Back

Major and Minor Inorganic Plant Nutrients

BGY C56H3 Lecture 5 - October 16, 2000

- 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 SiO_2, 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.

- N is always present and most abundant as a gas. Small quantities of ammonia (NH4+), nitrate (NO_3), 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 NO_3 moves easily through soils and is rapidly lost from land even in natural drainage systems.
- Denitrification, bacterial reduction of NO_3 to N_2 gas occurs at low DO levels in sediments and hypolimnion of some lakes.
- major forms of N available to bacteria, fungi, and plants are NO_3^- 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 N_2 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 NO_3 to N_2 gas is done by facultatively anoxic bacteria. Donate electrons to NO_3^- during respiration at low O_2 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 NO_3. 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 - NH_2. Conversion of NO_3 to N is 2 step process , NO_3 --> NO2 --> NH4+.
- NO_3 can only be metabolized after transformation by nitrate reductase. Induction period for enzyme is long and thus increased NO_3 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 NO_3.
- 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.

- $NH3 + H_2O$ <----> 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

- 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 (PO_4^{3-}), 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 PO_4-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% PO_4-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. **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

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.

this page was created by the Environmental Information Office at I.E.S., and was last changed August 10, 2000

Environmental Research and Teaching
at the University of Toronto
2000