Environmental Chemistry of Water

Lecture #2
### Table 11.1 Important Properties of Water

<table>
<thead>
<tr>
<th>Property</th>
<th>Effects and Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent solvent</td>
<td>Transport of nutrients and waste products, making biological processes possible in an aqueous medium</td>
</tr>
<tr>
<td>Highest dielectric constant of any common liquid</td>
<td>High solubility of ionic substances and their ionization in solution</td>
</tr>
<tr>
<td>Higher surface tension than any other liquid</td>
<td>Controlling factor in physiology; governs drop and surface phenomena</td>
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<tr>
<td>Transparent to visible and longer-wavelength fraction of ultraviolet light</td>
<td>Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water</td>
</tr>
<tr>
<td>Maximum density as a liquid at 4°C</td>
<td>Ice floats; vertical circulation restricted in stratified bodies of water</td>
</tr>
<tr>
<td>Higher heat of evaporation than any other material</td>
<td>Determines transfer of heat and water molecules between the atmosphere and bodies of water</td>
</tr>
<tr>
<td>Higher latent heat of fusion than any other liquid except ammonia</td>
<td>Temperature stabilized at the freezing point of water</td>
</tr>
<tr>
<td>Higher heat capacity than any other liquid except ammonia</td>
<td>Stabilization of temperatures of organisms and geographical regions</td>
</tr>
</tbody>
</table>
Sources and Uses of Water: The Hydrosphere

Contains or is covered by water including:
- Wetlands
- Oceans (97%)
- Rivers, Streams
- Lakes
- Ponds
- Groundwater (\& Soil water = 0.5%)
- Ice [snow packs, glaciers, polar ice caps] (2%)
- Atmosphere (0.0001%)

- Provides us with the water we drink
Sources and Uses of Water: Freshwater Availability

- Total Global Water
- 2.5% of Total Global Freshwater
- 97.5% Salt Water
- 68.9% Glaciers and Permanent Snow Cover
- 0.3% Freshwater Lakes and River Storage. Only this portion is renewable
- 0.9% Other including soil moisture, swamp water and permafrost
- 29.9% Fresh Groundwater

Sources and Uses of Water: Hydrologic Cycle

Take note of the processes involved in the hydrologic cycle

Ref.: http://www.uwsp.edu/geo/faculty/riter/geog101/modules/hydrosphere/hydrologic_cycle.html
Sources and Uses of Water: Water use

Water-use categories:
Public supply (water delivered to our homes and businesses)
Domestic (water use at home)
Commercial
Industry
Irrigation (water for growing crops, golf courses, etc.)
Thermoelectric power (electrical-power generation, other than hydroelectric)
Mining
Livestock (water for cows, chickens, horses, etc.)
Hydroelectric power (power produced at dams)
Wastewater treatment (sewage treatment)
Sources and Uses of Water: Water use

One way of better understanding the Nation's water use is to look at what we use water for, as represented by different categories of water use.

Ref.: http://ga.water.usgs.gov/edu/graphicshtml/totpie95.html
Water Use Trends in The USA

Water usage has been decreasing since the 1980s. Decrease is due to conservation and recycling particularly in industrial and agricultural (irrigation) sectors.

Figure 11.2 Trends in water use in the United States (data from U.S. Geological Survey).
Figure 11.1 The hydrologic cycle, quantities of water in trillions of liters per day.


**Problems Inhibiting Water supply**

1. Uneven distribution (particularly precipitation)

2. Deterioration of water system due to:
   a. Overdevelopment (e.g. Florida coast)
   b. Irrigation demands overpowering aquifers (e.g. Ogallala aquifers)
   c. Pollution
Characteristics of Bodies of Water

Types of bodies of water

**Surface water** – Streams, lakes, reservoirs

**Wetlands** – Flooded areas with shallow water table

**Estuaries** – Arms of the oceans into which streams flow thus enabling the mixing of fresh and salt water
Characteristics of Bodies of Water: 
Stratification

Epilimnion: from surface to thermocline. This region is hotter particularly in the summer

Thermocline: the region that has the steepest drop of temperature (or Metalimnion)

Hypolimnion: from below the thermocline to the bottom. This region is colder.

