

## Nitrogen fixation: Anthropogenic enhancement-environmental response

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**Abstract.** In the absence of human activities, biotic fixation is the primary source of reactive N, providing about 90-130 Tg N yr<sup>-1</sup> (Tg = 10<sup>12</sup> g) on the continents. Human activities have resulted in the fixation of an additional ≈140 Tg N yr<sup>-1</sup> by energy production (≈20 Tg N yr<sup>-1</sup>), fertilizer production (≈80 Tg N yr<sup>-1</sup>), and cultivation of crops (e.g., legumes, rice) (≈40 Tg N yr<sup>-1</sup>). We can only account for part of this anthropogenic N. N<sub>2</sub>O is accumulating in the atmosphere at a rate of 3 Tg N yr<sup>-1</sup>. Coastal oceans receive another 41 Tg N yr<sup>-1</sup> via rivers, much of which is buried or denitrified. Open oceans receive 18 Tg N yr<sup>-1</sup> by atmospheric deposition, which is incorporated into oceanic N pools (e.g., NO<sub>3</sub>, N<sub>2</sub>). The remaining 80 Tg N yr<sup>-1</sup> are either retained on continents in groundwater, soils, or vegetation or denitrified to N<sub>2</sub>. Field studies and calculations indicate that uncertainties about the size of each sink can account for the remaining anthropogenic N. Thus although anthropogenic N is clearly accumulating on continents, we do not know rates of individual processes. We predict the anthropogenic N-fixation rate will increase by about 60% by the year 2020, primarily due to increased fertilizer use and fossil-fuel combustion. About two-thirds of the increase will occur in Asia, which by 2020 will account for over half of the global anthropogenic N fixation.

### Introduction

Reactive nitrogen (NO<sub>x</sub>, NH<sub>x</sub>, and organic N) plays an important role in many environmental processes (Note: NO<sub>x</sub> = NO<sub>x</sub> (NO + NO<sub>2</sub>) + any other single N species with an oxygen atom; NH<sub>x</sub> = NH<sub>3</sub> plus aerosol NH<sub>4</sub><sup>+</sup>). Even though the atmosphere is 78% nitrogen (N), most biological systems are N limited on physiological timescales [Schlesinger, 1991; Vitousek and Howarth, 1991] because most biota are unable to use N<sub>2</sub>. Reactive N enhances ecosystem productivity, and conditions of N deficiency provide ecological niches for organisms that can convert unreactive N<sub>2</sub> to reactive forms by N fixation. Once converted, N can be used by biological systems until it is converted back to N<sub>2</sub> by denitrification.

In addition to being important to biological systems, reactive N also affects the chemistry of the atmosphere. At very low NO<sub>x</sub> concentrations, O<sub>3</sub> is chemically destroyed in the troposphere, although at higher levels of NO<sub>x</sub>, there is net O<sub>3</sub> production. NH<sub>3</sub> is a major source of alkalinity in the atmosphere and a source of acidity in soils. Although N<sub>2</sub>O is not viewed as a reactive form of N in the troposphere, it adsorbs IR radiation and acts as a greenhouse gas. In the stratosphere, N<sub>2</sub>O impacts O<sub>3</sub> concentrations. Thus any change in the rate of formation of reactive N (or N<sub>2</sub>O), its global distribution, or its accumulation rate can have a fundamental impact on many environmental processes.

This paper discusses the transfers of N between unreactive N<sub>2</sub> and its reactive forms and the impact human activities have on these processes. Our paper's basic premise derives from Delwiche [1970] who stated that in the absence of human activities the transfer of N from unreactive to reactive forms and back again is about balanced, that is, there is little accumulation of reactive N relative to the amount transferred. As Delwiche [1970] stated, human activities have now changed this situation. Not only do human activities convert N from unreactive to reactive forms at the same rate as nature, but the fate of anthropogenically fixed N is uncertain. We address four questions: (1) How do the rates of N fixation by anthropogenic processes compare with those from natural processes and how do they impact the environmental distribution of N?; (2) Is N fixed by human activities accumulating in the environment? If so, where?; (3) What are the potential consequences of N accumulation?; and (4) How will the rate of N-fixation change in the future?

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## Fixation and Distribution of Nitrogen: Preindustrial and Present

### Preindustrial World

**Introduction.** We have analyzed three issues concerning the preindustrial patterns of fixed N: What were the fixation rates, were fixation and denitrification rates balanced, and what was the extent of distribution of reactive N away from the point of fixation?

Two natural processes convert unreactive  $N_2$  to reactive N, lightning and biological N fixation (BNF) by bacteria. Lightning is relatively unimportant as a reactive N source. Although recent estimates of oxidized N from lightning are as high as  $100 \text{ Tg N yr}^{-1}$  [Liaw et al., 1990]. Logan [1983] pointed out that  $20 \text{ Tg N yr}^{-1}$  is the maximum allowed by nitrate deposition in remote areas, and a recent survey by M. G. Lawrence et al. (Lightning and atmospheric chemistry: The rate of atmospheric NO production, submitted to *Handbook of Atmospheric Electrodynamics*, 1994) estimated new bounds of  $1\text{--}8 \text{ Tg N yr}^{-1}$ . A recent three-dimensional chemical transport simulation (W. J. Moxim, personal communication, 1992) gave bounds of  $3\text{--}5 \text{ Tg N yr}^{-1}$ . For the purposes of this paper, we have used  $3 \text{ Tg N yr}^{-1}$  (Figure 1a). As discussed below for terrestrial and marine ecosystems, in the preindustrial world, BNF was always significantly greater than lightning.

**Terrestrial ecosystems.** Preindustrial BNF in terrestrial ecosystems is estimated to have been about  $90\text{--}130 \text{ Tg N yr}^{-1}$  [Stedman and Shetter, 1983] (Figure 1a).  $N_2$  production from denitrification is on the same order ( $80\text{--}180 \text{ Tg N yr}^{-1}$  [Stedman and Shetter, 1983, Figure 3]) (Figure 1a); so, in the absence of human activities, the amount of N fixed is approximately balanced by the amount of N converted back to  $N_2$  [Delwiche, 1970; Stedman and Shetter, 1983; Schlesinger, 1991]. The rate of  $N_2O$  produced by preindustrial terrestrial denitrification is about  $5.7 \text{ Tg N yr}^{-1}$  [Schlesinger, 1991]. Certainly there are other estimates of these rates [e.g., Ver et al., 1994; Mackenzie, 1994]; the absolute magnitude of the fluxes is not the key point but rather that the conversion of N between reactive and unreactive forms in the preindustrial world is approximately balanced.

Once formed, fixed N could have been converted to organic N ( $N_{org}$ ) within the fixing organism or lost from the organism as reduced inorganic N ( $NH_4^+$ ). Ultimately,  $N_{org}$  could also have been converted to  $NH_4^+$  by mineralization of dead organic matter. As long as N stayed in its reduced form, it probably remained in the local environment because of its affinity for soil adsorption sites and its rapid uptake by biota. A certain proportion of the reduced N was nitrified to  $NO_3^-$ . The rate of nitrification was highest when another element became limiting or when an ecosystem's biotic component was reduced (e.g., from fire, blowdowns, defoliation, or seasons with limited growth). Nitrification mobilizes N, and  $NO_3^-$  could have been distributed by hydrologic processes downstream to locations where denitrification was favored and where N was converted to  $N_2$  or  $N_2O$ . In the preindustrial world, hydrologic losses of N from the region of fixation were minimized because of the limiting nature of N in ecosystem processes. Transfers of N from continents via river inputs to coastal oceans are either stored in sedi-

ments or denitrified to  $N_2$  [Seitzinger, 1988; Ver et al., 1994]. Transport of reactive N beyond the coastal margin was thus minimal. About 10 to 30% of the N formed by terrestrial nitrogen fixation was lost to the marine environment via rivers, illustrating the demand and retention of reactive N by terrestrial ecosystems in the preindustrial world.

In the preindustrial world a small amount of reactive N was also redistributed from terrestrial ecosystems via the atmosphere.  $NH_3$  is naturally emitted by volatilization from vegetation/soils, wild animal waste, and biomass burning. Dentener and Crutzen [1994] estimated that vegetation/soil and "wild animals" emit  $5.1$  and  $2.5 \text{ Tg N yr}^{-1}$  (Figure 1a). Schlesinger and Hartley [1992] similarly estimated  $10 \text{ Tg N yr}^{-1}$  are volatilized from a combination of these sources. If the preindustrial human population was  $\approx 10\%$  of the present population, then the  $NH_3$  emissions from biomass burning would have been approximately  $10\%$  ( $0.5 \text{ Tg N yr}^{-1}$ ) (J. Langner, private communication, 1992) of present emission rates ( $5 \text{ Tg N yr}^{-1}$ ) [Schlesinger and Hartley, 1992]. NO is also emitted to the atmosphere by microbial processes (e.g., nitrification) and biomass burning. Yienger and Levy [1994] estimated that microbial processes in soils currently release about  $6 \text{ Tg N yr}^{-1}$ , of which  $4 \text{ Tg N yr}^{-1}$  are natural. We have estimated that NO production from natural biomass burning in the preindustrial world was about  $10\%$  of the current total ( $8.5 \text{ Tg N yr}^{-1}$ ) or about  $0.8 \text{ Tg N yr}^{-1}$ . Thus in addition to the  $35 \text{ Tg N yr}^{-1}$  of reactive N transferred to the oceans via the rivers, an additional  $4.8 \text{ Tg N yr}^{-1}$  of NO and  $8.1 \text{ Tg N yr}^{-1}$  of  $NH_3$  were emitted to the atmosphere (Figure 1a) for distribution to downwind terrestrial and marine ecosystems (Figures 1a and 2).

Other estimates of the losses of reactive N to the atmosphere and the oceans are generally within a factor of 2 of our estimates. The general agreement that a small amount of N was lost from terrestrial ecosystems to the atmosphere and to the open oceans supports our view that the rate of N fixation by terrestrial ecosystems was approximately equal to the rate at which reactive N was denitrified to  $N_2$  and that most of the fixed N was not extensively distributed from its origin.

**Marine ecosystems.** Estimates of oceanic BNF indicate that fixation is relatively uniformly distributed among ocean basins, with approximately half in nearshore benthic environments [Carpenter, 1983; Capone, 1983]. BNF by the planktonic cyanobacterium *Trichodesmium*, which has a fairly cosmopolitan distribution over the warmer oceans, reportedly accounts for  $10 \text{ Tg N yr}^{-1}$  globally [Carpenter, 1983]. However, in a recent reanalysis of the historical abundance of *Trichodesmium* in the tropical North Atlantic and Caribbean, Carpenter and Romans [1991] estimated that its average rate of N fixation ( $33 \text{ mg m}^{-2} \text{ d}^{-1}$ ) accounts for  $40\text{--}200 \text{ Tg N yr}^{-1}$  (depending on the boundaries of the selected region). Including other common oceanic N-fixing organisms may as much as double these estimates [Carpenter and Romans, 1991]. This large range in estimates of marine BNF derives from (1) uncertainties in the abundance of the N-fixing plankton [Carpenter and Romans, 1991] and (2) the order-of-magnitude uncertainties in the specific N-fixation rates under natural environmental conditions [Carpenter, 1983; Carpenter et al., 1987; Carpenter and Romans, 1991].

