

Chapter III. Processes

F. Land-Based N Sources and Their Delivery to Coastal Systems

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For: Nitrogen in the Marine Environment

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I. INTRODUCTION

Inputs to terrestrial systems of newly fixed N₂ (the conversion of relatively inert N₂ gas to more bioavailable N forms) have more than doubled as a result of human activities including synthetic N fertilizer production, cultivation of legume crops, and combustion of fossil fuels (Vitousek & Matson, 1993; Galloway et al., 2004). A portion of this chemically-combined N is transported to coastal waters where it can lead to changes in coastal ecosystem function (e.g. Nixon, 1995; Valiela et al., 1997; Carpenter et al., 1998; Deegan et al., 2002; Rabalais et al., 2002; Glibert et al., 2005a; Boynton and Kemp THIS BOOK). Changes in phytoplankton species composition, alteration and loss of seagrass habitats, and increases in carbon fixation, extent and duration of anoxic and hypoxic water, harmful algal blooms, and coral reef degradation are some of the effects associated with excess N inputs to coastal systems (e.g., Nixon, 1995; Carpenter et al., 1998; NRC 2000; Diaz, 2001; Anderson et al., 2002; Rabalais, 2002) as reviewed in Paerl and Piehler (THIS BOOK).

Rivers are the major pathway for delivery of land-based N sources from watersheds to coastal systems (Fig. 1). In addition, submarine groundwater discharge and direct atmospheric deposition can be important pathways for delivery of land-based N sources. This chapter focuses on export of N by rivers to the coastal zone (i.e., estuaries, bays, continental shelves) and includes investigations of: 1) spatial patterns of river N export, by N form; 2) N sources (natural and anthropogenic) and other factors controlling the form and magnitude of N transport by rivers from watersheds; 3) temporal patterns in river export of N (e.g., inter-decadal, inter-annual, seasonal, events); and 4) effects of

human modification of discharge (dams, consumptive water use) on N export. We also include brief discussions of coastal N loading via submarine groundwater discharge and direct atmospheric N deposition to coastal waters. Site specific case studies as well as regional and global perspectives are presented.

We specifically address land-based inputs of N to the coastal zone in this chapter.

Biological N₂-fixation occurring within coastal and open ocean regions can contribute substantial additional inputs of N at some times and locations (Carpenter and Capone, THIS BOOK; Hopkinson and Giblin, THIS BOOK). Of particular note is N from oceanic N₂-fixation which is transported onto continental shelves from advection of open ocean waters and can considerably exceed land-based N sources to continental shelves (e.g., Seitzinger and Giblin, 1996; Fennel et al., 2006).

II. SPATIAL PATTERNS IN AMOUNT AND FORM OF RIVER N EXPORT

Biologically available (combined) N transported by rivers to coastal systems occurs in several forms. These forms include dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and particulate nitrogen (PN). DIN is made up of three major components (nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonium (NH₄⁺)). DON is operationally defined as organic N that can pass through a filter with a minimum pore size of 0.2 -1 μm. PN is the N that is retained by the filter. DON and PN each are composed of complex mixtures of specific N-based compounds, most of which are chemically uncharacterized at the molecular level, although considerable advances are being made

(Bronk 2002; Benner, 2002; Koch et al., 2005; Seitzinger et al., 2005a; Bronk and McCarthy, this book; Aluwihare and Meador, this book).

From a nitrogen mass balance perspective, understanding total N export from watersheds to coastal systems may be sufficient. However, information about the various forms of N transported by rivers is important in order to understand factors controlling N export and effects of N inputs on coastal systems. This is because factors controlling export of N from watersheds are not the same for all N forms, as discussed below. Furthermore, different forms of N have different ecosystem effects. For example, all of the DIN pool is generally considered to be bioavailable, while only a portion of river transported DON is readily available for uptake by micro-organisms, including bacteria and some phytoplankton (Bronk, 2002; Seitzinger et al., 2002a). In particular DON is implicated in the formation of some coastal harmful algal blooms (Paerl, 1988; Berg et al., 1997 and 2003; Granéli et al., 1999; Glibert et al., 2005a and b). Particulate and dissolved species can have very different impacts on receiving ecosystems. Of course, it is also not sufficient to understand N alone; other bioactive elements (e.g., phosphorus, silica, carbon, etc.) must also be considered in order to fully understand effects of nutrient inputs to coastal systems (Conley et al., 1993; Turner et al., 1998). In this chapter we focus on only N, while recognizing the importance of other elements. Recent global perspectives on river export of P and C can be found in Mackenzie et al., (1998), Smith et al., (2003), Harrison et al., (2005a and b), and Van Drecht et al., (2005).

A. Approaches

During the last several decades there have been many studies quantifying and characterizing N export by individual rivers to the coastal zone through direct measurements of N concentrations and water discharge (e.g. Wollast, 1983; Boynton et al., 1995; Nixon et al., 1995; Eyre and Pont, 2003; Jordan et al., 2003; Appendix I). In addition, a number of relatively complex, deterministic models of river nitrogen flux have been developed and applied to individual rivers (e.g., GWLF, Haith and Shoemaker, 1987; HSPF, Bicknell, et al. 1997; SWAT, Srinivasan et al., 1993; Lee et al., 1999; Filoso et al., 2004). Several of these, as well as other models, have been described recently in Alexander et al. (2002).

However, syntheses of results from individual studies have been rarer. One of the first global syntheses of measurements of river N export, by N form, was by Meybeck (1982). Since then, several databases have been created documenting measured N export from rivers for specific regions (e.g., Alexander et al., 1996 – U.S.; Lewis et al., 1999 – South America; Holmes et al., 2000 - Arctic; UNEP/MAP 2003 - Mediterranean; EEA 1998-Europe; Appendix 1) and globally (Peierls et al., 1991; Meybeck and Ragu, 1995; Smith et al. 2003; LOICZ; GEMS-Water Triennial Reports). The creation of these databases has highlighted the large variation among rivers, both in terms of N yield (kg N km^{-2} watershed yr^{-1}) and N load ($\text{kg N watershed}^{-1} \text{ yr}^{-1}$; Appendix 1), and made it possible to develop a more refined understanding of patterns of N export at local, regional and global scales. For example, regional syntheses of measured N fluxes have characterized rates of N export in the Northeast US (Boyer et al., 2002), Eastern and Gulf US (Castro et al.,

2001), and in relatively unimpacted rivers in the Americas (Lewis et al., 1999). These studies have shown that fluxes of TN to the coastal zone can vary substantially on a regional scale and that TN export correlates reasonably well with N inputs to watersheds (Sources contributing to N export are discussed in detail in Section III).

Development of databases for a wide range of rivers also has made it possible to develop models that are widely applicable without tuning to individual basins. This is particularly important because in many basins around the world there is inadequate observational data on surface water quantity and quality. In some regions, such as the US, the number of river locations monitored (e.g., by the US Geological Survey) for water quality and discharge has decreased dramatically in the past decades; in some other world regions open access to data is still very limited. Progress continues to be made in the development of remote-sensing-based measurements for rivers and streams to obtain continuous data on water discharge (Brakenridge et al., 2005) and automated sensors capable of measuring concentrations of dissolved and particulate constituents (e.g. Johnson and Coletti, 2002). However, until these techniques are substantially improved and widely implemented, we must rely on models to estimate N export from watersheds which have few or no available measurements of nutrient export.

Significant progress has been made in the development and application of spatially explicit regional and global models of N export by rivers to the coastal zone as a function of watershed N inputs and biogeophysical properties (e.g., Howarth et al., 1996; Jordan and Weller, 1996; Seitzinger and Kroeze, 1998; Caraco and Cole, 1999; Alexander et al.,

2000; Smith et al., 2003; Green et al., 2004; Van Drecht et al., 2003; Harrison et al., 2005b; Beusen et al., 2005; Boyer et al., 2006). One of the first models to explain N export by a wide range of rivers globally related human population to nitrate export (Peierls et al., 1991). That model was further developed with additional parameters, including nonpoint sources related to agricultural fertilizer use and atmospheric N deposition, point source sewage inputs, and hydrological parameterization (Caraco and Cole, 1999). Global databases of input parameters were then applied which resulted in the first spatially explicit, global view of DIN export as a function of N inputs to watersheds (Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Seitzinger et al., 2002b). A model describing TN export by rivers as a function of atmospheric deposition and net anthropogenic N inputs (NANI model) was developed using data from rivers in the North Atlantic Basin (Howarth et al., 1996). A modified version of the NANI model has now been applied to global databases (Boyer et al., 2006). The SPARROW model (Spatially Referenced Regression on Watershed attributes; Smith et al., 1997) relates TN export by rivers with spatial data on watershed N sources, landscape characteristics, and stream properties. The SPARROW model has been applied to a range of rivers in the US and New Zealand (e.g., Alexander et al., 2000 and 2001; McBride et al., 2000). A non-spatial, global model has examined changes in the biogeochemical cycles N, P, C and S over decadal to century time scales (Mackenzie et al., 1998).

A system of spatially explicit, global nutrient export models has recently been developed by the Global Nutrient Export from Watersheds (Global NEWS) working group (Seitzinger et al., 2005b). The Global NEWS system of models includes models that

predict annual average export of DIN, DON, and PN for individual river basins globally (P and C forms are also included). These sub-models are referred to as NEWS-DIN, NEWS-DON and NEWS-PN, respectively. The NEWS-DIN model predicts DIN yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$) as a function of water runoff, inorganic N fertilizer application, manure N excretion, sewage N inputs, atmospheric N deposition, and biological N_2 -fixation (described in detail in Dumont et al., 2005). NEWS-DIN also includes N retention and loss terms such as N retention in river networks, N retention in dammed reservoirs, N loss via consumptive water use, and N removed from a watershed via harvesting and grazing. The NEWS-DON model predicts DON yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$) as a function of water runoff, inorganic N fertilizer application, manure N excretion, sewage N inputs, and biological N_2 -fixation (described in detail in Harrison et al., 2005b). It contains many of the same retention and loss pathways as NEWS-DIN. NEWS-PN is somewhat different in that it predicts PN yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$) as a function of land-use, precipitation intensity, landscape rugosity, and lithology (described further in Beusen et al., 2005).

B. Patterns

According to global model predictions, total N export by rivers at the global scale is approximately $40\text{-}65 \text{ Tg N yr}^{-1}$ under 1990s conditions (Van Drecht et al., 2003; Green et al., 2004; Galloway et al., 2004; Boyer et al., 2006; Seitzinger et al., 2005b). It is remarkable how small the range of estimates is, given the uncertainties in modeling approaches, global input data bases, and availability and quality of measurements of river TN export. Though this consistency is encouraging, some of it may result from the fact that there is considerable overlap between TN-export datasets used to calibrate each of

these models, and some overlap in the input data sets used to apply the models (van Drecht et al. 2005).

Relatively few large rivers account for a large proportion of the N exported to coastal zones globally for all N forms, based on NEWS model predictions. For example, the 25 rivers with the greatest water discharge globally (<0.5% of the rivers with a watershed > 2,500 km²) account for approximately half of the exported DIN and DON, and about a quarter of the exported PN, globally (Table 1). Some of the highest rates of TN export (>100 Gg N yr⁻¹) by individual rivers occur in Europe and southern and eastern Asia, although high export is also predicted for a number of rivers in North America, Africa, and South America (Fig. 2). The highest rates of TN export are often, although not always (e.g., Amazon), estimated to occur in large rivers with substantial anthropogenic N inputs.

If we distinguish N export by form, at the global scale, DIN and PN export are approximately equal in magnitude (~25 Tg yr⁻¹ and 30 Tg yr⁻¹, respectively), with each accounting for approximately 40% of global TN export, according to NEWS-model-predictions (Fig. 3). In contrast, global DON export is substantially less (~12 Tg yr⁻¹), and accounts for approximately 20% of TN export. (The C exported in the dissolved organic and particulate matter amounts to 170 and 197 Tg C yr⁻¹, respectively, according to NEWS model predictions; Harrison et al., 2005b and Beusen et al., 2005) There is, however, substantial spatial variability in both the magnitude and form of N exported to the coastal zone (Appendix 1; Fig. 4).

There are a number of hot-spots and cold-spots for N yield (N export per km² watershed) that are consistent across all N forms. For example, regions with high runoff such as northern South America, tropical West Africa, and Indonesia have high predicted yields for DIN, DON and PN (Fig. 4) (Seitzinger et al., 2005b). Conversely, arid regions such as the southwestern US, Northern Africa, and Australia all have low predicted yields for all N forms.

Substantial differences in the magnitude of export of the N forms are observed in many regions. For example, regions with high rates of human activity such as the NE US, Western Europe, and China all have high predicted rates of DIN export, but relatively lower predicted rates of DON and PN export (Fig. 4). South Asia and Southeast Asia have high predicted rates of DIN and PN export, but generally lower predicted rates of DON export. High predicted DIN yields in these regions are likely due to the high rates of human activity in these regions and the high predicted PN yield is likely due to the mountainous nature of the region. Basins where DON constitutes the largest pool of exported N are widely distributed, with a slight tendency to occur more frequently in northern boreal basins (Figs. 4 and 5).

When we aggregate predicted N export by latitude, several interesting patterns emerge. DIN constitutes the largest single form of N exported to coastal zones in north temperate regions, but PN constitutes the largest fraction of exported N from the rest of the world's latitudinal regions (Fig. 5; Table 2). The greatest fraction of exported N occurring as

DON is in arctic latitudes, where approximately a quarter of the exported N is DON. DON constitutes a somewhat smaller proportion of N exported from other latitudinal bands (17-20%). Although most of the exoreic land surface area is located in the north temperate latitude band, the greatest rates of N export for all N forms occur in the north tropical latitude band (Table 2; Figs. 4 and 5). This is due largely to the high rates of water runoff in tropical regions, though in many regions high levels of human activity also play an important role (Seitzinger et al., 2005b). The above discussion of the differences in the spatial patterns of river export of the various N forms demonstrates the need to explicitly include parameterization of the different N forms in watershed N export models.

Where does the river N enter the coastal zone? Some rivers discharge into estuaries while others (primarily large rivers) discharge directly to continental shelves (e.g., Mississippi, Zaire). Of the river N entering estuaries, a portion is permanently removed within the estuary by denitrification or burial, with the remainder exported to continental shelves. How much of river transported N enters estuaries and how much reaches continental shelves? Using NEWS model predictions of global river TN export ($\text{DIN} + \text{DON} + \text{PN} = 65 \text{ Tg TN y}^{-1}$) and arguments presented in Seitzinger et al. (2006), we estimate the following distribution. Rivers discharge 50 Tg N y^{-1} to estuaries and 15 Tg N y^{-1} (from large rivers) directly to continental shelves (Fig. 3). Estuaries export 38 Tg N y^{-1} of their river N to continental shelves, bringing total inputs of river N to continental shelves to 53 Tg N y^{-1} . Therefore, estuaries (directly) and continental shelves (directly plus indirectly) receive about equal amounts of river N. Most of the river transported N does not enter

the open ocean, but is denitrified in estuarine and continental shelf sediments (reviewed in Seitzinger et al. 2006).

III. SOURCES OF N AND FACTORS CONTROLLING N EXPORT

Both natural and anthropogenic factors are important in controlling among-watershed differences in DIN, DON, and PN export. Natural N sources include N₂-fixed by lightning and biological N₂-fixation (Fig. 1). Prior to recent anthropogenic increases in N fixation, the amount of naturally-fixed N washed into surface waters was likely controlled by a mixture of biological N₂-fixation rates and hydrology, with high rates of runoff transferring a relatively large proportion of the naturally fixed N into surface drainage waters. The tight coupling between runoff and N export in relatively unimpacted tropical and temperate rivers supports this conceptual model (Lewis et al., 1999). Major anthropogenic sources of fixed (bioavailable) N inputs to watersheds include inputs of newly fixed N from agricultural sources (inorganic fertilizers and biological N₂-fixation by crops) and atmospheric N deposition, as well as recycled N from animal manure, human sewage, and industrial sources.

A. Approaches

Nitrogen isotope studies and watershed modeling are two approaches that have been used to identify the contribution of different watershed sources of N to river N export. For example, differences in the $\delta^{15}\text{N}$ signature of biogenic (plants, soils) and lithogenic (rock) PN has been used to infer that biogenic sources accounted for only ~10% of the total PN exported from the mainstem of the Lanyang-His River in Taiwan (Kao and Liu, 2000). The $\delta^{15}\text{N}$ signature of nitrate has been used to indicate differences in N sources in

watersheds (e.g., Böhlke et al. 1997; Mayer et al., 2002; Billen et al., 2005). For example, increases over time in the $\delta^{15}\text{N}$ signature of nitrate in groundwater beneath agricultural land were used to relate increases in groundwater nitrate concentration to a change in the sources of N for crops from biological N_2 -fixation plus mineralization to primarily synthetic fertilizer (Böhlke 2002). $\delta^{15}\text{N}$ signatures were used to demonstrate a strong link between N in estuarine organisms and land-based anthropogenic N sources in several shallow coastal systems in the Northeast US (McClelland and Valiela, 1998; Martinetto et al. 2006).

Another approach to estimating the relative importance of N sources within a watershed entails the use of models. Models have been used to estimate the relative importance of various land-based N sources at basin, region and global scales. Numerous models have been developed for use in individual watersheds (e.g., Lee et al., 1999; Alexander et al., 2000; Valiela et al., 2000; Billen et al., 2001; Donner et al., 2004). Though these models are useful for the watersheds to which they have been tuned, these models are generally difficult to apply to regional and global scale questions as the input data required for these models are often unattainable at regional and global scales. Furthermore, they often require coefficients to be tuned to specific system types through sampling programs that would be resource-prohibitive at the regional or global scale.

