



**KTH Architecture and
the Built Environment**

PHYSICAL PROCESS EFFECTS ON CATCHMENT-SCALE POLLUTANT TRANSPORT-ATTENUATION, COASTAL LOADING AND ABATEMENT EFFICIENCY

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ABSTRACT

Pollutants follow various subsurface and surface water pathways from sources within a catchment to its outlet and may cause detrimental effects on downstream water quality and ecosystems. Along their different transport pathways through a catchment, pollutants may be attenuated subject to different physical and biogeochemical processes. In this thesis, physical process effects on such catchment-scale pollutant transport and attenuation, resulting coastal pollutant loading and its efficient abatement are investigated. For this purpose, pollutant transport-attenuation is modeled both generically using a Lagrangian Stochastic Advective-Reactive (LaSAR) approach and site specifically for the Swedish Norrström basin using the GIS-based dynamic nitrogen transport-attenuation model POLFLOW. Furthermore, the role of such modeling for catchment-scale pollutant abatement is also investigated by use of economic optimization modeling.

Results indicate that appropriate characterization of catchment-scale solute transport and attenuation processes requires accurate quantification of the specific solute pathways from different sources in a catchment, through the subsurface and surface water systems of the catchment, to the catchment outlet. The various physical processes that act on solute transported along these pathways may be quantified appropriately by use of relevant solute travel time distributions for each water subsystem that the pathways cross through the catchment. Such distributions capture the physical solute travel time variability from source to catchment outlet and its effects on reactive pollutant transport. Results of this thesis show specifically that neglect of such physical solute travel time variability in large-scale models of nitrogen transport and attenuation in catchments may yield misleading model estimates of nitrogen attenuation rates.

Results for nitrogen abatement optimization in catchments further indicate that inefficient solutions for coastal nitrogen load reduction may result from simplifying physical transport assumptions made in different catchment-scale nitrogen transport-attenuation models. Modeling of possible future nitrogen management scenarios show also that slow nitrogen transport and reversible mass transfer processes in the subsurface water systems of catchments may greatly delay and temporally redistribute coastal nitrogen load effects of inland nitrogen source abatement over decades or much longer. Achievement of the national Swedish environmental objective to reduce the anthropogenic coastal nitrogen loading by 30% may therefore require up to a 40% reduction of both point sources, for achieving a fast coastal load response, and diffuse sources, for maintaining the coastal load reduction also in the long term.

Key words: Efficient pollutant load abatement; groundwater-surface water interactions; biogeochemical cycles; nitrogen; Lagrangian stochastic travel time approach; GIS.

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LIST OF PAPERS APPENDED

This thesis comprises a summary of following appended papers that are referred to in the text by roman numerals:

- I **Lindgren, G.A.**, G. Destouni, and A.V. Miller, Solute transport through the integrated groundwater-stream system of a catchment, *Water Resour. Res.*, 40, W03511, doi:10.1029/2003WR002765, 2004.
- II **Lindgren, G.A.** and G. Destouni, Nitrogen loss rates in streams: Scale-dependence and up-scaling methodology, *Geophys. Res. Lett.*, 31, L13501, doi:10.1029/2004GL019996, 2004.
- III Darracq, A., **G.A. Lindgren**, V. Cvetkovic, and G. Destouni, Effects of neglecting solute travel time variability on modeled nitrogen attenuation rates in streams (submitted to *Environmental Science & Technology*).
- IV **Lindgren, G.A.**, I.-M. Gren, and G. Destouni, Effects of nitrogen transport-attenuation modeling on the efficiency of coastal nitrogen load abatement (in revision for publication in *Environmental Science & Technology*).
- V **Lindgren, G.A.**, A. Darracq, and G. Destouni, The dynamics of coastal load responses to inland nitrogen source abatement (to be submitted).

CONTRIBUTIONS TO THE PAPERS

My specific contributions to each of the papers were:

- I Main model programming and computer simulations, collaborative interpretation of results, and main responsibility for writing the paper.
- II Contributions to model development, main model programming and computer simulations, collaborative interpretation of results, and main responsibility for writing the paper.
- III Main contribution to the included generic analysis of travel time variability and its role for up-scaled in-stream nitrogen attenuation rates.
- IV Classification of nitrogen transport-attenuation models, collaborative interpretation of results, and main responsibility for writing the paper.
- V Computer simulations, collaborative interpretation of results, and main responsibility for writing the paper.

LIST OF PAPERS NOT APPENDED

Conference publications

- Lindgren, G.A., G. Destouni, and I.-M. Gren, Quantification capability requirements for efficient decrease of combined agricultural, industrial, and household water pollutant loads in a catchment. 15th Stockholm Water Symposium – Drainage Basin Management – Hard and Soft Solutions in Regional Development, August 21-27, Workshop 5, 2005.
- Lindgren, G.A. and G. Destouni, Diffuse nitrogen inputs into streams: Direct experimental-model comparison and up-scaling of loss rates in streams, Eos Trans. AGU, 85/(47), Fall Meet. Suppl., Abstract H12B-02, 2004.
- Lindgren, G.A. and G. Destouni, On the role of the hyporheic zone in catchment-scale solute transport through streams. State of the planet, International Union of Geodesy and Geophysics XXIII General Assembly, Sapporo, Japan, 2003.
- Lindgren, G. and V. Cvetkovic, Colloid retention in Äspö crystalline rock: A generic computational assessment. Radionuclide Retention in Geologic Media, Workshop Proceedings, OECD/NEA, 2002.

Reports

- Lindgren, G. and G. Destouni, National case study 3. Sweden. In ERMITE Report: D3 Institutional Relationships, The European Commission Fifth Framework Programme, Energy, Environment and Sustainable Development, Contract No EVK1-CT-2000-0078, University of Oviedo, 2002.
- Lindgren, G. and G. Destouni, 3.2 2nd Swedish Stakeholder Meeting. In ERMITE Report: D 7 Workshop Reports, The European Commission Fifth Framework Programme, Energy, Environment and Sustainable Development, Contract No EVK1-CT-2000-0078, University of Oviedo, 2001.
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1 INTRODUCTION

Water flows from the soil surface of a catchment (drainage basin, watershed) along different subsurface and surface pathways to the catchment outlet. Solutes follow this water flow, disperse, interact with the subsurface porous medium and the stream sediments through physical and biogeochemical exchange processes, and may be transformed by biogeochemical reactions or radioactive decay.

The catchment-scale water flow processes are essential for providing water to ecosystem and human needs, and the solute transport through the catchment is a basic mechanism in various essential biogeochemical cycles, such as the carbon (Hope et al., 1994) and nutrient cycles (Howarth et al., 1996). This redistribution of water and solutes in catchment systems may, however, also cause detrimental effects, for instance, when solutes are transported downstream to locations where they act as pollutants, degrade water quality and possibly harm ecosystems (Lindqvist et al., 1991; Kreuger, 1998; Conley, 1999). The dispersal of pollutants through catchments is in many cases unintentional, as for instance the leaching of pesticides into ground- and surface waters. But in other cases the water flow through catchments is considered an effective means for disposal and dispersal of pollutants, for instance, for wastewater discharges.

