Water Chemistry 5

Evaluating Water Quality

WATER QUALITY ASSESSMENT

Water quality:
physical, chemical, biological characteristics

Acceptable quality varies with intended use, for example:
Recommended Threshold Odor Number is for drinking water is 3 whereas it is 0 for brewing
PHYSICAL CHARACTERISTICS: Turbidity

Turbidity – the clarity of water

Transparency of natural water bodies is affected by human activity, decaying plant matter, algal blooms, suspended sediments, and plant nutrients.

Turbidity provides an inexpensive estimate of total suspended solids TSS concentration.

Turbidity has little meaning except in relatively clear waters but is useful in defining drinking-water quality in water treatment.

Secchi disk measures how deep a person can see into the water (feet). Reflects euphotic zone. Can’t be used in shallow water.

Other methods for measuring turbidity are:

- Jackson Turbidity Units (JTU) depth candle can be seen
- Nephelometer Turbidity Units (NTU) light scattering from a tungsten lamp (white light)
- Formazin Nephelometric Units (FNU) light scattering from an LED (light emitting diode, infrared) calibration uses microspheres of the polymer formazin

Units are roughly equivalent.

Duration of Turbidity is an Important Factor

http://waterontheweb.org/under/waterquality/turbidity.html
Nephlometer Turbidity Units (NTU)

**PHYSICAL CHARACTERISTICS: Color**

Blue - Transparent water with low dissolved solids
<table>
<thead>
<tr>
<th>PHYSICAL CHARACTERISTICS: Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red - An iron mine pit lake in northeast Minnesota</td>
</tr>
<tr>
<td>(some algae cause red color)</td>
</tr>
</tbody>
</table>

**PHYSICAL CHARACTERISTICS: Color**
Left - Reddish-Orange - iron Precipitate from AMD
Right - Reddish Silt in Malaysia River
Green-Blue Tapajos meets the Brown-Yellow Amazon River
Brown-Yellow = dissolved organic materials, humic substances from soil, peat, or decaying plant material

PHYSICAL CHARACTERISTICS: Color
Green due to water rich in phytoplankton and other algae

http://www.ozestuaries.org/indicators/Images/swan_algae.jpg
www.samford.edu/schools/artsci/biology/wetlands/basics/importance.html
PHYSICAL CHARACTERISTICS: Color

Verbal descriptions of color are unreliable and subjective.

EPA Secondary Drinking Water Recommendation is for color of less than 15 Platinum Cobalt Units (PCU).

1 unit - the color of distilled water containing 1 milligram of platinum as potassium chloroplatinate per liter.

Color is reduced or removed from water through the use of coagulation, settling and filtration techniques.

PHYSICAL CHARACTERISTICS: Solids

Total Solids (TS) - the total of all solids in a water sample.

Total Suspended Solids (TSS) - the amount of filterable solids in a water sample; filters are dried and weighed.

Total Dissolved Solids (TDS) - nonfilterable solids that pass through a filter with a pore size of 2.0 micron, after filtration the liquid is dried and residue is weighed.

EPA Secondary Drinking Water Recommendation is for TDS of less than 500mg/L.

Volatile Solids (VS) - Volatile solids are those solids lost on heating to 500 degrees C - rough approximation of the amount of organic matter present in the solid fraction of wastewater.
PHYSICAL CHARACTERISTICS: Temperature

Temperature should be measured in the field.
Temperature affects a number of water quality parameters such as dissolved oxygen which is a chemical characteristic.

AESTHETIC CHARACTERISTICS: Odor Taste

<table>
<thead>
<tr>
<th>Compound</th>
<th>Odor</th>
<th>Evaluated Volume is 200mL</th>
<th>Threshold Odor Number TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin from algae</td>
<td>Earthy Grassy</td>
<td># of parts of sample mixed with distilled water per 200mL of mixture</td>
<td># when odor is first noticed when starting with a dilute sample in which odor cannot be detected</td>
</tr>
<tr>
<td>2-methylisoborneal from algae</td>
<td>Musty</td>
<td>200 (undiluted)</td>
<td>1</td>
</tr>
<tr>
<td>Amines from algae</td>
<td>Fishy</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Chlorine from disinfectants</td>
<td>Bleachy</td>
<td>70</td>
<td>3</td>
</tr>
<tr>
<td>Aldehydes from ozonation</td>
<td>Fruity</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>Iron or Manganese</td>
<td>Rusty Metallic</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>Iron bacteria</td>
<td>Earthy</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Ammonial</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>Hydrogen Sulfide from organisms/minerals</td>
<td>Rotten Eggs</td>
<td>8.3</td>
<td>24</td>
</tr>
<tr>
<td>Organic Sulfides</td>
<td>Rotten Cabbage</td>
<td>5.7</td>
<td>35</td>
</tr>
<tr>
<td>Methane gas</td>
<td>Garlic</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>Skatole (a compound in feces)</td>
<td>Fecal</td>
<td>2.8</td>
<td>70</td>
</tr>
</tbody>
</table>

