Evaluating the Impact of Methane in Soil Gas on the Potential for Vapor Intrusion of Petroleum Hydrocarbons

Methane from Biofuels – Webinar, NEIWPCC
Wednesday, October 8 from 1:30 – 4:00 (EDT)

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1. Introduction

2. An approach to evaluate the impact of methane in soil gas on the potential for vapor intrusion of petroleum hydrocarbons – George DeVauil, Shell Global Solutions US Inc.

3. Emergency response to spills – Mark Toso, Minnesota PCA
   a. How methane is formed in the subsurface using case studies of sites
   b. Remediation, surface spills, and ecological impacts

4. Recent research on ethanol blended fuel spills and potential for methane generation and transport – Bill Rixey, University of Houston
By way of Acknowledgement:


Overview: Potential Methane Issues

Potential Sources:
- Biogenic methane from organic sources
- Natural gas transmission and distribution systems
- Reservoirs and storage, coal, petroleum, natural gas

Representative Examples:
- Measurement of shallow methane in the course of a vapor intrusion investigation
- Risk evaluation of some motor fuels (>E20) for methane and vapor intrusion potential

KEY IDEAS:
- Determine how much methane is okay.
- Both concentration and flux (or flow) are important.
Biogenic Methane: What’s the issue?

Biogenic methane generation – makes gas:

Example (with some steps missing):

- ethanol (liquid)
- methane (gas)
- carbon dioxide (gas)

\[
2 \text{CH}_3\text{CH}_2\text{OH} \rightarrow 3 \text{CH}_4 \uparrow + \text{CO}_2 \uparrow
\]

Similar for other organics, including petroleum

Compare to methane oxidation:

can be equal volume or decrease

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]
Methane – Scenarios / Conceptual Model

Focus Area Here: **Shallow Soil Gas** to Enclosure Migration

- Flammable liquid releases to enclosed spaces; explosion overpressure consequences; emergency response; mitigation methods; climate change

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**NOT COVERED**

- Cess pool in crawl space
- Effervescent tap water
- Bubbling / gassy water well
Overview: Risks and Hazards

Methane Hazards:

- **Direct:**
  - **Flammability**
    - In enclosures; not within soil gas
    - LFL (LEL) – Lower Flammability Limit: 5.4% v/v in air (21% O₂)
  - **Toxicity**
    - Asphyxiation (O₂ displacement); same as some other gases (N₂, He, Ar, …)
    - For methane toxicity criteria are higher than flammability criteria

- **Indirect:**
  - **Effect on other chemicals**
    - O₂ demand – for biodegradable chemicals
    - induced advection
Methane Flammability: Concentration and Flow (or Flux)

Concentration
- Within enclosure - flammable > 5.4%v/v
- In soil gas – potentially flammable once mixed with air > 14.1%v/v

Flux or Flow
- Enclosure (crawl space) > 5 to 95 L/min; 0.8 to 3.3 m/day
- Enclosure (residential) > 57 to 230 L/min; 0.34 to 1.4 m/day

KEY POINT:
- Flammability requires both high methane concentrations and high flow or flux.

• Values above for 100% LFL.
• ‘Safety factors’ (e.g. 10% LFL for human-occupied spaces) often applied.
Hazard Screening: Methane in Shallow Soils

Review / existing information: known risks & hazards of methane

- Comparison to guidance on mine safety, natural gas distribution systems, municipal landfill gas migration, feedlots, methane seeps, regional ordinances

Table: screening criteria

<table>
<thead>
<tr>
<th>Shallow Soil Gas Concentration</th>
<th>Indoor Air Concentration</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>None Available</td>
<td>&lt;0.01%v/v</td>
<td></td>
</tr>
<tr>
<td>0.01 to &lt;1.25%v/v</td>
<td>&gt; 1.25%v/v</td>
<td></td>
</tr>
<tr>
<td>&lt;1.25 to 5%v/v</td>
<td>No further action</td>
<td></td>
</tr>
<tr>
<td>&gt;5 to 30%v/v</td>
<td>No further action unless ΔP &gt;2 in. H₂O</td>
<td></td>
</tr>
<tr>
<td>&gt;30%v/v</td>
<td>Collect indoor air data</td>
<td>Evaluate on case-by-case basis</td>
</tr>
</tbody>
</table>

