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Subsurface Petroleum Vapor Intrusion to Indoor Air: Attenuation Due to Biodegradation

6th International Seminar on Remediation and Redevelopment of Contaminated Sites, October 27-28, 2008. Centro Universitário Senac, Campus Santo Amaro, Sao Paulo, Brazil.

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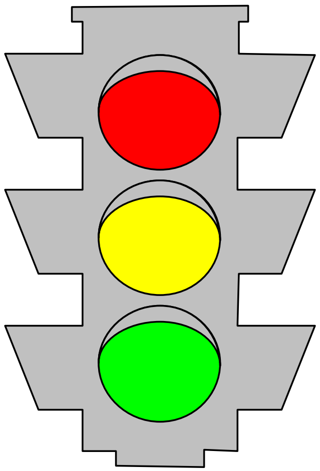
Petroleum Vapor Intrusion Sites

Decision Process : Classes of Sites

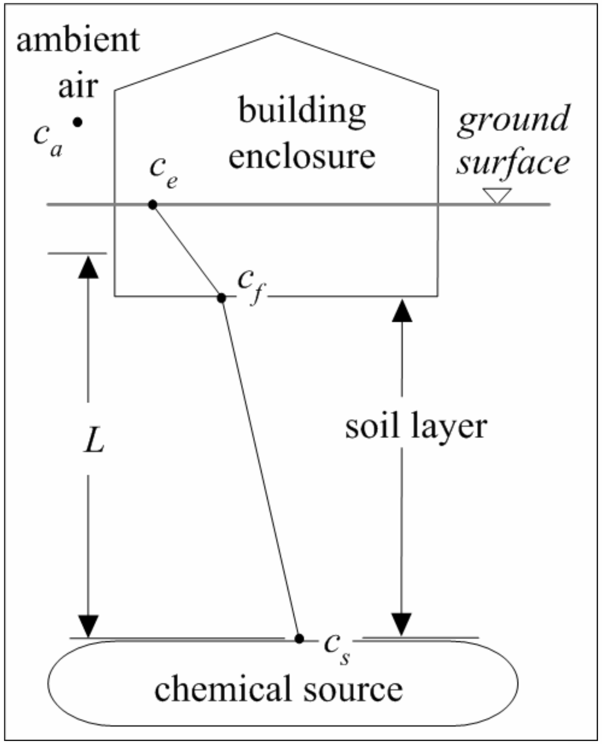


- Immediate Action
  - Flammable conditions
  - Gasoline in basement or connected sumps
- Not sure
  - 'noise' of background ambient air or indoor emission sources
  - Need more 'lines of evidence'
- Not a problem
  - Low source concentrations
  - Greater foundation to source separation
  - Significant biodegradation

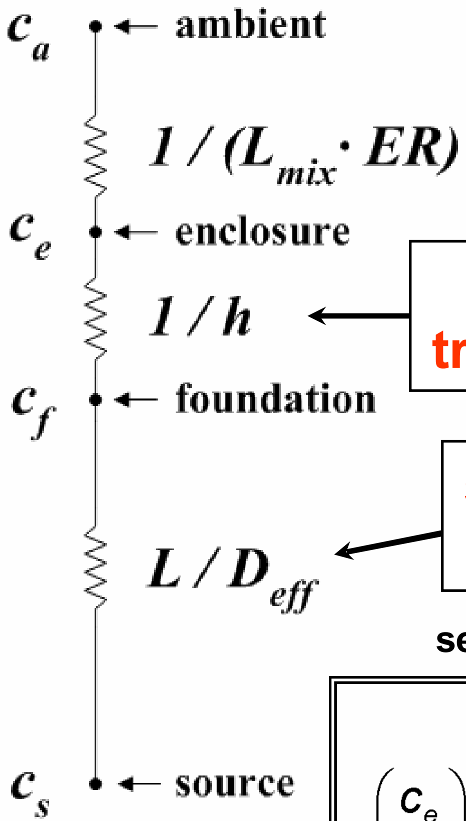
- Current VI Evaluation Process has High Positive Error Rates
  - Screening identifies an issue but no actual issue exists
  - Action : Improve Process to Improve Confidence [fewer errors]
- Risk Assessment Perspective:
  - Public Health (receptor view) – Indoor Air Quality ← ***Not covered here***
  - Contaminated Land Management (source view) ← **Focus**

Simple Conceptual Model

Use series resistance model: steady, constant, 1-D, no biodegradation



[laterally extensive]



mixing height
air exchange rate

foundation mass
transfer coefficient (lumped)

source (or sample) depth
soil diffusion coefficient

series **resistance** attenuation factor:

$$\left(\frac{c_e}{c_s}\right) \approx \left(\frac{c_e - c_a}{c_s - c_a}\right) = \frac{\left(\dfrac{1}{L_{mix} \cdot ER}\right)}{\left(\dfrac{1}{L_{mix} \cdot ER} + \dfrac{1}{h} + \dfrac{L}{D_{eff}}\right)}$$

