Environmental Microbiology Course 8

Biogeochemical Cycles Assoc. Prof. Dr. Emrah Şefik Abamor

Biogeochemical Cycle-Definition

A biogeochemical cycle is one of several natural cycles, in which *conserved matter* moves through the *biotic* and *abiotic* parts of an <u>ecosystem</u>.

In biology, conserved matter refers to the finite amount of matter, in the form of atoms, that is present within the Earth.



 The main chemical elements that are cycled are: carbon (C), hydrogen (H), nitrogen (N), oxygen (O), phosphorous (P) and sulfur (S). These are the building blocks of life, and are used for essential processes, such as *metabolism*, the formation of *amino acids*, *cell respiration* and the building of tissues.

Biogeochemical Cycles

Perfect versus Imperfect Cycles

More important is whether a cycle has an atmospheric reservoir readily available to ecosystems.

If so, such a cycle is called a "perfect" cycle, since these nutrients are not "lost" a long periods of time.

Perfect versus Imperfect Cycles



Perfect versus Imperfect Cycles Those cycles that lack an atmospheric stage are purely sedimentary. In sedimentary cycles, nutrients can become fixed in rocks or sediments at the bottom of the ocean.

Perfect versus Imperfect Cycles

They are potentially lost to ecosystems for long periods of time. Hence, these are "imperfect" cycles. Examples: Phosphorous Magnesium Iron Calcium Potassium

The Sulfur Cycle

The **sulfur cycle** is the collection of processes by which sulfur moves to and from minerals (including the waterways) and living systems.

IMPORTANCE OF SULFUR CYCLE

- 1. Sulfur is a component of most proteins and some vitamins.
- Sulfate ions (SO₄ ²⁻) dissolved in water are common in plant tissue. They are part of sulfur-containing amino acids that are the building blocks for proteins.
- 3. Sulfur bonds give the three dimensional structure of amino acids.
- 4. Many animals, including humans, depend on plants for sulfur-containing amino acids.

Sulfur

- I 6 Sulfur 32.06
- In nature: it can be found as the pure element, and as sulfide and sulfate minerals.
- Commercial uses: fertilizers, gunpowder, matches, insecticides, fungicides, vitamins, proteins and hormones.
- It is critical in the environment, climate and the health of ecosystems.
- Its the 10th most abundant element in the universe and 7th most abundant element in our body.
- Amino acids: Cystein and methionine

Biological importance

• Amino acids: Methionine and Cysteine



- Therefore important part of proteins, enzymes etc.
- Vitamins

Sulfur Cycle

 Source: ocean sediments, rocks, minerals



How is sulfur added to the environment?

- 1. Hydrogen Sulfide (H_2S)
 - Colorless, highly poisonous, rotten egg
 - Volcanoes
 - Anaerobic decomposers (swamps, bogs)
- 2. Sulfur Dioxide (SO_2)
 - Volcanoes
- 3. Sulfate salts (SO4²⁻) (particulates ammonium sulfate)
 - Sea spray, dust storms, forest fires
 - Then taken up by plants





4. Dimethyl sulfide (DMS) (CH₃SCH₃)

- Produced by marine organisms
- Condensation nuclei to form clouds
- If DMS can function as condensation nuclei, how can DMS alter the climate?
 - Increase cloud cover, weather
- In atmosphere
 - DMS \rightarrow SO₂ \rightarrow SO₃ \rightarrow H₂SO₄ (sulfuric acid)
 - Basis of acid rain/deposition



How do humans alter the S cycle? • SO₂

- Burn coal, oil releasing sulfur
- Refine sulfur containing petroleum for gas, heating oil
- Convert metal mineral ores into free metals copper, lead and zinc







Sulfur Cycle



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Steps of Sulfur Cycle

4 main steps:

Mineralization

Microbial oxidation

Sulphate reduction

Assimilation

1.Mineralization:

 organic sulfur change into inorganic forms, such as hydrogen sulfide (H₂S), elemental sulfur, as well as sulfide minerals.

