On the fate of anthropogenic nitrogen

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This article provides a synthesis of literature values to trace the fate of 150 Tg/yr anthropogenic nitrogen applied by humans to the Earth's land surface. Approximately 9 TgN/yr may be accumulating in the terrestrial biosphere in pools with residence times of ten to several hundred years. Enhanced fluvial transport of nitrogen in rivers and percolation to groundwater accounts for ≈35 and 15 TgN/yr, respectively. Greater denitrification in terrestrial soils and wetlands may account for the loss of ≈17 TgN/yr from the land surface, calculated by a compilation of data on the fraction of N_2O emitted to the atmosphere and the current global rise of this gas in the atmosphere. A recent estimate of atmospheric transport of reactive nitrogen from land to sea (NO_x and NH_x) accounts for 48 TgN/yr. The total of these enhanced sinks, 124 TgN/yr, is less than the human-enhanced inputs to the land surface, indicating areas of needed additional attention to global nitrogen biogeochemistry. Policy makers should focus on increasing nitrogen-use efficiency in fertilization, reducing transport of reactive N to rivers and groundwater, and maximizing denitrification to its N_2 endproduct.

biogeochemistry | denitrification | nitrogen cycle

Numerous papers have documented the current human impacts to the global nitrogen cycle; humans have approximately doubled the input of available nitrogen to the Earth's land surface, largely through the industrial production of nitrogen fertilizer (1–3). Some environmental effects are obvious, including the expanding summertime hypoxic zone in the Gulf of Mexico (4) and rising concentrations of nitrous oxide in Earth's atmosphere (5). Other consequences, such as the health impacts of nitrate in drinking water are less clear (6).

This paper provides some composite estimates of the fate of nitrogen applied to the Earth's land surface, focusing on four sinks—the biosphere, groundwater, fluvial transport to the sea, and denitrification. An additional movement of terrestrial nitrogen—atmospheric transport of NH_x, NO_y, and other forms to the oceans—is also considered using recent literature values. The residence time of reactive nitrogen in vegetation and soils can vary over a wide range of values, depending on vegetation and its age, affecting the permanence of the biospheric sink. None of these fluxes can be estimated precisely; the goal is to provide preliminary estimates of their relative role, which can indicate potential policy solutions to the global nitrogen problem.

Providing a balanced global nitrogen budget is not easy: the element has numerous valence states and gaseous forms that escape notice and travel long distances in the atmosphere. We have little understanding of the fate of the applied nitrogen, except to note that mass-balance studies of agricultural fields indicate that a lot of it must escape from the local point of application (7, 8).

The Biosphere. Nitrogen limits net primary production over much of the Earth's land surface (9), and to a large extent, the human impact on the global nitrogen cycle stems from our attempt to alleviate nitrogen deficiencies in agriculture by the application of fertilizer (10). Globally, ≈10% of applied nitrogen is contained in food (11); most nitrogen remaining is lost to the environment during food production and after human ingestion. There is some long-term retention of nitrogen applied to agricultural soils (8, 12–14), but much is lost to runoff, to *situ* denitrification, and to gaseous forms of nitrogen (e.g., NH_3 and NO_x) that are deposited downwind (15). Combined with emissions of NO_x from fossil fuel combustion, the latter produce a chronic nitrogen enrichment of natural ecosystems, with documented effects on forests (16), deserts (17), grasslands (18, 19), coastal ecosystems (20, 21), and oceans (22).

Anthropogenic nitrogen indirectly delivered to forests can accelerate their growth, resulting in greater biomass (23, 24). The results from fertilizer trials in forestry are instructive, indicating that ≈25–30% of the applied nitrogen is retained in biomass (25) and a similar amount retained in forest soils (Table 1). Generally, coniferous forests retain more nitrogen than deciduous forests. Anthropogenic nitrogen deposited from the atmosphere may allow for the apparent acceleration of forest growth in response to rising carbon dioxide concentrations in Earth's atmosphere (41) and explain the limited evidence for progressive nitrogen limitation in CO_2-enrichment studies (42). Humans have increased the atmospheric deposition of nitrogen on land by ≈46 TgN/yr (43), with about one-third of that deposited in forests (18 TgN/yr) (44), where trees provide a potential long-term sink for nitrogen in biomass. If ≈50% of nitrogen deposition is stored within the ecosystem, then ≈9 TgN/yr might be sequestered in terrestrial biomass until harvest or natural mortality. Some of this nitrogen is returned to the atmosphere as NO_x or N_2 when woody biomass is burned (pyrodenitrification) (45) and eventually nitrogen is released from decomposition, but a net sink for nitrogen on land is consistent with the apparent sink for carbon in terrestrial biomass. Goodale *et al.* (46) suggest that the retention of atmospheric nitrogen by forests in the eastern U.S. may be as high as 73%, consistent with the current sink for carbon—0.3 to 0.58 PgC/yr—in U.S. forests, many of which are recovering from agricultural land abandonment a few decades ago (47).