Simple Conceptual Model

two methods, or lines of evidence: flow & concentration

1. Flow Resistance - Building Parameters
   - building data (HVAC design); foundation data; define 'over predictive' values
   - site-by-site validation - uncertain (radon experience)
   - foundation flow is both ways (in-out)

   ER, L_{mix}, h

2. Chemical Concentration
   - Influence of indoor sources, ambient air : 'noise'
   - Small differences: $(c_e - c_a) / (c_s - c_a)$ → large errors

   c_e, c_s, c_a

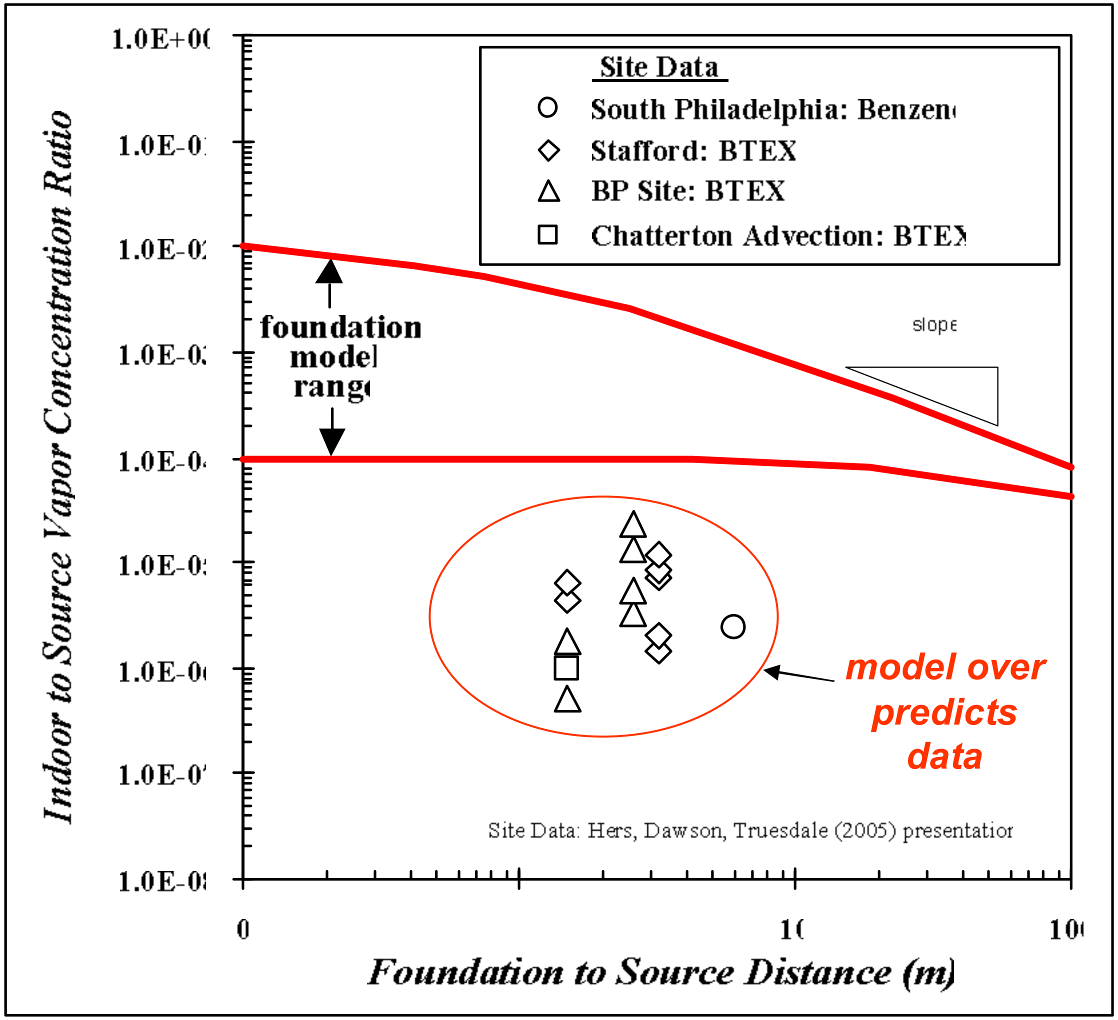
- Independent Validation:
  - Both methods agree? Not for building / below foundation concentration ratios
  - directly below foundation and indoor air → high variability
- Improved Application Requires:
  - Small c_e / c_s → Less confounding ambient 'noise' influence
  - Include More Soil Resistance, or
  - Screen further from building (including soil separation) → less 'noise' influence

