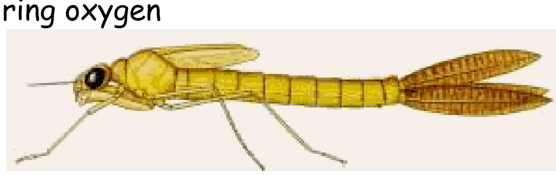
CHEMICAL COMPOSITION OF NATURAL WATERS

DISSOVLED GASES

Oxygen (and E_h)

Why important?

- product of photosynthesis
- needed for aerobic respiration - Much of an aquatic organisms energy budget is devoted to acquiring oxygen



- affects availability of nutrients

Given that:

- photosynthesis - *Who photosynthesizes in aquatic systems?*

carbon dioxide + water ---light---> organic carbon + oxygen + water

- aerobic respiration - *Who respires in aquatic systems?*

organic carbon + oxygen ---------> carbon dioxide + water + useable energy

What are the sources and sinks for oxygen in aquatic systems?

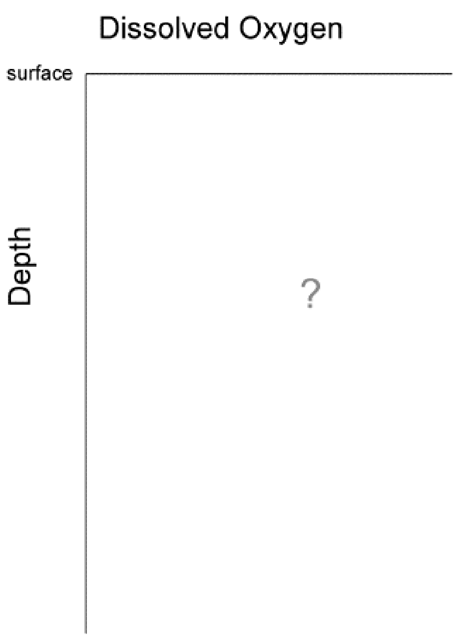
Because primary productivity strongly affects oxygen, changes in oxygen can be used to estimate productivity.
Because cellular respiration strongly affects oxygen, changes in oxygen can be used to estimate organic matter in water (biochemical oxygen demand or BOD).

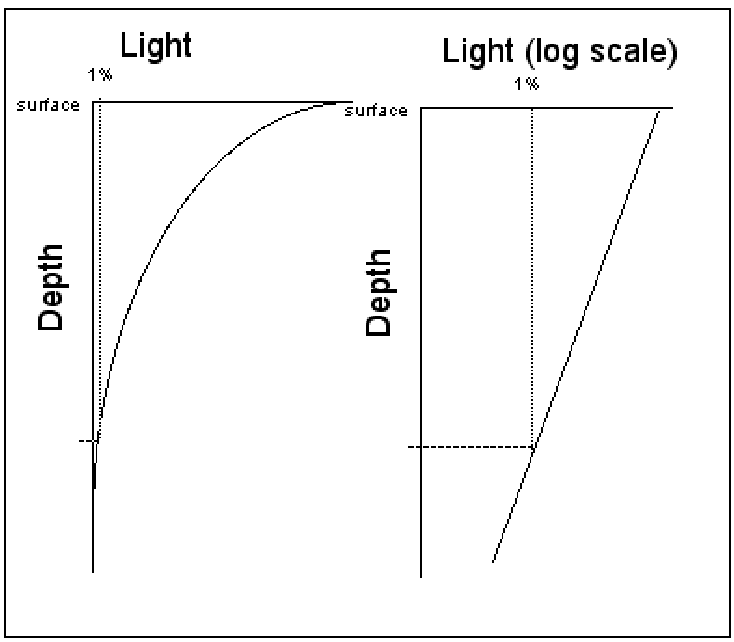
What are other possible sources and sinks for oxygen?

