Assessing Vapor Intrusion at Petroleum Hydrocarbon Sites

2008 Annual National Tanks Conference
March 16, 2008
Atlanta, Georgia
<table>
<thead>
<tr>
<th>Time</th>
<th>Session Title</th>
<th>Presenter(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:30</td>
<td>Welcome, Introductions, Safety Issues</td>
<td>Harley Hopkins, API</td>
</tr>
<tr>
<td>12:45</td>
<td>API Overview and Work on VI issues</td>
<td>Harley Hopkins</td>
</tr>
<tr>
<td>1:25</td>
<td>Petroleum Vapor Intrusion Site Conceptual Model</td>
<td>Todd Ririe</td>
</tr>
<tr>
<td>1:55</td>
<td>Principals of Vapor Movement and Attenuation</td>
<td>Blayne Hartman</td>
</tr>
<tr>
<td>2:25</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>2:45</td>
<td>Evaluating the Vapor Intrusion Pathway: Nationwide Study of Subsurface Petroleum Hydrocarbon Vapor Occurrence and Attenuation</td>
<td>Robin Davis, Utah Department of Environmental Quality</td>
</tr>
<tr>
<td>3:15</td>
<td>Case Studies to Evaluate HC Vapor Migration</td>
<td>Todd Ririe</td>
</tr>
<tr>
<td>3:35</td>
<td>Methods to Assess Vapor Intrusion &amp; Sampling issues</td>
<td>Blayne Hartman</td>
</tr>
<tr>
<td>4:15</td>
<td>Summary and Final Discussion</td>
<td>Harley Hopkins</td>
</tr>
</tbody>
</table>
Instructor Biographies

Robin Davis, Utah Department of Environmental Quality
168 North 1950 West
Salt Lake City, Utah 84116
Tel: 801-536-4177
Email: rvdavis@utah.gov

Robin holds a Bachelor of Science in Geology. Since 1976, she has worked for the states of California, Arizona and Utah in hydrologic investigations and petroleum remediation. She has helped develop state guidance for risk-based corrective action, monitored natural attenuation and site investigations. Robin’s most recent work includes optimizing site investigations for studying the vapor intrusion pathway, and the study of subsurface petroleum hydrocarbon vapor occurrence and attenuation at sites in the United States and Canada.

Blayne Hartman, H&P Mobile Geochemistry
2470 Impala Dr.
Carlsbad, CA 92075
Tel: 760-804-9678
Email: bhartman@handpmg.com

Dr. Hartman is a nationally recognized expert on soil vapor sampling, soil vapor analysis, and vapor intrusion. He has provided training on soil gas methods and vapor intrusion to County and State regulatory agencies in over 30 states, many of the EPA regions, the DOD, and numerous stakeholder groups and consultants. He has written numerous articles on the collection, analysis, and interpretation of soil vapor data, including chapters in four textbooks. He has participated in technical workgroups on soil vapor methods for EPA, CA-EPA, CA Regional Water Boards, County of San Diego, ITRC & ASTM; has reviewed/edited instructional manuals for the EPA OUST and Superfund groups, and lectured on soil gas methods in the EPA-OSWER vapor intrusion seminars. Over the past four years, Dr. Hartman has been a contributing author/editor to vapor intrusion and soil gas guidance documents to federal EPA, CA-EPA, San Diego County, ITRC, DOD, API, and more than 20 individual State documents.
Harley Hopkins, API
1220 L Street NW
Washington, DC 20005
Tel: 202-682-8318
Email: hopkins@api.org

Harley Hopkins is a manager in the Regulatory and Scientific Affairs Department of the American Petroleum Institute (API). Since 1991, he has managed research projects on the fate, transport and remediation of petroleum hydrocarbons in soil and groundwater, resulting in numerous API publications. He provides technical assistance within API on oil and natural gas waste, vapor intrusion and free-product remediation. Mr. Hopkins is a Certified Professional Geologist in the State of Virginia.

Todd Ririe, BP
6 Centerpointe Dr
La Palma, CA 90623
Tel: 714-670-3062
Email: todd.irie@bp.com

Todd has a BA degree in geology from Cornell College, and a PhD degree in geology from the University of Iowa. Todd has over 20 years of experience in applied geology, geologic instruction, and environmental applications of geology. Since 1990, his primary responsibility has been on environmental projects primarily focused on petroleum hydrocarbon site assessment and application of effective remedial approaches to reach closure. Work has included projects throughout the U.S., Southeast Asia, and South America. His current position is the environmental technology coordinator for BP in the Western United States.
Assessing Vapor Intrusion at Petroleum Hydrocarbon Sites

2008 Annual National Tanks Conference
March 16, 2008
Atlanta, Georgia
Proposed Format

- Informal
- Get acquainted: Instructors and participants
- Ask or submit questions
Goals

Gain knowledge to do smarter site screening

Gain knowledge on collecting the best data for evaluating petroleum hydrocarbon bioattenuation
Resource Documents at www.api.org/vi

• Collecting and Interpreting Soil Gas Samples from the Vadose Zone

• Identification of Critical Parameters for the Johnson and Ettinger (1991) Vapor Intrusion Model

• Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Empirical Assessment of Soil Gas Vertical Profile Data

• Assessing the Significance of Subsurface Contaminant Vapor Migration to Enclosed Spaces: Site-Specific Alternatives to Generic Estimates
API Work in Progress

• “Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings: Evaluation of Low Strength Sources Associated with Dissolved Gasoline Plumes”
  – Visit poster session

• Review of site data
In this part or the training, we will briefly review the existing EPA draft guidance, some of the current States guidances, the ITRC guidance, and the just released ASTM standard. If you are a consultant or RP, you need to know which agency has jurisdiction and what their vapor intrusion policy is in order to know what approaches are allowed and what the acceptable levels are.
This is the web page for the EPA draft vapor intrusion guidance. From here, the guidance and other supporting materials can be downloaded. The document is a lengthy and difficult read. It is available at: (http://www.clu-in.org/conf/tio/vapor/resource.cfm)
The EPA 2002 OSWER guidance consists of 3 tiers comprised of 6 questions. The EPA proposed changes to the draft guidance in March 2006 that was supposed to go into effect in 2006 but they never were instituted.
### DRAFT Exterior Decision Matrix

<table>
<thead>
<tr>
<th>Concentration in Soil Gas</th>
<th>Concentration in Groundwater</th>
<th>Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well above level of concern</td>
<td>Interior sampling or mitigation</td>
<td>Possible vadose source; Interior sampling or mitigation</td>
</tr>
<tr>
<td>Around level of concern</td>
<td>Interior sampling or mitigation</td>
<td>Interior sampling or mitigation</td>
</tr>
<tr>
<td>Well below level of concern</td>
<td>Consider geologic setting¹, verification sampling in select locations</td>
<td>Consider geologic setting¹, verification sampling in select locations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NFA unless nearby property has unacceptable risks (verification, monitoring)</td>
</tr>
</tbody>
</table>

¹ Review subsurface stratigraphy, depth to water, to determine presence, integrity, effectiveness of geologic barriers to vapor migration.

This is one idea being contemplated by EPA for site screening using only exterior data. As you can see, there is only one box that does not require any further action in this matrix. This is still very much in the draft stages and is being discussed by EPA with experts and stakeholders.
Many States have developed or are developing their own VI guidance because they don’t agree with EPA’s or they find it too confusing. Some States currently have written guidance, others have drafts, and others are pondering. Some States are still trying to figure it all out and have asked for training on the subject.
At the time of this writing, this is a summary of the preferences of various States. Most prefer active soil gas. A few prefer indoor air measurements. Groundwater data can be used to filter which sites need to be evaluated for the VI pathway, but most States won’t allow you to use additional GW data to get out once you are in. Few States are allowing soil matrix data to be used. Flux chambers are not readily accepted because of unfamiliarity.
ITRC VI Guidance

- Practical How-to Guide
- Stepwise Approach
- Discussion of Investigatory Tools
- Thorough Discussion of Mitigation
- Scenarios Document
- Classroom Training in 2008

ITRC finished its vapor intrusion guidance document in early 2007. Internet training was given in 2007 and classroom training is starting in 2008.
What it Is . . . What It Is Not!