Include: + L / D_{eff} ! *In absence of 'source' in interval*

Issue – (No-Bio) Model to Data Comparison

- Includes well characterized sites
- limited or no indoor ‘background’ chemical contribution
- Johnson and Ettinger (J&E) Model with ‘bounding range’ of parameter inputs
- indoor air concentrations over-predicted by up to 5 orders of magnitude

Measured vs. Predicted (No-Bio) Data



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Include Biodegradation in Simple Model

In soil layer: aerobic biodegradation (first-order kinetics);
All else: same assumptions

For chemicals:

$$\left(\frac{c_e}{c_s}\right) = \frac{\left(\frac{1}{L_{mix} \cdot ER}\right)}{\mathbf{A} \cdot \left(\frac{1}{L_{mix} \cdot ER} + \frac{1}{h}\right) + \mathbf{B} \cdot \left(\frac{L_a}{D_{eff}}\right)}$$

$$\mathbf{A} = \left(\frac{exp(\alpha_a) + exp(-\alpha_a)}{2}\right)$$

$$\mathbf{B} = \left(\frac{exp(\alpha_a) - exp(-\alpha_a)}{2 \cdot \alpha_a}\right)$$

$\alpha_a \to 0$: $\mathbf{A} \to 1, \mathbf{B} \to 1$ $\left(\frac{c_e}{c_s}\right) \to$ **same as no biodegradation result**

$\alpha_a \to$ larger: $\mathbf{A} \to$ *much* larger, $\mathbf{B} \to$ *much* larger $\left(\frac{c_e}{c_s}\right) \to$ ***much* smaller**

$$\alpha_a \approx \frac{\text{aerobic length}}{\text{reaction length}} \approx \frac{\text{aerobic residence time}}{\text{reaction time}}$$

α_a	A	B
→ 0	1	1
1	1.5	1.2
10	10^4	10^3

Large α_a → huge effect

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Aerobic Petroleum Biodegradation

- **Petroleum Readily Degrades**
  - **In aerobic conditions**
  - **At Rapid Rates**

- **Data Analysis Yields Rates**
  - **empirical**
  - **water-phase θ_w – soil moisture**
  - **pseudo- first order (aerobic)**
  - **geometric mean first-order rates:**

k_w = 0.79 /hr (BTEX)

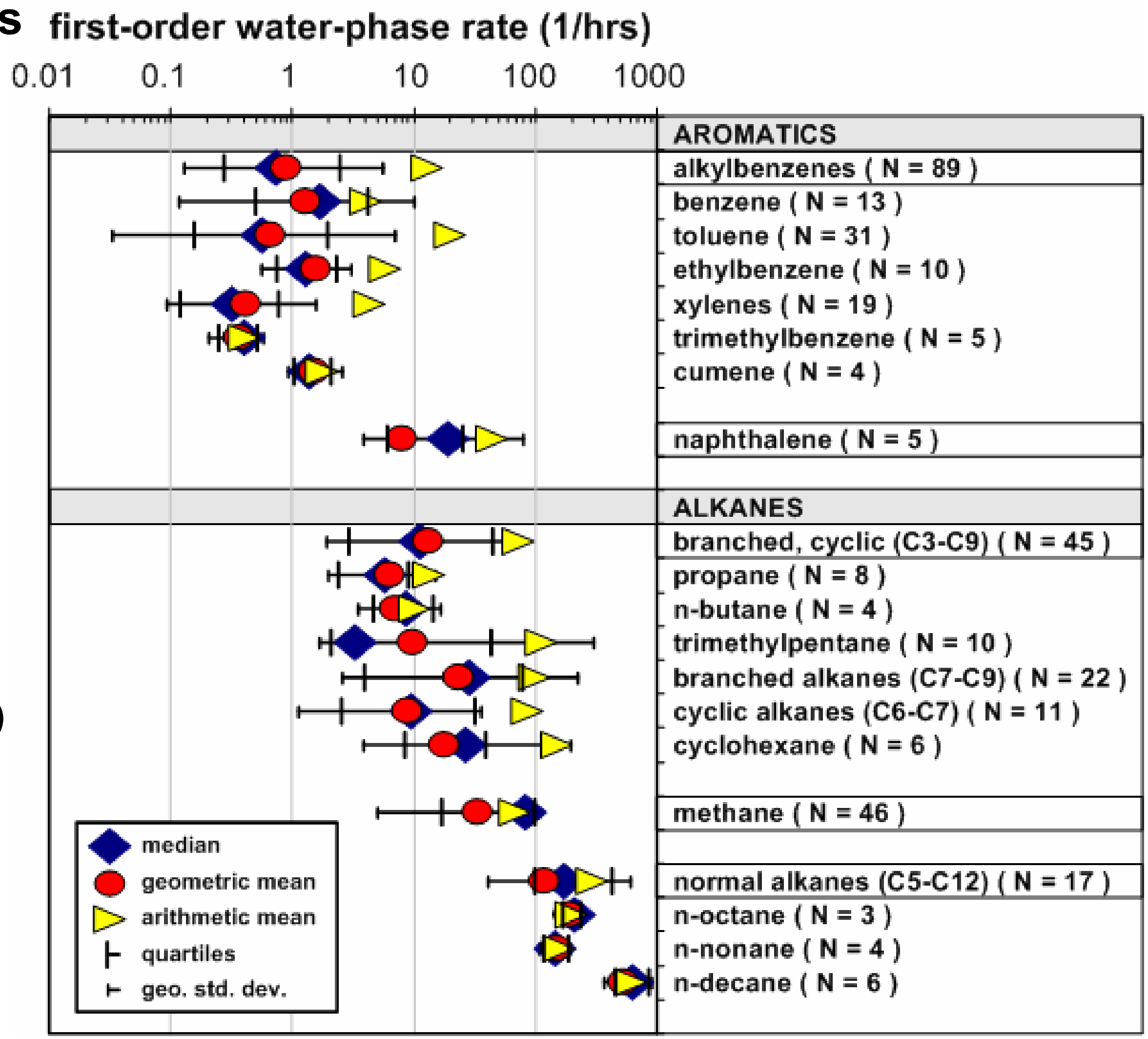
k_w = 71 /hr (aliphatics)