Regional scale modeling analyses have been done for 15 watersheds in the NE US (Boyer et al., 2002), 31 watersheds in the eastern and Gulf coasts of the US (Castro et al., 2001), and for the coterminous US divided into 15 regions (Jordan and Weller 1996). These analyses were limited to predicting export of TN only or nitrate only, not individual N

forms, and examined the magnitude of various N sources to those watersheds but did not explicitly estimate the contribution of each source to the river export. Due to different rates of retention of N sources in watersheds, relative inputs of different N sources are not equal to their relative contributions to N export. However, insights from these studies are still quite useful. In addition to these regional studies, the recent development of global nutrient export models (such as the NEWS and some of the other models described in section II) has made it possible to estimate the spatial distribution of the contributions of various land-based N sources to coastal N export globally.

B. Patterns

In their regional modeling analysis, Boyer et al. (2002) found that TN sources to watersheds varied substantially throughout the NE US. However, averaged across all the 15 study watersheds, atmospheric N deposition constituted the greatest N input (31% of total N inputs); net inputs of food and feed constituted the second largest source of N to these watersheds (25%), followed by agricultural N₂-fixation (24%), fertilizer use (15%), and forest N₂-fixation (5%) (Boyer et al., 2002; Driscoll et al., 2003). Castro et al. (2001) found similar patterns for TN sources to NE watersheds, but also found that sources of TN to watersheds differed substantially by region, with N fertilizer being substantially more important in Mid-Atlantic, Southeastern, and Gulf Coast watersheds than in Northeast US watersheds.

At the global scale, it is possible to use NEWS models to make several predictions regarding watershed N sources driving the regional patterns of N export. First, human activity is estimated to be responsible for approximately 60% of the global export of DIN

to coastal zones and has significantly increased DON export in many regions as well (Dumont et al., 2005; Harrison et al., 2005b) (Fig. 6; Tables 3 and 4). Total anthropogenic point and non-point sources of DON in rivers are estimated to be over three times greater in the tropics (1.85 Tg N/y) than temperate latitudes (0.51 Tg N/y) and account for a larger proportion of total DON (Table 4). Despite the massive scale of human intervention in the N cycle that has altered the input and transport of N by rivers (and the atmosphere) to coastal zones, natural sources still dominate the export (i.e., are the single largest source) of DIN, DON and PN from many watersheds in Arctic regions and in much of South America and Africa (Fig. 6). In the case of DON, natural sources still account for approximately 80% of export globally (Harrison et al., 2005b).

Fertilizer is estimated to be the single most important source of exported DIN in north temperate latitudes, contributing 37% of the exported DIN, according to NEWS-DIN (Fig. 6; Table 3). N_2 -fixation is estimated to be the largest contributor in tropical and Arctic regions, contributing over half of the exported DIN in each region. N_2 -fixation is estimated to contribute the smallest proportion of exported N in the industrialized north temperate range (~24%). Manure was estimated to contribute a relatively small fraction of exported DIN (11-25%) in most latitude bands, but was estimated to contribute a substantial proportion (39%) of the exported DIN in the south temperate range. N deposition was most important in the Arctic, contributing an estimated 14% of the exported DIN, and least important in the south temperate range (5%). When examined at the level of large latitudinal regions, sewage point sources constitute a fairly small fraction of exported DIN and DON (<5% and <10%, respectively). However, in

individual basins, sewage point sources can dominate DIN and DON export (Fig. 6). Most of the point-source-dominated basins are arid, and therefore have very small predicted rates of diffuse source (natural or anthropogenic) N input (Fig. 6).

It is important to note that often only a relatively small percentage of the total N inputs to the landscape are exported by rivers to the coast. Data from a variety of coastal watersheds throughout the world, indicate that, on average, approximately 25% of total net nitrogen inputs from anthropogenic plus natural sources is exported by rivers as TN to the coast (Boyer et al., 2006; Fig. 3). Similarly, estimates for watersheds throughout the North Atlantic Basin suggest that about 25% of anthropogenic N inputs are exported by rivers (Howarth et al., 1996). There can be considerable variation among basins in the percentage of N inputs that are exported by rivers. For example, the percentage of N loaded onto basins from point and non-point sources (both anthropogenic and natural) that is exported as DIN ranged from 0.0001% to 43%, based on NEWS-DIN model predictions (Dumont et al., 2005). Rivers which exported the largest fraction of their watershed N inputs had high water runoff ($>1 \text{ m yr}^{-1}$); rivers exporting the smallest fractions had extensive damming or very low annual precipitation and runoff. According to NEWS-DIN, in exoreic dry areas of Africa, Asia, Australia and North America where runoff is less than 0.1 m yr^{-1} (30% of the exoreic world), only 5% (on average) of N applied to watersheds is exported to coastal waters as DIN. Export from these arid systems is predicted to be low because there is very little runoff to transport soluble nitrogen (nitrate) from the soil and unsaturated zone to streams.

A number of caveats must be considered in the discussion of large-scale patterns of N sources. There is considerable variation among watersheds in a region in the relative importance of various N sources. Global models primarily focus on relatively large basins (25,000 km²). These large watersheds account for ~72% of global water discharge and 79% of exoreic land area and thus likely a large proportion of N export. However, small coastal watersheds drain most of the coastline globally. For example, out of 6,152 watersheds identified globally in a simulated topological network (STN-30p), 93% of them are entirely contained in coastal grid cells (0.5° latitude x 0.5° longitude) that are immediately adjacent to an ocean (Vörösmarty et al., 2000). Therefore, while small coastal watersheds may not appear to contribute much coastal N at regional and global scales, they are very important in determining rates and patterns of N delivery to many of the world's estuaries, and thus important in affecting coastal ecosystems and water quality where much of the world's population lives.

IV. TEMPORAL PATTERNS IN RIVER EXPORT OF N

Temporal variability of river N export spans a range of scales from geological (e.g., glacial, inter-glacial) to hourly. On human time scales, long-term trends occur over decades associated with changes in anthropogenic N inputs to watersheds (Meybeck, 2003), interannual variability can be associated with differences in weather patterns, and intra-annual variability occurs on seasonal, diurnal and event (e.g. storm) scales.

Variability on all of these scales can affect the response of coastal ecosystems to N inputs (Grenz et al., 2000; Deegan et al., 2002; Paerl and Piehler, 2006 this book).

A. Long-Term Trends

Long term (multi-decadal) records of N export from watersheds are rare and generally limited to nitrate. In general, human-impacted rivers demonstrate higher NO_3^- loads than non-impacted rivers, and the NO_3^- loads increase over time as anthropogenic N inputs to those watersheds increase. For example, an approximately 30-year record for the Yangtze River (Changjiang River), China, demonstrates over an order of magnitude increase in NO_3^- export as human population and agricultural activity have increased in the watershed (Yan et al., 2003) (Fig. 7). Several-fold increases in NO_3^- export have also been observed in the Mississippi (Goolsby and Battaglin, 2001), Seine (Billen et al., 2001), Scheldt (Billen et al., 2005), and Susquehanna (Hagy et al., 2004) basins associated with changing anthropogenic watershed activities (Fig. 7). In contrast, as expected, relatively stable NO_3^- export is observed in basins with relatively low and stable levels of human activity, such as in the Yukon and S. Dvina Rivers (Alexander et al., 1996; Holmes et al., 2000) (Fig. 7).

At the global scale, TN river export to coastal systems is estimated to have approximately doubled between 1860 and 1990, due to anthropogenic activities on land (Galloway et al., 2004). Over the next 50 years the human population is predicted to increase markedly in certain world regions, notably Southern and Eastern Asia, South America, and Africa (United Nations, 1996). Growing food to feed the expanding world population will require increased use of nitrogen and phosphorus fertilizers (Alcamo et al., 1994; Bouwman et al., 1995; Bouwman, 1997). Increased industrialization, with the associated combustion of fossil fuels and NO_x production, is predicted to increase atmospheric

deposition of N (Dentener et al., 2006; IPCC, 2001). Thus, unless substantial technological innovations and management changes are implemented, increasing food production and industrialization will undoubtedly lead to increased export of N to coastal ecosystems (Galloway et al. 2004), with resulting water quality degradation. For example, inorganic N export to coastal systems is predicted to increase 3-fold by the year 2050 (relative to 1990) from Africa and South America (Fig. 8) (Kroeze and Seitzinger, 1998; Seitzinger et al., 2002b). Substantial increases are predicted for Europe (primarily from eastern Europe) and N. America. Alarming large absolute increases are predicted for eastern and southern Asia; almost half of the total global increased N export is predicted for those regions alone.

Increases in river N export over time often correlate relatively well with increases in N inputs to watersheds. However, the response of river N export to *decreases* in watershed N inputs is not necessarily as rapid or well understood. In at least one case, the Patuxent River (MD, USA), point source reductions in N resulted in rapid reductions in N export (Boynton et al., 1995; Jordan et al., 2003). However, N export is generally dominated by non-point sources, not point sources (Carpenter et al., 1998; Seitzinger et al., 2005b; Dumont et al., 2005; others), so substantially reducing N export often requires a reduction in non-point N inputs. Reductions of non-point nutrient inputs have been attempted in a number of systems, but response of river N export to these reductions is often much slower and less predictable than responses to reductions in point sources (Stålnacke et al., 1999).

The complex response of N export to nonpoint reductions is well illustrated by Eastern European rivers. Despite a drastic reduction in fertilizer use and animal production as a result of the economic decline in the former Soviet Union and in Eastern Europe in the early 1990's, DIN concentrations showed statistically significant downward trends in only 4 of 12 sites studied in Latvian Rivers (study period 1987-1998) (Stålnacke et al., 2003). No decreases were reported in nitrogen export from major Eastern European rivers such as the Vistula and Oder Rivers in Poland (1989-1995) (Stålnacke, 2005) or the Danube River (at Reni; 1995-2000) (Behrendt et al., 2005a). Only moderate decreases in TN or nitrate export by the Elbe River to the North Sea were measured (1985-2000) (Hussian et al., 2004). A number of factors have been proposed to explain the weak response of river N export to decreases in diffuse sources of N in the watersheds, including the long-water transit times of water in soils and in aquifers and continued mineralization of the large pools of organic N which have accumulated over time in soils. The above examples demonstrate the uncertainty in our knowledge of the response of river N export to decreases in N inputs to watersheds after prolonged periods of high inputs and the need for future research.

B. Interannual Variability

In addition to long-term trends, there is also substantial inter-annual variation in N export (Fig. 7). There are several potential causes for this inter-annual variability, including: year-to-year variation in climate, variation in N inputs, changes in land-use, or changes in the relative timing of N application and runoff events. For example, inter-annual variation in climate is a major factor affecting river water discharge, and discharge is an

important variable controlling non-point N (natural or anthropogenic) export. This is observed in the long-term pattern (1945-2001) of nitrate export by the Susquehanna River to Chesapeake Bay which was strongly affected by interannual and interdecadal differences in river discharge (Hagy et al., 2004). Similarly, in the Odra River interannual variation (1960 to 2000) in DIN load and discharge showed similar patterns (Behrendt et al., 2005b). It is not clear whether the positive relationship between discharge and N export is simply due to increased hydrologic connectivity between potential N sources and flowing surface waters under wetter conditions or whether higher discharges also reduce N removal by denitrification in the river and on the landscape. The overall effect of water discharge on DIN, DON and PN export is indicated by the importance of water discharge as an explanatory variable in models that predict N export (TN as well as each of the N forms) across a wide range of rivers/watersheds globally (Caraco and Cole, 1999; Smith et al., 2003; Harrison et al., 2005b; Dumont et al., 2005; Smith et al., 1997). This is consistent with analysis of data from 16 major watersheds in the Northeastern US in which watersheds with higher discharge exported a greater fraction of the net anthropogenic N inputs (Howarth et al. 2006). Future changes in water discharge in various world regions are predicted in response to changing climate (due to natural and anthropogenic effects). Already, increases in water discharge in the 6 largest Eurasian Arctic rivers which appear to be related to global warming have been documented (7% from 1936 to 1999) (Peterson et al., 2002; McClelland et al., 2004); the effect of such changes in river flow on N export in these rivers is under investigation. A preliminary estimate of the effect on TN export of increases in precipitation and discharge due to future climate change indicated that TN export by the Susquehanna

River to Chesapeake Bay might increase by 3 to 17% by 2030 and by 16 to 65% by 2095 (Howarth et al., 2006).

It is possible to examine the relationship between climate and N export by de-trending long-term data and evaluating the strength of the relationship between de-trended N export and water discharge via regression analysis. When this analysis is done, we find that discharge exerts a relatively strong effect on NO_3^- export in some rivers, explaining approximately half of the variability in NO_3^- export from the Mississippi and Yukon River basins. This is similar to what others have found for the Mississippi using other approaches (Goolsby and Battaglin, 2001). However, curiously, in other rivers (e.g. the Yangtze, Seine, and Severnaya Dvina), there is little or no detectable relationship between water discharge and NO_3^- export through time, even when changes in N inputs are accounted for.

C. Seasonal Variability

The response of coastal ecosystems to river nutrient inputs depends, in part, on the seasonal pattern of the N delivery, including seasonal changes in the form of N delivered (e.g., DIN, DON and PN). Most studies of river nutrient export only report annual rates and often only report TN export. Where seasonal patterns of N export by individual river basins have been reported, a number of patterns have been observed, and the different forms of N can exhibit different patterns of export (e.g., Lesack et al., 1984; Alexander et al., 1996; Eyre and Pont, 2003) (Figs. 9 and 10). Seasonal patterns are observed in both N concentration and in N export (Fig. 10).

One might expect that river nutrient export from point sources would show a constant export rate, with concentration varying inversely with discharge, while rivers dominated by diffuse sources would show an export rate more directly related to discharge with less variation in concentration with discharge (Billen et al., 2005). However, to our knowledge this dynamic has not yet been demonstrated across a broad range of rivers, or with consideration of the N form. Seasonal patterns of river nutrient export may be complicated by seasonal variations in biological retention (plant uptake) or removal (e.g. denitrification) within soils or within the river network. Extremes of river discharge with season, such as occur in monsoonal regions, would be expected to greatly affect river N export. The natural seasonal cycle of N export can also be markedly dampened by dams such as demonstrated in California's Mokelumne River, as compared to a similar, but undammed neighboring river (Ahearn et al., 2005). In this case, dams shifted the pulse of nitrate export from winter to summer, and distributed the winter pulse of TN evenly throughout the year.

Despite a general lack of synthetic understanding regarding seasonal dynamics of N export from rivers, some initial work has been done at the global scale to estimate seasonal patterns of TN export by world rivers. Green et al., (2004) simply distributed annual river TN export for individual rivers based on the pattern of monthly water discharge (Fig. 11). This approach suggests that Arctic rivers exhibit the largest TN export during the summer (June –August). Many Northern Hemisphere temperate latitude rivers are predicted to have highest TN export during winter (December-

February) or spring (March-May), according to this approach. A comparison of the seasonal pattern of model predicted TN export for the Mississippi River (Fig. 11) with measured export (Fig. 9) suggests that, at least for this river, discharge alone can capture the major patterns in seasonal variation of TN export. Additional analyses we have conducted for the Sacramento, San Joaquin, and Yukon Rivers are consistent with the above suggesting that, while the absolute magnitude of N export is highly dependent upon watershed N inputs, the overall seasonal patterns in TN export can be relatively well predicted from the seasonal pattern in river water discharge. However, the pattern in other rivers is not as straight forward and will require more comprehensive analyses.

D. Diel Variability

Shorter term variations in nutrient export due, for example, to diel variations in N processing, can also be significant and may affect coastal ecosystem processes. A study in the highly productive, subtropical Yaqui Valley region in Mexico suggests that night-time anoxia can shut down nitrification and coupled nitrification-denitrification, thereby substantially changing the amount and form of exported N on a time-scale of hours (Harrison et al., 2005c). Similarly, a study of three rivers in the Midwest US showed a decrease in denitrification during the night (Laursen and Seitzinger 2004). The San Joaquin River, a highly productive river in California, also exhibits pronounced diel fluctuations in N concentrations and dynamics (Dahlgren, Pers. Comm.). In the case of the Mexican stream, the authors estimated that failing to measure night-time N fluxes would lead to a 17-38% underestimate of N export during their 24-hour study period (Harrison et al., 2005c). However, understanding the impact of diel variation in N

cycling on longer term (seasonal and annual) patterns and magnitudes of N flux will require additional work. Also, the effects of diel variation on downstream ecosystems of the observed hourly changes in N concentrations and forms have yet to be explored.

E. High Intensity, Low Frequency Events

Tropical storms, typhoons, or hurricanes, depending on their strength and geographical context, often deliver torrential rains. Increased river flow during such high intensity, low frequency rainfall events can transport a major portion of annual river N load to coastal systems. Historically, there has been a paucity of data on such events due to their irregular and extreme nature and the generally manual nature of water sample collection for nutrient analyses. However, with the use of *in situ* automatic water samplers and nutrient analysis systems, data from such events can now more readily be captured.