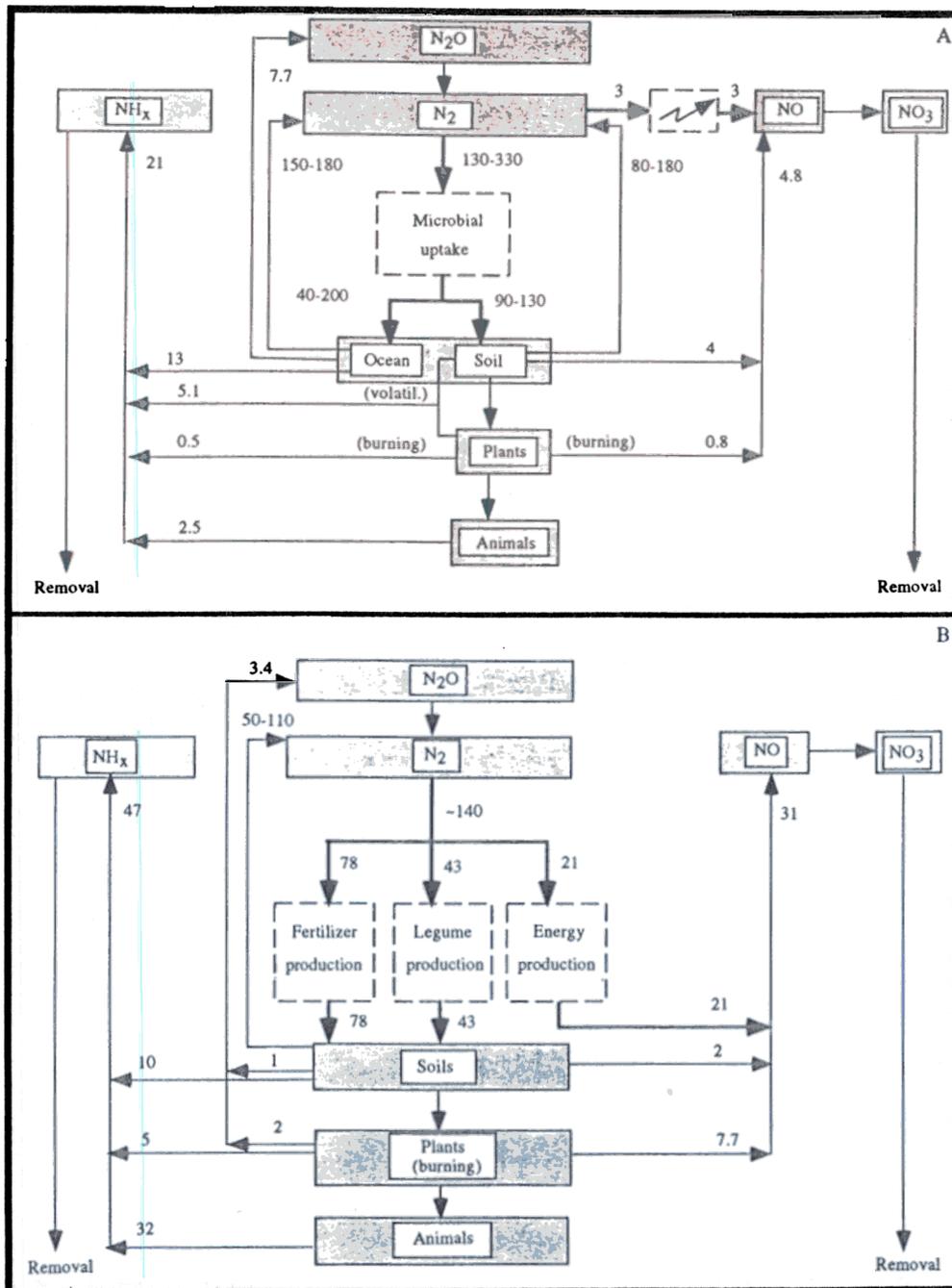


Figure 1. Global N-fixation rates and emission to the atmosphere (Tg N yr<sup>-1</sup>) from (A) preindustrial and (B) anthropogenic sources. The boxes with dashed borders represent processes that convert unreactive N to reactive N.

Our oceanic denitrification estimates of 150-180 Tg N yr<sup>-1</sup> (Figure 1a) were relatively equally divided between water column and sediments. Oceanic denitrification on the order of 80 Tg N yr<sup>-1</sup> is concentrated in areas of the tropical Pacific (50 Tg N yr<sup>-1</sup>) and Indian (30 Tg N yr<sup>-1</sup>) Oceans [Codispoti and Christensen, 1985; Codispoti, 1989; Naqvi et al., 1986] where surface production is high. Christensen et al. [1987] estimated denitrification in marine sediments at 50-75 Tg N yr<sup>-1</sup> although some of these rates may be low by

up to a factor of 4 [Devol, 1991]. The uncertainties in both the specific rates of denitrification and the extrapolation to global estimates appeared to be less than those for marine N fixation. Early marine BNF estimates (30 Tg N yr<sup>-1</sup>) were substantially lower than marine denitrification estimates, suggesting a nonsteady state condition in the marine N cycle. The higher, and somewhat more speculative, estimates of oceanic N fixation indicated that the oceans may have been in approximate balance.

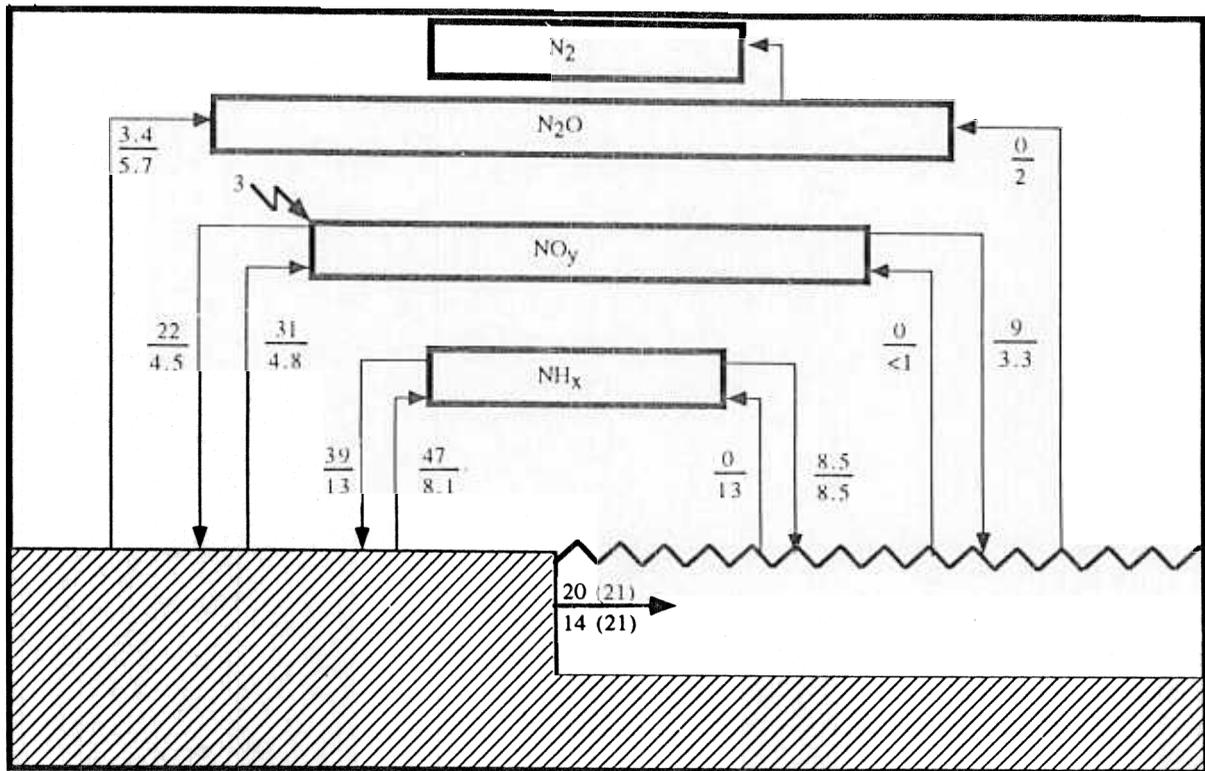


Figure 2. Reactive N produced by anthropogenic (upper value) and preindustrial (lower value) processes ( $Tg\ N\ yr^{-1}$ ) distributed among the atmosphere, continents, and oceans. Riverine fluxes in parentheses are for particulate organic nitrogen (PON); other riverine fluxes are for dissolved N.

The mobility of reactive N is very different in oceanic versus terrestrial environments. In seawater, the movement of the environment itself through currents and eddies can widely redistribute all forms of N. Ocean currents produce horizontal structure in nitrate distribution although various horizontal and vertical mixing processes act to homogenize concentration gradients. Vertical gradients in reactive N are maintained by constant biological activity. In most of the world's oceans, surface waters are nearly devoid of nitrate. Nitrate introduced to surface waters by physical mixing is incorporated into organic matter and efficiently transported back below the illuminated upper layers. Inputs of reactive nitrogen from atmospheric deposition and BNF will also be quickly transferred to middepths. There are significant stocks of dissolved organic nitrogen in the surface ocean, but the biological availability of this nitrogen is unclear. Globally, BNF is broadly distributed in warm oceans and shallow sediments although denitrification is concentrated on productive shelves and at middepths in the water columns of a few highly productive areas of the Indian and Pacific Oceans. Thus on decade-to-century timescales, sufficient nitrate must be transported to local denitrification sites in the ocean.

In addition to denitrification, other processes remove reactive N from the ocean: Emission to the atmosphere and deposition of  $N_{org}$  to marine sediments. Schlesinger and Hartley [1992] estimated that  $13\ Tg\ N\ yr^{-1}$  of  $NH_3$  are emitted to the atmosphere from the world's oceans (Figure 1a). Logan [1983] estimated that  $< 1\ Tg\ N$  is emitted from

the oceans as  $NO$  each year. We have assumed that much of the N emitted was redeposited onto the oceans (Figure 2). Sedimentation of organic N to the sea floor probably results in the deposition of  $10\text{--}20\ Tg\ N\ yr^{-1}$  [Wollast, 1991]. Most sedimentary N is converted to nitrate, some of which is liberated to overlying waters and some is denitrified in sediments [Seitzinger, 1988].

In summary, in the preindustrial world, BNF in terrestrial and marine ecosystems and lightning added about 90 to 130, 40 to 200, and  $3\ Tg\ N\ yr^{-1}$ , respectively, to the reactive N pool (Figure 1a). The redistribution of this reactive N was limited either within terrestrial ecosystems or between terrestrial and marine ecosystems. Of the 90–130  $Tg\ N\ yr^{-1}$  of reactive N produced by terrestrial ecosystems, about 35  $Tg\ N\ yr^{-1}$  was lost to coastal oceans via the rivers and about 13  $Tg\ N\ yr^{-1}$  was emitted to the atmosphere, 4.8  $Tg\ N\ yr^{-1}$  as  $NO$  and 8.1  $Tg\ N\ yr^{-1}$  as  $NH_x$ . Of the 40 to 200  $Tg\ N\ yr^{-1}$  of reactive N produced in the oceans, most was probably denitrified in the ocean; only about 13  $Tg\ N\ yr^{-1}$  as  $NH_x$  was emitted to the atmosphere and a similar amount was buried in the sediments.

What was the fate of the N distributed via riverine and atmospheric transport? The answer to this question sets the stage for our later discussion on anthropogenic impacts on the distribution of reactive N.

