Key Advances in Vapor Intrusion Assessments at Contaminated Sites

October 30, 2014
Welcome and Introductions

Rula Deeb, Ph.D.
Webinar Coordinator
Welcome and Introductions

Rula Deeb, Ph.D.
Webinar Coordinator
Webinar Agenda

- ReadyTalk instructions for audience
  Dr. Rula Deeb, Geosyntec (5 minutes)

- Overview of SERDP and ESTCP, and webinar series goals
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)

- Validated Methods to Distinguish Between Vapor Intrusion and Indoor Sources of Volatile Organic Compounds
  Dr. Thomas McHugh, GSI (30 minutes + Q&A)

- Multi-Year Monitoring of a House Overlying a Dilute Chlorinated Hydrocarbon Plume: Implications for Vapor Intrusion Pathway Assessment
  Dr. Paul Johnson (30 minutes + Q&A)

- Final Q&A session
  Moderated by Rula Deeb
SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Deputy Director
SERDP

- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management
ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance
Scales of Research

SERDP

ESTCP

Small reaction vessels

Columns, microcosms

Tanks, large reactors

Test cells, controlled field sites

Field sites

SERDP & ESTCP Webinar Series (#1)
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms
Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment
SERDP and ESTCP Launch a Webinar Series

<table>
<thead>
<tr>
<th>DATE</th>
<th>WEBINARS AND PRESENTERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 30, 2014</td>
<td>Key Advances in Vapor Intrusion Assessments at Contaminated Sites</td>
</tr>
<tr>
<td></td>
<td>• Dr. Paul Johnson (Arizona State University)</td>
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<td></td>
<td>• Dr. Thomas McHugh (GSI Environmental)</td>
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<tr>
<td>November 6, 2014</td>
<td>New Tools for Advancing our Understanding of Marine Mammal Behavioral Ecology</td>
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<td></td>
<td>• Dr. Kelly Benoit-Bird (Oregon State University)</td>
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<tr>
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<td>• Dr. Patrick Miller (St. Andrews University)</td>
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<td>November 20, 2014</td>
<td>Novel Sampling Approaches for Improving the Management of Contaminated Sediment Sites</td>
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<td>• Dr. Philip Gschwend (Massachusetts Institute of Technology)</td>
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<td>• Dr. Bart Chadwick (SPAWAR Systems Center Pacific)</td>
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<td>December 4, 2014</td>
<td>Waste to Energy Technologies</td>
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<td>• Mr. Patrick Scott (Lockheed Martin)</td>
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<td></td>
<td>• Mr. Steven Cosper (U.S. Army Engineer Research and Development Center, Construction</td>
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<td>Engineering Research Laboratory)</td>
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</table>
Validated Methods to Distinguish Between Vapor Intrusion and Indoor Sources of Volatile Organic Compounds

Thomas McHugh, Ph.D.
GSI Environmental
Validated Methods to Distinguish Between Vapor Intrusion and Indoor Sources of Volatile Organic Compounds

ESTCP ER-201025 and ER-201119
Thomas McHugh, GSI Environmental
Project Team Members

- Lila Beckley, GSI
- Ignacio Rivera-Duarte, Navy SSC Pacific

- Kyle Gorder, Hill AFB (left)
- Erik Dettenmaier, Hill AFB (now Chevron) (right)
Vapor Intrusion vs. Indoor Sources

- Overview of VI investigations
- Indoor sources of VOCs
- On-site GC/MS analysis protocol
- Stable isotope analysis
- Recommendations
Vapor Intrusion vs. Indoor Sources

Overview of VI Investigations
- Indoor Sources of VOCs
- On-site GC/MS Analysis Protocol
- Stable Isotope Analysis
- Recommendations
Vapor Intrusion: The basics

- Definition: Vapor intrusion is the vapor-phase migration of volatile organic compounds (VOCs) from the subsurface into indoor air.

VOCs in Indoor Air

Vapors in the subsurface

Effect on indoor air quality?
Why Focus on Indoor Air Testing?

