Shell Global Solutions

Indoor Air Vapor Intrusion with Oxygen-Limited Biodegradation from a Subsurface Gasoline Source

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The Next Great Environmental Challenge -- An Update
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Outline of Presentation

- Introduction
- Modeling Chemical Vapor Transport
  - With biodegradation
  - Single chemical - BTEX results
  - Oxygen
    - Demand and Availability
  - Framing Results

Indoor Vapor Intrusion from Subsurface Sources

Identifying Potential (chronic) indoor vapor intrusion problems

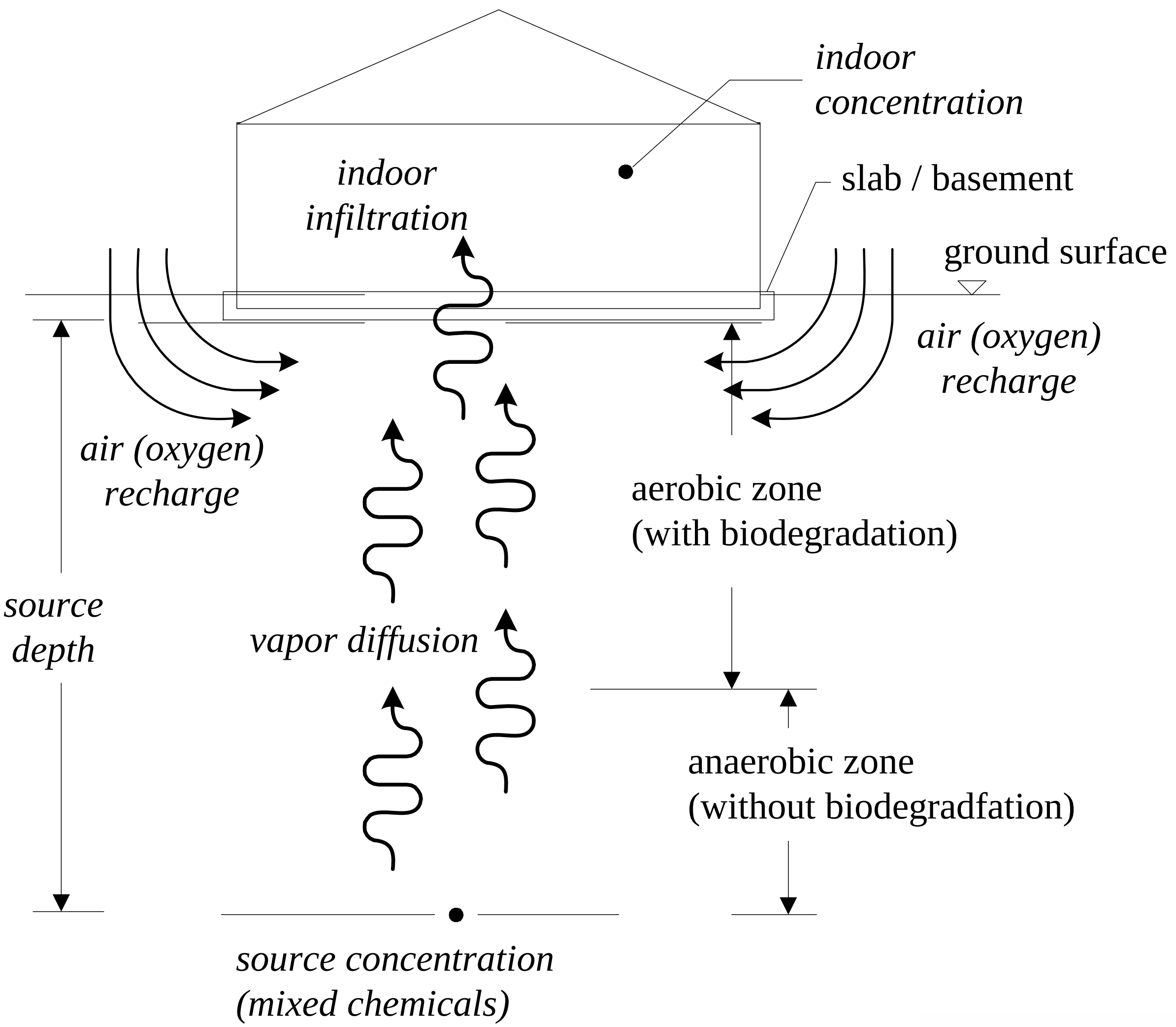
Direct Measurement

- Limited Measurable Concentration Ranges
  - Background conc., detection limits, saturated vapor limits
  - Confounded by other sources of identical chemicals in indoor air
  - Complicated by Land Use Changes