DeVaull, ES&T (2007)

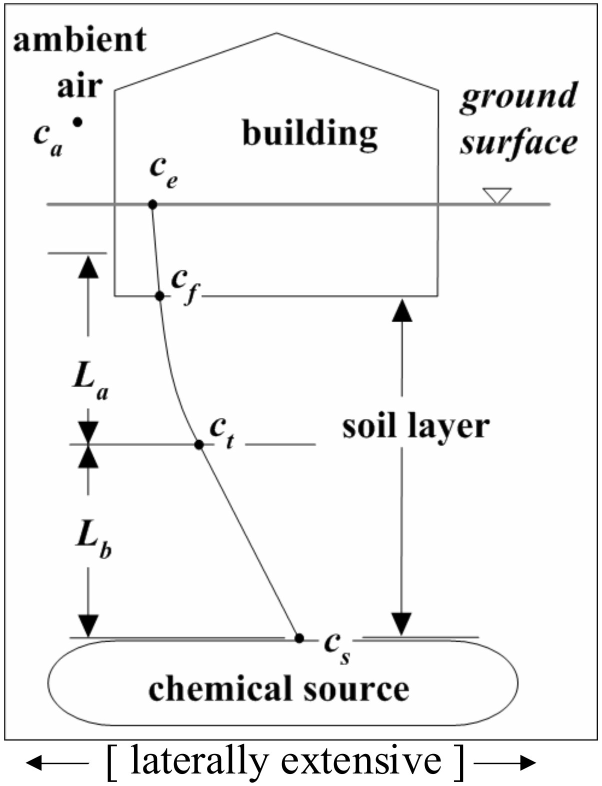
- **Additional investigation:**
  - **Generally consistent results**
    - **More detail (chemical-specific)**
  - **Better established limits**
    - **nutrients, oxygen,**
    - **biomass, kinetics**

