

Industrial Ecology and Global Change

Edited by

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Preface

A Novel Dialog

The 1992 Global Change Institute on Industrial Ecology and Global Change was held in Snowmass, Colorado, from July 19 to 31, 1992. Its principal written product is this book.

The institute was designed to encourage some of the first organized discussions between two communities: (1) natural scientists studying global change, and (2) a community that has focused on technological and policy responses to environmental constraints and on the underlying forces driving human activity. In the jargon of global change researchers, but probably nowhere else, this second community is called the "human dimensions" community.

The priority of the natural scientists studying global change is to understand the earth and its ecosystems—to get the science straight. For the past two decades these scientists have been knitting together previously independent disciplines, such as oceanography, atmospheric chemistry, and ecology, while consciously postponing reaching out beyond natural science.

During the same period, a human dimensions community has been forming, which takes as its starting point whatever current level of imperfect understanding of environmental science is available. This community has been trying to anticipate future levels of human impact on the environment—drawing on historical and economic studies of resource use in industry and agriculture, and on studies of contemporary environment-society interactions in all parts of the world. The human dimensions community has also been designing options for environmentally responsive technology and social organization, and they have been exploring the factors that determine whether such options will be successfully pursued.

The U.S. government agencies who have long sponsored the global change research of the natural scientists were the sponsors of the institute. As a member of the human dimensions community, working for many years on energy efficiency as a response to environmental constraints, I was asked to organize the institute. My charge was to create a dialog between the two communities.

There was indeed a gap to be bridged. The two communities scarcely knew one another and were unaware of many of the ways in which they need one another. The institute did much to educate the two communities about the character of their

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interdependence, and the opportunities for collaboration. Entering the institute, *industrial ecology* was a phrase looking for a mission; emerging from the institute, *industrial ecology* had the mission of blending the complementary kinds of understanding provided by these two communities.

Models of the earth system rooted exclusively in the natural sciences are adequate for capturing the essentials of preindustrial times, when the environmental consequences of human activity were largely local. Such modeling becomes progressively inadequate as one moves to a description of today's earth and then to projections into the future. For a time, many global natural scientists believed that the human dimensions community could provide deterministic submodels of the future course of human activity for direct incorporation into earth-system modeling. While no such naiveté about forecasting was in evidence at Snowmass, the natural scientists attending nonetheless had been unaware of the vigor of the analysis undergirding environment-driven scenarios. They were introduced to a wide-ranging effort on the part of the human dimensions community over the past two decades to explore new technologies, policies, and patterns of economic development. This body of work has direct consequences for the design of robust global modeling and monitoring. It also suggests a new task for global environmental science: to provide a deeper understanding of the environmental consequences of alternative futures.

In turn, the human dimensions community drew its own lessons from the institute. We became more aware of the profound incompleteness of environmental science when posed in the framework of societal problem-solving. In tracking a long-lived organic molecule or metal atom through the environment (say, from atmospheric emission, to soil deposition, to uptake by a plant, to incorporation into the human body, to health effect), there are islands of well-developed science in a sea of partial understanding. Gas exchange at the earth's surface, crucial to the nitrogen cycle and ecosystem function, is determined by processes involving soil bacteria that are poorly understood. An understanding of the impacts of chemicals on the health of almost all organisms other than humans scarcely exists.

Moreover, every ignorance is transient, and no area of certainty is safe from reappraisal. Important discoveries in environmental science are made almost every week.

One message of this incompleteness for the human dimensions community, it seems to me, is to become intimately involved with environmental natural science as a living and breathing enterprise. The better we know our way around, the more we will become aware of new puzzles and new discoveries, and the more we can expect help from the natural scientists in refining our previous prescriptions.

A second message is that whenever asked for advice by political and industrial leaders, the human dimensions community should not recommend strategies that create massive, difficult-to-reverse commitments to specific technologies and policies. Broadly based approaches, and parallel development of preliminary ideas, are preferable.

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A Little History

Institute Number Five

The 1992 Global Change Institute was the fifth in a sequence, and its scope is related to its place in that sequence. The first three institutes dealt with issues in which the role of human beings was secondary. Early on, the fourth institute (1991) and ours were planned as a pair, with the idea that between them they would address the principal global environmental impacts arising from human activity.¹

The global change natural scientists called for two efforts: "land use/cover" (in 1991) and "industrial metabolism" (in 1992). We will say more about the phrase, "industrial metabolism," in a moment. First, what about the dichotomy expressed by two (and only two) "human dimensions" institutes?

From one viewpoint, this pairing was intended to divide human activities into *rural* and *urban*. From another, it was intended to distinguish two classes of effects of human activity on climate: effects on *surface reflectivity (albedo)* and effects on *atmospheric gas concentrations*. From a third, *physical* modifications of the landscape vs. all *chemical* effects. These dichotomies are not congruent: nitrogen fertilizer is rural and chemical, and it affects both albedo and gas concentrations.

The 1991 Global Change Institute, Global Land-Use/Cover Change, focused on agriculture, forestry, and settlement. It dealt with erosion, desertification, and salinization of lands as a result of irrigation. Its core discipline was geography.

Because of the priority of servicing global environmental science, important human relationships to the natural environment were not caught in the nets of either of the two institutes. Neither institute did justice to human health and human sensibilities. Neither institute made room for informed discussion of lung function, or carcinogenesis, or sterility, or epidemics. Nor did either institute consider in much depth the sorts of aesthetic insults that arise from the degraded transparency of mountain air or from the polyethylene bottle discarded years before at the side of a trail.

Industrial Metabolism and Industrial Ecology

Both "industrial ecology" and "industrial metabolism" are phrases associated with important antecedents of our institute. One research program, carried out under the banner of *industrial metabolism*, has viewed the industrial system as a single entity and has explored its system-wide transformations of materials. Its leaders, Robert Ayres and William Stigliani, both participants in our institute, have been conducting seminal studies of materials flows through the world's industrial system. They have focused on the long-term habitability of the planet, with a corresponding emphasis on documenting the routes to toxification of the global environment.

¹ The sixth Global Change Institute (1993) returned to a pure-science theme, the global carbon cycle.

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A parallel research program, under the banner of *industrial ecology*, launched by Brad Allenby, Robert Frosch, Tom Graedel, and Kumar Patel (Graedel and Patel were institute participants) has emphasized the industrial firm as agent of change, and has located its analysis at the level of specific industries. Of special interest are the relationships among industries, and the opportunities for the wastes of one industry to become useful inputs to a second.

The word "industrial" has had different meanings for the two groups. "Industrial," in the phrase "industrial metabolism," refers to the totality of civilization. In the phrase, "industrial ecology," it refers, more narrowly, to the activities of specific industrial producers. Industrial metabolism addresses transportation; industrial ecology addresses the automobile, aircraft, petroleum, tire, battery, and other transport industries.

Our institute strove to weave together both strands of research and to demonstrate their enhanced value in combination. It was my decision not to invent a third phrase, but rather to choose one of the two and to set out deliberately to expand its meaning. I chose "ecology" over "metabolism." I am gambling that the phrase "industrial ecology" can be transformed by our exercise, and others, to carry the larger meaning given expression in this book. "Industrial ecology" is intended to mean both the interaction of global industrial civilization with the natural environment and the aggregate of opportunities for individual industries to transform their relationships with the natural environment. It is intended to embrace all industrial activity, specifically including agriculture; both production and consumption; and national economies at all levels of industrialization.

The Snowmass Institute

The most demanding rule of the institute was that everyone had to be in attendance for the full two weeks. In combination with the remoteness of the site, this rule made us feel and act like a sequestered jury. The site was beautiful and hikeable. We lost track of much of the outside world.

None of the 50 participants knew even one-half of the others before the institute began. More important, none of us was fluent in even one-half of the disciplinary languages. Deliberate confrontation was the organizing principle behind assignments to subgroups and assignments as official "reader" of another's paper.

The Institute and This Book

Interchanges among institute participants during and after the Global Change Institute have shaped all of the chapters of this book. Many of the chapters are based on drafts that were revised at the institute. Several multiauthored chapters are the result of collaborations initiated there. A few chapters were written by participants after the institute, at the urging of the editors, to close some gaps.

The institute was structured around three Working Groups:

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- I. Grand Nutrient Cycles
- II. Exotic Intrusions
- III. Implementation of Industrial Ecology.

The five sections of this book reflect this structure: Section 1 contains five cross-cutting papers; Sections 2 and 3 contain the papers exploring the topics addressed in Working Groups I and II, respectively; and Sections 4 and 5 address, respectively, the implications of the themes of Working Group III for industrial firms and for governments.

An interesting ecological distinction is inherent in the purviews of Working Groups I and II. Working Group I explored human intrusions into the grand biogeochemical cycles (carbon, nitrogen, phosphorus, sulfur). Working Group II gave its attention to those human intrusions that are largely unfamiliar ("exotic," "xenobiotic") from the point of view of the ecosystem (such as "toxic" chemicals, metals, and radioactivity). The distinction is analogous to the distinction between visiting a country where you speak the language and where you don't: we and the plants both speak organic carbon, but only we speak polychlorinated biphenyl. The two categories of involvement of human activity with the earth as a whole are qualitatively different.

Working Group III worked off the axis defined by the first two. It adopted an action orientation towards industrial ecology, while searching for general principles. It explicitly considered current industrial practices and productive strategies for change.

Throughout the second week at Snowmass, the Working Groups concentrated on preparing written reports. Little of this writing is found verbatim in this book. The reports were valiant efforts, full of interesting ideas. Many of these ideas are found in this book in the form of supplementary papers, revised versions of papers, and introductions to sections. But some of the efforts have been left on the cutting room floor, when the editors judged that the work remaining to be done was beyond our powers.

Statement of Goals

I conclude with the seven goals in front of us during the institute:

1. To add coherence to the thinking about industrial ecology, by clarifying what is more and less important and what is well and poorly understood. In short, to launch a field.
2. To inform and give guidance to those activities currently under way or being planned, in industry and elsewhere, designed to reduce the adverse environmental impacts of industrial activities.
3. To locate industrial ecology within broader research fields, in particular, within global change research.
4. To help creative individuals find productive research strategies in industrial ecology.

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5. To foster interactions that lead to joint research.
6. To lower thresholds in key federal agencies and corporations for the financial support of research in industrial ecology.
7. To produce a written record, in the form of a book, that is worth reading and keeping around.

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Human Impacts on the Carbon and Nitrogen Cycles

Robert U. Ayres, William H. Schlesinger, and Robert H. Socolow

Abstract

Human activities are substantially modifying the global carbon and nitrogen cycles. The global carbon cycle is being modified principally by the burning of fossil fuels, and also by deforestation; these activities are increasing the carbon dioxide concentration of the atmosphere and changing global climate. The nitrogen cycle is being modified principally by the production of nitrogen fertilizer, and also by the planting of legumes and the combustion of fossil fuels; these activities are more than doubling the rate of fixation of nitrogen and contributing to the unbalanced productivity and acidification of ecosystems. With the aim of quantifying these disruptions, the principal flows among reservoirs in preindustrial times and today are estimated in the framework of simplified models. The methane sub-cycle of the carbon cycle and the nitrous oxide subcycle of the nitrogen cycle are also discussed from this viewpoint.

The Grand Cycles

Carbon (C), nitrogen (N), sulfur (S), and phosphorus (P), the important biochemical building blocks of life, find their way to plants and animals, thanks to the interplay of biological and geochemical processes. Each of the four elements moves from one chemical state to another and from one physical location to another on the earth's surface in a closed loop, or "cycle." In view of their central role in life on this planet, the four cycles are here termed the "grand nutrient cycles."

The cycles are powered by solar energy, in conjunction with the earth's gravity and geothermal energy. The nutrients flow among "reservoirs." The reservoirs of interest are life forms (living and dead plants and animals), the soil, the oceans and other water bodies, the atmosphere, and rocks. The quantity of nutrient stored in a reservoir (the reservoir's "stock" of nutrient) changes whenever the total nutrient flows in and out of the reservoir are not equal.

In the grand nutrient cycles, one may identify three classes of reservoirs, shown in Figure 1:

The Grand Cycles

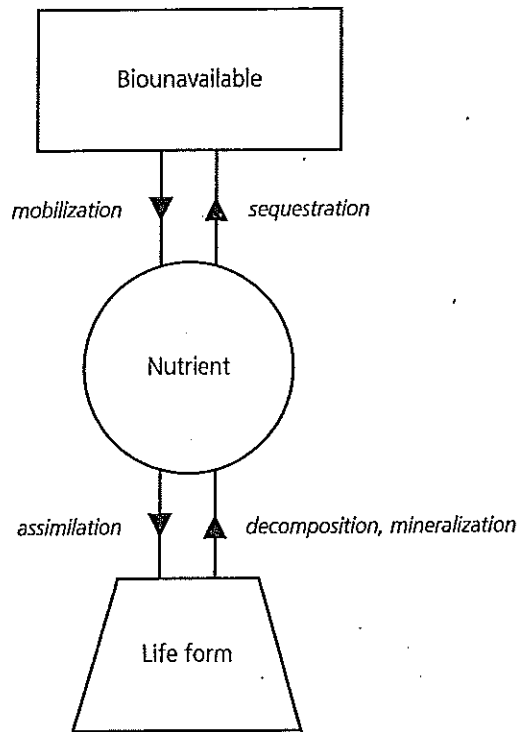


Figure 1. Basic elements of a grand nutrient cycle, presented as two subcycles. In the upper subcycle, the element is exchanged between a bio-unavailable reservoir and a nutrient reservoir. In the lower subcycle, the element is exchanged between a nutrient reservoir and a reservoir of life forms—living and dead plants and animals. Not shown, but possible, is the direct flow of an element from a life form to a bio-unavailable reservoir.

