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AP42 Section:	9.2.1
Background Ch	2
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THE NITROGEN CYCLE

Sect #13

Nitrogen is 79 percent of the atmosphere, but it cannot be used directly by the large majority of living things. It must first be "fixed" by specialized organisms or by industrial processes

by C. C. Delwiche

Although men and other land animals live in an ocean of air that is 79 percent nitrogen, their supply of food is limited more by the availability of fixed nitrogen than by that of any other plant nutrient. By "fixed" is meant nitrogen incorporated in a chemical compound that can be utilized by plants and animals. As it exists in the atmosphere nitrogen is an inert gas except to the comparatively few organisms that have the ability to convert the element to a combined form. A smaller but still significant amount of atmospheric nitrogen is fixed by ionizing phenomena such as cosmic radiation, meteor trails and lightning, which momentarily provide the high energy needed for nitrogen to react with oxygen or the hydrogen of water. Nitrogen is also fixed by marine organisms, but the largest single natural source of fixed nitrogen is probably terrestrial microorganisms and associations between such microorganisms and plants.

Of all man's recent interventions in the cycles of nature the industrial fixation of nitrogen far exceeds all the others in magnitude. Since 1950 the amount of nitrogen annually fixed for the production of fertilizer has increased approximately fivefold, until it now equals the amount that was fixed by all terrestrial ecosystems before the advent of modern agriculture. In 1968 the world's annual output of industrially fixed nitrogen amounted to about 30 million tons of nitrogen; by the year 2000 the industrial fixation of nitrogen may well exceed 100 million tons.

Before the large-scale manufacture of synthetic fertilizers and the wide cultivation of the nitrogen-fixing legumes one could say with some confidence that the amount of nitrogen removed from the atmosphere by natural fixation processes was closely balanced by the amount returned to the atmosphere by organisms that convert organic nitrates to gaseous nitrogen. Now one cannot be sure that the denitrifying processes are keeping pace with the fixation processes. Nor can one predict all the consequences if nitrogen fixation were to exceed denitrification over an extended period. We do know that excessive runoff of nitrogen compounds in streams and rivers can result in "blooms" of algae and intensified biological activity that deplete the available oxygen and destroy fish and other oxygen-dependent organisms. The rapid eutrophication of Lake Erie is perhaps the most familiar example.

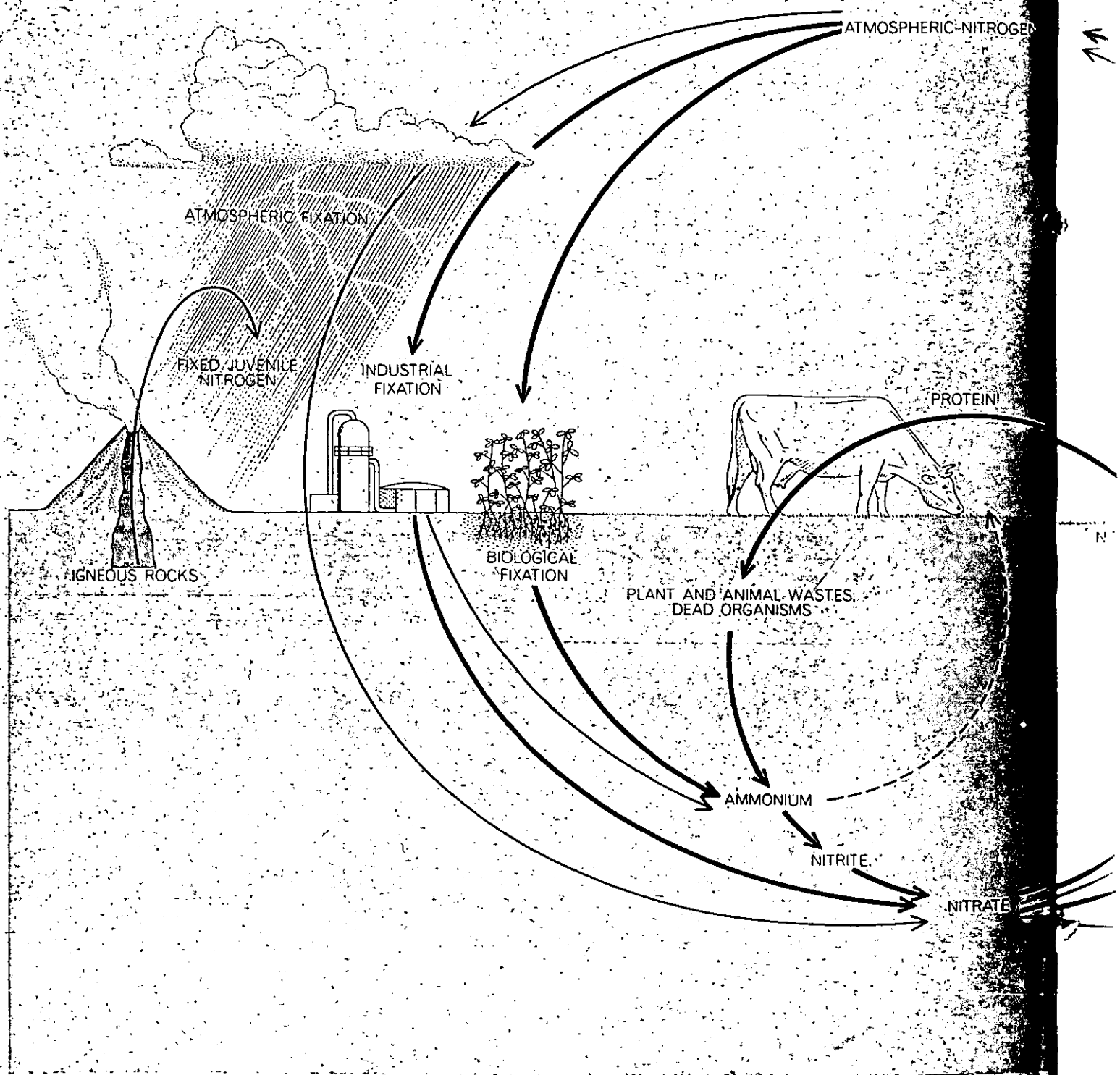
To appreciate the intricate web of nitrogen flow in the biosphere let us trace the course of nitrogen atoms from the atmosphere into the cells of microorganisms, and then into the soil as fixed nitrogen, where it is available to higher plants and ultimately to animals. Plants and animals die and return the fixed nitrogen to the soil, at which point the nitrogen may simply be recycled through a new generation of plants and animals or it may be broken down into elemental nitrogen and returned to the atmosphere [*see illustration on next two pages*].