ITRC VI document is . . .
- Guidance
- Flexible
- Informative
- Iterative
- Broad ranging

ITRC VI document is NOT . . .
- Regulation
- Prescriptive
- Restrictive
- Linear
- Limited

More details on the ITRC guidance
The ITRC scenarios document gives a recommended step-by-step approach for a variety of site scenarios, including 2 with petroleum hydrocarbons.
Regulatory Approach for HC Sites

- **Range of Regulatory Approaches:**
  - USEPA: 2002 Guidance not recommended for UST sites
  - ASTM – Critical distance reduced from 100’ to 30’
  - Some regulatory agencies include a 10X biodegradation factor
  - ITRC: Use vertical profile to demonstrate

- **Evidence suggests these approaches are overly conservative for most petroleum release sites**

Presently, most vapor intrusion guidances ignore bioattenuation. For those that discuss or consider it, there is a range of approaches to account for it. Some States simply decrease the distance of concern. Some give a 10 times allowance (typically by increasing screening levels) for bioattenuation. There is general recognition that these regulatory approaches tend to be overly conservative.
ASTM just completed a standard for vapor intrusion as it applies to property transactions. The standard was released on March 3, 2008. Because it uses larger screening distances, it will increase the number of sites that need to have a vapor intrusion assessment.
ASTM VI Standard

*Vapor Intrusion Condition (VIC)* is defined as “the presence or likely presence of any volatile chemical of concern in existing or planned structures on a property resulting from an existing release or a past release from contaminated soil or groundwater on the property or within close proximity to the property, at a concentration that presents or may present a human health risk.”

The Standard defines a new term/acronym: the Vapor Intrusion Condition.
The ASTM standard consists of 4 tiers. Tier 1 & 2 are analogous to Tier 1 in the ASTM Phase 1 standard.
The Standard identifies the following search distances. Note the long distances for the initial (Tier 1) search.

Slide courtesy of Anthony Buonicore, Chairman ASTM VI Task Group
Liability concerns is a big part of vapor intrusion. Those at risk include consultants, property owners (past, current & future), lenders, and insurance companies.

Slide courtesy of Anthony Buonicore, Chairman ASTM VI Task Group
Goals of a Site Conceptual Model

- Provide an understanding of the existing environmental and geologic conditions at the site based on available information.
- Minimize or eliminate any unnecessary activities.
- Prioritize site based on risk to human health and the environment.
- Based on the SCM, provide a clear path forward towards closure.
Generalized Site Conceptual Model for Vapor Intrusion
Data Needs to Constrain VI Site Conceptual Model

- Sample spacing
- Collection depths (vertical profile)
- Sub slab samples-needed?
- Gas data: O₂, CO₂, CH₄, plus HC’s
- Soil physical parameters:
  - Soil Moisture
  - Permeability
  - Porosity
  - TOC
Slide Topic: Industry experience with petroleum vapor intrusion

Based on industry experience, petroleum vapor intrusion impacts are generally associated with:

1) Direct NAPL impacts on a building foundation
2) NAPL or dissolved hydrocarbon impact on building sump
3) NAPL impact on preferential flow pathway or
4) Diffusion of vapors from subsurface NAPL source

Slide Presentation: Discuss industry experience with petroleum vapor intrusion impacts

Key Points:

Current USEPA VI guidance provides GW screening concentrations for benzene and other petroleum hydrocarbons in the low ug/L range (i.e., 5 ug/L for benzene). These low screening concentrations are not consistent with industry experience that vapor intrusion impacts are not associated with low concentrations of petroleum hydrocarbons dissolved in groundwater.
When is a SCM Needed?

- Prior to initiation of site assessment activities.
- When site circumstances or conditions change or whenever new data are acquired.
- Whenever a health risk assessment or receptor pathway investigation is initiated.
- Whenever a closure document or correction action plan is submitted.
Discussion Topics for Petroleum Hydrocarbon VI SCM’s

- What soil gas data are needed for petroleum hydrocarbon vapor intrusion SCM’s?
- Examples of sites with petroleum hydrocarbon vapor intrusion to indoor air?
- How should we deal with background ambient air values of benzene when developing a SCM for indoor air?
- What data are needed to screen out low risk sites from detailed analysis of the vapor intrusion pathway?
There are a number of basic principles that need to be understood in order to understand and effectively manage the vapor intrusion pathway. Some of these principles you may not have had in school or have never really used them, so you are rusty. We will be using them throughout the rest of this seminar so we will review them now.
The Most Common Goof

1 ug/L Benzene equals:

a) 1 ppbv
b) 1 ppmv
c) 330 ppbv
d) None of the Above

Vapor units is one of the most common mistakes being made by practitioners in this field. Let’s see how you do:
The Most Common Goof

Sent: Wednesday, November 20, 2007 11:36 AM
Subject: VI Question
Blayne,

I have a technical question for you. I’m worried that some deep soil gas data I just collected might have been compromised by ambient air leakage from the surface. The measured oxygen level was 44% much higher than we expected in deeper soil gas. The data are attached. What is your opinion?

An e-mail regarding units. See if you can spot the error.
How do Vapors Move?

Movement (Flux) = K d?/dx

where: K is a proportionality constant
d?/dx is a gradient

<table>
<thead>
<tr>
<th>Property</th>
<th>Equation</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Momentum:</td>
<td>Flux = K dH/dx</td>
<td>hydraulic cond</td>
</tr>
<tr>
<td>Heat (Poisson’s):</td>
<td>Flux = Φ dT/dx</td>
<td>thermal cond</td>
</tr>
<tr>
<td>Mass (Fick’s):</td>
<td>Flux = D dC/dx</td>
<td>diffusivity</td>
</tr>
</tbody>
</table>

Momentum, Heat, Mass ALL Move from High to Low

The fundamental equation describing momentum, heat, and mass movement is the same. Movement or flux is equal to a proportionality constant times a gradient. For momentum (groundwater or balls), the equation is known as Darcy’s Law. For heat, the equation is known as Poisson’s Law. For mass, it is known as Fick’s Law. The proportionality constant is known as the diffusivity or diffusion coefficient (D).

Balls, heat, and mass all move the same way: downhill, hot to cold, high to low concentration. As you will see, people often tend to forget this fundamental concept and make incorrect decisions.
Knowledge of Fick’s Law enables one to determine the direction of soil gas movement, and hence the direction of the source, from vertical gradients of the soil gas. Three types of common profiles are shown for sources at different locations in the vadose zone. Note that the flux is down the concentration gradient even when the flux is going “uphill” with respect to depth in the vadose zone.
**How Fast do Things Move?**

\[
\text{Distance} = (2\times D_e \times t)^{1/2}
\]

where: \( D_e \) is effective diffusivity, \( t \) is time

Vapors through the Vadose Zone:
- \( D_e = 0.01 \text{ cm}^2/\text{sec} \)
- \( \text{Distance} = (2\times0.01 \times 31,000,000) = 800 \text{ cm/yr} \)

Vapors through Liquid (into/out of GW):
- \( D_e = 0.000001 \text{ cm}^2/\text{sec} \)
- \( \text{Distance} = (2\times0.000001 \times 31,000,000) = 8 \text{ cm/yr} \)

**Transport in Vadose Zone 100 times faster than in GW**

An estimate of how fast contaminants move in the vadose zone can be obtained by a simple calculation based upon the diffusivity.

