Organic Leaching Science

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Outline

- Review of key leaching issues related to use of tests and modeling.
- How batch tests relate to more realistic leaching in the environment.
- How do we determine when equilibrium conditions are observed?
- How can we deal with kinetic limitations?
- Conclusions/suggestions.

Key Leaching Issues

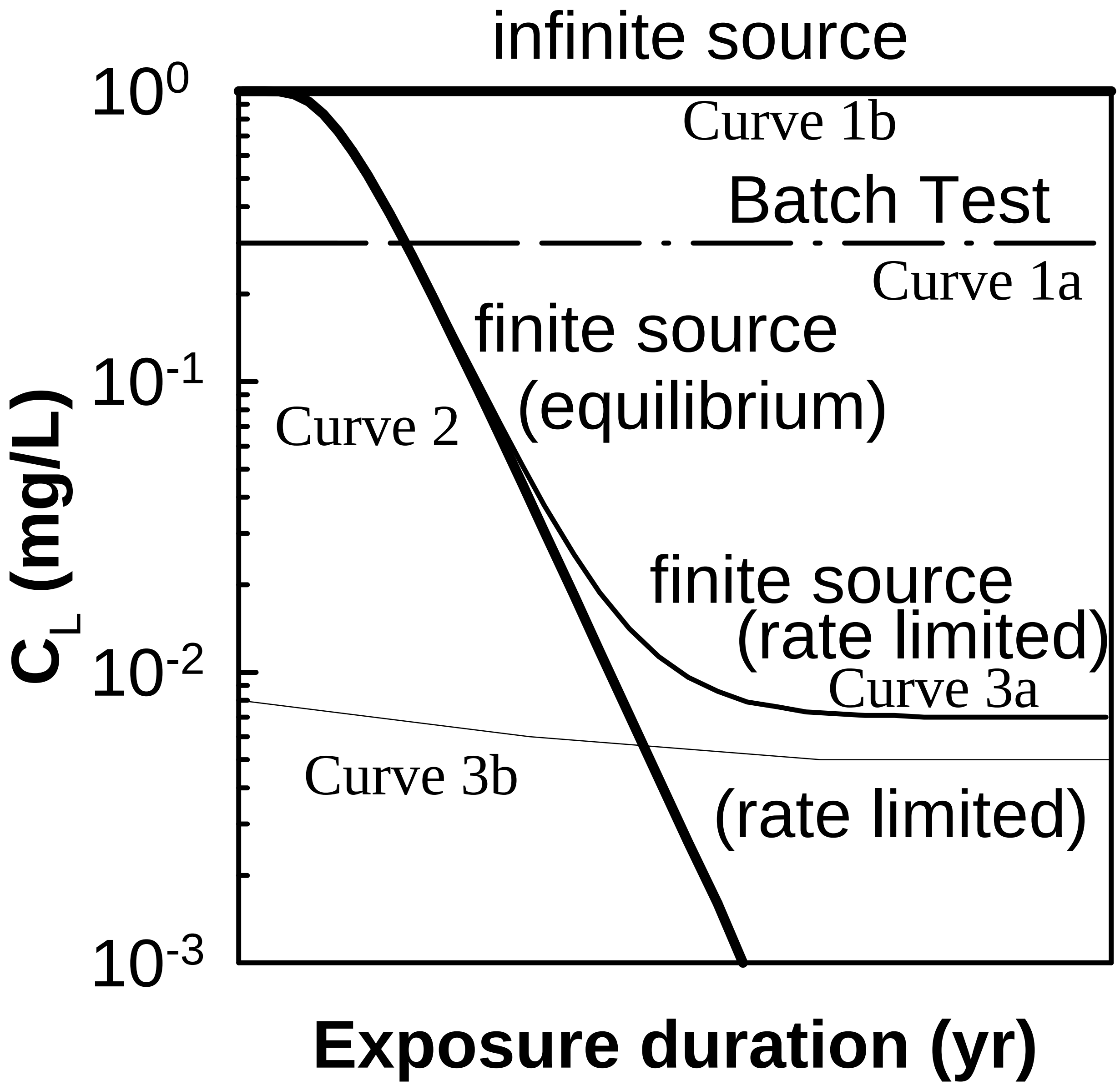
- What is the role of batch tests for describing leaching for organic compounds?
- How do we incorporate factors such as presence of residual NAPL, kinetics and various loss processes?

