Practical 4: Open Systems and Kinetics

1. The volume of the oceans is 1.37×10^{21} L; the global riverine input to the oceans is 3.6×10^{16} L/y. Calculate the residence times in the ocean (relative to riverine input) of the following chemical species given the observed concentrations:

Element	Conc. In Rivers (mol/L)	Conc. In Oceans (mol/L)
K	3.4×10^{-5}	1.02×10^{-2}
Fe	7.2×10^{-7}	1×10^{-9}
Cu	1.6×10^{-7}	4.0×10^{-9}
Si	1.9×10^{-4}	1.0×10^{-4}

Elements are removed from seawater by a number of mechanisms including precipitation, adsorption and biological uptake. Can you speculate as to what fundamental properties of these elements might explain the vast differences in residence times? (Note: in seawater, Fe is in the +3 oxidation state while Cu is in +2 state.)

2. Consider an element X exchanging between two geochemical reservoirs A and B. Let M_a and M_b be the masses of X in reservoirs A and B, respectively; let t_a and t_b be the residence times of X in reservoirs A and B, respectively. Further let $M = M_a + M_b$ be the total mass of X in the two reservoirs combined.

a. Show that at steady state, $M_a = M / (1 + \{ t_b / t_a \})$
b. In the limit $t_a >> t_b$ what controls the value of M_a?

3. The current concentration of Hg in the oceans is 5×10^{-12} mol/L while that in rivers is 4×10^{-10} mol/L. Hg is lost in the ocean by ‘scavenging’ onto sinking particles and incorporated into the sediments. As in the Hg-atmosphere example in lecture, assume that the kinetics of scavenging is first order so that the output flux due to scavenging is

$$F_{scav} = kV[Hg]$$

Where k is our first-order rate constant and V is the volume of the ocean (1.37×10^{21} L). Evaluate what k must be if the [Hg] in the oceans are at steady state. To do this, note that steady state requires that

$F_{riv} - F_{scav} = 0$

(we're ignoring input/output to the atmosphere and hydrothermal vents etc.). the global riverine flux of Hg to the oceans is 3.6 x 10^{16} L/y x $[Hg]_{river}$.

Now calculate the change in ocean [Hg] with time if we increased the riverine flux by a factor of 2. How long will it take for us to see a significant change in marine [Hg]?

4. A stream (5000 m^3/day) enters a pond (1000 m^3) situated above a mine-tailings pile. The tailings pile contains $PbCO_3$ which is found to dissolve with a rate law

$$R_{diss} = kA(C_s - C)$$

with *k* = 0.2 /m^2 $PbCO_3$ -day. C_s is the saturation concentration of $PbCO_3$ which, at the pH of the pond, is 15.0 mole $PbCO_3$/m^3 water. *A* is the surface area of exposed $PbCO_3$ per m^3 of water and is equal to 1 m^2 $PbCO_3$/m^3 water.. The outflow stream from the pond has a flow rate of 5000 m^3/day.

Set up a simple box model for the situation and calculate the steady-state concentration of Pb^{2+} in the pond. How does it compare with the equilibrium saturation concentration? What is the residence time of dissolved Pb in the pond?

If you know some calculus, can you figure out how long it took the pond to reach steady state?

5. A sewage inflow with total dissolved organic carbon of 25 mg C/kg-water enters a pond that contains 10000 kg water. The inflow rate of the sewer is 100 kg-water/day. Respiration in the lake occurs with first-order kinetics with a rate constant of 0.02 /hour. Water leaves the lake at a rate of 300 kg/day (the volume of the lake is constant, however due to input by rain and other streams..). What will be the steady state concentration of dissolved organic carbon in the water?