Contaminants move through the vadose zone by molecular diffusion at a rate of 800 cm/yr, which is 8 m/yr, or approx. 25 ft/yr, or 1 inch a day.

Contaminants move through liquid (into or out of) 100 times slower because the diffusion coefficient for liquids is 10,000 times lower. Thus, volatilization of contaminants out of an undisturbed water interface (e.g., groundwater) is glacially slow and typically orders of magnitude below equilibrium. This is a crucial concept when using groundwater data to calculate soil gas concentrations. Calculated soil gas values will always be over estimated.
Contaminant Partitioning

Groundwater to Soil Gas (Henry’s Constant):

\[ H = \frac{C_{sg}}{C_w}, \text{ so, } C_{sg} = C_w \times H \]

Example: \( H_{\text{benzene}} = 0.25 \) (dimensionless)

For GW Conc = 10 ug/L

\[ C_{sg} = 10 \times 0.25 = 2.5 \text{ ug/L} \]

Assumes Equilibrium. Very Rarely Achieved
(no mixers or blenders in the subsurface)

Partitioning refers to the distribution of molecules between different phases. Partition coefficients are determined empirically by laboratory measurement. The partition coefficient for water to air partitioning (e.g., groundwater to soil gas) is called the Henry’s Constant or Henry’s Law. It simply is a ratio of the concentration in the air to the concentration in the water. It is simple to calculate the soil gas concentration from groundwater data or the reverse from the dimensionless Henry’s constant.

Henry’s constants are based upon equilibrium being reached. The container was vigorously mixed. Mixers do not exist in the subsurface so equilibrium not reached and actual soil gas concentrations are far below calculated ones.
This slide shows data from the NY Endicott site comparing measured soil gas concentrations near groundwater to groundwater concentrations. The line shows the predicted values based upon equilibrium partitioning using the Henry's constant. You can see that the vast majority of points fall orders of magnitude below the calculated values. This proves that soil gas values predicted by groundwater are over-estimated.

Slide courtesy of Dr. William Wertz, NYDEC
This slide compares measured soil gas concentrations to soil gas concentrations predicted from co-located soil phase data for petroleum hydrocarbons. You can see that the vast majority of measured values fall orders of magnitude below the calculated values. This proves that soil gas values for hydrocarbons predicted from soil data are likely to be over-estimated. The same is not necessarily true for chlorinated solvents.
A common term in the vapor intrusion “community” is the attenuation factor also called the alpha factor. The soil gas alpha factor is a ratio of the indoor air concentration to the soil gas concentration. The groundwater alpha factor is a ratio of the indoor air concentration to the groundwater concentration times its Henry’s constant.

Since indoor air values are lower than subsurface values, alpha factors tend to be less than 1, hence lower numbers mean greater attenuation. Thus, inverse alpha factors are often easier to understand.

The EPA draft guidance uses very stringent alpha factors, determined empirically from a limited data base. More recent and larger data bases (IBM Endicott) are showing that the alphas should be orders of magnitude lower, especially for petroleum hydrocarbons.
In the draft VI guidance, alpha factors can are summarized vs. depth in Figure 3. As you can see in Figure 3a, the highest soil gas alpha is 0.002 at 5 feet below the structure. The inverse is 500.

For groundwater, Figure 3b shows the highest alpha is ~.001. The inverse is 1000.
Johnson and Ettinger Model

\[ \alpha = \frac{C_{\text{indoor}}}{C_{\text{vs}}} = \frac{D_{\text{eff}} A_B}{Q_{B} L_T} \exp \left( \frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{eff}}^\text{crack} \eta A_B} \right) \]

\[ = \frac{D_{\text{eff}} A_B}{Q_{B} L_T} \exp \left( \frac{D_{\text{eff}}^\text{crack} A_B}{Q_{\text{soil}} L_{\text{crack}} \eta} \right) - 1 \]

While this equation is in terms of an alpha factor, in reality, what the the J-E model is trying to do is estimate a value for the effective diffusivity, the proportionality constant in Fick’s Law that we talked about previously. There is no easy way to do this because too many factors influence this term. As you can see, there are many variables, some of which can not be directly measured or easily measured.
Measured attenuation factors for hydrocarbons can be orders of magnitude below “no-degradation” model predictions.

Slide compliments of Robbie Ettinger, Geosyntec
Using Alpha Factors to Calculate Screening Levels

For Soil Gas:

\[ C_{sg} = \frac{C_{\text{indoor}}}{\alpha_{sg}} \]

For Groundwater:

\[ C_{gw} = \frac{C_{\text{indoor}}}{(H \ast \alpha_{gw})} \]

Example: \( C_{\text{in}} \) benzene = 0.3 ug/m³

\[ C_{sg} (5') = \frac{0.3}{0.002} = 150 \text{ ug/m}^3 \]

\[ C_{gw} = \frac{0.3}{(0.20 \ast 0.0005)} = 30 \text{ ug/L} \]

By using alpha factors, one can calculate target levels or allowable levels for soil gas and groundwater by knowledge of the acceptable indoor air concentration.

By allowable level, I mean the concentration of a contaminant in the indoor air, soil gas, groundwater, or soil that fails the upward vapor risk calculation. It also is referred to as risk based screening level (RBSL), target level, ESL, PRG, acceptable value, look-up value, screening level, etc. This term will be used quite frequently throughout the remainder of this seminar.

Many consultants are not familiar with using alphas and calculate incorrect target values.
A summary of the alpha factor and corresponding acceptable soil gas levels for various States and the EPA draft guidance shows large variation and illustrates the main point: the levels are variable from State to State.

Notice the difference in fail values for the different EPA VI guidance questions.

<table>
<thead>
<tr>
<th>State</th>
<th>Alpha</th>
<th>1/Alpha</th>
<th>Fail Level (ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>0.002</td>
<td>500</td>
<td>150</td>
</tr>
<tr>
<td>CA-DTSC</td>
<td>0.002</td>
<td>500</td>
<td>42</td>
</tr>
<tr>
<td>CT</td>
<td>0.0013</td>
<td>770</td>
<td>192</td>
</tr>
<tr>
<td>NJ (Subslab)</td>
<td>0.05</td>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>EPA Q4</td>
<td>0.1</td>
<td>10</td>
<td>3.1</td>
</tr>
<tr>
<td>EPA Q5</td>
<td>0.002</td>
<td>500</td>
<td>155</td>
</tr>
<tr>
<td>EPA Q6</td>
<td>0.1</td>
<td>10</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Risk based screening levels vary from state to state and guidance to guidance. Acronyms are plentiful. The VI professional needs to know what they are, where they come from, and how and when to use them.
Allowable indoor air concentrations are so low because of the ultra conservative assumptions that are used, especially in regards to exposure time.
### Reasonable Exposure Times?
(Benzene 1e-6 risk, 5' deep SG sample)

<table>
<thead>
<tr>
<th>Agency</th>
<th>Residential</th>
<th>Workplace</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>OEHHA</td>
<td>36</td>
<td>61*</td>
<td>1.7</td>
</tr>
<tr>
<td>DTSC</td>
<td>42</td>
<td>84</td>
<td>2</td>
</tr>
<tr>
<td>SF ESLs</td>
<td>85</td>
<td>145*</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Corrected for ventilation rate

**Note: Ratio Should be 5**

This table gives a summary of the ratio of the allowed soil gas value for benzene for workplace vs. residential settings for three California agencies published RBSLs. The OEHHA & SF ESL values have been reduced by a factor of two to take out the effect of the different ventilation rate between residential and commercial settings that is incorporated in their tabulated values. The ratio assuming workplace exposure times of 8 hours/day, 250 days/year, for 25 years should be 5. The agency values are about 2.5 times too conservative.
Screen Out More Sites By:

• Using Correct Risk Level
  – 1 in 1 million: Residences, Schools, Hosp
  – 1 in 100,000: Commercial Settings (cumulative)
  – 1 in 10,000: Mitigation Required

• Adopting More Realistic Exposure Times
  – Workplace: 8 hrs/day, 250 days/yr, 25 yrs (5x)
  – School: 8 hrs/day, 180 days/yr, 6 yrs (30x)

• Accounting for Bioattenuation

More sites will be screened out if more realistic screening criteria are used such as more realistic exposure times, especially for schools and hospitals, and adopting more reasonable risk criteria. For State reimbursement funds, reasonable screening of sites will prevent draining the fund balances.
Evaluating the Vapor Intrusion Pathway

Nationwide Study of Subsurface Petroleum Hydrocarbon Vapor Occurrence & Attenuation

by
Robin V. Davis, P.G.
Project Manager
Utah Department of Environmental Quality
Leaking Underground Storage Tanks
rvdavis@utah.gov

Vapor Intrusion Work Shop & Session, March 16-19, 2008
20th Annual National Tanks Conference, Atlanta, Georgia

Thanks to: NEIWPCC, EPA, ASTSWMO, API
Purpose

- Explore why so many LUST sites exist nationwide, but so few report vapor intrusion to indoor air
- Evaluate mechanisms & show characteristics of subsurface bio-attenuation of petroleum hydrocarbon vapors
- Determine when VI pathway is complete & if further actions are necessary (e.g., sub-slab)
- Apply Subsurface Bio-Attenuation Factors for petroleum hydrocarbons to avoid unnecessary, costly VI investigations

- Guide uses Johnson-Ettinger (J&E) Model to develop generic screening levels for soil vapor & groundwater to protect VI pathway.
- J&E Model does not consider bio-attenuation of petroleum hydrocarbons (works well for non-degradable compounds: solvents).
- Guide therefore recommends it NOT be used for VI evaluation at UST sites.
- Guide recommends forming work group of EPA & state regulators to further study behavior of subsurface petroleum associated with VI pathway.
2003-2005: EPA OUST Work Group for Petroleum Hydrocarbons & VI Pathway, CONCLUSIONS:

High-quality site data necessary for evaluating petroleum hydrocarbon occurrence & attenuation

- Soil vapor concentrations: multi-depth, sub-slab
- Dissolved concentrations
- Groundwater depth & gradient
- Contaminant source zone extent
- Soil type

Large volume data necessary to understand trends

Compile data in a way that yields meaningful interpretations
SCOPE

- Compile & evaluate large volume of nationwide data, high-quality, readily accessible, from well-studied sites:
  - 243 soil vapor sampling events (82 events since LUSTLine #52, May 2006) (183 soil vapor sample points/wells)
  - 51 sites/geographic locations nationwide, United States & Canada (Colorado data analyzed separately)

- Compare findings at nationwide sites to representative Utah Case Study, Hal’s Chevron

- Compare nationwide measured vapors to models & quantify differences
Map Key

- Number vapor sample events per state

- Colorado data analyzed separately, 3907 SV events

- Chatterton Research Site, British Columbia

- Ottawa, Ontario

- Unknown location “Refinery Site”
**Profile of Multi-Depth Vapor Monitoring Well & Signature Characteristics of Vapor Bio-Attenuation**

Hydrocarbon concentrations high in source zone, O2 depleted, CO2 generated. As vapors diffuse upward through clean soil, hydrocarbons deplete, O2 & CO2 return to atmospheric proportions.

**EXPLANATION**
- **Oxygen, %**
- **Carbon Dioxide, %**
- **Benzene, ugm3**
- **TPH, ug/m3**

**Contaminated soil zone**
- **Depth to groundwater**
- **Edge of free product 0.1 ft thick**
- **Benzene 1,000 ug/L**

**AF** Subsurface Bio-Attenuation Factor, generally in clean soil: *Shallow SV / Deep SV*
Insignificant AF in shallow source zone. Significant AF overlying strong source with 2-7 feet clean overlying soil.

Tour de Plume

DEPARTMENT OF ENVIRONMENTAL QUALITY
Case Study: Hal’s Chevron, Green River, Utah, continued

Insignificant AF overlying weak dissolved plume where benzene 1000-5000 ug/L

Tour de Plume

EXPLANATION
- Underground Sewer Line
- Underground Water Line
- Overhead Power Line
- Underground Product Line
- Horizontal Well Location

- Vapor Well Nest
- Monitoring Well
- Manhole

Approach Stream/Wellhead (4000-5000)

[Map and diagram with labeled locations and data points]
Nationwide Examples of Significant Attenuation

AF 1E-04 to 1E-05

Very Strong Sources with 5 to 7 feet Clean Overlying Soil

Coachella, CA COA-2
(Ririe, et al 2002)
AF 1E-04

Beaufort, SC NJ-VW2
(Lahvis, et al., 1999)
AF 1E-05

Benzene (ug/m3)

O2 & CO2 (% V/V)
Nationwide Examples of Insignificant Attenuation...

AF ~1E+00 to 1E-01
Very Strong, Shallow Sources, Little Clean Overlying Soil

Conneaut, OH VMP-1
(Roggemans, 1998; Roggemans et al., 2001)
AF 7E-01

Salina Cash Saver VMW-1
Utah DEQ, 7/07
AF 1E-01 (excludes sub-slab)
OA <3.6E+00

FP on GW
Nationwide Examples of Insignificant Attenuation

**AF 1E+00 to 4E-02**

Very Weak Source Strength, Little Hydrocarbon to Degrade

---

Newport Beach, CA (Ririe, et al 2002)
NB-2
AF 1

Side Lake Store, MN
(Minnesota Pollution Control, 2004)
VP-1
AF 4E-02

---

**O2 & CO2 (% V/V)**

---

**Benzene (ug/m3)**

Dissolved Benzene 1000 to 5000 ug/L

---

Dissolved Benzene 1100 ug/L
Example of Overlooked Significant Attenuation

**Shallow vapor point set too deep at 5 feet shows insignificant attenuation**

Mission Valley Terminal, San Diego, CA
TA-03
AF 1E+00

**Shallow vapor point in nearby well set ~2 feet higher shows significant attenuation**

Mission Valley Terminal, San Diego, CA
SV-16-AS, AMS 2/23/2004
AF 1E-03
KEY FINDINGS FROM FIELD DATA

- Characteristics of vapor occurrence & attenuation at Hal’s Chevron Case Study are consistent with 242 other events nationwide.

- Significant vapor bio-attenuation with 2 to 7 feet clean overlying soil
  - AF 1E-02 to 1E-05

- Insignificant vapor bio-attenuation over weak dissolved plumes & in areas with no clean overlying soil
  - AF >1E-02

- Weak dissolved plumes with clean overlying soil, vapor intrusion pathway not complete:
  - Benzene ≤5,000 ug/L
  - TPH ≤10,000 ug/L
Compare Nationwide Field Data to Results Predicted by Johnson-Ettinger Model (1991)

- J&E excellent screening tool, cautious, biological degradation not considered

Model assumes vapors migrate by diffusion through vadose zone, vapor concentrations decrease upward to predicted sub-slab concentrations. Those sub-slab vapors migrate across foundations & enter overlying buildings by advection. Indoor vapors are diluted according to building air exchange rate.

