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Modèles de bilans de nutriments à l'échelle du bassin de drainage: Comparaison entre approches déterministe et statistique pour la modélisation de l'atténuation de nutriments dans le réseau hydrographique du bassin Norrström, Suède.

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RESUME

La complexité des sources de nutriments et des processus qui contrôlent leur transport et leur atténuation limite notre compréhension du problème de pollution majeur qu'est l'eutrophisation et la possibilité de prévoir le transport des nutriments depuis leur émission jusqu'à la côte, à travers les grands bassins de drainage. Il existe actuellement un certain nombre d'approches quantitatives pour décrire ces processus, avec des différences en termes, notamment, de méthode de calibration, de résolutions spatiale et temporelle, du niveau de complexité des processus représentés, ou de la prise en compte de la spatialisation de l'information. Cette diversité rend difficile les démarches comparatives multi-modèles, qui s'avèrent pourtant nécessaire dans l'optique de la gestion durable des ressources en eaux. Nous avons donc inventorié et comparé de façon qualitative un certain nombre d'approches couramment utilisées pour la modélisation du transport et l'atténuation des nutriments à l'échelle du bassin de drainage, et proposons une typologie de ces modèles. Nous avons ensuite étudié de façon concrète la faisabilité et l'intérêt d'une confrontation entre une description biogéochimique détaillée de l'atténuation des nutriments dans le réseau hydrographique et une approche par calibration entre propriétés hydrauliques du réseau et export de nutriments par le réseau. Pour cela, nous avons appliqué au bassin de drainage Norrström, en Suède, à la fois l'approche déterministe RIVERSTRAHLER et l'approche statistique/empirique POLFLOW. Cette comparaison nous permet d'identifier les pistes importantes de recherche et les problèmes à examiner afin d'améliorer notre connaissance du système et des processus en jeu. La confrontation des résultats de différents modèles se révèle délicate mais largement bénéfique : la combinaison de leurs limites et potentiels peut conduire au développement de recommandations plus fiables et mieux adaptées à la gestion durable des ressources en eaux et au traitement des problèmes de pollution.

SUMMARY

Currently, a relatively large number of differing modelling approaches are used to represent nutrient transport and attenuation in medium to large river basins. With the general purpose of understanding, explaining and predicting nutrient river-export fluxes and eutrophication pollution problems, all those models investigate the potential effects of past, present and future human disturbances on watersheds and water resources. Major differences in spatial and temporal resolutions, geographical strategies and/or assumed representations of the biological, physical and chemical controlling processes may make it difficult for scientists to adopt comparative multi-model approaches that are nevertheless necessary for drawing robust and sound recommendations to decision-makers. Here, we identify and qualitatively discriminate a number of such commonly-used models in order to provide an insight into main differences and similarities, and we suggest a possible generic classification in the form of typological trees. This organized inventory is further illustrated by a comparative, quantitative study: we apply both the deterministic RIVERSTRAHLER model and the statistical/empirical POLFLOW approach for modeling nitrogen and phosphorus transport and attenuation in the drainage network of the Norrström drainage basin, Sweden. The feasibility and credits of comparing two such different approaches are tested and validated, with the emergence of interesting further research issues that may help our understanding of the system and involved processes. Confrontation of model results appears clearly fundamental in that limits and capabilities of different approaches may be beneficially used together for serving deeper knowledge and authoritative scientific grounds for water resource management and pollution mitigation.

SOMMAIRE

INTRODUCTION

1) Eutrophication: a worldwide pollution problem for the environmental quality of coastal and marine waters

Nutrients –nitrogen (N), phosphorus (P) and silicon (Si)- are vital elements for life in rivers and seas. The natural process of nutrient enrichment of freshwater, terrestrial and marine ecosystems is therefore a prerequisite for ecological functioning and not in itself an environmental problem. Eutrophication, i.e. an excess amount of nutrients and organic matter, in turn, may lead to increased rates of primary production which triggers various physical, chemical and biological changes in plant and animal communities, as well as changes in processes in and on the bottom sediments, and changes in level of oxygen supply to surface water and oxygen consumption in deep waters (e.g. Cederwall & Elmgren 1990; Kronvang et al. 1993). The susceptibility of ecosystems to the ecological effects of nutrient overenrichment may vary because of additional site-specific factors such as light availability, the extension of algae grazing by zooplankton and benthic suspension feeders, and the flushing frequency of the water system (Howarth et al. 2000).

The accelerated growth of algae and higher forms of plant life is mainly caused by excess of nitrate, nitrite, ammonium (inorganic N), and orthophosphate (inorganic P). A too little amount of N or P may disrupt the balance between nutrient atoms (the Redfield ratios of 16 atoms of N and 20 atoms of Si for 1 atom of P) and hinder further algal growth, and a new input of the "missing nutrient" is therefore seen as a controlling factor for primary production. The relative abundances of those and other elements are also highly important in controlling eutrophication. Excess of nitrogen and phosphorus relative to silicon which limits the growth of diatoms tends to favour production of non-siliceous phytoplankton, macroalgae and macrophytes, who promote internal cycling of the nutrients rather than their removal from the system. In fact, toxic algal blooms may more frequently become prevalent in systems where silicon is in relatively short supply and loads of nitrogen and phosphorus are large (Officer and Ryther 1980). The concept of growth limitation is at the centre of the research, and of the management and mitigation efforts, related to the pollution problem of eutrophication (Smith et al. 1999).

Nevertheless, determining which is the limiting nutrient in a specific system is a difficult issue because of the dynamic aspect and the complexity of the controlling processes, and is still much at debate. It has been traditionally thought that freshwater bodies were P-limited whereas estuaries and coastal systems were rather characterized by a N limitation (e.g. Howarth et al. 2000, Howarth & Marino 2006). Large increases are expected in multiple N sources, on the one hand, and systems may have become more sensitive to decreased P emissions following a more stringent control on this nutrient, on the other hand. P input controls have been recommended for reducing eutrophication in the upstream freshwater systems as well as the receiving coastal waters (Conley 2000, Cugier et al. 2005). Because improvement of upstream freshwater quality may be beneficial to coastal and marine receiving waters (Howarth & Marino 2006), control of both N and P for an effective management of water resources is, with reason, called for in the EU Water Framework Directive (Chave 2001).

Eutrophication is indeed today one of the major water quality problems facing Water Authorities in European countries (Garnier et al. 2005), and is the most widespread water quality problem in the United States and many other nations (Carpenter et al. 1998). Nutrient pollution is estimated to affect, moderately or severely, more than 60 percent of United States' coastal rivers and bays, while, in Europe, the Baltic, North, Adriatic, and Black Seas have all experienced eutrophication problems (Howarth et al. 2000). Indeed, anthropogenic inputs of nutrients to the Earth's surface and the atmosphere have greatly increased during the past two centuries (Smith et al. 1999,

Vitousek et al. 1997, Galloway et al. 2003). This has led, worldwide, to the undesirable disturbance to the balance of life and to the water quality, with the particularly troubling ecological impacts of decreased biodiversity, changes in species composition and dominance, and toxicity effects.

Enhanced growth of phytoplankton is not only disrupting the normal functioning of ecosystems but also impacting the human society by altering the resource value of rivers, lakes, and estuaries. In addition to health problems, the availability of amenities or services such as recreation, fishing, hunting, and aesthetic enjoyment may be hindered by the impairment of water resources and ecosystems (Carpenter et al. 1998). The significance, in terms of biogeophysical, social and economical impacts, of eutrophication motivates the need of integrated strategies to prevent and control N and P excess in surface waters.

2) Catchment-scale management of nutrient loads to coastal and marine waters

2a) Catchment-scale nutrient transport from land to coast

The watershed approach provides a basic unit for management of water resources which is well adapted to the multi-sector, interdisciplinary and cross-sector aspects of the eutrophication issue. The watershed is a physical unit with a clear boundary that hydrologically integrates the interactive compounds and subsystems of the ecosystem, and allows for promoting participative and active integration of the public, scientists, managers and decision-makers (UNEP-IETC 1999). In the Water Framework Directive adopted by the European Union in 2001, integrated river basin management is the key concept and approach to achieve and maintain good status for all surface waters (rivers, lakes, transitional and coastal waters) and ground waters by 2015, and to prevent deterioration and ensure the conservation of existing high water-quality.

Implementation and compliance of this and/or other environmental policies or agreements (e.g. for the Baltic Sea: the Agenda 21 for the Baltic Sea Region (Baltic 21, 1996) or the Helsinki Commission (HELCOM, Baltic Marine Environment Protection Commission, 1993) require methods for investigating and evaluating river water quality, and deriving and assessing management practices. Catchment-scale models are important support tools for that purpose if they can link physico-chemical variables to additional hydromorphological and biological quality elements (Horn et al. 2004) as well as relate them to the constraints set by human activity in the watershed. The use of models, together with monitoring programs, is needed when dealing with the eutrophication pollution problem for: understanding the catchment system and determining the nutrient sources and pathways, for developing scenarios and providing basis for decision-making, for evaluating impacts of present and future control and mitigation measures (Grizzetti 2005).

Catchment-scale models of nutrient transport and attenuation from land to coast, investigate, quantify and predict the fate of nutrients from the input source to the export at the outlet of the catchment. The external supply of nutrient to aquatic systems is a multi-source and multi-pathway process, because wastewater and industrial effluents (point sources), runoff from agriculture, pasture, rangeland, and urban areas, leachage from landfill sites or septic systems, atmospheric deposition and other activities that potentially generate contaminants (diffuse sources) all contribute to the external nutrient load via groundwater, surface water and atmospheric inputs. The relative contribution of the different sources to the eutrophication of a specific water system may vary temporally and also depend upon the considered nutrient since agriculture has in general been estimated as the major source of N, whereas point sources and

soil erosion are considered as the main responsible for P enrichment. P is indeed more easily and strongly sorbed to soil particles than N for which leaching and groundwater transport are more significant. Nutrient accumulation in soils is in fact one of the reasons why nonpoint sources are particularly troublesome (Smith et al. 1999) because of their long residence time there.
When traveling through the different water pathways from their input location to the river system, and along the river network down to the catchment outlet, nutrients are affected by retention (delay) and attenuation processes.. In the soil and groundwater zones, inorganic P may be retained, taken up by plants, immobilized, firmly bound to soil particles. N inorganic forms may be retained, taken up by plants, nitrified, denitrified, immobilized in or remineralized from organic matter. The grassland, woodland, wetland or even non-vegetative interface between land and a flowing surface water body, known as riparian zone, is a particularly effective natural biofilter, intercepting nonpoint pollution between the source and the water (Carpenter et al. 1998). Those buffer zones naturally trap sediments and pollutants, including nutrients, and are therefore significant in improving water quality by lowering nutrient concentrations in both surface runoff and water flowing through subsurface and groundwater to the streams. Particularly efficient denitrification of nitrate in the riparian wetlands has been suggested, and quantified, at the scale of small or even large river systems (Billen & Garnier 2000). Although most effective means of prevention is from the primary source, restoration of damaged riparian zones is to be seen as an important instrument for water quality management and mitigation at the catchment-scale, by cleaning waters even before entering the river network which will carry pollutants all the way downstream to the catchment outlet.

2b) The role of riverine attenuation: from emissions to loads

Freshwater systems, fed by surface runoff and groundwater flow, play an important role in conveying nutrients from the point and diffuse, natural and anthropogenic sources within drainage basins, to the sinks constituted by coastal and marine waters (Rabalais 2002, Donner et al. 2004). The discrepancy between nutrient mass inputs to and associated nutrient mass outputs from the river system of a catchment is explained by significant in-stream nutrient retention and attenuation processes and can not be neglected (e.g., Billen et al. 1991, Howarth 1996, Peterson et al. 2001). Processes such as denitrification, organic matter burial in sediments, sediment sorption, and plant and microbial uptake affect the amount of N and P that is transported along water pathways (Billen et al. 1991, Saunders & Kalff 2001, Seitzinger et al. 2002).

The interactions between hydrological, meteorological, physico-chemical, biological processes are highly complex. Understanding the link between anthropogenic activities and riverine nutrient export, and the nutrient controls of the eutrophication pollution problem requires a modeling approach capable of integrating and explaining field observations (Garnier et al. 2005). However, appropriate use of independent experimental measurements is still under debate. It is, for example, not yet clear how to scale up well-defined nutrient removal processes across the range of stream sizes over catchment river networks (Wollheim et al. 2006).

3) Objectives of the thesis

The conceptualization of temporal variability, spatial distribution and heterogeneity of streams and contributing flowpaths, and involved processes, needs blurring system boundaries rather than accentuating them (Fisher et al. 2004). Integration of landscape and waterscape within catchment-scale nutrient fate modeling is necessary, but understanding and prediction of nutrient transport and attenuation from land to coast in large drainage basins are limited by the complexity of sources and of the controlling transport and attenuation processes. Currently, there exists a large range of varying modeling approaches for quantifying nutrient cycling in river

systems. This thesis aims at providing an insight into main differences and similarities between these models (Part I) and is illustrated by a comparative study of applying two such different approaches to the case-study area of the Norrström drainage basin in Sweden (Part II).

3a) Inventory and comparison of current N and P catchment-scale budget modeling approaches

Although, or maybe because, model development for quantification of nutrient riverine export from large watersheds has been progressing (Alexander et al. 2002), common modeling approaches to nutrient transport and attenuation at river-basin scale may currently rely on a large range of different assumptions and different description methods of nutrient sources, catchment characteristics and involved physical and biogeochemical processes. In general, modeling approaches may differ in terms of levels of spatial resolution and process complexity, geographic distribution account, temporal resolution, calibration methods (Alexander et al. 2002).

The first objective of this thesis is to provide an organized inventory or a possible generic classification of some major currently-used modeling approaches published in the literature for nutrient (N and/or P) transport and attenuation at the scale of medium to large river network catchments. Section *1* of Part I clarifies the criteria and models used for designing the suggested typological trees of such quantification methods, shown in 2) and discussed in 3) of Part I.

3b) Comparison between deterministic and statistical approaches to in-stream nutrient attenuation in the Norrström drainage basin, Sweden

In-stream nutrient attenuation may be deterministically described on the basis of known controlling biogeochemical variables and processes, or may alternatively be parameterized through site-specific calibration of varying levels of black-box-type relations. The second objective of this thesis is to investigate and test the differences and potential benefits from applying detailed biogeochemical description of nutrient in-stream attenuation compared to using calibrated simpler relationships between hydraulic properties and nutrient riverine export.

This comparative investigation will use as a case study area the Norrström drainage basin, located in the center of Sweden and draining into the Baltic Sea (see section *1*, Part II). We apply to this drainage basin: i) the distributed, catchment-scale model Polflow (section *2*, Part II) in which nutrient attenuation in the river network is quantified by use of a calibrated relationship with topographic slope and water flow; and ii) the mechanistic, drainage network Riverstrahler model (section *3*, Part II) that simulates nutrient transfer from land-based sources to the sea through the drainage network, by coupling a biogeochemical process description to a hydrological model. Section *4* finally presents, discusses and compares the results of those two different approach applications.

Part I:

MODELING APPROACHES TO NITROGEN (N) AND PHOSPHORUS (P) CATCHMENT-SCALE BUDGET

In spite of the difficulties linked to the complexity of the involved processes, model development for quantification of nutrient riverine export from large watersheds has been considerably progressing during the last decades (Alexander et al. 2002). A review of the international scientific literature on past and current attempts of nutrient transport and attenuation quantification at river-basin scale indicates, however, that current modeling approaches generally rely on a large range of different assumptions and different description methods of nutrient sources, catchment characteristics and involved physical and biogeochemical processes. Although site-specific observations should be the basis for adequate representation of the reality, and although specific regional needs, demands and conditions have to be accounted for when promoting sustainable use and management of water resources, general applicability of modeling approaches is also required, for example, for comparative investigations, transboundary issues and confidence-building in decision-making supporting tools. Identification and clarification of the different spatial, temporal, and process-related characteristics of different models are needed to enable their sound manipulation.

This literature-based study aims at providing an organized inventory of some major currently-used modeling approaches for nutrient (Nitrogen and/or Phosphorus) transport and attenuation at the scale of medium to large river network catchments. While reviewing of model efficiency to reproduce observations falls far outside the scope of our study, we suggest a possible generic classification in the form of typological trees, for enlightening major differences and similarities in model approaches.

1) Criteria for a possible typology of quantification methods for nutrient transport and attenuation

The modeling approaches which are included in this classification are all quantification methods for nutrient transport and attenuation, applied at the scale of medium to large river basin systems for estimating nutrient loads at basin's outlet and eventually further investigating source apportionment, management scenarios, impact analysis, water quality controlling factors etc. We did not included analytical approaches that solve, at the scale of infinitesimal elements, the differential equations provided by the fundamental laws of physics and chemistry, either deterministically (parameters are viewed as well-defined local quantities that can be assigned unique values at each point in space-time and can be determined by suitable laboratory/field experiments) or stochastically (parameters and variables are treated as random fields whose probability distribution is seeked). In stochastic analytical approaches such as the Lagrangian stochastic advective reactive travel time (LaSAR) approach, that may be applied to parcel/particle of water and solute for modeling the transport of non-reactive tracers and reactive solutes such as Total Nitrogen (Lindgren & Destouni 2004, Lindgren et al. 2006), sorption or biogeochemical reactions that affect the solute parcel depend on travel time. Deterministic analytical approaches such as the physically based, distributed, integrated hydrological and water quality coupled modeling system MIKE SHE/11-DAISY (e.g. Styczen et al. 1999) may require extensive model data and physical parameters, as well as a great deal of technical expertise, making it difficult to set up the model at the scale of large catchments. Input-output flow analysis are not included neither: usually used for estimating capital flows in economic systems or material flows in

political and socioeconomic systems and ecological systems, they have been suggested as a successful tool for quantifying coupled natural and cross-sectoral flows of water, nutrients in catchments (Baresel & Destouni 2005). Given the scope of this study, we don't include those approaches because they have not been yet systematically applied at the regional scale for straightforwardly quantifying nutrient fluxes and retention although their applicability for such purpose has been proved and recognized.

Table 1 specifies which models are included, as well as their general basic equations/principles for representation of nutrient attenuation processes, the required model input data, and a list of some main watersheds where those models have been applied. Catchment size may range from 500 to 300 000 km^2. All models have been successfully validated in diverse catchment areas and are all capable of satisfactorily estimating nutrient stream export. Nevertheless, although those methods may be commonly compared and are all able to reproduce monitoring data, they may differ in many ways, from spatial scale and resolution to temporal scale and process-complexity.

Table 1: List of nutrient transport and attenuation models included in the typology suggested in this study; basic equations or principles for attenuation process representation; input data to the models; sample of the main watersheds where the model has been applied.

