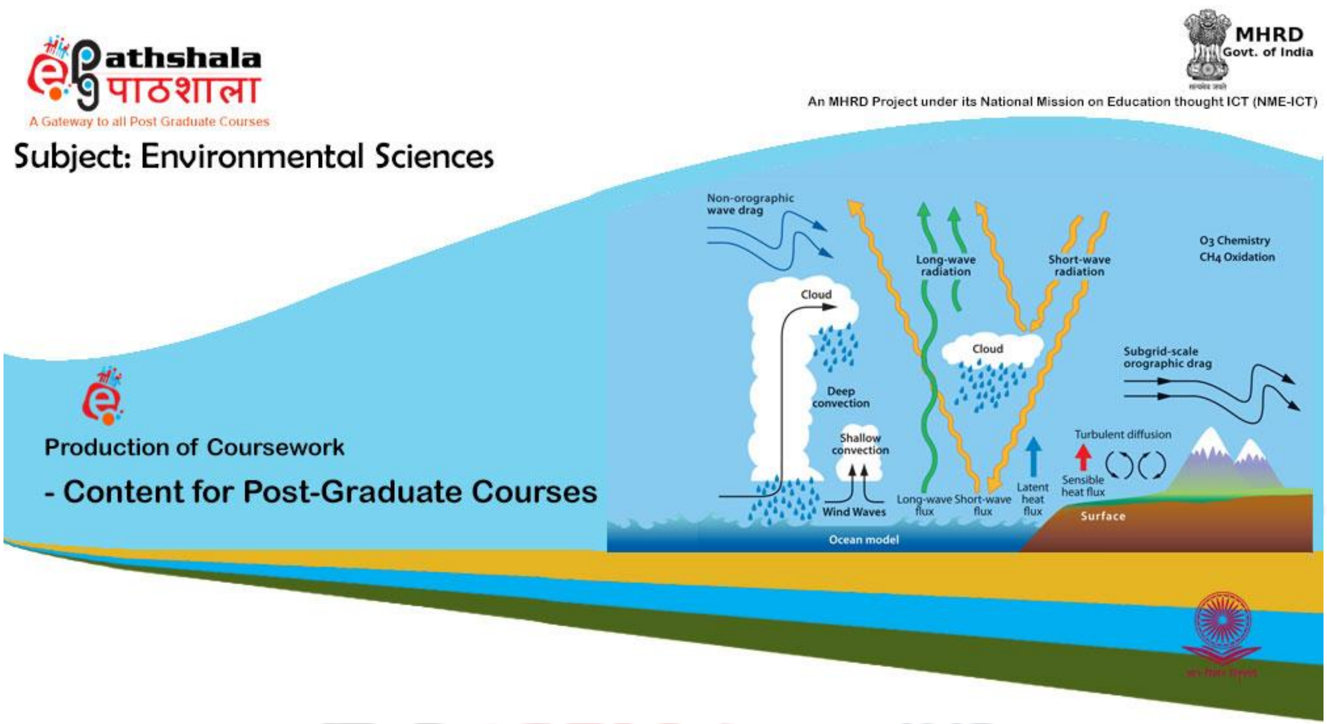

Paper No: 8 Atmospheric Processes

Module: 31 Biogeochemical Cycles

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1. Learning Outcomes

The objectives of this module are to:

- define the concept of biogeochemical cycles
- inform the reader in detail key elemental cycles in nature
- discuss the effect and feedbacks of different cycles

2. Introduction

Biogeochemical cycles describe the pathway through which the essential elements move through the biotic and abiotic components of the system and vice versa. For an ecosystem to exist, continuous cycling of elements is very essential. Every biogeochemical cycle possess two components namely the reservoir and exchange pool. The reservoir is normally the abiotic component which is usually large and slow moving. The exchange pool is small but active exchange occurs between the biotic and abiotic component. The elemental cycles parallel to the energy flow, however they differ in the abiotic factor. Energy flow cycle is solar driven and while the elemental cycle is highly conservative and the chemical elements are obtained from the small pool and retained within the system.

