A Review for the US Navy of Best Practices, Knowledge and Data Gaps, and Research Directions for Vapor Intrusion

Todd McAlary and Robert Ettinger, Geosyntec Consultants
Paul Johnson, Arizona State University
Bart Eklund, URS
Heidi Hayes, Air Toxics Limited
Tim Shields, Richard Brady Associates
Bart Chadwick and Ignacio Rivera-Duarte, SPAWAR Systems Center Pacific

Environment, Energy and Sustainability Symposium
Denver, May 2009
**A Review for the US Navy of Best Practices, Knowledge and Data Gaps, and Research Directions for Vapor Intrusion**

**Geosyntec Consultants, 427 Princess Street, Suite 429, Kingston, ON K7L 5S9,**

Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 4-7 May 2009 in Denver, CO. U.S. Government or Federal Rights License
Scope

• Conduct desk-top study to improve vapor intrusion pathway assessments at Navy sites
  ▪ Review and document best practices
  ▪ Identify technology and knowledge gaps
  ▪ Recommend areas for focused research
• Develop an integrated strategy for cost-effective reduction of the overall uncertainty
Focus Areas

- Technically defensible sub-surface sampling
- Passive air sampling methods
  \[ F = A \times D \times (\delta C/\delta x) \]
- Distinguish background vs vapor intrusion sources
Common VI Investigation Approach:
1) Select VI Guidance Document (from dozens)
2) Collect and analyze samples of various media
3) Compare concentrations to screening levels

- Often ambiguous outcomes:
  - spatial and temporal variability
  - background sources
  - data biases and gaps
Sampling

- Groundwater
- Bulk Soil
- Near-Slab Soil Gas
- Sub-Slab Soil Gas
- Indoor Air
- Outdoor Air

None are perfect, some less than others
# Matrix for Guidance on Selection of Soil Gas Sampling Methods with Compatible DQO Results


<table>
<thead>
<tr>
<th>Downhole Sampling System</th>
<th>Sample Collection Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Syringe</td>
</tr>
<tr>
<td>Increase Quality</td>
<td>Low/Low</td>
</tr>
<tr>
<td>Direct Sampling</td>
<td></td>
</tr>
<tr>
<td>PRT System</td>
<td></td>
</tr>
<tr>
<td>Implants</td>
<td></td>
</tr>
<tr>
<td>Gas Wells</td>
<td></td>
</tr>
</tbody>
</table>

*Note: The table illustrates the selection of sample collection methods based on the downhole sampling system and the increase in quality. The methods are ordered from Low/Low to High/High.*
Data Quality

High concentrations of both benzene and oxygen in the same soil gas sample is unexpected.

Were there leaks?

(Courtesy API)
Spatial Variability

Several orders of magnitude range in concentrations

(McAlary et al., 2007)

(Luo et al., 2006)

(Wertz, 2006)
Spatial and Temporal Variability

Indoor Air Radon (Marley, 2001)

Indoor Air VOC (McAlary et al., 2002)

Soil Gas @ 5 ft bgs (McAlary, 2008)

Soil gas @ 15 ft bgs (McAlary, 2008)
Is there really any correlation? Why so poor?