Large increases in river nutrient export associated with hurricanes have been documented in rivers in the Chesapeake Bay watershed and in the Neuse River watershed (North Carolina, USA) (Chesapeake Research Consortium, 1976; Paerl et al., 2005). In years with hurricanes that travel inland and deposit large amounts of rain (e.g., hurricanes Fran 1996 and Floyd 1999), the annual DIN load to Pamlico Sound from the Neuse River can be twice as large as during non-hurricane years (Paerl et al., 2005). DON load is also elevated (Paerl, pers comm.). In the Lanyang-His in Taiwan, a small subtropical river with a forested watershed, as much as 90% of the annual load of suspended matter can be transported during a single typhoon, although water discharge is often <10% of the annual total runoff (Kao and Liu, 1996 and 2000).

In arid regions the majority of water and nutrients in un-dammed rivers can be exported during a few major storms. In a study of 7 subtropical, Australian rivers, approximately 75% of the annual TN load was delivered in 20% of the time (2 10-day flood periods during 1996; Eyre and Pont, 2003). This contrasts with a number of temperate systems in which it takes 23-52% of the time to deliver 75% of the annual TN load (Eyre and Pont, 2003). Different N forms also exhibited different patterns of discharge in this study of Australian rivers, with DON typically accounting for a relatively constant proportion (60-80%) of the total N load in each non-flood month and PN increasing in importance during flood months (Eyre and Pont, 2003).

V. EFFECTS ON N EXPORT OF LONG-TERM HUMAN MODIFICATION OF DISCHARGE

Human modification of water discharge associated with dams and consumptive water use can greatly decrease river N export. Both dissolved and particulate N forms are affected. Dams trap particulates and also can increase the water residence time, which can increase the proportion of N inputs that are denitrified or buried. Consumptive water use (e.g. irrigation) transfers N out of the river system to terrestrial soils where it can be assimilated by crops, fixed by soils, or denitrified, and therefore not transported downstream. Consumptive water use also can influence PN export by decreasing water flow, which increases suspended sediment trapping within the river system.

Over 45,000 dams at least 15 m high are in operation today around the world (World Commission on Dams, 2000; Vorosmarty et al., 2003). There are many additional

smaller dams. For example, there are more than 79,000 registered dams in the US alone (National Inventory of Dams). While soil erosion due to anthropogenic activities has increased sediment transport by global rivers by over 2 billion metric tons/y, the amount of sediment reaching the world's coast has decreased by about 1.4 billion metric tons, due to retention in reservoirs (Syvitski et al., 2005). Globally, trapping of suspended sediments behind dams is estimated to have decreased the modern sediment transport to coastal systems by about 26% (Vorosmarty et al., 2003; Syvitski et al., 2005). PN data are often not available for pre and post dam conditions. However, there is a reasonably strong, non-linear relationship between total suspended sediment (TSS) and PC, PN, or PP based on data from a wide range of world rivers, so that PN and PC can be estimated based on TSS export (Ittekkot and Zhang, 1989; Beusen et al., 2005). Globally, approximately 4-7 Tg y⁻¹ of PN are estimated to be buried with sediments in large reservoirs alone (about 600), which is equivalent to a reduction of 14-23% of the current global export of PN (Seitzinger et al., 2002b; Beusen et al., 2005). Substantial additional PN is undoubtedly trapped in the tens to hundreds of thousands of small reservoirs around the world (Smith et al., 2001).

Dams can increase water residence time in a river, thereby increasing denitrification and decreasing N export to coastal systems (Seitzinger et al., 2002c; Dumont et al., 2005). Globally, denitrification is estimated to remove about 31 Tg N/y in lakes and reservoirs, with about 11 Tg N yr⁻¹ in large lakes and reservoirs and 20 Tg N y⁻¹ in small lakes (Seitzinger et al., 2006). These estimates are associated with considerable uncertainty, but (given that global N export by rivers is about 60 Tg yr⁻¹; Bouwman et al., 2005;

Boyer et al., 2006; Seitzinger et al., 2005b) suggest that human modification of rivers may significantly impact river N export.

The degree to which dams increase N removal by denitrification in a given river depends on a number of factors, such as placement of dams within the watershed, reservoir water residence time, reservoir depth, and the proportion of the river N that passes through reservoirs. Analysis of 16 rivers in the Northeastern US suggested that while any one reservoir could remove a substantial portion of the N input to that reservoir, at the scale of the whole river, the total amount of N removed in all dams within a watershed decreased the export of N to the coastal zone by less than 10% (Seitzinger et al., 2002c). In general, a relatively small proportion of the N inputs to those rivers passed through reservoirs. However, reservoirs with long water residence times, which intercept a large proportion of a basin's water and N load, can have a marked effect on export of N to coastal systems. The Nile provides a dramatic example. Nitrate export is estimated to have decreased by more than a factor of ten due to closure of the high dam at Aswan in 1965 (Nixon, 2003). Denitrification in reservoirs is predicted to also have a marked effect on N export in a number of other rivers heavily influenced by dams such as the Colorado, Rio Grande, Orange, and Huang He (Dumont et al., 2005). Interestingly, N export by the Nile is estimated to now exceed the pre-dam export due to increased fertilizer use, changes in agricultural draining, increasing human population, and marked extensions of urban water and wastewater systems, and the Nile delta fishery now surpasses that immediately preceding the dam (Nixon, 2003).

VI. GROUNDWATER

Submarine groundwater discharge (SGD) is a potentially important but as yet poorly quantified source of nutrients to coastal systems (Burnett et al. 2003; Slomp and Van Cappellen, 2004). The discharge of groundwater into the sea has been known since Roman times, when offshore springs were used as a source of freshwater (reviewed by Burnett et al., 2003). However, recognition of the potential importance of SGD as a source of nitrogen to coastal systems has been relatively recent (e.g., Johannes, 1980; D'Elia et al., 1981; Capone and Bautista 1985; Valiela and D'Elia, 1990; Valiela et al., 2002; Burnett et al., 2003; Slomp and Van Cappellen, 2004). Coastal systems in which SGD is an important source of N tend to be those characterized by shallow, permeable (sand, limestone) coastal aquifers with high rates of groundwater recharge (Slomp and Van Cappellen, 2004).

Nitrogen concentrations in submarine groundwater are influenced by many of the same natural and anthropogenic watershed characteristics that control river water concentrations. A model that predicts total dissolved N loads in groundwater to shallow estuaries for watersheds underlain by unconsolidated sands, has been developed and successfully applied to a number of systems on Cape Cod, MA (USA) (Valiela et al., 2000 and 2002). Inputs to the model include N in wastewater (via septic systems), fertilizer use, and atmospheric deposition. Quantifying N inputs to coastal waters, however, is complicated by high spatial and temporal variability. In addition to geologically determined preferential flow-paths, large changes in nitrogen concentrations can occur during groundwater movement through the aquifer and coastal sediments. In

particular, groundwater nitrate can be removed by denitrification, and diagenesis of organic matter in the coastal sediments can add nitrogen or change the composition of nitrogen species in the groundwater (Capone and Slater, 1990; Valiela et al., 1990; Nowicki et al., 1999).

Despite difficulties, there are a number of studies at both local and regional scales in which SGD of nitrogen (generally only nitrate measurements) has been quantified within the context of whole system N budgets. SGD has been shown to be an important N source in some coral reefs areas (e.g., D'Elia et al. 1981; Corbett et al. 1999; Umezawa et al. 2002), shallow coastal lagoons and bays (Valiela and D'Elia, 1990; Capone and Bautista 1985; Capone and Slater, 1990; Valiela et al., 1990 and 2002; Moser, 1997; Gobler and Boneillo, 2003), and salt marsh dominated systems (Krest et al., 2000). In a number of systems, N inputs from SGD equal or exceed river inputs (Table 5).

At regional scales, there are also examples in which SGD of nitrogen equals or exceeds river fluxes. For example, DIN fluxes in groundwater discharges through salt marshes along the South Carolina coast are estimated to be equivalent to input from major rivers in this region ($\sim 60 \times 10^6 \text{ mol y}^{-1}$) (Krest et al., 2000) (Table 5).

Regional and global scale budgets of SGD and nutrients are very difficult to formulate with confidence. However, most estimates of SGD at the global scale range from about 6-10% of surface water inputs (reviewed by Burnett et al., 2003), with large variations in time and space. If we assume that the water budget is a rough proxy for dissolved N

inputs, then SGD could transport approximately 4 Tg N yr⁻¹ to coastal systems (10% of global river DIN plus DON transport). While at the global scale, SGD may be a relatively small source of N to coastal systems, it is becoming increasingly clear that at local and regional scales it can be a very important term in some cases (Table 5). There is a need for greater understanding of SGD as a coastal N source and for the formulation and application of spatially explicit models of groundwater N inputs.

VII. ATMOSPHERIC DEPOSITION DIRECTLY TO COASTAL WATERS

Atmospheric N deposition can be an important source of N to coastal and open ocean ecosystems. The potential importance of N in atmospheric deposition has been recognized for over twenty years (e.g., Correll and Ford, 1982; Paerl, 1985; Duce, 1986). Recognition of the importance of atmospheric deposition as a source of N to coastal waters increased rapidly following the analysis by Fisher and Oppenheimer (1991) for a number of coastal systems, including Chesapeake Bay. Atmospheric deposition to watersheds contributes to diffuse N loads in rivers as discussed previously in this chapter. In this section we are specifically referring to N deposited (wet and dry) directly to the surface of coastal and open ocean waters.

N in rainwater includes both DIN (nitrate, nitrite, ammonium) and DON. Gas phase N species in the atmosphere contributing to dry deposition include ammonia, nitric acid and organic N compounds. Particulate N can also be associated with dust and organic debris, and deposited either as dry deposition or with rainfall. Globally, anthropogenic sources account for over 70% of NO_x and 65% of ammonium deposition (Galloway et al., 2004).

Sources of organic N compounds are not well known although a significant fraction (up to 80%) is available to plankton communities as a nitrogen source (Timperley et al., 1985; Peierls and Pearl, 1997; Seitzinger and Sanders, 1999).

In some estuaries and coastal embayments, atmospheric deposition directly to the water surface can account for a substantial fraction of N input (as much as 40% of the N inputs from river plus atmospheric inputs; Table 6). However, the relative importance of atmospheric deposition as an N source varies considerably among coastal systems and depends on a number of factors, including the nature of watershed N sources and the relative sizes of the contributing watershed and receiving estuary (Valigura et al., 2001).

In continental shelf regions, there is also a wide range in the relative magnitude of atmospheric N deposition. For example, in North Atlantic shelf regions, direct atmospheric deposition can accounting for from as little as 5% to more than half of the land-based N input (rivers plus direct atmospheric deposition) (Table 6). The proportion of land-based N inputs that are from atmospheric deposition depends not only on the magnitude of river N export, but also the area of shelf over which atmospheric N is deposited (Nixon et al., 1996; Seitzinger and Giblin, 1996). At the global scale, atmospheric N deposition to continental shelves ($\sim 8 \text{ Tg N y}^{-1}$) is estimated to account for about 17% of total N inputs from land-based sources (Table 6). This is based on estimated N inputs to global continental shelves from rivers that includes river N exported from estuaries and N delivered from large rivers that discharge directly to shelves (Fig. 3 and Seitzinger et al., 2006). These atmospheric deposition estimates do

not include DON, as we know of no measurements for DON in rainwater collected directly from continental shelf locations. However, we estimate that DON may comprise anywhere from 20% to 80% of the total dissolved N in rainwater (Cornell et al., 1995; 2001 and 2003; Valigura et al., 2001; Mace et al. 2003).

Open ocean regions receive significant amounts of land-based N from atmospheric deposition ($\sim 25 \text{ Tg N y}^{-1}$ Dentener pers. comm.). This estimate of atmospheric deposition does not include dissolved organic nitrogen (DON), which may account for 20% to as much as 80% of the total dissolved N in rainwater in remote marine locations (Cornell et al., 1995; 2001 and 2003; Mace et al. 2003). Keeping in mind that this estimate of DON is uncertain because of the limited number of measurements, including DON could increase current estimates of N deposition to oceanic regions by a factor of 1.25 to 5 or to 31 to 125 Tg N/y, increasing it to the range of estimated oceanic biological N_2 -fixation ($57\text{-}152 \text{ Tg y}^{-1}$; Mahaffey et al. 2005; Carpenter and Capone, this book).

VIII. SUMMARY AND FUTURE DIRECTIONS

In the past several decades, considerable progress has been achieved toward a comprehensive understanding of land-based N inputs to coastal waters (estuaries, bays and continental shelves). Local studies of patterns and controls of N export have been carried out and synthesized. These syntheses have, in turn, been used to develop spatially explicit regional and global models that can be used to estimate the patterns and magnitudes of N input to coastal ecosystems, as well as the N sources in watersheds and other factors controlling N export. We now have reasonable, though still quite uncertain,

estimates of land-based N inputs to coastal waters globally via a number of different pathways, including rivers ($\sim 60 \text{ Tg N yr}^{-1}$), submarine groundwater discharge (roughly 4 Tg N yr^{-1}) and direct atmospheric deposition (8 Tg N yr^{-1}). A better understanding of the magnitude of different forms of N is also developing. Globally, approximately 40% of river transported N is in the form of DIN and PN, with DON comprising approximately 20%.

There is substantial variability in the magnitude of N inputs to coastal regions, as well as the contribution of different sources driving that export, that is starting to be addressed by spatially explicit models. There are now many watersheds throughout the world with high yields (i.e., $\text{kg N exported by rivers to the coastal zone km}^{-2} \text{ watershed yr}^{-1}$) of N. Some of the highest rates of TN yield occur in watersheds in Europe and southern and eastern Asia. These are watersheds with high anthropogenic N inputs and N export is dominated by DIN, with fertilizer being the single largest N source of that DIN.

Anthropogenic factors, however, are not always responsible for high rates of N yield from watersheds, and high yields are not always dominated by DIN. Watersheds with high water runoff, such as the Amazon and Congo, are estimated to have high yields of all N forms (DIN, DON and PN). In much of Oceania, a combination of high water runoff and anthropogenic activity lead to high yields of all N forms. Throughout most of the world, non-point sources (natural and/or anthropogenic) dominate N export, regardless of N form. This includes fertilizer which is estimated to be the single most important source of exported DIN in many north temperate latitude watersheds; manure is estimated to contribute a substantial portion of the exported DIN in a number of

watersheds scattered throughout temperate and tropical latitudes. Except for some watersheds in the Eastern United States, atmospheric deposition does not appear to be the dominant source driving DIN export. Despite the massive scale of human intervention in the N cycle which has affected transport of N by rivers, natural sources (N_2 -fixation) are still the single largest contributor of DIN, DON and PN from many watersheds in the Arctic, South America and Africa. PN export may be one of the largest uncertainties in river N export. Its potential importance is suggested by current estimates that PN accounts for about 40% of global river TN export, and that it constitutes the largest fraction of exported N from all regions, except the north temperate zone, when information is aggregated at the larger scale of major latitudinal zones (tropical, temperate, and arctic regions). Within a region, all the patterns noted above can vary among individual watersheds. Differences in the spatial patterns of river N export among N forms, in combination with differences in coastal ecosystem effects of these different N forms, highlight the need to explicitly include parameterization of the different N forms in watershed N export models.

Often only a relatively small proportion of the total N inputs to a watershed are exported by rivers to the coast, although the range is considerable (e.g., <1% to >40%). Much of the N is denitrified within the soil and freshwater ecosystems. Hydrology has a large impact on the proportion of N exported by rivers with the largest proportion exported from watersheds with high water runoff (>1 m yr⁻¹) and lowest from basins with extensive damming or very low annual precipitation and runoff.

There is still much important work that needs to be done to understand patterns and controls of different N forms delivered to coastal waters. Below we highlight a few of these needs. At present, there is considerably more information on DIN inputs than other forms of N. The ability to predict seasonal or event driven changes in export, by N form, is largely limited to intensive studies in individual watersheds, as at present most regional and global N export models are only able to predict mean annual river export from large river basins. A comprehensive synthesis of seasonal patterns of river nutrient export that includes different N forms, as well as the factors contributing to those seasonal patterns, is needed. Such an analysis should include rivers across a wide range of geographic, hydrological, geological, and human disturbance regimes. These studies should also include small coastal watersheds which drain a large portion of the land immediately adjacent to the coastline globally, but which have often received less attention than larger watersheds. There is also a need for better integration of terrestrial biogeochemistry and ecosystem models with river nutrient export, including multiple element interactions. All the above are particularly pressing needs in tropical and subtropical systems, which are simultaneously the most poorly understood and subject to the greatest anticipated increases in N loading. While there has been relatively good success with relating increases in N inputs to watersheds to increases in N export by rivers, there is considerable uncertainty in our knowledge of the response of river N export to decreasing N inputs to watersheds after prolonged periods of high inputs. Given the suggested large magnitude of N entering marine systems from atmospheric DON deposition, research is needed to obtain better quantitative information DON deposition and to determine

whether the source of that DON is from land-based processes in which case it is an input of new N to the oceans, or whether it is from volatilization of DON from the oceans, in which case it would not represent new N, but rather more of a recycled N input.

