UNDP I GEF
DANUBE REGIONAL PROJECT

February 2007

PROVISION OF TECHNICAL SUPPORT ON DANUBE NUTRIENTS

FINAL REPORT

WORKING FOR THE DANUBE AND ITS PEOPLE

AUTHORS

PREPARED BY:

Vienna University of Technology

Institute for Water Quality, Resources and Waste Management

AUTHORS:

Helmut Kroiss

Matthias Zessner

Christoph Lampert

Vienna University of Technology

Institute for Water Quality, Resources and Waste Management

Karlsplatz 13

1040 Vienna

PREFACE

The Vienna University of Technology, Institute for water Quality, Resources and Waste Management (IWA) has been contracted by the UNDP-GEF Danube Regional Project to carry out activities within the DRP's objective of “Reinforcement of monitoring, evaluation and information systems to control transboundary pollution, and to reduce nutrients and harmful substances”. The main objective of this activity is to provide the UNDP/GEF DRP and the ICPDR Secretariat technically robust analyses of the nutrient state in the Danube River Basin and the Black Sea North West Shelf. These analyses are built on the earlier work of daNUbs project using readily available data where possible.

Three separate parts of work have been carried out (chronological order):

1. Support of Stefan Speck for a study on cost efficient mitigation of nutrient emissions
2. Comparison of current levels of nutrients in the Danube River with the 1997 levels and an assessment of the dissolved oxygen levels in the NW shelf of the Black Sea
3. Basic considerations on the introduction if phosphate free detergents in the Danubian countries

Further IWA participated in the Stakeholder Seminar “Phosphates in detergents: Latest developments in the Danube River Basin” in Bucharest on the 25 January 2007. The results of scenario calculations in respect to the use of P-containing detergents and the full implementation of the Urban Waste Water Treatment Directive were presented.

The objective was to raise awareness of the impact of the nutrients from laundry detergents and to discuss options to minimise their environmental impacts.

TABLE OF CONTENTS

LIST OF ANNEXES

LIST OF TABLES

LIST OF PICTURES AND GRAPHS

ABBREVIATIONS

CEE	Central and Eastern Europe
ICPDR	International Commission for the Protection of the Danube River
IWA	Institute for Water Quality, Resources and Waste Management, Vienna University of Technology
Q	Discharge of the river
MQ	Mean discharge
STTP	Sodium tripolyphosphate
T	Temperature
TIN	Total Inorganic Nitrogen
TNMN	Transnational monitoring network
UWWTD	Urban Waste Water Treatment Directive
Var	Variant
WWTP	Waste water treatment plant

EXECUTIVE SUMMARY

Main objective of the services carried out was to provide the UNDP/GEF DRP and the ICPDR Secretariat technically robust analyses of the nutrient state in the Danube River Basin and the Black Sea North West Shelf.

The analyses are built on the earlier work of daNUbs project using readily available data where possible.

Three separate parts of work have been carried out (chronological order):

> Comparison of current levels of nutrients in the Danube River with the 1997 levels and an assessment of the dissolved oxygen levels in the NW shelf of the Black Sea
> Support of Stefan Speck for a study on cost efficient mitigation of nutrient emissions
> Basic considerations on the introduction if phosphate free detergents in the Danubian countries

To derive cost efficient measures it has to be taken into account that emissions are modified via their transport from the area of emission to the area of discharge (denitrification, adsorption). Emissions from waste water treatment plants are mainly in the form of dissolved Phosphate which is immediately highly available for algae production. P-emissions via erosion are mainly in particulate form which is only partly available for algae-production. Particulate P- emissions provide a potential P-source which can be partly mobilised in the case of anaerobic conditions in the waters which are a result of eutrophication.

A mere focus on the reduction of the nutrient-discharge to the WBS could lead to a deterioration of smaller rivers or local groundwater. A comprehensive strategy as outlined in the Water Framework Directive including the quality of surface waters as well as ground water should be aimed at.

Transported nutrient loads in River Danube are highly influenced by physical factors as water discharge and temperature. The influence of these physical factors on yearly loads may outweigh anthropogenic impacts by far. Relatively high nutrient loads in 2005 are a result of the relatively high flow situation of this year.

Eliminating the two effects temperature and annual discharge a slight decrease in the Dissolved inorganic Nitrogen-loads transported in the Danube can be detected between 1996 and 2005.

TP-loads are heavily influenced by high flow events. A comparison of different time periods has to consider high flow events above average. Between 1997 and 2004/2005 no significant difference in total P-loads can be detected. The PO_4-P loads slightly decreased in the period 2004 – 2005 as compared to the period 1996-1998 (about 10 % of the yearly load).

The level of oxygen saturation at the bottom of WBS has significantly improved between the 80ies and 1996. No dramatic changes in the period between 1996 and 2003 can be interpreted from existing data. The data base is not appropriate to demonstrate changes between 1996 and 2003 in detail.

Scenario calculations have been carried out to show the effects of different consumption of P-containing detergents on the P-emissions from waste water treatment plants assuming full implementation of the Urban Waste Water Directive and the whole Danube Basin is considered as sensitive area.

If the average consumption of P-containing detergents exceeds 0.65 gP/inh.d (including automatic dish washing detergents) the emission will be higher as in the year 2004.

55 to 70% of the P-emission will stem from settlements between 2.000 and 10.000 inhabitants as for these areas no P-removal is required by the UWWTD.

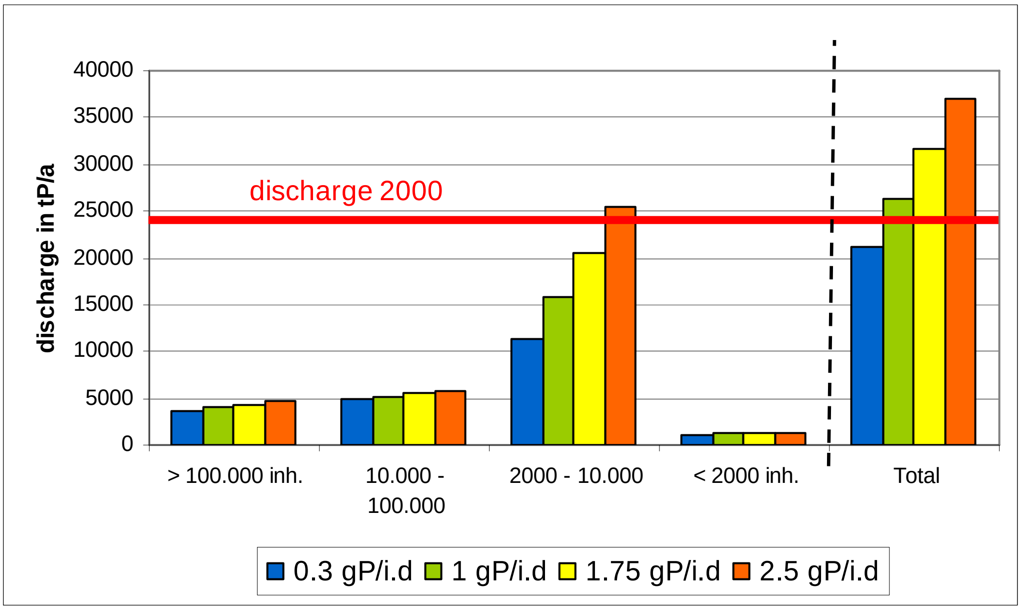


Figure 1: Mean P-discharge in different scenarios in tP/a.

Sewage sludge represents a considerable source of P.

The amounts of additional sludge production due to the replacement of P containing detergents by e.g Zeolites or due to the precipitation of P are similar (increase by 10 - 20%).

The costs of precipitants for P-removal compared to the total costs (investment costs plus operation costs) for sewer development and waste water treatment are very small.

1. INTRODUCTION

The Vienna University Institute for Water Quality Resources and Waste management was contracted to provide the UNDP/GEF DRP and the ICPDR Secretariat with technically robust analyses of the nutrient state in the Danube River Basin and the Black Sea North West Shelf. These analyses should be built on the successful earlier work of daNUbs project using readily available data where possible.

The following main activities were carried out within this assignment:

> Comparison of current levels of nutrients in the Danube River with the 1997 levels

> To provide as up-to-date as possible assessment of the dissolved oxygen levels in the NW shelf of the Black Sea

> Basic considerations on the introduction of phosphate free detergents in the Danubian countries including scenario calculations considering the introduction of P-free or reduced-P detergents and the full implementation of the Urban Waste Water Treatment Directive

> Support of Stefan Speck for a study on cost efficient mitigation of nutrient emissions

Further IWA participated

> in the Stakeholder Seminar “Phosphates in detergents: Latest developments in the Danube River Basin” in Bucharest on the 25 January 2007. The objective was to raise awareness of the impact of the nutrients from laundry detergents and to discuss options to minimise their environmental impacts. The results of scenario calculations in respect to the use of P-containing detergents and the full implementation of the Urban Waste Water Treatment Directive were presented by IWA.

> in the Regional Conference on Nutrient Pollution Control in the Danube-Black Sea Basin held on 3–6 October 2006 in Chisinau, Moldova Objective was to facilitate the sharing of lessons and experiences in the Danube-Black Sea Strategic Partnership Program. A special focus of the Conference was to develop an indicator framework for investments that could be used across similar Global Environment Facility-sponsored Strategic Partnerships being developed and implemented in the Mediterranean, Africa, and East Asia.

2. CURRENT NUTRIENT LEVELS IN THE DANUBE

Sources: Data from 1996 – 2002: TNMN database

Data from 2003 – 2005: Romanian data from station Reni

2.1. Nitrogen

Figure 2 shows the development of daily discharge and total inorganic nitrogen loads (TIN = NO_3-N + NO_2-N + NH_4-N) as well NH_4-N-loads at measuring days from 1996 to 2005. The high fluctuation of river discharge and the high fluctuation of nitrogen loads are evident. In addition to anthropogenic pressure (discharges from municipal and industrial point sources, agricultural activities and air pollution by burning processes) nitrogen loads in the Danube River depend to a high degree on physical factors.

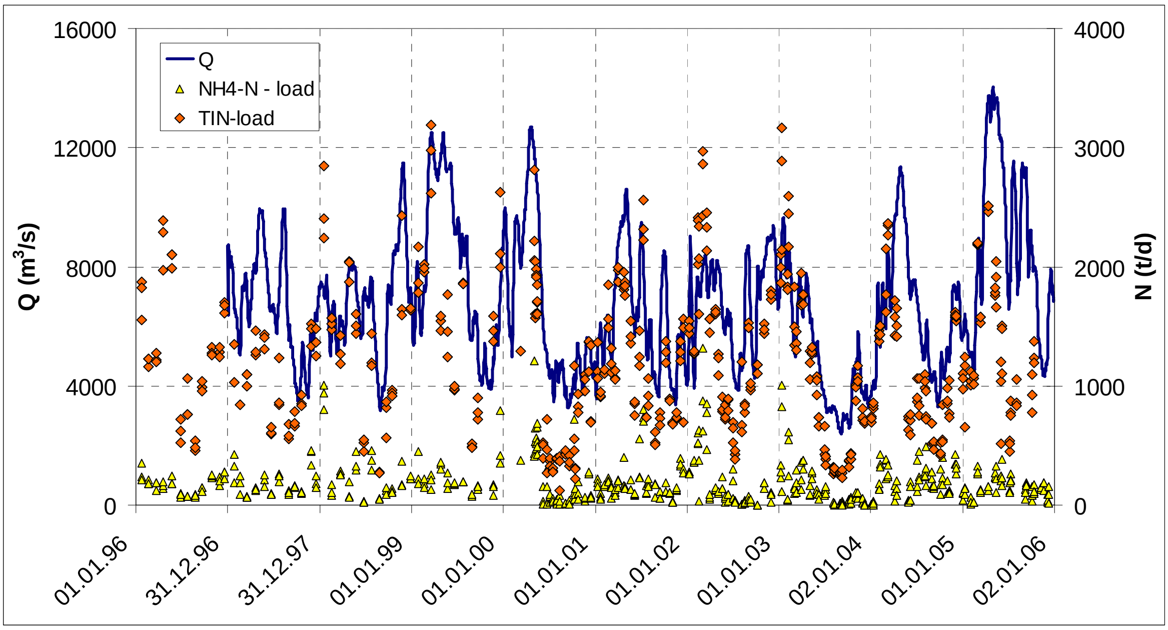


Figure 2: TIN and NH4-N-loads and Danube discharges at Reni from 1996-2005

2.1.1. Dissolved Inorganic Nitrogen (DIN)

A clear relation can be shown between the water temperature of the river and the TIN concentrations (influence of denitrification in the river, see Figure 3) and between the river discharge and the river load of TIN (influence of nitrogen discharge via groundwater and surface runoff, see Figure 4). The short term influence of these physical factors on TIN loads in river Danube can outweigh anthropogenic influences by far. Thus, the evaluation of changes in anthropogenic pressure based on the comparison of yearly loads can be misleading.