- Run model based on field data to obtain J&E predictions, plot & compare predicted results to field data
Very Strong Sources with 4 to 7 feet
Clean Overlying Soil

Model Under-Predicts Attenuation by 100x to 100,000x
Very Strong Sources with No Clean Overlying Soil

Model Closely Predicts Attenuation
Weak Sources with Little Hydrocarbon to Attenuate

Model Under-Predicts Attenuation by 1x to 100x
Total Petroleum Hydrocarbon Vapor Evaluation

Very high source strength,
TPH 180,000,000 ug/m³
Kent, OH VMP-1
(Roggemans, 1998; Roggemans et al., 2001)
AF 2E-03

High source strength,
TPH 100,000,000 ug/m³
Akron, OH VMP-1
(Roggemans, 1998; Roggemans et al., 2001)
AF 1E-03

Moderate source strength,
TPH 18,000,000 ug/m³
Beaufort, SC NJ-VW2
(Lahvis, et al., 1999)
AF 8E-05

Dissolved TPH
67,100 ug/L
Comparison of TPH Field Profiles to 3-D Numerical Model


**Very Strong Vapor Source**

Model under-predicts attenuation 10x to 100x

**Strong Vapor Source**

Model under-predicts attenuation 100x

**Moderate Strength Vapor Source**, common at most LUST sites

Model under-predicts attenuation ≤10x
Comparison of High-Quality Field Data to 2 Models

- **J&E Model**
  - Under-predicts benzene vapor attenuation up to 100,000x in strong source areas with up to 7 feet clean overlying soil.
  - Accurate prediction, under-prediction by ≤10x in weak source areas & in strong source areas with little clean overlying soil.
  - CONCLUSION: Partitioning from free- & dissolved phase to vapor phase greatly over-predicted (Henry’s Law Constant).

- **Abreu & Johnson Model**
  - Fairly accurate predictions in moderate strength sources with as little as 5 feet clean overlying soil, under-predicts vapor attenuation by <10x.
  - Under-predicts vapor attenuation by 10x to 100x in high strength sources, <7 feet clean overlying soil required.
# RECOMMENDED 100-FOLD ATTENUATION FACTOR TO EPA 2002 OSWER GUIDE (residential)

## COARSE-GRAINED SOIL

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Depth feet bls</th>
<th>Soil Gas Concentrations ug/m³</th>
<th>Groundwater Concentrations ug/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>J&amp;E Predicted</td>
<td>Proposed</td>
</tr>
<tr>
<td>Benzene</td>
<td>≤5</td>
<td>3.1</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>&gt;5</td>
<td>31</td>
<td>3,100</td>
</tr>
<tr>
<td>TPH (1,3,5-trimethylnzene)</td>
<td>≤5</td>
<td>60</td>
<td>6,000</td>
</tr>
<tr>
<td></td>
<td>&gt;5</td>
<td>600</td>
<td>60,000</td>
</tr>
</tbody>
</table>
# RECOMMENDED 1 TO 10-FOLD ATTENUATION FACTOR TO EPA 2002 OSWER GUIDE (residential)

## FINE-GRAINED SOIL

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Depth feet bls</th>
<th>Soil Gas Concentrations ug/m³</th>
<th>Groundwater Concentrations ug/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>J&amp;E Predicted</td>
<td>Proposed</td>
</tr>
<tr>
<td><strong>Benzene</strong></td>
<td>≤5</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>&gt;5</td>
<td>500</td>
<td>5,000</td>
</tr>
<tr>
<td><strong>TPH (1,3,5-trimethlybenzene)</strong></td>
<td>≤5</td>
<td>5,000</td>
<td>5,000</td>
</tr>
<tr>
<td></td>
<td>&gt;5</td>
<td>9,000</td>
<td>90,000</td>
</tr>
</tbody>
</table>
WHEN DOES VAPOR INTRUSION OCCUR?

Catastrophic petroleum releases

_Sudden release cannot displace water-saturated soil, vapors transport quickly_

Main St, Gunnison, Utah

Responsible Party

Telephone Company

Law Office

Business

GAS
WHEN DOES VAPOR INTRUSION OCCUR?

Modified building HVAC systems, not to code, no air exchange

Free product on GW directly beneath building
VAPOR INTRUSION WORK GROUPS

- API-funded contractor (GSI) compiling & analyzing national petroleum vapor data in Access database (includes Colorado data)

- ASTM Vapor Intrusion Task Group E 50.02.06
  - “Assessment of Vapor Intrusion into Structures on Property Involved in Real Estate Transactions,” final March 3, 2008
  - VERY CAUTIOUS: Requires assessment of VI pathway for petroleum hydrocarbons within 528 feet (1/10 mile) of property

- EPA OUST put Work Group for Petroleum Hydrocarbons “on hold”
Case Studies to Evaluate Hydrocarbon Vapor Attenuation in the Vadose Zone

G. Todd Ririe
BP
La Palma, CA
## Attenuation Factors

<table>
<thead>
<tr>
<th>Type of Data</th>
<th>U.S. EPA Attenuation Factor</th>
<th>2002 Guidance</th>
<th>2007 Guidance*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow Soil Gas</td>
<td>0.1</td>
<td></td>
<td>0.02 (residential)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.002 (industrial)</td>
</tr>
<tr>
<td>Deep Soil Gas</td>
<td>0.01</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ground Water</td>
<td>0.001</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*Value expected to be included in revised U.S. EPA guidance due out in 2007.

An attenuation factor is simply the ratio of the two concentrations: the indoor air and the subsurface media. For soil gas, the relationship can be expressed as:

\[ X_{\text{indoor}} = \left[ X_{\text{soil gas}} \right]^{\alpha} \] (Eq. 2-1)

Where:
- \( X_{\text{indoor}} \) = Concentration of VOC in indoor air (\( \mu g/m^3 \));
- \( X_{\text{soil gas}} \) = Concentration of VOC in soil gas (\( \mu g/m^3 \)); and
- \( \alpha \) = Attenuation coefficient (unitless).

Note that smaller numbers = greater attenuation in this calculation.
Case Study #1
Free Product Under Active Distribution Facility

- Sandy Soil-Desert Area
- Groundwater at 10 feet
- Free Product (gasoline and diesel)
- Clean Soils (where soil gas collected)
- Large Asphalt Slab
- Non slab area little vegetation no irrigation
Case Study #1-Map of Distribution Facility

- Free Product Plume on Water
- Hydrocarbons Dissolved in Water

- Above Ground Storage Tanks
- COA-1 (No Asphalt Cover)
- COA-2
- COA-3
- Loading Rack
- Plant Office and Warehouse
- Garage

Approx. Scale (Feet)
Vertical Profile of Soil Gases at Distribution Facility

Attenuation before oxygen threshold of 4-5%

Free product is at 10 feet
Degradation here is a first order decay constant (reason for log scale). For example at 2 feet attenuation of 0.1 to 100, equivalent to attenuation factor of 1000, or in comparison to earlier slide 0.001 factor.
Model case 1 is simple source concentration to atmospheric concentration by diffusion alone. Case 2 is a two-layer model with a slab factor to account for leakage through slab cracks.
Case Study #2
Home Over Former Oil Field Sump

• Sandy to silty sandy soils - Central Coast
• Perched Water 4 ft (Groundwater > 60 feet)
• Predominantly crude oil
• Affected soil 4-15 feet bgs
  – TPH 100 to 10000 mg/kg
  – Benzene < 0.1 mg/kg
  – BTEX < 30 mg/kg (mostly < 1 mg/kg)
• Slab under house
• Non-slab area formerly irrigated
One Way to Start Collecting Indoor Air Samples

Probably want to get permission before going into homes for indoor air or subslab gas sampling.
Collecting soil gas samples adjacent to a home is still preferable to doing subslab sampling and can be done while minimizing impact.
Subslab samples can be collected in the driveway adjacent to the home which is preferable to going in the house for this type of sampling.
Home over Sump

Bare Sand

Grass

Concrete

Garage

Sample Locations

- Single Story
- Slab on grade
- Heating only (no AC)

- Nested probes
- Sub-slab probe

3 m
Vertical Profile of Soil Gases at House over Sump

SG-4
No Slab

SG-12
Sub-Slab
Case Study #3
GW Plume Under Service Station

- Sandy Soils - S. CA beach area
- Groundwater at 5.5 feet
- Dissolved gasoline plume (1 to 3 ppm)
- Predominantly Clean Soils
- Former service station now demolished
- Bare ground, no irrigation
- No slab
Collecting Soil Gas as Service Station Site
Service Station-Sandy Soils over GW Plume

Clean Soils

Some Soil Contamination

Depth (feet)

O₂ Concentration (%)

CO₂ Concentration (%)

CH₄ Concentration (ppm)

Benzene Concentration (ppm)
Case Study #4
Building Over Oil Field

• Clay-rich soils-Orange County
• Deep groundwater- 120 feet
• Clean Soils
• Shallow oil field (several thousand ft)
• New construction forced soil gas analysis
• Slab under buildings over 50 yrs old
Location of Building on Edge of Oil Field
Building over Oil Field

Soil Gas Under Slab = 3, 4, and 5.