In view of the essential role of water flow and solute transport through catchment systems for supporting ecosystems and human needs and the adverse effects caused by anthropogenic solute loads, there is a need for management of inland water resources in general and of solute loads

from catchments in particular. This need is, for instance, recognized in the European Union Water Framework Directive (European Commission, 2000) that requires water resources management based on a catchment perspective.

A prerequisite for effective management of solute loads is a quantitative prediction of the downstream effects of possible pollutant management measures in catchments (Gren et al., 2000; Gren et al., 2002; Baresel and Destouni, 2006). Such quantification of the catchment response to various changes within a catchment requires an understanding of the catchment-scale solute transport system. This includes understanding of the transport of non-reactive solutes, which are only affected by physical processes (e.g., Nyberg et al., 1999) and the transport of reactive solutes, which in addition to the physical processes are also affected by biogeochemical processes acting along the source-to-coast pathways (e.g., Rinaldo et al., 2005).

Among many different reactive pollutants that affect water quality, the example case of catchment-scale transport and attenuation of nitrogen is important to study. Excess coastal nitrogen loading promotes coastal eutrophication in many parts of the world, and the need for management of nitrogen loading to the sea is widely recognized (e.g., HELCOM 1993; Nixon, 1995; Howarth and Marino, 2006). Moreover, nitrogen is interesting because it enters the catchment both through point source inputs to streams, such as wastewater discharges, and through diffuse inputs, for instance, onto the soil through nitrogen fertilizer application, or directly onto surface waters by atmospheric

deposition. From these various sources, nitrogen follows different source-to-coast pathways, with generally different physical solute transport and attenuation conditions (van Breemen et al., 2002; Baresel and Destouni, 2005). In consequence, nitrogen is a suitable example pollutant of environmental interest, for which it is important to investigate physical process effects on its transport-attenuation, coastal loading and abatement efficiency.

The general objective of this thesis is to contribute to the understanding and quantification of physical solute transport processes on catchment scale, and of their effects on the attenuation, ultimate coastal loading and efficient abatement of pollutants in catchments. More specific objectives have been to investigate and give answers to the following main questions

- How should catchment-scale solute transport and attenuation processes be char-

acterized for appropriate quantification of coastal solute discharges resulting from different inland solute sources?

and with nitrogen as a specific solute example of environmental importance

- Do differences in common basic assumptions that underlie catchment-scale nitrogen transport-attenuation models have any implications of practical importance for efficient nitrogen management within catchments?
- How does coastal nitrogen loading respond to different inland nitrogen source reduction scenarios, and what do resulting catchment response dynamics imply for nitrogen source management aimed at reducing coastal nitrogen loads?

2 METHODS

In Papers I-III and V, mathematical modeling of catchment-scale solute transport is used as basic investigation tool. In Paper IV, the implications of such transport modeling are combined with economic catchment-scale nitrogen abatement optimization. In the following, the modeling tools/approaches used in the present thesis are presented and the suitability of these approaches for the different investigations discussed. For details on the model set-up, parametrization, input data and numerical methods the appended Papers I-V are referred to.

2.1 Solute transport modeling with the LaSAR approach

For modeling non-reactive tracer and reactive solute transport in Papers I, II, and partly also in Paper III the **L**agrangian **s**tochastic **a**dvective **r**eactive travel time (LaSAR) approach is applied. (In Paper I the acronym LaSAS is used instead of LaSAR to emphasize that this particular study considers only physical sorption and not general reaction processes) The LaSAR approach has been widely used in groundwater studies (e.g., Cvetkovic and Shapiro, 1990; Destouni and Cvetkovic, 1991; Cvetkovic and Dagan, 1994; Destouni et al., 1994; Ginn et al., 1995; Simmons et al., 1995; Destouni and Graham, 1995, 1997; Berglund and Cvetkovic, 1996; Cvetkovic and Dagan, 1996; Cvetkovic and Haggerty, 2002) and also in surface water studies (Gupta and Cvetkovic, 2000, 2002; Haggerty et al., 2002).

In the LaSAR approach small parcels or particles of water and solute are considered that

move along trajectories in space and to which the spatial coordinate system is assigned (hence Lagrangian approach). These trajectories are not known deterministically and are therefore represented statistically (hence stochastic approach). The parcel/particle movement along each trajectory is assumed to be advective only, neglecting local solute dispersion (hence advective approach). Field-scale solute transport is thus conceptualized as a spatially variable advective movement of many small solute parcels/particles from their respective input locations and along their respective trajectories to a common control plane. Each parcel/particle travels a certain time τ from source to control plane. Considering sufficiently many parcels/trajectories, which together capture the statistical properties of the entire transport domain, the travel times of the individual parcels can be aggregated into a travel time distribution (hence travel time approach), which expresses the large-scale physical solute spreading that results from random advective heterogeneity of inert tracer transport. Sorption or biogeochemical reactions that affect the solute parcel depend on travel time, which is used in this framework for decoupling solute transport and reaction problems.

The conceptual set up of the LaSAR approach was suitable for the studies in Paper I-II for several reasons. The LaSAR approach is applicable to solute transport problems in both subsurface and surface water systems, and can account for different processes and parameterizations in each subsystem. This is important, because physical and biogeochemical pro-

cesses may be quite different in these subsystems, for instance due to differences in biogeochemical properties and water residence times. The LaSAR conceptualization emphasizes that transport occurs along trajectories, which may cross boundaries between different water subsystems of a catchment, e.g. the groundwater-surface water interface, thus expressing that the different water subsystems are hydrologically linked. Moreover, the conceptual decoupling of solute transport and reaction processes emphasizes the need to also independently analyze and quantify the different physical and biogeochemical processes acting on solutes, as exemplified here in Papers I-III.

2.2 GIS based catchment-scale solute transport modeling

In Papers III and V, the problem of solute transport-attenuation modeling on the catchment-scale is focused on nitrogen and the specific modeling tool represented by the POLFLOW model (deWit, 2001; deWit and Bendoricchio, 2001; Mourad and van der Perk, 2004; Darracq and Destouni, 2005; Darracq et al., 2005), which is programmed in the geographic information system (GIS)-based PCRaster modeling language (van Deursen, 1995). In PCRaster the catchment is represented by a raster map. Each grid cell in this raster defines a geographic location to which different types of data can be assigned, which are then represented in separate maps.

The handling of data in such a GIS is useful for modeling of nutrient transport-attenuation on the catchment-scale, because spatial heterogeneity of model inputs and parameters can be represented in different, but spatially corresponding and coupled GIS-maps. Moreover, input data that are necessary for hydrological flow and nutrient transport modeling is commonly stored in GIS format and therefore available data sets can readily be used in a GIS-based modeling approach.

