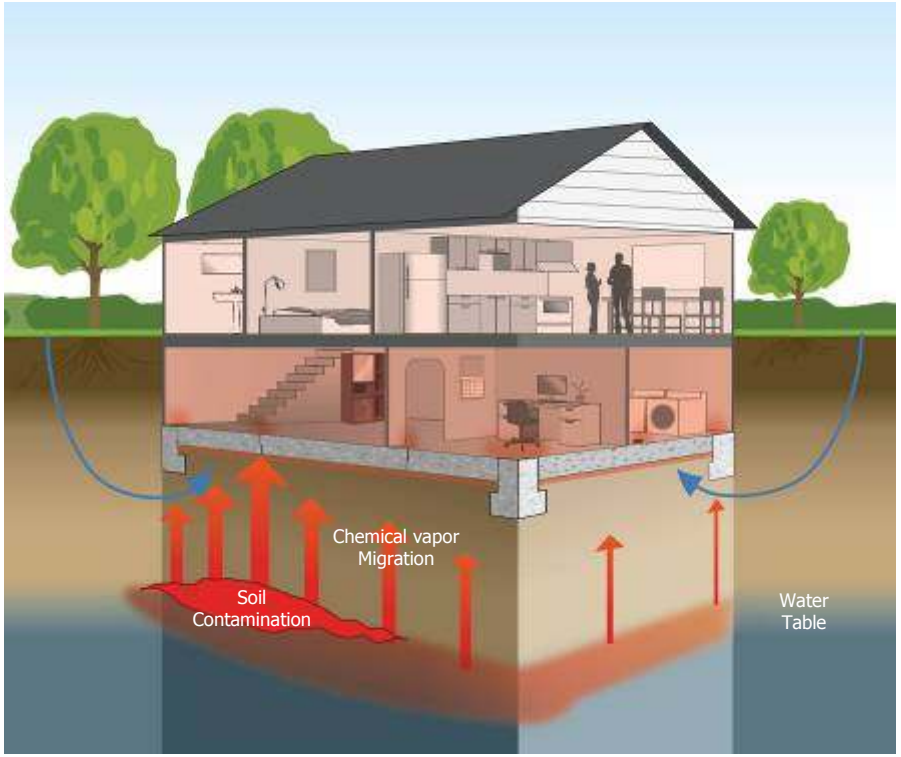
Prediction, Measurement and Mitigation of Soil Vapour Intrusion at Contaminated Sites



ISPRA Workshop
Roma, 27 Luglio 2010

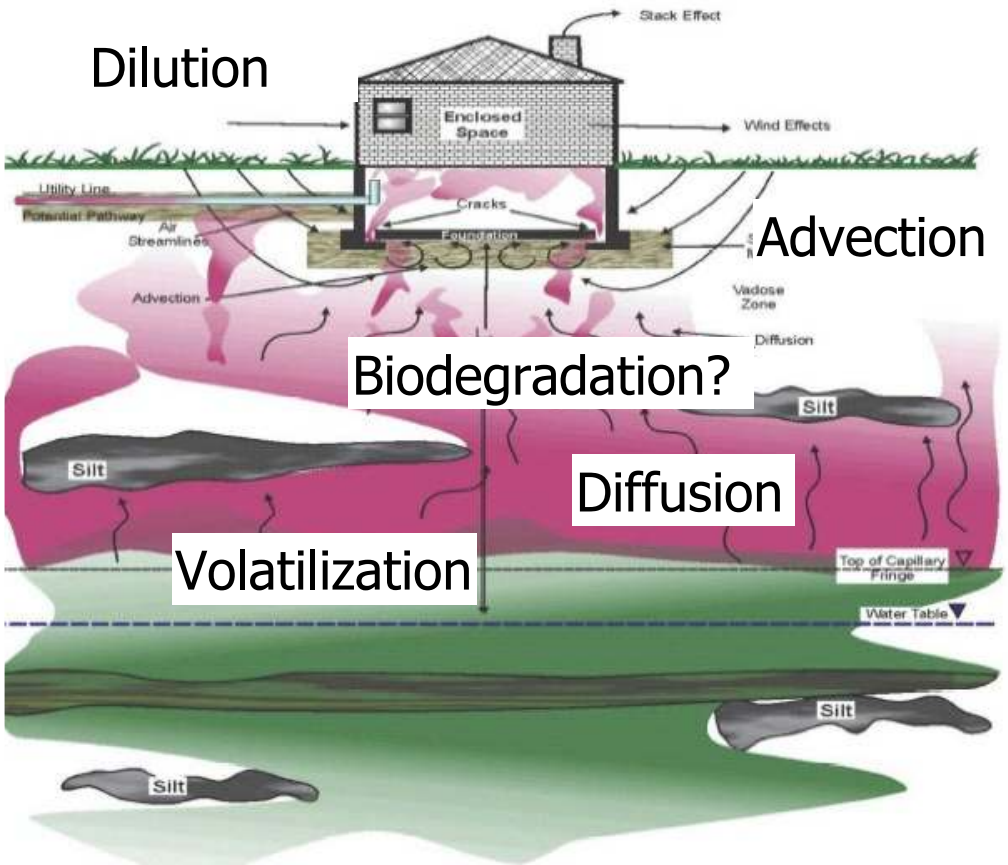
Dr. Ian Hers
Golder Associates Ltd.
Vancouver, BC

Golder Associates

Presentation Outline

- Introduction
- Learning from decade of site data
- Multiple lines of evidence approach
- Soil vapour methods
- Non-VOC measurement methods (expanded tool box)
- Modeling and empirical data comparisons
- Biodegradation research
- Vapour intrusion mitigation
- Conclusions

What is Vapour Intrusion?



- **Volatilization** of chemicals from groundwater or soil contamination
- **Diffusion** due to differences in chemical concentrations
- **Biodegradation** of petroleum hydrocarbon vapours as oxygen migrates downward
- **Advection** of soil gas into a building at a lower pressure than outdoor air due to stack effect (rising warm air), wind, or heating and ventilation; this sweeps upward migrating vapors into the building
- **Dilution** of vapors inside building due to ventilation

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Why is Vapour Intrusion Pathway Important

- Vapour intrusion (VI) is a ***potential*** exposure pathway at sites with volatile chemicals – represents many sites!
- There are an increasing number of identified sites with significant vapour intrusion impacts; ***majority*** of these are chlorinated solvent sites, with ***fewer*** petroleum sites
- At some sites may be safety (explosion, axyphiant) hazards due to methane or combustible vapours

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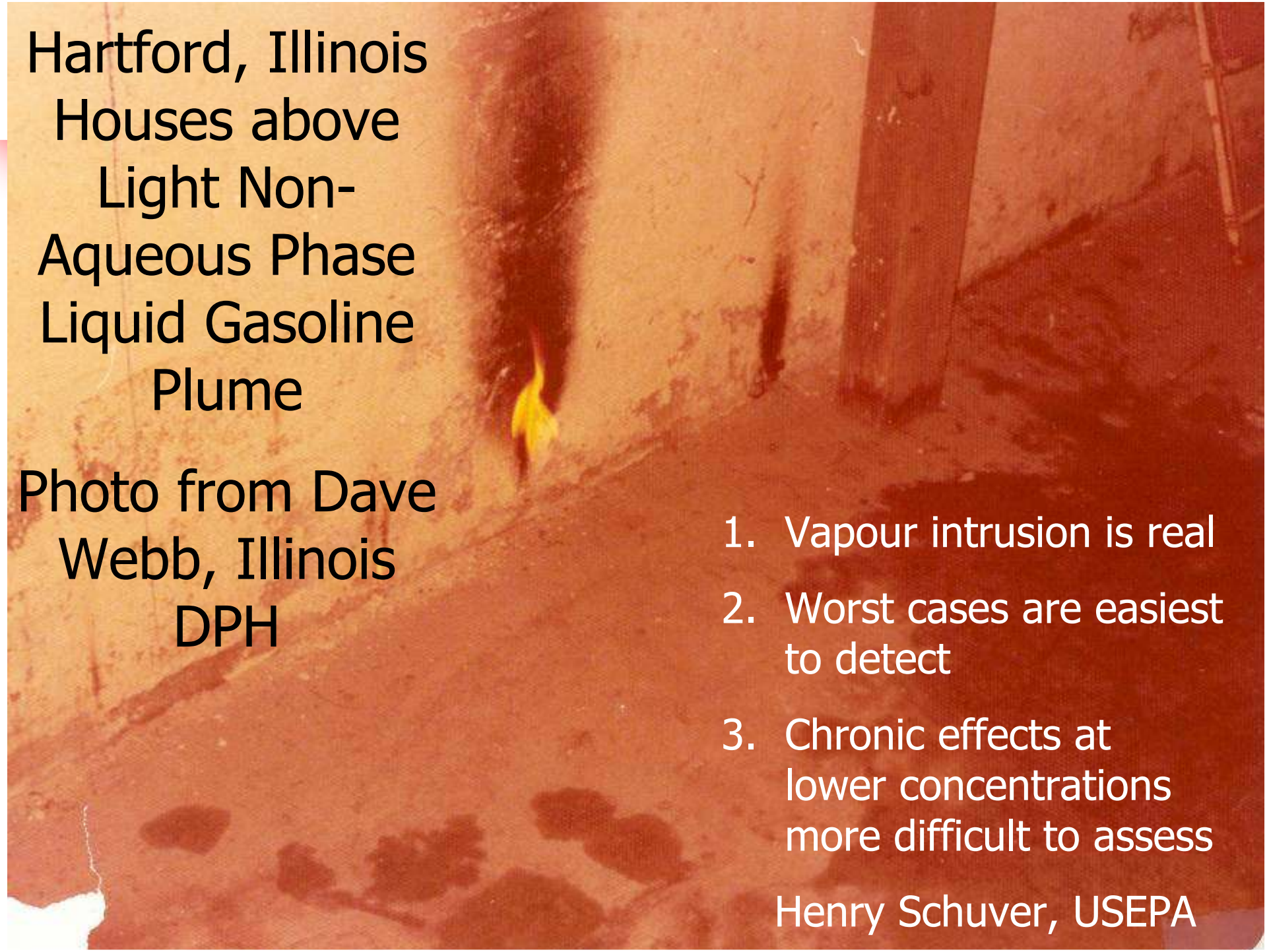


Hartford, Illinois Houses above Light Non-Aqueous Phase Liquid Gasoline Plume

Photo from Dave Webb, Illinois DPH

1. Vapour intrusion is real
2. Worst cases are easiest to detect
3. Chronic effects at lower concentrations more difficult to assess

Henry Schuver, USEPA

Town is a time bomb!

It's sitting on sea of gasoline — and could blow up at any minute

It's a town that could explode at any minute!

The 1,700 residents of Hartford, Ill., are sitting on a ticking time bomb — because the whole town rests on an underground pool of close to four MILLION gallons of gasoline leaked from refinery pipes.

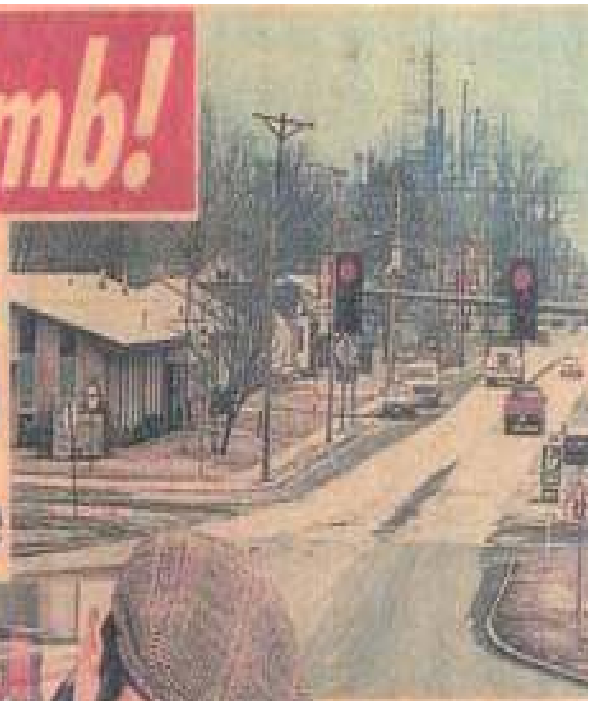
At any moment, a lit match or even a spark could ignite the ever-present gasoline fumes. The village has even put up street signs warning drivers not to leave their car motors running.

It's no empty threat — fires have already erupted at two homes when gas fumes ignited.

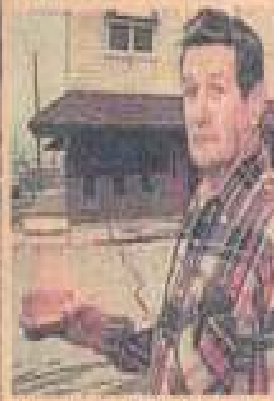
A year ago, the house that Harold and Norma Settles had built and lived in for 25 years caught fire and exploded, destroying the home and a lifetime of possessions.

"According to the fire department, the gas

— Even the dirt burns



POWDER KEG: The tow of Hartford, Ill., (above) soaking in gasoline Edwin Gallagher (belo shows — he got this j full from a well.



partment of Public Hea says the gas fumes "ar terrible threat to pu health" that can cause irr

Scope of Problem

- Vapor intrusion (VI) is a ***potential*** exposure pathway at sites with volatile chemicals (represents many sites!)
  - Manufacturing sites (esp. with chlorinated solvents)
  - PCE dry cleaners (~ 75% contaminated)
  - Fuel spills (gas stations, tank farms, refineries)
  - Coal tar/creosote sites (manufactured gas plant sites)
  - Brownfields sites
  - Landfills
  - Mercury?

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Why is Vapour Intrusion Pathway Important

- Inhalation is not voluntary - we breath ~ 20,000 L/day, and spend up to 90% of our time indoors
- Inhalation toxicity tends to be greater than for ingestion route resulting in very low chronic risk-based air concentrations for some chemicals
- Exposures to trichloroethylene of particular concern
- In US (and Canada to lesser extent), vapour intrusion has become a high profile issue, with an increasing number of class action law suits (in hundreds of millions of dollars)

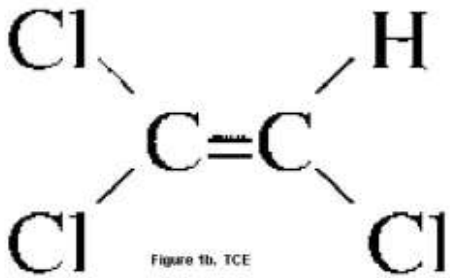

Figure 1b. TCE

[1] Toxic Chemical Exposure Reduction Act brought forward by Senator Hilary Clinton and others http://www.tceblog.com/posts/1147841386.shtml

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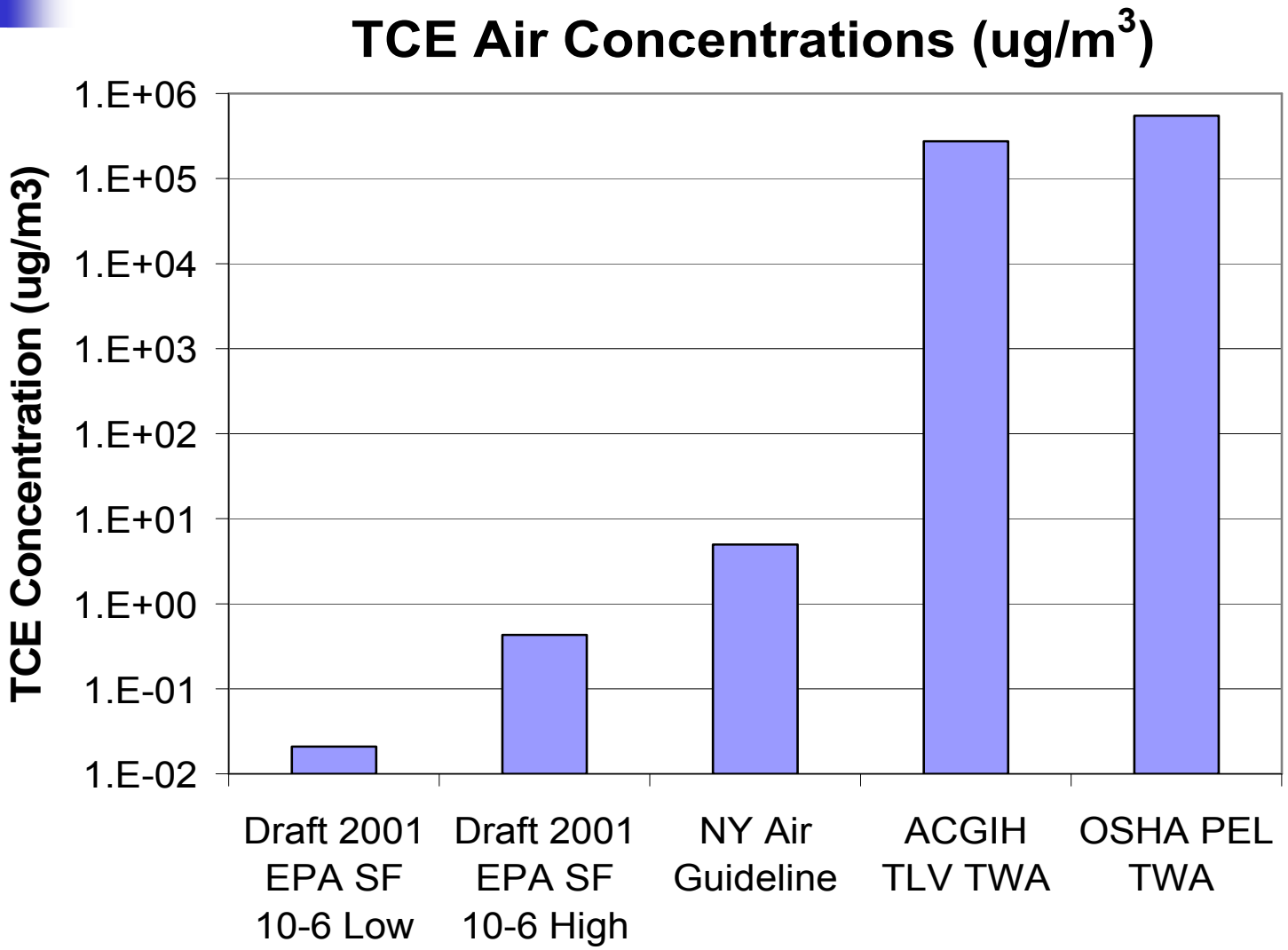
Draft USEPA Toxicity Factors

Residential Risk-Based Air Concentrations (ug/m^3)

	Trichloroethylene			Tetrachloroethylene	
	USEPA	WHO	HC	USEPA	HC
Carcinogen Risk-based air concentration for 10-5 cancer risk	2.5 Draft October 2009 Toxcity assessment unit risk 4E-6 (ug/m^3)$^{-1}$	23 2000 Air Guideline	16	0.5 to 5 Draft June 2008 unit risk 2E-6 to 2E-5 per ug/m^3)	NA
Non-carcinogen Reference conc-entration (RfC)	5 Draft October 2009 Toxicity Assessment		5 Draft	600 Draft	360
Residential "Back-ground" Air Conc.	**50th = 0.3** **95th = 1.6**			**50th = 1.6** **95th = 7.4**	

No amortization included in above calculations
Some regulatory jurisdictions apply source allocation factor of 0.2 to RfC
Residential background from in-progress USEPA study of 13 sites, ~ 2400 buildings tested, values are arithmetic means of percentiles
HC = Health Canada

Industrial Hygiene versus Risk Assessment World (TCE)



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Denver Post Articles
(4 impacted sites in Colorado)

Regulations fail to protect U.S. residences from gases

By Mark Obmascik
Denver Post Staff Writer

join the discussions

Sunday, January 06, 2002 - Patricia Brice nearly died from lupus - after her twin daughters convulsed with seizures. Ralph Miller woke up paralyzed down his right side. While Bob Gillette battled an inoperable brain tumor, his mother died of liver cancer.

More than 4,900 people in a five-state federal study suffered strokes, anemia and urinary tract disorders, including prostate trouble, at rates double or triple the national average.

All these people lived in homes polluted with toxic gas.

Post / Helen H. Davis

The Hamilton Sundstrand factory in

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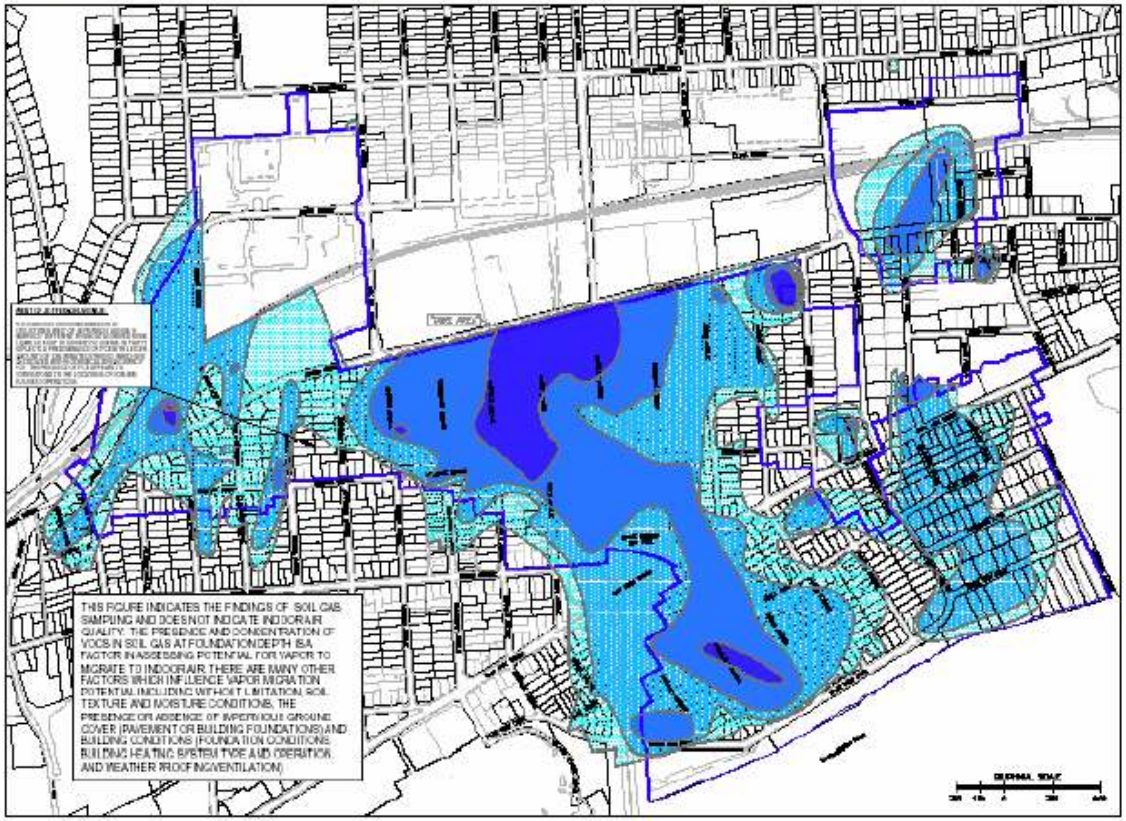
Two Examples

Redfield Site, Colo., & IBM,Endicott, NY

> 11 DCE action level



Outline of 11DCE In groundwater & IAQ

TCE in groundwater

With Permission from:
D. Folkes, Envirogroup, Inc.
http://www.epa.gov/epaoswer/osw/meeting/pdf02/folkes.pdf

McDonald, 2004

Mercury at Daycare Center

For Immediate Release: August 7, 2006
Contact: Bill Boteler (202) 265-733
MERCURY-LADEN DAY-CARE CENTER IN NEW JERSEY IS NO ANOMALY — Lax State Brownfield Laws Make Tragedy an "Accident Waiting to Happen"
Washington, DC — The discovery of toxic mercury vapors in a day-care center built on the site of a former thermometer factory last week is just the latest in a series of toxic scandals to rock New Jersey. A weak state law and political pressure to quickly re-develop old toxic sites, called brownfields, make such events "an accident waiting to happen," according to Public Employees for Environmental Responsibility (PEER).
More than 30 children, ranging in ages from 8 months to 3 years, were exposed to toxic mercury vapors at the Kiddie Kollege day-care center in Franklinville, New Jersey. The state Department of Environmental Protection (DEP) and the Department of Health issued a joint closure order for the center on July 28th following indoor air sampling which detected mercury vapors.

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Chlorinated Hydrocarbon Challenge

- A combination of:
  - Persistent and mobile chemicals (e.g., PCE, TCE)
  - Often long dissolved plumes migrated below buildings
  - Source zones that are difficult to remediate
  - Many buildings are underpressurized and have openings for vapour intrusion (VI) to occur
  - Low (and often changing!) toxicity thresholds
- Have resulted in vapour intrusion pathway being risk driver at many sites

Draft USEPA (2002) OSWER VI Guidance

- **Tier 1 Screening**
  - Preliminary screening
    - Volatile and toxic compounds present?
    - Buildings present (30 m off-set)?
    - Health effects, noxious odors, explosive levels? (immediate response)
  - Generic screening values based on following Attenuation Factors:
    - Groundwater: 0.001
    - External soil vapor : 0.01 ?
    - Subslab soil vapor: 0.1 ?

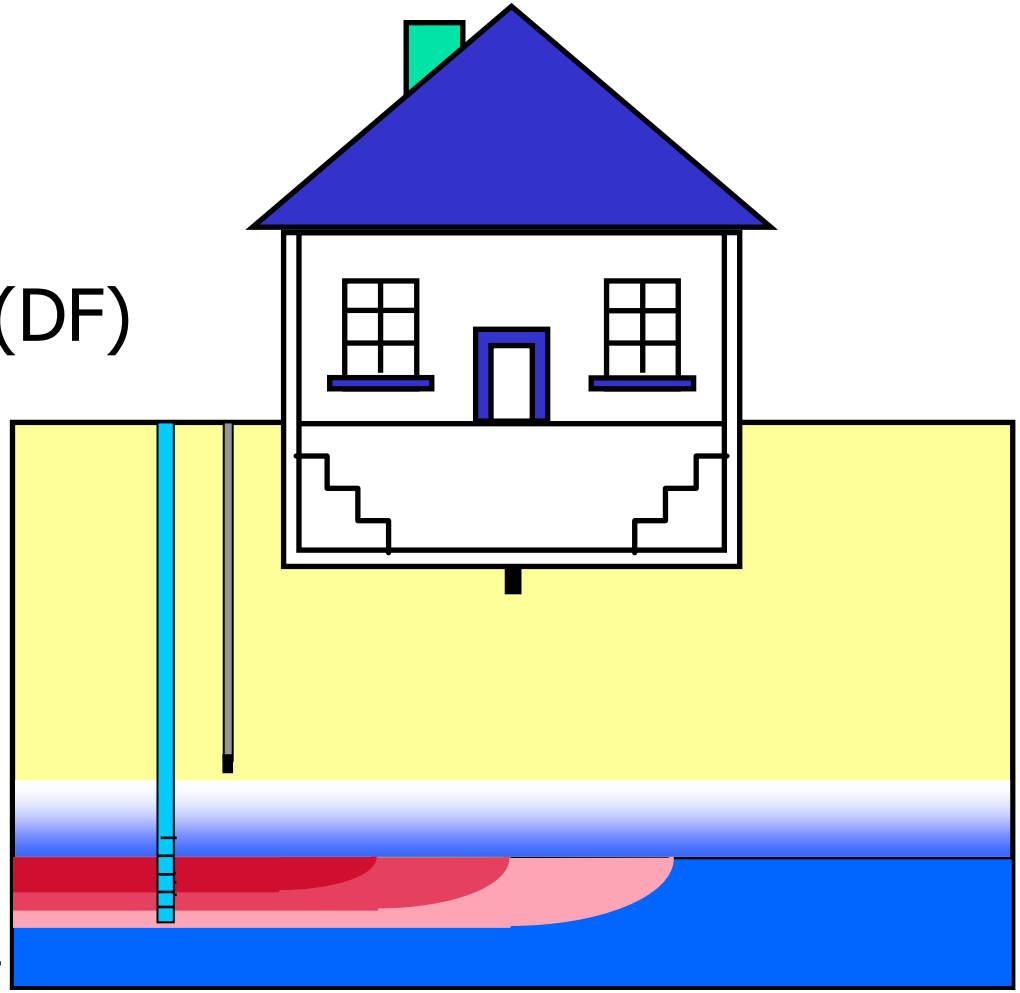
Very low generic groundwater screening values for some chemicals (ug/L)!	
TCE	5[1]
PCE	11
Benzene	14

ILCR = 1×10^{-5}

[1] The risk-based groundwater concentration (for 10^{-5} ILCR) is lower than 5 ug/L but as policy decision EPA set lower limit equal to the drinking water maximum concentration limit ("MCL")

Attenuation Factor ("alpha") Definition

- α = vapor attenuation factor (AF) ("alpha")
- AF = 1/dilution factor (DF)



Groundwater $\alpha = C_{air}/C_{vapor}$

$C_{vapor} = C_{water} * H'$

Soil vapor $\alpha = C_{air}/C_{soil\ vapor}$

Subslab $\alpha = C_{air}/C_{subslab\ vapor}$

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Draft USEPA (2002) OSWER VI Guidance

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  - Preliminary screening
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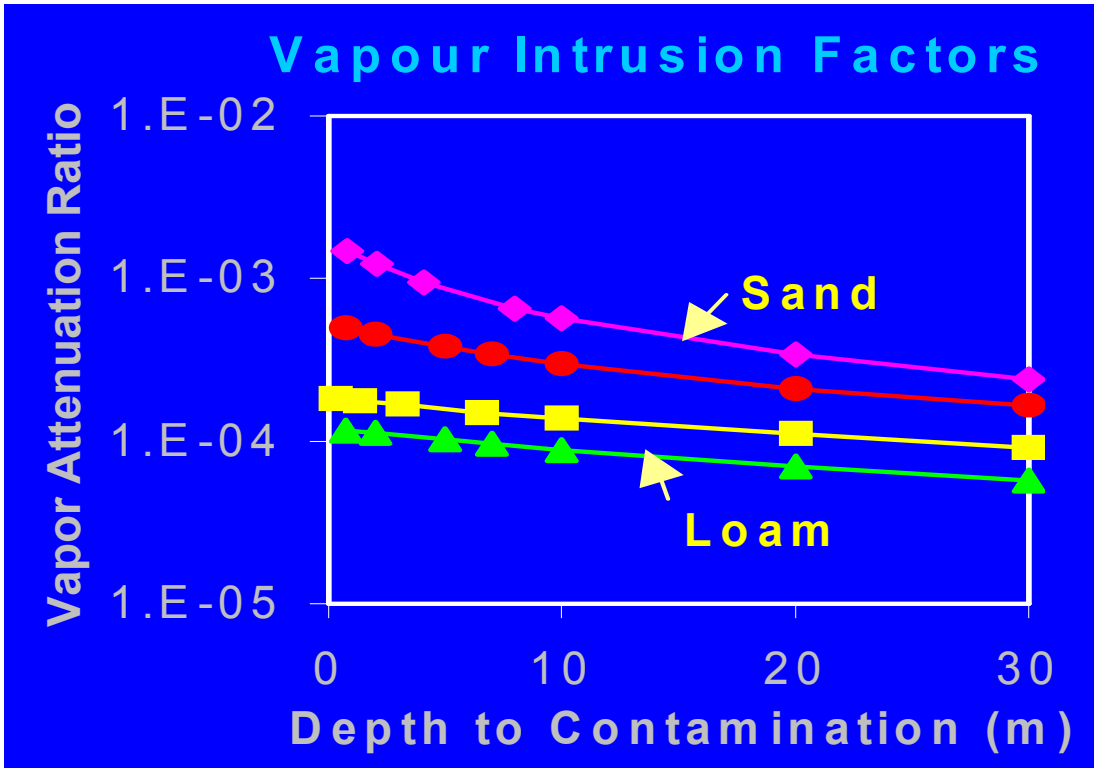
Draft USEPA (2002) OSWER VI Guidance

- **Tier 2 Screening (under review)**
  - Attenuation factor curves derived from Johnson and Ettinger (J&E) model based on soil type and depth for **groundwater** and **soil vapour** for benzene (surrogate)

Attenuation factors for groundwater to indoor air →



Draft USEPA (2002) OSWER VI Guidance

- **Tier 3 Site Specific Assessment**
  - Additional site specific data
  - J&E model or other models
  - Emphasis on multiple lines of evidence ***including*** indoor air & subslab vapor data (USEPA discourages modeling only)
- **Health Canada**
  - Similar approach, slightly different attenuation factor curves, adjustment for biodegradation and source depletion

Historical Milestones

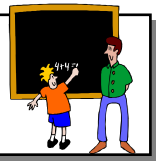
Early IAQ Concerns (1970's & early 1980's) (VOCs as Carcinogens)

↓

Early Experience (1980's)
(Love Canal, 1985; Hillside MA School 1989)

↓

Johnson & Ettinger Model (1991) **[The beginning of the end…]**



↓

Early Guidance (1990's)
(EPA Air/Superfund 1992, ASTM E-1739 1
MA 1992 **[Limited knowledge of pathway…]**

↓

Experience (~ 2000 on)
("Colorado" Sites, Endicott, NY)
[We need to take this pathway seriously …]

↓

Recent Guidance (2005 on
(EPA 2002, CA 2005, NJ 2005,ITRC 2007, ASTM 2010, BC SABCS 2010)
[Hmmm…Lot of different approaches]

- 20 year process for:

►**Recognition**
►**Science**
►**Experience**
►**Guidance**

- Knowledge improving but questions (and misconceptions!) remain

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Conceptual Site Model Overview

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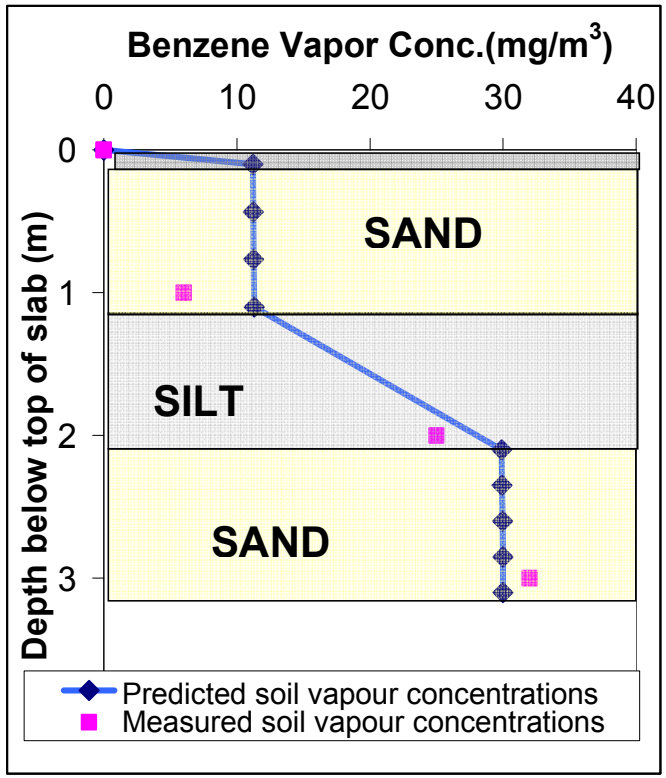
Diffusion

- Chemicals move from high to low concentrations, in all directions from source (3-D)
- Described by Fick's Law

$$\text{Flux} = D^{eff} * (\Delta C_v) / \Delta Z$$

- Diffusion coefficient (rate) in air is 4 orders-of-magnitude higher than in water, therefore **moisture content** is a key property, and controls effective diffusion coefficient

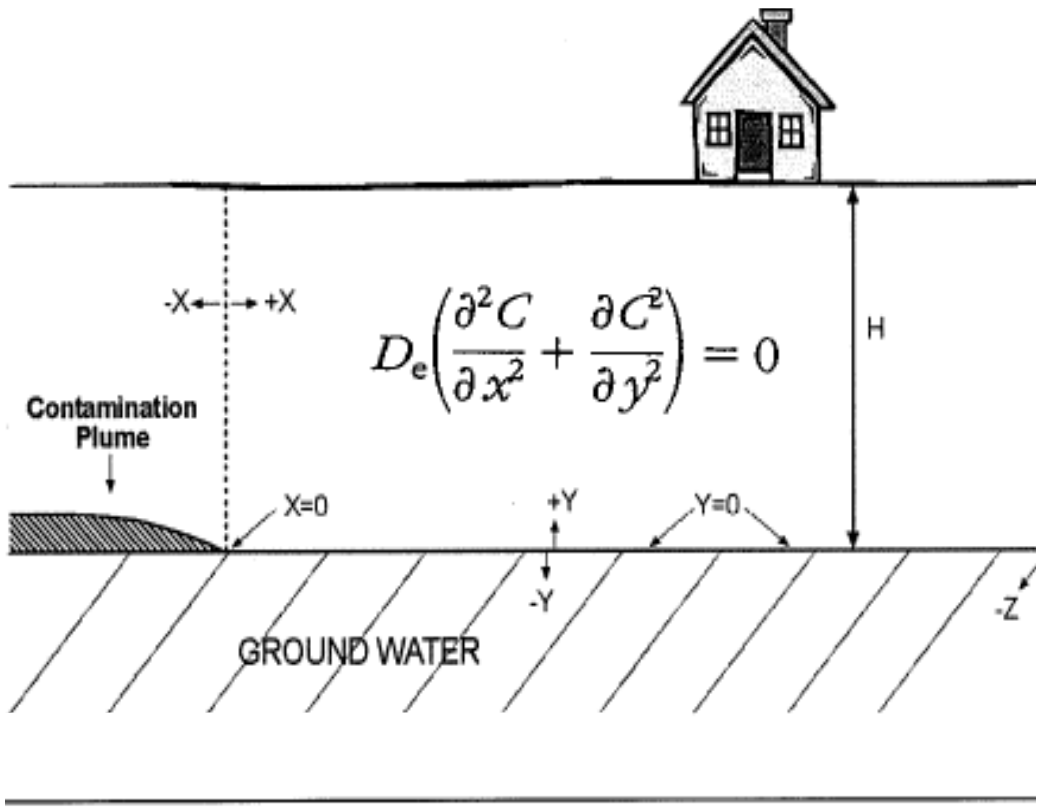
Influence Wet Layer

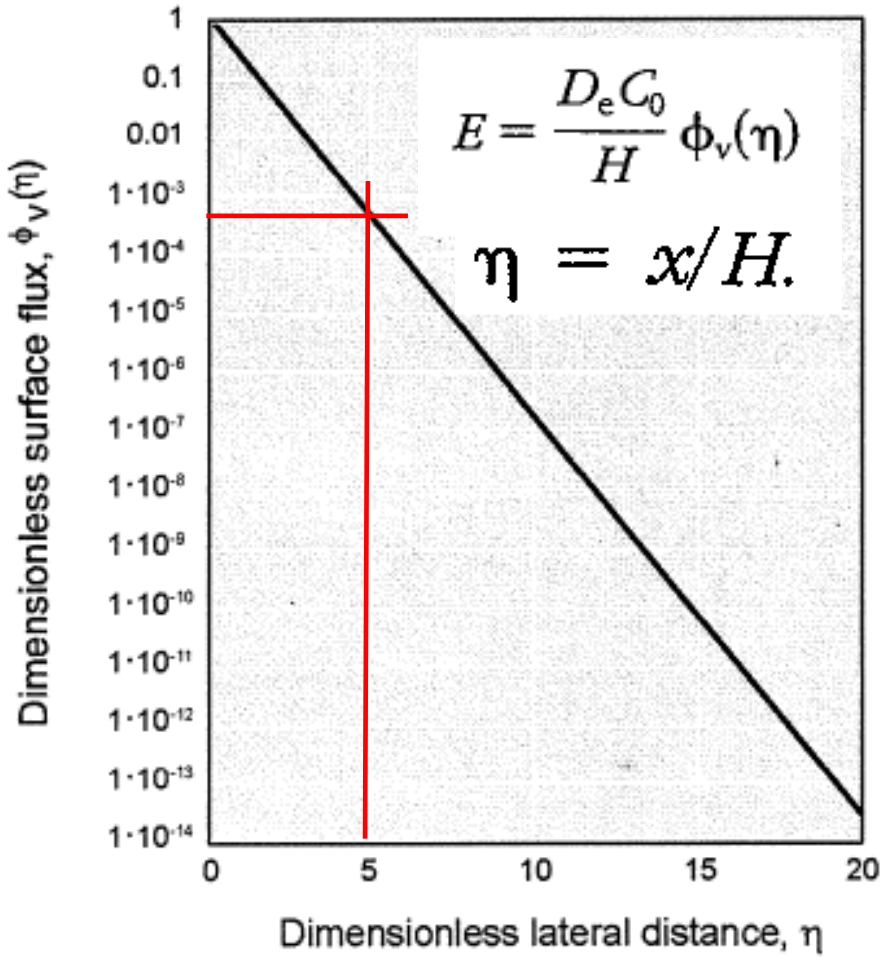


$$D^{eff} = D_{air} * (\theta_v^{3.33} / \theta^2) * + D_{water} / H' * (\theta_w^{3.33} / \theta^2)$$

Lateral Diffusion

(Lowell and Eklund, 2003)





Lowell, P. and B. Eklund, 2003. VOC Emission Fluxes as a Function of Lateral Distance from the Source. Environmental Progress, V23, N1.

Transient Vapour Migration

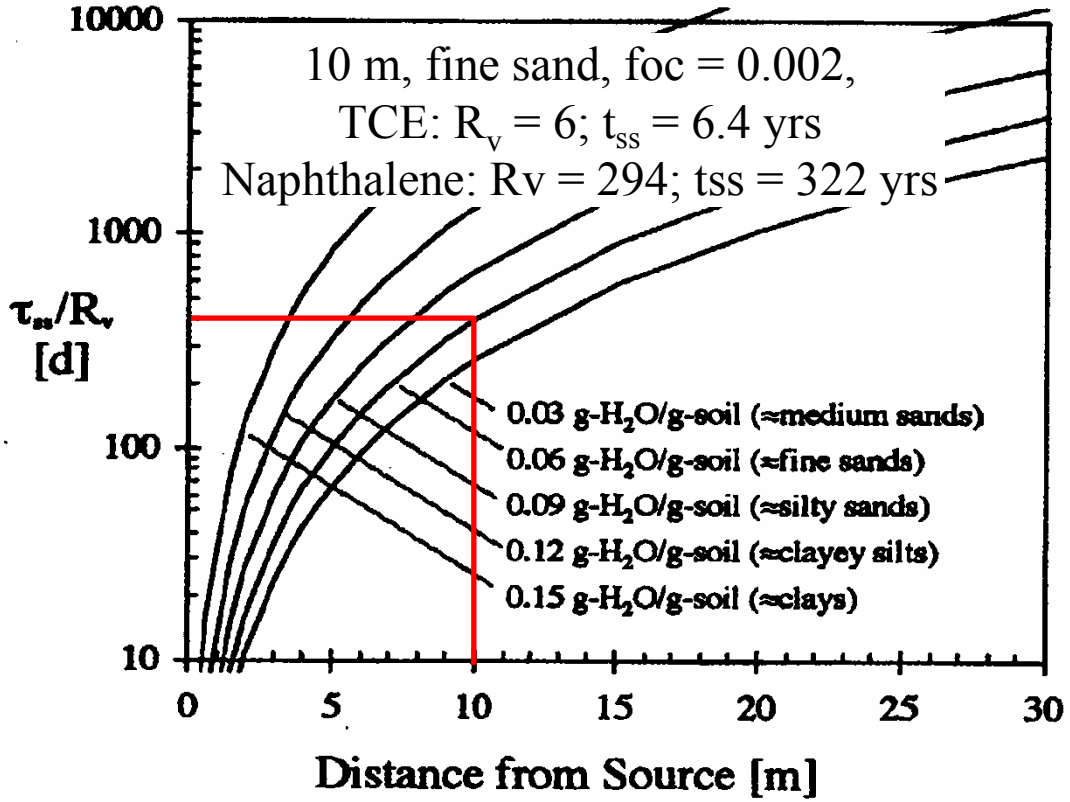


FIGURE 3

Estimated time for nonretarded chemicals to reach near steady vapor concentratic (τ_{ss}/R_v) at the distance L from a source. For retarded compounds multiply the (τ_{ss}/R_v) va by the retardation factor R_v defined in Eq. 4.

Solution transient diffusion equation with step-change b.c. at zero time

$$\tau_{ss} = \frac{R_v\, \theta_v\, L^2}{D_v^{eff}}$$

$$R_v = 1 + \frac{\rho_b K_d}{\theta_v H'} + \frac{\theta_w}{\theta_v H'}$$

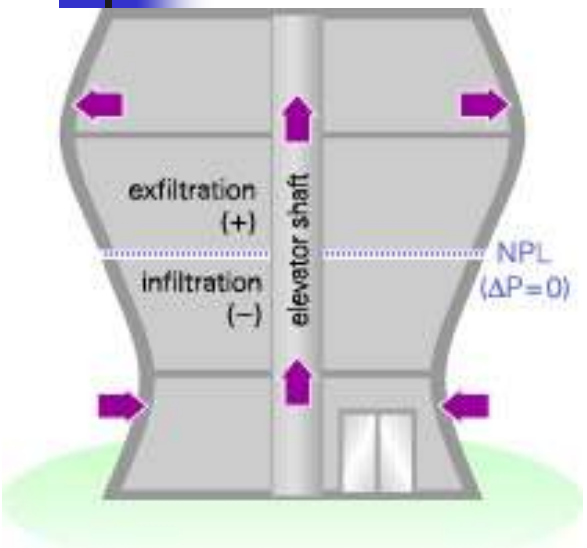
$$K_d = K_{oc} * f_{oc}$$

Johnson, P.C. 1999. Assessing the Significance of Subsurface Contaminant Vapor Migration to Enclosed Spaces: Site-Specific Alternatives to Generic Estimates. J. Soil Contamination., 8(3), 389-421.Inputs example: K_{oc} = 166, f_{oc} = 0.002, ρ_d = 1.6, H' = 0.42, θ_w = 0.01, θ_v = 0.3

Advection

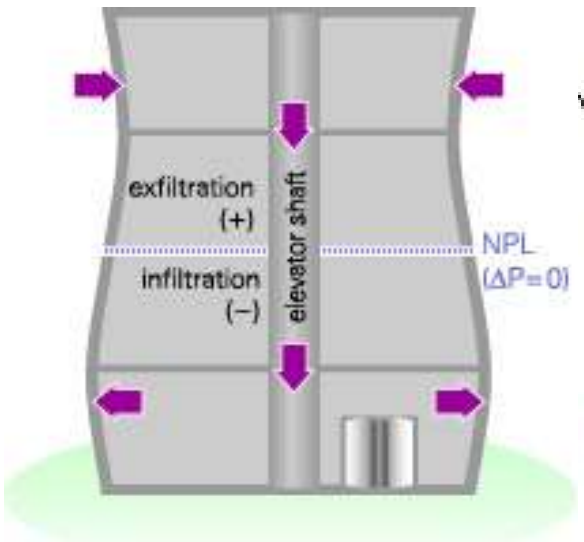
- Key factors are pressure gradients (ΔP) and permeability of soil (usually controls) & foundation
- Causes of ΔP are temperature differences (stack effect), wind, fans, HVAC system, fireplace
- Residential buildings often depressurized - wintertime ΔP in Canada, northern US typically 2 - 10 Pa (Nazaroff *et al.*, 1985; Nazaroff 1992, Figley, 1997 (CMHC))
- Commercial buildings will vary depend on design (balanced, supply (+ ΔP), exhaust (-ΔP)), height of building, time of day, season
- Dynamic process – recent research indicates buildings can breath both ways

Stack and Wind Effects



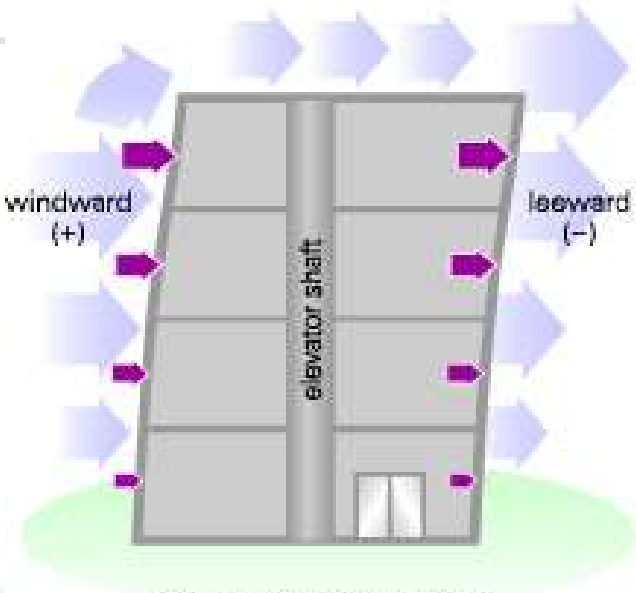
Winter (normal) stack effect

- Inward-swinging doors may not latch
- Exfiltrating indoor air drives moisture into building envelope



Summer (reverse) stack effect

- Outward-swinging doors may stand open
- Infiltrating outdoor air drives moisture into building envelope

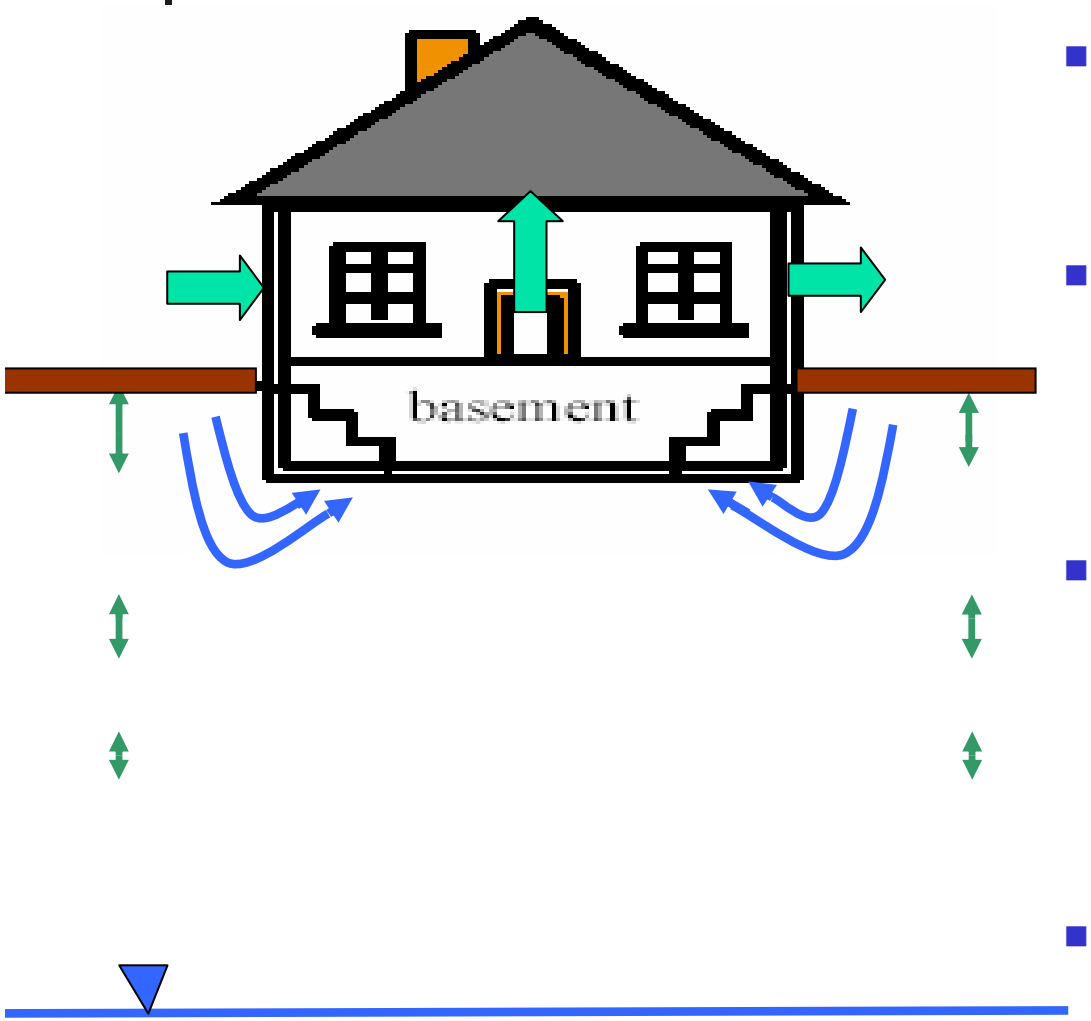


Seasonal effects of wind

- Summer: Wind drives moisture-laden outdoor air into windward envelope
- Winter: Exfiltrating indoor air carries moisture into leeward envelope

Stack effect: Warm air rising in building causes outward air pressure in upper storeys and inward air pressure near base of building, warm air that escapes replaced by air and soil gas entering lower regions. http://www.trane.com/commercial/library/vol31_2/#forces

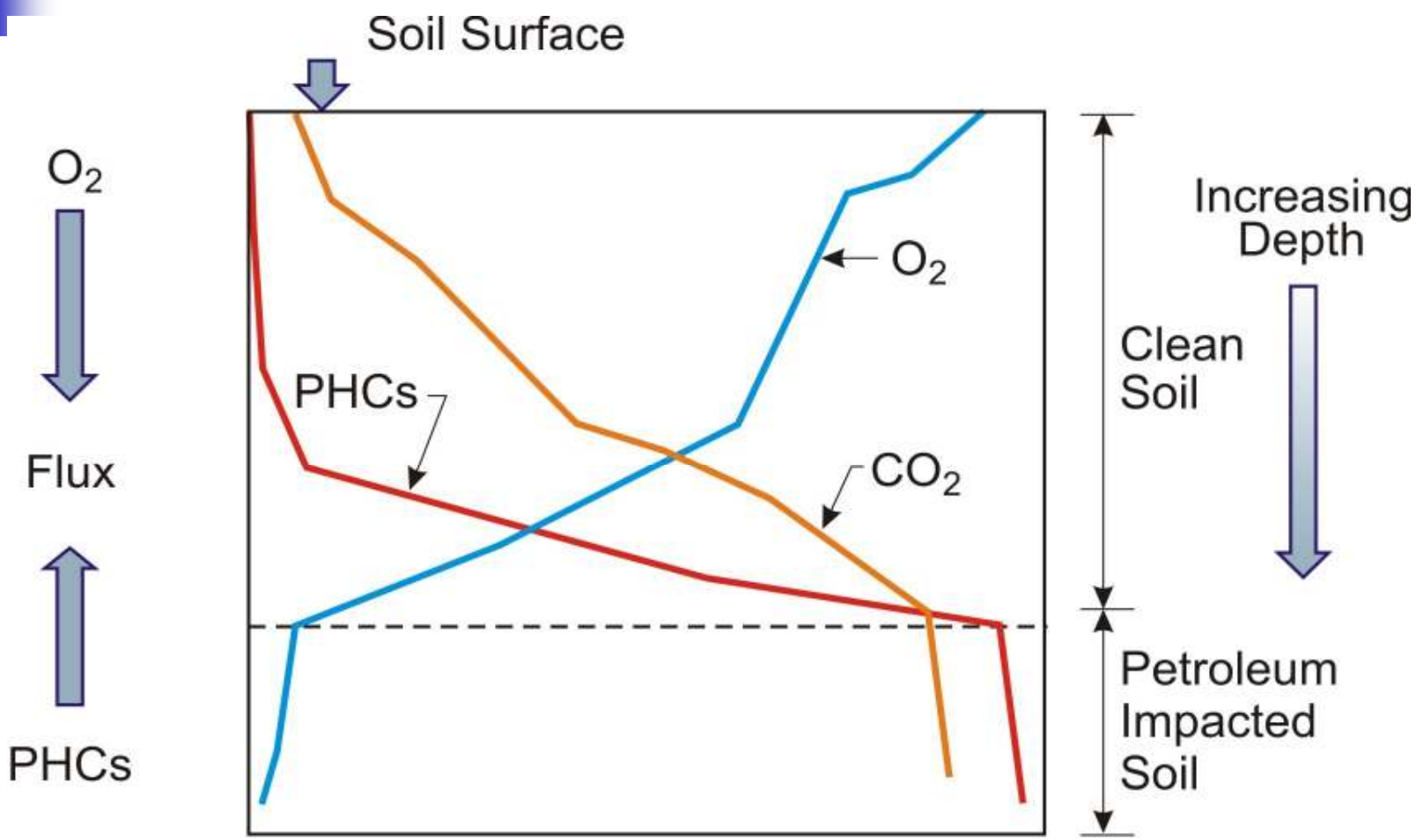
Barometric Pumping



- Maximum change barometric pressure ~ 2 to 3 % (24 hrs)

  (Massman & Farrier, WRR, 1992, 28 (3), 777-791).
- Piston Effect: maximum compression of soil gas at ground surface ~ 2 to 3% of unsaturated zone thickness
- Piston effect may be significant at sites with coarse-grained soil where depth to water table >~ 10 m
- What are implications for shallow soil gas sampling?

Conceptual Aerobic Biodegradation Profile



$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

VI Potential Matrix

Factor	Increased VI Potential	Decreased VI Potential
Chemical volatility	Higher	Lower
Contamination form	Product above water table	Dissolved contamination
Biodegradation	Chlorinated solvents (recalcitrant)	Petroleum hydrocarbons (when O_2 present)
Soil type	Coarse	Fine
Soil moisture	Dry	Wet
Soil permeability	High	Low
Depth to contamination	Shallow (especially when wet basement, sumps)	Deep (but not that sensitive to depth)
Proximity of contamination	Contamination below building	Contamination laterally removed from building
Building pressure	Negative pressure	Positive pressure
Building size and mixing volume	Smaller	Larger
Building foundation	Basement with cracks (but generally not that sensitive)	Slab-at-grade (but generally not that sensitive)

Learning from Decade of Site Data Collection

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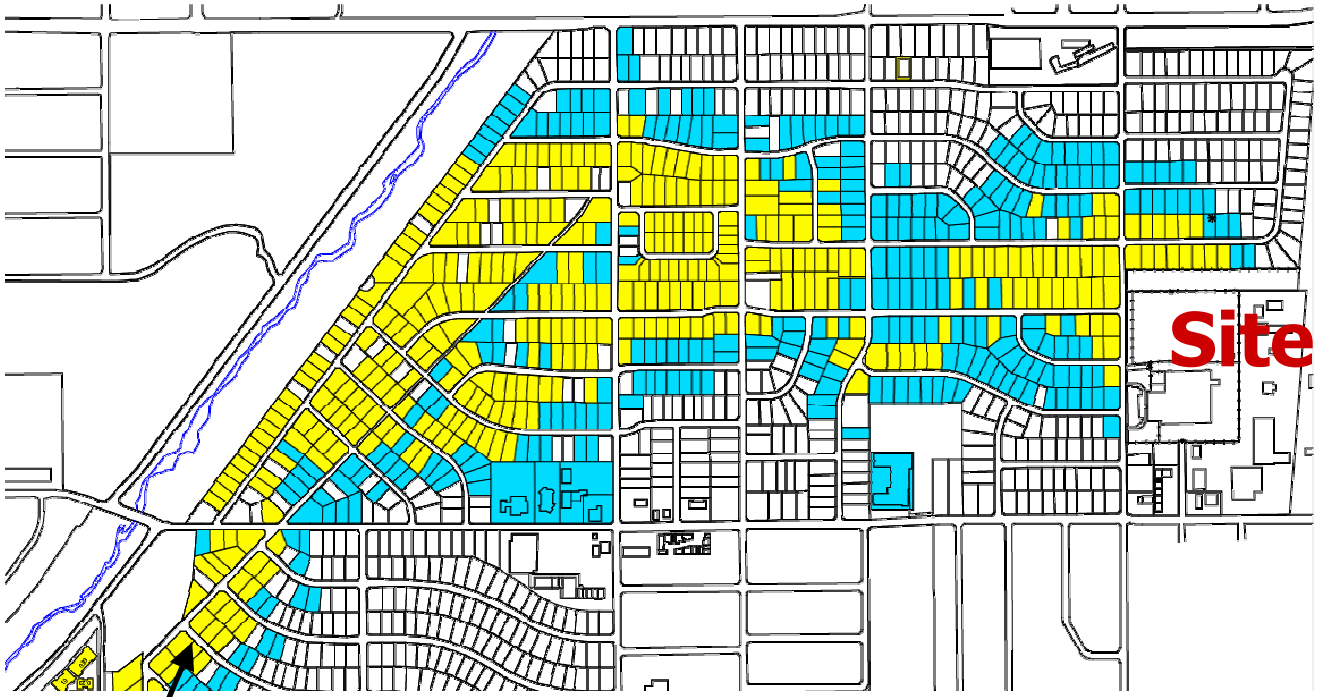
Redfield, Colorado
(D.Folkes, Envirogroup)



> 11-DCE action level in air (0.49 ug/m^3)

- Source rifle manufacturer
- Large TCE and 1,1-DCE plume below residential area
- Impacts observed for basement, crawlspace, slab-on-grade houses and groundwater depths over 9 m

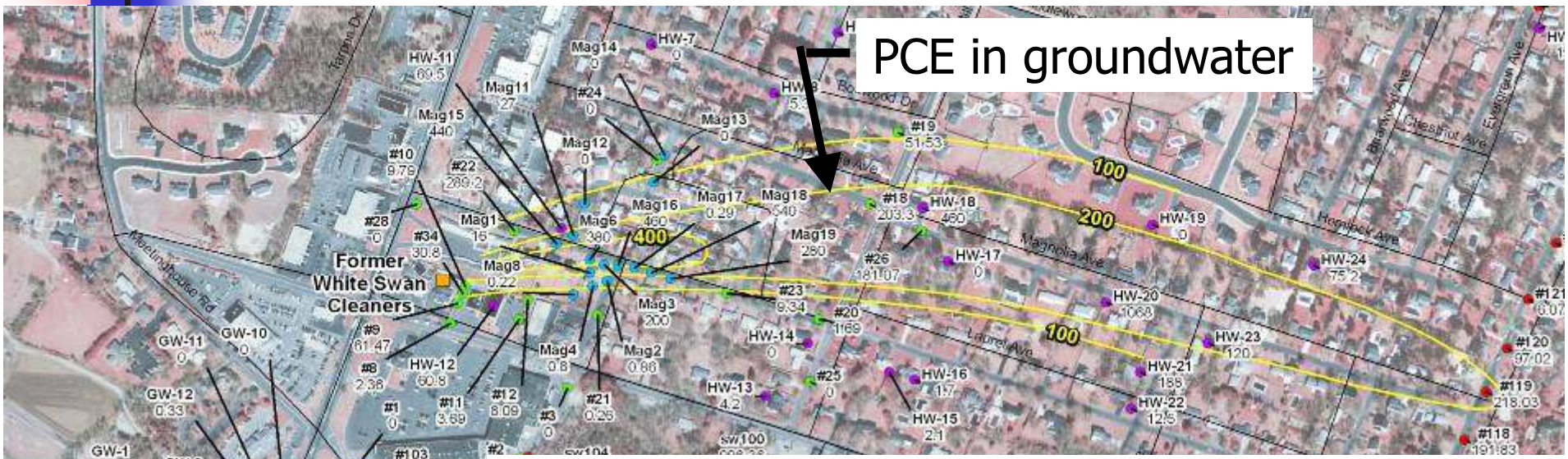
Over 350 buildings have been mitigated

Cambridge, Ontario
(November 21, 2007 public meeting; AMEC)

- Large TCE plume
- 120 wells
- 4000 IAQ samples
- TCE concentration air in 260 homes > 2.3 ug/m^3
- 187 homes mitigated
- Chemical oxidation selected for source treatment

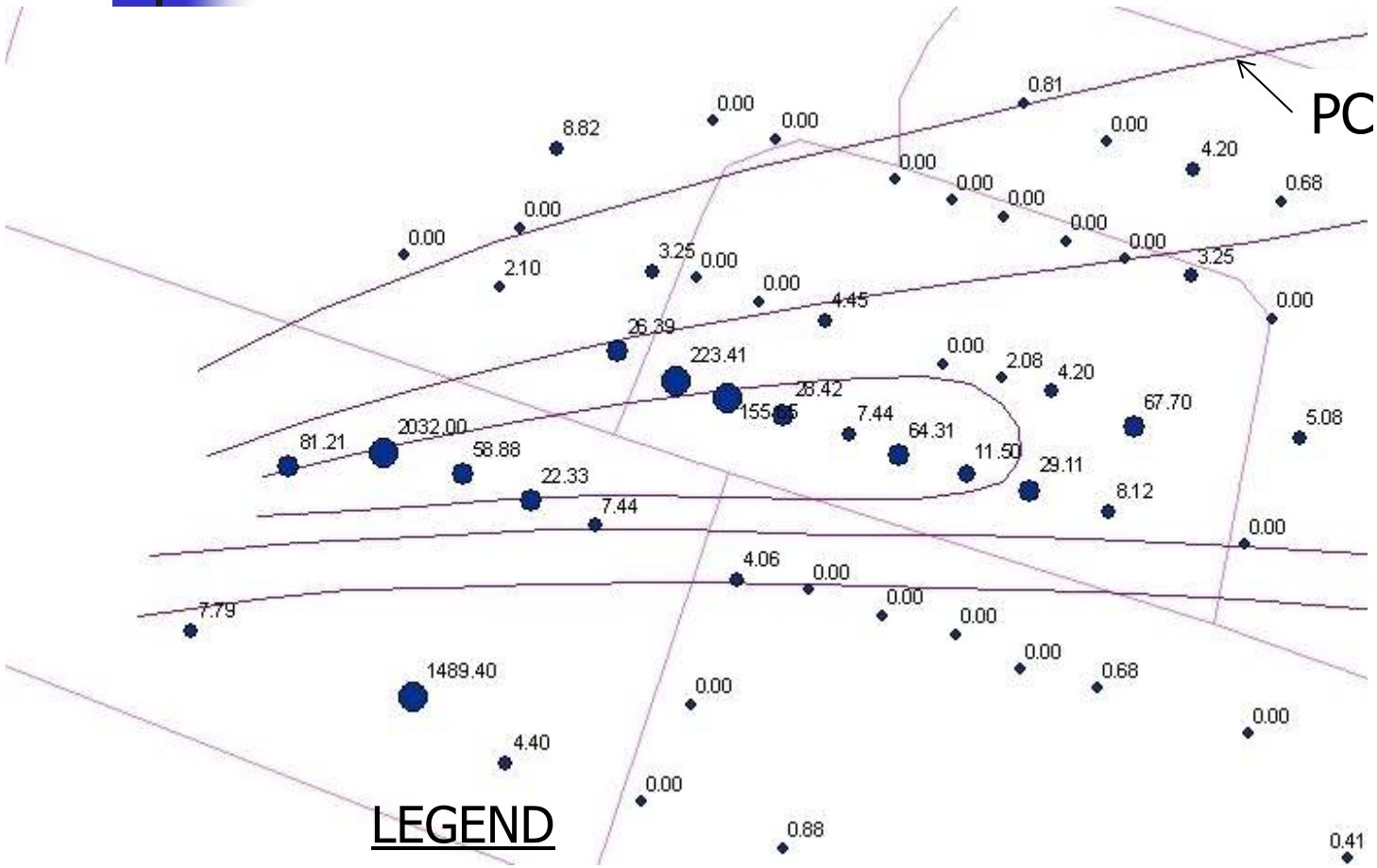
Wall Township, New Jersey

(NJDEP-Golder research study)



- Dry cleaners source of two large PCE plumes (2 by 3 km!), sand, depth to groundwater = 6 m
- PCE concentrations in groundwater in source > 500 ug/L
- Max indoor PCE concentrations!: Residential ~ 2000 ug/m^3, Commercial ~ 1500 ug/m^3

Wall Township, New Jersey
(NJDEP-Golder research study)



LEGEND

- PCE concentration indoor air (ug/m^3)

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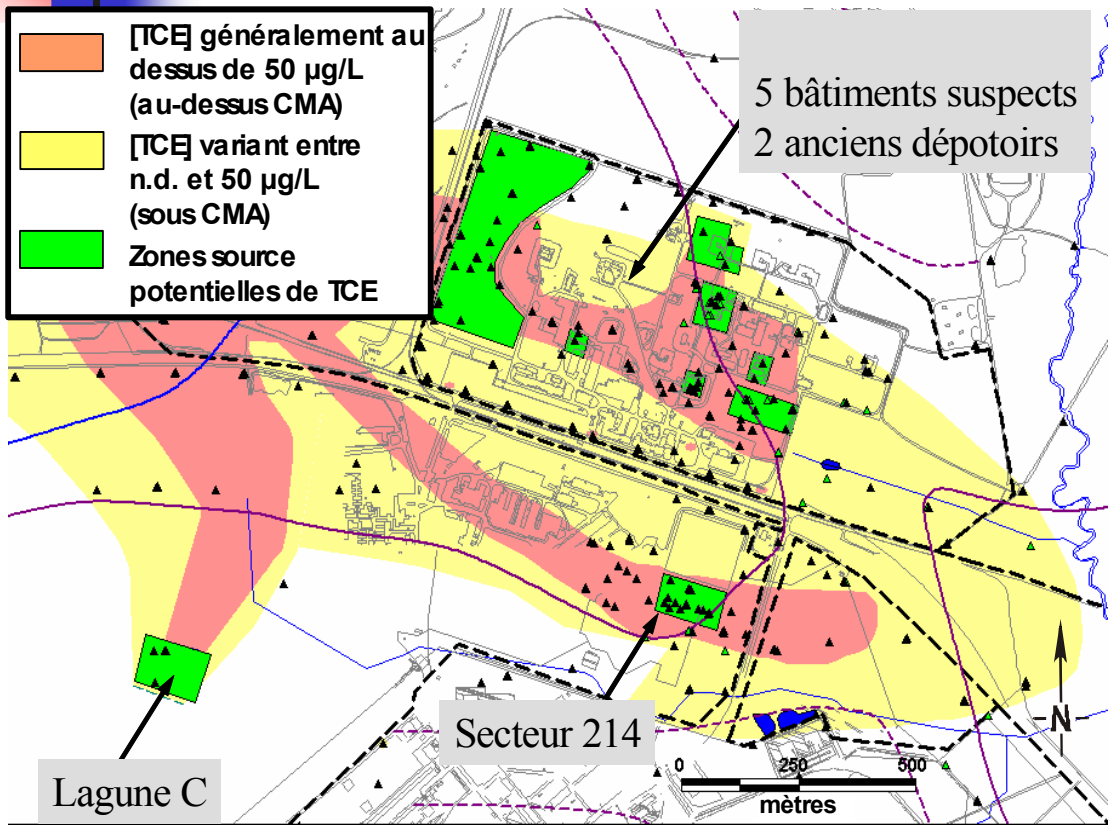
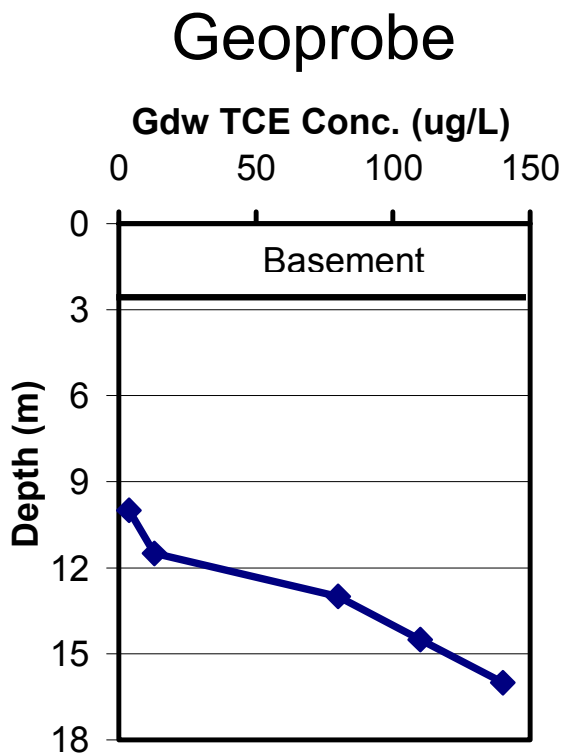
TCE Site
(over 2 km long plume)