Riverine inputs were an important N source for coastal productivity. The N was probably efficiently taken up by phytoplankton and ultimately buried in sediments or denitri-

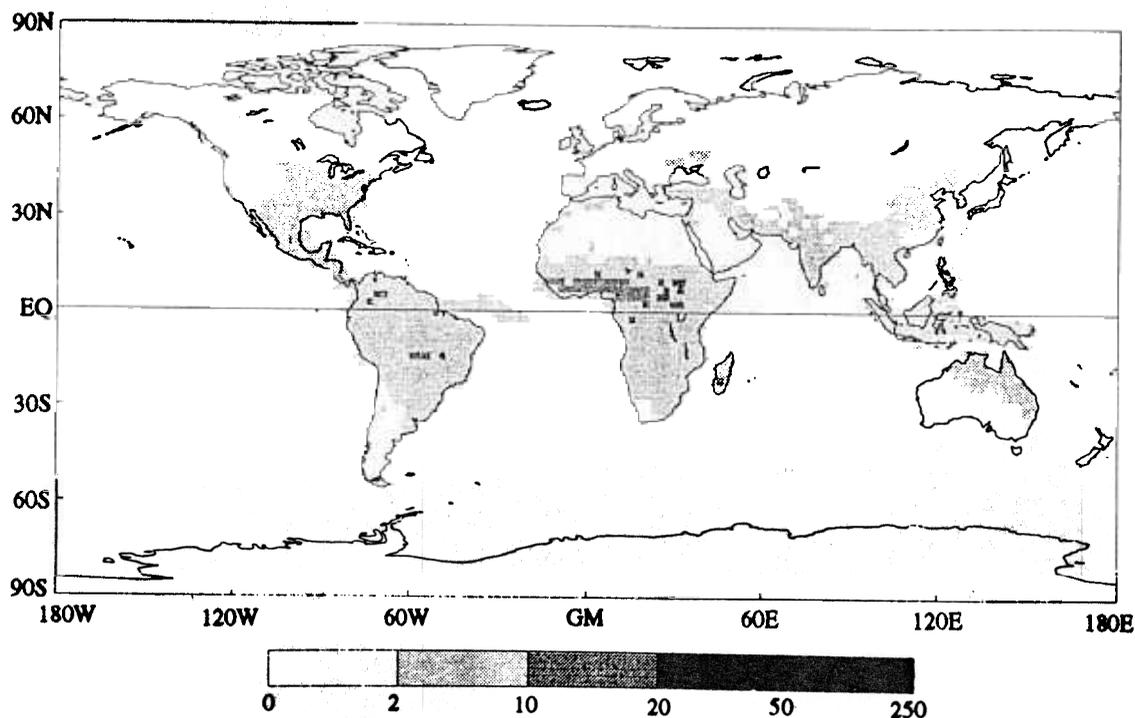


Figure 3. Preindustrial atmospheric  $\text{NO}_y$  deposition ( $\text{mmol N m}^{-2} \text{yr}^{-1}$ ).

fied [Seitzinger, 1988; Ver et al., 1994]. Hence there was little additional distribution of the reactive N.

Reactive N emitted to the atmosphere had much more extensive distribution. It was transported from its point of emission and deposited elsewhere as reactive N, where it could have had an immediate impact on ecosystem productivity without having to go through the N-fixation process. The redistribution of N emitted by natural processes

can be addressed with atmospheric models. Using natural emissions of NO as an input to the Geophysical Fluid Dynamics Laboratory (GFDL) Chemical Transport Model on a  $2.4^\circ \times 2.4^\circ$  grid, we have estimated  $\text{NO}_y$  deposition rates (Figure 3). The amount of atmospheric  $\text{NO}_y$  transported and deposited in ecosystems can be compared to the amount of  $\text{NO}_x$  emitted by dividing estimates of deposition rates by estimates of emission rates for individual grid cells (Figure

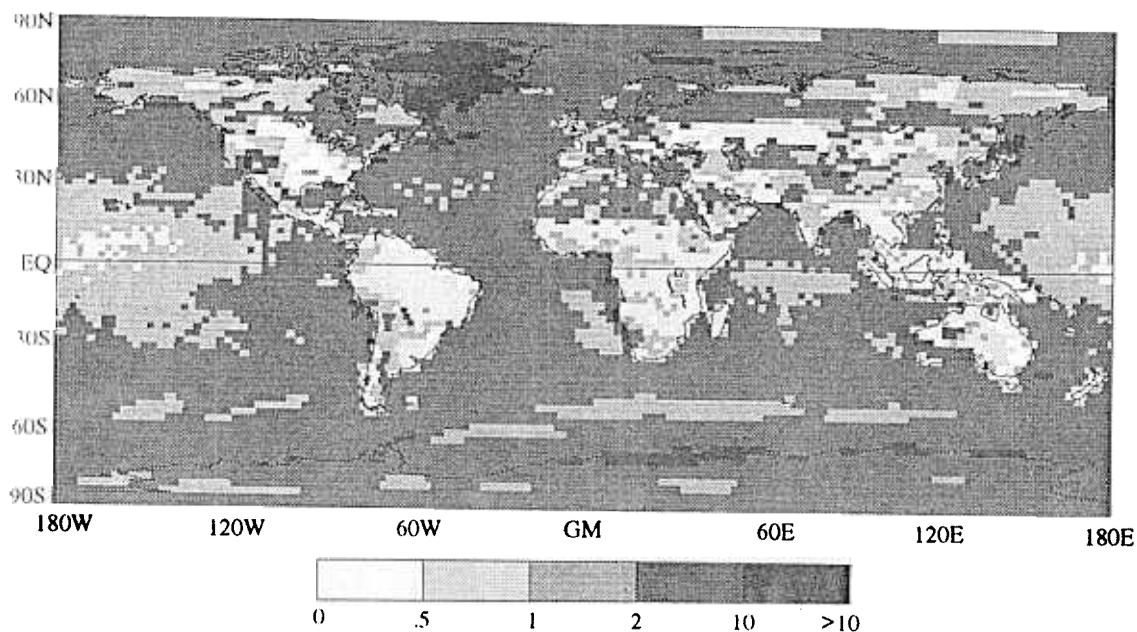


Figure 4. The ratio of preindustrial  $\text{NO}_y$  deposition to NO emission showing N distribution.

4). In essence, this calculation provides a measure of the supply of N from external sources (i.e., deposition) versus the atmospheric leakage of N from internal sources (i.e., emission). For terrestrial ecosystems of the preindustrial world, the ratio rarely exceeded 2; little (compared to current world, see below) N was gained by one ecosystem from atmospheric leakages from another, upwind ecosystem. For  $\text{NH}_x$ , Dentener and Crutzen [1994] compiled natural emissions of  $\text{NH}_3$  and used the MOGUNTIA model ( $10^\circ \times 10^\circ$  grid) to estimate  $\text{NH}_x$  deposition rates. Although their data are not displayed in a form we could use to perform an analysis similar to that for  $\text{NO}_y$ , redistribution of  $\text{NH}_3$  would probably also have been limited in the preindustrial world because of the shorter lifetime of  $\text{NH}_x$  relative to  $\text{NO}_y$ .

In the preindustrial world there was net atmospheric transfer of  $\text{NO}_y$  from continents to the oceans. We have estimated that  $4.8 \text{ Tg N yr}^{-1}$  of  $\text{NO}_x$  were injected into the atmosphere from continents and  $3 \text{ Tg N yr}^{-1}$  from lightning, leading to the deposition of  $4.5 \text{ Tg N yr}^{-1}$  onto continents and  $3.3 \text{ Tg N yr}^{-1}$  onto oceans (Figure 2). For  $\text{NH}_x$  the situation was reversed. We have estimated that  $8.1$  and  $13 \text{ Tg N yr}^{-1}$  of  $\text{NH}_3$  were emitted to the terrestrial and marine atmospheres and that  $13 \text{ Tg N yr}^{-1}$  and about  $8.5 \text{ Tg N yr}^{-1}$  were deposited in terrestrial and marine ecosystems (Figure 2). The basis for this estimate is discussed in the following section. The uncertainties of these  $\text{NH}_x$  estimates were large. Given the range of global emission estimates for marine and terrestrial systems [Schlesinger and Hartley, 1992], the values could easily have been reversed. Assuming that these values were correct, there was limited net atmospheric transfer of reactive N between the continents and the oceans. Riverine losses to the oceans were large (about  $35 \text{ Tg N yr}^{-1}$ , Figure 2) relative to the uncertainty in the net atmospheric exchange of  $\text{NH}_x$  between continents and oceans. However most N was retained in the coastal environment or converted to  $\text{N}_2$  and little was transported to the deep ocean. Therefore we have concluded that in the preindustrial world, there was limited exchange of reactive N between the open ocean and the continents. What exchange occurred was probably from atmospheric transport.

We have drawn several general conclusions from this view of the N biogeochemical cycle in preindustrial times.

(1) BNF was the primary process that converted N from an unreactive to a reactive form. Most reactive N was emitted back to the atmosphere as  $\text{N}_2$ ; that is, the rates of formation and loss of reactive N were approximately in balance.

(2) Of the 90 to  $130 \text{ Tg N yr}^{-1}$  of reactive N formed in terrestrial ecosystems, about one-third was lost as reactive N to the coastal ocean and 10-15% to the atmosphere, with much of the atmospheric N being redeposited on the continents. There was limited net exchange of reactive N between continents and the open ocean.

(3) Oceanic N was strongly redistributed from cosmopolitan fixation sites to the more local denitrification sites. Current estimates of BNF were highly variable. Either oceans were out of balance over centuries or N-fixation rates were underestimated. Of the reactive N formed in oceans, about  $13 \text{ Tg N yr}^{-1}$  was emitted to the atmosphere as  $\text{NH}_3$ , with much being deposited back onto the ocean surface.

(4) In the natural preindustrial terrestrial world, N fixation could be characterized as "fixation without extensive redistribution." The ecological reservoirs downstream (except for coastal marine ecosystems) or downwind of a given reservoir were not significantly influenced by fixation within that reservoir.

#### Present World

Times have changed. Globally, human activities now convert  $\text{N}_2$  to reactive forms at about the same rate as biotic N fixation. Three types of anthropogenic activities produce reactive N: The production of energy, the production of fertilizer, and the cultivation of legumes and other crops.

Energy produced by combustion of coal, petroleum products, and natural gas causes unreactive  $\text{N}_2$  to be directly converted to reactive NO at a rate of about  $21 \text{ Tg N yr}^{-1}$  (Table 1) [Levy and Moxim, 1989]. Some of this reactive N is from  $\text{N}_{\text{org}}$  contained in fossil fuel being converted to NO; but, since  $\text{N}_{\text{org}}$  is sequestered in fossil-fuel deposits, we have regarded it as the equivalent of newly fixed N (in reality, mobilized) by anthropogenic activities. From 1960 to 1986, fossil-fuel combustion has increased annually by about 2.7% (Figure 5).

Table 1. Conversion of Unreactive N to Reactive N by Energy and Fertilizer Production in the Present and Future

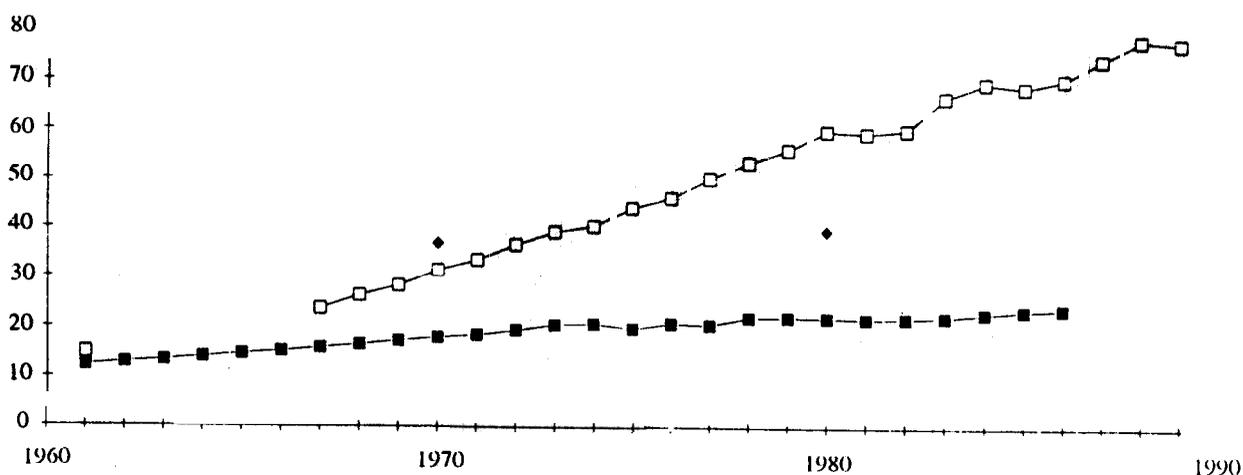
	Energy		Fertilizer	
	Present	2020	Present*	2020
<i>More-developed Regions</i>				
US and Canada	7.6	10.1	13.3	14.2
Europe**	4.9	5.2	15.4	15.4
Australia	0.3	0.4	---	---
Japan	0.8	0.8	---	---
Subtotals	13.5	16.5	28.7	29.6
<i>Less-developed Regions</i>				
Asia**	3.5	13.2	35.9	85.1
Mexico, Latin, South America	1.5	5.9	1.8	4.5
Africa	0.7	4.2	2.1	5.2
FSU	2.2	5.7	10.0	10.0
Subtotals	5.7	29.1	49.8	104
Totals	21.2	45.6	78.5	134

\*Data for present fertilizer N consumption are for 1989 [United Nations, 1992].