The nitrogen transport-attenuation processes are represented as mass balances over the grid cells, in which various subsurface-surface water interactions are quantified. The upstream-downstream (water flow and nutrient mass input-output) relations between grid cells are assigned and calculated based on a digital elevation map of the catchment. Conceptually this implies a division of the nitrogen transport-attenuation problem into two different scales, the grid cell scale over which transport-attenuation processes are averaged, and the catchment scale over which a spatial distribution mapping of transport-attenuation parameters is calculated and represented. In Paper III and V, the grid cell scale represents the highest spatial resolution scale available for required input and calculated output data. In Paper III, the grid cells are for comparative purposes also aggregated to sub-catchments of different sizes, in order to investigate effects of using coarse model resolution scales in the nitrogen transport-attenuation modeling.

2.3 Catchment-scale optimization of nitrogen source abatement

In Paper IV, the effects of specific nitrogen transport-attenuation processes on catchment-scale nitrogen abatement efficiency are investigated by use of economic optimization modeling (Söderqvist, 1996; Gren et al., 1997, 2000ab, 2002; Shortle et al., 1998; Elofsson, 2000, 2003). In such an optimization model, the conditions for economically optimal abatement solutions within a catchment are formulated with a set of equations, including objective functions and constraints. The objective function is a mathematical formulation of the objective of the optimization. In Paper IV, the objective is formulated as either minimization of total costs or maximization of net benefits of coastal nitrogen load abatement. The objective function quantifies in monetary terms the total costs of different nitrogen abatement measures or the total net benefits of these measures, based on cost

and benefits functions that depend on nitrogen source and coastal nitrogen load reductions.

Economically optimal abatement solutions to various possible nitrogen transport-attenuation model scenarios must account for the underlying catchment-scale nitrogen transport-attenuation system and also fulfill given constraints, such as political or legal coastal nitrogen load reduction targets. The constraints ensure that these targets are fulfilled in the optimal solution, which requires in turn quantification of re-

sulting coastal nitrogen load reduction subject to various possible inland nitrogen abatement measures. The optimization problem of catchment-scale nitrogen abatement, given a range of different possible approaches to quantifying nitrogen transport-attenuation in catchments, was solved in Paper IV by use of the computer based optimization algorithms "The General Algebraic Modeling System" (GAMS; Brooke et al., 1996).

3 PHYSICAL SOLUTE TRANSPORT PROCESSES (PAPER I)

In Paper I, transport of non-reactive solute through a catchment is studied. From analysis of time series of chloride contents in precipitation and stream water, Kirchner et al. (2000) inferred that the catchment system acts as a fractal filter, which implies that the stream response to catchment-wide solute inputs at the surface exhibits both a fast initial peak and a long tail in form of a power-law type breakthrough curve (BTC). The power spectra of such BTCs have power-law slopes around 1.

The objective of Paper I was to analyze the physical process basis underlying the catchment-scale solute transport system. For this purpose a model was developed based on the LaSAR approach that integrates solute transport through the groundwater and stream water systems of a catchment. This model was then used to analyze the response at the catchment stream outlet to a pulse input of non-reactive solute over the entire catchment surface and to investigate which transport process combinations may be dominant in yielding reported fractal temporal solute spreading. The following specific factors and processes causing temporal solute spreading were investigated: a catchment-wide source extent; the combination of fast overland/storm flow and slow groundwater pathways; advective variability in the subsurface caused by subsurface flow heterogeneity; transport by preferential subsurface flow and associated solute mass transfer between mobile and immobile water zones; and solute ex-

change between the stream water and the hyporheic zone.

The analysis of different physical transport process effects on resulting catchment-scale BTCs was based on the conceptual model illustrated in Figure 1. A pulse input of solute is uniformly distributed over the entire catchment surface and then follows either the overland flow path 1, or the subsurface flow path 2, before entering the stream and being transported to the catchment outlet. The transport along these pathways was modeled using the LaSAR approach, which in Paper I was further developed from the subsurface model of Destouni and Graham (1995) and the surface water models of Gupta and Cvetkovic (2000, 2002) to account for transport through the integrated subsurface-surface water systems of a catchment.

Fractal BTC responses at catchment outlets could among the investigated physical transport factors and processes only be explained by the combined effects of the large source extent, advective variability among and along subsurface transport pathways, and transport through preferential flowpaths with associated delaying solute mass transfer effects. Furthermore, it was found necessary that a relatively large fraction of solute input mass follows the groundwater flow paths and that the mass transfer rate to mean subsurface advection velocity ratio falls within a certain range.

The main controlling factors of the temporal spreading of non-reactive solute at the catchment outlet were thus found to be subsurface so-

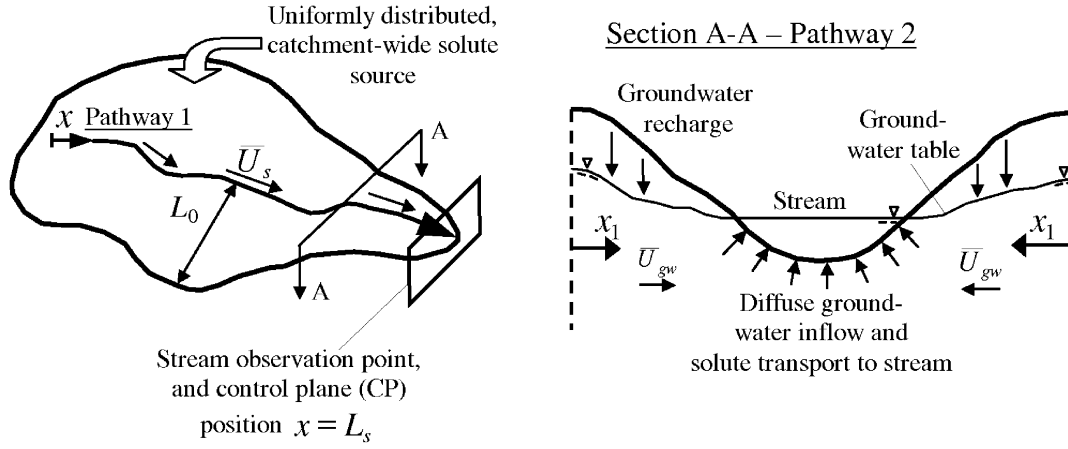


Figure 1. Schematic illustration of the considered integrated soil-groundwater-stream system of a catchment.

lute transport processes. However, the stream influence can not be neglected, even if the direct solute transport contribution of the fast pathway 1 (Figure 1) is small. The stream transport part still influences the overall solute transport through groundwater into streams and then fur-

ther to the catchment outlet. Furthermore, for reactive solute transport, in-stream reaction processes may be important, for instance for quantification of in-stream nitrogen attenuation studied in the following papers.

4 PHYSICAL SOLUTE TRAVEL TIME VARIABILITY EFFECTS ON IN-STREAM NITROGEN ATTENUATION (PAPER II)

To effectively mitigate excess nitrogen discharges from land to sea, and associated adverse effects on coastal ecosystems, different inland sources' contributions to the coastal nitrogen load have to be quantified. Besides estimation of the different nitrogen source inputs, this requires quantification of the nitrogen transport-attenuation along their different source-to-coast pathways. One possible approach is to fit first-order attenuation (or loss) rates λ_s^* to nitrogen input and output loads in a stream reach or sub-catchment, assuming a single representative travel time for the entire stream reach or sub-catchment (Smith et al., 1997; Alexander et al., 2000, 2002). Resulting attenuation rates λ_s^* are then used as basic parameters for quantification of the contribution of different sources to coastal nitrogen loading and comparison of nitrogen rates in different catchments.

