Evaluation of the Effect of Vadose Zone Biodegradation on Vapor Intrusion at Petroleum Hydrocarbon Sites

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Vapor Intrusion at Petroleum Release Sites

- EPA OUST reports confirmed releases at 470,000 locations (360,000 closed), but vapor intrusion (VI) is found to be significant at very few locations
- Evaluation of VI at these sites via indoor air measurements is difficult due to background effects
  - Distinguish contribution from sub-surface sources
  - Target concentrations may be below background levels
- Vadose-zone biodegradation has been shown to attenuate vapor intrusion of petroleum hydrocarbons. This should influence:
  - Site assessment approach
  - Regulatory screening levels

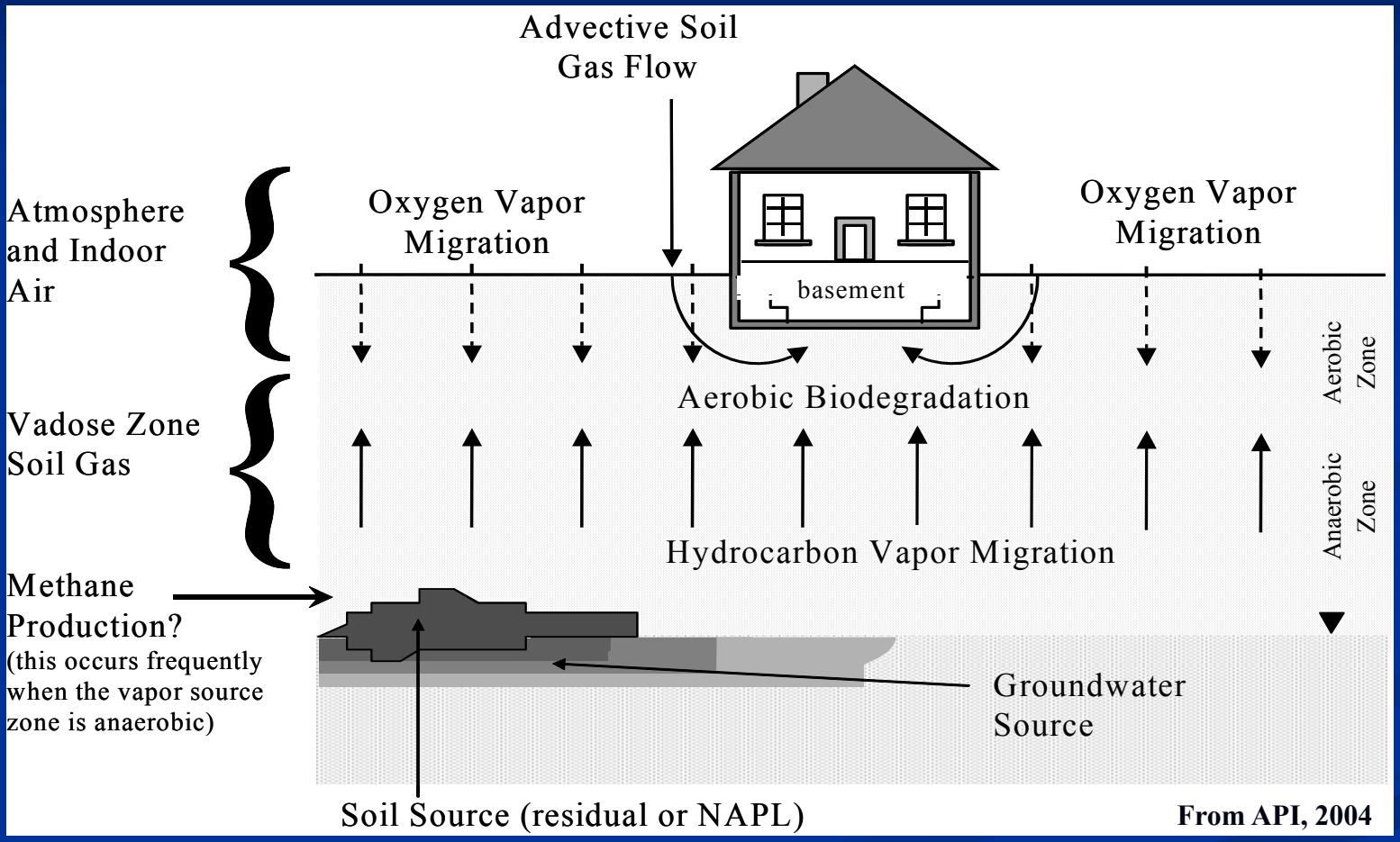
Regulatory Approach for Petroleum Sites

- Range of regulatory approaches to address VI assessment for petroleum hydrocarbons
  - USEPA: 2002 Draft Guidance not recommended for UST sites
  - Many regulatory agencies follow ASTM or 2002 USEPA Draft Guidance Examples
    - Leads to low screening levels (e.g., < 5 ug/L in groundwater)
  - A few regulatory agencies include a 10X biodegradation factor
- Empirical evidence suggests these approaches are overly conservative for most petroleum release sites

Outline

- Background on vadose zone biodegradation
- Modeling approaches
- Site characterization/assessment strategy
- Modeling study to evaluate VI screening criteria for petroleum compounds

Vapor Intrusion with Biodegradation Conceptual Model



Vapor intrusion attenuation factor: $\alpha = C_{indoor} / C_{soil\ gas}$

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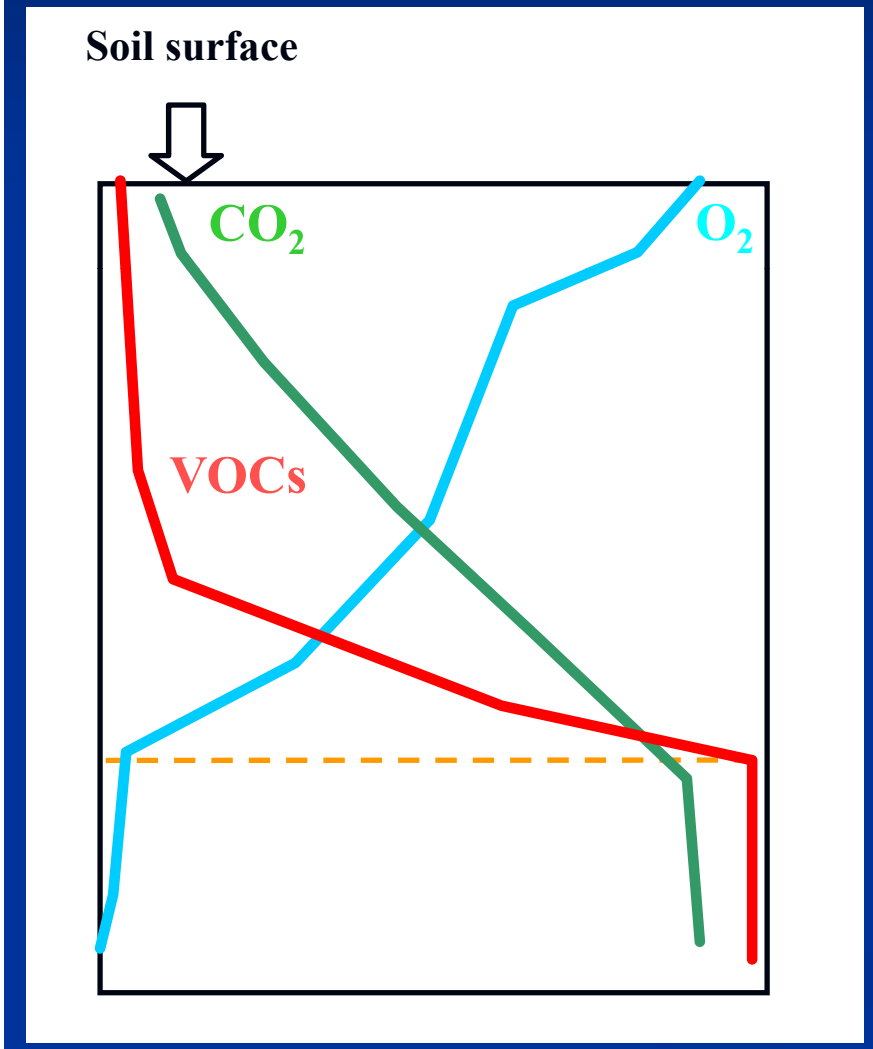
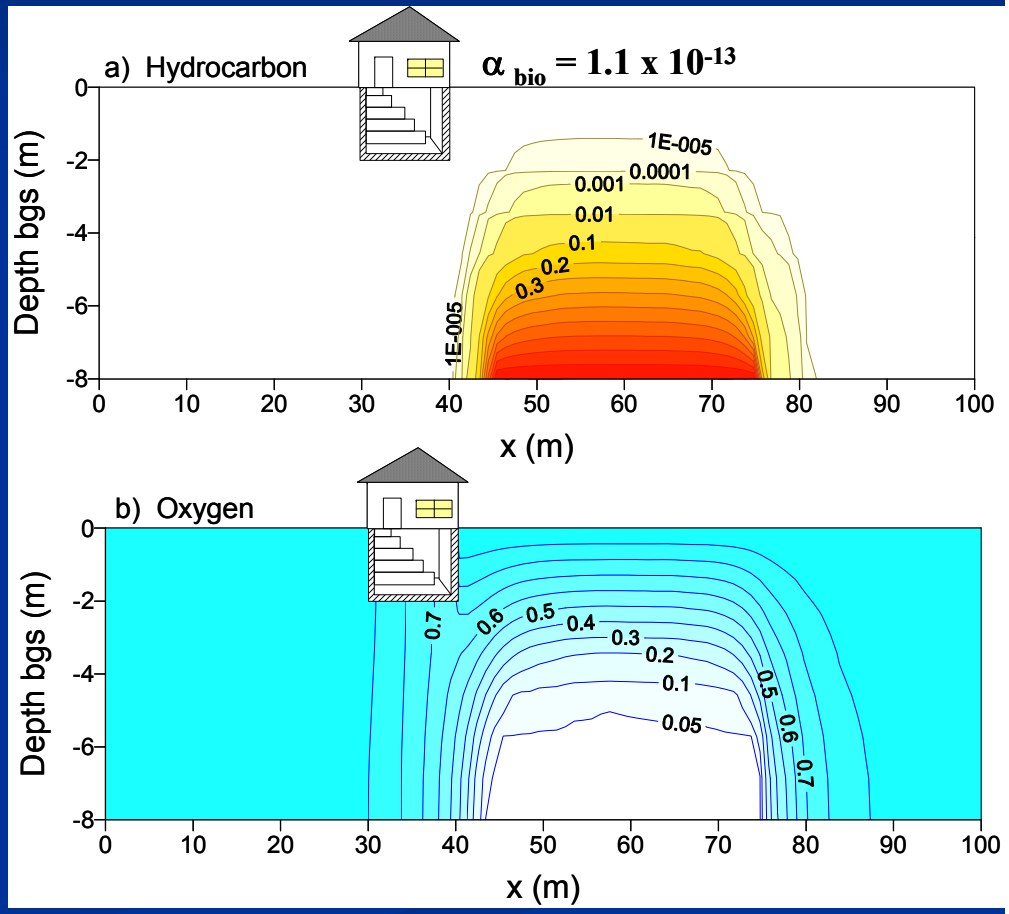
Vapor Intrusion with Biodegradation Conceptual Models (Chemical Distribution)





(Abreu and Johnson, 2005, 2006)