- (1) *Bio-unavailable reservoirs*, which store nutrients in forms that cannot be incorporated into plant or animal life without first being transformed chemically to some intermediate. (In the figures in this chapter, these reservoirs are shown as rectangles.)
- (2) *Nutrient reservoirs*, which store nutrients in forms that are bioavailable, i.e., forms where the nutrients can be incorporated directly into plants without a chemical intermediate. (In the figures in this chapter, these reservoirs are shown as circles.)
- (3) *Reservoirs of life forms*, plants and animals, either alive or dead. (In the figures in this chapter, these reservoirs are trapezoids, reflective of the trophic levels of a food chain.)

Some important vocabulary is presented in Figure 1. An element passes from a bio-unavailable reservoir to a nutrient reservoir by *mobilization*; an example is the transformation of atmospheric nitrogen by nitrogen-fixing bacteria. An element passes in the reverse direction, from a nutrient reservoir to a bio-unavailable one by *sequestration*; an example is the return of nitrogen to the atmosphere from the

nutrient reservoir by the action of denitrifying bacteria¹. Transport of an element from a nutrient reservoir to plant or animal life is called *assimilation*; a special case, applying to carbon, is photosynthesis. Transport of the nutrients in plant and animal matter back to the nutrient reservoirs takes various forms, including (in the case of carbon) *decomposition* of plant matter and (in the case of nitrogen) *mineralization*.

To focus the discussion in this chapter, we will explore only the carbon and nitrogen cycles. (The sulfur and phosphorus cycles raise few new conceptual issues.) The chemical forms of carbon and nitrogen encountered in this chapter are grouped below.

Carbon

There are two bio-unavailable reservoirs: oxidized carbon in the form of carbonate (CO_3^{2-}) in sedimentary rocks like limestone, and reduced organic carbon, known as "kerogen," also in sediments. Methane (CH_4) in the atmosphere is largely bio-unavailable: once in the atmosphere it is more likely to be oxidized to carbon dioxide than to be absorbed as methane by microbes. The carbon in the nutrient reservoir is present principally as bicarbonate ion (HCO_3^-) in water and carbon dioxide (CO_2) in the atmosphere. In the atmosphere, both CO_2 and CH_4 are important greenhouse gases. Newly photosynthesized plant matter may be represented by the hypothetical molecule CH_2O , which has approximately the same 1:2:1 ratio of carbon to hydrogen to oxygen atoms as average plant material.

Nitrogen

The principal bio-unavailable reservoir is atmospheric nitrogen, present almost exclusively in diatomic form (N_2); 78% of the molecules of the atmosphere are N_2 molecules. Mobilization is initiated by breaking the $\text{N}\equiv\text{N}$ bond, producing available nitrogen in both oxidized and reduced forms: principally nitrate (NO_3^-) and ammonium ion (NH_4^+), respectively. Certain bio-available gases transfer nitrogen among reservoirs but remain in the atmosphere for only a short time before being rained out and returning to the nutrient pool: ammonia (NH_3) and several oxides of nitrogen (collectively referred to as NO_x), including nitrogen dioxide (NO_2) and nitric oxide (NO). Nitrous oxide (N_2O) is a bio-unavailable gas with a long residence time in the atmosphere; it is the most important nitrogen-containing greenhouse gas and is a useful tracer for biological processes. In plants nitrogen usually appears in an amine group ($-\text{NH}_2$).

Persistence and Stability of Cycles

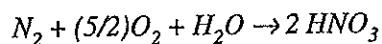
If biological processes were to cease, the grand nutrient cycles would wind down, as the many chemical reactions proceeded toward chemical equilibrium—the

¹ In discussions related to the greenhouse effect, *sequestration* (usually referring only to carbon) is used differently: "carbon sequestration" is the accumulation of carbon in some reservoir that prevents carbon dioxide from reaching the atmosphere.

The Grand Cycles

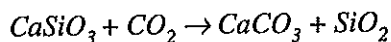
most stable (highest entropy) state of the atomic constituents. Gradually, for example, the chemically reduced carbon in life forms would combine with oxygen, until all the carbon became carbon dioxide (or, dissolved in water, carbonic acid). There is much more oxygen than reduced carbon available at or near the surface of the earth, so that if only reactions of oxygen with reduced carbon were proceeding toward chemical equilibrium, most of the atmospheric oxygen would remain.

However, a second process, the oxidation of atmospheric nitrogen, would also proceed, and it would indeed consume most of the atmospheric oxygen. The nitrogen would be gradually oxidized in the ocean, forming nitric acid, which is the most stable thermodynamic state of oxygen, nitrogen, and water in combination. The reaction is:



If this reaction were to proceed to chemical equilibrium, nearly all of the oxygen in the atmosphere would be used up while consuming about ten percent of the atmosphere's nitrogen. The nitric acid would accumulate in the ocean and turn it into a strongly acidic solution with a pH of 1.5 (Lewis and Randall, 1923). Thus, sunlight-driven biological processes play a major role in driving the earth away from chemical equilibrium and sustaining the chemical environment on earth that is compatible with life as we know it.²

Each of the grand nutrient cycles is stabilized by negative feedback. We give two examples: a long-term and a short-term feedback loop operating within the carbon cycle. On a scale of millions of years the carbon dioxide concentration in the atmosphere is stabilized by a geological negative feedback loop powered by geothermal energy deep in the earth. The carbon dioxide in the atmosphere is slowly consumed by *weathering*, an aqueous process where silicate rocks are transformed to silica (SiO_2), while the carbon travels to the sea in bicarbonate ion (HCO_3^-). Later, in the oceans, bicarbonate is incorporated as calcium carbonate in the shells of zooplankton and phytoplankton. The shells then drift to the ocean floor, where they accumulate as sediments. The overall reaction is:



If there were no chemical reaction in the reverse direction, nearly all the carbon in the atmosphere and biosphere, and even the carbon dioxide in solution in the oceans, would slowly disappear.

The reverse process, producing silicates and carbon dioxide from carbonates and silica, does indeed occur under conditions of high temperature and pressure deep in the earth, where the sediments are carried by tectonic processes. The

² Moving toward chemical equilibrium in the absence of biological processes would involve other chemical reactions as well, such as the reduction of ferric oxides by buried organic carbon, releasing further carbon dioxide. Today, this is a biotic, anaerobic process..

carbon dioxide is then vented to the atmosphere through volcanic eruptions or hot springs. There is a negative feedback, because the rise in carbon dioxide concentration in the atmosphere (such as might result, for example, from a period of greater than average volcanic activity) accelerates the chemical weathering of silicate rocks, reducing the atmospheric carbon dioxide concentration toward its earlier level.

A second negative feedback loop, based on the biological process of *carbon fertilization*, is controversial, but it may have played a role in the past in maintaining a relatively constant distribution of carbon dioxide between the atmosphere and the biosphere over shorter periods of time. When there was a short-term increase in the atmospheric concentration of carbon dioxide (such as might have resulted from a higher than average biomass destruction by forest fires), the rate of photosynthesis may have increased, if adequate quantities of other necessary nutrients and water were available. If such an increase in the rate of photosynthesis produced a greater stock of carbon in plants and soil, the carbon dioxide concentration in the atmosphere would have gradually fallen toward its previous value. The controversy in this instance concerns whether the stock of carbon in biomass can substantially increase in the short term, or whether increased photosynthesis is more or less immediately accompanied by increased respiration and decomposition, with no net increase in reduced carbon.

This short-term feedback mechanism may also operate when fossil fuel is burned, but only partially. Carbon fertilization may remove some of the carbon dioxide initially emitted into the atmosphere, in favor of an increase in the stock of carbon in the biosphere, but the atmospheric carbon dioxide concentration will remain elevated above its earlier level.

Preindustrial Steady State—But Imbalance Today Due to Human Activity

We will assume in this chapter that in preindustrial times (from a few thousand to about one hundred years ago) each grand cycle maintained a dynamic steady state, which is very different from the static chemical equilibrium just described. In a dynamic steady state the flows among reservoirs are not zero; rather, the flows are constant and balance one another. An external energy source powers these flows.

None of the grand nutrient cycles is in steady state now. For example, as seen in the ice core data in Figure 2, nitrate deposition rates were approximately constant in Greenland for nearly 200 years, until about 1950, and have roughly doubled since then. The increases measured in the ice may reflect the growth of nitric oxide emissions in the United States.

In this chapter we will attempt to quantify the departure today from preindustrial conditions, for both carbon and nitrogen, by making quantitative estimates of stocks and flows, first in preindustrial times and then today. This is an exercise full of uncertainty, in spite of the considerable progress made in recent years, as local measurements have been extended to greater numbers of places and conditions,

The Grand Cycles

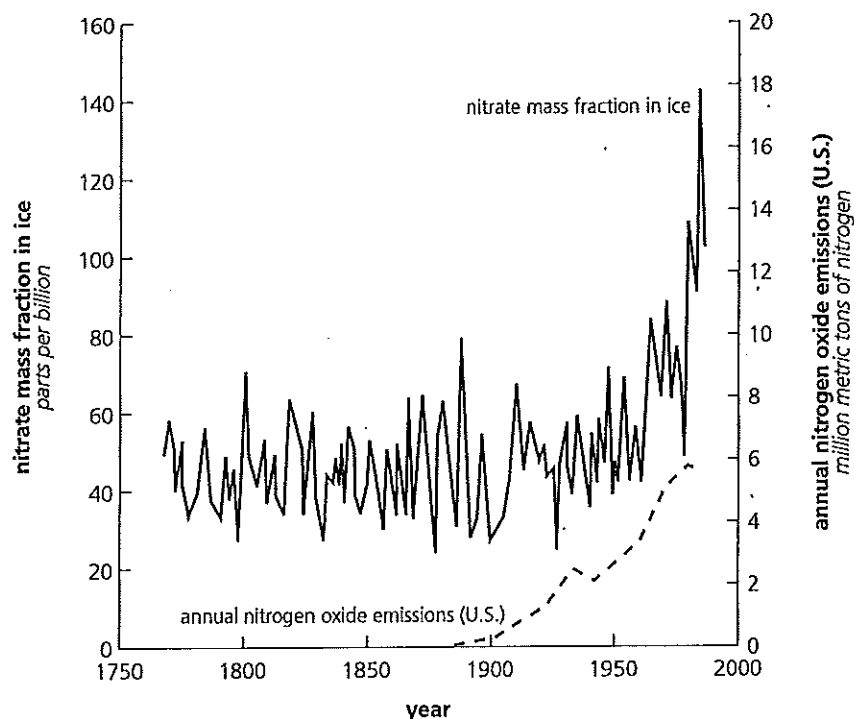


Figure 2. A 200-year record of nitrate in layers of an ice pack in South Greenland shows a relatively constant concentration until 1950 and more than a doubling in the next 30 years. Also shown (dashed line) are annual emissions of nitric oxides to the atmosphere from fossil fuel combustion in the United States (as estimated in U.S. Environmental Protection Agency, 1985, and graphed in Galloway, 1989). The trends in emissions and ice core concentrations are roughly parallel. (Modified from Mayewski et al., 1990. Reprinted with permission from *Nature*. © 1990 Macmillan Magazines Limited.)

and as modeling of processes has become more sophisticated. Our intent is to demonstrate some suggestive lines of argument.

It is instructive to develop indices that capture the degree of imbalance in the grand nutrient cycles brought about by human activities. Two kinds of indices are helpful:

- (1) indices in the form of fractional annual change in the stock of a nutrient in some reservoir arising from human activity;
- (2) indices in the form of ratios, with the nutrient transport resulting from current human activity in the numerator and the related nutrient transport resulting from *all* processes (natural + human) in the denominator.

As we will discuss further, a good and widely used index for the carbon cycle is the first kind: the rate of increase in the stock of carbon dioxide in the atmosphere. It has currently averaged almost one-half percent per year. One good index for the nitrogen cycle is the second kind: a ratio based on nitrogen fixation—the creation

of bioavailable nitrogen from the reservoir of N_2 in the atmosphere. That ratio, today, is about one-half; that is, nitrogen fixation associated with current human activity accounts for about half of all nitrogen fixation.

The imbalance of the carbon cycle has received much attention in recent years, because increases in the carbon dioxide concentration in the atmosphere are closely coupled to potential global climate change. Difficult as it is to make comparisons across cycles, human activity has probably made the nitrogen cycle even more unbalanced than the carbon cycle at this time. The disruption of the global nitrogen cycle may have received less attention because mostly it leads to changes in nutrient balances (and thereby, to changes in ecosystems) rather than to changes in sea level and patterns of rainfall. People more easily empathize with climate change than with nutrient change, but the consequences for human well-being can be severe in either case.

