Biogeochemical Cycles

Note: The chemical equations in these notes are not all balanced chemical equations; they are meant to simply describe key parts of chemical processes and in certain cases other details have been intentionally left out.

CARBON CYCLE

The carbon cycle transports carbon throughout the biosphere, hydrosphere, lithosphere and atmosphere.

- In absence of human disturbance the exchange of carbon throughout Earth's systems takes place in a balanced and steady state.
- This balance is important to the climate system (nature's thermostat), which sets the background for our environment: carbon dioxide (CO_2) and methane (CH_4) are greenhouse gases, which help determine global temperatures.

Biosphere

Carbon is required for formation of organic compounds in living things.

- 20% body weight; basis of organic molecules that form membranes, tissues, proteins, carbs, and energy.

Movement of carbon throughout the carbon cycle depends largely on photosynthesis, respiration, & decomposition.

- Carbon in carbon dioxide in the atmosphere and in water is moved to carbon in glucose via **photosynthesis** by producers.
  - $6\ CO_2 + 6\ H_2O + \text{Energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$
- Carbon in glucose is moved to atmospheric carbon in carbon dioxide by **cellular respiration**.
  - $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{Energy}$
- Carbon in glucose ($C_6H_{12}O_6$) is moved to carbon in organic molecules by synthesis reactions in living things (DNA, amino acids, proteins, cellulose, carbohydrates etc.).
- **Decomposition**: Aerobic and anaerobic respiration, i.e. decomposition of organic material (breaking down dead plants and animals), releases carbon dioxide and methane to the atmosphere, respectively.

Hydrosphere

CO_2 dissolves in ocean water and becomes part of marine sediments, as well as the skeletons of marine organisms.

- Carbon Exchange between atmosphere and ocean:
  - Atmospheric CO_2 dissolves into ocean water: CO_2 (atmospheric) $\rightleftharpoons$ CO_2 (dissolved in ocean water)
  - CO_2 (dissolved) reacts with ocean water to produce carbonic acid:

    $$CO_2 \text{ (dissolved)} + H_2O \rightleftharpoons H_2CO_3$$
  - Ionization: $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (bicarbonate ion); $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (carbonate ion)
  - $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (calcium carbonate) in shells/skeletons of aquatic organisms
  - $CaCO_3$ or Calcium Carbonate i.e. limestone is buried, long period of time

Lithosphere

Carbon Sedimentation and Burial:

- In the oceans, bicarbonate can combine with calcium to form limestone (calcium carbonate, $CaCO_3$,). Calcium carbonate precipitates (falls out of solution) to the ocean floor to form limestone via sedimentation. It's a slow process, but has accumulated much carbon over time!
- Carbon in limestone ($CaCO_3$) that has been exposed to Earth's surface is released slowly to carbon in carbon dioxide when exposed to oxygen and/or water i.e. *weather and erosion*.

Fossil Fuels:

- A small fraction of organic carbon in dead biomass (e.g. ancient swamp forests or ancient ocean phytoplankton) that was rapidly buried beneath layers of sediments before it could decompose, fossilized over millions of years and as a result of a combination of time, heat, and pressure to become coal, oil, and natural gas; i.e. fossil fuels.

Atmosphere

Extraction & Combustion

- Carbon locked in organic molecules (hydrocarbons) in fossil fuels is converted to atmospheric carbon in carbon dioxide by combustion (burning to produce energy to power cars and produce electricity).
- Removal of fossil fuels from the Earth and burning them (combustion) releases carbon, in the form of carbon dioxide, to the atmosphere.
- For example, the combustion of methane (the primary component of natural gas; used to heat homes, cook, and generate electricity) releases carbon dioxide to the atmosphere: $CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$.

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Human Interventions in the Carbon Cycle:

- **Large Scale Deforestation**: Reduces carbon reservoirs (natural carbon storage in forests; i.e. *sequestration*) *and* adds atmospheric carbon as a product of decomposition of wood (stumps and slash); also the removal of vegetation through deforestation reduces uptake of atmospheric carbon dioxide (through photosynthesis).
- **Burning Fossil Fuels**: Carbon stored (sequestered) in fossil fuels for millions of years (old carbon) is released during combustion as carbon dioxide.
- **Burning Biomass**: Either from forest fires or for slash and burn agriculture (burning forests to clear land for cropland or pastureland) releases CO_2 to the atmosphere (new carbon).
- **Raising Cattle:** Livestock such as cows are ruminant animals. This means they have a symbiotic relationship with gut bacteria and other microbes that live in their rumen (one chamber in the cow's four chambered stomach). These microbes are fiber digesters that convert feed such as grass, corn, or soybeans into a product that can be digested by the animal. This process, enteric fermentation, produces methane, which is exhaled by the animal (through belching or flatulence).
- **Making cement:** To produce cement, limestone and other clay-like materials are heated in a kiln at 1400°C. Coal, a fossil fuel, is the typical fuel used to heat the kilns and it takes a lot of coal to get a kiln to 1400°C.
- **Waste Incineration:** burning trash (municipal solid waste; MSW) releases carbon to the atmosphere.
- **Destruction/Draining of Wetlands:** Draining wetlands for agriculture and urban development releases carbon to the atmosphere.