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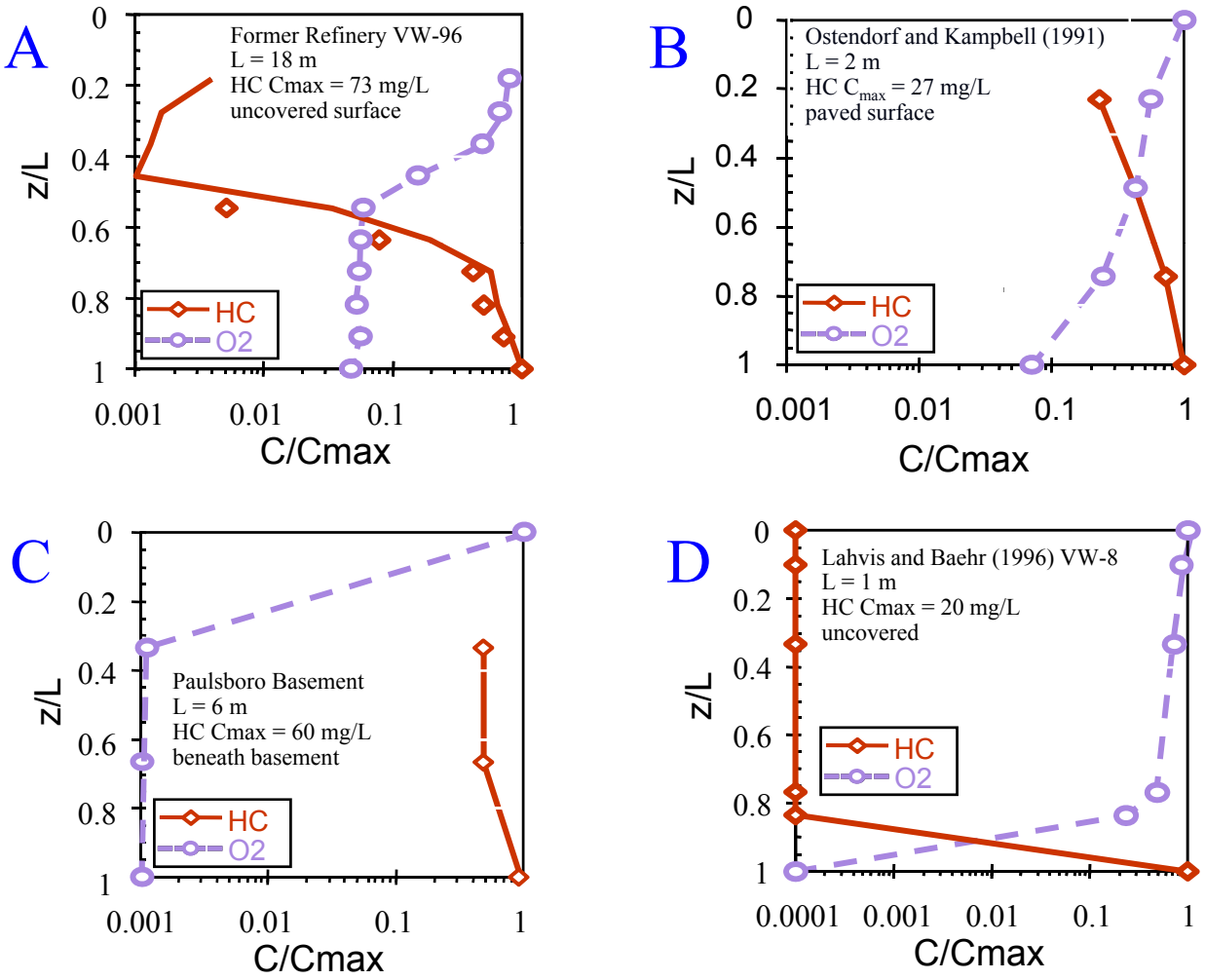
Evidence of Vadose Zone Biodegradation

- **Fitzpatrick and Fitzgerald, 1996**
  - Review data collected from large set of sites with VOCs located near buildings.
  - Marked difference in attenuation factors for chlorinated solvents compared to hydrocarbons.
  - Conclude that aerobic degradation is significant for petroleum hydrocarbons sites.
- **Various Site Studies**
  - Researchers collect hydrocarbon and oxygen soil gas data.
  - Evidence of biodegradation:
    - Oxygen depletion with depth
    - Hydrocarbon depletion near surface
    - Carbon dioxide generation with depth

Evidence of Vadose Zone Biodegradation

EXAMPLE SOIL GAS PROFILES



(Roggemans et al., 2001)

SOIL GAS PROFILES BEHAVIORS

A: Oxygen Transport Limited

B: Degradation Rate Limited

C: Oxygen Deficient

D: Source Diffusion Limited

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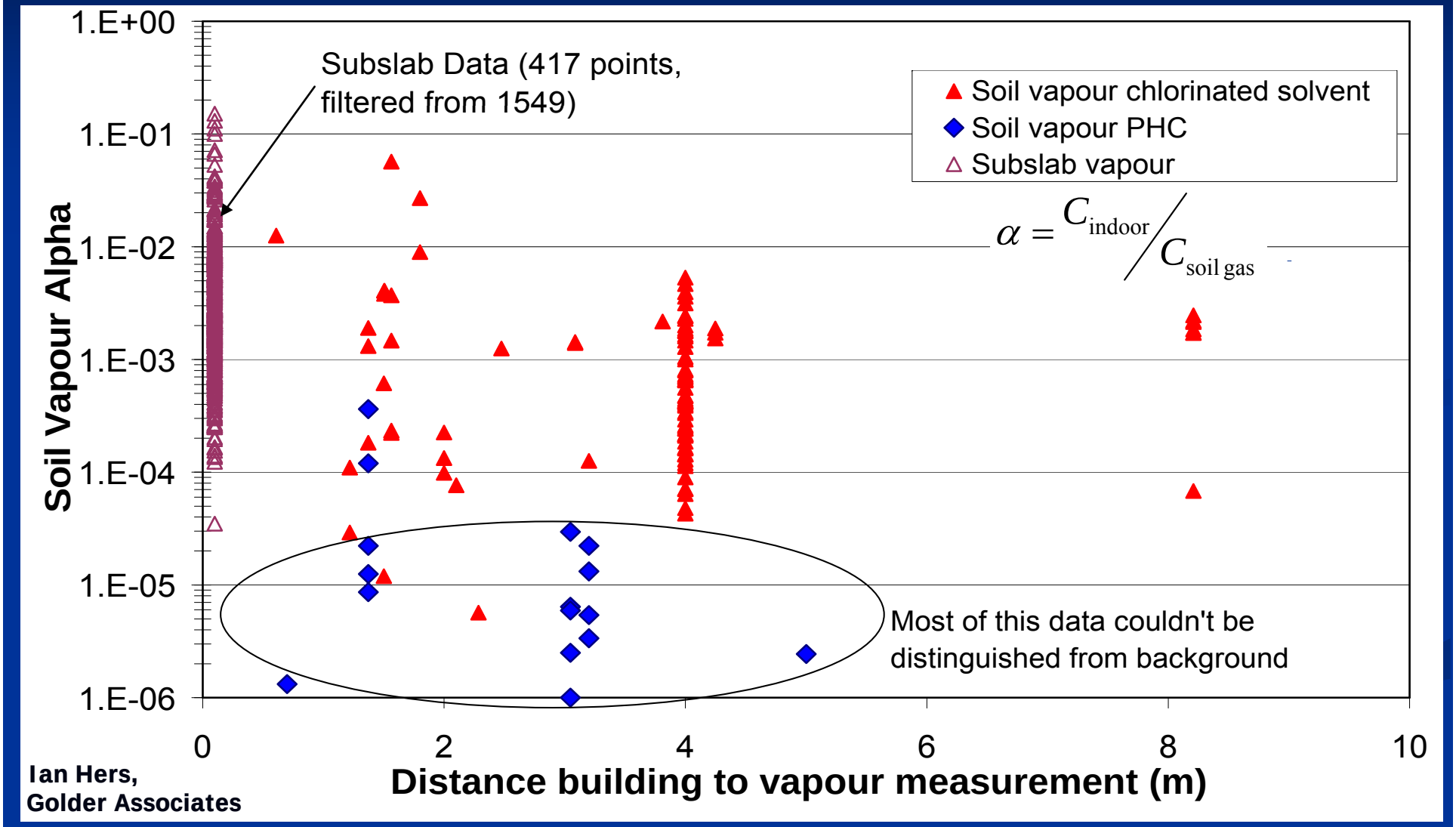
Empirical Attenuation Factor – USEPA Database



Ian Hers,
Golder Associates

(residential, filtered data 100X subslab vapor, 1000X external soil vapor)

Conditional Criteria for Aerobic Biodegradation

1. Microbes are present

   BTEX degrading microbes found in every soil investigated

2. Oxygen

   greater than ~0.1 mg/L in soil pore water
   (0.3% v/v in pore air)

3. Energy Source

   food (hydrocarbons)

4. Inorganic Mineral Nutrients

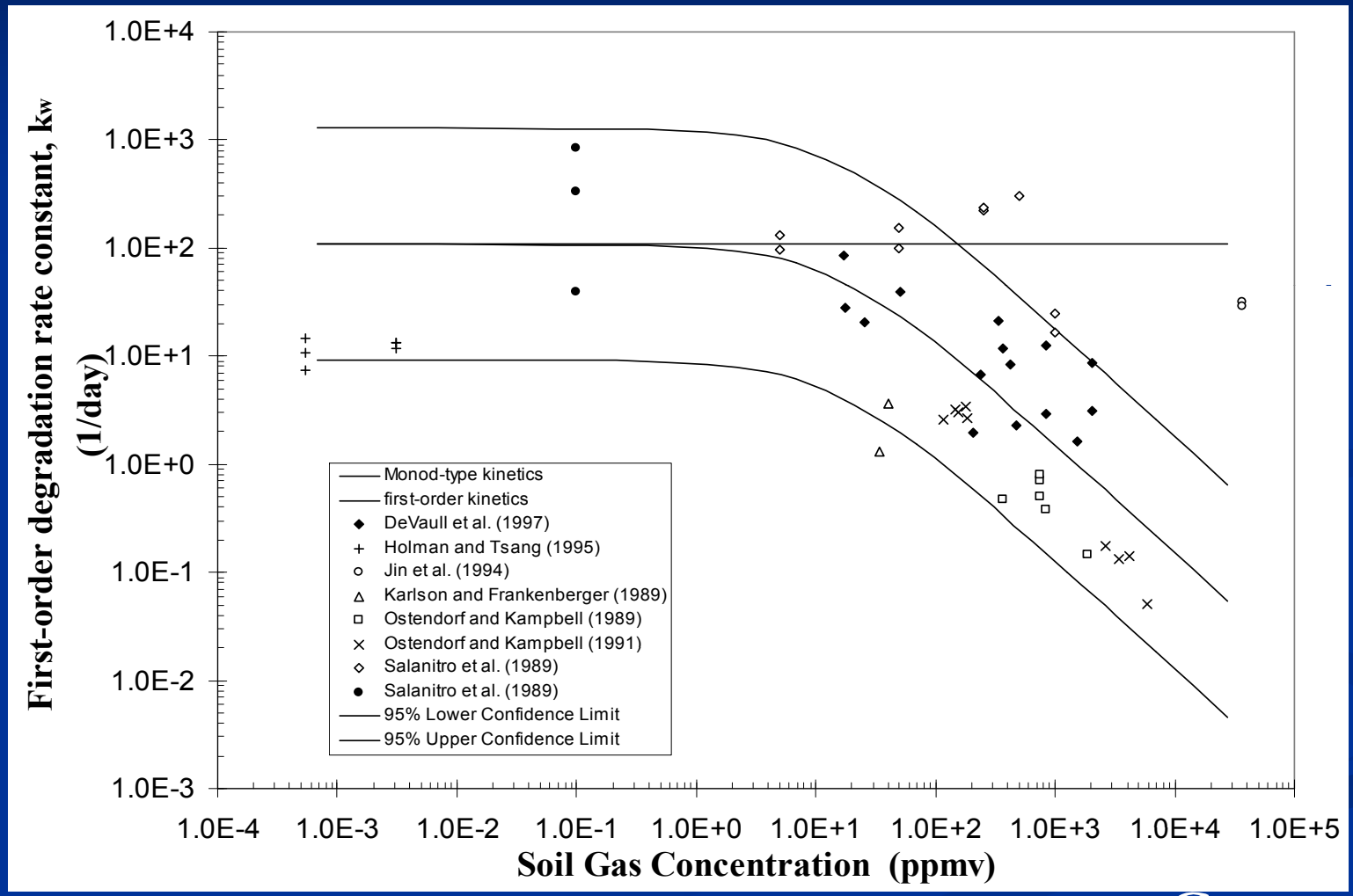
   nitrate, phosphate, ammonia at natural background levels.