2. Oxidation:

- Oxidation of elemental sulphur and inorganic sulphur compounds (such as H₂S, sulphite and thiosulphate) to sulphate (SO4) is brought about by chemoautotrophic and photosynthetic bacteria.
- Oxidation of hydrogen sulfide produces elemental sulfur.
- Further oxidation of elemental sulfur produces sulfate.
- Sulfide may be oxidized to elemental sulfur aerobically by species of *Thiothrix* and *Beggiatoa* and anaerobically by the purple sulfur bacteria. Both of these groups are primarily aquatic microbes.

- In soil, the predominant microbes involved in the oxidation of sulfide to elemental sulfur belong to the genus *Thiobacillus*.
- For the following two "generic" reactions, the first is typical of oxidation of sulfide to sulfur, and the second of oxidation of sulfide to sulfate. As shown in the diagram to the left, the rate-limiting step is mediated by the enzyme sulfite oxidase (cofactors for the enzyme are Mo and Fe).

3. Reduction:

- Sulphate can be reduced to hydrogen sulphide (H₂S) by sulphate reducing bacteria (eg.*Desulfovibrio* and *Desulfatomaculum*) and may diminish the availability of sulphur for plant nutrition.
- The reduction process is particularly favored by the alkaline and anaerobic conditions of the soil, as the organisms use sulphate as a source of oxygen supply.
- Besides the strict autotrophs of the genus *Thiobacillus*, there are several other members which are facultative autotrophs capable of reducing H₂S and drive energy from it.

For e.g. calcium sulphate is attacked under anaerobic condition by the members of the genus *Desulfovibrio* and *Desulfatomaculum* to release H₂S.

CaSO₄ + 4H₂ => Ca(OH)₂ + H₂S + H₂O Hydrogen sulphide produced by the reduction of sulphate and sulphur containing amino acids decomposition is further oxidized by some species of green and purple phototrophic bacteria (*eg. Chlorobium, Chromatium*) to release elemental sulphur.

 $CO_2 + 2H_2 + H_2S => (CH_2O) + H_2O + 2S$

4. Assimilation:

- The sulphates and sulphuric acid, when dissolved in water, are made available for plant growth.
- The plants utilize the sulphates to form various amino acids, hormones, growth factors, etc.
- They are either eaten away by the animals are also in some form or other returned to the soil.
- When the various complex orgnic sulphur compounds reach the soil, they are attacked by the soil organisms and the cycle of events continues.



Key Processes and Prokaryotes in the Sulfur Cycle

Process	Organisms	
Sulfide/sulfur oxidation (H ₂ S Aerobic	\rightarrow S ⁰ \rightarrow SO ₄ ²) Sulfur chemolithotrophs (<i>Thiobacillus</i> , <i>Beggiatoa</i> , many others) Purple and green phototrophic	
Sulfate reduction (anaerobic)	bacteria, some chemolithotrophs	
Sumate recucion (anaerosic)	Desulfovibrio, Desulfobacter Archaeoglobus (Archaea)	so
Sulfur reduction (anaerobic) ((S ⁰ → H ₂ S) Desulfuromonas, many hyperthermophilic Archaea	1
Sulfur disproportionation (S ₂	$(O_3^{2-} \rightarrow H_2S + SO_4^{2-})$ Desulfovibrio, and others	
Organic sulfur compound ox	idation or reduction (CH ₃ SH → CO ₂ + H ₂ S) (DMSO → DMS) Many organisms can do this	
Desulfurylation (organic–S \rightarrow	⊢ H ₂ S) Many organisms can do this	



(a) Degradation of Organic Compounds to Release H₂S:

(i) Degradation of proteins (proteolysis) liberates amino acids which generally contain sulphur.

Protein degradation Amino acid

(ii) Enzymatic activity of many heterotrophic bacteria result in the release of H₂S from further degradation of sulphur containing amino acids.

(b) Oxidation of Hydrogen Sulphide (H₂S) to Elemental Sulphur:

Hydrogen sulphide undergoes decomposition to produce elemental sulphur by the action of certain photosynthetic sulphur bacteria, e.g., members belonging to the families Chlorobiaceae (Chlorobium) and Chromatiaceae (Chromatium).