For both cycles, if change occurs gradually, manifestations of disruption and strategies for mitigation are matched to a scale of decades or centuries. However, faster change from non-linear effects cannot be ruled out.

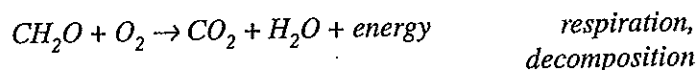
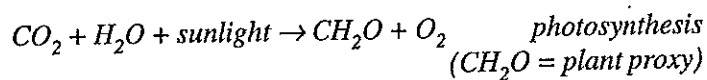
The Carbon Cycle

The Preindustrial Carbon Cycle

In preindustrial times the concentration of carbon dioxide in the atmosphere was roughly constant, but it has been rising for more than a century. In the middle of the last century about 280 of every million molecules in the atmosphere were carbon dioxide molecules (280 parts per million by volume, or 280 ppmv). Today the value has risen by 25%, to about 355 ppmv. The current rate of increase is about 0.4% per year.

In the carbon cycle, shown schematically in Figure 3, carbon dioxide is removed from the atmosphere and reduced carbon is incorporated directly into plants by the process of photosynthesis. A portion of the sunlight that drives photosynthesis is stored as chemical energy in the plant. Unlike the nitrogen cycle (see below), the carbon cycle involves no intermediary stages, which is why we call the carbon dioxide in the atmosphere a nutrient reservoir but the diatomic nitrogen in the atmosphere a bio-unavailable reservoir. The reduced carbon returns to carbon dioxide by respiration while the plant is alive and as part of the process of decomposition once the plant has died. The decomposition is accomplished by microfauna, bacteria, and fungi, acting upon plant litter and fine roots (Schlesinger, 1991).

The two key chemical reactions (each the reverse of the other) are:



Preindustrial Global Carbon Cycle

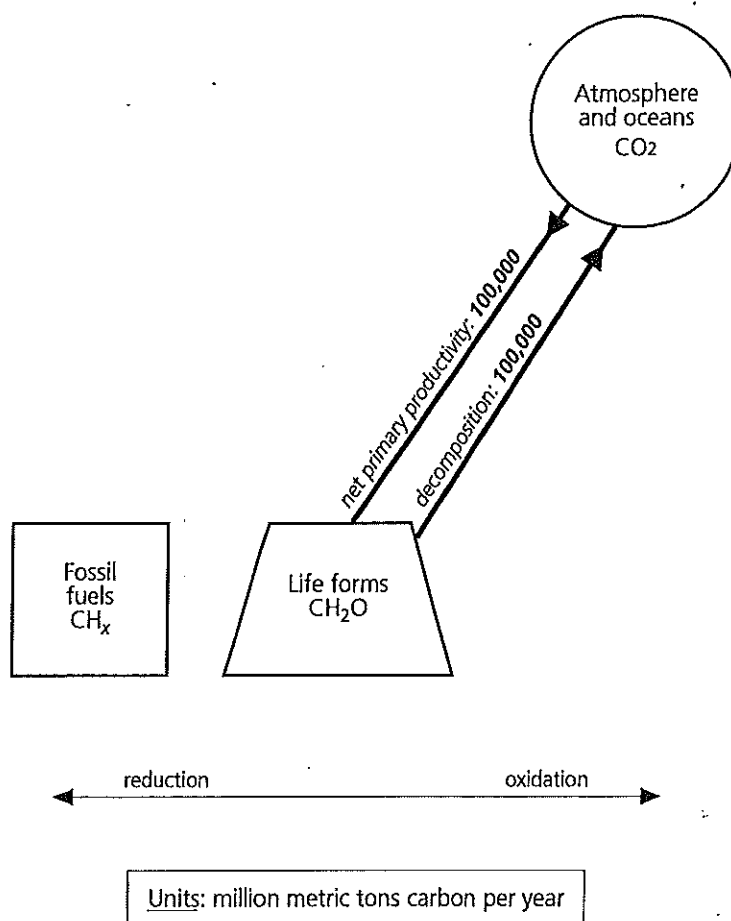


Figure 3. The preindustrial global carbon cycle. Flows are assumed in balance, with the reservoir of fossil fuels still untapped. The atmosphere is shown as a nutrient reservoir, rather than a bio-unavailable reservoir, because plants draw nutrient carbon directly from the reservoir of atmospheric carbon dioxide, without an intermediate step.

In quantifying the rate of carbon exchange between the biosphere and the atmosphere, one must distinguish *gross primary productivity* from *net primary productivity*. The process of photosynthesis is accompanied by a substantial amount of the reverse reaction—nearly simultaneous respiration that releases some of the incident energy to support plant metabolism. Gross primary productivity measures the rate of photosynthesis, and net primary productivity measures the actual rate of increase of the stock of organic carbon. Net primary productivity is generally the quantity of greater interest, because it measures the build-up of plant matter during a growing season.

As displayed in Figure 3, the global net primary productivity is about 100,000 million metric tons³ of atmospheric carbon per year. The data shown in Figure 4 are evidence that for the eight-hundred-year period from 1000 to 1800, the carbon flow due to global net primary productivity was in balance with an equal flow of carbon from the land and oceans to the atmosphere due to plant decomposition; these ice core data show carbon dioxide levels that varied only within about 10 ppmv, or 4% (Siegenthaler and Sarmiento, 1993).

Disaggregating the annual net primary productivity for land and sea, 60,000 million metric tons of carbon is incorporated into land vegetation and 40,000 million metric tons of carbon is incorporated into phytoplankton in the oceans (Schlesinger, 1991). These flows from the atmosphere to land and sea are matched by approximately equal flows back to the atmosphere⁴—but seasonally displaced, so that there is a net increase of standing biomass throughout the northern hemisphere spring and summer and an equal net decrease during its fall and winter. This seasonal cycle is seen in measurements of the atmospheric carbon concentration. Figure 5 shows the famous data from Mauna Loa, Hawaii, where carbon dioxide concentrations in the atmosphere have been measured continuously since 1958; the concentration is about two percent greater at the spring peak than at the minimum the following autumn.

A net primary productivity on land of 60,000 million metric tons of carbon per year can be converted into an average productivity by dividing by the land area on earth (15 billion hectares⁵), obtaining 4 metric tons of carbon per year per hectare. Relative to this average rate, the productivity of marshes is about triple, the productivity of estuaries and tropical forests is about double, the productivity of grassland is about half, and the productivity of desert scrub is less than one tenth (Harte, 1988). Agriculture in most climates, managed with the help of fertilizers, other chemicals, and perhaps irrigation, can achieve a net primary productivity comparable to estuaries—i.e., 8 metric tons of carbon (about 20 metric tons of dry biomass, as CH₂O) per hectare per year.

Methane

Methane (CH₄) has its own subcycle. Methane flows from land and sea to the atmosphere as a consequence of *methanogenesis*, or methane production from organic matter. Two of the principal processes involving methanogenesis are (1) the decay of plant matter a few centimeters below the water surface in rice paddies, bogs, and other wetland environments, and (2) the conversion of cellulose to

³ A metric ton is 1000 kilograms, or about 2200 pounds, about 10% larger than the familiar 2000-pound ton.

⁴ Even in a dynamic steady state, the flow from atmosphere to the land will exceed the flow from the land to the atmosphere, because of the flow of carbon nutrient from land to sea (in *runoff*). However, less than one percent of the carbon photosynthesized on land flows into the sea before being oxidized. We will see below that for nitrogen the corresponding fraction (flow to the sea in chemically reduced form, divided by fixation rate on land) is much higher.

⁵ A hectare is 10,000 square meters, or 2.47 acres.

The Grand Cycles

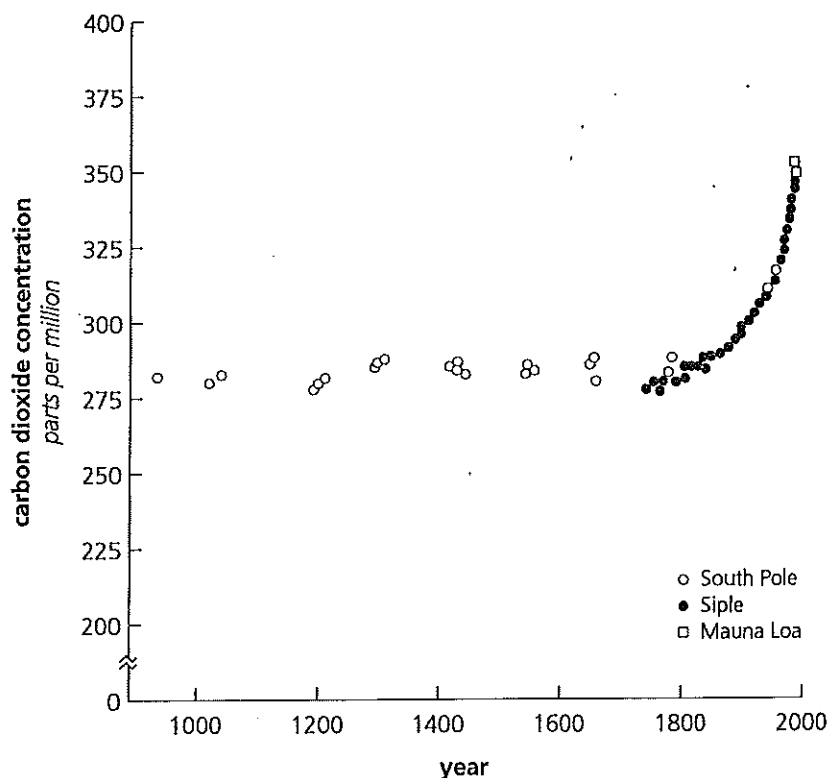


Figure 4. A 1000-year record of atmospheric carbon dioxide concentration. Data are from ice cores at the South Pole (open circles) and at the Antarctic base in Siple (closed circles), except for the rightmost two points, which are from Mauna Loa, Hawaii. (Source: Siegenthaler and Oeschger, 1987. Reprinted with permission from Munksgaard International Publishers Ltd., Copenhagen, Denmark, © 1987.)

carbon dioxide and methane by bacteria working in the stomachs and intestines of cattle, followed by belching.⁶

Very little of the methane in the atmosphere is metabolized by living organisms directly. The fate of most methane molecules is to be oxidized abiotically to carbon dioxide in the atmosphere, slowly and through many steps. The cycle is closed when photosynthesis again produces organic matter.

We know the size of the preindustrial reservoir of atmospheric methane quite accurately—about 1500 million metric tons, corresponding to a concentration of about 700 methane molecules for every billion molecules of atmosphere (0.7 ppmv). The rates of flow in and out of this reservoir must have been nearly equal, because over many centuries the methane concentration in the atmosphere was nearly constant. However, we do not know the preindustrial rates of flow of methane as accurately as the stock. Today, the *residence time* of methane in the

⁶ Again representing plant matter by the artificial molecule, CH_2O , the reaction, schematically, is:
 $2 \text{CH}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4$.

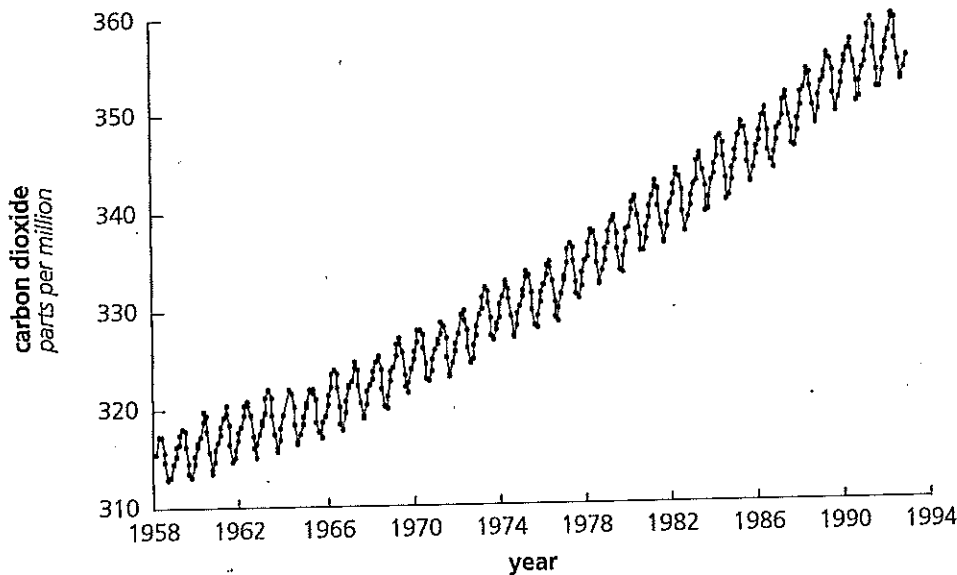


Figure 5. Monthly average concentration of atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. The data show both a seasonal variation (presumed to be due to the exchange of carbon between the atmosphere and vegetation) and a steady rise in annual average value (presumed to be due principally to human activity). The concentration is in parts per million by volume (ppmv) of dry air. A good model of the seasonal variation uses a shape that is exactly the same for each year, except for an increasing amplitude that doubles in about 100 years. The interannual variation is fitted by an unconstrained smooth curve. Data at other observing stations show nearly the same interannual variation, but each station shows a different seasonal pattern. (Data and model are in Keeling et al., 1989; data are updated in Keeling and Whorf, 1993.) The line shown here simply connects successive data points; it is not a model.

atmosphere is 10 years (that is, about one tenth of the methane in the atmosphere is oxidized to carbon dioxide in one year). If the residence time of methane in the atmosphere was also ten years in preindustrial times, the rate of flow of carbon in the form of methane in and out of the atmosphere would have been 150 million metric tons of carbon per year. However, in preindustrial times the oxidation mechanism that removes methane from the atmosphere may have been stronger than today, in which case the preindustrial residence time would have been shorter and the preindustrial flows of methane in and out of the atmosphere would have been larger.

