Water Chemistry -- Dissolved Gases -- Oxygen

I. Properties of dissolved gases

    A. Solubility -- How much gas will dissolve in water?

        1. Pressure -- as pressure increases, solubility increases

        2. Temperature -- as temperature increases, solubility decreases

        3. Salts -- as TDS increase, solubility decreases exponentially

        4. Concentration -- Henry's law

    At constant temp. the amount of gas absorbed by a given volume of liquid is proportional to the pressure in atmospheres that the gas exerts

        [gas] = K_H ρ_{gas}

          K_H (Henry's constant) is a solubility factor, varying from gas to gas

 O_2 in atmosphere ~20.3% = 0.203 atm

        K_H @ 20oC = 1.39 $\dfrac{mmol\,O_2}{kg\,H_2O \times atm}$ (for pure water)

          amount of O_2 that will dissolve in water at 20^oC

$$[O_2] = (0.203\,atm)\left(\frac{1.39\,mmol\,O_2}{kg \times atm}\right) = 0.282\,\frac{mmol\,O_2}{kg} = 9.03\,\frac{mg\,O_2}{kg}$$

    B. Oxygen

        1. Used in respiration

        2. Important in chemical reactions

        3. Oxygen dynamics:

          (a) respiration uses oxygen

          (b) bacterial decomposition uses oxygen

          (c) photosynthesis makes oxygen

$$(\quad 6CO_2 + 6H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2 \quad)$$
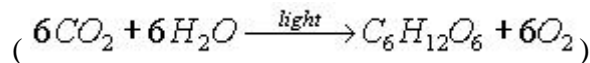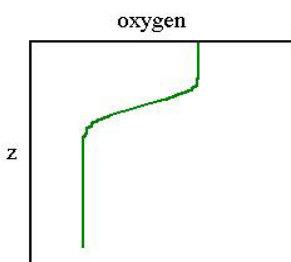
          (d) atmosphere contains a large reserve of oxygen

    C. Carbon dioxide -- about 200 X more soluble than oxygen.

     - Follows the 100% saturation curve.

     - Organism effects:

        i. Respiration

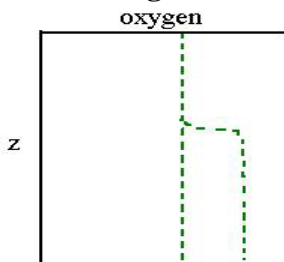   ii. Photosynthesis

II. Oxygen curves

    A. **Clinograde**

- Hypolimnetic oxygen depletion
- Respiration and decomposition increase as lake productivity increases

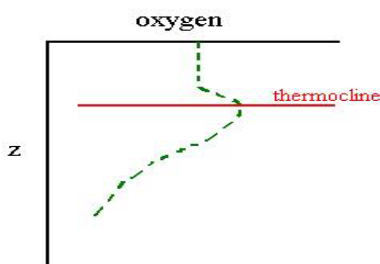B. **Orthograde**

- Oligotrophic lakes -- low production, little respiration
- Also higher oxygen solubility due to lower temperature
- If two lakes have the same productivity on an areal basis, one may be clinograde and one orthograde based on basin shape


C. **Positive heterograde**

- due to photosynthesis at the thermocline
- light penetration to metalimnion where there is slow mixing so that any oxygen produced stays around and builds up; some input of nutrients from hypolimnion increases growth from hypolimnion increases growth
- '**deep chlorophyll layer**' - depends on water transparency
- could also be due to input of oxygen-rich river water that is denser than surface water

D. **Negative heterograde**
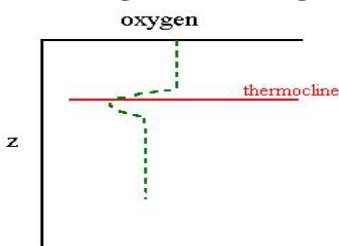
1. can be due to respiration of algae at night, or respiration of dense layer of zooplankton
2. density gradient slows the rain of detritus ('marine/lake snow') around thermocline, more respiration of organic matter   (could also be effluent output there)

3. morphology -- bench; more sediment area per water volume at a given depth so lots of respiration at that depth

E. Diel cycle of epilimnetic oxygen content
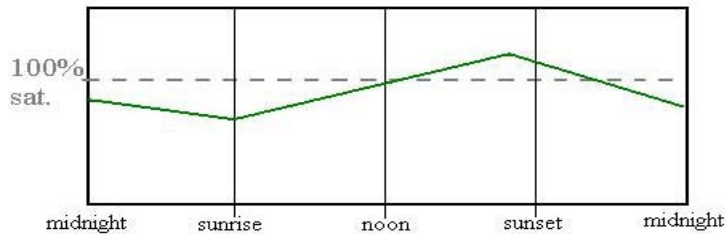
F. **Oxygen deficit** -- how much oxygen is used up from decomposition of material falling from the productive <u>trophogenic zone</u> to the <u>tropholytic zone</u>

    amount of oxygen consumed by decomposition in the hypolimnion gives an estimate of the productivity of the lake

Inorganic Carbon and pH

I. Controls on CO_2
   A. Photosynthesis
   B. Respiration
   C. Atmosphere
   D. Geologic inputs
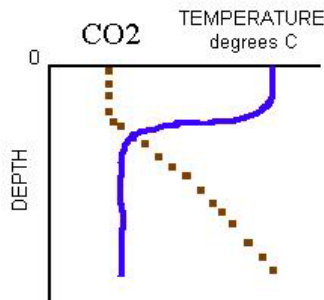
II. Forms of carbon --
  A. Forms and examples of each

	PARTICULATE	**DISSOLVED**

ORGANIC	Living organisms
	Dead organic material
		Soluble organics:
		   DOC (dissolved organic carbon)
		   Amino acids
		   Sugars

INORGANIC	$CaCO_3$
	Carbonates of Mg, K, Na, etc. (minerals)
		DIC (dissolved inorganic carbon)
		   CO_2
		   H_2CO_3
		   HCO_3^-
		   CO_3^{2-}

  B. Carbon cycle – how C moves between these boxes

III. Dissolved inorganic carbon, DIC
    Distribution of DIC as a function of pH – See figure 11-1, Wetzel

IV. pH
  A. Reactions and definitions
$$H_2O \leftrightarrow H^+ + OH^-$$

3

$$K_{water} = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14}$$

(dissociation product constant)

by definition concentration of water = 1

$$pH = -\log_{10}[H^+]$$

if [H+] = 10^{-7} molar, pH = 7

B. Common pH values
   1. If distilled water reacts with CO_2, get H_2CO_3 and pH ~5.6
   2. Rain with pH less than 5.6 is said to be 'acid rain'
   3. Most lakes range in pH from 6-9
   4. Low pH lakes
      a. pH < 2; usually due to volcanically produced H_2SO_4 or mine wastes
      b. pH 3.3-4.5 -- Sphagnum bogs – exchange of cations for H^+ by the plants
      c. Acid deposition
   5. High pH in lakes
      a. Carbonates present – Ca, Mg, Na or K (saline lakes, pH>8)
      b. High rates of photosynthesis (decrease CO_2, increase pH)

