

Chapter-10

Transformation of Sulfur, Iron and Manganese in Soil

Sulfur (S) is an essential element for the growth and activity of all living organisms. It is one of the ten major bio-elements required by organisms in relatively high concentrations (i.e., $> 10^{-4}M$). Sulfur is required for the synthesis of the amino acids cysteine, cystine, and methionine. It plays an active role in plants, animals, and microorganisms as an important constituent vitamins, hormones, and structural components, and for other metabolically important molecules such as coenzyme A. for example, the disulfide bond formed between cysteine residues helps stabilize the tertiary structure of proteins.

Sulfur is an important source of metabolic energy for many bacteria. For example, certain chemoautotrophic bacteria obtain energy for cell growth and division by oxidizing reduced sulfur compounds. In fact, some exotic ecosystems, such as hot sulfur springs and hydrothermal vent communities, are driven by energy generated in the oxidation of sulfur, which they use to fix carbon.

This chapter introduces the basic principles of the sulfur cycle and the microorganisms that drive it. This information will give one an appreciation of how important it is to understand the biogeochemistry of sulfur and other elements.

The Sulfur Cycle in Agroecosystems and Terrestrial Environments

The sulfur cycle bears many similarities to the nitrogen cycle. Both of these elements exist in a number of oxidation states and undergo similar types of chemical reactions and biological transformation, including volatilization. The majority of sulfur is found in the lithosphere. Most nitrogen on earth is also in the lithosphere; however, dinitrogen in the atmosphere is the major pool of biologically available nitrogen. Only a small portion of the sulfur pool is found in the atmosphere, and most sulfur that cycle through the atmosphere is because of human activities. In fact, since the Industrial Revolution, increased burning of fossil fuels has almost doubled the rate of sulfur entering the atmosphere to approximately $1.5 \times 10^{11} \text{ kg S yr}^{-1}$. The volatilization of sulfur as hydrogen sulfide, carbonyl sulfide, and dimethyl sulfide, for example, from marine algae, marsh lands, mud flats, plants, and soils also contributes to the global circulation of sulfur through the atmosphere.

The nature and quantities of the various sulfur pools in surface soils are basis for sulfur cycling in terrestrial environments. These sulfur pools are influenced by pedogenic factors such as

climate, regional vegetation, and local topography. For example, the total sulfur content of soils ranges from 0.002 to 10%, with the highest levels in tidal flats, and in saline, acid sulfate, and organic soils.

Nature and Forms of Organic and Inorganic Sulfur in Soil

Organic sulfur constitutes more than 90% of the total sulfur present in most surface soils. However, the precise nature of the organic sulfur compounds in soil cannot be clearly identified. Thus, organic sulfur is grouped into two broad categories, organic sulfates and carbon-bonded sulfur. Example of these organic compounds are given in Figure 15-1. Organic sulfates (R-O-S) include sulfates esters (C-O-S), sulfamates (C-N-S), and sulfated thioglycosides (N-O-S). Organic sulfates constitute 30 to 75% of total organic sulfur in soil. Carbon-bonded (C-S) includes the sulfur present in amino acids, proteins, polypeptides, heterocyclic compounds (e.g., biotin and thiamin), sulfinates, sulfones, sulfonates, and sulfoxides. A large portion of carbon-bonded sulfur of amino acids may constitute up to 30% of the organic sulfur in soil.

Inorganic forms of sulfur account for less than 25% of the total sulfur in most agricultural soils. Sulfur exists in a number of forms with a wide range of oxidation states. Sulfide, elemental sulfur, sulfite, thiosulfate, tetrathionate, and sulfate are the main forms of inorganic sulfur in agricultural soils. Sulfate is the most common form of inorganic sulfur found in well-aerated agricultural soils, whereas sulfides account for less than 1% of total sulfur and measurable quantities of thiosulfate and tetrathionate are usually detected only in soils treated with sulfur fertilizer or those receiving pollutants.

Table 15-3 important forms of sulfur and their oxidation states.

