TCE Fate and Transport, as Related to Vapor Intrusion

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NEWMOA/Brown SRP Workshop on
TCE Vapor Intrusion: State of the Science, Regulations and Technical Options
May 2015

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Vapor intrusion involves the migration of chemical vapors in the soil and groundwater to enter buildings through foundation cracks and joints. Sometimes vapor intrusion can result in long-term exposure of contaminants at harmful levels.

- Affects maybe 1/4 of the estimated inventory of 500,000 US brownfields sites.
- At present, no general EPA guidance, though draft guidance has been prepared.
- States regulate, but often very different standards in use.
- Also jurisdictional issues - who is in charge- OSHA? EPA? State?
- No agreement on site investigation practices.
- Limited use of quantitative modeling- very fieldwork based, empirical.

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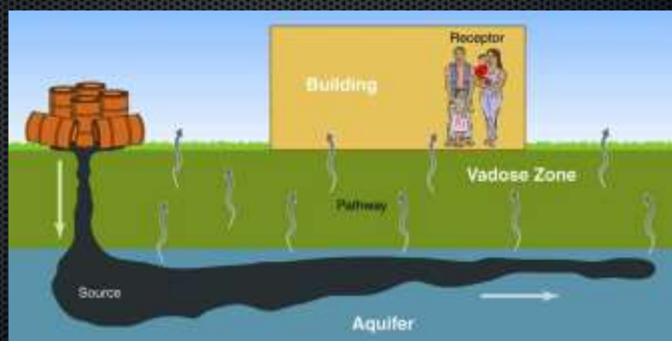
In environmental health risk assessment, for there to be a human health risk there must be a completed exposure pathway, involving identification of a

- **Source** **(Source strength variability? Where to measure?)**
- **Migration Route** **(Temporal Effects? Preferential Pathways?)**
- **Receptor** **(Backgrounds? Where to measure?)**

-Does depth to GW matter?

-Does rain/ice make a difference? Other Seasonal/weather effects?

-What about non-VI background? Is subslab sampling the answer?



(Interstate Technology & Regulatory Council, 2007

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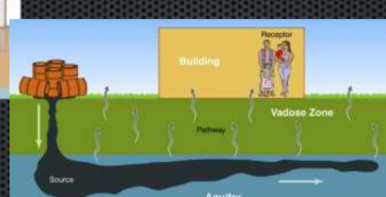
What is wrong with this picture?



Not appropriate for trichloroethylene (TCE), which is a DNAPL

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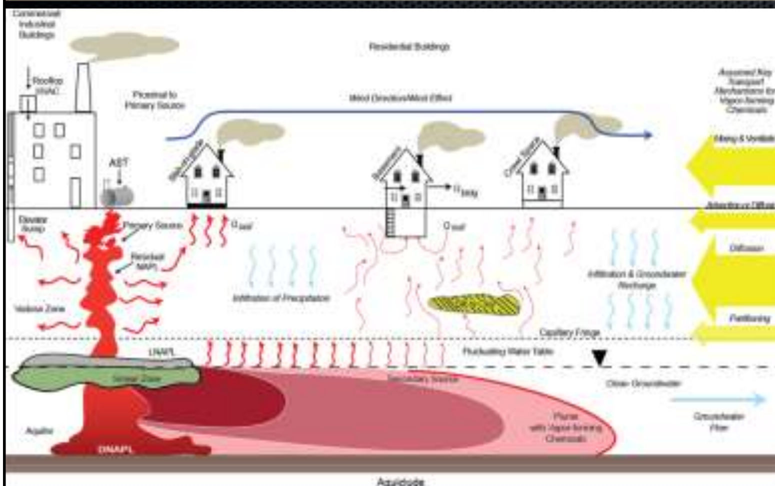

Source characterization may be tricky with DNAPLs

Also, there is Increasing understanding of the complexity of transport

From a presentation by Larry Schnapf, Schnapf LLC, Cherry Hill, NJ. September 2014