- **Goal:** Quickly and accurately determine if vapor intrusion is resulting in VOC concentration exceedances in indoor air

  - Find and remove indoor sources of VOCs to allow for accurate evaluation of vapor intrusion
  - Directly measures exposure concentrations
  - Quickly and accurately determine need to response action

**Key point:** The evaluation methods presented here save time and money by distinguishing between VI and indoor sources of VOCs
Typical VI Evaluation Process

**Screening Steps**

1. **CHEMICAL CRITERIA**
   - Chemicals could cause VI impact based on volatility and toxicity
   - Yes → **SOIL/GW SCREENING**
   - No → NFA

2. **DISTANCE CRITERIA**
   - Current or future receptors within 30 to 100 ft (10 to 30 m) of edge of impacted area
   - No → **SOIL/GW SCREENING**

3. **SOIL/GW SCREENING**
   - Soil/GW concentration > VI screening levels*
   - Yes → **FIELD MEASUREMENTS**
   - No → NFA

4. **SOIL GAS / SUBSLAB**
   - Soil gas concentration > VI screening levels
   - Yes → NFA
   - No → NFA

5. **INDOOR AIR**
   - Indoor air and/or sub-slab concentrations weight-of-evidence indicate vapor intrusion impact
   - Yes → Mitigation
   - No → NFA

---

*VI screening levels: Volatile Inventory Screening Levels.*
Sub-Slab Samples

- **What**: VOC concentrations under building
- **How**: Sample points through building floor
- **Problems**
  - Spatial variability
  - Attenuation factor (e.g., radon)
  - Downward migration of indoor VOCs
  - May miss sewer and other preferential pathways

Key point: Sub-slab/soil gas data can miss a subsurface source (false negative) or detect an indoor source (false positive)
Let’s Go Indoors: The Challenge

- Testing of indoor air is most direct way to identify vapor intrusion impacts
- Indoor sources of VOCs are ubiquitous (e.g., cleaners, glues, plastic, etc.)
- Detection of VOCs in indoor air does not necessarily indicate vapor intrusion

Key point: Indoor air samples are easy to collect; no extrapolation required to estimate exposure
Let’s Go Indoors: Data Interpretation

- Monitor, if needed to evaluate temporal variability
  - Cost effective options available
- No Further Action

- Identify source (indoor vs. VI)
- Mitigate source, if needed
  - Remove indoor source
  - Intercept subsurface source

Key point: Interpretation of indoor air data is very simple (if you can identify the source)
Vapor Intrusion vs. Indoor Sources

- Overview of VI investigations
- Indoor sources of VOCs
  - On-site GC/MS analysis protocol
  - Stable isotope analysis
  - Recommendations
Petroleum Hydrocarbons

- Sources of VOCs in indoor air
Petroleum Hydrocarbons

- Sources of VOCs in indoor air
Chlorinated Solvents

- Email bulletin, October 2010

Topics, trends and news in the environmental industry...

Technical Update

TCE Contamination Affects Community's Water Wells

“The TCE, which was banned from public use in the 1970s, was detected at levels greater than the U.S. EPA's maximum contaminant level for public drinking water.”

Key point: Many people believe that TCE and other chlorinated solvents are no longer used in industrial operations or consumer products
Chlorinated Solvents

Key point: Chlorinated VOCs are legal and are still used in a wide variety of consumer products currently available for purchase.
Vapor Intrusion vs. Indoor Sources

- Overview of VI investigations
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- Recommendations
On-Site Analysis: Portable GC/MS

- Inficon HAPSITE®
- Key features
  - GC/MS and MS-Only operating modes
  - Custom GC/MS methods
    - Positive ID for 5-10 compounds
    - ~6 min sample turn time
    - Low quantitation limits
- Can use off-site samples for “definitive” decision-making (i.e., comparison to screening levels)

Key point: Approach relies on instrument with rapid sample throughput, high sensitivity and precision, quantitative and semi-quantitative capabilities
On-Site Analysis

- Area by area results

**Goal**: Find the source

Prior Lab Sample > Screening Level triggered need for on-site testing
On-Site Analysis (Cont’d)

- Room by room results – Upstairs

Goal: Find the source
On-Site Analysis (Final Step)

Ion Intensity

E6000 Industrial Strength Adhesive

E6000 Adhesive

Around Closed Drawers

Around Closed Drawers

Around Closed Drawers

Inside Top Drawer

Top Drawer (Closed)

Top Drawer (Closed)

14:00 16:00 18:00 20:00 22:00 24:00
On-Site Analysis (Final Step)

- Indoor source

- Vapor entry point

PCE Ion Intensity (%)

TCE Survey Response
Building Pressure Control Option

General concept

1. Use controlled negative pressure to turn on vapor intrusion
2. Evaluate potential for vapor intrusion using on-site analysis procedure
3. “Make it worse” to address temporal variability

