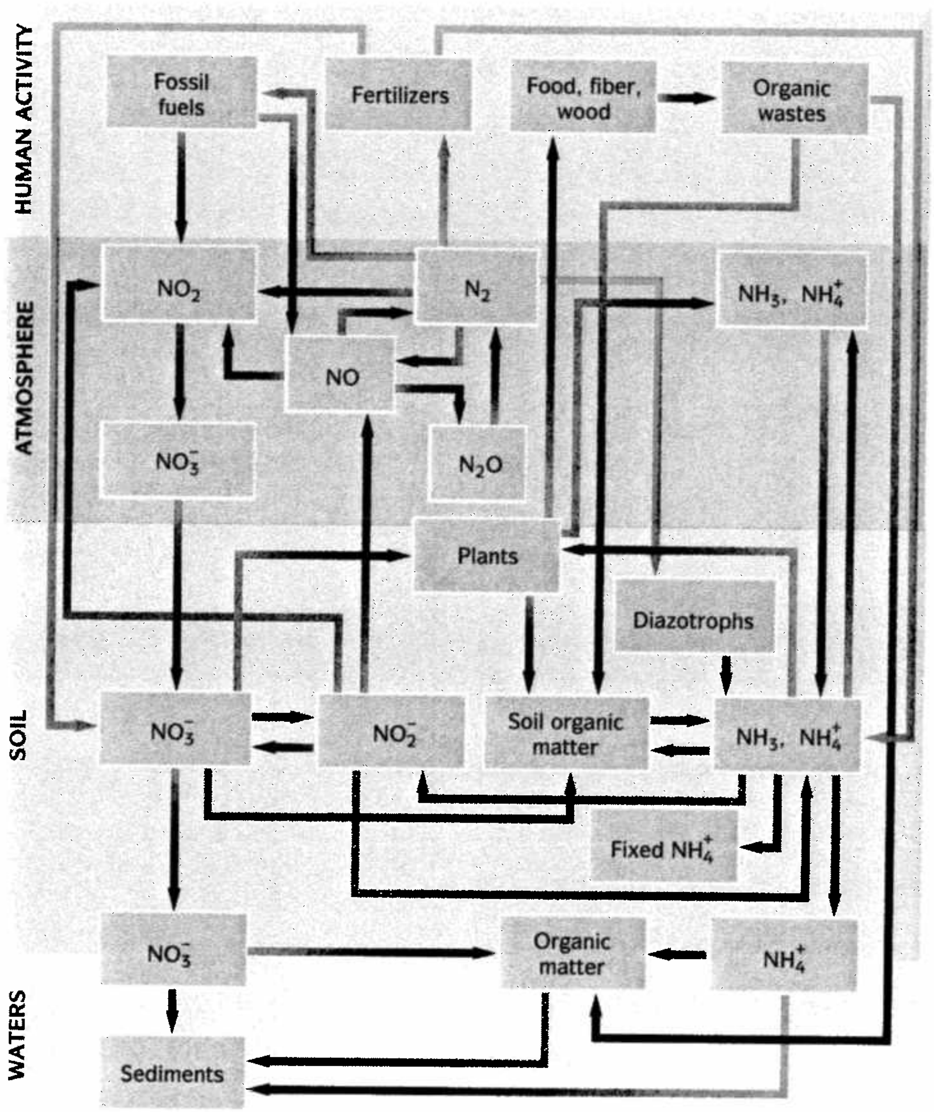
CHAPTER 5

Reactive Nitrogen in the Biosphere

The nitrogen stored in the bodies of all the people on Earth adds up to a minuscule reservoir. In 2000 the world population of 6.1 billion people—with a mean mass of 50 kg per person, and proteins averaging about 15 percent of body weight—stored about 6 Mt of nitrogen, equal to only about one-billionth of the atmosphere's nitrogen stores. But in order to maintain, and to gradually expand, this negligible reservoir, we now add to the world's agricultural soils the mass of reactive nitrogen at least five times as large as we did just before the end of the nineteenth century.

The reactive nitrogen that we introduce in synthetic fertilizers and combustion gases now rivals the total fixed by all bacteria in natural terrestrial ecosystems. Moreover, in every intensively cultivated region, and especially where large-scale agriculture is a neighbor to cities and industry, inputs from human activity are greatly surpassing natural flows of reactive nitrogen. On smaller scales, from local watersheds to individual fields, they dominate natural flows by more than an order of magnitude.

Our large-scale interference in nitrogen's biospheric flows began with the emergence of agriculture and increased only very slowly with the development of intensive farming. The invention of a



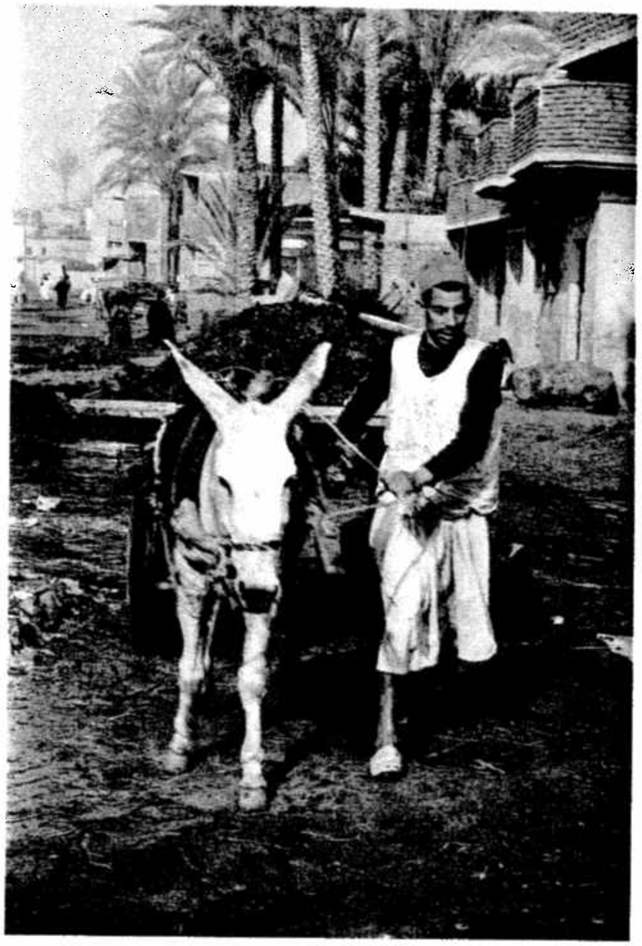
The terrestrial nitrogen cycle centered on plants. Red arrows show only the principal direct human interferences (were the diagram to trace indirect effects just about every arrow would have to be red). Biofixation (N_2 to diazotrophs) is, of course, a natural process, but we have been intensifying it by planting every year more than one-tenth of the world's cultivated land with leguminous food and feed crops. The fixed NH_4^+ pool represents the nutrient bound in clay lattices and not available for rapid cycling.

commercial method for synthesizing ammonia was the breakthrough that raised human intervention in the nitrogen cycle to an entirely new level—and the application of synthetic fertilizers remains responsible for the largest share of reactive nitrogen introduced by humans into the biosphere. During the late 1990s, synthetic fertilizers contributed annually about 80 Mt N, compared to at least 30 Mt N fixed by leguminous crops. Gaseous emissions from the combustion of fossil fuels contain close to 30 Mt N a year.

Human activities thus add around 140 Mt of reactive nitrogen a year to the biosphere, in both oxidized and reduced compounds. The first class, commonly subsumed under the NO_y label, is made up largely of NO_x, NO_3^-, HNO_3, and N_2O; the second class, bundled under the NH_x label, contains NH_3, NH_4^+, and NH_4SO_4. These compounds are found throughout the biosphere, from deep aquifers (containing leached NO_3^-) to cumulonimbus clouds (absorbing volatilized NH_3), and beyond them to the stratosphere (where N_2O destroys ozone). Although their augmented presence in the biosphere has received much less public attention than the rising levels of CO_2, these compounds, too, have diverse and potentially serious consequences.

Nitrogen and Traditional Agriculture

The earliest farmers relied on nature to supply the nitrogen their crops needed. This nitrogen came from the mineralization of dead organic matter, from atmospheric deposition, and from free-living diazotrophs. Settled farmers in regions where cultivable land was scarce were the first to face the necessity of augmenting the natural nitrogen supply. Their crops needed a greater supply of nutrients if the farmers were to get larger harvests from the same area of land. The common practice of burning unused crop residues returned mineral nutrients to the soil, but it released nearly all phytomass nitrogen to the atmosphere. Farmers often plowed in straws or stalks not needed for household fuel, bedding, or animal feed, but these plant parts are relatively poor in nitrogen. Consequently, this practice recycled only a small fraction of the element assimilated by crops.



Transporting manure to fields and distributing it to plants have been unappealing and laborious tasks in all traditional agricultures. This Egyptian peasant, and his donkey, get at least a bit of modern relief from the rubber wheels on the manure cart.

One set of practices succeeded particularly well in expanding nitrogen's soil stores: farmers would gather organic wastes—above all animal and human excrements and crop residues, but also food-processing wastes, wild grasses, leaves, and aquatic plants—let the wastes ferment, then apply them repeatedly to field or garden crops. These practices—requiring a great deal of unappealing and heavy labor—eventually reached their highest intensity in western Europe, Egypt, and East Asia. The Chinese commonly applied more than 10 t of fermented wastes per hectare every year, and Dutch applications peaked at more than 30 t of manure per hectare a year during the nineteenth century.

How much nitrogen the applied manure contained is difficult to estimate. The element's share in fresh organic wastes is highly variable, but generally low (usually just between 1 and 2 percent for all but poultry manures and legume crop residues). Moreover, a large part of the nitrogen is lost during fermentation and after field spreading, above all as NH_3 escapes into the air through volatilization and NO_3^- into waters through leaching. These losses can add up to more than two-thirds, or even four-fifths, of the nitrogen initially present. In some cases, the recycled nitrogen actually made available to crops might amount to no more than the nitrogen brought in precipitation (around 10 kg N/ha a year)—or it could greatly surpass all natural inputs and supply almost 100 kg N/ha a year.

Traditional farmers could add larger, and much more stable, amounts of additional nitrogen only by deliberately including leguminous plants as part of their crop rotations. All ancient agricultures depended on leguminous crops as a leading source of nitrogen. Archaeologists have found the remains of peas and lentils together with barley and wheat in the earliest settled communities of the Middle East. Farmers in ancient China rotated soybeans, beans, peas, and peanuts with millets, wheat, and rice. Lentils were the dominant legume cultivated in India, but Indians also grew peas, chickpeas, and pigeon peas. Medieval and premodern Europe favored peas and beans, sub-Saharan Africa peanuts, cowpeas, and bambara groundnuts. Beans were commonly grown in the same plot with corn by all settled New World cultures. These practices owed their virtually universal success to the fact that they not only enriched soil with nitrogen, but also produced a crop supplying amino acids that were missing in cereal grains.

The ancients often used legumes as green manures—incorporating immature plants into soil by hoeing or plowing. Theophrastus, a Greek botanist of the fourth century B.C., noted that "the bean best reinvigorates the ground" and that it also rots easily, "wherefore the people of Macedonia and Thessaly turn over the ground when it is in flower." Romans adopted and extended this practice. All the great sources of Roman agronomic wisdom—Cato, Varro, Pliny, and Collumela—extol legumes. Collumela correctly recognized that "of all legumes, alfalfa is the best."

