

CHAPTER

17

Transformations of Sulfur

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... sulfur is a devilish substance. . . discharged from the bowels of the earth, by volcanoes or evil-smelling hot springs . . . surely the effluent of Hell itself. . .

—J. R. Postgate

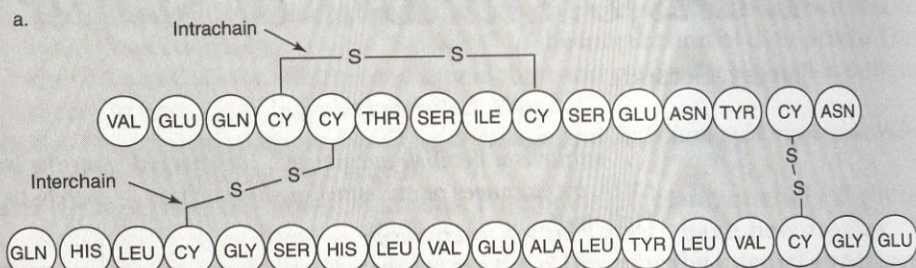
Sulfur (S) is an essential element for the growth and activity of all living organisms. It is one of the ten major bio-elements required by organisms in relatively high concentrations (i.e., $> 10^{-4}M$). Sulfur is required for the synthesis of the amino acids cysteine, cystine, and methionine. It plays an active role in plants, animals, and microorganisms as an important constituent of 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 (Box 17-1).

Sulfur is an important source of metabolic energy for many bacteria. For example, certain chemoautotrophic (chemolithotrophic) bacteria obtain energy for cell growth and division by oxidizing reduced sulfur compounds (Chapter 3). 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 (Box 17-2). These environments also support diverse communities of microorganisms (Box 17-3).

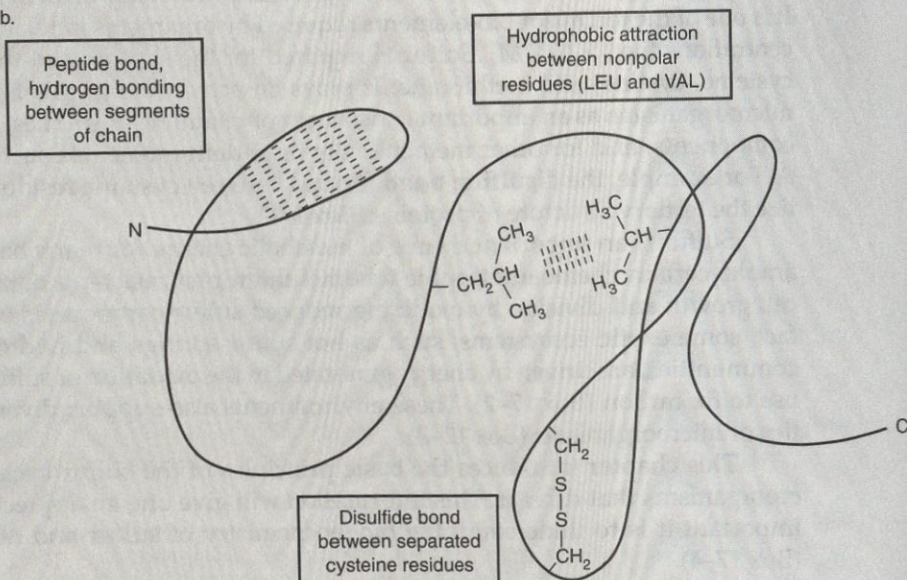
This chapter introduces the basic principles of the sulfur cycle and the microorganisms that drive it. This information will give one an appreciation of how important it is to understand the biogeochemistry of sulfur and other elements (Box 17-4).

BOX 17-1**Disulfide Bonds Stabilize Protein Structure**

A disulfide bond is a covalent linkage between two sulfur atoms. This type of linkage is commonly found in polypeptides and protein molecules and may occur as an interchain or intrachain bond between sulfur-containing amino acids. This type of bond is not common to all proteins, but is usually critical to those that do possess it.



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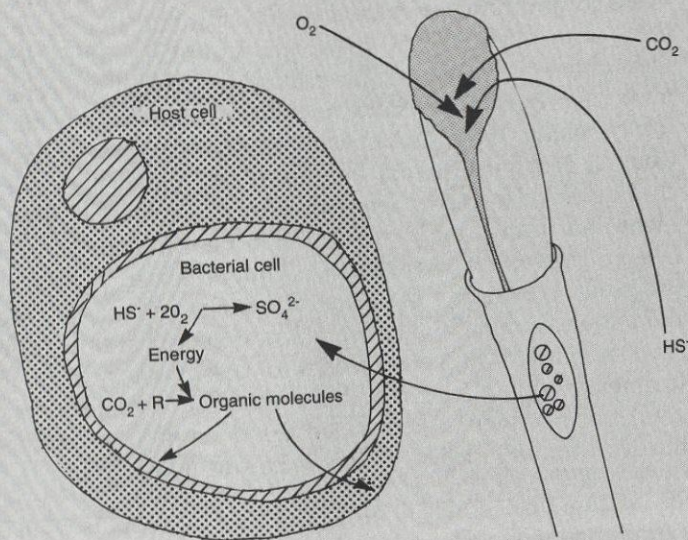


(a) Amino acid sequence of two polypeptide chains illustrating how intrachain and interchain disulfide covalent bonds form between cysteine residues. (b) Diagrammatic representation of how disulfide bonds and other stabilizing forces confer a unique spatial conformation on proteins. Not all types of forces or their frequency of occurrence are shown.

Life Without Light: The Importance of Chemosynthesis

All life requires energy. Furthermore, it is clear that the sun's energy, trapped through photosynthesis, is the driving force for **primary productivity** in all ecosystems. Almost all, that is! About 25 years ago scientists made one of the most startling discoveries of twentieth-century biology. They found bizarre, exotic biological communities living in the deep ocean where hydrothermal fluids rise through the earth's crust. The communities at these deep sea thermal vents consist of giant tubeworms and masses of large clams. Life here is sustained by primary productivity based on microbial sulfur oxidation (Jannasch and Mottl, 1985).

Hydrogen sulfide is the most abundant compound in the deep sea thermal vent fluid. This compound is extremely toxic to higher animals, but some sulfur-oxidizing bacteria can use it as an energy substrate. Considerable energy is released when hydrogen sulfide is oxidized. Through a process called **chemosynthesis**, analogous to photosynthesis, vent bacteria employ chemical



Bacteria found in symbiosis with tube worms at hydrothermal vents use chemosynthesis to fix carbon to make organic compounds. Shown is the breathing organ attached to the body of the worm, *Riftia pachyptila*, which contains the symbiotic association. The bacteria use the hydro-sulfide ion (HS^-) and oxygen (O_2) to generate chemical energy (chemosynthesis). The hydro-sulfide ion serves as the electron donor; the energy is released when HS^- and O_2 are combined, driving a series of reactions called the Calvin cycle. In the Calvin cycle, organic compounds are formed as the carbon dioxide (CO_2) present in both vent water and sea water is fixed. In this illustration, R stands for the auxiliary compounds, including CO_2 -fixing enzymes, involved in the cycle. Note that sulfuric acid is produced as a by-product. The process is analogous to photosynthesis, in which green plants use light energy to fix carbon dioxide and form organic compounds.

