Physical characteristics of water

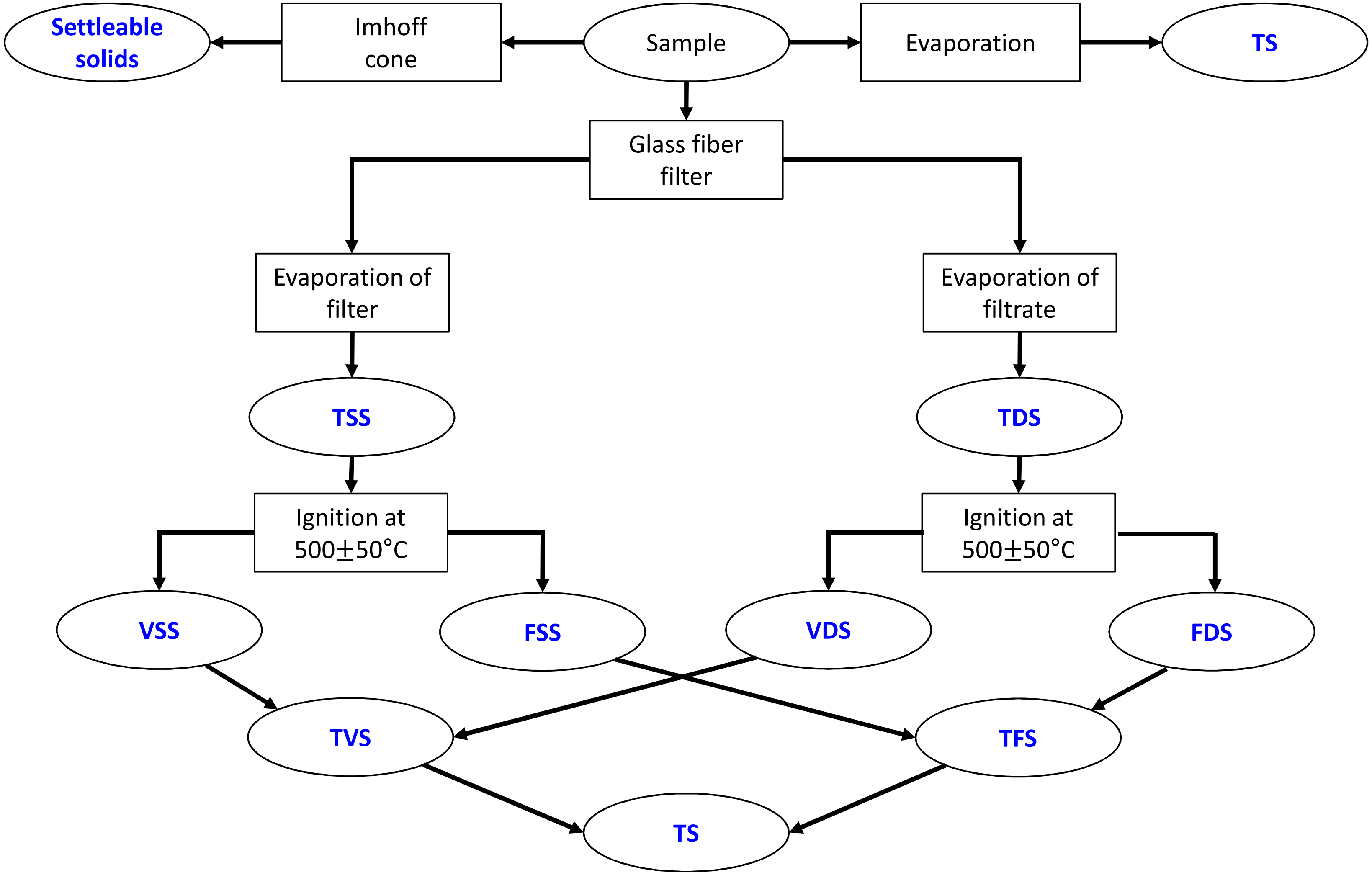
Solids

- All constituents of water other than water and dissolved gases
- **Dissolved vs. suspended**
  - Penetrates vs. retained on a filter
  - Filter with a pore size of 0.45 – 2 μm is used
- **Fixed vs. volatile**
  - Remains vs. volatilized at 500±50℃
  - Volatile solids are considered to be <u>organic</u>: used to differentiate organics and inorganics