Because much of the terminology used to describe steps in the nitrogen cycle evolved in previous centuries it has an archaic quality. Antoine Laurent Lavoisier, who clarified the composition of air, gave nitrogen the name azote, meaning without life. The term is still found in the family name of an important nitrogen-fixing bacterium: the Azotobacteraceae. One might think that fixation would merely be termed nitrification, to indicate the addition of nitrogen to some other substance, but nitrification is reserved for a specialized series of reactions in which a few species of microorganisms oxidize the ammonium ion (NH_4^+) to nitrite (NO_2^-) or nitrite to nitrate (NO_3^-). When nitrites or nitrates are reduced to gaseous compounds such as molecular nitrogen (N_2) or nitrous oxide (N_2O), the process is termed denitrification. "Ammonification" describes the process by which the nitrogen of organic compounds (chiefly amino acids) is converted to ammonium ion. The process operates when microorganisms decompose the remains of dead plants and animals. Finally, a word should be said about the terms oxidation and reduction, which have come to mean more than just the addition of oxygen or its removal. Oxidation is any process that removes electrons from a substance. Reduction is the reverse process: the addition of electrons. Since electrons can neither be created nor destroyed in a chemical reaction, the oxidation of one substance always implies the reduction of another.

One may wonder how it is that some organisms find it profitable to oxidize

BLUE-GREEN ALGAE, magnified 4,200 diameters on the opposite page, are among the few free-living organisms capable of combining nitrogen with hydrogen. Until this primary fixation process is accomplished, the nitrogen in the air (or dissolved in water) cannot be assimilated by the overwhelming majority of plants or by any animal. A few bacteria are also free-living nitrogen fixers. The remaining nitrogen-fixing microorganisms live symbiotically with higher plants. This micrograph, which shows blue-green algae of the genus *Nostoc*, was made by Herman S. Forest of the State University of New York at Geneseo.

nitrogen compounds whereas other organisms—even organisms in the same environment—owe their survival to their ability to reduce nitrogen compounds. Apart from photosynthetic organisms, which obtain their energy from radiation, all living forms depend for their energy on chemical transformations. These transformations normally involve the oxidation of one compound and the reduction of another, although in some cases the compound being oxidized and the compound being reduced are different molecules of the same substance, and in other cases the reactants are fragments of a single molecular species. Nitrogen can be cycled because the reduced inorganic compounds of nitrogen can be oxidized by atmospheric oxygen with a yield of useful energy. Under anaerobic conditions the oxidized compounds of nitrogen can act as oxidizing agents for the burning of organic compounds (and a few inorganic com-



NITROGEN CYCLE, like the water, oxygen and carbon cycles, involves all regions of the biosphere. Although the supply of nitrogen in the atmosphere is virtually inexhaustible, it must be combined with hydrogen or oxygen before it can be assimilated by higher plants, which in turn are consumed by animals. Man has intervened in the historical nitrogen cycle by the large-scale cultivation of nitrogen-fixing legumes and by the industrial fixation of nitrogen. The amount of nitrogen fixed annually by these two expedients now exceeds by perhaps 10 percent the amount of nitrogen fixed by terrestrial ecosystems before the advent of agriculture.

pounds), again with a yield of useful energy.

Nitrogen is able to play its complicated role in life processes because it has an unusual number of oxidation levels, or valences [*see illustration on page 141*]. An oxidation level indicates the number of electrons that an atom in a particular compound has "accepted" or "donated." In plants and animals most nitrogen exists either in the form of the ammonium ion or of amino ($-NH_2$) compounds. In either case it is highly reduced; it has acquired three electrons by its association with three other atoms and thus is said to have a valence of minus 3. At the other extreme, when nitrogen is in the highly oxidized form of the nitrate ion (the principal form it takes in the soil), it shares five of its electrons with oxygen atoms and so has a valence of plus 5. To convert nitrogen as it is found in the ammonium ion or amino acids to nitrogen as it exists in soil nitrates involves a total valence change of eight, or the removal of eight electrons. Conversely, to convert nitrate nitrogen into amino nitrogen requires the addition of eight electrons.

By and large the soil reactions that reduce nitrogen, or add electrons to it, release considerably more energy than the reactions that oxidize nitrogen, or remove electrons from it. The illustration on page 142 lists some of the principal reactions involved in the nitrogen cycle, together with the energy released (or required) by each. As a generalization one can say that for almost every reaction in nature where the conversion of one compound to another yields an energy of at least 15 kilocalories per mole (the equivalent in grams of a compound's molecular weight), some organism or group of organisms has arisen that can exploit this energy to survive.

The fixation of nitrogen requires an investment of energy. Before nitrogen can be fixed it must be "activated," which means that molecular nitrogen must be split into two atoms of free nitrogen. This step requires at least 160 kilocalories for each mole of nitrogen (equivalent to 28 grams). The actual fixation step, in which two atoms of nitrogen combine with three molecules of hydrogen to form two molecules of ammonia (NH_3), releases about 13 kilocalories. Thus the two steps together require a net input of at least 147 kilocalories. Whether nitrogen-fixing organisms actually invest this much energy, however, is not known. Reactions catalyzed by enzymes involve the penetration of activation barriers and not a simple change in energy between a set of initial reactants and their end products.

