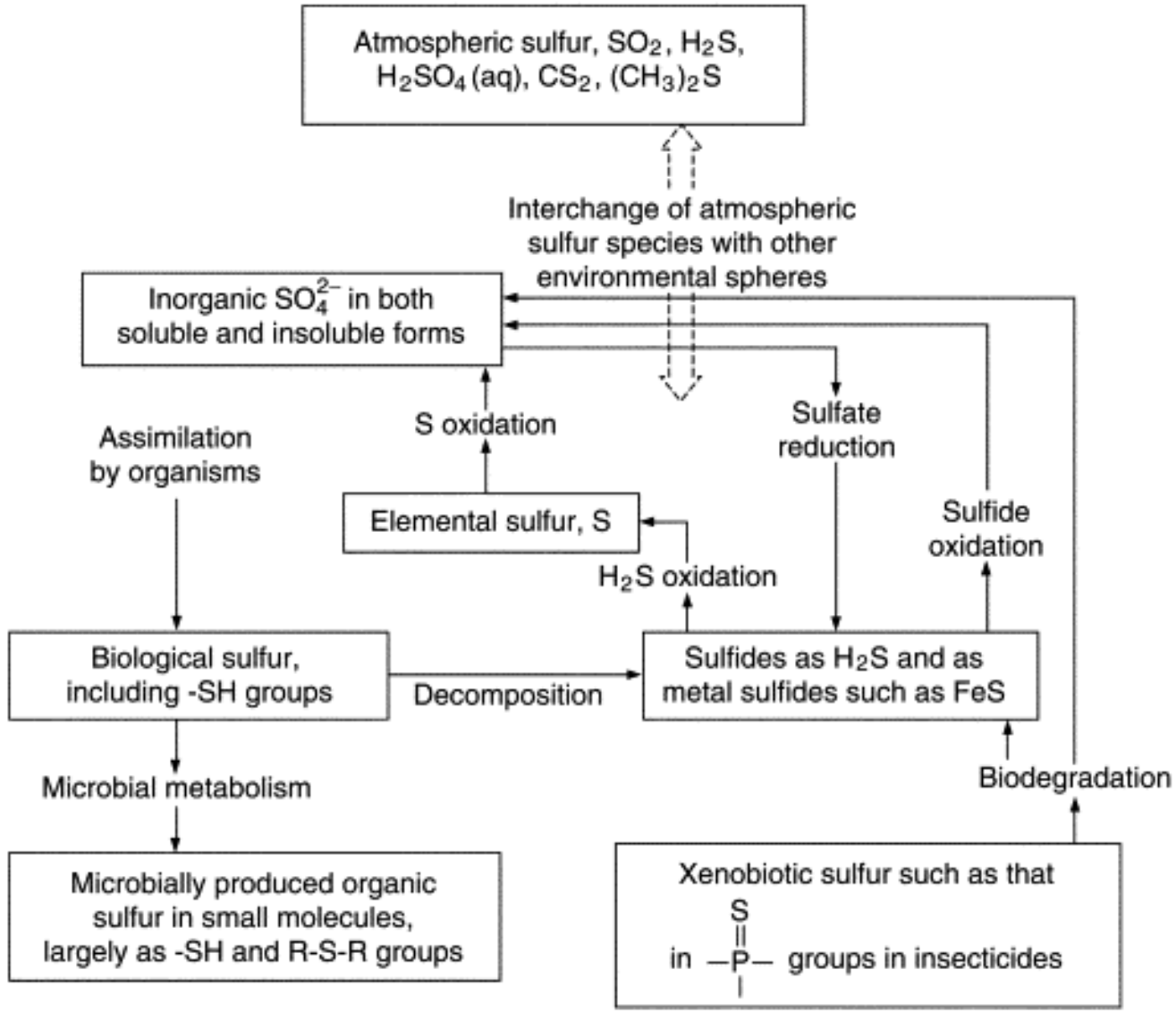
Sulfur Cycle

Introduction

- Sulfur, an essential element for the macromolecules of living things, is released into the atmosphere by the burning of fossil fuels, such as coal.
- As a part of the amino acid cysteine, it is involved in the formation of disulfide bonds within proteins, which help to determine their 3-D folding patterns, and hence their functions.
- Atmospheric sulfur is found in the form of sulfur dioxide (SO_2) and enters the atmosphere in three ways:
  - from the decomposition of organic molecules,
  - from volcanic activity and geothermal vents, and
  - from the burning of fossil fuels by humans.
- On land, sulfur is deposited in four major ways:
  - precipitation,
  - direct fallout from the atmosphere,
  - rock weathering, and
  - geothermal vents
- Atmospheric sulfur is found in the form of sulfur dioxide (SO_2), and as rain falls through the atmosphere, sulfur is dissolved in the form of weak sulfuric acid (H_2SO_4).
- Sulfur can also fall directly from the atmosphere in a process called **fallout**. Also, the weathering of sulfur-containing rocks releases sulfur into the soil.
- These rocks originate from ocean sediments that are moved to land by the geologic uplifting of ocean sediments.
- Terrestrial ecosystems can then make use of these soil sulfates (SO_4^-), and upon the death and decomposition of these organisms, release the sulfur back into the atmosphere as hydrogen sulfide (H_2S) gas.

…Introduction

- Sulfur enters the ocean via runoff from land, from atmospheric fallout, and from underwater geothermal vents.
- Some ecosystems rely on chemoautotrophs using sulfur as a biological energy source.
- This sulfur then supports marine ecosystems in the form of sulfates.
- Human activities have played a major role in altering the balance of the global sulfur cycle.
- The burning of large quantities of fossil fuels, especially from coal, releases larger amounts of hydrogen sulfide gas into the atmosphere.
- As rain falls through this gas, it creates the phenomenon known as acid rain.