- 8-10 m to water table, steep TCE gradients shallow groundwater, low indoor TCE (~ 1-2 ug/m^3) levels detected some houses, difficult to distinguish from background

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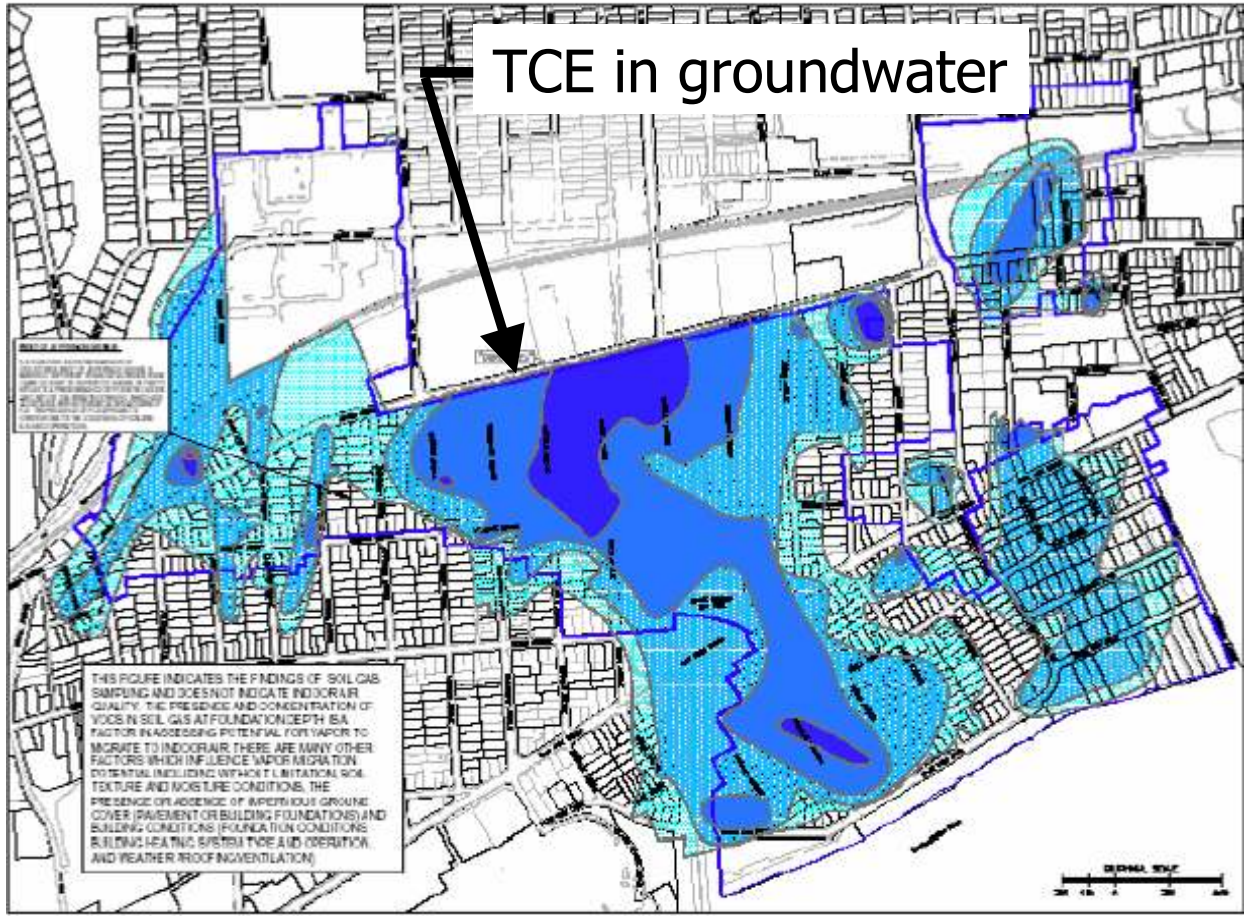
Endicott, New York
(G. McDonald, NYDOH)



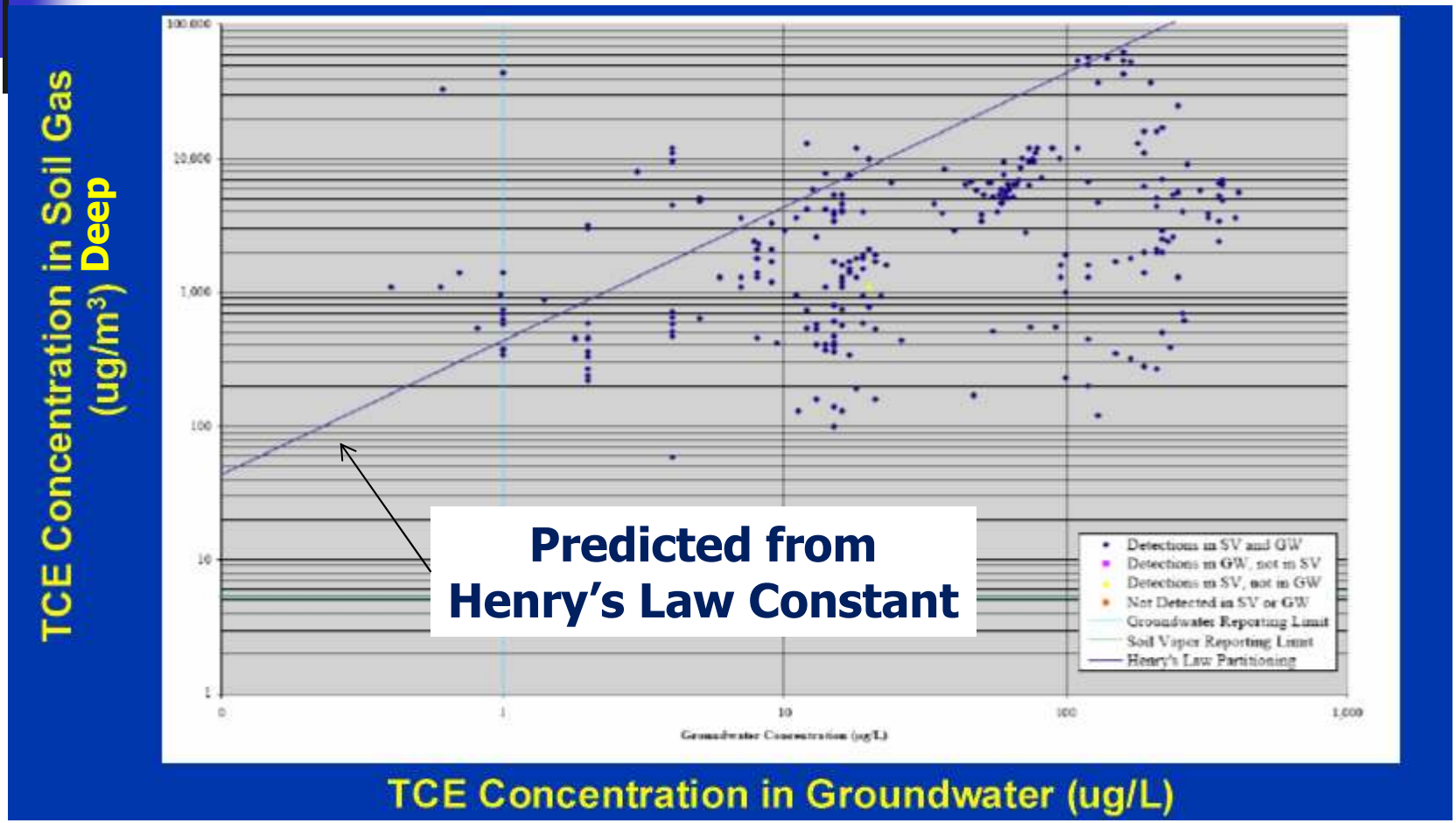
- Large TCE plume
- Highly variable plume and soils (sand & gravel, with fine soil layers) make difficult to predict indoor impacts
- 480 owners offered mitigation system + greater of $10,000 or 8% property value

Many buildings have been mitigated

http://tceblog.powerblogs.com/posts/1111819548.shtml

Endicott, NY Monitoring

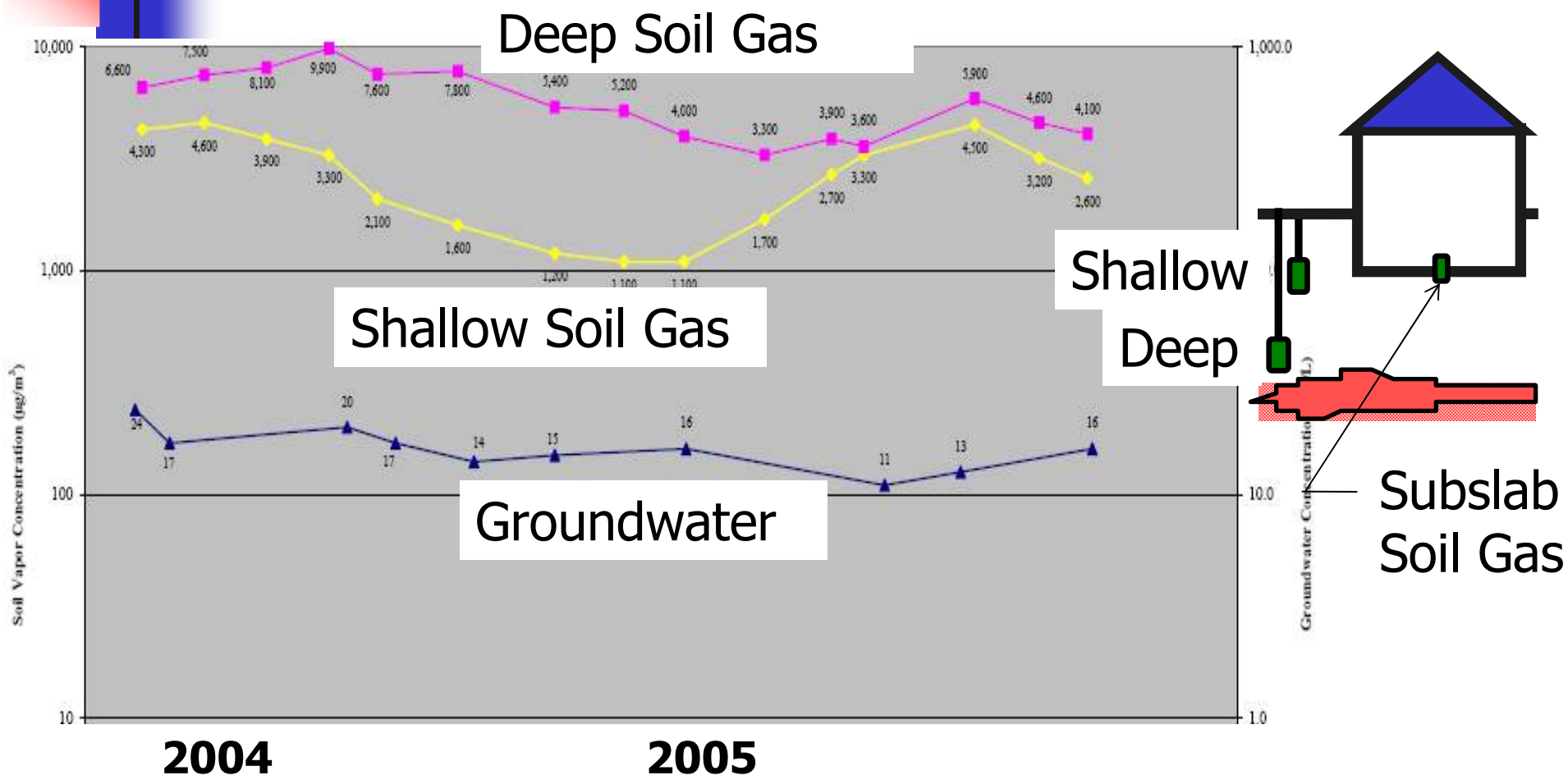
(Bill Wertz, NYSDEC)



Lot of variability. For sand & gravel, measured vapour often within ~10X of predicted from Henry's Law.

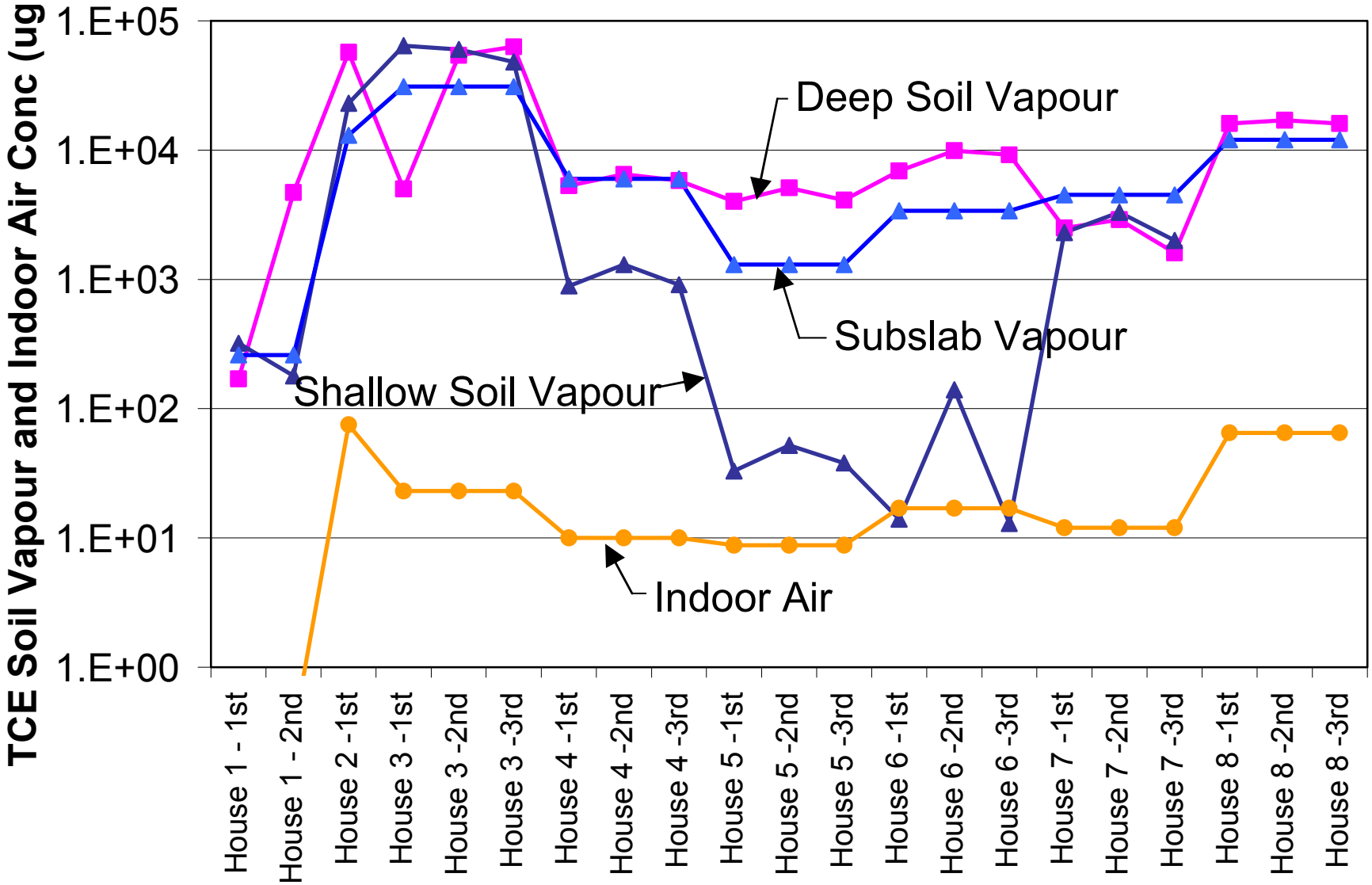
Endicott, NY Monitoring

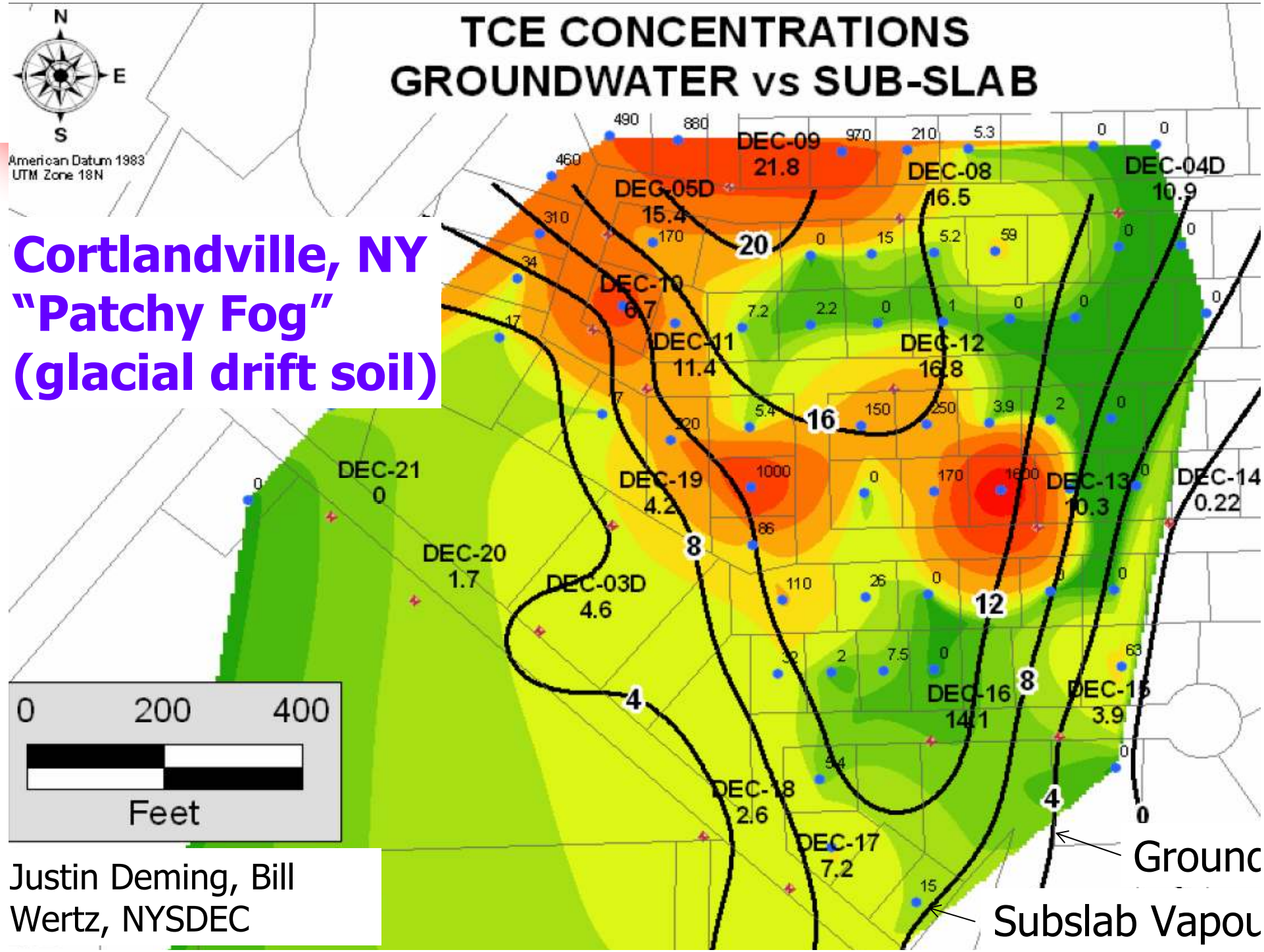
(Bill Wertz, NYSDEC)



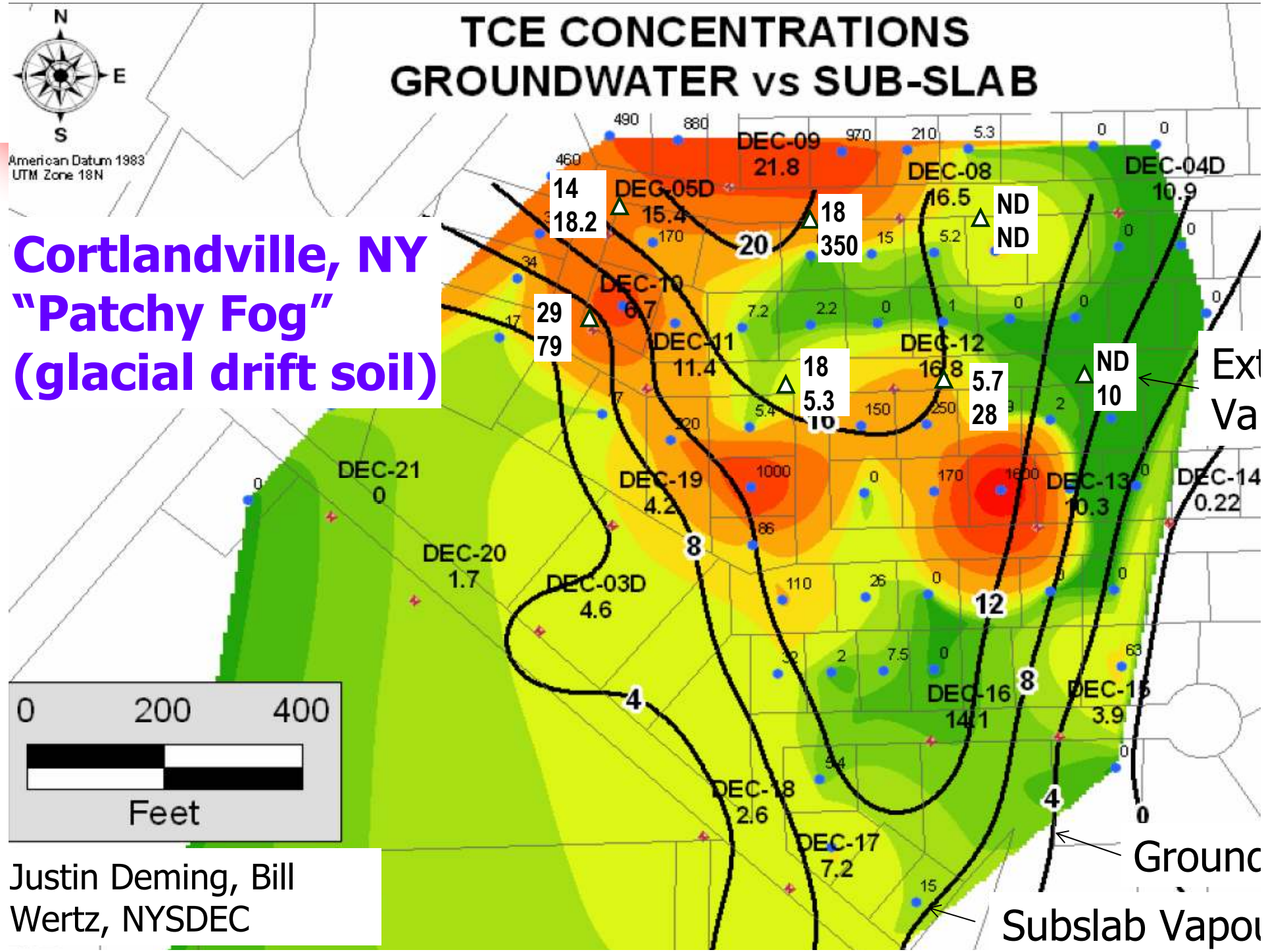
Deeper soil vapour less variable than shallow

Endicott Case Study





Justin Deming, Bill Wertz, NYSDEC



Justin Deming, Bill Wertz, NYSDEC

796
H-056
OA-56, ND
FF-56, 0.54
BA-56, 0.86
SSA-56, 5.4
SSB-56, ND
SSC-56, 5.3
804
H-024
OA-24, ND
FF-24, 0.54
BA-24, 0.54
SS-24, 150
808
H-053
OA-53, ND
FF-53, 0.45
BA-53, 0.51
SSA-53, ND
SSB-53, 250
SSC-53, ND
798
H-058
FF-58, 2.9
BA-58, 4.2
SSA-58, 1000
SSB-58, 120
SSC-58, 39
805
H-028
OA-028, ND
B1-028, ND
B2-028, ND
SS1-028, ND
SS2-028, ND
SS3-028, ND
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H-060
FF-60, 3.8
BA-60, 5.0
SSA-60, 170
SSB-60, ND
SSC-60, 31
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H-059
OA-59, ND
FF-59, 2.4
BA-59, 3.1
SSA-59, 86
SSB-59, ND
SSC-59, ND
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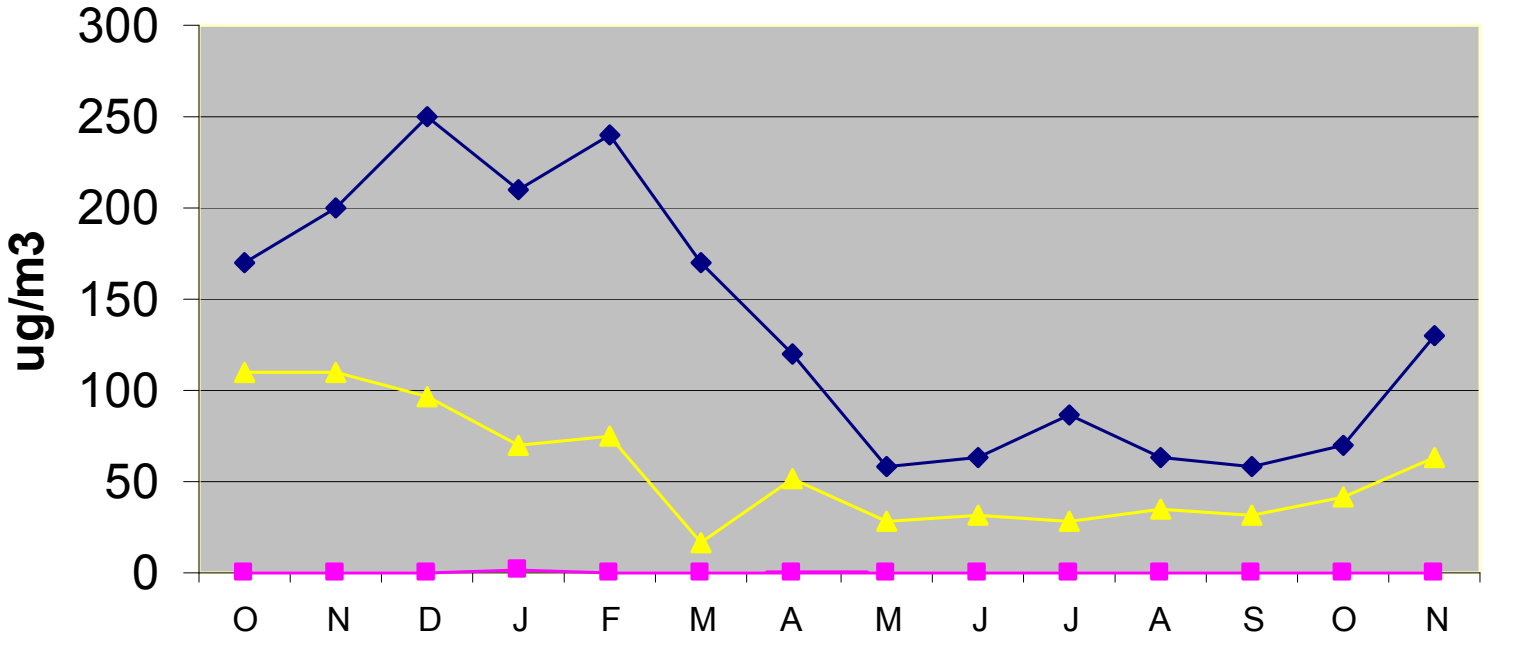
H-013
OA-013, ND
FF-013, 0.86
BA-013, 0.81
804
H-077
OA-077, ND
FF-077, 0.70
BA-077, 0.75
SSA-077, 1.3
SSB-077, 26
808
H-022
OA-022, ND
FF-022, ND
BA-022, ND
SS1-022, ND
SS2-022, ND
SS3-022, ND

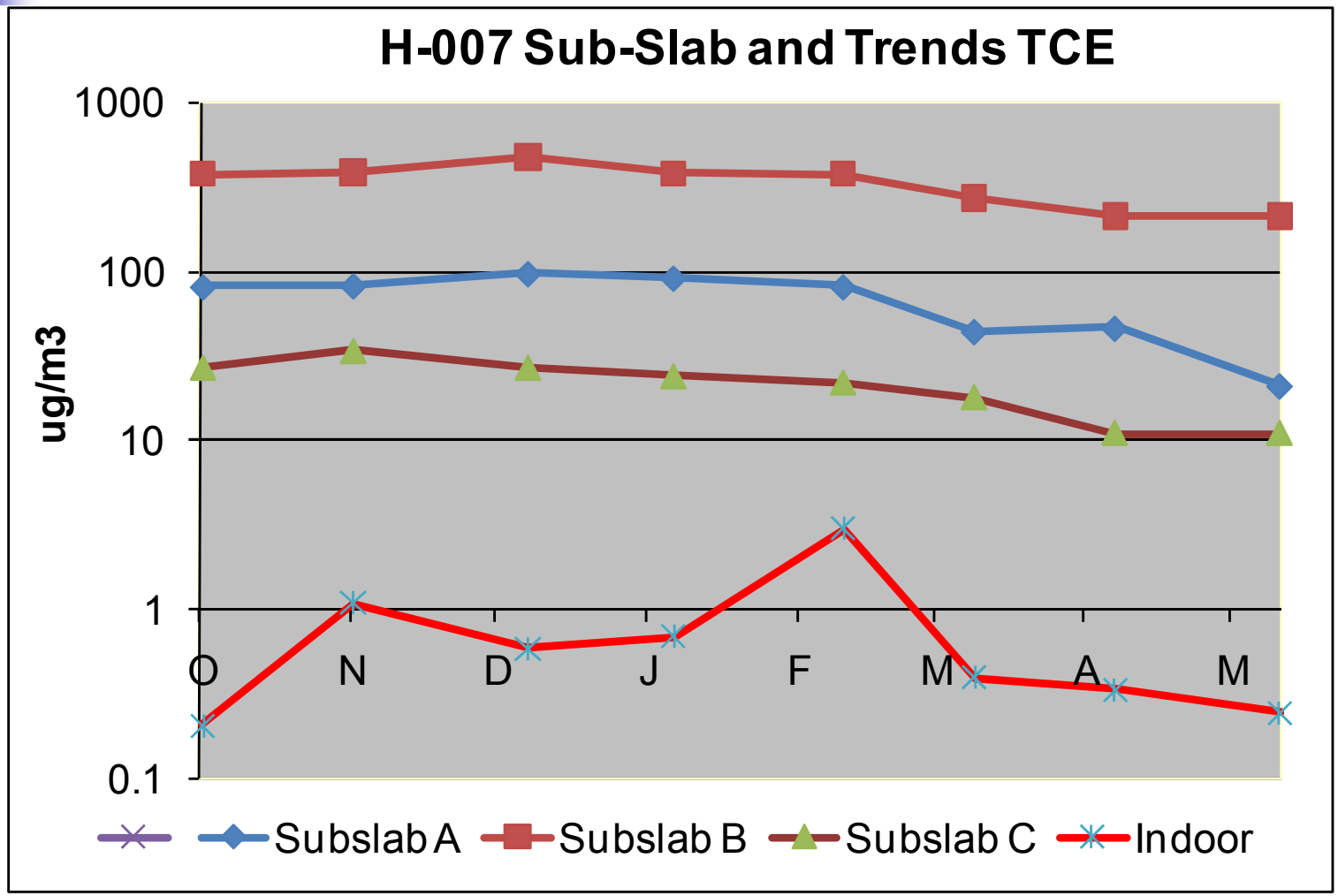
Cortlandville, NY Subslab Monitoring of House (Bill Wertz, NYSDEC)

TCE measured at 3 different locations below house



Significant spatial and temporal variability!

Cortlandville, NY Subslab Monitoring of House (Bill Wertz, NYSDEC)

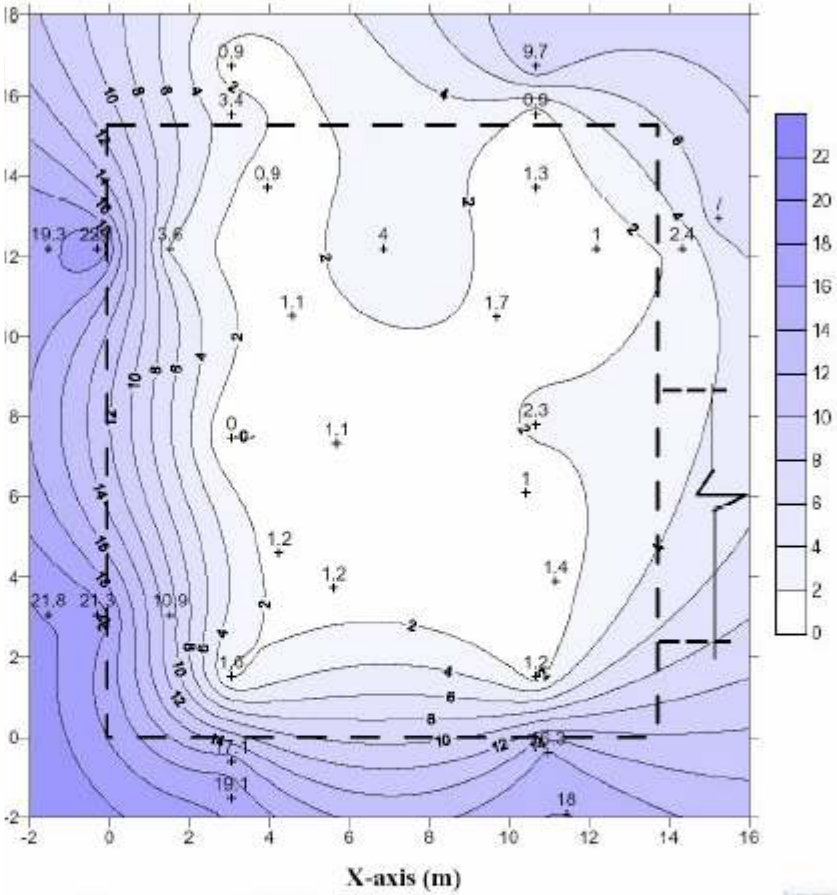


Casper, WY Research Site

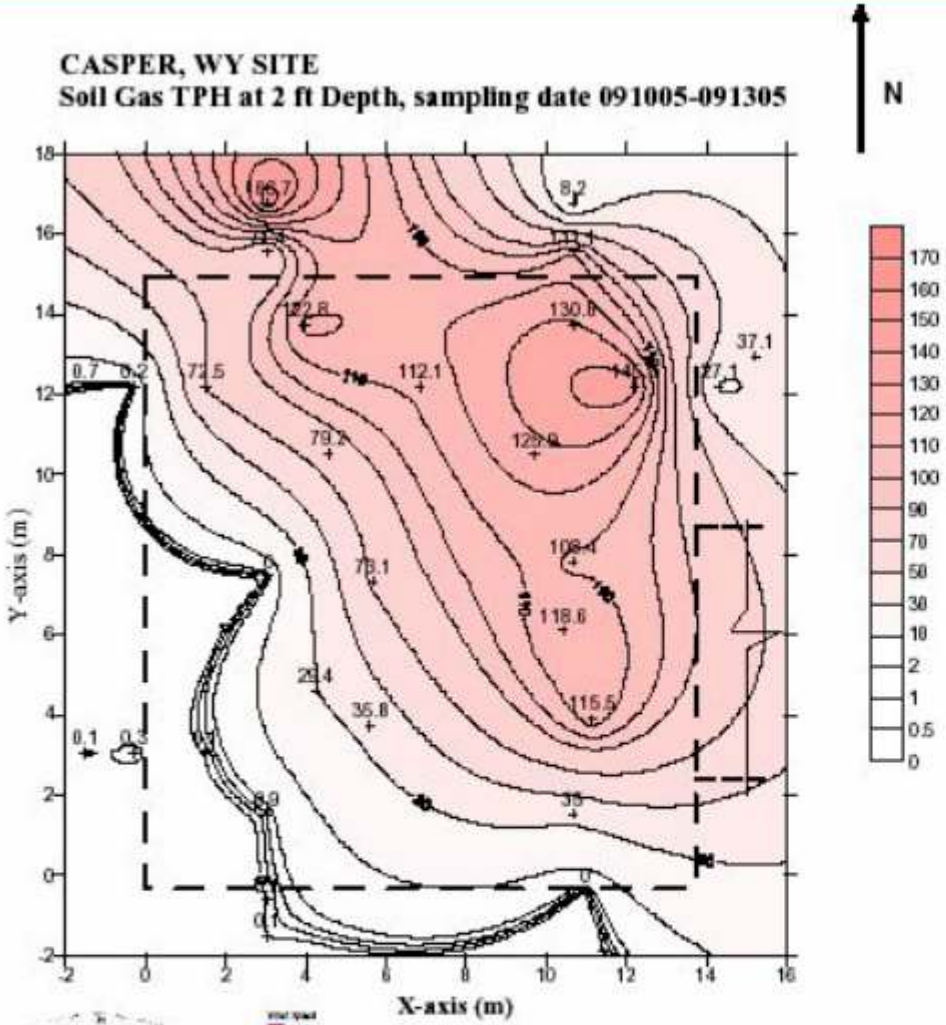
(Paul Johnson, ASU)

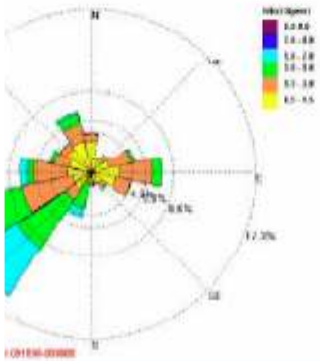
- Light petroleum distillate (gasoline)
- Soil is mixture sand, gravel and fill
- Water table 3.5 to 4.5 m below ground

CASPER, WY SITE
Soil Gas O2 Conc. at 2 ft Depth [091005-091305]



CASPER, WY SITE
Soil Gas TPH at 2 ft Depth, sampling date 091005-091305

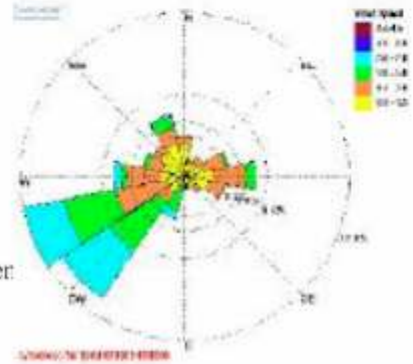




Legend:

Building boundary

0.2 Location and oxygen concer



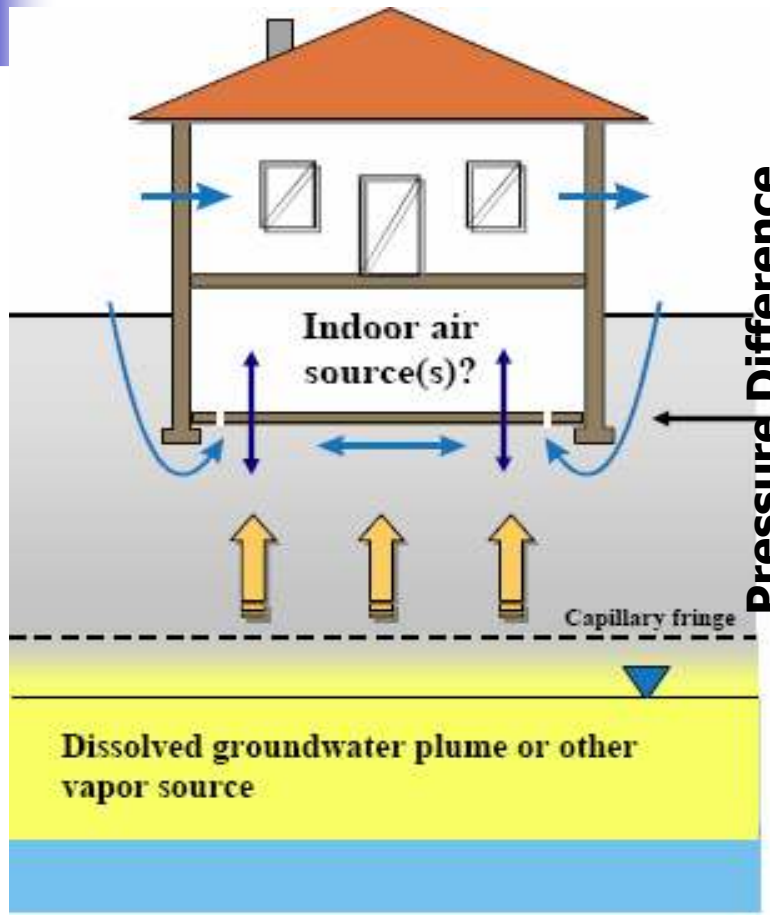
Legend:

Building boundary

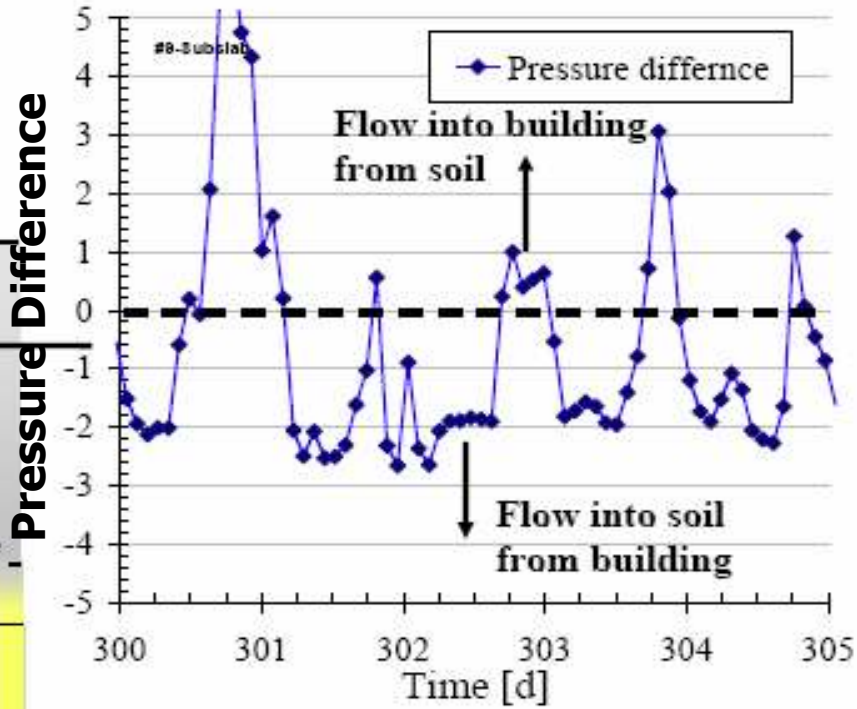
0.2 Location and its TPH concentration in mg/L

Casper, WY Research Site

(Paul Johnson, ASU)



Pressure difference across slab

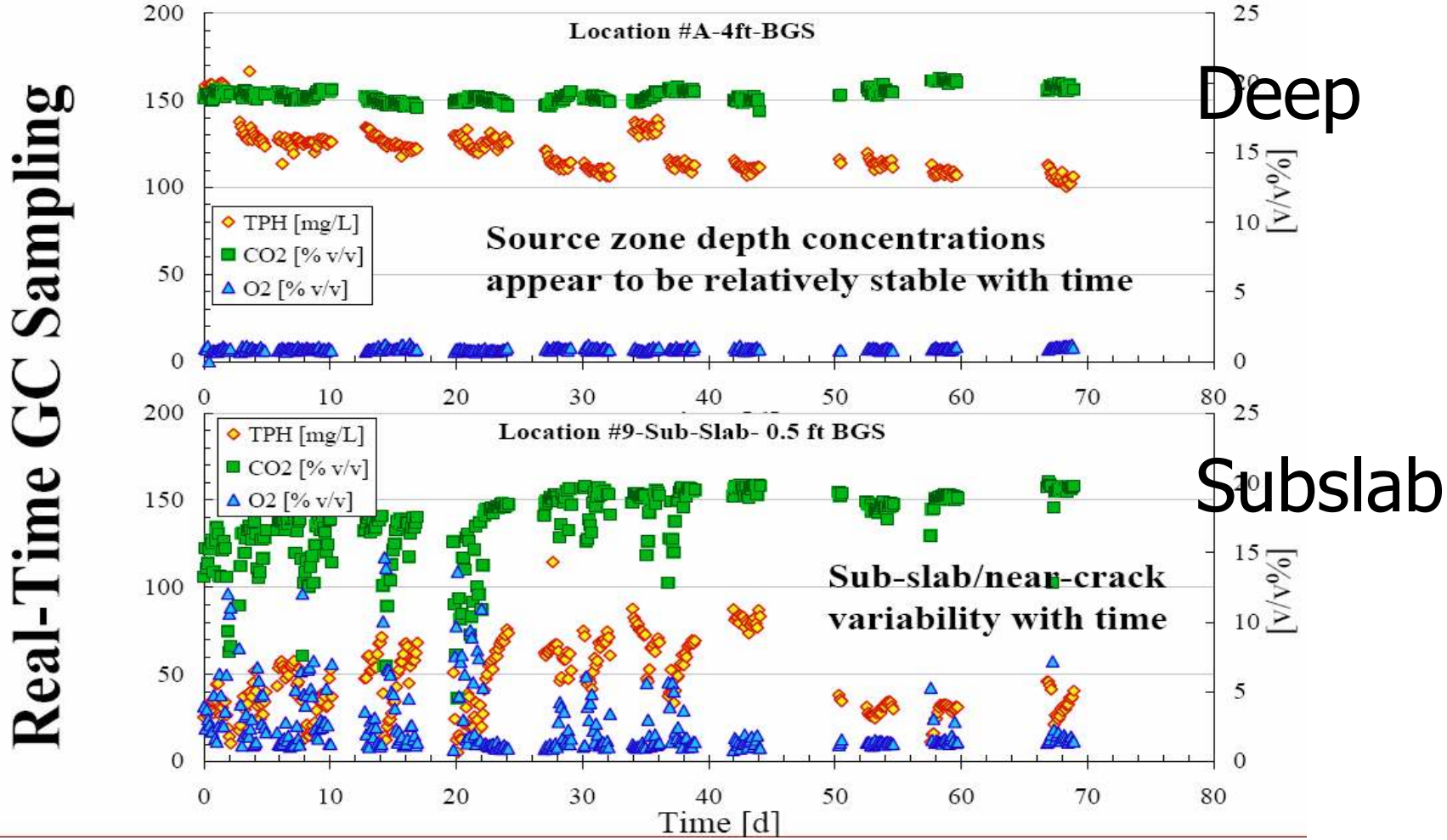


Temporal Variability
Building Breathing

Buildings can "breath" both ways! (think about implications for subslab vapour sampling)

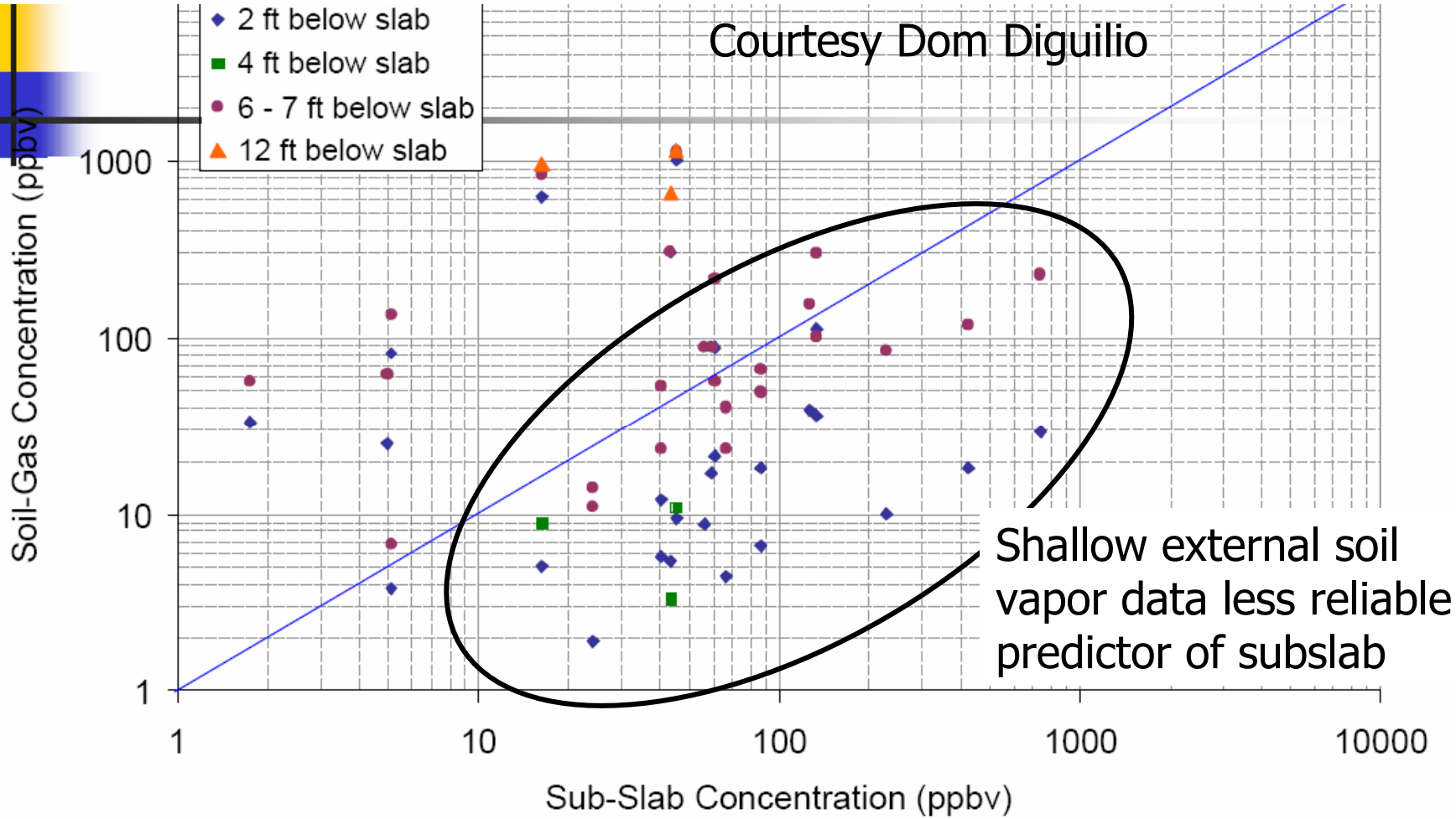
Casper, WY Research Site

(Paul Johnson, ASU)



Deeper soil vapour shows less variability

USEPA Raymark Site Research Study – Comparison External and Subslab Soil Gas

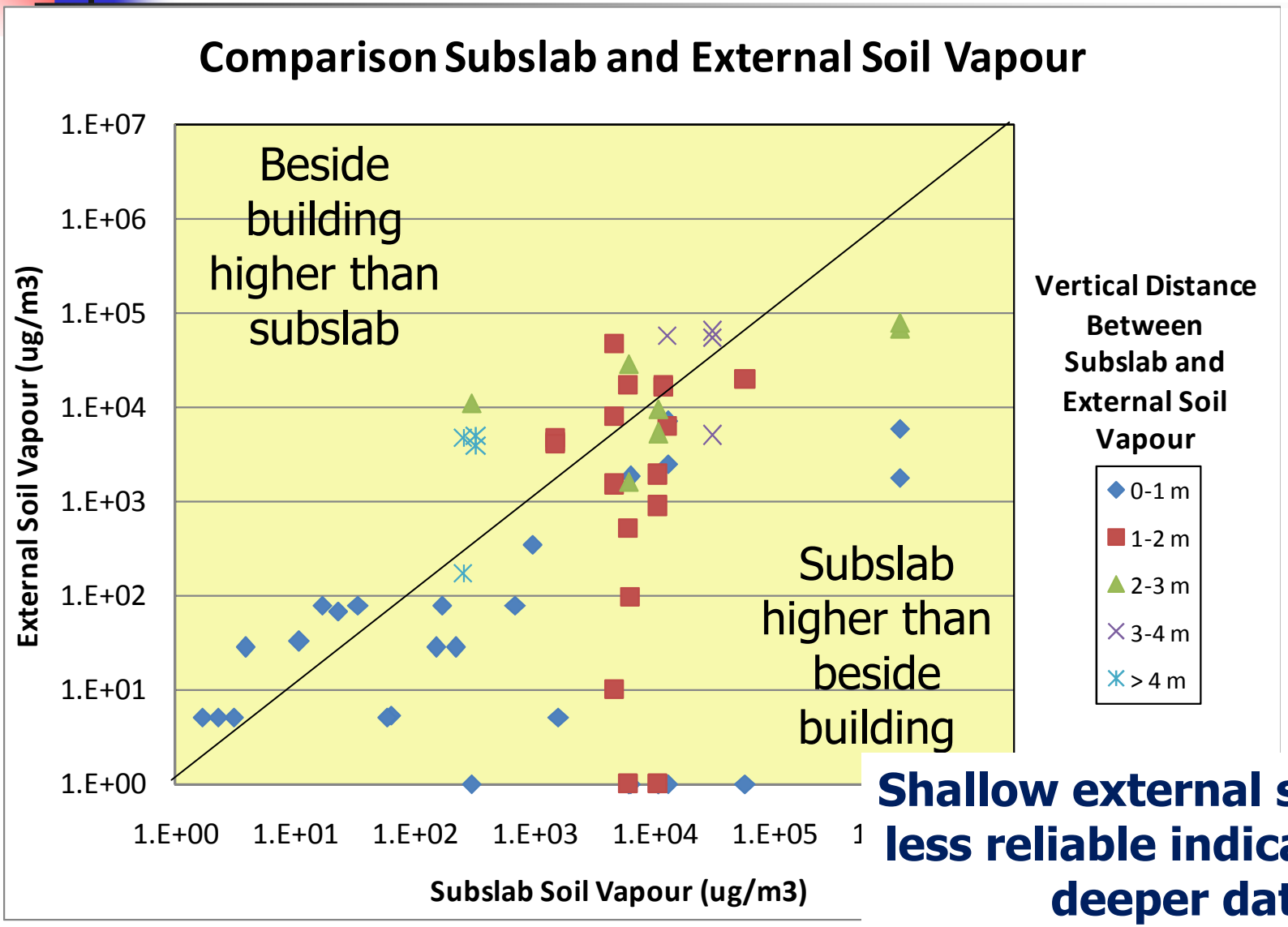


Soil-gas samples 1 meter (2 – 4 ft) below a slab systematically under-predicted sub-slab concentration. No clear pattern was present for soil-gas samples 2 meters (6 – 7) feet below a slab indicating that conservative estimation of sub-slab concentration would have required soil-gas measurement in excess of 2 meters.

Diapositiva 49

m1 I find this slide confusing - results not readily apparent.
mzgraggen; 12/10/2006

USEPA Database - Updated by Health Canada (2010)

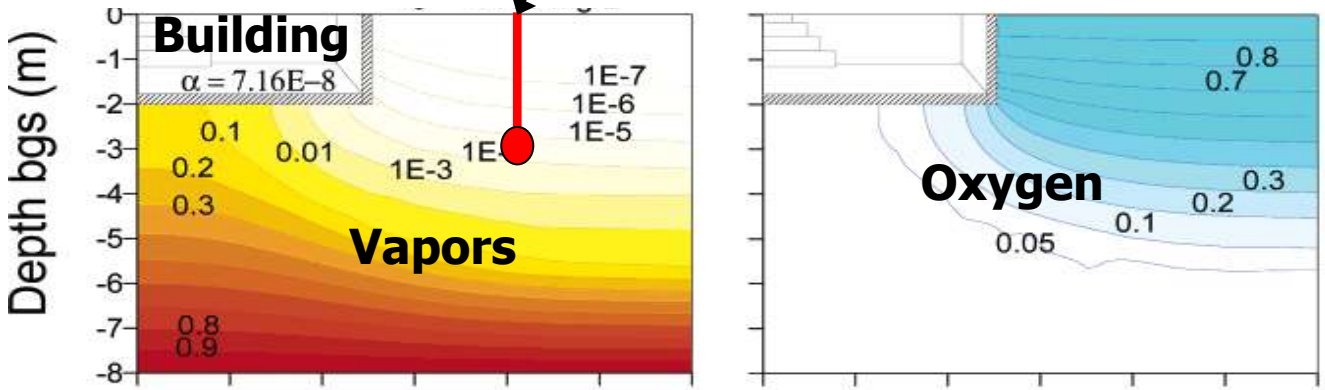


Shallow external soil vapor less reliable indicator than deeper data

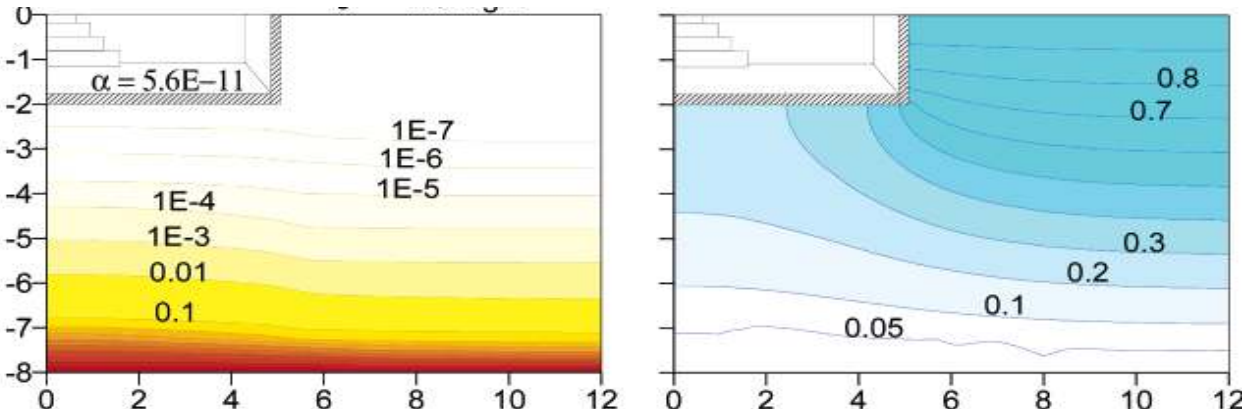
Modeling Study

(Illustrates spatial variability
& effect of biodegradation)

What if you sample out here?



V. High gasoline concentrations



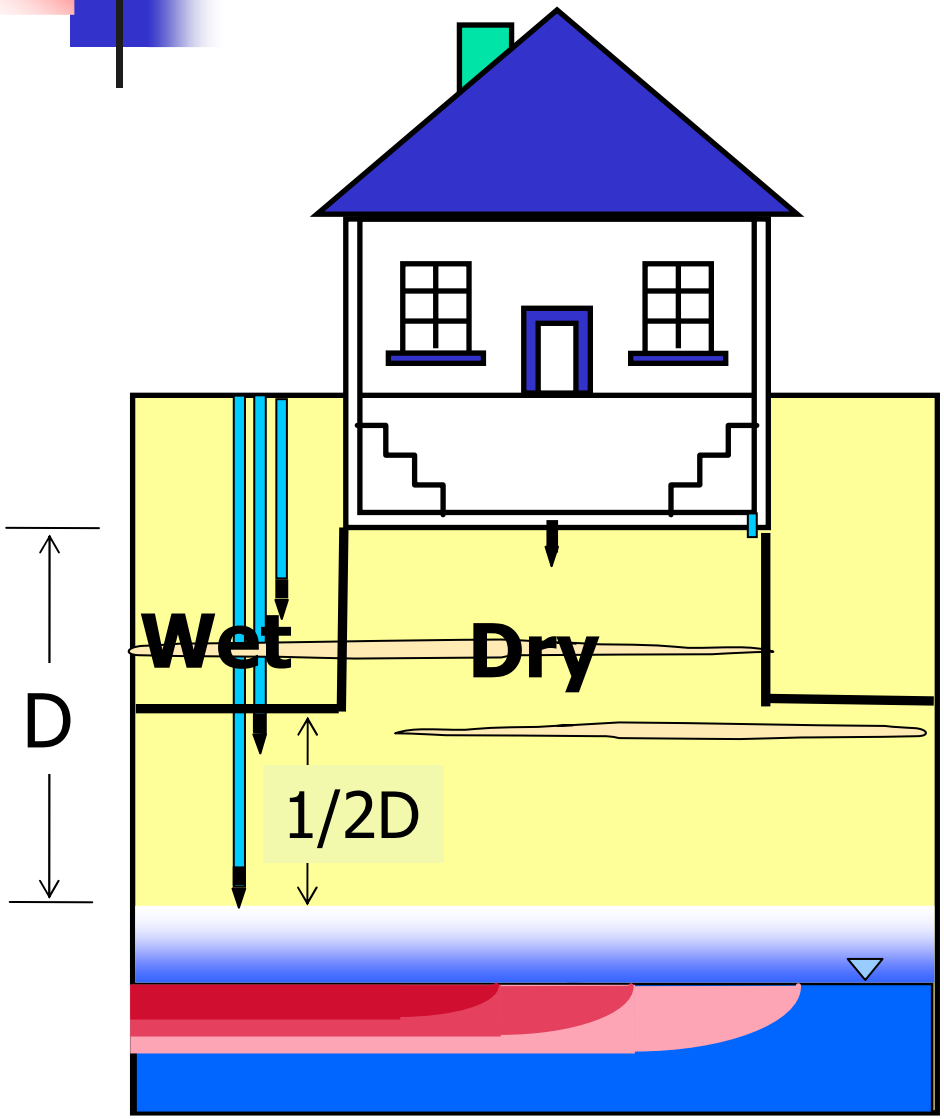
Slightly lower gasoline concentrations

3-D Numerical Model

(this is a slice through the house)

Abreu & Johnson, ES&T, 2005

Where to Collect Soil Vapour Samples?