Runoff and Fluvial Losses. A large number of studies have examined nitrogen losses in surface runoff. Most of these focus on dissolved NH_4^+ and NO_3^-, but forms of dissolved organic nitrogen increasingly are recognized to contribute to the total (48). Compiling data from watersheds in the northeastern United States, Van Breemen *et al.* (49) found that rivers transported ≈23% of the nitrogen applied to their watersheds (*cf.* 26%; 15% for nitrate only) (50, 51). Recent work by Schaefer and Alber (52) suggests that transport from watersheds in warm temperate regions may be lower than in colder regions, but globally, if 23% of applied N (150 TgN/yr) is lost to riverflow, I estimate that the flux in rivers has increased from a preindustrial value of 27 TgN/yr (43) to a current value of 61.5 TgN/yr, for a net sink for anthropogenic N of 34.5 TgN/yr. Independent estimates of the recent anthropogenic riverine flux (19 TgN/yr)

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Table 1. Fate of exogenous nitrogen applied to forest ecosystems, including studies that recorded changes in plant, litter, and soil organic matter.

					Percent recovery							
							Soil					
Forest type	Starting age, yrs	Method	Annual application, kgN/ha per yr	Duration of study, yrs	Plants	Litter	Extractable	Organic	Leachate	Gaseous flux	Total measured recovery, %	Reference
Coniferous forests												
Pinus resinosa	50	Treatment-control	50	9	19	35	2	24	2	Tr	82	26; soil data from ref. 27
Pinus contorta	11	^{15}N Urea	100	8	17	4	0	41			62	28
		$^{15}NH_4NO_3$	100	8	20	3	0	38			61	
		$NH_4{}^{15}NO_3$	100	8	8	2	0	18			28	
Pinus elliottii	11	Treatment-control	56	2	25	9		21			55	29
			224		27	6		12			45	
Pinus radiata	16	Treatment-control	117	9	15	5		21			51	30
Pseudotsuga menziesii	7	^{15}N	112	2	30			38			68	31
Pseudotsuga menziesii	35	$^{15}NH_4$	5	2	33	22		24	2		81	32
			50	2	29	15		22	33		99	
Pinus sylvestris	45	$^{15}NH_4$	5	2	10	46		20	10		86	
			50	2	17	21		15	17		71	
Pinus sylvestris	120–240	^{15}NH	100	2	30	2		51			82	33
		$^{15}NO_3$			38	2		37			76	
Pinus nigra	36	Treatment-control	84	3	19	21		153			193	34
			168	3	16	5		172			193	
			336	3	7	1		79			87	
			504	3	9	8		54			71	
Picea abies	15	$^{15}NH_4$	1	2	14	63		25			102	35
		$^{15}NO_3$		2	25	46		33			104	
Picea abies	250	N-15	30	2	13	13		63	10		99	36
Picea abies	75	$^{15}NO_3$	35	1	45	16		17	4		82	37
Picea sitchensis	35	$^{15}NO_3$	35	3	32	47		1	25		105	
			35	3	32	17		15	35		99	
			75	3	20	11		15	35		97	
Deciduous forests												
Fagus grandifolia	40	$^{15}NO_3$	28	4	3	3		1			7	38
			56		3	2		1			6	
Fagus–Acer	38	Treatment-control	40	2	0		14		0		14	39
			160		7		6		0		13	
			520		9		13		3		25	
Quercus	50	Treatment-control	50	9	14	55	$<$1	16	3	Tr	87	26; soil data from ref. 27
Acer Saccharum	88	$^{15}NO_3$	30	5	14	3	0	0	1		18	40

(53) and the total transport of N in the world's rivers, 59 TgN/yr (54) and 54 TgN/yr (55), are roughly compatible with these estimates. Much of the reactive N in rivers is denitrified in the coastal zone, returning N_2 to the atmosphere (56). As fertilizer use expands globally, increases in the fluvial transport of nitrogen are likely to occur worldwide (57).

Groundwater. Public health agencies have long recognized that excessive nitrate in water leads to the sometimes fatal condition in infants known as methemoglobinemia (58) and that regions of intensive agriculture and fertilizer use often have high concentrations of NO_3^- in groundwater (59, 60). Inasmuch as the nitrate concentrations in groundwater in many remote areas show near-zero values, the high nitrate concentrations found in agricultural areas are likely to be of anthropogenic origin. Compiling the results of several surveys, Spalding and Exner (61) found nitrate-N $>$ 3 mg/L in 9.4% to 23.6% of wells in domestic areas of the rural United States. Similarly, Nolan *et al.* (62) compiled nitrate concentrations reported from 1,280 wells across the continental United States, calculating a median value of 8.3 mgNO_3 per liter (1.9 mgN/L; *cf.* 3.4 mgNO_3/L; ref. 63). The field sampling in these studies may be biased toward problematic regions, but the value of 1.9 mgN/L can be used to provide a lower-limit estimate of the anthropogenic impact on the annual flux of nitrogen to groundwater, if we assume that it might otherwise be nitrogen-free.