Such comparison of resulting in-stream attenuation rates λ_s^* between catchments has indicated considerable decrease of attenuation rate with stream depth (Alexander et al., 2000). Locally measured nitrogen attenuation rates λ_s , however, were in other studies found to be much more constant when appropriately normalized with flow variables (Peterson et al., 2001). Modeled nitrogen attenuation rates thus appear to depend on whether or not hydrological transport factors are neglected in their quantification.

The objective of Paper II was to relate locally measurable nitrogen attenuation rates λ_s

to large-scale calibrated rates λ_s^* and to investigate possible hydrological transport and scale dependence effects. The conceptual catchment-scale transport model for investigating this relation is illustrated in Figure 2. Nitrogen is applied uniformly over the entire catchment surface and then follows subsurface transport pathways to the groundwater stream interface, where nitrogen mass enters the stream distributed along its entire length. Furthermore, an example nitrogen point source is also putting nitrogen mass into the stream.

The main result of Paper II is illustrated in Figure 3, which shows that neglect of in-stream travel time variability leads to large-scale calibrated attenuation rates λ_s^* that are generally different from independently measurable local-scale rates λ_s . The difference between the two attenuation rate parameters depends on mean advective travel time $\bar{\tau}_L$ through the stream to its sub-catchment outlet and exhibits considerable dependence on stream/sub-catchment scale. This scale-dependence increases with increased in-stream travel time variability. The scale effect is further larger when the single assumed representative travel time τ_d for λ_s^* calibration is around $0.5\bar{\tau}_L$ than for $\tau_d = \bar{\tau}_L$.

Derived close form expressions for the λ_s^*/λ_s relation, moreover, show that the point source delivery factor α_{ps} , which quantifies the fraction of point source nitrogen input that reaches the catchment outlet, generally differs from a

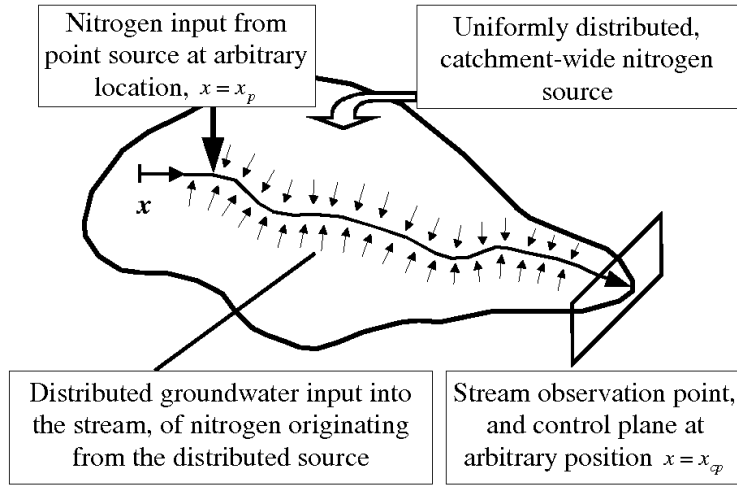


Figure 2. Schematic illustration of the considered nitrogen source distribution and catchment-scale transport problem.

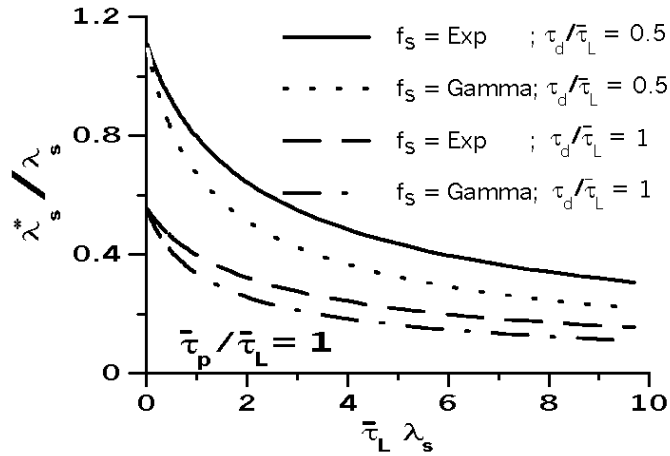


Figure 3. Resulting normalized nitrogen loss rate estimate λ_s^*/λ_s , as function of dimensionless quantity $\tau_L \lambda_s$ for example values of 10% point source and 90% diffuse source inputs to the catchment and 10% nitrogen attenuation in the subsurface water system (Smith et al., 1997, Arheimer and Brandt, 2000) and for different physical solute travel time distributions $f_s(\tau_s)$, and $\tau_p/\tau_L = 1$.

corresponding distributed source delivery factor α_{ds} in streams. The difference is explained by the difference between physical in-stream solute travel time distributions for point and diffuse source inputs to streams.

These results indicate that in-stream nitrogen attenuation rates λ_s^* that are calibrated in large-scale nitrogen transport-attenuation models are not comparable to independently measurable local-scale attenuation rates λ_s . If such

model scale dependence of λ_s^* is not properly addressed the interpretation of underlying biogeochemical processes may be confused by travel time variability effects. Moreover, such scale-dependence may imply generalization and predictability limits, because it is not clear how nitrogen attenuation rates that are calibrated on certain model resolution scales can appropriately be applied to different scales or sites.

5 CATCHMENT-SPECIFIC EFFECTS OF TRAVEL TIME VARIABILITY ON IN-STREAM NITROGEN ATTENUATION (PAPER III)

Several studies have noted that in-stream nitrogen attenuation per stream length appears to decrease with increasing stream depth (e.g. Smith et al., 1997; Alexander et al., 2000). This behavior has been interpreted as a decrease of in-stream first-order nitrogen attenuation rate with stream depth (Alexander et al, 2000), with the reasoning that the biogeochemically active stream-sediment interface area per water volume unit decreases with stream depth. However, the results of Paper II indicate that nitrogen attenuation rates may also just appear to decrease with increasing model resolution scale due to neglect of physical solute travel time variability.

To distinguish physical and biogeochemical process effects on nitrogen attenuation per unit stream length and their possible stream depth dependence, Paper III uses model results of nitrogen transport and attenuation in the specific Swedish Norrström drainage basin (Figure 4; Darracq and Destouni, 2005; Darracq et al., 2005; Destouni and Darracq, 2006). Paper III further extends the previous modeling with new results that explicitly quantify the variability of in-stream advective nitrogen travel time, its specific dependence on stream depth and its total statistics in model resolution units of different scales within this basin. By use of these site-specific results and extension of the generic results of Paper II to account for different possible forms of in-stream travel time variability, Paper III analyzes if and why neglect of in-stream

travel time variability on large model resolution scales may really produce such considerable effects in modeled nitrogen attenuation rates, as indicated by Paper II.

