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SPECIAL ISSUE:
PHYSICS AND
THE ENVIRONMENT



Sunset in Colorado.

(the disturbance of natural systems by people) but about air and water. One can of course study human environmental impacts directly, but eventually one will come upon limits to understanding of the underlying natural systems.

The article about air, by Jeffrey Kiehl (page 36), focuses on clouds, and the article about water, by Robert Toggweiler (page 45), focuses on deep ocean transport. Both articles convey the heroic efforts of natural scientists to get the science straight—to combine modeling and measurement, sampling and intuition. Both articles communicate profound incompleteness. There are islands of well-developed science in a sea of partial understanding. Every ignorance is transient, and no area of certainty is safe from reappraisal.

Fuel cells and flows of materials. The final two articles explore environmentally inspired transformations of the industrial landscape. The article by Sivan Kartha and Patrick Grimes (page 54) addresses an energy conversion device, the fuel cell, that may have the potential to bring the age of combustion to a close by offering improved efficiency and dramatically reduced emissions through electrochemistry. The article by Robert Frosch (page 63) addresses how we might change the industrial system to retain materials much longer before returning them to the environment.

Two vitally important issues are not addressed ade-

quately in this small set of articles. No article deals directly with the immense cleanup required to undo the carelessness of the past (especially in the discarding of persistent organic chemicals, metals and radionuclides); better science and technology are needed urgently to tame the astronomical costs of achieving today's restoration goals. And no article deals directly with the potential of advanced energy systems based on renewables or nuclear fission or nuclear fusion to loosen at least a few of the environmental constraints.

A system called Earth. Within the framework of physics, the Earth is merely a special case. As physicists we forgo some of the cherished generality of our discipline when we confront Earth's particular geochemistry and life forms. Yet in return we encounter marvelous detail in each of the subdisciplines engaged in extracting Earth's secrets. When we venture into new fields our relative lack of specialized knowledge is sometimes even an advantage, allowing us to see important connections and freeing us to challenge prevailing dogmas.

Learning the meaning of Earth's fences is a task that the entire global community must address. The particular skills and habits of mind of physicists are assets sorely needed.

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HUMAN IMPACTS ON THE NITROGEN CYCLE

Fertilizer production and other human activities have more than doubled the global rate of nitrogen fixation since preindustrial times. The resulting imbalance is contributing to ecosystem disruption, ozone depletion, greenhouse effects and other environmental problems.

Ann P. Kinzig and Robert H. Socolow

Humans are greatly perturbing the global nitrogen cycle. Perhaps the best evidence for this perturbation comes from air trapped in layers of quasipermanent ice in the Arctic and the Antarctic. Ice cores taken from these two polar regions give us a 2000-year record of the Earth's atmospheric composition. This record indicates a striking constancy in nitrous oxide concentrations, at approximately 285 parts per billion, for nearly 1500 years. (See figure 2.) Since about 1600 AD, however, nitrous oxide concentrations have been increasing, and the present-day atmospheric burden of this gas is greater than at any other time in the past two millennia. Furthermore, nitrous oxide concentrations continue to increase, currently at a rate of about 0.3% per year.1 These variations indicate that many nitrogen flows are now larger than in preindustrial times, and other evidence suggests that human activity is responsible. (See figure 1.)

These increased flows of nitrogen should be of some concern to humankind. The anthropogenic disruptions of the nitrogen cycle have led to the eutrophication (or excessive fertilization) of coastal waters, characterized by increases in algal blooms and decreases in dissolved oxygen. Urban smog, potentially dangerous nitrate levels in drinking water, stratospheric ozone depletion, greenhouse effects and the leaching of nutrients from soil are further consequences of these increased nitrogen flows.

To understand how to alleviate these effects, we must first understand the nitrogen cycle itself. Nitrogen cycles operate on many spatial and temporal scales, from the fast, microscopic scale of amino acid production and deg-

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radation to the very slow, global tectonic processes whereby nitrogen is subducted below the Earth's crust and later returned to the biosphere by volcanoes. Our discussion will concentrate on global-scale biological nitrogen cycles (excluding tectonic cycling), with particular attention to nitrogen cycling within terrestrial ecosystems.

The global biogeochemical cycle

In its simplest form, the global biogeochemical nitrogen cycle consists of three major reservoirs—the atmosphere, the oceans and terrestrial ecosystems—and the flows among them. (See figure 3.) Nearly all of the energy that drives the flows within the nitrogen cycle ultimately derives from the Sun; photosynthesis converts this radiant energy to chemical energy, which is then stored in living and dead organic matter.