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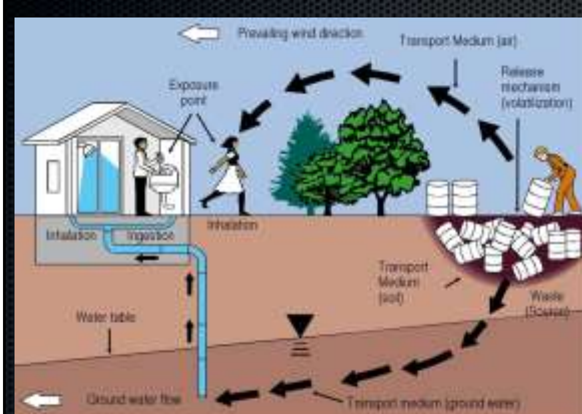
Other exposure routes can come into play (including resident-caused exposures)



From NEWMOA- “Improving Site Investigation”

Dose from drinking 2L/day of 5 µg/L TCE in water (EPA MCL) is same as from breathing 20m^3/day of air containing 0.5 µg/m^3-
Second is harder to control

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Background Sources

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The TCE issue has just exploded in the VI field – more controversy on what is "safe"

- US EPA IRIS (2011) - RfC=2 µg/m^3, HQ (1) = 2.1µg/m^3, ELCR (10^{-6}) = 0.48 µg/m^3, ELCR (10^{-5}) = 4.8 µg/m^3
- OSHA (PEL- 8 hr) = 537,000 µg/m^3, NIOSH (10 hr) = 134,000 µg/m^3
- Now, risk based indoor air levels are shifting to non-cancer endpoints (e.g. developmental; FCM, thymus weight)
- New "prompt" or "urgent" action levels being based upon RfC- mitigation may be required in weeks or days; may involve temporary relocation. But will the FCM RfC values stand?
- TCE found at 2/3 of Superfund sites

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EPA recommends mitigation for vapor intrusion cancer risks at 10^{-5} or 10^{-6}

Radon cancer risk @ 2 pCi/L

Non-smokers: 4 per 1000 risk ($10^{-2.4}$)

Smokers: 32 per 1000 risk ($10^{-1.5}$)

Important policy implications regarding being protective against VI risk

One in four homes contain radon in excess of EPA action level of 4 pCi/L
In some towns 50% of homes are above this level.

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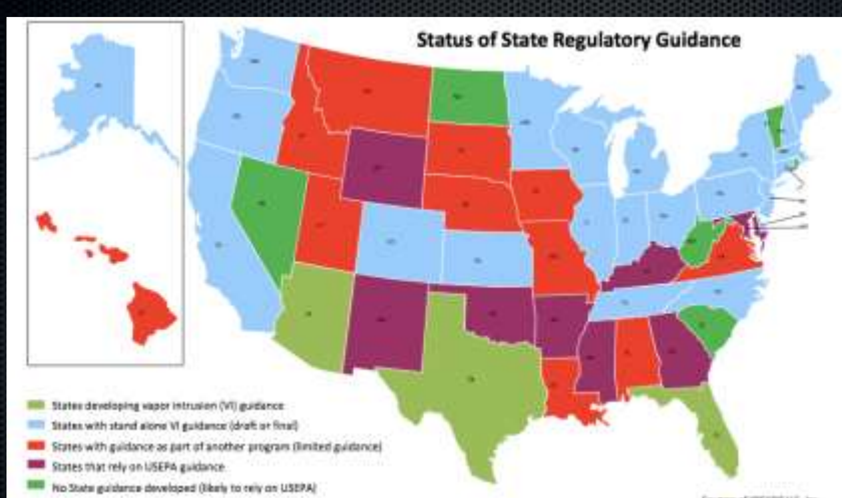
A patchwork of regulations



And it's a fluid situation

- Final, final interim, or draft stand-alone VI guidance document or appendix
- Most guidance documents published after 2006
- VI focus in the northeastern states (industrial legacy, climate, property)
- Several states have updated existing final guidance (e.g., CA, NC, NJ, NH, WS…)

From a Presentation by Laurent Levy, Gradient Corp. May 2014

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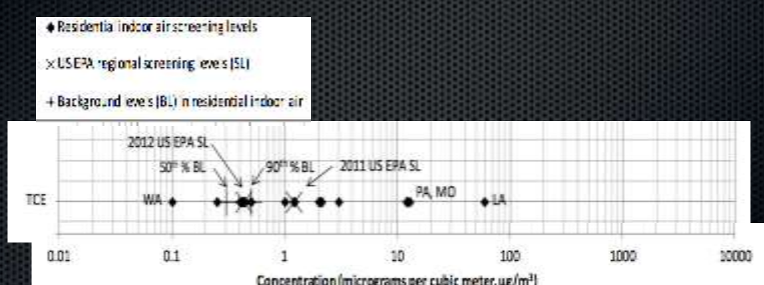
What levels of TCE are used by regulators?