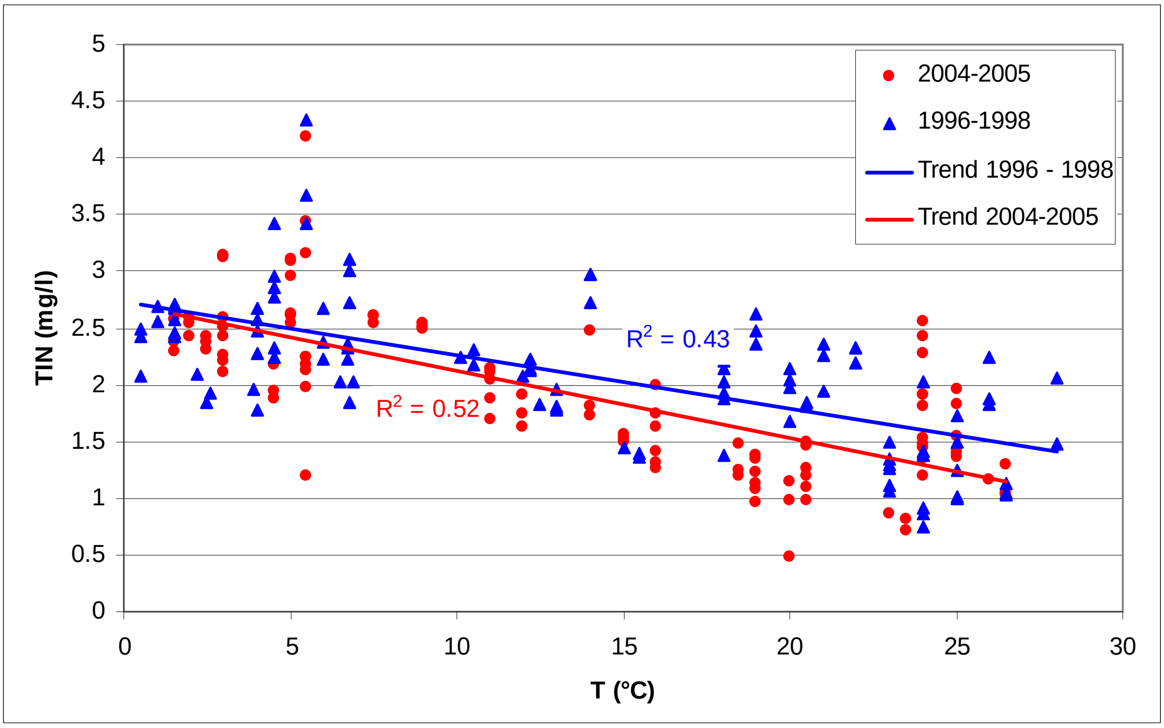


Figure 3: TIN-concentrations and temperature in the Danube River at Reni

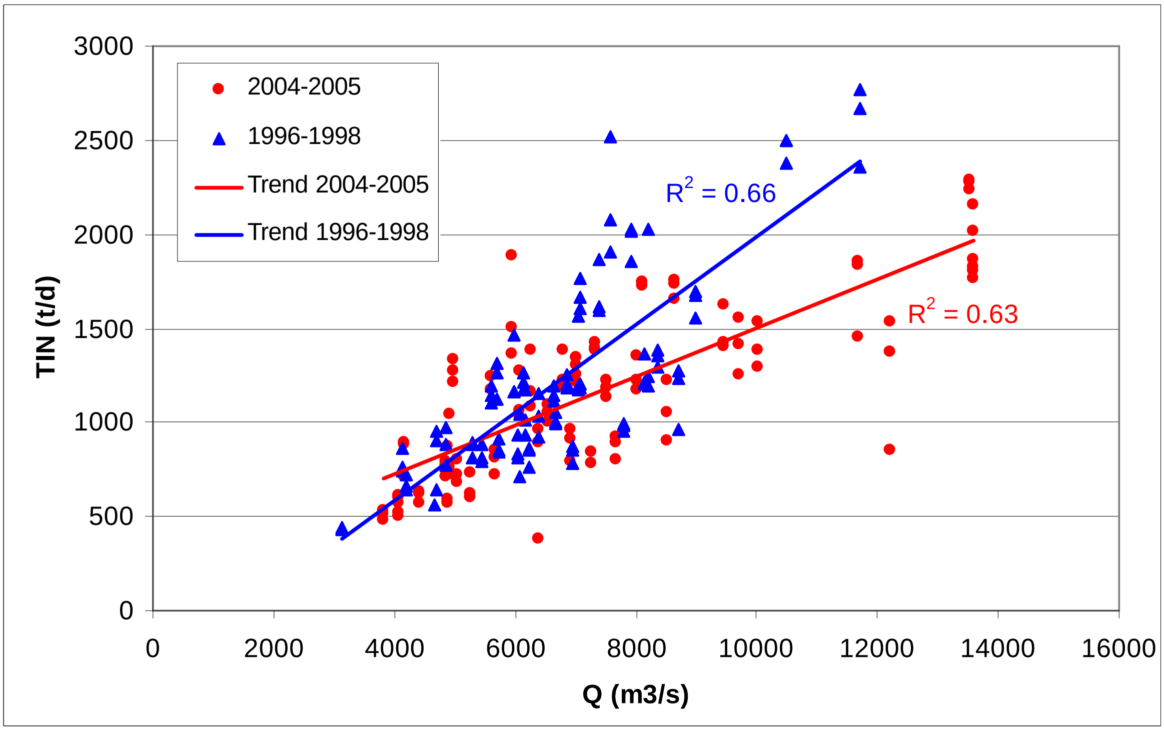


Figure 4: TIN-loads and river discharges of the Danube River at Reni

Based on the method of load calculation agreed within ICPDR an increasing TIN load between 2003 and 2005 is detected. This increase is due to the increasing water discharge during this period. If the influence of Q and T on the calculation of the development of TIN loads over the years is eliminated by calculation based on the functions in Figure 3 and Figure 4, the development of loads shows a slightly decreasing tendency.

Calculative elimination of Q was done based on

$\text{TIN-load}_{Q,i} = \text{TIN-load}_{ICPDR,i} \,.\, MQ_{1996\text{-}2005}/MQ_i$ with

$\text{TIN-load}_{Q,i}$	TIN-load of the year i with calculative elimination of the influence of fluctuations of MQ
$\text{TIN-load}_{ICPDR,i}$	TIN-load of a year i calculated with the method agreed upon at the ICPDR
$MQ_{1996\text{-}2005}$	Mean flow of the period 1996-2005
MQ_i	Mean flow of the year i

Calculative elimination of T was done based on the relation shown in Figure 3 with the following equation:

$c_{14,4;\,i} = c_i + (T_i - 14{,}4) \,.\, 0{,}057$

$c_{14,4;\,i}$	TIN concentration at the time i adjusted to a temperature of 14,4°C
14,4 °C	Mean temperature of the period 1996-2005
c_i	Measured TIN concentration at the time i
T_i	Measured temperature at the time i

Load calculations have been repeated based on the “normalised” concentration $c_{14,4;\,i}$.

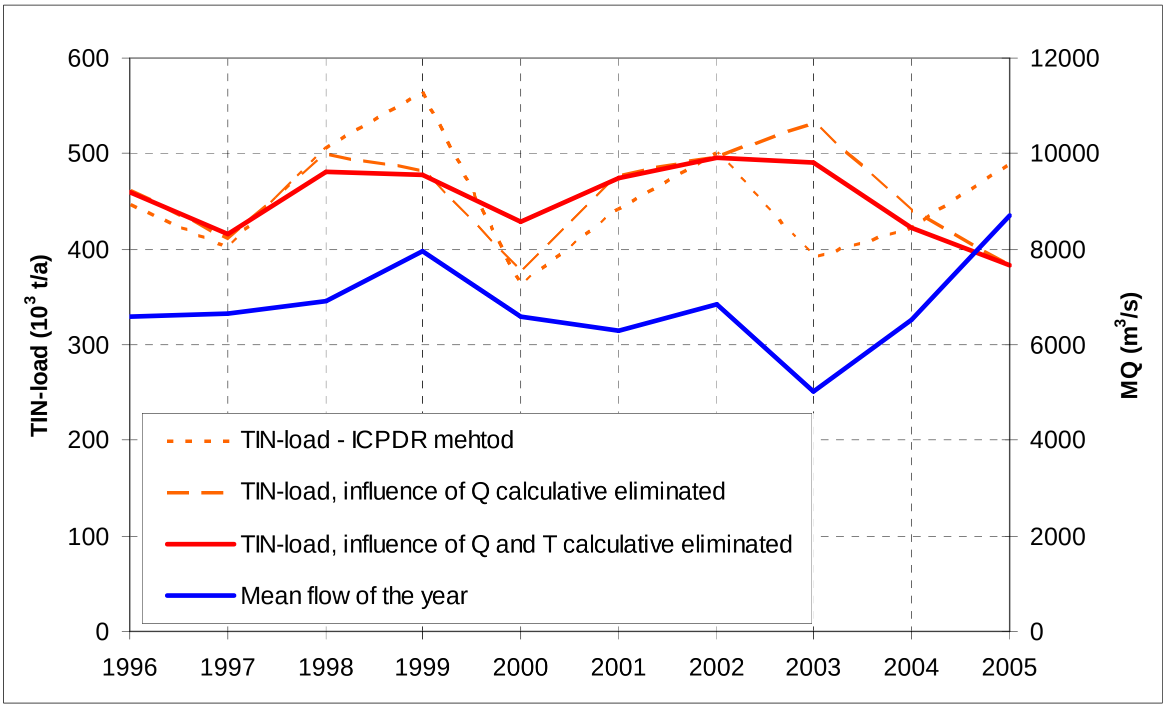


Figure 5: Yearly TIN loads and Danube discharges at Reni from 1996-2005

Despite the fact, that due to high Danube flows the transported TIN-loads have been relatively high in 2005, the Figure 3 to Figure 5 indicate that for comparable flow and temperature situations a slight decrease of nitrogen levels can be detected from the period 1996-1998 to the period 2004-2005. The TIN concentrations at higher temperatures as well as the TIN-loads at higher flows are slightly lower in the period 2004-2005. After calculative elimination of the influence of differences in Q and T between the periods the TIN-load in the period 2004-2005 is about 10 % lower than in the period 1996-1998, which still can not be seen as a significant trend. Changes of anthropogenic pressure at this level of difference only can be evaluated based on emission assessment.

2.1.2. Ammonium

If the Ammonium loads at different days are plotted against the flow (Figure 6), again a slight decrease of loads in the period 2004–2005 compared to the period 1996-1998 can be detected. Expressed as yearly loads this decrease is about 10 % of the yearly load.

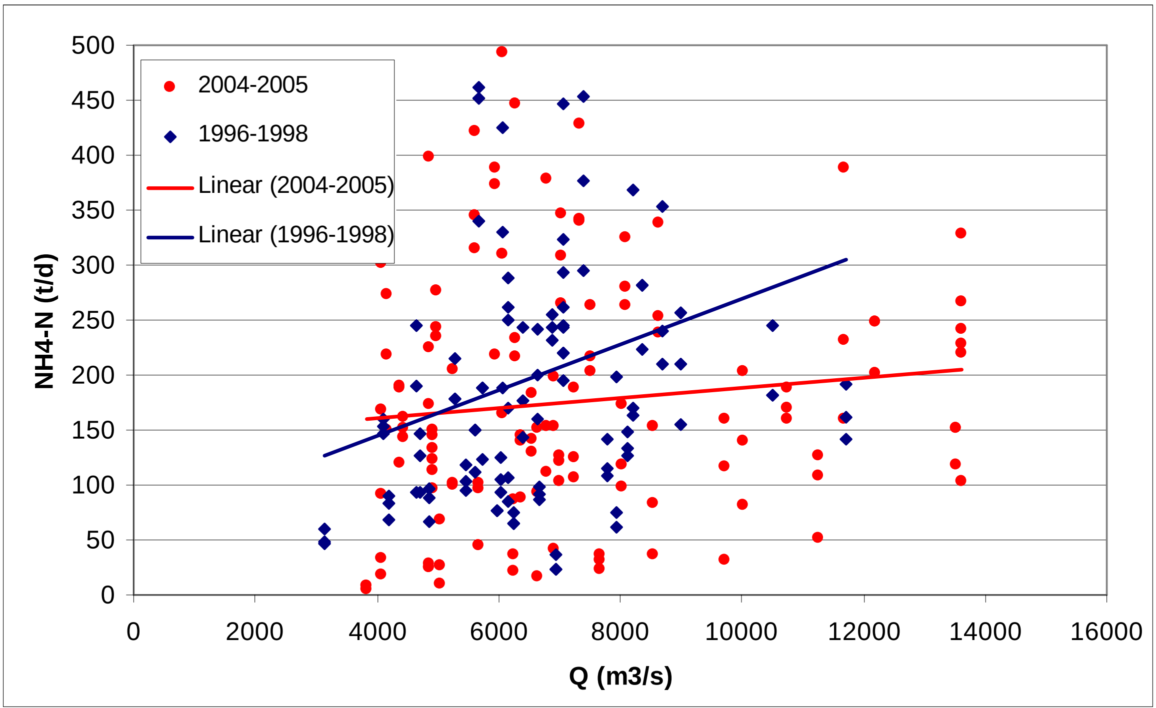


Figure 6: NH_4-N-loads and river discharges of the Danube River at Reni

2.2. Phosphorus

Similar as the TIN-loads, the TP loads show a high fluctuation (Figure 7). In contrary to the TIN-loads there is no linear but a disproportionate relation between loads and flow (Figure 8). High flow situations lead to a mobilization of suspended solids which highly influences the transport of TP. The TP load is significantly higher at increasing water levels compared with falling water levels. The TP loads at high flow situations are not directly related to anthropogenic emissions. Yearly TP-loads are highly influenced by TP transport at high flow and thus strongly depend on the number and intensity of high flow situations.

