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# Nitrogen inputs to rivers, estuaries and continental shelves and related nitrous oxide emissions in 1990 and 2050: a global model

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# Abstract

The purpose of the current paper is to estimate future trends (up to the year 2050) in the global geographical distribution of nitrous oxide (N<sub>2</sub>O) emissions in rivers, estuaries, and continental shelf regions due to biological processes, particularly as they are affected by anthropogenic nitrogen (N) inputs, and to compare these to 1990 emissions. The methodology used is from Seitzinger and Kroeze (1998) who estimated 1990 emissions assuming that N<sub>2</sub>O production in these systems is related to nitrification and denitrification. Nitrification and denitrification in rivers and estuaries were related to external inputs of nitrogen to those systems. The model results indicate that between 1990 and 2050 the dissolved inorganic nitrogen (DIN) export by rivers more than doubles to 47.2 Tg N in 2050. This increase results from a growing world population, associated with increases in fertilizer use and atmospheric deposition of nitrogen oxides (NOy). By 2050, 90% of river DIN export can be considered anthropogenic. N<sub>2</sub>O emissions from rivers, estuaries and continental shelves are calculated to amount to 4.9 (1.3 – 13.0) Tg N in 2050, of which two-thirds are from rivers. Aquatic emissions of N<sub>2</sub>O are calculated to increase faster than DIN export rates: between 1990 and 2050, estuarine and river emissions increase by a factor of 3 and 4, respectively. Emissions from continental shelves, on the other hand, are calculated to increase by only 12.5%.

#### Introduction

Nitrous oxide (N<sub>2</sub>O) is one of the major greenhouse gases in the Earth's atmosphere. The atmospheric concentrations of nitrous oxide (N<sub>2</sub>O) have been increasing for several decades due to human activities (Khalil and Rasmussen, 1992). The increase of atmospheric N<sub>2</sub>O is of environmental concern for two reasons. Most importantly, nitrous oxide is one of the radiatively active gases in the Earth's atmosphere (Wang et al., 1976). Thus, increasing concentrations of N<sub>2</sub>O contribute to global warming. Nitrous oxide has a relatively high Global Warming Potential of 310 (CO<sub>2</sub> = 1) (Houghton et al., 1995). In addition, it plays a role in stratospheric ozone depletion (Crutzen, 1970; Hahn and Crutzen, 1982).

Most of the atmospheric N<sub>2</sub>O is of biogenic origin, being produced by bacteria during nitrification and denitrification (Bouwman et al., 1995). The relative importance of the different anthropogenic sources has been the subject of considerable scientific discussions during the past fifteen years (Bouwman, 1995). While energy use and industry are important sources of anthropogenic N2O, food production is considered to be the main anthropogenic source (Houghton et al., 1995). Since pre-industrial times, global emissions of N<sub>2</sub>O have increased from about 11 (8 – 14) Tg N yr<sup>-1</sup> to 16 (13 – 20) Tg N per year (Houghton et al., 1995). During the next century, emissions of N2O may increase at an accelerated rate and it may be difficult to reduce emissions of N<sub>2</sub>O on a global scale, since production of this gas is closely related to production of food for a growing population (Kreileman and Bouwman, 1994; Kroeze, 1994; Nevison et al., 1996).

Most previous studies of the impact of anthropogenic N inputs to terrestrial systems on N<sub>2</sub>O emissions have focused on agricultural soils, and indicate that about 1.25 (0.25 - 2.25)% of the fertilizer N is lost from the soil as N<sub>2</sub>O (Bouwman, 1996). However, indirect emissions of N<sub>2</sub>O associated with fertilizer N after it leaves the agricultural fields also must be considered. Two major pathways leading to indirect emissions are:

- N<sub>2</sub>O production in downstream aquatic ecosystems following leaching of fertilizer N from agricultural soils, and
- 2). N<sub>2</sub>O production associated with utilization of agricultural crops once they leave the field (e.g. human sewage, livestock waste).

In a recent study by Nevison et al. (1996), both direct (short term) and indirect (long term) effects of fertilizer use on  $N_2O$  emissions were examined. They concluded from their global model results that in total 2% of the fertilizer N is lost as  $N_2O$  by direct plus indirect emissions. Similarly, Mosier et al. (this volume) indicated that, globally, indirect  $N_2O$  emissions resulting from agriculture may equal direct soil emissions from agricultural fields.

An additional source of anthropogenic N inputs to both terrestrial and aquatic ecosystems is atmospheric deposition (Fisher et al., 1988; Galloway et al., 1995). This is another reason why  $N_2O$  emissions from both terrestrial and aquatic ecosystems likely have increased, and will continue to increase, as a result of increased atmospheric N deposition (Galloway et al., 1995; Seitzinger and Kroeze 1998). Atmospheric N deposition is predicted to increased several fold during the next 20 years due to human activities (Galloway et al., 1995).

The purpose of the current paper is to estimate future trends in the global geographical distribution of N<sub>2</sub>O emissions in rivers, estuaries, and continental shelf regions due to biological processes, particularly as they are affected by anthropogenic N inputs associated with food production and atmospheric deposition. We focus on a comparison of the years 1990 and 2050. The geographical distribution of N inputs to rivers and estuaries and resultant N2O emissions were previously estimated for the year 1990 (Seitzinger and Kroeze, 1998). In the present paper we utilize databases developed for the year 2050 to estimate increased N inputs to rivers, estuaries and continental shelves and resultant N<sub>2</sub>O emissions in 2050. We use a model grid of 1° latitude by 1° longitude grid to estimate N<sub>2</sub>O emissions, for consistency with the International Biosphere Geosphere Program, Global Environmental Inventory Activity (GEIA).

#### Methodology

The methodology for estimating the global distribution of N loading and associated  $N_2O$  emissions from rivers, estuaries and continental shelves in the year 2050 is based on the approach developed previously for 1990 estimates (see Seitzinger and Kroeze (1998) for a comprehensive presentation of methodology development and rationale). The following is a short summary of that approach, plus a description of the modifications used to develop the 2050 scenario. The basic assumption of the approach is that  $N_2O$  production in these systems is related to nitrification and denitrification (Boxes 1, 2). Nitrification and denitrification in rivers and estuaries are related to external inputs of nitrogen to those systems:

> $N_2O$  production = f(nitrification, denitrification) = f(N input)

Using a model grid of 1° latitude by 1° longitude, the global landmass was divided into 177 watershed regions that transport their water to 303 estuarine gridcells. Estuaries were located in the gridcells at the mouths of major world rivers. The watershed database of Cogley (1994) was modified for this purpose. The N input into an estuarine gridcell was calculated as the total N export by rivers in the watershed involved.

