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)

25 minutes

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Webinar Outline

1. **Introduction**
2. ***An approach to evaluate the impact of methane in soil gas on the potential for vapor intrusion of petroleum hydrocarbons* – George DeVaull, 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:

- **Wilson, J. T., M. Toso, D. Mackay, N. de Sieyes, G. E. DeVaull, What's the Deal with Methane at LUST Spill Sites? Parts 1& 2: LUSTLine, #72, February 2013; #71, September 2012.**
- **Ma, J., W. G. Rixey, G. E. DeVaull, B. P. Stafford, P. J. J. Alvarez, Methane Bioattenuation and Implications for Explosion Risk Reduction along the Groundwater to Soil Surface Pathway above a Plume of Dissolved Ethanol, Environ. Sci. Technol., 2012, 46, 6013–6019.**
- **Sihota, N.J., O. Singurindy, and K. U. Mayer, 2011. CO_2 efflux measurements for evaluating source zone natural attenuation rates in a petroleum hydrocarbon contaminated aquifer, Environ. Sci. Technol., 45:482-488.**
- **Sepich, J. E., Methane Soil Gas Identification and Mitigation, ASCE San Antonio, April 20, 2012.**
- **Eklund, B., Proposed Regulatory Framework for Evaluating the Methane Hazard due to Vapor Intrusion, EM Magazine, Air & Waste Management Asso., awma.org, February 2011, 10-14.**

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 – <u>makes gas</u>:**

Example (with some steps missing):

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

$$2\,CH_3CH_2OH \rightarrow 3\,CH_4 \uparrow + CO_2 \uparrow$$

Similar for other organics, including petroleum

Compare to methane oxidation:
can be equal volume or decrease

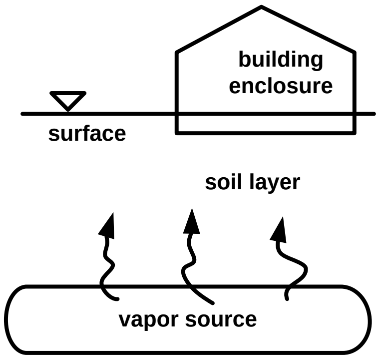
(gas) (gas) (gas) (gas or liquid)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Methane – Scenarios / Conceptual Model

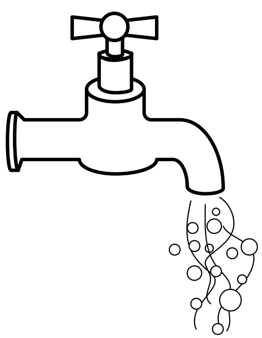
Focus Area Here: <u>Shallow</u> <u>Soil</u> <u>Gas</u> to Enclosure Migration

yes

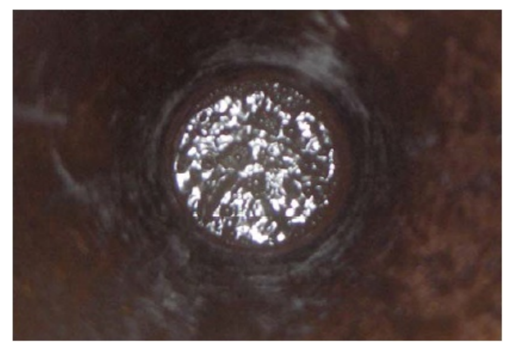


shallow methane source

cess pool in crawl space



effervescent tap water



bubbling / gassy water well

NOT COVERED

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

Overview: Risks and Hazards

Methane Hazards:

- **<u>Direct:</u>**
  - **Flammability** PART 1
    - **In enclosures; not within soil gas**
    - **LFL (LEL) – Lower Flammability Limit: 5.4% v/v in air (21% O_2)**
  - **Toxicity**
    - **Asphyxiation (O_2 displacement); same as some other gases (N_2, He, Ar, …)**
    - **For methane toxicity criteria are higher than flammability criteria**
- **<u>Indirect:</u>** PART 2
  - **Effect on other chemicals**
    - **O_2 demand – for biodegradable chemicals**
    - **induced advection**

Methane Flammability: Concentration and Flow (or Flux)

PART 1

- **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 (crawlspace) > 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

1

<u>Review / existing information:</u> 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**

Shallow Soil Gas Concentration[a]	Indoor Air Concentration			
	None Available	<0.01%v/v	0.01 to <1.25%v/v	> 1.25%v/v
<1.25 to 5%v/v	No further action		No further action[b]	Immediately notify authorities, recommend owner/operator evacuate building
>5 to 30%v/v[c]	No further action unless ΔP >2 in. H_2O[b]			
>30%v/v[c]	Collect indoor air data	Evaluate on case-by-case basis		

<u>Notes:</u>
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)

Methane Soil Gas Hazard Screening: Interpretation

Other Comparisons / Notes / Examples

- **Guidance: California DTSC "manure"**

  A Guidance Prepared for the Evaluation of Biogenic Methane in Constructed Fills and Dairy Sites, California EPA, Department of Toxic Substances Control, March 28, 2012

  - **San Diego – rescinded ordinance**

  1999. Methane discovered in San Diego housing developments; 2001. Ordinance imposed.

  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 H_2O) okay for relatively impermeable caps (intact concrete, silt, clay); otherwise might need adjustment**

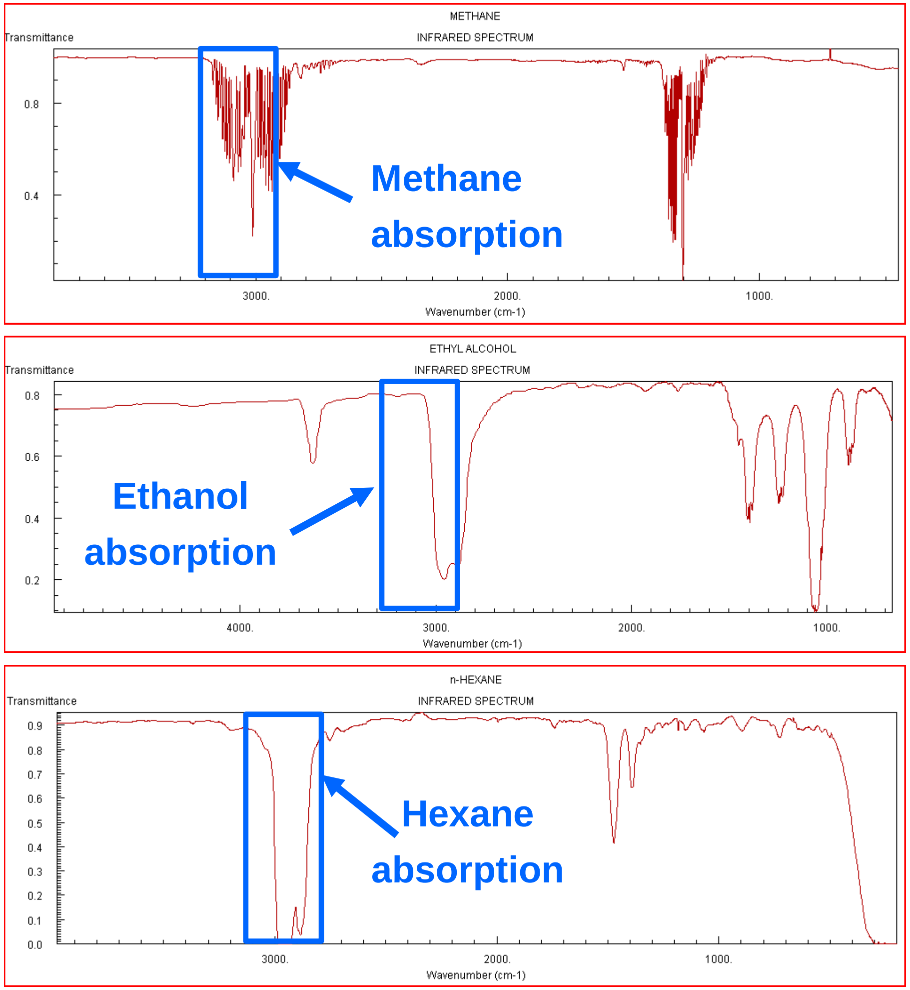
- **Other possible options:**

Methane Detection: care needed in measurement

- **Landfill Gas meters, handheld meters**
  - **3.41um (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!