REFERENCES

- Ahearn, D.S., Sheibley, R.W. and Dahlgren R.A. (2005). Effects of river regulation on water quality in the lower Mokelumne River, California. *River Res. Appl.* **21**, 651-670.
- Alcamo, J., Kreileman, G.J.J., Krol, M.S., and Zuidema, G. (1994). Modeling the global society-climate system: Part 1: Model description and testing. *Water Air Soil Poll.* **76**, 1-35.
- Alexander, R. B., Slack, J. R. Ludtke, A. S., Fitzgerald, K. K. and Schertz T. L. (1996). Data from selected U.S. Geological Survey national stream water quality monitoring networks (WQN). U.S.G.S. Digital Data Series DDS-37. *U. S. Geological Survey*.
- Alexander, R.B., Smith, R.A., and Schwarz, G.E. (2000). Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* **403**, 758-761.
- Alexander, R.B., Smith, R.A., Schwarz, G.E., Preston, S.D., Brakebill, J.W., Srinivasan, R., and Pacheco, P. (2001). 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, R.A. Valigura, R.B. Alexander, M.S. Castro, T.P. Meyers, H.W. Paerl, P.E. Stacey, and R.E. Turner [Eds.], Washington, D.C., American Geophysical Union, pp. 119-170.

- Alexander, R.B., Johnes, P.J., Boyer, E.W., and Smith, R.A. (2002). A comparison of models for estimating the riverine export of nitrogen from large watersheds, *Biogeochemistry*, 57/58, 295-339.
- Aluwihare, L.I. and Meador, R. THIS BOOK. Chemical composition of marine dissolved organic nitrogen.
- Anderson, D. M., Glibert, P. M. and Burkholder, J. M. (2002). Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. *Estuaries* **25**, 704-726.
- Behrendt, H., van Gils, J., Schreiber, H., and Zessner, M. (2005a). Point and diffuse nutrient emissions and loads in the Danube basin with the revised model. III. Long Term Changes. *Archiv Hydrobiologia, Suppl. Large Rivers*, **16**, 221-247..
- Behrendt, H., D. Opitz, R. Korol, and M. Stronszka. (2005b). Changes of the nutrient loads of the Odra River during the last century – their causes and consequences. Presentation at ICID 21st European Regional Conference "Integrated Land and Water Management: Towards Sustainable Rural Development," Frankfurt, Germany.
- Benner, R. (2002). Chemical composition and reactivity, Chapter 3, pp. 59-90, *In* Hansell, D.A., and Carlson, C.A. [Eds.], "Biogeochemistry of marine dissolved organic matter." Academic
- Berg, G. M., Glibert, P.M., Lomas, M.W., and Burford, M.A. (1997) Organic nitrogen uptake and growth by the chrysophyte *Aureococcus anophagefferens* during a brown tide event. *Marine Biology* **129**, 377-87.

- Berg, G.M., Balode, M., Purina, I., Bekere, S., Bechemin, C., Maestrini, S.Y. (2003). Plankton community composition in relation to availability and uptake of oxidized and reduced nitrogen. *Aquatic Microb. Ecol.* **30**, 263-74.
- Beusen, A.H.W., Dekkers, A.L.M., Bouwman, A.F., Ludwig, W. and Harrison, J. (2005). Estimation of global river transport of sediments and associated particulate C, N, and P, *Global Biogeochem. Cyc.* **19**, GB4S05, doi:10.1029/2005GB002453.
- Bicknell, B.R., Imhoff, J.C., Kittle, J.L.Jr., Donigan, A.S.Jr., and Johanson, R.C. (1997). Hydrological simulation program – fortran user's manual for release 11. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, U.S.A. EPA/600/R-97/080.
- Billen, G., Garnier, J., Ficht, A., and Cun, C. (2001). Modeling the response of water quality in the Seine River Estuary to human activity in its watershed over the last 50 years. *Estuaries* **24**, 977-993.
- Billen, G., Garnier, A. and Rousseau, V. (2005). Nutrient fluxes and water quality in the drainage network of the Scheldt basin over the last 50 years. *Hydrobiologia* **540**, 47-67.
- Böhlke, J.K. (2002). Groundwater recharge and agricultural contamination. *Hydrogeology Journal* **10**, 153-179.
- Böhlke, J.K., Ericksen, G.E., and Revesz, K. (1997). Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern Chile and southern California, USA. *Chem. Geol.* **136**, 135-152.

- Bouwman, A.F. (1997). Long-term scenarios of livestock-cropland use interactions in developing countries. *Land Wat Bull.* 5. Food and Agriculture Organization of the United Nations, Rome, Italy.
- Bouwman, A.F., Vanderhoek, K.W., and Olivier, J.G.J. (1995). Uncertainties in the global sources distribution of nitrous oxide. *J Geophys Res-Atmos.* **100**, 2785, 2800.
- Bouwman, A.F., Van Drecht, G., Knoop, J.M., Beusen, A.H.W., and Meinardi, C.R. (2005). Exploring changes in river nitrogen export to the world's oceans, *Global Biogeochem. Cyc.*, **19**, doi:10.1029/2004GB002341.
- Boyer, E.W., Goodale, C.L., Jaworski, N.A. and Howarth, R.W. (2002). Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A., *Biogeochemistry*, **57/58**, 137-169.
- Boyer, E.W., Howarth, R.W., Galloway, J.N., Dentener, F.J., Green, P.A. and C.J. Vörösmarty (2006). Riverine nitrogen export from the continents to the coasts. *Global Biogeochem. Cyc.*, **20**, GB1S91, doi:10.1029/2005GB002537.
- Boynton, W. R., Garber, J.H., Summers, R. and Kemp, W.M. (1995) Inputs, Transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* **18**, 285-314.
- Boynton, W.R. and Kemp, W.M. THIS BOOK. *Estuaries*.
- Brakenridge, G.R., Nghiem, S.V., Anderson, E., and Chien, S. (2005). Space-based measurement of river runoff. *EOS Transactions of the American Geophysical Union* **86**, 185-192.

- Bronk, D.A. (2002). Dynamics of DON, Chapter 5, pp. 153-247, *In* Hansell, D.A., and Carlson, C.A. [Eds.], “Biogeochemistry of marine dissolved organic matter.” Academic Press, San Diego, California.
- Bronk, D.A. and McCarthy, M.D. THIS BOOK. Analytical methods for the study of nitrogen.
- Burnett, W.C., Bokuniewicz, H., Huettel, M. Moore, W.S. and Taniguchi, M. (2003). Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* **66**, 3-33.
- Capone, D.G. and Bautista, M.F. (1985). A groundwater source of nitrate in nearshore marine sediments. *Nature* **313**, 214-216.
- Capone, D.G. and Slater, J.M. (1990). Interannual patterns of water table height and groundwater derived nitrate in nearshore sediments. *Biogeochemistry* **10**, 277-288.
- Caraco, N. F., and Cole, J.J. (1999). Human impact on nitrate export: an analysis using major world rivers. *Ambio*, **28**, 167-170.
- Carpenter, S., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., and Smith, V.H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.* **8**, 559-568.
- Carpenter, E.J., and Capone, D.G. (In press 2006). Chapter Processes: N₂ fixation. *In* “Nitrogen in the marine environment,” Capone, D. Carpenter, E. Bronk, D. and Mulholland, M. [Eds.], Academic Press.

- Castro, M.S., Driscoll, C.T., Jordan, T.E., Reay, W.G., Boynton, W.R., Seitzinger, S.P., Styles, R.V., and Cable J.E. (2001). Contribution of atmospheric deposition to the total nitrogen loads to thirty-four estuaries on the Atlantic and Gulf Coasts of the United States, *In* “ Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective, Coastal and Estuarine Studies” pp. 77-106, AGU.
- Conley, D. L., Schleske, C.L. and Stoermer, E.F. (1993). Modification of the biogeochemical cycle of silica with eutrophication. *Mar. Ecol. Prog. Ser.* **101**, 179-92.
- Corbett, D.R., et.al., 1999. Patterns fo groundwater discharge into Florida Bay. *Limnol. Oceanogr.* **44**, 1045-1055.
- Correll, D., and D. Ford. (1982) Comparison of precipitation and land runoff as sources of estuarine nitrogen. *Estuar. Coast. Shelf Sci.*, **15**, 45-56.
- Cornell, S., Rendell, A., and Jickells, T. (1995). Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* **376**, 243-246.
- Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., and Zhuang L.-Z. (2001). Organic nitrogen in Hawaiian rain and aerosol, *J. Geophys. Res.*, 106(D8), 7973-7984, 10.1029/2000JD900655.
- Cornell, S., Jickells, T. D., Cape, J. N., Rowland, A. P. and Duce, R. A. (2003). Organic nitrogen deposition on land and coastal environments: a review of methods and data. *Atmospheric Environment* **37(16)**, 2173-2191.

Chesapeake Research Consortium (CRC). (1976). The effects of tropical storm Agnes on the Chesapeake Bay estuarine system. Chesapeake Research Consortium, Publication No. 54. Johns Hopkins University Press, Baltimore, Maryland.

Deegan, L.A., Wright, A. Avayzian, S.G., Finn, J.T., Golden, H., Merson, R.R., and Harrison, J.A. (2002). Nitrogen loading alters seagrass ecosystem structure and support of higher trophic levels. *Aquat. Conserv.: Mar. Freshwater Eco.* **12**:193-212.

D'Elia, C.F., Webb, K.L., and Porter, J.W. (1981). Nitrate-rich groundwater inputs to Discovery Bay, Jamaica: a significant source of N to local reefs? *Bull. Mar. Sci.* **31**, 903-910.

Dentener, F., Drevet, J., Lamarque, J. F., Bey, I., Eickhout B., Fiore, A. M., Hauglustaine, D., Horowitz, L. W., Krol, M., Kulshrestha, U. C., Lawrence, M., Galy-Lacaux, C., Rast, S., Shindell, D., Stevenson, D., Van Noije, T., Atherton, C., Bell, N., Bergman, D., Butler, T., Cofala, J., Collins, B., Doherty, R., Ellingsen, K., Galloway, J., Gauss, M., Montanaro, V., Müller, J. F., Pitari, G., Rodriguez, J., Sanderson, M., Solmon, F., Strahan, S., Schultz, M., Sudo, K., Szopa, S. and Wild, O. (2006), Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation, *Global Biogeochem. Cycles*, **20**, GB4003, doi:10.1029/2005GB002672.

Devol, A. (200x). Denitrification (title of chapter?). This Book.

Diaz., R.J. (2001). Overview of hypoxia around the world. *J. Environ. Qual.* **30**, 275-281.

- Donner, S.D., C.J. Kucharik, and J.A. Foley. (2004). Impact of changing land use practices on nitrate export by the Mississippi River. *Global Biogeochem. Cyc.* **18**: GB1028, doi:10.1029/2003GB002093.
- Driscoll, C.T., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C.L., Groffman, P.M., Hopkinson, C., Lambert, K., Lawrence, G. and Ollinger, S. (2003). Nitrogen Pollution in the Northeastern United States: Sources, Effects, and Management Options. *BioScience*, **53**, 357–374.
- Duce, R. (1986). The impact of atmospheric nitrogen, phosphorous, and iron species on marine biological productivity, p. 497-529. In “The role of air-sea exchange in geochemical cycling,” Buat-Menard, P. [Ed.], D. Reidel, Norwell, Massachusetts.
- Dumont, E., Harrison, J.A., Kroeze, C. Bakker, E.J., and Seitzinger, S.P. (2005). Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: results from a spatially explicit, global model. *Global Biogeochem. Cyc.*, **19**, GB4S02, doi:10.1029/2005GB002488.
- European Environment Agency (1998). Europe’s environment: Statistical compendium for the second assessment, report, Copenhagen.
- Eyre, B.D. and Pont, D. (2003). Intra- and inter-annual variability in the different forms of diffuse nitrogen and phosphorus delivered to seven sub-tropical east. *Australian estuaries*, **57**, 137-148.
- Filoso, S; Vallino, J, Hopkinson, C, Rastetter, E, Claessens, L. (2004). Modeling nitrogen transport in the Ipswich River Basin, Massachusetts, using a hydrological simulation program in fortran (HSPF). *J.Am. Water Resour.Assoc.* **40**, 1365-1384.

- Fisher, D. and Oppenheimer, M. (1991). Atmospheric nitrogen deposition and the Chesapeake Bay estuary. *Ambio* **20**, 102-108.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., and Vörösmarty, C.J. (2004) Nitrogen cycles: past, present and future, *Biogeochemistry*, **70**, 153-226.
- Garrison, G.H., Glenn, C.R., and McMurty, G.M. (2003). Measurement of submarine groundwater discharge in Kahana Bay, O'ahu, Hawaii. *Limnol. Oceanogr.* **48**, 920-928.
- GEMS, <http://www.gemstat.org/>
- Glibert, P.M., Seitzinger, S., Heil, C.A., Burkholder, J.M., Parrow, M.W., Codispoti, L.A., and Kelly, V. (2005a). The role of eutrophication in the global proliferation of harmful algal blooms. *Oceanography*, **18**: 199-209.
- Glibert, P.M., Harrison, J., Heil, C. and Seitzinger, S. (2005b). Escalating worldwide use of urea – a global change contributing to coastal eutrophication. *Biogeochemistry*: DOI 10.1007/s10533-3070-0.
- Gobler, C.J. and Boneillo, G.E.. (2003). Impacts of anthropogenically influenced groundwater seepage on water chemistry and phytoplankton dynamics within a coastal marine system. *Mar. Ecol. Prog. Ser.* **255**, 101-114.

- Goolsby, D.A., and Battaglin, W.A. (2001). Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. *Hydrol. Process.* **15**, 1209-1226.
- Granéli, E., Carlsson, P., and Legrand, C., (1999). The role of C, N, and P in dissolved and particulate organic matter as a nutrient source for phytoplankton growth, including toxic species. *Aquat. Ecol.* **33**, 17-27.
- Green, P.A., Vörösmarty, C.J., Meybeck, M., Galloway, J.N., Peterson, B.J., and Boyer, E.W (2004). Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on topology, *Biogeochemistry* **68**, 71-105.
- Grenz C., Cloern, J.E., Hager, S.W., Cole, B.E. (2000). Dynamics of nutrient cycling and related benthic nutrient and oxygen fluxes during a spring phytoplankton bloom in South San Francisco Bay (USA). *Mar. Ecol. Prog. Ser.* **197**, 67-80.
- Hagy, J.D., Boynton, W.R., Keefe, C.W., and Wood, K.V. (2004). Hypoxia in Chesapeake Bay, 1950-2001: Long-term change in relation to nutrient loading and river flow. *Estuaries*, **27**, 634-658.
- Haith, D.A., and Shoemaker, L.L. (1987). Generalized watershed loading functions for stream flow nutrients. *Water Res. Bull.* **23**, 471-478.
- Harrison, J., Seitzinger, S. Caraco, N. Bouwman, L. Beussen, A. and Vörösmarty, C. (2005a) Dissolved inorganic phosphorus export to the coastal zone: results from a new, spatially explicit, global model (NEWS-SRP). *Global Biogeochem. Cyc.*, **19**, GB4S03, doi:10.1029/2004GB002357.

- Harrison, J.H., Caraco, N.F. and Seitzinger, S.P. (2005b). Global patterns and sources of dissolved organic matter export to the coastal zone: results from a spatially explicit, global model, *Global Biogeochem. Cyc.*, **19**, GB4S04, doi:10.1029/2005GB002480.
- Harrison, J. A., Matson, P.A. and Fendorf, S. (2005c) Effects of a diel oxygen cycle on nitrogen transformations and greenhouse gas emission in a eutrophied, subtropical stream, *Aquatic Sciences*, doi:10.1007.s00027-005-0776-3, 1-8.
- Holmes, R. M., Peterson, B.J., Gordeev, V.V., Zhulidov, A.V., Meybeck, M., Lammers, R.B. and Vörösmarty, C.J. (2000). Flux of nutrients from Russian rivers to the Arctic Ocean: can we establish a baseline against which to judge future changes? *Water Resour. Res.* **36**, 2309-2320.
- Hopkinson, C.S. and Giblin, A.E. THIS BOOK. Nitrogen dynamics of salt marsh ecosystems.
- Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., and Zhao-Liang, Z. (1996). Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* **35**, 75-139.
- Howarth, R.W., Swaney, D., Boyer, E.W., Marine, R., Jaworski, N. and Goodale, C. (2006). The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. *Biogeochemistry*, DOI 10.1007/s10533-006-9010-1.

- Hussian, M., Grimvall, A., and Petersen, W. (2004). Estimation of the human impact on nutrient loads carried by the Elbe River. *Environ. Monit. Assess.* **96**, 15-33.
- Hwang, D.W, Kim, G., Lee, Y.W., and Yang, H.S. (2005). Estimating submarine inputs of groundwater and nutrients to a coastal bay using radium isotopes. *Mar. Chem.* **96**, 61-71.
- IPCC, Climate Change 2001: Synthesis Report. *A Contribution of Working Groups, I, II, and III to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press, pp. 398, 2001.
- Ittekkot, V. and Zhang, S. (1989) Pattern of particulate nitrogen transport in world rivers. *Global Biogeochem. Cyc.* **3**, 383-391.
- Johannes, R.E. (1980). The ecological significance of the submarine discharge of ground water. *Mar. Ecol. Prog. Ser.* **3**, 365-373.
- Johannes, R.E., and Hearn, C.J. (1985). The effect of subsurface groundwater discharge on nutrient and salinity regimes in a coastal lagoon off Perth, West Australia. *Estuar. Coast. Shelf Sci.* **21**, 789-800.
- Johnson K.S. and Coletti L.J. (2002) In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep-Sea Research Part I – Oceanographic Research Papers* **49** (7): 1291-1305.
- Jordan, T.E., and Weller, D.E. (1996), Human contributions to terrestrial nitrogen flux. *BioScience* **46**: 655-664.