\*\*Europe and Asia are defined as the portion of the Eurasian continent to the east and west of the Ural Mountains, respectively.

Source: NO estimates are from Galloway et al. [1994].

Conversion measured in teragrams nitrogen per year ( $\text{Tg N yr}^{-1}$ ).



**Figure 5.** Temporal trends in N fixed by human activities ( $\text{Tg N yr}^{-1}$ ). (Sources: Data for N fixed by combustion in 1960 and 1970 from *Dignon and Hameed* [1989]; for 1970 to 1986 from *Hameed and Dignon* [1992]; for the years between 1960 to 1970 from *Dignon and Hameed* [1989] are interpolated. See the text for sources of data for N fixation by fertilizers and legume and rice cultivation.)

Fertilizer production converts about 79 Tg N of unreactive  $\text{N}_2$  to reactive  $\text{NH}_3$  (Table 1) [United Nations, 1992]. This value agrees well with other recent estimates (e.g., 84 Tg N  $\text{yr}^{-1}$ , *Schlesinger and Hartley* [1992]; 78 Tg N  $\text{yr}^{-1}$ , *Constant and Sheldrick* [1992]; 71 Tg N  $\text{yr}^{-1}$ , *Matthews* [1994]). From 1967 to 1989, fertilizer production has increased annually by 5.3% (Figure 5).

The third activity, cultivation of legumes and other crops, converts  $\text{N}_2$  to reactive N by increasing the rate of biological N fixation (BNF). To estimate the amount of BNF by legumes, we needed to know the area planted and the BNF rate per unit area. Legumes are generally grouped as soybeans, groundnuts (e.g., peanuts), pulses (e.g., lentils), and forage (e.g., alfalfa, clover). *Burns and Hardy* [1975], relying on FAO data [*Erus*, 1970], stated that the cultivation area of these legume classes is about  $250 \times 10^6$  ha (Table 2). Although they provide data for pulses, soybeans, and groundnuts, they do not provide specific data for forages but rather have a category entitled "others." We have assumed that the bulk of this category is forages. More recent data on cultivation areas of pulses, soybeans, and groundnuts were available for 1980 and 1990 [FAO, 1993] but not for forages. We have estimated the cultivation area of forages for 1980 and 1990 by assuming that they increase at the same rate as the total of the other classes. Thus we have estimated the areas of legume cultivation in 1980 and 1990 to be  $280 \times 10^6$  and

$310 \times 10^6$  ha, respectively. Given our assumptions, there was significant uncertainty about these estimates. If the cultivation area of forages does not in reality increase at the same rate as the other crops, then it was an overestimate. The increase in legume yield per unit area over the last few decades may have compensated for any overestimate.

The rate of N fixation varies considerably both within and among legume types. Several recent studies [e.g., *Ayers et al.*, 1994; *Kinzig and Socolow*, 1994] used the estimate of  $140 \text{ kg N ha}^{-1}$  for all legume types based on a review by *Burns and Hardy* [1975]. However, as discussed in *LaRue and Patterson* [1981], this value may be too large by a factor of 2. In their review, *LaRue and Patterson* presented ranges of 9 to  $290 \text{ kg N ha}^{-1}$  for forage crops, 14.7 to  $263 \text{ kg N ha}^{-1}$  (average  $75 \text{ kg N ha}^{-1}$ ) for soybeans in North America, and 10 to  $222 \text{ kg N ha}^{-1}$  for pulses. They concluded that no legumes have valid estimates for the amount of N they fixed. More recently, *Keyser and Li* [1992] reviewed the range of BNF in soybeans from nine investigations. The range of the median BNF rates from those studies is 72 to  $201 \text{ kg N ha}^{-1}$ . Given the uncertainty of BNF rates, we have estimated a range of legume fixation of 70 to  $140 \text{ kg N ha}^{-1}$ . This value combined with legume cultivation area gave global fixation rates of 18-35, 20-39, and 22-43 Tg N  $\text{yr}^{-1}$  for 1970, 1980, and 1990, respectively. Cultivation of rice and other crops promotes N fixation by blue-green algae [*Watanabe*, 1986]. In 1970,  $135 \times 10^6$  ha were planted in rice [*Burns and Hardy*, 1975]. In 1980 and 1990, about  $144 \times 10^6$  and  $147 \times 10^6$  ha were planted in rice [FAO, 1993]. At a N-fixation rate of  $30 \text{ kg N ha}^{-1}$  [*Burns and Hardy*, 1975], about 5 Tg N is fixed by rice cultivation in each of those years. In addition, *Burns and Hardy* estimate that nonlegume crops other than rice supply an additional 5 Tg N  $\text{yr}^{-1}$  of fixed N. Thus for 1970, 1980, and 1990, we have estimated that the ranges of N fixation due to cultivation were 28-45, 30-49, and 32-53 Tg N  $\text{yr}^{-1}$  of reactive N. Keeping in mind the uncertainties of these numbers, we have used values of 36, 40, and 43 Tg N  $\text{yr}^{-1}$  for 1970, 1980, and 1990, respectively, for this paper.

**Table 2.** Cultivation Areas of Legumes

	Pulses	Soybeans	Groundnuts	Forages	Total
1970	63	34	18	135	250
1980	61	50	19	150*	280
1990	68	56	20	170*	310

Cultivation measured in hectares ( $10^6$  ha).

From 1970 to 1990, the annual rate of increase was 0.6% anthropogenic N fixation is  $\approx 140 \text{ Tg N yr}^{-1}$  (Figure 1b), with most of the increase occurring over the last few decades from the production of fertilizers (Figure 5).

Substantial N fixed by anthropogenic processes is redistributed. About  $20 \text{ Tg N yr}^{-1}$  of anthropogenic N are carried in dissolved forms by rivers and injected into the coastal ocean [Duce *et al.*, 1991], about equal to the natural riverine flux of dissolved N ( $14 \text{ Tg N yr}^{-1}$  [Meybeck, 1982]) (Figure 2). Riverine discharge of anthropogenic particulate organic nitrogen (PON) is more challenging to estimate because of difficulties in differentiating between preindustrial and anthropogenic PON. We have assumed that a doubling in particulate organic carbon (POC) discharge caused by human activities [Wollast and Mackenzie, 1989] meant that PON discharge also doubled. Thus the anthropogenic PON flux would be equal to the preindustrial flux of  $21 \text{ Tg N yr}^{-1}$  [Meybeck, 1982], and the riverine input of anthropogenic N would be 20 and  $21 \text{ Tg N yr}^{-1}$  for dissolved N and PON, respectively (Figure 2). The atmosphere received an even greater portion of the anthropogenic reactive N (Figure 1b). Energy production directly injects  $21 \text{ Tg N yr}^{-1}$  into the atmosphere [Levy and Moxim, 1989]; much of the remaining  $109 \text{ Tg N yr}^{-1}$  added to terrestrial ecosystems from fertilizer application and from legume and rice cultivation are emitted into the atmosphere.  $\text{NH}_3$  is emitted directly from fertilized fields,  $10 \text{ Tg N yr}^{-1}$  [Schlesinger and Hartley, 1992]. Animal husbandry on natural or managed pastures results in  $\text{NH}_3$  emissions to the atmosphere ( $32 \text{ Tg N yr}^{-1}$  [Schlesinger and Hartley, 1992]) from the hydrolysis of urea.  $\text{NH}_3$  is also emitted to the atmosphere by biomass burning ( $5 \text{ Tg N yr}^{-1}$  [Schlesinger and Hartley, 1992]). NO is emitted to the

atmosphere from fertilized soils ( $2 \text{ Tg N yr}^{-1}$  [Yienger and Levy, 1994]) and biomass burning ( $7.7 \text{ Tg N yr}^{-1}$  [Levy *et al.*, 1991]), as is  $\text{N}_2\text{O}$  (about  $3.4 \text{ Tg N yr}^{-1}$  [Schlesinger, 1991]).

Although the atmosphere receives much of the reactive N formed by anthropogenic activities, its storage is only temporary because reactive N compounds have residence times of hours to days. Some reactive N emitted to the atmosphere is deposited back onto continents, the rest is deposited to oceans; the atmosphere merely transports N from one point to another. Once deposited, reactive N reenters the biosphere. In a sense, the atmosphere allows reactive N to hopscotch about the world. Reactive N is emitted, transported, deposited, reemitted, transported, etc. The critical questions are as follows: What is the extent of the redistribution via atmospheric transport? and What is the ultimate fate of the N? Is it accumulated or converted back to unreactive  $\text{N}_2$ ?

We have assessed the degree of atmospheric distribution of  $\text{NO}_y$  in the present world by revisiting the estimates of N deposition calculated by the GFDL Chemical Transport Model (Figure 6). Relative to the "past" world (Figure 3), extensive amounts of reactive N are being redistributed through atmospheric transport. In addition, we have determined the amount of N deposited to ecosystems relative to mined the amount of N deposited to ecosystems relative to the amount emitted from ecosystems by dividing present-day deposition rates by current  $\text{NO}_y$  emission rates (Figure 7). In contrast to the preindustrial world when deposition/emission ratios were generally  $<2$  for continents (Figure 4), they now range up to 100. These figures illustrate that the adage "fixation without redistribution" no longer applies. For

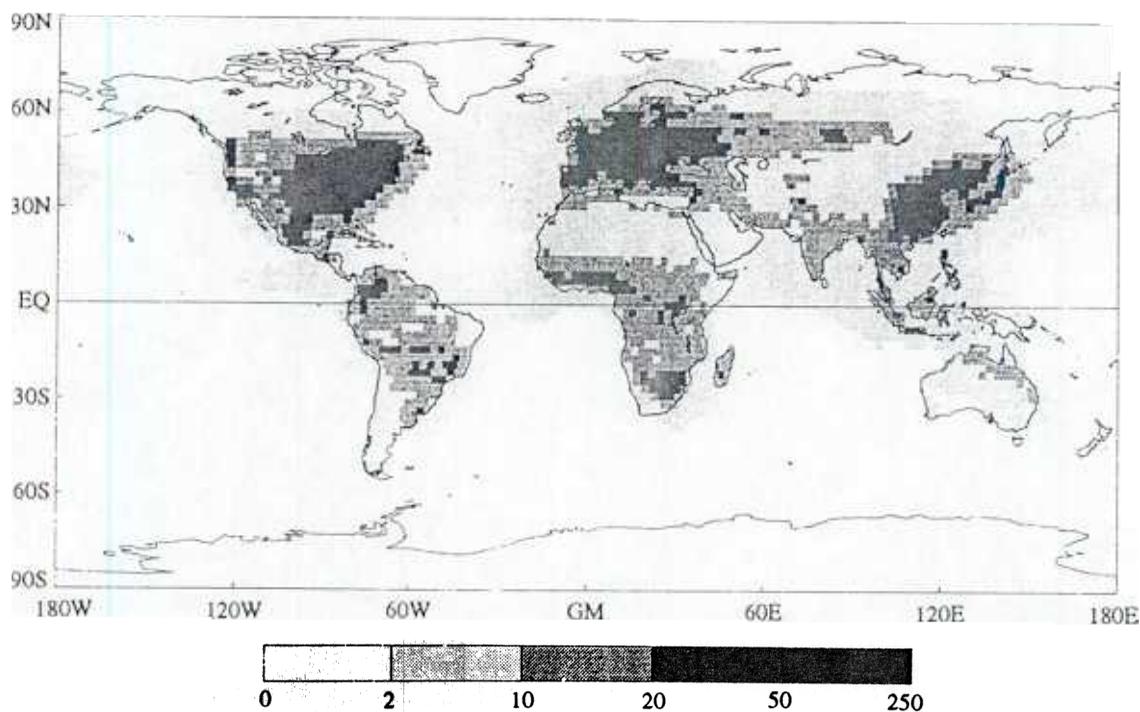


Figure 6. Current atmospheric  $\text{NO}_y$  deposition ( $\text{mmol N m}^{-2} \text{ yr}^{-1}$ ).

