Biogeochemical Cycles

ACADEMIC SCRIPT

1. Introduction

A *biogeochemical cycle* or *cycling of substances* or *substance turnover* is the cycling pathway by which chemical elements required by life moves through both biotic (biosphere) and abiotic (lithosphere, atmosphere and hydrosphere) compartments of Earth. A cycle is a series of change which comes back to starting point and which can be repeated. The term "biogeochemical" tells us that biological, geological and chemical factors are involved. The plants and animals that live and then die are the *bio part*; the earth that they decompose into comprises the *geo part*; and the process by which organic matter returns to the chemical elements in the earth is explained by *chemical part*. These chemical nutrients include Carbon, Oxygen, Nitrogen, Phosphorous, Sulphur and Water.

These elements cycle in either a gas cycle or a sedimentary cycle. In a *gas cycle,* elements move through the atmosphere. In a *sedimentary cycle,* elements move from land to water to sediment. Carbon cycle, nitrogen cycle and oxygen cycle are examples of Gas cycle whereas phosphorous cycle and sulphur cycle are examples of Sedimentary cycle.

2. Nitrogen Cycle

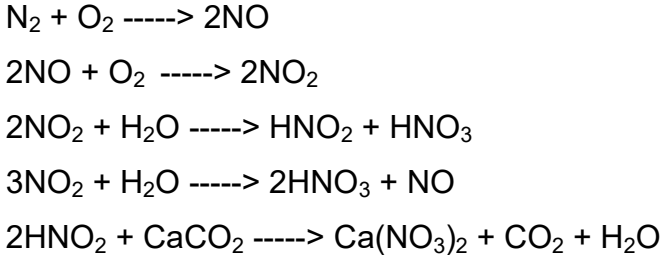
Nitrogen is one of the very important elements on earth as it is a component of amino acids, proteins, vitamins, DNA, RNA, etc. Earth's atmosphere contains around 78% nitrogen. However, plants and animals cannot use it directly in its elemental form from the atmosphere. This elemental form of nitrogen is used by plants only after it gets converted into inorganic nitrogen containing compounds like nitrites (NO_2^-), nitrates (NO_3^-), ammonia (NH_4^+), nitrous oxide (N_2O), nitric oxide (NO) or inorganic nitrogen (N_2). These conversions are done by various kinds of bacteria and other micro-organisms. Thus, the ***nitrogen cycle*** is the process by which nitrogen is converted in its various chemical forms by biological and physical process.

Nitrogen cycle consists of various steps:

Nitrogen fixation
Nitrogen assimilation
Ammonification
Nitrification
Denitrification
Sedimentation

Nitrogen fixation: Nitrogen fixation is the process by which free nitrogen of atmosphere is converted into biologically available form of nitrogen. There are four ways for nitrogen fixation,

1. **Physiochemical fixation**- during lightning and at the time of electric discharge in clouds, the nitrogen of atmosphere combines with oxygen and produces different kinds of nitrogen oxides. These oxides of nitrogen get dissolved in water to form nitrates and other nitrogenous compounds. This can be summarized as shown here,



$N_2 + O_2$ -----> $2NO$
$2NO + O_2$ -----> $2NO_2$
$2NO_2 + H_2O$ -----> $HNO_2 + HNO_3$
$3NO_2 + H_2O$ -----> $2HNO_3 + NO$
$2HNO_2 + CaCO_2$ -----> $Ca(NO_3)_2 + CO_2 + H_2O$

2. **Biological nitrogen fixation-** In this kind of fixation atmospheric nitrogen gets converted into nitrites and nitrates by free-living bacteria, symbiotic bacteria and by blue green algae.

Free living bacteria such as *Azobacter*, *Clostridium* etc. fix nitrogen of atmosphere in the soil by combining the gaseous nitrogen of atmosphere with the hydrogen that is obtained from respiratory pathway to form ammonia.

Symbiotic bacteria like *Rhizobium* living in the root nodules of legumes cannot fix the nitrogen solely. These bacteria invade the roots or leaves and stimulate the formation of root nodules or leaf nodules, which are kind of harmless over growth of cells as a 'tumour'. The union of these bacteria and nodule cells are able to fix the atmospheric nitrogen under low oxygen condition and nitrogenase enzyme reduces nitrogen to ammonia.
Certain species of lichens also have nitrogen-fixing ability.