IR Spectrum

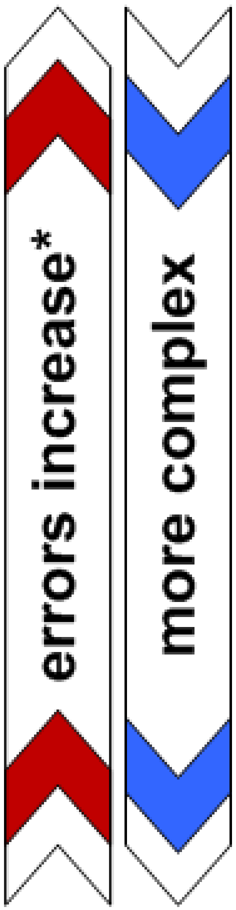


http://webbook.nist.gov

Jewell, K., J. T. Wilson, Ground Water Monitoring & Remediation, 31, 2011, 82–94.

Soil Gas Modeling: *can use a combination of meth*

1



Models: Gas Flow in Porous Media	
	Applicability:
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, $1 = \Sigma X_i$ • Imposed flux constraint, $u_{v,total} = \Sigma u_i$ • 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

1

Model

- **Solution of Stefan-Maxwell equations**

  Unidirectional diffusion of (CO_2 + CH_4) in stagnant air (N_2 + O_2)

  Thorstenson and Pollock (1989)

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

$$Pe_x = \frac{u_{v,i} \cdot x}{D_i}$$ **Peclet number**

X_i **mole fraction**

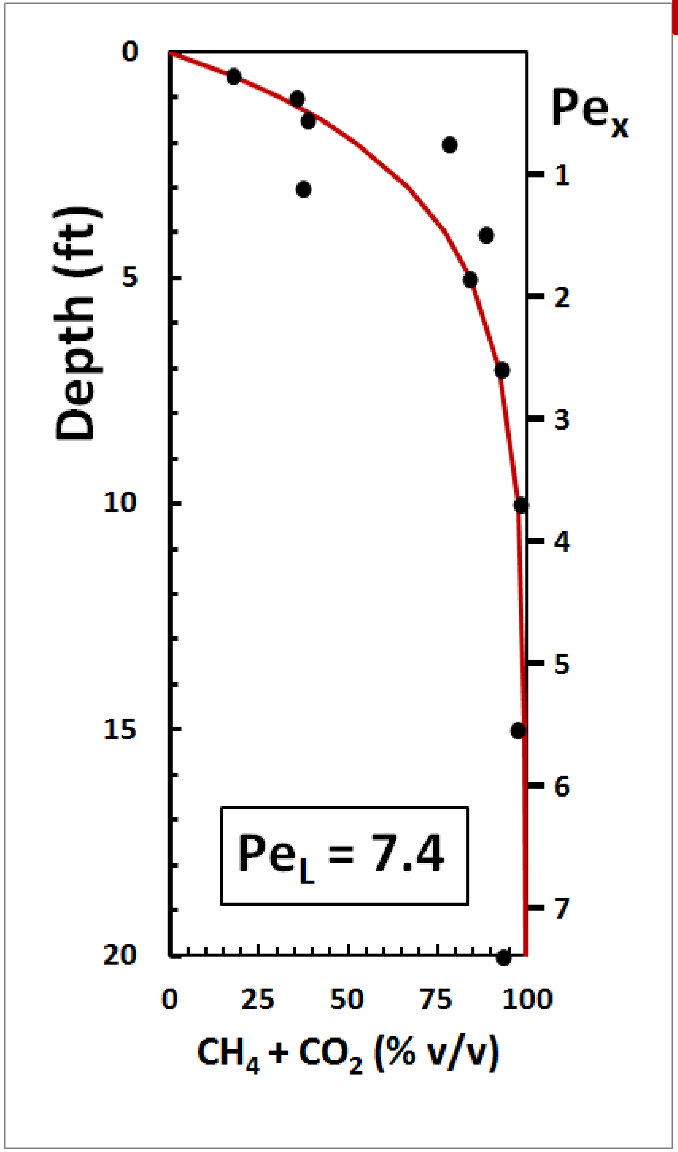
Data

- **Vertical profile – methane in soil gas**

  Lundegard, et al., 2000

71% CH_4 + 23% CO_2 = 94% at depth

78% N_2 in air → *must have been displaced*



Additional Parameter: Nitrogen Gas

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- **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.**

$$Pe_L = \frac{u_v}{D_i / L} = -\ln\left(\frac{X_{N_2}(at\ depth)}{X_{N_2}(atmosphere)}\right)$$

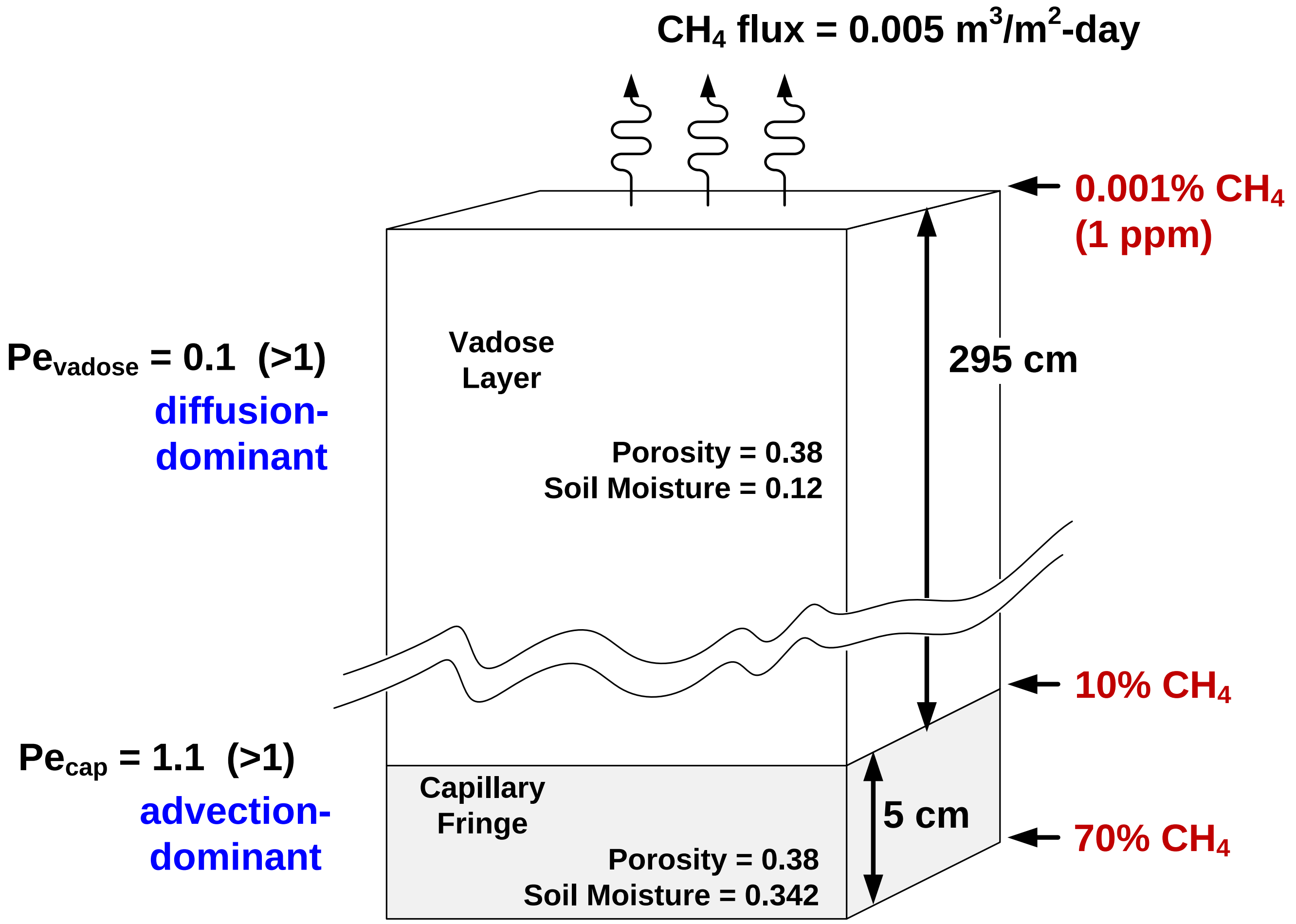
$$Pe_L < 1 \quad ; \quad X_{N_2}(at\ depth) > 0.29$$ ***for diffusive flow***

