EXERCISE 8

Mercury in the Florida Everglades

A canal carries water from the Everglades Agricultural Area into one of the water conservation districts. Last year, phosphate levels were unusually high in Lake Okeechobee and surrounding waters. Algal levels exploded in response. Now, the algae have died back and the sediments are enriched with organic matter. There is concern that this could shift the Hg speciation toward greater levels of methyl Hg.

A section of the canal has been chosen for detailed study. This reach is believed to receive Hg from both sediments and from the air. Your firm has been retained by the South Florida Water Management District (SFWMD) as a consultant to assist with this study. Your job is to examine the part of the Hg that derives from atmospheric inputs. A preliminary set of calculations is desired in order to better design the subsequent (and expensive) field sampling campaign. Address the following points and prepare a summary report to Dr. H.G. Marsh, the environmental specialist for the SFWMD mercury project.

Background
Elemental Hg\(^0\) accounts for about 99% of atmospheric Hg. A recent air monitoring study found that the concentrations of elemental Hg in the air over the Everglades had an average value of 20 pg/m\(^3\), which is typical of areas in proximity to heavy urban development.

For a specified partial pressure of Hg\(_{\text{g}}\), MINTEQ will calculate the inorganic Hg speciation. MINTEQ calculates the equilibrium between Hg\(^0\)\(_{\text{g}}\) and the dissolved elemental (zero-valent) Hg species or Hg\(^0\)\(_{\text{aq}}\). MINTEQ also automatically calculates the aqueous equilibrium with dissolved mercurous ion which consists of a pair of Hg\(^+\) ions (+I state) in the species Hg\(_2\)\(^{2+}\).

Methylmercury however is in the +II oxidation state and forms from the Hg(II) or mercuric ion. Because Hg(II) hydrolyzes so strongly, the dominant aqueous species (in the absence of any other ligands) is Hg(OH)\(_2\), which thus is the form of the mercuric component in MINTEQ. To find the concentration of t Hg(OH)\(_2\) and the various other Hg(II) species, you must tell MINTEQ to consider redox couple Hg(I)/Hg(II), or in MINTEQ components: Hg\(_2\)\(^{2+}\)/Hg(OH)\(_2\). Once this is specified, along with any other appropriate redox couples, the output will include the activity of Hg(OH)\(_2\).

The aqueous concentration of the dissolved (not gas-phase) species Hg(CH\(_3\))\(_2\) must be calculated indirectly from MINTEQ output. As described in the notes, you can use the mass action ratio for the formation of Hg(CH\(_3\))\(_2\) in order to calculate the concentration of this species:

\[
( \{ \text{Hg(CH}_3)_2 \}_\text{aq} ) / ( \{ \text{Hg(OH)}_2 \} \{ \text{CO}_3\^{2-} \}^2 \{ \text{H}^+ \}^{20} \{ \text{e}^- \}^{16} ) = 10^{84.7}
\]

Or:

\[
\{ \text{Hg(CH}_3)_2 \}_\text{aq} = \{ \text{Hg(OH)}_2 \} \{ \text{CO}_3\^{2-} \}^2 \{ \text{H}^+ \}^{20} \{ \text{e}^- \}^{16} 10^{84.7}
\]

Data:
Water samples taken from the bottom of the canal have the following average analysis:

pH 7.0  
Na = 53 mg/L  
Fe(II)T = 3.4 mg/L  
SO4 = 32 mg-S/L  
Sulfide = 16 mg-S/L

The water in the canal appears to be well buffered at pH 7.0 and is in equilibrium with atmospheric CO₂. The average temperature in this subtropical climate is about 25°C.

Average air concentration of Hg(g) = 20 pg/m³  
(Remember that MINTEQ needs this expressed as a partial pressure in atm.)

1. Although dissolved oxygen was not reported, the water analysis should tell you that the water sampled was anoxic.
   A. Use a simple thermodynamic calculation to demonstrate that if dissolved oxygen were present (the water was at a typical oxic pe), that essentially no Fe(II) or S(-II) could be present. (This will verify that the water sampled must be anoxic.) Show your calculation.
   B. If some disturbance of the canal such as a storm or a speeding boat were to mix the bottom water with well oxygenated surface water, what inorganic oxygen demand would the lower water exert in mg/L? (In other words, how many mg/L of D.O. would be consumed by the complete oxidation of the reduced species in the bottom water?) Show your calculations.
   C. How does this oxygen demand compare to the saturated D.O. of about 9 mg/L?
   D. What are the water quality implications of this finding for the canal?