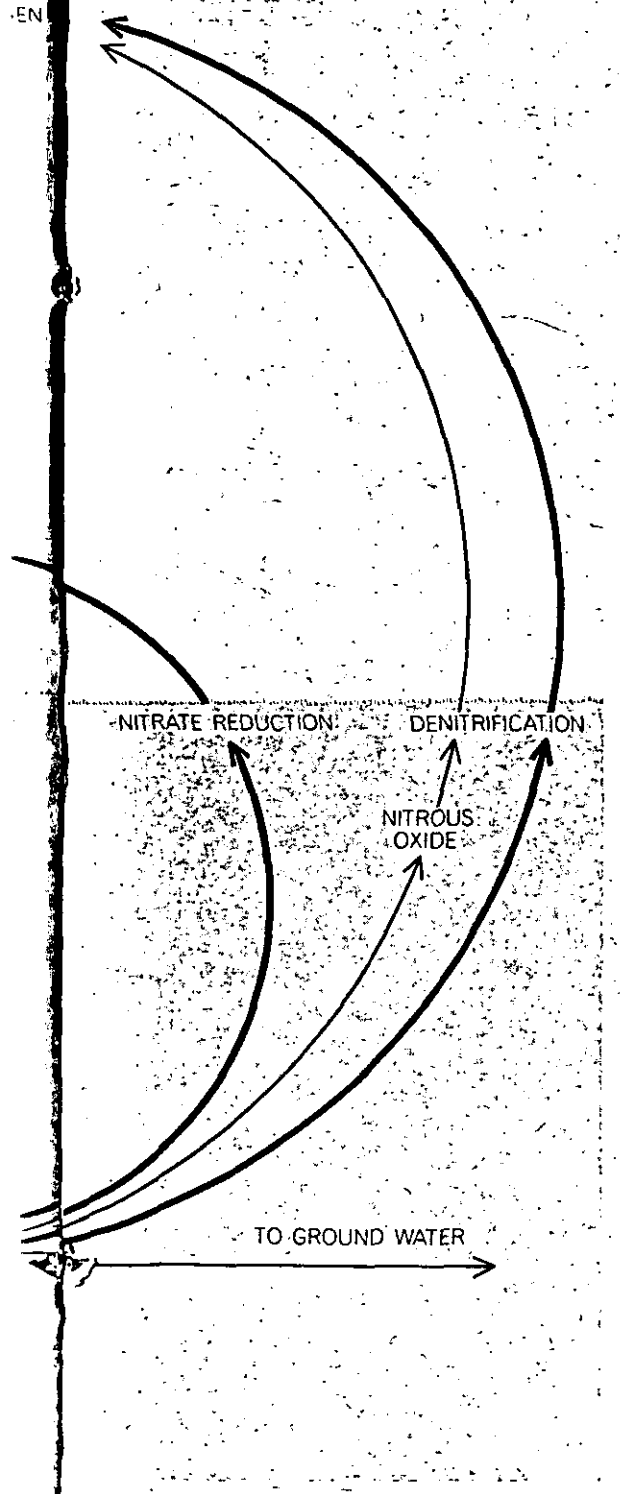
Once ammonia or the ammonium ion has appeared in the soil, it can be absorbed by the roots of plants and the nitrogen can be incorporated into amino acids and then into proteins. If the plant is subsequently eaten by an animal, the nitrogen may be incorporated into a new protein. In either case the protein ultimately returns to the soil, where it is decomposed (usually with bacterial help) into its component amino acids. Assuming that conditions are aerobic, meaning that an adequate supply of oxygen is present, the soil will contain many microorganisms capable of oxidizing amino acids to carbon dioxide, water and ammonia. If the amino acid happens to be glycine, the reaction will yield 176 kilocalories per mole.

A few microorganisms represented by the genus *Nitrosomonas* employ nitrification of the ammonium ion as their sole source of energy. In the presence of oxygen, ammonia is converted to nitrite ion (NO_2^-) plus water, with an energy yield of about 65 kilocalories per mole, which is quite adequate for a comfortable existence. *Nitrosomonas* belongs to the group of microorganisms termed autotrophs, which get along without an organic source of energy. Photoautotrophs obtain their energy from light; chemoautotrophs (such as *Nitrosomonas*) obtain energy from inorganic compounds.

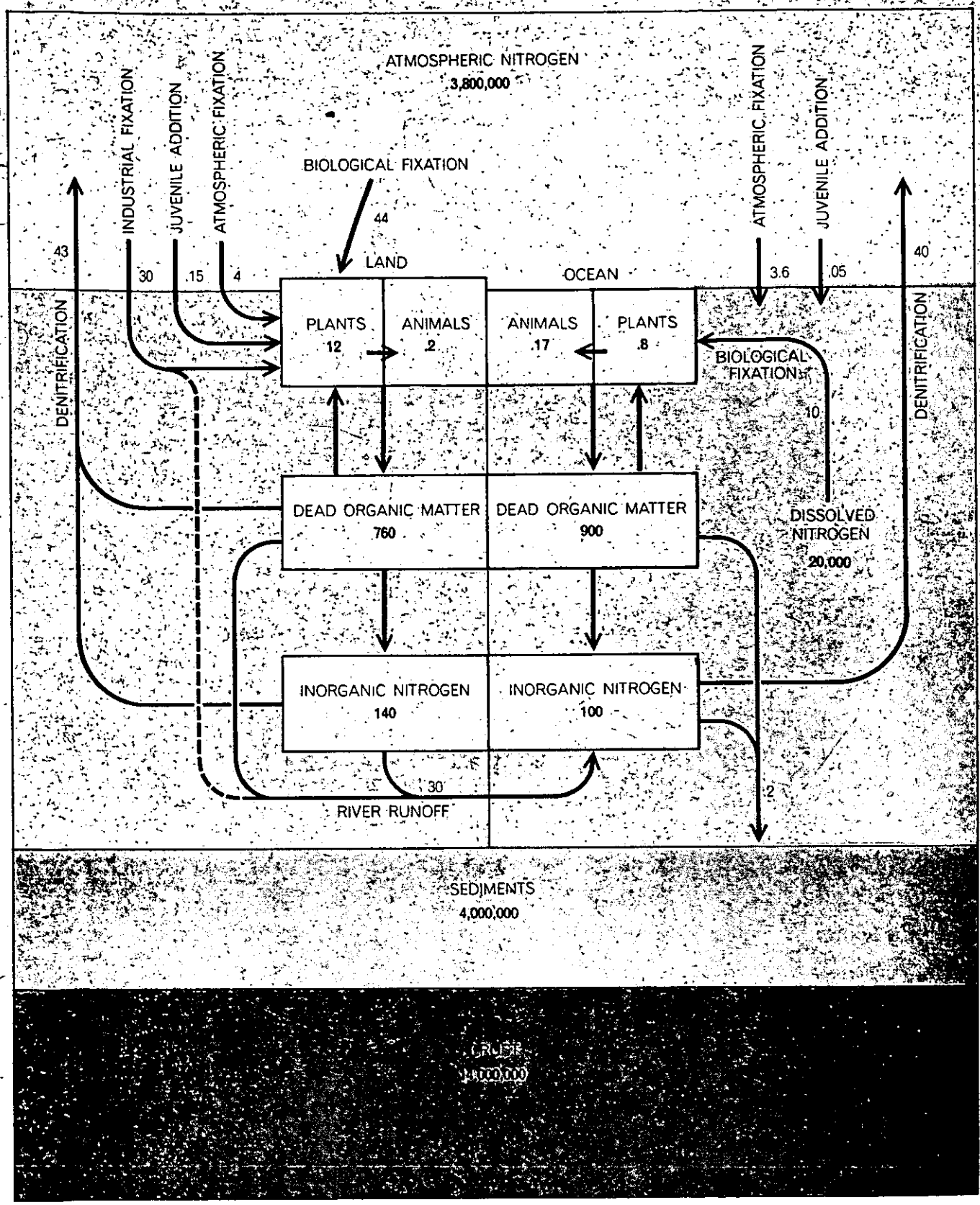
There is another specialized group of microorganisms, represented by *Nitrobacter*, that are capable of extracting additional energy from the nitrite generated by *Nitrosomonas*. The result is the oxidation of a nitrite ion to a nitrate ion with the release of about 17 kilocalories per mole, which is just enough to support the existence of *Nitrobacter*.