5. Water

   moist soil (available water greater than wilting potential)

From DeVaull et al., 1997

Summary of BTEX Degradation Rates



From DeVaull et al., 1997

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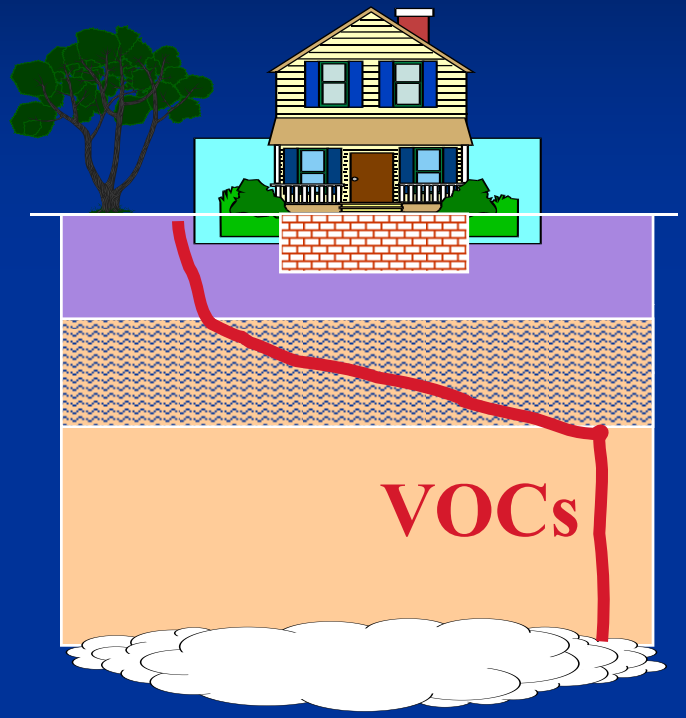
Biodegradation Modeling

- Different models with varying levels of sophistication are available
  - **Screening Bio-Model (Lahvis, 2006)**
    Biodegradation throughout vadose zone
  - **Dominant Layer Model (Johnson et al., 1999)**
    Biodegradation in user-defined degradation zone
  - **Oxygen Limited Model (DeVaull, 2007)**
    Biodegradation in zone of sufficient oxygen
  - **Three Dimensional Model (Abreu & Johnson, 2005)**
    Numerical code calculating VOC and oxygen fate and transport

Dominant Layer Model (DLM)

(Johnson, et al., 1999)



Mixing in Breathing Zone

Convective Transport into Building

Biodegradation Zone

Diffusive Transport

Partitioning

- Requires additional data collection for bio indicators
- Calibrate model with site soil gas profile data to determine biodegradation parameters

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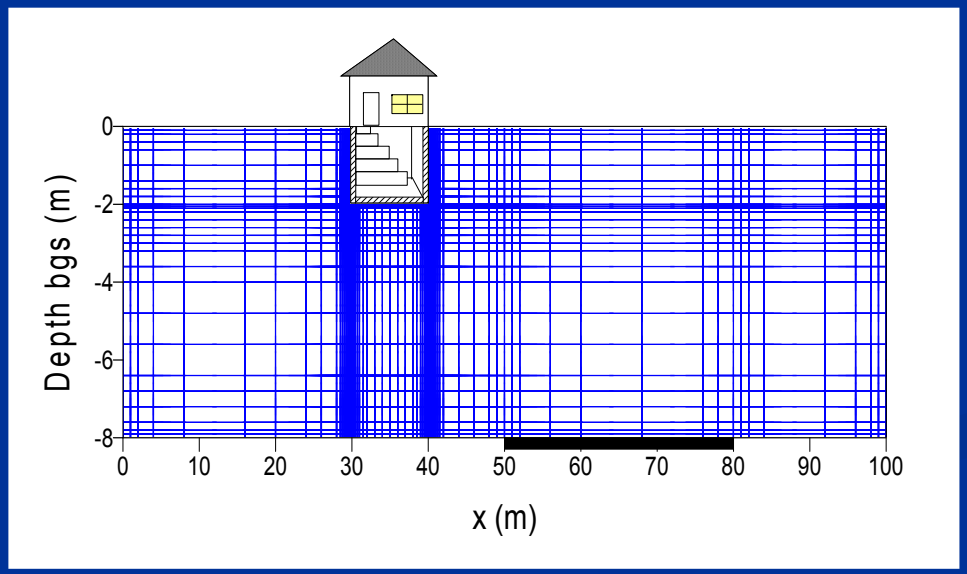
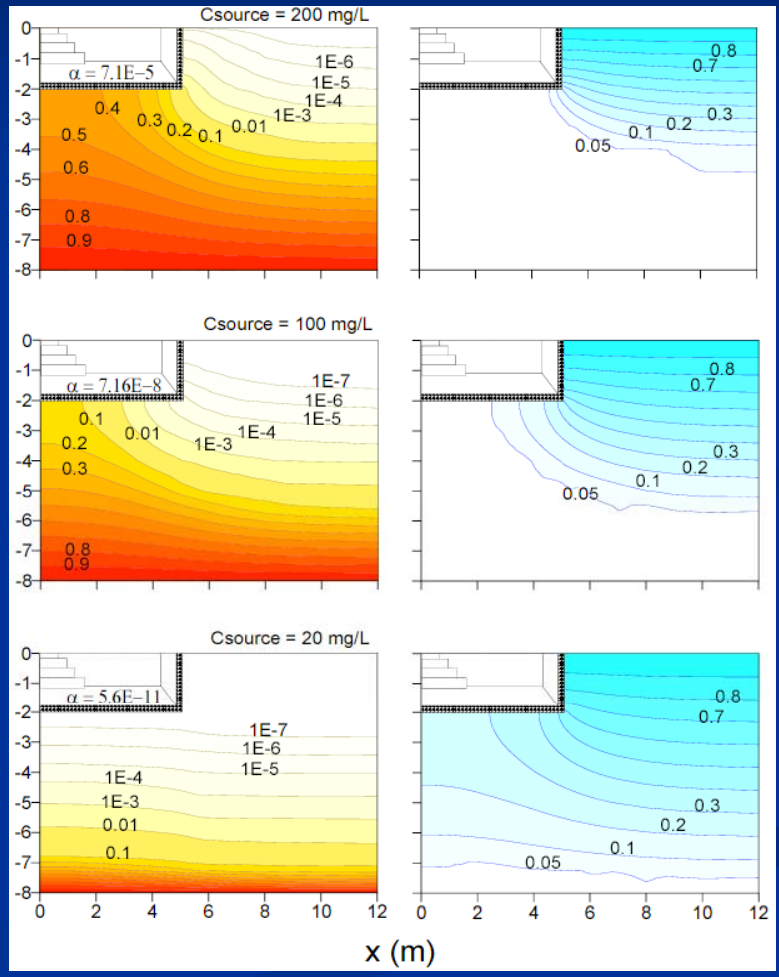
Three-Dimensional Numerical Model

(Abreu and Johnson, 2005)

- Model Description
  - 3-D vadose zone F&T model
  - Evaluate building type, source scenarios, and biodegradation kinetics
- Model Results
  - Impact of biodegradation
  - Significance of lateral migration





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Key Transport Phenomena

Hydrocarbon Flux from Source

- Diffusion rate from source
  - Source concentration
  - Effective diffusion coefficient
  - Diffusion path length
- Degradation rate
  - Kinetics
  - Oxygen availability

$$\frac{d^2C_{HC}}{dz^2} - \delta_{HC} C_{HC} = 0$$

$$\delta_{HC} = \frac{\lambda_{HC}\,\theta_w\,L^2}{D_{eff}\,H}$$

Oxygen Flux from Surface

- Diffusion rate from source
  - Surface flux
  - Effective diffusion coefficient
  - Diffusion path length
- Degradation rate
  - Kinetics
  - Oxygen utilization

$$\frac{d^2C_{O2}}{dz^2} - \delta_{O2} C_{O2} = 0$$

$$\delta_{O2} = \frac{\lambda_{O2}\,\theta_w\,L^2}{D_{eff}}$$

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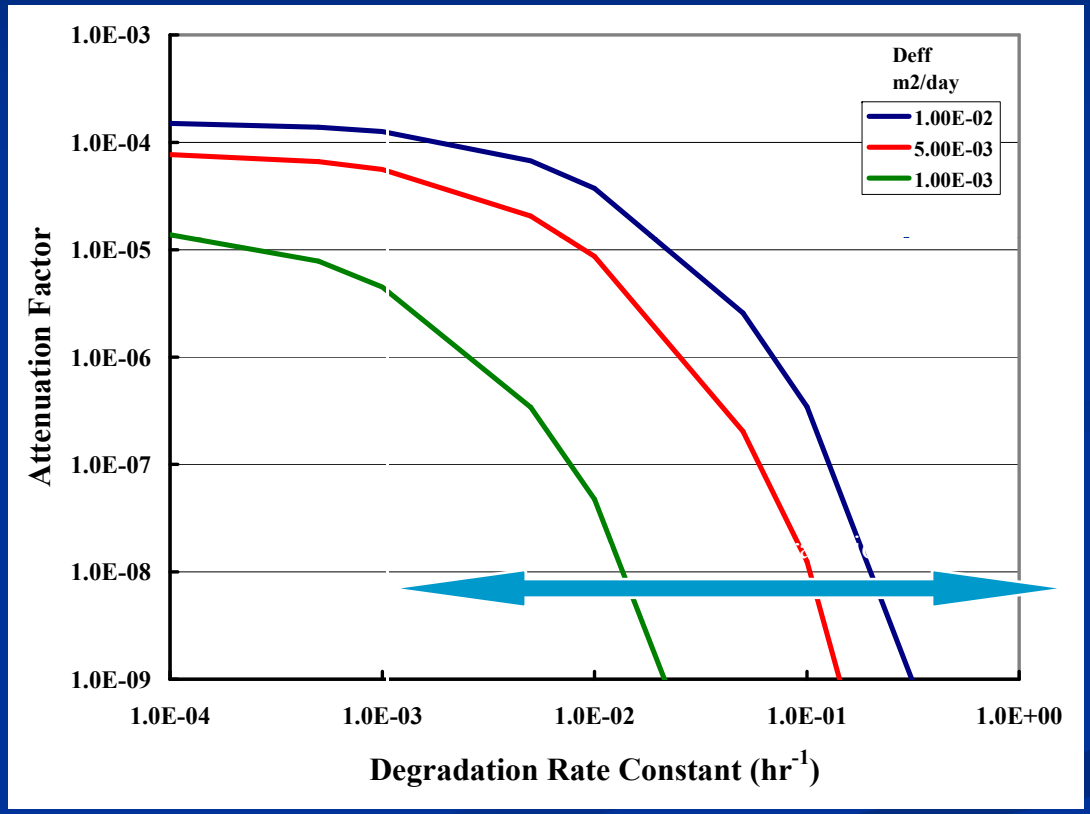
Vadose Zone Biodegradation