Example:

 $CO_2 + 2H_2S \xrightarrow{Photosynthetic sulphur}_{bacteria} (CH_2O)_x + H_2O + 2S$

Some non-sulphur purple bacteria, e.g., Rhodospirillum, Rhodopseudomonas, and Rhodomicrobium, which are facultative phototrophs and grow aerobically in the dark and anaerobically in the light, can also degrade H₂S to elemental sulphur.



(c) Oxidation of Elemental Sulphur to Sulphates:

Elemental form of sulphur accumulated in soil by earlier described processes cannot be utilized as such by the plants. It is oxidized to sulphates by the action of chemolithotrophic bacteria of the family Thiobacteriaceae (Thiobcicillus thiooxidans).

Example:

 $2S + H_2O + 3O_2 \xrightarrow{Thiobacillus}{thiooxidans} 2H_2SO_4$

Sulphates are the compounds that can readily be taken by the plants and are beneficial to agriculture in the following three ways:

(i) It is the most suitable source of sulphur and is readily available to plants.

(ii) Accumulation of sulphate solubilizes organic salts that contain plant nutrients such as phosphates and metals.

(iii) Sulphate is the anion of a strong mineral acid (H_2SO_4) and prevents excessive alkalinity due to ammonia formation by soil microorganisms.

Sulphate is assimilated by plants and is incorporated into sulphur containing amino acids and then into proteins. Animals fulfill their demand of sulphur by feeding on plants and plant products.

(d) Reduction of Sulphates:

Sulphate is first reduced to H₂S by sulphate reducing microorganisms under anaerobic conditions. Many bacteria including species of Bacillus, Pseudomonas, Desulfovibrio do this work. The mechanism of sulphate reduction to hydrogen sulphide involves, firstly, the reduction of sulphate to sulphite utilizing ATP and, secondly, reduction of sulphite to hydrogen sulphide.

The whole mechanism of the reduction of sulphate to hydrogen sulphide by Desulfovibrio desulfuricans, the most important bacterium of this reduction, can be represented as follows:

$$SO_4$$
 "ATP SO_3 " S_2O_3 " S''
 $S'' S_3 O_6$ "

Sulphur cycle

- Microorganisms contribute greatly to the sulfur cycle.
- Photosynthetic microorganisms transform sulfur by using sulfide as an electron source, allowing *Thiobacillus and* similar *chemolithoautotrophic* genera.
- In contrast, when sulfate diffuses into reduced habitats, it provides an opportunity for different groups of microorganisms to carry out sulfate reduction.
- For example, when a usable organic reductant is present, Desulfovibrio uses sulfate as an oxidant.
- This use of sulfate as an external electron acceptor to form sulfide, which accumulates in the environment, is an example of a dissimilatory reduction process and anaerobic respiration.

- In comparison, the reduction of sulfate for use in amino acid and protein biosynthesis.
- Other microorganisms have been found to carry out dissimilatory elemental sulfur reduction.
- These include Desulfuromonas, thermophilic archaea and also cyanobacteria in hypersaline sediments.
- Sulfite is another critical intermediate that can be reduced to sulfide by a wide variety of microorganisms, including *Alteromonas* and *Clostridium*, as well as *Desulfovibrio* and *Desulfotomaculum*.