SAB Leaching Test Issues

- L/S ratio
- Kinetics
- pH
- Colloid/emulsion formation/oily phase
- Particle size reduction
- Volatile losses
- Interactions with other wastes

- L/S ratio, kinetics, and aspects of the oily phase issue will be addressed in this presentation.

Batch vs. More Realistic Leaching Behavior



How Can One Translate Batch Data to More Realistic Leaching ?

Comparison of Batch and Fixed-bed Leaching for Oily Wastes

- Approach for obtaining appropriate leaching parameters from batch tests.
- Use of batch parameters to describe fixed-bed leaching.

Required Parameters from Batch Tests

- C_{Lo} - leachate concentration at a leachate/ waste ratio extrapolated to zero.
- K_w - partition coefficient.

Determination of K_w and C_{Lo} for a Given Waste

K_w and C_{Lo} can be determined for a given waste from:

- a batch test and waste analysis.
- multiple batch leachate tests.

Alternatively, K_w and C_{Lo} can be estimated for a given waste from:

- oil content or TPH.
- application of Raoult's Law.

Modeling Batch Extraction

(I) Single batch extraction and waste analysis:

$$K_w = \frac{C_{To}}{C_L} - \frac{V^L}{M_w} \qquad C_{Lo} = \frac{C_{To}}{K_w}$$

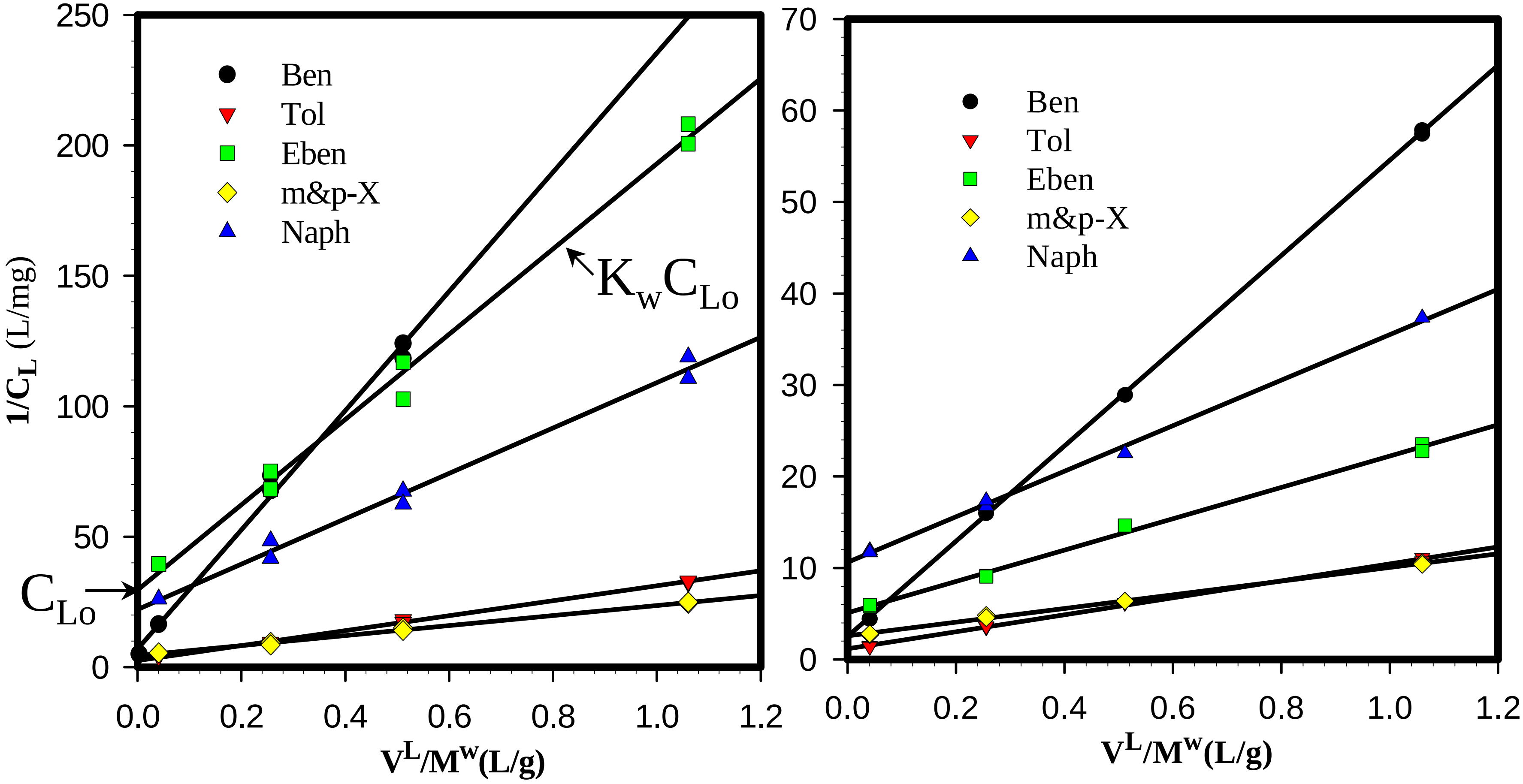
(II) Multiple batch extractions at various leachate/waste ratios:

$$\frac{1}{C_L} = \frac{1}{K_w C_{Lo}}\left(\frac{V^L}{M_w}\right) + \frac{1}{C_{Lo}}$$

C_L = leachate concentration emanating from waste (mg/L)
C_{Lo} = leachate concentration (mg/L)
C_{To} = initial total concentration (mg/kg)
K_w = waste-leachate partition coefficient (L leachate/kg waste)
V^L = volume of leachate (L)
M_w = mass of waste (kg)

$$C_T = K_w C_L$$

Multiple Batch Leachate Tests



Crude Oil Tank Bottoms Sludge

Hydrorefining Catalyst

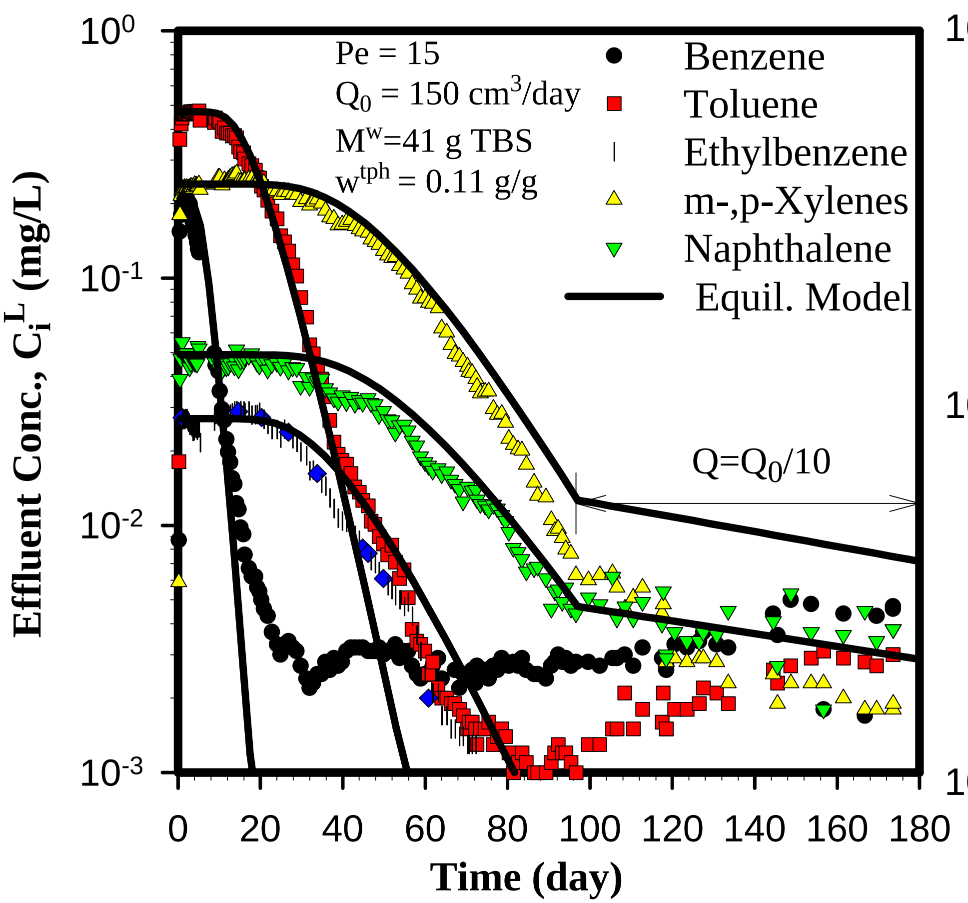
Theoretical Description of Fixed-Bed Leaching (Equilibrium Conditions)

$$\frac{C_L}{C_{Lo}} = 1 - \frac{1}{2} erfc\left[\sqrt{\frac{Pe}{4t^*}}(1-t^*)\right] - \frac{1}{2} exp(Pe) erfc\left[\sqrt{\frac{Pe}{4t^*}}(1+t^*)\right]$$

