# CE/ESM 479/579 Fate and Transport
# PROBLEM SET 9 - 2016

1. A bacterial culture growing on the herbicide 2,4,5-T is observed to have the growth parameters listed below. (4 points)

    a. What is the rate of 2,4,5-T uptake in g/(cell day) if the substrate concentration is 8.0 mg/L?
    b. Prepare a plot of the Michaelis-Menten relationship for this system over a sufficient range of concentration that you can see the full range of uptake rates (linear as well as asymptotic approach to $V_{max}$.)
    c. What is the pseudo-first-order uptake rate in in units of L $cell^{-1}$ $d^{-1}$ that applies to this system at very low substrate levels?
    d. From the graph in part (b), what is the approximate range of concentration that you expect is valid for the linear approximation?

    $V_{max}$ = 3.6 x 10-$^{5}$ g $cell^{-1}$ $d^{-1}$
    $K_s$ = 1.9 x $10^{-3}$ g $L^{-1}$

2. A 1.7-kg adult osprey eats 0.08 kg/d of lake trout containing 0.25 ppm of Arochlor 1254 PCB. Assume that the eagle excretes all PCB congeners with a mean first-order rate constant of 0.0l5/day. (6 points; 2 points each)

    a. Estimate the steady-state total-PCB concentration in the osprey.
    b. What is the bioaccumulation factor (BAF) between the trout trophic level and the osprey level?
    c. If the average sediment concentration of Arochlor 1254 is 65 μg/kg in the lake where the osprey feeds, what is the overall BAF for the system as referenced to sediment (not aqueous) concentrations. (This approach is commonly used for highly hydrophobic compounds that are difficult or impossible to measure in water, but which can be detected in sediments.)

3. A True Story: On July 14, 1991, a train derailed on a bridge in Northern California spilling approximately 19,500 gal of the soil fumigant sodium metam (Vapam™) into the Sacramento River, 70 km upstream from Shasta Lake, California's largest reservoir. The spill killed almost all aquatic life in the river.

```
    H    S
    |    ||
H3C-N-C-S-,  Na+
```

Sodium salt of metam

In an aqueous environment, metam (which is highly soluble) hydrolyzes to form methyl isothiocyanate and $H_2S$ as the major products:

```
    H    S
    |    ||
H3C-N-C-S-  +  H2O  →  H3C-N=C=S  +  H2S  +  OH-
```

$$H_3C\text{-}N(H)\text{-}C(=S)\text{-}S^- + H_2O \rightarrow H_3C\text{-}N\text{=}C\text{=}S + H_2S + OH^-$$

Metam Methyl isothiocyanate

Rate constants for this reaction are:

$k_a' = 320\ M^{-1}\ s^{-1}$
$k_n = 2 \times 10^{-8}\ s^{-1}$

(Methyl isothiocyanate is a highly toxic "soil fumigant" gas produced when the metam solution reacts with soil moisture, or in this case, river water. The isothiocyanate will volatilize from the river to the atmosphere, but for this problem we are focusing on the amount of metam itself and so we will *not* consider air-water transport here. The last question below touches on this assumption.)

Metam also undergoes indirect photolysis to form methyl isothiocyanate with a pseudo-first-order rate constant of approximately $1.0 \times 10^{-4}\ s^{-1}$.

Imagine this spill happened today. The California Regional Water Quality Control Board urgently needs your advice about the maximum concentrations of metam that will be encountered at different points along the Sacramento River. (5 points; 1 point each)

a. Calculate the maximum concentration (in moles per liter) of Na+ (which behaves as a conservative tracer) and metam that will be encountered, both at the town of Dunsmuir (10 km downstream from the spill) and *also* at the point where the Sacramento River reaches Shasta Lake (70 km downstream from the spill). You can assume an instantaneous input of metam across the cross section of this small stream.

b. What is the *relative* importance of the three processes of longitudinal dispersion, overall hydrolysis, and indirect photolysis in attenuating (reducing) the peak concentration of metam between Dunsmuir and Shasta Lake? Quantify your answer: show a *quantitative* comparison of the relative effect of each process on the peak concentration at the entrance to Shasta Lake. For example, you could show values of $C_s/C_d$ where $C_s$ is concentration at Shasta, and $C_d$ is the $C_{max}$ at Dunsmuir and $C_s$ is the $C_{max}$ at Shasta, calculating the C values using just ONE process at a time. E.g., $C_{max}$ for only dispersion with no decay, then $C_{max}$ for the dispersive case but with decay factors added one at a time. Comment on how your results show what is the most important attenuation factor(s): dispersion, hydrolysis, photolysis, or a combination? You can also show the effects of decay by comparing the behavior of the unreactive $Na^+$ with that of the reactive metam.

c. Another way to compare at least the two chemical decay processes: what are the half-lives for hydrolysis and indirect photolysis? What does this tell you about their relative importance.

d. California officials are also concerned about the *total mass* of metam entering Shasta Lake. What can you tell them about the relative importance of dispersion, hydrolysis, and photolysis in reducing the input of *total* metam mass.

e. Data are not available as to the Henry's law constant for metam. Why is this not a problem and that air-water exchange is not an issue with metam?

