GROUND-WATER MICROBIOLOGY AND GEOCHEMISTRY

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with the atmosphere, ensures rapid and complete cycling of carbon. Carbon cycling in local flow systems closely resembles the kinds of processes that occur in soils, unsaturated zones, and other near-surface environments.

Intermediate and Regional Flow Systems The carbon cycle in intermediate and regional flow systems tends to be much different than in local flow systems. One difference is the relative importance of organic carbon from surface decomposition of organic matter. The ultimate source of organic carbon is, of course, photosynthesis. However, organic carbon originally deposited with the sediments tends to be much more important in intermediate and regional flow systems. This reflects the relatively slow recharge rates from the surface. Because recharge rates are generally slow, DOC or POC fluxes from surface sources also tend to be low.

Some time after deposition, often millions of years, a ground-water flow system is established and slow oxidation of the organic carbon continues. In or near the outcrop areas of the aquifer, oxidation of organic matter may occur aerobically. However, with the consumption of dissolved oxygen, oxidation under anaerobic conditions quickly becomes the dominant process. Oxidation is not confined to the sandy aquifers exclusively, but also occurs in clayey confining beds. It is rare that anaerobic oxidation proceeds only via fermentation. Rather, fermentation and oxidation by mineral electron acceptors tend to be coupled. Because of the presence of confining beds, there is little connection between aquifers and the surface. Therefore, CO_2 and other carbonate species generated by these anaerobic oxidation processes accumulate in solution.

The progress of carbon cycling in intermediate and regional flow systems can have several different outcomes. If the ground water remains isolated from the surface by means of structural traps or other geologic features, then much of the DIC may ultimately be precipitated as carbonate cements. This effectively removes that carbon from the carbon cycle for long periods of time. A more common outcome, however, is the eventual discharge of ground water to the surface by means of springs or by diffuse upward discharge. This type of discharge accounts for the occurrence of mineral springs, such as those at Saratoga Springs, and countless other artesian seeps. The occurrence of CO_2-charged waters at these springs is thus an inevitable manifestation of carbon cycling in these subsurface environments.

On a large scale, in terms of both time and space, it is clear that complete truncation of the carbon cycle (and thus the oxygen and hydrogen cycles) in intermediate and regional ground-water systems is rare. Even dissolved carbonate species from organic carbon oxidation that become sequestered as carbonate cements will eventually return to the cycle when the sediments are uplifted and eroded. The concept of cycle truncation, therefore, is useful only when considering the time frame of human life and history. This time frame, however, is the one of special importance and interest, particularly in cases of anthropogenic contamination.

9.3 THE NITROGEN CYCLE

While the carbon, oxygen, and hydrogen cycles involved both macroorganisms and microorganisms in producing and decomposing organic compounds, the nitrogen

cycle involves only microorganisms and some abiotic processes. Nitrogen in the atmosphere is present primarily as N_2 gas, which is a particularly stable compound. Under ambient atmospheric conditions, oxidized (NO_3) or reduced (NH_3) nitrogen compounds are not produced from N_2. However, such compounds are produced nonbiologically during electrical storms as well as in the higher atmosphere where photochemical processes are important. These nitrogen compounds are then carried to the earth's surface by precipitation. At the earth's surface, however, microbially mediated nitrogen fixation—the production of organic nitrogen compounds from N_2—and microbial nitrogen oxidation and reduction are the sole nitrogen-cycling processes.

A schematic representation of the nitrogen cycle is shown in Figure 9.7. Molecular nitrogen gas is fixed aerobically by a number of microorganisms including *Azotobacter, Rhizobium*, and many species of *Cyanobacteria*. Anaerobically, N_2 is fixed by members of the genus *Clostridium*.

The production of organic nitrogen compounds, such as ammonia, from molecular nitrogen requires a relatively high amount of energy input by microorganisms. The overall reaction of ammonia formation is approximately

$$N_2 + 6H + 16ATP \rightarrow 2NH_3 + 16ADP + 16\ P$$
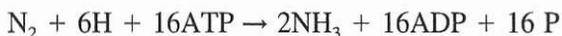
Thus, a cell must spend about 8 ATP molecules in order to synthesize a single molecule of ammonia. From this it is clear that microorganisms can only afford to actively fix nitrogen if a ready supply of energy, either from photosynthesis (in the *Cyanobacteria*), symbiotic plants (as in Rhizobium), or from organic carbon (as in *Clostridia*). The high "cost" of nitrogen fixation is a crucial factor in nitrogen cycling in ground-water systems.