	Basic equation(s)/principle(s) for nutrient transport and attenuation process representation	**Required input data**	**Watersheds**
Behrendt Behrendt 1996, Behrendt & Opitz 1999	Load weighted nutrient retention= $a * x^b$, where a and b are calibrated and x is specific runoff q or hydraulic load. Or also: Instream retention per catchment area= $a * q^b * C^c$, where C is the nutrient observed concentration; a, b and c are calibrated parameters	Specific runoff, river surface area, nutrient emissions to streams (from point and diffuse sources), nutrient loads	Rhine and Elbe (Germany), Loire (France), Oder, Vistula (Poland) basins
Cawaqs Flipo 2005, Flipo et al. 2006	Based on Rive model : kinetic formulation for each process describing the instream dynamics of nutrients and plankton	Meteorological data, soil types, agricultural practices, river flows, piezometric heads, crop growth, nitrate aquifer concentrations	Grand Morin basin (Seine) (France)
Green Grizzetti 2005, Grizzetti et al. 2005a, 2005b	Nutrient outlet load = $L = DS * exp(-\beta y) * exp(-\alpha x) + PS * exp(-\alpha x) + \varepsilon$, where α and β are calibrated in-stream and on-land loss parameters and x and y are chosen explanatory variables for stream and land retention, ε is an error term	Few land and waterscape characteristics (e.g. rainfall, topographic wetness index, low flow, river length) point emissions (PS), diffuse emissions (DS) (included fertilizers and livestock), nutrient loads	Wash basin (UK), Zelivka (Czech Republic), Vilaine (France) basins, Odense river basin (Denmark)
HBV-NP Arheimer & Wittgren 1994, Arheimer & Brandt 1998, Bergström et al. 1987, Brandt 1990	$\frac{d(cV)}{dt} = \sum\{c_{in}V_{in}\} + D + P - \Phi - cV_{out}$, where c is concentration, V is water volume, in and out means in- and outflow, Φ = retention for example: Retained inorganic N mass= $\Phi_{IN\_R} = k_6 * \overline{T_{10}} * \sum c_{in}V_{in}$, where c_{in} and V_{in} are concentration and water volume at initial time step, T10 is 10-day mean air temperature, k6 is a calibrated parameter.	Meteorological data, point inputs (P), atmospheric deposition on water surfaces (D), land-use specific soil-leaching concentrations, river discharge and nutrient concentrations	Subbasins of Sweden, Estonia, Germany
Howarth Howarth et al. 1996, 2006	*Log(Nutrient fluxes)=* $a + b * log(\ population\ density\ )$ or also *Nutrient fluxes=(ax+b)*NANI+c* where a, b and c are calibrated parameters and x can be either precipitation or discharge, and NANI are net anthropogenic nitrogen inputs	Precipitation, discharge, population, net anthropogenic nutrient (point and diffuse) inputs (NANI), nutrient fluxes	major rivers draining into the North Atlantic Ocean, major watersheds in Northeastern United States

Inca Inca-N: Whitehead et al. 1998a, Wade et al. 2002b; Inca-P: Wade et al. 2002c	Differential equations for describing losses in plant/soil system and instream: nitrification, denitrification, sediment setting / resuspension, precipitation, sorption/desorption, biological uptake (in terms of mass)-reaction rates are calibrated.	Temporal meteorological and hydrological series, basin characteristics, land use percentages, growing seasons, point inputs, diffuse emissions (included fertilizers and livestock)	River Tywi (South Wales), Great Ouse (Eastern England), Kennet (Southern England)
Moneris Behrendt 2002	Based on Behrendt – Regression laws	Point and diffuse emissions, water and nutrients discharges	German river basins
Polflow De Wit et al. 2000, De Wit 2001	Denitrification in soils: regression on N surplus and depending on soil type Denitrification in groundwater: regression on residence times and infiltration. Instream nutrient retained fraction= $\frac{1}{rn1*(1000*slope+1)*discharge^{rn2}}$, where rn1 and rn2 are calibrated parameters	Meteorological data, topographic slope, basin landscape characteristics, land use, point and diffuse surplus emissions, water and nutrient discharges	Rhine and Elbe basins, Lake Peipsi in Estonia and Latvia, Swedish Norrström drainage basin
RivR-N Seitzinger et al. 2002	Removed nutrient fraction= $a*(D/T)^b$, where D is the water body depth, T is water time of travel a and b are calibrated parameters.	River characteristics (depth, time of travel), data on emissions and load observations or data on retention fraction	major watersheds in Northeastern United States
Sparrow Smith et al. 1997, Preston & Brakebill 1999, Alexander et al. 2000, McBride et al. 2000, Alexander et al. 2001	Nutrient outlet load = $L=\Sigma\beta*s*exp(-\alpha Z)*exp(-\delta T)$, where α and β are calibrated in-stream and on-land loss parameters and Z and T are sets of explanatory variables for land and stream retention, ε is an error term	Basin characteristics (air temperature, precipitation, land-surface slope, soil permeability, stream density, and wetland area) and drainage network characteristics (discharge, time of travel), discharge data, point emissions, diffuse emissions (included fertilizers and livestock), nutrient loads	Chesapeake Bay watershed, Mississippi River and its tributaries, watersheds of major U.S. estuaries, watersheds of New Zealand
Swat Arnold et al. 1998, 1999	Command structure and algorithmic routines for describing water, nutrient and pesticide routing and transformation in the watershed, in streams and ponds	Meteorological data, topographic slope, soils, land use, nutrient emissions, agricultural management strategies	Watersheds in Australia, Belgium, Germany, India, Kenya, South Africa and the USA
Riverstrahler /Sénèque Billen et al. 1994, Garnier et al. 1995, Garnier et al. 2002, Ruelland et al. 2005	Kinetic formulation for each process describing the instream dynamics of nutrients, phytoplankton, zooplankton, bacteria (Rive model)	Meteorological data, drainage network morphology, land use, point emissions, nutrient concentrations of superficial and base flows to streams, water and nutrient discharges	Seine River system, the Mosel (France/ Germany), the Scheldt (France/ Belgium), the Danube river basins, the tropical Red River (North Vietnam and South China), subarctic Swedish watersheds

Classification criteria

The several models we consider here may concern the basin drainage network only, or the watershed system, i.e. including part of or all the soil and groundwater landscape-components as well. Between the emission source and the river basin outlet, nutrients travel through drainage basin landscape and waterscape. Transport via the soil and the groundwater is affected by physical and biogeochemical processes that retain (delay) or even irreversibly attenuate the proportion of nutrients reaching the river network. Site-specific characteristics of the soil system strongly determine the transport of nutrients via the soil to the river network, with soil properties, crop features, fertilization programme and soil management being of major importance for both nitrogen and phosphorus (De Wit, 1999). Conditions in the aquifer and

groundwater residence time determine when and how much of the nutrients finally reach the river network via groundwater pathways. The main retention/attenuation processes of denitrification, biological assimilation and physical mass transfer processes also occur all along the river system, and empirical studies showed for example that 30 to 80% of nitrogen input to rivers may be removed during transport through the river networks (Seitzinger et al, 2002).

Three distinct systems within the entire river catchment area may then be distinguished in terms of the environment where transport and attenuation processes are represented: i) the total catchment that includes the river network, the hydrological catchment, the plant/crop and livestock system of the watershed ii) the hydrological catchment that consists of the soil compartment below root zone and the aquifer compartment, iii) the river system by itself, gathering all surface water bodies within the drainage basin area . Figure 1 illustrates the spatial organization of a catchment from such a perspective that clearly separates vegetation system and human society, from soil and aquifer compartments on the one hand, from the drainage network on the other hand. In terms of modeling, such distinction implies differences in treating the functioning and impact of human use of land, especially in agricultural areas where account for nutrient imbalance between nutrient inputs and export through food and feeds might be or not included in the approach depending on whether the total or only the hydrological catchment is modeled. Resulting significance in terms of model entries and variables will be discussed further in the following. In the typology we suggest, models concerning the hydrological or total catchment are regrouped under the term watershed models, although we specify within the typological tree which models explicitly account for nutrient cycling above the root zone.

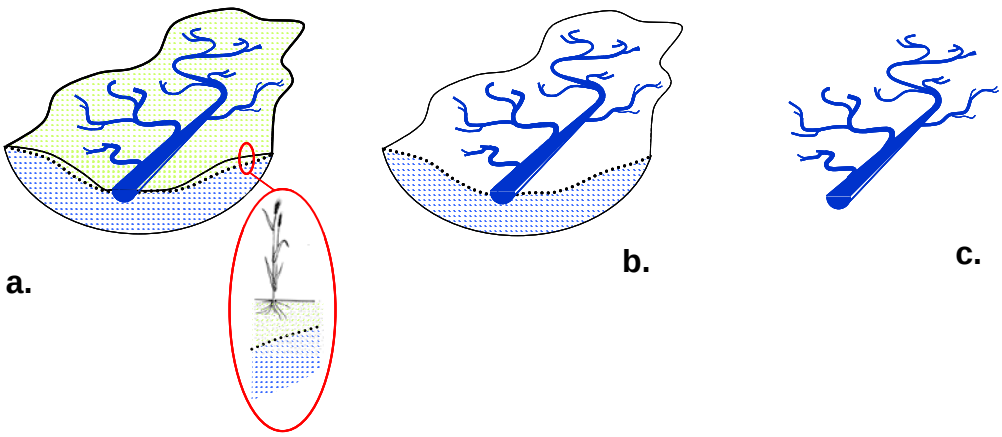

Figure 1: Schematic description of a catchment, according to the distinction in this study between (a) total catchment, including the soil-vegetation system, (b) the hydrological catchment and (c) the drainage network sensu stricto

A further classification criterion within the considered models is the account for, or neglect of, spatial variability over the considered system. Lumped approaches consider that sources and sinks are homogeneously distributed in space within the modeled system, and both the system characteristics and the represented processes are therefore assumed to be uniform and equal over the system. Even though such assumption may be necessary where source inputs and sinks, or watershed attributes, cannot be spatially referenced, it may seem rather coarse and yield a number of uncertainties as soon as those lumped methods are extended to large scale drainage basins (Alexander et al., 2002). Lumped models have however been found to satisfactorily reproduce nutrient exports in cases where detailed knowledge is not needed (e.g. Grizzetti et al. 2005a). Fully distributed models have been developed to account for spatial variability of processes,

nutrient inputs and watershed characteristics, and have shown to possibly improve the accuracy of predictions of stream export and the interpretability of model coefficients (Smith et al., 1997; Alexander et al., 2000, 2001). Detailed spatial referencing may however yield large constraints in terms of data requirement and calibration complexity. Semi-distributed models illustrate the intermediary case where sub-basins are divided into uniform units (e.g., in terms of landuse, or vegetation zones). Most often, depending on data availability and spatial resolution, models may consist of a compromise between fully distributed and totally lumped methods, adapting also to the level of process-description details.

The chosen representation of the processes controlling the fate of nutrients may range from very simplified to extremely complex description. Statistical regressions consist in simple correlations of stream monitoring data with watershed sources and landscape properties and provide empirical estimates of nutrient stream export, based on a few explanatory variables, also called predictors (Alexander et al., 2002). The commonly-low data and time requirements of such methods explain their popularity for modeling nutrient fate in large river basins, in addition to the large gap between the actual scale at which the processes occur, and the model scale. Nevertheless, as soon as forecasting, i.e. explaining and describing the evolution in time of nutrient export and its dependence on the several controlling factors, is needed, mathematical models should be used for mechanistically describing the physical and biogeochemical underlying processes. Such causal, detailed approaches necessarily include seasonal patterns, and allow for understanding the mechanisms involved in the estimation. However, intensive data and calibration requirements may limit the application of mechanistic, complex models in large watersheds, in addition to the problem of appropriately extrapolating spatial and temporal processes from scaled experiments to full-sized natural systems (U.S. EPA, 2001). In reality, here again, the argument separating causal versus empirical models can be challenged by the recognition that mechanistic models necessarily involve some degree of empiricism. While very detailed deterministic descriptions tend to reduce site-specificity to generically explain nutrient stream export with no or minimized need for calibration, hybrid methods are based on empirical relations for quantifying processes which interactions are mechanistically expressed. Distinction between statistical, hybrid and mechanistic approaches is the third criterion of our suggested classification of models.

Furthermore, the approaches under consideration in this study may differ considerably in terms of the variables described. All combinations of multi-element (i.e. accounting for both nitrogen and phosphorus) and/or multi-form (i.e. accounting for a number of forms of the modeled element, among for example inorganic or organic, dissolved or attached to suspended or sediment matter) approaches are possible. Total nitrogen *TotN* is the sum of: i) organic nitrogen *orgN* (both dissolved in such forms as amino acids, proteins, urea and humic acids, and particulate in plants and animals and their remains), and ii) inorganic nitrogen *inorgN*. *InorgN* groups together dissolved inorganic nitrogen *DIN* (*DIN*=nitrate *NO3-N*+nitrite *NO2-N*+ammonium *NH4-N*) and particulate inorganic nitrogen (*NH4-N* adsorbed onto mineral particles). Total phosphorus *TotP* is the sum of: i) organic phosphorus (both dissolved, and particulate in plants and animals and their remains) and ii) inorganic phosphorus that consists in dissolved inorganic phosphorus (also called soluble reactive phosphorus, the sum of orthophosphate and polyphosphates) and particulate inorganic phosphorus (in minerals, or on the mineral surfaces of iron oxyhydroxides). Because almost each model considers a unique set of nutrient element or form, that may even vary from a model application site to another depending on available monitoring data, the specificity of each model as to what variable(s) is(are) considered does not stand for a classification criteria by itself, but is nevertheless included in the bottom part of the typological trees presented in the following. Its degree of complexity is largely correlated with that of the model representation of the processes.

2) Example typology for some existing currently-used budget models

Figures 2a)-b) illustrate a possible typology of some currently-used approaches for modeling nutrient transport and attenuation in medium-to-large river basins. The classification consisted in firstly separating modeling approaches of the drainage system only, from watershed models that include, to some varying levels, the landscape components. Model names appear in the center of the typological trees; when the approach was not given any specific name or acronym, it is directly designated by the name of the first author in published references where the approach was originally presented. Bottom entrance of each tree allows for discrimination by the variables that are modeled in each approach, both in terms of what element and what form(s) of that element are included. Top entrance of each tree classifies the approaches according to whether they account for, or neglect, the spatial variability of inputs and attributes that exists within the modeled system. Furthermore, following those geographical criteria, models can be grouped according to the general approach used for representing and quantifying the different processes.

Based on our non-exhaustive sample of considered models and the unavoidably subjectively-chosen criteria, a number of general model families come out: statistical regressions lumped over the drainage network; deterministic, distributed models of the drainage network; approaches lumped over the watershed in the form of input/output analysis, statistical regressions or hybrid (mixed statistical/mechanistic) approaches; and hybrid or deterministic approaches which both may be semi- or fully-distributed over the watershed.

Representation of the seasonality of dominant processes and nutrient river exports can only be achieved through detailed description of the mechanisms involved. Figures 2a)-b) show that the varying level of mechanism complexity in the Seneque (Billen et al. 1994, Garnier et al. 1995, Garnier et al. 2002, Ruelland et al. 2005), HBV-NP (Arheimer & Wittgren 1994, Arheimer & Brandt 1998, Bergström et al. 1987, Brandt 1990,), Inca (Inca-N: Whitehead et al. 1998a, Wade et al. 2002b; Inca-P: Wade et al. 2002c), Swat (Arnold et al. 1998, 1999) and Cawaqs (Flipo 2005, Flipo et al. 2006) approaches also gives them forecasting capabilities, i.e. the possibility to describe, quantify and explain the temporal and seasonal evolution of various nutrient-form export. Because those approaches describe some of the physical and biogeochemical driving processes, controlling factors may further, and relatively easily, be subject to different scenarios for assessing their significance and for analyzing past and future trends. Despite its daily resolution, the HBV-NP dynamic mass-balance model stands out as a rather hybrid than mechanistic approach, where processes are physically distinguished but, to a relatively large degree, empirically quantified. Moreover, within the family of models accounting for seasonality, the HBV-NP (hybrid), Inca and Swat (mechanistic) models differ from the fully spatially-referenced, mechanistic, total catchment Cawaqs model and drainage network Seneque model, in that they are semi-distributed approaches: model equations are solved at the resolution of sub-basin zones distinguished according to altitude and vegetation (HBV-NP), land-use (Inca), or soil-type and land-use (hydrological units (HU) in Swat). Whatever the system under consideration and the level of spatial variability accounting, very high level of process description detail may yield generic models for which calibration is not needed, e.g. Riverstrahler/Seneque model of drainage network or Swat model of total catchment, possibly implying, however, a constraining complexity and required amount of data. Choice of those or similar modeling approaches is mainly driven by the need of understanding eutrophication phenomena and explaining cause-effect process interactions.

Relatively coarser approaches, such as empirical relationships based on statistical regressions (RivR-N model in Seitzinger et al. 2002; Howarth et al. 1996, 2006; Behrendt 1996, Behrendt & Opitz 1999; Green model in Grizzetti 2005, Grizzetti et al. 2005a, 2005b), can predict, i.e.

estimate, nutrient export at a certain period or point in time. Explanatory variables are few so as to limit calibration exercises, while number of rivers or catchments on which the regression is based should be as large as possible to ensure statistical representativeness.

Figures 2a)-b) show that statistical approaches usually lump quantification over the considered system, although the Green model stands out as a distributed model at the European scale, with a sub-basin resolution more adapted to its specific objective: to provide an efficient, little data-demanding tool for the implementation of European environmental regulations, allowing, for example, for identification of hot spots on which best management practices may be focused. A compromise between reduction of required data and goal-adapted level of detail for accounted processes is the purpose of hybrid methods such as the Moneris lumped model (Behrendt 2002), the Sparrow distributed model (Smith et al. 1997, Alexander et al. 2001) and the Polflow distributed model (De Wit et al. 2000, De Wit 2001). The Moneris and Sparrow total catchment models, as well as the Polflow model, or Howarth et al. (1996, 2006) statistical regression, do not model the nutrient imbalance between mineral and organic fertilizer inputs and crop fixation on one hand, and animal and crop export on the other hand. Those approaches do not explicitly account for crop efficiency and export, but account for crop and livestock systems through some lumped parameter, or are directly fed with given or estimated data on nutrient surplus at the soil surface or net anthropogenic inputs. This draws an important difference with total catchment approaches that integrate human society's behavior and activities and in which nutrient surplus, i.e. the nutrient amount that potentially can runoff to the river network through various pathways, constitute a variable estimated by the model and therefore already possibly dependent on model assumptions and settings.

3) Conclusion

We have suggested a qualitative typology for different approaches to nutrient transport-attenuation modeling at medium-to-large river basin scales. The exercise has shown us the difficulty in clearly identifying the specific characteristics of existing models without reading guides and manuals, and, maybe even more importantly, it has underlined the confusion one may experience in front of a jungle of approaches which differences may not be justified, or at least undoubtedly require further explanations, so as to guarantee a sound use of such tools. The several criteria used for defining general model families and emphasize main differences and crossings corresponded to questions such as: which system within the river catchment is considered, at what spatial resolution, is spatial variability accounted for, what is the level of process description detail, and which variables are modeled. Such identification and classification may be important to keep in mind in a time when simulation and prediction models are increasingly required for abatement and prevention of nutrient pollution. Comparative multi-model approaches have up to now mostly aimed at proving one or the other model capability to reproduce observations, and/or justifying its use. Lindgren et al. (2006), however, have shown that main differences in simplifying *a priori* assumptions in different nitrogen transport-attenuation modeling approaches may have significant implications for abatement efficiency of nitrogen loads from land to the sea, with the main conclusion that management of coastal load abatement should be based on multi-model approach. Our study aimed at providing a general picture of common approaches to nutrient transport and attenuation catchment-scale modeling. In addition to the general qualitative criteria on which this typology is based, quantification details of transport-attenuation processes in different approaches may then also be thoroughly investigated and clarified to the scientific community in order to optimize our use of existing models and facilitate necessary comparative studies.