Compound	Formula	Oxidation state(s) of sulfur
Sulfide	S_2^{2-}	-2
Polysulfide	S_n^{2-}	-2, 0
Sulfur*	S_8^0	0
Hyposulfite (dithionite)	$S_2O_4^{2-}$	+2
Sulfite	SO_3^{2-}	+4
Thiosulfate*	$S_2O_3^{2-}$	-1, +5
Dithionate	$S_2O_6^{2-}$	+6
Trithionate	$S_3O_6^{2-}$	-2, +6
Tetrathionate	$S_4O_6^{2-}$	-2, +6
Pentathionate	$S_5O_6^{2-}$	-2, +6
Sulfate	SO_4^{2-}	+6

Microbial Transformation of Sulfur in Soil

The sulfur cycle-emphasizing soil and plant sulfur transformations in agroecosystems-is illustrated in Figure 15-2. The major forms of sulfur in soil include elemental sulfur (S^0), sulfides (S^{2-}), sulfates (S^{6+}), and organic sulfur compounds. Most of this sulfur enters the soil as soluble inorganic forms produced during the weathering of minerals, from fertilizers and atmospheric deposition, or as soluble organic and inorganic forms the decomposition of organic matter. Losses of sulfur occur through leaching, surface runoff, volatilization, and crop removal.

Soil microorganisms drive the sulfur cycle. Hence, sulfur undergoes many microbially mediated transformations in soil, including:

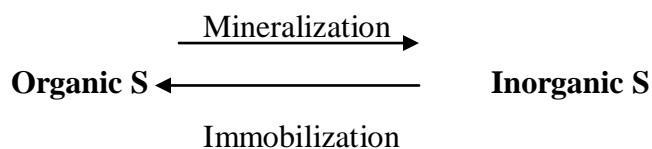
- oxidation and reduction reactions,
- mineralization and immobilization reactions, and
- volatilization reaction

The soil microbial biomass is the key driving force behind all sulfur transformations. The biomass acts as both a source and sink for inorganic sulfate, whereas microbial activity regulates both the fluxes of sulfur between different pools (inorganic sulfate, labile organic sulfur, and resistant organic sulfur) and the losses of sulfur from these pools (e.g., conversion of complex organic sulfur compounds into mobile forms that may be lost by leaching). Most of the sulfur in soil (75 to 90%) is found in organic complexes. These complexes are either stable, passive fractions that turn over very slowly or active, dynamic fractions that are readily transformed or metabolized. Actually, the continuum of sulfur organic complexes in soil ranges from very old, stable (e.g., organic sulfur found in the amino acid cysteine) fractions. The microbial biomass is the engine for the conversion of passive fractions into active fractions, and vice versa. This is illustrated in the following diagram, where the relative flux of sulfur between pools is reflected in the size of the arrows depicting microbial conversion:

Understanding the sources, sinks, and transformations of sulfur in soil is crucial to ensure adequate supplies of sulfur for the biota of various ecosystems and to protect the environment from the detrimental effects too much sulfur. Because microorganisms are so important for the conversions between the active and passive organic matter pools, any factor that disturbs or otherwise has an impact on the microbial biomass influence sulfur cycling. For example, crop rotations and soil cultivation typically increase sulfur cycling in soil. When a soil is cultivated, it is mixed and churned and broken up into smaller pieces. This increases soil aeration and exposes

soil particles and organic matter that were previously “hidden” from the soil microflora. Fresh organic matter, containing different ratios of carbon, nitrogen, phosphorus, and sulfur, is mixed into the soil. Some microbial biomass is activated due to the flush of available nutrients, and some of the biomass might be killed. For example, fungal hyphae help to hold soil aggregates together; as cultivation breaks up these aggregates, the hyphae are broken, resulting in dead biomass. This dead biomass is now available to be mineralized. As new microbial biomass is formed during decomposition of the newly exposed or added “active” organic material, nutrient elements (carbon, nitrogen, phosphorus, sulfur, and micronutrients) are cycled back and forth between active and passive states as organic and inorganic forms of the element. The overall consequence is increased nutrient cycling.

Similarly, interactions among different microbial groups, such as predation and parasitism, tend to increase the turnover rate of microbial biomass sulfur and hence affect sulfur fluxes. One can think of this in the following way. Bacteria and fungi store sulfur in the organic and inorganic sulfur compounds that comprise their cells. When predators, such as soil amoebae, eat bacterial cells or pieces of fungal hyphae, that biomass material (labile or active sulfur pool) is broken down into smaller, non-metabolized sulfur containing organic fragments resistant to further metabolism by the amoebae, which are excreted into the soil, along with any inorganic sulfur or metabolizable organic sulfur not needed by the amoebae for growth. The excess inorganic sulfur or metabolizable organic sulfur is now available for plants and other organisms to use. This is an example of the processes of **mineralization** and **immobilization** of nutrients.