V. Carbonate buffering system

   A. Reactions
      1. Hydration reaction $CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3$

$$[CO_2]_{aq}$$

      2. dissociation reaction $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
      3. dissociation reaction $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$
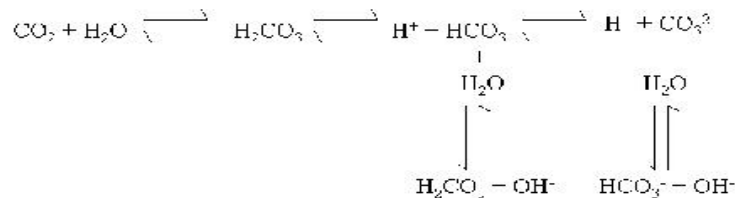
   B. Solving equations
      1. Basic principles
         (a) What is distribution of C species?
         (b) What happens when one or more species is changed – when the system is perturbed?
         (c) If we know any 2 quantities, then we can determine the others
      2. System of equations

         a. K_w
         $$K_{water} = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14}$$

         b. K_1
         $$\frac{[H^+][HCO_3^-]}{[CO_2][H_2O]} = 10^{-6.3}$$
         Do not put water in the denominator – is 1

         c. K_2
         $$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

d. $K_{sp}(CaCO_3)$

$$K_{sp(CaCO_3)} = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]} = 10^{-8.4}$$

solids also are 1

VI. Alkalinity

A. Definition = measure of the buffering capacity of the water; capacity of water to neutralize an acid

Sum of the anions of weak acids

$$[ALK]_{total} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + borate + silicate...$$

In practice for most lakes: $[ALK]_{total} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$
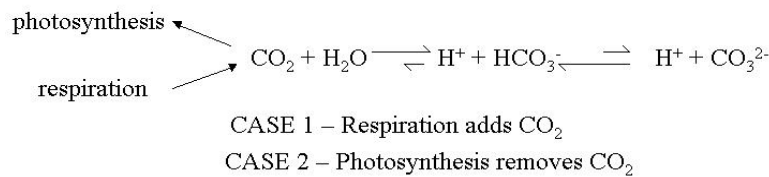
B. Changes in and control of alkalinity

CLOSED SYSTEMS – ALKALINITY IS CONSERVED

Changes in and control of alkalinity

The important reactions are respiration and photosynthesis –

in these two reactions (which add and subtract CO_2),
alkalinity is conserved, it neither increases nor decreases

photosynthesis

respiration

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

CASE 1 – Respiration adds CO_2
CASE 2 – Photosynthesis removes CO_2

1. CASE 1
   a. respiration adds CO_2
      Remember, $[HCO_3^-] + 2[CO_3^{2-}]$ = constant

2. CASE 2 -- Photosynthesis removes CO_2
      Opposite of CO_2 addition case

Open systems
alkalinity not necessarily conserved

Respiration and photosynthesis in the presence of $CaCO_3$

a. Respiration $\longrightarrow$ CO_2 $\longrightarrow$ HCO_3^-

$CaCO_{3(s)}$ $\longrightarrow$ CO_3^{2-}

Calcium carbonate dissolves
and causes an increase in CO_3^{2-},
thus increasing alkalinity

b. Photosynthesis $\longleftarrow$ CO_2 $\longleftarrow$ HCO_3^-

$CaCO_{3(s)}$ $\longleftarrow$ CO_3^{2-}

Precipitate calcium carbonate
and decrease alkalinity;
Marl; whitings.

5
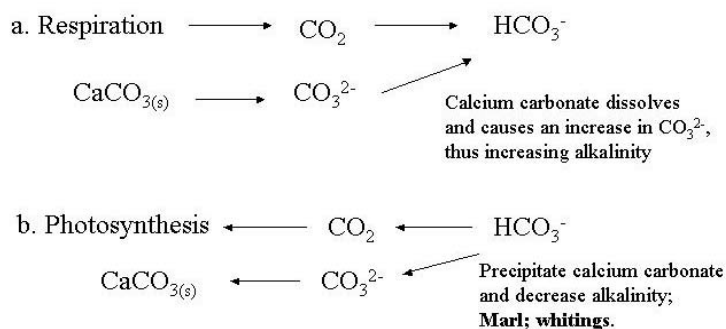
4. Buffering aspects – What happens when acid or bases are added to the system?

buffering aspects

Add acid – consume alkalinity

←

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$+ \qquad\qquad +$$

$$H_2O \qquad\qquad H_2O$$

$$\Updownarrow \qquad\qquad \Updownarrow$$

$$H_2CO_3 + OH^- \qquad HCO_3^- + OH^-$$
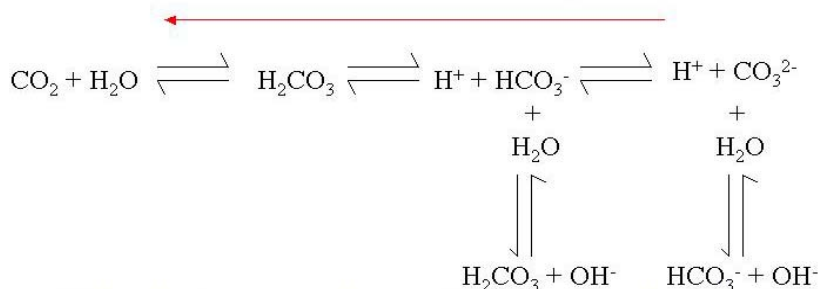
- pH doesn't change as much as would expect due to this buffering
- Can measure alkalinity as the equivalents of acid required to
   convert all CO_3^{2-} and HCO_3^- to CO_2

1. add acid – consume alkalinity
2. add base – increase alkalinity and increase pH
3. carbonate system prevents pH from changing as much as expected from amount of acid or base added.

VII. Flux to atmosphere (atmospheric controls)
    A. boundary layer model

Flux of CO_2 to the atmosphere

If water is supersaturated with CO_2 it will escape to the atmosphere

ATMOSPHERE

boundary layer   [CO2]eq Henry's constant
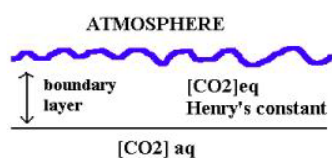
[CO2] aq

Boundary layer model
  In boundary layer have
  only molecular diffusion.

$$FLUX = -D \times \frac{dC}{dz} = D \times \frac{[CO_2]_{aq} - [CO_2]_{eq}}{z}$$

Very hard to measure the boundary layer directly
where z is the thickness of the boundary layer; related to wind speed

