PROBLEM SET VI
SORPTION PHENOMENA ON SOILS

1. Given the following chemical data, which of the following cations would you expect to adsorb preferentially to goethite (justify your answer):

Ni^{2+}: Electronegativity = 1.8; z/r = 6; pK_h (hydrolysis constant) = 9

Cd^{2+}: Electronegativity = 1.6; z/r = 4; pK_h (hydrolysis constant) = 12

2. Two adsorptives were found to specifically adsorb to a particular adsorbent. One of the adsorbates formed a monodentate surface complex while the other formed a bidentate binuclear surface complex. Which one of these would be more readily desorbed from the adsorbent (Justify your answer).

3. You are the Senior Environmental Soil Chemist for Dredco Environmental Inc. Your company has been awarded a large contract to clean up trace element contaminated sites throughout the southeast. The first two sites you look at are located in Central Alabama and Southeast Florida. The contaminants are the same; Pb^{2+}, Cr^{3+}, and Ni^{2+}. The site characterization data shows the following:

AL site, pH =6.5, 45 % clay, clay mineralogy = Fe-oxides, Kaolinite, and trace amounts of 2:1 layer silicates, CEC = 8 cmol(+)/kg, OM = 0.20%.

FL site, pH = 5.0, 10% clay, clay mineralogy = illite, vermiculite, small amount of Ti and Si oxides, CEC = 4 cmol(+)/kg, OM = 0.75%.

As the senior Environmental Soil Chemist you need to prioritize the sites. Which site would you begin work on first? Justify your answer.

4. Explain why Fe- and Al oxides are more reactive than Si- and Ti-oxides?

5. You have a soil that is dominated by Fe- and Al-oxides and has high concentrations of Pb^{2+}. The pH of the soil is 6.0. Can you think of any possible ways to desorb and remove the majority of the Pb^{2+} based on your knowledge of sorption phenomena.

6. Arsenate (H_3AsO_4) is similar to phosphate forming strong bonds with Fe-oxides. An industrial waste-water effluent has high concentrations of arsenate. This arsenate needs to be removed before the water can be discharged into a nearby stream. The pH of the water is near 5.0. How would you remove the arsenate from the wastewater?

7. In high-selenium soils of some arid regions, selenate is a problem pollutant in the drainage water of irrigated fields, while selenite is not. Develop a plausible argument based on chemical principles to explain this observation.

8. Explain (in chemical terms) why oxyanions that are weak acids tend to adsorb on Al- and Fe oxides at a pH that is near their pKa values.

9. Cu^{2+}, Cd^{2+}, and Pb^{2+} all show enhanced adsorption on Al hydroxide after the surface has adsorbed phosphate. Describe a bonding mechanism that would explain this effect.

10. Both the langmiur and Freundlich equations are used to describe ion sorption on soils and soil constituents. Can the fit of experimental data to these equations provide information on the adsorption mechanism? Why or why not?

12. Arsenic in the oxidized form (H_3AsO_4) adsorbs strongly on variable charged surfaces with the maximum adsorption near pH 4. Arsenic in the reduced from ($As(OH)_3$) adsorbs less strongly with maximum adsorption near pH 7. Given the fact that H_3AsO_4 is a much stronger acid than As(OH)3, explain this behavior.

13. Would you expect natural attenuation to be more prevalent in a well developed soil from the Valley and Ridge (mixed mineralogy: secondary clay minerals, Fe-oxides) or a soil from the eastern part of the coastal plane (primary minerals, low OM and secondary minerals). Justify your answer.