Classification of photosynthetic bacteria

- Two broad groups:
- 1) Anoxygenic photosynthetic bacteria
- 2) Oxygenic photosynthetic bacteria

	Plant photosynthesis	Bacterial photosynthesis
Organisms	Plants, algae, cyanobacteria	Purple and green bacteria
Type of chlorophyll	Chlorophyll-a and absorbs 650-750nm	bacteriochlorophyll and
		absorbs 800-1000nm
Photosystem I	present	present
(cyclic		
photophosphorylation)		
Photosystem I	present	absent
(noncyclic		
photophosphorylation)		
Produces O ₂	yes	no
Photosynthetic	H ₂ O	H ₂ S, other sulfur compounds or
electron donor		certain organic compounds

Oxygenic photosynthesis

 $6CO_2 + 12H_2O + \text{light energy} \longrightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O_6$ glucose oxygen water carbon water dioxide Anoxygenic photosynthesis $CO_2 + 2H_2A + light energy \longrightarrow [CH_2O] + 2A + H_2O$ carbohydrate carbon electron water dioxide donor*

 $*H_2A = H_2O$, H_2S , H_2 , or other electron donor

Anoxygenic Photosynthesis

- Uses light energy to create organic compounds, and sulfur or fumarate compounds instead of O₂
- Occurs in purple bacteria, green sulfur bacteria, green gliding bacteria and heliobacteria
- Uses bacteriochlorophyll pigments instead of chlorophyll
- Uses one photosystem (PS I) to generate ATP in "cyclic" manner

Anoxygenic photosynthetic bacteria

- Some photosynthetic bacteria can use light energy to extract electrons from molecules other than water.
- These organisms are of ancient origin, presumed to have evolved before oxygenic photosynthetic organisms.
- Anoxygenic photosynthetic organisms occur in the domain Bacteria and have representatives in four phyla – Purple-Sulphur Bacteria, Purple non-Sulphur Bacteria, Green-Sulfur Bacteria, Green non-Sulfur Bacteria.

- Anoxygenic photosynthesis depends on electron donors such as reduced sulphur compounds, molecular hydrogen or organic compounds.
- They are found in fresh water, brackish water, marine and hypersaline water.
- Anoxygenic photosynthetic bacteria have been divided into three groups on the basis of pigmentation: purple bacteria, green bacteria and heliobacteria.

Purple Bacteria

- The anoxygenic phototrophs grow under anaerobic conditions in the presence of light and do not use water as electron donor as higher plants.
- They grow autotrophically with CO₂ and hydrogen or reduced sulphur compounds act as electron donor.
- The pigment synthesis is repressed by O_{2.}

- Purple bacteria contain Bchl a and b as photosynthetic pigment.
- The colour of purple bacteria shows brown, pink brownred, purple-violet based on carotenoid contents.
- The photosynthetic pigments are innfluenced by light intensity. At high intensity, photo-apparatus is inhibited.
- Carotenoids give rise to purple colour; mutants lack carotenoids are blue green reflecting the actual colour of BChl a.
- Purple Bacteria are of two types: purple-suphur bacteria and purple non-sulphur bacteria.

Purple PhototrophicBacteria

- Purple Sulfur Bacteria
 - Use hydrogen sulfide (H₂S) as an electron donor for CO₂ reduction in photosynthesis
 - Sulfide oxidized to elemental sulfur (S°) that is stored as globules either inside or outside cells
 - Sulfur later disappears as it is oxidized to sulfate (SO₄²⁻)

Purple PhototrophicBacteria

- <u>Purple Sulfur Bacteria</u> (cont'd)
 - Many can also use other reduced sulfur compounds, such as thiosulfate (S₂O₃²⁻)
 - All are *Gammaproteobacteria*
 - Found in illuminated anoxic zones of lakes and other aquatic habitats where H₂S accumulates, as well as sulfur springs

Green Bacteria

- Instead of green in colour, these are brown due to the presence of carotenoids components.
- They are gram-negative.
- They contain BChl c, d and e plus small amount of Bchl a.
- The photosyntheic apparatus is chlorosomes.
- They do not require vitamins for their growth.
- Green bacteria are of two types: green sulphur bacteria and green non-sulphur bacteria.