Water constituents

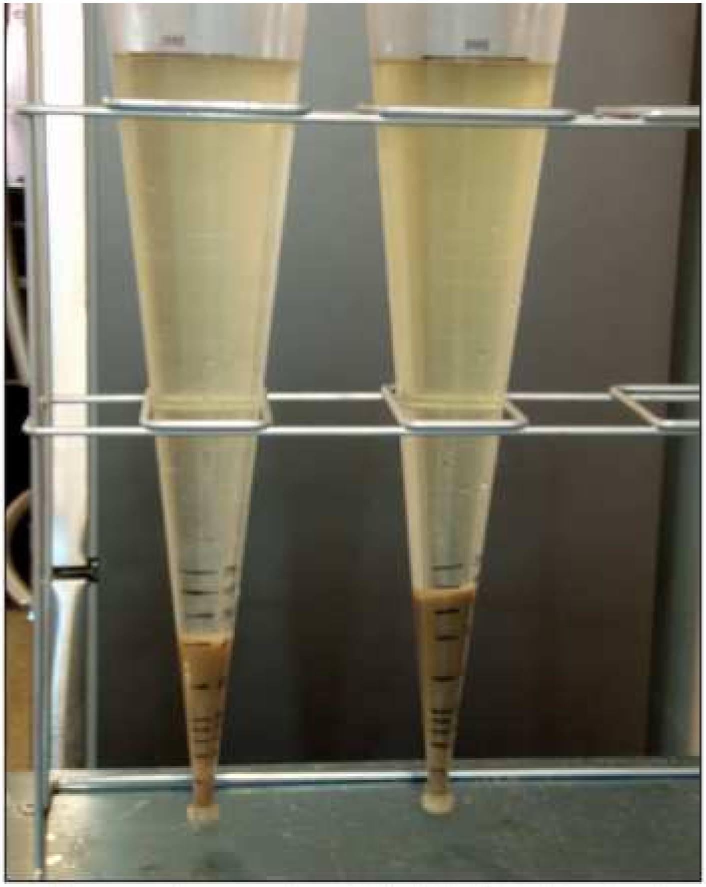
- **Suspended matter**
  - Operationally defined as the material that retained on a 0.45 µm filter
  - Colloids: 1 nm – 1 µm in size
  - Includes mineral colloids, microorganisms and their debris, organic polymers
  - Influences:
    - Contaminant transport
    - Light attenuation
    - Disinfection efficiency
    - Aquatic habitat

Solids – content analysis



Solids content analysis – settleable solids

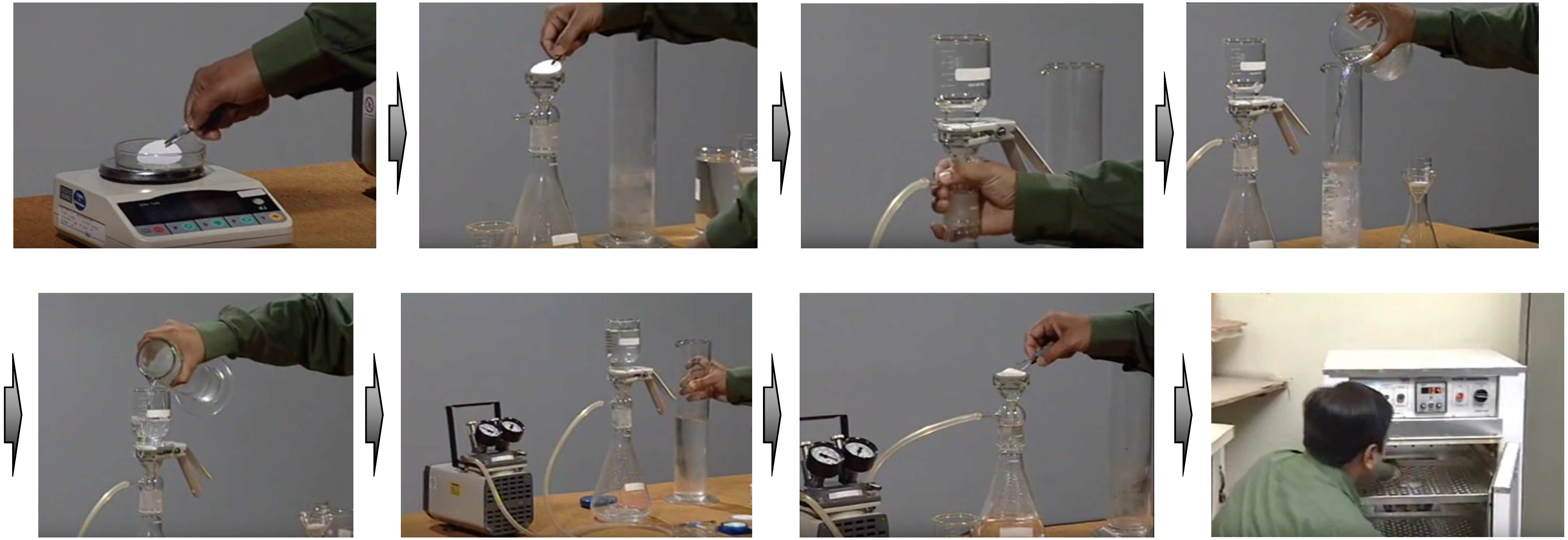
#1



Add 1L in Inhoff cone, wait for 1 hr for settling & record the volume of the thick, bottom layer (reported as mL/L)

Solids content analysis – suspended solids

#2



#3

Solids content analysis

Q: The following test results were obtained for a wastewater sample. All the tests were performance using a sample size of 50 mL. Determine the concentrations of TS, TVS, TSS, VSS, TDS, and VDS.