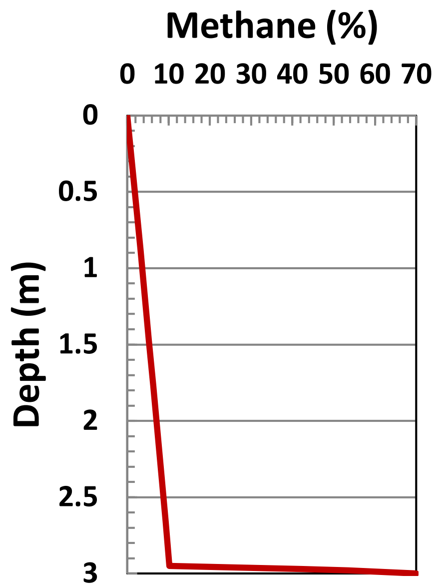
X – mole fraction • Pe_L – Peclet number

u_v – Darcy velocity • L – depth • D_i - effective diffusion coefficient

Methane: in wet soils

- Example 70% Methane at bottom of a (wet) capillary fringe
  - Peclet numbers Add (in layers):
  - $Pe_{total} = Pe_{cap} + Pe_{vadose} = 1.2$ (>1) ← advection-dominated





Conclusions: Methane Flammability

In Soil Gas Screening:

PART 1

- **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)**
  - **<u>Measure of nitrogen deficit</u> in subsurface soil gas can also indicate displacement / advection due to methane gas flow**

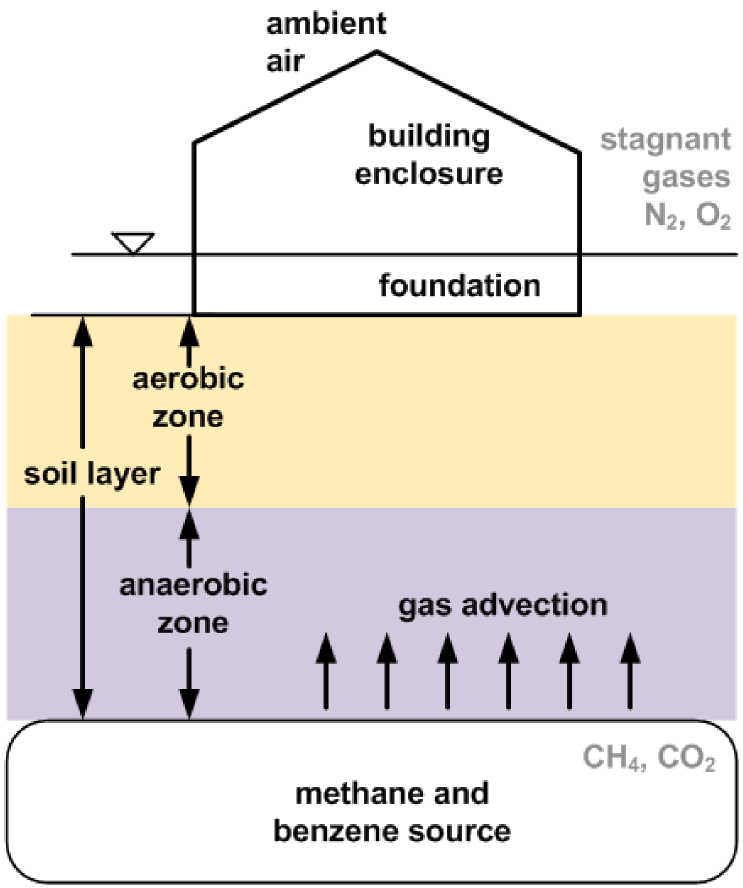
KEY IDEAS:

- **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)

PART 2



- **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
    - EPA OUST Draft Guidance, reports http://www.epa.gov/oust/cat/pvi/
    - Lahvis et al., 2012: Vapor Intrusion Screening Criteria for Application at Petroleum UST Release Sites. Groundwater Monitoring and Remediation.
  - 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)

Modeling

2

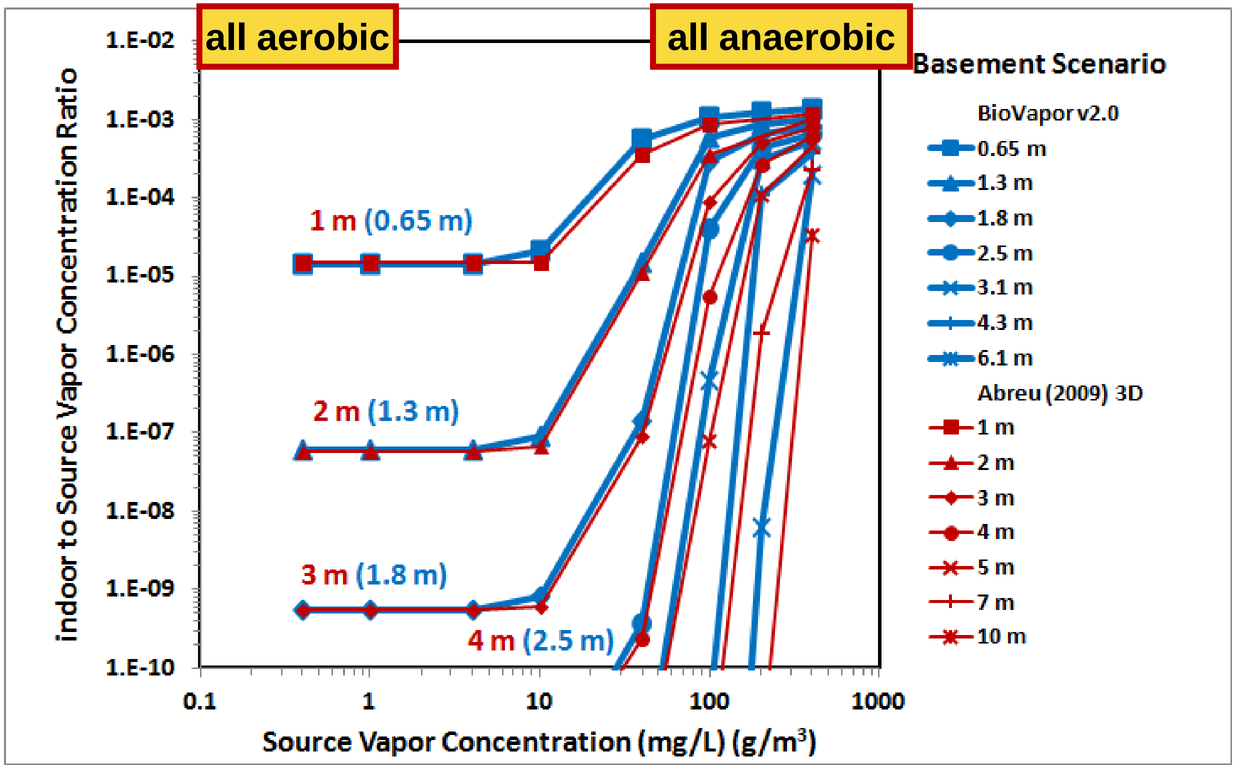
- **Use:**
  - **Advective-Diffusion Solution with Oxygen-limited Biodegradation**
    - **Derived algebraic solution for oxygen-limited aerobic biodegradation with imposed advection.**
    - **Very similar to 'BioVapor' model with imposed advection.**
  - **Impose additional constraints:**
    - **Maximum 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

2

- As an example, without advection –
- Use the same type of nomagram 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

