From Ditch to Delta
Nutrient retention in running waters

Promotoren:

Prof. Dr. M. Scheffer
Hoogleraar Aquatische Ecologie en Waterkwaliteitsbeheer,
Wageningen Universiteit, Nederland

Prof. Dr. A.A. Koelmans
Persoonlijk hoogleraar bij de leerstoelgroep Aquatische Ecologie en
Waterkwaliteitsbeheer, Wageningen Universiteit, Nederland

Samenstelling promotiecommissie:

Dr. B. Kronvang, National Environmental Research Institute, Silkeborg, Denmark
Prof. Dr. R.W.P.M. Laane, Universiteit van Amsterdam
Prof. Dr. Ir. O. Oenema, Wageningen Universiteit
Prof. Dr. J.T.A. Verhoeven, Universiteit Utrecht

Dit onderzoek is uitgevoerd binnen de onderzoeksschool WIMEK-SENSE

From Ditch to Delta
Nutrient retention in running waters

Jeroen de Klein

Proefschrift

Ter verkrijging van de graad van doctor
Op gezag van de rector magnificus
Van Wageningen Universiteit
Prof. Dr. M.J. Kropff
In het openbaar te verdedigen
Op vrijdag 6 juni 2008
Des namiddags om half twee in de aula

De Klein, J.J.M. 2008
From Ditch to Delta, Nutrient retention in running waters
PhD-thesis Wageningen University, Wageningen, The Netherlands –
with references – with summary in English and Dutch
ISBN: 978-90-8504-930-2

Contents

Chapter 1

General Introduction

Jeroen de Klein

General Introduction

Background

Nutrient loads and retention in surface waters

Eutrophication has been among the main water quality issues since decades (Ærtebjerg *et al.* 2001). It is caused by excess loads of nutrients (mainly nitrogen and phosphorus) from point and diffuse sources, accelerated by increased anthropogenic activity in the river basins. Major contributing sources are point loads from urban areas and industries, and diffuse emissions from agricultural activity, related to excess fertilizer application (Carpenter *et al.* 1998).

In surface waters, high nutrient concentrations can lead to excessive growth of phytoplankton resulting in a deterioration of the aquatic ecosystem (Smith 2003). Water clarity decreases, oxygen is depleted resulting in fish kills and odour problems, biodiversity declines and harmful toxic algal blooms occur more frequently. This also impairs the use of water for drinking, industry, agriculture, recreation, and other purposes (Boesch 2002). The negative effects on the ecosystem and the value of its services to society can be considerable. For instance, the societal costs of freshwater eutrophication in England and Wales are estimated at £ 75-115 million.yr^{-1} (Pretty *et al.* 2003). Eutrophication also affects coastal marine systems. In the mid 90-ties the total load of nitrogen and phosphorus to the North Sea amounted to around 1100 GgN.y^{-1} and 65 GgP.y^{-1}, of which more than half originated from the Rhine catchment (Figure 1.1). Although recent data analysis indicate that the loads have decreased, the coastal zones of the North Sea are still classified as high risk areas for eutrophication (OSPAR 2003).

The abatement of eutrophication is generally focused on reducing nutrient concentrations in the affected surface waters. This consists of two stages. First, ecological and accompanying chemical targets must be set, that protect the waters from undesirable effects. Secondly, to reach the targets measures should be developed and implemented to reduce the emission of nutrients to the surface waters (Laane *et al.* 2005). When developing a policy to regulate emission, it is important to note that the link between emission levels and the final concentrations in the downstream waters is not straightforward. Numerous studies show that the sum of the emissions can deviate quite strongly from the load at the outflow of the catchments (Svendsen & Kronvang 1993; Van Breemen *et al.* 2002). During transport through the ditches, streams and rivers physical and biochemical processes transform, remove or release nutrients, generally resulting in a sink of nutrients in the surface water system. The difference between the total incoming emissions and the exported loads out of the catchment is commonly indicated as *Retention.*

For design of emission reduction measures and evaluation of effectiveness it is essential to have a quantitative insight in the fate of nitrogen and phosphorus in surface waters (Kronvang *et al.* 2005). Nutrients budgets at different scales still contain considerable errors and uncertainties, which largely can be contributed to retention processes (De Vries *et al.* 2003; Nixon *et al.* 1996)

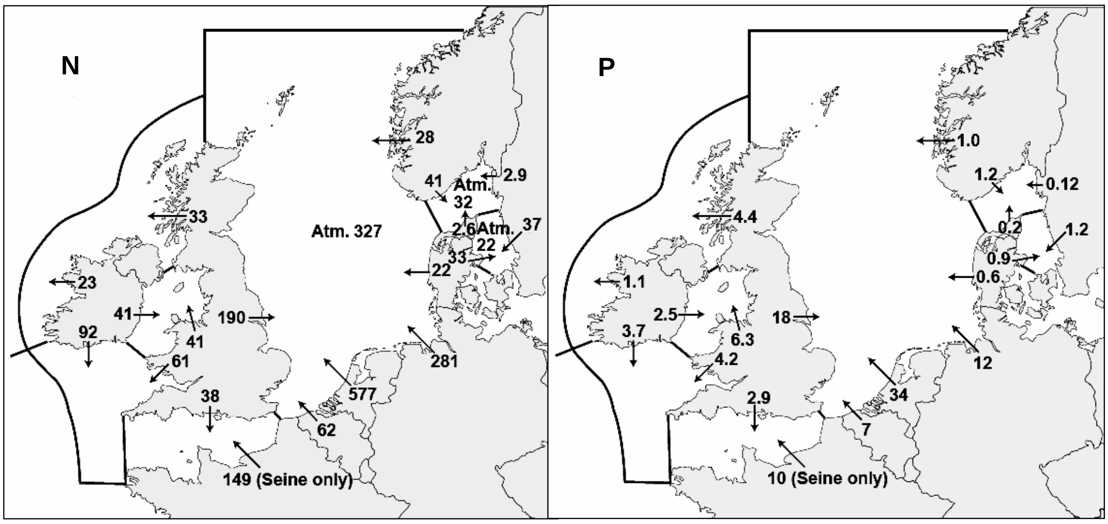


Figure 1.1 *Nitrogen and phosphorus loads to the North Sea in 1995 in Gg.y^{-1} (maximum estimates) (data from OSPAR 1997)*

Definition of retention

There is no complete consensus on the definition of retention (Kronvang *et al.* 2004). Some authors distinguish between retention and removal, in which the former is defined as a temporary storage in biomass or sediment and the latter is used to express a more permanent elimination like gaseous losses of nitrogen via denitrification. However, it is common practice to apply the term retention for the total removal, both temporary and permanent, that is detected within the timeframe used for the analysis.

For this thesis I defined retention as follows: The difference between the incoming load and the exported load within a certain timeframe and within certain spatial boundaries.

The timeframe is usually a season or a year, but depending on the scope of the research other time frames can be used too. Examples of different spatial boundaries are: a catchment, a network of ditches, a river stretch or a lake.
In most cases the outgoing load is smaller than the incoming load, indicating that the water system act as a sink for nutrients. In that case retention has a positive value. However, situations can exist with net release of nutrients, for instance in lakes with loaded sediments or streams during periods of high flow conditions. In such cases retention has a negative value.

Retention may be expressed in absolute terms (eq.1) or relative to the incoming mass flux (eq.2).

$$RET_a = M_{in} - M_{out} \quad \text{(eq.1)} \qquad RET_f = \frac{M_{in} - M_{out}}{M_{in}} \quad \text{(eq.2)}$$

with: RET_a = absolute retention (mass.time^{-1})
RET_f = relative retention or retention fraction (-)
M_{in} = incoming mass load over the system boundaries (mass.time^{-1})
M_{out} = outgoing mass load over the system boundaries (mass.time^{-1})

The rates of individual retention process are generally expressed in mass.area^{-1}.time^{-1} in which *area* relates to area of surface water or sediment. Alternatively, the rates can be expressed in mass.mass^{-1}.time^{-1} in which the second *mass* relates to mass of biofilms, plant biomass or sediment.

Nutrient retention processes

During transport in the surface water system nitrogen and phosphorus are subject to various processes transforming them (e.g. between inorganic-organic and dissolved-particulate) or removing them from the water system (Figure 1.2 and Figure 1.3). Both biotic and abiotic mechanisms regulate the relative pool sizes and transformations of N and P compounds within the water column and the sediment. Biotic processes include assimilation, decomposition, mineralization, nitrification and denitrification. Abiotic processes include sedimentation, adsorption by sediments, and exchange processes between the water column and the sediment on one side and the atmosphere on the other side (Reddy *et al.* 1999).

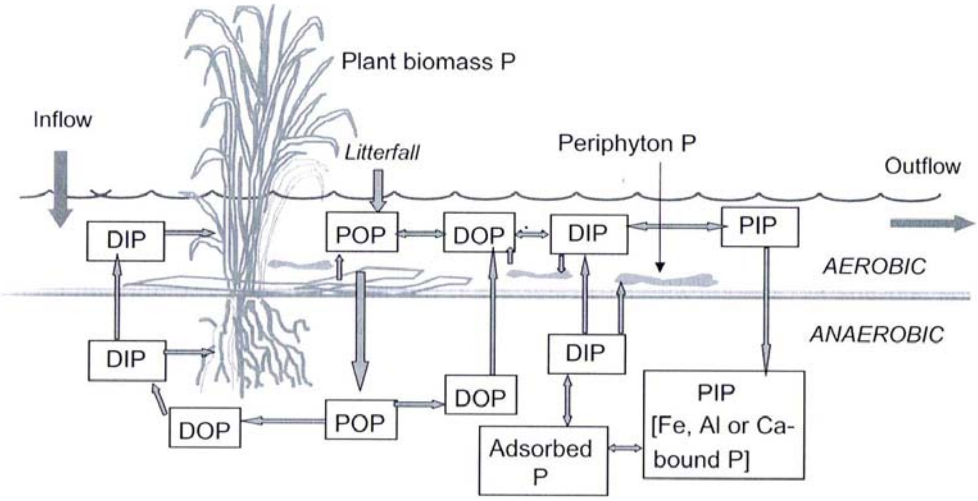


Figure 1.2 *Phosphorus cycle in shallow vegetated fresh waters. Phosphorus fractions include dissolved inorganic (DI), dissolved organic (DO), particulate inorganic (PI) and particulate organic (PO), (from Dunne & Reddy 2005).*

The main processes that remove N and P from the water phase are sedimentation, uptake by primary producers (algae and macrophytes) and denitrification (just N).

Settling of suspended particulate material with N and P will decrease the concentration in the water phase. Oppositely, settled material can be resuspended again by bioturbation, water flow or wind influence, releasing nutrients to the water column. The status of the water system, the period and the temporal and spatial scale of investigation determine whether there is a net sedimentation or resuspension flux.

In small waters with little flow, a net sedimentation will often occur, and when followed by burial this can result in a permanent removal of nutrients (Brenner *et al.* 2006). This is especially the case when watercourses are dredged for maintenance. In the case of phosphorus, such retention is possible even in the absence of dredging. This is because phosphorus may be bound irreversibly in sediments under some conditions (Macrae *et al.* 2003). Often, the fraction of particulate P is far larger than the fraction dissolved P in the water column (Bowes, House & Hodgkinson 2003). Therefore, sedimentation and subsequent burial or dredging is the main retention mechanism for phosphorus in surface waters (Reddy *et al.* 1999).

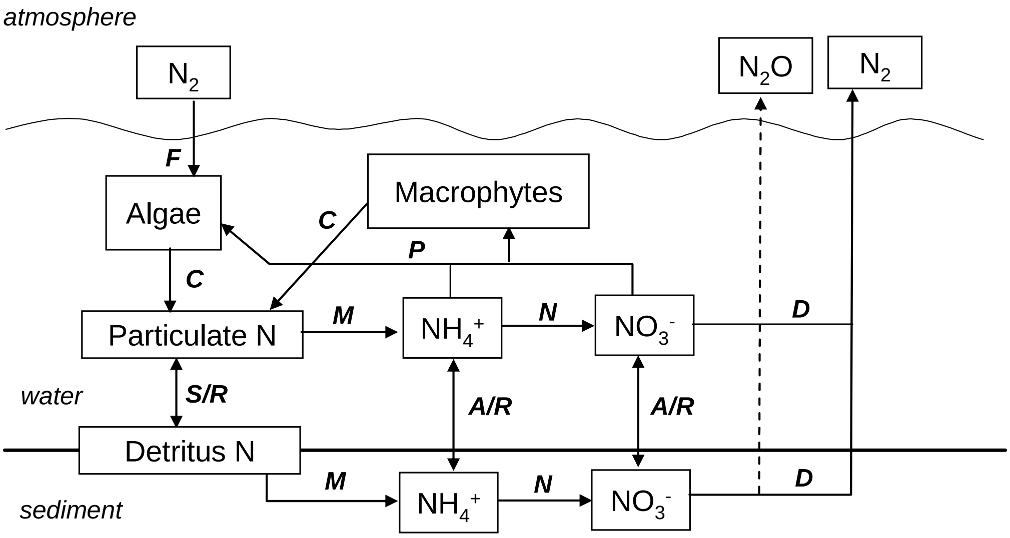


Figure 1.3 *Simplified nitrogen cycle in fresh waters.*
(F=fixation, S/R=sedimentation/resuspension C=decomposition, M=mineralization, N=nitrification, D=denitrification, A/R=absorption/release)

In general, the larger part of nitrogen compounds in running waters is dissolved, mainly inorganic (NO_3^- and NH_4^+). Lacking large quantities of particulate N sedimentation contributes less to nitrogen retention compared to phosphorus (Nixon *et al.* 1996).
Aquatic macrophytes and algae assimilate dissolved inorganic nutrients for biomass production. In the growing season this may lead to a significant reduction of nutrient concentrations in the water column (Bernot *et al.* 2006). In unmanaged aquatic systems the removal of nutrient is only temporary, as mineralization of biomass during fall releases the nutrients again (Clarke 2002). Net retention of nitrogen taken up by plants and algae occurs only when part of the biomass is stored in or on top of the sediment in the form of inert detritus. Obviously, retention of nutrients may be increased by harvesting the aquatic vegetation (Gumbricht 1993). In any case, the accumulation of nutrients in macrophyte and algal biomass usually contributes little to retention in natural waters, as the absolute biomass quantities are generally low and the average nitrogen content of the biomass is in the order of 1 % and for phosphorus in the order of 0.1% (Saunders & Kalff 2001). In constructed wetlands specific management and selection of the vegetation type can enlarge the effectiveness of this removal mechanism (Langergraber 2005; Reinhardt *et al.* 2005).

Denitrification is the main process removing nitrogen in the aquatic environment (Nixon *et al.* 1996; Seitzinger 1988). In the absence of oxygen, facultative anaerobic bacteria use nitrate as the final H acceptor in respiration. In this process nitrate is transformed to gaseous forms of nitrogen (mainly N_2 and some N_2O) that escape to the atmosphere (Gumbricht 1993). The rate of denitrification in aquatic systems can be particularly high if there is a large supply of nitrate and degradable organic carbon, and oxygen concentrations are low. Such conditions occur in the anaerobic layer of the sediment, but also in biofilms on submerged macrophytes and other substrates (Eriksson & Weisner 1997). In waters with a high external input of nitrogen the supply of nitrate for denitrification often comes largely from the water column. However, when water column nitrate becomes limiting nitrate may be supplied largely by nitrification of ammonium. The latter process, known as coupled nitrification-denitrification, is common in fresh surface waters (Van Luijn *et al.* 1999).

In summary, most phosphorus retention in fresh water systems is due to sedimentation and adsorption to sediment. By contrast, the major retention mechanism for nitrogen in fresh waters is denitrification.

Role of aquatic vegetation in nutrient retention

Ditches, brooks, floodplains of rivers and littoral zones of lakes may harbour abundant vegetation. Such aquatic macrophytes may promote retention of nutrients in these water bodies (Clarke 2002). Different mechanisms are involved. In running waters with abundant aquatic vegetation the flow velocity can be reduced significantly (Madsen *et al.* 2001; Clarke 2002). Field studies show that reduction of flow velocities can range up to a factor 10 to 20 compared to unvegetated waters (Sand-Jensen 1998; Schulz *et al.* 2003). The reduced flow implies an increase of the hydraulic residence time allowing the impact of nutrient transformation processes to increase. Decreased flow also leads to an increase in sedimentation and a reduction of resuspension (James, Barko & Eakin 2002; Madsen *et al.* 2001), implying retention of particulate nitrogen and phosphorus. Uptake for growth also reduces nitrogen and phosphorus concentrations, albeit often only temporally, as mentioned earlier.

Last but not least, macrophytes can stimulate denitrification. This is because the plants provide substrate for epiphytic biofilms of denitrifying bacteria (Eriksson & Weisner 1997; Schaller *et al.* 2004), but also because plants supply degradable organic matter that for the denitrification process (Bastviken *et al.* 2007; Weisner *et al.* 1994). In addition, microgradients in redox potential found in plant beds may stimulate the coupled nitrification-denitrification process (Eriksson & Weisner 1999; Kadlec & Knight 1996).

Taken together these mechanisms tend to lead to a high retention of nitrogen and phosphorus in macrophyte dominated fresh waters, compared to unvegetated water systems.

Quantification methods

For estimation of nutrient retention in the aquatic environment different approaches exist (Reddy *et al.* 1999). Here I briefly highlight the merits and drawbacks of the four main approaches, based respectively on mass balances, process rates, empirical relations and deterministic models.

Mass balances.

In mass balance approaches the total retention is estimated from the difference between measured incoming and outgoing loads. This net retention does not provide information on specific internal transformations. Estimating retention with a mass balance approach implies that the uncertainty may be substantial, since the errors and uncertainties of the separate mass fluxes are all reflected in the unknown item, i.e. retention. However, by combining mass budgets of several catchments patterns can be recognized that enable extrapolation of the results to comparable situations (Behrendt & Opitz 1999; Van Breemen *et al.* 2002).

Process rates.

Measurements of individual process provide information on the rates of transformation and removal of nitrogen and phosphorus. Denitrification is probably the most intensively studied, both in the laboratory and under field conditions. In a review of denitrification research in aquatic ecosystems it was found that lakes, rivers, estuaries and coastal zones are studied quite intensively, whereas measurements in smaller water systems (headwaters, ditches) are rare (Pina-Ochoa & Alvarez-Cobelas 2006). The study also suggests that there may be about an order of magnitude of variation in denitrification rates. Reported annual rates range from around 0.3 $\text{molN.m}^{-2}.\text{y}^{-1}$ in estuaries and coastal zones to around 2 $\text{molN.m}^{-2}.\text{y}^{-1}$ in lakes and rivers. Importantly, within the water types even larger differences in denitrification rate are found. Several factors may contribute to such within-system variation. For instance losses of particulate nitrogen and phosphorus through sedimentation are variable, depending on the settling properties of the particles, flow conditions and dimensions of the water system. In addition, presence of macrophyte stands strongly promotes sedimentation rates. Research in the river Spree (Germany) showed sedimentation rates of 0.1-0.2 $molP.m^{-2}.y^{-1}$ and 1-2 $molN.m^{-2}.y^{-1}$ in dense vegetated areas, accounting for up to 25% of the total nutrient retention (Schulz *et al.* 2003). Such variability implies that up-scaling measured process rates to estimate their contribution to retention on larger scales may introduce considerable errors if data are scarce.

Empirical relations.

The dependency of nutrient retention on environmental conditions can also be expressed in simple empirical relations. For instance, for deep lakes Vollenweider showed that the ratio of phosphorus concentration to inflow concentration is related in a simple way to hydraulic residence time (OECD 1982). Similar relations were derived for shallow lakes (Portielje & Van der Molen 1999) and nitrogen retention in lakes (Windolf *et al.* 1996). Also for streams and rivers empirical relations for nutrient retention have been developed, with hydrological conditions as the major explanatory factor (Behrendt & Opitz 1999; Seitzinger *et al.* 2002). Empirical relationships have their well known problems. For instance, a major pitfall of such models is application of the empirical relationship outside the scope that they were derived for. Nonetheless, these methods have proven to be useful in delivering rough estimates of retention in lakes and river catchments on basis of scarce data, a.o. (Arheimer & Liden 2000; Jensen *et al.* 2006).

Deterministic modeling.

An obvious alternative approach to prediction of future developments is the use of deterministic models in which knowledge about the main processes driving an aquatic ecosystem is combined in a set of mathematical equations. A major proble is that all the important mechanisms should be incorporated and hence such models easily become very complex. For simulation the values of the parameters and coefficients have to be set, few of which can actually be determined accurately for specific field situations. Therefore parameters usually need to estimated by fitting the model to data. This implies large uncertainty about the realism of the model, as good results can easily be obtained for the wrong reasons (Scheffer, Bakema & Wortelboer 1993). Nonetheless such models can be useful, especially for exploring hypothesis about the functioning of the system, and obtaining an estimate of the relative importance of different mechanisms.

Various models describing the fate of nutrients in the aquatic environment at different scales have been developed. An example of a complex nutrient and vegetation model is PC-Ditch (Janse 1998). The model comprises nutrient transformations and vegetation growth and transitions, at the scale of an individual watercourse. It has been applied to set critical values for nutrient loads to drainage ditches. INCA is an example of a catchment scale model. It simulates dynamically the nutrient export from different land-use types within a river system, and the in-stream nitrogen and phosphorus concentrations (Wade *et al.* 2002).

Objectives and outline of this thesis

Objectives of the thesis research

The brief overview in this introduction shows that despite the effort that has been put in quantifying and explaining nutrient retention in surface waters, we are still poorly equipped if it comes to accurate prediction of retention and the way in which it may be affected by different water management strategies.

The overall objective of the research reported in this thesis research is to elucidate the fate of nitrogen and phosphorus in running waters and to provide tools that may be used for estimating the effects of different river catchment management plans on nutrient loads.

Outline of this thesis

This thesis addresses various water types at different scales, and covers experimental work as well as data analysis and modeling. Special attention is paid to ditches and headwaters and the role of aquatic vegetation. First I address the nitrogen and phosphorus budgets on a national scale (chapter 2). In this research an alternative method for estimating nutrient loads to the coastal zones is presented, taking into account different pathways and retention processes. Additionally, the propagation of the uncertainties in load calculations and retention estimates on the final loads is studied.

Subsequently (chapter 3) experimental research of denitrification in drainage ditches is presented. The rates of denitrification in ditches were largely unknown, whereas there may be a great potential to remove nitrogen in areas with dense networks of ditches. In addition to quantification of the denitrification rates this research addresses the effect of temperature conditions, an important issue in the light of climate change.

In chapter 4 I present a model of fate of nutrients and suspended matter in streams dominated by aquatic vegetation. The dynamics of growth and decomposition of submerged macrophytes, nutrient transformations and sedimentation and resuspension are studied under various simulated conditions. In the following chapter (5) this model is applied to simulate a lowland stream, and analyze the potential impact of submerged macrophytes and management options on retention of nutrients.

In chapter 6 I develop an empirical model for nutrient export and retention, based on basic catchment properties and nutrient emissions. I test this approach on time series of measurement data of 13 lowland catchments. Using the model, nutrient export can be estimated on a monthly basis, thus showing seasonal dynamics.

Going back to a large scale approach, I present nutrient budgets in subregions of the EU-countries (chapter 7), predicting surface water nutrient concentrations in the far future, assuming agricultural practices to continue unchanged.

Finally, in chapter 8 I reflect on the main results and present a simplified concept of how to deal with nutrient issues in water management.

References

Ærtebjerg G., Carstensen J., Dahl K. & Hansen J. (2001) Eutrophication in Europe's coastal waters, pp. 86. Copenhagen: European Environment Agency.

Arheimer B. & Liden R. (2000) Nitrogen and phosphorus concentrations from agricultural catchments - influence of spatial and temporal variables. *Journal of Hydrology,* **227**, 140-159.

Bastviken S. K., Eriksson P. G., Ekstrom A. & Tonderski K. (2007) Seasonal denitrification potential in wetland sediments with organic matter from different plant species. *Water Air and Soil Pollution,* **183**, 25-35.

Behrendt H. & Opitz D. (1999) Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia,* **410**, 111-122.

Bernot M. J., Tank J. L., Royer T. V. & David M. B. (2006) Nutrient uptake in streams draining agricultural catchments of the midwestern United States. *Freshwater Biology,* **51**, 499-509.

Boesch D. F. (2002) Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. *Estuaries,* **25**, 886-900.

Bowes M. J., House W. A. & Hodgkinson R. A. (2003) Phosphorus dynamics along a river continuum. *Science of the Total Environment,* **313**, 199-212.

Brenner M., Hodell D. A., Leyden B. W., Curtis J. H., Kenney W. F., Gu B. H. & Newman J. M. (2006) Mechanisms for organic matter and phosphorus burial in sediments of a shallow, subtropical, macrophyte-dominated lake. *Journal of Paleolimnology,* **35**, 129-148.

Carpenter S. R., Caraco N. F., Correll D. L., Howarth R. W., Sharpley A. N. & Smith V. H. (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications,* **8**, 559-568.

Clarke S. J. (2002) Vegetation growth in rivers: influences upon sediment and nutrient dynamics. *Progress in Physical Geography,* **26**, 159-172.

De Vries W., Kros J., Oenema O. & De Klein J. (2003) Uncertainties in the fate of nitrogen II: A quantitative assessment of the uncertainties in major nitrogen fluxes in the Netherlands. *Nutrient Cycling in Agroecosystems,* **66**, 71-102.

Dunne E. J. & Reddy K. R. (2005) Phosphorus biogeochemistry of wetlands in agricultural watersheds. In *Nutrient management in agricultural watersheds. A Wetlands Solution* (ed. E. J. Dunne, K. R. Reddy & O. T. Carton), pp. 105-119. Wageningen, The Netherlands: Wageningen Academic Publishers.

Eriksson P. G. & Weisner S. E. B. (1999) An experimental study on effects of submersed macrophytes on nitrification and denitrification in ammonium-rich aquatic systems. *Limnology and Oceanography,* **44**, 1993-1999.

Eriksson P. G. & Weisner S. E. B. (1997) Nitrogen removal in a wastewater reservoir: The importance of denitrification by epiphytic biofilms on submersed vegetation. *Journal of Environmental Quality,* **26**, 905-910.

Gumbricht T. (1993) Nutrient Removal Processes in Fresh-Water Submersed Macrophyte Systems. *Ecological Engineering,* **2**, 1-30.

James W. F., Barko J. W. & Eakin H. L. (2002) Water quality impacts of mechanical shredding of aquatic macrophytes. *Journal of Aquatic Plant Management,* **40**, 36-42.

Janse J. H. (1998) A model of ditch vegetation in relation to eutrophication. *Water Science and Technology,* **37**, 139-149.

Jensen J. P., Pedersen A. R., Jeppesen E. & Søndergaard M. (2006) An empirical model describing the seasonal dynamics of phosphorus in 16 shallow eutrophic lakes after external loading reduction. *Limnology and Oceanography,* **51**, 791-800.

Kadlec R. H. & Knight R. L. (1996) *Treatment Wetlands.*: Lewis Publishers, Baco Raton,.

Kronvang B., Bechmann M., Lundekvam H., Behrendt H., Rubaek G. H., Schoumans O. F., Syversen N., Andersen H. E. & Hoffmann C. C. (2005) Phosphorus losses from agricultural areas in river basins: Effects and uncertainties of targeted mitigation measures. *Journal of Environmental Quality,* **34**, 2129-2144.

Kronvang B., Hezlar J., Boers P., Jensen J. P., Behrendt H., Anderson T., Arheimer B., Venohr M. & Hoffmann C. C. (2004) Nutrient Retention Handbook. Software Manual for EUROHARP-NUTRET and Scientific review on nutrient retention., pp. 103 pp. Oslo, Norway: NIVA.

Laane R., Brockmann U., van Liere L. & Bovelander R. (2005) Immission targets for nutrients (N and P) in catchments and coastal zones: a North Sea assessment. *Estuarine Coastal and Shelf Science,* **62**, 495-505.

Langergraber G. (2005) The role of plant uptake on the removal of organic matter and nutrients in subsurface flow constructed wetlands: a simulation study. *Water Science and Technology,* **51**, 213-223.

Macrae M. L., English M. C., Schiff S. L. & Stone M. A. (2003) Phosphate retention in an agricultural stream using experimental additions of phosphate. *Hydrological Processes,* **17**, 3649-3663.

Madsen J. D., Chambers P. A., James W. F., Koch E. W. & Westlake D. F. (2001) The interaction between water movement, sediment dynamics and submersed macrophytes. *Hydrobiologia,* **444**, 71-84.

Nixon S. W., Ammerman J. W., Atkinson L. P., Berounsky V. M., Billen G., Boicourt W. C., Boynton W. R., Church T. M., Ditoro D. M., Elmgren R., Garber J. H., Giblin A. E., Jahnke R. A., Owens N. J. P., Pilson M. E. Q. & Seitzinger S. P. (1996) The fate of nitrogen and phosphorus at the land sea margin of the North Atlantic Ocean. *Biogeochemistry,* **35**, 141-180.

OECD. (1982) Eutrophication of Waters - Monitoring, Assessment and Control, pp. 154. Paris: Organization for Economic Co-Operation and Development.

OSPAR. (2003) Integrated Report 2003 on the Eutrophication Status of the OSPAR Maritime Area Based upon the First Application of the Comprehensive Procedure.

OSPAR. (1997) Overview of the results of the comprehensive study on riverine inputs and direct discharges (RID) in 1995 and the comprehensive atmospheric monitoring programme (CAMP) in 1995.: Oslo and Paris Commissions.

Pina-Ochoa E. & Alvarez-Cobelas M. (2006) Denitrification in aquatic environments: A cross-system analysis. *Biogeochemistry,* **81**, 111-130.

Portielje R. & Van der Molen D. T. (1999) Relationships between eutrophication variables: from nutrient loading to transparency. *Hydrobiologia,* **408**, 375-387.

Pretty J. N., Mason C. F., Nedwell D. B., Hine R. E., Leaf S. & Dils R. (2003) Environmental costs of freshwater eutrophication in England and Wales. *Environmental Science & Technology,* **37**, 201-208.

Reddy K. R., Kadlec R. H., Flaig E. & Gale P. M. (1999) Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology,* **29**, 83-146.

Reinhardt M., Gachter R., Wehrli B. & Muller B. (2005) Phosphorus retention in small constructed wetlands treating agricultural drainage water. *Journal of Environmental Quality,* **34**, 1251-1259.

Sand-Jensen K. (1998) Influence of submerged macrophytes on sediment composition and near-bed flow in lowland streams. *Freshwater Biology,* **39**, 663-679.

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

Schaller J. L., Royer T. V., David M. B. & Tank J. L. (2004) Denitrification associated with plants and sediments in an agricultural stream. *Journal of the North American Benthological Society,* **23**, 667-676.

Scheffer M., Bakema A. H. & Wortelboer F. G. (1993) Megaplant - a Simulation-Model of the Dynamics of Submerged Plants. *Aquatic Botany,* **45**, 341-356.

Schulz M., Kozerski H. P., Pluntke T. & Rinke K. (2003) The influence of macrophytes on sedimentation and nutrient retention in the lower River Spree (Germany). *Water Research,* **37**, 569-578.

Seitzinger S. P. (1988) Denitrification in Fresh-Water and Coastal Marine Ecosystems - Ecological and Geochemical Significance. *Limnology and Oceanography,* **33**, 702-724.

Seitzinger S. P., Styles R. V., Boyer E. W., Alexander R. B., Billen G., Howarth R. W., Mayer B. & Van Breemen N. (2002) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry,* **57**, 199-237.

Smith V. H. (2003) Eutrophication of freshwater and coastal marine ecosystems - A global problem. *Environmental Science and Pollution Research,* **10**, 126-139.

Svendsen L. M. & Kronvang B. (1993) Retention of Nitrogen and Phosphorus in a Danish Lowland River System - Implications for the Export from the Watershed. *Hydrobiologia,* **251**, 123-135.

Van Breemen N., Boyer E. W., Goodale C. L., Jaworski N. A., Paustian K., Seitzinger S. P., Lajtha K., Mayer B., Van Dam D., Howarth R. W., Nadelhoffer K. J., Eve M. & Billen G. (2002) Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. *Biogeochemistry,* **57**, 267-293.

Van Luijn F., Boers P. C. M., Lijklema L. & Sweerts J. (1999) Nitrogen fluxes and processes in sandy and muddy sediments from a shallow eutrophic lake. *Water Research,* **33**, 33-42.

Wade A. J., Durand P., Beaujouan V., Wessel W. W., Raat K. J., Whitehead P. G., Butterfield D., Rankinen K. & Lepisto A. (2002) A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrology and Earth System Sciences,* **6**, 559-582.

Weisner S. E. B., Eriksson P. G., Graneli W. & Leonardson L. (1994) Influence of Macrophytes on Nitrate Removal in Wetlands. *Ambio,* **23**, 363-366.

Windolf J., Jeppesen E., Jensen J. P. & Kristensen P. (1996) Modelling of seasonal variation in nitrogen retention and in-lake concentration: A four-year mass balance study in 16 shallow Danish lakes. *Biogeochemistry,* **33**, 25-44.

Chapter 2

Nutrient loads to the Dutch part of the North Sea: sources, pathways, and uncertainties

Jeroen de Klein[1], Danneke Verhagen-Bakker[2], Remi Laane[3] & Theo Prins[3]

[1] *Wageningen University and Research Centre, Wageningen, The Netherlands*
[2] *Nelen & Schuurmans consultants, Utrecht, The Netherlands*
[3] *Deltares, Delft, The Netherlands*

Nutrient loads to the Dutch part of the North Sea: sources, pathways, and uncertainties.

Abstract

We present a novel method to estimate nutrient loads from river basins to the coastal areas. The method is a good alternative, when measurements in river outlets are unavailable or are highly uncertain due to the complex hydrology in the transition from fresh water streams to estuaries and coastal zones. In addition, with this method it is possible to quantify the contribution of different sources and areas to the final load to the sea, by identifying the specific pathways and retention processes during transport.

The method is applied to the Netherlands, resulting in nutrient loads to the Dutch part of the North Sea. By means of a Monte Carlo simulation the uncertainties in the estimated loads are quantified. In the period 1995 to 2005.the average load amounted to 336 ± 41 $Gg.y^{-1}$ total nitrogen and 17.5 ± 3.9 $Gg.y^{-1}$ total phosphorus, of which transboundary sources contributed 75 to 80%. However, expressed per area catchment and per inhabitant, the Dutch part of the river basins contributed equal or even more, compared to the neighboring countries.

The total retention of N and P in the surface waters was 136 ± 36 $GgN.y^{-1}$ and 9.9 ± 2.2 $GgP.y^{-1}$. Although river retention fractions are estimated to be not more than 4-9%, the largest part of the nutrients was retained within the main river system, due to high cumulative loads. This implies that increasing nutrient retention capacity in the rivers, for instance by restoring floodplains, can potentially reduce the nutrient loads to the North Sea.

Introduction

Eutrophication of fresh waters and coastal zones

Eutrophication of both fresh waters and coastal zones is of increasing general concern in many countries. Although substantial progress has been made in combating eutrophication, European policy has consistently identified eutrophication as a priority issue for water protection (European Communities 2005). Eutrophication is caused by an increase in the amount of nutrients being discharged to the water body. As a result algal production will accelerate, and a variety of following impacts may occur, including nuisance and toxic algal blooms, depleted dissolved oxygen, and loss of submerged aquatic vegetation, undesirable disturbance of the balance of organisms present in the water, and deterioration of the water quality (Smith 2003). Besides disturbance of the aquatic ecosystem, eutrophication in coastal and fresh water areas can lead to socio-economic consequences, such as reduced recreational value and drinking water treatment costs (Pretty *et al.* 2003).

For the protection of the marine environment the contracting parties of OSPAR assessed the status of their coastal zones, estuaries and fjords around the North Sea, regarding eutrophication and related effects (OSPAR 2003). The assessment revealed that the investigated waters show increased riverine N and P inputs, both from direct sources as from increased transboundary nutrient inputs. As a result of this many of the assessed coastal areas, fjords and estuaries show elevated levels of chlorophyll-a, and nuisance or toxic phytoplankton biomass. On basis of this assessment coastal regions are classified as Problem Area, Potential Problem Area or Non Problem Area. For the Netherlands it was concluded that the Dutch coastal North Sea waters, Dutch Ems and Western Scheldt estuaries and Dutch Wadden Sea must all be classified as 'Problem Areas' (Figure 2.1).

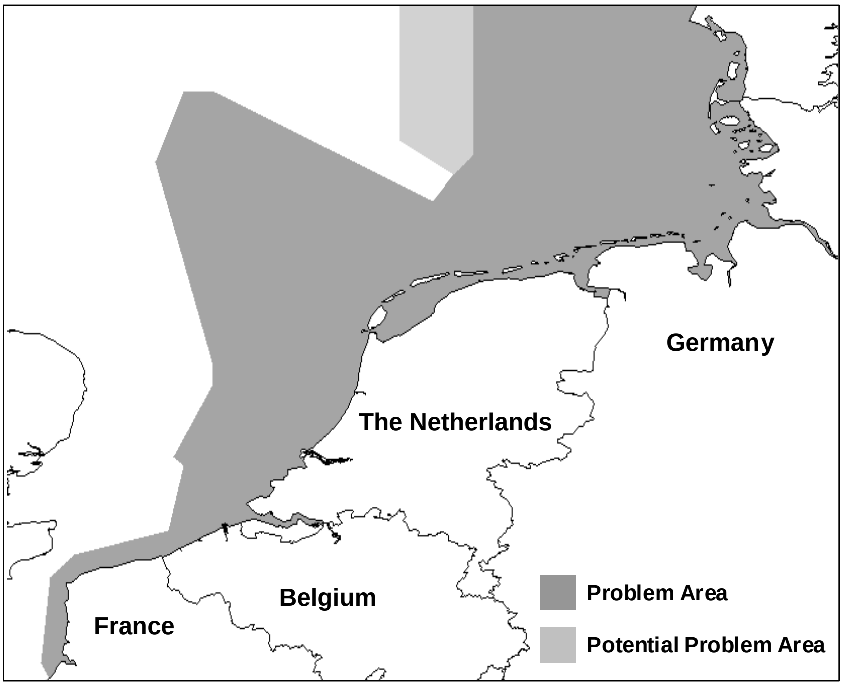


Figure 2.1 *Classification of Dutch coastal waters according to OSPAR eutrophication status assessment (OSPAR 2003).*

The elevated concentrations of nutrients in the coastal zones are mainly caused by the rivers, which accumulate nutrients from the catchments discharging at the rivers. They account for 65 – 80 % of the total nitrogen inputs and for 80 – 85 % of the total phosphorus inputs (OSPAR 2000). Atmospheric deposition also contributes substantially to the nitrogen input, up to 30% of the load to the North Sea (OSPAR 2000).

Although progress has been made in reducing the point emissions to the surface waters, nutrient loads are still high (EEA 2005). The main source of nitrogen is run-off from agricultural land. Most of the phosphorus comes from households and industry discharging treated or untreated wastewater (EEA 2005). Quantitative insight in nutrient loads as well as the magnitude of the separate sources is essential for a proper evaluation of emission reduction measures. Moreover, nutrient transformation during transport through the streams and rivers will significantly affect the final loads to the coastal zones and the rates of transformation must be known (Crouzet *et al.* 1999; Neal & Heathwaite 2005).

Calculation of riverine loads from concentrations measurements and discharges, as prescribed by OSPAR contain substantial uncertainties (De Vries & Klavers 1994). Especially in estuaries with tidal influence mass transport is often difficult to assess. This, among others, hampers the set up of reliable nutrient budgets and therefore identification of major contributing sources.

In this study an alternative method (flow-path approach) is presented to estimate nutrient loads to the Dutch coastal zones of the North Sea and the contribution of individual sources. Different path-ways and route specific retention of nutrients in freshwaters are taken into account.

Objectives of the study

The objectives of this study were:

- to quantify the loads of N and P to the Dutch part of the North Sea coastal zones via the discharge points of the main rivers in the period 1995 to 2005, taking into account nutrient retention in the transporting fresh waters;
- to identify the contribution of regional sources in the Dutch part of the Rhine, Meuse and Scheldt catchment, and the contribution of transboundary nutrient import to the total loads to the coastal zones;
- to estimate the uncertainties in the nutrient load calculations.

Methods

General approach

The general approach of the research is setting up mass balances of total nitrogen (N) and total phosphorus (P) over the Dutch surface waters for each year in the period 1995-2005. By quantifying the sum of the sources and retention the final load to the North Sea is determined. To account for regional conditions and different pathways budgets are set up for 19 individual subcatchments covering the whole Netherlands. The subcatchment borders are defined in the national policy document Water Management 21st century (see Annex 2.1). The mass balances per subcatchment contain the following items:

In:	Import from Belgium and Germany and/or upstream subcatchments
	Diffuse sources in the Netherlands (NL)
	Point sources in the Netherlands (NL)
Out:	Retention in surface waters and estuaries.
	Load to downstream subcatchments and/or to the coastal zones.

Via the so-called flow-path approach the nutrient loads through the subcatchments are coupled. The final results are total annual loads of nitrogen and phosphorus to the North Sea, quantified separately for the main river discharge points

Input Sources

Transboundary loads from Belgium and Germany via the rivers Rhine, Meuse and Scheldt are calculated from measurements at the monitoring stations at Lobith, Eijsden and Doel (see Annex 2.1). Discharges are measured daily and nutrient concentrations weekly to bi-weekly (Riza 2004). Annual loads of total N and P are calculated using the 'weighted concentration method' (De Vries & Klavers 1994).

Diffuse sources consist of leaching from nature areas, agricultural landuse, and atmospheric deposition directly on surface water. Emissions from agriculture are calculated with the modeling tool STONE (Wolf *et al.* 2003). This is a deterministic model that calculates annual emissions in 6000 subregions, covering the whole country. Inputs for the model are fertilizer application and atmospheric deposition on the soil.

For atmospheric deposition on surface water a uniform value is used (Emissieregistratie 2007). The atmospheric load is calculated, related to the total area of open water in the subcatchment.

Point sources consist of direct emissions from industry and domestic sources (direct or via the waste water system). Total loads are calculated from data of the national Emission Registration database (Emissieregistratie 2007). In the database data of 2440 drainage areas are collected, which are summarized for this study per subcatchment.

Flow-path approach

The basis of the flow-path approach is coupling of the 19 subcatchments from upstream to downstream. The nutrient budgets of the separate subcatchments are thus not independent from each other. A subcatchment receives nutrient loads from upstream subcatchments or from transboundary rivers and it transfers loads to downstream subcatchments and finally the coastal area of the North Sea. During transport through the subcatchment nutrients are retained in the regional waters and the main river system including the estuary (Figure 2.2).

Water discharges through the main river system, that connects the subcatchments, are determined with the national distribution model, consisting of a network of main river sections and large lakes (Annex 2.1) (Driesprong-Zoeteman 2004).

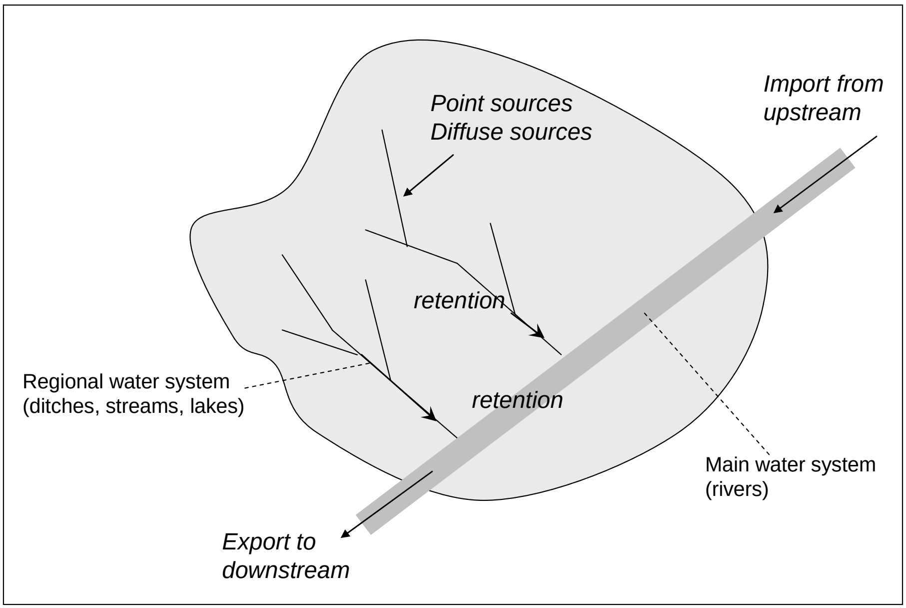


Figure 2.2 *Calculation of nutrient flows within a subcatchment*

Retention of nutrients

Many studies have been conducted on retention of nutrients in surface water. Part of this concerned quantifying process rates of the main nutrient retention processes like denitrification of nitrogen (Pina-Ochoa & Alvarez-Cobelas 2006) and sedimentation of particulate P (Reddy *et al.* 1999). On the other hand research has been focused on setting up nutrient balances of water systems or catchments. Retention is thus determined from the difference of total incoming and outgoing load (e.g. Kronvang *et al.* 2004).