Groundwater flux (i.e., the new inputs to the saturated zone) is estimated at 10^{16} liters annually (64), $\approx$10% of global terrestrial precipitation and roughly compatible with the traditional assumption that the base flow of rivers carries $\approx$10% of precipitation to the sea (65). If we assume that the groundwater flux in North America is proportional to the global surface runoff generated there (14%) (66), then the input of nitrate to groundwater in North America is $\approx$3 TgN/yr (1.9 mgN/L $\times$ 0.15 $\times$ 10^{16}L/yr; equivalent to $\approx$1.15

kgN/ha/yr for North America). This analysis does not consider additional nitrate that is transported to and denitrified in the saturated zone, which is included (44 TgN/yr) as part of the global estimate of denitrification (see below; 56). Anthropogenic inputs of nitrogen in North America are ≈20% of the world's total (67), so the global flux of nitrogen to groundwater may be as large as 15 TgN/yr. Because the mean residence time of groundwater is often thousands of years (68), it offers a long-term sink for nitrogen. Among comparative estimates, Lin *et al.* (69) developed a model to predict nitrate leaching of 12 TgN/yr to groundwater, adding to a preindustrial background flux of 14 TgN/yr. Van Drecht *et al.* (55) suggest that 10% (≈5 TgN/yr) of the nitrogen transport in rivers stems from groundwater, where N is largely derived from historical fertilizer use.

Some recent studies report large nitrogen accumulations in the vadose zone of desert ecosystems, totaling ≈3,000 to 15,000 TgN globally (70, 71). This nitrate has accumulated over an unknown period, so the pool is difficult to relate and probably not relevant to the fate of a large fraction of the anthropogenic nitrogen emitted during the past 100 years. The rate of accumulation of this nitrate in deserts (≈1 kgN/ha/yr) (72) may indicate a lower limit for the transport of nitrate to groundwater, with higher values expected in more mesic regions.

Denitrification. Environmental scientists are increasingly realizing the complexity of microbial transformations of nitrogen in soils and sediments (73, 74). Whereas many early textbooks of microbiology recognized nitrate and N_2 gas as the sole products of nitrification and denitrification, respectively, we now realize that a small percentage of the nitrogen passing through these biochemical pathways is released as NO and N_2O (75). N_2O is of particular interest, because it is a powerful greenhouse gas in Earth's atmosphere and destroys stratospheric ozone. Studies of the stable isotopes of nitrogen have sharpened our perceptions of nitrogen biogeochemistry; accumulations of the heavier isotope of nitrogen (^{15}N) in soils (76) suggest that denitrification is more widespread and of greater significance than we realized just a few years ago. For one wet tropical forest, Houlton *et al.* (77) attribute 24 to 53% of ecosystem losses of nitrogen to denitrification. Losses of nitrogen to the atmosphere via denitrification on the land surface result in a global mean residence time for nitrogen on land of ≈100 years (68).

Seitzinger *et al.* (56) compiled data for denitrification from a variety of ecosystems, estimating the current global rate of 573 TgN/yr, with 22% (124 TgN/yr) stemming from the land surface and 110 TgN/yr from wetlands. These high values are somewhat difficult to reconcile with estimates nitrogen inputs to the land surface, especially if we assume that the nitrogen cycle was in steady-state in the preindustrial era. For comparison, Galloway *et al.* (43) suggest global denitrification of 389 TgN/yr, with ≈100 TgN/yr derived from upland and freshwater environments. Some of this flux is natural, but at least a portion is stimulated by anthropogenic additions of nitrogen fertilizer to the land surface, thus representing a sink for applied nitrogen. Globally, N_2O comprises ≈2.6–3.9% of the denitrification flux, calculated by using the global N_2O flux from soils, wetlands, and the sea surface (5) and global denitrification from Seitzinger *et al.* (56) or Galloway *et al.* (43), respectively.