(Dawson, 2008)
### Table 3. Residential Screening Levels for Selected VOCs

<table>
<thead>
<tr>
<th>State</th>
<th>Benzene Ground Water</th>
<th>Benzene Soil Gas</th>
<th>Benzene Indoor Air</th>
<th>TCE Ground Water</th>
<th>TCE Soil Gas</th>
<th>TCE Indoor Air</th>
<th>PCE Ground Water</th>
<th>PCE Soil Gas</th>
<th>PCE Indoor Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska</td>
<td>5</td>
<td>3.1</td>
<td>0.31</td>
<td>5</td>
<td>0.22</td>
<td>0.022</td>
<td>5</td>
<td>8.1</td>
<td>0.81</td>
</tr>
<tr>
<td>California</td>
<td>NA</td>
<td>36.2</td>
<td>0.084</td>
<td>NA</td>
<td>528</td>
<td>1.22</td>
<td>NA</td>
<td>180</td>
<td>0.41</td>
</tr>
<tr>
<td>Colorado</td>
<td>15</td>
<td>NA</td>
<td>0.23</td>
<td>5</td>
<td>NA</td>
<td>0.016</td>
<td>5</td>
<td>NA</td>
<td>0.31</td>
</tr>
<tr>
<td>Connecticut</td>
<td>130</td>
<td>2,400</td>
<td>3.3</td>
<td>27</td>
<td>752</td>
<td>1</td>
<td>340</td>
<td>3,798</td>
<td>5</td>
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<tr>
<td>Indiana</td>
<td>95-850</td>
<td>250 - 1400; 25 - 140&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.5</td>
<td>4.6 - 700</td>
<td>120 - 2000; 2 - 200&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.2 - 4.1</td>
<td>7.4 - 1100</td>
<td>320 - 5200; 32 - 520&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.2 - 10</td>
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<tr>
<td>Louisiana</td>
<td>2,900</td>
<td>NA</td>
<td>12</td>
<td>10,000</td>
<td>NA</td>
<td>59</td>
<td>15,000</td>
<td>NA</td>
<td>110</td>
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<tr>
<td>Maine</td>
<td>NA</td>
<td>NA</td>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>2,000</td>
<td>NA</td>
<td>0.3</td>
<td>30</td>
<td>NA</td>
<td>1.37</td>
<td>50</td>
<td>NA</td>
<td>0.04</td>
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<tr>
<td>Michigan</td>
<td>5,600</td>
<td>150</td>
<td>2.9</td>
<td>15,000</td>
<td>700</td>
<td>14</td>
<td>25,000</td>
<td>2,100</td>
<td>42</td>
</tr>
<tr>
<td>Minnesota</td>
<td>NA</td>
<td>1.3-4.5</td>
<td>1.3-4.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>2,000</td>
<td>95</td>
<td>1.9</td>
<td>50</td>
<td>54</td>
<td>1.1</td>
<td>80</td>
<td>68</td>
<td>1.4</td>
</tr>
<tr>
<td>New Jersey</td>
<td>15</td>
<td>16</td>
<td>2</td>
<td>1</td>
<td>27</td>
<td>3</td>
<td>1</td>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>New York</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ohio</td>
<td>14</td>
<td>31</td>
<td>3.1</td>
<td>--</td>
<td>122</td>
<td>12.2</td>
<td>11</td>
<td>81</td>
<td>8.1</td>
</tr>
<tr>
<td>Oklahoma</td>
<td>5</td>
<td>3.1</td>
<td>0.27</td>
<td>5</td>
<td>0.17</td>
<td>0.017</td>
<td>5</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Oregon</td>
<td>160</td>
<td>NA</td>
<td>0.27</td>
<td>6.6</td>
<td>NA</td>
<td>0.018</td>
<td>78</td>
<td>NA</td>
<td>0.34</td>
</tr>
<tr>
<td>Pennsylvania</td>
<td>3,500</td>
<td>NA</td>
<td>2.7</td>
<td>14,000</td>
<td>NA</td>
<td>12</td>
<td>42,000</td>
<td>NA</td>
<td>36</td>
</tr>
</tbody>
</table>

**Notes:**
1. Units are µg/L for groundwater and µg/m³ for soil gas and indoor air.
2. See individual state guidance documents for additional information, including limitations and exceptions.
3. Trigger or action levels for mitigation based on indoor air concentrations may be higher than the screening levels shown.

<sup>a</sup> Second range of values shown is for sub-slab soil gas.

<sup>b</sup> Chronic exposure value.
Background vs Target Levels

MTBE background has been dropping faster than others.

Background exceeds 10-g cancer risk level.
Resolving Background

Compound Ratios (MTBE vs Benzene)

Trilinear Plots

Compound ratio plots from sub-surface and indoor air samples may help distinguish interior sources

Multi-linear diagrams
Summary of Current Best Practices

• Current approaches often result in uncertainty
  ▪ Spatial and temporal variability, positive and negative bias

• Uncertainty can be managed with LOTS of data
  ▪ Gets expensive, and doesn’t necessarily resolve issues

• Background is almost always a challenge
  ▪ Not always easily resolved

• Some new approaches are being tested on an ad hoc basis, but more formal studies need to be done to facilitate regulatory approval
Research Directions