Retention processes vary among the different types of surface waters (stream, river, lake) (Pina-Ochoa & Alvarez-Cobelas 2006). For lowland stream catchments it has been calculated that nutrient retention in surface water can be considerably, but also variable (0.25 – 0.75, expressed as fraction of the total emissions) (e.g. Behrendt & Opitz 1999; Svendsen & Kronvang 1993). Measurements in headwater streams showed that at least half of the incoming inorganic nitrogen load is retained (Peterson *et al.* 2001). Nitrogen removal in 16 catchments in the US, in area ranging from 400 to 20,000 km^2, was around 0.4 – 0.6 (Seitzinger *et al.* 2002). The same study revealed that relative nitrogen retention decreases with increasing river Strahler order, indicating a higher retention fraction upstream compared to downstream river reaches.

In large rivers in the Netherlands (Rhine and Waal) retention of nitrogen is generally very low (0-0.03) and for phosphorus this is usually not higher then 0.05 to 0.10 (Van Der Lee, Venterink & Asselman 2004). The same range of retention values was reported for the Humber River and estuary (UK) in the present state (Jickells *et al.* 2000). For the Mississippi watershed it was found that relative retention of nitrogen reduces with increasing dimension of the water courses (Alexander, Smith & Schwarz 2000). In that study, for small streams a 1st order retention coefficient of 0.45 day^{-1} was calculated and for large rivers around 0.015 day^{-1}. In the sections of the distribution model and the 19 regional subcatchments of this study an average residence time of 2 days is estimated. With the reported 1st order retention coefficient this results in a relative retention factor of 0.6 for streams and 0.03 for rivers.

Analysis of data of a large number of shallow lakes in the Netherlands, covering the period 1980-1996, indicated retention factors of 0.1 to 0.35 for nitrogen and 0 to 0.70 (average 0.45) for phosphorus (Portielje & Van der Molen 1999). In a study of shallow Danish lakes, with hydraulic residence time below 0.25 year, retention of nitrogen was calculated in the range of 0.18 to 0.38 (Windolf *et al.* 1996). An overview of retention factors and calculations methods is reported in the Nutrient Retention Handbook of the Euroharp-project (Kronvang *et al.* 2004).

On basis of the reported studies, and taking into account typical Dutch conditions, we set average retention factors for all water types (table 2.1). These factors represent relative retention, i.e. the fraction of the total incoming load that is retained in the surface water.

Table 2.1 *Estimated average annual retention factors (-) per water type (± indicates average range found in literature).*

Water type	N	P	References
small ditches and headwater streams (< 3 m width)	0.5 ±0.1	0.3 ±0.05	(Peterson *et al.* 2001) (De Klein *et al.* 2008)
ditches and streams (3 tot 6 m width)	0.6 ±0.1	0.5 ±0.1	(Alexander *et al.* 2000) (De Klein *et al.* 2008)
streams (> 6 m width)	0.6 ±0.1	0.5 ±0.1	(Seitzinger *et al.* 2002) (Behrendt & Opitz 1999)
Shallow lakes	0.25 ±0.05	0.45 ±0.1	(Windolf *et al.* 1996) (Portielje & Van der Molen 1999)
rivers	0.04 ±0.01	0.09 ±0.02	(Alexander *et al.* 2000) (Van Der Lee *et al.* 2004)

Overall nutrient retention for all subcatchments is estimated as an area-weighted average factor of small ditches, ditches, streams and lakes. The main river system is treated separately. Here, the retention factor for rivers is applied, except for the lakes in Zeeland and Lake IJssel, for which the retention factor for lakes is used.

Besides the type of surface waters, an important explanatory factor for the variability of retention on a catchment scale is the total area of open water within the catchment. With the run off this determines the displacement time ($m.y^{-1}$), or specific run off ($m.y^{-1}$), in the catchment (Seitzinger *et al.* 2002; Venohr *et al.* 2005). To account for these hydrological conditions, retention factors are corrected for the area of surface water in the subcatchments (spatially variable), and the annual precipitation (temporally variable), related to average conditions in the Netherlands (Eq. 1).

$$C_{SR} = \left(\frac{P / P_{av}}{F_{sw} / F_{sw-a}} \right)^{a} \qquad \text{(Eq.1)}$$

with:
C_{SR} = correction factor for specific runoff (-)
P = Annual precipitation (m)
P_{av} = Average annual precipitation (m)
F_{sw} = Fraction of surface water area (-)
F_{sw-a} = Average fraction of surface water area in the Netherlands (-)
a = power value (-);

The power a expresses the rate of influence of hydraulic residence time on nutrient retention. Various researchers reported values for a, ranging from -0.18 (Windolf *et al.* 1996) to -0.49 (Venohr *et al.* 2005), with P retention being less influenced by hydrological conditions (a closer to zero). We set the value for a at -0.2 for P and -0.4 for N. The total area of surface water and the distribution over the different water types are determined for all subcatchments from digital maps (250 by 250 m grid).

Verification of calculated loads to the North Sea

The flow-path approach results in calculated loads to the North Sea, taking into account retention in the regional waters and the main river system. To verify this method we quantified the loads to the North Sea based on measurements at the river outflow locations (Annex 2.1). Additionally, the loads were compared with calculations in the frame of OSPAR (Pätsch & Lenhart 2004). It should be noted that the ‘measured’ loads are based on the same set of data. However, due to different calculation methods the outcomes are not identical and will differ to a certain extent.

Uncertainties

Like all (model) calculations the presented method for estimating nutrient loads to the North Sea contains uncertainties. These are uncertainties in the input data, river load estimates, retention coefficients etc. For the nitrogen budget on a national level the uncertainties related to all relevant measurement techniques, calculation methods, lack of data etc. are described (Kroeze *et al.* 2003). For evaluation of the results and comparing with results of other studies it is essential to gain quantitative insight in the uncertainties of the final outcomes.

The flow-path approach used in this study consists of a series of calculations, which are all dependent. This hampers the evaluation of the propagation of the uncertainty in a straightforward way. Therefore, we calculated the uncertainties in the loads to the North Sea by means of a Monte Carlo simulation (Vose 1996).

It is expected that the transboundary loads contribute most to the total nutrient load of the Dutch freshwater system, and therefore also to the uncertainties. An extensive study on uncertainties in calculated loads of dissolved and suspended matter in large rivers was done by De Vries & Klavers (1994). The researchers analyzed high-frequency measurement series of ammonium, chloride and suspended matter in Rhine and Meuse. By sub-sampling the total data set the effect of monitoring frequency and calculation method on the *accuracy* (indicating the systematic error) and the *precision* (confidence interval, indicating the random error) were studied. It was concluded that for the weighed concentration method (used in this study) with biweekly concentration measurements the accuracy is high (systematic error is negligible). However, the precision (expressed as a 95% confidence interval) can be considerable and is variable for the different substances. For chloride the precision was ±5-10% and for suspended matter ±20-30%. For this study, we averaged the precision of chloride and ammonium for total nitrogen load and of suspended matter for total phosphorus load. For uniformity the confidence intervals are converted to standard deviation (divided by 1.96). Uncertainties were estimated for all input data and coefficients on basis of literature and expert judgment. We assumed normal distributions for all inputs and coefficients, characterized by a mean and a relative standard deviation (table 2.2).
The Monte Carlo simulation was run 2000 times, with random selection of input values from the normal distributions. By subsequently discarding the uncertainties of certain inputs and rerunning the Monte Carlo simulation the contribution of individual inputs to the final uncertainty is determined.

Table2.2 *Coefficients of variance (CV, as % of mean value) of the inputs and parameters in the flow-path calculation.*

Variable	CV (%)	Remarks
Loads of transboundary rivers	6, 12, 50	6% N, 12% P (Rhine), 50% P (Meuse); (De Vries & Klavers 1994)
Point sources (NL)	20	Explication document Emission Registration
Diffuse sources (NL)	30	Validation Stone; (De Vries *et al.* 2003)
Atmospheric deposition	15-30	(just for N)(Bleeker & Duyzer 2003)
Retention factors	17-25	Range in literature (see table 2.1)

Results and discussion

Emissions to surface water and load to the North Sea via the main Dutch rivers

For the period 1995-2005 yearly average nitrogen and phosphorus budgets are calculated including the loads of the main Dutch rivers to the North Sea (table 2.3 and 2.4). These years represent considerable differences in average precipitation and river discharges. Tables 2.3 and 2.4 show that the main part of the nutrient load to the Dutch surface waters is coming from the transboundary rivers Rhine, Meuse and Scheldt, on average 73% for N and 68% for P respectively. It should be noted that atmospheric deposition is completely regarded as an inland source, which may be argued. Part of the atmospheric pollution is also transboundary, however this is difficult to assess and the total contribution of this source is minor in the total budget.

Furthermore, the calculations show that on average 71% of the total N load to the surface water reached the coastal waters and 29 % of the load was retained during transport in the water system (1995-2005). For total P the surface water retention was even 37 % and the export load to the North Sea 63 % of the total emissions to the surface water. Although retention factors are the smallest in the rivers, the largest part (65-71%) of the total nutrient removal in the surface waters is in the main river system. The load transported through the rivers is the sum of all transboundary and internal sources and therefore absolute retention is relatively large. This is consistent with what was observed for river catchments in the US; relative retention decreases with increasing dimensions, while absolute retention increases due to the cumulative load of the upstream area (Seitzinger *et al.* 2002).

Table 2.3 *Total Nitrogen budget of the fresh surface water system in the Netherlands for the years 1995 to 2005 (Load to North Sea and retention calculated with flow-path approach).*

Nitrogen (GgN.y-1)												Average 1995-2005	
	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	load	%
Input													
Transboundary rivers	469.0	288.0	296.0	404.0	372.0	354.6	384.3	424.9	247.9	270.0	254.3	342.3	73.0
Point sources (NL)	43.0	45.4	43.9	40.7	37.0	53.0	49.0	46.0	44.9	44.7	44.5	44.7	9.5
Diffuse sources (NL)	88.3	40.7	42.0	145.5	83.2	86.7	81.7	70.5	33.9	58.0	45.0	70.5	15.0
Atmospheric deposition	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	2.5
Output													
Retention (regional waters)	47.0	39.4	37.8	70.6	43.3	51.5	49.6	43.5	37.0	47.5	41.3	46.2	9.8
Retention (main river system)*	109.1	80.1	80.0	111.0	89.0	91.0	97.6	102.5	72.5	79.8	74.2	89.7	19.1
Load to North Sea	455.9	266.3	275.8	420.3	371.6	363.5	379.5	407.1	228.9	257.1	240.0	333.3	71.1

* including lake IJssel and Zeeland delta waters

Table 2.4 *Total Phosphorus budget of the fresh surface water system in the Netherlands for the years 1995 to 2005 (Load to North Sea and retention calculated with flow-path approach).*

Phosphorus (GgP.y^{-1})												Average 1995-2005	
	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	load	%
Input													
Transboundary rivers	23.3	15.6	16.6	23.7	24.6	19.2	12.8	29.1	13.8	14.6	10.7	18.5	68.3
Point sources (NL)	7.0	6.7	6.5	5.6	6.0	4.4	4.4	3.9	3.5	3.3	3.1	4.9	18.1
Diffuse sources (NL)	3.8	2.2	2.2	6.4	4.0	4.3	4.7	4.6	2.3	3.5	3.0	3.7	13.6
Atmospheric deposition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Output													
Retention (regional waters)	3.1	3.6	2.9	4.1	3.0	2.9	3.1	2.6	2.1	2.4	2.2	2.9	10.7
Retention (main river system)*	8.7	6.5	7.0	9.2	9.1	7.0	5.4	9.9	5.5	5.9	4.5	7.1	26.2
Load to North Sea	22.3	14.4	15.4	22.4	22.5	18.0	13.4	25.1	12.0	13.1	10.1	17.1	63.1

* including lake IJssel and Zeeland delta waters

Among the years, large differences in the emissions and exported loads can be seen. The period 1995-2005 comprises different hydrological years. 1996 and 2003 were very dry with a precipitation sum of 576 and 631 mm, whereas 1998 was extremely wet (precipitation 1240 mm). The average precipitation in the evaluated period was 839 $mm.y^{-1}$ (Figure 2.3). It is likely that the sum of precipitation will affect the magnitude of nutrients exports and possibly also the share of inland sources to the exports. Regression analysis revealed an increase of the variables with increasing precipitation. However, most of the relations are weak and not significant. An explanation of the weak relations may be that the variation in precipitation is only partially reflected in the Rhine discharge at Lobith, which is the main contributor of the transboundary loads (Figure 2.3). Apparently, a large precipitation sum in the Netherlands does not automatically imply large precipitation in the rest of the Rhine catchment. Moreover, the Rhine discharge is for a large part originating from glaciers.

A significant relation ($p<0.02$) was found between annual precipitation and the contribution of inland nitrogen sources to the export to the North Sea. The latter increases with increasing precipitation. This may be due to the increase of diffuse emissions, mainly leaching from agricultural areas, in relatively wet years.

In general, annual precipitation is not a good predictor for annual nutrient loads to the North Sea.

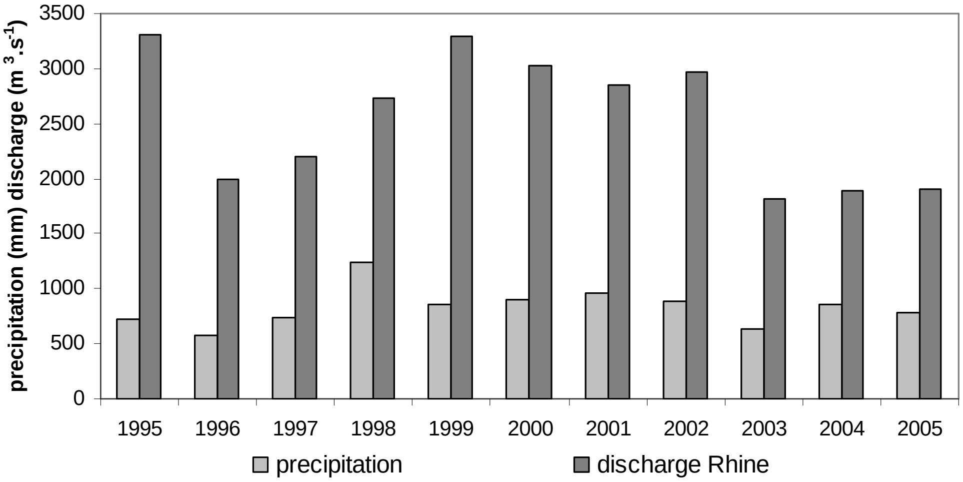


***Figure 2.3** Annual average precipitation in the Netherlands and average discharge of the Rhine at the German-Dutch border.*

Uncertainty analysis

The results of the Monte Carlo simulations are summarized in table 2.5. Values and uncertainties for all inputs, retention and load to the North Sea are presented as an average value, standard deviation (SD) and the coefficient of variance (CV; standard deviation relative to the mean). Figure 2.4 shows the frequency distributions of the final outcome, i.e. the average nutrient loads to the North Sea in the period 1995-2005.

Table 2.5 *Results of Monte Carlo simulations (2000 repetitive calculations)*

Period 1995-2005		N			P	
	mean	SD	CV	mean	SD	CV
	Gg.y^{-1}	Gg.y^{-1}	%	Gg.y^{-1}	Gg.y^{-1}	%
Transboundary rivers	343.2	16.8	5.4	18.7	2.2	12.6
Point sources (NL)	45.5	2.3	5.6	4.9	0.4	7.9
Diffuse sources (NL)	71.9	5.4	8.3	3.8	0.4	10.1
Atmospheric deposition	11.7	1.7	16.0	-	-	-
Retention	136.1	15.8	12.7	9.9	1.1	11.7
Load to North Sea	336.2	20.6	6.7	17.5	2.0	12.3

The outcome of the Monte Carlo simulation is normally distributed and the mean values correspond with the average data presented in table 2.3 and 2.4. This was expected, since the inputs for the calculations were set as normally distributed, with an expectation of the mean error at zero.

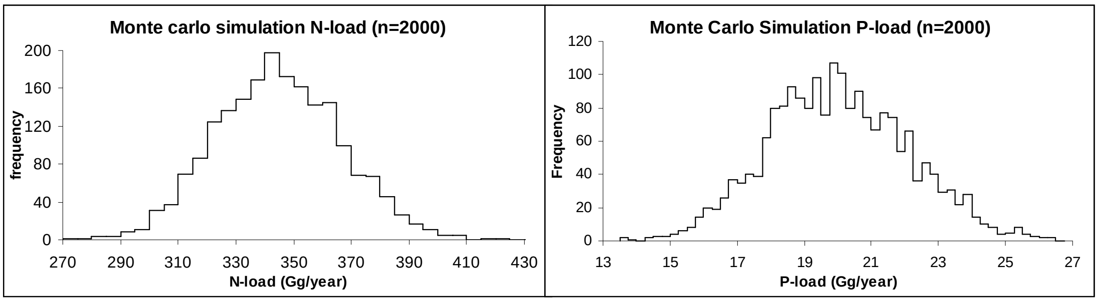


Figure 2.4 *Frequency distribution of the Monte Carlo calculation results (average nutrient loads to the North Sea in the period 1995-2005)*

The coefficient of variance of the load to the North Sea is 6.7 % for N and 12.3 % for P. The higher value for P is due to a higher uncertainty in the calculation of river P loads.

Phosphorus is mainly transported as particulate matter, whereas nitrogen is mainly dissolved. Generally, quantification of suspended matter load contain more uncertainty compared to the load of dissolved substances (De Vries & Klavers 1994). The 95% confidence interval for the average load to the North Sea is 336 ± 41 GgN.y^{-1} and 17.5 ± 3.9 GgP.y^{-1}.

Further analysis of the results of the Monte Carlo simulation revealed that the main contributors to the uncertainty in the final outcome were the transboundary loads (41-50%) and retention (39-47%). The latter is dominated by the uncertainty of the retention in the main water system (rivers).

The coefficients of variance (table 2.5) are lower than the basic coefficients of variance of the different inputs and parameters (table 2.2). For atmospheric deposition and point and diffuse sources this is caused by the fact that all 19 regions are treated separately with their own random sampling of the input values. An overestimation in one region may thus be compensated by an underestimation in another region and visa versa. So the CV of the total input on a national scale becomes lower than the CV's in the individual regions. This can only be applied when uncertainties in the data are related to regional conditions and not to systematic errors in the applied models and calculations methods.

To gain insight in the effect of this assumption we calculated the average load to the North Sea again, now with one standard deviation of all the regions. In this case one random sampling in the normal distribution was applied to all regions. For atmospheric deposition and point sources this revealed a negligible effect on the final outcome. For diffuse sources a limited increase in CV was observed from 8.3 to 9.2% for N and from 10.1 to 12.8% for P. For the retention in different water types and the three transboundary loads the calculations are independent and it is obvious to treat the sampling of input values from the probability function separately.

Verification of the loads calculated with the flow-path approach

In figure 2.5 the calculated nutrient loads to the North Sea via the Dutch main rivers are compared with 'measured' loads at the discharge points. These loads are in fact calculated from measurements of N and P concentrations and discharges. In this paper we use the term 'measured' to distinguish with the calculations of the flow-path approach. The error bars indicate the 95%-confidence intervals for the calculated loads based on the results of the Monte Carlo simulation.

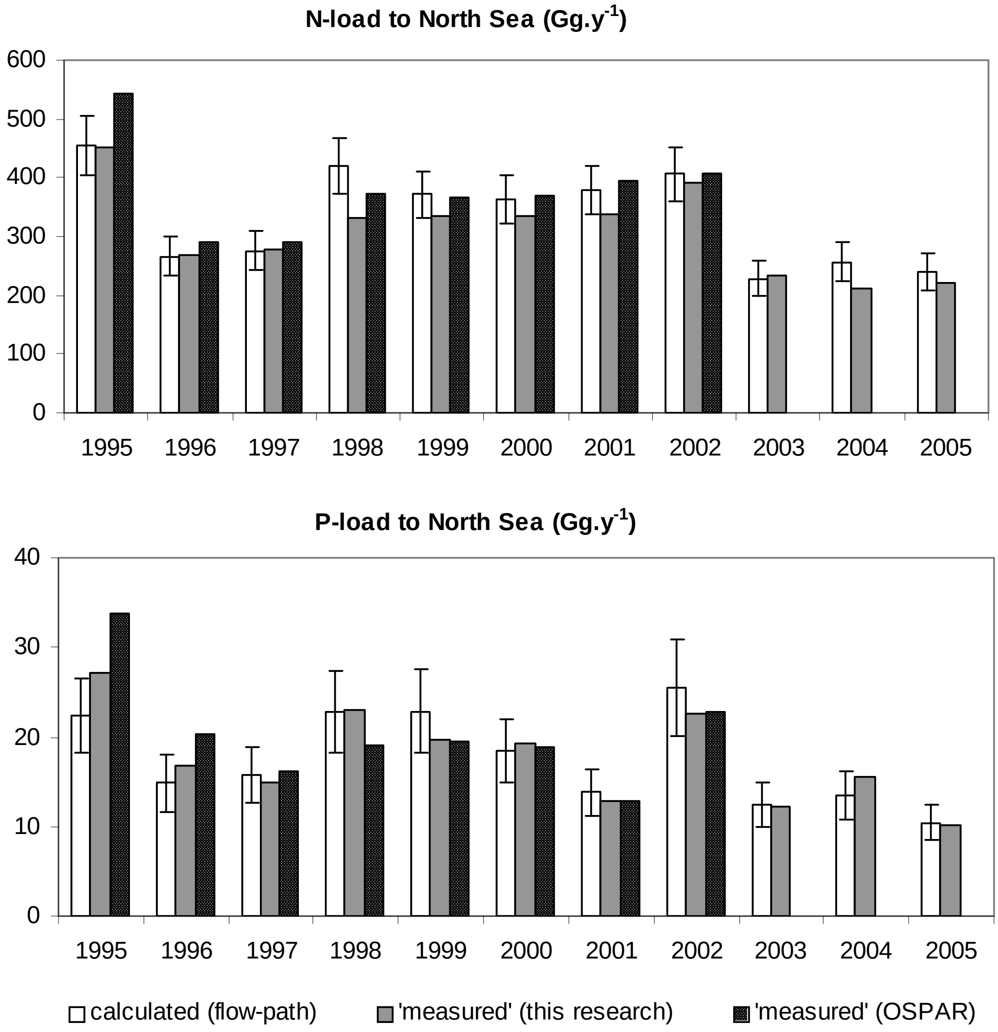


Figure 2.5 *Calculated and measured annual average loads of nitrogen and phosphorus to the North Sea via the main Dutch rivers (error bars represent 95%-confidance interval)*

A reasonable agreement is found between the calculated loads (flow-path) and the sum of the ‘measured’ loads at the river discharge points of the Dutch coast, especially taking into account the estimated uncertainties (Figure 2.5). But also differences can be seen. To determine nutrients loads in coastal zones and estuaries is difficult, as the influence of tide hampers an exact measurement of discharges. Combined with uncertainty related with discontinuous concentration measurements this results in large uncertainties. Although in the study for OSPAR (Pätsch & Lenhart 2004) uncertainties are not discussed, it is likely that load calculations in transitional waters contain larger uncertainties than at monitoring stations in the rivers evaluated by De Vries & Klavers (1994). Differences between 'measured' loads are mainly due to the different calculated methods. We used the weighted concentration method whereas OSPAR loads were calculated with the interpolation method.

The years 2003-2005 show remarkable low loads for both N and P. This is due to relatively low discharge of the Rhine in that period. Average discharges were < 1900 $m^3.s^{-1}$, which is even lower than in the extreme dry year 1996. 2003 was also dry, but for 2004 and 2005 no obvious explanation can be given.

From the validation we can conclude that in general the flow-path approach generates plausible loads to the North Sea, which justifies the additional analysis of calculation results.

Contribution of inland and transboundary sources to the final loads to the North Sea

The contribution of different sources to the total emissions to the Dutch surface waters (table 2.3 and 2.4) is not by definition equal to the share in the final loads to the North Sea. Through different path-ways and regional differences in retention, the ratio between foreign and inland sources can deviate. The here presented flow-path approach enables the quantification of the internal sources and transboundary loads separately and determination of the individual contributions to the final load to the North Sea (table 2.6).

Table 2.6 *Contribution of transboundary annual average loads and inland sources to the load to the North Sea (average 1995-2005).*

	N	P
Total load to North Sea ($Gg.y^{-1}$)	333	19.7
Share of transboundary sources	80.8 %	77.9 %
Share of inland sources	19.2 %	22.1 %

The annual average contribution of inland sources to the eventual load to the North Sea in the period 1995-2005 is 19 % for N and 22 % for P, whereas the share in the emissions to the surface water was 27% and 32% respectively (see table 2.3. and 2.4). In regional surface waters the relative retention of nutrients is larger than in the main rivers, which decreases the share of inland sources to the loads on the marine waters.

It may be expected that the share of transboundary and inland sources is related to the size of the catchment and the number of inhabitants (Billen *et al.* 1999). The Dutch part of the Rhine, Meuse and Scheldt is relatively small. Therefore, we expressed the transboundary and inland nutrient loads per square kilometer catchment area and per inhabitant (table 2.7).

Table 2.7 *Catchment characteristics, transboundary and inland annual average nutrient loads per square kilometer catchment area and per inhabitant (1995-2005)*

Total of Rhine, Meuse and Scheldt		
Catchment area outside the Netherlands	199200	km^2
Catchment area in the Netherlands	37700	km^2
Inhabitants outside the Netherlands	61.2	10^6
Inhabitants in the Netherlands	16.4	10^6
	N	P
Transboundary load to North Sea (Gg.y^{-1})	270	14
Inland load to North Sea (Gg.y^{-1})	66	4
Transboundary load per area (Kg.km^{-2}.y^{-1})	1357	69
Inland load per area (Kg.km^{-2}.y^{-1})	1751	106
Transboundary load per inhabitant (Kg.y^{-1})	4.4	0.23
Inland load per inhabitant (Kg.y^{-1})	4.0	0.24

Per area catchment the Dutch contribution to the North Sea loads is significantly larger than from the neighboring countries. Expressed per inhabitant the differences are small.

Per area and per inhabitant exports from the Rhine, Scheldt and Meuse, as calculated from this study, are compared with data from other river basins (table 2.8). Presented data are from different periods and calculated with different methods. However, some general conclusions can be drawn. The Rhine, Scheldt, Meuse catchment exhibits comparable fluxes as from the PO and Danish sound basins.

In intensively populated river basins riverine fluxes can range up to 1500 kgN.km^{-2}.y^{-1} and around 100 kgP.km^{-2}.y^{-1}. This is about 20 times higher than basins under ‘pristine’ conditions, for which fluxes of around 75 kgN.km^{-2}.y^{-1} and 5 kgP.km^{-2}.y^{-1} were estimated (Howarth *et al.* 1996). On a per inhabitant basis, however, the largest fluxes are found in less populated basins. Apparently, the exported nutrient loads are determined by both the size of the drainage area and the number of inhabitants.

Table 2.8 *Basin characteristics and annual average nutrient loads per square kilometer drainage area and per inhabitant from various river basins.*

			Per Inhabitant ($kg.y^{-1}$)		Per Area ($kg.km^{-2}.y^{-1}$)	
Basin	Population (10^6)	Area (10^3 km^2)	N	P	N	P
Rhine, Scheldt, Meuse [a]	77.6	237	4.3	0.23	1418	76
The Netherlands [a]	16.4	38	4.0	0.24	1751	106
Total Baltic Sea (1996-2000) [b]	83.1	1735	9.3	0.47	446	23
Danish Sounds (1996-2000) [b]	5.2	29	7.3	0.32	1316	58
Po (1990-1995) [c]	16.0	70	6.6	0.51	1514	117
Danube (1989-1992) [d]	76.0	817	9.9	0.66	918	61
Mississippi (1989-1991) [e]	64.0	3230	28	1.70	563	33

[a] this study; [b] (Morth *et al.* 2007); [c] (de Wit & Bendoricchio 2001); [d] (Garnier *et al.* 2006); [e] (Howarth *et al.* 1996)

Conclusions

The presented flow-path method enables the estimation of annual average nutrient loads to coastal zones from emission data and discharges from the main rivers. It accounts for retention of nutrients, both in the large rivers and in the regional surface waters. For the Dutch coastal zone it was found that estimated loads in the period 1995-2005 differ slightly from the measurements at the river outlets (3-8% for N and 1-6% for P depending on the calculation method for the riverine nutrient loads). Given the uncertainties in both the calculated and the ‘measured’ loads we can state that these do not significantly deviate from each other. Thus, the flow-path approach may be a good alternative to estimate loads to coastal areas, when measurements in river outlets are unavailable or are highly uncertain due to the complex hydrology in the transition from fresh water streams to estuaries and coastal zones.

With the presented method it is also possible to apportion the source areas within the river basin. In the period 1995 to 2005 the average nutrient loads to the Dutch part of the North Sea amounted to 336 ± 41 $Gg.y^{-1}$ total nitrogen and 17.5 ± 3.9 $Gg.y^{-1}$ total phosphorus, of which transboundary sources contributed 75 to 80%. However, expressed per area catchment and per inhabitant, the Dutch part of the river basins contributed equal or even more, compared to the neighboring countries. Moreover, it revealed that the share of separate sources in the emissions to the surface water is different from the share in the final loads to the North Sea. This is caused by different path-ways and subsequent retention processes.

The total retention of N and P in the surface waters was 136 ± 36 GgN.y^{-1} and 9.9 ± 2.2 GgP.y^{-1}. Although river retention fractions are estimated to be not more than 4-9%, the largest part of the nutrients was retained within the main river system, due to high cumulative loads. This implies that increasing nutrient retention capacity in the rivers, for instance by restoring floodplains, can potentially reduce the nutrient loads to the North Sea. Therefore, the concept of different pathways and route-specific retention should be taken into consideration when emission reduction measures are evaluated.

References

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

Behrendt H. & Opitz D. (1999) Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia,* **410**, 111-122.

Billen G., Garnier J., Deligne C. & Billen C. (1999) Estimates of early-industrial inputs of nutrients to river systems: implication for coastal eutrophication. *Science of the Total Environment,* **244**, 43-52.

Bleeker A. & Duyzer J. (2003) Belasting van het oppervlaktewater door atmosferische depositie-berekening van directe depositie van 18 probleemstoffen naar water. (in Dutch). Apeldoorn: TNO.

Crouzet P., Leonard J., Nixon S., Rees Y., Parr W., Laffon A., Bøgestrand J., Kristensen P., Lallana C., Izzo G., Bokn T. & Bak J. (1999) Nutrients in European ecosystems, pp. 156. Copenhagen: European Environment Agency.

De Klein J., Aalderink R. H. & Portielje R. (2008) Modeling the impact of aquatic macrophytes and management strategies on nutrient retention in streams. Chapter 5, this thesis. *submitted*.

De Vries A. & Klavers H. (1994) Riverine fluxes of pollutants: monitoring strategy and calculation methods. *European Water Pollution Control,* **4**, 12-17.

De Vries W., Kros J., Oenema O. & De Klein J. (2003) Uncertainties in the fate of nitrogen II: A quantitative assessment of the uncertainties in major nitrogen fluxes in the Netherlands. *Nutrient Cycling in Agroecosystems,* **66**, 71-102.

De Wit M. & Bendoricchio G. (2001) Nutrient fluxes in the Po basin. *Science of the Total Environment,* **273**, 147-161.

Driesprong-Zoeteman A. (2004) Quickscan Herkomstanalyse Stofstromen. Analyse van herkomst, gedrag en verspreiding van 12 landelijke probleemstoffen in Nederlands oppervlaktewater (in Dutch). pp. 102. Dordrecht: Rijkswaterstaat RIZA.

EEA. (2005) Source apportionment of nitrogen and phosphorus inputs into the aquatic environment, pp. 103. Copenhagen: European Environment Agency.

Emissieregistratie. (2007) Jaarcijfers 2005 (in Dutch). MNP, Bilthoven; CBS, Voorburg; RIZA, Lelystad; Alterra, Wageningen; SenterNovem, Utrecht en TNO-MEP, Apeldoorn.

European Communities. (2005) Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Towards a Guidance Document on Eutrophication Assessment in the Context of European Water Policies., pp. 133.

Garnier J., Cebron A., Tallec G., Billen G., Sebilo M. & Martinez A. (2006) Nitrogen behaviour and nitrous oxide emission in the tidal Seine River estuary (France) as influenced by human activities in the upstream watershed. *Biogeochemistry,* **77**, 305-326.

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. & Zhu Z. L. (1996) Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry,* **35**, 75-139.

Jickells T., Andrews J., Samways G., Sanders R., Malcolm S., Sivyer D., Parker R., Nedwell D., Trimmer M. & Ridgway J. (2000) Nutrient fluxes through the Humber estuary - Past, present and future. *Ambio,* **29**, 130-135.

Kroeze C., Aerts R., van Breemen N., van Dam D., van der Hoek K., Hofschreuder P., Hoosbeek M., de Klein J., Kros H., van Oene H., Oenema O., Tietema A., van der Veeren R. & de Vries W. (2003) Uncertainties in the fate of nitrogen I: An overview of sources of uncertainty illustrated with a Dutch case study. *Nutrient Cycling in Agroecosystems,* **66**, 43-69.

Kronvang B., Hezlar J., Boers P., Jensen J. P., Behrendt H., Anderson T., Arheimer B., Venohr M. & Hoffmann C. C. (2004) Nutrient Retention Handbook. Software Manual for EUROHARP-NUTRET and Scientific review on nutrient retention., pp. 103 pp. Oslo, Norway: NIVA.

Morth C. M., Humborg C., Eriksson H., Danielsson A., Medina M. R., Lofgren S., Swaney D. P. & Rahm L. (2007) Modeling riverine nutrient transport to the Baltic Sea: A large-scale approach. *Ambio,* **36**, 124-133.

Neal C. & Heathwaite A. L. (2005) Nutrient mobility within river basins: a European perspective. *Journal of Hydrology,* **304**, 477-490.

OSPAR. (2003) Integrated Report 2003 on the Eutrophication Status of the OSPAR Maritime Area Based upon the First Application of the Comprehensive Procedure.

OSPAR. (2000) Quality Status Report 2000, Region II – Greater North Sea., pp. 136 + xiii. London: OSPAR Commission.

Pätsch J. & Lenhart H. (2004) Daily Loads of Nutrients, Total Alkalinity, Dissolved Inorganic Carbon and Dissolved Organic Carbon of the European Continental Rivers for the Years 1977-2002, pp. 165. Hamburg, Germany: Zentrum für Meeres- und Klimaforschung der Universität Hamburg, Institut für Meereskunde.

Peterson B. J., Wollheim W. M., Mulholland P. J., Webster J. R., Meyer J. L., Tank J. L., Marti E., Bowden W. B., Valett H. M., Hershey A. E., McDowell W. H., Dodds W.

K., Hamilton S. K., Gregory S. & Morrall D. D. (2001) Control of nitrogen export from watersheds by headwater streams. *Science,* **292**, 86-90.

Pina-Ochoa E. & Alvarez-Cobelas M. (2006) Denitrification in aquatic environments: A cross-system analysis. *Biogeochemistry,* **81**, 111-130.

Portielje R. & Van der Molen D. T. (1999) Relationships between eutrophication variables: from nutrient loading to transparency. *Hydrobiologia,* **408**, 375-387.

Pretty J. N., Mason C. F., Nedwell D. B., Hine R. E., Leaf S. & Dils R. (2003) Environmental costs of freshwater eutrophication in England and Wales. *Environmental Science & Technology,* **37**, 201-208.

Reddy K. R., Kadlec R. H., Flaig E. & Gale P. M. (1999) Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology,* **29**, 83-146.

Riza. (2004) MWTL Monitoring Zoete Rijkswateren (in Dutch). pp. 128. Lelystad: Riza, Afdeling Informatie en Meettechnologie Meetnetten.

Seitzinger S. P., Styles R. V., Boyer E. W., Alexander R. B., Billen G., Howarth R. W., Mayer B. & Van Breemen N. (2002) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry,* **57**, 199-237.

Smith V. H. (2003) Eutrophication of freshwater and coastal marine ecosystems - A global problem. *Environmental Science and Pollution Research,* **10**, 126-139.

Svendsen L. M. & Kronvang B. (1993) Retention of Nitrogen and Phosphorus in a Danish Lowland River System - Implications for the Export from the Watershed. *Hydrobiologia,* **251**, 123-135.

Van Der Lee G. E. M., Venterink H. O. & Asselman N. E. M. (2004) Nutrient retention in floodplains of the Rhine distributaries in The Netherlands. *River Research and Applications,* **20**, 315-325.

Venohr M., Donohue I., Fogelberg S., Arheimer B., Irvine K. & Behrendt H. (2005) Nitrogen retention in a river system and the effects of river morphology and lakes. *Water Science and Technology,* **51**, 19-29.

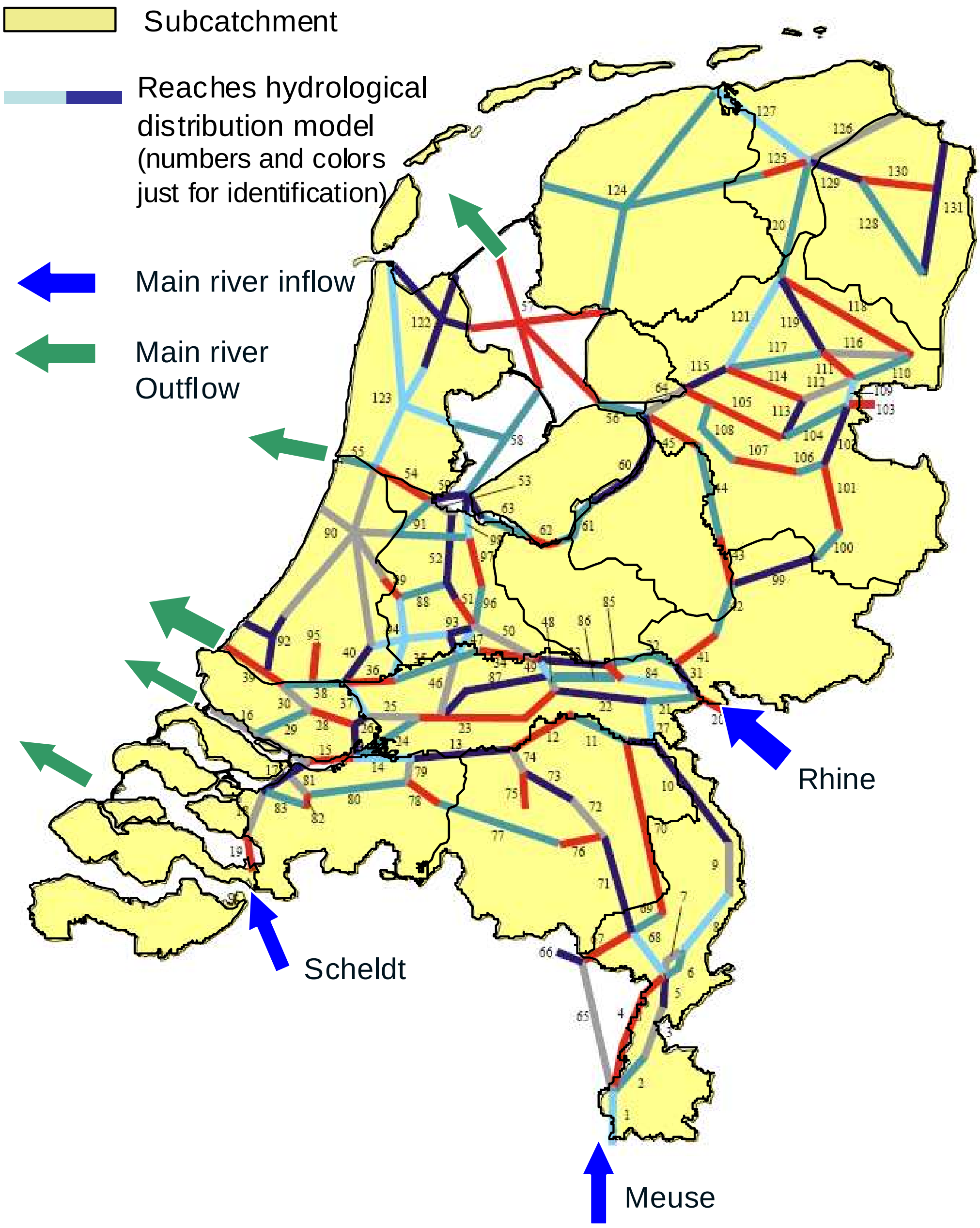
Vose D. (1996) *Quantitative risk analysis: a guide to Monte Carlo simulation modelling*. New York: John Wiley & Sons, Inc.

Windolf J., Jeppesen E., Jensen J. P. & Kristensen P. (1996) Modelling of seasonal variation in nitrogen retention and in-lake concentration: A four-year mass balance study in 16 shallow Danish lakes. *Biogeochemistry,* **33**, 25-44.

Wolf J., Beusen A. H. W., Groenendijk P., Kroon T., Rotter R. & van Zeijts H. (2003) The integrated modeling system STONE for calculating nutrient emissions from agriculture in the Netherlands. *Environmental Modelling & Software,* **18**, 597-617.

Annex 2.1

Overview subcatchment and hydrological distribution model



Chapter 3

Effect of temperature on denitrification in vegetated ditches

Jeroen de Klein, Jayne Rattray and Els Faassen

Wageningen University and Research Centre, Wageningen, The Netherlands

(Submitted)

Effect of temperature on denitrification in vegetated ditches

Abstract

Water column and sediment denitrification rates were measured *in situ* in vegetated ditches using ^{15}N Isotope Pairing Techniques. Weekly and daily measurements were conducted in summer and fall to study the effect of environmental and weather conditions.

Denitrification in drainage ditches ranged from 200 to 350 μmol.m^{-2}.h^{-1} during summer months and from 50 to 150 μmol.m^{-2}.h^{-1} in the fall. In general, rates were comparable to denitrification rates previously reported for rivers and wetlands.

We estimated the annual removal of nitrogen from agricultural ditches, via denitrification to be 15 gN.m^{-2}.y^{-1}. In areas with a dense network of drainage ditches this represents a high potential for removal of nitrogen, leached from agricultural areas. Our results suggest that denitrification in ditches can remove more than 50% of the total diffuse inputs.

The main driver for temporal variability of denitrification rates in vegetated ditches was found to be water temperature. The overall Arrhenius temperature coefficient was 1.28, which is significantly higher than reported coefficients so far.

The high temperature dependency means that with a temperature rise of 3 ^{o}C, as foreseen in IPCC scenarios denitrification in ditches could double.