Figure 5a illustrates that in-stream nitrogen attenuation rates k_{cell}^r (following here the specific notation of Paper III) that are calculated based on a constant 1km^2 grid-cell model resolution scale, show no particular dependence on stream depth. In contrast, in-stream attenuation rates k_{sc}^r that are calculated from aggregated model results to larger sub-catchment resolution scales exhibit an artificial dependence on stream depth. Because the k_{sc}^r quantification is solely based on aggregation of the finer resolution grid-cell data that also underlie the stream-depth independent k_{cell}^r quantification, the k_{sc}^r depth-dependence can only be an artifact of inappropriate up-scaling.

Figure 5b shows separately the two factors that determine the in-stream nitrogen attenuation rates on the cell (k_{cell}^r) and sub-catchment (k_{sc}^r) scales. One factor is the inverse physical nitrogen travel time through a cell $1/T_{cell}^r$, which increases with stream depth and another the negative value of the natural logarithm of relative nitrogen output per nitrogen input mass for a cell $-\ln(M_{cell}^{out}/M_{cell}^{in})$, which decreases with stream depth. The product of these two factors is k_{cell}^r , which is independent of stream depth. For the sub-catchment resolution scale, however, the increase of inverse representative travel time $1/T_{sc}^r$

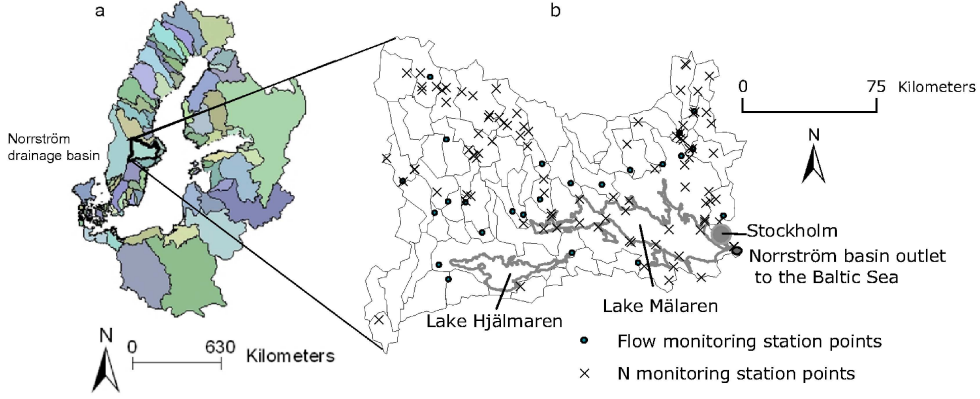


Figure 4. a) Location map of the Norrström drainage basin within the entire Baltic Sea drainage basin; b) (Sub)catchments and monitoring station locations for water flow and Nitrogen measurements in the Norrström drainage basin.

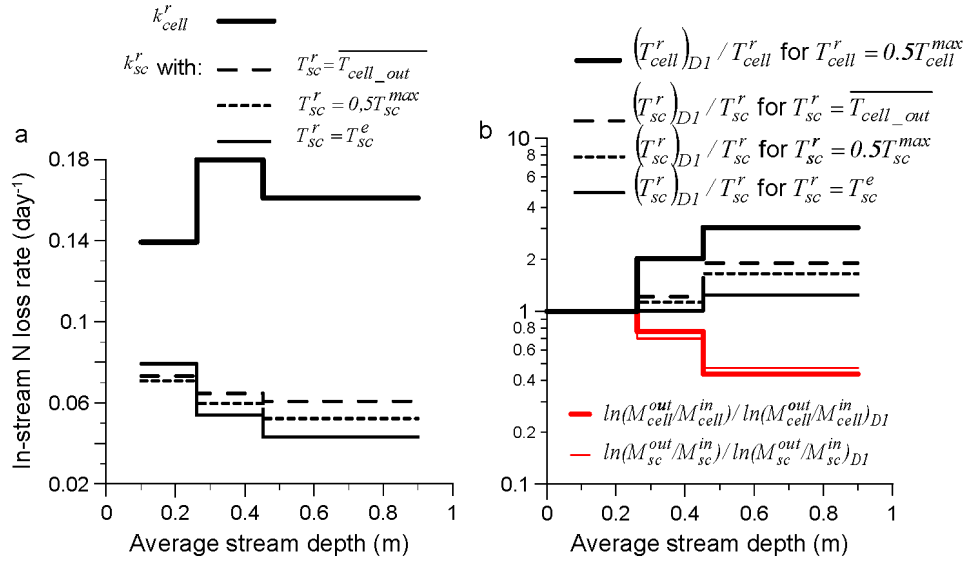


Figure 5. a) Average values of nitrogen attenuation rate k_{cell}^r on grid-cell scale (thick solid line) for cells of different stream-depth classes, compared with average values of nitrogen attenuation rate on (sub)catchment scale k_{sc}^r (thin lines) for (sub)catchments of different stream-depth classes, with k_{sc}^r for each (sub)catchment obtained using three different possible quantifications of a single representative travel time T_{sc}^r for the sub-catchments (for different T_{sc}^r quantifications see Table 1 in Paper III). b) Average nitrogen mass output/input relation factor $\ln(M_{cell}^{out}/M_{cell}^{in})$ on the grid-cell scale (thick red line) and $\ln(M_{sc}^{out}/M_{sc}^{in})$ on the (sub)catchment scale (thin red line) for different stream-depth classes relative to their respective average values for the smallest stream depth class ($0 < D1 < 0.26$ m), and average inverse travel time factor $1/T_{cell}^r$ on the grid-cell scale (thick black line) and $1/T_{sc}^r$ on the (sub)catchment scale (with different thin black lines for different T_{sc}^r quantifications) for different stream-depth classes relative to their respective average values for the smallest stream-depth class ($0 < D1 < 0.26$ m).

is smaller than that of inverse grid-cell travel time $1/T_{cell}^r$ and does not compensate for the decrease of the negative natural logarithm of relative nitrogen output per nitrogen input in the sub-catchment $-\ln(M_{sc}^{out}/M_{sc}^{in})$. The result is that $k_{sc}^r = -\ln(M_{sc}^{out}/M_{sc}^{in})/T_{sc}^r$ artificially decreases with stream depth.

This particular k_{sc}^r depth-dependence artifact is explained by the information loss implied by the T_{sc}^r averaging over the underlying variability of local in-stream travel times T_{cell}^r , which masks the full stream-depth dependence of physical nitrogen travel time and forces its effect on relative nitrogen mass delivery $M_{cell}^{out}/M_{cell}^{in}$ and M_{sc}^{out}/M_{sc}^{in} to appear instead as a stream depth dependence of calibrated large-scale nitrogen attenuation rates, k_{sc}^r . Neglect of travel time variability, however, has also more general and greater effects on the overall magnitude of modeled nitrogen attenuation

rates on different resolution scales, as exemplified by the difference in magnitude between the two rates k_{sc}^r and k_{cell}^r in Figure 5a.