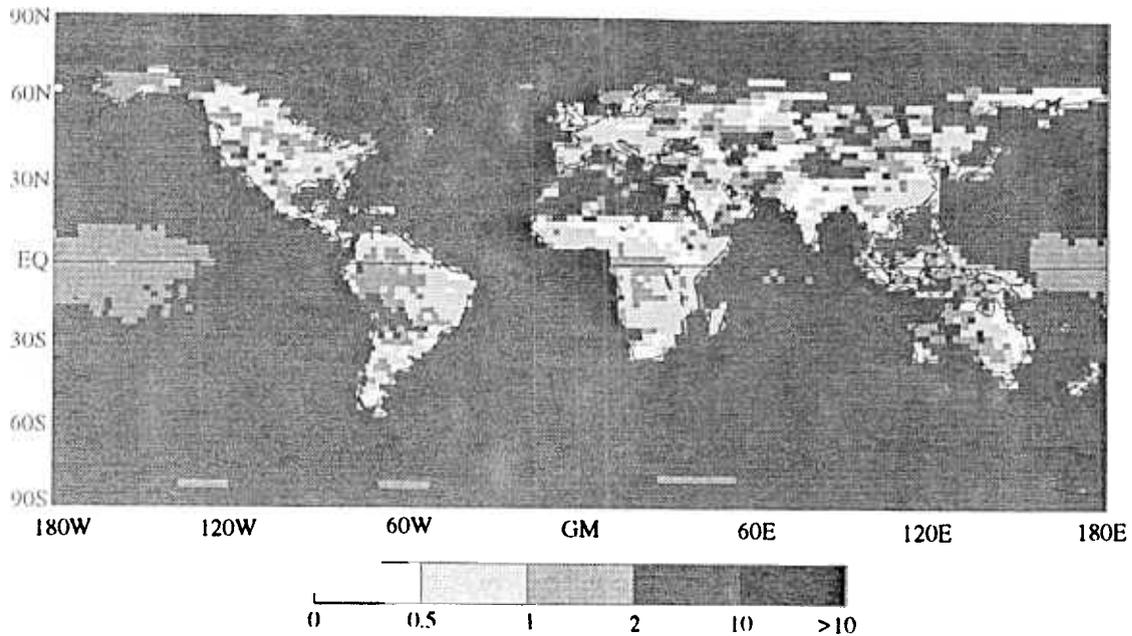


Figure 7. The ratio of current  $\text{NO}_y$  deposition to current  $\text{NO}$  emission showing N distribution.

example,  $\text{NO}$  emitted to the atmosphere of the United States can be transported to Europe [Levy and Moxim, 1989; Whelpdale and Galloway, 1994]. N deposited to midocean ecosystems has increased by several fold [Duce *et al.*, 1991; Owens *et al.*, 1992; Whelpdale and Galloway, 1994; Galloway *et al.*, 1994]. A history of the global transport of reactive N is available from ice cores from Greenland [Mayewski *et al.*, 1986; Laj *et al.*, 1992] and Antarctica [Langway *et al.*, 1994] that show substantial increases in ammonium and nitrate in recently deposited layers.

Anthropogenic N emitted to the atmosphere can either be redeposited into terrestrial ecosystems or transported and deposited into marine ecosystems. We have estimated that, of the  $31 \text{ Tg N yr}^{-1}$  of  $\text{NO}_x$  emitted to the atmosphere by anthropogenic activities, 22 and  $9 \text{ Tg N yr}^{-1}$  of  $\text{NO}_y$  are deposited to terrestrial and marine ecosystems, respectively (Figure 2). We have also estimated that the total  $\text{NO}_y$  (natural and anthropogenic) deposited to the ocean is about  $12 \text{ Tg N yr}^{-1}$ , which agrees well with the  $14 \text{ Tg N yr}^{-1}$  estimated by Duce *et al.* [1991]. We have used two methods to estimate natural and anthropogenic  $\text{NH}_x$  deposited to the ocean surface. First we have applied the 3.3:9 proportion found for oxidized N to the total  $\text{NH}_x$  deposition rate of  $17 \text{ Tg N yr}^{-1}$  ( $16.8 \text{ Tg N yr}^{-1}$  [Duce *et al.*, 1991]) to calculate natural and anthropogenic marine  $\text{NH}_x$  deposition rates of 4.2 and  $13 \text{ Tg N yr}^{-1}$ , respectively. Because of the shorter atmospheric residence time of  $\text{NH}_x$ , this technique probably underestimated natural  $\text{NH}_x$  deposition on the ocean. We could have assumed that the  $13 \text{ Tg N yr}^{-1}$  emitted to the marine atmosphere was redeposited to the ocean and that the difference between  $13 \text{ Tg N yr}^{-1}$  and  $17 \text{ Tg N yr}^{-1}$  ( $4 \text{ Tg N yr}^{-1}$ ) represented net anthropogenic  $\text{NH}_x$  deposition on the ocean. However, just as the previous techniques underestimated the natural deposition rate, this approach would have overestimated the rate given the likelihood that natural

$\text{NH}_x$  was transported from the marine to the continental atmospheres. Therefore for the purposes of this paper, we have taken a middle ground and have assumed that, of the  $17 \text{ Tg N yr}^{-1}$  of  $\text{NH}_x$  deposited in the ocean, half is from natural sources and half from anthropogenic sources, with about a factor of 2 uncertainty. In the preindustrial world, the uncertainties in the emission estimates were such that we were unable to determine the relative magnitude of  $\text{NH}_x$  emissions from marine and terrestrial systems and thus determine whether the oceans or the continents served as net source areas. However, for the current world there is substantial atmospheric transfer of anthropogenic  $\text{NH}_3$  (and  $\text{NO}_y$ ) to ecosystems of the open ocean.

Therefore of the atmospheric  $\text{NO}_y$  and  $\text{NH}_x$  emitted from anthropogenic activities, about 70 and 80%, respectively, are redeposited to terrestrial ecosystems; the balance (about  $18 \text{ Tg N yr}^{-1}$ ) is transported to the marine atmosphere and deposited at sea. Another  $41 \text{ Tg N yr}^{-1}$  of anthropogenic reactive N is injected into oceans via rivers for a net total of about  $59 \text{ Tg N yr}^{-1}$  of anthropogenic N transferred from the land to the ocean. Compared to the preindustrial transfer of about  $35 \text{ Tg N yr}^{-1}$ , this additional source of reactive N almost triples delivery of reactive N from terrestrial to marine ecosystems (Figure 2). Three comparisons with the preindustrial world can be made.

(1) On continents, human activities are now producing reactive N at the same rate as natural processes ( $130\text{--}150$  and  $90\text{--}130 \text{ Tg N yr}^{-1}$ , respectively).

(2) The release of reactive N from continents to coastal oceans via rivers has about doubled, from  $35$  to  $76 \text{ Tg N yr}^{-1}$ . The net atmospheric transfer of N from continents to the open ocean has increased from near zero to about  $18 \text{ Tg N yr}^{-1}$ .

(3) In the preindustrial world the atmospheric distribution of N was relatively limited compared to the amount that was

fixed and about 10 to 20% was leaked to the atmosphere from terrestrial and marine ecosystems as reactive N (Figure 1a). In the modern world, about 55% of the N fixed by human activities is emitted to the atmosphere (Figure 1b). Absolute emissions of reactive N to the atmosphere have increased from about 29 Tg N yr<sup>-1</sup> in the preindustrial world to 107 Tg N yr<sup>-1</sup>, currently. This increase allows more reactive N to be redistributed to ecosystems far from the point of fixation. The N<sub>2</sub>O emission rate to the atmosphere has increased from 7.7 to about 11 Tg N yr<sup>-1</sup>.

### Is N Accumulating? Or "The Case of the Missing Nitrogen"

Currently, humans are mobilizing C by burning fossil fuels, producing cement (5.5 ± 0.5 Pg C yr<sup>-1</sup>) (Pg = 10<sup>15</sup>), and changing land use (1.6 ± 1.0 Pg C yr<sup>-1</sup>). The atmospheric pool of CO<sub>2</sub> has increased (3.2 ± 0.2 Pg C yr<sup>-1</sup>) but not as rapidly as one might guess given the size of the estimated oceanic uptake (2.0 ± 0.8 Pg C yr<sup>-1</sup>) and forest regrowth (0.5 ± 0.5 Pg C yr<sup>-1</sup>) in the middle and high-latitude northern hemisphere [Schimel *et al.*, 1994]. The remainder of the C is "missing" and the search for it is an area of active investigation.

The situation with N is similar. Humans are fixing ≈140 Tg N yr<sup>-1</sup>. Where is it going, and once we find it, what is it doing? Possible fates for the reactive N produced by human activities are (1) denitrification to N<sub>2</sub> and (2) accumulation in the atmosphere, soils, groundwater, land vegetation, oceans, and marine sediments. This section sets boundaries on our uncertainties about the fate of the missing N. The task is a critical one for, if N is accumulating, there could be ecosystem impacts and substantial feedbacks to other phenomena on hemispheric and global scales [Garrels *et al.*, 1975].

#### Atmosphere

Atmospheric N<sub>2</sub>O concentrations are increasing at about the same relative rate that anthropogenic N fixation is increasing [Vitousek, 1994]. However, the amount of the increase (3 Tg N yr<sup>-1</sup> [Weiss, 1981; Keller *et al.*, 1986]) is small relative to the amount of N that humans convert from unreactive to reactive forms (≈140 Tg N yr<sup>-1</sup>).

Undoubtedly, a significant fraction of the N fixed by human activities denitrifies to N<sub>2</sub>. However, unlike N<sub>2</sub>O, atmospheric concentrations of N<sub>2</sub> are too large to detect a change. Therefore either denitrification must be measured directly or a method to measure it indirectly must be developed.

Direct measures show a strong potential for denitrification in groundwater. With their anaerobic nature and with sufficient concentrations of organic substrate [e.g., Ronen *et al.*, 1988; Spalding and Parrott, 1994], groundwater reservoirs are excellent sites for denitrification. Unfortunately, denitrification rates in groundwater vary considerably and the ability to predict them is site-specific at best [Korom, 1992]. Forested ecosystems can also have appreciable denitrification rates since they are moist and rich in organic matter (e.g., organic debris dams in streams and soil microsites) especially during certain times of the year (e.g., spring snowmelt

[Groffman *et al.*, 1992]). In addition, if nitrate begins to accumulate because of increased deposition, then denitrification rates can increase [Melillo, 1981; Johnson, 1992]. Again, however, because of the variability of denitrification rates in soils, the possibility of directly measuring any change in the global flux is problematic.