In the soil there are numerous kinds of denitrifying bacteria (for example *Pseudomonas denitrificans*) that, if obliged to exist in the absence of oxygen, are able to use the nitrate or nitrite ion as electron acceptors for the oxidation of organic compounds. In these reactions the energy yield is nearly as large as it would be if pure oxygen were the oxidizing agent. When glucose reacts with oxygen, the energy yield is 686 kilocalories per mole of glucose. In microorganisms living under anaerobic conditions the reaction of glucose with nitrate ion yields about 545 kilocalories per mole of glucose if the nitrogen is reduced to nitrous oxide, and 570 kilocalories if the nitrogen is reduced all the way to its elemental gaseous state.

The comparative value of ammonium and nitrate ions as a source of nitrogen for plants has been the subject of a number of investigations. One might think that the question would be readily resolved in favor of the ammonium ion: its valence is minus 3, the same as the valence of nitrogen in amino acids, whereas the valence of the nitrate ion is plus 5.



A cycle similar to the one illustrated also operates in the ocean, but its characteristics and transfer rates are less well understood. A global nitrogen flow chart, using the author's estimates, appears on the next page.



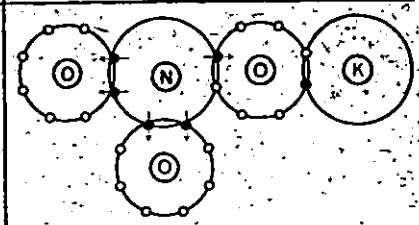
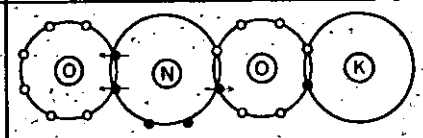
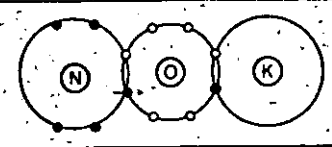
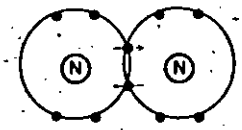
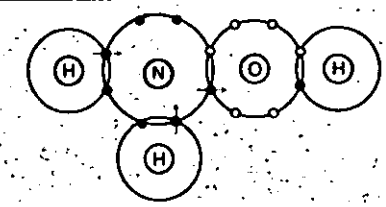
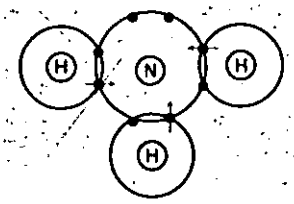
DISTRIBUTION OF NITROGEN in the biosphere and annual transfer rates can be estimated only within broad limits. The two quantities known with high confidence are the amount of nitrogen in the atmosphere and the rate of industrial fixation. The apparent precision in the other figures shown here reflects chiefly an effort to preserve indicated or probable ratios among different inventories. Thus the figures for atmospheric fixation and biological fixation in the oceans could well be off by a factor of 10. The figures for inventories are given in billions of metric tons; the figures for transfer rates (*color*) are given in millions of metric tons. Because of the extensive use of industrially fixed nitrogen the amount of nitrogen available to land plants may significantly exceed the nitrogen returned to the atmosphere by denitrifying bacteria in the soil. A portion of this excess fixed nitrogen is ultimately washed into the sea but it is not included in the figure shown for river runoff. Similarly, the value for oceanic denitrification is no more than a rough estimate that is based on the assumption that the nitrogen cycle was in overall balance before man's intervention.

On this basis plants must expend energy to reduce nitrogen from a valence of plus 5 to one of minus 3. The fact is, however, that there are complicating factors; the preferred form of nitrogen depends on other variables. Because the ammonium ion has a positive charge it tends to be trapped on clay particles near the point where it is formed (or where it is introduced artificially) until it has been oxidized. The nitrate ion, being negatively charged, moves freely through the soil and thus is more readily carried downward into the root zone. Although the demand for fertilizer in solid form (such as ammonium nitrate and urea) remains high, anhydrous ammonia and liquid ammoniacal fertilizers are now widely applied. The quantity of nitrogen per unit weight of ammonia is much greater than it is per unit of nitrate; moreover, liquids are easier to handle than solids.