- Degradation rate dependent on hydrocarbon content as well as oxygen content
- Attenuation factor decreases as degradation increases
- Vadose-zone biodegradation may result in orders of magnitude reduction in attenuation factor



Potential impact on attenuation factor: 10 to >>1000 x

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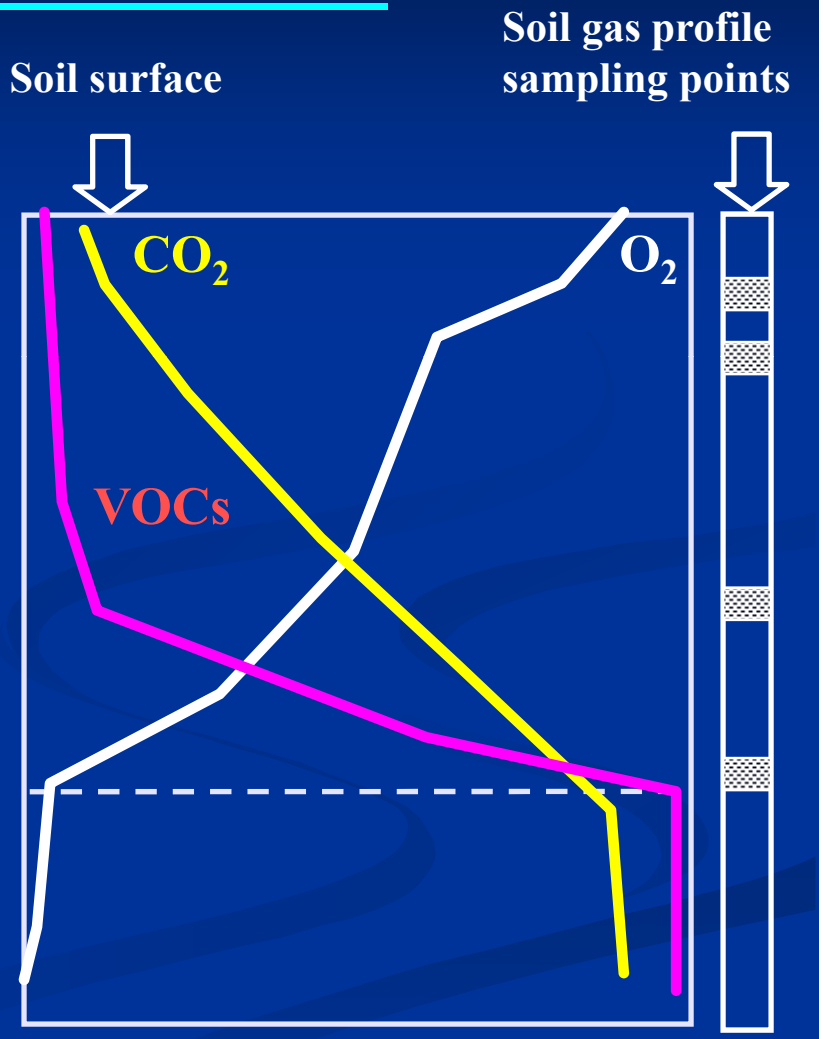
Investigation Approach to Evaluate Vadose-Zone Biodegradation

- Follow approach of API, 2005 and Johnson et al., 1999 to quantitatively evaluate soil gas profile data
- Data collection
  - Soil gas profile
  - Lithology and soil physical properties
- Data analysis
  - Data consistency
  - Vapor transport modeling
- Reduce uncertainty in vadose zone vapor transport component of VI modeling



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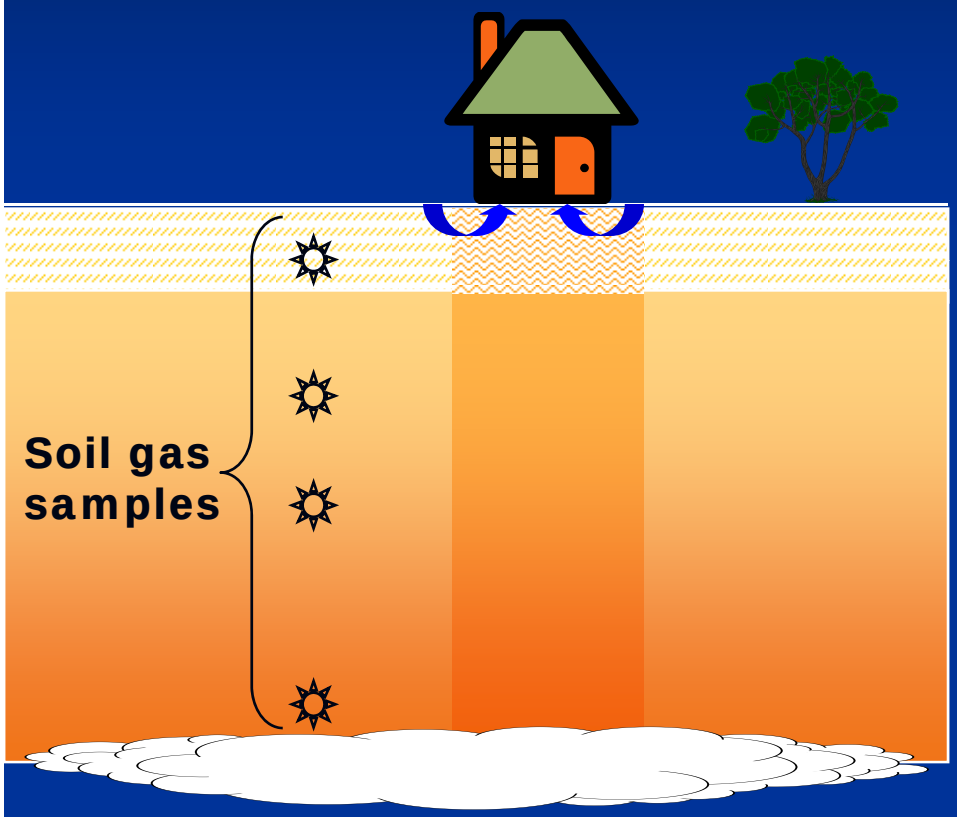
Soil Gas Profile Data



- Soil gas profile underneath building may be different than that outside building footprint.
- Often sub-slab data is unavailable (e.g., site redevelopment)
- Evaluate soil gas data to address uncertainty in sub-surface transport (diffusion and biodegradation)
- Reassess vapor intrusion evaluation from subsurface source (include convection and ventilation effects)

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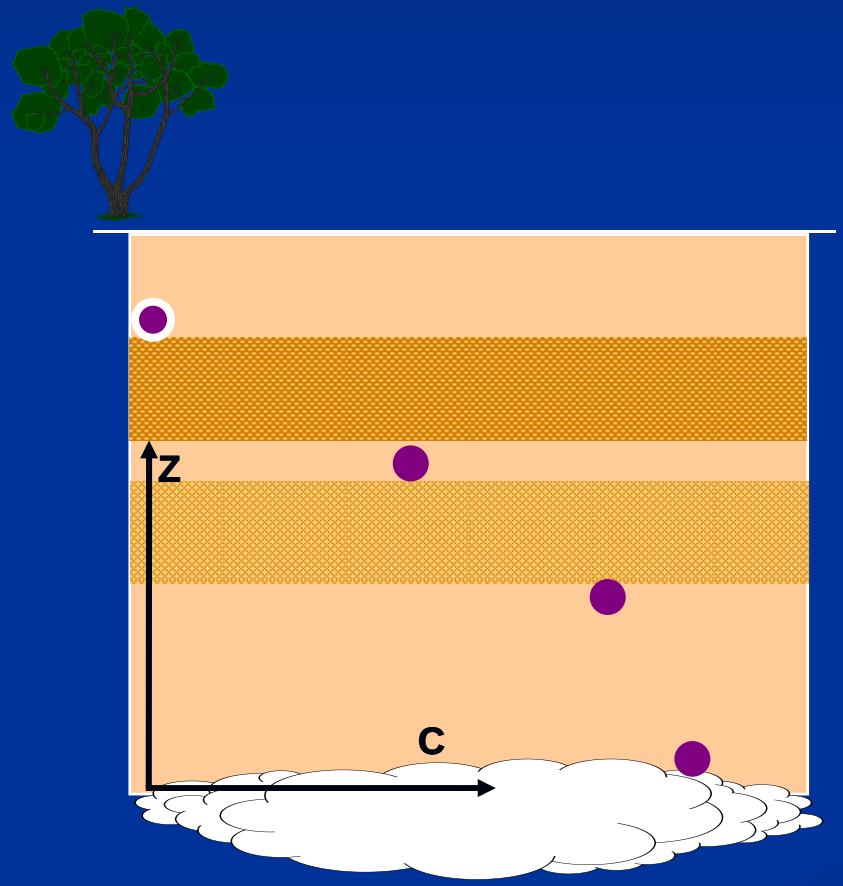
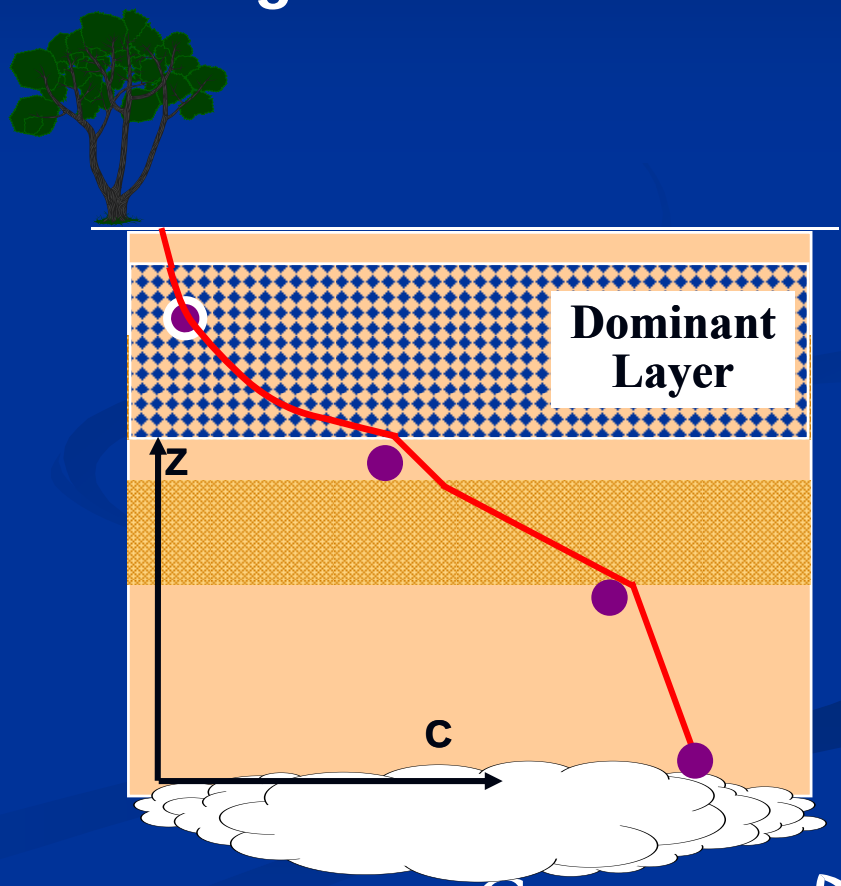
Modeling Process
Biodegradation Scenario