For every methane molecule in the atmosphere in preindustrial times there were about 400 carbon dioxide molecules, and today the ratio is just over 200, but these ratios understate the relative importance of atmospheric methane. In the atmosphere today, an additional molecule of methane makes a much greater contribution to the greenhouse effect than an additional molecule of carbon dioxide, because of differences in the absorption of infrared radiation by the two gases, and because there is much less methane to begin with. Adding a methane molecule to the

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current atmosphere increases the greenhouse effect about 20 times as much as adding a molecule of carbon dioxide.

Human Impacts on the Carbon Cycle

Figure 6 presents rough estimates of the additions to the preindustrial carbon cycle brought about by human activity. Especially prominent are: (1) the combustion of fossil fuels, and (2) land-use changes that affect the global stock of biomass and the rates of biotic processes.

Combustion of Fossil Fuels

There is a huge reservoir of buried, dispersed, organic carbon, some of which has been aggregated by geological processes and transformed by heat and biological activity to form coal, petroleum, and natural gas. Humans are adept at finding and extracting these buried hydrocarbons wherever large amounts are in one place. We are commercializing such resources at increasing depths below the surface and at increasing depths of water when offshore. Extraction and combustion of these fuels have contributed significantly to altering the atmospheric CO₂ balance.

In 1991, approximately 5900 million metric tons of carbon were transferred physically from underground hydrocarbon reservoirs to the atmosphere, while being transformed chemically from reduced carbon to carbon dioxide. The 5900 is the sum of 2600 from oil, 2300 from coal, and 1000 from natural gas (Marland, 1993). Approximately three-fourths of the world's primary energy consumption derives from the combustion of these fuels. (See the chapter by Williams in this volume, especially its Figure 1, which gives global 1985 data. Then, the remaining one-fourth of primary energy was, roughly, 15% plant biomass, 5% hydropower, and 5% nuclear power.)

Coal combustion delivers less energy with each carbon atom than does oil, and oil less than natural gas. The reason is that coal has less than one hydrogen atom per carbon atom, oil has about two, and natural gas (which is largely methane) has almost four, and energy is released from the oxidation of both carbon and hydrogen. Hence, an intermediate-term strategy for reducing carbon transfer to the atmosphere from fossil fuels is to shift fossil fuel use away from coal and toward natural gas (provided leakage of unburned natural gas to the atmosphere can be kept very low).

A longer range strategy, explored in the chapter by Williams (this volume), is to substitute plant matter (biomass) for fossil fuel. Williams suggests that five to ten percent of global biomass oxidation could be arranged to occur within energy conversion facilities that produce electricity and gaseous and liquid fuels, permitting an equivalent amount of fossil fuel to be left below ground. Without human intervention, this biomass oxidation would occur in a dispersed manner (decay on the forest floor, for example), producing energy in forms too dilute to harness to human technology. The biofuels industry could be based on renewable plantations, where carbon absorption from the atmosphere in new plant growth stays in approximate

Human Additions to the Global Carbon Cycle

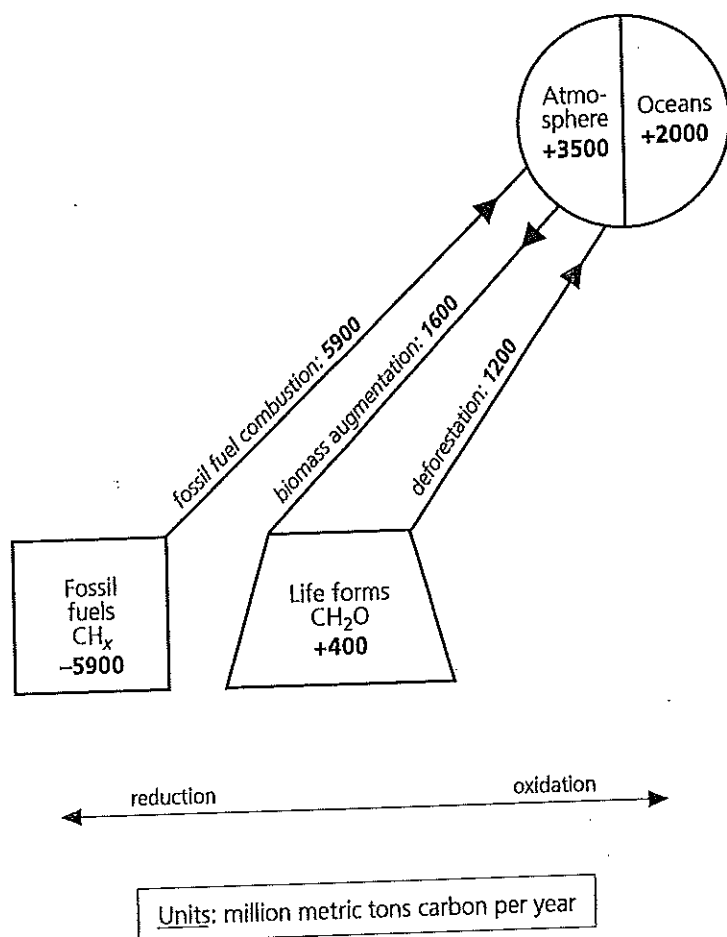


Figure 6. Human additions to the preindustrial global carbon cycle. Changes in reservoir stocks are shown by entries inside the boxes and sum to zero. Human impacts, dominated by the combustion of fossil fuels and by deforestation, lead to an increase in carbon dioxide in the atmosphere and bicarbonate in the oceans. The estimates shown here assume the "missing" carbon is in land plants (see text). The chemical structure of fossil fuels is stated as CH_x to emphasize that the ratio (x) of hydrogen atoms to carbon atoms in fossil fuels is variable, ranging from 4 for natural gas to less than 1 for coal. The rate of combustion of fossil fuels and the rate of increase in the atmospheric stock are known accurately; the other estimates are highly uncertain.

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balance with carbon emission to the atmosphere from biofuel use. Then there would be no net transfer of carbon dioxide to or from the atmospheric reservoir.

Land-Use Changes

Deforestation affects the global carbon cycle (Houghton, 1993). Estimates of the rate of deforestation globally have been considerably improved with the help of the LANDSAT satellites, whose photographs of the earth have high spatial resolution. We estimate a rate of 10 million hectares per year. (Earlier estimates were sometimes twice as high.)⁷ The total area of tropical forest remaining on the earth is about 1800 million hectares, so about one-half percent of remaining forest is lost to deforestation each year.

To convert the rate of loss in hectares per year to a carbon flow from land to atmosphere in metric tons of carbon per year, we multiply by 120 metric tons of carbon per hectare, a typical value for the net change in the carbon content of a hectare of primary rainforest, allowing for secondary growth⁸. We find that deforestation accounts for a flow of about 1200 million metric tons of carbon per year from the land to the atmosphere.

Fossil fuel combustion and deforestation are responsible for the two most important anthropogenic increments to the preindustrial flow of carbon dioxide from the land to the atmosphere. We see that their sum is about 7100 million metric tons per year. It is an important measure of the incompleteness of environmental science today that we cannot fully account for the fate of this additional flow. From Figure 5 we can infer that roughly half this excess anthropogenic flux, or 3500 million metric tons of carbon per year, is accumulating in the atmosphere, so about 3600 million metric tons of carbon per year must be accumulating either in the oceans or in terrestrial biomass. The oceans appear to take up about 2000 million metric tons of carbon per year (Siegenthaler and Sarmiento, 1993). The remainder, 1600 million metric tons of carbon per year, is called the "missing" carbon, which can be in one of only two places. Either the "missing" carbon has gone into the oceans, which would mean that carbon processes in the ocean are misunderstood, or the "missing" carbon is accumulating in terrestrial biomass elsewhere than at the sites of deforestation, where small changes in total terrestrial biomass are very difficult to detect.

The missing carbon may be going into the temperate forests of North America and Russia, increasing their stock of biomass in spite of increased timber and woodpulp harvesting. Arguments in support of the growth of temperate forests include: (a) *history*—the North American forests were cut down in recent centuries

⁷ The largest single region of deforestation is the Amazon basin, where the estimated deforestation rate from the clearing of closed-canopy primary forest is about 2 million hectares per year (Skole and Tucker, 1993).

⁸ We assume the carbon content of the biomass before and after deforestation to be, respectively, 160 and 40 metric tons per hectare. A more accurate calculation would take into account the delay between deforestation and plant decomposition: only about one-half of the biomass on deforested land will decompose in the first year (Houghton, 1991). It would also take into account year-to-year changes in regional deforestation rates and the multiple fates of land after deforestation.

and are growing back, still approaching their full size; (b) *CO₂ fertilization*—plants often grow more quickly when the concentration of carbon dioxide in their immediate environment is increased, a fact often exploited in greenhouses; and (c) *nitrogen fertilization*—plants often grow more quickly when additional nitrogen is supplied. In drawing Figure 6, for specificity, we have assumed the “missing” carbon is augmenting the global stock of biomass.

The anthropogenic component of atmospheric CO₂ influx may seem small: the 7100 million metric tons of carbon per year injected into the atmosphere from fossil fuel burning and deforestation is about 12% of the 60,000 million metric tons per year of terrestrial net primary productivity. But the anthropogenic term is not balanced, and so the carbon dioxide concentration in the atmosphere keeps growing. The build-up of carbon dioxide in the atmosphere accounts for roughly half of the total anthropogenic greenhouse effect, with the other half assigned to changes in the concentrations of several other trace gases in the atmosphere. Thus, a 12% perturbation within a grand nutrient cycle can have significant impacts.

Modifications of the Methane Subcycle

Human perturbations have also disrupted the methane subcycle. In the past two decades, the rate of increase in the concentration of methane in the atmosphere has averaged about 1% per year, more than twice the rate of increase in the concentration of carbon dioxide. In the last hundred years the methane concentration has more than doubled: the stock of carbon in the form of methane in the atmosphere today is about 3600 million metric tons, corresponding to a concentration of 1.7 ppmv.

The preindustrial methane flux into the atmosphere from anaerobic bacterial action has been augmented by an expansion of wet rice cultivation in the Orient and of cattle and sheep husbandry worldwide. Another important anthropogenic source, discussed by Harriss in this volume, is methane leakage from the natural gas system, at the wellheads and along the transmission and distribution systems.

Moreover, the methane destruction mechanism in the atmosphere is being diminished by an increase in emissions of carbon monoxide (CO). The hydroxyl radical (OH) is the principal scavenger of both molecules, so an increase of CO emissions into the atmosphere results in fewer OH molecules available to scavenge methane, thereby increasing methane's residence time and concentration in the atmosphere⁹.

The Nitrogen Cycle

The Preindustrial Nitrogen Cycle

The four-reservoir model of the nitrogen cycle presented in Figure 7 captures the cycle's most essential components. There are two subcycles. In the subcycle of “new” nitrogen, the flows on land are between atmosphere and soil. In the subcycle of “recycled” nitrogen, the flows on land are between soil and plants.

⁹ The electrically neutral hydroxyl radical (OH) that is chemically active in the atmosphere is not to be confused with the electrically negative hydroxide ion (OH⁻) found in aqueous solutions.

