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

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Houston, Texas, USA
Petroleum Vapor Intrusion Sites

Decision Process: Classes of Sites

<table>
<thead>
<tr>
<th>Immediate Action</th>
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</thead>
<tbody>
<tr>
<td>• Flammable conditions</td>
</tr>
<tr>
<td>• Gasoline in basement or connected sumps</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Not sure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• ‘noise’ of background ambient air or indoor emission sources</td>
</tr>
<tr>
<td>• Need more ‘lines of evidence’</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Not a problem</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low source concentrations</td>
</tr>
<tr>
<td>• Greater foundation to source separation</td>
</tr>
<tr>
<td>• Significant biodegradation</td>
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</tbody>
</table>

• 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
  • Contaminated Land Management (source view)

Not covered here

Focus

G. E. DeVaul, Shell Global Solutions, September 2008
Simple Conceptual Model

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

- **mixing height**
- **air exchange rate**
- **foundation mass**
- **transfer coefficient (lumped)**
- **source (or sample) depth**
- **soil diffusion coefficient**

**Series resistance attenuation factor:**

\[
\frac{c_a}{c_s} = \left(\frac{c_a - c_s}{c_s - c_a}\right) = \frac{1}{\left(\frac{L_{mix} \cdot ER}{L_{mix} \cdot ER + \frac{1}{h + \frac{L}{D_{eff}}}}\right)}
\]
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)

2. Chemical Concentration
   - Influence of indoor sources, ambient air : ‘noise’
   - Small differences: \( \frac{c_e - c_a}{c_s - c_a} \) → large errors

   - 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

   \[ \text{Include: } + L / D_{eff} ! \quad \text{In absence of ‘source’ in interval} \]
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
Include Biodegradation in Simple Model

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

For chemicals:

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

\[
A = \frac{\exp(\alpha_a) + \exp(-\alpha_a)}{2}
\]

\[
B = \frac{\exp(\alpha_a) - \exp(-\alpha_a)}{2 \cdot \alpha_a}
\]

\[
\alpha_a \to 0 \quad : \quad A \to 1, \quad B \to 1 
\]

\[
\left( \frac{c_e}{c_s} \right) \to \text{same as no biodegradation result}
\]

\[
\alpha_a \to \text{larger} \quad : \quad A \to \text{much larger}, \quad B \to \text{much larger} \quad \left( \frac{c_e}{c_s} \right) \to \text{much smaller}
\]

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

Large $\alpha_a \Rightarrow$ huge effect

<table>
<thead>
<tr>
<th>$\alpha_a$</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\to 0$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>$10^4$</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>
Aerobic Petroleum Biodegradation

• Petroleum Readily Degrades
• In aerobic conditions
• At Rapid Rates

• Data Analysis Yields Rates
  • empirical
  • water-phase $\theta_w$ – soil moisture
  • pseudo-first order (aerobic)
  • geometric mean first-order rates:
    
    $k_w = 0.79$ /hr (BTEX)
    $k_w = 71$ /hr (aliphatics)

DeVauail, ES&T (2007)

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

\[
\alpha_a = L_a \cdot \frac{k_w \cdot \theta_w}{D_{eff} \cdot H}
\]

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

<table>
<thead>
<tr>
<th>Air Flow (L/min)</th>
<th>Reference</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air flow through foundation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 to 7</td>
<td>Nazaroff et al., (1985)</td>
<td>Measured</td>
</tr>
<tr>
<td>5</td>
<td>USEPA (2002)</td>
<td>Recommended</td>
</tr>
<tr>
<td>1 to 10</td>
<td>Hers et al., (2003)</td>
<td>Measured</td>
</tr>
<tr>
<td>3.09 to 5.1</td>
<td>Abreu et al. (2007)</td>
<td>Modeled</td>
</tr>
<tr>
<td>Air flow below foundation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2 (0.5 to 1.25)</td>
<td>Lundegard et al., (2008)</td>
<td>Measured (O₂ demand)</td>
</tr>
</tbody>
</table>

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:**
  - DeVauill (2007) + foundation
  - Match model parameters
  - Scaling parameter:
    \[ Y_f \approx \frac{O_2 \text{ demand [as if all aerobic]}}{O_2 \text{ demand}} \]
    - Bigger \( \rightarrow \) more limited \( O_2 \)
    - Beyond a specified distance indoor / source attenuation factor decreases precipitously

![Graph showing indoor to subsurface concentration ratio vs source to foundation distance](image)
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
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) cm³/cm³-soil
- Residential Basement Scenario
- Target Indoor Air Criteria: $c_e = 4.16$ ug/m³
  - 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/m³

Soil Porosity: 0.38 cm³-void/cm³-soil
Soil Moisture: (range) 0.05 to 0.25 cm³/cm³-soil

(in gasoline)
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)…
Thank you