Soil Gas Profile Data



Vapor Diffusion / Degradation Model



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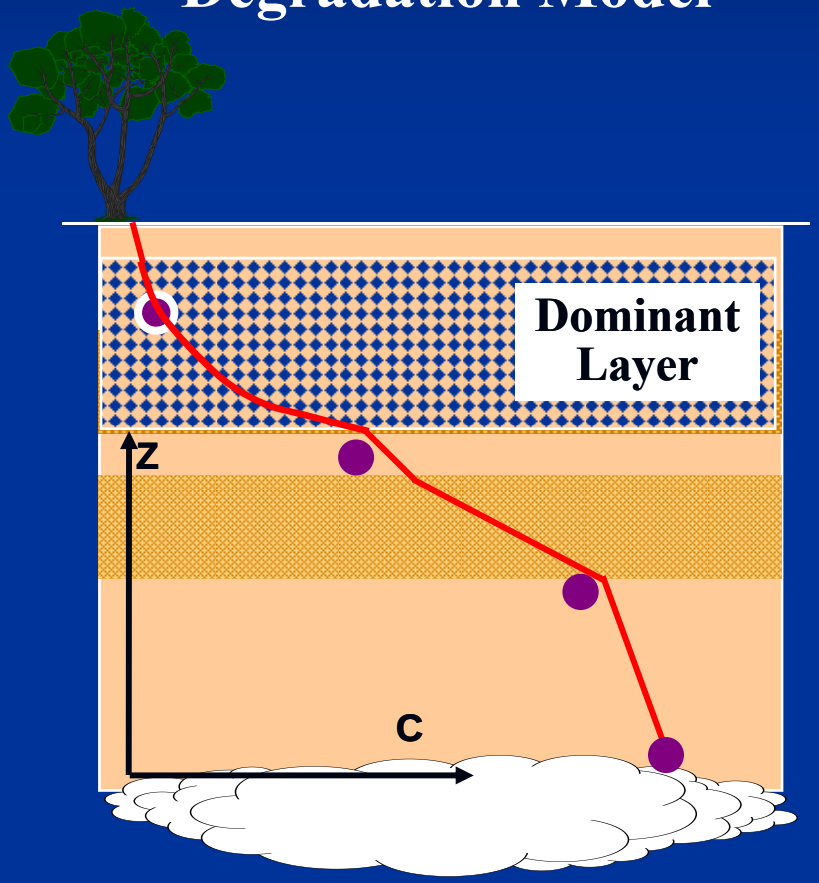
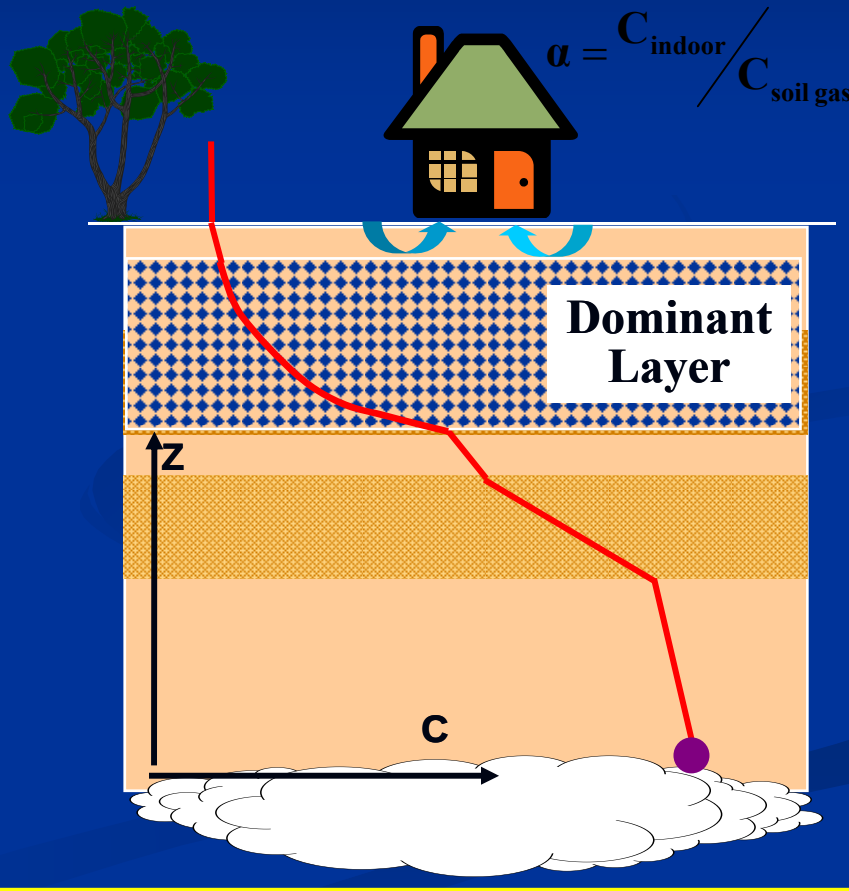
Modeling Process
Biodegradation Scenario

Vapor Diffusion / Degradation Model



Vapor Intrusion Model



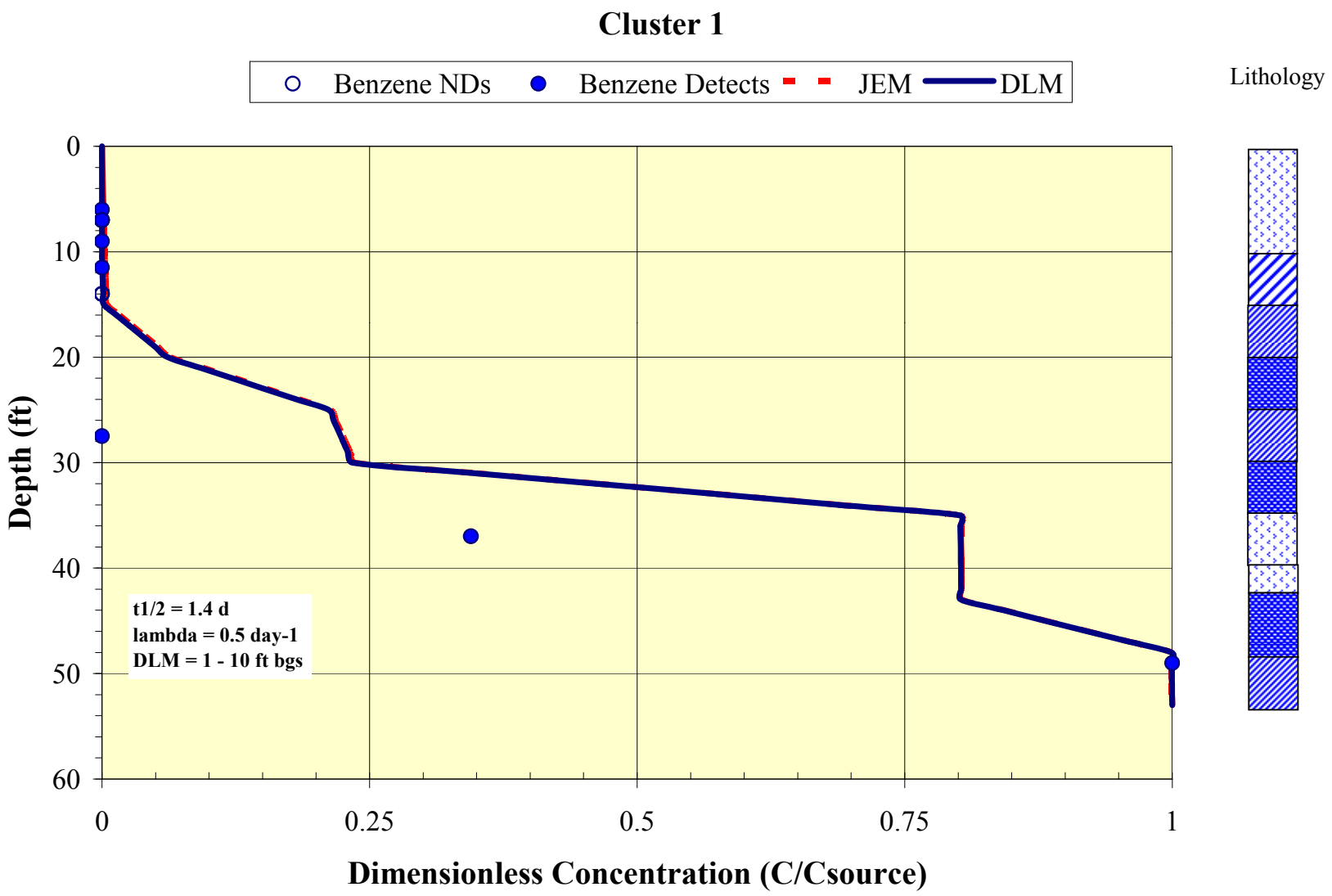
Modeling process considers site-specific hydrogeology, vadose-zone biodegradation, and accounts for potential building effects on soil gas profile

Example Evaluation
Chemical Release Site

Approach:

- Soil gas VOC concentration profile data and soil property data available (benzene primary chemical of concern)
- Use DLM to develop conservative site-specific estimates for biodegradation rate and biodegradation interval
- Assess data consistency (profiles for degradable and recalcitrant compound)
- Compare VI attenuation factors to no-degradation scenario

Soil Gas Profiles



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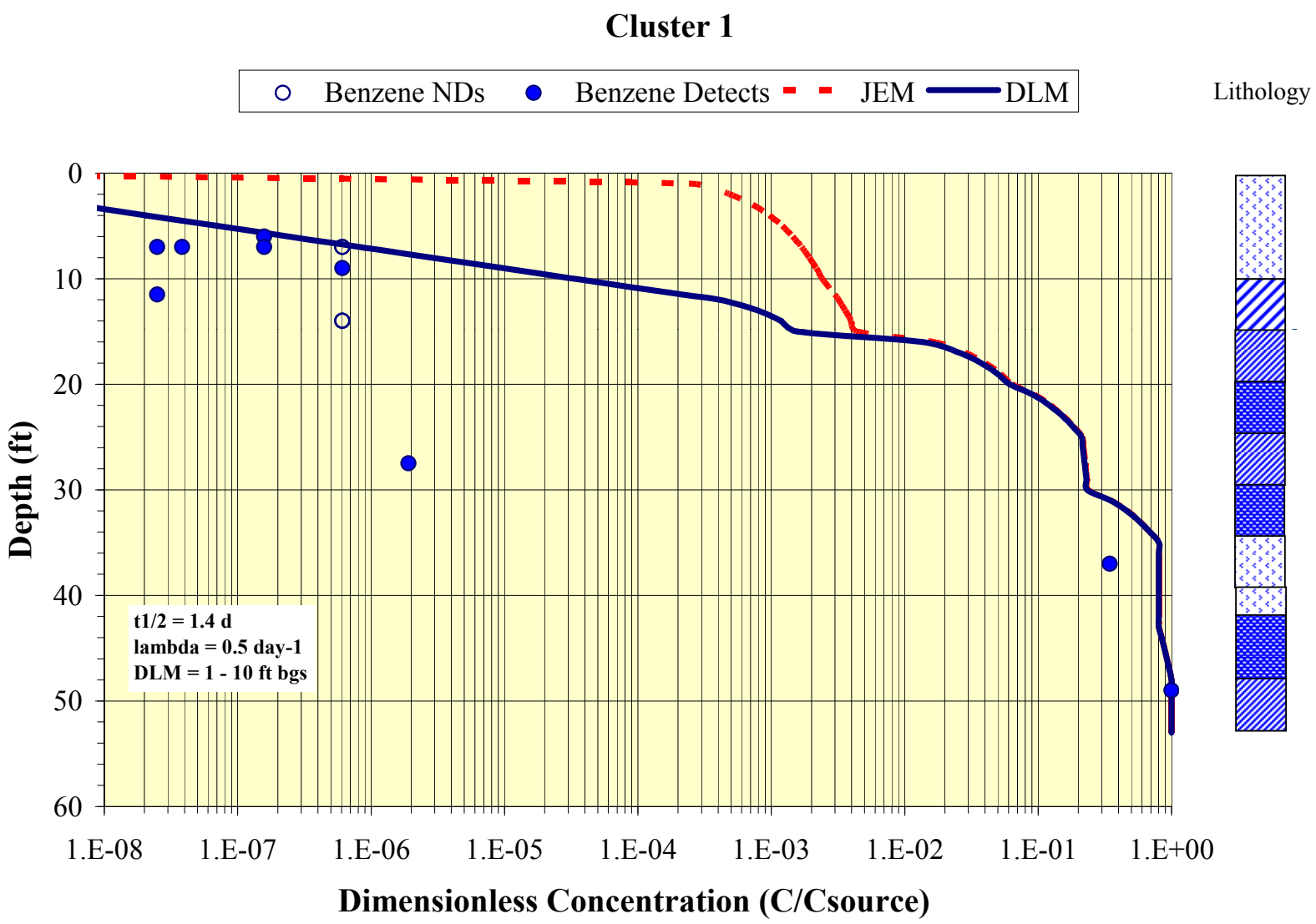
Soil Gas Profiles