- **Acid rain** is corrosive rain caused by rainwater falling to the ground through sulfur dioxide gas, turning it into weak sulfuric acid, which causes damage to aquatic ecosystems.
- Acid rain damages the natural environment by lowering the pH of lakes, which kills many of the resident fauna; it also affects the man-made environment through the chemical degradation of buildings.


Atmospheric sulfur, SO_2, H_2S, H_2SO_4 (aq), CS_2, $(CH_3)_2S$
Interchange of atmospheric sulfur species with other environmental spheres
Inorganic SO_4^{2-} in both soluble and insoluble forms
Assimilation by organisms
S oxidation
Sulfate reduction
Elemental sulfur, S
Sulfide oxidation
H_2S oxidation
Biological sulfur, including -SH groups
Decomposition
Sulfides as H_2S and as metal sulfides such as FeS
Microbial metabolism
Biodegradation
Microbially produced organic sulfur in small molecules, largely as -SH and R-S-R groups
Xenobiotic sulfur such as that in —P(=S)— groups in insecticides

The Microbial Sulfur Cycle

- Sulfur is one example of an element whose transformation and fate in the environment are critically dependent upon microbial activities.
- Sulfur is the 10th most abundant element in the universe and the sixth most abundant element in microbial biomass.
- By virtue of its chemical properties, particularly the wide range of stable redox states, sulfur plays important roles in central biochemistry as a structural element, redox center, and carbon carrier.
- In addition, redox reactions involving reduced and oxidized inorganic sulfur compounds can be utilized by microbes for the generation and conservation of biochemical energy.
- Microbial transformation of both inorganic and organic sulfur compounds has had a profound effect on the properties of the biosphere and continues to affect geochemistry today.
- A biogeochemical cycle which describes these transformations is comprised of many oxidation-reduction reactions.
- For instance, H_2S, a reduced form of sulphur, can be oxidized to sulphur or sulphate by a variety of microorganisms.
- Sulphate, in turn, can be reduced back to sulphide by sulphate reducing bacteria.

