SOIL VAPOR INTRUSION FIELD RESEARCH PROGRAM - EVALUATION OF SOIL VAPOR ATTENUATION ABOVE RESIDUAL MGP IMPACTS AT SITE IN WISCONSIN

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Outline

- Project Objectives
- Site Characterization Methods
- Overview of Site Characterization Results
- Capping Study
- Modeling Methods
- Modeling Results
- Conclusions
Project Objectives

• Characterize the soil vapor intrusion (SVI) potential at remediated MGP sites with residual impacts

• Assess the significance of *vadose zone natural attenuation* (VZNA) for biodegradation of MGP chemicals

• Use site studies to evaluate alternative characterization methods to assess SVI for sites with buildings and sites with future development potential

• Assess approaches/methods for mitigation of SVI
Site Characterization Methods

• Passive Gore Sorber survey
• Soil and groundwater quality testing
• High resolution soil gas profiling, and repeated sampling to obtain temporal data
  • Field analysis of O₂, CO₂, CH₄ by Landtec GEM-2000; Hydrocarbons by PID
  • Laboratory analysis TO-15, TO-17, Modified 8260
• Soil physical property testing
• Monitoring soil moisture using capacitance probe
• Real-time polymerase chain reaction (PCR) molecular testing
Soil Moisture Study
Study Area Characterization Results

• Depth to groundwater is approximately 10 ft.
• Localized residual NAPL near to water table
• Benzene and naphthalene groundwater concentrations equal to 2300 μg/L and 940 μg/L, respectively
• Vadose zone soils are dense clayey, silty sand fill (area excavated to ~12 ft.) with high water-holding capacity, localized deep gravel in one area; in-filled channel near study area with organic matter
• Anaerobic biodegradation in deep vadose zone, aerobic biodegradation (of MGP-vapors & CH₄) & rapid attenuation of hydrocarbon vapors between primarily 6 and 8 ft. depth
• PCR analysis indicated aromatic hydrocarbon-utilizing bacteria are locally present but not uniformly distributed
What is Vapor Composition and Relative Attenuation?

- Extended PIANO analyte list
- Aromatics ~67% (benzene highest concentration), aliphatics ~ 33%
- BTEX vapors attenuate to greater degree than iso-parafins (e.g., iso-pentane)
- Naphthalene concentration low even in deep vapor! (equal to or less than 200 ug/m³)
Capping Study

• Bioattenuation is a significant process under current conditions
• How might vapors change under future development scenario?
• Broader context are recent efforts to develop screening approaches for degradable hydrocarbons (e.g., exclusion factors based thickness of clean soil, attenuation reduction factors (e.g., 10X, 100X)
• How would this site fit this framework?
Capping Study

• Would attenuation change with cap simulating building slab?!  
• Cap constructed July 2009  
• July 2009 – present  
  – Field analysis (O2, CO2, CH4, PID)  
  – Lab analyses (TO-15, TO-17)  
• Soil moisture monitoring using capacitance probe and data logger
Vapor Transport Modeling

• Conventional vapor transport models generally simulate:
  • Molecular diffusive transport,
  • Aerobic first-order biodegradation, and
  • Soil gas advection through an external pressure gradient (e.g., depressurized building, barometric pumping)

“Multi-component Modeling - Stefan-Maxwell Equations – Knudson Diffusion - Dusty Gas Model?”

Dusty Island Universe
Modeling Study – Set up

Constant O₂ Conc.  
\( C_{O_2} = 20.9\% \)

Constant O₂ Conc.  
\( C_{O_2} = 20.9\% \)

Cap

No Flow Boundary

Soil

No Flow Boundary

0.05 m

15.2

20 m

20 m

3.6 m

Constant Hydrocarbon Concentration \( C_{HC} \)

Two components:

Hydrocarbon = 0.5 mg/L (~0.15%) (Most model runs assume all vapors are benzene)

Methane = 6%
Modeling Study – Transient Results Just Below Center of Cap

- Model predicts ~ 3 years for steady state conditions for benzene to be achieved.
Modeling Study – Oxygen

Post-cap data, $O_2$ depletion over ~5 months

Relatively good match modeled and measured data
Modeling Study – Oxygen Sensitivity Post-capping

Oxygen - G3

Oxygen Concentration (%)

Depth (ft)

10X higher diffusion rate through cap

much higher $O_2$ sensitive!