Redrawn from Tunnicliffe (1992). Used with permission.

BOX 17-2 (continued)

rather than light energy to fix inorganic carbon to make organic compounds. More surprisingly, the giant tube worms and clams living at the vent are in a symbiotic relationship with these sulfur-oxidizing bacteria that live in their tissue. This is truly a remarkable example of how life adapts to extreme environments and is found where least expected. In fact, it now appears that microbial life exists in all environments with an oxidizable energy source and favorable conditions for microbial life.

BOX 17-3***Biodiversity of Sulfur Bacteria at Hydrothermal Sea Vents***

Oceanic hydrothermal vents are sulfur-rich environments supporting diverse communities of microorganisms. Initial studies of the bacteria associated with these vents relied on culturing of hyperthermophiles and mesophiles, including sulfur-reducing bacteria. Molecular studies have offered new tools for detecting novel bacteria. Fluorescent in situ hybridization (FISH) using 16S rRNA-specific probes to study microbial diversity (see Chapter 4) is a useful tool, because phylogenetic trees can be constructed including novel bacteria detected in these vents. For example, novel bacteria identified from a mid-Atlantic ridge vent included members of the genus *Desulfurobacterium*, whereas other sequences were related to *Betaproteobacteria*, the group containing the genus *Acidithiobacillus*. Some sequences belong to the ϵ -*Proteobacteria*, which were also detected at hot springs at Yellowstone National Park. Using gene probes for dissimilatory bisulfate reductase genes (primers highly effective with *Desulfovibrio*, *Desulfobulbus*, and *Desulfobacter* spp.), bacteria were also detected at sea vents. These studies provide clues to the evolutionary origins of terrestrial sulfur bacteria.

BOX 17-4***Sulfur Can Be Good or Bad for the Environment***

Although sulfur is considered a macronutrient, its availability to the biota can be limiting in some ecosystems; then it must be applied as a supplement or fertilizer. However, in other instances, too much sulfur is a pollutant. For example, burning high-sulfur-content (e.g., bituminous and lignite) coals produces gaseous sulfur emissions that can become components of acid

BOX 17-4 (continued)

precipitation. Microbial oxidation of reduced sulfur minerals associated with coal seams and the subsequent leaching of the resulting oxyanions (e.g., SO_4^{2-}) gives rise to acid mine drainage that can pollute streams or acidify reclaimed soils. Finally, sulfur is important for many industrial processes; it can be used, for example, in the production of chemicals, concrete, and asphalt. As one reads this chapter, it will become evident that sulfur is an essential, versatile, and economically and ecologically important element.

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 transformations, including volatilization. The majority of sulfur is found in the **lithosphere** (Table 17-1). 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 cycles 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 1.5×10^{11} 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. Biological sources of sulfur volatilization total about 4.05×10^{10} kg S yr⁻¹.

The nature and quantities of the various sulfur pools in surface soils are the 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. The impact of pedogenic factors on the total sulfur concentrations in the surface is clear when comparing values for soils from diverse geographic areas, as shown in Table 17-2.

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. Examples of these organic compounds are given in Figure 17-1. Organic sulfates (R-O-S) include sulfate esters (C-O-S),

TABLE 17-1 Estimated Quantities of Sulfur in Major Sulfur Pools

Pool	Mass (kg S)
Atmosphere	3.6×10^9
Hydrosphere	1.3×10^{18}
Oceans	1.3×10^{18}
Marine organisms	2.4×10^{10}
Fresh waters	3.0×10^{12}
Ice	6.0×10^{12}
Lithosphere	24.1×10^{18}
Igneous rocks	5.0×10^{18}
Metamorphic rocks	11.4×10^{18}
Sedimentary rocks	7.7×10^{18}
Evaporites	5.1×10^{18}
Shales	2.0×10^{18}
Limestones	0.1×10^{18}
Sandstones	0.3×10^{18}
Soils	2.6×10^{16}
Soil organic matter	1.0×10^{13}
Biosphere	7.6×10^{12}

Adapted from Pierzynski et al. (2000).

TABLE 17-2 Amounts and Distribution of Sulfur in Some World Soils

Type of Soil	Location	Total S (mg kg ⁻¹)
Agricultural	Alberta, Canada	80-700
	Brazil	43-398
	British Columbia, Canada	214-438
	Iowa, U.S.	78-452
	New South Wales, Australia	38-545
	New Zealand	240-1360
	Nigeria	25-177
	Queensland, Australia	11-725
	Saskatchewan, Canada	88-760
	West Indies	110-510
	Alberta, Canada	364-1593
	British Columbia, Canada	162-2328
	Forest	Germany
Illinois, U.S.		112-555
New Hampshire, U.S.		452-1563
New York, U.S.		452-1563
Carolinias, U.S.		3000-35000
Tidal marsh	Carolinias, U.S.	3000-35000
	Iowa, U.S.	55-618
Surface	Iowa, U.S.	55-618
Organic	England	7405
Acid	Scotland	300-800
Calcareous	Scotland	460-1790
Volcanic	Hawaii, U.S.	180-2200

Adapted from Pierzynski et al. (2000) and Paul and Clark (1989).

