Back

WATER CHEMISTRY in LAKES
BGY C56H3 Lecture 4 - Oct 2, 2000

IONIC COMPOSITION (SALINITY)

- Ionic composition (salinity) of freshwaters is a measure of the inorganic ion concentration. Units are mg/L or m.eq/L where meq/L = mg/L x (charge/molecular weight)
- Salinity is governed by runoff of soil and rock in drainage basin, atmospheric precipitation, and balances between evaporation and precipitation. In open lakes (those with stream outflows), salinity is governed by chemistry of inflows. In closed lakes (no stream outflow) salinity is governed by precipitation and evaporation, e.g., saline lakes such as the Dead Sea, Great Salt Lake.
- Salinity dominated by 4 major cations: Ca^{2+}, Mg^{2+}, Na^+, and K^+
- Salinity also dominated by 4 major anions: HCO_3^-, $CO_3^=$, $SO_4^=$, and Cl^- (chloride).
- Other elements (e.g., N and P) are important biologically, but are minor components of ionic composition of water
- Proportions of major cations are Ca > Mg Na > K and proportions of major anions are CO_3 > SO_4 > Cl.
- Conservative elements: concentrations of Mg, Na, and K and Cl are high but are relatively conservative and undergo minor spatial and temporal fluctuations due to biotic utilization or biotically mediated changes in environment, i.e., very little is used by biota.
- Dynamic elements: Ca, CO_3, and SO_4 concentrations are lower, but are dynamic, i.e., their concentrations are strongly influenced by biotic metabolism. Concentrations of dynamic elements exhibit more seasonal variability.

TOTAL DISSOLVED SOLIDS

- Salinity is measured as quantity of solids remaining after water sample is evaporated to dryness at 105 C. Consists of total inorganic salts and organic material and means essentially the same thing as Total Dissolved Solids (TDS).
- Measured TDS often does not agree well with TDS calculated by summing dissolved constituents largely due to loss of CO_2.
- Freshwaters usually have salinities (TDS) < 1000 mg/L; brackish waters (> 1000 to 20,000 mg/L) are too saline to be potable (drinkable) but are not as saline as full strength seawater (35,000 mg/L - parts per thousand). Brines are significantly more saline than seawater.
- **SOFT** waters have low salinity and are usually derived from drainage of acidic igneous rocks (e.g., Canadian Shield). Commonly have salinity of < 50 mg/L and cationic proportions of Ca > Na > Mg > K. Anionic proportions are: Cl >= SO_4 > CO_3.
- **HARD** waters contain large concentrations of alkaline earth metals derived from drainage of calcareous rock (e.g., Limestone bedrock). Cationic proportions are Ca > Mg >= Na > K and anionic proportions are CO_3 > SO_4 > Cl.

CONDUCTIVITY

- Conductivity is convenient but indirect way to measure TDS in the field using a meter.
- Conductivity is the reciprocal of electrical resistance measured between two electrodes 1 cm^2 in area and 1 cm apart (umhos/cm - reciprocal of ohms). Usually corrected to standard temperature of 20 C.
- More ions in solution the lower its resistance to flow and hence the higher its conductivity. Distilled water is an excellent insulator because it has few dissolved ions.

ALKALINITY

- Alkalinity is numerically the total amount of base in the water and is determined by titration with a strong acid to equivalency points dictated by pH values at which contributions of bases such as hydroxide, carbonate, and bicarbonate are neutralized. Standard endpoint of titration is pH 4.5.
- Usually imparted by HCO_3^-, $CO_3^=$, and OH^-. Borate $(B(OH)_4)$, silicic acid, bisulfide (H_2S), organic anions and OH^- and H^+ are usually present in much smaller concentrations compared to latter three ions and phosphates.
- Alkalinity is usually expressed as mg/L (or ppm) as $CaCO_3$. This assumes that alkalinity results only