Green Sulphur Bacteria

- Family: Chlorobiaceae
- They are non-motile, rods, spiral and cocci.
- Chlorosomes are present in the cell.
- They are strictly anaerobic and obligate phototroph.
- Deposit sulphur extracellularly.
- Mol % G+C is 45-58.
- Eg; Chlorobium, Prostheochloris, Pelodictyon, Chloroherpeton



Sulfur cycle, Robertson and Keyenen (2006)

Colorless Sulfur Bacteria

- Comprises a very heterogeneous group of chemoautotrophic bacteria
- Use of reduced forms of S as e- source
- Most of them require O₂ as e- acceptor, but a few are able to grow anaerobically using nitrogen oxides



Colorless Sulfur Bacteria

- Thiobacillus
- Thiomicrospira
- Thiosphaera
- Sulfolobus
- Acidianus
- Thermothrix
- Thiovulum
- Beggiatoa
- Thiothrix
- Thioploca
- Thiodendron
- Thiobacterium
- Macromonas
- Achromatium
- Thiospira



3. Sulfur- and Iron-Oxidizingacteria

Sulfur-Oxidizing Bacteria

- Grow chemolithotrophically on reduced sulfur cmpds
- Two broad classes
 - Neutrophiles
 - Acidophiles (some also use ferrous iron (Fe²⁺)
- <u>Thiobacillus</u> (rods)
 - Sulfur compounds most commonly used as electron donors are H₂S, S^o, S₂O₃²⁻; generates sulfuric acid
- <u>Achromatium (spherical cells)</u>

Common in freshwater sediments

 Some obligate chemolithotrophs possess special structures that house Calvin cycle enyzmes (<u>carboxysomes</u>)

- Beggiatoa
 - Filamentous, gliding bacteria
 - Found in habitats rich in H₂S
 - e.g., sulfur springs, decaying seaweed beds, mud layers of lakes, sewage polluted waters, and hydrothermal vents
 - Most grow mixotrophically
 - with reduced sulfur compounds as electron donors
 - and organic compounds as carbon sources
 - Thioploca
 - Large, filamentous sulfur-oxidizing bacteria that form cell bundles surrounded by a common sheath
 - Thick mats found on ocean floor off Chile and Peru
 - Couple anoxic oxidation of H₂S with reduction of NO₃⁻ to NH₄⁺

Sulfur Cycle





Sulphur production

- a) After the death of plants and animals, they are decomposed by microbes like Aspergillus, Neurospora and Esherichia releasing hydrogen sulpgide (H₂S)
- $ightarrow SO_4^{2-} + 2H^+ \rightarrow H_2S + 2O_2$
- ✓ The high concentration of H₂S in deeper parts of aquatic ecosystems e.g. below 200 meters in the Black sea,does not allow the survival of higher animals. Similarly fish is unable to survive.

b) A part of H₂S is oxidized to soluble sulphates by sulphur bacteria like Thiobacillus while Beggiatoa (colourless sulphur bacteria) oxidise a part of H₂S to elemental sulphur. The oxidation of H₂S releases energy which is used iin their chemosynthetic matabolism involving reduction of carbon dioxide. \blacktriangleright 6CO₂ + 12H₂S $\xrightarrow{\text{Energy}}$ C₆H₁₂O₆ + 6H₂O + 12S ✓ The remaining passes into reservoir pool in deep sediments. From the sea, sulphur goes back to land in three ways i.e. food chains, sea sprays and geological upheavals.

- c) Many industries release SO₂ into atmosphere. As the lichens are very sensitive to SO₂, they disappear in polluted air containing SO₂.
- d) Fossil fuels on burning release SO₂ into the atmosphere e) Volcanic emissions also add sulphates to soil and air.
- ✓ Sulphur cycle is an imperfect cycle as sulphur has the potential for being bound under anaerobic conditions to cations like iron and calcium to form highly insoluble ferrous sulphate (FeS) ferric sulphate (Fe₂S₃, pyrite) or calcium sulphate (CaSO₄).

Phosphorus cycle



Introduction

- The phosphorus cycle is the movement of phosphorus from the environment to organisms and then back to the environment.
- The phosphorus cycle may also be referred to as the *mineral cycle or sedimentary cycle*.
- Unlike the other cycles, phosphorus cannot be found in air in the gaseous state.
- The phosphorus cycle is the **SLOWEST** cycle.
- The atmosphere does not play a significant role in the movement of phosphorus, because phosphorus and phosphorus-based compounds are usually solids at the typical ranges of temperature and pressure found on Earth.
- On the land, phosphorus (chemical symbol, P) gradually becomes less available to plants over thousands of years, because it is slowly lost in runoff.