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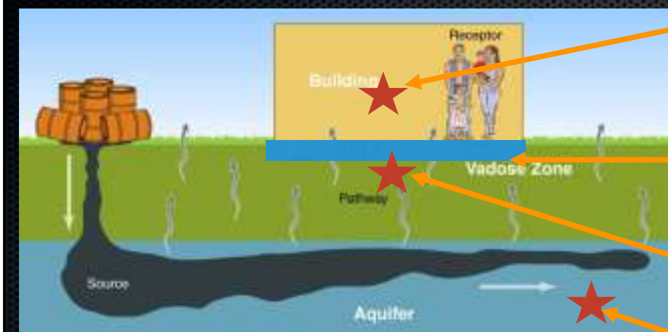


Indoor air sample

Foundation Slab

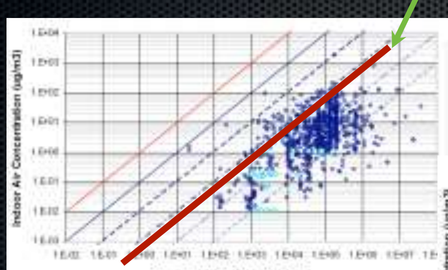
Subslab Soil Vapor Sample Location

Groundwater sample location (convert to source strength using Henry's Law)

- Screening values- which to use? Levels?
  - Groundwater (Henry's Law), soil gas
  - Subslab, indoor air
- How many samples taken over what time?

U.S. EPA uses empirical "attenuation factor" approach for predicting indoor air concentrations

- Based upon many field measurements.
- $C_{indoor}/C_{subslab}$ = 0.1 (resistance of slab)
- $C_{indoor}/C_{groundwater\ source}$ =0.001



Groundwater Source- reflects resistance of soil plus slab

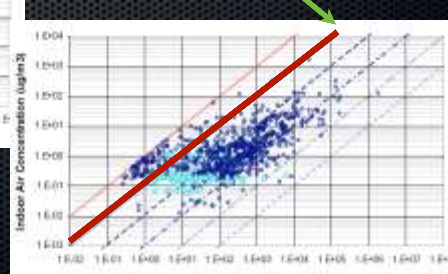


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Table 2. Residential screening levels for selected VOCs.

State	Benzene Groundwater	Benzene Soil Gas	Benzene Indoor Air	TCE Groundwater	TCE Soil Gas	TCE Indoor Air	PCE Groundwater	PCE Soil Gas	PCE Indoor Air
Alaska	5	3.1	0.31	5	0.22	0.022	5	8.1	0.81
California	NA	36.8	0.084	NA	528	1.22	NA	180	0.41
Colorado	15	NA	0.23	5	NA	0.016	5	NA	0.31
Connecticut	130	2480	3.3	27	752	1	340	3798	5
Indiana	85-850	250-1400; 25-140[a]	2.5	4.6-700	120-2000; 2-200[a]	1.2-4.1	7.4-1100	320-5200; 32-520[a]	3.2-10
Louisiana	2,900	NA	12	10,000	NA	58	15,000	NA	110
Maine	NA	NA	10[b]	NA	NA	NA	NA	NA	NA
Massachusetts	3000	NA	0.3	30	NA	1.37	50	NA	0.04
Michigan	5800	150	2.9	15,000	700	14	25,000	2100	42
Minnesota	NA	1.3-4.5	1.3-4.5	NA	NA	NA	NA	NA	20
New Hampshire	2000	95	1.8	50	54	1.1	80	68	1.4
New Jersey	15	16	2	1	27	3	1	34	3
New York	NA	NA	NA	NA	NA	5	NA	NA	100
Ohio	14	31	3.1	–	122	12.2	11	81	8.1
Oklahoma	5	3.1	0.27	5	0.17	0.017	5	0.33	0.33
Oregon	160	NA	0.27	6.6	NA	0.018	78	NA	0.34
Pennsylvania	3500	NA	2.7	14,000	NA	12	42,000	NA	38

Notes: Units are μg/L for groundwater and μg/m³ for soil gas and indoor air. See individual state guidance documents for additional information, including limitations and exceptions. Trigger or action levels for mitigation based on indoor air concentrations may be higher than the screening levels shown. [a]Second range of values shown is for subslab soil gas. [b]Chronic exposure value.