Over 99.9% of the nitrogen in global biogeochemical reservoirs is stored in a form inaccessible to almost all living organisms: diatomic nitrogen either in the atmosphere or in solution in the ocean.2 The strong triple bond of the N=N molecule makes it nearly inert. To most of the biosphere, therefore, the nitrogen in the atmosphere is like the ocean to a thirsty person; amazingly abundant but not quite in the right chemical form. Only a few species of aquatic and terrestrial bacteria and blue-green algae can convert N₂ into ammonium (NH₄+) through the process of biological nitrogen fixation. This biological pathway provides the dominant natural flow of fixed nitrogen on the planet. Lightning, however, provides a nonbiological pathway for nitrogen fixation, oxidizing N2 to nitric oxide (NO), which is rained out as nitrate (NO₃-) within days. Satellites record approximately 100 flashes of lightning per second (or 3 billion flashes per year); each flash on average oxidizes about 1 kilogram of N2 to nitric oxide.³ The product, a fixation rate of 3×10^{12} grams of nitrogen per year [3 Tg(N)/yr], is only a few percent of the rate of biological nitrogen fixation, though nitrogen was fixed exclusively by lightning and in the shock waves



Measurements of emissions of trace gases (such as N₂O and NO) from fields of fertilized sugarcane in Maui, Hawaii, provide us with information on the global nitrogen cycle and how human activity is modifying it. See the box on page 29 for a description of this type of measurement. (Courtesy of Pamela Matson, University of California at Berkeley.) Figure 1

of meteors before the origin of life on this planet.⁴ Humans have approximately doubled the global rate of nitrogen fixation, from the 130 Tg(N)/yr fixed in preindustrial 'times by terrestrial and aquatic bacteria and blue-green algae to the nearly 280 Tg(N)/yr fixed today.^{4,5}

The nitrogen fixed in terrestrial and aquatic ecosystems must somehow be "unfixed," or else the atmosphere would eventually run out of nitrogen (though even at today's rate of fixation it would take 12 million years!). The N_2 molecule is reconstituted and returned to the atmosphere via denitrification. Except for a small amount of pyrodenitrification in forest, grassland and agricultural fires, denitrification is accomplished nearly entirely by another specialized group of bacteria.

The terrestrial cycle

"Opening" any of the three reservoirs presented in figure 3 reveals layer upon layer of internal cycles. We will describe here only the first layer of the terrestrial nitrogen cycle, which has four major reservoirs and four major flows. (See figure 4.) The four reservoirs are plants, soil microorganisms (bacteria and fungi), dead organic matter and inorganic nitrogen (ammonium and nitrate). Plants account for about 94% of the nitrogen in living organisms in terrestrial ecosystems, while microorganisms and animals contain only 4% and 2%, respectively, of the nitrogen in living organisms. Soil invertebrates can play an important role in the nitrogen cycle through their redistribution and comminution (or pulverization) of detritus. Larger animals, however, do not usually play a significant role in nitrogen-cycling processes, except in some agricul-

tural or heavily grazed systems.7

The four major processes that move nitrogen within the terrestrial nitrogen cycle are:

be death of plants and microorganisms

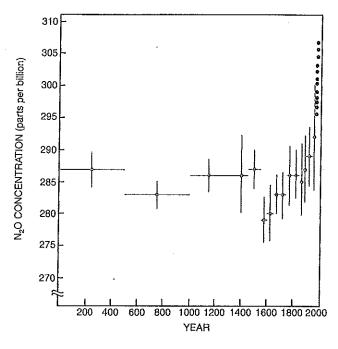
▷ mineralization, or liberation of nitrogen as ammonium, which occurs when microorganisms, in search of energy, attack amino acids and break the bond between a carbon atom and an amino group (NH₂)

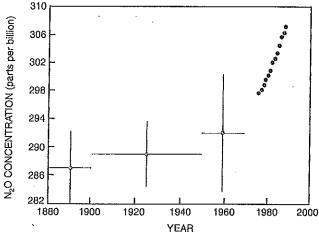
> assimilation, or uptake of inorganic nitrogen by plants > immobilization, or uptake of inorganic nitrogen by microorganisms.

Furthermore, ammonium is oxidized to nitrate (nitrification) within the reservoir of inorganic nitrogen.

In addition to the nitrogen flows within terrestrial ecosystems, there are flows of nitrogen into and out of ecosystems. The flows of nitrogen into an ecosystem include the anthropogenic and natural nitrogen fixation already mentioned. In addition, both wet and dry deposition can deliver nitrogen compounds from the atmosphere to terrestrial ecosystems. Nitrogen can move in surface runoff or in groundwater from one ecosystem to another. Nitrogen can be lost from a system through leaching, denitrification, ammonia volatilization and harvesting of plant material.

The analogy of the thirsty person at the seashore continues within the terrestrial nitrogen cycle, where the vast majority of nitrogen is unavailable to plants for a second reason. Plants require primarily inorganic forms of nitrogen—ammonium and nitrate—for their nutrition, but about 96% of the nitrogen in terrestrial ecosystems is bound up in dead organic matter. (See figure 3.) While





"labile" organic matter decomposes easily and quickly, releasing nitrogen for use by plants and microorganisms, other, "recalcitrant" dead organic matter can sequester nitrogen for hundreds or thousands of years.