Introduction

Denitrification is a major process removing nitrogen from surface waters and is therefore an important mechanism for the control of eutrophication (Seitzinger 1988). It is a dissimilative process in which a whole range of organisms including heterotrophic and lithotrophic bacteria, fungi, and archaea can transform nitrate to nitrous oxide or nitrogen gas. Denitrification requires anaerobic conditions and the availability of degradable organic carbon as the electron donor and nitrate (instead of oxygen) as an electron acceptor (Burgin & Hamilton 2007). Nitrate can be supplied either from external sources or from ammonium oxidation (nitrification). In systems with low internal inputs of nitrate the main nitrogen removal pathway is coupled nitrification-denitrification, which requires both aerobic and anaerobic conditions (Van Luijn *et al.* 1999). Over short distances, aerobic and anaerobic sites can be present in sediment layers or in epiphytic biofilms. In wetlands and ditches, submerged macrophytes support the denitrification process by offering attachment surfaces for denitrifying biofilms. In addition, macrophytes supply organic carbon from plant litter and from living biomass (Bachand & Horne 2000; Weisner *et al.* 1994). Moreover, by growth and respiration, macrophytes determine the oxic conditions in the water column to a large extent. Therefore, it is clear that aquatic vegetation plays a crucial role for denitrification in shallow water bodies.

Artificial drainage systems have been constructed to facilitate agricultural practices. These drainage systems typically consist of a network of shallow ditches (< 1 m deep) ranging from one to a few meters wide. During wet periods ditches transport surface runoff and subsurface drainage water away from agricultural fields, whereas in dry periods water is supplied for infiltration. In most agricultural areas in the lower parts of Western Europe and North-America, ditches are the dominant water type (Strock, Dell & Schmidt 2007) (Oenema, van Liere & Schoumans 2005). For the Netherlands, the total length of ditches ranging from one to six meters in width is estimated at almost 300,000 km (Janse 1998). In the western provinces, the density ranges from 8 to 12 km of ditches per km^2. Ditches are generally eutrophic due to high nutrient loading from adjacent fields. Leaching of nitrogen and phosphorus originates from excess fertilizer applications and from mineralization of the organic soils (Oenema & Roest 1998; van Beek *et al.* 2004). Analysis of about 3000 sampling locations in Dutch ditches (1985-2005) showed that mean total-N concentrations ranged from 2 to 9.7 $mgN.l^{-1}$ (10- and 90-percentile respectively) with a median value of 4.2 $mgN.l^{-1}$. Average total P concentrations ranged from 0.11 to 1.7 $mgP.l^{-1}$ (median 0.32 $mgP.l^{-1}$). Excess phosphorus is stored in sediments and plant biomass, whereas nitrogen is cycled faster between the different soluble forms and organic matter (Burgin & Hamilton 2007) (Reddy *et al.* 1999).

The permanent removal of nitrogen via denitrification results in a decrease of nitrogen concentrations and thus the subsequent nitrogen loads to downstream regions (Pina-Ochoa & Alvarez-Cobelas 2006). Rates of denitrification in the aquatic environment have been studied intensively, at different scales and in a variety of water types (a.o. (Seitzinger 1988) (Dong *et al.* 2000; Pattinson, Garcia-Ruiz & Whitton 1998; Pina-Ochoa & Alvarez-Cobelas 2006). Denitrification rates can be highly variable, both temporally and spatially (Seitzinger 1988; Pina-Ochoa & Alvarez-Cobelas 2006). Most research has been conducted on wetlands, rivers, estuaries and coastal areas, whereas denitrification studies in ditches are rare. The physical dimensions of ditches can be compared to the head waters of streams and brooks. However, in ditches the hydrological residence time is generally much longer and more variable (hours to weeks). In addition, primary production, including macrophyte growth is much larger in ditches. Therefore, previously reported denitrification rates may not be representative for what might be expected in ditches.

Like many microbial processes, a major factor influencing the rates of denitrification is temperature. Generally, higher water temperatures enhance biochemical processes in natural aquatic systems, which usually have temperatures in the range of 5-25 ^{o}C (Schwoerbel 1984). An increase in temperature results in a faster cycling of carbon, nutrients and oxygen both in the water column and the sediment. Experimentally, the direct effect of temperature on the rate of denitrification has shown that the activity of denitrifying bacteria increases with increasing temperature, with optimum rates occurring from 30-35 ^{o}C (Stanford, Dzienia & Vanderpol 1975) (Pfenning & McMahon 1997). Temperature also indirectly affects N-removal by denitrification, due to stimulation of mineralization and nitrification, resulting in higher nitrate availability. To complicate the matter further, the effect of temperature on denitrification is also affected by primary production, since denitrification is very sensitive to the presence of dissolved oxygen (Christensen *et al.* 1990). In particular, the productivity of epiphytic biofilms regulates small scale oxic and anoxic conditions and thus influences potential denitrification rates (Eriksson & Weisner 1997). In addition, denitrification can be inhibited by primary producers through competition for ammonium and nitrate (Cabrita & Brotas 2000). We have constructed a flow diagram summarizing hypothesized direct and indirect effects of temperature on denitrification (Figure 3.1).

In this study we explore how denitrification measured in situ in ditches varies over time and estimate the overall effect of temperature on this complex process.

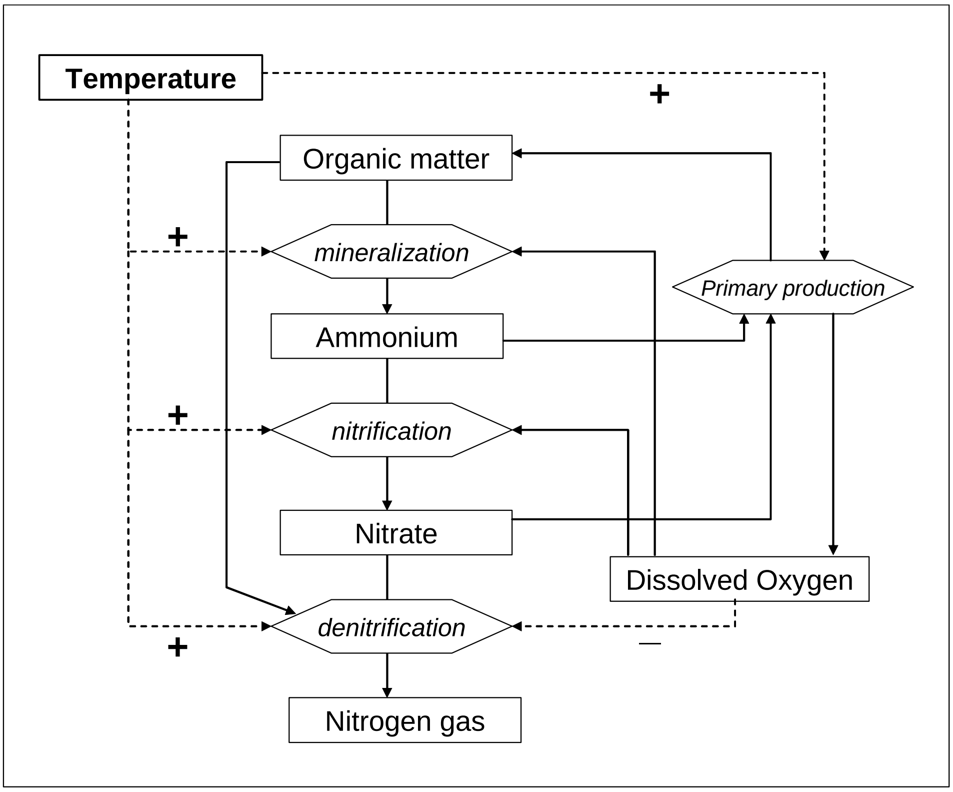


Figure 3.1 *Schematic presentation of the effect of temperature on nitrogen cycling in aquatic systems.*

Methods

Study site

The field study was conducted in an experimental ditch system at Wageningen University. The ditches were originally constructed in the 1970’s for research on water flow patterns in vegetated ditches. During the last 30 years the watercourses were managed according to typical agricultural practices, resulting in vegetated ditches with a variety of submerged macrophytes (e.g. *Potamogeton sp., Elodea*, *Hydrocharis*) and patches of floating duckweed (*Lemna sp.*). Inflow of groundwater from a reservoir was regulated with a pump and both inflow and outflow were measured using V-notch weirs. An impermeable layer under the ditches prevented interaction with groundwater and enabled the setup of adequate water and nutrient budgets. For the entire experiment, conducted between July and September 2001 and July and November 2002, the water flow was set at 1.5 $l.sec^{-1}$, which resulted in a water residence time of 4 days. During all experiments, the ditches were artificially elevated to a concentration of ~1-2 mg N l^{-1} NO_3^-, to mimic the nitrate concentrations commonly found in agricultural ditches in the Netherlands. The nitrate solution was prepared using agricultural grade KNO_3 fertilizer and demi-water, and was added to the inflow water using a Watson-Marlow pump.

Setup of experiments

First, a pilot study was performed between July and September 2001, to optimize the experimental setup and to study the difference between measurements taken during the day (13.00–16.00) and at night (1.00-4.00). In the same experiment the effect of macrophytes on denitrification was investigated. We measured sediment and water column denitrification on bare sediment, sediment covered with *Elodea* and sediment with floating plants (*Hydrocharis morsus-ranae)*, during both the day and night, all in triplicate.

Subsequent to the pilot study, weekly denitrification sampling sessions were conducted between July and August 2002, and daily measurements were taken for 20 days in September and October. In order to measure during a range of different weather conditions, additional spot sampling was also performed in October and November, when precipitation increased and temperature decreased.

Denitrification measurements

Denitrification is often measured under laboratory conditions, using water and sediment samples removed from *in situ* conditions (Pina-Ochoa & Alvarez-Cobelas 2006). Therefore, potential denitrification rates are most commonly determined by manipulating the *in situ* environmental conditions (Bastviken *et al.* 2007; Dong *et al.* 2000). In order to gain a better idea of the actual rate of denitrification *in situ*, we measured denitrification in the ditch itself, using small enclosures. For the detection of denitrification we selected the ^{15}N isotope-pairing technique (Nielsen 1992).

During the pilot study and the first period of weekly sampling we used three separate cylindrical chambers that were pushed a few centimeters into the sediment, remaining there for a period of ca. 3 hours. The placement and removal of the cylinders caused some disturbance of the sediment and the macrophytes. We assumed this to be of minor effect during the 7 day interval time between sampling. However, to avoid this disturbance during the daily sampling, we designed and constructed a split-box measuring device, which consisted of three identical chambers (Figure 3.2). The bottom part of the box was placed on and pushed partly into the sediment, and was left there for the entire research period (Figure 3.2, top). The top part was securely attached to the bottom section, only when the measurements were actually conducted, from 09.00 to 12.00 (Figure 3.2, bottom). This procedure enabled *in situ* conditions and processes to continue during most of the day and avoided stirring up the sediment at every occasion measurements were taken. The three chambers represented replicates of denitrification rates.

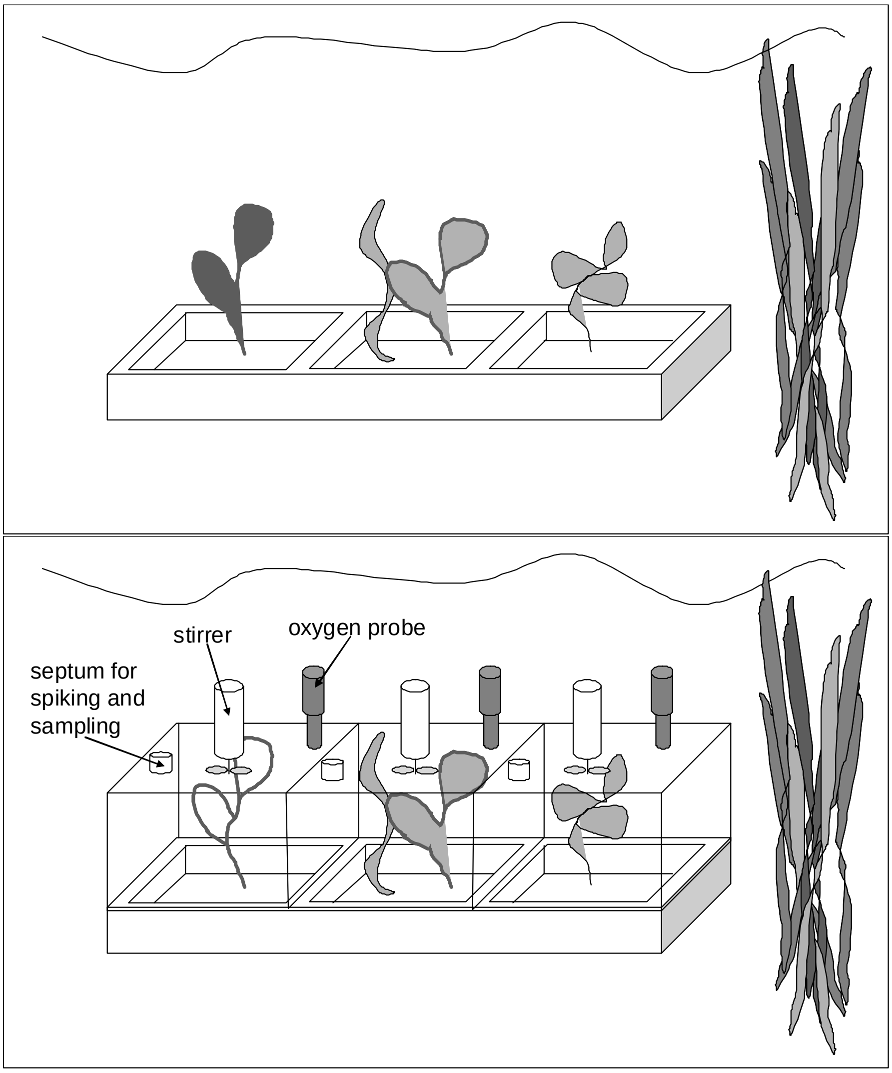


Figure 3.2 *In situ denitrification measurement enclosures.*
Top figure: open during normal conditions; bottom figure: closed during measurements.

Denitrification rates were determined *in situ* using IPT adapted from the NICE (Nitrogen Cycling in Estuaries) protocol handbook (Dalsgaard 2000). With this method denitrification of both nitrate sources, water column and nitrification, can be determined (Steingruber *et al.* 2001). We placed Perspex chambers on the ditch bottom, enclosing part of the water column and submerged macrophytes. After placement of the sampling enclosures the system was left to settle for 30 minutes before switching on the stirrers. Each chamber was spiked using 1 molar $^{15}NO_3^-$, (99% purity) resulting in a $^{15}NO_3$-concentration of 0.5 to 0.9 mgN.l^{-1} in the chambers. Water (containing the gaseous isotopes $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$) was sampled 0.5, 1.5 and 2.5 hours after spiking, using syringes (5 ml), and injected into 10 ml Exetainer ® (Labco, High Wycombe) glass sampling tubes. The Exetainer ® tubes were pretreated with 100 µl of ZnCl (50% w/v), to terminate further biological activity, and tightly sealed using caps with a rubber septum. Subsequently the tubes were flushed for 2 minutes with helium gas (250 ml min^{-1}) using a syringe system, and equilibrium pressure in the tubes was attained using a helium balloon. Directly prior to sampling, 5 ml of helium gas was extracted from the sampling tubes, to make a vacuum space for the 5 ml water sample. After injecting the water sample the Exetainer® tubes were kept refrigerated prior to analyzing the nitrogen $^{29}N_2$ and $^{30}N_2$ isotopes using isotope ratio mass spectrometry (IRMS).

For calibration of the absolute amount of N_2-gas measured with IRMS, six standard solutions were prepared in triplicate. 5 ml of gas was removed from pre-prepared Exetainer ® tubes (see above) and 5 ml of re-aerated (to atmospheric concentrations) demi-water was injected. Volumes of 0, 50, 100, 200, 300 and 400 µl N_2 gas were subsequently added to the tubes using glass syringes. Exetainer ® tubes containing standard solutions and samples (removed from refrigeration) were placed in a shaker for ~ 30 min to induce equilibrium between water sample and headspace. Isotopic ratios of the N_2 gas in the headspace was analyzed using a Finnigan MAT, type Delta C, isotope ratio mass spectrometer (IRMS). To account for instrumental drift during the IRMS analysis, a reference gas was analyzed with every sample.

Field measurements and analyses

During the experiment, dissolved oxygen concentrations (DO) and temperature in the ditch was measured continuously using an O_2 /temperature probe and recorded using a data logger. DO and temperature was also measured in all the sampling chambers, at the same time denitrification samples were taken, and before and after each experiment. Additionally, EC (electric conductivity) and pH were measured in the surrounding ditch water using a pH/ conductivity probe.

Nutrient samples were collected in the surrounding ditch water. Half of the nutrient samples were filtered through a 45 μm filter. Filtered samples were analyzed for NH_4^+, NO_3^-, NO_2^- and PO_4^+. Unfiltered samples were analyzed for total nitrogen and total phosphorus.

During August and September, the sediment oxygen demand (SOD, in $gO_2.m^{-2}.d^{-1}$) was measured at three locations. A pyramid shaped hood (bottom area 0.5 by 0.5 m) with a small stirrer and oxygen probe was placed gently at the sediment surface. After 15 minutes of sediment resettling, the stirrer was switched on and the dissolved oxygen concentration under the hood was recorded every 5 minutes, until DO dropped by 2-3 $mg.l^{-1}$. From the initial slope of the DO concentration profile the SOD was calculated

Results

Pilot study

In the pilot study we measured denitrification rates which ranged from 0 to 277 $\mu mol.m^{-2}.h^{-1}$. The average rate during daytime was 74 (SD ±58, n=18) and during the night 142 (SD ±77, n=18) $\mu mol.m^{-2}.h^{-1}$, which differed significantly ($p=0.005$). The effect of aquatic vegetation and time of measurement is presented in Figure 3.3.

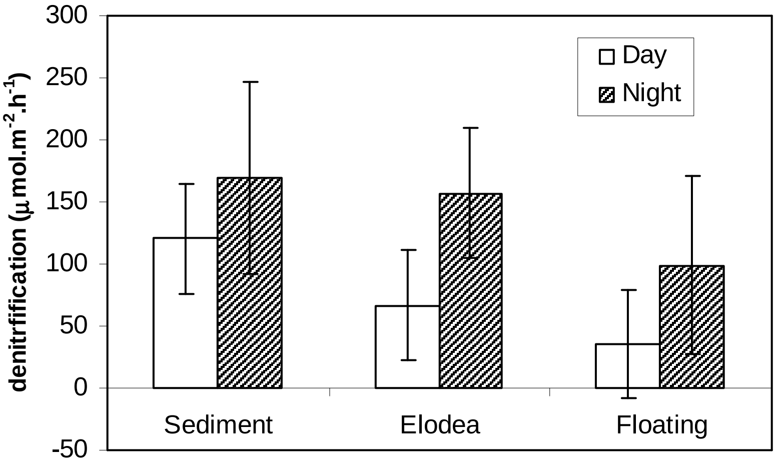


Figure 3.3 *Denitrification rates measured during day and night, for sediment with no vegetation, sediment and elodea, and sediment and plants with floating leafs (error bars indicate standard deviation; n=6).*

Between the groups only non-vegetated sediment and floating plants differed significantly (ANOVA, posthoc test Bonferroni, $p<0.05$). Within the groups, only for Elodea there was a significant difference between day and night denitrification (one-way ANOVA). The results indicate that in this ditch floating aquatic vegetation had a negative effect on denitrification during summer, whereas presence of submerged macrophytes (Elodea) did not affect the total rates of denitrification.

Denitrification rates

Measured denitrification rates, including nitrate concentrations and the water temperature measured during the second research period are plotted in Figure 3.4. In the weekly measurements during July and August we observed average denitrification rates ranging from 200 to 350 μmol.m^{-2}.h^{-1}. Standard deviations were high, which indicates a high spatial variability among the individual chambers.

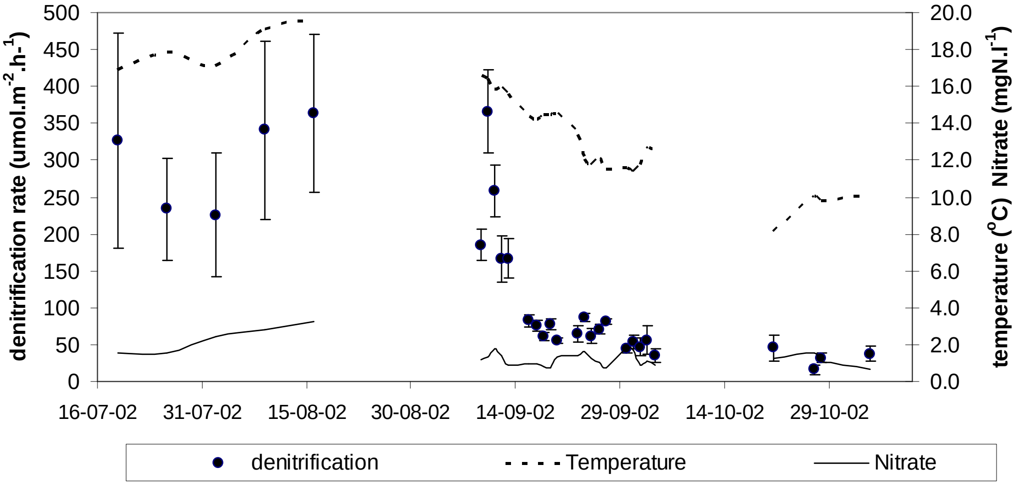


***Figure 3.4** Denitrification rates, water temperature and nitrate concentration in the enclosure chambers (error bars for denitrification rates indicate the standard deviation; n=3)*

In the second period, the daily measurements in September and October, denitrification rates began around the same level as measured in the summer. However, within a short period, denitrification rates dropped to 150 μmol.m^{-2}.h^{-1}, and then gradually decreased to around 50 μmol.m^{-2}.h^{-1}. Remarkably, differences between the three chambers decreased in this period, compared to the summer; standard deviations dropped from average 36 % to average 16 %. At the end of October and November denitrification rates ranged from 20 to 50 μmol.m^{-2}.h^{-1}. From July to October the macrophyte composition and biomass was observed to be more or less stable with respect to species type and density. Over this period, no large changes or sudden shifts in aquatic vegetation appearance were observed.

Effect of environmental conditions

To evaluate the relationship of various environmental conditions on denitrification we performed a correlation analysis. Kolmogorov-Smirnov normality tests indicated that some of the combined data was not normally distributed. Data were transformed using various techniques (logarithmic, square root, and arcsin) and the transformations resulting in the best fit was chosen by analyzing and comparing quantile/quantile plots. Variables which displayed a normal distribution without transformation were temperature, dissolved oxygen (DO) and electrical conductivity (EC). After logarithmic transformation the variables NH_4^+ and NO_3^- were normally distributed. The remaining variables did not display normal distribution even after transformation. For this reason, both Pearsons correlation and the non-parametric Spearman rank correlation coefficients were calculated, and the latter are used for correlations involving variables that were not normally distributed (Table 3.1).

Table 3.1 *Pearsons correlation (bold data) and Spearman rank correlation matrix showing relationships between all variables (n=29). Temp= water temperature, DEN = denitrification rate*

	DO	pH	Temp	EC	NH_4^+	NO_3^-
pH	-0.00					
Temp	-0.63**	-0.12				
EC	**-0.04**	0.51**	**0.18**			
NH_4^+	**-0.31**	-0.21	**0.73****	**0.39**		
NO_3^-	**-0.31**	0.09	**0.39**	**0.59****	**0.57****	
DEN	-0.60**	-0.15	0.85**	0.11	0.75**	0.41*

***Correlation is significant at the 0.01 level (2-tailed).*
**Correlation is significant at the 0.05 level (2-tailed).*

Scatter plots are used to examine the significant correlations further (Figure 3.5).

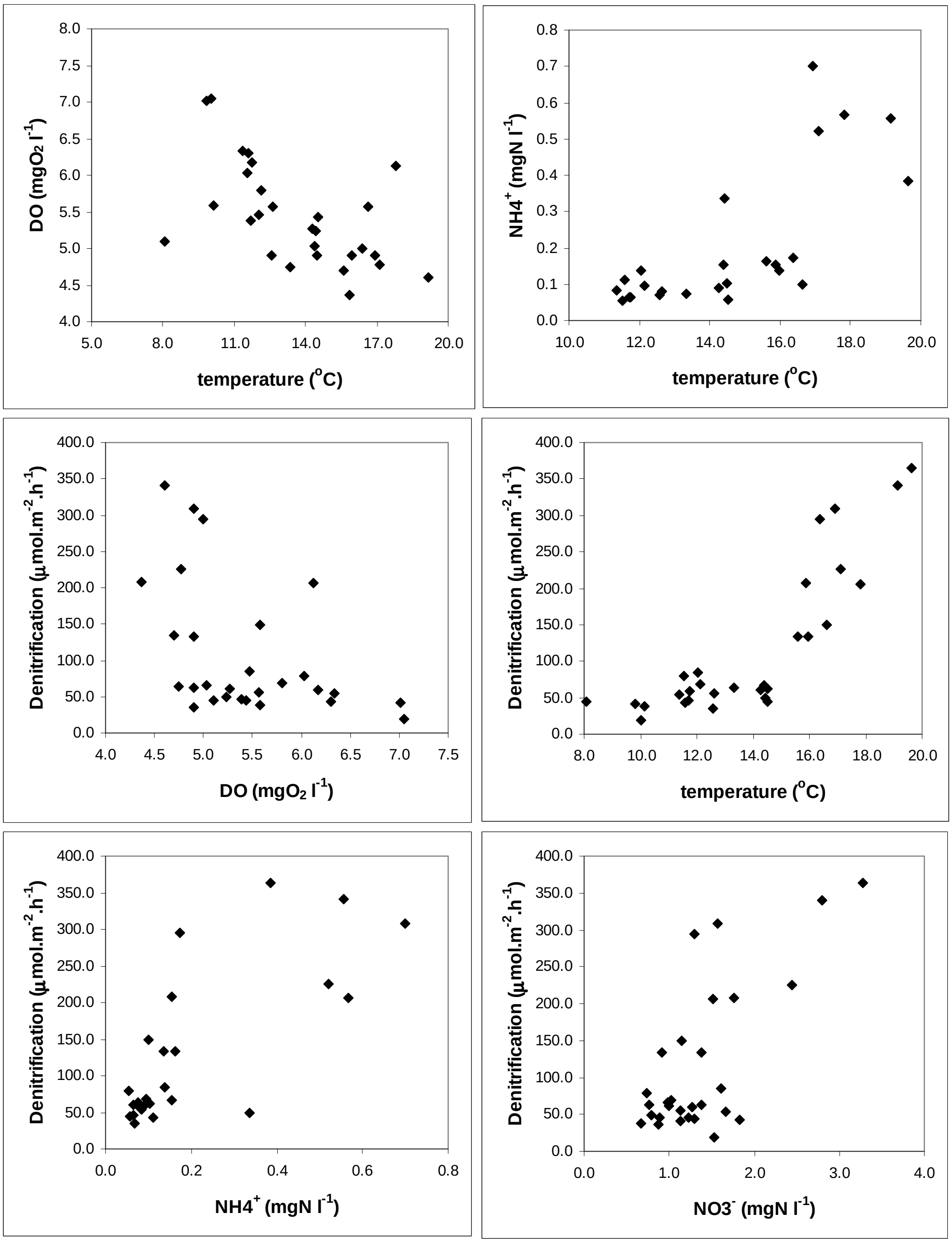


Figure 3.5 *Scatter plots of denitrification and environmental conditions*

Denitrification rates correlate most strongly with temperature and ammonium (Figure 3.5). At the same time temperature and ammonium are also strongly correlated, implying that both factors can not be treated separately when explaining rates of denitrification. Moreover, there is an inverse correlation of denitrification rates and DO. From the scatter plots we observe that at low oxygen concentrations denitrification rates range from low to high, indicating the presence of other limiting factors, but at high oxygen concentrations denitrification was never high. The rates of denitrification are also, albeit less significantly, correlated to nitrate concentrations. In contrast with ammonium, nitrate is not correlated with temperature. We also performed a stepwise regression analysis (both backward and forward selection) on the combined data (SPSS 2005). This revealed only temperature as a significant predictor for denitrification (adj. $r^2 = 0.71$; $p<0.001$). However, like most biochemical processes the effect of temperature on the rate of denitrification is not linear. Rather, it can be expressed with a modified Arrhenius temperature dependency (equation 1),

$$DR_T = DR_{20}\theta^{(T-20)} \qquad \text{(eq. 1)}$$

were DR_T and DR_{20} are denitrification rates ($\mu mol.m^{-2}.h^{-1}$) at temperature T and 20 °C respectively, and θ (theta) is the temperature coefficient (Kadlec & Knight 1996; Thomann & Mueller 1987). Typical values for the temperature coefficient range from 1.0 to 1.15 for various biochemical processes (Thomann & Mueller 1987). For nitrogen cycling reactions (mineralization, nitrification, and denitrification) in treatment wetlands (Kadlec & Reddy 2001) found temperature coefficients varying from 1.05 to 1.24.

We fitted the model (eq.1) with the measured data using regression analysis on log-transformed data (SPSS 2005). Optimal values were 430 $\mu mol.m^{-2}.h^{-1}$ for DR_{20} and 1.29 (-) for theta (r^2 =0.79; $p<0.001$ for both parameters) (Figure 3.6). Adding NH_4^+, NO_3^- and DO as other factors (non-linear regression) did not improve the model.

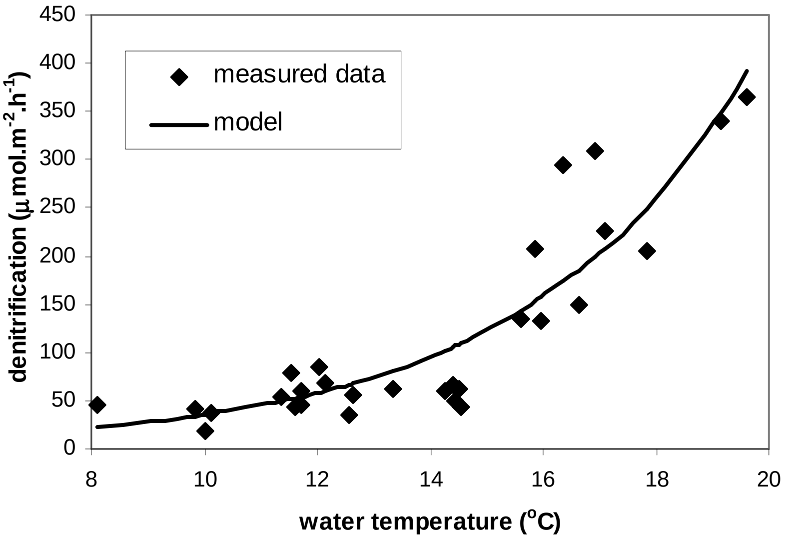


Figure 3.6 *Effect of water temperature on denitrification rates; measured data and fitted model (eq 1).*

Extrapolation to annual denitrification

Now we have established a relationship between denitrification rates and water temperature, the potential rates of denitrification during the different seasons can be calculated, resulting in an estimation of denitrification over an annual cycle. In our experiment, nitrate concentrations were elevated artificially to mimic a higher background level, and to increase the level of labeled ^{15}N-nitrate for the measurements. In water systems with low external input of nitrogen, nitrate concentrations may become depleted during the summer period, as a result of primary production and denitrification (Cabrita & Brotas 2000). This is often observed in Dutch ditches with low runoff and high residence time during summer. Thus, for an appropriate estimation of annual denitrification, inhibition by low nitrate concentrations needs to be taken into account. The response of denitrification rates to increasing and decreasing nitrate concentrations can often be described by Michaelis Menten-type kinetics (Monod). Half-saturation concentrations generally range from 25 to 50 µM NO_3^-, i.e. 0.35 to 0.70 mgN.l^{-1} (Bachand & Horne 2000; Seitzinger 1988). We calculated monthly denitrification rates in a standard ditch, based on the temperature model expanded with a monod-limitation factor for nitrate (eq. 2), with M_N being the half saturation value (0.5 mgN.l^{-1}).

$$DR_T = DR_{20}\theta^{(T-20)}\frac{NO3}{NO3+M_N} \qquad \text{(eq. 2)}$$

To compensate for the nutrient limitation DR_{20} was recalculated at 582 µmol.m^{-2}.h^{-1}. Average monthly temperature and nitrate concentrations in ditches were derived from the Dutch Limnodatabase. The seasonal variation of temperature, nitrate and estimated denitrification is presented in Figure 3.7.

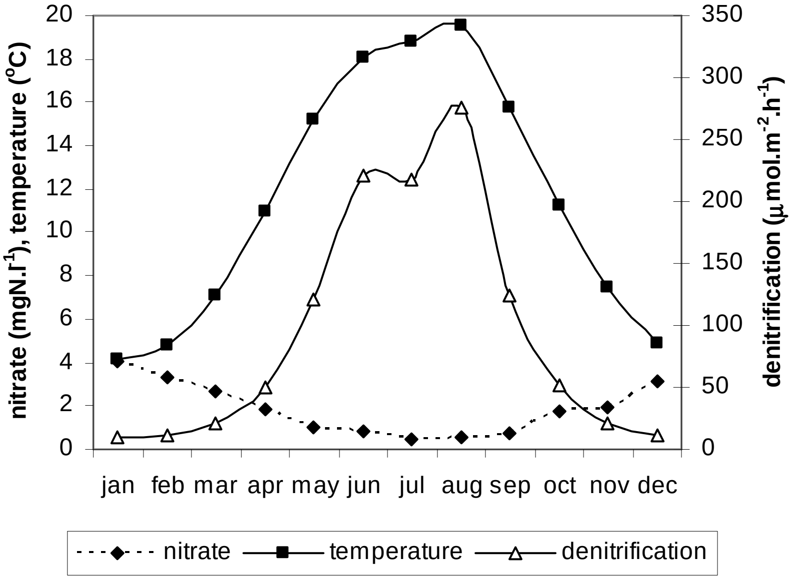


Figure 3.7 *Extrapolated (modeled) monthly denitrification in ditches in the Netherlands, at average monthly nitrate and temperature conditions.*

Estimated monthly denitrification increases and decreases in accordance with the temperature profile. In addition, we observe a small decrease during summer, due to limiting nitrate concentrations. This pattern is supported by previous research, which states that spring and fall peaks can be explained largely by two factors: temperature and nitrate concentration (Hasegawa & Okino 2004; Pattinson *et al.* 1998). The average of all the monthly denitrification rates was 117 µmol.m^{-2}.h^{-1}, which corresponds to an annual denitrification rate of 14.4 gN.m^{-2}.y^{-1}.

In view of the potential effects of temperature rise due to climate change, we also analyzed measured temperatures in Dutch ditches, in search for trends. Analysis of measurements at 3000 locations in the period 1980-2005 shows an average yearly trend of +0.06 ^{o}C.year^{-1} (Kendall Seasonal Slope Estimator, significant at 0.05 level). Average monthly temperature and estimated trends are presented in Figure 3.8.

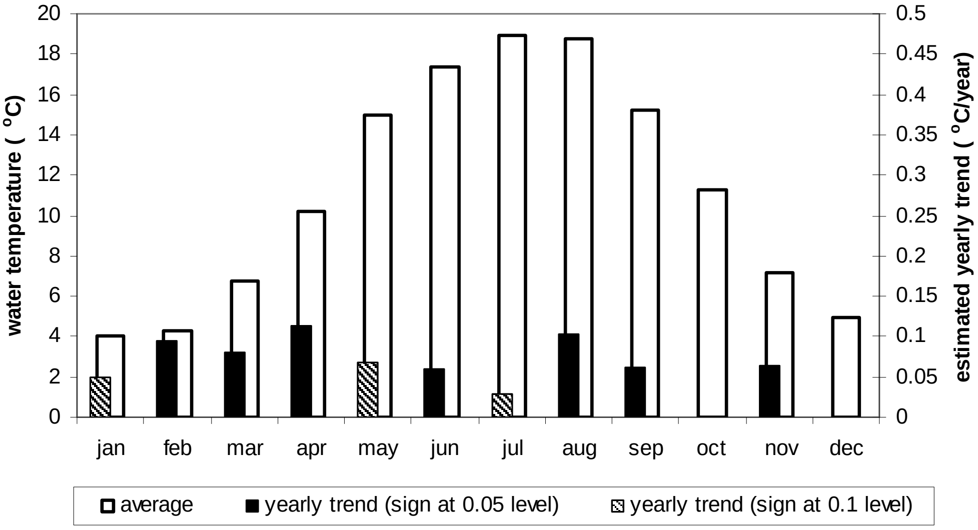


Figure 3.8 *Average monthly water temperature in ditches in the Netherlands (1982-2005), and estimated yearly trend in same period (Seasonal Kendall Slope Estimator).*

Discussion

Timing of denitrification measurements

Several studies have reported differences in denitrification rates during the day and night, and with light and dark incubations, however results have been contrasting. Some researchers report inhibition of anoxic denitrification during illumination, as a result of photosynthesis in the uppermost sediment layers and in epiphytic biofilms (Eriksson 2001; Sorensen, Jorgensen & Brandt 1988; Venterink, Hummelink & Van den Hoorn 2003). Others found stimulation of nitrification during the daytime, resulting in the increased rate of coupled nitrification-denitrification (Laursen & Seitzinger 2004; Risgaard-Pedersen *et al.* 1994). Still others found that denitrification rates were similar in both light and dark incubated sediments (Cabrita & Brotas 2000). In the pilot study we found that the highest denitrification rates occurred during the night, and the rates were in the range of 20 to 50 % higher, compared to the daytime measurements. Differences between the day and night measurements were largest when submerged macrophytes were abundant, indicating that photosynthesis and respiration, driving a diurnal pattern in dissolved oxygen concentration, were key factors. From continuous DO measurements an average diurnal pattern of DO in the experimental ditches was constructed that showed minimum DO around 07:00 and a maximum around 17:00. Analyses of 26 days continuous measurements showed that average DO between 09:00 and 12:00 deviated by only 1.0% (±SD 1.1) from 24 hour averages. Therefore, we took our measurements during these hours, which seem most appropriate to obtain results getting as close as possible to daily average denitrification rate.

Denitrification rates compared to other studies

During summer, denitrification rates ranged from 200 to 350 μmol.m^{-2}.h^{-1}. This is within the range of what has been reported as average values for rivers and lakes (Pina-Ochoa & Alvarez-Cobelas 2006). Specifically for headwaters of agricultural streams, denitrification rates of 10 – 350 μmol.m^{-2}.h^{-1}(Royer, Tank & David 2004) and 223 μmol.m^{-2}.h^{-1} (mean value) (Inwood, Tank & Bernot 2005) have been measured. However, numerous studies of individual sites show highly variable rates of denitrification, both spatially and temporally. For instance (Laursen & Seitzinger 2002) estimated denitrification rates ranged from 270 to >10.000 μmol.m^{-2}.h^{-1} in agricultural streams. In wetlands highly variable denitrification rates have also been measured (Sirivedhin & Gray 2006; Vymazal 2007). To relate our results to those of previous studies, a distinction should be made between reported *potential* and *actual* denitrification rates. In table 2 an overview of some reported data is presented, restricted to rates of *actual* denitrification in wetlands, not treating waste water. In addition, the results are expressed in per area units, in contrast to per gram sediment or biofilm organic matter. It can be seen that the denitrification rates in the Wageningen test ditches fit in the range of rates for constructed and natural wetlands.

Table 3.2 *Some data of actual denitrification rates in wetlands, not treating waste water*

Water system	*Denitrification (μmol.m^{-2}.h^{-1})*	*Reference*
Disturbed and undisturbed wetlands	20 - 260	(Seitzinger 1994)
Constructed wetland	345	(Reinhardt *et al.* 2006)
River Floodplain Wetlands	70 - 110	(Venterink *et al.* 2003)
Created riverine wetlands	328 - 778	(Hernandez & Mitsch 2007)

Temperature dependency

The main driver for temporal variability of denitrification in the Wageningen test ditches was temperature, with a temperature coefficient (theta) of 1.28. Specifically for denitrification rates, values for theta of 1.15 to 1.18 have been reported (Bachand & Horne 2000) and 1.07 to 1.14 for denitrification in a temperature range of 10 to 25 ^{o}C (Kadlec & Reddy 2001). In our whole system, the effect of temperature was not only restricted to the denitrification process itself, but also involved other processes supporting the nitrogen removal. We suggest that decomposition and nitrification, supplying organic matter and nitrate for denitrification, were also enhanced by increasing temperature. This might explain why our overall temperature coefficient was significantly higher than values found for the single process coefficient.
Adding other factors did not improve the temperature model. For DO and NH_4^+ this was expected since they are strongly correlated with temperature.

Besides the modified Arrhenius equation (eq.1), there are alternative ways to describe temperature dependency. It has been found that the effect of temperature on denitrification enzyme activity was better fitted with the model of Ratkowsky than with the Arrhenius equation (Pelletier *et al.* 1999).This model relates the square root of denitrification to temperature and is thought to describe better the effect of low temperatures. On the other hand, from the results of this study (Figure 3.6) a threshold of 15^{o}C can be postulated, above which denitrification increases linearly with temperature. Below this threshold denitrification rates are low and without temperature dependency. A similar transition of temperature dependency above 15^{o}C was also found for denitrification rates in soils (Keeney, Fillery & Marx 1979). The parameters of the 3 optional models were fitted to the measured data (table 3.3).

Both the visual and the calculated model performance (adjusted R^2) are lowest for the Ratkowsky model. For the highest and the lowest temperatures large deviations from the measured data are found. The threshold model has the best fit, indicating a temperature independency up to 15^{o}C, followed by a linear increase in warmer conditions. However, variability of denitrification with temperature below 15^{o}C has been reported by various researchers (Bachand & Horne 2000; Pfenning & McMahon 1997; Seitzinger 1988). Moreover, in this whole system measurement several subsequent processes are involved, all with different temperature dependencies (Kadlec & Reddy 2001). Thus, a gradual increase in the overall denitrification rate seems more likely to be realistic.

Table 3.3 *Options for temperature-denitrification models for this experiment. (DEN is denitrification rate (μmol.m^{-2}.h^{-1}), T is water temperature in ^{o}C).*

Temperature Model	*Equation (best fit parameters on measured data)***	*Adj R^2*
Modified Arrhenius	$DEN = 430 * 1.28^{(T-20)}$	0.79
Ratkowsky	$\sqrt{DEN} = 1.36 * (T - 8.4)$	0.76
Threshold 15^{o}C	If $T < 15$, $DEN = 53.5$ If $T > 15$, $DEN = 54.6 * T - 703$	0.84

*** all models significant; p<0.001*

Organic carbon

The amount and quality of the available organic matter was not specifically studied in the ditch system. However, a layer of fine organic material was observed on the ditch bottom, and course biofilms covered most of the submerged vegetation, both which represent a pool of degradable organic matter. Measurements of sediment oxygen demand (3.4 ± 0.1 gO_2.m^{-2}. day^{-1}) suggest a high organic matter content and high decomposition rate (Thomann & Mueller 1987) (Seitzinger & Giblin 1996). It was also suggested that sediment organic matter (expressed as % of dry weight) may represent a better measure of C availability, at the point of denitrification in the anoxic benthos, than stream water DOC (Arango *et al.* 2007).These findings support our assumption that in this system, organic matter was not likely to be a factor limiting denitrification.

Potential of nitrogen removal from an agricultural ditch landscape

In the Netherlands, estimates of diffuse inputs of nitrogen to surface waters in agricultural areas, drained by ditches, range from 25 to 30 kgN.ha^{-1}.y^{-1} (Oenema & Roest 1998). We estimate an annual nitrogen removal through denitrification in vegetated ditches of almost 15 gN.m^{-2}.y^{-1}. Assuming a dense network of ditches covering around 10% of the catchment area this can be expressed as 15 kgN.ha^{-1}.y^{-1}. This implies that from the total load to the surface waters, at least 50% is already removed from the drainage ditches, and thus not transported to downstream surface waters. Similar removal rates have been found in headwater streams (Peterson *et al.* 2001). During seasons of high biological activity, the reaches of headwater streams typically export less than half of the input of dissolved inorganic nitrogen from their watersheds. It is clear that ditches contain a high potential for self-purification. However, it is likely that the actual removal rates depend strongly on the presence and type of aquatic vegetation. The denitrification potential of vegetated ditches has been found to be 2-4 times higher compared to non-vegetated ditches (Ullah & Faulkner 2006). In addition, a mixture of submerged and floating plants in combination with emergent plants and grasses are recommended for improving denitrification rates (Bachand & Horne 2000). On the other hand our pilot study indicated reduced denitrification rates under floating vegetation as compared to submerged vegetation or unvegetated water.