From Eklund, Folkes, Kabel, Farnum, in EM, 2007.

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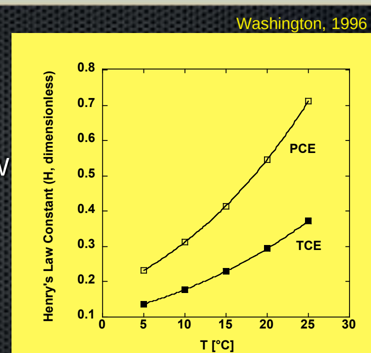
Henry's Law relates expected soil vapor concentrations to $C_{\text{groundwater source}}$

$$C_{\text{soil gas}} = H\, C_{GW}$$

Washington, 1996



Shallow groundwater temperatures (Collins, 1925)

If MCL for TCE in drinking water is 5 μg/L leads to about 1 mg/m³ soil gas.
EPA recommends non-cancer toxicity level inhalation conc. of 2 μg/m³ (1.2 μg/m³ cancer screening level at 10^{-6})

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Table 4. Attenuation values used in state VI guidance

State	Attenuation Coefficients: Groundwater	Shallow Soil Gas	Deep Soil Gas	BTEX	Crawl Spaces
Alaska	0.001	0.1	0.01	NA	NA
California	NA	0.01 - 0.002	same as shallow	NA	0.002
Colorado	NA	0.1 (subslab)	NA	NA	1
Connecticut	0.001	0.001	NA	NA	NA
Indiana	NA	subslab = 0.1 soil gas = 0.01	0.01	NA	1
Louisiana	NA	NA	NA	NA	NA
Maine	NA	NA	NA	NA	NA
Massachusetts	Based on J&E model	NA	NA	Adjusted by 10x	NA
Michigan	Based on J&E model	0.02	0.002	NA	NA
Minnesota	NA	NA	NA	NA	NA
New Hampshire	Based on J&E model	0.02	0.02	Groundwater values adjusted by 10x	1
New Jersey	Based on J&E model	0.02	NA	0.002	1
New York	NA	NA	NA	NA	NA
Ohio	0.001	0.1	0.01	NA	NA
Oklahoma		0.1 (subslab)	0.1 (8-10 ft)	NA	1
Oregon	0.002	NA	NA	NA	NA
Pennsylvania	NA	0.01	NA	NA	NA

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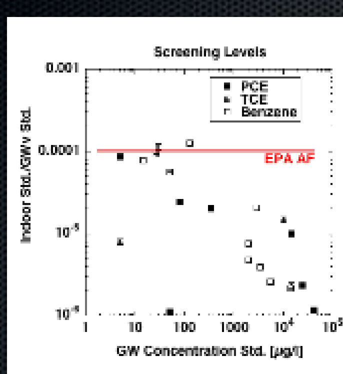

Data for CO, LA, CT, MA, NH, MI, PA. Henry's Law constants for benzene, TCE and PCE from EPA website, 25° C

Higher GW Concentration Standards associated with higher assumed AFs. That is, you can afford to accept higher GW values the greater the assumed attenuation of vapors by soil.

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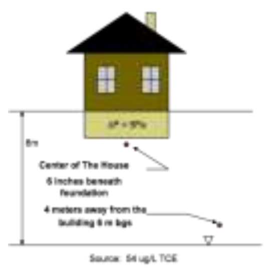
Subslab Sample Reliability?



We simulated various sampling points at different depths and locations using a sampling rate of 6L/8hr.

Photos from
O' Brien and Gere

But before discussing the simulations, consider what the EPA database shows about subslab samples and their relationship to indoor air samples.