Though frequently an insignificant reservoir in terms of quantity of nitrogen stored, soil microorganisms are crucial to the existence and control of the interreservoir flows of nitrogen, including the decomposition, mineralization, nitrogen fixation, nitrification and denitrification processes already discussed. Bacteria and blue-green algae are the most primitive organisms known, with a genesis that dates back to more than 3 billion years ago. They are also the most common living organisms on the planet. The biochemical versatility of populations of soil bacteria and fungi allows for the degradation of all natural organic compounds and many (but not all) man-made organic compounds as well.⁸

The relationship between plants and microorganisms in the soil system is simultaneously competitive and mutualistic. Plants and microorganisms compete for the inorganic nitrogen needed by both communities for biosynthesis and growth. On the other hand, microorganisms and plants are mutually dependent. The carbon that microorganisms need for biosynthesis, growth and energy is fixed by plants in photosynthesis and delivered to soil

Atmospheric concentration of nitrous oxide (N₂O) over the past two millennia as measured directly from the atmosphere (red) and from bubbles trapped in layers of polar ice (blue). Horizontal bars indicate the period that each ice-core value is averaged over; vertical bars indicate 90% confidence limits for those averages. The dip near 1500 could be due to a reduction in microbial activity caused by the "Little Ice Age." Human disruptions of the nitrogen cycle are probably responsible for the steeply increasing levels of N₂O in recent years. (Adapted from M. A. K. Khalil, R. A. Rasmussen, J. Geophys. Res. 97, 14 651, 1992.) Figure 2

microorganisms through root exudates, litter fall and plant death. The nitrogen needed by plants for biosynthesis and growth is liberated by microbially mediated decomposition. Interesting questions arise as to how the evolutionary pressures exerted by this simultaneous competition and mutualism serve to structure ecosystems and to control the flows of nitrogen.⁹

Many terrestrial ecosystems have "closed" nitrogen cycles, in the sense that rates of nitrogen input or loss are small compared with internal rates of nitrogen cycling. Mature and undisturbed ecosystems, in particular, are associated with low losses of nitrogen to groundwater or to the atmosphere. These closed cycles can be attributed to a relative balance between nitrogen supply and plant and microbial nitrogen demand. 10 For example, the ability of plants and microorganisms to take up available nitrogen quickly can reduce the amount of nitrogen available for leaching or denitrification, "closing" the system to nitrogen losses. Managed or disrupted ecosystems, on the other hand, often have "open" nitrogen cycles, with inflows and outflows of nitrogen that are comparable to or even exceed internal cycling rates.2 Fertilization and land clearing, and the consequent disruption of nitrogen production and uptake, are frequently associated with accelerated nitrogen loss due to denitrification and leaching.11

Perturbations due to human activities

The approximate doubling of the rate of nitrogen fixation is probably the most important perturbation of large-scale nitrogen cycling caused by human activity in the industrial age. The increased fixation is largely the result of production of nitrogen fertilizer, whose first step, making NH₃ from N₂, mimics at high temperatures and pressures (typically about 500 °C and 300 atmospheres) what bacteria and blue-green algae accomplish with enzymes at ambient temperature and atmospheric pressure. The rate of nitrogen fixation due to fertilizer production today is approximately 90 Tg(N)/yr. 5

Because nitrogen availability limits crop growth for many combinations of soils and crops, it has been relatively easy to increase crop yields by supplementing natural sources of available nitrogen with synthetic sources, though one gets diminishing returns. An instructive model of a typical US corn field 12 shows a grain yield of 4 metric tons (4×10^6 grams) of corn per hectare in the absence of fertilizer, 7 t/ha when fertilizer is applied at 100 kg(N)/ha, and 8 t/ha when fertilizer is applied at 200 kg(N)/ha. Since corn is about 1.3% nitrogen by weight,

the harvested grain contains 39 of the first 100 kilograms of nitrogen added as fertilizer, but only 13 of the second 100. (In the US, corn production is more commonly reported in bushels; a bushel is 30.3 liters, and there are about 25 kg of corn in a bushel.)

The large-scale use of fertilizer is a relatively recent phenomenon. Night soil, dung and recycled crop wastes have been the traditional means of returning nitrogen to the soil system. Figure 5 shows that the total global use of nitrogen fertilizer in 1960 was only about 10 million metric tons of nitrogen per year, about one-tenth of today's levels. Furthermore, nitrogen fertilizer use is likely to continue to increase so that a growing world population may be fed. 13

The planting of leguminous crops (such as soybean and alfalfa) and the combustion of fossil fuels are the second and third most important human activities that increase nitrogen fixation rates. (See figure 6.) Leguminous crops host symbiotic nitrogen-fixing bacteria in their root nodules. The 250 million hectares of leguminous crops currently cultivated worldwide increase nitrogen fixation over preindustrial levels by about 40 Tg(N)/yr.⁵

Fossil fuel combustion fixes as NO nitrogen that had previously been sequestered either as atmospheric N2 or as fuel-bound nitrogen deep underground. Globally the two processes are about equally important, and they fix nitrogen at a combined rate of about 20 Tg(N)/yr.5 Atmospheric N2 is the dominant source of nitrogen when liquid fuels are burned in gasoline and diesel engines and in aircraft gas turbines, while fuel-bound N is the dominant source of nitrogen in coal combustion at power plants. This difference arises in part because coal is an order of magnitude richer in nitrogen than are refined fuels such as gasoline, diesel and jet fuel (typically 1% versus 0.1% nitrogen by weight). Also, the formation of NO from atmospheric N₂ depends strongly on temperature, and the combustion temperatures in power plant boilers are generally lower than those in internal combustion or gas turbine engines, because there is less of a constraint to burn fuel rapidly.