Until the end of the 19th century little was known about the soil organisms that fix nitrogen. In fact, at that time there was some concern among scientists that the denitrifying bacteria, which had just been discovered, would eventually deplete the reserve of fixed nitrogen in the soil and cripple farm productivity. In an address before the Royal Society of London, Sir William Crookes painted a bleak picture for world food production unless artificial means of fixing nitrogen were soon developed. This was a period when Chilean nitrate reserves were the main source of fixed nitrogen for both fertilizer and explosives. As it turned out, the demand for explosives provided the chief incentive for the invention of the catalytic fixation process by Fritz Haber and Karl Bosch of Germany in 1914. In this process atmospheric nitrogen and hydrogen are passed over a catalyst (usually nickel) at a temperature of about 500 degrees Celsius and a pressure of several hundred atmospheres. In a French version of the process, developed by Georges Claude, nitrogen was obtained by the fractional liquefaction of air. In current versions of the Haber process the source of hydrogen is often the methane in natural gas [*see illustration on page 143*].

As the biological fixation of nitrogen and the entire nitrogen cycle became better understood, the role of the denitrifying bacteria fell into place. Without such bacteria to return nitrogen to the atmosphere most of the atmospheric nitrogen would now be in the oceans or locked up in sediments. Actually, of course, there is not enough oxygen in the atmosphere today to convert all the free nitrogen into nitrates. One can imagine, however, that if a one-way process were to develop in the absence of denitrifying bacteria, the addition of nitrates to the ocean would make seawater slightly more acidic and start the release of carbon dioxide from carbonate rocks. Eventually the carbon dioxide would be taken up by plants, and if the carbon were then deposited as coal or other hydrocarbons, the remaining oxygen would be available in the atmosphere to be combined with nitrogen. Because of the large number of variables involved it is difficult to predict how the world would look without the denitrification reaction, but it would certainly not be the world we know.

The full story of the biological fixation of nitrogen has not yet been written. One would like to know how the activating enzyme (nitrogenase) used by nitrogen-fixing bacteria can accomplish at ordinary temperatures and pressures what

VALENCE	COMPOUND	FORMULA	VALENCE ELECTRONS
+5	NITRATE ION	NO_3^-	
+3	NITRITE ION	NO_2^-	
+1	NITROXYL	[HNO]	
0	NITROGEN GAS	N_2	
−1	HYDROXYLAMINE	$HONH_2$	
−3	AMMONIA	NH_3	

NITROGEN'S VARIETY OF OXIDATION LEVELS, or valence states, explains its ability to combine with hydrogen, oxygen and other atoms to form a great variety of biological compounds. Six of its valence states are listed with schematic diagrams (*right*) showing the disposition of electrons in the atom's outer (valence) shell. The ions are shown combined with potassium (K). In the oxidized (+) states nitrogen's outer electrons complete the outer shells of other atoms. In the reduced (−) states the two electrons needed to complete the outer shell of nitrogen are supplied by other atoms. Actually the outer electrons of two bound atoms spend some time in the shells of both atoms, contributing to the electrostatic attraction between them. Electrons of nitrogen (N) are in color; those of other atoms are black dots or open circles. The nitroxyl radical, HNO, is placed in brackets because it is not stable. It can exist in its dimeric form, hyponitrous acid (HONNOH).

takes hundreds of degrees and thousands of pounds of pressure in a synthetic-ammonia reactor. The total amount of nitrogenase in the world is probably no more than a few kilograms.

The nitrogen-fixing microorganisms are divided into two broad classes: those that are "free-living" and those that live in symbiotic association with higher plants. This distinction, however, is not as sharp as it was once thought to be, because the interaction of plants and microorganisms has varying degrees of intimacy. The symbionts depend directly on the plants for their energy supply and probably for special nutrients as well. The free-living nitrogen fixers are indirectly dependent on plants for their energy or, as in the case of the blue-green algae and photosynthetic bacteria, obtain energy directly from sunlight.

Although the nitrogen-fixation reaction is associated with only a few dozen species of higher plants, these species are widely distributed in the plant kingdom. Among the more primitive plants whose symbionts can fix nitrogen are the cycads and the ginkgos, which can be traced back to the Carboniferous period of some 300 million years ago. [*see bottom illustration on page 145*]. It is probable that the primitive atmosphere of the earth contained ammonia, in which case the necessity for nitrogen fixation did not arise for hundreds of millions of years.

Various kinds of bacteria, particularly the Azotobacteraceae, are evidently the chief suppliers of fixed nitrogen in grasslands and other ecosystems where plants with nitrogen-fixing symbionts are absent. Good quantitative information on the rate of nitrogen fixation in such ecosystems is hard to obtain. Most investigations indicate a nitrogen-fixation rate of only two or three kilograms per hectare per year, with a maximum of perhaps five or six kilograms. Blue-green algae seem to be an important source of fixed nitrogen under conditions that favor their development [*see illustration on page 136*]. They may be a significant source in rice paddies and other environments favoring their growth. In natural ecosystems with mixed vegetation the symbiotic associations involving such plant genera as *Alnus* (the alders) and *Ceanothus* (the buckthorns) are important suppliers of fixed nitrogen.