Dissolved inorganic nitrogen (DIN) export by world rivers to estuaries

#### Model formulation

N loading rates by rivers to estuaries are modeled (Nmodel) as a function of N inputs to watersheds from fertilizer use, human sewage, and atmospheric N deposition. The N-model is based on Caraco and Cole (in press), who developed a relationship between measured nitrate export by thirty-five rivers as a function of nitrogen input to those rivers from various point and non-point sources. Their relationship refines that previously developed between river transport of nitrate and population density (Peierls et al., 1991; Cole et al., 1993), and builds on relationships developed for estimating P transport as a function of point and nonpoint sources (Caraco, 1995). Nitrate export by rivers  $(NO3exp_{riv})$  is calculated as a function of point source N inputs to rivers from human sewage (Psources), and nonpoint N inputs from fertilizer use (Fert<sub>ws</sub>) and atmospheric deposition ( $Ppt_{ws}$ ) to the soils in the watershed (Caraco and Cole, in press):

$$NO3exp_{riv} = EC_{riv} * [Psources + EC_{ws} * (Ppt_{ws} + Fert_{ws})]$$

Point source inputs (Psources), or sewage loading, are calculated using per capita nitrogen production per year, multiplied by the portion of the watershed population that lives in urban areas. This essentially assumes that only people living in cities are on sewage systems that discharge as point sources. In our application of the N-model we assumed that if the average population density of a gridcell equalled or exceeded 250 km<sup>-2</sup>, all human sewage produced in the cell was discharged to streams or rivers. The percent urbanization decreased proportionally as the population density decreased below 250 km<sup>-2</sup> (similar to value used by U.S. census bureau to define urban fringe). The fraction of the nonpoint inputs (atmospheric deposition and fertilizer) to the watershed that is exported to the river is defined by the watershed export coefficient  $(EC_{ws})$  which is calculated as a function of the water runoff. The fraction of the total nonpoint and point N input to the river that is exported by the river as nitrate is defined by the river export coefficient (EC<sub>*riv*</sub>). For all rivers, the river export coefficient is set at 0.7 according to the original model formulation of Caraco and Cole (in press).

The input data needed for the model include gridded data for runoff, population density, fertilizer use and atmospheric deposition of nitrogen oxides (NOy). The global data bases that we used are summarized in Table 1. DIN (nitrate + nitrite + ammonia) export was calculated from nitrate export assuming that 84% of DIN is nitrate (based on Meybeck, 1982).

The N-model was found to be a relatively good predictor of river nitrate export based on a comparison of model calculated nitrate export with measured export for twenty-nine rivers (linear regression analysis;  $r^2 = 0.84$ ) (Seitzinger and Kroeze, 1998). This strong correlation is similar to that reported in the original model developed by Caraco and Cole (in press) and demonstrates that application of spatially explicit global data bases to our modification of their model is reasonable. Fertilizer use, atmospheric deposition and human population in a watershed are good indicators for nitrate export by world rivers (Caraco and Cole, in press). This may seem in contrast with findings by Howarth (this volume) for the North Atlantic, where a strong correlation exists between atmospheric deposition (sum of wet and dry deposition of  $NH_x$  and  $NO_{\nu}$ ) and total N export from non-point sources from ten temperate regions draining into the North Atlantic  $(r^2 = 0.93)$ . We found, however, that for the 29 world rivers included in our analysis the correlation between atmospheric NO<sub>y</sub> deposition (wet and dry) in the watershed and nitrate export by rivers is relatively weak  $(r^2 = 0.41)$ . The two analyses are not directly comparable because we are comparing atmospheric deposition to DIN export, while Howarth (this volume) compared atmospheric deposition to total N export. In addition, our analysis was based on individual rivers and their watersheds, while Howarth's was a regional analysis. However, our analysis indicates that across a range of watersheds in North and South America, Europe, Asia and Africa, atmospheric deposition alone is not as good an indicator of river DIN export.

#### 2050 databases

For the 2050 simulation we used gridded  $(1 \times 1^{\circ})$  projections of population density, fertilizer use and NOy deposition for a business-as-usual scenario (Table 1). The gridded 2050 population database was compiled using United Nations country-based (medium) projections (United Nations, 1996) for population growth through 2050. The gridded 2050 database was created by multiplying the 1990 population in each gridcell by the 1990 - 2050 UN predicted population increase in the country where the gridcell was located. Similarly, for fertilizer use, we used fertilizer growth rates for 13 world regions distinguished in the Integrated Climate Model IMAGE (Alcamo et al., 1994) and applied these to 1990 gridded country-based fertilizer use from Bouwman et al. (1995). The 2050 fertilizer growth rates for developing countries are from Bouwman (1997). For other world regions we used the IMAGE 'conventional wisdom' projections (Kreileman and Bouwman, 1994). The regional and national projections for population and fertilizer use were gridded using the country to grid information as available in the EDGAR database (Olivier et al., 1996). The NOy deposition database for 2050 was calculated by the Moguntia model (Dentener, personal communication) for the IPCC IS92a scenario (Houghton et al., 1995). Finally, water runoff may change in the future as a result of climate change or land use; however, to what extent is uncertain. We therefore tentatively used the gridded GGHYDRO water runoff database for 1990 in the 2050 projections as well (Cogley, 1994).

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Table 1. Global databases used for 1990 (Seitzinger and Kroeze 1998) and 2050 (current study) N-model calculations

Parameter Human population	1990 Lerner et al. (1988) updated to the year 1990 using FAO data (Bouwman et al., 1995); 1° × 1° grid originally constructed from national population statistics	2050 United Nations (1996) country-based (medium) projections used to update 1990 data base
Atmospheric NO <sub>y</sub> deposition	modeled dry and wet deposition of HNO <sub>3</sub> and dry deposition of natural and anthropogenic NO <sub>x</sub> (NO, NO <sub>2</sub> , NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> , and PAN) from Dentener and Crutzen (1994) for 1990; 10° × 10° grid.	modeled dry and wet deposition of HNO <sub>3</sub> and dry deposition of natural and anthropogenic NO <sub>x</sub> (NO, NO <sub>2</sub> , NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> and PAN) calculated by Dentener (pers. comm.) using Moguntia model for the IPCC IS92a scenario; $10^{\circ} \times 10^{\circ}$ grid.
Synthethic fertilizer use	Bouwman et al. (1995) based on FAO data for national fertilizer consumption in the year 1990; $1^{\circ} \times 1^{\circ}$	1990 data base updated using fertilizer growth rates for developing countries from Bouwman (1997) and for other world regions from Kreileman and Bouwman (1994)
Water runoff	GGHYDRO database release 2.1 (Cogley, 1994); $1^{\circ} \times 1^{\circ}$ grid	GGHYDRO database release 2.1 (Cogley, 1994); $1^{\circ} \times 1^{\circ}$ (same as 1990)

Note: FAO, Food and Agriculture Organization; PAN, peroxyacetic nitric anhydride; GGHYDRO, global hydrographic; EDGAR, emission database for global atmospheric research

# Nitrification and denitrification rates and associated $N_2O$ production

Rates of nitrification and denitrification in rivers and estuaries are estimated as a function of the nitrogen inputs to those systems calculated by the N-model (see above) (Seitzinger and Kroeze, 1998). In the following, we briefly describe this methodology, as well as the emission factors used to relate  $N_2O$  production rates associated with nitrification and denitrification.

# River denitrification and nitrification

The rates of nitrification and denitrification in rivers are not well known. Estimates of the magnitude of Nremoval via denitrification range from 1 to 75% of the external nitrogen inputs based on mass balance models and/or from measurements of denitrification (reviewed by Seitzinger, 1990; Howarth et al., 1996). In the base case run of our model, we have assumed that denitrification removes 50% of DIN inputs to rivers, given the wide range of nitrogen removal by denitrification reported in rivers. An additional model run was conducted assuming that 25% of DIN inputs to rivers are removed by denitrification. In the base case, DIN inputs to rivers thus equal two times DIN export and river denitrification is calculated as one times the DIN export by rivers. Few studies have related river nitrification rates to environmental parameters (Billen, 1975; Lipschultz et al., 1986). In the base case run of our model, we assume all DIN entering rivers is nitrified once during river transport, thus the amount of N nitrified in a river equals twice the amount of DIN exported by the river to estuaries. Addition model runs were conducted assuming that 20% or 50% of DIN inputs to rivers is nitrified.

