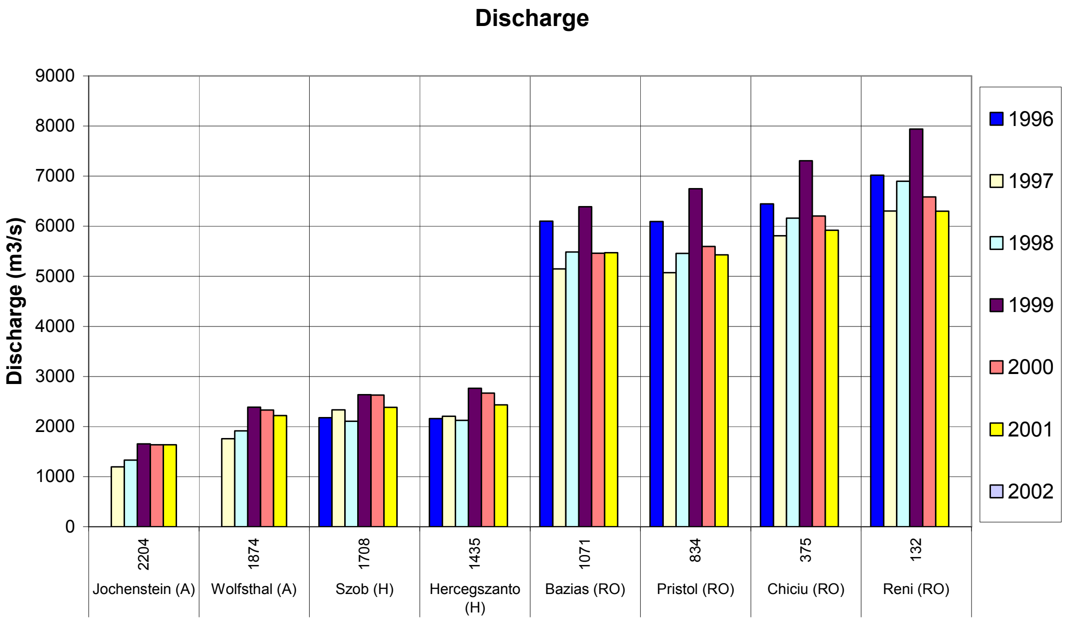

Figure 3-1: Annual discharges at selected stations along the Danube.

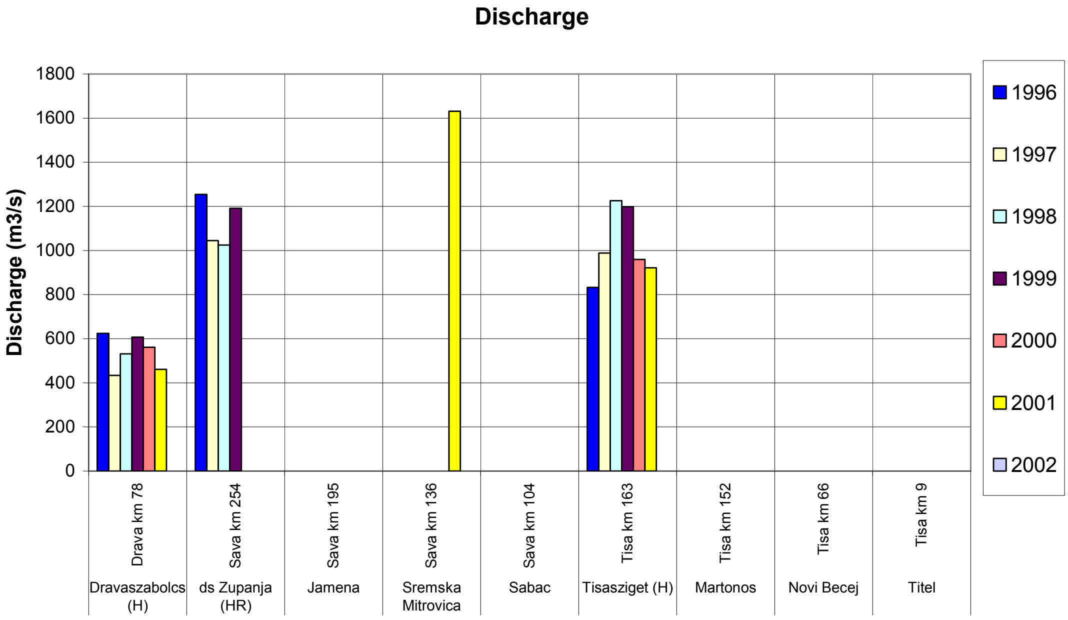

Figure 3-2: Annual discharges at selected stations along the main tributaries.

3.2.2 River concentrations

In order to detect spatial and temporal trends, the available data were used to calculate yearly averaged concentrations:

- the calculations were based on the profile average concentrations for those stations where 3 locations in the profile (L, M and R) are defined;
- the averages were computed in two steps: first a monthly (discharge weighted) average was computed, and next the monthly values were again averaged;
- the results were accepted if more than 9 samples were available in one particular year, while no restrictions were imposed on the distribution of these 9 samples over the year (consequently in some cases the yearly loads are computed even if sampling was done in less than 9 calendar months).

Total Inorganic Nitrogen (sum of ammonium, nitrites and nitrates)

Figure 3-3 shows that the highest values are encountered in the upper Danube (Jochenstein and Wolfsthal). The concentrations become substantially lower towards the Iron Gates (up to Pristol), to increase again in the lower part (Chiciu, Reni). The minimum in the middle part could be due to a conversion to organic nitrogen due to algae blooms, or due to the inflow of water from the Drava-Sava-Tisa. Figure 3-4 shows relatively low concentrations in these tributaries. The information from 2001 for the stations from Serbia-Montenegro is consistent with the information from the other stations, except for the Sava. The data for the Sava stations in Serbia-Montenegro in 2001 indicate a decrease in the lower Sava.

Organic Nitrogen

Organic nitrogen is not sampled frequently enough at a sufficient number of stations to provide a coherent picture of the spatial gradients. Moreover, large discrepancies exist between the Slovak and Hungarian stations along their common border stretch of the Danube. Figure 3-5 and Figure 3-6 provide an overview of all available data.

Total Nitrogen (sum of Total Inorganic and Organic Nitrogen)

Total nitrogen is not sampled frequently enough at a sufficient number of stations to provide a coherent picture of the spatial gradients. Again, significant discrepancies exist between the Slovak and Hungarian stations along their common border stretch of the Danube. Therefore, the data are not presented.

Total Phosphorus

Figure 3-7 shows that the concentration of total phosphorus tends to increase in a downstream direction up to the station Hercegszanto (situated upstream of the confluences of the Drava-Tisa-Sava). Further downstream, from the Iron Gates onwards to the Danube, the concentrations drop markedly. The concentrations in the Tisa at Tiszasziget are significantly higher than the concentrations in the Danube (Figure 3-8). The data for the Tisa stations in Serbia-Montenegro in 2001 indicate a strong decrease in the lower Tisa to levels similar to those in the Danube. The limited data for the Sava indicate that the concentrations in this tributary could be significantly higher than the concentrations in the Danube. The difference between Bazias and Pristol (Iron Gates section) is small, suggesting a small overall retention in the Iron Gates.

The information from 2001 for the stations from Serbia-Montenegro is consistent with the information from the other stations, except for the Sava (as mentioned above).

Suspended Solids

Figure 3-9 shows a relatively low average concentration up to Hercegszanto, with higher values in some years at some stations. At Bazias the concentrations suddenly increase, while they decrease again towards the Delta. Figure 3-10 shows very high concentrations in the Tisa, which could well be responsible for the sudden increase in the Danube between Hercegszanto and Bazias. The concentrations in the Drava and Sava are relatively small. The difference between Bazias and Pristol (Iron Gates section) is small, suggesting a small overall retention in the Iron Gates.

The information from 2001 for the stations from Serbia-Montenegro is consistent with the information from the other stations.

Chlorophyll-α

Chlorophyll-α is not sampled frequent enough at a sufficient number of stations to provide a complete picture of the spatial gradients. Nevertheless some observations can be made. Figure 3-11 shows a gradual increase from the German part of the Danube up to Dunafoldvar (from 5 to 25 μg/l). Figure 3-12 illustrates that the Drava river shows small concentrations (about 5 μg/l) and the Tisa moderate values (about 15 μg/l). In the lower Danube section few data are available. From Chiciu onwards the values are well below 5 μg/l.

Silicates

Silicates are not sampled frequent enough at a sufficient number of stations to provide a complete picture of the spatial gradients. Data are available for the station Borovo in 1998-1999 (8.9-11.5 mg SiO_2/l) and for a number of Romanian stations in 2002 (7.7-10.3 mg SiO_2/l).

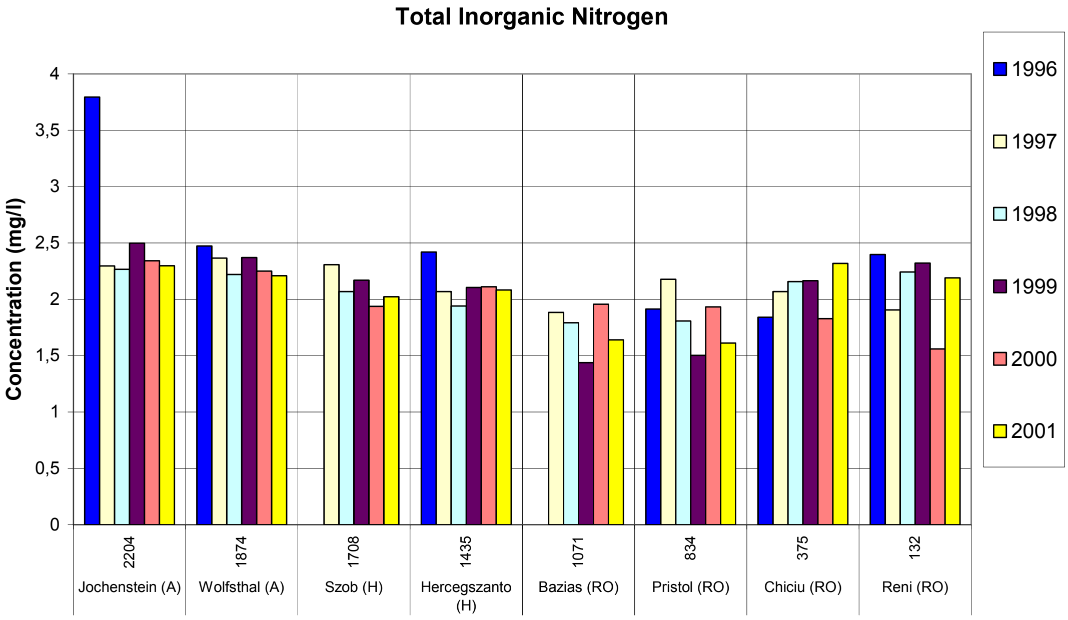

Figure 3-3: Yearly averaged concentrations of TIN at selected stations along the Danube.

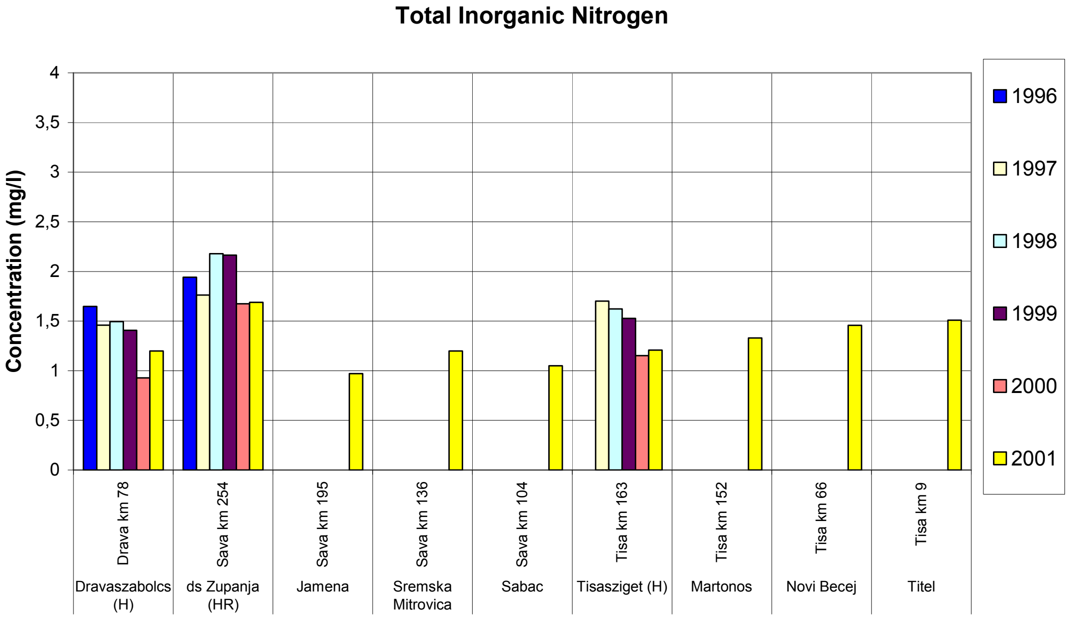

Figure 3-4: Yearly averaged concentrations of TIN at selected stations along the main tributaries.

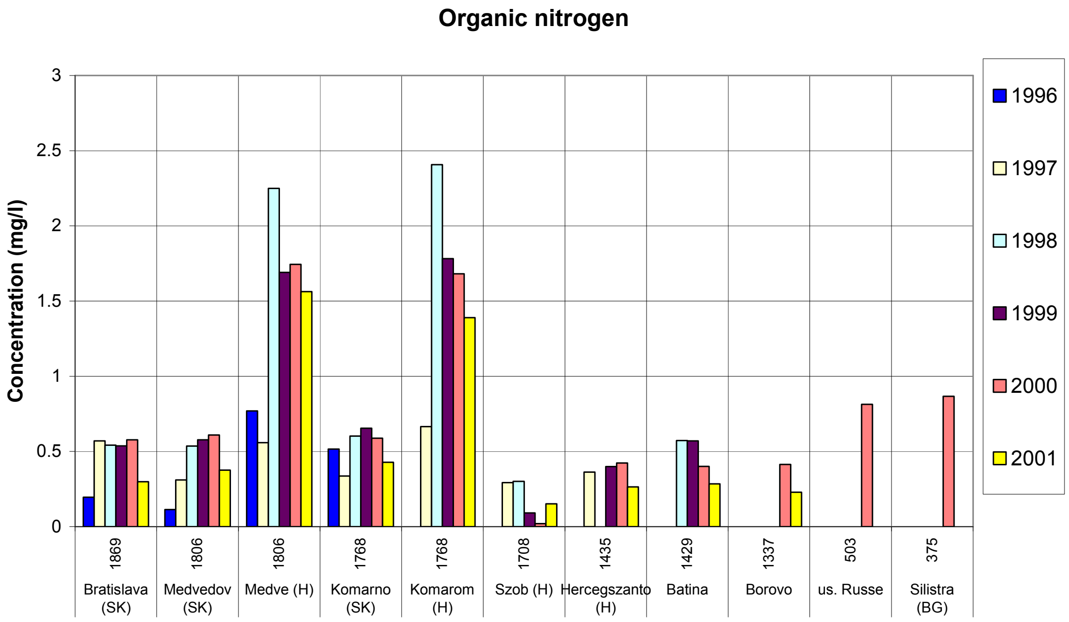

Figure 3-5 Yearly averaged concentrations of Org.N at stations along the Danube.

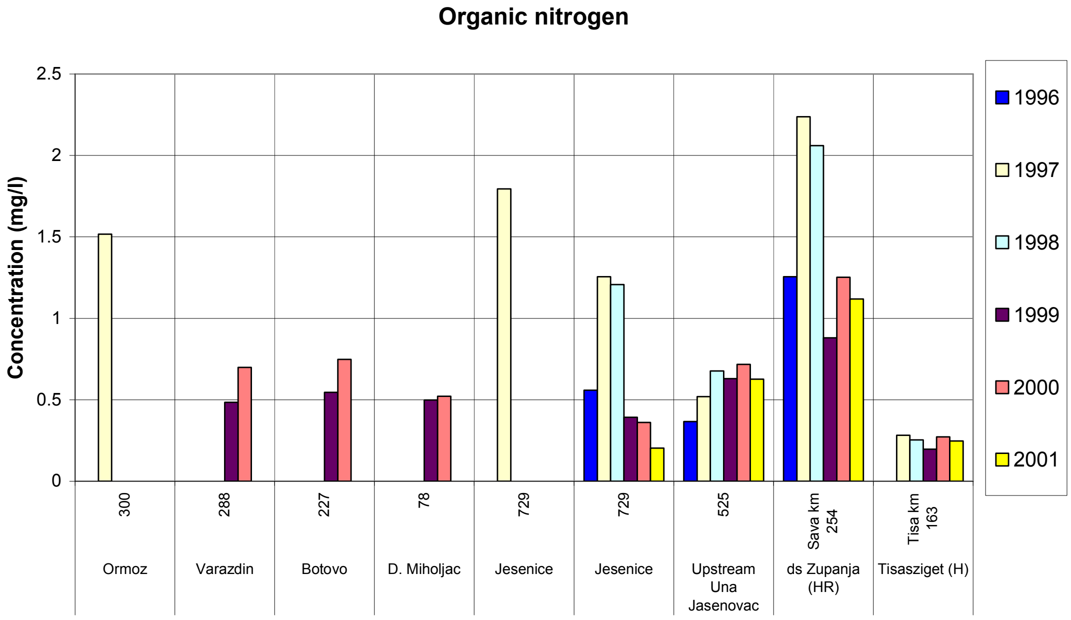

Figure 3-6 Yearly averaged concentrations of Org.N at stations along the main tributaries.

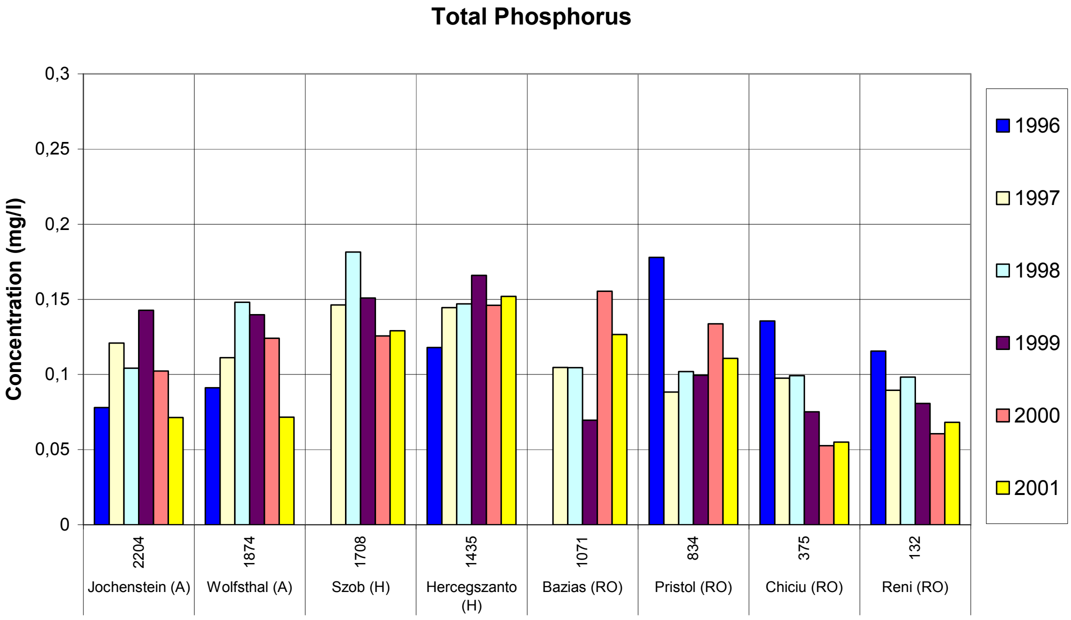

Figure 3-7: Yearly averaged concentrations of total P at selected stations along the Danube.

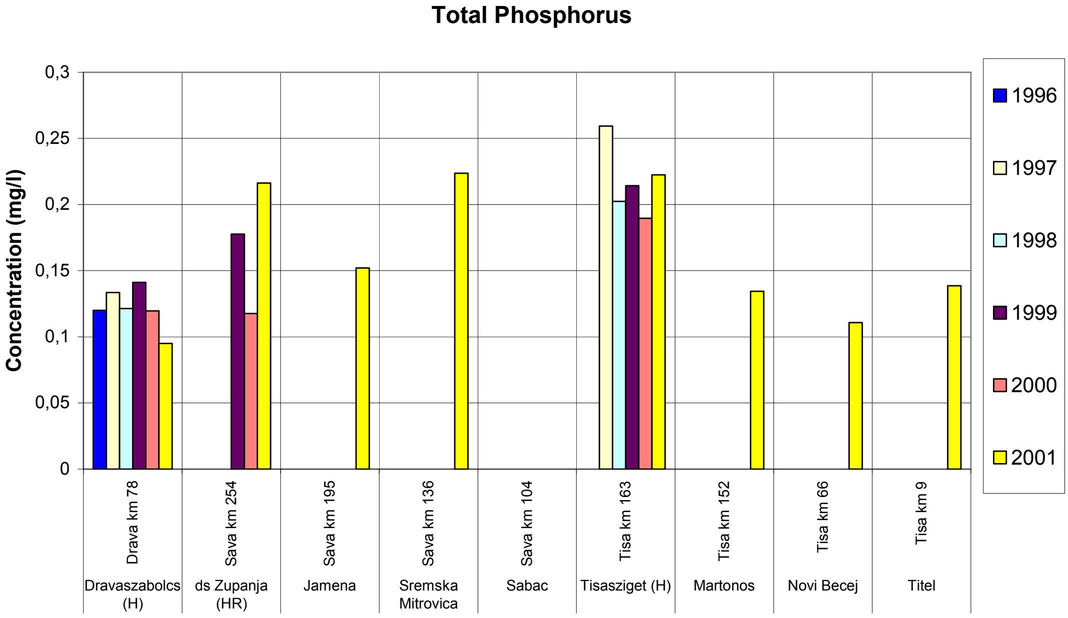

Figure 3-8: Yearly averaged concentrations of total P at selected stations along the main tributaries.

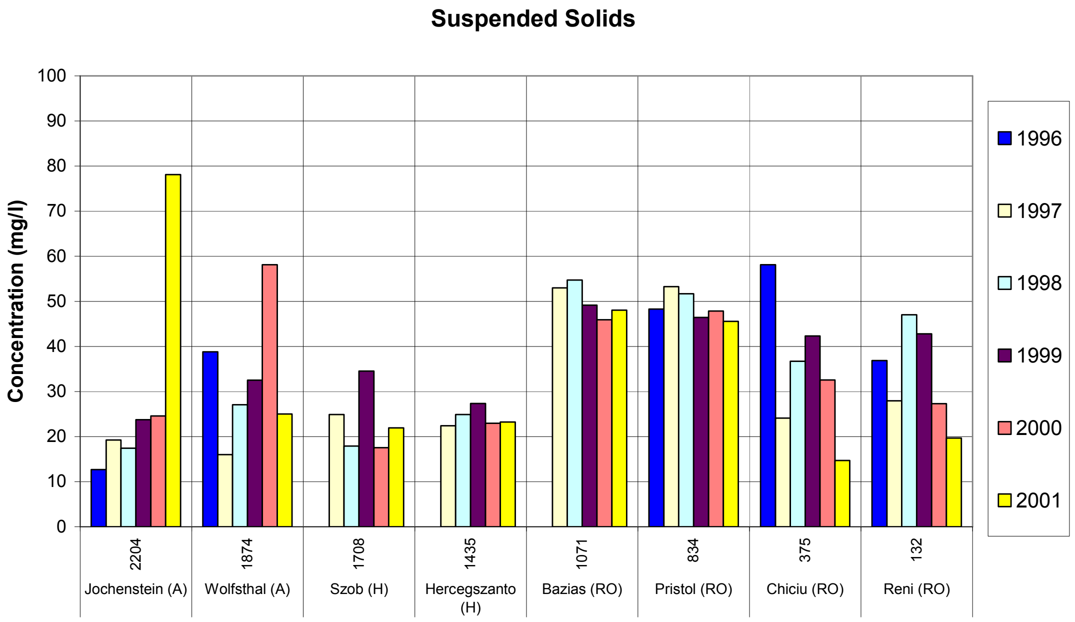

Figure 3-9: Yearly averaged concentrations of Suspended Solids at selected stations along the Danube.

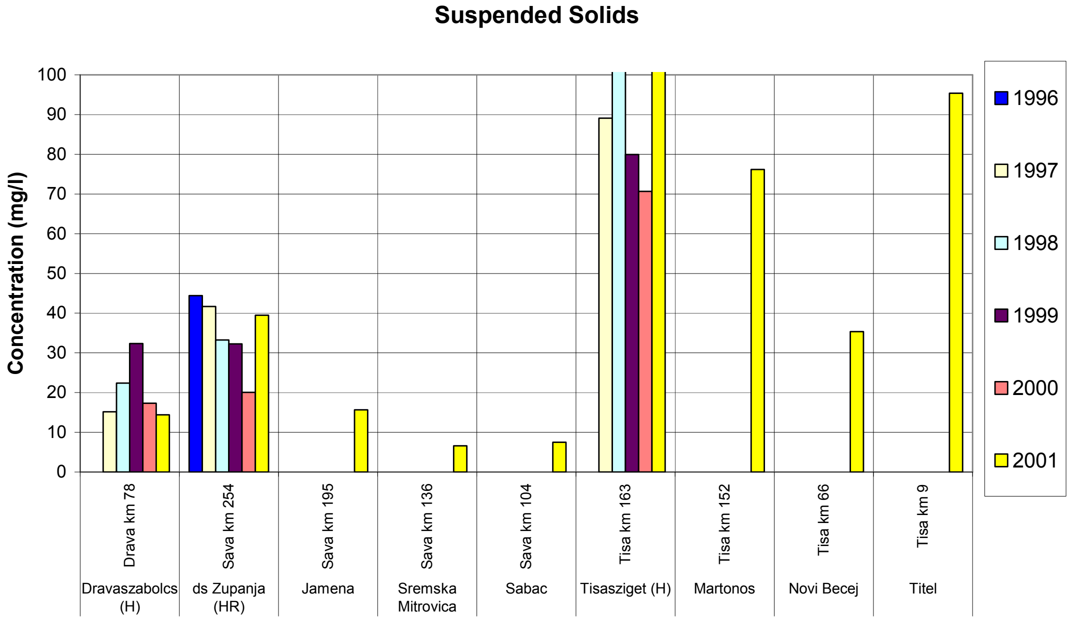

Figure 3-10: Yearly averaged concentrations of Suspended Solids at selected stations along the main tributaries.

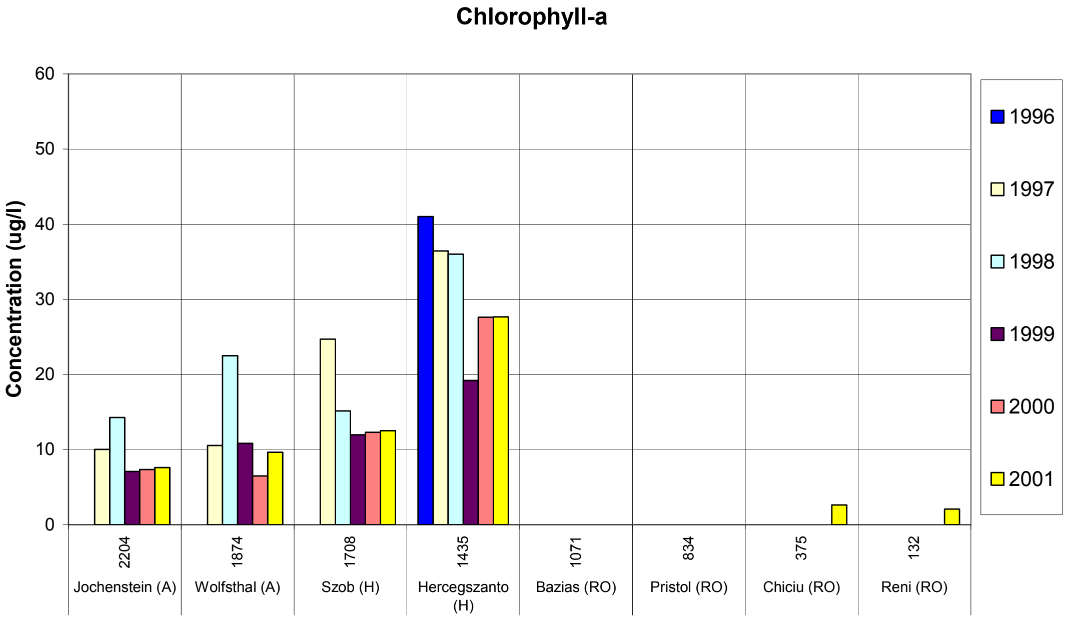

Figure 3-11: Yearly averaged concentrations of Chlorophyll-α at selected stations along the Danube.