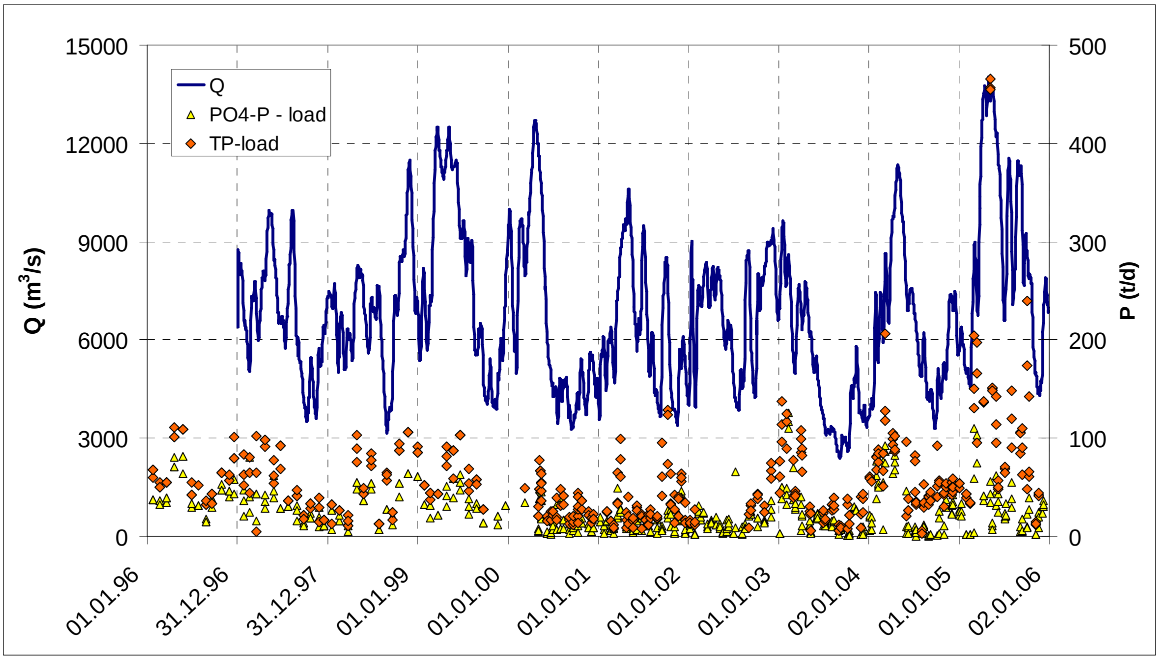


Figure 7: TP and PO_4-P-loads and Danube discharges at Reni form 1996-2005

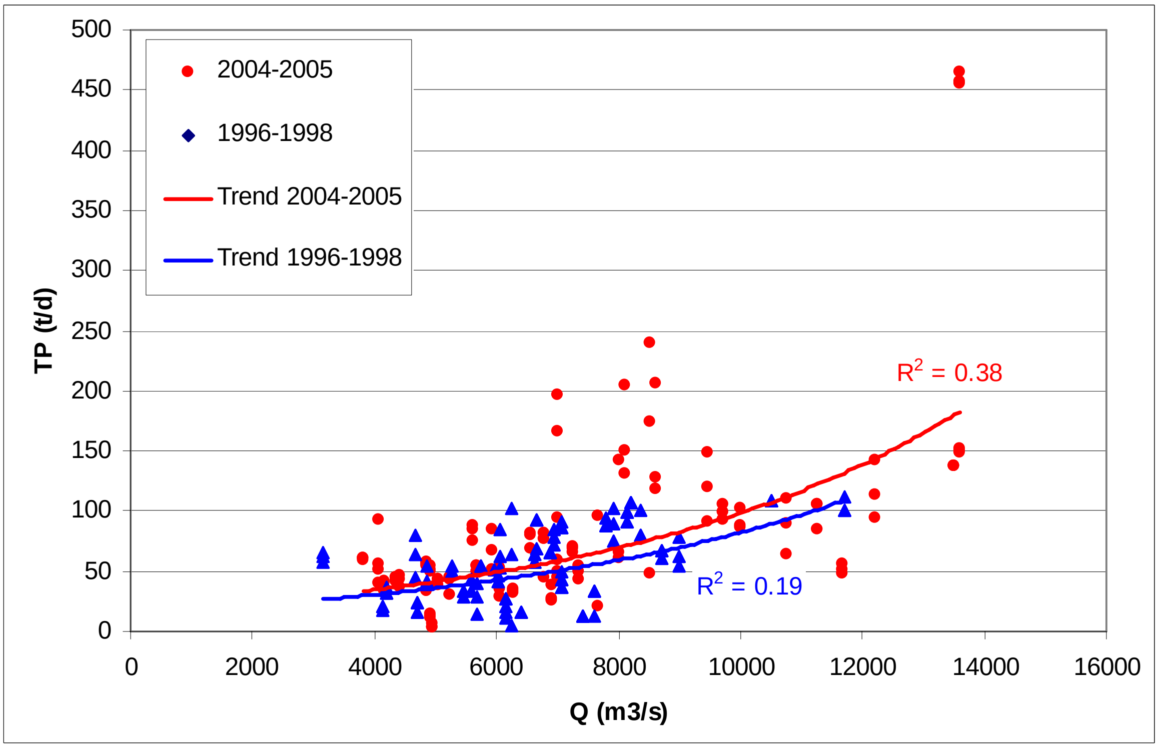


Figure 8: TP-loads and river discharges of the Danube River at Reni

TP loads of the period 1996-1998 compared to the TP loads of the period 2004-2005 at corresponding flow situations show no significant differences (figure 8). However the picture for 1999- 2001 is completely different. TP loads do not rise in the same relation to the increasing flow as in the other periods. As already indicated during the daNUbs project (2005) the TP-measurements of the TNMN-dataset at Reni for the period beginning with 2000 show significantly lower values as compared to other stations and other data sources. In this project the hypothesis was that these values are measured from filtered sample only.

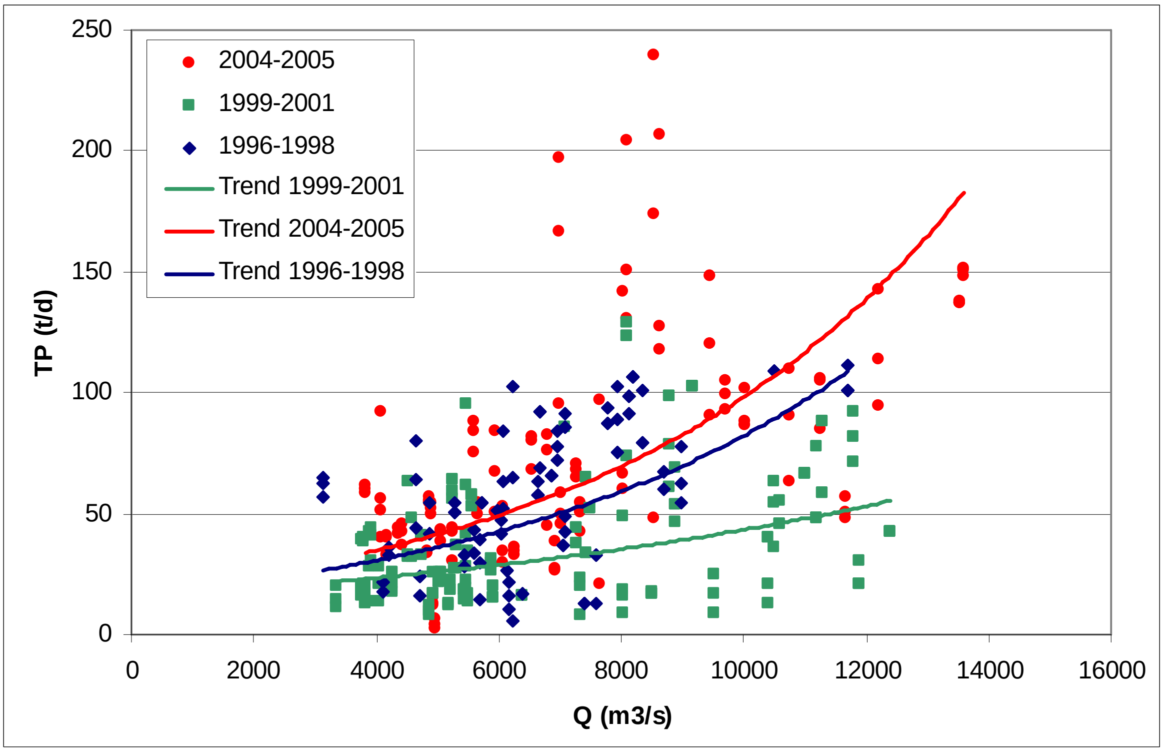


Figure 9: TP-loads and river discharges of the Danube River at Reni

The yearly loads calculated based on the method agreed upon at the ICPDR show a sharp increase in 2005. This increase is due to an increase of suspended solid transport at high flow situations of this year. To eliminate this influence of high flow events for a comparison of the TP-levels in 2004-2005 to the levels of 1997, the load calculation (Figure 10) was done a second time based on data from flow situations with less than 7000 m^3/s only. Based on these calculations it can be seen that there is no significant difference in loads between 1997 and the values of the period 2004-2005. Very low TP loads in the period 2000 – 2001 probably are based on measurements representing the TP-concentration of filtered samples only (instead of unfiltered samples in the years before and afterwards).

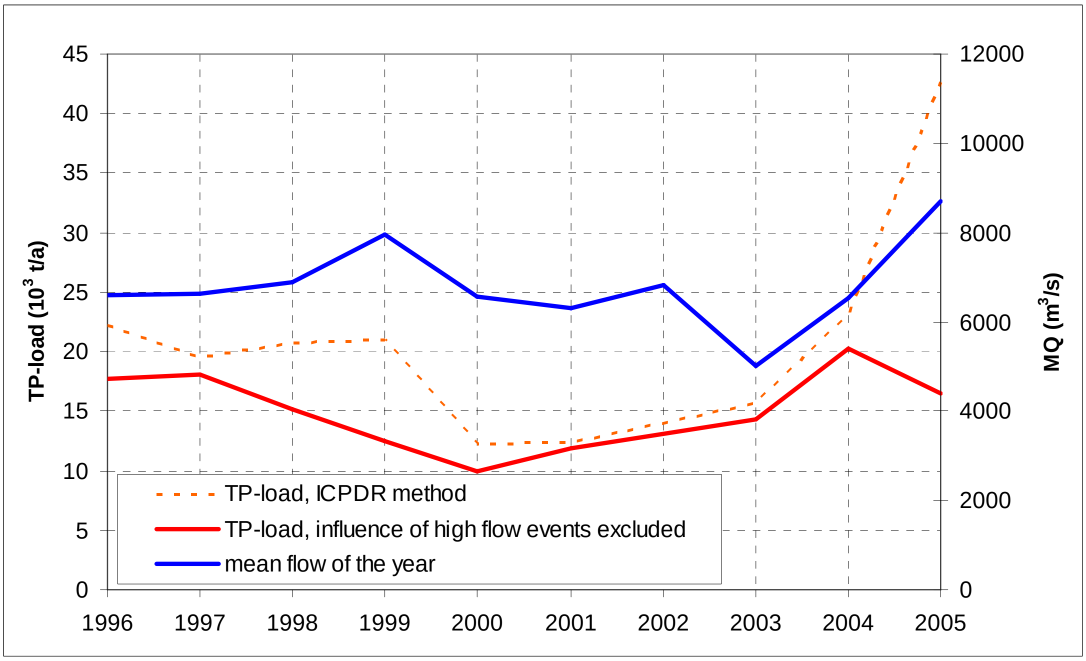


Figure 10: Yearly TP-loads and Danube discharges at Reni form 1996-2005

If the PO_4-P loads at different days are plotted against the flow (Figure 11), a slight decrease of loads in the period 2004 – 2005 as compared to the period 1996-1998 can be detected. Expressed as yearly loads this decrease is about 10 % of the yearly load.

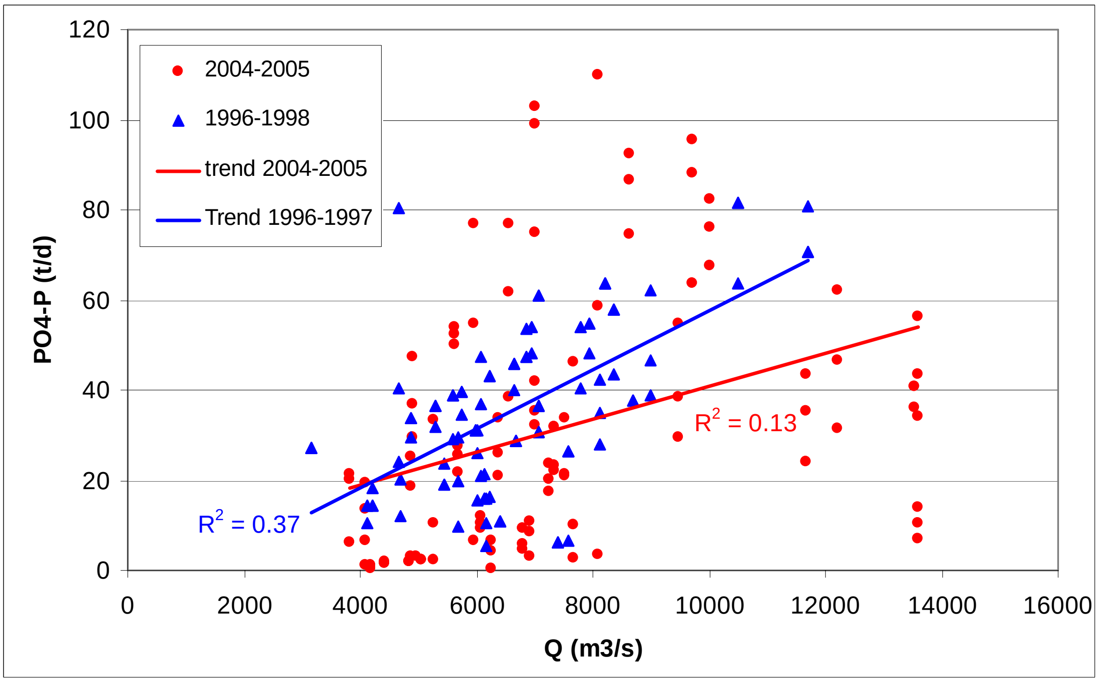


Figure 11: PO_4-P-loads and river discharges of the Danube River at Reni

2.3. Updated figures with trends since 1988

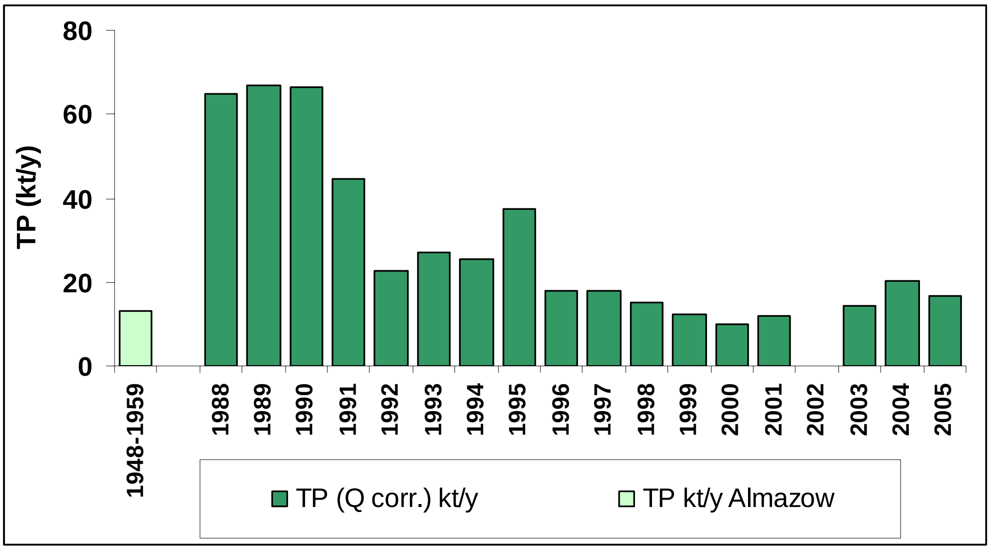


Figure 12: River Danube annual total phosphorus loads (corrected for annual discharge) to the Black Sea

