Fate & Transport of Chemicals in the Environment

Homework #7 University of South Florida
Due Wednesday, March 23, 2022 Prof J A Cunningham

1. (25 pts) In the Tampa Bay region, most of our household garbage ("municipal solid waste," or MSW) is incinerated. However, in most of the country, MSW is landfilled rather than incinerated. When MSW is put in a landfill, some of it decays or decomposes, releasing methane gas. That can be a good thing if the methane is harvested for energy, but it can be a safety hazard and a source of greenhouse-gas emissions if the methane release is uncontrolled. I was wondering how much methane is generated over the lifetime of a landfill. How would we figure that out? – with a mass balance, of course!

   Suppose the rate of MSW addition to a landfill is Q. The units are mass/time. A mass fraction f_d of the MSW decomposes, a mass fraction f_w is water or moisture, and the remainder $(1–f_d–f_w)$ is inert. The rate of MSW decomposition looks something like a first-order process: at any given time t, the rate of decomposition (in units mass/time) is linearly proportional to $M(t)$, the mass of decomposable MSW in the landfill at that time. Let's call the rate coefficient k.

   a. Write a mass balance for the mass of decomposable MSW in the landfill. You should end up with a differential equation in the form $\mathrm{d}M/\mathrm{d}t = \ldots$

   b. Solve the differential equation to derive a formula for $M(t)$, the mass of decomposable MSW in the landfill at any time t.

   Now we need to know how much methane is generated when the MSW decomposes. Suppose that the decomposable MSW is (by mass) 44.17% carbon, 5.91% hydrogen, 42.50% oxygen, 0.73% nitrogen, and 6.69% other. (I read that in a book somewhere, but I don't remember where.)

   c. Find an empirical molecular formula $C_aH_bO_cN_d$ for decomposable MSW, ignoring the 6.69% of "other". Note that a, b, c, and d do <u>not</u> need to be integers. (Sorry, Simon.)

   d. The stoichiometry for methane production is

      $$C_aH_bO_cN_d + n\,H_2O \rightarrow m\,CH_4 + s\,CO_2 + d\,NH_3$$

      where $n = (4a – b – 2c + 3d)/4$
      $m = (4a + b – 2c – 3d)/8$
      $s = (4a – b + 2c + 3d)/8$

      Based on this stoichiometry, find how many moles of methane gas are generated per 1 kg of decomposable MSW that decays. We will call this Y, the yield. The units are (kg methane generated)/(kg decomposable MSW that decays).

problem 1 continues →

1. continued

   e. Recall that the rate of MSW decomposition is linearly proportional to $M(t)$, and now we know that Y kg of methane are generated per kg of MSW decayed. Derive a formula for the rate of methane generation as a function of time.

   f. In part (e), you found the rate of methane generation at any time t. The total mass of methane that has been generated by time t is the integral of the rate expression. Integrate your expression from part (e) to derive a formula for the total mass of methane generated by time t. Don't forget to use an appropriate initial condition.

   Suppose that for a particular landfill, Q = 200,000 kg/d and $f_d = 0.45$. These are pretty realistic values. Let's also suppose that $k = 0.1\ \text{yr}^{-1}$. I don't actually know if that is a realistic value, but let's assume it is OK for this analysis.

   g. Suppose the lifetime of the landfill is 40 years. Graph your function from part (f). What is the total mass of methane generated in 40 years? What do you conclude about landfills as possible sources of methane?

   h. NOT REQUIRED – just because I was interested -- graph the mass of decomposable MSW in the landfill over the 40-year lifetime. It should eventually reach a steady-state value, when the rate of MSW addition equals the rate of MSW decay. Does it look like steady state is reached within the 40-year lifetime of the landfill?

2. (15 pts) This problem is based on one that I saw in a well-known text book by Masters & Ela, *Introduction to Environmental Engineering and Science*.

   The Plateau Creek carries 5.0 m^3/s of water that has a concentration of selenium (Se) equal to 0.0015 mg/L. Se is a naturally occurring element that living organisms (including humans) need in small doses, but it is toxic at high concentrations. On the banks of the Plateau Creek is a large farm called Salinas Farms. Salinas Farms withdraws 1.0 m^3/s from Plateau Creek for irrigation (with the Se concentration given above). During irrigation, the irrigation water picks up Se from the salts in the soil. Half of the irrigation water is lost to the crops and to evaporation, but the other half returns back to Plateau Creek. The irrigation run-off that returns to the creek contains 1.0 mg/L of Se.

   a. If Salinas Farms irrigates continuously, what will be the steady-state concentration of Se in the creek downstream of the farm (after the irrigation run-off returns to the creek)? Report your answer to two significant digits. Hint: draw a picture, and perform a mass balance. You can assume that Se is non-reactive, and that there are no other sources of Se into the creek.

problem 2 continues →

2. continued

   b. The level you found in part (a) was deemed too high. It was toxic to the fish in Plateau Creek. To keep the Se concentration in the river below 0.04 mg/L, how much water can Salinas Farms withdraw? (Assume that at the new extraction rate, 50% of the extracted water is lost, and 50% returns to the creek at a concentration of 1.0 mg/L, just as before.) Report your answer in units of m^3/s, and report two significant digits. Hint: draw a picture, and perform a mass balance.

