

Global foundations for reducing nutrient enrichment and oxygen depletion from land based pollution, in support of the





Report 1

Approaches for modeling nutrient dynamics, transfer, and impacts along the aquatic continuum from land to ocean

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About the GEF-Global Nutrient Cycle Project

Project objective: to provide the foundations (including partnerships, information, tools and policy mechanisms) for governments and other stakeholders to initiate comprehensive, effective and sustained programmes addressing nutrient over-enrichment and oxygen depletion from land based pollution of coastal waters in Large Marine Ecosystems.

Core project outcomes and outputs:

- the development and application of quantitative modeling approaches: to estimate and map
 present day contributions of different watershed based nutrient sources to coastal nutrient
 loading and their effects; to indicate when nutrient over-enrichment problem areas are likely to
 occur; and to estimate the magnitude of expected effects of further nutrient loading on coastal
 systems under a range of scenarios
- the systematic analysis of available scientific, technological and policy options for managing nutrient over-enrichment impacts in the coastal zone from key nutrient source sectors such as agriculture, wastewater and aquaculture, and their bringing together an overall Policy Tool Box
- the application of the modeling analysis to assess the likely impact and overall cost effectiveness of the various policy options etc brought together in the Tool Box, so that resource managers have a means to determine which investments and decisions they can better make in addressing root causes of coastal over-enrichment through nutrient reduction strategies
- the application of this approach in the Manila Bay watershed with a view to helping deliver the key tangible outcome of the project – the development of stakeholder owned, cost-effective and policy relevant nutrient reduction strategies (containing relevant stress reduction and environmental quality indicators), which can be mainstreamed into broader planning
- a fully established global partnership on nutrient management to provide a necessary stimulus and framework for the effective development, replication, up-scaling and sharing of these key outcomes.

Project partners:

- Chilika Development Authority
- Energy Centre of the Netherlands
- Global Environment Technology Foundation
- Government of India Lake Chilika Development Authority
- Government of the Netherlands
- Government of the Philippines
- Government of the United States
- Intergovernmental Oceanographic Commission of UNESCO
- International Nitrogen Initiative
- Laguna Lake Development Authority
- Partnerships in Environmental Management for the Seas of East Asia
- Scientific Committee on Problems of the Environment
- University of Maryland
- University of the Philippines
- University of Utrecht
- Washington State University
- World Resources Institute

Implementing Agency: United Nations Environment Programme

Executing Agency: UNEP- Global Programme of Action for the Protection of the Marine Environment from Land-Based Activities (GPA)

Approaches for modeling nutrient dynamics, transfer, and impacts along the aquatic continuum from land to ocean

Report 1 of component B1 of GEF project "Global foundations for reducing nutrient enrichment and oxygen depletion from land based pollution, in support of Global Nutrient Cycle"

Overview of existing tools for source-impact analysis of nutrients in LMEs and their target audiences

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A.F. Bouwman^{1,2}

J.A. Harrison³

¹ Department of Earth Sciences–Geochemistry, Faculty of Geosciences, Utrecht University, Utrecht, The Netherlands

² PBL Netherlands Environmental Assessment Agency, Bilthoven, The Netherlands.

³ School of Earth and Environmental Sciences, Washington State

University, Vancouver, Washington, USA.

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1. Introduction

Before reaching the open ocean, nutrients from land transit through the continuum formed by soil, groundwater, riparian zones, rivers, lakes, estuaries and coastal marine areas (Figure 1). These systems act as successive filters, often retaining a large fraction of the nutrients initially mobilized from land. Retention of the aquatic continuum not only affects the amount of nutrients reaching the ocean; it also modifies the ratio in which C, N, P and Si are transferred, and the form of each of these elements.

Eutrophication has been defined in various ways (e.g. Nixon, 1995), but central to all definitions is the concept that enrichment by nutrients causes enhanced biomass and/or growth rate of algae, which in turn leads to an undesirable disturbance in the balance of organisms present in the water and to the quality of the water body concerned. The result of eutrophication is often an increase in total algal biomass, frequently dominated by a single species or species group, sometimes harmful algae, resulting in a harmful algae bloom (HAB) (Hallegraeff, 1993;Anderson et al., 2002;Glibert et al., 2005;Heisler et al., 2008). The effects of HABs include overgrowth and shading of sea grasses, oxygen depletion of the water from algal and bacterial respiration (especially on death of the algal biomass), suffocation of fish from stimulation of gill mucus production, direct toxic effects on fish and shellfish (Anderson et al., 2002;Landsberg, 2002;Backer and McGillicuddy Jr., 2006). An additional problem with high-biomass harmful algal blooms is a reduced transfer of energy to higher trophic levels, as many HAB species are not efficiently grazed, resulting in a decreased transfer of carbon and nutrients to fish stocks when HAB species replace more readily consumed algal species (e.g. Mitra and Flynn, 2006).

Eutrophication as a result of nutrient loading was first evident in lakes and rivers as they became choked with excessive growth of rooted plants and floating algal scums, prompting intense study in the 1960's-70's and culminating in the scientific basis for banning phosphate detergents (a major source of P, the most frequent culprit in eutrophication of lakes) in many OECD countries, and upgrading sewage treatment to reduce wastewater N and P discharges to inland waters. Symptoms of eutrophication in estuaries and other coastal marine ecosystems (where N is the most frequent contributor to eutrophication) including hypoxia and harmful algal blooms were clearly evident by the 1980's (Zhang et al., 2010;Rabalais et al., 2010).

Currently, eutrophication negatively affects rivers, lakes, and estuaries worldwide, and is the foremost aquatic ecosystem management problem. There is mounting evidence that climate change will exacerbate eutrophication and its associated negative impacts (Baron et al., 2012, Michalak et al., 2013). This underscores the need to

develop approaches to examine interactions among disturbances and to incorporate ecological principles into management and restoration activities (Stanley et al., 2010). Disturbance of biogeochemical cycles by human activities calls for an integrative consideration of biogeochemical fluxes between the atmosphere, terrestrial and aquatic ecosystems. However, such integration of knowledge has been hampered by the historical separation between the approaches and cultures of terrestrial and aquatic sub-disciplines of biogeochemistry.

Models are essential to improve our understanding of the interaction between multiple processes in different landscape elements in river basins (Figure 1) and to better predict the transfer of nutrients from land to sea in a changing world. Various conceptual models have been developed that differ in their disciplinary rooting and bias, the spatial and temporal domain and resolution, the comprehensiveness of ecosystem coverage and the level of detail of processes that are included. A comparative study of conceptual models for nutrient transfer along the aquatic continuum from land to ocean is, therefore, needed.

Much ecological theory focuses on interactions between organisms in a homogeneously mixed, non-spatial environment. This simplifies mathematical representation of natural systems and facilitates experimental design, but is an unrealistic oversimplification. Predictions from models that lack spatial explicitness are often fundamentally different from predictions of models that account for spatial distributions in their representation of interactions among individuals, populations or chemical substances. For example, models describing competition or predation where individuals only interact when they are close enough, may predict co-existence; other models that consider the water as a box without spatial distribution, may predict exclusion of one species. Also, in a water column that is partially mixed where light comes from the surface and nutrients have to be mixed into the illuminated surface layer, strong gradients in algal concentration and primary production will develop, and total production may differ from that modeled for a well-mixed water column. An extensive discussion of ecosystem models is in Soetaert and Herman (2009). Here, we provide a brief summary of various approaches used to model nutrient transport and coastal effects, and outline some examples of some of the current models used for simulating river biogeochemistry (section 2). We also summarize several approaches to evaluating ecosystem status and water guality, ranging from indicators to complex models,(section 3).

2. Modeling the transport of nutrients from land to the ocean

	С	Ν	Р	Si
Weathering	DIC		DIP	DSi
Leaching	DIC, DOC	DIN	DIP, DOP	
Erosion/surface runoff	POC	PN	PP	ASi
Wastewater discharge (including aquaculture)	POC	DIN, DON, PN	DIP, DOP, PP	
Atmospheric deposition		DIN		

Table 1. Sources of C, N, P, and Si, by form, in rivers

2.1. Model approaches

In the last decades there have been a number of significant developments in the field of water-quality modelling, resulting in a variety of water-quality models. There is a large body of literature that describes individual models and processes. There are many ways to classify in-stream biogeochemistry models. For example, Cox (2003) used a scheme where the spatial dimension, processes, data types and temporal scale are used to subdivide models for in-stream biogeochemistry (Figure 2). However, for describing the fate of nutrients at the scale of a landscape from the source to the river mouth, we need to consider not only in-stream processes, but also the delivery processes.

Two fundamentally different approaches exist. The first category is the lumped approach, that combines all processes between the soil and the river mouth in a few parameters in simple, mostly empirical models (Figure 3a). The second is the distributed approach, where the transport of nutrients is separately described for the land, groundwater, riparian zones and river compartment (Figure 3b). Processes in each of these compartments can be empirical, mechanistic, or a hybrid approach.

2.2. Lumped river basin approaches

Generally, lumped approaches assume limited a priori knowledge of biogeochemical processes, but provide empirical estimates of the aggregate supply and loss of nutrients through the use of conventional stream monitoring data, which are often readily available in large watersheds with mixed land use. Anthropogenic N sources constitute the principle predictor variables in these models. Some of the models (e.g. Howarth et al., 1996) make use of literature rates of N processing (crop N fixation, N removal in crops) to estimate agricultural source inputs. Recent examples include regressions of N export from large watersheds on population density (Peierls et al., 1991), net anthropogenic sources (Howarth et al., 1996), atmospheric deposition, and measures of per capita energy consumption by humans (Meybeck, 1982). These models explain up to 80 percent of the spatial variation in N export. In contrast to complex deterministic models, these statistical methods have the advantage of being readily applied in large watersheds. Moreover, statistical approaches are capable of quantifying errors in model parameters and predictions.

Quasi-empirical models (Kroeze and Seitzinger, 1998;Caraco and Cole, 1999) of nitrate-N export from the largest rivers of the world were recently developed using empirical regression methods and literature-based rate coefficients. These models were developed for estimating N budgets at the continental scale and evaluating the effects of cultural sources on N export in some of the largest river basins of the world. These models indicate that the large variations in nitrate export among rivers worldwide can be largely explained by several major N sources and relatively simple descriptors of N removal on the landscape and in rivers. Nitrate export is modeled as a function of point sources, the diffuse inputs of fertilizer and atmospheric deposition, statistically calibrated runoff (discharge per unit drainage area) coefficients, and a literature-based in-stream loss coefficient. Model predictions of export were highly correlated (r-squared > 80%) with measured export for 35 of the largest rivers of the world. The stronger correlations of nitrate with population density than observed for total dissolved N has been suggested as an indication that nitrate measurements more readily display the effects of anthropogenic activities on river export in these rivers (Caraco and Cole, 1999).

Building on the models developed to estimate N or nitrate export, recently a range of quasi-empirical models was developed to model the various nutrient forms, i.e. dissolved inorganic and organic N, P and carbon, and particulate N, P and carbon, and sediments (Seitzinger et al., 2005). Revised models were more recently presented (Seitzinger et al., 2010;Mayorga et al., 2010). However, the accuracy of these global models has not been established for smaller watersheds (<25,000 km²).

Although hey have ben applied to gain insight into the magnitudes and sources of nutrients at regional-to-global scales, and to provide insight into historic and future

trajectories of water quality, these simple correlative models are limited in some respects. Firstly, all these methodologies work at the seasonal scale at best. Secondly, lumped river export models represent sources and sinks as homogeneously distributed in space, and do not separate terrestrial filters from in-stream loss processes. Thirdly, regression approaches have in common that they rarely account for nonlinear interactions between sources and loss processes, which makes them less useful for assessing the complex interactions induced by disturbance. Finally, lumped models may not be appropriate when systems may evolve from a source to a sink depending on the forcing and history(Turner et al., 2008;Cox et al., 2009).