EPA secondary standard for drinking water:

- Geosmin from algae: Earthy Grassy
- 2-methylisoborneal from algae: Musty
- Amines from algae: Fishy
- Chlorine from disinfectants: Bleachy
- Aldehydes from ozonation: Fruity
- Iron or Manganese: Rusty Metallic
- Iron bacteria: Earthy
- Ammonia: Ammonial
- Hydrogen Sulfide from organisms/minerals: Rotten Eggs
- Organic Sulfides: Rotten Cabbage
- Methane gas: Garlic
- Skatole (a compound in feces): Fecal
CHEMICAL CHARACTERISTICS

Commonly measured chemical parameters are:

- pH
- Alkalinity
- Hardness
- Nitrates, Nitrites, & Ammonia
- Phosphates
- Dissolved Oxygen & Biochemical Oxygen Demand

Portable laboratories and test kits

Chemical Characteristics: pH

The pH of water determines the solubility of many ions and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium).

EPA secondary drinking water recommendation pH 6.5 ~ 8.5
Chemical Characteristics pH – Scaling/Corrosion

Influences whether a water will be scale-forming or corrosive

Langelier Saturation Index (LSI)
- Determines if calcium carbonate will precipitate
  - LSI = pH – pHₘ
  - pH = actual pH value measured in the water
  - pHₘ = pH of the water in equilibrium with solid CaCO₃
  - If LSI > 0 calcium carbonate will precipitate
  - If LSI < 0 calcium carbonate won’t precipitate

\[
\begin{array}{c|c|c|c|c}
\text{pHₘ – precipitate} & \text{pHₘ – no precipitate} \\
1 & 14 \\
\end{array}
\]

Ryznar Index
- Determines the degree of scale formation versus corrosion
  - RI = 2 pHₘ – pH
  - If RI < 5.5 heavy scale will form
  - If 5.5 < RI < 6.2 scale will form
  - If 6.8 < RI < 8.5 water is corrosive
  - If RI > 8.5 water is very corrosive

<table>
<thead>
<tr>
<th>Scale Formation</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy</td>
<td>5.5</td>
</tr>
<tr>
<td>Neutral</td>
<td>6.2</td>
</tr>
<tr>
<td>Corrosive</td>
<td>6.8</td>
</tr>
<tr>
<td>Very Corrosive</td>
<td>8.5</td>
</tr>
</tbody>
</table>

\[
\text{pH of the water in equilibrium with solid CaCO}_3 = -\log \left( \frac{\gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}] \gamma_{\text{HCO}_3^-} [\text{HCO}_3^-]}{K_{SP}} \right)
\]

where 
\[
K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \text{equilib constant}
\]
\[
\gamma_i = \text{activity coeff}
\]
\[
K_{SP} = \text{solubility product}
\]
Determine the Langelier & Ryznar indexes for the Denver water supply

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Conc. (mg/L)</th>
<th>Conc. (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>179</td>
<td>-</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>42</td>
<td>1.05 x 10^{-3}</td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>115</td>
<td>1.89 x 10^{-3}</td>
</tr>
</tbody>
</table>

pH = 7.9, Temp = 20°C

Determine the value of pH_s
Determine the Langelier index
Determine the Ryznar index

Carbonate Equilibrium Constants as a Function of Temperature

<table>
<thead>
<tr>
<th>T, °C</th>
<th>K_m</th>
<th>K_1</th>
<th>K_2</th>
<th>K_{sp}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.02 x 10^{-7}</td>
<td>2.75 x 10^{-11}</td>
<td>8.13 x 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3.46 x 10^{-7}</td>
<td>3.24 x 10^{-11}</td>
<td>7.08 x 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>3.80 x 10^{-7}</td>
<td>3.72 x 10^{-11}</td>
<td>6.03 x 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.17 x 10^{-7}</td>
<td>4.17 x 10^{-11}</td>
<td>5.25 x 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.58 x 10^{-3}</td>
<td>4.47 x 10^{-7}</td>
<td>4.68 x 10^{-11}</td>
<td>4.57 x 10^{-9}</td>
</tr>
<tr>
<td>40</td>
<td>5.07 x 10^{-7}</td>
<td>6.03 x 10^{-11}</td>
<td>3.09 x 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>5.07 x 10^{-7}</td>
<td>7.24 x 10^{-11}</td>
<td>1.82 x 10^{-9}</td>
<td></td>
</tr>
</tbody>
</table>

K_m = \frac{[H_2CO_3]}{[CO_2]_{aq}} \quad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}