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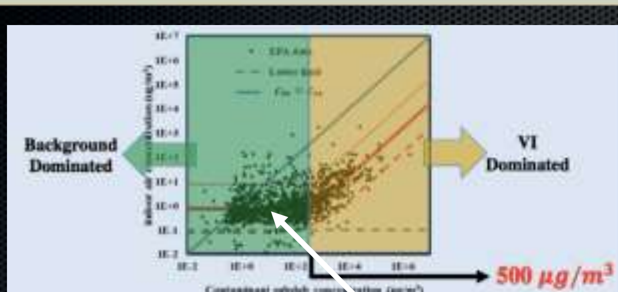

There is often great significance given to subslab values- but does this always make sense?

Little dependence of indoor air concentration on subslab values, because indoor air values dominated by "background" sources

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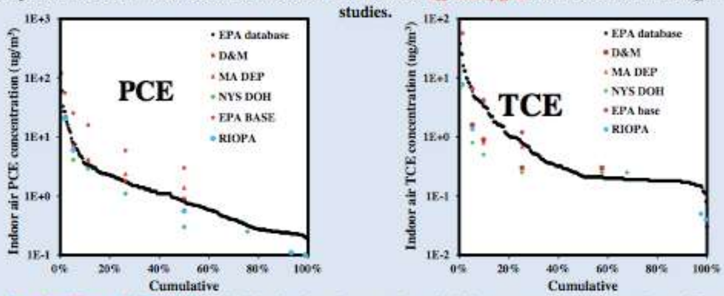
Comparison between the EPA database indoor air results when c_{ss} <500 $\mu g/m^3$ and other non-VI background studies.



There is no significant difference seen in distributions between low subslab concentration cases and non-VI cases.

When do you really look to VI, as opposed to other sources (e.g., consumer products)?

A 1000 m^3 volume house, 2 $\mu g/m^3$ indoor air contaminant level has an air inventory of 2 mg contaminant- can sorption processes contribute to the observed phenomena?

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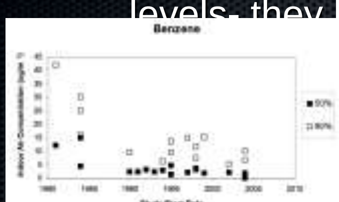
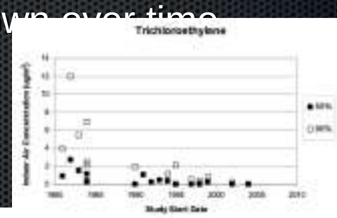
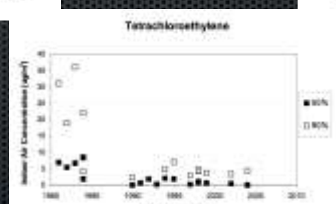
Need to watch what values you assume for background levels- they have gone down over time







Source: Background Indoor Air Concentrations of VOCs in North American Residences: A Compilation of Statistics and Implications for Vapor Intrusion by Helen Dawson (EPA)

- A number of VOCs have typical (median) background concentrations above the 10^{-6} risk level (benzene, carbon tetrachloride, chloroform, methylene chloride, PCE)
- Several others exceed 10^{-6} risk levels about 10% of time (1,2-DCA, TCE, vinyl chloride)

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Can we begin to do better by applying advanced engineering modeling tools?

EPA Screening Model Approach

- Based upon a 1-dimensional (1-D) model developed by Paul Johnson and Robbie Ettinger in 1991, based on earlier Radon work of Nazaroff and others.

$$\frac{D_{eff} A_B}{L_T}(C_{source} - C_{ck}) = Q_{ck} \times \frac{\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) C_{ck} - C_{indoor}}{\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) - 1}$$

$$Q_{ck} \times \frac{\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) C_{ck} - C_{indoor}}{\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) - 1} = Q_{building} * C_{indoor}$$