from $CaCO_3$ and HCO_3^- which is reasonable in most surface water where pH ranges from 5.5 to 8.4. These pHs favour HCO_3 formation which buffers the water against pH changes.
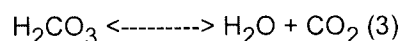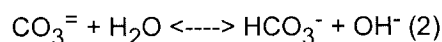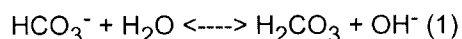
- Softwater lakes - low alkalinity, low buffering capacity, susceptible to acid precipitation, e.g., lakes on the Canadian Shield
- Hardwater lakes - high alkalinity, high buffering capacity, not susceptible to acid precipitation, e.g., lakes off the Canadian Shield in regions dominated by limestone bedrock.

pH and Buffering

- pH controls chemical state of many nutrients including CO_2, phosphate, Fe, ammonia, and trace metal speciation. pH of most lakes is controlled by reactions involving the carbonate system.
- CO_2 gas dissolves in water to form soluble CO_2. Equilibrium depends on the partial pressure in the atmosphere

$$CO_2 \longleftrightarrow CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_{3-} + H^+ \longleftrightarrow CO_3^= + 2H^+ = DIC$$
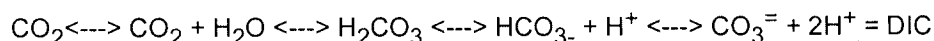
- CO_2 content of atmosphere averages about 0.034% globally. CO_2 is about 200X more soluble in water than O_2. Amount of CO_2 dissolved in water from atmosphere is about 1.1 mg/L at 0 C, 0.6 mg/L at 15 C, and 0.4 mg/L at 30 C.
- CO_2 dissolved in water is derived from atmosphere and as a by-product of P/S.
- Total amount of DIC, which is usually present as HCO_3 and CO_3, depends on Ca and Mg concentrations.
- Ca and Mg found in calcareous bedrock as $CaCO_3$, $Ca(Mg)(CO_3)_2$. Normally relatively insoluble in water but if CO_2 present will dissolve releasing CO_3 which is rapidly converted to HCO_3 at normal surface pH (5.5-8.5).
- As long as CO_3 supply continues, buffering capacity will be maintained. Softwater lakes CO_3 supply from bedrock is relatively small and can be rapidly exhausted by acidic precipitation, resulting in pH decrease.
- pK1 is 6.43 at 15 C, pK2 is 10.43 at 15 C.
- Below pH 6 essentially all dissolved carbonate species are in form of H_2CO_3 and above pH 7 all is in form of HCO_3^-. Above pH 10.43, activity of HCO_3 rapidly becomes small.
- In most natural waters $[CO_3^=]$ is small compared to $[HCO_3^-]$ because pH values vary from about 5.5 to 8.5.
- Buffering of water with respect to pH occurs when protonated and unprotonated species are both present in significant concentrations: at pH 6.4 this is H_2CO_3/HCO_3^- at pH 10.33 this is $HCO_3^-/CO_3^=$

$$HCO_3^- + H_2O \longleftrightarrow H_2CO_3 + OH^- \quad (1)$$

$$CO_3^= + H_2O \longleftrightarrow HCO_3^- + OH^- \quad (2)$$

$$H_2CO_3 \longleftrightarrow H_2O + CO_2 \quad (3)$$

- The above reactions explain buffering action of alkaline waters. Water resists pH change as long as these equilibria are present. Addition of proton neutralizes OH^- formed by dissociation of HCO_3^- and $CO_3^=$. However, more are formed immediately by reaction of carbonate with water as long as reservoir of carbonate ion is present. pH remains unchanged until supply of $CO_3^=$ or HCO_3^- is exhausted.
- Addition of OH^- reacts with bicarbonate $HCO_3^- + OH^- \longleftrightarrow CO_3^= + H_2O$

DISSOLVED ORGANIC CARBON (DOC) or DOM

- DOC or dissolved organic matter (DOM) in lakes is ultimately derived from P/S and is categorized into two types based on source:
    1. Allochthonous DOM - derived from material formed in the surrounding drainage basin (outside the lake itself) and brought into the lake through runoff or via wind. Generally imparts a brownish

colour to water; and

2. Autochthonous DOM - derived from material formed by P/S within the lake itself. Generally the result of decomposition of dead organisms but also some compounds released extracellularly during active growth of algae and macrophytes.

