

# WATER TREATMENT

## SKAA 2012

### WATER QUALITY PARAMETERS (CHEMICAL – NUTRIENTS, HARDNESS, ALKALINITY)

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# NUTRIENTS

- Carbon, Nitrogen and Phosphorus are crucial elements needed by animal and plants to live
- C – from  $\text{CO}_2$ , degradation of organic compounds
- N,P – limiting factors

# NUTRIENTS

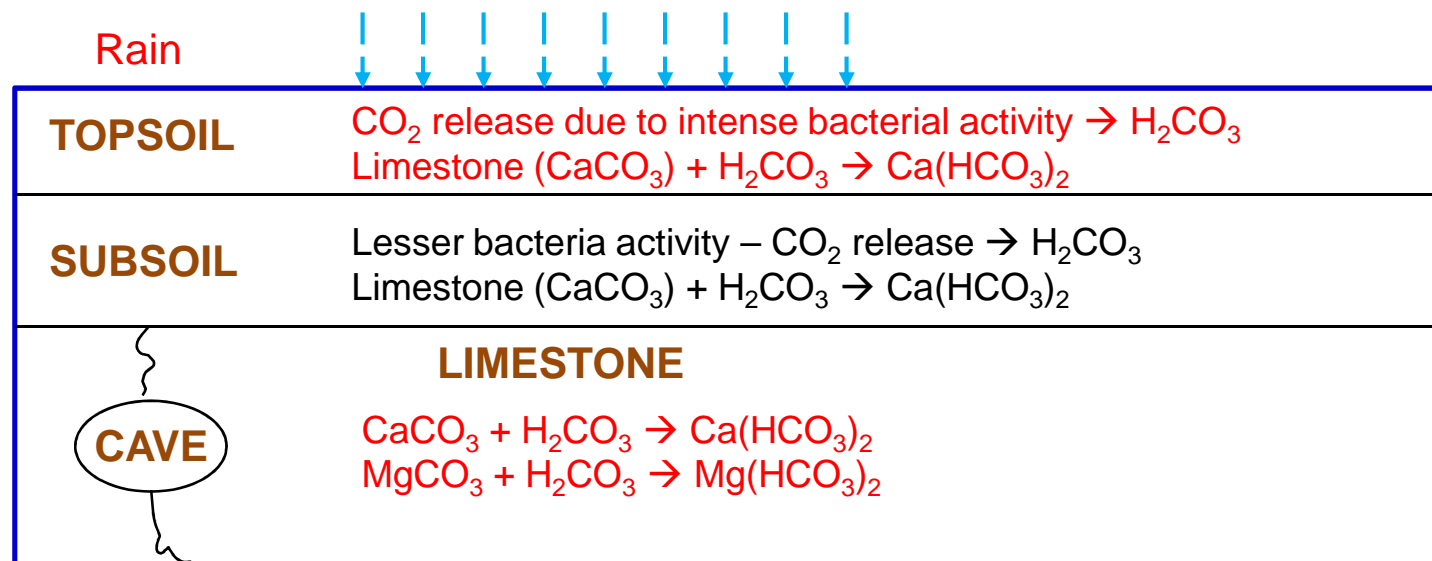
- Nitrogen (N)
  - Present in the form of ammonia or ammonium found in complex mixture of organic compounds such as proteins, amino acids and amino sugars
  - Sources:
    - Element for protein, chlorophyll and biological compounds
    - Decomposition to a simple compound  
Protein  $\rightarrow$  Amino acid  $\rightarrow$   $\text{NH}_3$   $\rightarrow$   $\text{NO}_2^-$   $\rightarrow$   $\text{NO}_3^-$
    - Animals and human wastes, chemicals (fertilizers)
  - Effects:
    - Poisoning in human and animal babies (baby blue syndrome – insufficient of oxygen in the blood due to the substitution of  $\text{NO}_3^-$  &  $\text{NO}_2^-$  in the blood vessel)
    - Excessive algae and aquatic plants breeding
    - Potential formation of nitrosamines and nitrosamides that can cause cancer in various tissue. However, these formation can be inhibited by the consumption of Vitamin C.
  - MCL: Total nitrate-N and nitrite-N  $<10$  mg/L

# NUTRIENTS

- **Phosphorus (P)**
  - An essential requirement for the growth of algae and other biological organisms
  - In the form of orthophosphates ( $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}_3\text{PO}_4$ ), condensed phosphate and organic phosphate
  - Sources:
    - Readily present in soil
    - Fertilizers
    - Human wastes (organic phosphates)
    - Domestic wastes (element in detergent)
  - Effects:
    - Algae blooms
    - $> 0.2 \text{ mg/L}$  – interfere the coagulation process in water treatment plant

# HARDNESS

- Definition: A measure of “multivalent” cations in water such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{3+}$
- Due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in water and is expressed as an equivalent concentration as calcium carbonate (**Total Hardness =  $\text{Ca}^{2+} + \text{Mg}^{2+}$** )
- Source:
  - Dissolved from rocks and soils (natural mineral on earth) due to bacterial activity (release as  $\text{CO}_2$ )



# HARDNESS

- Effects:
  - Excessive soap usage
  - Precipitate formation in hardware:

Affect cleaning (e.g. laundry (rough and scratchy clothes), dishwashing (spots on glasses and dishes), shower (film build up on bathtub, faucets, sink; sticky and dull feeling on hair))
  - Precipitate formation in pipe
    - ↑ Temperature & pH : Hard water build up scales in pipe and cause low water pressure
  - Water taste bitter ( $\text{CaCO}_3$ )

Contribution of other ions to water hardness is always  $< 1 \text{ mg/L}$  – insignificant

# HARDNESS

- Characterization of water hardness
  - Soft water:  $< 75 \text{ mg/L CaCO}_3$
  - Moderately hard water:  $75\text{-}150 \text{ mg/L CaCO}_3$
  - Hard water:  $150\text{-}300 \text{ mg/L CaCO}_3$
  - Very hard water:  $>300 \text{ mg/L CaCO}_3$
- Types of water hardness

(Total Hardness = Carbonate Hardness + Non-carbonate Hardness)

  - Carbonate hardness
  - Non-carbonate hardness

# HARDNESS

Example:

Calcium	=	29.0	mg/L
Magnesium	=	16.4	mg/L
Sodium	=	23.0	mg/L
Potassium	=	17.5	mg/L
Bicarbonate (as $\text{HCO}_3^-$ )	=	171.0	mg/L
Sulphate	=	36.0	mg/L
Chloride	=	24.0	mg/L

- Convert the above concentrations from mg/L to meq/L,
- What is the hypothetical combination?
- Find the water hardness in terms of mg/L as  $\text{CaCO}_3$



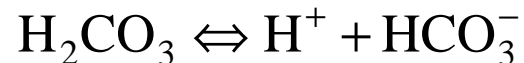
# ALKALINITY

- Definition:
  - The measure of ions in water to neutralize acid
  - A measure of its capability to neutralize acid
  - The quantity of strong acid required to titrate the solution to pH near 4.7
- In natural water, alkalinity is due to the salts of weak acids (bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ) and hydroxide ( $\text{OH}^-$ ) ions)
- Sources:
  - Mineral dissolved in water and air
  - Human activities such as detergent (in wastewater), fertilizers, pesticides, etc
- Effects:
  - Non-pleasant taste
  - Reaction between alkaline constituent and cation (positive ion) produces precipitation in pipe

# ALKALINITY

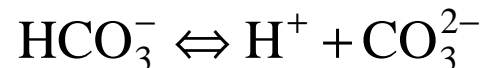
- In water hardness section, we learnt that
  - Bacteria activity release  $\text{CO}_2$  which dissolved in water as carbonic acid,  $\text{H}_2\text{CO}_3$  (pH 4.7)

pKa 6.35:  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  are at equilibrium



$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

pKa 10.33:  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are at equilibrium



$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

# ALKALINITY

- The specific concentration of each species can be computed when each fraction of the species is determined

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\alpha_{\text{H}_2\text{CO}_3} = \alpha_0 = \frac{[\text{H}_2\text{CO}_3]}{C_T} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$

$$\alpha_{\text{HCO}_3^-} = \alpha_1 = \frac{[\text{HCO}_3^-]}{C_T} = \frac{[\text{H}^+]K_1}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$

$$\alpha_{\text{CO}_3^{2-}} = \alpha_2 = \frac{[\text{CO}_3^{2-}]}{C_T} = \frac{K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$

# ALKALINITY

- We know that,
  - Alkalinity is the amount of strong acid needed to titrate the solution to pH near 4.7
  - Major alkalinity constituents include  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$
  - For acids & bases, one equivalent is one mole of  $\text{H}^+$
  - Therefore,

$$[\text{ALK}] \text{ meq/L} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

# ALKALINITY

- The concentration of carbonate and bicarbonate ions can be calculated if the pH and total alkalinity is known.

$$[\text{ALK}] \text{ meq/L} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ @ } 25^\circ \text{C}$$

$$[\text{HCO}_3^-] = \frac{\left( [\text{ALK}] - \frac{K_w}{[\text{H}^+]} + [\text{H}^+] \right)}{\left( 1 + \frac{2K_2}{[\text{H}^+]} \right)}$$

$$[\text{CO}_3^{2-}] = \frac{\left( [\text{ALK}] - \frac{K_w}{[\text{H}^+]} + [\text{H}^+] \right)}{\left( 1 + \frac{[\text{H}^+]}{2K_2} \right)}$$

# ALKALINITY

- The concentration of carbonate and bicarbonate ions can be calculated if the pH and total alkalinity is known.

$$[\text{ALK}] \text{ meq/L} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

$$[\text{HCO}_3^-] = C_T \alpha_1$$

$$[\text{CO}_3^{2-}] = C_T \alpha_2$$

$$[\text{ALK}] \text{ meq/L} = C_T (\alpha_1 + 2\alpha_2) + \left( \frac{K_w}{[\text{H}^+]} \right) - [\text{H}^+]$$

# ALKALINITY VS HARDNESS

- When alkalinity  $<$  total hardness

Carbonate hardness (mg/L) = alkalinity (mg/L)

- When alkalinity  $\geq$  total hardness

Carbonate hardness (in mg/L) = total hardness (in mg/L)

# REFERENCES

- American Water Works Association (2011). *Water Quality and Treatment: A Handbook on Drinking Water 6<sup>th</sup> Edition*, James K. Edzwald (Ed.), McGraw-Hill: USA
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- Sawyer, C.N., McCarty, P.L. & Parkin, G.F. (1994). *Chemistry for Environmental Engineering*, McGraw-Hill: Singapore