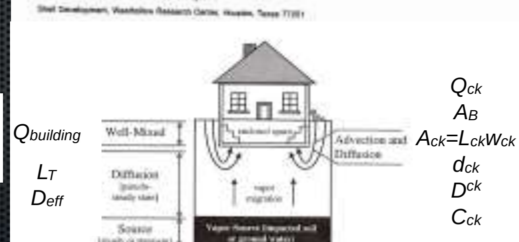
$$\alpha = \frac{C_{indoor}}{C_{source}} = \frac{\frac{D_{eff} A_B}{Q_{building} L_T} \exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right)}{\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) + \frac{D_{eff} A_B}{Q_{ck} L_T}\left(\exp\left(\frac{Q_{ck} d_{ck}}{A_{ck} D^{ck}}\right) - 1\right) + \frac{D_{eff} A_B}{Q_{building} L_T}}$$

Everything leaving the source enters the house- unrealistic, but a consequence of 1-D.

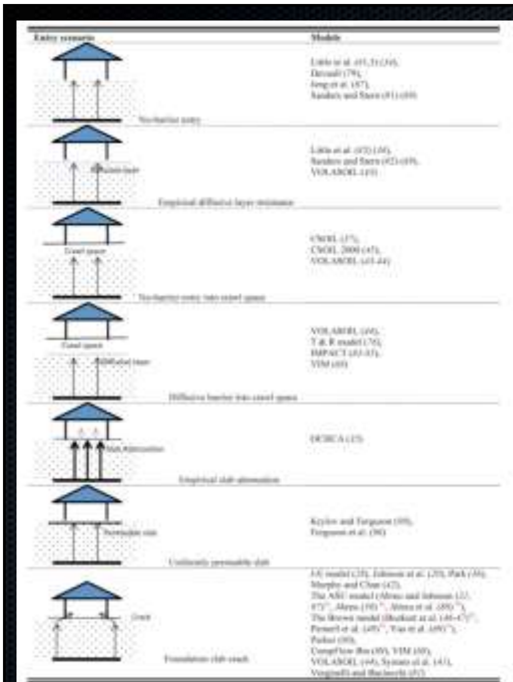
Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings

Paul C. Johnson* and Robert A. Ettinger

Shell Development, ... Research Center, Houston, Texas ...



Attenuation factor depends upon $Q_{building}$



Many mathematical models of VI being developed worldwide.

Differ based on where the main attenuation is assumed

Source: Yao et al., *Env. Sci. Tech.*, *47*, 2457-2470 (2013).

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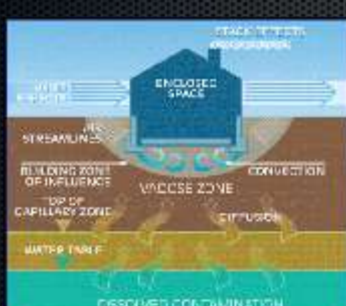
Brown University Modeling Approach

- A finite element computational package (Comsol) used to describe transport processes.



•Set finite element model domain.
•Typically assume a perimeter crack in the foundation.
•Assume "Stack Effect" creates an in-house negative pressure of 5 Pa.

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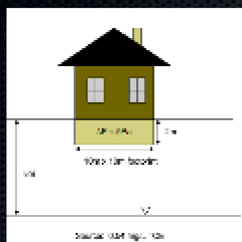
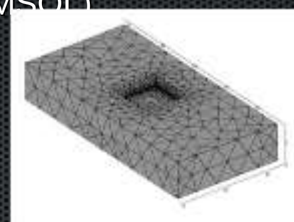
3-D Modeling Approach- Finite Element Solver (COMSOL)





Typically model 1 to 5 mm perimeter cracks

3-step solution method

1. Solve for gas advective flow through soil (Darcy's Law).
2. Solve for species transport via advection and diffusion.
3. Indoor air concentration is calculated using the species flow rate into the structure.

$$q = \frac{-k\rho}{\mu}\nabla\phi \qquad \phi = gz + \int_{p_0}^{p}\frac{dp}{\rho}$$

→

$$J_T = q \cdot C + D_{eff}\nabla C \qquad D_{eff} = d_i^{air} \cdot \frac{\eta_g^{10/3}}{\eta_T^{2}}$$