2.3. Distributed models

Nutrients reach surface water through atmospheric deposition, soil leaching, groundwater transport, and surface runoff, and direct discharge of wastewater from human activities (Table 1). Each of these pathways requires a different modeling approach. Two distinct approaches are available to describe the transfer of nutrients through groundwater and via surface runoff from land to surface water, i.e. (i) Semi-distributed (hybrid) models that use simple export coefficients that lump several processes between the surface and the point where nutrients enter surface water, including withdrawal of nutrients in harvested agricultural crops, and biogeochemical processes in soils, groundwater and riparian zones; (ii) Distributed models where the water flow is modelled explicitly as a medium for transport and biogeochemical processing. These two approaches are briefly discussed below.

2.3.1. Hybrid models

The hybrid approaches expand on conventional regression methods by using a mechanistic model structure in correlating measured N flux in streams with spatial data on N sources, landscape characteristics (e.g. soil permeability, temperature), and stream properties (e.g. streamflow, travel time) (Haith and Shoemaker, 1987;Smith et al., 1997;Preston and Brakebill, 1999;Alexander et al., 2000;McBride et al., 2000). It has been shown that models can be improved by spatially referencing N sources and watershed attributes to surface water flow paths, defined according to a digital drainage network, and imposing a mass-balance constraints (Smith et al., 1997;Alexander et al., 2000;Alexander et al., 2001).

A common approach to estimating stream export is to apply the reported yields (mass of nutrient per unit drainage area) from small, homogeneous watersheds to the variety of land types contained within larger heterogeneous basins ('export coefficient' approach). Export coefficient modelling is a watershed or catchment scale, semidistributed approach which calculates mean annual total N (and total P) loading delivered to a water body (freshwater or marine) as the sum of the nutrient loads exported from each nutrient source in the catchment.

$$L = \sum_{i=1}^{n} E_i(A_i(I_i)) + p$$
(1)

where *L* is the nutrient loss, *E* is the export coefficient for source *i*, *A* is the area of catchment occupied by land use type i, or number of livestock type i, or of people, *l* is the input of nutrients to source *i*, and *p* is the input of nutrients from precipitation. For human wastes, the export coefficient reflects the use of phosphate rich detergents and dietary factors in the local population, and is adjusted to take account of any treatment of the wastes prior to discharge to a water body.

Riverstrahler (Billen and Garnier, 2000) allows for analyzing, apart from other disturbances, the impact of changing nutrient load and changing nutrient ratios, and potential saturation of retention processes such as denitrification and P retention by sediment. The RIVE Model is the biogeochemistry component of Riverstrahler. RIVE consists of 23 variables, including nutrients (nitrate and ammonium, phosphate, dissolved silica), dissolved and particulate organic matter (as two classes of biodegradability), two taxonomic groups of phytoplankton (diatoms and non-diatoms), one group of zooplankton dominating in rivers (rotifers), and bacteria. The models includes a detailed description of the phytoplankton and zooplankton dynamics, organic-matter bacterial degradation, nutrient chemistry and nutrient exchanges across the water-sediment interface.

Because the nutrient yields for given land types are highly variable, reflecting variations in climatic conditions, nutrient sources, and terrestrial and aquatic loss processes, these methods can produce imprecise and potentially biased estimates of export when extrapolated to other areas and larger scales (Beaulac and Reckhow, 1982;Frink, 1991).

To obtain reliable estimates of the export potential, this approach requires detailed information on the location of sources in watersheds and the landscape and climatic conditions. Refinement of the export coefficient method in the United Kingdom has produced more robust models capable of accurately simulating the nutrient export response to temporal changes in nutrient source inputs and land and waste management practices at the watershed and regional scales (Johnes, 1996;Johnes and Butterfield, 2002).

Export coefficients are expressed as a percentage of nutrient inputs (rather than mass per unit area as in conventional export methods), allowing the simulation of the effect of historical land-use changes and management in watersheds. In the U.K., where long-term source and monitoring information is, the model has been extensively validated and applied nationally to all watersheds in England and Wales. Other watershed models have been developed that represent a mixture of deterministic and export-coefficient approaches. A recent model of watershed export combined the deterministic budget approach with literature-based export coefficients for different land types and source inputs (Castro et al., 2003). This model produced mixed results in applications to the drainages of 34 major estuaries of the United States (Castro et al., 2003) with the method tending to overestimate the riverine export from agricultural watersheds.

Hybrid types of models described as 'loading functions' e.g. GWLF (Haith and Shoemaker, 1987) represents a compromise between the export coefficient method and the complexity offered by simulation models. These models have mechanistic water and sediment transport components (Howarth et al., 1991) with nutrient dynamics often described by simple empirical relations (Haith and Shoemaker, 1987). Model parameters may be obtained from the literature or statistically estimated if sufficient data are available. Applications have been made to eastern U.S. watersheds as large as several thousands of square kilometers (e.g.Lee et al., 2000;Howarth et al., 1991).

A recently developed hybrid approach SPARROW (SPAtially Referenced Regression On Watershed attributes) (Smith et al., 1997) expands on conventional regression methods by using a mechanistic model structure in correlating measured N flux in streams with spatial data on N sources, landscape characteristics (e.g. soil permeability, temperature), and stream properties (e.g. streamflow, water time of travel). The model, which separately estimates the quantities of N delivered to streams and the outlets of watersheds from point and diffuse sources, has been applied nationally in the United States (Smith et al., 1997) with separate studies of N flux in the Chesapeake Bay watershed (Preston and Brakebill, 1999), the Mississippi River and its tributaries (Alexander et al., 2000; Alexander et al., 2008), the watersheds of major U.S. estuaries (Alexander et al., 2001), and watersheds of New Zealand (McBride et al., 2000). By spatially referencing N sources and watershed attributes to surface water flow paths, defined according to a digital drainage network, and imposing a massbalance constraint, the model has been shown to improve the accuracy of predictions of stream export and the interpretability of model coefficients (Smith et al., 1997; Alexander et al., 2000; Alexander et al., 2001). Model estimates of in-stream nutrient loss and stream nutrient export from watersheds of various land-use types are generally consistent with literature rates (Jackson et al., 2003).

2.3.2. Fully distributed models

Distributed models include various landscape components, delivery processes and transfers, including surface runoff, transport to aquifers, transport through aquifers,

the delivery to riparian zones, and bypass flow directly to streams and rivers, and instream biogeochemical processes. Ideally, models include all these processes and transfers, but often landscape compartments distinguished in models are lumped (e.g. aquifers and riparian zones).

There is a range of models available. Some of the commonly used watershed-scale hydrologic and nonpoint-source pollution models are listed in Table 3. These models simulate all the components of a landscape, usually with the hydrology as the basis of calculations. Therefore, these models generally have a time scale of one day or less.

In a recent review, Borah and Bera (2003) compared a range of continuous and eventbased models for watershed-scale hydrology and nonpoint-source pollution. As the continuous models are most relevant for assessing the impacts of changing nutrient loading and dam construction, Table 3 provides a summary of some commonly used models.

A common aspect of these models is that they all require large amounts of data that may be difficult to collect in all countries. To avoid this data problem, some models allow the user to run the model at different levels of water quality complexity. Data availability is a key problem in developing the river biogeochemistry models. Except for a limited number of intensively studied systems, data on the input of nutrients and transfer to the adjacent or downstream compartments in a river basin are scarce. This means that often the sediment, C, and nutrient concentrations at one particular place in the system may be known, for example in the stream, and that the processing and retention in those landscape elements delivering to the stream are either poorly known or not known at all. The problem of missing information is not easily solved and will require targeted and appropriately-scaled data collection efforts coupled to model calibration or development.

Model	Temporal scale	Description	Reference
AnnAGNPS	Day or less	Annualized Agricultural nonpoint- source pollution model, annualized version of AGNPS for continuous simulation of hydrology, erosion, transport of nutrients, sediment and pesticides	Young et al. (1995); Bingner and Theurer (2013)
ANSWERS- continuous	Day or less	Areal Nonpoint Source Watershed Environment Response Simulation, expanded with elements from other models (GLEAMS, EPIC) for nutrient transport and inputs	Bouraoui et al. (2002)
Hydrological Simulation Program - Fortran	Hour	Continuous watershed simulation of water quantity and quality at any point in a watershed developed for US- Environmental Protection Agency (EPA).	USEPA (2011); Skahill (2004)
SWAT	Day	Soil Water Assessment Tool to predict the impact of management on water, sediment and agricultural chemical losses in large ungauged river basins	Arnold and Fohrer (2005)
MIKE-SHE	Variable, depending on numerical stability	Comprehensive, distributed, physically based model to simulate water, sediment and water quality parameters in 2-dimensional overland grids, one-dimensional channels, and 1-dimensional unsaturated and 3- dimensional saturated flow layers, with both continuous and single event simulation capabilities	Refsgaard and Storm (1995)
Riverstrahler	Reach, decade	Riverstrahler allows for analyzing, apart from other disturbances, the impact of changing nutrient load and changing nutrient ratios, and potential saturation of retention processes such as denitrification and P retention by sediment. While in-stream processes are modelled with a mechanistic	Garnier et al. (1995); Billen et al. (2000)

Table 3. Examples of models for watershed-scale distributed simulation of nutrient transport in river basins.

		model, the delivery processes are described with coefficients, lumping soils, aquifers and riparian zones	
INCA	Day	Integrated flow and nitrogen model for multiple source assessment in catchments	Wade et al. (2002); Whitehead et al. (1998b); Whitehead et al. (1998a)
IBIS-HYDRA	Variable, 1 day to 1 year	Land surface and terrestrial ecosystem model model IBIS with hydrology model HYDRA, used for modeling dissolved inorganic nitrogen fluxes and removal	Donner et al. (2002) and Donner et al. (2004)

2.3.3. Components of distributed models

Point sources of Nutrients

The export coefficient approach described above is also used for wastewater flows (e.g. Van Drecht et al., 2009; Johnes and Butterfield, 2002). For human wastes, the export coefficient reflects the use of phosphate rich detergents and dietary factors in the local population determining N and P excretion, and is adjusted to take account of any treatment of the wastes prior to discharge to a water body using the following equation:

$$E_{\rm sw}^{\rm N} = E_{\rm hum}^{\rm N} D(1 - R^{\rm N}) \tag{2}$$

where E_{sw}^{N} is the N emission to surface water (kg person⁻¹ yr⁻¹), E_{hum}^{N} is the human N emission (kg person⁻¹ yr⁻¹), *D* is the fraction of the total population that is connected to public sewerage systems (no dimension), and R^{N} is the overall removal of N through wastewater treatment (no dimension). For P a similar method is used that accounts for the contribution of P-based detergents.

Models to compute wastewater from inland aquaculture operations are available, for example a global model that uses country-scale fish and shellfish production data, characteristics of aquaculture production systems, such as major feed and nutrient inputs, feed conversion ratios, nutrient assimilation efficiencies for mollusks and digestibility for finfish, and nutrient removal by the harvest of mariculture product (Bouwman et al., 2013b;Bouwman et al., 2011). Spatial allocation within each country yet needs to be developed, for example based on maps (FAO, 2012b, a) or on the basis of allocation rules (depending on the species, allocation in lakes, reservoirs, or rivers, or spreading of the activity in agricultural land).

Non-point sources of nutrients (surface transport)

Turning to sediment production processes, there is large uncertainty regarding the relative contribution of different sediment production processes, i.e. hill slope sediment delivery, gully formation, mass movement (slumps) and channel bank erosion (Syvitski et al., 2005). Various approaches with different levels of complexity are generally used to model sediment delivery. Due to the large spatial variation in soil-physical and landscape characteristics, models describing particle detachment and transport require extensive field surveys or substantial calibration, and their application remains limited to hill slopes or smaller catchments (Table 5). Models describing soil loss at the plot and landscape scale need to be extended with re-sedimentation within the landscape, since sediment delivery to streams generally decreases along with travel distance. Predictions at the catchment scale are often based on a sediment delivery ratio (Table 5), i.e. the proportion of the detached sediment that is actually delivered to the channel system.

Lithology, hydrology, relief, climate (storm events), and land use direct these masswasting processes which influence the balance between bedrock, soil, and vegetation delivered to waterways and thus the transported amount of POM associated with minerals versus more labile POM not bound to mineral particles (e.g. the conceptual approach of Blair et al., 2004).

