CHEMICAL REACTIONS: PRODUCTION AND DECAY

How is mass created or destroyed?

- Chemical reactions (hydrolysis, redox, precipitation/dissolution)
- Biodegradation (microbial, plant uptake)
- Radioactive decay

Reaction that destroys one species (decay) can create another (production).

- TCE $\rightarrow$ cis 1,2-DCE $\rightarrow$ Vinyl Chloride $\rightarrow$ Ethene
- ${}^{232}_{90}\mathrm{Th} \rightarrow {}^{228}_{88}\mathrm{Ra} \rightarrow {}^{228}_{89}\mathrm{Ac}$

Reaction end products:

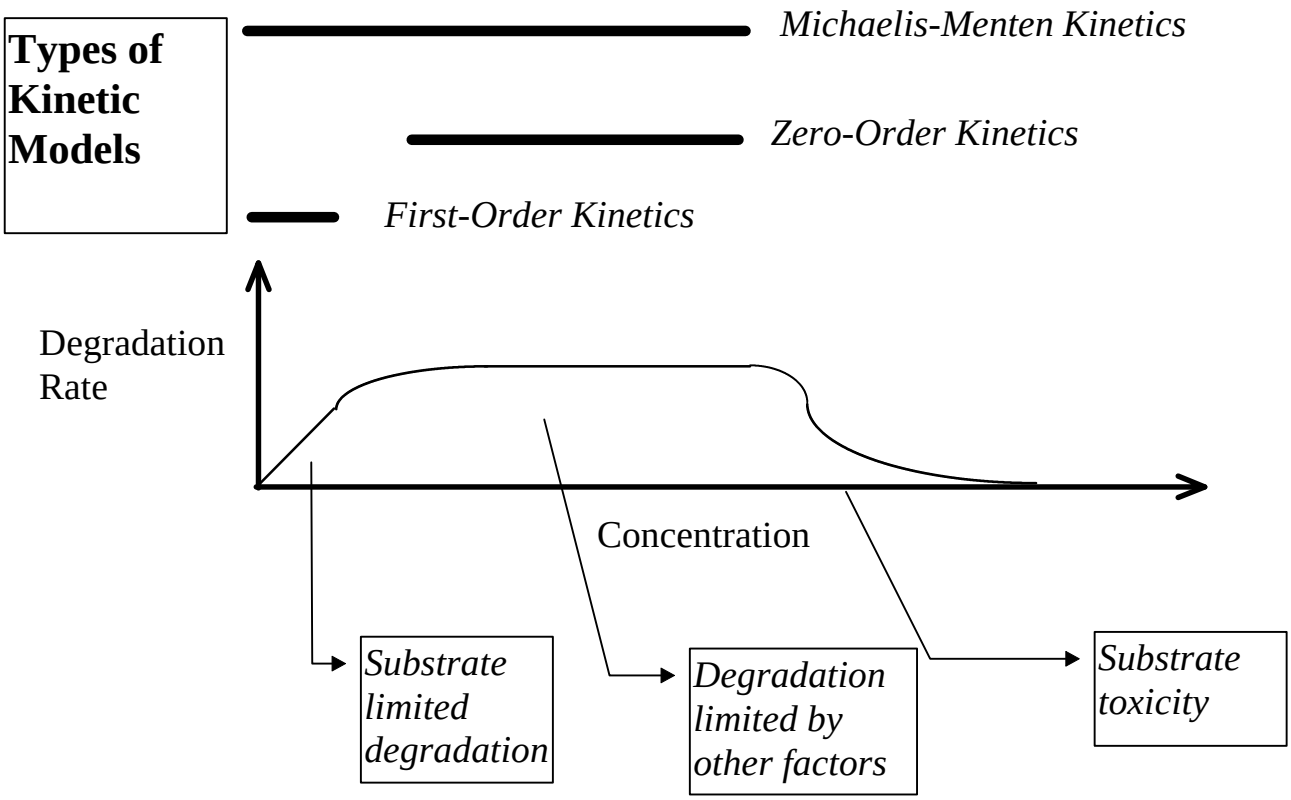
- Organic compounds oxidized to CO_2, H_2O, etc.--Irreversible
- Radioactive Decay: Irreversible
- Redox reactions with metals: May change oxidation state and therefore solubility (e.g.: $Fe^{+2} \rightarrow Fe^{+3}$), but reaction is reversible.