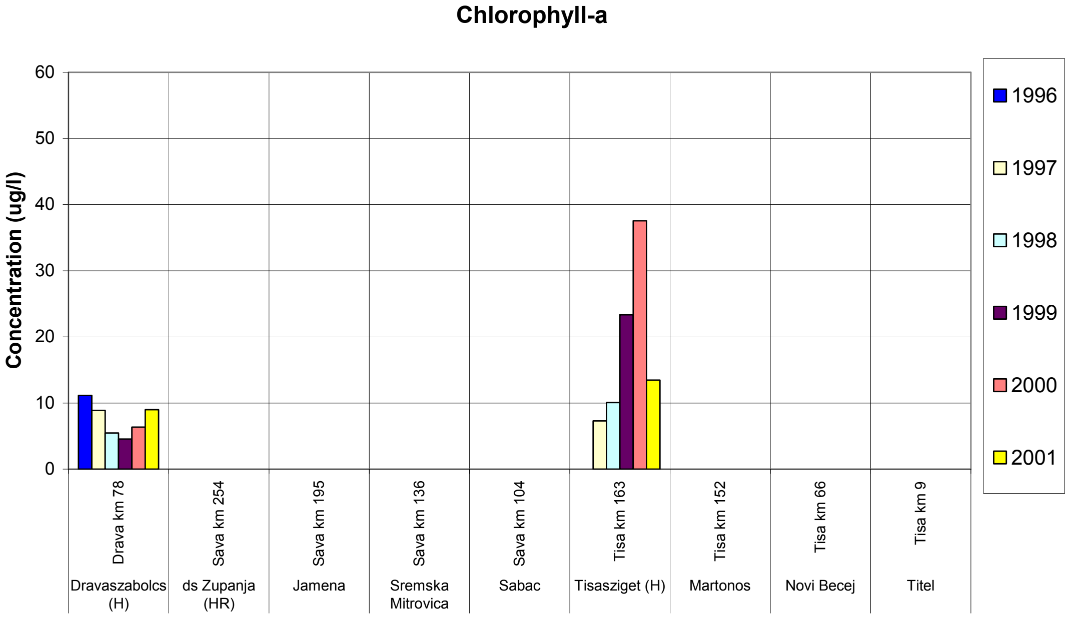

Figure 3-12: Yearly averaged concentrations of Chlorophyll-α at selected stations along the main tributaries.

3.2.3 River loads

The available data were used to carry out load calculations. The method used was the one agreed by the Danube countries under the umbrella of the ICPDR (ICPDR, 2000). The following assumptions were made:

- the load calculations were based on the profile average concentrations for those stations where 3 locations in the profile (L, M and R) are defined;
- the load calculations were carried out per year;
- the load calculations were accepted if more than 9 samples were available, no restrictions were imposed however on the distribution of these 9 samples over the year: consequently in some cases the yearly loads are computed even if sampling was done in less than 9 calendar months.

There are two ways to compute the river loads: one using the river discharge data on the sampling days only, and one using daily discharge records. Although the latter is more accurate, it can not be applied for the years 1996-1997 since for those years no daily discharge records are available. Because temporal coverage is important, we have used the former method. For reference however, we have compared the results of both methods (see Appendix B). The conclusion is that the results from both methods correlate very well for total P, TIN and suspended solids ($r^2 > 0.99$). The differences between the methods are usually smaller than 5%, with the highest differences occurring for suspended solids.

The results are presented for a number of characteristic locations (see Table 3-1).

Nitrogen loads (TIN)

Figure 3-13 and Figure 3-14 present the calculated river loads in the Danube and in its main tributaries. The river TIN loads show a spatial gradient very similar to the river discharge. There is however a larger year-to-year variation, especially in the lower Danube.

Phosphorus loads (TP)

Figure 3-15 and Figure 3-16 present the calculated river loads in the Danube and in its main tributaries. The river TP loads show a different spatial gradient from the river discharge and the nutrient loads. The loads show a maximum downstream of the inflowing tributaries Drava, Tisa and Sava and decrease over the Bulgarian-Romanian Danube stretches. Again, there is a very substantial year-to-year variation.

The spatial distribution of the phosphorus loads shows a strong anomaly in 2000-2001: the loads in Chiciu and Reni are dramatically lower than the loads of the preceding years. This drop does not occur at the upstream stations. In other words: in 2000-2001 there is a strong decrease of the calculated river load downstream of Pristol. This decrease can not be observed in the years 1996-1999.

Loads of suspended solids

Figure 3-17 and Figure 3-18 present the calculated river loads in the Danube and in its main tributaries. The river load of suspended solids shows a very strong increase downstream of the inflowing tributaries Drava, Tisa and Sava. Figure 3-18 shows that the Tisa may well be responsible for the sudden increase of the Danube river load in the middle section. Again, there is a very substantial year-to-year variation.

The spatial distribution of the suspended solids loads shows a strong decrease of the calculated river load downstream of Pristol in 1997, 2000 and 2001. This decrease can not be observed in the other years.

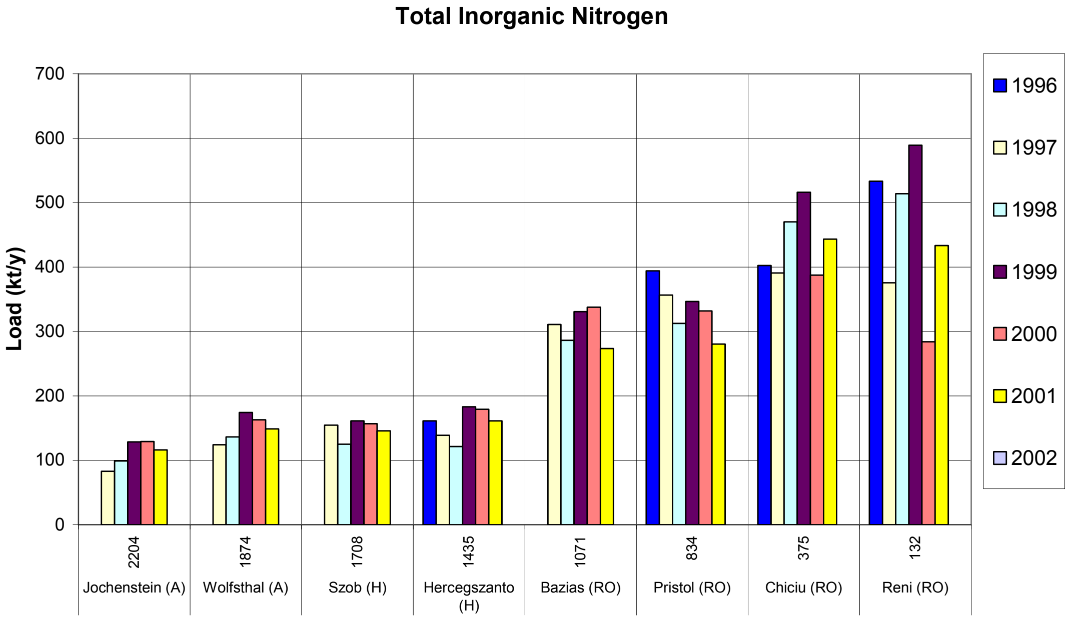

Figure 3-13: Annual loads of Total Inorganic Nitrogen at different stations along the Danube.

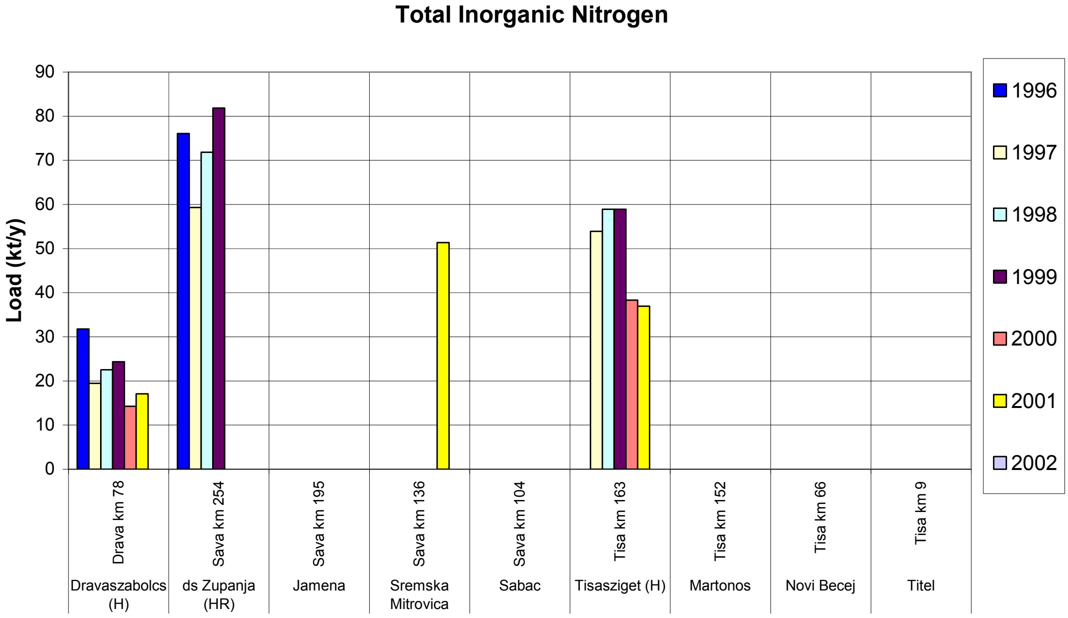

Figure 3-14: Annual loads of Total Inorganic Nitrogen at different stations along the main tributaries.

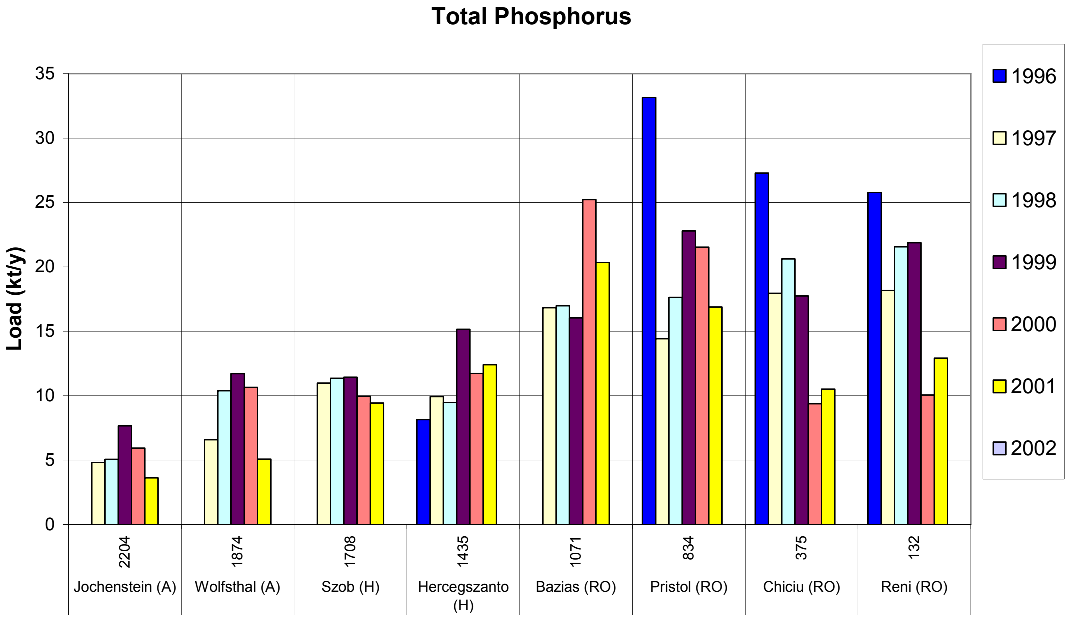

Figure 3-15: Annual loads of Total Phosphorus at different stations along the Danube.

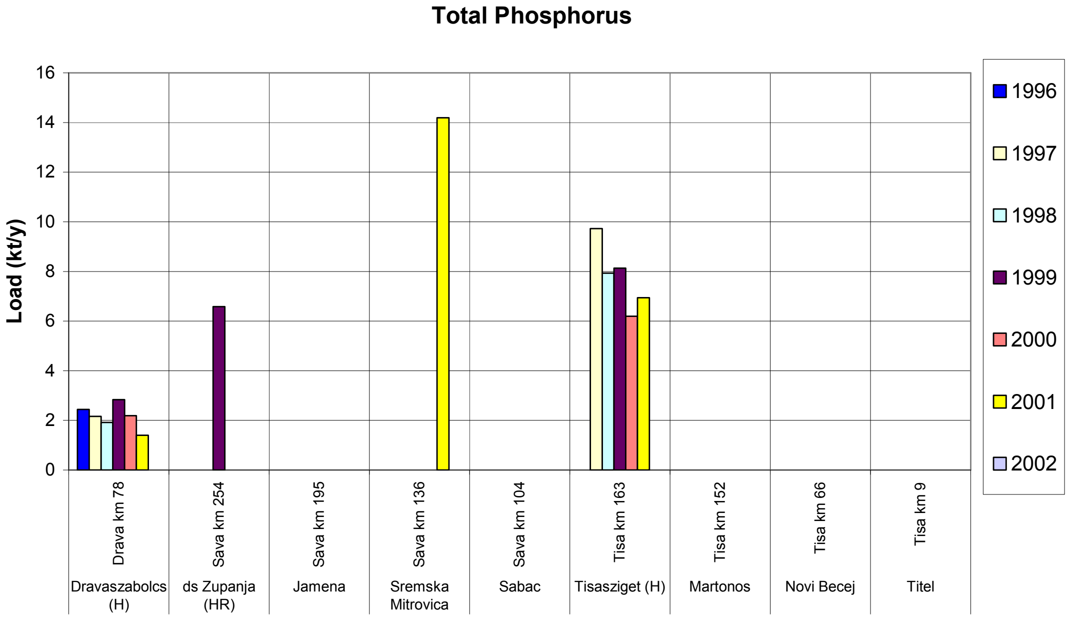

Figure 3-16: Annual loads of Total Phosphorus at different stations along the main tributaries.

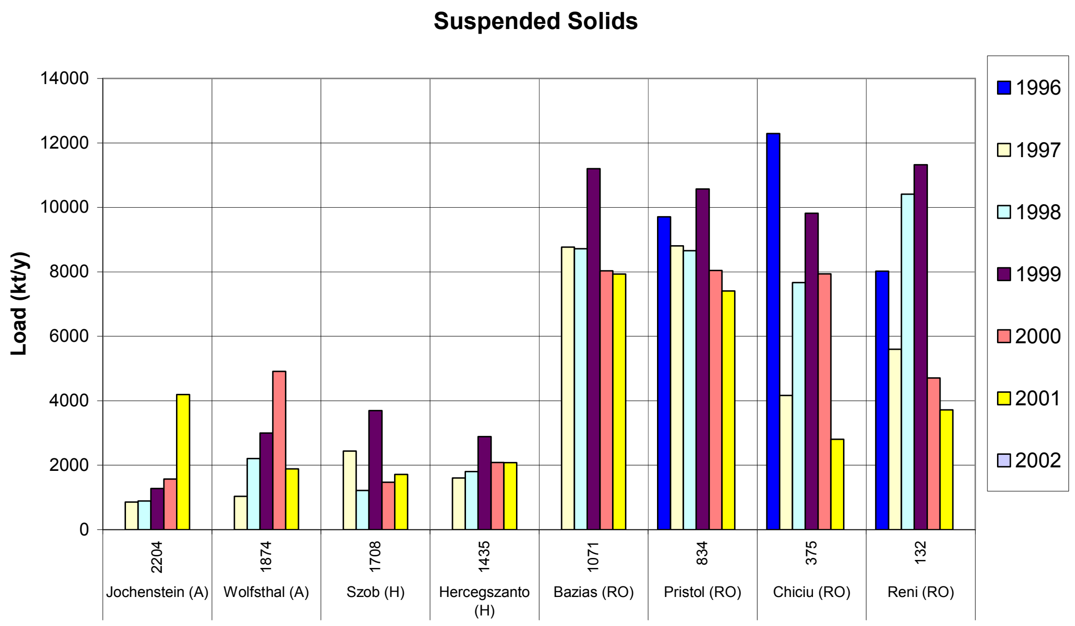

Figure 3-17: Annual loads of Suspended Solids at different stations along the Danube.

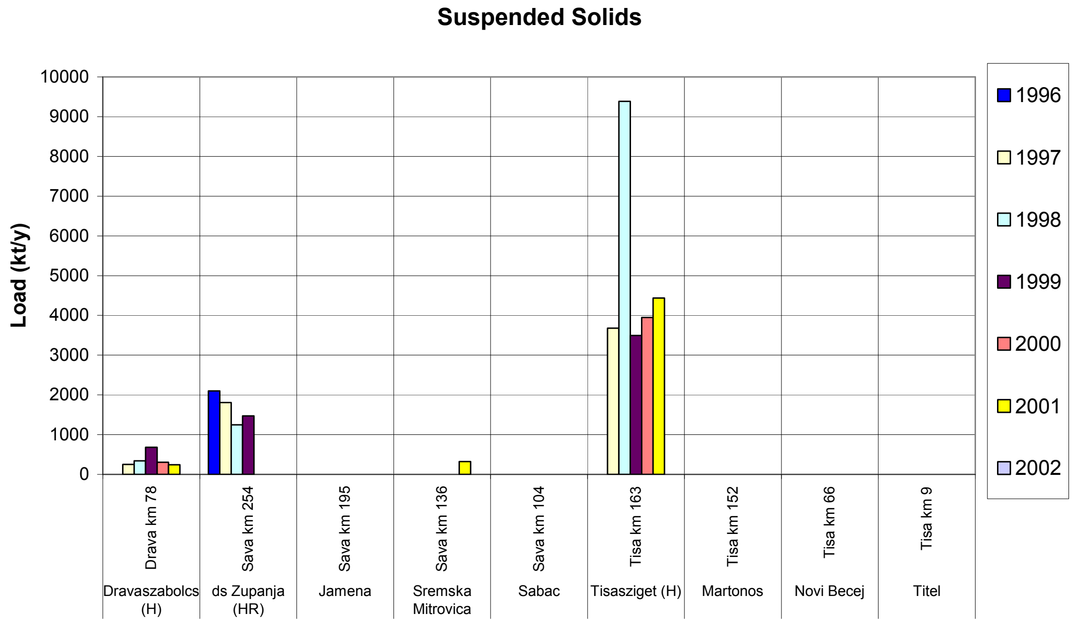

Figure 3-18: Annual loads of Suspended Solids at different stations along the main tributaries.

3.3 Discussion of the data

3.3.1 Sampling and analysis of total phosphorus

During the analysis of the data we found with regard to the sampling and analysis of total phosphorus:

- It could not be verified that the analysis of total P is done on unfiltered and homogenised samples.
- The methods of analysis are not always reported.
- The analysis methods reported to be used in the Czech Republic, Slovakia, Bulgaria, Germany, Moldova, Slovenia and Ukraine do not mention an explicit digestion or mineralization step, which implies that possibly certain species of P are not included in the analysis results.
- No reference is made to the desorption of sorbed fraction.
- The analysis methods reported are in all occasions of a spectrometric or spectrophotometric nature, except those used in the Romanian laboratories (colorimetry).

3.3.2 Water and nutrient balances

The available data have been used to produce water and nutrient balances for the network sections listed in Table 3-2.

Table 3-2: River network sections used to calculate water and nutrient balances.

Network section	**Method of computation**
Upper and middle Danube (German, Austrian, Slovakian and Hungarian stretches)	From data at Hercegszanto (km 1435)
Drava river	From data at Dravaszabolcs (km 78)
Tisa river	From data at Tiszasziget (km 163) , supported by data from Serbian stations for 2001
Sava river (+ Velika Morava)	Discharge computed from a water balance (Bazias, minus Upper/Middle Danube, minus Drava, minus Tisa) Nutrient loads estimated from the river discharge and the concentration estimated from data at Zupanja supported by data from Serbian stations for 2001
Serbian section (km 1430-1070) with inflows of Drava, Sava and Tisa	Discharge assumed zero Nutrient balances from the difference between Bazias (km 1071) and Hercegszanto (km 1435)
Iron Gates section	From the difference between Pristol (km 834) and Bazias (km 1071)
Lower Danube (Bulgaria, Romania)	From the difference between Reni (km 132) and Pristol (km 834)

Figure 3-19 presents the results from the water balance in absolute amounts, while Figure 3-20 presents the results relative to the average over the period 1996-2001.

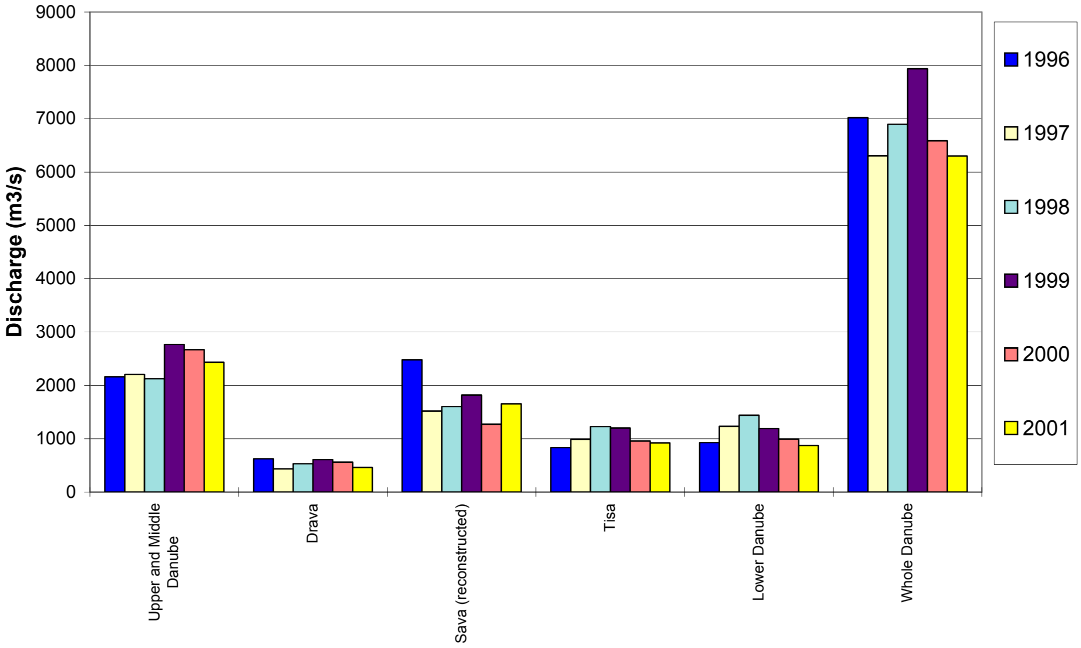

Figure 3-19: Discharges from different sections of the river network (absolute values).

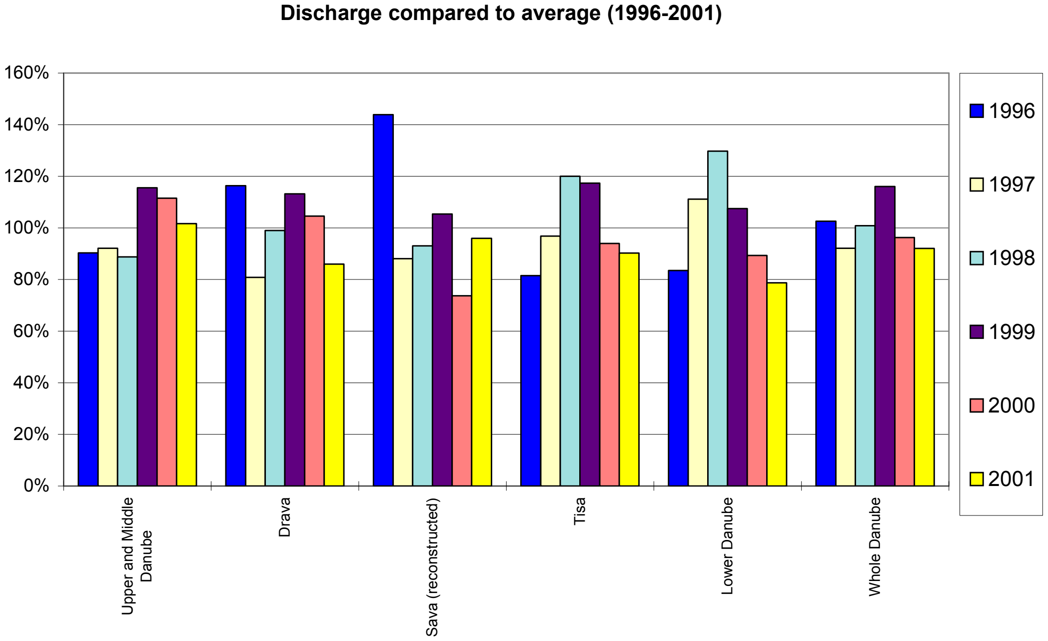

Figure 3-20: Discharges from different sections of the river network (values relative to the average over 1996-2001).

The average Danube discharge is 6842 m3/s. Compared to the long term yearly average of 6550 m3/s reported by Stancik ea. (1988) 1996-2001 is a relatively wet period in the Danube basin. The upper and middle Danube and its tributaries, upstream of the Hungarian-Croatian border contribute 35% (roughly 1/3), the large tributaries Drava, Sava, Tisa and

Velika Morava contribute 48% (roughly ½) while the lower Danube contributes 17% (roughly 1/6).

For the Danube as a whole, the individual years deviate less than 10% from the average, except for 1999, which has a 16% higher flow than the average. Looking at the sub-sections we see difference pictures. The upper and middle Danube has lower discharges in 1996-1998 and higher discharges in 1999-2001. The Drava and Sava show similar characteristics: the years 1996 and 1999 have the highest flows. The Tisa and the lower Danube also have similar characteristics: the highest discharges occurred in 1997-1999.

Figure 3-21, Figure 3-22 and Table 3-3 present the balances for Total Inorganic Nitrogen and Total Phosphorus.

Table 3-3: Results from the water and nutrient balances computations.

River section	**Water balance (m3/s) (1996-2001)**	**Balance of TIN (kt/y) (1997-2001)**	**Balance of TP (kt/y) (1997-2001)**
Upper and middle Danube	2392	157	11.7
Drava	536	20	2.1
Sava (reconstructed)	1725	70 to 95[1]	8.4
Tisa	1021	49	5.2 to 7.8[2]
Serbia	0	-13 to +12	-8.4 to –11.0
Iron Gates	57	18	-0.4
Lower Danube	1110	134	-1.7
Whole Danube	6842	460	16.9

The TIN balance demonstrates a consistent picture of the catchment. The contributions from the Upper/Middle Danube and from the large tributaries reflect more or less their contribution to the river flow. As expected, the contribution of the Iron Gates area is small. The fact that it is positive should not be given too much attention: the value is probably insignificant in view of the limited accuracy of the computed loads. The average contribution from the lower catchment is relatively high compared to its contribution to the river discharge. This is consistent with the observation that the concentrations increase in this part of the river. The balance over the Serbian section does not present a significant result, due to the large uncertainty in the Sava load.

The contribution from the lower Danube varies very strongly between the individual years. This contribution is computed as the difference between the computed river loads at Reni and at Pristol, and is influenced by errors in the computed loads at both stations. These errors probably have a random component. Therefore, the variation between the years is probably an artefact stemming from the limited accuracy of the results at Reni and Pristol.

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[1] *The value 95 is obtained by adopting the average concentration at Zupanja, the value 70 is obtained by adopting a concentration 0.5 mg/l lower than the concentration at Zupanja (assumption based on Serbian data for 2001, see Figure 3-4).*

[2] *The value 7.8 is obtained by adopting the load at Tiszasziget, the value 5.2 is obtained by applying a reduction of 1/3 (based on the observed concentration decrease over the Serbian stretch of the Tisa in 2001, see Figure 3-8).*

The TP balance shows a very confusing picture. The contributions from the Upper/Middle Danube and from the large tributaries reflect more or less their contribution to the river flow. In this case, the Serbian section is responsible for a substantial retention (about 1/3 of the incoming load). The Iron Gates section does not show a significant change of the river load. This is unexpected in view of earlier studies reporting the Iron Gates area to be a major sink of phosphorus (van Gils, 1999). The average contribution from the lower catchment is negative. This is difficult to understand. It will be studied in detail below.
Many parts of the balance vary strongly between the individual years. This is the result of the limited accuracy of the load computations.