McHugh et al., ESTCP Project ER-200707
Case Study: Warehouse

- 20,000 sqft supply distribution warehouse
- Many potential indoor and subsurface VOC sources
Conventional vs. On-Site Protocol

Conventional Protocol

<table>
<thead>
<tr>
<th>Conventional Program</th>
<th>No. Samples</th>
<th>TCE Concentration</th>
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<tbody>
<tr>
<td>Indoor Air (8 hr)</td>
<td>2</td>
<td>1.2 – 1.5 ug/m³</td>
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<td>3</td>
<td>1.5 – 320 ug/m³</td>
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<tr>
<td>Groundwater</td>
<td>2</td>
<td>55 - 96 ug/L</td>
</tr>
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</table>

Diagram showing TCE concentrations in different areas:

- IA-1: TCE 1.5 µg/m³
- IA-2: TCE 1.2 µg/m³
- AA-1: TCE < 0.038 µg/m³
- SS-1: TCE 43 µg/m³
- SS-2: TCE 320 µg/m³
- SS-3: TCE 1.5 µg/m³

TCE in groundwater: 55-110 µg/L
Conventional vs. On-Site Protocol

Conventional

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On-site protocol (baseline evaluation, 22 samples)

3 HAPSITE samples:
TCE 0.97 – 1.7 ug/m³

8 HAPSITE samples:
TCE 0.81 – 2 ug/m³

5 HAPSITE samples:
TCE 0.75 – 1.8 ug/m³

6 HAPSITE samples:
TCE 1.5 – 4.1 ug/m³
Pressure Control Results

1. Indoor Source
   - trans-1,2-DCE (ug/m³)

2. Subsurface Source
   - TCE (ug/m³)

3. Indoor Source
   - trans-1,2-DCE (ug/m³)
Vapor Intrusion vs. Indoor Sources

- Overview of VI investigations
- Indoor sources of VOCs
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- Stable isotope analysis
- Recommendations
Technology Description

- Stable isotope fractionation
  - Kinetic Effect: Biodegradation causes enrichment in PCE containing $^{13}$C

Key Point: Differences in isotope ratios between samples can indicate different sources: indoor vs. subsurface
Applications of CSIA to Vapor Intrusion

Example A: Indoor Source is Primary Source of PCE in Indoor Air

Example B: Subsurface Source is Primary Source of PCE in Indoor Air

Range for indoor sources
Application Protocol

1. Subsurface sample locations
Protocol (Cont’d)

2. Choose indoor air sample locations

3. Collect samples per validated steps
   - Estimate sample concentrations to ensure collection of correct sample mass
Protocol (Cont’d)

4. Interpret results per matrix

- **Indoor Source**
  - Strong Evidence
- **Subsurface Source**
  - Supporting Evidence
- **Mixed Indoor and Subsurface Source**

= Range for indoor sources
Vapor Intrusion vs. Indoor Sources

- Overview of VI investigations
- Indoor sources of VOCs
- On-site GC/MS analysis protocol
- Stable isotope analysis

Recommendations
Recommendations

- Goal: Quickly and accurately determine if vapor intrusion is resulting in VOC concentration exceedances in indoor air
  - Measure VOC Concentration
  - Compare to applicable screening level
  - VI vs. Indoor Source
    - On-site analysis
    - Isotope analysis
    - Building pressure control
- Temporal variability concern: low cost indoor air monitoring using passive samplers
- Real vapor intrusion: Mitigate

Indoor Air Testing

Source Identification

Follow up as needed
# Validation Studies: On-Site Analysis

<table>
<thead>
<tr>
<th>Investigation Method</th>
<th>Validation Study</th>
<th>Publications</th>
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<tbody>
<tr>
<td><strong>On-Site GC/MS Analysis</strong>: Use real-time compound-specific analysis to follow the “smoke trail” back to the indoor source of vapor entry point</td>
<td>ESTCP ER-201119 Google “ESTCP ER-201119” for project report and application protocol</td>
<td>Beckley et al., 2014, Env. Forensics, 15(3), 234-243 Gorder and Dettenmair, 2011, GWMR, 31(4), 113-119</td>
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## Validation Studies: Isotopes

<table>
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<tr>
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<tbody>
<tr>
<td><strong>Compound-Specific Isotope Analysis (CSIA):</strong> Use the isotope fingerprint of the target VOC to distinguish between vapor intrusion and indoor sources of VOCs</td>
<td>ESTCP ER-201025 Google “ESTCP ER-201025” for project report and application protocol</td>
<td>McHugh et al., 2011, ES&amp;T, 45(14), 5952-5958 Kilsch et al., 2013, J. Chromatography A, Vol. 1270, pp. 20-27</td>
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</tbody>
</table>
## Validation Studies: Pressure Control

