# Chemical characteristics of water I

# Today's class

- Water constituents composing total dissolved solids (TDS) – ionic species
- Nutrients – N & P
- pH & electrical conductivity (EC)
- Alkalinity, hardness, sodium adsorption ratio

# 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 ($SiO_2$)

# Dissolved ion analysis

**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 |

# Major ionic species in water

Firstly, calculate concentrations in meq/L units:

(conc. in meq/L) = (conc. in mg/L) / (Ionic weight, IW) x (oxidation number)

| Cations | IW (g/mole) | Conc. in mg/L | Conc. in meq/L |
|---|---|---|---|
| $Ca^{2+}$ | 40.1 | 93.8 | 4.68 |
| $Mg^{2+}$ | 24.3 | 28.0 | 2.30 |
| $Na^{+}$ | 23.0 | 13.7 | 0.60 |
| $K^{+}$ | 39.1 | 30.2 | 0.77 |
| | | | ∑(cations) = 8.35 |

| Cations | IW (g/mole) | Conc. in mg/L | Conc. in meq/L |
|---|---|---|---|
| $HCO_3^{-}$ | 61.0 | 164.7 | 2.70 |
| $SO_4^{2-}$ | 96.1 | 134.0 | 2.79 |
| $Cl^{-}$ | 35.5 | 92.5 | 2.61 |
| | | | ∑(anions) = 8.10 |

# Major ionic species in water

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

$$\left|\sum (anions) - \sum (cations)\right| = 0.25$$

$$0.1065 + 0.0155 \sum (anions) = 0.23$$

Therefore,

$$\left|\sum anions - \sum cations\right| > \left(0.1065 + 0.0155 \sum anions\right)$$ (not acceptable)

Source of error:

- measurement error of one or more ions
- missing one or more significant ions

# 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

When problems with biodegradable organic matter (dissolved oxygen depletion) & suspended solids are cleared..

→ N & P would be the next target of wastewater treatment

<Nakdong River, Korea>

<Chesapeake Bay, USA>

# 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 and life
  - One of the major elements in cells (~12% of cell dry mass)
  - Human excretion by urine accounts for 70~80% of N reaching wastewater treatment plants (excreted as urea)
  - Nitrogen fertilizers widely used to promote plant growth

# Haber-Bosch process

$N_2 + 3H_2 \rightarrow 2NH_3$

- Currently main industrial procedure for the production of $NH_3$
- Use of catalysts to produce ammonia on an industrial scale at a reasonable price
- Nobel Prize (1918, 1931)

## How fertiliser helped feed the world

2 January 2017


By Tim Harford
50 Things That Made the Modern Economy, BBC World Service

**It has been called one of the greatest inventions of the 20th Century, and without it almost half the world's population would not be alive today.**

A hundred years ago two German chemists, Fritz Haber and Carl Bosch, devised a way to transform nitrogen in the air into fertiliser, using what became known as the Haber-Bosch process.

- $NH_3$ – 2nd most produced single chemical in the world
- Haber-Bosch consumes 1% of world's fossil fuel energy resources & 50% of total produced $H_2$

# Fate of Organic-N & urea in wastewater & env.

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

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

**<urea hydrolysis>**

# Fate of N released into the environment

- Ammonia is oxidized serially by certain groups of bacteria

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

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

**<nitrification>**

- Nitrate ($NO_3^-$) and nitrite ($NO_2^-$) 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>**

# Other processes involving N in the environment

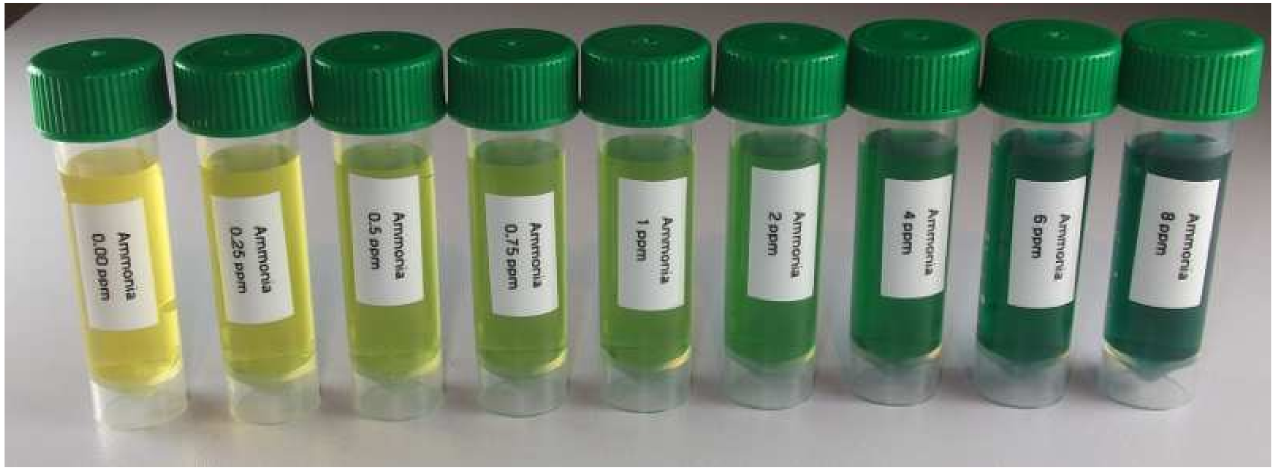
- Uptake by organisms
  - Animals: organic-N form only
  - Microorganisms and plants: $NH_3$ (most common), $NO_3^-$, $N_2$
  - Uptake of $N_2$ and subsequent conversion to organic-N is called "nitrogen fixation" (by limited number of bacterial species)