- Collect near source soil vapour (Health Canada minimum ½ way between building and source)
- Minimum 2 sides building
- Vertical profiles of O_2, CO_2, CH_4 concentra-tions can help evaluate bioattenuation

Lateral Soil Vapor Transect

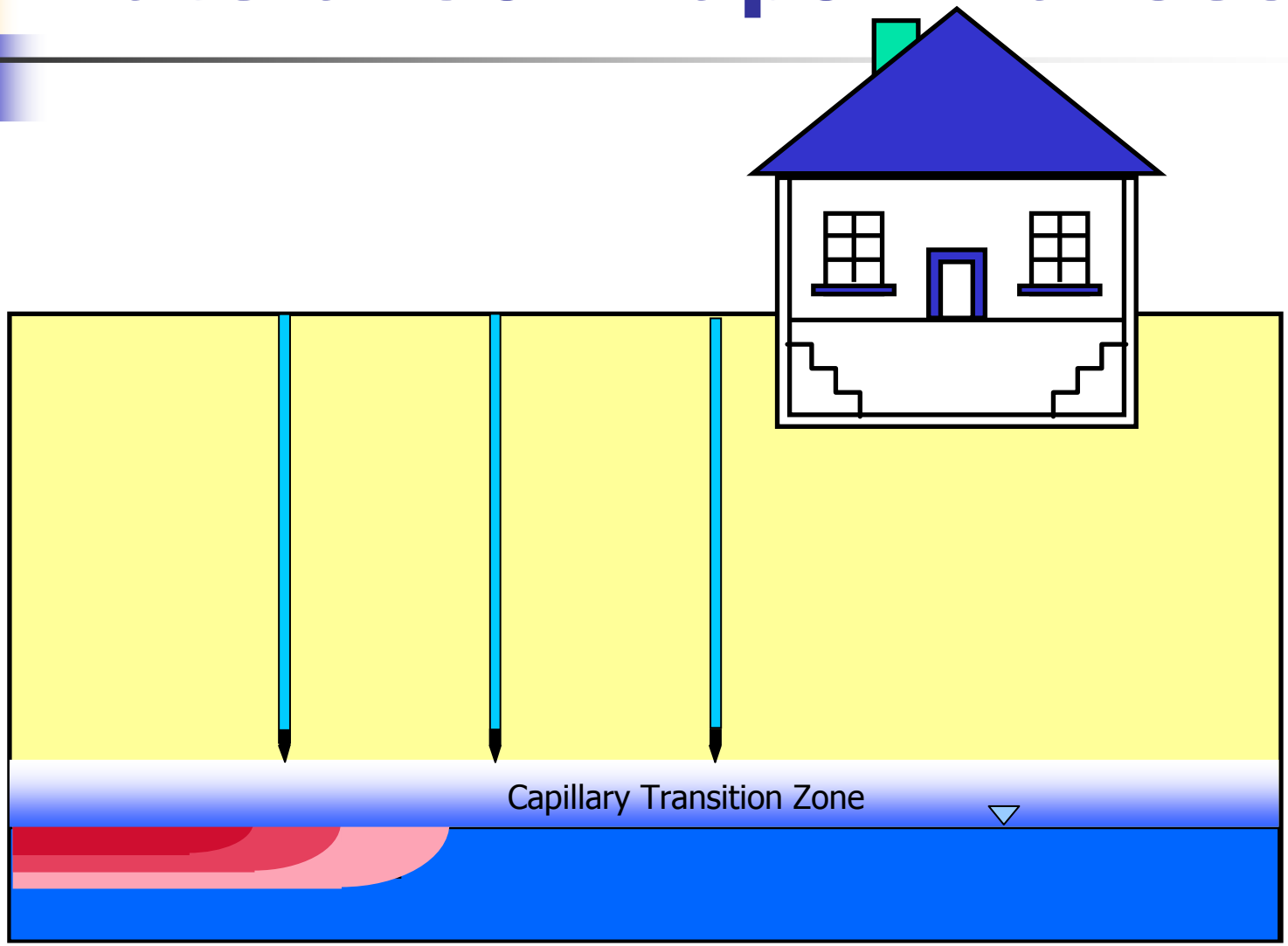
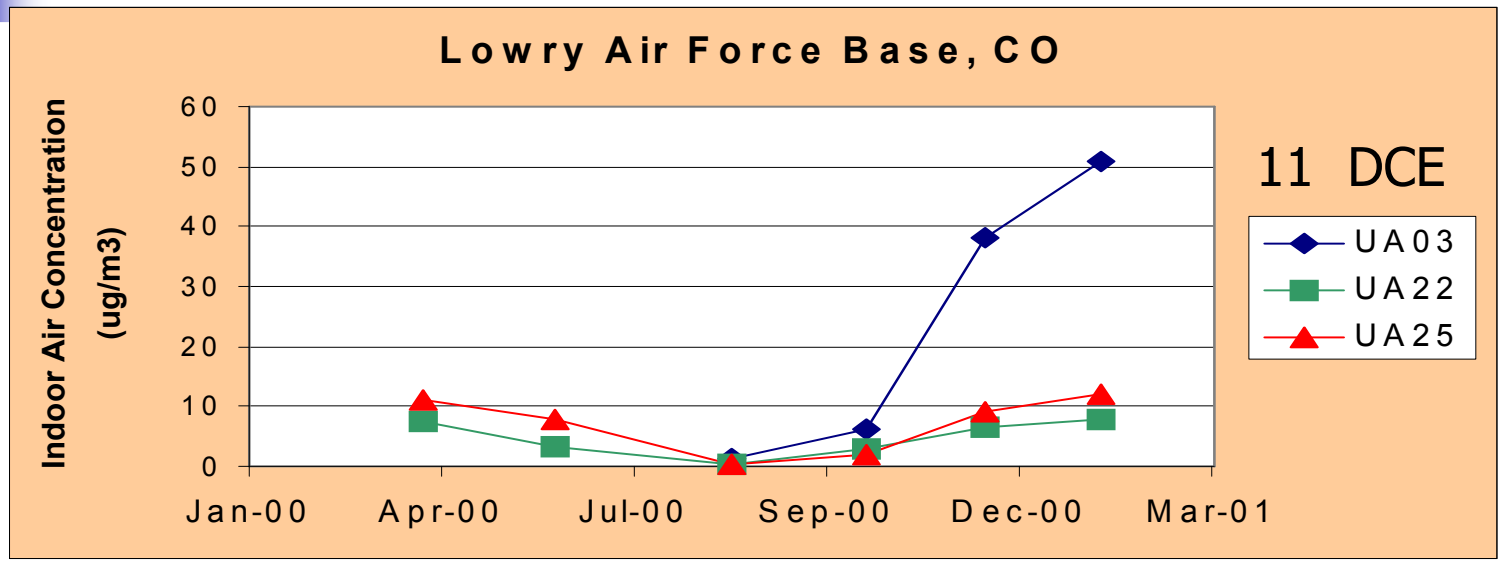


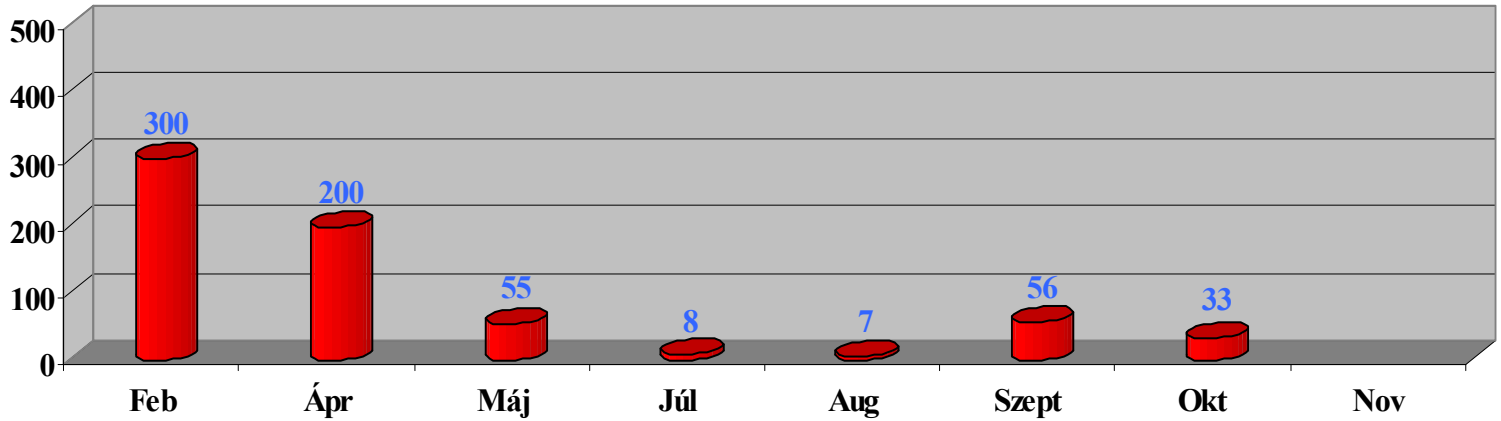
Figure 3.2 Lateral Transect Concept

Long-term Indoor Air Variability



H. Dawson

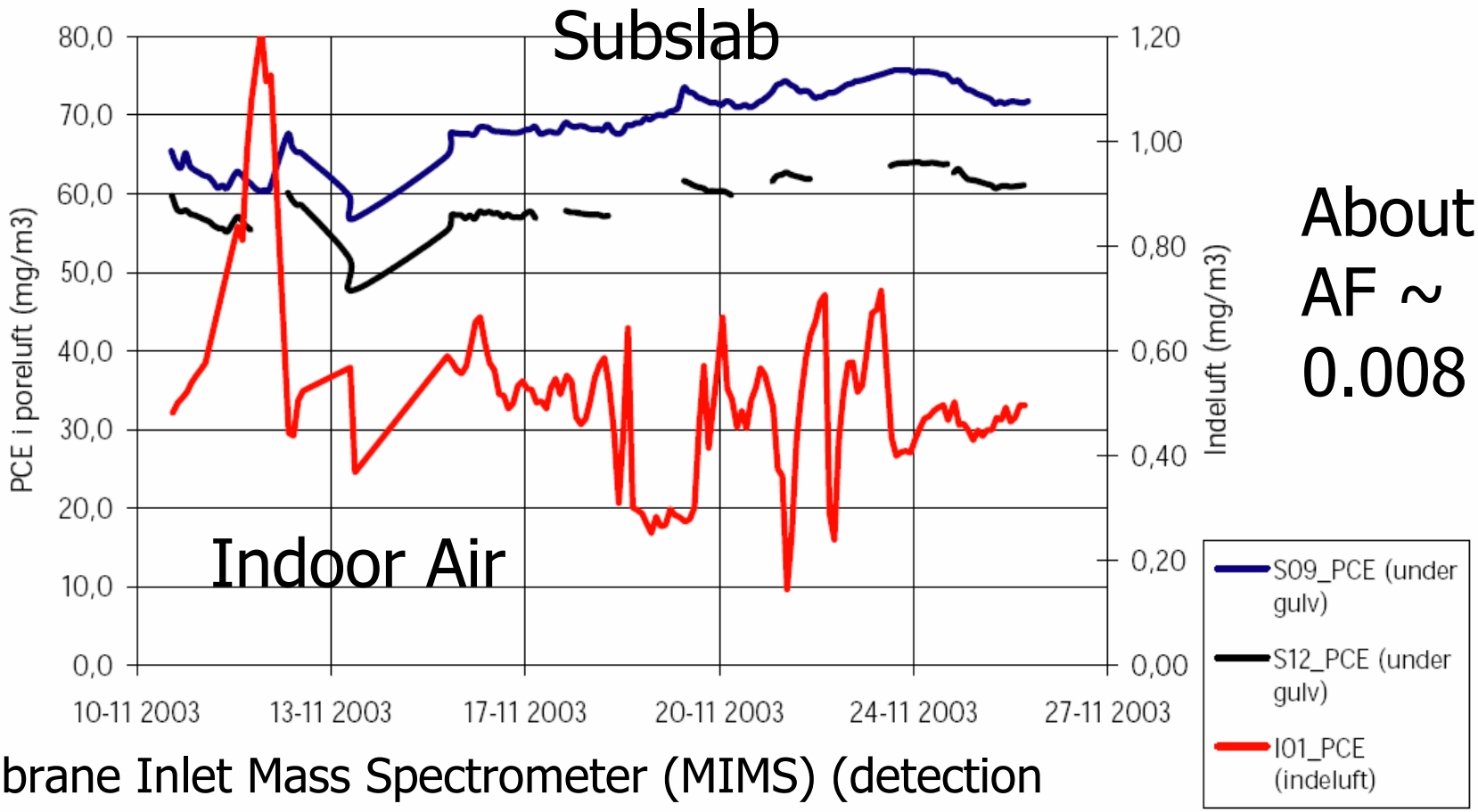
Site in Europe TCE



I. Hers

Short-term Indoor Air Variability

Danish Site Basement Monitoring

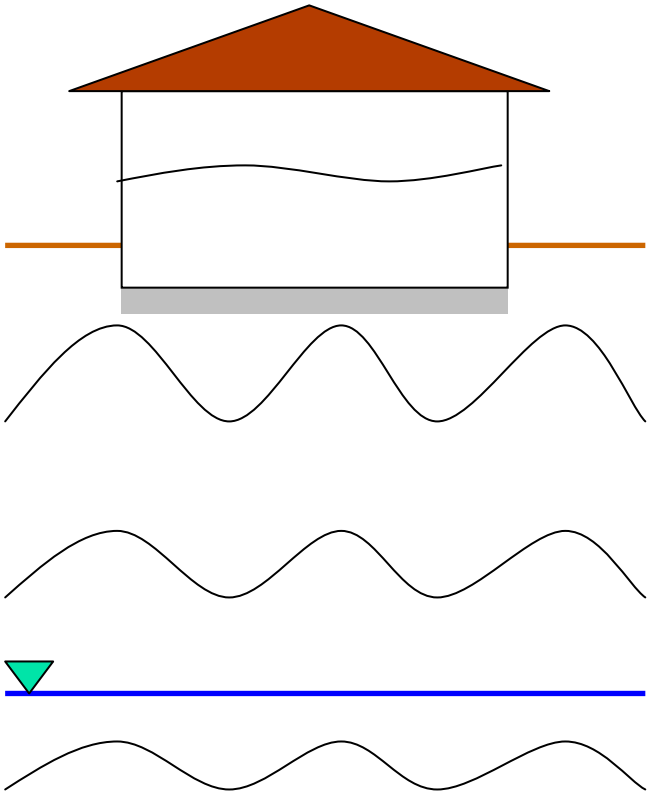


About AF ~ 0.008

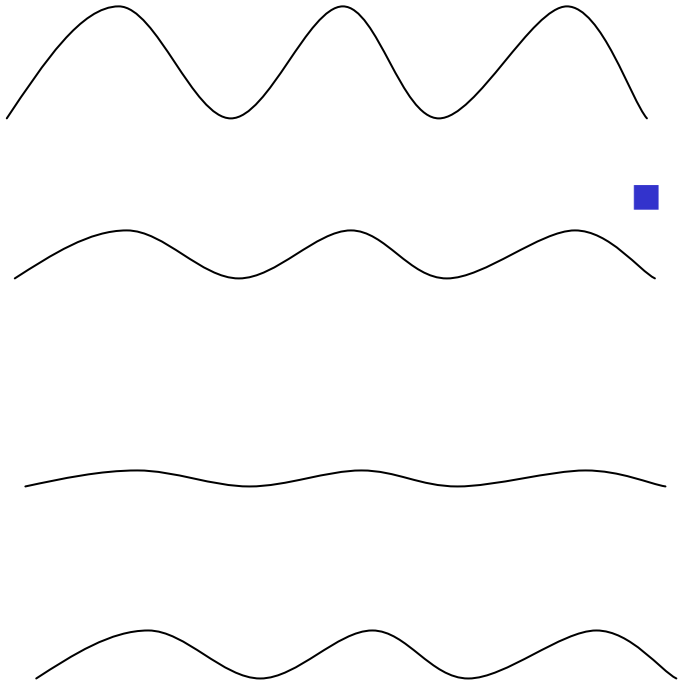
Membrane Inlet Mass Spectrometer (MIMS) (detection limit 0,5µg/m3

Conceptual Model

Spatial Variability



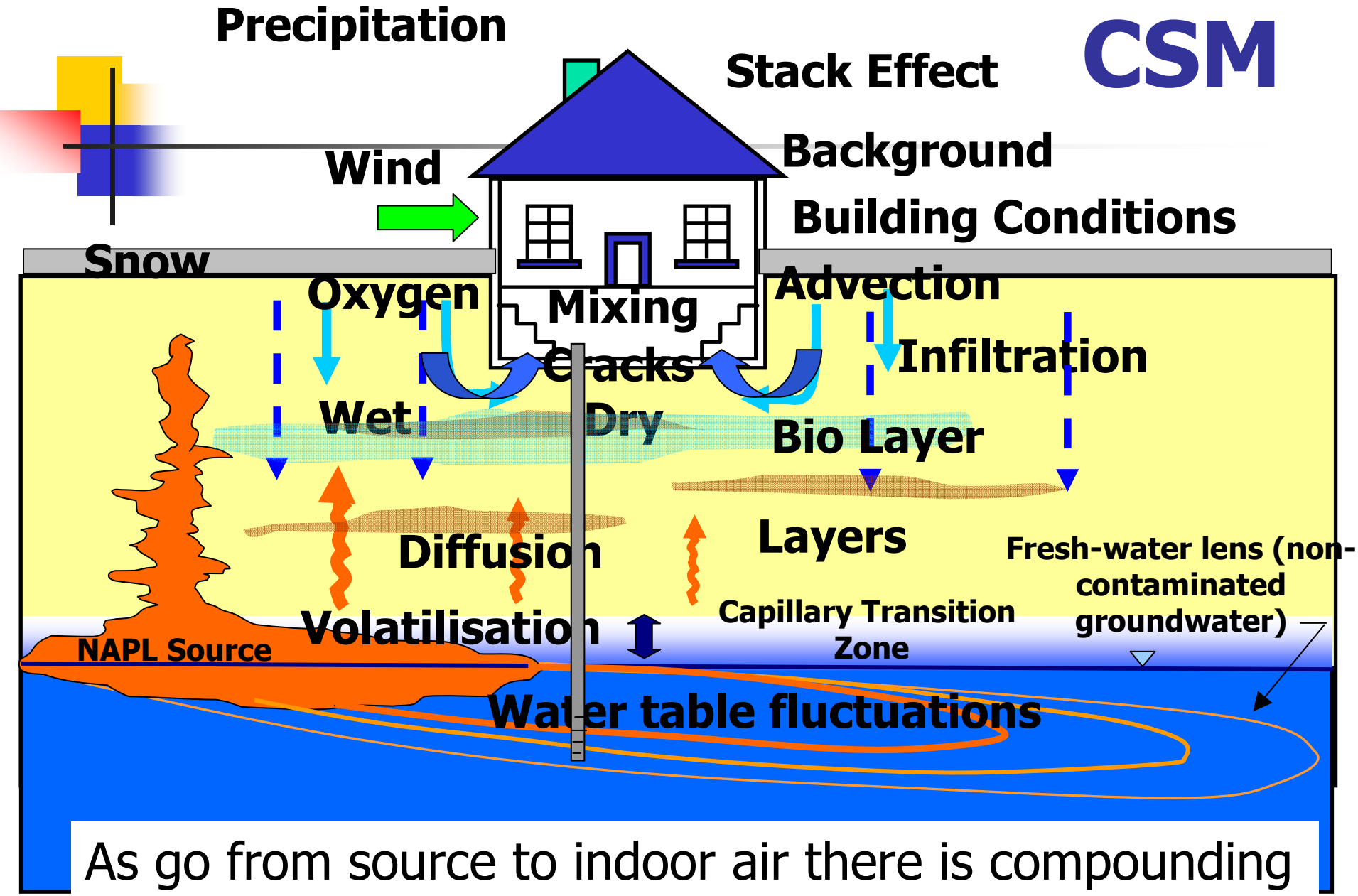
Temporal Variability



- What are Implications for sampling?

Courtesy of D. Folkes, Nov. 10, 2006 presentation (modified by H.Shuver and I. Hers)

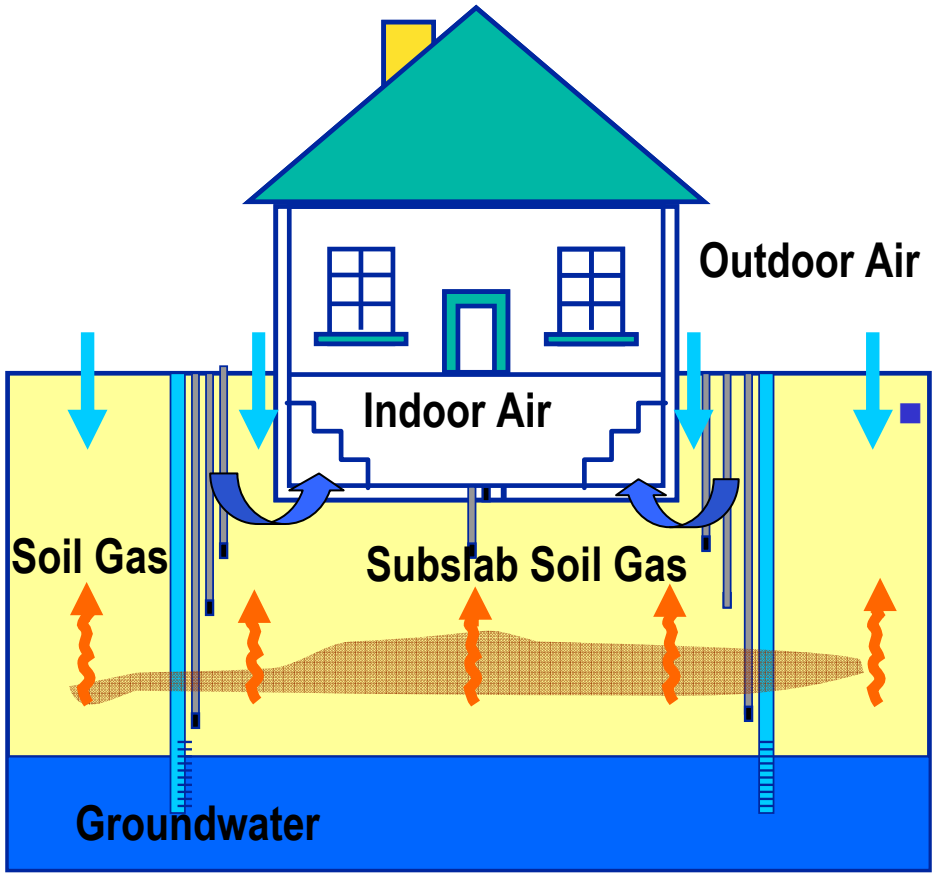
CSM



As go from source to indoor air there is compounding effect of variability – 4-dimensional problem!

Multiple Lines of Evidence

(Emerging Approach in US)



- **What is MLE?**
  - Sample different media (soil gas, groundwater, soil, air?) and locations, also non-VOC data (geology, biodegradation, building pressures, etc.
- **Why MLE?**
  - Reduce uncertainty
  - Determine whether pathway is complete and can reduce conservatism
  - How much data is needed? Cost? Sampling should be strategic.

Pro's & Con's Different Media

Media	Pro's	Con's
Soil	Data may be available, low cost, low temporal variability	Partitioning highly uncertain, high spatial variability
Ground water	Data may be available, low cost, moderate temporal variability	Partitioning uncertain, not representative if unsaturated zone source
External soil vapour	Avoids partitioning, more direct indication exposure, may integrate sources	Spatial variability moderate to high, temporal variability moderate, method issues
Subslab vapour	Closer to receptor, avoids lateral variability	Intrusive, cost, small scale spatial variability can be high
Air	Most direct indication (only for existing building)	Intrusive, cost, temporal variability moderate to high, background issues

Soil Vapour

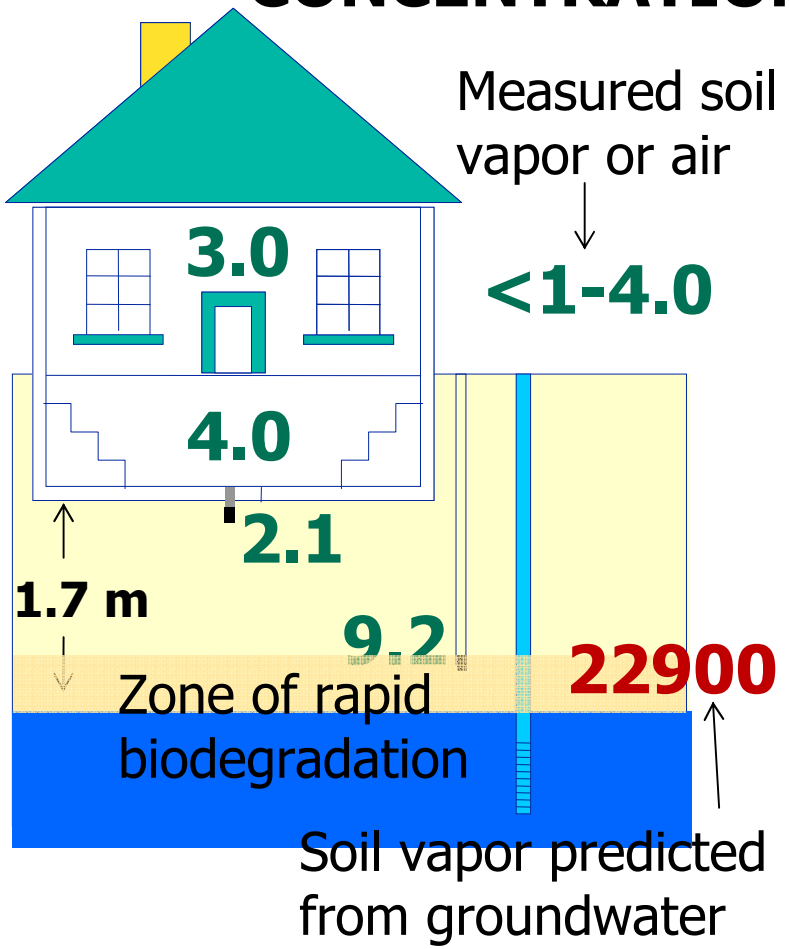
- Advantage more direct indication of potential exposure, no need for partitioning
- Variability in concentrations - significant spatial and temporal variability in soil vapour observed
  - Deep near-source vapour tends to be more temporally stable and less spatially variable
  - Shallow soil vapour - Influenced by geologic variability, biodegradation, barometric pumping, building, utilities
- Influence of building (rain and oxygen "shadow")
- How will future changes in site conditions affect soil vapour results?

Soil

- US guidance approach has been not to use soil, but instead use groundwater and soil vapour, because of inaccuracy in partitioning models
- Experience is that for
  - Chlorinated solvents, there is a poor correlation between soil and soil vapour
  - Petroleum hydrocarbons, there is a better correlation
- New guidance in British Columbia allows use of soil for petroleum hydrocarbon but not chlorinated solvents (DNAPL, specific gravity > 1 g/cm3)

Why MLE? – Pathway Completeness NJDEP-Golder Research Project

BENZENE CONCENTRATIONS

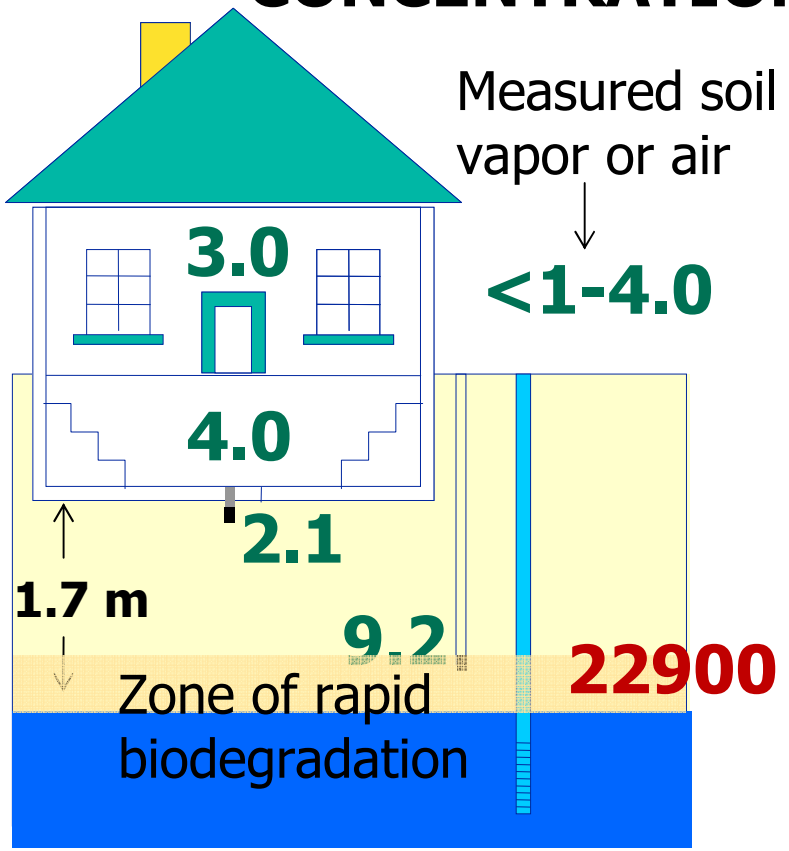


Evidence for incomplete pathway and possible background source

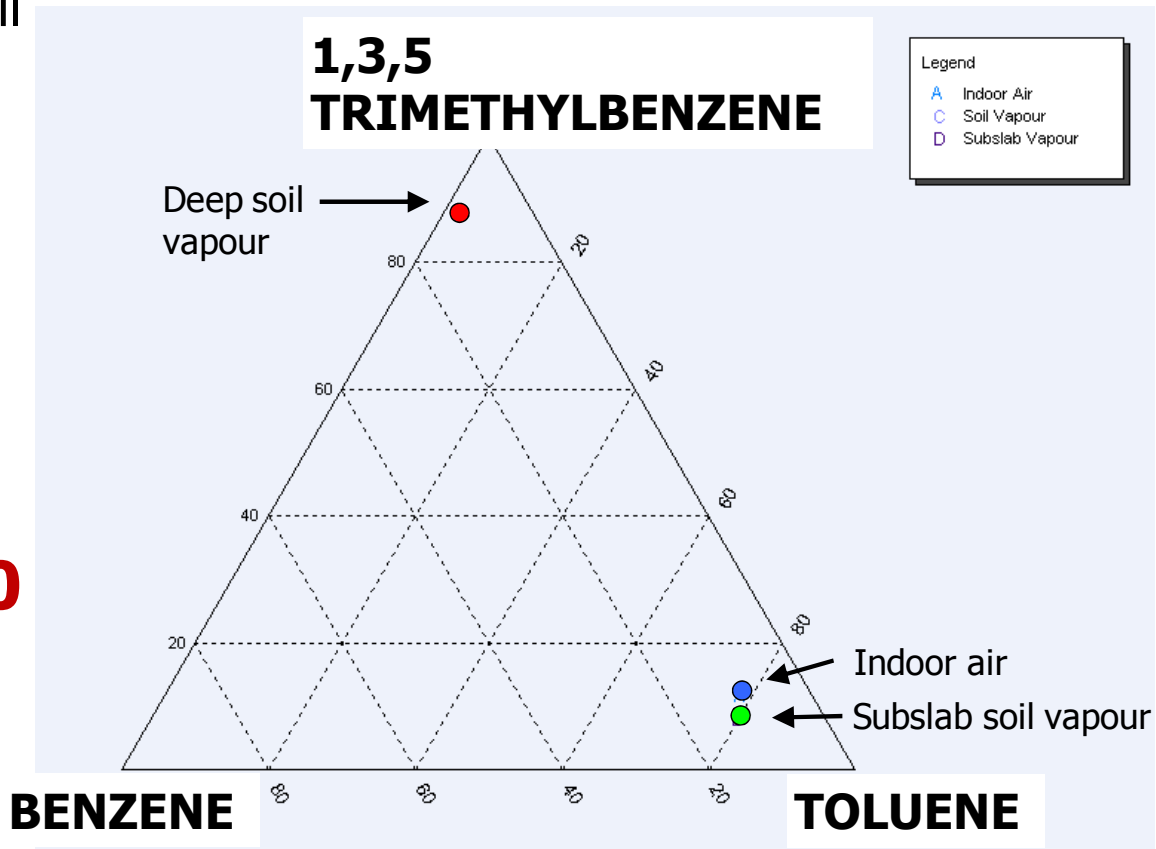
- Similar indoor and outdoor concentrations
- Subslab/Indoor concentrations that are < 10
- Indoor benzene within range of published background concentrations
- CSM model consistent with vadose zone attenuation

Why MLE? – Pathway Completeness NJDEP-Golder Research Project

BENZENE CONCENTRATIONS



- Compound ratio's, e.g., trilinear plots



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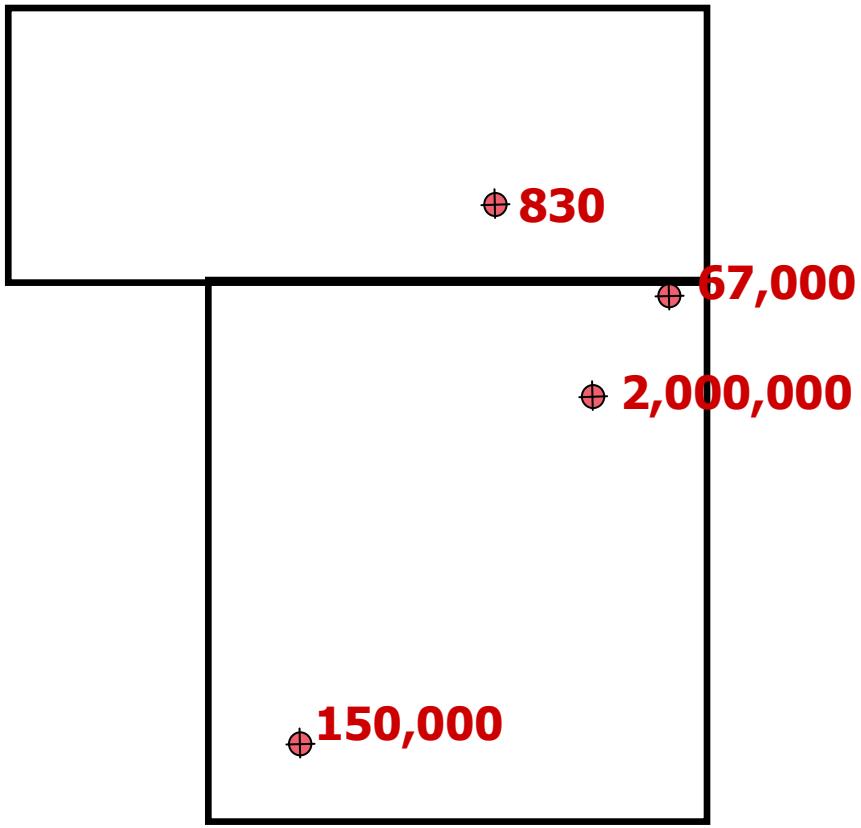
Why MLE?- Source Characterization Former Industrial Building



Subslab (5cm) VPH (~ TPH) Vapor Concentrations (ug/m^3) – Subsurface Contamination Problem – Right?

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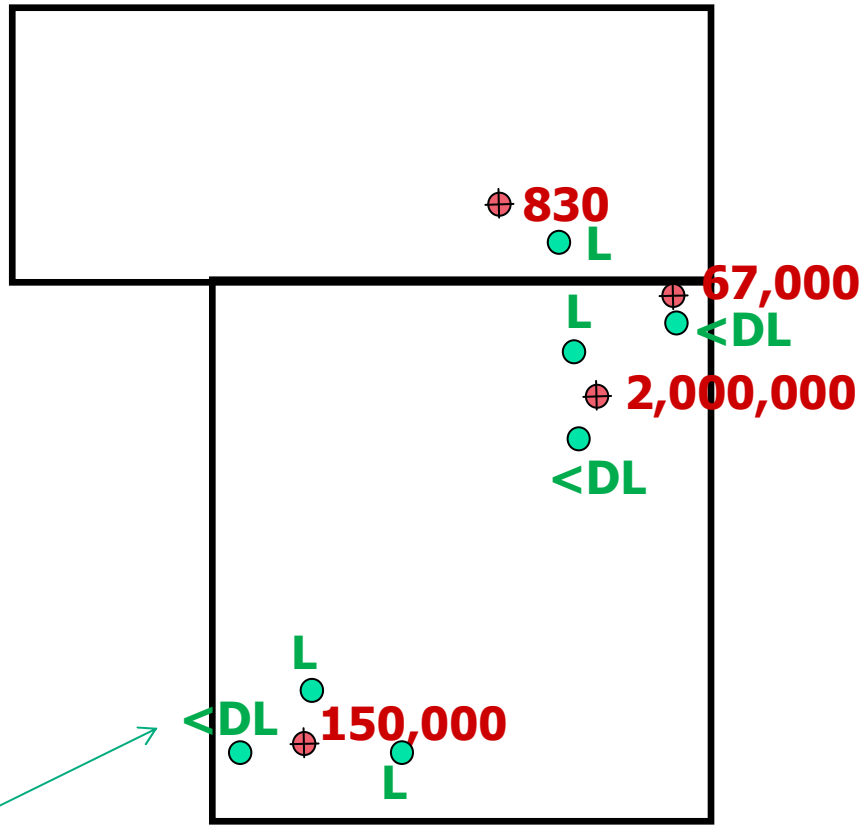
Why MLE?- Source Characterization Former Industrial Building



Soil Vapor VPH Concentrations at 1 m depth

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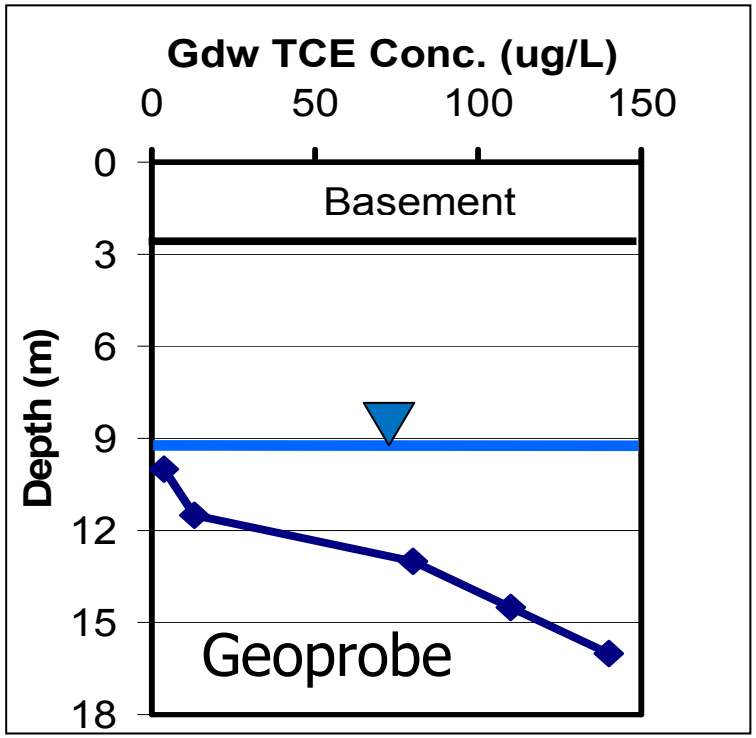
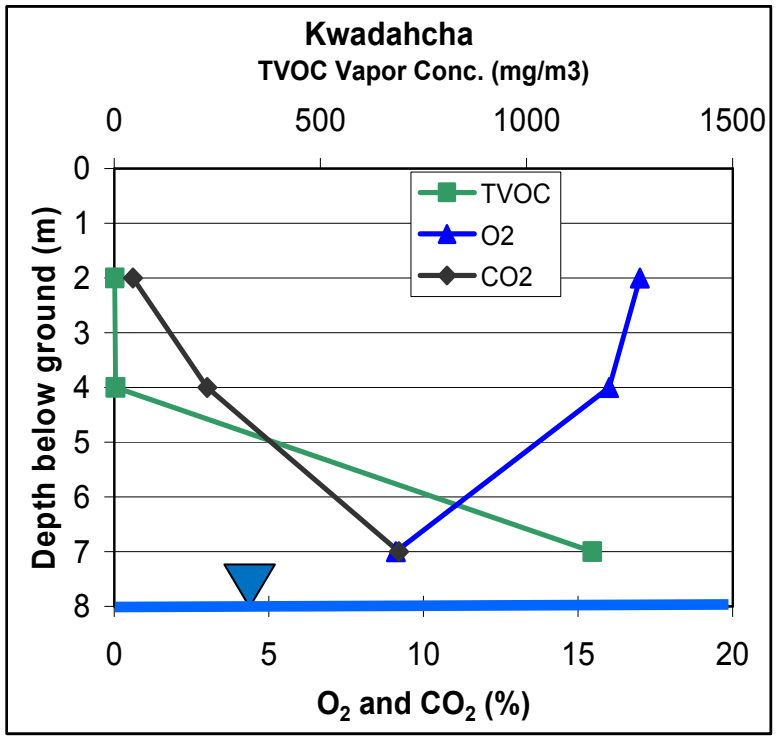
Vertical Profiles Can Help Assess Pathway Completeness

Groundwater Profile



Groundwater concentration decreases near water table

Soil Vapor Profile



Soil vapour profiling indicates aerobic biode-gradation at diesel site

MLE Dry Cleaner Case Study

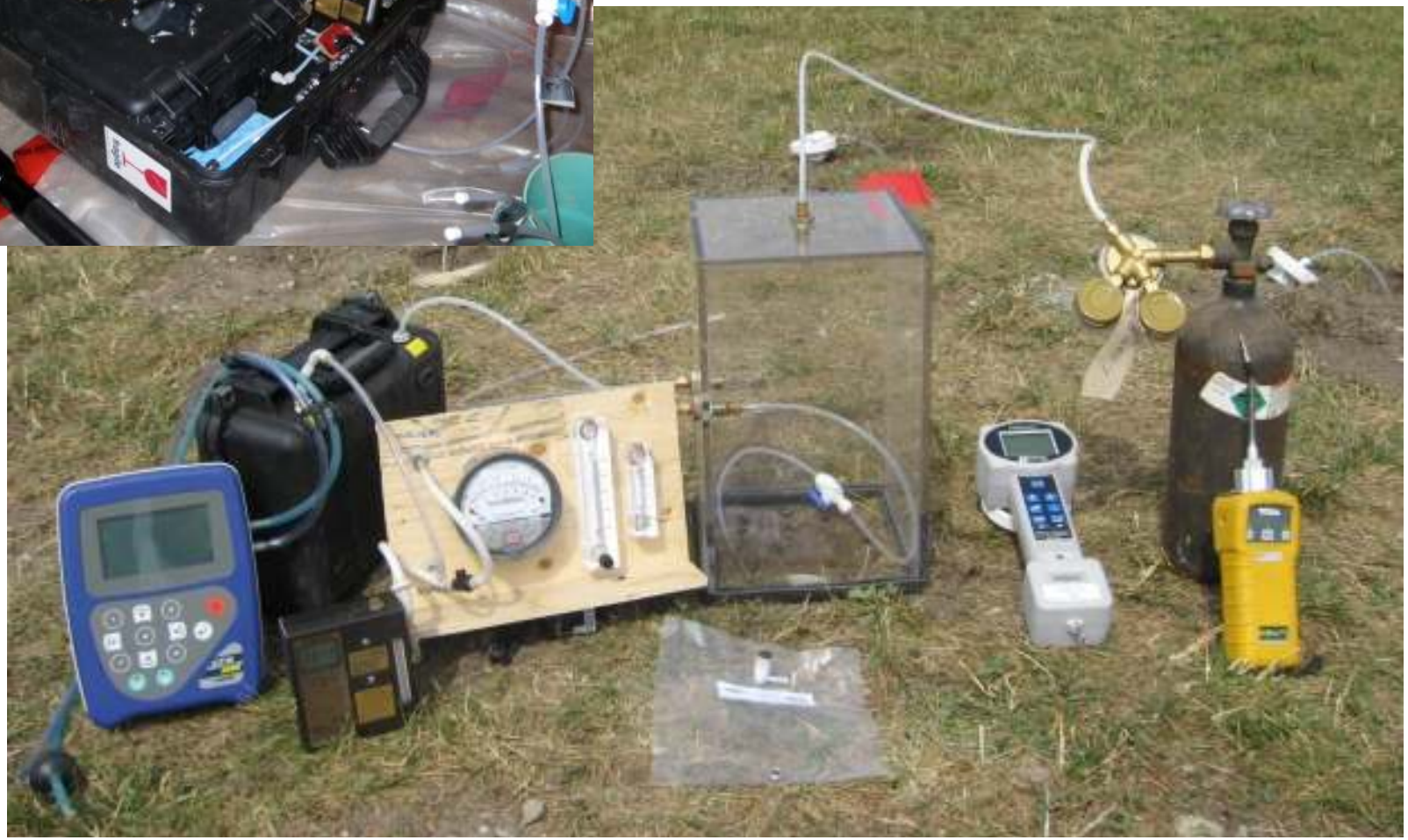
- **Soil vapour**: TCE > draft BC vapor criteria
- **Regulator required IAQ tests**: Indoor TCE ~ 0.16 to 5 ug/m^3 > draft BC air criteria of 0.3 ug/m^3 in several stores
- What is next step?

Soil Vapor-Air Alpha's

	Sports	Florist	Glasses	Dry * cleaning
PCE	2.E-03	1.E-03	6.E-03	7.E-02
TCE	1.E-04	1.E-04	3.E-04	6.E-03

* drop-off / pick-up only

Soil Gas Sampling and Analysis



Soil Vapour Methods

- Similar or higher level of care than groundwater
- Low-flow, low purge sampling
- Carefully seal boreholes
- Leak tracer tests to test seals and sampling trains

"Geoprobe"

Helium tracer test

Anyone like to come to Canada for some soil gas sampling?

Soil Gas Sampling Process

- Selection of probe and sampling train materials
- Test blanks
- Installation of probes
- Probe equilibration (and possible "conditioning" of probe)
- Flow and vacuum check
- Leak tracer test
- Purging and sampling
- Field screening
- Collection of samples for laboratory analysis

Probe Materials

- Probes: Stainless steel, rigid PVC
- Tubing: **Best**: Teflon, Nylon (Nylaflow) Polyetheretherketone (PEEK); **Don't Use**: Tygon, silicon, LDPE
- Always use new materials properly stored (except temporary driven probes)
- Always seal probe when not sampling (they breathe)
- Never use glues or tape

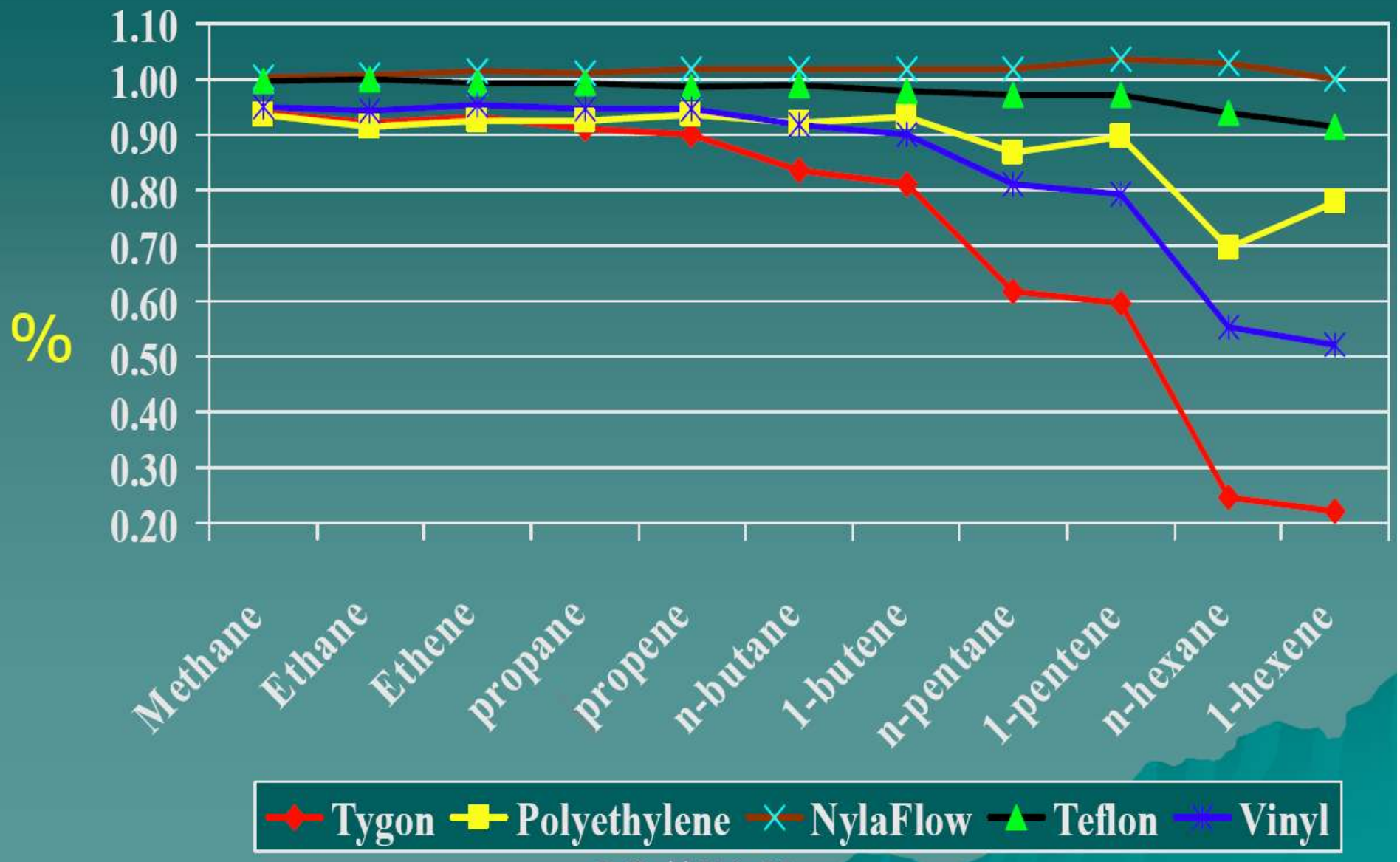
For tubing study see Hayes *et al,* 2006. *The Impact of Sampling Media on Soil Gas Measurements. Proc. Of AWMA VI– The Next Great Environmental Challenge – An Update*, Sept 13-15, LA, CA (Air Toxics website) (*e.g.*, LDPE (0.6 m long): toluene artefact of 14 ug/m^3, naphthalene recovery of 12%)

Tubing Sorption Study by Air Toxics Laboratory

- Air Toxics tested recovery of simulated soil gas through 0.6 m long tubing of different types
- Nylaflow, Teflon, PEEK generally performed well, polyethylene less well (not recommended)
- However, naphthalene recovery for Nylaflow (31%) was low compared to Teflon (87%)
- Nylaflow and Teflon are recommended tubing materials, but Nylaflow commonly used because less expensive
- We now have methods by where we can analyze for naphthalene but may loose much of it if we use Nylaflow – more research needed

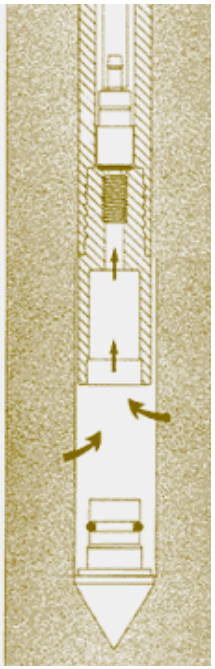
Hayes *et al,* 2006. *The Impact of Sampling Media on Soil Gas Measurements. Proc. Of AWMA VI– The Next Great Environmental Challenge – An Update*, Sept 13-15, LA, CA (Air Toxics website)

50 Ft Tubing Test



Soil Gas Probes

- Temporary direct push sampler with retractable screen (Geoprobe or AMS system) – Key is avoiding leakage
- Permanent probes installed in boreholes or using direct push – **Mini-well** (19 mm dia rigid PVC, 30 cm long) or **Implant** (13 mm dia, 15 cm long) – **Key is sealing probe**



Geoprobe implant

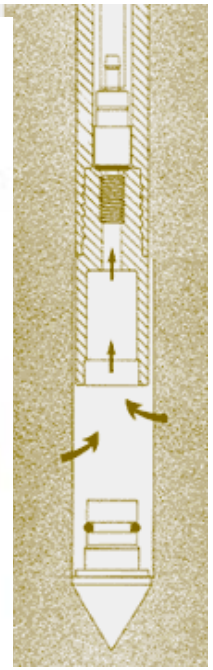
Very small sampling tips not recommended

Temporary Probes

- Driven ("slam bar") probes
  - Disadvantages leakage along outside of probe, fracturing fine-grained soils, small open area, generally not recommended

- Direct push sampler with retractable screen
  - Eg.,Geoprobe PRT system
  - Can go deeper
  - Multiple samples
  - Contaminant drag-down?

Geoprobe Method

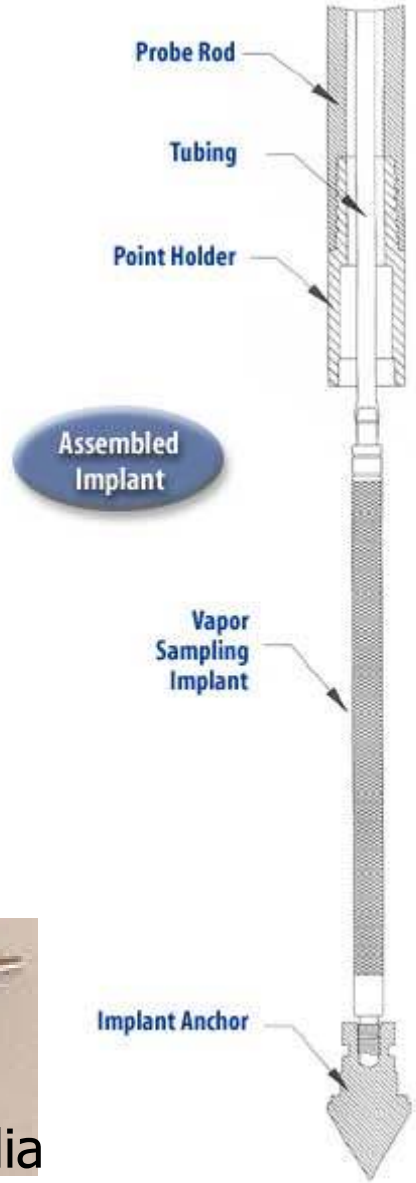


Permanent Probes

- Installed in Drilled Boreholes
  - Smaller diameter PVC pipe (3/4 inch) with 1′ long screen (No. 20 slot)
- Installed using Direct Push Technology
  - "Small implants" connected to ¼" tubing
  - Advantage small purge volumes
- Key is sealing borehole
  - Granular bentonite above sand pack and grout to surface

Geoprobe Implant

6" long, 0.5" dia



Sampling Existing Groundwater Monitoring Wells

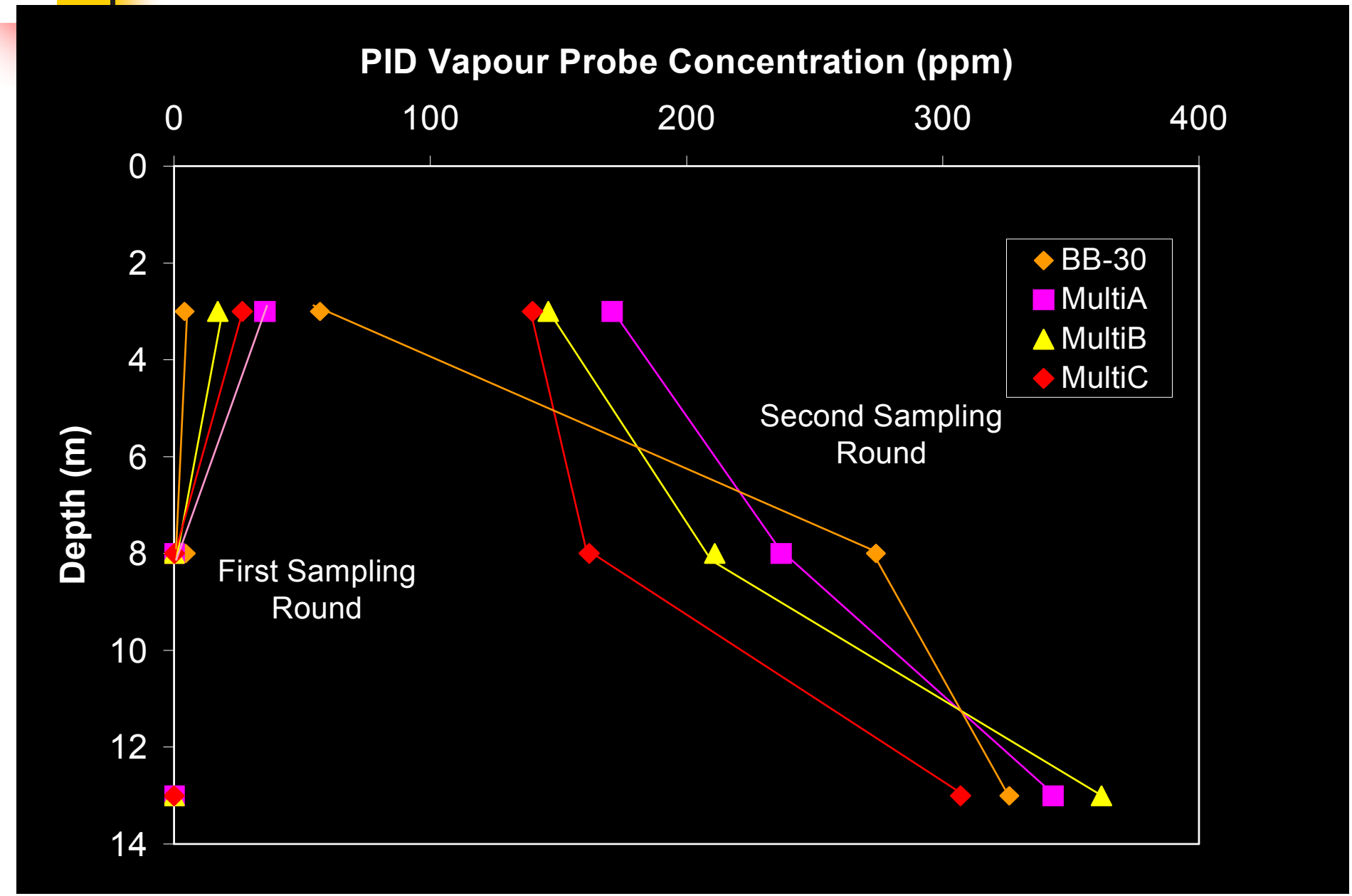
- Screen must be above capillary fringe (min 0.5 m above water table, maybe more for fine-grained)
- Borehole annulus must be well sealed
- Requires larger purge volumes (remove at least 3 standing volumes, if well is venting purge until concentrations stabilize)
- May be some volatilization from water table
- May not provide desired vertical discretization
- Although there are potential limitations, if wells pass leak test, sampling existing wells can provide useful data

Granular Seals

Soil Gas Probe Equilibration

- Drilling and construction of filter pack causes disturbance to soil vapour equilibrium
- Suggested **equilibration** times (by vapour diffusion) are:
  - Driven probe (~30 min)
  - Geoprobe implant (day)
  - Auger drilling (two days)
  - Air rotary (few weeks)

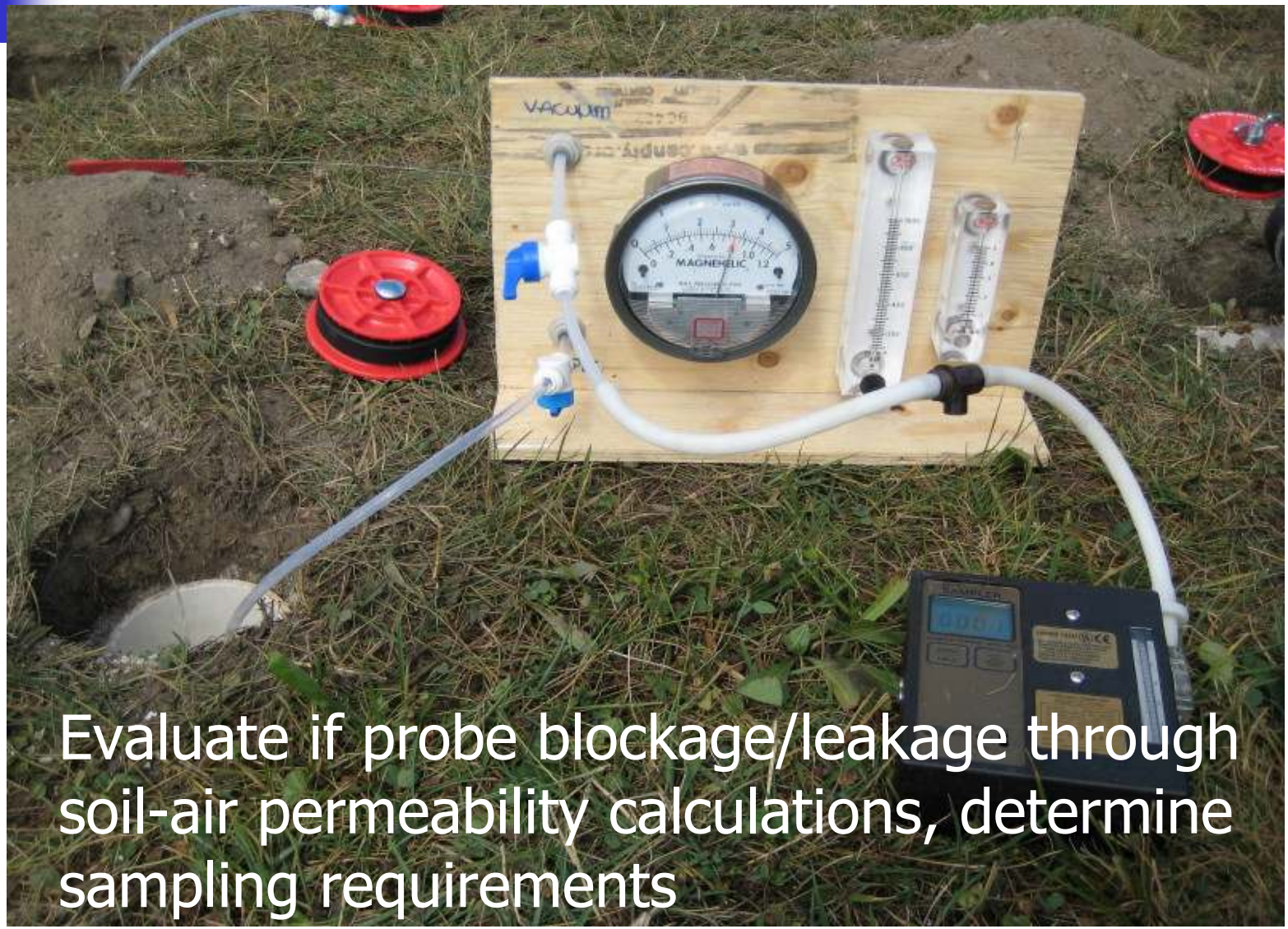
Why Equilibration Needed for Air Rotary



"Flow & Vacuum" Check
(probe performance test)

- Much higher vacuum than expected (based on soil-air permeability calculations on next slide) suggests probe blockage, much lower could indicate leak
- While it is possible to collect soil gas samples at up to 250 cm H20 vacuum, challenges are:
  - Requires specialized pumps for bag or tube sampling
  - Summa canisters partially filled
  - Possible contaminant stripping effect if vacuum were to be comparable to chemical vapor pressure, e.g., benzene VP = 150 cm H_20
- Recommend reducing flow such that vacuum is less than 40 cm H20 vacuum

"Flow & Vacuum" Check
(probe performance test)



Evaluate if probe blockage/leakage through soil-air permeability calculations, determine sampling requirements

Soil-air Permeability Testing – Steady State Solutions

Method 1: Spherical Flow to a Point

(Garbesi et al. 1995, Water Resources Research, 32, 3, 547-560, March 1996)

$$k = \mu Q / (S \, \Delta P_f)$$

Method 2: Radial Flow to Well

(Johnson et al. 1990, GWMR, 10, 2, p159-178, Spring)

$$Q = H * \pi * (k/\mu) * P_p * (1-(P_{atm}/P_p)^2) / \ln(R_p/R_i))$$

$$k = Q * \mu * \ln(R_p/R_i) / [\, H * \pi * P_p * (1-(P_{atm}/P_p)^2)]$$

Correction Klinkenberg Effect

$$k = k_{cor} (1 + b / P)$$

ΔP_f = pressure difference between surface & probe tip (g/cm-sec^2)

S = shape factor, for spherical pressure source, S = $4\pi r$ where r = probe radius (cm)

K = permeability (cm^2)

μ = viscosity (g-cm/sec)

Rp = radius probe (cm)

Ri = radius influence (cm)

P_p = pressure probe (g/cm-sec^2)

Q = flow (cm^3/sec)

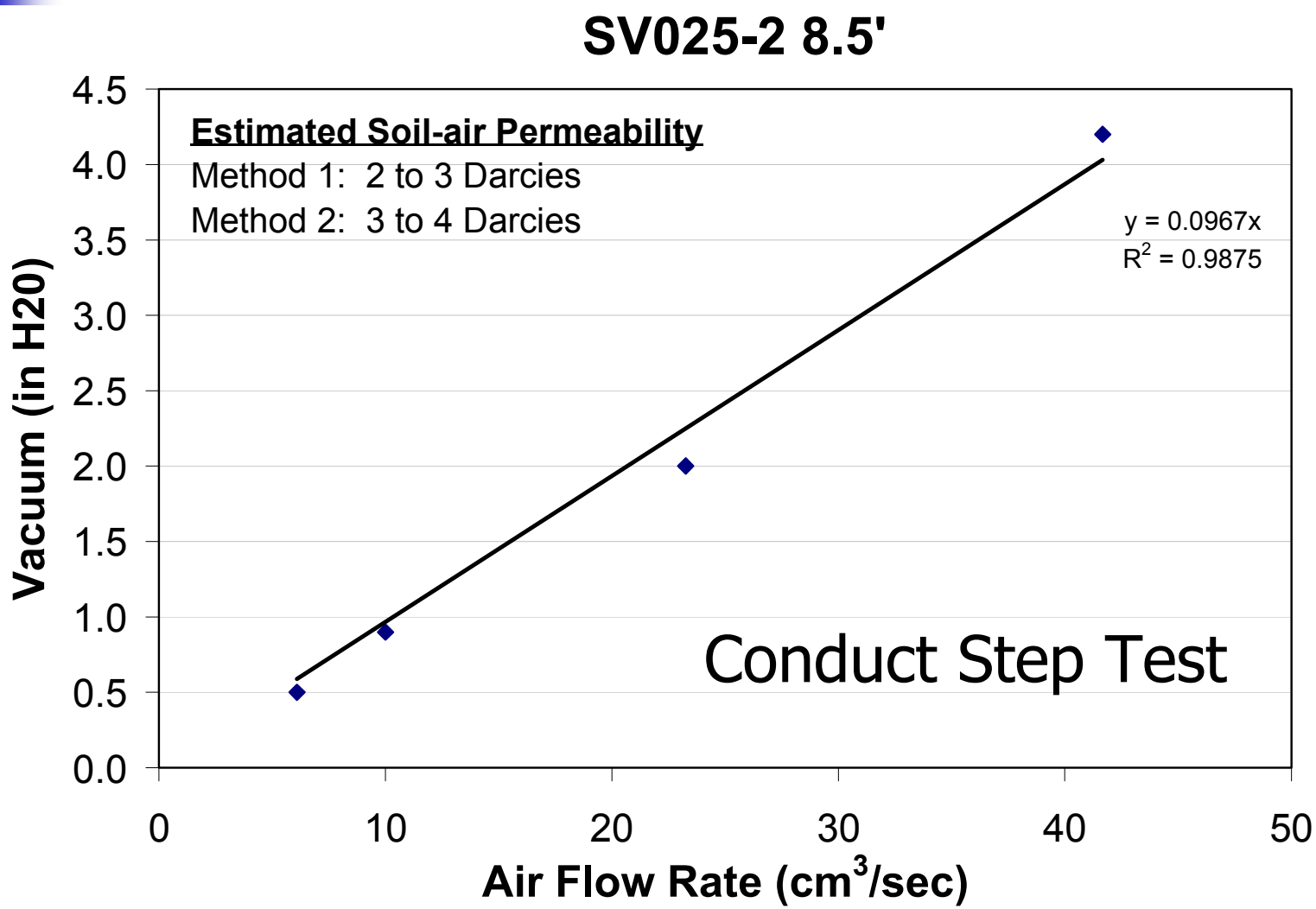
H = height well screen (cm)

P = pressure (atm)

b = empirical correction factor (0.05)

1.013E6 g/cm-sec^2 = 1 atm

IBM San Jose
Probe Performance Testing



Leak Tracer Test

- **Helium**: Measures potential leakage along probe annulus and probe fitting; Use sensitive helium field detector (Mark MGD-2002); Fill shroud such that He > 20%, If:
  - He soil gas /He shroud > 1% then fix probe

Advantages: real time data, doesn't interfere with analysis, readily available

Disadvantages: can not easily check for leaks in sampling train fittings

Leak Tracer Test (cont.)

- **Iso-propanol**: Wrap rag soaked with iso-proponal around probes & fittings, analyze for iso-propanol
- Advantages: Inexpensive
- Disadvantages: no real time measurement, cross contamination possible, can affect analysis

- **Difluoroethane**: Used in California
- [1] http://www.equipcoservices.com/contactus.html

Leak Test Tracers: Pros & Cons

Isopropanol		Helium	
Pros	Cons	Pros	Cons
Readily Available		Readily Available	
Inexpensive	Cross contamination possible	Fairly inexpensive	Separate analysis needed
	Can interfere with VOC analysis, even if leak is small	Will not interfere with VOC analysis, even when large leak is present	
	More difficult to measure onsite	Can measure onsite (handheld) to postpone sampling and/or calculate “before” concentration	

Helium Leak Tracer

Leakage = He soil gas /He shroud

Leakage > 1-10% then fix probe

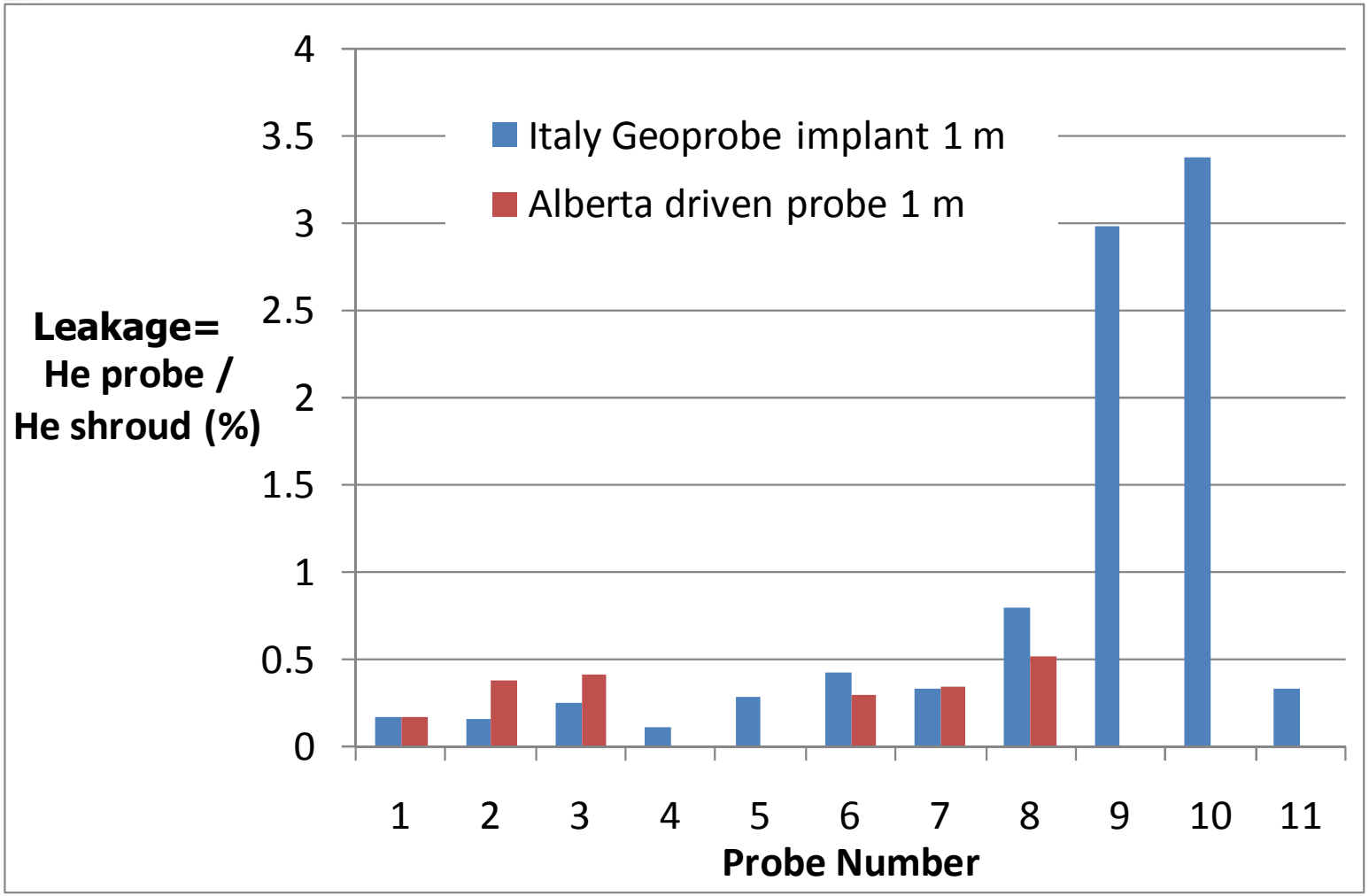
Mark MGD-2002

Golder Soil Vapour Training Course

Fill Bag with Helium
(David Olson, SPL)

This is why you
need helium leak tracer!

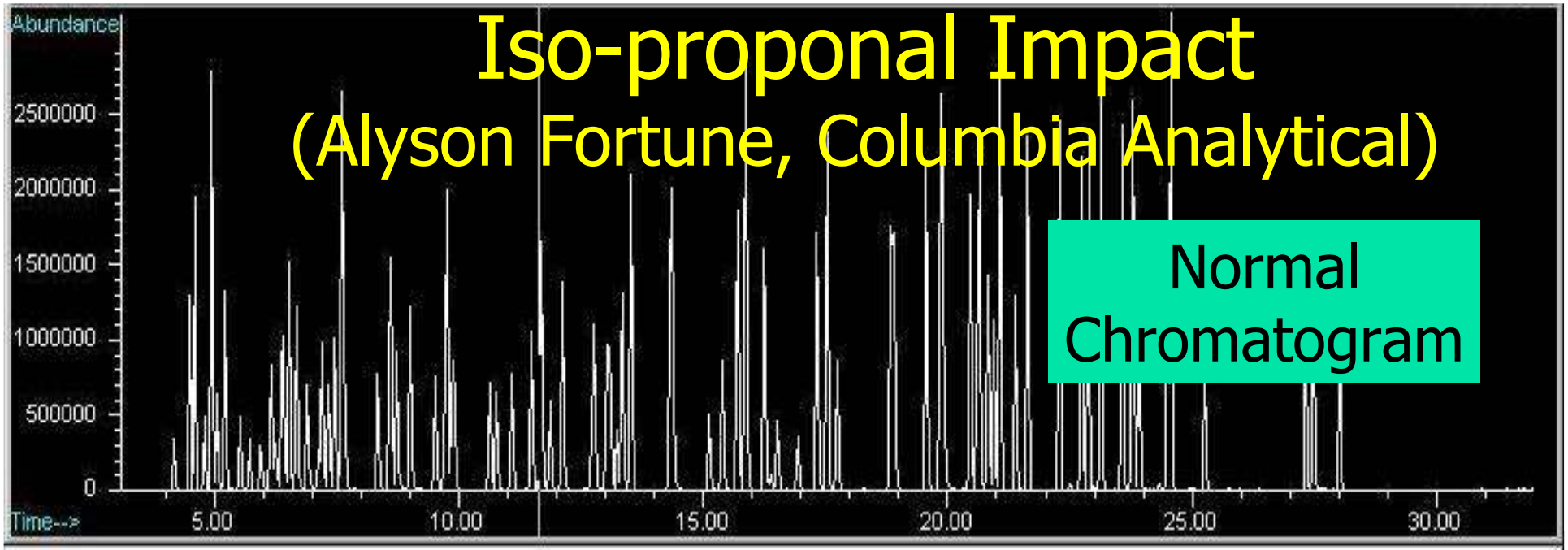
Golder Helium Leak Tracer Results

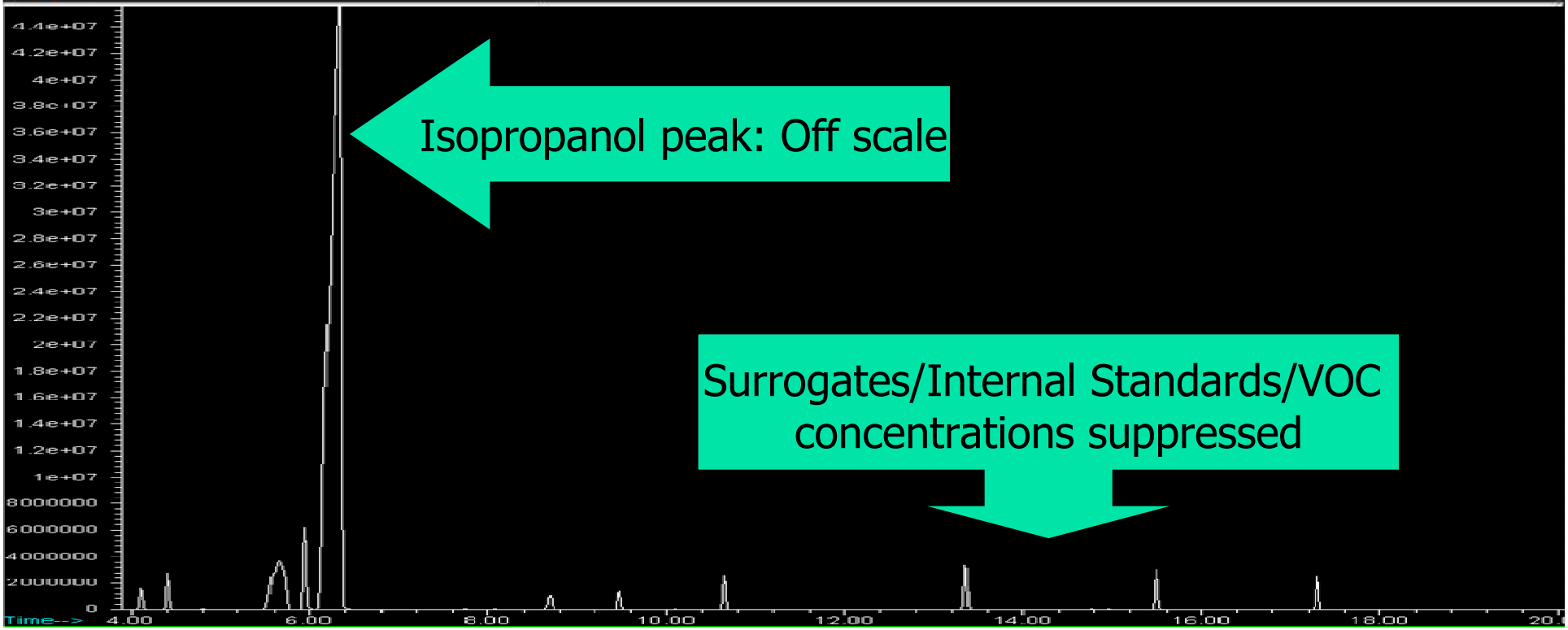


Helium Leak Tracer Experience

- Maxxam Helium Leak Tracer – Leakage Results of 48 Summa Tests (courtesy Petro Oh, Maxxam)
  - 2 results above 20% (24 and 23%)
  - 4 results between 5 and 10% (5.4, 6.6, 8.9, 6.0%)
  - 5 results between 1 and 5% (4.5, 1.1, 3.1, 2.9, 2.3%)
  - 37 below 0.5%
- McAlary et al. (2009) – 7 of 135 probes constructed in low permeability materials had leakage above 5%

Iso-proponal Impact
(Alyson Fortune, Columbia Analytical)





Theoretical Calculation

(Alyson Fortune, Columbia)

- Only a small amount of liquid tracer getting through causes a BIG problem!
  - Use IPA soaked rags, assume IPA is at a concentration 10% of its saturated vapor pressure around the sample probe
  - Even a 0.1% leak will yield concentration of 5.8 ppmV (that's 5800 ppbV or 14,257 $\mu g/m^3$) —OFF SCALE in the TO-15 Analysis

Shut-in Vacuum Test

- Measure vacuum dissipation within sampling train, create vacuum of 10 inches water, should essentially not loose any vacuum over 5 minutes when connections are tight
- Can also pressurize sampling train and conduct soap bubble test

Soil Gas Probe Purging and Sampling

- Goal generally is representative sampling near probe (unless large volume sampling to obtain integrated measurement)
- Purge **3 probe volumes** before collecting sample for analysis (generally do not include filter pack in calculation)
- Flow rate **20 to 200** ml/min, unless larger diameter probes where higher flows may be justified for purging (but not sampling)
- Monitor vacuum, if vacuum exceeds **10 inches** H_20, reduce flow rate

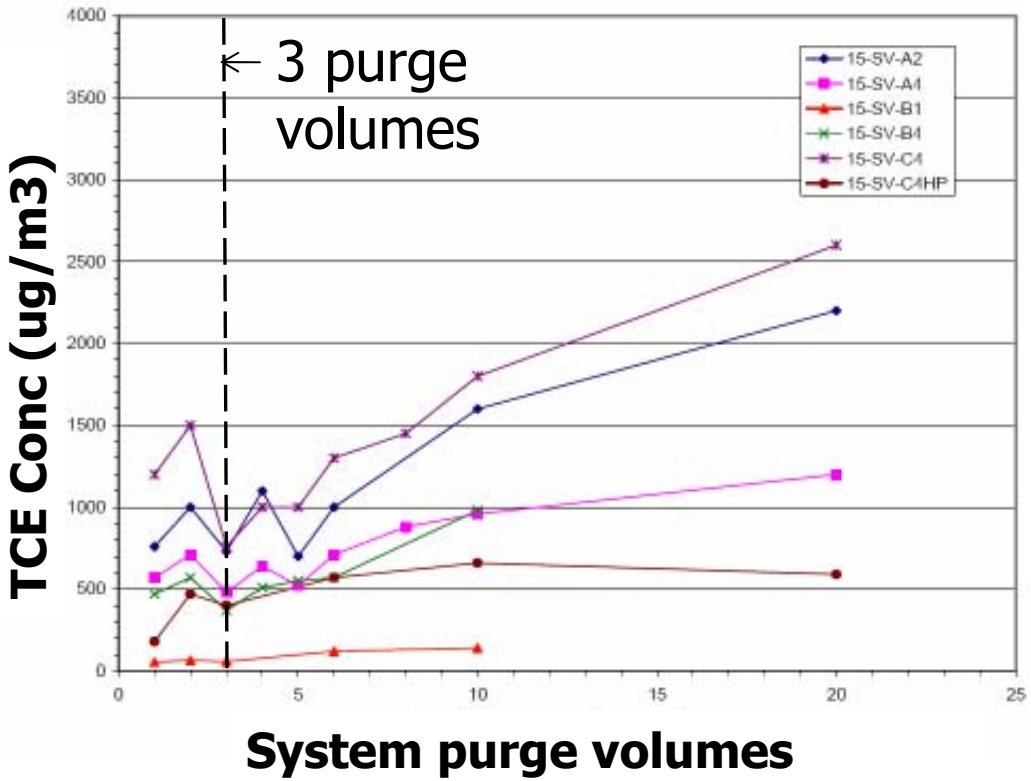
Purging and Sampling – Alternative Methods

- Method 1: Collect multiple soil gas samples during purging and measure PID, O_2, CO_2 concentrations and collect sample when stabilized (analogous to groundwater)
- Method 2 (California 2010 Protocol): Conduct purge volume test at subset of probes where measure PID, O_2, CO_2 after 1, 3 and 10 purge volumes. Optimal purge volume corresponds to volume where maximum PID concentration obtained.