3. **Industrial N-fixation-** Under great pressure, at a temperature of 600°C, an iron catalyst, hydrogen and atmospheric nitrogen combine to form ammonia.

4. **Combustion of fossil fuels-** Automobile engines and thermal power plants release various nitrogen oxides (NO_X).

Nitrogen assimilation: Inorganic nitrogen in form of nitrites, nitrates and ammonia is taken up by plants from soil. Plants utilize these inorganic nitrogenous compounds to produce organic nitrogenous compound like amino acids, proteins, enzymes, nucleic acid, chlorophyll etc. Animal consumes plants and thus they get nitrogenous organic compound in their body.

Ammonification: The dead organic remains of plants and animals as well as excreta of animals are decomposed by number of microorganisms that convert the organic nitrogen into ammonia. In decomposition, protein, urea, uric acid etc. of animals get converted into the ammonia in the presence of ammonifying bacteria such as *Bacillus ramosas*, *Bacillus vulgaris* and *Bacillus mycoides.*

Nitrification: In this step ammonia, which was produced in previous step, get converted into nitrite and nitrates. *Nitromonas* and *Nitococus* bacteria carry out conversion of ammonia to nitrites. The equation of this reaction is

$2NH_3 + O_2$ ---> *Nitromonas,*
Nitococus -----> $2NO_2^- + 2H^+ + 2H_2O$ + Energy

Conversion of nitrites to nitrate is brought about by bacteria like *Nitrobacter* and *Penicillium* (a fungus).

$2NO_2 + O_2$ ----> *Nitrobacter* -----> $2NO_3^-$ + Energy

Denitrification: In this step, denitrifying bacteria like *Pseudomonas, Micrococus denitrificans, Thiobacillus denitrificans* etc. converts ammonia, nitrites and nitrate into molecular nitrogen. The reaction can be summarized as

NO_3^- (Nitrate) -----> NO_2^- (Nitrite) -----> NO (Nitrous oxide) -----> N_2O (Nitricoxide) -----> N_2 (Nitrogen)

Sedimentation: Nitrates present in soil sometimes gets locked up in the rocks. This is called the sedimentation of nitrogen. During weathering nitrates is released by conversion into nitrogen.

Thus nitrogen is fixed by microbes. Fixed nitrogen is absorbed by plants via food chain. Organic nitrogen enters into consumers and all dead remains is acted upon by decomposer and again nitrogen gets back to atmosphere in its molecular form.

In this way nitrogen cycle keeps on operating in cyclic manner.

3. Phosphorous Cycle

Phosphorous is a major constituent of life sustaining biomolecules, biological membranes, energy rich compounds (ATP) and nucleic acids. In addition, many animals also need large quantities of this element to make shells, bones, exoskeleton and teeth. It also functions as a buffering agent in maintaining acid base homeostasis in human body. The ***phosphorous cycle*** describes the movement of phosphorous through lithosphere, hydrosphere and biosphere. It is a sedimentary cycle.

Sources of Phosphorous:

Due to rains and weathering, phosphates from rocks leach to soil. Much of the leached phosphate from soil runs off to ocean due to rain and soil erosion and thus makes phosphorous pool in the ocean.

Fate of phosphorous in soil and ocean:

In soil, phosphates reacts with iron oxide, aluminum hydroxides, clay surface, organic particles and become incorporated.

The phosphorous pool of soil is in four different forms, which are,

1. Inorganic phosphorous available directly for plant
2. Organic phosphorous which is not available to plant directly
3. Adsorbed phosphorous which is phosphate bound chemically with soil particles (unavailable to plants readily)
4. Mineralized phosphorous (unavailable to plants readily)

Mineralization and Immobilization:

Mineralization is conversion of organic phosphorous to $H_2PO_4^-$ or HPO_4^- by microbial activity. Slow desorption over a long period of time makes little adsorbed phosphorous available for plants. Primary mineral phosphorous like iron phosphate and mineral phosphate become plant available phosphate due to weathering. Certain microbes and symbiotic fungi at plant roots create acidic condition due to which phosphorous gets available to plant from its minerals.

