Chemical characteristics of water I

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

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

** ∑ values in meq/L*

- 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-})

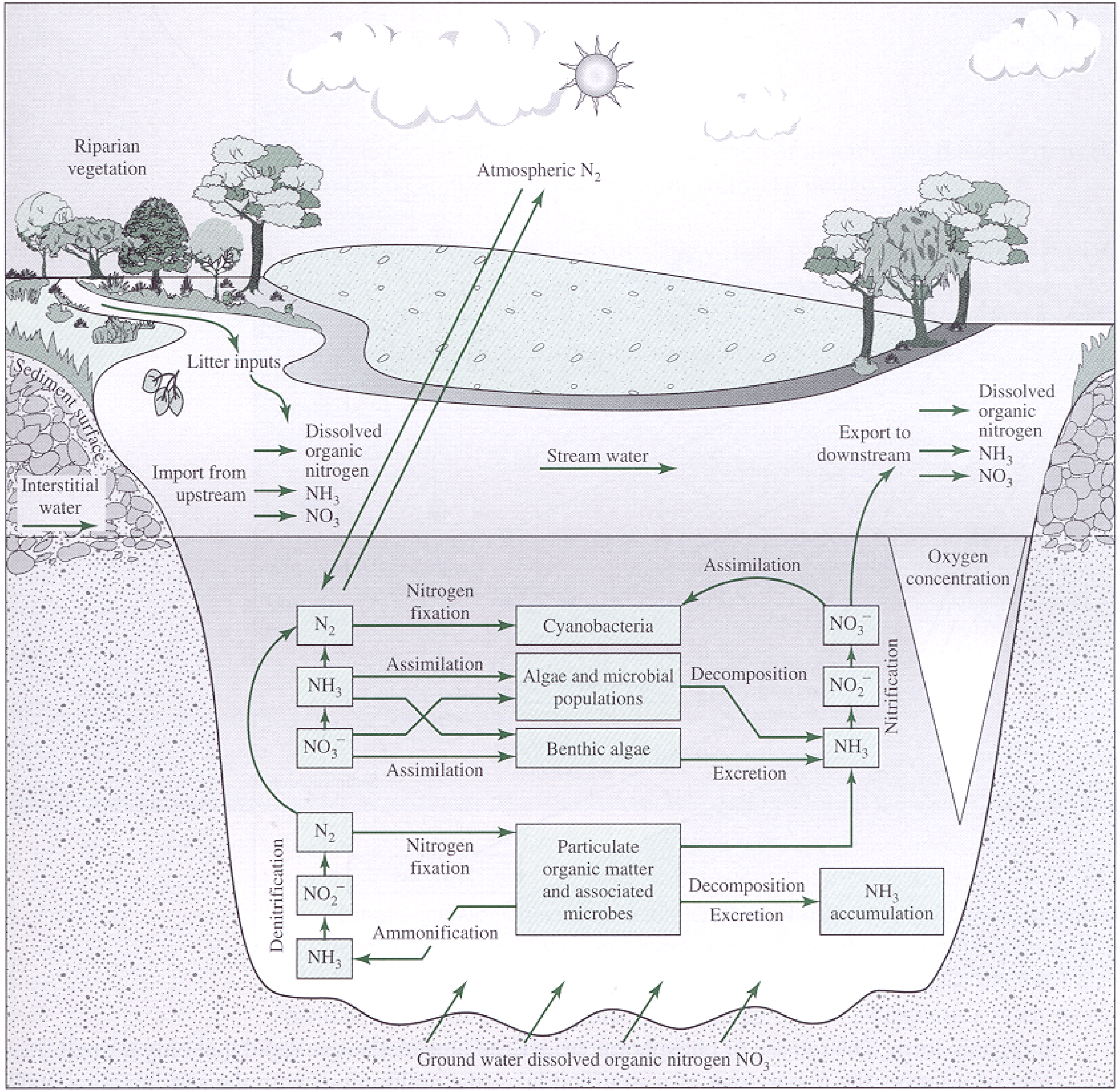
- Mostly derived from contact of the water with mineral deposits
- Some from bacterial and algal activity (ex: NH_4^+, NO_3^-, NO_2^-, CO_3^{2-}, S^{2-})