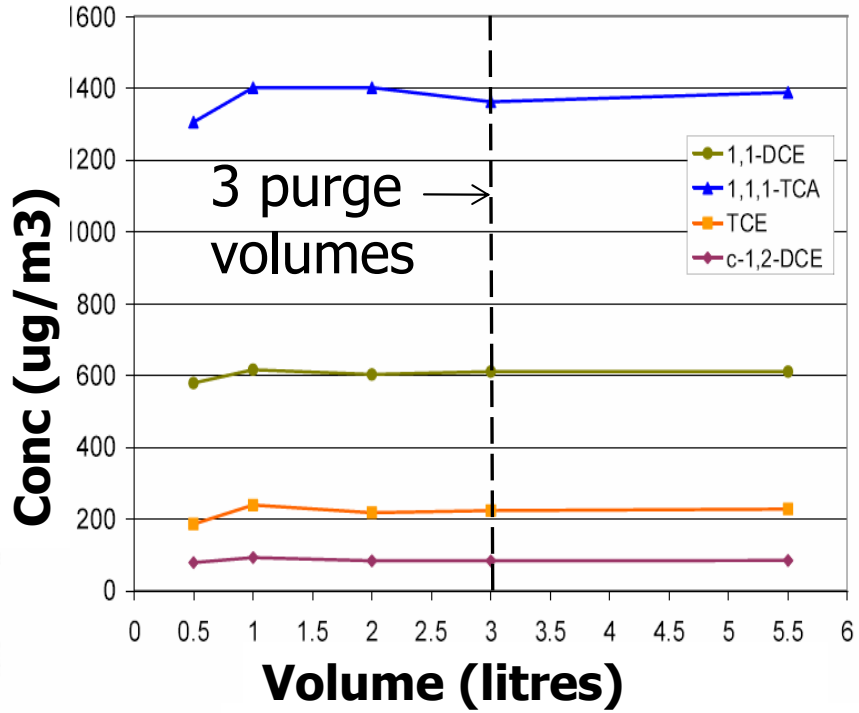
Currently consider these optional methods – more research needed on stability criteria and purge volume tests

Purging Volume Studies

TetraTech (2007)
(for USEPA)



USEPA Raymark Site
(USEPA, 2006)



Purging Rate Studies

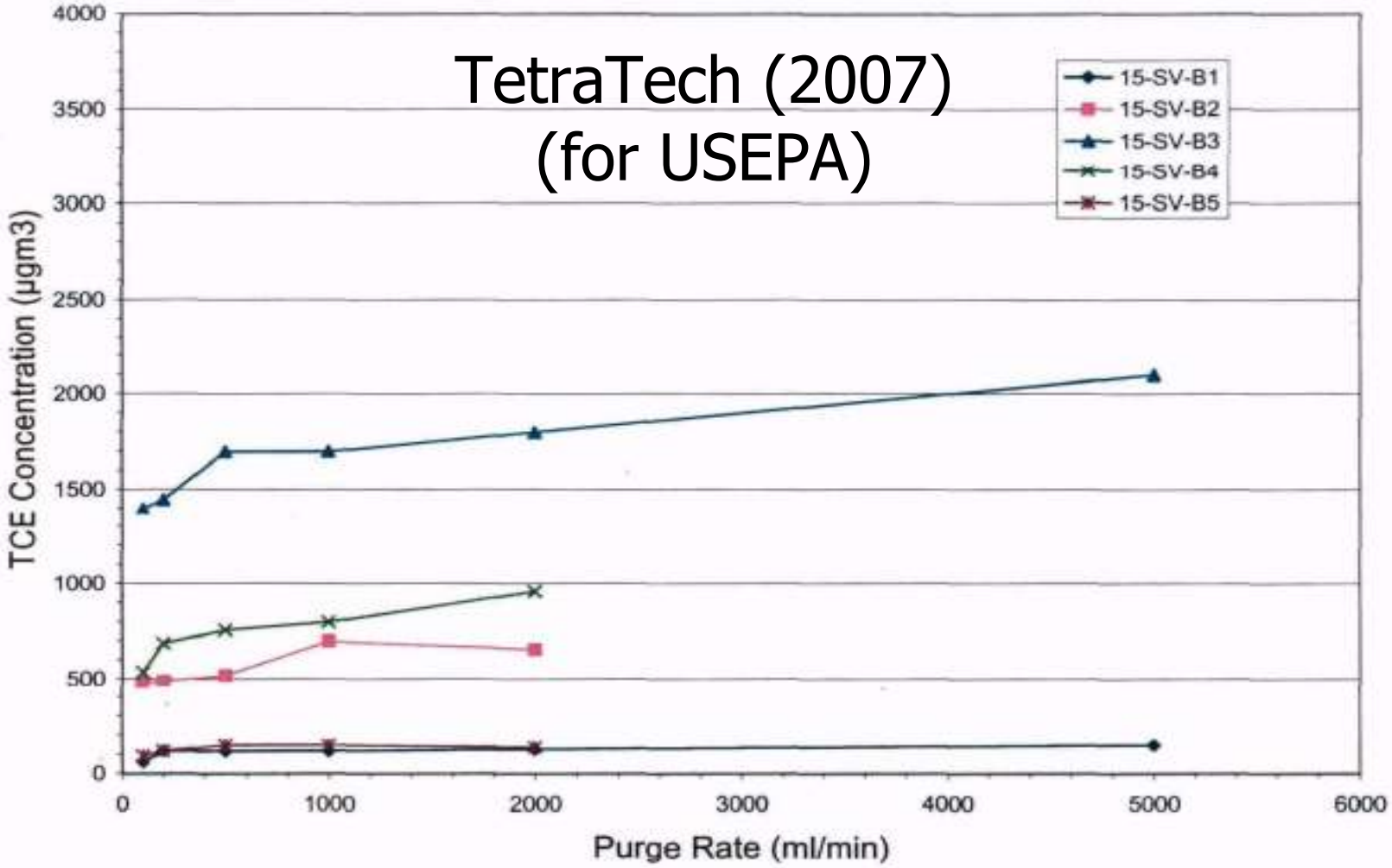


Figure 4-5. Linear Plot of Purge Rate Experiment Data

Modified Active Gas Sampling (MAGS)

(High Purge Volume Sampling)

Golder Jacksonville Office

- Subslab sampling below larger building will only characterize tiny fraction of soil gas relative to total volume
- Example 20,000 L air in 20 m by 20 m by 0.2 m thick layer with θ_a = 0.25
- Remove larger volumes of soil gas to obtain composite sample, take multiple PID measurements over time, with lesser number of laboratory analyses
- Qualitatively may help identify where sources are located (triangulation)

Modified Active Gas Sampling (MAGS)

Mathematics of 1-D Radial Flow

$$Q_w = H\left(\frac{\pi k}{\mu}\right)\left(\frac{P_w}{\ln(R_w / R_I)}\right)\left(1-\left(\frac{P_{RI}}{P_w}\right)^2\right)$$

$$R_{It} = \left(\frac{Qt}{\pi H \theta_a}\right)^{1/2}$$

$$V_p = \pi R_I^2 H \theta_a$$

Purge volume

$$t = V_p / Q$$

Time for 1 purge volume

- Can also adjust flow for foundation leakage using Hantush-Jacob formula for leaky aquifer (McAlary et al., 2010)

Procedure

- 300 to 2000 L/min blower capable of ~ 100 cm H20
- Extraction well and multiple probes
- Measure pressure extension from extraction point to obtain ROI (10% of vacuum at extraction point)
- Measure PID concentrations over time

Vacuum Chamber Sampling

- Use vacuum chamber to obtain Tedlar bag sample
- Minimizes potential for intrusion air from pumps and connections (which can leak)
- Avoids contaminating pump
- Better for low flow and low permeability soil sampling

Screening using Field Detectors

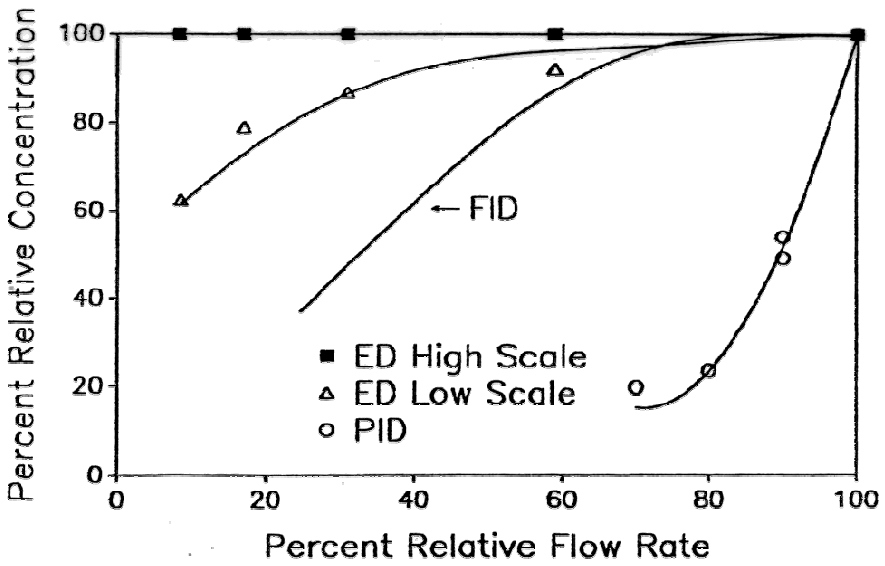
- Photoionization detector (PID) – organic vapours
- Electrochemical cell O_2, CO_2
- Infrared CH_4 – Landfills
- Catalytic - combustible vapours – petroleum sites
- Helium detector

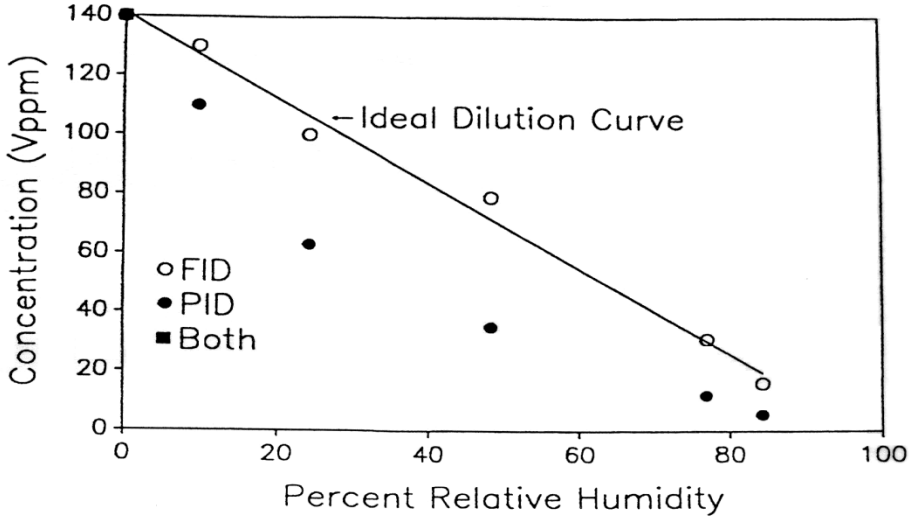
Field Detectors Simple but Potential Pitfalls

- Cross sensitivity
  - Helium detector – methane bias results high
  - Infrared CH4 – petroleum hydrocarbons or solvents bias results very high – recommend laboratory analysis
- Combustible gas detector
  - Poisoned by minor elements, element ages, only accurate at lower concentrations (less than 5% combustible gas)
- PID
  - Moisture and dust bias results high
  - Sensitivity varies depending on VOC response factors (chloroethenes can be detected w\ 10.6 eV lamp, chloroethanes require 11.7 eV)

Field Detector Research

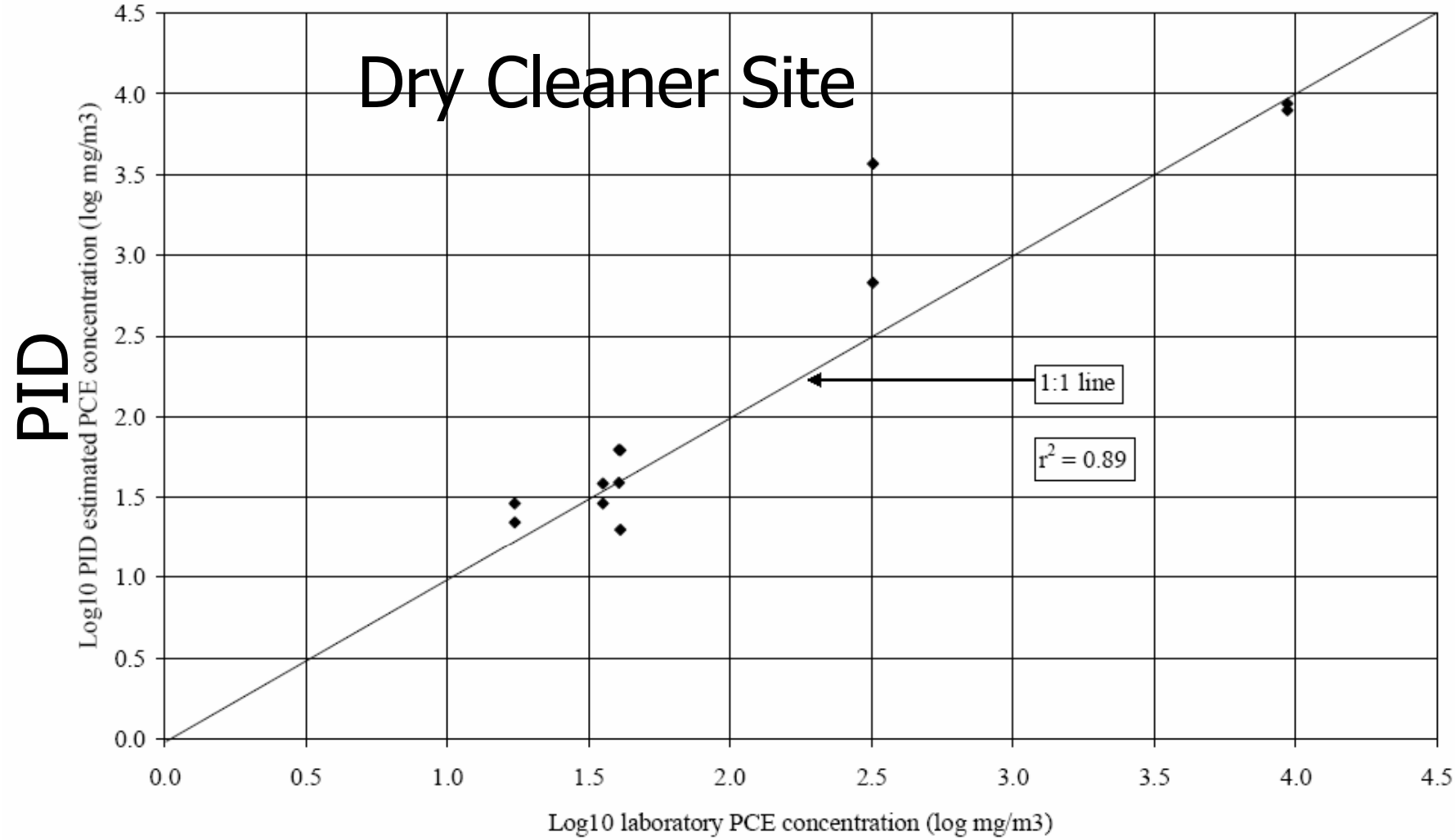
Robbins et al. GMR, Summer '90.





(a)

/ISION DATE: 06/03/29 10:21AM By: NVeloso CADD FILE: N:\Bur-Graphics\Projects\2004\1412\04-1412-131\Drafting\cad\P041412131-12.dwg



PROJECT
BENTALL
DRY CLEANER INVESTIGATION
VANCOUVER, B.C.

TITLE
LABORATORY SOIL VAPOUR PCE CONCENTRATION VERSUS PID ESTIMATED PCE CONCENTRATION

Golder Associates

PROJECT No. 04-1412-131			FILE No. P041412131-12	
DESIGN	GB	23MAR06	SCALE N/A	REV. –
CADD	NV	23MAR06		
CHECK	IH	23MAR06	FIGURE 4-7	
REVIEW				

Some Soil Gas Do's and Don'ts

- Conduct leak tracer test probes and valve
- Use Teflon or Nylaflow tubing, do not use polyethylene
- Use small diameter probes and purge volumes, unless goal is larger volume sampling
- Don't use quick-set grouts with volatile additives (QUIKRETE), watch for cutting oils on metal tips/probes (test blanks)
- Be aware of cross interferences for field detectors, e.g., He detector affected by CH4, Infrared CH4 detector affected by some hydrocarbons (specific guidance to follow)
- Be careful with hardware associated with canisters
- Measure flow rate and vacuum
- Always collect light gas data (O2, CO2, CH4)
- Watch units

Overview Lab Methods

Type Sampler and COPC	Sample Extraction/Method	Detector	Approx. Lowest DL	Com-ment
Syringe - VOC	N/A (Modified 8021/8260	GC/PID, GC/MS	50-500 ug/m^3	5 to 60 ml
Charcoal type Sorbent – VOC	Solvent extraction (OSHA7, NIOSH1501)	GC/FID	~ 0.5 ug BTEX	50 ug/m^3 (10 L)
Charcoal type sorbent – VOC	Solvent Extraction (OSHA7, NIOSH1501)	GC/MS	~ 0.1 ug BTEX, 20 ug TVOC	10 ug/m^3 (10 L)
Molecular Sieve sorbent – VOC	Thermal extraction (TO-17)	GC/MS	~ 0.01 to 0.001 ug	0.1-1 ug/m^3 (10 L)
Resin Sorbent – Semi-volatile	Solvent extraction (TO-13A)	GC/MS	~ 0.01 ug	1 ug/m^3 (10 L)
Canister – VOC	Whole air (TO-15)	GC/MS	~ 1 - 5 ug/m^3	
Canister – VOC	Whole air (TO-15)	GC/MS Low Level	~ 0.05 ug/m^3	Depends on lab
Canister - VOC	Whole air (TO-15)	GC/MS SIM	~ 0.01 ug/m^3	Depends on lab

Canister Sampling

USEPA Method TO-15 "Summa" Canister

- "Whole air" sample collected in evacuated canister that is either passivated electro-polished stainless steel (Summa) or glass-lined steel (SilcoCan™)
- Time-integrated sampling either using **mass flow controller** (more uniform sampling rate to 5 in Hg vacuum) or **critical orifice** (non-linear)
- Cryo-focusing (-70°C) followed by GC/MS analysis
- Under full-SCAN mode, typical reporting limits (RLs) are 1-2 ug/m^3; some labs offer "low level" full-SCAN ~10X lower, or Selective Ion Mode (SIM) at ~ 100X lower
- Heaviest compound that can be quantified is naphthalene (but recovery poor ~ =<50%, requires care!)

USEPA TO-15 Canister - Analytes

- USEPA Method TO-15 list ~70 cmp'ds hydrocarbons, halogenated solvents, consumer products
- Some labs have developed forensics PIANO list (parafins, iso-parafins, aromatics, naphthenes, olefins)
- Debate on whether SilcoCans should be used for reduced sulpher compounds - Two recent studies indicated poor recovery for aged glass-lined canisters for H_2S and certain mercaptans (use Tedlar bags?)
- May also request tentatively identified compounds (TICs)

Got Sulfur? Analytical Methods in Odor Threshold Range. Andy Rezendes, Alpha Analytical Labs, Inc.
Performance of Aged vs. New Glass-Lined Canister & Tedlar Bags in the the Analysis of Reduced Sulfur - #104. Wade Bontempo, Air Toxics Ltd.

USEPA TO-15 Canister Cleaning

- Canisters cleaned through heating and purging with inert gas (N2 or air)
- Recommend individual certification of canister and flow controller for indoor air analysis, for soil vapour (higher detection limits) batch certification acceptable
- Flow controller should also be certified
- Some laboratories segregate cans used for cleaner and dirtier environments

Summa Canisters – TO-15 – Lab QA/QC

Laboratory QC includes:

- 5-point calibration of GC/MS
- Primary gaseous calibration standards
- Secondary source calibration checks (70-130%)
- Lab blank (purified air) and lab blank spike
- Sample Duplicate analysis
- Sample Matrix Spike (60-140%)
- Addition of gaseous surrogates prior to analyses

Summa Canisters – TO-15 – Field QA/QC

- Check hardware and connections
- Measure pressure prior to and after sampling, should be residual vacuum left in canister[1], lab also measures vacuum (get this data)
- Field duplicates with splitter upstream of flow controllers (i.e., two controllers used)
- Equipment blank mandatory if sampling train re-used, optional but good practice if new materials
- Blank where Summa filled with high purity gas (N_2) or field spike using gaseous calibration standard is considered optional

[1] For every 1,000 ft altitude vacuum reduced ~ 1 in Hg.

Method Blank

(Alyson Fortune, Columbia)

- Canister filled with humidified ultra zero air
- Blank must be analyzed in the same manner as samples (e.g. if TICs are analyzed in sample, associated blank must also look for TICs)
- Shows cleanliness of analytical system prior to sample analysis (run daily)
- After highly contaminated samples, lab should analyze "instrument blank" or equivalent to demonstrate that system is again clean

RESULTS OF ANALYSIS

(Alyson Fortune, Columbia)

Client: **CLIENT NAME**
Client Sample ID: **CLIENT SAMPLE ID**
Client Project ID: **PROJECT ID**

CAS Project ID: LAB ID
CAS Sample ID: LAB SAMPLE ID

Test Code: EPA TO-15
Instrument ID: Tekmar AUTOCAN/Agilent 5973inert/6890N/MS8
Analyst: Rusty Bravo
Sampling Media: Summa Canister
Test Notes:

Date Collected: NA
Date Received: NA
Date Analyzed: 1/17/08
Volume(s) Analyzed: 1.00 Liter(s)

CAS #	Compound	Result µg/m³	MRL µg/m³	Result ppbV	MRL ppbV	Data Qualifier
75-01-4	Vinyl Chloride	ND	0.50	ND	0.20	
75-35-4	1,1-Dichloroethene	ND	0.50	ND	0.13	
156-60-5	trans-1,2-Dichloroethene	ND	0.50	ND	0.13	
75-34-3	1,1-Dichloroethane	ND	0.50	ND	0.12	
1634-04-4	Methyl tert-Butyl Ether	ND	0.50	ND	0.14	
156-59-2	cis-1,2-Dichloroethene	ND	0.50	ND	0.13	
107-06-2	1,2-Dichloroethane	ND	0.50	ND	0.12	
71-55-6	1,1,1-Trichloroethane	ND	0.50	ND	0.092	
71-43-2	Benzene	ND	0.50	ND	0.16	
79-01-6	Trichloroethene	ND	0.50	ND	0.093	
108-88-3	Toluene	ND	0.50	ND	0.13	
127-18-4	Tetrachloroethene	ND	0.50	ND	0.074	
100-41-4	Ethylbenzene	ND	0.50	ND	0.12	
179601-23-1	m,p-Xylenes	ND	1.0	ND	0.23	
95-47-6	o-Xylene	ND	0.50	ND	0.12	

ND = Compound was analyzed for, but not detected above the laboratory reporting limit.
MRL = Method Reporting Limit - The minimum quantity of a target analyte that can be confidently determined by the referenced method.

Laboratory Control Spike (LCS)

(Alyson Fortune, Columbia)

- Canister filled with humidified ultra zero air and fortified with a known concentration of target compounds
- LCS should contain most if not all compounds on the sample list
- LCS should be made from a separate source than the initial calibration standard
- Check of calibration accuracy

Laboratory Control Spike (LCS)

(Alyson Fortune, Columbia)

- Results expressed as % Recovery– 100% is optimal.
  - Generally 70-130% Recovery acceptable
  - Laboratory may also keep Control Charts for lab specific acceptable recovery limits

RESULTS OF ANALYSIS

Alyson Fortune, Columbia

Client: **CLIENT NAME**
Client Sample ID: **CLIENT SAMPLE ID**
Client Project ID: **PROJECT ID**

CAS Project ID: LAB ID
CAS Sample ID: LAB SAMPLE ID

Test Code: EPA TO-15
Instrument ID: Tekmar AUTOCAN/Agilent 5973inert/6890N/MS8
Analyst: Rusty Bravo
Sampling Media: Summa Canister
Test Notes:
Container ID: AC00953

Date Collected: 1/15/08
Date Received: 1/16/08
Date Analyzed: 1/17/08
Volume(s) Analyzed: 1.00 Liter(s)

Initial Pressure (psig): -1.3 Final Pressure (psig): 3.5

Canister Dilution Factor: 1.36

CAS #	Compound	Result µg/m³	MRL µg/m³	Result ppbV	MRL ppbV	Data Qualifier
75-01-4	Vinyl Chloride	ND	0.68	ND	0.27	
75-35-4	1,1-Dichloroethene	ND	0.68	ND	0.17	
156-60-5	trans-1,2-Dichloroethene	ND	0.68	ND	0.17	
75-34-3	1,1-Dichloroethane	ND	0.68	ND	0.17	
1634-04-4	Methyl tert-Butyl Ether	ND	0.68	ND	0.19	
156-59-2	cis-1,2-Dichloroethene	ND	0.68	ND	0.17	
107-06-2	1,2-Dichloroethane	ND	0.68	ND	0.17	
71-55-6	1,1,1-Trichloroethane	ND	0.68	ND	0.12	
71-43-2	Benzene	**0.78**	0.68	**0.24**	0.21	
79-01-6	Trichloroethene	ND	0.68	ND	0.13	
108-88-3	Toluene	**1.1**	0.68	**0.29**	0.18	
127-18-4	Tetrachloroethene	ND	0.68	ND	0.10	
100-41-4	Ethylbenzene	ND	0.68	ND	0.16	
179601-23-1	m,p-Xylenes	ND	1.4	ND	0.31	
95-47-6	o-Xylene	ND	0.68	ND	0.16	

ND = Compound was analyzed for, but not detected above the laboratory reporting limit.
MRL = Method Reporting Limit - The minimum quantity of a target analyte that can be confidently determined by the referenced method.

LABORATORY CONTROL SAMPLE SUMMARY

Alyson Fortune, Columbia

Client: **CLIENT NAME**
Client Sample ID: **Lab Control Sample**
Client Project ID: **PROJECT ID**

CAS Project ID: LAB ID
CAS Sample ID: LAB SAMPLE ID

Test Code: EPA TO-15
Instrument ID: Tekmar AUTOCAN/Agilent 5973inert/6890N/MS8
Analyst: Rusty Bravo
Sampling Media: Summa Canister
Test Notes:

Date Collected: NA
Date Received: NA
Date Analyzed: 1/17/08
Volume(s) Analyzed: NA Liter(s)

CAS #	Compound	Spike Amount ng	Result ng	% Recovery	CAS Acceptance Limits	Data Qualifier
75-01-4	Vinyl Chloride	24.8	**22.4**	**90**	61-127	
75-35-4	1,1-Dichloroethene	27.8	**26.1**	**94**	77-116	
156-60-5	trans-1,2-Dichloroethene	26.5	**26.0**	**98**	74-118	
75-34-3	1,1-Dichloroethane	26.8	**24.9**	**93**	74-118	
1634-04-4	Methyl tert-Butyl Ether	26.8	**24.7**	**92**	72-119	
156-59-2	cis-1,2-Dichloroethene	27.0	**26.3**	**97**	74-117	
107-06-2	1,2-Dichloroethane	26.3	**23.8**	**90**	72-117	
71-55-6	1,1,1-Trichloroethane	26.8	**24.7**	**92**	78-114	
71-43-2	Benzene	27.0	**23.6**	**87**	73-111	
79-01-6	Trichloroethene	27.3	**24.7**	**90**	80-116	
108-88-3	Toluene	26.5	**23.8**	**90**	76-116	
127-18-4	Tetrachloroethene	26.0	**23.6**	**91**	77-118	
100-41-4	Ethylbenzene	26.3	**24.4**	**93**	79-116	
179601-23-1	m,p-Xylenes	62.5	**58.2**	**93**	80-117	
95-47-6	o-Xylene	29.8	**27.8**	**93**	80-116	

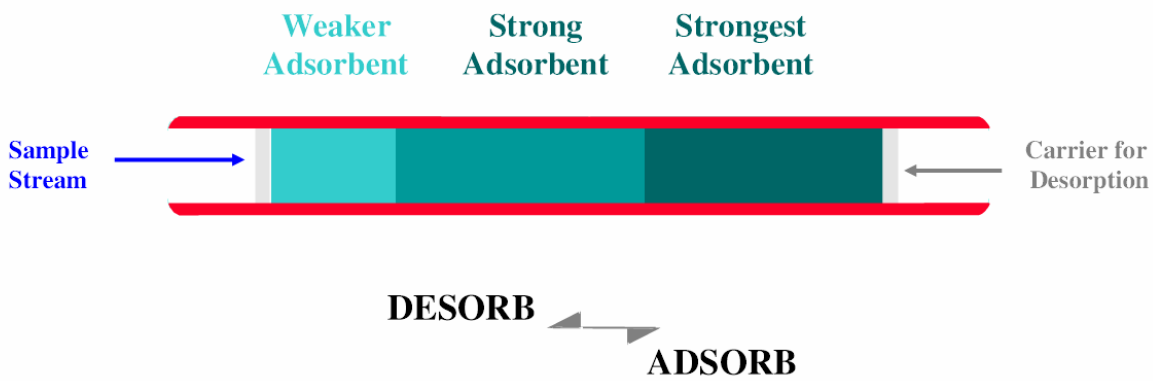
Summa Canisters

Active Sorbent Tubes

Active Sorbent Tubes

Active Sorbent Tube (USEPA Method TO-17)

- Concentration estimated from mass absorbed, flow rate and sampling time
- Thermally desorbed and analyzed by GC/MS
- Typically multi-bed sorbents are utilized



Active Sorbent Tube (USEPA Method TO-17)

- Soil vapour presents challenges – Ideal sorbent will quantify broad range of compounds, will be hydrophobic, minimize breakthrough and prevent irreversible or slow desorption (carryover) – area of active research!
- Safe sampling volume (SSV) is key
- DL 0.05 to 0.001 ng
- Depending on sorbent, able to quantify a broad range of compounds from vinyl chloride to multi-ring PAHs

TO-17 Thermal Tube Research

- Laboratories trying different sorbents (Supelco 300, Air Toxics, Carbotrap, Carbotrap)
- One laboratory[1] combined several graphitized sorbents of increasing strength to collect wide volatility range (e.g., Tenax, Carbograph 1TD, and Carbograph 5 TD), they found
  hydrophobic sorbents not good (e.g. Carbosieve S-III)), another lab developing tubes with Elmer Perkins[2]
- Drying tubes are used by some laboratories (not recommended)
- CARO study found breakthrough for dichlorodifluoromethane (MW=121), chloromethane (MW=50.5) but not for vinyl chloride (MW=62.5)

1 Hayes et al. 2007. Proc. AWMA Specialty Conf. VI, Sept 07, Providence, RI (Air Toxics)

2 www.caro.ca. See presentation on their tubing study

Sorbent Tubes – TO-17 – Field QA/QC

- Avoid moist conditions when sampling
- Field duplicates collected using splitter
- Analysis of front and back of tube or tubes in series to check for breakthrough
- May want to collect two samples over different sampling durations
- Trip blank
- Equipment blank – to check sampling train
- Pump calibrated before use, and flow checked during sampling – important for soil vapour
- Equipment blank mandatory – see TO-15

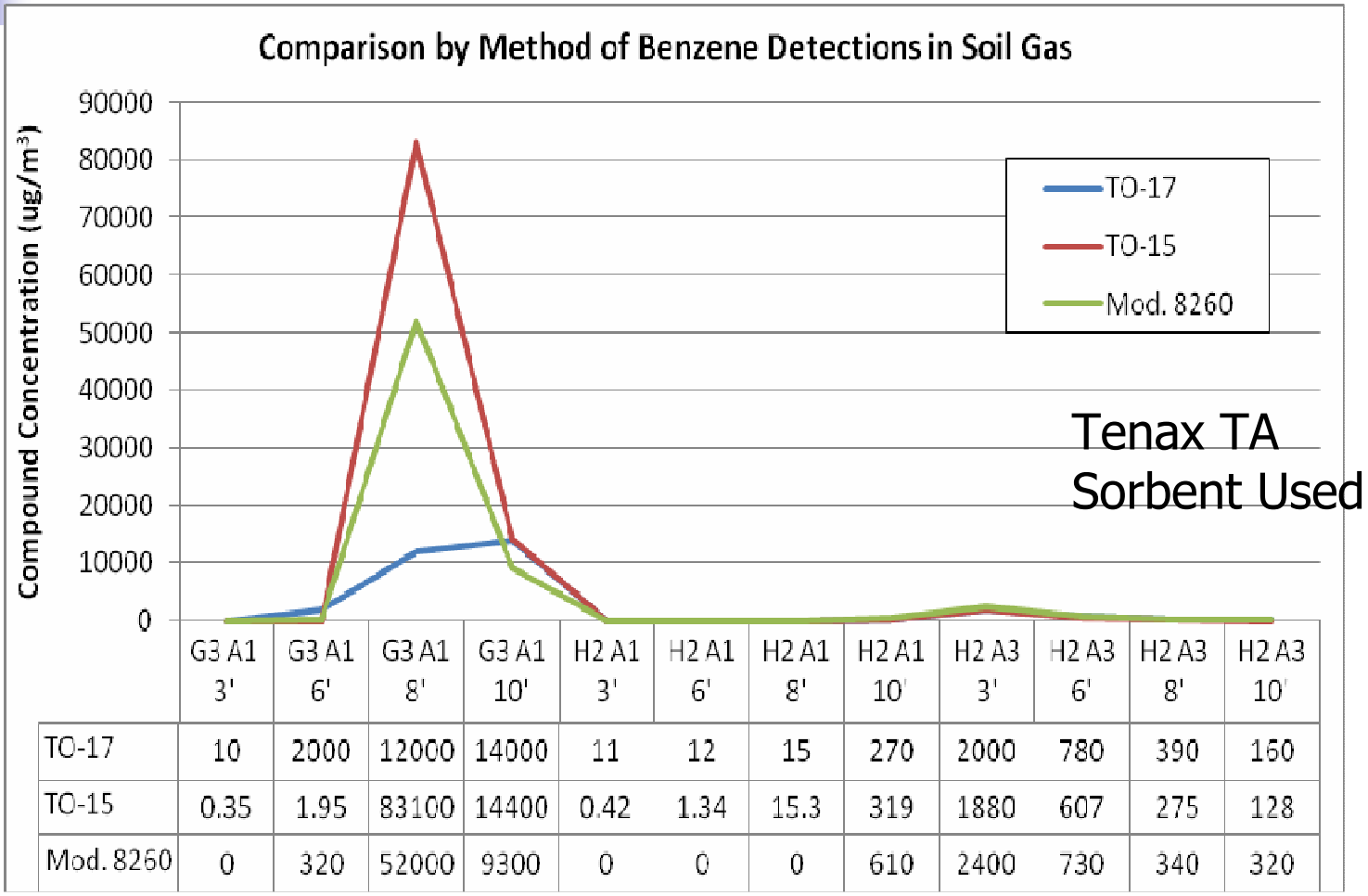
Comparison of TO-15 and TO-17 Methods

	Advantages	Disadvantages
TO-15 Summa	• Whole air sample • No pump required • Good recovery lighter molecular weight compounds	• Proper cleaning of canister & flow controller essential • Hardware • Poor recovery Naphthalene and heavier compounds • Some labs do not permit TPH > 5ppm
TO-17 Sorbent	• Easier to clean tube • Better recovery heavier molecular weight compounds • Easier to transport	• Pump required and must confirm flow rates in field • Potential for breakthrough (lab must validate the sorbent used) • Sorbent affected by moisture

Both methods acceptable, but require experienced samplers and laboratory

Blayne Hartman, H&P Geochemistry

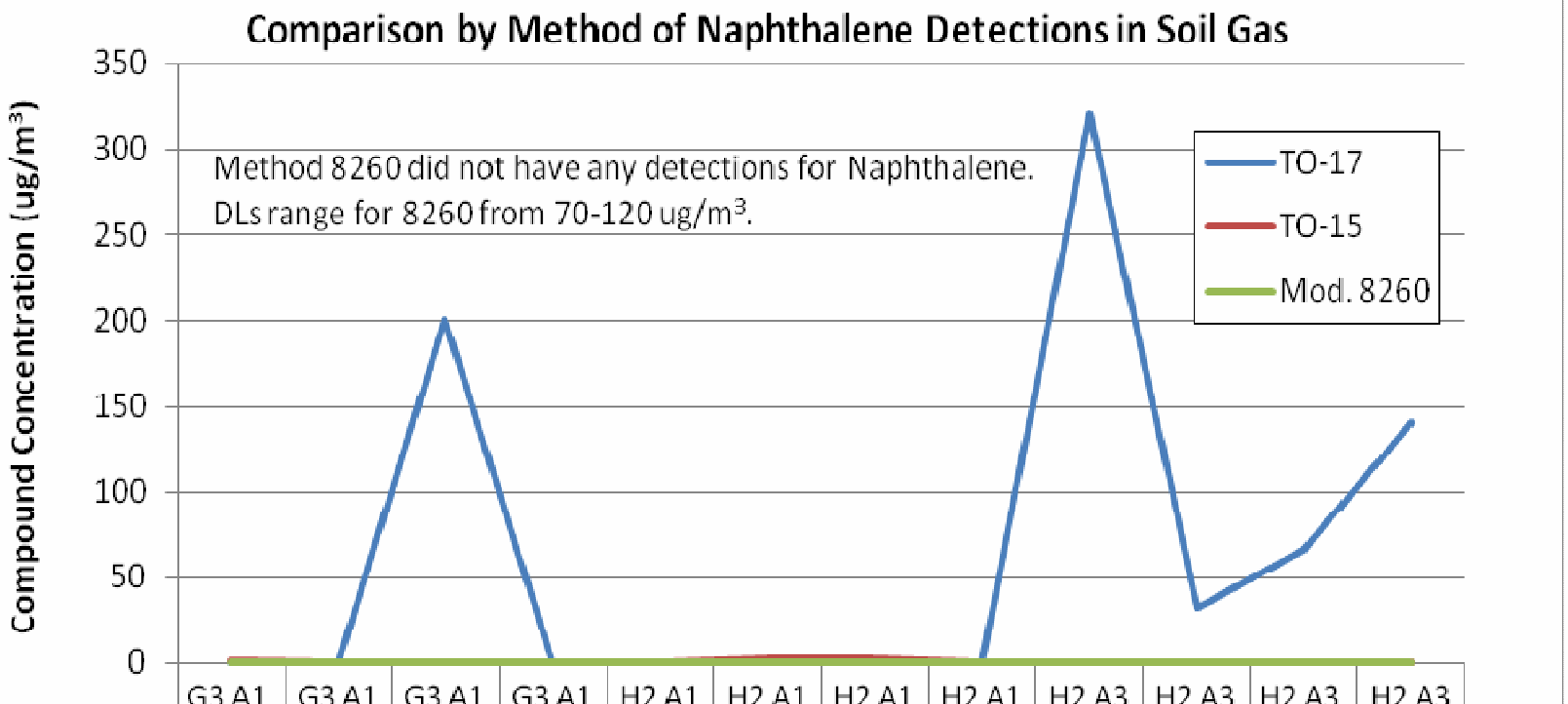
EPRI Research Study - Comparison of 8260, TO-15 &B TO-17 for Benzene



	G3 A1 3'	G3 A1 6'	G3 A1 8'	G3 A1 10'	H2 A1 3'	H2 A1 6'	H2 A1 8'	H2 A1 10'	H2 A3 3'	H2 A3 6'	H2 A3 8'	H2 A3 10'
TO-17	10	2000	12000	14000	11	12	15	270	2000	780	390	160
TO-15	0.35	1.95	83100	14400	0.42	1.34	15.3	319	1880	607	275	128
Mod. 8260	0	320	52000	9300	0	0	0	610	2400	730	340	320

Good agreement except for high concentration samples

EPRI Research Study - Comparison of 8260, TO-15 &B TO-17 for Naphthalene



	G3 A1 3'	G3 A1 6'	G3 A1 8'	G3 A1 10'	H2 A1 3'	H2 A1 6'	H2 A1 8'	H2 A1 10'	H2 A3 3'	H2 A3 6'	H2 A3 8'	H2 A3 10'
TO-17	0	0	200	0	0	0	0	0	320	32	66	140
TO-15	1.1	0	0	0	0	1.89	2.15	0	0	0	0	0
Mod. 8260	0	0	0	0	0	0	0	0	0	0	0	0

Other Sorbent Tube Methods

- **Modified NIOSH 1501/OSHA 7 Sorbent Tube**
  - GC/MS recommended (seen false positives with GC/FID)
  - Not as wide a range of VOCs as multi-bed thermal desorption tubes (for example, vinyl chloride difficult to analyze, also not possible to analyze for naphthalene)
  - Solvent extraction by carbon disulphide (CS_2)
  - Coconut Shell Carbon (CSC) or Anasorb™ 747 (beaded carbon) are commmon sorbents
  - DL depends on flow rate and duration (practically ~ 5 to 10 ug/m^3, may depend on matrix interferences) – not sufficiently low for indoor air analysis

Other Sorbent Tube Methods

- **USEPA TO-13A Sorbent Tube**
  - Semi-volatiles (naphthalene & other PAHs) by **GC/MS**
  - Amberlite XAD-2 resin tube for **vapour-phase**
  - Polyurthane foam & glass fibre filter for **particulate-phase** (not needed for soil vapour)
  - Soxhlet extraction, solvent exchange and concentration
- **USEPA TO-2 Sorbent Tube** (rarely used)
  - Wide range of VOCs by **GC/MS,** thermal desorption method
  - Tenax (poly 2,6-diphenyl phenaxylene oxide) (EPA TO-2)
  - Tenax GC problems with artifacts (benzaldehyde and phenol), retention low boilers and stability, replaced with Tenax TA
  - Multiple use causes problems – cleaning and retention problems

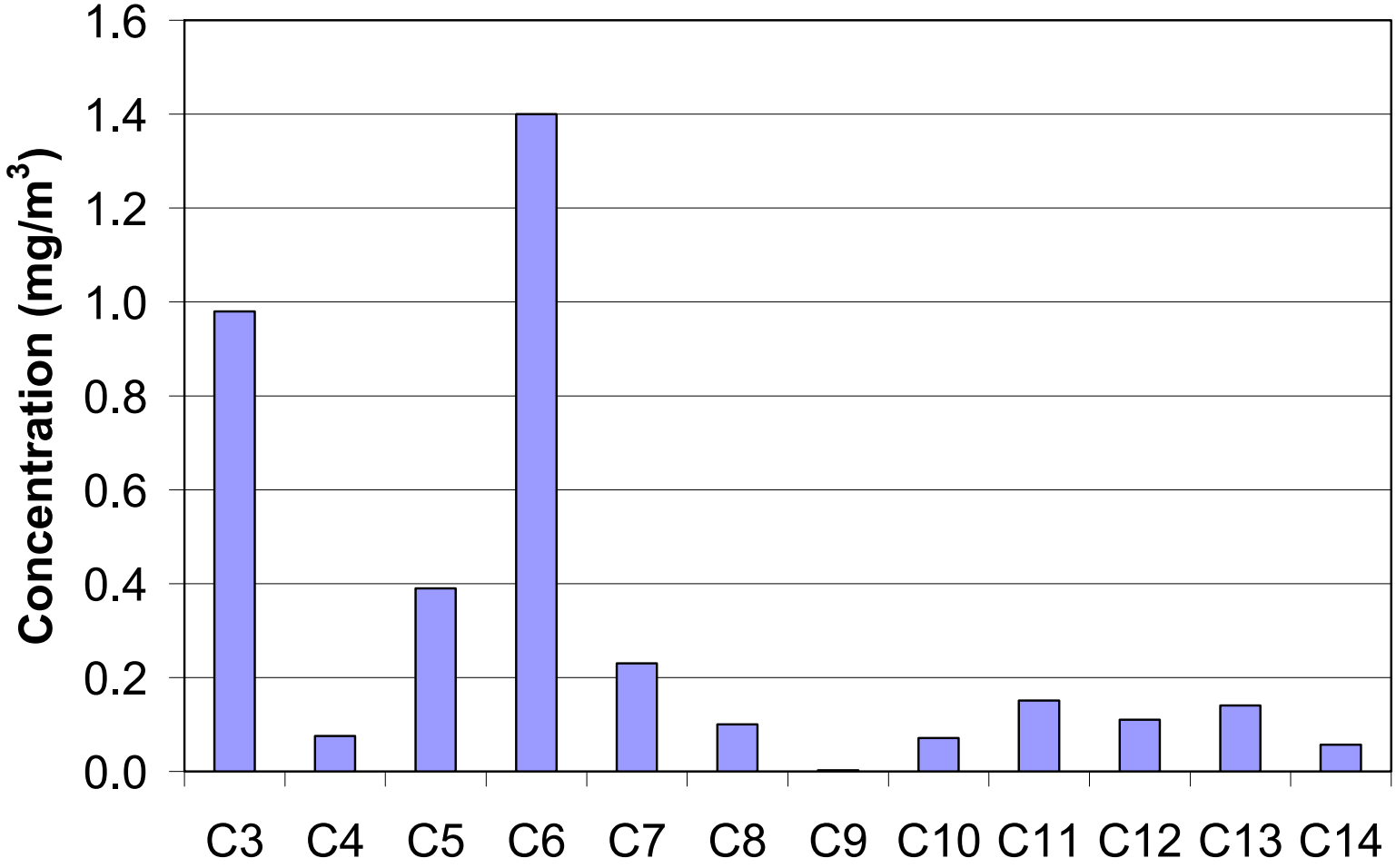
Sorbent Tubes Sampling Time Calculator

Chemical	**Criteria**	ALS Tube DL	Minimum Volume to reach Criteria	Desired Volume (Criteria/5)	Flow rate	Sampling Time	
	mg/m3	ug	L	L	L/min	min	Media
Benzene	**0.05**	0.1	2.0	10.0	0.2	50	CSC
Ethylbenzene	**2.81**	0.1	0.0	0.2	0.2	1	CSC
Toluene	**10.53**	0.2	0.0	0.1	0.2	0.5	CSC
Total Xylenes	**0.51**	0.15	0.3	1.5	0.2	7	CSC
n-hexane	**0.56**	0.5	0.9	4.5	0.2	22	CSC
Naphthalene	**0.01**	0.1	11.9	59.4	0.2	297	XAD-2
TVOC(6-10)	**10.00**	20	2.0	10.0	0.2	50	CSC
TVOC(10-19)	**10.00**	20	2.0	10.0	0.2	50	CSC
CWS Aliphatic (C>6-C8)	**51.66**	5	0.1	0.5	0.2	2	CSC
CWS Aliphatic (C>8-C10)	**2.81**	5	1.8	8.9	0.2	45	CSC
CWS Aliphatic (C>10-C12)	**2.81**	5	1.8	8.9	0.2	45	CSC
CWS Aliphatic (C>12-C16)	**2.81**	5	1.8	8.9	0.2	45	CSC
CWS Aromatic (C>7-C8)	**1.12**	5	4.5	22.3	0.2	111	CSC
CWS Aromatic (C>8-C10)	**0.56**	5	8.9	44.5	0.2	223	CSC
CWS Aromatic (C>10-C12)	**0.56**	5	8.9	44.5	0.2	223	CSC
CWS Aromatic (C>12-C16)	**0.56**	5	8.9	44.5	0.2	223	CSC

Other Laboratory Methods (cont.)

- **USEPA 18 (Tedlar bag or canister)**
  - Carbon ranges by **GC/FID**
  - n-alkane carbon range equivalents C1-C12
- **USEPA 3C or ASTM 1946 (Tedlar Bag or Canister)**
  - O_2, CO_2, N_2 by **GC/FID/TCD**
  - C1 to C3 Hydrocarbons (methane, ethane, propane)
  - Keep holding times as short as possible (< 48 hours)

EPA 18


Concentration (mg/m3)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14

Selection of Analytical Method and Laboratory

- Contaminants of Potential Concern (CPOCs)
- Detection limits and sampling duration
- Cost, lab experience, certification (SCC or CAEAL), measures to reduce cross contamination such as solvent free areas
- TO-15 and TO-17 methods both acceptable for wide range of compounds, TO-15 better if analyte list includes very light compounds, TO-17 better if heavier compounds (Naphthalene or heavier)
- Both canister and sorbent tube methods require experienced samplers and laboratory

How to identify CPOCs?

- USEPA 2002 Draft VI Guidance
  - $C_v > C_{air}^T$ /0.1 then "vapour COPC"
  - C_v = theoretical equilibrium from pure-phase vapour pressure or Henry's Law assuming pure-phase solubility
  - C_{air}^T = health risk-based air concentration
  - Screening approach results in four-ring PAHs and PCBs included as COPCs (> 100 chemicals) – overly conservative?
- USEPA Soil Screening Guidance ('96) – volatile definition:
  - Molecular weight < 200 g/mole, or
  - Henry's Law constant > = 1x10-5 atm-m3/mole
- BC Ministry of Environment
  - Henry's Law constant > = 1x10-5 atm-m^3/mole
  - Vapour pressure > 0.05 Torr
  - Compounds heavier than tridecane (nC13) and naphthalene would not be volatile, practically based on compounds that are mobile and "seen" in vapour

Detection Limit Calculation

- DL = C_{air} * DF / SF
- C_{air} = health based acceptable air concentration
- DF = conservative dilution factor, e.g., DF = 50 for soil vapor
- SF = safety factor of 5-10 preferred
- Example TCE
  - C_{air} = 5 ug/m^3 (HC non-carcinogen residential), DF = 50, SF = 5, DL ~ 50 ug/m^3
- May want to lower DL so that you can use data for background and forensic comparisons

Recommended Analytical Parameters

Contamination Type	Field Screening	Analytical Parameters	Laboratory Methods
Petroleum Hydrocarbons – Downstream factilities	Organic vapours (PID); light gases(O_2, CO_2, CH_4) (multigas detector)	**Gasoline**: BTEX, hexane, trimethylbenzenes, naphthalene, HC fractions **Diesel**: BTEX, naph-thalene, trimethyl-benzenes,decane, HC fractions	TO-17, OSHA 7 or NIOSH 1501 (sorbent tube) or USEPA TO-15 (Summa canister) (some methods limited for naphthalene
Petroleum Hydrocarbons - Upstream	As above	As above, except may add sulphur-based compounds	ASTM D-5504 (Tedlar bag or SilcoCan)

Additional compounds gasoline: 224-trimethylpentane (M), cyclohexane (M), pentane (M), methylcyclohexane (M), 1,3-butadiene (relatively toxic compound), 1,2-dibromoethane (leaded gasoline), 1,2-dichloroethane (leaded gasoline), MTBE (additive)

M = Marker compounds useful for evaluating fate and transport
HC = hydrocarbon fractions

Recommended Analytical Parameters

Contamination Type	Field Screening	Analytical Parameters	Laboratory Methods
Chlorinated Hydrocarbons – Dry Cleaner	Organic vapours Light gases (VC)	Focussed list VOCs (unless forensics)[1]	Generally recommend Summa canister
Halogenated Hydrocarbons, solvents, other VOCs -	Organic vapours, Light gases (VC)	VOC Full scan (70+ compounds TO-15)	Generally recommend Summa canister

1 **Tetrachloroethylene, trichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, vinyl chloride,** chloroform, chloroethane, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethylene, carbon tetrachloride, methylene chloride (bold chemicals are screening list for sites with only PCE impacts)

http://www.drycleancoalition.org/chemicals/ChemicalsUsedInDrycleaningOperations.htm

Recommended Analytical Parameters

Contamination Type	Field Screening	Analytical Parameters	Laboratory Methods
Coal-tar, creosote	Organic vapours, Light gases	BTEX, styrene, trimethylbenzenes, naphthalene, decane, HC fractions	As above, except add TO-17 or TO-13A (resin tube)
Other (Hg?, organo-metallic compounds, CN-)	Draeger tubes for some compounds	Compound specific analyses (sorbent tubes or impingers)	Compound specific analyses (sorbent tubes or impingers)

Additional compounds coal tar: methylnaphthalenes, indane, indene, thiophene, aliphatics, pentanes – more research is needed to determine whether methylnaphthalenes, indane, indene are an issue

Analytical Parameters – Hydrocarbon Fractions

1. CCME Canada Wide Standards Petroleum Hydrocarbon Compounds
http://www.ccme.ca/assets/pdf/phc_standard_1.0_e.pdf
- Aliphatic C6-C8,C>8-10, C>10-12,C>12-16
- Aromatic C>7-8 (mostly TEX), C>8-10, C>10-12, C>12-16

2. US TPH Criteria Working Group
http://www.aehs.com/publications/catalog/contents/tph.htm
- Aliphatic C5-C6, C>6-C8,C>8-10, C>10-12,C>12-16
- Aromatic benzene (6.5), toluene (7.6), C>8-10, C>10-12, C>12-16

3. Massachusetts Approachhttp://
- Aliphatic VPH: C5-C8, C11-22; EPH C9-18
-Aromatic VPH: BTEX, C9-10, EPH: C11-22, PAHs

CCME Approach for Hydrocarbon Fractions

$$SQG_{slice_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)
$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target water quality guideline for fraction *i*
$MF_{subfraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

	Soil	Water	Vapour
Fraction 1	Default	Default	Default
Aliphatics C6-C8	55	58.4	84.4
Aliphatics C>8-C10	36	6.5	15.1
Aromatics C>8-C10	9	35.1	0.49
Total	100	100	100
Fraction 2			
Aliphatics C>10-C12	36	2.4	76.6
Aliphatics C>12-C16	44	0.15	20.6
Aromatics C>10-C12	9	60.4	2.3
Aromatics C>12-C16	11	37.1	0.53
Total	100	100	100

For soil vapour, one option is to just test for F1 and use default conversion factors, but this is quite inaccurate, better to analyze 1 or 2 samples for sub-fractions

Expanded VI Tool Box (non-VOC measurement approaches)

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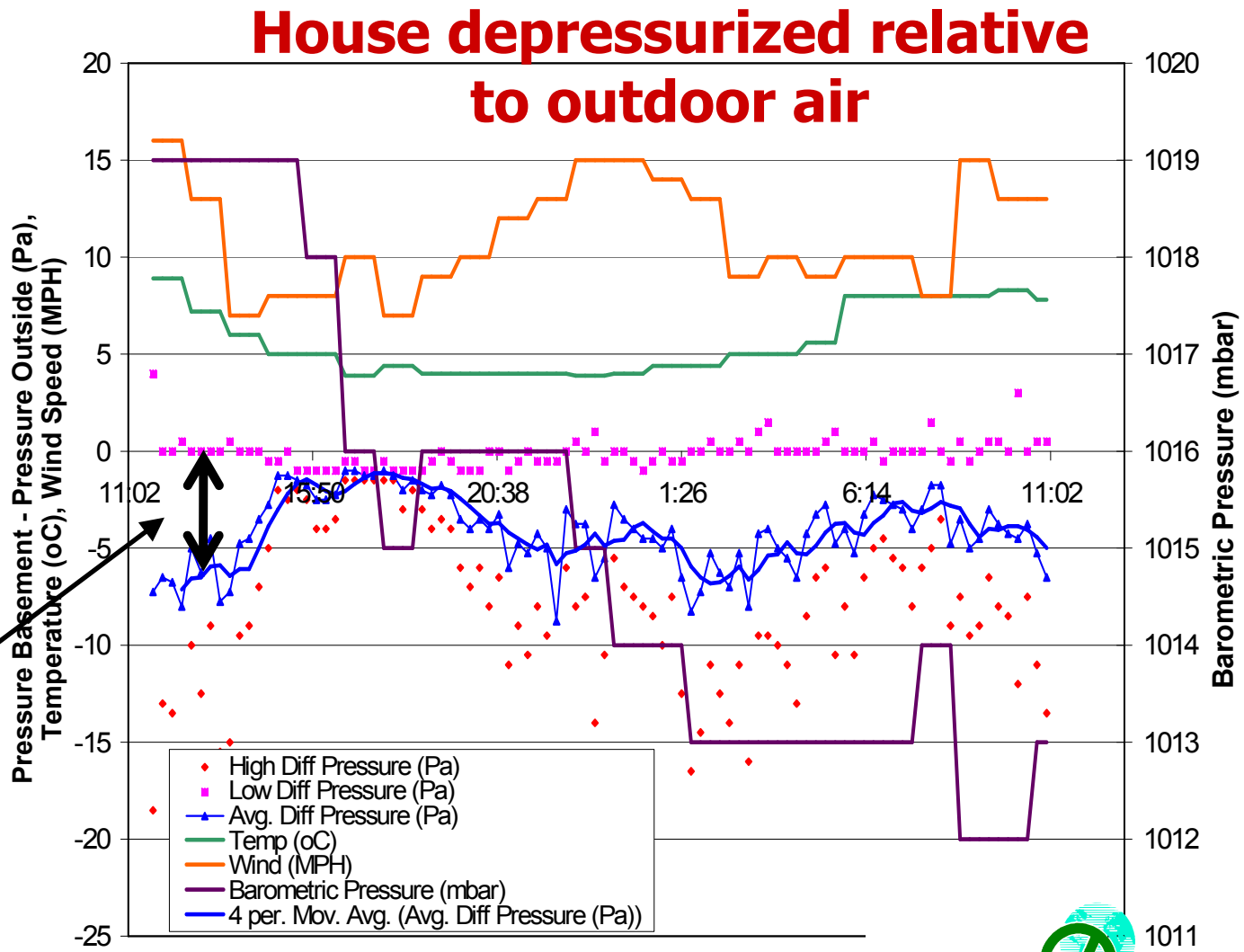
Expanded VI Tool Box

- Building pressure measurements
- HVAC information (exhaust & make-up)
- Building pressure manipulation
- Vapour intrusion tracer (radon, helium, other)
- Building ventilation tracer (CO_2, SF_6)
- Foundation Permeability test
- Infrared Camera

Pressure Monitoring House
Golder-NJDEP Research Study

ΔP



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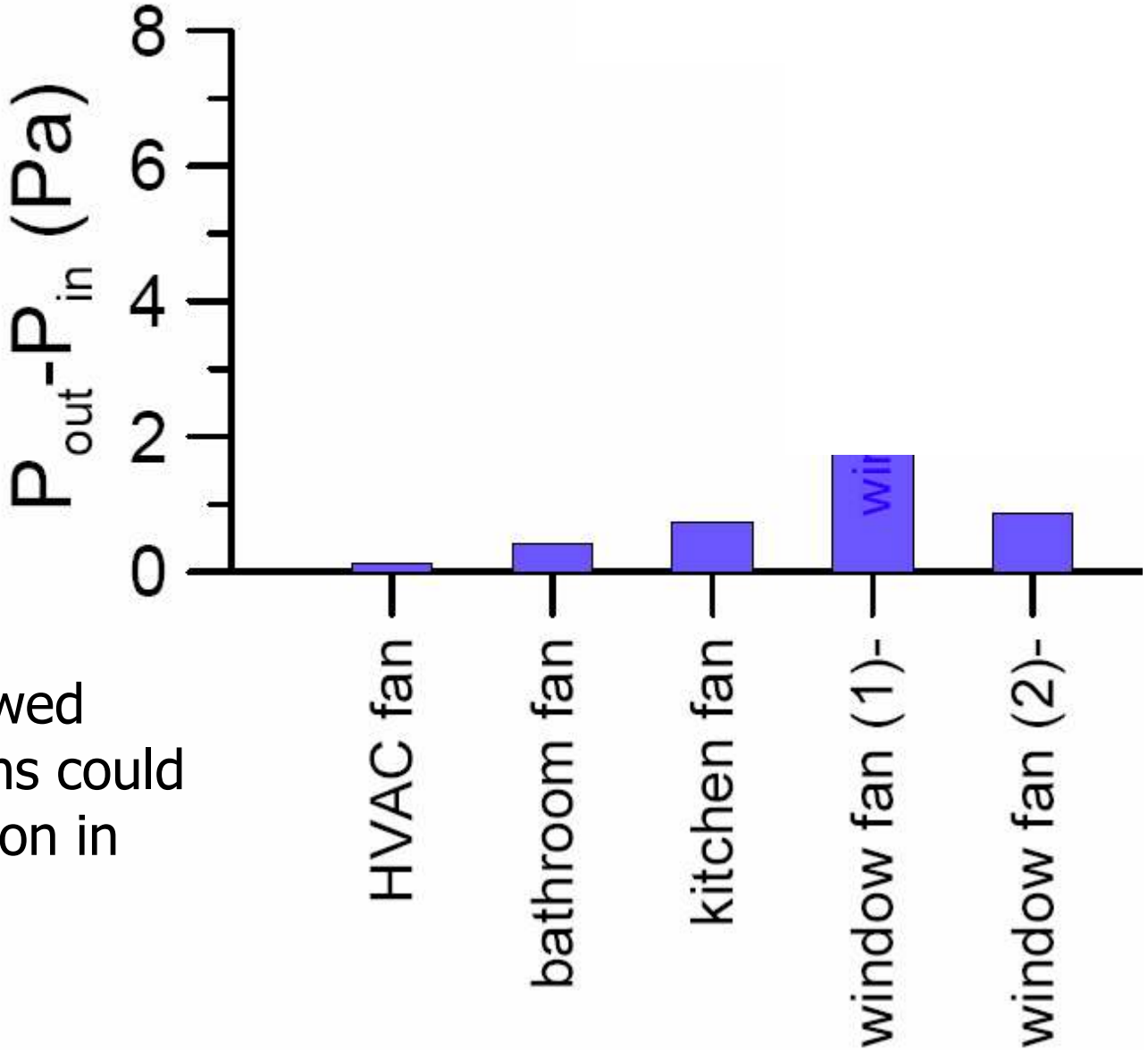
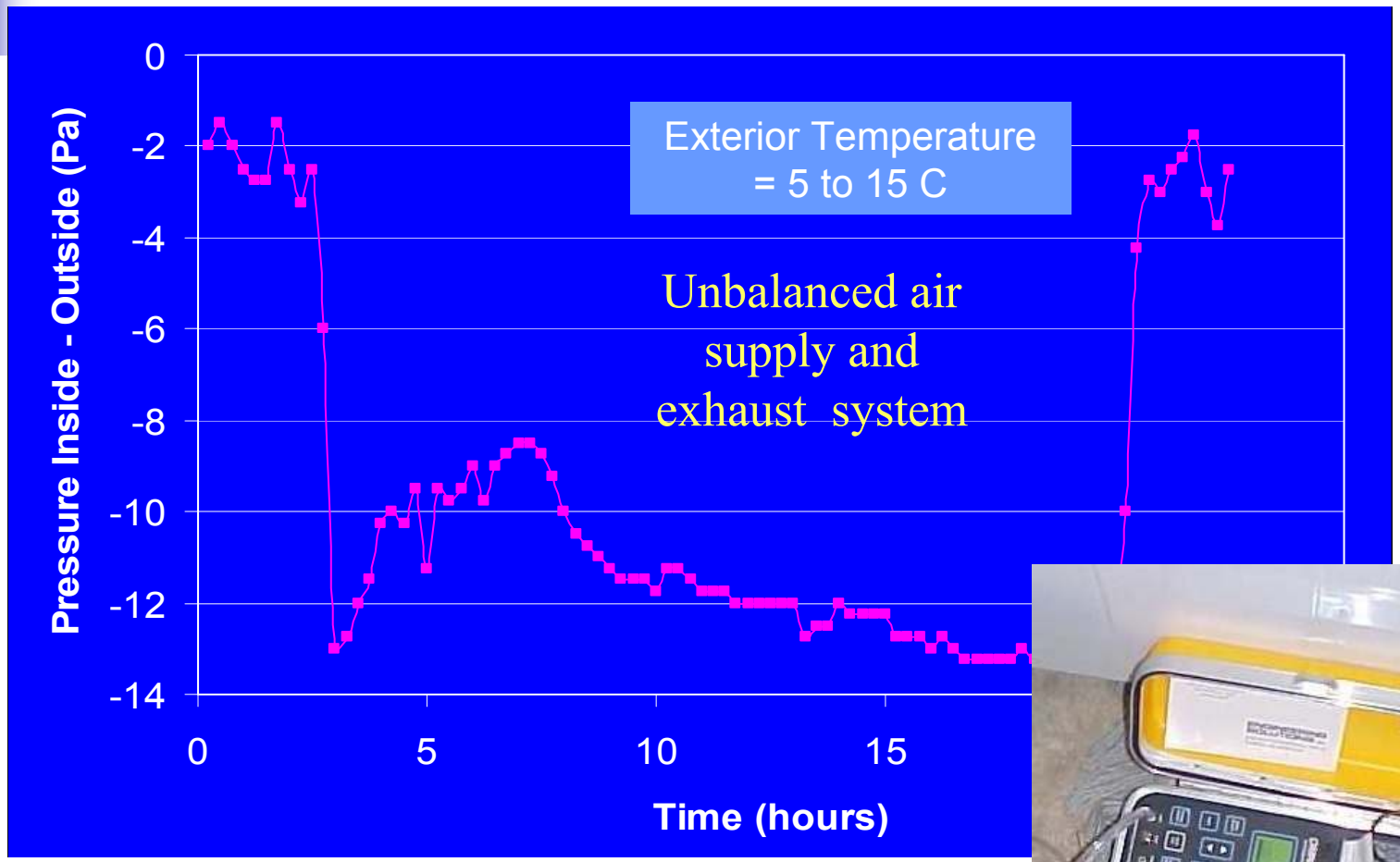
Pressure Monitoring - House



- **Purpose**: Data showed how operation of fans could cause depressurization in warm climate

Pressure Monitoring - School



- **Purpose**: Develop CSM, determine if correlation pressure and indoor VOCs

HVAC Information

(Joe Daniel, Stoller Corporation, 2005)

- Blower tests are sometimes conducted for energy/ventilation studies – Leakage quantified as scfm/ft2/Pa

Total Outdoor Air Supplied (scfm)	175,316	(20% of total)
Total Exhaust (scfm)	140,253	
Net Inflow (scfm)	35,063	(*F*)
Building Surface Area (ft^2)	970,292	(*A*)
Average Industrial Leakage ($scfm/ft^2/Pa$)	0.019	(*L*)
Net Pressure (Pa)	2	(= *F*/*AL*)

Implication: ***Some*** commercial buildings designed/ operated under +ΔP; significantly reduces the potential for VI.

