Lecture 1: Environmental Chemistry, Global Carbon Cycle

- A major part of environmental and forensic chemistry is analytical.
  - → In environmental chemistry, we try to find how natural processes work and then find out how humans have impacted on such processes.
  - → Includes atmospheric chemistry, aqueous chemistry, solid-state chemistry and surface chemistry.
  - → Environmental chemistry is also related to green chemistry - the study of chemical processes to minimise negative environmental impacts.
- Plant photosynthesis is what converts atmospheric CO_2 into higher-energy biomass, represented by $\{CH_2O\}$.

$$CO_2 + H_2O \xrightarrow{hv} \{CH_2O\} + O_2$$

- The opposite of photosynthesis is respiration - it breaks down biomass and releases energy.
  - → It can occur in the presence of oxygen (aerobic respiration) or absence of oxygen (anaerobic respiration)

$$Aerobic: \{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$$
$$Anaerobic: C_6H_{12}O_6 + 3NO_3^- + 3H_2O \rightarrow 6HCO_3^- + 3NH_4^+$$
$$Anaerobic: C_6H_{12}O_6 + 3SO_4^{2-} \rightarrow 6HCO_3^- + 3HS^- + 3H^+$$

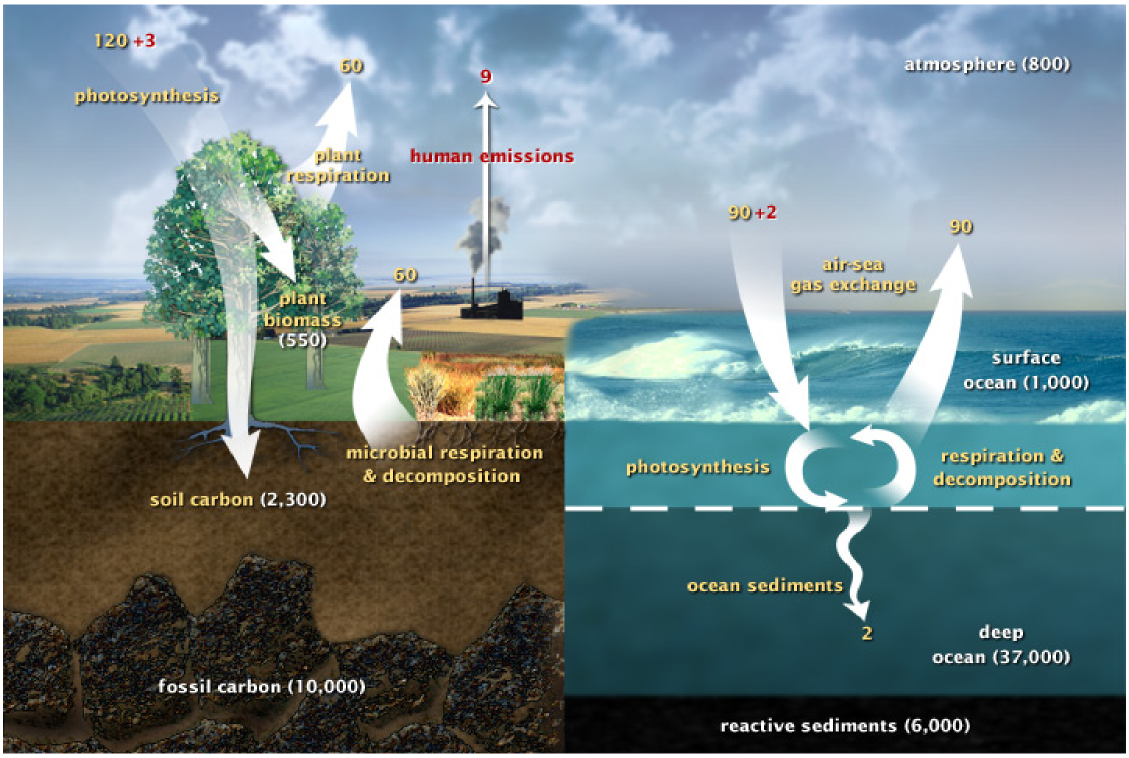
- For this lecture, you need to be able to recall oxidation numbers (covered in first year).
  - → It shows the distribution of electrons within molecules or ions.
  - → Elements have an oxidation number of zero.
    - <u>Example</u>: He, N_2, H_2, O_2 etc.
  - → Effectively shows the charge of an atom.
    - <u>Example</u>: O^{2-} (-2), Cl^- (-1) etc.
  - → Electrons in molecules and polyatomic ions are assigned to the more electronegative atom (way of representing things - doesn't show the true position of electrons).
- Cycles of matter usually refer to elemental cycles such as the nitrogen cycle and the carbon cycle.
  - → Often refer to interchange of matter between reservoirs such as between the geosphere, hydrosphere, atmosphere and biosphere.
  - → Organisms are a part of the biogeochemical cycles.
  - → Ultimately powered by solar energy.
- The carbon cycle is important for biological systems (living stuff).
  - → Carbonates also play in important role in water systems, often acting as a buffer.
  - → The atmosphere contains carbon dioxide (7.5×10^{15} kg C).
- Carbon is regularly changed from biotic to abiotic forms.
  - → Biotic forms include those with an oxidation state of 4 such as $C_6H_{12}O_6$.