#### Estuarine denitrification and nitrification

The amount of N removed by denitrification in estuaries is currently easier to predict than it is in rivers. The amount of N removed by denitrification is equivalent to a relatively constant percentage (50%) of external DIN loading in a variety of estuaries (Seitzinger, 1988). Those estuaries vary in a number of characteristics including N loading rates (25 to 516  $10^{-6}$ mol DIN  $m^{-2}$  estuary  $h^{-1}$ ), extent of intertidal area (<1% to 50%), and latitude (subtropical to subarctic). We used this relationship between denitrification and DIN loading rates to calculate estuarine denitrification in our model; denitrification rates were calculated as 50% of the riverine DIN loading rates. Recent studies indicate that water residence time in estuaries also is a good predictor of the percent of total N inputs removed by denitrification (Nielsen and Rasmussen,

1995; Nixon et al., 1996) ( $r^2 = 0.75$  from Nixon et al. (1996) data). Although admittedly water residence time is likely to affect the amount of N denitrified, we did not incorporate water residence time into our model because we are estimating denitrification based on DIN inputs (not total N inputs) and the relationship between DIN input and denitrification is equally as good at predicting denitrification ( $r^2 = 0.81$ ) as the residence time model of Nixon et al. (1996). Furthermore, information was not available to calculate water residence time in the 303 estuarine gridcells. Similarly, in practice information is not available to include water residence time in rivers in a global model.

Reported pelagic nitrification rates in estuaries generally range from 0–22  $\mu$ mol l<sup>-1</sup> d<sup>-1</sup> (reviewed by Berounsky and Nixon, 1993). While estuarine nitrification rates have been shown to be affected by a number of factors including ammonia concentrations, temperature (Berounsky and Nixon, 1985, 1993), oxygen (Helder and De Vries, 1983; Billen, 1975), suspended particulate matter (Helder and De Vries, 1983; Owens, 1986), and light (Olson, 1981), no predictive factor has been developed to estimate pelagic nitrification rates across a range of estuaries. Therefore, for nitrification rates in estuaries we assumed that pelagic nitrification is equal to 1.2 times benthic denitrification, based on studies in Narragansett Bay (Berounsky and Nixon, 1993; Seitzinger et al., 1984), where benthic nitrification rates are about 1.2 times the denitrification rates.

#### Continental shelf denitrification and nitrification

Continental shelf areas are treated with the least amount of detail in the model. In the 1990 scenario, N2O production associated with denitrification in continental shelf sediments was estimated by extrapolating previously estimated denitrification rates for low, middle and high latitudes in the North Atlantic (Seitzinger and Giblin, 1996) to shelf areas in those latitudes in other basins. N<sub>2</sub>O production associated with pelagic nitrification was estimated by applying depth average rates of nitrification measured in shelf waters of the western U.S. to the global shelf area. We define continental shelves as the area with water depths less than 200 meters. The USDOC/NOAA ETOPO-5 bathymetry database (Edwards, 1986) is used to calculate the area of continental shelves for various regions.

Future  $N_2O$  emissions from continental shelf regions are predicted to increase due to increased anthropogenic N inputs to shelf regions. Both N export from estuaries and atmospheric N deposition directly to shelf waters are expected to increase. To explore the resultant magnitude of increased N<sub>2</sub>O emissions we first estimated increased continental shelf nitrification and denitrification based on expected increased export of N from estuaries to continental shelves globally between 1990 and 2050. While the amount of N exported from estuaries is a function of a number of parameters (e.g. water residence time, temperature, etc.), we assumed for the current calculation that the percent of the N exported remains constant, although the absolute amount increases as the input increases. Therefore, we calculated the increased export of N, globally, to continental shelves associated with increased DIN inputs to estuaries (as calculated by the N-model) based on the difference between the DIN inputs to estuaries in 1990 and 2050. We then used the average percent of N exported from estuaries in the North Atlantic (50%), as estimated by Nixon et al. (1996), as the global average percent exported. All of the increased N input to continental shelves was assumed to be denitrified on the shelf. This was based on previous analyses which indicate that essentially all current N export from estuaries is denitrified in shelf sediments (Christensen et al., 1987; Seitzinger and Giblin, 1996). Nitrification in shelf waters globally was estimated to increase by the same percent as the calculated increase in denitrification in shelf sediments globally. The effect of increased atmospheric N deposition on shelf processes was not explored in the current model.

#### N<sub>2</sub>O Emission factors

Nitrous oxide emissions (kg N yr<sup>-1</sup>) are estimated as 0.3% of nitrification and denitrification rates (in kg N yr $^{-1}$ ), except for river and estuarine gridcells with external N inputs exceeding 10 kg N ha<sup>-1</sup> yr<sup>-1</sup>; for the latter an emission factor of 3% was used. These emission factors are based on a variety of studies (Seitzinger and Kroeze, 1998) which suggests that the ratio of N<sub>2</sub>O:N<sub>2</sub> fluxes is generally within the range 0.1 - 0.5%, although in heavily polluted sediments yields up to 6% have been observed (Nishio et al., 1983; Jensen et al., 1984; Seitzinger, 1988). For example, in estuarine mesocosms and regions of an estuary receiving different N loading rates, the ratio of N<sub>2</sub>O:N<sub>2</sub> increased linearly (r=0.97 calculated from data by Seitzinger and Nixon, 1985). Additional model runs were conducted using threshold values of 5 and 50 kg N ha<sup>-1</sup> yr<sup>-1</sup> (external N inputs) for the high emission factor (3%) step function) as well as using an emission factor that increased linearly as a function of external N inputs.

For pelagic nitrification the same N<sub>2</sub>O emission factors of 0.3% and 3% were used in the model as for denitrification. The N2O yields (moles N2O-N per mol of NO<sub>2</sub><sup>-</sup>) during nitrification measured in cultures of nitrifying bacteria were between 0.2 and 0.3% at atmospheric oxygen levels (20 kPa), with enhanced yields of 10% N<sub>2</sub>O found at reduced O<sub>2</sub> concentrations (0.5 kPa) (Goreau et al., 1980). Recent field studies in an Antarctic lake reported high N<sub>2</sub>O yields for nitrification ( $\sim$ 8%) even at near atmospheric oxygen levels, with yields increasing further to near 30% at low oxygen concentrations (Priscu et al., 1996). Lowered oxygen concentrations may be expected in rivers and estuaries receiving high nutrient loading rates. Therefore, in the present model formulation, N<sub>2</sub>O emission factors for pelagic nitrification of 0.3% and 3% were used for river and estuarine gridcells with external N inputs  $<10 \text{ kg N} \text{ ha}^{-1} \text{ yr}^{-1} \text{ and } >10 \text{ kg N}$ ha<sup>-1</sup> yr<sup>-1</sup>, respectively. For continental shelf regions, a constant N<sub>2</sub>O emission factor of 0.3% was used for both denitrification and nitrification (Seitzinger and Kroeze, 1998).

#### **Results and discussion**

#### 1990 calcaulations

The results for 1990 have been published previously (Seitzinger and Kroeze, 1998) and are included here for comparison with the 2050 results.