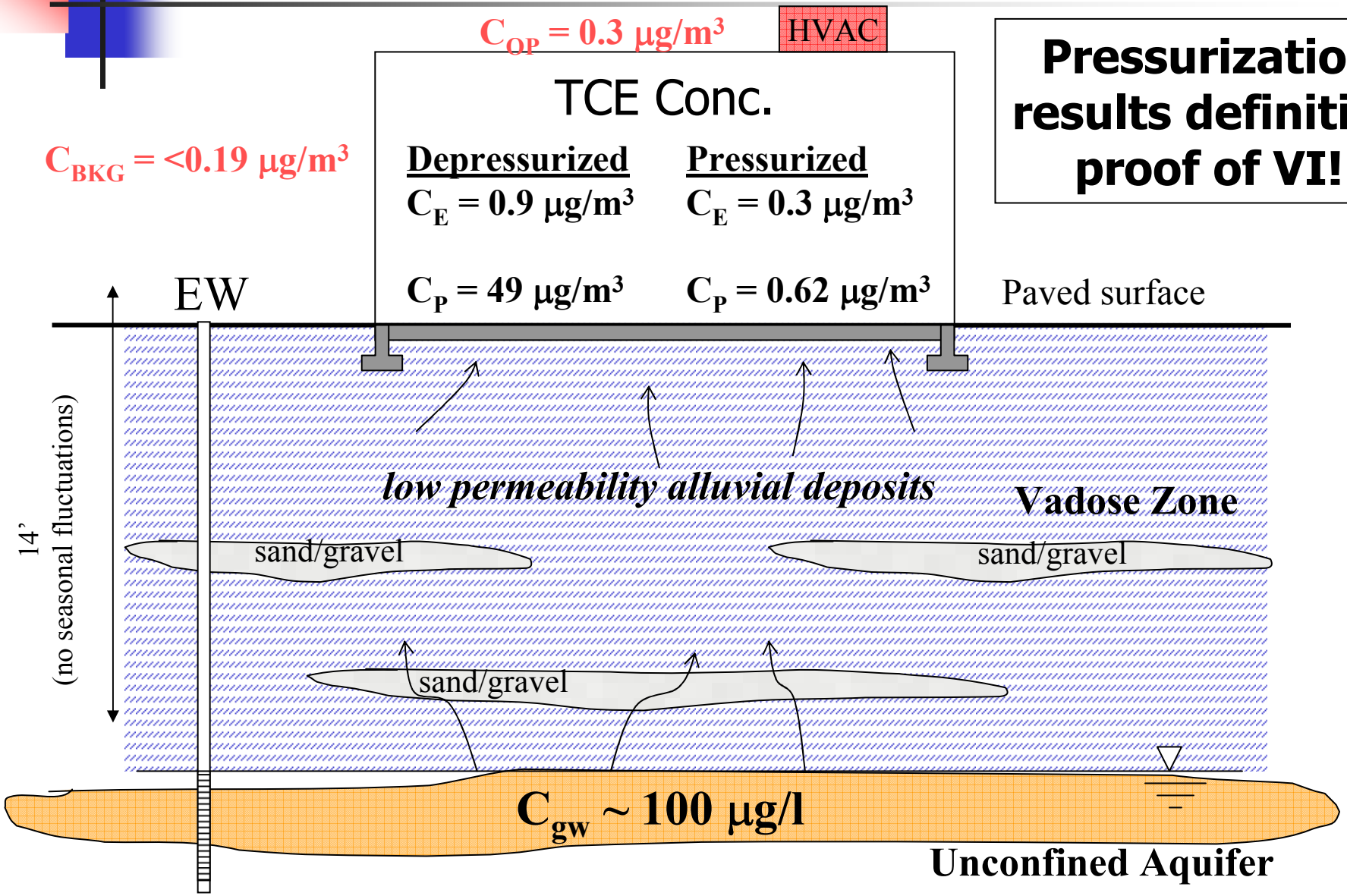
Building Pressure Manipulation

Blower Door

- Monitor indoor VOC concentrations under positive and negative pressure
- For smaller buildings may be able to use blower door
- **Purpose**: Separate vapour intrusion from background sources, may also be mitigation method

Commercial Building VI Study
(Wozniak et al., AEHS, 2004)

Pressurization results definitive proof of VI!

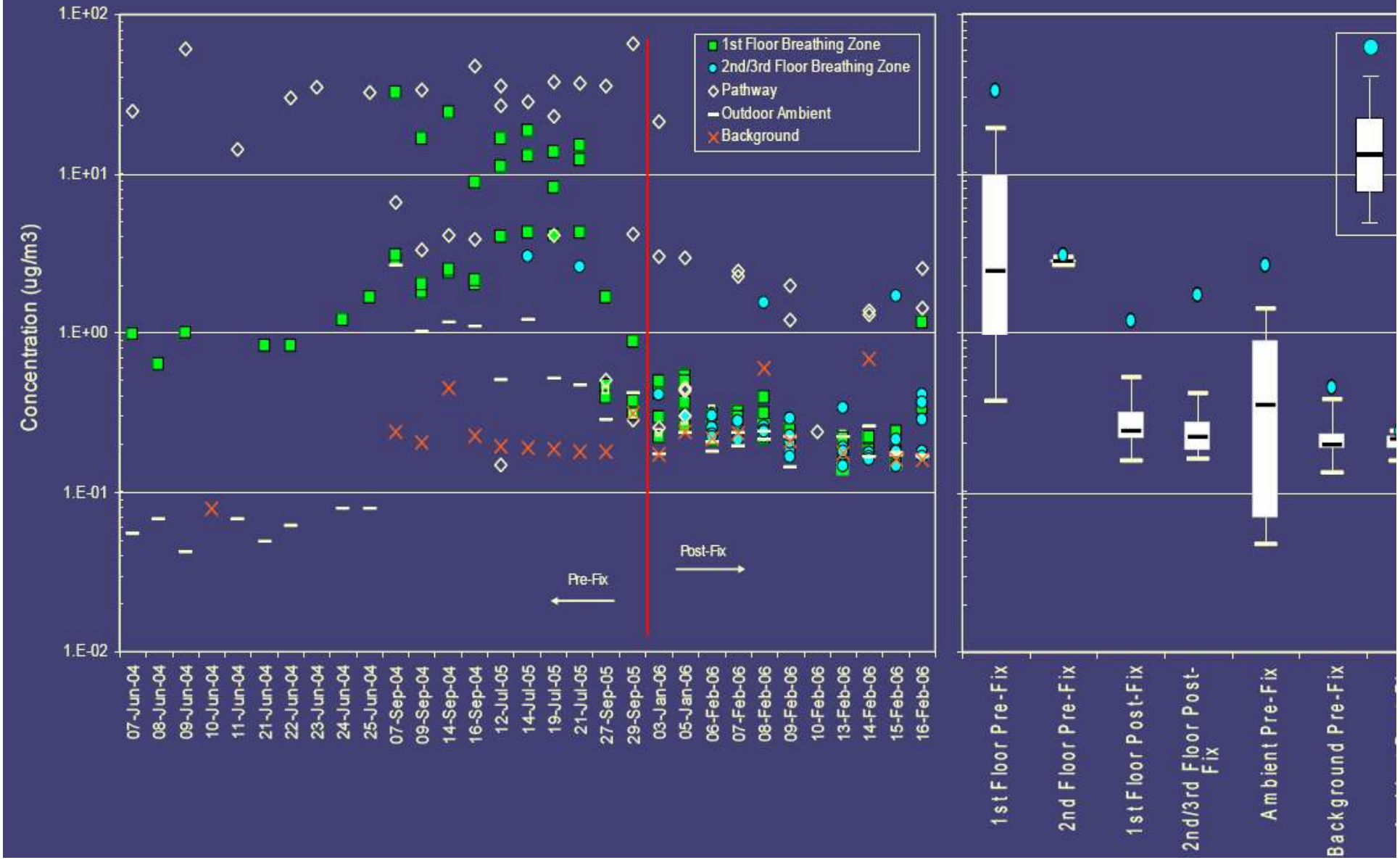


Moffett AFB Hanger
(D. Brenner, AWMA, 2006)

TES

TCE Results

Moffett AFB D. Brenner, AWMA, 2006



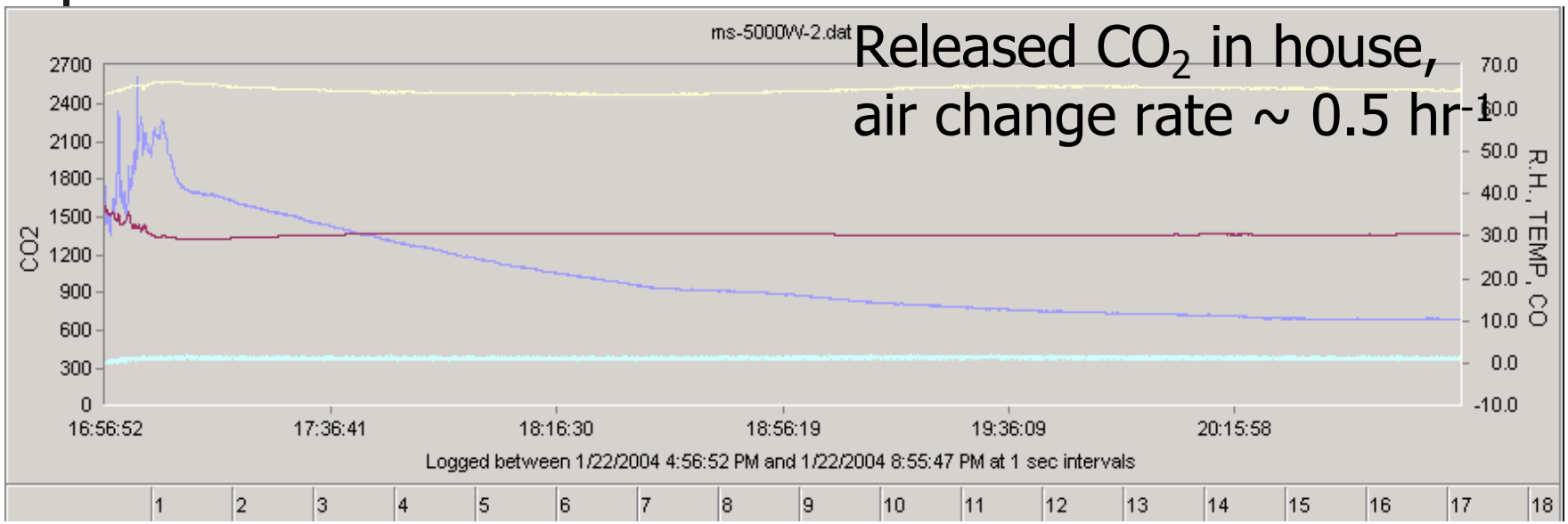
Vapour Intrusion Tracer

- ESTCP study[1]: Rn is effective tracer if 1) Rn conc. in soil > several hundred pCi/L, 2) indoor Rn > outdoor Rn, 3) Rn sensitivity ~ 0.1 pCi/L 4) Correct for Rn decay

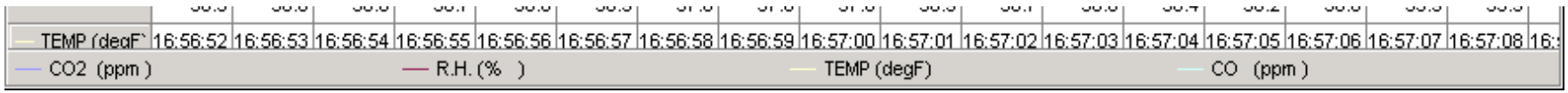
[1] McHugh et al. 2008. Use of Rn Measurements for Evaluation of VOC Intrusion. Environmental Forensices, 9 ,107-114.

- Golder has found sensitive real time radon monitoring effective for evaluating vapour intrusion pathways
- Recent Danish study injected 5% H2, 95% N2 as tracer
- **Purpose**: Estimate attenuation factors, identify pathways, separate vapour intrusion from background sources

Ventilation Tracer Test
Golder-NJDEP Research Project



ASTM E-741-00. 2000. Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution



- **Purpose**: Mass flux calculations, input for modeling purposes

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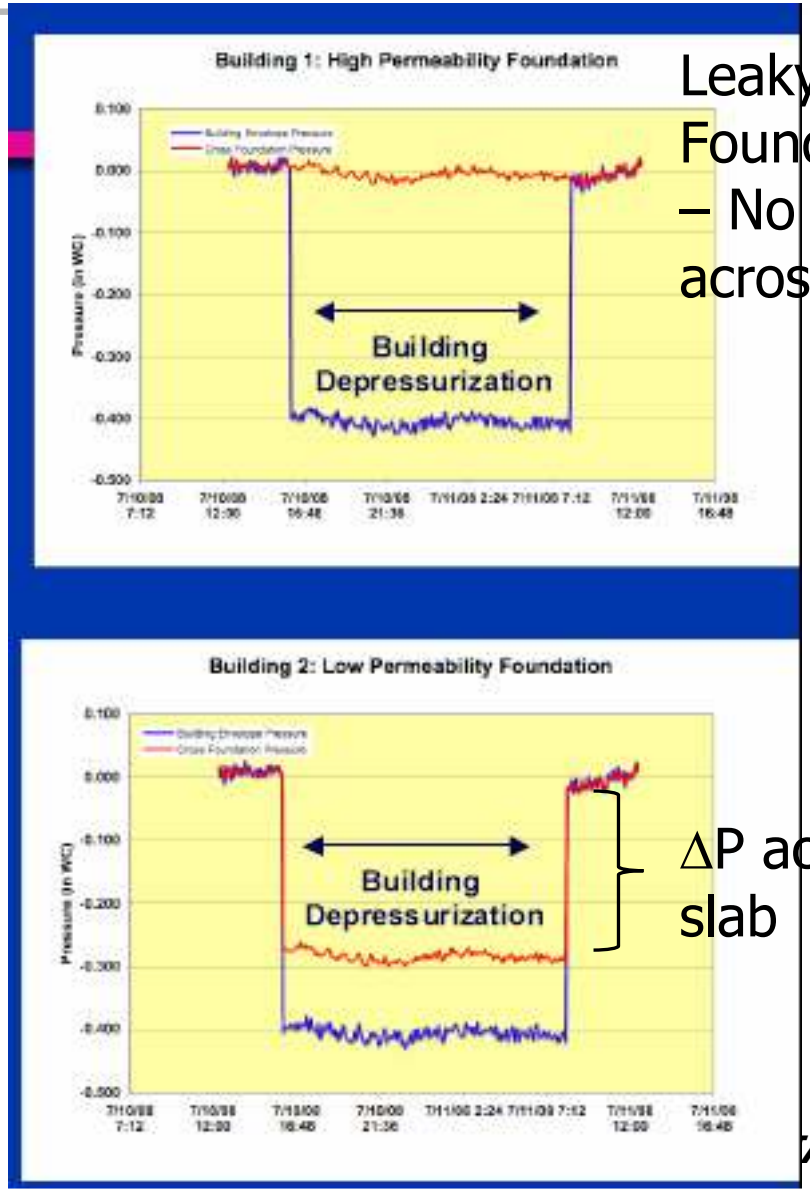
Foundation Permeability

(Tom McHugh, GSI)

- Measure differential pressure between building and outdoor air and building and subslab soil
- If foundation is leaky than there will be little pressure drop across slab
- **Purpose**: Evaluate potential for VI, obtain information for mitigation



Leaky Foundation – No ΔP across slab

ΔP across slab

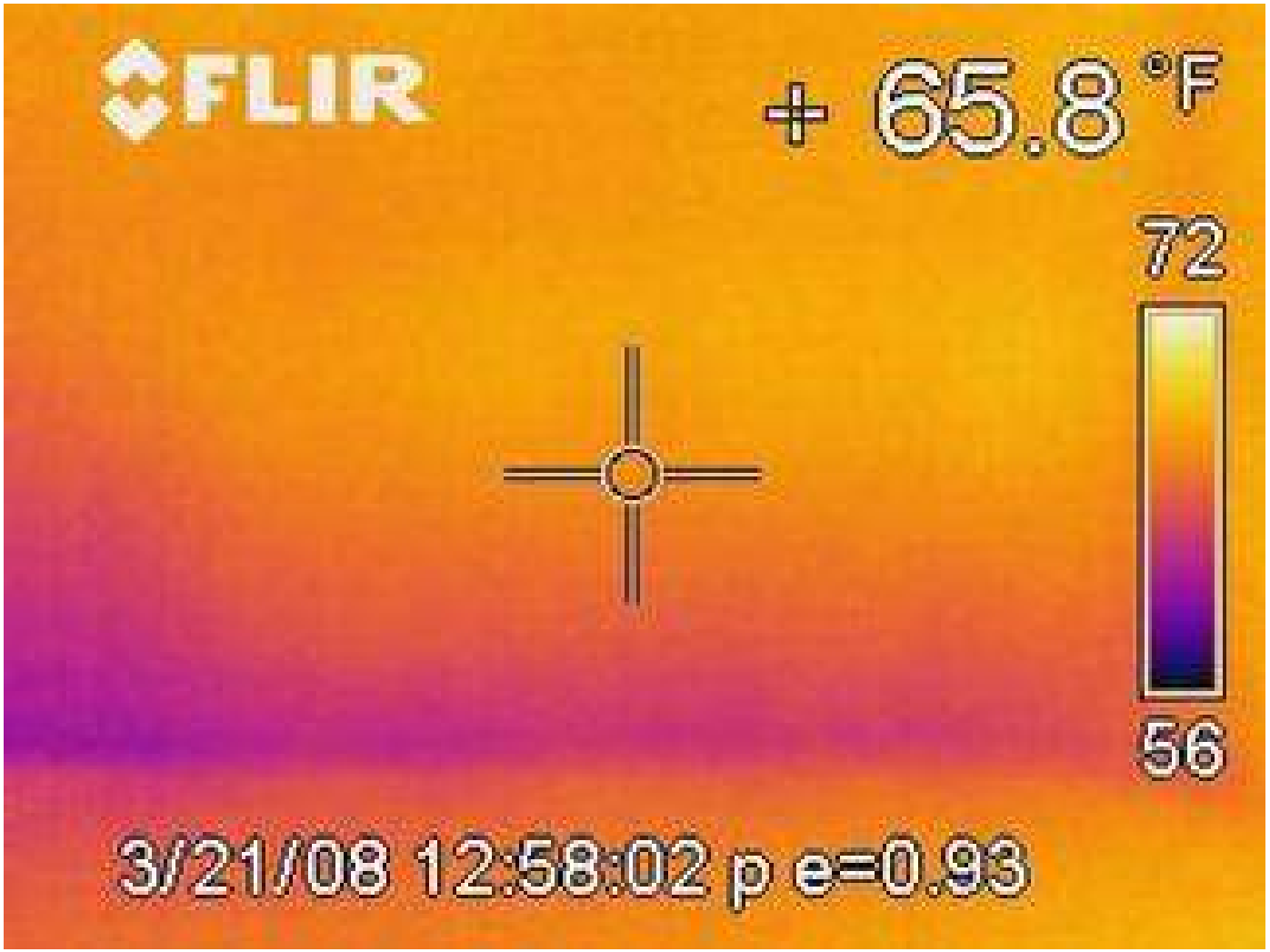
ATES

Diagnosis – Good Seal?

(Pete Granholm, Apex)

Thermal Image of Same Wall

(Pete Granholm, APEX)



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Modeling and Comparisons to Empirical Data

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Modeling Context

- Models have essential role in helping develop regulatory screening levels
- Help understand sensitive inputs and influence of different transport processes
- Simple software or spreadsheets are also useful but concern over misuse and abuse

- Lack of familiarity with more sophisticated models
- Models should incorporate key physical processes (e.g., biodegradation when appropriate)
- Prediction is only as good as validation and calibration

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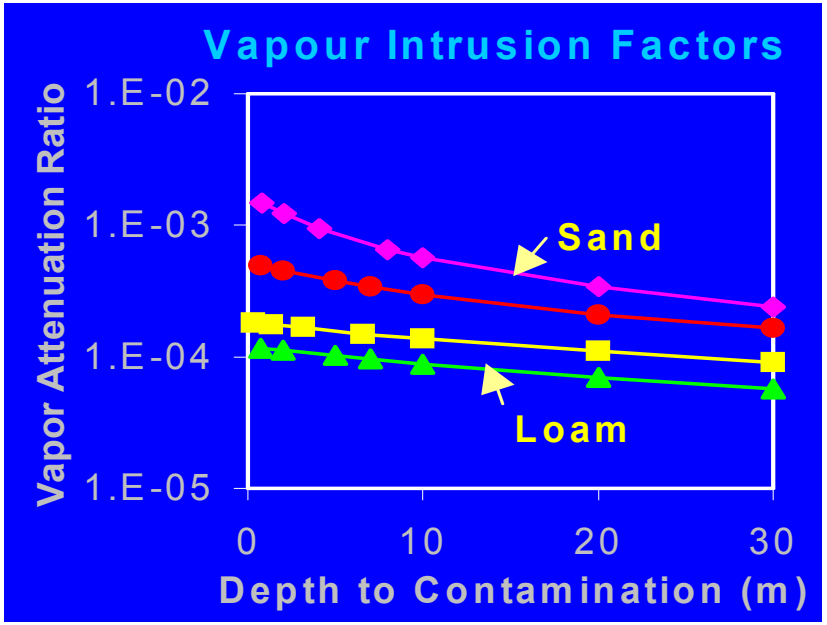
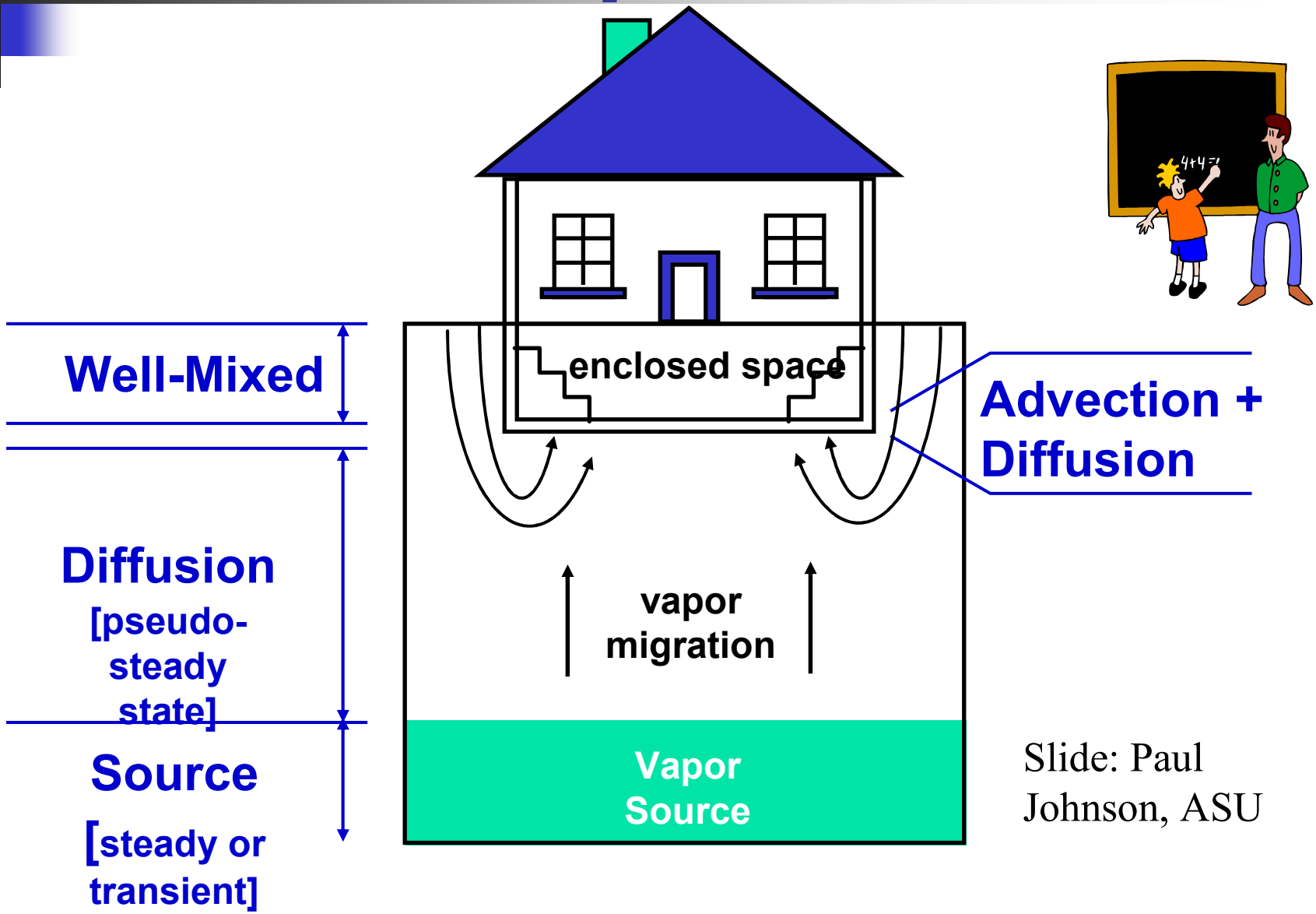
Draft USEPA (2002) & Health Canada VI Guidance

- **Tier 2 Screening**
  - Attenuation factor using J&E model based on soil type and depth
  - USEPA is currently reviewing approach, further validation is needed particularly for soil vapour



Johnson and Ettinger (1991) Conceptual Model



Slide: Paul Johnson, ASU

Johnson & Ettinger Model Attenuation Factor

$$\alpha = \frac{\left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] \exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) + \left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] + \left[\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right]\left(\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) - 1\right)}$$

Primary Parameters

- D_{eff} = Effective diffusion coefficient
- L_T = Depth to source
- A_B = Building area in contact with soil
- Q_B = Building ventilation rate
- Q_{soil} = Soil gas convection rate
- D_{crack} = Eff. diff. coeff. through cracks
- L_{crack} = Crack thickness
- η = Building crack factor

Secondary Parameters

- D_{eff} = fn(H, D_{water}, D_{air}, θ_T, θ_w) *for each layer*
- $L_T = \Sigma(L_i)$
- Q_{soil} = fn(k, ΔP, rcrack, zcrack, xcrack)

$$Q_{Soil} = \frac{2\pi \Delta P k_v X_{crack}}{\mu \ln\left[2 Z_{crack} / r_{crack}\right]}$$

Perimeter Crack Model

Diffusive Flux in Soil

Diffusive flux in vadose zone determined by:

$$Flux = D_{eff} \cdot \frac{dC}{dZ}$$

where

$$D_{eff} = D^{air} \frac{\theta_v^{10/3}}{\theta_t^2} + \frac{D^{H_2O}}{H'} \frac{\theta_w^{10/3}}{\theta_t^2}$$

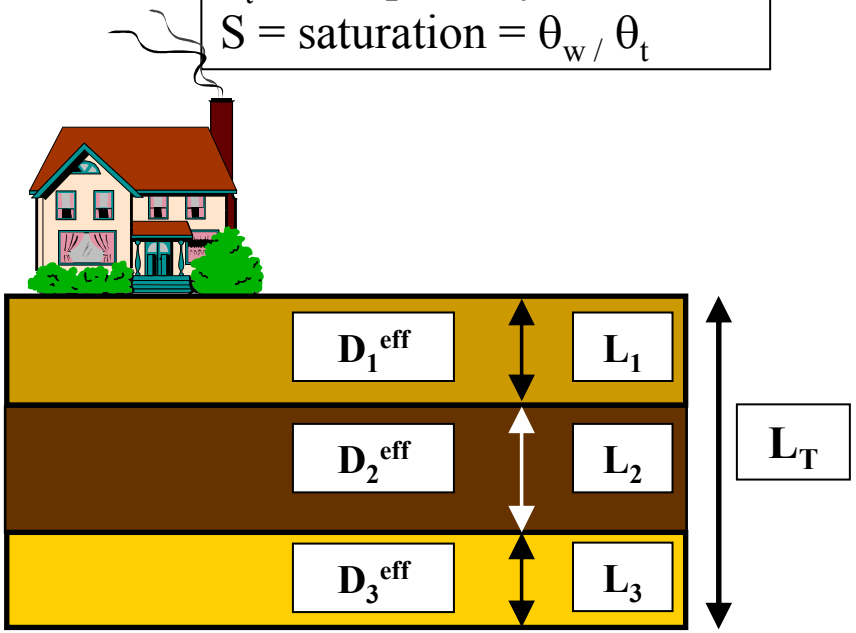
Tortuosity Factor

"Millington & Quirck (1961) Relationship

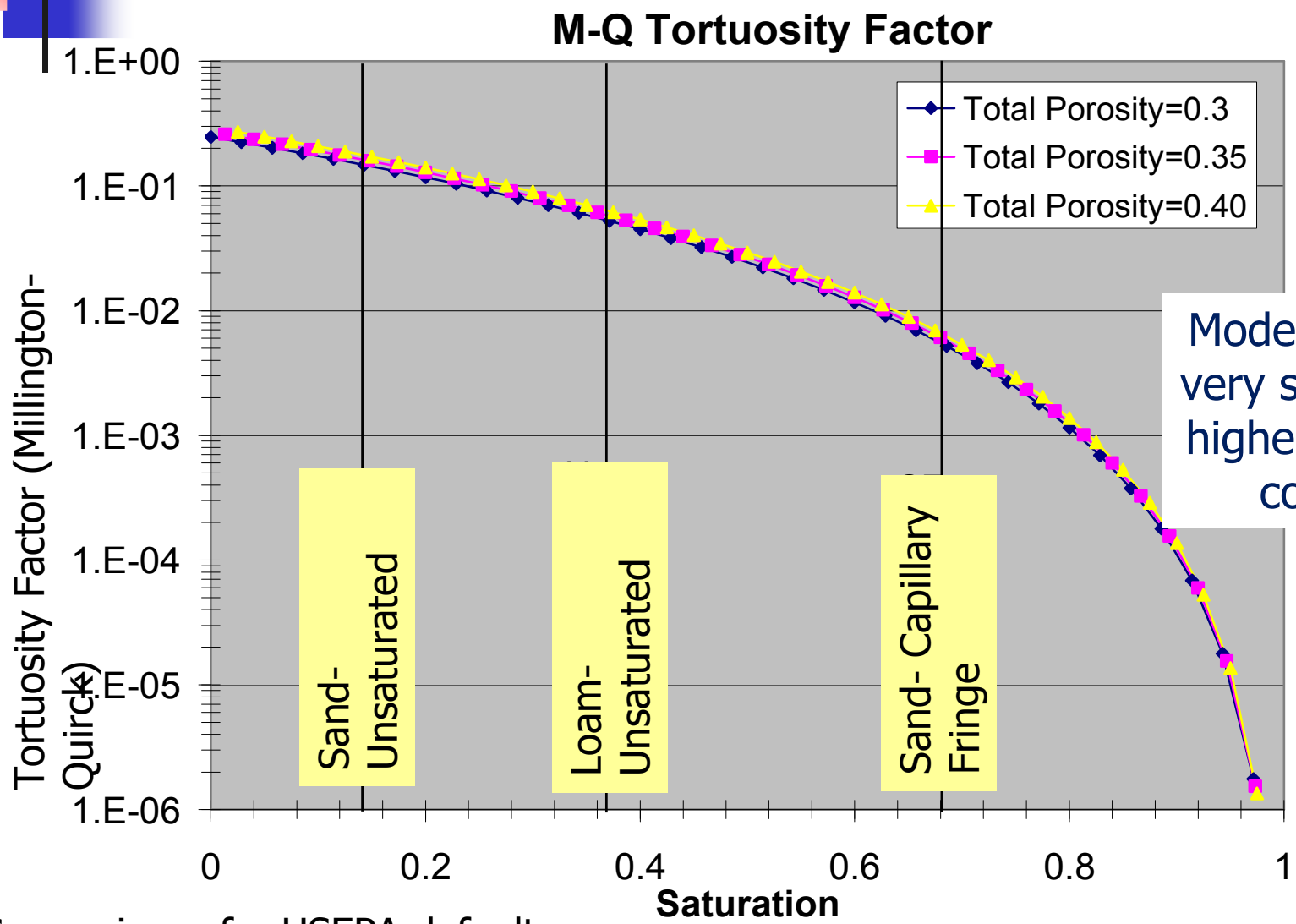
D_{eff} = Effective diff. coeff.
D^{air} = Diff. coeff. in air
D^{H2O} = Diff. coeff. in water
H' = Henry's Law coeff.
θ_v = air-filled porosity
θ_w = water-filled porosity
θ_t = soil porosity
S = saturation = θ_w / θ_t

For Layered Media:

$$D_T^{eff} = L_T \left(\sum \frac{L_i}{D_i^{eff}} \right)^{-1}$$



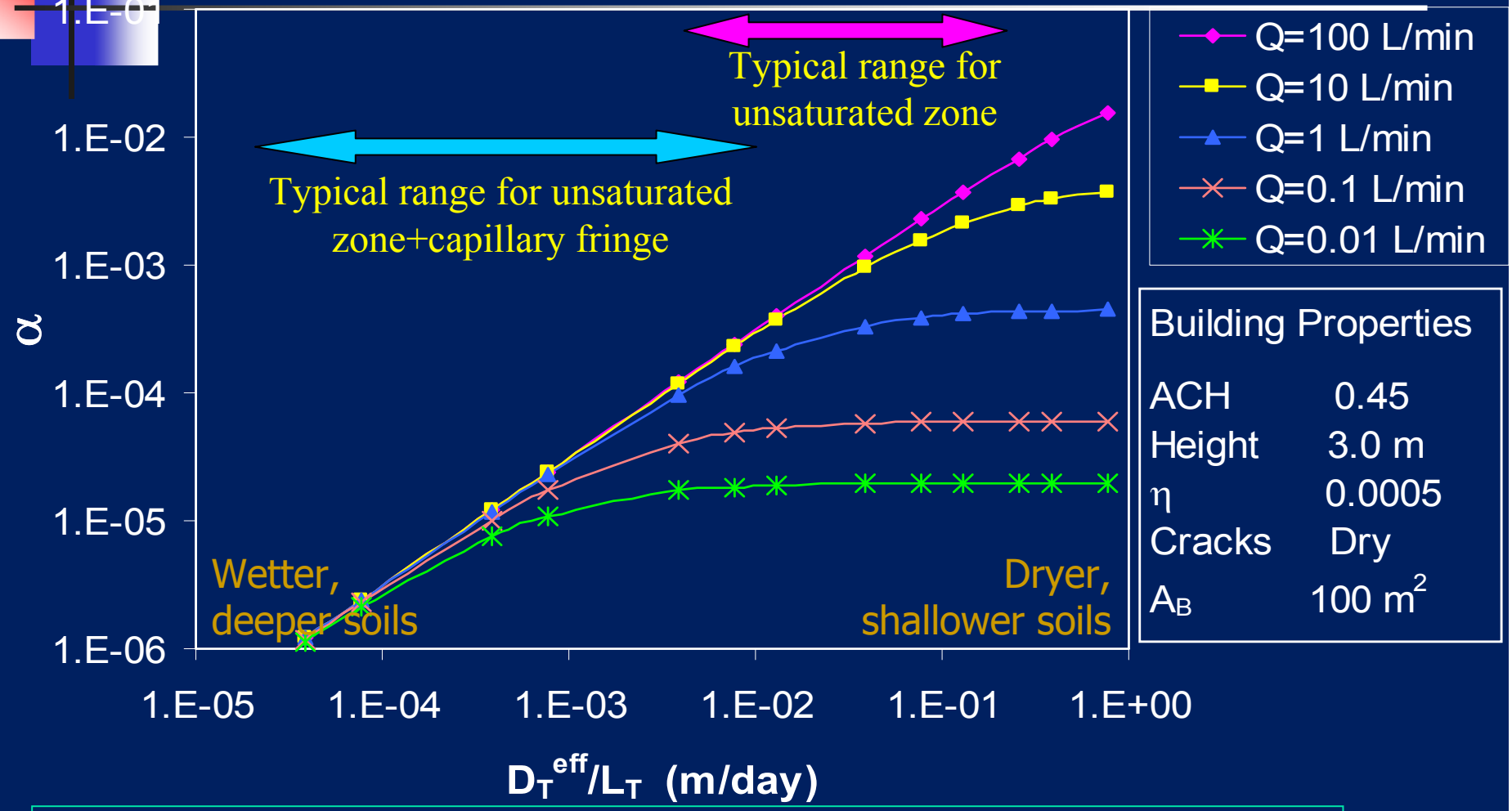
Tortuosity Factor Sensitivity



Model becomes very sensitive at higher moisture content!

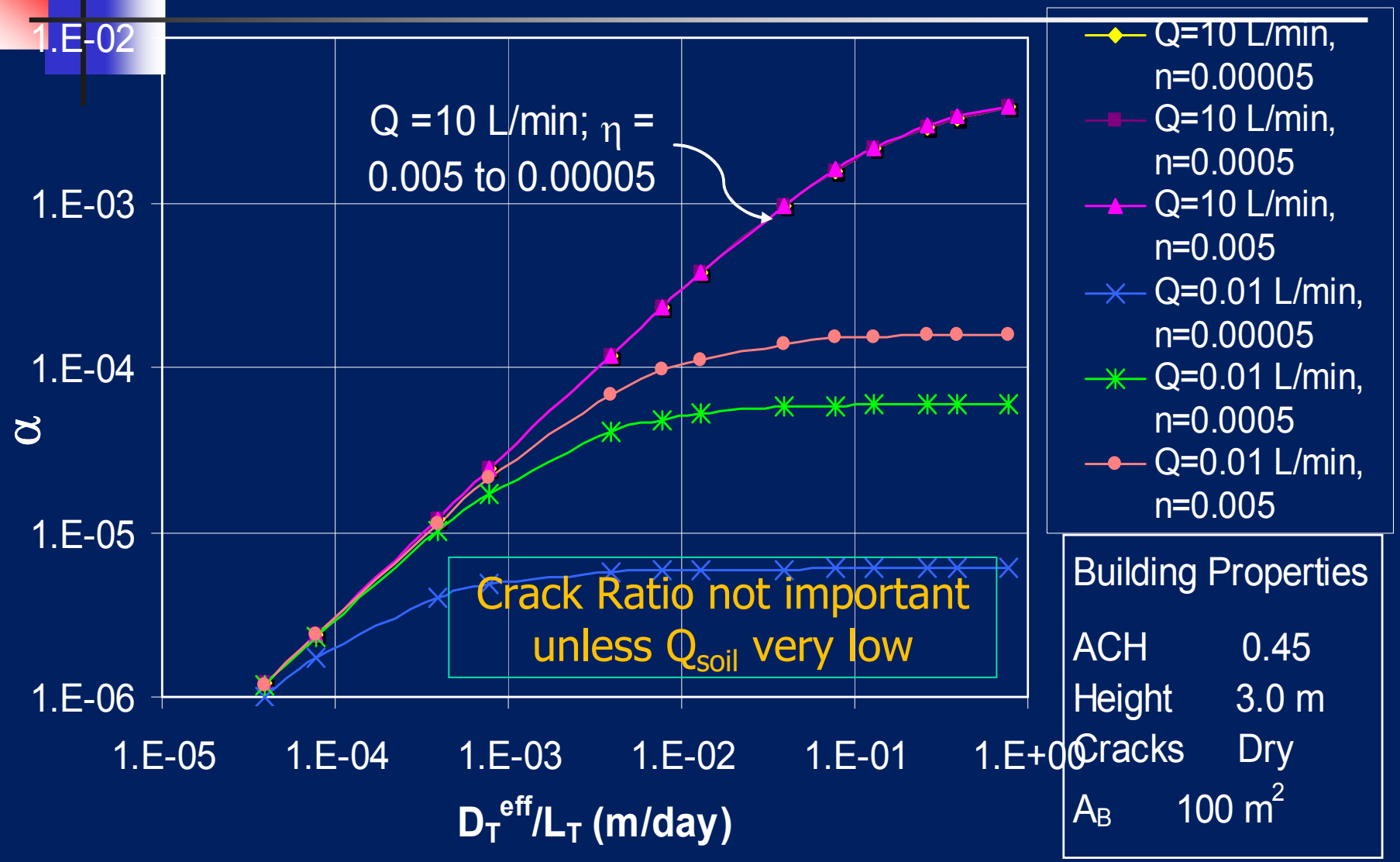
Comparisons for USEPA defaults

J&E Sensitivity



Model highly sensitive to Q_{soil} for shallow contamination and dry soils, less sensitive for groundwater source

J&E Sensitivity



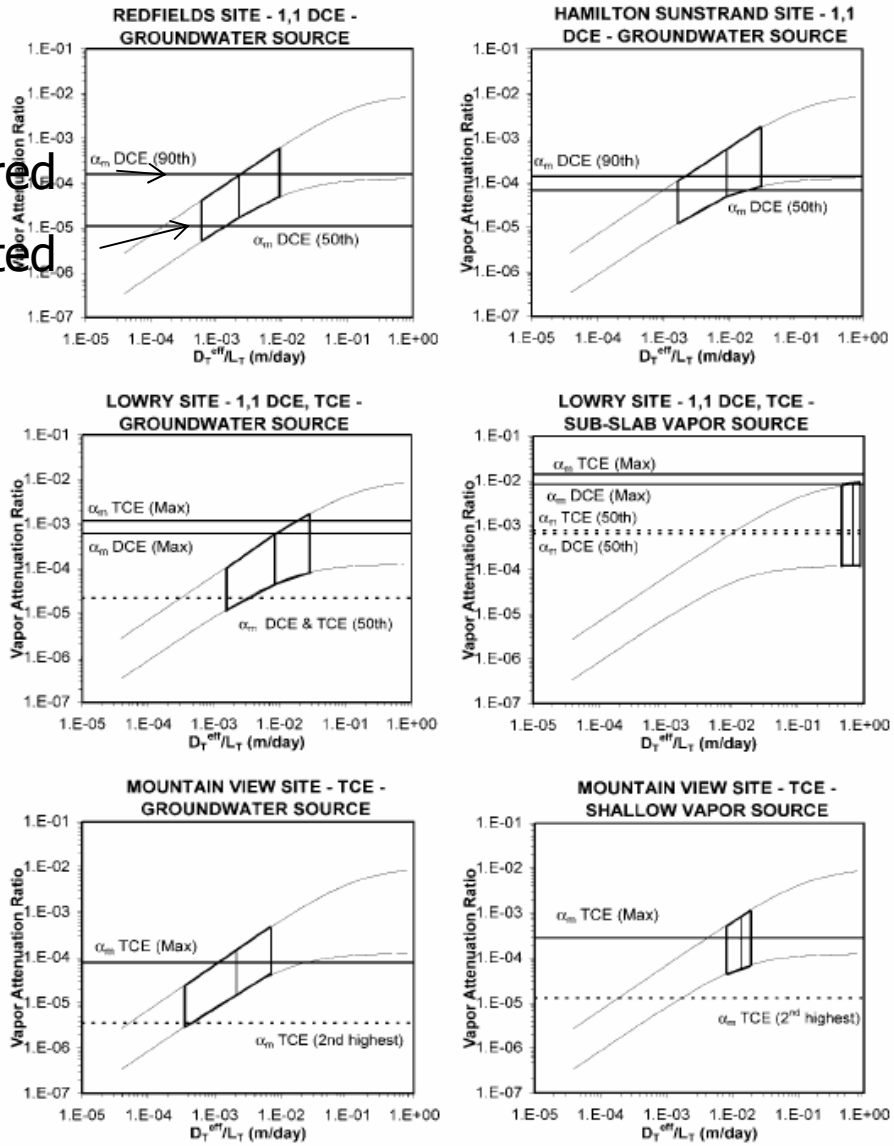
Building Properties

ACH	0.45
Height	3.0 m
Cracks	Dry
A_B	100 m^2

J&E Model Comparisons (GWMR 2003)

Measured

Predicted



Evaluation of the Johnson and Ettinger Model for Prediction of Indoor Air Quality
Hers, Zapf-Gilje, Johnson, Li
GWMR 2003, 23 (2)

Conclusion: When data evaluated on site specific basis (with good quality data) J&E reasonable order of magnitude predictor (with appropriate inputs)

J&E Model Sensitivity

	Building Depressurized (advection & diffusion)	Building Not Depres-surized (diffusion)
High D_T^{eff}/L_T (shallow)	Q_{soil} (advection controlled)	Building Crack Ratio & Properties
Moderate D_T^{eff}/L_T	Q_{soil} and Moisture Content	Building Crack Ratio & Properties
Low D_T^{eff}/L_T (deep)	Moisture Content (diffusion controlled)	Moisture Content

- Sensitivity to moisture content increases when capillary fringe modeled (groundwater to indoor air)
- Indoor air concentrations proportional (i.e., linear) to source concentrations, ventilation rate and building height

Generalized Sensitivity Assessment of the J&E (1991) Model - Back to Basics

- **The output only depends on three parameters (A, B, C)**
- **If you understand sensitivity to those three parameters, you can quickly assess the sensitivity to any specific input.**

$$\alpha = \frac{[A]\exp(B)}{\exp(B) + [A] + \left[\frac{A}{C}\right](\exp(B) - 1)}$$

$$A = \left[\frac{D_T^{eff}}{E_B\,(\frac{V_B}{A_B})\,L_T}\right] \quad B = \left[\frac{(\frac{Q_{soil}}{Q_B})\,E_B\,(\frac{V_B}{A_B})\,L_{crack}}{D_{crack}^{eff}\,\eta}\right]$$

$$C = \left[\frac{Q_{soil}}{Q_B}\right]$$

P.C. Johnson. 2002. Sensitivity Analysis and Identification of Critical and Non-Critical Parameters for the Johnson and Ettinger (1991) Vapor Intrusion Model. API Technical Bulletin. Also (2005 in Ground Water Monitoring and Remediation)

Paul Johnson in critical parameters paper recommends V/A of 2 to 3 where A is defined as the subsurface foundation area (base and walls). V/A is not equal to the mixing height.

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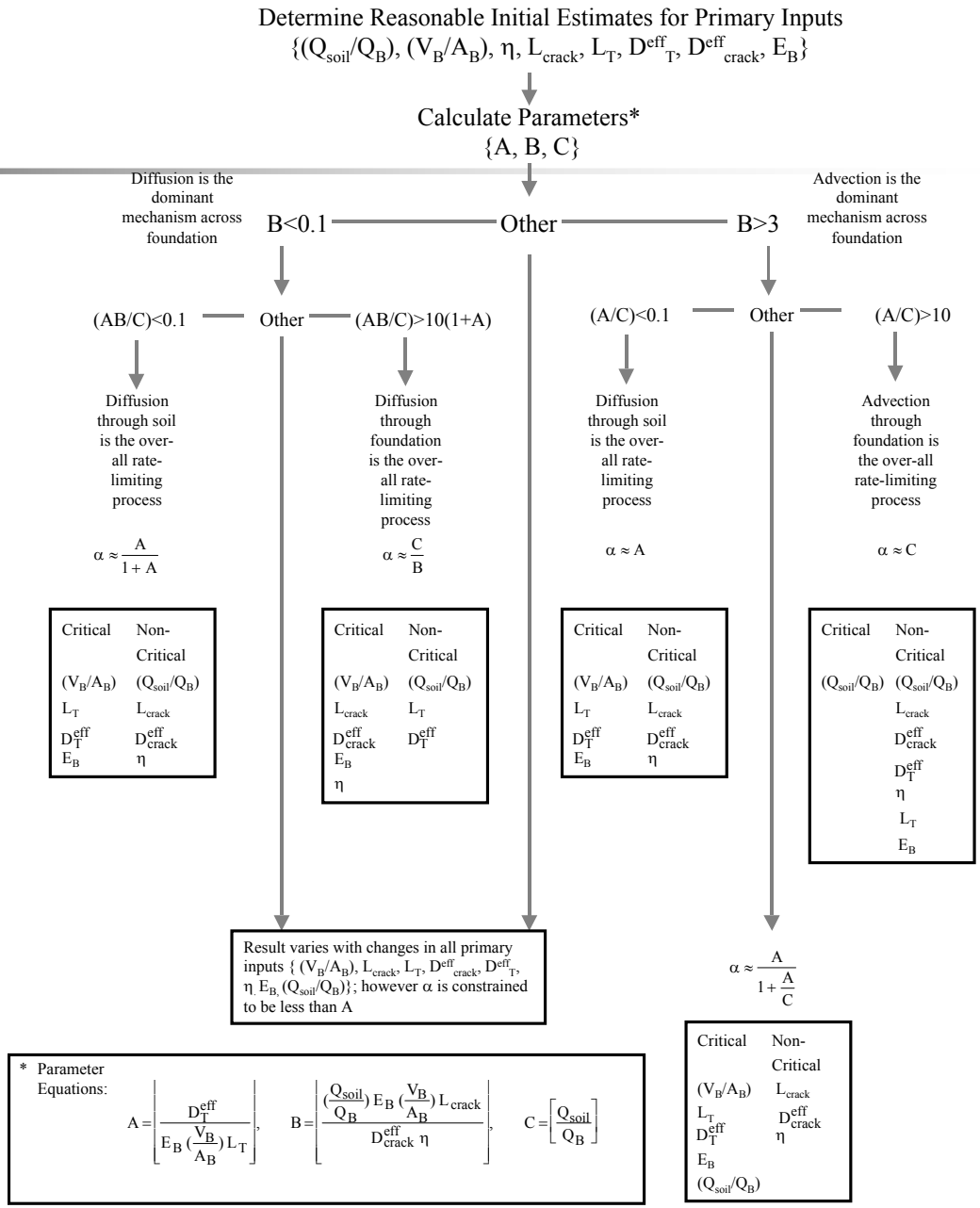
Generalized Sensitivity Assessment of the J&E (1991) Model:

Flowchart Summary



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Draft USEPA (2002) OSWER VI Guidance

- **Tier 1 Screening**
  - Preliminary screening
    - Volatile and toxic compounds present?
    - Buildings present (30 m off-set)?
    - Health effects, noxious odors, explosive levels? (immediate response)
  - Generic screening values based on following Attenuation Factors:
    - Groundwater: 0.001
    - External soil vapor : 0.01 ?
    - Subslab soil vapor: 0.1 ?

Very low generic groundwater screening values for some chemicals (ug/L)!	
TCE	5[1]
PCE	11
Benzene	14

ILCR = 1×10^{-5}

[1] The risk-based groundwater concentration (for 10^{-5} ILCR) is lower than 5 ug/L but as policy decision EPA set lower limit equal to the drinking water maximum concentration limit ("MCL")

Key Inputs for J&E Model

- Water-filled porosity (θ_w or $S = \theta_w/\theta_t$)
- Soil gas advection rate (Q_{soil} or Q_{soil}/Q_{build})
- Building vapour mixing height (H)
- Building air exchange (ACH)
- Building footprint area

`Normalized` parameters can also help establish reasonable bounds for input parameters – see Johnson (2005)

Presentation that will be sent will include additional slides on modeling and how input parameters were derived

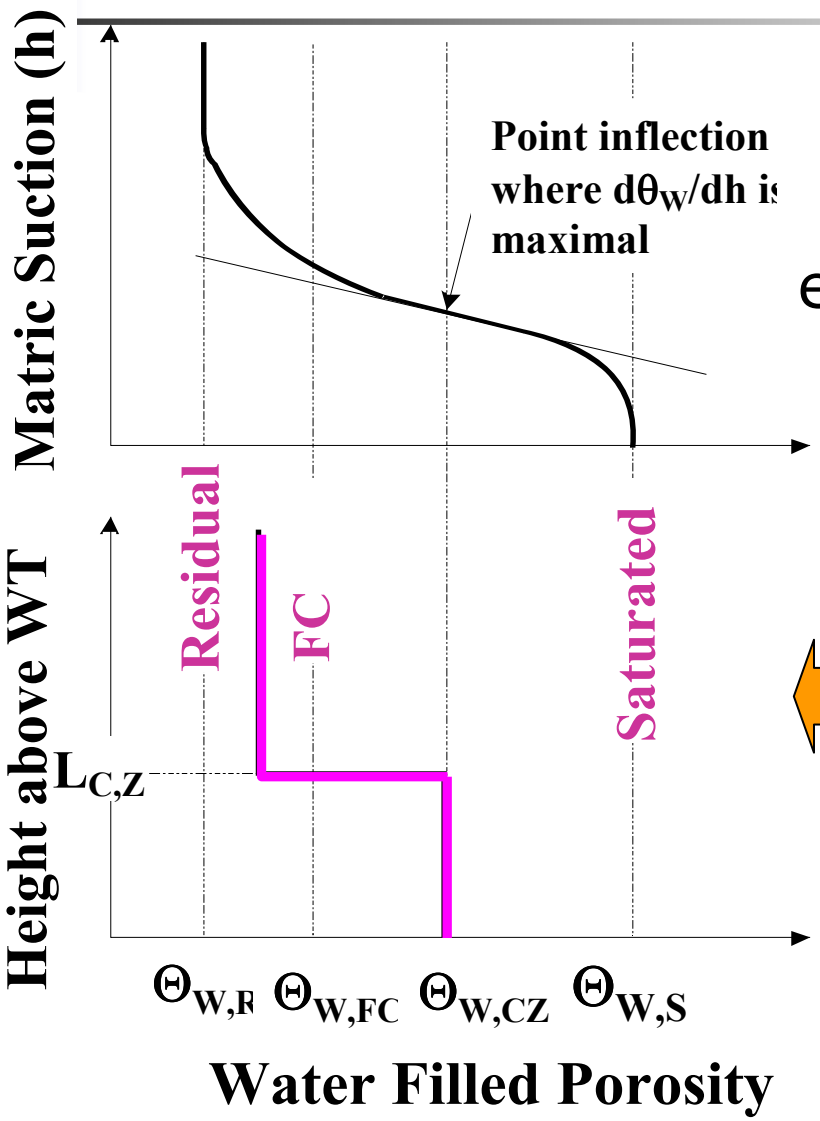
Key Health Canada Inputs for J&E Alpha Curves

	Qsoil (L/min)	Qsoil/ Qbuild (-)	Mixing Height (m)	Air Change Rate (hr-1)	Building Footprint Area (m^2)
Residential	10	4.5E-3	3.66	0.35	100
Commercial	7	4.5E-4	3.0	1.0	300

	Θ_T	$\Theta_{w,unsat}$	$S_{unsaturated}$	$\Theta_{w,cap\ fringe}$	$S_{cap\ fringe}$
Sand	0.375	0.055	0.14	0.32	0.68
Loam	0.399	0.148	0.37	0.332	0.83

USEPA inputs similar (except no commercial scenario)

Water-Filled Porosity



Water Retention Curves
e.g. Van Genuchten model

HC/ USEPA guidance use simplified water retention model to estimate water content from default Van Genuchten parameters published for different soil textures (Schaap & Lej, 1998)

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USEPA Spreadsheet Soil Moisture Parameters

U.S. Soil Conservation Service (SCS) Soil Texture	Total (Saturated) Porosity θ_s (cm^3/cm^3)	Unsaturated Zone: Residual Water-Filled Porosity θ_r (cm^3/cm^3)	Unsaturated Zone: Field Capacity Water-Filled Porosity 1/3 bar 333	Unsaturated Zone: Mean Water-Filled Porosity $(FC_{1/3bar}+\theta_r)/2$ $\theta_{w,unsat}$ (cm^3/cm^3)	Capillary Transition: $\theta_{w,cap}$ Cap @ air-entry $\theta_{w,cap}$ (cm^3/cm^3)	Capillary Transition: Height Cap Zone Fetter (94) (cm)
Clay	0.459	0.098	0.33	0.215	0.412	81.5
Clay Loam	0.442	0.079	0.26	0.168	0.375	46.9
Loam	0.399	0.061	0.24	0.148	0.332	37.5
Loamy Sand	0.39	0.049	0.10	0.076	0.303	18.8
Silt	0.489	0.05	0.28	0.167	0.382	163.0
Silt Loam	0.439	0.065	0.30	0.180	0.349	68.2
Silty Clay	0.481	0.111	0.32	0.216	0.424	192.0
Silty Clay Loam	0.482	0.09	0.31	0.198	0.399	133.9
Sand	0.375	0.053	0.055	0.054	0.253	17.0
Sandy Clay	0.385	0.117	0.28	0.197	0.355	30.0
Sandy Clay Loam	0.384	0.063	0.23	0.146	0.333	25.9
Sandy Loam	0.387	0.039	0.17	0.103	0.320	25.0
Loamy Sand	0.39	0.049	0.10	0.076	0.303	18.8

- **Van Genuchten water-retention model used with Schaap & Leij curve fit parameters**
- **USEPA semi-site specific alpha curves are for four representative soil types**

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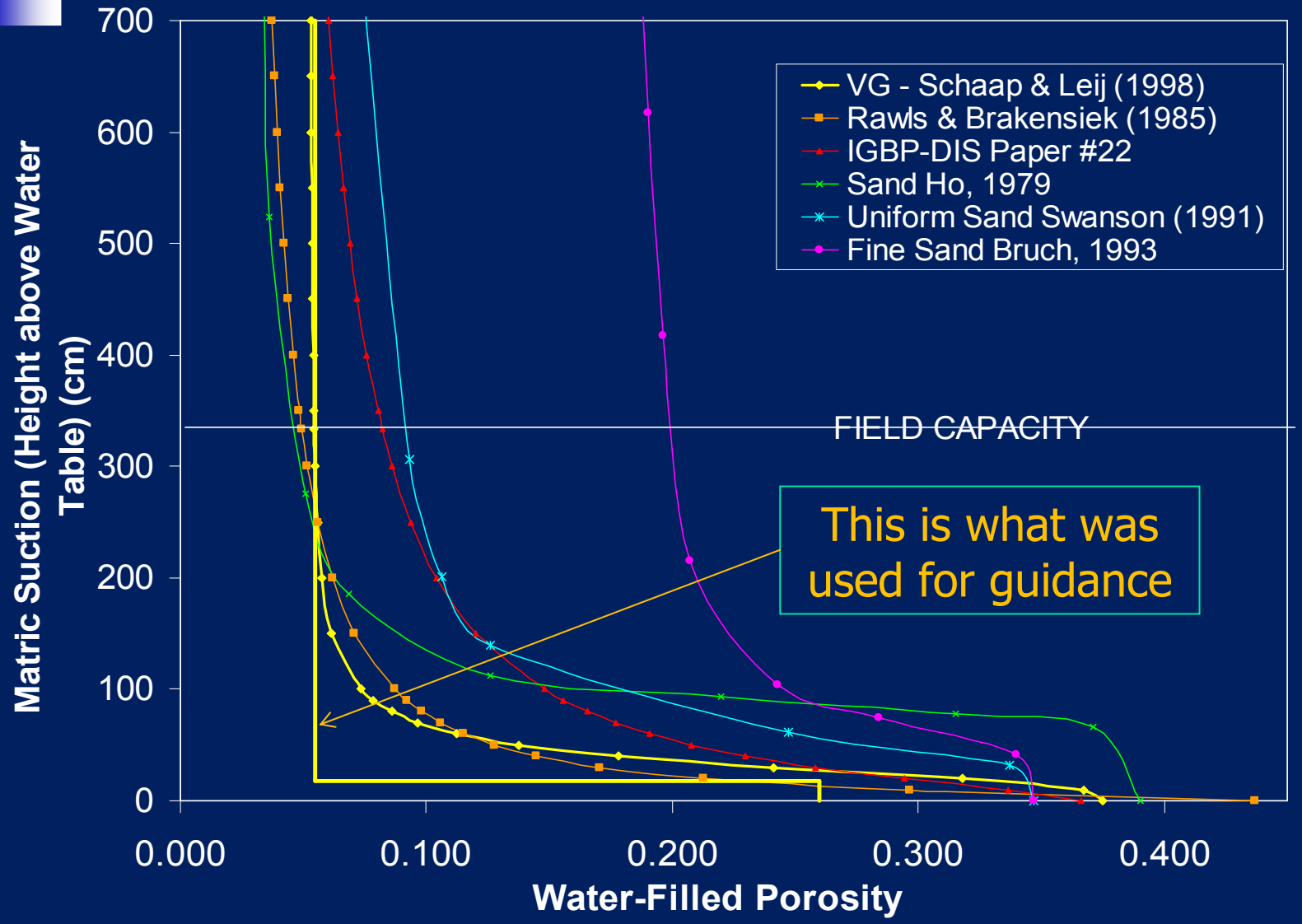
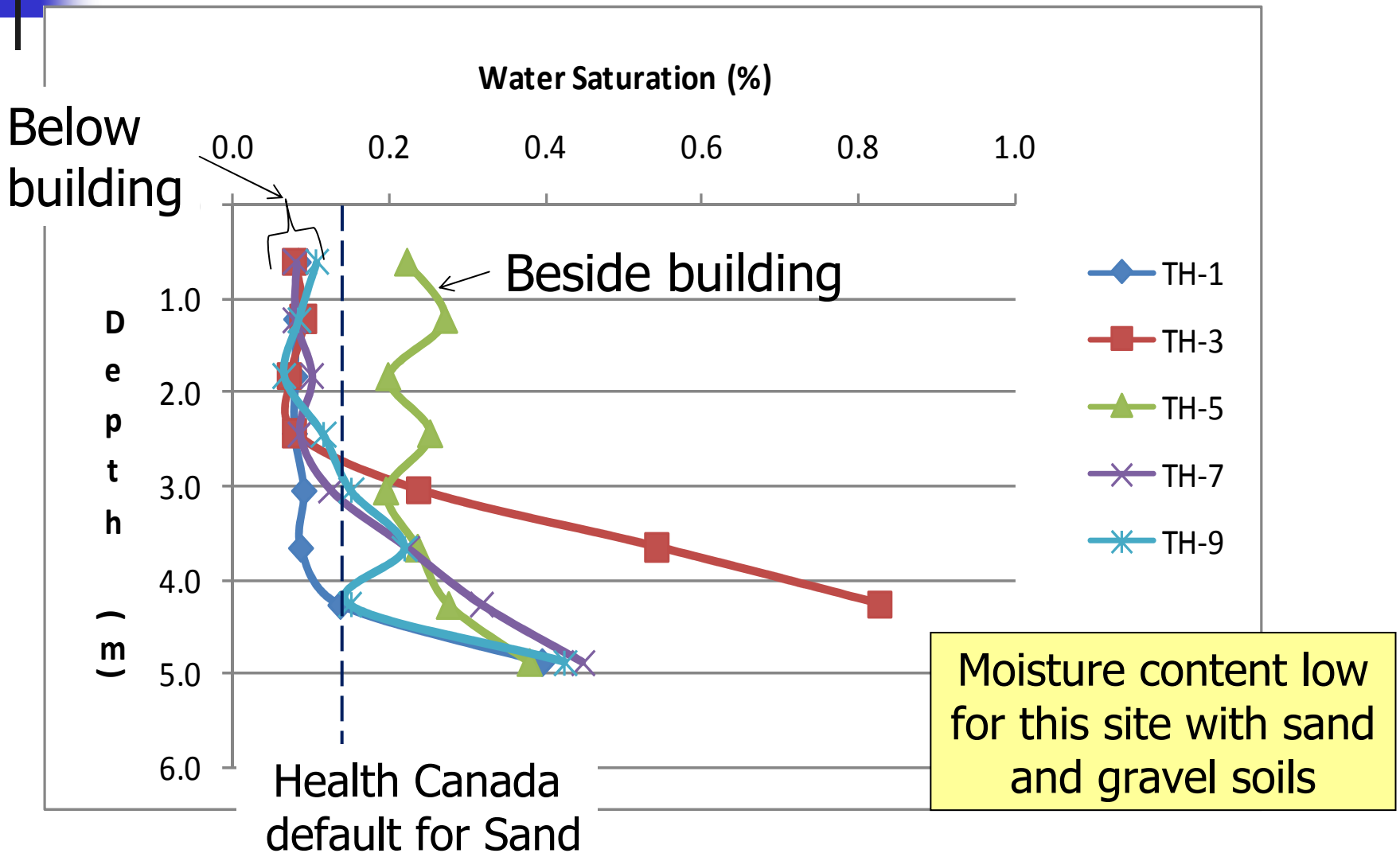
Comparison of Water Retention Curves for Sand



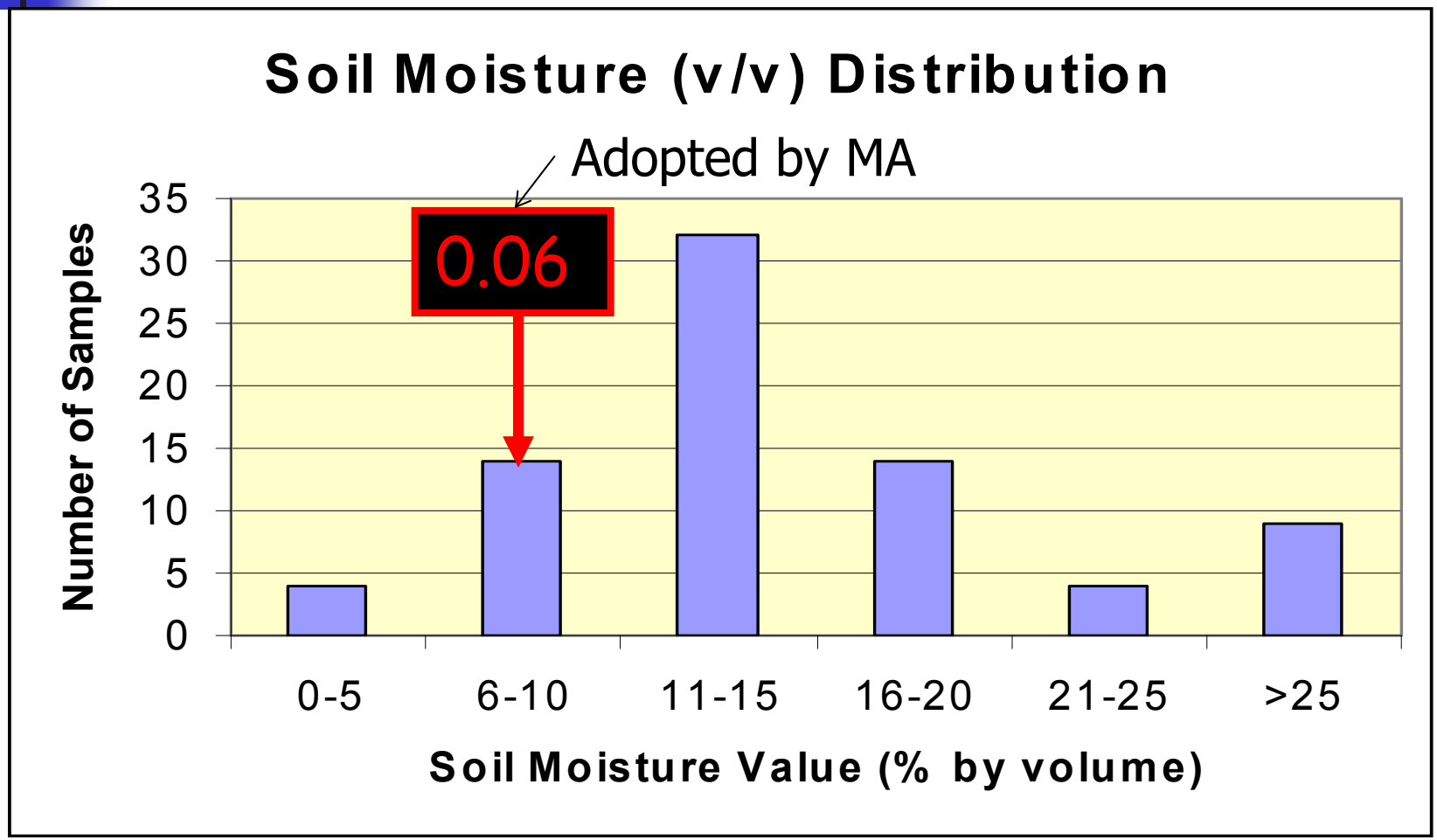
Health Canada-Golder Research Site

Courtesy Lindsay Smith, Health Canada



Moisture content low for this site with sand and gravel soils

Massachusetts Soil Moisture Below Buildings (P.Locke)



*Moisture (w/w) to Soil Moisture(v/v)

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Soil Gas Advection (Qsoil & Qsoil/Qbuild)

- Can estimate using Perimeter Crack Model, but accuracy uncertain, therefore Qsoil estimated using measurement data
- Tracer test data from research studies
  - Q_{soil} ~ 1 to 10 L/min small to moderate sized house and coarse soils (maybe 0.1 to 1 L/min for finer soil)
- USEPA database indicate that subslab to indoor air attenuation factors typically range from ~ 0.0001 to 0.01 (see empirical data slides)
- Based on mass balance on next slide, the attenuation factor is ~ equal to Qsoil/Qbuild
- Little commercial data

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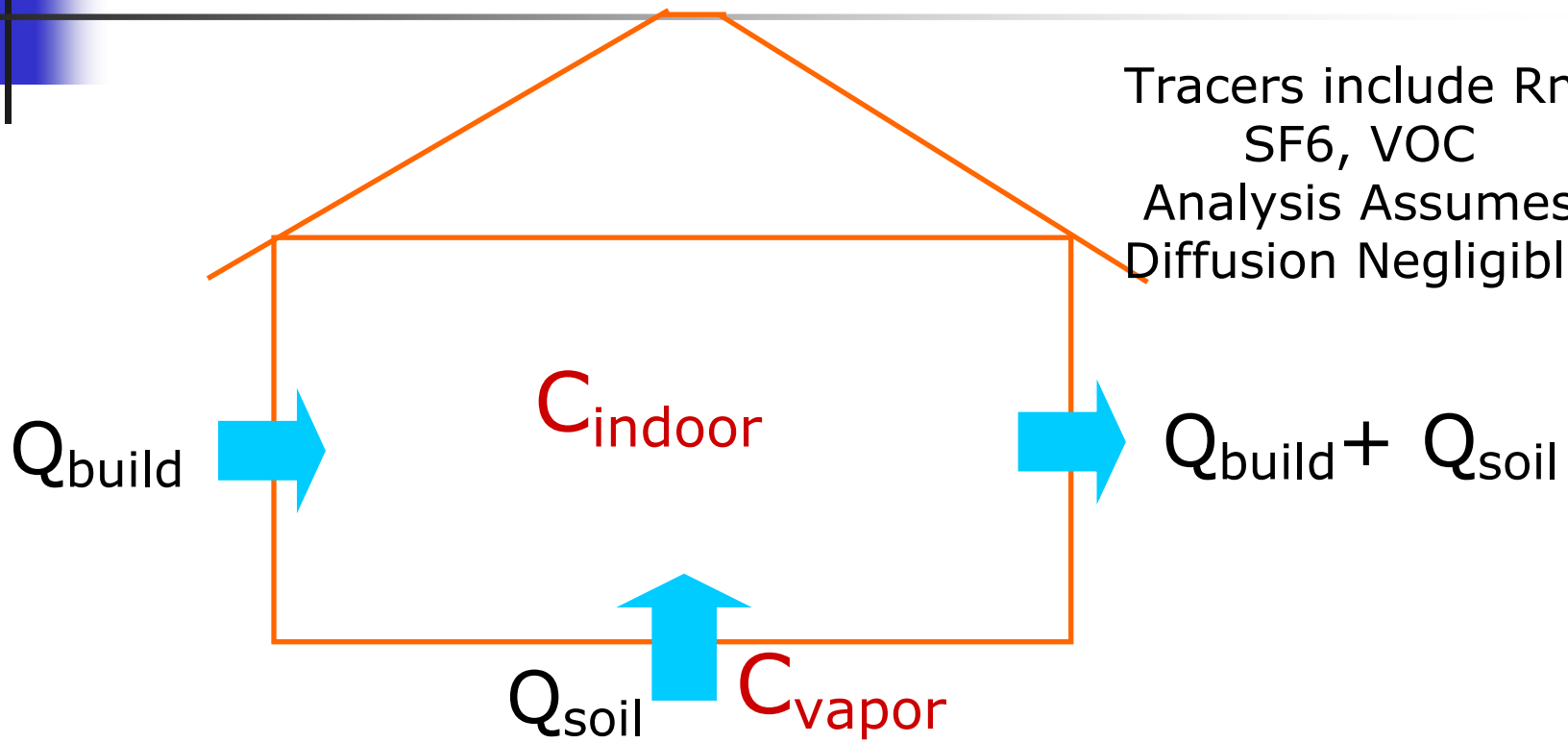
Mass Balance Calculations