Mountains covering only a small fraction of the area of a river basin, can supply a large part of the material transported by the river, and thus regulate the ecological characteristics of river reaches and floodplains downstream (e.g. the Amazon, McClain and Naiman, 2008). A recent sediment delivery and transport model was developed for large river basins (Loos et al., 2009). The model approach is mechanistic and spatially explicit with a 3 by 3 km resolution and a monthly temporal resolution; it uses global data on terrain elevation, vegetation cover, land use, and soil types to calculate sediment detachment and transport to the stream system. An elaborate version of the model also calculates sediment production by bank erosion, deposition in reservoirs, and conveyance loss due to floodplain sedimentation along the drainage network. Simulation results for large rivers (Rhine, Mississippi, Mekong) range between a factor of 1.2 – 2 around observed values.

Non-point sources of nutrients (transport through the shallow subsurface)

The WEKU model developed by (Kunkel and Wendland, 1997b;Wendland et al., 2001) derives estimates of N surpluses from agriculture based on (Gömann et al., 2004) from total N inputs (biological N_2 fixation, N fertilizer, atmospheric N deposition and animal manure). The displacement of N surpluses into ground water is assumed to be equal to the ratio of ground water recharge to surface runoff. This long-term annual ratio is obtained from annual average precipitation for 1961-1990 using base-flow conditions that depend on area characteristics (e.g. geology, depth of ground water) according to Kunkel and Wendland (2002).

The soil N surpluses may be denitrified mainly in the root zone. Using the Michaelis-Menten approach, denitrification conditions in soil are combined with the N surplus calculated according to Gömann et al. (2004), and the residence times of the percolating water in the root zone calculated as a function of average field capacity and the water percolation rate.

Similarly, in the global approach of Van Drecht et al. (2003) the recharge flux of nitrate was calculated as the excess N available for leaching, based on estimates of N loading, crop uptake, ammonia volatilization, and soil processes, including soil denitrification. The partitioning of runoff into surface runoff and ground water recharge

was estimated by Klepper and Van Drecht (1998) on the basis of characteristics such as soil texture, thickness of aquifer, geology, slope and other factors.

Non-point sources of nutrients (transport through the shallow subsurface)Groundwater transport and retention

Groundwater N transport takes place over large distances and long time-scales. Due to long residence times, the groundwater system may act as a temporary sink for N. Groundwater is also a permanent sink for reactive N through the exothermic process of denitrification, the reduction of NO_3^- to nitrous oxide (N₂O) and molecular N (N₂). The ground water flowing into draining surface water is generally a mixture of water with varying residence times in the ground water system (Figure 1). The nitrate concentration in ground water depends on the historical year of water infiltration into the saturated zone and on the denitrification loss during its transport. Hence, for simulating the outflow concentration of nitrate from the ground water system, both the transport of water and residence time and the solute transport and denitrification in the ground water system need to be considered.

A range of models exist for describing water and nutrient fluxes in ground water at different scales. Various models have been developed to estimate NO₃⁻ transport and reactivity in groundwater at the basin scale (Meinardi et al., 1995;Ledoux et al., 2007;Kunkel and Wendland, 1997a;de Wit, 1999;Beaujouan et al., 2002;Birkinshaw and Ewen, 2000). Many of these basin-scale models require local spatial and temporal information on soil and aquifer properties, land use and climate.

The quantification of residence times with the WEKU model (Kunkel and Wendland, 1997b;Wendland et al., 2001) is in many cases restricted to unconsolidated rock aquifers, i.e. aquifers with laminar flow conditions. The residence time is calculated for complete flow paths from the point of recharge to that of discharge to surface water. The NO₃⁻ concentration within a grid cell in reduced aquifers is determined by the residence time of ground water in the grid, the denitrification constant (half-life) and the NO₃⁻ recharge. The estimation of the parameter values of denitrification kinetics was done separately for the ground water bearing formations occurring in the Ems and Rhine river basins. The aquifers in glaciofluviatile sands and moraine deposits in the Ems basin were classified as reduced, while consolidated schists and limestone areas in the Rhine basin were classified as oxidized (nonreducing) (Figure 2).

In the global approach of Van Drecht et al. (2003) the NO₃⁻ concentration of the outflow for shallow and deep ground water is calculated by combining the effects of residence time, historical fertilizer inputs and denitrification (half-life). Recently, Keuskamp et al. (2011) presented an improved version of the Van Drecht et al. (2003) model to assess NO₃⁻ transport and denitrification model for the European scale based

on the reaction progress of denitrification. The model accounts for the large spatial heterogeneity and is extended with simulation of N_2O production in groundwater. The model uses detailed physiogeographical information and a multi-scale approach. Small-scale hydrological processes like surface runoff and infiltration are modelled together with large scale processes such as regional groundwater flow. The shallow and deep systems have separated pathways and domains and are operating independently. The computation scale is 1 by 1 km in space and 1 year in time. Balancing water- and material flows is done at the catchment scale as defined in the Catchment Characterization and Modelling (CCM) database (JRC-IES, 2007).

A major problem of ground water denitrification models is their unability to simulate NO₃⁻ storage. For example, Gömann et al. (2004) and Behrendt et al. (2000) describe mean residence times, but do not explicitly calculate the storage component. Although the model of Van Drecht et al. (2003) is also static, the ground water storage component can be computed indirectly as the unaccounted for term in the mass balance (see Bouwman et al., 2013a). Similarly, in the dynamic POLFLOW model (De Wit et al., 2002) with a time integration of 5 years ground water storage is calculated for each grid cell from the mass balance.

Base flow of continental groundwater contributes freshwater to both river flow and to SGD under many climatic conditions and in various types of aquifers (Church, 1996;Moore, 1996). This freshwater SGD occurs in places where aquifers are connected hydraulically with the sea through permeable sediments or rocks and where the aquifer head is above sea level. Submarine groundwater flows into the coast at the interface between freshwater and seawater (the mixing zone) where the unconfined aquifer outcrops at the beach (Moore, 1996;Church, 1996). Box modeling has shown that coastal N input via SGD has the potential to significantly affect coastal zone nutrient cycling at the global scale (Slomp and Van Capellen, 2004). Typological approaches for estimating SGD have been suggested (Bokuniewicz et al., 2003), and recently a spatially explicit global approach was presented (Beusen et al., 2013).

Transport through riparian zones

In the approach of Billen and Garnier (2000), a transfer coefficient is used to express the fraction of NO_3^- contained in ground water entering the surface water through riparian areas. Measurements of NO_3^- concentrations in aquifers are used to compute the N concentration in (sub)surface and base (deep ground water) flow. The value of the transfer coefficient is obtained by adjusting simulated values with observed NO_3^- concentrations.

A conceptual model was developed for describing subsurface NO_3^- transport and removal in riparian areas (Vidon and Hill, 2006, 2004b, a;Vidon and Hill, 2004c). In this

model topography is an approximate predictor of water table gradient influencing fluxes entering the riparian zones and their flow direction. Moderate to steep slope are likely to produce greater fluxes than gentle slopes with similar depth of permeable sediments (Vidon and Hill, 2004a). The NO_3^- removal is linked with topography and depth to a confining layer at the upland-riparian zone margin, and is affected by depth and texture of permeable sediments in the riparian zone (Vidon and Hill, 2004b).

Modeling processes in riparian areas requires spatial information on where these zones are located, including their hydrogeological conditions. For example, (Vidon and Hill, 2006) notes that it is important to determine the extent to which spatially explicit data can be used to identify the key landscape variables for the above models. Topography can be determined using maps and Digital Elevation Models (DEMs) at various resolutions and scales. However, even maps at the 1:10000 to 1:20000 scale to determine the topography of riparian areas and adjacent upland perimeter slope may have limitations. At such scales the contour interval is 5 m. This will cause limitations for riparian areas with less than 5 m of difference in elevation between the upland and riparian area.

A recent first attempt to model the delivery of nutrients to riparian zones by aquifers, by-pass flow, and denitrification within the riparian soils, was presented by Bouwman et al. (2013a). Since it is impossible to know the location of riparian areas at the 0.5 by 0.5 degree resolution used in this study, and with all the simplifications in the simulation of the N inflow to riparian areas and denitrification, the model results are only a first attempt to quantify riparian denitrification and N₂O emissions. The model results are strongly sensitive to total water flow, soil N budget, and N inflow from shallow aquifers, suggesting a need for additional work to constrain these elements.

In-stream processes and retention

In-stream processes are described with approaches ranging from simple export coefficients (e.g. Van Drecht et al., 2003) or relationships between the hydraulic load of rivers (runoff divided by catchment area (e.g. Behrendt and Opitz, 1999), to hybrid approaches, spiraling concept, and process-based models. The latter three types will be discussed in more detail.

The term nutrient spiraling (Table 1) was coined to describe the cycling of nutrients as they are assimilated from the water column into benthic biomass, temporarily retained, and mineralized back into the water column (Webster, 1975). Spiraling is a lumped steady-state model concept where suspended and solution components both are transported and interact with static components such as sediment. The fate of a molecule in a stream is described as a spiral length, which is the average distance a molecule travels to complete a cycle from the dissolved inorganic state in the water

column, to a streambed compartment, and eventually back to dissolved inorganic form in the water column (Stream_Solute_Workshop, 1990). Using this concept, Ensign and Doyle (2006) found that within-stream networks, larger streams and headwaters are equally important in buffering downstream ecosystems (lakes, estuaries, and oceans) from nutrient pollution.

Examples of mechanistic models include HSPF (USEPA, 2011;Skahill, 2004), CE-QUAL2E (Brown and Barnwell Jr., 1987), NUSWALITE (Siderius et al., 2005), and RIVE (Sferratore et al., 2005;Garnier et al., 2000;Billen and Garnier, 2000). A few of these models will be discussed with more detail.

QUAL2E includes two basic processes: (i) net sedimentation of particles containing nutrients, and (ii) algal growth and settling. N cycling consists of a stepwise transformation from organic N to ammonia, then to nitrite, and finally to nitrate; however, denitrification is not included. Organic N may also be removed from the stream by settling. The P cycle is similar to the N cycle. The death of algae transforms algal P into organic P. Organic P is mineralized to a soluble P fraction that is available for uptake by algae. Organic P may also be removed from the water column by settling. No P sorption and desorption processes or dependencies on oxic/anoxic conditions are considered. Settled particles during low flow conditions. Nutrient removal in standing water bodies is based on a completely mixed, steady-state, mass balance approach that uses a constant settling rate and ignores any transformations between different forms of N and P. The model enables the user to specify nutrient settling rates for each water body or wetland in the catchment, and this has led some to suggest that this model is over-determined.

The NUSWALITE model comprises four main processes: (i) uptake and release of nutrients by plant biomass, (ii) decomposition of organic P and N to mineral fractions, (iii) adsorption/desorption of P on mineral particles, and (iv) loss of N by denitrification and the loss of P by sedimentation. Two fractions of plant biomass are considered – a drifting fraction that can be transported with water flow (algae, floating macrophytes) and an immovable fraction having roots in the sediment. Growth is influenced by radiation, turbidity, temperature, and nutrient status. Growth of living biomass generates a nutrient uptake demand. The nutrient content of the living biomass is considered as a constant fraction of the biomass dry weight. The oxygen cycle is not explicitly described. The N and P cycles consist of two pools, a mineral and organic, and the interaction between water and sediment is described by an equilibrium equation. (Siderius et al., 2005).

MIKE-11 is an advanced dynamic 1-D model of flow and water quality in streams. It can simulate the hydrodynamics of branched and looped rivers and estuaries, and can be used to simulate solute transport and transformations in complex river systems (e.g. Zhu et al., 2008). Even more than the above models QUAL2E and NUSWALITE, MIKE-11 requires large amounts of data that may be difficult to collect. To avoid this data problem, MIKE-11 allows the user to run this model at different levels of water quality complexity.