![Diagram of lake stratification](image.png)

Figure 11.4 Stratification of a lake.
Aquatic Chemistry: Fundamentals

Major aquatic Chemical processes

Figure 11.5 Major aquatic chemical processes.
**Water Quality: Alkalinity**

A measure of the buffering capacity of the Carbonate-Bicarbonate ions and, to some extent, the hydroxide ions of water.

These three ions all react with hydrogen ions to reduce acidity and raise pH.

\[
\begin{align*}
\text{HCO}_3^- + \text{H}^+ & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CO}_3^{2-} + \text{H}^+ & \rightarrow \text{HCO}_3^- \\
\text{OH}^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

Note: alkalinity (a measure of buffer capacity) is different from pH, a measure of H\(^+\) concentration.
Water Quality : Alkalinity

Alkalinity Unit:
ppm (mg/l) as calcium carbonate (CaCO₃) for all three ions

Water with:
- > 100 ppm CaCO₃ is considered alkaline and should be treated.
- < 100 ppm CaCO₃ is considered "soft" or mildly alkaline.
Water Quality: Alkalinity

Environmental Impact of Alkalinity:

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes.

Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes.

Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.
Water Quality: Acidity

Acidity is the ability of water system to neutralize OH⁻.

Acidity results from weak acids such as:
- \( \text{H}_2\text{PO}_4^- \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \) (major contributors)
- Protein, fatty acids
- Acidic metal ions (e.g. \( \text{Fe}^{3+} \), \( \text{Al}^{3+} \))

\[
\text{Al} (\text{H}_2\text{O})_6^{3+} \rightarrow \text{Al} (\text{H}_2\text{O})_5^{2+} + \text{H}^+ \\
\text{Fe} (\text{H}_2\text{O})_6^{3+} \rightarrow \text{Fe} (\text{H}_2\text{O})_5^{2+} + \text{H}^+
\]
**Water Quality : Acidity**

The term *free mineral acid* is used in place of acidity when strong acid such as $\text{H}_2\text{SO}_4$ and/or $\text{HCl}$ is the focus. Such as in acid mine water.

**Measurement:**

Total acidity is measured by titration to phenolphthalein end point ($\text{pH}=8.2$)

But methyl orange ($\text{pH} 4.3$) is used for determination of free mineral acid.
Water Quality : Acidity

Importance of acidity

- pH 6 – 9 is the best for aquatic life
- needed to calculate the amount of lime or chemical required for neutralizing acidic water.
Water Quality: Metal ions

Sources

Metal ions enter into water system through:

- Dissolutions of rock or soil containing the metals, usually in the form of metal salts. (e.g. Ca & Mg as their carbonates from limestone)

- Discharges from sewage treatment and industrial plants.
Water Quality: Metal ions

Major metal ions affecting chemistry of water are:
- $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ & $\text{Fe}^{3+}$
  - their $\text{CO}_3^{2-}$, $\text{HCO}_3^-$, & $\text{OH}^-$ impacts the alkalinity and hardness of water
  - Their concentration affects the toxicity of other metal ions

Minor constituents:
- $\text{Al}^{3+}$, $\text{Ba}^{2+}$, $\text{Cd}^{2+}$, $\text{Cr}^{3+}$, $\text{Pb}^{2+}$, $\text{Mn}^{2+}$, $\text{Zn}^{2+}$ & $\text{Na}^+$

The toxicity of metals depends on
  - solubility
  - pH
  - Chemical form (oxidation state, salt, complex etc)
  - Concentration of other cations
Water Quality: Metal Ions

Bare ions do not exist in water. They are hydrated with a shell of water or other strong bases – e.g. \( \text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow \text{Fe(H}_2\text{O)}_6^{3+} \)

They may bond or coordinate with other species present.