INTEGRATION OF NUTRIENT CYCLES

Types of Reactions
  A. Dissolved inorganic carbon/alkalinity
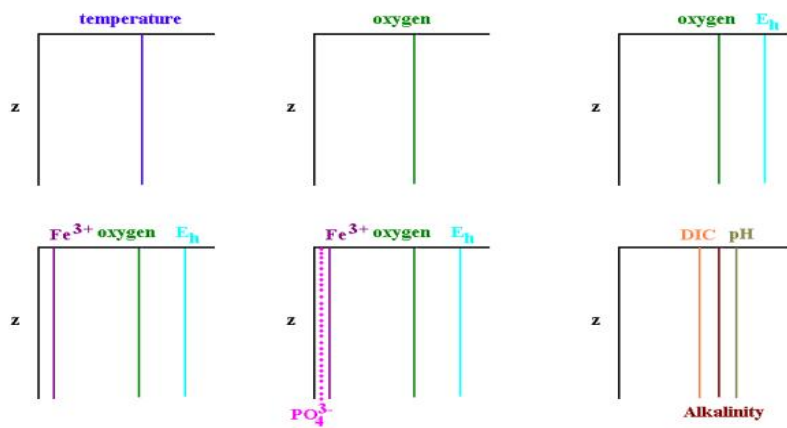   1. PS/Resp. cause -/+ CO_2 , +/- pH , +/- O_2
  B. Redox Reactions
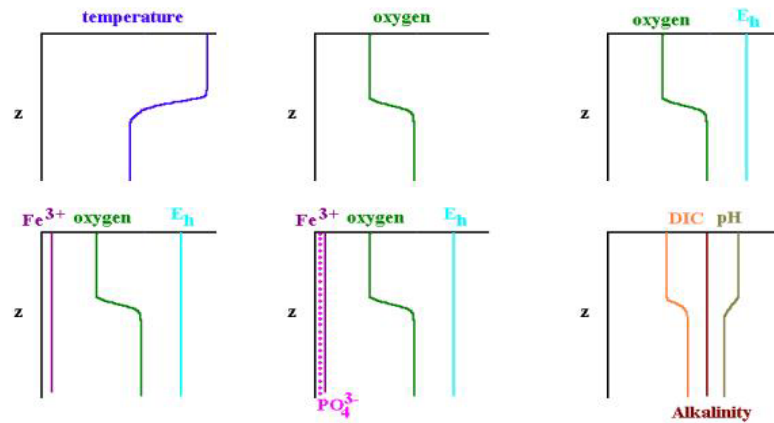   1. +/- O_2 cause change in E_h
  C. PO_4 and Fe (solubility)
    1. +/- Eh changes Fe solubility and PO_4 co-precipitation

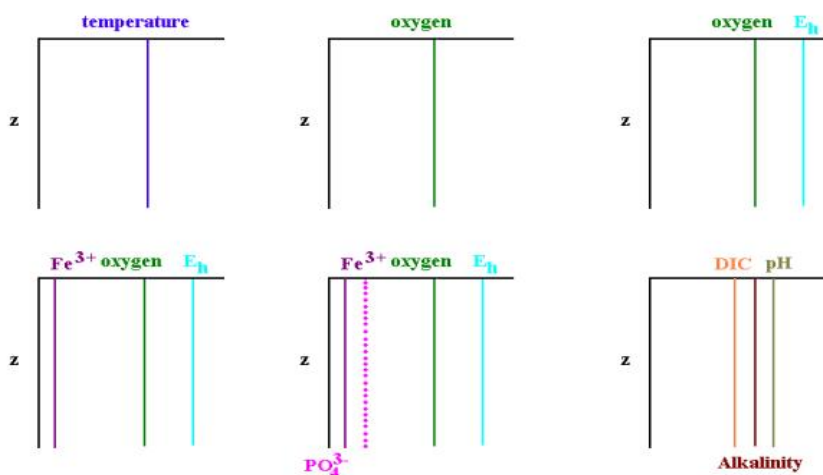# OLIGOTROPHIC LAKE AT SPRING OVERTURN

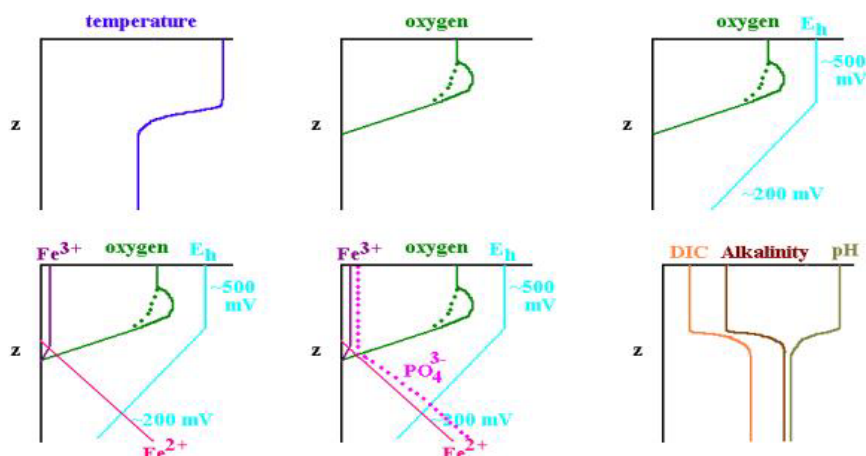# OLIGOTROPHIC LAKE AFTER STRATIFICATION

In an oligotrophic lake, the redox sequence of reactions occurs in the sediments

EUTROPHIC LAKE AT SPRING OVERTURN

DAYTIME PATTERNS
EUTROPHIC LAKE AFTER STRATIFICATION

In a eutrophic lake, the redox sequence of reactions occurs in the water column

HYPOLIMNETIC VALUES

LAKE STATUS	[O2]	Eh	Fe^{+2}	H_2S	PO_4^{3-}
Oligotrophic	High (orthograde)	400-500 mV	Absent	Absent	Very low
Mesotrophic	Much reduced (clinograde)	400-500 mV	Absent	Absent	Low
Eutrophic	Much reduced or absent (clinograde)	~250 mV	High	Absent	High
Hypereutrophic	Absent	<100 mV	Decreasing (formation of FeS)	High	Very high

PHYTOPLANKTON ECOLOGY II

IV. Nutrient requirements
   A. Macro and micronutrients
     1. Macronutrients:
       a. C,H,O
       b. Ca,Mg,Na,K,S,Cl (usually abundant)
       c. N,P,Si (diatoms) – often limiting
     2. Micronutrients: Fe, Mn, Cu, Zn, B, Mo (N fixation), V, Co (B_{12})
   B. Minimum levels and toxicity
   C. **Redfield ratio**
     1. Algal composition – elemental ratios in marine environments
     2. Element: C   H   O   N   P   S   Fe
       # atoms: 106   263   110   16   1   0.7   0.01
     3. Variability in the ratios of these elements actually found in algae is often used as an indicator of nutrient status/nutrient limitation
       a. N:P = 16 growing well, not P limited
       b. N:P >30 not enough P in cell; may be an indication of P limitation
   D. Growth curves – general