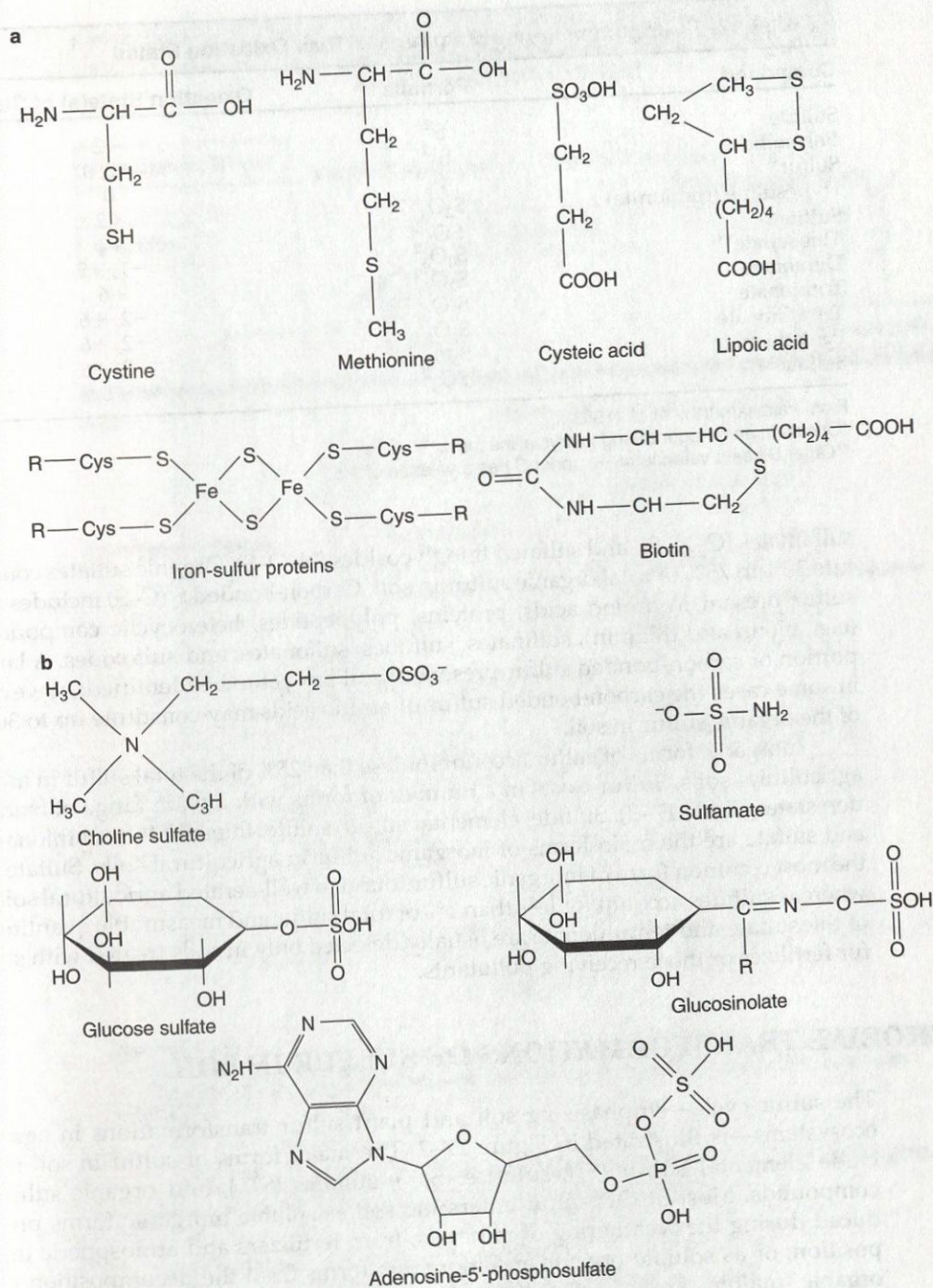


FIGURE 17-1
 Examples of some of the organic sulfur compounds found in soils. (a) Amino acids and other compounds containing carbon-bonded sulfur. Note that lipoic acid also has a disulfide bond. (b) Compounds that possess ester sulfate bonds (e.g., C-O-S and C-N-S). This class of compounds is sometimes used by microorganisms to store sulfur, although some bacteria are able to store elemental sulfur.

TABLE 17-3 Important Forms of Sulfur and Their Oxidation States

Compound	Formula	Oxidation State(s) of Sulfur
Sulfide	S^{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

From Vairavamurthy et al. (1993).

*Occurs in an octagonal ring in crystalline form.

**Outer S has a valence of -1; inner S has a valence of +5.

sulfamates (C-N-S), and sulfated thioglycosides (N-O-S). Organic sulfates constitute 30% to 75% of total organic sulfur in soil. Carbon-bonded S (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 present in soil has yet to be identified; however, in some cases the 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 (Table 17-3). 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.

MICROBIAL TRANSFORMATIONS OF SULFUR IN SOIL

The sulfur cycle—emphasizing soil and plant sulfur transformations in agroecosystems—is illustrated in Figure 17-2. 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 from the decomposition of organic matter. Losses of sulfur occur through leaching, surface runoff, volatilization, and crop removal.

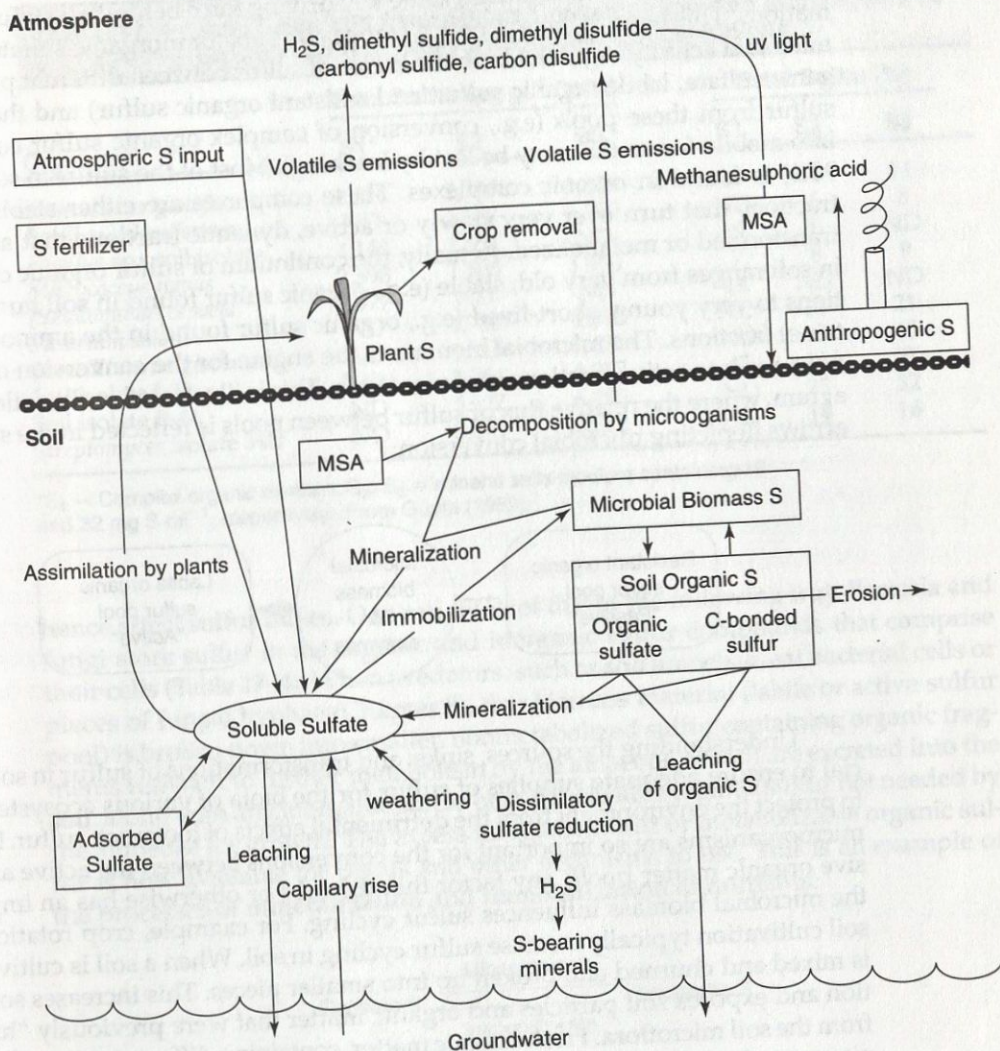
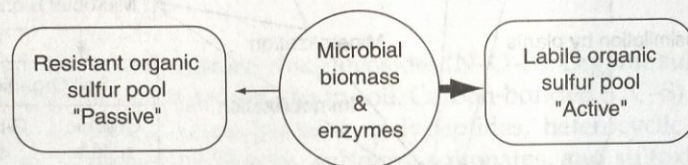