Mass of evaporating dish = ***53.5433 g***

Mass of evaporating dish + residue after evaporation at 105°C = ***53.5794 g***

Mass of evaporating dish + residue after ignition at 500°C = ***53.5625 g***

Mass of filter paper after drying at 105°C = ***1.5433 g***

Mass of filter paper + residue after drying at 105°C = ***1.5554 g***

Mass of filter paper + residue after ignition at 500°C = ***1.5476 g***

Solids content analysis

Mass of evaporating dish = ***53.5433 g***

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Mass of filter paper + residue after drying at 105°C = ***1.5554 g***

Mass of filter paper + residue after ignition at 500°C = ***1.5476 g***

$$\boldsymbol{TS} = \quad \frac{(53.5794 - 54.5433)\ g\ \times\ 10^3\ mg/g}{0.05\ L} = 722\ mg/L$$

$$\boldsymbol{TVS} = \quad \frac{(53.5794 - 54.5625)\ g\ \times\ 10^3\ mg/g}{0.05\ L} = 338\ mg/L$$

$$\boldsymbol{TSS} = \quad \frac{(1.5554 - 1.5433)\ g\ \times\ 10^3\ mg/g}{0.05\ L} = 242\ mg/L$$

$$\boldsymbol{VSS} = \quad \frac{(1.5554 - 1.5476)\ g\ \times\ 10^3\ mg/g}{0.05\ L} = 156\ mg/L$$

$$\boldsymbol{TDS} = \quad TS - TSS = 722 - 242 = 480\ mg/L$$

$$\boldsymbol{VDS} = \quad TDS - VSS = 338 - 156 = 182\ mg/L$$

Turbidity

- A measure of clarity of water
- Unit: nephelometric turbidity units (NTU)
- Measured by the intensity of light scattered by a water sample
- Suspended and colloidal matter increases turbidity
  - No general, direct relationship between TSS and turbidity, but at certain conditions, turbidity may be used to estimate TSS

$$TSS, mg/L \cong TSS_f \times T$$

TSS_f = conversion factor, mg TSS/L/NTU

ex: 2.3-2.4 for secondary effluent;

1.3-1.6 for secondary eff. filtered by sand filter

T = turbidity, NTU;

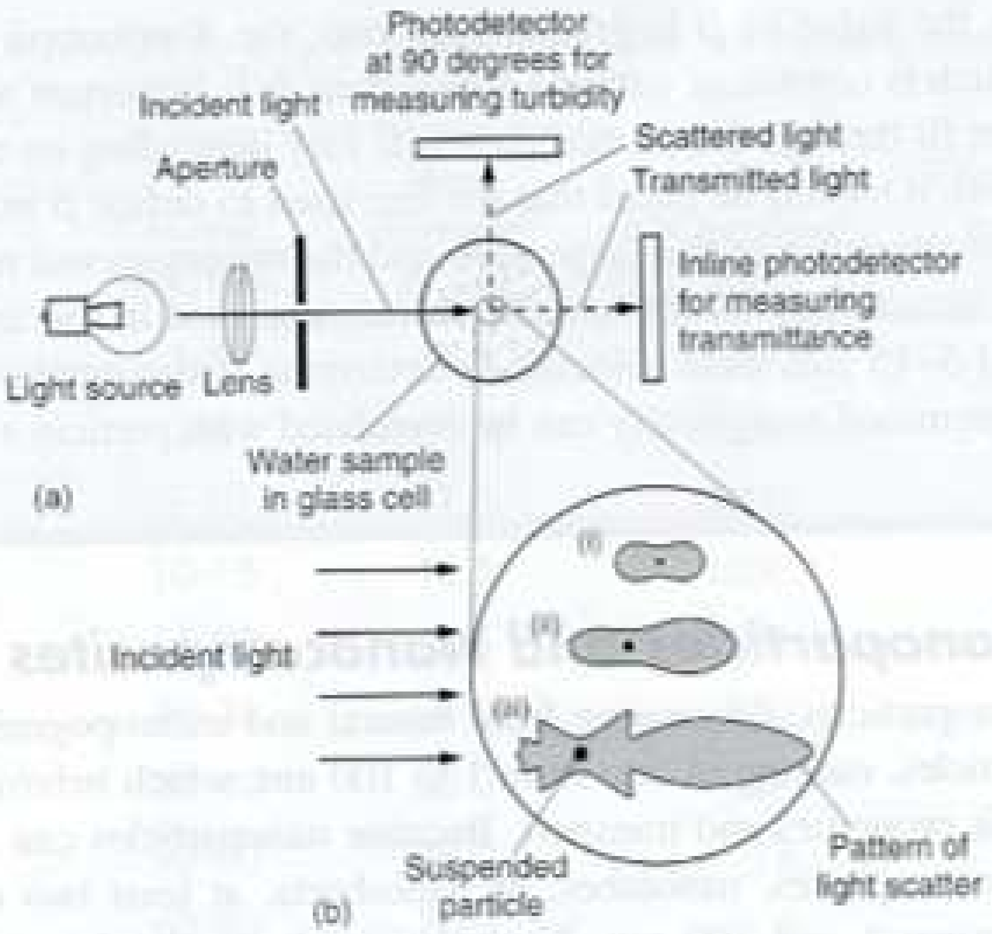
  - Turbidity can be measure real-time, on-line (TSS cannot)