8

Stationary

Decline

Exponential growth

Lag

LOG number of algal cells

time
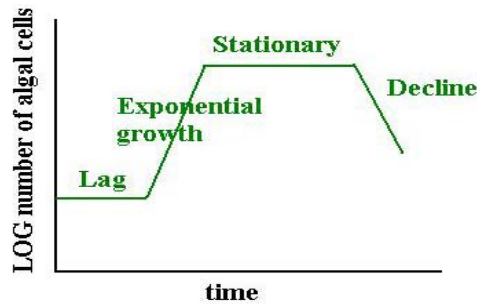
1. r = growth of population = μ - d
    2. μ = specific growth rate (division rate of one cell)
    3. d = death rate
    4. Lag phase
    5. Exponential growth: r>0, μ >d
    6. Stationary phase: μ =d
    7. Decline (death): r<0, μ <d
 E. Growth rates -- Nutrient uptake velocity
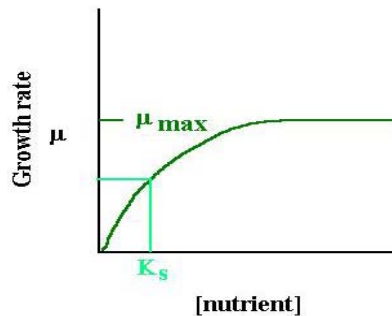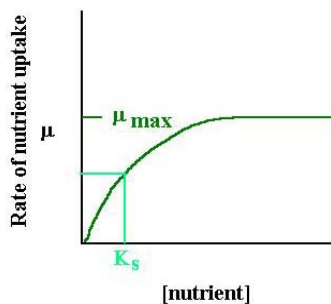   1. Growth and nutrient uptake curves generally follow the same pattern
    2. Generally follows a Monod Growth Curve/ Michaelis-Menton uptake curve

Rate of nutrient uptake

μ μ_{max}

K_s

[nutrient]

Growth rate

μ μ_{max}

K_s

[nutrient]

3. $$\mu = \frac{\mu_{max} * S}{K_s + S}$$

    a. μ = growth rate (or nutrient uptake rate)
    b. S = substrate concentration
    c. K_s = substrate concentration where growth rate is half of maximum

 F. Factors affecting uptake rate
    1. Cell size – amount of surface area relative to volume; surface area/volume gets lower as cell gets bigger
        ($4\Pi r^2$ = area of a sphere; $4/3\Pi r^3$ = volume; so A/V = 3/r)
    2. Nutritional state of cell
        a. **Luxury uptake** – cells take up more than they need
        b. Inhibition by internal stores
    3. Transport limitation
        a. sinking speed or swimming speed
        b. turbulence
    4. Inducible enzyme systems affect Ks
    5. Toxicity effects (if nutrient abundance too high)

 G. Determining the limiting nutrient – How do we determine the limiting nutrient?
1. **Liebig's law of the minimum**- only 1 thing limits growth at any one time (something else may be close)
                nutrient in shortest supply relative to needs
2. Bioassay techniques

Lakes and Reservoirs Chemical and Biological Processes

- Major nutrients: N, P, S, K, Mg, Ca
- Minor nutrients: Fe, Mn, Si, B, Mo, Zn, Cu, Co, Na - required in trace amounts
- Solubility and availability of inorganic nutrients is dependent on chemical species (ionic form), which is a function of pH and redox, e.g., Fe dynamics, and complexing with DOC.
- Requirement for Fe and Mn is established but for other micronutrients situation is not so clear. No universal requirement for all.
- Concentration and availability of micronutrients is usually adequate in most natural waters to sustain algal growth
- DOC is important regulator of micronutrient availability through its complexing (chelating) abilities.
- Complexing by DOC may increase physiological availability of many micronutrients, e.g., Fe, Mn
- Other micronutrients are toxic in excess or when complexed organically to point availability exceeds tolerance limits, e.g., Cu is micronutrient but also well known herbicide used to control algal blooms.

Iron (Fe) and Manganese (Mn)

- Typical Fe levels in lakes ranges from 50 to 200 ug/L, consisting of $Fe(OH)_3$, organically-bound Fe (to DOC), adsorbed to particles, particulate Fe.
- Fe required in enzymatic pathways (cytochromes) of chlorophyll and protein synthesis and in respiratory metabolism (hemoglobin).
- Mn concentrations in surface waters range from 10 to 850 ug/L, average is 35 ug/L
- Mn is essential for assimilation of NO_3, in P/S, and is catalyst for many enzyme-mediated metabolic reactions.
- Under epilimnetic conditions, pH 5-8, well oxygenated, $E_7 >= 0.56$ V, most Fe is found as ferric hydroxide, which is practically insoluble. Thus, availability of Fe in trophogenic zone is limited.
- $Fe(OH)_3$ exists mainly as in floculent suspension, which will remain on filters with 0.5 um pore size.
- Can also form a finer precipitate with colloidal properties that will go through 0.5 um pores. These particles are usually positively charged, except at high pH, and will attract negatively charged particles such as phosphate (PO_4^{3-}), clay particles, organic ions ($COOH^-$).

Fe-P interactions

- Under oxygenated conditions (e.g., in the epilimnion or at overturn) ferrous (Fe^{2+}) is oxidized to ferric (Fe^{3+})
- Fe^{3+} forms $Fe(OH)_3$ or $FePO_4$ if phosphate is present. Both are relatively insoluble and so precipitate out of solution.
- Some PO_4^{3-} is also adsorbed on $Fe(OH)_3$ colloid.
- In lakes with clinograde oxygen curves, during summer stratification:
  1. Ferric iron is reduced to ferrous which is more soluble, freeing PO_4^{3-}. Reduction usually occurs at sediment water interface.
  2. Fe concentration in hypolimnion increases throughout stratification but is practically undetectable in epilimnion.
  3. Hypolimnion operates as Fe trap.
- At overturn:
  1. water column is oxygenated oxidizing Fe^{2+} to Fe^{3+} liberating PO_4^{3-} which is mixed throughout water column causing algal bloom
 2. PO_4^{3-} rapidly forms $FePO_4$ or becomes adsorbed to $Fe(OH)_3$

Silica

- Si moderately abundant as SiO2, relatively unreactive but is important in cycles of diatom algae
- Diatoms use large quantities of Si in formation of cell structure (shell-like outer casing). Large marine deposits of dead diatoms harvested as diatomaceous earth.
- Availability of silica influences species succession and productivity of phytoplankton
- Si decreases in epilimnion during spring circulation and during stratification. In eutrophic lakes Si may be reduced below detection limits due to diatom growth and sedimentation of dead diatoms into bottom waters.
- Early in spring phytoplankton algae undergo conspicuous growth. Many species are involved but diatoms usually are predominant algae in spring maximum.
- Spring max declines abruptly as Si levels fall below 0.5 mg/L due to diatom utilization and sedimentation.
- Mixing of water at fall overturn may cause second bloom of diatoms as Si sedimented into hypolimnion is dispersed throughout lake.

NITROGEN

- Sources

    1. Atmosphere - diffusion
    2. Stream and river inflows
    3. Precipitation directly on the lake surface
    4. N fixation - bacteria and blue-green algae. Significance varies: in eutrophic lakes may be major source but in oligotrophic lakes is minor source.