**Consider some useful information:**

The Sacramento River in this region is a small stream and at this time of year has a discharge of 46 cfs ($ft^3/s$), a mean depth of 1.2 ft, a mean width of 4.1ft, a constant pH of 7.8, and a longitudinal dispersion coefficient = $1.6 \times 10^2$ $m^2$ $min^{-1}$.

Vapam™ has a commercial formulation that is 33% by weight sodium salt of metam, with 67% neutral aqueous solvent. The density of the commercial formulation is 1.2 g/mL, and a molecular weight of 129.2 g/mol for sodium salt of metam.

---

The following is an article from the Los Angeles Times about the Dunsmuir spill.

PERSPECTIVE ON THE ENVIRONMENT : Biological Hiroshima on the River : We need better regulation of toxic pesticides. But real safety lies in reducing their use.

July 18, 1991|LAWRIE MOTT and MARC REISNER | Lawrie Mott is a senior scientist with the Natural Resources Defense Council, based in San Francisco. Marc Reisner is the author of "Game Wars: The Adventures of an Undercover Wildlife Agent" (Viking Penguin, 1991) Dunsmuir.

The name of the place deservedly evokes images of Scotland. This section of the Upper Sacramento River, one of the last almost-free-flowing stretches of water in the state, was until Sunday one of our last blue-ribbon native trout fisheries. Today, it is a biological Hiroshima. Thousands of fish--10-pound wild trout!--countless ducks, river otters, insects and other life forms were killed by a 19,500-gallon pesticide spill from a derailed train.

Officials are still trying to determine what caused the derailment Sunday night, but the facts now available demonstrate again how vulnerable we are to ultra-toxic chemicals, and how fate or accident or carelessness can knock to pieces our efforts to shield ourselves and the environment from harm.

A 97-car Southern Pacific train was en route from Long Beach to Pasco, Wash. Only 11 cars were loaded and only one contained hazardous materials. Seven cars and one engine jumped the tracks. Only one car fell into the river, but it was full of the pesticide Vapam, or metam-sodium, a fumigant used before crop planting to kill insects, weeds and fungi in soil--in other words, everything.

The first official record of the spill on Sunday night read "creek name unknown"-- this for a river that ultimately becomes drinking water for 22 million Californians. Until noon Monday, the state Office of Emergency Services thought that just 1,000 gallons of the pesticide had spilled. Officials did not think that the chemical was toxic because the tank car carried no warning, which federal law requires when substances classified as hazardous are being transported. Only when fish started dying did officials learn otherwise.

This winding canyon section of track has been the scene of other derailments. In 1976, a similar accident resulted in a chemical spill and serious fish kills. State records show eight "major derailments" in the area between 1981 and 1989, though with less-serious consequences.

Perhaps the consequences of even Sunday's spill would not have been so severe if this chemical had been named a hazardous substance by the Department of Transportation. Then the tank car would have been labeled and emergency response presumably would have been more effective. It is almost impossible to believe that a pesticide designed to kill all living organisms in soil has not been classified as hazardous.

Metam-sodium belongs to a pesticide family with an ugly history. Soil fumigants are notorious for their toxicity-- others including DBCP, EDB and Telone II have all been outlawed because of carcinogenicity. The use of metam-sodium has increased as these other chemicals have been banned. Metam-sodium breaks down almost immediately on contact with water into hydrogen sulfide and methyl isothiocyanate, or MITC, which is extremely irritating to skin, eyes and the respiratory system. It is a less-potent cousin of methyl isocyanate, which killed more than 2,000 people at Bhopal, India, in 1984. Available studies seem to indicate that MITC does not cause cancer, reproductive toxicity or other chronic hazards to humans. That is good news for the Californians who may receive this chemical in their drinking water. But what about a state wild trout fishery--already plundered by water diversions and dams--that has just suffered the worst single-day-loss in its history? And miles of wild-river ecology killed off literally bank-to-bank?

There are old lessons here that we should already have learned. The federal transportation safety regulations failed to protect public health and the environment from this toxic chemical, just as they failed to protect Alaska from the Exxon Valdez. Many other toxic chemicals are transported daily throughout this country, through far more populous areas. Certainly the transportation regulatory system needs immediate scrutiny and probably a serious overhaul.

It has been reported that more than 20 state and federal government agencies were involved in the response to this spill. Lack of communication and coordination resulted in serious delays. Perhaps if the one-day-old California Environmental Protection Agency had been born last year, the response to this spill would have been more effective.

But the fundamental lesson of the Dunsmuir spill is that pesticides, no matter how tightly regulated or controlled, can be fiendishly toxic. These compounds, designed to kill or control unwanted pests, be they insects, weeds, fungi or rodents, are lethal by definition.