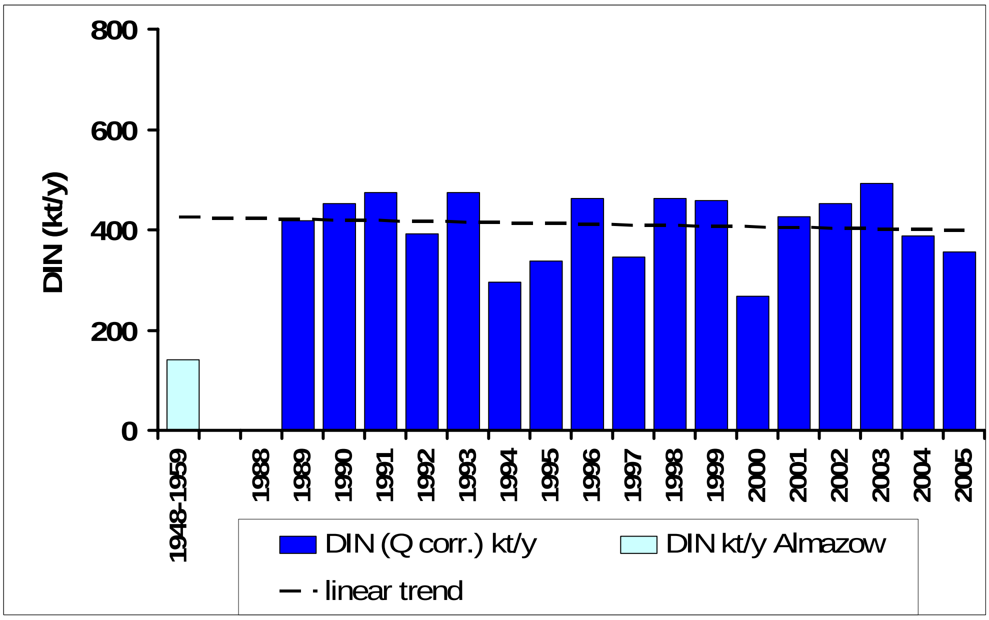


Figure 13 : River Danube annual inorganic nitrogen loads (corrected for annual discharge) to the Black Sea

3. DISSOLVED OXYGEN LEVELS IN THE NW-SHELF OF THE BLACK SEA

Source: Cosiasu et al. (2003-2005) Deliverables: D7.1 Romanian report; D7.3 Romanian annual reports 2001-2002; and D7.6 "Summary report on field and laboratory work in 2001-2003 in comparison with previous observations in the Western Black Sea" from the project "Nutrient Management in the Danube Basin and its Impact on the Black Sea" supported under contract EVK1-CT-2000-00051 by the Energy, Environment and Sustainable Development (EESD Programme of the 5th EU Framework Programme, http://danubs.tuwien.ac.at)

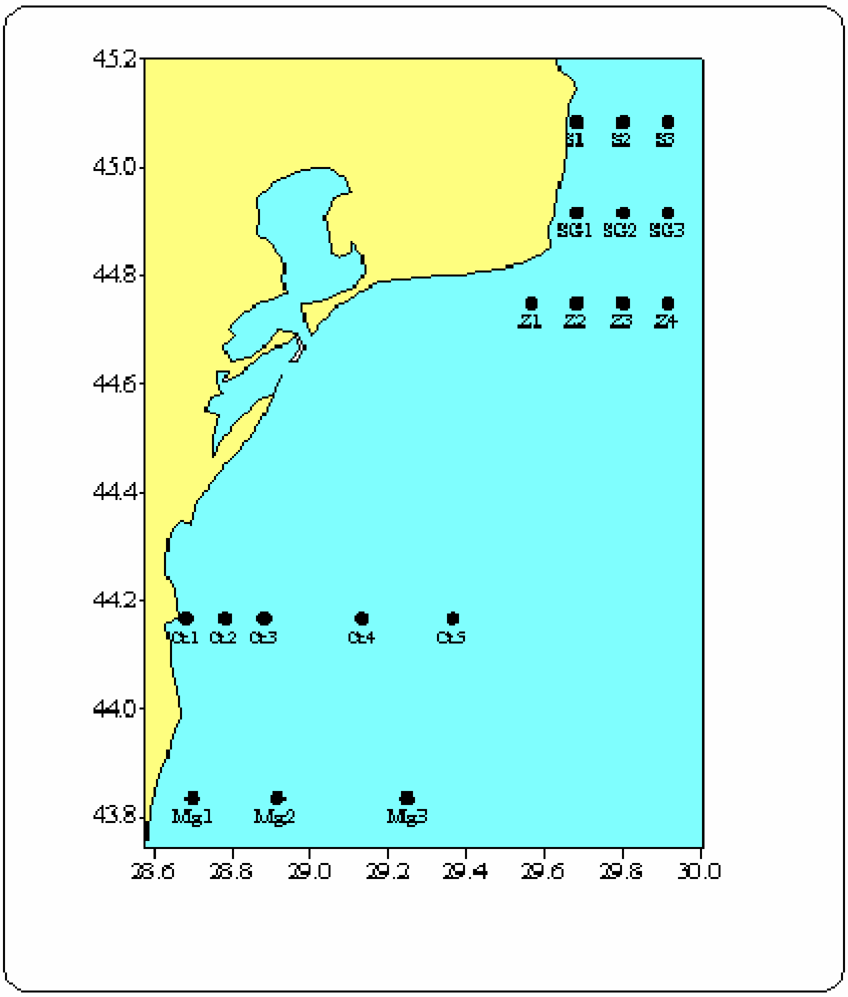


Figure 14: Monitoring locations in the Western Black Sea Shelf (WBS):

SG ... Sf. Georghe; Z ... Zaton, Ct ... Constanta, Mg ... Mangalia

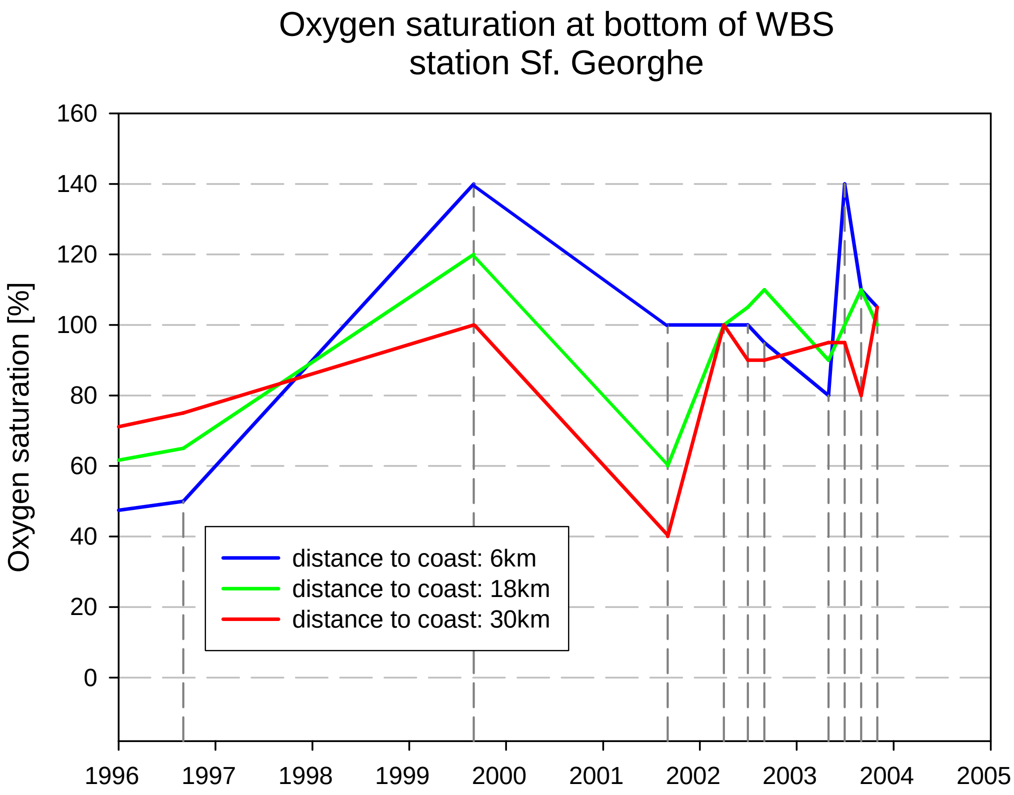


Figure 15: Oxygen saturation at bottom of WBS, station Sf. Georghe

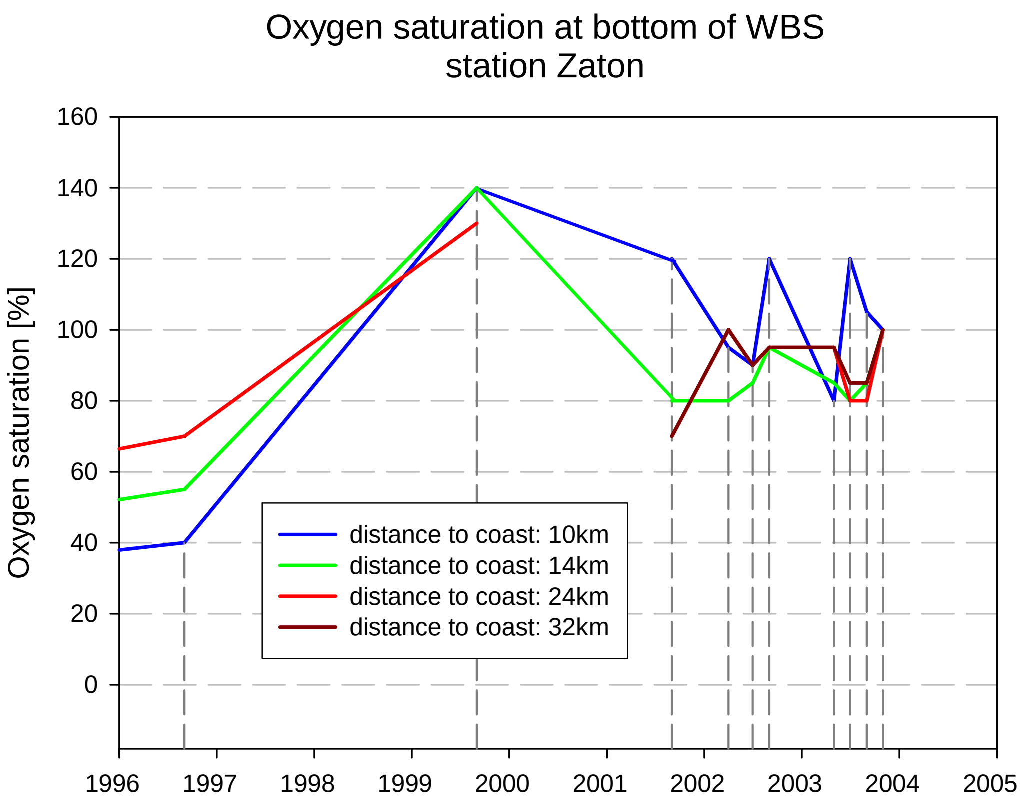


Figure 16: Oxygen saturation at bottom of WBS, station Zaton

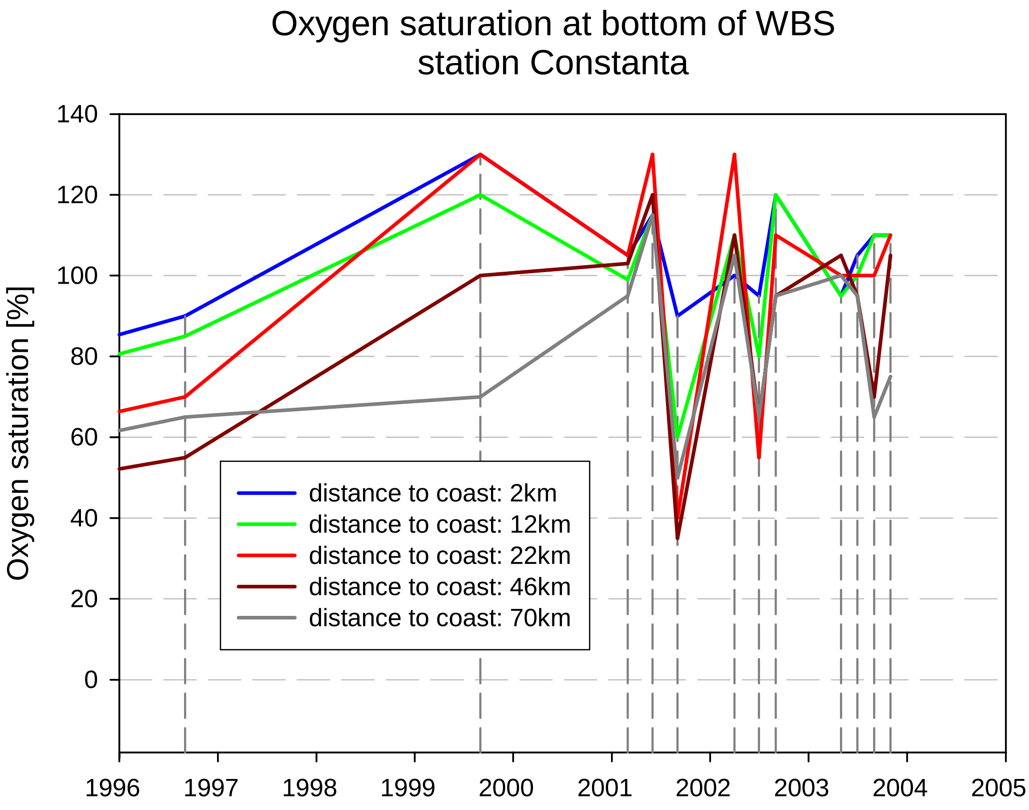


Figure 17: Oxygen saturation at bottom of WBS, station Constanta

Figure 15 to Figure 17 show the development of oxygen saturation at the bottom of the Western Black Sea shelf area (WBS) of the transects St. George, Zaton and Constanta from 1996 to 2003. These figures indicate an improvement of oxygen saturation in this period. Going more in detail it becomes clear that the measurement from 1996 was done in September, representing the season at which in the years 2001-2003 the lowest oxygen saturation appeared as well. If only the autumn values are compared only for the stations very close to the coast (2 resp. 6 or 10 km distance) an increase can be seen in oxygen saturation between 1996 and 2003. Especially the oxygen saturation at Constanta station has not improved compared to 1996. Nevertheless, the improvement since the 80ies, where large zones of anoxia (bottom oxygen saturation = 0 %) have been detected, is obvious.