FIGURE 17-2 Conceptual sulfur cycle in agroecosystems. Numbers represent flux estimates ($\text{kg ha}^{-1} \text{yr}^{-1}$) for sulfur transformations in western Canadian soils. From Schoenau and Germida (1992). Used with permission.

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 reactions.

The soil microbial biomass is the key driving force behind all sulfur transformations. This 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 soil humus) fractions to very young, short-lived (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 of 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 influences 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.

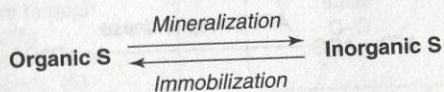
Similarly, interactions among different microbial groups, such as predation and parasitism, tend to increase the turnover rate of microbial biomass sulfur and

TABLE 17-4 Total Sulfur and Ester Sulfate Content of Selected Microorganisms Grown in Culture with Varying Sulfur Concentrations

Organism	Total Sulfur ($\mu\text{g g}^{-1}$ Cells)			Ester Sulfur (%)		
	S1*	S2	S3	S1	S2	S3
<i>Arthrobacter globiformis</i>	1,626	1,706	1,850	23	10	14
<i>Bacillus licheniformis</i>	ND	1,667	1,700	ND	6	8
<i>Bacillus</i> sp., soil isolate	1,142	1,054	ND	19	10	ND
<i>Micrococcus flavus</i>	2,398	1,500	1,950	7	8	9
<i>Pseudomonas cepacia</i>	2,477	ND	ND	16	ND	ND
<i>Fusarium solani</i>	ND	4,750	4,900	ND	13	21
<i>Penicillium nalgiovensis</i>	ND	1,815	2,450	ND	45	45
Soil isolate J-20	2,800	3,764	4,017	45	14	27
Soil isolate P-44	ND	5,527	6,400	ND	25	32
<i>Streptomyces</i> isolate 34L	ND	3,043	3,072	ND	14	16

*S₁ = Complex organic medium; S₂, S₃ = mineral salts medium containing 16 and 32 mg S ml⁻¹, respectively. From Gupta (1989).

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 (Table 17-4). When predators, such as soil amoebae, eat bacterial cells or pieces of fungal hyphae (Chapter 8), that biomass material (labile or active sulfur pool) is broken down into smaller, nonmetabolized 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 remineralized. 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 *assimilatory 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 reaction of SO_4^{2-} -S incorporation into amino acids is shown in Figure 17-3.

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 esters (Table 17-4; Fig. 17-1). 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 (Chapter 13), especially as organic sulfates.

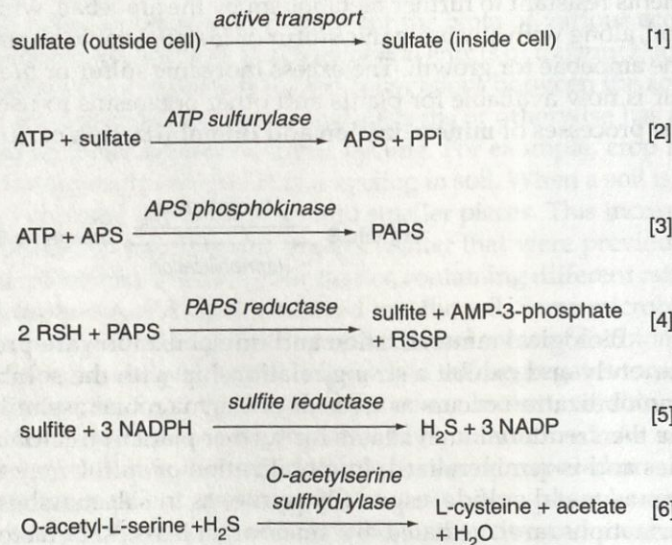


FIGURE 17-3

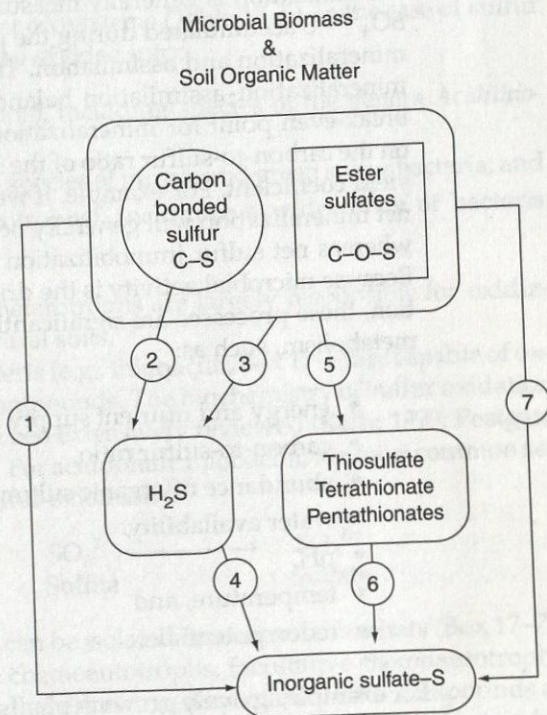
Assimilatory reduction of sulfate and formation of cysteine. RSH stands for thioredoxin; its reduced form is regenerated from the oxidized form through reduction by NADPH. *Redrawn from Gottschalk (1979). Used with permission.*

Mineralization

Mineralization of organic sulfur in soil is largely mediated by microbial activity. The various known pathways of sulfur mineralization are summarized in Figure 17-4. Carbon-bonded sulfur is mineralized through either oxidative (aerobic) decomposition or desulfurization (anaerobic) processes, whereas various sulfatases are involved in the mineralization of sulfate esters (Box 17-5). The mineralization process may be cell mediated, involving viable microbial cells, or enzymatic, involving enzymes such as sulfatases. In the case of cellular mineralization, 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 increases in the sulfate-sulfur pool in soil. In the case of enzymatic mineralization, those elements that exist as sulfate esters are hydrolyzed by intracellular or extracellular enzymes. This process occurs mainly outside the cell and may be regulated by end product inhibition, or the sulfate level. Cellular mineralization is controlled by the microbial need for carbon and energy sources, whereas enzymatic mineralization is controlled by factors influencing enzyme synthesis, activity, and kinetics.