# 1990 DIN export

World rivers exported 20.8 Tg N yr<sup>-1</sup> as dissolved inorganic nitrogen (DIN) to estuaries in 1990, according to the N-model; almost 90% of the DIN exported by world rivers is in the Northern Hemisphere (Tables 2 and 3; Figure 2). On an ocean basis, the calculated DIN export to the Atlantic and Indian Oceans are of similar magnitude (5.4 Tg N yr<sup>-1</sup>, 4.6 Tg N yr<sup>-1</sup>), with inputs to the Pacific being approximately 50% greater (7.9 Tg N yr<sup>-1</sup>). Natural DIN export rates are estimated to amount to 5 Tg N  $yr^{-1}$ , indicating that human activities have increased DIN export rates by a factor of 4 (Table 4). Thus, human activities have a considerable impact on DIN transport in world rivers. The N-model indicates that export of anthropogenic DIN by rivers can be predominantly attributed to fertilizer N (58%), followed by sewage (24%) and atmospheric deposition (18%). It should be realized that in the current model formulation, DIN export that is due to sources not explicitly accounted for, are attributed to fertilizer, point sources and atmospheric deposition, while in reality part of it may in fact be from for instance biological  $N_2$  fixation or other inputs (Galloway et al., 1995; Howarth et al., 1996; Jordan and Weller, 1996).

The N-model predicted DIN export (20.8 Tg N  $yr^{-1}$ ) for 1990 is in good agreement with an earlier estimate by Duce et al. (1991) of  $20 \text{ Tg N yr}^{-1}$  as nitrate. Galloway et al. (1995) estimate that total N export to oceans is 41 Tg N yr<sup>-1</sup>, which is in reasonable agreement with our estimate assuming that 60% of the total nitrogen is inorganic (Meybeck, 1982). Our estimate is higher than an estimate for 1970 (7 Tg N yr<sup>-1</sup> as total N) by Meybeck (1982), which may reflect the actual increase. Our calculated DIN export rates are also in good agreement with estimates extrapolated from data by Howarth et al. (1996) for large regions of the North Atlantic. Howarth et al. (1996) use a combination of measured export rates and extrapolations from data collected in similar regions to estimate riverine total nitrogen fluxes to the North Atlantic. We extrapolated DIN export rates from these estimates, based on data on the relative composition of inorganic and total N for a number of the major rivers. The respective N-model and Howarth et al. (1996) estimates are 0.8 and 0.7 Tg DIN yr<sup>-1</sup> for 0–20 °N including the Amazon; 1.5 and 1.8 Tg DIN yr<sup>-1</sup> for 20–45 °; and 0.6 and 0.5 Tg DIN  $yr^{-1}$  for 45–66° N (Seitzinger and Kroeze, 1998).

#### 1990 N<sub>2</sub>O emissions

Worldwide N2O emissions from rivers, estuaries and continental shelves are calculated to be 1.9 (range 0.9 - 9) Tg N yr<sup>-1</sup> in 1990 (Table 4, Figure 3). Rivers contribute 55% to these emissions, estuaries 11% and continental shelves 33%. Approximately 95% of N<sub>2</sub>O emissions from rivers and estuaries take place in the Northern Hemisphere, in line with the regional distribution of DIN export by rivers (Table 3). Over 90% of the current N2O emissions from rivers and estuaries are considered anthropogenic. The N-model indicates that an amount of N equivalent to about 1% of the N input from fertilizers, atmospheric deposition and sewage to watersheds is lost as N2O in rivers and estuaries. Globally, anthropogenic emissions of N2O from rivers and estuaries (1.2 Tg N yr<sup>-1</sup>) could account for approximately 20% of the current global anthropogenic N<sub>2</sub>O emissions, and are similar in magnitude to a number of previously identified sources including

	Watershed <sup>a</sup>	Runoff <sup>a</sup>	Popu	lation	Fertiliz	zer Use	NOy De	eposition
Oceanic Region			1990 <sup>a</sup>	2050 <sup>b</sup>	1990 <sup>a</sup>	2050 <sup>c</sup>	1990 <sup>a</sup>	$2050^{d}$
	$10^3 \text{ km}^2$	km <sup>3</sup>	millions	millions	Gg N/yr	Gg N/yr	Gg N/yr	Gg N/yr
Arctic	20730	4466	68	70	1618	2610	2681	3101
North Atlantic (west) 45-66 N	6793	2695	57	77	2088	2730	1631	1479
North Atlantic (west) 20-45 N	6678	1879	217	327	9119	14217	2486	3938
North Atlantic (west) 0-20 N	3141	2695	76	153	810	3371	423	1066
North Atlantic (east) 45-66 N	1540	1057	181	177	5490	7309	823	698
North Atlantic (east) 20-45 N	1228	191	53	66	1015	2231	117	254
North Atlantic (east) 0-20 N	4364	1756	170	598	204	1815	692	1176
South Atlantic (west) 0-20 S	8968	7877	86	150	373	1558	1311	2416
South Atlantic (west) 20-45 S	4264	1255	118	201	557	2330	530	1191
South Atlantic (west) 45-66 S	438	162	2	3	0	0	6	13
South Atlantic (east) 0-20 S	5046	1979	67	265	36	321	1276	1945
South Atlantic (east) 20-45 S	698	26	21	53	147	1307	86	283
South Atlantic (east) 45-66 S	0	0	0	0	0	0	0	0
Total Atlantic	43157	21572	1048	2070	19838	37279	9384	14459
North Pacific (west) 45-66 N	3882	1281	72	92	3009	6560	525	975
North Pacific (west) 20-45 N	6264	3699	1239	1590	17801	41046	1706	4288
North Pacific (west) 0-20 N	1515	1262	113	194	969	2910	275	575
North Pacific (east) 45-66 N	3182	2724	11	15	323	422	248	222
North Pacific (east) 20-45 N	1801	272	51	82	528	1351	247	435
North Pacific (east) 0-20 N	1018	945	44	88	581	2432	111	388
South Pacific (west) 0-20 S	6232	6919	228	429	1664	5808	415	696
South Pacific (west) 20-45 S	2692	928	17	26	359	469	99	110
South Pacific (west) 45-66 S	0	0	0	0	0	0	0	0
South Pacific (east) 0-20 S	778	957	13	25	150	626	45	106
South Pacific (east) 20-45 S	389	478	7	12	75	313	23	53
South Pacific (east) 45-66 S	0	0	0	0	0	0	0	0
Total Pacific	27752	19465	1794	2553	25459	61937	3695	7849
North Indian	9980	5129	1260	2555	11251	42985	1681	5444
South Indian	7215	2391	140	405	991	5714	790	1448
Total Indian	17195	7521	1400	2960	12242	48698	2470	6892
Baltic Sea	2084	750	91	92	2429	3568	1235	1104
Black Sea	2524	660	185	191	5610	9687	1070	1651
Caspian Sea	2881	455	83	102	2452	4358	733	1282
Mediterranean Sea	5609	907	239	454	3961	13601	1232	2198
Total European Seas	13098	2772	598	839	14451	31213	4269	6235
Total	121933	55795	4908	8493	73608	181736	22500	38536

*Table 2.* Inputs to N model for 1990 and 2050 (watershed area, runoff, population, fertilizer use and NOy deposition) for 31 oceanic regions. Column totals may not be exact due to rounding

<sup>*a*</sup> See Seitzinger and Kroeze (1998); <sup>*b*</sup> from UN (1996); <sup>*c*</sup> based on Bouwman (1997) and Kreileman and Bouwman (1994); <sup>*d*</sup> from Dentener (personal communication).