2. Since Hg levels are expected to be small relative to other constituents, it is logical to first look at the chemistry of the major elements in the system without adding Hg (i.e., no equilibration with atmospheric Hg). Calculate the chemical speciation of the canal bottom water for the two scenarios below. Be sure to report the pe and E₉ (in mV) for both scenarios and briefly explain why the pe changes.
   A. Speciation at equilibrium if no solids are allowed to form. As usual, highlight the major species. Report pe and E₉ (in mV).
   B. Check the saturation indices and see which iron sulfide species could form. Crystalline FeS minerals (such as mackinawite) form very slowly and pyrite (FeS₂) will typically not form at all under these conditions, but amorphous FeS(ppt) can readily form. Allow this solid to form if appropriate and recalculate the speciation at equilibrium. The composition of the solution changes, but does the pe change? Explain why or why not. The Equilibrated Mass Distribution Table will help you explain this. (Note also, elemental S will not precipitate under these conditions)
   C. What does the composition of the water sample suggest about the mineral phases in the bottom sediments?

3. Calculate the expected Hg speciation for the canal water at equilibrium with the atmosphere. I recommend a stepwise process as follows:
   A. For no reason I can figure out MINTEQ has the following quirk. If I took the saved input file from the previous step and added Hg(g), it crashed every time, no matter what I did.
However, if you reset the input file and start from scratch in the following order, I got it to converge properly every time:
1. Type in the Na+, HS-, SO4 conc’s and specify pH, HS- redox couple and the CO2 and Hg gases.
2. Run to verify it works.
3. Now add Fe2+ and run to verify it works.
4. Allow FeS(ppt) as possible solid and run.
5. If all went well (always did for me) record speciation and pe/Eh.

This is a classic example of something that plagues MINTEQ: unpredictable instability with complex redox problems. If you run across it in the future, do what I did, and just try reconstructing the problem from scratch and try rearranging the order in which you add redox active components.

B. Now go back and add in the Hg2+2/Hg(OH)2 redox couple to get the Hg(II) species. Record the speciation.

C. Present and discuss the speciation of Hg. Focus on the relative importance of Hg(I) and Hg(II) as well as which species are significant within each redox state. How important here is the “major” Hg(OH)2 species of Hg(II) and why?

4. Now let’s consider methylmercury. Although dimethylmercury can dissociate in water to become monomethylmercury ion, assume that the only organic species in solution is the dimethylmercury. Ignore the biological degradation of (di)methylmercury. MINTEQ does not perform the equilibration between Hg(OH)2 and dissolved Hg(CH3)2 so you must do the calculation yourself, using the equation given on the first page, and as discussed in class. Obtain the necessary species activities from the final MINTEQ output.

A. What is the molar concentration of Hg(CH3)2 ?
B. What is the relative distribution of organic and total inorganic Hg in the system?
C. What is the concentration of Hg(CH3)2 in ng/L and how does this compare to:
   1. The typically observed range in Everglades waters of 1-5 ng/L?
   2. The level at which serious toxicity is expected: 12 ng/L

   **Hint:** Do part 5 before you address these questions.

5. Direct Eh measurements from a few centimeters deep in the sediments showed pe values of about -6.1, and some evidence suggests that this number has been getting steadily more negative in recent years as a result of the eutrophic build-up of organic matter.

A. What microbial processes are typical at pe = -6.1?
B. Explain why your bottom water had a different pe, and does that makes sense?
C. Recalculate the concentration of Hg(CH3)2 in ng/L at pe = -6.1. How does this compare to:
   1. The typically observed range in Everglades waters of 1-5 ng/L?
   2. The level at which serious toxicity is expected: 12 ng/L

D. How does the methymercury level respond to a small, say, +/- 0.1 unit, change in pe? Comment on why the increasing eutrophication may be of great concern to the methymercury problem.