Aquatic vegetation composition and abundance is strongly affected by anthropogenic management of the water body (Evans *et al.* 2007). It would therefore be good if we would have a better insight in the effect of different plant types on self cleaning capacity. With the knowledge, appropriate management of vegetation in drainage ditches can be tuned to optimize the removal of biologically available forms of N from drainage water.

Possible implications of changing climate on denitrification

Due to global warming, the temperature of air and surface waters has been predicted to rise over the coming decades (KNMI 2006). The Intergovernmental Panel on Climate Change has developed different scenarios indicating a temperature rise from one to several ^{o}C in the next 50 to 100 years (IPCC 2007). Our analysis of data from ditches in the Netherlands shows that an increase in water temperature is already visible.

The outcome of our research implies that, with θ (theta) being 1.28, a temperature rise of 1 ^{o}C results in an increase of denitrification rates by 28%, and 110% at a temperature rise of 3 ^{o}C. Obviously, these are potential values, assuming that other factors controlling denitrification do not become limiting. Nevertheless, the results show that there might be a significant impact of global warming on the permanent removal of nitrogen from surface waters.

References

Arango C. P., Tank J. L., Schaller J. L., Royer T. V., Bernot M. J. & David M. B. (2007) Benthic organic carbon influences denitrification in streams with high nitrate concentration. *Freshwater Biology,* **52**, 1210-1222.

Bachand P. A. M. & Horne A. J. (2000) Denitrification in constructed free-water surface wetlands: II. Effects of vegetation and temperature. *Ecological Engineering,* **14**, 17-32.

Bastviken S. K., Eriksson P. G., Ekstrom A. & Tonderski K. (2007) Seasonal denitrification potential in wetland sediments with organic matter from different plant species. *Water Air and Soil Pollution,* **183**, 25-35.

Burgin A. J. & Hamilton S. K. (2007) Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment,* **5**, 89-96.

Cabrita M. T. & Brotas V. (2000) Seasonal variation in denitrification and dissolved nitrogen fluxes in intertidal sediments of the Tagus estuary, Portugal. *Marine Ecology-Progress Series,* **202**, 51-65.

Christensen P. B., Nielsen L. P., Sorensen J. & Revsbech N. P. (1990) Denitrification in Nitrate-Rich Streams - Diurnal and Seasonal-Variation Related to Benthic Oxygen-Metabolism. *Limnology and Oceanography,* **35**, 640-651.

Dalsgaard T. (2000) *Protocol handbook for NICE-nitrogen cycling in estuaries*. Copenhagen, Denmark: National Environmental Research Institute,.

Dong L. F., Thornton D. C. O., Nedwell D. B. & Underwood G. J. C. (2000) Denitrification in sediments of the River Colne estuary, England. *Marine Ecology-Progress Series,* **203**, 109-122.

Eriksson P. G. (2001) Interaction effects of flow velocity and oxygen metabolism on nitrification and denitrification in biofilms on submersed macrophytes. *Biogeochemistry,* **55**, 29-44.

Eriksson P. G. & Weisner S. E. B. (1997) Nitrogen removal in a wastewater reservoir: The importance of denitrification by epiphytic biofilms on submersed vegetation. *Journal of Environmental Quality,* **26**, 905-910.

Evans R. O., Bass K. L., Burchelt M. R., Hinson R. D., Johnson R. & Doxey M. (2007) Management alternatives to enhance water quality and ecological function of channelized streams and drainage canals. *Journal of Soil and Water Conservation,* **62**, 308-320.

Hasegawa T. & Okino T. (2004) Seasonal variation of denitrification rate in Lake Suwa sediment. *Limnology,* **5**, 33-39.

Hernandez M. E. & Mitsch W. J. (2007) Denitrification in created riverine wetlands: Influence of hydrology and season. *Ecological Engineering,* **30**, 78-88.

Inwood S. E., Tank J. L. & Bernot M. J. (2005) Patterns of denitrification associated with land use in 9 midwestern headwater streams. *Journal of the North American Benthological Society,* **24**, 227-245.

IPCC. (2007) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

Janse J. H. (1998) A model of ditch vegetation in relation to eutrophication. *Water Science and Technology,* **37**, 139-149.

Kadlec R. H. & Knight R. L. (1996) *Treatment Wetlands.*: Lewis Publishers, Baco Raton,.

Kadlec R. H. & Reddy K. R. (2001) Temperature effects in treatment wetlands. *Water Environment Research,* **73**, 543-557.

Keeney D. R., Fillery I. R. & Marx G. P. (1979) Effect of Temperature on the Gaseous Nitrogen Products of Denitrification in a Silt Loam Soil. *Soil Science Society of America Journal,* **43**, 1124-1128.

KNMI. (2006) Climate Change Scenarios 2006 for the Netherlands, pp. 82. De Bilt, The Netherlands.

Laursen A. E. & Seitzinger S. P. (2004) Diurnal patterns of denitrification, oxygen consumption and nitrous oxide production in rivers measured at the whole-reach scale. *Freshwater Biology,* **49**, 1448-1458.

Laursen A. E. & Seitzinger S. P. (2002) Measurement of denitrification in rivers: an integrated, whole reach approach. *Hydrobiologia,* **485**, 67-81.

Nielsen L. P. (1992) Denitrification in Sediment Determined from Nitrogen Isotope Pairing. *Fems Microbiology Ecology,* **86**, 357-362.

Oenema O. & Roest C. W. J. (1998) Nitrogen and phosphorus losses from agriculture into surface waters; The effects of policies and measures in The Netherlands. *Water Science and Technology,* **37**, 19-30.

Oenema O., van Liere L. & Schoumans O. (2005) Effects of lowering nitrogen and phosphorus surpluses in agriculture on the quality of groundwater and surface water in the Netherlands. *Journal of Hydrology,* **304**, 289-301.

Pattinson S. N., Garcia-Ruiz R. & Whitton B. A. (1998) Spatial and seasonal variation in denitrification in the Swale-Ouse system, a river continuum. *Science of the Total Environment,* **210**, 289-305.

Pelletier F., Prevost D., Laliberte G. & van Bochove E. (1999) Seasonal response of denitrifiers to temperature in a Quebec cropped soil. *Canadian Journal of Soil Science,* **79**, 551-556.

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

Pfenning K. S. & McMahon P. B. (1997) Effect of nitrate, organic carbon, and temperature on potential denitrification rates in nitrate-rich riverbed sediments. *Journal of Hydrology,* **187**, 283-295.

Pina-Ochoa E. & Alvarez-Cobelas M. (2006) Denitrification in aquatic environments: A cross-system analysis. *Biogeochemistry,* **81**, 111-130.

Reddy K. R., Kadlec R. H., Flaig E. & Gale P. M. (1999) Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology,* **29**, 83-146.

Reinhardt M., Muller B., Gachter R. & Wehrli B. (2006) Nitrogen removal in a small constructed wetland: An isotope mass balance approach. *Environmental Science & Technology,* **40**, 3313-3319.

Risgaard-Pedersen N., Rysgaard S., Nielsen L. P. & Revsbech N. P. (1994) Diurnal-Variation of Denitrification and Nitrification in Sediments Colonized by Benthic Microphytes. *Limnology and Oceanography,* **39**, 573-579.

Royer T. V., Tank J. L. & David M. B. (2004) Transport and fate of nitrate in headwater agricultural streams in Illinois. *Journal of Environmental Quality,* **33**, 1296-1304.

Schwoerbel J. (1984) *Handbook of limnology*. Chichester, UK.: Ellis Horwood Ltd.

Seitzinger S. P. (1988) Denitrification in Fresh-Water and Coastal Marine Ecosystems - Ecological and Geochemical Significance. *Limnology and Oceanography,* **33**, 702-724.

Seitzinger S. P. (1994) Linkages between Organic-Matter Mineralization and Denitrification in 8 Riparian Wetlands. *Biogeochemistry,* **25**, 19-39.

Seitzinger S. P. & Giblin A. E. (1996) Estimating denitrification in North Atlantic continental shelf sediments. *Biogeochemistry,* **35**, 235-260.

Sirivedhin T. & Gray K. A. (2006) Factors affecting denitrification rates in experimental wetlands: Field and laboratory studies. *Ecological Engineering,* **26**, 167-181.

Sorensen J., Jorgensen T. & Brandt S. (1988) Denitrification in Stream Epilithon - Seasonal-Variation in Gelbaek and Rabis-Baek, Baek, Denmark. *Fems Microbiology Ecology,* **53**, 345-354.

SPSS. (2005) *SPPS for Windows v. 15.0*. Chicago, IL, U.S.A: SPSS Inc.

Stanford G., Dzienia S. & Vanderpol R. A. (1975) Effect of Temperature on Denitrification Rate in Soils. *Soil Science Society of America Journal,* **39**, 867-870.

Steingruber S. M., Friedrich J., Gachter R. & Wehrli B. (2001) Measurement of denitrification in sediments with the N-15 isotope pairing technique. *Applied and Environmental Microbiology,* **67**, 3771-3778.

Strock J. S., Dell C. J. & Schmidt J. P. (2007) Managing natural processes in drainage ditches for nonpoint source nitrogen control. *Journal of Soil and Water Conservation,* **62**, 188-196.

Thomann R. V. & Mueller J. A. (1987) *Principles of surface water quality modeling and control*. New York: Harper & Row.

Ullah S. & Faulkner S. P. (2006) Denitrification potential of different land-use types in an agricultural watershed, lower Mississippi valley. *Ecological Engineering,* **28**, 131-140.

van Beek C. L., van den Eertwegh G., van Schaik F. H., Velthof G. L. & Oenema O. (2004) The contribution of dairy farming on peat soil to N and P loading of surface water. *Nutrient Cycling in Agroecosystems,* **70**, 85-95.

Van Luijn F., Boers P. C. M., Lijklema L. & Sweerts J. (1999) Nitrogen fluxes and processes in sandy and muddy sediments from a shallow eutrophic lake. *Water Research,* **33**, 33-42.

Venterink H. O., Hummelink E. & Van den Hoorn M. W. (2003) Denitrification potential of a river floodplain during flooding with nitrate-rich water: grasslands versus reedbeds. *Biogeochemistry,* **65**, 233-244.

Vymazal J. (2007) Removal of nutrients in various types of constructed wetlands. *Science of the Total Environment,* **380**, 48-65.

Weisner S. E. B., Eriksson P. G., Graneli W. & Leonardson L. (1994) Influence of Macrophytes on Nitrate Removal in Wetlands. *Ambio,* **23**, 363-366.

Chapter 4

AquaVenus, a model for Aquatic Vegetation, Nutrients and Suspended matter in small surface waters

Jeroen de Klein

AquaVenus, a model for Aquatic Vegetation, Nutrients and Suspended matter in small surface waters

Abstract

A simulation model was set up to evaluate nutrient retention in vegetated headwater streams, with focus on the effect of macrophytes. It combines dynamic water flow modeling with mechanistic macrophyte growth and nutrient processes. Interactions are kept relatively simple, restricted to the relations that affect nutrient retention. Despite the simplifications the model is able to predict nutrient concentrations and macrophyte biomass quite well in a dynamic upper region of a lowland stream. The simulations showed that average annual nitrogen retention was 25% of the incoming load. Retention was mainly due to denitrification (75%). Annual phosphorus retention was 30%, predominantly from sedimentation (92%). The average simulated summer denitrification rate was 560 $\mu mol.m^{-2}.h^{-1}$, which is in agreement with reported data from vegetated streams and wetlands.

Introduction

In addition to their drainage function and ecological values, ditches and headwater streams have a potential to improve water quality by removing nutrients (Strock, Dell & Schmidt 2007). In lowland areas and flat polder landscapes these waters have a relatively long residence time compared to fast running streams in hill slope catchments. Moreover, due to the shallowness, the water courses are generally dominated by macrophytes and require maintenance (mowing and dredging) to preserve their hydraulic capacity (Janse 1998). There is an increasing awareness of the possibilities ror optimizing the purification capacity, combined with the hydrological and ecological function (Evans *et al.* 2007; Scholz & Trepel 2004), especially regarding the demand of the European Water framework Directive to achieve good ecological status of all surface waters by 2015.

The important role of macrophytes in retaining nutrients in surface waters is generally acknowledged (Clarke 2002; Gumbricht 1993). Mechanism, related to water plants, that stimulate nutrient retention include: a) nutrient uptake for biomass production; b) obstruction of water flow, increasing water residence time; c) stimulation of particulate material sedimentation and reduction of resuspension risks; d) offering suitable substrate for denitrifying epiphytic biofilms. Studies on natural vegetated waters have predominantly been focused on individual processes, and quantifying the rates of retention in field conditions. Studies that address design and management options that may improve the retention capacity in small running waters are rare. Several ecological models for macrophyte growth have been presented, mostly focusing on different aspects. Examples are vegetation dynamics and survival (Scheffer, Bakema & Wortelboer 1993), harvesting strategies (van Nes *et al.* 2002), light climate (Best *et al.* 2001) and nutrient induced shifts (Janse & Van Puijenbroek 1998). In addition, models are constructed to study flow obstruction effects of macrophytes in running waters (e.g. (Green 2006)). However, to our knowledge, models that interrelate hydrodynamics, macrophyte growth and nutrient retention have not been set up so far.

In this paper, an integrated dynamic deterministic model for water flow, macrophyte growth and nutrient fates is presented and tested. It combines an existing hydrodynamic modeling tool and a new nutrient and macrophyte model. Both parts run simultaneously, which enables simulating effect of flow on water quality and macrophytes, and visa versa. In a second paper (De Klein, Aalderink & Portielje 2008) the model is applied to explore the effects of maintenance and design options on nutrient retention.

Model description

The model is set up to explore the influence of macrophyte growth, flow regimes, stream morphology and management options on the retention of nitrogen and phosphorus. Therefore, complex ecological interactions and feedbacks are left out or lumped to simple relations, with a focus on the effect of submerged macrophytes on physical and biochemical processes. A major simplification is that we treat all macrophytes as one single biomass pool, disregarding different growth forms and competition between species. Since we focus on macrophyte dominated stream headwaters and ditches, algae are left out, as well as other functional groups like macro-invertebrates and fish.

The presented model is an application within Duflow®, a 1-dimensional modeling package for water movement and water quality (Stowa / MX-systems 2004). It enables the calculation of unsteady flow in networks of canals, rivers and channels with the full Saint-Vernant equations for river flow, resulting in water level, discharge and velocity in all sections and for all time steps. The water quality module describes transportation of substances in free surface flow with the 1-D advection-dispersion equation. Both flow and substance transport equations are solved numerically. For additional transformation processes mathematical formulations can be supplied by the user, in the form of differential equations.

The AquaVenus model is such a set of equations. It includes processes in the water column, assumed to be well mixed, and sediment storage and release (Figure 4.1). Simulated state variables are biomass of submerged macrophytes (M), dissolved inorganic nitrogen (NO3, NH4), particulate nitrogen (PN), sediment nitrogen (Nbod), dissolved inorganic phosphorus (DP), particulate phosphorus (PP) and sediment phosphorus (Pbod). To achieve closed nutrient budgets suspended matter is expressed as PN and PP, and settled material as Nbod and Pbod. Part of the macrophyte biomass is transformed in inert detritus, which is regarded as a permanent sink.

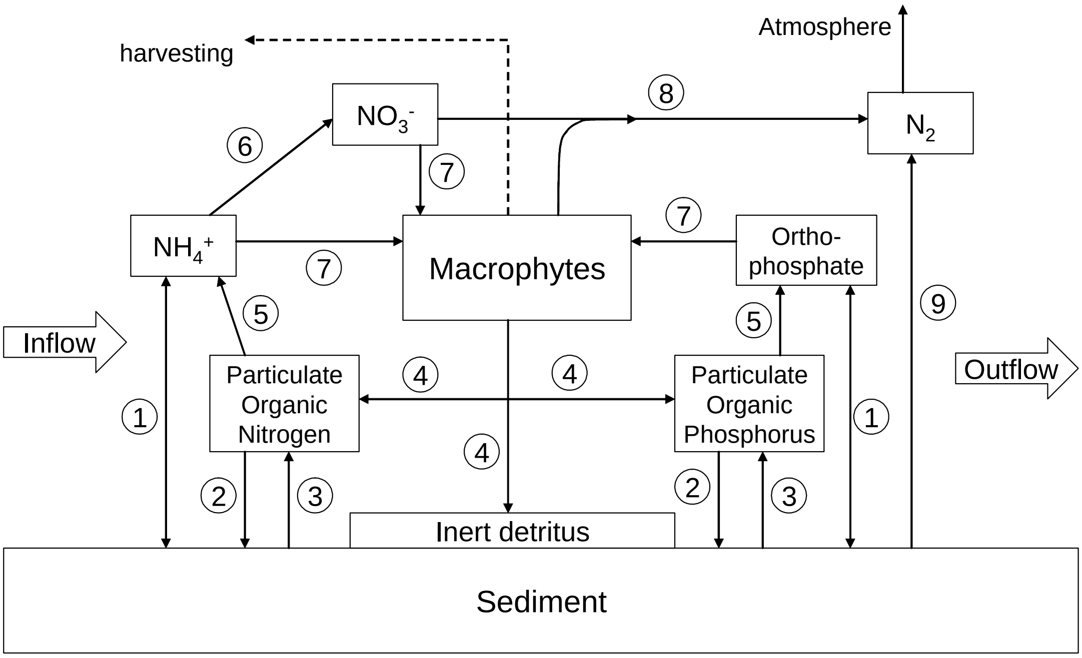


Figure 4.1 *Pathways and processes of Nitrogen and Phosphorus in the model AquaVenus. (Processes: 1. sediment release/absorption, 2. sedimentation, 3. resuspension, 4. decomposition, 5. mineralization, 6. nitrification, 7. macrophyte uptake (net growth), 8. epiphytic biofilm denitrification, 9. sediment denitrification.)*

Macrophyte growth

Macrophyte growth is driven by nutrient, temperature and light limited photosynthesis, and a loss rate that includes both respiration and decay and a harvest rate (*Hv*). Plant biomass is treated as a ‘bottom’ variable, meaning that it is not transported by water flow. Nutrient limitations are described using a Michaelis-Menten type kinetics and temperature dependence with a modified Arrhenius equation (Table 4.1).

The light climate in the water column is dealt with in two sections (Figure 4.2). The top section is the open water above the macrophyte stand; here a light extinction according to Lambert-Beer's law is used (Scheffer 1998). The bottom section is occupied by macrophytes, where available light is determined by background extinction and self-shading of the plants. For photosynthesis, light limitation according to Steele is integrated over the depth *Hm* and over the day (Thomann & Mueller 1987). The height of the macrophytes is calculated from the maximum height, and the biomass using a hill-function.

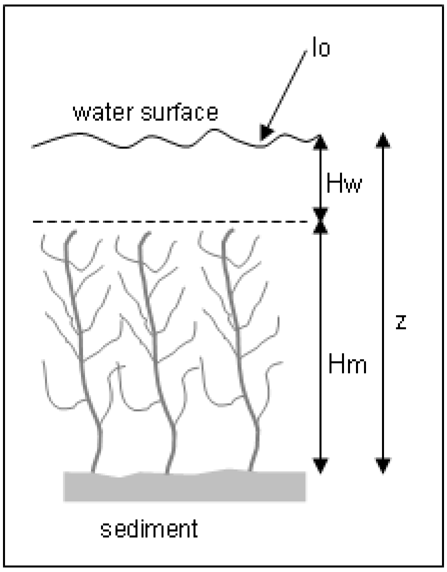


Figure 4.2 *Representation of he height of the total water column (z), the free water column (Hw) and macrophyte stand (Hm) (all in m). Io is light intensity at the water surface (W.m^{-2})*

Nutrient cycling processes

Nutrient cycling processes are sediment release/absorption, decomposition, mineralization, nitrification, denitrification and macrophyte uptake. Most equations are taken from well accepted basic eutrophication models (Brown & Barnwell 1987; Reichert *et al.* 2001; Thomann & Mueller 1987)(Table 4.2.). Denitrification is split up in sediment denitrification and denitrification by epiphytic biofilms. The latter is dependent on available substrate, i.e. submerged macrophyte biomass (Eriksson & Weisner 1999).

In addition, sedimentation and resuspension are important processes for particulate nitrogen and phosphorus. Both process rates are partially determined by the biomass of macrophytes, as water plants capture particles and reduce resuspension by stabilizing the top layer of the sediment. Suspended sediment processes are described using the equations of Partheniades and Krone (Blom & Aalderink 1998). In this concept current flow induces bottom shear stress. In case shear stress is below the lower critical value than particles will settle, whereas above the upper critical value resuspension of settled material will occur. Shear stress between both critical values will induce nor sedimentation nor resuspension.

Flow reduction by macrophytes

Macrophyte stands in running waters generally reduce the flow, resulting in decreasing flow velocities and increasing water levels. In the hydraulic module of Duflow this is described as:

$$Q = A * (1 - A_M) * C * \sqrt{R_1 * \frac{\partial H}{\partial x}} + A * A_M * W * \frac{\partial H}{\partial x} \qquad (22)$$

where Q = discharge ($m^3.s^{-1}$), A = cross-sectional area of the water course (m^2), A_M = vegetated fraction of the cross-section (m^2), C = Chezy- coefficient ($m^{½}$ $.s^{-1}$), R_1 = hydraulic radius of unvegetated part (m), $\delta H/\delta x$ = slope (-), W = conductivity rate of the vegetated part ($m.s^{-1}$) (Arcadis 2004). In the water quality module the value of A_M is calculated from the macrophyte biomass (eq. 23) and since both modules run simultaneously this will directly affect the flow.

$$A_M = \frac{Hm}{z} * \frac{M^x}{(M^x + K_B{}^x)} \qquad (23)$$

with K_B the macrophyte half saturation value of vegetated area ($g.m^{-2}$).

Table 4.1 *Macrophyte growth and light climate equations (parameters explained in annex 4.1)*

Variable / function	**Unit**	**Model equation**	
Macrophyte biomass	$g.m^{-2}$	$\frac{dM}{dt} = (netgr - Hv) * M$	(1)
Net growth rate	d^{-1}	$netgr = \mu_{MAX} * f(T) * f(Nu) * f(L) - Loss$	(2)
Temperature limitation	-	$f(T) = \Theta_M{}^{(T-20)}$	(3)
Nutrient limitation	-	$f(Nu) = \min(\frac{DIN}{DIN + K_N}, \frac{DP}{DP + K_P})$; $DIN = NH4 + NO3$	(4)
Preference for Ammonium uptake	-	$pNH4 = \frac{NH4 * NO3}{(NH4 + K_{MN}) * (NO3 + K_{MN})} + \frac{NH4 * K_{MN}}{DIN * (K_{MN} + NO3)}$	(5)
Height of the macrophyte stand	m	$Hm = H\max * \frac{M^y}{(M^y + K_H{}^y)}$	(6)
Light at top of macrophyte stand	m	$I_M = I_0 * e^{-\varepsilon_w * Hw}$	(7)
Total extinction coefficient	m^{-1}	$\varepsilon = \varepsilon_w + \lambda_M * M$	(8)
Light limitation	-	$f(L) = \frac{2.718}{\varepsilon * Hm} * \left(\exp(-\frac{I_M}{I_{opt}} * \exp(-\varepsilon * Hm)) - \exp(-\frac{I_M}{I_{opt}}) \right)$	(9)

Table 4.2 *Nutrient cycles equations (parameters explained in annex 4.1)*

Variable / function	**Unit**	**Model equation**	
Ammonium-N	$gN.m^{-3}$	$\frac{dNH4}{dt} = -netgr * \frac{M}{z} * pNH4 * Nm + k_{MI} * \Theta_{MI}{}^{(T-20)} * PN - k_{NI} * \Theta_{NI}{}^{(T-20)} * NH4 + \frac{Nflux}{z}$	(10)
Nitrate-N	$gN.m^{-3}$	$\frac{dNO3}{dt} = -netgr * \frac{M}{z} * (1 - pNH4) * Nm - k_{DEN} * \Theta_{DEN}{}^{(T-20)} * NO3 + k_{NI} * \Theta_{NI}{}^{(T-20)} * NH4$	(11)
Particulate N	$gN.m^{-3}$	$\frac{dPN}{dt} = -k_{MI} * \Theta_{MI}{}^{(T-20)} * PN + DECOM * \frac{M}{z} * Nm * (1 - FD) - \frac{Sd}{z} * PN + \frac{Rs * Nss}{z}$	(12)
Sediment N	$gN.m^{-2}$	$\frac{dNbod}{dt} = Sd * PN - Rs * Nss$	(13)
Decomposition rate	d^{-1}	$DECOM = -netgr$; *if netgr < 0*	(14)
Denitrification rate	d^{-1}	$k_{DEN} = (\frac{k_{sd}}{z} + D_{bf} * M)$	(15)
Dissolved P	$gP.m^{-3}$	$\frac{dDP}{dt} = -netgr * \frac{M}{z} * Pm + k_{MI} * \Theta_{MI}{}^{(T-20)} * PP + \frac{Pflux}{z}$	(16)
Particulate P	$gP.m^{-3}$	$\frac{dPP}{dt} = -k_{MI} * \Theta_{MI}{}^{(T-20)} * PP + DECOM * \frac{M}{z} * Mp * (1 - FD) - \frac{Sd}{z} * PP + \frac{Rs * Pss}{z}$	(17)
Sediment P	$gP.m^{-2}$	$\frac{dPbod}{dt} = Sd * PP - Rs * Pss$	(18)

Variable / function	Unit	Model equation	
Shear stress	Pa	$\tau = 1000 * (0.1 * Vs * \frac{K_s}{K_s + M})^2$	(19)
Sedimentation rate	m.d^{-1}	$Sd = Vss * (1 - \frac{\tau}{\tau_{sed}})$; if $\tau < \tau_{sed}$	(20)
Resuspension rate	g.m^{-2}.d^{-1}	$Rs = Rflux * \frac{K_r}{K_r + M} * (\frac{\tau}{\tau_{res}} - 1)$; if $\tau > \tau_{res}$	(21)

Study site and field research

The Duflow-AquaVenus model is applied to a small lowland stream headwater catchment, Gooiermars (Figure 4.3). It drains runoff and regional seepage from 150 ha grassland and natural forest. Watercourses range from 0.5 to 4 m in width, and 0.2 to 0.8 m in depth, all with abundant macrophytes during the growing season. Annual average residence time of the water is in the range of one day.

At the outflow monitoring station discharge is measured continuously and in 2002 biweekly samples for nutrient analyses have been taken. During the summer of 2006 an extensive fieldwork was set up, to deliver input data and validation data for the model (data not all reported here). At 5 locations in the mean stream and 5 locations in the side streams sediment cores were sampled for nutrient release experiments. At 10 locations in the main stream macrophyte biomass was harvested in 0.5 m by 0.5 m squares, representative for the density and composition of the macrophyte community. Wet and dry weights from the biomass have been measured at 5 dates from April to October. From a sub-sample of the different macrophyte species nitrogen and phosphorus content has been determined. Groundwater was sampled at 3 dates and analyzed for nutrients.

Simulation approach

The model was run over a 1 year period, both 2002 and 2006, simulating seasonal dynamics of water flow, physical and biochemical processes and macrophyte growth. Groundwater inflow data were derived from an existing regional groundwater model.

First, an indication of the sensitivity of the simulation for parameter settings was obtained, by subsequently increasing and decreasing the parameter values with 20 % and evaluating the effect on some key factors (growth rate, maximum biomass and average nitrogen and phosphorus concentrations). Parameters were selected for evaluation, based on known sensitivity in other macrophyte models (Giusti & Marsili-Libelli 2005; Janse 1998; Scheffer *et al.* 1993) or difficulty to get independent estimates of values for.

Subsequently, we estimated parameter values by calibrating the model with measured nutrient data from the year 2002. Unfortunately, no macrophyte biomass data were available for calibration. Therefore, biomass was calibrated using seasonal data and maximum biomass from other studies in running waters (Champion & Tanner 2000; Sand-Jensen *et al.* 1989). The model was validated with measured data of the field research in 2006. Nutrient concentrations at the outflow point and average macrophyte biomass in the main watercourse upstream the outflow were evaluated. Finally, separate process rates and nutrient budgets were retrieved from the simulation results to study contribution of removal processes to the nutrient retention.

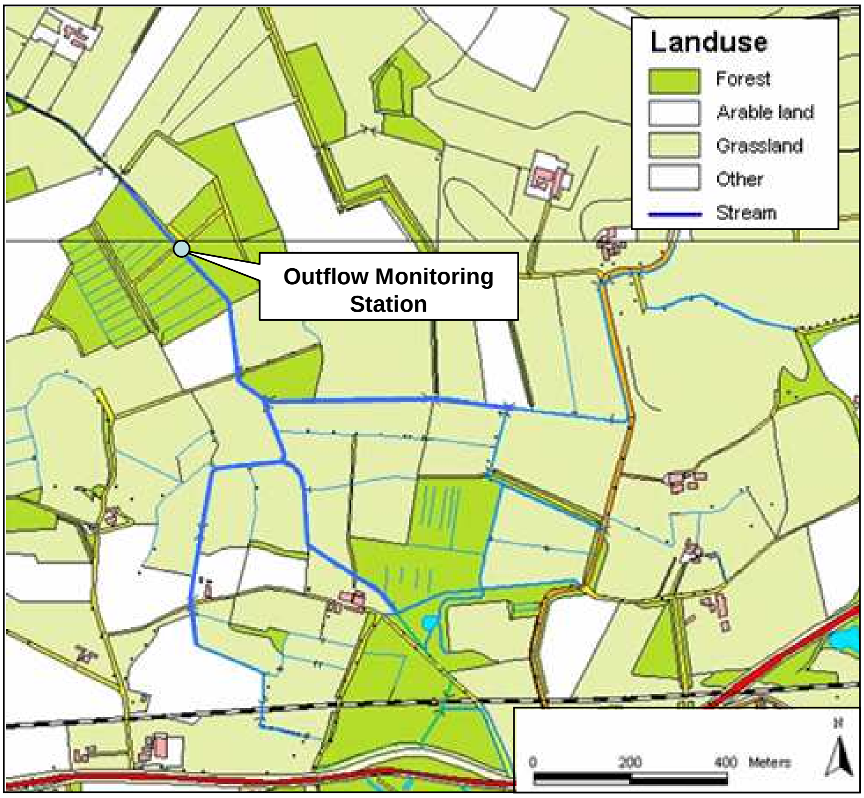


Figure 4.3 *The Gooiermars research area.*

Results

The sensitivity evaluation revealed that changing some parameters had a large impact on the net macrophyte growth, maximum biomass and average nutrient concentration. Parameters with the largest effect on the biomass were maximum growth rate (μ_{max}), optimal light intensity for growth (I_{opt}), the self-shading coefficient (λ_M) and sediment denitrification rate (k_{sd}).

The model was calibrated for nutrient concentration at the outflow point of the catchment. Generally, the range of the concentration is simulated quite well for all variables, except PO_4-P (Figure 4.4). This is due to low measured values, often below the detection limit (0.01 mgP.l^{-1}). The seasonality, higher in winter and lower in summer, is reproduced quite well.

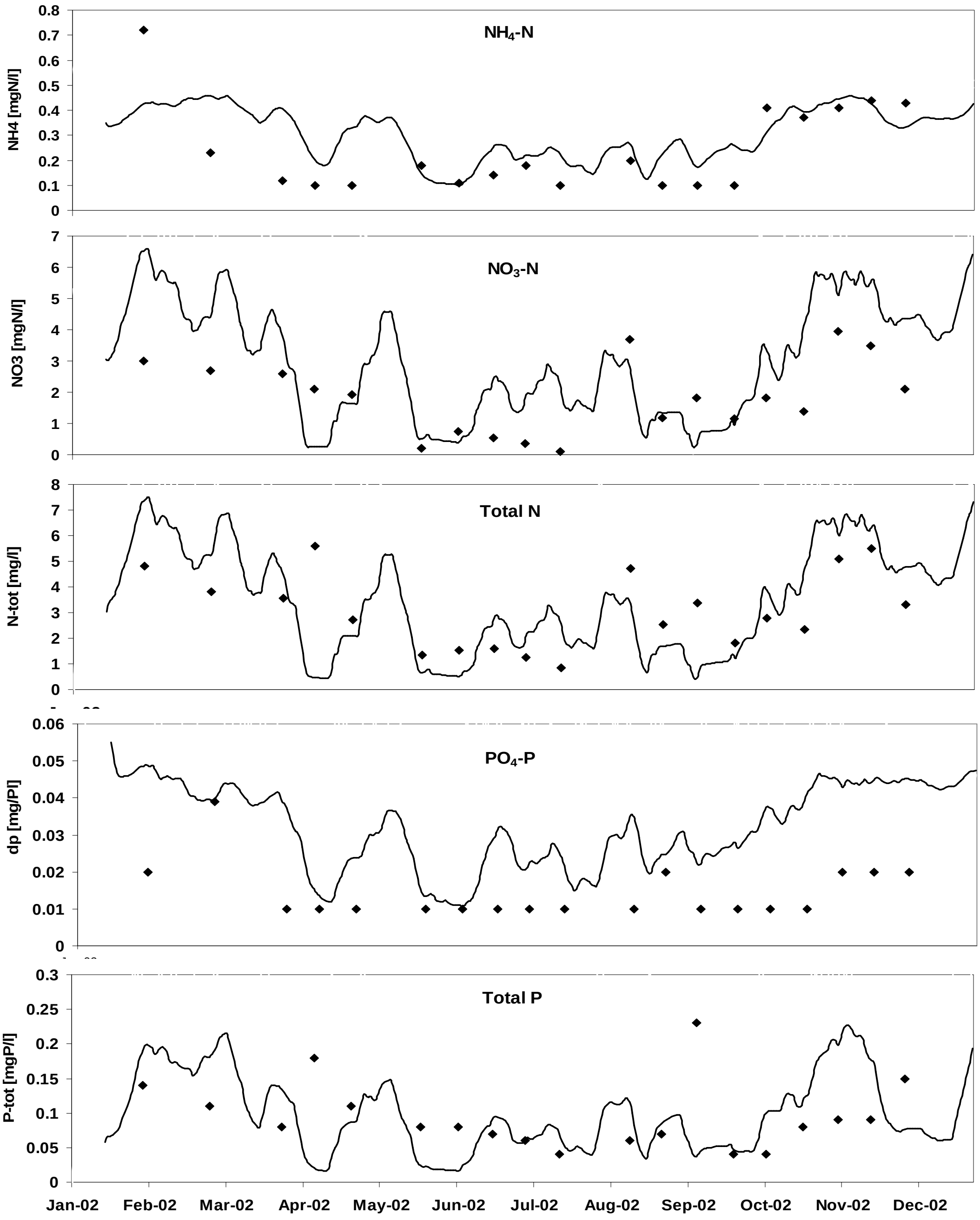


Figure 4.4 *Calibration results of the model with data from 2002. (line is model; dots are measurement data).*

Validation of the model with the field data of 2006 also showed fairly good results (Figure 4.5). Ranges of concentration N and P are in good agreement, although not all dynamics of nutrients are simulated correctly. The model fits macrophyte biomass measurements remarkably well. The sharp decrease in the modeled biomass (end of June) is due to an enforced reduction of biomass, representing a mowing event that actually took place that date. To demonstrate the effect of the mowing, a simulation without mowing is also presented (dashed line).

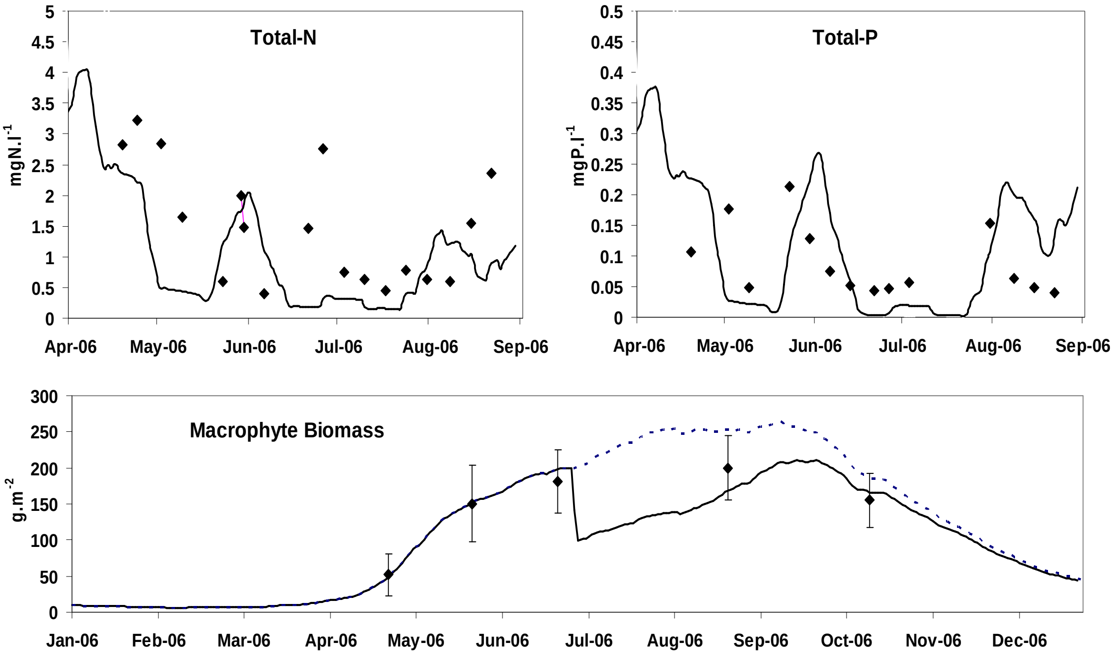


Figure 4.5 *Validation results of the model with data from 2006. Solid line is model; dots are measurement data. Error bars for macrophyte biomass indicate standard deviation (n=10). Dashed line for macrophyte biomass is simulation with no harvest in July.*

The standard simulation scenario consisted of actual hydrological and meteorological conditions in 2006, internal loading from sediment release and a limited harvesting during one occasion. Average hydraulic residence time from the sources to the outlet of the catchment were 1.6 d in the summer period (April to September), and 0.5 d in the winter period (October to March). For the same periods nutrient budgets are calculated and contribution of the main processes to the retention (Table 4.3). Summer retention (around 40%) differs from winter retention (around 20 %.) due to longer residence time and the presence of macrophytes. During summer, nutrients are stored in the biomass.

In winter they are released again by decomposition. The main retention processes are denitrification for nitrogen and sedimentation for phosphorus. The average summer denitrification rate was 560 µmol.m^{-2}.h^{-1}. This is substantial, but in good agreement with reported data of vegetated streams and wetlands (Pina-Ochoa & Alvarez-Cobelas 2006).

Table 4.3 *Residence time, nutrient budgets and contribution of retention processes, simulated for actual conditions in 2006.*

	N		P	
	Summer	Winter	Summer	Winter
Hydrological residence time				
Average residence time (d)	1.6	0.5	1.6	0.5
Nutrient Budgets				
Inflow and internal loading (kg)	1626	3980	118	270
Export load (kg)	965	3261	68	202
Retention (kg)	661	719	50	68
Retention fraction (-)	0.41	0.18	0.42	0.25
Contribution to retention				
Biomass accumulation (%)	6.4	-5.1	9.0	-5.4
Sedimentation (%)	16	27	90	97
Denitrification (%)	77	74	0	0
Detritus (%)	0.4	4.4	0.7	8.5

Discussion

Off course, actual interactions between nutrients, macrophytes, sediment and water flow are more complex than simulated with the AquaVenus model. For example, macrophyte stands mediate flow conditions on one hand, but conversely water movement affects the growth of submersed macrophytes. Additionally, sediment biochemical processes and redox conditions that may influence nutrient absorption and release are omitted. In the model macrophytes are modeled as a lumped total biomass, whereas not all macrophytes species show the same effects on flow and retention processes (Clarke 2002).

However, making the model more complex generates more parameters for which values have to be set. This introduces more uncertainties and may not make the model much more accurate. The results from the Gooiermars simulations show reasonable agreement with the measured nutrient and biomass data, and resulting retention and process rates are also in line with literature data. Clearly, this does prove that the model is in fact correct, as there is always a real possibility that good results are produced for the wrong reasons. Therefore it is important that we use the model to explore changes in retention mechanism rather than to really predict nutrient concentrations.

Acknowledgements

Rutger Engelbertink is gratefully acknowledged for his extensive fieldwork in the Gooiersmars region, and Wilfred Wiegman (waterboard Groot-Salland) for providing water quality and catchment data.

References

Arcadis. (2004) Beheer en onderhoud van watergangen; toepassingen in Duflow. (in Dutch), pp. 14. Apeldoorn, The Netherlands: Arcadis.

Baldwin D. S., Mitchell A. M., Rees G. N., Watson G. O. & Williams J. L. (2006) Nitrogen processing by biofilms along a lowland river continuum. *River Research and Applications,* **22**, 319-326.

Bartleson R. D., Kemp W. M. & Stevenson J. C. (2005) Use of a simulation model to examine effects of nutrient loading and grazing on Potamogeton perfoliatus L. communities in microcosms. *Ecological Modelling,* **185**, 483-512.

Best E. P. H., Buzzelli C. P., Bartell S. M., Wetzel R. L., Boyd W. A., Doyle R. D. & Campbell K. R. (2001) Modeling submersed macrophyte growth in relation to underwater light climate: modeling approaches and application potential. *Hydrobiologia,* **444**, 43-70.

Blom G. & Aalderink R. H. (1998) Calibration of three resuspension/sedimentation models. *Water Science and Technology,* **37**, 41-49.

Champion P. D. & Tanner C. C. (2000) Seasonality of macrophytes and interaction with flow in a New Zealand lowland stream. *Hydrobiologia,* **441**, 1-12.

Clarke S. J. (2002) Vegetation growth in rivers: influences upon sediment and nutrient dynamics. *Progress in Physical Geography,* **26**, 159-172.

EPA. (1985) Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling (Second Edition): EPA.

Eriksson P. G. & Weisner S. E. B. (1999) An experimental study on effects of submersed macrophytes on nitrification and denitrification in ammonium-rich aquatic systems. *Limnology and Oceanography,* **44**, 1993-1999.

Eriksson P. G. & Weisner S. E. B. (1997) Nitrogen removal in a wastewater reservoir: The importance of denitrification by epiphytic biofilms on submersed vegetation. *Journal of Environmental Quality,* **26**, 905-910.

Evans R. O., Bass K. L., Burchelt M. R., Hinson R. D., Johnson R. & Doxey M. (2007) Management alternatives to enhance water quality and ecological function of channelized streams and drainage canals. *Journal of Soil and Water Conservation,* **62**, 308-320.

Giusti E. & Marsili-Libelli S. (2005) Modelling the interactions between nutrients and the submersed vegetation in the Orbetello Lagoon. *Ecological Modelling,* **184**, 141-161.

Green J. C. (2006) Effect of macrophyte spatial variability on channel resistance. *Advances in Water Resources,* **29**, 426-438.

Gumbricht T. (1993) Nutrient Removal Processes in Fresh-Water Submersed Macrophyte Systems. *Ecological Engineering,* **2**, 1-30.

Herb W. R. & Stefan H. G. (2003) Integral growth of submersed macrophytes in varying light regimes. *Ecological Modelling,* **168**, 77-100.

James W. F., Barko J. W. & Butler M. G. (2004) Shear stress and sediment resuspension in relation to submersed macrophyte biomass. *Hydrobiologia,* **515**, 181-191.

Janse J. H. (1998) A model of ditch vegetation in relation to eutrophication. *Water Science and Technology,* **37**, 139-149.

Janse J. H. & Van Puijenbroek P. (1998) Effects of eutrophication in drainage ditches. *Environmental Pollution,* **102**, 547-552.

Kadlec R. H. & Knight R. L. (1996) *Treatment Wetlands.*: Lewis Publishers, Baco Raton,.