In addition to planting legumes, many Asian farmers took advantage of a symbiosis between *Azolla pinnata*, a small floating freshwater fern common in tropical Asia, and *Anabaena azollae*, a nitrogen-fixing cyanobacterium living in a cavity of the fern's leaflet. Many farmers in Asia today still rely

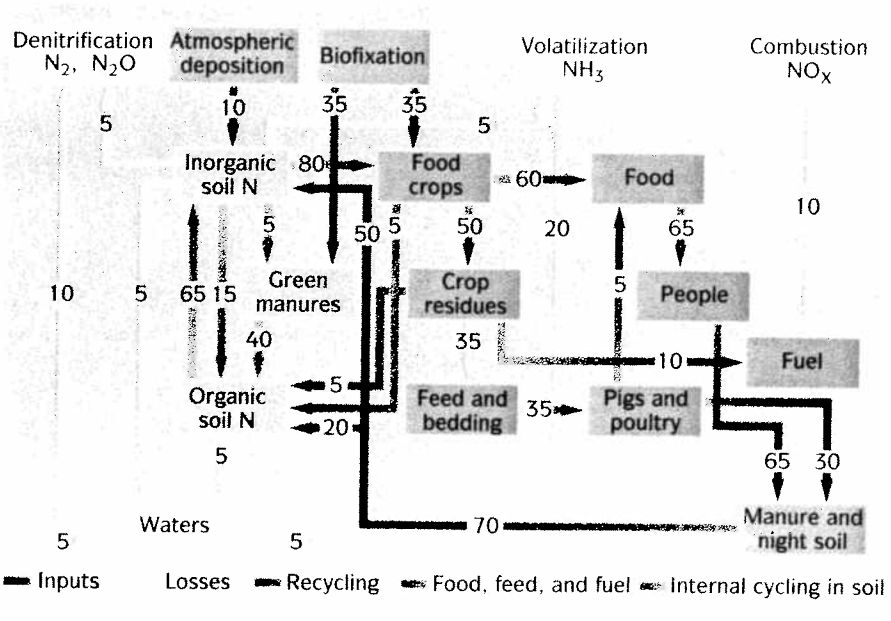
Tiny plants of *Azolla* fern, whose leaf folds harbor nitrogen-fixing *Anabaeana*, cover the surface of a rice field.

on *Azolla* and its symbiont. They grow the fern in nurseries and distribute it over flooded rice fields, where the floating *Azolla* can double its mass in just a few days. Then, after draining away the water, they plow the *Azolla* in and transplant rice seedlings from their nurseries. If the fern regenerates too vigorously, its dense mats surrounding the growing rice plants must be buried by hand so that its continuous growth does not reduce the crop yield. Its mineralized nitrogen helps to raise rice yields in paddies throughout monsoonal Asia, from tropical Indonesia to subtropical China.

Some nutrient flows in traditional intensive agricultures can be reconstructed from a variety of historical sources. Naturally, the oldest extant descriptions offer little in the way of quantitative information, but ancient Chinese records contain a sprinkling of revealing numbers. For example, the *History of the Han Dynasty* implies that during the fourth century B.C. in the state of Wei a typical peasant was expected to provide each of his five family members with nearly half a kilogram of grain a day. That is equal to North China's mean during the 1950s, before the introduction of irrigation pumps and synthetic fertilizers.

More modern sources range from Stamford Raffles's meticulous descriptions of farming in early nineteenth-century Java to John L. Buck's comprehensive surveys of cropping in China during the 1920s and 1930s. These accounts contain figures on crop yields and animal husbandry, as well as on such farming inputs as manure applications. They allow a fairly good reconstruction of nitrogen flows and carrying capacities in the world's most productive traditional farming practices.

I have used this diverse information to prepare detailed nitrogen balances for a number of preindustrial agroecosystems. The simplest, and oldest, ones produced a single crop in a field each year, and relied on extensive fallowing. In the most complex traditional systems, farmers rotated more than half a dozen crops, produced up to three crops a year from



The nitrogen flows in traditional intensive Chinese farming, as formerly practiced in Sichuan. The Chinese assiduously recycled organic matter to provide high nitrogen inputs, and their efforts actually resulted in a slow accumulation of the nutrient (about 15 kg N/ha a year) in the organic soil pool.

the same field, and recycled organic wastes intensively. The fertile parts of China's subtropical region are the best example of this kind of farming, which supported higher population densities than any other purely organic agriculture.

In early permanent agricultures, the nitrogen supplied by farmers almost always amounted to less than one-fifth of all nitrogen available to plants, and commonly less than one-seventh, or even one-tenth. These agricultures could not support more than two people per hectare of farmland even in regions of fertile soils and plentiful water. The fields of ancient Egypt supported a mean of between 1.5 and 2 people per hectare, those of northern China below two people until the Tang dynasty (A.D. 618–906), and the average for the whole basin of Mexico before the Spanish conquest in 1519 was about four people per hectare.

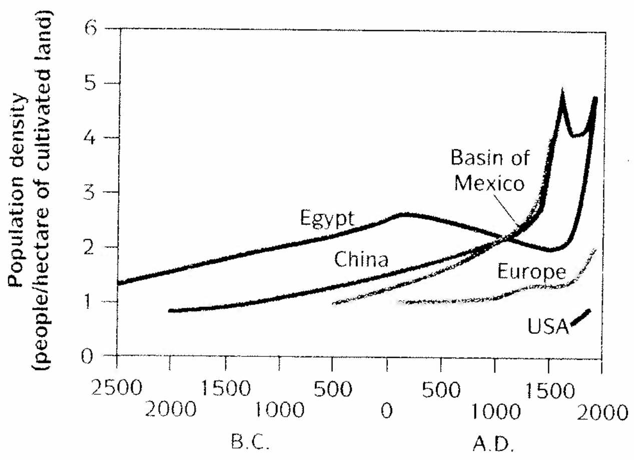
By the early nineteenth century Dutch farmers supplied up to three-quarters of all their fields' nitrogen, and at the same time peasants in South China's most productive regions provided shares that were similarly high. The Chinese relied on a combination of recycled human and animal wastes, green manures, food legumes, and, in the rice region, fixation by *Anabaena-Azolla*; together these inputs provided annually up to around 200 kg N per hectare of arable land, enough to produce 200 to 250 kg of food protein.

This protein output determined the maximum number of people that could be supported in the overwhelmingly vegetarian societies of the preindustrial world. In places where peasants could grow crops year-round on good soils, a hectare of farmland could support as many as 11 to 15 people, all deriving about nine-tenths of their food energy from staple grains. The Aztecs achieved similar peak densities by cultivating extraordinarily productive *chinampas*: these were fields, raised above the shallow lake waters of the basin of Mexico, enriched by nitrogen from alluvial muds and recycled plant residues.

Chinampas, raised fields in the Valley of Mexico, were extraordinarily productive. Their corn and vegetable harvests played a critical role in sustaining the population of Tenochtitlán, the great Aztec capital founded in 1325. The small remaining area of chinampas is now a park.

China's overall population densities had to be much lower than the mean densities possible in the most productive areas: not all farmland could yield so much, and some had to be used to produce nonfood crops, above all fibers. A region harvesting two crops a year supported just over six people per hectare in the early twentieth century, and the national mean was over five people per hectare of arable land. A density of about five people per hectare was also the highest level, albeit with diets richer in meat and including dairy products, that the best farming areas in Europe could achieve.

But unlike China or the Netherlands, most European countries arrived at the nitrogen barrier relatively late. For many centuries, whenever the output became inadequate, they simply converted more forests, grasslands, or wetlands to fields: average yields remained low, but larger areas produced more food. Only when these conversions reached their practical limit did the intensification of nitrogen flows become the only way to increase harvests. Yet the amount of recyclable wastes that could be applied to fields is obviously limited by crop yields and by the number of animals and people. Only one option was available to early modern societies looking for a way to greatly expand the nutrient supply: a more intensive planting of leguminous forages, such as clover and alfalfa, that would provide fodder for livestock.



The population densities supportable by traditional farming reached their maxima in the irrigated agricultures of China and Egypt and in the Basin of Mexico before the European conquest. European dryland farming was much less productive, as was the extensive grain cropping practiced in the nineteenth-century United States.

The more fodder was grown, the more livestock could be raised, and the more manure produced. Moreover, these leguminous forages fixed more nitrogen than they consumed in a growing season, leaving some of it in the soil to be assimilated by cereals or oil crops that followed forages in rotations. The combination of nitrogen fixed by legumes, manure returned to fields, and more abundant crop residues plowed in after harvests produced increased yields in many European countries. First adopted in northwestern Europe, this new agricultural system allowed a huge transfer of labor from farming to industry. English historian G. P. H. Chorley believes that it is not fanciful to conclude that this now so neglected innovation was of comparable significance to steam power in the economic modernization of Europe during the nineteenth century.

But this strategy is feasible only in areas where farmland is relatively plentiful. In other regions a more fitting choice would be to rotate leguminous food grains (beans, peas, lentils) more frequently with staple cereals. But this practice, too, has its drawbacks: legumes have lower yields than cereals, they are more difficult to digest, and they cannot be made easily into bread or noodles.

Beneficial though it was, the introduction of forage legumes did not solve the long-term challenge of providing enough nitrogen. As soon as nineteenth-century agronomists had understood the element's critical role in food production and learned of its scarcity in reactive form, they began to worry that the nitrogen supply would become inadequate. In contrast, the other two required macronutrients—potassium and phosphorus—were found to be much less frequently the factors limiting crop yields, and they were also much easier to supply. For potassium it was largely a matter of mining abundant potash (K_2O) deposits, whereas phosphorus became readily available with the commercialization of superphosphate production (the treatment of phosphate rocks with H_2SO_4 to convert them into more soluble compounds). The invention of this process stimulated the discovery of rich phosphate deposits after 1870.

No comparably simple solutions were available for nitrogen, and by the late 1890s a looming nitrogen barrier threatened all intensive agricultures. Various forms of fertilizer had been tried during the century, but none proved adequate in the long run. Both the inorganic nitrogen from Chilean nitrates ($NaNO_3$), discovered in 1821, and organic guano, deposited over millennia by birds in the rainless climate of some tropical islands, could provide only a temporary reprieve: the relatively small deposits clearly could not support the anticipated expansion of harvests in the twentieth century.

Some farmers fertilized their crops with ammonium sulfate, $(NH_4)_2SO_4$, recovered from coking ovens, but this compound made only a marginal contribution. Another source of fertilizer was the cyanamide process, in which coke (nearly pure carbon) reacts with lime (CaO) and the resulting CaC_2 combines with nitrogen to produce $CaCN_2$. Although this technique was successfully commercialized in Germany in 1898, its potential output was limited, and its energy requirements were very high.

The energy requirements for another promising source of nitrogen—the production of nitrogen oxides by blowing a mixture of nitrogen and oxygen through an electric spark—were also very high. Before the end of the eighteenth century Henry Cavendish had showed that the sparking of nitrogen and oxygen would produce nitrogen oxides, readily convertible to nitric acid, which, in turn, is used to produce fertilizer nitrates. Although the reaction was easily accomplished in a laboratory, it demanded inexpensive electricity for large-scale commercialization. Norway, with its cheap hydroelectricity, used the process after 1903, but its total output remained small.

