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

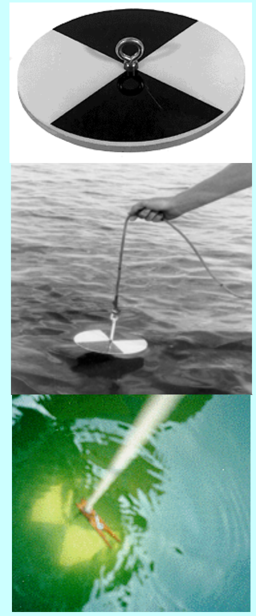
Turbidity has little meaning except in relatively clear waters but is useful in defining drinking-water quality in water treatment

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

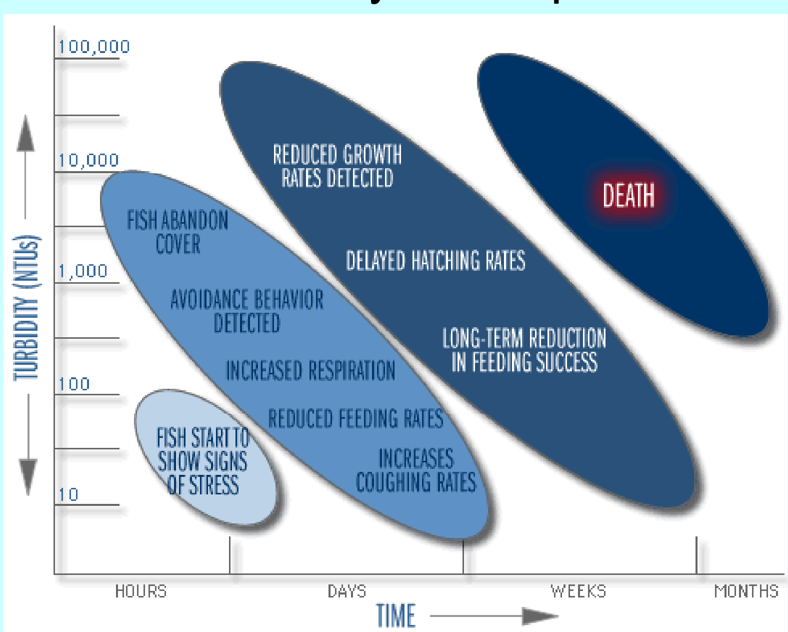
Other methods for measuring turbidity are

Jackson Turbidity Units (JTU) depth candle can be seen
Nephlometer 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 <u>roughly</u> equivalent



Duration of Turbidity is an Important Factor



http://waterontheweb.org/under/waterquality/turbidity.html

Nephlometer Turbidity Units (NTU)

PHYSICAL CHARACTERISTICS: Color

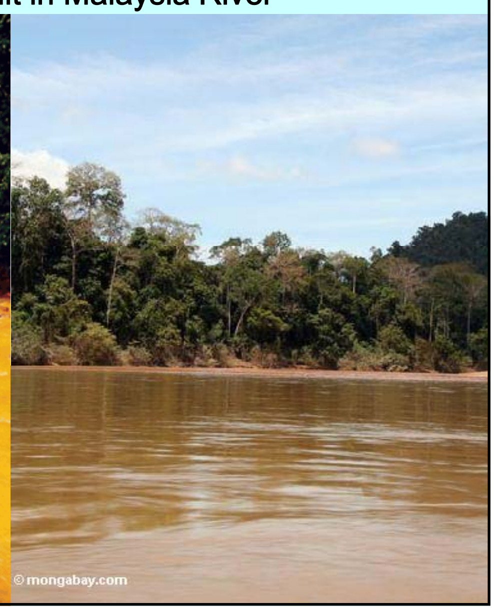
Blue - Transparent water with low dissolved solids

PHYSICAL CHARACTERISTICS: Color

Red - An iron mine pit lake in northeast Minnesota
(some algae cause red color)

PHYSICAL CHARACTERISTICS: Color

Left - Reddish-Orange - iron Precipitate from AMD
Right - Reddish Silt in Malaysia River