The crucial enzyme system involved with nitrogen fixation is nitrogenase, a complex molecule consisting of an iron-molybdenum protein and two iron proteins.
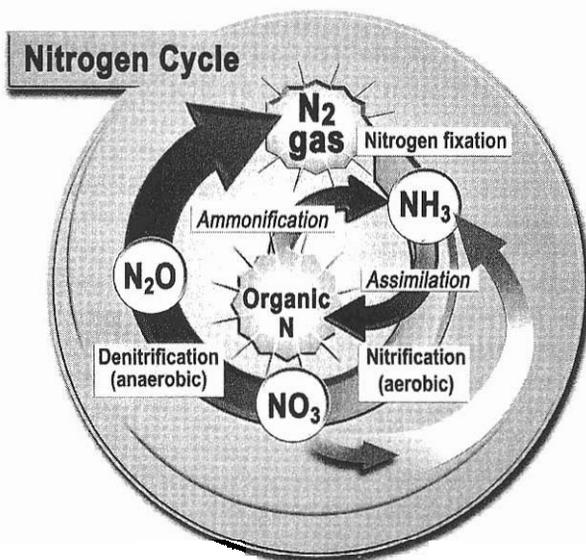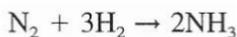

Figure 9.7. The nitrogen cycle.

The general mode of nitrogenase action is for the two iron proteins to reduce the iron-molybdenum protein to a low enough state so that the triple bond of the N_2 molecule may be broken and hydrogens attached to the nitrogen atoms:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Once the nitrogen cycle is initiated by N_2 fixation, the nitrogen cycle can continue (Fig. 9.7). Ammonia (NH_3) produced by N_2 fixation may be assimilated into proteins by microorganisms and by some macroorganisms such as plants. Upon the death of these organisms, the nitrogen present in proteins may be returned to ammonia via deamination processes.

Under aerobic conditions, ammonia may be oxidized to nitrite (NO_2^-) by speciallized nitrifying bacteria such as *Nitrosomonas*. Nitrite is then further oxidized to nitrate (NO_3^-) by other nitrifying bacteria, such as *Nitrobacter*. These combined nitrification processes are the basis of producing nitrate fertilizers from human and animal wastes, procedures that have been used by farmers for millennia. Once complete oxidation of nitrogen is accomplished, the nitrate may be assimilated by a variety of microorganisms and incorporated as NH_2 groups in proteins by either plants or microorganisms. Note that the assimilation into proteins involves the reduction of nitrate. This assimilative nitrate reduction production is a process carried out by a large number of microorganisms.

In addition to being available as a component in protein synthesis, the nitrate ion can function as an electron acceptor in bacterial metabolism. Under anaerobic conditions, nitrate is the most thermodynamically favored electron acceptor and is used by a number of facultatively anaerobic bacteria, including many *Pseudomonas* species. Nitrate reduction coupled to respirative energy production is referred to as *denitrification* to distinguish it from assimilative nitrate reduction. Denitrification occurs in a number of steps, each of which is catalyzed by different microorganisms, in the order $NO_3 \rightarrow NO_2 \rightarrow N_2O \rightarrow N_2$.

As was the case with the oxygen and carbon cycles, the nitrogen cycle is driven primarily by solar energy. The manner in which some microorganisms gain access to the solar energy, however, is interesting and very important for agricultural applications. Members of the bacterial genus *Rhizobium* have evolved a symbioic relationship with several plants, most notably legumes (soybeans and related crops). In symbiotic nitrogen fixation, *Rhizobium* infects the root hairs of the host plant, forming nodules. Within these nodules, the plant supplies sugars to the bacteria. This energy supply gives the bacteria the wherewithal to produce the large amounts of ATP needed to fix nitrogen. This fixed nitrogen is then made available to the plant, which uses it for protein synthesis and growth. It is this symbiotic relationship that is responsible for the relatively high protein content of soybeans and other legumes.