Similarly, the RIVE model (Billen and Garnier, 2000) explicitly calculates in-stream nutrient retention within the drainage network as the result of biological (algal uptake, denitrification) and physical-chemical processes (adsorption, sedimentation). Like MIKE-11, RIVE is a 1-D model, describing the processes within a river reach or strahler order.

In summary, most mechanistic models describe algal growth, death and settling, and decomposition and mineralization to organic compounds, adsorption/desorption of particulate P on mineral particles, and denitrification. These models move towards an integration of ecology with hydromorphology (Vaughan et al., 2009) and geomorphology (Thorp et al., 2006) by linking ecology, biogeochemistry and the physical habitat. The complexity of mechanistic models often creates intensive data and calibration requirements, which generally limits their application at large scales (large watersheds, or greater). It is also important to recognize that these so-called mechanistic models often have empirical components.

3. Coastal marine ecosystems

3.1. Introduction

	Carbon	Nitrogen	Phosphorus	Silica
River export	DIC, DOC,PC	DIN, DON, PN	DIP, DOP, PP	DSi, ASi
Wastewater	DIC, DOC, PC	DIN, DON, PN	DIP, DOP, PP	
Subterranean groundwater discharge		DIN, DIP		DSi
Atmospheric deposition	DIC	DIN		
Aquaculture	DIC, DOC,PC	DIN, DON, PN	DIP, DOP, PP	
Organic detritus remineralization	DIC, DOC, PC	DIN, DON	DIP, DOP	DSi

Table 2. Sources of sediment, C, N, P, and Si in coastal marine ecosystems

Rivers transport nutrients to downstream ecosystems where they can affect lake and coastal receiving waters. When considering the inflow of nutrients to coastal seas, various sources can be distinguished, each with its own nutrient signature (Table 2). Also, the importance of these nutrient sources is variable, for example the river export may be dominant in some coastal marine ecosystems, while direct wastewater discharge to coastal marine ecosystems may be important near large cities close to the coast.

When nitrogen (N) and phosphorus (P) are discharged in excess over silicon (Si) with respect to the requirements of diatoms, these will be limited and nondiatoms, often undesirable algal species, will develop instead (Billen and Garnier, 1997, 2007;Conley, 1997;Officer and Ryther, 1980;Turner and Rabalais, 1994;Rabalais et al., 2002). There are different approaches to assess eutrophication of coastal ecosystems, ranging from simple indicators to complex ecosystem models. These different approaches will be discussed in more detail below.

3.2. Indicator approaches

Sometimes, when an assessment of ecosystem status is desired, it is easier to use an index of water quality of ecosystem status than to run a model. Water quality indices (WQIs) are formulated to give a single value to the water quality of a source on the basis of various indicators. WQIs have been widely used in the past three decades, but the concept was first introduced more than 150 years ago, in 1848, in Germany where the presence of absence of certain organisms was used as an indicator of the water quality. Since then different countries have developed and applied different classification systems for water quality based on the amount of pollution or the presence of absence of specific organisms.

The first modern WQI was presented by Horton (1965), who selected the most commonly measured variables for his index: dissolved oxygen, pH, coliform bacteria, specific conductance (as a proxy for total dissolved solids and carbon chloroform extract), alkalinity, and chloride. Wastewater treatment (the fraction of human population served) was used as an abatement indicator.

Since then, a series of WQI approaches has been developed, specific to the local or regional situation within a country, the purpose (monitoring or abatement), or the type of water (surface water or groundwater, freshwater or coastal water) (Abbasi and Abbasi, 2012).

In the Water Framework Directive (WFD) of the European Union (EC, 2000), a method is developed for the definition of water quality. The ecological quality of surface water according to the WFD consists of several elements including biological quality, general physico-chemical conditions and the concentration of specific pollutants. The water quality of N and P are two elements of the general physico-chemical conditions (EC, 2000).

Recently, an Indicator of Coastal Eutrophication Potential (ICEP) was proposed (Billen and Garnier, 2007). ICEP is calculated on the basis of riverine N, P and Si deliveries, allowing to determine the possible problems resulting from a new production of nonsiliceous algae sustained by external inputs of N and/or P brought in excess over silica, e.g. in limiting conditions for the diatom growth. Compared to N:P ratios which are often considered (for example, Glibert et al. (2008)), the ICEP adds information about the role of Si in determining potential eutrophication impacts of changing element stoichiometry.

The ICEP represents the potential impact of the riverine deliveries to the coastal zone, and does not take into account the particular morphological, climatic and hydrological conditions that locally determine the response of the marine algae in the receiving coastal zone (Nixon, 2009;Rabouille et al., 2008).

3.3. Model approaches

3.3.1. General

A good model should describe the available data, represent the system's dynamics and produce emergent properties. Too much model complexity leads to uncertainty and problems in interpretation of the model dynamics. In contrast, too little complexity means that the models cannot reproduce the system behaviour in a realistic manner (Raick et al., 2006). There is a trade-off between complexity and generality in models.

Marine plant functional types are defined largely by the geochemical transformations made by the group of organisms, for instance calcifiers, silicifiers, dimethyl-sulphide producers, pico heterotrophs, etc. In marine ecosystems, widely different classes of organisms often fill each of these descriptions, and it is not clear whether a useful classification can be made without going to considerably greater detail. A fundamental problem is therefore, to find the appropriate level of complexity for ecosystem models with skills to predict biogeochemical processes.

The type of ecosystem model employed also depends on the objectives of the study. Complex models may be useful to improve the understanding of the system's dynamics. Very few studies of the effects of model complexity have been made (Allen et al., 2010). One of such studies concluded that a certain degree of sophistication in the formulation of some biogeochemical processes is required to simulate realistic behaviours. For example, the phytoplankton competition, the potential carbon or N limitation of the zooplankton ingestion, and the model trophic closure. Raick et al. (2006) concluded that in general the best-

seas.		
Туре	Application	Example
0-D	Global coastal types	Laruelle (2009)
1-D	Westerschelde	Soetaert and Herman (1995)
	Various estuaries in USA	Evans and Scavia (2013)
	Various rivers and estuaries	MIKE (Refsgaard and Storm,
		1995;Zhu et al., 2008;Arndt et
		al., 2011); MIKE 21 Warren and
		Bach (1992)
	Scheldt	CONTRASTE (Regnier et al.,
		1997)
	North Sea	Baretta et al. (1995)
	Belgian coast	Gypens et al. (2008)
		MIRO (Lancelot et al.,
		2005;Lancelot et al., 2007)
	Black sea	Grégoire et al. (2008)
	Veerse Meer; North Sea; Sea of Marmara; Venice Lagoon;	Blauw et al. (2009)

Table 3. Examples of models for describing biogeochemistry in estuaries and coastal seas

performing model is a 9 state-variable model that has the functional group diversity removed, but includes the bacterial loop and unbalanced algal growth.

The recently developed global biogeochemical box model (Laruelle, 2009) using a spatially-explicit coastal typology (including deltas, tidal systems, lagoons and fjords) (Dürr et al., 2011) is such a zero-dimensional model. Each coastal box comprises a simple representation of the N and P biogeochemical cycles including explicit pools of dissolved and particulate matter for both nutrients, primary production and uptake by phytoplankton. The parameterization of the transformation rates connecting the various reservoirs and water residence time within each box depends on the coastal type.

Fluxes are formulated in 1-D models as directed movement (advection-like fluxes) or to random movement (diffusion-like or dispersive fluxes). For water bodies like estuaries, the 1-D advection-dispersion reaction equation can be used to describe transport and reaction along the length axis, provided that vertical and lateral gradients are negligible. As the cross-sectional surface along the length axis is variable, it is common to use flow-rates rather than velocities. An example is the model of Soetaert and Herman (1995) that couples pelagic and benthic processes in one model for the Westerschelde in The Netherlands. For lakes that can be considered to be horizontally homogeneous, it is more common to model processes as a function of water depth. One-dimensional models can be used to model processes in two or three-dimensional (3-D) domains, depending on the assumptions on how concentrations will change in space. An important requirement of spatially explicit models is that the boundary conditions need to be specified. Hence, if the spatial domain is bounded, what happens with substances at these boundaries. In contrast, the spatial domain may extend to infinity. In a 1-D estuarine model, the upstream boundary is generally the river, and the downstream boundary is the sea. Transport models can only be solved if it is specified what happens at these physical boundaries.

The use of complex ecosystem models containing sufficient detail has become possible and attractive thanks to the progress in modern computing power, next to progress in ecosystem theory. About two decades ago, the simple nutrientsphytoplankton-zooplankton-detritus (NPZD) models were embedded in three dimensional general circulation models providing the physics of the system (e.g. Sarmiento et al., 1993). The current trend in marine ecosystem modelling is to include complex models in general circulation models (Gregg et al., 2003;Le Quéré et al., 2005;Cotrim da Cunha et al., 2007).

Sometimes it is useful to subdivide the model in a number of distinct zones, each having a unique set of equations. For example, in sediment models oxic, suboxic and anoxic zones can be distinguished, each having distinct metabolic pathways. In these multi-layered models, the boundary conditions at the interface between the layers need to be specified. Commonly, the boundary conditions are based on continuity of concentration or continuity of flux.

3.3.2. Modelling nutrient impacts on the development of HABs

For describing algal bloom development, models need to have an explanatory predictive capacity for individual species responding to changing conditions and changing nutrient availability. Process models often require the use of functional type approaches. There are different levels of complexity. At the most basic level processes are represented by single nutrient based nutrient-phytoplankton-zooplankton (NPZ) models (Fasham et al., 1990). Such approaches may not be adequate to describe emergent properties (new proprties arising when a system exceeds a certain level of complexity) because of interconnectivity in ecosystems. Three groups of models will be briefly discussed, i.e. ecophysiology, organismal life cycles and benthic pelagic coupling.

One approach to modelling HAB physiology within a complex ecosystem is to represent the HAB species with a detailed model, and to use aggregate models for other groups. This approach has been coined a rhomboid strategy (De Young et al., 2004). Detailed descriptions of non-HAB species may be warranted, e.g. for

descriptions of prey growth dynamics in support of mixotrophic HABs, of specific predators or of indicator species that may not have a close association with the HAB.

A close coupling between organismal life cycle stages is likely in systems impacted by eutrophication. This is important for both HAB species and other components of the ecosystem. Eutrophication can stimulate the formation of temporary or long-term resting stage (e.g. encystement, and excystment) (Steidinger and Garcés, 2006). Germination and subesequent migration of organisms is a route for the transfer of particulate nutrients from sediments to the water column, which is important for those species in the system that interact with HAB species. These processes affect the removal and transformations of nutrients for HAB development, as well as predator-prey interactions. Linkage between these processes, climate and weather events, and other conditions are important.

Benthic-pelagic coupling of biogeochemical and trophic interactions are important, because most HABs are associated with growth and activity and advection within the water column, typically associated with systems such as shallow coastal areas, lakes, estuaries. Beyond the empirical description of benthic biogeochemical processes, there are series of trophic and life-cycle interactions such as bioturbation and also abiotic events that may promote fluxes of nutrients in and out of the benthic zone.

Many of the above issues have been included in existing models for individual HAB species (Ishizaka et al., 2006;Moita et al., 2003). Fuzzy logic models were used to develop the Harmful Algal Blooms Expert System (HABES) model to predict the conditions favouring blooms and harmful effects from seven HAB species from various European waters (Blauw et al., 2006). Numerical models that include feedbacks are needed to explore ecosystem response beyond the current climate conditions. Follows et al. (Follows et al., 2007) and later work (Dutkiewicz et al., 2009) provide a conceptual framework which can be the basis of models describing emergent ecosystems combining generic cells with food web interactions, but requires modifications to be useful for HAB predictions.

3.3.3. Modelling impact of nutrient on the development of hypoxia

Several types of models, ranging from simple to complex ones, have been very useful to improve our understanding of the diverse aspects of hypoxia (Peña et al., 2010). Models have been used to synthesize the observations, understand ecosystem functioning and to predict hypoxia events or situations (Zhang et al., 2010).