Tracers include Rn, SF6, VOC
Analysis Assumes Diffusion Negligible



$\alpha = C_{indoor}/C_{vapor} \sim Q_{soil}/(Q_{soil}+Q_{build}) \sim Q_{soil}/Q_{build}$

If know Q_{build}, then can estimate Q_{soil}
Keep in mind tracer test α is for source directly below building

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Radon & Early VI Tracer Tests

Study	Building	Soil Type	Tracer	ΔP	Q_{soil}/Q_{build}	Q_{soil} (L/min)	Q_{soil}/Area (L/m^2)	Q_{soil}/Area-ΔP (L/m^2-Pa)
Olson & Corsi (2001)	House w\basement Paulsboro	Sand, some silt	SF_6	3.6 to 6.2	0.003 to 0.01	5.8 to 6.7	0.18 (6.2 Pa)	0.03
Mose & Mushrush (1999)	Houses Virginia	N/A	Radon	N/A	0.003 to 0.02	N/A	N/A	N/A
Hers (Chatterton) (1998)	Experimental Greenhouse	M. Sand	BTX	10 to 30	0.0003 to 0.0006	2.7 to 4.2	N/A	0.005 to 0.01
Fischer et al. (1996)	Small Commercial Building	F. Sand	SF_6	3	0.0002 to 0.0004	1.4 [1]	0.018	0.006
Garbesi et al. (1993)	Small Experimental Basement	F. Sand	N/A	10	N/A	9.7		0.04
Little et al. (1992)	Houses USA	N/A	Radon	N/A	0.0016 (Avg)	N/A	N/A	N/A
Garbesi & Sextro (1989)	House w\basement	Sandy Loam to Loamy Sand	SF_6	30	~0.001	67 (Best)	N/A	0.01(Best)
Rezvan et al. (1989)	Houses	Gravel	Rn	N/A	0.0079 to 0.045	17 to 96[2]	N/A	N/A

1 Estimated by Fischer et al (1996) from wind-loading (Qbuilding not available)
2 Estimated using assuming values for house volume (366 m3) and AEH (0.35/hr) (Qbuilding not available)
3 Cyclohexane, MTBE, Pentane, 2,2,4-Trimethylpentane

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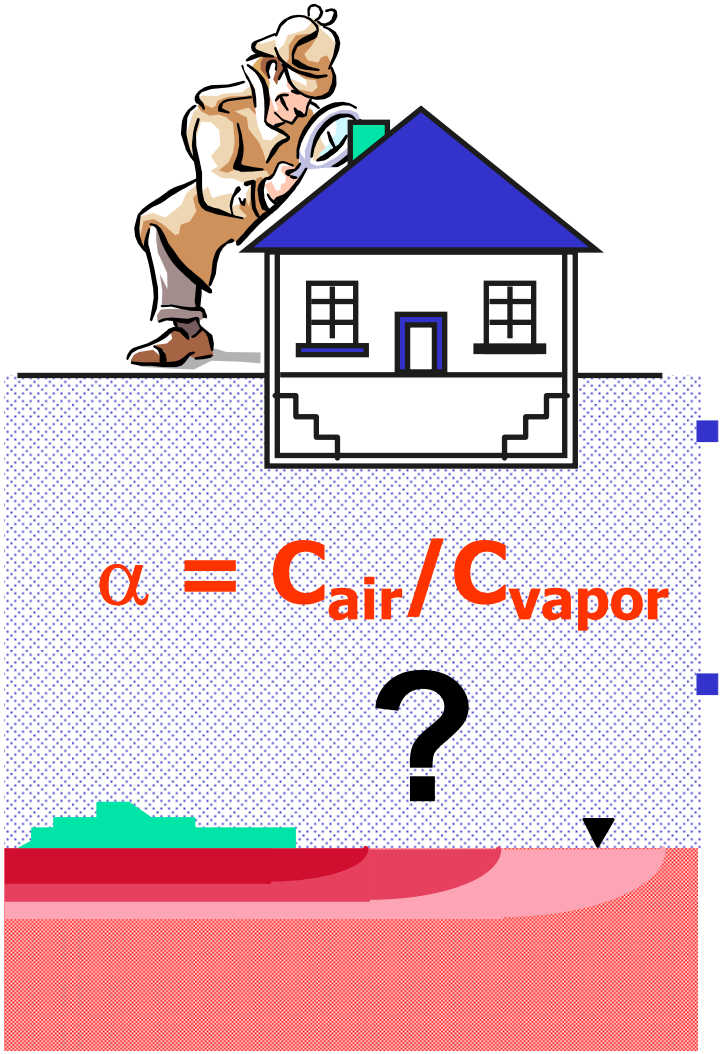
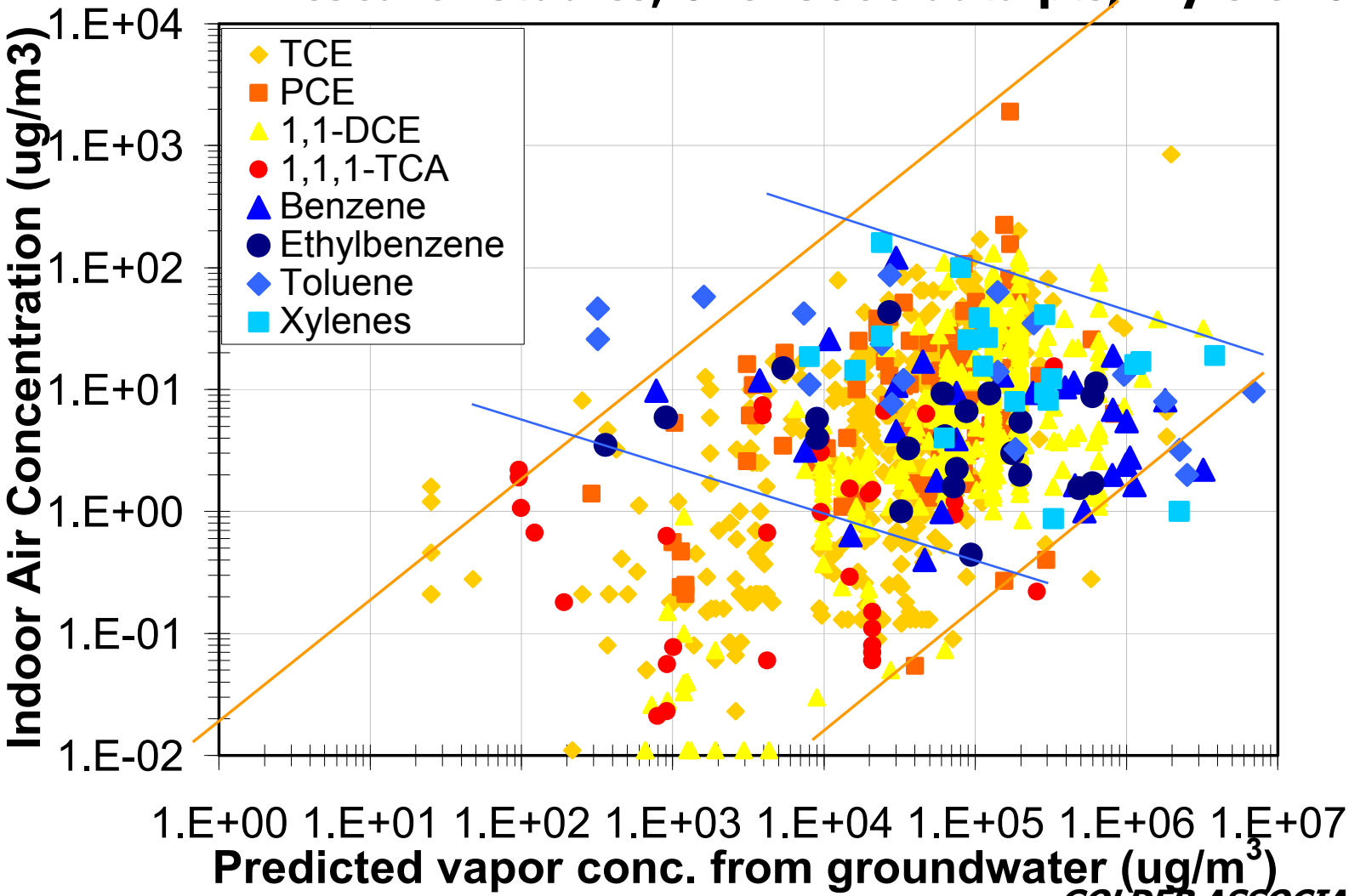
Empirical Data Analysis



- USEPA Database (2004-2008)[1]
  - Over 42 sites, > 2000 data points
  - Analysis of attenuation factors
  - Data evaluation & filtering process was essential to address bias data due to background and poor quality data
- Health Canada
  - BTEX data added in 2009[1]
  - Current adding chlorinated solvent data
- Empirical analysis has helped to:
  - Develop screening criteria
  - "Validate" J&E model

Empirical Data
(USEPA, 2007 database + Health Canada)

2 research studies, over 3000 data pts, 4 yrs effort



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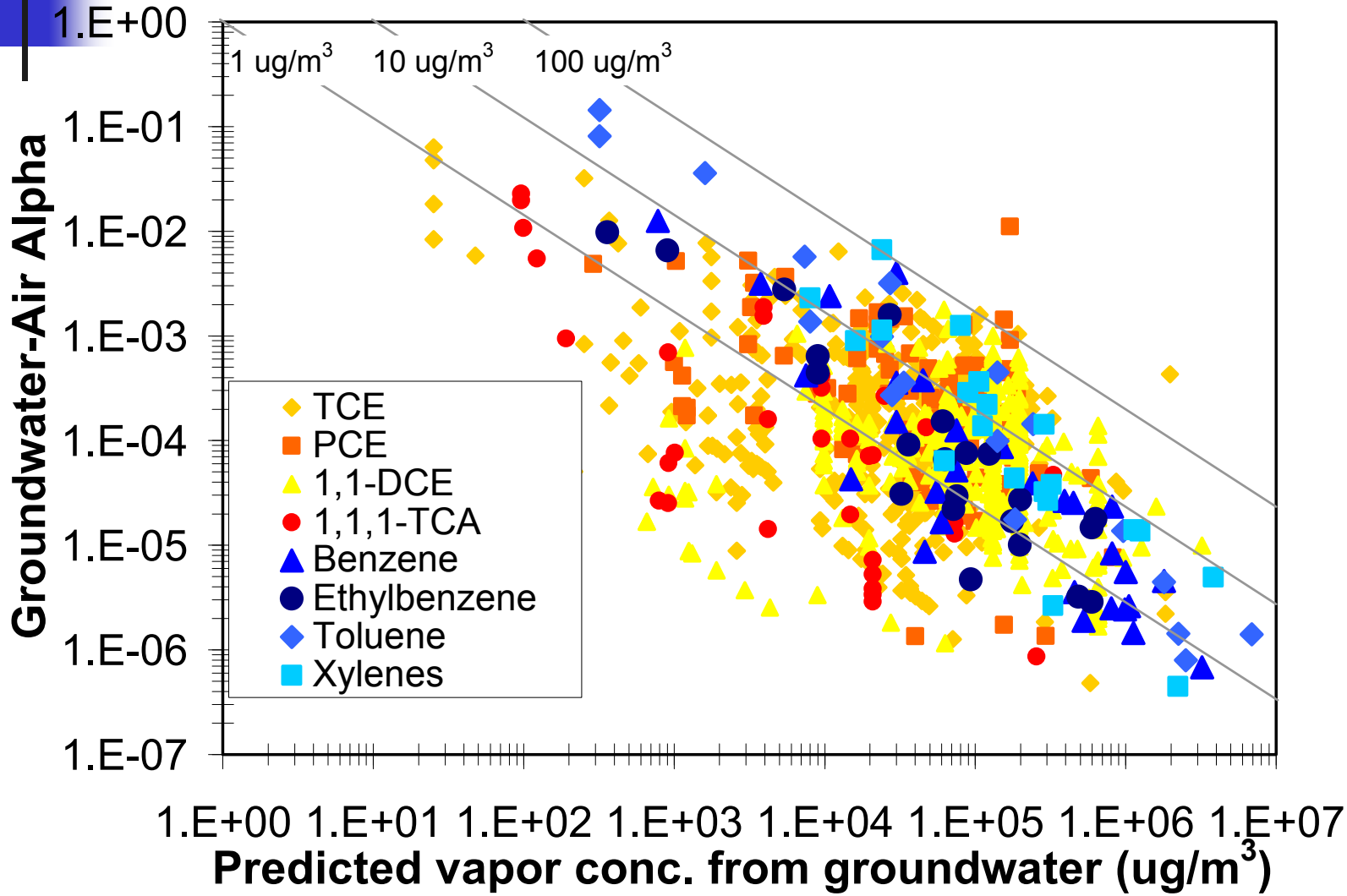
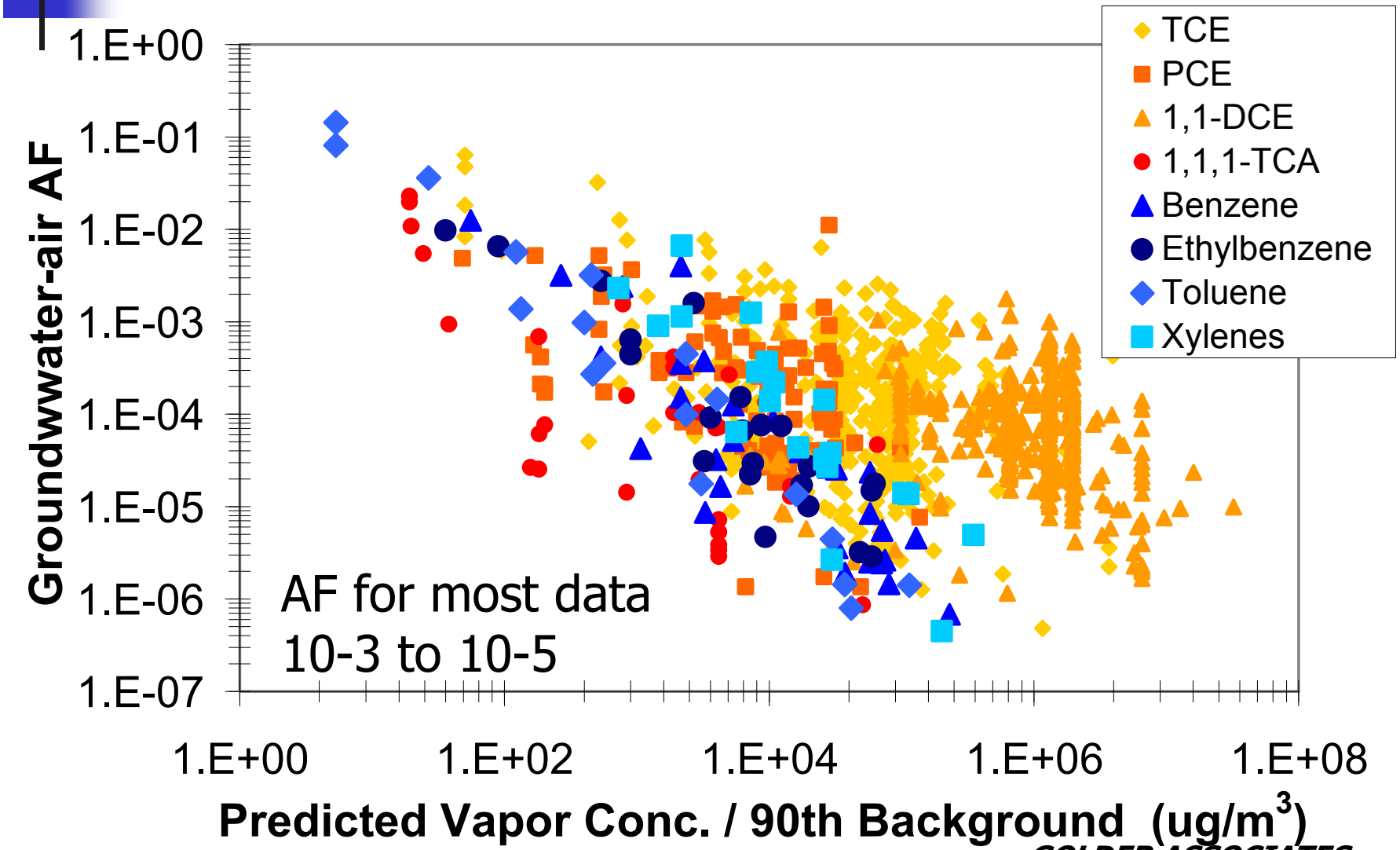
Empirical Data
(USEPA, 2007 database + Health Canada)



Empirical Data
(USEPA, 2007 database + Health Canada)



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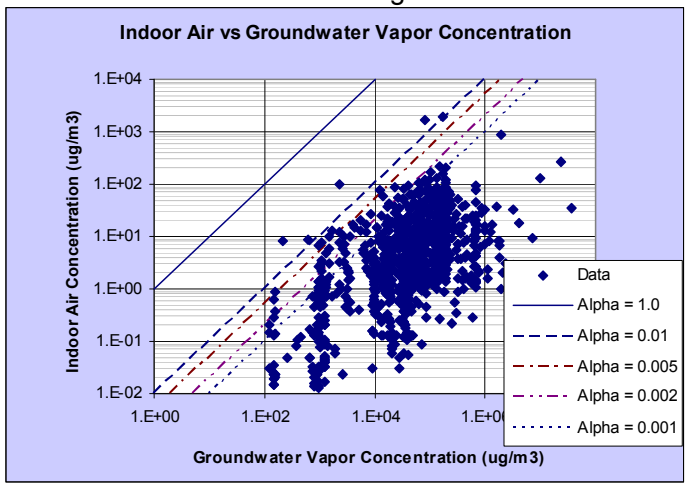
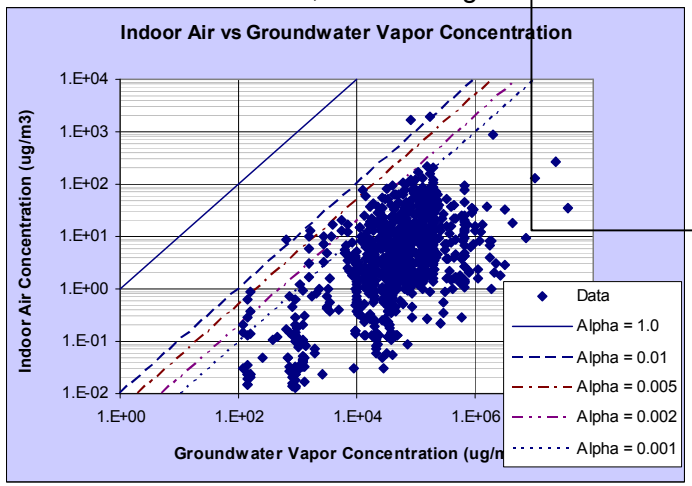
Groundwater-Air Attenuation Factor

Progressive Filtering on Source Strength

GW > 100 X Background

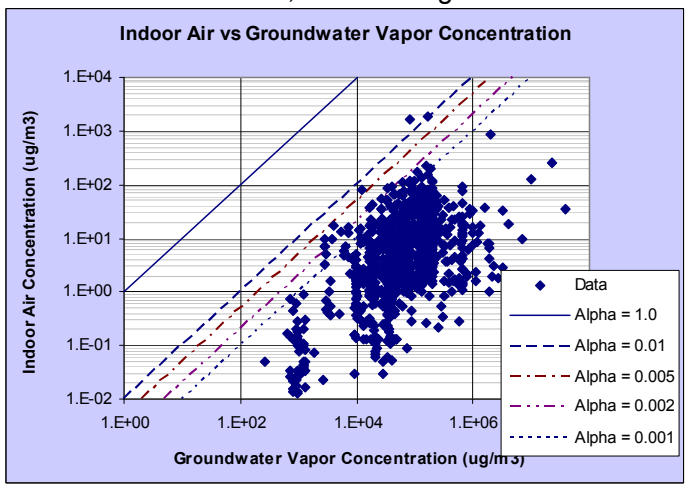


GW > 1,000 X Background

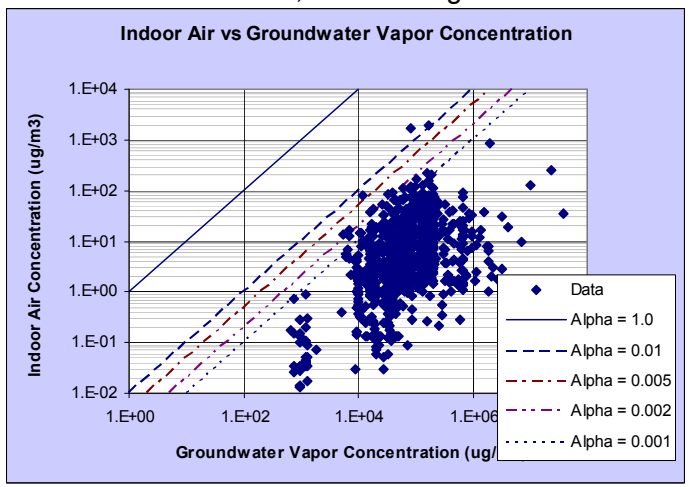


Vapour predicted from GW Conc > Multiplier x 90th literature background

GW > 5,000 X Background



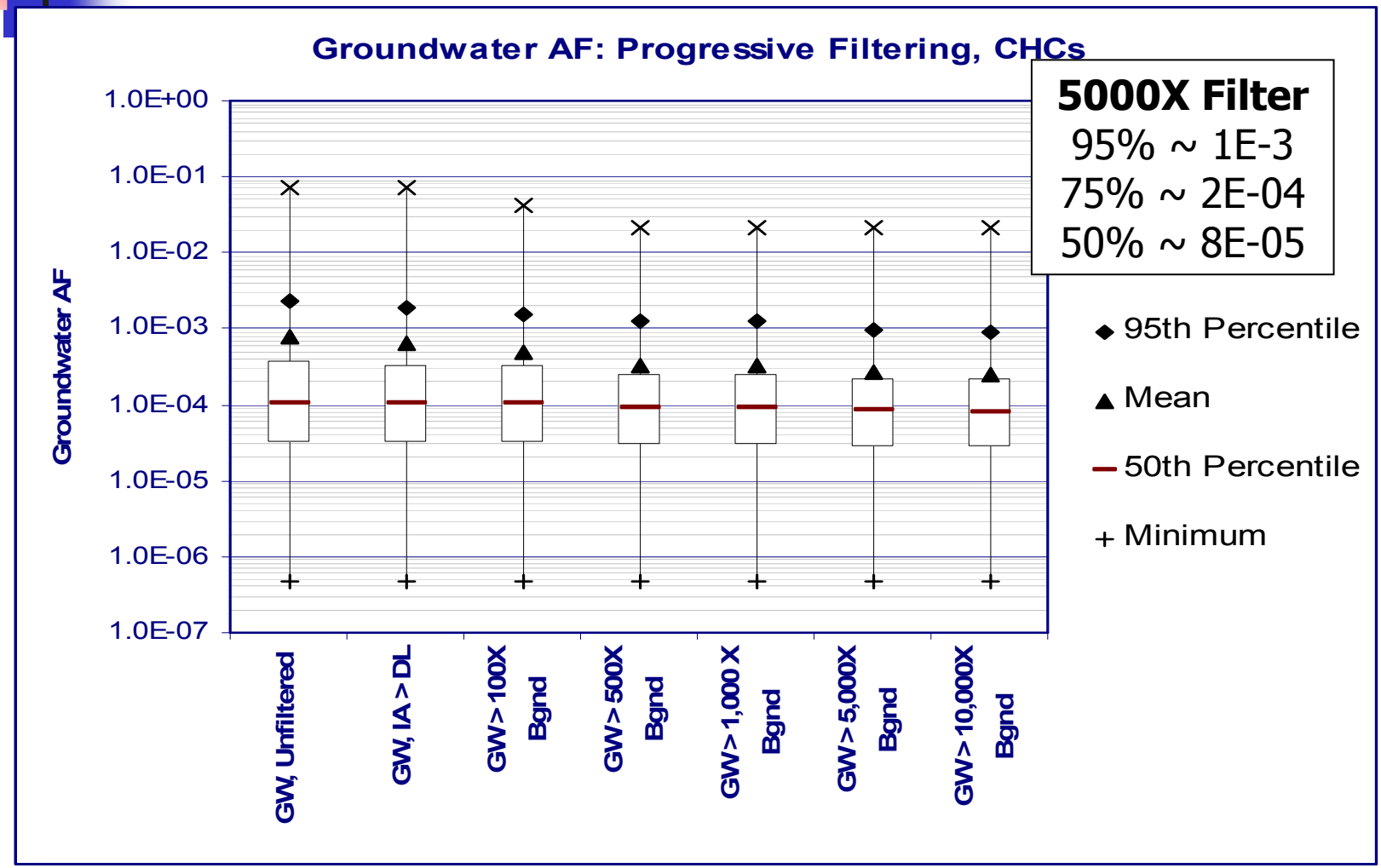
GW > 10,000 X Background



Study by Helen Dawson, Ian Hers, Robert Truesdale, presented AWMA Conference, Rhode Island, Sept 2007

Groundwater-Air Attenuation Factor

Progressive Filtering on Source Strength

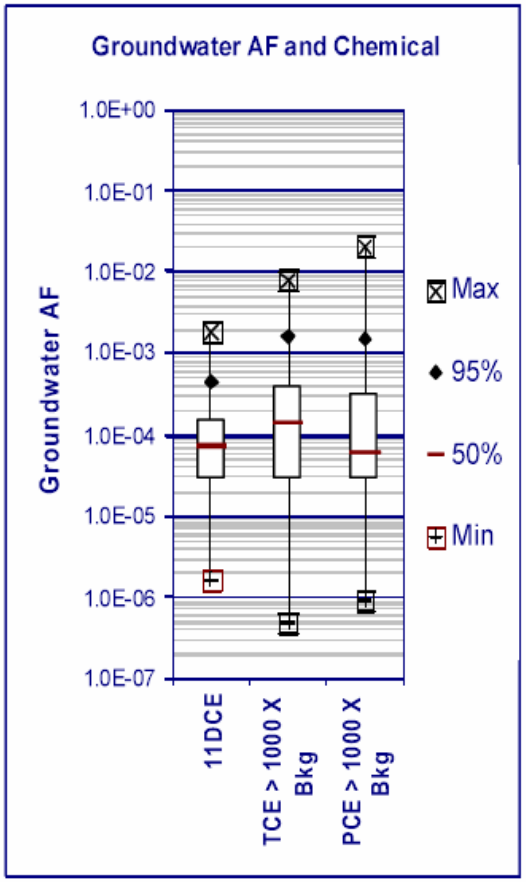


AF = indoor air/vapour conc. from groundwater

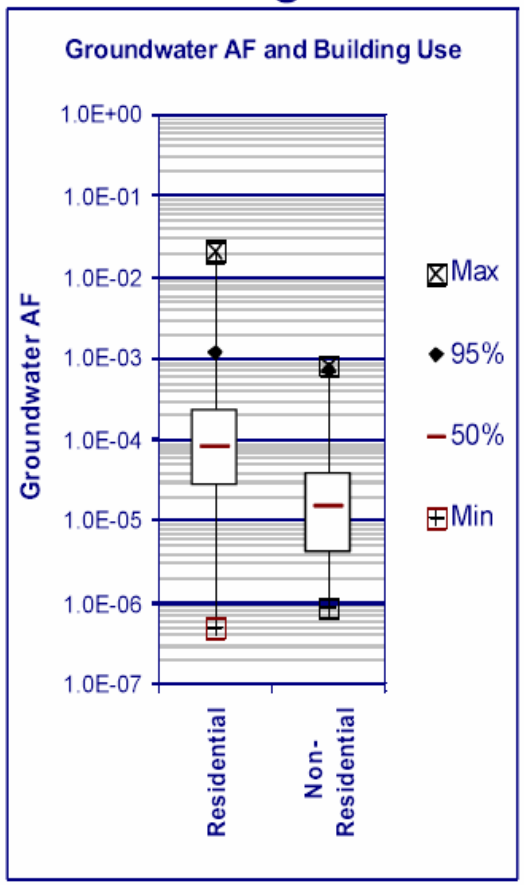
Groundwater-Air Attenuation Factor

Progressive Filtering on Source Strength

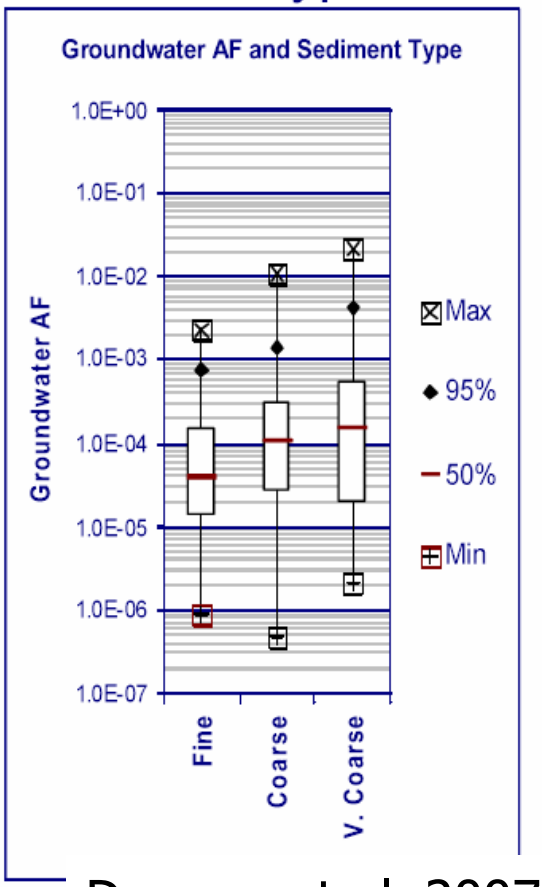
Chemical



Building Use



Soil Type

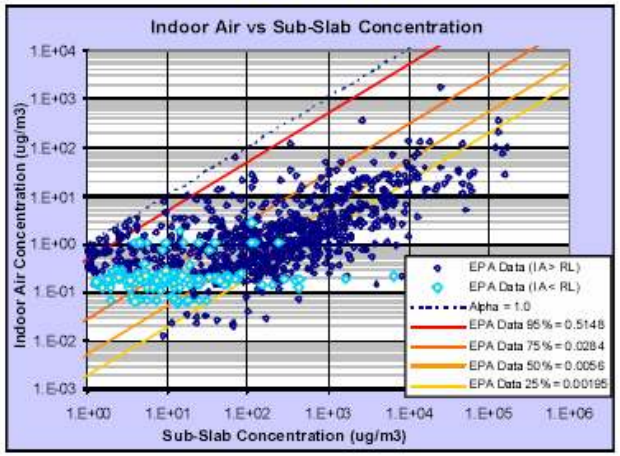


Dawson et al, 2007

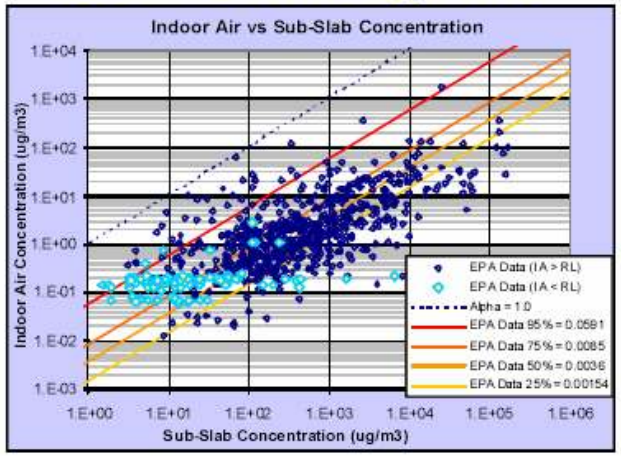
Subslab-Air Attenuation Factor

Progressive Filtering on Source Strength

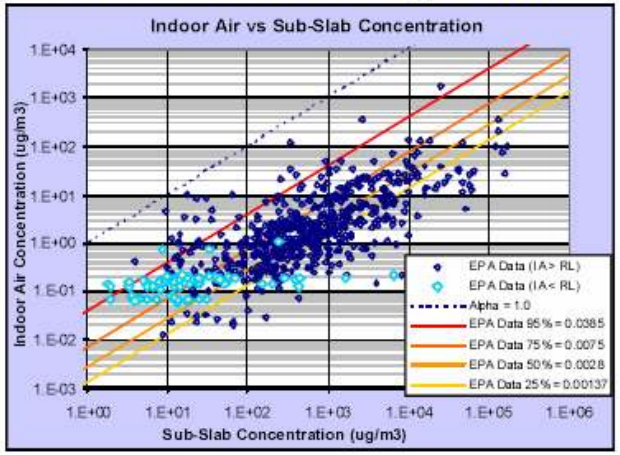
Css > DL



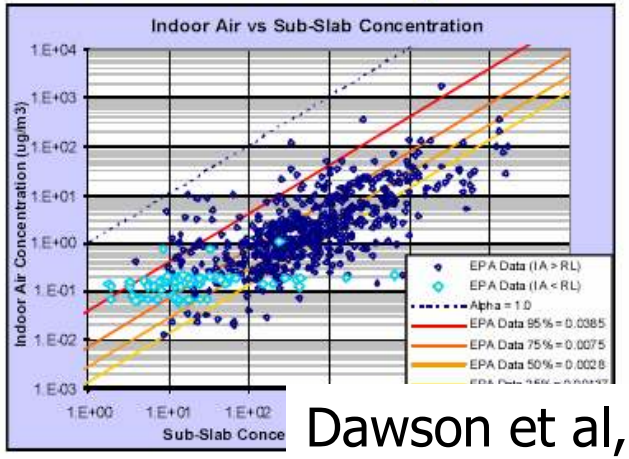
Css > 10 X Background



Css > 30 X Background



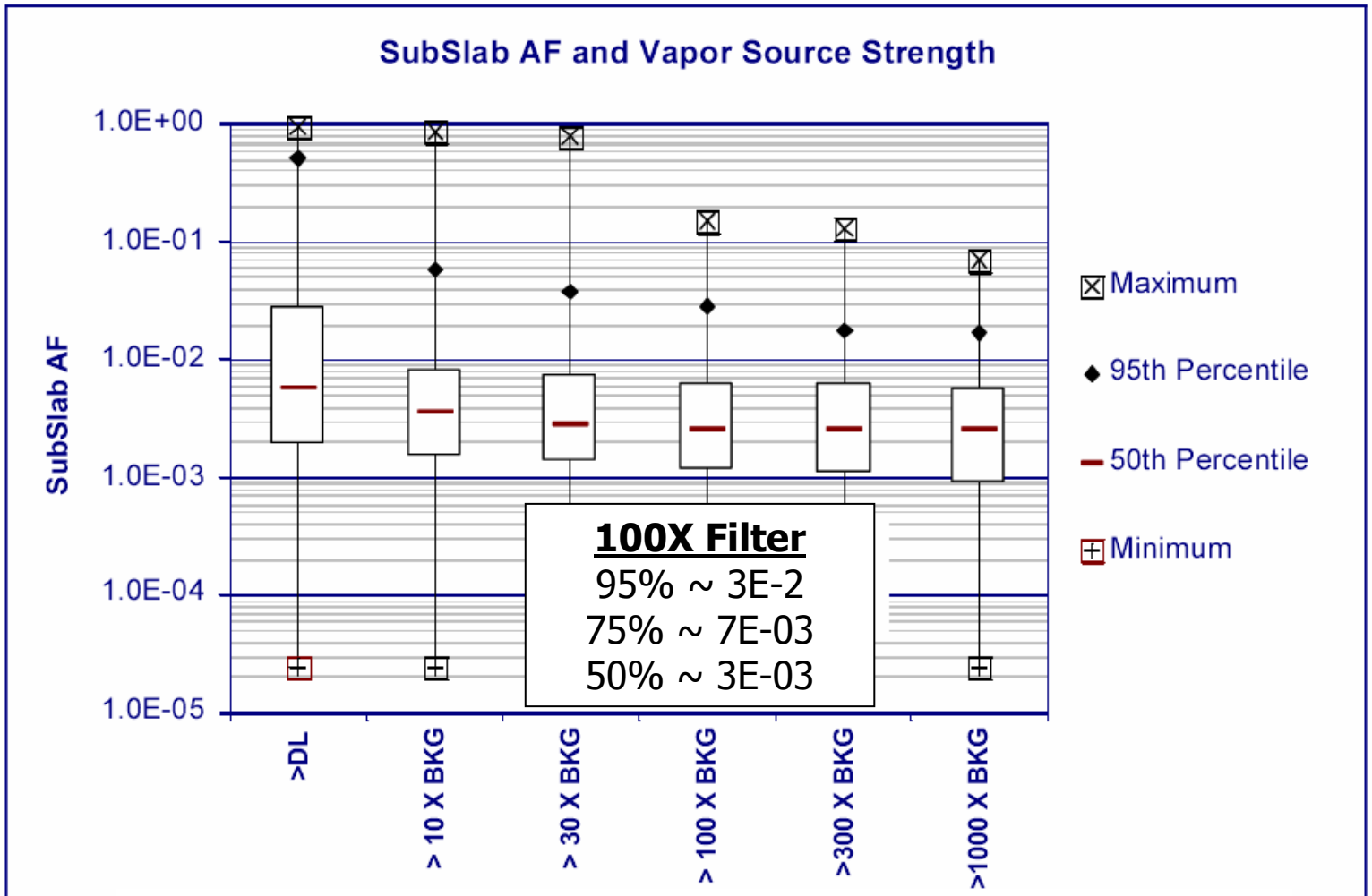
Css > 100 X Background



Dawson et al, 2007

Subslab-Air Attenuation Factor

Progressive Filtering on Source Strength

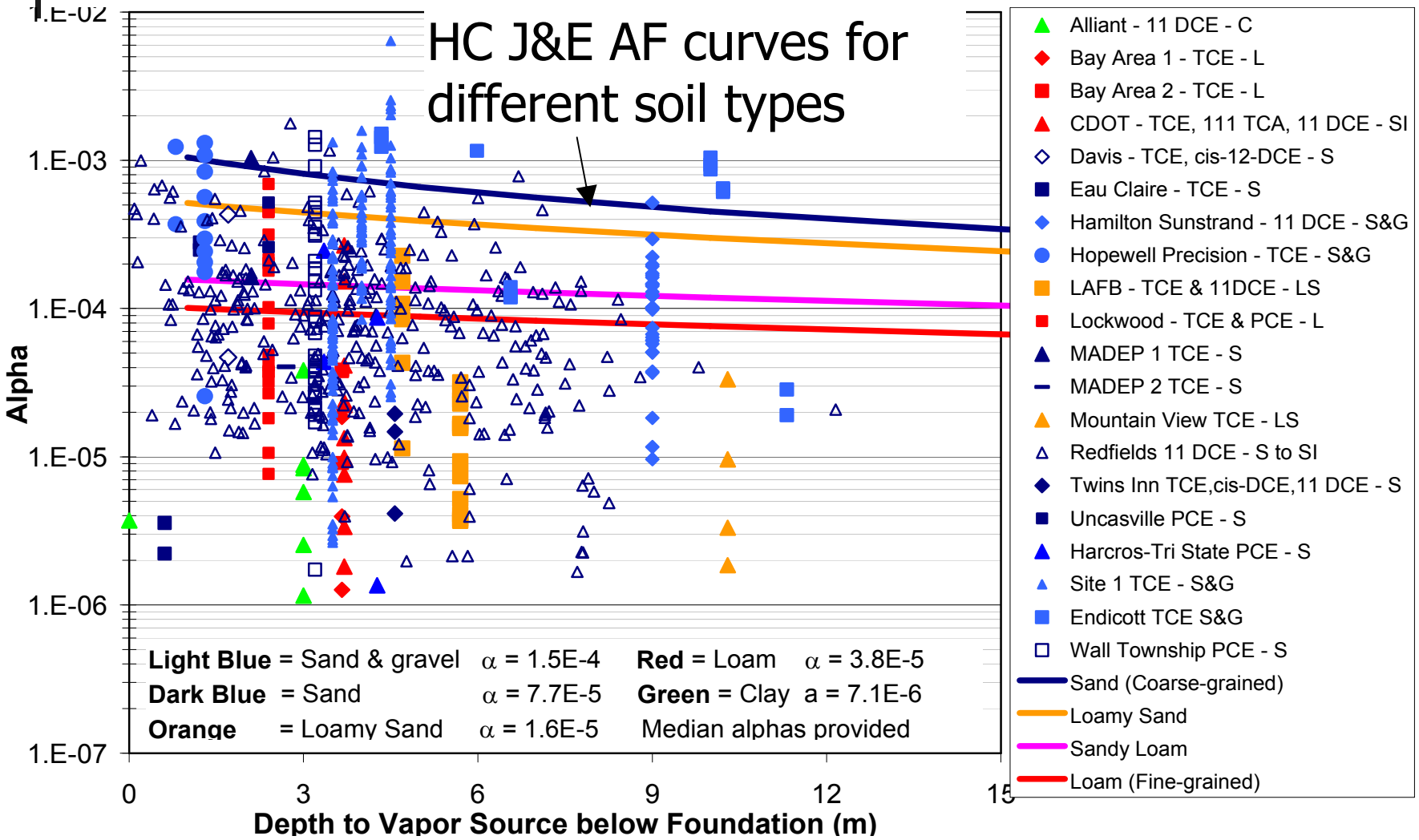


Filtered dataset 440 data points, 88% residential, 12% commercial (little difference in commercial data)

2007

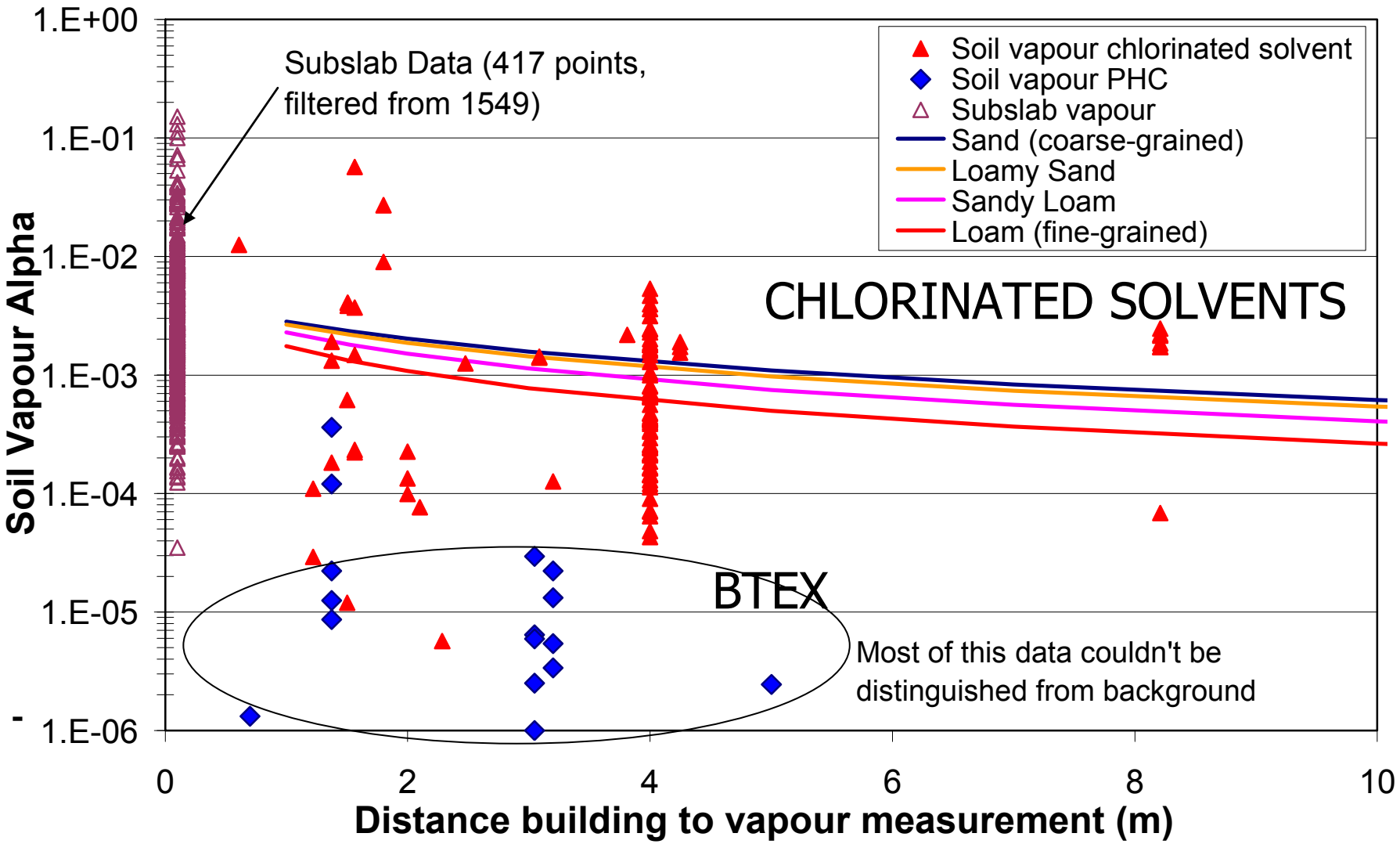
Health Canada Validation
J&E Groundwater AFs

(chlorinated solvents, filtered >5,000-10,000 background,2007 data)

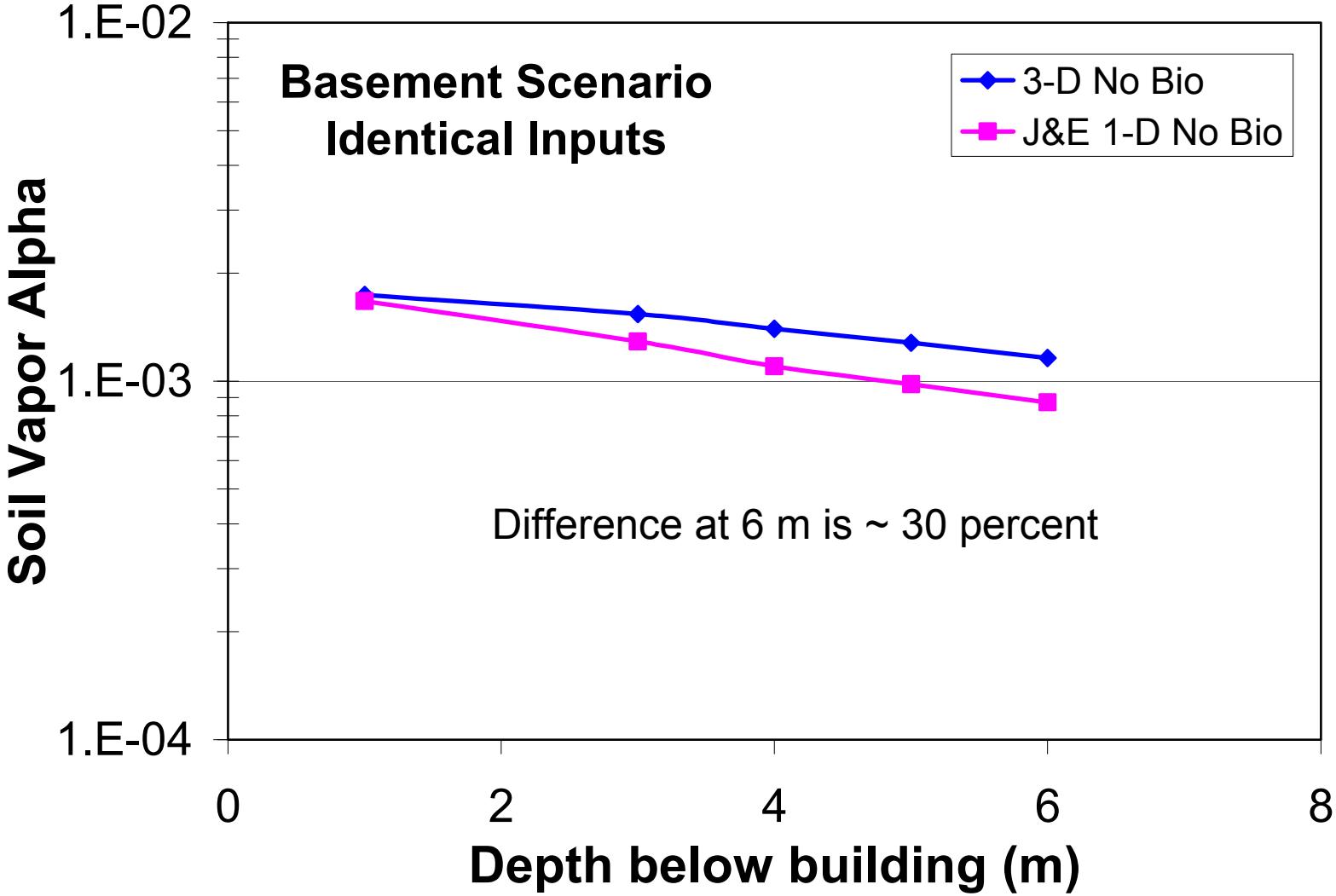


Health Canada Validation J&E Soil Vapour AFs

(chlorinated solvents, filtered >100-1000 background, 2007 data)



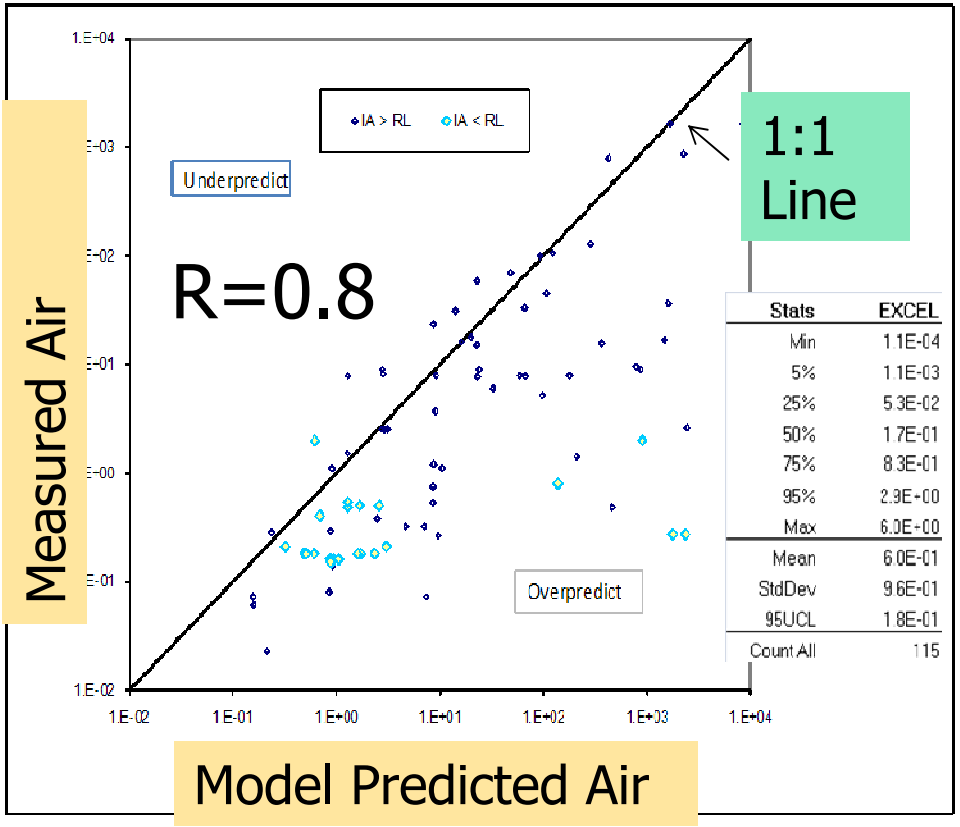
Comparison 3-D & J&E (1-D) Model



Health Canada 2010 Study

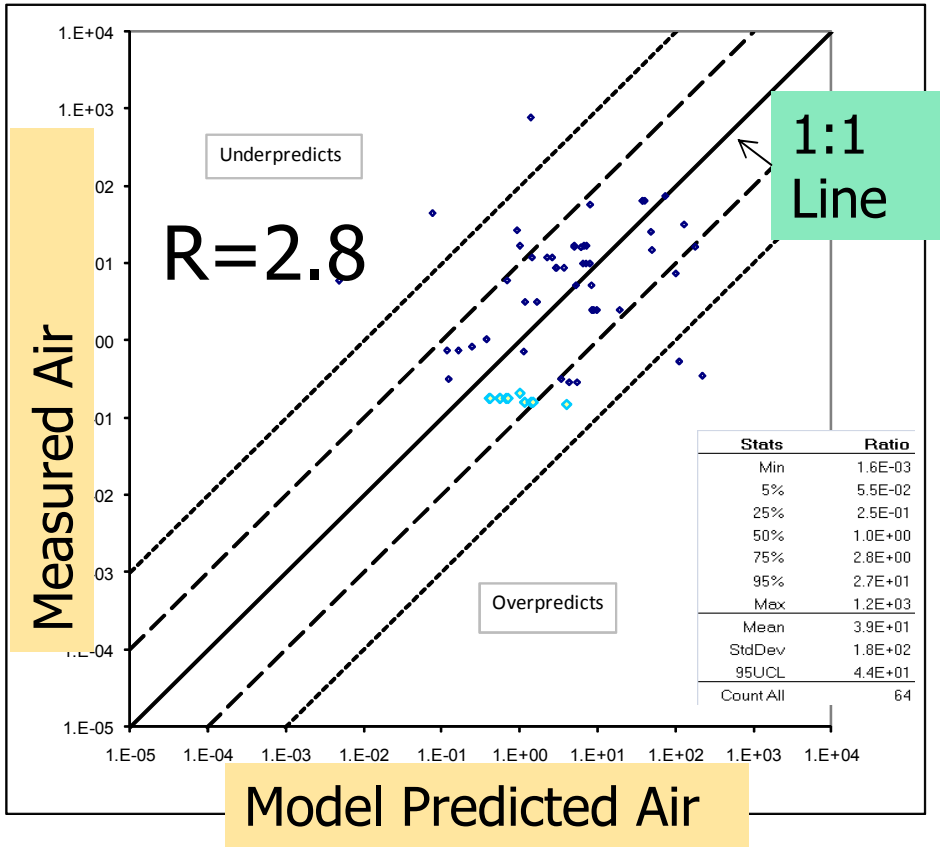
(chlorinated solvents)

Groundwater (1000X background filter)



Stats	EXCEL
Min	1.1E-04
5%	1.1E-03
25%	5.3E-02
50%	1.7E-01
75%	8.3E-01
95%	2.9E+00
Max	6.0E+00
Mean	6.0E-01
StdDev	9.6E-01
95UCL	1.8E-01
Count All	115

Soil Vapour (100X background filter)



Stats	Ratio
Min	1.6E-03
5%	5.5E-02
25%	2.5E-01
50%	1.0E+00
75%	2.8E+00
95%	2.7E+01
Max	1.2E+03
Mean	3.9E+01
StdDev	1.8E+02
95UCL	4.4E+01
Count All	64

R = 75th percentile Measured/Predicted

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Golder projects commercial subslab alpha data

Site	Location	Building Type	Building Foundation	Date	Chemical	Sampling ID	Subslab Vapour (ug/m^3)	Indoor Air (ug/m^3)	Empirical Alpha
1	Vancouver	Industrial	Slab-at-grade	Feb-08	PCE	Location 1	2350000	270	1.1E-04
						Location 2	44000	58	1.3E-03
						Location 3	120000	53	4.4E-04
						Location 4	240000	19	7.9E-05
						Location 5	96	47	4.9E-01
2	Victoria	Commercial (shopping mall)	Slab-at-grade	Nov-07	TCE	Location 1	920	0.25	2.7E-04
						Location 2	1600	0.16	1.0E-04
						Location 3	1600	0.2	1.3E-04
						Location 4	920	5.1	5.5E-03
3	Surrey	Commercial (shopping mall)	Slab-at-grade	N/A	PCE	Location 1	236000	5.2	2.2E-05
						Location 2	52000	14	2.7E-04
4	Vancouver	Commercial (shopping mall)	Slab-at-grade	Feb-06	PCE	Location 1	9340000	55	5.9E-06
							50th percentile		2.0E-04

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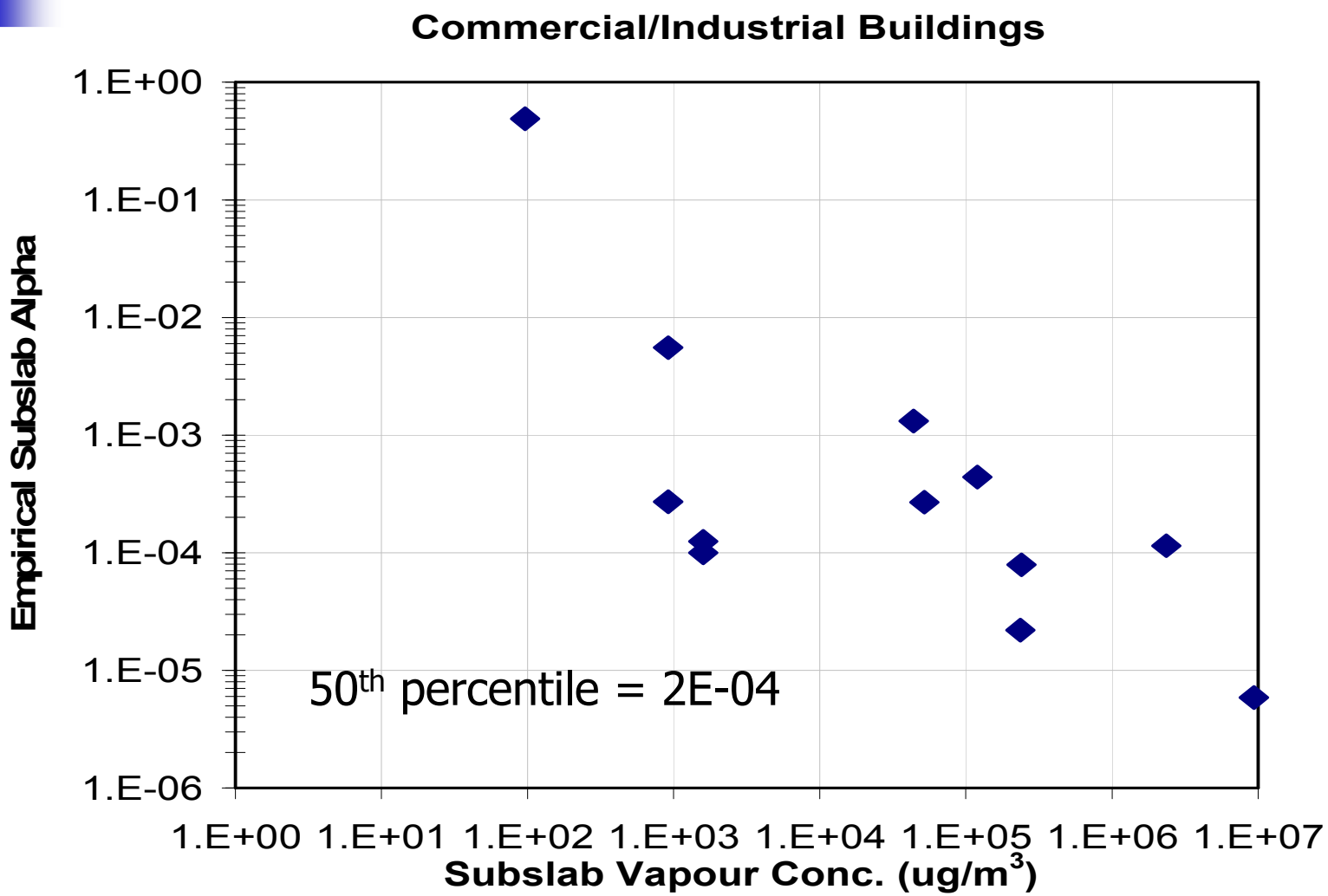
Golder projects commercial subslab alpha data



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Empirical Data and Modeling Conclusions

- There is much variability in empirical data – this has led some to conclude should test indoor air (but there are limitations with this approach)
- Comparison of Health Canada J&E Model defaults to 75th percentile empirical data indicate:
  - Chlorinated solvents: J&E Reasonable approximate predictor of ***groundwater to indoor air attenuation*** factors but slightly underpredicts ***soil vapour to indoor air attenuation*** factors, but predictions improve when using deep near source vapour data or maximum data
  - Petroleum hydrocarbons: J&E overpredicts attenuation factors for petroleum hydrocarbon compounds

Model Summary
(more than just J&E!)

MODEL TYPE		Diffusion	Gas-Phase Advection	Water Infiltration	Sorption	Biodegradation	Crawlspace	Source Depletion	Slab Resistance	Building mixing	Comments
STEADY STATE 1-D ANALYTICAL											
Johnson and Ettinger (1991)	US	X	X					X	X	X	Source depletes by mass removed
ASTM (1995)	US	X							X	X	
Ferguson et al (1995)	UK	X	X					X	X	X	Source degrades by 1st-order model
Johnson Dominant Layer 1st-order BIO ('98)	US	X	X			X			X	X	
Johnson O_2-limited 1st-order BIO (2000)	US	X	X			X			X	X	
Volasoil (2000)	NL	X	X				X		X	X	Includes advection in vadose zone
Parker biodegradation model (VAPEX) (2003)	US	X				X				X	
Devaull O_2-limited 1st-order BIO (2007)	US	X	X			X			X	X	BioVapor Model ES&T 2007 (41)
TRANSIENT 1-D ANALYTICAL											
Jury et al. (1983, 1990)	US	X		X	X	X					
Sanders and Stern (1994)	US	X	X		X	X					
Robinson & Tuczynowicz (2005)	AUS	X			X	X	X			X	
NUMERICAL											
Lahvis and Baehr (R-UNSAT)	US	X		X	X	X					
Mendoza 2-D (VapourT)	CAN	X	X		X						
Hers 2-D (2000, 2000)	CAN	X	X		X	X					
Abreu and Johnson 3-D ASU (2005, 2006) (US	US	X	X		X	X			X	X	
Pennell 3-D Brown University (2007)	US	X	X		X	X			X	X	
Mayer Jourabachi 3-D UBC (2010)	CAN	X	X	X	X				X	X	Multi-component included(CH_4, CO_2)

Site Specific Modeling

- J&E model appropriate starting point for chlorinated solvents, for groundwater and soil vapour
- Need guidance on reasonable ranges for inputs and estimation methods, e.g., soil-air permeability tests, differential pressure measurements, building ventilation, etc.
- Better model needed for different foundations e.g. crawlspace
- For petroleum hydrocarbons, J&E generally too conservative, for soil important to use model that includes source depletion (e.g., Jury or Robinson and Turcynowicz)

Software Modeling Tools

1. Health Canada Preliminary Detailed Quantitative Risk Assessment (PQRA & DQRA J&E spreadsheets)
2. USEPA Superfund Spreadsheets
3. RISC Model 4 (Developed for BP by Lyn Spense)
4. GSI Toolkit
5. Golder J&E-BIO Spreadsheet
6. BioVapor Model (DeVaull model, details in Biodegradation section)
7. Abreu-Johnson 3-D numerical Model (with building)
8. VapourT (2-D numerical model, no building)
9. Probabilistic models (Crystal Ball, Gold Sim)?
10. Virginia Trench Model (construction worker)

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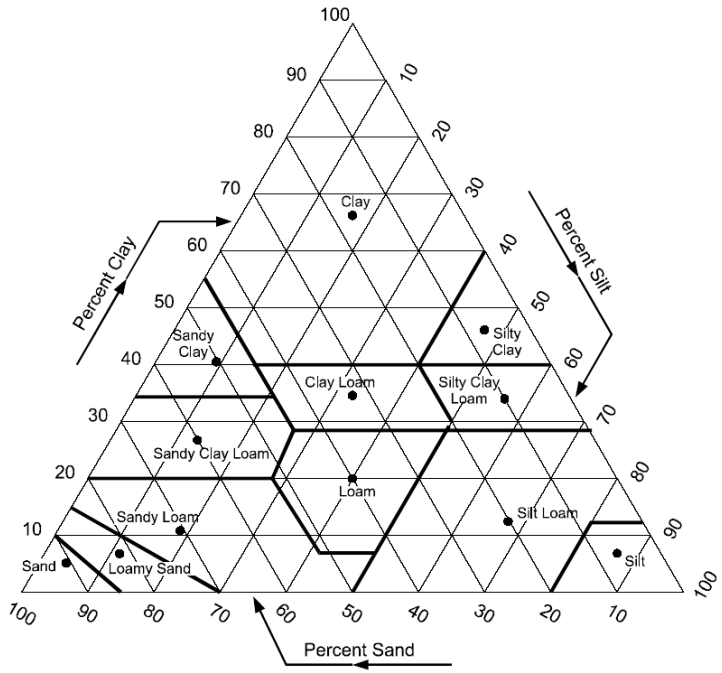
Guidance on J&E Inputs
(θ_w & S= θ_w/θ_t)

Measure

- Undisturbed sample, measure moisture content and bulk density
- Challenges are non representativeness if beside building and temporal change

HC/USEPA Approach

1. Grain size test
2. Soil type from textural triangle
3. Estimate water-filled porosity from VG model defaults (previous slides)



If you are going to use measured values, take samples below building or make sure do not deviate too far from HC defaults

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Guidance on J&E Inputs – USEPA Spreadsheet

U.S. Soil Conservation Service (SCS) Soil Texture	Total (Saturated) Porosity θ_s (cm^3/cm^3)	Unsaturated Zone: Residual Water-Filled Porosity θ_r (cm^3/cm^3)	Unsaturated Zone: Field Capacity Water-Filled Porosity 1/3 bar 333	Unsaturated Zone: Mean Water-Filled Porosity $(FC_{1/3bar}+\theta_r)/2$ $\theta_{w,unsat}$ (cm^3/cm^3)	Capillary Transition: $\theta_{w,cap}$ Cap @ air-entry $\theta_{w,cap}$ (cm^3/cm^3)	Capillary Transition: Height Cap Zone Fetter (94) (cm)
Clay	0.459	0.098	0.33	0.215	0.412	81.5
Clay Loam	0.442	0.079	0.26	0.168	0.375	46.9
Loam	0.399	0.061	0.24	0.148	0.332	37.5
Loamy Sand	0.39	0.049	0.10	0.076	0.303	18.8
Silt	0.489	0.05	0.28	0.167	0.382	163.0
Silt Loam	0.439	0.065	0.30	0.180	0.349	68.2
Silty Clay	0.481	0.111	0.32	0.216	0.424	192.0
Silty Clay Loam	0.482	0.09	0.31	0.198	0.399	133.9
Sand	0.375	0.053	0.055	0.054	0.253	17.0
Sandy Clay	0.385	0.117	0.28	0.197	0.355	30.0
Sandy Clay Loam	0.384	0.063	0.23	0.146	0.333	25.9
Sandy Loam	0.387	0.039	0.17	0.103	0.320	25.0
Loamy Sand	0.39	0.049	0.10	0.076	0.303	18.8

- **Van Genuchten water-retention model used with Schaap & Leij curve fit parameters**
- **USEPA semi-site specific alpha curves are for four representative soil types**

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Guidance on J&E Inputs
(θ_w & S= θ_w/θ_t)

Johnson (2005) Critical Parameters[3]

- S_{sand}: 0.05 to 0.1
- $S_{mixtures\ sands,\ silts,\ clays}$: 0.1 to 0.28
- S_{clays}: 0.28 to 0.54

Advanced estimation approaches (rare for VI)

- Estimate from grain size & other soil properties using ROSETTA[1] (free USDA software) or SOILPARA[2]
- Data mining - SoilVision and API soil parameter database (match database to site physical properties
- Measure Van Genucthen parameters undisturbed soil samples (capillary tests>$500)

[1] http://www.ussl.ars.usda.gov/MODELS/rosetta/rosetta.htm.

[2] http://www.scisoftware.com/products/soilpara_details/soilpara_details.html

[3] Johnson, P. 2005. Identification of Critical Parameters for the Johnson and Ettinger (1991) Vapor Intrusion Model, GWMR, Spring.

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Guidance on J&E Inputs: Qsoil & Qs/Qb

1. Simplest approach is to adjust Qs so that the Qs/Qb stays approximately equal to the Health Canada defaults for attenuation factor curves
2. Scale default Q_s relative to building area
3. Use Perimeter Crack model to estimate Q_s
   - Should consider measuring soil-air permeability and differential pressure between building and air

- Recommend $Q_s/Q_b = 10^{-4}$ to 10^{-2}, with values toward upper end of range for coarse-grained soils and value toward lower end of range for fine-grained soil

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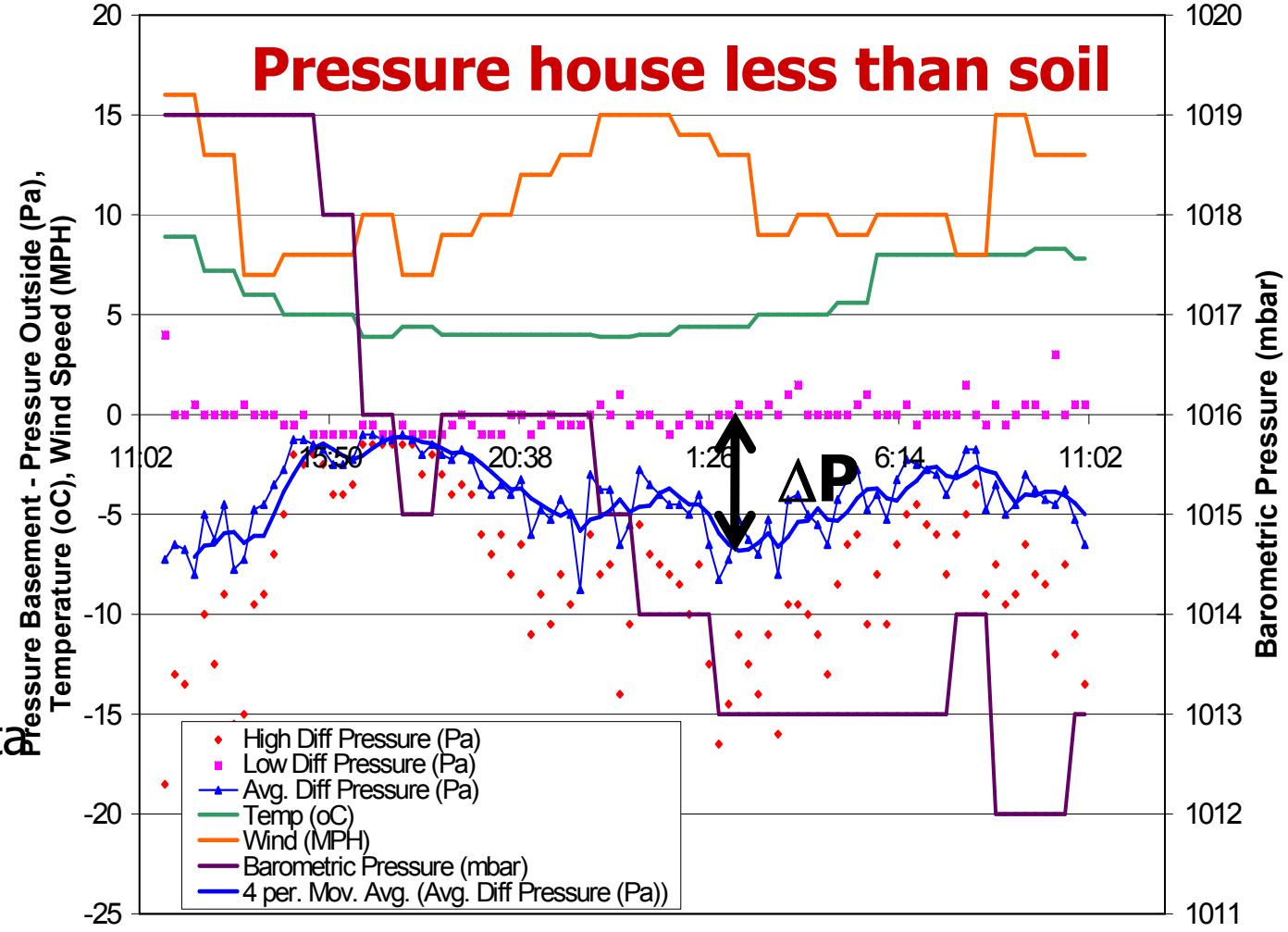
Guidance on J&E Inputs: Measuring ΔP



Some questions: data representativeness? Use average value?