Reaction Rates:

- Rapid: Acid-base reactions
- Predictable First-Order rates: Radioactive decay
- Slow: Redox, Precipitation/Dissolution
- Stoichiometric Considerations: Mass balance must be maintained!

Redox reactions are often so slow that a catalyst is needed to make the reaction happen in meaningful time scales. <u>Microorganisms</u> often supply the <u>catalysts (enzymes)</u> in aquatic environments.

How does biodegradation rate "typically" vary with concentration?



- Low concentrations: Degradation rate limited by availability of chemical - first-order kinetics.
- Higher concentrations: Plenty of chemical available for degradation; rates limited by other factors (oxygen availability, microbial population, etc.) - rate independent of chemical concentration or zero-order kinetics.
- Low through high concentrations: Michaelis-Menten kinetics
- Very high concentrations: Chemical becomes toxic to microorganisms - degradation rate declines.

Choose model that fits concentration range of interest.

Modeling Kinetics:

[1] "Instantaneous" Reaction

If the reaction rate is very fast compared to other factors (i.e., transport), then the reaction can be considered "instantaneous."

$$aA + bB \rightarrow cC$$

If chemicals A and B react "instantaneously," at any time step A and B will react until one or both compounds are depleted.

If $\frac{C_A}{a\,MW_A} > \frac{C_B}{b\,MW_B}$ at t=t:

Then:

$$\int_t^{t+\Delta t} \phi_A dt = -\theta \frac{a\,MW_A}{b\,MW_B} C_B$$

units: $M\,L^{-3}$ media

$$\int_t^{t+\Delta t} \phi_B dt = -\theta C_B$$

$$\int_t^{t+\Delta t} \phi_C dt = -\theta \frac{c\,MW_C}{b\,MW_B} C_B$$

Examples:

- Biodegradation of petroleum compounds is "fast" compared to the rate that diffusion can supply oxygen to groundwater. The BIOPLUME models simulate the transport of oxygen and hydrocarbons separately. At each time step, hydrocarbons and oxygen at a given location react stoichiometrically until either compound is depleted.
- Neutralization of HCl by $CaCO_3$.

[2] Zero-Order Kinetics

When decay rate is INDEPENDENT of concentration:

$$\phi = -\theta k_0 \qquad \text{units of } k_0 = M\, L_w^{-3}\, T^{-1}$$

Problem: Mass will be removed at this rate regardless of concentration--negative concentrations can result!

Example:

- Cometabolization of vinyl chloride by toluene degraders (degradation of VC is a side-effect).

[3] First-Order Kinetics:

Decay rate is proportional to concentration

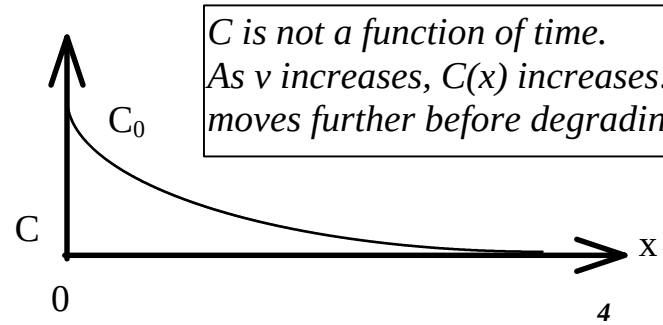
$$\phi = -\theta k_1 C \qquad \text{units of } k_1 = T^{-1}$$

- Mathematically simple
- Avoids mass imbalance problems of zero-order kinetics
- Valid when the substrate is the reaction-limiting component (i.e., at low concentrations!)
- Valid for radioactive decay

$$\theta_w R \frac{\partial C_w}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + \theta_w D_w \frac{\partial^2 C_w}{\partial x^2} - \theta_w k C_w$$

If you have a constant source term, at long times (steady state solution) and for small values of D_w:

$$C(x) = C_0 \exp\left(-\frac{kx}{v}\right)$$



C is not a function of time.
As v increases, C(x) increases: plume moves further before degrading.