Nutrients

- **N & P as major nutrients of interest**
  - 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)

Nitrogen cycle in the environ-ment



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)

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

Nitrogen cycle

- Fate of N released into the environment
  - Organic-N is degraded by bacteria to urea and NH_3
  - Urea is easily hydrolyzed to NH_3

    Urea hydrolysis

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

  - 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>

Nitrogen cycle

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

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

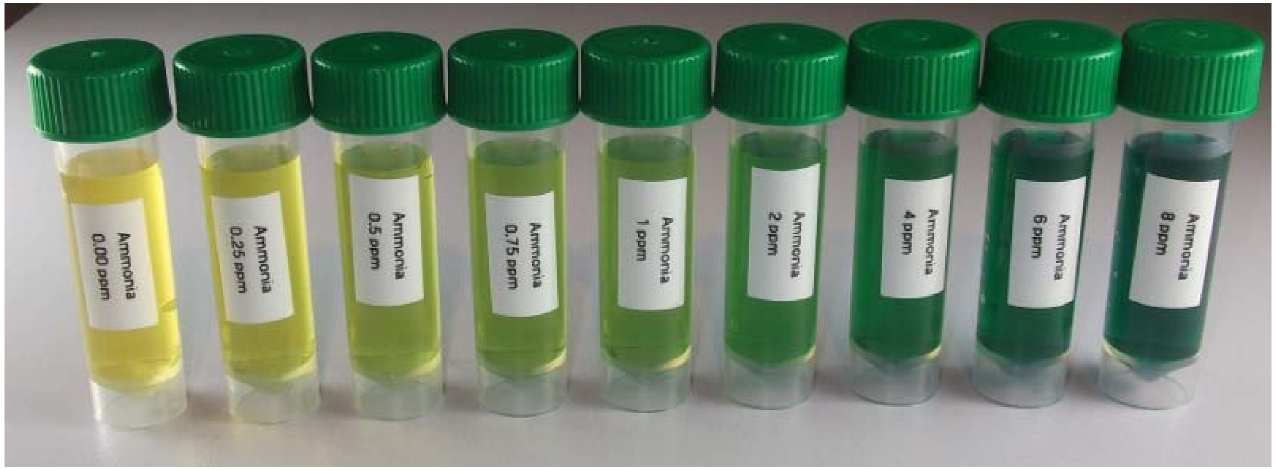
<denitrification>

- Note nitrous oxide (N_2O) is a potent greenhouse gas (greenhouse gas potential 265-298 time greater than CO_2)
- N_2O may be released as an intermediate of both nitrification and denitrification

Measurement of N 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
- To determine organic-N only by the Kjeldahl method, the water is first heated to remove NH_3 by volatilization

General methods for measuring ions



Colorimetric method

- Add chemical agents that will react with the compound to be measured to form products that have a color
- Measure absorbance by spectrophotometer or compare the color with standards

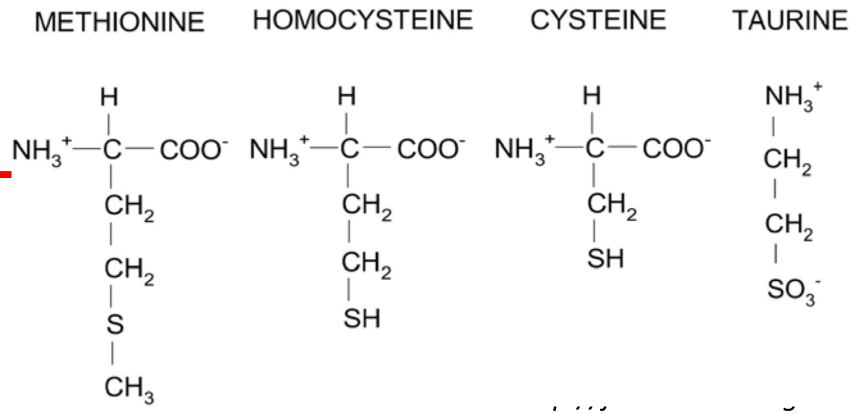
Ion chromatography (IC)