Turbidity

#4

Figure 2-12

Determination of turbidity by light scattering: (a) schematic of turbidity apparatus and (b) typical light scattering patterns for small (i), intermediate (ii), and large (iii) particles.



Color

- Natural water may have yellowish color
  - Major contributor: DOM
- Fresh wastewater is in light brownish-gray color; as anaerobic condition develops, the water gets darker and eventually turn black (septic water)

#5

#6

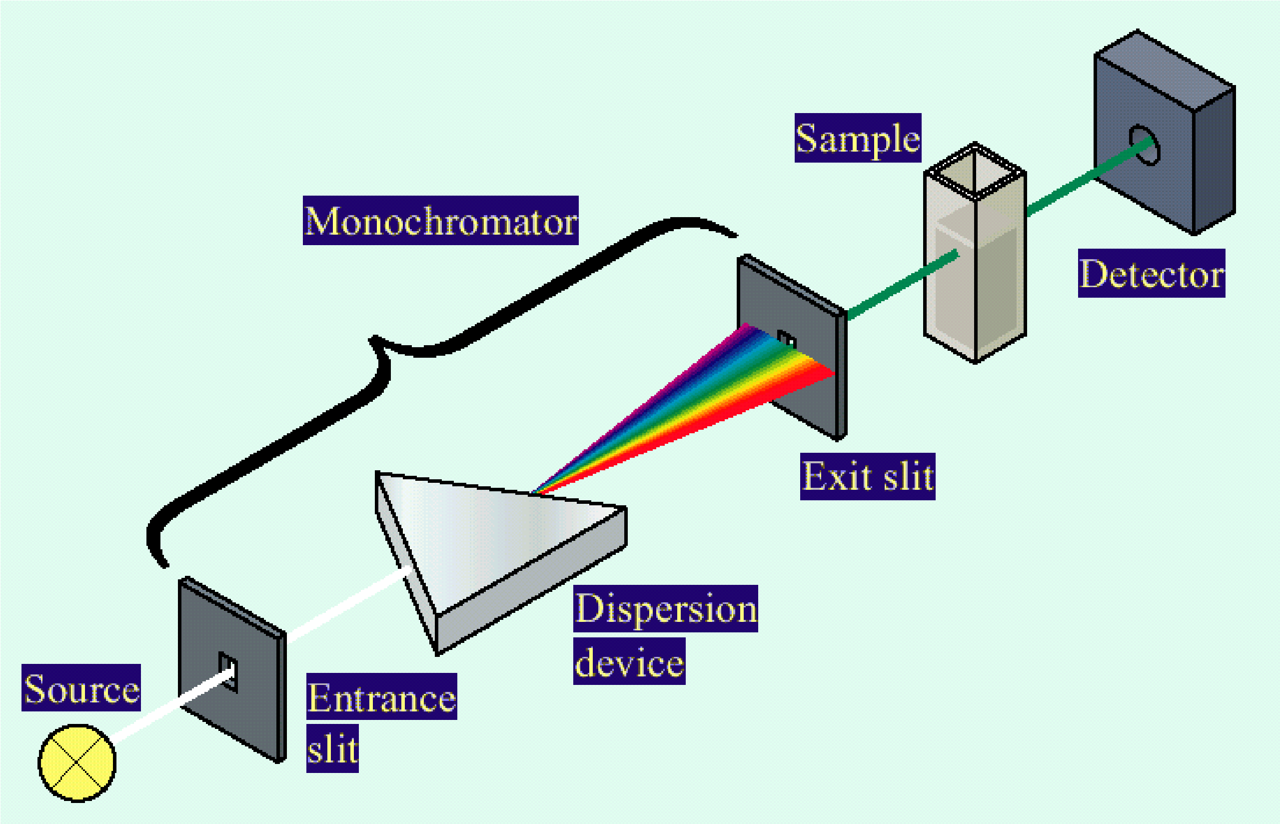
Light absorption

- **Absorbance**
  - A measure of the amount of light absorbed by the constituents in a solution
  - Typically measured at a wavelength of 254 nm using a spectrophotometer
  - Function of solute property, concentration, light path length, and light wavelength

