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Use of Predictive Models in Vapor Intrusion Investigations

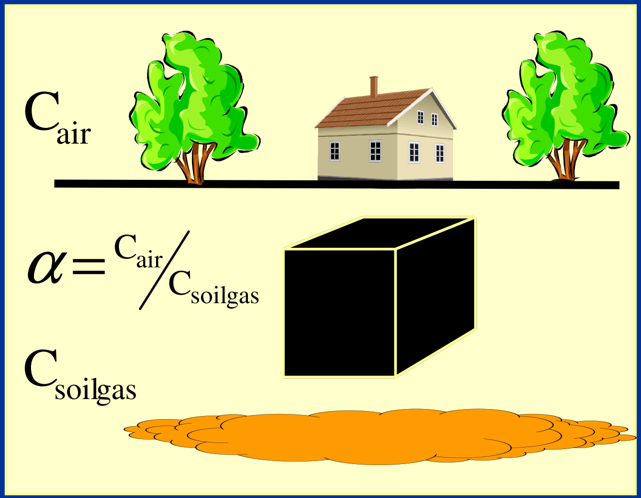
Matthew Lahvis (Shell Global Solutions)

Vapor Intrusion - The Next Great Environmental Challenge

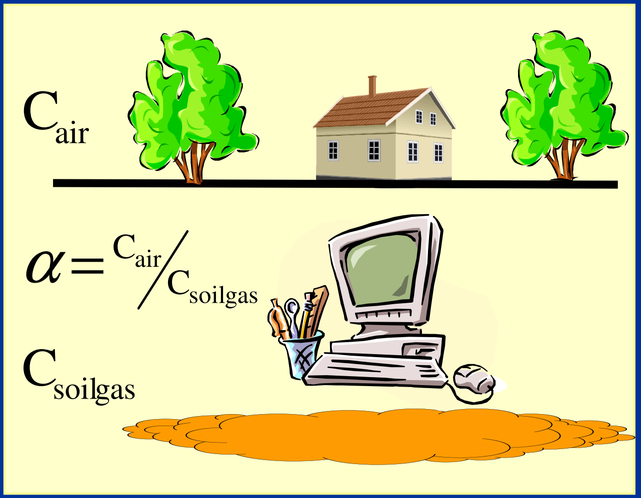
Air and Waste Management Assoc., September 13-15, 2006, Los Angeles, Ca.

Overview

- **PART I**
  Issues with the Use of Predictive Models



- **PART II**
  Predictive Model for Screening Dissolved-Phase Petroleum Hydrocarbon Sites



- **Summary**

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Issues

POSITIVES

- models if used properly, can help:
  - guide SIs (identify sensitive parameters), avoid unnecessary sampling
  - identify relevant transport processes
  - quantify unknowns
  - predict uncertainties

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Issues (Cont'd.)

NEGATIVES

- processes governing VI can be highly variable and are not easily quantified
  - nobody expects models to predict the future exactly
    - what degree of confidence is acceptable? (stakeholder implications)
    - prediction is only as good as the calibration/validation
- general unfamiliarity with more sophisticated models
- most widely accepted VI models are either too conservative or too simple (i.e., do not account for relevant processes, such as biodegradation)

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Issues (Cont'd.)

MAJOR CONCERNS

- there is a tendency for misuse and abuse of models

- applications beyond simple spreadsheets not generally performed and acceptance generally limited

  -restricted use for site-specific applications

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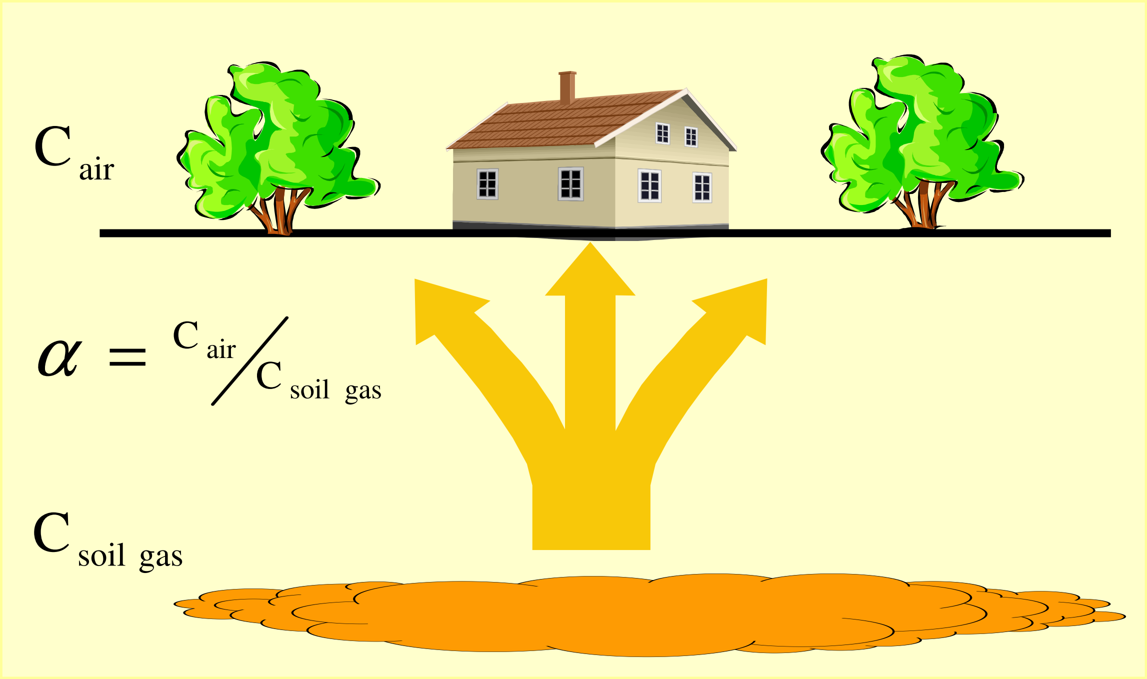
General Conceptual Site Model (CSM)