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Preindustrial Global Nitrogen Cycle

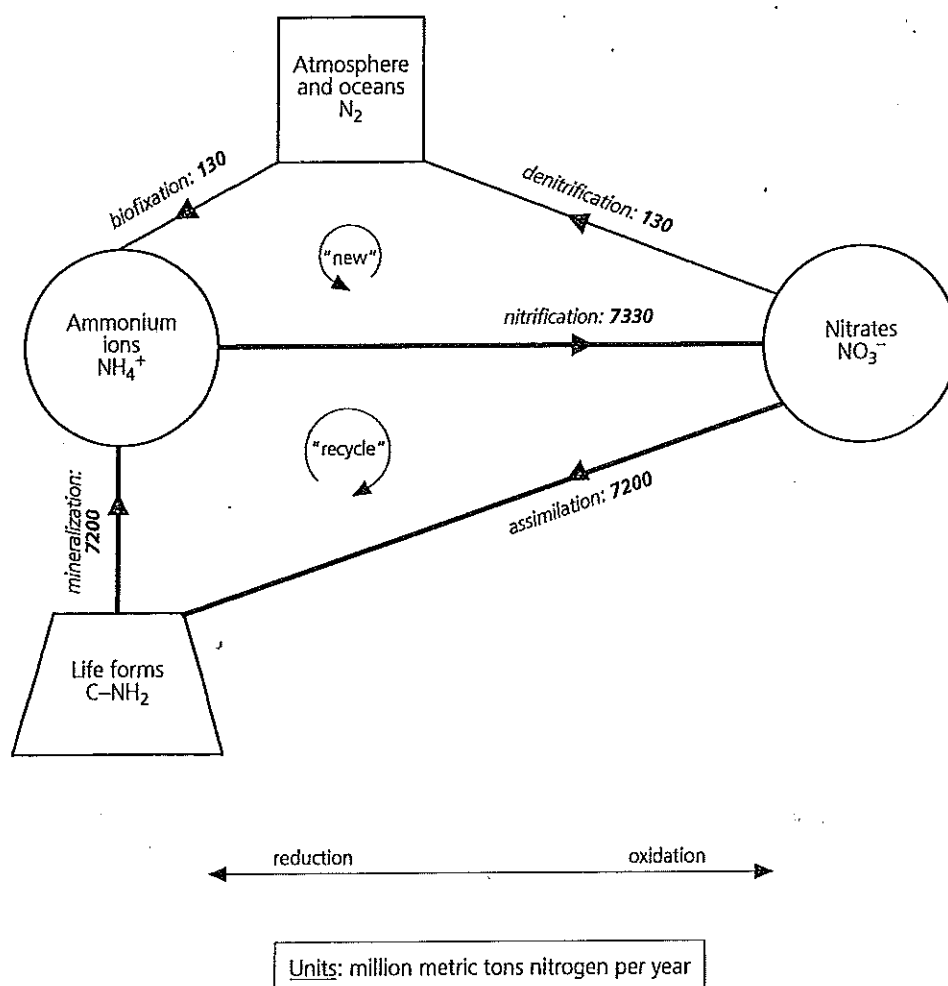


Figure 7. The preindustrial nitrogen cycle, modeled with four reservoirs and two subcycles. The subcycle of "new" nitrogen exchanges nitrogen between the atmosphere and the nutrient pool. This subcycle is shown unidirectional, reflecting the fact that biological organisms can neither convert atmospheric N_2 directly to nitrate nor convert reduced nitrogen to N_2 . Nitrogen fixation directly to nitrate, as in lightning and fires, is small and not shown (see text). The subcycle of "recycled" nitrogen, involving much larger flows, is an oversimplification, in that most plants can and do receive a portion of their nutrients directly from the reduced nitrogen in the soil (a flow running in the opposite direction from the flow marked "mineralization"). The sum of land and ocean flows is shown; Table 1 disaggregates these estimates for land and sea separately.

In the first subcycle, the $N\equiv N$ bond is broken and restored. The nitrogen flowing through this subcycle is called "new" nitrogen, because in this subcycle molecular nitrogen from the atmosphere replenishes the nutrient pool of ammonium and nitrate ions. In the second subcycle, nitrogen is "recycled," and the total stock of nutrient nitrogen remains unchanged. In a well established ecosystem the flows of "recycled" nitrogen are much larger than the flows of "new" nitrogen. We elaborate on these subcycles below.

The Subcycle of "New" Nitrogen

In the subcycle of "new" nitrogen, diatomic nitrogen (N_2) is transformed into available N by *nitrogen fixation*, principally *biofixation*. Because plant and animal life can utilize as nutrients both nitrates and ammonium ions, but not diatomic nitrogen, all life ultimately depends on nitrogen fixation. Most plants and animals get their nitrogen from other plants and animals. But the whole process cannot get started without specially adapted nitrogen-fixing microorganisms that catalytically disassemble and chemically reduce N_2 to ammonium ion (NH_4^+). Biofixation is accomplished by a few specialized bacteria and blue-green algae. The most important of the bacteria is *Rhizobium*, which fixes nitrogen symbiotically after attaching itself to the roots of legumes, such as alfalfa. An important nitrogen-fixing blue-green algae is *Anabaena*, a leftover from the early evolutionary history of the earth. We estimate that preindustrial biofixation occurred at a rate of about 130 million metric tons of nitrogen per year: 100 on land and 30 in the sea.

A second, much smaller, non-biological pathway to nitrogen fixation, not shown in Figure 7, involves the fixation of nitrogen by lightning. Lightning bolts oxidize atmospheric N_2 to nitric oxide (NO), which is rained out as nitrate (NO_3^-) within days. Lightning fixes about 3 million metric tons of nitrogen per year (Borucki and Chameides, 1984). There are about 100 flashes per second (or 3 billion per year), a rate well estimated by satellites; each flash fixes about 1 kilogram of nitrogen as nitric oxide, a mass known with an uncertainty of about a factor of three (Lawrence *et al.*, 1993).

Nitrogen in plant matter is largely found in reduced form, as amine ($-NH_2$) groups incorporated into organic molecules. *Nitrification*—the conversion of an amine or ammonium ion into a nitrate ion—plays a crucial role in increasing the movement of nitrogen in the environment. Nitrification is an aerobic process involving bacteria of the genera *Nitrosomonas* and *Nitrobacter*. The oxidation of the nitrogen is generally accompanied by the reduction of carbon dioxide, thereby assimilating carbon and linking the carbon and nitrogen cycles.

In *denitrification*, which closes the "new" nitrogen cycle, nutrients are removed from the nutrient pool as a result of the restoration of the $N\equiv N$ bond and the transformation of nitrogen back into N_2 , or, infrequently, nitrous oxide (N_2O)¹⁰.

¹⁰ It is unfortunate that *nitrification* and *denitrification* are the names of two processes that in no sense reverse one another. The two processes that reverse one another—in the sense of disassembling and reassembling the $N\equiv N$ bond—are *nitrogen fixation* and *denitrification*.

The Grand Cycles

Biological denitrification requires anaerobic environments, and is accomplished by a specialized set of bacteria, notably in the genus *Pseudomonas*. These bacteria are able to oxidize organic matter using oxygen extracted from the nitrate ion. Thus, denitrification creates a second link between the carbon and nitrogen cycles.¹¹

Forest and brush fires are a pathway to non-biological denitrification known as *pyrodenitrification*. In pyrodenitrification, two nitrogen atoms that were in separate molecules in plants or soil bind to one another to make N_2 , as the result of a sequence of high-temperature reactions¹² (Bowman, 1991; Kuhlbusch *et al.*, 1991). In the absence of a fire, most of the nitrogen in living organisms is recycled, and only a small fraction is denitrified; but in a fire much of the nitrogen is denitrified (Logan, 1983). A forest or brush fire, therefore, short-circuits the nutrient recycling system¹³.

The preindustrial rates of global denitrification and global nitrogen fixation should have been approximately equal, assuming a steady state. From our earlier assumptions about fixation (130 million metric tons of nitrogen via biofixation and almost negligible net nitrogen fixation via lightning and fires), about 130 million metric tons of nitrogen would have been returned to the atmosphere each year (see Figure 7). Uncertainties abound, because measurements of denitrification rates are as difficult as measurements of biofixation rates¹⁴.

Consider the nitrogen flows, separately, for the land and the sea. In preindustrial times there would have been a net nutrient flow from land to sea, yet, by our assumption of a steady state, no net nutrient accumulation on land or in the sea. Bioavailable nitrogen is transferred, as *runoff*, from land to sea, principally via rivers. In a balanced land-sea cycle one finds: (1) greater fixation than denitrification on land, leading to net nutrient availability; (2) transport of this net nutrient from land to sea (runoff); and (3) less fixation than denitrification in the sea—less by an amount equal to the runoff.

¹¹ Additional sources of oxygen for bacteria in anaerobic environments are sulfates (SO_4^{2-}), manganese dioxide (MnO_2) and ferric hydroxide ($Fe(OH)_3$). The corresponding processes link carbon cycling to sulfur, manganese, and iron cycling. Bacteria have greater difficulty extracting oxygen from the phosphate ion PO_4^{3-} (which yields phosphine (H_3P), a gaseous compound), because the energy required to break the oxygen-phosphorus bond is very large; the strength of this bond accounts for the fact that phosphate molecules are the major energy carriers in living organisms.

¹² Atmospheric chemists and experts in combustion have focused principally on the production not of the principal gaseous nitrogen product of a fire, N_2 , but of the gas that carries away most of the rest of the nitrogen from a fire, nitric oxide (NO). Their focus is explained by the fact that NO in the atmosphere participates in chemical reactions that affect the balance of other gases in the atmosphere, while N_2 is inert. However, from the perspective of the subcycle of "new" nitrogen, the passage of a nitrogen atom from a plant or animal to a molecule of N_2 in the atmosphere is more consequential than the passage of the same atom to a molecule of NO. In only a few days the NO is washed out of the atmosphere as nitrate in rain or snow, and if it falls on the land, it becomes a nutrient for another plant (Schlesinger, 1991).

¹³ *Pyrofixation* is still another nitrogen process related to biomass fires. In pyrofixation nitric oxides are produced not from nitrogen originally in the biomass but (as with lightning) from N_2 in the atmosphere.

¹⁴ Comparing the carbon cycle in Figure 3 with the subcycle of "new" nitrogen in Figure 7, we see that in nature reduced carbon is oxidized directly to the dominant atmospheric gas, CO_2 , but reduced nitrogen is not oxidized directly to the corresponding gas, N_2 . The biological subcycle of "new" nitrogen is a three-step cycle (fixation-nitrification-denitrification-fixation), while a direct analog of the carbon cycle would be a two-step cycle (fixation-denitrification-fixation) that does not occur.

We estimate that preindustrial runoff carried 20 million metric tons of nitrogen per year from land to sea. The rates of preindustrial denitrification on land and in the oceans would have been, in million metric tons of nitrogen per year, 80 (100 minus 20) and 50 (30 plus 20), respectively. Land and sea values are disaggregated in Table 1.

One year of such flows can affect only a tiny fraction of the 3,900,000,000 million metric tons of nitrogen contained in the reservoir of the global atmosphere. A cycle involving an annual flow in and out of the atmosphere of 130 million metric tons removes and returns just one part in 30 million of the stock in a year. Because the nitrogen in the atmosphere is nearly all bio-unavailable N_2 , however, life depends on this trickle of fixed "new" nitrogen. Changing the size of the trickle will affect plant and animal life.

The Subcycle of "Recycled" Nitrogen

In the subcycle of "recycled" nitrogen, the flows of nitrogen from reservoir to reservoir do not break or restore the $N \equiv N$ bond, and therefore do not change the amount of nitrogen in the global nutrient pool. (In local ecosystems, of course, the amount of nutrient nitrogen can either increase as a result of inputs such as acid precipitation, or decrease as a result of loss mechanisms such as leaching.) In Figure 7, the subcycle of recycled nitrogen, like the subcycle of new nitrogen, has three steps. As drawn, Figure 7 oversimplifies what is found in nature by showing plants obtaining all nitrogen from nitrates, not from nitrogen in chemically reduced form. In fact, the processes of nitrogen *assimilation* by plants can begin with nitrogen in either oxidized or reduced form. Nitrogen in reduced form—as the ammonium ion (NH_4^+) or amine group ($-NH_2$)—is acceptable to most plants. However, many plants absorb nitrogen preferentially in the form of nitrate ion (NO_3^-), and some plants cannot absorb the ammonium ion at all and must wait for nitrification to present the nitrogen as nitrate.

In the subcycle of recycled nitrogen, nutrients are retrieved from life forms by *mineralization*, a strange name for a process where decomposers, as a byproduct of obtaining energy from the oxidation of reduced carbon in plantlife, transform the reduced nitrogen in plant and animal matter into simpler molecules (especially NH_4^+) that still contain nitrogen in reduced form, but that no longer have carbon-nitrogen bonds. The process of *nitrification* completes the subcycle of recycled nitrogen, just as it completes the subcycle of new nutrients; it is the one process common to the two subcycles.

The total flow of recycled nitrogen is estimated in Figure 7 to be 7200 million metric tons of nitrogen per year. In Table 1 this flow is disaggregated: 1200 on land and 6000 in the sea. The rate on land is about twelve times the magnitude of flow of new fixed nitrogen, so in preindustrial times about 92% of the nitrogen on land was recycled. In the oceans, an even greater percentage was recycled; the recycling rate was 200 times the biofixation rate.