$$\alpha_a = L_a \cdot \sqrt{\frac{k_w \cdot \theta_w}{D_{eff} \cdot H}}$$

Effective diffusion **Henry's Law**



Model: Impose Oxygen Limits

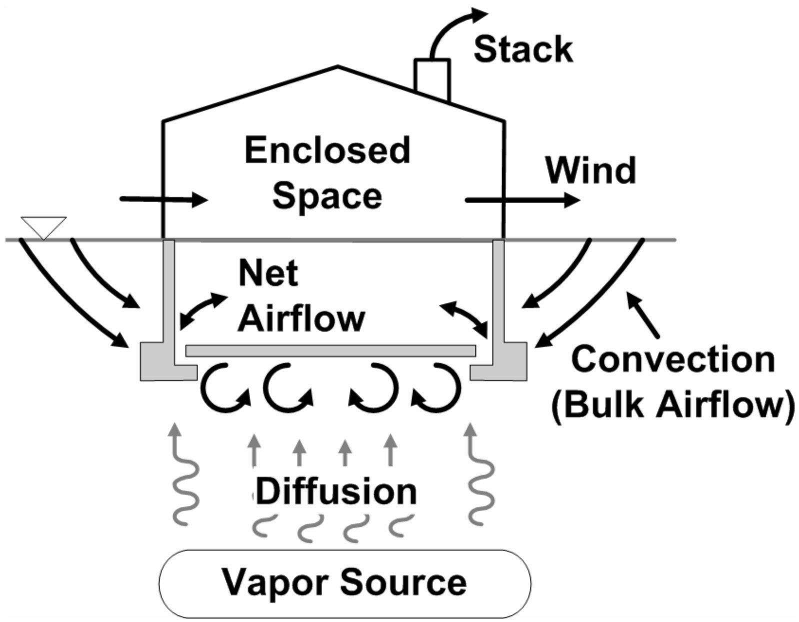


- Divide the homogeneous soil layer:
  L_a - Shallow aerobic region with biodegradation
  L_b - Deep anaerobic region - no biodegradation
- Coupled Chemical / Oxygen Eqns.
  - Multiple Oxygen Sinks in Soil
    - Chemical mixtures, Basal "baseline" soil
  - O_2 Demand less than O_2 Availability
- O_2 in Soil Limited by:
  1. O_2 in Advective Airflow Under Foundation, and / or
  2. Diffusion of O_2 through soil to reaction zone (Ambient O_2 maximum)

Convective Airflow Below Foundation

measured and estimated rates

Air Flow (L / min)	Reference	Basis
Air flow through foundation		
3.3 to 7	Nazaroff et al., (1985)	Measured
5	USEPA (2002)	Recommended
1 to 10	Hers et al., (2003)	Measured
3.09 to 5.1	Abreau et al. (2007)	Modeled
Air flow below foundation		
6.2 (0.5 to 1.25)	Lundegard et al., (2008)	Measured (O_2 demand)



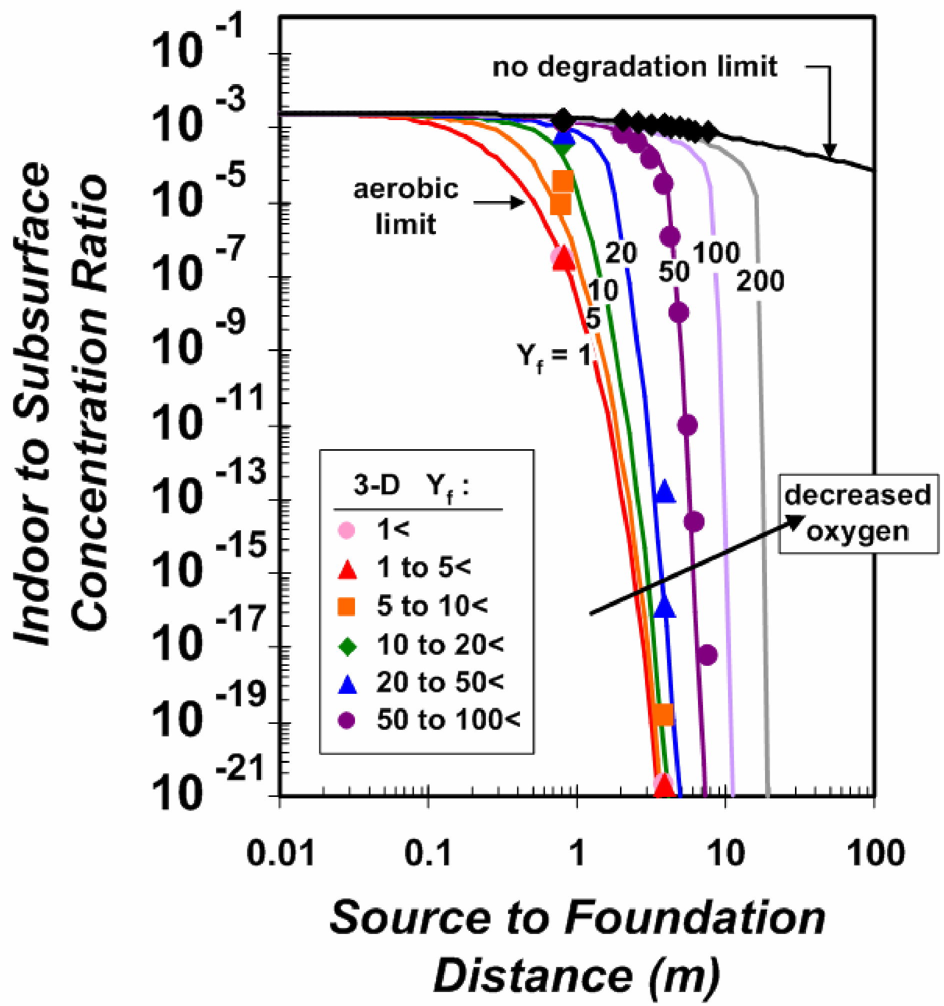
Pressure-driven airflow below and through a building foundation