In some cases, the symbiotic relationship between the plant and the microorganism has reached the molecular level. For example, *Rhizobium* is an obligate aerobe, but the activity of nitrogenase is irreversibly destroyed by exposure to oxygen. A specialized protein called leghemoglobin controls access of oxygen to the nodule in order to allow respiration and nitrogen fixation to continue simultaneously. In order to construct leghemoglobin, *Rhizobium* carries the gene for one portion of the protein molecule, whereas the plant carries the gene for another portion. Thus, nitrogen fixation requires both organisms. This is a classic example

of true symbiosis, where each partner requires the other in order to carry out critical life functions.

9.3.1   Nitrogen Cycling in Ground-Water Systems

The behavior of nitrogen species in ground-water systems is strongly affected by three key aspects of the nitrogen cycle. The first of these is that fixation of organic nitrogen from N_2 requires a tremendous input of energy. In oligotrophic ground-water systems, this necessarily places limits on the rate and amount of nitrogen fixation that takes place. Second, the oxidation of organic nitrogen to nitrate (nitrification) takes place only under aerobic conditions. Third, denitrification takes place only under anaerobic conditions. These aspects ensure that nitrate accumulation in ground water requires oxygenated conditions and that nitrate depletion requires anoxic conditions.

In the case of the oxygen and carbon, we saw that the lack of solar energy input in ground-water systems effectively truncated the cycles, resulting in depletion of oxygen and accumulation of carbonate species. In the case of the nitrogen, however, the behavior differs depending on the oxygen status of the ground-water system. Under aerobic conditions nitrification may take place, but the alternate side of the cycle, denitrification, cannot take place. Thus, under aerobic conditions, the cycle truncates after nitrification and nitrate accumulates in solution. Under anaerobic conditions, the reverse is true—nitrate can be converted to N_2 via denitrification, but nitrification is blocked. This generally results in depletion of nitrogen species in anaerobic ground-water systems.

The occurrence of nitrate in ground water is a significant public health issue that has received considerable attention over the years. Excessive intake of nitrate in infants has been linked to methemoglobinemia, often referred to as the "blue baby syndrome," by depleting oxygen in the bloodstream. Furthermore, intake of nitrate has been linked to rates of mortality from gastric cancer. Because of these health concerns, the processes that influence nitrate and nitrogen species mobility in ground water have been closely studied.

As a practical matter, the cycling of nitrogen in ground-water systems is strongly influenced by human activities. Nitrogen fertilizers are widely used in agricultural practice, and the application of these often affects nitrogen cycling in particular systems. Similarly, organic nitrogen is present in a number of waste products, notably sewage effluents, and discharge of these impacts nitrogen cycling. It is convenient, therefore, when considering nitrogen cycling in ground-water systems to distinguish between different kinds of human impacts on ground-water systems. In human-impacted ground-water systems, the principal sources of nitrogen are (1) animal excrement and manure, (2) nitrogen fertilizers, and (3) sewage effluents.

Animal Excrement and Manures   Many studies have documented that animal excrements can impact nitrate concentrations in local flow systems. For example, Robertson (1979) showed that nitrate concentrations in a shallow water table aquifer in Delaware tended to be associated with confined feeding operations of poultry or cattle. Furthermore, Robertson (1979) showed that there was a general decrease in nitrate concentrations with well depths.

These observations can be readily interpreted in the context of the nitrogen cycle. Animal manure contains organic nitrogen in the form of ammonia. Under the aerobic conditions at land surface, ammonia is converted to nitrate via nitrifying bacteria. This nitrate is soluble and readily leaches into the shallow ground-water aquifer. This aquifer tends to be aerobic near the water table surface and so nitrate accumulates in solution. However, in deeper portions of the aquifer, where anaerobic conditions are more common, nitrate concentrations decrease due to denitrification reactions. The accumulation of nitrate in this aquifer is therefore primarily dependent on the delivery of nitrate and the presence or absence of oxygen.

The relationship between the delivery of nitrate to local flow systems and the application of manure to fields has also been widely studied. In one such study in eastern Pennsylvania, Gerhart (1985) showed that concentrations of nitrate in a shallow aquifer mirrored recharge events. As water levels in the well rose, reflecting recharge from rainfall events, concentrations of nitrate increased significantly. In general, nitrate concentrations in the ground water were higher during periods of recharge than between periods of recharge.

