

# The Nitrogen Cascade

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*Human production of food and energy is the dominant continental process that breaks the triple bond in molecular nitrogen ( $N_2$ ) and creates reactive nitrogen (Nr) species. Circulation of anthropogenic Nr in Earth's atmosphere, hydrosphere, and biosphere has a wide variety of consequences, which are magnified with time as Nr moves along its biogeochemical pathway. The same atom of Nr can cause multiple effects in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on human health. We call this sequence of effects the nitrogen cascade. As the cascade progresses, the origin of Nr becomes unimportant. Reactive nitrogen does not cascade at the same rate through all environmental systems; some systems have the ability to accumulate Nr, which leads to lag times in the continuation of the cascade. These lags slow the cascade and result in Nr accumulation in certain reservoirs, which in turn can enhance the effects of Nr on that environment. The only way to eliminate Nr accumulation and stop the cascade is to convert Nr back to nonreactive  $N_2$ .*

*Keywords: nitrogen cascade, fertilizer, forest dieback, eutrophication, ozone, denitrification*

**T**he chemical elements nitrogen (N), carbon (C), phosphorus (P), oxygen (O), and sulfur (S) are all necessary for life. With one exception, they are generally available in global reservoirs to sustain life forms ranging from single-cell organisms to vertebrates. Of these elements, N has the greatest total abundance in Earth's atmosphere, hydrosphere, and biosphere; it is ironic that N is the element least readily available to sustain life. The total amount of N in the atmosphere, soils, and waters of Earth is approximately  $4 \times 10^{21}$  grams (g)—more than the mass of all four of these other elements combined (Mackenzie 1998). However, more than 99% of this N is not available to more than 99% of living organisms. The reason for this seeming contradiction is that while there is an abundance of N in nature, it is almost entirely in the form of molecular nitrogen, a chemical form that is not usable by most organisms. Breaking the triple bond holding the two N atoms together requires a significant amount of energy—energy that can be mustered only in high-temperature processes or by a small number of specialized N-fixing microbes.

We divide the N compounds in nature into two groups: nonreactive and reactive. Nonreactive N is  $N_2$ ; reactive N (Nr) includes all biologically, photochemically, and radiatively active N compounds in Earth's atmosphere and biosphere. Thus, Nr includes inorganic reduced forms of N (e.g., ammonia [ $NH_3$ ] and ammonium [ $NH_4^+$ ]), inorganic oxidized forms (e.g., nitrogen oxide [ $NO_x$ ], nitric acid [ $HNO_3$ ], nitrous oxide [ $N_2O$ ], and nitrate [ $NO_3^-$ ]), and organic compounds (e.g., urea, amines, proteins, and nucleic acids).

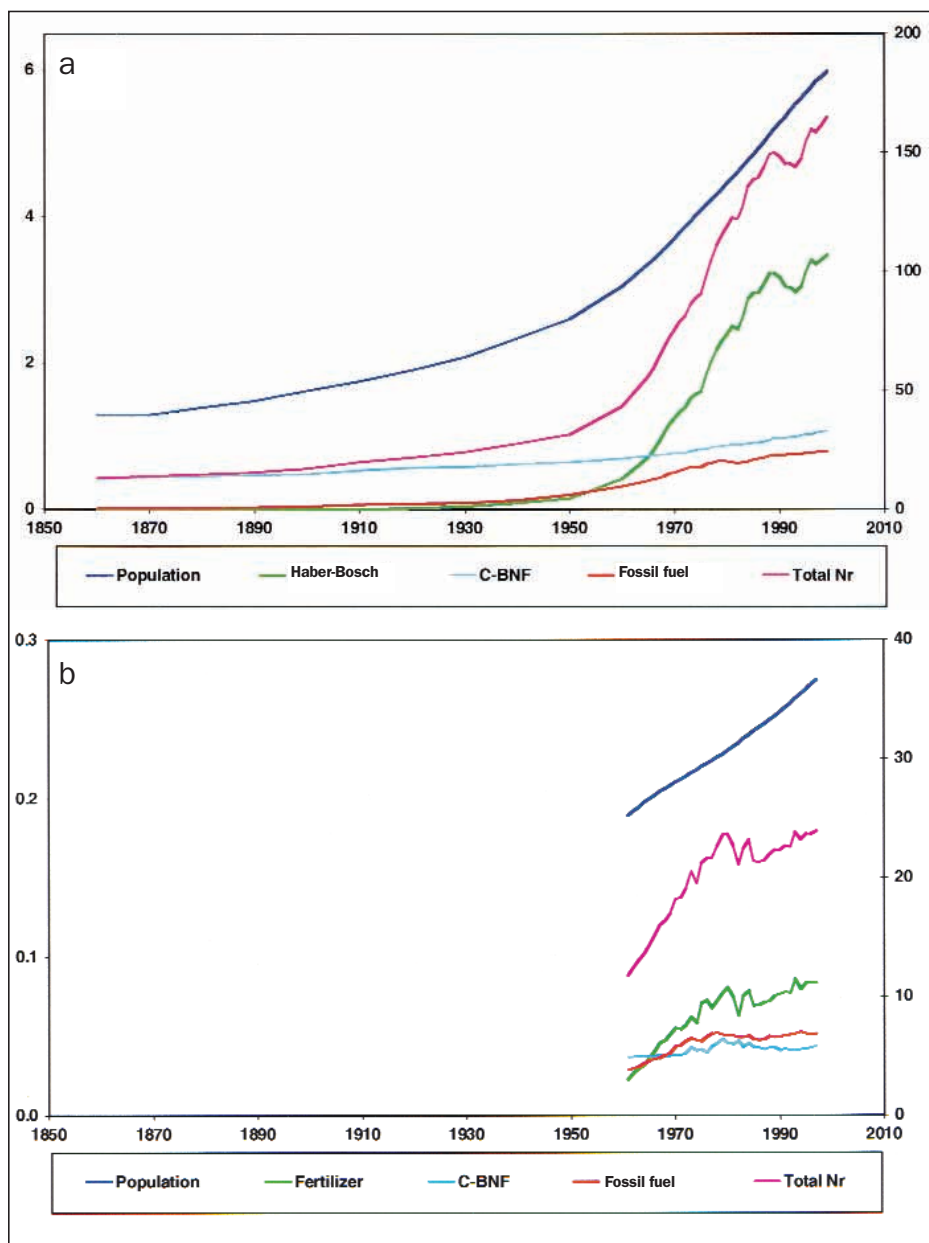
In the prehuman world, creation of Nr from  $N_2$  occurred primarily through two processes, lightning and biological nitrogen fixation (BNF). Reactive N did not accumulate in environmental reservoirs because microbial N fixation and denitrification processes were approximately equal (Ayres et al. 1994).

This is no longer the case. Reactive N is now accumulating in the environment on all spatial scales—local, regional, and global (Galloway et al. 1995). During the last few decades, production of Nr by humans has been greater than production from all natural terrestrial systems. The global increase in Nr production has three main causes: (1) widespread cultivation of legumes, rice, and other crops that promote conversion of  $N_2$  to organic N through BNF; (2) combustion of fossil fuels, which converts both atmospheric  $N_2$  and fossil N to reactive  $NO_x$ ; and (3) the Haber-Bosch process, which converts nonreactive  $N_2$  to reactive  $NH_3$  to sustain food production and some industrial activities.

The global rate of increase in Nr creation by humans was relatively slow from 1860 to 1960. Since 1960, however, the rate of increase has accelerated sharply (figure 1a). Cultivation-induced Nr creation increased from approximately 15 teragrams (Tg) N per year in 1860 to approximately 33 Tg N per year in 2000. Reactive N creation through fossil fuel combustion increased from less than 1 Tg N per year in 1860 to approximately 25 Tg N per year in 2000. Reactive N creation from the Haber-Bosch process went from 0 before 1910 to

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**Figure 1.** (a) Global population trends from 1860 to 2000 (billions, left axis) and reactive nitrogen (Nr) creation (teragrams nitrogen [Tg N] per year, right axis). “Haber-Bosch” represents Nr creation through the Haber-Bosch process, including production of ammonia for nonfertilizer purposes. For 1920, 1930, and 1940, we assumed that global total Nr production through the Haber-Bosch process was equivalent to global anthropogenic fertilizer production (Smil 2001). For 1950 onward, data on Nr creation through the Haber-Bosch process were obtained from USGS Minerals (Kramer 1999). “C-BNF” (cultivation-induced biological nitrogen fixation) represents Nr creation from cultivation of legumes, rice, and sugarcane. The C-BNF rate for 1900 is estimated to be approximately 15 Tg N per year (Vaclav Smil, University of Manitoba, Winnipeg, Canada, personal communication, January 2002). The C-BNF rates for 1860, 1870, 1880, and 1890 were estimated from population, using the 1900 data on population and Nr creation. For 1961–1999, Nr creation rates were calculated from crop-specific data on harvested areas (FAOSTAT 2000) and fixation rates (Smil 1999). Decadal data from 1910 to 1950 were interpolated between 1900 and 1961. “Fossil fuel” represents Nr created from fossil fuel combustion. The data from 1860 to 1990 are from a compilation from Elisabeth Holland, based on Müller (1992), Keeling (1993), and Holland and Lamarque (1997). These data agree well with those recently published by van Aardenne and colleagues (2001) for decadal time steps from 1890 to 1990. The data for 1991 to 2000 were estimated by scaling emissions of nitrogen oxides to increases in fossil fuel combustion over the same period. “Total Nr” represents the sum created by these three processes. (b) US population trends from 1961 to 1997 (billions, left axis; FAO 2000) and Nr creation (Tg N per year, right axis; Howarth et al. 2002a).

more than 100 Tg N per year in 2000, with about 85% used in the production of fertilizers. Thus, between 1860 and 2000, the anthropogenic Nr creation rate increased from approximately 15 Tg N per year to approximately 165 Tg N per year, with about five times more Nr coming from food production than from energy production (Galloway et al. 2002).