Biological mineralization and immobilization are processes that occur concurrently and exhibit a strong relationship with the soluble sulfate pool in soil. Immobilization occurs as a result of the microbial assimilation of nutrients that are then rendered unavailable for further plant or microbial uptake until the cell dies and is re-mineralized. Immobilization of sulfur may also involve precipitation as metal sulfide, especially pyrite, as in salt marshes, because these transformations are mediated by microorganisms, soil factors that influence the growth and activity of microorganisms (e.g., pH, temperature, and moisture) also affect the rate of sulfur transformations. To estimate or predict the available sulfur status of soils, it is necessary to understand the factors that influence these processes.

Immobilization (Assimilation)

Microbial assimilation and conversion of inorganic sulfate into organic sulfur through the *assimilation sulfate reduction pathway* leads to temporary immobilization of sulfur from plant or microbial availability. This process involves ATP sulfurylase and two energy-rich sulfate nucleotides, APS (adenosine 5-phosphosulfate) and PAPS (3'-phosphoadenosine-5'-phosphosulfate). The overall reactions of SO_4^{2-} incorporation into amino acids is shown 15-3.

Most of the sulfur accumulated by microorganisms is in the form of amino acids in proteins; however, microorganisms also accumulate sulfate esters, sulfonates, vitamins, and cofactors. Some microorganisms, such as fungi, accumulate especially large amounts of sulfate ester. This is important because organic sulfates (e.g., sulfate esters and thioglucosides) are considered to be the most labile form of organic sulfur in soil and may comprise up to 30 to 70% of the organic sulfur in surface soils. The relative proportion of fungal biomass to bacterial biomass in soil (approximately 2:1) underscores the potential importance of microorganisms accumulating ester-sulfur compounds.

Typically, the addition of inorganic SO_4^{2-} -S to soil leads to its quick incorporation into the organic sulfur fractions via microbial assimilation. The rate and magnitude of this immobilization is increased in the presence of an energy source, such as metabolizable organic matter or addition of easily degradable carbon sources like glucose. Later, much of this accumulated sulfur is found in the fulvic acid fractions, especially as organic sulfates.

Mineralization

Mineralization of organic sulfur in soil is largely mediated by microbial activity. The various known pathways of sulfur mineralization are summarized in 15-4. Carbon-bonded sulfur is mineralized either through oxidative (aerobic) decomposition or desulfurization (anaerobic) process, whereas various sulfatases are involved in the mineralization of sulfate esters. The mineralization process may be direct (i.e., cell mediated), involving viable microbial cells, or indirect (i.e., cell-free, enzyme mediated), involving enzymes such as sulfatases. In the case of direct mineralization, elements such as nitrogen and sulfur in direct association with carbon are mineralized; elements such as nitrogen and sulfur in direct association with carbon are mineralized as microorganisms oxidize the organic carbon compounds to obtain energy. Heterotrophic soil microorganisms decompose organic sulfur compounds to grow; as the carbon-sulfur bond is broken, the sulfur is released usually as sulfide. Because this process involves actively growing microorganisms, their requirement for sulfur may meet or even exceed the

sulfur supplied by the substrate. Thus net mineralization of sulfur by this process may not be reflected by increase in the sulfate-sulfur pool in soil. In the case of indirect mineralization, those elements that exist as sulfate esters are hydrolyzed by intracellular or extracellular enzymes. This process, also known as enzymatic mineralization, occurs mainly outside the cell and may be regulated by end product inhibition, or the sulfate level. Direct mineralization is controlled by the microbial need for carbon and energy sources, whereas indirect mineralization is controlled by factors influencing enzyme synthesis, activity, and kinetics.

Factors Affecting the Mineralization of Sulfur in Soil

Mineralization is generally measured as net mineralization, either the amount of SO_4^{2-} -S accumulated during the period of study or the difference between gross mineralization and assimilation. Thus, for higher net mineralization to occur, the mineralization-assimilation balance has to be driven toward mineralization. A break-even point for mineralization and immobilization can be calculated based on the carbon-to-sulfur ratio of the substrate, the decomposing organisms, and the yield coefficient. For example, if we consider the decomposition of crop residues, net mineralization will generally occur with a carbon-to-sulfur ratio of 200 or less, whereas net sulfur immobilization will occur when the ratio is greater than 400/1. Because microbial activity is the driving force for mineralization and immobilization, these processes are significantly influenced by all factors affecting microbial metabolism, such as:

- energy and nutrient supply,
- carbon-to-sulfur ratio,
- abundance of organic sulfur,
- water availability,
- pH,
- temperature and
- redox potential.