$$6CO_{2(g)} + 6H_2O_{(l)} \xrightarrow{hv} C_6H_{12}O_{6(s)} + 6O_{2(g)}$$
$$6CO_2 + 24e^- + 24H^+ \rightleftharpoons C_6H_{12}O_6 + 6H_2O$$
$$\mathrm{hv} + 12\mathrm{H_2O} \rightleftharpoons 6\mathrm{O_2} + 24\mathrm{e^-} + 24\mathrm{H^+}$$

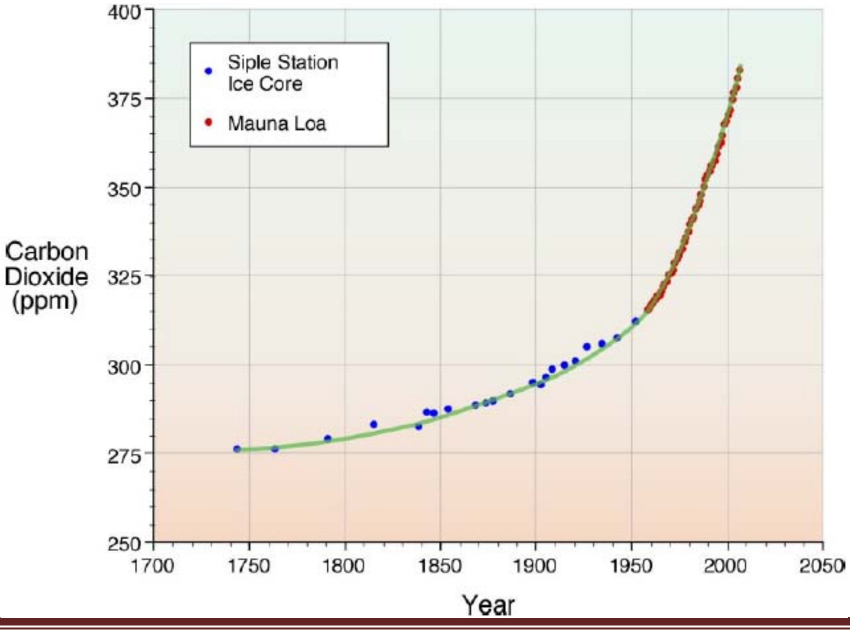
  - → Abiotic forms include those with an oxidation state of 0 such as CO_2.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} + energy$$
$$C_6H_{12}O_6 + 6H_2O \rightleftharpoons 6CO_2 + 24e^- + 24H^+$$

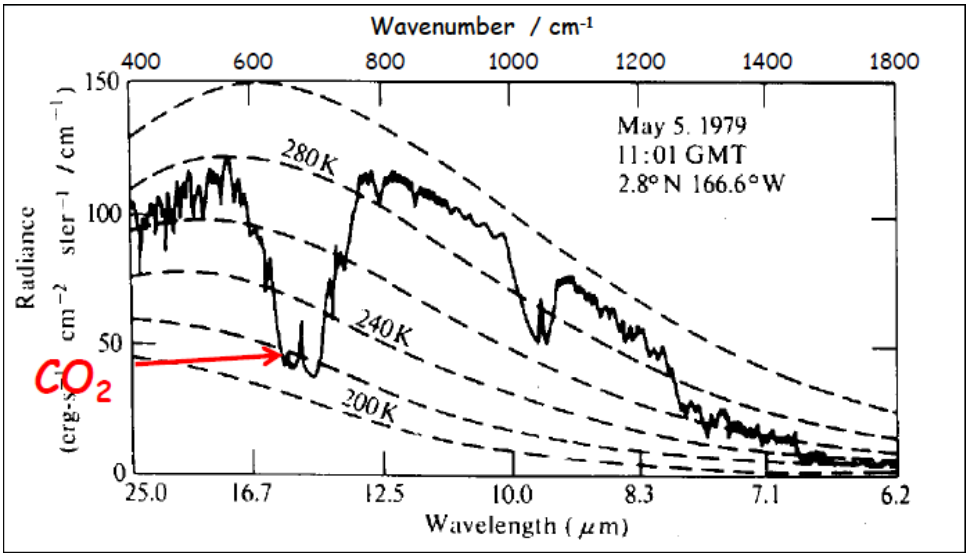
- There are two types of carbon cycles: fast and slow carbon cycles.
  - → The fast carbon cycle is measured in a lifespan - between 10^{15} and 10^{17} grams of carbon move through the fast carbon cycle each year.
  - → The slow carbon cycle is the cycle through a series of chemical reactions and tectonic activity, carbon takes 100-200 million years to move between rocks, soil, ocean and atmosphere in the slow carbon cycle. About 10^{13} and 10^{14} grams of carbon move through the slow carbon cycle every year.
    - Human emissions are around 10^{15} grams per year.