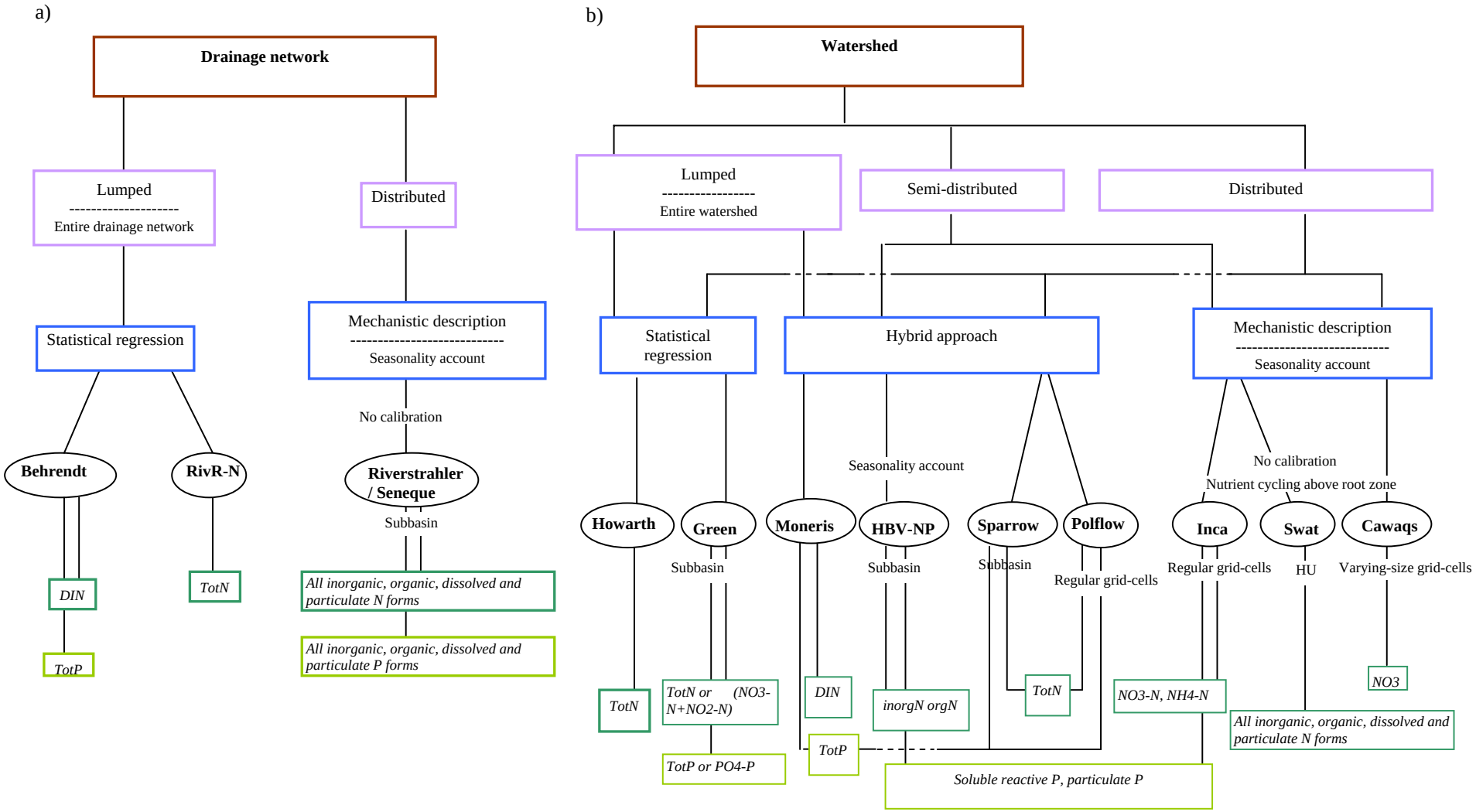

Figure 2: Typological trees of some nutrient transport and attenuation models of: a) the drainage network, b) the watershed system.

Part II :

COMPARING STATISTICAL-REGRESSION AND MECHANISTIC-DESCRIPTION APPROACHES FOR MODELING NUTRIENT ATTENUATION IN STREAMS IN THE NORRSTRÖM BASIN, SWEDEN

Eutrophication by large-scale nutrient over-enrichment threatens coastal and marine environmental quality over the world. The Baltic Sea is one of the world's most severely affected seas by human activities and in spite of, and years after, international agreements on large nutrient input reductions its status has not yet been significantly improved (Wulff et al. 2001), mostly due to its semi-enclosed topography and strong anthropogenic pressures that make it particularly vulnerable.

The Swedish Norrström basin drains into the Baltic Sea through Lake Mälaren outflow into the Stockholm Archipelago. The water quality of Lake Mälaren, and its surrounding watershed, is at stake for the regional supply of freshwater as well as, more generally, for water resource management in the drainage basins of the Baltic Sea Region. Because of major pressures on the natural water resources of the Norrström basin exerted mainly by agriculture, industries and steadily increasing population, and whereas water quantity in natural systems may be sufficient for meeting human and ecological needs within the basin (Baresel & Destouni, 2005), water quality remains a major problem for achieving sustainable water management.

The Norrström basin may be a good example case-study for investigating, understanding and predicting the functioning of nutrient transport and attenuation through the system, for example for further quantifying downstream responses, in the inland water resources, in the Stockholm Archipelago or in the Baltic Sea, to pollution mitigation measures in the catchment.

For this purpose, different quantification approaches may tackle with different strategies and perspectives the complex interacting roles of physical transport and biogeochemical processes. In this study we have applied to the Norrström basin, two such different approaches: (i) the distributed, catchment-scale model POLFLOW that simply and directly relates nutrient attenuation in the river network to topographic slope and water flow; and (ii) the drainage-network model RIVERSTRAHLER that deterministically describes biogeochemical processes. We intend: i) to test the feasibility of applying and comparing those methods, ii) to investigate and explain resulting differences and similarities in terms of nutrient budgets and general or particular information that can be yielded from interpreting each approach outputs.

1) Case-study area

1a) The Baltic Sea environmental status and management

The Baltic Sea is the largest brackish water body on earth, covering 415 000 km^2 and with a volume of 22 000 km^3 and average saline content of 0.7 percent. There are nine countries bordering the Baltic Sea region, with a coast line of approximately 20 000 km and a total population of around 100 million people within the water catchment area. The Baltic Sea is a relatively shallow inland sea in northeast Europe with its only exchange to more open seas being a very narrow link to the North Sea between Norway, Sweden and Denmark. On average, it takes twenty years for the water to be replaced. As a semi-enclosed marginal sea, the Baltic Sea ecosystem is particularly sensitive to all anthropogenic changes that can affect economical and

political conditions in the surrounding countries that already show different levels of use as well as protection of the natural resources.
Eutrophication, the excess of nutrients transported by surface runoff and groundwater flow through the terrestrial environment and streams, lakes and rivers, remains the major environmental problem in the Baltic Sea (Elmgren, 2001). In the past few years, increasing blooms of blue-green algae have caused much debate in the countries around the Baltic region. In warm summers, beaches have been riddled with thick carpets of algae, and vast slicks of algae have been adrift in the open sea.

Trends in oxygen declining concentrations and loss of fish habitat, namely, in the deep basins of the Baltic Seas, 50 years ago, led to awareness in the Swedish coastal seas, where eutrophication problems were visible as massive algal blooms including Cyanobacteria and other toxin producers, anoxic dead zones in bottom waters of deep basins with disturbance of food chains, and, in shallower nearshore, frequent lower transparency, the development of littoral mats of filamentous green algae and the disappearance of Fucus and eelgrass beds (Boesch et al. 2006).

Nutrient inputs from land-based sources (both diffuse and point sources) to many of Sweden's coastal bays and estuaries had indeed increased substantially above background levels: four-fold and eight-fold increase in nitrogen and phosphorus inputs to the Baltic Sea since the mid-19th century were reported (Larsson et al. 1985). Efforts have been undertaken for decreasing nutrient emissions from point sources (Phosphorus removal in sewage treatment plants appeared at the beginning of the 1970s and nitrogen removal was added from the beginning of the 1990s to sewage treatment plants larger than 100000 equivalent inhabitants) and diffuse sources with agricultural origin (through reduction of phosphorus, and more slightly nitrogen, mineral fertilizer use. However, a number of Sweden's east coast systems show higher phytoplankton biomass relative to many other east coast waters, as a consequence of increased anthropogenic nutrient sources. The inner Stockholm Archipelago is one such typical system (Boesch et al. 2006). This highly important Swedish recreational area is fed by three kinds of sources: i) freshwater inputs from Lake Mälaren in Stockholm, that discharges 80% of the total phosphorus and 60% of the total nitrogen that enter the inner Archipelago, ii) discharges from large sewage treatment plants that serve the metropolitan area of Stockholm and that discharge most of the dissolved inorganic nitrogen (66% on an annual basis but 84% during summer months and growing season) and most of the dissolved inorganic phosphorus (20% on an annual basis but 56% during summer months and growing season) and iii) additional, not very-well known nor quantified inputs from permanent or seasonal homes on the shores or the islands of the Archipelago (Boesch et al. 2006). The administrative catchment of Lake Mälaren is called the Norrström drainage basin.

1b) The Norrström drainage basin

The Norrström drainage basin is the main part of the Swedish water management district Northern Baltic Proper, one of the five water districts established for catchment-scale water resource management, as legally required by the European Water Framework Directive (WFD 2000/60/EC). Cooperation in the Baltic Sea Region was yet established already some decades ago. The Agenda 21 for the Baltic Sea region was launched in 1996 (Baltic 21) to push the region towards sustainable development. The Helsinki convention in 1974 established cooperation between the bodies of the Helsinki commission that works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental cooperation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. A new convention was signed in 1992 in the light of political changes and developments in international environmental and maritime law. Inland waters as well as the water

of the sea itself and the sea bed were included and land-based pollution was also integrated by taking measures in the whole catchment of the Baltic Sea (HELCOM 2004).

The Norrström drainage basin extends over Stockholm county, Uppsala county, Södermanland county, Västmanland county and Örebro county, with a total area of about 22000 km^2 (Figure 3). Not only in terms of area, but also in population (over 1.7 millions), the Norrström basin is an interesting case study area where stakes are important. Noticeable land-use changes occurred around both lakes Mälaren and Hjälmaren (third and fourth largest lakes in Sweden) in the after war period, namely a strong shift towards urbanization around Stockholm where one third of the Swedish population is living today. Despite rapid growing of cities and settlement of industries around the lakes, agriculture and farming are still traditionally present in that clay- and till-rich area which is part of the fertile belt covering the southern part of Sweden. In terms of land-use coverage, the Norrström drainage basin consists of 4% built-up areas, 36% agricultural and open land, 49% forest (mostly in the north-west of the basin), 1.5% wetlands and 9.5% inland waters, including Lakes Mälaren and Hjälmaren.

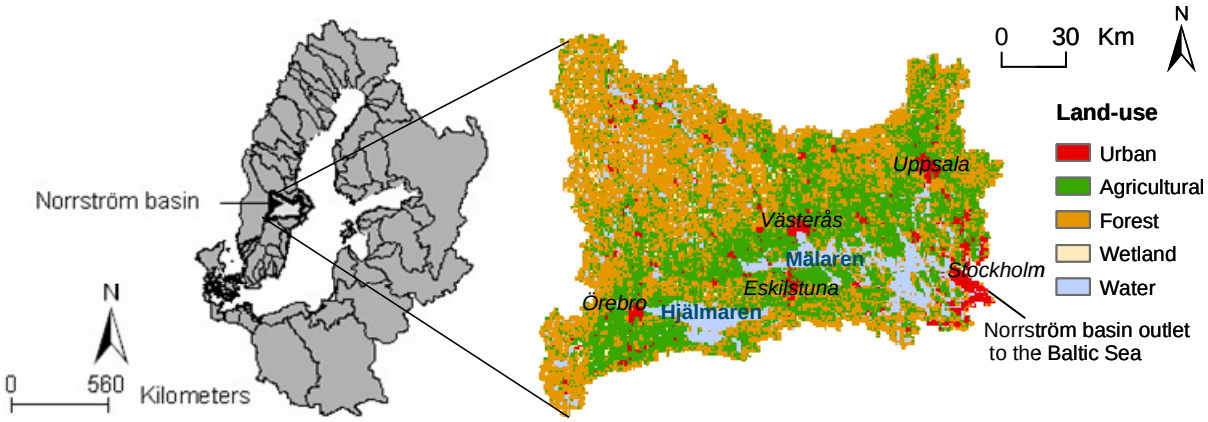

Figure 3: Location of the Norrström basin in Sweden and in the Baltic Sea Region (left), and land-use map of the catchment with main cities and lakes (right).

The Norrström basin is mostly flat and its relief is rather smooth than broken, with a maximum elevation of 450 m in the more hilly north-western part of the basin, and average elevation around 40-50 meters above sea-level. The bedrock in the area is granitic and gneiss-granitic. Quaternary deposits are mostly thin (maybe up to a maximum of 5 meters) and mostly glacial clayey tills, with a relatively high groundwater table that explains the richness of the area in lakes and wetlands. Average temperature is around 15 °C in summer, about -2ºC in winter. The average annual temperature is about 7 °C. Average precipitation in the Norrström basin is typically about 600 mm/year and the basin is covered by snow approximately 3 to 4 months per year, between December and April.

2) Modelling N and P transport and attenuation in the Norrström basin with the POLFLOW model

2a) POLFLOW model description

The POLlutant FLOW (POLFLOW) model (de Wit 1999, de Wit et al. 2000, de Wit 2001) is a distributed, catchment-scale, semi-empirical (or hybrid) model for estimating water flow and nutrient (total nitrogen and total phosphorus) transport and attenuation from pollution sources to the basin outlet, at a time step of 5 years and a spatial resolution of 1 km^2. Mostly based on hydrological models from Wendland (1992) and Meinardi et al. (1994), the POLFLOW approach

was developed and calibrated for the Rhine and the Elbe basins. The model was further applied in the drainage basin of Lake Peipsi in Estonia and Latvia (Mourad et al. 2003, Mourad & Van der Perk 2004), and in the Swedish Norrström drainage basin (Greffe 2003). The POLFLOW model is embedded in PCRaster, a raster-based Geographic Information System (GIS) modelling tool. Nutrients are routed through the river network by use of spatial functions while dynamic functions describe the transport delay in the soil and groundwater, and retention through the drainage network.

The water flow module estimates runoff, groundwater recharge indices, and groundwater residence times that will be used as (constant) inputs to the nutrient transport module. More specifically, the water flow module yields annual average (over 10 years) runoff as the difference between annual average precipitation and actual evapotranspiration, estimated as a function of precipitation and temperature. Groundwater recharge indices are related to topographic slope, soil type, texture, aquifer type, groundwater level, land cover, and January temperature, and groundwater residence times are related to aquifer conductivity, porosity, thickness, local slope, and groundwater recharge.

Nutrients are assumed to follow water flow paths (vertical or horizontal), over and/or through the soil surface into underlying groundwater before reaching the streams. In each cell of the rasterized river basin, contributing nutrient fluxes from surface runoff, slow and very slow groundwater runoffs are estimated from diffuse emissions below the root-zone (i.e. surplus emissions, estimated independently as the amount available for further runoff and infiltration), and basin and climatic characteristics, based on empirical relations and general basic principles. Nitrogen loss to atmosphere by denitrification in the soil and groundwater systems is described following Wendland (1992) based on residence times in and characteristics of aquifers. Topography-induced local drainage direction network routes water and nutrients, and a lumped attenuation model is applied to all surface water cells and accounts for hydraulic properties (slope and water flow) for determining the nutrient quantity that is further transported downstream the drainage network, after receiving diffuse inputs and additional point emissions. Figure 4 illustrates coarsely the principles of the transport model.

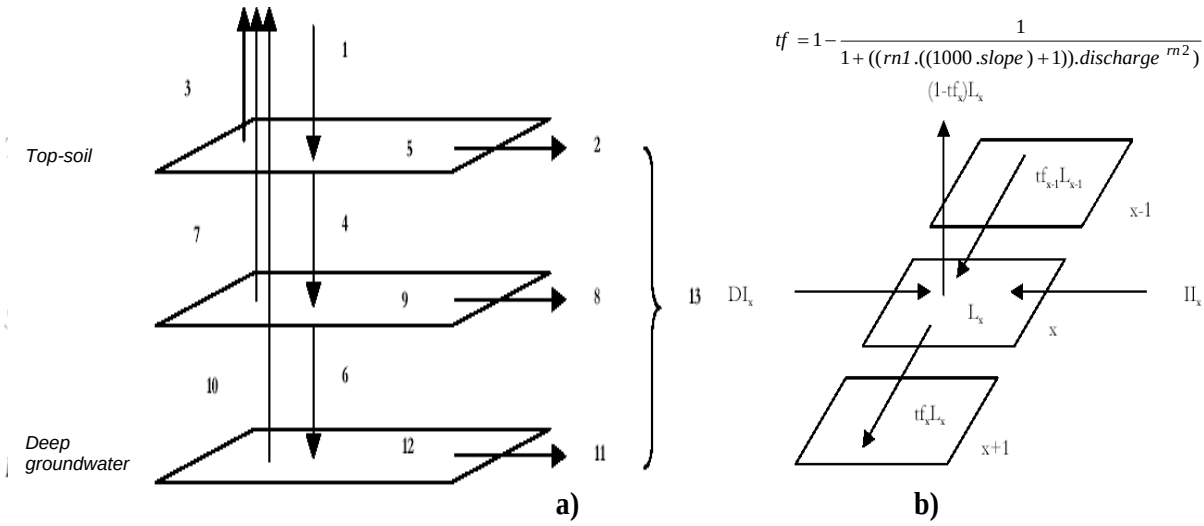

Figure 4: Underlying principles of the POLFLOW transport model (after De Wit, 2001).
(a) Division into three subsystems. Numbering refers to the processes involved in the transport of nutrients from soil into surface waters. 1: addition of diffuse emissions to the nutrient content of soil, 2: surface runoff and erosion, 3: denitrification in soil, 4: leaching from surface to shallow groundwater, 5: new nutrient content for the soil input for next time step, 6: leaching from shallow to deep groundwater, 7: denitrification in shallow groundwater, 8: shallow groundwater runoff to surface water, 9: new nutrient content in shallow groundwater, input for next time step, 10: denitrification in deep groundwater, 11: deep groundwater runoff to surfacewater, 12: new nutrient content

in deep groundwater, input to next step, 13: total input to surface waters via surface and groundwater runoff. (b) Transport from cell to cell in the river network. Using the local drainage direction to route the nutrients through the river system, each cell is connected to its lowest neighbour, all the way down to the basin outlet (De Wit, 1999) tfx is the fraction of nutrients transported from one cell to the next one downstream, (1-tfx) is the retention loss and decay in the river. Parameter m1 quantifies the basic loss in a segment of the river network and the dependence of tf on the slope, m2 quantifies the change of the value of the transport fraction through the river system, Lx is the nutrient load in the cell, x. DIx stands for the direct emissions and IIx, for the indirect emissions from surface and groundwater runoffs.