Nitrous oxide (N_2O) is a byproduct of nitrification and denitrification and is increasing in Earth's atmosphere by ≈0.3%/yr (5). The approach to estimating recent changes in global denitrification is to divide the observed increase in N_2O in Earth's atmosphere (≈4 TgN/yr) by an estimate of the ratio of N_2O to the total of N_2+N_2O produced by soil microbes. Table 2 (see also Table S1)includes values for the N_2O to (N_2+ N_2O) ratio in the efflux from a variety of ecosystems under natural and N-fertilized conditions. As noted in many earlier reports (78), there is considerable range in these values. For wetlands, including stream and lake sediments, the values are always low; N_2 dominates the efflux in anerobic environments (79–81). For upland ecosystems, a significant percentage of the efflux occurs as N_2O, with an unknown proportion of this derived from nitrification rather than denitrification. The mean ratios N_2O/(N_2 + N_2O) for upland, agricultural, and wetland soils are 0.49, 0.37, and 0.082, respectively. To provide an estimate of the human impact on terrestrial denitrification, assume that the rise in N_2O in Earth's atmosphere is solely from denitrification on land. If 53% of denitrification occurs in the upland soils, dominated by agriculture, with a ratio of 0.37, and 47% occurs in wetlands with a ratio of 0.08 (57), then the weighted mean ratio is 0.23, and the calculated total rate of denitrification is now 17 TgN/yr greater than in preindustrial times. Any contributions of N_2O from nitrification would reduce this value, because it would not be associated with the production of N_2. An identical estimate for the human-induced change in terrestrial denitrification is given by Galloway *et al.* (43).

Table 2. Mean N_2O-yield values from various laboratory and field studies of denitrification

Ecosystem	N_2O-N/(N_2+N_2O)N
Agricultural soils	0.375 ± 0.035 (SE)
Soils under natural or recovering vegetation	0.492 ± 0.066 (SE)
Freshwater wetlands and flooded soils	0.082 ± 0.024 (SE)

Full dataset is available as Table S1.

Seitzinger (82) compiled data showing a wide range of values for the N_2O/(N_2+N_2O) mole fraction in the gaseous efflux from coastal marine ecosystems. Most values were very low, but see ref. 83. Near-shore denitrification may be as large as 79 TgN/yr (56), of which 21 TgN/yr may derive from human distribution of available nitrogen (43). Thus, a substantial fraction of the nitrogen leaving the land surface is likely to be denitrified in coastal waters. In this analysis, changes in pelagic denitrification are assumed to be minor (43), potentially with a significant fraction contributed by the anammox reaction that produces no N_2O (73).

Xu *et al.* (84) report significant correlations in the flux of CO_2 and N_2O from soils (*cf.* ref. 85). Soil denitrification and N_2O flux may increase globally as future, rising atmospheric CO_2 stimulates plant growth, accumulation of carbon in soils, and greater denitrification. Kammann *et al.* (86) report large increases in the loss of N_2O from a grassland grown under Free Air CO_2 Enrichment (FACE) conditions. In contrast, Phillips *et al.* (87) found only small changes in the flux of N_2O from soils in a forest grown at ambient +200 μl/L atmospheric CO_2.

Atmospheric Transport of Available Nitrogen to the Marine Environment. Atmospheric transport of reduced and oxidized nitrogen trace gases and various forms of organic nitrogen to marine ecosystems represents an additional sink for anthropogenic nitrogen applied to the land surface. Duce *et al.* (22) indicate that the flux of these constituents to the ocean surface has increased by 48 TgN/yr from preindustrial times to 2000, representing a net sink for anthropogenic nitrogen from the land surface. Nearly 70% (33 TgN/yr) is derived from inorganic forms—NH_x and NO_y—and the rest is organic N. For the 1990s, comparable values for the inorganic portion are 25 TgN/yr (43) and 39 TgN/yr (88). Of course, the atmospheric transport of reactive nitrogen from land to sea via the atmosphere is recognized as a major source of nitrogen causing environmental degradation in coastal waters and perhaps also in the open ocean (22).

Conclusions

The sum of these preliminary, generally upper-limit estimates of sinks for anthropogenic nitrogen applied to land is ≈124 TgN/

Table 3. Budgets for nitrogen on the global land surface

	Pre-industrial	Human derived	Total
Inputs			
Biological nitrogen fixation	120	20[†]	140
Lightning	5	0	5
Industrial N-fixation	0	125[‡]	125
Fossil fuel combustion	0	25	25
Totals	125	170	295
Fates			
Biospheric increment	0	9	9
Riverflow	27	35	62
Groundwater	0	15	15
Denitrification	92*	17	109
Atmospheric transport to the ocean	6	48	54
Totals	125	124	249

All values are TgN/yr. Unless otherwise indicated, preindustrial values and human-derived inputs are for the mid-1990s from Galloway *et al.* (43) and Duce *et al.* (22). Fates of anthropogenic nitrogen are derived in this paper.

*To balance.

[†] Net of human activities.

[‡] Ref. 89 for 2007.

yr—slightly less than the current estimate of the industrial production of available nitrogen by humans (150 TgN/yr; 125 Tg from industrial production plus 25 Tg from fossil fuel combustion; Table 3). Thus, the budget for the terrestrial portion of the modern nitrogen cycle is nearly balanced, although a number of the "sinks" (e.g., surface and groundwater pollution) are associated with serious environmental problems. Further work will be needed to refine these estimates and identify other sinks for anthropogenic nitrogen applied to the land surface. Studies of nitrogen retention in fertilized agricultural soils (12) and of submarine discharges of nitrogen to coastal marine environments (83, 90, 91) are worthy of examination.