This behavior reflects the two-step nature of nitrate delivery to shallow ground-water systems. First, the ammonia present in manure must be oxidized to nitrate by nitrifying bacteria under aerobic conditions, often at or near land surface. Second, nitrate produced by this reaction must be delivered to the ground-water system by means of vertically percolating recharge. If the aquifer being recharged is aerobic, nitrogen cycling truncates at this point and nitrate accumulates in ground water. If the aquifer grades from aerobic to anaerobic, as commonly occurs along aquifer flowpaths, the nitrogen cycle continues through denitrification and nitrate does not accumulate in solution. Again, the nitrogen cycle truncates at this point, this time because of the lack of nitrogen fixation.

Sewage Effluents   Another important source of nitrogen to ground water in human-impacted local flow systems is by the discharge of sewage effluents. The ground water quality problems generated by sewage effluents have been widely studied worldwide. In the United States, one place where this problem has been studied particularly closely is on Long Island, New York.

Long Island is underlain by coastal plain sediments of the Magothy aquifer, which is in turn overlain by coarse-grained sediments of glacial origin. The coarse, organic matter–poor glacial sediments generally contain dissolved oxygen at or near atmospheric saturation. This allows nitrate to accumulate in solution. Much of Long Island has been dependent on septic drains for disposal of sewage effluent. This has, in some places, resulted in significant accumulations of nitrate in ground water.

The influence of septic systems on nitrate accumulations in ground water of Long Island was studied by Katz et al. (1980). Katz and his coworkers made a statistical comparison of nitrate concentrations in unsewered residential areas, where septic tanks were the predominant method of sewage disposal, and sewered areas where sewage was collected for treatment. Surprisingly, there was no significant difference found in mean nitrate concentrations between sewered and unsewered areas over a 15-year period. The data, however, did indicate some differences. For example, the unsewered areas were much more likely to have nitrate concen-

trations greater than 20 mg/L than the sewered areas. Furthermore, while there was little difference in nitrate concentrations, concentrations of ammonium were significantly lower in the sewered area relative to the unsewered area.

These differences can be interpreted in the context of nitrogen cycling in this ground-water system. For example, a major source of dissolved nitrogen from sewage is the deamination of organic matter to produce ammonia and ammonium ions. In the unsewered areas, therefore, a major portion the nitrogen cycle appears to be deamination followed by nitrification. In the sewered areas, in contrast, deamination was much less important. Katz et al. (1980) suggested that sewage effluents were a more important source of dissolved nitrogen in the unsewered areas than in sewered areas. Furthermore, it was suggested that the lack of significant nitrate differences between the two areas reflected applications of nitrate fertilizers.

Perhaps the most comprehensive study of microbial denitrification associated with sewage effluents in local flow systems was described by Smith and Duff (1988). These investigators measured rates of denitrification in a 4-km-long sewage effluent plume on Cape Cod, Massachusetts. Near the source of the effluent, nitrate concentrations exceeded 50 mg/L. As water in the plume moved downgradient, however, concentrations of nitrate decreased below detectable level.

Smith and Duff (1988) obtained samples of aquifer sediments along the hydrologic gradient and measured rates of denitrification using the acetylene block technique. In this technique the final step of denitrification, conversion of N_2O to N_2, is blocked by adding acetylene to sediment slurries. The accumulation of N_2O gas in the slurry vial thus gives an estimate of the overall rate of denitrification. Using this technique, Smith and Duff found that rates of denitrification decreased as nitrate concentrations decreased along the flowpath. Furthermore, rates of denitrification in the plume were greater than in the pristine portion of the aquifer. Denitrification of nitrate to N_2, rather than nitrate reduction to ammonia (Fig. 9.7), was the predominant reductive process in this system.

Perhaps the most interesting finding of this study was that denitrifying activity in the contaminated plume was not limited by the availability of nitrate. Rather, the limiting factor to denitrification rates was the availability of a suitable organic carbon substrate. In anaerobic aquifers in which measurable concentrations of nitrate persist for any distance along the flowpath, denitrification must be limited by factors other than nitrate availability. In such cases, carbon limitation is often responsible for the observed persistence of nitrate.

