Chemical characteristics of water

Major ionic species in water

Cations	Anions
Calcium (Ca^{2+})	Bicarbonate (HCO_3^-)
Magnesium (Mg^{2+})	Sulfate (SO_4^{2-})
Sodium (Na^+)	Chloride (Cl^-)
Potassium (K^+)	

- Derived from contact of the water with mineral deposits
- Relatively high in groundwater, low in surface water
- Determining the accuracy of water ion content analysis:

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

- Most dissolved inorganics are in ionic form
  - Major nonionic: silica (SiO_2)

Major ionic species in water

Q: Determine the acceptability of the following water analysis.

Cations	Conc. (mg/L)
Ca^{2+}	93.8
Mg^{2+}	28.0
Na^{+}	13.7
K^{+}	30.2

Anions	Conc. (mg/L)
HCO_3^-	164.7
SO_4^{2-}	134.0
Cl^-	92.5

Minor ionic species in water

Cations		Anions	
Aluminum (Al^{3+})	Copper (Cu^{2+})	Bisulfate (HSO_4^-)	Nitrite (NO_2^-)
Ammonium (NH_4^+)	Iron, ferrous (Fe^{2+})	Bisulfite (HSO_3^-)	Phosphate, mono- ($H_2PO_4^-$)
Arsenic (As^+)	Iron, ferric (Fe^{3+})	Carbonate (CO_3^{2-})	Phosphate, di- (HPO_4^{2-})
Barium (Ba^{2+})	Manganese (Mn^{2+})	Fluoride (F^-)	Phosphate, tri- (PO_4^{3-})
Borate (BO_4^{3-})		Hydroxide (OH^-)	Sulfide (S^{2-})
		Nitrate (NO_3^-)	Sulfite (SO_3^{2-})

- Mostly derived from contact of the water with mineral deposits
- Some from bacterial and algal activity (ex: NH_4^+, NO_3^-, NO_2^-, CO_3^{2-}, S^{2-})

Nutrients

- **N & P**
  - Essential for life
  - Most often limiting nutrients in the environment

- **Nitrogen (N)**
  - Exist in various oxidation states: +5, +3, +2, +1, 0, -2, -3
  - Important nitrogen-containing compounds for water quality
    - Organic nitrogen; ammonia (NH_3), nitrite (NO_2^-), nitrate (NO_3^-), urea [$CO(NH_2)_2$], nitrogen gas (N_2)

Nutrients

- Nitrogen cycle: Uptake by organisms
  - Uptake by microorganisms and plants: NH_3 (most common), NO_3^-, N_2 → produce proteins
  - Conversion of N_2 to organic-N by bacteria is called "nitrogen fixation" (by limited number of bacterial species)
  - Human contribution to nitrogen cycle: Haber-Bosch process

    $N_2 + 3H_2 \rightarrow 2NH_3$
  - Uptake by animals and humans: nitrogen must be in organic form (protein)

- Nitrogen cycle: release from organisms
  - Animals excrete urea and other forms of organic-N (ex: proteins)
  - Dead organisms → release organic-N into the environment

Nutrients

– Nitrogen cycle: Fate of released N in the environment

- Organic-N is degraded by bacteria to urea and NH_3
- Urea is easily hydrolyzed to NH_3

  Urea hydrolysis

$$H_2N - \overset{\overset{\displaystyle O}{||}}{C} - NH_2 \;+\; H_2O \xrightarrow{\;urease\;} 2NH_3 \;+\; CO_2$$

- Ammonia is oxidized serially by certain groups of bacteria:

$$NH_4{}^+ + 1.5\,O_2 \xrightarrow{\;Nitrosomonas\;} NO_2{}^- + 2H_2O + 4H^+$$

$$2NO_2{}^- \;+\; O_2 \xrightarrow{\;Nitrobacter\;} 2NO_3{}^-$$

<nitrification>

Nutrients

- Nitrate and nitrite is reduced by various types of bacteria to produce nitrogen gas (N_2) by series of reactions:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

(note: N_2O is a potent greenhouse gas)