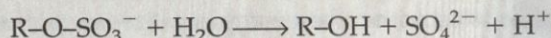
FIGURE 17-4

Known pathways for mineralization of organic sulfur compounds in soil: (1) biological (direct) mineralization during the oxidation of carbon as an energy source; (2) hydrolysis of cysteine by cysteine desulphydrolase; (3) anaerobic mineralization (desulfurization) of organic matter; (4) biological oxidation of hydrogen sulfide to sulfate through elemental sulfur and sulfite; (5) incomplete oxidation of organic sulfur into inorganic sulfur compounds; (6) biological oxidation of tetrathionate to sulfate through sulfide; and (7) biochemical (indirect) mineralization when sulfate esters are hydrolyzed by sulfatases. Adapted from Lawrence (1987).



BOX 17-5***Enzymes Drive Mineralization of Sulfate Esters in Soil***

Sulfatases (technically referred to as sulfohydrolases EC 3.1.5) are enzymes that hydrolyze sulfuric acid esters, where the linkage with sulfate is in the form of R-O-S and R represents a diverse group of organic moieties. This reaction can be shown as follows:



Arylsulfatase is by far the most studied enzyme involved with sulfur cycling in soil. This is because organic sulfates are abundant in soil, and hence arylsulfatase may play an important role in the mineralization of organic soil sulfur. The enzyme may be extracellular or associated with cell debris, and its activity is easily determined based on colorimetric assays.

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. 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.

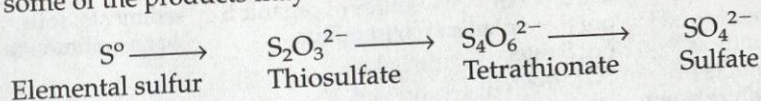
For example, actively growing plants may significantly increase sulfur mineralization in soils. Plants supply energy sources to the rhizosphere in the form of root ex-

updates 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 available to plants and may even result in reduction of that pool when the microbial demand exceeds the rate of sulfur mineralization. Different plants excrete different types and amounts of root exudates and require different amounts 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:

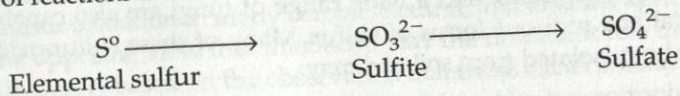


Many different microorganisms are important for the oxidation, reduction, and cycling of sulfur in soil and other ecosystems (Table 17-5). In the case of sulfur oxidation, the microorganisms can be divided into:

- chemoautotrophs (lithotrophs), including species of the genera *Acidithiobacillus* and *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, Box 17-6) are capable of oxidizing reduced inorganic sulfur compounds. The biochemistry of sulfur oxidation by thiobacilli growing *in vitro* has been extensively reviewed (Kelly, 1999; 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 (Box 17-7). 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**,

TABLE 17-5 Sulfur-Using Bacteria Occurring in Soil and Aquatic Habitats

Group	Sulfur Conversion	Habitat Requirements	Habitat Example	Examples 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 $\text{S}^0 \rightarrow \text{HS}^-$ $\text{SO}_3^{2-} \rightarrow \text{HS}^-$	anaerobic; organic substrates available; light not required	anoxic sediments and soils	<i>Desulfomonas</i> <i>Desulfovibrio</i> <i>Desulfotomaculum</i> <i>Desulfuromonas</i> <i>Campylobacter</i>
Obligate and facultative autotrophs that use reduced S as an energy source	$\text{HS}^- \rightarrow \text{S}^0$ $\text{S}^0 \rightarrow \text{SO}_4^{2-}$ $\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$	$\text{H}_2\text{S} - \text{O}_2$ interface; light not required	mud; hot springs; mine drainage; soils	<i>Acidithiobacillus</i> <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>Rhodospseudomonas</i>
Heterotrophs that use organic S compounds as energy sources or that hydrolyze esters	org S $\rightarrow \text{HS}^-$ org S \rightarrow volatile org S ester $\text{SO}_4 \rightarrow \text{SO}_4^{2-}$	source of organic S compounds	sediments; soils; water column	Many
Microorganisms that use SO_4^{2-} or H_2S in biosynthesis	$\text{SO}_4^{2-} \rightarrow$ protein $\text{HS}^- \rightarrow$ protein $\text{SO}_4^{2-} \rightarrow \text{DMSP}^*$	nonspecific	sediments; soils; water column	Many

*dimethylsulfoniumpropionate

From Cook and Kelly (1992). Used with permission.

which can use mixtures of inorganic and organic compounds simultaneously. The thiobacilli differ in their physiological characteristics and in the reduced sulfur compounds used as energy sources (Table 17-6). The majority of these thiobacilli are obligate aerobes, although some, such as *Thiobacillus denitrificans*, can grow anaerobically by using nitrate as a terminal electron acceptor. Other species of thiobacilli use electron donors such as ferrous iron (*A. 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.

BOX 17-6**Taxonomic Changes in the Classification of the Genus *Thiobacillus***

The use of 16S rRNA sequences and DNA-DNA hybridization led to the recent reclassification of many *Thiobacillus* species. *Acidithiobacillus thiooxidans* and *A. ferrooxidans* were formerly *Thiobacillus* spp., as were *Halothiobacillus halophilus*, *H. hydrothermalis*, and *Thermithiobacillus tepidarius*. Bacteria formerly called *Thiobacillus* spp. are now classified into different subclasses of *Proteobacteria*.

Taxonomic changes in the classification of the genus *Thiobacillus*.

<i>Current name</i>	<i>Old name</i>	<i>Characteristics</i>
<i>Acidithiobacillus</i> spp.	<i>T. thiooxidans</i> <i>T. ferrooxidans</i> <i>T. caldus</i> <i>T. albertensis</i>	Acidophilic
<i>Halothiobacillus</i> spp.	<i>T. neapolitanus</i> <i>T. halophilus</i> <i>T. hydrothermalis</i>	Halophilic
<i>Thermithiobacillus</i> spp.	<i>T. tepidarius</i>	Warm-water dwelling
<i>Thiobacillus</i> spp.	<i>T. thioparus</i> <i>T. denitrificans</i> <i>T. aquaesulis</i>	

Adapted from Kelly and Wood (2000).