Water Runoff and Soil Erosion:

Water carries away dissolved phosphorous from applied manure and fertilizers as well as particulate (soil bound) phosphorous, which gets trapped in sedimentary rocks. Soil erosion control decreases phosphorous losses by slowing water flow over soil surface and increasing infilteration.

Phosphorous cycling between biotic and abiotic components:

Plants absorb phosphorous from soil and via food chain it becomes integral part of different trophic level consumers. Both producers and consumer's dies and decomposition of both submit phosphorous back to soil. Similarly, in the ocean phosphorous from water is passed to phytoplanktons to zooplanktons and from zooplanktons to fishes via food chain. Excreta and death of marine organisms return phosphorous to water. Small amount of phosphorous is returned to lithosphere from ocean by marine birds' excreta known as 'Guano', which contains plenty of, phosphorous.

The deposited sediment of phosphorous remains out of circulation and makes cycle imperfect.

4. Sulphur Cycle

Sulphur is an essential element of biological molecules in small quantities. It is a component of three amino acids, which are cysteine, cystine and methionine. Besides that certain vitamins and enzymes also contain sulphur. The ***sulphur cycle*** is the collection of processes by which sulphur moves to and from minerals (including the waterways) and living system.

Sources of Sulphur:

Sulphur is mainly found on earth as sulphates in soil, water and rock or as free sulphur. Rainwater running over the rock causes leaching of sulphur from rock. This leached sulphur by rain water gets soaked in soil whereas some amount run off to lake, river and ocean. In ocean it may get locked in sedimentary rocks. The largest physical reservoir of sulphur is the Earth's crust where sulphur is found in gypsum ($CaSO_4$) and Pyrite (FeS_2). Atmosphere contains sulphur dioxide (SO_2) and methane sulfonic acid ($CH_3SO_3^-$), Volcanic activity releases some hydrogen sulphide into the air.

Cycling of sulphur between sulphates and sulphides:

After death of autotrophs and heterotrophs, their decomposition takes place and in this process biologically incorporated sulphur is mineralized by bacteria. Sulphur is directly reduced to hydrogen sulphide by *Desulphovibrio* and *Aerobacter*.

$SO_4^{2-} + 2H^+ \text{-----> } H_2S + 2O_2$

Thus higher concentration of H_2S starts to build up in anaerobic or deeper portion of aquatic ecosystem. A part of H_2S is oxidized to soluble sulphates by sulphur bacteria like *Thiobacillus* and *Beggiatoa*.

$6CO_2 + 12\ H_2S \text{ -----> } C_6H_{12}O_6 + 6H_2O + 12S$

Some amount of sulphur remains in deep sea. From sea it gets back to land via food chain, sea sprays and due to geological upheavals.

The SO_2 and SO_3 are released into the atmosphere by burning of fossil fuel. When there is rain, these SO_2 and SO_3 gets dissolved in rain water forming sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4) respectively. These fall on earth as 'acid rains'. On reaching soil, sulphurous acid and sulphuric acid form sulphates with metals. Sulphates are in turn used by plants and animals and thus *cycle keeps operating.*

5. Oxygen Cycle

Oxygen is a basic element of life and it is part of several essential biomolecules. It is one of the major gaseous components of atmosphere and in form of O_3, Ozone it provides protection of life. It constitutes about 21% of the atmosphere and is ubiquitous. The ***oxygen cycle*** involves movement of oxygen and its storage in different forms as well as its oxidative reactions with various elements. This cycle is important because it helps to shield Earth from majority of harmful Ultraviolet (UV) radiation turning it to harmless heat before it reaches earth's surface.

Sources of Oxygen:

Oxygen is stored in three main reservoirs: the atmosphere, the total content of biological matter within the biosphere and lithosphere. Most of this oxygen is not on its own or free

moving, but part of chemical compounds such as silicates or oxides and as water in the oceans. An additional source of atmospheric free oxygen comes from photolysis, whereby high energy UV radiation breaks down atmospheric water and nitrous oxide into component atoms. The free H and N atoms escape into space leaving O_2 in the atmosphere.