IMPORTANCE OF PHOSPHOROUS CYCLE

- 1.Phosphorous is an essential nutrient of both plants and animals.
- 2. It is part of DNA molecules which carry genetic information.
- 3. It is part of ATP and ADP) that store chemical energy for use by organisms in cellular respiration.
- 4. Forms phospholipids in cell membranes of plants and animal cells.
- 5. Forms bones, teeth, and shells of animals as calcium phosphate compounds.

- Low concentration of P in soils reduces plant growth, and slows soil microbial growth.
- Soil microorganisms act as both sinks and sources of available P in the biogeochemical cycle.
- Locally, transformations of P are chemical, biological and microbiological: the major long-term transfers in the global cycle, however, are driven by tectonic movements in geologic time.
- Humans have caused major changes to the global P cycle through shipping of P minerals, and use of P fertilizer, and also the shipping of food from farms to cities, where it is lost as effluent.





The Phosphorus Cycle

Phosphorus cycle has two major steps

I. Conversion of organic to inorganic

II. Conversion of inorganic to organic P

Phosphorus Cycle

- Overall Transformations of Phosphorus
 Soil Organisms
 - Break down organic phosphate into to inorganic phosphates
 - Then convert inorganic phosphates to orthophosphate (PO₄³⁻)
 - Orthophosphate is water soluble and readily used by most plants and microorganisms
 - When plants & animals die decomposers convert organic phosphate back into inorganic phosphate
 - Phosphorus is often the limiting nutrient in many environments

The Phosphorus Cycle (continue)

- * Conversion of insoluble forms of phosphorus such as calcium phosphate Ca(HPO₄)₂ into soluble forms principally to PO₄³⁻ is also carried out by microorganisms
- * Organic P in dead plant and animal tissue, animal waste products is converted bacterially to PO₄ ³⁻
- * PO₄ ³⁻ releases to the environment is then incorporated into plant and animal tissue



Mineralization :

- Organic phosphorus compounds (e.g., phytin, inositol phosphates, nucleic acids, phospholipids) are mineralized to orthophosphate by a wide range of microorganisms that include bacteria (e.g., B. subtilis, Arthrobacter), actinomycetes (e.g., Streptomyces), and fungi (e.g., Aspergillus, Penicillium).
- Phosphatases are the enzymes responsible for degradation of phosphorus compounds.

Assimilation :

- Microorganisms assimilate phosphorus, which enters in the composition of several macromolecules in the cell.
- Some microorganisms have the ability to store phosphorus as polyphosphates in special granules

Precipitation of Phosphorus Compounds:

- The solubility of orthophosphate is controlled by the pH of the aquatic environment and by the presence of Ca²⁺,Mg²⁺, Fe³⁺ and Al^{3+.}
- When precipitation occurs, there is formation of insoluble compounds such as hydroxyapatite (Cal0(PO4)6(OH)2, vivianite Fe3(PO4)2. 8H2O or variscite AlPO4.
 2H2O.



Recycling and the role of decomposers



Dependence on oxygen and carbon dioxide

Animals need oxygen for respiration Plants produce oxygen in photosynthesis

Animals produce carbon dioxide in respiration Plants use up carbon dioxide in photosynthesis

The process of decay uses up oxygen and produces carbon dioxide

This interdependence is represented by the **Carbon Cycle**

Atmospheric carbon dioxide

Production of carbon	Uptake of carbon
dioxide	dioxide
Burning of fuel: wood, coal, oil and gas.	Photosynthesis in plants
Respiration in all organisms	Absorption by the oceans
Decay of organic matter	

Dependence on bacteria

-Most bacteria are beneficial

-They break down dead organisms into simpler substances

-Soil bacteria make mineral salts available to plants

-Bacteria and fungi are called decomposers