- Mixing in Breathing Zone
- Convective Transport into Bldg
- Diffusive Transport to Breathing Zone
- Impacted Soil and/or Groundwater in Equilibrium with Soil Gas

KEY POINTS:

- **CSM is specific to certain models (e.g., 1-D)**
- **Important to collect necessary data to determine if model is applicable to CSM**

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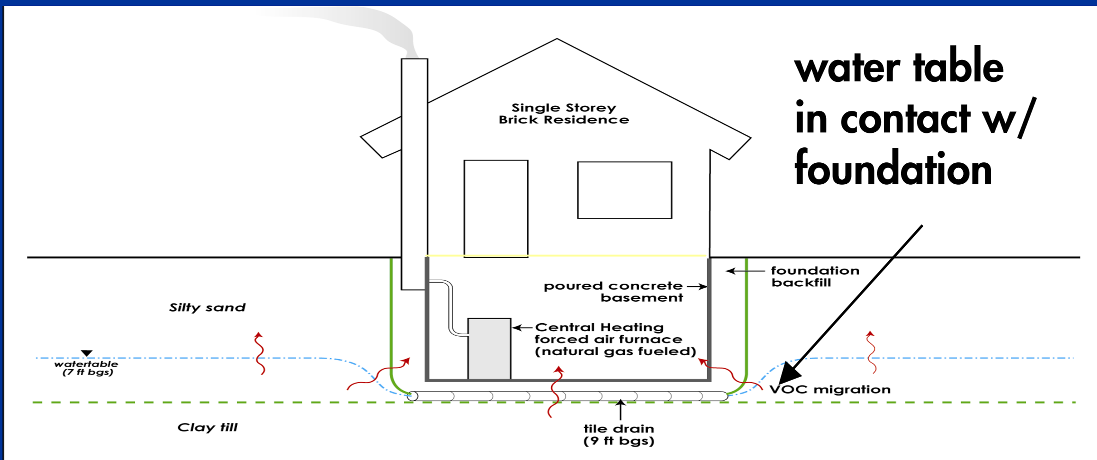
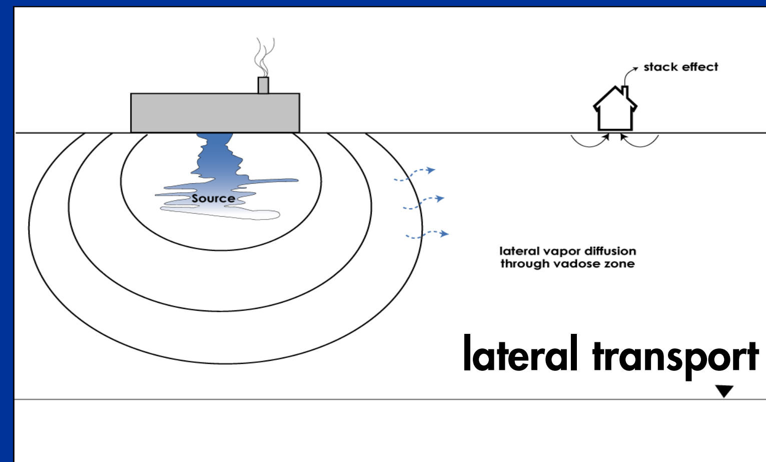
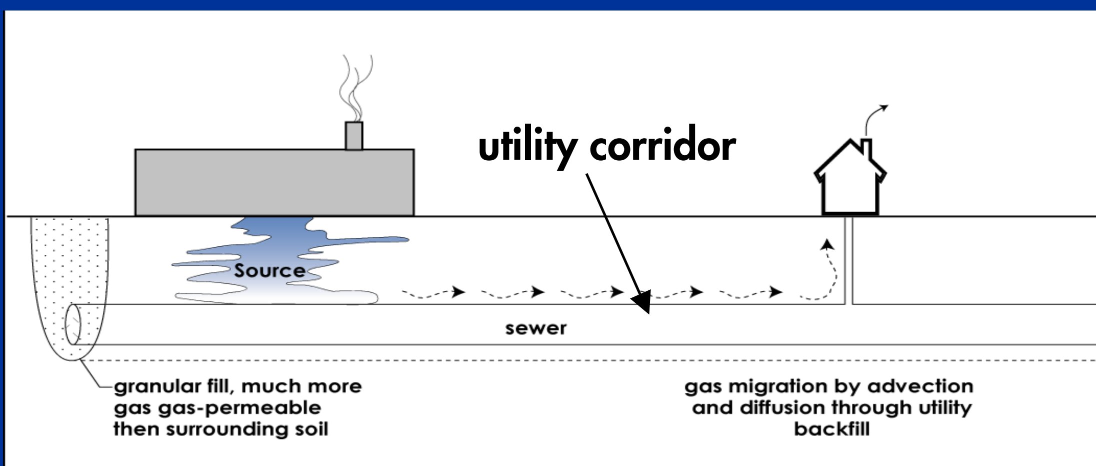
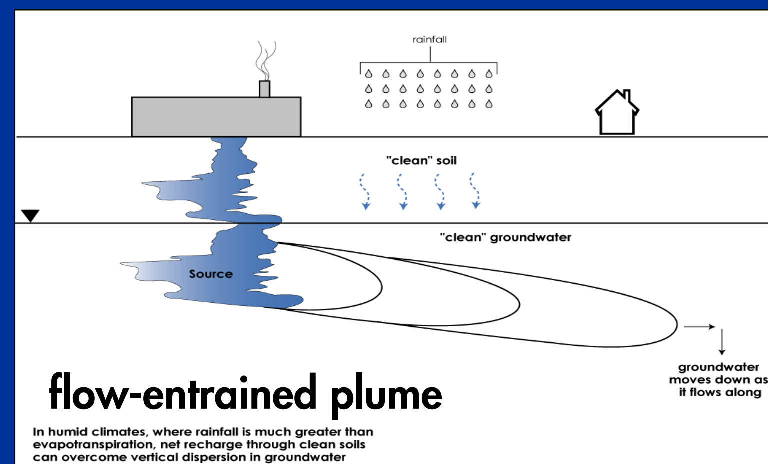
Factors to Consider in CSM