NITROGEN CYCLING

- N can exist in multiple oxidation states
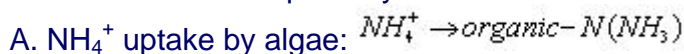
    -3 0 +3 +5
    NH_4^+ N_2 NO_2^- NO_3^-
    reduced   oxidized
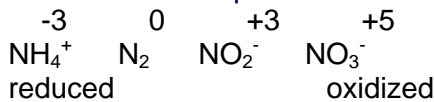
- Aquatic N cycle

Aquatic Nitrogen Cycle
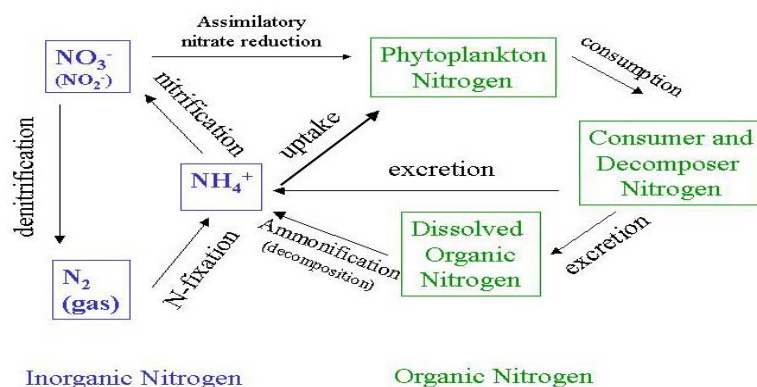
- Reactions within the aquatic cycle

    A. NH_4^+ uptake by algae: $NH_4^+ \rightarrow organic - N(NH_3)$

B. **Ammonification** -- ammonium production through decomposition of organic matter: $organic-N(NH_3) \rightarrow NH_4^+$

NH$_4$OH toxic

C. **Nitrification** -- NH$_4^+$ conversion to NO$_3^-$ (oxidation; bacterial gain of energy)

$$NH_4^+ + \frac{3}{2}O_2 \leftrightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + \frac{1}{2}O_2 \leftrightarrow NO_3^-$$

D. NO$_3^-$ uptake by algae (<u>**assimilatory nitrate reduction**</u>): NO$_3^-$ to organic-N(NH$_3$)

$$NO_3^- + H^+ \rightarrow NH_3 - organic$$

E. **Denitrification** -- dissimilatory NO$_3^-$ to N$_2$ (reduction)

$$CH_2O + NO_3^- + 2H^+ \leftrightarrow CO_2 + \frac{1}{2}N_2 + 2H_2O$$

F. **Nitrogen fixation** -- N$_2$ to organic-N(NH$_3$); cyanobacteria

Is very energy expensive -- 76 kcal/mole N

- Nitrogen cycle and N limitation
    A. Patterns
        In most cases, P is limiting to algal growth in lakes
        N most often limiting to algal growth in oceans and estuaries

    B. How can you get N limitation?

N cycle and N vs. P limitation
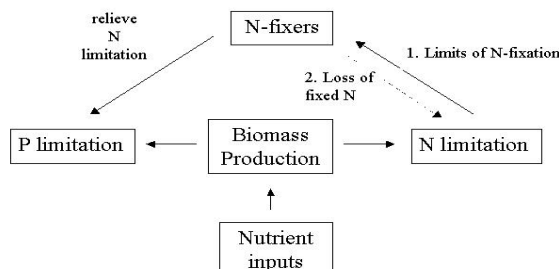
1. Loss of fixed N -- denitrification

2. Limits on N fixation
    a. light -- the N - N triple bond in atmospheric N$_2$ is hard to break -- requires lots of light energy.
    b. trace elements are limiting -- iron and molybdenum needed to fix N
    c. too little phosphorus for N-fixing cyanobacteria to grow
    d. CO$_2$ can be limiting (only on short time scales)

- N is always present and most abundant as a gas. Small quantities of ammonia (NH4+), nitrate (NO3), nitrite (NO2), urea, and dissolved organic compounds of N are also present. Nitrate is most important in aquatic systems.
- Concentration and rate of supply of nitrate is related to landuse practices in watershed since NO3 moves easily through soils and is rapidly lost from land even in natural drainage systems.

- Denitrification, bacterial reduction of NO3 to N2 gas occurs at low DO levels in sediments and hypolimnion of some lakes.
- major forms of N available to bacteria, fungi, and plants are NO3- and NH4+. N fixation and denitrification are ultimate sources and sinks of combined N available to algae.
- Nitrogen fixation is restricted to certain blue-green algae (*Aphanizomenon, Anabaena, Gleotrichia, Nodularia,* and *Nostoc*) and is the transformation of N2 gas to ammonia by enzyme reaction. Important because it may be major source of new N, but is not a universal phenomenon in all lakes.
- Denitrification of NO3 to N2 gas is done by facultatively anoxic bacteria. Donate electrons to NO3- during respiration at low O2 levels which occur in lake muds or anoxic hypolimnia.
- No known organisms denitrify NH4+.
- Loss of nitrate in oxygen-depleted waters can occur by denitrification or other biological transformations. Conversion of nitrate to NH4+ involves uptake and then decomposition and usually accounts for all observed losses of NO3. Thus open water dentrification is usually insignificant.

NO$_3$ and NO2

- Plant cells use reduced N, which is usually transferred intracellularly as amino acid group - NH2. Conversion of NO3 to N is 2 step process , NO3 --> NO2 --> NH4+.
- NO3 can only be metabolized after transformation by nitrate reductase. Induction period for enzyme is long and thus increased NO3 uptake is slow relative to NH4+ uptake. Presence of ammonium causes direct feedback inhibition and repression of nitrate reductase. Usually ammonium levels are too low to cause this inhibition.
- Nitrate levels are not usually toxic in water, about 1 mg/L; NO2 is only present briefly in small quantities.
- Concentrations follow regular seasonal pattern - biological uptake lowers concentration in spring, and summer in photic zone. During fall and winter, releases from sediments, tributary inflows, precipitation and replenishment from hypolimnion increase nitrate and sometimes ammonium.

Ammonia

- Usually present as ammonium (NH4+) which is more reactive than NO3.
- Rapidly taken up by phytoplankton and plants, but persists in small quantities because it is major excretory product of aquatic animals.
- Ammonia is highly toxic to aquatic organisms.
- NH3 + H2O <----> NH4OH <-----> NH4+ + OH-
- ammonium ion is harmless but NH4OH is toxic; toxicity varies with pH, DO, temperature, hardness, species and age. Usually < 0.1 mg/L in freshwaters.

PHOSPHORUS

- Forms and Measurement of P
  - Total **P = DIP + DOP + PP**
    i. DIP – (<5%) dissolved inorganic phosphorus -- PO_4^{3-} polyphosphates
    ii. DOP – dissolved organic phosphorus -- often organic colloids; less quickly available
  - Alkaline phosphatase enzyme mediates can be an indicator of P limitation
    iii. PP – particulate phosphorus -- often largest percentage of P in lakes (>70%)
  - most P is in organic matter -- living or dead organisms;
  - some particulate P is mineral P (not as bioavailable)
  - phosphate adsorbed onto clays
  - Measurement of phosphorus

- soluble reactive phosphate (SRP) and scientists long thought this was PO_4^{3-}
- BUT, measurement procedure actually digests some organics, too

- P is not needed in large quantities for growth, but is one of most common limiting elements on land and in water. There are 3 reasons:

    1. P-containing minerals are scarce geochemically, so normal nutrient supply from rock breakdown will be P-poor;
    2. No gaseous phase in P-cycle so there is no equivalent to N-fixation; and
    3. P is sufficiently reactive to be tightly bound to soils.
- 3 types of P are normally measured:
    1. particulate phosphorus (PP) - remains on 0.45 um filter. Includes organic and inorganic forms of P, e.g., organisms (bacteria, plant, animal), minerals such as hydroxyapatite, phosphate adsorbed on clay, phosphate adsorbed on dead organisms
    2. soluble phosphate (SP) - filtrate that goes through 0.45 um filter. Consists of orthophosphate (PO43-), polyphosphates (including detergents), colloidal phosphorus (large molecular aggregations that disperse slowly if at all), and low MW P-esters.
    3. dissolved total Phosphorus (TP) - 90% is PP and 10% SP
- Soluble Phosphorus consists of 2 fractions:
    1. Soluble reactive phosphorus (SRP - determined by molybdenum blue method) consisting mostly of orthophosphate (PO4). Good approximation of biologically available P for algal, macrophyte and bacterial growth.
    2. Soluble unreactive phosphorus (SUP).