$$A(\lambda) = log_{10}(I_0/I) = \varepsilon(\lambda)Cx$$

$A(\lambda)$ = absorbance at wavelength λ (unitless)
I_0= light intensity at light source (mW/cm^2)
I = light intensity at distance x from the light source (mW/cm^2)
$\varepsilon(\lambda)$ = molar absorptivity of the light-absorbing solute at wavelength λ (L/mole-cm)
C = concentration of light-absorbing solute (mole/L)
x = light path length (cm)

Light absorption



#7

- Absorptivity

$$k(\lambda) = \frac{A(\lambda)}{x} = \varepsilon(\lambda)C$$

$k(\lambda)$ = absorptivity (cm^{-1})

Odor

- Offensive odor usually occur in anaerobic conditions
- Most commonly reported as “Minimum Detectable Threshold Odor Concentration (MDTOC)”
- Quite subjective property

Odorous compounds in water

Odorous compound	Chemical formula	Odor quality
Amines	CH_3NH_2, $(CH_3)_3NH_2$	Fishy
Ammonia	NH_3	Ammoniacal
Diamines	$NH_2(CH_2)_4NH_2$, $NH_2(CH_2)_5NH_2$	Decayed flesh
Hydrogen sulfide	H_2S	Rotten eggs
Mercaptans	CH_3SH, $CH_3(CH_2)SH$, $(CH_3)_3CSH$, $CH_3(CH_2)_3SH$	Decayed cabbage or skunk
Organic sulfides	$(CH_3)_2S$, $(C_6H_5)_2S$	Rotten cabbage
Skatole	C_9H_9N	Fecal matter

Odor

- MDTOC determination example

mL sample	**mL pure water**	**Odor**
100 mL	0 mL	Present
50 mL	50 mL	Present
25 mL	75 mL	Barely detectable
10 mL	90 mL	Absent

$$MDTOC = 100\ mL / 25\ mL = 4$$

Temperature

- Chemical and biochemical reaction rates increase with temperature
  - van’t Hoff-Arrhenius relationship

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2}$$

k = *reaction rate constant*

T = *temperature (K)*

E = *activation energy (J/mole)*

R = *ideal gas constant (8.314 J/mole-K)*

  - Modification of van’t Hoff-Arrhenius relationship

    For a practical range of water temperature, $E/RT^2 \approx constant$

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

k_1 = *reaction rate at* T_1

k_2 = *reaction rate at* T_2

θ = *temperature coefficient*

van’t Hoff-Arrhenius when E/RT^2≈const.

$$d(\ln k) = \frac{E}{R} \cdot \frac{dT}{T^2}$$

$$\int_{lnk_1}^{lnk_2} d(\ln k) = \frac{E}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$lnk_2 - lnk_1 = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{k_2}{k_1} = exp\left[\frac{E}{RT_1T_2}(T_2 - T_1)\right]$$

$$let \quad \theta = exp\left(\frac{E}{RT_1T_2}\right)$$

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

Temperature

- Gas solubility decrease with temperature

  ex) saturated dissolved oxygen DO: 13.1 mg/L @ 4℃, 9.1 mg/L @ 20℃, 7.5 mg/L @ 30℃

- Most organisms have distinct temperature ranges within which they reproduce and compete
- Slightly higher temp. in domestic wastewater and much higher temp. in cooling water → can damage aquatic ecosystem
  - Low saturation DO, faster oxygen consumption rate by microorganisms → DO depletion
  - Direct effect of temperature increase on aquatic organisms
- Heat recovery from wastewater of current interest

References

#1) http://bioaqua.vn/en/marine-shrimp-biofloc-systems-basic-management-practices/

#2) https://www.youtube.com/watch?v=GJSe_Deo-_0

#3) https://www.ebsbiowizard.com/total-suspended-solids-tss-volatile-suspended-solids-vss-2-1071/

#4) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill, p. 84.