- Two major groups of substances comprise DOM:
  1. NonHumic Substances - carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments, and other low molecular weight organic compounds. Usually used and degraded by microorganisms (labile) and so have rapid flux rates within a lake
  2. Humic Substances - amorphous, brown or black coloured hydrophilic (water loving) and acidic complexes formed by microbial activity on plant and animal matter. Largest constituent of organic matter in soil and water. Have relatively high molecular weights (450 - 10,000 g) and resistant to microbial degradation. Therefore, they persist with long residence times in lakes

- Two types of humic substance:
  1. Fulvic acids - low MW (450) carboxylic aliphatic acids that bind Mg, Na, Co, Mn, Fe, Cu, and Zn and are very stable to chemical and biological oxidation, and
  2. Humic acids - high MW (up to 10,000 or more) condensation products of phenols, quinones, and amino acids. Bind Fe and are extremely stable (resistant to degradation). Have brownish/red colour.

- DOM has several functions in lakes:
  1. DOM influences water transparency and so is a determinant of photic zone depth. In dystrophic lakes (brown-water lakes, heavily stained with high humic content from allochthonous sources) water colour is so dark that planktonic productivity is low.
  2. Many DOM compounds are weak acids or their salts and thus they provide some, minimal buffering capacity to maintain pH.
  3. Many compounds, particularly fulvic acids, bind metal ions, affecting the availability and assimilation capacity of inorganic substances. DOM acts as chelating agent, incorporating metal into a stable ring structure. This can increase physiological availability of reactive ions such as Fe and Mn or reduce the availability of substances toxic to certain organisms.
  4. Water chemistry can be altered through interactions of DOM and other constituents of water. E.g., DOM is adsorbed by clay which in turn sorbs P through interaction of PO_4^{3-} and Al^{3+}; humic acids chelate Al and so free up PO_4^{3-}, and
  5. Many DOM compounds, particularly nonhumus, are easily used by heterotrophic bacteria within lakes and some algal species (source of essential nutrients). If adsorbed on colloids and large food particles, then large filter feeding invertebrates may use them.

DISSOLVED OXYGEN

- Dissolved oxygen (DO) is essential to metabolism of all aquatic organisms that possess aerobic respiratory biochemistry.
- Sources of O_2 from atmosphere (by diffusion) and from P/S inputs and hydromechanical distribution are counterbalance by consumptive metabolism.
- Rates of O_2 utilization in relation to synthesis allow us to evaluate, very approximately, the metabolism of a lake as a whole.

Solubility of O_2 in Water

- air contains 20.95% O_2 by volume, the bulk 79% being nitrogen, plus 0.003% CO_2
- O_2 is more soluble in water than N_2, so amount of O_2 dissolved in water is about 35%, rest is N_2 even though pressures are equal.
- Solubility of O_2 decreases nonlinearly with increasing temperature. Also affected by pressure as well so equilibrium of atmospheric O_2 with $[O_2]$ in water depends on atmospheric partial pressure or altitude of lake surface.
- % saturation can be determined from nomograms that take into account temperature and elevation (partial pressure)
- Amount of gas that can be held in water by combined atmospheric and hydrostatic pressure (due to water above) at a particular depth is called ABSOLUTE SATURATION.
- Actual pressure (P_z) at a given depth (in atmospheres) is

$$P_z = P_o + 0.0967 \text{*} z,$$

where P_o is surface pressure and z is depth (m).
- Salinity also reduces O_2 solubility, exponentially with increasing salt content. O_2 solubility in normal seawater (35 parts per thousand) is about 20% less than in freshwater.
- Principal method of O_2 analysis is Winkler method, based on chemical fixation of O_2 and colorimetric titration against reagents of known reaction with concentration.