The Synthesis of Ammonia

The fundamental breakthrough in the quest for an abundant and affordable nitrogen fertilizer came only with the brilliant invention of ammonia synthesis by Fritz Haber and Carl Bosch. Carl Bosch was hired in April 1899, fresh with a doctorate in chemistry from the University of Leipzig, by the Badische Anilin- und Sodafabrik (BASF), Germany's leading chemical company. Eight months later he started to work on the synthesis of ammonia, turning to this effort full-time in 1902. For years he had little to show for his work, and it was Fritz Haber, who worked since 1894 at the Technische Hochschule in Karlsruhe, who demonstrated to the BASF a promising experimental process for ammonia synthesis.

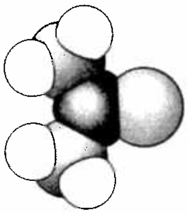
Haber began his work in 1903, by proving that ammonia could be synthesized at a temperature of "just" 1000 °C in the presence of an iron catalyst, which he selected after testing more than 1000 materials. But the yield of this reaction was negligible, and Haber's real success came only when the physicist Walther Nernst, who later received a Nobel Prize for formulating the third law of thermodynamics, pointed out that increasing the pressure should further lower the reaction temperature. In 1909 Haber and his assistant Robert Le Rossignol employed pressures of 175–200 atmospheres and temperatures of 550–600 °C to synthesize ammonia in the presence of an osmium catalyst.

As with so many chemical processes, converting this bench reaction to an engineering reality was an immense challenge. Carl Bosch had lost the experimental race, but he found a brilliant solution to the second difficulty after BASF acquired the rights to Haber's process. Bosch built a double-walled reaction chamber that solved the greatest design problem, the deterioration of the metal when subjected simultaneously to high temperatures and pressures. He contained the high temperature within an inner wall of soft, low-carbon steel and forced a pressurized mixture of cold hydrogen and nitrogen into the space between the inner and outer walls. Consequently, the inner shell was subject to equal pressure from both sides, and although the strong outer shell was under high pressure, it remained much cooler. Bosch also adapted to the process a cheaper way of generating hydrogen by passing steam over hot coke.

The first commercial factory for ammonia synthesis was completed at Oppau near Ludwigshafen am Rhein in 1913—but the ammonia it produced was used initially not to increase crop yields, but to serve as a feedstock for making explosives. Shortly after the beginning of World War I in 1914 the plant's ammonia began to be used in the production of nitric acid, and a new plant with a capacity of 130,000 tonnes was completed at Leuna near Merseburg before the end of the war. The output from these plants was enough to make Germany self-sufficient in the sodium nitrate (synthesized from NH_3) needed for producing explosives. Undoubtedly, the Haber-Bosch synthesis was critical in prolonging World War I: blockaded Germany could do without imports of Chilean nitrates, and its troops had enough ammunition to keep launching devastating offensives on all fronts for nearly four years, until the spring of 1918.

The commercial diffusion of the Haber-Bosch synthesis proceeded slowly for several decades. The first nitrogen fertilizers based on ammonia were produced in the early 1920s, but the economic setbacks of the 1930s and of World War II kept global ammonia synthesis below 5 Mt until the late 1940s. As with many other innovations of the late nineteenth and early twentieth centuries, the time of widespread commercial application came only during the 1950s. Farmers applied higher amounts of nitrogen first to a few major crops in regions where yields were already high (northwestern Europe, the U.S. Corn Belt, Japan's Kanto plain). But, even in the United States more than one-third of all farmers still did not use any synthetic fertilizers by the late 1950s. Then several improvements in the Haber-Bosch synthesis led to a major leap in the efficiency of ammonia synthesis, and to lower fertilizer prices.

Better compressors and lower reaction pressures sharply cut the consumption of electricity (by more than 90 percent), and made possible larger and more economical plants. At the same time, natural gas almost completely displaced coal as both the fuel and the feedstock (the source of hydrogen for NH_3



Urea
$CO(NH_2)_2$

Granules of urea, the world's most important nitrogen fertilizer.

Carl Bosch and Fritz Haber

The stories of Carl Bosch and Fritz Haber combine admirable scientific triumph and profound personal tragedy. In 1919 Bosch became head of BASF's managing board, and in 1925 of IG Farbenindustrie's board, and his leadership was essential in developing the hydrogenation of brown coals at Leuna. This process converted coal to synthetic gasoline, a fuel that eventually helped Hitler to prolong World War II. Bosch received a richly deserved Nobel Prize for chemistry of high-pressure reactions in 1931, but he became increasingly depressed after Hitler's rise to power in 1933. Bosch died in 1940—before his protégé Carl Krauch led IG Farbenindustrie into Auschwitz and historical infamy.

Fritz Haber's fate was more tragic still. In 1911 he became the Director of the Kaiser Wilhelm Institute of Physical Chemistry, where he developed, at the request of the German Gen-

Carl Bosch (1874–1940), the brilliant chemical engineer who turned Haber's concept into commercial reality.

synthesis), a substitution that further lowered the energy cost of the process. Finally, the adoption of a nickel catalyst, or one made of iron, potassium, and calcium combined, increased the reaction yield.

The earliest, coal-based, ammonia plants needed more than 100 MJ to synthesize a kilogram of ammonia; by 1950 plants using natural gas typically needed less than 50 MJ of energy; and the best plants in the year 2000 synthesize one kilogram of ammonia with less than 30 MJ of energy consumed as natural gas and electricity. The U.S. firm M. W. Kellogg Company is the most important provider of this efficient synthesis: more than 150 of its large-scale plants were on stream or on order in 1995, compared to just 25 plants designed by its main competitor.

Ammonia, containing 82 percent nitrogen, became the leading nitrogen fertilizer in North America. But because it is a gas under normal atmospheric pressure, it requires special means of

Fritz Haber (1868–1934), the inventor of the catalytic synthesis of ammonia.

eral Staff, the use of chlorine gas against entrenched troops. He hoped that this invention would bring a speedier victory to Germany and thus end the protracted suffering of trench warfare. The first chlorine gassing at Ypres on April 22, 1915, led to massive allied casualties. On its eve, Haber's wife, Clara Immerwahr, committed suicide. A year later Haber became the Chief of the German Chemical Warfare Service, and when the armistice came the Allies considered him a war criminal. Nonetheless, the Swedish Academy awarded him the Nobel Prize for chemistry in 1919 for the revolutionary ammonia synthesis. Disillusioned and depressed, he continued his research until Nazi anti-Semitism forced him into exile in England. He died in Basel, en route to Italy, in 1934.

These two great *dramatis personae* are now hardly remembered by anyone other than industrial chemists—yet their invention, unchanged in its fundamentals but greatly improved in its performance, is the source of by far the most far-reaching human intervention in the global nitrogen cycle.

shipping, storage, handling, and application (it is injected into soil through hollow tubes). All this is obviously costly, so fertilizer plants commonly proceed one step further. They use ammonia that they produce to synthesize urea, $CO (NH_2)_2$, a solid compound that contains more nitrogen (almost 47 percent) than any other solid fertilizer. Urea granules are easily bagged, stored, and broadcast by hand onto small fields. During the early 1990s urea supplied about two-fifths of the world's fertilizer nitrogen, and it had three-quarters of the fastest growing market, in East Asia.

The Growing Dependence on Nitrogen Fertilizers

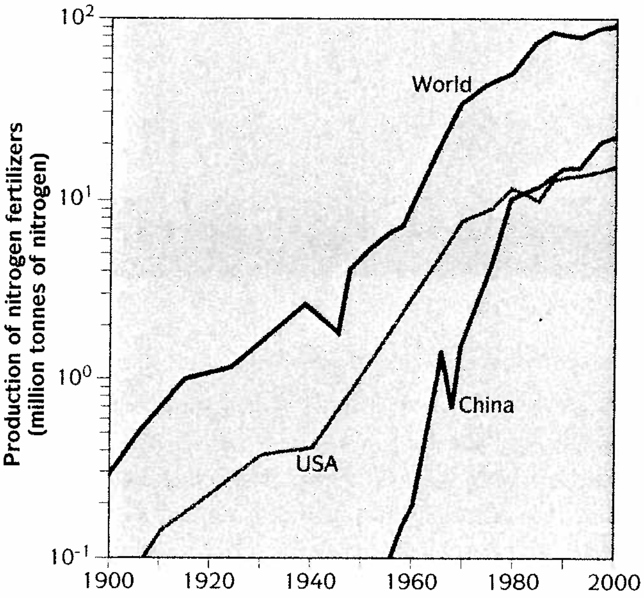
Growth of the global output of nitrogen fertilizer resumed its exponential rate after the end of World War II, reaching 10 Mt a year by the end of the 1950s. The total output had more than quadrupled by 1975, and it nearly doubled again by 1990. As a result, half of all nitrogen fertilizer produced between 1913 and 2000 has been synthesized since 1976. At the same time, there has been a shift in the shares used in rich and poor countries. In the early 1960s rich countries applied more than nine-tenths of all fertilizer nitrogen, but by 1980 their share was down to two-thirds and the rich and poor worlds had drawn level by 1988. By 2000 the poor countries were applying about three-fifths of the fertilizer nitrogen used worldwide.

Half a century ago synthetic nitrogen fertilizers made a marginal difference to global food output—but without their rising application the global population would not have surpassed 5 billion on its way to yet another doubling by the middle of the twenty-first century. In the mid-1990s the world's farmland received annually about 170 Mt of nitrogen, and synthetic compounds supplied about 45 percent of that total, while crop harvests removed about half. Since plants on the average absorb roughly half of all applied fertilizer, this means that synthetic compounds now provide half of all nitrogen used by the world's crops. And because crops supply, indirectly through animal feed as well as directly, about three-quarters of all nitrogen in edible proteins (the rest comes from fish catches and from livestock raised by grazing), synthetic nitrogen fertilizers supplied protein for at least every third person worldwide.

This conclusion is both an overestimate and an underestimate of the global importance achieved by the Haber-Bosch synthesis. The conclusion is an overestimate because nitrogen fertilizers in rich countries have not been used to secure survival or decent nutrition, but rather to satisfy a rising demand for animal foods. Western nations could halve their meat and dairy consumption and still enjoy adequate nutrition. In the world's most populous nations, in contrast, the use of nitrogen fertilizers is a matter of existential necessity.

China provides an enlightening illustration. In the early 1960s the Chinese applied on the average less than 10 kg N/ha, compared to about 20 kg N/ha in the United States. By the late 1990s China had to feed 600 million more people while coping with the net loss of at least one-fifth of its farmland. The only way the country could achieve the yields it so urgently needed was to accelerate its use of nitrogen fertilizers.

In the early 1980s China became the world's largest consumer of fertilizer nitrogen, and a decade later the world's largest producer. By 2000 Americans applied an average of about 60 kg N/ha—but the Chinese average was 190 kg N/ha, and in the country's most intensively cultivated provinces (occupied by some 300 million people) it surpassed 300 kg N/ha. A hectare of farmland receiving over 300 kg N can now produce annually enough food



The global rise in the production of synthetic nitrogen fertilizers. China is now both the largest producer and the largest user of nitrogen fertilizers.

for more than 20 people on a high-protein diet, and for more than 30 people on a diet that is largely vegetarian.