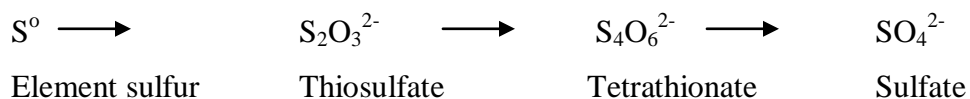
For example, actively growing plants may significantly increase sulfur mineralization in soils. Plants supply energy sources to the rhizosphere in the form of root exudates that increase microbial growth and activity, thus increasing sulfur mineralization. However, the re-assimilation of inorganic sulfates released by the growing microorganisms may result in no increase in the sulfur pool when the microbial demand exceeds the rate of sulfur mineralization.

Different plants excrete different types and amounts of root exudates and require different amount of sulfur for growth. Hence, crop rotations can have a significant impact on sulfur cycling in soil.

Microbial Oxidation of Inorganic Sulfur Compounds

Chemoautotrophic and Chemoheterotrophic Sulfur Oxidation

The abiotic oxidation of reduced sulfur compounds can occur to a limited extent in soils, but microbial reactions clearly dominate the process. For example, the biological oxidation of elemental sulfur in soils apparently takes place primarily via the following sequence of reactions (i.e., those most common to heterotrophs), although some of the products may result from abiotic side reactions:

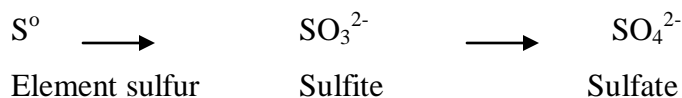


Many different microorganisms are important for the oxidation, reduction, and cycling of sulfur in soil and other ecosystems. In the case of sulfur oxidation, the microorganisms can be divided into:

- chemoautotrophs (lithotrophs), including species of the genus *Thiobacillus*,
- photoautotrophs, including species of purple and green sulfur bacteria, and
- chemoheterotrophs (organotrophs), including a wide range of bacteria and fungi.

The chemoautotrophs and chemoheterotrophs are largely responsible for oxidizing sulfur in most aerobic, agricultural soils.

Many chemoautotrophic bacteria (e.g., thiobacilli) are capable of oxidizing reduced inorganic sulfur compounds. The biochemistry of sulfur oxidation by thiobacilli growing in vitro has been extensively reviewed (Postgate and Kelly, 1982; Pronk et al., 1990). For acidophilic thiobacilli, the most common sequence of reactions involved in sulfur oxidation is:



A great variety of thiobacilli can be isolated from natural habitats. They include obligate acidophilic chemoautotrophs, facultative chemoautotrophs (thiobacilli that grow autotrophically with reduced inorganic sulfur compounds as energy sources, but are also capable of heterotrophic growth), and **mixotrophs**, which can use mixtures of inorganic and organic compounds simultaneously. The thiobacilli differ in

Table 15-5 Sulfur-using bacteria occurring in soil and aquatic habitats.