Soil Gas Outside Slab = 1, 2, 6 and 7.
Hand augering outside building

Clayey soil at 5 to 10 feet below surface
Drilling through concrete slab

Augering below slab
Outside of mobile lab

On site analysis with mobile lab
First set of preview data collected with hand-driven probe

Constructing dedicated sample points
Dedicated Soil Gas Probes

Tygon Tubing

6” Bentonite Seal

12” Sand Pack

Native Soil

6” Bentonite Seals

Native Soil Backfill

Native Soil

12” Sand Pack

Soil Gas Sample Tip

Soil Gas Sample Tip
Vertical Profile of Soil Gases—Building over Oil Field

Depth (feet)

O₂ Concentration (%)

CH₄ Concentration (ppmv)

No Slab
Sub-Slab
SUMMARY

- Four case studies evaluated HC vapor migration using vertical profiles
- HC vapors showed attenuation when soils were clean
- Oxygen levels under slabs were greater than 5% in all cases examined
- Oxygen levels above 5% are a good barrier to upward migrating HC vapors
- Methane used as a surrogate for benzene

CH4 easier to measure at low levels in the field, instrumentation to do this is readily available, easy to document biodegradation using isotopic approach, extensive literature exists on bio-attenuation of CH4-particularly in landfills
In this part of the seminar, we will discuss the primary techniques used to assess the vapor intrusion pathway, including the pros & cons of each.

Methods to Assess VI

• Indoor Air Sampling
• Predictive Modeling
• Measure Flux Directly
• Soil Gas Sampling
• Supplemental Tools/Data
Vapor intrusion risk assessments are complicated by a variety of factors or fundamental problems.

1. Inconsistent and contradictory regulations coupled with site-specific conditions make the process complicated and slow.

2. Vapors and vapor intrusion are a new area for most environmental professionals. A general lack of expertise among regulators, consultants, subcontractors and the public often results in things being done incorrectly (e.g., program design or sampling or analysis) or in a lot of work being done needlessly (using incorrect screening levels).

3. Ultra-conservative risk based screening levels results in few sites screening out and the vast majority screen in.
The keys to effective vapor intrusion assessments are picking the proper approach, determining the correct screening levels, sample & analyze correctly and efficiently, know when and how to use supplemental assessment tools, and to know how to demonstrate bioattenuation if petroleum hydrocarbons are the COC.
The most important ingredient for cost effective and efficient VI investigations is the experience of the person/firm doing the collection. Is the collection being done by a firm that has prior experience? Is it a routine part of their services or an occasional part? Do they put experienced people in the field who can think or junior staff who aren’t well versed? This applies to the consultant and their subcontractors.

Soil gas, like soil, is not homogenous in most cases. So you need enough data to give decent coverage near, around, or under the receptor. Simpler collection systems with small volumes are advantageous as there is less to go wrong and enable higher production per day (20+ samples per day). Less expensive analytical methods (8021, 8260) enable more analyses for reasonable cost. Real-time data can be extremely helpful to track soil gas contamination laterally and vertically.

Legal considerations often dictate what additional work needs to be done at what standards.

All of these issues affect the investigation progress.
Approach Generalizations

- Indoor Air
  - Always find something
  - Multiple sampling rounds: time consuming & expensive
- Groundwater Data
  - Typically over-predicts risk
- Soil Gas Data
  - Transfer rate unknown
- Sub-slab Soil Gas Data
  - Transfer rate unknown
  - Intrusive

Each investigatory approach has pros and cons that must be considered before choosing the one to use at a site.
Indoor Air Measurement

• Pros:
  – Actual Indoor Concentration
• Cons:
  – Where From?
    • Inside sources (smoke, cleaners)
    • Outside sources (exhaust, cleaners)
  – No Control
  – Higher chance of false positives
  – Snapshot, limited data points
  – Expensive!!

Measuring indoor air might seem to be the most direct and simplest approach, but it has its share of problems. The biggest problem is complications from background sources of contaminants. Many commonly used household products contain some of the target compounds of concern. For example, benzene from gasoline, PCE from dry cleaned clothes, TCA from degreasing cleaners. In addition, the protocols are laborious, intrusive, offer little control, and are expensive. For these reasons, the EPA and many States shy away from this method. However, this method may still be the method of choice if the contaminant of concern is not one commonly found in household products (e.g., 1,1 DCE).
Groundwater Data

- Preexisting Data Often Exist
  - Over proper well screen interval?
  - Coverage typically limited; interpolation
- Gather New Data
  - Well location, construction, sampling
- Perched/clean water layer?
- Likely Will Over-predict VI Risk

At many sites, groundwater data already exist. But, it may not be from a well screened across the interface. Plus, coverage often is limited so you have to interpolate the data.

Some States prefer groundwater data. Or if groundwater is very shallow, it may be the only option. If you are going to collect new groundwater data, be sure that the well locations and construction are correct.

Also, be sure that you aren’t sampling perched water infiltrating from the surface.
Soil Phase Data

- Soil data generally not acceptable in VI Assessment
- Existing soil data – line of evidence
  - Can “screen in” sites
  - Cannot be used alone to “screen out” sites
- Convert to soil gas concentrations
  - Partitioning equations exist. Likely overestimate.

Soil phase data are generally not acceptable for VI investigations by most States. This is because equilibrium partitioning is rarely achieved so it is difficult to predict soil vapor concentrations from soil phase data, and hence in turn, the vapor intrusion risk.

In the absence of soil gas data, existing soil data is typically used as a line of evidence

- Soil data can be used to “screen in” sites, but cannot be used alone to “screen out” sites
- Soil data may have elevated reporting limits or volatilization losses, therefore non detect (ND) in soil does not mean “no potential for VI”

- One can convert soil data to soil gas concentrations using partitioning equations. This result provides an estimate of the soil gas concentration in the vadose zone.

- If soil sampling is conducted, perform the sampling using accepted methods that minimize VOC losses
Modeling

• Pros:
  – Can Use GW, Soil (?), Soil Gas Data
  – Relatively Easy
• Cons:
  – Which Version to Use?
  – No Validation – Erroneous Conclusions
  – Often Too Restrictive
  – Can Tweek to Your Pleasure

The use of models to calculate an indoor air concentration, and in turn a health risk, is commonplace. Existing models use groundwater, soil, or soil gas data and are relatively easy to use. In general, if default parameters are used, they tend to overcalculate the risk for most situations.