<table>
<thead>
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<th>Investigation Method</th>
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<tbody>
<tr>
<td><strong>Building Pressure Cycling</strong>: Change the building pressure to turn on and turn off vapor intrusion in real time</td>
<td>ESTCP ER-200707 Google “ESTCP ER-200707” for project report and application protocol</td>
<td>McHugh et al., 2012, ES&amp;T, 46(9), 4792-4799</td>
</tr>
<tr>
<td></td>
<td></td>
<td>USEPA Environmental Technology Verification (ETV) Program: <a href="http://www.epa.gov/etv/vrvs.html">http://www.epa.gov/etv/vrvs.html</a></td>
</tr>
</tbody>
</table>
For additional information, please visit http://www.serdp-estcp.org

Speaker Contact Information:
temchugh@gsi-net.com; 716-876-9261
Q&A Session 1
Multi-Year Monitoring of a House Overlying a Dilute Chlorinated Hydrocarbon Plume: Implications for Vapor Intrusion Pathway Assessment

Paul Johnson, Ph.D.
Arizona State University
Lessons Learned from Monitoring a House Overlying a Dissolved Chlorinated Hydrocarbon Plume Under Natural and Controlled Depressurization Conditions

SERDP Project ER-1686

Paul C. Johnson
Ira A. Fulton Schools of Engineering, Arizona State University
(w/C. Holton, P. Dahlen, H. Luo, K. Gorder, E. Dettenmaier)
SERDP ER-1686 Overview

**Objective:** Collect a long-term and high-frequency vapor intrusion (VI) data set

**Why?:** It does not exist. Needed to answer key VI pathway assessment plan questions – major data gap in the VI field

**Goal:** Increase confidence and cost-effectiveness in VI pathway assessment

**Data Collection:**

- **Phase I:** Natural conditions (921 days)
- **Phase II:** Controlled building under-pressurization condition (325 days)
- **Phase III:** Controlled under-pressurization and natural conditions, with modifications to subsurface infrastructure (460+ days)

Data: CHCs and radon in indoor air and soil gas, pressure differentials, exchange rate, environment (wind, temperature, etc.), tracer gas, effective diffusion coefficients
**MLE* VI Pathway Assessment Paradigm**

- Heavy weighting of indoor air data
- Decisions made using a few samples
- Sometimes short sampling windows or seasonal data (e.g., fall, winter)
- Usually 24-h indoor samples; might include portable detectors or passive samples

**Question:** Do MLE outcomes depend on plan specifics? (date/time/season, number of samples, sampling duration)

* MLE = multiple lines of evidence
“When IA samples are being collected as a primary assessment tool for the determination of the VI pathway, the sample event should take place between November 1 and March 31. Based on seasonal weather patterns, these dates are generally “worst case” conditions for VI to occur.

Assuming there are no other contradictory lines of evidence, the single round of indoor/ambient air samples should be able to determine whether the VI pathway is complete.”
Controlled Pressure Method (CPM) Testing

- Proposed alternative to sampling under natural conditions
- One-time short-term test

Questions: Will CPM outcomes depend on application date, season, duration?

How do CPM results compare with true impacts under natural conditions?
Sun Devil Manor (Layton, UT)

- 10 – 60 mg/L TCE and 1,1 DCE in groundwater
- 1500 pCi/L radon in soil gas
Monitoring and Characterization
Results: Variability Along the VI Pathway

Key Result: Near-source data more consistent in time and space than near-surface data
Key Result: Value of intrusive sub-slab sampling not clear

Observations from SDM

<table>
<thead>
<tr>
<th>Media and Depth</th>
<th>Spatial Variations</th>
<th>Temporal Variations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indoor Air (lower level)</td>
<td>Unknown</td>
<td>1000X</td>
</tr>
<tr>
<td>Sub-slab Soil Gas</td>
<td>10X – 100X</td>
<td>10X</td>
</tr>
<tr>
<td>3-ft BS Soil Gas</td>
<td>10X</td>
<td>2X</td>
</tr>
<tr>
<td>6-ft Below Slab Soil Gas</td>
<td>3X</td>
<td>50% (about mean)</td>
</tr>
<tr>
<td>Shallow Ground water</td>
<td>2X</td>
<td>50% (about mean)</td>
</tr>
</tbody>
</table>
Results: Variability Along the VI Pathway