Figures courtesy of T. McAlary









- CSM must be valid for model application
- the predictive calculation is only as good as the investigative process itself

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Model Selection

Model	Published	1-D Vertical	Multi-Dimensional	Diffusion	Gaseous-Phase Advection	Slab Resistance	Infiltration	Biodegradation	Analytical	Numerical	Transient
Jury et al.	1983/1990	X		X			X	X	X		X
Johnson and Ettinger (1991)	1991	X		X	X	X			X		
Orange County Health Care Agency	1991	X		X		X			X		
Little et al.	1992	X		X	X				X		X
Sanders and Stern	1994	X		X	X			X	X		X
Ferguson et al.	1995	X		X	X	X		X	X		X
Jeng et al.	1996	X		X				X	X		X
R-UNSAT (Lahvis and Baehr)	1997	X	X	X			X	X	X	X	X
Krylov and Ferguson	1998		X	X	X			X	X	X	
Dominant Layer Model (Johnson et al.)	1998/1999	X		X	X	X		X	X		
Oxygen Limited Model (Johnson et al.)	2000	X		X	X	X		X	X		
Parker	2003	X	X					X			
Abreu and Johnson	2005		X	X	X	X		X		X	X

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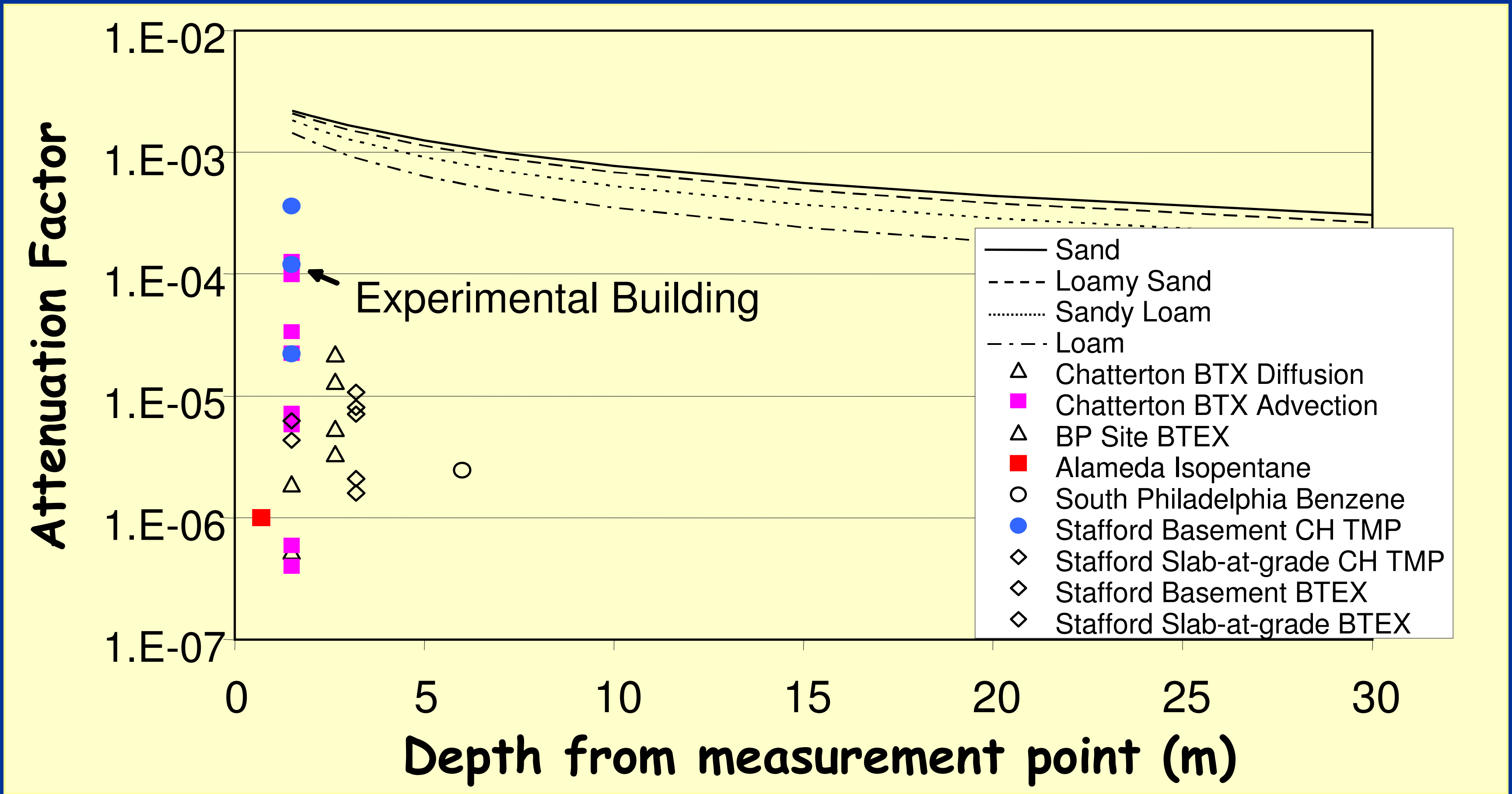
Measured vs. Conservative Model -- Hydrocarbons



- measured AFs for petroleum hydrocarbons can be orders of magnitude less than semi-site specific screening levels

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Hers, Dawson, & Truesdale (2005)

Screening Model for Dissolved-Phase Petroleum-Hydrocarbon Sites

Governing Transport Equation
1-D Vertical (steady-state)

$$D\frac{\partial^2 G}{\partial z^2} - \lambda C = 0$$

diffusion

biodegradation

D = effective diffusion coefficient
λ = first-order rate constant
C = aqueous-phase concentration
G = gaseous-phase concentration
z = distance