As in the global system, the Nr creation rate in the United States has increased over the last few decades. In 1961, the United States created Nr at a rate of approximately 8 Tg N per year (figure 1b). By 1997, the Nr creation rate was approximately 25 Tg N per year. Companion papers in this issue (Aber et al. 2003, Driscoll et al. 2003, Fenn et al. 2003a, 2003b) discuss Nr biogeochemistry in the United States, with a focus on the Northeast and the West.

The remarkable changes in the N cycle have resulted in a wide variety of changes, both beneficial and detrimental, to the health and welfare of people and ecosystems. A large portion of the human population of the world is sustained today because Nr is provided as synthetic fertilizers and cultivation-induced BNF (Smil 2000). But there are also some significant worrisome consequences. First, Nr is widely dispersed by hydrologic and atmospheric transport processes. Second, Nr is accumulating in the environment because Nr creation rates are greater than rates of

Nr removal through denitrification to nonreactive  $N_2$ . Third, Nr creation and accumulation is projected to continue to increase in the future as human populations and per capita resource use increase. Fourth, Nr accumulation contributes to many contemporary environmental problems. For example:

- Increases in Nr lead to production of tropospheric ozone and aerosols that induce serious respiratory illness, cancer, and cardiac disease in humans (Pope et al. 1995, Follett and Follett 2001, Wolfe and Patz 2002).
- Forest and grassland productivity increase and then decrease wherever atmospheric Nr deposition increases significantly and critical thresholds are exceeded; Nr additions probably also decrease biodiversity in many natural habitats (Aber et al. 1995).
- Reactive N is responsible (together with S) for acidification and loss of biodiversity in lakes and streams in many regions of the world (Vitousek et al. 1997).
- Reactive N is responsible for eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal ecosystems. It is now considered the biggest pollution problem in coastal waters (e.g., Howarth et al. 2000, NRC 2000, Rabalais 2002).
- Reactive N contributes to global climate change and stratospheric ozone depletion, both of which have impacts on human and ecosystem health (e.g., Cowling et al. 1998).

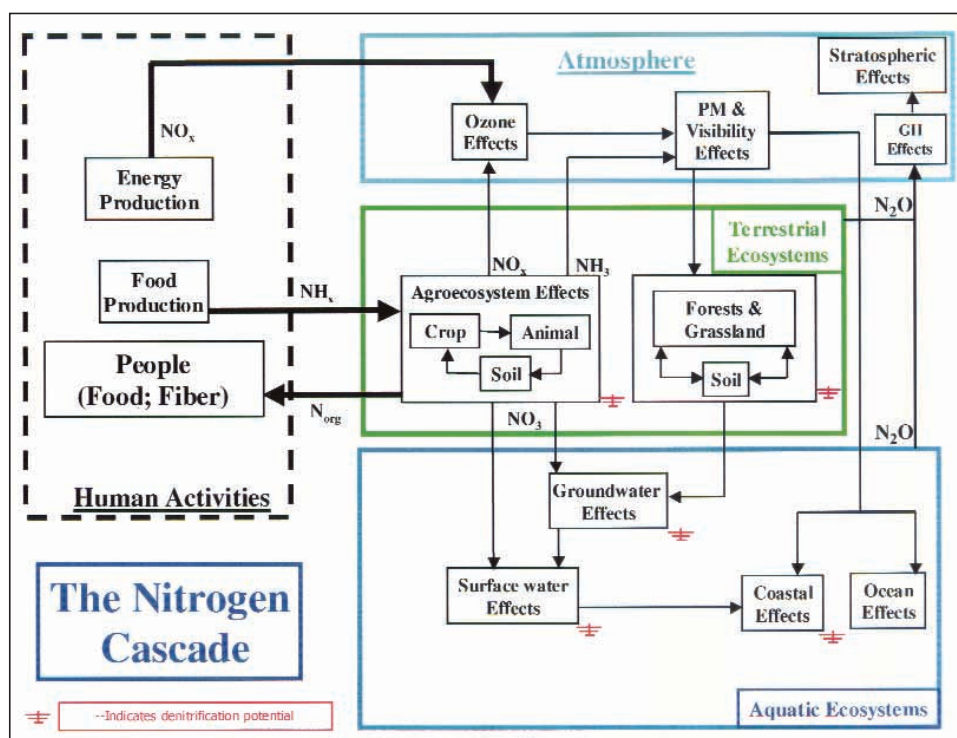
This article focuses on the multiple linkages among the ecological and human health effects of Nr molecules as they move from one environmental system to another. This phenomenon is called the N cascade (Galloway 1998), which we define as the sequential transfer of Nr through environmental systems and which results in environmental changes as Nr moves through or is temporarily stored within each system.

We use figure 2 as a frame of reference for two illustrative scenarios of the Nr cascade. In the first example, energy production by fossil fuel combustion results in the conversion of atmospheric  $N_2$  (or fossil Nr) into  $NO_x$ . In sequence, an atom of N mobilized as  $NO_x$  in the atmosphere can first increase ozone concentrations, then decrease atmospheric visibility and increase concentrations of small particles, and finally increase precipitation acidity. Following deposition to the

terrestrial ecosystem, the same N atom can increase soil acidity (if a base cation is lost from the system), decrease biodiversity, and either increase or decrease ecosystem productivity. If discharged to the aquatic ecosystem, the N atom can increase surface water acidity and lead to coastal eutrophication. If the N atom is converted to  $N_2O$  and emitted back into the atmosphere, it can first increase greenhouse warming potential and then decrease stratospheric ozone.

The second example illustrates a similar cascade of effects of Nr from food production. In this case, atmospheric  $N_2$  is converted to  $NH_3$  in the Haber-Bosch process. The  $NH_3$  is used primarily to produce fertilizer. About half the Nr fertilizer applied to global agroecosystems is incorporated into crops that are harvested from fields and used for human food and livestock feed (Smil 1999, 2001). The other half is transferred to the atmosphere as  $NH_3$ ,  $NO$ ,  $N_2O$ , or  $N_2$  or is lost to aquatic ecosystems, primarily as  $NO_3^-$ . Once transferred to these downstream or downwind systems, the N atom is part of the cascade. Depending on its chemical form, Nr will enter the cascade at different places. An important characteristic of the cascade is that once it starts, the source of the Nr (e.g., fossil fuel combustion or fertilizer production) becomes irrelevant. Nr species can be rapidly interconverted from one Nr form to another. Thus, the critical step is the formation of Nr in the first place.

The simplified conceptual overview in figure 2 does not cover some important aspects of the N cascade. It ignores the internal cycling of Nr within each component of the



**Figure 2.** Illustration of the nitrogen (N) cascade showing the sequential effects that a single atom of N can have in various reservoirs after it has been converted from a nonreactive to a reactive form. Abbreviations: GH, greenhouse effect;  $NH_3$ , ammonia;  $NO_3^-$ , nitrate;  $NO_x$ , nitrogen oxide;  $N_2O$ , nitrous oxide; PM, particulate matter.

ecosystem; it does not account for long-term Nr storage; and it does not account for all the pathways that Nr follows as it flows from one “box” or effect to another. The following sections describe these characteristics in greater detail, first for the atmosphere (troposphere and stratosphere), next for terrestrial ecosystems (agroecosystems, forests, and grasslands), and finally for aquatic ecosystems (groundwater, wetlands, streams, lakes, rivers, and marine coastal regions). The coverage for these systems is not meant to be exhaustive but rather to give an overview of how each system behaves and interacts with other systems within the cascade. We do not consider the N cycle of the open ocean, because little of the Nr created by human activities on land reaches the open ocean (Nixon et al. 1996, Seitzinger and Giblin 1996, Chen and Wang 1999).

The cascade of Nr from one system to another is enhanced if there is limited potential for Nr accumulation or loss of N<sub>2</sub> through denitrification within a given system and thus increased potential for transfer to the next system. There is a lag in the cascade if there is a large potential for accumulation within a system. The cascade decreases if there is a large potential for denitrification to N<sub>2</sub> within a system (table 1). Thus, at each stage of the N cascade, we evaluate the potential for

- accumulation and cycling of Nr within the system;
- loss of Nr through conversion to N<sub>2</sub> by denitrification;
- transfer of Nr to other systems; and
- effects of Nr within the system.