2b) POLFLOW modeling of the Norrström basin

Table 2 provides a summary of available data for the Norrström basin. We provide here additional information on their further processing and preparation as appropriate inputs to the POLFLOW model.

Table 2: Sources of input data to the POLFLOW model
NB: all maps were rasterised to 1km^2 grid cells

POLFLOW Module:	Input data	Location	References
Water fluxes	Monthly precipitation 1992-2001	18 stations (see Figure 5)	Swedish Meteorological and Hydrological Institute (SMHI)
	Monthly temperature 1992-2001	5 stations (see Figure 5)	SMHI
	Hydrogeological data (soil capacity, bedrock capacity, bedrock type)		Geological Survey of Sweden (SGU)
	Elevation map		GTOPO30/HYDRO1K, US Geological Survey
	Slope		Derived from the elevation map
	River network		Digital Chart of the World; SMHI Water Systems in Sweden paper map
	Land cover	See Figure 3	BALANS data set from the Baltic Drainage Basin Project
	Soil map		SGU
	Water discharge monthly measurements	25 stations (see Figure 6)	SMHI
Nutrient transport	Nutrient point and diffuse emissions (annual fluxes, averaged on 1985-1999)		TRK project, Swedish University of Agricultural Sciences (SLU)
	Measured chemical variables in streams	62 stations (see Figure 6)	SLU, Institution for Environmental Analysis

As indicated in Table 2, input data for nutrient emissions were taken from the Swedish national database of nutrient sources at the drainage basin scale (Brandt & Ejhed 2003*B*), with five different types of nutrient sources (six for nitrogen) given for our specific case study: point sources (industries and wastewater treatment plants), atmospherically deposited Nitrogen (deposition on lakes), runoff from urban areas (inputs to streams based on concentration measurements, and accounting already for denitrification in soil), runoff from agricultural land (emissions below root zone calculated with independent model of agricultural systems), diffuse emissions from houses not connected to public sewage systems, and emissions from forested areas (inputs to streams based on concentration measurements). Originally given as annual fluxes lumped over sub-basins, data on diffuse emissions were re-distributed to account for land-use, i.e. runoff from urban areas was for example equally distributed over all cells with urban land-use.

As the POLFLOW modeling of the Norrström basin has an annual time step, meteorological input data available monthly for the period 1992-2001 (Figure 5) were averaged for yielding long-term average annual values.

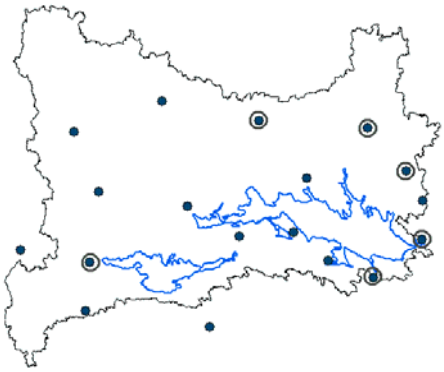

Figure 5: Location of stations used in the POLFLOW modelling of the Norrström basin for meteorological input data (all stations provided monthly precipitation in mm/yr between 1992 and 2001, circled stations provide as well monthly temperatures).

The nearest neighbour method was applied for spatially distributing precipitation and temperature data over cells of the basin. Since no data were available on actual or potential evapotranspiration, Meinardi et al. (1994)'s method, based on Turc (1954) and Langbein (1949), was applied to our case study using precipitation and temperature data. Potential evapotranspiration (EPOT in mm/yr) is estimated according to Langbein (1949): $EPOT = 325 + 21T + 0{,}9T^2$, while actual evapotranspiration (EACT in mm/yr) is estimated according to Turc (1954): $EACT = P/(0.9 + P^2/EPOT^2)^{0.5}$, where T is average annual temperature in °C and P is annual precipitation in mm/yr.

Validation data to the water flow module were annually averaged for comparison with modelled average annual water flows. For the nutrient flow module, because measurements were not available at similar locations, available total nitrogen and total phosphorus concentrations were averaged for yielding annual average concentrations which were then further multiplied by modeled annual water discharge for providing "observed" annual nutrient fluxes to be compared with modeled annual nutrient fluxes.

2c) Calibration and validation of the POLFLOW modeling

Modeled annual average water discharges (see location of stations in Figure 6, blue dots) resulted from the uncalibrated water flow module, whereas modeled discharges of total nitrogen and total phosphorus resulted from 5-parameter calibration of the transport modules (Table 3).

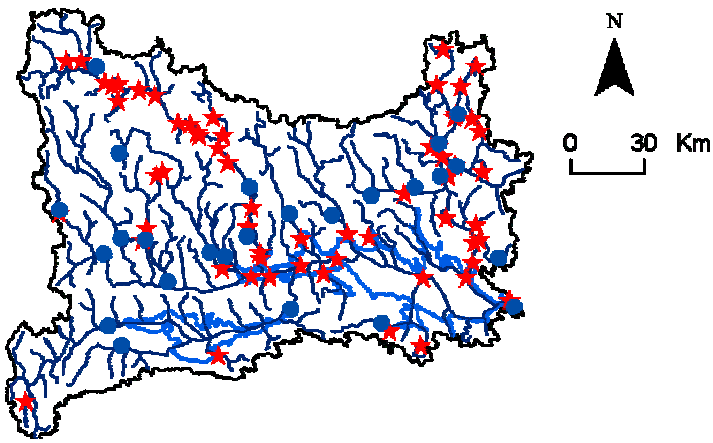

Figure 6: Location of stations used for the validation of the POLFLOW modelling of the Norrström basin (blue dots for water discharge, red stars for water quality).

Table 3: Parameter values before and after calibration for modeling the Norrström basin
Uncalibrated values are referred to as the ones originally used by De Wit (1999) in the Rhine and Elbe basins

Parameter	Role of the parameter	Original / Calibrated value for total nitrogen	Original / Calibrated value for total phosphorus
sr	Weights the effect of surface runoff and erosion ($year^{-1}$)	0.00075 / 0.00025	0.00075 / 0.00005
gr	Weights the effect of groundwater runoff (mm/year)	200 / 270	200 / 200
pms	Estimates the maximum storage of nitrogen in soil (-)	1.5 / 2.3	100 / 100
rn1	Loss parameter quantifying the "basic" loss in a river network segment ($s.m^{-3}$)	50 / 35	6.5 / 30
rn2	Loss parameter quantifying the decrease of relative loss in downstream direction	0.5 / 0.4	0.9 / 0.9

Figure 7a shows the resulting agreement between modeled and measured annual averages of water discharge at 25 observation stations in streams of the Norrström basin (see location in Figure 6, blue dots).

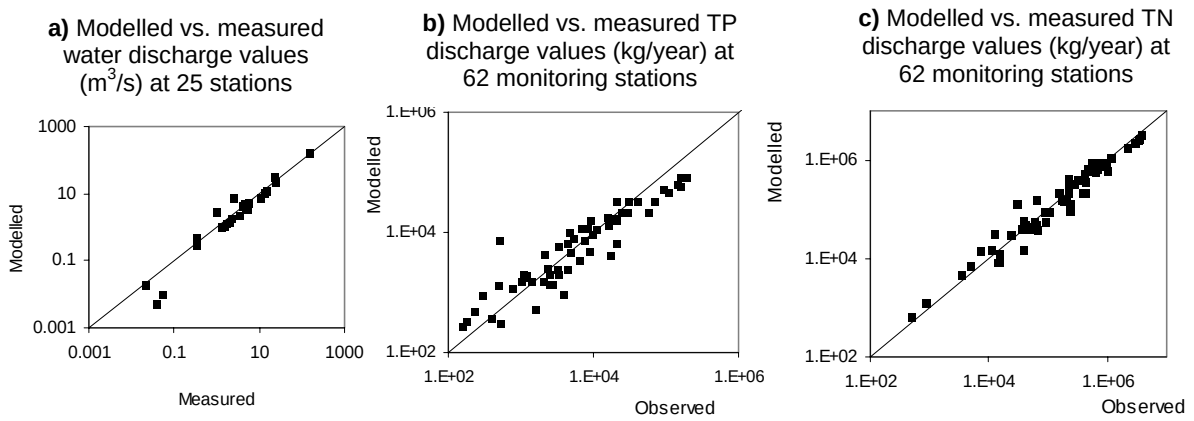

Figure 7a: Modelled vs. measured water discharges; b) Modelled vs. measured total phosphorus fluxes; c) Modelled vs. measured total nitrogen fluxes.

The value of R^2 for the water discharge model was 0.992, with a prediction bias, in terms of median prediction error, of -17.4%, and a prediction error variability (interquartile range) of 33.3%. Figures 7b-c show the resulting goodness-of-fit between calibrated (5-parameter calibration) model results and observation-based annual average values of total phosphorus (Figure 7b) and total nitrogen (Figure 7c) discharge at 62 measurement stations (see location in Figure 6, red stars). The value of R^2 for the total nitrogen discharge module was 0.980, with a prediction bias, in terms of median prediction error, of -4.35%, and a prediction error variability (interquartile range) of 51%. The value of R^2 for the total phosphorus discharge module was 0.85, with a prediction bias, in terms of median prediction error, of -2.43%, and a prediction error variability (interquartile range) of 112.67%.

3) Modelling N and P in-stream attenuation in the Norrström drainage network with the RIVERSTRAHLER model

3a) RIVERSTRAHLER model description

The mathematical model RIVERSTRAHLER (Billen et al. 1994, Garnier et al. 1995) aims at representing the complex biogeochemical processes involved in the nutrient and plankton dynamics at the scale of the whole drainage network of large, human impacted, river systems (Billen & Garnier 2000), by use of the concept of stream order (Strahler 1957). RIVERSTRAHLER was originally and extensively developed for the Seine river system (e.g., Billen et al. 1994, Garnier et al. 1995, Billen & Garnier 2000, Billen et al. 2001, Cugier et al. 2005, Garnier et al. 2005), to deterministically simulate phytoplankton seasonal dynamics by considering hydrological, morphological, bottom-up and top-down controlling factors, as well as the circulation of carbon, nitrogen, phosphorus and silica through the compartments of the river system. The model was further applied to several other European river systems, namely the Mosel (Garnier et al. 2000), the Scheldt (Billen et al. 2005), the Danube (Garnier et al. 2002), the tropical Red River (Garnier & Billen 2002), and the Nordic Swedish rivers Kalix & Lule (Sferratore et al. 2006).

A main assumption of the RIVERSTRAHLER approach is that the differences in model constraints (hydrological, geomorphologic and climatic factors, and point and diffuse inputs) yield the characteristics of the ecological functioning of the studied river, rather than differences in the kinetics of the simulated biological and physico-chemical processes (Garnier et al. 2000)

The RIVERSTRAHLER model couples the idealized hydrological model HYDROSTRAHLER and the ecological model RIVE. In HYDROSTRAHLER, specific runoff is the sum of two components (Figure 8): (sub)-surface runoff, contributed by direct runoff and snow melt, and base flow from infiltration to groundwater. The five parameters involved in the hydrological description of the basin (snow melt rate, soil saturation level, sub-surface runoff rate, infiltration rate, base flow rate) are considered homogenous over the whole watershed area and are calibrated so as to get the best fit between measured and modelled specific runoff.

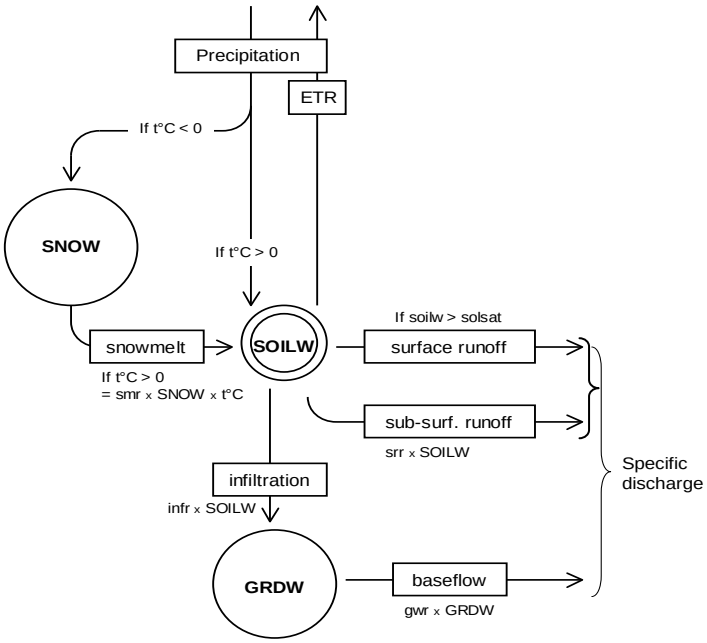

Figure 8: Conceptual model for the calculation of specific discharge from precipitation, evapo-transpiration and temperature (from Sferratore et al. 2006).

For distributing the water flows within the different water bodies, RIVERSTRAHLER considers 3 types of "objects" connected to each other within the drainage network; (i) the hydrological network of *sub-basins* is idealized as a regular scheme of confluence of tributaries with increasing stream order and average morphological characteristics. (ii) *major river branches* are represented with a higher level of geographical realism and a kilometric resolution; (iii) *reservoirs* (lakes, ponds, dams), branched to either certain streamorder rivers of basin or to a river branch, are considered as perfectly mixed waterbodies. In all these objects, the same description of the biogeochemical processes is assumed, with the specific constraints exerted by the hydrology.

Additional constraints on the river system are the nutrient and suspended matter inputs from the watershed: point sources (as total inputs to same order-streams), and diffuse sources after transport through the superficial and groundwater pathway (based on assumed concentrations assigned to HYDROSTRAHLER-resulting runoff components). The RIVE model (Figure 9) consists of a large number of variables including inorganic suspended matter, nutrients (Nitrate and ammonium, phosphate, dissolved silica), dissolved oxygen, dissolved and particulate organic matter, phytoplankton (diatoms and non-siliceous algae), zooplankton and bacteria (heterotrophs and nitrifiers) (e.g., Garnier et al. 2000). The processes accounted for include phytoplankton dynamics (photosynthesis, algal growth, lysis, etc), zooplankton dynamics (growth, grazing, mortality, etc), bacterioplankton dynamics (hydrolysis, growth, excretion, sedimentation etc), nitrification and phosphorus dynamics (including exchanges of inorganic phosphorus between dissolved and particulate phases; Garnier et al. 2005), and benthos remineralisation. Temperature dependence is also taken into account. Detailed kinetic formulation of the processes and values of the parameters (mostly experimentally derived) can be found for instance in Garnier et al. (2002).

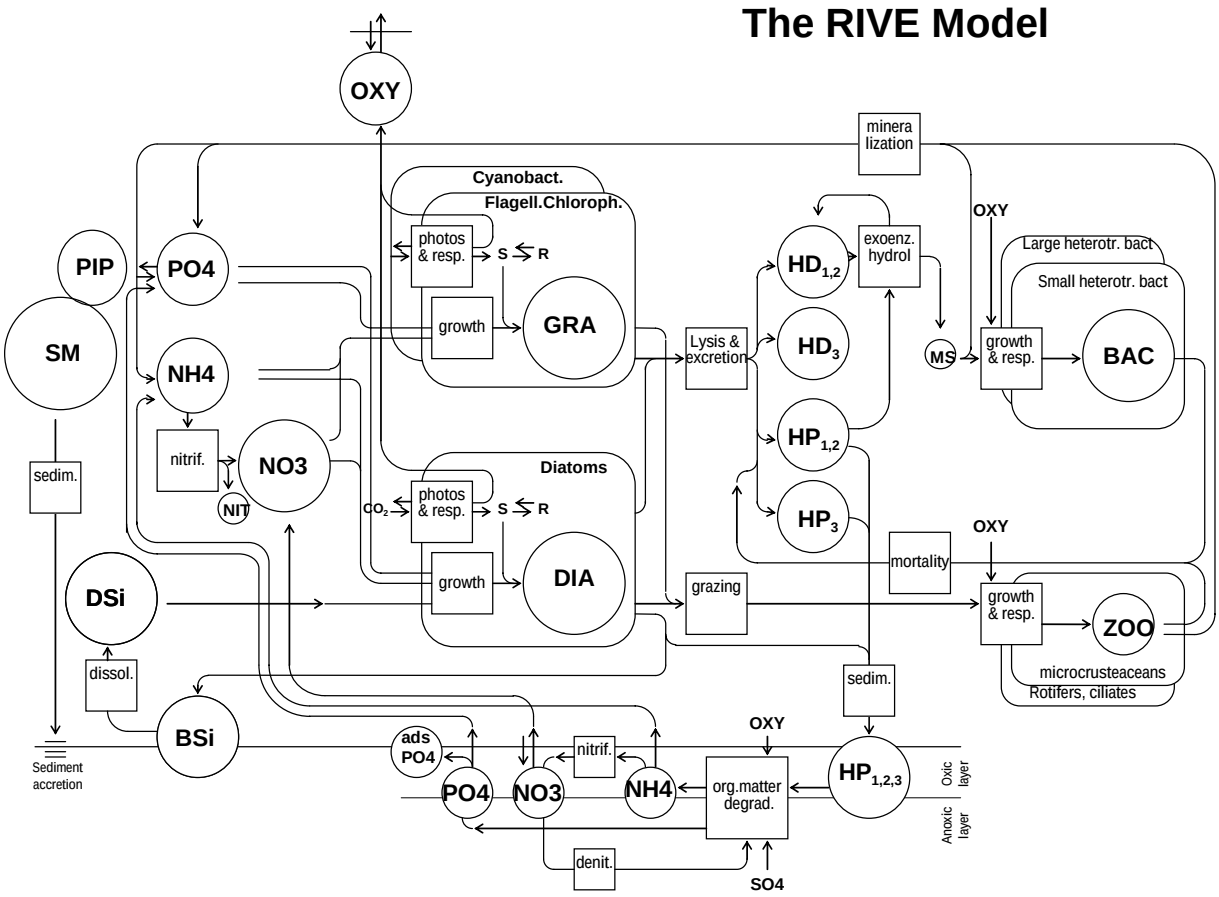

Figure 9: The conceptual scheme of the RIVE model

3b) RIVERSTRAHLER modeling of the Norrström basin

In order to improve the geographical resolution of the application and to account for the heterogeneity in land-use over the entire watershed, the Norrström basin was divided into three distinct sub-basins (Figure 10): the Northwestern zone, characterised by the main presence of forest, wetlands and small lakes, and draining into Lake Mälaren; the Southwestern area, occupied mainly by agriculture and the urban area of Örebro, as well as the presence of Lake Hjälmaren just upstream the outlet to Lake Mälaren; and the Northeastern zone with the city of Uppsala, covered by agricultural land and lakes, and which drains into Lake Mälaren next to the main city of Stockholm. In this first approach, both lakes Hjälmaren and Mälaren were considered as independent perfectly mixed reservoirs (see morphological characteristics in Table 4) downstream their respective contributing drainage basins (Southwestern basin, for Lake Hjälmaren; all three sub-basins and the proper Mälaren basin, for Lake Mälaren). Figure 11 and 12 provide with details on morphological and land-use characteristics of the different zones that were distinguished within the Norrström basin.