Sub-slab

3 ft BGS

6 ft BGS

August

January

February
Indoor Air Concentrations

Winter Months

Holton et al., ES&T, 2013, 47, 13347-13354
Indoor Air Concentrations

Spring Months

Holton et al., ES&T, 2013, 47, 13347-13354
Indoor Air Sampling Plans and Decision-Making

1. Create synthetic 24-h sample data from high temporal resolution data

2. Divide samples into four seasons
   • Fall, Winter, Spring, Summer

3. Perform 10,000+ simulations for three VI pathway assessment plans
   • 4 samples (Fall, Winter, Spring, Summer)
   • 2 samples (Winter, Summer)
   • 2 samples (Winter, Winter)

4. Analyze statistics, assess decision
Results: Analysis of Sampling Outcomes

- High potential for false negative result concerning VI occurrence
- High potential to incorrectly characterize long-term exposure
- High potential to incorrectly characterize maximum short-term exposure
  - About half of all 24-h samples would come back non-detect
  - Only about 50% chance that sample results would have a mean concentration inside a 10X range about the true mean concentration

Holton et al., ES&T, 2013, 47, 13347-13354
Temporal Changes in Indoor Air – Others

Folkes et al., *GWMR*, **2009**, 29 (1), 70-80.
Colorado CHC, UK radon, etc.

Sweden homes
Other Lessons Learned from Phase I

- **Indoor Sources**
  - Can create subsurface soil gas plumes
  - This can confound MLE data interpretation in ways not previously anticipated

- **Radon**
  - VI behavior different from CHCs at this site
  - Not useful as quantitative surrogate

Indoor tracer appearance in sub-slab soil gas
Other Lessons Learned from Phase I

Strong correlation only with indoor-outdoor temperature difference

Focus Sampling on ΔT>5°C?
Phase II: Controlled Pressure Method (CPM)

- House maintained at constant underpressurization (11 Pa outdoor-indoor)
- Tracer gas released at known rate
- TCE, radon, and tracer monitored in blower exhaust
- QB and emission rates into house calculated
- Compare vs. natural conditions
Results: Controlled $\Delta P$ Emission Rates

Results are relatively constant with time.

Results do not depend on date, time, or season.

Blower speed reduced.
# Comparison: CPM vs. Natural Conditions

## Concentration Comparison

<table>
<thead>
<tr>
<th></th>
<th>TCE [μg/m³]</th>
<th>Radon [pCi/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Condition</strong></td>
<td><strong>Natural Conditions (128 to 730 d)</strong></td>
<td><strong>CPM (780 to 1045 d)</strong></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td>0.35</td>
<td>9.3</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td>0.068</td>
<td>9.1</td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td>&lt;0.04</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**CPM Results**

>> long-term average exposure concentrations

CPM results are similar to maximum impacts under natural conditions

No false negatives in CPM test results
Phase II: Other Observations

Natural Conditions

CPM Conditions
Land Drain Discovery and Manipulation
Phase III: Close land drain lateral

- Maintain house at constant underpressurization for about 3 months
- Turn off blower, study house under natural conditions for about a year
Phase III Observations

CPM Conditions
Land Drain Open

Natural Conditions
Land Drain Open

Natural Conditions
Land Drain Closed

CPM Conditions
Land Drain Closed
Conclusions

- Be cautious when extrapolating shallow soil gas and indoor air measurements beyond that point-in-space and time.
- There is a risk of false negatives (and false positives) when using current guidance to assess VI occurrence; there is also the risk of mischaracterizing VI exposure.
- Controlled-pressure method testing looks promising as a one-time short-term “Yes/No” VI pathway test; greater confidence in results than for sampling under natural conditions.
- Contributing VI pathways are difficult to identify with current site and pathway characterization information and tools; not sure yet if this is important or not.

Note: this is a unique one-of-a-kind data set; we do not yet know if observations at this site are representative of VI behavior at other sites.
For additional information, please visit:
https://www.serdp-estcp.org/Featured-Initiatives/Cleanup-Initiatives/Vapor-Intrusion

https://iavi.rti.org/WorkshopsAndConferences.cfm

Speaker Contact Information
paul.c.johnson@asu.edu; (480) 965-9115
Q&A Session 2
The next webinar is on Thursday November 6

New Tools for Advancing our Understanding of Marine Mammal Behavioral Ecology

Please take a moment to complete the survey that will pop up on your screen when the webinar ends.