Notes:

a) Shallow soil gas: Maximum methane soil gas value for area of building footprint.
b) Landowner or building owner/manager should identify indoor sources and reduce/control emissions.
   If no sources are found, additional subsurface characterization and continued indoor air monitoring are recommended.
c) ΔP > 2 in. water: The potential for pressure gradients to occur in the future at a given site should be considered.

Table based on Eklund (2011) and Sepich (2008)
Other Comparisons / Notes / Examples

- **Guidance: California DTSC “manure”**
  

- **San Diego – rescinded ordinance**
  
  
  June 2002. MTRANS (Methane Transport Model)
  
  April 2005. San Diego County repeals ordinance requiring methane gas testing on mass graded lots within the unincorporated areas of the County.

**GET**

- **Soil Gas Criteria (<5%, <30%) overestimates potential enclosure risk**

  - Differential Pressure (2-in H₂O) okay for relatively impermeable caps (intact concrete, silt, clay); otherwise might need adjustment

- **Other possible options:**
Methane Detection: care needed in measurement

- Landfill Gas meters, handheld meters
  - 3.41μm (nominal) absorption band
    - For methane
    - Responds to other hydrocarbon gasses
    - Also responds to ethanol
- Carbon Filter Trap?
  - In front of detector
  - Traps most hydrocarbons
  - Ethanol not sorbed by carbon

• Petroleum and ethanol also detected by IR gas meters!


http://webbook.nist.gov
Soil Gas Modeling: can use a combination of methods

<table>
<thead>
<tr>
<th>Models: Gas Flow in Porous Media</th>
<th>Applicability:</th>
</tr>
</thead>
</table>
| **Diffusion (Fick's law)**      | • Low concentration, $X_i << 1$
|                                 | • Low advection, $u_{v,total} << D_{eff,i} / L$
| **Advective-Diffusion**         | • Low concentration, $X_i << 1$
|                                 | • Specified advection, $u_{v,total}$ [from uncoupled flow estimate]
| **Stefan-Maxwell**              | • Total concentration, $1 = \sum X_i$
|                                 | • Imposed flux constraint, $u_{v,total} = \sum u_i$
|                                 | • Low pressure gradient, $\Delta P << P$
| **‘Dusty Gas’**                 | • Fully coupled diffusive flux and viscous flux (pressure-driven)
|                                 | • Strong gas / wall (‘dust’) interaction.

- $X_i$, mole fraction (mole/mole)
- $(R \cdot T / P)$, molar volume (m$^3$/mole)
- $c_i = X_i / (R \cdot T / P)$, mole concentration (mole/m$^3$)
- $u_{v,i} = (R \cdot T / P) \cdot N_i$, Darcy flux (m$^3$/m$^2$-hr)
- $N_i$, molar flux (mole/m$^2$-hr)
- $D_{eff,i}$, effective diffusion coefficient (m$^2$/hr)
- $L$, distance (m)
- $P$, pressure (Pa)

*errors increase for higher concentration, concentrations, and pressure gradients

Ref: Thorstenson and Pollock (1989)
Example: Field Data

Model

- Solution of Stefan-Maxwell equations
  Unidirectional diffusion of \((\text{CO}_2 + \text{CH}_4)\)
  in stagnant air \((\text{N}_2 + \text{O}_2)\)
  Thorstenson and Pollock (1989)

\[
X_i(s) = 1 - \left(1 - X_i(s = 0)\right) \cdot \exp\left(-\frac{u_{v,i} \cdot x}{D_i}\right)
\]

\[
P_{E_x} = \frac{u_{v,i} \cdot x}{D_i} \quad \text{Peclet number} \quad X_i \quad \text{mole fraction}
\]