Synthetic compounds now supply almost three-fifths of all nitrogen required by China's crops, and because more than nine-tenths of the country's food protein comes from crops, about half of all nitrogen in China's food protein originates in the Haber-Bosch synthesis. That process thus ensures the survival of more than 500 million people in China. A number of other crowded countries are developing a similarly high dependence on nitrogen fertilizers.

Every country producing annually more than about 100 kg of protein per hectare is in this category. This rate is the regional or national maximum that can be achieved by traditional farming, providing a barely adequate and largely vegetarian diet. In the early 1990s the group of countries surpassing this rate included, besides China (producing 250 kg protein/ha), Egypt (500), Indonesia (170), Bangladesh (170), the Philippines (125), and Pakistan (110). India is on the threshold, but about half of its protein already comes from land that yields well above the maximum for traditional farming.

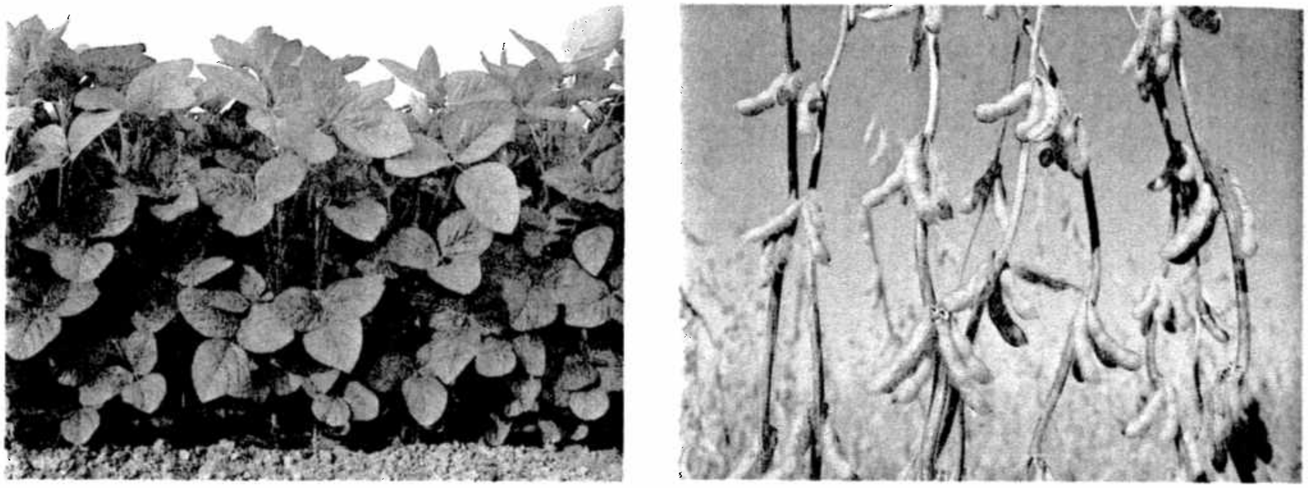
The expansion of the Haber-Bosch synthesis did not eliminate traditional ways of providing nitrogen to crops. The growth of animal husbandry has made recyclable organic wastes more available, and in some places it has led to extraordinarily high applications of manure. In Miyazaki prefecture in Japan, the annual output of nitrogen in animal wastes now prorates to an astounding 600 kg per hectare of cropland. Adding so much manure to cropland saturates the soil with nutrients, and the surplus not assimilated by crops can cause serious water pollution. In the Netherlands the output of cattle and pig manure reached nearly 100 Mt (in fresh weight) a year by the mid-1980s—and in 1987 a new Dutch law limited the amount a farmer can spread on his own land, creating stockpiles of waste.

Legumes are still planted extensively—they are grown on about a tenth of the world's cropland—but less frequently to be fed to humans. Affordable animal protein has displaced the protein from legumes in all rich countries. This substitution, now underway in Asia and Latin America, has brought the cultivation of food legumes to a nearly universal decline. Among large populous countries only India has been expanding its planting of lentils and peas. In contrast, U.S. plantings of soybeans grown for feed (and also for oil) rose from just a few thousand hectares in the 1930s to nearly 30 Mha by the late 1990s. These fields produce more than 50 Mt a year. Brazil has expanded its plantings even faster, from a negligible harvest in the early 1960s to more than 30 Mt in the late 1990s.

How Much Nitrogen Do Legumes Fix?

While leguminous crops are obviously important in terms of their nutritional contribution, economic value, and planted area, it is much less clear how much nitrogen they actually fix. There is no simple way to measure biofixation, even in the laboratory, and neither of the two most common methods of assessing biofixation in crops is really satisfactory. Similar, or even greater, uncertainties of measurement and interpretation arise when using other methods. Even a perfect technique could not overcome the challenge of generalizing across wide ranges of climates, soils, cultivars, crop densities, and microbial strains. Not surprisingly, published rates of nitrogen fixation for common cultivated legumes differ at least two- to threefold, and for some species they diverge by an order of magnitude. This is true for the soybean, the world's most important, and hence most studied, feed legume.

Soybean fixation rates have been measured at extremes of 15 and 330 kg N/ha a year. A very large fixation range has been also found for the



Growing soybean plants (left) and mature, drying pods of the legume (right). Now the world's most important leguminous grain crop, soybeans are cultivated mostly as a high-quality animal feed.

most widely cultivated food legume, the common bean (*Phaseolus*). Measured annual maxima have surpassed 100 kg N/ha, but in general the plant has just about the lowest fixation rates among food legumes: in many fields in its Latin American homeland, it provides only a few kilograms of nitrogen per hectare a year, and its typical contributions are below 60 kg N/ha.

The practice of applying synthetic fertilizers further compounds the difficulties in estimating biofixation by leguminous crops. Adding mineral nitrogen at low rates can stimulate nodule formation and nitrogenase activity, but adding a lot can suppress them. Given the variety of rhizobia, crop cultivars, and soils, there is no sharply defined transition between the two states: spreading as little as 15 kg N/ha at sowing reduces fixation in some bean cultivars, while applying nearly three times the amount has no depressing effect on others. Moreover, adding even relatively high levels of fertilizer nitrogen may stimulate nodulation when accompanied by additional phosphorus and sulfur.

Because of all these uncertainties, it is no exaggeration to conclude that we do not have a truly representative biofixation rate for a single major leguminous crop; that the average multipliers commonly used to calculate regional or global biofixation for all leguminous crops are hardly better than guesstimates; and that there may have been a general tendency to overestimate actual fixation rates in the field.

On the other hand, estimates of biofixation in the tropics probably underrate contributions from such woody forage legumes as *Leucaena* and *Sesbania*, which produce anywhere between 100 and 300 kg N/ha a year. We may find that new discoveries call for another upward readjustment of tropical biofixation rates. The largest gain could come from recognizing the major contributions made by newly identified diazotrophs. Certainly the most impres-

Measuring Biofixation in Crops

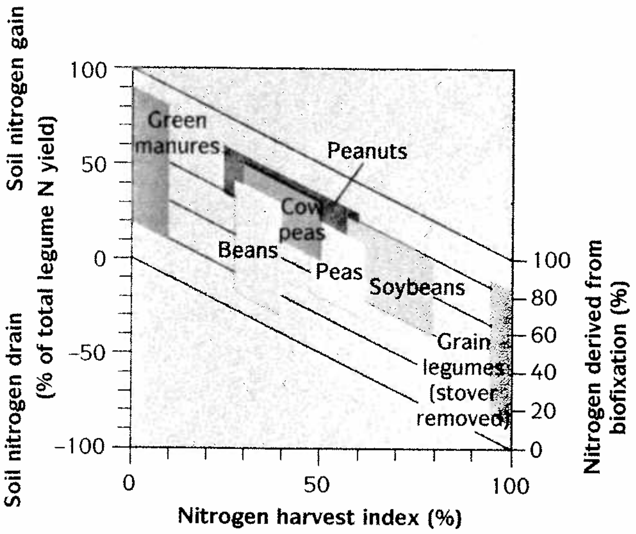
The first of the two common methods for assessing biofixation, introduced in the 1940s, makes use of the stable isotope ^{15}N. The assessment starts with researchers applying fertilizer enriched by ^{15}N to increase soil's $^{15}N/^{14}N$ ratio beyond the atmosphere's 0.3663 percent. While a specifically chosen nonfixing species, used as a reference, will get its nitrogen from soil, nitrogen-fixing species will take a large portion of the nutrient from the air instead. The isotopic ratio of the absorbed nitrogen will be thus lower in nitrogen-fixing plants. The difference between the two isotopic ratios in the species being compared reveals how much nitrogen the legume fixed. This method makes it possible to measure, with a single harvest, the total amount of the nutrient assimilated during a growing season.

Inevitably, the choice of reference plant affects the technique's accuracy. Ideally, both plants should have a similar rate of growth and maturation, and their roots should penetrate an identical volume of soil containing the same amount of ^{15}N. These requirements are rarely met. But even in the unlikely case that they are, no two reference species would give identical fixation estimates because of their different rates of nutrient assimilation, immobilization, mineralization, and nitrogen loss.

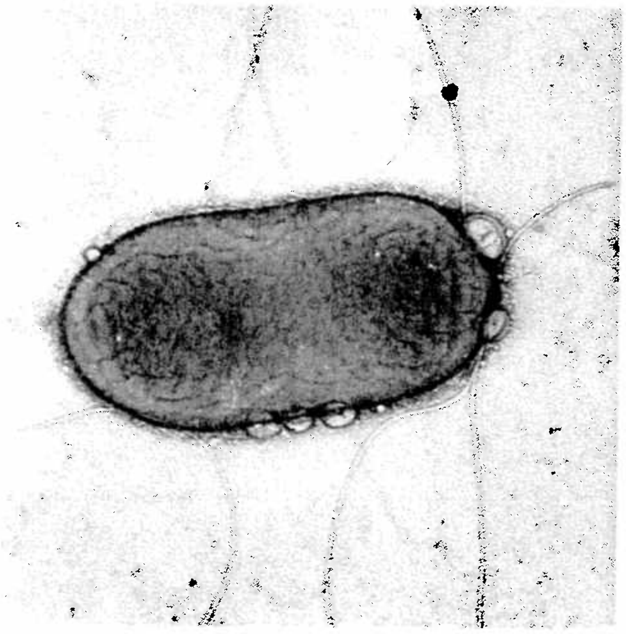
By far the most common way to determine the rate of bacterial nitrogen fixation is to measure the activity of nitrogenase, the enzyme that splits N_2. The assay, introduced during the late 1960s, is sensitive and specific. Unlike the ^{15}N technique it is also easy to perform, fast, and cheap—but it provides only a momentary glimpse of nitrogenase activity, and it does so in an indirect and approximate fashion. Nitrogenase reduces a number of other triple-bonded molecules besides N_2, including acetylene, and the assay measures the enzyme's reduction of acetylene to ethylene.