Table 4: Morphological characteristics of Lakes Mälaren and Hjälmaren, after Willén 2001a.

	Surface (km^2)	Volume (km^3)	Average depth (m)	Regulation amplitude (m)	Maximum length (km)	Minimal volume (10^6 m3)	Maximal volume (10^6 m3)
Mälaren	898	14.4	16.04	0.95	110	13973	14827
Hjälmaren	464	3	6.47	0.5	63	2884	3116

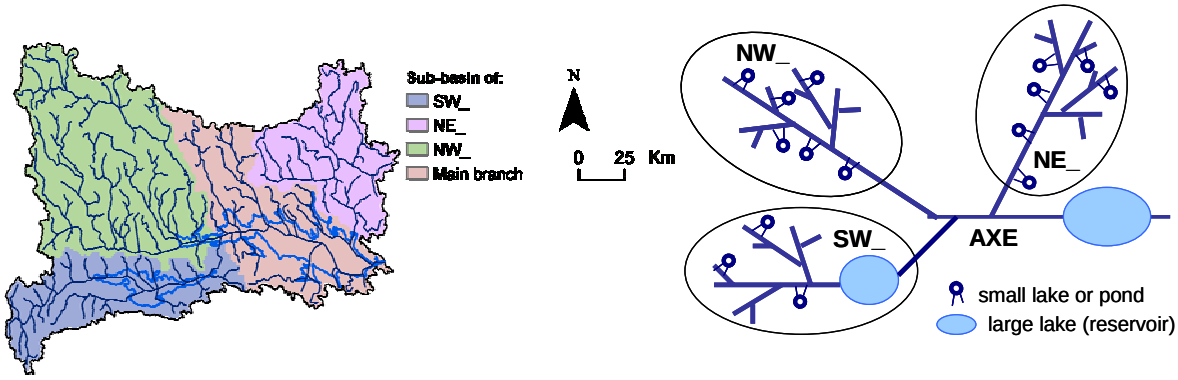

Figure 10: Left: Location of the sub-basins SW_ (Southwestern area), NE_ (Northeastern area), NW_ (Northwestern area) and the drainage basin of the main branch within Lake Mälaren, and right: conceptual RIVERSTRAHLER representation of the Norrström basin.

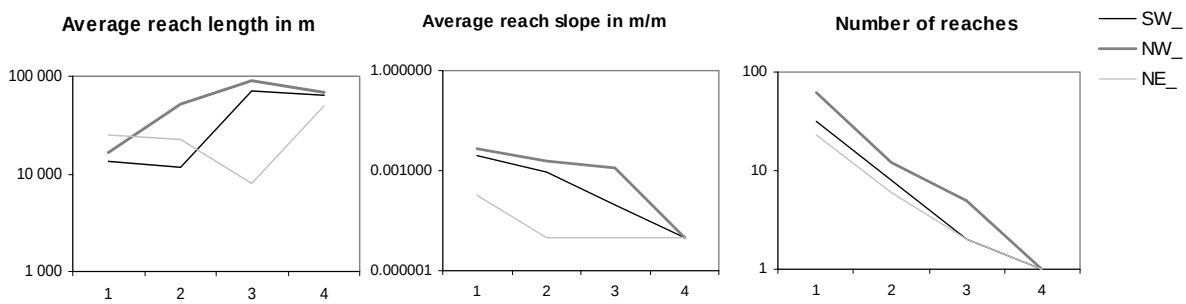

Figure 11: Morphological characteristics of the Norrström basin

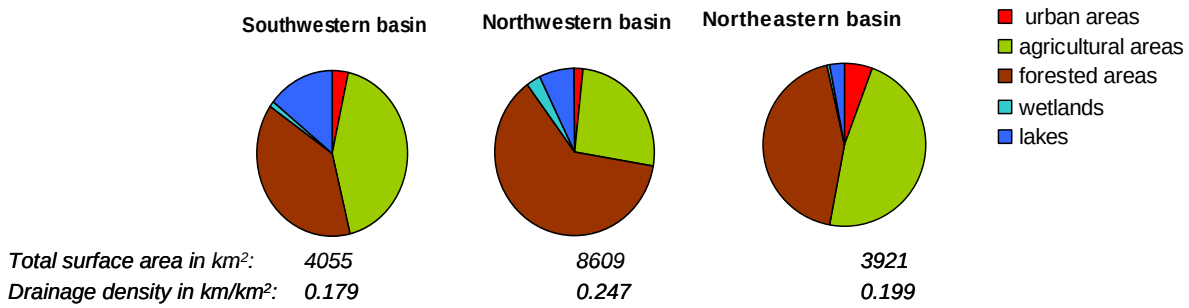

Figure 12: Land-use characteristics of the Norrström basin

The methodology of the RIVERSTRAHLER model application to the Norrström basin is described in Figure 13. Hydrological parameters (in AJUSTHYD models) were optimized for each basin, with the hypothesis, based on available hydrological data (Figure 14), that lakes do not exert a significant role in smoothing hydrology and the variability of water discharges, as there are regulated for minimizing water level variations.

For each basin, calculated runoffs were further used as inputs to biogeochemical models RIVBAS. The biogeochemical functioning of Lakes Hjälmaren and Mälaren was treated with a specific reservoir routine RIVRES. The main branch receives the outlet discharges of the three basins (southwestern, northwestern and northeastern), and is connected at its downstream point to the large reservoir representing Lake Mälaren. Resulting discharges at the outlet of the lake provides with information on the transport and attenuation of the whole drainage network of the Norrström basin, with the additional possibility to interpret average data on each order of each basin.

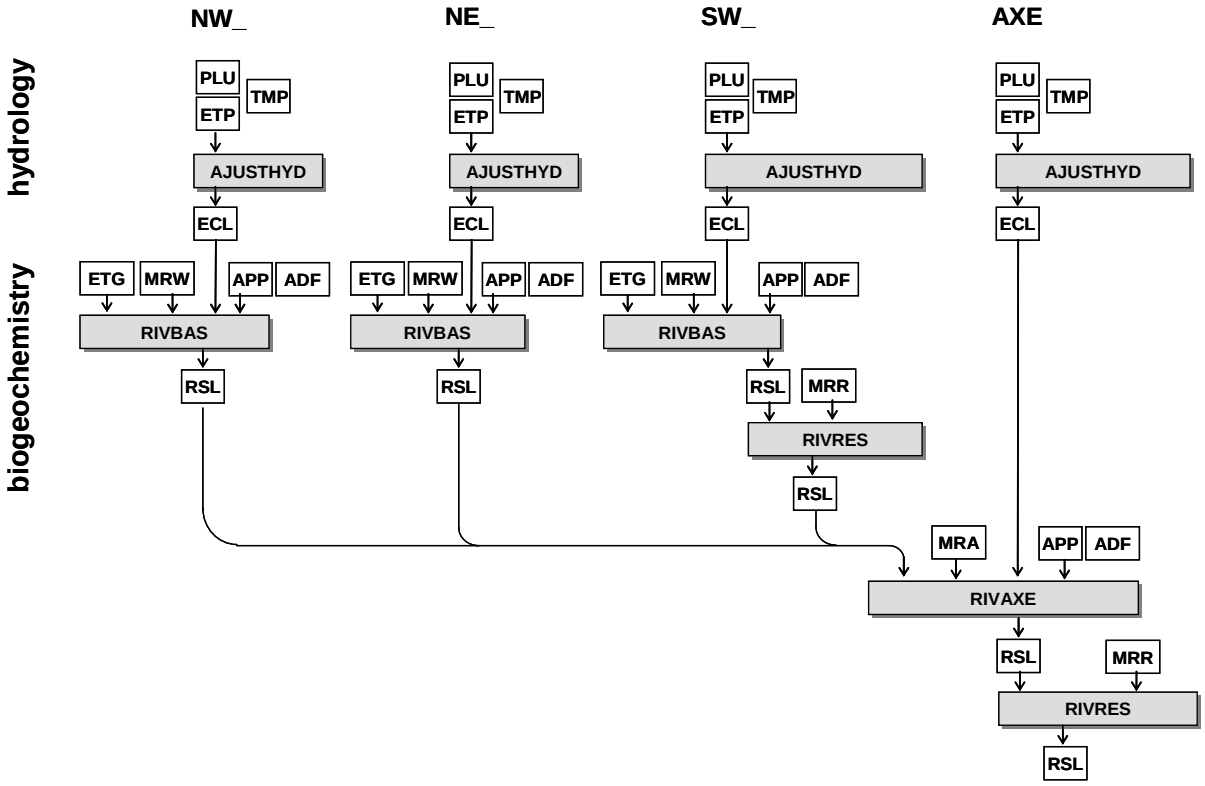

Figure 13: Methodology used in the application of the RIVERSTRAHLER approach to the Norrström basin.

.PLU, .ETP and .TMP are meteorological input files to the hydrological model while .ECL are resulting runoff files. .MRW , .ETG and .MRR contain morphological information on basin drainage network, ponds or bogs and lakes. .APP and .ADF are point and diffuse emissions files. .RSL are the model ouput files.

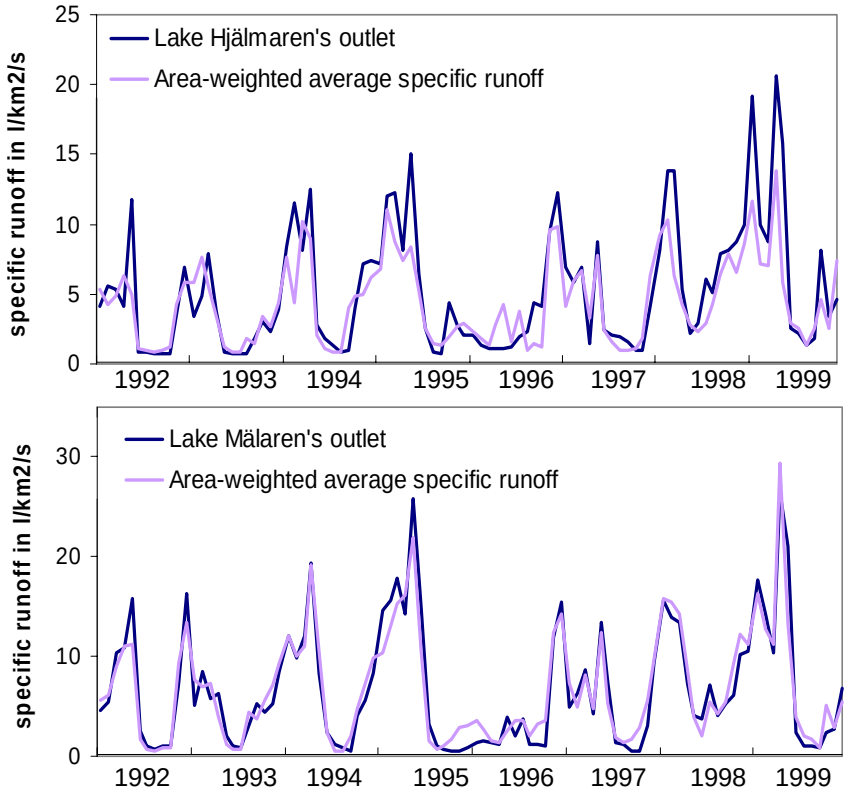

Figure 14: Comparison between observed contributing specific runoff from the drainage basin and observed outlet water discharge for (top) Lake Hjälmaren and (down) Lake Mälaren. For Lake Mälaren, specific runoffs from basins SW_, NW_, NE_ and the proper drainage basin of the main branch were weighted with their surface area for yielding a representative average of contributing runoff.

As a complement to Table 2 which provides for a summary of available data for the Norrström basin, we give here additional information on their further processing and preparation as inputs to the RIVERSTRAHLER model. Availability of input data limited the time-step resolution of the model application to the Norrström basin: a monthly resolution was the best to be achieved and data were adapted to comply with the daily (for hydrology) or decadal (for biogeochemistry) original temporal-resolution approach. Meteorological data (precipitations and temperatures) for the period 1992-2001 were spatially distributed using the nearest neighbour method. Figure 15 provides for summary information on meteorological conditions in the Norrström basin.

Monthly potential evapotranspiration (ETP in mm/month) was calculated based on Turc's formula (1961) based on monthly atmospheric temperature (T in °C), total solar radiation (Ig in cal.cm^{-2}.d^{-1}) and sunshine duration (h in hours): $ETP = (Ig + 50) * \frac{0,4T}{T + 15}$.

Total solar radiation Ig is calculated by: $Ig = IgA * (0,18 + 0,62 * \frac{h}{H})$ where IgA is the energy of solar radiation in the absence of atmospheric attenuation (cal.cm^{-2}.d^{-1}) and h/H is the relative duration of sunshine, H being the duration of the astronomic day and h the duration of the sunshine period per day.

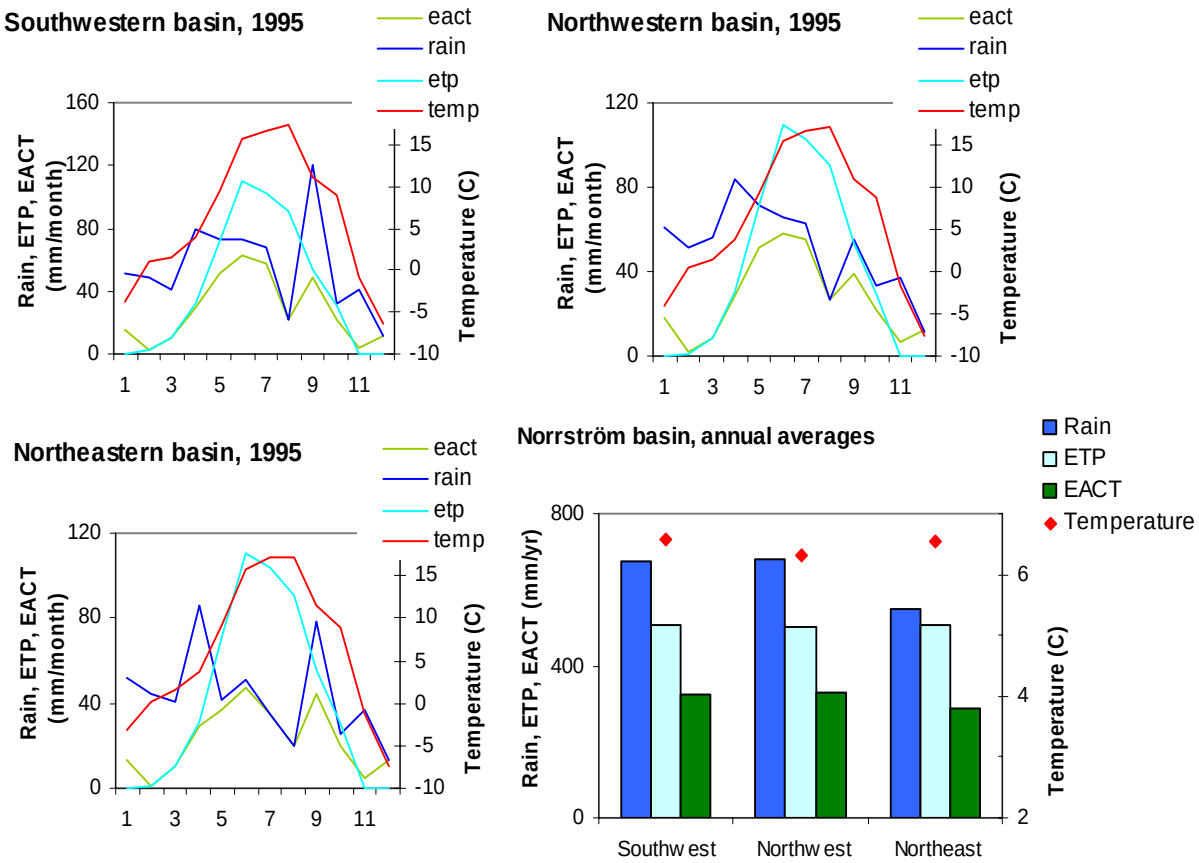

Figure 15: Meteorological characteristics of the Norrström basin zones.

Point nutrient emissions to the drainage network of each zone were derived from the same information as used for the POLFLOW modeling (TRK project, SMHI). Because nitrate, ammonium and orthophosphate fluxes per day are needed instead of total nitrogen and total phosphorus as in POLFLOW, point emissions from waste water treatment plants and industries were derived from equivalent-inhabitant data for each station (Table 5). Inorganic nitrogen emissions were considered to be in all cases in the form of 10% ammonium and 90% nitrate.

Table 5: Hypothesis for point emission calculation for RIVERSTRAHLER modelling

	Emission per inhabitant per day	Retention in secondary treatment plants (eq. inhab.<10000)	Retention in tertiary treatment plants (eq. inhab.<100000)	Retention in advanced tertiary treatment plants (eq. inhab.>100000)
Suspended matter	80 g	92%	95%	95%
Total Nitrogen	12 g	40%	53%	65%
Total Phosphorus	2 g	92%	95%	95%
Carbon	8 g	92%	95%	95%

To account for diffuse emissions to streams each flow component ((sub)-surface and base flows) was related to certain concentrations of nitrogen, phosphorus, silica, carbon and suspended matter. Because of lack of data, typical land use-specific concentrations were assumed based on previous applications and expert knowledge, and weighted by land use characteristics of each zone. Riparian zones were assumed to perform additional 80% nitrate attenuation, while

agricultural drainage was assumed to affect 20 to 30% of riparian zones. Assuming possible long groundwater residence times promoting significant denitrification in aquifers, nitrate concentrations in base flow was reduced by a factor 5 compared to nitrate concentrations in (sub)surface runoff.

Table 6: Summary of assumed concentrations for calculation of diffuse nutrient and suspended matter inputs to streams

	Land-use:	Forested	Grassland	Arable land	Urban
In (sub)surface:	Nitrate (mgN/l)	0,5	1	12	2
	Suspended matter (mg/l)	50	70	350	500
	Particulate inorganic phosphorus(gP/kgMES)	0,14	0,8	1	1,5
	Ammonium (µmol/l)	3,36			
	Silica (µmol/l)	120			
In aquifers:	Nitrate (mgN/l)	0.1	0.2	2.4	0.4
	Suspended matter (mg/l)	15	20	25	100
	Ammonium (µmol/l)	1,00			
	Silica (µmol/l)	130			

3c) Validation of the RIVERSTRAHLER modeling

Validation of both RIVERSTRAHLER hydrological and biogeochemical modules was based on monthly water discharges (either specific in l/km²/s or accumulated in m³/s), and monthly water quality data (concentrations) at a number of selected stations in each zone, preferably close to the outlet or downstream/upstream lakes. Figure 16 shows the location of those chosen stations for validation of water flows and water quality in each zone.