Biogeochemical Cycle of Phosphorus in Lakes

- Sources:
    1. Stream and river inflows (erosion)
    2. Wind and aerial deposition
    3. Sewage
    4. Internal recycling from sediments

- Sinks

    1. Sedimentation of dead organic matter
    2. Chemical precipitation with Fe, Ca, and Al compounds (colloidal P). Precipitation with Fe is important part of recycling when fall turnover occurs.
- Most P is present particulate P in living and dead biomass; small amounts are excreted as soluble organic P compounds, which some phytoplankton are able to convert to PO4 by releasing alkaline phosphatase

- Phytoplankton are able to overcome P-deficits in 3 ways:
    1. luxury consumption - uptake of more PO4 than required for growth and storage as polyphosphates granules in cells;
    2. ability to use phosphate at low levels - Most lakes phosphate growth constant, Ks, is low for natural phytoplankton. Generally 1-3 ug/L PO4-P, which means enzyme system is not saturated much of the time. May be species differences in K, which may play a role in species succession. Because PO4 is rapidly recycled, rate of P uptake is important. High uptake rate may compensate somewhat for lack of ability to remove P at low levels.
    3. Alkaline Phosphatase - enzyme which cleaves bond between PO4 and organic molecule to which it is attached. Enzyme is produced in response to P-deficiency and is released in free dissolved form into environment. Is unique to P metabolism.

Recycling of P

- P is excreted by fish and zooplankton among phytoplankton. Excreted P consists of about

50% PO4-P and rest as organic P.
- In some cases zooplankton excretion may supply most of daily phytoplankton demand.
- DO has role in controlling P release from sediments. When sediment-water interface becomes anoxic, PO4 moves rapidly into water above due to Fe kinetics.

Rooted Macrophytes

- uptake of P occurs through leaves when water is rich in PO4.
- Main method macrophytes obtain P is absorption of PO4 directly from interstitial soil water. Losses occur by direct excretion or death and decomposition.

Controlling and Limiting Factors

- **Aquatic systems in semi-arid climates tend to have excess P and be N-limited**
- **Aquatic systems in temperate climates tend to have excess N and be P-limited**
- Limiting nutrient concept (paraphrasing Leibig's Law of the Minimum) states that: the ...yield of any organism is determined by the abundance of the substance that, in relation to the needs of the organism, is least abundant in the environment .
- P is typically the limiting nutrient in most temperate FW systems. The exception is Si which may limit diatoms forming spring blooms.
- Nutrient sufficient phytoplankton C : N : P = 106 : 15 : 1 (Redfield Ratio).

  1. Theoretically most limiting nutrient

      - '*Ecological stoichiometry*' -- Ratio of elements in plankton and other organisms (oceanographer *Redfield* in the 1950's)
      - Found an average phytoplankton composition of (**Redfield Ratio**)

C	H	O	N	P	S
106	263	110	16	1	0.7

      - Compared with available nutrient ratios
      - He considered P to be the most limiting nutrient even though it is only ~1% organic matter BECAUSE the amount of P available to organisms is much less than the *amount required* relative to these other elements
      - Also implies that if nothing else is limiting, then increasing P can theoretically generate >100X the weight of added P in algae

  2. Algal biomass versus total P
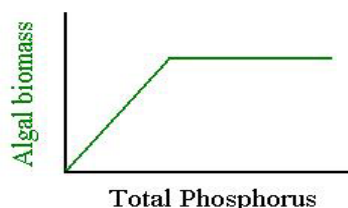
  1. **Controlling Factors** - factors that influence metabolic rate but do not enter into metabolic chain, i.e., they alter the activation state of metabolites, e.g., temperature
  2. **Limiting Factors** - factors that alter the rate of supply of metabolites or removal of waste products, e.g., P or N.
  3. **Lethal Factors** - factors that destroy the organism through disturbance of the metabolic chain, e.g., high temperature will cause protein denaturation.

- Main sources of P is soil erosion carried in by inflowing rivers; precipitation is main source of N (water-soluble)

- Most P is carried as inorganic and organic particulates. During erosion PO4 is carried sorbed to clay particles as silt. Flow of P into rivers is correlated with average slope of drainage basin.
- Climate influences sediment and nutrient transport
- Temperate areas rainfall spread out and lots of vegetative cover. Soil erosion is minimal.
- Semi-arid areas rainfall tends to be torrential, vegetative cover is minimal so soil erosion is extensive
- Nutrients such as P and Fe which are transported adsorbed to soil particles, move easily in semi-arid areas
- N, S, and Si are usually present in soluble form and are easily transported by clear or muddy H_2O
- P loading versus mean depth -- trophic state classification
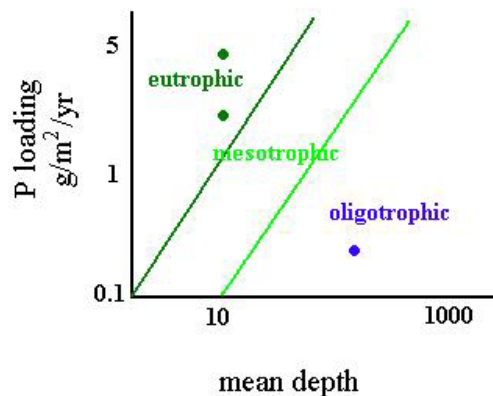
Lake Productivity Classification	Total Phosphorus μg/L
Ultra-oligotrophic	<5
Oligotrophic	5-10
Mesotrophic	10-30
Eutrophic	30-100
Hypereutrophic	>100

- Sources of P
    - i. weathering of calcium phosphate minerals, especially apatite [$Ca_5(PO_4)_3OH$]
    - ii. mostly stored in marine deep ocean sediments
    - iii. anthropogenic P is now often much greater than natural inputs of P in many watersheds -- sewage, urban runoff, agriculture,
        - "**cultural eutrophication**"
        - - '**point source**' – sewage (treated or untreated), industry...
        - - '**nonpoint source**' – e.g., agriculture – animal waste, fertilizers
- Modes of Entry of P to aquatic systems
    - i. Precipitation – dust in air
    - ii. Groundwater –P adsorbs to soil particles
    - iii. Surface runoff
- Decomposition and excretion
    - i. well-developed, efficient recycling of P
    - ii. P excreted by animals is rapidly taken up by algae and bacteria
    - iii. often one major function of decomposition is the liberating of usable P

$$organic - P \rightarrow PO_4^{3-}$$

    - iv. Lack of oxygen due to decomposition actually feeds back and affects the availability of PO_4^{3-} through some more redox reactions.
- Redox reactions

