Homework #1 - Solutions

Due: March 29, 2016 (Tue), in class

- 1. Select one from the environmental or public health outbreaks related to water quality that occurred recently (2000-present) in your own country. Briefly (in less than 3 paragraphs) describe the contaminants of concern, causes, effects, and solutions adopted if there were any. (20 points)
- 2. Suggest at least four different roles that dissolved organic matter plays in the biochemistry and transport of contaminants in natural waters. (20 points)

Answer)

This question is designed to challenge students so as to encourage in-depth literature review in this topic. Dissolved organic matter (DOM) have various effects on the biochemistry in rivers, lakes, estuary area, and oceans. Much of those are quite popular topics in environmental science research. Followings list several effects of DOM on the biochemistry and transport of contaminants in natural waters.

- 1) DOM can be a nutrient source for aqueous ecosystem, providing carbon, nitrogen, and others.
- 2) DOM plays a significant role in carbon cycling in natural waters, transporting carbons produced in the upstream ecosystem towards downstream
- 3) Many DOMs are weak acids (humic substances are divided into humic acids and fulvic acids those are acids!), therefore affecting the pH in water.
- 4) DOM is involved in photochemical degradation of contaminants. (note: DOM acts as a photosensitizer, that is, DOM absorbs light, get excited, and transfer the energy to other molecules, that leads to the degradation of some contaminants.)
- 5) DOM absorbs light, so the light penetration into water is reduced by the presence of

DOM. This affects the growth of photosynthesizing organisms and photodegradation of chemicals in water.

- 6) DOM forms complexes with heavy metals and sorb organic contaminants, making those contaminants (apparently) dissolved in water. This leads to enhanced transport of the contaminants along with the water flow. (note: here "apparently dissolved" means that the substance is not dissolved in a free form, but in a form associated with other substances. For example, some hydrophobic organic contaminants have very low solubility in water, so they are mostly dissolved in water as a DOM-associated (or DOM-sorbed) form, not as a free form.)
- 7) Formation of DOM-heavy metal complexes and organic contaminant sorption by DOM also affects the fate of those contaminants in water, including chemical reactions, biodegradation, and volatilization.
- 8) Formation of DOM-heavy metal complexes and organic contaminant sorption by DOM also affects the toxicity of those contaminants. Generally, it is expected that the toxicity is reduced as the DOM-bound fraction is less available to organisms.
- 3. Determine the molarity and mole fraction of 43% ethanol in water (volume/volume basis). Assume that when ethanol is mixed with water, the total volume remains unchanged (for example, if 1.0 L ethanol and 1.0 L water is mixed, the total volume is 2.0 L). Use the following values:

density of ethanol = 0.78 kg/L

density of water = 1.00 kg/L

(10 points)

Answer)

MW of ethanol $(C_2H_5OH) = 2 \times 12 + 1 \times 6 + 16 \times 1 = 46 g/mole$

 $molarity(ethanol) = \frac{0.43 \ L \ ethanol/L \ solution \times 0.78 \ kg \ ethanol/L \ ethanol \times 10^3 \ g/kg}{46 \ g/mole}$

= 7.29 M

Moles of water in 1 L solution =

$$\frac{(1-0.43)\ L\ water/L\ solution \times 1.00\ kg\ water/L\ water \times 10^3 g/kg}{18\ g/mole} = 31.7\ moles/L$$

 $mole\ fraction(ethanol) = \frac{7.29\ mole/L}{(7.29+31.7)\ mole/L} = 0.187$

4. Determine the TS, TVS, TFS, TSS, TDS, VSS, FSS, VDS, and FDS of a water sample using the following data. All analyses are made using 50 mL of the water sample. (10 points)

Mass of residue in evaporating dish after evaporation at $105^{\circ}C = 36.0 \text{ mg}$ Mass of residue in evaporating dish after ignition at $500^{\circ}C = 34.0 \text{ mg}$ Mass of residue on filter paper after evaporation at $105^{\circ}C = 12.0 \text{ mg}$ Mass of residue on filter paper after ignition at $500^{\circ}C = 11.0 \text{ mg}$

Answer)

$$TS = \frac{36.0 \text{ mg}}{0.05 L} = 720 \text{ mg/L}$$

$$TVS = \frac{(36.0 - 34.0) \text{ mg}}{0.05 L} = 40.0 \text{ mg/L}$$

$$TFS = TS - TVS = 720 - 40 = 680 \text{ mg/L}$$

$$TSS = \frac{12.0 \text{ mg}}{0.05 L} = 240 \text{ mg/L}$$

$$TDS = TS - TSS = 720 - 240 = 480 \text{ mg/L}$$

$$VSS = \frac{(12.0 - 11.0) \text{ mg}}{0.05 L} = 20.0 \text{ mg/L}$$

$$FSS = TSS - VSS = 240 - 20 = 220 \text{ mg/L}$$

$$VDS = TVS - VSS = 40.0 - 20.0 = 20.0 \text{ mg/L}$$

 $FDS = TFS - FSS = 680 - 220 = 460 \ mg/L$

5. Using the following data for water sample analysis, i) determine the acceptance of the analysis for sample 1 and ii) predict SO_4^{2-} concentration in sample 2 as mg/L based on electroneutrality.