## Atmosphere

The atmosphere receives Nr mainly as air emissions of NO<sub>x</sub>, NH<sub>3</sub>, and N<sub>2</sub>O from aquatic and terrestrial ecosystems and of NO<sub>x</sub> from combustion of biomass or fossil fuels. NO<sub>x</sub> and

NH<sub>x</sub> (NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>) can accumulate in the troposphere on a regional scale. But because NO<sub>x</sub> and NH<sub>x</sub> have a short residence time in the atmosphere and lack potential to form N<sub>2</sub> by denitrification, almost all Nr emitted as NO<sub>x</sub> and NH<sub>x</sub> is transferred back to Earth's surface within hours to days. There is some internal cycling of Nr within the atmosphere. Together with volatile organic C compounds, increased concentrations of NO<sub>x</sub> can lead to increased concentrations of ozone and other photochemical oxidants in the atmosphere. Ultimately much of the NO<sub>x</sub> is converted to HNO<sub>3</sub>, which is either converted to an aerosol (e.g., ammonium nitrate) or deposited on land, surface waters, or other surfaces. NH<sub>3</sub> emitted to the atmosphere is either deposited or transformed into an ammonium aerosol (e.g., ammonium bisulfate or ammonium sulfate). Before deposition, ammonium aerosols contribute to fine particulate matter and regional haze concentrations in the atmosphere.

Six major atmospheric effects are associated with increased NO<sub>x</sub> and NH<sub>3</sub> emissions: (1) Fine particulate matter decreases atmospheric visibility; (2) elevated ozone concentrations enhance the greenhouse potential of the atmosphere; (3) ozone and fine particulate matter have serious impacts on human health (Pope et al. 1995); (4) ammonia plays an important role in the direct and indirect effects of aerosols on radiative forcing and thus on global climate change (Seinfeld and Pandis 1998, Penner et al. 2001; Russell Dickerson, University of Maryland, College Park, MD 20742, personal communication, March 2003); (5) ozone deposition can decrease productivity of crops, forests, and natural ecosystems; and (6) atmospheric deposition of NH<sub>x</sub>, NO<sub>y</sub> (all oxidized forms of nitrogen other than N<sub>2</sub>O), and organic forms of Nr can contribute to ecosystem acidification, fertilization, and eutrophication.

N<sub>2</sub>O and NO<sub>x</sub> are produced during both nitrification and denitrification. Addition of Nr to agroecosystems leads to increased N<sub>2</sub>O and NO<sub>x</sub> emissions. Nitrous oxide has a

**Table 1. Characteristics of different systems relevant for the nitrogen cascade.**

System	Accumulation potential	Transfer potential	N <sub>2</sub> production potential	Links to systems down the cascade	Effects potential
Atmosphere	Low	Very high	None	All but groundwater	Human and ecosystem health, climate change
Agroecosystems	Low to moderate	Very high	Low to moderate	All	Human and ecosystem health, climate change
Forests	High	Moderate, high in places	Low	All	Biodiversity, net primary productivity, mortality, groundwater
Grasslands	High	Moderate, high in places	Low	All	Biodiversity, net primary productivity, groundwater
Groundwater	Moderate	Moderate	Moderate	Surface water, atmosphere	Human and ecosystem health, climate change
Wetlands, streams, lakes, rivers	Low	Very high	Moderate to high	Atmosphere, marine coastal systems	Biodiversity, ecological structure, fish
Marine coastal regions	Low to moderate	Moderate	High	Atmosphere	Biodiversity, ecological structure, fish, harmful algal blooms



tropospheric residence time of approximately 100 years and is increasing in the troposphere at a rate of approximately 0.25% per year (Prather et al. 2001). Nitrous oxide is a greenhouse gas in the troposphere and, when transferred to the stratosphere, decreases the concentration of stratospheric ozone. As discussed above,  $\text{NO}_x$  can contribute to increased tropospheric ozone and decreased atmospheric visibility.

In summary, the residence time for most Nr species in the atmosphere is short. There is an internal cascade of effects:  $\text{NO}_x$  increases the potential first for ozone and then for aerosol formation. Except for  $\text{N}_2\text{O}$ , there is very limited potential for long-term storage of Nr (and thus limited lag time), but there are significant effects from Nr while it remains in the atmosphere. There is no potential for denitrification back to  $\text{N}_2$  within the troposphere, and there is a large potential for Nr transfer to the next receptor—terrestrial and aquatic ecosystems (table 1).

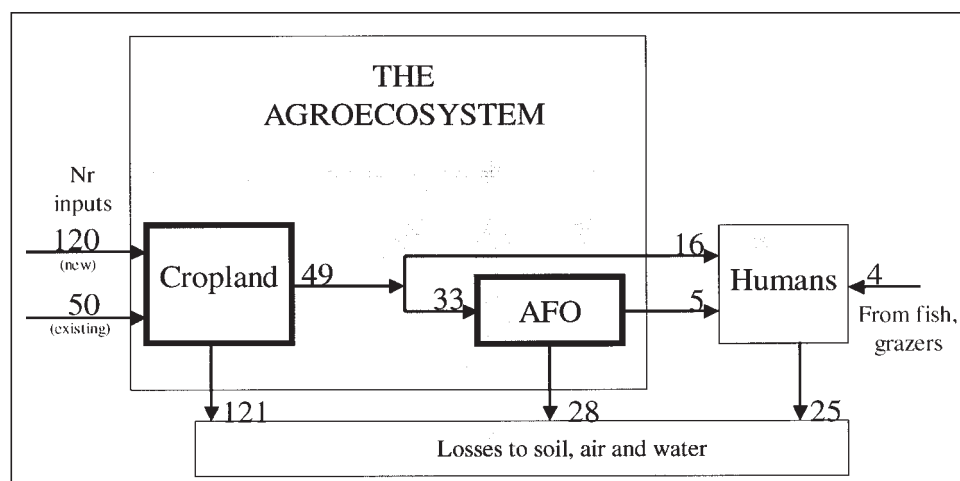
### Terrestrial ecosystems

This section discusses the nitrogen cascade in three types of terrestrial ecosystems—agroecosystems, forests, and grasslands.

**Agroecosystems.** Intensively managed agroecosystems and, even more, concentrated animal feeding operations (CAFOs, also called “factory farms”) are only the latest technical means by which human needs and dietary preferences are major drivers of change in the N cycle. About 75% of the Nr created globally by humans is added to agroecosystems to sustain food production. About 70% of that Nr is from the Haber-Bosch process and about 30% from cultivation-induced BNF (figure 1a). Smil (2001) estimates that about 40% of the people alive today owe their life to the production and wide use of fertilizers produced by the Haber-Bosch process.

The agroecosystems of the world consist of two general types: (1) crop production systems, composed of primary producers; and (2) animal production systems, composed of secondary producers. Crop agroecosystems produce cereal grains, fruits, vegetables, and commercial fibers through the uptake of mostly inorganic Nr, other nutrients, and water, using sunlight as the energy source. Crop production is sustained by indigenous sources of Nr in the soil; by wet and dry deposition of Nr from the atmosphere; by biological N fixation; by recycling of crop residues, animal

manure, and human waste; and by application of synthetic Nr fertilizers. The residence time of Nr within crop agroecosystems can be years to decades because of the large pool of organic matter in the soil. Cassman and colleagues (2002) report substantial indigenous soil Nr reserves; for example, a typical irrigated rice soil in Asia contains about 2800 kilograms (kg) N per hectare (ha) in the upper 20 centimeters (cm). Fertile prairie soil in the Corn Belt of the United States often contains about 4000 kg N per ha in the upper 20 cm of the soil profile. However, usually less than 5% of this indigenous supply is available for crop uptake in a given season. Thus, the annual crop yield is determined primarily by the amount of Nr added. Nearly all of this added Nr is lost from most agroecosystems over the course of a year. On a global basis, about 120 Tg N from new Nr (fertilizer and cultivation-induced BNF) and about 50 Tg N from previously created Nr (e.g., crop residue, animal manure, and atmospheric deposition) is added annually to crop agroecosystems (Smil 2001, 2002). Of this amount, about 33 Tg N per year is consumed by animals and about 16 Tg N per year is consumed by humans (figure 3). The remainder (about 121 Tg N per year) is lost to the atmosphere (as  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$ ) or to waters (as dissolved and particulate Nr) or is part of the material reintroduced to crop systems during the next cropping cycle. Smil (1999) estimates that only a small amount (about 4 Tg N per year) of the 170 Tg N per year introduced accumulates in crop agroecosystems. Generally, the more Nr that is added to crop agroecosystems, the more is lost through air and water pathways. Once lost, the released Nr can cascade through natural ecosystems, where it alters their dynamics and



**Figure 3.** Major reactive nitrogen (Nr) flows in crop production and animal production components of the global agroecosystem. Croplands create vegetable protein through primary production; animal production utilizes secondary production to create animal protein. Reactive nitrogen inputs represent new Nr, created through the Haber-Bosch process and through cultivation-induced biological nitrogen fixation, and existing Nr that is reintroduced in the form of crop residues, manure, atmospheric deposition, irrigation water, and seeds. Portions of the Nr losses to soil, air, and water are reintroduced into the cropland component of the agroecosystem (Smil 2001, 2002). Numbers represent teragrams of nitrogen per year; AFO, animal feeding operations.

in many cases decreases their ability to provide ecosystem services (table 1).