PHYSICAL CHARACTERISTICS: Color

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

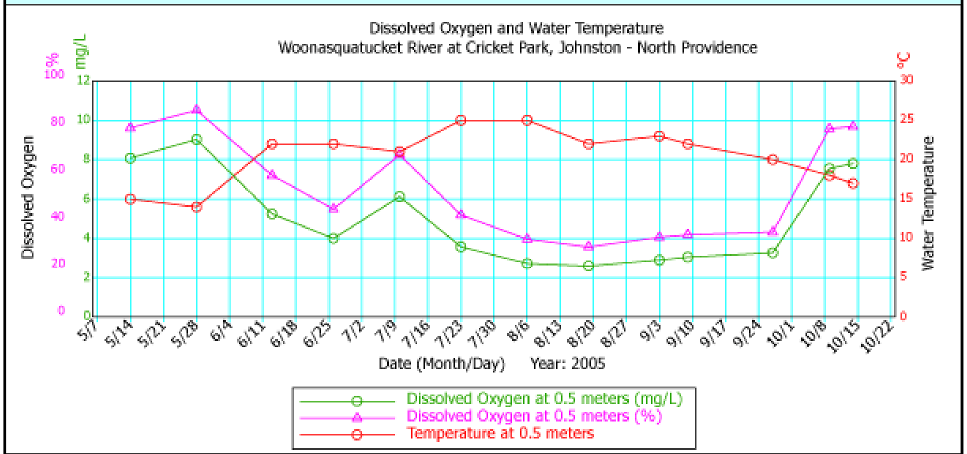
Total Dissolved Solids (TDS) - nonfilterable solids that pass through a filter with a pore size of 2.0 micron, after filtration the liquid is dried and residue is weighed

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



www.woonasquatucket.org/waterqualitydata2005.htm

AESTHETIC CHARACTERISTICS: Odor Taste

Compound	Odor
Geosmin from algae	Earthy Grassy
2-methylisoborneal from algae	Musty
Amines from algae	Fishy
Chlorine from disinfectants	Bleachy
Aldehydes from ozonization	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

Evaluated Volume is 200mL # of parts of sample mixed with distilled water per 200mL of mixture	Threshold Odor Number TON # when odor is first noticed when starting with a dilute sample in which odor cannot be detected
200 (undiluted)	1
100	2
70	3
50	4
35	6
25	8
17	12
8.3	24
5.7	35
4	50
2.8	70
2	100

EPA secondary standard for drinking water

CHEMICAL CHARACTERISTICS

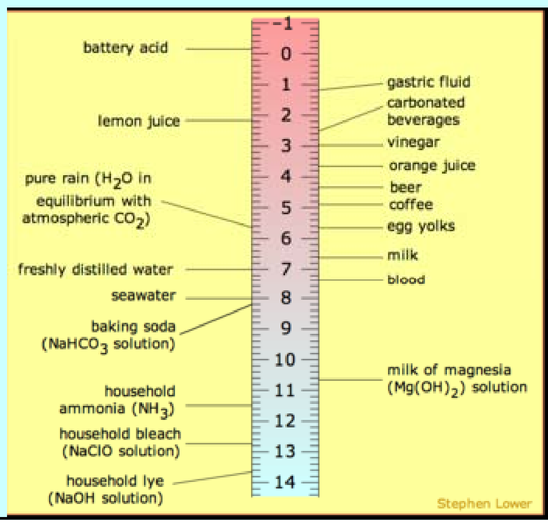
Commonly measured chemical parameters are:

- 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)



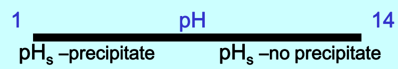
EPA secondary drinking water recommendation pH 6.5 ~ 8.5

Chemical Characteristics pH – Scaling/Corrosion

Influences whether a water will be scale-forming or corrosive

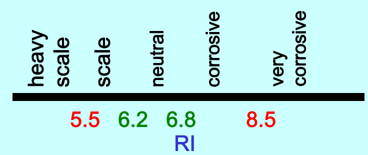
Langelier Saturation Index (LSI)

- Determines if calcium carbonate will precipitate
  - LSI = pH – pH_s
  - pH = actual pH value measured in the water
  - pH_s = pH of the water in equilibrium with solid $CaCO_3$
  - If LSI > 0 calcium carbonate will precipitate
  - If LSI < 0 calcium carbonate won't precipitate



Ryznar Index

- Determines the degree of scale formation versus corrosion
  - RI = 2 pH_s – 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



Chemical Characteristics pH – Scaling/Corrosion

pH of the water in equilibrium with solid $CaCO_3$

$$pH_S = -\log\left(\frac{K_2\,\gamma_{Ca^{+2}}[Ca^{+2}]\,\gamma_{HCO_3^-}[HCO_3^-]}{K_{SP}}\right)$$

$$\text{where}\quad K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = \text{equilib constant}$$

$$\gamma_i = \text{activity coeff}$$

$$K_{SP} = \text{solubility product}$$

Determine the Langelier & Ryznar indexes for the Denver water supply

Constituent	Conc. (mg/L)	Conc. (mol/L)
TDS	179	-
Ca^{+2}	42	1.05×10^{-3}
HCO_3^-	115	1.89×10^{-3}
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