[4] Michaelis-Menten Kinetics:

Decay rate transitions from first-order at low concentrations to zero order at high concentrations.

$$\phi = -\theta k_{max}\left(\frac{C}{K_m + C}\right)$$

units: $k_{max} = T^{-1}$

$K_m = M\,L^{-3}$

- Valid over greater range than first-order kinetics
- Avoids mass imbalance problems of zero-order kinetics
- Mathematically more complex
- Typical of enzymatic processes such as biodegradation

Example: Petroleum hydrocarbon biodegradation

$$\text{Hydrocarbons} + G[\text{Oxygen}] \rightarrow \text{Decay Products}\left(C0_2, H_2O\right) + Y[\text{cells}]$$

Source/Sink Terms:

$$\phi_H = -\theta M_t \mu\left(\frac{C_H}{K_H + C_H}\right)\left(\frac{C_O}{K_O + C_O}\right)$$

Hydrocarbon degradation term

$$\phi_O = -\theta M_t \mu G\left(\frac{C_H}{K_H + C_H}\right)\left(\frac{C_O}{K_O + C_O}\right)$$

Oxygen degradation term

Cell decay

$$\Sigma\phi_M = \theta M_t \mu Y\left(\frac{C_H}{K_H + C_H}\right)\left(\frac{C_O}{K_O + C_O}\right) + \theta k_c Y C_{OC} - \theta b M_t$$

Cell source and sink terms

Cell growth due to hydrocarbon degradation

Cell growth due to natural carbon sources

The variables used in the source/sink equations are:

C_H = hydrocarbon concentration in fluid (ML^{-3})
C_O = oxygen concentration in fluid (ML^{-3})
M_t = total aerobic microbial concentration (ML^{-3})
μ = maximum hydrocarbon utilization rate per unit mass of aerobic microorganisms (T^{-1})
Y = microbial yield coefficient (g cells/g hydrocarbon)
K_H = hydrocarbon half-saturation constant (ML^{-3})
K_O = oxygen half-saturation constant (ML^{-3})
k_c = first-order decay rate of natural organic carbon
C_{OC} = natural organic carbon concentration (ML^{-3})
b = microbial decay rate (T^{-1})
G = ratio of oxygen to hydrocarbon consumed

The governing equations are:

Hydrocarbons:	Sorption/advection/dispersion/sink
Oxygen:	Advection/dispersion/sink
Microbes:	Sink/source (no transport)

What does it mean?

- When concentration of hydrocarbon or oxygen is low, the decay rate is dependent on that concentration (chemical availability limits degradation rate).
- When concentration of hydrocarbon or oxygen is high, the decay rate is constant with respect to that constituent (decay rate reaches some maximum value, increasing the concentration will no longer increase the degradation rate).
- Degradation rate depends on the amount of microbes, and more microbes will grow when hydrocarbon and oxygen are available.

STOICHIOMETRY AND PRODUCTION:

Mass balance must be maintained.

When a compound decays, the amount of daughter products must be in proportion to the parent compound.

Production rate constants are DEPENDENT on decay rate constants.

Example: Estimate production rate constants from decay rate constants for reductive dehalogenation of PCE.

Reactions:

$$C_2Cl_4 + 2e^- + H^+ \rightarrow C_2Cl_3H + Cl^-$$

tetrachloroethene trichloroethene

$$C_2Cl_3H + 2e^- + H^+ \rightarrow C_2Cl_2H_2 + Cl^-$$

trichloroethene dichloroethene

$$C_2Cl_2H_2 + 2e^- + H^+ \rightarrow C_2ClH_3 + Cl^-$$

dichloroethene chloroethene

$$C_2ClH_3 + 2e^- + H^+ \rightarrow C_2H_4 + Cl^-$$

chloroethene ethene

First-Order Decay Terms:

PCE: $\phi_{PCE\,decay} = -\theta k_{PCE} C_{PCE}$

TCE: $\phi_{TCE\,decay} = -\theta k_{TCE} C_{TCE}$

DCE: $\phi_{DCE\,decay} = -\theta k_{DCE} C_{DCE}$

VC: $\phi_{VC\,decay} = -\theta k_{VC} C_{VC}$

Questions:

- Write the production terms for TCE, DCE, VC, ethene, and Cl^-
- If $k_{PCE} = k_{TCE} = k_{DCE} = k_{VC} = 1\ yr^{-1}$, what are the production rate constants for the compounds above?