Data

- Vertical profile – methane in soil gas
  Lundegard, et al., 2000

71% \(\text{CH}_4\) + 23% \(\text{CO}_2\) = 94% at depth

78% \(\text{N}_2\) in air \(\rightarrow\) must have been displaced
Additional Parameter: Nitrogen Gas

- Low values of differential pressure are hard to measure
- The potential for significant advection may also be evaluated by measure of nitrogen (N\(_2\)) in soil gas.
- Nitrogen is nearly conserved
- Ensure the N\(_2\) value is measured directly; or reasonably estimable by a balance of all of the other gases and vapors.

\[
P_{e_L} = \frac{u_v}{D_i / L} = -\ln \left( \frac{X_{N_2}(\text{at depth})}{X_{N_2}(\text{atmosphere})} \right)
\]

\[
P_{e_L} < 1 \quad ; \quad X_{N_2}(\text{at depth}) > 0.29 \quad \text{for diffusive flow}
\]

\(X\) – mole fraction \hspace{1em} \(Pe_L\) – Peclet number

\(u_v\) – Darcy velocity \hspace{1em} \(L\) – depth \hspace{1em} \(D_i\) – effective diffusion coefficient
Methane: in wet soils

- Example 70% Methane at bottom of a (wet) capillary fringe

- Peclet numbers Add (in layers):
  - $P_{\text{e\_total}} = P_{\text{e\_cap}} + P_{\text{e\_vadose}} = 1.2$ (>$1$) $\leftarrow$ advection-dominated

CH$_4$ flux = 0.005 m$^3$/m$^2$-day

- $P_{\text{e\_vadose}} = 0.1$ (>1) diffusion-dominant
- $P_{\text{e\_cap}} = 1.1$ (>1) advection-dominant
Conclusions: Methane Flammability

In Soil Gas Screening:

- Methane Screening Concentrations in soil gas can be relatively high (5%, 30%) and still conservative [that is, overestimating potential flammability risk].

- Advective contribution

  - Flux can be high enough to generate a pressure gradient
  - Differential pressure criteria (2-in water) can be measurable under an intact cap (concrete, clay)
  - Measure of nitrogen deficit in subsurface soil gas can also indicate displacement / advection due to methane gas flow

KEY IDEAS:
- Acceptable methane screening values are high (>5%, >30%).
- Both concentration and flux (or flow) are important.
Potential effect of methane

On transport and degradation of other chemicals (benzene)

- **Scenario:**
  - **Methane**
    - dominant oxygen sink
    - dominant source of advection
  - **Benzene**
    - Low levels
  - **Sand Soil**
  - **Typical concrete foundation**
  - **Source to foundation:** 3m

- **Apply:**
  - ‘Oxygen-Limited Aerobic Biodegradation’
  - With Methane Advection
Screening methods

- Exclusion Distances (source to foundation separation distances)
  - Examples: 6 ft dissolved phase source, 15 ft LNAPL source

- Developed from a field-measured data set which includes gasoline releases at up to 10% ethanol
- Ethanol which can generate methane
- These Exclusion Distances are valid for up to E10 (10% ethanol)
Use:

- Advective-Diffusion Solution with Oxygen-limited Biodegradation
  - Derived algebraic solution for oxygen-limited aerobic biodegradation with imposed advection.
  - Very similar to ‘BioVapor’ model with imposed advection.

Impose additional constraints:

- Maximum 100%v/v soil gas sum
- Advection is due only to soil gas concentration gradients; imposes an upper bound advection from Stephan-Maxwell equation for singly advective diffusion (advecting methane, stagnant air)
Sensitivity Analysis

In Soil Gas Screening

- As an example, without advection –
- Use the same type of nomogram to interpret the effect of advection

For methane:
- Apply this type of analysis using one selected source depth (3 m) and a range of source advection rates
- Plot on this slide: the source advection rate is zero.