<denitrification>

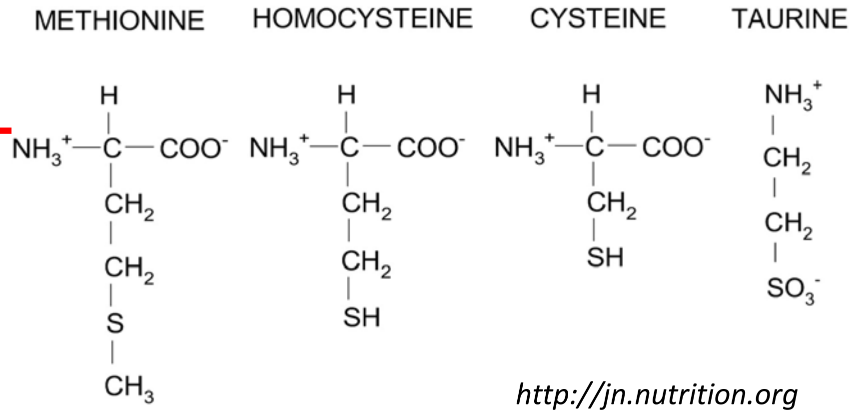
– Measurement of nitrogen in water

- Each ionic species can be measured by ion chromatography or colorimetric methods
- Organic nitrogen is determined by the Kjeldahl method: organic-N is degraded by acid and heat to ammonium and then ammonium content is determined
- **Total Kjeldahl nitrogen (TKN)** = organic-N + ammonia-N

Nutrients

- **Phosphorus (P)**
  - Used..
    - in fertilizers
    - for corrosion control in water supply and industrial cooling water
    - in synthetic detergents
  - P-containing compounds relevant to water quality
    - Orthophosphates: PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, H_3PO_4
      - Can be directly utilized by organisms
      - Easily measured by colorimetric methods / ion chromatography
    - Polyphosphates ($(PO_3)_6^{3-}$, $P_3O_{10}^{5-}$, $P_2O_7^{4-}$, …) and organic phosphates
      - Needs breakdown to orthophosphates for biological metabolism / analysis

Nutrients



http://jn.nutrition.org

- **Sulfur (S)**
  - Essential element for life
    - C, H, O, N, **S**, P, K, …
    - Required in the synthesis of proteins, released when protein degrades
  - Reduced biologically under anaerobic conditions

$$Organic\ matter + {SO_4}^{2-} \rightarrow S^{2-} + H_2O + CO_2$$

    - Anaerobic conditions occur in sediment, subsurface, sewers, and anaerobic processes in wastewater treatment
    - The sulfide ion (S^{-2}) may combine with hydrogen to form hydrogen sulfide gas (H_2S)

$$S^{2-} + 2H^+ \rightarrow H_2S$$

pH

$$pH = -log_{10}[H^+]$$

- Ionization constant of water

$[H^+][OH^-] = K_w$ $K_w = 10^{-14}$ at 25°C

$p \equiv -log_{10} \rightarrow pH + pOH = 14$ at 25°C

Q: pH in pure H_2O at 25°C?

Electrical conductivity (EC)

- A measure of an ability of a solution to conduct an electrical current
- Unit: millisiemens per meter (mS/m) or microsiemens per centimeter (μS/cm)
- Electrical current is transported by ions in a solution → related to the concentration of ions in a solution

Conductivity meter & probe
http://coleparmer.com

Electrical conductivity (EC)

- Conversion between EC and ionic concentration
  - Conc. of each ionic species in water and EC

$$EC \cong \sum_i (C_i \times f_i)$$

EC = electrical conductivity (μS/cm)
C_i = conc. of ionic species i in solution (meq/L)
f_i = conversion factor

Cations	f_i [(μS/cm)·(meq/L)$^{-1}$]
Ca^{2+}	52.0
Mg^{2+}	46.6
K^+	72.0
Na^+	48.9

Anions	f_i [(μS/cm)·(meq/L)$^{-1}$]
HCO_3^-	43.6
CO_3^{2-}	84.6
Cl^-	75.9
NO_3^-	71.0
SO_4^{2-}	73.9

Electrical conductivity (EC)