Consequences? All of the aforementioned are significantly altering Earth's carbon budget (balance) and are increasing atmospheric CO_2 causing an increase in greenhouse effect resulting in global warming. Some environmental problems that result from increased carbon dioxide concentrations are:

- Global warming will cause climate change which will cause climate zones to shift and some species may not be able to adapt and may therefore become extinct.
- Melting of ice caps and glaciers causing sea level rise, as a result coastal habitats will be flooded.
- Increased absorption of carbon dioxide by the oceans will lead to ocean acidification (carbonic acid), which inhibits shell formation of marine organisms.

Carbon Sinks and Reservoirs

- The Earth's largest reservoir of carbon is sedimentary rock such as limestone (old carbon).
- Oceans are the second largest reservoir of carbon on Earth. Carbon is stored in the oceans in three ways: **1)** dissolved carbon dioxide in ocean water; **2)** in living things in ocean such as shells, skeletons, and coral reef; and **3)** in photosynthetic phytoplankton.
- Trees of *old growth forest* that live for thousands of years are a major terrestrial carbon sink.
- Glaciers, ice, and permafrost are a major terrestrial carbon sink that can store carbon for thousands to millions of years.
- Sedimentary rocks such as limestone are major terrestrial carbon sink that can store carbon for thousands to millions of years.
- Soil: Carbon is incorporated into soil by many natural processes including volcanism and decomposition of organic material. Therefore, soil is major terrestrial carbon sink that can store carbon for thousands of years.
- Wetlands and bogs are major terrestrial carbon sinks that can store carbon in plants, soil, and water for thousands of years.

For more information on sources and sinks:
https://enviroliteracy.org/air-climate-weather/climate/sources-sinks/

Biogeochemical Cycles

NITROGEN CYCLE

The nitrogen cycle transports nitrogen throughout the biosphere, hydrosphere, lithosphere and atmosphere.

- In absence of human disturbance the exchange of nitrogen throughout Earth's systems takes place in a balanced and steady state. This balance is important to the function of terrestrial and aquatic ecosystems.

The Role of Nitrogen:

- Nitrogen is required for proteins, nucleic acids in living things.
- Nitrogen is a building block of various essential organic molecules – especially proteins & nucleic acids.
- Plant chlorophyll requires nitrogen for photosynthesis
- It is a limiting nutrient in many ecosystems – typically, addition of nitrogen leads to increased productivity.
- Nitrogen compounds and ions such as ammonia, ammonium ion, nitrate and nitrates are water-soluble: can be leached (dissolved in water and transported) from soil and enter groundwater.
- Nitrogen is an essential plant nutrient, but is altering functional diversity of ecosystems.

Nitrogen Cycle Processes (*That you must know!)*

Plants and animals cannot use free nitrogen gas in the atmosphere. They must have nitrogen in "fixed" form.

- Nitrogen is fixed by lightning, ***bacteria*** in soil in terrestrial ecosystems and cyanobacteria in aquatic systems.
  - **Nitrogen Fixation:** $N_2 \rightarrow NH_3/NH_4^+$
    - Free N_2 in atmosphere is "fixed" by nitrogen-fixing bacteria to NH_3 (ammonia):
      $$N_2 + 3H_2 \rightarrow 2NH_3$$
    - Nitrogen fixing bacteria (rhizobium) live in nodules on the roots of leguminous plants (soybeans, peas, clover, and alfalfa.)
    - Gaseous nitrogen reacts with hydrogen to produce ammonia (NH_3) and ammonium ions (NH_4^+)

  - **Nitrification:** $NH_3 \rightarrow NH_4^+ \rightarrow NO_2^-/NO_3^-$
    - Water in the soil reacts with ammonia (NH_3) to form NH_4^+ (ammonium ion)
    - Another specialized species of bacteria performs nitrification once ammonium has formed:
      $NH_4^+ \rightarrow NO_2^-$ (nitrite; toxic) NO_3^- (nitrate; plant nutrient)

  - **Assimilation:** NH_3 or NH_4^+ or NO_2^- or $NO_3^- \rightarrow$ organic compounds (proteins)
    - Producers (plants) take up nitrogen in the form of ammonia, ammonium, nitrite, or most readily nitrate for use to make nucleic acids and proteins; the building blocks of plant tissue.
    - Consumers then get fixed nitrogen by eating plants, insects, or other animals.