The comparative magnitude of these fluxes gives some indication of where better environmental management might reduce human impacts on natural and managed ecosystems. All efforts to minimize human impacts on the global nitrogen cycle will benefit from improved efficiency in the application of nitrogen fertilizer (92). With the era of cheap energy now ending, economics alone may dictate a greater efficiency of fertilizer use. However, policy makers should consider future regulations on losses of nitrogen to runoff and perhaps even to institute a cap-and-trade system to reduce wasteful inputs to the global nitrogen cycle.

The loss of applied nitrogen in rivers causes substantial disruption to estuarine and coastal marine ecosystems (93). To minimize such transport, land-use planning should encourage the maintenance and expansion of wetland ecosystems that convert nitrate to N_2 (Table 2 and Table S1). Considering the large human inputs of available nitrogen to the Earth's land surface, humans appear to have caused a surprisingly small change in the flux of N_2 to the atmosphere from denitrification (17 TgN/yr). The efficiency of denitrification in streams appears to decrease as nitrate concentrations increase (94). Efforts to increase the rate of denitrification, while minimizing the by-product flux of N_2O, may be effective ways to reduce the environmental impact of fertilizer nitrogen (95, 96). Clearly even the modest flux of nitrogen to groundwater is problematic in regions depending on this resource for drinking water. More efficient use of fertilizer and efforts to increase vadose-zone denitrification may protect groundwater resources for future generations.

The sink for nitrogen in trees and soils appears modest (9 TgN/yr), but large enough to support a significant, simultaneous global sink for carbon in these ecosystem components. In contrast, on fertilized agricultural lands, the enhanced sink for carbon in soil organic matter is often substantially discounted by the CO_2 emissions during fertilizer production (97). Inadvertent nitrogen deposition in natural ecosystems has important adverse consequences (16, 98), but it may alleviate progressive nitrogen limitation to forest growth under high CO_2.

The largest net sink for anthropogenic nitrogen, atmospheric transport from the terrestrial to the marine realm, reflects the importance of airborne pathways and transformations of nitrogen compounds, much of which is derived from combustion sources. Many of the deposited compounds impact the productivity and health of coastal and continental shelf ecosystems. Better management of emissions from agriculture will help preserve the integrity of coastal ecosystems and their fisheries.

Overall, our understanding of the nitrogen cycle and the development of effective policies to reduce inadvertent losses of anthropogenic nitrogen to the environment is analogous to our understanding of the carbon cycle in the late 1960s. Humans are adding nitrogen to the Earth's surface; we do not know where it all goes, but we do know that increasing concentrations of nitrogen in unexpected places will cause significant environmental damage that we will all learn to regret.

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1. Vitousek PM, *et al.* (1997) Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol Applic* 7:737–750.
2. Galloway JN, *et al.* (2008) Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* 320:889–892.
3. Gruber N, Galloway JN (2008) An Earth-system perspective of the global nitrogen cycle. *Nature* 451:293–296.
4. Rabalais NN, Turner RE, Wiseman WJ (2002) Gulf of Mexico hypoxia: AKA, ''The Dead Zone.'' *Ann Rev Ecol System* 33:235–263.
5. Denman KL, *et al.* (2007) in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change*, eds Solomon S *et al.* (Cambridge Univ Press, Cambridge, UK), pp 499–587.
6. Powlson DS, *et al.* (2006) When does nitrate become a risk for humans? *J Environ Qual* 37:291–295.
7. Isermann K (1993) in *Interactions of C, N, P and S in Biogeochemical Cycles and Global Change*, NATO SAI Series Vol I-4, eds Wollast R, MacKenzie FT, Chou L (Springer, Berlin), pp 79–121.
8. Stevens WB, Hoeft RG, Mulvaney RL (2005) Fate of nitrogen-15 in a long-term nitrogen rate study: II. Nitrogen uptake efficiency. *Agronomy J* 97:1046–1053.
9. LaBauer DS, Treseder KK (2008) Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. *Ecology* 89:371–379.
10. Smil V (2001) *Enriching the Earth* (MIT Press, Cambridge, MA).
11. Galloway JN, Cowling EB (2002) Reactive nitrogen and the world: 200 years of change. *Ambio* 31:64–71.
12. Schindler FV, Knighton RE (1999) Fate of fertilizer nitrogen applied to corn as estimated by the isotopic and difference methods. *Soil Sci Soc Am J* 63:1734–1740.
13. Fritschi FB, Roberts BA, Rains DW, Travis RL, Hutmacher RB (2004) Fate of nitrogen-15 applied to irrigated Acala and Pima cotton. *Agronomy J* 96:646–655.
14. Jagadamma S, Lal R, Hoeft RG, Nafziger ED, Adee EA (2007) Nitrogen fertilization and cropping systems effects on soil organic carbon and total nitrogen pools under chisel-plow tillage in Illinois. *Soil Tillage Res* 95:348–356.
15. Aneja VP, *et al.* (2008) Workshop on agricultural air quality. State of the science. *Atmos Environ* 42:3195–3208.
16. Aber JD, *et al.* (2003) Is nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* 53:375–389.
17. Brooks M (2003) Effects of increased soil nitrogen on the dominance of alien annual plants in the Mojave desert. *J Appl Ecol* 40:344–353.
18. Stevens CJ, Dise NB, Mountford JO, Gowing DJ (2004) Impact of nitrogen deposition on the species richness of grasslands. *Science* 303:1876–1879.
19. Clark CM, Tilman D (2008) Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. *Nature* 451:712–715.
20. Boulart C, *et al.* (2006) Atmospherically-promoted photosynthetic activity in a well-mixed ecosystem: Significance of wet deposition events of nitrogen compounds. *Estuarine Coastal Shelf Sci* 69:449–458.