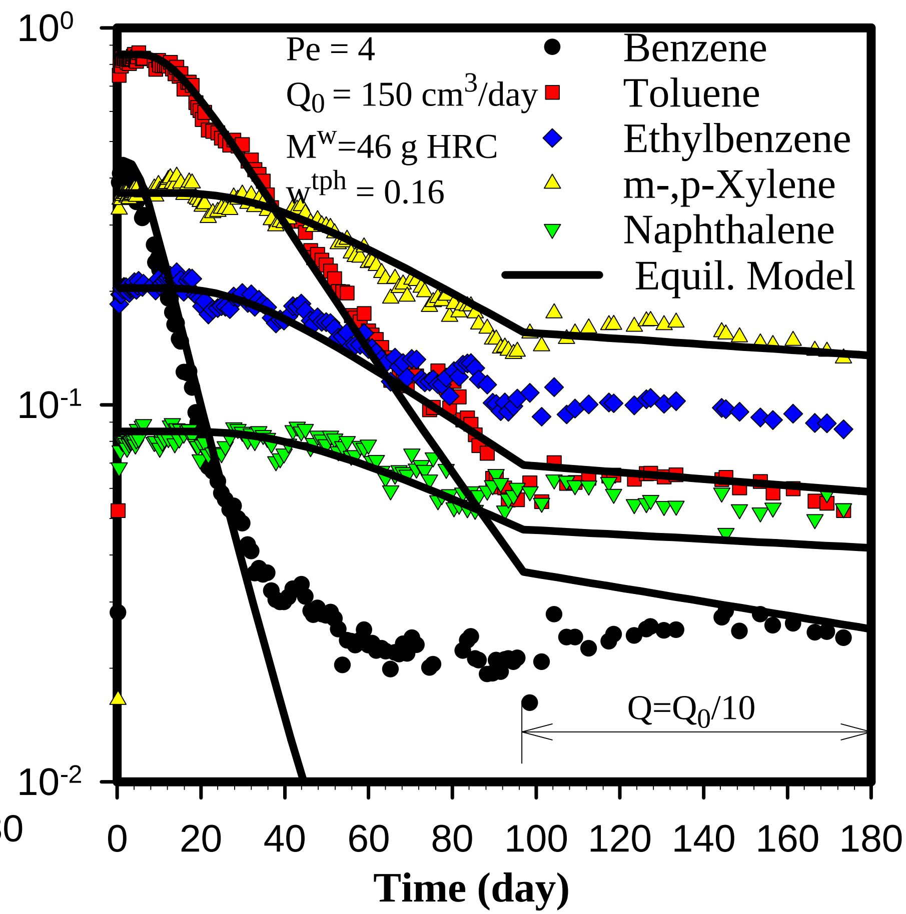
C_L = leachate concentration emanating from waste (mg/L)
C_{Lo} = initial (t=0) leachate concentration (mg/L)
t^* = non-dimensionalized leaching time, $(Qt)/(M_w K_w)$
Q = leachate flow rate (L/day)
M_w = mass of waste (kg)
K_w = waste-leachate distribution coefficient (L/kg)
Pe = Peclet number in waste zone, $v_y L/D_y$

K_w and C_{Lo} can be determined independently from Batch leaching tests.

Fixed-Bed Leaching Curves



Crude Oil Tank Bottoms Sludge



Hydrorefining Catalyst

- Curves were generated from batch parameters with a theoretical <u>equilibrium</u> dissolution model. Asymptotic concentrations reflect rate-limited release.

Conclusion

- A simple batch test <u>can</u> be used to describe more realistic leaching

Caveats:

(1) for equilibrium leaching conditions &

(2) in the absence of other loss processes,

e.g., volatilization and degradation.

