Water constituents

What's in water

- **Microorganisms**
  - Native vs. Introduced; Oligotrophic vs. Eutrophic
  - Millions to billions per mL or g
  - Complex consortia
    - Species makeup: f(T, O_2, pH, nutrients, etc.)
  - Indicators & pathogens

- **Dissolved inorganics**
  - Major vs. trace
  - Nutrient vs. contaminant

What's in water

- **Dissolved organics (DOM)**
  - Simple vs. polymeric
  - Biodegradable vs. recalcitrant
  - Natural vs. anthropogenic

- **Suspended matter**
  - Operational definition: retained on 0.45 µm-filter
    - Mineral colloids; organic polymers; bacteria
    - Aggregation & sorption
  - Contaminant sink, transport consequences

Microbes

- **$C_5H_7O_2N$ – approx. microbial chemical formula**
  - Dry weight basis; Cell is composed of ~90% water by weight
- **Other major constituents**
  - P: ~0.07 mole/mole cell material
  - S, Mg, Ca, K, Na: ~0.02-0.03 mole/mole cell material
  - Fe: more than trace, less than major
- **Trace constituents**
  - Cr, Co, Mn, Mo, Ni, Se, W, V, Zn
  - Constituents of enzyme systems
  - Need a little, but ***too much is toxic***

Dissolved inorganics

- **Major constituents of surface & groundwaters (ppm+)**
  - Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, SiO_2
- **Others important to life (ppb~ppm)**
  - O_2; Fe; N (NO_3^-, NH_3); P (PO_4^{3-})
    - N & P: rapid uptake by biota
    - P: strongly sorbed to minerals
    - Fe: low solubility in aerobic waters (Fe^{3+}) and moderate pH
- **Special cases**
  - Oxygen absent: high Fe^{2+}, S^{2-}
  - Low pH – high Fe^{3+}
- **Total dissolved solids (TDS): primarily ions**
  - Surface water < groundwater < seawater

Dissolved inorg. - electroneutrality

- **Electroneutrality principle**

$$\sum cations\ (in\ eq/L) = \sum anions\ (in\ eq/L)$$

- **May use the following condition to determine the accuracy of water ion content analysis**

$$\left|\sum anions - \sum cations\right| \leq \left(0.1065 + 0.0155 \sum anions\right)$$

** ∑ values in meq/L*

Dissolved inorg. - electroneutrality

- **Ionic strength**

$$I = \frac{1}{2}\sum_i (C_i \times {z_i}^2)$$

C_i = concentration of ionic species i (M)

z_i = charge of ionic species i

  - Significance: in dilute solutions (*I* ~< 10^{-3} M) the ions behave independently of each other, but as ion concentration increases, ion interactions become significant, decreasing the activity of the ions

- **Activity vs. molarity ({ } vs. [ ])**

$$\{i\} = \gamma_i [i]$$

  - $\gamma_i \cong 1$ in dilute solutions (for most natural waters except for seawater, this would be acceptable for crude calculations)
  - Güntelberg equation (for *I* < 0.1):

$$log_{10}\,\gamma_i = -\frac{0.5{z_i}^2 I^{0.5}}{1 + I^{0.5}}$$

Organics in natural waters

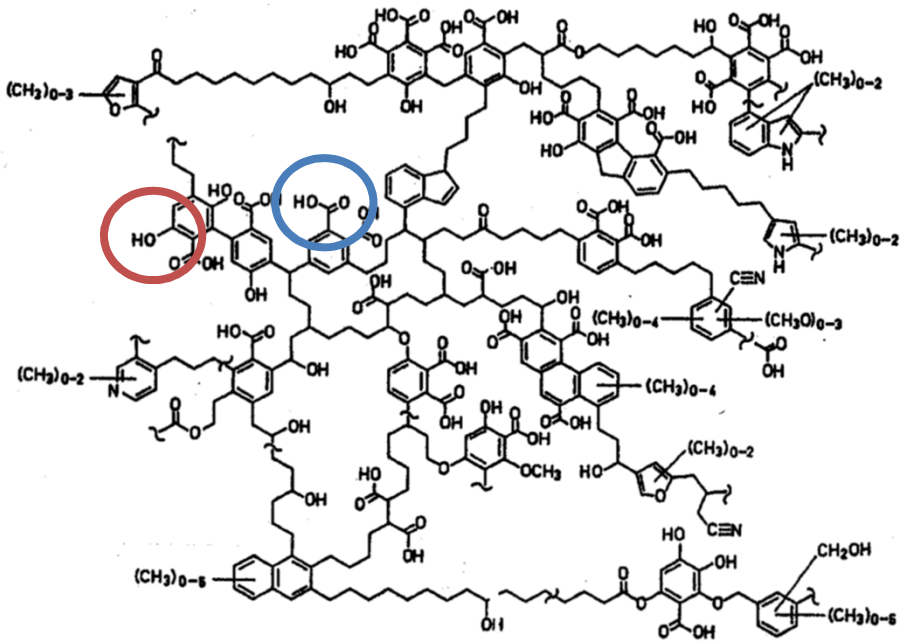
- **Simple sugars, amino acids, etc.**
  - Concentrations typically very low – easily degraded, assimilated
- **Microbial polymers**
  - Important components of biofilms, flocs, aggregates
  - In some cases may have significant dissolved concentrations
- **Humic substances**
  - Typically the primary component of dissolved & particulate organic matter (DOM, POM)
    - Resistant to degradation
    - Many ions & hydrophobic compounds sorb strongly to humics