Nitrogen Fertilizers   Nitrogen fertilizers are a significant source of nitrate contamination of ground water. Nitrogen fertilizers may be composed of a number of nitrogen compounds, including anhydrous NH_3, NH_4NO_3, $(NH_4)2HP_2O_5$, and urea. In general, nitrogen delivered to the soil as NH_3 or NH_4^+ is retained better than nitrogen delivered as nitrate. Ammonium, being a positively charged ion, tends to adsorb to the negatively charged silicate minerals present in soils. The negatively charged nitrate ion, however, is repelled from mineral-grain surfaces and moves freely with percolating pore water, effectively leaching it from the soil.

The impacts of agricultural nitrogen applications on the chemical composition of ground water has been extensively studied. In the United Kingdom, agricultural nitrogen applications to fields overlying a chalk aquifer have been studied by Gray and Morgan-Jones (1980). This study documented the accumulation of nitrate in

three well fields tapping the chalk aquifer over a 40-year period. One of these well fields in particular showed a close correlation between agricultural activity and nitrate concentrations. In the early 1940s, when fertilizer applications were lowered because of World War II, concentrations of nitrate decreased. However, over the next 30 years, as agricultural activity progressively increased, concentrations of nitrate in the ground water increased dramatically. These accumulations reflected the familiar pattern of nitrification in the soil zone, followed by nitrate leaching into and accumulating in an aerobic local flow system.

Nitrate contamination of ground water due to fertilization practices is an important water-quality issue in the midwestern United States. Corn, an important crop in the Midwest, requires large amounts of nitrogen for yields to be economically viable. It is common practice for corn growers to apply as much as 180 lbs N/acre/yr in order to obtain sufficient yields. Nitrogen applied in this manner is rapidly depleted from soil both by plant uptake and by nitrification followed by leaching of nitrate into ground water.

In one study of the impacts of such practices on ground-water quality, Spalding et al. (1978) showed that zones of nitrate contamination in ground water were closely correlated with coarse-textured, well-drained soils. This reflected rates of nitrification, rates of leaching, and the occurrence of oxygenated conditions in the water-table aquifer. This general pattern has been observed in many locations and is characteristic of nitrate contamination of ground water.

Municipal Wastes In addition to animal excrements, sewage effluents, and agricultural fertilizers, municipal wastes that have been disposed in landfills may be important sources of nitrogen contamination to ground water. An example of such nitrogen contamination is given by Baedecker and Back (1979) in describing a municipal landfill in Delaware. The source of the nitrogen species in the ground water was organic nitrogen in the refuse. Near the landfill, ground water was anaerobic and most of the nitrogen was present as reduced organic nitrogen and ammonium. However, as the contaminated water moved downgradient and mixed with the ambient oxygenated ground water, concentrations of reduced nitrogen decreased and concentrations of nitrate increased. Baedecker and Back (1979) described this behavior using a nitrogen index, defined as the ratio of reduced nitrogen species (determined by Kjeldahl digestion) to nitrate. As ground water became progressively more oxygenated, the nitrogen index decreased. This reflected the progressive nitrification of reduced nitrogen with the production of nitrate.

Since anaerobic conditions are more likely in and near landfills of municipal waste, the pattern described by Baedecker and Back (1979) is probably the most common. However, patterns of nitrogen cycling are very sensitive to the availability of oxygen, and other patterns may occur. A very different pattern of nitrogen cycling was described near a municipal landfill and waste-water holding cells in North Dakota (Bulger et al., 1989). This study showed that nitrate was the primary nitrogen species emanating from the landfill under oxidizing conditions. However, once the nitrate plume intersected a plume of high dissolved organic carbon, which was anaerobic, the nitrate was progressively reduced to NH_4^+. This pattern indicates that denitrification, with the conversion of NO_3 to N_2, is not the only pathway of nitrate reduction found in ground-water systems. In this case, nitrate is apparently reduced to NH_4^+ as the plume becomes anaerobic.