Biogeochemical cycles are categorized into two types: Gaseous and sedimentary. Atmosphere remains the reservoir for gaseous and earth crust is the reservoir for sedimentary cycle. Carbon, nitrogen and oxygen are included in gaseous biogeochemical cycle and phosphorus and Sulphur are grouped under sedimentary cycle. The sedimentary cycle consists of two phase, one water phase and the other soil/ sediment phase. The elements gets weathered and dissolved in the water phase, moves through the biotic components and returns back to the sediment phase. Unlike sedimentary cycle, the movement is very rapid within the gaseous cycle as it involves the atmosphere as reservoir. Since the cycle involves the geological, biological and chemical component in the cycle it is termed as biogeochemical cycle.

The important biogeochemical cycles are discussed in the following section.

3. Elemental cycles

3.1. Carbon cycle

Carbon cycle is one of the important atmospheric cycles. The cycle mainly portrays the circulation of carbon between the atmospheric gas carbon dioxide, assimilation of carbon as organic matter via photosynthesis and its subsequent release back into the atmosphere through respiration. Figure 1 depicts the carbon circulation through the carbon cycle. As we all know carbon is an important constituent of all life molecule. It is present in air as carbon dioxide (0.03%) and as carbonates and bicarbonates (CO_3^-, HCO_3^-) or molecular CO_2 (aq) in surface water and groundwater. It is also present in minerals associated mainly with magnesium and calcium as carbonates. Coal, lignite, petroleum and natural gas are the sources of carbon fixed due to high pressure and temperature deep below the earth's surface. The organic matter fixed as oil shale is termed as hydrocarbonaceous kerogen and it contributes a major portion of the fixed carbon.