Group	Sulfur conversion	Habitat requirements	Habitat example	Example of Genera
Heterotrophs that use Oxidized S species as Electron acceptors	$\text{SO}_4^{2-} \rightarrow \text{HS}^-$ $\text{S}_2\text{O}_3^{2-} \rightarrow \text{HS}^-$ or S^0 $\text{S}^0 \rightarrow \text{HS}^-$ $\text{SO}_3^- \rightarrow \text{HS}^-$	anaerobic; organic substrates available; light not required	anoxic sediments and soils	<i>Desulfomonas</i> <i>Desulfovibrio</i> <i>Desulfotomaculum</i> <i>Desulfurmonas</i> <i>Campylobacter</i>
Obligate and facultative Autotrophs that use Reduced S as energy source	$\text{HS}^- \rightarrow \text{S}^0$ $\text{S}^0 \rightarrow \text{SO}_4^{2-}$ $\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$	H_2S - O_2 interface; light not required	mud; hot springs; mine drainage; soils	<i>Thiobacillus</i> <i>Thiomicrospira</i> <i>Achromatium</i> <i>Beggiatoa</i>
Phototrophs that use Reduced S as an electron donor	$\text{HS}^- \rightarrow \text{S}^0$ $\text{S}^0 \rightarrow \text{SO}_4^{2-}$	anoxic; H_2S ; Light	Shallow water; anoxic sediments; metalimnion or hypolimnion; anoxic water	<i>Chlorobium</i> <i>Chromatium</i> <i>Ectothiorhodospira</i> <i>Thiopedia</i> <i>Rhodopseudomonas</i>
Heterotrophs that use Organic S compounds as Energy sources or that Hydrolyze esters	$\text{Org S} \rightarrow \text{HS}^-$ $\text{Org S} \rightarrow \text{Volatile Org S}$ $\text{Ester SO}_4 \rightarrow \text{SO}_4^{2-}$	source of organic S compounds	Sediments; soils; water column	Many
Microorganisms that use SO_4^{2-} or H_2S in biosynthesis	$\text{SO}_4^{2-} \rightarrow \text{protein}$ $\text{HS}^- \rightarrow \text{protein}$ $\text{SO}_4^{2-} \rightarrow \text{DMSP}$	nonspecific	Sediments; soils; water column	Many

their physiological characteristics and in the reduced sulfur compounds used as energy sources.

The majority of these thiobacilli are obligate aerobes, although some, like *Thiobacillus denitrificans*, can grow anaerobically by using nitrate as a terminal electron acceptor. Other

species of thiobacilli use electron donors such as ferrous iron (*T. ferrooxidans*) and thiosulfate (*T. thioparus*) in addition to sulfur.

Although thiobacilli can oxidize sulfur to plant-available sulfate in some soils, this process is also evidently mediated by many different heterotrophic soil microorganisms. Bacteria, such as *Arthrobacter*, *Bacillus*, *Micrococcus*, and *Pseudomonas*, some actinomycetes, and a wide range of fungi are also capable of oxidizing elemental and reduced forms of sulfur. Many of these sulfur-oxidizing heterotrophs have been isolated from soil and may:

- oxidize sulfur, producing mainly thiosulfate,
- oxidize sulfur, producing sulfate, and
- oxidize thiosulfate to sulfate.

The pathway by which heterotrophic microorganisms produce these sulfur oxyanions has not been established, although several studies suggest that it is enzymatic in fungi. Apparently, no energy is derived by the organisms through these oxidations, and the transformations are incidental to the major metabolic pathways. Because the heterotrophic organisms are generally more numerous in soils than chemoautotrophs, mixed populations of heterotrophs probably play the dominant role in sulfur oxidation in many aerobic, neutral, and alkaline agricultural soils.

The opposing view that thiobacilli play the dominant role in sulfur oxidation in soils is largely based on the observation that these bacteria achieve rates of sulfur oxidation in culture far in excess of those achieved by heterotrophs growing under the same conditions. Most thiobacilli are facultative or obligate chemoautotrophs, which means that they can oxidize sulfur independently of the supply of available organic carbon. Marked increases in numbers of thiobacilli may follow the addition of reduced forms of sulfur to some soils, supporting the concept that populations of thiobacilli are important oxidizers of the added sulfur. However, no consistent correlation has been found between sulfur-oxidation rates and the numbers of thiobacilli. Sulfur oxidation is generally low in soils that lack these organisms and is accelerated in soil inoculated with thiobacilli. It is probable that in many soils the initial oxidizers of reduced sulfur compounds are heterotrophic organisms until the pH is reduced sufficiently to permit oxidation by chemolithotrophs. In addition, there is good evidence that **consortia** of heterotrophs and autotrophs working together to bring about the oxidation of sulfur in agricultural soils.