Modeling

- Include relevant physical information
  - Combine existing (or readily available) information into a model
- Key features:
  - Aerobic biodegradation in unsaturated-zone soils
    - Oxygen consumption
      - Multiple biodegrading chemicals, soil respiration
    - Oxygen availability
      - Oxygen under building foundations
  - Keep it Simple

Indoor Vapor from Subsurface Soil and Groundwater: model diagram



Indoor air vapor intrusion model
(no degradation)

indoor air

effective diffusion coefficient (m^2/day)

separation distance (m)

$$AF = \frac{c_e}{c_s} = \left(\frac{D_{eff} / L_T}{L_{mix} \cdot ER} \right)$$

source

air exchange rate (1/day)

mixing height (m)

- Neglects foundation resistance
  - and all foundation parameters (as in the Johnson and Ettinger model)
- A soil layer is needed for biodegradation, therefore:
  - presume soil diffusion-dominated chemical vapor transport in soil
  - negligible foundation resistance for chemical vapor transport
- Additional assumptions:
  - steady-state, one-dimensional, homogeneous soils, constant source concentration, infinite lateral extent of source, no other chemical sources or sinks, well-mixed building, …

Indoor air vapor intrusion model aerobic biodegradation (single chemical)

- L_T: = (L_a + L_b) distance from source to foundation (m)
- L_a : aerobic soil depth (m)
- L_b : anaerobic soil depth (m)
- L_R : diffusion - reaction length (m)
- α_a : = L_a / L_R

$$\frac{c_e}{c_s} = \left(\frac{D_{eff}}{L_{mix} \cdot ER} \right) \cdot \frac{2}{L_b \cdot (e^{-\alpha_a} + e^{\alpha_a}) - L_R \cdot (e^{-\alpha_a} - e^{\alpha_a})}$$

- With:
  - first-order aerobic biodegradation
  - no biodegradation in anaerobic soil layer
- Additionally:
  - Same assumptions as no-biodegradation model …