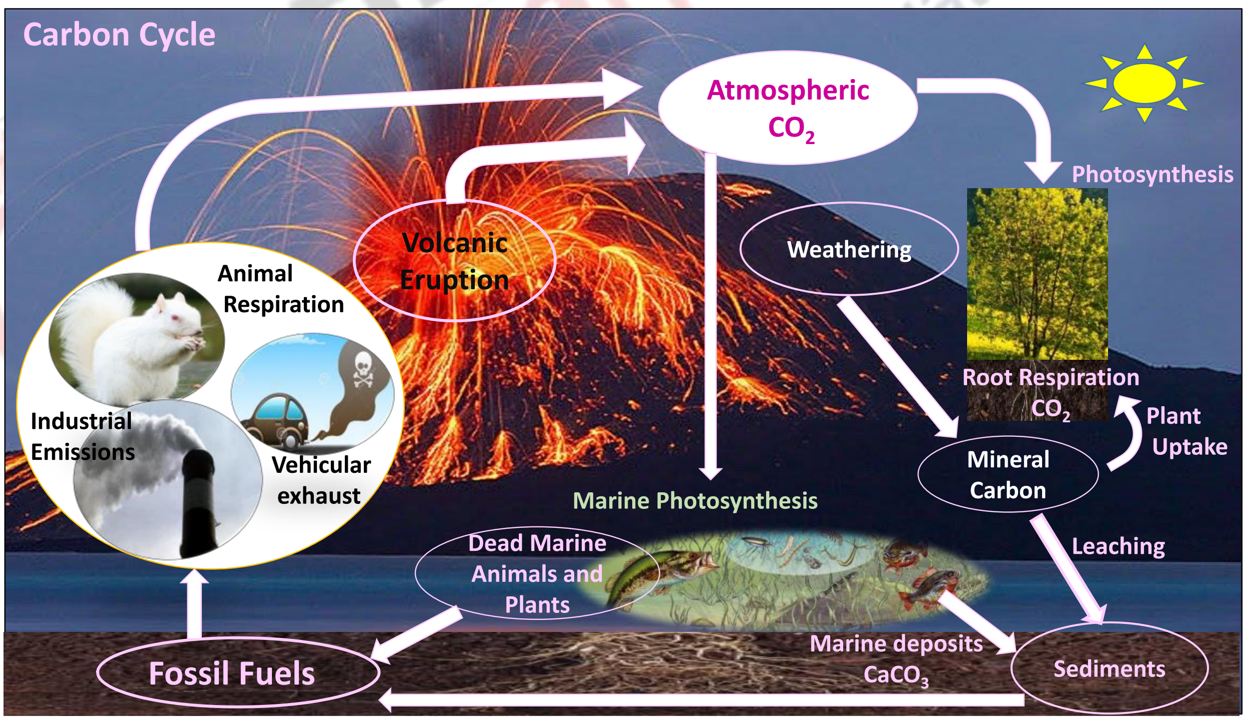

Figure 1 Global carbon cycle

Carbon is an element that cannot be broken down or converted into simpler ones. The amount of carbon in the earth is fixed but the dynamic nature of the earth moves it from one form to the other, between living to non-living. The carbon cycle occurs in a series of steps. It begins with the fixing of carbon in the biological systems by capturing solar energy via the process of photosynthesis. Plants utilize the carbondioxide from the atmosphere and fix them as carbon in their various plant parts. The carbon is gradually transferred to herbivores, carnivores and other life forms through the food chain. The animals through the process of respiration inhales oxygen and release the carbon as carbondioxide back to the atmosphere. The death and decay of plants and animals returns the carbon back to the soil by the action of decomposers such as bacteria, fungi etc. Microorganisms play a crucial role in carbon cycle by mediating a number of biochemical reactions. They degrade and fix organic carbon which later is transformed through various biochemical reactions into fossil fuels such as coal, lignite, peat, petroleum etc. Majority of the organic contaminants (xenobiotics) are degraded by the microorganisms to release the carbon back into the soil.

Carbon circulates within the ocean too where the photosynthetic algae fixes carbondioxide and produce biomass. The carbon dioxide gas from the atmosphere dissolves in the water to form weak carbonic acid. The carbonic acid further dissociates into hydrogen ions and bicarbonate ions. The hydrogen ions react with the minerals and alters them resulting in clay and other ions such as sodium, potassium and calcium. Corals, a marine organism precipitates calcium and bicarbonates to form calcium carbonate. Calcium carbonate is stored in the sediments in the ocean floor as reserves. The calcium carbonates in the sediments are metamorphosed in deep subduction zones and orogenic belts. During volcanic eruptions, a huge amount of CO_2 is evolved from the mid oceanic ridges and hot spot volcanoes. The metamorphosed calcium carbonate is the source of CO_2 released from the ocean. The released carbon dioxide once again cycles back in three routes: dissolved in ocean water, some are bound as carbonate rocks and some bound as biomass.

Thus, carbon cycle is very vital because carbon is the backbone of life on earth. It has a lot of sources and sinks. The speed of carbon movement from source to sink is not same all the time and it varies for sources. Carbon cycle is altered by various anthropogenic emissions leading to impacts on global level. The impacts caused by anthropogenic activity are provided below.

- Burning fossil fuels leads to the release of huge amount of CO_2
- As discussed earlier, trees sequester carbon dioxide during photosynthesis. Deforestation increases the level of in CO_2 air
- Alteration in CO_2 level due to man-made activities causes increase in temperature of the earth due to greenhouse effect
- The global warming results in destruction of the earth due to sea level rise, floods, drought, increased temperature and changing weather patterns.

3.2. Oxygen cycle

Oxygen is an important element playing a vital role in the environment. It is highly reactive gas which turns to a bluish liquid at -183° C. Figure 2 depicts the oxygen cycle. It circulates between the atmosphere and bound forms of oxygen (chemically and biological bound) eg. Water, carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen dioxide, organic matter and minerals. Atmosphere is the huge reservoir of free oxygen containing almost 21% oxygen. The biosphere has some free oxygen released by the living organisms by the process of photosynthesis. Majority of oxygen is present in the