- Conversion between EC and ionic concentration
  - Applying generic composition of ionic species in water, EC can be used to estimate the ionic strength and TDS of a solution

$$I = EC\ (in\ \mu S/cm) \times (1.6 \times 10^{-5})$$

Tchobanoglous & Schroeder (1985) Water Quality

$$TDS\ (mg/L) = EC\ (in\ \mu S/cm) \times (0.55\ - 0.70)$$

Metcalf, Eddy, AECOM (2014) Wastewater Engineering

Alkalinity

- The capacity of water to neutralize acid
- Determined by titrating water with a strong acid to pH=4.5

$$Alk\ (eq/L) = (HCO_3^-) + (CO_3^{2-}) + \cdots + (OH^-) - (H^+)$$

$$= [HCO_3^-] + 2[CO_3^{2-}] + \cdots + [OH^-] - [H^+]$$

Include $B(OH)_4$, PO_4^{3-}, HPO_4^{2-}, $SiO(OH)_3$, etc. if significant

- Most of the time, practically:

$$Alk\ (eq/L) \cong [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

- Most of the time, at neutral pH:

$$Alk\ (eq/L) \cong [HCO_3^-]$$

More common unit for Alk: "mg/L as $CaCO_3$"
<u>Conversion</u>
Alk (in mg/L as $CaCO_3$)
= Alk (in meq/L) x 50 mg $CaCO_3$/meq

Hardness

- The term used to characterize a water that does not lather well (react with soap to form a scum)

- Caused by polyvalent cations in water (+2, +3, …); mostly Ca^{2+} & Mg^{2+}

- These ions are also easily precipitated to produce scales in pipes transporting hot water

$$Ca^{2+} + 2HCO_3^{-} \xrightarrow{\Delta H} CaCO_3 + CO_2 + H_2O$$

http://www.watersoftenerbest.blogspot.com

http://www.proenv.com

Hardness

- Total hardness (TH)
  - Technically: the sum of all polyvalent cations

$$TH(eq/L) = (Ca^{2+}) + (Mg^{2+}) + (Fe^{3+}) + (Fe^{2+}) + (Ba^{2+}) + \cdots = \sum_{i=1}^{n} (X^{m+})_i$$

  - Practically (most of the time): the sum of Ca^{2+} & Mg^{2+}

$$TH(eq/L) \cong (Ca^{2+}) + (Mg^{2+}) = 2[Ca^{2+}] + 2[Mg^{2+}]$$

"mg/L as $CaCO_3$" is more common for hardness as well!

- Carbonate hardness (CH) and noncarbonate hardness (NCH)
  - CH: the maximum amount of hardness that can be associated with carbonates (HCO_3^- and CO_3^{2-})
  - NCH = TH - CH
  - When **TH > Alk** (≈ [HCO_3^-]): **CH = Alk**, NCH = TH - CH
  - When **TH ≤ Alk**: **CH = TH**, NCH = 0

Sodium adsorption ratio (SAR)

- Related to the agricultural production
  - Important property for irrigation water

- High sodium (Na^+) content in soil reduces soil permeability!
  - Most clay surfaces are negatively (-) charged
    → Cations are attached to clay surfaces
  - Attachment of Na^+ ion on clay surfaces
    → swelling of clay
    → soil pore size ↓
    → soil permeability ↓
    → crop productivity ↓
  - So, irrigation of water with high Na^+ content can result in replacement of Ca^{2+} and Mg^{2+} in soil, resulting in low crop productivity

Sodium adsorption ratio (SAR)

$$SAR = \frac{(Na^{+})}{\sqrt{\frac{(Ca^{2+}) + (Mg^{2+})}{2}}}$$

SAR < 3: low risk

3 ≤ SAR ≤ 6: slight to moderate risk

SAR > 6: high risk

Organic content

- Contaminated water contains various kinds of organic compounds
  - Proteins, carbohydrates, fats and oils, urea, etc. from food and human wastes
  - Synthetic organic compounds
  - Organics released to waters → consumption of dissolved oxygen by microorganisms → anaerobic (septic) condition → destroy aquatic environment (ex: fish kills), odor problems, production of toxic compounds, etc.
  - Removal of organic compounds is one of the major target for wastewater treatment
- Measurement of organic content as a whole
  - Biochemical oxygen demand (BOD)
  - Chemical oxygen demand (COD)
  - Total organic carbon (TOC)