Temperature affects concentration of oxygen

- solubility (measurements of dissolved oxygen (D.O.) can be expressed in **mg/l** or **percent saturation**).
- diffusion
- metabolism

What will oxygen vertical profiles look like? Why? What factors will affect profile?



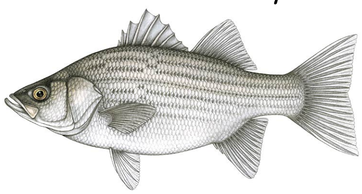


Will all lakes have similar profiles?
All lakes, being at the bottom of their drainage basin, will collect nutrients and sediments over time.
As more nutrients accumulate year after year, how should oxygen profiles change?

EUTROPHICATION

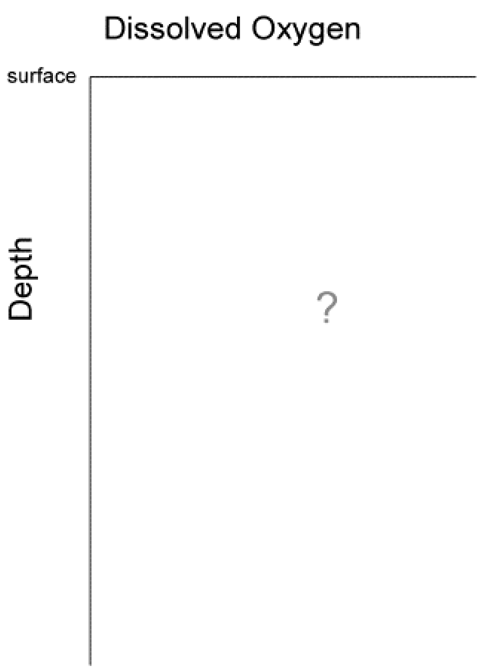
Oligotrophic ---- Mesotrophic ---- Eutrophic

What are the consequences of this for organisms with a particular temperature preference?



How will oxygen change with distance from the sediment-water interface in sediments of lakes where more than 1% of surface light reaches the bottom?

How should oxygen profiles change over seasons?



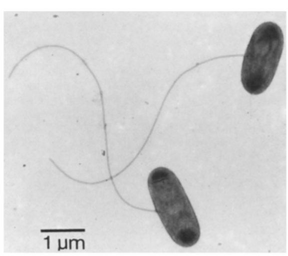
Tolerances of organisms:

- General critical level - 4 mg/l for 24 h to maintain a diverse assemblage

- <2 mg/l - most organism die or become dormant

- 1-2 mg/l - organism must be physiologically adapted (modified gills, specialized blood pigments...)

- O mg/l - certain bacteria that utilize oxidized compounds as an electron acceptor



E_h (Redox potential)

Redox potential (also known as reduction potential, oxidation / reduction potential, ORP, pE, ε, or E_h) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. It is a measure of how reducing an environment is.

Measuring this transfer of electrons between chemical species as the **reduction potential** is analogous to measuring the transfer of hydrogen ions between chemical species as the pH .

Redox potential determine which metabolic processes can occur for cellular respiration (i.e. which molecules will be used as the electron acceptor) and therefore which types of organisms can make a living at a given depth in the water column and sediment. As an environment becomes anoxic, electron activity is high, E_h values become negative, and the metabolic process used to extract energy from organic matter through cellular respiration ($(CH_2O)_n$ --> CO_2) shifts:

$(CH_2O)_n$ -- --> CO_2

(organic

carbon)

e^-

oxic environment ($+E_h$)	O_2 -> H_2O	animals, plants, protists, and aerobic bacteria
anoxic	NO_3 -> N_2	certain anaerobic bacteria
even more anoxic	$Fe^{+3}PO_4$ -> Fe^{+2} + PO_4	certain anaerobic bacteria
strongly anoxic ($-E_h$)	SO_4^{-2} -> H_2S	certain anaerobic bacteria

(http://www.ecasatoolbox.org.uk/the-toolbox/eia-country/book-of-protocols/sediment-redox-potential-eh)

Redox potential (Eh) is measured by the voltage (electric potential) difference using an electrode that is inserted down a sediment core often to detect the depth at which redox values change abruptly (normally on the scale of millimeters to centimeters).