K_{sp} = \text{Solubility product for CaCO}_3

pH = 7.9, Conc. (mol/L)

Ca^{2+} 1.05 x 10^{-3}
HCO_3^- 1.89 x 10^{-3}
Chemical Characteristics: RedOx Potential

Redox = Oxidation + Reduction
Oxidation: substance loses or donates electrons (e⁻)
Reduction: substance gains or accepts electrons (e⁻)

OILRIG Oxidation Is Loss Reduction Is Gain

Redox reactions can be thought of as reactions involving transfer of oxygen

\[ 2Mg + O_2 = 2MgO \]

In solution chemistry it is generally more convenient to consider redox reactions as electron transfers

\[ Fe^{3+} + e^- = Fe^{2+} \]

The redox potential is a number defining how much gaining or losing of e⁻ a system might do – essentially activity of electrons (unit in volts)

Chemical Characteristics RedOx Potential Eh

Redox Potential can be measured on site

Redox Potential (Eh) can be calculated using the Nernst equation:

\[ Eh = E^0 + \frac{RT}{nF} \ln K_{sp} \]

where
- \( E^0 \) = standard potential (at 25°C & 1 atm pressure)
- R = gas constant (kcal/(mol*K))
- T = temperature (K)
- F = Faraday constant (23.1 kcal/V)
- n = number of electrons transferred in the reaction (or \( \frac{1}{2} \) reaction)
- \( K_{sp} \) = solubility product

\( \log K_{sp} = \frac{-\Delta G^°}{2.303RT} \)

Eh of groundwater generally ranges from -400 to 800 millivolts (mV)

Measure Eh during purging and immediately before and after sampling using a direct-reading meter because purging can aerate the water and change the chemistry.
Redox reactions in groundwater are usually controlled by microbial activity so Eh depends upon and influences rates of biodegradation.

Eh can be an indicator of some geochemical activities (e.g., sulfate reduction).

Eh of groundwater indicates location of contaminant plumes undergoing anaerobic biodegradation due to lower Eh in the plume than upgradient.

Biodegradation can reduce contaminants in groundwater (natural and enhanced).

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**Eh-pH DIAGRAM**

- Stability limits of water at 25°C and 1 bar
- At conditions above the top dashed line, water is oxidized to O₂
- At conditions below the bottom dashed line, water is reduced to H₂
- No natural water can persist outside these stability limits for any length of time
- Water in nature is usually between pH 4 and pH 9
Eh-pH conditions of waters in various environments

**Eh-pH DIAGRAM**

Eh-Ph diagram can be used to show the fields of stability for solid & dissolved ionic species.

Iron will be mobile in groundwater only under the Eh-pH conditions where Fe²⁺ and Fe³⁺ are stable in the diagram (i.e. under strongly acidic conditions at any Eh, or under reducing conditions under typical pH conditions).
Chemical Characteristics: HARDNESS
high multi-valent ion content

Hard water is found in about 85% of USA

Prevents lathering/sudsing - hotter water and extra rinse cycles may be required

Fabric appearance declines & life may be reduced

Minerals may clog pipes & cause excessive wear on moving parts

Solutions:
– Distill water to remove the calcium and magnesium
– Soften the Water - Replaces calcium and magnesium ions with sodium or potassium ions
– Cation exchange
  Strong adsorption » » » Weak adsorption
  \[ Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+ > H^+ \]
HARDNESS
measured in grains per gallon gpg

1 grain of hardness = the amount of calcium and magnesium equal in weight to a kernel of wheat

1 grain = 64.8 mg of calcium carbonate dissolved in 1 gallon
= 1 part in 70,000 parts of water
= 14.3 ppm

<table>
<thead>
<tr>
<th>Classification</th>
<th>mg/l or ppm</th>
<th>grains/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>0 - 17.1</td>
<td>0 - 1</td>
</tr>
<tr>
<td>Slightly hard</td>
<td>17.1 - 60</td>
<td>1 - 3.5</td>
</tr>
<tr>
<td>Moderately hard</td>
<td>60 - 120</td>
<td>3.5 - 7.0</td>
</tr>
<tr>
<td>Hard</td>
<td>120 - 180</td>
<td>7.0 - 10.5</td>
</tr>
<tr>
<td>Very Hard</td>
<td>180 &amp; over</td>
<td>10.5 &amp; over</td>
</tr>
</tbody>
</table>

http://water.usgs.gov/owq/hardness-alkalinity.html
Chemical Characteristics: NITROGEN (N)

Nitrogen gas (N₂) makes up 78.1% of the Earth’s atmosphere.

An essential nutrient required by all plants and animals for formation of amino acids (the molecular units that make up protein).