21. Scavia D, Bricker SB (2006) Coastal eutrophication assessment in the United States. *Biogeochemistry* 79:187–208.
22. Duce RA, *et al.* (2008) Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 320:893–897.
23. Pregitzer KS, Burton AJ, Zak DR, Talhelm AF (2008) Simulated chronic nitrogen deposition increases carbon storage in northern temperate forests. *Global Change Biol* 14:142–153.
24. Hyvonen R, *et al.* (2008) Impact of long-term nitrogen addition on carbon stocks in trees and soils in northern Europe. *Biogeochemistry* 89:121–137.
25. Nadelhoffer KJ, *et al.* (1999) Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature* 398:145–148.
26. Magill AH, *et al.* (2000) Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems* 3:238–253.
27. Nadelhoffer KJ, Colman BP, Currie WS, Magill A, Aber JD (2004) Decadal-scale fates of ^{15}N tracers added to oak and pine stands under ambient and elevated N inputs at the Harvard Forest (USA). *Forest Ecol Manage* 196:89–107.
28. Preston CM, Mead DJ (1994) Growth response and recovery of ^{15}N-fertilizer one and eight growing seasons after application to lodgepole pine in British Columbia. *Forest Ecol Manage* 65:219–229.
29. Mead DJ, Pritchett WL (1975) Fertilizer movement in a slash pine ecosystem. II. N distribution after two growing seasons. *Plant Soil* 43:467–478.
30. Neilsen WA, Pataczek, Lynch T, Ryrke R (1992) Growth response of *Pinus radiata* to multiple applications of nitrogen fertilizer and evaluation of the quantity of added nitrogen remaining in the forest system. *Plant Soil* 144:207–217.
31. Heilman PE, Dao TH, Cheng HH, Webster SR, Christensen L (1982) Comparison of fall and spring application of N-15-labelled urea to douglas fir. 2. Fertilizer nitrogen recovery in trees and soil after two years. *Soil Sci Soc Am J* 46:1300–1304.
32. Koopmans CJ, Tietema A, Boxman AW (1996) The fate of 15N enriched throughfall in two coniferous forest stands at different nitrogen levels. *Biogeochemistry* 34:19–44.
33. Melin J, Nommik H, Lohm U, Flowerellis J (1983) Fertilizer nitrogen budget in a Scots pine ecosystem attained by using root-isolated plots and N-15 tracer technique. *Plant Soil* 74:249–263.
34. Proe MF, Dutch J, Miller HG, Sutherland J (1992) Long-term partitioning of biomass and nitrogen following application of nitrogen fertilizer to Corsican pine. *Can J For Res* 22:82–87.
35. Buchmann N, Gebauer G, Schulze ED (1996) Partitioning of ^{15}N-labled ammonium and nitrate among soil, litter, below- and above-ground biomass of trees and understory in a 15-year old *Picea abies* plantation. *Biogeochemistry* 33:1–23.
36. Schleppi PL, *et al.* (1999) Simulation of increased nitrogen deposition to a montane forest ecosystem: Partitioning of the added ^{15}N. *Water Air Soil Poll* 116:129–134.
37. Tietema A, Emmett BA, Gundersen P, Kjonaas OJ, Koopmans CJ (1998) The fate of ^{15}N-labelled nitrogen deposition in coniferous forest ecosystems. *Forest Ecol Manage* 101:19–27.
38. Nadelhoffer KJ, *et al.* (1995) The fate of ^{15}N-labelled nitrate additions to a northern hardwood forest in eastern Maine, USA. *Oecologia* 103:292–301.
39. Christ M, Zhang Y, Likens GE, Driscoll CT (1995) Nitrogen retention capacity of a northern hardwood forest soil under ammonium sulfate additions. *Ecol Applic* 5:802–812.
40. Zak DR, Pregitzer KS, Holmes WE, Burton AJ, Zogg GP (2004) Anthropogenic N deposition and the fate of $^{15}NO_3^-$ in a northern hardwood ecosystem. *Biogeochemistry* 69:143–157.
41. Magnani F, *et al.* (2007) The human footprint in the carbon cycle of temperate and boreal forests. *Nature* 447:848–850.
42. Finzi AC, *et al.* (2006) Progressive nitrogen limitation of ecosystem processes under elevated CO_2. *Ecology* 87:15–25.
43. Galloway JN, *et al.* (2004) Nitrogen cycles: Past, present, and future. *Biogeochemistry* 70:153–226.
44. Hudson RJM, Gherini SA, Goldstein RA (1994) Modeling the global carbon cycle-nitrogen-fertilization of the terrestrial biosphere and the missing CO_2 sink. *Global Biogeochem Cycles* 8:307–333.