The attenuation rates k_{cell}^r for the cell and k_{sc}^r for the sub-catchment scale are both calculated with the assumption of a single representative travel time for each scale T_{cell}^r and T_{sc}^r , respectively. They both neglect variability of sub-grid travel time due to many different physical transport mechanisms that are discussed in detail in Papers I, II, and V. This variability may be represented by different travel time probability density functions (pdfs) for different site conditions. Closed form expressions that couple nitrogen attenuation rates with such travel time pdfs are presented in Papers II-III, making it possible to explicitly relate locally measurable nitrogen attenuation rates to calibrated rates on large model scales.

6 NITROGEN TRANSPORT-ATTENUATION EFFECTS ON CATCHMENT-SCALE ABATEMENT EFFICIENCY (PAPER IV)

Management of coastal nitrogen load reductions should follow an efficient nitrogen source abatement strategy in the coastal catchments that contribute to the coastal load. This requires identification of optimal allocation of nitrogen abatement measures in the catchment, either minimizing the costs of achieving given coastal load targets (Gren et al., 1997, 2000ab, 2002; Shortle et al., 1998; Elofsson, 2000, 2003), or maximizing the net benefits of reducing the coastal loads (Söderqvist, 1996). The allocation of nitrogen abatement measures is optimal if it is not possible to further decrease the cost for achieving coastal load targets or increase the net benefits of the nitrogen abatement by reallocating abatement measures within the coastal catchments.

In Paper IV, main differences between basic assumptions of some different nitrogen transport-attenuation modeling approaches (Haith and Shoemaker, 1987; Grimvall and Stålnacke, 1996; Johnes, 1996; Smith et al., 1997; Arheimer and Brandt, 1998; deWit, 2001; Paper II) are identified and classified for further investigation of whether such model differences may have any implications for abatement efficiency of nitrogen loads from land to the sea. For this investigation purpose, an economic optimization model for catchment-scale abatement of coastal nitrogen loads (Gren et al., 1997, 2000ab, Elofsson, 2000, 2003; Wulff et al., 2001) was developed and parameterized with

example data from the catchments of Southern Sweden discharging into the Baltic Sea.

Four classes of nitrogen transport-attenuation models are differentiated and classified with regard to different basic a priori assumptions: class a) models that neglect nitrogen attenuation along the source-to-coast pathways through catchments (Haith and Shoemaker, 1987); class b) models that quantify nitrogen attenuation separately in the subsurface and the surface stream water sub-systems of a catchment, but assume equal nitrogen attenuation for all source inputs to each sub-system (Smith et al., 1997; Arheimer and Brandt, 1998; deWit, 2001); class c) models that distinguish the relative nitrogen attenuation for different sources, but not between the different water sub-systems in a catchment (Grimvall and Stålnacke, 1996; Johnes, 1996); and finally class d) models that quantify nitrogen attenuation separately for both different water sub-systems of a catchment and different sources (Rinaldo et al., 2005; Paper II). For comparison, it has been common for catchment-scale models of nitrogen abatement optimization to assume the same relative nitrogen attenuation for all sources and water sub-systems within a catchment (Gren et al., 1997, 2000ab, Elofsson, 2000, 2003; Wulff et al., 2001).

The different classified nitrogen-attenuation model assumptions lead to two main different optimization rule expressions. The more general rule (equations 2-3 in Paper IV) is based

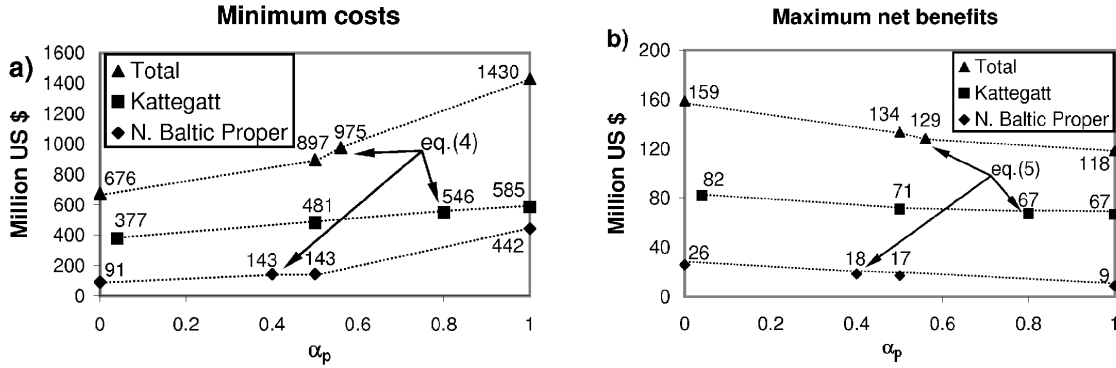


Figure 6. Optimization results for reducing the total coastal nitrogen (N) loading for the example separate sub-catchments Kattegatt and Northern Baltic Proper, and for the total N loading from all Baltic Sea catchments of Southern Sweden. Results are shown in terms of: a) the more general minimum annual cost solution of equation (2) in Paper IV for a 50% N load reduction under different possible α_p - α_d combinations, along with the corresponding solution of simplified equation (4) in Paper IV assuming $\alpha_p = \alpha_d$; and b) the maximum annual net benefit solution of equation (3) in Paper IV for different possible α_p - α_d combinations, along with the corresponding solution of simplified equation (5) in Paper IV assuming $\alpha_p = \alpha_d$.

on separately quantified nitrogen mass delivery fractions to the coast from point (α_p) and diffuse (α_d) sources in a catchment. The other, simplified rule assumes instead that $\alpha_p = \alpha_d$ (equations 4-5 in Paper IV). In consequence, different optimal allocations of nitrogen source measures may result from use of different nitrogen transport-attenuation models according to the above-described classification. Without any need for economic efficiency considerations, however, the nitrogen load data for the catchments of Southern Sweden indicate that class a) models are not suitable for deriving efficient management strategies, because considerable nitrogen attenuation does occur along source-to-coast pathways. Furthermore, subsurface nitrogen attenuation in the example southern Swedish catchments has been estimated to be close to 1 (Arheimer et al., 1998), implying that $\alpha_p \approx \alpha_d$ in nitrogen transport-attenuation models of class b), which thus support the corresponding simplified abatement optimization rule (equations 4-5 in Paper IV). In contrast, class c) and d) models generally require use of the more

general abatement optimization rule (equations 2-3 in Paper IV).

Figure 6 illustrates optimization results for reduction of the coastal nitrogen loading, for different α_p (and associated α_d values) model assumptions in the example Baltic Sea sub-catchments of Kattegatt and Northern Baltic Proper, and for the total Baltic Sea catchments of Southern Sweden. The results show that the use of simplified rules for nitrogen abatement optimization may lead to considerably inefficient abatement strategies. The largest difference between the two different optimization rules is obtained for the example catchment case of the Northern Baltic Proper, for which minimum costs for different α_p model assumptions range from 36% lower to 3 times higher than the minimum costs resulting from the simplified optimization rule. How large the differences between different α_p and α_d model assumptions may be in catchments can generally only be addressed by class d) models, which are the only ones allowing for independent process-based quantification of α_p , α_d and the latter's different water sub-system components.