The rates of assimilation of carbon and nitrogen must be related, because plant growth involves a fairly predictable ratio of carbon to nitrogen uptake. Our numbers

Table 1: Preindustrial and contemporary nitrogen cycle (units: million metric tons of nitrogen per year)

Process	Preindustrial Flow			Human Additions			Flow Today		
	Land	Sea	Total ¹	Land	Sea	Total ²	Land	Sea	Total
Subcycle of "new" nitrogen									
Fixation									
Life forms (reduced N)	100	30	130	40	—	40	140	30	170
Fertilizer (reduced N)	—	—	—	90	—	90	90	—	90
Combustion of fossil fuels (oxidized N)	—	—	—	20	—	20	20	—	20
Runoff (reduced N)	-20	20	0	-20	20	0	-40	40	0
Nitrification ³	80	50	130 ³	100	20	120 ³	180	70	250
Denitrification	80	50	130	50	20	70	130	70	200
Subcycle of "recycled" nitrogen									
Assimilation	1200	6000	7200	160	—	160	1360	6000	7360
Mineralization	1200	6000	7200	130	—	130	1330	6000	7330
Nitrification ³	1200	6000	7200 ³	130	—	130 ³	1330	6000	7330
Build-up in reservoirs									
Life forms	—	—	—	30	—	30	30	—	30
Amine nutrients	—	—	—	10	—	10	10	—	10
Nitrate nutrients	—	—	—	40	—	40	40	—	40
Atmosphere and oceans as N ₂	—	—	—	-80	—	-80	-80	—	-80

¹ See Figure 7.

² See Figure 9.

³ The two rows are combined in Figures 7 and 9.

for global annual uptake on land—60,000 million metric tons of carbon and 1200 million metric tons of nitrogen—are consistent with an “average” plant that incorporates carbon and nitrogen at a C/N mass ratio of 50 to 1 (about 60 to 1 on an atom for atom basis). There is a steady enrichment for carbon as plants grow and woody tissue develops, however, so these C/N ratios underestimate the ratio for carbon and nitrogen *stored* in plants. (In other words, the residence time of carbon in plants is longer than the residence time of nitrogen.) As a result, the older the plant tissue, the higher the ratio of carbon to nitrogen. The trunks of trees have C/N mass ratios of 150 or more, leaves less than 50, and algae in the oceans perhaps 10. Soil on average has a C/N mass ratio of 12 to 15 (Schlesinger, 1991).

Nitrous Oxide

There are 2.5 million N_2 molecules for every nitrous oxide (N_2O) molecule in the atmosphere. Still, nitrous oxide makes a powerful contribution to the greenhouse effect (molecule for molecule, additional N_2O is several hundred times as effective as additional carbon dioxide), while minute fractional changes in N_2 are unimportant. Accordingly, much effort has been devoted to understanding the global cycle of nitrous oxide (N_2O) and to documenting its build-up in the atmosphere in recent years.

The N_2O concentration in air up to 2000 years old trapped in layers of permanent ice has been analyzed (see Figure 8). The data reveal that until about two hundred years ago the concentration of nitrous oxide was relatively constant at about 285 ppbv, or 285 molecules of N_2O per billion molecules of atmosphere (Khalil and Rasmussen, 1992). This concentration corresponds to a reservoir of 1400 million metric tons of nitrogen as N_2O in the atmosphere.

Nitrous oxide enters the atmosphere as a minor byproduct of nitrification and denitrification. These flows must have been balanced by removal processes, or *sinks*. The only known sinks for N_2O are in the stratosphere, where destruction by solar ultraviolet photons or by activated atomic oxygen yields either N_2 or nitric oxide (NO). The destruction rate by these two mechanisms is such that one out of every 150 N_2O molecules in the atmosphere is destroyed every year. (An equivalent statement is that the residence time of N_2O in the atmosphere is 150 years.) Unlike the situation with methane, the strength of the destruction mechanism for N_2O in the atmosphere has hardly changed since preindustrial times. This permits an accurate estimate of the preindustrial rate of transfer of N_2O into and out of the atmosphere; it is equal to the size of the reservoir of atmospheric N_2O divided by the residence time, or about 10 million metric tons of nitrogen per year.

Human Impacts on the Nitrogen Cycle

A Doubling of Nitrogen Fixation

Figure 9 and Table 1 present rough estimates of the many additions to the preindustrial nitrogen cycle brought about by human activity. Every aspect of the cycle has been modified in the industrial age. Probably the most important modification

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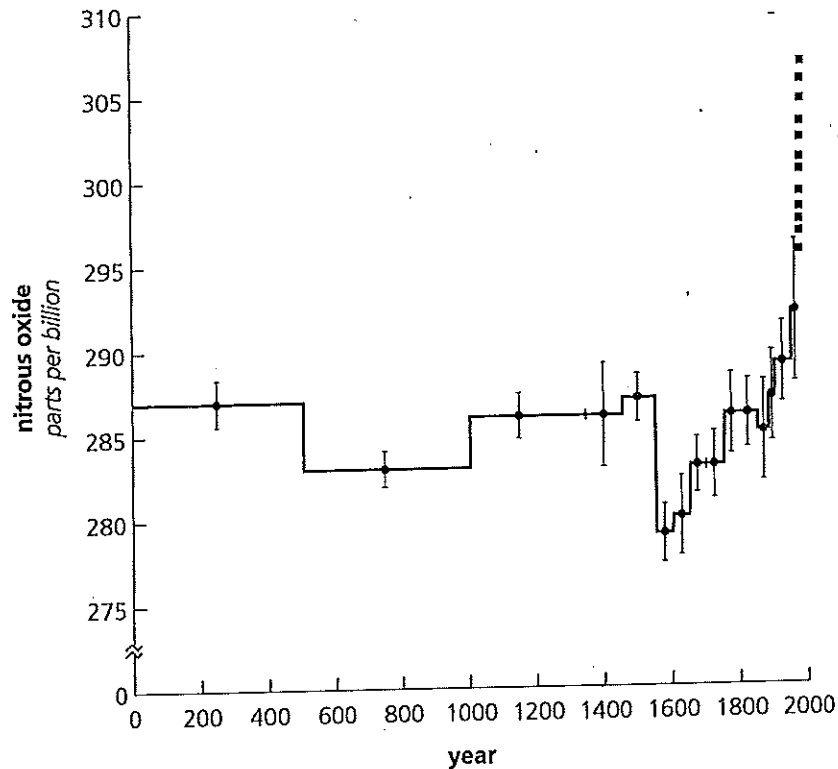


Figure 8. A 2000-year record of the atmospheric concentration of nitrous oxide (N_2O). The data since 1975 are direct measurements in the atmosphere. Earlier data are obtained from bubbles trapped in layers of polar ice. Data are averages from ice cores in the Arctic (at the Crete and Camp Century sites) and the Antarctic (Byrd Station). There is a 90% chance that a larger data set from similar cores for the same time period would give an average value within the vertical error bars. The data show little variation around an average concentration of about 285 N_2O molecules in every billion molecules of atmosphere (285 ppbv) in preindustrial times and a rise at a rate of about 1 ppbv per year in recent years. Modified from Table 2 and Figure 3 of Khalil and Rasmussen, 1992.

is the doubling of the rate of nitrogen fixation. We will trace the doubling of nitrogen fixation to three human activities. In decreasing order of importance they are:

- (1) the production of nitrogen fertilizer,
- (2) the increased planting of leguminous crops, and
- (3) the combustion of fossil fuels.

What are the likely impacts of this doubling of preindustrial global fixation rates, and of almost certain further increases in fixation rates in the future? Worldwide, local ecosystems are being affected in two ways: by changes in nutrient balances and by changes in environmental acidity.

Nitrogen is a limiting ingredient in many ecosystems, so an increased input of fixed nitrogen generally increases net primary productivity. Unfortunately, in natural ecosystems, increased net primary productivity generally means ecosystem

Human Additions to the Global Nitrogen Cycle

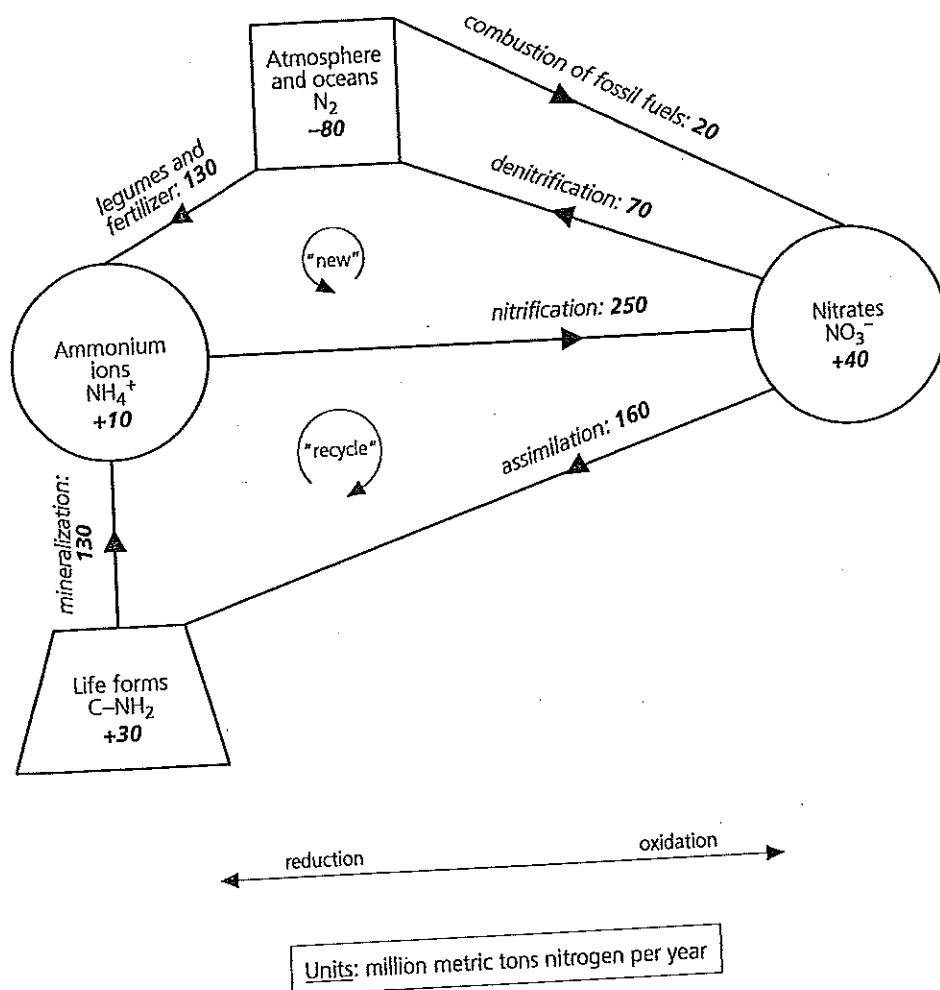


Figure 9. Human additions to the preindustrial global nitrogen cycle. Changes in reservoir stocks are shown by entries inside the boxes and sum to zero. Human impacts on the nitrogen cycle are dominated by the use of fertilizers, the planting of leguminous crops, and the combustion of fossil fuels. A build-up of nitrogen stocks in life forms and as nutrients is assumed, and detailed flows are modeled using additional arbitrary, but plausible assumptions (see text). Table 1 gives a further disaggregation that distinguishes land and sea.

disruption, because there will be differential growth of some species relative to others.

An increase in fixed nitrogen input does not necessarily increase local acidity. At locations of increased concentrations of chemically reduced nitrogen (ammonium ions and amines), the environment becomes less acidic, while at loca-

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tions of increased concentrations of oxidized nitrogen (nitrates), the environment becomes more acidic. Both changes are disruptive. Globally and in most precipitation, the net effect is increased acidity, because nitrogen is a weak base when in reduced form but a strong acid when in oxidized form, and the nitrification process is continually oxidizing the ammonium ion.

An increase in the acidity of ecosystems, such as lakes, degrades them, in part, by mobilizing aluminum and other metallic ions that formerly were bound firmly to soil particles. The increased acidity "uses up" the alkaline buffering capacity in the soil (in the form of calcium and magnesium ions). Aluminum poisoning may be one of the causes of the European *Waldsterben* (forest death) that has decimated some forests in central Europe. Similar toxicity problems may arise from the mobilization of heavy metals like lead, cadmium, arsenic, and mercury (Stigliani, 1988). An increase in local acidity also leaches nitrates from soils; when leached nitrates percolate through soils into groundwater, nitrate concentrations sometimes reach unacceptable levels. One long-term effect of a net increase in global acidity is an increase in rock weathering, as weathering by carbonic acid is supplemented by faster processes due to nitric and sulfuric acid (Cronan, 1980).

Fertilizer. Nitrogen fertilizer production creates the single largest disturbance of the global nitrogen cycle assignable to human activity. Because nitrogen is a limiting factor in many agricultural regions, it has been relatively easy to increase crop yield by supplementing natural sources of available nitrogen with synthetic sources. The flow today is approximately 90 million metric tons of nitrogen per year (Smil, 1991).

As seen in Figure 10, the intensive use of nitrogen fertilizer is a new phenomenon. Levels of use associated with traditional agricultural practices, such as fertilizing with nightsoil and recycled crop wastes, are many times smaller. As recently as 1960 the total global use of nitrogen fertilizer was only about 10 million metric tons of nitrogen per year, or one tenth of today's levels (Smil, 1991).