45. Kuhlbusch TA, Lorbert JM, Crutzen PJ, Warneck P (1991) Molecular nitrogen emission from denitrification during biomass burning. *Nature* 351:135–137.
46. Goodale CL, Lajtha K, Nadelhoffer KJ, Boyer EW, Jaworski RA (2002) Forest nitrogen sinks in large eastern U.S. watersheds: Estimates from forest inventory and an ecosystem model. *Biogeochemistry* 57:239–266.
47. Pacala SW, *et al.* (2001) Consistent land- and atmosphere-based US carbon sink estimates. *Science* 292:2316–2320.
48. Perakis SS, Hedin LO (2002) Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. *Nature* 415:416–419.
49. Van Breemen N, *et al.* (2002) Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. *Biogeochemistry* 57:267–293.
50. Howarth RW, *et al.* (2006) The influence of climate on average nitrogen export from large watersheds in the northeastern United States. *Biogeochemistry* 79:163–186.
51. Caraco NF, Cole JJ (1999) Human impact on nitrate export: An analysis using major world rivers. *Ambio* 28:167–170.
52. Schaefer SC, Alber AM (2007) Temperature controls a latitudinal gradient in the proportion of watershed nitrogen exported to coastal ecosystems. *Biogeochemistry* 85:333–346.
53. Green PA, *et al.* (2004) Pre-industrial and contemporary fluxes of nitrogen through rivers A global assessment based on topology. *Biogeochemistry* 68:71–105.
54. Boyer EW, *et al.* (2006) Riverine nitrogen export from the continents to the coasts. *Global Biogeochem Cycles* 20:GB1S91.
55. Van Drecht G, Bouwman AF, Knoop JM, Beusen AHW, Meinardi CR (2003) Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Global Biogeochem Cycles* 17:1115.
56. Seitzinger S, *et al.* (2006) Denitrification across landscapes and watersheds. *Ecol Applic* 16:2064–2090.
57. Bouwman AF, Van Drecht G, Knoop JM, Beusen AHW Meinardi CR (2005) Exploring changes in river nitrogen export to the world's oceans. *Global Biogeochem Cycles* 19:GB1002.
58. Knobeloch L, Saina B, Hogan A, Postle J, Anderson H (2000) Blue babies and nitrate-contaminated well water. *Environ Health Perspec* 108:675–678.
59. Almasri MN, Kaluarachchi JJ (2004) Assessment and management of long-term nitrate pollution of ground water in agriculture-dominated watersheds. *J Hydrol* 295:225–245.
60. McMahon PB, *et al.* (2008) Source and transport controls on the movement of nitrate to public supply wells in selected aquifers of the United States. *Water Resour Res* 44:W04401.
61. Spalding RF, Exner ME (1993) Occurrence of nitrate in groundwater—a review. *J Environ Qual* 22:392–402.
62. Nolan BT, Hitt KJ, Ruddy BC (2002) Probability of nitrate contamination of recently recharged groundwaters in the coterminous United States. *Environ Sci Tech* 36:2138–2145.
63. Rupert MG (2008) Decadal-scale changes of nitrate in ground water of the United States, 1988–2004, *J Environ Qual* 37(5 Suppl):240–S248.
64. Zektser IS, Loaiciga HA (1993) Groundwater fluxes in the global hydrologic cycle: Past, present, and future. *J Hydrol* 144:405–427.
65. Alley WM, Healy RW, LaBaugh JW, Reilly TE (2002) Flow and storage in groundwater systems. *Science* 296:1985–1990.
66. Berner EK, Berner RA (1996) *Global Environment: Water, Air, and Geochemical Cycles* (Prentice Hall, Upper Saddle River, NJ).
67. Galloway JN (2004) in *The Treatise on Geochemistry*, ed Schlesinger WH (Elsevier, Amsterdam), Vol 8, pp 557–583.
68. Schlesinger WH (1997) *Biogeochemistry: An Analysis of Global Change* (Academic, San Diego).
69. Lin B-L, Sakoda A, Shibasaki R, Suzuki M (2001) A modeling approach to global nitrate leaching caused by anthropogenic fertilization. *Water Res* 35:1961–1968.
70. Walvoord MA, *et al.* (2003) A reservoir of nitrate beneath desert soils. *Science* 302:1021–1024.
71. Graham RC, Himas DR, Wood YA, Amrhein C (2008) Large near-surface nitrate pools in soils capped by desert pavement in the Mojave desert, California. *Geology* 36:259–262.