4. BASIC CONSIDERATIONS ON THE INTRODUCTION OF PHOSPHATE FREE DETERGENTS

Eutrophication is of major concern in the Danube Region and especially in the receiving Sea, the Western Black Sea. The ecological situation in the Black Sea has improved considerably in the last decade (reduced eutrophication, disappearance of anoxic conditions, regeneration of zoo-benthos and phytoplankton). However the improvement was only partly due to the effect of measures of environmental policy, like nutrient removal at waste water treatment plants (WWTPs) or the ban of P-containing laundry detergents. To a considerable part the reduction is caused by the economic crises in several countries in Central and Eastern Europe.

There are two major developments that endanger the improvements in the Western Black Sea observed, i.e. which will lead to an increase of nutrient emissions:

- The economy in these countries will redevelop in the coming years
- The (full) implementation of the Urban Waste Water Treatment Directive (UWWTD).

The challenge towards policy nowadays is to enable economic development without increasing nutrient emissions again (as in the 70ies and 80ies) above “critical loads” for the Western Black Sea. This means: efforts have to be taken to provide space for the anticipated increase of nutrient emissions. Otherwise the ecology of the Black Sea will deteriorate again.

The introduction of P-free laundry detergents is considered to be a fast and efficient measure to reduce nutrient emissions into surface waters.

The following 3 basic considerations are evaluated more in detail in the following chapters:

1. Scenario development for nutrient emissions via waste water treatment plants in respect to the amounts of detergents used
2. Aspects of the management of the limited resource phosphate
3. Costs of waste water treatment: P-removal, sludge management

4.1. Scenario development

Already in the daNUbs project several scenarios have been developed. Some main differences to the scenarios developed below shall be depicted:

- In the daNUbs scenarios also an increase of the economy was assumed.
- In the scenarios developed now, a further distinction was made between the sizes of the settlements. In total 4 categories were defined: A = settlements > 100.000 inhabitants; B = settlements 10.000 - 100.000 inhabitants; C = settlements 2.000 – 10.000 inhabitants; D = settlements < 2.000 inhabitants. The classification is based on the figures given in the study (“Nutrient balances for Danube countries”, PHARE EU/AR/102A/91). The former Yugoslavia was not included in that study. For Serbia relevant data was retrieved from the ICPDR webpage (http://www.icpdr.org/icpdr-pages/serbia.htm), for Bosnia and Croatia it was assumed to have the same distribution as Serbia. For Romania statistical data for the year 2004 was used.

4.1.1. Scenario development basic assumptions

The scenarios developed now are based on the following basic assumptions:

- Connection to sewer systems: All areas except those below 2000 inhabitants are completely (100%) connected to sewer system and corresponding waste water treatment plants. For Germany in addition 77% and for Austria 36% of these areas (reflecting the situation in 2004) are connected.
- All areas connected to WWTPs are considered to be "sensitive" areas according the UWWTD. This means if some regions would be declared as non-sensitive areas, the P-loads emitted by the treatment plants in these regions would be considerably higher.
- The P-removal efficiency of treatment plants is according the UWWTD:
    - > 100.000 pe: effluent concentration 1 mgP/l
    - 10.000 – 100.000 pe: effluent concentration 2 mgP/l
    - Optional for both categories mentioned: 80% reduction in relation to the inflow load
    - Less than 10.000 pe: secondary treatment; For secondary treatment a removal of 0.6 gP/pe was assumed.
- The amount of sewer infiltration water influences the P-concentration in the raw waste water and as a consequence the efforts required to meet the effluent quality standards differ; calculation were carried out with 100 l (low) and 200 l (high) sewer infiltration water per inhabitant.
- The amount of detergents consumed per inhabitant and day were varied as follows: In Western countries like Austria, Germany or Suisse, the maximum consumption of P-containing laundry detergents amounted up to 3 g P/inh.d. It has to be recognized that the composition of detergents has changed in the last decades. For instance the total amount of Sodium tripolyphosphate (STPP) contained in washing powders has been reduced from 50% to about 25% (or even less). Therefore "modern" P-containing laundry washing powders use less STPP per washing. Depending on the hardness of the washing water 4 to 13 kg [Fox et al. 2002] of washing powders are consumed per inhabitant. Assuming a consumption of 4 – 13 kg washing powder with an STPP concentration of 25% per inhabitant would mean a specific P-emission of 0.7 – 2.2 gP/inh.d.

  In the last years a considerable increase in the use of P-containing detergents in automatic dishwasher products was observed in Germany and Austria amounting to about 0.3 g P/inh.d. It is almost out of discussion that it is currently not possible to replace STPP in these products. Therefore the "Zero-Laundry P-detergent scenario" would mean a P-detergent consumption of 0.3 g P/inh.d. This amount is included in all other Scenarios as well.

  The following assumptions have been made:
    - 0.3 gP_{det}/inh.d: this is the amount used in Germany or Austria in dish washing products etc., but no P-containing laundry detergents
    - 1.0 gP_{det}/inh.d: 0.7 gP/inh.d in laundry detergents + 0.3 gP/inh.d dish washing products; for D and A the amounts of 0.3 gP/inh.d were used
    - 1.75 gP_{det}/inh.d; 1.45 gP/inh.d in laundry detergents + 0.3 gP/inh.d dish washing products; for D and A the amounts of 0.3 gP/inh.d were used
    - 2.5 gP_{det}/inh.d: 2.2 gP/inh.d in laundry detergents + 0.3 gP/inh.d dish washing products; for D and A, the amounts of 0.3 gP/inh.d were used

The Scenario with 1.75 gP/inh. probably is the worst case. The Scenario with 2.5 gP/inh.d is highly unlikely, as (i) not all areas in the Danube Basin have very hard water (meaning that the washing powder consumption is increased) and (ii) there will be a share of P-free detergents in the future.

> The contribution from industry was assumed to be on the same level as in 2000
> The specific emission per inhabitant excluding detergents is 1.65 gP/inh.d
> The water consumption of 1 pe: 150 l
> For the 4 categories of settlements (A, B, C, D) assumptions for the amount of industrial pe (pe_{ind}) were made as follows: A: 1.2 pe_{nd}/inhabitant.day, B and C: 1 pe_{nd}/inh.d, D: 0.2 pe_{nd}/inh.d; These assumptions are based on recent studies in Austria reflecting well developed economic activities. In respect to the economic transition process with lower economic intensity in the CEE countries the following reduction for the amount of pe_{ind} per inhabitant.d have been done for the calculations: A, D: 0%, CZ, SK, HU, SL: minus 25%, all others: minus 50%
> P-Emissions from industry: 1.1 gP/$pe_{ind.}$d

According these assumptions 18% of the population is not connected to a sewage treatment plant (about 14.5 Mio. inhabitants).

4.1.2. Scenario results

As a base for comparison for the scenario results: The current emissions via waste water treatment plants amount to about 24 kt P.

In total 32 different scenarios were evaluated:

4 different areas (A, B, C, D), 4 different assumptions on the use of detergents (0.3, 1.0, 1.75, 2.5 g P in detergents per inhabitant and day) and 3 different removal efficiencies for the Areas A and B (2 different sewer infiltration rates (100l/inh., 200l/inh. and 80% removal rate).

The following results depict the mean P-emissions for the four different areas and the 4 different consumptions of P-containing detergents. The results of the other scenarios are included in the Annex.

The following main results were obtained:

> Only in the Scenarios with 0.3 g P_{det} the emissions of P from point sources can be lower than in 2000.
> The highest P- loads are emitted in the Area C (settlements between 2.000 and 10.000 inhabitants): 54 to 69% of the total P-emissions.
> The introduction of P-free laundry detergents in the Danubian countries would save emissions of 5 kt P/a compared to the 1gP/inh.d Scenario and 10.5 kt P/a compared to the 1.75 gP/inh.d Scenario.
> For treatment plants with more than 100.000 pe the emissions increase with increasing consumption of P-containing detergents by up to 4 kt P.
> Doubling the sewer infiltration water (from 100 to 200 l/inh.d) increases the discharge of P by 2 kt /a.

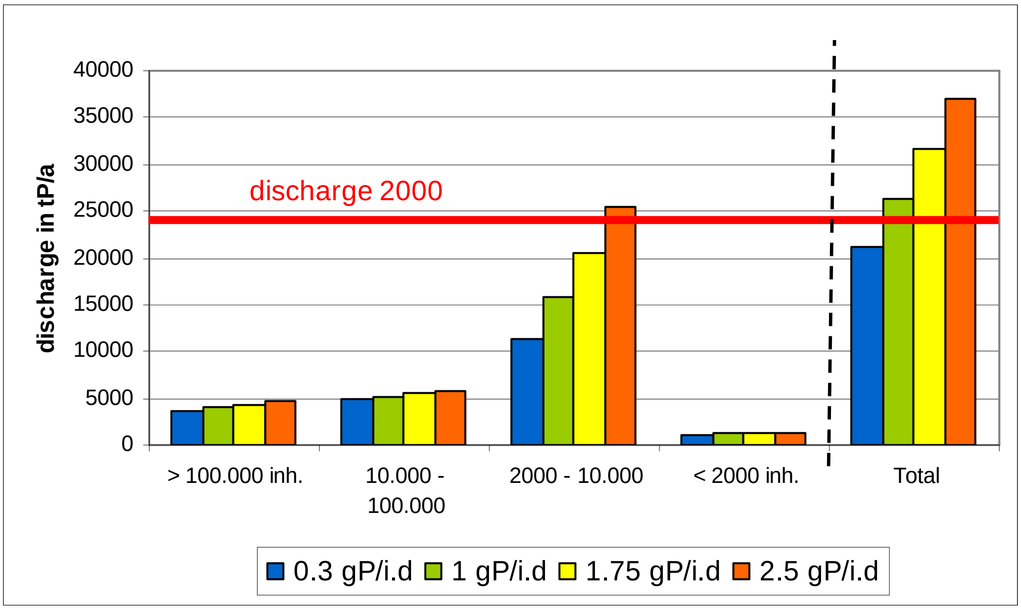


Figure 18: Mean P-discharge in different scenarios in tP/a.

The following figure shows the results of the 3 variants with different sewer infiltration rates (Var 1 and Var 2) and the calculations based on the 80% removal rate (Var 3)

If the average consumption of P-containing detergents exceeds 0.65 gP/inh.d (including automatic dish washing detergents) the emission will be higher as in the year 2004.

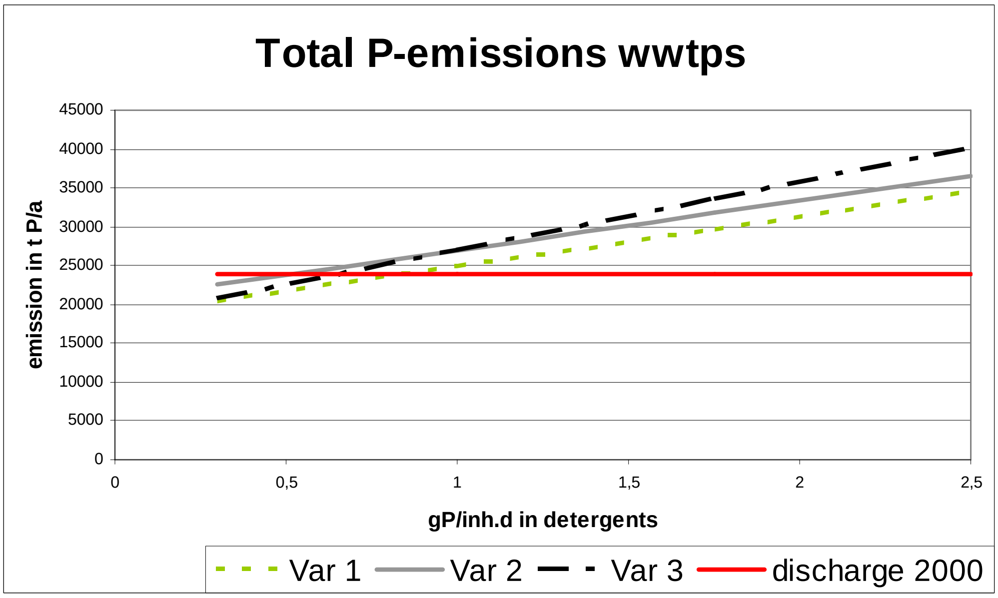


Figure 19: P-emissions from WWTPs of the 3 variants considered

Storm water overflow: Based on experiences in Austria the total P-load emitted via storm water over flow is less than 3% of the total P-load in the raw waste water. The emission of P via storm water overflow is relatively important in areas with P-removal. Assuming a P-removal of 80% would mean that the contribution of storm water overflow amounts to 15% of the P-emissions.

Assumption: 3% of the total P-load is discharged directly to the surface waters:

Depending on the Scenario considered in total 2 to 3 kt P will be discharged untreated into the receiving waters via storm water overflow.

The P-output from households and industry amounts from 77 kt P (in the 0.3 g P/inh. Scenario) to 128 kt P (2.5 g P/inh.d). Out of this about 15% are discharged partly to septic tanks and partly directly into the river system causing additional P-loads in the rivers which are not included in the Scenario calculations.

The overall removal efficiency of waste water treatment plants is about 65%.

4.1.3. Reliability and Uncertainties of Scenario calculations

In the scenario calculations it was assumed that the whole Danube Basin is considered as a sensitive area. If parts would be defined as non-sensitive areas the requirements to waste water treatment would be lower and the resulting emissions considerably higher.

> Essential for the scenario calculations is the share of the population living in the different settlement categories, especially in those below 2000 inhabitants (where no sewer system and no treatment is required according the UWWTD) and in those from 2000 to 10.000 inhabitants (biological treatment required in sensitive areas). Romania is due to its size a key country in the Danube Basin. The data and statistics evaluated for Romania for the year 2004 differ from those for the other countries (e.g. population in settlements below 2000 inhabitants: Serbia: 27% Romania in 2004: 4.2%). As this data represents the official data base and as the *Implementation Plan for Directive 91/271/EEC concerning urban waste water treatment for Romania* is based on this data it was used it for the scenario calculations.
>
> Using averages of the other Danubian countries for Romania would lower the emissions to surface waters by 3 to 7 kt per year. In this case the emissions in the 1g P/inh.d-Scenario would amount to the emissions in 2000 (see Annex Figure 29).

