1.020 Ecology II: Engineering for Sustainability
Spring 2008

Lecture 08_3 Outline: Chemical Kinetics, Dechlorination

Motivation/Objective

Develop model to evaluate impact of source size and microbial degradation rates on time-dependent concentrations of chlorinated hydrocarbons (TCE and daughter products). System is open -- flowing water dissolves NAPL and transports dissolved constitiuents out of system.

Approach

1. Define system (open), chemicals of interest (compartments). Identify unknowns (mass of non-aqueous liquid trichlorethene $M_{trinapl}$ and concentrations of dissolved tricholorethene C_{tri}, dichlorethene C_{di}, vinyl chloride C_{vc}, and ethane C_{eth}).
2. Identify chemical reactions, write mass balance equation for each chemical (rate form)
3. Relate gain and loss terms in each balance equation to unknowns.
4. Specify inputs and solve the coupled mass balance eqs. for the unknowns (MATLAB).
5. Examine impacts of initial NAPL mass and degradation rates on concentration time histories.

Concepts and Definitions:

Define multiple system properties (e.g. chemical concentrations).

Write separate mass balance for each chemical/compartment (*i = trinapl, tri, di, vc, eth*):

$$\frac{dM_{CV,i}}{dt} = \dot{m}_{in,i} - \dot{m}_{out,i} + \dot{m}_{gain,i} - \dot{m}_{loss,i}$$

Express masses & concentrations in moles and then convert to kg after solving equations

Mass gain and loss rates are related to rate of chemical reaction:

For: $aC_A + bC_B \rightarrow pC_P + qC_q$ Reaction rate $r = \frac{1}{a}\frac{\dot{m}_{loss,A}}{V} = \frac{1}{b}\frac{\dot{m}_{loss,B}}{V} = \frac{1}{p}\frac{\dot{m}_{gain,P}}{V} = \frac{1}{q}\frac{\dot{m}_{gain,Q}}{V}$

r depends on concentrations, may be derived from law of mass action for elementary reactions.

For the dechlorination example:

1 mole *trinapl* dissolves to form 1 mole *tri* at constant rate:

$$\dot{m}_{loss,trinapl} = \dot{m}_{gain,tri} = \begin{cases} qC_s & M_{trinapl} > 0 \\ 0 & M_{trinapl} = 0 \end{cases}, \quad \dot{m}_{gain,trinapl} = 0, \quad (q = \text{flow rate}, C_s = \text{solubility})$$

$C_{tri} \rightarrow C_{di} \rightarrow C_{vc} \rightarrow C_{eth}$ (1 mole reactant yields 1 mole product in each of 3 reactions).

These dechlorination reactions are first-order:

$$\dot{m}_{loss,tri} = \dot{m}_{gain,di} = Vr_{tri} = Vk_{tri}C_{tri} \qquad \dot{m}_{loss,di} = \dot{m}_{gain,vc} = Vr_{di} = Vk_{di}C_{di}$$

$$\dot{m}_{loss,vc} = \dot{m}_{gain,eth} = Vr_{vc} = Vk_{vc}C_{vc} \qquad \dot{m}_{loss,eth} = Vr_{eth} = Vk_{eth}C_{eth}$$

$\dot{m}_{out,i} = qC_i$ for dissolved chemicals, $\dot{m}_{out,trinapl} = 0$, $\dot{m}_{in,i} = 0$ for all chemicals.

Complete Mass Balance Equations:

Insert $\dot{m}_{in,i}$, $\dot{m}_{out,i}$, $\dot{m}_{gain,i}$, $\dot{m}_{loss,i}$ into mass balances for all 5 chemicals. See MATLAB code.

Model Results

Note how inputs affect times required for decay, sequence of concentration peaks.