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

# Measurement of N in water

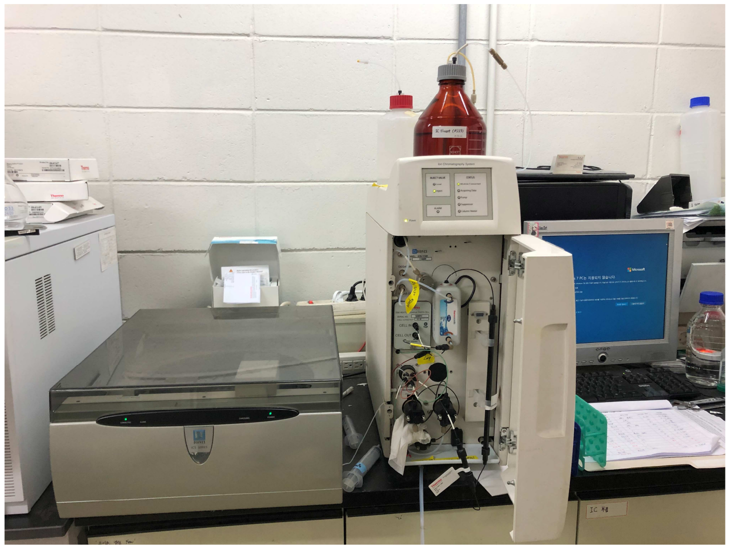
- Each ionic species can be measured by ion chromatography or colorimetric methods
- Organic nitrogen is determined by the Kjeldahl method: organic-N is degraded by acid and heat to ammonium and then ammonium content is determined
- **Total Kjeldahl nitrogen (TKN)** = organic-N + ammonia-N
- To determine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



*IC at Water Quality & Environment Lab., SNU*

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

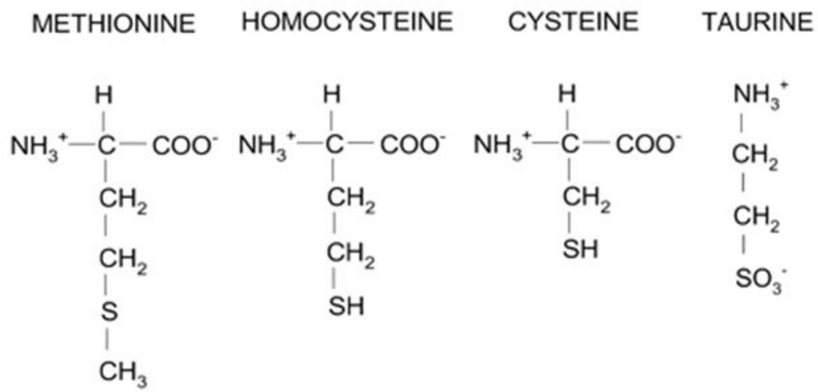
# Phosphorus (P)

- Used..
  - in fertilizers
  - for corrosion control in water supply and industrial cooling water
  - in synthetic detergents

- Most often growth-limiting element for algae in fresh water

- 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 ($(PO_3)_6^{3-}$, $P_3O_{10}^{5-}$, $P_2O_7^{4-}$, …) & organic-phosphorus
    - 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

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

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

**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

# 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

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

# $CaCO_3$ precipitation – temperature effect

Recall from the env. eng. course:

$$HCO_3^{\ -} = H^+ + CO_3^{\ 2-}\ , \quad K_{a2} = 10^{-10.33} = 4.68 \times 10^{-11} \quad \text{(at 25°C)}$$