> No change in the population was assumed. There are indications that the population will decrease in several Danubian countries in the coming years. Probably the decrease depends on the economic development in these countries. Furthermore it would not be possible to distinct in which areas (categories of settlements) the decrease will take place – probably people from larger settlements are more mobile to go abroad, people from small settlements will move to the cities etc.

> No development of industrial activities (of industry connected to municipal waste water treatment plants) was assumed.

> No estimations on other industrial and agricultural point sources have been carried out.

> Probably also several settlements less than 2000 inh. will be (partly) sewered or will discharge partly untreated waste water into the river systems.

- According the *Implementation Plan for Directive 91/271/EEC concerning urban waste water treatment for Romania* there will be a time lag between the number of inhabitant connected to sewers and the treatment of the collected waste water (e.g. 2010: collection system to be provided for 60.8% of the total pe, waste water treatment to be provided for 50.5% of the total pe). For the year 2018 no time lag is foreseen (100 % of the waste water collected will be treated).

4.2. Aspects of the management of the limited resource phosphate

Phosphate rock is a limited resource and need to be managed properly. The phosphate-reserves will last according to different estimations between 88 [Global 2000, 1976] and 500 years [Finck, 1992], and those having low Cadmium concentrations are even more limited (Semi Island Kola: 1 mg Cd/kg DM, Taiba / Senegal: 68 – 111 mg Cd/kg DM) [Sauerbeck and Rietz, 1980]. Additionally, the production of mineral N- and P-fertilizers demands (fossil) energy input.

Sewage sludge contains considerable amounts of nutrients that can be reintegrated into the nutrient cycle. Together with the nutrients sewage sludges contain potentially hazardous substances having different origins. The heavy metal contents of sewage sludge can be highly influenced by diffuse sources (corrosion of roofings, etc.) [Zessner and Lampert, 2002]. These substances might be accumulated on the long run in the environment if their quantity is not properly considered. Furthermore the use of precipitants (side products of industry) for P-removal is an additional source of heavy metals (esp. Ni, Cr but also Cd, Hg and Pb). Therefore only precipitants with low concentrations of heavy metals shall be employed.

Sludge can be

- used directly in agriculture: only if the concentrations of harmful substances in the sludge are acceptable (aspect of soil protection); low costs
- used after combustion: partly a separation of atmophilic elements (like Cd and Hg) can be gained; organic hazard compounds are destroyed, no hygienic problems; conditioning needed before use; high costs

Material balances show:

- Less than 3% of the annual P-input into soils is eroded and therefore lost.
- A considerable part of the P-input into the soil remains in the soil (increase in the P-stock of soils) - this is not a loss of P and shall be considered as an interim storage.
- About 70% of the P-emissions from households are included in the waste water, the remaining 30% in solid wastes. Using P-containing detergents increases the share of waste water.

As a conclusion: relevant losses of P only (can) occur via waste water and the final disposal of sludge (in landfills, non agricultural areas).

The emissions to the environment (underground, direct discharges) from households in the Danube Basin not connected to sewer systems and WWTPs are in the same order of magnitude as the P-fertilizer consumption in Austria 2004.

The P-load of the sewage sludge in the Scenario 1.75 gP/inh.d is almost 4 times higher as the total P-fertilizer consumption in Austria in 2004.

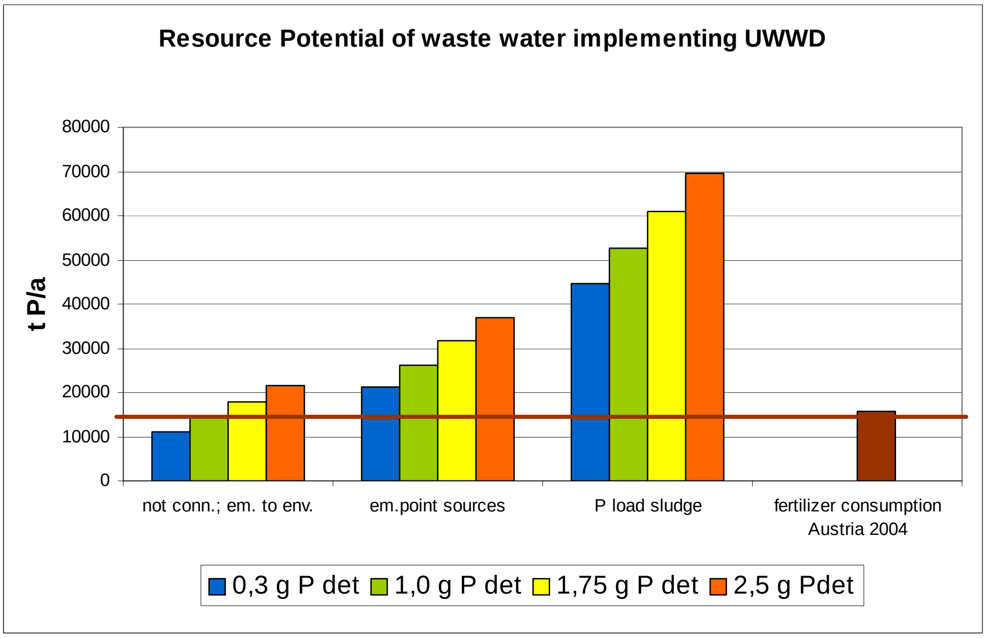


Figure 20: Amount of P in various P-flows in comparison with the P-fertilizer consumption in Austria 2004

4.3. Costs of sludge management and P-removal

In the following rough estimations on the additional amounts of dry matter of sewage sludge produced due to the replacement of P-containing detergents respectively due to P-precipitation in the WWTPs above 10.000 pe are given.

No detailed information will be provided on

- the additional sludge volume,
- the costs of dewatering,
- costs of storage, etc..

For the sludge production in treatment plants without P-removal an amount of 40g dm/pe.d was assumed. Implementing the UWWTD will lead to an annual total (biological) sludge production of about 1.65 Mio t dm. As the implementation of the UWWTD requires P-removal in all plants > 10.000 pe additional amounts of sludge will be produced. The amount of additional sludge produced in these plants is based on the following assumptions:

Calculation of the P-amount to be precipitated:

- Removal of 0.6 gP/pe due to biological treatment
- Total load minus P-load removed by biological treatment minus P-load in the effluent = P-load to be precipitated

Calculation of the specific amount of additional dm/kg P:

- Precipitant per kg P: 1.8 kg Fe/kg P, 0.87 kg Al/kg P

> Beta-value: 1.8 (Beta value: molar ratio of precipitant (Fe, Al) : P)
> Sludge production: 2.5 kg dm/kg Fe (Beta = 1,5), 4 kg dm/kg Al (Beta = 1.5)

These assumptions lead to an additional dm production of 9.7 kg dm/kg P using Fe, and 7.5 kg dm/kg P using Al.

A replacement of P-containing detergents by e.g. Zeolites would increase the production of sewage sludge. The Zeolite consumption in Germany amounted in 1999 to 4.5 g/inh.d. 61 mio people using the same amount (which should be comparable to the "reliable" worst case of 1.75 g P/inh.d. used in detergents) produces almost the same amount of sewage sludge as the P-precipitation in all plants above 10.000 pe.

The amounts of additional sludge production due to the replacement of P-containing detergents by e.g. Zeolites or due to the precipitation of P are similar (increase by 10-20%).

This means that the costs for sludge management would be similar for these two options.

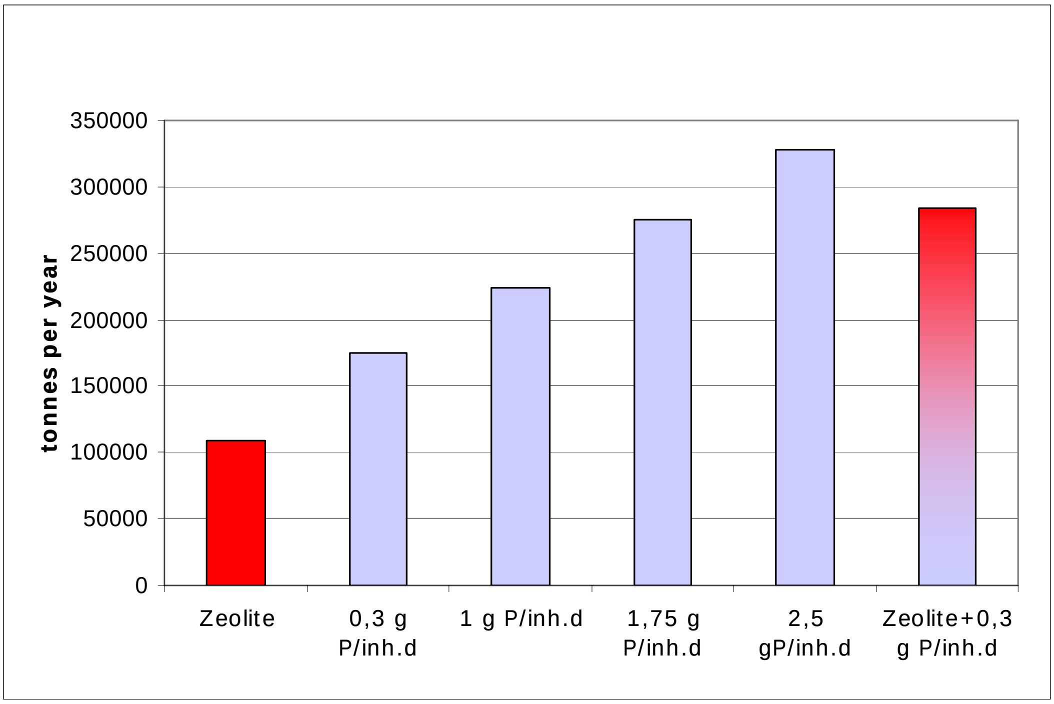


Figure 21: Increase of sludge dry matter due to P-precipitation in treatment plants above 10.000 pe or due to the replacement of P-containing laundry detergents by Zeolite in t/a (mean of the variants are used)

The main difference exists for the costs of precipitants for P-removal.

The following diagram depicts the additional need of precipitants in the 3 variants considered (two different sewer infiltration rates (Var 1 and Var 2) and calculations based on the 80% removal rate (Var 3)) compared to the "zero-laundry P-detergent scenario" of 0.3 gP/inh.d.

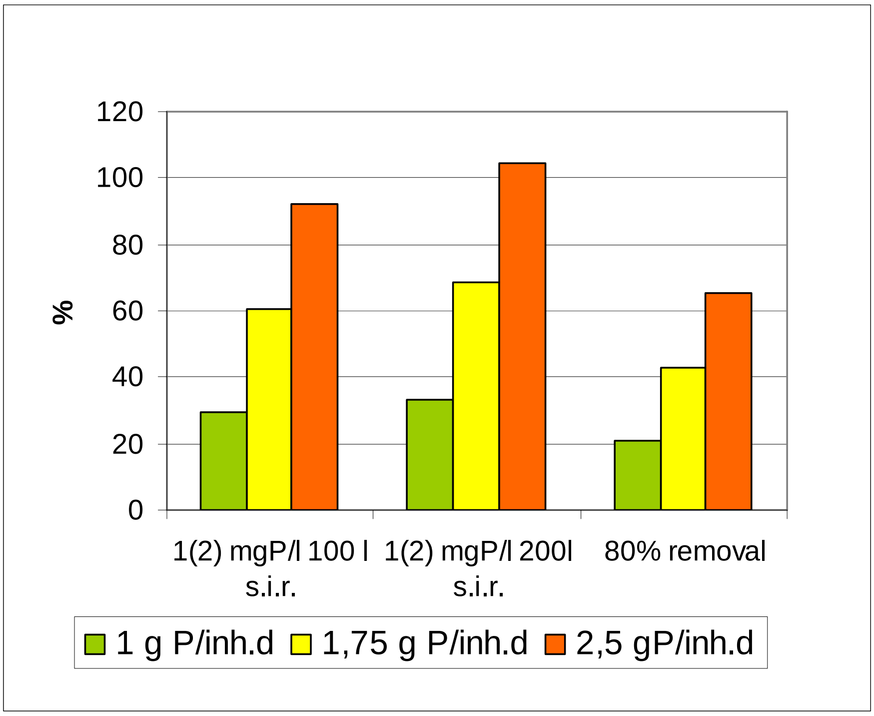


Figure 22: Additional need for precipitants of 3 variants in % of the "Zero laundry detergent Scenario" (0.3 g P/inh.d from detergents)

The mean amount of precipitants increase (compared to Scenario: 0.3 g P/inh.d in dish washing detergents) by about 30% in the 1.0 gP/inh.d Scenario and by about 60% in the 1.75 gP/inh.d Scenario. In the latter Scenario the annual operation costs of the treatment plants would increase slightly by about 4 %.

In respect that

> the costs for sewer development are higher as those for the waste water treatment and

> the operation costs amount to about 40% of the total costs of the waste water treatment

the increase of the total costs of waste water management (collection + treatment) due to P-precipitation is very small.

4.4. Different sources - different forms of P

Relevant P-emissions in 2000 stem from diffuse sources, mainly from the erosion of soils. Therefore it is also possible to reduce P-emissions in the agricultural sector.

However there is a big difference in P- emissions from waste water treatment plants and from erosion:

Emissions from waste water treatment plants are mainly in the form of dissolved Phosphate which is immediately highly available for algae production. On the contrary P-emissions via erosion are mainly in particulate form which is only partly available for algae-production. These emissions provide a potential P-source which can be partly mobilised in the case of anaerobic conditions in the waters which are a result of eutrophication.

The different forms of P and consequently the different availability for algae growth shall be considered in the innovative mechanisms for cost efficient mitigation of nutrient emissions when measures on emission reductions from different sectors are compared.

To keep the mobilisation of the particulate P-source low, the discharge of dissolved P-forms has to be kept low in order to avoid eutrophication.

5. ISSUES FOR INNOVATIVE MECHANISMS FOR COST EFFICIENT MITIGATION OF NUTRIENT EMISSIONS

In September 2006 a document was established to support Stefan Speck in his work on innovative mechanisms for cost efficient mitigation of nutrient emissions from diffuse sources in large catchments. In the following section relevant issues to be tackled by innovative mechanisms are depicted. Definitions of technical terms included in the document can be found in the ANNEX.

A mere focus on the reduction of the nutrient-discharge to the WBS could lead to a deterioration of rivers or local groundwater. A comprehensive strategy as outlined in the Water Framework Directive including the quality of surface waters as well as ground water should be aimed at.