	N <sub>2</sub> O Emissions Rivers		N <sub>2</sub> O Emissions Estuaries		DIN Export By Rivers		
Oceanic Region	1990 <sup>a</sup>	2050	1990 <sup>a</sup>	2050	1990 <sup>a</sup>	2050	
-	N/yr	t N/yr	t N/yr	t N/yr	t N/yr	t N/yr	
Arctic	3734	4799	1369	1760	414840	533217	
North Atlantic (west) 45-66 N	5171	5860	1896	2149	574510	651123	
North Atlantic (west) 20-45 N	23816	122973	7103	12942	1468405	2466405	
North Atlantic (west) 0-20 N	3657	91305	1341	18802	406329	1401063	
North Atlantic (east) 45-66 N	136534	167108	44799	61273	1525611	1862579	
North Atlantic (east) 20-45 N	8219	10680	624	916	189082	277511	
North Atlantic (east) 0-20 N	2076	36633	761	3702	230644	1121741	
South Atlantic (west) 0-20 S	4500	9927	1650	3640	500014	1103041	
South Atlantic (west) 20-45 S	2146	31759	787	2206	238483	668627	
South Atlantic (west) 45-66 S	9	19	3	7	1028	2139	
South Atlantic (east) 0-20 S	2078	12294	762	1800	230853	545373	
South Atlantic (east) 20-45 S	169	752	62	276	18737	83534	
South Atlantic (east) 45-66 S	0	0	0	0	0	0	
Total Atlantic	188374	489311	59788	107713	5383697	10183135	
North Pacific (west) 45-66 N	3643	7367	1336	2701	404734	818589	
North Pacific (west) 20-45 N	443121	943554	81902	299517	5307381	10483940	
North Pacific (west) 0-20 N	3885	101203	1424	3711	431614	1124481	
North Pacific (east) 45-66 N	1363	1565	500	574	151460	173844	
North Pacific (east) 20-45 N	1071	1921	393	704	118958	213455	
North Pacific (east) 0-20 N	2124	67529	779	24760	236013	888140	
South Pacific (west) 0-20 S	9567	291458	3508	10797	1062999	3271888	
South Pacific (west) 20-45 S	531	717	195	263	58971	79628	
South Pacific (west) 45-66 S	0	0	0	0	0	0	
South Pacific (east) 0-20 S	753	2756	276	1011	83696	306273	
South Pacific (east) 20-45 S	377	1378	138	505	41848	153136	
South Pacific (east) 45-66 S	0	0	0	0	0	0	
Total Pacific	466434	1419448	90450	344544	7897674	17513373	
North Indian	296345	1103932	57529	388594	4198466	12970400	
South Indian	3565	87108	1307	31939	396144	1526628	
Total Indian	299910	1191040	58837	420533	4594610	14497028	
Baltic Sea	20812	23537	2001	2411	606382	730490	
Black Sea	53357	109334	3015	28178	913725	1453391	
Caspian Sea	2794	4767	1025	1748	310497	529611	
Mediterranean Sea	15873	27401	5820	10047	708510	1735502	
Total European Seas	92836	165039	11861	42383	2539114	4448994	
Total	1051287	3269636	222304	916933	20829935	47175748	

*Table 3.* Model results for 1990 and 2050 ( $N_2O$  emissions and DIN export by rivers) for 31 oceanic regions. Column totals may not be exact due to rounding

<sup>*a*</sup> From Seitzinger and Kroeze (1998).

Table 4. Global fluxes of dissolved inorganic nitrogen (DIN) by world rivers, combined rates of pelagic nitrification and sediment denitrification in continental shelves, and  $N_2O$  emissions in rivers, estuaries and continental shelves in 1990 and 2050. Ranges are based on ranges in emission factors

$(Tg N yr^{-1})$	1990 <sup><i>a</i></sup> (Tg N yr <sup>-1</sup> )	2050
DIN export by rivers	20.8	47.2
of which natural	5	5
Continental shelf nitrification plus denitrification <sup>b</sup>	214	240
N <sub>2</sub> O flux		
Rivers	1.05 (0.19 – 1.87)	3.27 (0.42 - 4.25)
Estuaries	0.22 (0.07 - 0.69)	0.92 (0.16 - 1.56)
Continental Shelves	0.64 (0.64 - 6.43)	0.72 (0.72 - 7.22)
Total	1.92 (0.90 - 8.99)	4.91 (1.30 – 13.0)

<sup>*a*</sup> from Seitzinger and Kroeze (1998).

<sup>b</sup> only includes denitrification coupled to sediment nitrification.

agricultural soils (1 Tg N yr<sup>-1</sup>), biomass burning (0.5 Tg N yr<sup>-1</sup>), industrial sources (1.3 Tg N yr<sup>-1</sup>) and cattle and feed lots (0.4 Tg N yr<sup>-1</sup>) (Bouwman et al., 1995; Houghton et al., 1995).

#### 2050 projections

We used the N-model to estimate DIN export by rivers and associated N<sub>2</sub>O emissions for the year 2050 for a business-as-usual scenario (i.e. assuming that current trends continue) as described above. The N-model relates river DIN export rates to: river runoff, population density, fertilizer use and atmospheric deposition of nitrogen oxides (NOy) in the watershed considered. Changes in the absolute amount, as well as global distribution, of these parameters between 1990 and 2050 then are reflected in the model output. Assuming that the current relationship between river DIN export and N inputs to watersheds remains similar, the 2050 projection should provide reasonable insight into future potential patterns in DIN export and N<sub>2</sub>O emissions, following assumed developments in future population growth, fertilizer use and atmospheric deposition. However, the 2050 projections can only be regarded as a first order estimate for future conditions due to the obvious uncertainties in predicting both N inputs globally from the various N sources and changes in point and non-point source nutrient control measures in watersheds.

#### Future population, fertilizer use and NOy deposition

#### Population

The model results indicate that by 2050, 8.5 billion people will live in exoreic watersheds (i.e. watersheds draining to oceans), which is an increase of more than 70% relative to 1990 (Table 2). Both in 1990 and 2050, more than 80% of the people living in exoreic watersheds are found in the Northern Hemisphere, while more than 50% of the world population lives in regions draining into the North Indian and North Pacific Ocean. Approximately 35% (~1.3 billion) of the population increase is in watershed areas draining into the North Indian Ocean. However, population increases in Atlantic (1 billion) and Pacific (~0.8 billion) watersheds are also substantial. Of all continents, Africa shows the largest relative population growth with an estimated tripling to about 2 billion people in 2050.

#### Fertilizer use

The modelled global fertilizer use in the exoreic watersheds increases by 145% between 1990 and 2050, from 74 Tg N to 182 Tg N per year (Table 2; Figure 1). Thus the relative growth in fertilizer use globally (145%) is over two times the population growth (70%). This implies an increase in the globally averaged per capita fertilizer use from 15 kg/person to 21 kg/person per year. The increase in fertilizer use differs per region as described in the methodology section. On an oceanic region basis, the largest absolute



1990 and 2050 (predicted) N Inputs to Global Exoneic Watersheda

*Figure 1.* Nitrogen inputs from synthetic fertilizer, NOy atmospheric deposition, and point sources to global exoreic watersheds for 1990 and 2050 (predicted).

increase in fertilizer use are found in the western North Pacific between  $20^{\circ}$  and  $45^{\circ}$  N (primarily China) (23 Tg N) and in the Indian Ocean (36 Tg). The input data that we use from Bouwman (1997) show large increases in fertilizer use by 2050 relative to 1990 in Africa, Asia and Latin America. In Northern Africa, Latin America and watersheds draining into the Indian Ocean, for instance, fertilizer use in 2050 exceeds the 1990 use by a factor of approximately 4 to 5. For China, Japan, and South East Asia combined increases by approximately a factor of 2.5 are predicted in exoreic regions.