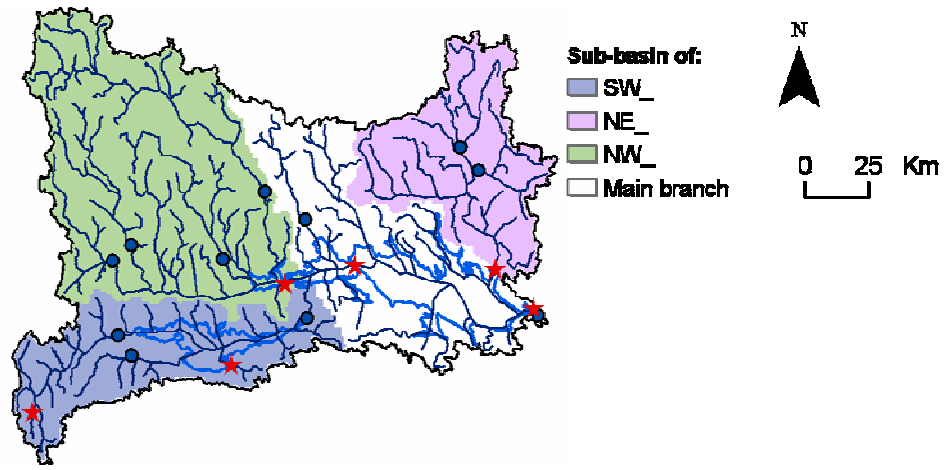

Figure 16: Location of the stations selected for validation (blue dots for water discharge, red stars for water quality) of the RIVERSTRAHLER modeling of each zone of the Norrström basin.

Parameters of the hydrological model were optimized (Table 7) so that calculated daily runoff best fits monthly-observed water discharges (Figure 17). The obtained values of the Nash criteria ranged between 0.257 and 0.509.

Table 7: Values of the hydrological parameters adjusted on data from the Norrström basin

Parameters of the hydrological model:	Adjusted value			
	SW_	NW_	NE_	Main Branch
Soil saturation level (mm)	125	100	150	80
Infiltration rate (day^{-1})	0.006	0.003	0.001	0.005
(Sub)surface runoff rate (day^{-1})	0.01	0.021	0.005	0.02
Groundwater runoff rate (day^{-1})	0.0005	0.002	0.0015	0.002
Snow melt rate ($day^{-1}.°C^{-1}$)	0.009	0.0015	0.005	0.005

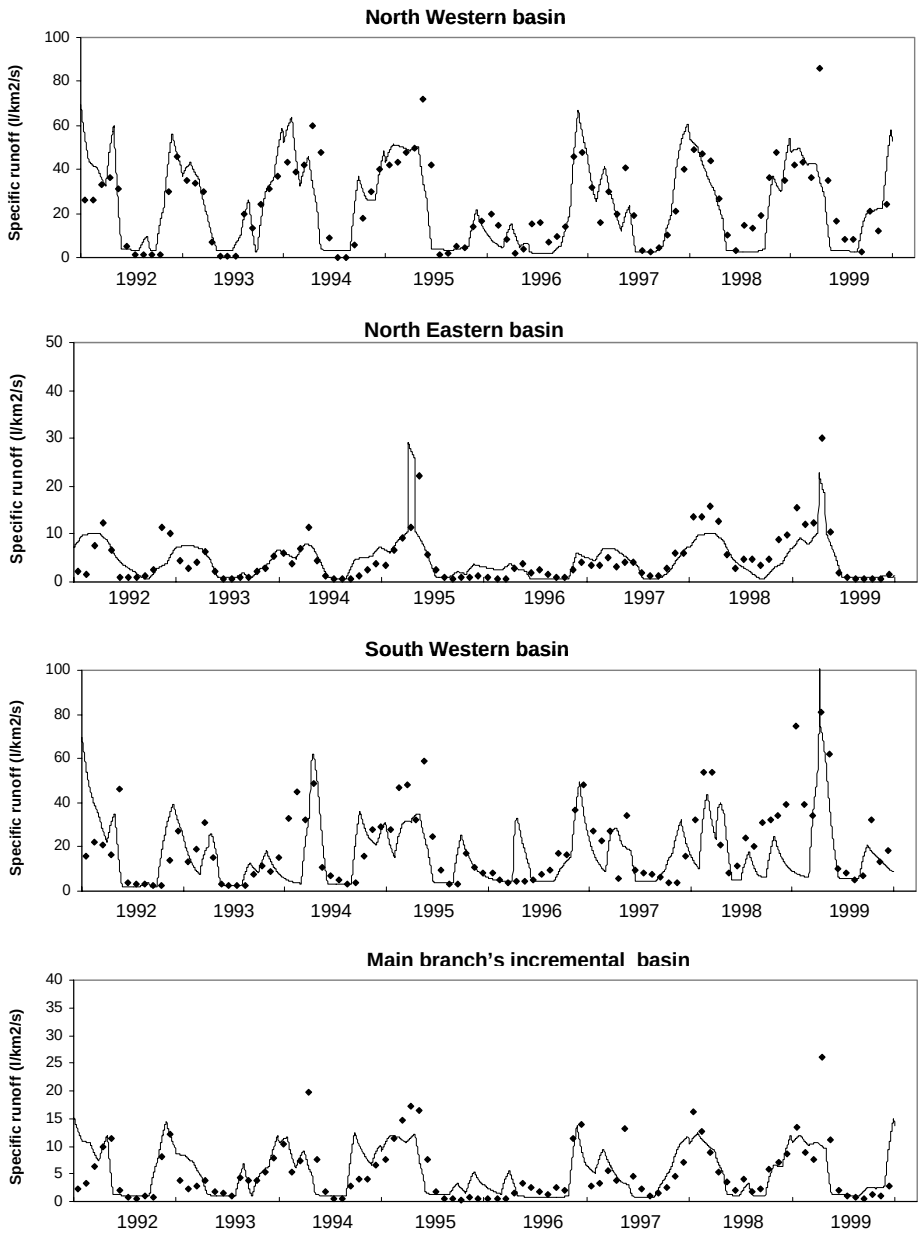

Figure 17: Observed vs. calculated water discharges (specific runoff in $l/km^2/s$) at the selected stations (see Figure 16) for, from top to bottom: Southwestern basin, Northwestern basin, Northeastern basin and drainage basin of the main branch of the Norrström basin.

Biogeochemistry of the Norrström basin was modeled with RIVERSTRAHLER for the years 1995 to 1999, with the hydrologically validated years 1992-1994 yielding stabilized initial conditions. Available water quality data at a monthly time resolution consisted in all or part of the following variables (depending on the considered station): water temperature, oxygen concentration, nitrates (nitrate+nitrite), ammonium and total nitrogen concentrations, orthophosphate and total phosphorus concentrations, total organic carbon concentration and chlorophyll-a concentration. Given the rather coarse time-resolution of the available water quality data, validation of the RIVERSTRAHLER modelling of the distinct sub-basins and of the whole Norrström basin favoured fitting the range of observed concentrations to precisely matching seasonality. Figures 18 a-d illustrate water quality results of RIVERSTRAHLER model runs, and compare calculated versus observed concentrations in total nitrogen, total phosphorus and phytoplankton, at the outlet of each sub-basin and for the whole Norrström. Monthly data were available every second year only. We were in general not able to satisfactorily reproduce the observed trends in nitrate seasonal patterns, the model being unable to simulate the observed low levels during summer, low flow periods. This is particularly the case for the NE_ basin where the highest population density is present and where the model predicts high levels of nitrate due to low dilution of nitrate-rich effluents of wastewater treatment plants. Keeping in mind the actual purpose of the present modelling exercise, and in spite of some remaining unconsistencies between predicted and observed concentrations, we considered that the range of our estimations were good enough for yielding coherent average annual export fluxes to be compared with POLFLOW results in term of loading and retention in streams and lakes.

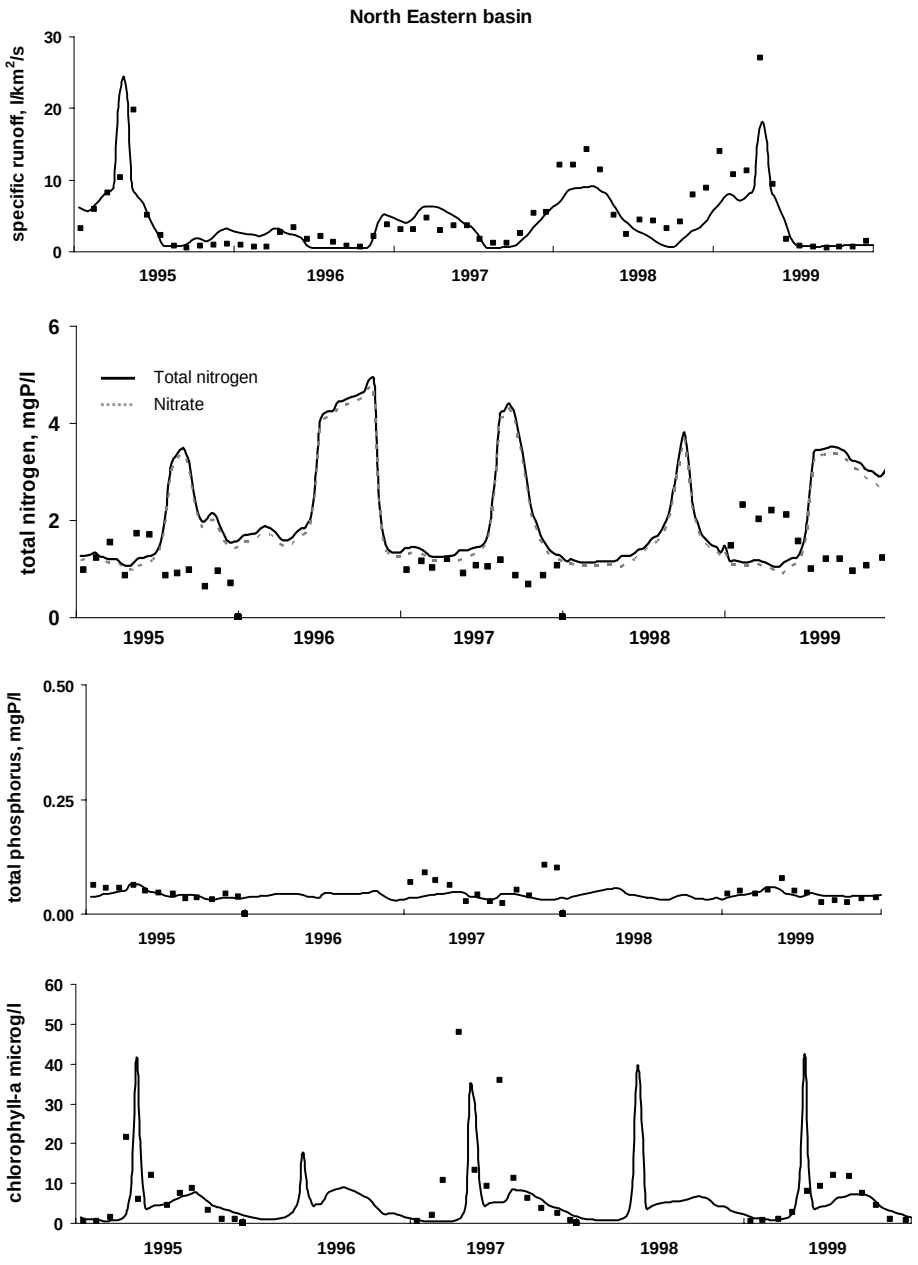

Figure 18a: Observed vs. RIVERSTRAHLER calculated specific runoff, concentrations in total nitrogen, total phosphorus and phytoplankton.

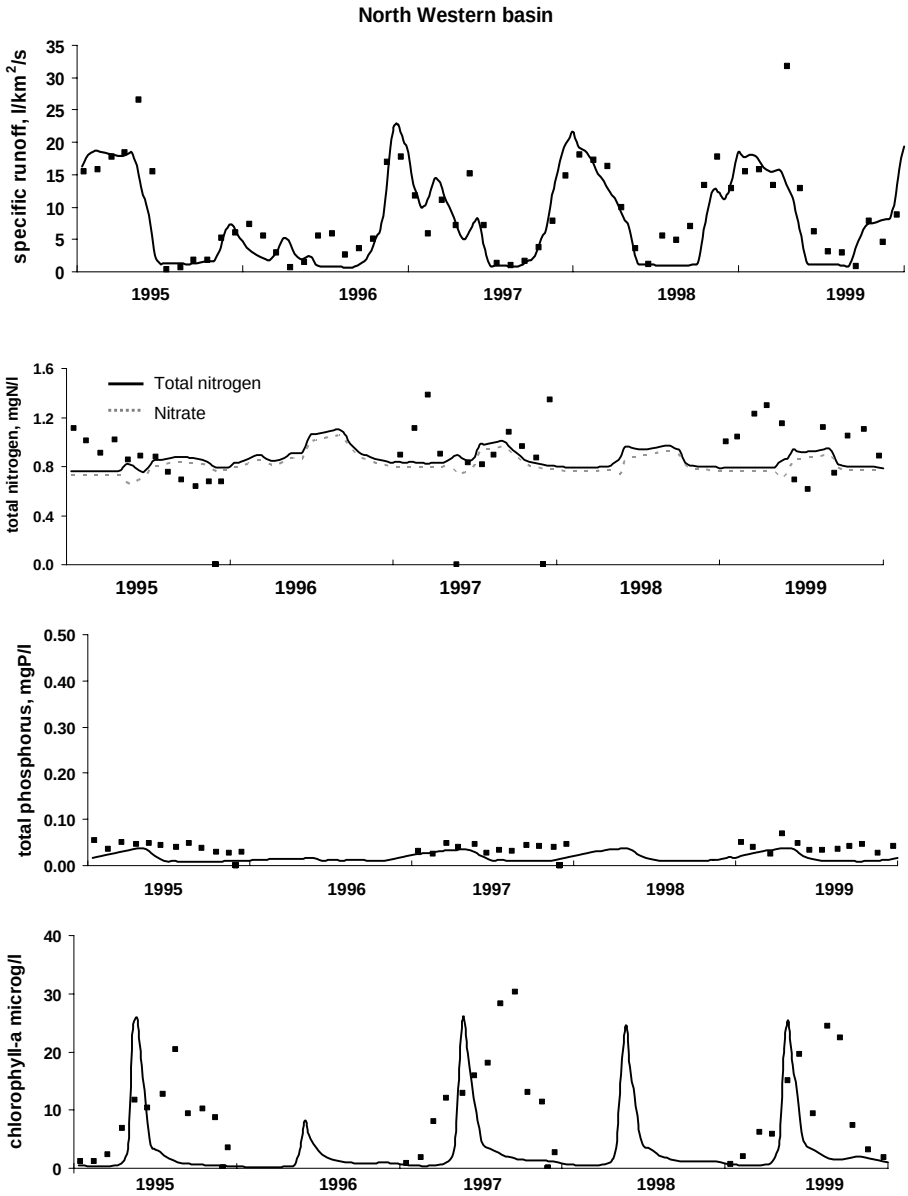

Figure 18b: Observed vs. RIVERSTRAHLER calculated specific runoff, concentrations in total nitrogen, total phosphorus and phytoplankton.

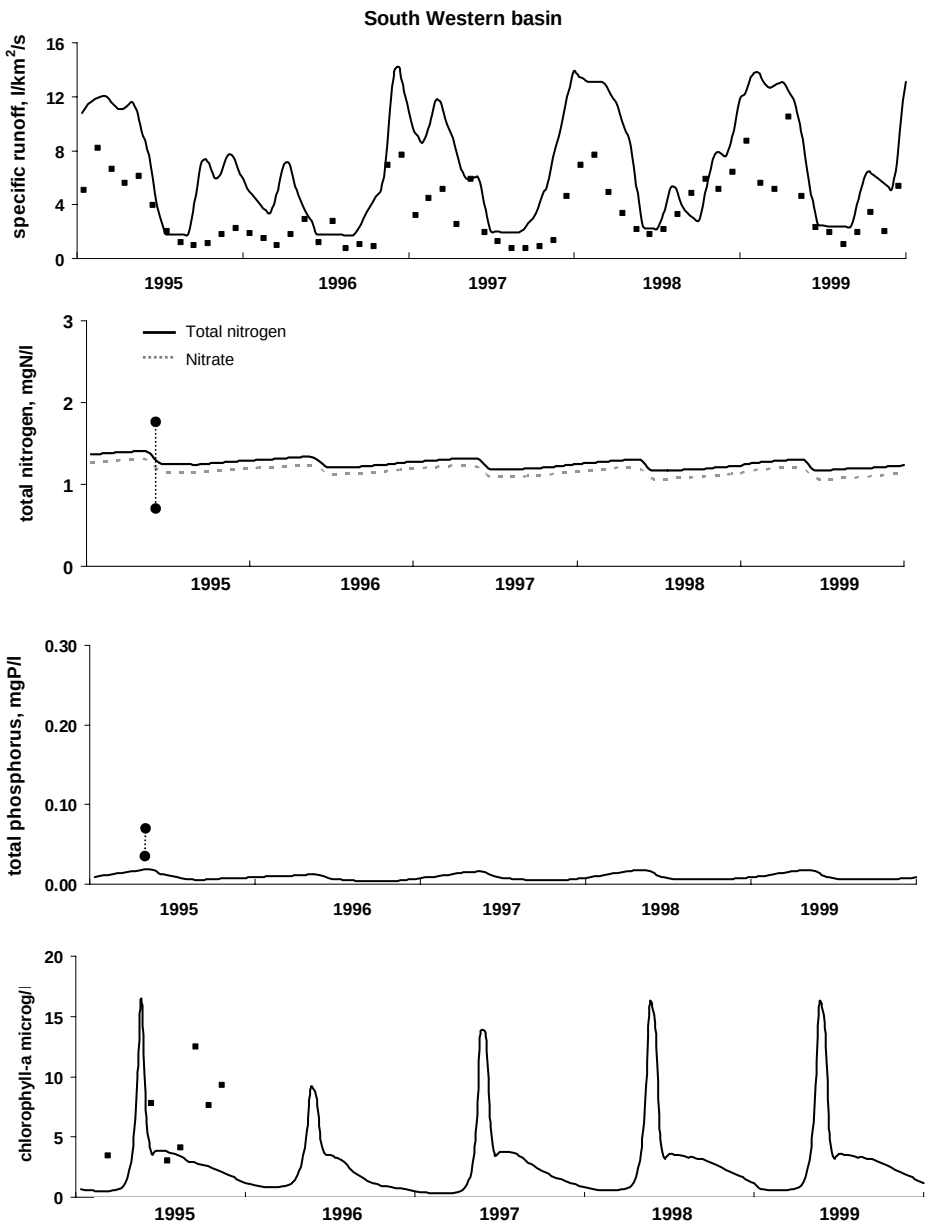

Figure 18c: Observed vs. RIVERSTRAHLER calculated specific runoff, concentrations in total nitrogen, total phosphorus and phytoplankton.. Only a few data were available, at this stage, at or close to the outlet of Lake Hjälmaren. RIVERSTRAHLER resulting concentrations downstream South Western basin are shown here only to illustrate that obtained values are in the range of resulting concentrations in the other basins. Growth season mean values of total nitrogen and total phosphorus in Lake Hjälmaren between 1985-1995 are cited by Willén (2001b) and are represented here by a range bar to allow some level of comparison. Chlorophyll-a concentrations (dot plot) in Lake Hjälmaren were available for the year 1995 only from Swedish University of Agricultural Sciences' database.