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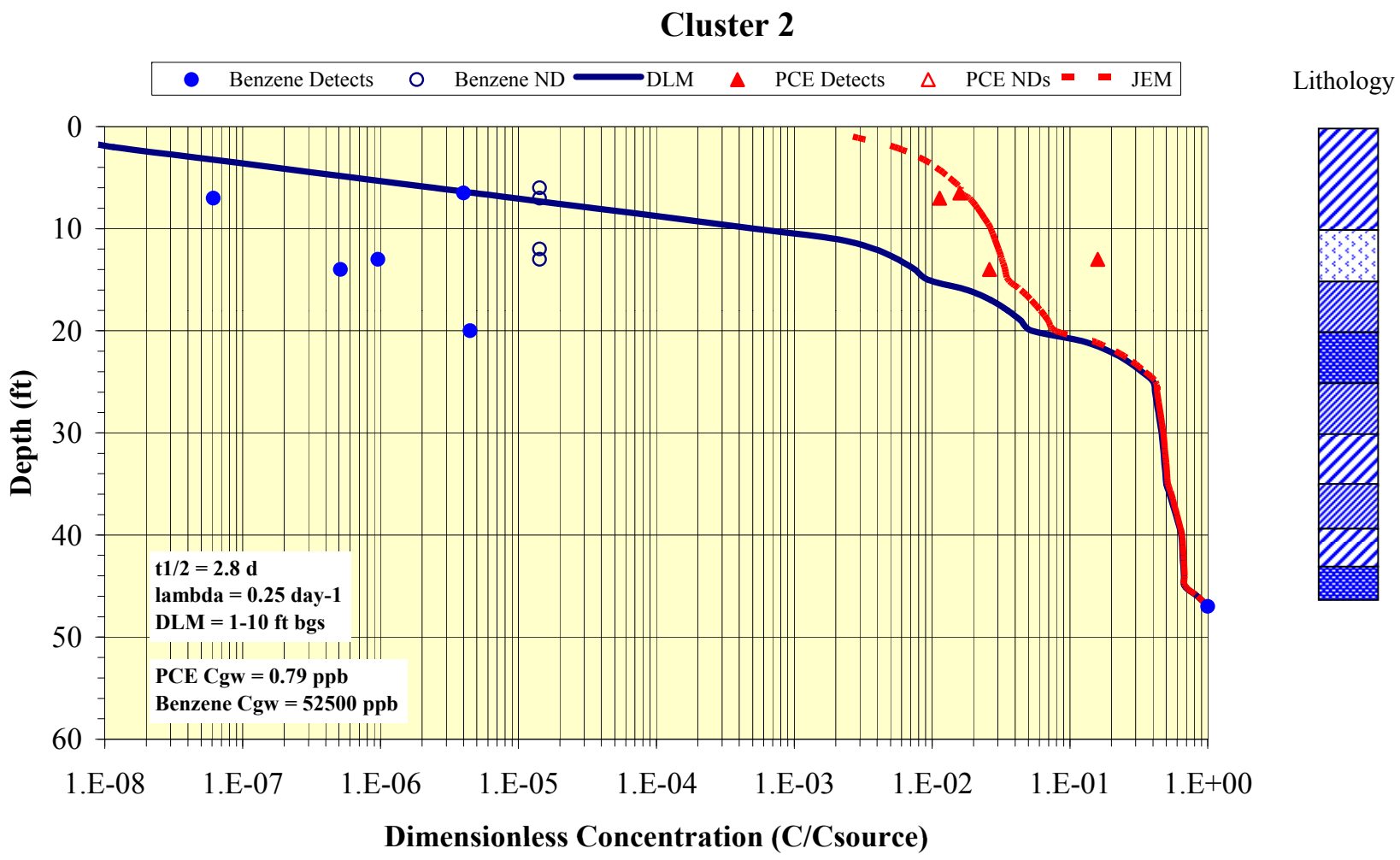
Biodegradable vs. Recalcitrant Compounds



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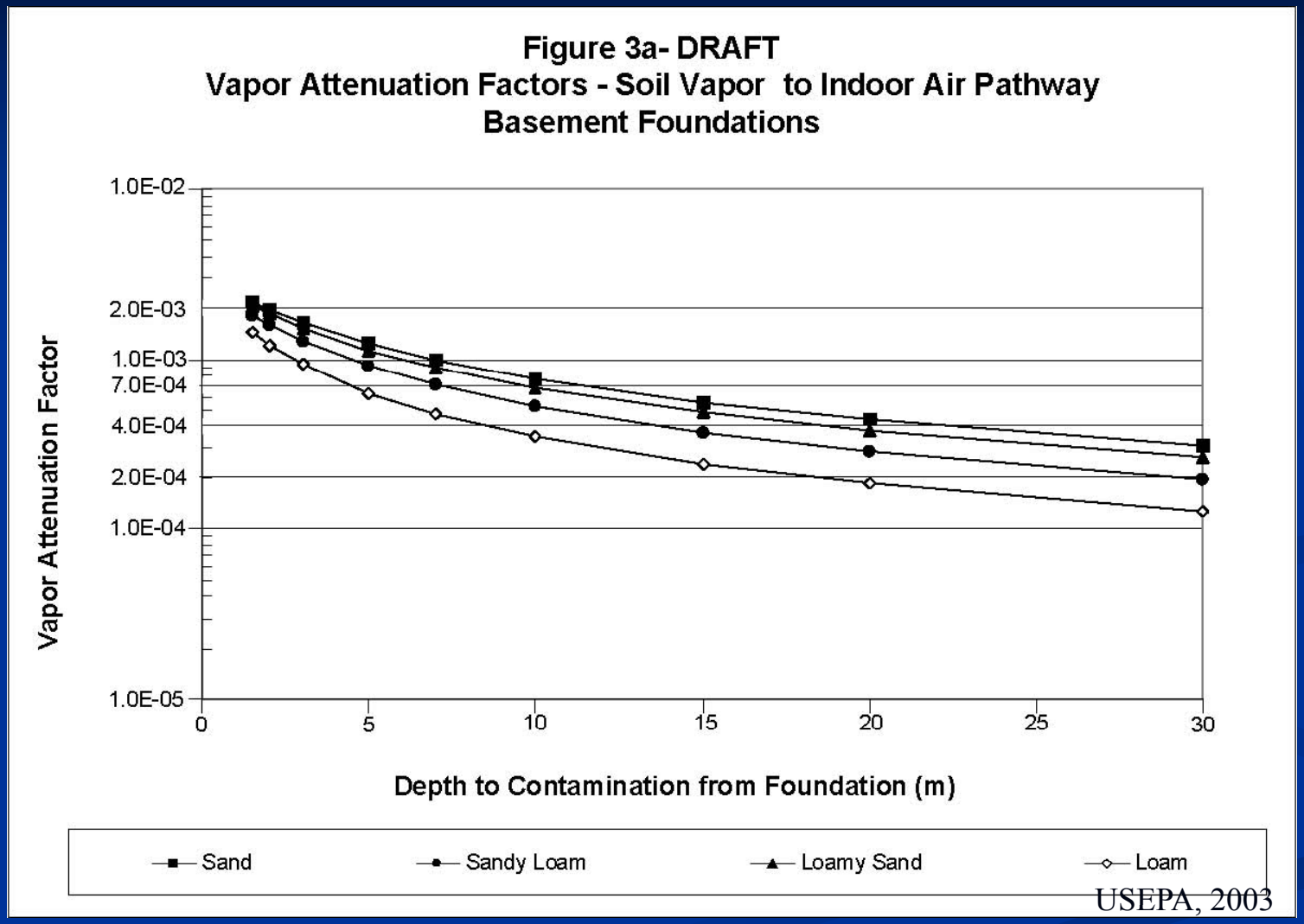
Biodegradation Modeling Results

- Benzene soil gas profiles demonstrate that vadose zone biodegradation is significant
- Dominant Layer Model can be used to simulate soil gas profiles
- Calculated degradation rate constants are conservative and consistent with literature values (0.05 – 0.6 per day)
- Conservative estimates result in 2 to 3 orders of magnitude reduction in predicted contaminant vapor intrusion

Modeling Evaluation of VI Screening Criteria for Biodegradable Compounds

- Abreu and Johnson 3-D model used to calculate vapor intrusion attenuation factors for various site conditions:
  - Source strength and depth
  - Soil type
  - Building type
  - Degradation rate
- Improve understanding of the key factors that affect vapor intrusion for aerobically biodegradable conditions
- Improve VI screening approach and sampling criteria for low source concentration (e.g. dissolved phase) petroleum hydrocarbon sites

"Look-up" a Semi Site Specific Attenuation Factor



USEPA, 2003

Available AF presented in regulatory guidance documents do not consider biodegradation.

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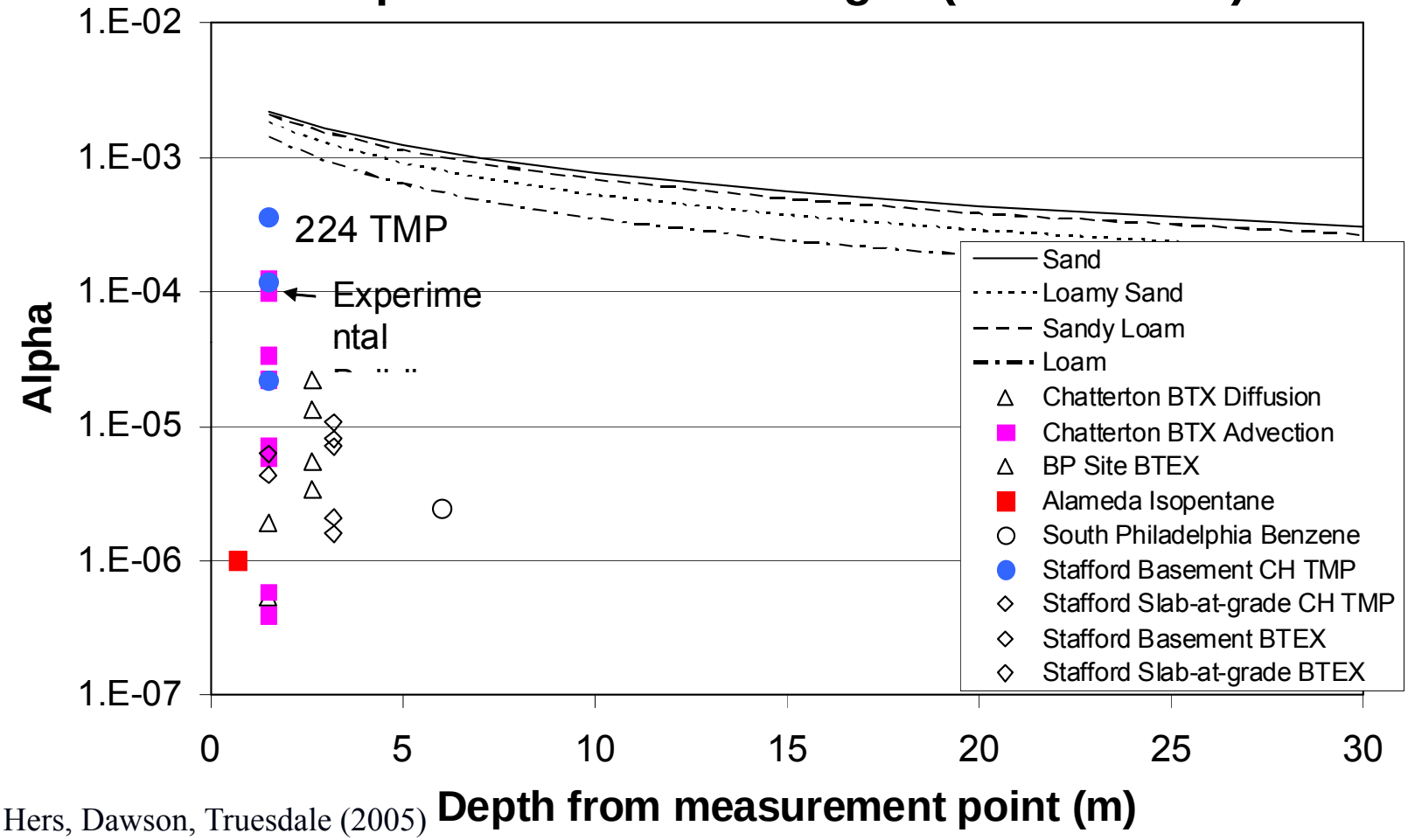
Petroleum Hydrocarbon Site Soil Vapor Alpha Comparison to USEPA Fig. 3 (filtered data)