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

BOX 17-7

Phylogenetic Diversity of *Thiobacillus*

Phylogenetic tree based on 16S rRNA gene-sequence data analysis of members of the *Proteobacteria*, showing "*Thiobacillus*" species in each of the α -, β -, and γ -subclasses. T- type strain Redrawn from Kelly and Wood (2000). Used with permission.

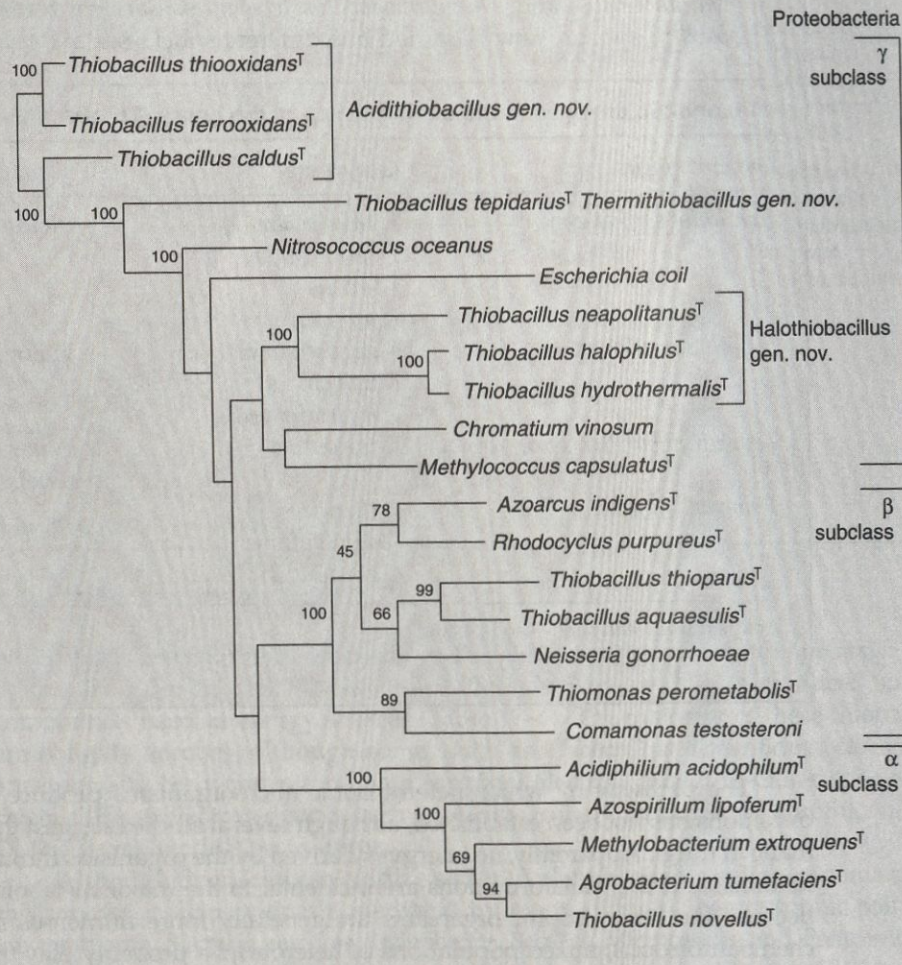


TABLE 17-6 Characteristics of Species of Sulfur Chemolithotrophs

Species	Electron Donor	Electron Acceptor	Facultative Heterotroph	Facultative Anaerobe	pH Optimum
<i>Acidithiobacillus thiooxidans</i>	H ₂ S, S ⁰ , S ₂ O ₃ ²⁻	O ₂	-	-	2.2
<i>Acidithiobacillus ferrooxidans</i>	S ⁰ , S ₂ O ₃ ²⁻ , Fe ²⁺	O ₂	+	-	3.0
<i>Halothiobacillus neapolitanus</i>	S ⁰ , S ₂ O ₃ ²⁻	O ₂	-	-	6.6
<i>Thiobacillus kabobis</i>	S ⁰	O ₂	-	-	ND
<i>Thermithiobacillus tepidarius</i>	S ₂ O ₃ ²⁻	O ₂	-	-	7.0
<i>Thiobacillus thioparus</i>	S ⁰ , S ₂ O ₃ ²⁻ , NCS ⁻	O ₂ , NO ₂ ⁻	-	+	6.9
<i>Thiobacillus denitrificans</i>	S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻	O ₂ , NO ₃ ⁻	-	+	7.0
<i>Thiomonas intermedius</i>	S ₂ O ₃ ²⁻	O ₂	+	-	ND
<i>Thiobacillus novellas</i>	S ₂ O ₃ ²⁻	O ₂	+	-	8.4
<i>Acidiphilium acidophilus</i>	ND	O ₂	+	-	3.0
<i>Thiobacillus organoparus</i>	ND	O ₂	+	-	ND
<i>Paracoccus versutus</i>	S ₂ O ₃ ²⁻	O ₂ , organic-C	+	+	8.2
<i>Thiomonas perometabolis</i>	S ₂ O ₃ ²⁻ , S ⁰	O ₂	+	-	ND

Adapted from Germida and Janzen (1993), Konopka et al. (1986), Kuenen and Beudeker (1982), and Kelly and Wood (2000).
 ND = no data

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 incidence of thiobacilli, except that rates of sulfur oxidation are generally low in soils that lack these organisms and are 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 work together to bring about the oxidation of sulfur in agricultural soils.

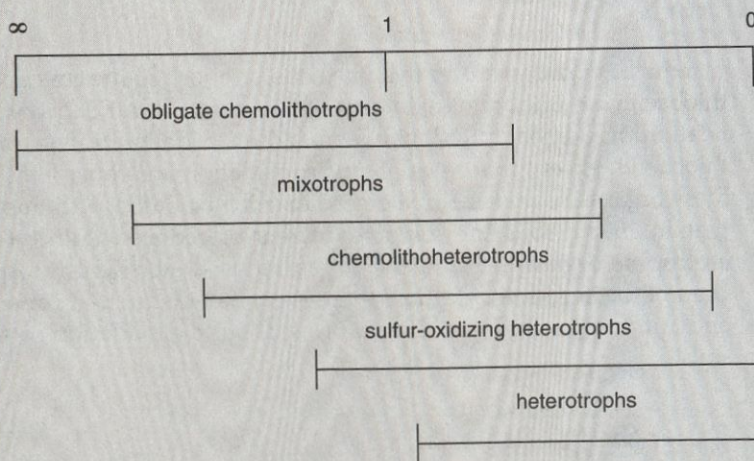
Other Sulfur Bacteria

Other bacteria may also oxidize sulfur compounds. The gliding sulfur oxidizers include those bacteria that have a gliding motion on the substratum; 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 soils. 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 has 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

BOX 17-8**Predicting the Occurrence of Sulfur-Oxidizing Microorganisms in Different Habitats**

Consider a hot sulfur spring like those found in Yellowstone National Park, United States. The molar ratio of inorganic sulfur compounds to organic substrates in the water is very large (e.g., lots of dissolved, reduced sulfur compounds in the water and very little organic matter), hence we predict that obligate autotrophic (e.g., chemolithotrophic) sulfur-oxidizing bacteria would be abundant. We also know these bacteria are thermophiles because they are living in water at a temperature greater than 60°C. Alternatively, in a soil that contains 1% organic matter and 0.01% thiosulfate, or elemental sulfur, the ratio of inorganic sulfur compounds to organic substrates would be very small, and thus heterotrophic sulfur-oxidizing organisms would be abundant.