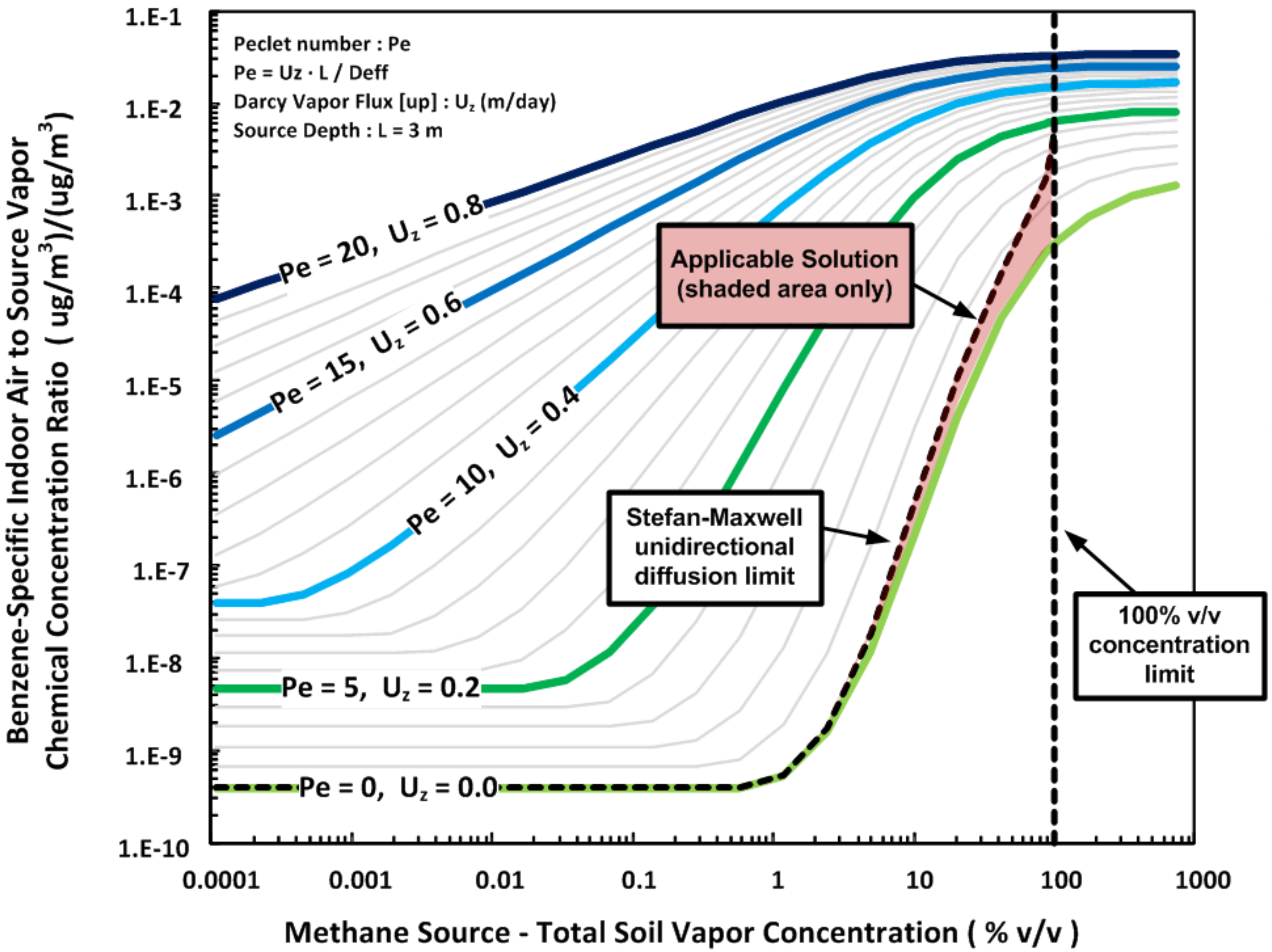
•Plot on this slide: the source advection rate is zero.

- 3D: Abreu 2009: GWM&R
  - & API Publ. 4555
- Basement Scenario
- Matched Parameters
  - Except "Depth"

Model Results – Sensitivity Analysis

2

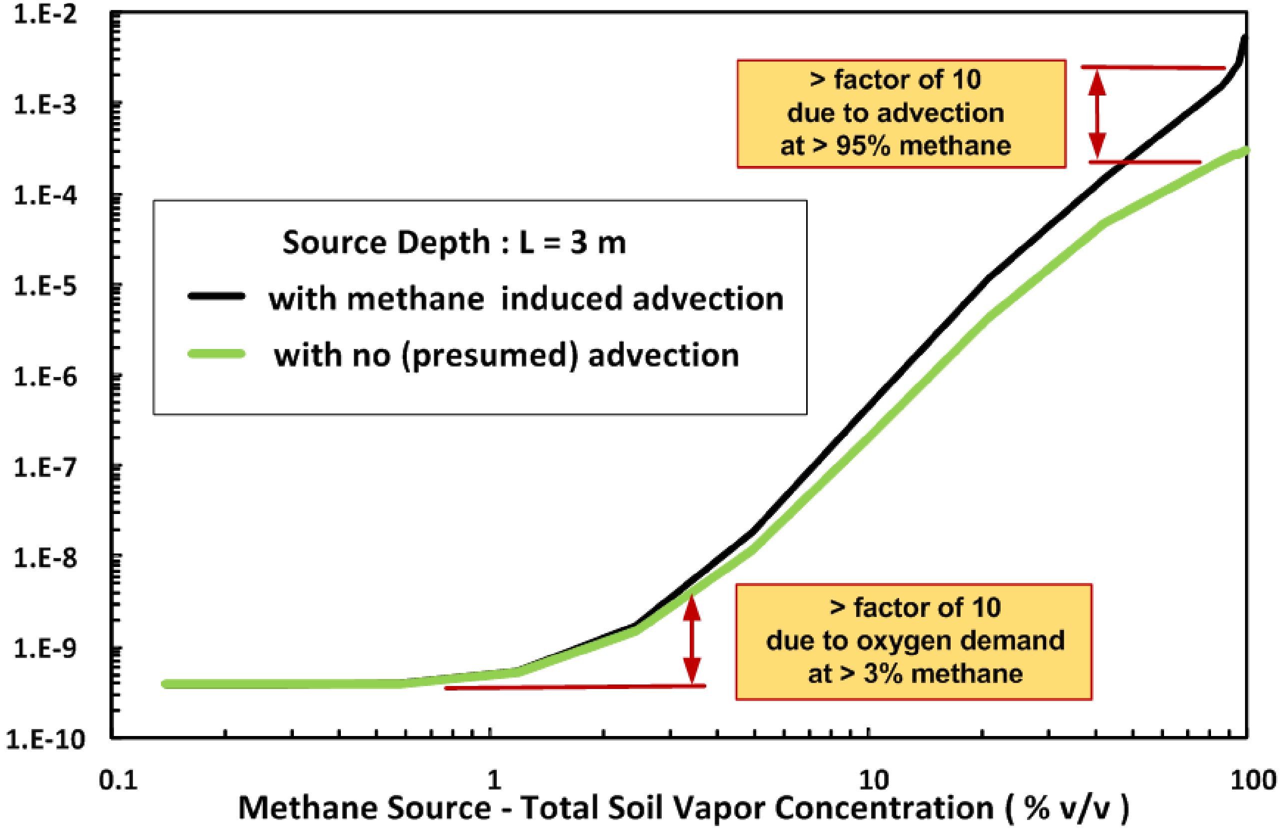
- **Effect of Methane Source on Benzene Attenuation Factor (Ex**



Conclusions: Effect of methane on other chemicals

2

- 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) : 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