  - **Ammonification (a.k.a. Mineralization):** organic compounds $\rightarrow NH_3$
    - Eventually all organisms die and their tissue decompose.
    - Fungal and bacterial decomposers break down organic material found in dead bodies and waste products and convert organic compounds back into inorganic compounds; Such as inorganic forms of nitrogen like ammonia or ammonium ions (NH_3/NH_4^+).

  - **Denitrification:** NH_3 or $NH_4^+ \rightarrow NO_2^-$ and/or $NO_3^- \rightarrow N_2$ (nitrogen gas) and N_2O (nitrous oxide)
    - The final step that completes nitrogen cycle.
    - In a series of steps, another group of bacteria convert ammonia or ammonium ions into nitrate then to atmospheric nitrogen compounds: the gases nitrous oxide (N_2O) and nitrogen gas (N_2).

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Human Interventions in the Nitrogen Cycle:

- **Agriculture:**
  - Surface runoff of nitrogen based fertilizers and livestock waste (manure is rich in nitrogen and phosphorus), throughout large watersheds adds excess nitrogen to downstream aquatic systems. This leads to *eutrophication* in aquatic ecosystems such as the Gulf of Mexico or Chesapeake Bay, for example. Nitrogen and phosphorus stimulate growth of algae causing massive algal blooms. When the algae die, aerobic decomposers break them down; this depletes the water of oxygen, causing dead-zones or massive die-offs of aquatic organisms.
  - Nitrous oxide (N_2O) is released to the atmosphere from off gassing of fertilizers and decomposition of manure by bacteria. Nitrous oxide (N_2O) is a potent greenhouse gas. The impact of 1 pound of N_2O on warming the atmosphere is almost 300 times that of 1 pound of carbon dioxide.
- **Untreated Discharge of Sewage:** Untreated discharge of sewage can also lead to eutrophication.
- **Destruction of forest, grasslands, and wetlands:** With such destruction, nitrogen that was stored in plants and soils is released to aquatic systems and atmosphere as gaseous compounds.
- **Forest Fires:** Nitric oxide is produced when forests burn. Heat energy catalyzes a reaction in which combines N_2 and O2, present in atmosphere, combine to form nitric oxide ($N_2 + O_2 \rightarrow 2NO$). This nitric oxide then reacts with atmospheric water vapor (clouds) to produce nitric acid, acid rain ($NO_2 + H_2O \rightarrow HNO_3$).
- **Burning Fossil Fuels:** Burning fossil fuels, such as gasoline, allows for high temperatures to catalyze a reaction in which combines N_2 and O2, present in atmosphere, combine to form nitric oxide ($N_2 + O_2 \rightarrow 2NO$). This nitric oxide then reacts with atmospheric water vapor (clouds) to produce nitric acid, acid rain ($NO_2 + H_2O \rightarrow HNO_3$).

PHOSPHORUS CYCLE

The phosphorus cycle is a *sedimentary cycle* and therefore *does not have an atmospheric component*. Phosphorus cycles through water, the earth's crust, and living organisms, *but not the atmosphere!* Phosphorus cycles slowly because it is dependent on geologic processes. Weathering from water releases phosphorus in rocks to aquatic systems. It is eventually transported by streams and rivers to the ocean and buried in bottom sediments where it is stored for long periods of time, becoming rock again. Phosphorus may again be exposed to the surface through geologic uplift, such as mountain building. When near the surface it is slowly released from rock or soil minerals, by weathering (rainfall and surface runoff), as phosphate ($P0_4^{3-}$). Phosphorus does not easily dissolve in water and is not readily leached; rather it precipitates out of solution and clings tightly to soil. Because of this very little phosphorus reaches groundwater, then to streams, rivers, and lakes. Since it is not plentiful it is not readily available to be taken up by plants (mineralization and assimilation). This scarcity makes it an important limiting factor for plant growth. Phosphorus may also be broken-down from organic forms (plant and animal tissue) to phosphate ($P0_4^{3-}$) by decomposer microbes.