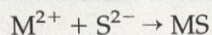
molar ratio of inorganic sulfur compounds to organic substrates



compounds and organic substrates during energy-limiting growth conditions (Kuenen and Beudeker, 1982; Box 17-8).

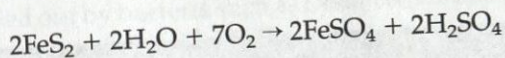
Biogenesis and Oxidation of Metal Sulfides

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:

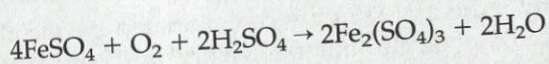


Many sulfate-reducing bacteria, such as *Desulfovibrio* spp. or *Desulfotomaculum* spp., are involved in the biogenesis of sulfides of antimony, cobalt, cadmium, iron, lead, nickel, and zinc. The extent of metal-sulfide genesis depends on many factors, the most important of which is the relative toxicity of the metal ion. In nature, this toxicity is probably reduced when the metal ions are adsorbed 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.

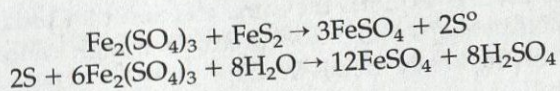
The oxidation of metal sulfides in soil involves both chemical and microbial processes and, as a result, is a more complex process than is sulfur oxidation. Chalcocite (Cu_2S), chalcopyrite (CuFeS_2), galena (PbS), pyrite (FeS_2), and nickel sulfide (NiS) are just a few examples of metal sulfides that are subject to microbial transformations. For example, the biological oxidation of pyrite follows a series of oxidation steps described in the following equations. These biotic oxidations 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:



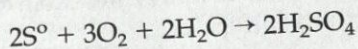
This reaction is then followed by the bacterial oxidation of ferrous sulfate, generally by *A. ferrooxidans*:



This reaction occurs chemically but can be accelerated 10^6 to 10^8 times by thiobacilli. Subsequently, ferric sulfate is reduced and pyrite oxidized by a strictly chemical reaction.



The elemental sulfur produced is finally oxidized by *A. thiooxidans* and *A. 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 *A. 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 (Box 17-9). For example, acid mine drainage contaminates several thousand kilometers of streams in the Appalachian coal mining region of the United States. Alternatively, they can be used in a beneficial manner in the bioremediation of soils contaminated with metals (Box 17-10) or in the bioextraction of precious metals from low-grade ores not suitable for smelting.

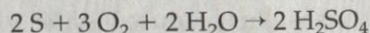
BOX 17-9***Problems Associated with Sulfur Oxidation***

Oxidation of reduced sulfur compounds leads to the formation of acidic products. As a consequence, sulfur oxidation can have detrimental effects on the environment. This is especially true in the case of sulfide minerals such as pyrite (FeS_2). Some of the more serious problems associated with sulfur oxidation include:

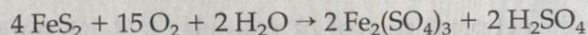
- formation of acid mine drainage,
- formation of acid sulfate soils,
- corrosion of concrete structures, and
- corrosion of metals.

BOX 17-10***Metal Bioremediation Using Sulfur Bacteria***

Many industrial sites are contaminated by metals, including arsenic, cadmium, copper, chromium, mercury, lead, and zinc. These are typically toxic to animals, including humans, and can bioaccumulate in plants. Hence, it is important to remediate these soils. Typically, chemicals such as strong acids are added to soil or sludge to leach heavy metals, but the cost of this process is often inhibitory. Using sulfate-oxidizing microorganisms is an alternative. This process exploits the same reaction that produces acid mine drainage. *Acidithiobacillus thiooxidans* produces a high concentration of sulfuric acid, dissolving heavy metals in soil:



Alternately, where iron is present in the soil, *Acidithiobacillus ferrooxidans* can also produce sulfuric acid:



These reactions can drop the pH to as low as 1.5, providing an environment where leaching easily occurs. Many heavy metals can be dissolved up to 80%. After leaching, metals can be recovered by sulfate-reducing bacteria. The soil or sludge can be moved to an anaerobic bioreactor, where sulfate-reducing bacteria like *Desulfovibrio* spp. can remove both acidity and metals. The rate and efficiency of these processes depends on the soil type, inoculum density, and the initial soil pH.

MICROBIAL REDUCTION OF INORGANIC SULFUR COMPOUNDS

Bacterial Sulfate Reduction

The reduction of sulfate to hydrogen sulfide is mediated mainly by anaerobic, sulfate-reducing bacteria. This process may be significant in anaerobic, water-logged 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 14. 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. (Table 17-7). 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

TABLE 17-7 Dissimilatory Sulfate-Reducing Bacteria

Genera	<i>Desulfobacter</i> , <i>Desulfobulbus</i> , <i>Desulfococcus</i> , <i>Desulfonema</i> , <i>Desulfosarcina</i> , <i>Desulfotomaculum</i> , <i>Desulfovibrio</i>
General characteristics	Strict anaerobes Grow at mildly acid to mildly alkaline pH
Substrates	Generally mesophilic, but some species thermophilic Most sulfate reducers will also reduce sulfite and thiosulfate Some species reduce elemental sulfur
Habitats	Organic matter utilization varies with genus and species As a group, capable of completely oxidizing fatty acids from C1 to C18, lactate, pyruvate, low-molecular-weight alcohols, and some aromatic compounds Anaerobic sediments of freshwater, brackish water, and marine environments, thermal regions, water-logged soils, and animal intestines.

From Trudinger (1986). Used with permission.