Indirect techniques are also unsatisfactory. Weier *et al.* [1993] assessed an indirect method for measuring how much N<sub>2</sub> is emitted to the atmosphere by measuring the ratio of N<sub>2</sub>:N<sub>2</sub>O emitted by different soil types. They found that this ratio varies too much to assess quantitatively the N<sub>2</sub> flux using N<sub>2</sub>O measurements. Keeping these difficulties in mind, we have estimated the change in the global flux of N<sub>2</sub> from denitrification by assuming that the N<sub>2</sub>:N<sub>2</sub>O ratio (weight) in denitrification in the preindustrial world was about 14-32 (based on an estimate of preindustrial denitrification on land of 80-180 Tg yr<sup>-1</sup>, Figure 1a) and that the increased flux of N<sub>2</sub>O (3.4 Tg N yr<sup>-1</sup>, Figure 1b) is from denitrification of N mobilized by human activities. Using these assumptions, an increment of 3.4 Tg N yr<sup>-1</sup> of N<sub>2</sub>O in the atmosphere would imply that N<sub>2</sub> from denitrification has increased about 50-110 Tg N yr<sup>-1</sup>. As the range indicates, there was much uncertainty in this number. In addition, because some processes produce N<sub>2</sub>O but not N<sub>2</sub> (e.g., nitrification, nylon production), a rate based on N<sub>2</sub>O emissions to the atmosphere would be an overestimate. Thus at that point, we were unable to determine the amount of anthropogenic N denitrified to N<sub>2</sub>. Given the potential magnitude of the sink, it is an area critical to any future research.

#### Continents

Human activities on continents fix ≈140 Tg N yr<sup>-1</sup>. Of this, 41 Tg N yr<sup>-1</sup> enter the coastal ocean via rivers, 18 Tg N yr<sup>-1</sup> are deposited to the ocean from the atmosphere, and 3.4 Tg N yr<sup>-1</sup> are emitted to the atmosphere as N<sub>2</sub>O. The remaining ≈80 Tg N yr<sup>-1</sup> are either stored or denitrified to N<sub>2</sub>. Our estimate of denitrification of anthropogenic N (50-110 Tg N yr<sup>-1</sup>) brackets the remainder. However, as discussed, there were large uncertainties about many of our estimates, especially N<sub>2</sub> production. Hence storage of N within continental systems is highly likely. The following paragraphs put limits on the extent of storage possible in groundwater, biomass, and soils. Storage may be active or inactive. In the former, N is actively cycled among the subcompartments of natural ecosystems (e.g., soils, living and dead biomass, surface waters, etc.); in the latter, N is removed from circulation (e.g., stored in deep continental reservoirs). For our purposes, inactive storage was equivalent to N<sub>2</sub> produced by denitrification; the N was not available for interaction with other components of the environment.

Many terrestrial ecosystems are N limited; thus reactive N can be stored by an increase in biomass or an increase of N in soil organic matter. Johnson [1992] reviewed the results from the Integrated Forest Study and other studies and concluded that N is preferentially stored as net gains in biomass as opposed to storage in soil. In contrast, Aber *et al.* [1993] in a study of the fate of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> added to Harvard Forest, Massachusetts, concluded that N is retained

primarily in the soil organic pool and is not lost from the system until it is no longer limiting. *Nadelhoffer et al.* [1993], following the fate of  $\text{NH}_4^+$  added to a hardwood forest at the Bear Brook watershed in Maine, concluded that most N is stored in the soil pool and not in vegetation. The fate of  $\text{NO}_3^-$  additions is different. One-fourth to one-third of the  $\text{NO}_3^-$  applied to the forest plots is found in the above-ground biomass and surface soil and plant and microbial assimilation are about equally important in retaining  $\text{NO}_3^-$  additions to that forest [*Nadelhoffer et al.*, 1995]. Thus forested ecosystems by virtue of their N-limited character are potentially strong sinks for storing anthropogenic N. *Dixon et al.* [1994] estimated that forests, especially in temperate regions, are accumulating  $0.7 \text{ Pg C yr}^{-1}$ . With an average organic N content of vegetation of 1%, this represents a global accumulation of about  $7 \text{ Tg N yr}^{-1}$ . They point out that changes in land-use practices could result in additional C and thus N storage. Therefore the potential for N to accumulate in terrestrial organic matter is large but the magnitude is unknown.

Anthropogenic N can also be stored in groundwater. In a recent review, *Spalding and Exner* [1993] stated that the concentrations of  $\text{NO}_3^-$ , the most common aquifer contaminant, are increasing. *Madison and Brunett* [1985] and a follow-up analysis by *Lee and Nielsen* [1989] showed that nitrate concentrations in the groundwater of the United States are elevated in much of the nation's agricultural regions. Increases in nitrate concentrations can be substantial. As *Hallberg and Keeney* [1993] reported that between the 1930s and 1980s, nitrate concentrations in an aquifer in the Big Spring Basin area increased from  $<1 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$  to  $10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ . It is difficult to assess how much N is stored in groundwater aquifers without knowing aquifer sizes or how representative the data are. However, we were able to set some bounds on the amount of N stored in groundwater using the following calculation. About  $4200 \times 10^3 \text{ km}^3$  of groundwater are within a half mile of the earth's surface [*van der Leeden et al.*, 1990]. When we assumed that anthropogenic N was stored only in the top 100 m of soil, the groundwater volume became  $5.2 \times 10^{17} \text{ L}$ . When we raised the nitrate concentration of groundwater by  $1 \text{ mg N L}^{-1}$ , groundwater stored about  $500 \text{ Tg N}$ . Thus groundwater is potentially a large reservoir for anthropogenic N. Whether it is in reality will require extensive information about the 3-dimensional distribution of nitrate in the world's groundwaters, the residence time of nitrate in groundwater, the formation rate of new groundwaters and the depletion rate of old groundwater.

#### Ocean: Coastal

Of the  $\approx 140 \text{ Tg N yr}^{-1}$  fixed by human activities,  $59 \text{ Tg N yr}^{-1}$  (40%) are injected into oceans, of which  $41 \text{ Tg N yr}^{-1}$  are from river flow into the coastal ocean and  $18 \text{ Tg N yr}^{-1}$  are from atmospheric deposition on the open ocean.

There are three primary fates of N injected into the coastal ocean: Storage in coastal sediments as  $\text{N}_{\text{org}}$ , denitrification to  $\text{N}_2$ , or export to the open ocean. The general coastal cycle begins with river input and is followed by biotic uptake, deposition of organic matter, oxidation of reduced N to  $\text{NO}_3^-$ , and then denitrification to  $\text{N}_2$ . Alternatively,  $\text{NO}_3^-$

in the water column can diffuse into the sediments and be denitrified directly. Denitrification is the most likely sink for N injected into the coastal/shelf environment. Anaerobic environments required for denitrification are extensive in sediments of the coastal and shelf oceans, thus it is not surprising that denitrification is a major process [*Christensen et al.*, 1987]. *Seitzinger* [1988] found that the range of denitrification rates is greater in coastal marine sediments than in lake or river sediments, with the highest rates in systems with substantial amounts of anthropogenic nutrient inputs. *Seitzinger* [1988] also found that much of the organic N mineralized in coastal marine sediments is denitrified and that the denitrification rate exceeds the N-fixation rate in almost all coastal marine ecosystems and that denitrification in estuaries is a sink for 40 to 50% of the natural and anthropogenic inputs of dissolved inorganic N to estuaries from the surrounding watershed. The importance of denitrification in coastal and shelf oceans is supported by *Nixon et al.* [1995] and S. P. *Seitzinger* and A. E. *Giblin* (Estimating denitrification in North Atlantic continental shelf sediments, submitted to *Biogeochemistry*, 1995) who reported that denitrification rates on continental shelves are greater than riverine inputs and thus require a net input of nitrate from the open ocean to balance sediment denitrification. Thus it is likely that little of the riverine N injected into the coastal ocean is transported beyond the shelf region. It is either denitrified or stored in sediments.

#### Ocean: Open

Exclusive of the cross-shelf transport of riverine N, open oceans also receive significant anthropogenic N from atmospheric deposition ( $18 \text{ Tg N yr}^{-1}$ ). There are three possible fates of the N deposited to the open ocean: Deposition to the ocean floor, accumulation in deep water, or emission of  $\text{N}_2$  to the atmosphere. Deposition to the deep ocean floor is not a major sink. Although all atmospheric N deposited into oceans is rapidly incorporated into organic matter, only 1-2% of total surface production is deposited in deep marine sediments and most is decomposed in deep waters to  $\text{NO}_3^-$ . Total long-term burial in deep-ocean sediment is currently estimated to be of the order of  $0.4 \text{ Tg N yr}^{-1}$  [*GESAMP*, 1987]; and, even if this rate is low by a factor of 10, it is still an order of magnitude less than atmospheric deposition. *Duce et al.* [1991] stated that the large difference between the atmospheric input and the pelagic burial rate suggests that there must be a large flux of N gases to the atmosphere (e.g.,  $\text{N}_2$ ). The imbalance between historical oceanic N-fixation rates ( $30 \text{ Tg yr}^{-1}$ ) and denitrification rates ( $150\text{-}180 \text{ Tg yr}^{-1}$ ) [*Christensen et al.*, 1987; *Codispoti and Christensen*, 1985] supports this conclusion. If more recent and higher N-fixation rates are accurate, then oceans may be closer to balance and the net exchange of  $\text{N}_2$  may be small. (It is intriguing that the oceanic N-fixation rate may be sensitive to trace metals like iron and that trace element fluxes to oceans may also have increased significantly because of human activity.) However, oceanic denitrification rates or  $\text{N}_2$  fluxes to the atmosphere do not have to increase to compensate for increased atmospheric deposition of anthropogenic N. Additional N may also accumulate in deep oceans as either  $\text{NO}_3^-$  or dissolved  $\text{N}_2$ . Both pools are very

large compared to anthropogenic fluxes, approximately  $10^5$  Tg N for  $\text{NO}_3^-$  and  $10^7$  Tg N for dissolved  $\text{N}_2$  [Laws, 1983]. Globally, total anthropogenic N inputs to oceans would not measurably change concentrations of any N constituent (e.g., approximately 0.02% per year for  $\text{NO}_3^-$ ).

In summary, anthropogenic N is accumulating in soils, groundwater, and vegetation. However, given the extensive variability in the magnitude of the storage mechanism and the potentially large rate of denitrification production of  $\text{N}_2$ , we were unable to set bounds on the accumulation rates. As discussed below, it is critical that these rates be determined.

### N Is Accumulating: So What?

We have known for some time that reactive N initially entering the environment has many effects. Nitrogenous fertilizer and domestic legumes have been introduced "on purpose" and have created more productive agricultural systems. The local negative effects are primarily associated with  $\text{NO}_3^-$  loss to aquatic ecosystems resulting in unplanned fertilization and more methemoglobinemia.  $\text{NO}_x$  is emitted to the atmosphere from fossil-fuel combustion "by accident," and it has both local and regional deleterious impacts. Tropospheric  $\text{O}_3$  is enhanced by emissions of  $\text{NO}_x$  and associated hydrocarbons and, over many regions,  $\text{O}_3$  concentrations and the acidity of atmospheric deposition are now much higher than in preindustrial times. Consequences of increased rural  $\text{O}_3$  involve both human health and ecosystems. The primary consequence of more  $\text{HNO}_3$  deposited to ecosystems is short-term acidification of low-alkalinity streams and lakes during episodic events (e.g., snowmelt, storm runoff) [e.g., Galloway and Dillon, 1983]. Currently, the rates at which reactive N is created exceed N-fixation rates in unmanaged terrestrial ecosystems and reactive N is apparently accumulating in the environment. The following section explores some hemispheric and global consequences of this N accumulation.

#### Atmosphere

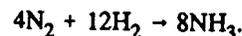
Several authors have discussed the consequences of increased atmospheric reactive N levels.  $\text{O}_3$  mixing ratios may have already more than doubled over the midlatitude, northern hemisphere continental troposphere because of increased anthropogenic pollution, primarily  $\text{NO}_x$  emissions [e.g., Crutzen, 1988; Kley et al., 1988]. Calculations from the three-dimensional GFDL Chemical Transport Model predicted that  $\text{NO}_x$  levels would continue to increase throughout most of the northern hemisphere, which in turn might lead to significant increases in tropospheric  $\text{O}_3$  [Galloway et al., 1994]. Chameides et al. [1994] estimated that 9 to 35% of the world's cereal crops are currently exposed to  $\text{O}_3$  concentrations that have the potential to cause crop-yield reductions. In addition, they calculated that increasing  $\text{NO}_x$  emissions will cause a threefold increase in plant exposure to tropospheric  $\text{O}_3$  by early next century in some midlatitude regions.