Transformed Equation
(dimensionless analysis)

$$\frac{\partial^2 C}{\partial x^2} - D_m C = 0$$

where,

$$D_m = \frac{\lambda L^2}{D H}, \quad x = \frac{z}{L}$$

D_m = scales biodegradation and diffusion
H = Henry's Law constant **L = distance**

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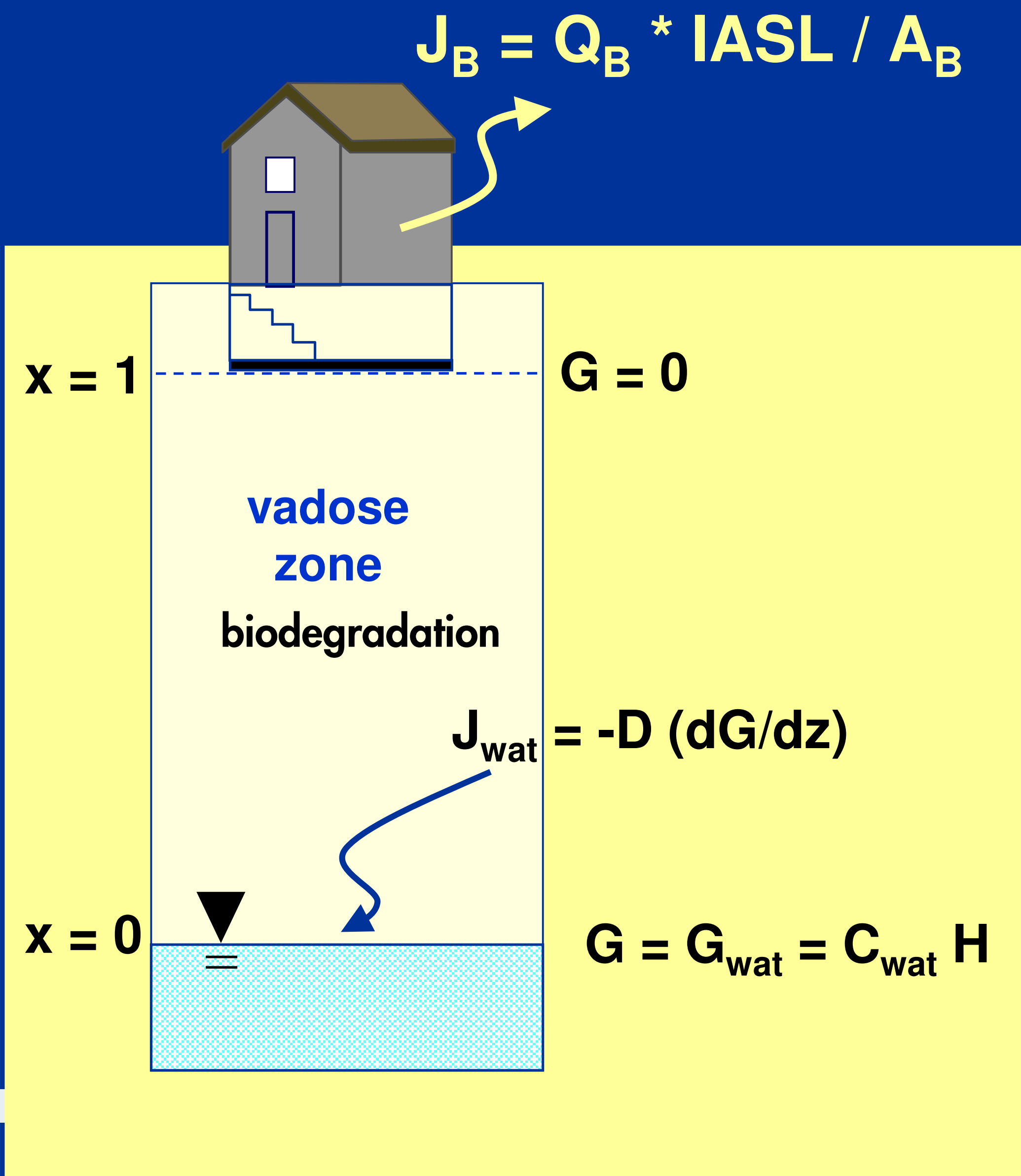
Boundary Conditions and Model Assumptions



- 1-D, uncoupled transport (conservation of mass)
- conservative with respect to diffusive transport
  - at x = 1, G = 0
- first-order kinetics
- uniform soil properties - weighted avg. diffusion coeff.
- equilibrium partitioning
- may not be appropriate for all applications (advection >> diffusion)

General Site-Specific Application: Predict Risk-Based Screening Level (RBSL)

a) calculate mass flux to indoor air (J_B): $J_B = Q_B * IASL / A_B$

b) calculate D_m: typical knowns - depth to groundwater (L); soil type (D), Henry's Law (H); typical unknown - biodegradation rate (λ)

Default Values	***D(benzene)* = 0.12 m²/d (sand, EPA *spreadsheet*) (Default)** **For unsaturated soils and BTEX concentrations in pore water < 0.2 mg/L, kinetics first order apply:** **λ (avg.) = 5.8 d^{-1}** **λ (lower 95%) = 0.5 d^{-1}** **λ (default) = 0.25 d^{-1}**

$$D_m = \frac{\lambda L^2}{D H}$$

c) apply type curve, determine RBSL/J_B

d) predict RBSL

* *DeVaull et al.* (1997)
assumes moisture content = 0.054 (sand, EPA spreadsheet)