Consequences of increased nitrogen fixation

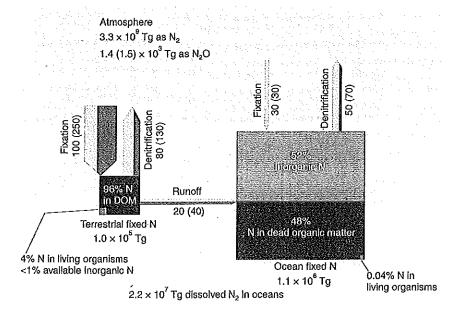
The consequences of increased nitrogen fixation are manifold. They include disruptions of the nitrogen budgets of natural and managed ecosystems, leaching of nutrients from soils, effects on stratospheric ozone chemistry, al-

terations in the greenhouse effect and direct impacts on human health.

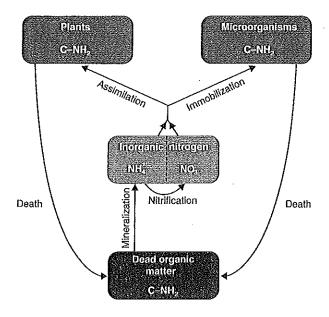
Nitrogen budgets of ecosystems. Nitrogen fixed by human activities disperses widely to unintended targets—sometimes up to hundreds of kilometers downwind or downstream. For example, nitrogen fixed during the combustion of fossil fuels and lofted into the atmosphere causes both wet and dry deposition of nitrate and nitric acid (HNO₃). Similarly, application of fertilizer based on urea (CO(NH₂)₂) or ammonium (NH₄⁺) results in the volatilization of ammonium (NH₃), the conversion of ammonia to ammonium in the atmosphere and the deposition of ammonium in precipitation. 14

Since many terrestrial ecosystems are nitrogen limited, nitrogen deposition may initially increase an ecosystem's net primary productivity. Inevitably, however, some species will assimilate the additional nitrogen more easily than others, causing differential growth of species and altering the species composition of the community. Altered species composition may reduce ecosystem biodiversity or otherwise change ecosystem function. Ecosystem productivity determines the rate at which the Earth's populations can harvest the goods supplied by ecosystems, such as food, fodder, fuel and fiber. In addition to supplying harvestable material resources, diverse and healthy ecosystems can reduce soil erosion from surface runoff, regulate local climate and help prevent outbreaks of pests and plant diseases. Many scientists recognize the urgency of characterizing the precise effects of anthropogenic disruptions on the flows of these (and many other) goods and services provided by ecosystems and collections of ecosystems. In particular, society needs a clearer view of the degree to which particular goods and services are unique to specific ecosystems or redundant across many different types of ecosystems.

A back-of-the-envelope calculation gives some indication of a relevant time scale for the terrestrial nitrogen deposition problem. Assuming that most of the terrestrially deposited inorganic nitrogen is either taken up by living organisms or stored in the most labile part (roughly 15%) of the dead organic matter pool, nitrogen stocks totaling approximately 20 000 Tg(N) are being affected by anthropogenic fixation. Figure 3 gives the net increase in nitrogen deposition on land (fixation minus runoff minus denitrification) as about 80 Tg(N)/yr. Dividing the



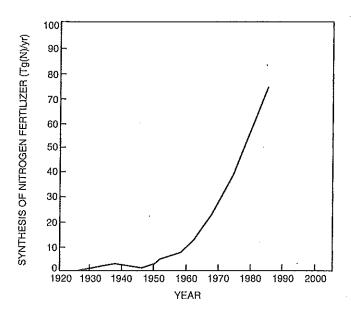
Global biogeochemical nitrogen cycle. Stocks of nitrogen are given in teragrams (Tg or 1012 grams); flows are given in Tg(N)/yr. Yellow portions of arrows indicate preindustrial flows; full arrows (and numbers in parentheses) indicate the current flows. Very little inorganic nitrogen (ammonium and nitrate) is available in terrestrial ecosystems because nitrogen transformations and uptake by plants and microbes are rapid. (Additional terrestrial stocks of inorganic nitrogen unavailable to living organisms, and not represented here, may be sequestered in the soil or held on the clay matrix.) Oceanic stocks of nitrogen include nitrogen stored in the deep oceans. Terrestrial stock estimates are taken from ref. 4, oceanic stock estimates from ref. 6, and flow estimates from ref. 5. Estimates of some global nitrogen stocks and flows can vary by as much as an order of magnitude.²³ Figure 3



stock by this flow yields 250 years as a rough estimate of the time required to double the stock of living and labile terrestrial nitrogen at the current rates of human perturbation of the nitrogen cycle. The analogous ratio for the greenhouse effect (stock of atmospheric carbon dioxide divided by the current annual increase in the stock) is similar—also roughly 200 years.