Animal agroecosystems produce dietary protein (milk, eggs, and edible meat) from the consumption of proteins produced by crop agroecosystems. Just as in crop agroecosystems, most of the Nr that enters the animal agroecosystem is lost to the environment over the course of a year. Animals receive Nr primarily through the consumption of amino acids in grains and other vegetation. The efficiency with which food animals use N from forage and grain varies greatly. Typical rates of N-use efficiency for production of human-digestible protein from feed grains and forages on farms are about 50% to 60% for fish, about 40% to 50% for poultry, about 35% to 40% for dairy, and about 15% to 30% for beef. On a global basis, 33 Tg N per year of grain produced by the crop agroecosystem is fed to animals (figure 3). Of this amount, about 15% is consumed by humans. The remaining Nr is lost as manure and waste (Smil 2001, 2002). The manure can be reused as fertilizer, but the Nr is often lost through air emissions (e.g.,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$ ) and through leaching of  $\text{NO}_3^-$  to ground or surface waters.

Humans consume about 25 Tg N per year, mostly as dietary protein. Of this amount, 64% comes from grain, 20% from CAFOs, and about 16% from fish and pasture grazing animals (figure 3).

A portion of the Nr added to agroecosystems is denitrified back to nonreactive  $\text{N}_2$  in systems that have high  $\text{NO}_3^-$  or  $\text{NH}_4^+$  concentrations, high organic matter, and low  $\text{O}_2$  concentrations, such as agricultural fields with high water content (e.g., wetland rice), those that receive large amounts of precipitation over a short time period (e.g., spring rains), and anaerobic manure storage systems. Unfortunately, the amount of  $\text{N}_2$  lost through denitrification in agroecosystems is poorly known. Oenema and colleagues (2001) reviewed  $\text{NO}_x$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  emissions from pastures; from animal housing systems; from manure slurry in tanks, silos, and lagoons; from manure heaps; and from slurry and manure applied to the soil. They concluded that our knowledge of gaseous losses from animal manure is greatest for  $\text{NH}_3$  and successively less for  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$ . Smil (1999) estimates that on a global basis 6% to 12% of the Nr added to agroecosystems is denitrified to  $\text{N}_2$ . In an analysis of agroecosystems in the Great Plains region of the United States, Del Grosso and colleagues (2001) used the DAYCENT model to show that  $\text{N}_2$  fluxes were small compared with  $\text{NO}$  and  $\text{N}_2\text{O}$  fluxes, primarily because of the semiarid characteristics of the region. They estimate that less than 5% of the applied Nr is lost as  $\text{N}_2$ . For large watersheds of the eastern United States, van Breemen and colleagues (2002) estimate by difference that up to 49% of the Nr input to agroecosystems is denitrified. In the Netherlands, with high levels of Nr production, 30% to 40% of the Nr applied is either stored or denitrified (Erismann et al. 2001). These large differences reflect in part regional variability in the conditions that promote denitrification (e.g., soil moisture) and the general uncertainty of the magnitude of denitrification.

In summary, global crop agroecosystems receive about 75% of the Nr created by human activity (Galloway and Cowling 2002). Most of this Nr is transferred to other systems along the N cascade; a much smaller portion globally is denitrified to  $\text{N}_2$  (table 1). Improving the efficiency of N use in major grain and animal production systems will require collaboration among ecologists, agronomists, soil scientists, agricultural economists, and politicians. A great need exists for accurate measurements of actual fertilizer N-use efficiency, N losses, and loss pathways in major crop and animal systems. Only in this way can we (a) identify opportunities for increased efficiency of N use through improved crop and soil management; (b) quantify N-loss pathways in major food crops, including CAFOs; and (c) improve human understanding of local, regional, and global N balances and N losses from major crop and animal systems.

**Forests.** Forests can be a major reservoir and a short- to long-term sink within the N cascade. Total Nr stocks in soils and biomass can range as high as 500 g N per square meter ( $\text{m}^2$ ). Inputs of Nr in unpolluted regions are 0.1 to 0.2 g N per  $\text{m}^2$  per year but can reach 5 or, very rarely, 10 g N per  $\text{m}^2$  per year (Dise and Wright 1995). Outputs as dissolved organic N in steamwater are low and relatively constant across sites (e.g., Goodale et al. 2000), while dissolved inorganic N (DIN) loss is quite variable and can be as low as zero or equal to deposition, depending on forest history and condition (Dise et al. 1998, Gundersen et al. 1998, Fenn et al. 2003a). In general, this means that Nr residence time within a forest is measured in hundreds to thousands of years, and thus there is a substantial opportunity for lags in the N cascade. However, human activity can shorten this residence time either by increasing inputs or by removing Nr through harvests, fires, or conversion to agriculture. Large reservoir size and relatively low turnover rates mean that human-induced changes in the Nr status of forests can have long-term effects, and previous land use history can play a large role in conditioning forest response to Nr additions (Goodale et al. 2000, Aber et al. 2003).

Our understanding of the responses of historically Nr-limited forests to increases in Nr deposition have been presented in summary diagrams of the process known as N saturation (figure 4; Aber et al. 1998). Four general stages along this continuum have been discussed. In highly Nr-limited (stage 0) systems, low Nr availability is reflected in low foliar N content and low net primary productivity. Plants and root symbionts compete effectively for mineralized  $\text{NH}_4^+$ , and net nitrification and  $\text{NO}_3^-$  leaching are minimal, while  $\text{N}_2\text{O}$  efflux is low to undetectable. In stage 1, increased Nr deposition gradually relieves Nr limitations on biological functions. Either through plant uptake or through direct incorporation into soil organic matter, added Nr enters into the N cycle of the forest and increases mineralization and cycling rates. Foliar Nr increases, as does productivity.

There are two critical thresholds in the N saturation process. The first is induction of net nitrification (stage 2). Thus, the

presence of net nitrification and extractable soil  $\text{NO}_3^-$  are key indicators of ecosystem Nr status. Field experiments have shown that there can be a significant delay between the initiation of Nr additions and the induction of detectable rates of net nitrification (Magill et al. 2000). Both  $\text{NO}_3^-$  leaching and  $\text{N}_2\text{O}$  effluxes are low but detectable during this period.

The second critical threshold occurs when Nr becomes a nonlimiting element for plant growth (stage 3). At this point, biological retention processes become less effective, and  $\text{NO}_3^-$  leaching losses increase substantially. Effluxes of NO and  $\text{N}_2\text{O}$  also may increase because of nitrification or denitrification processes (Davidson et al. 2000), which may become significant if soils are imperfectly or variably drained soils. In stage 3, experimental additions of Nr may decrease tree growth (e.g., Magill et al. 2000), while decreases in Nr deposition may increase tree growth (Beier et al. 1998, Boxman et al. 1998). Excess Nr may damage forests by causing nutrient imbalances and by increasing sensitivity to factors such as frost and attacks by fungi (Erisman and de Vries 2000).

There is substantial field documentation that N saturation does occur and that it is related to increases in atmospheric inputs. In a companion article in this issue of *BioScience*, Aber and colleagues (2003) analyze foliar, soil, and surface water chemistry from a large number of sites to test for patterns that coincide with strong Nr deposition gradients across the northeastern United States. Surface waters yield the clearest patterns because they integrate over large areas; the surface water data show increasing Nr leaching in response to increasing Nr deposition (Aber et al. 2003). These results are very similar to patterns observed in European forests. In an

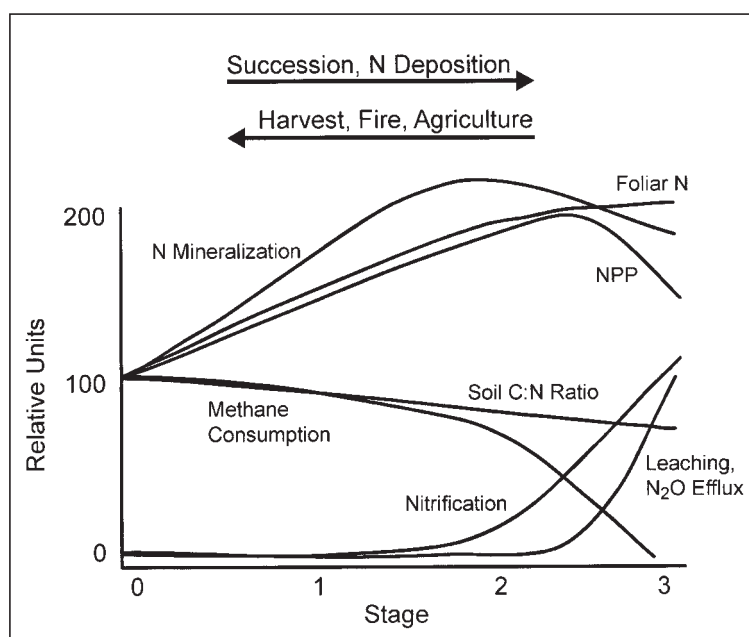
analysis of 139 forests, Dise and colleagues (1998) found that inorganic Nr leaching increased with Nr deposition as well as with changes in humus composition and soil acidity (figure 5).