T, °C	K_m	K_1	K_2	K_{sp}
5		3.02×10^{-7}	2.75×10^{-11}	8.13×10^{-9}
10		3.46×10^{-7}	3.24×10^{-11}	7.08×10^{-9}
15		3.80×10^{-7}	3.72×10^{-11}	6.03×10^{-9}
20		4.17×10^{-7}	4.17×10^{-11}	5.25×10^{-9}
25	1.58×10^{-3}	4.47×10^{-7}	4.68×10^{-11}	4.57×10^{-9}
40		5.07×10^{-7}	6.03×10^{-11}	3.09×10^{-9}
60		5.07×10^{-7}	7.24×10^{-11}	1.82×10^{-9}

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

K_{sp} = Solubility product for $CaCO_3$

pH = 7.9	Conc. (mol/L)
Ca^{+2}	1.05×10^{-3}
HCO_3^-	1.89×10^{-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 ½ reaction)
K_{sp} **= solubility product** $(\log K_{SP} = \frac{-\Delta_r G^o}{2.303RT})$

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

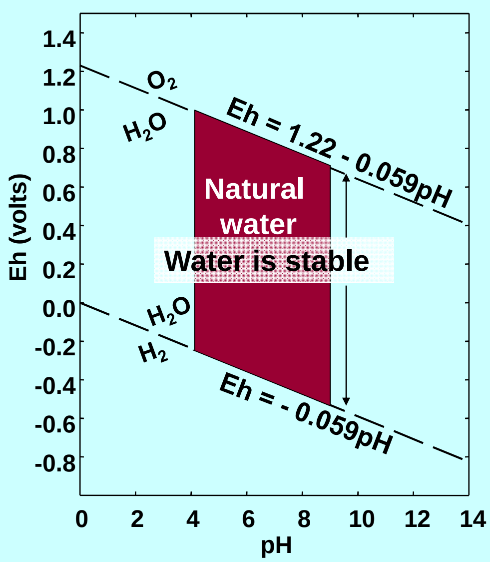
Redox reactions in groundwater are usually controlled by microbial activity so Eh depends upon and influences rates of biodegradation

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)

Eh-pH DIAGRAM



Stability limits of water at 25°C and 1 bar

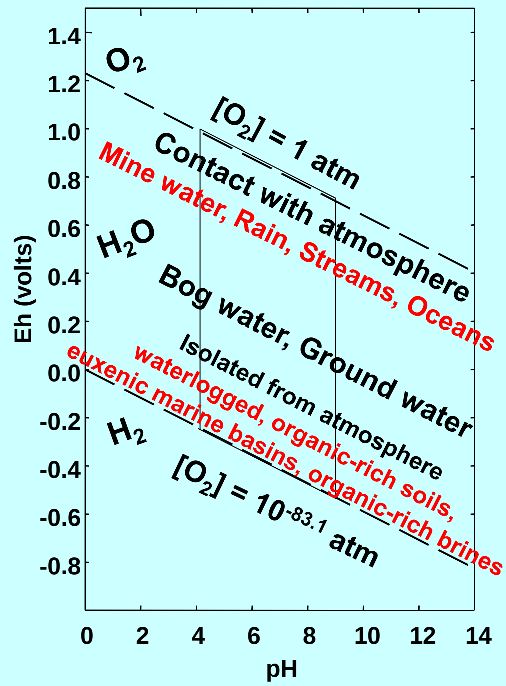
At conditions above the top dashed line, water is oxidized to O_2

At conditions below the bottom dashed line, water is reduced to H_2

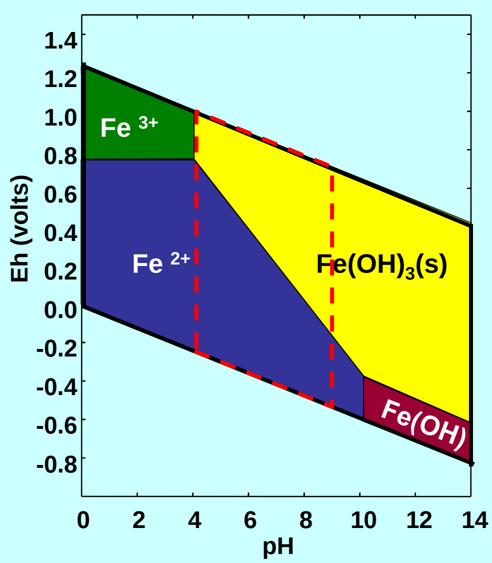
No natural water can persist outside these stability limits for any length of time