Hers, Dawson, Truesdale (2005)

Measured attenuation factors for hydrocarbons can be orders of magnitude below "no-degradation" model predictions. Determining AF for biodegradable compounds is more complex, but the idea is the same.

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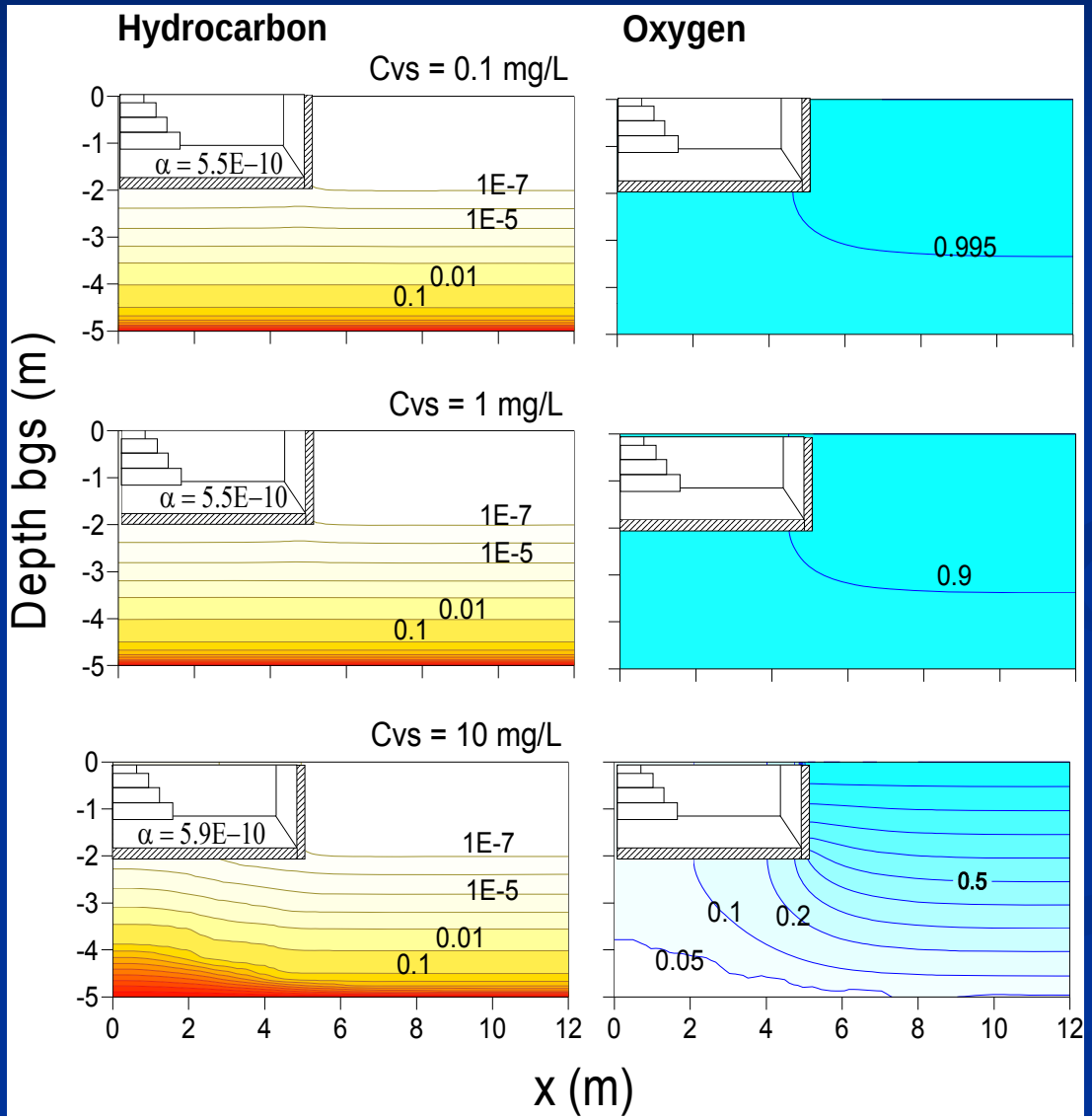
Variables Considered in Model

Variable	Range
Soil Type	Sand, silt
Building foundations	Slab-on-grade, basement
Foundation-source separation	1 - 10 m
Vapor source concentration	0.004 to 400 mg/L
Equivalent groundwater source concentration	*0.017 to 1700 mg/L*
First order degradation rates*	0, 0.079, 0.79, 2 hr^{-1}

* **Aqueous-phase biodegradation rates**

Effect of Vapor Source Concentration



- Oxygen utilization increases with increasing source concentration
- α decreases with lower source concentrations
- α has small dependence on source concentration at lower values
- Bio-attenuation is significant

Simulation Assumptions
Sand soil
Basement Scenario
Cvs = 0.1, 1, 10 mg/L
$\lambda = 0.79\ h^{-1}$

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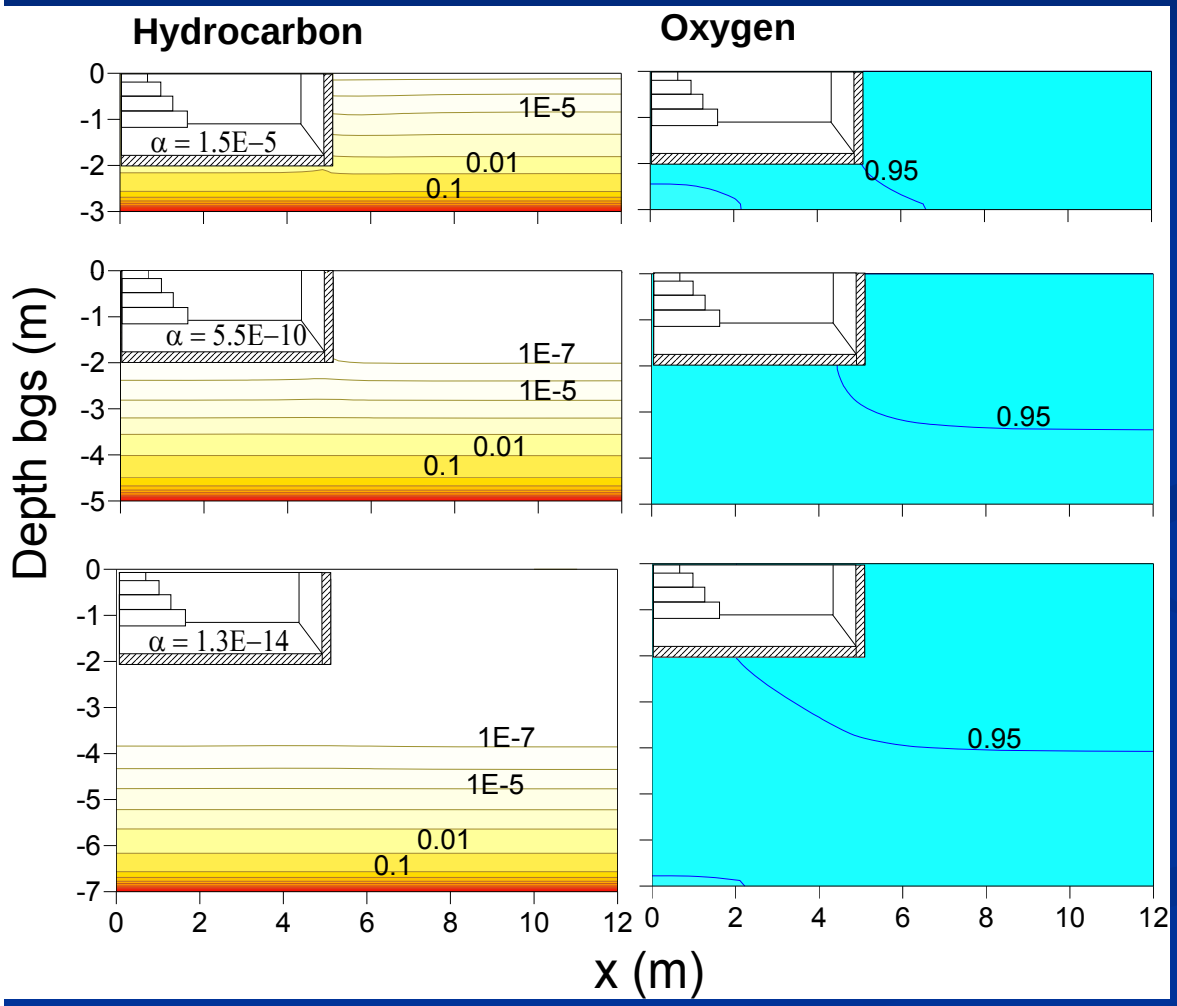
Effect of Vapor Source Depth



- Attenuation factor decreases with increasing depth to source
- At low source strength, small source-slab separation is necessary to promote significant bio-attenuation

Simulation Assumptions
Sand soil
Basement Scenario
Cvs = 1 mg/L
L = 1, 3, 5 m
$\lambda = 0.79\ h^{-1}$