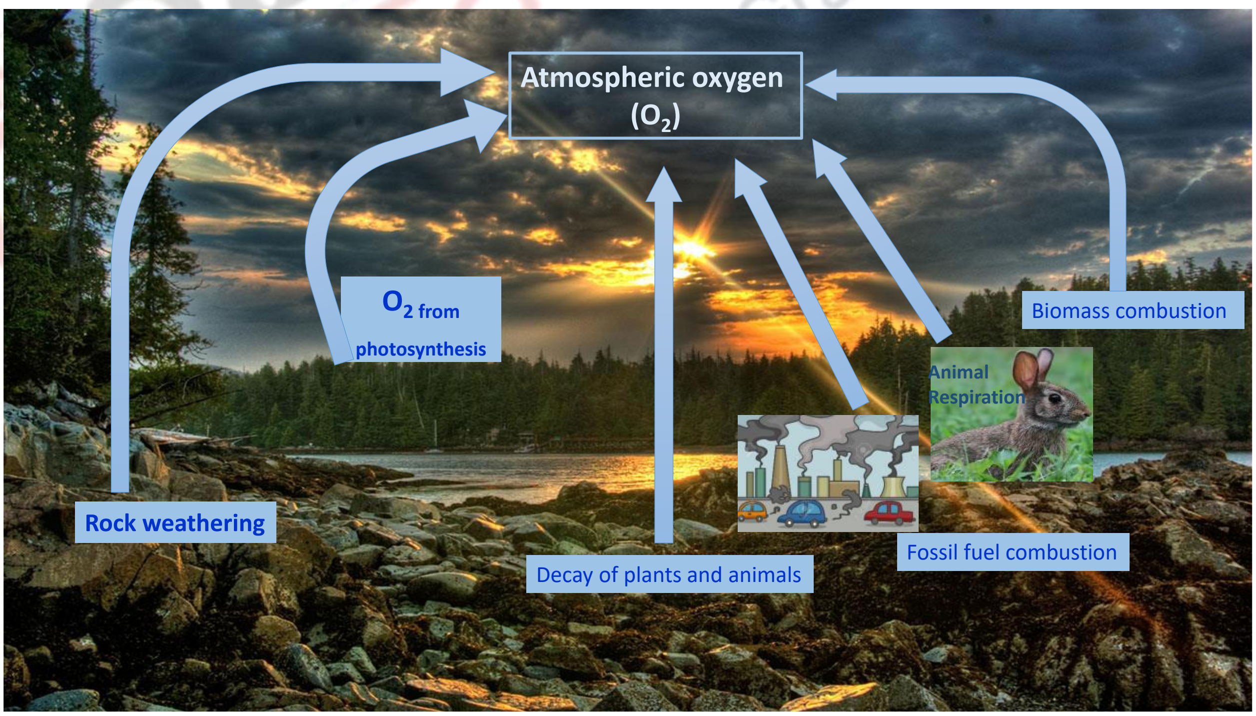

Figure 2 Oxygen cycle

lithosphere in the chemically bound form as silicates and oxides. Lithosphere is considered to be the largest source of oxygen than atmosphere.

The oxygen from the atmosphere is taken up by the living organisms through the process of respiration. During aerobic respiration, the oxygen combines with carbon and releases carbon dioxide which is used by plants in photosynthesis. The oxygen utilized in respiration is returned back to the atmosphere during the process of photosynthesis. Oxygen plays an important role in combustion of fossil fuels and methane resulting in release of CO_2, SO_x and NO_x. Inorganic substances and other minerals are also oxidized by oxygen. The degradation and decomposition of dead organic matter and waste generated from living organisms too requires oxygen. The aerobic bacteria involved in decomposition require oxygen for degradation of waste material.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

In the aquatic environment, Oxygen supports the aquatic life in the dissolved form (i.e) dissolved oxygen. Chemical weathering of materials resulted in release of oxygen present in combined forms in lithosphere. An important aspect of the oxygen cycle is the generation of stratospheric ozone. Oxygen is broken down by UV radiations into free oxygen radical which again combines with oxygen to form ozone in the stratosphere. The stratospheric ozone protects the earth from harmful UV radiations by absorbing them.

The Oxygen cycle is strongly tied with other biogeochemical cycles and influences them. Similar to other cycles, the oxygen cycle is also affected by the human activities. Increased burning of fossil fuels results in decreased oxygen and increased emission of carbon dioxide, thereby altering both the carbon and oxygen cycle.

3.3. Nitrogen cycle

Nitrogen is one of the most important and crucial biogeochemical cycle of the environment. It is a key nutrient for the living organisms and is a constituent of the organic molecules such as the amino acids, proteins, chlorophyll and nuclei acids. Before getting into the details of nitrogen cycle, it is essential to know some basic facts about nitrogen. Nitrogen is available in huge amount in the atmosphere. Almost 78% of air is composed of dinitrogen (N_2). Although atmosphere contains 78% of dinitrogen gas it is not available to the living organisms due to the inertness and non-reactive nature of N_2 due to the strong triple bond between the nitrogen atoms. Though dinitrogen gas is largely available in the atmosphere, it remains inaccessible to the living organisms. Only when dinitrogen gas is converted into ammonia it becomes accessible. Soil and oceans are the second major reservoir of nitrogen. Contrary, the biosphere constitutes just a minimum quantity of nitrogen (i.e) almost one million times lesser nitrogen than the atmosphere.