Qualitative Agreement 3-D & 1-D Models

- 3-D Model:
  - Abreu and Johnson (2006)
  - numerical, near foundation air convection
    - Air flow thru foundation (3.09 to 5.1 L/min)
    - Compare 107 of 116 results
- 1-D Model:
  - DeVaull (2007) + foundation
  - Match model parameters
- Scaling parameter :

$$Y_f \approx \frac{O_2 \text{ demand [as if all aerobic]}}{\text{actual } O_2 \text{ demand}}$$

  - Bigger → more limited O_2
  - Beyond a specified distance indoor / source attenuation factor decreases precipitously



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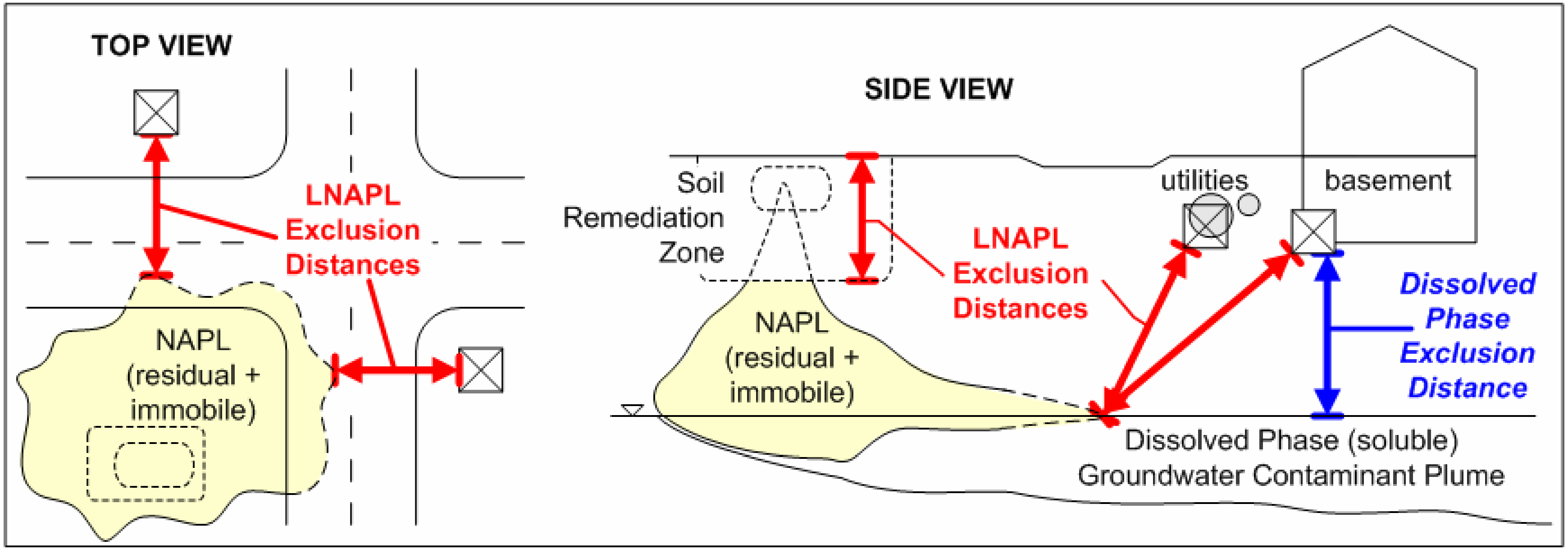
Example Exclusion Distances

For Petroleum Chemicals, UST Releases



Unlikely for Vapor Intrusion Issue if:

> 100 feet from LNAPL boundary

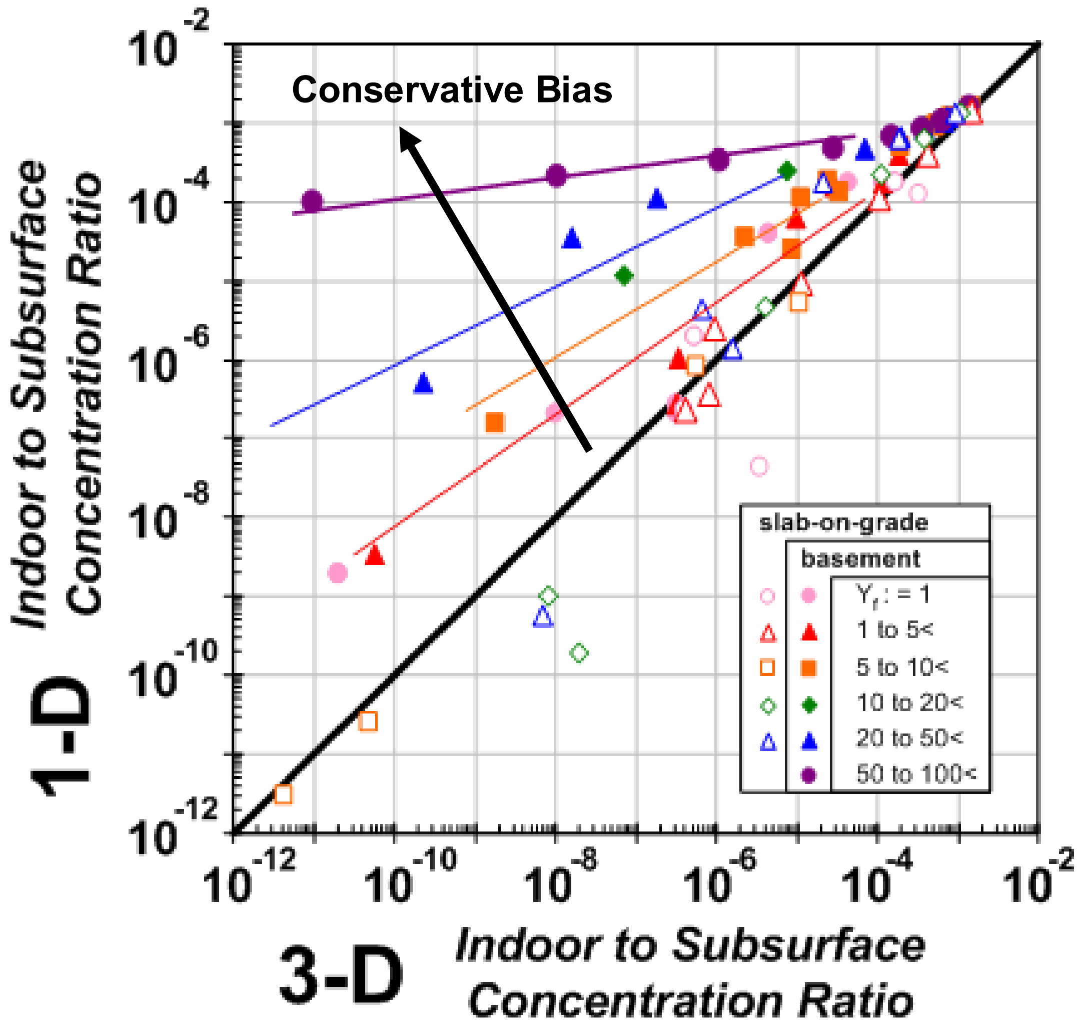
> 30 feet lineal distance from dissolved plume

to nearest possible structure in any direction.

Reference: ASTM E 2600-08: Standard Practice for Assessment of Vapor Intrusion into Structures …

1-D & 3-D Model Comparison

- 1-D indoor concentrations greater or equal to 3-D results
- Bias increases for higher oxygen demand
- Why?
  - 3-D model includes lateral oxygen diffusion from sides of foundation
- 1-D model can be used
- 3-D model may be more realistic and less over -conservative