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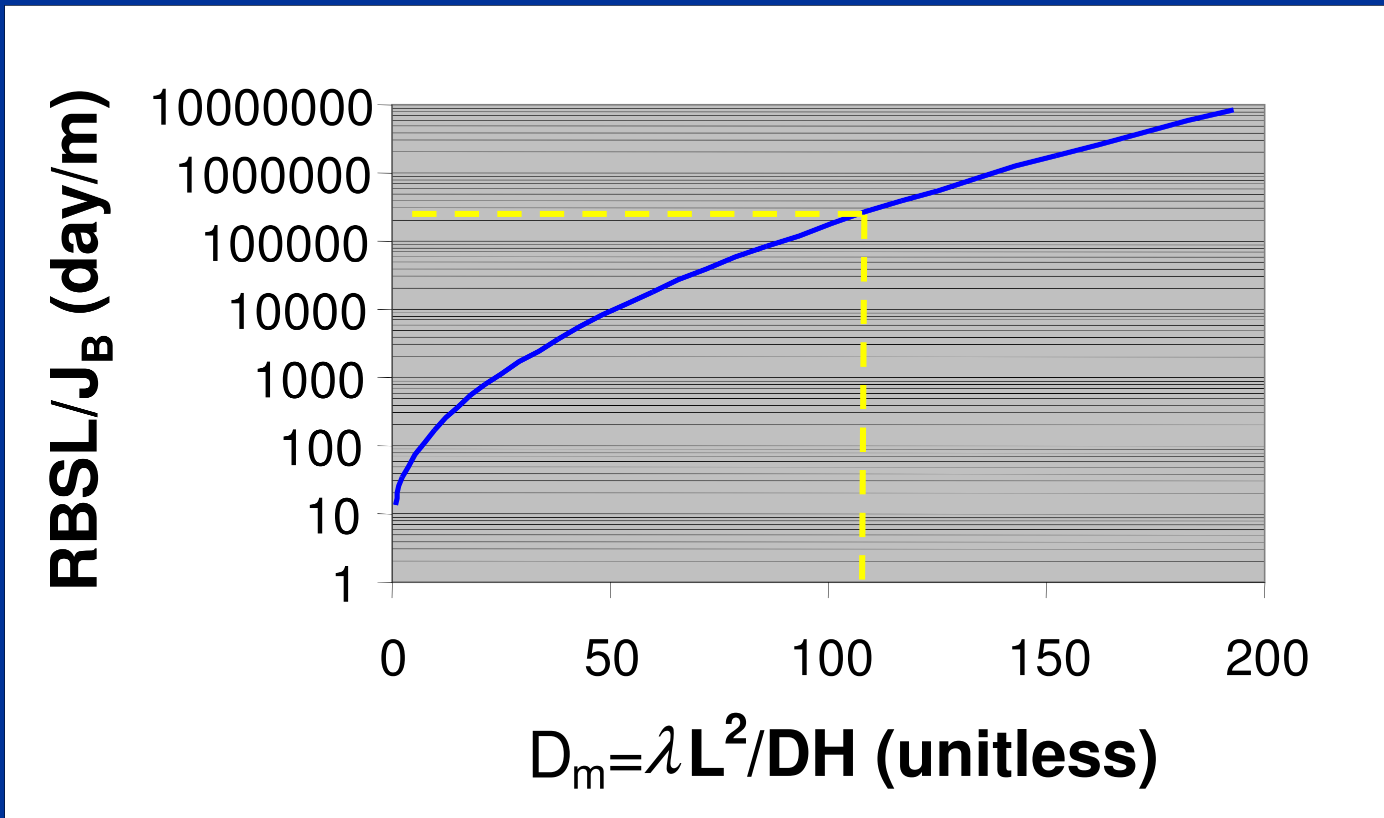
Application Cont'd. (example sand)



- calculate J_B
  ($J_B = Q_B$ * IASL / A_B)

  Q_B = 2,200 m^3/d
  IASL = 0.23 $\mu g/m^3$
  A_B = 100 m^2

- determine D_m

  $$D_m = \left(\frac{\lambda L^2}{DH} \right)$$

  λ = 0.25 d^{-1} (default)
  L = 3 m
  D = 0.12 m^2/d
  H = 0.21 (benzene)

- determine RBSL/J_B
- calculate RBSL (ppb)
  (RBSL = RBSL/J_B * J_B)

Biodegradation Rate	0.25 d^{-1}
J_B (mg/m^2-d) :	0.005
D_m (unitless) :	110
RBSL/J_B (d/m) :	215,000
RBSL (ug/L) :	1,100