7 COASTAL LOAD RESPONSES TO NITROGEN SOURCE MITIGATION (PAPER V)

Recent studies in Swedish (Arheimer and Brandt 2000; Arheimer et al., 2005; Baresel and Destouni, 2005) and Latvian (Stålnacke et al., 2003) catchments converge in indicating that it has been and may continue to be difficult to achieve targeted decreases of coastal nitrogen loads (for instance, 30% reduction of anthropogenic coastal nitrogen loads, as required by the national Swedish environmental objectives) with so far attempted nitrogen abatement strategies and measures. The objective of Paper V was to investigate and quantify the possible process basis of such difficulties in achieving set nitrogen reduction targets. For this purpose, the nitrogen input and transport-attenuation history and four possible future nitrogen management scenarios are simulated for the Swedish Norrström basin (Figure 4) with the dynamic GIS-based nitrogen transport-attenuation model POLFLOW (deWit, 2001; Darracq et al., 2005; Darracq and Destouni, 2005). In the future baseline scenario 0, nitrogen inputs are assumed to remain constant after year 2005. Scenarios 1-3 simulate instead a 40% step decrease in 2005 of nitrogen inputs from all agricultural sources (scenario 1), all point sources (scenario 2), and both agricultural and point sources (scenario 3), while all other nitrogen inputs remain constant at their 2005 levels.

Analysis of model inputs and results shows that the diffuse nitrogen mass inputs at the basin soil surface increased with about 240% from 1945 to 2005. The downstream transport effect of this input increase, however, is an only 30%

increase of total nitrogen input to the basin's surface waters. This considerably smaller increase of surface water inputs compared to soil surface inputs is explained by: a) large and only slowly changing inputs to surface waters from internal subsurface nitrogen accumulation and subsequent release; b) large, even though slowly reversible subsurface nitrogen attenuation of about 80%; and c) relatively large point source inputs directly into surface waters. For comparison with the subsurface nitrogen attenuation of 80%, the nitrogen attenuation in surface waters is about 55%.

Figure 7 shows further simulation results for the possible future nitrogen management scenarios 0-3, in terms of the resulting future deviation of coastal nitrogen load from its 2005 level, relative to a calculated 55% anthropogenic coastal load component in 2005. All scenarios show considerable short- and long-term dynamic effects on coastal nitrogen loading. The results for scenario 0 show remaining transient long-term effects of the nitrogen mass input history from 1945 to 2005. Scenario 1 yields a small initial effect of the 40% agricultural source reduction, which ultimately results in a 14% reduction of the anthropogenic coastal nitrogen load relative its 2005 value. The point source reduction scenario 2 yields a quick 25% decrease of anthropogenic coastal nitrogen load, but also an increasing long-term trend similar to that of scenario 0, which leads to an ultimate reduction of anthropogenic coastal nitrogen load of only about 10%. Scenario 3, with both diffuse

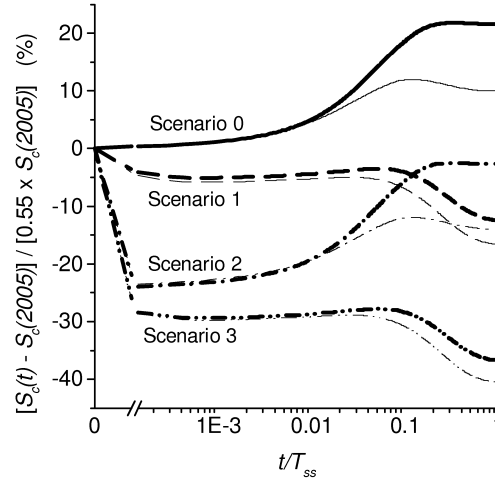


Figure 7. Relative temporal change $(S_c(t) - S_c(2005)) / (0.55 S_c(2005))$ of modeled coastal nitrogen (N) load $S_c(t)$ at the Norrström basin outlet from its 2005 value $S_c(2005)$ relative the calculated 55% anthropogenic $S_c(2005)$ component. Results are shown for the baseline scenario 0 (solid lines) and scenarios 1 (dashed lines), 2 (dash-dotted lines) and 3 (dash-dot-dotted lines) and for the model calibration versions of Darracq and Destouni (2005; thick lines) and Darracq et al. (2005; thin lines). Scenario 0 simulates constant N inputs at their 2005 values. Scenarios 1, 2, and 3 simulate a 40% step decrease from 2005 values of all agricultural N input sources, point N sources, and both agricultural and point N sources, respectively, with all other N inputs remaining constant at their 2005 levels. Time t is set to 0 in 2005 and is normalized with the time it takes to reach steady state (T_{ss}) in each model calibration version.

agricultural and point source reductions of 40%, is the only one able to yield both a quick and a long-term reduction of coastal nitrogen load. The quick and the total long-term reductions of anthropogenic coastal nitrogen load in scenario 3 are about 30% and 35%, respectively, thus fulfilling the associated national Swedish environmental objective.

Comparison of two different model calibration versions for these scenario simulations (Darracq and Destouni, 2005; Darracq et al., 2005) shows that modeled future coastal nitrogen load results agree well on the decadal time

scale (Figure 7). On longer time scales, however, different model calibration results diverge, reflecting a lack of long-term data for conclusive discrimination between different possible types and combinations of slow nitrogen transport and mass transfer processes in the subsurface water systems of the Norrström basin. To get a better understanding and quantification of slow subsurface transport and mass transfer processes, independent mechanistic modeling and observation of such processes and their surface water impact implications under various field conditions are required.

8 GENERAL DISCUSSION

8.1 Catchment-scale solute transport and attenuation process characterization

The interactions of subsurface and surface waters and the different source-to-coast pathways of pollutants from different sources are central for the quantification of solute transport-attenuation in catchments. Results in Paper I indicate that a large fraction of diffuse solute inputs to catchments follow subsurface water and solute transport and mass transfer pathways before entering streams and further being transported to the catchment outlets. Consequently, the solute transport processes in both subsurface and stream water systems of a catchment require appropriate coupled quantification.

Responses at the groundwater-stream interface and further on in the stream, to distributed non-reactive solute input over the entire stream catchment surface, are characterized by solute breakthrough curves (BTCs). These have been found to show early peaks and a long tails, i.e. large solute travel time variability (e.g., Kirchner et al., 2000; McGuire et al., 2005). To distinguish the underlying physical processes that in combination yield such BTCs, quantification of separate physical process effects is required that relies on and can be constrained by independently measurable parameters. By use of such process-based modeling, reported early peak, long-tailed BTCs are in Paper I explained by the combined effects of large source extent, advective variability along and among subsurface transport pathways, and subsurface transport through preferential flowpaths and associ-

ated delaying mass transfer effects of less mobile subsurface water zones.

In-stream solute transport, from a point source to the stream outlet, is also characterized by solute travel time variability, for instance due to advective variability and solute exchange with the hyporheic zone. Diffuse solute input from subsurface water into the stream yield further even greater in-stream travel time variability, due to the travel path length difference from different input locations along a stream to its outlet. For reactive solute, such as nitrogen, such travel time variability in both the subsurface and the surface water systems of catchments implies that the fraction of nitrogen mass delivered to a catchment outlet is in general different for point and distributed sources within the catchment (Paper II). In consequence, nitrogen and generally pollutant mass delivery factors for point and distributed sources need to be distinguished.