#### Continents

Terrestrial ecosystems require C and N in specified amounts. C:N weight ratios in woody tissues range from

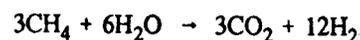
50:1 to 150:1 [Schindler and Bayley, 1993] although the range can be larger when all components of the terrestrial ecosystem are considered [e.g., Kinzig and Socolow, 1994]. With the advent of extensive combustion and fertilizer use, the amounts of C and N available for ecosystems have increased dramatically. The consequences of these changes depend on the relative increases in mobilization as well as the extent of C and N distribution beyond the point of mobilization.

We determined the relative rates of creating reactive C and N by calculating the C:N ratios of each of the three processes considered in this paper: Fossil-fuel combustion, combustion was the primary anthropogenic process mobilizing C and N, the C:N ratio of the mobilized material was about 200 (e.g., in 1980, fossil-fuel combustion released about 5200 Tg C [Boden et al., 1990] and 22 Tg N [Dignon and Hameed, 1989]), generally greater than terrestrial ecosystem requirements. However, the C:N ratios of fertilizer and legume production were quite different. Most anthropogenic fertilizer used in the world is either  $\text{NH}_3$  or urea produced from  $\text{NH}_3$  [Constant and Sheldrick, 1992]. The basic formation reaction for  $\text{NH}_3$  is

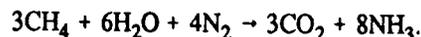


Production of fertilizer in this way requires significant energy for this endothermic reaction. Two processes are involved in the creation of reactive C and N by fertilizer production. The first is the combustion to supply the energy required for fertilizer production. The second is the actual production of  $\text{NH}_3$ . Natural gas is the most prominent fossil fuel generating energy used in fertilizer production. (Since the reactive C and N produced by combustion have already been accounted for above, we did not consider it further here.) For the second process,  $\text{N}_2$  comes from the atmosphere and  $\text{H}_2$  comes from reducing a feedstock (e.g.,  $\text{CH}_4$ ). Globally, the feedstocks are natural gas (79%), coal and coke (11%), naphtha (5%), oil (3%), and "other" (2%) [Constant and Sheldrick, 1992]. Most new fertilizer plants use natural gas as a feedstock although in China coal continues to dominate. Because natural gas prevails, we used that fuel in our stoichiometry calculations.

$\text{H}_2$  is generated in a reducing environment at high temperatures by the reaction of the feedstock with  $\text{H}_2\text{O}$



Combining the two reactions above yields an  $\text{NH}_3$  production reaction of



By weight the reactive C:N ratio of fertilization production is about 0.3.

The relative mobilization rates of reactive C and N from cultivating legumes presented a different situation. Legume cultivation creates reactive N from  $\text{N}_2$  by microbial activity. It does not create reactive C because existing reactive C ( $\text{CO}_2$ ) is used in photosynthesis. Therefore, legume (and rice) cultivation produces only reactive N.

Thus currently the C:N ratio is much lower. In 1980 the C:N ratio from combustion was  $\approx 200$ . When we included fertilizer and legume production (60 and 40 Tg reactive N produced from fertilizer and legume production, respectively, and 18 Tg reactive C produced from fertilizer production), the ratio dropped to  $< 50$ . Thus over the past century mobilization of reactive N has increased relative to C. N (as  $\text{NO}_y$  and  $\text{NH}_x$ ) has been extensively distributed throughout the atmosphere (e.g., for  $\text{NO}_y$  see Figures 6 and 7) and is available to terrestrial ecosystems at locations far removed from its point of mobilization.

It should be noted that the amount of P, another important nutrient, mobilized by human activities has also increased. In 1950 the N:P ratio (by weight) of fertilizer produced was 0.9, by 1970 it was about 7, and currently it is about 10 (after Turner and Rabalais [1991]), equivalent to that in woody tissue and soils [Melillo and Gosz, 1983]. However, although the increased rates of N and P mobilization have kept pace with ecosystem requirements [Garrels et al., 1975], the area impacted by P has generally been significantly less than that by N because P has no significant gas phase and it is readily adsorbed by particles although long-range transport of P can occur [e.g., Swap et al., 1992]. Thus its distribution beyond the point of application is primarily limited to hydrologic transport, which impacts freshwater and coastal ecosystems as a result of fertilizer runoff and sewage treatment.

Several examples manifest the increased supply of reactive N in terrestrial ecosystems. One consequence of N fertilization of natural ecosystems, perhaps first noted in lake eutrophication, is a loss of species diversity [e.g., Bakelaar and Odum, 1978; Tilman, 1982; Hueneke et al., 1990]. Studies of natural and experimental plant populations often show that increased plant growth in fertile conditions is associated with intense competition. Plant diversity has been remarkably reduced in a long-time fertilized pasture in Great Britain from 1856 to the present; many rare species have been replaced by a few aggressive weedy species that now dominate the community [Kempton, 1979]. Ecologists have ample theories to explain these observations; the maximum species diversity in natural communities will persist when resources are low so that each species is limited by a different resource and no one species can out compete the rest [Levin, 1970; Rosenzweig, 1971; Tilman, 1982]. Any resource added to such a community will lead to the dominance of the species that can most efficiently use that resource.

Atmospheric N deposited to the Netherlands ( $50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) is less than the amount of N used to fertilize pastures in Britain ( $144 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ), but recent trends in species diversity in the Dutch heathlands and pastures are similar to changes observed in fertilization experiments. Over large areas, formerly diverse pastures are now dominated by *Brachypodium*, which increases when fertilized [Bobbink, 1991]. In other areas grasslands of *Deschampsia* and *Molinia* have invaded *Calluna* heathlands [Heil and Diemont, 1983]. These plant communities are apparently changing because the competitive relations of the species are changing and because of changes in basic ecosystem processes. Unlike species losses from local, toxic industrial emissions, these changes in plant community structure

represent a regional loss of biotic diversity from persistent exposure to an effluent of the industrialized world that would seem, at first glance, to be benefiting plant communities. The ecosystem shows signs of eutrophication: It is more productive but with lower species diversity and a greater potential for  $\text{NO}_3^-$  loss [Van Vuuren et al., 1992]. Persistent atmospheric deposition of fixed N to forest ecosystems may eventually lead to retrogressive changes in ecosystem function. Aber et al. [1989] suggested that forests in the north-eastern United States are becoming N sources rather than N sinks because of extensive N deposition. Not only are the forests potentially impacted by the high rate of atmospheric deposition but they are also N sources to downstream ecosystems and to the atmosphere ( $\text{N}_2\text{O}$  emissions). Kauppi et al. [1992] suggested that the forests of central Europe are now growing much faster than they were several decades ago partly because excess N is being deposited from the atmosphere. Mohren et al. [1986] reported that Douglas fir stands in northwestern European lowlands have shifted from N limitation to P limitation because of increased atmospheric deposition of N.

In the process of fertilizing terrestrial ecosystems, reactive N accumulated in the environment might impact atmospheric  $\text{CO}_2$  concentrations by additional photosynthetic conversion of  $\text{CO}_2$  into organic C. There is a large potential for carbon storage in terrestrial ecosystems from N fertilization. We have estimated that about  $60 \text{ Tg N yr}^{-1}$  (Figure 2) of anthropogenic N are deposited to continents. If that N is taken up by long-lived terrestrial plants with C:N weight ratios of 50:1 to 150:1 (based on Schindler and Bayley [1993]), then up to 3 to  $9 \text{ Pg C yr}^{-1}$  could be stored in the biomass, more than enough to account for any missing carbon (about  $1.2 \text{ Pg C yr}^{-1}$ ). Several researchers have investigated this issue. Peterson and Melillo [1985] estimated that  $0.2 \text{ Pg C yr}^{-1}$  can be stored in terrestrial biomass by "nitrogen matching." More recently, Schindler and Bayley [1993] estimated that there is a possible carbon sink of 1 to  $2.3 \text{ Pg C yr}^{-1}$ . In a recent review, Schimel et al. [1994] estimated that 0.2 to  $1.0 \text{ Pg C yr}^{-1}$  may be stored in forests because of the 50 to  $60 \text{ Tg N yr}^{-1}$  of N deposition. A. R. Townsend et al. (Nitrogen deposition and terrestrial carbon storage: Linking atmospheric chemistry and the global carbon budget, submitted to *Ecological Applications*, 1995) estimated that the 1990 net uptake of  $\text{CO}_2$  from deposition of fossil-fuel N was between 0.2 and  $1.2 \text{ Pg C yr}^{-1}$ , with a best estimate of 0.3 to  $0.6 \text{ Pg C yr}^{-1}$ . However, their calculations did not include  $\text{NO}_y$  from non-fossil-fuel sources or any  $\text{NH}_x$ . Hudson et al. [1994] also concluded that N fertilization of temperate forests is an important sink for  $\text{CO}_2$ . They stated that up to 40% of the increase growth of the terrestrial biosphere may be from N fertilization based on N-deposition rates of 26- $30 \text{ Tg N yr}^{-1}$  to temperate and boreal forests. This range of N deposition was not inconsistent with our estimate of about  $60 \text{ Tg N}$  deposited to continents. These studies indicated that deposition of anthropogenic N has the potential to account for a substantial portion of the "missing" C. However, whether the potential is fulfilled is open to question. As Aber et al. [1993] and Nadelhoffer et al. [1993, 1995] illustrated, not all N deposited to forested ecosystems is stored in woody tissue; a substantial portion is stored in soil

organic matter with substantially lower C:N ratios than in woody biomass. Further resolution of this issue awaits detailed measurements of the fate of N deposited to forested ecosystems. Another potentially large storage reservoir for carbon is groundwater. When anthropogenic N is incorporated into organic matter and then is sequestered in groundwater, the associated carbon is removed from the atmosphere.

### Ocean

About 40% of the N fixed by human activities is injected into the ocean. Because this N is either denitrified to  $N_2$ , stored in coastal sediments as  $N_{org}$ , or stored in the deep ocean as nitrate or  $N_2$  (all very large pools), the long-term impact on oceanic water-column processes is probably minimal. Estuaries of major rivers, nearshore benthic environments, and coastal seas may have more prolonged, local effects. For example, N. F. Caraco (personal communication, 1994) has postulated that regions of the western Pacific coastal ocean have shifted from N limitation to P limitation because of extensive N fertilizer (relative to P and K fertilizers) use in China.

In some areas, anthropogenic N deposited from the atmosphere can change the natural N cycle of the upper ocean, particularly near the surface [Michaels *et al.*, 1993; Owens *et al.*, 1992; Paerl, 1985; Paerl and Fogel, 1994]. In the North Atlantic Ocean, deep-water nitrate concentrations are lower than in other oceans, and annual atmospheric inputs to this basin ( $10 \text{ Tg N yr}^{-1}$ ) are approximately 0.1% of the nitrate stock in the upper 1000 m (2% over 2 decades). This substantial input may change the upper-ocean nitrate gradients and nutrient-limitation patterns and perhaps, in some areas, switch the limiting factor from N to phosphate.