Carbon Dioxide (and pH)

Why is CO_2 important?

- Direct source of carbon for the production organic matter (biologically manufactured molecules)
- Acts as a buffer
- Part of global carbon cycle

- ([killer lakes])

__What are the sources of CO_2?__

- Respiration
- Diffusion (extremely soluble)
- Dissolution of limestone rock

__What are the sinks for CO_2?__

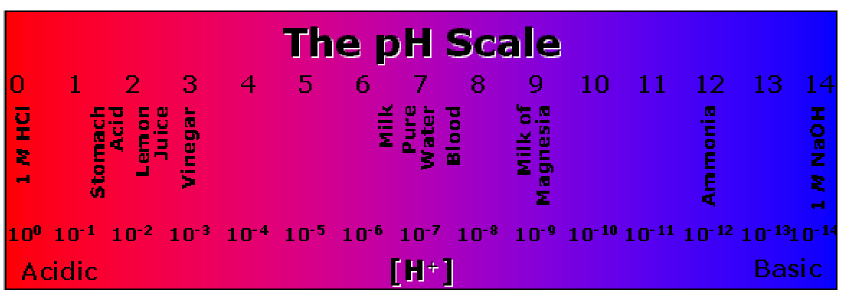
- Photosynthesis
- Diffusion
- Precipitation of insoluble $CaCO_3$

Most carbon in aquatic systems occurs as equilibrium products of carbonic acid, hence:

CO_2 affects pH and pH affects CO_2

[pH] is a measure of hydrogen ion activity.

pH = -log[H+]



Disassociation of Carbon dioxide in water:

$$H_2O + CO_2 \longleftrightarrow (H_2CO_3) \longleftrightarrow HCO_3^{-1} + H^+ \longleftrightarrow CO_3^{-2} + H^+$$

carbonic acid *bicarbonate* *carbonate*

Think of chemical equilibrium as a balance; if you dump something on one side, the equilibrium will shift to the other to maintain balance.

*What happens if you add **CO_2**?*

*What happens if you add **acid**?*

However **alkalinity** of water in aquatic systems will affect this and is affected by it.

Alkalinity is the capacity of water to except protons (H+) ("the buffer capacity" or "acid neutralizing capacity")
(**Hardness** is the concentration of polyvalent ions, principally calcium and magnesium, which tend to precipitate soap, and so is closely related to alkalinity where alkalinity is due to calcium carbonate, but not where it is due mainly to sodium carbonate or calcium sulfate)

The major source of alkalinity in freshwaters is $CaCO_3$
$Ca(HCO_3)_2$ <---> $CaCO_3$ (marl) + H_2O + CO_2

HCO_3^{-1} and CO_3^{-2} in H_2O tend to disassociate releasing OH^-, thus buffering water (resistance to change in pH)

Waters of low alkalinity (<20 mg/l) are poorly buffered, and the removal of carbon dioxide (CO_2) during photosynthesis results in rapidly rising pH.

<u>Bottom line:</u>

- waters are going to vary in their ability to resist change in pH due to hardness of water

- CO_2 (and all dissolved inorganic carbon) is most easily measured from calculations based on measures of pH (probe) and alkalinity (acid titration)