Researchers place detached nodules or plant roots into an airtight container, or put an airtight cover over a whole plant growing in the field. After injecting acetylene (C_2H_2) into the container, or into the enclosure, they take a baseline measurement; then, at regular intervals, they withdraw gas samples from containers or enclosures and analyze them chromatographically for ethylene. This information must be then converted to give the rate of nitrogen fixation. In theory, three molecule of C_2H_2 should be reduced for every molecule of N_2, but ratios actually measured have ranged from 1.5 to 8.4 for food and pasture legumes, and from 1.6 to 4.8 for woody species. Moreover, several uncontrollable factors can influence the results—brief variations in nitrogenase activity, for example, and differences among individual plants. To obtain a representative mean for the whole growing season would then require repeated assaying.

sive recent example is the discovery of *Acetobacter diazotrophicus* in 1988. This species, associated with Brazilian sugarcane, is not found in soil; it propagates only within stem cuttings and enters plants through damaged tissues. In some sugarcane varieties it can supply 60 to 80 percent of all the nitrogen a plant requires, equivalent to more than 200 kg N/ha a year.



Nitrogen withdrawals and contributions by leguminous crops. Some legumes fix less than half the nitrogen they need—but even soybeans, which fix 60 percent of their nitrogen, need to take nitrogen from the soil because only a small share of the nutrient incorporated in the plants can be recycled (i.e., they have a high nitrogen harvest index).



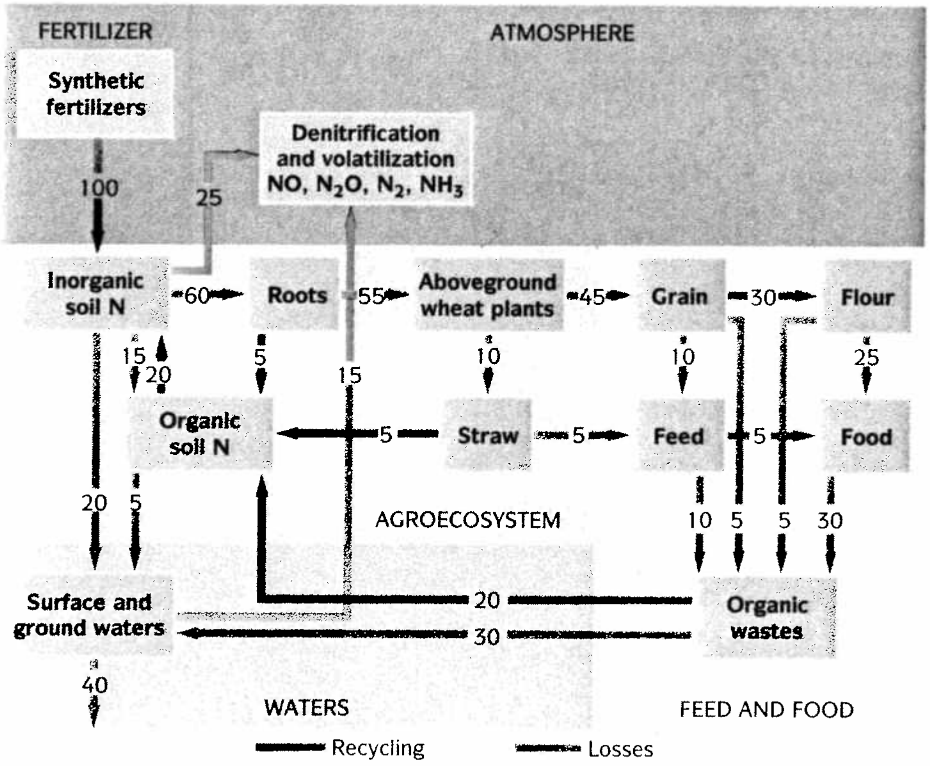
A transmission electron micrograph of *Acetobacter diazotrophicus*. These bacteria, about 3 μm long, live and multiply only inside sugarcane plants, providing these plants with a large share of the nitrogen they need.

Almost 20 estimates of total terrestrial biofixation have been published since the late 1950s; they range between extremes of 44 and 200 Mt N a year, but most of the estimates fit between 100 and 150 Mt N. Yet if we trace the origins of these estimates, we do not find that most fall in that relatively narrow range because of a reasonable agreement among independently derived values. Rather, older, apparently authoritative, estimates are simply being perpetuated. If the global fixation in cropfields amounts to just 30 Mt N a year (my lowest estimate), then synthetic fertilizers are already supplying nearly three times as much nitrogen as bacteria in croplands do. If, on the other hand, biofixation in crops and pastures adds as much as 80 to 90 Mt N (the highest published estimates), then bacteria (using nitrogenases) and humans (relying on the Haber-Bosch process) fix about the same amount of nitrogen.

How much nitrogen is available to nonleguminous crops that follow in the rotation is highly dependent on the share of the fixed nutrient taken up by the harvested legume seeds. This so-called nitrogen harvest index may be as low as 30 percent for beans and as high as 80 percent for soybeans. Plowing bean plant residues into the soil thus returns most of the fixed nitrogen, but soybeans, despite their reputation as prolific fixers of nitrogen, may not be even able to fix all the nutrient they need.

American plant physiologist Gary Heichel calculated that while a good soybean crop, which yields almost 2.5 t/ha, will incorporate in its grain, straw, and pods about 200 kg N/ha, the plants may fix less than 90 kg N/ha. Even when a soybean cultivar fixes more than half its nitrogen needs, and when its pods, leaves, and stems are completely recycled, the plants can remove from the soil nitrogen amounting to more than 50 or even 80 kg N/ha. Rather than being major providers of nitrogen to subsequent crops, some legumes thus actually claim a considerable amount of the nutrient stored in soil.

Even those legumes that do not usually produce a net nutrient loss (beans, peanuts, or chickpeas) are more valuable in crop rotations because of their sparing effect on soil than because they fix substantial quantities of nitrogen available for the following crop. Some field experiments suggest that even forage legumes are credited with contributing more nitrogen to the soil-plant system than they actually do. Six years of rotations in Minnesota demonstrated that corn yields were as high when the crop followed wheat as when it followed soybeans, or a sequence of wheat and alfalfa. In such cases, legumes may be more important for recycling organic matter, and for diversifying the cropping sequence, than for fixing nitrogen.



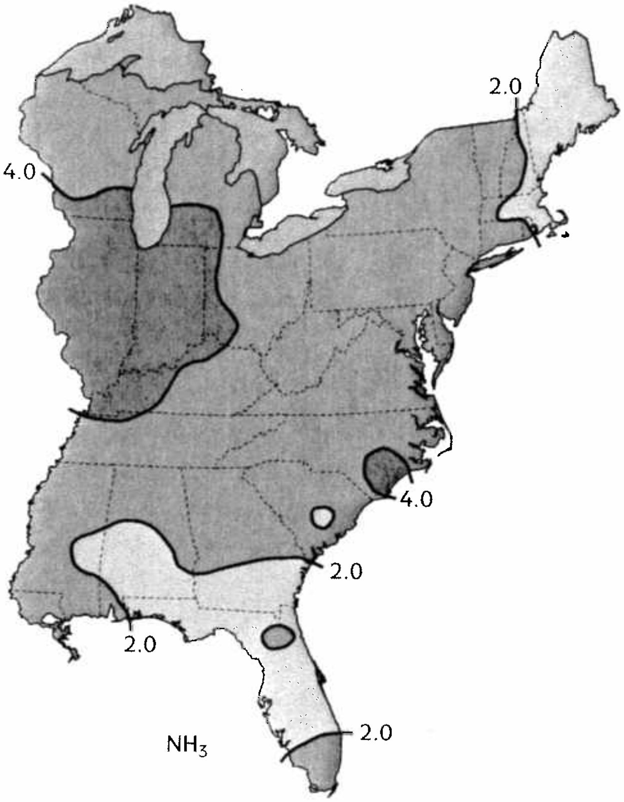
The fate of fertilizer nitrogen. The diagram shows the pathways taken by 100 units of nitrogen in a synthetic fertilizer when that fertilizer was applied to high-yielding (8 t/ha) French winter wheat in the early 1990s. One-quarter of the fertilizer nitrogen is transferred to foodstuffs, and two-fifths of the initial input eventually ends up in surface and ground waters.

Fertilizer Nitrogen in the Environment

Synthetic fertilizers make up the largest share of the nitrogen we are introducing to the biosphere, but they did not cause any notable environmental problems until the late 1950s. Intensive fertilization changed that in the years to follow. The reason is that not all the nitrogen in fertilizer is absorbed into plants, or even remains in soil—substantial amounts of the nutrient escape into the environment. The plants grown in most modern agroecosystems typically recover slightly less than half of all nitrogen applied to fields, and even the most efficient cropping sequences absorb only around 70 percent. A European survey found that during the 1980s high-yielding wheats assimilated between 38 and 70 percent of applied nitrogen in France and between 52 and 65 percent in the United Kingdom, but between a mere 18 and 37 percent in Greece. Animal husbandry incorporates even less of the supplied nitrogen. Dutch studies have shown that milk and cattle biomass retain only 20 percent of the nitrogen supplied in the grain feed and in the fertilizer used to produce grass.

Fertilizer nitrogen not assimilated by plants or used by animals can accumulate in soils, but most of it is lost to the atmosphere (through volatilization and denitrification) and to waters (washed out in runoff, carried in eroded topsoil, or leached out). Crops can also lose surprisingly large amounts of the nutrient directly from their aboveground parts. These losses commonly add up to about 10 kg N/ha; but up to 50 kg N/ha can be lost through leaching of soluble nitrates from leaf surfaces, from volatilization of NH_3 from leaves, and from the release of pollen and the decay of flowers and fruits.

The losses from volatilization can be high after the application of both animal manures and ammoniacal fertilizers. Solid compounds spread on the surface commonly lose 5 to 20 percent of their nitrogen, mostly within just a week after application. Ammonium bicarbonate (NH_4HCO_3), a highly volatile compound that still supplies at least a third of China's fertilizer needs, can lose up to one half its nitrogen by this means.



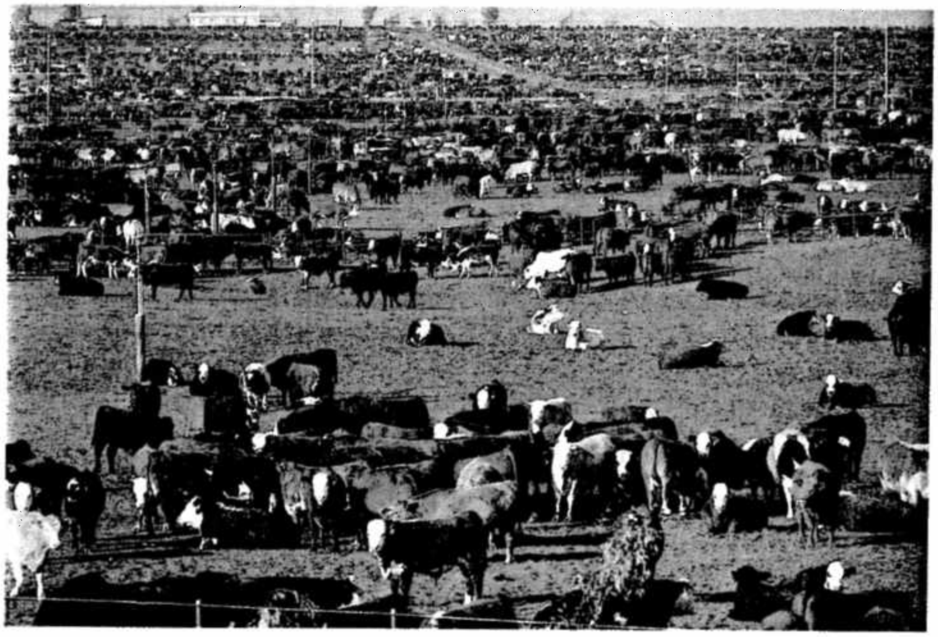
Ammonia deposition in the eastern United States 1998. Isolines show annual amounts of NH_3 in kilograms per hectare. The region downwind from the area of highest animal concentrations in the Midwest receives the highest inputs.