## Atmospheric NOy deposition

Global NOy deposition in exoreic watersheds is calculated to increase by 70%, from 22.5 Tg N in 1990 to 38.5 Tg N in 2050 (Table 2, Figure 1). This increase is consistent with a global increase in fossil fuel use as projected in the IS92a IPCC scenario (Houghton et al., 1995) which was used by Dentener (personal communication) to estimate global NOy deposition rates. As with fertilizer use, the largest absolute increases in NO<sub>y</sub> deposition are in the western North Pacific between 20° and 45° N (primarily China) (2.6 Tg N yr<sup>-1</sup>) and in the Indian Ocean (4.4 Tg N yr<sup>-1</sup>) (Table 2). However, substantial increases of at least 1 Tg N yr<sup>-1</sup> are noted for western N. America, Brazil, and regions draining into the Mediterranean Sea. Small decreases in NO<sub>y</sub> deposition (0.15 Tg N yr<sup>-1</sup> or less) are noted for the Baltic, regions draining into the Atlantic from Canada (>45° N) and Europe (45-66° N), and U.S. drainage into the Pacific.

#### Point sources

Point source inputs of DIN to surface waters double from 7.2 Tg N in 1990 to 14.3 Tg N in 2050 (Figure 1). This is a combined effect of population growth (70%) and increased urbanization. Since the model assumes that only urban areas discharge sewage to rivers directly, point sources increase faster than population density. Nevertheless, point sources (14 Tg N) are relatively small as compared to inputs from fertilizers (182 Tg N) and atmospheric deposition (38.5 Tg N) in 2050.

# Future DIN export

The calculated DIN export by rivers in 2050 amounts to 47.2 Tg N in 2050 (Table 4). Thus, estimated DIN export rates more than double relative to 1990 as a result of increasing population, fertilizer use and NOy deposition. This is in reasonable agreement with Den Elzen et al. (1997), if we assume that of their estimated total N export to world oceans (100 Tg N yr<sup>-1</sup> by 2050) about 60% is inorganic (Meybeck, 1982). By 2050, 90% of river DIN export can be considered anthropogenic, compared to an estimated 75% in 1990, assuming that natural DIN export rates amount to 5 Tg N (Seitzinger and Kroeze, 1998).

We calculate an increase in DIN input to all major world oceans and European Seas (Table 3 and Figure 2). The highest increase was found for the Indian Ocean both in relative (about a factor of 3) and absolute (about 10 Tg N) terms. This is consistent with the large increases in population, fertilizer use and  $NO_{y}$  deposition noted above. Inputs to the Pacific and Atlantic Oceans also increase substantially, approximately doubling, by 10 Tg N yr<sup>-1</sup> and 5 Tg N yr<sup>-1</sup>, respectively. The increases in DIN inputs to the Pacific are primarily from Asia and thus are located in the western side of the basin (Figure 2). Increased DIN inputs to the Atlantic also are primarily from watersheds in the western side of the basin (3 Tg N), with increased inputs from watersheds in the eastern basin being approximately half (1.7 Tg N) of those from North and South America combined. However, a considerable area of Europe and portions of North Africa and eastern Asia drain into the Mediterranean or Baltic Seas.



*Figure 2.* N-Model predicted DIN-N export by rivers in 1990 and 2050. Black bars and numbers represent Gg DIN-N yr<sup>-1</sup> exported in 1990; grey bars and numbers are predictions for 2050. Graphs are shown for combined inputs to latitudinal zones  $66^{\circ}-20^{\circ}$ N,  $20^{\circ}$ N- $20^{\circ}$ S and  $20^{\circ}-66^{\circ}$ S. Additional graphs are shown for the Arctic Ocean, Indian Ocean, Mediterranean Sea and Baltic Sea. Approximately 80–90% of the predicted DIN exported by world rivers in 1990 and 2050 occurs in the Northern Hemisphere. Totals may differ from Table 3 due to rounding. Units: Gg DIN-N and  $10^{3}$  Gg DIN-N for graphs.



*Figure 3.* Emissions of N<sub>2</sub>O from rivers, estuaries and continental shelves as calculated by the N-model for 1990 (a) and 2050 (b). Units: kg  $N/km^2$ .

Our model does not explicitly account for DIN export from the Baltic and Mediterranean Seas into the Atlantic Ocean and may therefore underestimate DIN inputs to the Atlantic. The increased DIN export in 2050 from the Baltic Sea in the Atlantic would be expected to be minimal because: (i) inputs to the Baltic are calculated to increase only moderately (0.6 to 0.7 Tg N) (Table 3), and (ii) currently only about 10% of total N inputs to the Baltic are exported to the Atlantic (summarized in Nixon et al., 1996). In contrast, river DIN exports to the Mediterranean are predicted to more than double by 2050, increasing by approximately 1 Tg N (Table 3). A recent evaluation of nitrate export from the Mediterranean suggests that currently between 0.7 and 3.1 Tg N as nitrate is exported to the Atlantic (Michaels et al., 1996), suggesting that an amount of nitrate at least equivalent to the 1990 N-model estimate of DIN inputs to the Mediterranean from rivers currently is being exported. If the same pattern holds for 2050, then DIN inputs to the Atlantic from the Mediterranean would increase by about 1 Tg N, resulting in approximately equivalent addi-



Figure 4. N-model predicted DIN export rates for world regions in 1990 and 2050.

tional inputs of DIN from both the eastern and western drainages to the Atlantic.

We present aggregated results for both 31 oceanic regions (Tables 2 and 3; Figure 3) as well as for 7 world regions (Figures 4 and 5). The 31 oceanic re-



Figure 5. N-model predicted  $N_2O$  emissions from rivers and estuaries for world regions in 1990 and 2050.

gions were chosen by subdividing the world oceans into large areas and include both continental shelf and estuaries located in the regions and the land area draining into these regions. The 7 world regions that are distinguished in Figures 4 and 5 follow continental boundaries and were included to facilitate comparison with human activities within these continents. If the data are examined on a world region basis (Figure 4) a trend consistent with the ocean basin scale (Table 3) is seen. As expected, developing regions (Africa, South America and Asia) show larger increases than the industrialized countries. Asia contributes over 50% to global DIN export by world rivers in 1990 and 2050.

# Future $N_2O$ emissions from rivers, estuaries and continental shelves

## Rivers and estuaries

Global N<sub>2</sub>O emissions from rivers, estuaries and continental shelves are calculated to be 4.9 (1.3 - 13.0) Tg N in 2050, of which two-thirds are from rivers (Table 4). Between 1990 and 2050, river and estuarine emissions increase by a factor of 3 and 4, respectively. These increases exceed the doubling of DIN export by rivers. The nonlinear increase in N<sub>2</sub>O emissions relative to DIN export is consistent with higher N<sub>2</sub>O emission factors for denitrification observed in aquatic systems exposed to high N inputs (Seitzinger and Nixon, 1985). In those studies, which were conducted in estuarine mesocosms and in regions of an estuary receiving different N loading rates, the ratio of N<sub>2</sub>O:N<sub>2</sub> increased linearly from 0.3% to over 6% as N loading increased.

The model results suggest that increased anthropogenic N loading to aquatic ecosystems by the year 2050 could significantly increase global N2O production. Approximately 90% of the 1990 N2O emissions from rivers and estuaries are estimated to be anthropogenic (Seitzinger and Kroeze, 1998). By 2050, over 95% of the aquatic emissions can be considered anthropogenic, following the same assumptions. Trends in atmospheric N<sub>2</sub>O indicate that the present net anthropogenic source is about 4 – 5 Tg N per year (Khalil and Rasmussen, 1992). By 2050, anthropogenic N2O emissions from rivers and estuaries (about 4 Tg N) are calculated to be similar to the current anthropogenic emissions from all sources. In order to verify these model predictions, more information on the effect of eutrophication on N2O production associated with nitrification and denitrification in aquatic ecosystems is required.