Accounting for the effect of NAPL residual

Effect of NAPL on Partitioning

Equilibrium partitioning:

$$C_T = K_w C_L$$

where:

water air **NAPL** soil partitioning

$$K_w = f\left(S_w + S_a K_H + S_o K_o\right) + r_b F K_d$$

avail. fraction

Note: The effect of NAPL is accounted for in measured values of K_w. This increases equilibrium partitioning.

Observed vs. Theoretical K_w

	TBS (tph = 0.11g/g)		HRC (tph = 0.16 g/g)		Soil (f_{oc} = 0.003)
	Measured	Theoretical[1]	Measured	Theoretical[1]	$0.63 f_{oc} K_{ow}$
Benzene	30	32	48	46	0.26
Toluene	85	131	126	190	0.93
Ethylbenzene	227	489	347	707	2.7
m-, p-Xylenes	180	480	298	694	3.0
Naphthalene	252	886	427	1280	4.4

[1] Raoult's Law (γ_i^o=1; MW_o=150)
TBS - crude oil tank bottoms dewatered sludge.
HRC - hydrorefining catalyst.

- Residual NAPL in oily wastes significantly increases K_w compared with K_d for sorption only.

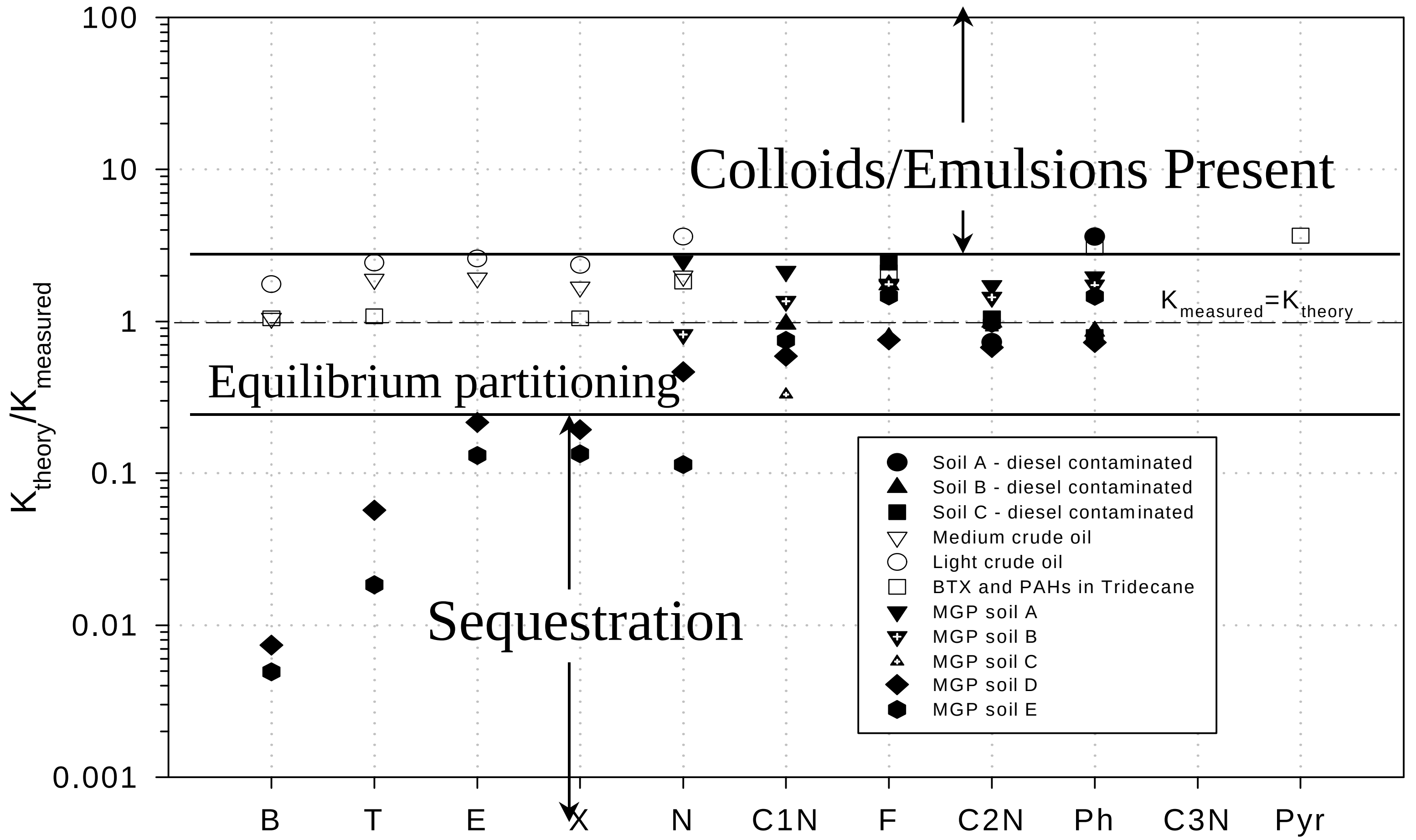
Theoretical Values of K_o

$$K_o = \frac{C_o}{C_L} = \frac{1}{g_i^{\,o}} \frac{MW_i}{MW_o} \frac{10^6}{S_i^{aq}}$$

K_o = oil-leachate partition coefficient ((L leachate/kg oil)
S_i^{aq} = subcooled solubility of contaminant in water (mg/L)
MW_i = molecular weight of chemical
MW_o = molecular weight of oil phase
γ_i^o = activity coefficient of chemical in oil phase in Raoult's Law sense (unitless)

Raoult's Law : $\gamma_i^o = 1$

Comparison of Theoretical (Raoult's Law) and Measured (48 hr Batch Experiments) Partition Coefficients



Notes:

1) diesel contaminated and MGP soils - $K_{measured}$ determined from single batch (48 hours) leachate and total waste analyses.