A trading system for nutrients has to be based on an agreement of the understanding of the system (quantification of nutrient fluxes) and on an agreement on indicators as benchmark for nutrient management (e.g. surpluses on soil, cattle density, emissions to surface waters, loads to the Black Sea).

Emission from agriculture in the CEE countries probably will increase. The strategy should enable economic growth and simultaneous ensure a “good” status of the environment.

The cost effectiveness of measures is only related to direct costs. Impacts e.g. on employment or costs of the health system are not included.

Management of nutrients is only possible if the sources of the nutrients as well as their fate in the catchment are known. For this purpose the flows, transformations and storage processes in terms of mass loads have to be identified and described. These processes take place as well in the soil, the groundwater as in the surface water.

The Danube river and its main tributaries play a minor role for N removal by denitrification. In respect to P, the Iron Gate I is still a major point sink (up to 40% of the total P-load entering the Iron Gate reservoir is deposited).

The Danube Delta does not play a dominant role in nutrient retention as > 90% of the nutrient load of the Danube passes the three main channels directly to the Black Sea.

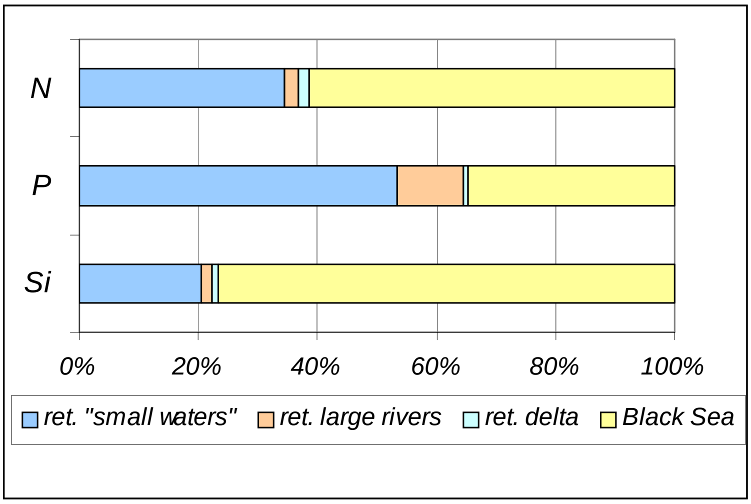


Figure 23: Emission to the river system and discharge to the Black Sea

Differences in the hydrology and hydrogeology of the catchments highly affect the amount of the total N emissions.

The quantification of the retention (denitrification) of nitrogen in soils and groundwater is **more important for the assessment of nitrogen emissions via groundwater as the surplus in soils**. In respect to emissions to surface water in comparison between regions the denitrification in groundwater may outweigh the influence of the surplus in soils.

Monitoring data- handle with care:

- Load calculations based on monitoring data from diffuse sources, especially via the groundwater do not reflect the current nutrient management. Depending on the residence time of the groundwater the current emission is the effect of management several years or even decades ago. This phenomenon has also to be considered for success control: measures taken now will show effects in the future.
- Impact of flow conditions:

  In respect to transport of P from the catchment to the receiving Sea, it can be concluded that there is no immediate influence of high flow or flood events in upstream parts of the Basin on the transport of P from the catchment to the receiving Sea. Particle-bound P is mobilised from the catchment (erosion) and the river bottom to a high extent at high flow events and transported at peak discharges downstream where retention by sedimentation of particles takes place. On the one hand this retention is a transport to floodplains. In this case it can be considered as more or less long term retention. On the other hand sedimentation takes place in the riverbed, as soon as the tractive effort of the river drops. In this second case the P-pool in the sediments of the sedimentation area will be increased. If anaerobic conditions in the sediment appear, part of the P will be transformed to soluble ortho-phosphate and will continuously contribute to the P transport to the receiving Sea. Part of the P-retained in the river sediment will be mobilised by resuspension at the next bigger high flow event. All together these alternating processes of suspension, transport, export to floodplains or sedimentation in the river bed with partly solution and partly resuspension at the next event decrease the share of the P transport during high flow events on the total loads transported in the more downstream parts of a catchment as compared to the more upstream parts. In the year of occurrence of an extreme flood event the P-transport of this year is dominated by the flood event. As average over many years the contribution of high flow events to the total P-transport still may be significant in smaller catchments. In a large catchment (e.g. river Danube) much smaller contributions of flood events on the total P-transport can be expected as average over many years.

  For the monitoring of P-loads this means that flood events have to be specifically addressed in tributaries anyway. In a large river the importance of event oriented load monitoring depends on the time scale considered. For calculations of yearly loads monitoring during flood events is still decisive. If average loads over 5 years and more are taken into consideration, monitoring at flood events is less decisive unless the probability of events increases significantly due to change of landuse practices in the catchment or due to climate change.

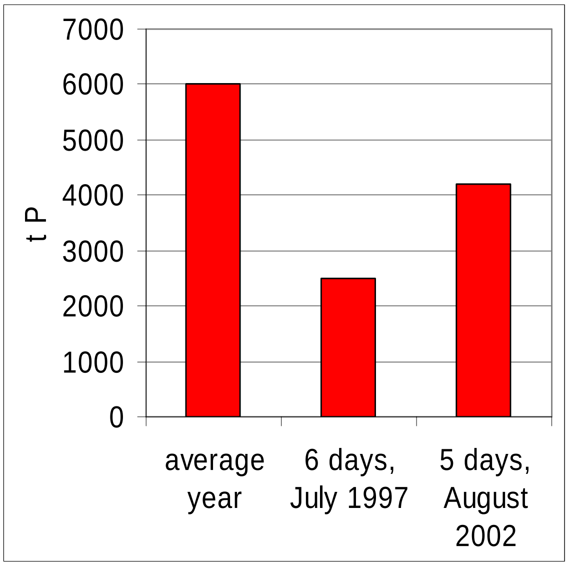


Figure 24: P-flow at high flow: Danube at Vienna

In general: Elevated concentrations (phosphate, nitrate, ammonia etc.) due to nutrient emissions affect the ground and surface water quality mainly in regions with low groundwater recharge rates and low river discharge (small rivers) as the dilution capacity is low. At the same time the retention of P and the removal of N by denitrification are high. These regions contribute only little to the total nutrient discharge to the Black Sea. In these areas emission reduction (at waste water treatment plants or best agricultural practice) is effective mainly for the protection of the local/regional water quality. **In such regions the influence of agricultural practice on N discharges via groundwater, differs completely depending on the distance (expressed in groundwater residence time) of an agricultural field related to surface waters.**

In regions with high groundwater recharge and high river discharge nutrient concentrations can be low, while the loads transported in the rivers are comparatively high (nutrient retention and losses during transport are low). Emission reduction in these regions effectively influences water quality of the Danube, the Delta and the Black Sea.

6. SUMMARY OF MAIN RESULTS

Results of the current level of nutrients in the Danube and dissolved oxygen in the NW shelf

> Transported nutrient loads in River Danube are highly influenced by physical factors as water discharge and temperature. The influence of these physical factors on yearly loads may outweigh anthropogenic impacts by far. Relatively high nutrient loads in 2005 are a result of the comparatively high flow situation of this year.

> If nutrient levels are compared at comparable flow situations, constant values up to a slight decrease can be detected between 1996-1998 and 2004-2005. Still this decrease is not significant. Changes in the emissions within this period can only be assessed based on emission calculations, as has been done till 2000 within the daNUbs project.

> As already indicated in the daNUbs-project the quality of phosphorus data at the Reni station is questionable.

> The level of oxygen saturation at the bottom of WBS has significantly improved between the 80ies and 1996. No dramatic changes in the period between 1996 and 2003 can be interpreted from existing data. The data base is not appropriate to demonstrate changes between 1996 and 2003 in detail. Only for the period 2001-2003 a good database exists from the daNUbs project.

Results of Scenario calculations on the effects of different consumption of P-containing detergents on the P-emissions from waste water treatment plants assuming full implementation of the Urban Waste Water Directive and the whole Danube Basin is considered as sensitive area.

> If the average consumption of P-containing detergents exceeds 0.65 gP/inh.d (including automatic dish washing detergents) the emission of P from WWTPs after full implementation of the Urban Waste Water Treatment Directive will be higher as in the year 2004 (emission in 2004: ca. 24 ktP).

> 54 to 69% of the P-emission will stem from settlements between 2.000 and 10.000 inhabitants as for these areas no P-removal is required by the UWWTD.

> The introduction of P-free laundry detergents in the Danubian countries would save 5 kt P/a compared to the 1gP/inh.d Scenario and 10.5 kt P/a compared to the 1.75 gP/inh.d Scenario.

> For treatment plants with more than 100.000 pe the emissions increase with increasing consumption of P-containing detergents by up to 4 kt P.

> In total 2 to 3 kt P will be discharged untreated into the receiving waters via storm water overflow.

> The amounts of additional sludge production due to the replacement of P containing detergents by e.g. Zeolites or due to the precipitation of P are similar (increase by 10-20%). This means that the costs for sludge management would be similar for these two options.

> The costs of precipitants for P-removal compared to the total costs (investment costs plus operation costs) for sewer development and waste water treatment are very small.

REFERENCES

Finck A. (1992). Dünger und Düngung. 2. Aufl., VCH-Verlagsgesellschaft mbH, Weinheim.

Fox K.K., Cassani G., Facchi A., Schröder F.R., Poelloth C., Holt M.S. (2002): Measured Variations in boron loads reaching European sewage treatment works. Chemosphere 47, 499 – 505

Sauerbeck D. and Rietz E. (1980). Zur Cadmiumbelastung von Mineraldüngern in Abhängigkeit von Rohstoff- und Herstellungsverfahren. Landw. Forschung, Sdhft. 37, pp. 685.

Zessner M. and Lampert C. (2002). The use of regional material balances in water quality management. Urban water, 4, pp. 73-83.

ANNEXES

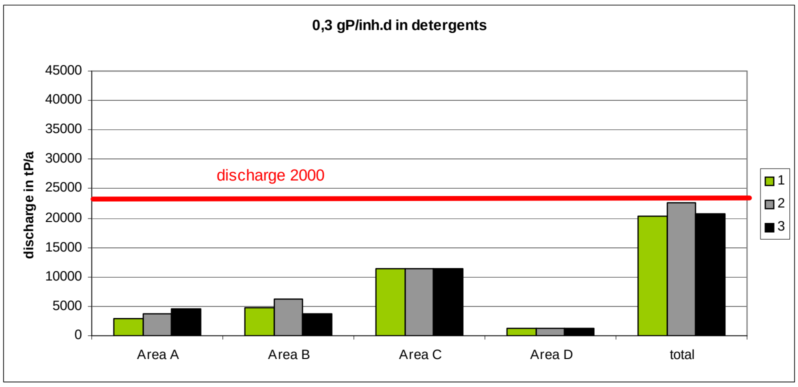
ANNEX 1

RESULTS OF SCENARIO CALCULATIONS

RESULTS OF SCENARIO CALCULATIONS

Table 1: Mean of Scenario calculations for emissions from municipal waste water treatment plants in tP/a

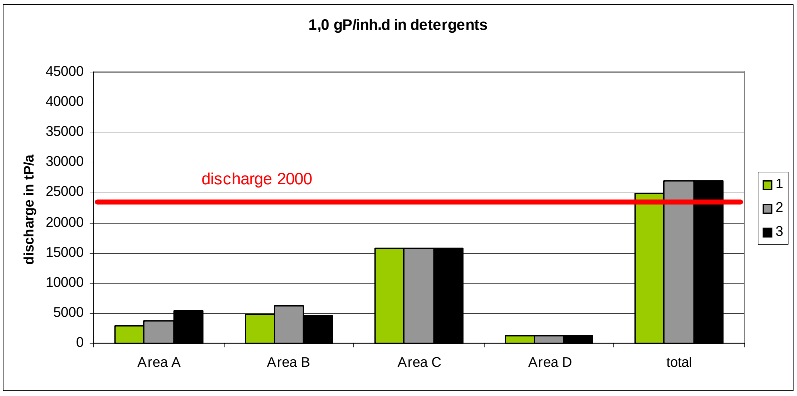
	consumption of P in detergents per inh.d			
emission in t P/a	0.3 gP/i.d	1 gP/i.d	1.75 gP/i.d	2.5 gP/i.d
> 100.000 inh.	3730	4015	4318	4621
10.000 - 100.000	4926	5211	5517	5822
2.000 - 10.000	11366	15844	20636	25428
< 2.000 inh.	1172	1188	1188	1188
Total	**21.194**	**26.258**	**31.659**	**37.060**



1:

The effluent concentration in area A is 1 mgP/l, in Area B 2 mgP/l. The infiltration rate amounts to 100 l/inhabitant.

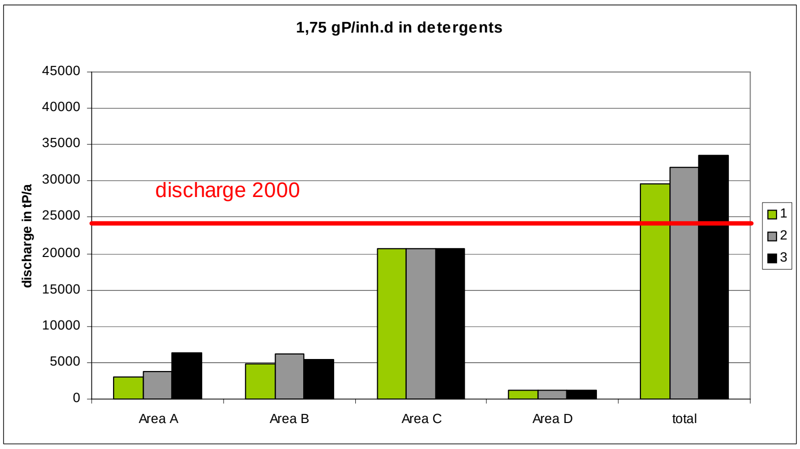
In the area C and biological treatment is applied.



2.

The effluent concentration in area A is 1 mgP/l, in Area B 2 mgP/l. The infiltration rate amounts to 200 l/inhabitant.

In the area C biological treatment is applied.



3:

80% P-reduction in relation to the inflow load

In the area C biological treatment is applied.