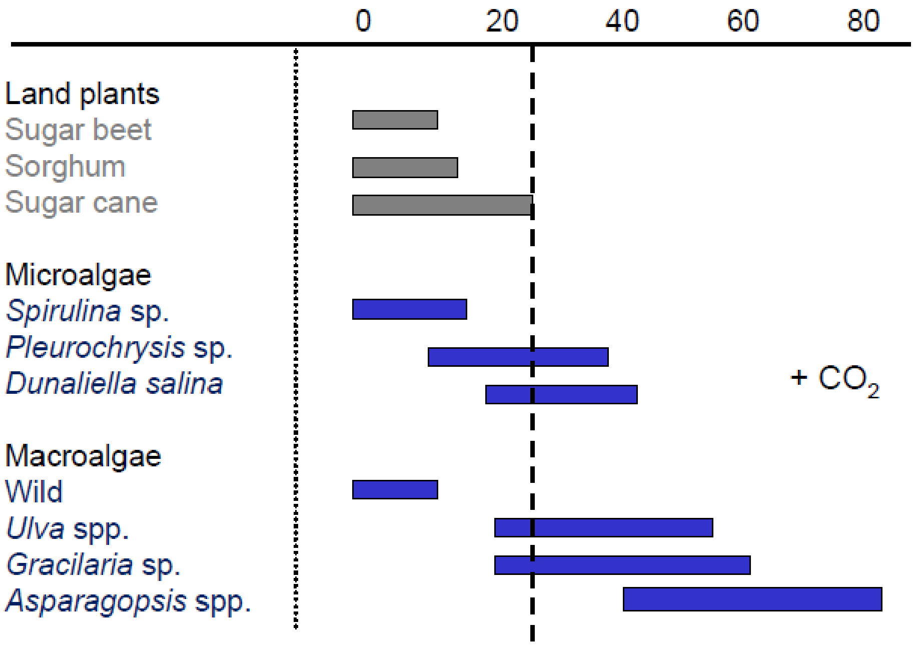
- The diagram above is of the fast carbon cycle and shows the movement of carbon between land, atmosphere, and oceans in billions of tons of carbon per year.
  - → Yellow numbers are natural fluxes, red are human contributions in billions of tons of carbon per year.
  - → White numbers are stored carbons.



- Carbon dioxide absorbs infrared radiation - the infrared spectrum of the Earth is below.
  - → More CO_2 means more infrared is absorbed.
  - → More CO_2 doesn't necessarily means more is absorbed - this is the case when all infrared is absorbed that CO_2 can absorb.