They may undergo various reactions:

1. **Acid-base**: \( \text{Fe(H}_2\text{O)}_6^{3+} \leftrightarrow \text{Fe(H}_2\text{O)}_5^{2+} + \text{H}^+ \)

2. **Precipitation**: \( \text{Fe(H}_2\text{O)}_6^{3+} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}_2\text{O} + \text{H}^+ \)

3. **Redox reaction**: \( \text{Fe(H}_2\text{O)}_6^{3+} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}_2\text{O} + \text{e}^- + \text{H}^+ \)

The metal ions undergo these processes to become more stable (achieve the least energetic electronic configuration).
Water Quality: Metal Ions

Various forms of metal ions include:

- Hydrated forms
- Hydroxy species
- Metal complexes (with organic and inorganic ligands)
- Organometallics (where metal is bonded directly to carbon in a compound)

The chemical form of a metal influences its:

- biological and chemical activities
- solubility,
- mobility or transport
- Bioaccumulation, bioavailability and toxicity
Water Quality: Metal Ions

Acidity of the hydrated metal ion:
- Decreases with increasing radius
- decreases in the order: $M^{3+} > M^{2+} > M^+$
Water Quality: Metal ions

Environmental Impact:

Ca & Mg are non-toxic and are easily absorbed by living organisms more readily than the other metals. Consequently, if the water is hard, the toxicity of a given concentration of a toxic metal is reduced.

Conversely, in soft, acidic water the same concentrations of metals may be more toxic.

At high pH, metal ions precipitate as their metal salts and are thus unavailable.
Aquatic organisms can bioaccumulate (or concentrate) certain metals (for example, mercury, lead, and cadmium).

*If more is absorbed than excreted, the levels can then build up over time to a toxic level.*

Permissible levels of metal in any water is determined by its intended use.

*Quality requirements vary for drinking, industrial, agricultural and recreational uses.*
Water Quality: Hardness

Hardness is due to the presence of multivalent metal ions which come from minerals dissolved in the water.

Ca and Mg are primarily responsible for hardness but Fe and Mn may also contribute.

Hardness is based on the ability of these ions to react with soap to form a precipitate or soap scum.

\[
2C_{17}H_{33}COO^- \cdot Na^+ + Ca^{2+} \rightarrow Ca(C_{17}H_{33}CO_2)_2(s) + Na^+
\]

Two kinds of hardness – Temporary and permanent.
Water Quality: Hardness

- Permanent hardness is caused by SO$_4^{2-}$, Cl$^-$ & NO$_3^-$ salts that remains after boiling.

- Temporary hardness is caused by CO$_3^{2-}$ and HCO$_3^-$ salts and can be removed by boiling:
  \[
  \text{Ca}^{2+} + 2 \text{HCO}_3^- = \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}
  \]

- Water with high concentration of CO$_2$ easily dissolves Ca from its carbonate:
  \[
  \text{CaCO}_3(s) + \text{CO}_2(g) = \text{Ca}^{2+} + 2 \text{HCO}_3^-
  \]
Water Quality: Hardness

• Concentration of dissolved CO$_2$ determines the extent of CaCO$_3$ dissolution

• The high concentration of Ca in freshwater is accounted for by CO$_2$ (g) from two sources:
  
  – CO$_2$ dissolved in water as a result of equilibrium between air and water
  
  – CO$_2$ produced as a result of biodegradation of organic matter in water, sediment and soil

{CH$_2$O} + O$_2$ $\rightarrow$ CO$_2$ + H$_2$O
Water Quality: Hardness

Environmental Impact:

Lowers the toxicity of other metals to aquatic life (e.g. Pb, Cd, Cr, & Zn).

Causes precipitation of other thereby reducing their bioavailability.

Hard water requires more soap and synthetic detergents for home laundry and washing,

Causes scaling in boilers and industrial equipment
# Water Quality: Hardness

## Classification of Water by Hardness Content

<table>
<thead>
<tr>
<th>Concentration mg/L CaCO₃</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 75</td>
<td>0 - 60</td>
</tr>
<tr>
<td>75 - 150</td>
<td>61 - 120</td>
</tr>
<tr>
<td>150 – 300</td>
<td>121 - 180</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>&gt;180</td>
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</tbody>
</table>

Ref. [http://water(nr.state.ky.us/ww/ramp/rmhard.htm](http://water.nr.state.ky.us/ww/ramp/rmhard.htm)

Water Quality: Hardness

Ref.: http://water.usgs.gov/owq/map1.jpeg