N must be "fixed" (combined) in the form of ammonia (NH₃) or nitrate (NO₃⁻) to be used for growth:
- \( \text{N}_2 + 8\text{H}^+ + \text{bacteria} = 2\text{NH}_3 + \text{H}_2 \)
- \( \text{NH}_3 + \text{O}_2 + \text{bacteria} = \text{NO}_2^- + 3\text{H}^+ + 2\text{e}^- \)
- \( \text{NO}_2^- + \text{H}_2\text{O} + \text{bacteria} = \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \)

Ammonia NH₃ (extremely toxic) continually changes to ammonium NH₄⁺ (relatively harmless) and vice versa, relative concentration depends on temperature & pH.

At higher temperatures and pH, more N is in the ammonia form.

NITROGEN cycle
5 main processes cycle nitrogen through the bio atmos & geosphere:
- nitrogen fixation
- nitrogen uptake (organism growth)
- nitrogen mineralization (decay)
- nitrification
- denitrification

http://www.mhhe.com/biosci/genbio/tlw3/eBridge/Chp29/animations/ch29/1_nitrogen_cycle.swf
### Chemical Characteristics: NITROGEN (N)

**Maximum Contaminant Level (MCL):**

- nitrite-N : 1 mg/L
- nitrate-N : 10 mg/L
- nitrite + nitrate (as N) : 10 mg/L

**Sources:**
- Fertilized areas; Sewage disposal; Feed lots; N cycle

**Potential Problems:**

- Infants <6mo convert nitrate to nitrite due to higher pH in their digestive system & could become seriously ill, and may die if untreated because the nitrite diminishes oxygen carrying capacity of their blood
- Excessive concentrations can lead to eutrophication

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### Chemical Characteristics: PHOSPHATES

**Secondary Drinking Water Standard EPA recommendation**

- total phosphate should be <0.05 mg/L (as phosphorus) in a stream where it enters a lake or reservoir
- total phosphate should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs

**Sources:**
- Erosion; Fertilizer; Sewage; Feed lots; Detergents

**Potential Problems:**

- Excessive concentrations can lead to eutrophication
- >4g/day may cause gastrointestinal discomfort & decrease bone density
EUTROPHICATION

increase in nutrients (typically nitrogen or phosphorus) resulting in excessive plant growth and decay, reducing oxygen availability

Eutrophication can cause too much plant growth either making food sources for fish inaccessible or literally suffocating them due to oxygen deprivation

Chemical Characteristics: DISSOLVED OXYGEN

Dissolved Oxygen DO mg/L – only gas routinely measured in water samples (depends on temperature, salinity, and pressure)

Analysis should be performed on site immediately after sampling

Oxygen enters the water by photosynthesis of aquatic biota transfer across the air-water interface

DO < 5mg/L stresses aquatic life (the lower the concentration, the greater the stress)

DO dependence on Temperature

www.woonasquatucket.org/waterqualitydata2005.htm
Biological Characteristics: FECAL COLIFORMS

Harmless bacteria ~ present in large numbers in feces and intestinal tracts of humans and other warm-blooded animals.

Environmental Impact
- Indicator of contamination with human or animal fecal material
- May indicate contamination by pathogens or disease producing bacteria or viruses

Criteria
- Swimming ~ fewer than 200 colonies/100 mL
- Fishing and boating ~ fewer than 1000 colonies/100 mL
- Domestic water supply ~ fewer than 2000 colonies/100 mL
- Drinking water ~ 0 colonies/100 mL

Biological Characteristics: BIOCHEMICAL OXYGEN DEMAND (BOD)

Biological Oxygen Demand is a measure of oxygen used by microorganisms to decompose organic waste (add a microorganism seed to all samples, seal sample from air, store in dark to prevent photosynthesis, subtract seeded control, measure decrease in DO).

Nitrates & phosphates are plant nutrients so may contribute to high BOD levels.

When BOD levels are high, dissolved oxygen decreases ⇒ fish and other aquatic organisms may not survive.

An index of the degree of organic pollution in water
- BOD level of 1-2 ppm - very good
- BOD level of 3-5 ppm - moderately clean
- BOD level of 6-9 ppm - somewhat polluted
Benthic macroinvertebrates are examined to assess the biological attributes of water quality. Their presence indicates a high quality of water, while their absence suggests water may be polluted.

**Biological Characteristics Specific to Surface Water**

[Image of Hess sampler]

**Water Quality Information References**

- **Colorado Department of Public Health and Environment - Water Quality Control Division**
  - [http://www.cdphe.state.co.us/wq/wqhom.asp](http://www.cdphe.state.co.us/wq/wqhom.asp)

- **U.S. EPA - National Primary Drinking Water Regulations**
  - [http://www.epa.gov/safewater/mcl.html](http://www.epa.gov/safewater/mcl.html)

- **U.S. Geological Survey - National Water Quality Assessment Program**

- **U.S. Department of Agriculture – Water Quality Information Center**