Cycling of Oxygen:

Plants mark beginning of Oxygen cycle as they are able to use the energy of sunlight to convert Carbon dioxide and water into carbohydrates and oxygen in a process called photosynthesis. Animals form the other half of oxygen cycle as they take in oxygen through process of respiration and release carbon dioxide (CO_2) into atmosphere. Fuels need oxygen for combustion so they take oxygen and release (CO_2) into atmosphere as a byproduct along with other gases like N_2, etc.

Oxygen is also cycled between biosphere and lithosphere. Marine organisms in the biosphere create calcium carbonate shell material ($CaCO_3$), which is rich in oxygen. When the organism dies, its shell is deposited on the shallow sea floor and buried over time to create the limestone sedimentary rock of lithosphere. Weathering processes initiated by organisms can also free oxygen from lithosphere. Plant and animals extract nutrient minerals from rocks and release oxygen in the process. The lithosphere mostly fixes oxygen in minerals such as silicates and oxides. When oxygen-bearing mineral is exposed to elements, a chemical reaction occurs that wears it down and in the process produces free oxygen.

Failures in the oxygen cycle within the hydrosphere can result in development of hypoxic zones.

6. Water Cycle (Hydrologic Cycle)

Water is indispensible for life and it can be said that it is the “matrix of life”. It is component part of all living tissue. 60% - 90% of the organisms’ body weight is due to water. It

remains incorporated in biomolecules of the body. It also acts as solvent for many organic and inorganic components. It is required for thermoregulation, for transportation of molecules and in hydrolytic digestion of nutrients. The ***water cycle***, also known as ***hydrologic cycle*** or the ***H_2O cycle*** describes continuous movements of water on, above and through the Earth via the land, atmosphere and oceans. The water cycle figures significantly in the maintenance of life and ecosystems.

Distribution of water:

Water covers 71% of Earth's surface. On earth 96.5% of total water is found in oceans and seas, 1.7% as groundwater, 1.7% in glaciers and in the ice caps at polar region. A small fraction is found in other large water bodies and 0.001% in the air as vapor, clouds and precipitation.

Water Cycling:

The three major steps of water cycle are precipitation, evaporation and condensation. In this regard there are two types of water cycles.

1. Global water cycle
2. Biological water cycle

1. Global water cycle:

The sun, which drives the water cycle, heats water in oceans, seas, lakes rivers etc., and eventually water precipitates on both lithosphere and hydrosphere. Every year 4.46×10^{20} gm water precipitates on the earth. Of this amount 0.99×10^{20} gm falls on land and 3.24×10^{20} gm falls on ocean surface. Evaporated water from the hydrosphere forms cloud. Clouds blow over the land and sea as rain, snow, hail and sleet. Some water content of the rain percolate through soil. Natural springs, manmade wells and pumps brings ground water to surface water. Again by evaporation and precipitation, cycle gets repeated. A major part of water is locked up in earth's crust and it is only released in small quantities during volcanic eruptions. Same way, the large store in polar ice caps has little effect on hydrological cycle due to negligible evaporation from them.

2. Biological water cycle:

In terrestrial ecosystem, source of water for autotrophs is underground water. Roots of plant absorb this water from soil and use it in different physiological processes. In aquatic life, plants and animals get water from aquatic body in which they live. In terrestrial ecosystem, animals get water from water reservoirs like rivers, ponds, lakes, etc. whereas humans get water from rivers and from ground water by making tube wells and pumps. Plants return water to environment by transpiration. Animals return water to air by transpiration, urination and excretion. Mammals excrete water as sweat, which evaporates. These vaporized water from plants and animals precipitate eventually.

Thus, in these ways biological water cycle remains operating.

7. Carbon Cycle

Carbon is considered as building block of life as it is main component of biological compounds and many minerals. Carbon is the best for joining of elements to form compounds necessary for life such as sugar, starch, fats and proteins. The ***Carbon cycle*** is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere and atmosphere of Earth.