Nitrogen exists in organic and inorganic (ammonia, nitrate) forms and in different oxidation states. Nitrogen is a highly interchangeable compound and hence undergoes transformations from one oxidation state to another according to the use of organisms. The transformations include nitrogen fixation, nitrification, denitrification and ammonification carried out by the microorganisms especially the bacteria and fungi. Figure 3 depicts the nitrogen cycle. Dinitrogen is made biologically available through nitrogen fixation. The conversion process is very energy demanding and only few prokaryotes can convert N_2 into biological nitrogen. Almost eight electrons and sixteen ATPs are

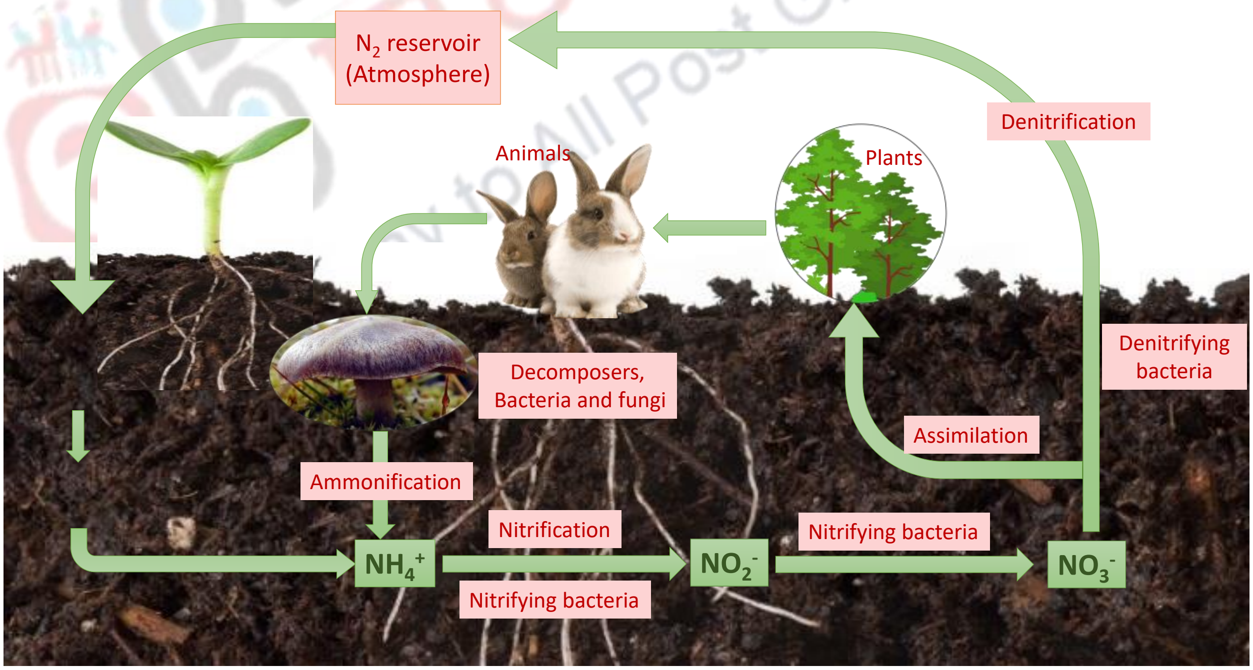

Figure 3 Nitrogen cycle

required to break the triple bond in dinitrogen gas. Lightning and certain industrial process also break the dinitrogen into biological available nitrogen. Some nitrogen fixers are free living and some exhibit symbiotic relationship with the host plant eg. *Rhizobium* in leguminous plants; Cyanobacteria in aquatic systems. The nitrogenase enzyme present in the nitrogen fixers catalyzes the reduction of N_2 to NH_3 (ammonia).

$$N_2 + 8H^+ + 8e^- \longrightarrow 2NH_3 + H_2$$

The ammonia is oxidized to nitrite and nitrate by the nitrifying bacteria through the process of nitrification. Two distinct steps are involved in nitrification. First step involves the oxidation of ammonia to nitrite via an intermediate, the hydroxylamine carried out by ammonia oxidizing bacteria. Ammonia oxidizing bacteria are autotrophic and involve two enzymes viz. ammonia monooxygenase and hydroxylamine oxidoreductase.