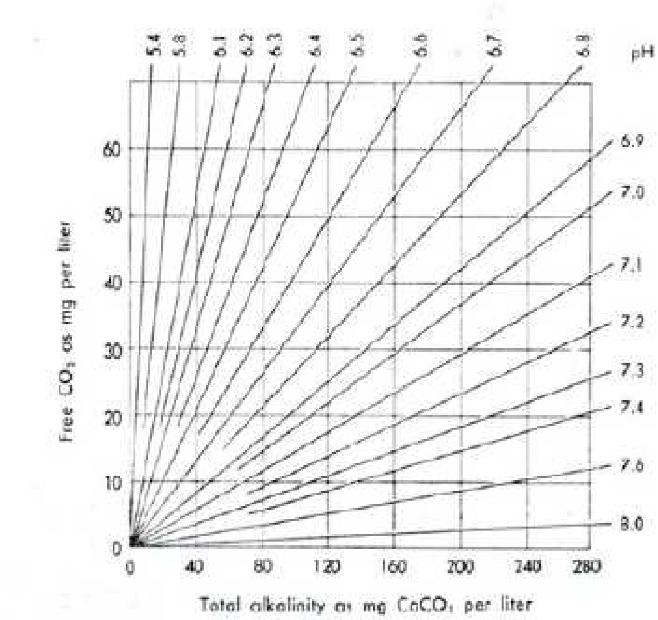
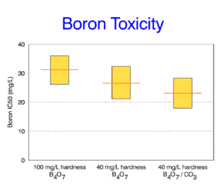


Fig. 12. Moore's nomograph for determination of free carbon dioxide concentration from pH and total alkalinity data.

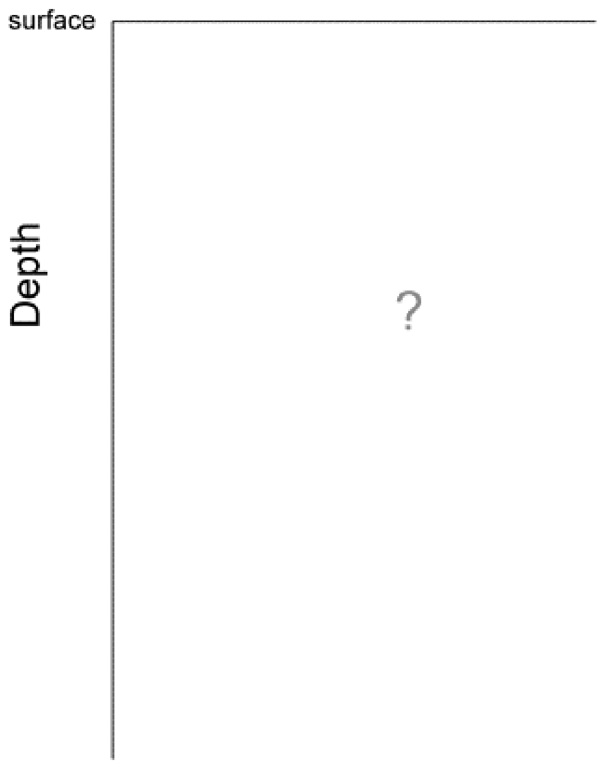
Assuming alkalinity does not vary greatly within a system, lower pH is a rough indication of CO_2 concentration.

(Hardness also influences toxicity of many substances)



http://www.pwrc.usgs.gov/resshow/wingr1rs/wingr1rs.htm

*What will **pH** depth profiles look like in Lake Allatoona during late summer?*



NUTRIENTS

Lieberg's Law of the Minimum: at any given instant, any metabolic process is limited by only one factor at a time; i.e. the nutrient in shortest supply **relative to demand**.

Carbon

Rarely limiting because carbon dioxide is highly soluble and diffuses easily from the atmosphere where is relatively abundant.

Phosphorus

Often limiting because:

- no gaseous phase, thus no nitrogen fixing equivalent

- often geochemically scarce
- binds with soils in watershed

Photosynthetic organisms require a N:P of ~7:1 (by weight), ~16:1 (by element)

Usually low 20 ug/l wordwide average. 200-700 very high

Why is phosphorus a needed element?

What are sources?