→

$$C_{indoor} = \frac{J_{Tck}}{A_e \cdot V_e + Q_{ck}}$$

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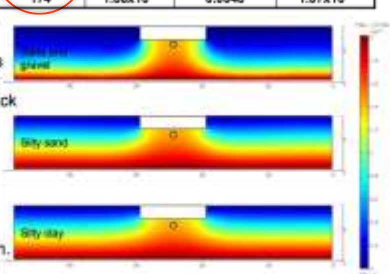
Subslab sample reliability?
Roughly same values, but 2 O.O.M. difference in indoor air

Where should samples be collected?

	soil Permeability	C sampling location (mg/m³)	C indoor Air (mg/m³)	Soil Gas Entry Rate (L/min)	$C_{indoor}/C_{sampling}$
Center of The House immediately beneath foundation	High (10^{-10} m²)	217	1.78	47.5	8.20×10^{-3}
	Moderate (10^{-11} m²)	190	0.27	4.75	1.41×10^{-3}
	Low (10^{-14} m²)	174	1.86×10^{-2}	0.0048	1.07×10^{-4}

The concentration values at the sampling point for all three cases are very similar; however, higher soil gas flow rate through the crack carries more contaminant vapor into the building, causing higher indoor air concentration for high permeability cases.

Sub slab sampling may lead to incorrect conclusions about the indoor contaminant concentration.



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Soil gas and subslab

- Subslab still very intrusive, and can be misleading
- Soil gas often misunderstood. “Open field” soil gas of limited value in understanding what happens in the presence of buildings, paving, or even frozen ground surface.

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How far is far enough??

$$D_e\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial C^2}{\partial y^2}\right) = 0$$

Solved simple 2-D Laplace Equation

insignificant at lateral distances of only η = 5. The value of 100 ft given in the U.S. EPA guidance is a conservative upper limit for sites with groundwater shallower than 10 ft and diffusion-limited vapor transport. Our work suggests that the risk from breathing contaminated indoor air from subsurface contamination need only be investigated for buildings within a relatively short distance (e.g., within one or two residential sized lots) from the edge of the contamination plume.

Lowell and Eklund, 2004

Echoed in various guidance documents, but challenged by Abreu and Johnson, 2005 for homogeneous soils.

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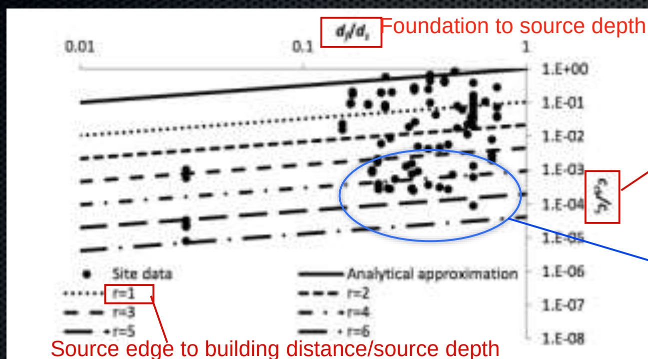
How close should GW Source measurements be?



Yao et al. *Vadose Zone Journal*,2013

Subslab to Source Concentration

Unusually high source to slab attenuation can have an origin in GW sources that are not really that "close"

Consider 2 m deep basement, 4 m deep source, sampling GW at r= 5 i.e., 20 m away, can lead to significant extra attenuation

Also, at what depth to sample GW?

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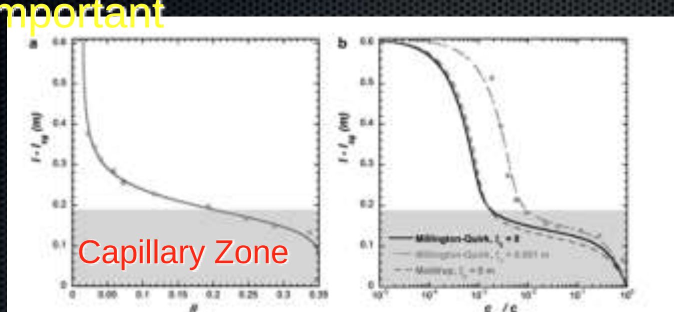
Capillary zone resistance is very important



From Shen et al., *Env. Engineering Sci.* , 2013

Shows extent to which open porosity filled with water; diffusion through water layer slow

Shows how dramatically COC concentration drops through capillary zone- big part of AF_{soil}

Relates to critical issue- the role of GW vertical concentration profiles

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Indoor Air sampling

Typical TO-15 with 6L summa

Intrusive, expensive, and is it even reliable as an indication of risk?

