Problem Set VII
Oxidation/Reduction Reactions

1. Define poise and give an example of a poised redoc reaction.

2. You have 100 grams of three of the same soil with a mixed mineralogy of kaolinite, vermiculite, quartz, a small amount of Fe-oxides and 0.25 % organic matter. To the first soil you add 100 ppm nitrate, to the second you add 8 grams of wheat flour, and to the third soil you add nothing. All 3 soils are submerged with water and you measure Eh over the next 3 months. Which soil would you expect to exhibit the lowest redox potential and why?

3. Why are electrode measured redox potentials and thermodynamically defined redox potentials not necessarily the same in soil solution?

4. What is the equilibrium concentration of Fe^{2+} in an aerated soil solution at pH=7, assuming that $Fe(OH)_3$ is the solid phase formed by Fe oxidation? (assume $P_{O2} = 0.2$ atm)

5. Why does one often find significant quantities of ferrous Fe (Fe^{2+}) and Mn^{2+} in a well aerated soil?

6. We talked about natural attenuation and its potential as a remediation technique. You have to decide if the following site would be a good candidate for natural attenuation of Pb^{2+}, Cu^{2+}, and Cr^{3+}. The soil is dominated by Fe-oxides and kaolinite with a high quantity of OM (5%). It is located in a valley that receives significant amounts of rainfall and has a fluctuating water table and during some times of the year may remain flooded. Would you recommend this site for natural attenuation, why or why not?

7. Soils in the Mekong Delta have been continuously submerged and used for rice production. These soils developed on marine deposits rich in pyrite. What might happen if these soils were drained so that they can be used for soybean production? Is this an example of an oxidation or a reduction reaction?

8. A soil adjacent to the new river becomes periodically flooded during the year. The soil may stay submerged for several weeks depending on the extent and duration of the flooding event. The soil contains about 2 % SOM, 6 % Fe-oxides, 0.5 % Mn-oxides, and is heavily fertilized with nitrate several time a year. After several weeks of flooding what do you think the redox potential will approximately reach (Eh). What reactions will poise the redox of the system?

9. Base on the diagram of pe vs pH for Iron from your notes; a solution has an Eh of 0.6V and a pH of 6.0, which form of Fe would dominate under these conditions?

10. From the half potentials listed in your notes develop the Eh-pH lines for the following half reactions (show all work): Assume Fe^{2+} and $Mn^{2+} = 1 \times 10^{-5}$

$Fe(OH)_3$ (s) + $3H^+$ + e- = Fe^{2+} + $3H_2O$ $\quad Eh^o = 1.057$

MnOOH (s) + $3H^+$ + e- = Mn^{2+} + $2H_2O$ $\quad Eh^o = 1.45$

Under reducing conditions which oxide would you expect to dissolve first and why?

11.EXTRA CREDIT (5 Points)

Shewanella putrefaciens can mediate the reduction of U^{6+} to U^{4+}. U^{6+} is soluble whereas U^{4+} is relatively insoluble. Similar to many redox active elements the oxidation state of uranium is extremely important factor in determining the mobility and toxicity of Uranium in the environment.

A typical reaction is as follows:

$$0.5UO_2(CO_3)_3^{4-} + H^+ + e^- \rightarrow 0.5UO_2 \text{ (uraninite solid)} + 1.5HCO_3^-$$

a. Calculate Eh^0 for this reaction at 25 C given Gf^0 (kJ mol^{-1}) = -1031.7 for UO_2, -2659.2 for $UO_2(CO_3)_3^{4-}$ and –586.8 for HCO_3^-.
b. Calculate the Eh for this reaction at pH = 5.7, $UO_2(CO_3)_3^{4-}$ =1 X 10^{-5} mol l^{-1} and the total carbonate, Ct= 3 X 10^{-2} mol l^{-1}. Hint : you will have to calculate the quantity of HCO_3^- present at pH = 5.7 (pk_1 = 6.37)