$$NH_3 + O_2 + 2e^- \longrightarrow NH_2OH + H_2O$$

$$NH_2OH + H_2O \longrightarrow NO_2 + 5H^+ + 4e^-$$

The second step involves the oxidation of nitrite to nitrate carried out by a specific group of bacteria nitrite oxidizing bacteria. *Nitrospira*, *Nitrobacter*, *Nitrococcus*, and *Nitrospina* are few of the nitrite oxidizing bacteria. Nitrate is highly soluble in water and hence gets leached out into the water body.

$$NO_2 + 0.5\ O_2 \longrightarrow NO_3$$

The biological nitrogen is returned back to the atmosphere by the process of denitrification. Denitrifying bacteria converts the nitrate to dinitrogen under anaerobic conditions with a series of intermediate nitrogen compounds such as NO_2, NO, N_2O.

$$2NO_3 + 10e^- + 12H^+ \longrightarrow N_2 + 6H_2O$$

Denitrification is carried out by anaerobic bacteria in soils, sediments, lakes and oceans. Denitrifying bacteria are chemoorganotrophs and require carbon for its growth. *Bacillus*, *Paracoccus* and *Pseudomonas* are some of the examples of denitrifying bacteria.

Plants take up nitrogen as ammonium (NH_4^+) and nitrate (NO_3^-) ion from the soil mixture. Ammonium is toxic at higher concentration and hence used less by the plants. The nitrogen enters into the animals and other trophic levels of the food chain via the plants. The waste generated by the animals, death and decay of plants and animals results in the generation of inorganic nitrogen via the decomposition process. The process by which the decomposers convert the ammonia (NH_3) into ammonium ion (NH_4^+) is called as ammonification. Bacteria, actinomycetes and fungi play an important role as decomposers. The ammonium is then available for plants and other microorganisms for growth.

Impact of human activities on nitrogen cycle

1. The N_2O which is produced as an intermediate during denitrification is a greenhouse gas and possess more global warming potential than methane and carbon dioxide.
2. The N_2O warms the atmosphere and leads to depletion of stratospheric ozone
3. Combustion of fuel at high temperature releases a huge amount of NO to the atmosphere which later gets converted to NO_2 and HNO_3 in the atmosphere. The HNO3 reaches the earth as acid rain and causes environmental and health effects.
4. As mentioned earlier, nitrate is readily soluble in water and leaches out into the water bodies. Excessive use of nitrate in fertilizers can contaminate ground and surface water which is harmful for the health of an individual especially the infants.
5. Agricultural run off and sewage discharge into water bodies leads to eutrophication problems
6. Deforestation also leads to alterations in nitrogen cycle.

3.4. Phosphorus cycle

Phosphorus is an element on the Earth and is present in water, soil and sediments. Phosphorous is not present in the atmosphere and hence lacks an atmosphere component in the cycle making the cycle endogenic. The availability of phosphorus in soil is very limited and this is the reason for application of phosphate fertilizers to enhance plant growth. Animals and humans obtain phosphorus through the food chain from plants and plant eating animals.

Phosphorus is an essential nutrient for animals and plants. It is a constituent of protoplasm and DNA with a major role in cell development and energy storage (ATP).

Cycling of phosphorus: Biogeochemical cycling of phosphorus through living and non-living element of the earth is called phosphorus cycle (Figure 4). Phosphorus is a limited nutrient commonly found in nature as orthophosphates (PO_4^{3-}). Its limitedness in the environment makes the cycle more crucial. Unlike carbon, the reservoir of phosphorus is rocks where deposition occurred for ages. They are found associated with minerals in the rocks. Hydroxyapatite, a calcium phosphate is the major reservoir of phosphate in the soil. Over the period of time, the geological process causes weathering and erosion of rocks containing phosphate ions and releases it into the soil and water bodies. Most of the phosphorus is lost to the sea where it gets deposited in the deep sediments. The marine organisms uplift the phosphorus in the sediments and reintroduce it into the cycle. The cycling of phosphorus from sea to land is comparatively slower due to loss of fish and other marine creatures for food and industrial purpose.

The phosphorus enters into the plant through absorption of phosphate ions from the soil and is carried to other animals via the food chain. After the consumption phosphate is assimilated into the ATP, nucleotides and other organic molecules (bones and biological membranes in the form of phospholipids) of the animals and man. After the death and decay of plants and animals these phosphates are released into the environment again. The organic forms of phosphate within the soil are provided to the plants by the bacteria which break down organic matter into inorganic forms of phosphorus through the process called as mineralization. The movement of phosphorus between the living beings and the environment is uneven due to the certain reasons. The reasons include (i) the phosphorus gets locked up in the bones of organisms, organic detritus and inorganic particles of the sediment; (ii) the phosphorus uptake in lakes is much faster than its release.