Organics in natural waters

- **Anthropogenic organics**
  - >100,000 synthetic chemicals in daily use
    - Pesticides, solvents, dyes, personal care products, anti-fouling agents, additives
    - >300,000,000 tons produced annually
  - Wide varying properties
    - Size, aqueous solubility, volatility, degradability, toxicity

Dissolved organics – humic substances

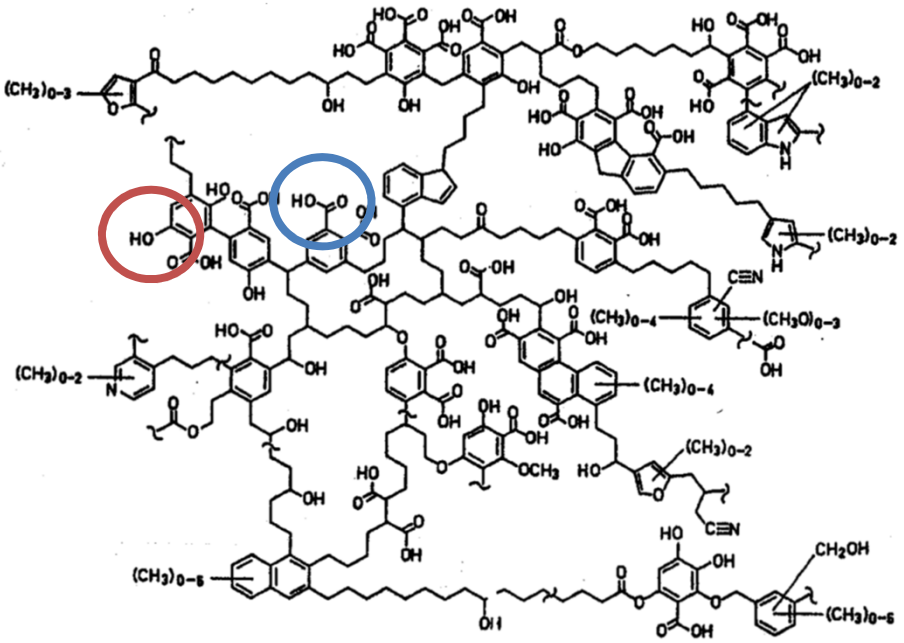
- **Acidic polymers**
  - ~3-15 mmoles/g, primarily
    - carboxylic
    - Phenolic OH
- **Wide varying composition**
  - There is no “humic molecule”
  - MWs from ~500 to >100,000

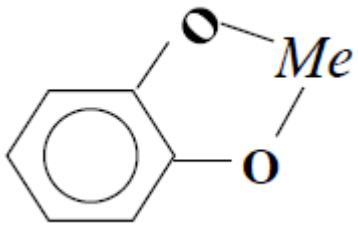


- **Molecular volume a function of pH, ionic strength**
  - Compact at high salinity, low pH
  - Extend at low salinity, high pH

Dissolved organics – humic substances

- **Hydrophilic/hydrophobic regions**
  - High affinity for many toxic organics
- **Coat minerals**
- **Photoactive**
- **High metal affinity**





Suspended matter

- **Not dissolved; potentially settleable (usually)**
  - Traditionally considered to be a material that retained on a 0.45 µm-filter
    - Colloids may be as small as a few nanometers