BOD

- Measurement of dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter

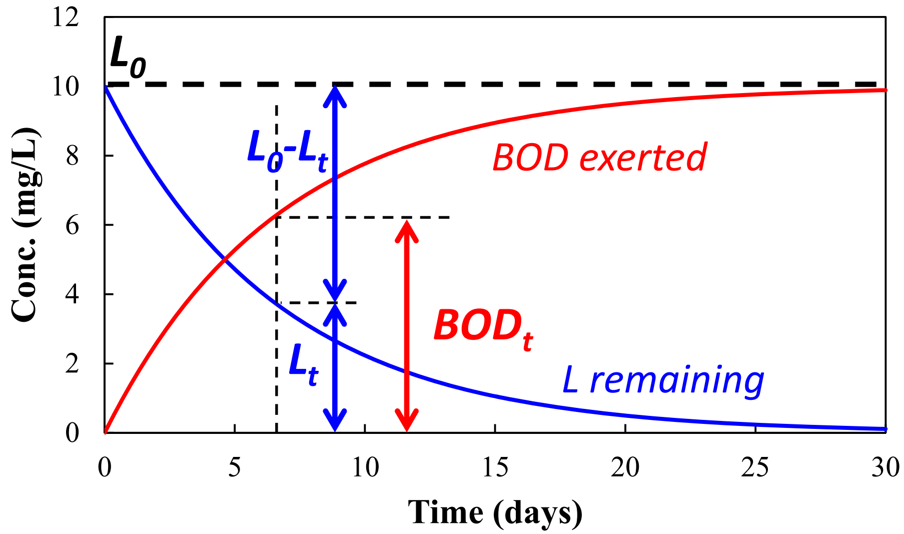
- **BOD test procedure**
  - The water sample is diluted such that the difference between the DO before and after the test can be determined (estimated BOD: 2-6 mg/L)
  - The diluted water sample inoculated with microorganisms that degrade organic matter
  - The diluted, inoculated water sample is incubated for a certain time period (usually 5 days)
  - The DO before and after the incubation is measured to determine the BOD of the sample

BOD

- Modeling BOD reaction: **assume first-order reaction**

$$\frac{d(L_t)}{dt} = -k_1 L_t$$

L_t = amount of organics remaining at time t (d) expressed in oxygen equivalents (mg O_2/L)
k_1 = first-order rate constant (1/d)



Integrating from *t=0* to *t*,

$$L_t = L_0\left(e^{-k_1 t}\right)$$

Note
$BOD_t = L_0 - L_t$
L_0 = UBOD

UBOD = ultimate BOD (mg/L)

BOD

→ $$BOD_t = UBOD - L_t = UBOD\left(1 - e^{-k_1 t}\right)$$

BOD_t = the BOD value at time t (mg/L)

- Temperature effect
  - modified van't Hoff-Arrhenius relationship:

$$k_{1_T} = k_{1_{20}} \theta^{T-20}$$

T = temperature in ℃

  - Typically used value of θ:
    1.056 (20-30°C) / 1.135 (4-20°C)