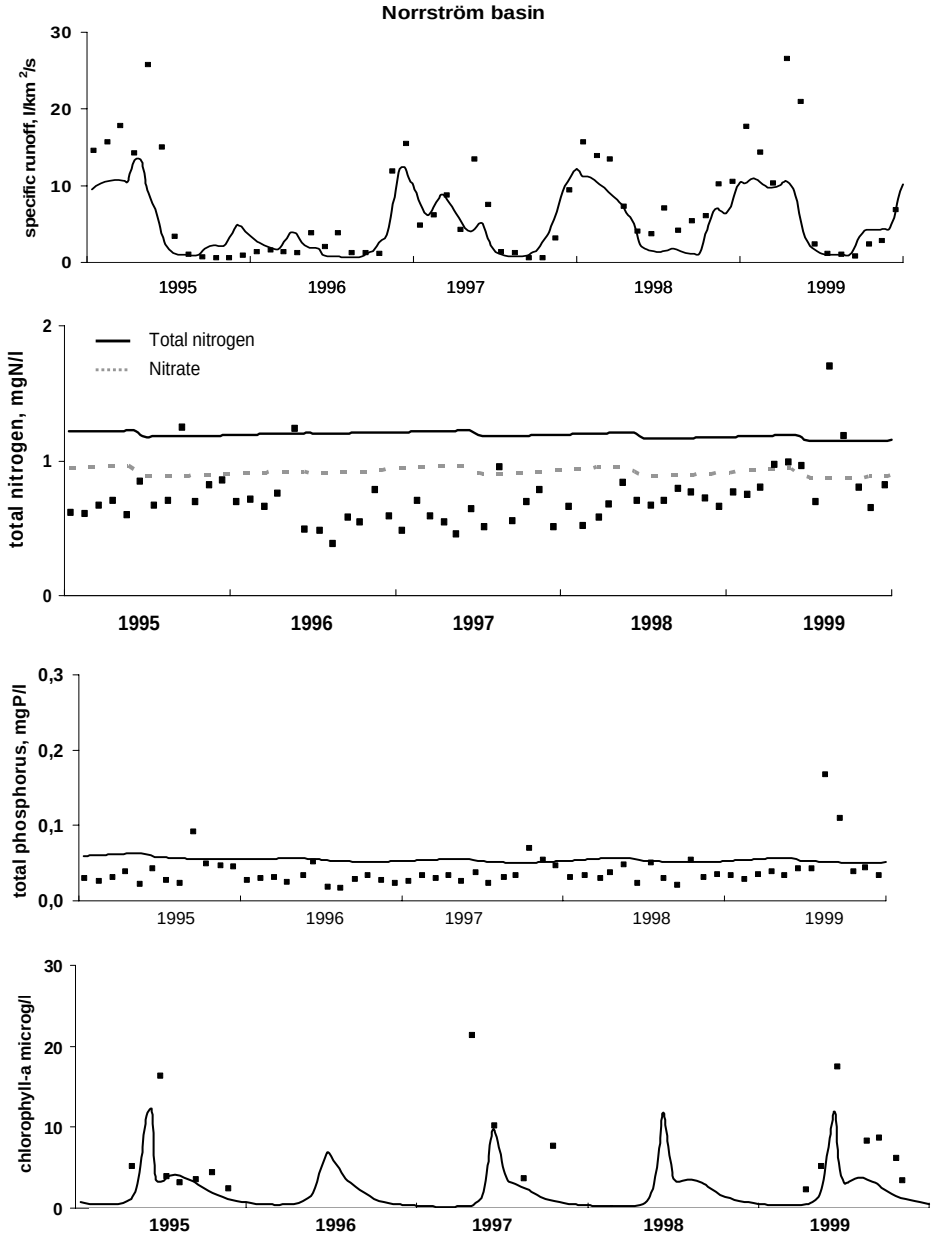

Figure 18d: Observed vs. RIVERSTRAHLER calculated specific runoff, concentrations in total nitrogen, total phosphorus and phytoplankton. In spite of no available observations, at this stage, calculated phytoplankton concentrations at the outlet of Lake Mälaren are consistent with data on chlorophyll-a concentrations measured in the easternmost station within Lake Mälaren (source: water quality database of the Swedish University of Agricultural Sciences).

The reservoir approach adopted for the modelling of Lakes Hjälmaren and Mälaren enabled estimating lake retention capacity in terms of relative attenuation of total nitrogen and total phosphorus concentrations. Lake Hjälmaren was found to retain 45% total nitrogen and 64% total phosphorus. Lake Mälaren was found to retain 22% total nitrogen and 9% total phosphorus. Such values are rather low compared to reported literature data (e.g. 56% total nitrogen retention and 70% total phosphorus retention in Kvarnäs 2001) and may be explained by the basic assumption and coarse representation we have adopted when considering Lake Mälaren as one homogenous well-mixed water body with average characteristics. Indeed, Lake Mälaren consists in reality mainly of an archipelago with numerous islands and a complex pattern

of subbasins within the lake (Willén 2001b): from the westernmost location of Lake Mälaren, a shallow unstrastified eutrophic lake is followed by a deep stratified mesotrophic lake, whose discharge is mixed close to Stockholm with the discharge from a deep stratified eutrophic lake located downstream the large city of Uppsala. We tested the sensitivity of the modeling to a simple changed representation of Lake Mälaren by two reservoirs in cascade, a small shallow lake followed by a larger and deeper lake: nitrogen retention in Lake Mälaren was as a consequence estimated to 25% while phosphorus retention was estimated to 13%. The isolation of the third lake in the northern area of Lake Mälaren receiving nutrient inputs from the agricultural and urban Northeastern sub-basin was however not accounted for in that simple variation. Flexibility in the RIVERSTRAHLER approach may allow us in future investigations to improve the conceptual representation of this complex but well-monitored large lake.

4) Results and discussion

Results of the RIVERSTRAHLER model for each year in the period 1995-1999 allowed to further calculate: i) average annual nutrient fluxes, to be compared to the observed fluxes at the Norrström basin outlet, and ii) 5-year average annual nutrient fluxes, to be compared with modeling results from the POLFLOW "black-box" representation of in-stream attenuation, based on regression on slope and water discharge. Figure 19 shows, for each basin (North East, North West, South West) 5-year average annual estimations of: nutrient outlet loads, nutrient diffuse and total (diffuse + point) inputs from both POLFLOW and RIVERSTRAHLER model Riparian nitrate retention is explicitly accounted for only in the former approach, so that we also present nitrogen RIVERSTRAHLER results that include riparian zones ("rz-incld" in Figure 19) or rather entirely isolate streams and lakes ("rz-excld" in Figure 19).

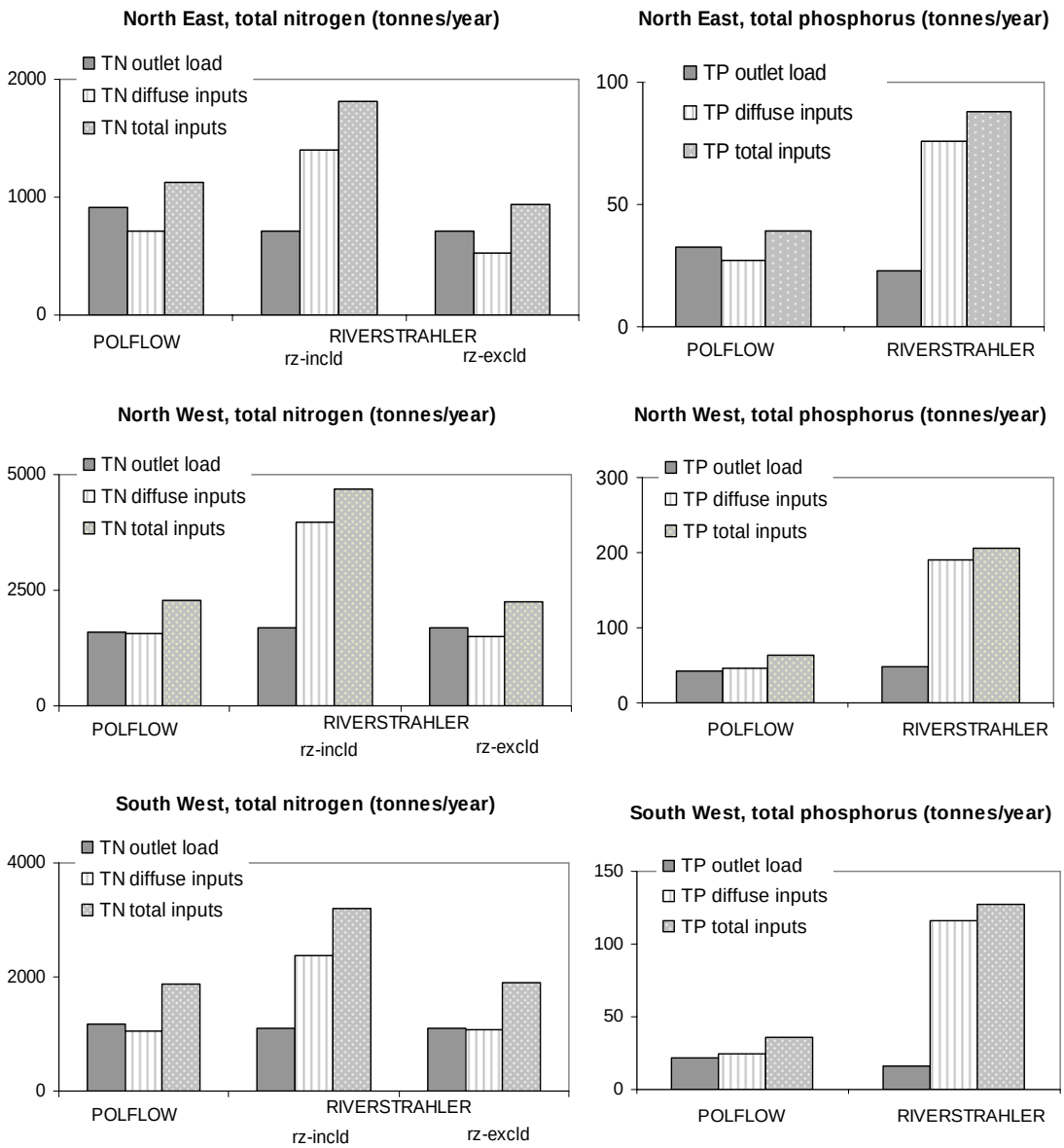

Figure 19: POLFLOW vs. RIVERSTRAHLER estimations of 5-year average annual nutrient balance in the Northwestern, Northeastern and Southwestern sub-basins of the Norrström watershed.

The rather good agreement between both models estimations of nutrient loads illustrated in Figure 19 suggests the feasibility of comparing those two significantly different approaches for modeling nutrient transport and attenuation in a large-scale river watershed like the Norrström drainage basin. Sub-basin retention was estimated by the POLFLOW model to 20%, 30% and 40%, for nitrogen and for phosphorus, respectively in the North Eastern, North Western and South Western sub-basins. The RIVERSTRAHLER approach estimated retention in drainage network (i.e. "after" riparian zone) to 24%, 25% and 42% of total nitrogen and to 74%, 77% and 88% of total phosphorus, respectively in the North Eastern, North Western and South Western sub-basins. Retention estimations by the two different approaches were in the same range for nitrogen, with a similar evaluation of relative contributions of the different sub-basins, but significantly lower in the case of phosphorus according to the POLFLOW modeling. Indeed, for a similar export load at the basin outlet, diffuse phosphorus inputs to streams in the POLFLOW approach are almost twice lower than estimated in the RIVERSTRAHLER approach.

POLFLOW- and RIVERSTRAHLER-calculated 5-year average annual export fluxes of total nitrogen and total phosphorus at the outlet of the Norrström basin are compared in Figure 20, together with observed nutrient loads. Error bars show minimum and maximum annual fluxes in the period 1995-1999 when such information is available, i.e. in observations and in RIVERSTRAHLER estimations.

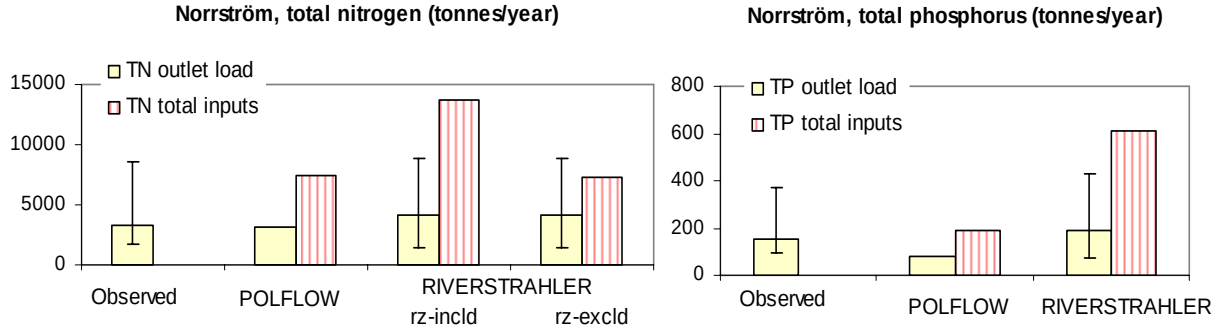

Figure 20: Observed vs. POLFLOW and RIVERSTRAHLER estimations of 5-year average annual nutrient fluxes at the outlet of the Norrström basin.

In general, both approaches seem to yield rather good estimates, with RIVERSTRAHLER even quite accurately capturing inter-annual ranges of nutrient fluxes. Basin-wide in-stream retention of nutrients (see summary in Table 8) is estimated to about 60% for total nitrogen and for total phosphorus by the POLFLOW approach. The RIVERSTRAHLER approach predicts 43% total nitrogen retention (after attenuation in riparian zones) and 70% total phosphorus retention in the whole drainage network of the Norrström basin.

Differences in retention assessment might be explained by slight overestimation of nitrogen load by RIVERSTRAHLER, and slight underestimation of phosphorus by POLFLOW, together with significant deviations between model estimation of diffuse sources, particularly noticeable for phosphorus. Riparian retention may be included in land retention of nutrient in the POLFLOW model, which is also accounted for in the RIVERSTRAHLER approach to modeling nitrogen transport and attenuation. For phosphorus, however, no riparian retention was assumed in RIVERSTRAHLER. Observation of such discrepancies raises important questions on how to evaluate diffuse inputs, but also on the retention description in different approaches that all manage to reproduce, sufficiently well, observed concentrations or loads. The POLFLOW model assumes the same retention representation by a regression on hydraulic and morphological characteristics. Although the corresponding parameters are nutrient specific, the values obtained by optimization for in-stream retention are quantitatively similar for total nitrogen and total phosphorus. The RIVERSTRAHLER approach uses nutrient-specific process description, and a sensitivity test on phosphorus diffuse emissions showed that the model always suggests higher retention of phosphorus than nitrogen.

Table 8: Retention within basin drainage network as calculated by RIVERSTRAHLER and POLFLOW models for the different sub-basins and the whole Norrström basin.

	Total nitrogen retention according to calculations by:		Total phosphorus retention according to calculations by:	
	RIVERSTRAHLER	POLFLOW	RIVERSTRAHLER	POLFLOW
Northwestern basin	25%	30%	77%	31%
Northeastern basin	24%	19%	74%	17%
Southwestern basin	42%	38%	88%	40%
Entire Norrström basin	43%	58%	70%	57%

The validation of each approach and such model comparison show that both models are sufficiently capable of reproducing observations, and allow for confrontation of resulting calculations of, for instance, nutrient retention in basin-wide drainage networks, relative contributions of sub-basins, future impacts and scenario analysis. At present and concerning this particular study, we have been able to practically show the feasibility of implementing two different modeling approaches, and of drawing and further quantitatively comparing modeling results in terms of potentially-useful information for decision-makers, in the context of basin management and eutrophication mitigation. In addition, we have identified a number of future interesting research issues that should help to providing with further system- and process-understanding. In general, our RIVERSTRAHLER hydrological and biogeochemical modelling of Norrström basin, at the present stage and based on a restricted amount of available data of the required quality, seems to systematically slightly underestimate water discharges, but rather satisfactorily account for export fluxes, which is consistent with a possible slight overestimation of nutrient concentrations at the outlet of the basin (as shown in Fig. 18). This supports our previous notice of the need to further investigate Lake Mälaren's retention capacity, with, namely, better accounting for bathymetry and heterogeneous morphology. Estimation of nutrient emissions from diffuse sources has been as well pointed out because of its complexity, significance and major uncertainty.

CONCLUSION

Environmental problems affecting a common natural resource, such as eutrophication of inland and coastal waters, are very much related to how human society functions. With issues of fluctuating and changing climate, of human endeavours in agriculture and industry, and of demographic development and redistribution, dynamic and integrated approaches are needed (Neal 2005) for complying with national and international environmental regulations (such as the European Water Framework Directive) and political agreements. The need for understanding and predicting transport and attenuation of water and nutrients, and chemicals in general, emphasize the usefulness of catchment science and modeling as critical guides for planning and assessing cost- and benefit-effective mitigation measures of pollution abatement. The complexity of sources and controlling processes at the scale of entire, relatively large watersheds intensifies the need of measurement data from a wide variety of areas as well as adequate upscaling methods. It reveals also the existence of major uncertainties in stakeholders' knowledge, and explains the resulting difficulties in translating these complexities into mathematical quantifications.

Such quantifications, however, have developed so much that instead of enhancing measurement campaigns and improving data availability, the number of different modeling approaches has inflated without clear agreement, nor maybe even consultation between different scientific teams, upon process representations and the strategies to adopt for reaching the ultimate purpose of developing sound tools for decision-makers in the context of pollution abatement and water resource management. This shared observation has been the starting point of the present study. We have here, therefore, aimed at: 1) qualitatively classifying a number of selected approaches to nutrient transport and attenuation modeling at medium-to-large river basin scales and 2) assessing the feasibility of quantitatively comparing, confronting and maybe cumulating the benefits of two such different approaches.

We suggest in the first part of this thesis a typology for a non-exhaustive list of approaches to nutrient transport and attenuation catchment-scale modeling. Because comparative multi-model approach to problem-solving appears of major importance, the identification of model characteristics and their qualitative classification may be helpful for later identifying differences and similarities in their results. However, the result itself of this exercise may not have been, as such, the most important outcome. The questions raised during the typology-building process have indeed been highly informative indicators of the complexity of understanding the data requirements of, the several assumptions in, and the general conceptual thinking behind widely-used models.