• New techniques and tools to minimize variability
• Real-time information
• Less expensive investigative tools
• Field demonstrations at “typical” sites
  ▪ Shallow Water Table (common for Navy)
  ▪ Large Slab-on-Grade Buildings
  ▪ Undeveloped Land
  ▪ Etc.
ESTCP Project 08 EB ER3-036 will compare 4 passive samplers to establish capabilities and limitations:

1) SKC Ultra II™ Badges
2) Perkin Elmer Tubes
3) PDMS Membrane samplers
4) Radiello™
Passive vs Active Sampling

Indoor Air

- PDMS vs Summa Canister or TAGA - Indoor Air Samples

Sub-Slab

- PDMS vs Summa Canister - Sub-slab Samples

Vent-Pipes

- PDMS vs Summa Canisters - HPV and Passive Vent Samples

Comparison to conventional methods is encouraging for samplers where the uptake rate is controlled and quantified (not all passive samplers do this)

(McAlary et al., 2009)
High Purge-Volume Sampling (Spatial Integration)

Buildings “inhale” about 0.1 to 10 L/min of soil gas = 1.6 to 160 million L over 30 years

Is a 1L soil gas sample a “representative elemental volume”? Why not 1,000 L? Or 10,000 L?
Trend in Concentrations vs Volume Removed can help to elucidate location of source.

(Creamer and McAlary, 2009)
Real-Time Portable Monitoring

- Foxboro TVA 1000 FID/PID
- HAPSITE Viper
- ppbRAE
- Tiger Microfast GC

Capabilities and limitations? (MSRAS, in press)
To what extent do sampling methods depend on the soil type?
Meteorological Data

Monitor Barometric Pressure and Gauge Pressure in a deep soil gas probe

If the Gauge Pressure is a mirror image of the Barometric pressure over time, deep soil gas MUST be pneumatically isolated from the atmosphere

(McAlary, 2003)
Pressure Cycling Strategies

Sample Building under Positive and Negative Pressure

positive pressure will reduce or eliminate vapor intrusion

(Berry-Spark et al., 2005)
Indoor Air concentrations were initially similar to predictions from soil gas data

>10X drop after building pressurized

(Berry-Spark et al., 2005)

Indoor Air concentrations were initially similar to outdoor air concentrations

No change when building pressurized
Pressure Cycling

Classic response of indoor air concentrations to sub-slab depressurization

1,1-DCE concentrations dropped by >100X

Other compounds unchanged (interior sources)
Building pressure is often influenced by the ventilation system, and can have a dramatic effect on vapor intrusion.
Mostly, we measure concentrations (it is easier)

But if we could measure flux, it might actually be more relevant

Key issue is the scale of measurement

can we use the whole building as a flux chamber?

\[
F = Q_{\text{soil}} \times [\text{VOCs}]_{ss}
\]

\[
[\text{VOCs}]_{VI} = \frac{F}{Q_{\text{building}}}
\]

\[
[\text{VOCs}]_{VI} = [\text{VOCs}]_1 - [\text{VOCs}]_2
\]
Extended Flow Controllers for Canisters
Indoor air samples from 1 day to 7 (temporal average)

Composite Sampling
Collect aliquots from multiple locations (spatial average)

Compound-Specific Stable Isotope Analysis
Look at $\text{C}^{13}/\text{C}^{12}$ to assess degradation (fingerprinting)

Use of Radon as a Tracer
where present naturally (building-specific $\alpha$-factor)
Current best practice often leads to uncertainty or ambiguity

Temporal and spatial variability

Very low target levels (analytical challenges and biases)

Background interferences

Several emerging methods may help to reduce uncertainty and cost

Temporal and spatial integration

Manipulating Building pressure – use the building like a flux box

New hardware – lower detection limits, greater portability, lower cost

Forensic tools and Tracers

Research is needed to demonstrate the capabilities and limitations

Detailed studies of selected sites or buildings

Comparative studies between technologies
Recommendations from Navy Panel

1) Passive sampling devices:
   Quantitative evaluation of average concentration,
   Differentiation between background and VI, and
   Regulatory acceptance

2) Pressure cycling for evaluation of background:
   Development of a practical & reliable SOP

3) Portable GC-MS:
   Quantification issues
   Regulatory acceptance
Acknowledgements

SPAWAR Systems Center Pacific
Code 71750
53475 Strothe Rd.
San Diego, CA 92152