How quickly Nr status or degree of N saturation can change is poorly known. Very Nr-poor sites receiving concentrated doses of DIN can retain over 100 g N per  $\text{m}^2$  before nitrification and  $\text{NO}_3^-$  leaching are induced (Magill et al. 2000). Richer sites receiving more dilute solutions can show an increase in  $\text{NO}_3^-$  loss immediately (Kahl et al. 1993). Less N appears to be required to move needle-leaved evergreens from stage 1 to stage 3 than is required for broad-leaved deciduous forests (Aber et al. 1995, 1998). Nitrogen saturation may occur quickly near large point sources of Nr (Erisman and de Vries 2000).

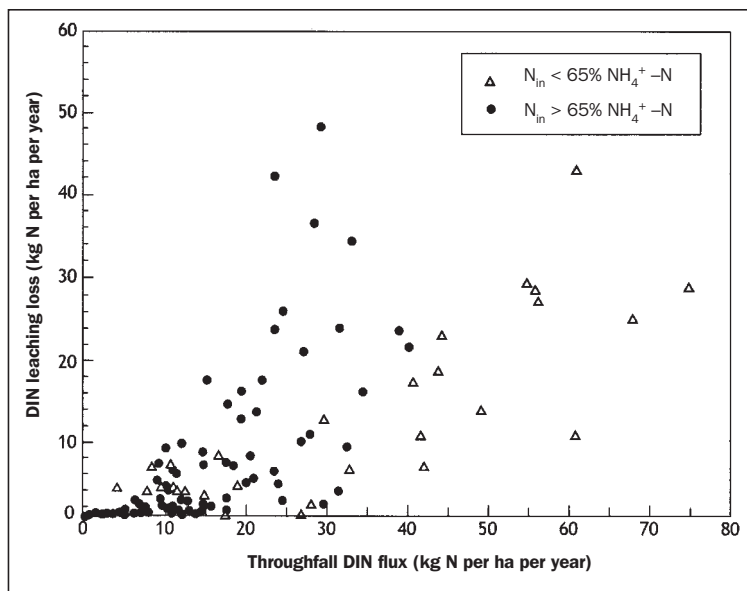
It is clear that most Nr retained in forests is held in soils (Nadelhoffer et al. 1999, Magill et al. 2000). Recent work suggests that either abiotic reactions between DIN and soil organic matter or assimilation and conversion by mycorrhizae may be important (Aber et al. 1998, Johnson et al. 2000, Dail et al. 2001). Understanding the kinetics and capacity of these or other retention mechanisms is key to predicting Nr retention rates and the role of forests in the N cascade.

To summarize the role of forests in the N cascade: (a) The residence times and lag times of Nr in forests can be years to centuries depending on forest history, type, and Nr inputs; (b) the effects of Nr accumulation in forests are numerous, mostly relating to changes in forest and microbial productivity and function; (c) there is significant potential for Nr to be transferred to the atmosphere as NO and  $\text{N}_2\text{O}$ , and especially to surface waters as  $\text{NO}_3^-$ , once Nr additions or availability exceed biotic requirements; and (d) relative to inputs in areas with high Nr deposition, there is a limited potential for Nr to be removed from the cascade by means of  $\text{N}_2$  formation.

**Grasslands.** Unmanaged grasslands receive most of their Nr from BNF and atmospheric deposition; the latter source is much more important where deposition rates are large. As with forests, temperate grasslands have the potential to be a major storage reservoir and a short- to long-term sink within the N cascade. At the Konza Prairie (tallgrass) site, for example, Nr stocks in soils and in biomass are on the order of 625 g per  $\text{m}^2$  and 6 to 25 g per  $\text{m}^2$ , respectively (Blair et al. 1998). Inputs of Nr in unpolluted regions are less than 1 g N per  $\text{m}^2$  per year but can reach 5 g N per  $\text{m}^2$  per year (Galloway and Cowling 2002). The residence times of Nr in grasslands can be decades to centuries, because most biomass is subsurface and decomposition rates are slow (Blair et al. 1998, Epstein et al. 2001). Given the N-limited nature of most grasslands and the long residence times, there is a large potential for significant internal cycling (including redistribution by grazing animals) and for Nr accumulation.



**Figure 4.** Changes in several ecosystem functions with increasing Nr availability or degree of N saturation (modified from Aber et al. 1998). Abbreviations: C, carbon; N, nitrogen;  $\text{N}_2\text{O}$ , nitrous oxide; NPP, net primary productivity.



**Figure 5.** Dissolved inorganic nitrogen (DIN, in kilograms per hectare per year) lost in runoff and seepage. Sites with throughfall DIN dominated by nitrogen from ammonium ( $\text{NH}_4^+-\text{N}$ ) are shown in open triangles (Dise et al. 1998).  $N_{in}$  represents N throughfall inputs.

Nr losses from grasslands can occur through hydrologic losses and atmospheric emission. Because precipitation rates and thus runoff rates in grasslands are low, atmospheric emissions are important, especially if fire is frequent; fire-induced Nr losses can be approximately equal to input by atmospheric deposition. For example, in ungrazed regions of the Konza Prairie, Nr losses from fire can approximate or exceed atmospheric Nr deposition inputs (Blair et al. 1998). However, some of these losses are in the form of  $\text{N}_2$  (Crutzen and Andreae 1990). For biomass burning in general, Kuhlbusch and colleagues (1991) estimate that  $\text{N}_2$  constitutes the largest flux of N gases emitted. Thus, if fire is frequent, some atmospheric Nr deposition resulting from human action may be returned to the atmosphere, partly as Nr and partly as  $\text{N}_2$ .

In addition to denitrification through fire, Nr can also be converted to  $\text{N}_2$  and lost from the grassland through microbial denitrification. However, because most grassland soils are well aerated, conversion of Nr to  $\text{N}_2$  through microbial denitrification is probably not an important process (Del Grosso et al. 2001). If retained in the grassland, accumulated Nr can lead to increases in productivity and loss of biodiversity (Tartowski and Howarth 2000).

Grasslands managed for animal production (e.g., cattle) are much more "leaky" with respect to loss of added Nr. The addition of fertilizer or grazing animals increases the amount of Nr that is available for loss, especially through the atmosphere (e.g.,  $\text{NH}_3$  [Sommer and Hutchings 1997] and  $\text{N}_2\text{O}$  [Fowler et al. 1997]). Thus, in managed ecosystems the effective residence times have the potential to be less than for unmanaged systems.

## Aquatic ecosystems

This section discusses the N cascade in three types of aquatic ecosystems: (1) groundwater; (2) wetlands, streams, lakes, and rivers; and (3) coastal systems.

**Groundwater.** The primary anthropogenic Nr source for groundwater on a global basis is leaching from agroecosystems, although in some regions human waste disposal can also be important (Puckett et al. 1999, Refsgaard et al. 1999, Hudak 2000, Nolan and Stoner 2000, Nolan 2001, van Egmond et al. 2002). Nitrate is the most common Nr species (Burkart and Stoner 2001). As in other systems considered in this article, there are three fates of Nr in groundwater: accumulation, conversion to  $\text{N}_2$ , and distribution to other systems through hydrologic pathways (e.g., as  $\text{NO}_3^-$ ) or atmospheric pathways (e.g., as  $\text{N}_2\text{O}$  or  $\text{NO}$ ). Although pollution can result in high levels of  $\text{NO}_3^-$  in some groundwater aquifers, the accumulation of N in groundwater is not a major sink for the N mobilized by human activity at either global or regional scales. In regions of intense agricultural activity in Europe and the United States, the average rate of accumulation of  $\text{NO}_3^-$  in groundwater amounts to at most a few percent of the N inputs from fertilizer and other sources (Howarth et al. 1996).

Nitrogen is lost from groundwater both through denitrification to  $\text{N}_2$  and through losses of Nr to surface waters and the atmosphere, but the relative mix of these fates is site dependent, as is the residence time of Nr in groundwater reservoirs. For example, in an intensive agricultural area in west-central Minnesota, about 40% of the Nr that entered the groundwater was denitrified, and the rest accumulated in the aquifer with little discharge to surface waters (Puckett et al. 1999, Puckett and Cowdery 2002). In the southeastern United States, some systems have high losses of  $\text{NO}_3^-$  and concomitant low  $\text{NO}_3^-$  concentrations, while other systems have low losses of  $\text{NO}_3^-$  and high  $\text{NO}_3^-$  concentrations (Nolan 1999). A review of several studies of denitrification in groundwater by Groffman and colleagues (1998) found similar degrees of variability.

Although the accumulation of Nr in groundwater is not a regionally or globally important sink relative to the amount of Nr created, the effects of elevated Nr in groundwater do pose a significant human health risk, because drinking water can become contaminated. In the human body,  $\text{NO}_3^-$  is converted to nitrite, which can cause methemoglobinemia by interfering with the ability of hemoglobin to take up  $\text{O}_2$ . Most cases of methemoglobinemia occur after consuming water with high concentrations of  $\text{NO}_3^-$ ; infants are particularly susceptible, as are people who receive kidney dialysis treatment (Follett and Follett 2001). For this reason, the World Health Organization recommends that  $\text{NO}_3^-$  concentrations in drinking water should be less than 10 milligrams (mg) N per liter. In the United States,  $\text{NO}_3^-$  concentrations exceed this level in more than 15% of groundwater samples from 4 of the 33 major regional aquifers most commonly used as sources of



drinking water (Nolan and Stoner 2000). Other effects associated with elevated concentrations of  $\text{NO}_3^-$  in drinking water include respiratory infection, alteration of thyroid metabolism, and cancers induced by conversion of  $\text{NO}_3^-$  to N-nitroso compounds in the body (Follett and Follett 2001).