Nitrogen fixed or mobilized by human activities can also affect the nitrogen budgets of aquatic ecosystems. One result has been the eutrophication of coastal waters. (Productivity in freshwater ecosystems tends to be limited by the availability of phosphorus, while nitrogen frequently limits productivity in saltwater ecosystems.) The Baltic and North Seas, the western Mediterranean and the Atlantic seaboard (including the Narragansett and Chesapeake Bays) have all been affected by nitrogen-induced eutrophication. The increased algal blooms and decreased oxygen supplies in eutrophic waters can have detrimental effects on fisheries and other aquatic populations.

Leaching of cations from soils. The surfaces of clay minerals and amorphous organic materials in the soil



Terrestrial nitrogen cycle in simplified form, with the major chemical form indicated for each of the reservoirs. The global terrestrial flows via mineralization, total uptake by plants and microorganisms, and total death are each approximately 1200 Tg(N) per year. These flows occur within the terrestrial box of figure 3. Figure 4

are negatively charged, and nutrient cations such as Ca²⁺, Mg²⁺, K⁺ and Na⁺ are held on this clay-organic matrix. These nutrient cations are gradually displaced from the soil matrix by hydrogen ions and thus become available for assimilation by plants. This cation-exchange capacity is a critical feature of the soil system: The retention of nutrients on the surface of soil particles prevents their being quickly leached away, beyond the reach of plant roots. The deposition of nitric acid on soil ecosystems, however, can increase the concentrations of hydrogen ions in soils (leading to acidic soils), which in turn can lead to mobilization of nutrients in excess of plant needs. The end result is that cation nutrients are leached away and lost from the system.

Acidification of soils can also mobilize aluminum and other metallic cations. Increased aluminum mobilization in terrestrial watersheds can elevate aquatic aluminum concentrations, killing fish and amphibians. Elevated aluminum concentrations in soil may be contributing to the *Waldsterben* (forest death) that has decimated some forests in central Europe. The mobilization of metals such as lead, cadmium, arsenic and mercury may cause similar toxicity problems.

Stratospheric ozone. A small but important subcycle of the global nitrogen cycle involves the flow of nitrous oxide (N_2O) from soils or oceans to the atmosphere. Nitrous oxide is produced as a by-product of nitrification and denitrification in soils and oceans. There are no known tropospheric chemical loss processes for N_2O ; instead, N_2O migrates to the stratosphere, where it is primarily destroyed by photodissociation into O atoms and N_2 . Approximately 10% of the N_2O in the stratosphere, however, is destroyed by activated atomic oxygen, yielding either nitric oxide (NO) or N_2 and O_2 . ¹⁶

The production of NO is important in stratospheric ozone (O_3) chemistry, since NO can catalytically destroy ozone via the following reactions:

$$\begin{aligned} NO + O_3 &\to NO_2 + O_2 \\ NO_2 + O &\to NO + O_2 \end{aligned}$$
 Net:
$$O + O_3 &\to 2O_2$$

These cycles involving NO and NO₂ (collectively known as NO₂), and similar cycles involving chlorine, bromine and OH radicals (and leading to the same net reaction),

Global nitrogen fertilizer production from 1920 to 1985. The cumulative production over this 65-year period is 1000 Tg, with half of that occurring between 1976 and 1985. (Adapted from V. Smil, in *The Earth as Transformed by Human Action, B. L. Turner II, W. C. Clark, R. W. Kates, J. F. Richards, J. T. Mathews, W. B. Meyer, eds., Cambridge U. P., Cambridge, England, 1991, p. 423.) Figure 5*

are among the principal reactions governing stratospheric ozone concentrations. 16,17 Ozone in the stratosphere absorbs incoming ultraviolet-B radiation (0.23–0.32 microns). DNA and proteins are sensitive to disruption at those

wavelengths.

Attempts to balance the global nitrous oxide budget have not yet been successful, and our understanding of the cause of the imbalance is inadequate. Nevertheless it is believed that fertilizer application and changes in land use are contributing to the observed increase in atmospheric nitrous oxide concentrations through their effects on global nitrification and denitrification rates. ¹¹ Current anthropogenically induced ozone losses, however, are attributable mostly to long-lived industrial chlorine-and bromine-containing compounds, especially the chlorofluorocarbons.

The impact of fertilizer use on stratospheric ozone via increased atmospheric N_2O concentrations should be compared with the similar impact of direct injection of NO into the stratosphere. The latter receives immense attention today in the aerospace community, which designs supersonic and hypersonic aircraft and their engines to meet anticipated regulatory constraints on NO emissions

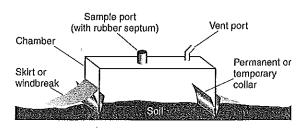
in the stratosphere and upper troposphere.