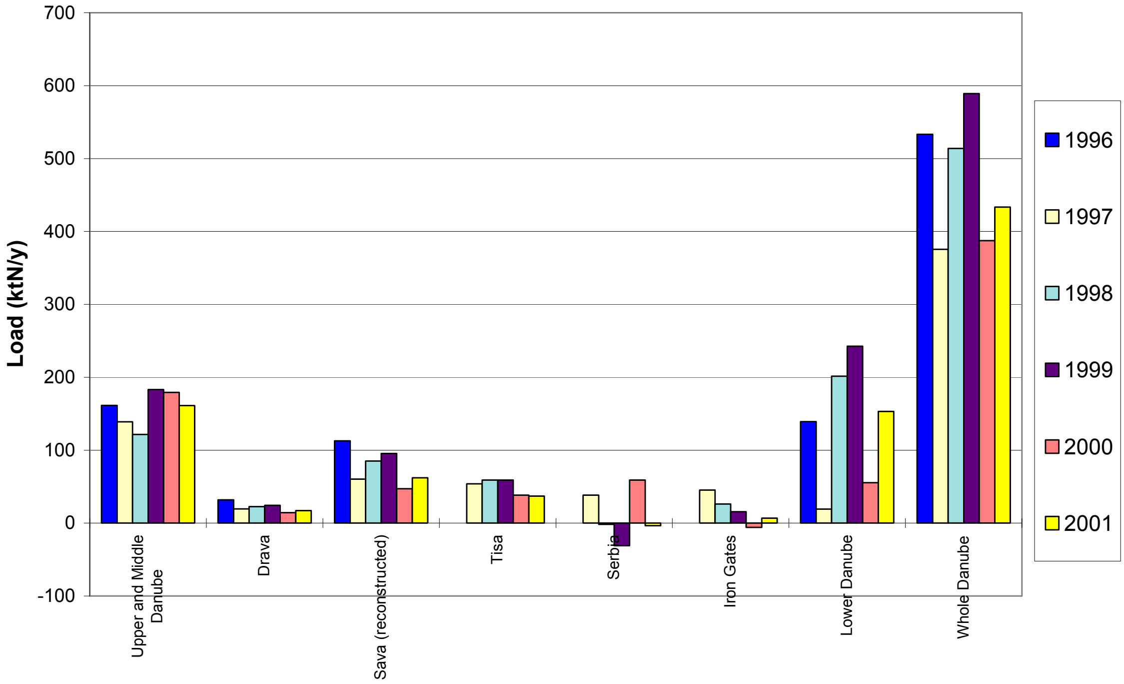

Figure 3-21: Nitrogen loads from different sections of the river network.

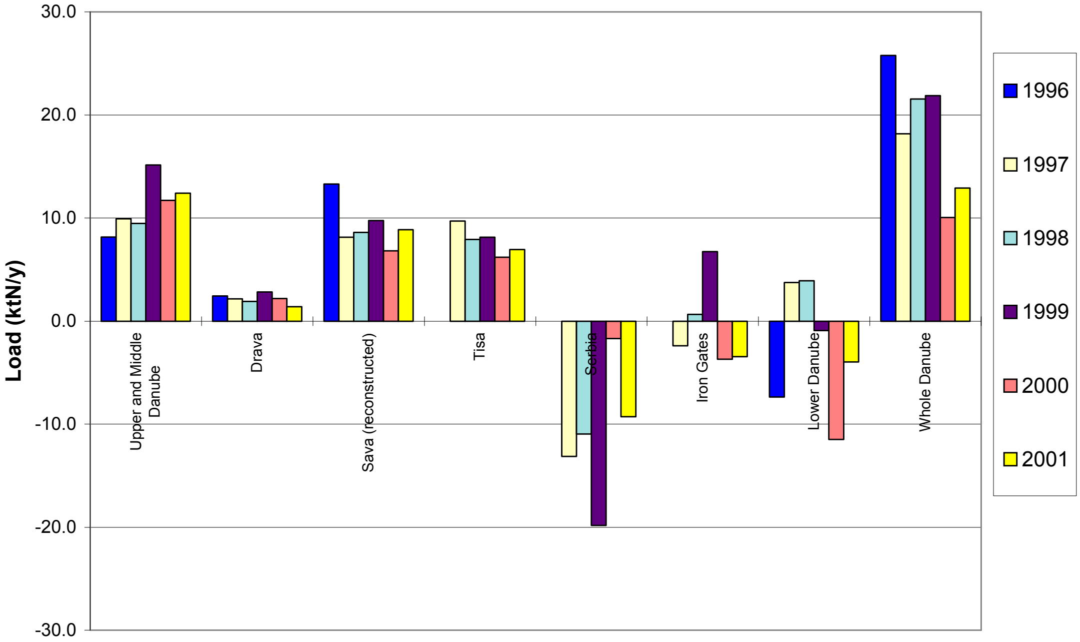

Figure 3-22: Phosphorus loads from different sections of the river network.

3.3.3 Detailed analysis of the Gabcikovo section

The Gabcikovo section of the Danube (between Bratislava and Komarno/Komarom) is of specific interest. Due to the construction of a dam and a power station with inlet and outlet channels, the river has been altered and a potential retention site for nitrogen and phosphorus has been created. The section has been studied by checking the data for the stations listed in Table 3-4.

Table 3-4: Stations analysed along the Gabcikovo section.

Station	**Locations in profile**	**River**	**Distance from mouth (km)**	**Comments**
Wien-Nussdorf (A)	R	Danube	1935	
Wolfsthal (A) / Bratislava (SK)	R M	Danube	1874 1869	ds Morava
Medve (H) / Medvedov (SK)	M M	Danube	1806	ds part of Gabcikovo area
Komarom (H) / Komarno (SK)	M M	Danube	1768	ds Gabcikovo
Szob (H)	LMR	Danube	1708	ds Vah, Nitra, Ipel, Hron

The nitrogen loads do not show a consistent trend over the Gabcikovo section. Probably, the spatial changes of the load are small compared to the inaccuracies introduced by the sampling and analysis and the load calculation.

While analyzing the phosphorus data, a remarkable difference was encountered between the computed loads at the stations Bratislava, Komarno and Medvedov on one hand, and the stations Wolfsthal, Komarom and Medve on the other hand. Figure 3-23 demonstrates this difference. The average load over the years 1997-2001 is about 1/3 lower at the Slovakian stations as compared to the Austrian/Hungarian stations. Figure 3-23 also shows that the annual discharges also show some differences, but that these are much smaller. The differences in the computed loads therefore have to be the result of differences in the observed concentrations.

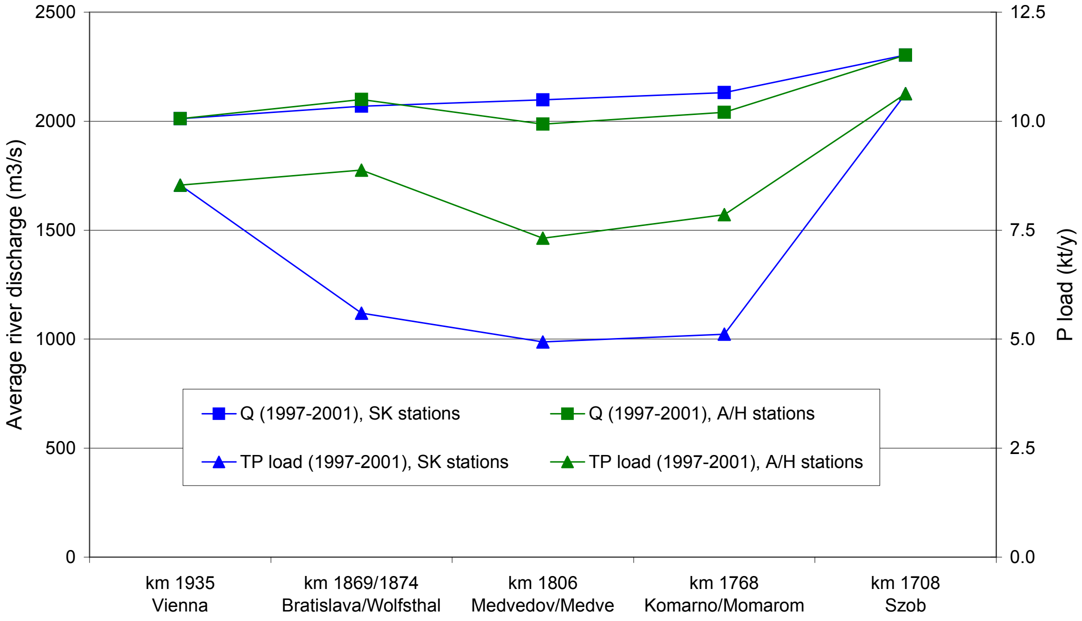

Figure 3-23: Computed river loads of total phosphorus and computed annual river discharges along the Danube (km 1935-1708).

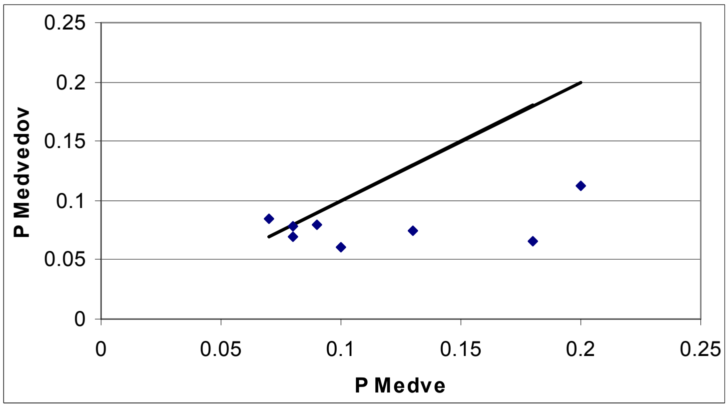

Figure 3-24: Relation between observed concentrations at Medve and Medvedov in 1999 (dates of sampling are identical).

Figure 3-24 illustrates the differences in the observed concentrations in 1999 at the stations Medve (H) and Medvedov (SK). According to the TNMN database, both stations take their samples at the middle of the river section, while in 1999 even the sampling dates were identical. The average concentration at Medvedov is substantially lower than that at Medve, while the correlation between the two is poor.

The data from Vienna and Szob have been used to further analyse the problem.
Accepting the values from the Austrian/Hungarian stations would imply accepting a small decrease (about 10%) of the river P loads between Wolfsthal and Komarom and a distinct increase (about 30%) between Komarom and Szob. The small decrease could be caused by retention in the Gabcikovo area, while the increase can be attributed to the inflow of P from some smaller tributaries from Slovakia, which cause an increase of the annual discharge of about 10%.
Accepting the values from the Slovakian stations would imply accepting a substantial decrease (about 35%) of the river load between Vienna and Bratislava, a small decrease (about 10%) of the river loads between Bratislava and Komarno and a distinct increase (about 100%!!) between Komarno and Szob. There is no explanation for the decrease between Vienna and Bratislava. The increase of 100% due to the inflow of the Slovakian tributaries, which cause an increase of the annual discharge of only 10%, is not realistic.

From the current analysis we derive the conclusion that the concentrations of total phosphorus measured at the Danube stations of Bratislava, Medvedov and Komarno are not representative for the Danube. We expect that this is the result of the sampling and analysis. Possible explanations are the filtering or homogenisation of the samples, or the digestion step during the analysis.

3.3.4 Detailed analysis of the Iron Gates and the Lower Danube sections

Above we have discussed that some of the available information for the Lower Danube section does not seem to be consistent: there seems to be a very small or even negative load of total phosphorus from this section. To further analyse this, we check the data for the stations listed in Table 3-5

Table 3-5: Stations used for the analysis of the Lower Danube section.

Station	Locations in profile	River	Distance from mouth (km)	Comments
Novo Selo (BG) / Pristol (RO)	LMR LMR	Danube	834	ds Iron Gates
Svishtov (BG)	MR	Danube	554	
Russe (BG)	MR	Danube	503	
us Arges (RO)	LMR	Danube	432	
Silistra (BG) / Chiciu (RO)	LMR LMR	Danube	375	
Reni	LMR	Danube	132	

We will focus on the analysis of the concentrations, since these are responsible for the possible inconsistencies. Figure 3-25 , Figure 3-26 and Figure 3-27 show the yearly averaged concentrations of TIN, TP and suspended solids.

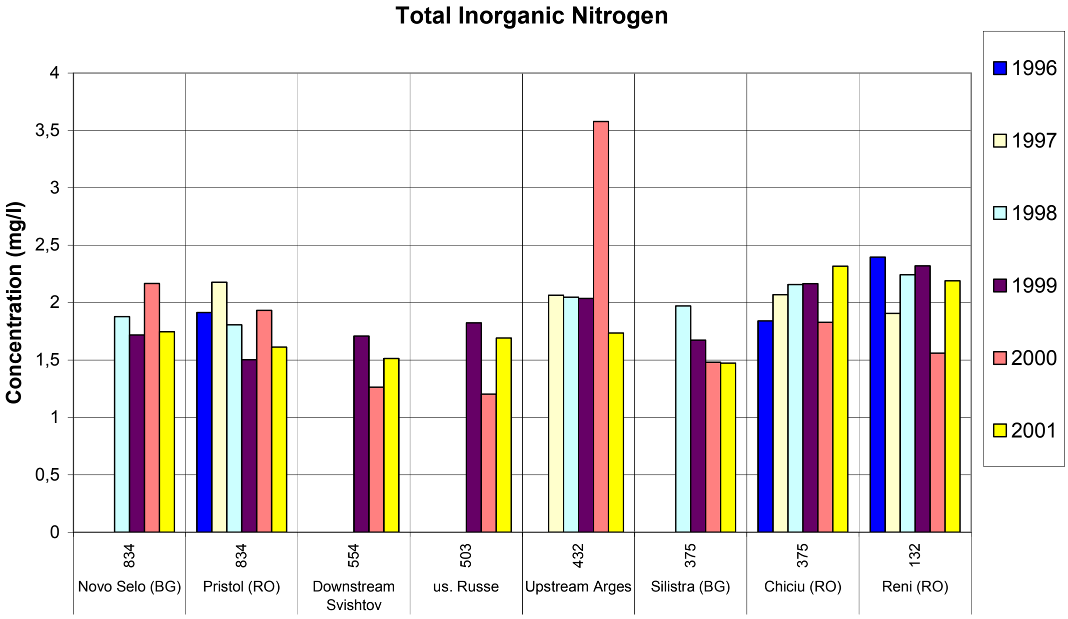

Figure 3-25: Annual averages of the concentrations of TIN along the Lower Danube.

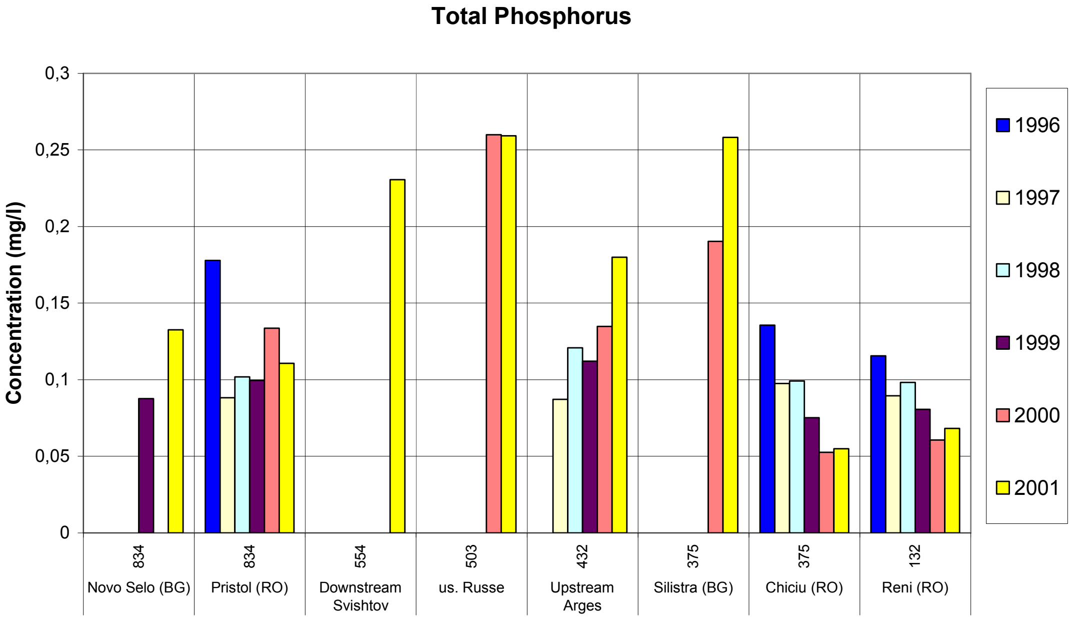

Figure 3-26: Annual averages of the concentrations of TP along the Lower Danube.

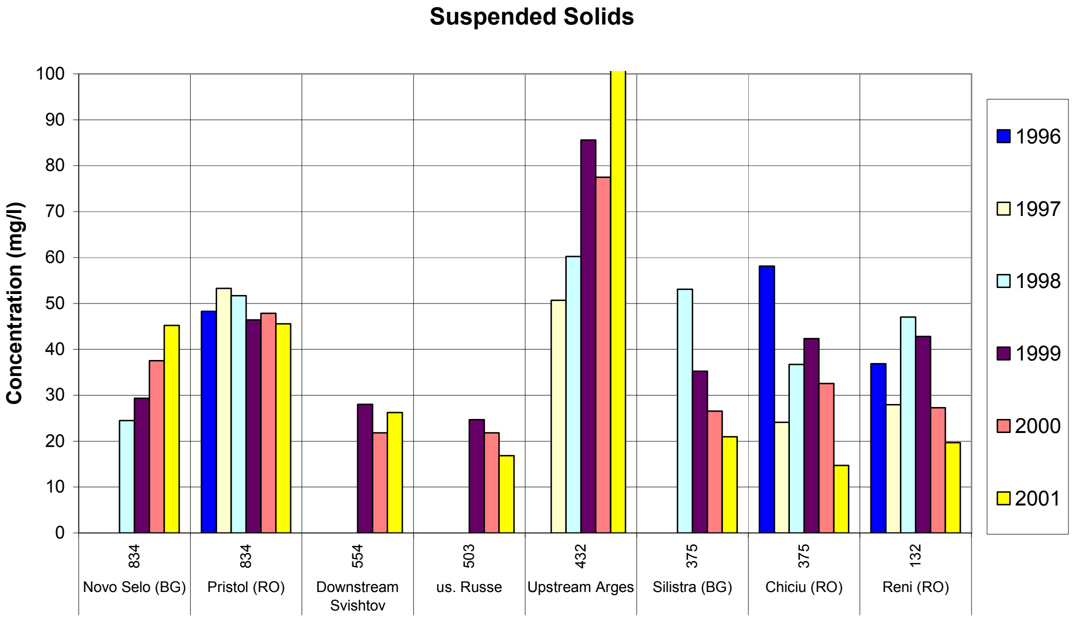

Figure 3-27: Annual averages of the concentrations of Suspended Solids along the Lower Danube.

The data for TIN seem reasonably consistent. The data at the opposite stations Pristol (RO) and Novo Selo (BG) are more or less equivalent. However, the concentrations measured at Silistra (BG) are systematically lower than those at the opposite Chiciu (RO) station. Looking at the whole profile downstream of Pristol/Novo Selo, it could be argued that the Bulgarian stations Svishtov, Russe and Silistra provide lower concentrations than the Romanian stations us Arges, Chiciu and Reni. The station us Arges shows very high concentrations in 2000.

The data for suspended solids also seem reasonably consistent, except for the station us Arges, which shows exceptionally high concentrations in 1999-2002. These high values are not observed at any other station. This time the data at the opposite stations Pristol (RO) and Novo Selo (BG) show systematic differences, while the data at the opposite stations Chiciu (RO) and Silistra (BG) are more or less equivalent.

The data for total phosphorus show significant inconsistencies. The station us Arges shows exceptionally high concentrations in 1999-2002. Again, these high values are not observed at any other station. The data at the opposite stations Pristol (RO) and Novo Selo (BG) are equivalent. There are very strong systematic differences however at the opposite stations Chiciu (RO) and Silistra (BG), for the years 2000-2001 when sufficient samples were taken at both stations. The latter shows yearly average concentrations which are 4 to 5 times higher (!) than the former.

Based on these observations, we conclude that the computed river loads on the Danube stations from Bazias to Reni are possibly too low. This may be caused by the fact that one or more fractions of total phosphorus are not included in the numbers, due to the sampling and analysis process.

Next, we conclude that it is highly unlikely that the Serbian section retains an amount of P in the order of 10 kt/y. If we assume that the average computed river load in Bazias is too low by 9.7 kt/y (34%), it follows that the retention is actually taking place in the Iron Gates section. The latter hypothesis is more likely.

Furthermore, we conclude that it is highly unlikely that there is no net inflow of phosphorus along the Lower Danube. If we assume that the computed river loads in Chiciu and Reni are too low by 7.6 kt/y (31%), it follows that the Lower Danube contributes a share proportional to its contribution to the river flow to the Danube P load.

Finally, there is a sharp decrease of the computed P loads at Chiciu and Reni in 2000-2001 (see Figure 3-15). Looking at the concentrations (Figure 3-7) it turns out that the decrease is more or less continuous over 1996-2001. The apparent sharp drop from 1999 to 2000 is partially the result of the high discharge in 1999. Still there seems to be a major sink of phosphorus downstream of the Iron Gates, which gradually developed in 1996-2001. As long as such a sink has not been identified, we consider this decrease an artefact.

Following these hypotheses, the “adjusted” P balance is listed in Table 3-6

Table 3-6: “Adjusted” balance of phosphorus.

River section	**Adjusted balance of TP (kt/y) (1997-2001)**
Upper and middle Danube	11.7
Drava	2.1
Sava (reconstructed)	8.4
Tisa	6.5
Serbia	0
Iron Gates	-10.2
Lower Danube	5.8
Whole Danube	24.5

This adjusted P balance represents no more than an estimate based on expert judgement. We will investigate the data from other information sources to firm up the estimate.

3.3.5 Relation between discharge and suspended solids

To investigate the effect of the frequency of sampling on the computed loads of phosphorus, we have checked the relation between the river discharge and the concentration of suspended solids at different stations along the Danube. This has been done after removing outliers (very high values at moderate discharges). A linear regression between both parameters has been carried out and the correlation coefficient has been determined. The result is summarised in Table 3-7.

Table 3-7: Relation between the river discharge and the concentration of SS for different stations along the Danube.

Station	**$\partial SS/\partial Q$ (g.s)**	**Correlation between SS and Q(R^2)**
Jochenstein	0.011	0.16
Wolfsthal	0.023	0.48
Hercegszanto	0.007	0.27
Bazias	0.002	0.04
Pristol	0.001	0.03
Chiciu	0.003	0.04
Reni	0.001	0.01

Table 3-7 clearly demonstrates that the correlation between SS and the river discharge is weak to non-existent. This may be caused by the fact that apparently no extreme discharges have occurred in the analysed period. (The range of flows in the data set does not include values higher than the local 1% exceedence value over the years 1998-2001.) Therefore, the data do not allow the analysis of the effect of the frequency of sampling on the computed loads of phosphorus.

4 Data collected at Sulina by the NIMRD, Constanta, Romania

4.1 Description of the data

The National Institute for Marine Research and Development (NIMRD) is a partner of *daNUbs*. NIMRD has collected a long time series of water quality data at the station Sulina (see *daNUbs* reports from Work Package 7). The sampling is done on weekdays. The results are reported as monthly averages over the period 1990-2002. Up to 2000, only the inorganic nutrients are analysed: ammonium, nitrites, nitrates, phosphates and silicates. From 2001 onwards, also total phosphorus is analysed, while in 2003 the analysis of total nitrogen is started. Sampling is done at the water surface. Further details of the sampling and analysis are not exactly known.

4.2 Presentation of the data

Figure 4-1 to Figure 4-4 show the monthly averages of the observed concentrations of TIN, phosphates, silicates and TP.

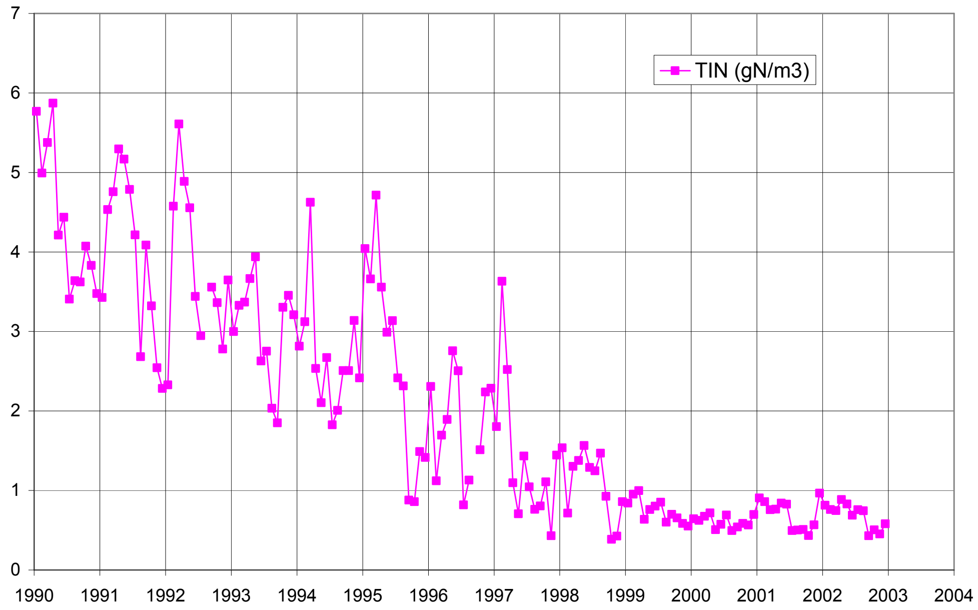

Figure 4-1: Observed concentration of TIN at Sulina (data from NIMRD, monthly averages of daily values).

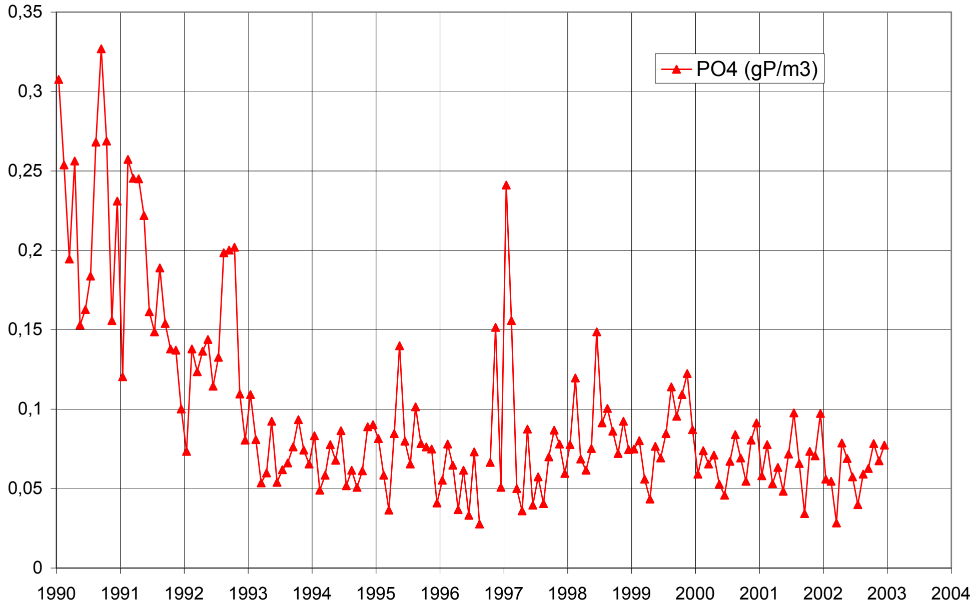

Figure 4-2: Observed concentration of phosphates at Sulina (data from NIMRD, monthly averages of daily values).