In summary, groundwater systems are accumulating Nr at low rates compared with rates of human mobilization of Nr in the landscape, but the effects of contaminated groundwater can nonetheless be significant. Nr is lost from groundwater through denitrification, through advection of  $\text{NO}_3^-$  to surface waters, and through conversion to gaseous Nr forms that diffuse or flow to the atmosphere. Just as there is a lag in Nr release in forests because of N saturation phenomena (figure 4), there is also a lag for Nr release from groundwater to surface water, although this is highly variable among sites (Groffman et al. 1998, Puckett and Cowdery 2002). At some time, the Nr introduced into groundwater will be transferred to surface water if the Nr is not permanently stored in groundwater or denitrified to  $\text{N}_2$ . If the inputs of Nr to groundwater systems decrease, then the decrease of the groundwater  $\text{NO}_3^-$  burden can be delayed for a significant amount of time because of the significant residence time of Nr in groundwater reservoirs.

**Wetlands, streams, lakes, and rivers.** Surface freshwater ecosystems consist of wetlands (e.g., bogs, fens, marshes, swamps, and prairie potholes), streams, lakes (including artificial reservoirs), and rivers. Surface freshwater ecosystems receive most of their Nr from their associated watersheds, from atmospheric deposition, and from BNF within the system. Nitrogen fixation is generally more important in eutrophic lakes and in some wetlands, where the process has been found to contribute between 5% and 80% of total Nr inputs (Howarth et al. 1988). There is limited potential for Nr accumulation within surface water ecosystems because the residence time of Nr within surface waters, like the water itself, is very brief. Residence times may be relatively longer in the sediments associated with wetlands and some larger lakes, but they are still short when compared with the residence times in terrestrial ecosystems.

Despite a short residence time, Nr cycling in surface fresh water can be very complex. In addition to dissolved  $\text{N}_2$ , inorganic oxidized and reduced forms of Nr can occur, as can organic forms of Nr. In most headwater systems, the inorganic forms of Nr ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) are present in low concentrations unless the waters are associated with N-saturated forests, grasslands, agroecosystems, or suburban landscapes. This is primarily because the intense cycling of Nr in the terrestrial portions of the watershed results in little runoff of Nr to streams. The little inorganic Nr that does reach the streams in pristine regions is usually denitrified or quickly incorporated into biomass by aquatic plants and then recycled through the hierarchy of consumers and decomposers unless Nr concentrations are high (Peterson et al. 2001). However, many headwater streams and lakes are now in highly disturbed

landscapes and thus have high  $\text{NO}_3^-$  concentrations, which can lead to eutrophication problems locally or farther downstream. In addition, for headwater streams and lakes draining poorly buffered soils, increased  $\text{NO}_3^-$  concentrations can result in stream acidification, with resultant impacts on biota.

In undisturbed areas in the temperate zone, the major terrestrial flux of Nr into surface waters may be organic Nr in the form of detritus or dissolved organic matter washed into lakes and streams (Lewis 2002, Perakis and Hedin 2002). Undisturbed tropical regions can have significant losses of  $\text{NO}_3^-$  (Lewis et al. 1999). In the presence of increased atmospheric deposition of inorganic Nr or significant land-use perturbations (e.g., urbanization or agriculture) in the terrestrial watershed, the amount of Nr delivered to streams and lakes may easily exceed the retention capacity of the aquatic system. There will then be little delay in the transport of N down the cascade unless the Nr is denitrified back to  $\text{N}_2$ . As discussed below, the potential for denitrification in wetlands, streams, lakes, and rivers is large.

Wetlands can generally be considered aggrading ecosystems where the additional Nr can come from adjacent waters and, in some cases, from BNF and atmospheric deposition. Wetlands are so efficient at removing Nr through denitrification (see below) that they are frequently constructed to remove Nr from effluent waters from a number of human activities. However, humans are also accelerating wetland removal. In many areas of the world, wetlands are being drained; nearly half the wetlands in the United States have been destroyed since 1780 (Gleick 1993). While wetlands can be efficient Nr sinks, their areal extent is limited (and becoming more limited) compared with that of terrestrial and oceanic sinks.

In summary, the potential for Nr accumulation in streams, lakes, rivers, and associated wetlands is small (table 1). While changes in Nr inputs to surface waters may significantly alter the internal cycles in these systems, from a global perspective such changes are merely extremely efficient avenues for propagating the effects of the N cascade from higher to lower components. Even though wetlands may delay or prevent this transfer locally, and denitrification may short-circuit some of the Nr transport along the way, surface freshwater ecosystems essentially move Nr from the mountains to the sea, ensuring that perturbations at one point in the cascade quickly lead to changes elsewhere.

**Coastal systems.** Coastal ecosystems (e.g., estuaries) receive most of their Nr from riverine and groundwater inputs; direct atmospheric deposition is an important source in some systems, and inputs from the ocean are important in others. These inputs have increased several-fold as a consequence of human activities (Howarth et al. 1996, Seitzinger and Kroeze 1998, NRC 2000, Howarth et al. 2002b). Because of the dynamic nature of coastal ecosystems, there is limited potential for Nr accumulation. In addition, although the potential for Nr transfer to continental shelf regions is large, there is limited transport to the shelf because of the high rates of

denitrification (mostly as  $N_2$ ), and the Nr that is transferred is mostly converted to  $N_2$  before its transport to the open ocean. With coastal systems acting as Nr sinks, atmospheric deposition becomes a potentially important source of Nr for the open ocean, especially in oligotrophic midocean gyres (figure 2).

Although Nr has a short residence time in coastal ecosystems compared with terrestrial ecosystems, the time it does spend there can have a profound impact on the coastal ecosystem. Primary production in most coastal rivers, bays, and seas of the temperate zone is limited by Nr supplies (Vitousek and Howarth 1991, Nixon et al. 1996, NRC 2000). As a consequence, greater Nr inputs lead to increased growth of algae. In moderation, this can be viewed as beneficial, as it can lead to increased production of harvestable fish (Nixon 1988, Jorgensen and Richardson 1996). However, high Nr inputs can also lead to excessive algal growth, or eutrophication. In the United States, the increased Nr flux is now viewed as the most serious pollution problem in coastal waters (Howarth et al. 2000, Rabalais et al. 2002). One-third of the nation's coastal rivers and bays are severely degraded, and another third have been moderately degraded from nutrient overenrichment (Bricker et al. 1999). The situation is probably equally severe in other regions of the globe where human activity is leading to high Nr inputs to the coast (e.g., the North Sea and the Baltic Sea).

In the tropics, P rather than N often limits relatively pristine coastal ecosystems. However, increased nutrient loading can shift these systems toward Nr limitation (McGlathery et al. 1994, Howarth et al. 1995) and, as in temperate-zone systems, Nr is a major contributor to coastal eutrophication in tropical coastal systems (Corredor et al. 1999, NRC 2000, Rabalais 2002).

One of the most obvious consequences of increasing Nr inputs to coastal waters over the past few decades has been an increase in the size of water masses that are anoxic (completely devoid of  $O_2$ ) or hypoxic (with concentrations of  $O_2$  less than 2 to 3 mg per liter). These so-called dead zones now occur in the Gulf of Mexico, the Chesapeake Bay, Long Island Sound, Florida Bay, the Baltic Sea, the Adriatic Sea, and many other coastal areas (Diaz and Rosenberg 1995, NRC 2000). The hypoxic water mass in the northern Gulf of Mexico has grown in size in recent summers to about 20,000 square kilometers and is clearly attributable to Nr pollution running down the Mississippi River (Goolsby et al. 1999, Rabalais et al. 1999, 2002, NRC 2000).

Other major effects of increasing Nr in coastal regions include loss of seagrass beds, macroalgal beds, and changes in coral reefs (Lapointe and O'Connell 1989, Valiela et al. 1997, Howarth et al. 2000, NRC 2000). Reactive N additions can increase the incidence and duration of harmful algal blooms (NRC 2000). Anoxic or hypoxic events and harmful algal blooms can lead to fish kills. Reactive N pollution can also lead to more subtle effects, with alterations of marine food webs that lead to decreased fish production (NRC 2000). Reactive

N pollution is a leading cause of loss of biotic diversity in marine ecosystems (NRC 1996, 2000).

In summary, Nr inputs to coastal ecosystems have increased significantly over the last few decades. Although most Nr is eventually denitrified to  $N_2$  within the coastal ecosystems and associated shelf, Nr pollution has significant and widespread impacts on various ecosystem components and on human health (table 1).