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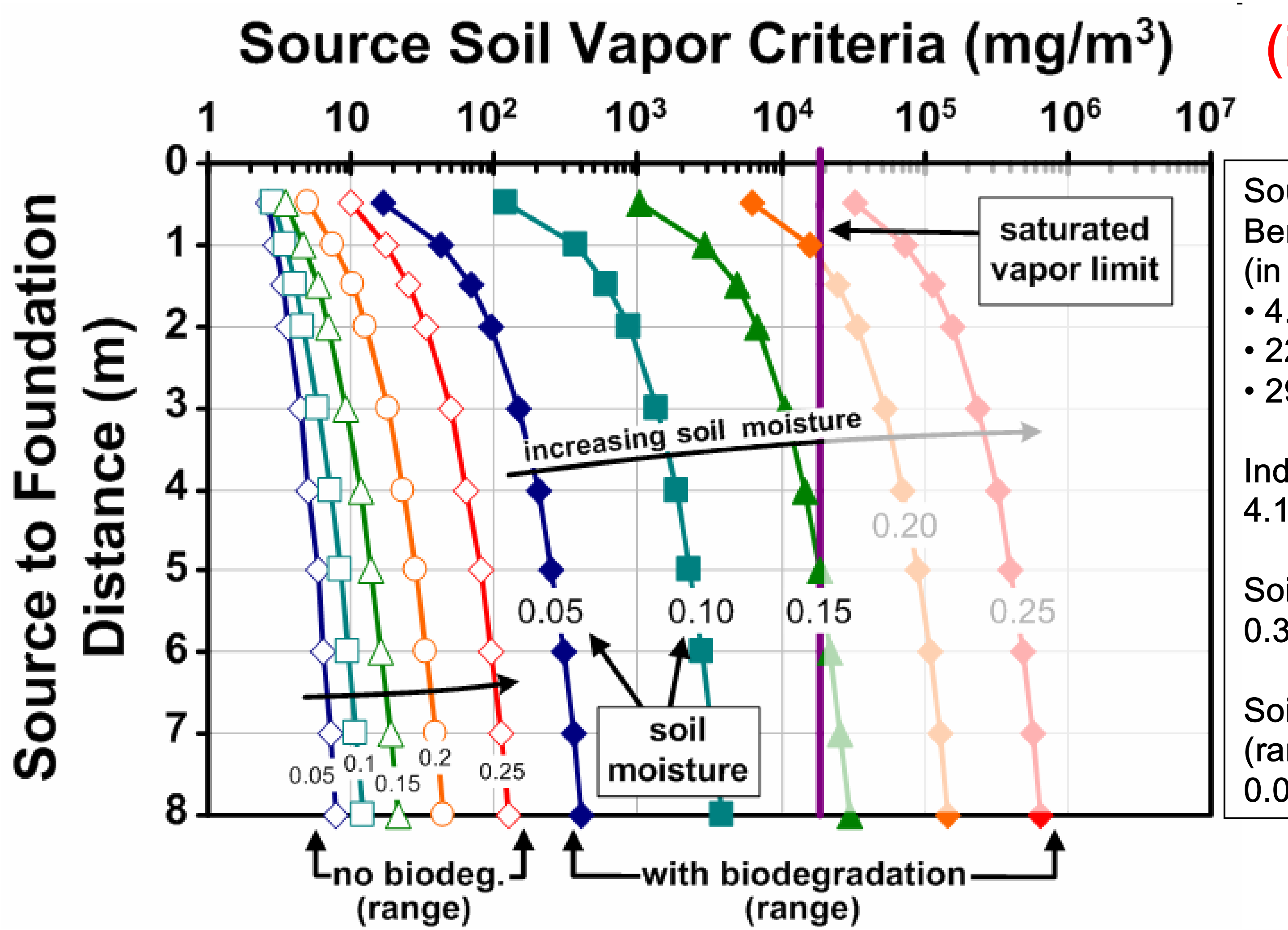
Calculate Screening Levels

Examples using the 1-D model

Benzene

- Chemical Vapor Source
  - (#2) Benzene in Gasoline (lightly weathered)
    - Saturated Vapor Limits Imposed
- Soils
  - Homogeneous, No capillary fringe, Porosity (0.38)
  - Varied Moisture Range (0.05, 0.1, 0.15, 0.2, 0.25) cm^3/cm^3-soil
- Residential Basement Scenario
- Target Indoor Air Criteria : c_e = 4.16 ug/m^3
  - Risk-Based Inhalation at 10^{-5} Risk, Residential Long-Term Scenario
  - Approximately 'Background' or Less
- Biodegradation
  - With and without
- For Example Only: Table / Values / Plots
  - Policy development, stakeholder agreement, caveats needed

Screening Levels: Benzene



Source :
Benzene
(in weathered gasoline)
- 4.8% in NAPL
- 22% m/m in vapor
- 29% m/m in water

Indoor Air Criteria :
4.16 ug/m^3

Soil Porosity :
0.38 cm^3-void/cm^3-soil

Soil Moisture:
(range)
0.05 to 0.25 cm^3/cm^3-soil

VI from Subsurface Sources to Indoor Air

Practical Application

- Include Oxygen-Limited Biodegradation for Petroleum
  - Less conservative, more realistic – equally protective
    - Likely Better Initial Screening with Lower False Error Rate
  - Qualitatively Consistent with Experience
    - Petroleum VI Appears to be ‘all or nothing’
      - Very Infrequent Actual Subsurface VI Problems
      - When Vapor Problems Occur, They are Significant
      - Available Evidence Supports Exclusion Distances
    - Model / Data Validation and Improvement
      - Model to Data Comparison in Pieces
        - Multiple Lines of Evidence (Concentration, Flow)
        - Empirical Parameters: Biodegradation Rates
        - Data Decimation (ND, ‘background’)
  - Practical Experience
    - Qualitative risk factors remain useful
      - Flammability, NAPL in close proximity, odors, …, checklists
      - Good Conceptual Models

Conclusions and Next Steps

- Modeling Confidence
  - Extensive biodegradation data - rates
  - 1-D to 3-D Comparison shown
    - Equivalent model assumptions and parameters produce equivalent result or conservative bias
    - Comparable models should produce comparable results
- Forward Plan
  - 1-D Spreadsheet Model with User Interface
    - Include Biodegradation
    - "Easy" to Use
    - Try it yourself
    - Work in Progress
    - Publications (updates)…

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Thank you