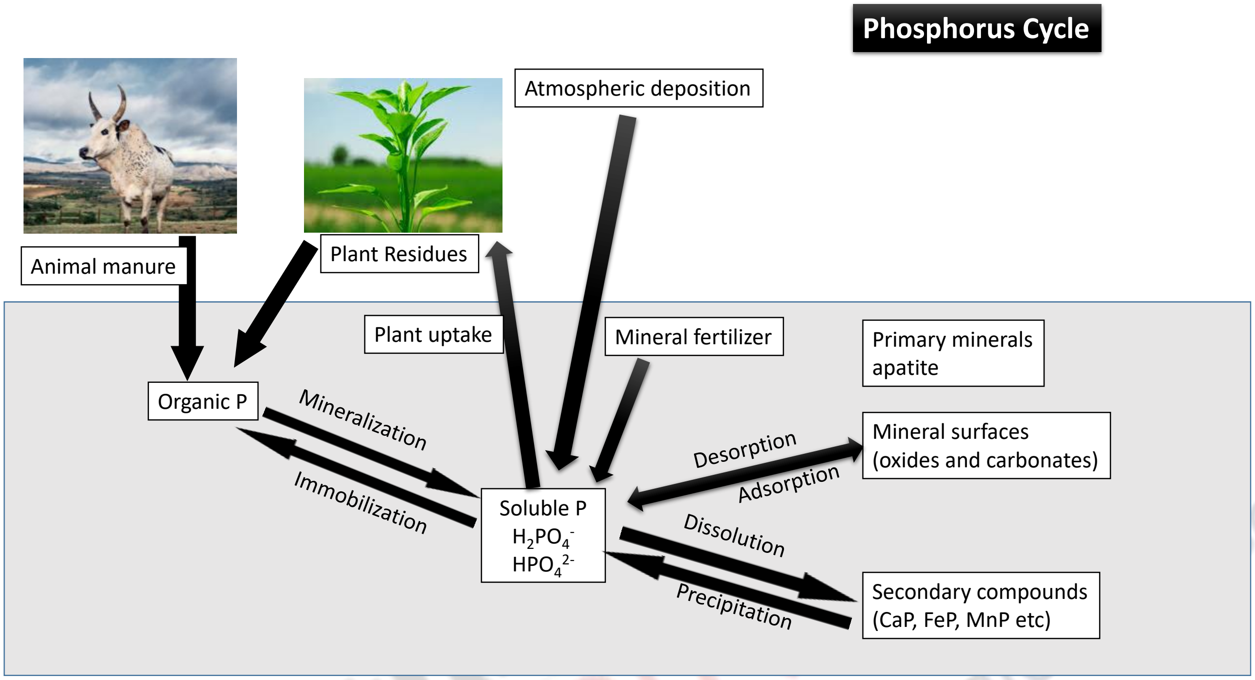

Figure 4 Phosphorus cycle

Impacts of anthropogenic activities on phosphorus cycle

The cycling of phosphorus is slowest among all biogeochemical cycles. However, the human interferences bring about changes in the cycle.

1. During certain times the phosphorus available in the soil are locked and made unavailable to plants. This results in excessive use of fertilizers causing intrusion of phosphate into the soil and water through seepage. Plants may not be able to utilize all of the provided phosphate fertilizers. The unused phosphate enters the water bodies through agricultural runoff. The phosphorus once again gets dissolved in ponds and lakes resulting in algal blooms and eutrophication.
2. Mining of apatite (calcium phosphate) from phosphate rocks for fertilizers and detergent preparation leads to huge release of phosphate into the soil.
3. Deforestation reduces the availability of phosphorus in soil
4. Discharge of sewage and other industrial effluents into the water bodies also disturb the phosphorus cycle.

3.5. *Sulphur cycle*

Sulphur is a yellow, odorless, nonmetallic element found in the earth's crust. It is an important constituent of protein and vitamin playing a vital role in protein and enzyme functioning in plants and animals. Sulphur is present naturally in the earth's crust, water bodies and atmosphere. Sulphur primarily occurs in the earth's crust in the form of gypsum ($CaSO_4$) and pyrite (FeS_2, PbS, and HgS). Oceans are the largest reservoir of sulphur. Around 2.6 g/L of sulphates are present in the oceans in addition to dissolved hydrogen sulfide gas, and elemental sulfur. Atmosphere is another source of sulphur (Sulphur dioxide, ammonium sulphate and sulphate particles, Hydrogen sulphide gas).