Sources of Carbon:

The major source of carbon is the atmospheric CO_2, CO_2 dissolved in water bodies of the earth and methane. Atmosphere contains 700×10^9 metric tonnes of CO_2 while water contains 35000×10^9 metric tonnes of CO_2. On an average, there is about 6 tonnes of carbon as CO_2 over each acre of Earth.

Movement of carbon in the ecosystem:

Photosynthesis and respiration are the two main biological processes, which count for biological cycling of CO_2 in the atmosphere.

***Photosynthesis*:**

All green plants, algae and phytoplankton's are able to carry out photosynthesis. In this complex process, after series of chemical reactions, simple sugar such as glucose is produced. Oxygen is produced as by-product. The process of photosynthesis can be summarized as:

$CO_2 + H_2O$ + Radiant energy -----> $C_6H_{12}O_6 + O_2$

The simple sugar is then converted to other biomolecules such as starch, fat, protein, cellulose etc. by different complex biochemical pathways. So it can be said that all the "matter "of the plant ultimately is produced as a result of photosynthesis.

Respiration:

The process of eating and being eaten transfers carbon from plant to successive trophic levels in food chain. Carbon in the form of different biomolecules get stored in animals and some amount of these biomolecules are utilized for cellular respiration and rest of it again count for biomass which may be consumed by animals of next trophic level in food chain. The process can be summarized as follows:

O_2 + Carbohydrate -----> Energy + Water + CO_2

In addition to this, decomposing micro-organisms break down dead material which releases carbon that goes back to carbon cycle. Some amount of carbon returns to environment in form of methane.

Cycling of the carbon from fossil fuels:

The direct emissions from burning fossil fuels transfer carbon from geosphere to atmosphere. Under, certain conditions, dead tissue may undergo partial decomposition. This causes formation of coal from plants and formation of natural gases and petroleum from marine organisms. Coal, natural gas and petroleum when burnt in automobiles, factories and powerhouses produce CO_2 that is added to atmosphere. Carbon tied up in fossilized organisms remains out of circulation for thousands of years.

Fate of carbon dioxide in oceans and seas:

Oceans contain the largest quantity of actively cycled carbon in the world. Carbon dioxide and other atmospheric gases dissolve in surface water. Dissolved gases are in equilibrium with the gases in the atmosphere. Carbon dioxide in atmosphere reacts with water to form weak acid that is carbonic acid.

$H_2O + CO_2$ <-----> H_2CO_3 (Carbonic acid)
H_2CO_3 <-----> H^+ (Hydrogen ion) + HCO_3^- (Bicarbonate ion)
HCO_3^- <-----> $H^+ + CO_3^-$ (Carbonate ion)

The carbonic acid causes weathering of rocks. As rocks get eroded, the clay ion like Ca++, Mg++ and carbon in form of HCO3- gets liberated from rocks. Sea animals that have calcium carbonate shell like clay, clam, cowry etc. possess ability to create shell from these dissolved ions in seawater. The reaction can be summarized as:

$2HCO_3 + Ca^{++}$ -----> $CaCO_3 + H_2O + CO_2$

Thus CO_2 and H_2O unite to form H_2CO_3 and thus cycling goes on and on. When organisms die their shells get accumulated as the limestone. Some of this carbon is returned to atmosphere via metamorphosis of this limestone due to heat and pressure in the deep region of the sea. Thus carbon dioxide is liberated from the limestone by this reaction:

$CaCO_3 + SiO_2$ (silicon dioxide) -----> $CaSiO_3$ (Calcium silicate) + CO_2

CO_2 formed in this way again contribute to formation of carbonic acid. Thus CO_2 passes through many phases and remain in cyclic utilization in seas.

The recycling of carbon is essentially a self-regulating mechanism.

8. Summary

Water, Nitrogen, Carbon, Phosphorous, Sulphur and Oxygen are the building blocks of life and they continually cycle through Earth's system, the atmosphere, hydrosphere, biosphere and lithosphere, on time scales that range from a few days to millions of years. Biogeochemical cycles are components of broader cycle that govern the functioning of planet Earth. These cycles are innately complex in nature and are pathways for transport and transformation of matter. They facilitate transfer of matter from one form to another and from one location to another on planet Earth.