2

- **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

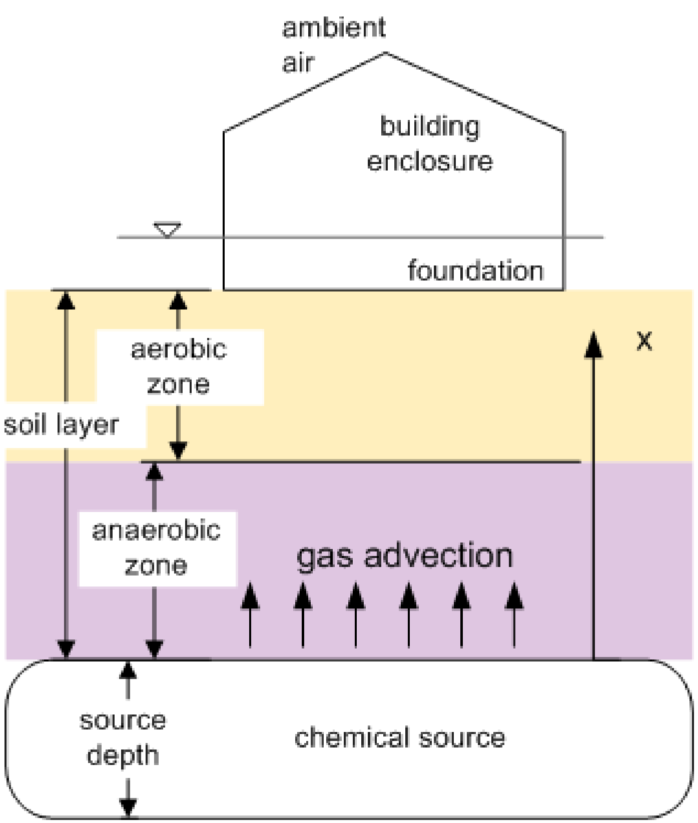
End

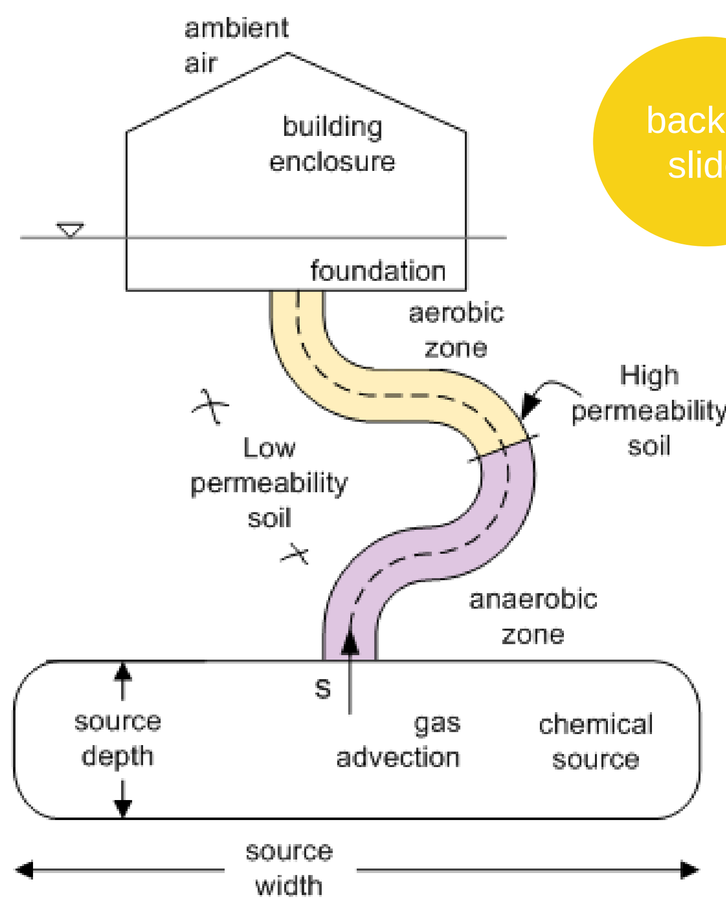
Thank you

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**





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Modeling: Soil gas flow

- high concentration of methane in soil gas; possible induced

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

$u_{v,i} = (R \cdot T / P) \cdot N_i$, Darcy flux (m^3/m^2-hr) • $(R \cdot T / P)$, molar volume (m^3/mole)

N_i, molar flux (mole/m^2-hr) • X_i, mole fraction (mole/mole) • D_i, effective diffusion coefficient (m^2/hr)

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- **Advective-Diffusion Eq. – no concentration constraint**
- **Fick's law – no advection**

$\sum^{mobile}_{gases} < 50\% v/v$: bias in flux $< 50\%$ • $\sum^{mobile}_{gases} > 80\% v/v$: bias in flux $> 100\%$

Key point:

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

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:**

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

- **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 atmosph gases, probably by methane gas.**
  - **The nitrogen value has been confirmed to be through calibrated 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.**

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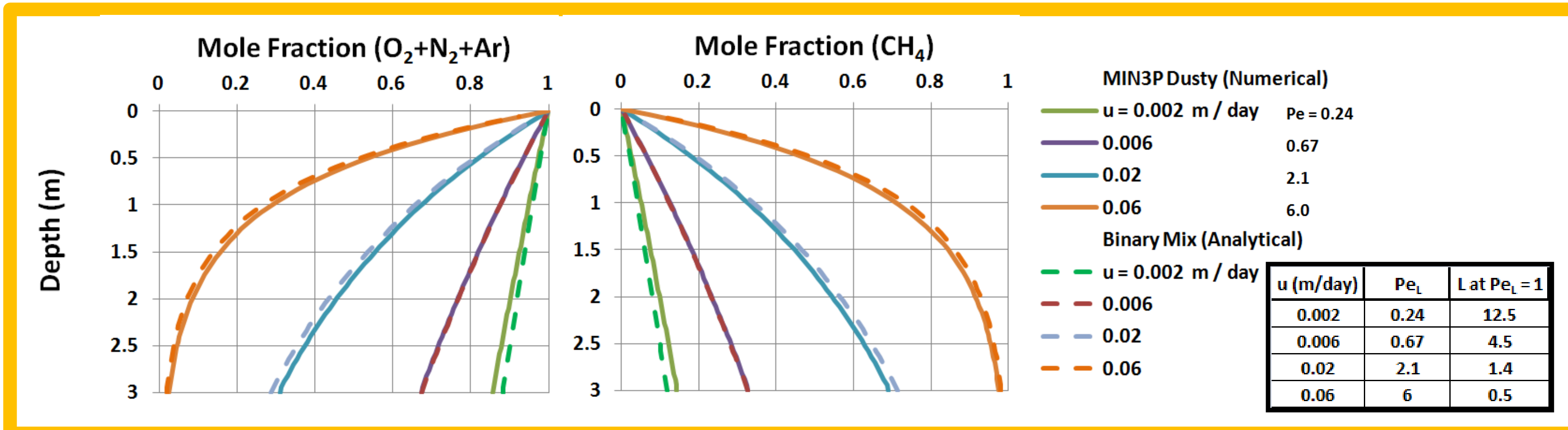
Modeling: Implementation

- **Binary non-reactive gas flow → mathematical solution**
- **Anything more complex → numerical solution**

Favorable comparison:

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



u (m/day)	Pe_L	L at Pe_L = 1
0.002	0.24	12.5
0.006	0.67	4.5
0.02	2.1	1.4
0.06	6	0.5