- Jordan, T. E., Weller, D.E., and Correll, D.L. (2003). Sources of nutrient inputs to the Patuxent River Estuary. *Estuaries* **26**, 226-243.
- Kao, S.J. and Liu, K.K. (1996). Particulate organic carbon export from a subtropical mountainous river (Lanyang-Hsi) in Taiwan. *Limnol. Oceanogr.* **41**, 1749-1757.
- Kao, S.J., and Liu, K.K. 2000. Stable carbon and nitrogen isotope systematics in a human-disturbed watershed (Lanyang-Hsi) in Taiwan and the estimation of biogenic particulate organic carbon and nitrogen fluxes. *Global Biogeochemical Cycles* 14(1): 189-198.
- Koch, B.P., Witt, M.R., and Engbrodt, R. (2005). Molecular formulae of marine and terrigenous dissolved organic matter detected by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Geochem. Et Cosmochim Acta* **69**,3299-3308.
- Kratzer, C. R., Dileanis P.D., Zamora, C., Silva, S.R., Kendall, C., Bergamaschi, B.A., and Dahlgren, R.A. (2004). Sources and Transport of Nutrients, Organic Carbon, and Chlorophyll *a* in the San Joaquin River Upstream of Vernalis, California, during Summer and Fall, 2000 and 2001. 03-4127, 1-113. Sacramento, CA, U.S. Geological Survey. Water-Resources Investigation Reports.
- Krest, J.M., Moore, W.S., and Gardner, L.R. (2000). Marsh nutrient export supplied by groundwater discharge: Evidence from radium measurements. *Global Biogeochem. Cycl.* **14**, 167-176.

- Kroeze, C. and Seitzinger, S.P. (1998). Nitrogen inputs to rivers, estuaries and continental shelves and related nitrous oxide emissions in 1990 and 2050: a global model. *Nutr. Cycl. Agroecosys.* **52**, 195-212.
- Laursen, A. E. and Seitzinger, S.P. (2004). Diurnal patterns of denitrification, oxygen consumption and nitrous oxide production in rivers measured at the whole-reach scale. *Freshwater Biol.* **49**, 1448-1458.
- Lee, K.Y., Fisher, T.R., Jordan, T.E., Correll, D.L., and Weller, D.E. (1999). Modeling the hydrochemistry of the Choptank River basin using GWLF and Arc/Info: 1. Model calibration and validation. *Biogeochemistry* **00**, 1-31.
- Lesack, L.F.W., Hecky, R.E., and Melack, J.M. (1984). Transport of carbon, nitrogen, phosphorous and major solutes in the Gambia River, West Africa. *Limnol. Oceanogr.* **29**, 816-830.
- Lewis, W.M.Jr, Melack, J.M., McDowell, W.H., McClain, M., and Richey, J.E. (1999). Nitrogen yields from undisturbed watersheds in the Americas. *Biogeochemistry* **46**, 149-162.
- LOICZ, Biogeochemical Modeling Node, <http://data.ecology.su.se/MNODE>.
- Mace K. A., Duce, R. A., and Tindale, N. W. (2003). Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia, *J. Geophys. Res.*, 108 (D11), 4338, doi:10.1029/2002JD003051.

- Mackenzie, F.T., Ver, L.M., and Lerman, A. (1998). Coupled biogeochemical cycles of carbon, nitrogen, phosphorous and sulfur in the land-ocean-atmosphere system, p.42-100. *In* “Asian change in the context of global climate change” Galloway, J.N. and Melillo, J.M. [Eds.], Cambridge University Press.
- Mahaffey, C. Michaels, A.F., and Capone, D.G. (2005). The conundrum of marine N₂ fixation. *American Journal Science* **305**: 546-595.
- Martinetto, P., Teichberg, M., Valiela, I. (2006). Coupling of estuarine benthic and pelagic food webs to land-derived nitrogen sources in Waquoit Bay, Massachusetts, USA. *Mar. Ecol. Progr. Ser.* **307**, 37-48.
- Mayer, B., Boyer, E.W., Goodale, C., Jaworski, N.A., van Breemen, N., Howarth, R.W., Seitzinger, S.P., Billen, G., Lajtha, K., Nadelhoffer, K., Van Dam, D., Hetling, L.J., Nosil, M., Paustian, K. and R. Alexander. (2002). Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. *Biogeochemistry* 57/58:171-197.
- McBride, G.B., Alexander, R.B., Elliot, A.H., and Shankar, U. (2000). Regional scale modeling of water quality. *Water and Atmosphere*, 8: 29-31. National Institute of Water and Atmospheric Research (NIWA), Auckland, New Zealand.
- McClelland JW and Valiela I. (1998). Linking nitrogen in estuarine producers to land-derived sources. *Limnol. Oceanogr.* **43**, 577-585.
- McClelland, J.W., Holmes, R.M., Peterson, B.J. Stieglitz, M. (2004). Increasing river discharge in the Eurasian Arctic: Consideration of dams, permafrost thaw, and fires as potential agents of change. *J. Geophys. Res. – Atmos.* 109, Art. no. D18102.

- Meade, R.H. (1996). River-sediment inputs to major deltas. *In* “Sea-level rise and coastal subsidence,” Milliman, J.D., Haq, B.U. [Eds.], Kluwer Academic Publishing, Dordrecht, pp. 63-85.
- Meybeck, M. (1982). Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci.* **282**, 401-450.
- Meybeck, M. (2003). Global analysis of river systems: from Earth system controls to Anthropocene syndromes. *Phil. Trans. R. Soc. London*, online DOI 10.1098/rstb.2003.1379.
- Meybeck, M.M. and Ragu, A. (1995). GEMS/Water contribution to the global register of river inputs, *GEMS/Water Programme (UNEP/WHO/UNESCO)*. World Health Organization, Geneva, Switzerland.
- Milliman, J.D., and Meade, R.H. (1983). Worldwide delivery of river sediment to the oceans. *J. Geol.* **100**, 525-544.
- Moore, W.S., Krest, J., Taylor, G., Roggenstein, E., Joye, S., Lee, R. (2002). Thermal evidence of water through a coastal aquifer: Implications for nutrient fluxes. *Geophys. Res. Lett.* **29**, art. 1704.
- Moser, F.C. (1997). Sources and sinks of nitrogen and trace metals, and benthic macrofauna assemblages in Barnegat Bay, New Jersey. Dissertation submitted to the Graduate School, Environmental Science – New Brunswick, Rutgers, The State University of New Jersey.
- National Inventory of Dams, <http://crunch.tec.army.mil/nid/webpages/nid.cfm>.

- Nixon, S.W. (1995). Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* **41**, 199-219.
- Nixon, S.W., Ammerman, J.W., Atkinson, L.P., Berounsky, V.M., Billen, G., Boicourt, W.C., Boynton, W.R., Church, T.M., Ditoro, D.M., Elmgren, R., Garber, J.H., Giblin, A.E., Jahnke, R.A., Owens, N.J.P., Pilson, M.E.Q., and Seitzinger, S.P. (1996). The fate of nitrogen and phosphorous at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry* **35**, 141-180.
- Nixon, S.W. (2003). Replacing the Nile: are anthropogenic nutrients providing the fertility once brought to the Mediterranean by a great river? *Ambio* **32**, 30-39.
- Nowicki, B.L., Requintina, E., Van Keuren, D., Portnoy, J. (1999). The role of sediment denitrification in reducing groundwater-derived nitrate inputs to Nauset Marsh estuary, Cape Cod, Massachusetts. *Estuaries*, **22**, 245-259.
- NRC. (2000). Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution. Washington, D.C., USA: *National Academy of Sciences*.
- Oberdorfer, J.A., Valentino, M.A., Smith, S.V. (1990). Groundwater contribution to the nutrient budget of Tomales Bay, California. *Biogeochem.* **10**, 199-216.
- Paerl, H.W. (1985). Enhancement of marine primary production by nitrogen-enriched acid rain. *Nature* **316**, 747-749.
- Paerl, H.W. (1988). Nuisance phytoplankton blooms in coastal, estuarine, and inland waters. *Limnol. Oceanogr.* **33**, 823-847.

- Paerl, H.W., Piehler, M.F., Valdes, L.M., Dyble, J., Moisaner, P.H., Pinckney, J.L. and Steppe, T.F. (2005). Determining anthropogenic and climatically-induced change in aquatic ecosystems using microbial indicators: An integrative approach. *Verh. Internat. Verein. Limnol.* **29**, 89-133.
- Paerl, H.W. and Piehler, M.F., (Submitted 2006). Nitrogen and marine eutrophication. Chapter *In* “Nitrogen in the marine environment,” Capone, D. Carpenter, E. Bronk, D. and Mulholland, M. [Eds.], Academic Press.
- Peierls, B.L. and Paerl, H.W. (1997). The bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton. *Limnol. Oceanogr.* **42**, 1819-1880.
- Peierls, B.L., Caraco, N.F., Pace, M.L., and Cole, J.J. (1991). Human influence on river nitrogen. *Nature* **350**, 386-387.
- Peterson, B.J., Holmes, R.M., McClelland, J.W., Vorosmarty, C.J., Lammers, R.B., Shiklomanov, A.I., Shiklomanov, I.A., and Rahmstorf, S. (2002). Increasing river discharge to the Arctic Ocean. *Science*, **298**, 2171-2173.
- Prospero, J.M., Barrett, K., Church, T., Dentener, F., Duce, R.A., Galloway, J.N., Levy II, H., Moody, J., and Quinn, P. (1996). Atmospheric deposition of nutrients to the North Atlantic Basin, pp. 27-74 *In* “Nitrogen cycling in the North Atlantic Ocean and its watersheds: report of the international SCOPE project.” Howard, R.W., [Ed.], Kluwer Academic Publishers, Dordrecht and Boston.
- Rabalais, N.N. (2002). Nitrogen in aquatic ecosystems. *Ambio* **31**, 102-112.

- Rutkowski, C.M., Burnett, W.C., Iverson, R.L., Chanton, J.P. (1999). The effect of groundwater seepage on nutrient delivery and seagrass distribution in the northeastern Gulf of Mexico. *Estuaries* **22**, 1033-1040.
- Seitzinger, S.P. and A.E. Giblin. (1996). Estimating denitrification in North Atlantic continental shelf sediments. *Biogeochemistry* **35**, 235-259.
- Seitzinger, S. P., and Kroeze, C. (1998). Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. *Global Biochem.Cyc.* **12**, 93-113.
- Seitzinger, S. P. and R. W. Sanders. (1999). Atmospheric inputs of dissolved organic nitrogen stimulate estuarine bacteria and phytoplankton. *Limnol. Oceanogr.* **44**, 721-730.
- Seitzinger, S.P., Sanders, R.W. and Styles, R.V. (2002a). Bioavailability of DON from natural and anthropogenic sources to estuarine plankton, *Limnol. and Oceanogr.* **47**, 353-366.
- Seitzinger, S.P., Kroeze, C., Bouwman, A.F., Caraco, N., Dentener, F. and Styles, R.V. (2002b). Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections, *Estuaries* **25**, 640-655.
- Seitzinger, S.P., Styles, R.V., Boyer, E.W., Alexander, R.B., Billen, G., Howarth, R., Mayer, B., and van Breemen, N. (2002c). Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. *Biogeochemistry* **57**, 199-237.

- Seitzinger, S.P., H. Hartnett, R. Lauck, M. Mazurek, T. Minegishi, G. Spyres, and R. Styles. (2005a). Molecular level chemical characterization and bioavailability of dissolved organic matter in streamwater using ESI mass spectrometry. *Limnology & Oceanography* **50(1)**:1-12.
- Seitzinger, S. P., Harrison, J.A., Dumont, E., Beusen, A.H.W., and Bouwman, A.F. (2005b), Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, *Global Biogeochem. Cyc.*, **19**, GB4S01, doi:10.1029/2005GB002606.
- Seitzinger, S.P., J. Harrison, J. Böhlke, A. Bouwman, R. Lowrance, B. Peterson, C. Tobias, G. Van Drecht. (2006). Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications*, **16(6)**, 2064-2090..
- Slomp, C.P., and Van Capellen, P. (2004). Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *J. Hydrol.* **295**, 64-86.
- Smith, R.A., Schwartz, G.E, and Alexander, R.B. (1997). Regional interpretation of water-quality monitoring data. *Wat. Resour.Res.* **33**: 2781-2798.
- Smith, S.V., Renwick, W.H., Buddemeier, R.W., and Crossland, C.J. (2001). Budgets of soil erosion and deposition for sediments and sedimentary organic carbon across the conterminous United States. *Global Biogeochem.Cyc.***15**, 697-707.

- Smith, S.V., Swaney, D.P., Talaue-Mcmanus, L., Bartley, J.D., Sandhei, P.T., McLaughlin, C.J., Dupra, V.C., Crossland, C.J., Buddemeier, R.W., Maxwell, B.A., and Wulff, F. (2003). Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean. *Bioscience* **53**, 235-245.
- Srinivasan, R., Arnold, J.G., Muttiah, R.S., Walker, D., and Dyke, P.T. (1993). Hydrologic unit modeling of the United States (HUMUS). In "Advances in Hydro-Science and Engineering, Vol. I Part A," Yang, S. [Ed.] pp. 451-456. Washington, D.C., USA.
- Stålnacke, P., Grimvall, A., Sundblad, K., and Wilander, A. (1999). Trends in nitrogen transport in Swedish rivers. *Environ. Monit. Assess.* **59**, 47-72.
- Stålnacke, P., Grimvall, A., Libiseller, C., Laznik, M., and Kokorite, I. (2003). Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *J. Hydrol.* **283**: 184-205.
- Stålnacke, P., (2005). Time scale in nutrient fate: examples from Eastern Europe. In: Proceedings of international workshop, "Where do fertilizers go?" ISPRA, Italy.
- Syvitski, J.P.M., Vörösmarty, C.J., Kettner, A.J., and Green, P. (2005). Impact of humans on the flux of terrestrial sediment to the global coastal ocean. *Science* **308**, 376-380.
- SWAT. (2002). Soil and water assessment tool (SWAT) user's manual: version 2000, TWRI Report. Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Srinivasan, R. and Williams, J.R. [Eds]. Texas Water Resources Institute, College Station, TX: TR-192:1-472.

- Timperley, M.H., Vigor-Brown, R.J., Kawashima, M., Ishigami, M. (1985). Organic nitrogen compounds in atmospheric precipitation: their chemistry and availability to phytoplankton. *Can. J. Fish Aquat. Sci.* **42**, 1171-1177.
- Turner, R.E., Qureshi, N., Rabalais, N.N., Dortch, Q., Justic, D., Shaw, R.F., Cope, J. (1998). Fluctuating silicate: nitrate ratios and coastal plankton food webs, *Proceedings of the National Academy of Sciences of the United States of America* **95**, 13048-51.
- Uchiyama, Y., Nadaoka, K., Roelka, P., Adachi, K., and Yagi, H. (2000). Submarine groundwater discharge into the sea and associated nutrient transport in a sandy beach. *Water Resour. Res.* **36**, 1467-1479.
- Umezawa, Y., Miyajima, T., Kayanne, H., and Koike, I. (2002). Significance of groundwater nitrogen discharge into coral reefs at Ishigaki Island, southwest of Japan. *Coral Reefs* **21**, 346-356.
- UNEP/MAP/MED POL. (2003). Riverine transport of water, sediments and pollutants to the Mediterranean Sea. MAP Technical Reports Series. Athens: United Nations Environment Programme-Mediterranean Action Plan. **141**, 1-111.
- United Nations (1996). Country population statistics and projections 1950-2050, Report, *Food and Agricultural Organization of the United Nations*, Rome, Italy, 1996.
- Valiela, I. and D'Elia, C. (1990). Groundwater inputs to coastal waters. Special Issue *Biogeochemistry* **10**, 328.

- Valiela, I., Costa, J., Foreman, K., Teal, J.M., Howes, B., and Aubrey, D. (1990).
Transport of groundwaterborne nutrients from watersheds and their effects on
coastal waters. *Biogeochemistry* **10**,177-197.
- Valiela, I., McClelland, J., and Hauxwell, J. (1997). [Macroalgal blooms in shallow
estuaries: Controls and ecophysiological and ecosystem consequences](#)
Limnol. Oceanogr. **42**,1105-1118.
- Valiela, I., Geist, M., McClelland, J. and Tomasky, G. (2000). Nitrogen loading from
watersheds to estuaries: Verification of the Waquoit Bay Nitrogen Loading
Model, *Biogeochemistry* **49**, 277-293.
- Valiela, I., Bowen, J.L., and Kroeger, K.D. (2002). Assessment of models for estimation
of land-derived nitrogen loads to shallow estuaries. *Appl. Geochem.* **17**, 935-953.
- Valigura, R.A., Alexander, R.B., Castro, M.S., Meyers, T.P., Paerl, H.W., Stacey, P.E.,
and Turner, R.E. [Eds.] (2001). In “Nitrogen loading in coastal water bodies: An
atmospheric perspective.” American Geophysical Union, Washington, D.C.,
USA.
- Van Drecht, G., Bouwman, A.F., Knoop, J.M., Beusen, A.H.W., and Meinardi, C.R.
(2003). Global modeling of the fate of nitrogen from point and non-point sources
in soils, groundwater, and surface water. *Global Biogeochem. Cycl.* **17**, 1115,
doi:10.1029/2003GB002060.