- Natural - phosphate bearing rock - (apatite)
- Human - fertilizers, detergents, sewage, soil erosion

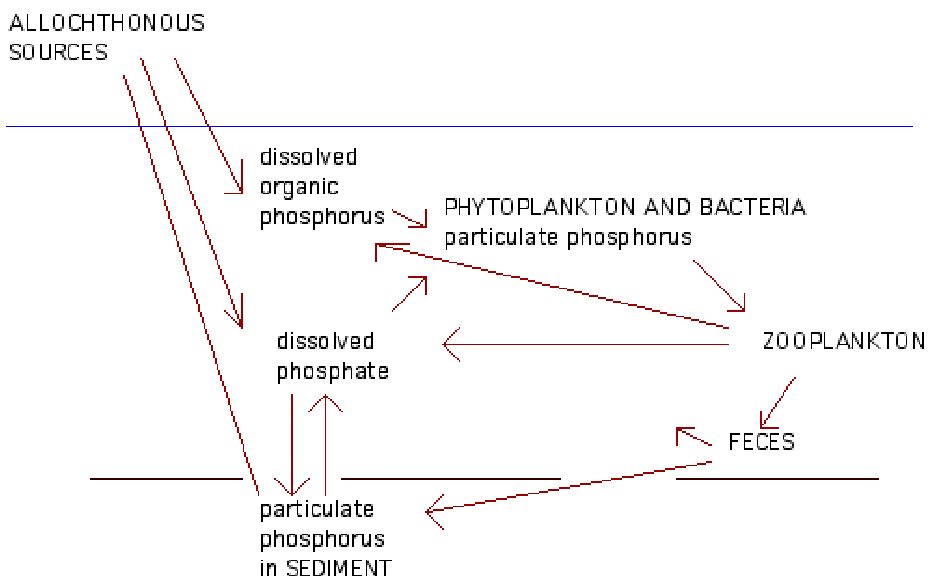
Forms:

- TOTAL SOLUABLE PHOSPHORUS
    - Dissolved Phosphate (orthophosphate PO_4^{-3}, and ions of phosphoric acid) - often estimated as "soluable reactive phosphorus"
    - (Inorganic polyphosphates)
    - Dissolved organic phosphorus
- TOTAL PARTICULATE PHOSPHORUS most phosphorus in freshwater tied up and **not immediately available** (but potentially available).
    - Phosphorous in living matter (bacteria, plant, and animal)
    - Phosphorous adsorbed by clays and other minerals

"Total Phosphorus" is a measure of both soluble and particulate phosphorus"

What forms of phosphorus are available to phytoplankton?

Some Major Pathways of Phosphorus in Aquatic Systems:

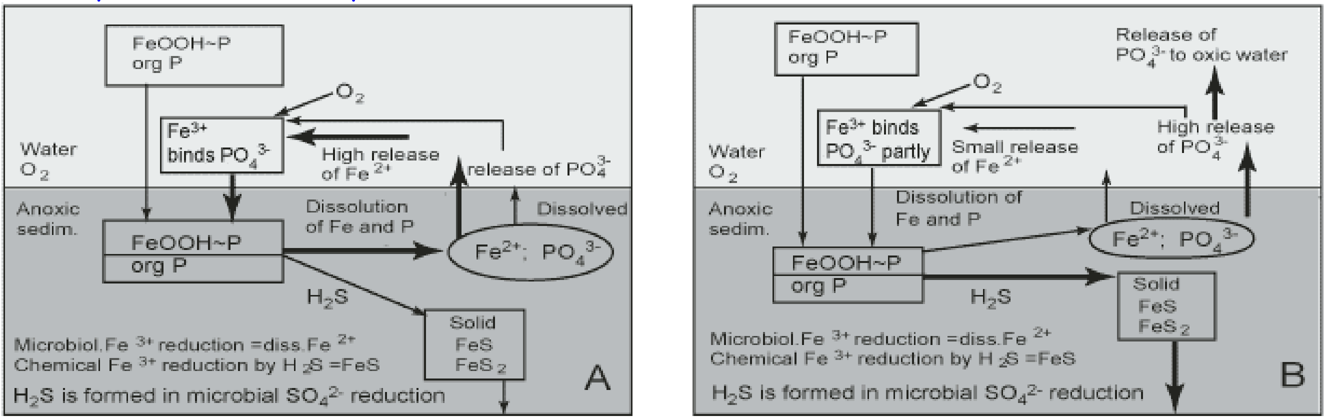


Availability of phosphorus in aquatic systems:
Depends on dissolved oxygen!!!