Aerobic Degradation Rates

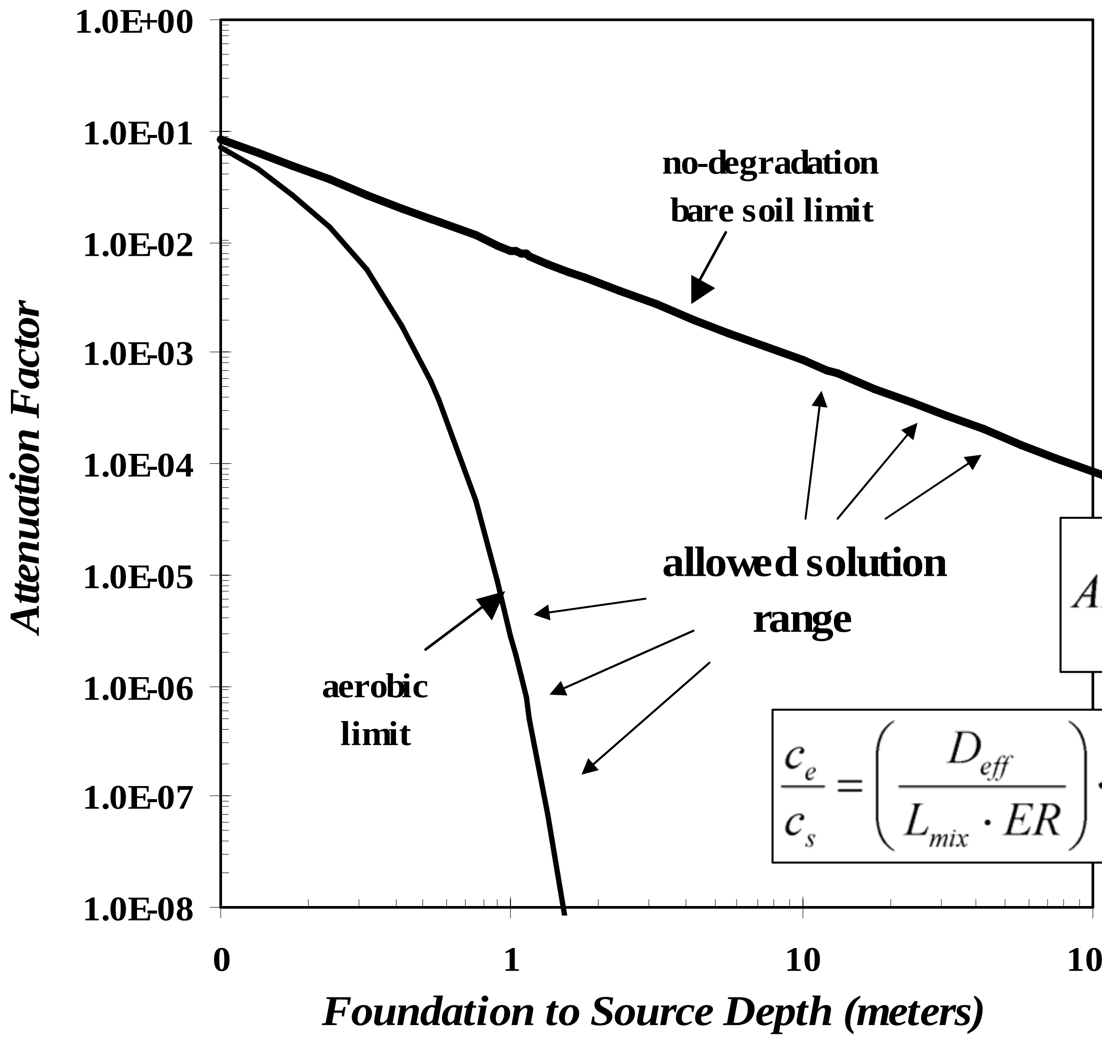
Chemical Biodegradation in soil vapor transport model appear only as L_R (cm)

$$L_R = (D_{eff} \cdot H / \; k_w \cdot \theta_w)^{1/2}$$

	BTEX Light Aromatics	Light Aliphatics (C5 - C10)
First-Order Rate, k_w:	0.79/hr	71/hr
Henry Law Coefficient, H:	~0.3	~55
Diffusive - reaction length, L_R: (approx. within a factor of 3 to 10)	~9 cm	~12 cm

- Includes vadose zone soils within ranges:
- θ_w = 0.039 to 0.22 cm^3/cm^3 soil moisture
- θ_T = 0. 36 to 0.49 cm^3/cm^3 soil porosity
- Aerobic only

aerobic biodegradation (single chemical)