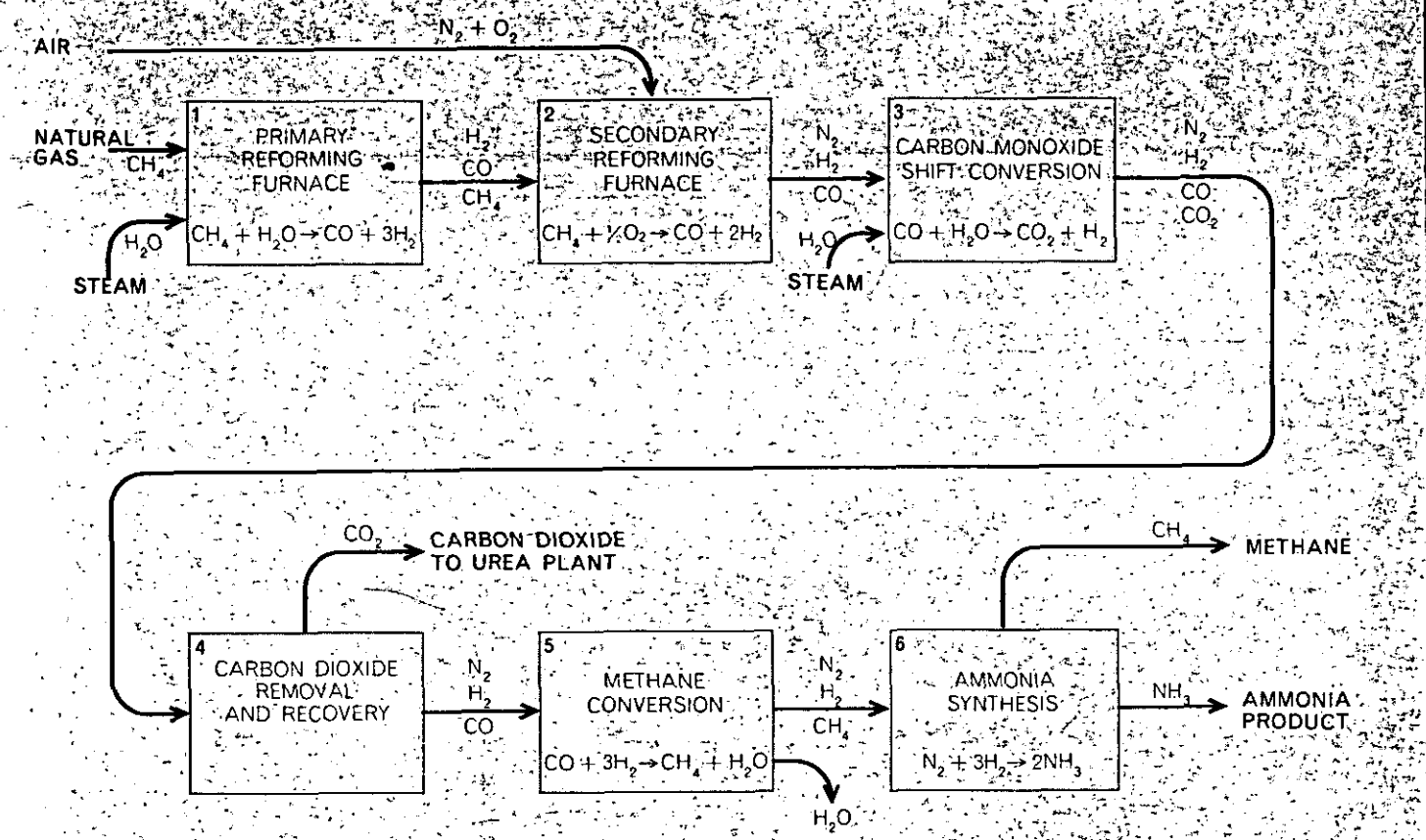
For the earth as a whole, however, the greatest natural source of fixed nitrogen is probably the legumes. They are certainly the most important from an agronomic standpoint and have therefore been the most closely studied. The input of nitrogen from the microbial symbionts of alfalfa and other leguminous crops can easily amount to 350 kilograms per hectare, or roughly 100 times the annual rate of fixation attainable by nonsymbiotic organisms in a natural ecosystem.

Recommendations for increasing the world's food supply usually emphasize increasing the cultivation of legumes not only to enrich the soil in nitrogen but also because legumes (for example peas and beans) are themselves a food crop containing a good nutritional balance of amino acids. There are, however, several obstacles to carrying out such recommendations. The first is custom and taste. Many societies with no tradition of growing and eating legumes are reluctant to adopt them as a basic food.

For the farmer legumes can create a more immediate problem: the increased yields made possible by the extra nitrogen lead to the increased consumption of other essential elements, notably potassium and phosphorus. As a consequence farmers often say that legumes are "hard on the soil." What this really means is that the large yield of such crops places

REACTION	ENERGY YIELD (KILOCALORIES)
DENITRIFICATION	
1 $C_6H_{12}O_6 + 6KNO_3 \longrightarrow 6CO_2 + 3H_2O + 6KOH + 3N_2O$ (GLUCOSE, POTASSIUM NITRATE; POTASSIUM HYDROXIDE, NITROUS OXIDE)	545
2 $5C_6H_{12}O_6 + 24KNO_3 \longrightarrow 30CO_2 + 18H_2O + 24KOH + 12N_2$ (NITROGEN)	570 (PER MOLE OF GLUCOSE)
3 $5S + 6KNO_3 + 2CaCO_3 \longrightarrow 3K_2SO_4 + 2CaSO_4 + 2CO_2 + 3N_2$ (SULFUR; POTASSIUM SULFATE, CALCIUM SULFATE)	132 (PER MOLE OF SULFUR)
RESPIRATION	
4 $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$ (CARBON DIOXIDE, WATER)	686
AMMONIFICATION	
5 $CH_2NH_2COOH + 1\frac{1}{2}O_2 \longrightarrow 2CO_2 + H_2O + NH_3$ (GLYCINE, OXYGEN, AMMONIA)	176
NITRIFICATION	
6 $NH_3 + 1\frac{1}{2}O_2 \longrightarrow HNO_2 + H_2O$ (NITROUS ACID)	66
7 $KNO_2 + \frac{1}{2}O_2 \longrightarrow KNO_3$ (POTASSIUM NITRITE)	17.5
NITROGEN FIXATION	
8 $N_2 \longrightarrow 2N$ "ACTIVATION" OF NITROGEN	-160
9 $2N + 3H_2 \longrightarrow 2NH_3$	12.8

ENERGY YIELDS OF REACTIONS important in the nitrogen cycle show the various means by which organisms can obtain energy and thereby keep the cycle going. The most profitable are the denitrification reactions, which add electrons to nitrate nitrogen, whose valence is plus 5, and shift it either to plus 1 (as in N_2O) or zero (as in N_2). In the process glucose (or sulfur) is oxidized. Reactions No. 1 and No. 2 release nearly as much energy as conventional respiration (*No. 4*), in which the agent for oxidizing glucose is oxygen itself. The ammonification reaction (*No. 5*) is one of many that release ammonium for nitrification. The least energy of all, but still enough to provide the sole energetic support for certain bacteria, is released by the nitrification reactions (*No. 6 and No. 7*), which oxidize nitrogen. Only nitrogen fixation, which is accomplished in two steps, calls for an input of energy. The true energy cost of nitrogen fixation to an organism is unknown, however.