**Denitrification potential in the wetland–stream–river–estuary–shelf continuum.** Along the entire aquatic continuum, from wetlands to headwater streams to the continental shelf and eventually to the open ocean, not only is Nr rapidly cycled among the various forms (e.g.,  $NH_4^+$ ,  $NO_3^-$ , and particulate and dissolved organic N), there is great potential for loss of Nr from the biosphere through the conversion of  $NO_3^-$  to  $N_2$  (denitrification). In this section we aim to identify places along the N cascade where Nr can be converted back into  $N_2$  or  $N_2O$ .

Conditions required for this conversion include (a) the presence of  $NO_3^-$  or nitrite (referred to collectively in this section as nitrate), (b) the presence of labile organic matter, and (c) the absence or low concentration of dissolved  $O_2$ . The most active sites for denitrification in aquatic systems are benthic sediments, which are often anoxic below the first few millimeters, even though the overlying water is well oxygenated. Even when nitrate concentrations are low in sediments, denitrification rates could be high if other conditions are favorable, because of the close spatial and temporal coupling of nitrification and denitrification. Denitrification also can occur in anoxic zones within the water column, with the primary source of nitrate coming from outside the zone of anoxia.

Increased inputs of Nr from anthropogenic sources can increase rates of denitrification along the entire aquatic continuum. As Nr inputs increase, they can increase the nitrate concentration in the water column and thus increase the diffusive supply of nitrate to the sediments. Increased inputs of Nr can also enhance primary production, particularly in Nr-limited estuarine and continental shelf waters, thus increasing organic matter deposition to the sediments and subsequent sediment nitrification and denitrification. However, if Nr inputs result in the water column becoming anoxic, sediment nitrification and consequently denitrification can markedly decrease. For example, in the Chesapeake Bay, denitrification in sediments underlying anoxic waters was low compared with periods of well-oxygenated bottom waters (Kemp et al. 1990). However, the net effect of persistent anoxic water in estuarine and continental shelf systems, where nitrate concentrations and rates of water advection are low, on total denitrification rates (in sediment plus water) is not well documented. On the other hand, in rivers such as the Seine and Scheldt, with high inputs of nitrate from upstream agricultural sources, more Nr was removed in the river by denitrification when the water was severely depleted in  $O_2$ , compared with times after improvements in sewage treatment

when the  $O_2$  concentrations in the river increased (Billen 1990).

The proportion of  $Nr$  inputs removed through denitrification has a similar range for lakes, rivers, and estuaries (generally from less than 10% to more than 80%). Is there an overall ecosystem property that can account for the wide variability in the proportion of the  $Nr$  inputs removed through denitrification? The residence time of water is an important factor controlling removal of  $Nr$  through denitrification in streams, lakes, rivers, and estuaries. The effect of water residence time is probably related to the time that  $Nr$  has to react in the ecosystem before it is transported to the adjacent downstream system. The relationship between the proportion of  $Nr$  inputs that are denitrified and the water residence time in an aquatic environment was originally shown for well-oxygenated and well-mixed shallow lakes (Kelly et al. 1987). This relationship was extended to river reaches and reservoirs and indicated that a smaller proportion of the  $Nr$  inputs were retained in a river reach (often 5% to 20%) compared with many lakes and reservoirs (from about 10% to more than 90%; Howarth et al. 1996). Recently, this relationship for stream and river reaches was incorporated into a stream and river network watershed model that was applied to 15 river networks in the northeastern United States (Seitzinger et al. 2002). The model results indicate that the  $Nr$  removal efficiency varies throughout a network of rivers and streams. Reaches in smaller streams remove a greater proportion of the  $Nr$  inputs to those reaches than reaches in larger rivers per se. However, the total amount of  $Nr$  removed by denitrification is greater in downstream reaches, because the total  $Nr$  inputs, primarily from the upstream watershed, are larger. At the scale of a whole wetland–stream–river network, the cumulative effect of continued  $Nr$  removal along the entire flow path from wetlands to small streams to larger rivers downstream can result in denitrification of as much as 30% to 70% of the total external  $Nr$  inputs to the river, although the proportion of  $Nr$  inputs removed by denitrification in a particular reach is generally quite small (often 1% to 20%).

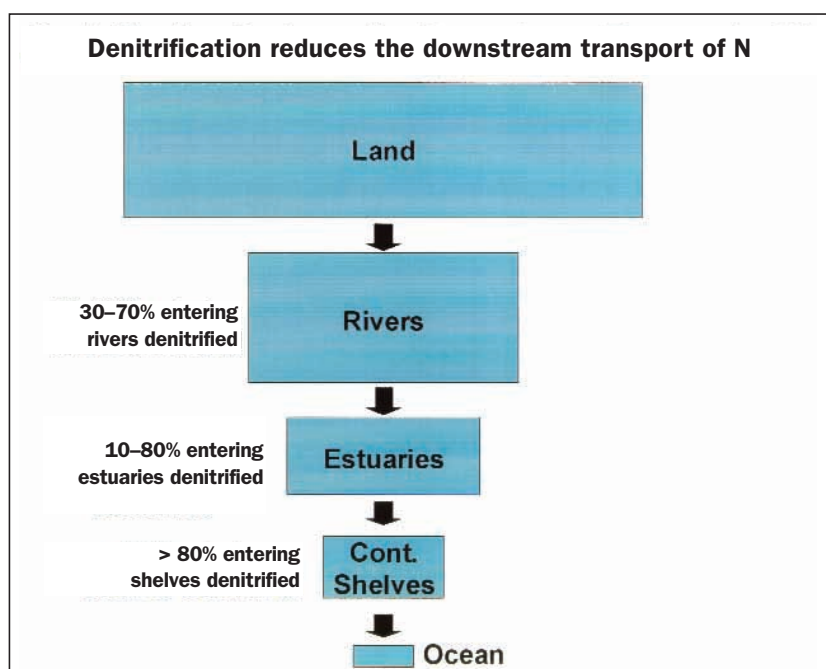
Physical alterations to rivers, such as channelization, can decrease water residence time and thus decrease denitrification within a river. Channelization of rivers also destroys riparian wetlands, which have a considerable capacity for  $Nr$  removal (Billen and Garnier 2000). Wetland restoration and the construction of new wetlands have been considered as options for decreasing  $Nr$  loading at local and regional scales. While individual wetlands are clearly active sites for denitrification, the overall contribution of wetlands to  $Nr$  removal at the whole-watershed scale generally is not well documented and warrants further analysis.

Reactive  $N$  not removed within the wetland–river network is transported to

estuaries or discharged by large rivers directly onto the continental shelf. In estuaries, water residence time again is an important factor controlling the proportion of  $Nr$  inputs that are removed by denitrification. A similar functional relationship to the ones demonstrated for lakes and rivers applies to estuaries. In estuaries with a water residence time ranging from 0.1 month to over a year, the total  $Nr$  inputs removed by denitrification ranged from less than 10% to approximately 75% (Nixon et al. 1996).

$Nr$  that has not been removed by denitrification in rivers or estuaries is subject to removal on the continental shelf (e.g., Devol and Christensen 1993, Laursen and Seitzinger 2001). In fact,  $Nr$  removed by denitrification in shelf sediments probably exceeds  $Nr$  exported to coastal areas by rivers. Detailed  $Nr$  budgets for continental shelf regions throughout the North Atlantic basin suggest that denitrification in continental shelf sediments is equal to or greater than inputs of  $Nr$  from land-based sources (Seitzinger and Giblin 1996). The additional  $Nr$  required to support the estimated denitrification rates in shelf sediments probably comes from the transport of  $Nr$  from oceanic regions across the slope–shelf boundary. Confirming this observation in another region, Chen and Wang (1999) found that the net denitrification rate in the East China Sea shelf is greater than the total riverine supply to the region. Additional measurements of denitrification and  $Nr$  inputs for other continental shelf regions throughout the world's oceans are needed to better understand the  $Nr$  balance and final fate of land-based  $Nr$  inputs.

In summary, nearly all of the  $Nr$  that is injected into surface waters is denitrified along the stream–river–estuary–shelf continuum (figure 6). While most of this  $Nr$  is converted to  $N_2$ , a fraction is converted to  $N_2O$  and  $NO$ . Model estimates



**Figure 6.** The transport of reactive nitrogen from terrestrial to oceanic systems decreases at each step along the river–estuarine–continental shelf system.

of global  $N_2O$  emissions suggest that rivers, estuaries, and continental shelves account for approximately 30% of the total global anthropogenic  $N_2O$  emissions (Seitzinger et al. 2000). As injections of Nr to rivers increase, so will the rates of creation of NO and  $N_2O$  (Seitzinger and Kroeze 1998).

### The nitrogen cascade: Linkages with other elements

Elevated atmospheric Nr can increase ozone, increase atmospheric fine particulate loadings, and enhance the impacts of aerosol sulfate on the atmospheric radiation balance. These are not the only important linkages. Because many natural ecosystems are N limited (e.g., temperate and boreal forests, grasslands, and temperate coastal waters), the increased abundance of Nr leads to increases in productivity, which in turn lead to increases in uptake of all other elements tied to productivity (e.g., calcium [Ca], C, P, potassium, and magnesium). Eventually, another element may replace N as the limiting element. For example, when temperate forested ecosystems reach stage 3 of N saturation, N becomes a non-limiting element for plant growth (figure 4). At that point, something else becomes limiting, and the basic biogeochemical nature of the forest changes. Other possible limiting materials are base cations, P, light, and water (e.g., Schulze 1989, DeHayes et al. 1999).