#5) https://www.solutionstrak.com/blog/wastewater-definitions/

#6) https://newsbeezer.com/vietnameng/rushing-the-sewage-black-stink-massively-poured-into-the-sea-da-nang/

#7) https://www.ssi.shimadzu.com/products/uv-vis-spectrophotometers/faqs/instrument-design.html

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)

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

- Aluminum (Al^{3+})
- Ammonium (NH_4^+)
- Arsenic (As^+)
- Barium (Ba^{2+})
- Borate (BO_4^{3-})
- Copper (Cu^{2+})
- Iron, ferrous (Fe^{2+})
- Iron, ferric (Fe^{3+})
- Manganese (Mn^{2+})

Anions

- Bisulfate (HSO_4^-)
- Bisulfite (HSO_3^-)
- Carbonate (CO_3^{2-})
- Fluoride (F^-)
- Hydroxide (OH^-)
- Nitrate (NO_3^-)
- Nitrite (NO_2^-)
- Phosphate, mono- ($H_2PO_4^-$)
- Phosphate, di- (HPO_4^{2-})
- Phosphate, tri- (PO_4^{3-})
- Sulfide (S^{2-})
- Sulfite (SO_3^{2-})

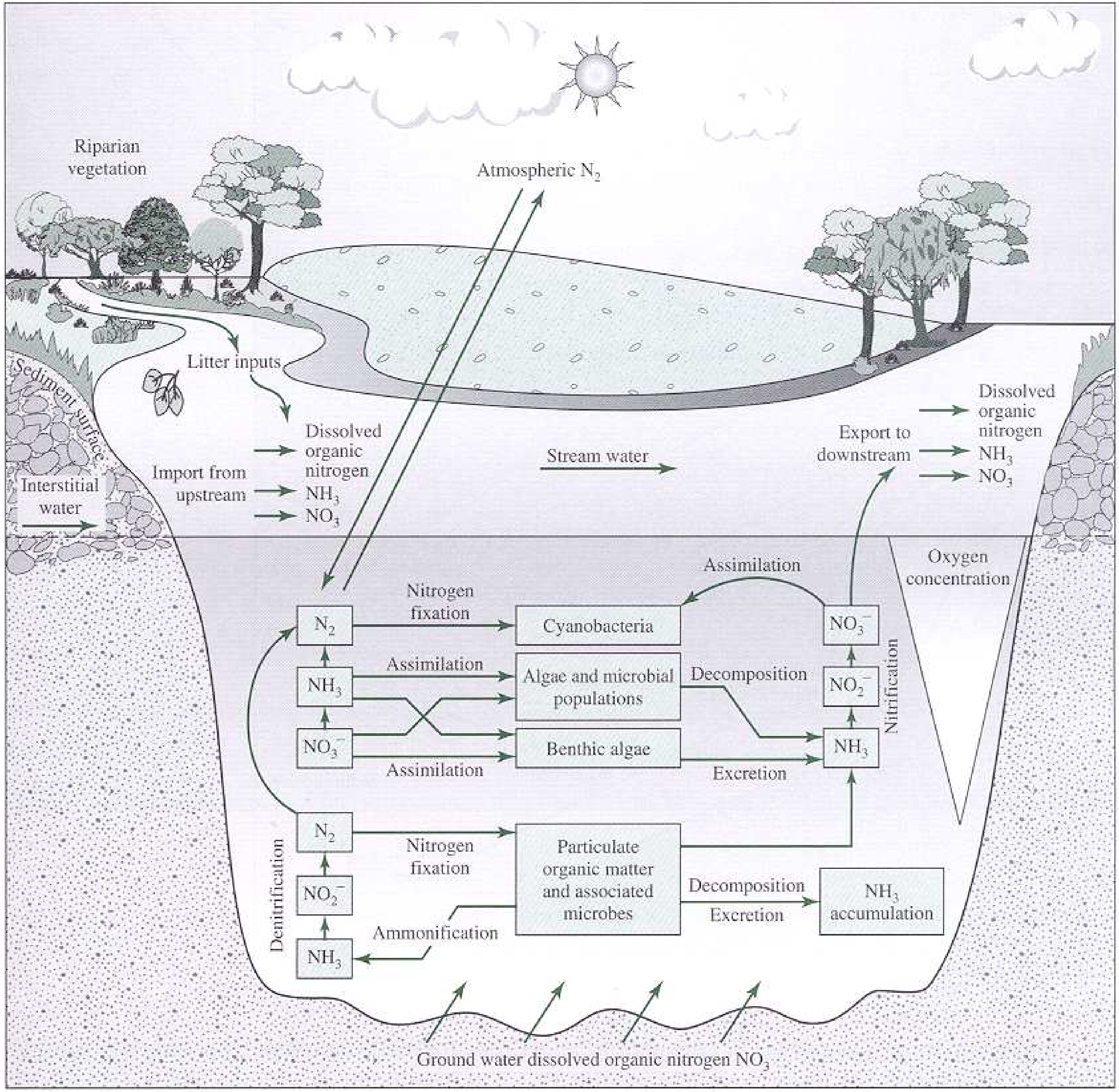
- Mostly derived from contact of the water with mineral deposits
- Some from bacterial and algal activity (ex: NH_4^+, NO_3^-, NO_2^-, CO_3^{2-}, S^{2-})