- For oily wastes, Raoult's Law is a useful measure of equilibrium behavior. Can be used to indicate presence of colloids/emulsions and sequestration (kinetics).

Conclusions Regarding Residual NAPL

- Residual NAPL has a significant impact on C_T vs. C_L relationship.
- Raoult's Law can be used to assess whether equilibrium conditions exist in batch tests.
- useful especially for oily wastes which tend to have high K_w.
- Raoult's Law can also be useful for estimating leaching in the absence of leach tests.

How can we determine when rate limitations exist?

I. By comparing with predicted leaching using batch tests at a fixed L/S ratio.

- useful for an initial assessment.

II. Using more definitive ROR tests.

How do we account for kinetics?

- Using rate of release (ROR) tests.
- Modified batch, fixed-bed and other rate of release (ROR) approaches have been developed.
- Rate constants can then be compared with those for other loss processes using an appropriate modeling framework.

Example ROR Methods

Current methods:

- Aqueous modified batch methods.
- Aqueous fixed-bed methods.

Alternative methods under development:

- Supercritical Fluid Extraction (SFE).
- Accelerated Solvent Extraction (ASE).
- Thermal Desorption Mass Spectrometry (TDMS).

Quantitative Treatment of Slow Release

A contaminant mass balance yields:

equil. release — rate-limited release — loss term

$$K_w \frac{dC_L}{dt} + r_b \frac{dq_2}{dt} = -\Lambda C_L$$

where:

water — air — **NAPL** — soil — partitioning

$$K_w = f\left(S_w + S_a K_H + S_o K_o\right) + r_b F K_d$$

avail. fraction

Quantitative Treatment of Slow Release (cont.)