- Phosphate in the presence of iron and oxygen will precipitate (i.e. insoluble) as **iron phosphate** ($FePO_4$)
- Other more complex processes , such adsorption to **clays**, also depends on oxygen.

The rate of these processes are sensitive pH, Eh, dissolved minerals, and silt properties. But essentially, phosphate in the presence of **iron** and **oxygen** will **precipitate** out as **iron (ferric) phosphate.**
In anoxic environments, phosphate becomes soluble and therefore available if transported to the photic zone.

[These processes are complex]



Where sulfur is plentiful, phosphate is soluble even in the presence of oxygen (B).

- The bottom line though is that free oxygen tends to make nutrients insoluble. Anoxic sediment can release phosphorus (as phosphate) up to 1000X faster than for oxic sediment.

To what degree is phosphorus available in lake in which free oxygen reaches to the bottom of the lake? (Under what conditions does this occur?)

oxidized microlayer:

Why is the sediment anoxic below the oxidized microlayer?

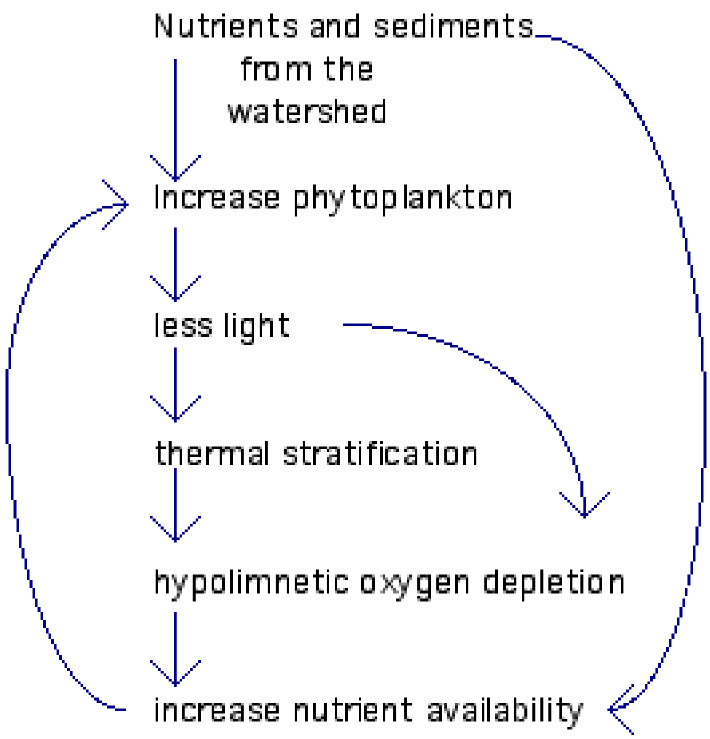
To what degree is phosphorus available in lake in which free oxygen does not reach to the bottom of the lake? (Under what conditions does this occur?)

anoxic sediments:

^P

What time of year should phosphorus be most available to phytoplankton in the photic zone?

How does the relationship between oxygen concentration and phosphorus availability affect the rate of eutrophication?



Will retention time of water in the lake affect the relationship between phosphorus loading and eutrophication?