3D: Abreu 2009: GWM&R
& API Publ. 4555
Basement Scenario
Matched Parameters
Except “Depth”
Model Results – Sensitivity Analysis

Effect of Methane Source on Benzene Attenuation Factor

(Ex)

- Peclet number: $\text{Pe} = \frac{U_z \cdot L}{D_{eff}}$
- Darcy Vapor Flux [up]: $U_z$ (m/day)
- Source Depth: $L = 3$ m

Applicable Solution (shaded area only)

Stefan-Maxwell unidirectional diffusion limit

100% v/v concentration limit

Benzene-Specific Indoor Air to Source Vapor Chemical Concentration Ratio (ug/m$^3$)/(ug/m$^3$)

Methane Source - Total Soil Vapor Concentration (% v/v)
Conclusions: Effect of methane on other chemicals

Effect of methane on benzene attenuation factor:

- A factor of 10x effect:
  - ~ 3% methane for oxygen demand
  - ~ 95% methane for advection

In the modeled scenario
Still worried about effect of methane?

On transport of other biodegradable chemicals?

- Some vapor intrusion models can still be applicable

- e.g. BioVapor ([www.api.org](http://www.api.org)) : diffusion, oxygen-limited biodegradation
  - Include methane concentration in the source composition
  - Check that vapor transport is ‘diffusion’ dominated
    - that is, relatively low source concentration
  - If conceptual model matches the site conditions, and modeled indoor air estimates for constituents of concern are acceptable, should be okay.
Conclusions: Effect of methane on benzene

- Effect of oxygen demand is more significant than advection
  - for biodegradable chemicals
  - Low (Total) Source concentration alone will ‘screen’ sites

- At higher methane source concentrations
  - High oxygen demand → higher attenuation ratios
  - Higher induced advection → higher attenuation ratios
  - Potential enclosure impacts may be greater than expected

- Need:
  - More estimates, more sensitivity evaluations

**KEY POINT:**

- Low Source Concentration → Low Oxygen Demand
  - Low Advection
End

Thank you

Reserved slides follow
Methane: Modeled Scenarios

- Presence of methane indicates (biogenic) gas generation & potential for source advection
- Conceptual models illustrating the potential effects of advective velocity on soil vapor intrusion
**Modeling: Soil gas flow**

- **high concentration of methane in soil gas; possible induced**

<table>
<thead>
<tr>
<th>Stefan-Maxwell</th>
<th>General relationship</th>
<th>Binary mixture (one stagnant gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-D_i \cdot \left( \frac{P}{R \cdot T} \right) \cdot \frac{dX_i}{ds} = N_i - X_i \cdot \sum N_i$</td>
<td>$\left( \frac{R \cdot T}{P} \right) \cdot N_{i[S-M]} = -\frac{D_i}{s} \cdot \ln \left( \frac{1 - X_i(s)}{1 - X_i(s = 0)} \right)$</td>
<td></td>
</tr>
</tbody>
</table>

- **Key point:** At high concentrations the diffusion rate of each gas is coupled to the diffusion rate of every other gas.

- **Advective-Diffusion Eq. – no concentration constraint**

- **Fick’s law – no advection**

  - $\sum_{gases}^{mobile} < 50\% \frac{v}{v}$ : bias in flux $< 50\%$
  - $\sum_{gases}^{mobile} > 80\% \frac{v}{v}$ : bias in flux $> 100\%$

  - **backup slide**
Example: Field Data

• Water-well soil gas data sampling. Inficon Micro 3000 GC analysis.
• Data courtesy John Wilson (August 2013).
• For gas samples taken 30 to 40 min into purging:

<table>
<thead>
<tr>
<th></th>
<th>methane %v/v</th>
<th>oxygen %v/v</th>
<th>nitrogen %v/v</th>
<th>carbon dioxide %v/v</th>
<th>C2 to C6+ (sum) %v/v</th>
<th>total %v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-1</td>
<td>57.0</td>
<td>7.2</td>
<td>16.2</td>
<td>16.8</td>
<td>0.9</td>
<td>98.1</td>
</tr>
<tr>
<td>MW-2</td>
<td>65.2</td>
<td>1.3</td>
<td>5.1</td>
<td>20.3</td>
<td>3.2</td>
<td>95.1</td>
</tr>
<tr>
<td>EPA-1 / MW-9</td>
<td>50.4</td>
<td>1.2</td>
<td>20.5</td>
<td>19.9</td>
<td>1.1</td>
<td>93.2</td>
</tr>
</tbody>
</table>

• Oxygen is low in MW-2 & MW-9; moderate in MW-1.
• Nitrogen (5.1 to 20.5 %v/v) is significantly less than atmospheric (79%v/v) throughout. This indicates displacement of nearly conserved atmospheric gases, probably by methane gas.
  • The nitrogen value has been confirmed to be through calibrated GC analysis and not estimated by difference (which is done by some labs / methods).
• The total vapors including gases and vapors sum to 93.2 to 98.1 % v/v. This is marginally lower than 100%, but nearly complete.
Modeling: Implementation

- Binary non-reactive gas flow $\rightarrow$ mathematical solution
- Anything more complex $\rightarrow$ numerical solution

*Favorable comparison:*

**MIN3P-Dusty (Molins and Mayer, 2007) to Thorstenson and Pollock (1989)**

Acknowledgement MIN3P Dusty: Parisa Jourabchi (Golder), Uli Mayer (UBC)
Potential Identified Issues from Consolidated survey:

- Active Municipal Landfills, Manure, Ethanol, Ethanol/Petroleum, Petroleum
- Source size & methane generation rate still matter
I. Flammability: Methane Concentration

- 5.4% methane in air is flammable (LFL)
  - Need at least 14.1% methane in soil gas (the rest: N\textsubscript{2}, CO\textsubscript{2}, etc.) to mix with air (21% O\textsubscript{2}) to yield a flammable mixture.

![Diagram showing flammability threshold]

- ‘Safety factors’ (10% LFL for occupied space)
- Soil gas is not flammable; Flame is ‘quenched’ in the soil matrix

**KEY POINT:**

- Flammability requires high methane concentrations in ‘open’ space (not soil gas).
Screening methods presume prior site assessment, characterization, and evaluation

A developed and validated conceptual model:

**Sources:**
- Buried organic matter
- Municipal landfills, leachate
- Released petroleum, ethanol, organic liquids
- Coal deposits, Peat soils
- Made land, fill areas
- Swamp land, Rice fields
- Septic tanks, Drainage fields
- Livestock containment, Manure pits
- Sewage and sewer gas
- Gas transmission and distribution lines

**Factors:**
- Source volume
- Gas generation rates
- Biodegradation
- Composition
- Gases present (CH₄, CO₂, ...)
- VOCs present

**Pathway Linkages:**
- Air connected soils
- Capping, Foundations
- Vapor diffusion
- Gas advection
- Sewers, Vents
- Gas ebullition
- On-site, off-site
- Sumps, Dry wells, Vaults
- Foundation cracks, Utility penetrations

**Factors:**
- Diffusion rates, Permeability
- Wet/dry soils
- Preferential flow
- Natural and man-made geology, Hydrogeology
- Atmospheric pressure changes
- Rising/falling water tables
- Soil gas venting
- Dewatering
- Paving, Hardscape

**Receptors:**
- Occupied enclosures
- Crawlsspaces
- Basements
- Current and future land use
- Soil flora, Soil fauna

**Factors:**
- Air exchange rates
- Residential / commercial
- Background concentrations
- Enclosure emission sources
- Hazards, exposure
- Direct toxicity
- Flammability
- Oxygen displacement
- Acute, chronic

backup slide
Differential Pressure Criteria

scenario: crawlspace
specified methane flux : 0.34 m / day
## II. Flammability: Methane Flux (or Flow)