In many regions of the world, where high primary production coincides with low degrees of water column mixing, eutrophication leads to recurrent hypoxia or anoxia. Essential for the modeling of hypoxia development is benthic-pelagic coupling, which refers to the dependence of processes in sediments on those in the water column. Below the euphotic zone, the benthic biogeochemical processes are essentially pelagically driven, as they are fuelled by deposition of material (e.g. organic matter) from the water column are affected by the overlying bottom water. In response to deposition events, sediments transform the deposited material (e.g. degradation, dissolution) and return transformation products (nutrients) to the water column. Part of those products becomes available for bacterial and phytoplankton production that ultimately may sink to the seafloor to fuel the benthic communities again (Soetaert et al., 2000).

Such models could also serve as a basis for setting goals for nutrient reduction

or for predicting effects of global change. By increasing the water temperature and river runoff, global change is likely to prolong stratification, reduce mixing, increase primary production, and decrease the solubility of oxygen, with important consequences on the extent of anoxic zones and benthic respiration. How this will affect the susceptibility of the system to eutrophication or the resilience to oligotrophication remains unclear. However, models can be used to assess possible impacts of such changes on hypoxia development (Soetaert and Middelburg, 2009).

Generic diagenetic models, i.e. benthic biogeochemical models, can accurately simulate sediment –water exchange fluxes. There are no limitations to couple these models to water column biogeochemical models, and during the last decades a number of such coupled models have been used, which have been arranged into a hierarchical set of levels of complexity by Soetaert et al. (2000). Highest complexity is achieved by so-called diagenetic models that explicitly describe the spatial segmentation of the sediment into biogeochemical zones (e.g. Soetaert et al. (1996) or Wijsman et al. (2002)). First approximation consists of ignoring the vertical extent and focusing on depth-integrated dynamic models (e.g. Middelburg et al. (1996) or Soetaert et al. (2000).

A next simplification is to ignore temporary storage of particulates. As soon as deposited, particulate matter are converted to dissolved form in this type of model. Further simplification by imposing a measured flux or bottom-water concentration may violate the principle of mass conservation, and are not appropriate for simulation of hypoxia (Soetaert et al., 2000).

A number of the models used to simulate biogeochemistry in rivers and estuaries, can also be employed to simulate hypoxic or anoxic events, for example MIKE (Refsgaard and Storm, 1995;Zhu et al., 2008;Arndt et al., 2011); MIKE 21 (Warren and Bach, 1992). Several recent model approached have been used to study, for example, sedimentary phosphorus dynamics (Reed et al., 2011), effects of oxygen depletion on diagenetic processes (Katsev et al., 2007;Ritter and Montagna, 1999), oxygen dynamics (Peña et al., 2010;Benoit et al., 2006) or biogeochemical processes in general (Pastor et al., 2011). An interesting development is the integration of biological and physical processes for generic application to ecosystems (Blauw et al., 2009). This model has been applied in a series of scenario studies, basic to several policy and management decisions and infrastructural developments (Zhang et al., 2010).

3.3.4. Modeling impacts of nutrients on fisheries production

A link between coastal N loading, primary production, and fisheries production has been recognized for several decades (Nixon, 1988), but it is only recently that quantitative models linking N loading to fisheries production have been proposed. These models range from empirical and correlative (e.g. Breitburg, 2002) to models that maintain balanced mass and energy budgets. One important, outstanding question is whether N inputs and associated hypoxia result in fisheries declines at high rates of N loading. There is some indication that coastal hypoxia can negatively affect fisheries (Breitburg, 2002), but increased fishing effort`, altered fishing patterns`, or fish movements may compensate for hypoxia-induced stress on fisheries`, making the signal of hypoxia on fisheries difficult to detect (Breitburg et al.;Breitburg et al., 2009a).

In addition to the development of empirical relationships between nutrient loading and fish production, there have also been several recent efforts to develop "end-to-end" models that examine the cumulative impact of multiple anthropogenic pressures (including, but not limited to) nutrient enrichment on marine ecosystems and fisheries. Examples of these kinds of models include Ecopath with Ecosim (EwE) (Christensen and Walters, 2004), OSMOSE (Shin and Cury, 2001, 2004) and Atlantis (Fulton et al., 2005). Increasingly, these models are closing nutrient cycles and including long-term climate forcing and environmental variability. Examples of these models include OSMOSE (Shin and Cury, 2001, 2004), Atlantis (Fulton et al., 2005), InVitro (McDonald et al., 2005), SEAPODYM (Loukos et al., 2003;Lehodey et al., 2003;Lehodey et al., 2008), and APECOSM (Maury, 2010). These models are typically applied in a single, local or regional setting. There are several current efforts to understand and quantify the relationship between N loading, hypoxia, and fisheries at the global scale. These include Hypoxia, Fisheries, and Nitrogen (HypoFiN), a LOICZ-supported effort to link measurements of N loading to end-to-end models of fishery production and ecosystem function and Nutrient-related Coastal Integrated Research Programme (N-CIRP), a UNESCO-funded effort to link coastal nutrient loading models to coastal impacts (this project).

Challenges currently facing the end-to-end modeling field include an increasing need for long simulation periods, non-stationarity resulting from a shifting climate, biodiversity and evolution, accurate representation of human causes of and responses to ecosystem and health stresses, and managing the inevitable uncertainty associated with complex, multi-faceted modeling efforts (Fulton, 2010).

Literature

Abbasi, T., and Abbasi, S. A.: Water quality indices, Elsevier, Oxford, 2012.

- Alexander, R. B., Smith, R. A., and Schwarz, G. E.: Effect of stream channel size on the delivery of nitrogen to the gulf of mexico, Nature, 403, 758-761, 2000.
- Alexander, R. B., Smith, R. A., Schwarz , G. E., Preston, S. D., Brakebill, J. W., Srinivasan, R., and Pacheco, P. A.: Atmospheric nitrogen flux from the watersheds of major estuaries of the united states: An application of the sparrow watershed model., in: Nitrogen loading in coastal water bodies: An atmospheric perspective.
 Monograph 57, edited by: Valigura, R., Alexander, R., Castro, M., Meyers, T., Paerl, H., Stacey, P., and Turner, R. E., American Geophysical Union, 119–170, 2001.
- Alexander, R. B., Smith, R. A., Schwarz, G. E., Boyer, E. W., Nolan, J. V., and Brakebill, J.
 W.: Differences in phosphorus and nitrogen delivery to the gulf of mexico from the mississippi river basin, Environmental Science and Technology, 42, 822-830, 2008.
- Allen, J. I., Aiken, J., Anderson, T. R., Buitenhuis, E., Cornell, S., Geider, R. J., Haines, K., Hirata, T., Holt, J., Le Quéré, C., Hardman-Mountford, N., Ross, O. N., Sinha, B., and While, J.: Marine ecosystem models for earth systems applications: The marquest experience, Journal of Marine Systems, 81, 19-33, 2010.
- Anderson, D., M., Gilbert, P. M., and Burkholder, J. M.: Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences, Estuaries, 25, 704-726, 2002.
- Arndt, S., Lacroix, G., Gypens, N., Regnier, P., and Lancelot, C.: Nutrient dynamics and phytoplankton development along an estuary-coastal zone continuum: A model study, Journal of Marine Systems, 84, 49-66, 2011.
- Arnold, J. G., and Fohrer, N.: Swat2000: Current capabilities and research opportunities in applied watershed modelling, Hydrological Processes, 19, 563-572, 2005.
- Backer, L. C., and McGillicuddy Jr., D. J.: Harmful algal blooms at the interface between coastal oceanography and human health, Oceanography, 19, 94-106, 2006.
- Baretta, J. W., Ebenhoh, W., and Ruardij, P.: The european regional seas ecosystem model a complex marine ecosystem model, Netherlands Jouranl of Sea Research, 33, 233-246, 1995.
- Beaujouan, V., Durand, P., Ruiz, L., Aurousseau, P., and Cotteret, G.: A hydrological model dedicated to topography-based simulation of nitrogen transfer and transformation: Rationale and application to the geomorphology-denitrification

relationship, Hydrological Processes, 16, 493-507 (doi: 410.1002/hyp.1327), 2002.

- Beaulac, M. N., and Reckhow, K. H.: Examination of land use nutrient export relationships, Water Resources Bulletin, 18, 1013-1024, 1982.
- Behrendt, H., and Opitz, D.: Retention of nutrients in river systems: Dependence on specific runoff and hydraulic load, Hydrobiologia, 410, 111-122, 1999.
- Behrendt, H., Huber, P., Kornmilch, M., Opitz, D., Schmoll, O., Scholz, G., and Ueby, R.: Nutrient emissions into river basins of germany, UBA, BerlinUBA Texte 23/2000, 261 pp., 2000.
- Benoit, P., Gratton, Y., and Mucci, A.: Modeling of dissolved oxygen levels in the bottom waters of the lower st. Lawrence estuary: Coupling of benthic and pelagic processes, Marine Chemistry, 102, 13-32, 2006.
- Beusen, A. H. W., Slomp, C. P., and Bouwman, A. F.: Global land–ocean linkage: Direct inputs of nitrogen to coastal waters via submarine groundwater discharge, Environmental Research Letters, 8, 034035, 10.1088/1748-9326/8/3/034035

2013.

- Billen, G., and Garnier, J.: The phison river plume: Coastal eutrophication in response to changes in land use and water management in the watershed, Aquatic Microbial Ecology, 13, 3-17, 1997.
- Billen, G., and Garnier, J.: Nitrogen transfers through the seine drainage network: A budget based on the application of the 'riverstrahler' model, Hydrobiologia, 410, 139-150, 2000.
- Billen, G., and Garnier, J.: River basin nutrient delivery to the coastal sea: Assessing its potential to sustain new production of non-siliceous algae, Marine Chemistry, 106, 148-160, doi:110.1016.j.marchem.2006.1012.1017, 2007.
- Bingner, R. L., and Theurer, F. D.: Annagnps pollutant loading model (<u>http://www.Ars.Usda.Gov/research/docs.Htm?Docid=5222</u>). Accessed 13 august 2013, 2013.
- Birkinshaw, S. J., and Ewen, J.: Nitrogen transformation component for shetran catchment nitrate transport modelling, Journal of Hydrology, 230, 1-17, 2000.
- Blair, N. E., Leithold, E. L., and Aller, R. C.: From bedrock to burial: The evolution of particulate organic carbon across coupled watershed-continental margin systems, Marine Chemistry, 92, 141-156, 2004.
- Blauw, A., Los, H., Bokhorst, M., and Erftemeijer, P.: Gem: A generic ecological model for estuaries and coastal waters, Hydrobiologia, 618, 175-198, 2009.
- Blauw, A. N., Anderson, P., Estrada, M., Johansen, M., Laanemets, J., Peperzak, L., Purdie, D., Raine, R., and Vantera, E.: The use of fuzzy logic for data analysis

and modelling of european harmful algal blooms: Results of the habes project, African Journal of Marine Science, 28, 365-369, 2006.