Kadlec R. H. & Reddy K. R. (2001) Temperature effects in treatment wetlands. *Water Environment Research,* **73**, 543-557.

Langergraber G. (2005) The role of plant uptake on the removal of organic matter and nutrients in subsurface flow constructed wetlands: a simulation study. *Water Science and Technology,* **51**, 213-223.

Laursen A. E. & Seitzinger S. P. (2002) Measurement of denitrification in rivers: an integrated, whole reach approach. *Hydrobiologia,* **485**, 67-81.

Pina-Ochoa E. & Alvarez-Cobelas M. (2006) Denitrification in aquatic environments: A cross-system analysis. *Biogeochemistry,* **81**, 111-130.

Reichert P., Borchardt D., Henze M., Rauch W., Shanahan P., Somlyody L. & Vanrolleghem P. (ed.) (2001) *River Water Quality Model No.1, IWA Scientific & Technical Report No. 12*. London: IWA Publishing.

Sand-Jensen K., Jeppesen E., Nielsen K., Vanderbijl L., Hjermind L., Nielsen L. W. & Iversen T. M. (1989) Growth of Macrophytes and Ecosystem Consequences in a Lowland Danish Stream. *Freshwater Biology,* **22**, 15-32.

Scheffer M. (1998) *Ecology of shallow lakes*. Population and community biology series. London [etc.]: Chapman & Hall.

Scheffer M., Bakema A. H. & Wortelboer F. G. (1993) Megaplant - a Simulation-Model of the Dynamics of Submerged Plants. *Aquatic Botany,* **45**, 341-356.

Scholz M. & Trepel M. (2004) Water quality characteristics of vegetated groundwater-fed ditches in a riparian peatland. *Science of the Total Environment,* **332**, 109-122.

Stowa / MX-systems. (2004) Duflow Manual, version 3.7, pp. 118. Delft, The Netherlands: Stowa / MX-systems.

Strock J. S., Dell C. J. & Schmidt J. P. (2007) Managing natural processes in drainage ditches for nonpoint source nitrogen control. *Journal of Soil and Water Conservation,* **62**, 188-196.

Thomann R. V. & Mueller J. A. (1987) *Principles of surface water quality modeling and control*. New York: Harper & Row.

van Nes E. H., Scheffer M., van den Berg M. S. & Coops H. (2002) Aquatic macrophytes: restore, eradicate or is there a compromise? *Aquatic Botany,* **72**, 387-403.

Annex 4.1 Parameter explication and values, and external variables.

(** **Bold** values from calibration, *italic* values measured at the research site).

Parameter	Description	Unit	Range	Used value**	Reference
D_{bf}	Specific biofilm denitrification	$m^2.d^{-1}.g^{-1}$	0.002 - 0.0025	0.002	Calculated from (Eriksson & Weisner 1997) (Baldwin *et al.* 2006)
FD	Fraction detritus production from vegetation loss	-	0.5 - 0.6	0.5	(Giusti & Marsili-Libelli 2005)
H_{max}	Maximum height of the vegetation	m	0.5 - 2	1	Plant specific
I_{opt}	Optimal light intensity	$W.m^{-2}$	50 - 400	**250**	Plant specific
K_B	Half saturation value for vegetated cross sectional area	$g.m^{-2}$	10 - 50	80	estimation
K_H	Half saturation value for macrophyte height	$g.m^{-2}$	10 - 50	100	estimation
k_{MI}	Mineralization rate constant	d^{-1}	0.1 - 0.3	0.1	(EPA 1985)
K_{MN}	Coefficient for ammonium preference	$g.m^{-3}$	0 - 1	0.5	(EPA 1985)
K_N	Half saturation value N for macrophyte growth	$g.m^{-3}$	0.04 - 0.12	0.1	(Bartleson, Kemp & Stevenson 2005)
k_{NI}	Nitrification rate constant	d^{-1}	0.2 – 0.4	0.2	(EPA 1985)
K_P	Half saturation value P for macrophyte growth	$g.m^{-3}$	0.01 - 0.05	0.01	(Bartleson *et al.* 2005)
K_r	Half saturation value resuspension inhibition	$g.m^{-2}$	100 - 150	100	estimation
K_s	Half saturation value orbital velocity reduction	$g.m^{-2}$	80 - 120	100	Calculated from (James, Barko & Butler 2004)
k_{sd}	Denitrification rate constant sediment	$m.d^{-1}$	0.1 - 0.2	**0.1**	Calculated from (Laursen & Seitzinger 2002) (Pina-Ochoa & Alvarez-Cobelas 2006)
Loss	Macrophyte loss rate	d^{-1}	0.01 - 0.04	**0.035**	(Bartleson *et al.* 2005; Giusti & Marsili-Libelli 2005; Herb & Stefan 2003)

μ_{max}	Maximum macrophyte growth rate	d^{-1}	0.05 - 0.30	**0.33**	(Giusti & Marsili-Libelli 2005; Herb & Stefan 2003; Janse 1998; Scheffer *et al.* 1993)
$Nflux$	Nitrogen release/fixation sediment	g.m^{-2}.d^{-1}	-0.1 - 0.5	*0.052*	(Giusti & Marsili-Libelli 2005)
Nm	Nitrogen content macrophytes	gN.g^{-1}	0.015 - 0.025	*0.02*	(Janse 1998; Kadlec & Knight 1996; Langergraber 2005)
Nss	Nitrogen content sediment	gN.g^{-1}	0.01 - 0.02	0.02	Site specific
$Pflux$	Phosphorus release/fixation sediment	g.m^{-2}.d^{-1}	-0.01 - 0.04	*0.0003*	(EPA 1985)
Pm	Phosphorus content macrophytes	gP.g^{-1}	0.002 - 0.005	*0.003*	(Janse 1998; Kadlec & Knight 1996; Langergraber 2005)
Pss	Phosphorus content sediment	gP.g^{-1}	0.002 - 0.005	0.002	Site specific
Θ_{DEN}	Temperature coefficient denitrification	-	1.04 - 1.06	1.04	(Bartleson *et al.* 2005; Kadlec & Reddy 2001)
Θ_{M}	Temperature coefficient macrophyte growth	-	1.04 - 1.06	1.05	(Bartleson *et al.* 2005; Kadlec & Reddy 2001)
Θ_{IM}	Temperature coefficient mineralization	-	1.04 - 1.06	1.04	(Bartleson *et al.* 2005; Kadlec & Reddy 2001)
Θ_{IN}	Temperature coefficient nitrification	-	1.04 - 1.06	1.06	(Bartleson *et al.* 2005; Kadlec & Reddy 2001)
$Rflux$	Resuspension rate	g.m^{-2}.d^{-1}	1000 - 1500	1200	Site specific
Vs	Settling velocity	m.d^{-1}	0.1 - 1	0.5	(Blom & Aalderink 1998)
W	Conductivity rate biomass	m.s^{-1}	100 - 300	100	(Arcadis 2004)
x	Hill function coefficient vegetated area	-	1 - 3	1	estimation
y	Hill function coefficient vegetation height	-	1 - 3	1	estimation
ε_{w}	Background extinction	m^{-1}	0.1 - 2	*0.5*	System specific (measurement)
λ_{M}	Specific macrophyte extinction	m.g^{-1}	0.01 - 0.025	**0.06**	(Herb & Stefan 2003; Sand-Jensen *et al.* 1989)
τ_{res}	Critical shear stress resuspension	pa	0.1 - 0.2	0.4	(James *et al.* 2004)
τ_{sed}	Critical shear stress sedimentation	pa	0.04 - 0.1	0.04	(Blom & Aalderink 1998; James *et al.* 2004)

External Variables

z	Water depth	m	From the hydrology module
Vs	Flow velocity	$m.s^{-1}$	From the hydrology module
Io	Day average light intensity	$W.m^{-2}$	Time series from meteorological station
T	daily temperature	^{o}C	Time series from meteorological station
Hv	Days of harvesting biomass	-	User defined time series

Chapter 5

Modeling the impact of aquatic macrophytes and management strategies on nutrient retention in streams

Jeroen de Klein[1], Hans Aalderink[2] & Rob Portielje[3]

[1] *Wageningen University and Research Centre, Wageningen, The Netherlands*
[2] *Arcadis Regio BV, Apeldoorn, The Netherlands*
[3] *Rijkswaterstaat RIZA, Lelystad, The Netherlands*

(Submitted)

Modeling the impact of aquatic macrophytes and management strategies on nutrient retention in streams

Abstract

For the implementation of the EU Water Framework Directive member states have to develop catchment management plans to achieve good ecological status of surface waters. To evaluate the effectiveness of management options there is a need for prediction tools. Quantifying retention of nutrients in surface waters is essential for abatement of eutrophication and for setting nutrient emissions limits. We developed and applied a mechanistic model to simulate the effect of management strategies and aquatic macrophytes on nutrient retention in streams. Simulation scenarios comprised changes in hydraulic residence time, macrophyte growth and sediment release in a summer en winter period. The results suggest that mediating residence time and maintenance of macrophytes may have large impacts on the retention of nutrients. From the simulation results we derived a metamodel that allows predicting nutrient retention without running the complex dynamic model.

Introduction

Eutrophication of standing waters and coastal zones is of great general concern. Abatement strategies are focused on reducing the emissions of nutrients to surface waters. In most countries largest diffuse emissions are related to agricultural land use in the river catchments. European policies (i.e. Nitrate Directive, Water Framework Directive) aim at reducing these emissions to protect groundwater quality and to achieve good ecological status of the surface waters. Besides emissions, also biochemical and physical processes during transport determine the fate of nutrients and their effects on aquatic ecosystems. Retention caused by these processes can lead to a considerable decrease in nutrient loads to downstream water bodies (Kronvang et al., 2004). There is an increasing recognition that besides morphological and hydrological improvement of rivers, restoration of internal biochemical processes should be addressed even more (Doyle et al., 2003).

In the budgets of nitrogen and phosphorus in the soil-ground water-surface water system, nutrient retention in surface waters can be considerable but is still highly uncertain (Reddy et al., 1999; Saunders and Kalff, 2001). Due to variability of the retention processes, both in space and time, it is difficult to quantify changes in nutrient loads during riverine transport. Based on process rates, mass balances and expert judgment several retention coefficients have been deducted by different researchers (e.g. Behrendt and Opitz, 1999; Kronvang et al., 2004). Although useful methods for retention estimation exist which can be generally applied, they usually do not account for specific local conditions, nor explicitly describe retention processes.

To develop mitigation strategies and to predict the effect of specific measures on water quality, there is a need for a more mechanistic approach. Management options specially refer to design of watercourses, presence and management of macrophytes, local hydrology, etc. In this paper we present results of simulations with a new process model. The overall objective is to set up a metamodel for estimating nutrient retention in surface waters. We define a metamodel as an abstraction of a complex simulation model that comprises the principal mechanistic concepts, without the need for a lot of data and modeling effort.

Model overview

The general approach for this study is to run a series of modeling scenarios, using the dynamic process-model AquaVenus. The model simulates seasonal variation of aquatic vegetation growth, nutrient fate and suspended matter. The results of the modeling scenarios are analyzed and transformed into simple input-output relations to derive a metamodel. AquaVenus consists of a series of equations reflecting the main processes of macrophyte biomass and nutrient in fresh water systems. In contrast to commonly used, algae growth dominated eutrophication models the emphasis of the model AquaVenus is on the specific role of submerged macrophytes on nutrient transformations and suspended matter behavior. Therefore the model is applicable for fresh waters that are dominated by aquatic vegetation like most lowland streams and small rivers, ditches and shallow lakes. On the other hand, the effect of the absence of macrophytes on nutrient retention can be evaluated, as is the case in many eutrophicated shallow lakes that are in the phytoplankton dominated turbid state (Scheffer, 1998). A detailed description of the model, parameter estimations and model performance is presented in De Klein (2008). An overview of the nutrient pathways and processes in the model is given in figure 5.1.

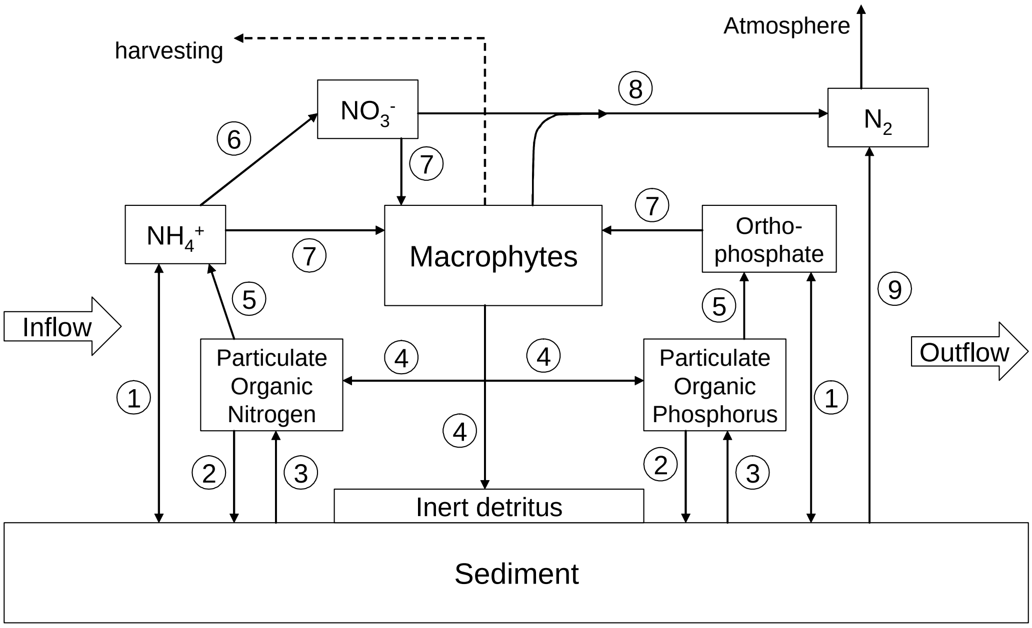


Figure 5.1 *Pathways and processes of Nitrogen and Phosphorus in the model AquaVenus. (Processes: 1. sediment release/absorption, 2. sedimentation, 3. resuspension, 4. decomposition, 5. mineralization, 6. nitrification, 7. macrophyte uptake (net growth), 8. epiphytic biofilm denitrification, 9. sediment denitrification.)*

Macrophytes play a distinct role in the retention of nutrients and suspended solids. This relates not only to biochemical processes but also to the physical environment. Four different mechanisms can be distinguished:
1. macrophytes can reduce flow velocities significantly, resulting in an increase of the hydraulic residence time:, 2. reduction of current velocity promotes the deposition and trapping of suspended particles within the macrophytes stands; 3. uptake of nitrogen en phosphorus by macrophytes; 4. macrophytes stimulate denitrification by supplying suitable substrate for denitrifying epiphytic biofilms.
These mechanisms are incorporated in AquaVenus in a straightforward way. The purpose of the model is to generate generic knowledge of nutrient retention and the effect of mitigation measures, with a limited number of equations and parameters. However, despite these simplifications the analysis of model behavior, calibration and verification shows satisfactory results in relation to the models objective (De Klein, 2008).

Methods

For this study the process model AquaVenus was linked to the 1D hydrodynamic modeling tool Duflow for modeling transport of water and substances (Aalderink et al., 1995). Duflow is recently expanded to allow modeling feedbacks of water quality on hydrology, such as the obstruction of flow by macrophytes. The model was applied for the upper part of a lowland stream (Gooiermars).

Gooiermars consists of several first and second order streams, with a total length of around 4 km. Average hydraulic residence time is 1.66 days in summer and 0.51 days in winter. Average slope is 0.4 m.km^{-1}. Most reaches are macrophyte dominated. A detailed description is presented in De Klein (2008).

Water flow, nutrient transport and processes were calculated dynamically for a period of one year, with a time step of one hour. We used different modeling scenarios reflecting varying conditions of water flow, release of nutrients from the sediment, profile redesign and vegetation maintenance. Several studies indicate that hydraulic residence time is an important factor for nutrient retention in fresh waters (Behrendt and Opitz, 1999; Seitzinger et al., 2002). We simulated N and P retention with varying residence times, by increasing (200%) and decreasing (40% and 20%) the groundwater flow to the watercourses, causing an inverse change in the residence time (50%, 250% and 500%). Groundwater concentrations were unchanged so total incoming loads varied proportional to the groundwater flow. To study the effect of higher incoming loads we calculated all above scenarios with and without nutrient release from the sediment. Sediment release in Gooiersmars under basic conditions is estimated at 0.06 gN m^{-2} d^{-1} and 0.01 gP m^{-2} d^{-1}. In scenarios with no release these rates are set to zero.

Furthermore, we examined the impact of macrophytes on retention by running two simulation scenarios: one with undisturbed vegetation growth and one without vegetation growth at all, and additionally two different scenarios with vegetation harvesting: cutting once the vegetation (July) to 10% of its actual biomass, and cutting three times (June, August, and October) to 50%.

Nutrient retention may benefit from changes in (hydro) morphological conditions in small water courses (Doyle et al., 2003), especially measures that enlarge the hydraulic residence time. We hypothesized that impacts of adapting residence time may be different when applying different types of measures. We studied three ways of mediating water residence time: a) increasing/decreasing the inflow of groundwater, b) applying a deeper/undeeper profile (and c) applying a wider profile.

For all scenarios nutrient retention of the whole water system was calculated by quantifying the total incoming and outgoing load of nutrients. To account for seasonality we distinguished a summer period (April –September) and a winter period (October –

March). Retention was calculated following $R = 1 - L_{out} / L_{in}$, where R is retention fraction (-) or relative retention, L_{in} is incoming nutrient load (g) and L_{out} is outgoing nutrient load (g). Loads are summarized over a half year period. Note, that for the retention calculation sediment release is regarded as an external source, so it is calculated in the incoming load (eq. 1).

$$L_{in} = (C_{av}.Q + S.A).D \quad (1) \qquad \text{and} \qquad C_{in} = C_{av} + \frac{S.A}{Q} \quad (2)$$

where C_{av} is discharge weighted average nutrient concentration of incoming flows (g m^{-3}), Q is total discharge of inflows (m^3 d^{-1}), S is nutrient release from sediment (g m^{-2} d^{-1}), A is total sediment surface (m^2), D is length of the evaluated period (d) and C_{in} is the apparent inflow concentration in the water system (g m^{-3}).

Results and Discussion

Simulation results

The simulations suggest that under basic conditions relative nitrogen retention is about 0.41 in summer and 0.18 in winter, and for phosphorus 0.42 and 0.25 respectively. Expressed as an average areal retention rate this amounts to 1150 kgN $ha^{-1}y^{-1}$ and 98 kgP $ha^{-1}y^{-1}$. These retention rates are in line of what is usually found in streams and rivers (Svendsen and Kronvang, 1993; Saunders and Kalff, 2001; Bernot et al., 2006). For the EU-project Euroharp data from a number of catchments were analyzed to design nutrient retention guidelines (Kronvang et al., 2004). The researchers suggested 840 kgN $ha^{-1}y^{-1}$ and 55 kgP $ha^{-1}y^{-1}$ as an average value for retention of nutrients in lowland rivers. Compared to these values our annual retention rates are higher, which can be explained by the nature of our modeled water system. Gooiermars is a network of upper reaches of a lowland river, whereas for Euroharp whole catchments are analyzed. It was found that headwaters and upper parts of river systems exhibit a higher relative nutrient retention compared to downstream reaches (Peterson et al., 2001; Wollheim et al., 2006).

Nutrient retention related to hydraulic residence time is presented in figure 5.2. This figure also shows the effect of diffusive nutrient release from the sediment. As was expected results show a strong increase of retention with increasing residence time. The relation is not linear, but approaches a saturation level indicating first order process kinetics. The consequence of this is addressed later.

As stated earlier retention is calculated with the input from sediment release treated as an external source. In theory retention may thus be independent from the rate of sediment release. For nitrogen this is indeed found. Extra N input is easily (de)nitrified so the retention fraction stays at the same level. However, in summer phosphorus retention decreases when there is nutrient flux from the sediment. P release increases the concentration of dissolved phosphorus which has to be transformed in particulate organic P via macrophyte growth and decomposition. This effect gets more pronounced at high residence times, where the relative contribution of the release flux to the total input load increases.

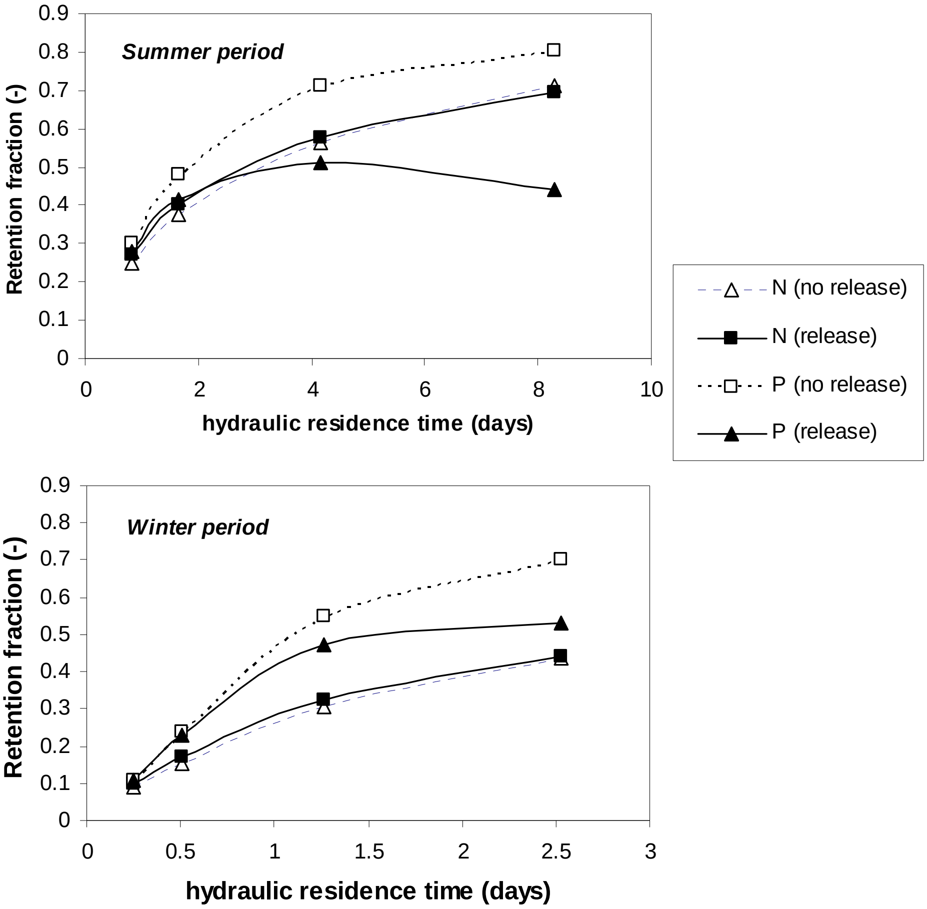


Figure 5.2 *Nitrogen (N) and phosphorus (P) retention with varying hydraulic residence time, under basic conditions (with release) and without release of N and P from the sediment.*

To study the mechanism of nutrient retention in our water system we quantified the separate process rates and set up a mass balance for N and P under basic conditions (figure 5.3). The inflow and outflow mass of N and P balance quit well. The maximum discrepancy was found for N in the summer period (3.7 %). On an annual basis this was less than 1.5 %. Inaccuracy can be explained by numerical errors in the model. The water budget showed an error of around 1 %. Accumulation in the water phase, due to differences in nutrient concentrations at the start and the end of the simulation period (not presented in figure 5.3), was less than 0.1 %.

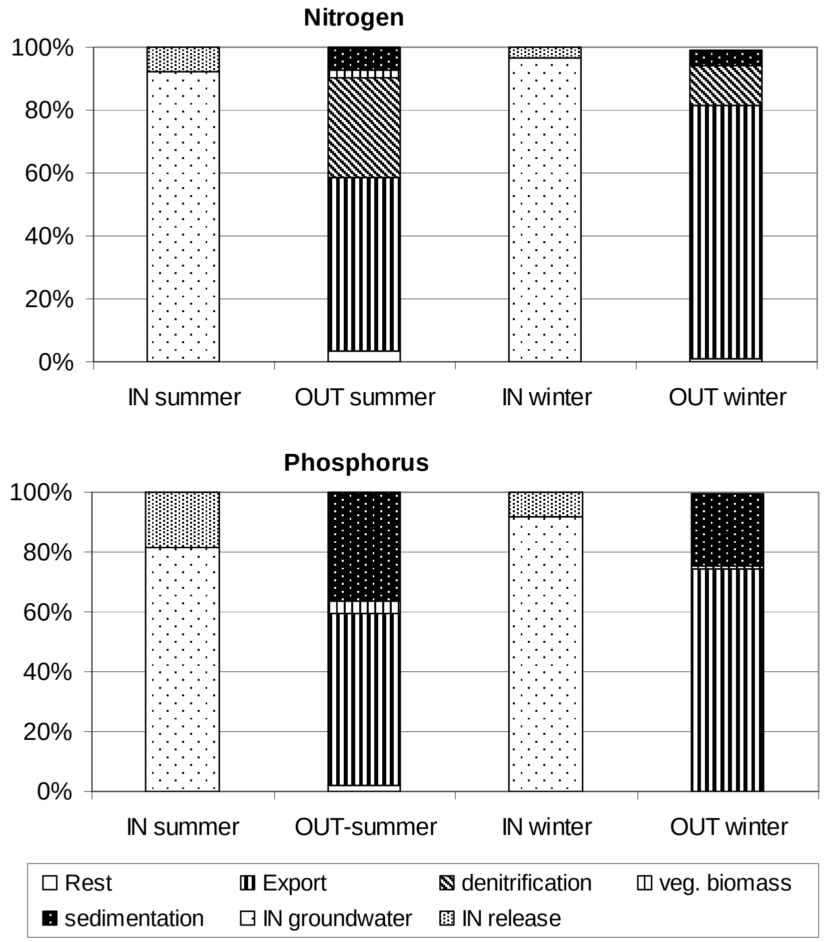


Figure 5.3 *Mass balance and relative contribution of retention processes for the modeled water system under basic conditions.*

An analysis of the process rates and verifications, presented in De Klein (2008) showed good agreement with other studies of nutrient retention mechanisms. The main mechanism for nutrient removal in the model is denitrification for nitrogen and sedimentation for phosphorus (figure 5.3). This is in line with results from many researches, (e.g. Kronvang et al. 2004; Schaller et al. 2004). Furthermore, nutrient uptake by macrophyte growth contributes less than 2 % to N and P retention. Even in permanently vegetated constructed wetlands this is usually no more than 4 -5 % (Langergraber, 2005).

Although the direct effect of macrophyte (uptake) may be small, the indirect effects on nutrient retention are substantial (Figure 5.4). An undisturbed growth of macrophytes may clearly stimulate nutrient retention in the summer period. For nitrogen the model predicts an increase of around 25 % and for phosphorus even around 60 % compared to a situation with no macrophyte growth. In the winter period no significant effect is predicted for phosphorus, and only a 19 % increase for nitrogen is computed.

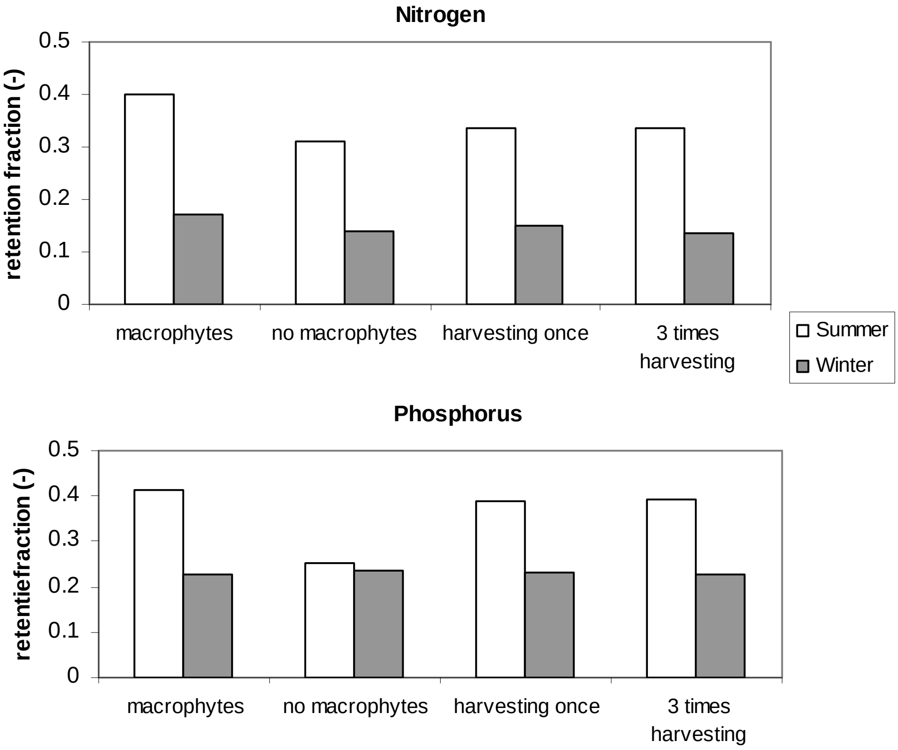


***Figure 5.4** Effect of presence and maintenance of macrophytes on nutrient retention, under basic conditions.*

Macrophyte stands promote sedimentation and reduce resuspension of organic particles, which are the main mechanism for P retention. Additional N removal is also explained by epiphytic biofilms denitrification. Nevertheless, the relative N retention is increased less by presence of macrophytes due to sediment denitrification, which is, in general, independent from the presence of vegetation (Schaller et al., 2004). In the model, harvesting of biomass during the growing season does in fact decrease the nitrogen retention compared to a situation without harvesting. The extra removal of nutrients via biomass harvesting and disposal does not counterbalance the (temporal) disturbance of macrophytes stands and its positive effect on retention by sedimentation and denitrification.

Alternative ways of manipulating residence time affect retention differently (Figure 5.5). The results show a clear difference in nutrient retention for different hydro-morphological measures. At comparable residence times the wide profile is most efficient in retaining nutrients, whereas the deep profile is less efficient. For the flow variation scenarios the watercourses profiles are kept at basic conditions. Differences in profiles can be expressed as the average width to depth ratio. For the wider profile this ratio is 11.5, for the basic profile 7.5 and for the deeper profile 4.0. These differences in width to depth ratios largely explain the differences in observed nutrient retentions, as the bottom related processes (macrophyte growth, sedimentation, and denitrification) dominate the retention mechanisms. For the deep profiles it can be observed that the advantage of increased residence time is neutralized by the increase in water depth and thus a decrease of the effect of benthic processes.

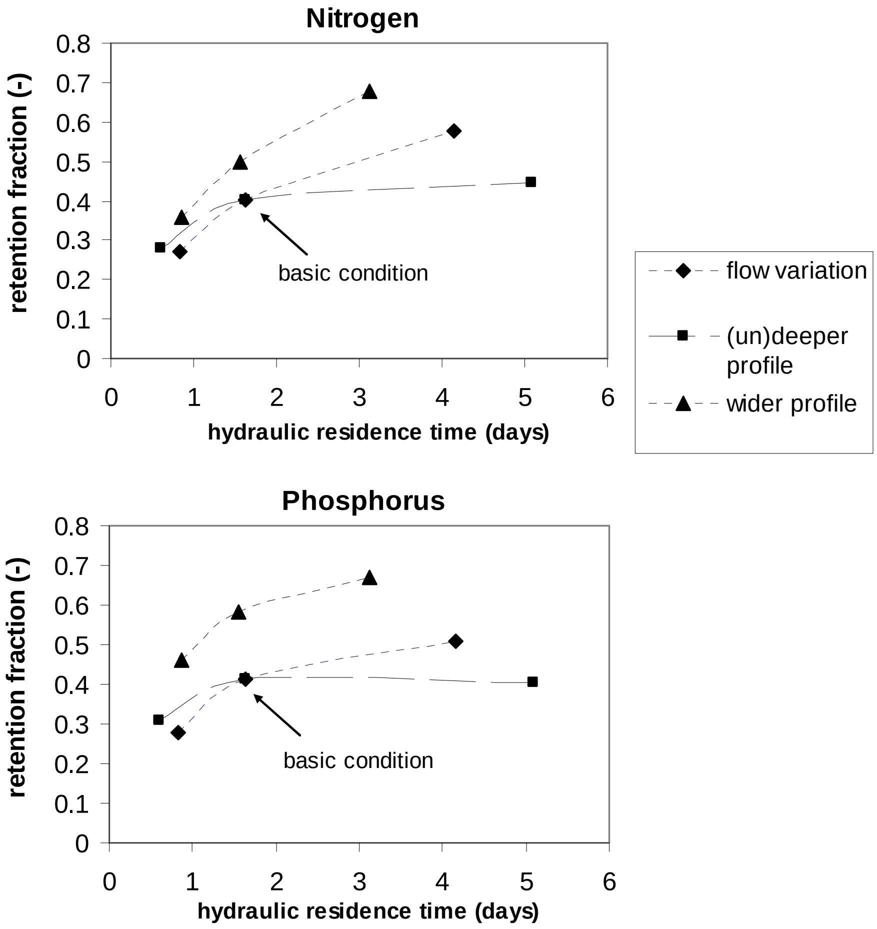


Figure 5.5 *Retention at varying residence time, resulting from changes in the watercourses profile, compared with varying residence time resulting from changes in water inflow rates (summer period).*

<u>Metamodel</u>

From the results we conclude that the main controlling factors for nutrient retention in streams and small rivers are hydraulic residence time, macrophytes and sediment release flux. To describe these relations quantitatively we suggest that a metamodel can be applied assuming an ideal mixed water system, since we evaluate half year periods and inflows are diffuse over the reaches. Because saturation levels of retention do not all approach 1, a 1st order decay rate and a zero order term should be used. The mass balance equation for a completely mixed water system yields:

$$V\frac{dC}{dt} = Q.C_{in} - Q.C - k_1.C.V + k_0.V \qquad (3)$$

where C is nutrient outflow concentration (g.m^{-3}), k_1 is 1st order decay rate (d^{-1}), k_0 is zero order term (g.m^{-3}.d^{-1}) and V is total water volume (m^3). For average hydraulic residence time T=V/Q (d) and assuming steady state (process rates are relatively fast compare to the half year period) the outflow concentration C and retention fraction R can be calculated as:

$$C = \frac{C_{in} + k_0.T}{1 + k_1.T} \quad (4) \qquad \text{and} \qquad R = 1 - \frac{C}{C_{in}} = 1 - \frac{1 + {}^{k_0}\!/_{C_{in}}.T}{1 + k_1.T} \qquad (5)$$

We argue that k_0 is related to complex interactions in the deterministic model and zero-order processes such as release from the sediment. Since C_{in} is also determined by sediment release we presume that both are related. Therefore k_0/C_{in} is replaced by k_a. As a consequence, retention calculation becomes independent from the apparent inflow concentration. To account for the effect of macrophytes we introduce a third parameter, indicating the influence of macrophytes M (-). Thus, we define our final metamodel as:

$$R = \left[1 - \frac{1 + k_a.T}{1 + k_1.T}\right].M \qquad (6)$$

The parameters are calibrated with the results of the process model retention calculations. For parameter estimation the solver option of MS-Excel is used, optimizing the R^2 (Table 5.1).

For most of the scenarios the metamodel fit to the simulations is very high (R^2>0.96). For P in summer with sediment release R^2 is lower but still 0.77. k_1 values for P are in the range of the sedimentation rates (1.5 d^{-1} in summer with macrophytes and 0.7 d^{-1} in winter). For nitrogen, k_1 values represent lumped 1st order process rates (mineralization, nitrification and denitrification) which are varying and cannot be link easily to the metamodel parameters.

Table 5.1 *Calibrated parameter values for the retention metamodel (eq. 6).*

	Summer				Winter			
	No release		Release		No release		Release	
	N	P	N	P	N	P	N	P
K_1	0.447	0.562	0.562	1.738	0.497	0.489	0.632	0.819
K_a	0.050	0.007	0.093	0.831	0.108	0.001	0.177	0.144
M (macrophytes)	1	1	1	1	1	1	1	1
M (no macrophytes)	0.77	0.61	0.77	0.61	0.81	1	0.81	1
R^2	*0.996*	*0.995*	*0.999*	*0.774*	*1.000*	*0.978*	*1.000*	*0.960*

To demonstrate the effect of the zero-order component in the metamodel we plotted AquaVenus results, metamodel and a straightforward 1st order decay model (Figure 5.6). The metamodel performance is better compared to that of the 1st order model; especially the saturation of retention at high residence times is predicted more accurately.

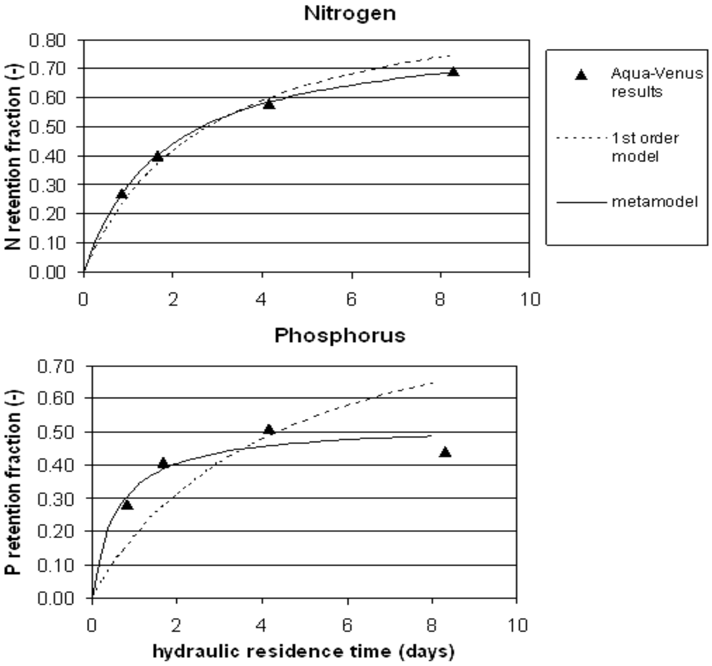


Figure 5.6 *Calculated nitrogen and phosphorus retention with the dynamic model AquaVenus, a 1st-order decay and the metamodel with parameters according to table 5.1. (Summer period at basic conditions, with release from the sediment).*

Conclusions

Our results indicate that hydraulic residence time and macrophyte biomass can have large effects on the retention of nutrients in streams. Longer residence time promotes the retention of N and P, saturating at long residence times to a maximum retention capacity. Macrophyte growth may promote retention processes up to 60% compared to a situation without macrophytes. Harvesting of macrophytes to remove nutrients has no effect or decreases nutrient retention. Our simulations suggest that redesign of watercourses to mediate water flow and hydraulic residence time can have different effects. A wider profile is predicted to enhance nutrient retention due to a higher sediment to water ratio. Deepening a profile has no effect or reduces retention, compared to a basic profile with comparable residence time.

The results of the complex mechanistic model can be approximated with a metamodel, containing a first and zero-order term. Metamodel calculations show good agreement with the simulations of AquaVenus. The retention metamodel allows estimating the effect of management options on nutrient retention in streams without the time effort and data demands of a complex dynamic model. This concept will be used in the development of an integrated evaluation tool for catchment management plans in the Netherlands.

References

Aalderink, R.H., Klaver, N.J., and Noorman., R. (eds) (1995) *Duflow V 2.0 Micro-computer package for the simulation of 1- dimensional flow and water quality in a network of open water courses.* In: Water Quality Modelling, proceedings of the international conference on water quality modeling. Orlando.

Behrendt, H., and Opitz, D. (1999) Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia* **410**: 111-122.

Bernot, M.J., Tank, J.L., Royer, T.V., and David, M.B. (2006) Nutrient uptake in streams draining agricultural catchments of the midwestern United States. *Freshwater Biology* **51**: 499-509.

Clarke, S.J. (2002) Vegetation growth in rivers: influences upon sediment and nutrient dynamics. *Progress in Physical Geography* **26**: 159-172.

De Klein. (2008) Aqua-VENUS; a mechanistic simulation model for nutrients in macrophyte dominated fresh waters. *Chapter 4, this thesis*.

Doyle, M.W., Stanley, E.H., and Harbor, J.M. (2003) Hydrogeomorphic controls on phosphorus retention in streams. *Water Resources Research* **39**.

Eriksson, P.G., and Weisner, S.E.B. (1999) An experimental study on effects of submersed macrophytes on nitrification and denitrification in ammonium-rich aquatic systems. *Limnology and Oceanography* **44**: 1993-1999.

James, W.F., Barko, J.W., and Butler, M.G. (2004) Shear stress and sediment resuspension in relation to submersed macrophyte biomass. *Hydrobiologia* **515**: 181-191.

Kronvang, B., Hezlar, J., Boers, P., Jensen, J.P., Behrendt, H., Anderson, T. et al. (2004) Nutrient Retention Handbook. Software Manual for EUROHARP-NUTRET and Scientific review on nutrient retention. Oslo, Norway: NIVA, p. 103 pp.

Langergraber, G. (2005) The role of plant uptake on the removal of organic matter and nutrients in subsurface flow constructed wetlands: a simulation study. *Water Science and Technology* **51**: 213-223.

Madsen, J.D., Chambers, P.A., James, W.F., Koch, E.W., and Westlake, D.F. (2001) The interaction between water movement, sediment dynamics and submersed macrophytes. *Hydrobiologia* **444**: 71-84.

Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L. et al. (2001) Control of nitrogen export from watersheds by headwater streams. *Science* **292**: 86-90.

Reddy, K.R., Kadlec, R.H., Flaig, E., and Gale, P.M. (1999) Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology* **29**: 83-146.

Sand-Jensen, K. (1998) Influence of submerged macrophytes on sediment composition and near-bed flow in lowland streams. *Freshwater Biology* **39**: 663-679.

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

Schaller, J.L., Royer, T.V., David, M.B., and Tank, J.L. (2004) Denitrification associated with plants and sediments in an agricultural stream. *Journal of the North American Benthological Society* **23**: 667-676.

Scheffer, M. (1998) *Ecology of shallow lakes*. London [etc.]: Chapman & Hall.

Schulz, M., Kozerski, H.P., Pluntke, T., and Rinke, K. (2003) The influence of macrophytes on sedimentation and nutrient retention in the lower River Spree (Germany). *Water Research* **37**: 569-578.

Seitzinger, S.P., Styles, R.V., Boyer, E.W., Alexander, R.B., Billen, G., Howarth, R.W. et al. (2002) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry* **57**: 199-237.

Svendsen, L.M., and Kronvang, B. (1993) Retention of Nitrogen and Phosphorus in a Danish Lowland River System - Implications for the Export from the Watershed. *Hydrobiologia* **251**: 123-135.

Weisner, S.E.B., Eriksson, P.G., Graneli, W., and Leonardson, L. (1994) Influence of Macrophytes on Nitrate Removal in Wetlands. *Ambio* **23**: 363-366.

Wollheim, W.M., Voosmarty, C.J., Peterson, B.J., Seitzinger, S.P., and Hopkinson, C.S. (2006) Relationship between river size and nutrient removal. *Geophysical Research Letters* **33**.

Chapter 6

Quantifying seasonal and annual retention of nutrients in lowland rivers at catchment scale.

Jeroen de Klein and Bart Koelmans

Wageningen University and Research Centre, Wageningen, The Netherlands

(submitted)

Quantifying seasonal and annual retention of nutrients in lowland rivers at catchment scale

Abstract

Nutrient retention in freshwater systems is usually calculated from mass balances or estimated from catchment characteristics as an average annual loss. However, to set accurate critical values for the protection of lakes and coastal areas, it is crucial to know the seasonal variation of the nutrient exports, especially for lakes with low residence times. This paper aims at improving methods for estimating in-stream nutrient retention and its seasonal variation. For 13 lowland river catchments in Western Europe, inputs to surface water and exports were calculated, on a monthly as well as an annual (average) basis. The catchments varied in size (21 to 486 km^2) and annual in-stream retention ranged from 23 to 84 % for N and 39 to 72 % for P.