Distribution of Dissolved Oxygen in Lakes

- Diffusion is slow. For [O_2] in water to reach equilibrium with atmosphere, water must circulate as at spring and fall turnovers or in epilimnion during summer.
- In idealized lake [O_2] at fall overturn is at or near 100% saturation (12-13 mg/L if temperature is about 4 C and altitude is near sea level). This concentration is based on physical control of diffusion, mixing, and saturation.

Orthograde O_2 Profile

- In oligotrophic lakes, O_2 with depth is relatively is constant. Depends on conditions at circulation (spring overturn) and physical mechanisms as summer stratification occurs. Lakes exhibiting this profile have no depletion related to biological activity or production of detectable magnitude.
- [O_2] in epilimnion decreases as temperature increases but remains in equilibrium with atmosphere. [O_2] increases as temperatures decrease in metalimnion and hypolimnion.
- Important characteristic of this O_2 profile is that saturation is more or less 100% with increasing depth.

Clinograde O_2 Profile

- Orthograde curve is rare. Oxidative processes occur constantly in hypolimnion, intensity a function of the amount of organic matter reaching the hypolimnion from the productive upper zones of the lake (trophogenic zone).
- [O_2] in hypolimnion becomes more reduced and undersaturated as stratification progresses. In eutrophic lakes, the hypolimnion may be rapidly depleted of O_2 a few weeks after stratification begins; anaerobic metabolism results.
- Principal cause of O_2 depletion in hypolimnion is bacterial oxidation of organic matter in the water column and especially at the sediment-water interface where bacterial decomposition is greatest.
- Plant and animal respiration can consume large amounts of O_2 but major consumption in lakes is due to bacterial respiration in decomposition of sedimenting organic matter.
- O_2 consumption by bacteria is great in all water layers, but in hypolimnion this consumption is not offset by renewal mechanisms of circulation and P/S that occur in epilimnion.
- Shift from aerobic to anaerobic metabolism in the hypolimnion excludes large volume of lake for habitation by plants and animals. Also, the shift results in a marked reduction in the efficiency of decomposition of organic matter.
- Fall overturn causes O_2 saturated water to be carried down to hypolimnion. When circulation is complete, [O_2] continues at saturation in accordance with solubility at existing temperatures.
- Ice formation interrupts O_2 exchange. Based on solubility relationships would expect O_2 profile essentially constant at saturation in relation to temperature at depth in oligotrophic lakes where biotic influences are minor.
- Such a profile is rare in dimictic lakes. Usually see a significant reduction in [O_2] with depth, which is particularly acute near sediment. Mechanisms: P/S occurs during winter at reduced rates in eutrophic lakes. Respiratory and chemical oxidation utilizing O_2 increase with depth as before. If heavy and prolonged snow cover occurs, may get winter-kill .

Variations - Metalimnetic Oxygen Maxima

- Most common variation that occurs during stratification. Referred to as POSITIVE HETEROGRADE CURVE

- Solubility of O_2 in epilimnion decreases with increasing summer temperatures and O_2 consumption in hypolimnion results in clinograde reduction with depth, result is absolute oxygen maximum in the metalimnion which may be at or above saturation.
- Nearly always result of O_2 production by algal populations that are adapted to low temperatures and low light intensities of metalimnion; also have access to nutrient concentrations that are higher in lower metalimnion than in epilimnion.
- Depth of O_2 maxima is correlated with water transparency, usually found at 3-10 m.