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 environment



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

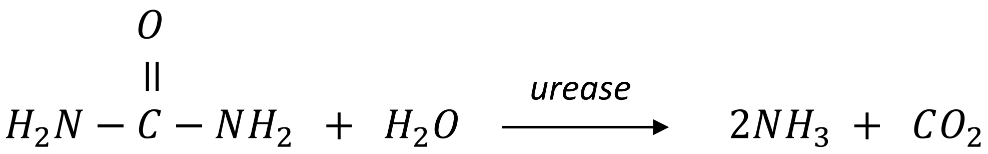
    $N_2 + 3H_2 \rightarrow 2NH_3$
  - Uptake by animals and humans: nitrogen must be in organic form (protein)

- 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>

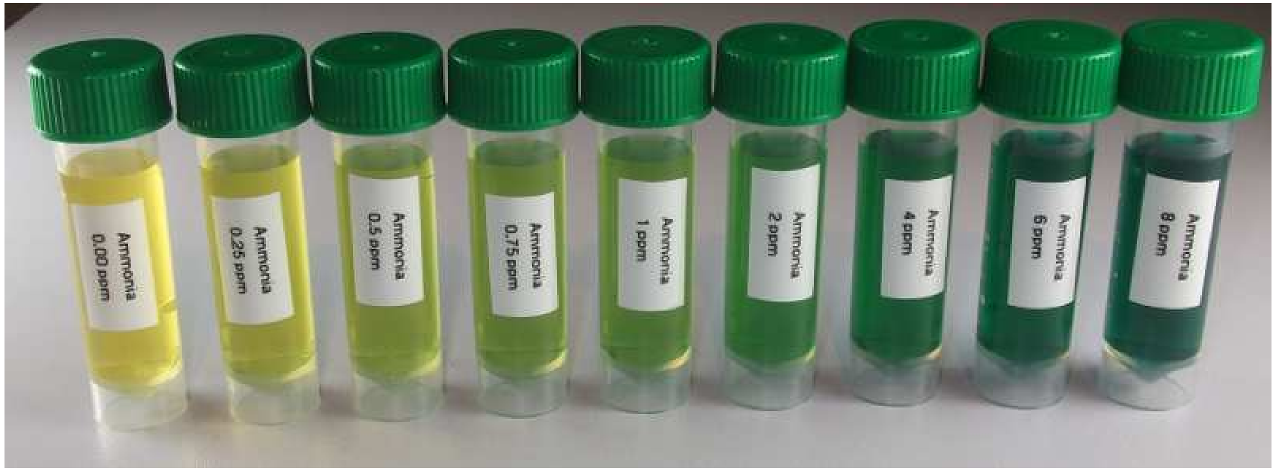
- Note nitrous oxide (N_2O) is a potent greenhouse gas (greenhouse gas potential 265-298 time greater than CO_2)
- N_2O may be released as an intermediate of both nitrification and denitrification