A novel calculation method is presented that quantifies monthly exports from lowland rivers based on an annual load to the river system. Inputs in the calculation are annual emission to the surface waters, average monthly river discharge, average monthly water temperature and fraction of surface water area in the catchment. The method accounts for both seasonal variation of emission to the surface water and seasonal in-stream retention. The similarity of calculated values and the calibration data was high (N: $R^2 = 0.93$; $p<0.0001$. P: $R^2 = 0.81$; $p<0.0001$). Validation of the equations also showed good results (model efficiencies for the separate catchments ranged from 31% to 95%, average 76%). This implies that exports of nitrogen and phosphorus on a monthly basis can be calculated with few input data, for a range of Western-Europe lowland rivers.

Our analysis shows that, in general, retention in summer is higher than in winter, resulting in lower summer nutrient concentrations than calculated with an average annual input. In shallow lakes with short water residence time, seasonal variation in nutrient load will have a greater impact on in-lake nutrient concentrations compared to larger lakes. This implies that accurate evaluation of critical thresholds for eutrophication effects requires that we take seasonal

variation in hydrology and nutrient loading into account. Our quantification method thus may improve the modeling of eutrophication effects in standing waters.

Introduction

Eutrophication of standing waters is a serious problem in many countries. Nutrients originate from point and diffuse sources. Subsequently, they are transported trough catchments and discharged to lakes and coastal areas. This results in an excessive growth of phytoplankton and absence of water plants (Scheffer 1998). In many countries much effort has been undertaken to reduce the loads of nutrients. However, in only few cases this has lead to an improvement of transparency and macrophyte abundance in the lakes. After all, the mechanisms related to increased nutrient loads in lakes are complex and despite numerous studies, nutrient transformations in lakes and streams are not completely understood (Thomann & Linker 1998).

Only part of the nutrients discharged to the surface water by leaching or erosion will eventually enter the coastal systems. Several budget studies on catchments show a substantial discrepancy between the emissions from the land to the head streams and the final export out of the catchment (Billen *et al.* 1999; Faafeng & Roseth 1993; Zessner & Kroiss 1999). For a number of European catchments, it was found that this discrepancy could not be explained by uncertainties in the budget calculations and measurements (Behrendt & Opitz 1999). Presumably, during riverine transport nutrient cycling takes place, almost always resulting in a net retention of nitrogen and phosphorus.

Estimates of nutrient retention in streams vary from around 10 to 60 % of the emission (e.g (Zessner & Kroiss 1999) (Reddy *et al.* 1999) (Garnier *et al.* 2002).). The underlying retention processes differ for phosphorus and nitrogen by the nature of the emissions. In general, more than 70% of total P and less than 10 % of total N is transported in rivers in particulate form (Svendsen & Kronvang 1993). For nitrogen, denitrification is an important retention mechanism, whereas phosphorus is mainly removed by sedimentation of particles. Furthermore, aquatic vegetation and algae take up nutrients for primary production.

The relative contribution of different retention mechanisms is related to meteorological and hydrological conditions and catchment properties. These conditions are: residence time in the stream (Behrendt & Opitz 1999) (Nixon *et al.* 1996; Zessner & Kroiss 1999); temperature (Rysgaard, Christensen & Nielsen 1995); presence of macrophytes (Clarke 2002; Eriksson & Weisner 1999) riparian area's (Hefting & de Klein 1998; Svendsen & Kronvang 1993); catchment size and area of surface water (Behrendt & Opitz 1999; Seitzinger *et al.* 2002b).

Furthermore, the retention of nitrogen and phosphorus is spatially separated. Nitrogen retention occurs mostly in headwater streams (Alexander, Smith & Schwarz 2000; Peterson *et al.* 2001), whereas most retention of phosphorus (sedimentation) mainly occurs at moderate flow velocities in downstream parts of the main river system (Alexander, Smith & Schwarz 2004; Reddy *et al.* 1999). Also the presence of lakes in the catchment should be considered. Lakes are known to be major nutrient sinks (Jennings *et al.* 2003; Kronvang *et al.* 2004).

To our knowledge, research on the seasonal variations of nutrient retention is limited to only few studies, whereas no studies are available for rivers. Rysgaard et al. (1995) Denitrification variability was measured in estuarine sediment (Rysgaard *et al.* 1995) and in a small lake (Ahlgren *et al.* 1994). Both studies indicated variability of denitrification rates related to temperature and availability of nitrate. Monthly phosphorus retention in 16 Danish lakes was calculated using mass balances (Søndergaard, Jensen & Jeppesen 2001). Results showed that P retention in eutrophic lakes is often negative during part of the summer, due to internal loading.

For river systems, hardly any information on seasonal retention is available. Catchment models used to asses critical loads to lakes or estuaries might benefit from addressing this seasonal retention. After all, seasonal (i.e. monthly) retention estimates may preserve critical thresholds**.** From the above we conclude that there is an urgent need for budget studies for European lowland rivers, addressing this seasonality in riverine retention. Catchment models should address this seasonal variation, as well as spatial variation and subsequent nutrient export to lakes.

The aim of this research is twofold. The first objective is to provide novel nutrient budgets and estimates of nutrient retention in 13 European lowland river catchments, covering a period of 3 to 10 years. The studied catchments are typical for rather flat agricultural areas in Western Europe. The second objective is to introduce and illustrate the relevance of seasonal variability of nutrient retention. A novel calculation method for seasonal retention and export of nutrients from rivers is presented. Using total annual emissions of nutrients from point and diffuse sources, monthly export loads from the catchment are estimated. The calculation method is calibrated for 7 lowland river systems and validated for 6 other catchments in the Netherlands, Germany, Ireland and Denmark.

It should be noted that in this paper in-stream retention in catchments is defined as the nutrient retention in the total drainage network and not in the terrestrial part of the catchment.

Methods

For the studied catchments nutrient budgets are set up to calculate in-stream nutrient retention for the whole catchment both on an annual and a monthly basis. Secondly, a regression model is constructed and tested that estimates nutrient exports on a monthly basis. Catchment data and calculation methods are describe below.

Catchment data

Water quality and discharge data are collected from 13 lowland river systems in The Netherlands, Germany, Ireland and Denmark. Data partly originate from routine monitoring programs of water management boards and partly from more intensive measurements in project studies. Measured data of river discharges and nutrient concentrations were available for several years within the period 1988-2002. Flows are measured with high frequency (hourly to daily). Nutrient datasets consist of multiple-year monitoring with weekly to monthly sampling frequencies.

Most catchments are used for agriculture, resulting in a substantial diffuse loss of nutrients to the environment. In table 6.1 general river and catchment data are presented. In the Flakkensee catchments (Germany) also large forested areas are present. The catchments’ slopes range from 0.3 to 19 ‰).

Table 6.1 *Characteristics of the lowland river catchments use for the analysis.*

River Catchment *	Period	Area (km^2)	surface water area (ha)	surface water (%)	mean slope (‰)	stream length (km)
Chaamse Beek (NL)	1996-2000	49.9	37	0,74	0,8	9,6
Beerze (NL)	1995-1998	247	269	1,09	0,9	36
Beerze (NL)	1990-1994	247	269	1,09	0,9	36
Hunze (NL)	1995-1998	250	350	1,4	0,3	30
Schuiten-beek (NL)	1988-1994	74.1	40	0,54	1,8	12
Hierdense beek (NL)	1994-1998	48.2	32	0,67	1,7	15,1
Groenlose Slinge (NL)	1997-2002	188	199	1,06	0,9	27,2
AA of Weerijs (NL)	1996-2000	148	138	0,93	0,5	19,3
Robe (Ireland)	2001-2003	285	512	1,8	19,3	60
Flakkensee Locknitz (Ger)	1999-2002	231	669	2,9	7,7	26
Flakkensee Wolsdorf (Ger)	1999-2002	141	698	4,95	5	20,9
Schaugraben (Ger)	1997-2002	20.8	21	1	1,17	9,6
Odense (Denmark)	1996-2001	486	875	1,8	10	35

** NL: The Netherlands, Ger: Germany*

Calculation of annual and monthly retention

In-stream nutrient retention is calculated from the difference between total emissions (diffuse and point sources) and export from the catchment. Retention is expressed as an absolute amount ($kg.ha^{-1}.y^{-1}$) as well as a percentage of the total input (relative retention).

Diffuse (agricultural) sources for the Dutch catchments are derived from simulations with the STONE nutrient emission tool (Wolf *et al.* 2003). The model was validated with data from different catchments (Oosterom & Groenendijk 2005). For the German and Irish catchments diffuse loads are estimated using export coefficient modeling with the MONERIS-model (Behrendt 2000). Diffuse sources for the Odense catchment (Denmark) are taken from the catchment analysis in the EUROHARP-project (Kronvang *et al.* 2003).

The Dutch STONE nutrient emission tool was designed to evaluate the effects of changes in the agricultural practice and policy measures on leaching of nitrogen and phosphorus from agricultural land areas to ground water and surface waters. STONE consists of a chain of mechanistic models, which were applied to over six thousand unique units that represent the variation in biophysical conditions in the Netherlands. The soil processes within STONE are calculated for each unique spatial unit and aggregated to regional scale. The basis is a complex, one-dimensional process-oriented model for simulating the cycling of carbon and nutrients in soils, resulting in fluxes of N and P to groundwater and surface water (for detailed description see (Wolf *et al.* 2003)).

The model MONERIS (MOdelling Nutrient Emissions in RIver Systems) was developed for the investigation of the nutrient inputs via various point sources and diffuse sources in German river basins. The sum of the diffuse nutrient inputs into the surface waters is the result of different pathways realized by several runoff components. Diffuse emissions pathways taken into account are atmospheric deposition, erosion, surface runoff, groundwater, tile drainage and paved urban areas (Behrendt 2000). Because different models were employed for different catchments, their concomitant emission estimates might be biased. Hence, the consistency of STONE and MONERIS was a priori tested by applying them both on two catchments. For both catchments, the results (available on request) from STONE and MONERIS agreed very well, so we could safely assume that the emission estimates contained no conceptual or systematic error. Point sources for all studied catchments are calculated from measured loads largely from wastewater treatment plants (WWTP's).

Nutrient exports out of the catchments are calculated from flow and concentration measurements. In order to quantify nutrient budgets for catchments, reliable calculations of mass-loads are essential. This requires high frequency monitoring of river discharge and nutrient concentrations. For all catchments in this study discharge was measured with high accuracy. On the other hand, nutrient concentrations were measured only daily to monthly. Especially monthly data might result in inaccurate mass-load calculations as short-term variations of nutrient concentrations in the rivers might be missed. However, by averaging measurement data of several years we lowered the risk of under- or overestimating export loads, especially when only monthly measurements were available.

First, monthly exports of nitrogen are calculated from average monthly discharge and average monthly concentrations. For phosphorus a relation between discharge and concentration is assumed (higher discharge, higher concentration) (De Vries & Klavers 1994). So, a correction is used for the average discharge at the concentration measurement dates compared to the average of all the discharge data.

Quantification of seasonal export and retention

The general concept of calculating monthly nutrient exports from catchments is presented in Figure 6.1.

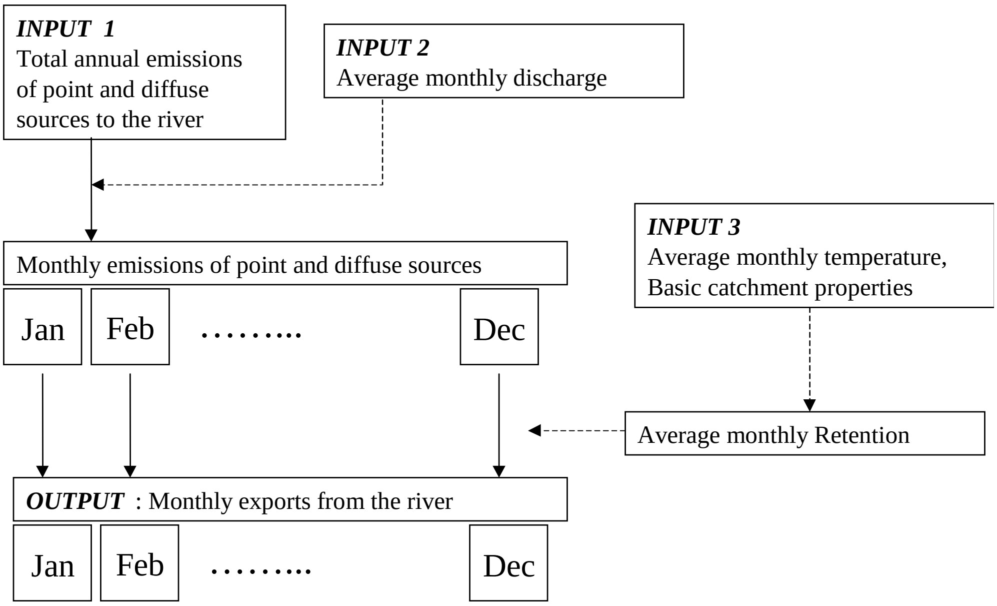


Figure 6.1 *Outline of the export and retention model.*

Primary input of the calculation is the total annual emission of diffuse sources and point sources of nutrients to the surface waters of the catchments. Since P-emissions mostly originate from erosion and N-emissions from leaching of groundwater (Behrendt 1996; Svendsen & Kronvang 1993) discharge is a major controlling factor of seasonal variations of the emissions. Consequently, the diffuse annual emission is divided over the months according to the discharge in a month relative to the total annual discharge (Input 2). Point emissions originate from different sources. In many cases effluents from WWTP and discharges of untreated wastewater contribute substantially (Behrendt 1996). Monthly averages of point sources usually show no large variations (Emissieregistratie 2007) and therefore are assumed to be constant over the year. Accordingly, from the annual emissions monthly emissions are derived using:

$$M_i = \frac{Q_i}{Q_t} * L_D + \frac{L_P}{12} \qquad (1)$$

with: M_i = monthly emission to surface water (kg.ha^{-1}), i =index for month
Q_i = average monthly discharge (m^3.s^{-1})
Q_t = average annual discharge (m^3.s^{-1})
L_D = total annual diffuse emission (kg.ha^{-1})
L_P = total annual point source emission (kg.ha^{-1})

During transport to the outlet of the catchment part of the nutrient emissions will be retained. Thus the export out of the catchment can be defined as:

$$E_i = M_i * (1 - R_i) \qquad (2)$$

with: E_i = catchment export mass load in month i (kg.ha^{-1})
R_i = Retention fraction (-)

The retention fraction can vary over the months and over the catchments. Several studies provide evidence that this retention is partly absolute (independent of the nutrient concentration at high nutrient availability) and partly relative to the nutrient concentration (at low nutrient concentrations) (Ekholm *et al.* 2000; Seitzinger *et al.* 2002b; Svendsen & Kronvang 1993). Another major factor is residence time of the water in the catchment, basically determined by the total volume of surface water and the runoff (Behrendt & Opitz 1999; Seitzinger *et al.* 2002b) . In accordance with above mentioned studies we defined Surface water area specific Runoff SR_i :

$$SR_i = \frac{Q_i}{SW} \qquad (3)$$

with: SR_i = surface water area specific runoff ($m^3.s^{-1}.ha^{-1}$)
Q_i = average (monthly) discharge ($m^3.s^{-1}$)
SW = total area of surface water in the catchment (ha)

River discharge is measured at the outlet of the catchment. SR represents the hydraulic load ($m.time^{-1}$) or water displacement. It is the thickness of the water layer that is displaced (refreshed) within a period of time. At constant average water depth, SR is an inverse measure of the residence time. Differences in surface water area, among catchments, are controlled by the density of the drainage and river network, but more importantly by the presence of ponds and lakes in the catchment. As an example, Figure 6.2 presents outlines and river networks of 4 catchments with varying area of surface water (0.54 to 4.9%).

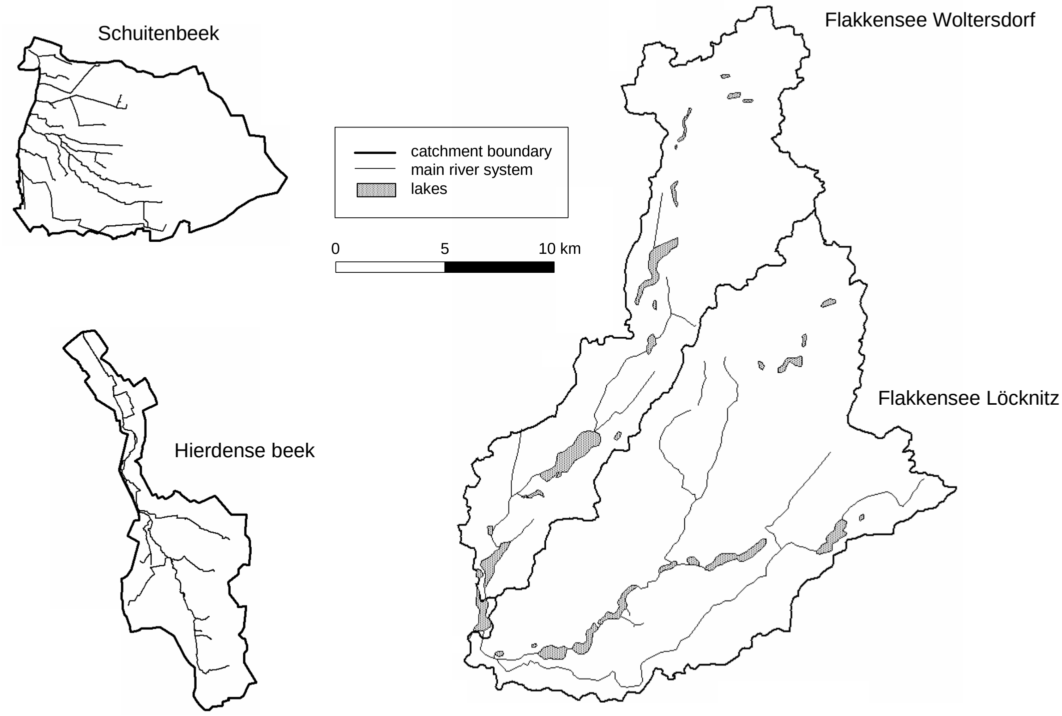


Figure 6.2 *Outlines and river networks of 4 representative study catchments with varying area of surface water. Schuitenbeek (0,54% area of surface water), Hierdense beek (0,67%), Flakkensee Woltersdorf (4,9%), Flakkensee Löcknitz (2,9%).*

Besides nutrient load and residence time, retention is controlled by temperature, especially for nitrogen reduction, due to biochemical denitrification. For many biochemical processes temperature is a driving force for seasonal variability (Kadlec & Reddy 2001; Pfenning & McMahon 1997). Combining these factors yields an a priori estimate of the retention fraction:

$$R_i = R_b * M_i^a * SR_i^b * K^{Ti-20} \tag{4}$$

in which: R_i = Retention fraction (-), i =index for month (-)

R_b = calibration coefficient (-)
M_i = monthly emission to surface water (kg.ha^{-1}), i = month
a = calibration coefficient for mass load weighted retention (-)
b = calibration coefficient for SW-area (-)
K = temperature coefficient (-)
Ti = average monthly temperature (ºC)

With the data of our 13 catchments the parameters R_b, a, b and K are calibrated using the NonLinearRegression-Analysis routine in SPSS (SPSS 2005). The similarity of measured and calculated values and the significance of the models were tested by linear regression. Calibration is performed with monthly loads of 7 catchments (n=84) and validation was done with the remaining 6 catchments. Model Efficiency (ME) was calculated for individual catchments using equation 5:

$$ME = \frac{\sum (Cm - \overline{Cm})^2 - \sum (Cm - Cs)^2}{\sum (Cm - \overline{Cm})^2} * 100\% \qquad (5)$$

with ME = model efficiency (100% is perfect fit)
Cm = individual measured value
Cs = individual model simulation value
$\overline{Cm}$ = mean of measured values

Results and discussion.

Firstly, average annual export and retention will be presented and differences between catchments will be addressed and analyzed. Secondly, seasonal patterns of nutrient retention and the controlling factors will be shown as well as the results of the seasonal retention model.

Average annual export and retention

Annual inputs, exports and retention of nitrogen and phosphorus in the studied lowland rivers are presented in table 6.2.

Table 6.2 *Average annual inputs (emissions) and exports in the lowland rivers (based on measured data)*

River	**TOTAL-N**			**TOTAL-P**		
	Total Input * ($kg.ha^{-1}.y^{-1}$)	**Export ($kg.ha^{-1}.y^{-1}$)**	**retention (%)**	**Total Input* ($kg.ha^{-1}.y^{-1}$)**	**Export ($kg.ha^{-1}.y^{-1}$)**	**retention (%)**
Chaamse beek	44,8	30,9	31,0	1,04	0,61	41,4
Beerze 90-94	28,8	19,3	33,0	1,25	0,49	61,0
Beerze 95-98	28,8	18,7	35,1	1,25	0,43	65,9
Hunze	30,1	12,7	57,8	1,23	0,36	70,8
Schuitenbeek	21,1	11,3	46,7	1,59	0,62	60,9
Hierdensebeek	14,8	11,9	19,8	0,67	0,28	58,6
Groenlose Slinge	57,5	42,6	25,9	1,58	0,88	44,0
AA of Weerijs	40,0	31,0	22,5	1,45	0,82	43,3
Robe	26,0	18,9	27,4	1,09	0,61	44,3
Flakkensee Lo	4,8	0,8	83,8	0,27	0,08	71,9
Flakkensee Wo	7,3	1,5	79,2	0,19	0,20	(-4,6**)
Schaugraben	15,6	8,3	46,6	0,33	0,17	48,6
Odense	43,8	20,3	53,6	0,75	0,46	39,2

** Total Input to the surface water per ha catchment area (sum of diffuse and point sources).*

*** questionable; probably a substantial input source is omitted; or catchment properties are not correct*

Average annual budgets from the 13 catchments show a substantial variability in the annual retention: 23 to 84 % for N; 39 to 72 % for P. Nevertheless, these values are well in the range of earlier studies (Kronvang *et al.* 2004) (Nixon *et al.* 1996; Svendsen & Kronvang 1993) (Behrendt 1996) (Seitzinger *et al.* 2002a).

It might be expected that nutrient loads contain errors, especially for phosphorus (De Vries & Klavers 1994). Due to increasing concentration with increasing flow rates, a limited number of peak-flows may account for a large proportion of the total P-load (Kuusemets & Mander 2002) (McKee, Eyre & Hossain 2000). When such peak flows are missed in the monitoring, P-export loads are underestimated, so that P-retention in the river system is overestimated.

N and P retention may be related to system variables as will be discussed below. We tested the correlation of N-retention to area specific runoff ($m^3.s^{-1}$ per area of total catchment). The observed correlation was weak (adj. $R^2=0.21$; $p=0.1$). Such a correlation does not account for the fraction of catchment area occupied by surface water. The highest retention values are found in the catchments were lakes are present, and point and diffuse emissions are relatively low. Nitrogen retention (Nret) appears to be correlated with Surface water area specific Runoff (*SR*) and nutrient input (Figure 6.3).
These results suggest that nitrogen retention (Nret as % of input) is proportional to Surface water area specific Runoff (SR) (eq. 6a) and to a certain extent to input loads (Ninput) (eq. 6b):

$$Nret \propto (SR)^{-0,44} \qquad (6a)$$

$$Nret \propto (Ninput)^{-0,38} \qquad (6b)$$

Multiple regression of N-retention to both SR and N-input did not yield a better model compared to 6a and 6b. Equation 6a implies that relative nitrogen retention will increase with decreasing SR. In fact, SR reflects hydraulic load or water displacement ($m.time^{-1}$). This can be regarded as an inverse measure for the residence time of water and nutrients in the catchment. Thus, lower SR results in longer residence times in which retention processes can proceed longer. The lower SR can be a result of either more surface water area in the catchment, or a lower river discharge.

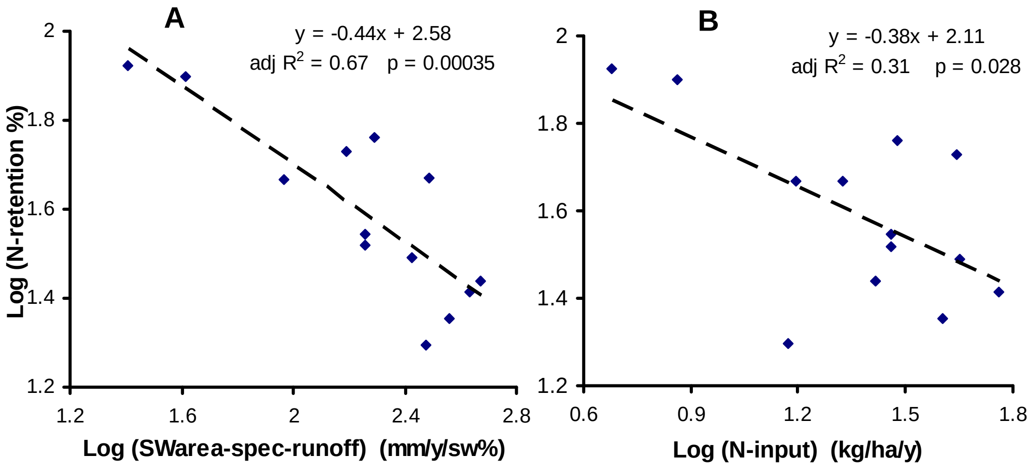


Figure 6.3 *Log- Log correlation of average annual Nitrogen retention to surface water area specific runoff (A) and N- input load(B).*

For phosphorus, no clear relation of annual retention to P-inputs and catchment hydrology is found. In the literature a few models for P-retention in streams and rivers have been reported. For lakes, a widely used concept is the Vollenweider equation, which relates concentration of P in the lake to concentration of P in the inflowing water, as a function of residence time (T): $P_{lake}/P_{in} = 1/(1+\sqrt{T})$ (OECD 1982). In the current study, we found no correlation between measured P-retention and P-retention as estimated with the Vollenweider equation ($R^2 < 0.1$; $p = 0.12$). This may be explained by the fact that the Vollenweider concept was derived for deep lakes in steady state, whereas in small lowland river catchments phosphorus concentrations and interactions with sediments are highly dynamic (Reddy *et al.* 1999) (House & Denison 1998) and simple relations are thus difficult to identify.

Load-weighted nutrient retention

For average annual data, equation 6b implies an inverse correlation of nitrogen retention with input loads. Relative N retention (% of input) relates to total input with an exponential term of -0.38. Hence, relative retention decreases with increasing input, and levels off at high inputs. At the same time absolute retention ($kg.ha^{-1}.y^{-1}$) might still increase. This contrasts to earlier reports. Many studies present models and retention estimates that are based on a first order removal process (Reddy *et al.* 1999) (Alexander *et al.* 2000) in which values for the first order N-removal rate range from 0.005 to 0.5 day^{-1}. Given a certain residence time this results in a retention fraction that is independent of the input. However, our data-analyses as presented in figure 6.3 and equation 6b show that this is not valid for our catchments.

Seasonal variation of export and retention

In Figure 6.4, representative examples of monthly data of 4 catchments are presented. The other catchments show similar trends. All the catchments clearly show seasonal variations in concentrations, loads and discharges. Discharges in these lowland catchments are directly dependent on the precipitation surplus, i.e. they are high in winter and low in summer. For nitrogen all catchments show a clear decrease of concentration in summer. Nitrogen uptake and denitrification are temperature dependent. So the decrease in exported N-load in summer is a result of the decrease of discharge as well as the decrease in concentration.

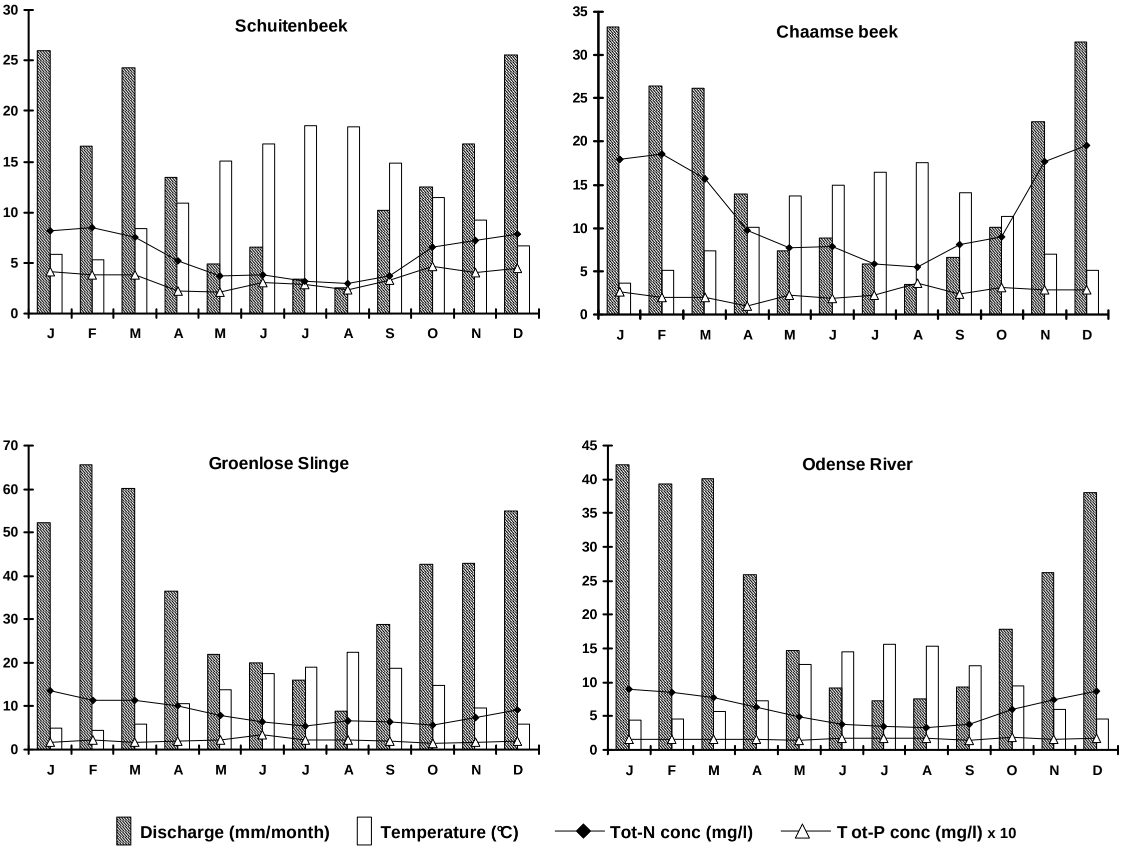


Figure 6.4 *Measured average monthly Discharge, Temperature and N- and P-concentrations in 4 representative lowland river catchments*

Monthly phosphorus concentrations show more random variations. On average, the winter concentration is a little higher than the summer concentration, which can be explained by the higher discharges in winter. However, the increase in P concentration with increasing discharge is especially seen during short peak flows. When averaged over a whole month, this effect is low.

From Figure 6.4 we can conclude that discharge as well as input loads are high in winter and low in summer. These data are strongly correlated due to the fact that loads are distributed over the year according to the pattern of discharge (for the diffuse sources). In the studied catchments point sources contribute only up to 10% of the total input. Furthermore, the temperature variations over the months show an opposite seasonal pattern as compared to discharge and input loads. In summary, there is a strong seasonal dependency of nutrient input loads, surface water area specific runoff and temperature

Quantifying seasonal export and retention

From the previous section we conclude that for our type of catchments the inputs used in the a-priori retention model (eq 4) are partially correlated. Consequently we performed non-linear-regression on more simple models. These models were based on equation 4, with stepwise exclusion of parameters and variables. The reduced models were tested for maximum model significance (F-test) and minimum range of confidence intervals for the parameters. As a result, monthly retention of nitrogen can be estimated from surface water area specific runoff (eq 7) (adj. R^2: 0.93, $p<0.0001$)

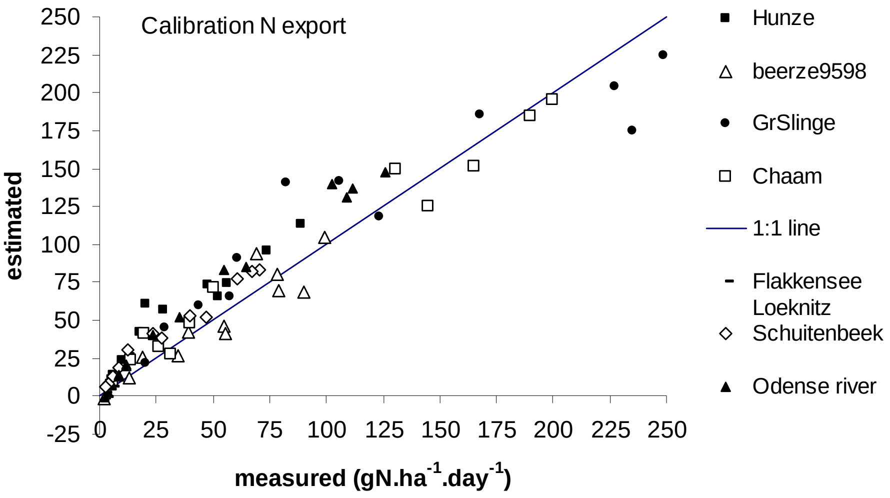
$$R_i = 0{,}0246 * \left(\frac{Q_i}{SW} \right)^{-0{,}57} \qquad (7)$$

The power value in equation 7 (-0.57) is different from the retention model based on annual averages (equation 6a) where the power value is -0.44. The 95% confidence interval for the power value in equation 7 ranged from -0.67 to -0.46 and in equation 6a from -0.63 to -0.25, so the difference is not significant.

Monthly phosphorus retention can be estimated from surface water area specific runoff (SR_i) and temperature (eq 8) (adj. R^2: 0.81, $p<0.0001$)

$$R_i = 0{,}253 * \left(\frac{Q_i}{SW} \right)^{-0{,}20} * 1{,}01^{(T_i - 22)} \qquad (8)$$

Results of the calibration and validation of the reduced models' monthly predictions are presented in Figure 6.5a and 6.5b. The similarity of measured and calculated values for the training set was high (N: R^2= 0.93; P: R^2= 0.81). Validation of the obtained model with data of the 6 remaining catchments also showed good results. The modelling efficiency for the individual catchments ranged from 31% to 95%, with an average of 76%.



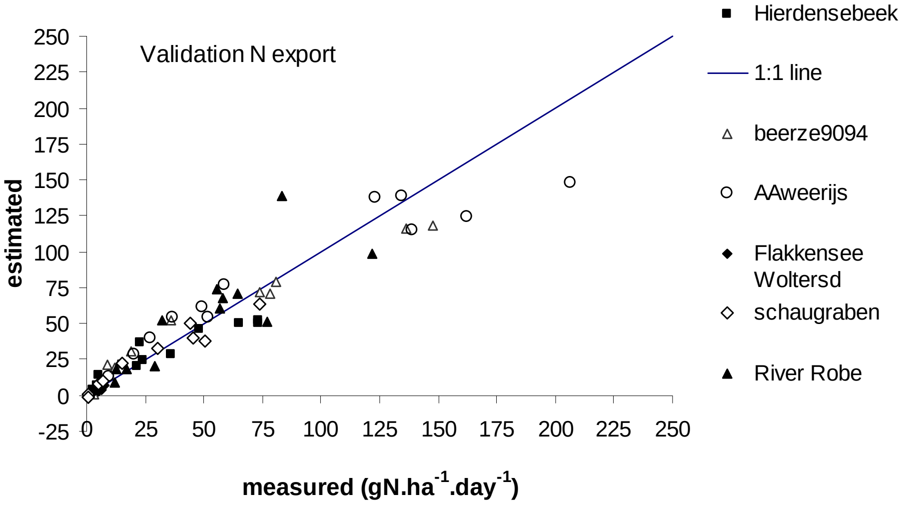


***Figure 6.5a**. Measured and calculated values of monthly exports for Nitrogen; calibration and validation (each data-point represents an average month in a specific catchment).*

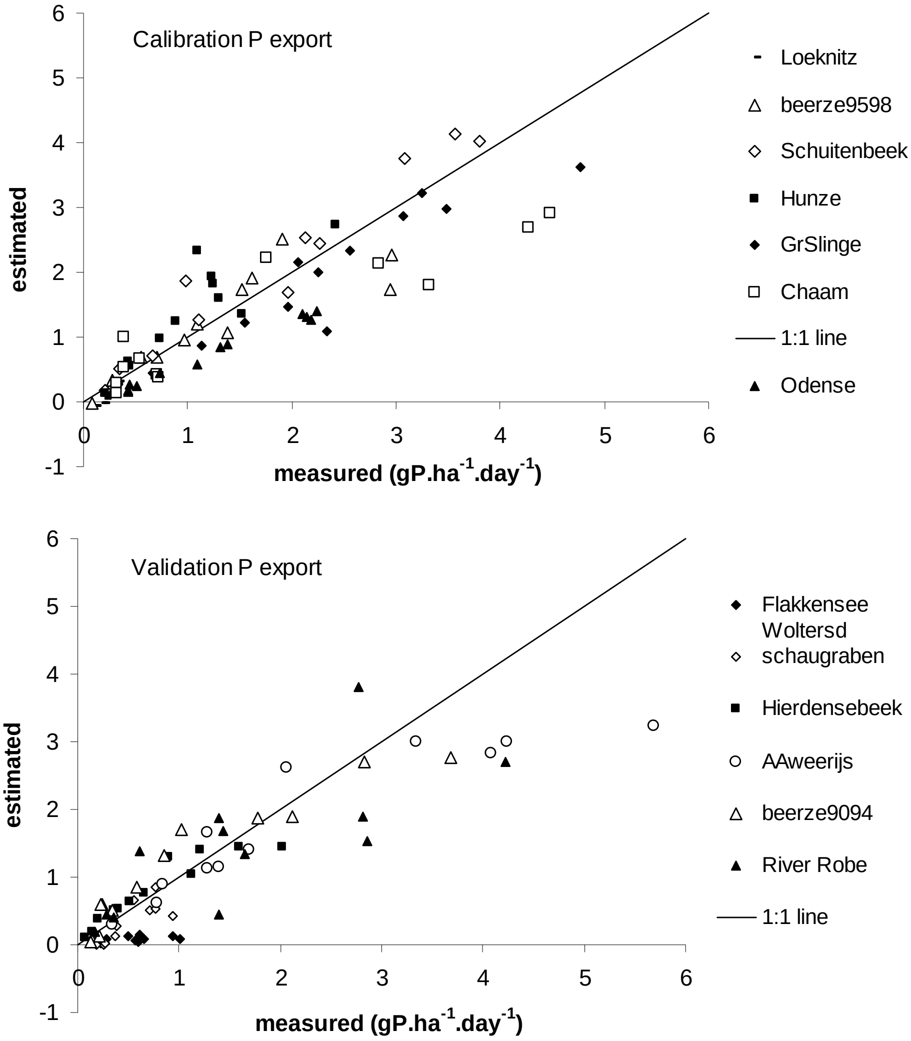


***Figure 6.5b**. Measured and calculated values of monthly exports for Phosphorus; calibration and validation (each data-point represents an average month in a specific catchment).*

The slightly poorer fit for phosphorus can be explained mechanistically. In our calculation method the distribution of the diffuse sources over the months is based on discharge. This assumes that nutrient concentrations in runoff water are constant. For nitrogen in lowland catchments research shows that this is plausible (Van den Eertwegh 2002). However, for phosphorus this might not always be true due to complex processes like (im)mobilization in soil and erosion.

The final models for N and P-retention estimates on a monthly basis (eq. 7 and 8) contain area-specific run-off (N and P) and temperature (P) as controlling input variables. This results in a seasonal pattern of relative nutrient retention (%). In Figure 6.6 this is presented for 2 representative catchments which differ in the area of surface water: Groenlose Slinge (~1 % surface water area) and Odense catchment (~2 % surface water area).

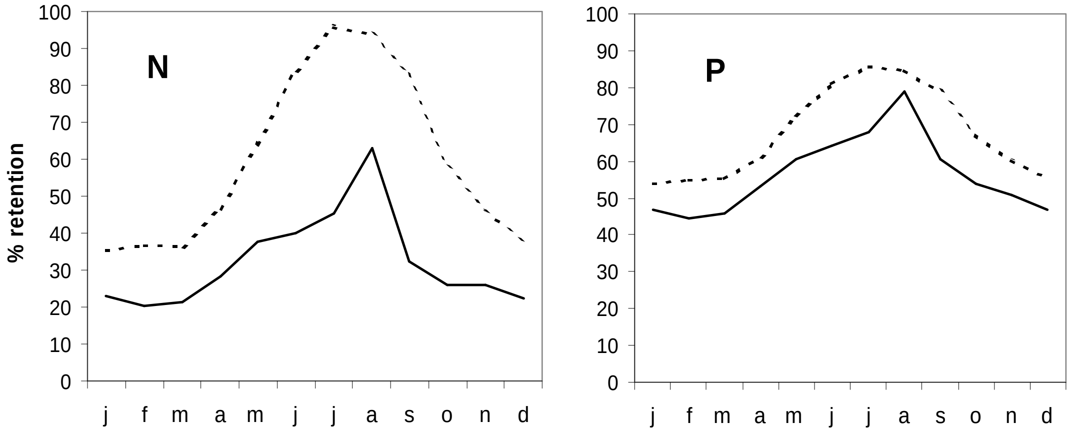


Figure 6.6 *Seasonal pattern of relative N and P retention (% of input) calculated with the calibrated retention models (equations 7 and 8). Two catchments with different surface water area are presented: Groenlose Slinge catchment (~1 % SW-area, solid line) and Odense catchment (~2 % SW-area, dotted line).*

All catchments show similar patterns for seasonal nutrient retention. Highest relative retention is found in summer. This is the combined effect of residence time and temperature. On the other hand, nutrient availability is higher in winter due to higher input loads. Therefore, the absolute nutrient retention (expressed in g.m^{-2}.day^{-1}) might increase during this period, but obviously not in the same range as the inputs. Both pictures in Figure 6.6 show that retention increases with increasing area of surface water in the catchment.

For both nitrogen and phosphorus SR is a crucial factor for the retention estimates. A study on nitrogen retention in 16 catchments in North-America revealed an inverse relation of nitrogen retention in river reaches with *displacement time* (average depth of the reach *D* divided by time of travel *T*) (eq. 9) (Seitzinger *et al.* 2002b).

$$Nretention \propto \left(\frac{D}{T}\right)^{-0,37} \qquad (9)$$

If we define travel time T as Volume/Flow-rate(Q) and Volume as SW-Area*Depth equation 9 can be written as

$$Nretention \propto \left(\frac{Q}{SW-area}\right)^{-0,37} \qquad (10)$$

Conceptually, this agrees to our relations (eq.6a and 7). A similar relation has been reported for N-retention in a study of 4 lowland catchments (size range 850-14.000 km2), with a power value of -0.49 for total-nitrogen (Venohr *et al.* 2005). In both referenced studies however, no confidence levels of the estimated parameters were reported. Although the power values found by these researchers differ to some extent from our models we can conclude that the relations are similar within error ranges whereas the theoretical background is consistent. Considering the smaller spatial scale (20-400 km^2) and the smaller time scale (monthly retention instead of annual average retention), it is remarkable that very similar relations are obtained for our catchments.

Figure 6.6 further shows that seasonal differences for phosphorus retention are smaller than for nitrogen. This might indicate that controlling factors like residence time and input loads are less dependent on the season. Furthermore, P-retention is strongly dependent on physical removal by sedimentation, which might be expected over the entire year.

On the other hand we extended the model of Surface water area specific Runoff for phosphorus with a temperature factor. This improved the modeling results, which indicates a relation with biochemical activity during spring and summer. Analysis of the phosphorus data in the rivers (Figure 6.4) shows that seasonal variability of P concentrations is less straightforward than for N. Generally, P-dynamics in rivers is considered more complex and strongly related to local catchment properties (House & Denison 1998; Jennings *et al.* 2003; Reddy *et al.* 1999). In our study in-stream retention is treated as a lumped factor. Underlying processes like (temporal) storage and mobilization, as well as permanent removal are not explicitly taken into account. In case of nitrogen, the predominant retention process is permanent loss by denitrification, which follows a clear seasonal pattern. For phosphorus however, the macrophyte uptake in spring and release in later month may complicate the monthly retention estimate. Furthermore, the large impact of peak-flows with alternating suspended matter resuspension and sedimentation prevent the setup of simple P-export and retention relations.