- P doesn't go through redox reactions itself, but it is influenced by the solubility of Fe, which changes due to its redox state
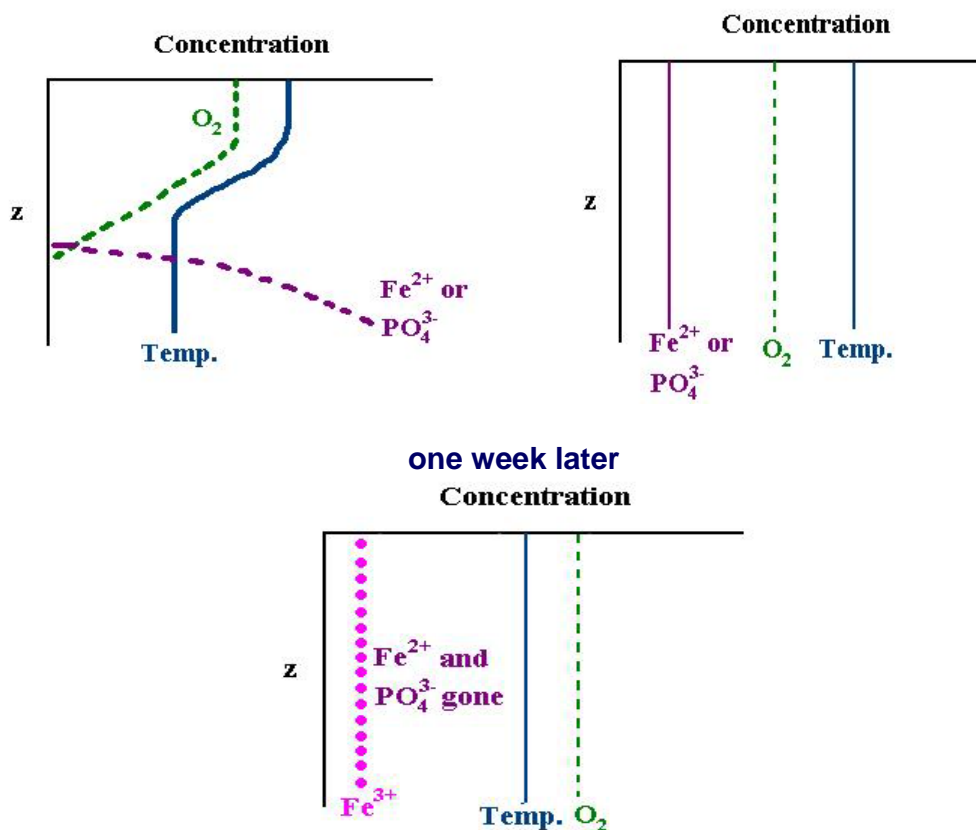
A. **Iron trap for P**
  - In oxygenated waters, iron is present as Fe^{3+} (ferric)

  - At pH<7 you get $Fe^{3+} + PO_4^{3-} \leftrightarrow FePO_4$ -- vivianite

  - At pH> or equal to 7 you get $Fe^{3+} + PO_4^{3-} + OH^- \leftrightarrow Fe_x(OH)_y(PO_4)_z$
  - **stratified lake day of turnover**

- What happens?
        i. Fe^{2+} is converted to Fe^{3+} due to presence of oxygen
        ii. Fe^{3+} goes to $Fe_x(OH)_y(PO_4)_z$, FeOH, and $FePO_4$
 - "**iron trap for P**", less available for algae
 - Can be a *critical point for eutrophication* -- when hypolimnion becomes anoxic, then more P is released and that increases the P recycling and loading from within the lake as well -- contributes to increased eutrophication.
 - As long as hypolimnion remains oxic, any phosphate in sediments will be trapped by iron trap as it comes to the sediment surface, even if the sediments are anoxic.

TROPHIC STATE

- **OLIGOTROPHIC LAKES** - tend to be deep with mean depths > 15 m and maximum depths > 25 m. Waters are transparent and have low density of plant life occurring at various depths. Nutrient supply is low in relation to the volume of water and dominant fish tend to be coldwater species such as lake trout.
- **EUTROPHIC LAKES** - are shallow with mean depths < 10 m and maximum depths < 50 m, have high nutrient supply in relation to volume and dense growths of plankton in the surface waters. Water column is turbid and biological productivity is high at all levels. Bottom waters become anoxic during summer stratification. Dominant fish tend to be warmwater species in the minnow and bass families.

- **MESOTROPHIC LAKES** - a convenient term for lakes that are borderline between oligotrophic and eutrophic. They are intermediate with respect to nutrient supply, depth, biological productivity, water clarity, and oxygen depletion in the hypolimnion. Yellow perch commonly reaches maximum abundance in mesotrophic lakes.
- These trophic descriptions of oligotrophic and eutrophic have no absolute meaning but are generally used now to: denote the nutrient status of a waterbody, or to describe the effects of nutrients on the general water quality and/or trophic conditions of a waterbody.
- Under natural conditions nutrient supply, basin form (morphometry), and climate are the most important determinants of lake trophic status (see the Rawson diagram from the first lecture).
    1. In a given climatic zone, lakes in nutrient rich soil are more productive than lakes of similar size and shape in areas of igneous rock drainage.
    2. In areas of comparable climate and geology, shallow lakes are found to be more productive than deep lakes.
    3. In lakes of comparable size and shape and similar geology, tropical lakes are more productive on an annual basis than lakes at high altitudes or latitudes (temperate regions).

LAKE SUCCESSION - NATURAL EUTROPHICATION

- Based on knowledge that oligotrophic lakes are deep and eutrophic lakes are shallow, early limnologists (Thienemann, Naumann) inferred that lakes must evolve toward a condition of eutrophy over geological periods of time. Thus, the ultimate fate of lakes was to become filled with sediments and eventually supplanted by grassed or forested land. Exceptions occur, such as the large Rift Valley lakes in Africa (e.g., Lake Victoria) where sinking of land may result in constant or sometimes increasing depths over geologically long periods of time.
- Lakes accumulate sediments at an average rate of about 1 mm/yr. Most lakes in Ontario are glacial in origin and so at most will have about 11,000-12,000 years of sediment in them.
- Support for the idea that there is a successional process in lakes from oligotrophic to eutrophic was found through examinations of the fossil remains of indicator organisms in the sediments. The deepest sediments (oldest deposits) tended to have a greater abundance of organisms found in well oxygenated conditions and the shallowest sediments (most recently deposited) tend to have more organisms tolerant of low oxygen conditions.
- However, there is more recent evidence that this support was derived from a biased selection of lakes that were only recently eutrophic, i.e., as a consequence of human activities. Also, there is evidence that some deep lakes evolved from a eutrophic state towards an oligotrophic state. Furthermore, in areas sensitive to climatic change the trophic state of a lake can be determined by climate alone. All of this is evidence that tends to contradict the idea of natural succession in lake development.
- Despite the evidence to the contrary, there is widespread acceptance of the **PROCESS OF NATURAL EUTROPHICATION**. Natural eutrophication is complex, immeasurably slow (geological time periods), and, for all practical purposes, it is irreversible under a given set of climatic conditions. It is caused by the change in form and depth of the basin as it gradually fills in with sediment. To reverse natural eutrophication, you would have to scour out the lake basin; a formidable task under any circumstances and certainly not practical with current technology! Nutrient supply does not change, or if it does, it decreases as soils become exhausted. The species changes that Thienemann, Naumann and others observed and attributed to changes in nutrient supply were caused by form-induced oxygen depletion.
- Lakes undergoing this natural successional process generally have good water quality and exhibit a diverse biological community throughout their existence. Algal growth is generally minimal or at least in balance with the input of nutrients.