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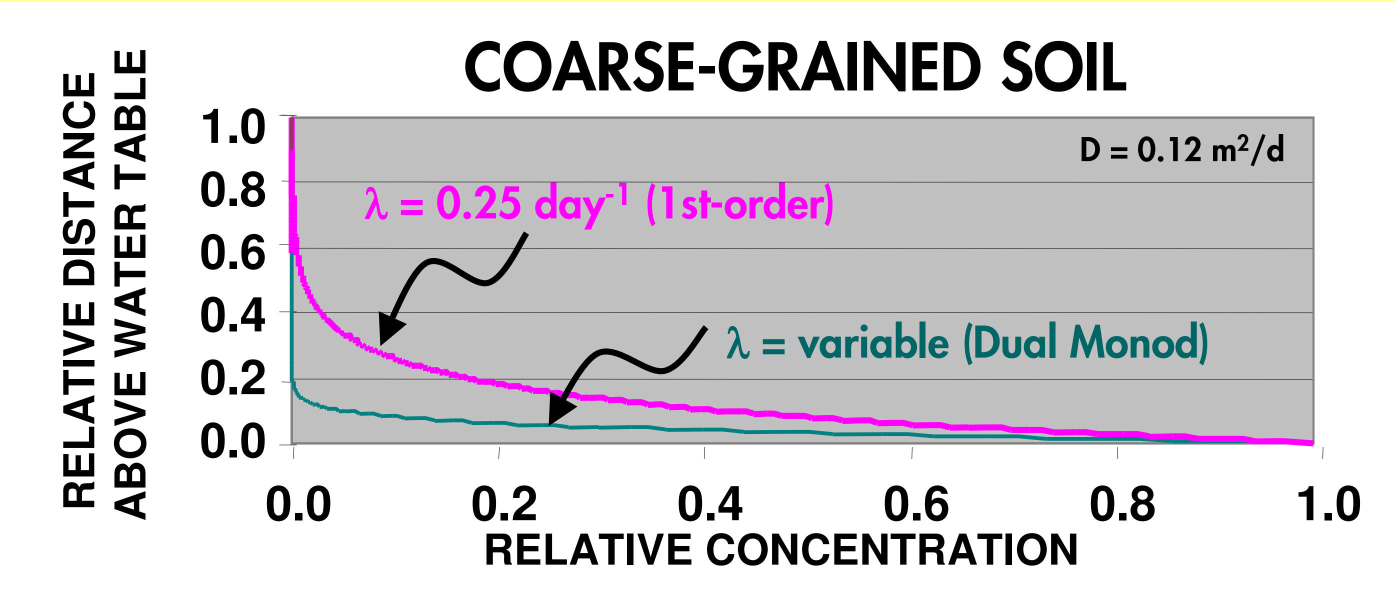
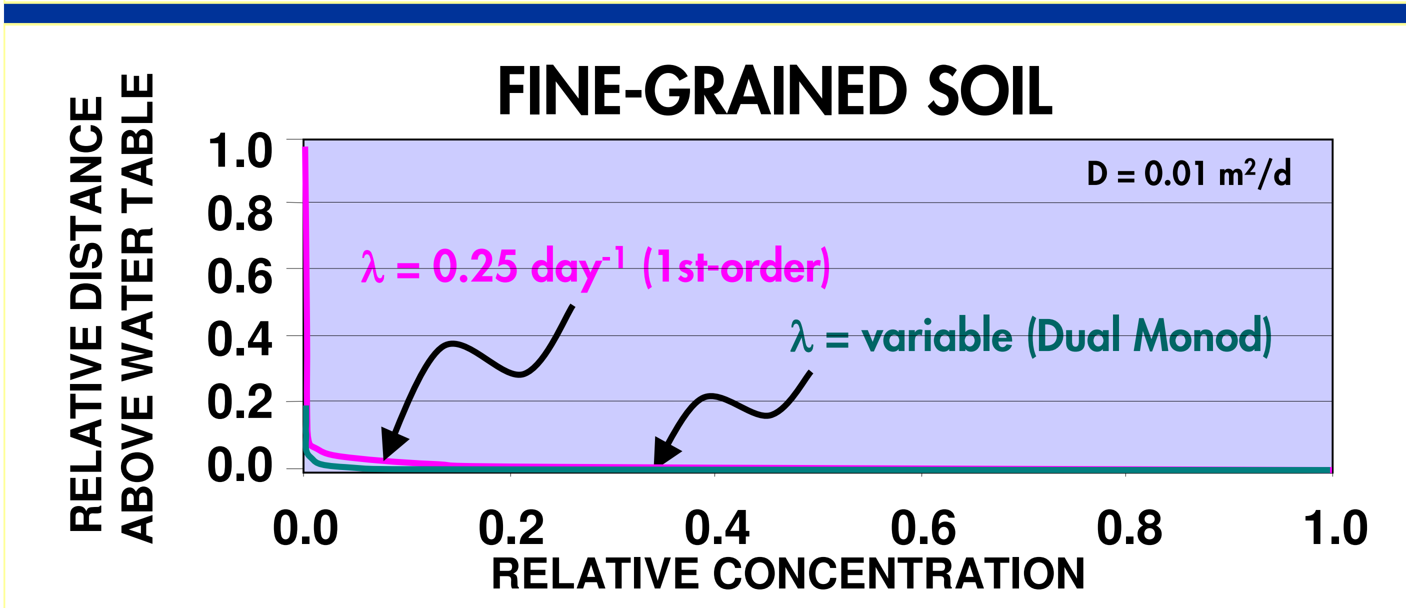
Validation of 1st-Order Kinetic Model





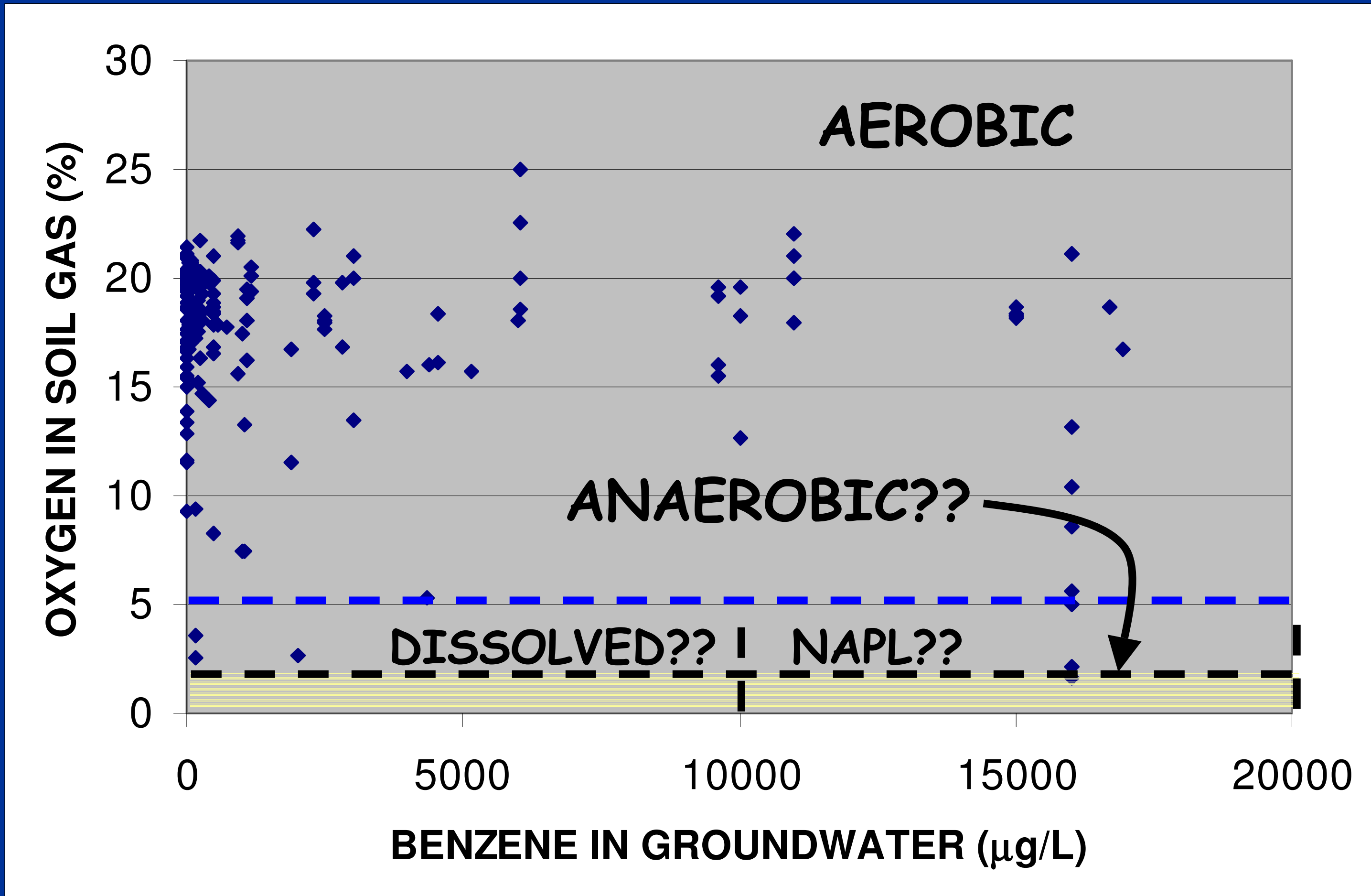
Is 1st-order kinetics assumption (λ = 0.25 d^{-1}) reasonable with respect to potential O_2 limited biodegradation?