### Methane Flux Criteria

<table>
<thead>
<tr>
<th>encloourse criteria (%v/v)</th>
<th>Methane Flow (L/min)</th>
<th>Methane Darcy Flux (m³/m²-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>residential building</td>
<td>5.4</td>
<td>57 to 230</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>5.4 to 21.7</td>
</tr>
<tr>
<td>crawlspace</td>
<td>5.4</td>
<td>5 to 95</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>0.5 to 9.0</td>
</tr>
</tbody>
</table>

### Estimated methane fluxes (and flows) for potential flammability:

- **Approximately ~ 0.33 to 3.3 m/day** to reach 5.4%v/v methane in enclosure
  - Advection required (relative to diffusion) at these flux velocities
  - Lower ranges with applied safety factors; higher ranges if ‘crack’ flow not entire foundation area

\[
\frac{Q_f}{A_f} = L_{mix} \cdot ER \left(\frac{1}{X_{CH4}} - 1\right)
\]
### Parameter definition and selection

#### 1-D geometry modeled

For each layer (foundation, soil):

<table>
<thead>
<tr>
<th>LAYERS:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-layer</td>
</tr>
<tr>
<td>$X_i(s = L) = 1 - \left(1 - X_i(s = 0)\right) \cdot \exp \left(- \frac{u_{v,i} \cdot L}{D_i}\right)$</td>
</tr>
<tr>
<td>2-layer</td>
</tr>
<tr>
<td>$X_i(L_2) = 1 - \left(1 - X_i(s = 0)\right) \cdot \exp \left(- \left(\frac{u_{v,i} \cdot L_1}{D_{i,1}} + \frac{u_{v,i} \cdot L_2}{D_{i,2}}\right)\right)$</td>
</tr>
</tbody>
</table>

- $u_{v,i}$, Darcy flux (m$^3$/m$^2$-hr)
- $L$, depth (m)
- $Pe_{i} = u_{v,i} \cdot L / D_i$, Peclet number
- $X_i$, mole fraction (mole/mole)
- $D_i$, effective diffusion coefficient (m$^2$/hr)
- $i$, mobile gas component

Within each layer, an area-weighted average:

<table>
<thead>
<tr>
<th>AREA: 2 sub-areas, $A_A, A_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$D_{i,avg} = \eta \cdot D_{i,A} + (1-\eta) \cdot D_{i,B}$</td>
</tr>
<tr>
<td>gas permeability</td>
</tr>
<tr>
<td>$k_{v,i,avg} = \eta \cdot k_{v,A} + (1-\eta) \cdot k_{v,B}$</td>
</tr>
</tbody>
</table>

Area weighted fraction: $\eta = A_A / (A_A + A_B)$
Model Scenario: Shallow Methane

Steady-state unidirectional diffusion in a binary gas mixture

Layered Compartments (one-dimensional):

- **Enclosure**
  - Mixing and dilution
  - Stagnant gases: Air (N₂, O₂, Ar)

- **Foundation (or cap)**
  - Specified resistance to flow [range]
  - Diffusion coefficient, permeability

- **Soil Layer**
  - Advection, diffusion, no (bio)degradation
  - Sand [diffusion coefficient, high permeability]

- **Source**
  - Generation (CH₄, CO₂) at depth; upward flux specified (worst-case for flammability is all methane)
Methane Hazard: modeled results

Key point:

• Soil gas concentration criteria (<5 & <30%) overestimates potential risk [below indicated depths]

Indoor methane: 5.4 %v/v
Methane flux: 0.34 m / day
Scenario: crawlspace
Criteria: 30% v/v methane, at > 0.28 m depth

Methane: 0.5 %v/v
Methane flux: 0.033 m / day
Scenario: crawlspace
Criteria: 5% v/v methane, at > 0.44 m depth
Differential Pressure

- 2-in H₂O differential pressure criteria
  - Presumes pneumatic connection between soil and enclosure
  - Requires a relatively impervious cap
    - From calculated pressure drop
    - 15 cm capping material

Key point:
- Differential pressure criteria require capped surface (concrete, silt, clay); may adjust downward for more permeable surfaces