L_R = 9 cm

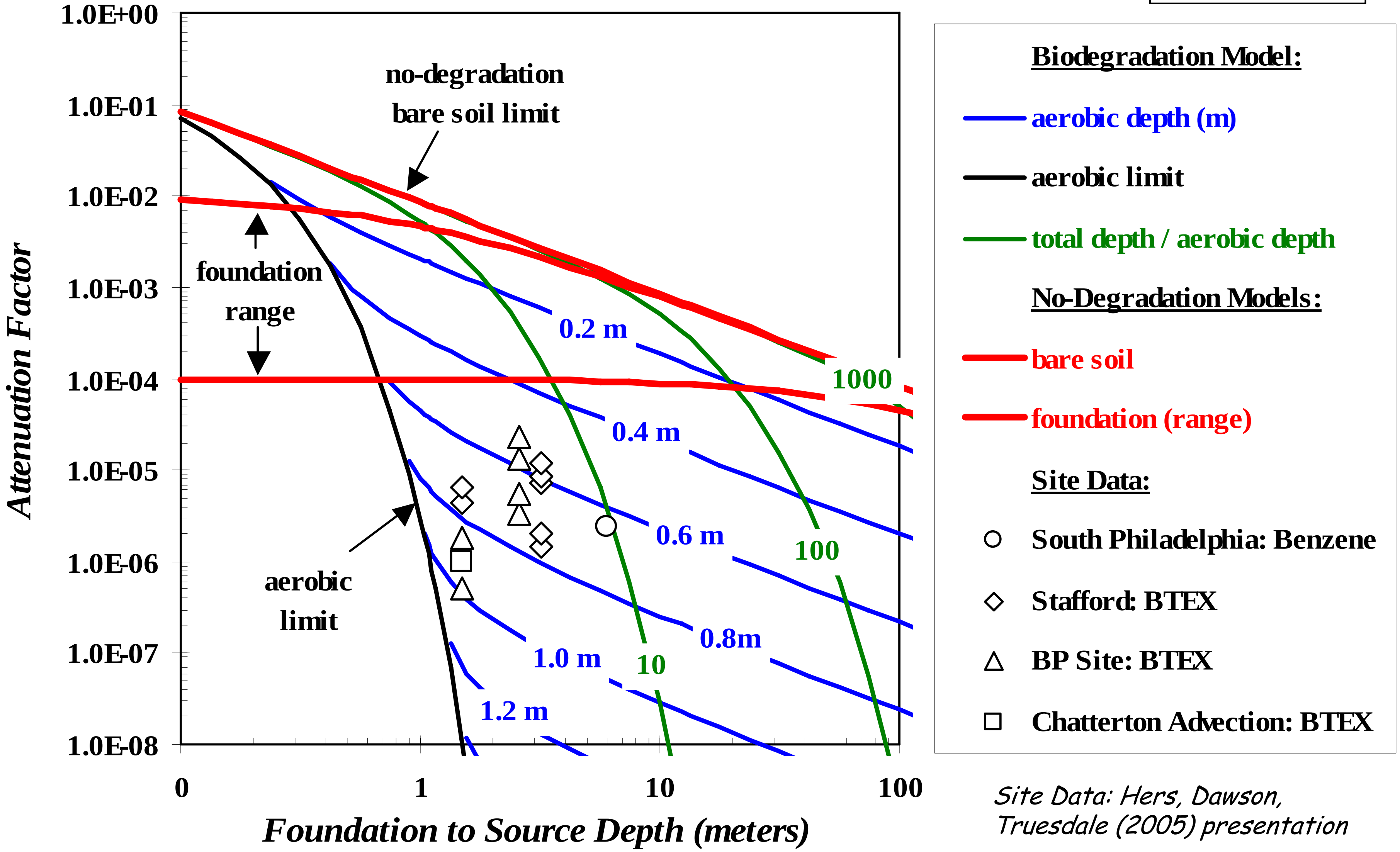
plot of model equation
- nominal bldg parameters.
- sandy soil

$$AF = \frac{c_e}{c_s} = \left(\frac{D_{eff} / L_T}{L_{mix} \cdot ER} \right)$$

$$\frac{c_e}{c_s} = \left(\frac{D_{eff}}{L_{mix} \cdot ER} \right) \cdot \frac{2}{L_b \cdot (e^{-\alpha_a} + e^{\alpha_a}) - L_R \cdot (e^{-\alpha_a} - e^{\alpha_a})}$$

Model / Data Comparison: BTEX

L_R = 9 cm



Site Data: Hers, Dawson, Truesdale (2005) presentation

Aerobic depth

How to get aerobic depth?

1. Direct measurement
   - Under foundations, building perimeters, exposed surfaces
2. Oxygen demand / availability balance
   - Model:
     - Coupled chemical degradation, respiration, and diffusion
     - empirical data relations
   - Combination - use model to identify data needs:
     - Example: measure oxygen concentration under building and correlate to aerobic depth

Indoor Vapor from Subsurface Soil and Groundwater

Model Developed

Includes existing, readily available, relevant information

Coupled set of algebraic equations: each chemical & oxygen transport

- Key features:
  - Diffusive oxygen & chemical vapor transport in vadose-zone soils
  - Include aerobic biodegradation
    - Oxygen consumption
      - Multiple biodegrading chemicals
      - Baseline soil respiration
      - Summation
    - Oxygen recharge
      - Convection and diffusion of oxygen into soil
      - Adjacent to and under building foundations
  - Match common model calculations when applicable
  - Simplifications
    - Homogeneous
    - One-dimensional
    - Steady-state
    - Algebraic Equations [fast computations]
- Peer Review Publication in Progress (submitted)