- Bokuniewicz, H., Buddemeier, R., Maxwell, B., and Smith, C.: The typological approach to submarine groundwater discharge (sgd), Biogeochemistry, 66, 145-158, 2003.
- Borah, D. K., and Bera, M.: Watershed-scale hydrologic and nonpoint-source pollution models: Review of mathematical bases, Transactions of the American Society of Agricultural Engineers, 46, 1553-1566, 2003.
- Bouraoui, F., Braud, I., and Dilaha, T. A.: Answers. A nonpoint-source pollution model for water, sediment, and nutrient losses, in: Mathematical models of small watershed hydrology and applications, edited by: Singh, V. P., and Frevert, D. K., Water Resources Publications, Highlands Ranch, Colorado, 833-882, 2002.
- Bouwman, A. F., Pawłowski, M., Liu, C., Beusen, A. H. W., Shumway, S. E., Glibert, P. M., and Overbeek, C. C.: Global hindcasts and future projections of coastal nitrogen and phosphorus loads due to shellfish and seaweed aquaculture, Reviews in Fisheries Science, 19, 331-357, 10.1080/10641262.2011.603849, 2011.
- Bouwman, A. F., Beusen, A. H. W., Griffioen, J., Van Groenigen, J. W., Hefting, M. M., Oenema, O., Van Puijenbroek, P. J. T. M., Seitzinger, S., Slomp, C. P., and Stehfest, E.: Global trends and uncertainties in terrestrial denitrification and n20 emissions, Philosophical Transactions of the Royal Society B: Biological Sciences, 368, 10.1098/rstb.2013.0112, 2013a.
- Bouwman, A. F., Beusen, A. H. W., Overbeek, C. C., Bureau, D. P., Pawlowski, M., and Glibert, P. M.: Hindcasts and future projections of global inland and coastal nitrogen and phosphorus loads due to finfish aquaculture, Reviews in Fisheries Science, 21, 112-156, 10.1080/10641262.2013.790340, 2013b.
- Breitburg, D.: Effects of hypoxia, and the balance between hypoxia and enrichment, on coastal fishes and fisheries, Estuaries, 25, 767-781, 2002.
- Breitburg, D. L., Craig, J. K., Fulford, R. S., Rose, K. A., Boynton, W. R., Brady, D. C., Ciotti,
 B. J., Diaz, R. J., Friedland, K. D., Hagy Iii, J. D., Hart, D. R., Hines, A. H., Houde, E.
 D., Kolesar, S. E., Nixon, S. W., Rice, J. A., Secor, D. H., and Targett, T. E.:
 Nutrient enrichment and fisheries exploitation: Interactive effects on estuarine living resources and their management, Hydrobiologia, 629, 31-47, 2009a.
- Breitburg, D. L., Hondorp, D. W., Davias, L. A., and Diaz, R. J.: Hypoxia, nitrogen, and fisheries: Integrating effects across local and global landscapes, Annual Review of Marine Science, 1, 329-349, 2009b.
- Brown, L. C., and Barnwell Jr., T. O.: The enhanced water quality models qual2e and qual2e-uncas documentation and user manual, US Environmental Protection Agency (EPA), Athens, GAEPA Document EPA/600/3-87/007, 1987.

- Caraco, N. F., and Cole, J.: Regional-scale export of c, n, p, and sediment: What river data tell us about key controlling variables, in: Integrating hydrology, ecosystem dynamics, and biogeochemistry in complex landscapes, edited by: Tenhunen, J. D., and kabat, P., Wiley and Sons, New York, 239-253, 1999.
- Castro, M. S., Driscoll, C. T., Jordans, T. E., Reay, W. G., and Boynton, W. R.: Sources of nitrogen to estuaries in the united states, Estuaries, 26, 803-814, 2003.
- Christensen, V., and Walters, C. J.: Trade-offs in ecosystem-scale optimization of fisheries management policies, Bulletin of Marine Science, 74, 549-562, 2004.
- Church, T. M.: An underground route for the water cycle, Nature, 380, 579-580, 1996.
- Conley, D. J.: Riverine contribution of biogenic silica to the oceanic silica budget, Limnology and Oceanography, 42, 774-777, 1997.
- Cotrim da Cunha, L., E. T. Buitenhuis, E. T., Le Quéré, C., Giraud, X., and Ludwig, W.: Potential impact of changes in river nutrient supply on global ocean biogeochemistry, Global Biogeochemical Cycles, 21, GB4007, doi:10.1029/2006GB002718, 2007.
- Cox, B. A.: A review of currently available in-stream water-quality models and their applicability for simulating dissolved oxygen in lowland rivers, Science of the Total Environment, 314-316, 335-377, 10.1016/S0048-9697(03)00063-9, 2003.
- Cox, T. J. S., Maris, T., Soetaert, K., Conley, D. J., Van Damme, S., Meire, P., Middelburg, J. J., Vos, M., and Struyf, E.: A macro-tidal freshwater ecosystem recovering from hypereutrophication: The schelde case study, Biogeosciences, 6, 2935-2948, doi:2910.5194/bg-2936-2935-2009, 2009.
- de Wit, M.: Nutrient fluxes in the rhine and elbe basins, Faculteit Ruimtelijke Wetenschappen, Utrecht University, Utrecht, 163 pp. pp., 1999.
- De Wit, M., Behrendt, H., Bendoricchio, G., Bleuten, W., and Van Gaans, P.: The contribution of agriculture to nutrient pollution in three european rivers, with reference to the european nitrates directive, European Water Management Online, EWA 2002. Hennef, Germany/Brussels, Belgium, 2002.
- De Young, B., Heath, M., Werner, F., Chai, F., Megrey, B., and Monfray, P.: Challenges of modeling ocean basin ecosystems, Science, 304, 1463-1466, 2004.
- Donner, S. D., Coe, C. T., Lenters, J. D., and Twine, T. E.: Modeling the impact of hydrological changes on nitrate transport in the mississippi river basin from 1955 to 1994, Global Biogeochemical Cycles, 16, 101029, 2002.
- Donner, S. D., Kucharik, C. J., and Oppenheimer, M.: The influence of climate on instream removal of nitrogen, Geophysical Research Letters, 31, L20509 20501-20505, 10.1029/2004gl020477

- 10.1029/2000JD000309; Donner, S.D., Kucharik, C.J., Evaluating the impacts of land management and climate variability on crop production and nitrate export across the Upper Mississippi Basin (2003) Global Biogeochem. Cycles, 17 (3), p. 1085., doi: 10.1029/2001GB001808; Donner, S.D., Coe, M.T., Lenters, J.D., Twine, T.E., Foley, J.A., Modeling the impact of hydrological changes on nitrate transport in the Mississippi River Basin from 1955 to 1994 (2002) Global Biogeochem. Cycles, 16 (3), p. 1043., doi:10.1029/2001GB001396; Donner, S.D., Kucharik, C.J., Foley, J.A., Impact of changing land use practices on nitrate export by the Mississippi River (2004) Global Biogeochem. Cycles, 18, pp. GB1028., doi:10.1029/2003GB002093; Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., The nitrogen cascade (2003) Bioscience, 53 (4), pp. 341-356; Goolsby, D.A., Battaglin, W.A., Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin. USA (2001) Hydrol. Processes, 15 (7), pp. 1209-1226; Groffman, P.M., Gold, A.J., Addy, K., Nitrous oxide production in riparian zones and its importance to national emission inventories (2000) Chemosphere, 2, pp. 291-299; Howarth, R.W., Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natura and human influences (1996) Biogeochemistry, 35, pp. 75-139; Kucharik, C.J., Foley, J.A., Delire, C., Fisher, V.A., Coe, M.T., Lenters, J.D., Young-Molling, C., Gower, S.T., Testing the performance of a Dynamic Global Ecosystem Model: Water balance, carbon balance, and vegetation structure (2000) Global Biogeochem. Cycles, 14 (3), pp. 795-826; Milly, P.C.D., Wetherald, R.T., Dunne, K.A., Delworth, T.L., Increasing risk of great floods in a changing climate (2002) Nature, 415, pp. 514-517; Peterson, B.J., Control of nitrogen export from watersheds by headwater streams (2001) Science, 292, pp. 86-89; Seitzinger, S.P., Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance (1988) Limnol. Oceanogr., 33, pp. 702-724; Seitzinger, S.P., Kroeze, C., Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems (1998) Global Biogeochem. Cycles, 12 (1), pp. 93-113; Seitzinger, S.P., Nitrogen retention in rivers: Model development and application to watersheds in the northeastern U.S.A (2002) Biogeochemistry, 57-58, pp. 199-237, 2004.
- Dürr, H. H., Laruelle, G. G., Van Kempen, C. M., Slomp, C. P., Meybeck, M., and Middelkoop, H.: World-wide typology of near-shore coastal systems: Defining the estuarine filter of river inputs to the ocean, Estuaries and Coasts, 34, 441-458, doi:410.1007/s12237-12011-19381-y, 2011.
- Dutkiewicz, S., Follows, M. J., and Bragg, J. G.: Modeling the coupling of ocean ecology and biogeochemistry, Global Biogeochemical Cycles, 23, GB4017, doi:10.1029/2008GB003405, 2009.

EC: Water framework directive, in, European Commission, 72, 2000.

Ensign, S. H., and Doyle, M. W.: Nutrient spiraling in streams and river networks, J. Geophys. Res., 111, G04009, 10.1029/2005jg000114, 2006.

- Evans, M. A., and Scavia, D.: Exploring estuarine eutrophication sensitivity to nutrient loading, Limnology & Oceanography, 58, 569-578, 10.431/lo.2013.58.2.0569, 2013.
- FAO: National aquaculture sector overview in, Fisheries and Aquaculture Department, Food and Agriculture Organization of the United Nations (<u>http://www.fao.org/fishery/naso/search/en</u>), Rome, 2012a.
- FAO: Fishery and aquaculture country profiles, in, Fisheries and Aquaculture Department, Food and Agriculture Organization of the United Nations (<u>http://www.fao.org/fishery/countrysector/FI-CP_SE/en</u>), Rome, 2012b.
- Fasham, M. J. R., Ducklow, H. W., and McKelvie, S. M.: A nitrogen-based model of plankton dynamics in the oceanic mixed layer, Journal of Marine Research, 48, 591-639, 1990.
- Follows, M. J., Dutkiewicz, S., Grant, S., and Chisholm, S. W.: Emergent biogeography of microbial communities in a model ocean, Science, 315, 1843-1846, 10.1126/science.1138544, 2007.
- Frink, C. R.: Estimating nutrient exports to estuaries, Journal of Environmental Quality, 20, 717-724, 1991.
- Fulton, E. A., Smith, A. D. M., and Punt, A. E.: Which ecological indicators can robustly detect effects of fishing?, ICES Journal of Marine Science, 62, 540-551, 2005.
- Fulton, E. A.: Approaches to end-to-end ecosystem models, Journal of Marine Systems, 81, 171-183, 2010.
- Garnier, J., Billen, G., and Coste, M.: Seasonal succession of diatoms and chlorophyceae in the drainage network of the seine river: Observations and modeling, Limnology and Oceanography, 40, 750-765, 1995.
- Garnier, J., Billen, G., and Palfner, L.: Understanding the oxygen budget and related ecological processes in the river mosel: The riverstrahler approach, Hydrobiologia, 410, 151-166, 2000.
- Glibert, P. M., Anderson, D. M., Gentien, P., Graneli, E., and Sellner, K. G.: The global, complex phenomena of harmful algal bloom, Oceanography, 18, 136-147, 2005.
- Glibert, P. M., Mayorga, E., and Seitzinger, S.: Prorocentrum minimum tracks anthropogenic nitrogen and phosphorus inputs on a global basis: Application of spatially explicit nutrient export models, Harmful Algae, 8, 33-38, 2008.
- Gömann, H., Kreins, P., Kunkel, R., and Wendland, F.: Model based impact analysis of policy options aiming at reducing diffuse pollution by agriculture. A case study for the river ems and a sub-catchment of the rhine, Environmental Modelling and Software, 20, 261-271, doi:210.1016/j.envsoft.2004.1001.1004, 2004.