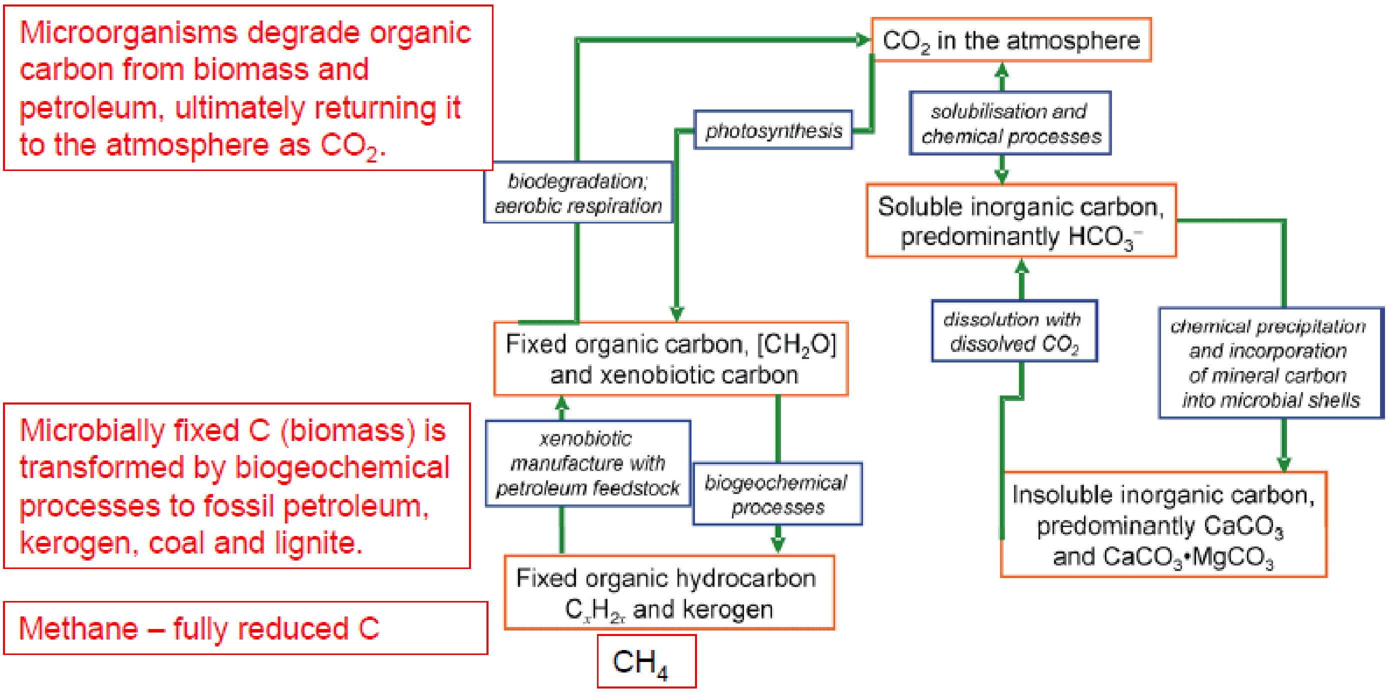
- Algae uses light energy to convert CO_2 and other nutrients (nitrates, phosphates etc) into biomass at or near the water surface.
  - → Excess of nutrients leads to eutrophication.
  - → Eutrophication is a result of excessive algal bloom and consumption of most or all dissolved oxygen in water, leaving anaerobic conditions in the water - this can also lead to production of toxins in the water from anaerobic respiration.
  - → Dead biomass can be degraded by several ways.
    - Near the surface, bacteria and oxygen lead to CO_2 production.
    - On land, fungi and bacteria produce waste products (organic and inorganic).
    - In deep waters, anaerobic bacterial degradation occurs.
- Algae is subject to research as a possible source of biofuels.
  - → Productivity is in g/m^2/day - mass is dry weight (dw).



- Fermentation are reactions where both the oxidising and reducing agents are organic.
  - → Example below.

$$2\{CH_2O\} \rightarrow CH_3COOH \rightarrow CH_4 + CO_2$$
$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

- Photosynthetic algae dominate as carbon fixing agents in aqueous environments - consumption of CO_2 to produce biomass makes water more alkaline which precipitates $CacO_3$.



Lecture 2: Nitrogen and Sulfur Cycle

- Nitrogen is an extremely important component of organic matter, particularly $-NH_2$ groups and as a nutrient in the form of nitrates.
  - → Like other cycles, nitrogen is also exchanged between various reservoirs.
    - Atmosphere: N_2, N_2O, NO, NO_2 etc.
    - Terrestrial: living organisms, organic material, ammonium salts/deposits, nitrate and nitrite ions.
    - Oceans: nitrates and nitrites.
- Nitrogen is abundant in the atmosphere as N_2 gas (78%) but it is very stable so nitrogen from the atmosphere needs to be fixated.
  - → Nitrates are present in soil and groundwater and nitrogen containing biomolecules.
  - → As nitrogen in the air is very stable, nitrogen availability depends on conversion to more chemically active forms, such processes are known as nitrogen fixation.
  - → Generally, nitrogen fixation converts elemental nitrogen to ammonia.
    - Generally, plants to this through aerobic and anaerobic microorganisms such as bacteria and algae using the enzyme, nitrogenase.

$$\boxed{3\{CH_2O\} + 2N_2 + 3H_2O \rightarrow 3CO_2 + 4NH_3}$$

    - Nitrogenase exists in both free-living aerobic and anaerobic bacteria and symbiotic bacteria. Relatively few aquatic microorganisms can fix nitrogen.