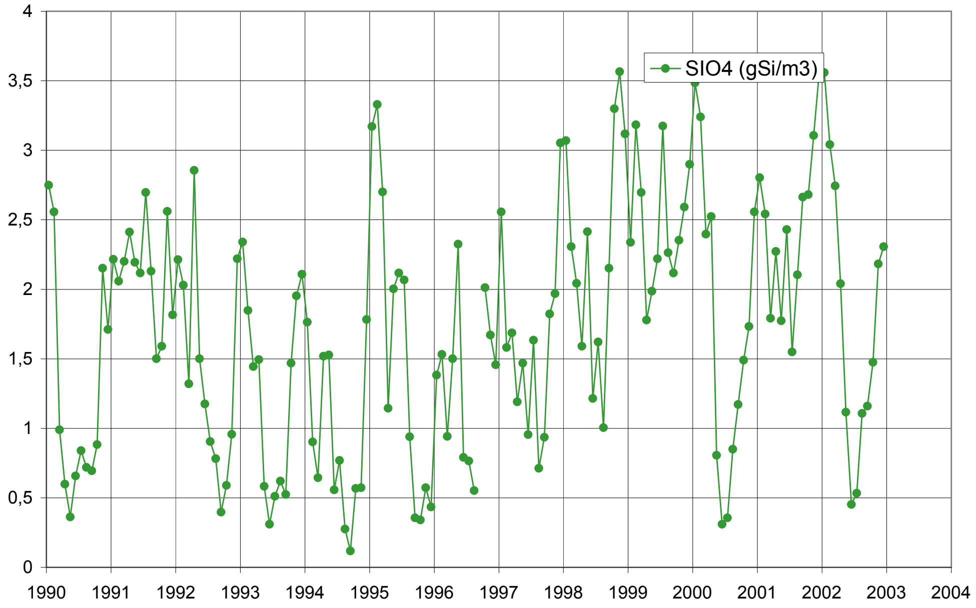

Figure 4-3: Observed concentration of silicates at Sulina (data from NIMRD, monthly averages of daily values).

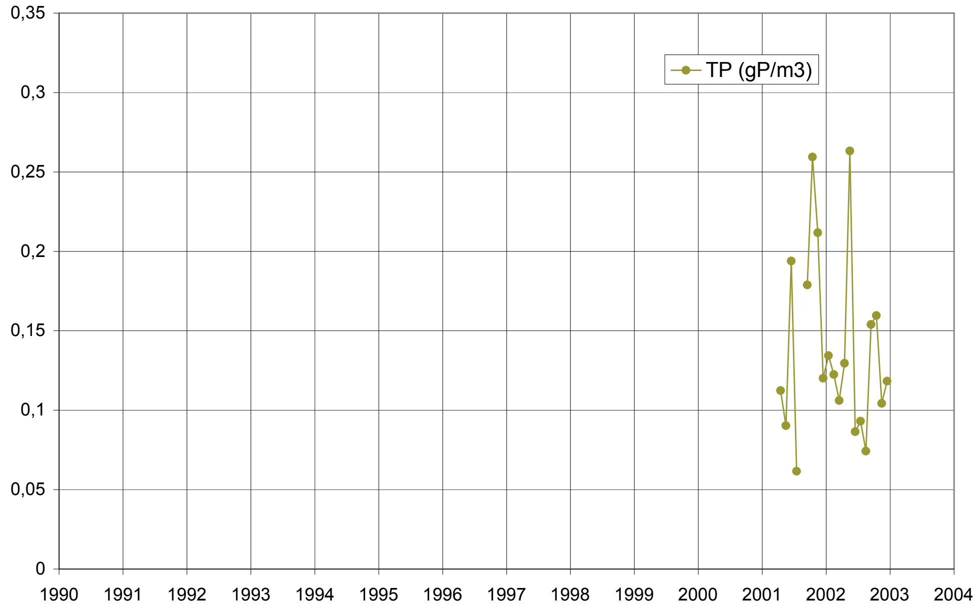

Figure 4-4: Observed concentration of total phosphorus at Sulina (data from NIMRD, monthly averages of daily values).

4.3 Discussion of the data

The concentration of TIN at Sulina shows a strong and continuous decrease during the period 1990-2002. The yearly averages (computed as the average of the monthly averages) show a reduction of more than a factor 7(!) between 1990 and 2000.

The cause of this strong decrease is not immediately evident. If we suppose that the concentration of TIN follows the concentration of total nitrogen and that the concentration at Sulina resembles the concentration of the Danube upstream of the Danube Delta, the Danube river load of nitrogen must show a similar decrease. From the research carried out about diffuse sources of nitrogen in large river basins we know that this is highly unlikely. Large stocks of nitrogen are formed in the ground water during periods of high fertilizer use. In the Danube basin such a period existed up to about 1990, before the successful implementation of nitrogen pollution reduction measures in Germany and Austria and before the economic collapse in the Central and Eastern European countries. Due to the existence of these stocks, the trends in the river loads follow the trends in the fertiliser use with a delay of at least a decade (Elbe, Rhine). And even then, the decrease in the river loads is usually not as strong as the decrease observed in Sulina.

Consequently, it can not be excluded that the observed concentrations of TIN at Sulina are not a valid indicator for the Danube nitrogen load. Local conditions of the water system and/or the sampling and analysis may be responsible for the decreasing trend in the local TIN concentration.

A final observation is that the typical yearly cycle of the concentration of TIN (governed by the yearly cycle of uptake by plants and denitrification) is hard to observe during 1998-2003.

The concentration of phosphates at Sulina shows a strong decrease during 1990-1992 and a more or less constant level afterwards. This can be related to the rapid decrease of point sources of P after the economic collapse in the Central and Eastern European countries.

The concentration of silicates at Sulina shows a strong variation over time. Generally, the summer values are lower than the winter values, probably due to the uptake of silicates by phytoplankton. The winter maxima vary from year to year, probably due to the variation of the hydrological conditions. The yearly average shows a distinct increasing trend. The average value over the period 1996-2000 equals about 400 kt/y.

5 *daNUbs* surveys

5.1 Description of the data

In the course of the *daNUbs* project, specific water quality data collection activities have taken place. They include:

- sampling at Vienna during an extreme flood event in 2002;
- sampling at different locations in the Gabcikovo area, during three periods of one week;
- sampling at different locations in the Iron Gates area, during three periods of one week;
- sampling at Isaccea (upstream of the Danube Delta) during different periods of 4 days, preceding the marine sampling cruises carried out in Work Package 7 of *daNUbs*.

Table 5-1 provides more details.

Table 5-1: Overview of *daNUbs* surveys.

	Vienna	**Gabcikovo**	**Iron Gates**	**Danube Delta**
Station(s)	Vienna	Bratislava (km 1869), Hrusov reservoir, Medve (km 1806)	Bazias (km 1071) Orsova (km 954) Gruia (km 849)	Isaccea (km 101)
Sampling locations in the profile	surface, middle	left, middle, right, at 0 and 5 m depth	left, middle, right, at 0 and 5 m depth	left, middle, right, at 0 and 5 m depth
Sampling period(s)	8-18 August 2002	7 day periods starting on: 9 August 2002 4 November 2002 25 November 2002	7 day periods starting on: 23 April 2002 24 June 2002 28 August 2002	4 day periods starting on: 2 October 2001 7 November 2001 4 June 2002 6 August 2002 8 October 2002
Sampling frequency	about 40 samples in 10 days	daily samples	daily samples	daily samples
Determinants	pH, temperature, DO, TOC, DOC, all P species, all N species, SiO2, suspended solids, conductivity, Cl, SO4	discharge temperature, DO, TOC, all P species, all N species, SiO2, suspended solids	discharge temperature, DO, TOC, all P species, all N species, SiO2, suspended solids	discharge temperature, DO, all P species, all N species, SiO2, suspended solids

5.2 Presentation of the data

The data from the station Vienna during the peak flood of August 2002 are presented in Figure 5-1, Figure 5-2 and Figure 5-3 (TU Vienna, 2003). They are compared with data from the first Gabcikovo survey, which took place during the same flood event.

The data for the Gabcikovo and Iron Gates surveys are presented by Laszlo (2004).

The results from the Isaccea surveys will be presented graphically in conjunction with the data from other sources in paragraph 8.1. The analysis of these data will be presented in the same paragraph.

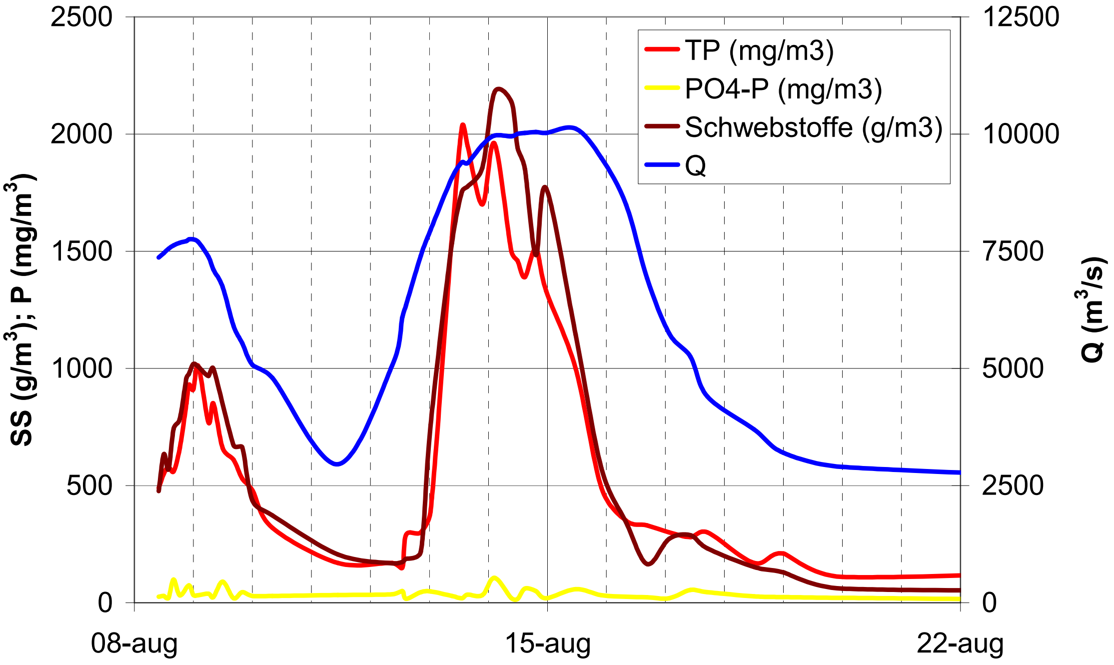

Figure 5-1: Simultaneous presentation of the river discharge, the concentration of SS and the concentration of phosphates and total P, measured at Vienna during the August 2002 flood.

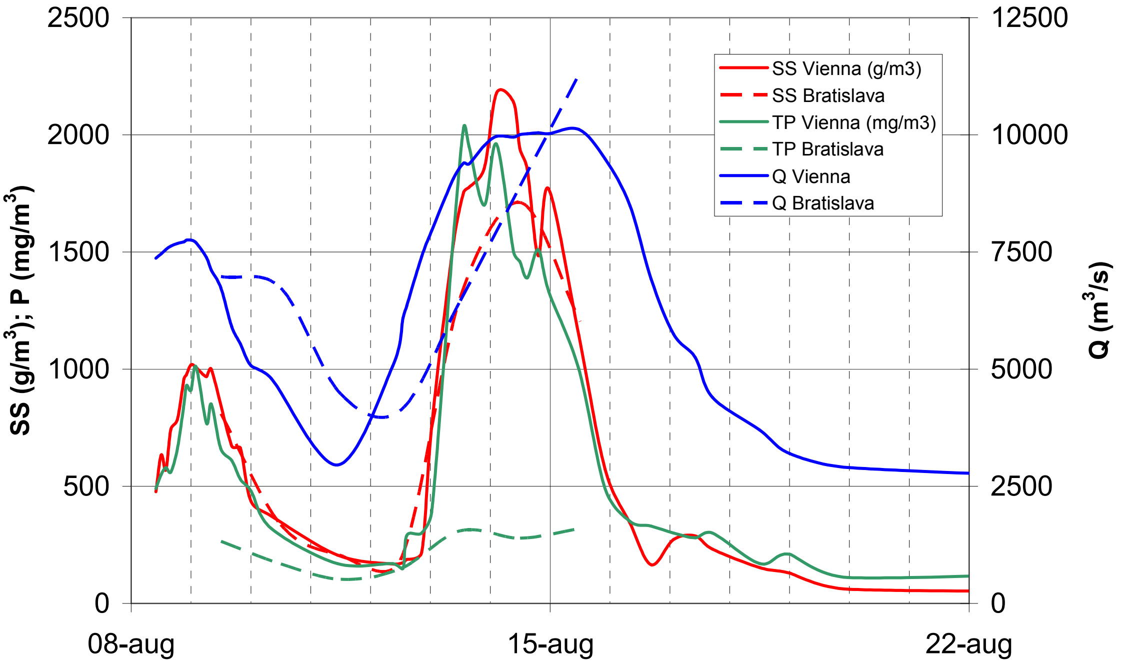

Figure 5-2: Simultaneous presentation of the river discharge, the concentration of SS and the concentration of total P, measured at Vienna and at Bratislava during the August 2002 flood.

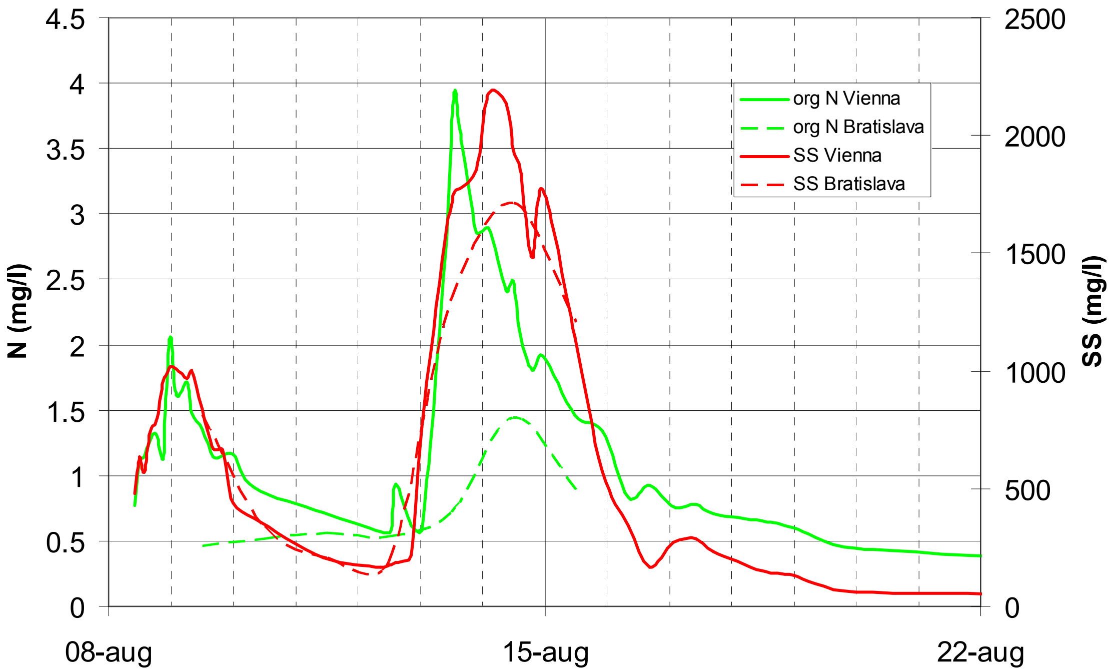

Figure 5-3: Simultaneous presentation of the concentration of SS and the concentration of organic N, measured at Vienna and at Bratislava during the August 2002 flood.

5.3 Discussion of the data

5.3.1 Vienna survey

From the presentation of the Vienna data some observations can be made.

- as expected, during the flood the concentration of suspended solids shows a sharp peak, with a maximum value of 2179 mg/l;
- the concentration of total phosphorus also shows a sharp peak, with a maximum value of 2 mg/l (!), which coincides with the peak in the suspended solids concentration;
- the concentration of ortho-phosphates is a small fraction of the total, and does not show a peak;
- the concentration of organic nitrogen (total minus inorganic) shows a similar sharp peak, with a maximum value of 3.9 mg/l, which again coincides with the peak in the suspended solids concentration;
- the P content of suspended solids (computed as (TP-PO4)/SS) is relatively low, mostly below 1000 mg/kg, during the high water period, while after the high water period this concentration increases to values of 1500-2000 mg/kg.

The total phosphorus load at Vienna during the survey period (8 August to 17 August) equals 4.7 kt (note that the average annual load at the TNMN station in Vienna-Nussdorf over the years 1997-2001 equals 8.5 kt!).

Comparing the data at Vienna with the data for Bratislava from the first Gabcikovo survey, some additional observations can be made:

- the discharge peak arrives in Bratislava at least a day later than Vienna, and the peak value is even higher (unfortunately the survey in Bratislava was stopped before the discharge started to decrease, so the actual peak value was not necessarily captured and the water quality at the back of the flood wave was not monitored);
- the concentration of suspended solids shows a similar peak in Bratislava as it does in Vienna (note the lower sampling frequency);
- the concentration of total P (max. 0.32 mg/l) does not show a peak similar to the one in Vienna (2 mg/l), for no apparent reason;
- a similar observation holds for organic nitrogen, where the Bratislava peak (1.44 mgN/l) is substantially smaller than the Vienna peak (3.9 mgN/l).

With regard to the low concentrations of organic N and total P at Bratislava, we suspect that the values observed at Bratislava are erroneous because of poor homogenisation of the samples.

5.3.2 Gabcikovo surveys

From the presentation of the data some observations can be made. Due to the high flow conditions during all three surveys and due to the relatively small size of the study area (63 km), the travel time from the first to the last station is in the order of one day only.

- During the first survey a high flood occurs. The other two surveys are also carried out under relatively high discharge conditions (local average flow is 2020 m3/s). Therefore, the surveys do not provide a complete picture of the variability of the water quality with the hydrological conditions.
- The discharge at Medve is substantially lower than the discharge at Bratislava and the Hrusov reservoir. The difference concerns the flow through parallel branches.
- The water temperature reflects the season of the surveys.
- The concentrations of DO are generally high (>9 mg/l) with higher values under colder conditions. The saturation has not been determined.
- The concentrations of TOC are rather variable. The highest values are observed in August, possibly due to phytoplankton activity.
- The concentrations of SS are extremely high during the August flood event. There is a substantial retention of SS along the reservoir. This is probably due to sedimentation in the floodplains.
- The concentrations of TotN partly reflect the normal seasonal cycle with lower values in the summer and higher values in the winter. At the end of the August survey however, the N content of the suspended matter makes the concentration of TotN increase. This effect can also be clearly observed in OrgN, and in ammonium due to the mineralization of OrgN. The concentrations of nitrates and TIN reflect the normal seasonal cycle with lower values in the summer and higher values in the winter. The concentration of OrgN is usually low (0.4 to 0.6 mgN/l) and does not show a seasonal variation.
- The concentrations of TotP vary between 0.1 and 0.2 mgP/l and show no clear trends, except during the peak flood period. The concentrations of phosphates vary between 0.04 and 0.12 mgP/l and show no clear trends.
- The concentrations of Si are in a rather narrow range of 7-9 mgSiO2/l (or 3-4 mgSi/l). There is no spatial trend. The August values tend to be a little higher, seemingly due to the flood conditions.

Table 5-2 summarises the average change of the concentration of certain key variables between the last and the first station. These numbers are indicative for the retention characteristics of the study area during the three cruises.

Table 5-2: Relative change of the concentrations of key variables over the Gabcikovo section during the *daNUbs* cruises.

Balance	**TOC**	**SS**	**TotN**	**TotP**	**SiO2**
	mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**
9-8-2002	-11%	-60%	-5%	-24%	-2%
4-11-2002	3%	-16%	-4%	-8%	-3%
25-11-2002	-8%	3%	-5%	-8%	-4%
Average	**-5%**	**-24%**	**-5%**	**-13%**	**-3%**

The results indicate a significant retention of SS and P. The retention of SS is clearly the strongest during the flood survey. This effect is also visible for TotP. The retention of P is consistent with the retention found from the TNMN data (which was about 10%!).

5.3.3 The Iron Gates surveys

From the presentation of the data some observations can be made. Due to the size of the study area (222 km), the travel time from the first to the last station varies from about 4 days (at 7000 m3/s) to about 8 days (at 4000 m3/s), see paragraph 7.1 for a further explanation.

- The first survey is carried under high flow conditions, the second under low flow conditions and the third under high to medium flow conditions (the local average flow is 5700 m3/s). Therefore, the surveys provide a reasonably good picture of the variability of the water quality with the hydrological conditions.
- The discharges at the three stations do not show systematic differences.
- The water temperature reflects the season of the surveys, while the June temperatures can be characterised as very high (indicating stratification?).
- The concentrations of DO are moderate to high (always >5 mg/l) with higher values under colder conditions. Undersaturation is common, indicating that the mineralization processes dominate primary production.
- The concentrations of TOC are rather variable. The highest values are observed in September. It is not immediately clear why this should be the case.
- The concentrations of SS show a remarkably small variability.
- The concentrations of all N species show extreme variations between the stations and between the different sampling days. There are no clear systematic differences between the individual cruises.
- The concentrations of TotP vary between 0.1 and 0.45 mgP/l. There is a clear longitudinal trend. The concentrations of phosphates vary strongly between 0.01 and 0.18 mgP/l and show no clear trends.
- The concentrations of Si vary strongly between the stations and between the different sampling days. While the first and second cruises show a substantial increase along the reservoir, the third cruise shows an opposite trend.

Table 5-3 summarises the average change of the concentration of certain key variables between the last and the first station. These numbers are partly indicative for the retention characteristics of the study area during the three cruises. It should be noted however that the retention time of the study area is of the same order as the duration of the surveys, which makes it difficult to consider the data in Table 5-3 as a real mass balance.

Table 5-3: Relative change of the concentrations of key variables over the Iron Gates section during the *daNUbs* cruises.

Balance	**TOC**	**SS**	**N Total**	**P Total**	**SiO2**
	mg/l	**mg/l**	**mgN/l**	**mgP/l**	**mg/l**
23.04.02	-12%	14%	-30%	-48%	226%
24.06.02	-51%	3%	0%	-42%	118%
28.08.02	-7%	0%	-3%	-38%	-66%
Average	**-23%**	**6%**	**-11%**	**-43%**	**92%**

The results indicate a significant retention of TOC and P, and to a lesser extent of N. The retention of TOC is probably connected to the fact that mineralization processes dominate primary production. The strong retention of P in combination with no retention of SS suggests that the retention mechanism in the Iron Gates area is different from that in the Gabcikovo area. The strong variations of the inorganic and organic species of N, of phosphates and of silicates demonstrate a strong biological activity in the area. This has an effect on the balance of N, but much more on P, which is apparently retained effectively. It is very well possible that organic particles drop to the sediment, where their P content is mineralised and subsequently fixated as a precipitate in the sediment. Note that the retention of P is consistent with the adjusted retention estimate from the TNMN data (about 35%!).

Figure 5-4 shows simultaneously the observations of the TotP concentration from the Iron Gates surveys and the TNMN data in the second and third quarter of 2002.

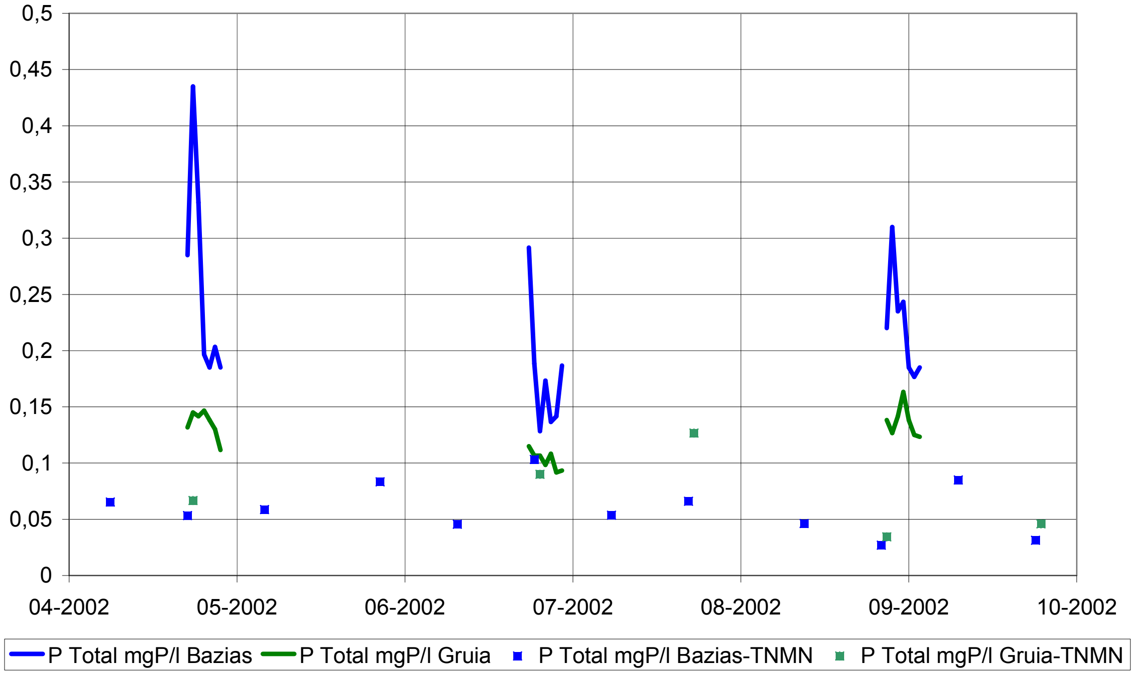

Figure 5-4: Simultaneous observations of the concentration of total P at the entrance (Bazias) and the exit (Gruia) of the Iron Gates reservoir during the *daNUbs* surveys (lines) and from regular TNMN monitoring data (points). It should be noted that the TNMN data are preliminary unverified data.

The figure clearly shows that the survey results support the assumption that the TNMN concentrations at these stations are too low. The difference is larger at Bazias, and smaller at Gruia. The survey data show a clear retention, while the original TNMN data do not show a similar phenomenon. These results have been used in support to the adjusted P balance discussed in paragraph 3.3.4.

6 The Joint Danube Survey (JDS)

6.1 Description of the data

Between 13 August and 19 September 2001 a survey along the Danube was carried out. From Neu-Ulm (km 2581) up to the Danube Delta the surface water, the suspended solids and the sediments were sampled and analysed. The survey included an extensive list of biological/ecological and chemical parameters, including the nutrients which are most interesting from the point of view of *daNUbs*.

Due to the nature of the survey, the data from JDS provide longitudinal profiles of all parameters of interest. The temporal variation was not a subject of study. The survey was carried out in the warmest part of the year, so that the observations are characteristic for that particular period.

6.2 Presentation of the data

The data are presented in a Technical Report (ICPDR, 2002). We refer to that report for the relevant graphs showing longitudinal profiles of water and sediment quality parameters.

6.3 Discussion of the data

The JDS report clearly discussed the methods of sampling and analysis. The analysis of the surface water samples was carried out after filtration, while the suspended sediments were analysed separately. Therefore, the parameters total phosphorus and organic nitrogen are not immediately comparable to those parameters from the other data sources mentioned in this report, since these (are supposed to) analyse unfiltered and homogenised samples.

The river discharge is low during the JDS. The discharge at the river mouth amounts 5460 m3/s.