Distinguishing Sources of Nitrogen Contamination   Because of the numerous sources of nitrogen contamination in ground-water systems, distinguishing whether contamination originated from agricultural fertilizers, animal wastes, or sewage effluents is often difficult. One method for distinguishing different sources of nitrogen contamination that has been widely applied is the use of stable nitrogen isotopes.

Nitrogen occurs as two stable isotopes, ^{15}N and ^{14}N. Ratios of these isotopes are commonly referred to a standard and reported as $\delta^{15}N$. Ranges of $\delta^{15}N$ for nitrogen from different sources are shown in Figure 9.8. Clearly, there is a wide difference between nitrogen present in fertilizers (-4 to $+2$ per mil) and nitrogen present in animal (and human) wastes ($+9$ to $+18$ per mil. All things being equal,
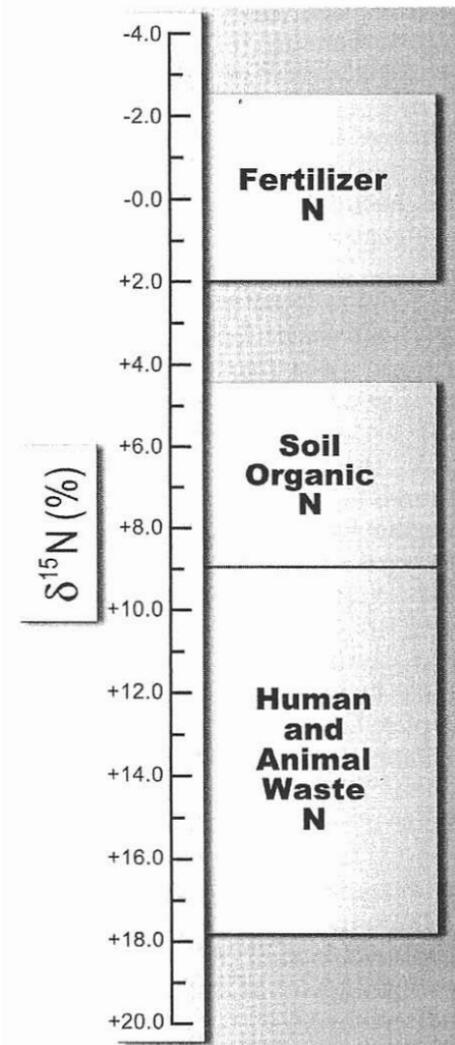
Figure 9.8. Range of nitrogen isotopes characteristic of different sources.

therefore, it should be possible to distinguish fertilizer nitrogen from animal waste nitrogen based solely on $\delta^{15}N$.

However, nitrogen isotopes are subject to a number of fractionation processes in the nitrogen cycle. For example, some ammonia nitrogen applied to soils is subsequently volatilized, resulting in enrichment in ^{15}N. In addition, denitrification also results in a ^{15}N enrichment as microorganisms tend to discriminate against the heavier isotope. These twin processes tend to enrich nitrate with ^{15}N after fertilizer application. For example, Gormly and Spalding (1979) showed that there is an inverse correlation between $\delta^{15}N$ and nitrate concentrations in ground water. This reflects the fact that ground water with lower concentrations of nitrate had undergone more denitrification than the high-nitrate water. However, volatilization and denitrification do not appear to increase $\delta^{15}N$ values above +10 per mil. As such, nitrogen isotopes may be used to distinguish between animal waste nitrogen contamination and fertilizer nitrogen contamination.

This technique has been applied on Long Island, New York, in order to distinguish between animal waste contamination and fertilizer contamination. For example, Flipse and Bonner (1985) showed that the del-15N values of nitrate under a heavily fertilized potato field and under a golf course were in the range of +6.5 to +6.2. While these values were significantly heavier than the fertilizers being applied (−.6 to +.2), they were lighter than the +10 values characteristic of animal wastes. Thus, while fractionation processes altered the isotopic signatures, the technique was still useful for distinguishing between fertilizer contamination and animal waste contamination.

Nitrate Accumulation Due to Dry-Land Farming Practices   While nitrogen species in ground water are commonly associated with contamination events, natural processes also contribute to delivery of nitrogen to ground water. In the soil zone, organic nitrogen produced by microbial nitrogen fixation is cycled through deamination, nitrification, and denitrification processes. Because organic nitrogen is often a limiting nutrient for both plant and microbe growth, it is unusual for ground water in pristine local flow systems to accumulate more than 1 or 2 mg/L dissolved nitrate. However, under some conditions, natural processes can contribute substantial nitrate concentrations to ground water.