$K_{a2}$ increases with increasing temperature:

$$K_{a2} = 2.75 \times 10^{-11} \quad \text{(at 5°C)}$$

$$K_{a2} = 6.03 \times 10^{-11} \quad \text{(at 40°C)}$$

Also recall:

$$K_{a2} = \frac{[CO_3^{\ 2-}][H^+]}{[HCO_3^{\ -}]}, \quad [CO_3^{\ 2-}] = K_{a2}\frac{[H^+]}{[HCO_3^{\ -}]}$$

⇨ Higher $CO_3^{-2}$ fraction when water is heated,
$Ca^{2+}$ is more likely to be precipitated as $CaCO_3$

# 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

# Why are we interested in $CaCO_3$?

Recall for the following precipitation reaction:

$$aA^{x+} + bB^{y-} = A_aB_b\ (s) \qquad K_{sp} = [A^{x+}]^a[B^{y+}]^b, \quad pK_{sp} = -log_{10}K_{sp}$$

Inspect the $pK_{sp}$ of potential Ca/Mg precipitates:

$$pK_{sp}\ (CaCO_3) = 8.55$$

$$pK_{sp}\ (MgCO_3) = 7.46$$

$$pK_{sp}\ (Ca(OH)_2) = 5.26$$

$$pK_{sp}\ (Mg(OH)_2) = 10.74$$

# 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

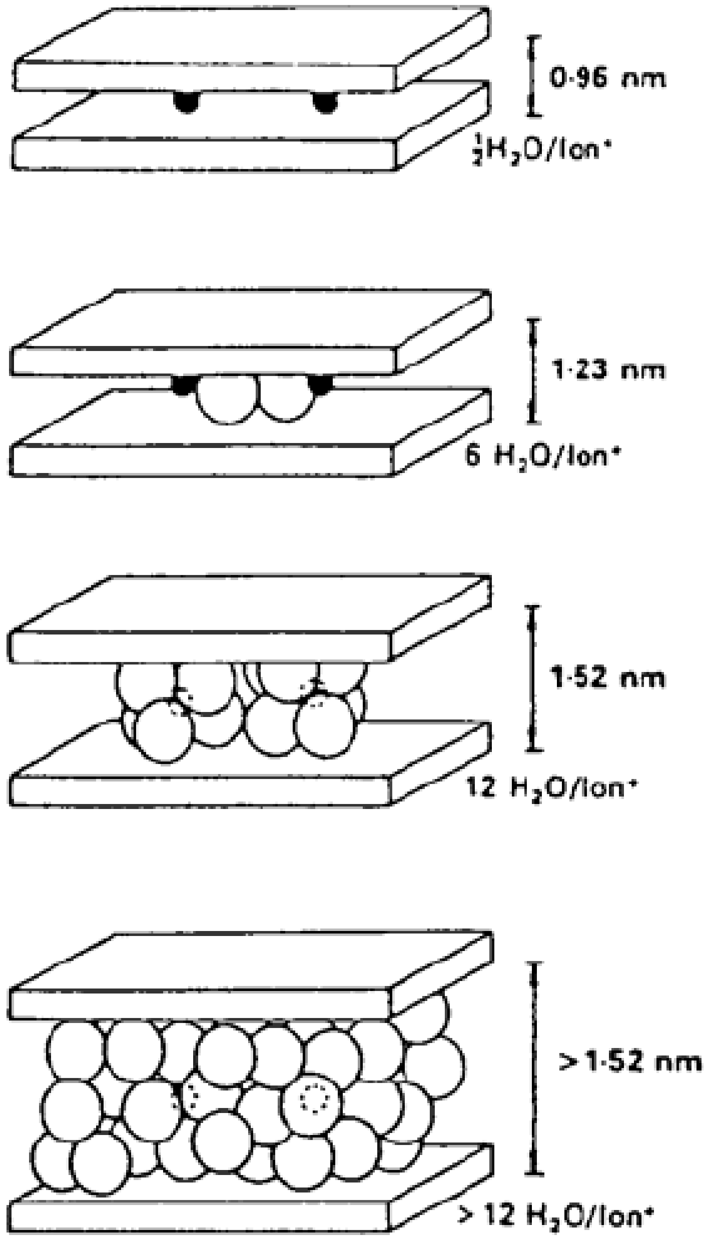
    → soil pore size ↓

    → 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

#7



# Sodium adsorption ratio (SAR)

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

***Note:***
*Here, ( ) denotes* *<u>meq/L</u>*, *not eq/L*

SAR < 3: low risk

3 ≤ SAR ≤ 6: slight to moderate risk

SAR > 6: high risk

# Key references

- Textbook sec 2-3, 2-4

# Next class

- Chemical characteristics of water II
  - Gross indicators of organic content: BOD, COD, TOC
  - Individual organic compounds