- Van Drecht, G., A.F. Bouwman, E.W. Boyer, P. Green, and S. Siebert. (2005). A comparison of global spatial distributions of nitrogen inputs for nonpoint sources and effects on river nitrogen export. *Global Biogeochem. Cyc.*, **19**, GB4S06, doi:10.1029/2005GB002454.
- Vitousek, P.M. and Matson, P.A. (1993). Agriculture, the global nitrogen cycle, and trace gas flux. In "The biogeochemistry of global change: radiative trace gases." Oremland, R.S. [Ed.], Chapman and Hall, New York, pp 193-208.
- Vörösmarty, C.J., Feteke, B., Meybeck, M., and Lammers, R.B. (2000). Global system of rivers: its role in organizing continental land mass and defining land-to-ocean linkages. *Global Biogeochem. Cyc.* **14**, 599-621.
- Vörösmarty, C.J., Meybeck, M., Feteke, B., Sharma, K., Green, P., and Syvitski, J.P.M. (2003). Anthropogenic sediment retention: major global impact from registered river impoundments, *Global and Planetary Change*, **39**, 169-190.
- Whitall, D.R., and Paerl, H.W. (2001). Atmospheric pollutants and trace gases: spatiotemporal variability of wet atmospheric nitrogen deposition to the Neuse River Estuary, North Carolina. *J. Environ. Qual.* **30**, 1508-1515.
- Wollast, R. (1983). Interaction in estuaries and coastal waters, Chapter 14 In: B. Bolin and R.B. Cook [Eds.] The major biogeochemical cycles and their interactions, SCOPE (Scientific Committee on Problems of the Environment), John Wiley and Sons, UK.
- World Commission on Dams. (2000). Dams and dam development: a new framework for decision-making. Earthscan, London, UK.

Yan, W.J., Zhang, S., Sun, P., and Seitzinger, S.P. (2003). How do nitrogen inputs to the Changjiang basin impact the Changjiang River nitrate: A temporal analysis for 1968-1997. *Global Biogeochem. Cycl.* **17**, 1091-1100.

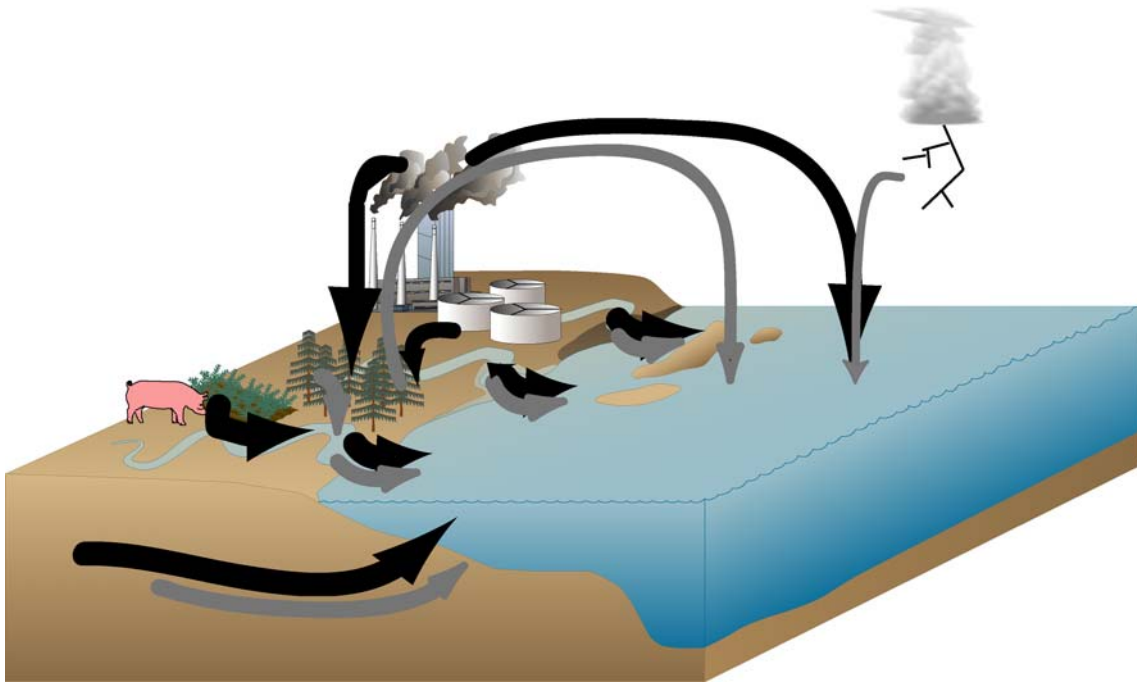


Figure 1. Land-based sources of N to coastal and marine waters from natural (grey arrows) and anthropogenic (black arrows) sources. Sources of N that contribute to river N export are represented including non-point inputs from atmospheric deposition from natural sources (soil emissions and lightning) and fossil fuel combustion, non-agricultural and agricultural biological N_2 -fixation, and synthetic fertilizer and livestock manure; point sources include wastewater treatment facilities. Some portion of watershed N inputs can enter coastal regions directly with submarine groundwater discharge. Atmospheric deposition directly to the surface of coastal and oceanic waters also is a transport pathway of land-based N. Figure created using the IAN symbol library (ian.umces.edu).

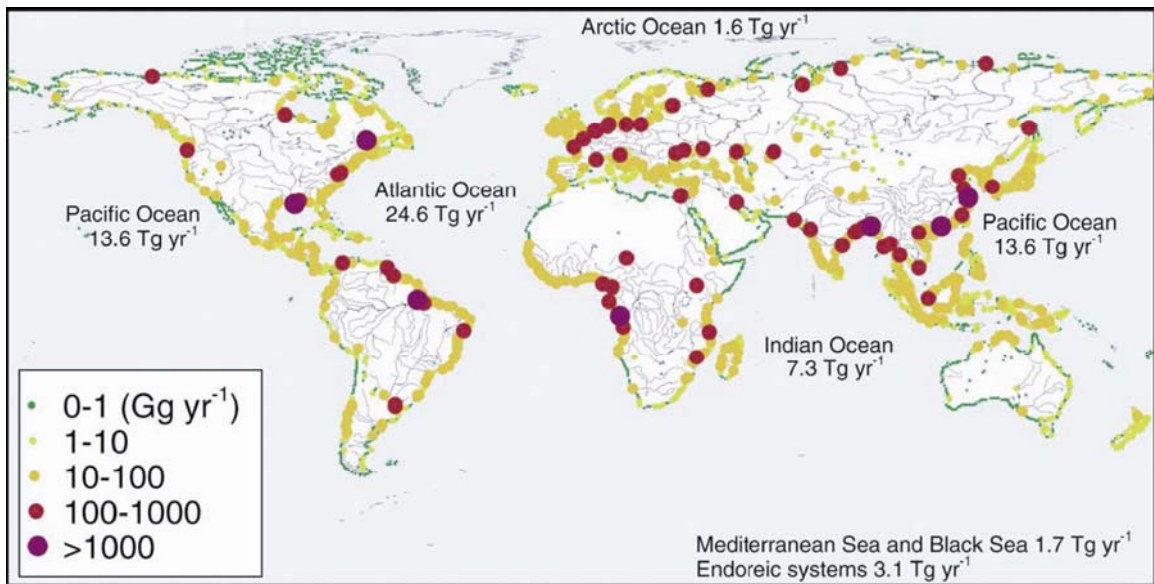


Figure 2 . Modeled river TN export to coastal areas from Van Drecht et al. (2003). Gg = 10^9 g and Tg = 10^{12} g.

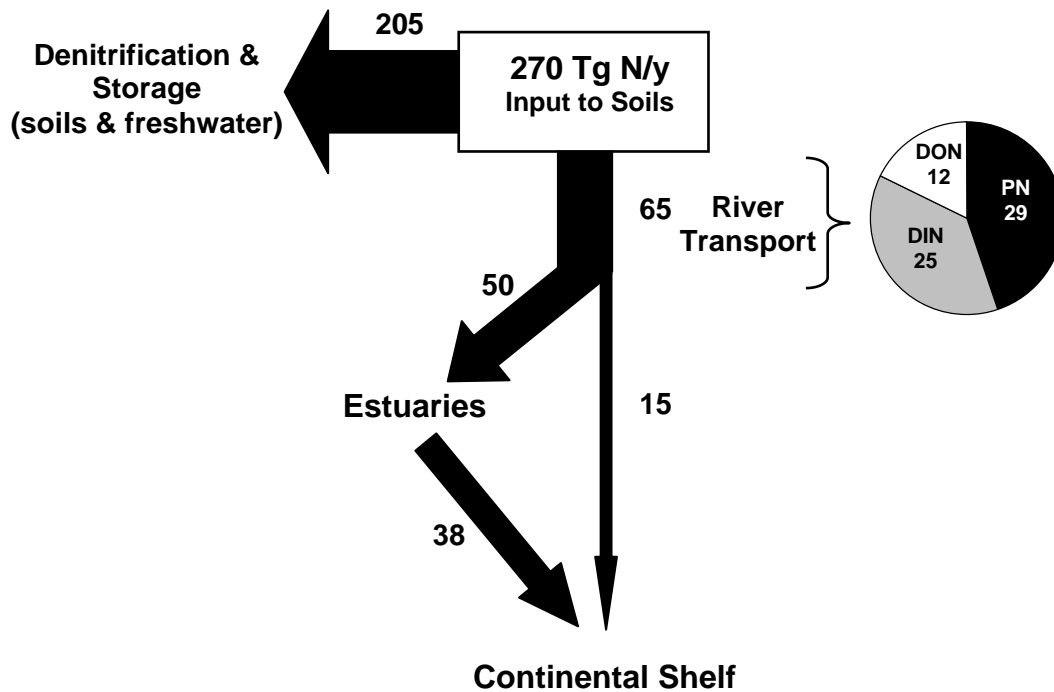


Figure 3. Globally, approximately 270 Tg of newly fixed N enters terrestrial soils each year from biological N₂-fixation (natural and agricultural), lightning, combustion of fossil fuels (leading to increased atmospheric N deposition), and synthetic fertilizer use as of the mid-1990's (Galloway et al. 2004). According to NEWS-model-predictions, 65 Tg N y⁻¹ of the N entering soils is exported by rivers to coastal systems as DIN, DON and PN [Dumont et al., 2005; Harrison et al., 2005b; Beusen et al., 2005]. We estimate that ~15 Tg of the river N is discharged by large rivers directly to the continental shelves. The other 50 Tg of river N enters estuaries, of which ~38 Tg is then exported to continental shelves. Units: Tg N/y (Tg = 10¹² g)

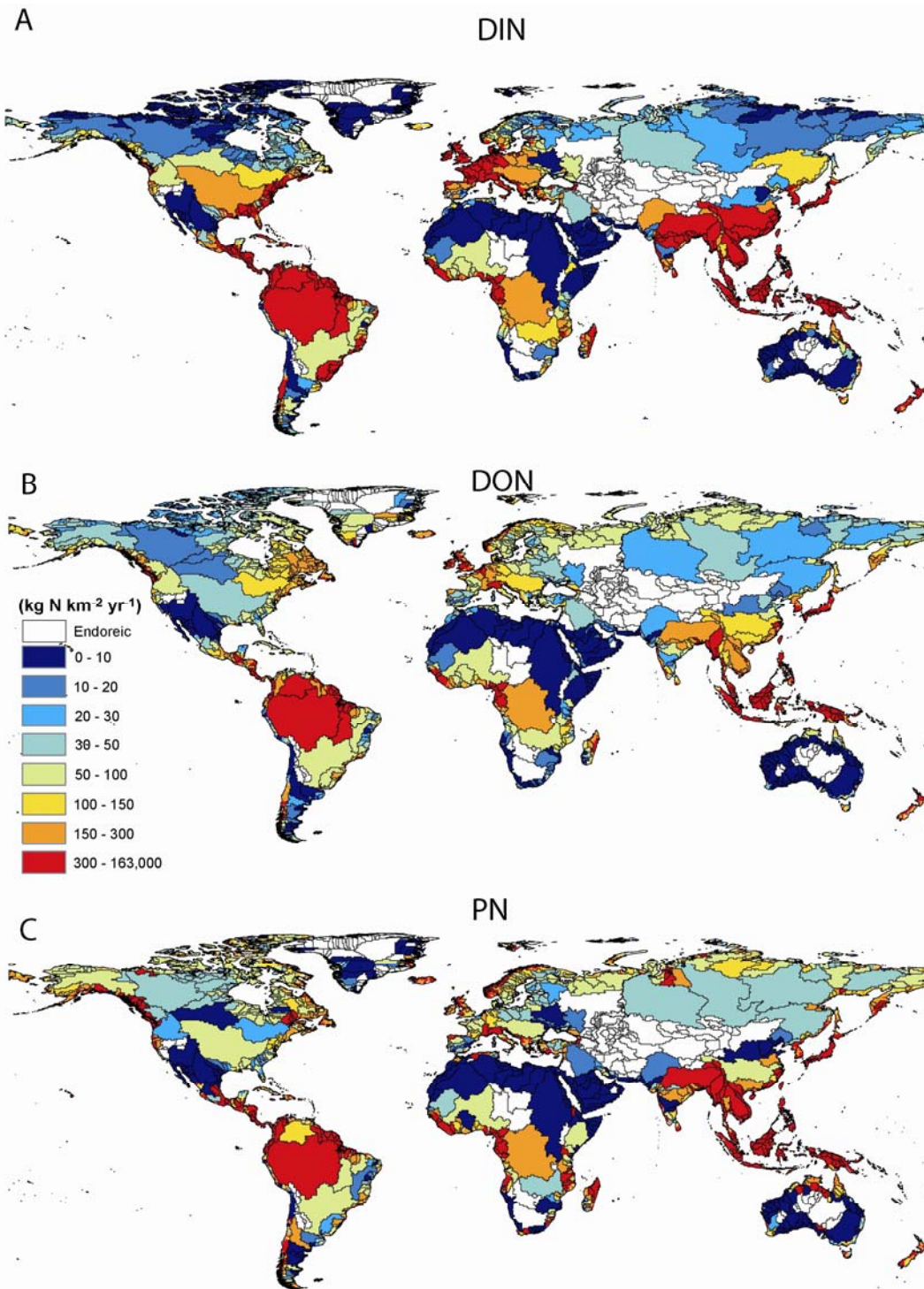


Figure 4. NEWS-model-predicted A) DIN, B) DON, and C) PN yield ((kg N km⁻² yr⁻¹) for 0.5 x 0.5 degree (latitude x longitude) or larger river basins globally for mid-1990's conditions. Model output replotted from Harrison et al., 2005b, Dumont et al., 2005, and Beusen et al., 2005.

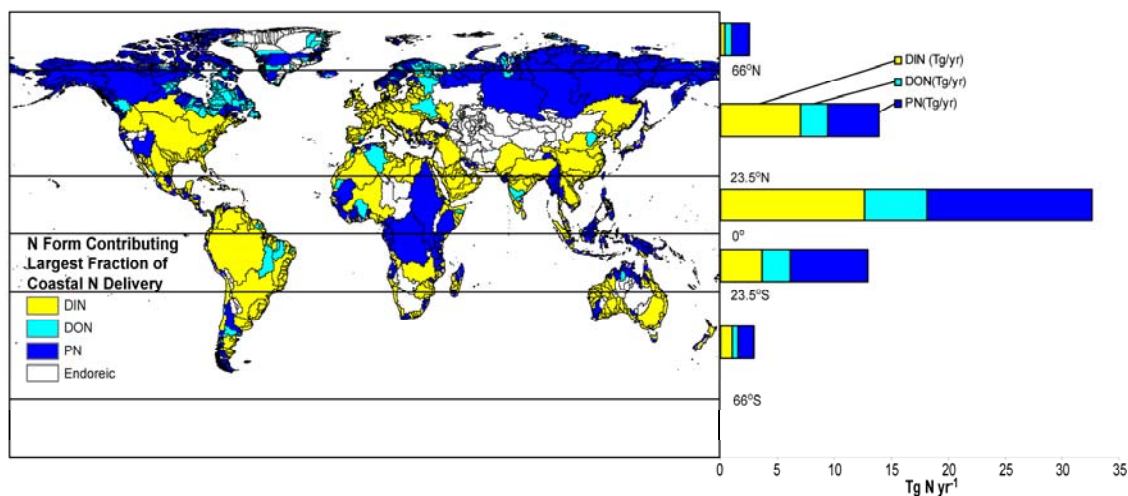


Figure 5. DIN, DON, and PN export to the coastal zone by latitude (mid-1990's). Dominant forms are shown by basin in map, and magnitudes of coastal TN export are represented by size of bars to right of map. Global map has been slightly distorted to make room for bar graph to right. Model predictions taken from Beusen et al., 2005, Dumont et al., 2005, and Harrison et al., 2005b.