INDUSTRIAL AMMONIA PROCESS is based on the high-pressure catalytic fixation method invented in 1914 by Fritz Haber and Karl Bosch, which supplied Germany with nitrates for explosives in World War I. This flow diagram is based on the process developed by the M. W. Kellogg Company. As in most modern plants, the hydrogen for the basic reaction is obtained from methane, the chief constituent of natural gas, but any hydrocarbon source will do. In Step 1 methane and steam react to produce a gas rich in hydrogen. In Step 2 atmospheric nitrogen is introduced; the oxygen accompanying it is converted to carbon monoxide by partial combustion with methane. The carbon monoxide reacts with steam in Step 3. The carbon dioxide is removed in Step 4 and can be used elsewhere to convert some of the ammonia to urea, which has the formula $CO(NH_2)_2$. The last traces of carbon monoxide are converted to methane in Step 5. In Step 6 nitrogen and hydrogen combine at elevated temperature and pressure, in the presence of a catalyst, to form ammonia. A portion of the ammonia product can readily be converted to nitric acid by reacting it with oxygen. Nitric acid and ammonia can then be combined to produce ammonium nitrate, which, like urea, is another widely used fertilizer.

a high demand on all minerals, and unless the minerals are supplied the full benefit of the crop is not realized.

Symbiotic nitrogen fixers have a greater need for some micronutrients (for example molybdenum) than most plants do. It is now known that molybdenum is directly incorporated in the nitrogen-fixing enzyme nitrogenase. In Australia there were large areas where legumes refused to grow at all until it was discovered that the land could be made fertile by the addition of as little as two ounces of molybdenum per acre. Cobalt turns out to be another essential micronutrient for the fixation of nitrogen. The addition of only 10 parts per trillion of cobalt in a culture solution can make the difference between plants that are stunted and obviously in need of nitrogen and plants that are healthy and growing vigorously.

Although legumes and their symbionts are energetic fixers of nitrogen, there are indications that the yield of a legume crop can be increased still further by direct application of fertilizer instead of depending on the plant to supply all its own needs for fixed nitrogen. Additional experiments are needed to determine just how much the yield can be increased and how this increase compares with the industrial fixation of nitrogen in terms of energy investment. Industrial processes call for some 6,000 kilocalories per kilogram of nitrogen fixed, which is very little more than the theoretical minimum. The few controlled studies with which I am familiar suggest that the increase in crop yield achieved by the addition of a kilogram of nitrogen amounts to about the same number of calories. This comparison suggests that one can exchange the calories put into industrial fixation of nitrogen for the calories contained in food. In actuality this trade-off applies to the entire agricultural enterprise. The energy required for preparing, tilling and harvesting a field and for processing and distributing the product is only slightly less than the energy contained in the harvested crop.

Having examined the principal reactions that propel the nitrogen cycle, we are now in a position to view the process as a whole and to interpret some of its broad implications. As other authors in this issue of *Scientific American* have explained, one must be cautious in trying to present a worldwide inventory of a particular element in the biosphere and in indicating annual flows from one part of a cycle to another. The balance sheet for nitrogen [*see top illustration on page 145*] is particularly crude because we do not have enough information to assign accurate estimates to the amounts of nitrogen that are fixed and subsequently returned to the atmosphere by biological processes.

Another source of uncertainty involves the amount of nitrogen fixed by ionizing phenomena in the atmosphere. Although one can measure the amount of fixed nitrogen in rainfall, one is forced to guess

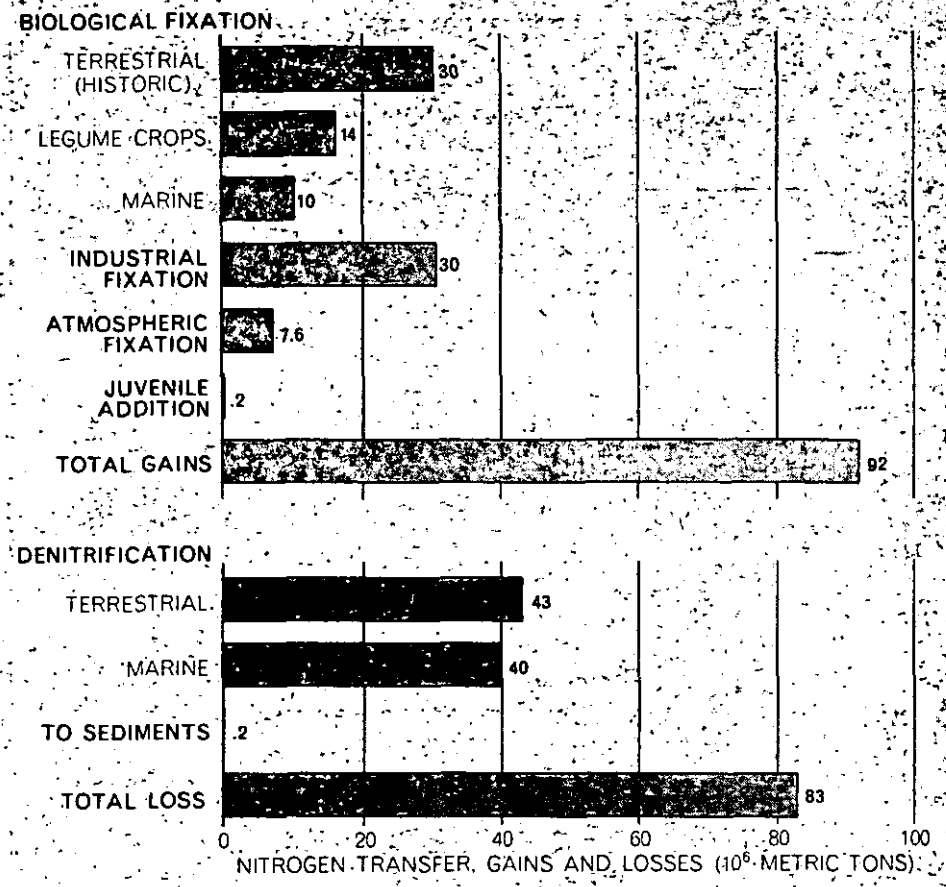
CROSS SECTION OF SOYBEAN ROOT NODULE, enlarged 22,000 diameters, shows portions of three cells that have been infected by the nitrogen-fixing bacterium *Rhizobium japonicum*. More than two dozen bacteria are visible, each surrounded by a membrane. After the bacteria have divided, within a few days, each membrane will contain four to six "bacteroids." This electron micrograph was made by D. J. Goodchild and F. J. Bergersen of the Commonwealth Scientific and Industrial Research Organization in Australia.

