## CH3041 Tutorial 2 Answers

1. The BOD test is routinely used for water quality analysis. Detail how the test works and why a simple DO reading is not sufficient to indicate the aerobic properties of the water.

In the BOD test at time = 0 a DO measurement is made to ascertain the DO level in the water before oxidation of organic matter has taken place The sample is diluted with a BOD diluent containing nutrients (Mg, Ca, Fe, P) that has been fully aerated. A Winkler titration (which relies on a stoichiometric reaction between  $Mn^{2+}$  and  $O_2$  followed by a subsequent  $I_2 / S_2O_3^{2-}$  titration) or an electrochemical DO probe are used to make the measurements (mg / L of dissolved oxygen).

The water sample is placed in a sealed BOD bottle and incubated at 20°C for 5 days and microbial oxidation of the organic matter in the water sample takes place.  $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$ T = 5d a second DO measurement is made to ascertain the DO level after oxidation.

The difference between the two DO measurements indicates the biochemical oxygen demand in the water, which is then related to the organic load of the water. Normal values in unpolluted water are around 2mg /L, high values are found in organically polluted water 1000s mg /L. A test which attempts to replicate the conditions found in natural waters and it best used for routine monitoring of water quality waterways as it takes 5 days per test.

The DO measurement only indicates the oxygen level in the water when the reading is taken. A DO reading is susceptible to considerable variations due to the ambient temperature. This is an important parameter but it does not indicate how close to running out of oxygen the water is. If there is substantial organic material in the water then a sudden burst of microbial activity may quickly remove all oxygen from the water and this is only indicated by a BOD (or roughly by a COD). Thus the BOD is a more useful indicator of the long term oxygenated state of the water, a low BOD and a good DO reading will indicate a healthy water.

2. Calculate the **pH** of a natural water given that the atmospheric CO<sub>2</sub> concentration is 350 ppm,  $K_{\rm H}$  for CO<sub>2</sub> is 3.38 x 10<sup>-2</sup> mol l<sup>-1</sup> atm<sup>-1</sup> and  $K_{\rm a}$  for the following equilibrium is 4.47 x 10<sup>-7</sup>.

 $CO_2(aq) + H_2O(l) \leftrightarrows HCO_3(aq) + H^+(aq)$ 

 $\%_i = ppmv_i \ge 10^{-4}$ 

 $p_i = (\%_i / 100) p_{atm}$ 

 $[i_{(aq)}] = p_i K_H$ 

 $p(CO_2) = (350 \times 10^{-4} / 100) \times 1 = 3.5 \times 10^{-4} \text{ atm}$ 

$$\begin{split} [CO_{2(aq)}] &= K_{H} \, p(CO_{2}) \qquad K_{H} = 3.38 e^{-2} \, \text{mol } l^{-1} \, atm^{-1} \\ &= 3.38 \, x \, 10^{-2} \, x \, 3.5 \, x \, 10^{-4} \, atm \\ &= 1.183 \, x \, 10^{-5} \, \text{mol } dm^{-3} \\ K_{a} &= [H^{+}]^{2} \, / \, [CO_{2}] = 4.47 \, x \, 10^{-7} \\ &= [H^{+}]^{2} \, / \, 1.183 \, x \, 10^{-5} \end{split}$$
 $[H^{+}] &= \sqrt{(4.47 \, x \, 10^{-7} \, x \, 1.183 \, x \, 10^{-5})} \\ &= 2.30 \, x \, 10^{-6} \, \text{mol } dm^{-3} \end{split}$ 

 $\begin{array}{ll} pH & = -\log_{10}[H^+] \\ & = -\log_{10} \\ & = 5.64 \end{array}$ 

3. Explain the term Base Neutralising Capacity (BNC). How does this parameter differ from the pH of a water sample?

Base Neutralising Capacity  $[BNC] = [HA] + [H^+] - [OH^-]$ The major acids [HA] are: H<sub>2</sub>CO<sub>3</sub>, fulvic & humic organic acids, HCl, H<sub>2</sub>SO<sub>4</sub>. BNC is the sum of all acids in a water that can be titrated to a fixed equivalent point using the strong base NaOH, it is the ability of the water to neutralise added base.

The total acidity is determined by titration to the phenolphthalein indicator endpoint (pH 8.2), while the titration of mineral acidity is found by titration to the methyl orange indicator endpoint (pH 4.3). The units are meg / L ( the mmol OH<sup>-</sup> equivalents titrated per litre).

The pH of a sample indicates the available  $H^+$  in the solution as an *intensity factor* of  $H^+$ . It is usually determined directly by measuring pH.

For a weak acid it must have a high concentration to generate an appreciable  $H^+$  intensity, due to only partial dissociation to give  $H^+$ , eg  $H_2CO_3$  A strong acid may have a low concentration and yet display a appreciable  $H^+$  intensity as it is fully dissociated eg. HCl.