The macro-chemical water quality parameters are presented in figures C2.1-1 to C2.2-11 in (ICPDR, 2002). The phytoplankton results (figure PPL-1/PPL-2 in (ICPDR, 2002)), indicate a smaller peak of about 40 µg/l chlorophyll-α in the German part of the Upper Danube and a large peak of about 120 µg/l chlorophyll-α in the Hungarian Danube stretch. Elsewhere the concentrations of chlorophyll-α are very low, often smaller than 10 µg/l and always smaller than 20 µg/l. This very distinct profile of phytoplankton biomass influences or rather dominates the chemical water quality as well. In particular:

- the pH and DO profiles show the river stretches were algae grow: CO2 is consumed (pH increases) and DO is produced;
- the pH and DO profiles show the river stretches were organic material is decomposed downstream of the algae bloom zone: CO_2 is produced (pH decreases) and DO is consumed;

- the suspended solids profile shows a maximum on the Hungarian Danube stretch, which is probably due to the presence of algae, while the content of suspended matter of a mineral nature is low due to the low flow conditions;
- the concentrations of ammonium and nitrites show a maximum in the river stretches were organic material is decomposed downstream of the algae bloom zone: these are intermediate products of the mineralization of organic nitrogen to nitrates;
- the concentration of nitrates decreases in the algae bloom zone, indicating the possible uptake by algae, and increases downstream after the mineralization of organic nitrogen to nitrates;
- the concentration of dissolved organic nitrogen (DON) does not show a clear relation with the phytoplankton profile: apparently this DON is of a non-algae nature;
- the concentration of organic nitrogen in suspended solids (PON) clearly reflects the phytoplankton profile;
- the concentration of organic nitrogen in the sediment shows the highest values in the areas where the phytoplankton profile shows blooms: this could be an indication that the phytoplankton profile measured during the JDS is representative for the average phytoplankton profile;
- the concentration of phosphates decreases in the algae bloom zone, indicating the possible uptake by algae, and increases downstream after the mineralization of organic phosphorus to phosphates;
- by comparing the profile of total (dissolved!) phosphorus and phosphates, it can be observed that there is an amount of “other dissolved phosphorus” in the water column which is certainly not negligible;
- the concentration of phosphorus in suspended solids (PP) reflects the phytoplankton profile, but less pronounced as in the case of PON: apparently in the case of PP material other than algae have a stronger effect on the solid phase, like adsorbed phosphates and phosphorus minerals;
- the concentration of phosphorus in the sediment shows somewhat higher values in the areas where the phytoplankton profile shows blooms, but less pronounced as in the case of PON;
- the ratio of N:P in suspended solids in the area where phytoplankton blooms occur is in the order of 6:1 to 8:1, but outside this zone as well as in the sediments the ratio of N:P drops to much lower values, say 2:1;
- the concentration of silicates decreases in the algae bloom zone, indicating the possible uptake by algae, and increases downstream after the mineralization of organic silica to silicates.

Note that according to the Iron Gates surveys the mineralization processes systematically dominate primary production in the Iron Gates area. This is consistent with the JDS data!

The JDS report does not present a profile of total nitrogen and phosphorus including the fractions in suspended solids. Therefore, we have constructed such profiles (see Figure 6-1 and Figure 6-2). The particulate fractions have been reconstructed as follows:

Part N = SSxNSS
Part P = SSxPSS

with:

SS	suspended solids (mg/l)
NSS	nitrogen concentration of SS (gN/g)
PSS	phosphorus concentration of SS (gP/g)

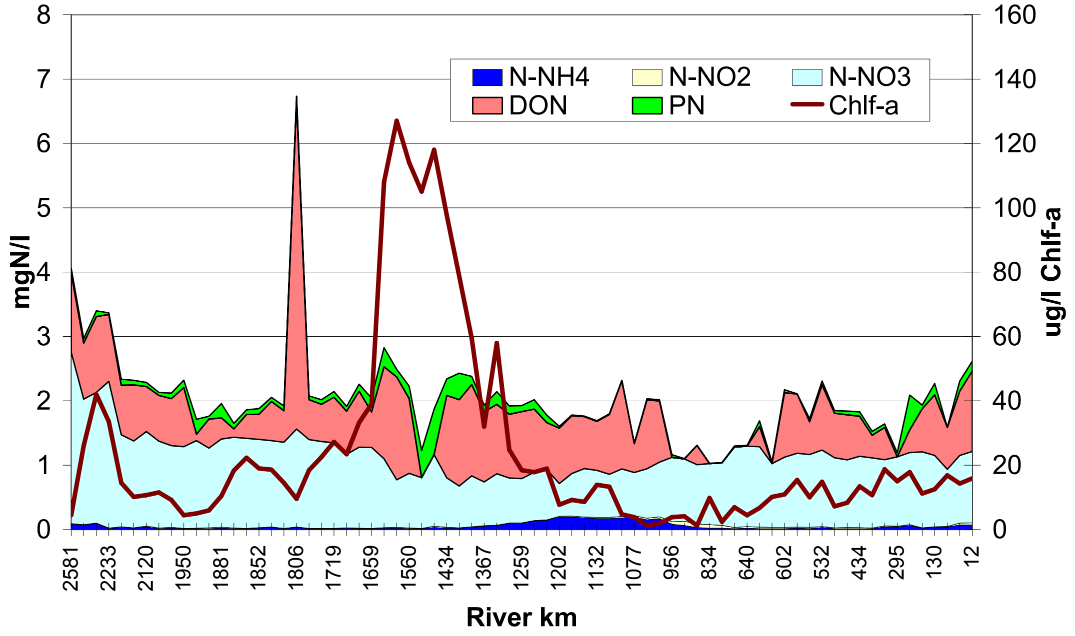

Figure 6-1: Profile of cumulative concentrations of N species along the Danube (Joint Danube Survey).

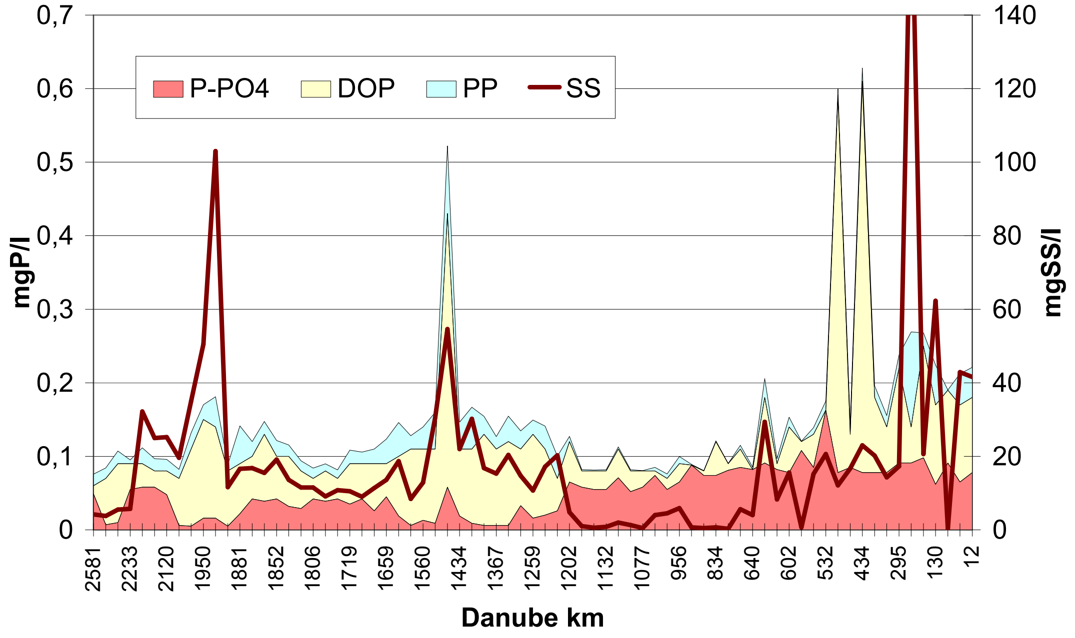

Figure 6-2: Profile of cumulative concentrations of P species along the Danube (Joint Danube Survey).

Figure 6-1 illustrates that the difference between TN and DIN is substantial: it consists of a fraction Dissolved Organic Nitrogen (median 0.7 mg/l, 34% of total N), and a fraction of Particulate Organic Nitrogen (median 0.07 mg/l, 3% of total N). The former is not directly related to phytoplankton blooms, while the latter is.

Figure 6-2 shows that there is a substantial fraction of P (median 46%) which is dissolved and not included in phosphates, while the contribution of particulate P is relatively small (median 13%): note that this is the result of the summer situation with low inorganic suspended matter and therefore low adsorbed P.

Figure 6-3 shows that the silica content of the river seems to be around 4 mg/l up to km. 1700. Towards km 1500, the concentration drops to about zero. Towards the downstream section the concentration recovers to a value between 2 mg/l and 4 mg/l. The section of lower Si values coincides with a phytoplankton bloom with values of chlorophyll-α up to 120 µg/l around km 1500.

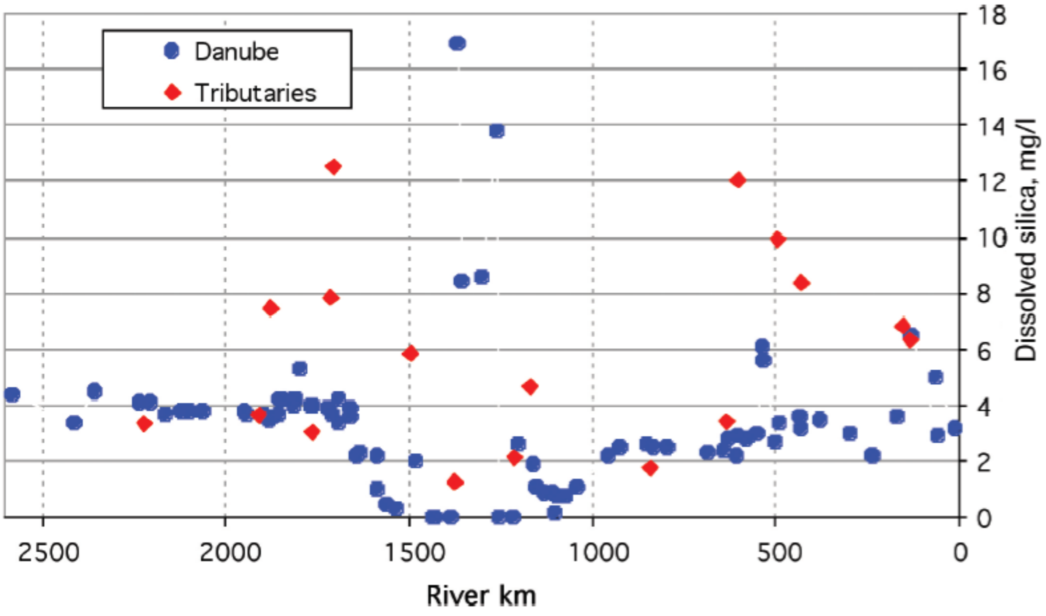

Figure 6-3: Observed profile of dissolved silica during the JDS

7 Additional literature

7.1 Data collected by Danube Delta National Institute

The Danube Delta National Institute in Tulcea, Romania (DDNI), is a partner of *daNUbs*. The DDNI has made available the results from their water quality monitoring at the upstream end of the Danube Delta.

The data include the following parameters: ammonium, nitrates (including nitrites), suspended solids, ortho-phosphates, total phosphorus and dissolved oxygen. The sampling frequency is not very high: over the period 1996-2001 48 samples are available.

The data from this source are not presented and discussed. In the first place, a preliminary analysis showed that the data set does not add a lot to the other data sets. Furthermore, the frequency of sampling is too low to allow load computations.

7.2 The flow velocity and the travel time in the Iron Gates section

Information related to the flow velocity has been derived from Perisic et al. (1990). The flow velocity varies as listed in Table 7-1.

Table 7-1: Flow velocity data for the Iron Gates section under different discharge conditions

	Q = 1900 m3/s	**Q = 3300 m3/s**	**Q = 9500 m3/s**	**Q = 11900 m3/s**
Upper Section	0.2	0.5	1.3	1.7
Middle Section	0.2	0.2	0.6	0.8
Lower Section	0.1	0.2	0.4	0.6

Information related to the travel time has been derived from the APC Expert Group under the ICPDR. The relevant information is listed in Table 7-2.

Table 7-2: Transport velocity of the cloud of pollutants, observed after the Baia Mare spill in 2000.

Location	**KM**	**Passage of peak concentration**	**Discharge (m3/s)**	**Velocity (m/s)**
Bazias (RO)	1071	15-02-00 14:00	8700	
Gura Vaii (RO)	941	17-02-00 18:00	8600	0.69
Timok mouth (BG)	845	19-02-00 09:00	8334	0.68

Based on this information we estimated the average velocity over the Iron Gates reservoir section during the *daNUbs* surveys as 0.6 m/s (at 7000 m3/s) to 0.3 m/s (at 4000 m3/s). For a total distance of 222 km this means a total travel time of 4.3 to 8.6 days.

7.3 Vertical concentration and transport gradients of suspended solids

A paper by Reschke ea. (2002) provides information about the vertical (and horizontal) concentration gradients of suspended solids. This information concerns one longitudinal survey carried out in June 1995. The Danube river discharge was high in this period (8300-9800 m3/s).

The results have been collected and presented graphically. Figure 7-1 shows the lateral variation of the observed concentrations of suspended solids along the Lower Danube.

The results show low concentrations of SS in the Iron Gates area (km 1070-850) and increasing concentrations towards the Delta. This is not in agreement with the averages from the TNMN data over 1996-2001. This is probably the result of the high flow conditions during the survey. It is striking that the lateral differences are very large. This strongly supports the TNMN practice of sampling at three locations in one particular cross-section.

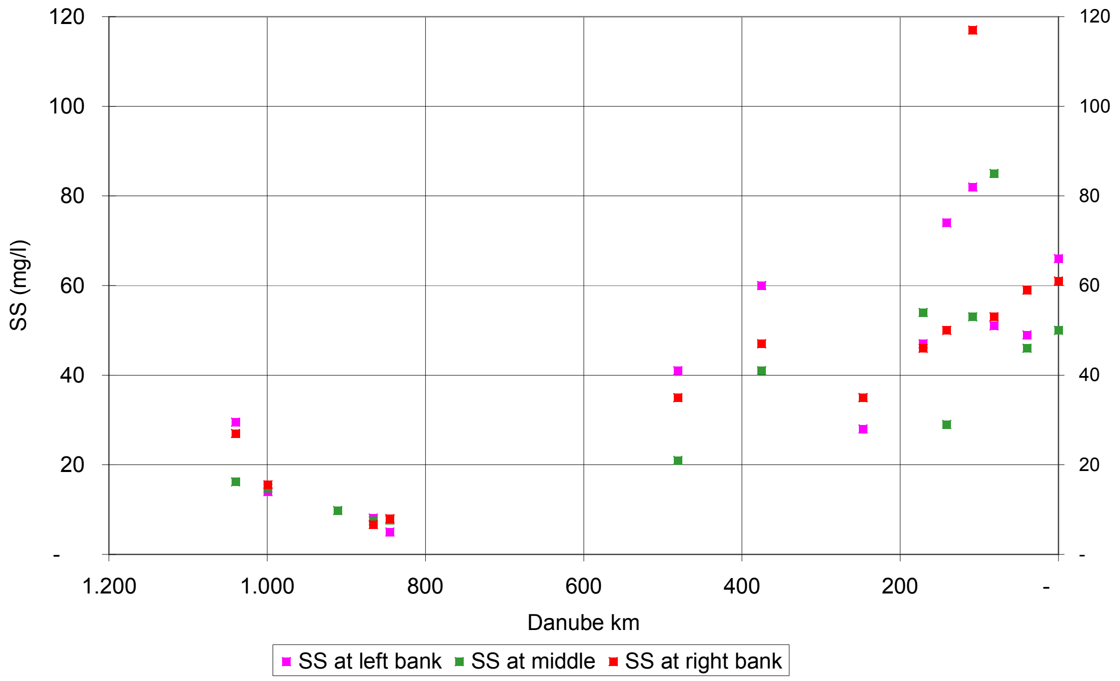

Figure 7-1: Observed concentrations of SS at different locations in the cross-section by Reschke (2002).

The results by Reschke also allow the analysis of the vertical concentration gradients of SS. This has been done as follows. At those locations where three samples were taken at different depths (typically up to about 75% of the total depth) the stream flow velocity has been estimated at these three depths, relative to the average velocity. A power law velocity profile was used:

$$\frac{u}{u_{average}} = (m+1)\left(\frac{y}{H}\right)^m , \quad m = 0.15$$

By multiplying this relative velocity with the local concentration of suspended solids a vertical profile of the suspended solids load was obtained. By comparing the integral of this profile with the surface concentration multiplied with the average velocity, an estimate was obtained for the error caused by neglecting the vertical concentration profile. Figure 7-2 shows the result. The results show that the correction factor amounts to 1.2 to 1.4.

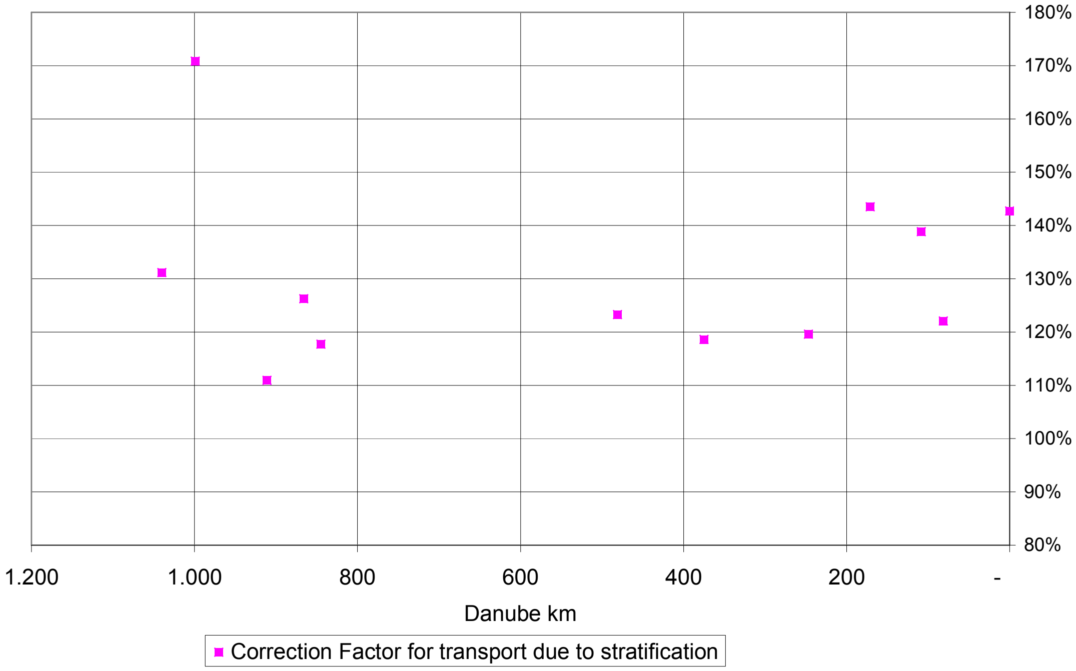

Figure 7-2: Error introduced by neglecting the vertical profile of the SS concentration and the stream flow velocity, based on data from Reschke (2002).

Finally, Reschke reports that the content of N of the suspended solids is in the range of 0.5-1.5%, which translates to 5000-15000 mgN/kgSS. This is consistent with the findings of the JDS.

7.4 Retention processes in the Iron Gates area

Two recent papers by Friedl ea. (2003) and by Teodoru ea. (2002) discuss and analyse the data collected during 2001 by the EAWAG Institute. The data were collected at different stations along the Iron Gates section by weekly sampling at three different depths. As far as we know, no integral publication of these data has taken place.

The papers conclude that there is no relevant retention (or mobilisation) of dissolved nutrients (Si, N, P), while the particular matter, including its nutrient content is retained for a substantial part. The estimate by Teodoru ea. is about 50%. This is fully in line with older research on which the first version of the DWQM was based (van Gils, 1999). Unfortunately, this is in apparent contradiction with the results from the *daNUbs* surveys, where there is no retention of SS, despite the fact that the retention of P is substantial.

Teodoru et al. investigated in particular the fate of dissolved silicates in the Iron Gates area. On the basis of the data presented in Figure 7-3, they conclude that there is no significant retention of dissolved silica in the Iron Gates section.

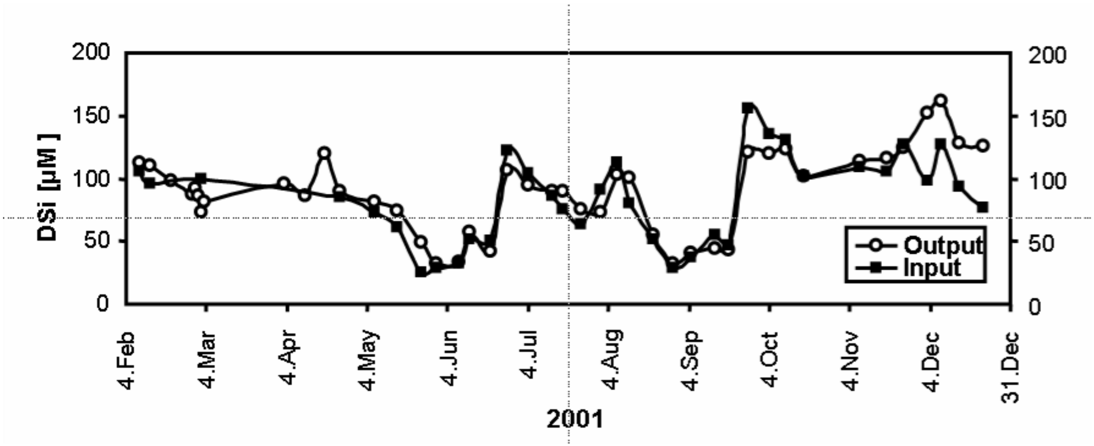

Figure 7-3: Observed concentrations of dissolved silica at the entrance and the outlet of the Iron Gates reservoir during 2001.

7.5 Silica concentrations observed during the Burgund survey

During a survey carried out in May and June 1998 in the upper and middle Danube stretch, the water quality was investigated. the inorganic silica content of the river was found to be between 0 and 1.5 mg/l (reported as SiO_2). The chlorophyll-α concentrations were in the range of 20 to 70 µg/l, with a clear inverse correlation between silica and chlorophyll- α. Oxygen saturation values were between 100 and 180%, with a clear correlation between oxygen saturation and chlorophyll- α.

7.6 Background silica concentrations in the Danube River Basin surface waters

Garnier et al. (2002) present a methodology to estimate the background silica concentrations in the Danube river basin on the basis of the lithology. The estimate is based on data from Meybeck. The values are in the range between 70 and 105 µM. On the basis of these concentrations and the water balance presented in chapter 3, the background "emissions" of silica in the Danube River Basin can be estimated at 515 ktSi/y.

7.7 Sediment regime of the Danube river

A report written by the Danube countries and the IHP of Unesco provides an overview of older historical data regarding the sediment load of the Danube (Rákóczi, 1993). Figure 7-4 provides an overview of the data. The figure shows the averages over the period 1956-1985 as well as the averages over the period 1976-1985. In general, the 1976-1985 decade shows smaller sediment loads than the average over 1956-1985.

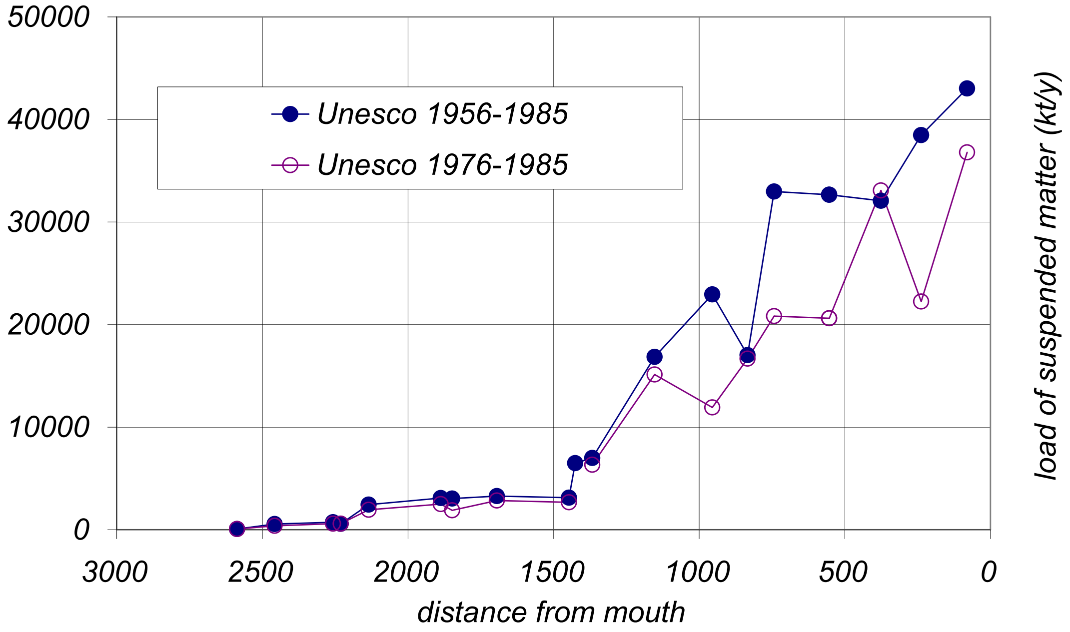

Figure 7-4: Longitudinal profile of historical sediment load data along the Danube.

The sediment yield of the whole catchment amounts to about 50 t/km^2/y. The sediment influx to the Danube is reported to be significantly affected by a number of relatively small tributaries, which feature a very large sediment yield, such as the Inn (2800 kt/y, 108 t/km^2/y), the Velika Morava (6900 kt/y, 184 t/km^2/y), the Olt (6800 kt/y, 284 t/km^2/y!) and the Siret (11800 kt/y, 248 t/km^2/y!). The annual loads have been derived from observations at discrete locations with a high frequency, especially during high flow episodes.

The load data presented above have been converted to “average” concentrations by dividing the loads by a representative annual discharge. Figure 7-5 presents the result. In this figure we have added the TNMN data as they were presented in Chapter 3.

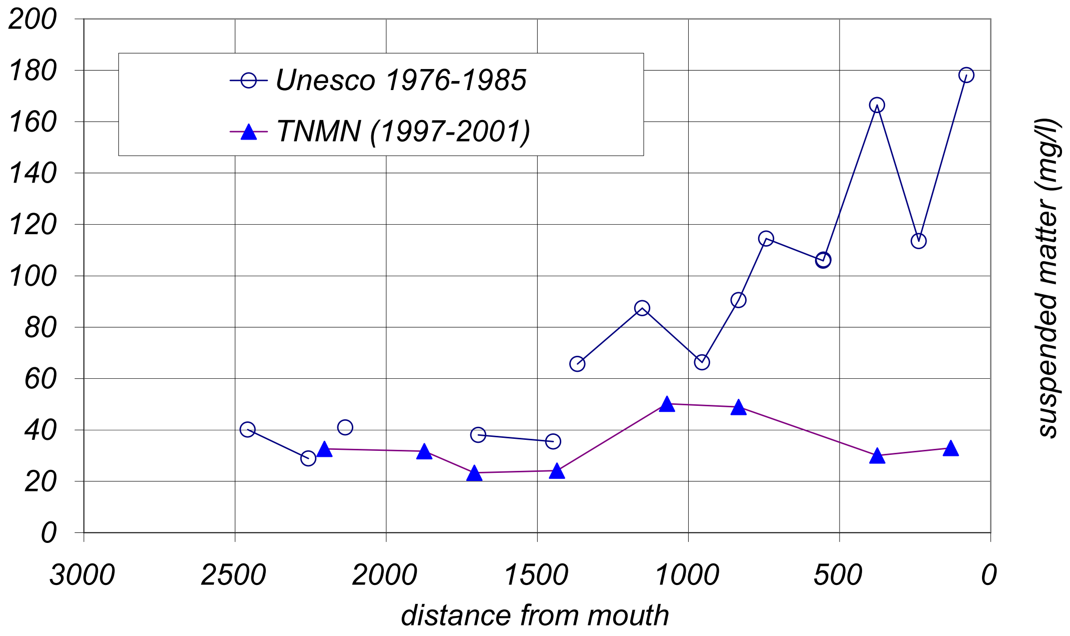

Figure 7-5: Longitudinal profile of average sediment concentration along the Danube.

Assuming that both data sources are comparable, the results show dramatic changes of the concentrations, especially in the downstream part of the Danube. This is probably the result of the ongoing damming of the Danube and its tributaries.

The results may not be comparable, due to the fact that the Unesco data are based on observations with a high frequency depending on the discharge, while the TNMN data have a frequency of 12/y or 24/y independent of the flow conditions.

8 Comparison of data from different sources

In the paragraph on the TNMN data we have already discussed the data from stations operated by different countries on two sides of the river, e.g. Medve/Medvedov and Chiciu/Silistra. At a number of occasions these data from different sources were useful to judge the quality of the data.

8.1 Water quality data at the station of Reni/Sulina

Several of the information sources herein provide data for the stations Reni and Sulina[3]. The results are presented in this paragraph.