The oceans are thought to be a significant sink for anthropogenic C although few explanations for this sink can be directly related to the anthropogenic changes in atmospheric C. For marine ecosystems, the input of anthropogenic N is one mechanism for linking a subsequent storage of carbon to an anthropogenic signal. Most anthropogenic reactive N added to the open ocean is quickly incorporated into organic matter (at a C:N ratio near the Redfield Ratio of 6.6 mol C/mol N) and transported and held below the surface thus maintaining the near-surface depletion. If all of the  $18 \text{ Tg N yr}^{-1}$  of reactive N deposited on the open ocean were sequestered in the main thermocline or stored in biomass at this ratio, it would account for a C storage of  $0.14 \text{ Pg C yr}^{-1}$ . Sinking particles in deep waters have a higher C:N molar ratio of 9-12 [Martin *et al.*, 1987; Honjo *et al.*, 1982]. Even if all the atmospheric deposition were sequestered at these ratios, it would account for less than  $0.3 \text{ Pg C yr}^{-1}$ . In fact, if all the reactive nitrogen added to the ocean ( $59 \text{ Tg N yr}^{-1}$ , Figure 1b) were sequestered at a C:N of 14 ( $\text{g g}^{-1}$ ), this process would only account for  $0.8 \text{ Pg C yr}^{-1}$ . Although these rates are significant in comparison to the size of the total oceanic sink ( $1\text{-}3 \text{ Pg yr}^{-1}$ ) [Sarmiento and Sundquist, 1992], the net long-term sequestration of carbon by this process must be lower than these rates since much of the nitrogen is remineralized in the main thermocline with a short residence time. The fate of anthropogenic nitrogen after it enters the ocean determines the effect of this mechanism in mediating anthropogenic carbon storage.

In summary, the increases in N mobilization relative to that of C and mobilization and distribution of N relative to P imply that large regions of the world where N has historically been the limiting factor are shifting to regions where N is in excess and some other nutrient (e.g., P) is becoming the limiting factor.

### Forecast for the Future

Anthropogenic N fixation is driven by two processes, energy and food production, each of which is controlled by two factors: human population and the standard of living. Both factors will probably increase with time. Future anthropogenic N-fixation rates can be estimated using past trends in energy, fertilizer use, and legume cultivation. For N fixation during fossil-fuel production, Galloway [1989] estimated that N emissions in 2020 will range from 30 to  $60 \text{ Tg N yr}^{-1}$ ; in 1980 the value was only about  $20 \text{ Tg N yr}^{-1}$ . More recently, Galloway *et al.* [1994] estimated that the 2020 value will be on the order of  $46 \text{ Tg N yr}^{-1}$  (Table 1), more than double the 1980 value, with the less-developed regions having the highest increase. This estimate agrees well with the 2025 estimate of Leggett *et al.* [1992] of  $43 \text{ Tg N yr}^{-1}$ .

Future N-fixation rates by fertilizer production are estimated by analyzing historical rates. Specifically, trends of regional fertilizer consumption in North/Central America, South America, Asia, the former USSR (FSU), and Africa are available for 1961-1989 (1961-1971 [United Nations, 1976], 1972-1979 [United Nations, 1981], and 1980-1989 [United Nations, 1992]). In 1989, about  $78 \text{ Tg N yr}^{-1}$  is fixed by fertilizer production and about  $50 \text{ Tg N yr}^{-1}$  is consumed in less-developed regions and the rest is consumed in more-developed regions (Table 1). These data showed that Asia has the greatest increase in consumption of fertilizer N.

From 1979 to 1989, fertilizer consumption increases by about 3.3% annually. When we projected that rate to 2020, the annual fixation rate increased to  $206 \text{ Tg N yr}^{-1}$  from the  $78 \text{ Tg N yr}^{-1}$  in 1989. However, the fertilizer industry will probably not be able to sustain such an increase. Production facilities are limited and recent political events in the Middle East and the FSU have already caused fertilizer N production to decrease [Constant and Sheldrick, 1992]. Reporting about an analysis by the World Bank's Fertilizer Working Group, Constant and Sheldrick predicted an annual growth rate of 1.47% through 2000-2001. Regionally, their annual growth rates are 3.07% for Africa, 0.21% for North America, 2.40% for Central America, 3.40% for South America, 2.92% for Asia, -1.17% for Europe, and -0.52% for the FSU. For our 2020 projections, we have modified these 2000-2001 estimates by assuming that the negative growth rates for the FSU and Europe will be zero over the longer time period we have used. In addition, we have combined the fertilizer consumption increases of 2.40% for Central America and 3.40% for South America into one rate of 3.07% for the entire area. We calculated an estimated 2020 value of  $134 \text{ Tg N yr}^{-1}$  (Table 1), which is equivalent to an annual increase of 1.8%. This was slightly

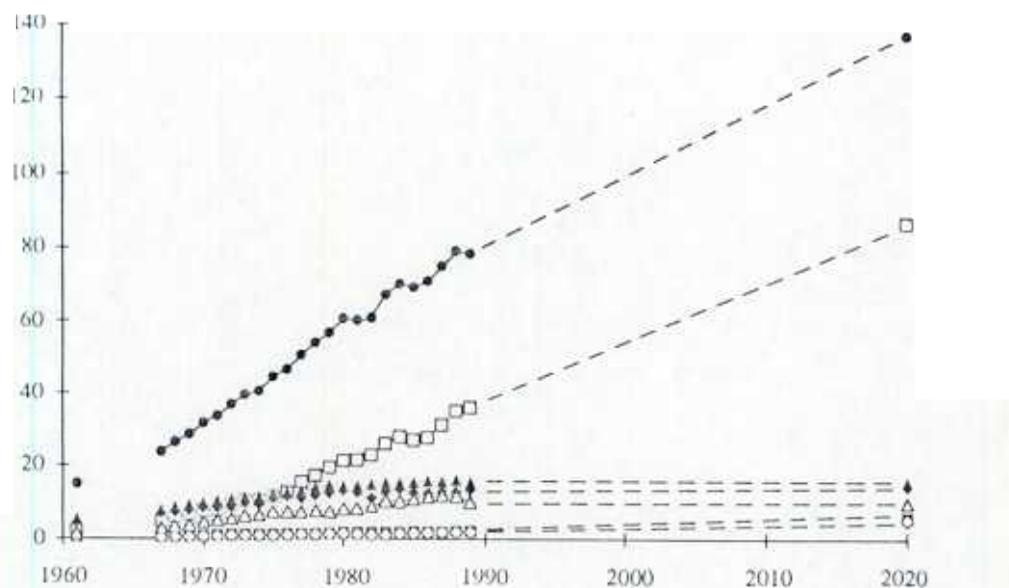


Figure 8. Projections of total fertilizer consumption ( $\text{Tg N yr}^{-1}$ ) to 2020 for the world (solid circle), Asia (open square), Europe (solid triangle), North and Central America (solid diamond), USSR (open triangle), Africa (solid square), South America (open diamond).

higher than the 1.5% of *Constant and Sheldrick* [1992] because of our assumptions about FSU and Europe. Fertilizer consumption increased the most in Asia (Figure 8). Over the period 1970–1990, legume cultivation increased by  $0.6\% \text{ yr}^{-1}$ . Extending this rate, we have predicted a 2020 value of about  $50 \text{ Tg N yr}^{-1}$ . Thus in 2020, we have estimated that the anthropogenic N-fixation rate will be of the order of  $230 \text{ Tg N yr}^{-1}$ , an increase of about  $90 \text{ Tg N yr}^{-1}$  from the current value of  $\approx 140 \text{ Tg N yr}^{-1}$  with about 60% of the increase (about  $55 \text{ Tg N yr}^{-1}$ ) coming from fertilizer production (Figure 9).

These estimates were, of course, tremendously uncertain. However, the direction of change was beyond question. Energy, fertilizer, and legume production, and hence N fixation, will certainly increase in the future. The implications of this increased fixation rate will depend on how much and where reactive N accumulated. If it accumulates, then the phenomena of N saturation of terrestrial ecosystems, loss of species, and the shift from N limitation of primary production to limitation by other nutrients will accelerate. In

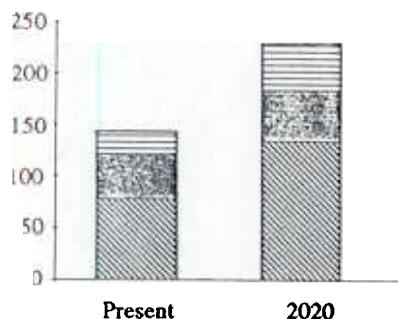


Figure 9. Current anthropogenic N fixation compared to that in 2020 ( $\text{Tg N yr}^{-1}$ ).

addition, there will be an increased capacity for long-term carbon storage by both terrestrial and marine ecosystems.

## Conclusions

The human activities of energy and fertilizer production and the planting of legumes cause unreactive N to be converted to reactive N at about  $\approx 140 \text{ Tg N yr}^{-1}$ , more than doubling the preindustrial terrestrial rate of N fixation ( $90$  to  $130 \text{ Tg N yr}^{-1}$ ). Substantial amounts of anthropogenic N are redistributed through the atmosphere and through aquatic ecosystems and by trade and transportation. Of the N fixed by anthropogenic processes,  $\approx 60 \text{ Tg N yr}^{-1}$  are transported to marine ecosystems by riverine ( $41 \text{ Tg N yr}^{-1}$ ) and atmospheric transport ( $18 \text{ Tg N yr}^{-1}$ ). Most riverine N is probably stored in coastal sediments or denitrified.

Of the remaining  $\approx 80 \text{ Tg N yr}^{-1}$ , a small portion, about  $3 \text{ Tg N yr}^{-1}$ , is released to the atmosphere as  $\text{N}_2\text{O}$ . Some N is also released to the atmosphere as  $\text{N}_2$ . Using a  $\text{N}_2:\text{N}_2\text{O}$  denitrification production ratio of 14 to 32, we have estimated that an increased rate of denitrification would convert about  $50$  to  $110 \text{ Tg N yr}^{-1}$  of reactive N back to  $\text{N}_2$ . However, this calculation was very uncertain. A variety of lines of evidence also supported the conclusion that reactive N is accumulating on continents in groundwater, soils, and vegetation. However, given the uncertainties we could set bounds on the accumulation rates, except to say that they might be significant.

The consequences of reactive-N accumulation vary by reservoir.  $\text{NO}_y$  influences the oxidizing capacity of the atmosphere and contributes to the acidity of atmospheric deposition. In addition,  $\text{N}_2\text{O}$ , although unreactive in the troposphere, is radiatively active and can act as a greenhouse gas. Many ocean regions are N limited. Additions from rivers or atmospheric deposition increase primary productiv-

ity in both coastal and open-ocean ecosystems. N accumulated on continents can cause N-limited forests and aquatic ecosystems to be more productive. Increased N availability causes a shift in the nutrient limitation status of both terrestrial and marine ecosystems. Groundwater N accumulation can impact human health from methemoglobinemia.

N accumulated in both continents and oceans impacts atmospheric CO<sub>2</sub> concentrations. In oceans, if anthropogenic N is stored in the biomass or results in a carbon storage in sediments or the deep ocean, it can be a C sink of at most 0.1 to 0.8 Pg C yr<sup>-1</sup> depending on the C:N ratio of the biomass. On continents, there is a potential for up to 9 Pg C yr<sup>-1</sup> to be stored in vegetation; however, the more likely value is <2 Pg C yr<sup>-1</sup>.

The N cycle is one of the most complicated of the biogeochemical cycles and as such presents special challenges when viewed in its entirety. One challenge is that many critical fluxes have large degrees of uncertainty about them (e.g., denitrification production of N<sub>2</sub>; N storage in groundwater). These uncertainties were reflected in the diversity of flux estimates reported in the literature. However, it is critical that, in our deliberations about the correct values, we do not lose sight of the bigger issues: Human activity is creating reactive N at the same rate as natural terrestrial processes; there is extensive atmospheric redistribution of reactive N to downwind ecosystems on hemispheric scales; there is extensive hydrologic redistribution of N to groundwater and coastal ecosystems; reactive N is accumulating in global reservoirs; some aquatic and terrestrial ecosystems are no longer N limited; some atmospheric processes have been modified. The evidence was strong on all these points. What is now required is a better understanding of the magnitude of increased N flux and storage so that we can precisely assess the consequences of N fixation by human activities at scales approximate to natural activities.

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