72. Hartsough P, Tyler SW, Sterling J, Walvoord M (2001) A 14.6-kyr record of nitrogen flux from desert soil profiles as inferred from vadose zone pore waters. *Geophys Res Lett* 28:2955–2958.
73. Arrigo KR (2005) Marine microorganisms and global nutrient cycles. *Nature* 437:349–355.
74. Leininger S, *et al.* (2006) Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature* 442:806–809.
75. Davidson EA, Keller M, Erickson HE, Verchot LV, Veldkamp D (2000) Testing a conceptual model of soil emissions of nitrous and nitric oxides. *Bioscience* 50:667–680.
76. Amundson R, *et al.* (2003) Global patterns of the isotopic composition of soil and plant nitrogen. *Global Biogeochem Cycles* 17:1031.
77. Houlton BZ, Sigman DM, Hedin LO (2006) Isotopic evidence for large gaseous nitrogen losses from tropical rainforests. *Proc Natl Acad Sci USA* 103:8745–8750.
78. Weier KL, Doran JW, Power JF, Walters DT (1993) Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. *Soil Sci Soc Amer J* 57:66–72.
79. Focht DD (1974) The effect of temperature, pH, and aeration on the production of nitrous oxide and gaseous nitrogen—a zero-order kinetic model. *Soil Sci* 118:173–179.
80. Riley WJ, Matson PA (2000) NLOSS: A mechanistic model of denitrified N_2O and N_2 evolution from soil. *Soil Sci* 165:237–249.
81. Kralova M, Masscheleyn PH, Lindau CW, Patrick WH (1992) Production of dinitrogen and nitrous oxide in soil suspensions as affected by redox potential. *Water Air Soil Poll* 61:37–45.
82. Seitzinger S (1988) Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnol Oceanogr* 33:702–724.
83. Tobias CR, Macko SA, Anderson IC, Canuel EA, Harvey JW (2001) Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: A combined groundwater tracer and in situ isotope enrichment study. *Limnol Oceanogr* 46:1977–1989.
84. Xu X, Tian H, Hui D (2008) Convergence in the relationship of CO_2 and N_2O exchanges between soil and atmosphere within terrestrial ecosystems. *Global Change Biol* 14:1651–1660.
85. Mathieu O, *et al.* (2006) Emissions and spatial variability of N_2O, N_2 and nitrous oxide mole fraction at the field scale, revealed with ^{15}N isotopic techniques. *Soil Biol Biochem* 38:941–951.
86. Kammann C, Muller C, Grunhage L, Jager H.-J (2008) Elevated CO_2 stimulates N_2O emissions in permanent grassland. *Soil Biol Biochem* 40: 2194–2205.
87. Phillips RL, Whalen SC, Schlesinger WH (2001) Influence of atmospheric CO_2 enrichment on nitrous oxide flux in a temperate forest ecosystem. *Global Biogeochem Cycles* 15:741–752.
88. Krishnamurthy A, Moore JK, Zender CS, Luo C (2007) Effects of atmospheric inorganic nitrogen deposition on ocean biogeochemistry. *J Geophys Res* 112:G02019.
89. US Geological Survey (2008) *Mineral Commodity Summaries* 2008, pp 118–119.
90. Slomp CP, Van Cappellen P (2004) Nutrient inputs in the coastal ocean through submarine groundwater discharge: Controls and potential impact. *J Hydrol* 295:64–86.
91. Leonte C, Ibanhez JS, Rocha C (2008) Submarine groundwater discharge as a nitrogen source to the Rio Formosa studied with seepage meters. *Biogeochemistry* 88:185–194.

92. Matson PA, Naylor R, Ortiz-Monasterio I (1998) Integration of environmental, agronomic and economic aspects of fertilizer management. *Science* 280:112–116.
93. Beman JM, Arrigo KR, Matson PA (2005) Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature* 434:211–214.
94. Mulholland PJ, *et al.* (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature* 452:202–205.
95. Hefting MM, Bobbink R, de Caluwe H (2003) Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *J Environ Qual* 32:1194–1203.
96. Bernhardt ES, Band LE, Walsh CJ Berke PE (2008) Understanding, managing, and minimizing urban impacts on surface water nitrogen loading. *Ann NY Acad Sci* 1134:61–96.
97. Schlesinger WH (2000) Carbon sequestration in soils: Some cautions amidst optimism. *Agric Ecosyst Envrion* 82:121–127.
98. Fenn ME, *et al.* (1998) Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. *Ecol Applic* 8:706–733.