Reactive nitrogen escapes from organic wastes in amounts that can rival those from fertilizers. And so the unprecedented rates of population increase during the twentieth century, and the equally unprecedented concentration of humanity in cities, have been yet another source of intensified nitrogen flows. In 1950 2.5 billion people produced less than 15 Mt of waste nitrogen, and only about a quarter of this release came from cities. By 2000 the flow of waste had risen nearly 2.5-fold, about half of it of urban origin.

And these increasingly concentrated flows are dwarfed by waste streams from domestic animals. In the early 1990s these animals surpassed wild mammalian vertebrates in mass by an order of magnitude, and the total mass of humanity by a factor of 2. Cattle accounts for the largest share, as there are more than 1.5 billion of these large animals. There are also nearly one billion pigs. These species void annually close to 80 Mt of waste nitrogen. About half is released in confinement and must be disposed of into nearby soils or into streams and ponds.

Average losses of nitrogen from animal wastes are high, usually around 30 to 40 percent, and easily 10 to 20 percent of the element escapes into the air while the manure is still stored in the farmyard. As ammonia from animal wastes volatilizes readily, regions with concentrated livestock farming have become major sources of such emissions. Because ammonia spends only a short time in the atmosphere, the areas with the highest rates of deposition are either identical to the areas with the highest rates of emission—or they lie a relatively short distance downwind.

European NH_x emissions peak in the Netherlands (more than 60 kg per hectare per year), Belgium, Denmark, and Bavaria; in the United States they are highest in the Corn Belt (from cattle, pigs, and fertilizers); China's top rates are in Sichuan province (from the world's highest concentration of pigs). Modern animal-raising facilities have become



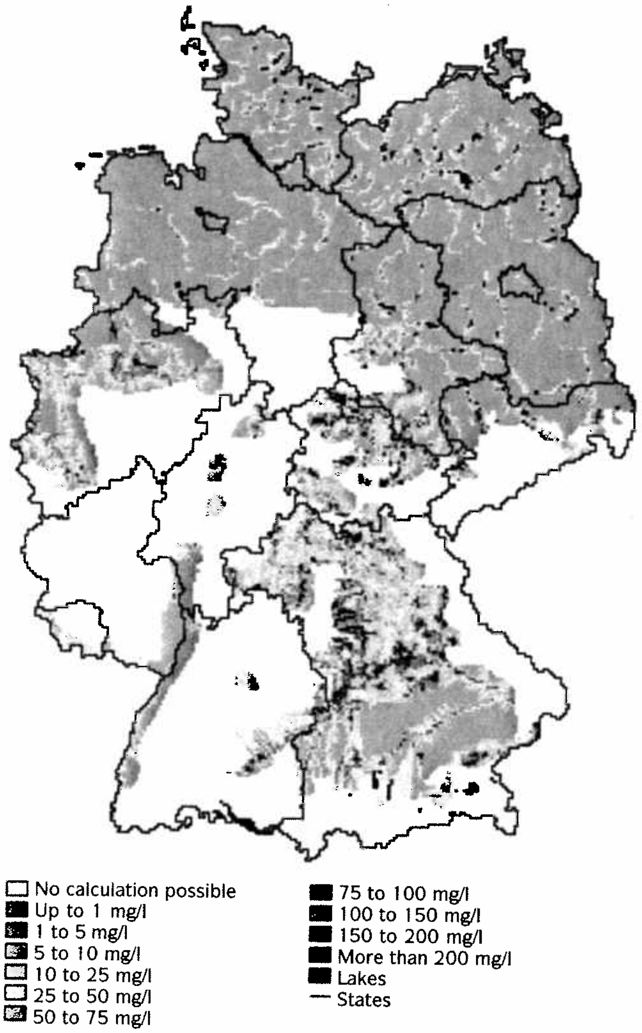
Huge beef feedlots—such as this one at Harris Ranch, California—are among the largest sources of concentrated ammonia emissions.

a highly concentrated source of atmospheric NH_3. Since volatilization removes around 25 kg N a year per head of cattle, a single large feedlot holding 80,000 animals may send annually skyward up to 2000 t nitrogen.

Even if only a quarter of all nitrogen voided in animal wastes were lost as NH_3, the annual flux would be close to 25 Mt N. Volatilization of ammoniacal fertilizers adds at least half as much as that total, and it may come close to matching it. Moreover, up to a quarter of the nitrogen present in coal is released as ammonia, adding to the compound's emissions from organic wastes and fertilizers. Global NH_3 emissions from fossil fuels are now about 15 Mt N a year.

Not all nitrogen escapes from fertilizers in the form of volatile ammonia. A large share of fertilizer ammonia and urea is eventually converted through bacterial nitrification to nitrates, and nitrate fertilizers, especially ammonium nitrate (NH_4NO_3), are also applied directly to crops. Nitrates are highly soluble in water, so the water in precipitation, irrigation flows, or a flood will dissolve a relatively large share of the compound present in the soil and carry it from the root zone into streams, lakes, and ponds.

Where the ground is permeable, precipitation can carry nitrates to the underlying groundwater. There, nitrates may remain long enough that denitrifying bacteria will convert them to unreactive N_2O and N_2, but in many instances they reenter surface waters fairly rapidly. A recent nationwide appraisal found the extreme residence times in Germany to be just a year in the southern limestone formations and more than 1000 years underneath the North German plain. As a result, the northern groundwater reemerges almost nitrate free, while water flowing from regions in the southern part of the country still holds most of the nitrates that originally seeped into it.



Potential nitrate concentrations are low in the aquifers of the North German Plain, where the water remains belowground more than 1000 years, but high in many parts of southern Germany, where residence times are much shorter.

As nitrogen application expanded in the 1950s and 1960s, the losses experienced through leaching remained negligible in North America's arid and semiarid plains and prairies. By the 1960s they had risen to between 20 and 30 kg N/ha in the Corn Belt, and to more than 50 kg N/ha in the most heavily fertilized parts of northwestern Europe. Nitrogen losses caused by erosion have remained negligible in well-managed rice fields even as fertilizer applications have risen—but the topsoil lost annually in the United States averages about 14 t/ha, and this mass takes away at least 55 kg of nitrogen. Iowa's mean soil loss is double the national average, and erosion removes the equivalent of 60 to 75 percent of all fertilizer nitrogen applied to a good corn crop. The astounding erosion on China's Loess plateau can strip away up to 200 t of topsoil a year, nearly all of it in just one or two intensive summer downpours.

Concerned about rising nitrogen losses, American biologist Barry Commoner began to write about the dangers of nitrates, and his claims helped to usher in the age of American environmental consciousness during the late 1960s. In a series of much publicized writings Commoner argued that intensive fertilization put the U.S. nitrogen cycle seriously out of balance, and that the nation's waters would soon contain unacceptably high levels of NO_3^-, posing health risks and promoting algal growth destructive to other aquatic life. He suggested that major steps be taken in order to prevent further dangerous deterioration, even including a reduction in the planting of crops.

Commoner's critics, most notably Samuel Aldrich, an expert on corn cultivation in the U.S. Midwest, were able to show his worst fears to be much exaggerated. During the early 1970s even rivers in the heavily fertilized Corn Belt did not have NO_3^- levels significantly higher than those of the 1950s, and these levels were well below the acceptable limit. Nitrate levels in the lower Mississippi, which drains watersheds receiving about two-fifths of all fertilizer nitrogen in the country, remained fairly constant until the early 1970s. Even though levels had risen more than fourfold by 1985, with three-quarters of the increase attributed to higher fertilizer applications, the river's total nitrogen loading was still only a fraction of the maximum acceptable level.

And an extensive survey of NO_3^- levels in Iowa found no undesirable effect on drinking water from deep wells during the late 1970s. Nearly all cases of high NO_3^- concentrations in shallow wells were traced to seepage from improperly stored manure. But such reassuring findings did not ultimately have lasting or universal validity. During the 1980s surveys discovered that almost 20 percent of Iowa wells had NO_3^- levels above the maximum contaminant limit (MCL). The contamination of these wells exposed about 130,000 of the state's rural residents to high-nitrate water. In 1990 the MCL was exceeded at public water-supply intakes on the Des Moines and Raccoon Rivers during much of spring and summer, an increase attributed to the leaching of fertilizer during a time of above-average precipitation following two dry years. The NO_3^- levels were found to exceed the MCL in roughly every fifth well in Illinois and Minnesota, and in about every seventh well in Kansas.

In western Europe, nitrate concentrations began to rise quickly in both groundwaters and surface waters during the early 1970s. A decade later they were either near or above the European Union's limit of 50 mg NO_3^-/L (or 11.3 mg N/L, virtually identical to the U.S. MCL) in a number of regions, especially in England and the Netherlands. During the 1980s western European nitrate levels were increasing with particular rapidity in the chalk aquifers of Champagne in northeastern France and the neighboring area of Belgium, and in the sands and gravels of Bavaria. Estimates attribute as much as 60 percent of these aquatic nitrates to the leaching of fertilizers.

Is Commoner being proved right? Yes—and no. The rising nitrate levels clearly show that human interference in the nitrogen cycle is intensifying—but the rise has not been translated into any worrisome health problems. Reactive nitrogen is the cause of unwelcome changes in some ecosystems—but there has been no general deterioration.

High nitrate levels in drinking water pose several potential health risks. The most dangerous risk is to infants, especially those younger than three months. A baby's gastrointestinal tract is distinguished by its lack of acidity. When it acquires acidity after infancy, this property prevents bacteria from reducing nitrate to nitrite, but in newborns exposed to high concentrations of NO_3^- these bacteria produce toxic levels of nitrites that can enter the bloodstream. There they change the ferrous iron (Fe^{2+}) of hemoglobin, the carrier and transmitter of oxygen, into the ferric iron (Fe^{3-}) of methemoglobin, which is incapable of carrying out these vital functions. The resulting disease is called methemoglobinemia, or, more commonly, blue baby disease.

The replacement of normal hemoglobin by methemoglobin causes first cyanosis of lips and skin (blue baby syndrome), then shortness of breath, and eventually suffocation as the blood turns chocolate brown. Fortunately, an infant treated in a timely manner with ascorbic acid or methylene blue will experience a complete recovery, and adequate intake of vitamin C provides good prevention.