- **Includes: mineral colloids, microbes and their debris, organic polymers**
  - Often found as aggregates, flocs that are mixtures of minerals, polymers, and microbial matter
  - Aggregates >0.45 µm may consist of many individual components <<0.45 µm

Suspended matter

- **Suspended mater influences:**
  - Contaminant transport
  - Light attenuation
  - Disinfection efficiency

http://chasebc.ca

Aqueous chemistry parameters

- **Units**
  - Mass/vol — kg/m^3, mg/L, …
  - #/vol — mole/L, # of organisms/mL
  - Transferable electrons or protons/vol — eq./L, meq./L
  - Mole fraction — mole/∑mole
- **Why different units?**
  - Engineers vs. chemists
  - Specific needs of the problem
- **Aggregate parameters**
  - BOD, COD, TOC
  - Hardness
  - Total PCBs

Aqueous chemistry parameters

- **Aggregate parameters**
  - Characterize important properties of mixtures
    - __OD (oxygen demand)
    - TO__ (total organic carbons (C), halides (X))
  - Conduct one analysis instead of many

- **__per__as__**
  - mg/L as $CaCO_3$ (for alkalinity & hardness)
  - mg/L as N
  - % as P_2O_5 or K_2O

Measures of (oxidizable) organic matter

- **BOD – Biochemical Oxygen Demand**
  - Measure of a water's biologically oxidizable constituents
    - Analyze [DO] in a water sample before & after controlled incubation
    - 5 day incubation is common
- **COD – Chemical Oxygen Demand**
  - Measure of a water's chemically oxidizable constituents
    - 2-3 hour reaction time
    - Generates liquid hazardous wastes
  - Doesn't oxidize organic N
- **TOC, DOC – Total/Dissolved Organic Carbon**
  - Measure of a water's organic carbon content
    - Analyze mass/concentration of CO_2 produced after chemical oxidation of a sample
    - Sampling time – a few minutes

BOD_5 vs COD vs TOC

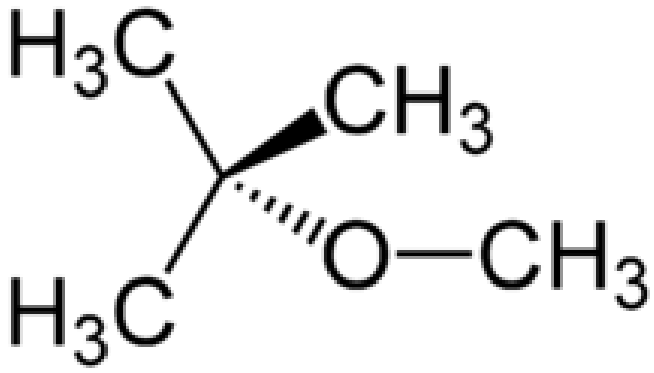
Compound	Formula	MW	BOD_5	COD	TOC	COD/TOC	TOC/MW	COD/MW
Methane	CH_4	16	??	64	12	5.3	0.75	4.0
MTBE	$C_5H_{12}O$	88	~0	240	60	4.0	0.68	2.7
Benzene	C_6H_6	78	??	240	72	3.3	0.92	3.1
Glucose	$C_6H_{12}O_6$	192	~192	192	72	2.7	0.38	1.0

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$$

$$C_5H_{12}O + 7.5O_2 \Leftrightarrow 5CO_2 + 6H_2O$$

$$C_6H_6 + 7.5O_2 \Leftrightarrow 6CO_2 + 3H_2O$$

$$C_6H_{12}O_6 + 6O_2 \Leftrightarrow 6CO_2 + 6H_2O$$



[MTBE]

Aqueous chemistry parameters – pH

- **$pH = -\log_{10}\{H^+\} \approx -\log_{10}[H^+]$**
  - For most natural waters 5<pH<9
    - Most aquatic life adapted for this range
  - $K_w = \{H^+\}\{OH^-\} = 10^{-14}$ @25°C
  - $pK_w = pH + pOH \approx 14$
  - Chemical speciation can be highly pH dependent

$$ROH \iff RO^- + H^+ \qquad K_a \approx \frac{[RO^-][H^+]}{[ROH]}$$

  - If pH < pK_a, protonated (associated)
  - If pH > pK_a, deprotonated (dissociated)