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 Fe^{2+} and Fe^{3+} 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

  $Al^{+3} > Ca^{+2} > Mg^{+2} > K^{+} = NH_4^{+} > Na^{+} > H^{+}$

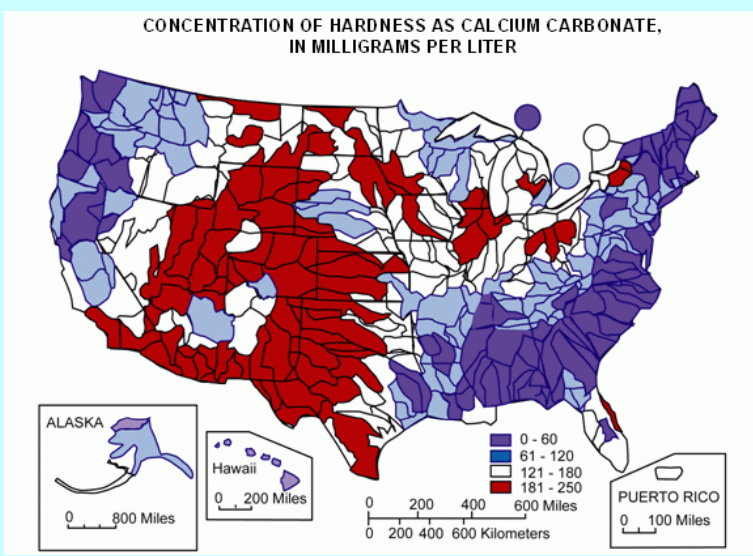
Web images from various commercial water softening web sites

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

Classification	mg/l or ppm	grains/gal
Soft	0 - 17.1	0 - 1
Slightly hard	17.1 - 60	1 - 3.5
Moderately hard	60 - 120	3.5 - 7.0
Hard	120 - 180	7.0 - 10.5
Very Hard	180 & over	10.5 & over



http://water.usgs.gov/owq/hardness-alkalinity.html

Chemical Characteristics: NITROGEN (N)

Nitrogen gas (N_2) 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 (NH_3) or nitrate (NO_3) to be used for growth

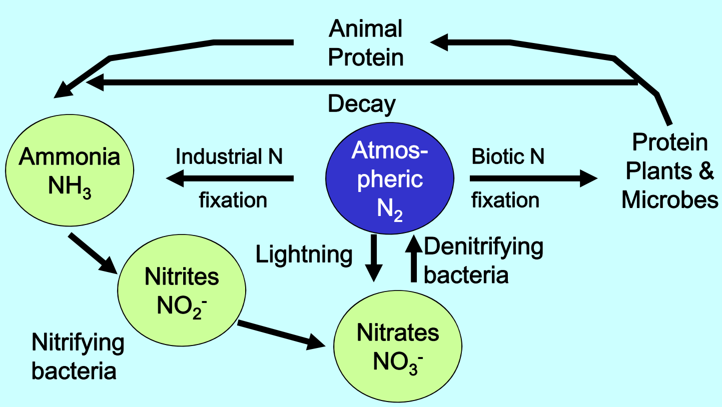
- $N_2 + 8H^+ + \text{bacteria} = 2NH_3 + H_2$
- $NH_3 + O_2 + \text{bacteria} = NO_2^- + 3H^+ + 2e^-$
- $NO_2^- + H_2O + \text{bacteria} = NO_3^- + 2H^+ + 2e^-$

Ammonia NH_3 (extremely toxic) continually changes to ammonium NH_4^+ (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 caryying capacity of their blood