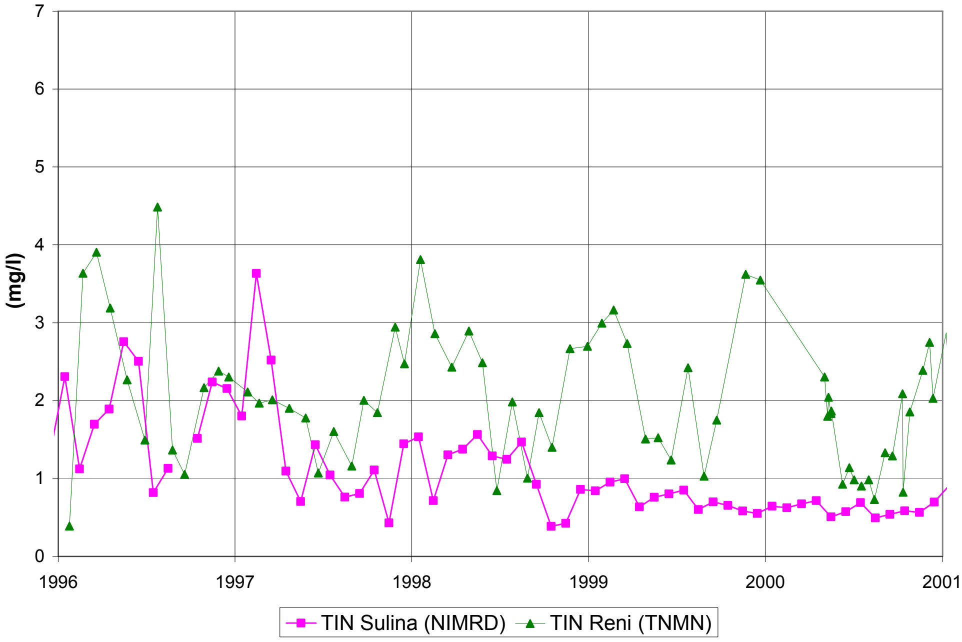

Figure 8-1: Concentrations of TIN at Reni/Sulina from different information sources (1996-2000).

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[3] *This paragraph presents TNMN data from the station of Reni, upstream of the Danube Delta. They are compared with data from NIMRD for the station of Sulina, situated at the downstream end of the Sulina branch, which carries about 20% of the Danube discharge. It should be noted that the concentrations at the TNMN station Sulina (not presented here) are comparable to those at the TNMN station Reni.*

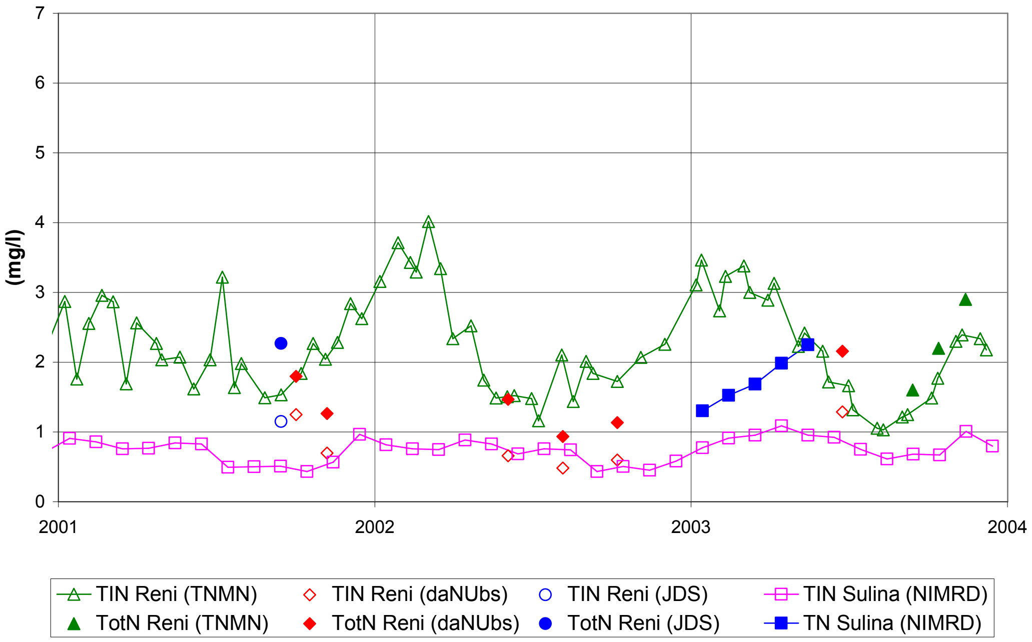

Figure 8-2: Concentrations of TIN and TN at Reni/Sulina from different information sources (2001-2003). The 2002-2003 TNMN data are preliminary unverified data.

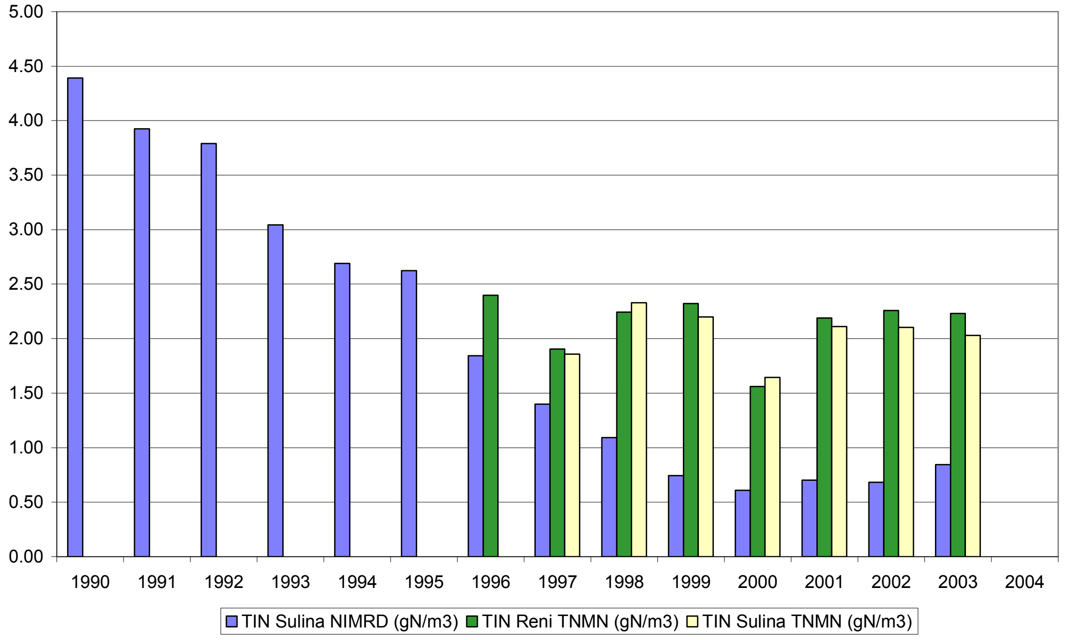

Figure 8-3: Annually averaged concentrations of TIN at Reni/Sulina from different information sources. The 2002-2003 TNMN data are preliminary unverified data.

Figure 8-1 to Figure 8-3 show that the consistency between the observed concentrations of TIN from TNMN and from NIMRD is problematic. The NIMRD data show very low concentrations and a very weak seasonal variation in recent years, and a very strong temporal gradient over the past decade. The data from the *daNUbs* surveys and from the JDS are included in Figure 8-2, both for TIN and for total N. From the comparison with the TNMN data it seems that the TIN data from TNMN agree better with the total N data from the *daNUbs* survey and from JDS. This is an indication that the sampling and analysis procedures for TIN may be less consistent than they seemed when we only considered the TNMN data.

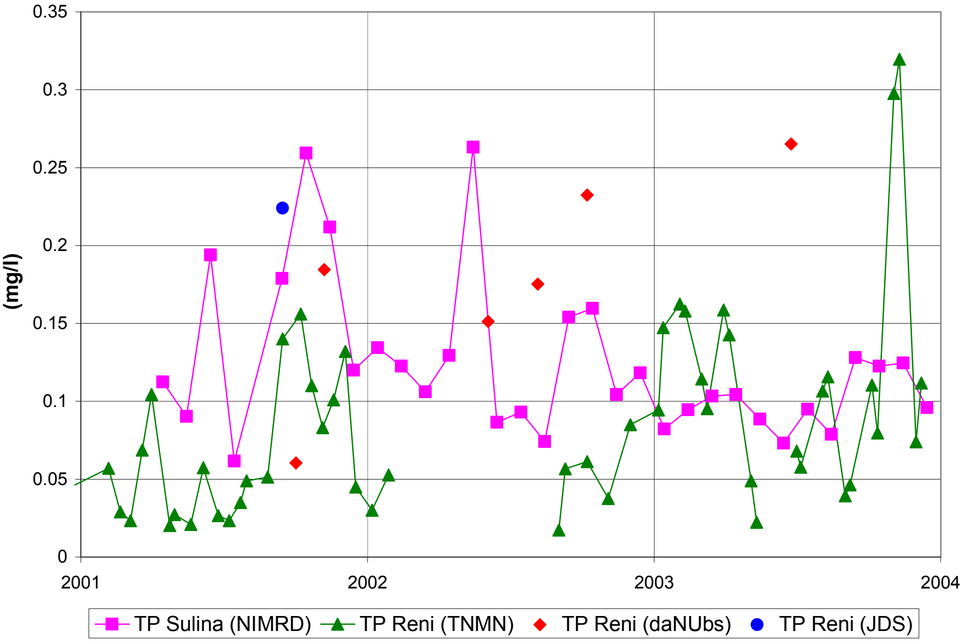

Figure 8-4: Concentrations of TP at Reni/Sulina from different information sources (2001-2003). The 2002-2003 TNMN data are preliminary unverified data.

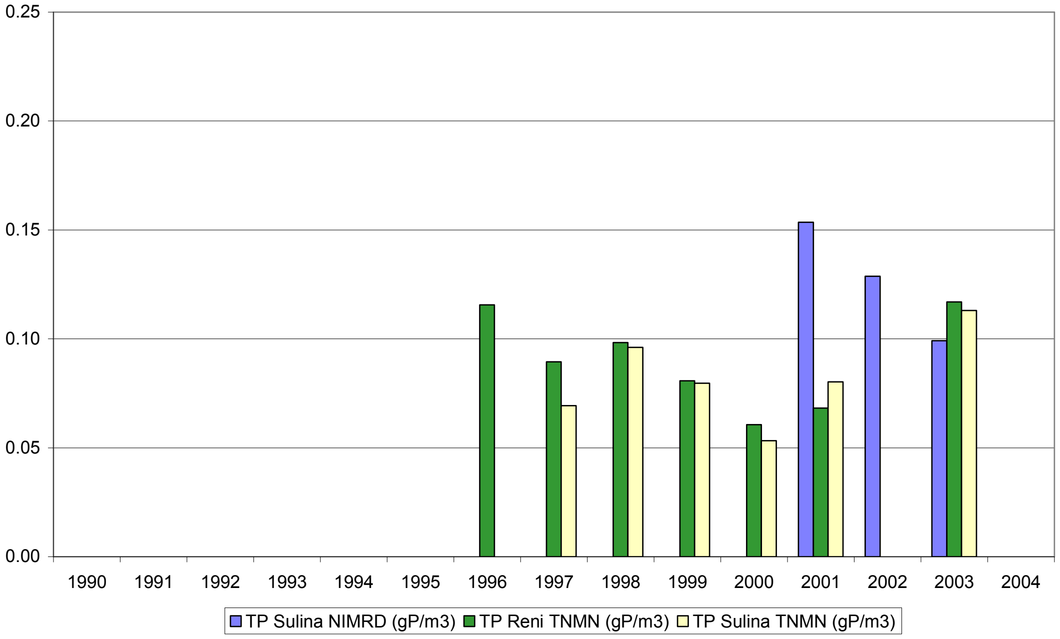

Figure 8-5: Annually averaged concentrations of TIN at Reni/Sulina from different information sources. The 2002-2003 TNMN data are preliminary unverified data.

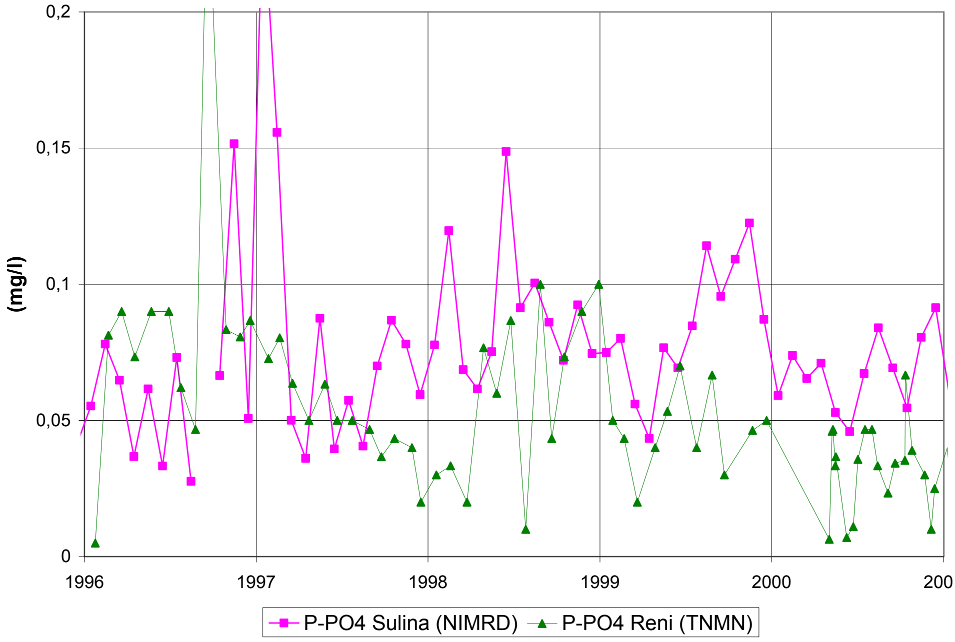

Figure 8-6: Concentrations of phosphates at Reni/Sulina from different information sources (1996-2000).

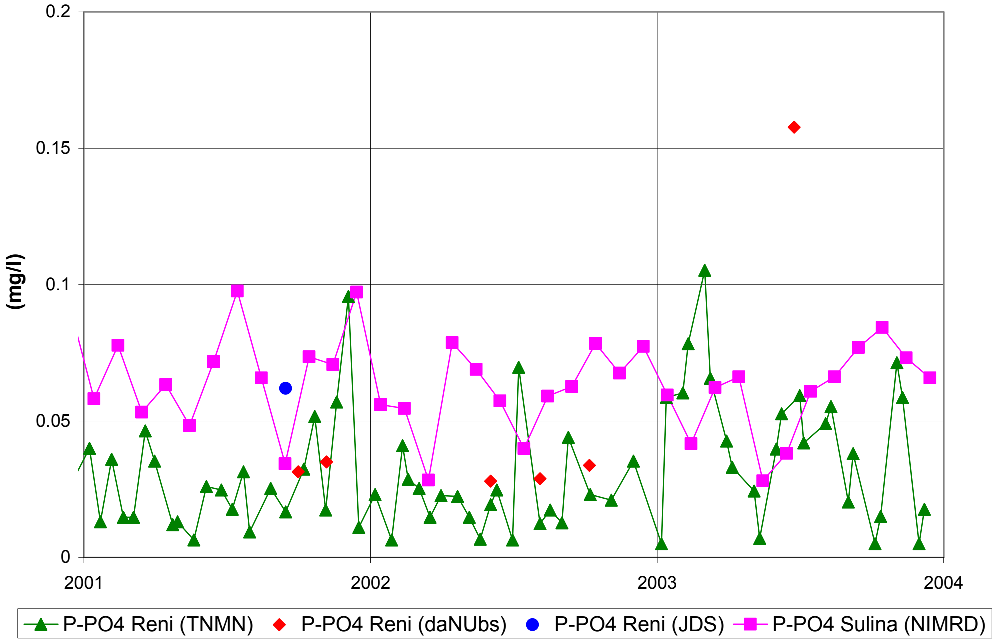

Figure 8-7: Concentrations of phosphates at Reni/Sulina from different information sources (2001-2003). The 2002-2003 TNMN data are preliminary unverified data.

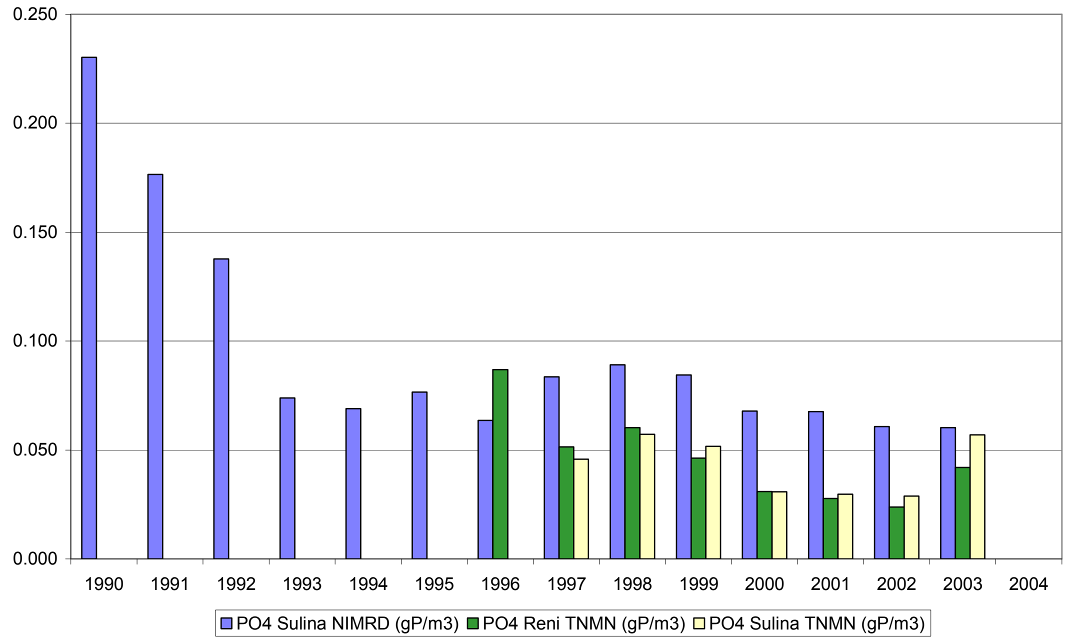

Figure 8-8: Annually averaged concentrations of phosphates at Reni/Sulina from different information sources. The 2002-2003 TNMN data are preliminary unverified data.

Figure 8-4 to Figure 8-8 show that the consistence between the observed concentrations of total P and phosphates from TNMN and from NIMRD is again poor. Especially in recent years, the NIMRD data show consistently higher concentrations. The data from the *daNUbs* surveys and from the JDS confirm that the consistence of data from different sources is troublesome. The JDS data agree better with the NIMRD data, whereas the *daNUbs* surveys match the NIMRD for total P and the TNMN data for phosphates.

The “adjusted P balance” presented in paragraph 3.3.4 assumes a river load at Reni of 24.5 kt/y. This is roughly the equivalent of an average concentration of 0.12 mgP/l. The data from the daNUbs surveys, from the JDS, from TNMN in 2003 and from the NIMRD indicate that this is not as unlikely as it seems from the 1996-2001 TNMN data.

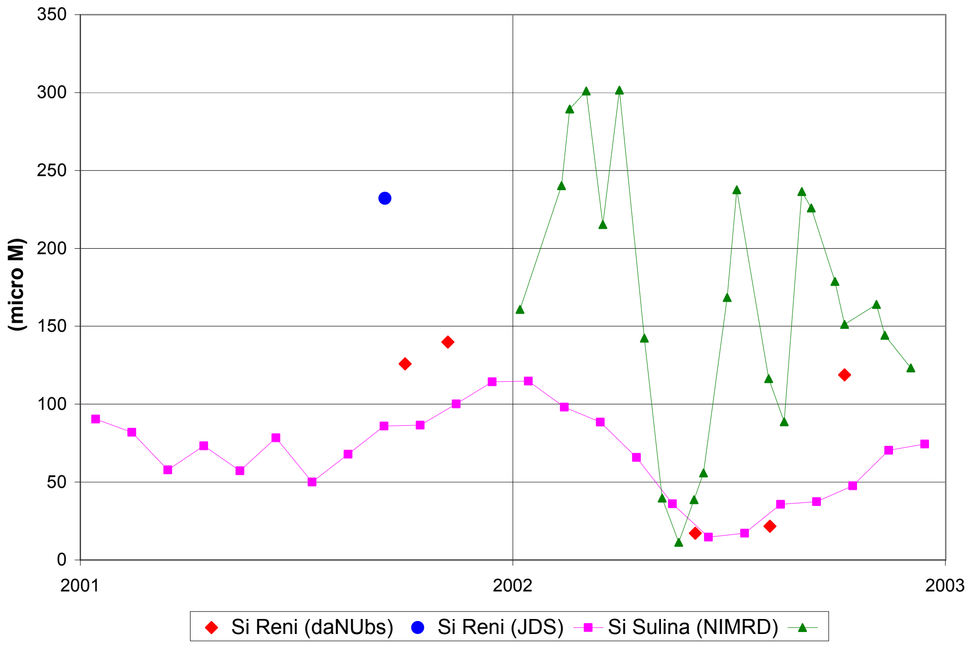

Figure 8-9: Concentrations of dissolved silica during 2001-2002, from different sources. The 2002 TNMN data are preliminary unverified data.

Figure 8-9 shows that the consistence between the observed concentrations of dissolved Si from the different sources is limited. The JDS number at the station of Reni is an outlier, the stations upstream and downstream show values in the order of 100 µM. This brings the JDS in close range with the other values.

8.2 Long term development of the Danube River loads[4]

Different information sources report historical data with regard to the Danube River loads of N and P. In this paragraph we repeat graphs presented by van Gils (1999), completed with the newly computed loads based on the TNMN data.
Figure 8-10 to Figure 8-13 present the results for the river discharge, for the loads of N and for the loads of P. These results are discussed in paragraph 9.1.2.

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[4] *This paragraph is written under the assumption that the data collected in the framework of the Bucharest Convention and the TNMN are correct. As such, it does not explicitly take into account the discussions listed in paragraph 8.1.*

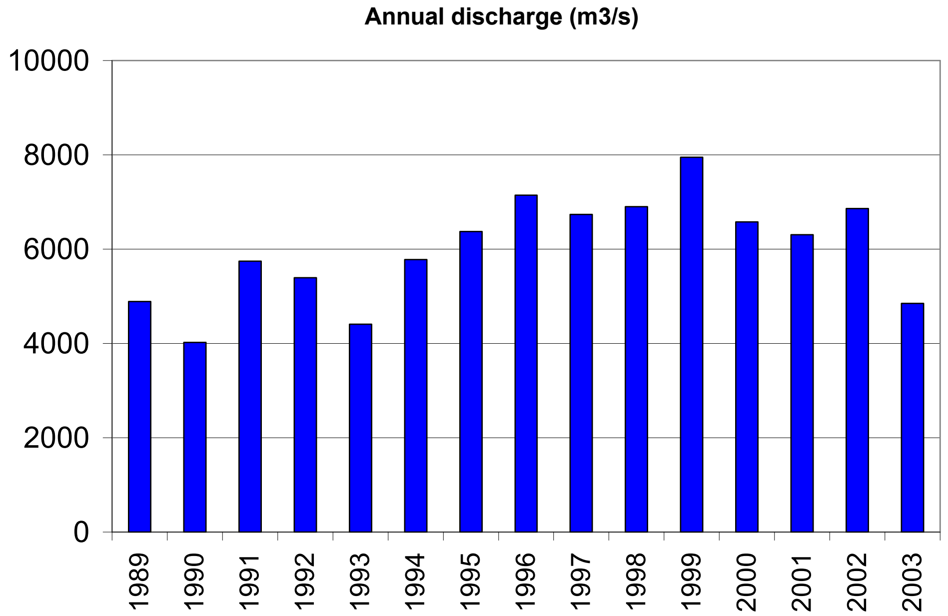

Figure 8-10: Annual discharge of the Danube.

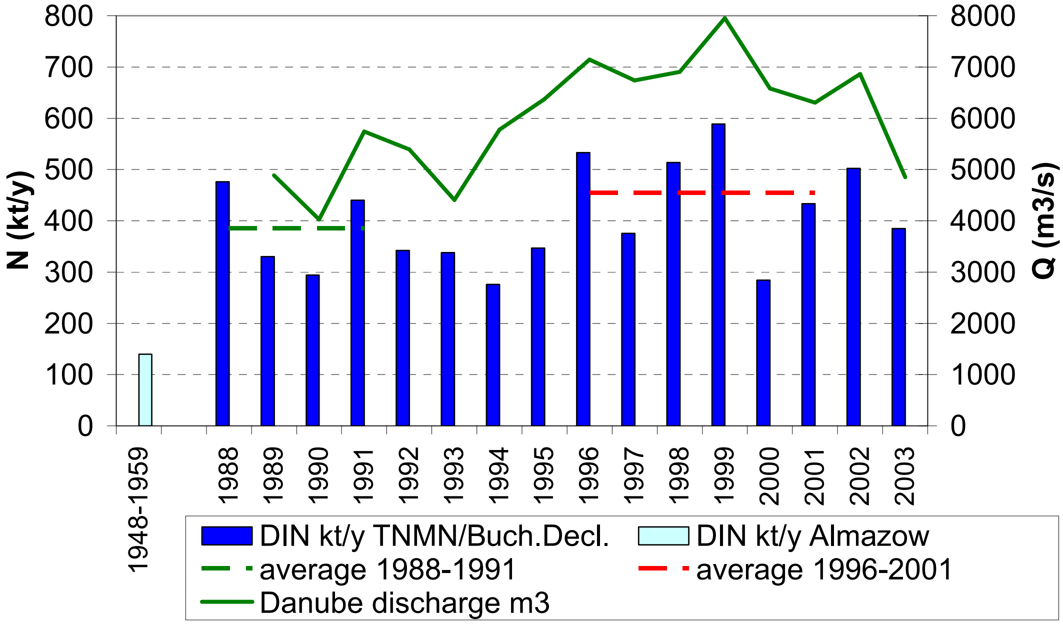

Figure 8-11: Annual nitrogen load of the Danube derived from different sources of information. The graph also shows the annual discharge and the averages over 1988-1991 and 1996-2001 respectively.

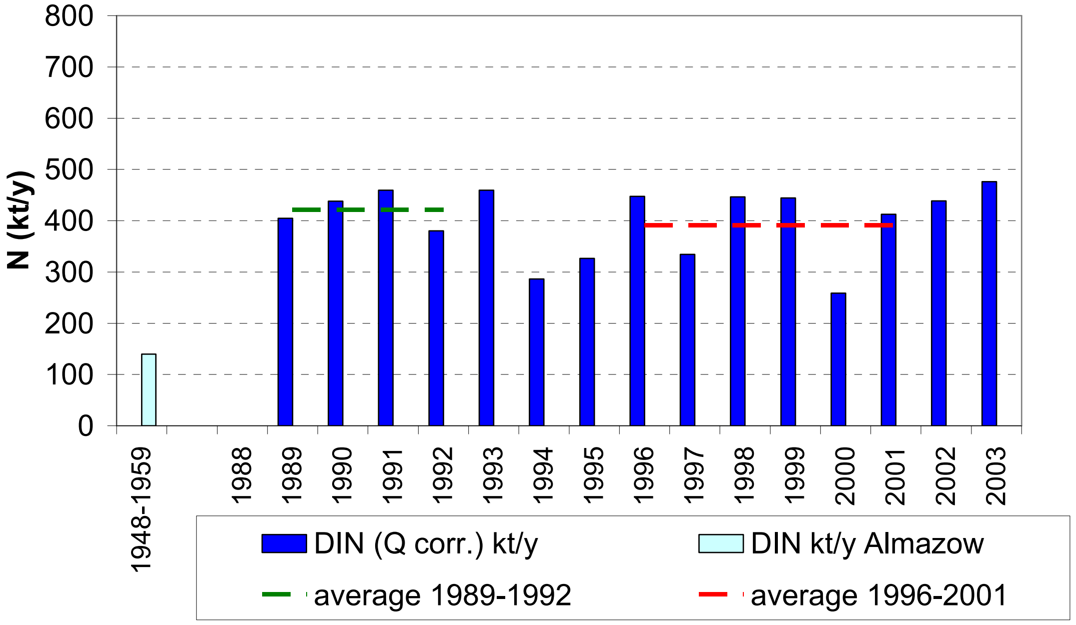

Figure 8-12: Annual nitrogen load of the Danube, corrected for the varying annual discharge. The averages over 1989-1992 and 1996-2001 respectively are also shown.