- Gregg, W. W., Ginoux, P., Schopf, P. S., and Casey, N. W.: Phytoplankton and iron: Validation of a global three-dimensional ocean biogeochemical model, Deep-Sea Research Part II: Topical Studies in Oceanography, 50, 3143-3169, 2003.
- Grégoire, M., Raick, C., and Soetaert, K.: Numerical modeling of the central black sea ecosystem functioning during the eutrophication phase, Progress in Oceanography, 76, 286-333, 2008.
- Gypens, N., Lancelot, C., and Soetaert, K.: Simple parameterisations for describing n and p diagenetic processes: Application in the north sea, Progress in Oceanography, 76, 89-110, 2008.
- Haith, D. A., and Shoemaker, L. L.: Generalized watershed loading functions for stream flow
- nutrients, Water Resources Bulletin, 23, 471-478, 1987.
- Hallegraeff, G. M.: A review of harmful algal blooms and their apparent global increase, Phycologia, 32, 79-99, 1993.
- Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison, W.
 C., Dortch, Q., Gobler, C. J., Heil, C. A., Humphries, E., Lewitus, A., Magnien, R.,
 Marshall, H. G., Sellner, K., Stockwell, D. A., Stoecker, D. K., and Suddleson, M.:
 Eutrophication and harmful algal blooms: A scientific consensus, Harmful
 Algae, 8, 3-13, 2008.
- Horton, R. K.: An index number system for rating water quality, Journal of the Water Pollution Control Federation, 37, 300-306, 1965.
- Howarth, R., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., and Zhao-Liang, Z.: Regional nitrogen budgets and riverine n & p fluxes for the drainages to the north atlantic ocean: Natural and human influences, Biogeochemistry, 35, 75-139, 10.1007/bf02179825, 1996.
- Howarth, R. W., Fruci, J. R., and Sherman, D.: Inputs of sediment and carbon to an estuarine
- ecosystem: Influence of land use, Ecological Applications, 1, 27-39, 1991.
- Ishizaka, J., Kitaura, Y., Touke, Y., Sasaki, H., Tanaka, A., Murakami, H., Suzuki, T., Matsuoka, K., and Nakata, H.: Satellite detection of red tide in ariake sound, 1998-2001, Journal of Oceanography, 62, 37-45, 2006.
- Jackson, C. J., Preston, N. P., Thompson, P. J., and Burford, M. A.: Nitrogen budget and effluent nitrogen components at an intensive shrimp farm, Aquaculture, 218, 397-411, 2003.

- Johnes, P. J.: Evaluation and management of the impact of land use change on the nitrogen and phosphorous load delivered to surface waters: The export coefficient modelling approach, Journal of Hydrology, 183, 323-349, 1996.
- Johnes, P. J., and Butterfield, D.: Landscape, regional and global estimates of nitrogen flux from land to sea: Errors and uncertainties, Biogeochemistry, 57/58, 429-476, 2002.
- JRC-IES: Ccm river and catchment database v2.1 (ccm2), Joint Research Center, Institute for Environmental and Sustainability (JRC-IES), Ispra, ItalyTechnical report EUR 22920 EN, EC-JRC, 2007 (<u>http://desert</u>. jrc.ec.europa.eu/action/php/index.php?action=view&id=23), 2007.
- Katsev, S., Chaillou, G., Sundby, B., and Mucci, A.: Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the lower st. Lawrence river estuary, Limnology and Oceanography, 52, 2555-2568, 2007.
- Klepper, O., and Van Drecht, G.: Waribas, water assessment on a river basin scale; a computer program for calculating water demand and water satisfaction on a catchment basin level for global-scale analysis of water stress, National Institute for Public Health and the Environment, BilthovenReport 402001009, 124, 1998.
- Kroeze, C., and Seitzinger, S. P.: Nitrogen inputs to rivers, estuaries and continental shelves and related nitrous oxide emissions in 1990 and 2050: A global model, Nutrient Cycling in Agroecosystems, 52, 195-212, 1998.
- Kunkel, R., and Wendland, F.: Weku. A gis supported stochastic model of groundwater residence times in upper aquifers for the supraregional groundwater management, Environmental Geology, 30, 1-9, 1997a.
- Kunkel, R., and Wendland, F.: Weku a gis-supported stochastic model of groundwater residence times in upper aquifers for the supraregional groundwater management, Environmental Geology, 30, 1-9, 1997b.
- Kunkel, R., and Wendland, F.: The growa98 model for water balance analysis in large river basins. The elbe case study, Journal of Hydrology, 259, 152-162, 2002.
- Lancelot, C., Spitz, Y., Gypens, N., Ruddick, K., Becquevort, S., Rousseau, V., Lacroix, G., and Billen, G.: Modelling diatom and phaeocystis blooms and nutrient cycles in the southern bight of the north sea: The miro model, Marine Ecology Progress Series, 289, 63-78, 2005.
- Lancelot, C., Gypens, N., Billen, G., Garnier, J., and Roubeix, V.: Testing an integrated river-ocean mathematical tool for linking marine eutrophication to land use: The phaeocystis-dominated belgian coastal zone (southern north sea) over the past 50 years, Journal of Marine Systems, 64, 216-228, 2007.
- Landsberg, J. H.: The effects of harmful algal blooms on aquatic organisms, Reviews in Fisheries Science, 10, 113-390, 2002.

- Laruelle, G. G.: Quantifying nutrient cycling and retention in coastal waster at the global scale, PhD, Geologica Ultraiectina. Mededelingen van de Faculteit Geowetenschappen Universiteit Utrecht No. 312, Utrecht University, Utrecht, 226 pp., 2009.
- Le Quéré, C., Harrison, S. P., Prentice, I. C., Buitenhuis, E. T., Aumont, O., Bopp, L., Claustre, H., Cotrim Da Cunha, L., Geider, R., Giraud, X., Klaas, C., Kohfeld, K. E., Legendre, L., Manizza, M., Platt, T., Rivkin, R. B., Sathyendranath, S., Uitz, J., Watson, A. J., and Wolf-Gladrow, D.: Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models, Global Change Biology, 11, 2016-2040, 2005.
- Ledoux, E., Gomez, E., Monget, J. M., Viavattene, C., Viennot, P., Ducharne, A., Benoit, M., Mignolet, C., Schott, C., and Mary, B.: Agriculture and groundwater nitrate contamination in the seine basin. The stics-modcou modelling chain, Science of The Total Environment, 375, 33-47, 2007.
- Lee, K. Y., Fisher, T. R., Jordan, T. E., Correll, D. L., and Weller, D. E.: Modeling the hydrochemistry of the choptank river basin using gwlf and arc/info: 1. Model calibration and validation, Biogeochemistry, 49, 143-173, 2000.
- Lehodey, P., Chai, F., and Hampton, J.: Modelling climate-related variability of tuna populations from a coupled ocean-biogeochemical-populations dynamics model, Fisheries Oceanography, 12, 483-494, 2003.
- Lehodey, P., Senina, I., and Murtugudde, R.: A spatial ecosystem and populations dynamics model (seapodym) - modeling of tuna and tuna-like populations, Progress in Oceanography, 78, 304-318, 2008.
- Loos, S., Middelkoop, H., van der Perk, M., and van Beek, R.: Large scale nutrient modelling using globally available datasets: A test for the rhine basin, Journal of Hydrology, 369, 403-415, 2009.
- Loukos, H., Monfray, P., Bopp, L., and Lehodey, P.: Potential changes in skipjack tuna (katsuwonus pelamis) habitat from a global warming scenario: Modelling approach and preliminary results, Fisheries Oceanography, 12, 474-482, 2003.
- Maury, O.: An overview of apecosm, a spatialized mass balanced "apex predators ecosystem model" to study physiologically structured tuna population dynamics in their ecosystem, Progress in Oceanography, 84, 113-117, 2010.
- Mayorga, E., Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., Bouwman, A. F., Fekete, B. M., Kroeze, C., and Van Drecht, G.: Global nutrient export from watersheds 2 (news 2): Model development and implementation, Environmental Modelling and Software, 25, 837-853, 2010.
- McBride, G. B., Alexander, R. B., Elliot , A. H., and Shankar, U.: Regional scale modelling of water quality. , National Institute of Water and Atmospheric Research (NIWA), Auckland, New ZealandWater and Atmosphere Vol. 8, 29-31, 2000.

- McClain, M. E., and Naiman, R. J.: Andean influences on the biogeochemistry and ecology of the amazon river, BioScience, 58, 325-338, 2008.
- McDonald, A. D., Little, L. R., Gray, R., Fulton, E., Sainsbury, K. J., and Lyne, V. D.: Multiple-use management strategy evaluation for coastal marine ecosystems using invitro, 2005, 2588-2594,
- Meinardi, C. R., Beusen, A. H. W., Bollen, M. J. S., Klepper, O., and Willems, W. J.: Vulnerability to diffuse pollution and average nitrate contamination of european soils and groundwater, Water Science and Technology, 31, 159-165, 1995.
- Meybeck, M.: Carbon, nitrogen and phosphorous transport by world rivers, American Journal of Science, 282, 401-450, 1982.
- Middelburg, J. J., Soetaert, K., Herman, P. J. M., and Heip, C.: Denitrification in marine sediments: A model study, Global Biogeochemical Cycles, 10, 661-673, 1996.
- Mitra, A., and Flynn, K. J.: Promotion of harmful algal blooms by zooplankton predatory activity, Biol. Lett., 2, 194-197, 2006.
- Moita, M. T., Oliveira, P. B., Mendes, J. C., and Palma, A. S.: Distribution of chlorophyll a and gymnodinium catenatum associated with coastal upwelling plumes off central portugal, Acta Oecologica, 24, S125-S132, 2003.
- Moore, W. S.: Large groundwater inputs to coastal waters revealed by 226ra enrichments, Nature, 380, 612-614, 1996.
- Nixon, S. W.: Physical energy inputs and the comparative ecology of lake and marine ecosystems, Limnology and Oceanography, 33, 1005-1025, 1988.
- Nixon, S. W.: Coastal marine eutrophication: A definition, social causes and future concertns, Ophelia, 41, 199-219, 1995.
- Nixon, S. W.: Eutrophication and the macroscope, Hydrobiologia, 629, 5-19, 2009.
- Officer, C. B., and Ryther, J. H.: The possible importance of silicon in marine eutrophication, Marine Ecolology Progress Series, 3, 83–91, 1980.
- Pastor, L., Cathalot, C., Deflandre, B., Viollier, E., Soetaert, K., Meysman, F. J. R., Ulses, C., Metzger, E., and Rabouille, C.: Modeling biogeochemical processes in sediments from the rhône river prodelta area (nw mediterranean sea), Biogeosciences, 8, 1351-1366, 10.5194/bg-8-1351-2011, 2011.
- Peierls, B. L., Caraco, N. F., Pace, M. L., and Cole, J. C.: Human influence on river nitrogen, Nature, 350, 386-387, 1991.
- Peña, M. A., Katsev, S., Oguz, T., and Gilbert, D.: Modeling dissolved oxygen dynamics and hypoxia, Biogeosciences, 7, 933-957, 2010.
- Preston, S. D., and Brakebill, J. W.: Application of spatially referenced regression modeling for

- the evaluation of total nitrogen loading in the chesapeake bay watershed, U.S. Geological Survey Water Resources Investigations Report 99–4054, 1999.
- Rabalais, N. N., Turner, R. E., Dortch, Q., Justic, D., Bierman, V. J., and Wiseman, W. J.: Nutrient-enhanced productivity in the northern gulf of mexico: Past, present and future, Hydrobiologia, 475, 39-63, 2002.
- Rabalais, N. N., Díaz, R. J., Levin, L. A., Turner, R. E., Gilbert, D., and Zhang, J.: Dynamics and distribution of natural and human-caused hypoxia, Biogeosciences, 7, 585-619, 10.5194/bg-7-585-2010, 2010.
- Rabouille, C., Conley, D. J., Dai, M. H., Cai, W. J., Chen, C. T. A., Lansard, B., Green, R., Yin, K., Harrison, P. J., Dagg, M., and McKee, B.: Comparison of hypoxia among four river-dominated ocean margins: The changjiang (yangtze), mississippi, pearl, and rhône rivers, Continental Shelf Research, 28, 1527-1537, 2008.
- Raick, C., Soetaert, K., and Grégoire, M.: Model complexity and performance: How far can we simplify?, Progress in Oceanography, 70, 27-57, 2006.
- Reed, D. C., Slomp, C. P., and Gustafsson, B. G.: Sedimentary phosphorus dynamics and the evolution of bottom-water hypoxia: A coupled benthic-pelagic model of a coastal system, Limnology and Oceanography, 56, 1075-1092, 2011.
- Refsgaard, J. C., and Storm, B.: Mike she, in: Computer models of watershed hydrology, edited by: Singh, V. P., Water Resources Publications, Highlands Ranch, Littleton, Colorado, pp. 809-846, 1995.
- Regnier, P., Wollast, R., and Steefel, C. I.: Long-term fluxes of reactive species in macrotidal estuaries: Estimates from a fully transient, multicomponent reaction-transport model, Marine Chemistry, 58, 127-145, 1997.
- Ritter, C., and Montagna, P. A.: Seasonal hypoxia and models of benthic response in a texas bay, Estuaries, 22, 7-20, 1999.
- Sarmiento, J. L., Slater, R. D., Fasham, M. J. R., Ducklow, H. W., Toggweiler, J. R., and Evans, G. T.: A seasonal three-dimensional ecosystem model of nitrogen cycling in the north atlantic euphotic zone, Global Biogeochemical Cycles, 7, 417-450, 1993.
- Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., and Bouwman, A. F.: Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of global news models and their application, Global Biogeochemical Cycles, 19, GB4S01, 10.1029/2004GB002606, 2005.
- Seitzinger, S. P., Mayorga, E., Bouwman, A. F., Kroeze, C., Beusen, A. H. W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B. M., Garnier, J., Harrison, J., Wisser, D., and Wollheim, W. M.: Global river nutrient export: A scenario analysis of past and future trends, Glob Biogeochem Cycles, 24, GB0A08, doi:10.1029/2009GB003587, 2010.