TCE:

$$\phi_{TCE\,production} = \theta k_{PCE} \frac{MW_{TCE}}{MW_{PCE}} C_{PCE}$$

Production rate = k_{PCE} (MW_{TCE}/MW_{PCE}) = 0.792 yr^{-1}

<u>Governing equation for TCE</u>:

$$\theta R \frac{\partial C_{TCE}}{\partial t} = -q \bullet \nabla C_{TCE} + \theta D \bullet \nabla^2 C_{TCE} - \theta k_{TCE} C_{TCE} + \theta k_{PCE} \frac{MW_{TCE}}{MW_{PCE}} C_{PCE}$$

Source term for TCE is function of PCE concentration
Cannot solve TCE GE without solving PCE GE!

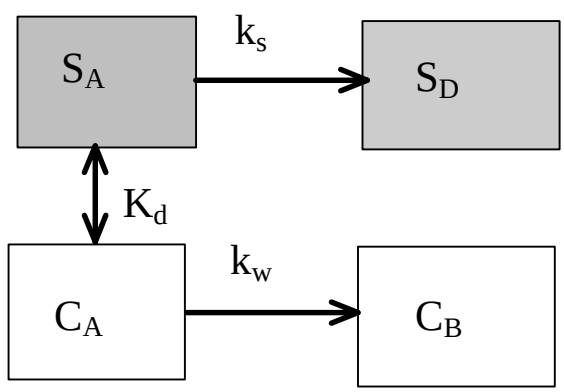
Cl^{-1}:

$$\phi_{Cl\,production} = \theta k_{PCE} \frac{MW_{Cl}}{MW_{PCE}} C_{PCE} + \theta k_{TCE} \frac{MW_{Cl}}{MW_{TCE}} C_{TCE} + \theta k_{DCE} \frac{MW_{Cl}}{MW_{DCE}} C_{DCE} + \theta k_{PCE} \frac{MW_{Cl}}{MW_{VC}} C_{VC}$$

DEGRADATION IN DIFFERENT PHASES: Assume different degradation processes/pathways in the aqueous and sorbed phases.

- Aerobic degradation in aqueous phase: A→B
- Anaerobic degradation in sorbed phase: A→D
- Different phases can mean different processes:
  - Different products.
  - Different rate constants.

Equilibrium Sorption



Sink terms:

$$\phi_s = -\rho_B k_s S_A \qquad \phi_w = -\theta_w k_w C_A$$

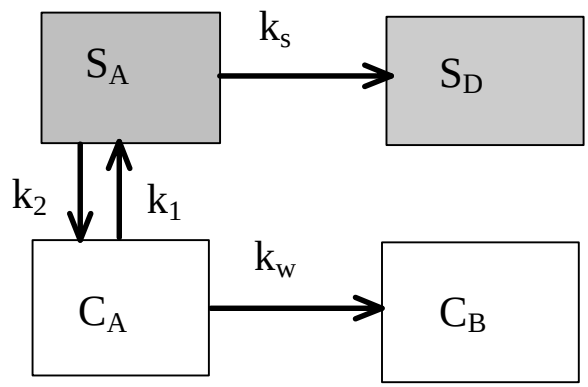
Governing Equation:

$$R\frac{\partial C_A}{\partial t} = -v_w\frac{\partial C_A}{\partial x} + D_w\frac{\partial^2 C_A}{\partial x^2} - k_w C_A - \frac{\rho_B}{\theta_w}k_s K_d C_A$$

$$= -v_w\frac{\partial C_A}{\partial x} + D_w\frac{\partial^2 C_A}{\partial x^2} - \left(k_w + (R-1)k_s\right)C_A$$

All degradation terms can be written in reference to aqueous phase concentration because sorption is "instantaneous."

Nonequilibrium Sorption:



Sink terms:

$$\phi_s = -\rho_B k_s S_A \qquad \phi_w = -\theta_w k_w C_A$$

Governing Equations:

$$\frac{\partial C_A}{\partial t} + \frac{\rho_B}{\theta_w}\frac{\partial S_A}{\partial t} = -v_w \frac{\partial C_A}{\partial x} + D_w \frac{\partial^2 C_A}{\partial x^2} - k_w C_A - \frac{\rho_B}{\theta_w} k_s S_A$$

Total medium MBE

$$\frac{\partial S_A}{\partial t} = k_2\left(K_d C_A - S_A\right) - k_s S_A$$

Solid phase MBE

Since solute in water and solid phases are not at equilibrium, separate MBE's (including decay terms) are written for each phase and are solved simultaneously.

Questions:

- What is the water phase MBE?
- Is decay likely to occur in the sorbed phase?