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Guidance on J&E Inputs: Building Mixing Height

- Function building height, leakage/mixing between floors, HVAC system (forced air versus electric heat?)
- Data suggests vapour well mixed within floors but stratification across floors, some data below:
  - Stafford (n=1): 2nd floor = 30% of basement
  - CDOT: 2nd floor = 20% of basement (apartments)
  - NY (n=6): 2nd floor = 53% of basement
  - Ogden (n=8): 2nd floor = 40% of basement
- Health Canada default = 3.6 m for 2-level house (50% reduction)

H not equal to V/A defined in Johnson's critical parameters paper – see extra slides

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Guidance on J&E Inputs: Air Exchange Hour (AEH)

- Processes are natural ventilation, infiltration and mechanical ventilation
- Depends on house construction, house use, HVAC system, season, climatic region
- Reported rates are 0.1 AEH for energy efficient "air-tight" houses to over 2 AEH[1]
- Avg. 3 residential CAN Studies: 0.36, 0.41, 0.44 AEH
- Murray & Burmaster (US residential, all seasons)
  - 10th = 0.21 AEH; 50th = 0.51 AEH; 90th = 1.48 AEH
- Health Canada default = 0.35 AEH residential, 1 AEH

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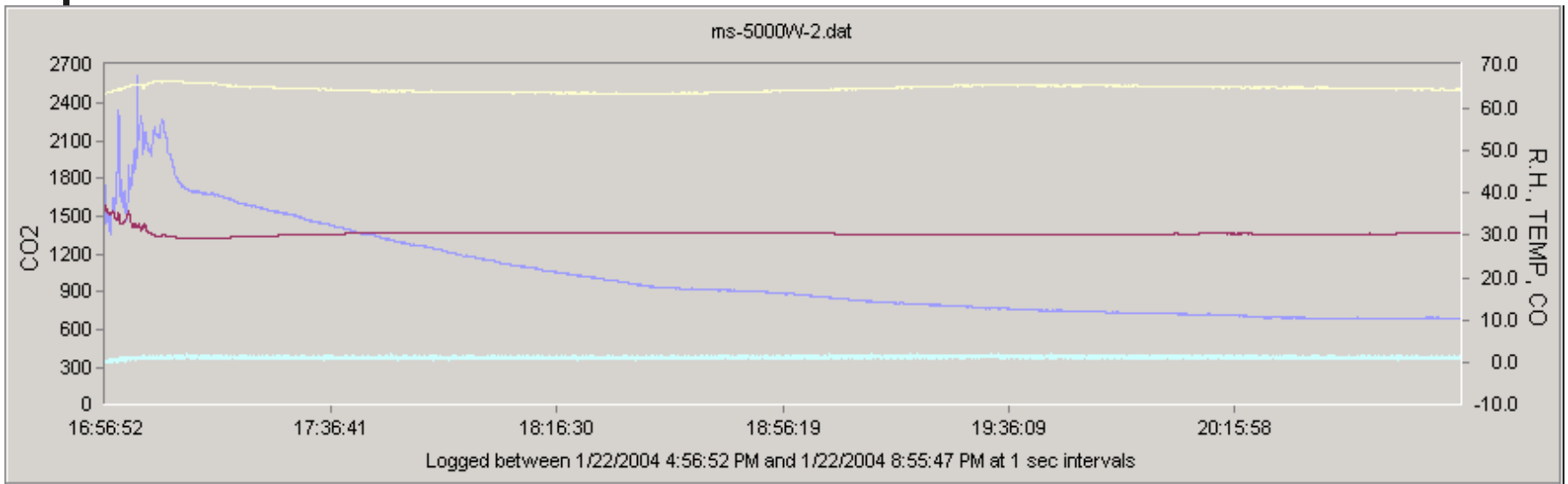
Guidance of J&E Inputs: CO_2 Ventilation Tracer Test



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
CO2 (ppm)	16:56:52	16:56:53	16:56:54	16:56:55	16:56:56	16:56:57	16:56:58	16:56:59	16:57:00	16:57:01	16:57:02	16:57:03	16:57:04	16:57:05	16:57:06	16:57:07	16:57:08	16:
	1685	1677	1679	1690	1711	1727	1745	1755	1752	1736	1708	1672	1631	1591	1549	1512	1483	
R.H. (%)	16:56:52	16:56:53	16:56:54	16:56:55	16:56:56	16:56:57	16:56:58	16:56:59	16:57:00	16:57:01	16:57:02	16:57:03	16:57:04	16:57:05	16:57:06	16:57:07	16:57:08	16:
	36.5	36.6	36.6	36.7	36.8	36.9	37.0	37.0	37.0	36.9	36.7	36.6	36.4	36.2	36.0	35.9	35.9	
TEMP (degF)	16:56:52	16:56:53	16:56:54	16:56:55	16:56:56	16:56:57	16:56:58	16:56:59	16:57:00	16:57:01	16:57:02	16:57:03	16:57:04	16:57:05	16:57:06	16:57:07	16:57:08	16:

CO2 (ppm) R.H. (%) TEMP (degF) CO (ppm)

ASTM E-741-00. 2000. Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution

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Guidance on J&E Input: Building Standard Ventilation Requirements

- AS 1668, Mechanical Ventilation for Acceptable Indoor Air Quality
- ASHRAE Standard 62-2004 Ventilation for Acceptable Indoor Air Quality
  - School: 13-15 cfm/person
  - Office: 17 cfm/person
  - Correctional facility: 10 cfm/person
  - General or office conference room: 6 cfm/person
- Blower door test and Lawrence Berkeley Lab Infiltration Model, accounts for wind, construction type, climate, and building height http://www-epb.lbl.gov/ventilation/program.html

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Guidance on J&E Inputs: Estimate AEH from Ventilation Calculations

- Vz = Rp Pz + Ra Az
- Vz = outdoor, clean airflow rate required in the breathing zone of the occupiable space(s)
- Rp = outdoor, clean airflow rate required per person, 2.5 L/s per person (5 cfm per person) for office spaces; default minimum 5 persons per 100 m2
- Pz = population, the number of persons expected to occupy the zone during typical usage
- Ra = outdoor, clean airflow rate required per unit area, 0.3 L/s-m2 (0.06 cfm/ft2) for office spaces
- Az = the net occupiable floor area of the zone [m2] (ft2)
- Vz = 2.5 L/s-person*5 person + 0.3 L/s-m2 * 100 m2 = 42.5 L/s
- AEH = 42.5 L/s * 3600 s/hr * 1 m3/1000 L / 100 m2 * 2.7 m = 0.57 hr-1

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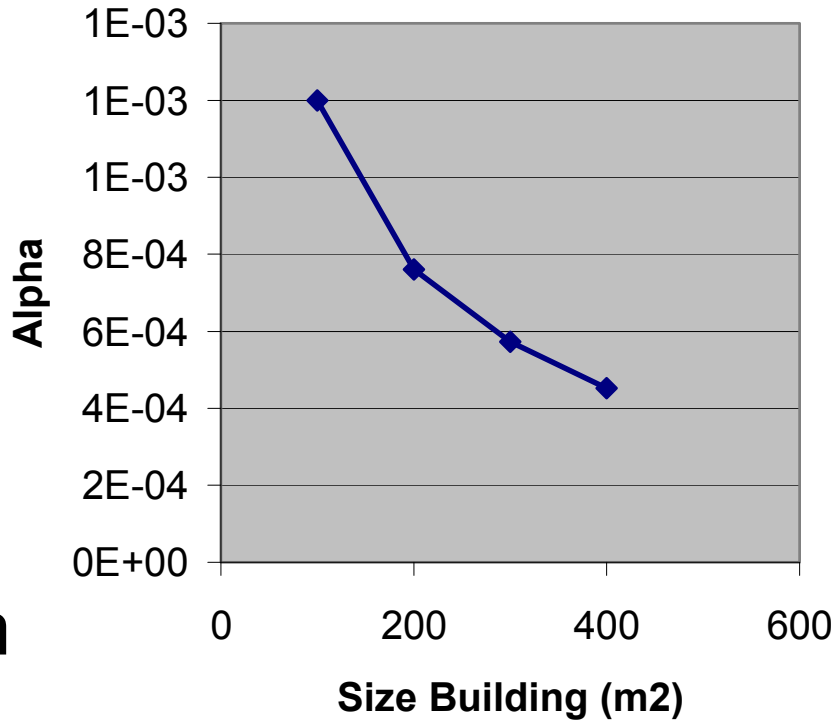
Guidance on J&E Inputs: Building Area

- Alpha moderately sensitive to building area
- But if Volume/Area of subsurface foundation ratio stays constant, then no change in alpha



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Guidance on J&E Inputs: Crack Ratio (η)

- Measure or back-calculate from tracer test? (or use intuition, P. Johnson)
- Figley & Snodgrass: 10 houses, hairline - 5 mm wide, most < 1 mm, total crack length: 2.5 - 17.3 m/house
- Eaton and Scott: Average 300 cm^2 edge crack Elliot Lake homes (η ~ 0.0003, assumed A = 100 m^2)
- Rezvan, Nazaroff: η ~ 0.0001 to 0.001 backcalculated from tracer test
- HC VI Default value = 1 mm wide edge crack & 100 m^2 house: Basement η = 0.0002, Slab-on-grade ~ 0.0004

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Health Canada Spreadsheets

- Preliminary Quantitative Risk Assessment (PQRA) and Detailed Quantitative Risk Assessment (DQRA) spreadsheets (multiple exposure pathways considered)
- PQRA
  - VI attenuation factor curve approach, two soil types coarse and fine-grained soil
- DQRA (two options)
  - VI attenuation factor curve approach
    - Four soil types
    - Adjustments for biodegradation, groundwater mass flux, source depletion
  - Site specific J&E modeling
- Extensive phys-chem database

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USEPA Superfund Spreadsheet

- USEPA Superfund Spreadsheets
  - Free software, good user's manual
  - Simplified (single layer) and advanced versions (three layers)
  - Intercalcs provide parameters such as effective diffusion coefficients, Qsoil, Alpha
  - Soil, groundwater and soil vapour source versions (groundwater version includes advection, unlike RISC), also inc. source depletion
  - Only model single chemical at a time
  - Model either calculates the soil gas advection rate (Qsoil), or the user may directly enter Qsoil

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USEPA Superfund Spreadsheet

- USEPA Superfund Spreadsheets
  - Either calculates risk, or backcalculates criteria
  - Chemical database with 100 chemicals (if you unlock cells password ABC, can add additional chemicals)
  - Error in groundwater model, when entering user defined soil type for capillary zone, total porosity for soil **type** is incorrect and is actually the total porosity for soil **stratum** above water table

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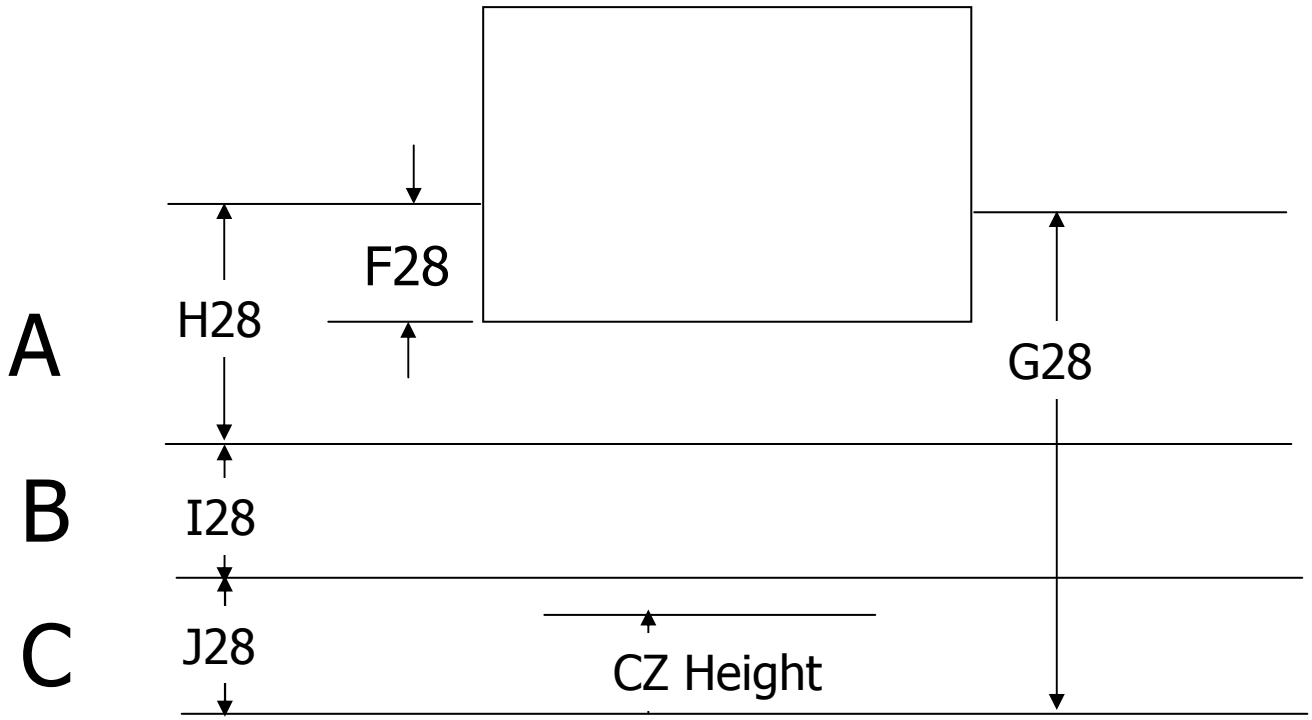
USEPA Superfund Spreadsheet



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GW-ADV
Version 3.1; 02/04

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES [ ]

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION (enter "X" in "YES" box and initial groundwater conc. below)

YES [X]

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (µg/L)	Chemical
74873	5.00E+01	Methyl chloride (chloromethane)

MORE ↓

ENTER Average soil/ groundwater temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to water table, L_{WT} (cm)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum directly above water table, (Enter A, B, or C)	ENTER SCS soil type directly above water table	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of L_{WT} (cell G28)							
10	10	30	13	16	1	C	S			1.00E-08

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
S	1.66	0.375	0.054	C	1.66	0.375	0.054	S	1.66	0.375	0.054

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
10	40	1000	1000	366	0.1	0.25	5

MORE ↓

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	30	30	350	1.0E-06	1

J&E Source Depletion

$$\langle \alpha \rangle = \frac{\rho_b \, C_R \, \Delta H_c \, A_B}{Q_{building} \, C_{source} \, \tau} \left(\frac{L_T^0}{\Delta H_c} \right) \left[\left(\beta^2 + 2 \, \Psi \, \tau \right)^{1/2} - \beta \right] \quad (2$$

re

$\langle \alpha \rangle$	=	Time-averaged finite source attenuation coefficient, unitless
ρ_b	=	Soil dry bulk density at the source of contamination, g/cm^3
C_R	=	Initial soil concentration, g/g
ΔH_c	=	Initial thickness of contamination, cm
A_B	=	Area of enclosed space below grade, cm^2
$Q_{building}$	=	Building ventilation rate, cm^3/s
C_{source}	=	Vapor concentration at the source of contamination, g/cm^3-v
τ	=	Exposure interval, s
L_T^0	=	Source-building separation at time = 0, cm

RISC Model

- RISC Model 4 (Lyn Spense)
  - Commercially available ($750?)
  - Multiple chemicals
  - Calculates fluxes
  - Includes two biodegradation models
  - Gdw-to-indoor air – not full J&E model (no advection)
  - When back-calculating criteria check that results converge
  - Has indoor and outdoor model
  - Probabilistic Monte Carlo capabilities for exposure model

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RISC Model

- Partitioning Model

$$C_w = \frac{C_T \rho_b}{\rho_b K_{oc} F_{oc} + \theta_w + \theta_a K_H}$$

$$C_w = xS \qquad x = \frac{m}{m_{TPH}}$$

- If Cw1 > Cw2 then residual saturation, use NAPL-vapour partitioning model, otherwise 3-phase model
- Risk manual suggests MW gasoline = 95 g/mol, see TPHCWG for other data, and

http://www.epa.gov/athens/learn2model/part-two/onsite/es.htm

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RISC Model Summary

Table 1 Vapour model options in RISC – based on J&E model approach

Assumption/ Fate and Transport Processes	Vapour model without degradation	Dominant Layer Model	Oxygen-limited model	Vapour model from groundwater
Source term	Soil gas or soil	Soil gas or soil	Soil gas or soil	Groundwater
Layering/ Heterogeneity	May have two layers	May have three layers	Homogeneous	May have two layers plus cap. fringe
Degradation	No	Yes, in middle layer	Yes, if oxygen conc. high enough	No
Model oxygen conc.	No	No	Yes	No
Considers pressure driven flow by building	Yes	Yes	Yes	No

Petroleum Vapour Model Comparison – Interim Report for CRC Care (G. Davis, Trefley, Paterson)

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Advection & Diffusion
Building

Boundary layer model
for O2 flux (Ko)

RISC Model

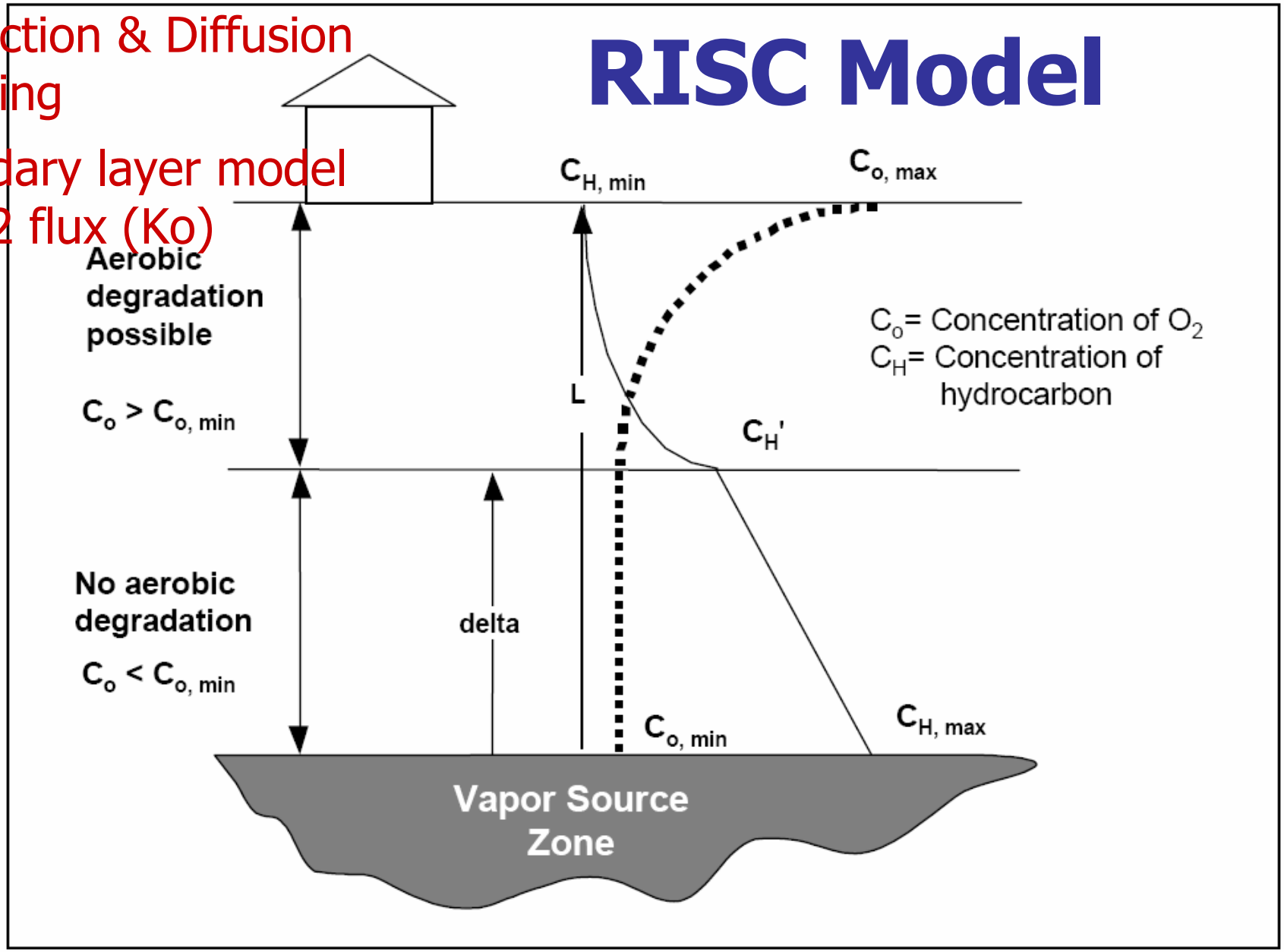

Figure K-1. Schematic of the Oxygen-Limited Vapor Transport Model.

RISC Model

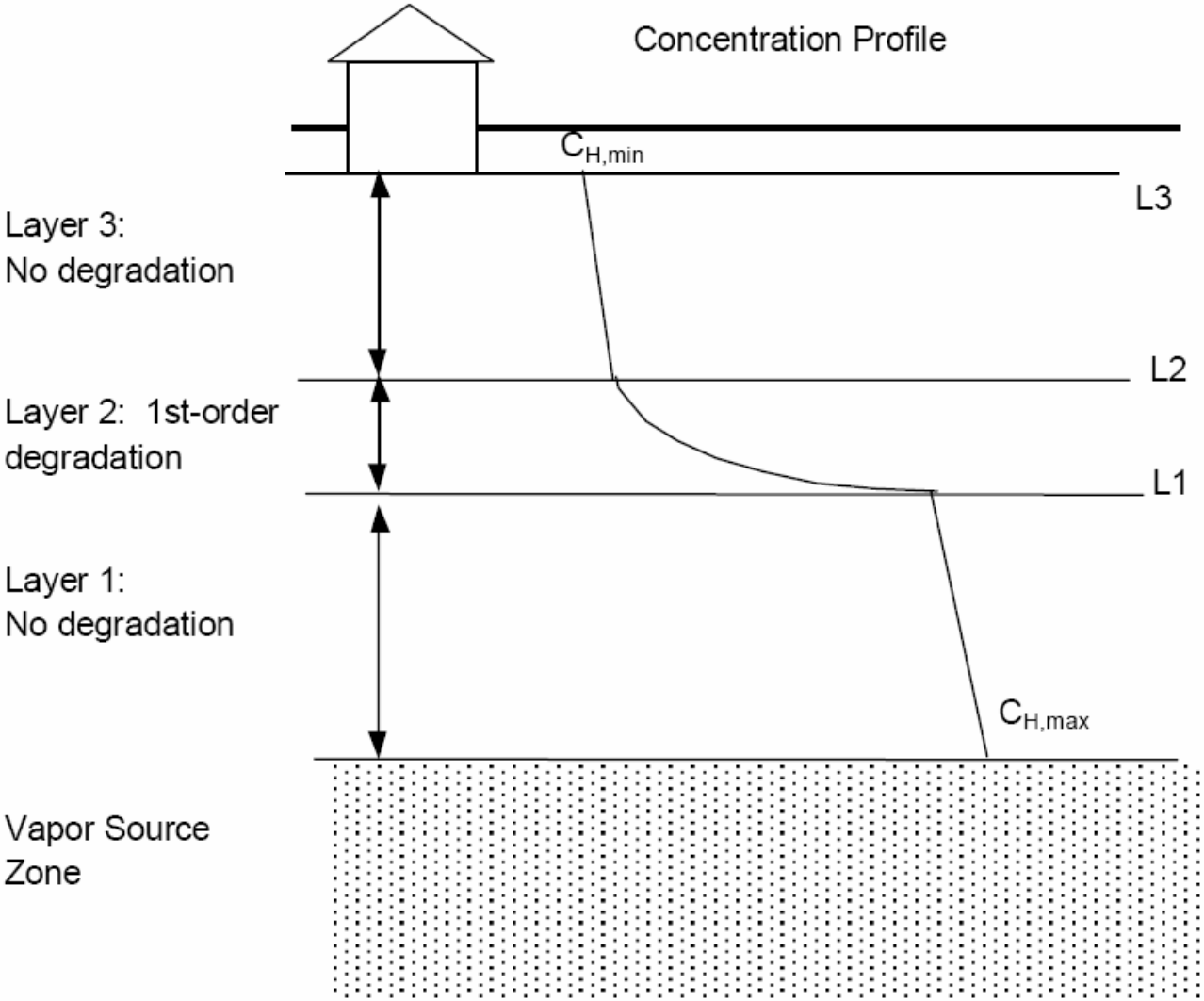

Figure J-1. Schematic of the Dominant Layer Vapor Transport Model.

Golder J&E-Bio Model

- Multiple layers, plots soil vapour concentrations, more graphical than EPA spreadsheets
- Biodegradation dominant layer (like RISC) but coupled to oxygen flux
- Crawlspace

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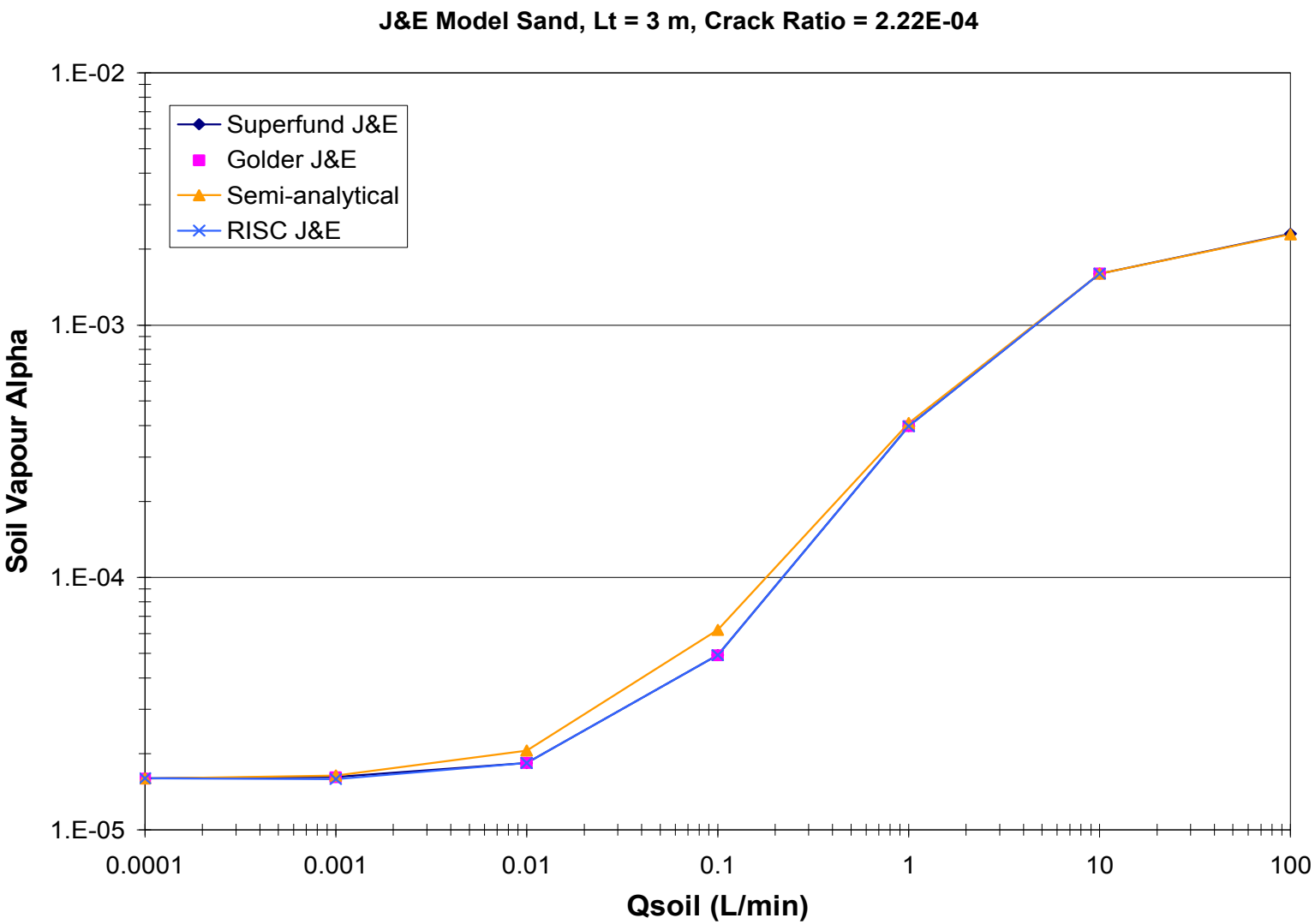
Golder J&E-Bio Model



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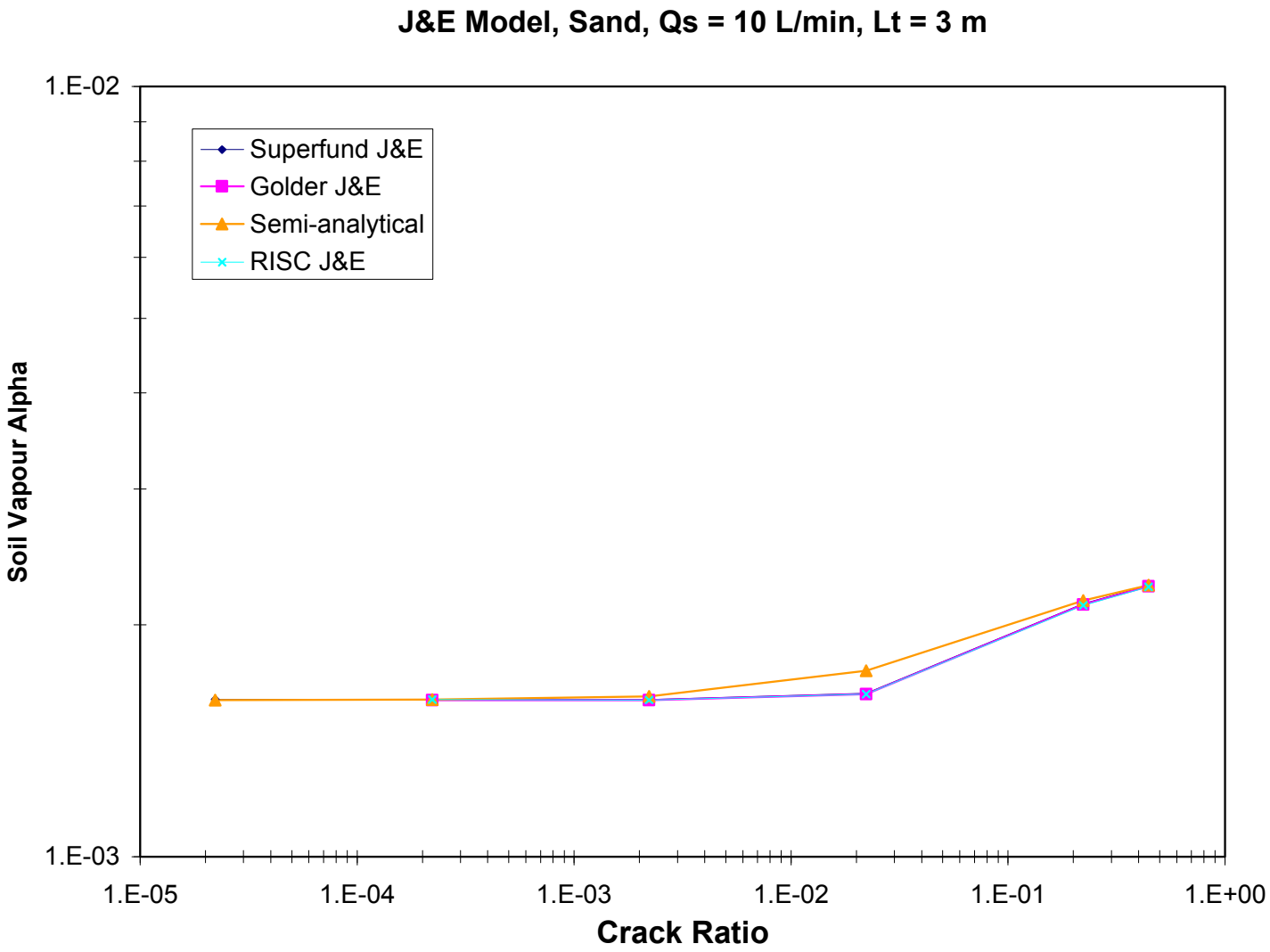
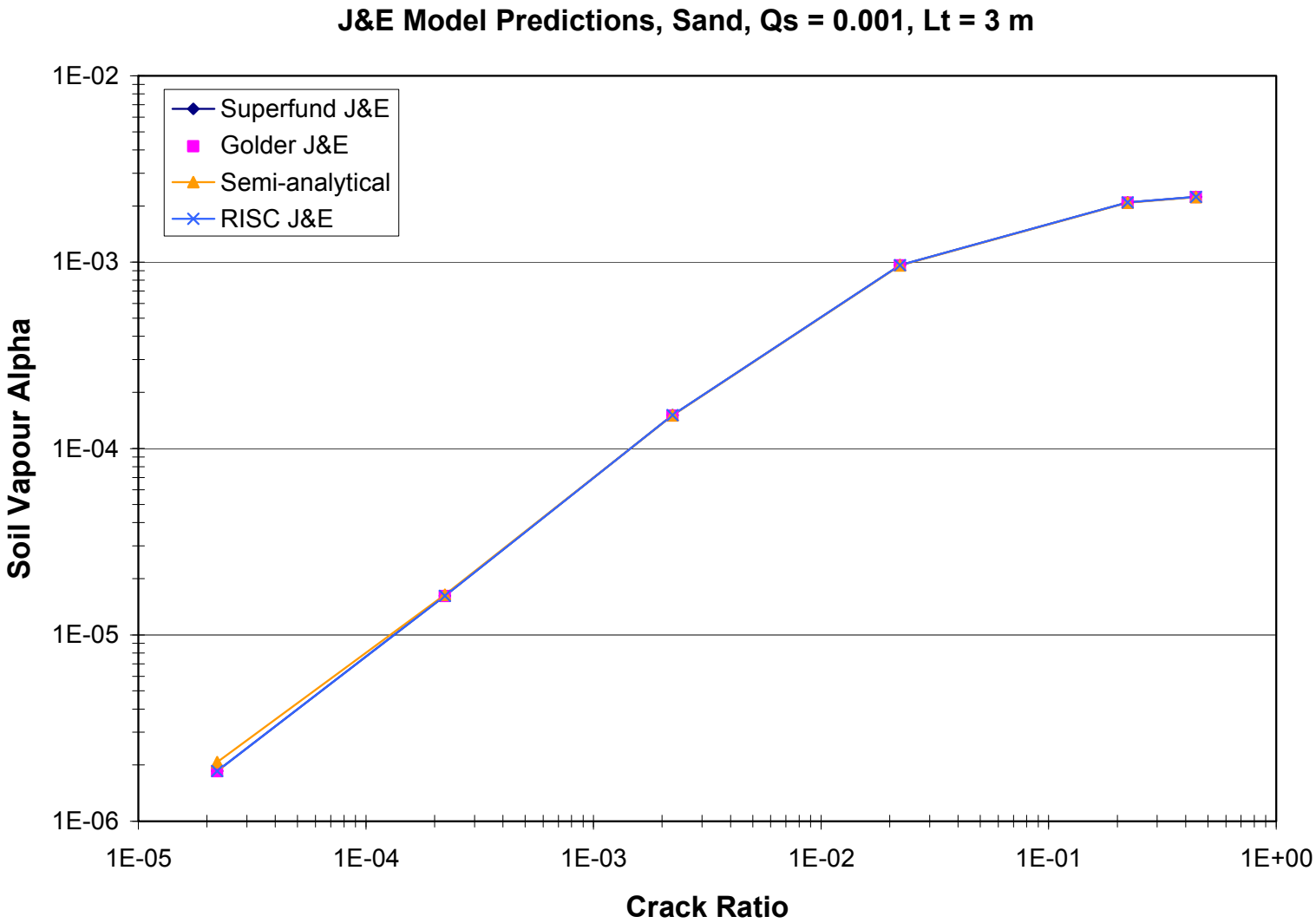
Golder J&E-Bio Model



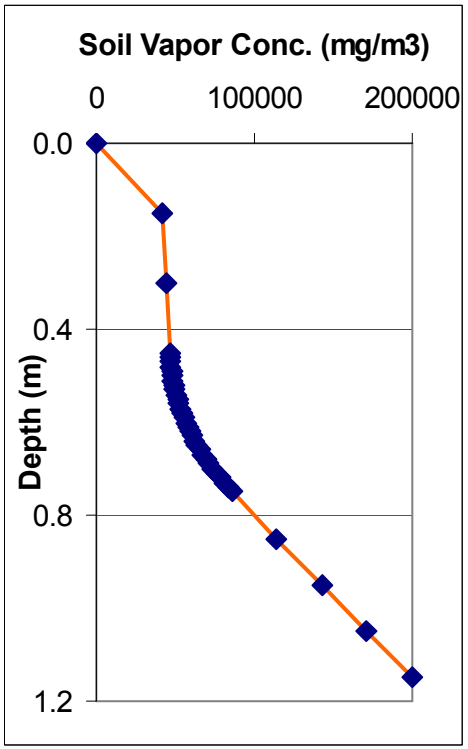
Golder J&E-Bio Model

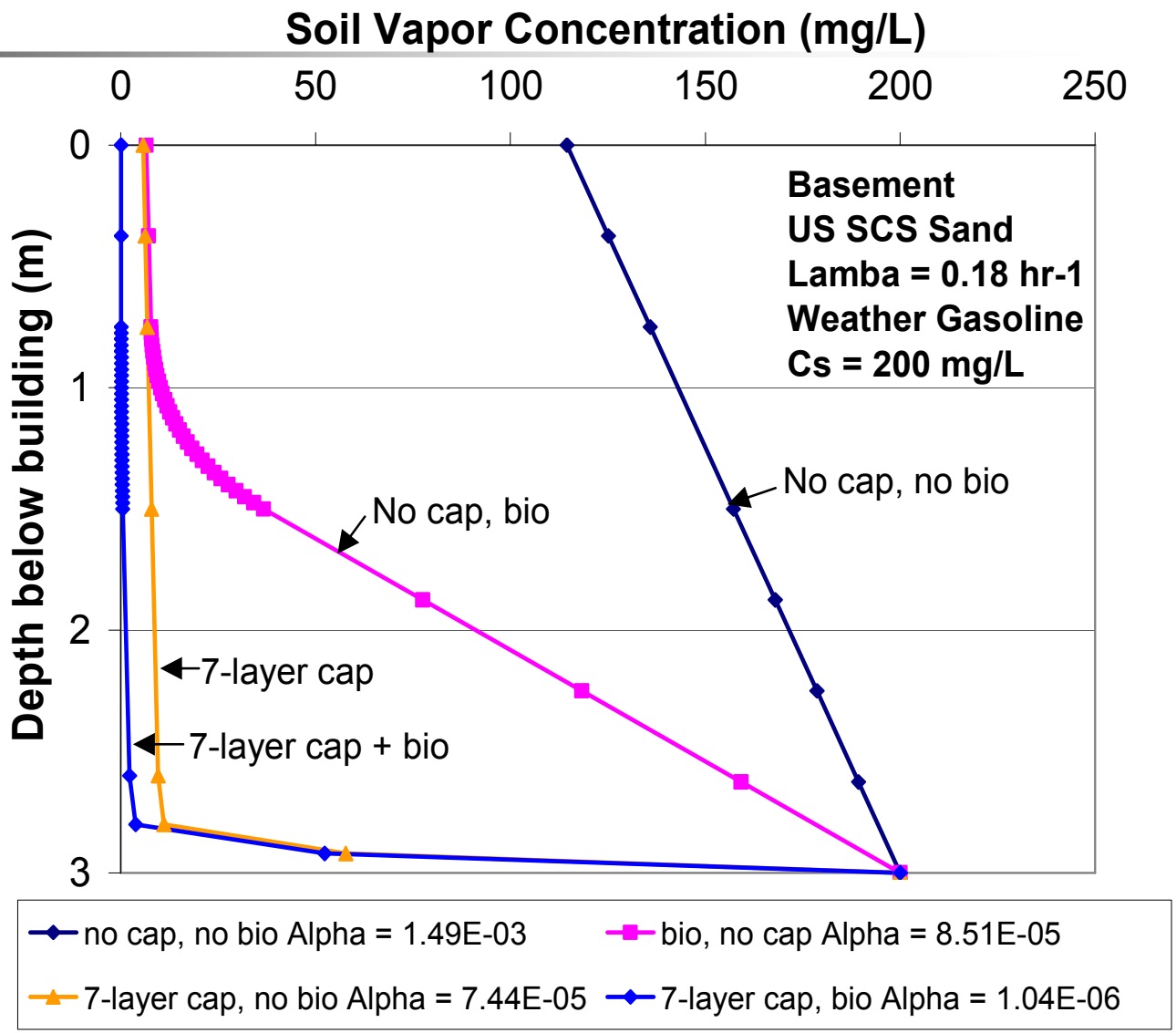


Golder J&E+Bio Semi-Analytical Model

Key point:

Significant attenua-tion predicted for combination capillary fringe and biodegradation (3 orders-of-magnitude in this case)





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Jury Model (appendices to USEPA 1996 Soil Screening Guidance)

$$\frac{\partial C_1}{\partial t} + \mu \; C_1 = D \; \frac{\partial^2 C_1}{\partial z^2} - V \frac{\partial C_1}{\partial z}$$

- Transient model for
  - Diffusion
  - Upward soil gas advection, downward infiltration of soil water
  - First order decay
  - Sorption
  - Uniform, homogenous soil, linear equilibrium partitioning

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Jury Reduced Solution Infinite Source

$$J_s = C_0 \, (D_E/\pi t)^{1/2}$$

J_s = Instantaneous emission flux, $\mu g/cm^2$-day

C_o = Initial soil concentration (total volume), $\mu g/cm^3$-soil

t = Time, days

D_E = Effective diffusion coefficient, cm^2/day (Equation 2).

Can use spreadsheet to integrate this to obtain time-averaged flux

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Jury Reduced Solution Finite Source

$$J_s = C_o\, e^{-m}\, (D_E/p\, t)^{1/2}\, \left[1 - \exp\left(-L^2/4\, D_E\, t\right)\right]$$

= Instantaneous emission flux, $\mu g/cm^2$ -day

= Initial soil concentration (total volume), $\mu g/cm^3$-soil

= Degradation rate constant, 1 /day

= Time, days

= Effective diffusion coefficient, cm^2 /day

= Depth from the soil surface to the bottom of contamination, cm

No boundary layer, OK when H is large

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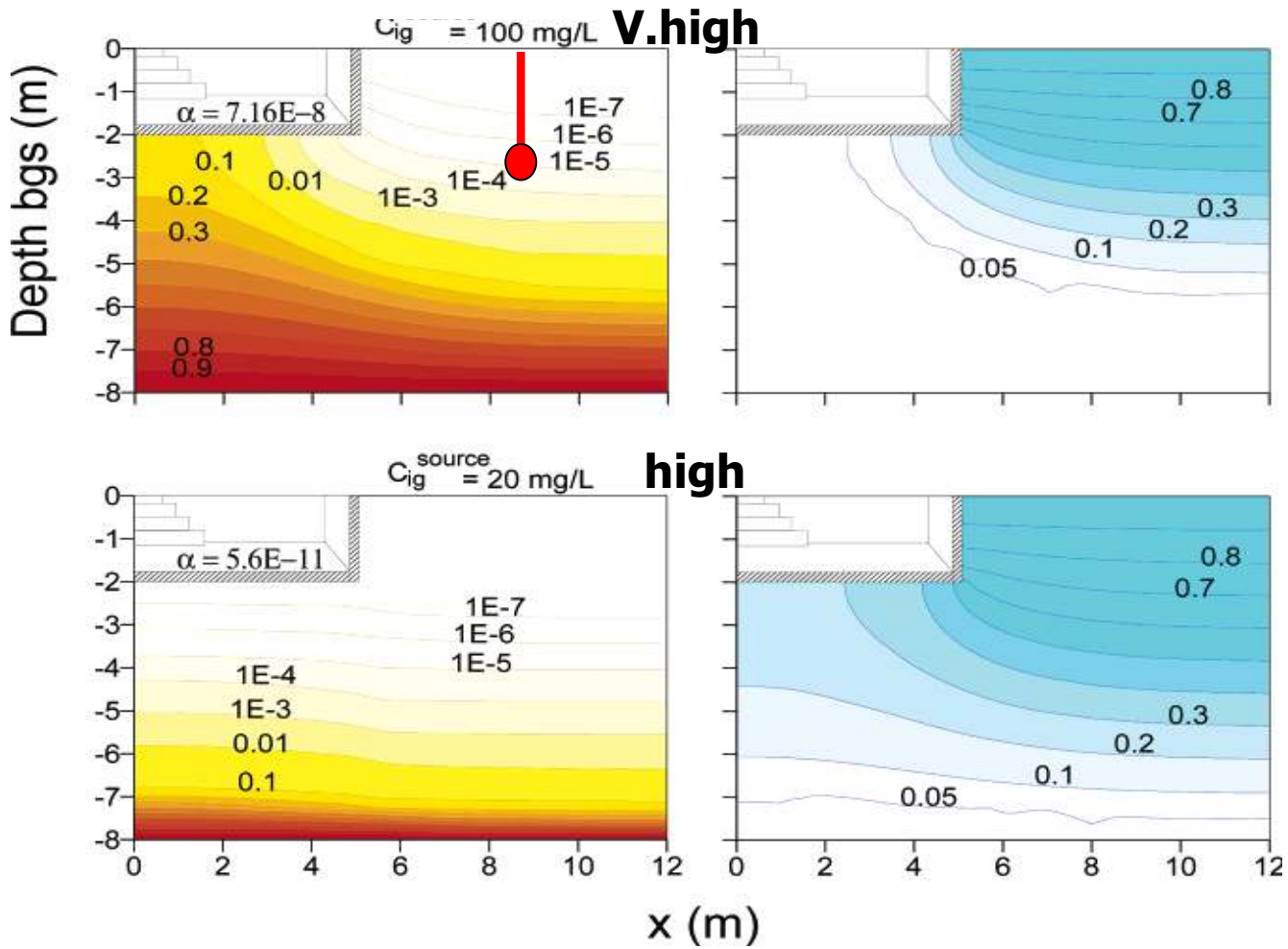
Robinson and Turczynowicz Model

- Started with Jury Model (time varying diffusion, sorption, first-order decay)
  - Coupled with crawlspace and indoor air module
  - 1-D diffusion & 3-D diffusion versions, 3-D version can incorporate partial source below building
  - Calculated health-based investigation levels (HIL) for 2 m thick contamination layer
    - Benzene = 3 mg/kg
    - Toluene = 40 mg/kg
    - Naphthalene = 30 mg/kg
  - Fortran code, theoretical equations complex

Three-Dimensional Soil Transportation Models for Volatiles Migrating from Soils to House Interiors N. I. ROBINSON1,∗ and L. TURCZYNOWICZ2
Transp Porous Med (2005) 59:301–323 © One- and Springer 2005

Abreu and Johnson 3-D Numerical Model

Soil Vapour above Gasoline NAPL



3-D Biodegradatic Modeling

by L. Abreu & P. Johnson, EST, 2005

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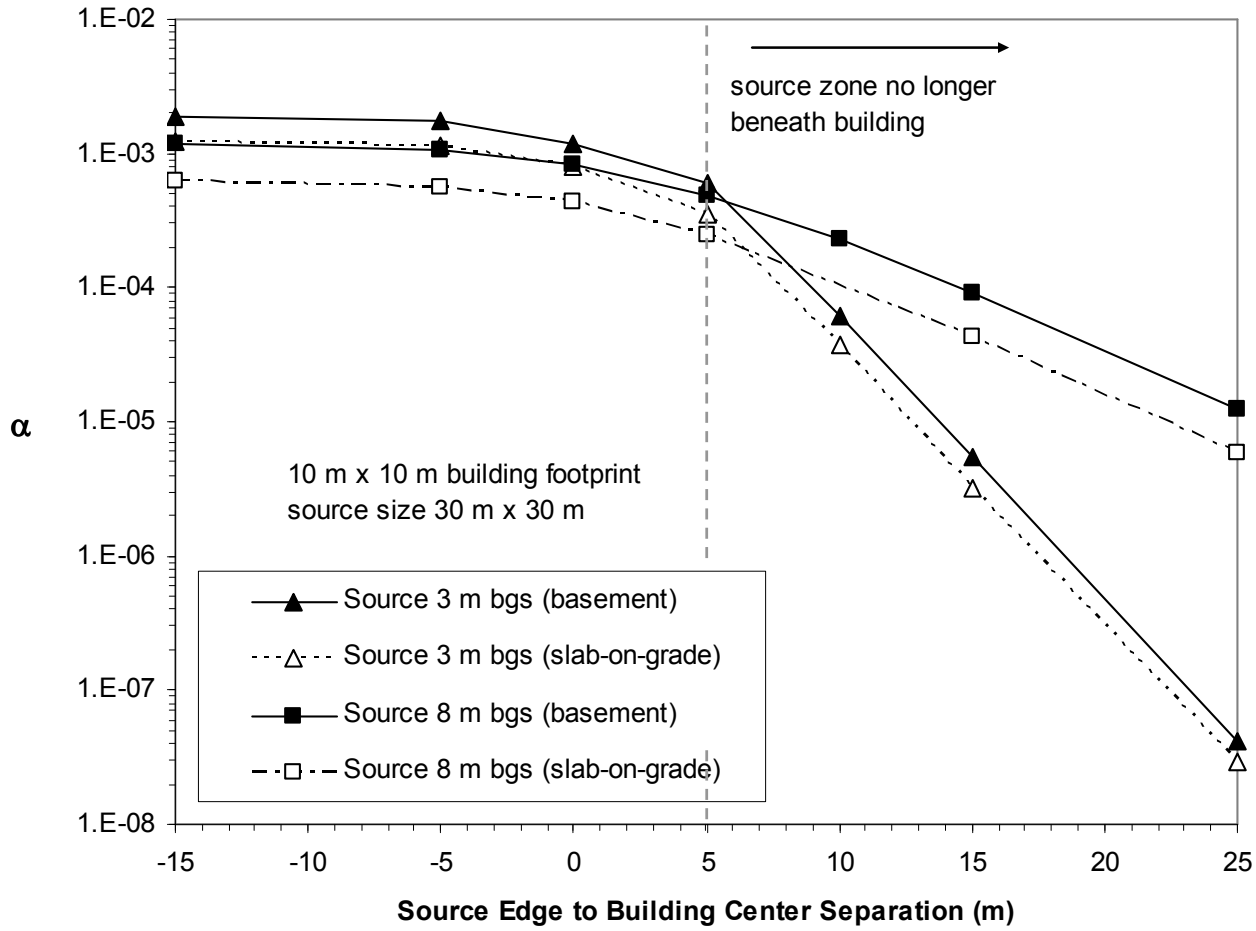
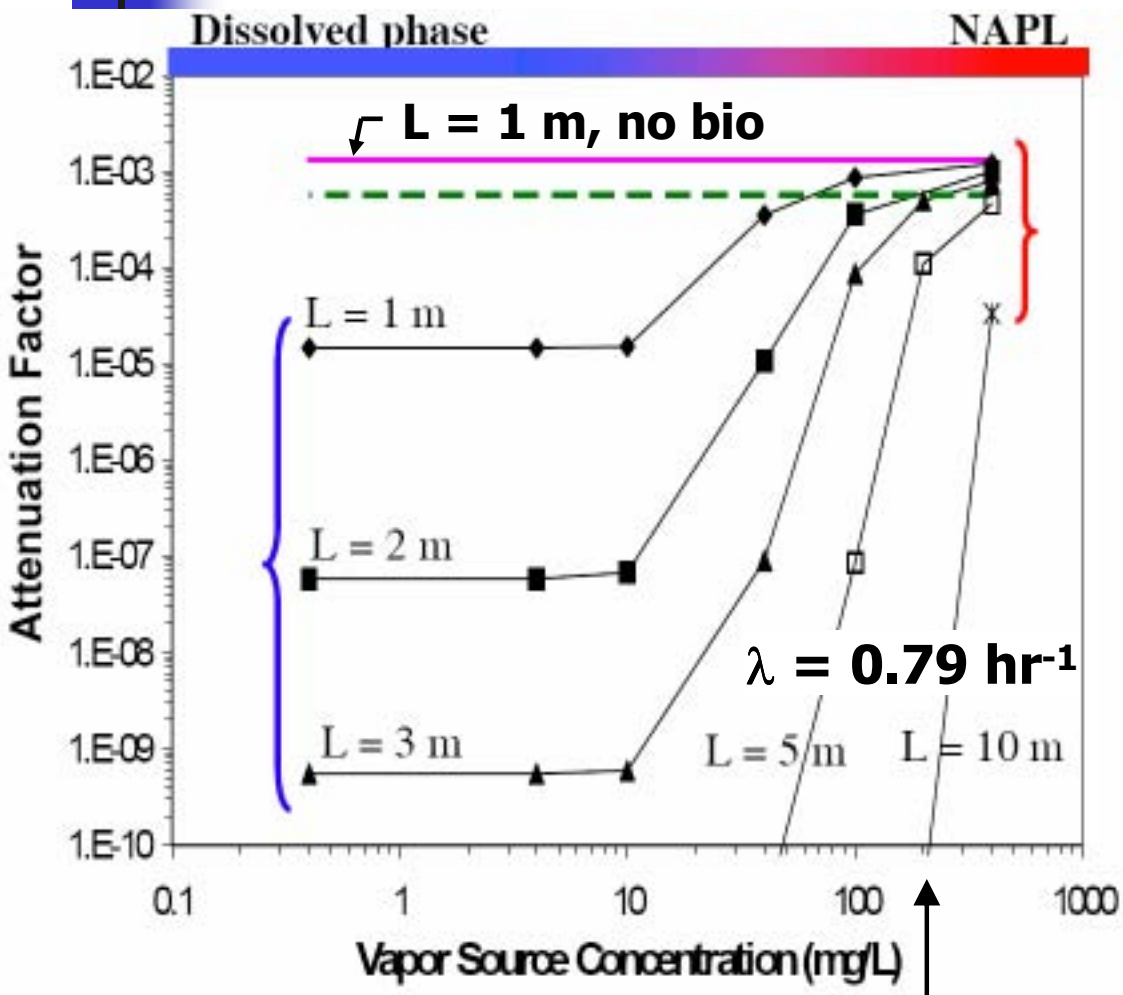
Abreu and Johnson 3-D Numerical Model



3-D Modeling
Abreu et al. (2007)

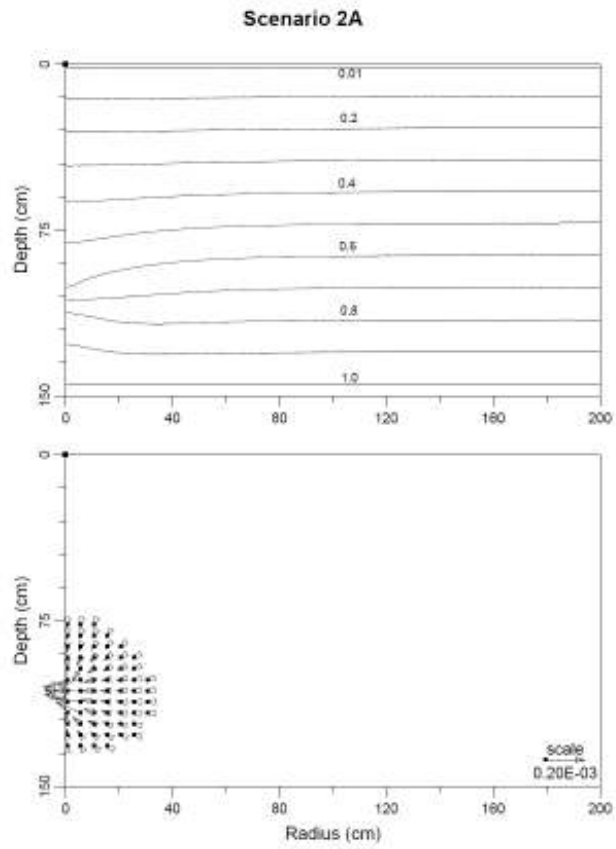


Case studies, TPH_g <= 200 mg/L

- House with basement
- Homogenous sand
- No capillary fringe assumed (conservative for dissolved phase)
- No O_2 replenishment by barometric pumping or wind (conservative)
- No low diffusivity surface cover (non-conservative – 2D modeling suggests may be significant for some cases)
- > 10X reduction in AF predicted most scenarios

VapourT Model

- 2-D numerical model
- Diffusion, gas-phase and liquid phase advection, density driven transport, dispersion, sorption
- No building component, no decay
- Used for recent SABCS project to simulate soil vapour sampling



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Virginia Trench Model

- Groundwater **< 15 ft depth**, groundwater pools in excavation: Volatilization model based on gas and liquid phase mass transfer coefficients is coupled with box model
- Groundwater **> 15 ft. depth**, groundwater below bas of trench: Diffusion model coupled with box model
- Urban canyon studies suggest minimal mixing W/D < 1, ACH = 2 hr-1; when W/D > 1, ACH = 360 hr-1
- http://www.deq.virginia.gov/vrprisk/tables.html (vrp37.xls and vrp38.xls)
- http://www.deq.virginia.gov/vrprisk/raguide.html

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Recent Biodegradation Research

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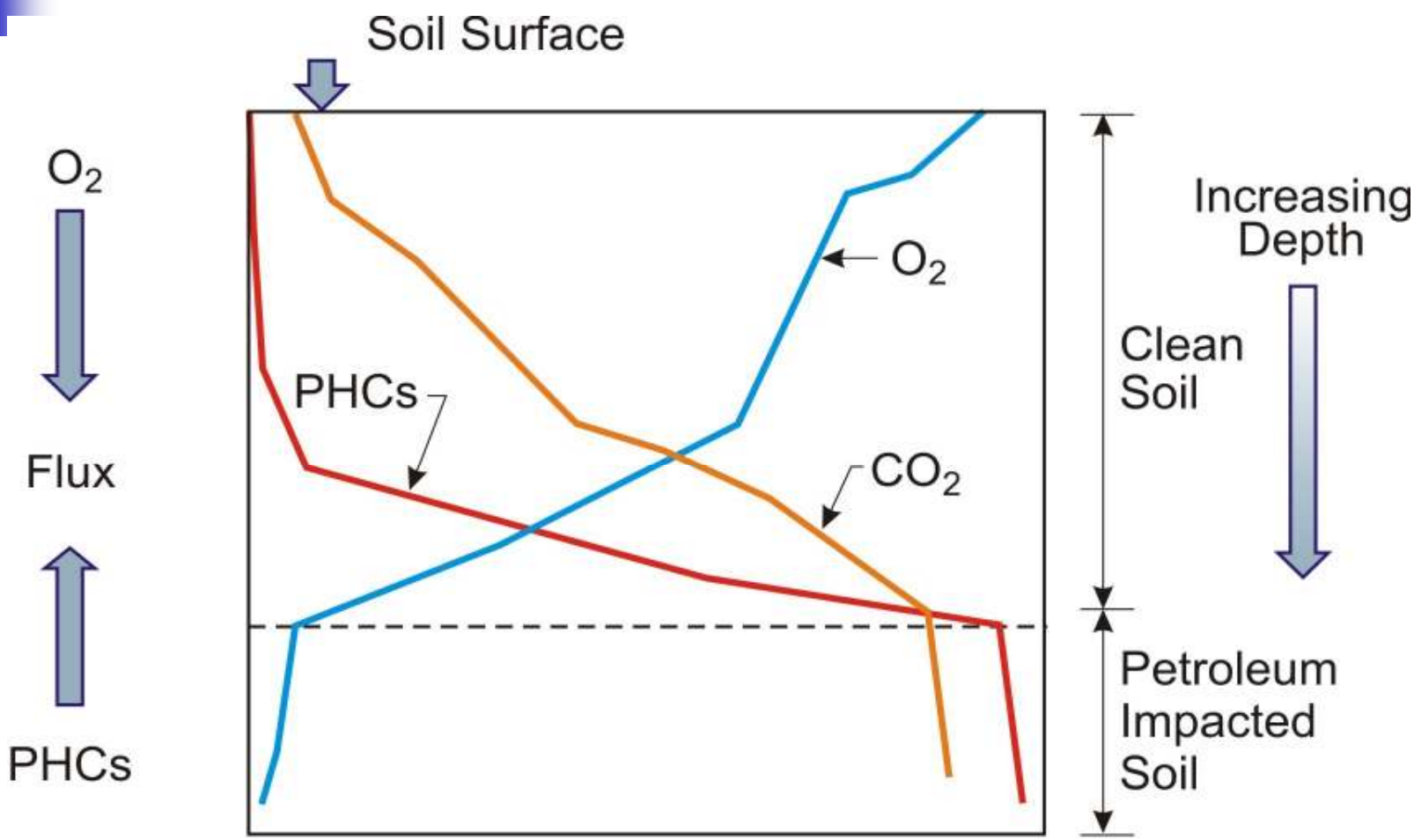
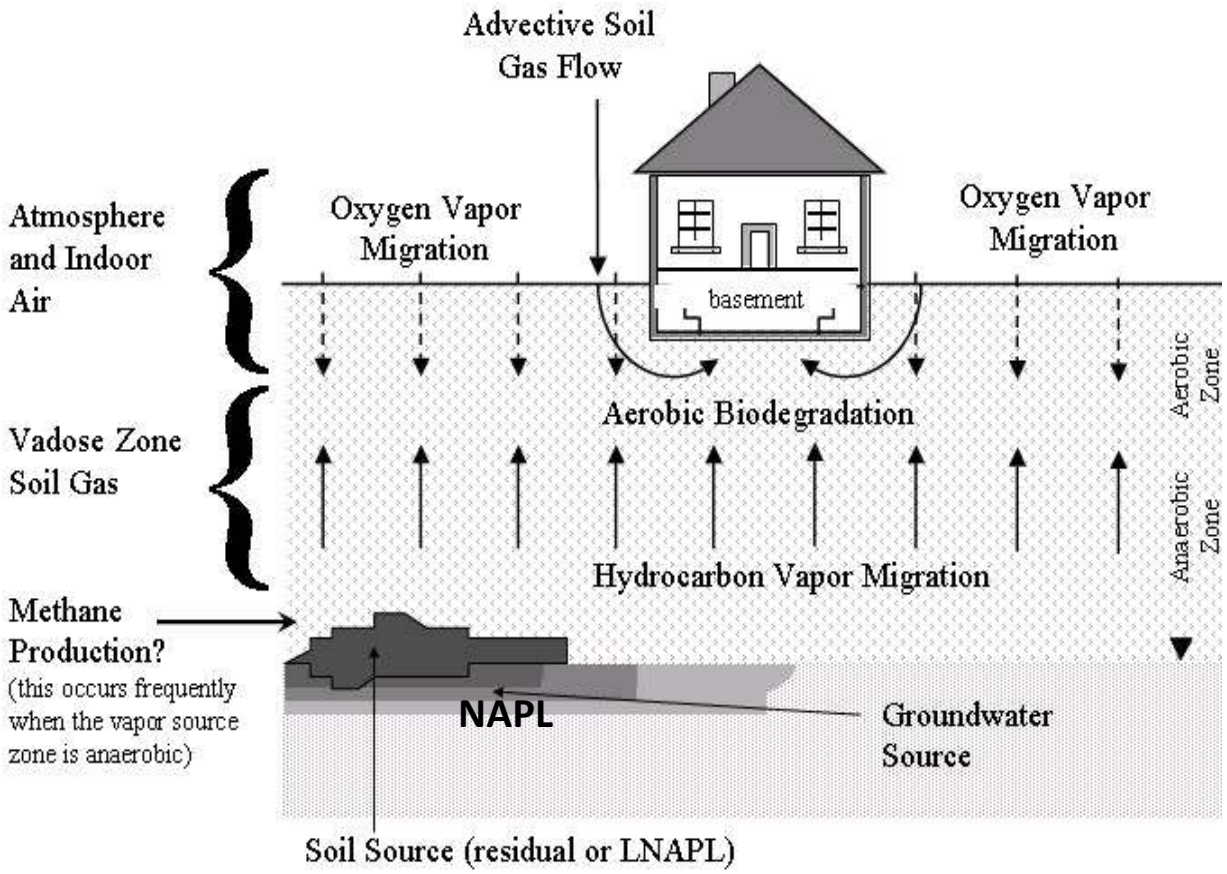
Conceptual Hydrocarbon Vapour Profile



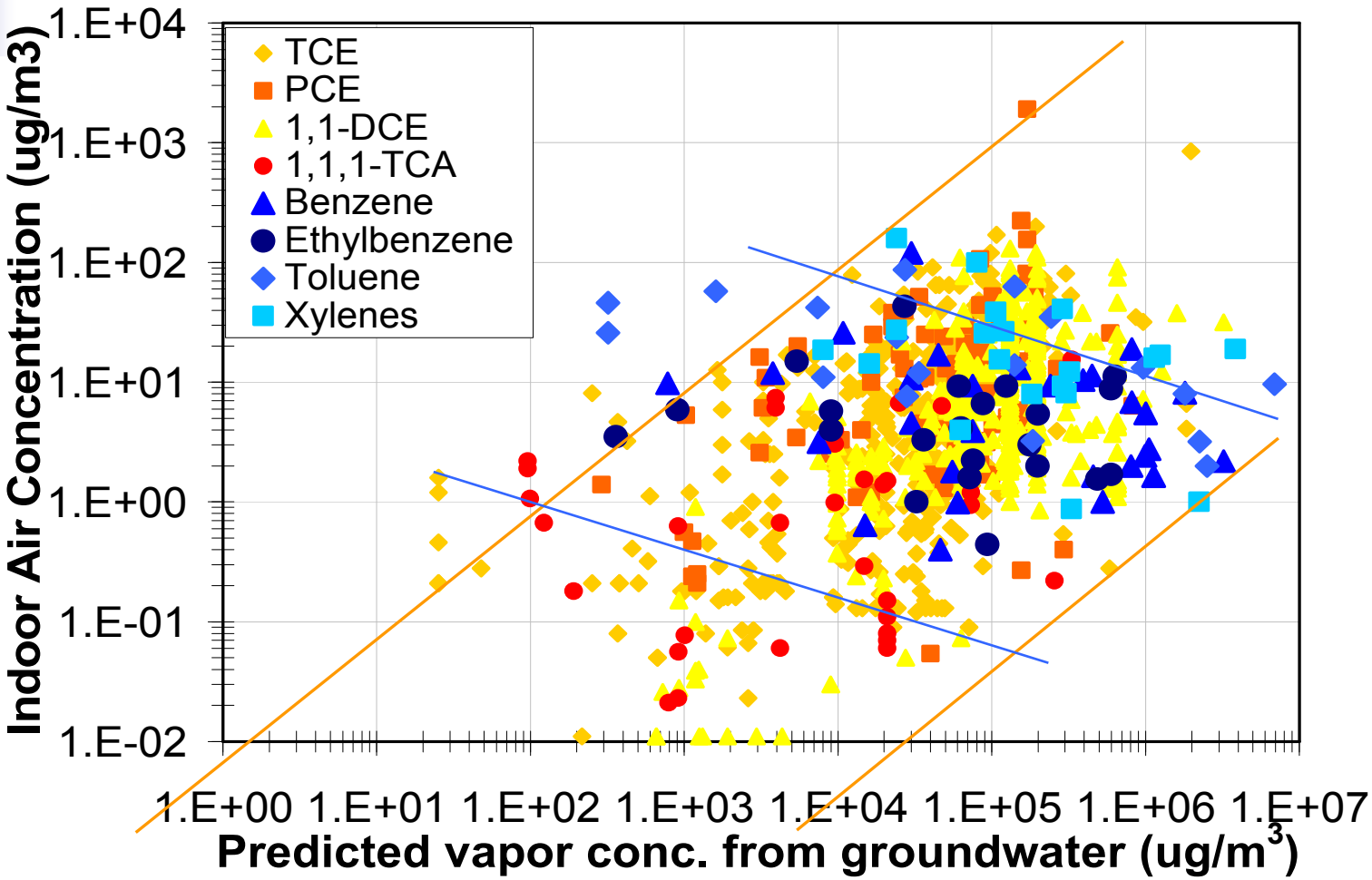
$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

Biodegradation CSM



- Aerobic biodegradation of PHC (BTEX, aliphatic HCs) vapours readily occur, key is whether sufficient O_2 below building
- First order decay constants ~ 0.1-100 hr^{-1}
- Key factors
  - Source strength
  - Separation distance
  - Capping effect
  - Soil type

Empirical Groundwater-Air Database
(USEPA plus HC BTEX data, mostly residential)