Variations - Metalimnetic Oxygen Minima

- Exhibits NEGATIVE HETEROGRADE CURVE and is observed less frequently than maxima.
- Mechanisms behind formation are not clear: large amounts of oxidizable material produced in the epilimnion and brought into the lake from the drainage basin sinks continuously. Rate of sinking is slowed by the denser metalimnion allowing more time for bacterial decomposition. Decomposition is greater in metalimnion than the hypolimnion because temperatures are warmer.

- O_2 regime of most dimictic lakes of the temperate zone is governed largely by quantities of organic matter received during stratification, either produced within the lake or produced within the drainage basin and brought into the lake.
- Artificial loading of lakes with organic matter can effectively and rapidly exceed processing capacity of the lake. Resulting effects on aerobic organisms are direct and immediate. Indirect effects on biogeochemical cycling and productivity are more gradual.

OXYGEN DEFICITS

- **Absolute Oxygen Deficit** - difference between observed concentration at prevailing temperature and saturation value at 4 C. Problem: this measure assumes that oxygen content at spring circulation is the saturation value at 4 C, which may not be true.
- **Areal Hypolimnetic Oxygen Deficit (AHOD)** - amount of oxygen lost per unit area of hypolimnion per unit time between spring circulation and the height of summer stratification
- Since the amount of organic matter synthesized in the trophogenic zone (photic zone) that rains into and decomposes in the tropholytic zone (aphotic zone, usually metalimnion and hypolimnion) is reflected by the rate at which hypolimnetic oxygen is used, AHOD is often used as a general measure of the productivity of a lake.
- Note that the dynamics of oxygen utilization are not this simple and that some of the organic matter undergoing decomposition may be allochthonous, thus AHOD should be used cautiously and only in a general comparative way to approximate lake productivity.

REDOX POTENTIAL

- Change in oxidation state of metal ions and some nutrients is defined as REDOX or reduction-oxidation potential.
- Redox (E_h) is the electrical voltage which exists between 2 electrodes, one made of hydrogen and the other of the material under study.
- At neutral pH, 25 C, and fully oxygenated, most lakes have redox of about +500 mV, e.g., $E_7 = 500$ mV (7 indicates that redox is corrected to pH 7)
- Redox potential is related to pH and O_2 concentration: redox decreases by 58 mV per 1 pH unit increase; reduction in O_2 saturation from 100% to 10% decreases redox by 30 mV.
- Oxidizing and reducing conditions in lakes usually defined in relation to Fe system since it is an important substance that undergoes redox reactions that affects availability of nutrients
- Oxidizing Conditions - $E_7 > 200$ mV which means that Fe^{3+} (ferric iron) exists and is visible on sediments as a light brown, orange colour.
- Reducing Conditions - $E_7 < 200$ mV and ferrous iron (Fe^{2+}) exists. Ferrous iron gives sediments a black colour.

- Oxidizing conditions are thermodynamically stable and most oxidized forms of metals (Fe) and nutrients (N, P) are present, e.g., NO_2, NO_3, SO_4, Fe^{3+} salts
- Reducing conditions favour the formation of ammonia, Fe^{2+} salts, sulphides, etc.
- Reduced microzone is formed at sediment-water interface where most of redox reactions occur.

- Most redox reactions are carried out by bacteria which gain energy from converting substances to thermodynamically favoured state as O_2 and redox potentials change.
- Oxidized microzone on sediment surface is important since ferric Fe^{3+} is produced which binds with phosphate as insoluble oxide, trapping Fe, P in sediments.
- Low O_2 near mud-water interface lowers redox and releases nutrients such as PO_4^{3-} and reduced Ferrous Fe^{2+}. This occurs in lakes with clinograde oxygen profile.
- Redox changes are important to primary production in lakes.
- Redox can be measured but usually measuring DO is sufficient since it controls redox.

WATER CHEMISTRY SUMMARY

- Three major controlling parameters:
    1. Conductivity/salinity/ionic strength
    2. pH, which measures proton activity
    3. pE, which measures electron activity