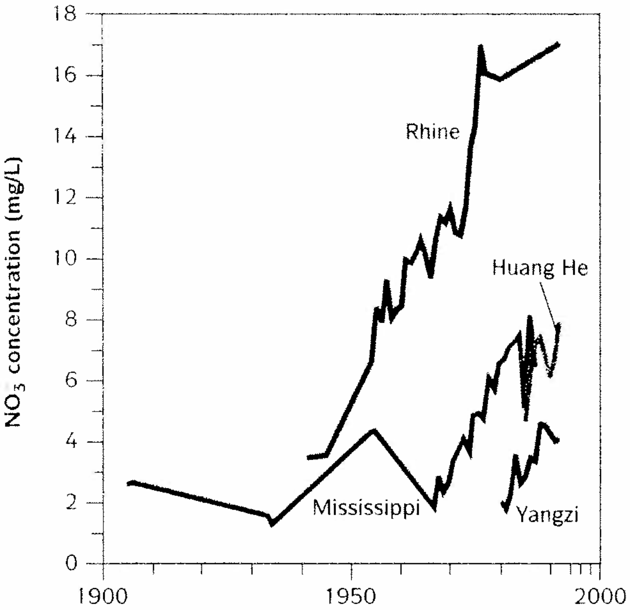
Only a few thousand cases of methemoglobinemia have been documented since 1950; in the largest outbreak, which struck in Hungary between 1976 and 1982, the disease affected more than 1300 children. Nevertheless, there must have been many times as many unreported mild occurrences in rich countries, and a large number of acute cases in poor ones. As nearly all known cases followed the drinking of water with more than 100 mg NO_3^-/L, the World Health Organization recommended in 1970 that the maximum level of nitrates allowed be set to 50 mg/L, a limit widely accepted in countries around the world.

The chronic consequences of drinking water with high nitrate concentrations are much harder to determine. One suspected effect has received a great deal of attention: nitrate-contaminated water may cause a higher incidence of some cancers in adults. A variable fraction of the NO_3^- present in drinking water is reduced by bacteria in saliva to NO_2^-, adding to the quantity of nitrites taken directly, mostly from cured meats. NO_2^- then reacts with amines to produce carcinogenic N-nitroso compounds. But the strength of this link between nitrates and cancer remains controversial.

An epidemiological association between high NO_3^- intake and esophageal cancer was first reported from Chile in 1970, and a large number of studies followed that suggested a higher incidence of gastric, urinary bladder, and intestinal cancers. But a clear attribution of these cancers to any single cause is impossible, since many factors contribute to their onset. Even if nitrates in water could be unequivocally implicated, they are not the only source of nitrate in our diets. In fact, most of the nitrate that we take in (about four-fifths of the total daily intake in the United States) comes from vegetables, above all from beets, celery, spinach, lettuce, and radishes, and our bodies may synthesize an amount that matches that total, or even surpasses it.

Moreover, a British study, which measured NO_3^- and NO_2^- levels in saliva, found that their concentrations were significantly higher in areas where the risk of stomach cancer was low. Perhaps most reassuringly, gastric cancer has been declining throughout the Western world just as nitrogen applications have undergone an unprecedented increase.

The effects of aquatic nitrogen on ecosystems are much easier to demonstrate, and they are certainly much more costly. Nitrogen enters waters not only through the leaching of fertilizers: in all populated areas much nitrogen comes from the dumping of urban sewage; and in some watersheds nitrates and ammonia resulting from fossil fuel combustion and volatilization contribute a significant amount as they settle or wash down from the atmosphere. These sources have brought the annual totals of nitrogen entering watersheds to about 30 kg N/ha in the eastern United States, and to more than 60 kg N/ha in parts of northwestern Europe and Japan. Loads are climbing toward similar levels in China's coastal provinces.



Increasing nitrate concentration in some of the world's major rivers.

Much of the nitrogen entering watersheds is carried by streams to the ocean as nitrate and in dissolved organic compounds. Total annual outflows of nitrogen from the most intensively fertilized and most densely populated watersheds are now surpassing 10 kg N/ha, an order of magnitude above the natural rates. The average NO$_3^-$ concentrations in the most affected rivers (the Thames, Rhine, Meuse, and Elbe) are now two orders of magnitude above the mean in unaffected streams. In the early 1990s more than a tenth of western Europe's rivers had NO$_3^-$ levels above the MCL, and nitrate levels are increasing in both of China's two largest rivers, the Huang He and Yangzi.

When a surfeit of nitrates exists in a body of water, the result is eutrophication, or the enrichment of surface waters with a commonly growth-limiting nutrient. The excessive presence of a previously scarce nutrient promotes the growth of algae and cyanobacteria. When these algal blooms die, their decomposition consumes aquatic oxygen, and the decline in oxygen may seriously reduce, and even eliminate, fish and shellfish species. Concerns about eutrophication eased somewhat with the demonstration that an excess of phosphorus, rather than nitrates, had been primarily responsible for unwanted algal growth in many fresh and coastal waters. The elimination of phosphates from laundry detergents diminished the threat—but did not remove it.

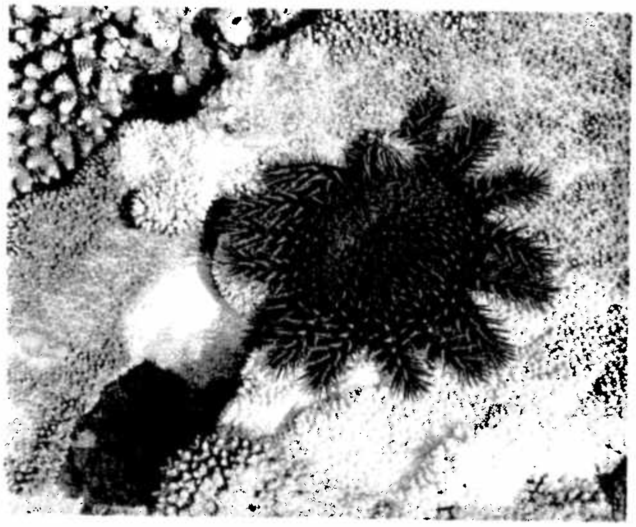
Above all, nitrogen-induced eutrophication threatens shallow lakes and coastal waters that receive high inflows of the nutrient from fertilizers

Eutrophication of ponds and lakes leads to an excessive growth of algae and, as in this photograph, of cyanobacteria.

commonly 40 to 60 percent of the total) and from the atmosphere. Among the largest affected lakes have been Florida's Okeechobee (recharged with runoff from heavily fertilized sugarcane fields) and East China's Tai Hu (formerly a major fishing area). Eutrophication has been particularly widespread in estuaries. These coastal ecosystems may receive nitrogen inputs that are 10 times, even more than a 100 times, higher than even a heavily fertilized field receives. Most estuaries in North America, including the Long Island Sound, San Francisco Bay, and the Mid-Chesapeake Bay, have the productivity of their plant and algae species clearly limited by nitrogen rather than by phosphorus.

The Baltic Sea, receiving annually almost 1.5 Mt N from agricultural runoff and atmospheric deposition, has been one of the most noticeably eutrophied marine ecosystems. In many places the oxygen-deficient, or outright exhausted, conditions of the sea's bottom sediments are attested to by the presence of extensive mats of *Beggiatoa*, bacteria that reduce CO_2 and produce sulfates in the absence of oxygen. The worst affected U.S. waters are in the Gulf of Mexico where nitrogen from the Mississippi and Atchafalya rivers creates every spring a large hypoxic zone that kills many benthic species. Appreciable eutrophication has also been observed in the Black, Mediterranean, and North Seas.

Perhaps the most worrisome reports come from the lagoon of the Great Barrier Reef, the world's largest coral formation, which extends about 2000 km along the coast of Queensland. Since the early 1950s, farming in the region has undergone an expansion that has quadrupled phosphorus applications and boosted nitrogen use nearly 10-fold. The resulting eutrophication of shallow waters threatens coral directly by smothering them with algal overgrowth, and indirectly by promoting the survival and growth of the larvae of *Acanthaster planci*, the crown-of-thorns starfish that has recently destroyed large areas of the reef. Eutrophication also seems to promote the growth of the nitrogen-fixing cyanobacterium *Oscillatoria*, and its blooms add almost as much nitrogen as the runoff.



A starfish *(Acanthaster planci)* feeding on coral; the white area has been already eaten.

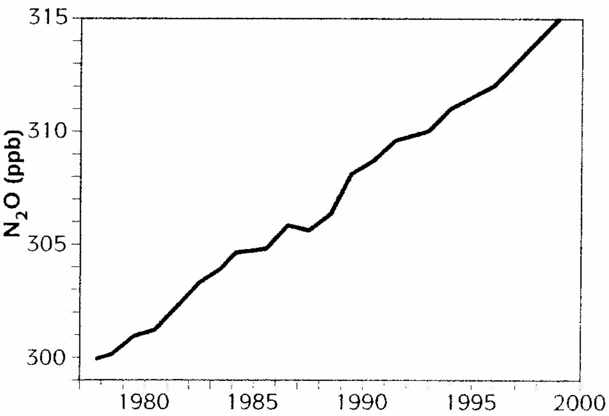
While the practices of modern, intensive agriculture have been a major source of undesirable nitrogen in waters, they have caused an unwelcome *decline* of the nutrient in topsoils. In the tropics a great deal of the highly volatile nitrogen from the surface layer is lost during fires set to convert forests to croplands. Cultivation further depletes the soil, since as much as 50 percent of the remaining nitrogen may be lost during the first 30 to 50 years of cropping. Fortunately, farmers can reduce these losses, or even reverse them, by applying fertilizers (regular manuring is particularly effective), recycling crop residues, and reducing the intensity of soil tillage.

A comprehensive review of typical European and U.S. agroecosystems found nitrogen gains in about three-quarters of all cases studied, with a mean annual increase of 35 kg N/ha. Without synthetic fertilizers, more than half these agroecosystems would have lost nitrogen. However, while the status of many of the rich world's soils may be slowly improving, most of the nonirrigated cropland in Asia, sub-Saharan Africa, and Latin America has been losing nitrogen. Annual losses of the nutrient in the three continents range mostly between 20 and 70 kg N/ha a year.

Nitrogen in the Atmosphere

Nitrogen's escape from the soil to the atmosphere became a matter of concern at almost the same time that the public started to worry about aquatic nitrates. Soil bacteria are continually denitrifying the nitrates in soils and waters, whether the nitrates came from fertilizers or were produced by the nitrification of ammonia from decomposed biomass. Denitrification produces N_2O, a gas that is unreactive in the troposphere, but that is involved in reactions high above it, reactions that may have undesirable consequences for all complex forms of life.

When N_2O is eventually mixed into the stratosphere, its reactions with excited oxygen (derived from the photodissociation of ozone) produce NO, and that oxide sets off a catalytic cycle of reactions that leads to the destruction of ozone. This cycle was first identified by Paul Crutzen in 1970, a finding rewarded in 1995 with a Nobel Prize in chemistry, and its operation is the reason for obvious concerns about the long-term effects of higher N_2O emissions that result from the increasing use of fertilizers.



Atmospheric levels of N_2O have risen by about 4 percent since regular monitoring began in 1977.

N_2O may account for all of the gas released in denitrification or be virtually absent; shares between 3 and 30 percent are common. The extent of the average N_2O losses from applications of fertilizer is highly uncertain: denitrification can account for just a fraction of one percent, or up to three-quarters of all postapplication losses of nitrogen. The loss of between 10 and 20 percent of all applied nitrogen as N_2O or N_2 is common.