how much is produced by ionization and how much represents nitrogen that has entered the atmosphere from the land or the sea, either as ammonia or as oxides of nitrogen. Because the ocean is slightly alkaline it could release ammonia at a low rate, but that rate is almost impossible to estimate. Land areas are a more likely source of nitrogen oxides, and some reasonable estimates of the rate of loss are possible. One can say that the total amount of fixed nitrogen delivered to the earth by rainfall is of the order of 25 million metric tons per year. My own estimate is that 70 percent of this total is previously fixed nitrogen cycling through the biosphere, and that only 30 percent is freshly fixed by lightning and other atmospheric phenomena.

Another factor that is difficult to estimate is the small but steady loss of nitrogen from the biosphere to sedimentary rocks. Conversely, there is a continuous delivery of new nitrogen to the system by the weathering of igneous rocks in the crust of the earth. The average nitrogen content of igneous rocks, however, is considerably lower than that of sedimentary rocks, and since the quantities of the two kinds of rock are roughly equal, one would expect a net loss of nitrogen from the biosphere through geologic time. Conceivably this loss is just about balanced by the delivery of "juvenile" nitrogen to the atmosphere by volcanic action. The amount of fixed nitrogen reintroduced in this way probably does not exceed two or three million tons per year.

Whereas late-19th-century scientists worried that denitrifying bacteria were exhausting the nitrogen in the soil, we must be concerned today that denitrification may not be keeping pace with nitrogen fixation, considering the large amounts of fixed nitrogen that are being introduced in the biosphere by industrial fixation and the cultivation of legumes. It has become urgent to learn much more about exactly where and under what circumstances denitrification takes place.

We know first of all that denitrification does not normally proceed to any great extent under aerobic conditions. Whenever free oxygen is available, it is energetically advantageous for an organism to use it to oxidize organic compounds rather than to use the oxygen bound in nitrate salts. One can conclude that there must be large areas in the biosphere where conditions are sufficiently anaerobic to strongly favor the denitrification reaction. Such conditions exist wherever the input of organic materials



BALANCE SHEET FOR NITROGEN CYCLE, based on the author's estimates, indicates that nitrogen is now being introduced into the biosphere in fixed form at the rate of some 92 million metric tons per year (*colored bars*), whereas the total amount being denitrified and returned to the atmosphere is only about 83 million tons per year. The difference of some nine million tons may represent the rate at which fixed nitrogen is building up in the biosphere: in the soil, in ground-water reservoirs, in rivers and lakes and in the ocean.

ASSOCIATIONS OF TREES AND BACTERIA are important fixers of nitrogen in natural ecosystems. The ginkgo tree (*left*), a gymnosperm, has shown little outward change in millions of years. The alder (*right*), an angiosperm, is common in many parts of the world.

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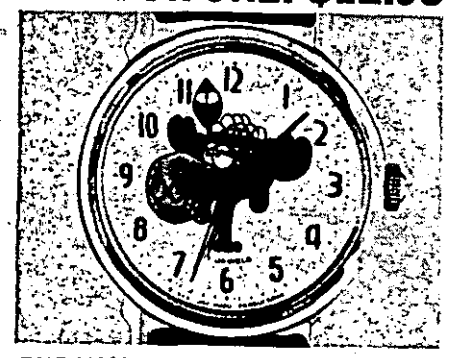

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exceeds the input of oxygen for their degradation. Typical areas where the denitrification process operates close to the surface are the arctic tundra, swamps and similar places where oxygen input is limited. In many other areas where the input of organic material is sizable, however, denitrification is likely to be proceeding at some point below the surface, probably close to the level of the water table.

There are even greater uncertainties regarding the nitrogen cycle in the ocean. It is known that some marine organisms do fix nitrogen, but quantitative information is scanty. A minimum rate of denitrification can be deduced by estimating the amount of nitrate carried into the ocean by rivers. A reasonable estimate is 10 million metric tons per year in the form of nitrates and perhaps twice that amount in the form of organic material, a total of about 30 million tons. Since the transfer of nitrogen into sediments is slight, one can conclude that, at least before man's intervention in the nitrogen cycle, the ocean was probably capable of denitrifying that amount of fixed nitrogen.

The many blanks in our knowledge of the nitrogen cycle are disturbing when one considers that the amount of nitrogen fixed industrially has been doubling about every six years. If we add to this extra nitrogen the amounts fixed by the cultivation of legumes, it already exceeds (by perhaps 10 percent) the amount of nitrogen fixed in nature. Unless fertilizers and nitrogenous wastes are carefully managed, rivers and lakes can become loaded with the nitrogen carried in runoff waters. In such waterways and in neighboring ground-water systems the nitrogen concentration could, and in some cases already does, exceed the levels acceptable for human consumption. Under some circumstances bacterial denitrification can be exploited to control the buildup of fixed nitrogen, but much work has to be done to develop successful management techniques.

The problem of nitrogen disposal is aggravated by the nitrogen contained in the organic wastes of a steadily increasing human and domestic-animal population. Ideally this waste nitrogen should be recycled back to the soil, but efficient and acceptable means for doing so remain to be developed. At present it is economically sounder for the farmer to keep adding industrial fertilizers to his crops. The ingenuity that has been used to feed a growing world population will have to be matched quickly by an effort to keep the nitrogen cycle in reasonable balance.