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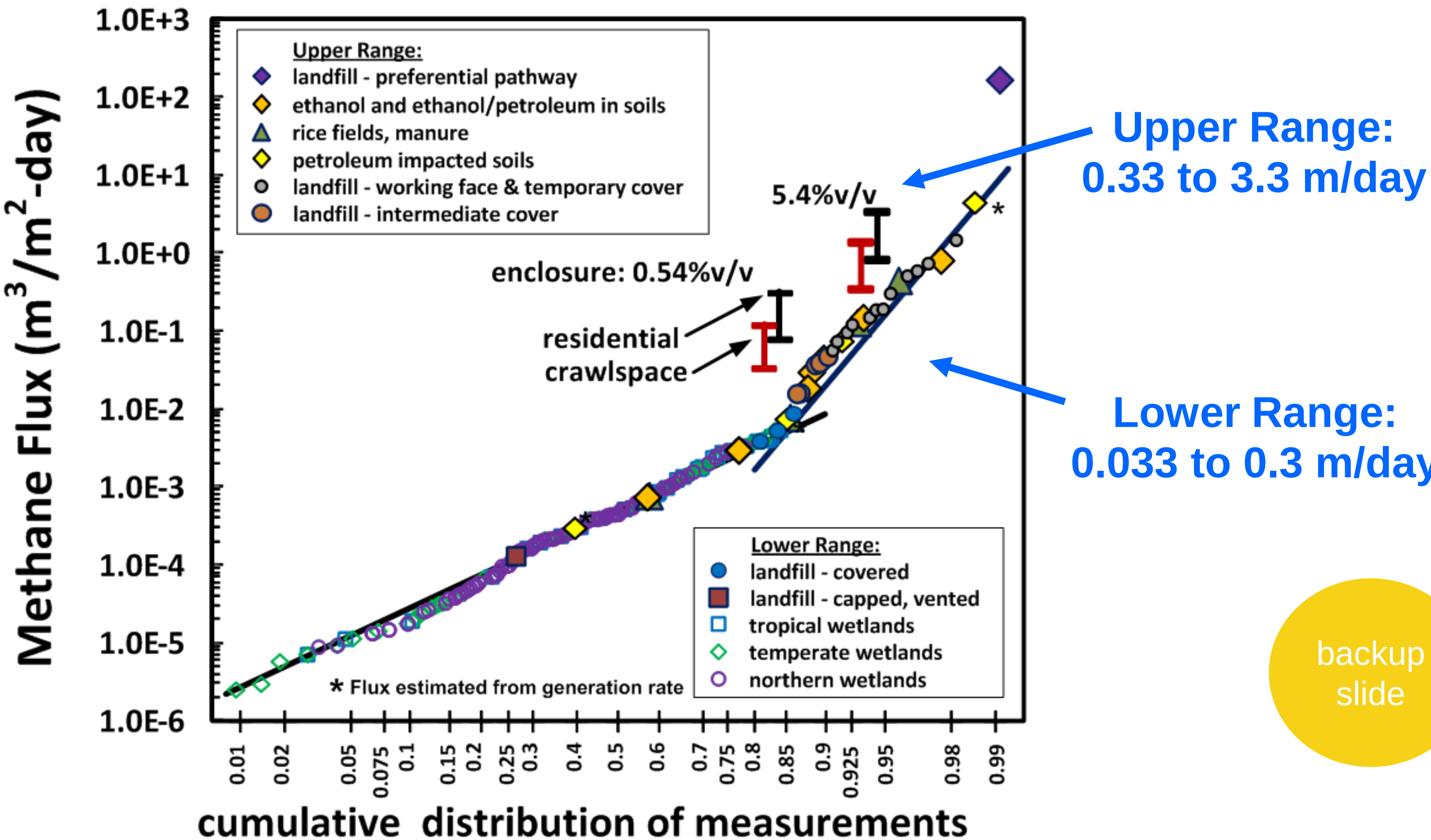
Acknowledgement MIN3P Dusty : Parisa Jourabchi (Golder), Uli Mayer (UBC)

Methane emission flux - survey



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- <u>Potential</u> Identified Issues from Consolidated survey:
  - Active Municipal Landfills, Manure, Ethanol, Ethanol/Petroleum, Petroleum
    - Source size & methane generation rate still matter

I. Flammability: Methane Concentration

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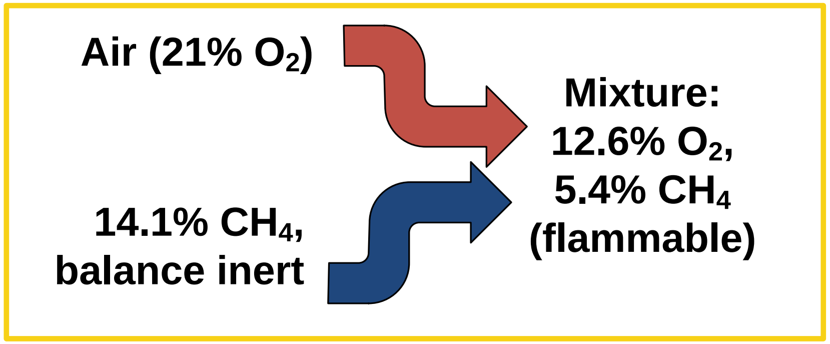
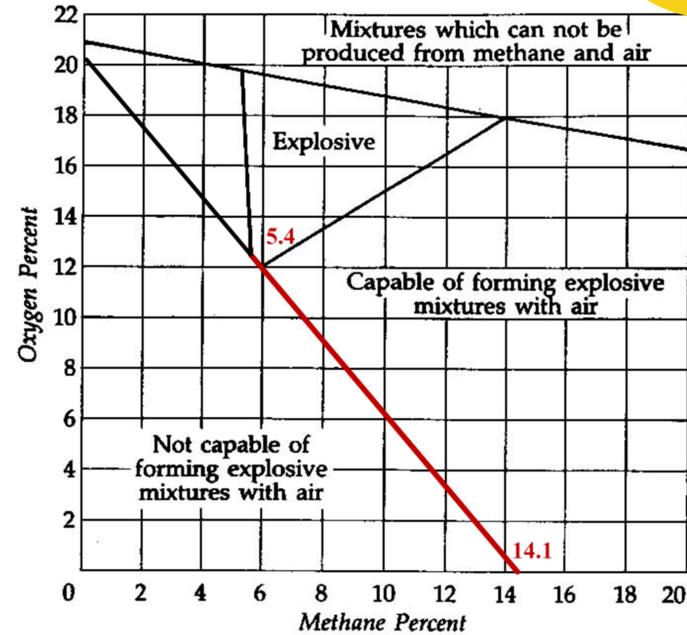
- 5.4% methane in air is flammable (LFL)
  - Need at least 14.1% methane in soil gas (the rest: N_2, CO_2, etc.) to m with air (21% O_2) to yield a flammable mix





Relation Between Quantitative Composition and Explosibility of Mixtures of Methane and Air

30 CFR § 57.22003, MSHA Illustration 27

  - 'Safety factors' (10% LFL for occupied space)
- Soil gas is not flammable; Flame is 'quenched' in 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

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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 (CH_4, CO_2, …)
- 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 pemetrations

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

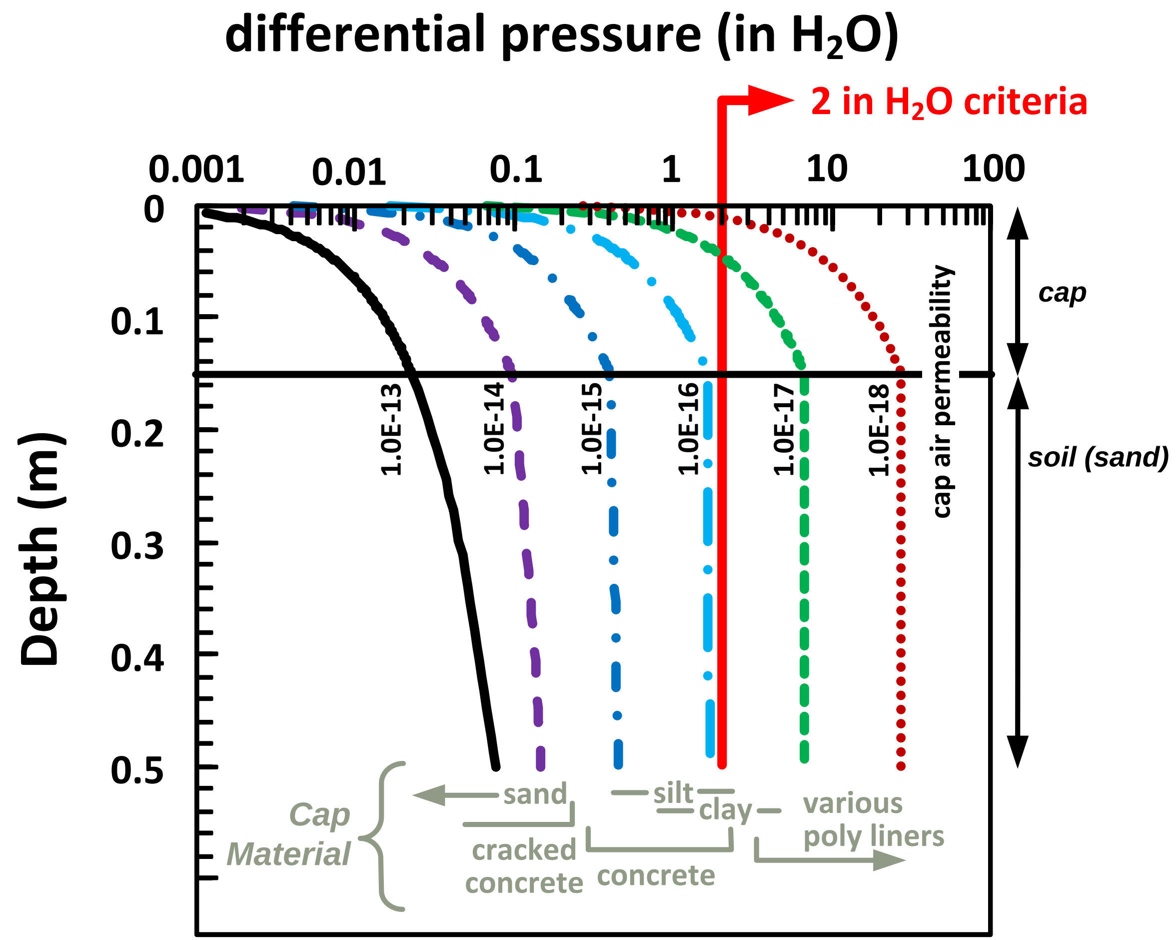
Receptors:

- Occupied enclosures
- Crawlspaces
- 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

Differential Pressure Criteria



scenario: crawlspace
specified methane flux : 0.34 m / day

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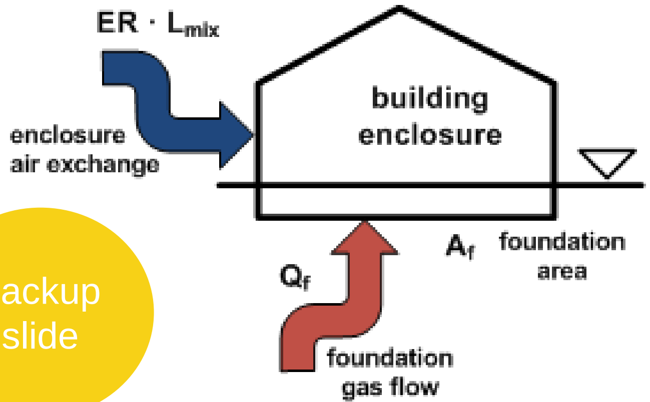
II. Flammability: Methane Flux (or Flow)



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air flow / area / mixing height / exchange rate / mole fraction

$$Q_f / A_f = L_{mix} \cdot ER / (1/X_{CH4} - 1)$$

	enclosure criteria (%v/v)	Methane Flow (L/min)	Methane Darcy Flux (m^3/m^2-day) (m/day)
residential building	5.4	57 to 230	0.82 to 3.3
	0.54	5.4 to 21.7	0.078 to 0.31
crawlspace	5.4	5 to 95	0.34 to 1.4
	0.54	0.5 to 9.0	0.033 to 0.13

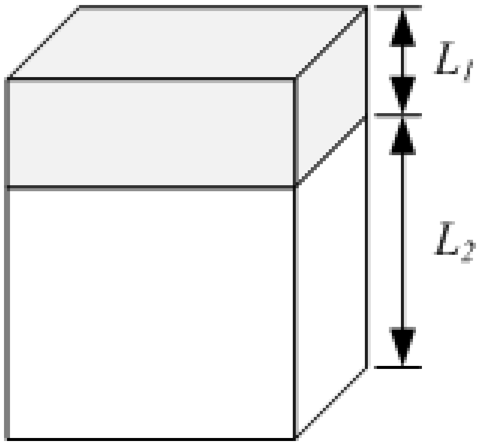
- **Estimated methane fluxes (and flows) for potential flammability:**
  - **Approximately ~ 0.33 to 3.3 m/day to reach 5.4%v/v methane in enclosure**
    - **Advection required (relative to diffusion) at these flux velocities**
    - **Lower ranges with applied safety factors; higher ranges if 'crack' flow not entire foundation area**

Parameter definition and selection

- **1-D geometry modeled**

For each layer (foundation, soil):

LAYERS:	
1-layer	$X_i(s=L)=1-(1-X_i(s=0))\cdot\exp\left(-\frac{u_{v,i}\cdot L}{D_i}\right)$
2-layer	$X_i(L_2)=1-(1-X_i(s=0))\cdot\exp\left(-\left(\frac{u_{v,i}\cdot L_1}{D_{i,1}}+\frac{u_{v,i}\cdot L_2}{D_{i,2}}\right)\right)$
$u_{v,i}$, Darcy flux (m^3/m^2-hr) • L, depth (m) • $Pe_L=u_{v,i}\cdot L/D_i$, Peclet number • X_i, mole fraction (mole/mole) • D_i, effective diffusion coefficient (m^2/hr) • i, mobile gas component	



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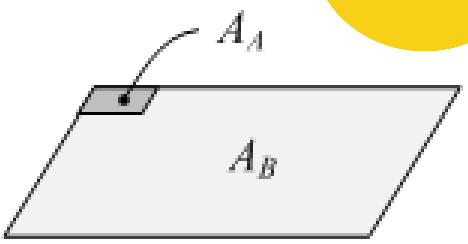
Within each layer, an area-weighted average:

AREA: 2 sub-areas, A_A, A_B	
diffusion coefficient	$D_{i,avg}=\eta\cdot D_{i,A}+(1-\eta)\cdot D_{i,B}$
gas permeability	$k_{v,i,avg}=\eta\cdot k_{v,A}+(1-\eta)\cdot k_{v,B}$
Area weighted fraction: $\eta=A_A/(A_A+A_B)$	



Model Scenario: Shallow Methane

Steady-state unidirectional diffusion in a binary gas mixture

1

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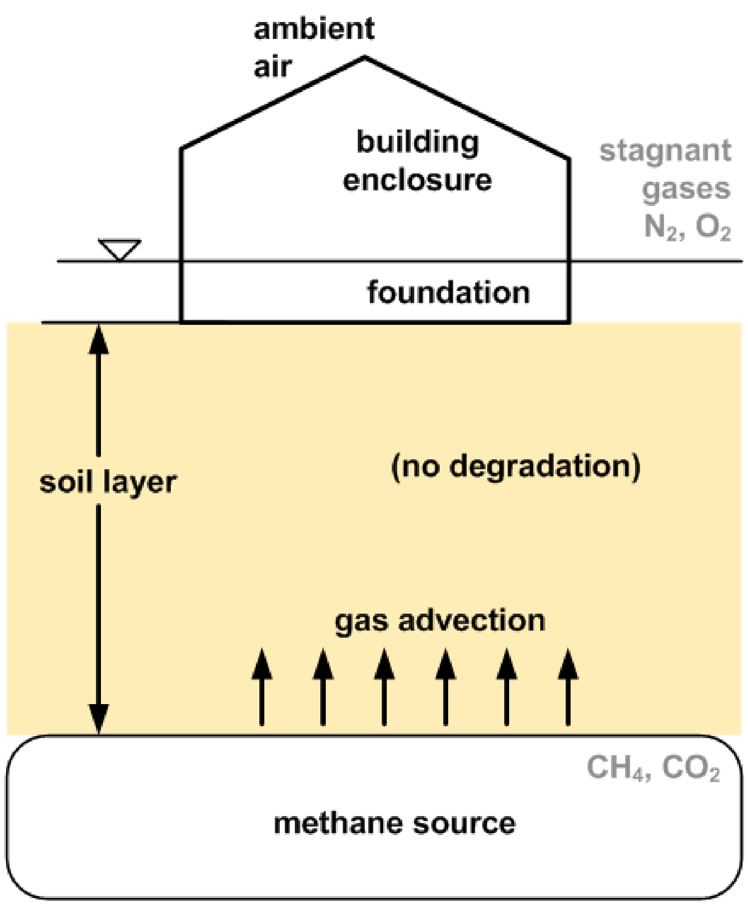

Layered Compartments (one-dimensional):

- **Enclosure**
  - **Mixing and dilution**
  - **Stagnant gases: Air (N_2, O_2, 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 (CH_4, CO_2) at depth; upward flux specified (worst-case for flammability is all methane)**