- Sferratore, A., Billen, G., Garnier, J., and Théry, S.: Modeling nutrient (n, p, si) budget in the seine watershed: Application of the riverstrahler model using data from local to global scale, Global Biogeochemical Cycles, 19, GB4S07, 10.1029/2005GB002496, 2005.
- Shin, Y. J., and Cury, P.: Exploring fish community dynamics through size-dependent trophic interactions using a spatialized individual-based model, Aquatic Living Resources, 14, 65-80, 2001.
- Shin, Y. J., and Cury, P.: Using an individual-based model of fish assemblages to study the response of size spectra to changes in fishing, Canadian Journal of Fisheries and Aquatic Sciences, 61, 414-431, 2004.
- Siderius, C., Groenendijk, P., Jeuken, M. H. J. L., and Smit, A. A. M. F. R.: Process description of nuswalite, Alterra, WageningenAlterra-Technical Report, 2005.
- Skahill, B. E.: Use of the hydrological simulation program fortran (hspf) model for watershed studies, System-wide Modeling, Assessment, Restoration and Technologies (SMART) / U.S. Army Engineer Research and Development Center (ERDC), 26, 2004.
- Slomp, C., and Van Capellen, P.: Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact, Journal of Hydrology, 295, 64-86, doi:10.1016/j.jhydrol.2004.1002.1018, 2004.
- Smith, R. A., GE Schwarz, G. E., and Alexander, R. B.: Regional interpretation of waterquality monitoring data, Water Resources Research, 33 2781–2798, 1997.
- Soetaert, K., and Herman, P. M. J.: Nitrogen dynamics in the westerschelde estuary (sw netherlands) estimated by means of the ecosystem model moses, Hydrobiologia, 311, 225-246, 1995.
- Soetaert, K., Herman, P. M. J., and Middelburg, J. J.: A model of early diagenetic processes from the shelf to abyssal depths, Gechimica et Cosmochimica Acta, 60, 1019-1040, 1996.
- Soetaert, K., Middelburg, J. J., Herman, P. M. J., and Buis, K.: On the coupling of benthic and pelagic biogeochemical models, Earth-Science Reviews, 51, 173-201, 2000.
- Soetaert, K., and Herman, P. M. J.: A practical guide to ecological modelling using r as a simulation program, Springer Science and Business Media b.v., 2009.
- Soetaert, K., and Middelburg, J. J.: Modeling eutrophication and oligotrophication of shallow-water marine systems: The importance of sediments under stratified and well-mixed conditions, Hydrobiologia, 629, 239-254, 10.1007/s10750-009-9777-x, 2009.

- Stanley, E. H., Powers, S. M., and Lottig, N. R.: The evolving legacy of disturbance in stream ecology: Concepts, contributions, and coming challenges, Journal of the North American Benthological Society, 29, 67-83, 10.1899/08-027.1, 2010.
- Steidinger, K. A., and Garcés, E.: Importance of life cycles in the ecology of harmful microalgae, in: Ecology of harmful algae, edited by: Granéli, E., and Turner, J. V., Springer, Heidelberg, 37-47, 2006.
- Stream_Solute_Workshop: Concepts and methods for assessing solute dynamics in stream ecosystems, Journal of the North American Benthological Society, 9, 95-119, 1990.
- Syvitski, J. P. M., Vörösmarty, C. J., Kettner, A. J., and Green, P.: Impact of humans on the flux of terrestrial sediment to the global coastal ocean, Science, 308, 376-380, 2005.
- Thorp, J. H., Thoms, M. C., and Delong, M. D.: The riverine ecosystem synthesis: Biocomplexity in river networks across space and time, River Research and Applications, 22, 123-147, 2006.
- Turner, R. E., and Rabalais, N. N.: Coastal eutrophication near the mississippi river delta, Nature, 368, 619-621, 1994.
- Turner, R. E., Rabalais, N. N., and Justic, D.: Gulf of mexico hypoxia: Alternate states and a legacy, Environmental Science & Technology, 42, 2323-2327, 10.1021/es071617k, 2008.
- USEPA: Hydrological simulation program fortran (hspf). <u>Http://www.Epa.Gov/ceampubl/swater/hspf/</u>, 2011.
- Van Drecht, G., Bouwman, A. F., Knoop, J. M., Beusen, A. H. W., and Meinardi, C. R.: Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater and surface water, Global Biogeochemical Cycles, 17, 1115, doi:10.1029/2003GB002060, 2003.
- Van Drecht, G., Bouwman, A. F., Harrison, J., and Knoop, J. M.: Global nitrogen and phosphate in urban waste water for the period 1970-2050, Global Biogeochemical Cycles 23, GB0A03, doi:10.1029/2009GB003458, 10.1029/2009GB003458, 2009.
- Vaughan, I. P., Diamond, M., Gurnell, A. M., Hall, K. A., Jenkins, A., Milner, N. J., Naylor, L. A., Sear, D. A., Woodward, G., and Ormerod, S. J.: Integrating ecology with hydromorphology: A priority for river science and management, Aquatic Conservation: Marine and Freshwater Ecosystems, 19, 113-125, 2009.
- Vidon, P. G., and Hill, A. R.: Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology, Biogeochemistry, 71, 259-283, 2004a.

- Vidon, P. G., and Hill, A. R.: Landscape controls on the nitrate removal in stream riparian zones, Water Resources Research, 40, W03201, doi:10.1029/2003WR002473, 2004b.
- Vidon, P. G., and Hill, A. R.: A landscape-based approach to estimate riparian hydrological and nitrate removal functions, Journal of the American Water Resources Association, August 2006, 1099-1112, 2006.
- Vidon, P. G. F., and Hill, A. R.: Landscape controls on the hydrology of stream riparian zones, Journal of Hydrology, 292, 210-228, 10.1016/j.jhydrol.2004.01.005, 2004c.
- Wade, A. J., Durand, P., Beaujouan, V., Wessel, W. W., Raat, K. J., Whitehead, P. G.,
 Butterfield, D., Rankinen, K., and Lepisto, A.: A nitrogen model for european catchments: Inca, new model structure and equations, Hydrol. Earth Syst. Sci., 6, 559-582, 2002.
- Warren, I. R., and Bach, H. K.: Mike 21: A modelling system for estuaries, coastal waters and seas, Environmental Software, 7, 229--240, 1992.
- Webster, J.: Analysis of potassium and calcium dynamics in stream ecosystems on three southern apalachian watersheds of contrasting vegetation, PhD, University of Georgia at Athens, Athens, 1975.
- Wendland, F., Kunkel, R., Grimvall, A., Kronvang, B., and Müller-Wohlfeil, D. I.: The soiln/weku model system – a gis-supported tool for the assessment and management of diffuse nitrogen leaching at the scale of river basins, Water Science and Technology, 45, 285-292, 2001.
- Whitehead, P. G., Wilson, E. J., and Butterfield, D.: A semi-distributed integrated nitrogen model for multiple source assessment in catchments (inca): Part i model structure and process equations, Science of the Total Environment, 210-211, 547-558, 1998a.
- Whitehead, P. G., Wilson, E. J., Butterfield, D., and Seed, K.: A semi-distributed integrated flow and nitrogen model for multiple source assessment in catchments (inca): Part ii - application to large river basins in south wales and eastern england, Science of the Total Environment, 210-211, 559-583, 1998b.
- Wijsman, J. W. M., Herman, P. M. J., Middelburg, J. J., and Soetaert, K.: A model for early diagenetic processes in sediments of the continental shelf of the black sea, Estuarine, Coastal and Shelf Science, 54, 403-421, 2002.
- Young, R. A., Onstad, C. A., and Bosch, D. D.: Agnps: An agricultural nonpoint source model, in: Computer models of watershed hydrology. Water resources publications, edited by: Singh, V. P., Highlands Ranch, Colorado, USA, 1001-1020, 1995.
- Zhang, J., Gilbert, D., Gooday, A. J., Levin, L., Naqvi, S. W. A., Middelburg, J. J., Scranton, M., Ekau, W., Peña, A., Dewitte, B., Oguz, T., Monteiro, P. M. S., Urban, E.,

Rabalais, N. N., Ittekkot, V., Kemp, W. M., Ulloa, O., Elmgren, R., Escobar-Briones, E., and Van der Plas, A. K.: Natural and human-induced hypoxia and consequences for coastal areas: Synthesis and future development, Biogeosciences, 7, 1443-1467, 10.5194/bg-7-1443-2010, 2010.

Zhu, Y. P., Zhang, H. P., Chen, L., and Zhao, J. F.: Influence of the south-north water diversion project and the mitigation projects on the water quality of han river, Science of the Total Environment, 406, 57-68, 10.1016/j.scitotenv.2008.088, 2008.

Figure captions

Figure 1. Schematic of the hydrological system in river basins, including the soil, groundwater, riparian zone and floodplain, and the stream or river, and with wastewater flows from urban areas.

Figure 2. Classification of river biogeochemistry models in common use.

Figure 3. Schemes for river biogeochemsitry models, including (a) lumped river-basin scale regression models; (b) distributed models.

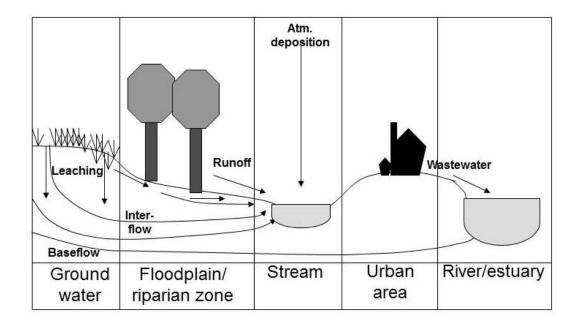


Figure 1.

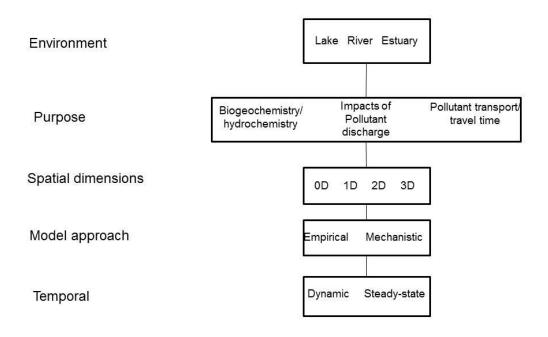
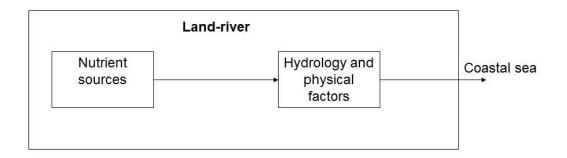


Figure 2.

a. Lumped regression models



b. Distributed models

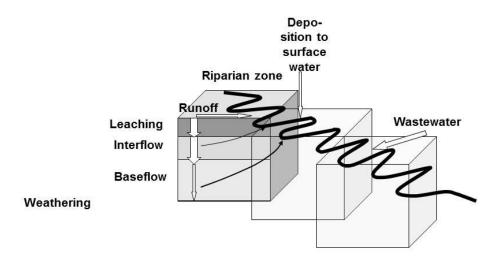


Figure 3.