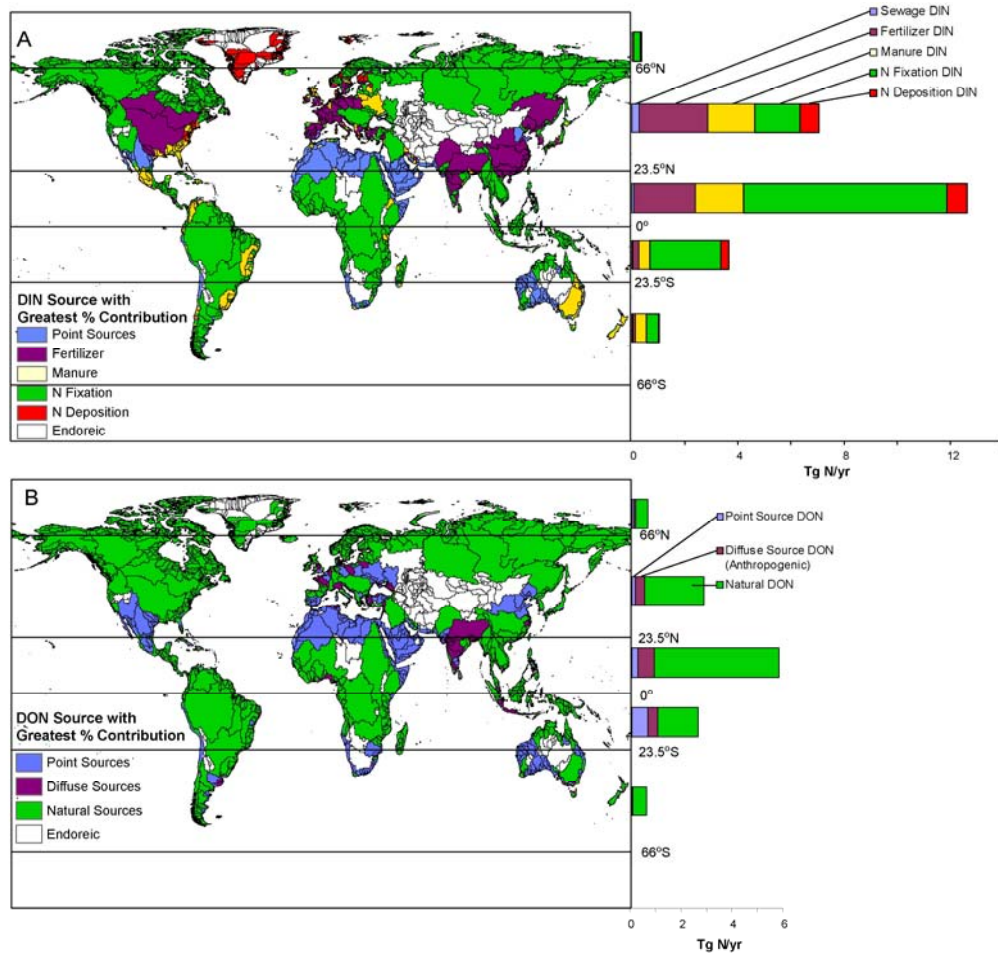


Figure 6. Dominant sources of N to the coastal zone by 0.5x 0.5 degree or larger basin and relative contributions of sources of exported DIN and DON by latitude band as predicted by NEWS-DIN (A) and NEWS-DON (B). Global maps have been compressed horizontally to fit both map and bar graph in same figure. For actual values of predicted DIN and DON, see Tables 3 and 4. Model predictions have been reprocessed from Harrison et al., 2005b and Dumont et al., 2005.

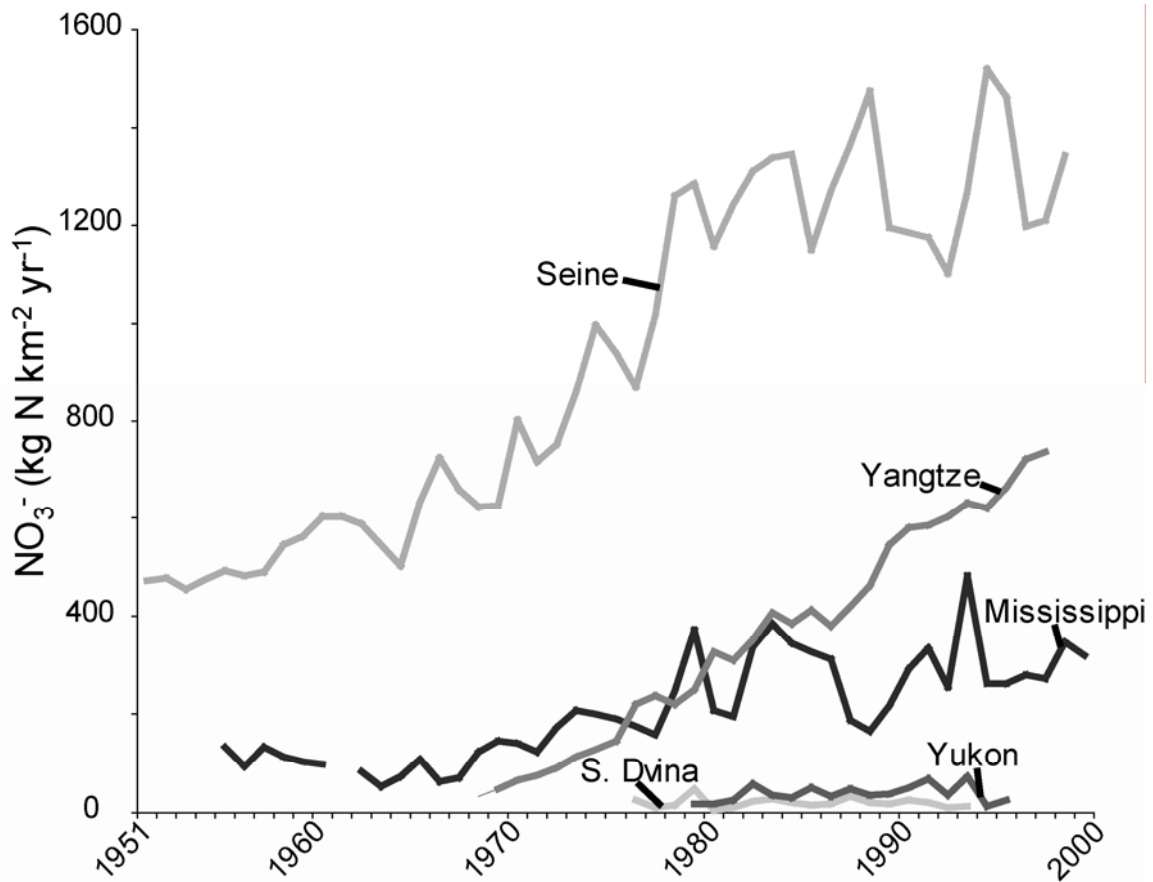


Figure 7. NO₃⁻ yield (kg N km⁻² yr⁻¹) trends for three human-impacted rivers (Seine, Mississippi, and Yangtze), and two relatively non-impacted rivers (Severnaya Dvina and Yukon). (Billen et al., 2001; Yan et al., 2003; Goolsby and Battaglin., 2001; Alexander et al., 1996; Holmes et al., 2000)

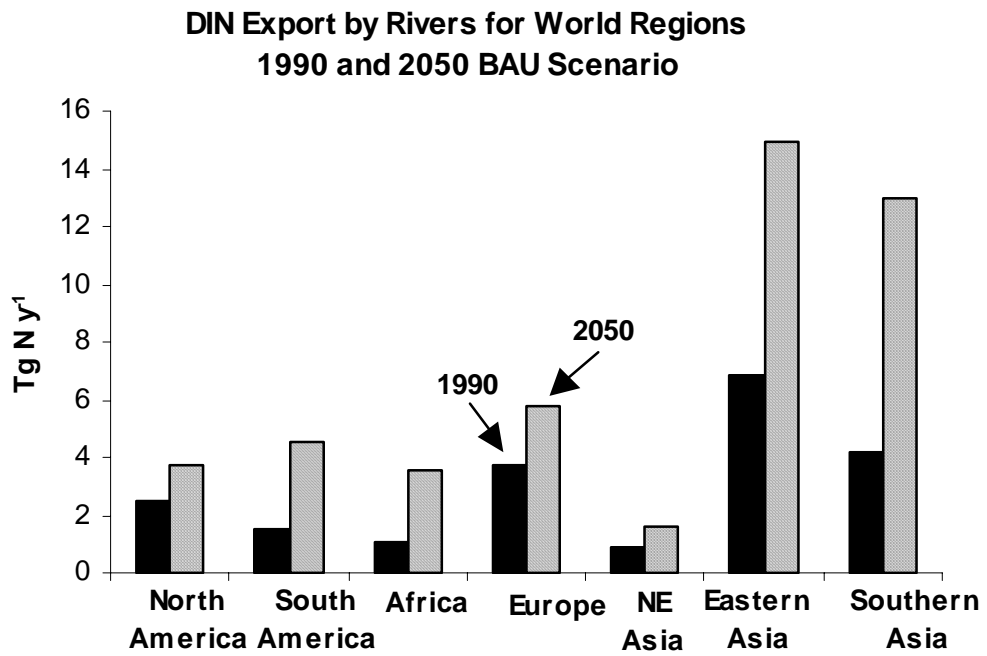


Figure 8. Predicted increases in DIN export to coastal systems between the years 1990 and 2050 under a business-as-usual (BAU) scenario. Modified from Kroeze and Seitzinger (1998).

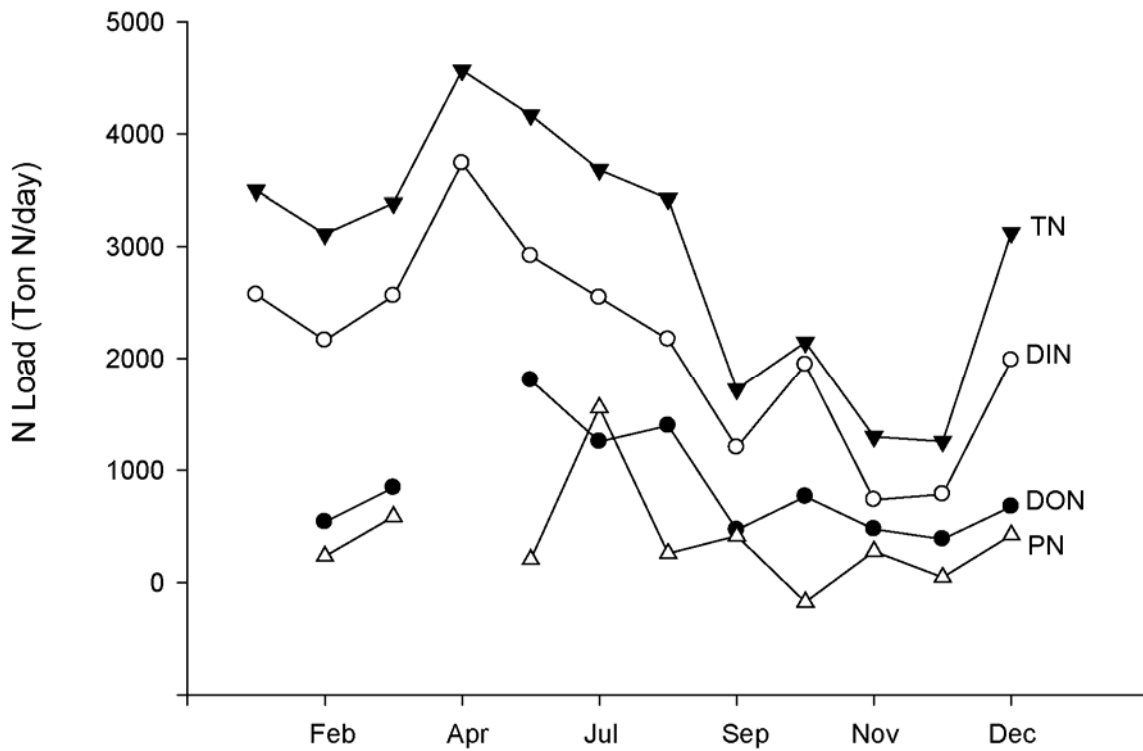


Figure 9. Mean annual N load for the Mississippi River at Belle Chase, LA (1979-1981), by N form, including total nitrogen (closed triangles), dissolved inorganic nitrogen (open circles), dissolved organic nitrogen (closed circles), and particulate nitrogen (open triangles) (Alexander, et. al., 1996). Units: metric Ton N/day

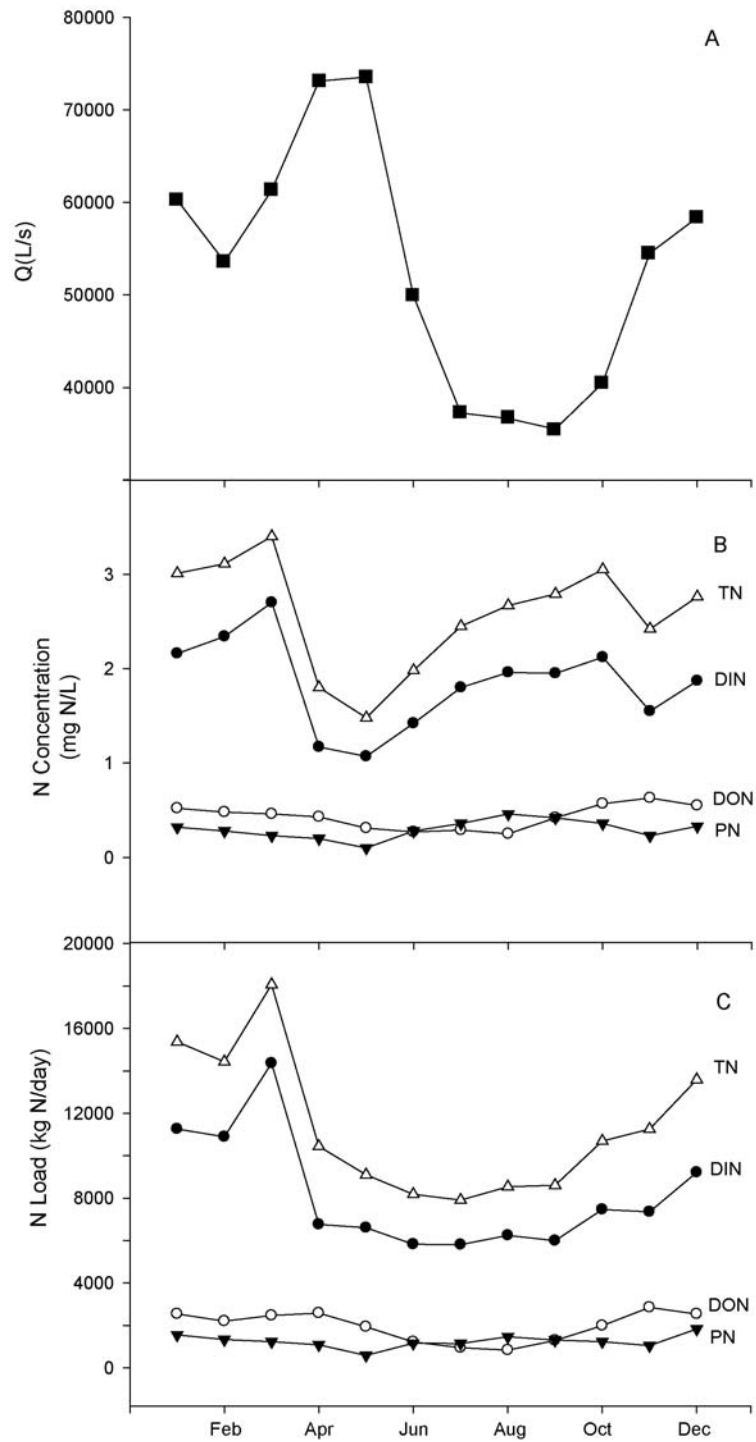


Figure 10. Seasonal discharge and N dynamics in the San Joaquin River (California, USA). Monthly average discharge (A), DIN (closed circles), DON (open circles), TN (open triangles), and PN (closed, inverted triangles) concentrations (B) and loads (C) are shown. Data from 2001-2002, (Kratzer et al., 2004).