Again much higher $O_2$ if only non-methane HCs modeled
Modeling Study - Methane

Methane - G3

CH₄ Soil Gas Concentration (%)

Methane concentrations slightly underpredicted

Most post-cap data

Pre-cap Model  Post-cap Model

Pre-cap Data
Measured carbon dioxide profile was unusual – More often profiles indicate higher CO₂ at depth.

One way we have been able to match measured data is to assume high calcite content minerals.
Modeling Study – Comparison Aromatics and Aliphatics

For these model runs divided non-CH₄ hydrocarbons into aromatics and aliphatics.

Aromatics (benzene) vs. Aliphatics (methylcyclohexane)

Different behavior observed; measured data consistent with model.
Modeling Study – Aromatics

Aromatics (benzene)

Benzene - G3

Soil Gas Concentration ($\mu g/m^3$)

Post-cap Data

Pre-cap Data

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Modeling Study – Results of Advection

For one model run, turned off advection – resulted in a 5% decrease in the methane flux.
Conclusions – Measured Data for Capping Condition

• A zone of oxygen depletion formed below cap and methane concentrations increased after several months
• Benzene concentrations increased slightly but there was still significant degradation observed (but was steady state reached?)
Conclusions – Some Things Modeling Showed

• Generally good comparison obtained between model predicted and measured concentrations (except CO₂)
• May take several years for steady state conditions to be reached for benzene
• Oxygen below cap is highly dependent on diffusion rate through the cap (a 10X change resulted in completely different profile!)
Conclusions – Some Things Modeling Showed (cont.)

• Critical to include methane oxidation demand (otherwise will over predict biodegradation)
• When methane concentrations are high (e.g., 6% in our case) a model that includes advection is more accurate (but difference is fairly small (5%))
• Less attenuation for aliphatic compared to aromatic hydrocarbons (consistent with data)
Conclusions – Big Picture and Future Directions

• Effect of cap not un-expected given elevated methane concentrations, however …

• Aerobic biodegradation is highly sensitive to oxygen diffusion through top boundary – how would this change if concrete slab was simulated? Or if there was a mechanism for oxygen recharge to below slab (e.g., wind, barometric pumping)

• Knowledge gained from modeling studies and empirical data provide basis for framework for identifying when biodegradation can be included in site screening and models
TO-17 Sorbent Media Comparative Study
New TO17 Sorbent Technology

Multi-bed ‘hydrophobic’ sorbent tube designed and tested by Perkin Elmer

Adsorbents

Sample Flow: Adsorb compounds

Sample Analysis: Desorb chemicals
TO17 Sorbent Comparison

**Weak**

- Little retention of water, ideal for high humidity soil vapor
- Good performance and sensitivity for naphthalene and PAHs through Pyrene
- Elevated RL for benzene due to background from Tenax
- Breakthrough observed for Benzene under high concentration conditions

**Weaker**

- Largely hydrophobic, designed and validated for soil vapor applications
- Good performance and sensitivity for benzene, naphthalene through Pyrene
- Low Benzene background translating into a lower reporting limit
- Retains benzene even when sampling high concentration soil vapor

- Tenax TA TO-17 Tubes
- SVI™ TO-17 Tubes
TO-17 Naphthalene + PAHs

- Naphthalene + PAH Detections using TO-17
  - April 2010 round: One site had detectable naphthalene levels by TO-17, no sites had detectable levels by TO-15

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tenax TA µg/m³</th>
<th>VI µg/m³</th>
<th>TO-15 µg/m³</th>
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<tr>
<td>Naphthalene</td>
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<td>7.4</td>
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<tr>
<td>2-Methylnaphthalene</td>
<td>12</td>
<td>&lt;5.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

- Air Toxics Ltd. has optimized PAHs on VI tube for next round, lowering RL by a factor of 10.