Solute travel time variability effects are, however, commonly ignored in large-scale nitrogen transport-attenuation modeling, for instance by assumption of single representative travel times for entire sub-catchments or stream reaches (Smith et al., 1997; Alexander et al., 2000, 2002). Such neglect of in-stream solute travel time variability leads to scale-dependence of resulting calibrated first-order nitrogen in-stream attenuation rates λ_s^* . Such scale-dependence generally implies considerable under- or overestimation of underlying independently measurable local nitrogen attenuation rates λ_s by λ_s^* (Paper II; Paper III). In consequence, calibrated large-scale λ_s^* values

are generally not comparable to local-scale λ_s values obtained by experimentation (e.g., Peterson et al., 2001). If the scale-dependence of λ_s^* is not properly addressed, for instance by application of up-scaling expressions proposed here in Papers II-III, the interpretation of underlying biogeochemical processes may be confused by physical travel time variability effects.

For example, depth dependence of in-stream nitrogen attenuation rates has been indicated in studies relying on attenuation rate calibration on different large model resolution scales (Smith et al.; 1997, Alexander et al., 2000, 2002). However, it is shown in Paper III that such depth-dependence of calibrated biogeochemical attenuation rates may be only apparent and may instead be explained by physical effects of decreasing solute travel time per transport length with increasing stream depth. The ultimate consequence of over-simplified physical process descriptions may be incorrect quantification of the impacts of different inland sources' on coastal nitrogen loading, which in turn may lead to inadequate recommendations for regulation, abatement and management of such sources (Darracq and Destouni, 2005; Paper IV).

8.2 Nitrogen transport-attenuation effects on nitrogen abatement efficiency

Different a priori assumptions of underlying transport-attenuation processes are used in different model representations of catchment-scale nitrogen transport and attenuation. For instance, some models entirely neglect nitrogen mass attenuation (Haith and Shoemaker, 1987), other models quantify nitrogen transport-attenuation based on process representations in different hydrological subsystems without distinguishing the effects of different source type contributions within these subsystems (Smith et al., 1997; Arheimer and Brandt, 2000; deWit, 2001), yet another type of models quantify source-specific nitrogen transport-attenuation but without distinguishing between the different water sub-

system components of that transport-attenuation (Grimvall and Stålnacke, 1996; Johnes, 1996), and finally some models quantify both source- and system-specific nitrogen transport-attenuation, based on underlying processes along transport pathways within and across different hydrologic subsystems (Paper II; Rinaldo et al., 2005).

Such different model representations of underlying transport-attenuation processes may result in large differences between modeled solutions for efficient resource allocation for nitrogen abatement in catchments (Paper IV). The choice of nitrogen transport-attenuation model may thus have significant implications for nitrogen abatement and management recommendations. In consequence, such abatement and management decisions should be based on comparative multi-model approaches, ideally including independent quantitative assumption testing of main transport-attenuation model differences.

8.3 Catchment response dynamics to nitrogen source abatement

In the short-term perspective of a few years, a relatively high 40% reduction of agricultural inputs to the Swedish Norrström drainage basin were simulated to yield a mere 5% reduction of anthropogenic coastal nitrogen load. In the same short-term period, a point source reduction of 40% would imply a substantially larger 25% reduction of the anthropogenic coastal nitrogen load component. Based on such a short term analysis, the management recommendation would be to reduce point sources and ignore diffuse sources of nitrogen in catchments.

The long-term scenario modeling in Paper V, however, suggests that slow nitrogen transport and reversible mass transfer processes in the subsurface and subsurface nitrogen inputs to surface waters control the long-term dynamics of catchment responses to diffuse nitrogen source abatement in the Swedish Norrström basin. Therefore, simulation of future coastal nitrogen loads show a slowly increasing long-term trend that counteracts much of the short-term

coastal load reductions that may be achieved by only point source abatement. Based on such a long-term scenario simulation perspective, the main management recommendation is therefore to reduce both point sources for a fast coastal load reduction response and diffuse sources for maintaining the coastal load reduction also in the long term.

For achievement of the national Swedish environmental objective, of a 30% reduction of anthropogenic coastal nitrogen loads, the long-term scenario simulations indicate a need for about 40% point source and 40% agricultural source reductions. These results are for uniform source input reductions over the entire Norrström basin, implying that smaller source

reductions may suffice for an efficient spatially non-uniform reduction strategy.

The difficulties of calibrated N transport-attenuation models to distinguish and discriminate among different possible slow subsurface transport and mass transfer processes imply a need for independent mechanistic quantification and observation of such processes under various field conditions. Local-scale measurement and controlled experimentation may then be used for constraining model parametrization, improving the understanding of the transport-attenuation system and in turn allowing for better prediction of nitrogen regulation, abatement and management effects.

9 CONCLUSIONS

This thesis has addressed questions relating to physical process effects on catchment-scale pollutant transport-attenuation, coastal loading, and efficient abatement. Specifically, these questions concern the appropriate characterization of the catchment-scale solute transport and attenuation processes, evaluation of different common transport-attenuation model assumption effects on efficient nitrogen abatement in catchments, and simulation of coastal nitrogen load responses to possible future nitrogen input changes. The findings in appended papers and above discussion may be summarized in the following main conclusions:

- An appropriate characterization of catchment-scale solute transport and attenuation processes requires quantification of the relative importance of solute pathways from different sources through the subsurface and surface water systems to coastal catchment outlets. Furthermore, the physical processes acting on the solutes that are transported along these pathways need to be quantified appropriately for each relevant subsystem, for instance by explicit use of physical solute travel time distributions. Such distributions capture the travel time variability from source to catchment outlet and are a prerequisite for adequate interpretation of biogeochemical process effects on reactive solute transport. Neglect of such physical solute travel time variability in calibrated large-scale transport-attenuation models may yield misleading attenuation rate quantifications and poor management recommendations. Finally, slow subsurface solute transport and mass transfer processes imply important long-term effects on large spatial scales and require mechanistically based quantification and up-scaling, because necessary long-term time-series of pollutant transport data for both model calibration and relevant validation are generally not available.
- Different a priori simplifying assumptions are made in different catchment-scale nitrogen transport-attenuation models. Such a priori assumptions may lead to considerably inefficient solutions for coastal nitrogen abatement. Nitrogen abatement and management decisions should therefore be based on comparative multi-model approaches, ideally including independent quantitative assumption testing of important transport-attenuation model differences.
- The slow nitrogen transport and reversible mass transfer processes in subsurface water systems may greatly delay and temporally redistribute coastal nitrogen load effects of inland nitrogen source abatement over decades or much longer. Achievement of the national Swedish environmental objective to reduce 30% of anthropogenic coastal nitrogen loading mass therefore require up to 40% reduction of both point sources for a fast coastal load reduction and diffuse sources for maintaining this reduction also in the long term.

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