CULTURAL EUTROPHICATION

- Human settlement in the drainage basin of a lake generally leads to clearing of the natural vegetation, the development of farms and cities. These activities in turn accelerate runoff from the land surface and increase the input of plant nutrients, i.e, the rate of nutrient supply is increased. Also, streams were convenient for disposing of household wastes and sewage,

adding to the nutrient load in the receiving water body. The addition of plant nutrients stimulates the growth of algae and other plants which in turn stimulates fish and other organisms in the food web. This phenomenon is called **CULTURAL EUTROPHICATION.**

- Cultural eutrophication is manifested by an intense proliferation of algae and higher plants and their accumulation in excessive quantities which can result in detrimental changes in water quality and biological populations and can interfere with human uses of that waterbody.

- During the last 2-3 decades, the term eutrophication has been used increasingly to mean the artificial and undesirable addition of plant nutrients, mainly P and N, to waterbodies. This can be misleading since what is undesirable in one water body may be desirable in other water bodies.

- During the last 2-3 decades, the term eutrophication has been used increasingly to mean the artificial and undesirable addition of plant nutrients, mainly P and N, to waterbodies.

- The perceived negative effects of cultural eutrophication include reduced water transparency and excessive algal and plant growth, which is highly visible and can interfere with uses and aesthetic quality of water. One consequence of such growths may be taste and odour problems in drinking water. Ecological consequences include hypolimnetic anoxia due to algal decomposition and fish kills and a rapid shift in species composition of the biological community. In tropical areas, diseases such as malaria may be enhanced by eutrophication because the insect vector, mosquitoes in the case of malaria, breeds in these waters.

- Some positive effects include enhance growth and biomass of fish and other organisms at all levels of the food web. But the species may not be the same as found in less eutrophic conditions (a potential negative).

- Cultural eutrophication is the rapid enrichment of water with nutrients derived from human activities. Main nutrients are P and N and they are derived from sewage, agricultural and livestock holding operations. This process is the result of an increase in nutrient supply to a constant volume of water, without any appreciable change in depth or form of the basin, as in natural eutrophication. The process is rapid and it is reversible by eliminating sources of nutrient sources. BUT, reverse means only a return to pre- human conditions. If a lake was mesotrophic prior to cultural eutrophication, it cannot be reversed to an oligotrophic state.

- The sequence of chemical and biological events associated with cultural eutrophication occurs independently of time and place, in contrast to natural eutrophication. Note that productivity per se (i.e., the rate at which new biomass is synthesized) is NOT the major problem associated with cultural eutrophication. Rather, it is excessive algal (and macrophyte) biomass (the amount of tissue present at a given time) which interferes with human uses of the water that is the problem. Although biomass can be directly proportional to productivity, it is often not the case.

- The three nutrients important to plant growth are P, N, and C but attempts to stop and reverse cultural eutrophication focus on P. WHY?

    1. Ratio of P:N:C in plant tissues on unit weight basis is 1P:7N:40C:100 dry weight:500 fresh weight. Thus, P can theoretically generate 500X its weight in living algae, N can generate 71X its weight (500/7), and C only 12X its weight (500/40). The amplifying effects on P and N on plant growth have been known for centuries and used in pond culture to trigger algal growth, which results in the transfer of energy to all higher levels in the food web, including fish.
    2. P and N are 1000X more concentrated in sewage effluents than in lake waters unaffected by humans.

3. Limiting nutrient concept - growth and yield are related to the abundance of that essential substance most scarce in the environment. There is lots of evidence showing that algal growth increases as P concentration in the water increases, at least up to a point after which other factors limit growth. The atomic ratio of P, N, and C in phytoplankton tissues is 1P:16N:106C. From this, many have surmised that P was the limiting nutrient for algal growth.

- Human waste: 540 g P/person/yr; N : P = 7.5 : 1
- Detergents: high % of P as polyphosphates

Symptoms of Cultural Eutrophication

1. Early stages symptoms consist of increase in phytoplankton standing crop (biomass) and biomass at other trophic levels
2. Algal blooms
3. Massive growths of Cyanophyta (blue-green algae or cyanobacteria)
4. Complete depletion of oxygen from hypolimnion shortly after stratification occurs: high concentrations of nutrients appear (due to redox reactions)
5. H_2S, NH_4^+, non-mineralized organic matter, CH_4 found in hypolimnion as a result of anaerobic respiration.
6. Invertebrate and fish communities change: species requiring high oxygen levels disappear, species tolerant of low oxygen levels dominate. Species diversity reduced.
7. Macrophytes and periphyton (attached algae) may increase.

Controlling Cultural Eutrophication

- Cultural eutrophication is a world-wide phenomenon and is of great economic importance in many areas. Because of this much effort has gone into developing models designed to provide predictions on the outcome of lake manipulations.

- Vollenweider developed one of the most practical models in 1968 based on comparative studies of European and North American lakes. In this model, the trophic status of a lake is a function of the rate of areal nutrient supply (g/m2/yr), basin form and flushing rate in the form of mean depth/hydraulic residence time. (Hydraulic residence time is the time required to fill a lake at present rates of inflow). Since it is impossible in any practical sense to manipulate mean depth or hydraulic residence time, this model was used to predict the likely effects of altering the rate of nutrient supply on lake trophic status. In fact, this model formed the basis for action in many jurisdictions for stopping cultural eutrophication.

- A second model, developed in 1974 by Dillon and Rigler was:

$$[TP] = (Lp/qs) * (1-R),$$
where TP is total phosphorus concentration (mg/L), Lp is the annual areal P loading (mg/m2/yr), qs is the annual areal water loading (mean depth/hydraulic residence time, m/yr) and R is the P retention coefficient = 1 - (annual outflow P load/annual inflow P load).

- Dillon and Rigler's model could be used to set a P concentration target and from that determine loadings required to achieve this target.

- Both models were used successfully in Ontario to stop and reverse cultural eutrophication.

- From a control perspective there are two sources of nutrients to a waterbody:
    1. **Point sources** - effluent discharges from a pipe, including municipal and industrial sewage, and

20

2. **Nonpoint sources** - diffuse runoff from land surface, including agricultural runoff from fields and feedlots and urban storm sewer discharges.

- P in municipal sewage treatment plants (STP) is usually bioavailable at the point of discharge (75->90% in the Great Lakes). Such P is in a soluble form and is easily and rapidly used by aquatic plants and so point sources discharging directly into lakes are usually most important sources of bioavailable P to consider in a control program.

- Control of cultural eutrophication focuses on P because it is the only nutrient of P, C, and N known to exert control on plant growth and because it is the most easily controlled nutrient from a human perspective. Both C and N have atmospheric sources which would negate efforts to control them in water.