Excessive concentrations can lead to eutrophication

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

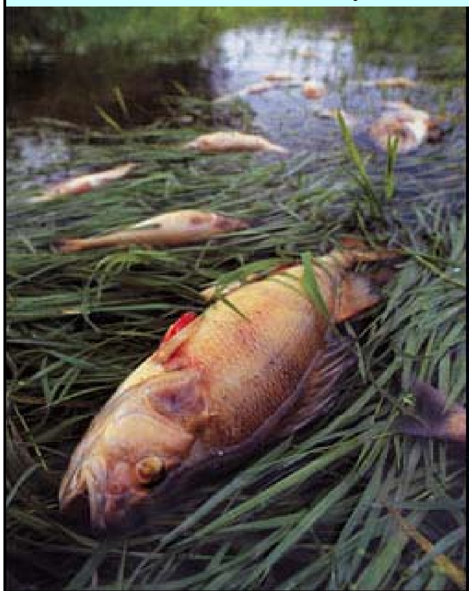
Potential Problems:

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



 Sources: http://www.whoi.edu/oceanus/viewArticle.do?id=2487 (left) and http://www.unep.or.jp/ietc/publications/short_series/lakereservoirs-3/IMG/photo_04.gif (right)

Chemical Characteristics: DISSOLVED OXYGEN

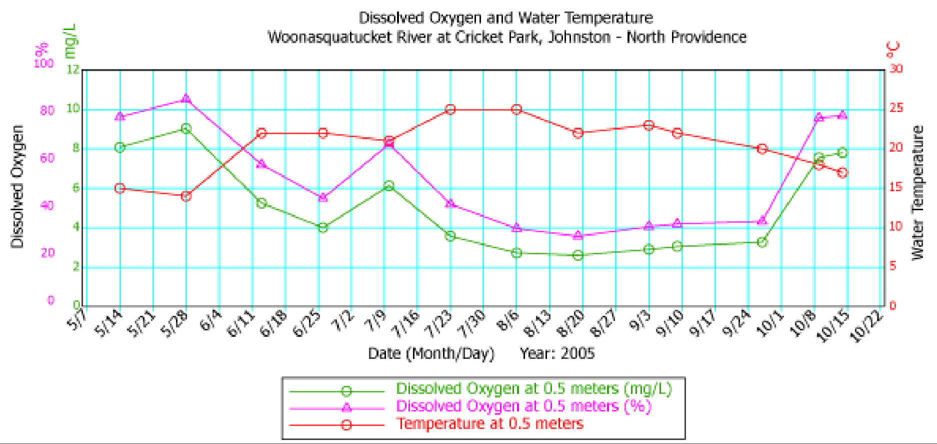
Dissolved Oxygen DO mg/L – only gas routinely measured in water samples (depends on temperature, salinity, and pressure)

Analysis should be performed on site immediately after sampling

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

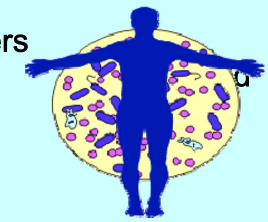
DO < 5mg/L stresses aquatic life (the lower the concentration, the greater the stress)

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 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

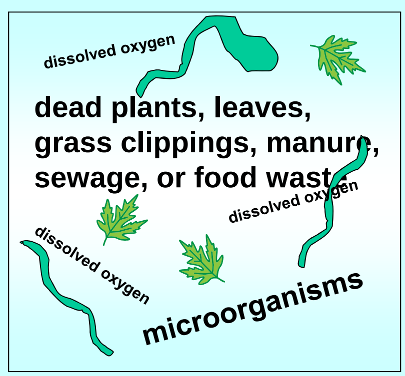
Criteria
- Swimming ~ fewer than 200 colonies/100 mL
- Fishing and boating ~ fewer than 1000 colonies/100 mL
- Domestic water supply ~ fewer than 2000 colonies/100 mL
- Drinking water 0 colonies/100mL

Biological Characteristics:
BIOCHEMICAL OXYGEN DEMAND (BOD)

Biological Oxygen Demand is a measure of oxygen used by microorganisms to decompose organic waste (add a micororganism 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

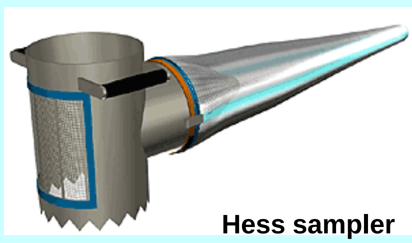


An index of the degree of organic pollution in water
BOD level of 1-2 ppm - very good
BOD level of 3-5 ppm - moderately clean
BOD level of 6-9 ppm - somewhat polluted

Biological Characteristics Specific to Surface Water

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.



Water Quality Information References

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

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

U.S. Geological Survey - National Water Quality Assessment Program
- **http://water.usgs.gov/nawqa/**

U.S. Department of Agriculture – Water Quality Information Center
- **http://www.nal.usda.gov/wqic/**