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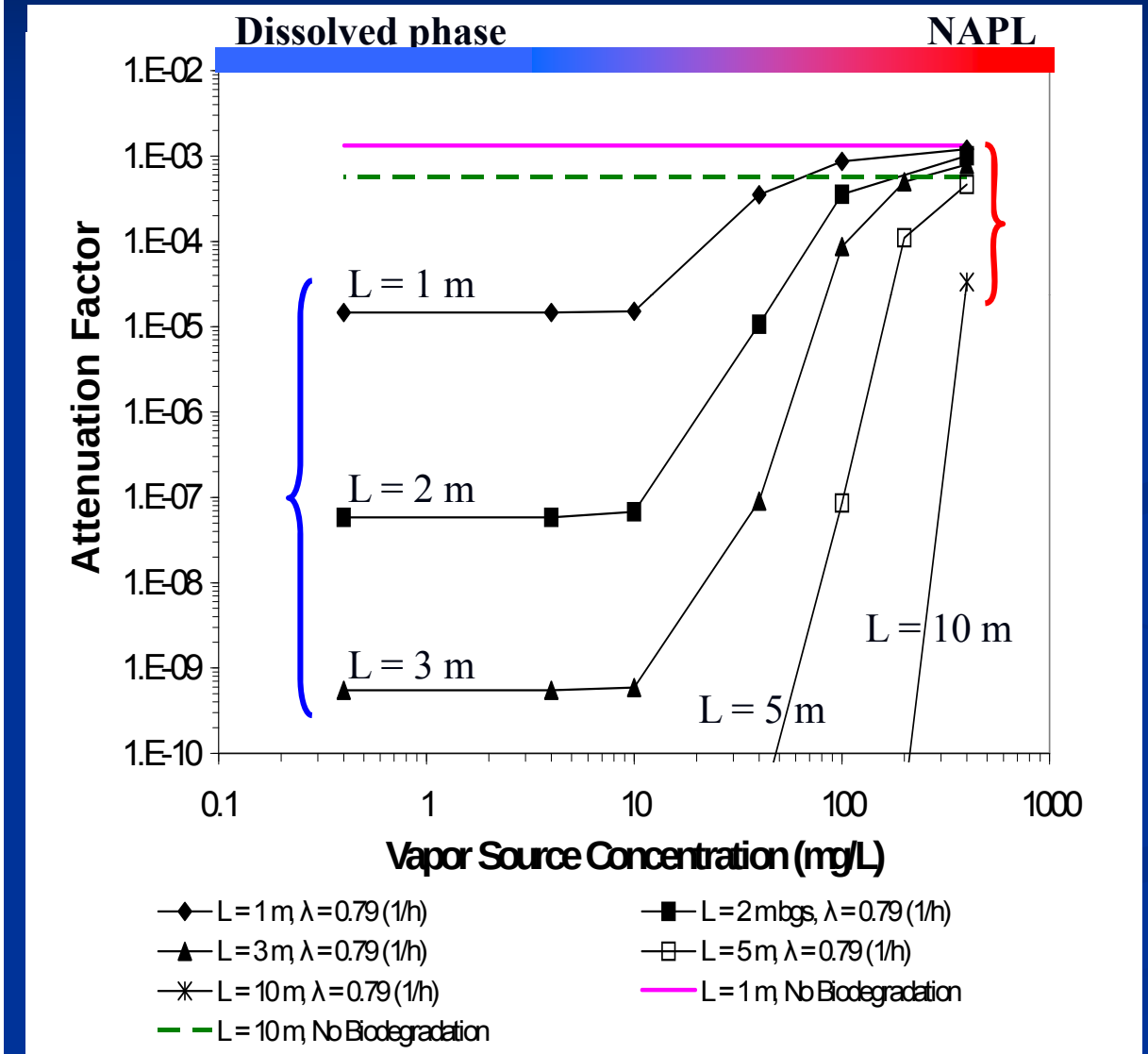
Effect of Source Concentration and Depth



- Biodegradation is likely to have a significant effect on α for non-NAPL sources
- This effect is more pronounced for deeper sources
- α has small dependence on source concentration at lower values
- For NAPL sources, effect of biodegradation on α may be limited due to oxygen depletion

Simulation Assumptions
Sand soil
Basement Scenario
$\lambda = 0.79\ h^{-1}$

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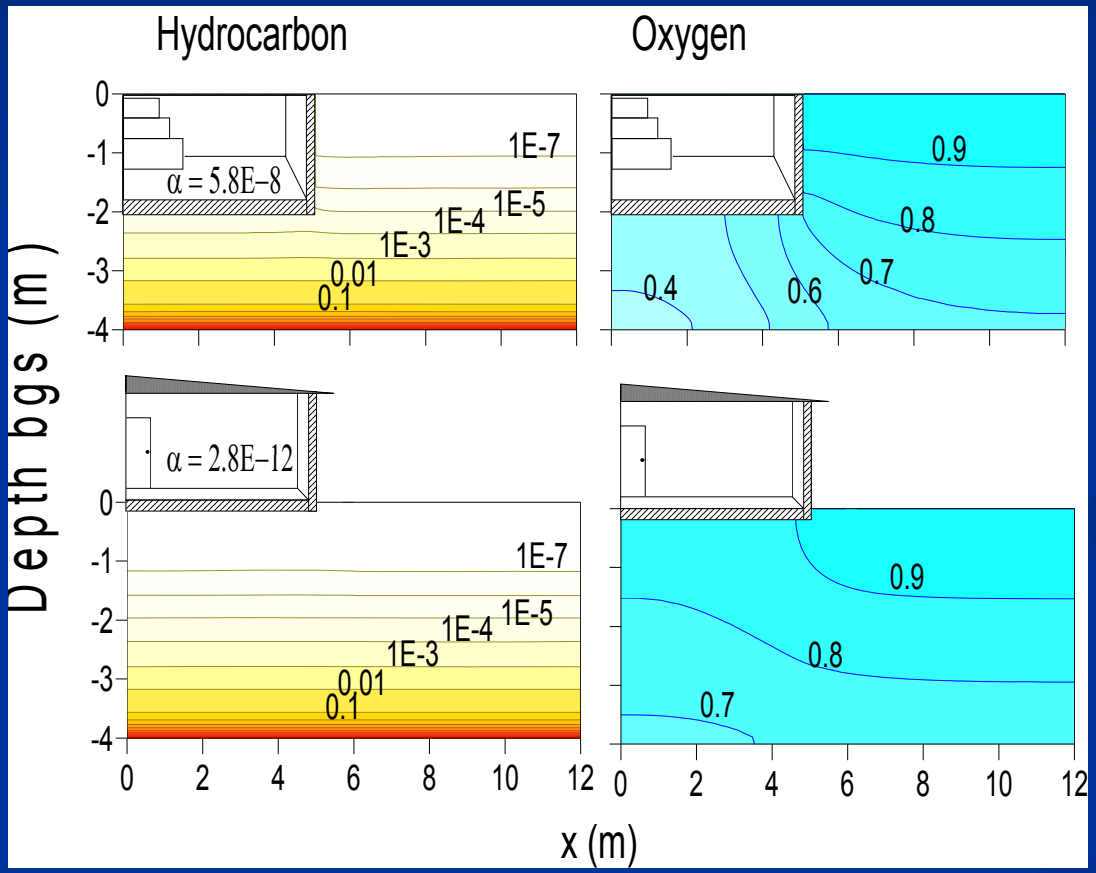
Effect of Building Type



At low source strength:

- Hydrocarbon soil gas profile is not affected by building type
- Near foundation soil gas sample represents sub-slab concentration for both foundations
- Bio-attenuation is significant for both foundations but is more pronounced for slab-on-grade

Effect of building type may be more evident with high strength, near foundation source

Simulation Assumptions
Sand soil
Cvs = 4 mg/L
$\lambda = 0.79\ h^{-1}$

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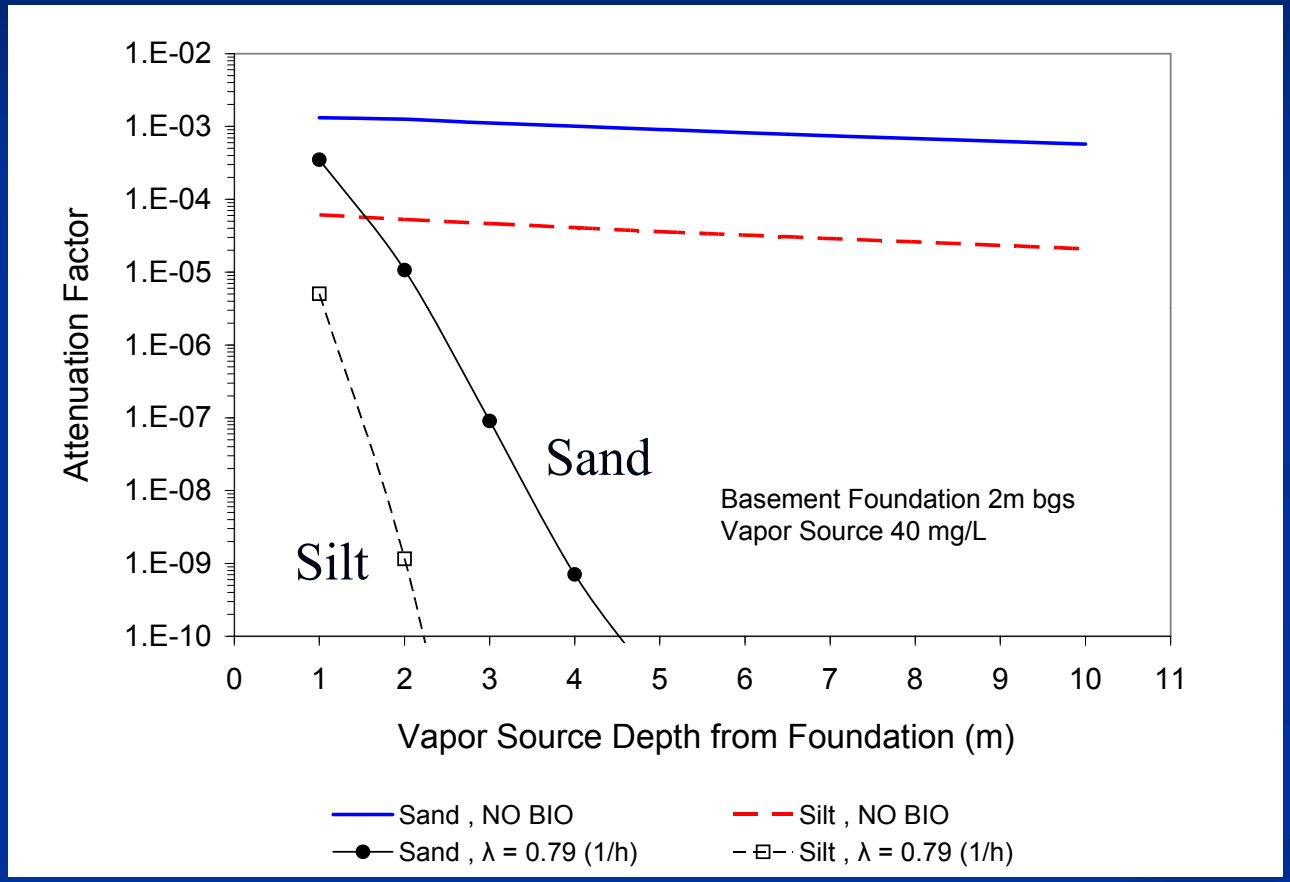
Effect of Soil Type and Source Depth



Simulation Assumptions
Basement Scenario
Cvs = 40 mg/L
$\lambda = 0.79\ h^{-1}$

Compare Results to Semi-Site Specific Attenuation Factors in USEPA 2002 Draft Guidance

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Modeling Study Implications

Findings of modeling study may be used to:

- Develop improved VI screening process
  - Use theory to help interpret field data
  - Define exclusion criteria which could then be simply validated with field data (e.g., O_2)
  - Will permit focus on sites with higher probability of VI concerns
- Develop sampling strategies
  - Near-slab soil gas sampling is appropriate for moderate to low concentration sources
  - Sampling strategy may be used to confirm/support site conceptual model

Conclusions

- Vadose-zone biodegradation significantly limits vertical migration of petroleum hydrocarbons from sub-surface sources
- Site-specific evaluation approach may be used to quantitatively assess bio-attenuation factors
- The effect of biodegradation on α is more substantial for moderate to low source concentrations (i.e. dissolved-phase) or larger source-foundation distances
- Incorporation of bio-attenuation for dissolved-phase petroleum hydrocarbon sites is supported