Matson and colleagues (2002) discuss how the globalization of Nr deposition raises questions concerning consequences of anthropogenic Nr for ecosystems in tropical regions, where P or Ca most likely limits production in humid tropical forest and savanna ecosystems with highly weathered soils. In many of these systems, Nr may already be a nutrient in excess, so many tropical humid forests may be naturally N saturated (Hall and Matson 1999).

### The nitrogen cascade: Possibilities for intervention

Nr accumulation in environmental reservoirs enhances the N cascade and its consequences on people and ecosystems. However, just as anthropogenic activities have substantially increased the rate of Nr formation, it is possible to intervene at critical points along the N cascade and make Nr less abundant. There are two ways to decrease total Nr: (1) decrease the rate of Nr creation during energy and food production or (2) convert Nr back to  $N_2$  following Nr creation and use.

**Decreasing the rate of reactive nitrogen creation.** There is no benefit to the Nr created during fossil fuel combustion. Nitrogen oxides are formed inadvertently during combustion either through oxidation of fossil-organic Nr in the fuel or through oxidation of atmospheric  $N_2$ . In both cases, the options for significantly decreasing  $NO_x$  emissions are numerous, either by using an alternative method to provide energy (e.g., hydrocarbon-based fuel cells) or by eliminating  $NO_x$  and other Nr species from the combustion products (Bradley and Jones 2002, Moomaw 2002). It is now technically feasible to decrease Nr creation from fossil fuel combustion to a point where it becomes just a minor disturbance to the global

cycle (Cowling et al. 2002). If that occurs,  $NO_y$  deposition to global ecosystems will decrease by about half, and the remaining major  $NO_x$  sources will be emissions from biomass burning and agricultural soils. Nr deposition to regional systems will also decrease. In the northeastern United States, if fossil fuel combustion were no longer a source of  $NO_x$ , Nr deposition to the research sites in the study by Aber and colleagues (2003) would decrease by more than 50% (Ollinger et al. 1993). Kroeze and colleagues (2001) examined the effect of instituting the maximum technical potential to decrease  $NO_x$  emissions in Europe on DIN export by European rivers in the year 2050. This scenario assumed that all countries apply maximum emission control in electricity generation, transport, and industry. This resulted in a decrease of approximately 80% in  $NO_y$  deposition to European watersheds relative to a business-as-usual scenario.

In food production, there is a benefit to Nr creation through the Haber-Bosch process and through cultivation-induced BNF. However, there is also inefficiency. Of about 170 Tg N of Nr added to global crop agroecosystems in 1995, only about 12% entered human mouths (figure 3; Smil 1999, 2002). Most of the rest was distributed to the environment without serving the purpose for which it was created.

There is ample opportunity to increase the efficiency of Nr use in food production and thus decrease the Nr creation rate. There are many ways of achieving this goal: (a) increase the efficiency of N use in crop and animal agriculture (Cassman et al. 2002), (b) increase Nr recycling within agroecosystems (i.e., if Nr is not incorporated into food the first time around, send it around again; Smil 2002), (c) increase use of cultivation-induced BNF (Roy et al. 2002), (d) provide incentives to reduce overfertilization (Howarth et al. 2002b), and (e) redistribute Nr from areas with high Nr production to areas where there is a need for Nr for food production (Erismann et al. 2001).

CAFOs offer large opportunities for improvement of N-use efficiency. In recent decades, livestock and meat processing industries have been transformed in many countries. Both vertical and horizontal integration have great potential to maximize N-use efficiency with integrated economic and advisory-service linkages among farmers, feed suppliers, animal-rearing advisers, and food-processing companies. These changes often lead to largely unforeseen Nr-induced environmental problems, mainly on local and regional scales. Thus, emphasis on economic efficiency without attention to Nr-induced health and environmental risks leads to externalization rather than internalization of these real costs.

If societies decreased their consumption of meat, there would be less demand for Nr created to produce food (Bleken 1997, Kroeze et al. 2001, Smil 2002). Howarth and colleagues (2002a) project that if the US population adopted a Mediterranean diet of approximately 6.3 kg meat per capita per year (about one-seventh of the supply in the United States), total inorganic N fertilizer consumption would decrease to about 6.9 Tg N per year by 2030—a 65% decrease. Kroeze and



colleagues (2001) report similar findings for the United States and Europe.

The projections for future Nr creation through the Haber-Bosch process depend to a large extent on the degree of intervention and on assumptions and preferences regarding human diets. A study of future fertilizer requirements up to the year 2030 projects that annual increases in fertilizer use will range from 0.7% to 1.3%, depending on assumptions about N-use efficiency (FAO 2000, Fixen and West 2002). In absolute terms, this means that N fertilizer use in 2030 will range from about 96 Tg N per year to 118 Tg N per year, compared with about 78 Tg N per year for the base period 1995–1997. Tilman and colleagues (2001) project that N fertilizer use will increase from 87 Tg N per year in 2000 to 135 Tg N per year in 2020. While the actual production of Nr in the future for fertilizer use is uncertain, it is clear that N demands for food production will increase.

**Increasing the conversion of reactive nitrogen to N<sub>2</sub>.** In most environmental reservoirs, N<sub>2</sub> formation is very limited (e.g., atmosphere, grasslands, and forested ecosystems) or counterproductive to the purpose of the system (e.g., agroecosystems). The wetland–stream–river–estuary–shelf continuum is the only system that provides this service naturally, at rates that are large relative to Nr inputs. However, before Nr is converted to N<sub>2</sub> in the continuum, a number of detrimental effects occur in forests, grasslands, and surface water ecosystems. For this reason, the next opportunity for intervention is immediately after Nr is used as a resource but before it is distributed to the environment. While there are probably other suitable points for intervention, we choose two: (1) Nr losses from animal and human waste and (2) Nr transfer from agroecosystems to surface waters.

Globally, animals and humans excrete about 75 Tg N per year and about 23 Tg N per year, respectively (Smil 1999). While this is about 80% of the Nr created for food production, some of it is reused, and not all of the remainder is easily collectible. For animals, of about 75 Tg N per year, about 28 Tg N per year are produced in CAFOs, and of that about 18 Tg N per year are recycled to agroecosystems, leaving about 10 Tg N per year as easily collectible waste Nr. For humans, in 2000, 47% of the world's population lived in an urban environment; of this 47%, 84% had their waste collected by a sewage system (6 March 2003; [www.worldbank.org/data/dataquery.html](http://www.worldbank.org/data/dataquery.html)). So, of about 23 Tg N per year contained in human waste that is generated annually, municipal sewage operations collect about 9 Tg N per year. Thus, of about 100 Tg N per year produced as Nr-containing waste by animals and humans, about 21 Tg N per year is not reused and is easily collectible, which increases the potential for a “denitrification intervention” unless other value-added products can be made using this N-rich resource (Cassman et al. 2002, Oenema and Pietrzak 2002).

The second intervention point is between agroecosystems and streams or rivers. Accepting that Nr leakages will occur from most agroecosystems and some forests, there is an

opportunity to take advantage of the fact that denitrification does occur in wetland and riparian areas (Hill 1996, Hill et al. 2000, Steinhart et al. 2000, Mitsch et al. 2001), and specific management activities can be used to create an environment that will increase this rate (e.g., Schipper and Vojvodic-Vukovic 2001). However, it is not enough to increase denitrification; the production of N<sub>2</sub> must also be optimized relative to N<sub>2</sub>O formation.

### Summary

The atmosphere directly receives about 15% of the Nr created by human activities as a consequence of energy production; all of it is deposited as Nr. Agroecosystems receive 75%, most of which is either transferred directly into the atmosphere or hydrosphere or lost to the environment during the process of food production and consumption. The remaining 10% of the Nr is used in industrial processes. The primary beneficial effect of Nr introduced into agroecosystems is human nutrition; other effects occur as the Nr from agroecosystems cascades through other environmental systems.

In the atmosphere, increased Nr concentrations have direct and indirect impacts on human and ecosystem health on a regional and global basis. Most of the Nr emitted to the atmosphere is deposited back to Earth's surface after hours to days. Increased Nr deposition to grasslands and forests has a residence time of years to centuries, introducing the potential for a large lag time in the cascade. Because the production of N<sub>2</sub> is small relative to Nr inputs, N accumulates in a reactive form, resulting in initially increased productivity and some loss of biodiversity, and ultimately some loss of productivity. Several regions of the world have already reached the point where accumulation has slowed and loss of Nr to the atmosphere and hydrosphere has increased.

Transfer of Nr from the atmosphere, agroecosystems, forests, and grasslands into the wetland–stream–river–estuary hydrosphere continuum is increasing and has resulted in numerous effects, including acidification, eutrophication, and human health problems. However, throughout the continuum there is a large potential for conversion of Nr to N<sub>2</sub>, especially in wetlands, large rivers, estuaries, and the continental shelf. Thus, while the N cascade begins at the point of Nr creation, and while Nr will accumulate in and cycle among, most terrestrial systems, the cascade reaches an end at the continental margins, where its primary continuation is N<sub>2</sub>O production during nitrification.

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