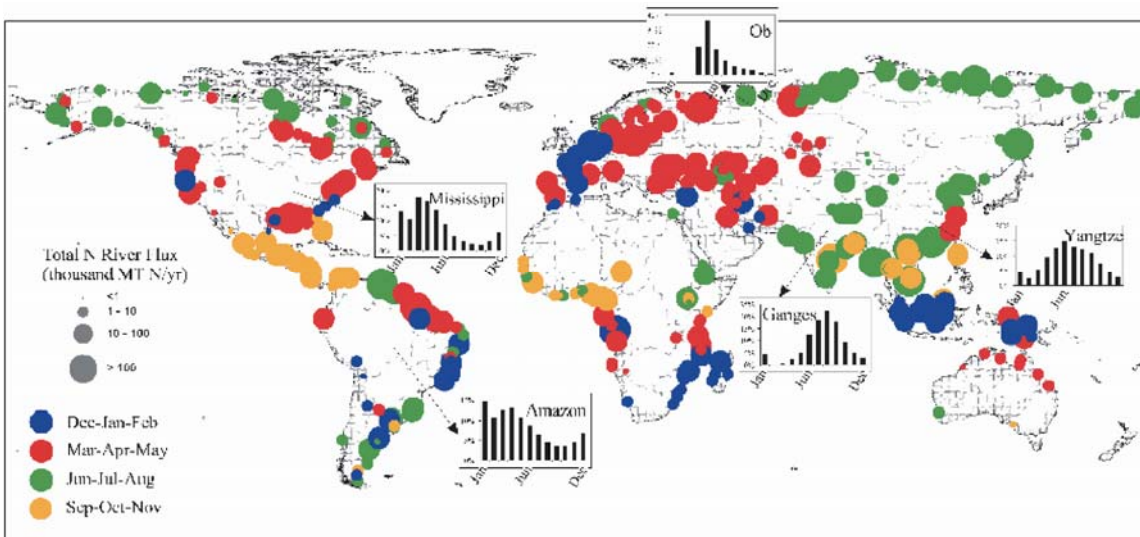


Figure 11. Global seasonal patterns of N export as predicted using hydrology alone. Hydrographs of five large, representative rivers are shown. Reprinted with permission from Green et al. (2004)

Table 1. The largest 25 rivers (in order of decreasing annual discharge; Milliman and Meade 1983; Meade 1996), river watershed areas, river discharge estimates, and NEWS-model-estimated DIN, DON, PN, and TN. Total exports from the 25 largest rivers and the percent of total global export for which these rivers account are also shown. Tg = 10¹² g

River Name	Receiving Ocean	Watershed Surface Area 10 ⁶ (km ²)	Q (km ³ /yr)	DIN (Tg N/basin/yr)	DON (Tg N/basin/yr)	PN (Tg N/basin/yr)	TN (Tg N/basin/yr)
Amazon	Atlantic Ocean	5.88893	6300	3.43	1.89	2.75	8.07
Zaire	Atlantic Ocean	3.73374	1250	0.82	0.68	0.82	2.32
Orinoco	Atlantic Ocean	1.03931	1200	0.50	0.48	0.15	1.13
Ganges	Indian Ocean	1.62681	970	2.17	0.32	1.29	3.78
Chang Jiang	Pacific Ocean	1.79304	900	1.05	0.16	0.14	1.35
Yenisei	Arctic Ocean	2.62072	630	0.07	0.08	0.11	0.26
Mississippi	Atlantic Ocean	3.20312	530	0.57	0.08	0.17	0.82
Lena	Arctic Ocean	2.50029	510	0.04	0.05	0.11	0.20
Parana	Atlantic Ocean	2.71483	470	0.26	0.19	0.16	0.61
Mekong	Pacific Ocean	0.757852	470	0.35	0.14	0.34	0.83
St. Lawrence	Atlantic Ocean	1.05277	450	0.15	0.14	0.03	0.32
Irrawaddy	Indian Ocean	0.40554	430	0.21	0.13	0.37	0.72
Ob	Arctic Ocean	3.10111	400	0.13	0.07	0.13	0.33
Amur	Pacific Ocean	1.79413	325	0.25	0.05	0.08	0.38
Mackenzie	Arctic Ocean	1.71057	310	0.03	0.03	0.07	0.13
Zhujiang	Pacific Ocean	0.408123	300	0.32	0.05	0.07	0.45
Salween	Indian Ocean	0.272866	300	0.06	0.03	0.09	0.18
Columbia	Pacific Ocean	0.731473	250	0.06	0.04	0.02	0.12
Indus	Indian Ocean	1.14155	240	0.19	0.02	0.02	0.23
Magdalena	Atlantic Ocean	0.251789	240	0.21	0.07	0.13	0.40
Zambezi	Indian Ocean	1.36377	220	0.14	0.09	0.06	0.29
Danube	Black Sea	0.787291	210	0.18	0.06	0.06	0.30
Yukon	Pacific Ocean	0.895236	195	0.02	0.03	0.05	0.10
Niger	Atlantic Ocean	2.23885	190	0.16	0.12	0.13	0.41
Purari	Pacific Ocean	0.0337825	150	0.02	0.01	0.03	0.07
<i>Total</i>		42.96	17440	11.38	5.02	7.41	23.81
<i>Total as Percent of Global Total</i>		38	47	48	46	27	38

Table 2. DIN, PN, DON, total N (TN) export (Tg N yr^{-1}) by rivers, and exoreic land surface area (10^6 km^2) for tropical (0° - 23.5°), temperate (23.5° - 66°), and polar (66° - 90°) latitude bands and global totals, based on Global NEWS model predictions for mid-1990's. For spatially explicit representation of data, see Figures 4 and 5.

Latitude Band	DIN (Tg N/yr)	DON (Tg N/yr)	PN (Tg N/yr)	Total N (Tg/yr)	Surface Area (10^6 km^2)
Arctic (66°N - 90°N)	0.4	0.6	1.6	2.5	17.0
North Temperate (23.5°N - 66°N)	7.0	2.8	4.5	13.9	43.8
North Tropical (0° - 23.5°N)	12.6	5.7	14.5	32.6	27.6
South Tropical (0° - 23.5°S)	3.7	2.5	6.8	12.9	15.0
South Temperate (23.5° S- 66°S)	1.0	0.6	1.4	2.9	10.8
<i>Totals</i>	<i>24.8</i>	<i>12.1</i>	<i>28.6</i>	<i>64.9</i>	<i>114.1</i>

Table 3. DIN sources: contribution of N sources in watersheds to the global DIN export by rivers by latitude bands and global total, as predicted by Global NEWS models for mid-1990's. Units: Tg N yr⁻¹

Latitude Band	Sewage DIN (Tg N/yr)	Fertilizer DIN (Tg N/yr)	Manure DIN (Tg N/yr)	N ₂ -Fixation DIN (Tg N/yr)	N Dep DIN (Tg N/yr)
Northern Polar (66°N -90°N)	0.01	0.01	0.04	0.25	0.05
Northern Temperate (23.5°N -66°N)	0.28	2.59	1.76	1.72	0.70
Northern Tropical (0°-23.5°N)	0.09	2.31	1.82	7.65	0.78
Southern Tropical (0° -23.5°S)	0.03	0.24	0.43	2.67	0.29
Southern Temperate (23.5° S-66°S)	0.03	0.11	0.41	0.45	0.05
<i>Totals</i>	0.44	5.26	4.46	12.74	1.87

Table 4. DON sources: contribution of N sources in watersheds to the global DON export by rivers by latitude bands and global total, as predicted by Global NEWS models, for mid-1990's. Units: Tg N yr⁻¹

Latitude Band	Point Source DON (Tg N/yr)	Diffuse Source DON (Tg N/yr)	Natural DON (Tg N/yr)
Northern Polar (66°N -90°N)	0.07	0.07	0.46
Northern Temperate (23.5°N -66°N)	0.13	0.35	2.28
Northern Tropical (0°-23.5°N)	0.23	0.63	4.79
Southern Tropical (0° -23.5°S)	0.61	0.38	1.55
Southern Temperate (23.5° S-66°S)	0.02	0.01	0.54
<i>Totals</i>	<i>1.06</i>	<i>1.44</i>	<i>9.62</i>

Table 5. Comparison of estimated N fluxes through submarine groundwater discharge (SGD) relative to river fluxes (modified from Slomp and Van Cappellen, 2004). Sites with relatively large SGD inputs relative to river inputs were specifically selected for this table.

Location	SGD N: river N	Reference
Coastal bays, New England	2:1 to 32:1	Valiela et al. (1990)
Perth Region, West Australia	3:1 to 5:1	Johannes (1980) and Johannes and Hearn (1985)
Kahana Bay, Hawaii	2:1	Garrison et al. (2003)
Florida Bay	~1: ~1	Corbett et al. 1999
Turkey Pt., St. Joseph Bay, Florida	1:1	Rutkowksi et al. (2000)
S. Carolina, salt marsh input	1:1	Krest et al. (2000)
S. Carolina, incl. offshore input	3.6:1	Moore et al. (2002)
Tomales Bay, CA, summer	7:1	Oberdorfer et al. (1990)
Tomales Bay, CA, winter	1:3.4	Oberdorfer et al. (1990)
Kashima Sea, Japan	1:420	Uchiyama et al. (2000)
Yeoja Bay, Korea	14:1	Hwang et al. 2005
Barnegat Bay, NJ	1:7	Moser 1997

Table 6. Proportion (as a percent) of N inputs to estuaries, bays and continental shelves from atmospheric deposition *directly to the water surface* compared to river plus atmospheric inputs. For open ocean regions atmospheric deposition is calculated as a percent of biological N₂-fixation plus atmospheric deposition, assuming river N inputs are removed within coastal and shelf sediments. For continental shelves the range includes uncertainties in river N inputs; for open ocean estimates, the range is that calculated with and without including DON in rainwater. See Fig. 6 for the contribution of atmospheric deposition in watersheds to river N export.

Receiving Waters	Percent Direct Atmospheric N to Water Surface	Reference
Estuaries and Bays		
Narragansett Bay, RI ^{1,2}	5%	Nixon 1995
Barnegat Bay, NJ ^{2,3}	40%	Moser 1997
Chesapeake Bay ^{1,4}	8%	Castro et al. 2001
Casco Bay, ME ^{1,4}	22%	Castro et al. 2001
Buzzards Bay ^{1,4}	19%	Castro et al. 2001
St. Catherine-Sapelo, GA ^{1,4}	37%	Castro et al. 2001
Tampa Bay, FL ^{1,4}	4%	Castro et al. 2001
Neuse River Estuary, NC ^{2,3}	5%	Whitall and Paerl 2001
Continental Shelves		
Global shelves ^{1,5}	17%	Seitzinger et al. 2006; This chapter
North Atlantic Shelf ^{1,5}		
Western 45°-66° N	29-50%	Nixon et al. 1996;
20°-45°	17-21%	Prospero et al. 1996
0°-20°	5 (incl. Amazon)	
Eastern 45°-66° N	40-55%	
20°-45°	17-29%	
0°-20°	3-5%	
Open Ocean	17-51%	This chapter
Global Coastal and Open Ocean	15-42%	This chapter

¹Wet & dry deposition; ²Inorganic and organic N; ³Wet deposition only; ⁴Nitrate only; ⁵Inorganic only

Appendix 1. DIN, DON, and PN yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$) and load ($\text{Ton N basin}^{-1} \text{ yr}^{-1}$) from a range of river basins for which data are available.

River	Continent	Basin area (km^2)	DIN yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$)	DIN load ($\text{Ton N basin}^{-1} \text{ yr}^{-1}$)	Source ^a	DON yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$)	DON load ($\text{Ton N basin}^{-1} \text{ yr}^{-1}$)	Source ^a	PN yield ($\text{kg N km}^{-2} \text{ yr}^{-1}$)	PN load ($\text{Ton N basin}^{-1} \text{ yr}^{-1}$)	Source ^a
Alabama	N. America	56894				241.9	13762.7	2			
Altamaha	N. America	41450	113.2	4692.1	2						
Amazon	S. America	5833000	172.5	1006192.5	1	172.8	1007942.4	1	180.6	1053639.0	1
Amur	Asia	1748000	79.7	139315.6	1						
Anabar	Asia	98550	11.7	1153.0	1	42.5	4188.4	1			
Appalachicola	N. America	54660	235.1	12850.6	2	157.5	8609.0	2			
Apure	S. America	170000	53	9010	5	80	13600	5	154	26180	5
Balsas	N. America	122600	73.1	8962.1	1						
Brazos	N. America	124600	56	6977.6	2	52.8	6578.9	2	1824.6	227340.1	1
Bug	Europe	68980	28.3	1952.1	4						
Caroni	S. America	95000	207	19665	5	235	22325	5	75	7125	5
Caura	S. America	47500	238	11305	5	400	19000	5	364	17290	5
Chang Jiang	Asia	1788000	327.5	585570.0	1						
Churchill (Hudson Bay)	N. America	302400	9.5	2872.8	1						
Colorado (CA)	N. America	638951				5.6	3578.1	2			
Colorado (Texas)	N. America	120800	24.2	2923.4	2	16.6	2005.3	2			
Columbia	N. America	729300	74.1	54041.1	1	0.0					
Colville	N. America	53535				750.2	40162.0	2			
Connecticut	N. America	25019				162.5	4065.6	2			
Copper	N. America	66990	325.2	21785.1	2	431.2	28886.1	2			
Dalalven	Europe	29820	56.7	1690.8	1						
Danube	Europe	817000				150.0	122550.0	1			
Daugava	Europe	83160	151.3	12582.1	3						
Don	Europe	421600	19.1	8052.6	1						
Elbe	Europe	148000	795.4	117719.2	1						

Gambia	Africa	42000							13.6	569.8	1
Ganges	Asia	1050000				28.2	29610.0	1	569.5	598018.9	1
Glama	Europe	47310	191.8	9074.1	1						
Guaviare	S. America	150000	124	18600	5			5			5
Huang He	Asia	890500	120.5	107305.3	1				1711.4	1524018.7	1
Hudson	N. America	43070	381.1	16414.0	1						
Indigirka	Asia	362000				59.5	21539.0	1			
Indus	Asia	1139000	136.9	155929.1	1						
Japura	S. America	300000	204	61200	5	184	55200	5	244	73200	5
Jurua	S. America	220000	182	40040	5	121	26620	5	144	31680	5
Kamchatka	Asia	50370	88.8	4472.9	1						
Khatanga	Asia	364000				94.3	34325.2	1			
Klamath	N. America	32080	71	2277.7	2	151.9	4873.0	2			
Kobuk	N. America	24657				303.6	7485.9	2			
Kolyma	Asia	663200	18	11937.6	1	70.0	46424.0	1			
Kuban	Europe	63630	330.9	21055.2	1						
Kuskowin	N. America	115400	136.9	15798.3	2	503.2	58069.3	2			
Lena	Asia	2433000	21.1	51336.3	1	96.6	235027.8	1			
MacKenzie	N. America	1787000				17.0	30379.0	1	46.3	82790.4	1
Madeira	S. America	1300000	130	169000	5	130	169000	5	203	263900	5
Meta	S. America	110000	214	23540	5			5			5
Mezen	Europe	75430	24.8	1870.7	1						
Mississippi	N. America	3191000	255.6	815619.6	1	139.4	444825.4	2	428.5	1367356.9	1
Murray	Australia	1028000	1.1	1130.8	1						
Narva	Europe	58010	73.3	4252.1	3						
Negro	S. America	620000	67	41540	5	248	153760	5	2	1240	5
Nemanus	Europe	96630	138.4	13373.6	1						
Neva	Europe	283500	74.1	21007.4	1						
Niger	Africa	1200000				16.9	20280.0	1			
Nile	Africa	2870000						1	0.1	389.4	1
Nueces	N. America	39956				22.5	899.0	2			
Nushagak	N. America	35300	105.3	3717.1	2	466.4	16463.9	2			
Ob	Asia	3015000	98	295470.0	1						

Odra	Europe	119400	389.8	46542.1	1							
Olenek	Asia	219000				65.6	14366.4	1				
Orange	Africa	1000000				1.5	1500.0	1				
Orinoco	S. America	1100000				164.8	181280.0	1	300.1	330103.4	1	
Paraguay River	S. America	363500		0	5			5	16	5816	5	
Paraiba do Sul	S. America	62760	185.2	11623.2	1							
Parana	S. America	2654000	43.9	116510.6	1	16.0	42464.0	1	39.7	105485.1	1	
Pechora	Europe	313100	64.7	20257.6	1							
Pee Dee	N. America	27640	219.3	6061.5	2	114.4	3162.0	2				
Penzhina	Asia	85540	25.5	2181.3	1				1500.3	128331.6	1	
Po	Europe	70000				224.0	15680.0	1				
Potomac	N. America	38300	395.7	15155.3	1	294.8	11290.8	2				
Rhine	Europe	164500	2200.4	361965.8	1							
Rio Coatzacoalcos	N. America	29497				565.5	16680.6	4				
Rio Grande (US)	N. America	801900	0.6	481.1	1	5.7	4570.8	2				
Roanoake	N. America	22458				79.2	1778.7	2				
Rufiji	Africa	186100	275.9	51345.0	1							
Sabine	N. America	18982				265.2	5034.0	2				
Sacramento	N. America	58690	38.1	2236.1	1	180.4	10587.7	2				
Saint John	N. America	52850	59.8	3160.4	1	264.0	13952.4	2				
Sakarya	Asia	56830	155	8808.7	1							
San Joaquin	N. America	35058				48.4	1696.8	2				
Savannah	N. America	25511				118.8	3030.7	2				
Sebou	Africa	38492				63.0	2425.0	4				
Seine	Europe	73190	1364.9	99897.0	1	100.0	7319.0	1				
Solimoes at Ica	S. America	1200000	240	288000	5	136	163200	5	390	468000	5	
St. Lawrence	N. America	1020000				9.9	10098.0	1				
Stikine	N. America	51170	233	11922.6	2	1159.2	59316.3	2				
Susitna	N. America	50246				744.0	37383.0	2				
Susquehanna	N. America	71860	493.2	35441.4	1	414.7	29800.3	2				
Tejo	Europe	73090	122.8	8975.5	1							
Tornionjoki	Europe	34510	9	310.6	1							
Trinity	N. America	47380	92.2	4368.4	2	114.4	5420.3	2				

Trombetas	S. America	130000	53	6890	5			5			5
Usumacinta	N. America	67890	562.2	38167.8	1						
Waikato	Oceania	13700							268.5	3679.1	1
Weser	Europe	45470	1204.7	54777.7	1						
Wisla	Europe	180000	371.8	66924.0	1						
Yana	Asia	224200	25.9	5806.8	1	46.2	10358.0	1			
Yenisei	Asia	2569000	43.1	110723.9	1						
Yukon	N. America	852700	30.6	26092.6	1	205.2	174974.0	2			
Zaire	Africa	3698000				57.6	213004.8	1			
Zhujiang	Asia	407100	523.3	213035.4	1						

^b 1 = Meybeck & Ragu [1995], 2 = USGS [Alexander et al., 1996], 3 = European Environmental Agency [EEA, 1998], 4 = GEMS-Water Triennial Reports, 5 = Lewis et al., 1999