Greenhouse effects. Nitrous oxide is also of interest in greenhouse policy. The 150-year mean life of $N_2\mathrm{O}$ in the atmosphere is far longer than the mean life of any other oxide of nitrogen. The combination of its atmospheric concentration and its particular frequencies of absorption of infrared radiation make nitrous oxide an important contributor (along with water vapor, carbon dioxide, methane and ozone) to the natural greenhouse effect—the effect that makes life possible by raising the Earth's average surface temperature from about -18 °C to +15 °C. The surface temperature increases because gases in the atmosphere trap infrared radiation emitted by the Earth and reradiate it back down to the surface. Human activities have increased the atmospheric budgets of many greenhouse gases and have consequently increased this downward infrared radiation; increases in nitrous oxide concentrations have contributed 5% of this increase in downward infrared radiation.1

Anthropogenic nitrogen fixation has additional greenhouse impacts as well. In some ecosystems, ammonium deposition has been shown to reduce methane (CH₄) consumption by soils, perhaps due to the inability of certain enzymes to distinguish between NH4+ and CH4.18 This decrease in soil consumption may contribute to the observed increase in methane in the atmosphere, though the global significance of this mechanism is still unknown. In addition, the increased availability of nitrogen in ecosystems due to human activities may be increasing the storage of carbon in plants and soils via nitrogen fertilization. Because carbon and nitrogen compounds are both required for the synthesis of biological material and both are released by the decomposition of organic material, the carbon and nitrogen cycles are tightly linked. Increases in available inorganic nitrogen in ecosystems may stimulate plant and microbial growth and increase the storage of carbon and nitrogen in dead organic matter.¹⁹ The magnitude of the increased carbon storage due to nitrogen fertilization will depend on the average C:N ratio of the reservoirs undergoing accretion. (See figure 7.)

In the absence of other perturbations or ecosystem responses, this effect of nitrogen fertilization would decrease the greenhouse effect by transferring carbon from the atmosphere to the biosphere. Anthropogenic nitrogen fertilization could be sequestering in terrestrial ecosystems some of the "missing" global carbon^{5,20}—the as yet unidentified flow of carbon out of the atmosphere and into

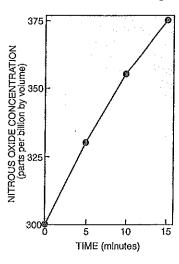
Measuring N₂O Fluxes



In the closed-chamber method for measuring fluxes of nitrous oxide (and other trace gases) a chamber is placed over the soil surface (as shown in figure 1). The efflux of gas from the soil is then proportional to the increase in gas concentration within the chamber over time—the slope $\Delta c/\Delta t$ of the line in a plot like that below. Gas samples are typically extracted from the sample port with a syringe for later analysis with, for example, a gas chromatograph. The gas in the chamber must be well mixed, either passively by diffusion (in small chambers) or actively with fans (in large chambers).

The data generally depart from linearity for reasons that experimenters identify and allow for. For example, as gas concentrations build up in the chamber, the flux from soil to air decreases due to the decreased concentration gradi-

ent. Also, surface winds may cause pressure fluctuations and turbulence around the chamber, resulting in the leakage of gas out of the bottom of the chamber. A windbreak can reduce this effect. The chamber itself can affect the fluxes by changing 'evaporation rates and surface temperatures. Consequently the chamber should remain on the sur-



face for the shortest possible time, although experimental runs must be long enough to detect the changes in gas concentration. In a typical N_2O experiment samples are extracted every 5 minutes for 20 minutes.

terrestrial or oceanic systems that seems to be required to balance the atmospheric CO₂ budget. A fully convincing global carbon budget, however, awaits additional research.

Direct impacts on human health. High concentrations of fixed nitrogen in both air and water have direct health impacts. The notorious photochemical smog that bedevils many of the world's cities today requires nitrogen oxides as precursors. Of all the instances of nitrogen fixation, probably none has received as much regulatory attention as nitrogen oxide emissions into urban air. Nitrate concentrations in water are also regulated, however, because while nitrates themselves are not particularly toxic, certain bacteria residing in vertebrate digestive tracts can convert the relatively benign nitrate (NO₃⁻) into

Annual nitrogen fixation due to human activities alone (right) now approximately equals the estimated preindustrial fixation rate (left). Figure 6

highly toxic nitrite (NO₂-). Human infants and farm animals are particularly likely to house such bacteria.

Reducing anthropogenic nitrogen fixation

In the framework of global and regional environmental change, anthropogenic disruptions of the nitrogen cycle may be as significant as anthropogenic disruptions of the carbon cycle—even though the nitrogen cycle has received far less attention. In particular, fertilizer use and legume production should perhaps be of as much concern to humans as fossil fuel use and deforestation, the principal

agents of disruption of the global carbon cycle.