L = 10 ft.
C_0 = 1,000 µg/L benzene

<u>Dual-Monod Parameters*</u>
max. rate constant
= 0.9 mg/L-hr
half sat. constant
= 0.2E-06 mg/L

from DeVault et al. (1997)

Initial Validation of Biodegradation Parameters

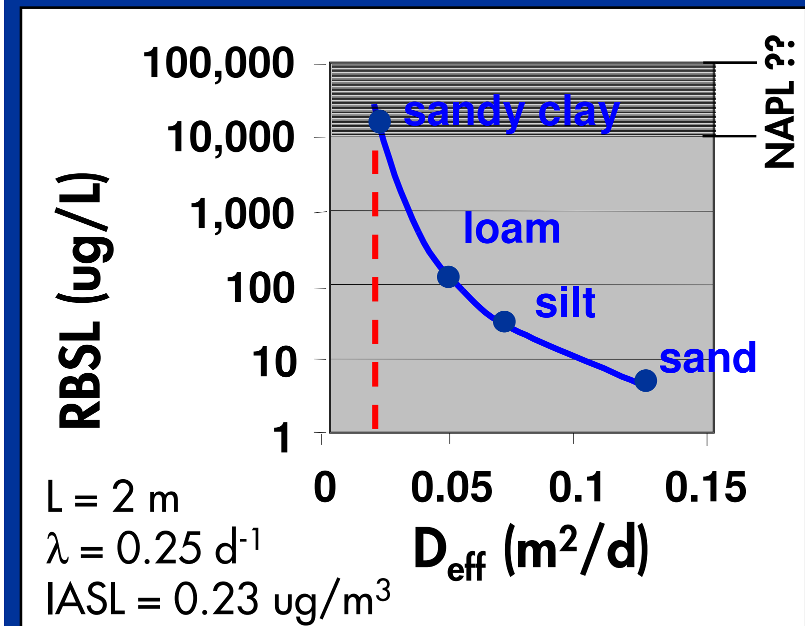


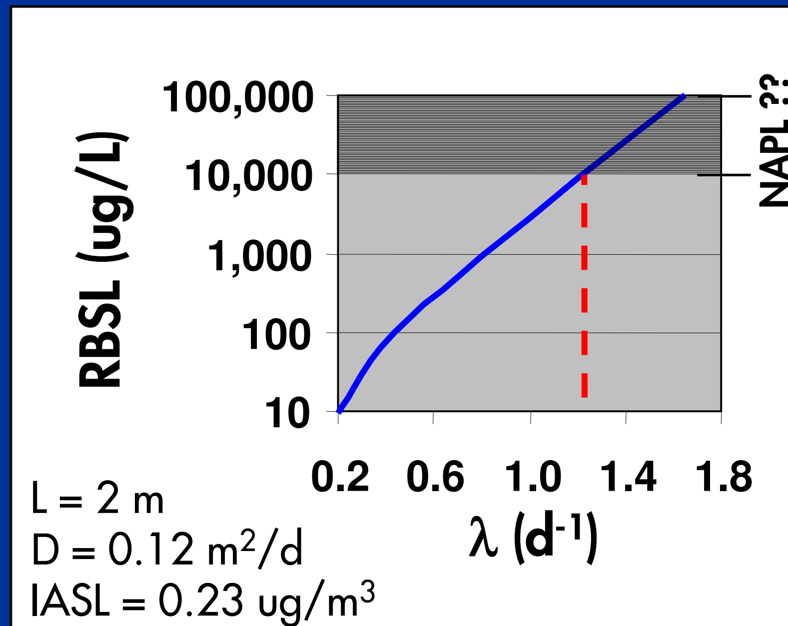
- aerobic conditions are observed in the unsaturated zone for all cases where benzene concentrations in groundwater < 10,000 ppb
- 3 events (< 1%) w/ limited O_2 (2% < O_2 < 5%) (clay, clayey silt)
- data appear to support 1st-order kinetics at dissolved-phase sites