Several versions currently exist with different default values for various parameters, so one must be careful to know what version they are using. Regulators must be careful with using modeling results for a number of reasons, one being that it is easy to try and change the values of some of the variables to get a passing value. As a result, some States will let you use the models as a screening tool, but not give complete closure.
How Well Does J-E Predict?  
(From GW & Soil Data)

- **Hydrocarbons**
  - Calculated SG value too high by 10-1000x
  - No bioattenuation (10 to 1000x reduction)
  OVER PREDICTS IN ALMOST ALL CASES

- **Chlorinated Solvents – Deep Source**
  - Calculated SG value too high by 10-1000x
  OVER PREDICTS IN MOST CASES

- **Chlorinated Solvents – Surface Source**
  - Calculated SG value too low by 10-1000x
  UNDER PREDICTS IN MOST CASES

If you are going to use the models/spreadsheets, you need to be aware of the limitations. If the groundwater or soil spreadsheets are being used, the spreadsheet calculates the soil gas concentration assuming equilibrium partitioning. This is likely to give a soil gas concentration orders of magnitude higher than actual values. Also, for hydrocarbons, there is no allowance for bioattenuation. So, the result is that the spreadsheet is likely to over predict risk for hydrocarbons in almost all cases, unless right at the surface. For chlorinated compounds, the spreadsheet is also likely to over predict, but not as much since bioattenuation is not as prevalent. But, if surface sources exist, then vapor clouds might exist and the actual soil gas concentration might be higher than calculated, so in turn, the risk will be underestimated.

Because these models tend to over-predict the risk, especially from groundwater and soil data, you should be careful to verify the predicted risk if they show you are failing.
Surface flux chambers are attractive because they give a direct measurement of the flux into the structure or out of the soil. This eliminates the need to know the effective diffusivity and the uncertainty inherent in the models. The biggest drawback with chambers is whether they can be placed in the proper locations in an existing structure. Also, few regulators, consultants, or vendors have used them, so they are unfamiliar of the protocols to use and how to interpret the data. As a result, regulatory acceptance is limited. In slab-on-grade structures or undeveloped lots or crawl spaces, surface flux chambers may be the best method to use. Chambers will also prove useful to support the presence of bioattenuation.
Photo of a static flux chamber equipped with a LandTech GEM 2000 real-time oxygen, carbon dioxide, and methane analyzer used to collect data continuously.
Measurement of soil gas is by far the most preferred approach around the country. Actual soil gas data are reflective of subsurface properties, are less expensive than indoor air measurements, and allow real-time results. The screening levels are also higher so there is less chance to be chasing blanks.

There are some drawbacks, including the lack of knowledge of the transfer rate, very restrictive screening levels for sub-slab data, and debate over how & where to collect samples.
Which Soil Gas Method?

- Active?
- Passive? (limited use)
- Flux Chambers? (limited use)

Active method most often employed for VI

There are three types of soil gas methods. Active refers to actively withdrawing vapor out of the ground. It gives quantitative values. Passive refers to burying an adsorbent in the ground and letting the vapors passively contact and adsorb onto the collector. It does not give quantitative data and hence cannot be used for risk applications, except for screening. Surface flux chambers were discussed previously.

The active method is the one most applicable to risk assessments.
VI Requires Much Lower DLs

- Typical Soil Gas Concentrations
  - MTBE & Benzene near gasoline soil: >100 ug/L
  - PCE under dry cleaner: >100 ug/L

- Soil Gas Levels a Threat to GW:
  - MTBE: >10 ug/L
  - BTEX/PCE: >100 ug/L

- Soil Gas Levels “Failing” EPA VI Criteria
  - Subslab: Benzene: 0.003 ug/L, PCE: 0.008 ug/L
  - At 5’: Benzene: 0.15 ug/L, PCE: 0.400 ug/L

The biggest difference between sampling soil gas for site assessments and for vapor intrusion is that we are measuring at concentration levels 1,000 to 10,000 times lower. So, the protocols require much greater care. At such low levels, the chances for false positives from equipment blanks are much greater.
There are two common ways to collect active soil gas samples: collection through a probe or rod driven into the ground or collection through a vapor well buried into the ground. Both methods give reliable data.

The vapor wells consist of small diameter, inert tubing and offer advantages when vertical profiles are desired or when repeated sampling events are likely. Multiple tubes can be “nested” in the same borehole.
Collection through the probe rod is advantageous if only one sampling round is required. Seals at the base of the probe are advisable, especially if depths are shallow and larger volume samples (>1 liter) are collected.
Soil vapor implants nested in same borehole at three different depths. This method is advantageous if repeated sampling is anticipated.
### Probe Considerations

- **Tubing Type**
  - Rigid wall tubing ok (nylon, teflon, SS)
  - Flexible tubing not (tygon, hardware store)
  - Small diameter best (1/8” or ¼”)

- **Probe Tip**
  - Beware metal tips (may have cutting oils)

- **Equilibration Time**
  - Effects by air knife, rotary, air percussion, sonic

- **Equipment Blanks**
  - Need to collect blank through collection system

Some of the issues that need to be considered when installing probes include:

**Tubing Type**: Small diameter tubing offers advantages over large PVC pipe. Flexible tubing tends to leak.

**Probe tip**: Metal tips may have blanks due to the cutting process.

**Equilibration time**: How long to wait, especially if air knives are used to clear holes or larger drill rigs are used?

**Equipment blanks**: need to collect blank through the collection system. Trip blanks not enough.
Soil Gas Sampling Issues

- Sample Size
  - Greater the volume, greater the uncertainty
  - Smaller volumes faster & easier to collect
- Containers
  - Canisters: More blank potential. Higher cost
  - Tedlars: Good for ~2 days. Easier to collect
- Flow Rate
  - Really not imp. But most agencies < 200 ml/min
- Tracer/Leak Compound
  - Crucial for sub-slab & larger sample volumes
  - Gases (He, SF6, Propane) & Liquids (IPA)

Lower detection levels requires more careful protocols. Important sampling considerations include sample volume, container type, flow rate, and leak testing to ensure valid samples are collected.

Smaller volumes require less complicated sampling systems and minimize the chances for leakage from the surface and desorption off soil. Recent studies have shown no difference in soil gas values regardless of whether small (0.5 L) or large (100 L) volumes are collected.

Sample containers must be inert, clean, and handled properly (no cooling or heat). Canisters have longer holding times, but have the potential for blanks (carry-over from previous samples), cost more, and can be trickier to fill. Tedlar bags are good for ~2 days, are less expensive, and suitable for concentrations of 1 ppbv or higher.

Sample flow rate is of concern to many agencies, but recent data are showing it not to be a factor.

Tracer/leak compounds are generally required to ensure sample integrity because small leaks can create significant effects at such low concentrations. The larger the volume extracted and the more complicated the sampling system, the greater the potential for leaks.
A 6-liter Summa can is about the size of a basketball. A 400 cc mini-can is about the size of a baseball.

Lower volumes give more control on sample location, require less time to collect, and minimize chances of breakthrough from the surface or other sampling zones in nested wells.

For soil gas samples, most labs only require 100 cc of sample, so small canisters (<1 liter) are sufficient volume.
A soil gas sample collection system used by a consulting firm. Extremely complex, lots of dead-volume for cross contamination, and numerous fittings for potential leaks.
Sample Collection

Collection of a soil vapor sample in a tedlar using a syringe. No power required, no complicated fittings. Leak/tracer can be applied prior to sample collection.
Soil vapor samples can be easily transferred from a tedlar bag into an evacuated canister in the field for longer holding times or for more security during sample shipping.
A variety of analytical methods are available to measure soil gas samples, but no federal guidance document exists specifying any one. Methods 8021 and 8260 are soil & water methods but give accurate results for soil gas samples at detection levels above 10 ug/m³. The toxic organic methods (TO) are designed for ambient air samples, so they give accurate results for soil gas samples at much lower detection levels. The TO methods require extensive hardware and are far more expensive.

The criteria for selection should be which method(s) reach the required detection limits.