The biogeochemical cycle of Sulphur consists of two components, the terrestrial and atmospheric component. Sulphur cycles between air, water, soil and living organisms. Weathering of rocks release the sulphur stored in the earth's crust. In addition to weathering, the Sulphur from the earth's crust is also released through volcanic eruptions. Sulphur dioxide and hydrogen sulphide gas is released from the active volcanoes. The organic matter in marshes, tidal flats, bogs, wetlands emit sulphur in the gaseous form (H_2S). Sea spray, forest fires and dust storms are also the sources of sulphate salts (ammoniaum sulphate) in the atmosphere. To summarize, sulphur enters the atmosphere from the land through four routes namely volcanic activity, soil dust, industrial activity and Sulphur reducing bacteria activity. Ocean acts as another major contributor of sulphur to the atmosphere. Aerosols of sea water, deep sea hydrothermal vents, dimethyl sulfide gas produced by the marine algae are the routes of Sulphur entry into the atmosphere. In the atmosphere, Dimethyl sulphide droplets act as nuclei for the condensation of water in the clouds thereby playing a major role in cloud cover and climate change. Dimethyl sulphide is finally converted to sulphur dioxide in the atmosphere.

The Sulphur dioxide when it comes in contact with air gets oxidized to forms Sulphur trioxide. Similarly, the hydrogen sulphide combines with oxygen to form Sulphur dioxide and Sulphur trioxide. The oxides of Sulphur react with water droplets in the atmosphere to form droplets of sulphuric acid. The ammonia present in the atmosphere also reacts with sulphuric acid to form ammonium sulphate salts. The droplets of sulphuric acid and ammonium sulphate salt reaches the earth as acid deposition which is harmful to plants, animals and human beings. Moreover, it changes the soil pH and acidifies the lakes in addition to chemical weathering of buildings. The Sulphur once again gets accumulated in the sediments of oceans, lakes and reservoirs. The Sulphur combines with iron to form ferrous sulphide and gives a black colour to the ocean sediments.

As mentioned earlier, Sulphur is an important constituent of the amino acids (cysteine and methionine) and proteins. Only few organisms utilize organic sulphur via amino acids, rest assimilates Sulphur in the inorganic form, the sulphate ions. Plants assimilate sulphate and from them Sulphur enters into the animals via the food chain. Death and decay of organisms releases the Sulphur back to the environment. Bacteria reduce sulphur and obtain energy both in the presence and absence of oxygen and other terminal electron acceptors. Sulphur reducing bacteria (SRB) are extremophiles belonging to domain archea. They live in hydrothermal vents and hot springs. Sulphate reduction can be assimilatory and dissimilatory. Sulfate (SO_4^{2-}) is reduced to organic sulfhydryl groups (R–SH) in assimilary pathway and desulfurization of sulfhydryl groups (R–SH) to hydrogen sulphide is the dissimilatory pathway. Desulfuromonas is an example of SRB that reduces sulphur to hydrogen sulfide. A special group of bacteria the photosynthetic green and purple sulfur bacteria and some chemolithotrophs oxidize H_2S (hydrogen sulfide) to produce elemental sulfur (S_o), oxidation state.

Impact of anthropogenic activities on Sulphur cycle

Similar to other biogeochemical cycles, the Sulphur cycle is also altered by the human activities. Some of them are mentioned below.

1. Burning of fossil fuels such as coal and oil results in release of oxides of Sulphur
2. Refining of petroleum products adds Sulphur to the atmosphere
3. Purification of Sulphur containing metallic ores also releases Sulphur dioxide to the atmosphere.

4. Summary

The chapter highlighted the importance of the biogeochemical cycles in the earth. The cycling of the elements among the biological, geological and chemical component of the environment is the biogeochemical cycle. It is very essential for proper functioning and survival of the ecosystem. Though each cycle is different from the other, its functioning is of utmost important for maintaining the structure and function of an ecosystem. Anthropogenic activities bring a lot of lot of alterations in the biogeochemical cycles which further adds on oil to the burning global issues.