Oxygen Demand

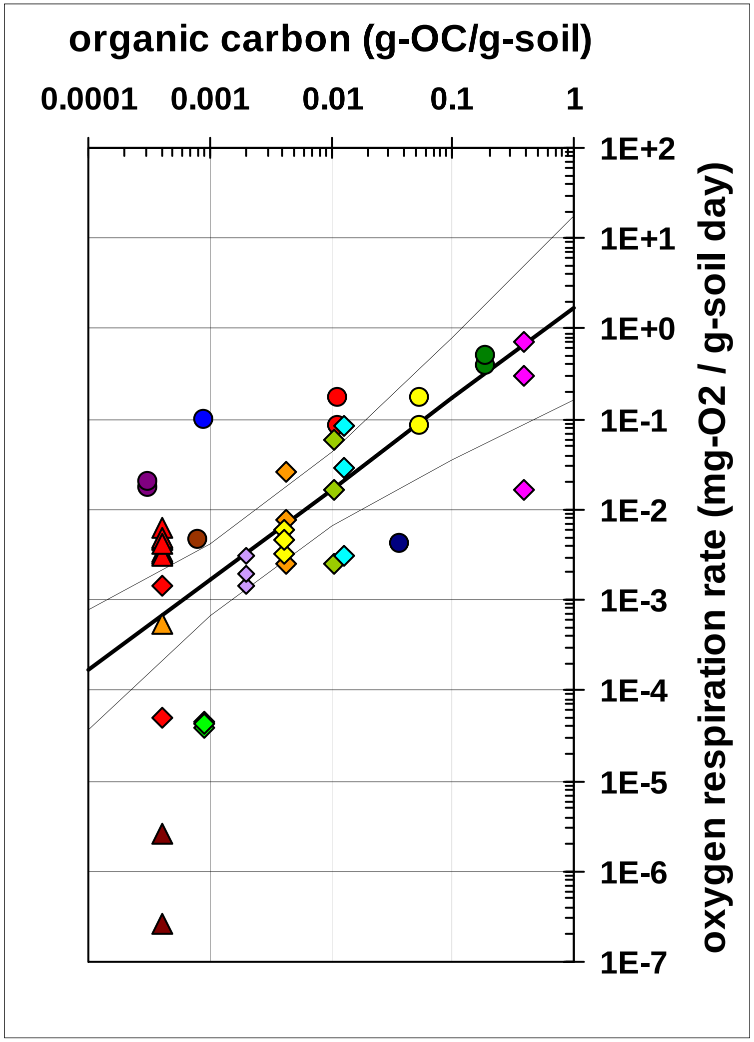
(1) Chemical Biodegradation

- Stoichiometric Sum of Chemicals

(2) Baseline Soil Respiration

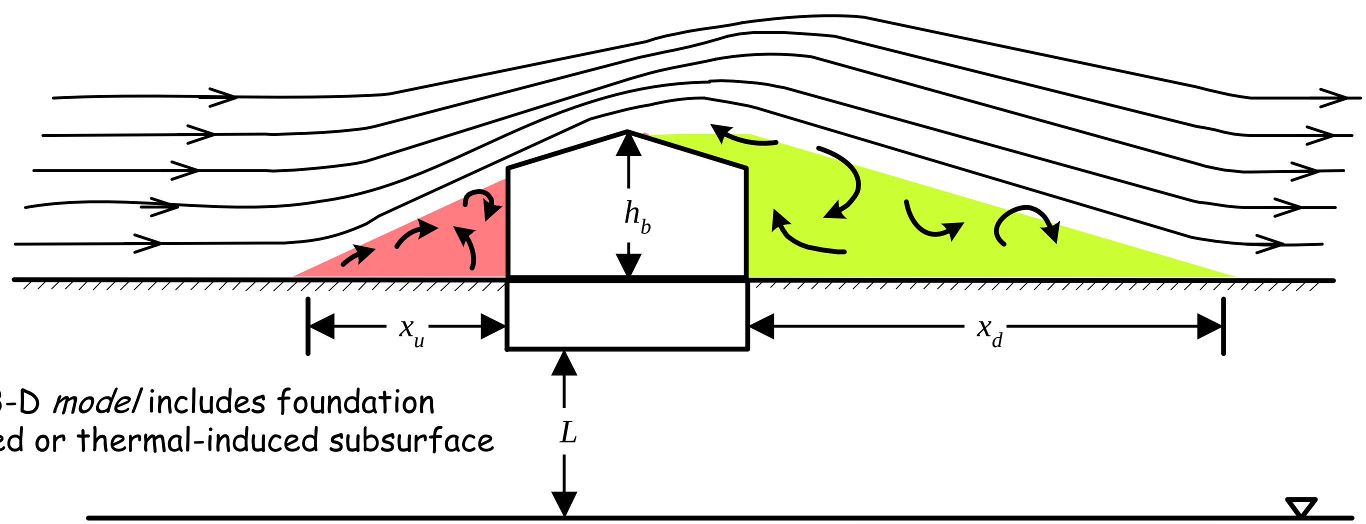
Unimpacted Soils Correlation:

- soil oxygen demand:
  ~ 1.69 mg-O^2/g-oc · day
- soil organic carbon:
  - 410 day half-life
  - factor of 10 (95%) confidence
- For:
  - peat, clay, silt, loam, sand, …
  - multiple data sources
- Bias:
  Increased scatter at lower f_{oc}
  ~ measurement error
  ~ type of f_{oc}
  ~ other factors
  ~ temperature, moisture



Oxygen Recharge

- Sub-Foundation flow of air - Oxygen Recharge
  - Hers, et al estimates range: 1 to 10 L-air/min soil vapor to indoor air
  - Equivalent oxygen mass flow should be conservative limit
- Scaling:
  - external - induced aerodynamic subsurface flow can be many times that of sub-grade to indoor air flow
  - Thermal-induced flow is at least that of subsurface to indoor air flow.
  - Characterization: available and in progress
    - API - Building characterization project(s)
    - USEPA - wake flow



Note: Abreu et al. (2006) 3-D *model* includes foundation crack flow, not wake-induced or thermal-induced subsurface flow external to building.

Example Model Estimates

(1) Apply a range of reasonable parameters (sensitivity)

- **Sources:**
  - Multiple petroleum gasoline compositions & concentrations
- **Soils:**
  - Ranges of soil porosity, moisture, soil organic carbon
- **Oxygen:**
  - Ranges of flux-limited oxygen (1-10 L/min)
  - Ranges of subsurface oxygen concentration