slow rate constant — slow fraction

$$\frac{dq_2}{dt} = k_2 \left[K_d \left(1 - F\right) C_L - q_2 \right]$$

leaching — volatilization — degradation

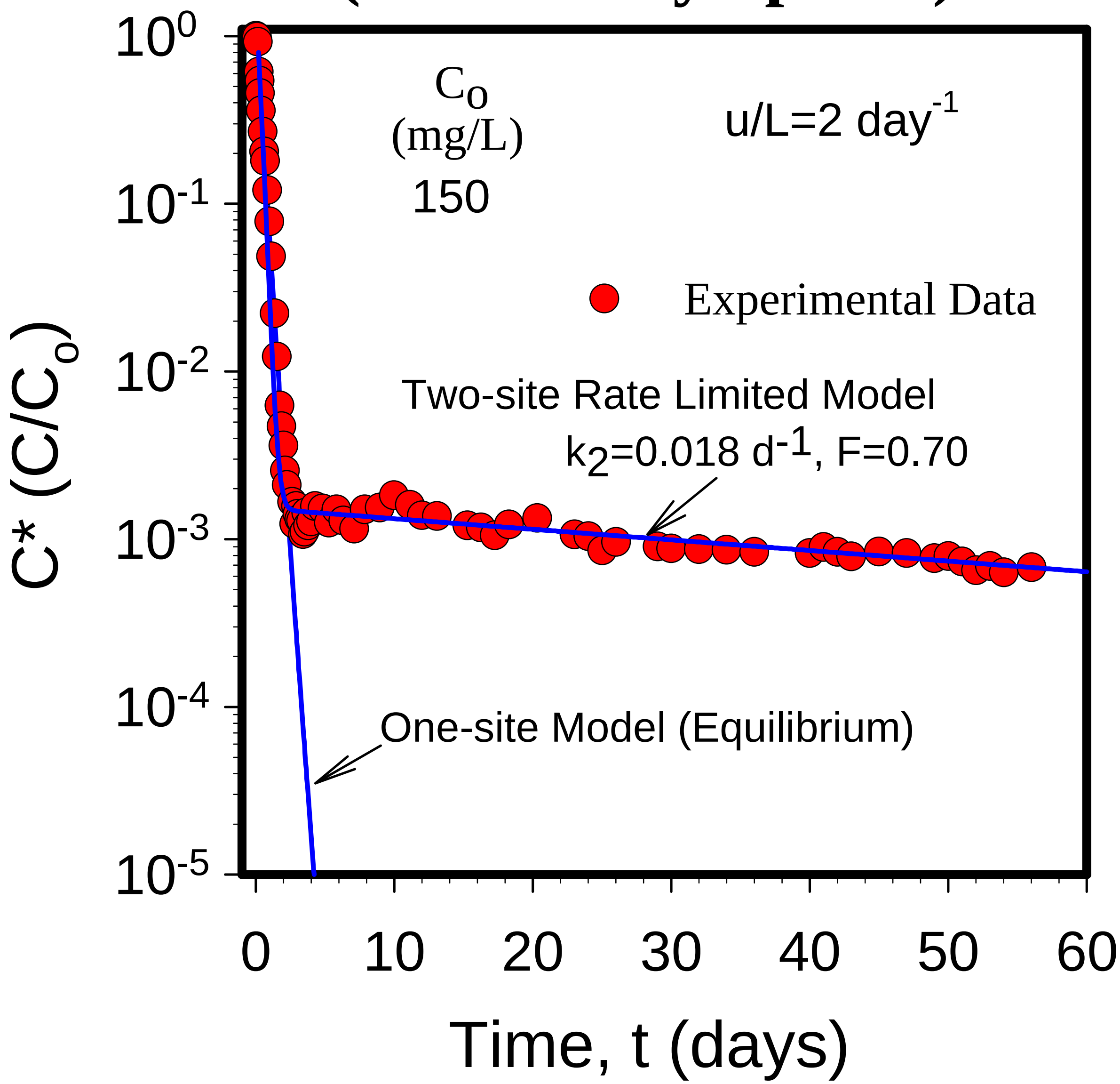
and

$$\Lambda = \frac{u}{L} + l_V + l_D$$

Slow Release Example

- Fixed-bed desorpion of benzene from an aged silty loam soil.
  - Measurements of k_2 and F.

Rate-limited Desorption of Benzene from a Silty Loam Soil (Laboratory Spiked)



When is Slow Release Important?

Relative to leaching:

$$k_2 r_b K_d (1 - F) < \frac{u}{L}$$

Relative to biodegradation or volatilization:

$$k_2 r_b K_d (1 - F) < l_V \ or \ l_D$$

Conclusions/Suggestions

- Simple batch tests are useful for describing leaching for organic compounds from oily wastes, esp. if equilibrium conditions occur.
- Separate test methods should be used to determine kinetics when needed.
- Estimation methods/separate tests should be used to account for other loss processes, e.g., volatilization and degradation.
- Appropriate tests should reflect a tiered approach to waste assessment.

Other Issues

- NAPL migration, volatilization, degradation.
- Lab-to-Field translation.
- Field-scale heterogeneities:
- soil type
- contaminant distribution
- paths for various transport processes, e.g., leaching, volatilization, etc.
- Sampling considerations.
- Modeling considerations.
- Other specific test related issues.