#### Continental shelves

Global N<sub>2</sub>O emissions from continental shelves are expected to be affected less by changes in terrestrial DIN inputs than estuaries and rivers because shelf regions also receive substantial nitrogen from the deep ocean (e.g. onwelling) (Seitzinger and Giblin, 1996). Approximately 50% of the increased DIN inputs to estuaries are predicted to be exported to the continental shelves (see 'Methodology'). If all of this increased DIN input is nitrified once and denitrified, the global emission of N2O from continental shelves is predicted to increase from 0.64 Tg yr<sup>-1</sup> to 0.72 Tg yr<sup>-1</sup>, or by 12.5%, between 1990 and 2050. The global increase in continental shelf N<sub>2</sub>O emissions is relatively small compared to the estimated increases from rivers and estuaries (Table 4), suggesting that the global emission of N<sub>2</sub>O from continental shelves may be less affected by human activities. Because of the small increase predicted for shelf areas on a global scale, we did not calculate increased N<sub>2</sub>O emissions for the 31 oceanic regions separately in the current model. We also did not include the effects of increased atmospheric N deposition on the global emission of N2O from continental shelves. Future model development could include those steps. Certain shelf regions undoubtedly will be affected more than others due to the relative increase in N inputs from anthropogenic sources compared to inputs from oceanic sources in specific areas (Howarth, this volume).

# Geographical distribution of N<sub>2</sub>O emissions

Both in 1990 and 2050 over 85% of the aquatic  $N_2O$ emissions take place in the Northern Hemisphere. This distribution is similar to that estimated from fertilized agricultural soils where the Northern Hemisphere accounts for at least 85% of the emissions (Bouwman et al., 1995). On a continent basis, Asia dominates the calculated N<sub>2</sub>O emissions in 1990 and 2050 (Figures 3 and 5). Asia also has the greatest absolute increase in N<sub>2</sub>O emissions. Of the 7 world regions that we distinguished, greatest absolute increases in N<sub>2</sub>O emissions are calculated for India and the region covering China, Japan and Southeast Asia (Figure 5). River plus estuarine emissions increase by approximately 1 Tg N  $yr^{-1}$ in each of those two regions (Table 3; Figure 5). This is in line with the relatively large increase in all three N inputs (population, fertilizer use and NO<sub>v</sub> deposition) in India and large increases in fertilizer use and  $NO_{\nu}$  deposition in China, Japan and Southeast Asia (Table 2). Europe is the third largest contributor in 1990 and 2050, on a world region basis. Emissions are relatively small from Africa, South America and North America in 1990. However, their increase on a percent basis by 2050 is similar to or exceeds the percent increase from India and the Asia region that includes China.

On a subregional scale we can distinguish several areas with high areal emissions (>50 kg N km<sup>-2</sup>) outside of Asia (Figure 3). Both in 1990 and 2050, those include large parts of western and central Europe and areas in the northeastern US. For 2050 we find also high emissions in much of Central America, areas in western equatorial Africa and areas in the US that surround the Gulf of Mexico. In contrast there are large areas in Siberia and Canada where the areal emissions are at least two orders of magnitude lower (<0.5 kg N km<sup>-2</sup>). It should be realized that other land-based sources (e.g. agricultural soils, industrial sources, etc.) add to the river gridcell emissions.

The highest areal emissions (>500 kg N per km<sup>2</sup> of gridcell) are calculated for estuarine gridcells. These are located in Asia, western Europe and in 2050 also in Central America. The watersheds draining into these estuaries all have high river N<sub>2</sub>O emissions (>50 kg N km<sup>-2</sup>), which reflects the large N inputs from anthropogenic sources.

Globally, in 1990 approximately 30% of river and estuarine emissions are estimated to be from tropical latitudes (0–20°), with approximately 50% from 20– $45^{\circ}$  and 15% from latitudes >45°. The dominance of mid to high latitudes is similar to the estimated

emissions from fertilized agricultural soils where the tropics (7%) are relatively small compared to the combined inputs from subtropics (20–35° N) (24%) and temperate regions (>35°) (69%) (Matthews, 1994). In contrast, from undisturbed soils about 85% of the N<sub>2</sub>O emissions have been estimated to be in the tropical/subtropical regions (30° S to 30° N) (Bouwman et al., 1993, 1995). By 2050 a shift to increasing importance of aquatic tropical emissions is predicted by the N-model, with about 55% of the river and estuarine N<sub>2</sub>O emissions from tropical latitudes (0–20°), approximately 40% from 20-45°, and 5% from latitudes >45°. This is consistent with the predicted future increase in N<sub>2</sub>O emissions from agricultural soils in tropical and subtropical latitudes (Matthews, 1994).

Most measurements of N<sub>2</sub>O production in rivers and estuaries have been made in temperate latitudes in North America or Europe. Given the N-model predicted current as well a future distribution of N<sub>2</sub>O production, there is a clear need for studies in a variety of tropical and subtropical latitudes, and in regions such as eastern and southern Asia. A similar lack of information on N<sub>2</sub>O flux measurements from agricultural fields in tropical and subtropical areas has been noted previously (Vitousek and Matson, 1993; Matthews, 1994).

## Model sensitivity

We investigated the sensitivity of the model output to a some relatively uncertain assumptions, including (i) the emission factors used and (ii) assumptions on nitrification and denitrification rates (Table 5). In the base case calculations we use two different emission factors to calculate N2O emissions from rivers and estuaries, depending on the rate of external N-inputs. In the 1990 model scenario, we investigated the effect of using different N-input threshold values for changing the emission factor (Seitzinger and Kroeze, 1998). Threshold values of 5, 20 and 50 kg N ha<sup>-1</sup> yr<sup>-1</sup> were compared to the base case of 10 kg N ha<sup>-1</sup> yr<sup>-1</sup>. The N-model calculated N2O emissions from rivers ranged from 0.19 - 1.28 Tg N yr<sup>-1</sup> compared to the base case of 1.05 Tg N yr<sup>-1</sup>; from estuaries the N<sub>2</sub>O emissions ranged from 0.07 – 0.39 Tg N yr<sup>-1</sup>, compared to the base case of 0.22 Tg N yr<sup>-1</sup>. Calculating the emission factor as a linear function of N inputs resulted in global N<sub>2</sub>O emissions that were only 25% to 30% less than the base case. Field studies of the N<sub>2</sub>O yield of nitrification and denitrification in a variety of geo-

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Table 5. Sensitivity of the calculated global  $N_2O$  emissions to model assumptions with respect to emission factors and nitrification / denitrification rates

	Model assumption	Calculated global N <sub>2</sub> O emission (Tg N yr <sup>-1</sup> )		
N <sub>2</sub> O Emission Factor (EF) <sup>a</sup>		rivers (1990) estuaries (1990)		
- base case	threshold for high EF: external N inputs exceeding 10 kg N ha <sup><math>-1</math></sup>	1.05 0.22		
- alternative case 1	threshold for high EF: external N inputs exceeding $5-50 \text{ kg N ha}^{-1}$	0.19 - 1.28 0.07 - 0.39		
- alternative case 2	EF increases linearly with external N inputs	25 – 30% lower		
River nitrification and denitrification		rivers (2050)		
- base case	all DIN input is nitrified once, 50% is denitrified	3.3		
- alternative case A	50% of DIN input is nitrified, 25% is denitrified	1.6		
- alternative case B	<ul><li>20% of DIN input is nitrified,</li><li>25% is denitrified</li></ul>	1		

<sup>a</sup> Seitzinger and Kroeze (1998).