High levels of application of nitrogen fertilizer are found today throughout the world. Remarkably, unlike the use of energy, automobiles, telephones, or most other products of industrialization, fertilizer use shows little correlation with average income levels across countries. One summary of recent rates of nitrogen fertilizer use across countries (in kilograms per hectare of arable land per year) finds a global average rate of 46—with the United States at 55, Japan at 145, and Egypt at 295 (Smil, 1991). It is widely believed that to feed a growing population the global rate of nitrogen fertilizer production must continue to increase for many decades.

Nitrogen fertilizer production usually begins with the reaction, at high pressure, of atmospheric nitrogen (N_2) with hydrogen from the methane (CH_4) in natural gas to produce ammonia (NH_3). The fertilizer is applied on the land both as ammonium (reduced nitrogen) and as nitrate (oxidized nitrogen). Each form has advantages. Ammonium fertilizer binds more tightly to clay and so is not as easily leached; nitrate fertilizer is more easily absorbed by plants, but is easily lost in

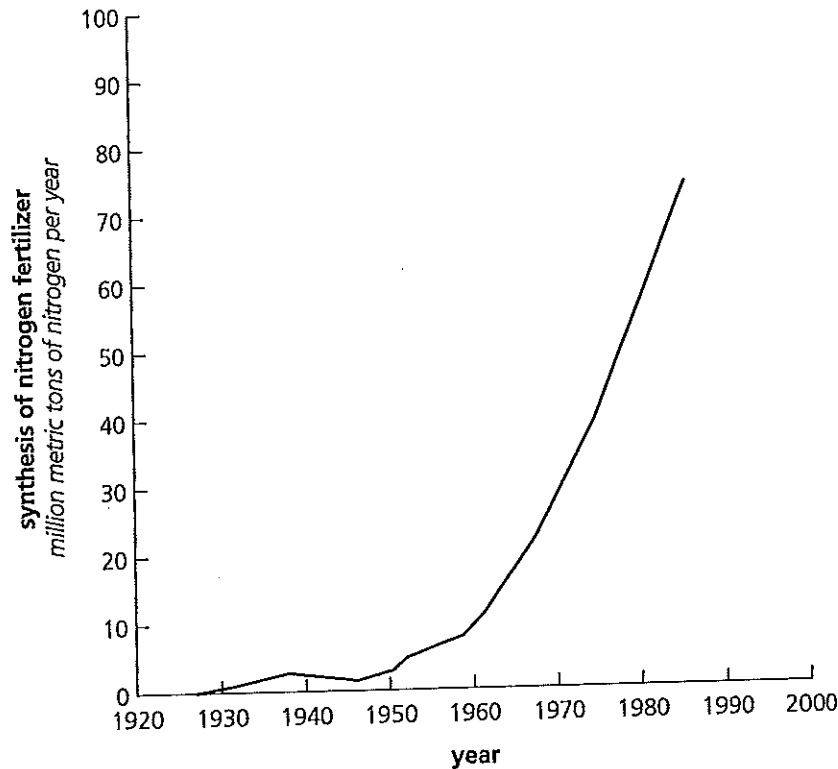


Figure 10. The global production of nitrogen fertilizer, 1920 to 1985. The cumulative production over this 65 year period is one billion metric tons; half of the production was between 1976 and 1985. (Source: Smil, 1991. Reprinted with permission of Cambridge University Press.)

runoff. Mostly, farmers opt for ammonium, delivered either as ammonia gas or, increasingly, as urea ($\text{CO}(\text{NH}_2)_2$). Nitrogen is mineralized from urea slowly enough that, like a time-release capsule, urea can have its positive effect over a longer period of time. Moreover, urea is a convenient, easy way to transport reduced nitrogen: it is 47% nitrogen by weight. Farmers frequently opt for applying the nitrogen in both reduced and oxidized form at the same time, in the form of ammonium nitrate.

Nitrogen fertilizer is used especially intensively on corn. In the United States in 1987 corn was grown on 21% of all the cropland but received 41% of all nitrogen fertilizer. On average, in that year's corn production, 153 kilograms of nitrogen was applied per hectare (137 pounds per acre), more than double the rate in 1965 (National Research Council, 1993).

A simple model of a "typical" cornfield, developed by the Committee on Long-range Soil and Water Conservation of the Board on Agriculture of the National Research Council, is helpful in understanding these rates of use (National Research Council, 1993). The model assumes a grain yield of 4 metric tons of corn per hectare (t/ha) in the absence of fertilizer, growing to 7 t/ha when fertilizer is

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applied at 100 kilograms of nitrogen per hectare and to 8 t/ha when fertilizer is applied at 200 kilograms of nitrogen per hectare¹⁵. There are the expected diminishing returns: the first hundred kilograms of nitrogen per hectare is three times as effective as the second hundred in adding to yield¹⁶.

Increased Planting of Leguminous Crops. Changes in agricultural practices affect the nitrogen cycle in several ways. A major direct effect arises from the worldwide cultivation of about 250 million hectares of leguminous crops, such as soybean and alfalfa, that are estimated to fix, annually, 35 million metric tons of nitrogen, an average of 140 kilograms of nitrogen per hectare (Burns and Hardy, 1975). We estimate that the increment in the nitrogen fixation rate, relative to preindustrial times, resulting from direct fixation by all crops is about 40 million metric tons of nitrogen per year. This change alone, therefore, adds 40% to our estimate of preindustrial nitrogen fixation by land plants.

Alterations of land use by human activity can affect the nitrogen cycle by changing the fraction of bioavailable nitrogen that is denitrified rather than assimilated (or, equivalently, the fraction that flows through the subcycle of new nitrogen rather than the subcycle of recycled nitrogen). Overall, agriculture increases denitrification. The increased mineralization and nitrification when natural vegetation is replaced by crops leads to enhanced denitrification at sites where nitrates are carried by runoff. This effect generally dominates any local decrease in denitrification (an anaerobic process) where plowing aerates the soil. While dramatically increasing crop yields, modern agriculture mines nitrogen from the soil.

Combustion of Fossil Fuels. The combustion of fossil fuels mobilizes about 20 million metric tons of nitrogen per year, by injection into the atmosphere as nitrogen oxides (Logan, 1983; Müller, 1992). Two distinct classes of combustion processes are about equally involved: (1) processes where most of the nitrogen has originated in the fossil fuel as *fuel-bound nitrogen*, as is the case with coal combustion at electric power plants; and (2) processes where most of the nitrogen has originated as N_2 in the atmosphere, as is the case with combustion in gasoline and diesel engines. In both cases the global pool of bioavailable nitrogen is being augmented by mobilization from a bio-unavailable pool of nitrogen—in the first case from nitrogen in the pool of buried hydrocarbons, in the second case from the pool of atmospheric N_2 . The rate of mobilization of nitrogen through fossil fuel combustion is about five times smaller today than the rate associated with nitrogen fertilizer production.

¹⁵ There are 40 bushels of corn in a metric ton. Thus, yields of 4, 7, and 8 metric tons per hectare are, respectively, 64, 112, and 144 bushels per acre, and application rates of 100 and 200 kilograms per hectare are, respectively, 89 and 178 pounds per acre.

¹⁶ The model can be taken further. Corn contains about 1.3% nitrogen. Thus the harvested grain retains 39 of the first 100 kilograms of nitrogen added as fertilizer, but only 13 of the second 100.

During the combustion of coal with one percent by weight of fuel-bound nitrogen (a typical concentration), about three-fourths of the fuel-bound nitrogen is emitted to the atmosphere as N_2 and one-fourth is mobilized as nitrogen oxides (NO_x) (Bowman, 1991, Figure 9)¹⁷. The production of NO_x from fuel-bound nitrogen is usually much larger than the production of NO_x from the N_2 in the air. Thus, we can estimate the rate at which fuel-bound nitrogen enters the global atmosphere today as NO_x , as a result of the combustion of coal. Coal combustion transfers 2300 million metric tons of carbon to the atmosphere (see above), and coal is about 70% carbon by weight (Harte, 1988), so about 3000 million metric tons of coal, containing about 30 million metric tons of nitrogen, are burned. Assuming that one fourth of the fuel-bound nitrogen becomes NO_x , about 8 million metric tons per year of nitrogen as NO_x are produced globally from coal combustion. This estimate is close to estimates obtained from detailed information about the actual range of coals and burning conditions (Müller, 1992).

Nitrogen oxides in the atmosphere, along with sulfur oxides, are the principal precursors of acid precipitation. The potential acidity carried to the land in precipitation today is the equivalent of about 17 million metric tons of hydrogen ion (H^+) per year—and the 17 is, roughly, 10 natural and 7 anthropogenic (Schlesinger and Hartley, 1992). Nitrogen oxides are also crucial precursors of photochemical smog. Accordingly, there is a large effort underway around the world to reduce NO_x formation in combustion, involving large investments in pollution control technology.

Reducing NO_x formation during coal combustion requires increasing the fraction of fuel-bound nitrogen that becomes N_2 . This can be accomplished by staged combustion—burning a part of the fuel as a fuel-rich mixture, then adding air downstream and burning the rest of the fuel as a fuel-lean mixture (Bowman, 1992). The alternative of recovering the NO_x from the combustion waste stream, for input into fertilizer production, would be a demonstration of linking two industries in the spirit of industrial ecology; its current economics are dubious.

The second class of combustion processes that fix nitrogen involve combustion conditions where the temperature is so high that the N_2 molecule can be oxidized. The highest temperatures achievable for combustion of fuels in air occur at a particular ratio of fuel to air, known as the stoichiometric ratio, where, approximately, all the carbon and hydrogen in the fuel is oxidized to carbon dioxide and water, with neither excess air nor excess fuel. At the temperatures associated with stoichiometric fuel-air mixtures, the $N\equiv N$ bond of atmospheric nitrogen is often broken, but at not much lower temperatures the $N\equiv N$ bond is

¹⁷ The lower the concentration of N in the fuel, the higher the NO fraction, because the key N_2 formation reaction ($NO + N \rightarrow N_2 + O$) is quadratic in the concentration of single-N species and so becomes relatively more important when there is more N around. When fuel is 0.1% N by weight (a typical value for petroleum products), combustion converts roughly one-fourth of fuel nitrogen to N_2 and three-fourths to NO (Bowman, 1991, Figure 9).

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likely to remain intact. Stoichiometric burning characterizes diesel and gasoline engines¹⁸.

Human beings are probably also increasing the rate of combustion of biomass, relative to preindustrial times. Human beings deliberately burn biomass to cook and to heat houses, to clear land in slash-and-burn shifting agriculture, to prepare land for replanting by burning crop residues, and for other reasons. These activities probably increase pyrodenitrification more than they increase pyrofixation, and thus they decrease the global stock of bioavailable nitrogen.

We summarize our estimates of nitrogen fixation (in units of million metric tons of nitrogen per year): human beings add 150 today (90 from fertilizer, 40 from leguminous crops, and 20 from combustion) to 130 in preindustrial times, thereby approximately doubling the preindustrial global rate of nitrogen fixation.

Other Modifications of the Nitrogen Cycle

An increase in the global nitrogen fixation rate is contributing indirectly to the increase of three other important flows of nitrogen, each of which has other causes as well. Relative to preindustrial times one finds:

- (1) a doubling of runoff of nitrogen from soils, reflecting erosion and other failures in land management;
- (2) at least a doubling of the rate of ammonia volatilization, reflecting, especially, large increases in the world's population of cattle; and
- (3) a 50% increase in nitrous oxide emissions, from 10 to 15 million metric tons of nitrogen per year, reflecting largely unidentified changes in land use.

A Doubling of Runoff. No symbol has been used more frequently to illustrate the misuse of land by human beings than the loss of topsoil through erosion. Nitrogen and other nutrients move with the topsoil and also percolate through the soil; the

¹⁸ The fixation of atmospheric N_2 by U.S. automobile driving may be estimated with reference to the pollution control standards for nitrogen oxide emissions. These emission standards are written in *grams of nitrogen oxides per mile*, to which we must add: (1) the "grams" in question are grams of nitrogen dioxide (NO_2), so a "gram" of nitrogen oxide is 0.30 grams of nitrogen; and (2) the "mile" in question is not a mile of actual driving, but a mile of driving on a standard driving cycle intended to represent average driving. The current U.S. federal nitrogen oxide standard is 1.0 grams per mile (0.62 grams per kilometer); driving with no pollution controls produces about 4.0 grams per mile (2.4 grams per kilometer) (Bowman, 1992); and improved pollution control technologies, involving catalytic reduction of nitric oxides to N_2 in the exhaust gases, can probably achieve 0.2 grams per mile (0.12 grams per kilometer) (Bowman, 1992). In the United States today, cars are driven about two trillion miles per year (more than 100 million cars driven more than 10,000 miles each per year). If, on average, U.S. driving exactly meets the current federal nitrogen oxide emission standard, approximately 0.6 million metric tons of nitrogen fixation per year would occur, and the investments in pollution control would have avoided another 1.8 million metric tons of nitrogen fixation.