- Sample is injected to a column which has different affinity to different ions
- An eluent continuously flushes the column and the ions flow out of the column at different times
- Concentration of each ion is determined by measuring electrical conductivity

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

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

$[H^+][OH^-] = K_w$ $\quad K_w = 10^{-14}$ 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 $CaCO_3$"

Conversion

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): 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**: **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

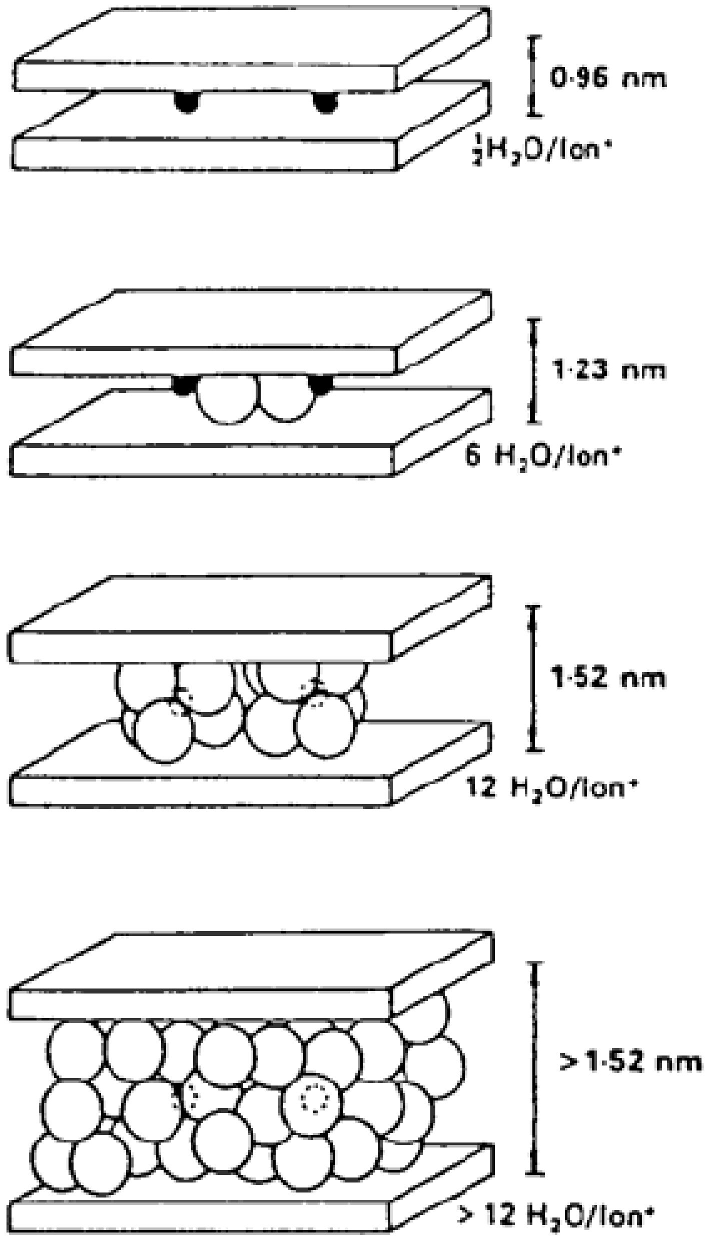
    → swelling of clay by introduction of water molecules between clay sheets

    → 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

Clay swelling by water addition



Savage et al., Ski report, 2005

Sodium adsorption ratio (SAR)

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

Note:
Here, ( ) denotes meq/L, not eq/L

SAR < 3: low risk

3 ≤ SAR ≤ 6: slight to moderate risk

SAR > 6: high risk