In the second part of this work, we concretely investigated the possibility to apply and compare two such different approaches, based on a restricted amount of time and available data. Both the deterministic, semi-distributed RIVERSTRAHLER approach and the statistical/empirical fully-distributed POLFLOW model were able to reproduce observations in total nitrogen and total phosphorus loads in the Norrström basin, Sweden. Results in terms of basin retention and relative contribution were comparable but raised a number of interesting issues to be further investigated, namely the account for lake morphology and the challenging estimation of diffuse emissions. Rather than opposing the models on the basis of their result disagreements, one may prefer to learn from both and improve the specific knowledge that each approach is able to yield: process and seasonality information from RIVERSTRAHLER, spatial characterization and land/water system integration from POLFLOW, for instance. In the perspective of yielding management recommendations, such confrontation of approach results might be highly necessary, for scientists to better understand the system and associated processes on one hand, for decision-makers to obtain more trustful supporting tools on the other hand.

REFERENCES

Alexander, R. B.; Smith, R. A.; Schwarz, G. E. Effect of stream channel size on the delivery of Nitrogen to the Gulf of Mexico. *Nature* **2000**, *403*, 758-761.

Alexander, R.B.; Smith, R.A.; Schwarz, G.E.; Preston, S.D.; Brakebill, J.W.; Srinivasan, R.;Pacheco, P.A. (2001) Atmospheric nitrogen flux from the watersheds of major estuaries of the United States: An application of the SPARROW watershed model. In: Valigura R, Alexander R, Castro M, Meyers T, Paerl H, Stacey P & Turner RE (Eds) Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective, American Geophysical UnionMonograph 57, pp 119–170

Alexander, R.B.; Johnes, P.J.; Boyer, E.W.; Smith, R.A. A comparison of models for estimating the riverine export of nitrogen from large watersheds**,** *Biogeochemistry* **2002**, *57/58*, 295–339.

Arheimer, B.; Wittgren, H.B. Modelling the effects of wetlands on regional nitrogen transport. *Ambio* **1994**, *23(6)*, 378-386.

Arheimer, B.; Brandt, M.. Modelling nitrogen transport and retention in the catchments of southern Sweden. *Ambio* **1998**, *27(6)*, 471-480.

Arnold, J.G.; Srinivasan, R.; Muttiah, R.S.; Williams, Jr. Large area hydrologic modeling and assessment part I: model development. *Journal of the American Water Resources Association* **1998**, *34(1)*, 73–89.

Arnold, J.G.; Srinivasan, R.; Muttiah, R.S.; Allen, P.M.; Walker, C. Continental scale simulation of the hydrologic balance. *Journal of the American Water Resources Association* **1999**, *35(5)*, 1037–1052.

Baresel, C.; Destouni, G. Novel Quantification of Coupled Natural and Cross-Sectoral Water and Nutrient/Pollutant Flows for Environmental Management Environ. Sci. Technol. **2005**, *39*, 6182-6190.

Behrendt, H. (2002) The Model System MONERIS, *EUROCAT WD, 22:* 10 pages.

Bergström, S.; Brandt, M.; Gustafson, A. Simulation of runoff and nitrogen leaching from two fields in southern Sweden. *Hydrological Science Journal* **1987**, *32(2-6)*, 191-205.

Billen, G.; Garnier, J.; Hanset, Ph. Modelling phytoplankton development in the entire drainage network: The RIVERSTRAHLER model applied to the Seine River system. *Hydrobiologia* **1994**, *289*, 119–137.

Billen, G.; Garnier, J.; Billen, C.; Hannon, E. (1995) Global change in nutrient transfer from land to coast: biogeochemical processes in river systems. GMMA, Free University of Brussels: 99 pp.

Billen, G; Garnier, J. Nitrogen transfers through the Seine drainage network: a budget based on the application of the Riverstrahler model. *Hydrobiologia* **2000**, *410*, 139-150.

Billen, G.; Garnier, J.; Ficht, A.; Cun, C. Modelling the response of water quality in the Seine River Estuary in response to human activity in the watershed over the last 50 years. *Estuaries* **2001**, *24*, 977-993.

Billen, G.; Garnier, J.; Rousseau, V. Nutrient fluxes and water quality in the drainage network of the Scheldt basin over the last 50 years. *Hydrobiologia* **2005**, *540*, 47-67.

Boesch, D., Hecky, R.; O´Melia, C.; Schindler, D.; S. Seitzinger 2006. Eutrophication of Swedish seas. Naturvårdsverket Report 5509, Naturvårsdverket, Stockholm (Sweden).

Brandt, M. Simulation of runoff and nitrogen transport from mixed basins in Sweden. *Nordic Hydrology* **1990**, *21*, 13-34.

Brandt, M.; Ejhed, H. TRK, *Transport - Retention - Ka¨llfördelning. Belastning p*Å *havet*; NaturvÅrdsverket Rapport 5247; Stockholm, Sweden, 2003.

Carpenter, S.R.; Caraco, N.F.; Correll, D. L.; Howarth, R. W.; Sharpley, A. N.; Smith, V. H. Non-point pollution of surface waters with Phosphorus and Nitrogen. *Ecological Applications* **1998***, 8(3)*, 559–568.

Cederwall, H.; Elmgren, R. Biological Effects of Eutrophication in the Baltic Sea, Particularly the Coastal Zone. *Ambio* **1990**, *14(3)*, 109-112.

Chave, P. **2001**. The EU Water Framework Directive – An Introduction. International Water Association.

Conley, D.J. Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia* **2000**, *410*, 87-96.

Cugier, P.; Billen, G.; Guillaud, J.F., Garnier, J.; Ménesguen, A. Modelling the eutrophication of the Seine Bight (France) under historical, present and future riverine nutrient loading. *J. Hydrology* **2005**, *304*, 381-396.

De Wit, M. J. M., 1999, Nutrients Fluxes in the Rhine and Elbe basins, Utrecht: Koninklijk Nederlands Aardrijkskundig Genootschap, Nederlandse Geografische Studies 259.

De Wit, M. J. M., 2001, Nutrients fluxes at the river basin scale. I: the PolFlow model, *Hydrological Processes*, 15, pp.743-759.

De Wit, M., Meinardi, C., Wendland, F., Kunkel, R., 2000, Modelling water fluxes for the analysis of diffuse pollution at the river basin scale, Hydrological processes, 14, pp. 1707-1723.

Donner, S.D.; Kucharik, C.J.; Oppenheimer, M. The influence of climate on in-stream removal of nitrogen. *Geophys. Res. Lett.* **2004**, 31, L20509.

Elmgren, R. 2001. Understanding impact on the Baltic ecosystem: changing views in recent decades. Ambio 30:222-231.

European Commission, Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, Official Journal of the European Communities, L 327/1, 2000.

Even, S.; Poulin, M. ; Garnier, J. ; Billen, G. ; Servais, P. ; Chesterikoff, A.; Coste, M. River ecosystem modelling: application of the PROSE model to the Seine river (France). *Hydrobiologia* **1998**, *373-374*, 27-45.

Fisher, S. G.; Sponseller, R. A.; Heffernan, J.B. Horizons in stream biogeochemistry: Flowpaths to progress. *Ecology* **2004**, *85*, 2369-2379.

Flipo, N. (2005) **M**odélisation intégrée des transferts d'azote dans les aquifères et les rivières : Application au bassin du Grand Morin. PhD Thesis, Ecole de Mines de Paris, France.

Flipo, N.; Even, S.; Poulin, M.; Théry, S.; Viavattene, C.; Ledoux, E. Modelling nitrate fluxes at the catchment scale using the integrated tool CAWAQS. Science of the Total Environment **2006** (accepted).

Galloway J.N.; Aber, J.D.; Erisman, J.W.; Seitzinger, S.P.; Howarth, R.W.; Cowling, E.B.; Cosby, B.J. The Nitrogen cascade. *Bioscience* **2003**, *53(4)*, 351-356.

Garnier, J.; Billen, G.; Coste, M. Seasonal succession of diatoms and Chlorophyceae in the drainage network of the Seine River: Observations and modelling. *Limnol. Oceanogr.* **1995**, *40(4)*, 750-765.

Garnier, J.; Billen, G.; Palfner, L. Understanding the oxygen budget and related ecological processes in the river Mosel: The Riverstrahler approach. *Hydrobiologia* **2000**, *410*, 151-166.

Garnier, J.; Billen, G. The Riverstrahler modeling approach applied to a tropical case study (the Red-Hong River, Vietnam): nutrient transfer and impact on the coastal zone. SCOPE. *Coll. Mar. Res. W.* **2002**, *12*, 51-65.

Garnier, J.; Billen, G.; Hannon, E.; Fonbonne, S.; Videnina, Y.; Soulie, M. Modeling transfer and retention of nutrients in the drainage network of the Danube River. *Estuar. Coast. Shelf Sci.* **2002**, *54(3)*, 285-308.

Garnier, J.; Nemery, J.; Billen, G. Nutrient dynamics and control of eutrophication in the Marne River system. *J. Hydrology* **2005**, *304*, 397-412.

Greffe, F., 2003, *Material transport in the Norrström drainage basin: Integrating GIS and hydrological process modelling*, Master Thesis, Department of Land and Water Resources Engineering, Royal Institute of Technology, Stockholm.

Grizzetti, B. (2005). Modelling Nitrogen and Phosphorus fate from point and diffuse sources at European scale. PhD thesis, Université Pierre et Marie Curie Paris VI.

Grizzetti, B.; Bouraoui, F.; de Marsily, G.; Bidoglio, G. A statistical approach to estimate nitrogen sectorial contribution to total load. *Water Science and Technology* **2005a**, *51(3-4)*, 83-90.

Grizzetti, B.; Bouraoui, F.; de Marsily, G.; Bidoglio, G. A statistical method for source apportionment of riverine nitrogen loads. *Journal of Hydrology* **2005b**, *304*, 302-315.

HELCOM 1993. *The Baltic Sea Joint Comprehensive Environmental Action Programme*; Baltic Sea Environmental Proceedings No. 48; Helsinki, Finland, 1993.

HELCOM 2004. 30 years of protecting the Baltic Sea: HELCOM 1974-2004. Baltic Marine Environment Protection Commission (Helsinki Commission), 2004.

Horn, A.L.; Rueda, F.J.; Hörmann, G.; Fohrer, N. Implementing river water quality modelling issues in mesoscale watershed models for water policy demands - an overview on current concepts, deficits, and future tasks. *Physics and Chemistry of the Earth* **2004**, *29*, 725–737.

Howarth, R.W.; Billen, G.; Swaney, D.; Townsend, A.; Jaworski, N.; Lajtha, K.; Downing, J.A.; Elmgren, R.; Caraco, N.; Jordan, T.; Berendse, F.; Freney, J.; Kudeyarov, V.; Murdoch, P.; Zhao-Liang, Z. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* **1996**, *35*, 75–139.

Howarth, R.; Anderson, D.; Cloern, J.; Elfring, C.; Hopkinson, C.; Lapointe, B.; Malone, T.; Marcus, N.; Mc Glathery, K.; Sharpley, A.N. Nutrient Pollution of Coastal Rivers, Bays, and Seas. *Issues in Ecology* **2000**, *7*, 1-15.

Howarth R. W.; Marino, R. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades, *Limnol. Oceanogr.* **2006**, 51(1, part 2), 364–376

Howarth, R.W.; Swaney, D.; Boyer E.W.; Marino, R.; Jaworski, N.; Goodale, C. The influence of climate on average nitrogen export from large watersheds in the North-Eastern United States. *Biogeochemistry* **2006**, DOI 10.1007/s10533-006-9010-1.

Kronvang, B.; Aertebjerg, G.; Grant, R.; Kristensen, P.; Hovmand, M.; Kirkegaard, J. Nationwide monitoring of nutrients and their ecological effects: state of the Danish aquatic environment. *Ambio* **1993**, *22(4)*, 176-187.

Kvarnäs, H. Morphometry and Hydrology of the Four Large Lakes of Sweden. *Ambio* **2001**, *30(8)*, 467–474.

Langbein WB (1949) Annual runoff in the United States. US Geological Survey Circular 52, Washington, DC.

Larsson U.; Elmgren, R.; Wulff. F. Eutrophication and the Baltic Sea: causes and consequences. Ambio 1985, 14, 9-14.

Lindgren, G.A.; Destouni, G. Nitrogen loss rates in streams: Scale dependence and up-scaling methodology. *Geophys. Res. Lett.* **2004**, *31*, L13501, doi:10.1029/2004GL019996.

Lindgren, G.A.; Gren, I-M.; Destouni, G. Effects of nitrogen transport-attenuation modelling on the efficiency of coastal nitrogen load abatement. Environmental Science and Technology 2006, accepted.

McBride, G.B.; Alexander, R.B.; Elliot, A.H.; Shankar, U. (2000) Regional scale modelling of water quality. Water and Atmosphere, Vol. 8 (pp 29–31). National Institute of Water and Atmospheric Research (NIWA), Auckland, New Zealand.

Meinardi, C., Beusen, A., Bollen, M., Klepper, O., 1994, Vulnerability to Diffuse Pollution of European Soils and Groundwater, National Institute of Public Health and Environmental Protection (RIVM), Report 4615001002, Bilthoven: RIVM

Mourad, D. S. J.; Van der Perk, M.; Gooch, G. D.; Loigu, E.; Piirima¨e, K.; StÅlnacke, P. *GIS-based quantification of future nutrient loads into Lake Peipsi/Chudskoe using qualitative regional development scenarios*. In *DipCon 2003. IWA Proceedings of the 7th International Specialised Conference on Diffuse Pollution and Basin Management, 17th-22nd August 2003*; Bruen, M., Ed.; University College Dublin, Dublin, 2003; Vol. 10, pp 105-111.

Mourad, D.; van der Perk, M. Modelling nutrient fluxes from diffuse and point emissions to river loads: the Estonian part of the transboundary Lake Peipsi/Chudskoe drainage basin (Russia/Estonia/Latvia). *Water Sci. Technol.* **2004**, *49* (3), 21-28.

Neal, C. Water and chemical fluxes through catchments. *Hydrology and Earth System Sciences* **2005**, *9(6)*, 569.

Peterson, B.J.; Wollheim, W.M.; Mulholland, P.J.; Webster, J.R.; Meyer, J.D.; Tank, J.L.; Martõ, E.; Bowden, W.B.; Valett, H.M.; Hershey, A.E.; McDowell, W.H.; Dodds, W.K.; Hamilton, S.K.; Gregory, S.; Morrall, D.D. Control of nitrogen export from watersheds by headwater streams. *Science* **2001**, *292(5514)*, 86-90.

Preston, D. P.; Brakebill, J. W. *Application of spatially referenced regression modeling for the evaluation of total nitrogen loading in the Chesapeake Bay watershed* (WRI Report 99-4054, USGS Water Resources Division MD-DE-DC, Maryland, 1999)

Rabalais, N. N. Nitrogen in aquatic ecosystems. *Ambio* **2002**, *31(2)*, 102-112.

Ruelland, D.; Billen, G.; Brunstein, D.; Garnier, J. SENEQUE: a GIS interface to the RIVERSTRAHLER model of the biogeochemical functioning of river systems. Submitted to Ecological Modelling, 2005.

Saunders D.L.; Kalff J.. Nitrogen retention in wetlands, lakes and rivers. *Hydrobiologia* **2001**, *443*, 205-212.

Seitzinger S.P. ; Styles R.V. ; Boyer E.W.; Alexander R.B.; Billen G.; Howarth R.W.; Mayer B.; Van Breemen N. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. *Biogeochemistry* **2002***, 57/58***,** 199–237.

Sferratore, A.; Billen, G.; Garnier, J.; Humborg, C.; Rahm, L. Modelling nutrient fluxes from sub-arctic basins: comparison of pristine vs. dammed rivers. In preparation, 2006.

Smith, R.A.; Schwarz. G.E.; Alexander R.B. Regional interpretation of water-quality monitoring data. *Wat. Resour. Res.* **1997**, *33*, 2781–2798.

Smith. V.H.; Tilman, G.D., Nekola, J.C. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution* **1999,** *100*, 179-196.

Strahler, A.H. Quantitative analysis of watershed geomorphology. *Trans. Am. Geophys. Union* **1957**, *38*, 913-920.

Styczen, M., M. Thorsen, A. Refsgaard, J. S. Christiansen, and S. Hansen. 1999. Non-point pollution modeling at different scales and resolution based on MIKE SHE. In: Proceedings of 3rd DHI Software Conference, June 7-11, 1999, Helsingør, Denmark.

Turc, L. Le bilan d'eau des sols: Relations entre les précipitations, l'évaporation et l'écoulement. *Ann. Agron.* **1954**, *5*, 491–595.

Turc, L. Évaluation des besoins en eau d'irrigation, évapotranspiration potentielle, formule simplifiée et mise à jour. *Ann agron.* **1961**, *12*, 13-49.

UNEP-IETC. 1999. *Planning and Management of Lakes and Reservoirs: An Integrated Approach to Eutrophication*. IETC Technical Publication Series 11.

U.S. EPA. 2001. Nutrient criteria technical guidance manual: estuarine and coastal marine waters. Office of Water, Washington, DC. EPA-822-B-01-003.

Vitousek, P.M.; Aber, J.D.; Howarth, R.W.; Likens, G.E.; Matson, P.A.; Schindler, D.W.; Schlesinger, W.H.; Tilman, D.G. Human Alteration of the Global Nitrogen Cycle: Sources and consequences, *Ecological Applications* **1997**, *7(3)*, 737-750.

Wade, A.J.; Durand, P.; Beaujouan, V.; Wessel, W.W; Raat, K.J.; Whitehead, P.G.; Butterfield, D.; Rankinen, K.; Lepisto, A. A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrology and Earth System Sciences* **2002b**, *6(3)*, 559–682.

Wade, A.J.; Whitehead, P.G.; Butterfield, D. The Integrated Catchments model of Phosphorus dynamics (INCA-P), a new approach for multiple source assessment in heterogeneous river systems: model structure and equations. *Hydrology and Earth System Sciences* **2002c**, *6(3)*, 583–606.

Wendland, F., 1992 Die Nitratbelastung in den Grundwasserlandschaften der "alten" Bundesländer (BRD), Berichte aus der Okologischen Forschung, Band 8. Jülich: Forschungszentrum Jülich (KFA).

Willén, E. Four Decades of Research on the Swedish Large Lakes Mälaren, Hjälmaren, Vättern and Vänern: The Significance ot Monitoring and Remedial Measures for a Sustainable Society. *Ambio* **2001a**, *30(8)*, 458-466.

Willén, E. Phytoplankton and Water Quality Characterization: Experiences from the Swedish large lakes Mälaren, Hjälmaren, Vättern and Vänern. *Ambio* **2001b**, *30(8)*, 529-537.

Whitehead, P.G.; Wilson, E.J.; Butterfield, D. A semi-distributed Nitrogen Model for Multiple Source Assessments in Catchments (INCA): Part 1 - Model Structure and Process Equations. *Sci. Tot. Env.* **1998a**, *210/211*, 547-558.

Wollheim, W. M.; Vörösmarty, C. J.; Peterson, B. J.; Seitzinger, S. P.; Hopkinson, C. S. Relationship between river size and nutrient removal. *Geophys. Res. Lett.* **2006**, *33*, L06410, doi:10.1029/ 2006GL025845.

Wulff, F.; Bonsdorff, E.; Gren, I-M.; Johansson, S.; Stigebrandt, A. Giving advice on cost effective measures for a cleaner Baltic sea: a challenge for science. *Ambio* 2001, *30(4-5)*, 254-259.