Other Sulfur Bacteria

Other bacteria may also oxidize sulfur compounds. The gliding sulfur oxidizer includes those bacteria that have a gliding motion on the substrate; their cells are arranged in **trichomes**. The most important members of this group in relation to sulfur-oxidation in soils are species of *Beggiatoa*, bacteria that participate in sulfide oxidation in the root zone of rice. All strains of *Beggiatoa* deposit sulfur intracellularly in the presence of hydrogen sulfide. Phototrophic bacteria, such as *Chromatium* and *Chlorobium*, also play an important role in sulfide oxidation in rice paddy soil, but not in aerobic agricultural soil. A number of nonfilamentous, chemolithotrophic sulfur-oxidizing bacteria, such as *Sulfolobus*, *Thiospira*, or *Thiomicrospira*, have also been isolated from special habitats, but the importance of these bacteria in sulfur oxidation in soils as yet to be determined. The activity of different groups of sulfur-oxidizing bacteria may be predicted based on the relative turnover rates of inorganic sulfur compounds and organic substrates during energy-limiting growth condition (Kuenen and Beubeker, 1982).

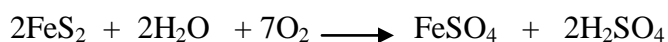
Biogenesis and Oxidation of Metal Sulfides

Metal sulfides may be formed through biotic or abiotic reactions. In both cases the metal sulfide results from the interaction between a metal ion and a sulfide ion



Many sulfate-reducing bacteria such as *Desulfovibrio* spp. or *Desulfotomaculum* spp., are involved in the biogenesis of sulfides of antimony, cobalt, cadmium, iron, lead, nickel, and zinc. The extent of metal-sulfide genesis depends on many factors, the most important of which is the relative toxicity of the metal ion. In nature, this toxicity is probably reduced when the metal ions are absorbed on clays or complexed with organic matter. The formation of metal sulfides during the mineralization of organic sulfur compounds is also possible, although little is known about this phenomenon.

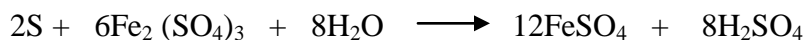
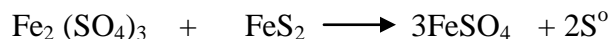
The oxidation of metal sulfides in soil involves both chemical and microbial processes and, as a result, is more complex process than is sulfur oxidation. Chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), galena (PbS), pyrite (FeS_2), and nickel sulfide (NiS) are just a few example of metal sulfide that are subject to microbial transformation. For example, the biological oxidation of pyrite follows a series of oxidation steps described in the following equations. These biotic oxidation are responsible for the formation of acid mine drainage and acid soil formation in surface mine spoils. First ferrous sulfate is formed as the result of an abiotic oxidation step:



This reaction is then followed by the bacteria oxidation of ferrous sulfate, generally by *T.ferrooxidans*;



This reaction occurs chemically but can be accelerated 106 – to 108- times by thiobacilli. Subsequently, ferric sulfate is reduced and pyrite oxidized by a strictly chemical reaction.



The elemental sulfur produced is finally oxidized by *T.thiooxidans* and *T.ferrooxidans*, and the acidity produced helps the whole process to continue.



Note the net production of 10 molecules of H_2SO_4 during the process.

Although several sulfur-oxidizing thiobacilli and heterotrophs can be isolated from acid sulfate soils in which pyrite is being oxidized, only *T. ferrooxidans* appears to play an important role in the process. The biological oxidation of sulfides and other reduced sulfur compounds can have severe consequences for the environment. For example, acid mine drainage contaminates several thousand kilometers of streams in the Appalachian coal mining region of the United States.

Microbial reduction of inorganic sulfur compounds

Bacterial Sulfate Reduction

The reduction of sulphate to hydrogen sulfide is mediated mainly by anaerobic, sulfate-reducing bacteria. This process may be significant in anaerobic, waterlogged soils, but is usually not important in well-aerated agricultural soils, except in anaerobic microsites. Nevertheless, sulfate reduction is a major component of the sulfur –cycle in soils exposed to waterlogging or periodic flooding, especially where readily decomposable plant residues are present.

Microorganisms reduce oxidized sulfur compounds by either an assimilatory or Dissimilatory process. Some use *assimilatory sulfate reduction* to meet their sulfur requirements. In *Dissimilatory sulfate reduction*, bacteria use sulfate as a terminal electron acceptor, and large quantities of hydrogen sulfide (H_2S) are released. This process is analogous to the denitrification process discussed in Chapter 12. Like most denitrification, dissimilatory sulfate reduction is a strictly anaerobic process. In this case it is carried out by bacteria such as *Desulfovibrio* spp., *Desulfomonas* spp., and *Desulfotomaculum* spp. these bacteria use end products of other fermentations such as lactate, malate, and ethanol as electron donors.