BOX 17-11***Consequences of Sulfate Reduction***

The activity of sulfate-reducing bacteria and the problems they pose can be seen in many examples from our daily lives:

- Sulfate-reducing bacteria are a major cause of corrosion of underground iron pipes, causing between \$1.6 and \$5 billion of damage in the United States in 1990.
- Turf managers find that sulfate-reducing bacteria can produce a black layer under golf course greens by using the organic matter in root exudates to reduce soil sulfates to ferrous sulfides.
- The water in the canals of Venice is polluted with hydrogen sulfide and, as a consequence, the gondolas of Venice turn black regardless of their original color.
- Not all activity by sulfate-reducing bacteria is bad, though. Sulfate-reducing bacteria can also be used in metal recovery and bioremediation of heavy-metal contaminated soils. Sources of heavy metal contamination include burning of fossil fuels, industrial processes, and sewage effluent. Leachate produced by sulfur-oxidizing bacteria can be transferred to bioreactors, where sulfur-reducing bacteria can remove acidity and toxic metals, producing an effluent with low levels of heavy metals that can be returned to the environment.

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 (Box 17-11).

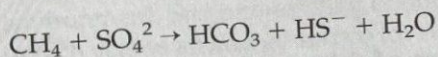
VOLATILIZATION OF INORGANIC AND ORGANIC SULFUR COMPOUNDS FROM SOIL

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 (Chapter 19, Box 17-12). Many different fungi and heterotrophic bacteria are responsible for the formation of these volatile compounds during the metabolism of organic sulfur compounds (Table 17-8).

BOX 17-12

Do Sulfate-Reducing Bacteria Help to Control Atmospheric Methane? Methane-Eating Microorganisms in a Sulfur-Rich Environment

The most potent of the greenhouse gases is methane, 10 trillion tons of which is produced by microorganisms and buried in the ocean floor. However, very little of the methane escapes to the atmosphere. Until recently, it was not understood what happens to the methane. It was hypothesized that bacteria assimilated methane, but most known methane-eating bacteria are aerobic, which obviously cannot survive deep in the ocean floor. However, it is known that sulfur-reducing bacteria can function under these conditions. Recently, scientists recognized that sulfate disappeared at the same place in the sediment as the methane (Boetius et al. 2000; Orphan et al. 2001). Investigation using a variety of tools revealed that methanotrophic archaea lived in association with sulfate-reducing bacteria like *Desulfosarcina* in the sediment layer. It is hypothesized that the consortia carry out the following reaction:



This biochemical symbiosis results in a highly efficient method of transferring intermediates, allowing microorganisms to consume methane that would otherwise cause heating of the earth that would make conditions unlivable for life as we know it. This is a good example of how novel bacteria are discovered in unique environments.

TABLE 17-8 Biochemical Origin of Volatile Sulfides Produced in Soils by Microbial Degradation of Organic Matter Under Aerobic and Anaerobic Conditions

Volatile Name	Formula	Biochemical Precursors
Hydrogen sulfide	H ₂ S	Proteins, polypeptides, cystine, cysteine, glutathione
Methyl mercaptan	CH ₃ SH	Methionine, methionine sulphoxide, methionine sulphone, S-methylcysteine
Dimethyl sulfide	CH ₃ SCH ₃	Methionine, methionine sulphoxide, methionine sulphone, S-methylcysteine, homocysteine
Dimethyl disulfide	CH ₃ SSCH ₃	Methionine, methionine sulphoxide, methionine sulphone, S-methylcysteine
Carbon disulfide	CS ₂	Cysteine, cystine, homocysteine, lanthionine, djenkolic acid
Carbonyl sulfide	COS	Lanthionine, djenkolic acid

From Andreae and Jaeschke (1992). Used with permission.

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 general soil fertility.

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.

Concrete Corrosion by Sulfur-Oxidizing Bacteria

Concrete sewer pipes are often corroded and sulfur-oxidizing bacteria seem to be the culprits. Concrete has a pH of around 12, so it is surprising to find that these bacteria are responsible, because sulfur-oxidizing bacteria are acidophilic. Microbial succession aids the corrosion process. It appears that the concrete is neutralized by carbonation and acidic H_2S followed by colonization by sulfate-producing bacteria. The first colonizers are moderately acidophilic *Thiobacillus* species, followed by *Acidithiobacillus thiooxidans*. Some studies have shown that this organism often occurs in relationship with acidophilic heterotrophic microorganisms, which degrade the organic compounds excreted by the sulfur-oxidizing bacteria. This helps

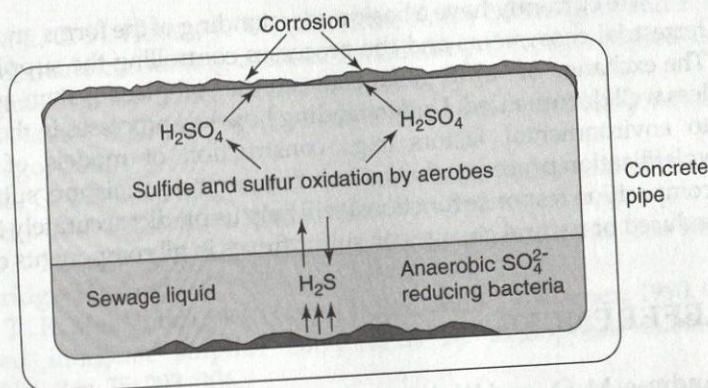
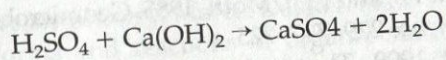


FIGURE 17-5
The activities of sulfate-reducing and sulfur-oxidizing bacteria in concrete sewer pipes can lead to serious corrosion problems. Hydrogen sulfide (H_2S) produced in the anoxic effluents diffuses to the top of the pipe where the actions of sulfur (sulfide)-oxidizing bacteria (e.g., *Acidithiobacillus*) convert it to sulfuric acid, which can corrode a few millimeters of the concrete per year. Eventually, the roof of the sewer pipe can collapse.

to maintain the acidic environment. Some co-existing organisms may oxidize H_2S , producing thiosulfate, which acts as an energy source for *A. thiooxidans*. Corroded concrete typically has a pH of 6.2 to 1.5.

The inner surfaces of sewer pipes are corroded in only certain areas of the pipe (Fig. 17-5). The anaerobic region covered by sewage water is typically not corroded, whereas the region near the top of the pipe is most corroded. In the sewer, H_2S is volatilized to the sewer atmosphere and dissolves in the condensate on the sewer's crown. Sulfur-oxidizing bacteria are capable of oxidizing the elemental sulfur. Several millimeters of concrete can typically be corroded each year. The actual corrosion occurs when the sulfuric acid produced by sulfide oxidation reacts with the calcium hydroxide binder in the concrete to form calcium sulfate.



In newer sewer systems, attempts are made to reduce the amount of anaerobic activity to control sulfuric acid production (Vincke, Boon, and Verstraete, 2001).

SUMMARY

Sulfur is an essential element for all living organisms and is the basis for primary productivity in some exotic communities. It exists in a number of oxidation states as inorganic 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 processes controlling the supply of sulfur to 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.

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