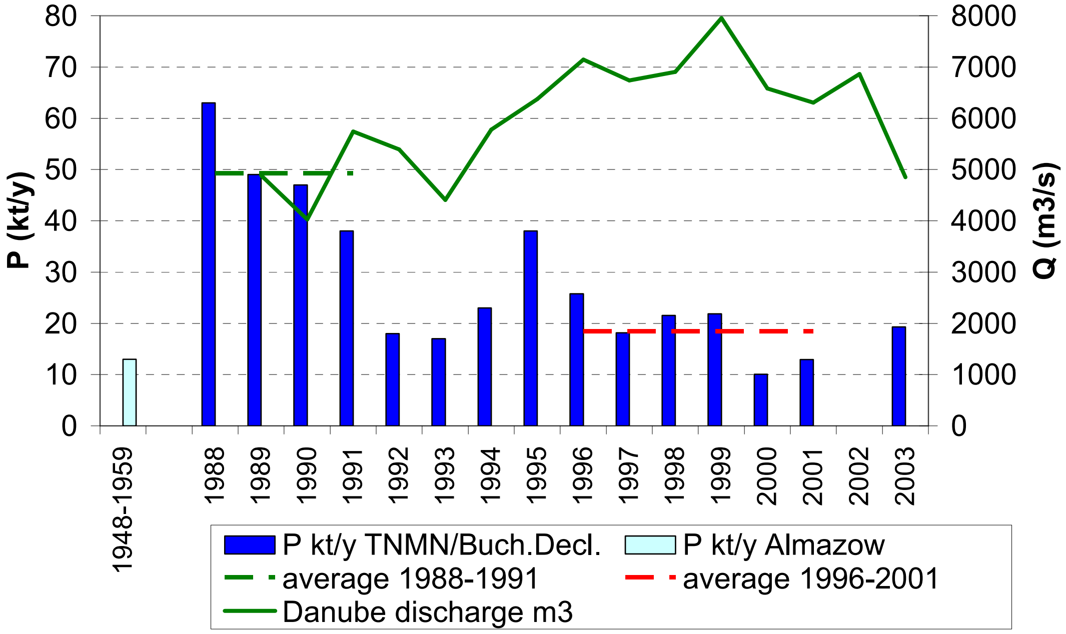

Figure 8-13: Annual phosphorus load of the Danube derived from different sources of information. The graph also shows the annual discharge and the averages over 1988-1991 and 1996-2001 respectively.

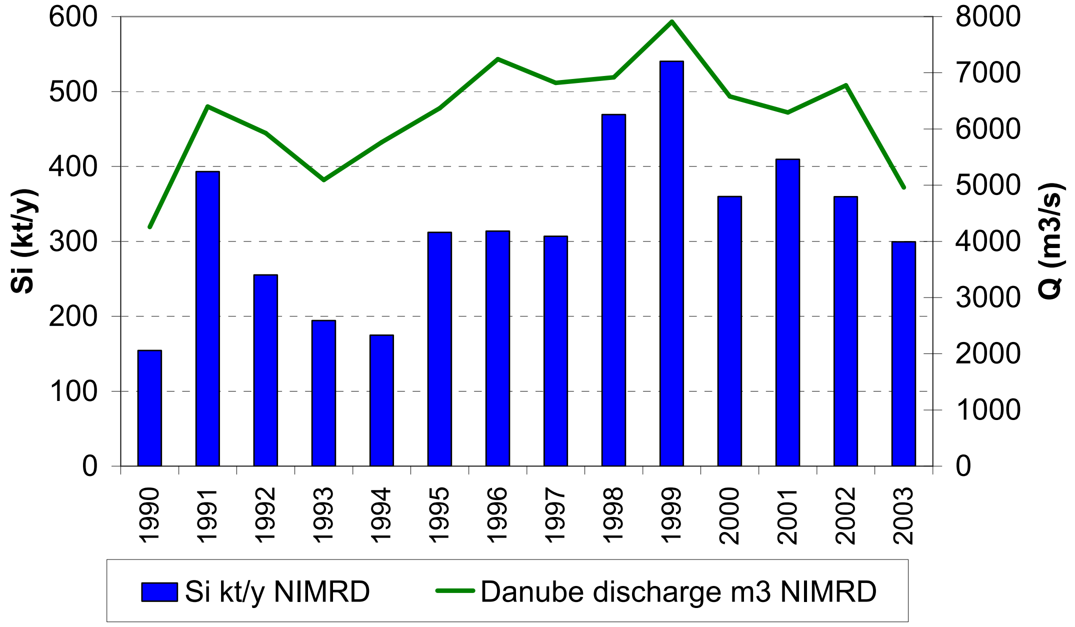

Figure 8-14: Annual loads of silicates at Sulina (also shown is the annual water volume).

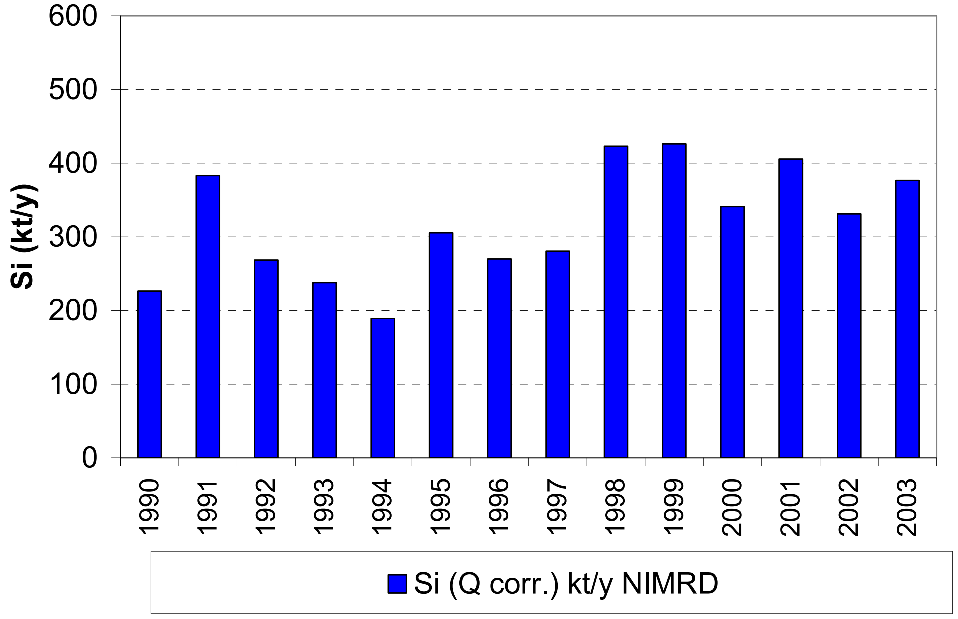

Figure 8-15: Annual loads of silicates at Sulina, corrected for the varying annual discharge.

The NIMRD data present the only long data series for dissolved silica. Figure 8-14 and Figure 8-15 present the results. There is a clear increasing trend in the last decade, even if the data are corrected for the variability of the annual discharge of the Danube river.

8.3 Compilation of data for organic N

The collected data contain limited information about the concentrations of organic N. This paragraph provides a summary.

Chapter 3 provides an overview of the observed concentrations of organic nitrogen in the TNMN database. This information is not complete and not completely consistent. It does show however that the concentration of organic nitrogen is not negligible. Figure 8-16 shows the only available rather complete time series for lower Danube stations (Silistra and Russe in 2000). These data show that a clear seasonal cycle seems not to be present.

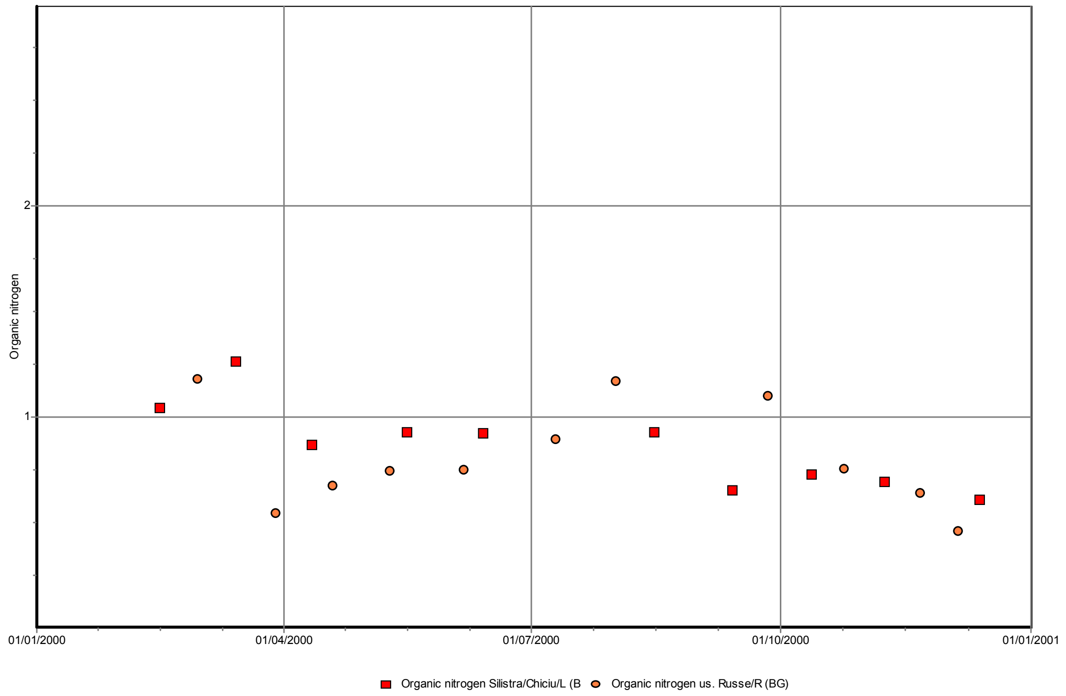

Figure 8-16 Time series of organic nitrogen at Silistra and Russe in 2000 (Source: TNMN).

The data from other information sources provide estimates for organic N at discrete locations for short periods of time. Table 8-1 provides an overview, where the concentration of organic N is expressed as a fraction of total nitrogen and as mgN/l.

Table 8-1: Overview of organic nitrogen data from various information sources

Station	Period	Observed fraction organic N in total N (average)	Observed concentration of organic N in mgN/l (average)
Gabcikovo section (Bratislava / Hrusov reservoir / Medve)	August 2002 (7 days)	28% / 25% / 25%	0.73 / 0.64 / 0.63
	November 2002 (7 days)	19% / 19% / 18%	0.54 / 0.55 / 0.48
	November 2002 (7 days)	17% / 17% / 16%	0.51 / 0.50 / 0.45

Station	Period	Observed fraction organic N in total N (average)	Observed concentration of organic N in mgN/l (average)
Iron Gates section (Bazias / Orsova / Gruia)	April 2002 (7 days)	37% / 45% / 45%	0.72 / 0.53 / 0.61
	June 2002 (7 days)	70% / 59% / 45%	1.07 / 0.78 / 0.67
	August 2002 (7 days)	48% / 70% / 69%	0.50 / 0.98 / 0.70
	August 2003 (1 day)	63% / 51% / 56%	1.33 / 0.94 / 1.10
Isaccea (upstream of Delta)	October 2001 (4 days)	30%	0.55
	November 2001 (4 days)	46%	0.57
	June 2002 (4 days)	55%	0.81
	August 2002 (4 days)	48%	0.46
	October 2002 (4 days)	45%	0.54
	June 2003 (4 days)	40%	0.87
Isaccea (Joint Danube Survey)	16 September 2001	50%	1.1

The coverage of the information in Table 8-1 is poor, both in time and in space. It does show however that the fraction of organic N is not negligible.

The concentrations of TIN upstream of the Delta are relatively high in the winter and relatively low in the summer. Furthermore, the Danube discharge shows seasonal variations. Consequently, the numbers listed in Table 8-1 are not immediately representative for the annual Danube load.
The previous estimate that the fraction of the organic N load at the Danube outflow point equals 22% of the TIN load (van Gils, 1999). If we assume that the concentration of organic N varies sinusoidally between 0.5 and 1.0 mgN/l, with the maximum value in the summer, we can compute the consequences for the Danube nitrogen load at Reni. The result for the data from 1996-2001 is an increase of 30-40% (average of 34%).

8.4 Compilation of data for silicates

Table 8-2 presents an overview of the available data with respect to the concentration of silicates.

Table 8-2: Overview of inorganic silica data from various information sources

Data source	Station	Period	Observed concentration in µM
MS Burgund Survey	Longitudinal profile along the Upper and middle Danube	May/June 1998	Range along river (^{1}): 0 – 25
Garnier et al. (2002)		1988-1990	Ranges per station (^{1}):
	Drava		33 - 100
	Sava (few data)		67
	Isaccea		0 – 100

Data source	**Station**	**Period**	**Observed concentration in** µM
Humborg et al. (1997)	Sulina	recent years	median: ≈ 60
daNUbs, WP4	Gabcikovo section (Bratislava / Hrusov reservoir / Medve)		Averages per station (1):
		August 2002 (7 days)	≈ 130
		November 2002 (7 days)	≈ 120
		November 2002 (7 days)	≈ 120
daNUbs, WP4	Iron Gates section (Bazias / Orsova / Gruia)		Averages per station (1):
		April 2002 (7 days)	26 - 83
		June 2002 (7 days)	22 - 95
		August 2002 (7 days)	24 – 70
daNUbs, WP4	Isaccea (upstream of Delta)		Averages (1):
		October 2001 (4 days)	132
		November 2001 (4 days)	147
		June 2002 (4 days)	18
		August 2002 (4 days)	23
		October 2002 (4 days)	125
		June 2003 (4 days)	26
JDS	Longitudinal profile	August/September 2001	Range along river (2): 0 – 143
Teodoru et a. (2002)	Iron Gates section, Bazias	Annual average over 2001 (bi-weekly sampled)	80
TNMN			Annual average (>8 samples) (1):
	Borovo	1998-1999	150 - 184
	Lower Danube	2002	133 – 167
NIMRD	Sulina	Average over 1996-2001	62 µM

1 Converted from mgSiO$_2$/l, using 1µM = 0.060 mgSiO2/l.
2 Converted from mgSi/l, using 1µM = 0.028 mgSiO2/l.

Figure 8-17 to Figure 8-19 present the sparse available data from the TNMN. Note that the available chlorophyll-α data indicate very low values in the lower Danube. The silica data show a clear seasonal cycle, with a lot of scatter. Simultaneous observations of chlorophyll-α are not available. The observed concentrations of dissolved oxygen however, indicate no significant oversaturation.

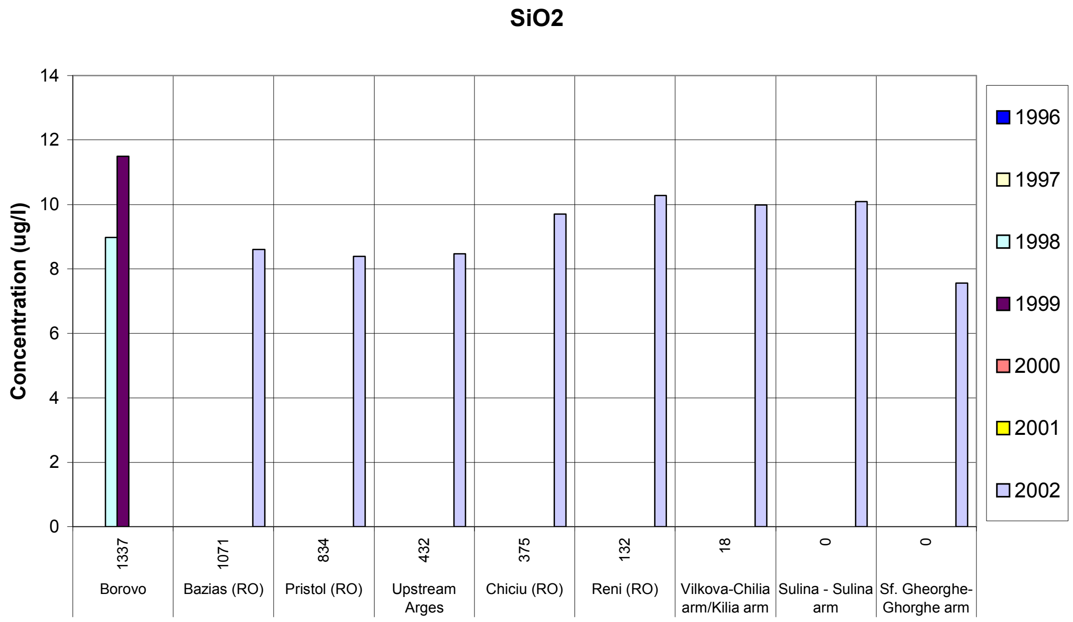

Figure 8-17: Yearly averages of SiO_2 (>8 samples) from the TNMN.

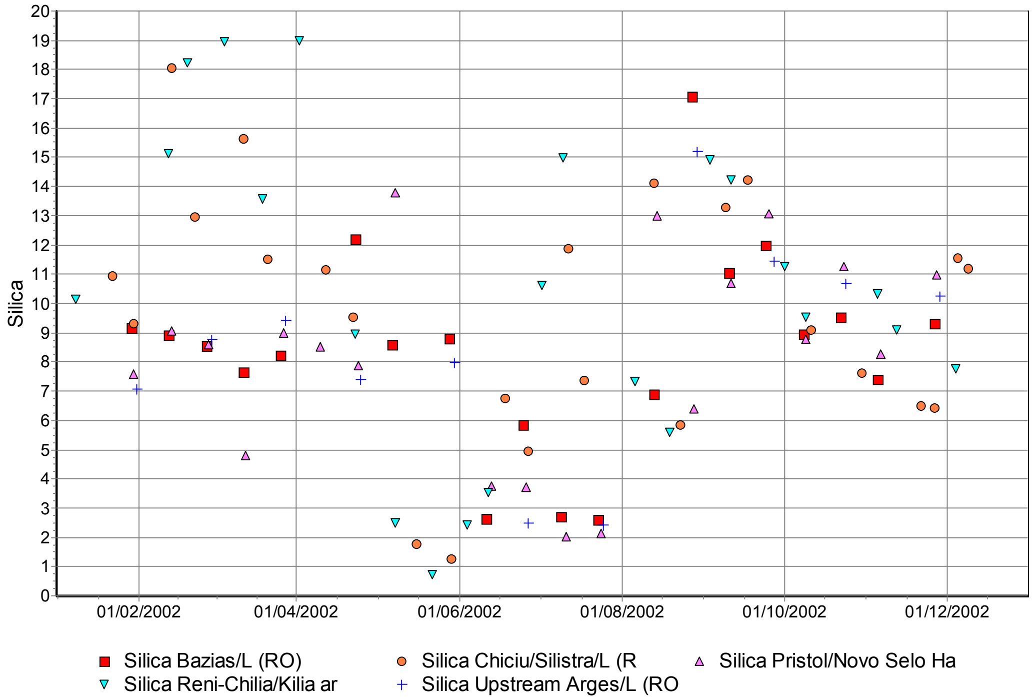

Figure 8-18: Selected observations of SiO_2 in the Lower Danube during 2002.

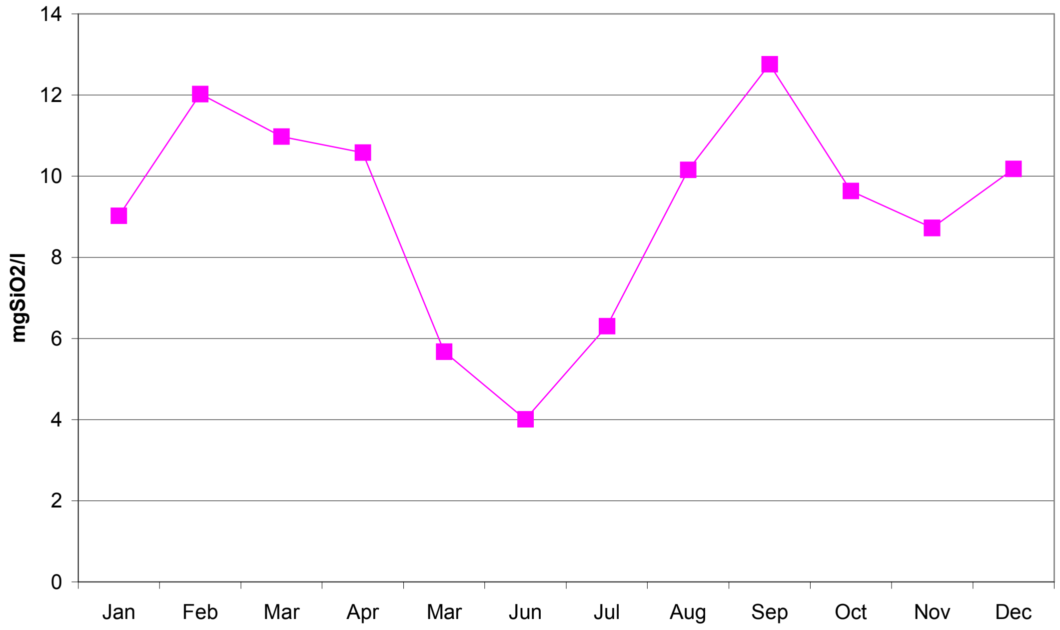

Figure 8-19: Monthly averages during 2002 at the stations Bazias, Chiciu, Pristol, us. Arges and Reni (TNMN).

Figure 8-20 illustrates that also the NIMRD data show a clear seasonal cycle. The winter values during recent years are between 80 and 100 µM. This is in line with the "background" values reported by Garnier et al. (2002).

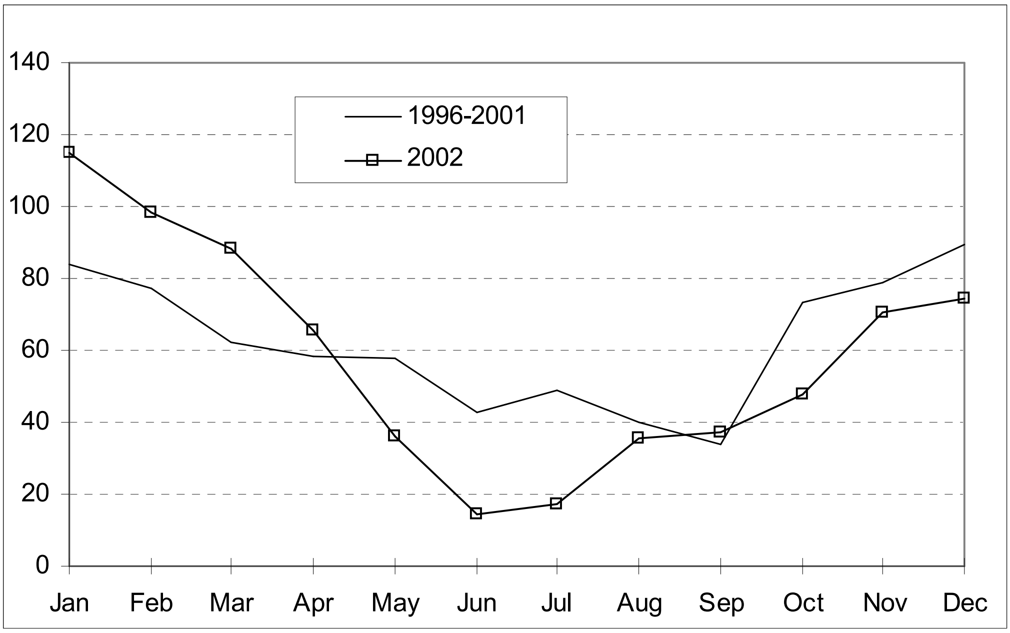

Figure 8-20: Monthly averaged concentrations of silicates at Sulina.

9 Conclusions and recommendations

9.1 Conclusions

9.1.1 Sampling and analysis

The Trans-National Monitoring Network (TNMN) forms an indispensable source of information. This initiative is of key importance for the International Commission for the Protection of the Danube River (ICPDR). Given the brief history of basin-wide co-operation under the umbrella of the ICPDR, and given the complexity of the basin from a socio-economical point of view, the achievements within the TNMN have been huge.

While we use the TNMN data as the corner stone for the current project, we believe we should be critical and also mention those elements of the TNMN programme, which deserve improvement. Since 2001 new stations in Serbia-Montenegro have been included in the TNMN. This is highly relevant, because the downstream sections of the Tisa and the Sava as well as the Iron Gates backwater area are situated in Serbia-Montenegro.

The overall picture of the spatial and temporal distribution of the river discharge, which emerges from the TNMN data is fully consistent. We therefore consider this information highly reliable.

A similar observation can be made with regard to Total Inorganic Nitrogen, be it that the accuracy of the concentrations and the computed river loads is probably somewhat lower. This is logical, since the sampling and analysis procedures have an inherent inaccuracy, and since the sampling frequency is not always very high. Nevertheless, these data are considered reliable in view of the objectives of *daNUbs*. When we consider the consistency of the TNMN data as a whole in comparison to data from other sources, the picture is less positive. Significant discrepancies have been found, which indicates that the sampling and analysis should be quality controlled with great care.

The reliability of the TNMN results of total phosphorus is problematic. At a number of occasions the TNMN data show internal inconsistencies. Moreover, there exist some inconsistencies between the TNMN data and data from other information sources. This means that the data for total P can only be used after making certain assumptions about what data are representative.

The spatial and temporal coverage of the TNMN data for Si is limited. Using also data from other information sources, still a rather complete image emerges. The units used are not consistent, and in some occasions conversion factors had to be assumed.

9.1.2 The Danube river loads of N, P and Si

The average Danube load of inorganic nitrogen in 1997-2001 is about 460 kt/y. If there is any trend at all during the last decade, it is an upward trend (see Figure 8-11). This trend may well be an artefact caused by the variability of the Danube annual water discharge (see Figure 8-12).

Based on the TNMN data, the average Danube load of total phosphorus in 1997-2001 is about 17 kt/y. In the early nineties of the last century a sharp decrease occurred, from about 50 kt/y to about 20 kt/y. The TNMN data indicate that a second sharp drop to about 10 kt/y occurred in the years 2000-2001.
We think there is good reason to doubt the TP data for 2000-2001. From a basin-wide analysis, the current Danube phosphorus load is estimated at about 25 kt/y.

Based on data from the NIMRD, the yearly average Danube load of dissolved silicate shows a distinct increasing trend. The average value over the period 1996-2000 equals about 400 kt/y. These numbers are consistent with the sparse available data from other sources.

9.1.3 Balances of N, P and Si

The analysis of the available data has resulted in the synthesis of a basin wide balance of (inorganic) nitrogen, phosphorus and (inorganic) silica. These balances are shown in Figure 9-1 to Figure 9-3, see also Table 3-3 and Table 3-6.

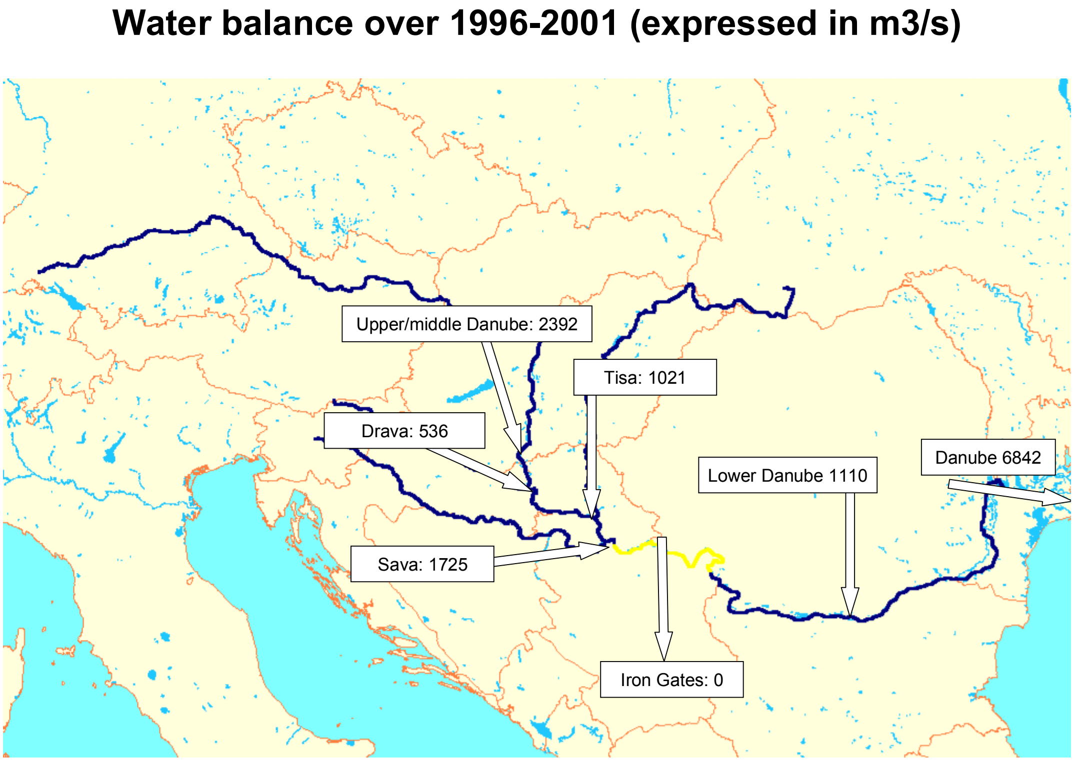

Figure 9-1: Water balance of the Danube river (1996-2001).