Water → Earth's Crust → Living Organisms
Phosphorus Sinks: sedimentary and igneous rock, ocean sediments

The Role of Phosphorus

- Phosphorus is required in the form of phosphate ions (PO_4^{3-}) for nucleic acids, DNA, ATP, phospholipids in cell membranes, bones, teeth, and shells of animals.
- It is a limiting factor for plant growth (plants can't really grow without it)– typically, addition of phosphorus leads to increased productivity, especially for freshwater aquatic systems.
- Thus, phosphorus is an essential plant nutrient. Animals get phosphorus by eating plants or other animals.
- As such, phosphorus is a crucial ingredient in artificial fertilizers. A readily available commercial form is Monoammonium phosphate (MAP): $NH_4H_2PO_4$.

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Human Interventions in the Phosphorus Cycle:

- **Mining:** Mining of phosphate for fertilizers and soap results in habitat loss and disrupts to ecosystems.
- **Destruction of forest, grasslands, and wetlands:** Removal of phosphorus from ecosystems by clearing of forests, and cutting down of vegetation in general, disrupts ecosystems as most of phosphorus is taken up in biomass.
- **Agriculture:** Excessive phosphate runoff from fertilizers and livestock waste (manure is rich in nitrogen and phosphorus), throughout large watersheds, adds excess phosphorus to downstream aquatic systems. This leads to *eutrophication* in aquatic ecosystems such as the Gulf of Mexico or Chesapeake Bay, for example. Nitrogen and phosphorus stimulate growth of algae causing massive algal blooms. When the algae die, aerobic decomposers break them down, which depletes the water of oxygen, causing dead-zones or massive die-offs of aquatic organisms.
- **Cleaning Detergents:** Although phosphates have generally been eliminated from dishwashing and laundry detergents in the U.S. and the European Union, they have not been completely eliminated globally. Phosphates from detergents are discharged from washing machines and eventually make their way into rivers and streams. This results in *eutrophication* and dead zones in aquatic ecosystems.

SULFUR CYCLE

The sulfur cycle transports sulfur throughout the biosphere, hydrosphere, lithosphere and atmosphere.
In absence of human disturbance the exchange of sulfur throughout Earth's systems takes place in a balanced and steady state.

- Sulfur is found in the atmosphere, organisms, ocean sediments, soil, rocks, and fossil fuels.
- Sulfur is a component of amino acids and proteins and plays a role in allowing some organisms to use oxygen.
- Sulfur is stored in underground rocks, minerals and soil.
- Sulfur is released into water and soil over time as rocks weather.
- Producers absorb sulfur through their roots in the form of sulfate ions (SO_4^{2-}).
- Plants take up sulfur as sulfate-cycles through food webs.
- H_2S (hydrogen sulfide), a toxic gas, dissolves into water of swamps and bogs through the anaerobic decomposition of organic matter.
- H_2S (hydrogen sulfide) and SO_2 (sulfur dioxide) is released into the atmosphere from natural processes such as volcanoes and other geothermal activity:
  - $H_2S + O_2 \rightarrow SO_2$
  - $SO_2 + O_2 \rightarrow SO_3$ (sulfur trioxide) or
  - $SO_2 + H_2O \rightarrow H_2SO_4$ (sulfuric acid)
  - This is naturally occurring acid rain. The sulfur is then returned to water and soil and taken up by plants.

Human intervention of the Sulfur Cycle:

- Coal contains sulfur and when burned, releases SO_2. Sulfur then reacts with atmospheric oxygen molecules to form sulfur trioxide ($SO_2 + O_2 \rightarrow SO_3$), and then sulfur trioxide reacts with water vapor (clouds and rain droplets) to form sulfuric acid, which is acid rain ($SO_3 + H_2O \rightarrow H_2SO_4$).
  - Acid rain slowly deteriorates plant tissue, inhibits photosynthesis, and weakens plants ability to withstand extremes such as heat, cold, and wind.
  - Also, as acid rain infiltrates the soil it leaches toxic heavy metals (that were immobilized in chemical bonds in the soil) such as arsenic, lead, and mercury. This leaching mobilizes them, freeing them up to be taken up by plants and animals. Here, through bioaccumulation through food chains, their toxicity will disrupt ecosystem function.
- Mining metals releases sulfur compounds into the environment. Copper, cold, and molybdenum metals are all found *sulfide ore deposits*. So, processing sulfide ore and extracting any of these useful metals releases sulfur compounds to the environment. Rainwater and surface runoff create acid mine drainage, which disrupts aquatic and terrestrial ecosystems; both through making systems acidic and by releasing heavy metals as described above for acid rain from burning coal.
- Mining coal also causes acid mine drainage.

Biogeochemical Cycles

WATER CYCLE