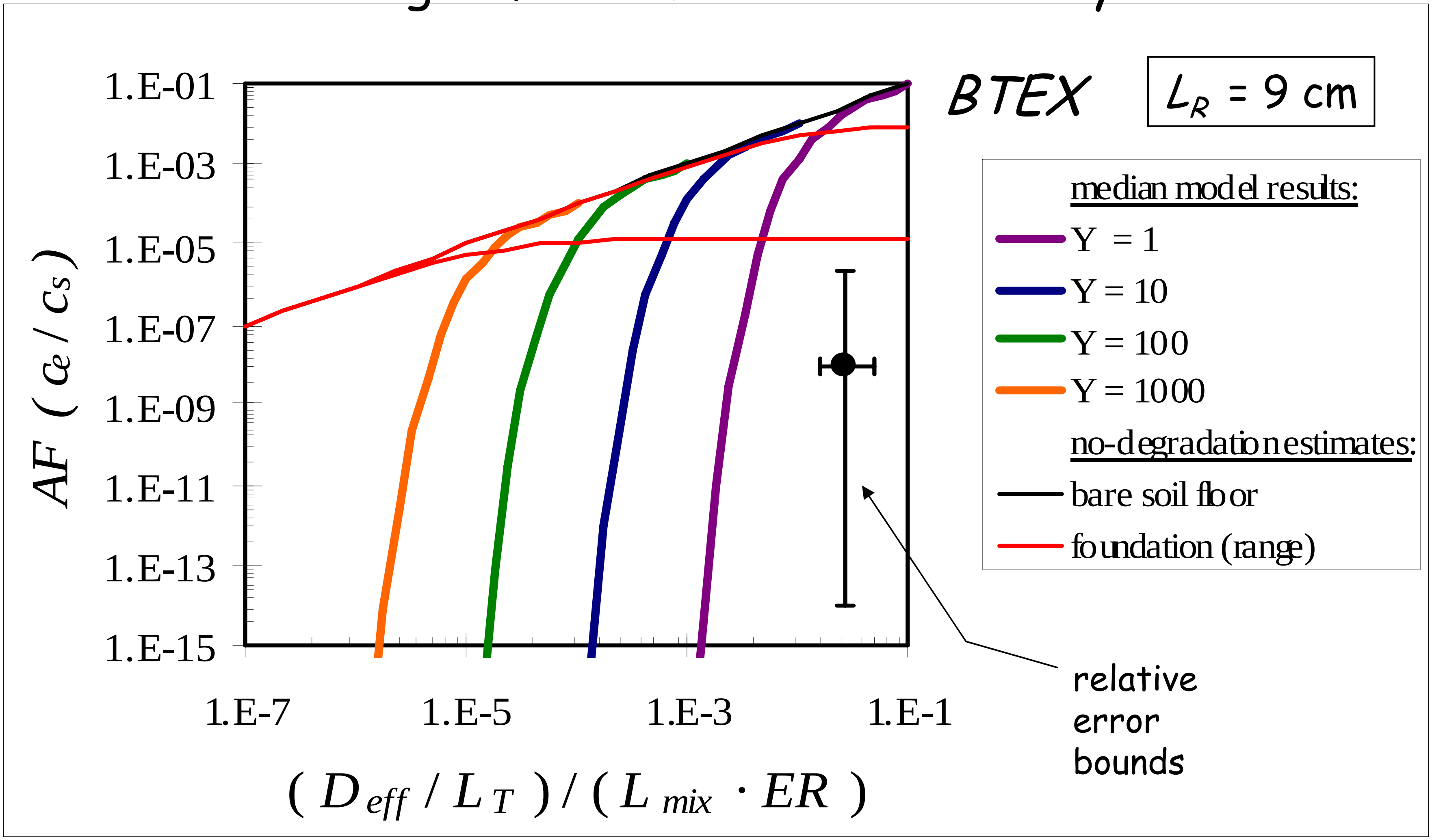
(2) Conservative Application

- **(overestimating impact)**
  - High chemical diffusion rates (sand soil, low moisture)
  - Low oxygen availability (1 L/min)
  - Specified Target Indoor Air Concentration

Multiple Model Runs

Model Results

Range of Parameters: Sensitivity



Scaling Parameter for Biodegradation

$Y = Y_c$ or Y_f : oxygen concentration or flux boundary condition

- Ratio of oxygen demand to oxygen availability (Defined)

flux:

$$Y_f = \frac{\sum_{i=1}^{N}(J_{e,i} - J_{s,i})}{\varphi_i \cdot J_{e,O_2}} + \left(\frac{L_T \cdot \rho_s \cdot \Lambda_{base,O_2}}{J_{e,O_2}}\right)$$

concentration:

$$Y_c = \left(\left(\frac{\sum_{i=1}^{N} D_{eff,i} \cdot c_{s,i}}{\varphi_i \cdot D_{eff,O_2} \cdot c_{e,O_2}}\right) - \left(\frac{L_T^2 \cdot \rho_s \cdot \Lambda_{base,O_2}}{2 \cdot D_{eff,O_2} \cdot c_{e,O_2}}\right)\right)^{\frac{1}{2}}$$

soil layer:

($Y < 1$) all aerobic . ($Y > 1$) partly aerobic . ($Y = 1$) O_2 avail. = O_2 demand