Methane Hazard: modeled results

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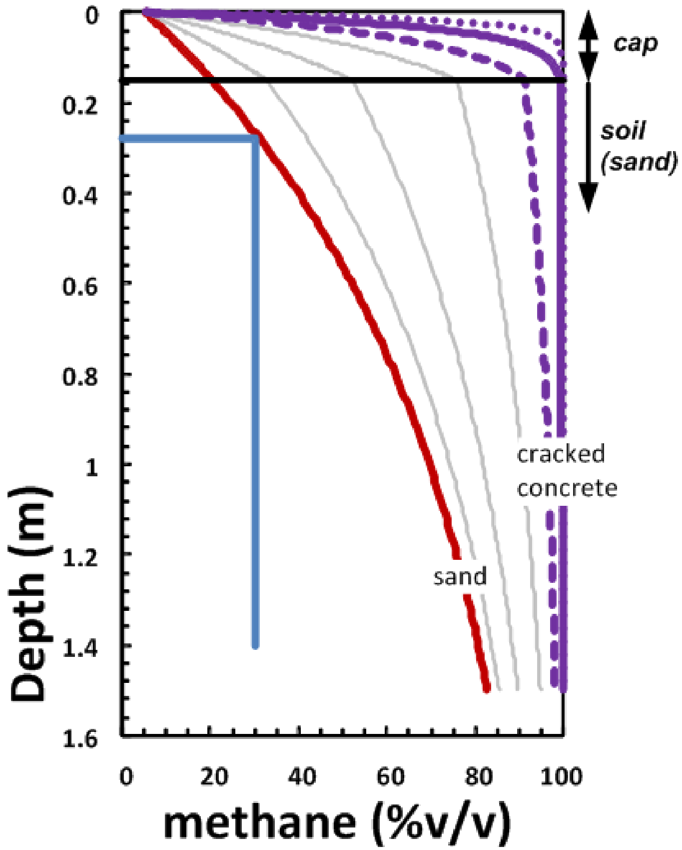
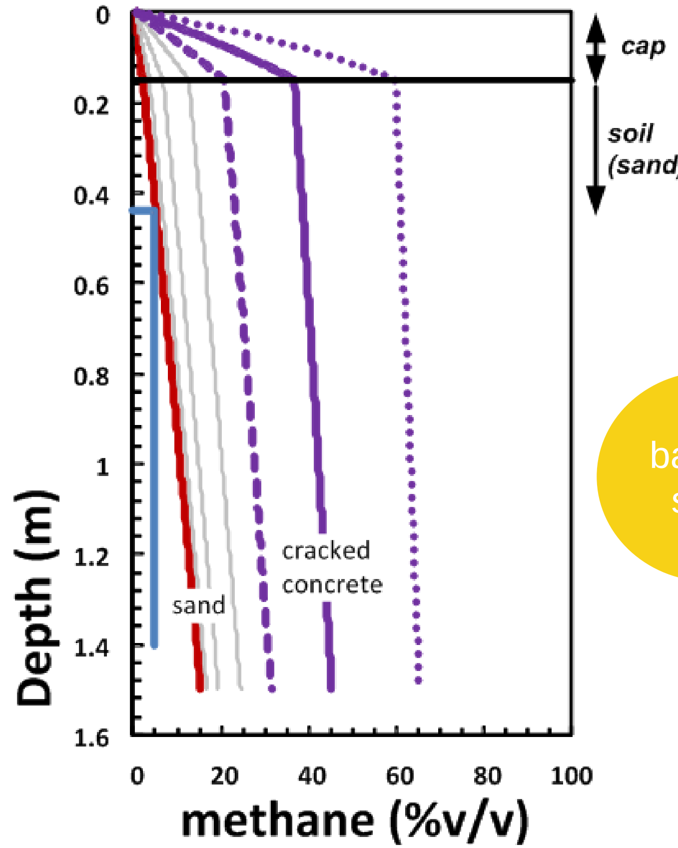


indoor methane : 5.4 %v/v
methane flux : 0.34 m / day
scenario: crawlspace
criteria: 30% v/v methane, at > 0.28 m depth



methane : 0.5 %v/v
methane flux : 0.033 m / day
scenario: crawlspace
criteria: 5% v/v methane, at > 0.44 m depth

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Key point:

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

Differential Pressure

- **2-in H_2O differential pressure criteria**
  - **Presumes pneumatic connection between soil and enclosure**
  - **Requires a relatively impervious cap**
    - **From calculated pressure drop**
    - **15 cm capping material**

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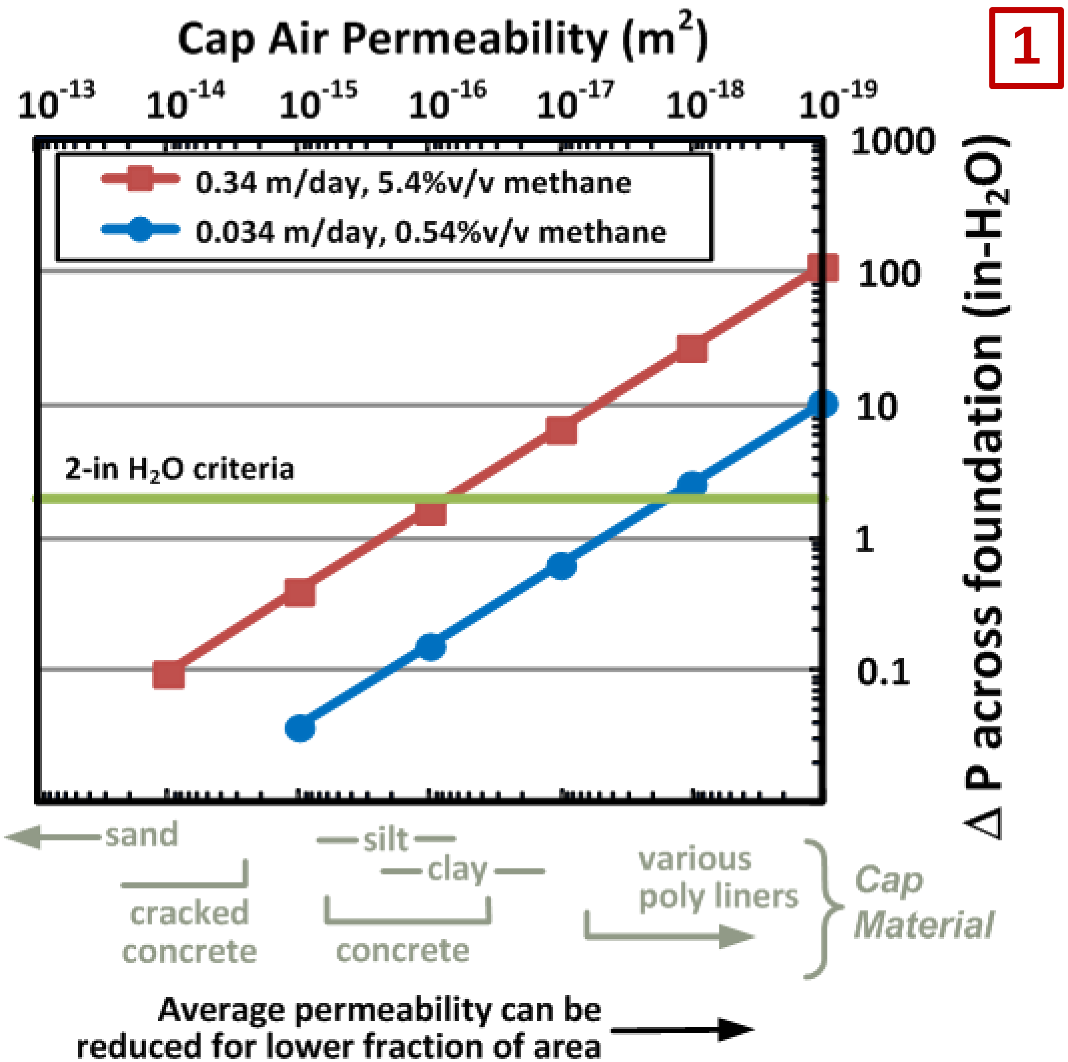

Key point:

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