Therefore, it can not be ruled out that the temperature factor in our model just represents a seasonal pattern without a clear deterministic background.

Annual retention based on monthly estimates

The previous sections showed that good estimates can be obtained for monthly nutrient retention, with the aim of predicting seasonal variation of nutrient loads to lakes and coastal areas. Nevertheless, many studies report nutrient budgets and retention estimates on an annual basis. Furthermore management decisions often require evaluation of annual budgets. In order to evaluate our seasonal model on an annual timescale we calculated annual retentions for our catchments by totalizing the monthly inputs and the predicted monthly exports, and compared these annual retentions with measured annual retentions (Figure 6.7). The agreement is reasonable for nitrogen, whereas for phosphorus a rather poor fit is obtained. As described earlier, this can be explained by the cumulative uncertainties of the monthly estimates of P-retention as described earlier.

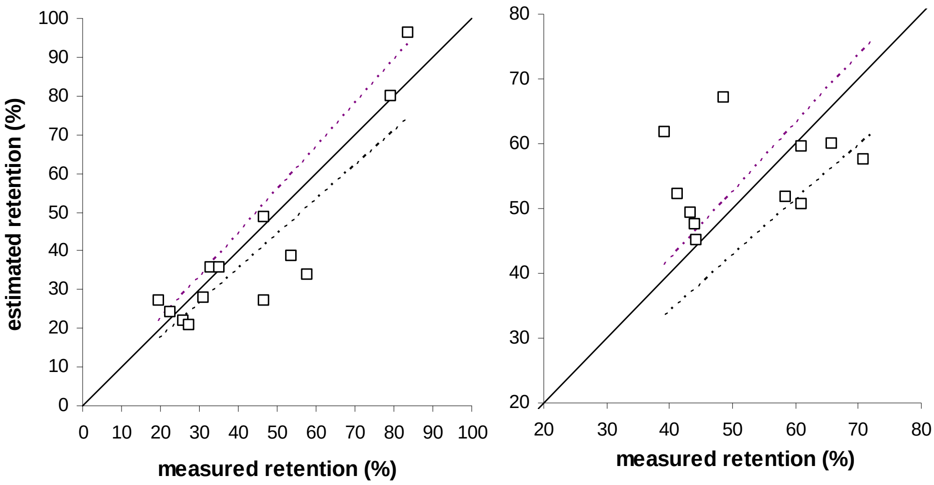


Figure 6.7 *Measured and estimated values of average annual retention of N and P. Annual retention is calculated based on the monthly inputs and predicted exports, including 95% confidence levels (dotted lines). Each data point represents annual N- or P-retention in a specific catchment.*

Conclusions

This research shows that in-stream retention in lowland river catchments is considerable and must be accounted for in nutrient budgets. Our analyses further show that variation of nutrient retention largely can be explained by the rate of nutrient emissions and the total area of surface water in the catchment. We conclude that dynamic modeling of eutrophication in standing waters may gain a lot from addressing seasonal variation in nutrient inputs. A new methodology to quantify this seasonality of nutrient retention is provided. Previous studies generally emphasized average annual retention and neglected seasonal variability. We introduce a novel simple calculation method that may adequately estimate monthly in-stream retention of nitrogen and phosphorus. The main controlling factors are discharge and area of surface water. In addition, for phosphorus also temperature serves as input. This quantification method may be applied to a wide range of western European lowland rivers, and may improve the estimation of nutrient load extremes.

Validation to data from six catchments confirmed the quality of the method. Further conceptual improvements can be made, by including complex dynamic processes, such as temporal storage and release in the drainage network.

Our analysis shows that, in general, retention in summer is higher than in winter, resulting in lower summer nutrient concentrations than calculated with an average annual input. In shallow lakes with short water residence time, seasonal variation in nutrient load will have a greater impact on in-lake nutrient concentrations compared to larger lakes. This implies that accurate evaluation of critical thresholds for eutrophication effects requires that we take seasonal variation in hydrology and nutrient loading into account. Our quantification method thus may improve the modeling of eutrophication effects in standing waters.

Acknowledgements

This study was conducted within the EU-project BUFFER (EVK1-1999-00094 "Key nutrient transport mechanisms important for the prediction of nutrient and phytoplankton concentrations in European standing waters"). Thanks to Buffer-partners from TCD (Dublin), IGB (Berlin) and NERI (Silkeborg) for providing catchment data.

Also Dutch water boards and Dr. G. Wriedt are gratefully acknowledged for providing river measurement datasets and Jan Roelsma (WUR-Alterra, NL) for the data of ANIMO-calculations.

References

Ahlgren I., Sorensson F., Waara T. & Vrede K. (1994) Nitrogen Budgets in Relation to Microbial Transformations in Lakes. *Ambio,* **23**, 367-377.

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

Alexander R. B., Smith R. A. & Schwarz G. E. (2004) Estimates of diffuse phosphorus sources in surface waters of the United States using a spatially referenced Watershed model. *Water Science and Technology,* **49**, 1-10.

Behrendt H. (1996) Inventories of point and diffuse sources and estimated nutrient loads - A comparison for different river basins in Central Europe. *Water Science and Technology,* **33**, 99-107.

Behrendt H. (2000) Nutrient emissions into river systems. Berlin: Institute of Freshwater Ecology and Inland Fisheries (IGB).

Behrendt H. & Opitz D. (1999) Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia,* **410**, 111-122.

Billen G., Garnier J., Deligne C. & Billen C. (1999) Estimates of early-industrial inputs of nutrients to river systems: implication for coastal eutrophication. *Science of the Total Environment,* **244**, 43-52.

Clarke S. J. (2002) Vegetation growth in rivers: influences upon sediment and nutrient dynamics. *Progress in Physical Geography,* **26**, 159-172.

De Vries A. & Klavers H. (1994) Riverine fluxes of pollutants: monitoring strategy and calculation methods. *European Water Pollution Control,* **4**, 12-17.

Ekholm P., Kallio K., Salo S., Pietilainen O. P., Rekolainen S., Laine Y. & Joukola M. (2000) Relationship between catchment characteristics and nutrient concentrations in an agricultural river system. *Water Research,* **34**, 3709-3716.

Emissieregistratie. (2007) Jaarcijfers 2005 (in Dutch). MNP, Bilthoven; CBS, Voorburg; RIZA, Lelystad; Alterra, Wageningen; SenterNovem, Utrecht en TNO-MEP, Apeldoorn.

Eriksson P. G. & Weisner S. E. B. (1999) An experimental study on effects of submersed macrophytes on nitrification and denitrification in ammonium-rich aquatic systems. *Limnology and Oceanography,* **44**, 1993-1999.

Faafeng B. A. & Roseth R. (1993) Retention of Nitrogen in Small Streams Artificially Polluted with Nitrate. *Hydrobiologia,* **251**, 113-122.

Garnier J., Billen G., Hannon E., Fonbonne S., Videnina Y. & Soulie M. (2002) Modelling the transfer and retention of nutrients in the drainage network of the Danube River. *Estuarine Coastal and Shelf Science,* **54**, 285-308.

Hefting M. M. & de Klein J. J. M. (1998) Nitrogen removal in buffer strips along a lowland stream in the Netherlands: a pilot study. *Environmental Pollution,* **102**, 521-526.

House W. A. & Denison F. H. (1998) Phosphorus dynamics in a lowland river. *Water Research,* **32**, 1819-1830.

Jennings E., Irvine K., Mills P., Jordan P., Jensen J.-P., Søndergaard M., Barr A. & Glasgow G. (2003) Eutrophication from agricultural sources. Seasonal Patterns & Effects of Phosphorus. Environmental RTDI Programme 2000-2006 Final Report, pp. 61. Wexford, Ireland: EPA.

Kadlec R. H. & Reddy K. R. (2001) Temperature effects in treatment wetlands. *Water Environment Research,* **73**, 543-557.

Kronvang B., Hezlar J., Boers P., Jensen J. P., Behrendt H., Anderson T., Arheimer B., Venohr M. & Hoffmann C. C. (2004) Nutrient Retention Handbook. Software Manual for EUROHARP-NUTRET and Scientific review on nutrient retention., pp. 103 pp. Oslo, Norway: NIVA.

Kronvang B., Larsen S., Jensen J. & Andersen H. (2003) Catchment report: River Odense Denmark. Trend analysis, retention and source apportionment,, pp. 20. Oslo, Norway: NIVA.

Kuusemets V. & Mander U. (2002) Nutrient flows and management of a small watershed. *Landscape Ecology,* **17**, 59-68.

McKee L. J., Eyre B. D. & Hossain S. (2000) Transport and retention of nitrogen and phosphorus in the sub-tropical Richmond River estuary, Australia - A budget approach. *Biogeochemistry,* **50**, 241-278.

Nixon S. W., Ammerman J. W., Atkinson L. P., Berounsky V. M., Billen G., Boicourt W. C., Boynton W. R., Church T. M., Ditoro D. M., Elmgren R., Garber J. H., Giblin A. E., Jahnke R. A., Owens N. J. P., Pilson M. E. Q. & Seitzinger S. P. (1996) The fate of nitrogen and phosphorus at the land sea margin of the North Atlantic Ocean. *Biogeochemistry,* **35**, 141-180.

OECD. (1982) Eutrophication of Waters - Monitoring, Assessment and Control, pp. 154. Paris: Organization for Economic Co-Operation and Development.

Oosterom H. & Groenendijk P. (2005) Toetsing van STONE 2.0 aan enkele stroomgebieden. In Dutch., pp. 68. Wageningen: WUR Alterra.

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

Pfenning K. S. & McMahon P. B. (1997) Effect of nitrate, organic carbon, and temperature on potential denitrification rates in nitrate-rich riverbed sediments. *Journal of Hydrology,* **187**, 283-295.

Reddy K. R., Kadlec R. H., Flaig E. & Gale P. M. (1999) Phosphorus retention in streams and wetlands: A review. *Critical Reviews in Environmental Science and Technology,* **29**, 83-146.

Rysgaard S., Christensen P. B. & Nielsen L. P. (1995) Seasonal-Variation in Nitrification and Denitrification in Estuarine Sediment Colonized by Benthic Microalgae and Bioturbating Infauna. *Marine Ecology-Progress Series,* **126**, 111-121.

Scheffer M. (1998) *Ecology of shallow lakes*. Population and community biology series. London [etc.]: Chapman & Hall.

Seitzinger S. P., Kroeze C., Bouwman A. F., Caraco N., Dentener F. & Styles R. V. (2002a) Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections. *Estuaries,* **25**, 640-655.

Seitzinger S. P., Styles R. V., Boyer E. W., Alexander R. B., Billen G., Howarth R. W., Mayer B. & Van Breemen N. (2002b) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry,* **57**, 199-237.

Søndergaard M., Jensen J.-P. & Jeppesen E. (2001) Retention and internal loading of phosphorus in shallow, eutrophic lakes. *The Scientific World,* **1**, 427-442.

SPSS. (2005) *SPPS for Windows v. 15.0*. Chicago, IL, U.S.A: SPSS Inc.

Svendsen L. M. & Kronvang B. (1993) Retention of Nitrogen and Phosphorus in a Danish Lowland River System - Implications for the Export from the Watershed. *Hydrobiologia,* **251**, 123-135.

Thomann R. V. & Linker L. C. (1998) Contemporary issues in watershed and water quality modeling for eutrophication control. *Water Science and Technology,* **37**, 93-102.

Van den Eertwegh G. (2002) Water and nutrient budgets at field and regional scale : travel times of drainage water and nutrient loads to surface water. Wageningen: Wageningen University.

Venohr M., Donohue I., Fogelberg S., Arheimer B., Irvine K. & Behrendt H. (2005) Nitrogen retention in a river system and the effects of river morphology and lakes. *Water Science and Technology,* **51**, 19-29.

Wolf J., Beusen A. H. W., Groenendijk P., Kroon T., Rotter R. & van Zeijts H. (2003) The integrated modeling system STONE for calculating nutrient emissions from agriculture in the Netherlands. *Environmental Modelling & Software,* **18**, 597-617.

Zessner M. & Kroiss H. (1999) Retention and losses of nutrients in the hydrosphere of Austria. *Water Science and Technology,* **40**, 59-66.

Chapter 7

Long-term effects of fertilizer use on European water quality

Jeroen de Klein[1], Paul Boers[2], Peter Schippers[1] & Marten Scheffer[1]

[1] Wageningen University and Research Centre, The Netherlands

[2] Rijkswaterstaat Riza, Lelystad, The Netherlands

Long-term effects of fertilizer use on European water quality

Abstract

Eutrophication is among the main threats to biodiversity and ecosystem functioning of European surface waters (Ærtebjerg *et al.* 2001; Beman, Arrigo & Matson 2005; Crouzet *et al.* 1999). Although fertilizer use is considered the main cause of this problem, definition of application limits that would protect freshwater and marine systems remains subject to scientific discussions (Boesch 2002; Parris 1998) and political debate (Crouzet *et al.* 1999; Kampas, Edwards & Ferrier 2002). Here we present a straightforward analysis of long-term consequences of fertilizer use for the aquatic environment. Assuming eventual saturation of nutrient storage capacity of soils and sediments, we calculate long- term surface water concentrations from nutrient surpluses in agriculture and net precipitation levels at the scale of European administrative regions. We predict that nutrient concentrations will exceed basic surface water targets in over 85% of the area. Implemented fertilizer application limits according to present legislation (European Commission 2002) will hardly improve this situation. Agricultural nutrient surpluses should be reduced an order of magnitude in most regions to be environmentally sustainable.

Introduction

In Europe agriculture and urban activities have lead to emissions of phosphorus and nitrogen to ground and surface waters (Carpenter *et al.* 1998; Crouzet *et al.* 1999) that may seriously affect biodiversity and functioning of aquatic ecosystems (Ærtebjerg *et al.* 2001). At present the nutrient load from agriculture represents a high proportion of the total anthropogenic load, 40-80% for nitrogen and 30-40% for phosphorus (OECD 2001). To reduce eutrophication risks in rivers, lakes and coastal areas both national and international action plans and regulations are developed and implemented. For instance both the Baltic Sea countries and North Sea countries (OSPAR 1997) have decided on a 50 % reduction in the nutrient load to areas likely to be affected by eutrophication and the European Union has issued the Nitrate Directive (European

Commission 2002) limiting nitrogen application to 170 kg ha^{-1} y^{-1}. Unfortunately the effectiveness of such regulations remains difficult to assess (Crouzet *et al.* 1999). Numerous tools are developed to describe nutrient transport and processes and to estimate loading of lakes and coastal zones (Schoumans & Silgram 2003). However, many of the processes involved in transportation and retention of nutrients in the landscape are still poorly understood, and predictions contain large uncertainties (Billen *et al.* 1995; Neal & Heathwaite 2005). A major problem is that we cannot validate the models, or assess the effectiveness of measures empirically as the time between reduction measures and new stable nutrient concentrations in standing waters may range up to decades and even centuries (Schippers *et al.* 2006) .

Methods

General approach

Here, we take an alternative approach to predict surface water concentrations. Assuming that current agricultural practice will continue, all storage capacity will eventually saturate and all excess of applied nutrients will then reach the aquatic environment. Depending on the precipitation surplus this leads asymptotic to long-term equilibrium concentrations of N and P in surface waters. By comparing these long-term equilibrium concentrations to commonly used surface water standards we evaluate impacts of fertilizer use. For our analysis we have set up a database of nitrogen and phosphorus surpluses in agricultural areas in Europe. For nitrogen we also estimated denitrification in soil and surface water. For phosphorus no permanent removal is assumed. We calculated average annual precipitation surpluses as the difference between annual precipitation and annual actual evaporation. Finally, we calculated long-term equilibrium concentration of N and P in surface water by dividing the (remaining) nutrient surplus (g.ha^{-1}.y^{-1}) by the precipitation surplus (m^{3}.ha^{-1}.y^{-1}).

Dataset and calculations

The spatial scale of this research reflects the entities from the European Nuts2 regions. NUTS (Nomenclature of Units for Territorial Statistics) is a European-wide geographical classification developed by the European Office for Statistics. Nuts2 roughly relates to major regions within countries, (counties, provinces etc.). In case of smaller countries there may be only one Nuts2 region. This spatial scale allows us to compare different countries and to identify differences within one country. The nutrient surpluses in agriculture are computed as the difference of all inputs and the outputs at the soil level.

Soil surface balances for nitrogen were obtained from Eurostat (Eurostat 1997) at the scale of Nuts2. For agricultural areas N-surplus was calculated from total inputs (manure, fertilizer, atmospheric deposition, and fixation) minus output (harvested crops). Data were available for the years 1993, 1995, 1997. For this study the average over these three was used. P-surplus data were only available for whole countries (Sibbesen & Runge-Metzger 1995). The national data were distributed over the Nuts2 regions proportional to the distribution of the nitrogen surpluses.

The precipitation surplus was calculated as precipitation minus evapotranspiration. Average annual precipitation was derived from the IMAGE 2.2 database, Global Climate Change Scenario's (Leemans *et al.* 1998). Data were aggregated from grid (0.5 x 0.5 grades) to the scale of Nuts2. Actual evapotranspiration was estimated from precipitation and temperature (Dingman 2002)

$$E_a = \frac{P}{\left[1 + \left(\frac{P}{E_p}\right)^2\right]^{0.5}} \qquad (1)$$

E_a = actuel Evapotranspiration (mm year^{-1})
P = precipitation (mm year^{-1})

$$E_p = 3.0 * 10^2 . \exp\left(\frac{17.3 \cdot T}{T + 237.3}\right) \qquad (2)$$

E_p = Potential Evapotranspiration (mm.y^{-1})
T = temperature in °C

Average temperature data were also obtained from the IMAGE 2.2 database. The calculated actual evapotranspiration was checked with several national water resources reports (Eurostat 2003; Mills 2002). All deviations from our calculations were less than 5 %.

Denitrification increases with temperature. Furthermore, large annual precipitation excess causes short residence times of nitrate in the soil and surface waters, resulting in low denitrification rates. This implies that gaseous N losses dominate in dry, warm climates.

Denitrification in soil and water, for separate regions was estimated based on temperature and precipitation surplus (Van Drecht *et al.* 2003). We defined the fraction of total N lost by denitrification (F_{denit}) as dependent on soil properties and climatic conditions

$$F_{denit} = 0.4 + F_K * F_R \tag{3}$$

where F_K (-) is the temperature effect on denitrification, F_R (-) is the effect of mean annual residence time of water and nitrate in the root zone and the surface water. The temperature effect F_K is calculated according to the Arrhenius equation

$$F_k = 7.94 * 10^{12} \cdot \exp\left(\frac{-E_a}{R \cdot K}\right) \tag{4}$$

where E_a is the activation energy (74830 J mol^{-1}), K is the mean annual temperature (Kelvin), and R the molar gas constant (8.3144 J $mol^{-1}K^{-1}$). The factor of mean annual residence time of the water F_R is given by

$$F_R = \frac{P_{av}}{P_{surp}} \tag{5}$$

where P_{surp} (mm $year^{-1}$) is the excess of precipitation over evapotranspiration, and P_{av} (mm $year^{-1}$) is used to convert P_{surp} to a ratio ($P_{av} = 400$).

Evaluation

To evaluate the calculated long-term equilibrium concentration in surface waters, we defined a classification, in which nutrient concentrations are set in classes ranging from ‘pristine’ to ‘severely polluted’ (table 7.1). Classification boundaries are based on the Trophic Classification Scheme for Lake Waters (OECD 1982) and standards for nutrients in fresh waters (Andersen, Conley & Hedal 2004; Crouzet *et al.* 1999).

Table 7.1 *Classification scheme for nitrogen en phosphorus in surface waters.*

Class*	**Tot-P conc. ($gP.m^{-3}$)**	**Tot-N conc. ($gN.m^{-3}$)**	**Remark**
Pristine	< 0.035	< 0.5	OECD oligotrophic to mesotrophic
Acceptable	0.035 – 0.08	0.5 – 1.0	OECD mesotrophic to eutrophic
Moderately polluted	0.08 - 0.15	1.0 – 2.2	Up to Dutch protection level for eutrophication of lakes
Polluted	0.15 – 1	2.2 – 5.0	Above Dutch protection level for eutrophication of lakes
Strongly polluted	1 – 5	5 – 11.4	Up to EU drinkingwater level (N)
Severely polluted	> 5	>11.4	Above EU drinking water level (N)

**Class definitions arbitrary; just for evaluation and presentation purposes*

Results

Long-term surface water (LTSW) concentrations are derived for all administrative (NUTS2) regions in the EU-countries (figure 7.1). Large differences can be seen. LTSW concentrations range from 0.03 to 26 mg l^{-1} total nitrogen and from almost zero up to18 mg.l^{-1} for total phosphorus. The highest concentrations can be found in the intensive agricultural areas of Western Europe (Netherlands, northern Germany, and Denmark). The calculations indicate that within the EU-countries 89% of the surface waters will eventually become moderately to severely polluted with phosphorus, and nitrogen limits would be exceeded in 52% of the area. We have to keep in mind that the LTSW concentrations presented here are averaged over agricultural and non-agricultural areas. This implies that local concentrations may become higher than indicated, especially in regions with a relative small proportion of agricultural area. Therefore we also calculated LTSW concentrations as an average over the agricultural areas of the separate regions (figure 7.2). This reveals that waters in the agricultural parts of 98% of the regions are projected to become moderately to severely polluted with phosphorus and 72% for nitrogen. In some regions classification shifts from ‘pristine’ to strongly or severely polluted, e.g. parts of Sweden and Finland.

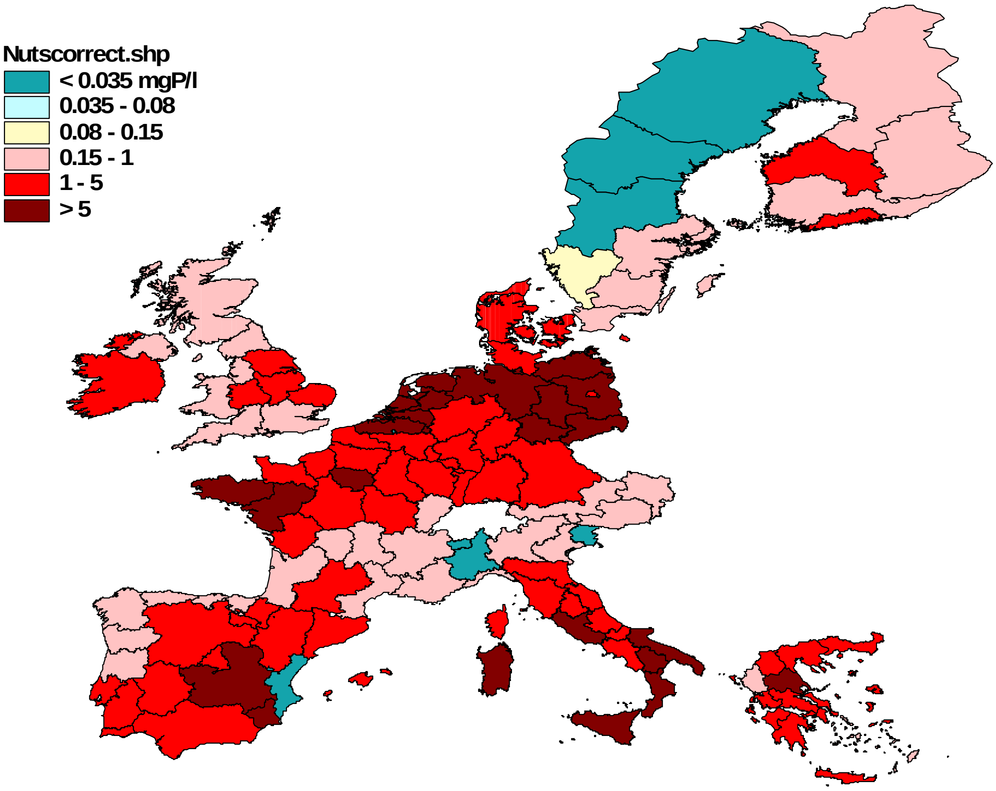


Figure 7.1a. *Long term surface water concentrations for* ***Phosphorus****, averaged over the whole Nuts-region (light and dark bleu is acceptable cf. table 7.1)*

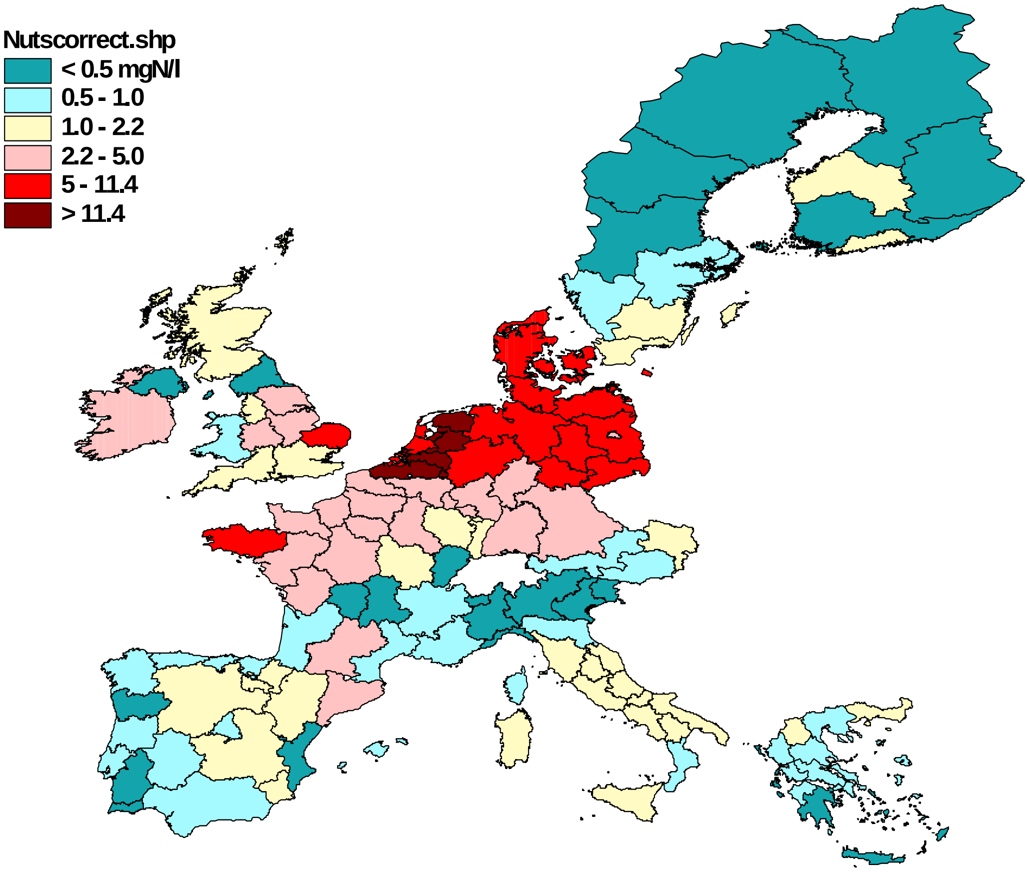


***Figure 7.1b**. Long term surface water concentrations for **Nitrogen**, averaged over the whole Nuts-region (light and dark bleu is acceptable cf. table 7.1)*

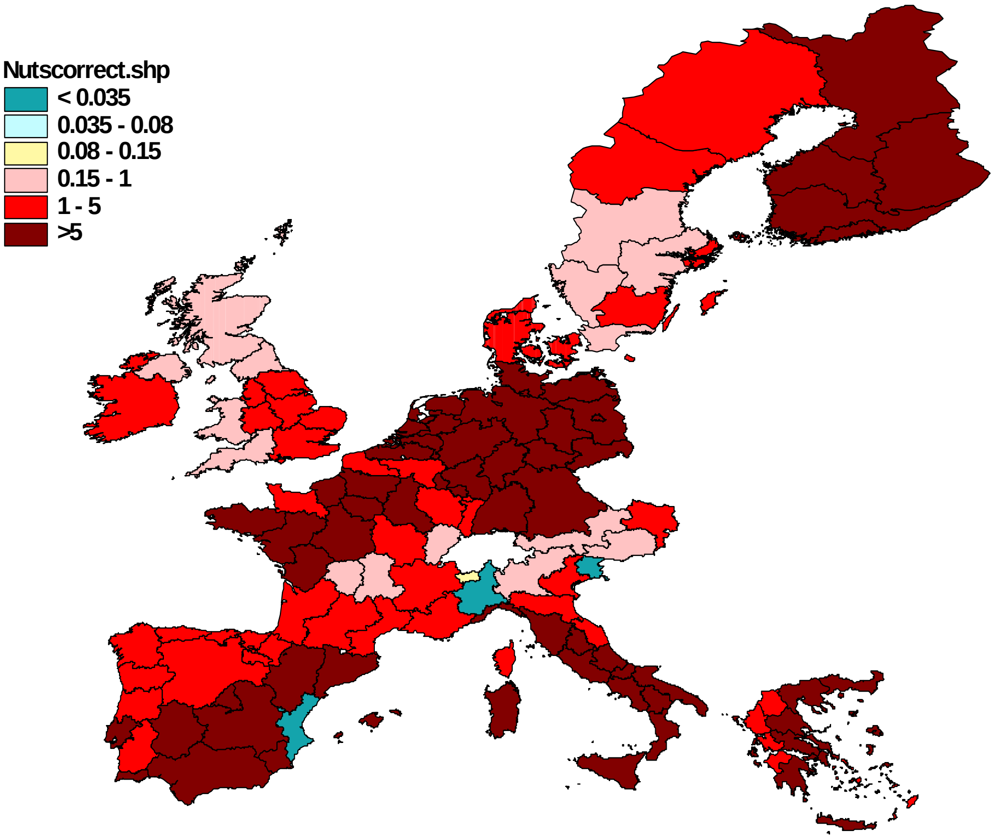


Figure 7.2a. *Long term surface water concentrations for **Phosphorus**, averaged over the agricultural area within the region (light and dark bleu is acceptable cf. table 7.1).*

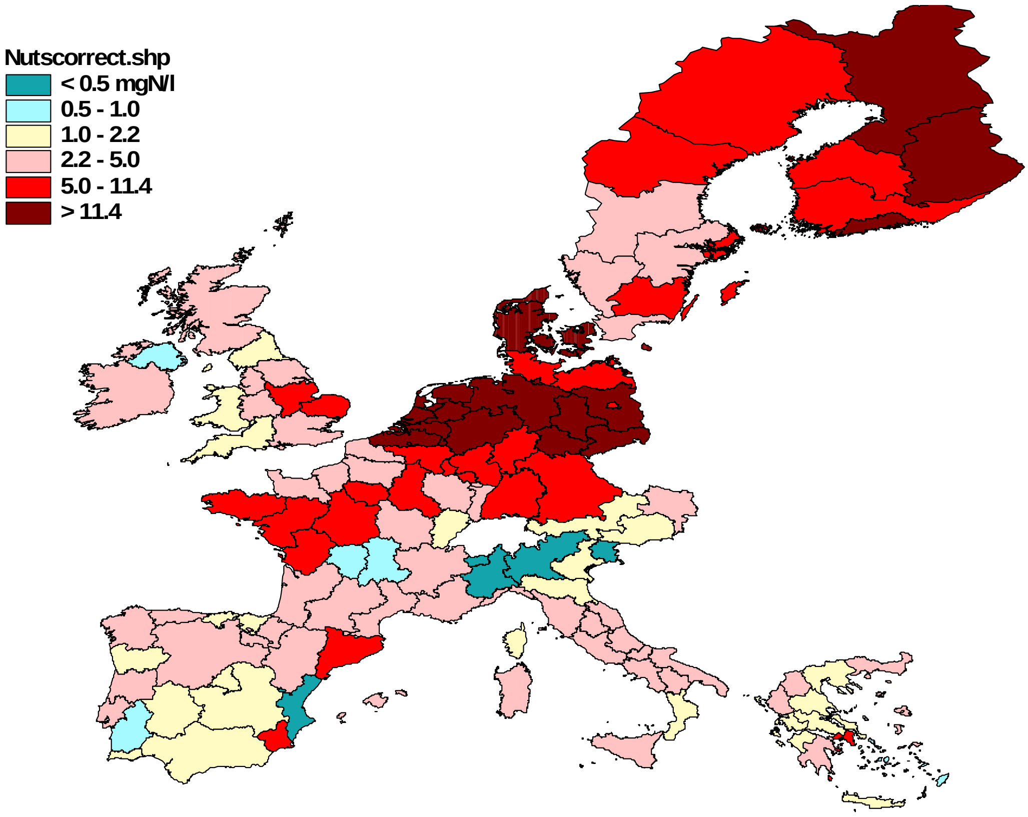


Figure 7.2b *Long term surface water concentrations for* ***Nitrogen****, averaged over the agricultural area within the region (light and dark bleu is acceptable cf. table 7.1).*

In only a few countries average projected LTSW concentrations remain at acceptable levels (figure 7.3), but large differences occur between regions within countries. For example in France LTSW concentrations range from 0.4 to 6.4 mg l^{-1} for nitrogen and in UK from 0.15 to 3.2 mg l^{-1} for phosphorus.

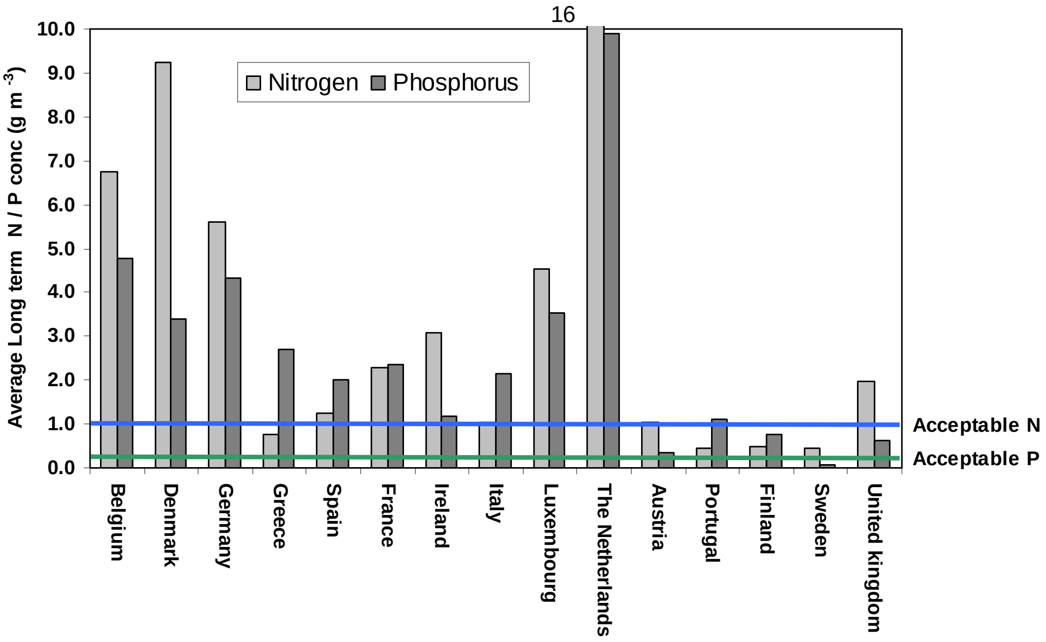


Figure 7.3 *Average long-term surface water nutrient concentration, area-weighted average per EU-country; horizontal lines indicate acceptable concentration limits.*

The regional differences are due to either variations in nutrient surpluses or variations in precipitation surpluses. In the UK the latter varies widely between regions (figure 7.4). This results, for example, in a classification ‘acceptable’ for the region Wales, whereas the classification for the region South-West is ‘polluted’, even though the nitrogen surplus in Wales is higher. Similar variability can be observed for Spain with comparable examples of classification differences. On the other hand in Germany precipitation surpluses are less variable, and differences in LTSW concentrations are mainly due to differences in nutrient surpluses. In countries such as France where both precipitation and nutrient surpluses are widely variable, the largest regional differences are found. The EU member states are implementing a fixed limit for nitrogen application to be applied in all regions (European Commission 2002). However, since projected surface water concentrations depend not only on net application but also on net precipitation (and for nitrogen also temperature), environmentally sustainable fertilizer use should depend on local climatic conditions.

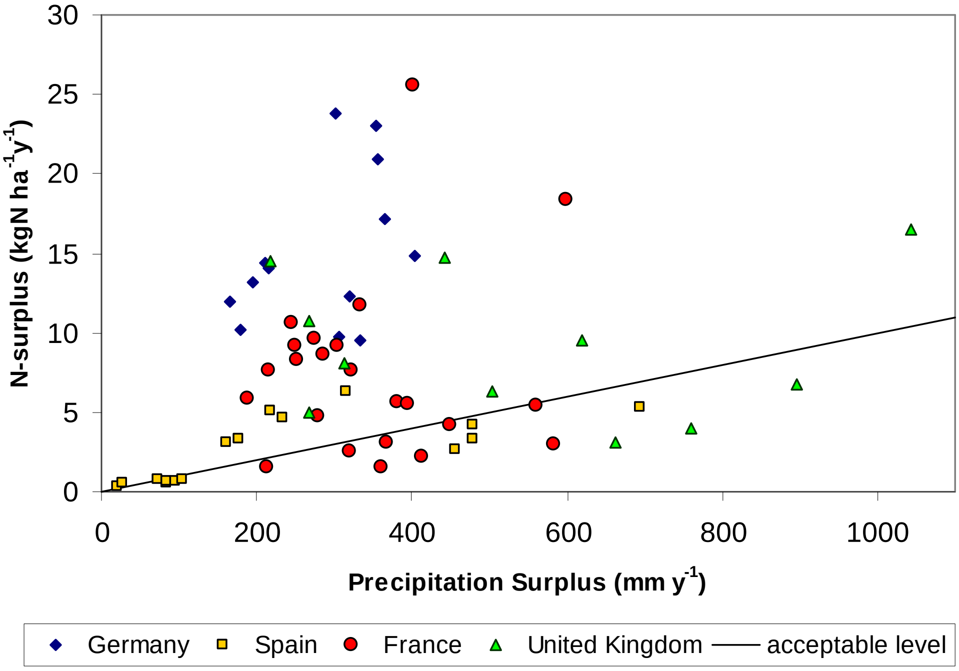


Figure 7.4 *Precipitation and Nitrogen surpluses in different regions of 4 EU-countries. Line represents combination of precipitation surplus and nitrogen surplus leading to a Long-term Surface Water N-concentration of 1 mgN l^{-1} (acceptable).*

To indicate admissible N-surpluses we calculated maximum N-surpluses, that lead to an ‘acceptable’ LTSW concentration (< 1 mg l^{-1}) (figure 7.5). High admissible surpluses are derived for warm and relative dry conditions due to high denitrification (sharp peak). Allowable surpluses subsequently decrease with increasing precipitation surplus, due to shorter residence times and thus smaller denitrification losses. Finally, admissible surpluses increase again at high precipitation surplus, as the dilution effect becomes dominant. Full implementation of the Nitrate Directive is thought to contribute significantly to solving environmental problems related to agriculture (European Commission 1999). However, assuming an efficiency of fertilizer use for crops of 60% (our database) (Oenema & Roest 1998; Van Drecht *et al.* 2003), the N-application limit of 170 kgN ha^{-1} y^{-1} implies an average N-surplus of 68 kgN ha^{-1} y^{-1}, which is far above the admissible surpluses we estimate (figure 7.5).

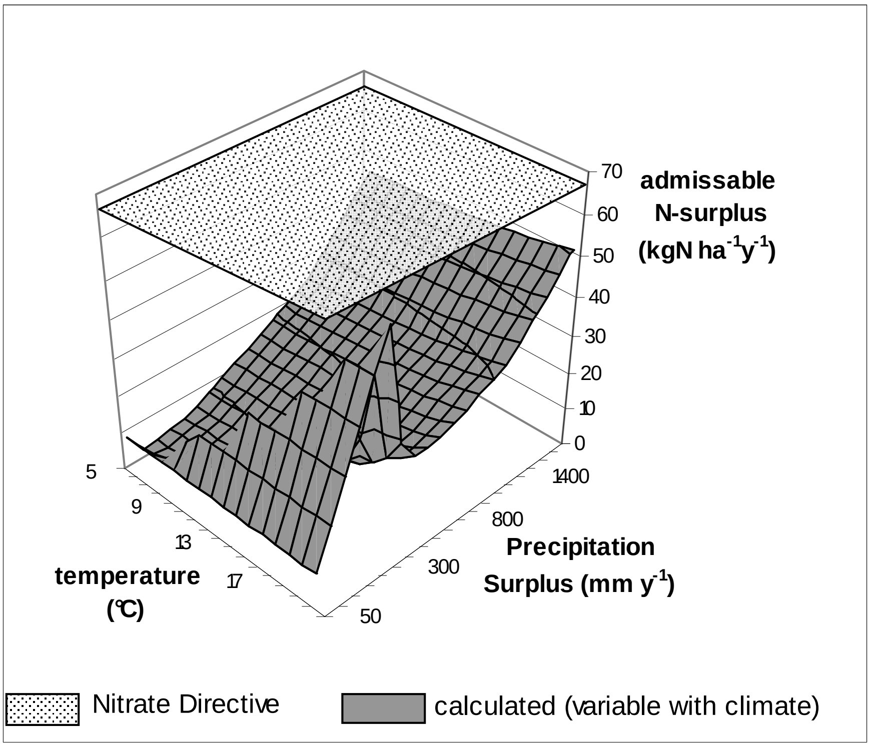


Figure 7.5 *Maximum admissible nitrogen surplus as a function of average annual temperature and precipitation surplus, to maintain 'acceptable' nitrogen surface water concentrations (<1 mgN/l). Light area represents N-surplus (68 kgN ha^{-1} y^{-1}) as a result of EU N-application limit on soils (170 kgN ha^{-1} y^{-1}); see text.*

Discussion

Obviously, the approach used in this study has the drawback that it refers to a status of the water quality that might be reached only after a long time. Indeed, the calculated Long-term Surface Water concentrations are much higher than generally measured in the surface waters at present and might seem unrealistic. However, the logic of our method is straightforward, and the first symptoms of long-term unsustainability are discernible already. For instance, according to the Dobris assessment (EEA 1995) 87% of the agricultural area in Europe has nitrate concentrations in the groundwater that are above the guide-level value of 25 mg l^{-1} (5.7 mgN/l), and 22% are above the maximum admissible concentration of 50 mg l^{-1} (11.4 mgN/l). For phosphorus the situation is more complex due to its immobility and accumulation of P in soils and fresh water sediments. This results in a potentially large time lag between the excessive application of phosphorus on soils and the observed effect in groundwater and surface waters {Schippers, 2006 #175. Nevertheless, eventually accumulation capacity for phosphorus will decrease, resulting in an increase in P-concentrations in the aquatic environment. In fact, due to heterogeneity in soils, an increase in P loading to surface water will already start before all accumulation capacity is depleted. A sharp increase in P-leaching may be observed from soils that exceed 25% saturation level; i.e. 25% of the P-binding capacity is occupied (Maguire & Sims 2002; Vanderzee, Leus & Louer 1989). Since there is no permanent P-removal process, comparable to denitrification, the eventual long-term effect of P-loading should be more pronounced than from N-loading. The effect may be somewhat ameliorated by an influx of P-binding compounds in some regions that may result in a permanent sink of P, that will not be saturated (Neal *et al.* 2002). However, this sink will usually be far less than the projected P-emissions.

Conclusions

Our study shows that in large parts of Europe, agriculture is judged as ‘environmentally unsustainable’. In most of the EU-countries Long-term Surface Water concentrations will greatly exceed acceptable levels of nitrogen and phosphorus. These estimations are conservative as we assume other anthropogenic sources and natural background emissions to surface waters to be negligible. Our analysis suggests that, in order to protect surface water quality, the N-application limit of 170 kgN.ha^{-1} y^{-1}, as defined in the EU Nitrate Directive, should be two- to twenty fold lower, depending on regional climatic conditions and strict P-regulations are needed.

Acknowledgements

This research was funded by the EC program BUFFER: “Key nutrient transport mechanisms important for the prediction of nutrient and phytoplankton concentrations in European standing waters”, contract number EVK1-CT-1999-00094.