Factors Influencing Sulfate Reduction

When a soil is flooded, electron acceptors become reduced in an ordered sequence: first oxygen, followed by nitrate, nitrite, manganic, and ferric compounds, and finally sulfate and carbon dioxide. Although the reduction of one compound does not have to be completed before another is reduced, oxygen and nitrate must be removed before the reduction of ferric and sulfate ions can occur. Because of this reaction sequence, sufficient ferrous ions generally are available to react with any hydrogen sulfide produced, and as a result, free hydrogen sulfide is rarely liberated from soils. Sulfate reduction increases with the period of soil submergence and following the addition of organic matter. Sufficient organic substrates to stimulate the process are also liberated from seeds and from roots into the rhizosphere, with the result that in paddy soils, blackening caused by ferrous sulfide deposits often occurs in the root region. There is evidence, however, that rice roots can aerate the soil sufficiently that ferric iron is observed on the root surface. In general, the rate of sulfate reduction increases with decreasing redox potential, with the optimum being a function of soil pH, around -300 mV at pH 7. Sulfate-reducing bacteria are active in soil, sediments, polluted water, oil-bearing strata, and shales. Their activity may be beneficial or detrimental to the surrounding environment and have serious economic consequences.

Volatilization of Inorganic and Organic Sulfur Compounds from Soil

A number of sulfur gases are released from soils, marshes, peats, and sediments or from anthropogenic sources. These gases may be inorganic or organic and play an important role in the cycling of sulfur through the atmosphere. Many different fungi and heterotrophic bacteria are responsible for the formation of these volatile compounds during the metabolism of organic sulfur compounds.

Environmental Aspects of Sulfur Pollutants

Acid Sulfate Soils

Acid sulfate soils contain sulfides, mainly in the form of pyrites, which may be oxidized to yield free and adsorbed sulfates, they are characterized by yellow mottling due to the formation of jarosites [$AFe_3(SO_4)_2(OH)_6$, where $a = K^+, NH_4^+, Na^+$ or H_3O^+], and have a pH typically below 4. Although these soils cover large areas of the tropics, they tend to be of only local importance in temperate regions. The acidification of these soils results from the abiotic and microbial oxidation of pyrite. Problems in producing crops on these soils occur because of aluminum and

manganese toxicity rather than to the direct effects of acidity. Acid sulfate soils can be reclaimed by:

- controlling the water table through adequate drainage,
- adding lime,
- planting crops tolerant of aluminum, manganese, and iron, and
- improving soil fertility generally.

Deposition of Atmospheric Sulfur in Soils

Soils subject to atmospheric pollution receive sulfur from the atmosphere largely in the form of dilute sulfuric acid. Thus, sulfate is the main sulfur ion entering soils from the atmosphere; smaller quantities of sulfite and bisulfite may also contaminate these soils. Atmospheric pollution deposits, consisting largely of soot, may also be locally important sources of reduced sulfur compounds, particularly in areas adjacent to industrial plants, such as coking and steel works. Because sulfate is the major sulfur ion entering soil from atmospheric pollution, we expect that the major sulfur transformations that occur involve sulfur assimilation and sulfur reduction rather than sulfur oxidation. However, when reduced sulfur compounds in the atmosphere are deposited on soils, they are rapidly oxidized.

Summary

Sulfur is an essential for all living organisms and is the basis for primary productivity in some exotic communities. It exists in a number of oxidation states as in organic and organic compounds that undergo a number of biotic and abiotic transformations. These transformations can be beneficial or detrimental to ecosystems depending on the forms and fluxes of sulfur. The cycling of sulfur through aquatic, terrestrial, and atmospheric ecosystems is similar to that of other elements, such as carbon and nitrogen, and is influenced by natural and anthropogenic processes.

We currently have a basic understanding of the forms and amounts of sulfur in terrestrial ecosystems and the process controlling the supply of sulfur plants. The exchange of sulfur gases between the soil-plant system and the atmosphere is less well documented. Understanding how key processes in the sulfur cycle respond to environmental factors (e.g., construction of models of mineralization and volatilization processes that include temperature, moisture, substrate, and microbial composition response functions) will help us predict accurately the impact of human-induced or natural changes on sulfur fluxes in all components of the biosphere.