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

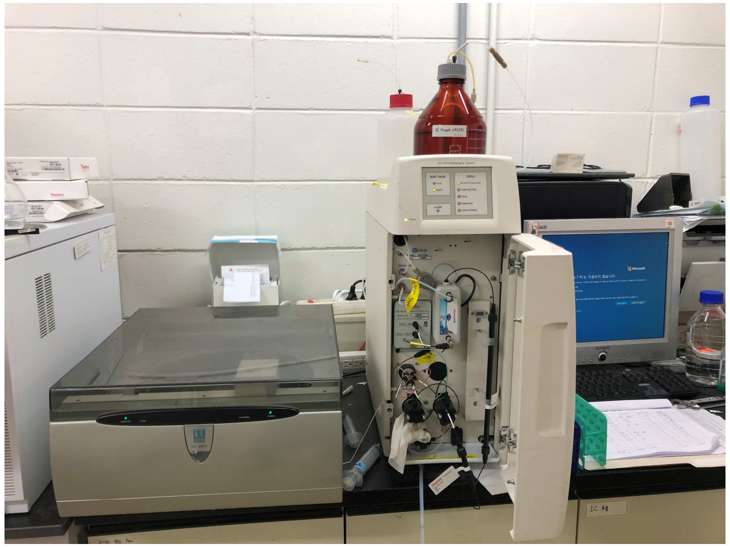
General methods for measuring ions

#2



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

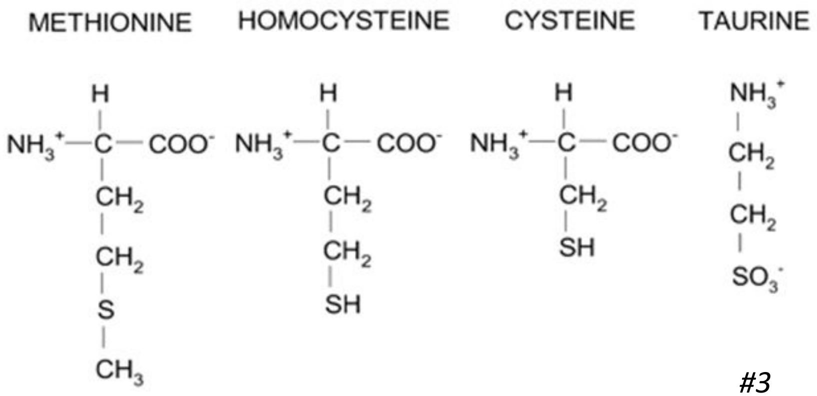
Ion chromatography (IC)

- 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
- 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

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

- 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

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

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

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

  - Most of the time, practically:

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

  - 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

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

#5

#6

$CaCO_3$ precipitation – temperature effect

Recall:

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

K_{a2} increases with increasing temperature:

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

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

Also recall:

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

⇨ Higher CO_3^{-2} fraction when water is heated,
Ca2+ 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:

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

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

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

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

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

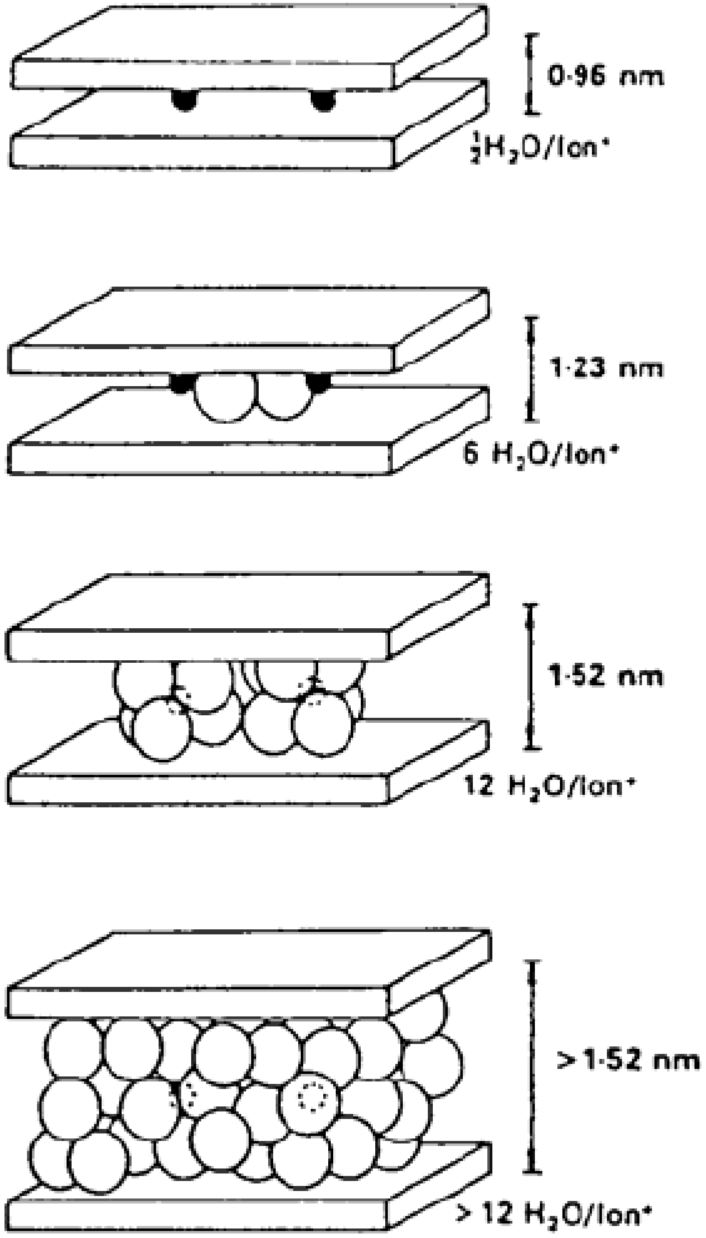
    → soil pore size ↓

    → 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 meq/L,
not eq/L

SAR < 3: low risk

3 ≤ SAR ≤ 6: slight to moderate risk

SAR > 6: high risk

References

#1) Davies, M. L., Masten, S. J. (2014) Principles of Environmental Engineering and Science, 3rd ed. McGraw-Hill (figure provided by the publisher).

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