Nitrogen

Sources:

- nitrogen fixation
- watershed

Sinks:

- Denitrification
- Outflow
- Sedimentation

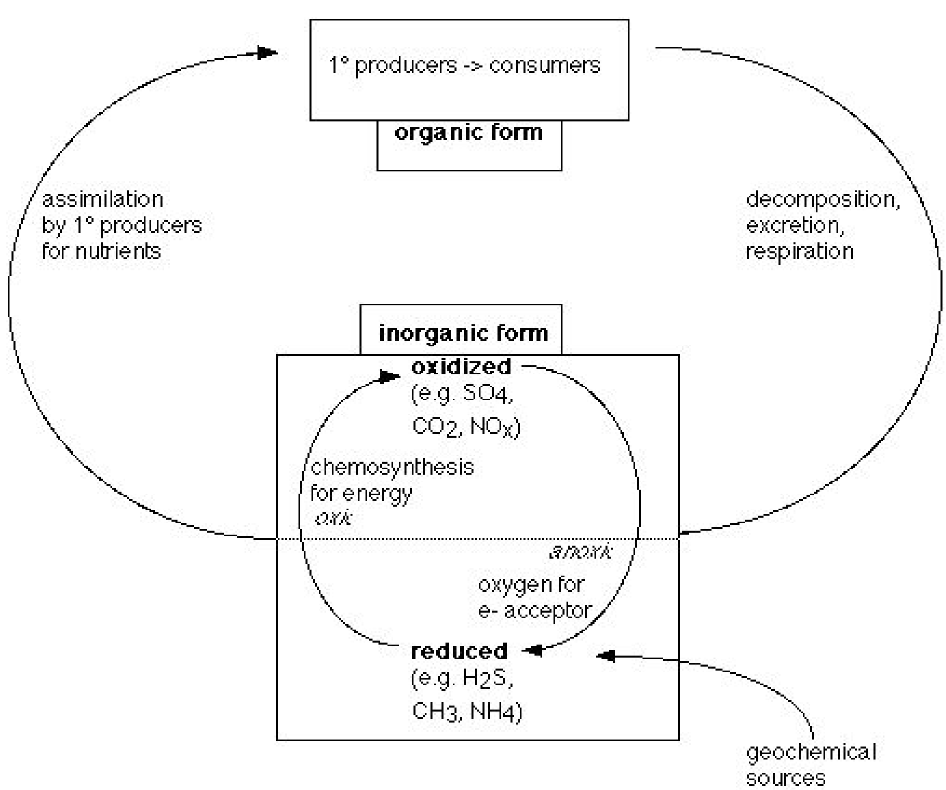
Tends to be limiting in ocean waters.

<u>Forms:</u>

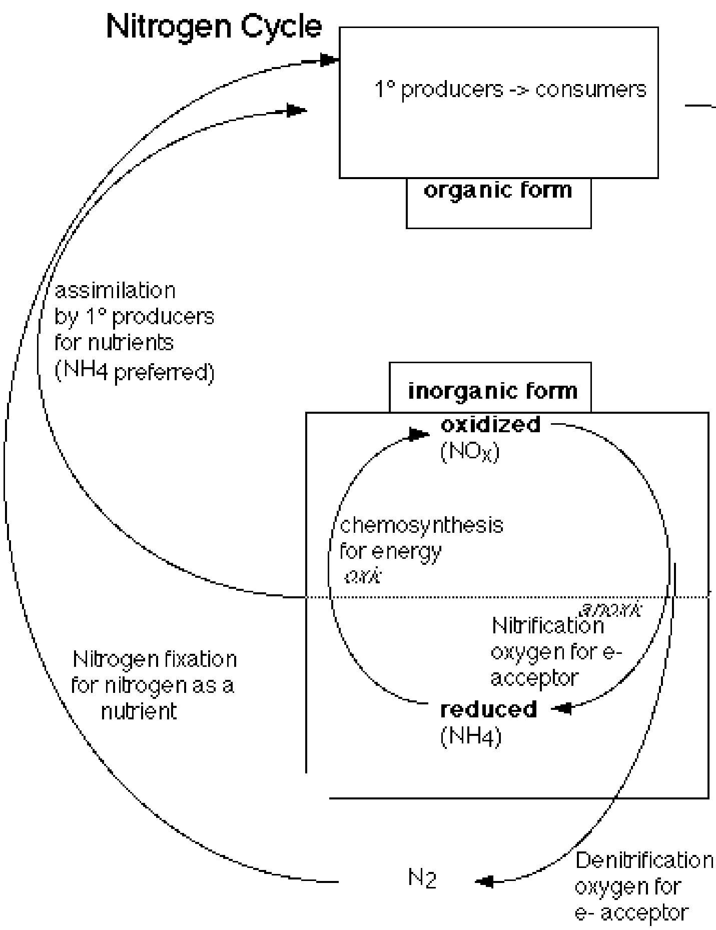
- Inorganic
  - Nitrogen gas N_2
  - Nitrate NO_3^-
  - Nitrite NO_2^-
  - Ammonium NH_4^+
- Organic forms - In freshwaters, typically 50% in organic form; larger forms less soluable