One example of this was given by Kreitler and Jones (1975). In 1968, several cattle in Runnels County, Texas, died of anoxia from drinking water produced from the water table aquifer. Upon analysis of the water, it was found to contain between 100 and 1,000 mg/L nitrate. This was surprising in that the use of nitrogen fertilizers for agriculture was minimal. What could be the source of the observed nitrate?

One possibility was that animal wastes were the principal source. In order to test this possibility, Kreitler and Jones (1975) examined the $\delta^{15}N$ of nitrate in the ground water. Surprisingly, the observed values were generally less and +10 per mil, indicating that animal wastes were not the principal source. These values, however, did generally match values of soil nitrogen that was present naturally. Prior to 1900, this area was covered with buffalo grass, the roots of which form a symbiotic relationship with nitrogen-fixing bacteria much like legumes. These soils, therefore, were naturally high in reduced nitrogen compounds. The advent of dry-land farming practices after 1900, particularly with increased oxygen delivery to

the newly plowed soils, resulted in the oxidation of soil nitrogen and subsequent leaching to the water table. This leaching was greatly accelerated by terracing the fields in order to capture and retain more moisture. The intriguing result, therefore, was the production of a nitrate contamination problem without human or animal application of nitrogen.

This is an excellent example of why considering elemental cycling processes are important to understand some ground-water chemistry problems. The accumulation of biochemically active elements in ground water always reflects the perturbation or truncation of one or more elemental cycles. These may be due to natural causes, such as nitrate accumulating due to truncation of the nitrogen cycle in an aerobic aquifer. On the other hand, the perturbation may reflect human influences, such as adding a nitrogen source (fertilizer) where no source existed before. In either case, the key to understanding the observed phenomenon is to consider the nature of the nitrogen cycle.

9.4   THE IRON CYCLE

Iron in the environment exists predominantly in either the reduced ferrous (Fe(II)) or oxidized ferric (Fe(III)) form. Ferrous iron is relatively soluble in water and is therefore quite mobile. Ferric iron, on the other hand, tends to form insoluble Fe(III) oxyhydroxides and is therefore relatively immobile. The iron cycle in most environments involves alternate reduction (mobilization) of ferric iron followed by oxidation (immobilization) of ferrous iron. Most of these reactions are microbially catalyzed under natural conditions.

A schematic diagram of the iron cycle is shown in Figure 9.9. Under anaerobic conditions, Fe(III) oxyhydroxides are reduced by a variety of microorganisms that use Fe(III) as a terminal electron acceptor. Curiously, the role of microorganisms in iron reduction has only recently been extensively studied. Prior to 1985, most geochemists and microbiologists considered Fe(III) reduction to be an abiological reaction initiated by "reducing conditions." However, with the isolation and characterization of Fe(III) reducing microorganisms in the late 1980s it became clear that this important component of the iron cycle is largely mediated by microbial processes (Lovley et al., 1991). Several microorganisms, including *Geobacter* and *Shewanella putrifaciens,* carry out this metabolic function.

Much of the Fe(II) generated by Fe(III) reduction remains sediment-bound, being sequestered in Fe(II)-bearing minerals such as illite or magnetite. A small percentage (1–5%) of the Fe(II) accumulates in solution, however, and moves in response to diffusion gradients or with flowing water. If dissolved Fe(II) is transported to an aerobic environment, it is subsequently oxidized to Fe(III) oxyhydroxides. This oxidation is highly excergonic and can take place spontaneously without microbial mediation. However, several types of microorganisms have evolved mechanisms to harness this available energy. These include representatives of the genera *Gallionella, Thiobacillus,* and *Leptothrix.* Because spontaneous oxidation of Fe(II) occurs much less rapidly at acidic pH, many of these microorganisms are specifically adapted to acidic environments. *Thiobacillus,* for example, has been widely described in streams impacted by acid-mine drainage. There is relatively little energy to be had from oxidizing Fe(II), and consequently, Fe(II)-