References

Ærtebjerg G., Carstensen J., Dahl K. & Hansen J. (2001) Eutrophication in Europe's coastal waters, pp. 86. Copenhagen: European Environment Agency.

Andersen J. H., Conley D. J. & Hedal S. (2004) Palaeoecology, reference conditions and classification of ecological status: the EU Water Framework Directive in practice. *Marine Pollution Bulletin,* **49**, 283-290.

Beman J. M., Arrigo K. R. & Matson P. A. (2005) Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature,* **434**, 211-214.

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

Boesch D. F. (2002) Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. *Estuaries,* **25**, 886-900.

Carpenter S. R., Caraco N. F., Correll D. L., Howarth R. W., Sharpley A. N. & Smith V. H. (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications,* **8**, 559-568.

Crouzet P., Leonard J., Nixon S., Rees Y., Parr W., Laffon A., Bøgestrand J., Kristensen P., Lallana C., Izzo G., Bokn T. & Bak J. (1999) Nutrients in European ecosystems, pp. 156. Copenhagen: European Environment Agency.

Dingman S. L. (2002) *Physical Hydrology (2nd Edition)*. New Jersey USA: Prentice Hall.

EEA. (1995) Europe's Environment: The Dobris Assessment. Luxembourg: European Environment Agency.

European Commission. (1999) Directions towards sustainable agriculture, pp. 30. Brussels: COMMISSION OF THE EUROPEAN COMMUNITIES.

European Commission. (2002) Implementation of Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources. Synthesis from year 2000 Member States reports, pp. 51. Luxembourg: Office for Official Publications of the European Communities.

Eurostat. (1997) Soil surface nitrogen balances in EU countries. Luxembourg: Office for Official Publications of the European Communities.

Eurostat. (2003) Statistics in focus: Water resources, abstraction and use in European Countries, pp. 8. Luxembourg: Office for Official Publications of the European Communities.

Kampas A., Edwards A. C. & Ferrier R. C. (2002) Joint pollution control at a catchment scale: compliance costs and policy implications. *Journal of Environmental Management,* **66**, 281-291.

Leemans R., Kreileman E., Zuidema G. & Alcamo J. (1998) The IMAGE User Support System: Global Change Scenarios from IMAGE 2.1, pp. Publication 4815006. Bilthoven: RIVM National Institute for Public Health and the Environment.

Maguire R. O. & Sims J. T. (2002) Measuring agronomic and environmental soil phosphorus saturation and predicting phosphorus leaching with Mehlich 3. *Soil Science Society of America Journal,* **66**, 2033-2039.

Mills G. (2002) Modelling the water budget of Ireland-evapotranspiration and soil moisture. *Irish Geography,* **33**, 99-116.

Neal C. & Heathwaite A. L. (2005) Nutrient mobility within river basins: a European perspective. *Journal of Hydrology,* **304**, 477-490.

Neal C., Jarvie H. P., Williams R. J., Neal M., Wickham H. & Hill L. (2002) Phosphorus-calcium carbonate saturation relationships in a lowland chalk river impacted by sewage inputs and phosphorus remediation: an assessment of phosphorus self-cleansing mechanisms in natural waters. *Science of the Total Environment,* **282**, 295-310.

OECD. (2001) Environmental Indicators for Agriculture, pp. 400. Paris: Organisation for Economic Co-operation and Development.

OECD. (1982) Eutrophication of Waters - Monitoring, Assessment and Control, pp. 154. Paris: Organization for Economic Co-Operation and Development.

Oenema O. & Roest C. W. J. (1998) Nitrogen and phosphorus losses from agriculture into surface waters; The effects of policies and measures in The Netherlands. *Water Science and Technology,* **37**, 19-30.

OSPAR. (1997) Overview of the results of the comprehensive study on riverine inputs and direct discharges (RID) in 1995 and the comprehensive atmospheric monitoring programme (CAMP) in 1995.: Oslo and Paris Commissions.

Parris K. (1998) Agricultural nutrient balances as agri-environmental indicators: an OECD perspective. *Environmental Pollution,* **102**, 219-225.

Schippers P., van de Weerd H., de Klein J., de Jong B. & Scheffer M. (2006) Impacts of agricultural phosphorus use in catchments on shallow lake water quality: About buffers, time delays and equilibria. *Science of the Total Environment,* **369**, 280-294.

Schoumans O. F. & Silgram M. e. (2003) Review and literature evaluation of nutrient quantification tools., pp. 120 pp. Oslo, Norway.

Sibbesen E. & Runge-Metzger A. (1995) Phosphorus Balance in European Agriculture_Status and Policy Options. In *Phosphorus in the Global Environment* (ed. H. Tiessen), pp. 43-57. New York: John Wiley & Sons.

Van Drecht G., Bouwman A. F., Knoop J. M., Beusen A. H. W. & Meinardi C. R. (2003) Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Global Biogeochemical Cycles,* **17**.

Vanderzee S., Leus F. & Louer M. (1989) Prediction of Phosphate-Transport in Small Columns with an Approximate Sorption Kinetics Model. *Water Resources Research,* **25**, 1353-1365.

Chapter 8

Synthesis

Jeroen de Klein

Synthesis

While many processes are involved in nutrient retention, some basic rules of thumb emerge from the work presented in this thesis and other studies. Firstly, the rates of retention differ depending on water types. In large rivers (Rhine) retention fractions are in the range of 25 to 35 % (Chapter 2). In the delivering stream catchments and smaller rivers we found retention ranging from 30 to 60%, with high variability (Chapter 6). For ditches and headwaters of streams retention rates are estimated in the range of 50 to 70% (Chapter 3 and 5). Generally, our work suggests that relative retention rates of nitrogen decrease with increasing stream order, whereas absolute retention increases with increasing stream order. This is in line with earlier findings (Alexander, Smith & Schwarz 2000; Seitzinger *et al.* 2002). For phosphorus fewer studies on retention in relation to stream order is available. Consequently, it is difficult to draw general conclusions. However, our results indicate that the highest relative retention is found in lakes and downstream parts of streams.

When it comes to explaining differences in retention, essentially two things matter: the rate of the processes involved and the time these processes have to ‘clean’ the water. The latter depends on hydraulic residence time, or properties related to that, such as *displacement time* (Seitzinger *et al.* 2002) or *specific runoff*. (Behrendt & Opitz 1999). If transport through a water system takes longer, nutrient retention is higher. However, the relation is not linear and only valid to a certain extent. At very high residence times retention will level off to a constant maximum value (chapter 5 and 6). The rates of the different processes involved in retention can differ widely depending on the environmental conditions. Denitrification, for instance, is strongly affected by the presence of an oxygen gradient (oxic-anoxic) and degradable organic matter. On the other hand, particulate phosphorus retention depends on sedimentation, resuspension and entrainment, governed by hydromorphological factors and biological activity. Importantly, as described in this thesis, aquatic macrophytes promote favorable conditions for both nitrogen and phosphorus retention in many ways. Therefore, the combination of residence time and the presence of vegetated areas determines much of the variation in nutrient retention.

Obviously, it is the combination of loading rates and retention rates that determines nutrient concentrations in the water flowing from a catchment to downstream waters which are potentially vulnerable for eutrophication. More precisely, we can predict these concentrations from a simple model (eq. 1).

$$C_E = \frac{k_0}{k_1} + (C_0 - \frac{k_0}{k_1}) e^{-k_1 t} \qquad \text{(eq. 1)}$$

With: C_E = concentration at the end of the system (g.m^{-3})
C_0 = upstream starting concentration (g.m^{-3})
k_1 = 1st order process rate (time^{-1})
k_0 = zero order process rate (g.m^{-}3.time^{-1})
t = time of travel or residence time (time)

Here, k_1 and k_0 are lumped process rates, reflecting all the relevant processes. In case of a net removal of nutrients the process rates have negative signs. In this concept the outflow concentrations are thus determined by three parameters: starting concentration (C_0), travel time (t) and process rates (k_0 , k_1). Measures to reduce the end concentration can be evaluated on their impact on these parameters, pointing at essentially three different ways to improve water quality.

I. Emission reduction (C_0).

The parameter C_0 represents an apparent starting concentration, which reflects all point sources and diffuse loads in combination with the hydrological conditions. In order to decrease the outflow concentrations of a water system, the first step would be reduction of the emissions. Obviously, limiting nutrient emissions to surface waters will directly reduce the exported loads. Good progress is made in reducing point loads, and combating diffuse losses from agriculture is studied intensively (Kronvang *et al.* 2005; Withers & Jarvis 1998). However, reducing diffuse emissions is complex and effects will be visible after longer time spans (Schippers *et al.* 2006). Reduction of the emissions of nitrogen and phosphorus to the surface waters should have first priority in the abatement of eutrophication. When this is not possible (e.g. due to natural loadings) or when the time spans of noticeable effects are long, measures in the water systems can be considered, as specified in the following sections.

II. Increasing hydraulic residence time (t).

Hydraulic residence time can be changed by enlarging the surface water volume and reducing the flow velocities. Practical ways to do this include introduction of obstructions, promoting the growth of aquatic vegetation, reconnection of stream meanders, reconnecting floodplains and restoring stream-side wetlands (Kronvang *et al.* 2005; Tockner *et al.* 1999).

III. Stimulation of purification rates (k_0, k_1).

Especially, small surface waters like drainage ditches and stream headwaters have a high potential nutrient removal in a naturally vegetated state (Chapters 3 and 5). As argued in this thesis, measures that stimulate the presence of a diverse aquatic macrophyte community in such waters may often contribute substantially to the retention rates of nitrogen and phosphorus. Also, reconnection of stream floodplains and restoration of wetlands may accelerate denitrification rates, not only by increasing residence times, but also by improving process conditions (Fennessy & Cronk 1997).

Obviously, measures may also have negative effects that should be taken into account. For instance, flooding of wetlands with river water may induce loss of biodiversity in the flooded ecosystem and increased emissions of greenhouse gasses (Verhoeven *et al.* 2006). Also, abundant macrophyte growth in streams and ditches may conflict with the drainage function of the water courses. However, in many cases more detailed analysis may reveal the potential for integrative solutions that result in a substantial net benefit.

Although details may differ between cases, the emerging picture is that while reduction emissions (I) remains important, much can be gained by enhancing nutrient retention through increased residence times (II) and creating conditions that promote purification rates (III). Restoration of streams, floodplains and inundation strips along running waters, as well as the stimulation and maintenance of a diverse aquatic macrophytes community, may significantly improve the capacity for nutrient retention, and fit well to the ecological objectives of stream restoration.

References

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

Behrendt H. & Opitz D. (1999) Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia,* **410**, 111-122.

Fennessy M. S. & Cronk J. K. (1997) The effectiveness and restoration potential of riparian ecotones for the management of nonpoint source pollution, particularly nitrate. *Critical Reviews in Environmental Science and Technology,* **27**, 285-317.

Kronvang B., Bechmann M., Lundekvam H., Behrendt H., Rubaek G. H., Schoumans O. F., Syversen N., Andersen H. E. & Hoffmann C. C. (2005) Phosphorus losses from agricultural areas in river basins: Effects and uncertainties of targeted mitigation measures. *Journal of Environmental Quality,* **34**, 2129-2144.

Schippers P., van de Weerd H., de Klein J., de Jong B. & Scheffer M. (2006) Impacts of agricultural phosphorus use in catchments on shallow lake water quality: About buffers, time delays and equilibria. *Science of the Total Environment,* **369**, 280-294.

Seitzinger S. P., Styles R. V., Boyer E. W., Alexander R. B., Billen G., Howarth R. W., Mayer B. & Van Breemen N. (2002) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry,* **57**, 199-237.

Tockner K., Pennetzdorfer D., Reiner N., Schiemer F. & Ward J. V. (1999) Hydrological connectivity, and the exchange of organic matter and nutrients in a dynamic river-floodplain system (Danube, Austria). *Freshwater Biology,* **41**, 521-535.

Verhoeven J. T. A., Arheimer B., Yin C. Q. & Hefting M. M. (2006) Regional and global concerns over wetlands and water quality. *Trends in Ecology & Evolution,* **21**, 96-103.

Withers P. J. A. & Jarvis S. C. (1998) Mitigation options for diffuse phosphorus loss to water. *Soil Use and Management,* **14**, 186-192.

Summary

Summary

Nutrient retention

Streams and rivers transport nutrients from point sources and diffuse loads to downstream lakes and coastal zones, leading to eutrophication in many places. However, not all the nutrients loaded to a river system reach the end. Often a substantial part of the nutrients is stored in biomass and sediments or transformed. The sum of all the removal processes is generally referred to as *retention*. If we want to predict the effect of change in loading to downstream systems, it is important to have quantitative insight in the nutrient retention. Also insight in the conditions that control the rate of retention may help defining strategies for enhancing retention.

The overall objective of the research reported in this thesis is to elucidate the fate of nitrogen and phosphorus in running waters and to provide tools that may be used for estimating the rate of retention and the effects of different river catchment management plans on nutrient loads.

Ditches and headwater streams

In fresh waters, the main nitrogen removal process is denitrification, transforming nitrate to nitrogen gas that is subsequently emitted to the atmosphere. In areas with a dense network of drainage ditches denitrification represents a high potential removal of nitrogen, but knowledge on the process rates in these waters is scarce. Chapter 3 reports on a study where water column and sediment denitrification rates were measured *in situ* in vegetated ditches using ^{15}N Isotope Pairing Techniques, during summer and fall. Denitrification ranged from 200 to 350 μmol.m^{-2}.h^{-1} during summer months and from 50 to 150 μmol.m^{-2}.h^{-1} in the fall. Extrapolating these results we estimated the annual removal of nitrogen from agricultural ditches, via denitrification, to be 15 gN.m^{-2}.y^{-1}. This suggest that denitrification in ditches may remove more than 50% of the total diffuse inputs. The main driver for temporal variability of denitrification rates in these vegetated ditches was found to be water temperature. The overall Arrhenius temperature coefficient was 1.28, which is significantly higher than reported coefficients so far. The high temperature dependency means that with a temperature rise of 3 ^{o}C, as foreseen in IPCC scenarios denitrification in ditches could double.

Water residence time and presence of macrophytes are also major controlling factors for nutrient retention. To explore the effect of submerged macrophytes and management options, a simulation model was set up that combines dynamic water flow

modeling with mechanistic macrophyte growth and nutrient processes (Chapter 4). Despite simplifications of complex relations, the model predicted nutrient concentrations and macrophyte biomass quite well in a dynamic upper region of a lowland stream. Simulations suggested that average annual nitrogen retention was 25% of the incoming load, and was largely caused by denitrification (75%). Annual phosphorus retention was predicted to be slightly more (30%), and to result predominantly from sedimentation (92%).

We applied the model to simulate the effect of management strategies and maintenance of aquatic macrophytes on nutrient retention in streams (Chapter 5). Simulation scenarios comprised changes in hydraulic residence time, macrophyte growth and sediment release in a summer and winter period. The results suggest that changing residence time and the regime of maintenance removal of macrophytes may have significant impacts on the retention of nutrients. From the simulation results we derived a metamodel that allows predicting nutrient retention without running the complex dynamic model.

Lowland river catchments

Nutrient retention in freshwater systems is usually calculated from mass balances or estimated from catchment characteristics as an average annual loss. However, to determine critical emission values for the protection of lakes and coastal areas, it is also important to know the seasonal variation of the nutrient exports, especially for lakes with low residence times. In such lakes high winter loads may not affect summer nutrient concentration, whereas summer peak loads may cause large risks for algal blooms. To obtain an insight in seasonal variability, we analyzed data from 13 lowland river catchments in Western Europe varying in size from 21 to 486 km^2 (Chapter 6). Inputs to surface water and exports from the catchments were calculated, on a monthly as well as an annual (average) basis. The estimated annual in-stream retention in these catchments ranged from 23 to 84 % for N and 39 to 72 % for P.

To quantify variation of emission to the surface water and seasonal in-stream retention we derived empirical relations from the data (7 catchments) and used these to predict monthly exports from lowland rivers from annual emission to the surface waters, average monthly river discharge, average monthly water temperature and fraction of surface water area in the catchment. Validation of the empirical equations for the remaining 6 catchments showed good results (R^2 for the separate catchments ranged from 0.31 to 0.95, average 0.76). This suggests that exports of nitrogen and phosphorus may be predicted on a monthly basis from limited data, for a range of Western-Europe lowland rivers. In general, retention in summer is higher than in winter. This implies that summer nutrient concentrations are lower than what would be predicted based on an average annual input. An important implication is that accurate prediction of effects of measures for eutrophication abatement requires that we take seasonal variation in hydrology and nutrient loading into account.

Nutrient loads to the North Sea

To estimate nutrient loads from large river basins to the coastal areas we developed a flow-path approach (Chapter 2). This approach computes nutrient loads to the coastal areas, based on emissions to the surface waters, area of surface water within the subcatchments, retention factors for different water types and discharge distribution among the subcatchments. This method may be an alternative, when measurements in river outlets are unavailable or are highly uncertain due to the complex hydrology in the transition from fresh water streams to estuaries and coastal zones. The method also allows an estimation of the contribution of different sources and areas to the final load to the sea, revealing the specific pathways and retention processes during transport.

The method is applied to predict nutrient loads to the Dutch part of the North Sea. By means of a Monte Carlo simulation the uncertainties in the estimated loads are quantified. In the period 1995 to 2005, the estimated load amounted around 335 $Gg.y^{-1}$ total nitrogen and 18 $Gg.y^{-1}$ total phosphorus, which is 65 to 70 % of the total emissions to the surface waters. The total retention of N and P in the surface waters was 30 to 35 % of the emissions. Expressed as a per area value, the export loads to the Dutch part of the North Sea are among the highest reported in large river basins. They are in fact around 20 times higher than the exports of ‘pristine’ river basins.

Although river retention fractions are estimated to be not more than 4-9%, the largest part of the nutrients was retained within the main river system, due to high cumulative loads. This suggests that increasing nutrient retention capacity in the rivers, for instance by restoring floodplains, can potentially reduce the nutrient loads to the North Sea substantially.

The European scale

Eutrophication is among the main threats to biodiversity and ecosystem functioning of European surface waters. Although fertilizer use is considered the main cause of this problem, definition of application limits that would protect freshwater and marine systems remains subject to scientific discussions and political debate.

In chapter 7 I present an approach to predict long-term consequences of fertilizer use for the aquatic environment. Assuming eventual saturation of nutrient storage capacity of soils and sediments, we calculate long- term surface water concentrations from nutrient surpluses in agriculture and net precipitation levels at the scale of European administrative regions. We predict that nutrient concentrations will exceed basic surface water targets in over 85% of the area. Implementing fertilizer application limits according to present legislation will hardly improve this situation. Agricultural nutrient surpluses should be reduced an order of magnitude in most regions to be environmentally sustainable. In addition, the analysis indicates that setting a fixed nutrient application standard for all regions is inappropriate. Importantly, fertilizer application limits should be region specific, accounting for spatial difference in rain fall and temperature. This is because in regions with less net precipitation, the same amount of fertilizer leads to higher concentrations.

Synthesis

In the last chapter I argue that the results in this thesis imply that management aimed at enhancing retention can help improving water quality in many cases. Certainly, reduction of the emissions of nitrogen and phosphorus to the surface waters should have first priority in the abatement of eutrophication. However, when this is not possible (e.g. due to natural loadings) or when there is a substantial time lag between emission reduction and noticeable effects, measures aimed at enhancing retention can be considered. Although details may differ between cases, the emerging picture is that much can be gained through increasing residence times and creating conditions that promote purification rates. Restoration of streams, floodplains and inundation strips along running waters, as well as the stimulation and maintenance of a diverse aquatic macrophytes community, may significantly improve the capacity for nutrient retention, and fit well to the ecological objectives of stream restoration.

Samenvatting

Samenvatting

Nutriënten retentie

Beken en rivieren transporteren nutriënten (vooral stikstof en fosfor), afkomstig van puntbronnen en diffuse lozingen, naar benedenstrooms gelegen meren en kustwateren. Dit leidt tot eutrofieringsverschijnselen in veel gebieden. Maar niet alle nutriënten die worden geloosd bereiken uiteindelijk de benedenstroomse wateren. Tijdens het transport vinden allerlei processen plaats, waardoor een aanzienlijk deel van de nutriënten wordt omgezet of vastgelegd in biomassa en het sediment. Het totaal van deze verwijderingsprocessen wordt aangeduid met de term *retentie*. Voor het voorspellen van het effect van maatregelen om de lozingen te verminderen (emissiereductie) is het noodzakelijk om kwantitatief inzicht te hebben in de nutriëntenretentie. Daarnaast draagt kennis van de sturende factoren bij aan het ontwikkelen van ingrepen om de retentie te stimuleren.

Het algemene doel van het onderzoek in dit proefschrift is het belichten van de lotgevallen van stikstof en fosfor in stromende wateren. Tevens wordt beoogd methoden te ontwikkelen om retentie te kunnen schatten en om ingrepen in wateren en stroomgebieden te kunnen beoordelen op hun effecten op nutriëntenvrachten.

Sloten en beekbovenlopen

In oppervlaktewater is denitrificatie het belangrijkste verwijderingsproces voor stikstof. Nitraat wordt omgezet in stikstofgas, dat verdwijnt naar de atmosfeer. In gebieden met een dicht netwerk van sloten kan in potentie veel stikstof verwijderd worden, maar kennis van denitrificatiesnelheden in dit type water is beperkt. Hoofdstuk 3 beschrijft een onderzoek waarin denitrificatie *in situ* wordt gemeten in sloten met vegetatie. De metingen zijn verricht met de ^{15}N Isotope Pairing Technique, gedurende de zomer en het najaar. Denitrificatie varieerde van 200 tot 350 μmol.m^{-2}.h^{-1} tijdens de zomer maanden en van 50 tot 150 μmol.m^{-2}.h^{-1} in de herfst. Geëxtrapoleerd naar een heel jaar schatten we de denitrificatiecapaciteit van sloten in agrarisch gebied op 15 gN.m^{-2}.y^{-1}. Dit betekent dat 50% van de totale jaarlijkse diffuse input via denitrificatie wordt verwijderd.

Voorts lieten de metingen zien, dat temperatuur de belangrijkste factor is voor temporele variatie van denitrificatie in dergelijke waterplantgedomineerde sloten. De totale Arrhenius temperatuur coëfficiënt was 1.28, dat beduidend hoger is dan tot nu toe gevonden waarden. De grote temperatuursafhankelijk houdt in, dat met een temperatuurstijging van 3 °C, zoals voorzien in de IPCC scenario's, denitrificatiesnelheden in sloten kunnen verdubbelen.

Verblijftijd van het water en de aanwezigheid van waterplanten zijn eveneens belangrijke sturende factoren voor retentie van nutriënten. Om het effect van waterplanten en verschillende beheersopties te onderzoeken is een simulatiemodel gemaakt, bestaande uit een hydrodynamisch model (watertransport) en een mechanistisch model voor groei van waterplanten en nutriëntenprocessen (hoofdstuk 4). Het model is toegepast op een netwerk van watergangen in de bovenloop van een laaglandbeek. Ondanks de simplificaties van complexe relaties bleek het model in staat concentraties van nutriënten en biomassa van waterplanten goed te voorspellen. De simulaties laten zien dat gemiddeld 25% van de jaarlijkse stikstofbelasting wordt vastgelegd of verwijderd, voornamelijk door denitrificatie (75%). Jaarlijkse fosforverwijdering werd berekend op 30%, voornamelijk door sedimentatie (92%).
We hebben het model ook toegepast om het effect van verschillende beheersopties en onderhoud van de vegetatie op de retentie van nutriënten te onderzoeken (hoofdstuk 5). De scenario's bevatten verschillen in verblijftijden, maaistrategieën voor de vegetatie en nalevering van nutriënten uit het sediment. De resultaten wijzen op een significant effect van deze factoren op de totale retentie van N en P. De resultaten van de modelberekeningen zijn gebruikt voor het afleiden van een zogenaamd metamodel. Hiermee kan een schatting van de retentie gemaakt worden op basis van enkele basiskenmerken, zonder dat daarvoor het hele dynamische model gerund hoeft te worden.

Stroomgebieden van laaglandbeken

Nutriëntenretentie in oppervlaktewatersystemen is vaak berekend aan de hand van massabalansen of geschat uit stroomgebiedskenmerken, als een gemiddelde jaarlijkse verwijdering. Maar voor het vaststellen van kritische belasting voor de bescherming van meren en kustwateren is het ook noodzakelijk de seizoensvariatie in beschouwing te nemen. Dat geldt vooral voor meren met relatief kleine verblijftijden. Hier kunnen belastingen in de winter mogelijk geen effect hebben op de zomerconcentraties, terwijl pieken in zomerbelasting kunnen leiden tot grote algenbloeien. Om dit te onderzoeken hebben we data van 13 stroomgebieden van laaglandbeken in Nederland, Duitsland Denemarken en Ierland geanalyseerd, variërend in oppervlakte van 21 tot 486 km^2 (hoofdstuk 6). Belasting van het oppervlaktewater en export uit de stroomgebieden zijn berekend op maandbasis en op jaarbasis. De geschatte jaarlijkse retentie in het oppervlaktewater bedroeg 23 tot 84% voor N en 39 tot 72% voor P. Uit de data zijn empirische relaties afgeleid die maandelijkse export en retentie schatten op basis van jaarlijkse emissies naar het oppervlaktewater, maandelijkse afvoer en watertemperatuur en de fractie oppervlaktewater van het totale stroomgebiedsoppervlak. De relaties zijn gekalibreerd met data van 7 stroomgebieden en gevalideerd met de overige 6 stroomgebieden. De resultaten van de validatie waren bevredigend (gemiddelde R^2 was 0.76). Met de empirische relaties kunnen export en retentie in laaglandbeken geschat worden op basis van een beperkte hoeveelheid data.

In het algemeen is de retentie in de zomer hoger dan in de winter. Dit betekent dat de zomerconcentraties lager zijn dan geschat op basis van een jaarlijkse retentie. Voor accurate beoordeling van maatregelen voor eutrofiëringbestrijding is het gewenst dat de seizoensvariatie in hydrologie en nutriëntenbelasting wordt meegenomen.

Nutriëntenbelasting van de Noordzee

Voor het berekenen van de vrachten aan nutriënten naar de kustwateren via de grote rivieren hebben we een zogenaamde stroombanenbenadering toegepast (hoofdstuk 2). Hiermee berekenen we nutriëntenbelasting van de kustwateren op basis van emissies naar het oppervlaktewater, oppervlakte open water in de deelstroomgebieden, retentiefactoren voor verschillende watertypen en verdeling van de waterafvoeren tussen de deelstroomgebieden. Deze methode kan een alternatief zijn voor vrachtberekeningen als metingen in de uitstroompunten van de rivieren niet beschikbaar of erg onzeker zijn. Met deze methode kan ook de individuele bijdrage van verschillende bronnen en deelstroomgebieden aan de totale vracht naar de Noordzee gekwantificeerd worden, rekening houdend met verschillende transportwegen en retentie onderweg.

Voor het Nederlandse deel van de Noordzee zijn aldus jaarlijkse vrachten berekend in de periode 1995-2005, waarbij de onzekerheden in de berekening zijn gekwantificeerd met een Monte Carlo simulatie. De gemiddelde jaarlijkse vracht bedroeg 335 $Gg.y^{-1}$ totaal stikstof en 18 $Gg.y^{-1}$ totaal fosfor. Dit is 65 tot 70 % van de totale emissies naar het oppervlaktewater, wat inhoudt dat tijdens het transport 30 tot 35% wordt vastgelegd of verwijderd. Wanneer de export wordt uitgedrukt per vierkante kilometer stroomgebied blijkt dat de vrachten naar het Nederlandse deel van de Noordzee tot de hoogste behoren van tot nu toe gerapporteerde vrachten van grote rivieren. De waarden zijn circa 20 keer hoger dan de ‘natuurlijke’ exports.

De retentie van nutriënten in de grote rivieren wordt geschat op 4 tot 9 % van de totale vrachten, maar in absolute zin is dat het meest van alle wateren, omdat de cumulatieve vrachten erg groot zijn. Dit betekent dat het stimuleren van retentie van nutriënten in de rivieren, bijvoorbeeld door het herstel van overstromingsgebieden, tot een belangrijke vermindering van de belasting van de Noordzee kan leiden.

Het Europese schaalniveau

Eutrofiering is een van de belangrijkste bedreigingen voor de biodiversiteit en het functioneren van het ecosysteem in Europese oppervlaktewateren. Overmatig gebruik van meststoffen in de landbouw wordt algemeen beschouwd als belangrijke veroorzaker van eutrofiering, maar het stellen van gebruikslimieten voor meststoffen om het water te beschermen zijn nog steeds onderwerp van wetenschappelijke en politieke discussies.

In hoofdstuk 7 presenteer ik een manier om lange termijn effecten van meststoffengebruik op de kwaliteit van het oppervlaktewater te voorspellen. Als we ervan uitgaan dat uiteindelijke alle opnamecapaciteit van bodems en sedimenten voor nutriënten uitgeput raakt kunnen we lange termijn evenwichtsconcentraties in het oppervlaktewater uitrekenen uit het bemestingsoverschot en de jaarlijkse neerslag in een gebied. Dit is gedaan voor alle EU deelgebieden (Nuts2 regio’s). We voorspellen dat in 85 % van alle gebieden de normen voor acceptabele waterkwaliteit worden overschreden, uitgaande van het bemestingsniveau van 1997. Invoering van de gebruiksnormen in overeenstemming met de huidige wetgeving zal de situatie nauwelijks verbeteren. In de meeste regio’s zouden de bemestingsoverschotten een orde grootte gereduceerd moeten worden om te kunnen spreken van milieukundige duurzaamheid. Verder toont de analyse aan, dat het toepassen van een uniforme gebruiksnorm voor alle gebieden niet zinvol is. In deze benadering zouden gebruiksnormen voor bemesting beter regionaal gedifferentieerd moeten worden, waarbij rekening wordt gehouden met regiospecifieke omstandigheden als neerslag en temperatuur.

Synthese

In het laatste hoofdstuk betoog ik dat de resultaten van het hier gepresenteerde onderzoek aangeven, dat het stimuleren van nutriëntenretentie in oppervlaktewater in veel gevallen kan bijdragen aan verbetering van de waterkwaliteit. Uiteraard heeft reductie van de emissies van N en P naar het oppervlaktewater eerste prioriteit bij het bestrijden van eutrofiering. Maar als dat niet mogelijk is (bijvoorbeeld in geval van natuurlijke belasting) of als maatregelen lastig in te voeren zijn of pas na lange tijd effect hebben, zijn maatregelen voor retentiebevordering zeker te overwegen.

Het zal van geval tot geval verschillen, maar het algemene beeld is dat veel gewonnen kan worden door de verblijftijd van het water te vergroten en verwijderingsprocessen te stimuleren. Herstel van beekprofielen, inundatiezones en uiterwaarden, alsmede het stimuleren van een gevarieerde aquatische vegetatie kunnen de retentiecapaciteit van stromende wateren aanzienlijk verbeteren. Deze maatregelen sluiten ook prima aan bij de ecologische doelen van beek- en rivierherstel.

Dankwoord

Dankwoord

Een aantal jaren geleden hadden we met de leerstoelgroep een studiedag over teamrollen. Uit de vragenlijsten en enquêtes die daaraan vooraf gingen kwam naar voren dat ik twee natuurlijke rollen vervul: de *brononderzoeker* en de *groepswerker.* Voor degene die bekend zijn met de teamrollentheorie van Belbin zal dit het een en ander kunnen verklaren over mijn keuzes van de afgelopen jaren. Vooral de eerste rol heeft me duidelijke parten gespeeld bij de totstandkoming van dit proefschrift. Een brononderzoeker wordt omschreven als een nieuwsgierige verkenner, op zoek naar ideeën, ontwikkelingen en mogelijkheden, zowel binnen als buiten de groep. Positief en enthousiast. Maar daar staan ook zwakheden tegenover: overenthousiasme, niet erg doelgericht, en vooral '*een brononderzoeker maakt niks af*'. Tijdens de studiedag kreeg ik hierover veelbetekenende blikken van een aantal collega's, en het is nog jaren onderwerp van gesprek geweest. Maar tegelijkertijd is dit proefschrift ook het bewijs van het tegendeel. Het is namelijk wel af.

In 1995 kwam ik, na 10 jaar waterschap en ingenieursbureau, terug naar Wageningen. Mijn ervaring in het veld waren nuttig bij het inbrengen van praktijkgerichte en toegepaste vraagstukken in het waterbeheer. In eerste instantie vooral bij het onderwijs. Toen al constateerden we dat voor een (vaste) aanstelling als Universitair Docent een promotie toch zeer gewenst was. Intussen zag ik collega's interessante onderzoeken doen en publicaties schrijven, maar door mijn brede interesse en veelheid aan contacten was het lastig een focus te vinden. Samen met mijn toenmalige collega's heeft het zich ontwikkeld richting het eutrofieringsonderzoek en de lotgevallen van nutriënten. Voor het EU-project Buffer ben ik wat specifieker gaan kijken naar retentie van nutriënten in stromende wateren en uiteindelijk is dat de leidraad van het proefschrift geworden.

Veel mensen hebben mij ondersteund en direct bijgedragen aan dit proefschrift. Van diegenen wil ik als eerste noemen mijn beide promotoren Marten Scheffer en Bart Koelmans. Zij hebben me alle vrijheid gegeven en onvoorwaardelijke steun om het op mijn manier te doen, en tegelijkertijd met gerichte prikkels me bij de les gehouden en doelgericht laten zijn. Mijn interpretatie van het begrip *deadline* heeft ongetwijfeld veel van hun incasseringsvermogen gevraagd. De interessante discussies en gerichte coaching, vooral in de laatste periode, hebben ervoor gezorgd dat het eindelijk allemaal op papier is terecht gekomen.

Ten tweede zijn er de co-auteurs die op enigerlei manier hebben bijgedragen aan de hoofdstukken. Dit zijn er een behoorlijk aantal vanuit verschillende richtingen, wat ongetwijfeld samenhangt met mijn rol als brononderzoeker. In volgorde van de hoofdstukken: Danneke Verhagen-Bakker (als student, en nu bij Nelen en Schuurmans), Remi Laane en Theo Prins (RIKZ, tegenwoordig Deltares); Jayne Rattray en Els Faassen (beide als student, en later als werk-collega); Rob Portielje (RIZA, tegenwoordig RWS Waterdienst) en Hans Aalderink (oud-collega, thans Arcadis); Bart Koelmans; Paul Boers (RIZA, tegenwoordig RWS Waterdienst), Peter Schippers (WUR-collega) en Marten Scheffer.
In de afgelopen jaren heb ik veel afstudeervakkers begeleid, met een grote verscheidenheid aan onderwerpen. In verreweg de meeste gevallen was de samenwerking plezierig en constructief. Een aantal studenten heeft direct bijgedragen aan het retentie-onderzoek. Naast de genoemde co-auteurs Danneke, Jayne en Els wil ik Rutger Engelbertink bedanken voor zijn omvangrijke veldwerk in de Gooiermars.

Maar zonder een prettige werkomgeving is het niet te doen. Ik verkeer in de gelukkige omstandigheid te mogen werken in het team van de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer. Een creatieve, collegiale staf, een fantastisch stel AIO’s en een groep ondersteuners, zonder wie sowieso heel weinig van de grond zou komen. En allemaal bereid om mee te denken en om werk van elkaar over te nemen. Zonder iemand te kort te willen doen bedank ik Frits Gillissen, John Beijer en Marijke Kuipers voor het feit altijd bij hen terecht te kunnen voor welke vraag of voor wat voor klus dan ook. Ik hoop dat het lukt om met z’n allen de goede sfeer binnen AEW vast te houden.
Twee keer heb ik een tijdelijke ‘uitstap’ gemaakt in de vorm van een detachering. Eerst naar het Riza in Lelystad (2005-2006). Ik bedank Paul Boers en Rob Portielje en de overige collega’s van de afdeling WIE voor het prettige en leerzame jaar van samenwerking. Vervolgens ben ik in deeltijd gaan werken voor het team Integraal Waterbeheer van Alterra. In dit team is een grote en unieke expertise op het gebied van modellen en toegepaste studies voor het waterbeheer aanwezig. Ik heb daar een aantal interessante projecten kunnen doen.

Velen van mijn familie en vrienden hebben het proces naar het proefschrift met belangstelling gevolgd en hebben zich ongetwijfeld afgevraagd of het er ooit nog eens van zou komen. Vaak begon het gesprek met een aarzelend ‘*mag ik je vragen hoe het gaat met ….’.* Maar belangstelling is nooit verkeerd, het helpt altijd een beetje. Speciaal was de noveen van Ans, een hart onder de riem bij de laatste negen dagen voor het inleveren van de leesversie. En Cecile en Michiel, bedankt dat jullie paranimfen wilden zijn, met de support van dichtbij en op afstand.

En tot slot: Willem, Guus, Daantje en Lien. Jullie hebben het allemaal van dichtbij meegemaakt. Met belangstelling, soms met ongeduld (“*is het nu nog niet af?”*), maar altijd met begrip voor mijn nukken en steun als het nodig was. We hebben wel eens bedacht dat 05-05-05 een mooie datum was om te promoveren; toen werd het 06-06-06, en uiteindelijk is het dus 06-06-08 geworden. Waarschijnlijk was het proefschrift er zonder jullie ook wel gekomen, misschien zelfs wat eerder dan nu. Maar daarmee wil ik alleen maar aangeven, dat jullie voor mij echt op de eerste plaats komen.

Curriculum Vitae

Curriculum Vitae

Jeroen de Klein is geboren op 21 juli 1959 in Gendt in de over-Betuwe. Daar is hij tot zijn 18^{e} jaar blijven wonen. In 1977 haalde hij zijn VWO diploma op het Canisius College te Nijmegen. Aansluitend is hij begonnen met de studie Milieuhygiëne aan de toenmalige Landbouwhogeschool te Wageningen. In het 2^{e} jaar koos hij voor de specialisatie waterkwaliteit en in 1984 haalde hij zijn doctoraaldiploma met als afstudeervakken waterzuivering, hydrobiologie en milieurecht. Jeroen heeft zijn stage gedaan bij het Limnologisch Instituut te Uppsala in Zweden.

Van 1985 tot 1990 was hij in dienst bij het Zuiveringsschap Oostelijk Gelderland (thans waterschap Rijn en IJssel) als medewerker waterkwaliteit. Daar heeft hij kennis gemaakt met veel facetten van het waterbeheer. Van monitoring tot dataverwerking; van beleidsadvisering tot integraal waterbeheersplan. Vervolgens werkte hij gedurende vijf jaar bij ingenieursbureau Tauw in Deventer als (senior) adviseur en projectleider.

In 1995 kreeg Jeroen de mogelijkheid om terug te keren naar ‘zijn’ vakgroep in Wageningen. Ondanks de beperkte zekerheid, een 0.5 aanstelling voor twee jaar en de rest zelf bijverdienen, was de combinatie van onderwijs, onderzoek en toegepaste projecten erg aanlokkelijk. Na enkele jaren volgde een vaste aanstelling als universitair docent bij, wat inmiddels was gaan heten, de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer. Daar werkt hij nu nog steeds.

Ter verbreding van de eigen horizon en voor het versterken van de contacten met de praktijk van het waterbeheer, is Jeroen van juni 2005 tot juni 2006 gedetacheerd geweest bij Rijkswaterstaat Riza in Lelystad. Na terugkeer in Wageningen volgde een nieuwe detachering, in deeltijd (0.6), bij het team Integraal Waterbeheer van WUR-Alterra en de resterende 0.4 bij de leerstoelgroep AEW.

List of publications

List of publications

Klein J.J.M. de; Aalderink R. H.; Portielje R. (2008) Modeling the impact of aquatic macrophytes and management strategies on nutrient retention in streams. (this thesis). *submitted*.

Klein J.J.M. de,;Rattray, J. and Faassen, E. (2008) Effect of temperature on denitrification in vegetated ditches. (this thesis). *submitted*.

Klein J.J.M. de; Koelmans, A.A. Quantifying seasonal and annual retention of nutrients in lowland rivers at catchment scale. (this thesis). *submitted*.

Klein, J.J.M. de; Portielje, R. (2007) Effecten van hydromorfologische ingrepen op de afleiding van de Mep/Gep voor nutriënten. Wageningen : Alterra, (Alterra-rapport 1611) - p. 47.

Klein, J.J.M. de (2007) Analyse van de vrachten stikstof en fosfor, op het Nederlandse deel van de Noordzee. Wageningen : Alterra, (Alterra-rapport 1612) - p. 43.

Klein, J.J.M. de; Brinkman, B. (2007) Effect of hydromorphological interventions on nutrient concentrations in surface waters
In: Proceedings of the 5th International Phosphorus Workshop, Silkeborg, Denmark, 3 - 7 September, 2007. - Aarhus : Aarhus Universitet, - p. 263 - 265.The 5th International Phosphorus Workshop (IPW5), 2007-09-03/ 2007-09-07

Klein, J.J.M. de; Brinkman, A.G. (2007) Effecten van hydromorfologische ingrepen op nutriëntenconcentraties en overige fysisch-chemische grootheden in oppervlaktewater
Wageningen : Alterra, (Alterra-rapport 1416) - p. 76.

Klein, J.J.M. de (2007) Analyse van de grootte en de herkomst van de vrachten stikstof en fosfor, via het oppervlaktewater, op het Nederlandse deel van de Noordzee. Wageningen : Alterra, (Alterra-rapport 1417) - p. 40.

Peeters, E.T.H.M.; Klein, J.J.M. de; Scheffer, M. (2007) Onderzoek naar het ecologisch functioneren van Nederlandse sloten
H twee O 40 (6). - p. 30 - 31.

Schippers, P.; Weerd, H. van de; Klein, J.J.M. de; Jong, B. de; Scheffer, M. (2006) Impacts of agricultural phosphorus use in catchments on shallow lake water quality: about buffers, time delays and equilibria
Science of the Total Environment 369 (1-3). - p. 280 - 294.

Smit, R.; Klein, J.J.M. de; Walvoort, D.J.J. (2006) Versterking van het zelfreinigend vermogen van oppervlaktewateren
In: 20 puzzelstukjes voor de KRW; een bloemlezing uit het onderzoek van Wageningen UR voor de Europese Kaderrichtlijn Water / Leenders, Ir T.P., Kwakernaak, Dr C., . - Wageningen : Alterra, (Alterra-rapport 1403) - p. 34 - 35.

Schippers, P.; Vermaat, J.; Klein, J.J.M. de; Mooij, W.M. (2004) The effect of atmospheric carbon dioxide elevation on plant growth in freshwater ecosystems. Ecosystems 7 (1). - p. 63 - 74.

Weerd, H. van de; Klein, J.J.M. de; Nes, E.H. van; Peeters, E.T.H.M. (2004) Ecologisch effect van nutriëntverwijdering in RWZI De Bilt op het oppervlaktewater. Wageningen Universiteit, - p. 22.

Vermeer, C.P.; Escher, M.; Portielje, R.; Klein, J.J.M. de (2003) Nitrogen uptake and translocation by Chara
Aquatic Botany 76 . - p. 245 - 258.

Kroeze C., Aerts R., van Breemen N., van Dam D., van der Hoek K., Hofschreuder P., Hoosbeek M., de Klein J., Kros H., van Oene H., Oenema O., Tietema A., van der Veeren R. & de Vries W. (2003) Uncertainties in the fate of nitrogen I: An overview of sources of uncertainty illustrated with a Dutch case study. Nutrient Cycling in Agroecosystems, 66, 43-69.

Vries, W. de; Kros, J.; Oenema, O.; Klein, J.J.M. de (2003) Uncertainties in the fate of nitrogen: II. a quantitative assessment of the uncertainties in major nitrogen fluxes in the Netherlands
Nutrient Cycling in Agroecosystems 66 (1). - p. 71 - 102.

Klein, J.J.M. de (2002)
Monitoring Spaarbekken/helofytenfilter te Laude (1997-2001) Wageningen : Wageningen Universiteit, (Eindrapport ; M326) - p. 56.