<u>Some Major Pathways of Nitrogen in Aquatic Systems:</u>

Generalized Nutrient Cycle



Depends on the **redox potential** of the environment



Vertical distribution of nitrogen in a stratified lake?

~~~~~~***lake surface***~~~~~~

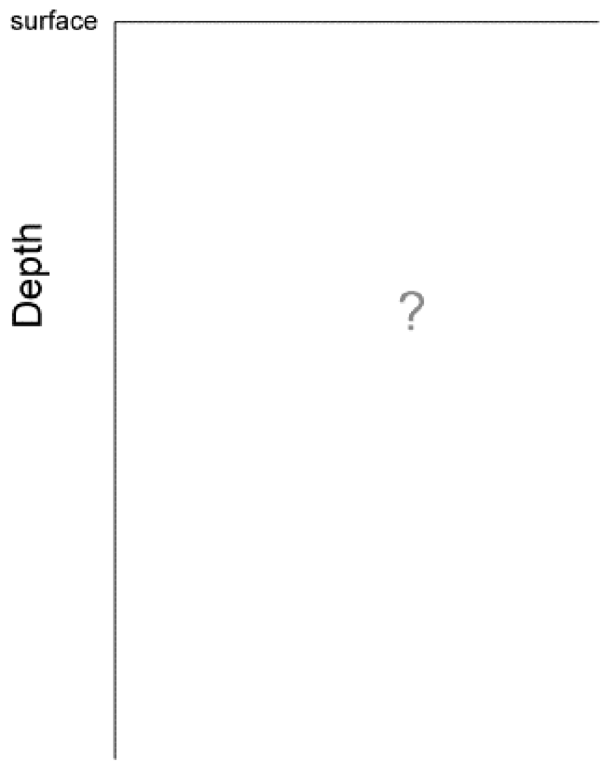
N_2-->Assim N (AssimN-->NH_4^+) NH_4^+ (NO_x) --> Assim N

-- NH_4^+--->NO_3 ---------------***metalimnion***-------

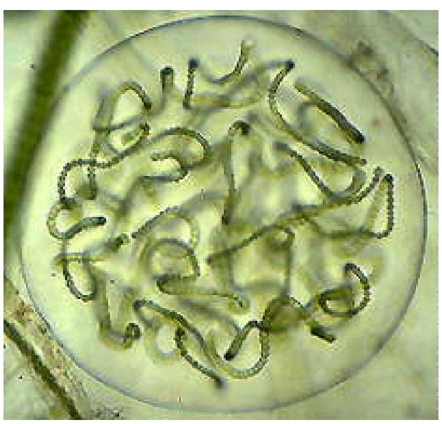
(N_2-->Assim N) AssimN-->NH_4^+

NO_3-->N_2 NO_3-->NH_4^+

____***sediment***_______
~~~~~~



Only a few genera of cynobacteria are capable of N-fixation in freshwaters (e.g. *Nostoc* & *Anabaena*)



Other nutrients

- Magnesium
- Calcium
- Silica
- Sulfur
- Other trace nutrients