Because strategies for reducing human impacts on the carbon cycle have been under development for several decades, looking to these strategies for guidance in addressing potentially harmful modifications to the nitrogen cycle seems a reasonable first step. In particular, there are likely to be many cost-effective strategies to achieve efficient use of nitrogen in food production, distribution and consumption that are analogs of the strategies for energy efficiency (effectively, efficient use of carbon) currently being developed and tested around the world.

Some examples of possible innovations in the production of food and fodder include:

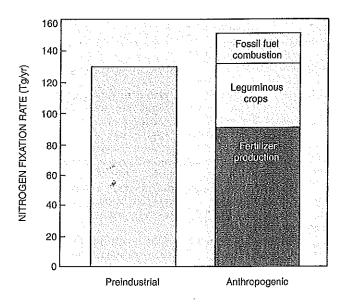
> new crop combinations and improved soil management to increase the yield at a given level of fertilizer use

> improved mechanisms and strategies for retaining natural and synthetic nitrogen in the soil system for subsequent availability to plants

bioengineered crops such as nitrogen-fixing corn.

Much can be achieved through wise management practices. For instance, many farmers use legumes in a crop rotation scheme, leaving the legumes in place and tilling them under, or returning the waste from cash-crop legumes. This increases nitrogen availability in the soil and also increases the soil's organic content, which can improve its water-holding capacity. Alternating a shallow-root crop with a more deeply rooted crop can reduce losses of nitrogen: The deeply rooted crop can assimilate nitrogen that has leached to lower layers of the soil system, and this nitrogen can then be returned to the surface soil in crop wastes. 21 As a complement to such technical innovations, a vigorous regime of regulations and market incentives (taxes, subsidies, tradable nitrogen-fixation permits and so on) would be appropriate.

Innovations in the distribution of food and fodder would include systems for recycling the nitrogen in wastes from feedlots and from sites of centralized food processing and consumption, as well as systems to reduce preconsumer spoilage (a particular problem in developing countries). Innovations in consumption (that is, innovations in end-use nitrogen efficiency) would include changes in the diets of people and domesticated animals. In particular, the diets of prosperous individuals could shift toward



a more protein-efficient diet that substitutes grain for (Production of 1 kilogram of beef or chicken in the US in recent years has required feed equivalent to about 14 or 2.5 kilograms of corn, respectively.22)

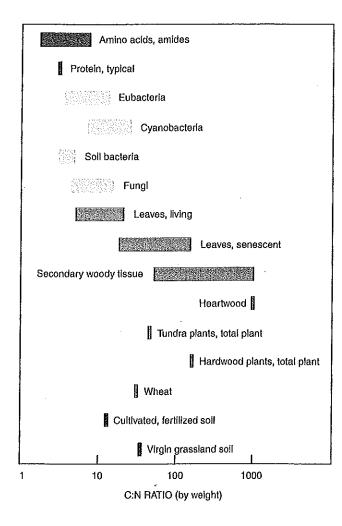
Nitrogen management, of course, also involves crops grown for purposes other than food and fodder, including crops for fiber, paper, timber and energy. For each of these crops a sustainable nitrogen management strategy would include mechanisms for leaving in place or recovering and reapplying the nitrogen in crop residues.

Public policy for agriculture today does not reflect the priorities suggested in this article. Although minimizing soil erosion and the consequent transport of nitrogen has been a historical target of agricultural policy, fertilizer production and use-the most important source of disruption of the nitrogen cycle—awaits creative policymaking.

The challenges ahead

Throughout recorded history, our species has derived from the biosphere not only the goods and services necessary for physical survival but also aesthetic pleasure, creative inspiration and spiritual renewal. Yet our growing population and increasing reliance on resource-consumptive technologies have created the potential for unprecedented anthropogenic disruption of the biosphere. Protection of the biosphere therefore becomes a priority. But we cannot protect what we do not understand. Policies and practices designed to protect the biosphere against the grosser insults of human activity must rest on a deep understanding of environmental sciences across a wide range of spatial and temporal scales.

The nitrogen cycle is emerging as an important focus of environmental science. It has become clear that human actions are significantly disturbing the stocks and flows of nitrogen. It is not yet possible, however, to assess accurately the significance for human beings of these disturbances of nitrogen cycling, either in absolute terms or relative to the disturbance of the global carbon cycle. The disturbance of the carbon cycle is probably leading to global warming, and the disturbance of the nitrogen cycle is probably leading to global fertilization. At an earlier time of anthropocentricity and ecological innocence, one might have supposed that warmer is better and more fertile is better too. Ecology teaches otherwise. Earth's ecosystems have evolved and adapted to past changes in environmental conditions, and will continue to evolve and adapt. But the changes being created by



humans today may be too rapid for ecosystem adaptation to outpace ecosystem damage on time scales relevant to humans. As we come to understand anthropogenic disruptions of the biosphere more deeply, we may find the nitrogen cycle sharing center stage as an agent of long-term environmental change.