An estimate of a decade ago assigning about 8 million metric tons of global nitrogen fixation to all "mobile sources" (Logan, 1983) may still be correct today, because (1) the total number of vehicle-kilometers traveled globally has increased, but (2) stronger pollution controls have been imposed. An accurate estimate requires knowledge of actual levels of emissions per vehicle-kilometer (which may be higher than the emission levels achieved by new cars on specific driving cycles), as well as actual vehicle-kilometers of use for all vehicle types (cars, trucks, and planes) around the world.

result is elevated concentrations of nitrogen ions in rivers, lakes, and groundwater. These increased nitrogen ion concentrations are due not only to poor land practices that result in the loss of nitrogen previously in the soil, but also to increased inputs of nitrogen. Globally today, the nitrogen flow from land to the oceans in runoff is about 40 million metric tons of nitrogen per year (Schlesinger, 1991), approximately double the nitrogen flow in runoff in preindustrial times. It follows that the annual input to land of bioavailable nitrogen is greater today than in preindustrial times by 130 million metric tons—the difference between 150 million metric tons of increased fixation (making the approximation that all anthropogenic additions are inputs to land, not sea) and 20 million metric tons of increased runoff.

A Doubling of Ammonia Volatilization. Ammonia is volatilized from soils at a much higher rate today than in preindustrial times. Ammonia does not accumulate in the atmosphere, because, although not easily oxidized, it is extremely soluble and reactive (Warneck, 1988). The ammonium ion returns to earth when ammonia combines in water droplets with nitric acid to form ammonium nitrate and with sulfuric acid to form ammonium sulfate and bisulfate—water-soluble salts which are quickly washed out of the atmosphere by rain. Ammonia volatilization redistributes bioavailable nitrogen on the land, and it depletes the total nutrient pool available to land plants when the ammonium ions volatilized from the land are delivered to the sea.

Increasing the flow of ammonia in a side loop of the nitrogen cycle should increase the concentration of ammonium ion relative to nitrate ion, other things being equal, because the residence time of nitrogen in reduced form will be increased by cycles of volatilization, rainout, and return to the soil, that are unaccompanied by oxidation. Increased ammonia volatilization provides some mitigation of the acidification of the environment that accompanies increased nitrogen fixation, because the increased stock of ammonia, amines, and ammonium ions chemically neutralizes part of the increased stock of nitrate. Each local disruption of the nitrogen cycle, however, be it an increase in acidity or alkalinity, affects the local natural ecosystem and its biodiversity. When change is rapid, some species will adapt faster than others, stressing the ecosystem in countless ways. As discussed in the chapter by Schlesinger in this volume, a rapid increase in bioavailable nitrogen in any form is likely to lead to a loss of biodiversity.

The principal source of increased volatilization of ammonia comes by a curious route involving cattle. There are about 1.3 billion head of cattle on earth today, and, on average, each is a processor that delivers to the atmosphere, annually, about 16 kilograms of nitrogen as ammonia (Schlesinger and Hartley, 1992). The nitrogen is originally ingested in food, then excreted largely as urea; the urea slowly decomposes and gives off ammonia, just as happens by design when urea is used as a nitrogen fertilizer. The annual flow of nitrogen from land to the atmosphere as ammonia, associated with the chemical decomposition of the urea from cattle, is estimated by simple multiplication to be an amazing 20 million metric tons of nitrogen.

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The estimated total global ammonia volatilization (in units of million metric tons of nitrogen per year) is 75; other principal contributors are: another 12 for urea from animals other than cattle, 10 from biological processes in unmanaged ecosystems, 9 from biological processes in fertilized soils, and 13 from processes at the surface of the ocean (Schlesinger and Hartley, 1992). The multiplier that best describes the volatilization of ammonia today relative to preindustrial times is obviously somewhat arbitrary (among other things, one needs to estimate the preindustrial animal population and its diet), but it seems safe to conclude that human activity has at least doubled the rate of ammonia volatilization.

A 50% Increase in Nitrous Oxide Emissions. Assuming the rate of removal of nitrous oxide (N_2O) from the atmosphere has not changed from its preindustrial value (10 million metric tons of nitrogen per year), its 150-year residence time implies that any increment in emissions relative to preindustrial times should appear as an almost equal increment in nitrous oxide in the atmosphere. In fact, the atmospheric concentration has increased from 285 to above 310 ppbv, and is climbing at a rate of about 1 ppbv per year, equivalent to a rate of increase in nitrogen in the atmosphere in the form of nitrous oxide of about 5 million metric tons of nitrogen per year. The additional nitrous oxide production due to human activity, therefore, should also be about 5 million metric tons of nitrogen per year, and the total emissions of N_2O from all sources today should be about 15 million metric tons of nitrogen per year. This is a 50% increase in emission rate, relative to preindustrial times.

A Model of an Unbalanced Nitrogen Cycle

Is human activity now resulting in a net build-up of bioavailable nitrogen? To answer this question we need to compare how human activity has affected (1) the rate of mobilization of N_2 from the atmosphere (nitrogen fixation), and (2) the rate of return of N_2 to the atmosphere (denitrification). We earlier estimated that human activity (increased fertilizer production, planting of nitrogen-fixing crops, and combustion) has increased the global nitrogen fixation rate by 150 million metric tons of nitrogen per year. Can we also estimate the increase in the global denitrification rate?

One way to estimate the global denitrification starts from our estimate, immediately above, that human activity has increased the rate of N_2O emission to the atmosphere by 5 million metric tons of nitrogen per year. We assume that the increase in N_2O emission is due exclusively to denitrification and that in denitrification there is some definite ratio between the rates of emission of N_2 and N_2O . (In denitrification, N_2 is the principal nitrogen product and N_2O is a minor nitrogen product.) We see that there will be a net build-up of nitrogen in plant life unless the N_2/N_2O ratio in denitrification is higher than 30¹⁹.

¹⁹ The ratio here is grams of nitrogen as N_2 divided by grams of nitrogen as N_2O . It is, equivalently, a ratio of molecules of N_2 to molecules of N_2O . It is about 1.6 times the corresponding ratio of grams of N_2 to grams of N_2O , since the molecular weight of N_2O is about 1.6 times the molecular weight of N_2 .

The key ratio, the relative production of N_2 and N_2O in denitrification, is not well known, but it is probably less than 30. By one estimate, for denitrification on land, this ratio is 16 (Council for Agricultural Science and Technology, 1976). We conclude that one likely result of human activity is an increase in the amount of nitrogen available to the earth's biota.²⁰

Figure 9 and Table 1 present a simple model of the increases in flows and stocks of nitrogen since preindustrial times. The specific numerical estimates in this model require several arbitrary, but plausible assumptions about the subcycles of "new" and "recycled" nitrogen. For the subcycle of "new" nitrogen, we assume: (1) the global increase in the annual denitrification rate is 70 million metric tons of nitrogen; (2) the resulting annual increase in nitrogen in biota, 80 million metric tons of nitrogen, occurs only on land; and (3) this annual increase, in millions of metric tons of nitrogen per year, is apportioned 30 to plants, 40 to nitrates, and 10 to amines.

As for the subcycle of "recycled" nitrogen, we assume that recycling of the anthropogenic increment of nitrogen has been established only to the extent that on land the flows of nitrogen into the pool of bioavailable reduced nitrogen from the "new" subcycle and from the "recycle" subcycle are equal; thus, incremental mineralization is assumed to be 130 million metric tons per year. Recall that for the preindustrial nitrogen cycle on land, mineralization was estimated to exceed biological fixation of reduced nitrogen by a ratio of 12 to 1; it seems reasonable that the time required to establish such efficient recycling would substantially exceed the time since large human disturbances began.

Is the Nitrogen Build-Up Related to the "Missing" Carbon?

An increase in the global stock of bioavailable nitrogen could well contribute to an increase in the stock of reduced carbon in terrestrial biomass, by the nitrogen fertilization effect discussed above. For a rough estimate of the rate at which nitrogen would be incorporated in terrestrial biomass to account for the 1600 million metric tons of "missing" carbon per year discussed earlier, we assume that all the missing carbon is in plants (rather than in soil carbon) and assume a C/N mass ratio for assimilation of 50 to 1 (see above). An annual build-up in plants of 1600 million metric tons of carbon would be accompanied by a build-up of 30 million metric tons of nitrogen. Such a rate is roughly consistent with the data above. A more careful comparison would take into account carbon and nitrogen flows into soils, and carbon and nitrogen flows associated with deforestation.

Over the next few decades, stock-and-flow models of the global nitrogen cycle similar to the one presented in Figure 9 and Table 1 will become better established. Such models will build on a more precise understanding of historical data and on

²⁰ The argument for a net build-up of nitrogen in plants today is even stronger when one takes into account that not all of the increase in N_2O in the atmosphere is due to increased N_2O emissions in denitrification. Other possible sources are (1) increased N_2O emissions during nitrification, and (2) direct N_2O emissions from industrial processes used to make nylon and explosives. If, for example, anthropogenic effects have increased the rate of emission of nitrogen as N_2O in denitrification by only 3 million metric tons of nitrogen per year, there will be a net build-up of nitrogen in plant life unless the N_2/N_2O molecular ratio in denitrification is higher than 50.

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hundreds of careful field studies of C-to-N ratios, N_2 -to- N_2O ratios, assimilation-to-sequestration ratios, and other factors affecting the flows of carbon and nitrogen in many kinds of ecosystems.

Policies to Address Disruptions in the Nitrogen Cycle—Preliminary Thoughts

One source of disruption of the nitrogen cycle already receives concerted attention in public policy—the formation of nitric oxides in the combustion of fossil fuels. The attention arises from concern for local and regional air pollution: nitrogen fixation in combustion contributes to photochemical smog and to acid precipitation. Soil erosion, a second source of disruption through its connection to nitrogen in runoff, has been a historic target of agricultural policy. However, policy addressing fertilizer production and use—the most important source of disruption of the nitrogen cycle—is much less developed.

Indeed, in the framework of global change, fertilizer use may well deserve as much attention as fossil fuel use, the principal agent of disruption of the global carbon cycle. The chapter by Gadgil (this volume) describes many of the strategies for energy efficiency (effectively, carbon efficiency) being developed and tested around the world. Each of the many current strategies to modify fossil fuel use has its analog for fertilizer.

Industrial ecology urges attention to be paid to policies that encourage the closing of loops in materials flows. In this instance, one would search for ways to recover the nitrogen in crop residues, in the wastes from feedlots, and in waste streams at sites of centralized food processing and food consumption.

More traditional policies would seek to promote technological innovations that would lead to a future food production, distribution, and consumption system with a much higher nitrogen utilization efficiency. Some examples on the production side include: (1) improved soil management (including new crops or varieties and new crop combinations) to increase yield at a given level of fertilizer use; (2) improved mechanisms to get the nitrogen in fertilizer incorporated into plants; and (3) bioengineered crops, like nitrogen-fixing corn. Policies addressing food distribution would seek to achieve the reduction of pre-consumer spoilage. Policies addressing consumption—end-use nitrogen efficiency—would consider changes in diet. Analogous policies would address crops grown for purposes other than food, including crops for energy. Policies could be market-based or regulatory and could operate at the local, regional, national, or international level. One could, for example, imagine a regime of tradable permits to fix nitrogen.

Conclusions

The simplified modeling presented throughout this chapter carries several messages. First, the principal processes that govern the global cycling of nutrients have been identified. Second, the roles of biological and geochemical processes are remarkably intertwined. Third, although the quantitative details of reservoir models are highly uncertain, numerical estimates of stocks and flows are constrained by mass balances

and by element ratios like C/N and molecular ratios like N_2O/N_2 in particular processes. Fourth, research in environmental science is steadily deepening our understanding of every aspect of the grand nutrient cycles. Fifth, the human impacts on the grand nutrient cycles are significant disturbances.

It is not yet possible to assess accurately the significance for human beings of the disturbance of the global nitrogen cycle—either in absolute terms or relative to the disturbance of the global carbon cycle. The disturbance of the global carbon cycle is probably leading to global warming, and the disturbance of the global 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: that the earth's ecosystems have adapted to today's climate and today's nutrient sources and are likely, on balance, to be damaged by any rapid change in environmental conditions. As environmental science becomes more deeply understood, the nitrogen cycle may well take center stage in studies of global change.

Comparing the global carbon and nitrogen cycles has particular messages for technology and policy. The global nitrogen cycle has strayed far from its preindustrial steady state, yet the nitrogen cycle is scarcely part of public discourse. The global carbon cycle, by contrast, is well known to the public via the greenhouse effect and deforestation. The principal human activity disturbing the carbon cycle, fossil fuel use, has long been the subject of innovations in technology and policy designed to reduce environmental impact. The principal human activity disturbing the nitrogen cycle, fertilizer use, has had less attention of this kind. Reasoning by analogy, it may be productive to think about fertilizer use in terms of the quantification of environmental externalities, the delivery of end-use efficiency, and the creation of competitive markets—ways of thinking about fossil fuel use that have led to some partial successes in the grand task of conducting the human enterprise within environmental constraints.

Acknowledgments

We have been helped immeasurably by general guidance and expert advice from Allison Armour, Tom Bowman, Francis Bretherton, Bill Chameides, Tom Graedel, John Harte, Wendy Hughes, Sivan Kartha, Aslam Khalil, Ann Kinzig, Pamela Matson, Steve Pacala, Vern Ruttan, David Skole, and Valerie Thomas.

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