Calculate for: Y = 1, 10, 100, 1000

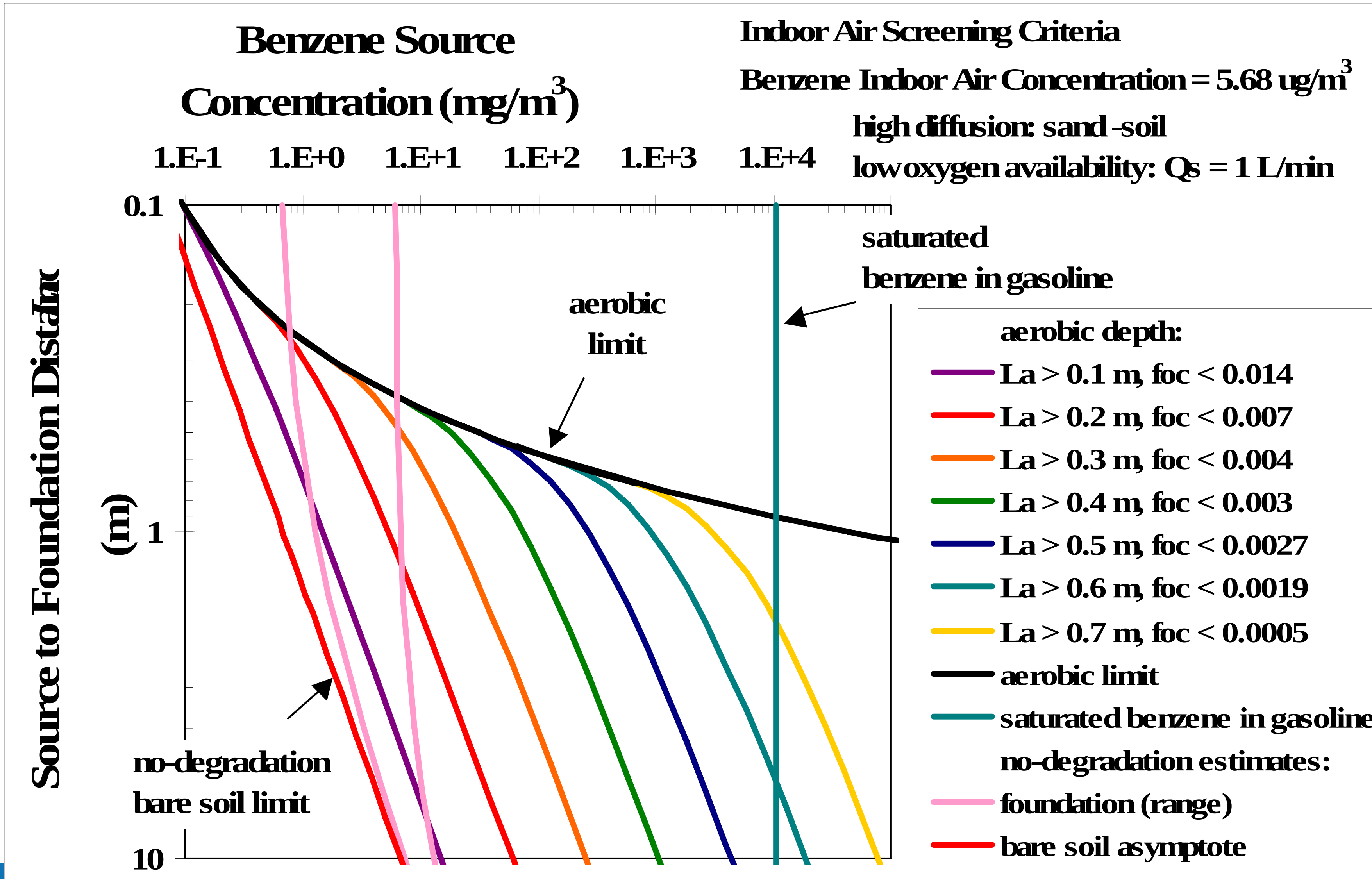
Result: $L_a / L_T = 1 / Y$

meaning: soil respiration dominates oxygen demand

(within most of the modeled parameter ranges)

Model Results

Conservative Parameters: Model Screening



Conclusions

- **Aerobic Biodegradation of Petroleum Vapor** -
  - biodegradation model
    - Includes Coupled Petroleum Vapor & Oxygen Transport in Soils
    - Oxygen demand: summed chemical biodegradation and soil organic carbon
    - Peer Review in progress (submitted)
  - Results
    - With significant biodegradation
      - "Exclusion Distance" may be a much better screening parameter than an "Attenuation Factor" (less sensitive to minor parameter variations)
      - "Exponential -like" concentration decrease with distance from source, not a linear decrease
      - building details can be unimportant, except as affecting oxygen recharge
    - Simple correlation is promising, Possible Examples:
      - no possible indoor vapor intrusion issue for BTEX if:
        - » Oxygen concentration below building > 2%, or,
        - » aerobic depth > 1.5 m below building, or,
        - » combination of soil organic carbon / source conc. / depth