Nitrogen cycles are scarcely part of current public discourse. The global carbon cycle, by contrast, is better known to the public because of its association with the greenhouse effect and deforestation. Fossil fuel use has increasingly been the subject of innovations in technology and policy designed to reduce environmental impacts on the global carbon cycle. We may be well advised to seek analogous innovations for fertilizer use if we are to succeed in the grand task of conducting the human enterprise within environmental constraints.

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References

 Intergovernmental Panel on Climate Change, World Meteorological Organization and the United Nations Environment Programme, Climate Change: The IPCC Scientific Assessment, J. T. Houghton, G. J. Jenkins, J. J. Ephraums, eds., Cambridge U. P., Cambridge, England (1990). Ratio of carbon to nitrogen in various terrestrial materials. These ratios are often used to estimate global stocks and flows of nitrogen from the somewhat better known values for carbon. Horizontal bars indicate ranges of estimates; vertical bars indicate single-value estimates for which ranges were not available. Plant selection (breeding, species choice) can alter the C:N ratios for the vegetation in an ecosystem, affecting total carbon storage per unit of available nitrogen. C:N ratios serve as useful constraints and indicators in the development of coupled models of C and N cycles. (Data from refs. 7, 8, 19 and 24.) Figure 7

- T. Rosswall, in Some Perspectives of the Major Biogeochemical Cycles, G. E. Likens, ed., Wiley, New York (1981), p. 25.
- M. G. Lawrence, W. L. Chameides, P. S. Kasibhatla, H. Levy II, W. Moxim, "Lightning and Atmospheric Chemistry: The Rate of Atmospheric NO Production," to appear in *Handbook* of Atmospheric Electrodynamics, vol. 1, CRC Press, Boca Raton, Fla.
- 4. W. H. Schlesinger, Biogeochemistry: An Analysis of Global Change, Academic, San Diego (1991).
- R. Ayres, W. Schlesinger, R. Socolow, in *Industrial Ecology and Global Change*, R. Socolow, C. Andrews, F. Berkhout, V. Thomas, eds., Cambridge U. P., Cambridge, England (1994), p. 121.
- R. Söderlund, T. Rosswall, in The Natural Environment and the Biogeochemical Cycles, O. Hutzinger, ed., Springer-Verlag, New York (1982), p. 61.
- J. Sprent, The Ecology of the Nitrogen Cycle, Cambridge U. P., Cambridge, England (1987).
- 8. E. A. Paul, F. E. Clark, Soil Microbiology and Biochemistry, Academic, San Diego (1989).
- J. Harte, A. P. Kinzig, Am. Naturalist 141, 829 (1993). A. P. Kinzig, "Mutualism and Competition Between Plants and Microorganisms: Implications for Nitrogen Allocation in Terrestrial Ecosystems," PhD dissertation, U. of Calif., Berkeley (1994).
- P. M. Vitousek, W. A. Reiners, BioScience 25, 361 (1975).
 P. M. Vitousek, L. R. Walker, in Colonization, Succession, and Stability, A. J. Gray, M. J. Crawley, P. J. Edwards, eds., Blackwell Scientific, Oxford (1986), p. 207.
- J. D. Aber, J. M. Melillo, Terrestrial Ecosystems, Saunders, Philadelphia (1991). P. M. Vitousek, P. A. Matson, in Biogeochemistry of Global Change, R. S. Oremland, ed., Chapman and Hall, New York (1991), p. 193.
- Natl. Res. Council, Soil and Water Quality: An Agenda for Agriculture, Natl. Acad. P., Washington, D. C. (1993).
- K. M. Constant, W. F. Sheldrick, World Nitrogen Survey, World Bank, Washington, D. C. (1992).
- W. H. Schlesinger, A. E. Hartley, Biogeochemistry 15, 191 (1992).
- 15. H. W. Paerl, Can. J. Fisheries Aquatic Sci. 50, 2254 (1993).
- J. P. D. Abbatt, M. J. Molina, Annu. Rev. Energy Environment 18, 1 (1993).
- G. Brasseur, S. Solomon, Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere, Reidel, Dordrecht, The Netherlands (1984).
- P. A. Steudler, R. D. Bowden, J. M. Melillo, J. D. Aber, Nature 341, 314 (1989).
- E. B. Rastetter, M. G. Ryan, G. R. Shaver, J. M. Melillo, K. J. Nadelhoffer, J. E. Hobbie, J. D. Aber, Tree Physiol. 9, 101 (1991).
- D. W. Schindler, S. E. Bayley, Global Biogeochem. Cycles 7, 717 (1993).
- C. R. Carroll, J. H. Vandermeer, P. M. Rosset, Agroecology, McGraw-Hill, New York (1990).
- US Dept. of Agriculture, Agricultural Statistics 1989, US Govt. Printing Office, Washington, D. C. (1989).
- See, for instance, D. A. Jaffe, in Global Biogeochemical Cycles, S. S. Butcher, R. J. Charlson, G. H. Orians, G. V. Wolfe, eds., Academic, San Diego (1992), p. 263.
- B. N. Richards, The Microbiology of Terrestrial Ecosystems, Longman Scientific and Technical, Harlow, England (1987).