   Note: A situation like this actually happened in real life in the 1970s and 1980s at the Kesterson Reservoir in California. It almost wiped out the local fish and bird populations from selenium poisoning. You can google "Kesterson reservoir selenium."

3. (20 pts) "The Zamboni problem" is based on a problem that appears in the text book *Environmental Engineering: Fundamentals, Sustainability, Design*, by Mihelcic and Zimmerman.

   If you attend an ice-hockey game, you will see the ice rink use a re-surfacing machine to treat the ice between periods. The most popular brand of ice re-surfacing machine is Zamboni; often the re-surfacing machine is just called "the Zamboni" (which, I admit, sounds much cooler than "the re-surfacing machine"). As far as I know, the Zamboni runs on a standard gasoline-powered internal combustion engine. This means that it emits carbon monoxide (CO) into the air as it operates. If the fuel injector has the right air-to-fuel ratio, the CO emission rate will be low, and it isn't a problem. But if the CO emission rate is too high, we could have a problem, because CO is being emitted into a closed space (i.e., the ice rink), and it is bad for your health at high concentrations.

   Suppose we have the following information about our favorite ice rink.

   - The volume of air inside the arena is $V = 5.0\times10^4$ m^3, and it is well mixed.
   - The arena is ventilated at a rate $Q = 4.0$ m^3/s.
   - The concentration of CO in the ventilation air pumped *in* to the arena is $C_I = 2.5$ mg/m^3.
   - Our poorly tuned Zamboni emits CO at a rate $E = 58$ mg/s as it operates.
   - CO is non-reactive.
   - When the Zamboni first starts operating, the concentration of CO in the air inside the arena is $C_0 = 2.5$ mg/m^3. However, that concentration might change over time because the Zamboni is emitting CO into the air.

problem 3 continues →

3. continued

   a. Write a mass balance for the mass of CO in the air inside the arena.

   b. Use your mass balance to derive a differential equation that describes the rate of change of the concentration of CO in the air. Your differential equation should be in the form *dC/dt* = …, where *C* represents the concentration of CO in the air inside the rink.

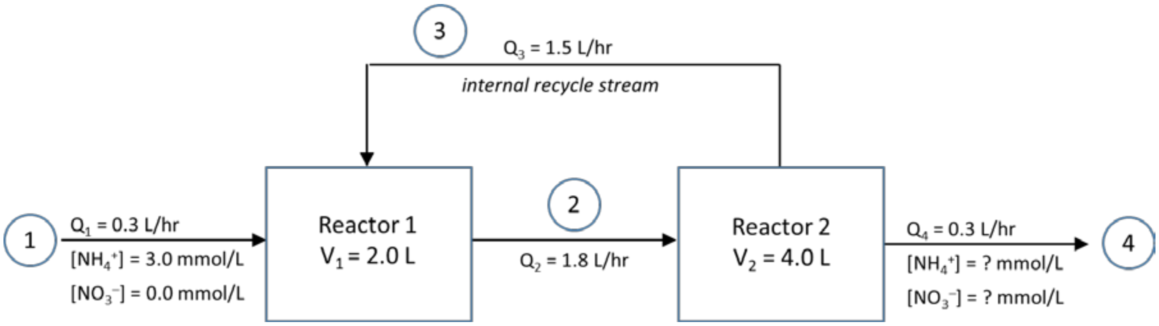
   c. If the Zamboni ran forever, eventually the concentration of CO in the air would reach a steady-state value. What would be the steady-state concentration of CO in the air inside the arena? Hint: you do <u>not</u> need to solve the differential equation from part (a) in order to answer this. Instead, how would your mass balance change for these conditions?

   d. Solve the differential equation to derive the following expression for the concentration of CO in the air inside the arena.

$$C(t) = \left(C_I + \frac{E}{Q}\right) - \left(C_I + \frac{E}{Q} - C_0\right) e^{-\frac{Q}{V}t}$$

   e. We want to be sure that the concentration of CO in the arena stays below 10 mg/m^3. How long (in minutes) would the Zamboni have to operate in order for the air concentration to exceed this level? Based on this, are you worried about attending an indoor ice-hockey game?

4. (20 pts) One of my former graduate students, Dr Hélène Kassouf, designed and built a laboratory-scale treatment system to remove ammonium (NH_4^+) and nitrate (NO_3^-) from wastewater. A schematic of her treatment system is shown below. (Actually, her treatment system was a little more complicated, but this simplified version is fine for the purposes of this assignment.) The four streams in the treatment system are numbered 1 through 4.