(unit: mg/L)

Ions	Sample 1	Sample 2
Ca ²⁺	76.0	120.0
Mg^{2+}	26.8	75.0
Na ⁺	23.0	1.86
\mathbf{K}^+	19.6	15.6
Cl	37.2	42.7
SO_4^{2-}	192.0	?
CO_3^{2-}	10.4	0.00
HCO ₃ -	126.5	156.9

(15 points)

Answer)

Following table can be constructed for concentration in meq/L:

Cations	Ion weight	Sample 1	Sample 2
Ca^{2+}	40.1	3.79	5.99
Mg^{2+}	24.3	2.21	6.17
Na^+	23.0	1.00	0.08
K^+	39.1	0.50	0.40
Sum		7.50	12.64

Ions	Ion weight	Sample 1	Sample 2
Cħ	35.5	1.05	1.20
SO_4^{2-}	96.1	4.00	?
CO_3^{2-}	60.0	0.35	0.00
HCO ₃ ⁻	61.0	2.07	2.57
Sum		7.46	3.77

i)

 $|\varSigma(anions) - \varSigma(cations)| = |7.46 - 7.50| = 0.04$

$$0.1065 + 0.0155 \times \Sigma(anions) = 0.1065 + 0.0155 \times 7.46 = 0.22$$

As the analysis result for sample 1 satisfies

 $|\Sigma(anions) - \Sigma(cations)| \le 0.1065 + 0.0155 \times \Sigma(anions)$, it is acceptable.

ii)

Based on electroneutrality, the concentration for SO_4^{2-} should be:

 $(SO_4^{2-}) = 12.64 - 3.77 = 8.87 \ meq/L$

 SO_4^{2-} equivalent mass = $\frac{96.1 g}{2 eq} = 48.1 g/eq = 48.1 mg/meq$

 SO_4^{2-} concentration in $mg/L = 8.87 meq/L \times 48.1 mg/meq = 427 mg/L$

6. Determine the alkalinity, total hardness, and carbonate hardness (in mg/L as CaCO₃) for the two water samples. (15 points)

Answer)

i) Alkalinity

 $Alk \!=\! \left(\! H\!C\!O_{\!3}^{-} \right) \!+\! \left(C\!O_{\!2}^{2-} \right) \!-\! \left(O\!H^{-} \right)$

Let's assume that (OH') is negligible. For sample 2, this assumption is valid as $[HCO_3^-] > 200 \times [CO_3^{2-}]$ (indicates that the solution pH is lower than 8). For sample 1, the assumption will be checked by question 7.

Sample 1: Alk(in meq/L) = 2.07 + 0.35 = 2.42 meq/L

Sample 2: Alk(in meq/L) = 2.57 meq/L

In mg/L as CaCO₃:

Sample 1: 2.42 meq/ $L \times 50$ mg/meq = 121 mg/L as CaCO₃

Sample 2: 2.57 meq/ $L \times 50$ mg/meq = 129 mg/L as CaCO₃

ii) Hardness

 $TH = (Ca^{2+}) + (Mg^{2+})$

Total hardness in mg/L as $CaCO_3$:

Sample 1: $(3.79+2.21) meq/L \times 50 mg/meq = 300 mg/L as CaCO_3$

Sample 2: $(5.99+6.17) meq/L \times 50 mg/meq = 608 mg/L as CaCO_3$

Carbonate hardness in mg/L as CaCO₃:

Sample 1: CH = Alk = 121 mg/L as $CaCO_3$ (: TH > Alk)

Sample 2: CH = Alk = 129 mg/L as $CaCO_3$ (: TH > Alk)

7. Estimate the pH of sample 1. Use $pK_{a2} = 10.3$ for carbonic acid. (10 points) Answer)

$$HCO_{3}^{-} = CO_{3}^{2-} + H^{+}$$
$$\frac{[CO_{3}^{2-}][H^{+}]}{[HCO_{3}^{-}]} = K_{a2}$$
$$pH = pK_{a2} + \log \frac{[CO_{3}^{2-}]}{[HCO_{3}^{-}]}$$

 $pH{=}\,10.3{+}\log\frac{0.173\;mM}{2{\cdot}07\;mM}{=}\,9.2$

Note that at pH=9.2, $(OH^{-}) = 10^{-4.8} eq/L = 0.016 meq/L$. This is negligible for the calculation of alkalinity (question 6).