Need a lot of care to avoid being misled by background.

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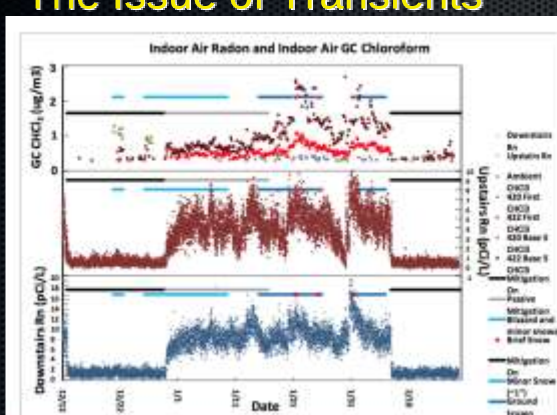
The Issue of Transients



Sample data from a 2013 AEHS Conference Workshop by Schumacher et al. Samples from a duplex in Indianapolis.

Note the wide variability over short sampling times.

Correlation with Radon not particularly good.

Seasonal variability in indoor air higher than in subslab.

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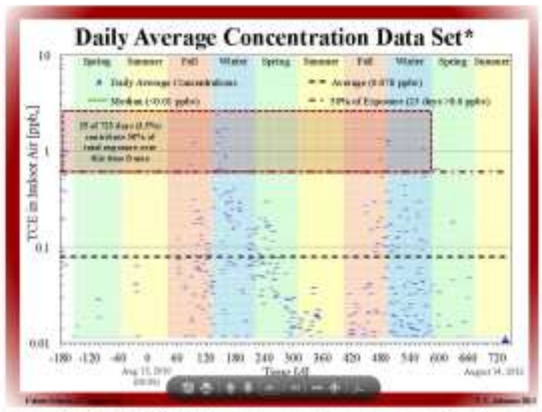
Episodic Peaks Drive Exposure

25 days (3.5%) present more exposure than the other 698 days



Dr. Paul Johnson's slide 20/48 - Note audio recording of presentation also available at:
https://iavi.rti.org/attachments/WorkshopsAndConferences/05_Johnson_03-19-13.pdf

Courtesy: Henry Schuver, EPA

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The majority of VI exposure could be unpredictable!

One time assessments are increasingly unlikely to be considered satisfactory…

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Paul Johnson, and Henry Schuver

Now What Do We Do?

Assuming that indoor air measurements will continue to be weighted heavily in future VI pathway assessment…

- evaluate the robustness of practicable combinations of different sampling durations and frequencies (daily, weekly, 3-weeks, seasonal)

What is a "robust" VI sampling plan?

One that produces data that lead to a high probability of correct and confident answers to questions like:

- Is the VI pathway complete?
- Are the indoor air concentrations and resulting exposures over periods of interest likely to exceed thresholds of concern?

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The Burden of Proof for Chemical VI

- Original Presumption:
  - VI pathway incomplete, until shown otherwise
- Evidence (from buildings over VI source areas):
  - Soil Gas Intrusion – occurs in episodic time periods
    - with some varying amount of subsurface chemical vapors
    - Assess. difficult, costly, and can be inaccurate
- Alternative (rebuttable) approach for CVI*
  - VI pathway is 'complete' to some degree (poss. Signif.)
    - Until demonstrated otherwise:

* As for Radon

From Henry Schuver, EPA

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Summary

- There exists a large variation in Attenuation Factors, for reasons that are only partly understood.
- Essential to consider background concentrations (and to measure or at least use current estimates).
- How close should a GW monitoring well be, to be reliable?
- There needs to be the awareness of transients, some very short term, some seasonal, and some very long time scale.

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Resources

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- United States Environmental Protection Agency (USEPA). *Vapor Intrusion Screening Level (VISL) Calculator*. Office of Solid Waste and Emergency Response (OSWER) and Office of Superfund Remediation and Technology Innovation (OSTRI), March **2012**.

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Courtesy: Professor Kelly Pennell, UKY