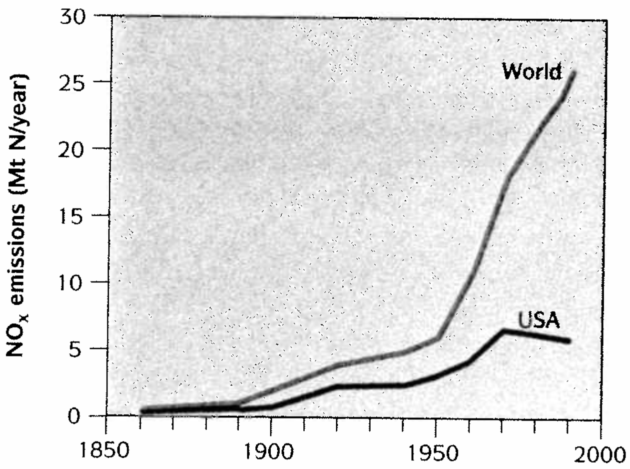
A number of modeling exercises done between the mid-1970s and the mid-1980s attempted to predict what would happen to ozone concentrations in the stratosphere if N_2O in the atmosphere doubled. They concluded that a doubling of N_2O concentrations would eventually reduce stratospheric ozone levels by as much as 10 to 16 percent. The timing of such a doubling is highly uncertain, but it now appears to be much further away than we thought in the mid-1970s. Since regular measurements began in 1977, the N_2O concentration in the troposphere, at about 315 ppb in 2000, has been rising by less than 0.25 percent a year.

After a decade of concern, the catalytic NO cycle was overshadowed in importance by a much more pernicious intervention—the destruction of ozone involving chlorine from chlorofluorocarbons (CFCs). This sequence of reactions was first outlined by Sherwood Rowland and Mario Molina in 1974 (and they were also rewarded in 1995 with the Nobel Prize in chemistry). Its effects were dramatically demonstrated in 1985 when researchers identified a pronounced decline in ozone levels above Antarctica in the spring months of September and October.

Now that CFCs are being eliminated, while rates of fertilization will continue to rise, N_2O may, once again, become the center of attention during the early decades of the twenty-first century.

In the mid-1980s N_2O began receiving attention as a minor, but far from negligible, greenhouse gas. Although the gas is three orders of magnitude less abundant than CO_2, it is a stronger absorber of infrared radiation. In fact, it is now responsible for about 6 percent of the direct tropospheric warming caused by all greenhouse gases except water vapor.

There is yet another connection between nitrogen and ozone: nitrogen in the form of NO_x promotes the formation of ozone in the troposphere, where it does harm. Since around 1950 industrial societies have been burning larger shares of fossil fuels at very high temperature in the boilers of large electricity-generating stations and in internal combustion engines. This combustion generates substantial amounts of nitrogen oxides. The nitrogen in these oxides comes from two sources: the fuel itself, where it is almost always present in minute amounts, and the atmosphere's store of N_2. The nitrogen in coals and oils represents on the order of one percent of their mass. Natural gases have usually less than 5 percent nitrogen, but the gas is commonly removed before combustion.



Emissions of nitrogen oxides have been on the rise worldwide, due to a combination of expanding electricity generation and growing automobile traffic. The U.S. share has declined thanks to stricter car emission controls.

Any nitrogen already in the fuel will be oxidized even at relatively low combustion temperatures, such as one might find when wood burns in smoldering wildfires or coal in simple household stoves. But at higher temperatures the N_2 in the air will dissociate and combine with oxygen to form NO_x (of which 95 to 98 percent is NO). Only a very small amount of NO_x is formed at temperatures below 1500 °C, but above that threshold their formation rises exponentially. Consequently, the combustion of one kilogram of coal in a large power-plant boiler can produce 10 times as much NO_x as the combustion of the same amount of coal in a small household stove. Internal combustion engines are also relatively large sources of NO_x. Even highly conservative estimates would have the amount of NO_x generated worldwide rising to about 2 Mt N by 1900 and then quintupling by 1950. Today humans are responsible for releasing about 40 Mt of NO_x a year, split about 4:1 between oxides from fossil fuel combustion and oxides from the burning of phytomass.

A problem arises when nitrogen oxides—mostly from fossil fuel combustion but also from microbial activity in heavily fertilized soils—react with volatile organic compounds (VOC) and CO. The presence of these three ingredients sets the stage for the development of seasonally very high concentrations of photochemical smog, a mixture of gases resulting from complex chains of chemical reactions powered by sunlight.

The American chemist Arie Haagen-Smit elucidated the chemistry of the photochemical smog syndrome in the early 1950s. The process starts with

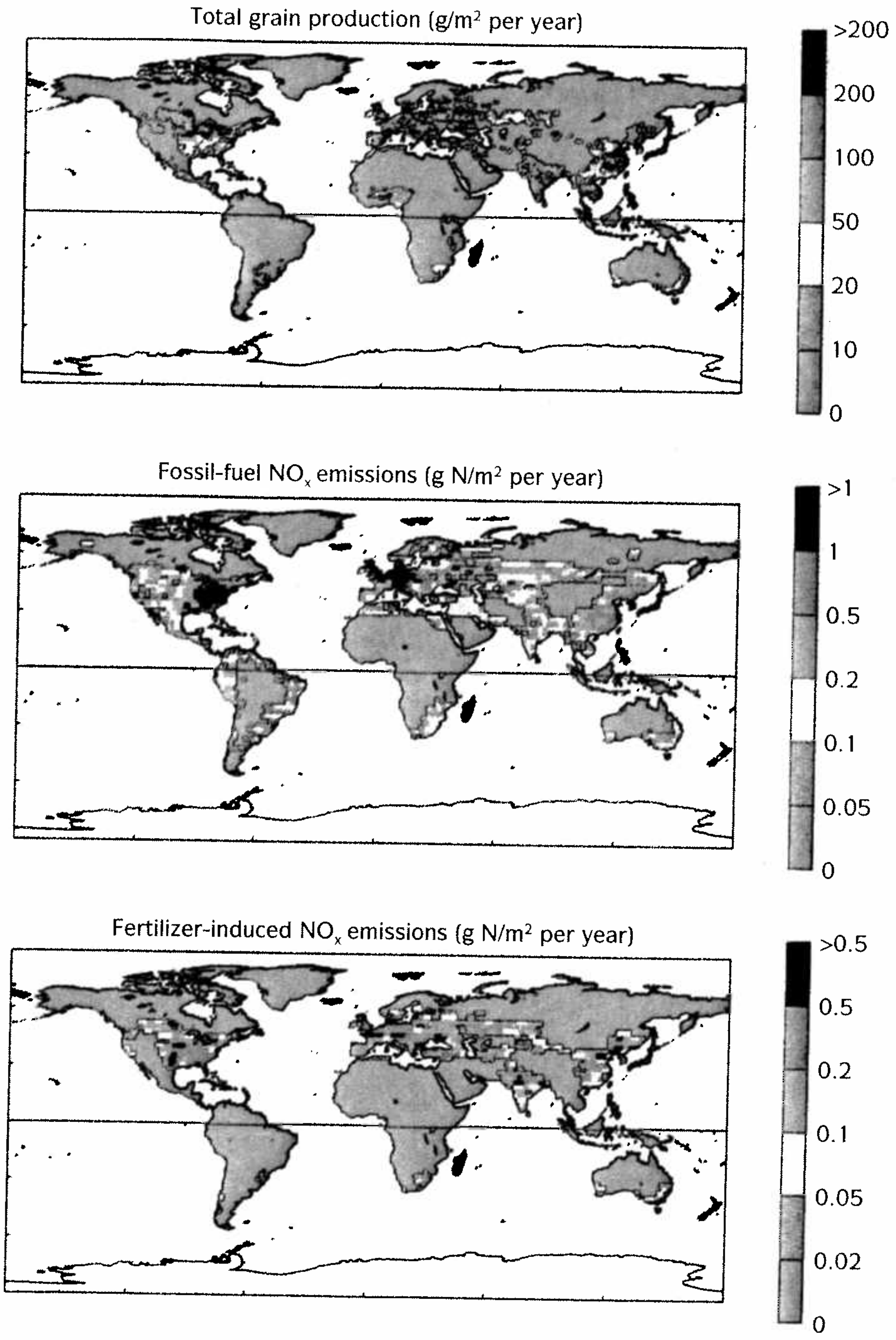
Heavy urban traffic—and heavy photochemical smog—in Bangkok, Thailand, typifies the ubiquitous degradation of air quality taking place in all large cities in warmer climates.

a rapid oxidation of NO to NO_2 involving a variety of reactive molecules (OH·, CO, hydrocarbons, aldehydes). The subsequent dissociation of NO_2 and oxidization of hydrocarbons leads to rising concentrations of ozone (O_3). One of the most aggressive oxidizing agents, O_3 impairs lung function, injures cells, limits the capacity for work and exercise, and lowers the resistance to bacterial infections. In plants it causes pigmentation, bleaching of leaves, and tissue death, and it damages textiles, dyes, rubber, plastics, and asphalt.

For some time after Haagen-Smit explained photochemical smog, it seemed that the phenomenon would remain confined to sunny subtropical climates, but rising NO_x and VOC emissions have brought summertime smog to all large cities of the northern hemisphere's densely inhabited mid-latitudes. Both Vancouver and London (at 50 °N) can have days when the smog level is comparable to that in Los Angeles (34 °N).

Photochemical smog and excessive O_3 concentrations have thus become a semipermanent presence in all tropical and subtropical cities and their surroundings—be it Bangkok, Taipei, Los Angeles, or Mexico City—and a recurring seasonal affliction of large cities in temperate climates. Elevated O_3 levels now afflict regions far larger than even such sprawling conurbations as Boston-Washington or Tokyo-Osaka. Persistent summertime high-pressure cells limit atmospheric mixing over the easternmost third of North America and allow concentrations to build up to harmful levels even in rural areas, especially in the southeastern United States.

William Chameides of the Georgia Institute of Technology points out that the largest three of these metro-agro-plexes—regions combining cities, industries, and large-scale agriculture—are already home to almost a third of the world's population. The three regions—western Europe, eastern North America, and East Asia—also account for about 75 percent of the worldwide use of fossil fuels and nitrogen fertilizers, and for about 60 percent of global food production. At least a tenth, but perhaps up to a third, of the world's cereal crops, and an even higher share of the vegetables and fruits, are grown in these regions. There, they are already exposed to O_3 levels above 50 to 70 ppb, the threshold



Metro-agro-plexes defined by total grain production, NO_x emissions from fossil fuels, and fertilizer-induced emissions of NO_x.

above which cumulative exposure during the growing season leads to damage.

Technical solutions to this problem are not easy to find. Only the world's strictest emissions controls have been able to prevent further air quality deterioration in southern California since the early 1970s—but these controls still cannot do away with frequent violations of the prescribed air quality standards. Scores of cities in North America and Europe are exceeding the highest desirable O_3 levels. Similarly, in spite of strenuous efforts by the Japanese, average annual values of NO_x released in urban areas in their country have hardly changed during the past 15 years.

The nitrogen oxides that contribute to photochemical smog are also readily oxidized to nitrates, and these compounds have been a source of yet another worrisome kind of environmental degradation. Although in most people's minds acid rain has been connected with sulfur emissions, nitrates have been major, and increasingly important, contributors to large-scale acidification of sensitive ecosystems. The next chapter will look at the causes and consequences of this process of biospheric change.