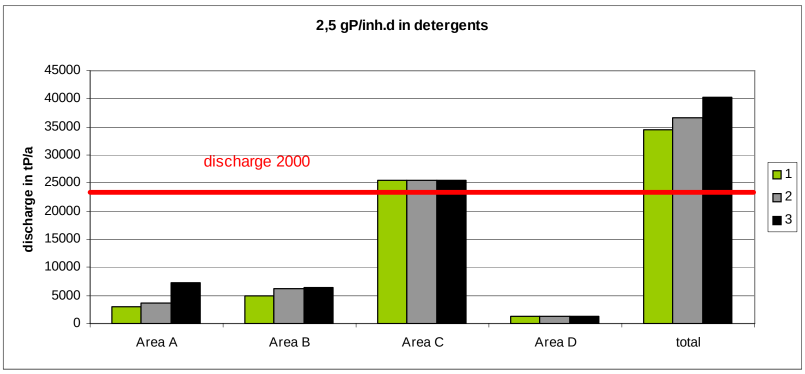


Figure 25: P-emissions in different settlement categories and different variants

The following diagrams show the different P-emissions depending on the use of P-containing laundry detergents.

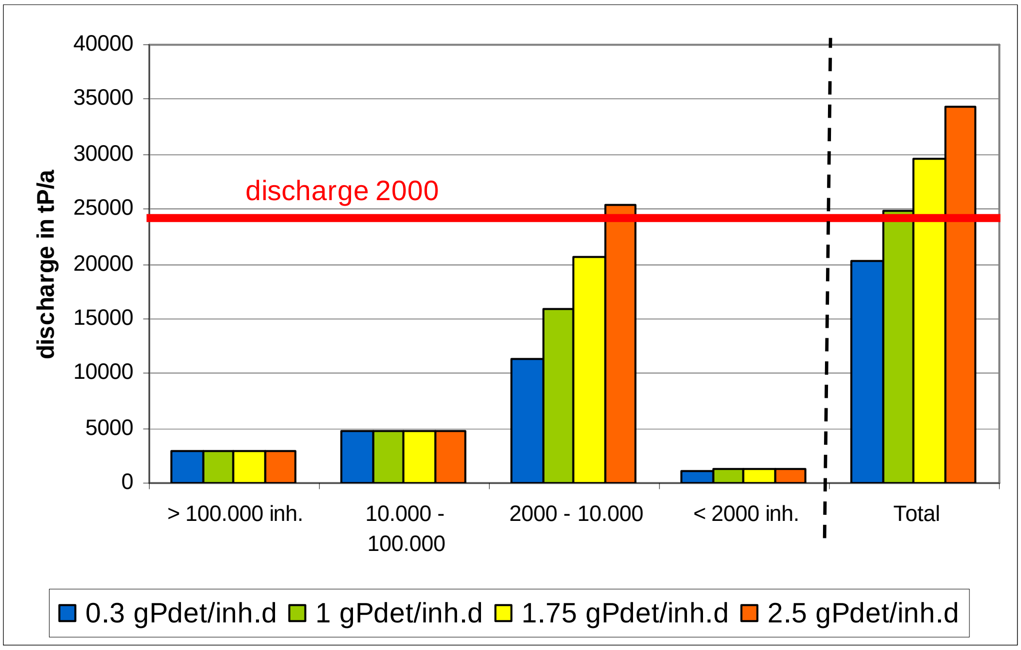


Figure 26: P-discharge of Variant 1: The effluent concentration in area A is 1 mgP/l, in Area B 2 mgP/l. The infiltration rate amounts to 100 l/inhabitant. In the area C biological treatment is applied.

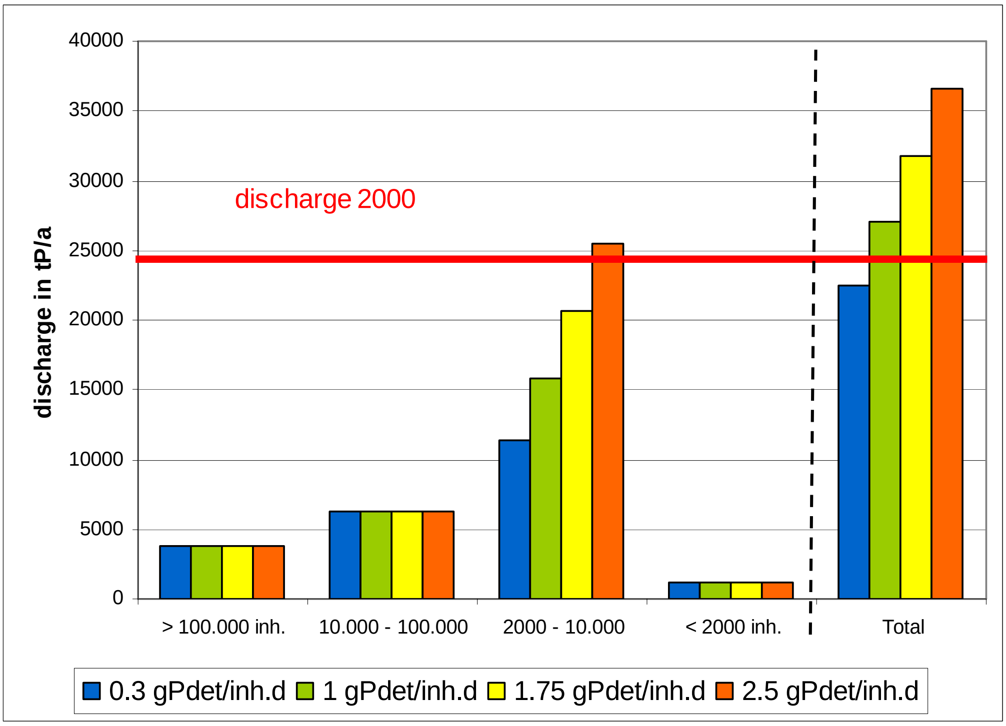


Figure 27: P-discharge of Variant 2: The effluent concentration in area A is 1 mgP/l, in Area B 2 mgP/l. The infiltration rate amounts to 200 l/inhabitant. In the area C biological treatment is applied.

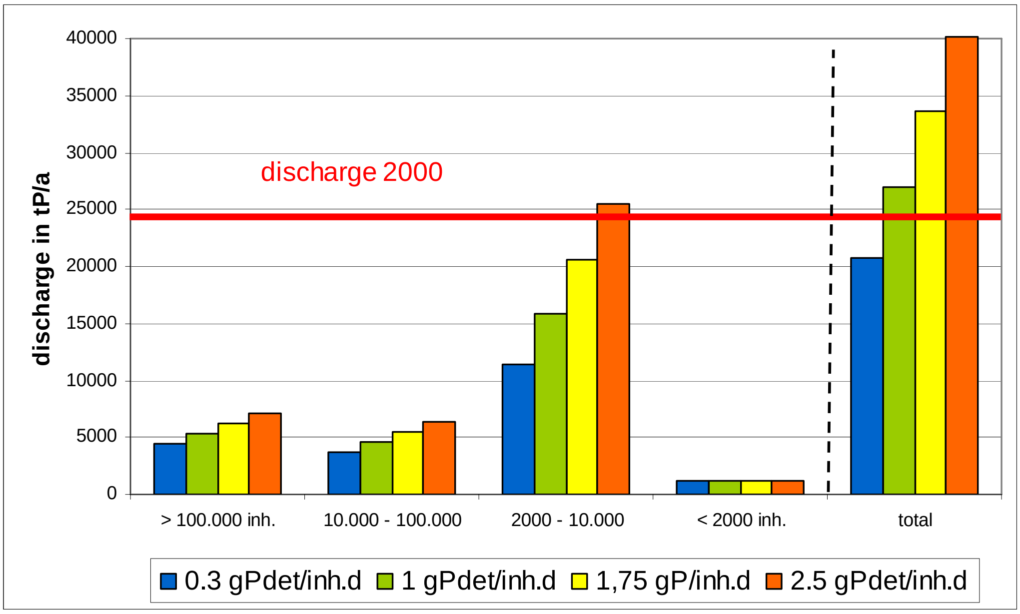


Figure 28: P-discharge of Variant 3: 80% P-reduction in relation to the inflow load. In the area C biological treatment is applied.

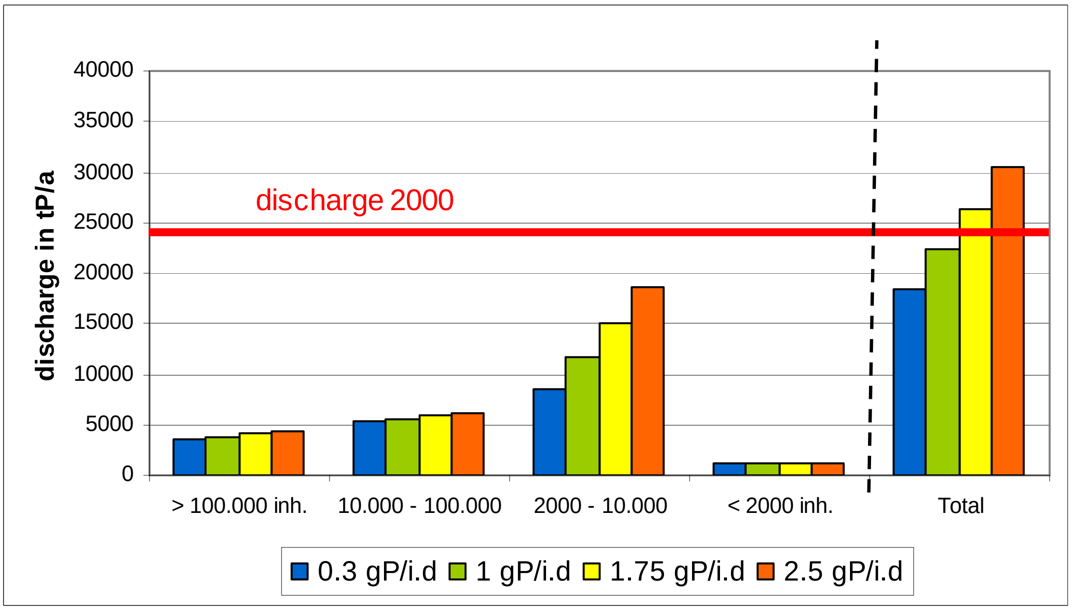


Figure 29: Emissions from WWTPs assuming "average" values for the percentage of the population in settlements from 2.000 – 10.000 and below 2.000 for Romania (mean of the 3 Variants).

ANNEX 2

DEFINITION OF TECHNICAL TERMS

DEFINITION OF TECHNICAL TERMS

Definitions of key technical terms prepared for Stefan Speck in order to support the work on key issues for innovative mechanisms for cost efficient mitigation of nutrient emissions from diffuse sources in large catchments.

Denitrification: The conversion of nitrite and nitrate nitrogen (after nitrification) to inert nitrogen gas (N_2). This process may occur in all parts of the water cycle and leads to a “loss” of nitrogen from the water system. The process requires that little or no oxygen be present in the system and that an organic food source be provided to foster growth of another type of bacteria. The resultant nitrogen gas is released to the atmosphere. In addition to N_2 also N_2O can be emitted. While N_2 is no harm for the environment, N_2O is a greenhouse gas and may also return by deposition to the soil – water system.

Emission: Refers to pollution being released or discharged into the environment from natural or man-made sources.

Erosion: The disruption and movement of soil particles by wind, water, or ice, either occurring naturally or as a result of land use.

Eutrophication: The fertilization of surface waters by nutrients that were previously scarce. Eutrophication through nutrient and sediment inflow is a natural aging process by which warm shallow lakes evolve to dry land. Human activities are greatly accelerating the process. The most visible consequence is the proliferation of algae. This algae eventually die and decompose, which reduce the amount of dissolved oxygen in the water.

Nonpoint Source (diffuse Source): A diffuse source of pollution that cannot be attributed to a clearly identifiable, specific physical location or a defined discharge channel. This includes the nutrients that runoff the ground from any land use - croplands, feedlots, lawns, parking lots, streets, forests, etc. - and enter waterways. It also includes nutrients that enter through air pollution, through the groundwater, or from septic systems.

Point Source: A source of pollution that can be attributed to a specific physical location; an identifiable, end of pipe "point". The vast majority of point source discharges for nutrients are from wastewater treatment plants, although some come from industries.

Nitrogen: N is used primarily by plants and animals to synthesize protein. Nitrogen enters the ecosystem in several chemical forms and also occurs in other dissolved or particulate forms, such as tissues of living and dead organisms. In water systems usually the dissolved forms are dominating.

Phosphorus: A key nutrient in the ecosystems; phosphorus occurs in dissolved organic and inorganic forms, often attached to particles of sediment. This nutrient is a vital component in the process of converting sunlight into usable energy forms for the production of food and fiber. It is also essential to cellular growth and reproduction for organisms such as phytoplankton and bacteria. Phosphates, the inorganic form are preferred, but organisms will use other forms of phosphorus when phosphates are unavailable.

Limiting nutrient: A nutrient, whose concentration in the environment of an organism, determines the growth and productivity of that organism.

Nutrient load: The term "nutrient load" refers to the mass or quantity of nutrients that pass out of a catchment or sub-catchment via a stream per unit of time. Nutrient load comprises direct and indirect input of waterborne and airborne nutrients from point sources and diffuse sources, as a result of land-based activities (driving forces) within the drainage area. This total input is caused by human activities as well as from natural sources.

The size of this input (load) can be indicated in different ways, for example as:

- tonnes of N or P /year = total annual input from all sources in all countries within the drainage area
- tonnes of N or P/year/source = e.g. tonnes of N from agriculture in all countries within the drainage area
- tonnes of N or P/year/country = e.g. tonnes of N from all sources in Austria

specific load:

- quantity per capita and year = e.g. kg N per person and year or
- quantity per ha and year = e.g. kg N per ha and year

Nutrient loads represent the emissions and inputs of nutrients from all sources (diffuse and point sources) upstream and include the effects of nutrient transport losses (e.g. from assimilation, chemical breakdown and storage due to sedimentation).

Nutrient loads can be measured by monitoring the outputs from catchments and sub-catchments. A nutrient load model can then be calibrated against this monitoring data. However, there are difficulties in measuring nutrient emissions if these are not to include any effect of transport loss and therefore, the results from studies may not be true nutrient emissions.

It seems that the major difference between nutrient emissions reported in the literature and nutrient loads that can be measured by monitoring outputs from catchments is a matter of scale. Scale refers to the size of the area of land used for measurement. The effect of transport losses in varying areas of land may explain, in part, the wide variation in reported nutrient generation rates (= specific loads) for the same landuse. In general: the larger the scale the better is the fit between emission estimates and the nutrient load calculated on the base of monitoring data.