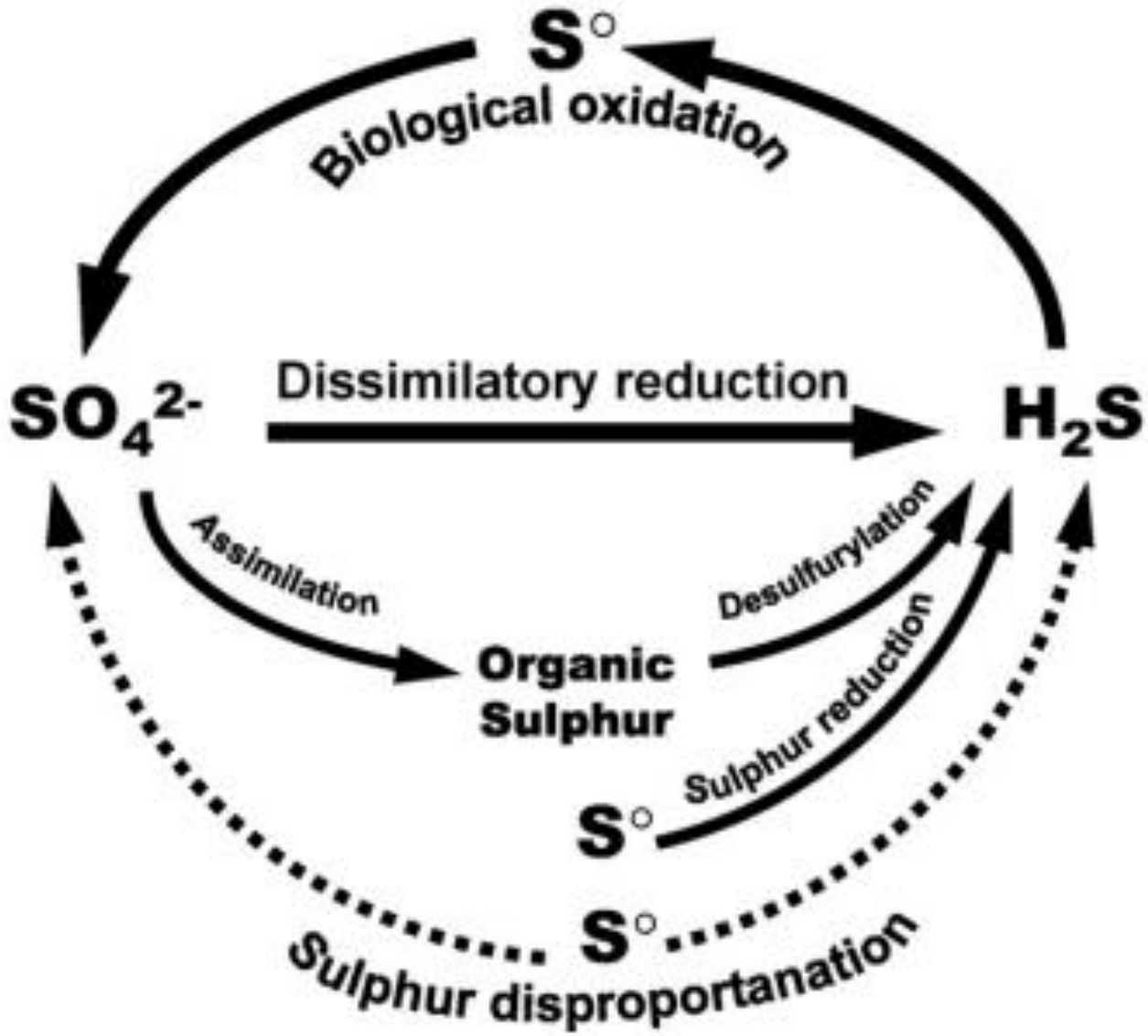


Fig. 1. Schematic representation of microbial sulphur cycle.

- The sulphur cycle consists of oxidative and reductive sides.
- **Sulphate on the reductive side** functions as an electron acceptor in metabolic pathways used by a wide range of microorganisms and is converted to sulphide.
- **On the oxidative side**, reduced sulphur compounds such as sulphide serve as electron donors for phototrophic or chemolithothrophic bacteria which convert these compounds to elemental sulphur or sulphate.
- A situation in which the reductive and oxidative sides of this cycle are not in balance could result in accumulation of intermediates such as sulphur, iron sulphide and hydrogen sulphide.
- **Sulphur disproportionation**, carried out by some species of sulphate reducing bacteria and other highly specialized bacteria, is an energy generating process in which elemental sulphur or thiosulphate functions both as electron donor and electron acceptor. Sulphur disproportionation results in simultaneous formation of sulphate and sulphide.

$$4S^0 + 4H2O \rightarrow SO4^{2-} + 3H2S$$

- In addition to the inorganic sulphur compounds, a vast array of organic sulphur compounds (i.e. sulphur containing proteins) are synthesized by microorganisms and considered part of the microbial sulphur cycle.
- Other organic sulphur compounds such as dimethyl sulfide, dimethyl disulphide, dimethyl sulfoxide, methanethiol, and carbon disulphide are also involved and affect the microbial sulphur cycle.

- In some cases, very neat cyclic reactions are possible.
- Habitats with a complete sulfur cycle are known as sulfureta.
- Both groups of bacteria may be found close to the border between the aerobic and the anaerobic habitats, and neither organism can grow in the other's space.
- Yet, they are totally dependent on sulfur compounds that diffuse between them.
- Such cycles are common in marine or estuarine sediments and are also evident in stratified water bodies and fixed film wastewater treatment systems