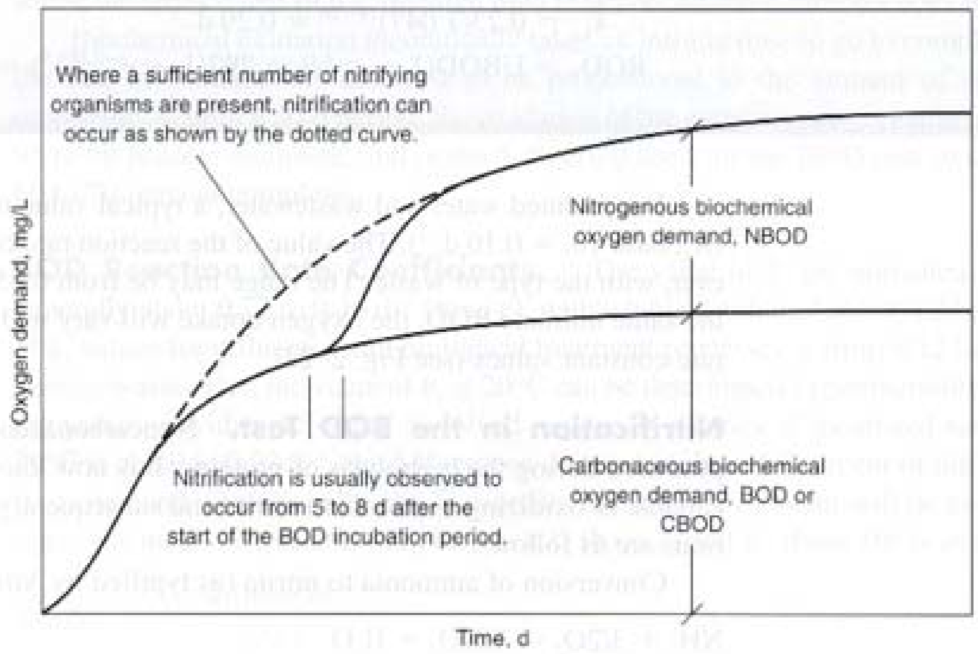
NBOD vs. CBOD

- Ammonia-nitrogen in wastewater may significantly contribute to the total oxygen demand by nitrification:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

Figure 2-24

Definition sketch for the exertion of the carbonaceous and nitrogenous biochemical oxygen demand in a waste sample.



Metcalf, Eddy, AECOM (2014)

NBOD vs. CBOD

- The oxygen demand associated with the oxidation of ammonia is referred to as nitrogenous biochemical oxygen demand (NBOD)
- Carbonaceous biochemical oxygen demand (CBOD): the oxygen demand associated with the oxidizable carbon in the sample
- When NBOD is significant, nitrification is suppressed by adding chemical agents for the measurement of CBOD

COD

- Measured by oxidizing the organic compounds in water using a strong oxidizing agent
- Oxidizing agent: potassium dichromate (K_2CrO_7 - more common) or potassium permanganate ($KMnO_4$)
- Can be fractionated into particulate and soluble COD
  - Soluble COD: readily biodegradable / nonbiodegradable
  - Particulate COD: slowly biodegradable / nonbiodegradable

COD

- **COD > BOD** because:
  - Many organics that are difficult to be oxidized biologically can be oxidized chemically (ex: lignin)
  - Inorganic substances in water may be oxidized by chemical oxidizing agents
  - Certain organic substances may be toxic to microorganisms used in the BOD test
  - When microorganisms grow, they utilize some fraction of organic compounds to synthesize cells instead of oxidizing them

TOC

- Measures all organic carbon in a water sample including those that cannot be chemically/biologically oxidized
- Can be fractionated into particulate/soluble TOC
- Three steps for measurement
  - **Acidification**: add acid to reduce the pH → removes carbonate species (inorganic carbon) from water
  - **Oxidation**: use heat, oxygen, ultraviolet radiation, or combination of those to oxidize organic carbon to CO_2
  - **Quantification**: measure the amount of CO_2 production with an infrared analyzer or other means
- TOC: measures amount of **C** / BOD & COD: measures amount of **O_2** consumed by oxidation

  → different COD/TOC ratio for different compounds!

BOD, COD, & TOC

Q: Determine the theoretical ratios of BOD_5/COD and COD/TOC for an organic compound represented by $C_5H_7O_2N$. Use the following assumptions:

- The compound can be completely mineralized biologically
- Only CBOD is considered for BOD
- The BOD first-order reaction rate constant, k_1, is 0.23/d

Individual organic compounds

- Some organic compounds have particular toxicity to humans and aquatic organisms → have to be regulated individually
- Sources
  - Commercial and industrial wastewater
  - Disinfection byproducts
  - Surface runoff from agricultural land (ex: pesticides)
  - Surface runoff from urban area (ex: oil spill, additives used for vehicles, sealant for pavements)
  - Pharmaceuticals and personal care products (PPCPs)
    - Mostly not regulated currently, but of recent interest

http://istc.Illinois.edu