In contrast a moderately high BNC may be found with a weak acid if it has a moderate concentration as this is a *capacity factor* that relates simply to the total concentration of the acid and not the liberated concentration of  $H^+$ . A strong acid with an equivalent pH will have a lower BNC as there will be a lower total concentration of the acid present.

4. List the major classes of acids that are found in natural waters and indicate their origin.

• Which acids are introduced into the environment by humans in significant quantities, indicate their origin.

(a)

 $H_2CO_3$  (carbonic acid) (weak acid) carbonate rocks are ubiquitous and the presence of  $CO_2$  as a minor atmospheric gas means this is the most important acid / base system in the environment.

Humic and Fulvic acids (weak acids) Polyprotic acids (can lose more than  $1 \text{ H}^+$ ) Complex polymeric organic acids - biodegredation of large polymeric plant materials such as lignins (rivers) or by the aggregation of smaller molecules such as triglycerides (oceans).

Humic substances can be pptd at pH = 2MW > 1000'sFulvic substances stay in soln at pH = 2(have more COOH and -OH groups)MW > 300'sHCl,  $H_2SO_4$ (strong acids)Volcanic sources(also called mineral acids)



5. Seawater is not simply evaporated river water. List the major 0 ions present in both natural waters and comment on the reasons that make the above statement true.

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	Major Ion Composition (mmol I <sup>-1</sup> , global averages)					
Ion	Riverwater	Seawater				
HCO <sub>3</sub> <sup>-</sup>	0.85	2	(being removed)			
$Ca^{2+}$	0.33	10	(being removed)			
$Na^+$	0.23	470				

Cl	0.16	550	
SiO <sub>4</sub> <sup>4-</sup>	0.16	0.1	(being removed)
$Mg^{2+}$	0.14	53	
$SO_4^{2-}$	0.09	28	
$\mathbf{K}^+$	0.03	10	(a source in oceans)

Ocean Input - Output Balance :			$(10^{12} \text{ mol } / \text{ y})$			
Ion	Inventory(x10 <sup>18</sup> mol)	River	Air	Other	CO <sub>3</sub> dep	<b>•</b> $\tau(10^6 \text{ y})$
Cl	710	+6.1	-6.1	-	-	131
$Na^+$	608	+8.5	-5.7	-2.8	-	78
Mg <sup>2+</sup>	69	+5.2	-0.3	-4.3	-0.6	14
$SO_4^{2-}$	37	+3.2	-0.3	-2.9	-	12
$\mathbf{K}^+$	13	+1.2	-0.1	-1.1	-	13
$Ca^{2+}$	13	+12.5	-0.1	+4.6	-17	1.1
"CO <sub>3</sub> "	3.1	+31.9	-	+2.5	-34.4	0.1
	Air = atmospheric - evap	orite cycli	ing.	Other = Ion	exchang	e / Hydrothermal / Pyrite Burial

Seawater is not simply evaporated riverwater, if this were the case we would expect to find the concentration of  $Mg^{2+}$  comparable to that of Cl<sup>-</sup> and the concentration of "CO<sub>3</sub><sup>2-</sup>" and Ca<sup>2+</sup> to be significantly higher than Na<sup>+</sup> and Cl<sup>-</sup>, which is clearly not the case.

As the river water hits the estuaries there is a rapid change in ionic strength this results in a substantial alteration in the ionic composition of the water that eventually arrives in the ocean. The colloid particles in the rive water rapidly sediment in the estuaries and cation exchange with these colloid particles alters the ionic ratios in the water.

Some ions are lost readily from the oceans in the bubbles due to wave breaking,  $Na^+Cl^-$  are good examples. The  $Na^+Cl^-$  ions are also lost through deposition in supersaturated regions as evaporite mineral deposits (eg. Halite).

The ocean floor is not chemically inert and some ions exchange with ion-exchange minerals on the sea floor Na<sup>+</sup> is an example. The most active areas for ion addition and removal are the deep sea hydrothermal vents in the vicinity of marine oceanic ridges: Mg, Si, K, Ca, Na and  $SO_4^{2-}$  are ions effected.

Many ions also react with pyritic material that is being buried on the sea floor, the pyritic material is formed, in particular  $FeS_2$  by the sulphate reduction which occurs in the sediments.

Carbonate deposition results in the removal of substantial amounts of  $CaCO_3$ , this occurs both through the large-scale biotic mechanism (eg. Great Barrier Reef) and in regions where the  $[CaCO_3]$  is significantly supersaturated and the mineral deposits directly (eg. oids).

Marine organisms also alter the Si balance where the incorporation of silicon into the framework of marine diatoms results in a significant removal mechanism for dissolved silicate ions.