When Dr Kassouf first started operating the treatment system, we were seeing good removal of NH_4^+, but we were detecting too much NO_3^- in the effluent. Let's figure out why.

problem 4 continues →

4. continued

In addition to the information shown in the figure above, we have the following information:

- Reactor 1 and Reactor 2 are both completely mixed flow reactors (also called continuously stirred tank reactors). We haven't covered that yet this semester, but probably you are familiar with this concept from a previous class.
- The system operates at steady state.
- In Reactor 1, NH_4^+ does not react. However, NO_3^- is removed (converted to N_2 gas) with a first-order rate coefficient $k = 0.33\ \text{hr}^{-1}$.
- In Reactor 2, NH_4^+ is converted to NO_3^- with first-order kinetics. The rate coefficient is $k = 4.0\ \text{hr}^{-1}$. Nitrate does not react in reactor 2.

Our job is to use this information to estimate the concentrations of NH_4^+ and NO_3^- in the effluent stream, i.e., stream 4.

a. Write a mass balance for NH_4^+. For the control volume, use the entire treatment system. Then use your mass balance to solve for $[NH_4^+]$ in the effluent (stream 4). Hint: use the information given above in the bullet points.

b. Now write a mass balance for NO_3^-. Use Reactor 2 for the control volume. Hint: think carefully about the source term in your mass balance. Clearly indicate which concentrations in the mass balance are known, and which are unknown. How many unknowns do you have?

c. Write another mass balance for nitrate. This time, for the control volume, use Reactor 1. Clearly indicate which concentrations in the mass balance are known, and which are unknown. How many unknowns do you have?

d. Solve for $[NO_3^-]$ in the effluent (stream 4). Hint: if you need another equation, think about how $[NO_3^-]$ in stream 3 is related to $[NO_3^-]$ in stream 4, remembering that Reactor 2 is a completely mixed flow reactor.

e. Notice that in the influent stream, $[NH_4^+] + [NO_3^-] = 3.0$ mmol/L. What is $[NH_4^+] + [NO_3^-]$ in the effluent stream? If we consider the contaminants together, what fractional removal did we achieve in the treatment system?

Eventually, Dr Kassouf figured out how to improve the removal of NO_3^-, but it was a tricky balancing act – she had to tune the oxygen supply just right to remove both NH_4^+ and NO_3^-. If the oxygen level wasn't tuned just right, we would get too much of one compound or the other. It was a pretty fun project!

5. (20 pts) The sediment of a particular lake is contaminated with the chlorinated pesticide lindane. Chemical properties of lindane are given in Table 2.3 of your text book. To be consistent with HW 4, let's use the following equations to describe the partitioning of lindane into the fish that live in the lake and into the organic compartments of the lake sediments:

$\log_{10}(\mathrm{BCF}) = 0.76 \log_{10}(K_{OW}) - 0.23$ for BCF in units L/kg

$\log_{10}(K_{OC}) = 1.00 \log_{10}(K_{OW}) - 0.20$ for K_{OC} in units L/kg

The concentration of lindane in the sediment of the lake is 50 mg/kg, and the lake sediment is 10% organic carbon by mass.

a. If the lake water and the lake sediment were in equilibrium, what would be the concentration of lindane in the water? We will call this concentration C^*.

Some people like to fish in the lake, and they like to eat the fish. We want to be sure that the people are not ingesting too much lindane when they eat the fish, because lindane is toxic. Therefore, we want to ensure that the concentration of lindane in the fish does not exceed 0.01 mg/kg (equivalent to 10 μg/kg).

b. Estimate/calculate the maximum concentration of lindane that can be in the lake water in order to keep the concentration in the fish below 0.01 mg/kg. We will call this concentration C^{max}.

So now we see a problem. If the water reaches equilibrium with both the sediment and the fish, then the fish will be unsafe to eat. We must hope that the release of lindane from the sediment into the water is slow. Suppose the overall mass-transfer coefficient (describing mass transfer of lindane from the sediment into the lake water) is denoted k_{LO}.

c. Write an expression for J, the mass flux of lindane from the sediment into the lake water. The concentration of lindane in the lake water should be denoted C.

Suppose the volume of the lake is $V = 5.0\times10^8$ L, and it has one inlet stream and one outlet stream, both flowing at a rate $Q = 2.4\times10^7$ L/d. There is some good news for us – in the lake, lindane degrades according to first-order kinetics, with a degradation rate coefficient $k_1 = 0.01\ \mathrm{d}^{-1}$.

d. Write a mass balance for the mass of lindane in the lake water. Then derive an equation for C (the concentration of lindane in the lake water) as a function of $k_{\mathrm{LO}}\,a$, where a is the specific interfacial area of the sediment-water interface.

e. Estimate/calculate the maximum allowable value of $k_{\mathrm{LO}}\,a$ that will keep the aqueous concentration (and hence the fish concentration) within acceptable limits.

f. Compare the maximum allowable value of $k_{\mathrm{LO}}\,a$ to the value of the degradation rate coefficient. What does this tell you (qualitatively) about the allowable value of $k_{\mathrm{LO}}\,a$? Based on this, what do you think about fishing in a lake where lindane was applied in the past?