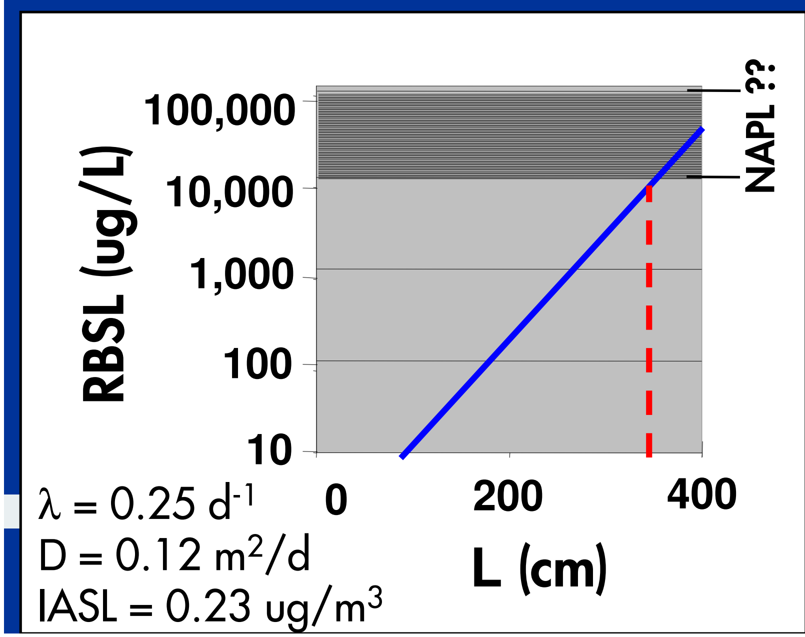
CO/UT Data Eval.

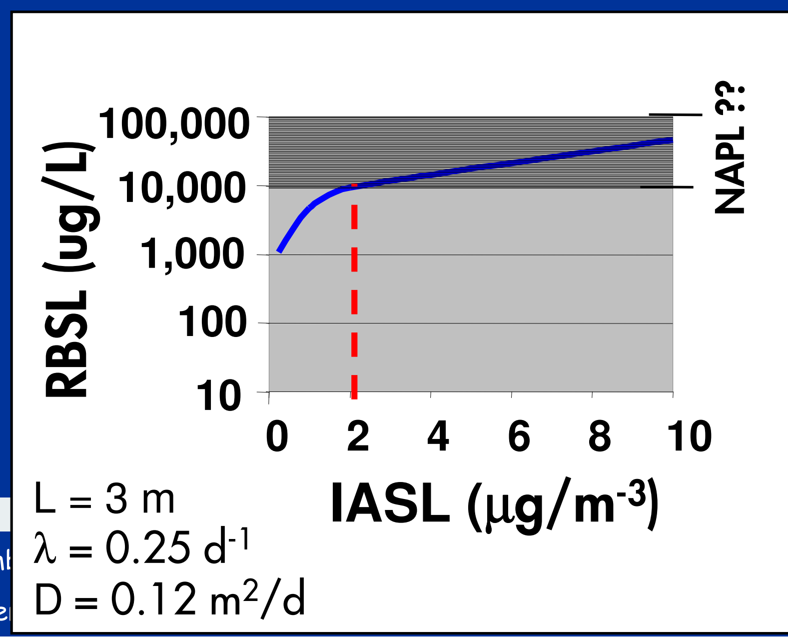
- 5822 soil vapor sampling events, 161 sites
- 696 events (O_2/CO_2 data)
- 447 events w/ O_2 + CO_2 > 18%
- 286 events w/ corresponding GW data
- 3 events (2 wells) w/ 2% < O_2 < 5 % (benzene < 10,000 ppb)
- 420/447 events w/ BTEX concs. in pore water < 0.2 mg/L (not, either C_{wat} benzene > 10,000 ug/L or UZ source implied)

Parameter Sensitivities





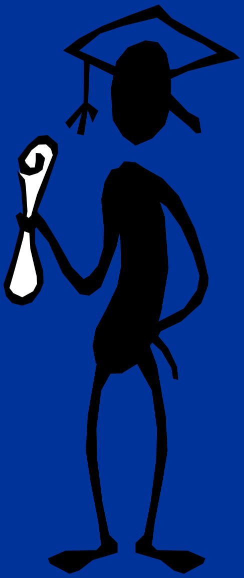




- sensitivities to λ, L, and D (fine-grained soil) imply AF is highly variable
- consistent with initial database analyses
- exclusion criteria (i.e., L = 3.5 m) more rational approach than "bioattenuation factor" at dissolved-phase sites

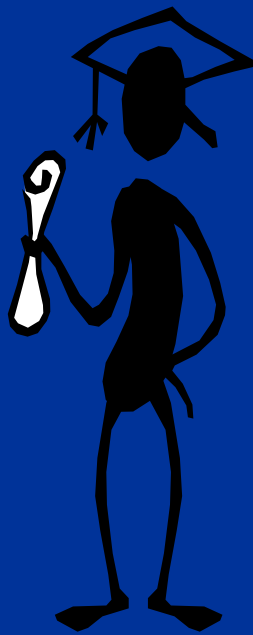
Summary

- if used appropriately, models can be extremely beneficial in guiding VI investigations (data collection)
- modeling is not appropriate without a basic understanding of the CSM (1-D transport)
- more sophisticated models (as opposed to conservative software) can be extremely helpful in refining predictions and limiting uncertainties, provided:
  - model assumptions and limitations are realized
  - sensitivities are sufficiently characterized
  - adequate field data is available to support application
  - bounds are placed on unknowns with significant variability



Summary (Cont.'d)

- for petroleum hydrocarbons, meaningful screening levels can only be established by accounting for biodegradation, especially at dissolved-phase only sites
- use of conservative 1st-order rate constant in screening-level model supported by initial evaluation of hydrocarbon database (> 2% O_2 present, BTEX concs. < 200 μg/L)
- application of screening model indicates current screening levels for benzene are far too conservative for dissolved-phase sites
- analysis indicates exclusion criteria (i.e., L = 3 m) is likely better approach than "bioattenuation factor"



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