Box 1. N-model (modified from Caraco and Cole, in press) for calculating DIN export by rivers (taken from Seitzinger and Kroeze, 1998)

N-model DINexp <sub>riv</sub> NO3exp <sub>riv</sub>	= 1.19 * NO3exp <sub>riv</sub> * WS = $EC_{riv}$ * [Psources + $EC_{ws}$ * (Ppt <sub>ws</sub> + Fert <sub>ws</sub> )] = 0.7 * [1.85*Popd*Urb + 0.4*WaterRunoff <sup>0.8</sup> * (Ppt <sub>ws</sub> +Fert <sub>ws</sub> )]
where	
EC <sub>riv</sub>	= River export coefficient (fraction N inputs to river that is exported to estuary as nitrate)
DINexp <sub>riv</sub>	= sum of natural and anthropogenic DIN export by river to estuary (kg N per watershed per year)
Fert <sub>ws</sub>	= fertilizer N use (kg N per $km^2$ of watershed per year)
NO3exp <sub>riv</sub>	= sum of natural and anthropogenic nitrate export by river to estuary (kg N per km <sup>2</sup> of watershed per year)
Popd	= population density (number of people per $km^2$ of watershed)
Psources	= point sources = sewage loading rates (kg N per km <sup>2</sup> of watershed per year)
Ppt <sub>ws</sub>	= total atmospheric NOy deposition (kg N per km <sup>2</sup> of watershed per year)
$EC_{ws}$	= Watershed export coefficient (fraction that is not retained)
Urb	= fraction of population living in urban areas
WaterRunoff	= water runoff (m <sup>3</sup> m <sup>-2</sup> yr <sup>-1</sup> )
WS	= watershed area $(km^2)$

graphic locations and across a range of environmental conditions are needed.

In addition, we tested the sensitivity of the model output for the assumed percent of N that is nitrified and denitrified in rivers. In the base case, 100% of the DIN input to rivers is nitrified and 50% of the DIN input is denitrified. We compared the predicted  $N_2O$ emissions from the base case to two other scenarios with reduced nitrification and denitrification: Case A) 50% of the DIN input is nitrified and 25% is denitrified and, Case B) 20% of the DIN input is nitrified and 25% is denitrified. These quite dramatic decreases in nitrification and denitrification reduced the predicted N<sub>2</sub>O emissions by 50 – 70%. In the base case, the predicted N<sub>2</sub>O emission from rivers is 3.3 Tg N yr<sup>-1</sup> (Table 4), which is reduced to 1.6 Tg N yr<sup>-1</sup>, with a 50% reduction in nitrification and denitrification (Case A), or reduced to 1 Tg N yr<sup>-1</sup> if nitrification is further reduced to 20% of the base case (Table 5).

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*Box 2.* Method to calculate  $N_2O$  emissions from river, estuaries, and continental shelves. Taken from Seitzinger and Kroeze (1998). A sensitivity analysis was performed for model parameters in bold italics (see Table 5)

 $N2O_{riv,est,con} = EF^*$  (NIT + DENIT)

#### Rivers

$$\begin{split} \text{NIT}_{riv} &= 1 \text{ * DINinput}_{riv} = 2 \text{ * DINexport}_{riv} \\ \text{DENIT}_{riv} &= 0.5 \text{ * DINinput}_{riv} = 1 \text{ * DINexport}_{riv} \\ \text{N2O}_{riv} &= EF_{riv} \text{ * } 3 \text{ * DINexport}_{riv} \end{split}$$

#### Estuaries

$$\begin{split} \text{NIT}_{est} &= 1.2 \text{ * DENIT}_{est} \\ \text{DENIT}_{est} &= 0.5 \text{ * DINexport}_{riv} \\ \text{N2O}_{est} &= EF_{est} \text{ * } 1.1 \text{ * DINexport}_{riv} \end{split}$$

#### Continental Shelves<sup>a</sup>

$$\begin{split} \text{NIT}_{con} &= 3.9 \ 10^6 \ \text{* Areacon} \\ \text{DENIT}_{con} &= 2.760 \ 10^6 \ \text{g km}^{-2} \ \text{in the region 45 - 90 degrees} \\ &= 8.074 \ 10^6 \ \text{g N km}^{-2} \ \text{in the region 20 - 45 degrees} \\ &= 4.395 \ 10^6 \ \text{g N km}^{-2} \ \text{in the region 0 - 20 degrees} \\ \text{N2O}_{con} &= \text{EF}_{con} \ \text{* (NIT}_{con} + \text{DENIT}_{con}) \end{split}$$

where DENIT = denitrification rate (g N yr<sup>-1</sup>) DINexport = DIN export, e.g. by river to estuary (g N yr<sup>-1</sup>) DINinput = external DIN input, e.g. by river to estuary (g N yr<sup>-1</sup>) EF= emission factor = 0.003, except for river and estuarine cells with external N input exceeding 10 kg N per hectare of watershed when EF = 0.03 NIT = nitrification rate (g N yr<sup>-1</sup>) N2O = N<sub>2</sub>O flux (g N yr<sup>-1</sup>) Aeracon = area (km<sup>2</sup>) of continental shelf (water depth < 200 meters) con = continental shelf sediment est = estuary riv = river ws = watershed

<sup>a</sup> nitrification and denitrification rates are for 1990; see text for 2050 calculations.

# Conclusion

Our scenario study indicates that DIN export rates by rivers may double between 1990 and 2050. Over half of the increase is predicted to be concentrated in eastern and southern Asia, resulting in significant increases in coastal eutrophication. Furthermore, our study indicates that emissions of N<sub>2</sub>O from rivers, estuaries and continental shelves may increase from 1.9 Tg N in 1990 to 4.9 Tg N in 2050, making anthropogenic N<sub>2</sub>O emissions from rivers and estuaries (about 4 Tg N) similar to the current increase in atmospheric N<sub>2</sub>O (Khalil and Rasmussen, 1992; Houghton et al., 1995). The estimated increase in N<sub>2</sub>O emissions by 2050 (approximately 3 Tg N) is a relatively large increase if compared to other published scenarios for anthropogenic N<sub>2</sub>O emissions. For instance, Houghton et al. (1995) estimate that fertilizer-induced emissions increase from 2.2 Tg N in 1990 to 4.2 Tg N in 2050, assuming that these emissions include fertilizer-induced soil emissions as well as degassing from polluted aquifers, but without accounting for N2O formation due to leaching of nitrogen into the aquatic environment. Other studies indicate that the total N<sub>2</sub>O emissions from agriculture, energy use, industry and waste may increase by 4 - 7Tg N  $yr^{-1}$  between 1990 and 2050, while the increase between 1990 and 2100 may amount to 4 - 13 Tg N  $yr^{-1}$  (Houghton et al., 1992, 1995; De Vries et al., 1994; Kreileman and Bouwman, 1994; Kroeze, 1994; Nevison et al., 1996). Most of these studies do not explicitly account for N<sub>2</sub>O formation in fresh water,

estuaries or continental shelves. Our study indicates that ignoring emissions in these aquatic ecosystems as influenced by nitrogen inputs from agriculture, energy use and waste handling, may result in a significant underestimation of the total anthropogenic emissions.

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