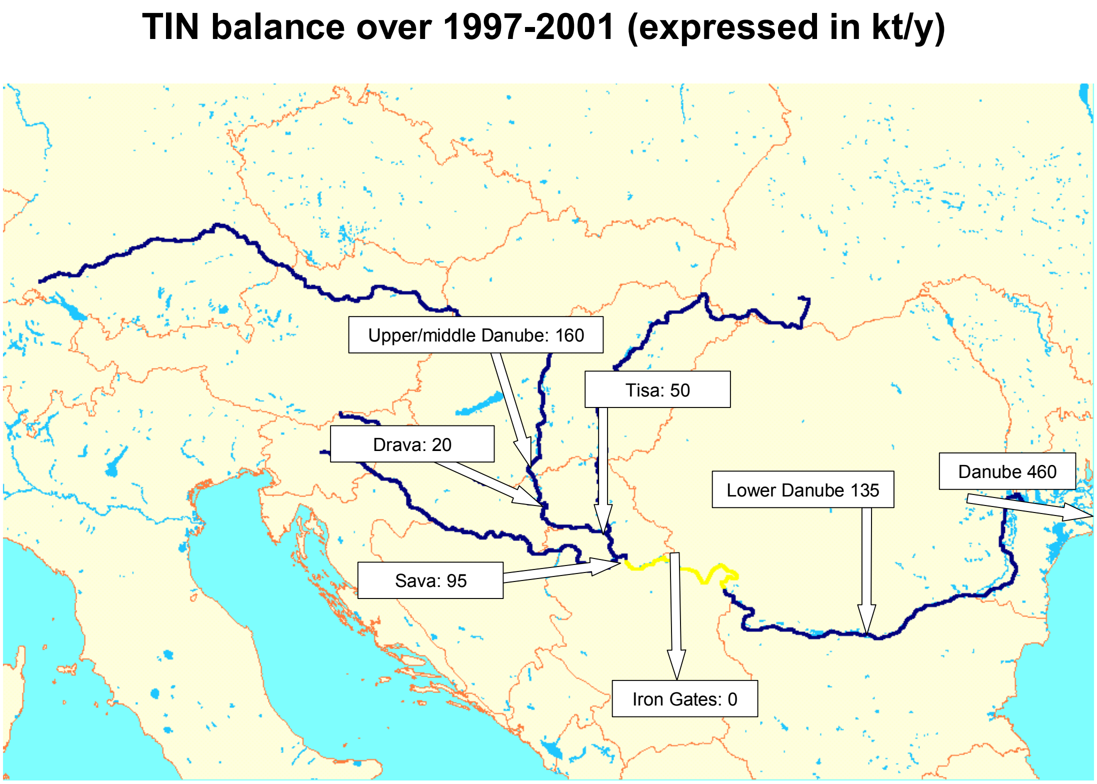

Figure 9-2: TIN balance of the Danube river (1997-2001).

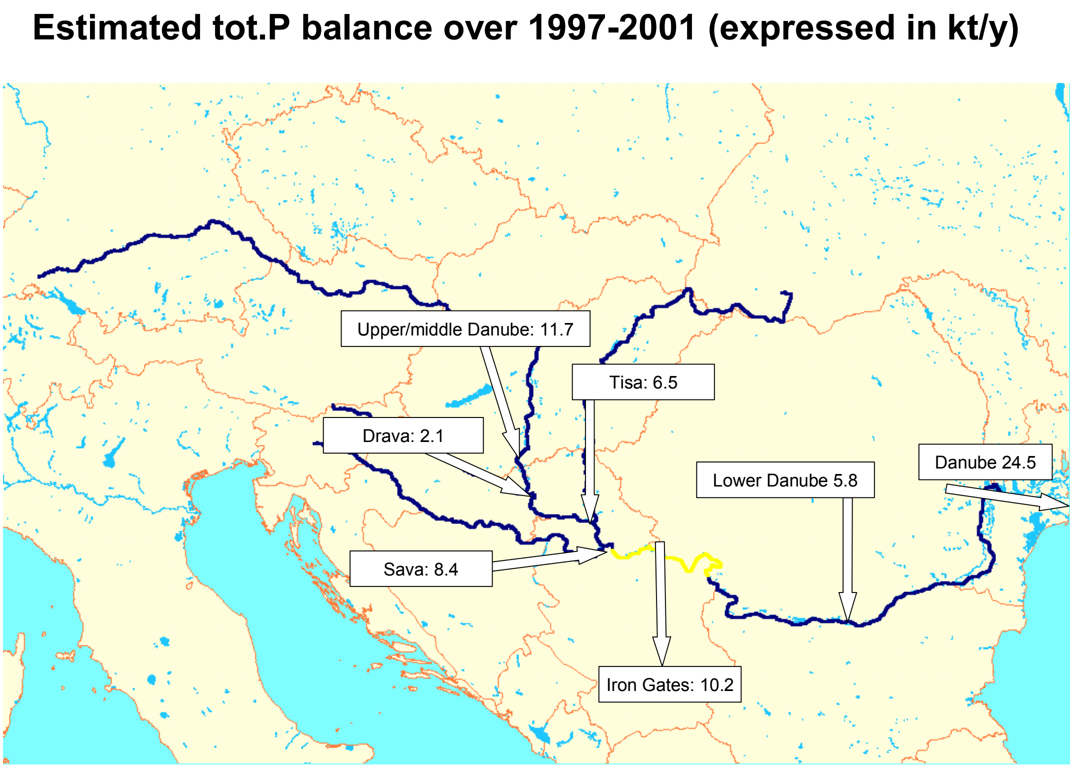

Figure 9-3: Estimated TP balance of the Danube river (1997-2001).

Only for phosphorus there are clear indications for the existence of limited areas with strong retention. The Gabcikovo area retains about 10% of the local load. The Iron Gates area probably retains about one third of the incoming phosphorus load. The available information is not consistent at this point, so this conclusion could not be reached with a 100% certainty.

The sparse available data do not allow the construction of a complete silicates balance as was done for N and P. The “emissions” of silica to the surface waters are estimated at about 515 kt/y (chapter 8). With the Danube river loads being about 400 kt/y, this implies a retention of about 22%.

9.1.4 Role of organic nitrogen

The available data reveal that there are two relevant forms of organic nitrogen. The dissolved organic nitrogen (DON) fraction has no direct relation with phytoplankton blooms. It consists for example of humic acids and it originates from organic matter in the soils. In the summer period it reaches concentrations of about 0.5 to 1.5 mgN/l. It is unknown how this value varies over the year.

The particular organic nitrogen (PON) fraction consists mainly of live and dead phytoplankton and therefore this fraction is directly connected to the phytoplankton blooms. This fraction is related to anthropogenic emissions, since the phytoplankton feeds on ammonium and nitrates from these emissions. The PON fraction is quite rapidly mineralised to ammonium and nitrates. In the summer period it reaches concentrations of up to about 0.3 mgN/l (equivalent to 15,000 mgN/kgSS) in areas of phytoplankton blooms. There are indications that on average the phytoplankton blooms are the strongest in the middle Danube. Near the delta the average phytoplankton density is small, so this PON fraction is less relevant there. In general this fraction is small.

High concentrations of PON can also occur during floods: values up to 4 mg/l have been observed in Vienna during the August 2002 flood. Such peaks are not associated with phytoplankton blooms: they are the result of erosion. The specific N content of solids in such peaks is lower: in the Vienna case about 1,500 mgN/kgSS. This fraction only reaches relevant concentrations during extreme floods.

Organic nitrogen is not sampled frequently enough at a sufficient number of stations to provide a coherent picture of the spatial gradients. Moreover, the handling and analysis of the collected samples does not seem consistent enough to guarantee full comparability. Under the present conditions, the only way to address the N balance is to look at TIN.

The sparse available data of organic nitrogen indicate that the fraction of organic nitrogen is certainly not negligible: it amounts to 15-70% of total N. There are indications that the contribution of organic N is smaller in the upper part of the Danube and higher in the lower part. This could imply that the TIN mass balance presents a slightly biased image of the nitrogen mass balance: an increasing part of the river load is transformed to organic nitrogen going in a downstream direction. Consequently, the downstream load is too small in relation to the upstream load.

It can be expected, if the concentrations of N in the Danube decrease due to emission reduction measures, that the relative importance of the organic N fraction increases.

9.1.5 Accuracy of the computed river loads of phosphorus

The effect of the sampling frequency on the computed loads of suspended solids (and therefore on the loads of TotP) is caused by a strongly increasing concentration of SS if the river discharge increases. Such a relation is only noticeable at high to extreme floods, when an annual sediment load is transported in a few days. Such a flood has been observed in 2002 in Austria and Slovakia. Unfortunately, the TNMN data for this year are not yet available, so that a check how far this event could be observed could not be made. It is possible that such extreme events only occur upstream of the Tisa and Sava confluences, since further downstream the Danube bed is so wide that only coinciding flood events on the Upper and Middle Danube, on the Tisa and on the Sava would cause similar conditions.

Under the conditions covered in 1996-2001 by TNMN data, there is no significant correlation between the river discharge and the SS concentration. Therefore, the theoretical effect of the sampling frequency on the computed loads of suspended solids (and therefore on the loads of TotP) could not be demonstrated and quantified on a basin-wide scale.

The effect of surface sampling only on the accuracy of the computed loads of suspended solids (and therefore on the loads of TotP) could be quantified for the Lower Danube during one particular survey. It was demonstrated that the real load of SS is 20 to 40% higher than the load computed based on surface samples only. The effect on the TotP loads is smaller, due to the fact that TotP also included a dissolved fraction which constitutes about half of the total. This leaves an error of about 10 to 20%, while it is not known if these numbers are valid under all conditions. Given the very limited accuracy of the sampling and analysis of TotP, this error seems to be not very relevant at the present state-of-the-art.

9.2 Recommendations

The TNMN should be maintained and strengthened as a main policy support tool of the ICPDR. It is important to routinely present and analyse the data, for example by carrying out load calculations, for stations with sampling at three locations in the profile (LMR).

At present, the sampling programme is not complete and/or not consistent for a number of relevant parameters. The TNMN could be strengthened considerably by paying more attention to:

- completion of organic nitrogen data (possibly separated in a dissolved and a particulate fraction);
- improvement of total phosphorus data (possibly separated in a dissolved and a particulate fraction);
- completion and improvement of silica data;
- completion of chlorophyll-α data;
- completion and improvement of suspended solids and total P data collected during flood events.

Sampling at multiple depths is certainly interesting. However, the expected profits in terms of the increase of the accuracy of the load calculations is relatively small, compared to the possible profits of a more harmonised sampling and analysis.

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A Modifications made to the TNMN data

Flow data
Flow at Vilkova, 18-4-1996, values 0 at L and R were removed.
Flow at Szob, 14-5-1997, value 1470 at R was replaced by 2470.
Flow at Tiszasziget, 27-8-1997, value 640 at R was replaced by 460.
Flow at Tiszasziget, 12/19/26-4-2000, 3/17/31-5-2000 and 2-8-2000, values at R were multiplied with 10.

Total P data
For the stations Basarbovo, Karantzi and Silistra the unit mg/kg was found to be an error and replaced by mg/l. For the stations Breclav, Dravaszabolcs, Dunafoldvar, Hercegszanto, Komarno and Lanzhot the data reported with the unit mg/kg were found to be sediment samples and therefore omitted from the data. The assessment was based on the sampling frequency of the parameter and the values of the parameter.

Total P, ortho-phosphates and nitrites
Unrealistically high values were assumed to be given in g/l, and subsequently multiplied with 0.001.

Chlorophyll-α
The data for the Romanian stations in 1996-2000 are given in the unit mg/l with unrealistic numbers. No correction could be applied, and the numbers have been neglected.
The data for Hungarian stations are given in mg/l and converted to μg/l.
The data for some Slovak stations are given in mg/l and converted to μg/l.
The data for Jochenstein (D) were listed with the unit mg/l, assumed was that the values are nevertheless given in μg/l.

B Comparison of computed river loads, by different methods

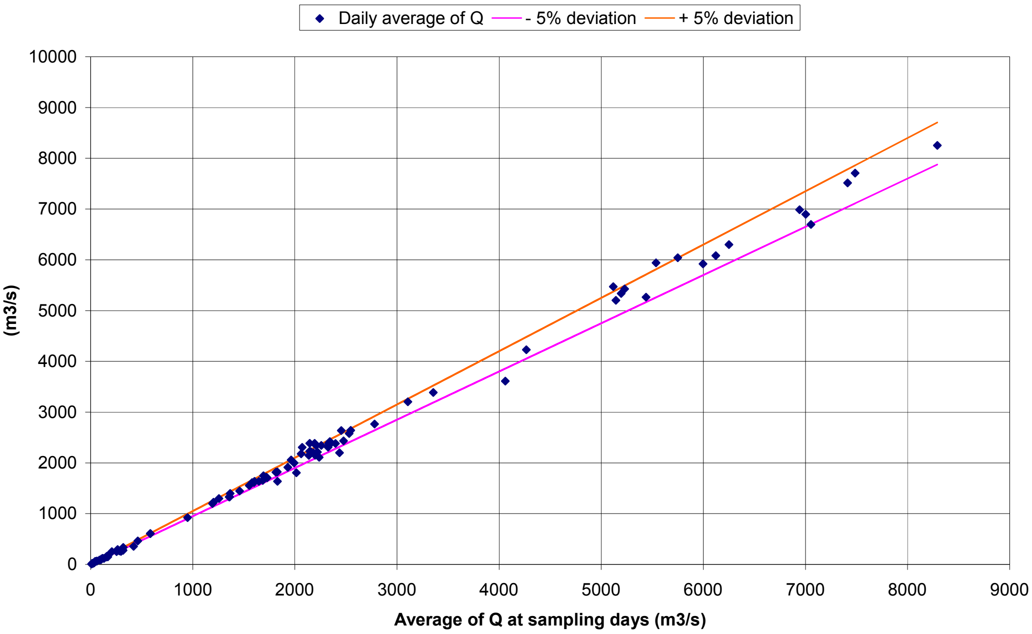

Figure B-1: Comparison of average discharge on sampling days only (plotted on the X-axis) and daily averaged discharge (plotted on the Y-axis). The blue and red lines indicate differences between both numbers larger than –5% and +5% respectively.

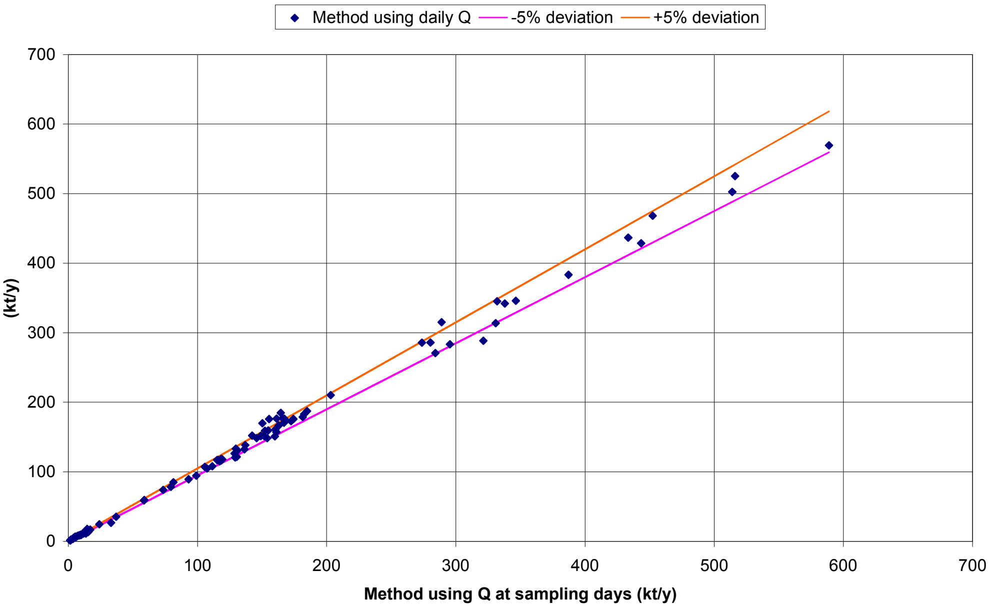

Figure B-2: Comparison of TIN loads computed by different methods. The results from the method using only the discharge at the sampling dates is plotted on the X-axis, while the result of the method using daily discharges is plotted on the Y-axis. The blue and red lines indicate differences between both methods larger than –5% and +5% respectively.

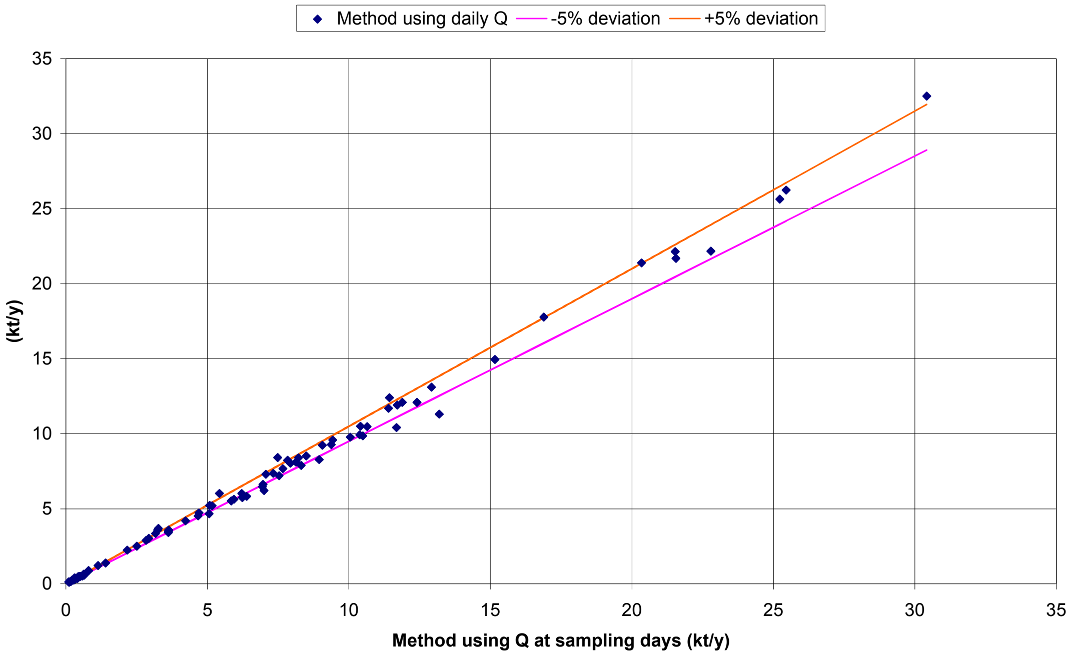

Figure B-3: Comparison of total P loads computed by different methods. The results from the method using only the discharge at the sampling dates is plotted on the X-axis, while the result of the method using daily discharges is plotted on the Y-axis. The blue and red lines indicate differences between both methods larger than –5% and +5% respectively.

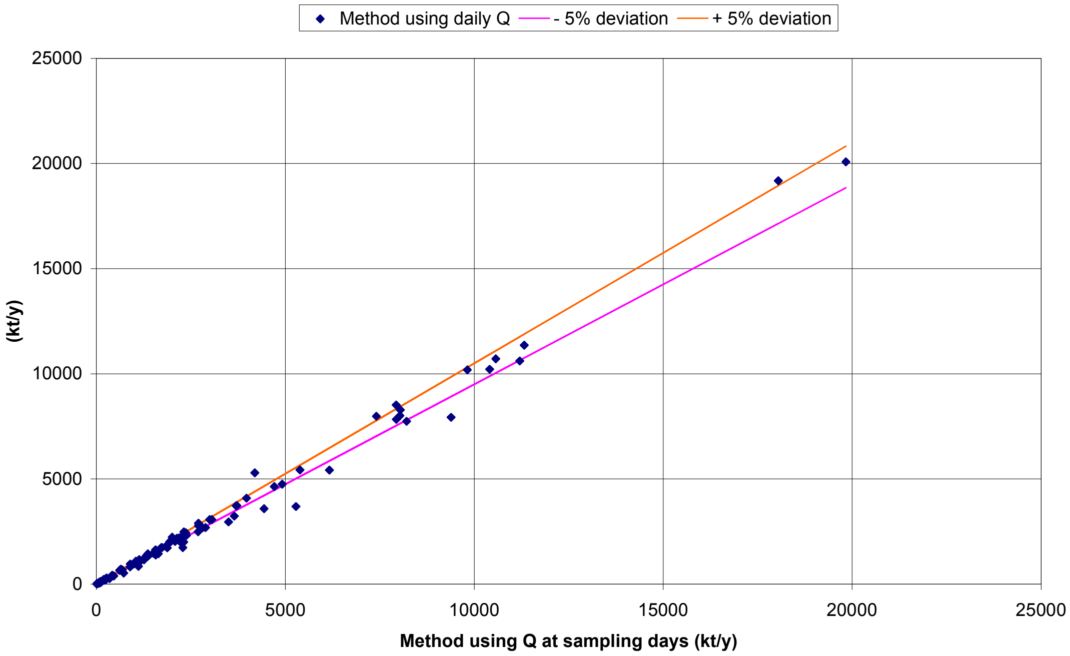

Figure B-4: Comparison of suspended solids loads computed by different methods. The results from the method using only the discharge at the sampling dates is plotted on the X-axis, while the result of the method using daily discharges is plotted on the Y-axis. The blue and red lines indicate differences between both methods larger than –5% and +5% respectively.

C TNMN stations (1996-2000)

The table below provides a full listing of the TNMN stations in the years 1996-2000.

Country Code	River Name	Town/Location Name	Distance [Km]	Altitude [m]	Catch-ment	DEFF Code	Loc
D01	Danube	Neu-Ulm	2581	460	8107	L2140	L
D02	Danube	Jochenstein	2204	290	77086	L2130	M
D03	/Inn	Kirchdorf	195	452	9905	L2150	M
D04	/Inn/Salzach	Laufen	47	390	6113	L2160	L
A01	Danube	Jochenstein	2204	290	77086	L2220	M
A02	Danube	Abwinden-Asten	2120	251	83992	L2200	R
A03	Danube	Wien-Nussdorf	1935	159	101700	L2180	R
A04	Danube	Wolfsthal	1874	140	131411	L2170	R
CZ01	/Morava	Lanzhot	79	150	9725	L2100	R
CZ02	/Morava/Dyje	Pohansko	17	155	12540	L2120	R
SK01	Danube	Bratislava	1869	128	131329	L1840	M
SK02	Danube	Medvedov/Medve	1806	108	132168	L1860	M
SK03	Danube	Komarno/Komarom	1768	103	151961	L1870	M
SK04	/Váh	Komarno	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov	1806	108	131605	L1470	M
H02	Danube	Komarom/Komarno	1768	101	150820	L1475	M
H03	Danube	Szob	1708	100	183350	L1490	LMR
H04	Danube	Dunafoldvar	1560	89	188700	L1520	LMR
H05	Danube	Hercegszanto	1435	79	211503	L1540	LMR
H06	/Sio	Szekszard-Palank	13	85	14693	L1604	M
H07	/Drava	Dravaszabolcs	78	92	35764	L1610	M
H08	/Tisza	Tiszasziget	163	74	138498	L1700	LMR
H09	/Tisza/Sajo	Sajopuspoki	124	148	3224	L1770	M
Sl01	/Drava	Ormoz	300	192	15356	L1390	L
Sl02	/Sava	Jesenice	729	135	10878	L1330	R
HR01	Danube	Batina	1429	86	210250	L1315	M
HR02	Danube	Borovo	1337	89	243147	L1320	R
IR03	/Drava	Varazdin	288	169	15616	L1290	M
HR04	/Drava	Botovo	227	123	31038	L1240	M
HR05	/Drava	D.Miholjac	78	92	37142	L1250	R
HR06	/Sava	Jesenice	729	135	10834	L1220	R
HR07	/Sava	us. Una Jasenovac	525	87	30953	L1150	L
HR08	/Sava	ds. Zupanja	254	85	62890	L1060	MR
BlH01	/Sava	Jasenovac	500	87	38953	L2280	M
BlH02	/Sava/Una	Kozarska Dubica	16	94	9130	L2290	M
BlH03	/Sava/Vrbas	Razboj	12	100	6023	L2300	M
BlH04	/Sava/Bosna	Modrica	24	99	10308	L2310	M
RO01	Danube	Bazias	1071	70	570896	L0020	LMR
RO02	Danube	Pristol/Novo Selo Harbour	834	31	580100	L0090	LMR
RO03	Danube	us. Arges	432	16	676150	L0240	LMR
RO04	Danube	Chiciu/Silistra	375	13	698600	L0280	LMR
RO05	Danube	Reni-Chilia/Kilia arm	132	4	805700	L0430	LMR
RO06	Danube	Vilkova-Chilia arm/Kilia arm	18	1	817000	L0450	LMR
RO07	Danube	Sulina - Sulina arm	0	1	817000	L0480	LMR
RO08	Danube	Sf.Gheorghe-Ghorghe arm	0	1	817000	L0490	LMR
RO09	/Arges	Conf. Danube	0	14	12550	L0250	M
RO10	/Siret	Conf. Danube Sendreni	0	4	42890	L0380	M
RO11	/Prut	Conf.Danube Giurgiulesti	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	834	35	580100	L0730	LMR

Country Code	River Name	Town/Location Name	Distance [Km]	Altitude [m]	Catch-ment	DEFF Code	Loc
BG02	Danube	us. Iskar - Bajkal	641	20	608820	L0780	R
BG03	Danube	Downstream Svishtov	554	16	650340	L0810	MR
BG04	Danube	us. Russe	503	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	375	7	698600	L0850	LMR
BG06	/Iskar	Orechovitza	28	31	8370	L0930	M
BG07	/Jantra	Karantzi	12	32	6860	L0990	M
BG08	/Russ.Lom	Basarbovo	13	22	2800	L1010	M
MD01	/Prut	Lipcani	658	100	8750	L2230	L
MD02	/Prut	Leuseni	292	19	21890	L2250	M
MD03	/Prut	Conf. Danube-Giurgiulesti	0	5	27480	L2270	LMR
UA01	Danube	Reni - Kilia arm/Chilia arm	132	4	805700	L0630	M
UA02	Danube	Vilkova-Kilia arm/Chilia arm	18	1	817000	L0690	M

In 2001, the following stations from Serbia-Montenegro have been included:

River	Town/Location	Distance (km)	Altitude (m)	Catchment (km²)	DEFF Code	Loc. profile
Danube	Bezdan	1427	83,15	210250	L2350	L
Danube	Bogojevo	1367	80,41	251253	L2360	L
Danube	Novi Sad	1258	74,52	254085	L2370	L
Danube	Zemun	1174	70,76	412762	L2380	R
Danube	Pancevo	1154,8	70,14	525009	L2390	L
Danube	Banatska Palanka	1076,6	68,58	568648	L2400	L
Danube	Tekija	954,6		574307	L2410	R
Danube	Radujevac	851	32,45	577085	L2420	R
Danube	Backa Palanka	1287		253737	L2430	L
/Tisa	Martonos	152	75,54	140130	L2440	R
/Tisa	Novi Becej	66	74,03	145415	L2450	L
/Tisa	Titel	8,9	72,55	157147	L2460	M
/Sava	Jamena	195	77,67	64073	L2470	L
/Sava	Sremska Mitrovica	136,4	75,24	87996	L2480	L
/Sava	Sabac	103,6	74,22	89490	L2490	R
/Sava	Ostruznica	17		37320	L2500	R
/Velika Morava	Ljubicevski Most	34,8	75,09	37320	L2510	R
/Sava/Drina	Badovinci				L2520	L