On-site data are extremely useful to ensure that the samples do not have tracer/leak levels above acceptable levels, provide real-time data for decision making, and to validate detections seen in the off-site data. If measured values are high, then the on-site methods (8021, 8260) are more appropriate to use than the ultra-sensitive TO methods. If on-site values are low or below detection, then the samples can be measured off-site by the TO methods.
New equipment allows on-site TO-15 analyses. New GC/MS equipment enables simultaneous Scan/SIM mode meaning you can measure for all VOCs (>60 compounds) at DLs < 10 ug/m3 while simultaneously measuring for a subset of compounds at lower detection levels (<2 ug/m3). Only 2 cc of sample are required for analysis, so much of the sampling hardware can be eliminated, reducing chances of false positives.

This capability enables real-time analysis in structures. This might eliminate need for unsupervised time-integrated sampling.
Are sub-slab samples necessary to collect? This issue is highly contested around the country and has huge ramifications. Sub-slab samples are much more intrusive, require access agreements, and often attorneys get involved, especially for private residences.
The draft VI guidance strongly advocates sub-slub samples and some State agencies agree. Some are fearful that the contaminants build-up under the slab ("ponding effect"). But, sub-slub sampling is intrusive and often leads to legal complications. By Fick’s law, the sub-slub concentration can be no higher than the source concentration, so if the source is below, collection of samples at the source depth or midway to the source will give useful data and not create as many legal headaches.

If high oxygen levels exist all around the slab at a shallow depth, and the slab small, there is a good chance that reaeration under the slab is occurring and sweeping contaminants clear.
Data from Endicott NY show a poor correlation between sub-slab soil gas and exterior, shallow soil gas. However, the data were not always collected at the same time and many of the exterior samples were collected far away from the slab.

Slide courtesy of Dr. William Wertz, NYDEC
Recent modeling by Dr. Lilian Abreau (Geosyntec Consultants) has shown that for hydrocarbons sources in the soil vapor less than 20 mg/L, there is unlikely to be any vapor intrusion risk. The benzene vapor concentration in equilibrium with gasoline is only 7.8 mg/L and data from 100 sites show maximum benzene vapor concentrations of less than 1 mg/L! So, unless the source very close to the receptor, there is no need to worry.

Slide courtesy of Dr. Lilian Abreau
How Often to Sample?

- Depth Below Surface
  - 3’ to 5’ bgs generally considered stable
  - Temporal Studies Ongoing
- Seasonal Effects – How Important?
  - Most studies show less than 5x
- Extreme Conditions?
  - Heavy rain
  - Extreme heating/cooling

Why Spend the $?

The closer to the surface, the more the potential temporal variation. Depths of 3’ to 5’ below the surface are generally considered deep enough to get repeatable data and resampling is not required by most agencies.

Historical radon data around houses show variations less than a factor of 7 in cold climates. Recent VOC data from Endicott show soil gas variations less than a factor of 4 over 15 months. Larger variations may be likely in areas of extreme temperature variation (northern climates), during heavy periods of precipitation, and when the structure’s heating or ventilation systems are operative.

In general, if the soil gas concentrations are below allowed levels by a factor of 10, there should be no need to repeat sampling.

If conditions suggest that temporal variations may be significant and if the measured values are close to the fail level, then repeated sampling may be appropriate and vapor implants are a good approach.
Recent data collected over 15 months from Endicott NY show very low variations in deep soil gas (max variation less than factor of 2) and sub-slab soil gas concentrations (max variation less than factor of 4). Hence, in most cases, it is not necessary to collect samples more than once.

Slide courtesy of Dr. William Wertz, NY-DEC
This is a plot of data recently collected for an EPA funded study by an automated instrument at Vandenberg AFB site from three probes at the same location but at different depth (3’, 8’, & 17’ bgs). This plot consists of over 500 points per probe collected once per hour over a 4 week period from mid March to mid April 2007. The soil gas concentrations varied by less than 10% over these four weeks even for probes only 3 feet below the surface.
Recent modeling by Dr. Lilian Abreau (Geosyntec Consultants) has shown that for hydrocarbons sources in the soil vapor less than 20 mg/L, there is unlikely to be any vapor intrusion risk. The benzene vapor concentration in equilibrium with gasoline is only 7.8 mg/L and data from 100 sites show maximum benzene vapor concentrations of less than 1 mg/L! So, unless the source very close to the receptor, there is no need to worry.

Slide courtesy of Dr. Lilian Abreau
Effect of Depth on $\alpha$

Results suggest that, for a given source vapor concentration, there may be a critical depth beyond which vapor migration is of little concern.

Recent modeling by Dr. Lilian Abreau (Geosyntec Consultants) and has shown that depth of the contamination source is also important.

Slide courtesy of Dr. Lilian Abreau
The end result of the recent modeling by Dr. Lilian Abreau (Geosyntec Consultants) is that one can now estimate the bioattenuation attenuation factor based upon depth to source and source strength. Note that for all concentrations below 10,000 ug/L, the attenuation factor is no higher than 1e-5. This is 4 orders of magnitude lower than the EPA VI guidance default value! Unless the source is within 3 feet of the receptor, the attenuation factor never exceeds 1e-3, still 2 orders of magnitude lower than the EPA default value.

Slide courtesy of Dr. Lilian Abreau, Geosyntec Consultants, and API.
Supplemental Tools/Data

• Site Specific Alpha Using Radon
  – Factor of 10 to 100. $100/sample
• Indoor Air Ventilation Rate
  – Factor of 2 to 10. <$1,000 per determination.
• Real-Time, Continuous Analyzers
  – Can sort out noise/scatter
• Pressure Measurements
  – Can help interpret indoor air results

There are some other inexpensive tools/data that can be applied to better evaluate some of the default model parameters and the vapor intrusion pathway. These tools/data have much more influence on the resulting risk than measurement of soil porosity and cost about the same.

Radon can be used to determine a site-specific alpha that may be 10 to 100 times lower than the default alpha allowed.

Tracers can be used to measure the room ventilation rates and may give values 2 to 10 times higher than the default value, especially for commercial sites.

For HCs, vertical profiles of the soil gas can demonstrate bioattenuation. In some States, the agencies allow for a 10 times reduction in risk if bioattenuation is demonstrated. Although the DTSC guidance recognizes bioattenuation, it currently gives no indication as to how the data will be interpreted.

Real-time analyzers can be used to locate problem houses, preferential pathways into structures, or sort out background scatter. Pressure measurements are helpful with indoor air data to possibly show a background source.
Practical Strategies
(Things to Do)

- Use Reasonable RBSLs
- Have Reasonable Distance Criteria
- Get Enough Data
- Allow Less Expensive Methods (8021, 8260)
- HCs: Vertical Profiles Around Structure
- Use Radon for Slab-Specific Alpha
- Measure Ventilation Rate
- Have Competent Consultants & Subs
- Check Your Units!!!!!!!!!!!

These are things you want to do/allow to practically and cost effectively assess this risk pathway.
A summary of existing documents on soil gas methods can be found at these locations:
Existing Documents & Training

- Soil Gas Sampling SOPs
  - Soil Gas Sampling, Sub-slab Sampling, Vapor Monitoring Wells/Implants, Flux Chambers (www.handpmg.com)
  - EPA-ORD Sub-slab SOP–Draft, Dr. Dom DiGuilio (www.iavi.rti.org/resources)

- Other
  - API Soil Gas Document (www.api.org/bulletins)
  - Robin Davis Lustline Article on Bioattenuation (Lustline June 2006, www.neiwpcc.org)

More documents.
VI Websites & Links

- www.handpmg.com
  - Soil Gas Information
  - Other Site Assessment Methods
  - Articles & Presentations
- www.itrcweb.org
- www.api.org
- http:iavi.rti.org

Useful vapor intrusion websites.