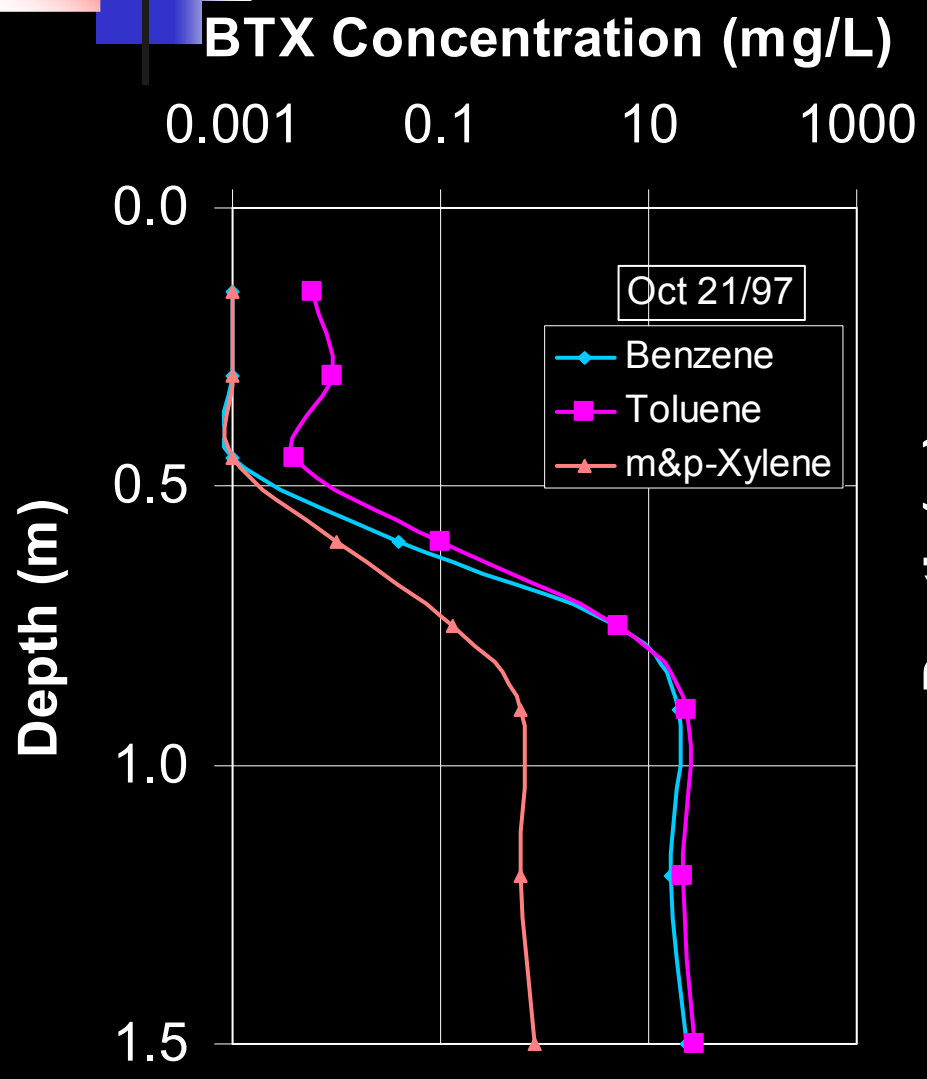
Key Point: No relation between subsurface and indoor air concentrations for BTEX chemicals

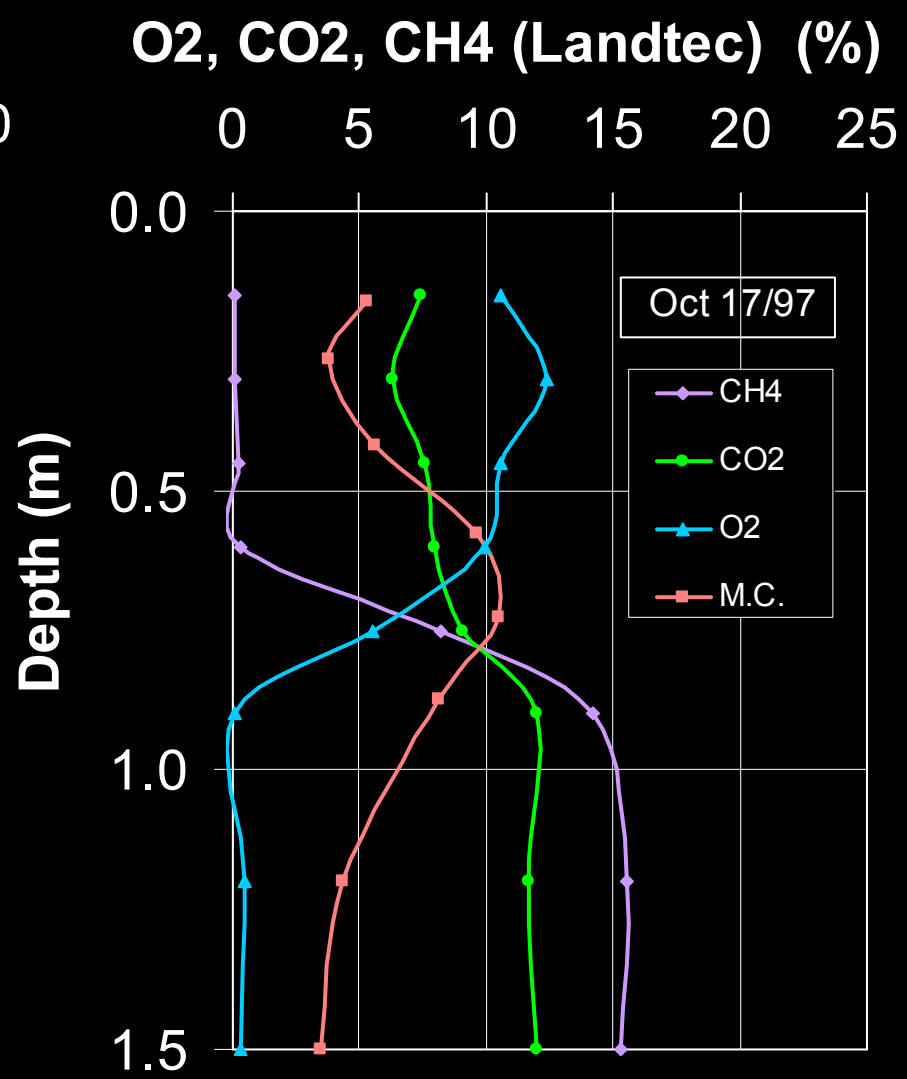
Selected Research Studies

- Chatterton Research Site (Hers Ph.D., 2000-2002)
- DeVaull research first decay rates (1997,2007)
- ASU-Chevron intensively monitored research sites - Casper, WY, Santa Maria, CA, Cleveland, OH
- Golder-New Jersey field-based research study and model development (Sanders and Hers, 2006)
- Golder Health Canada – CPPI empirical data review (2008)
- Golder-Shell-ASU Seasonal (Cold Climate) Study Canada (2009-2010)
- EPRI-Golder-UBC Field-based Research and Biodegradation Modeling using MIN3P (2009-2010)

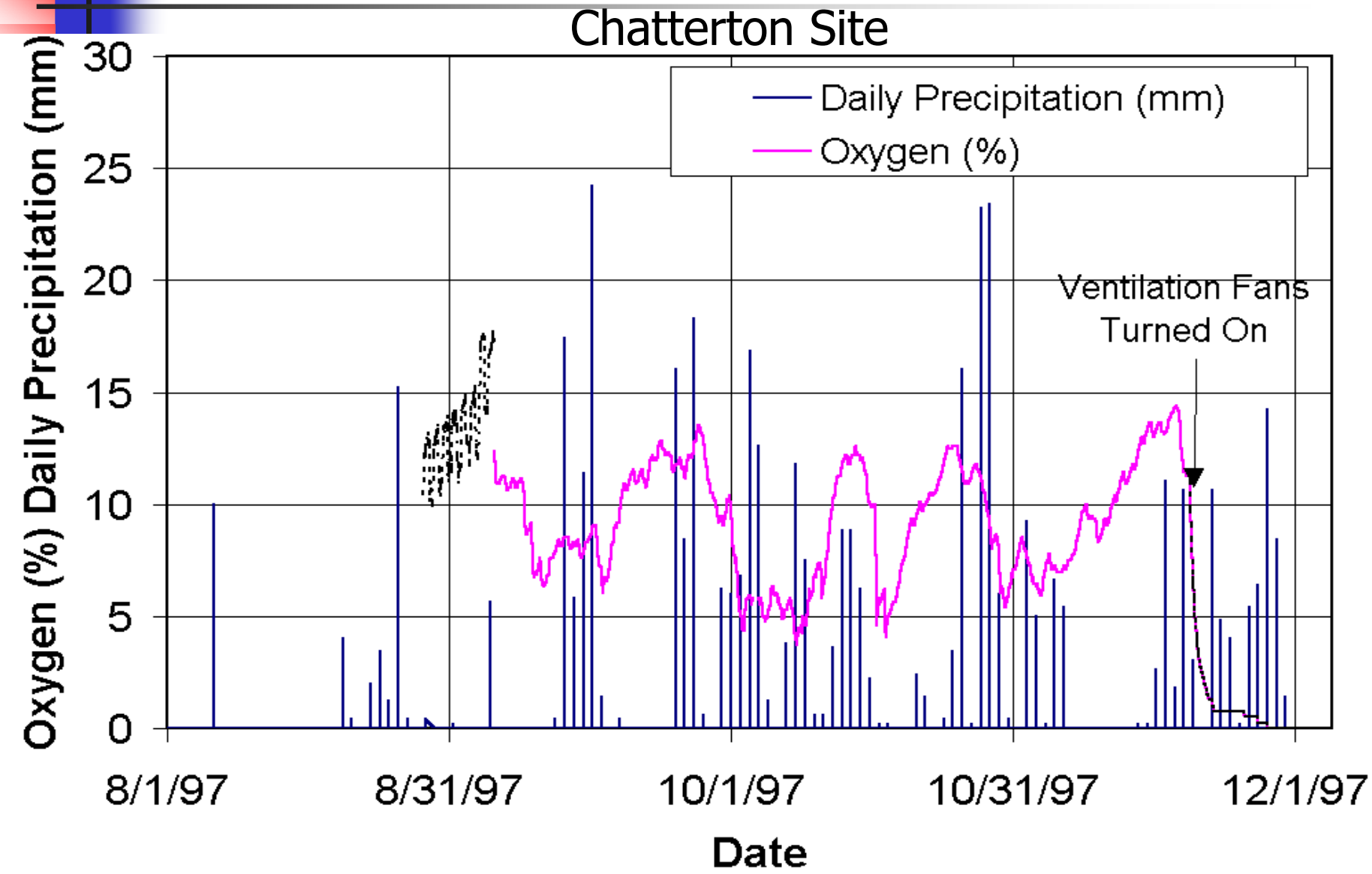
Chatterton Research Site

BTX VAPOUR BIODEGRADATION
(Chatterton Research Site)



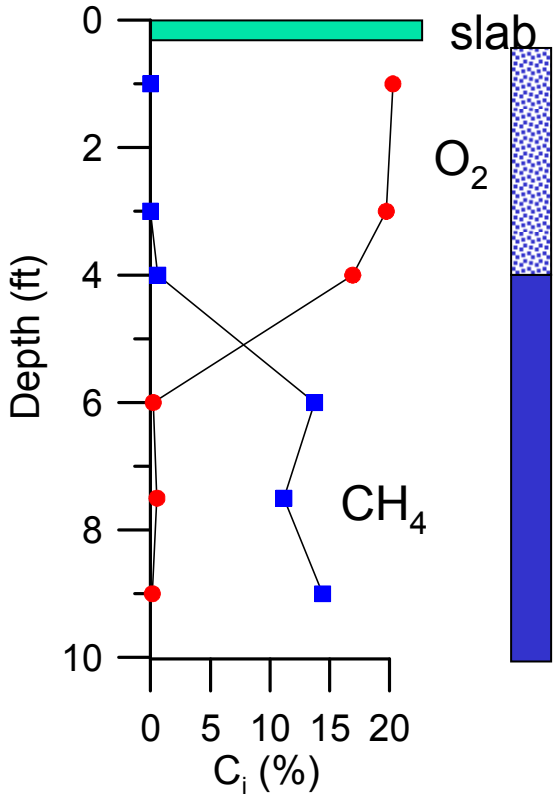


Precipitation Reduces Oxygen Below Slab

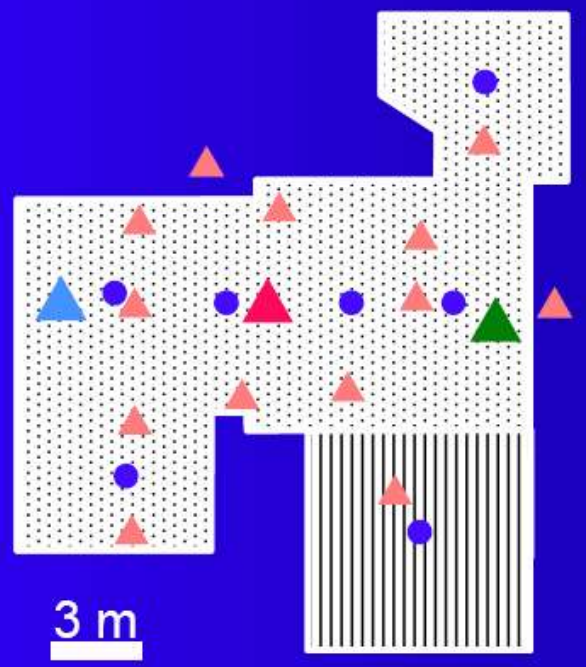


Santa Maria, CA Study
(Is O_2 Transport Below House Slow or Fast)

Paul Johnson, ASU, Paul Lundegard, Unocal and Paul Dahlen, Golder

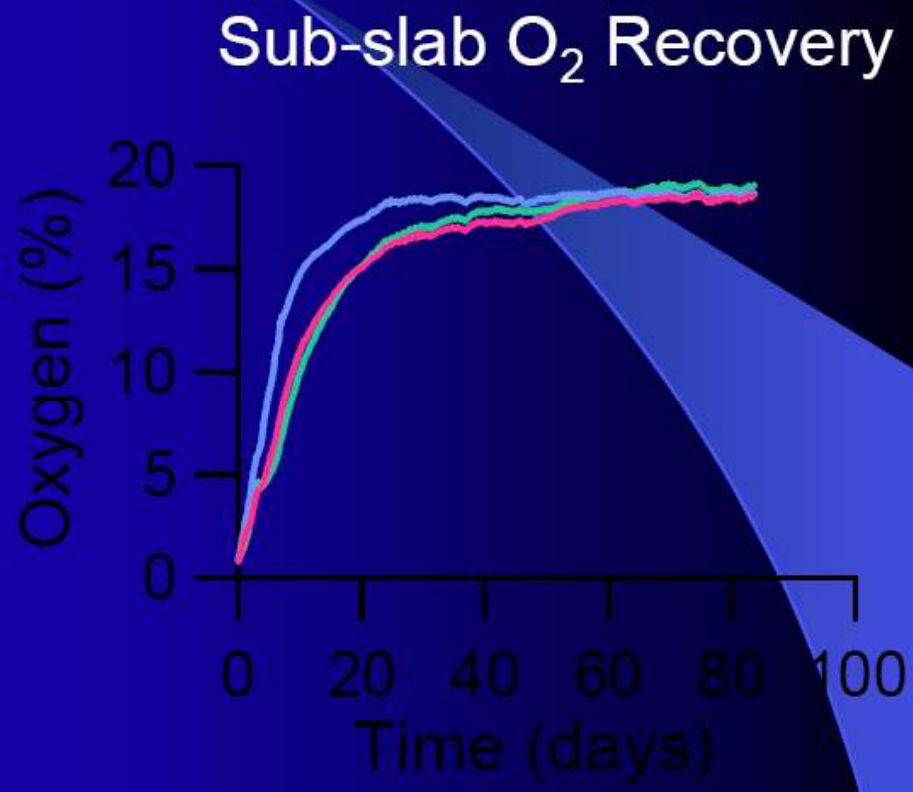


Sub-Slab O_2 Transport Experiment



N_2 injection

O_2 sensor

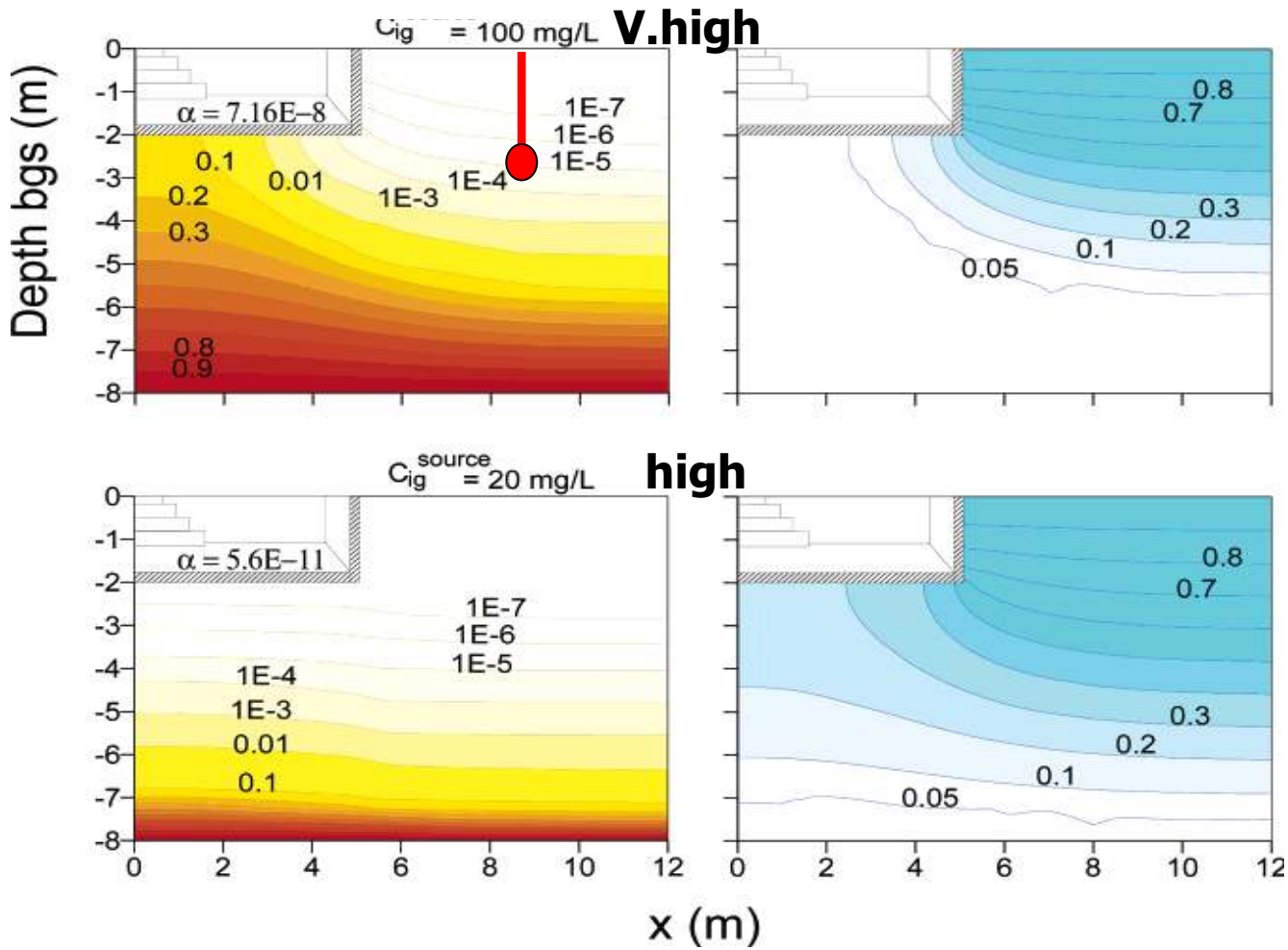


Diffusion most important, wind induced O_2 recharge also important. Rainfall can affect recharge

Paul Johnson, ASU, Paul Lundegard, Unocal and Paul Dahlen, Golder

Abreu and Johnson 3-D Numerical Model

Soil Vapour above Gasoline NAPL



3-D Biodegradatic Modeling

by L. Abreu & P. Johnson, EST, 2005

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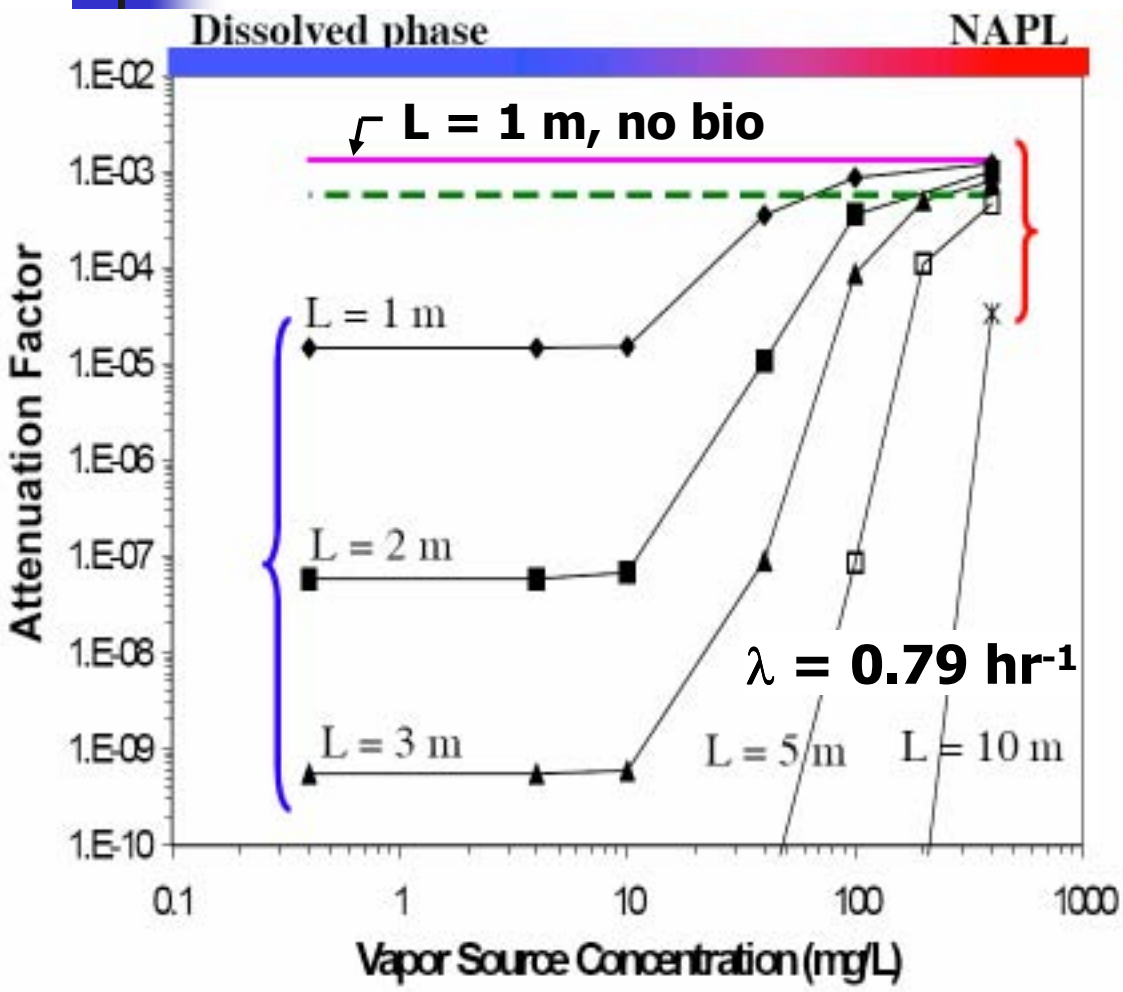
3-D Modeling
Abreu et al. (2007)

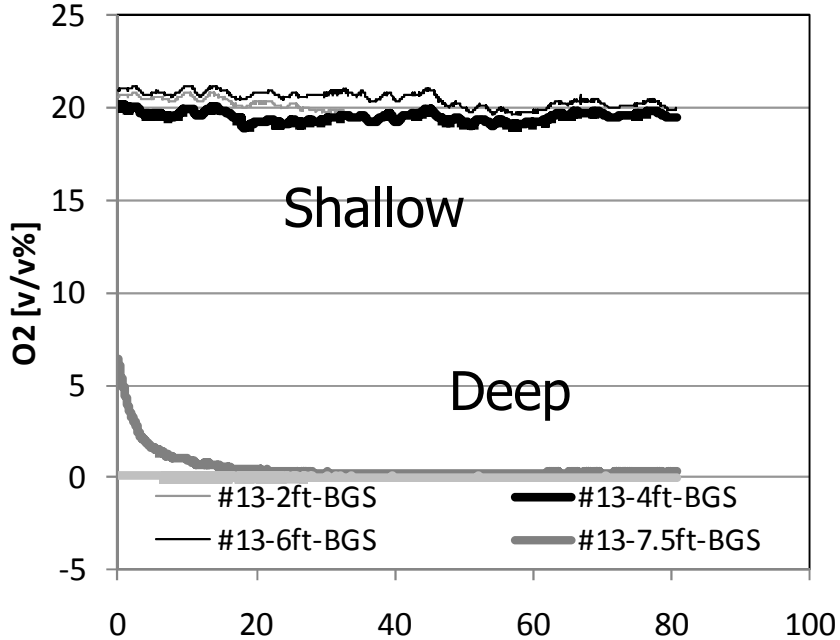


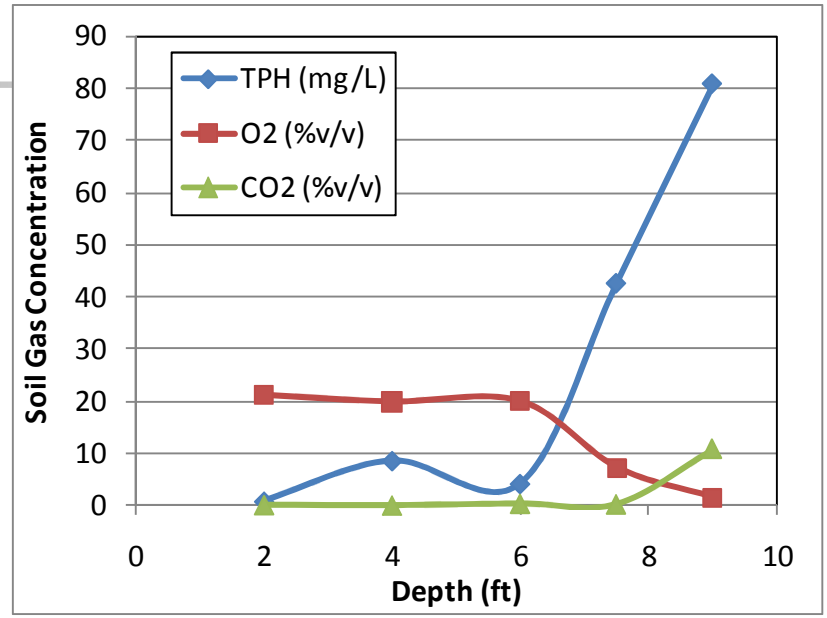
- House with basement
- Homogenous sand
- No capillary fringe assumed (conservative for dissolved phase)
- No O_2 replenishment by barometric pumping or wind (conservative)
- No low diffusivity surface cover (non-conservative – 2D modeling suggests may be significant for some cases)
- > 10X reduction in AF predicted most scenarios

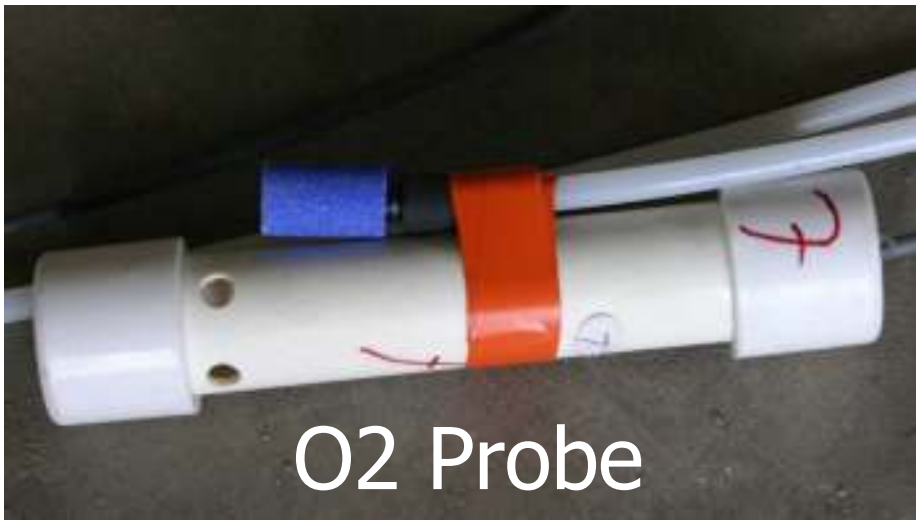
Shell Cold Climate (Seasonal) VI Study Canada

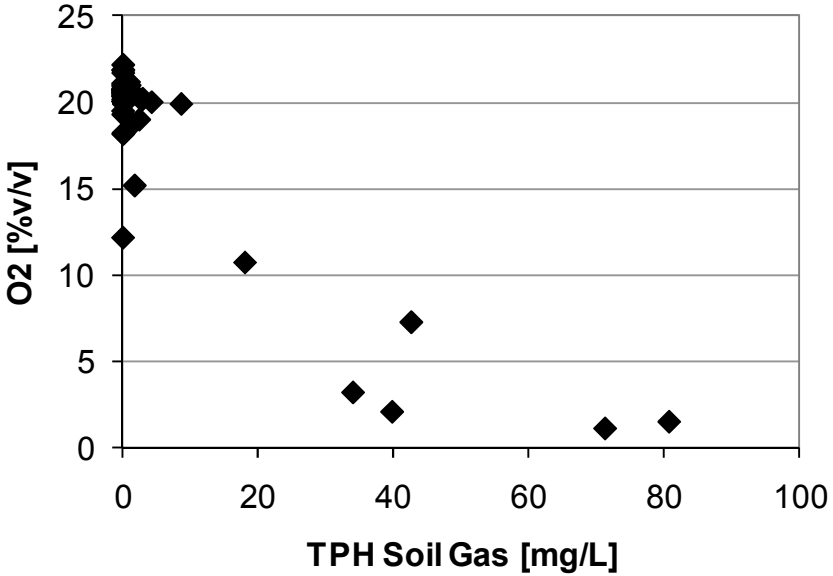
- How do seasonal factors affect soil vapour intrusion?
- High resolution sampling conducted at house at site above groundwater impacted with gasoline
  - Laboratory analysis of hydrocarbon concentrations, including detailed analysis (163 compounds!)
  - 50 O_2 sensors, 12 pressure sensors, 12 soil moisture and temperature sensors
  - Weather
- ASU 3-D VI model be used to evaluate field data
- Research team Shell (Dr. Matt Lahvis), Golder (Dr. Ian Hers) and Arizona State University (Paul Johnson, Paul Dahlen)

Shell Cold Climate VI Study

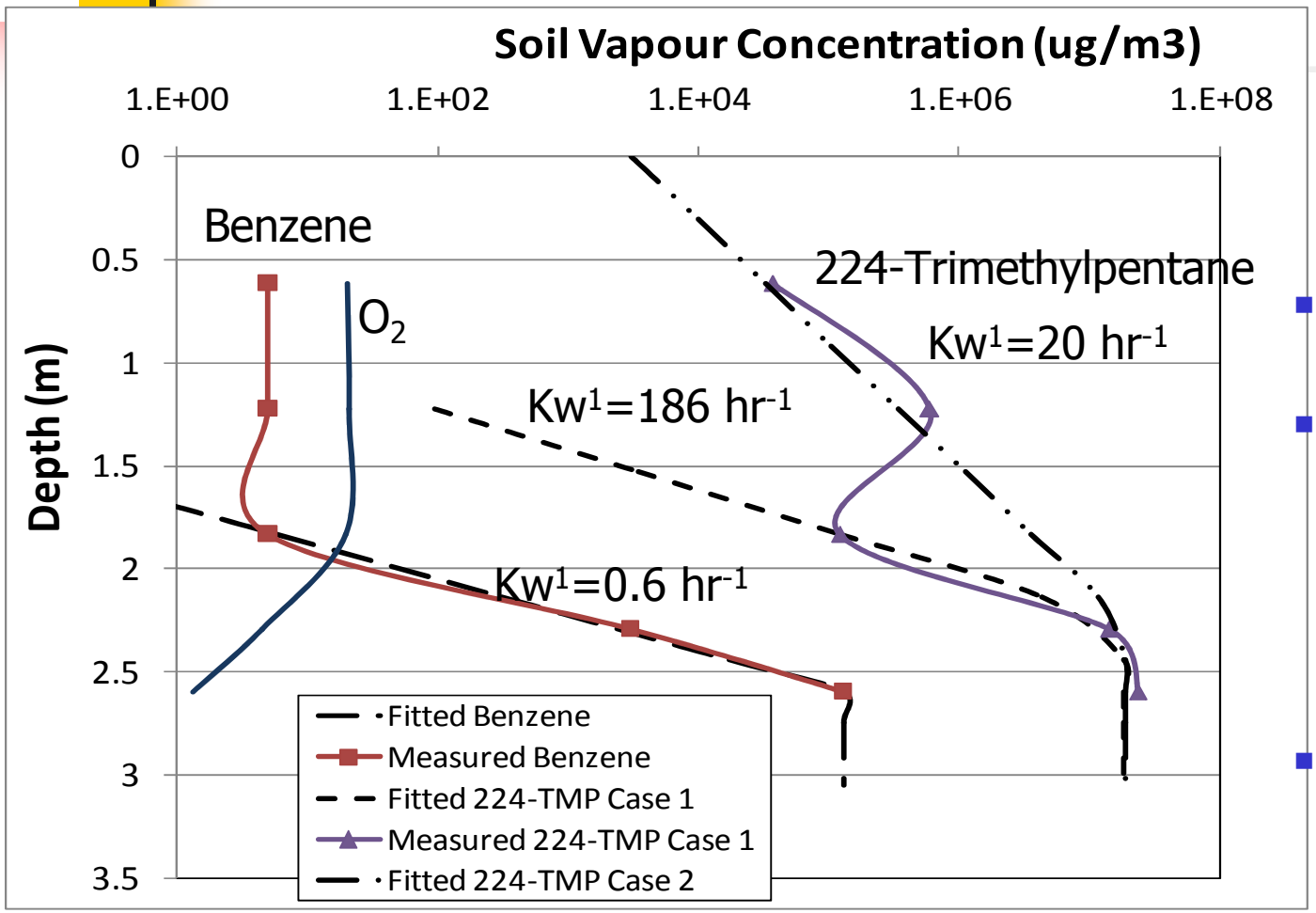








Shell Cold Climate



Soil gas above NAPL

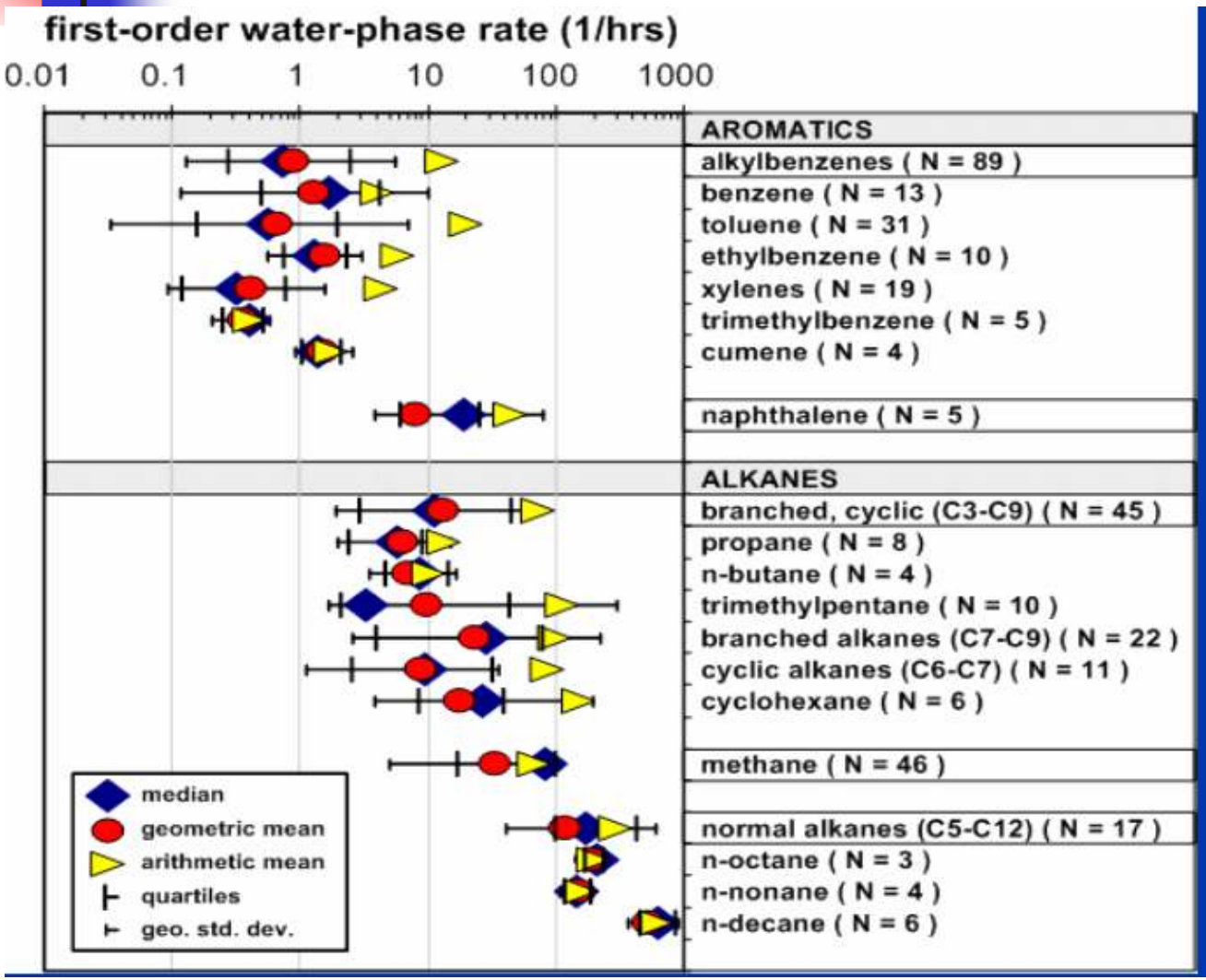
- BTEX vapours ~ 1% of total vapours
- What is the rest? Is it of toxicological concern? What are the fate & transport properties of these compounds?
- 224-TMP = 20%

Visual Fit Method to Estimate First-Order Decay Constants

$$c(z) = c(z_0) \cdot \exp(-z / L_R) \quad z < z_0; \qquad c(z) = c(z_0), \quad z > z_0$$

- $z = 0$ at surface; z_0 = profile 'knee', or zero oxygen, or water table
- Fit to obtain L_R reaction length; $L_R = (D_{eff} \cdot H / k_w \cdot \theta_w)^{0.5}$

DeVaull Review
First-Order Rates (ES&T 2007, 41)



- Petroleum rapidly biodegrades in vadose zone with oxygen
- Geometric mean fir order rates:
  - *BTEX* = 0.79 /hr
  - Aliphatics = 71 /hr
  (DeVaull, 2007)
- Biodegradation occurs in pore wate
- User can edit defau biodegradation rate

Dr. DeVaull is currently updating these rates

Health Canada- Golder VI Study
Northern Canada Site

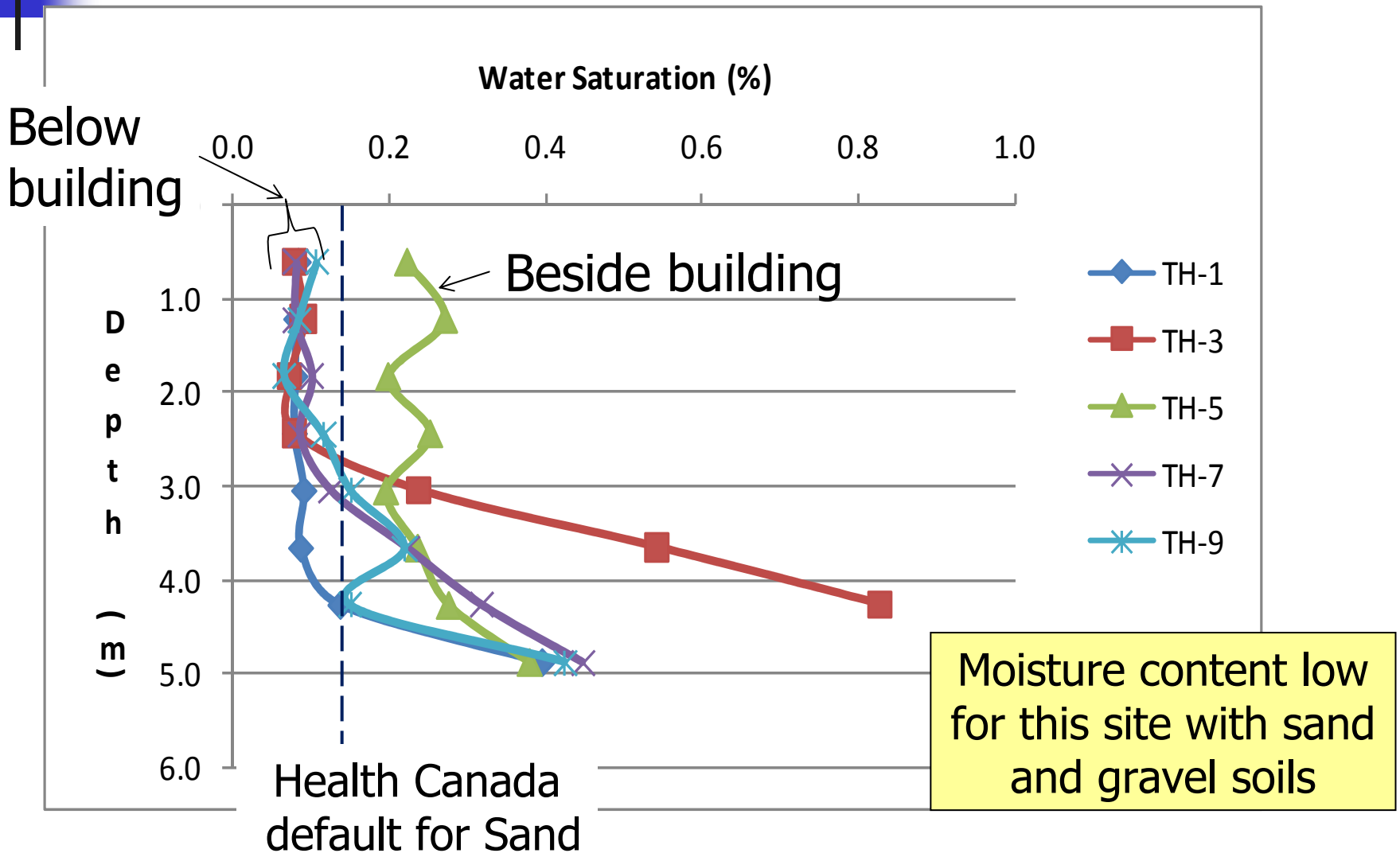
Courtesy Lindsay Smith, Health Canada

Health Canada- Golder VI Study
Northern Canada Site

Sampling Inside Heated Crawlspace

Health Canada-Golder VI Study
Northern Canada Site

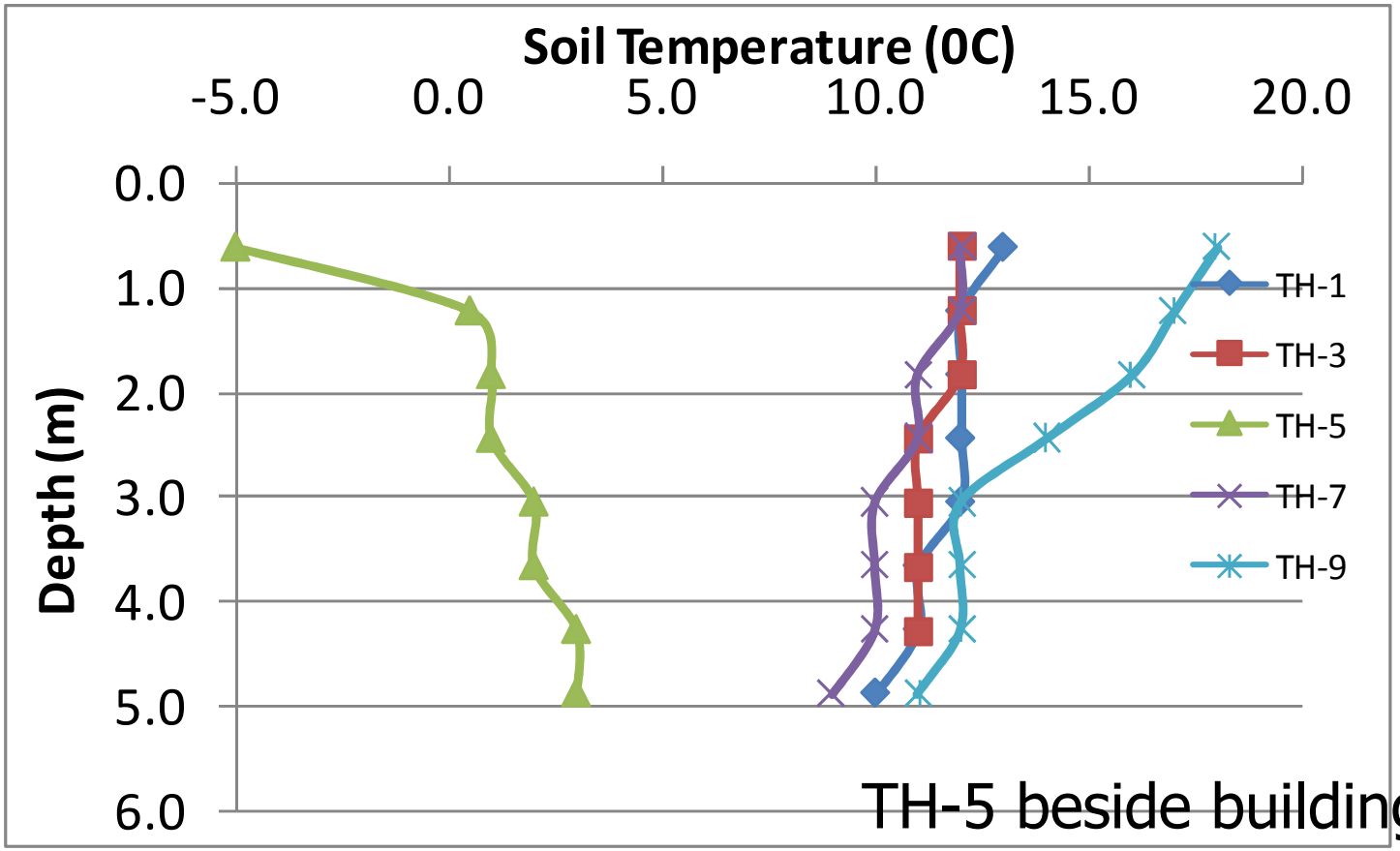
Courtesy Lindsay Smith, Health Canada



Moisture content low for this site with sand and gravel soils

Health Canada-Golder VI Study
Northern Canada Site

Courtesy Lindsay Smith, Health Canada

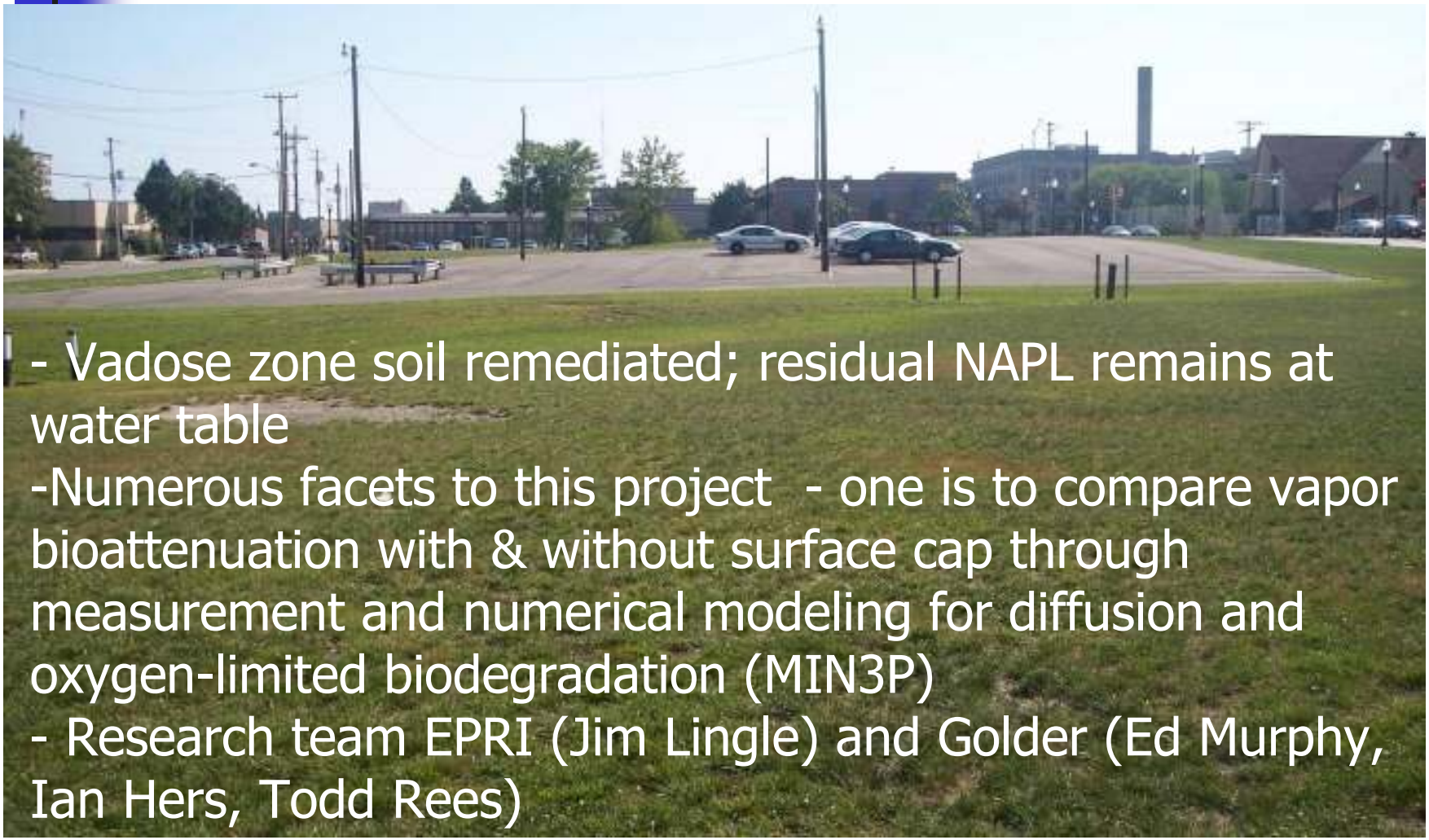


TH-5 beside building,
TH-1,3,7,9 below building

EPRI VI Research Study

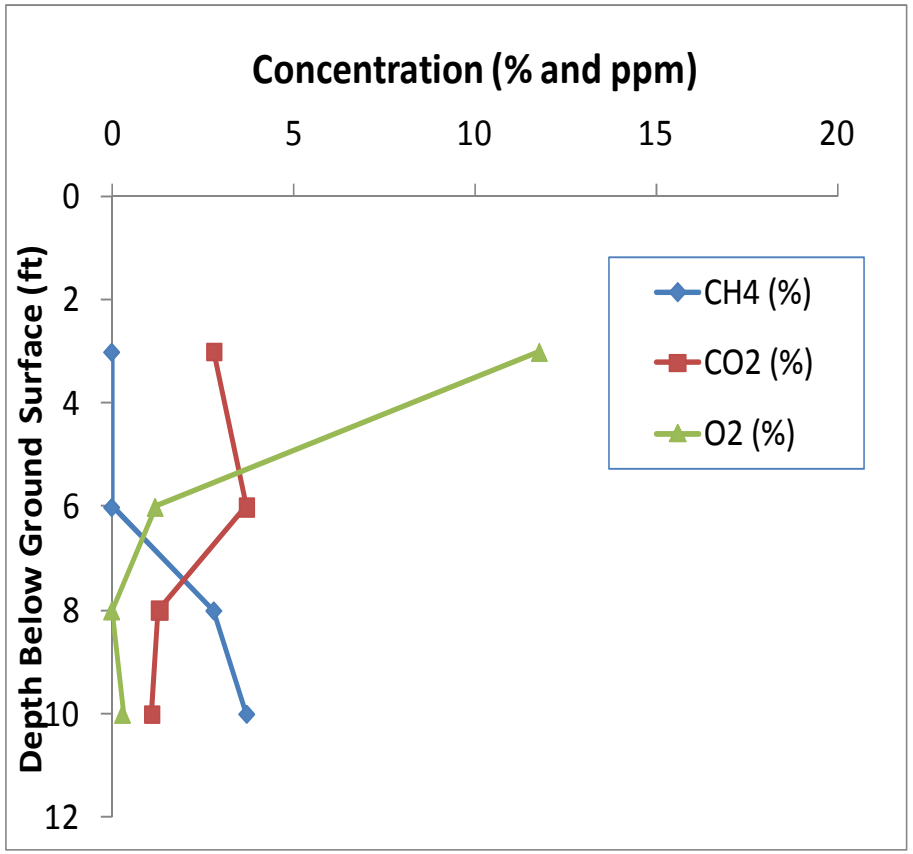
- Develop investigation methodologies to assess VI for (i) sites with buildings & (ii) future development scenario
- Characterize the VI potential at remediated MGP sites with residual impacts
- Assess the significance of vadose zone natural attenuation (VZNA), and in particular biodegradation of MGP chemicals
- Evaluate beneficial innovative, lower cost site characterization methods
- Assess approaches/methods for mitigation of VI
- Research team EPRI (Jim Lingle) and Golder (Ed Murphy, Ian Hers, Todd Rees)

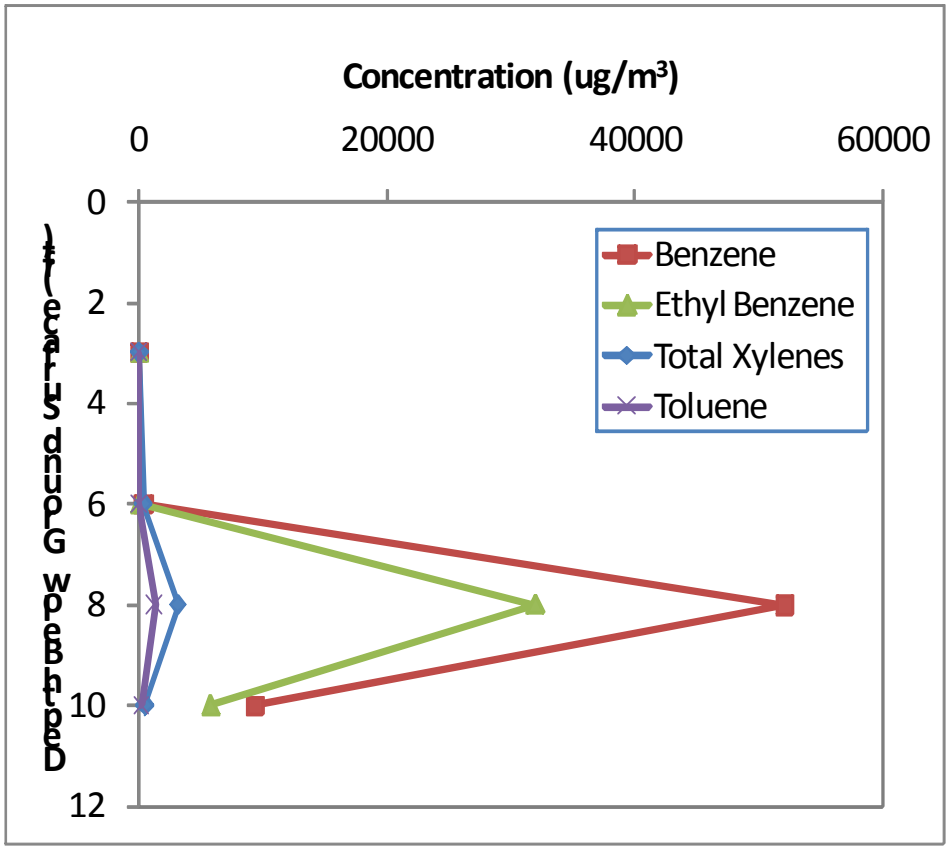
EPRI VI Research Study



- Vadose zone soil remediated; residual NAPL remains at water table
-Numerous facets to this project - one is to compare vapor bioattenuation with & without surface cap through measurement and numerical modeling for diffusion and oxygen-limited biodegradation (MIN3P)
- Research team EPRI (Jim Lingle) and Golder (Ed Murphy, Ian Hers, Todd Rees)

EPRI Research Study – Soil Gas Profiles without Cap



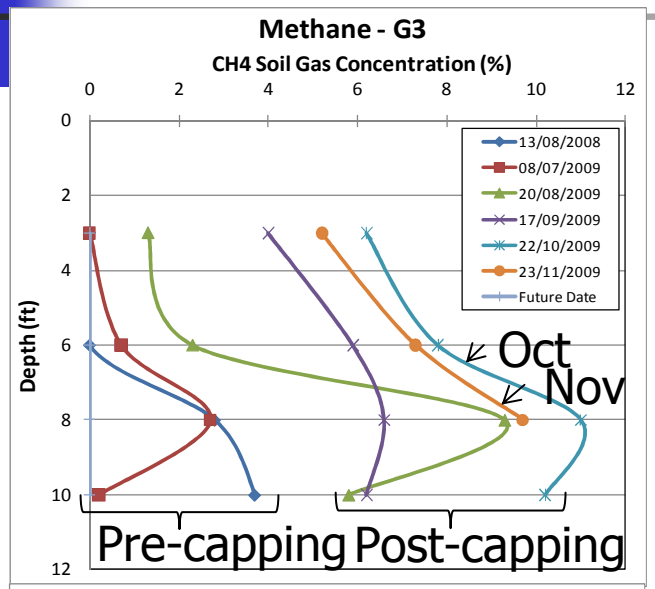


Placement of Topsoil

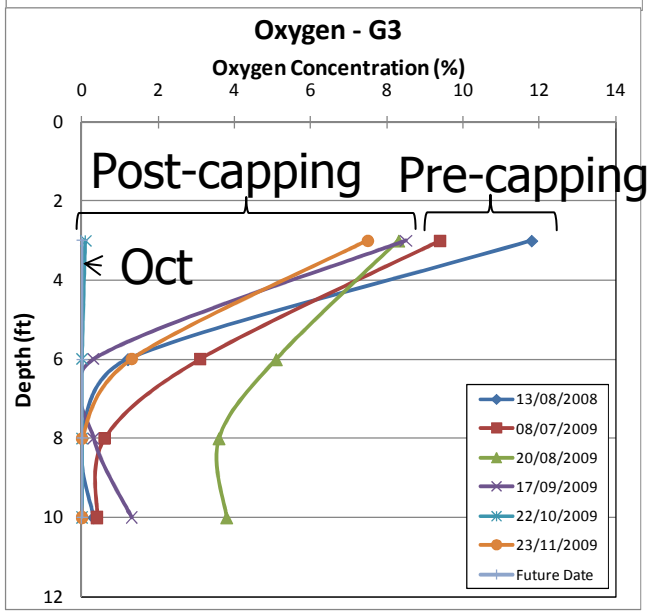
For more info see MGP 2010 presentation

Preliminary Monitoring Results

CH_4

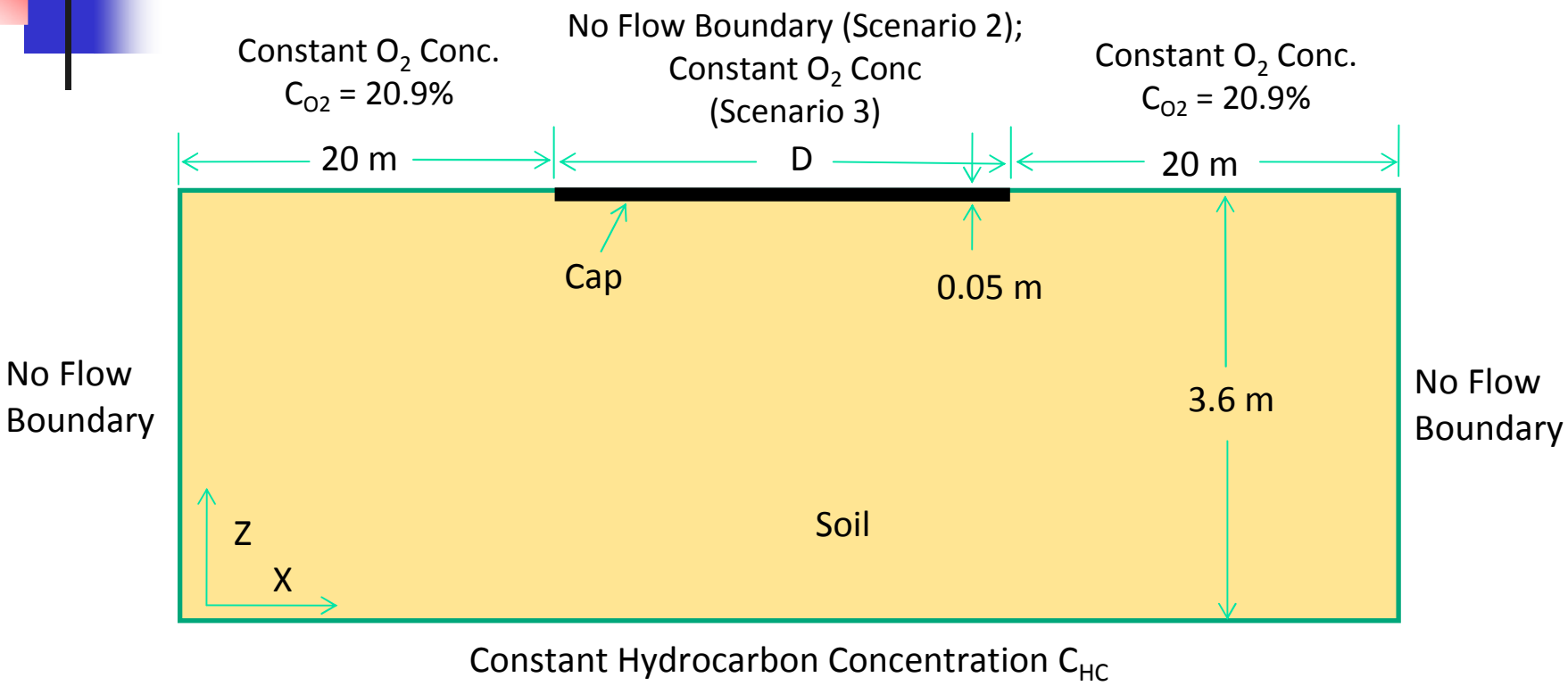


O_2



- Below-cap O_2 concentrations decreasing, CH_4 concentrations increasing
- Below-cap hydrocarbon (TO-15) concentrations also generally increased in shallow probes
- Differences in October/November may be due to water table (rose slightly, deep probe submerged in Nov.) or weather conditions
- Beside-cap concentration profiles did not exhibit apparent trends (although concentrations lower)

EPRI Research Study - Modeling



C_{HC} x,z (t = 0) = 0
C_{HC} (z = 0) = Constant

Scenarios:
1. No cap
2. Impermeable Cap, D = 15 m
3. Leaky Cap, D = 15 m

MIN3P - Diffusion and Oxygen-Limited First Order Decay

Recent Direction for Petroleum Hydrocarbons

- USEPA developing Petroleum Vapour Intrusion (PVI) Guidance, as part of this work are:
  - Developing empirical database
  - Screening approaches; under consideration are:
    1. Pathway **exclusion criteria** for dissolved or low strength petroleum sources:
    2. Adjust attenuation factors to include bioattenuation factor (e.g., 10X or 100X reduction)
  - Validate BioVapor Model

Recent Direction for Petroleum Hydrocarbons

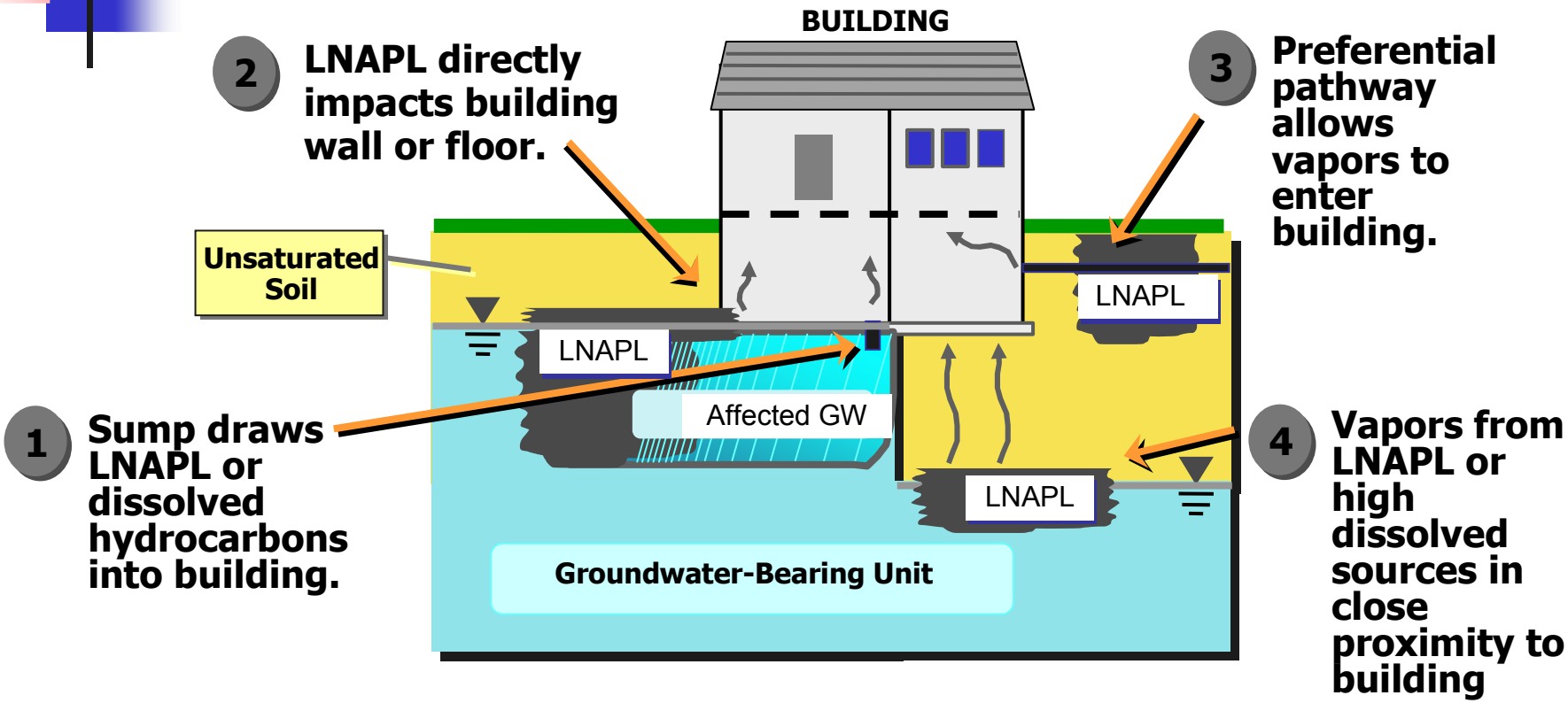
Possible exclusion criteria for dissolved or low strength petroleum sources:

1. Benzene < X mg/L Groundwater
2. TPH < Y mg/L
3. Minimum depth clean soil above contamination source = Z m
4. No NAPL
5. No significant capping effect
6. Oxygen in soil gas > X

- Significant interest industry and regulators for less conservative approaches

Causes of Petroleum Vapor Intrusion

Industry Experience

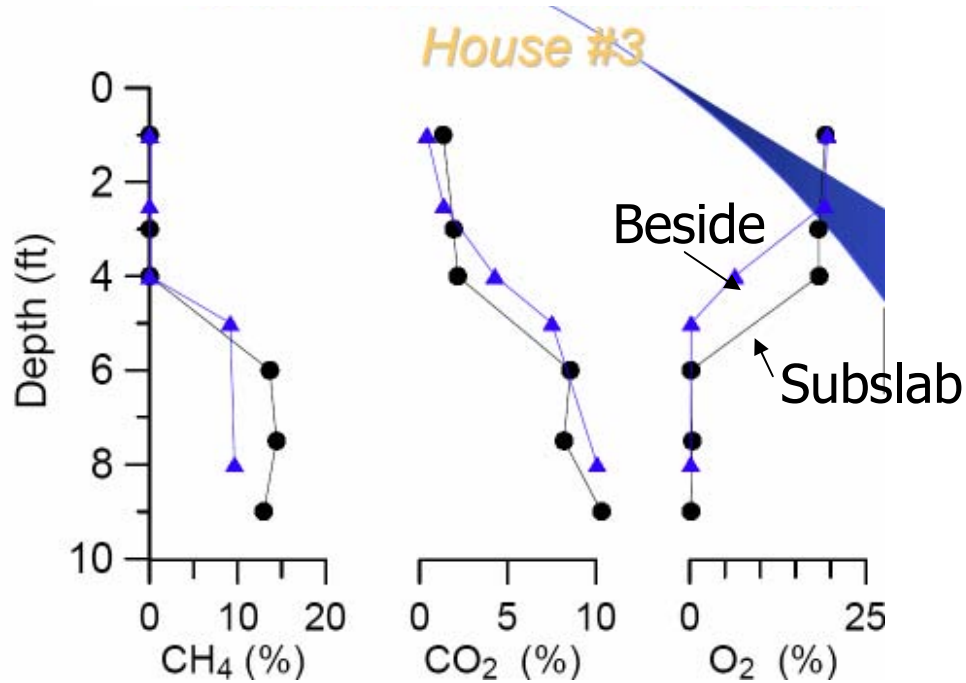


KEY POINT: **Vapor intrusion caused by LNAPL, contaminated soil, or high-dissolved sources in direct contact or close proximity to buildings/receptors**

Courtesy Todd Ririe, BP 2009 (AEHS Amherst conference; API)

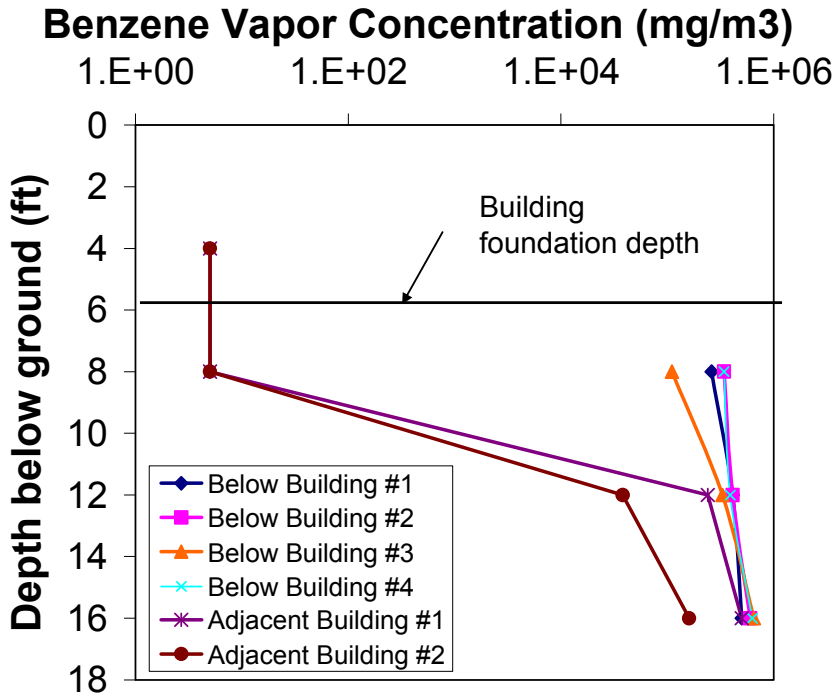
Capping Effect?

Santa Maria House, CA (Paul Lundegard, Unocal Oil Seeps)



No Capping Effect?

Paulsboro House, NJ (Gasoline NAPL, sand, sm. silt)

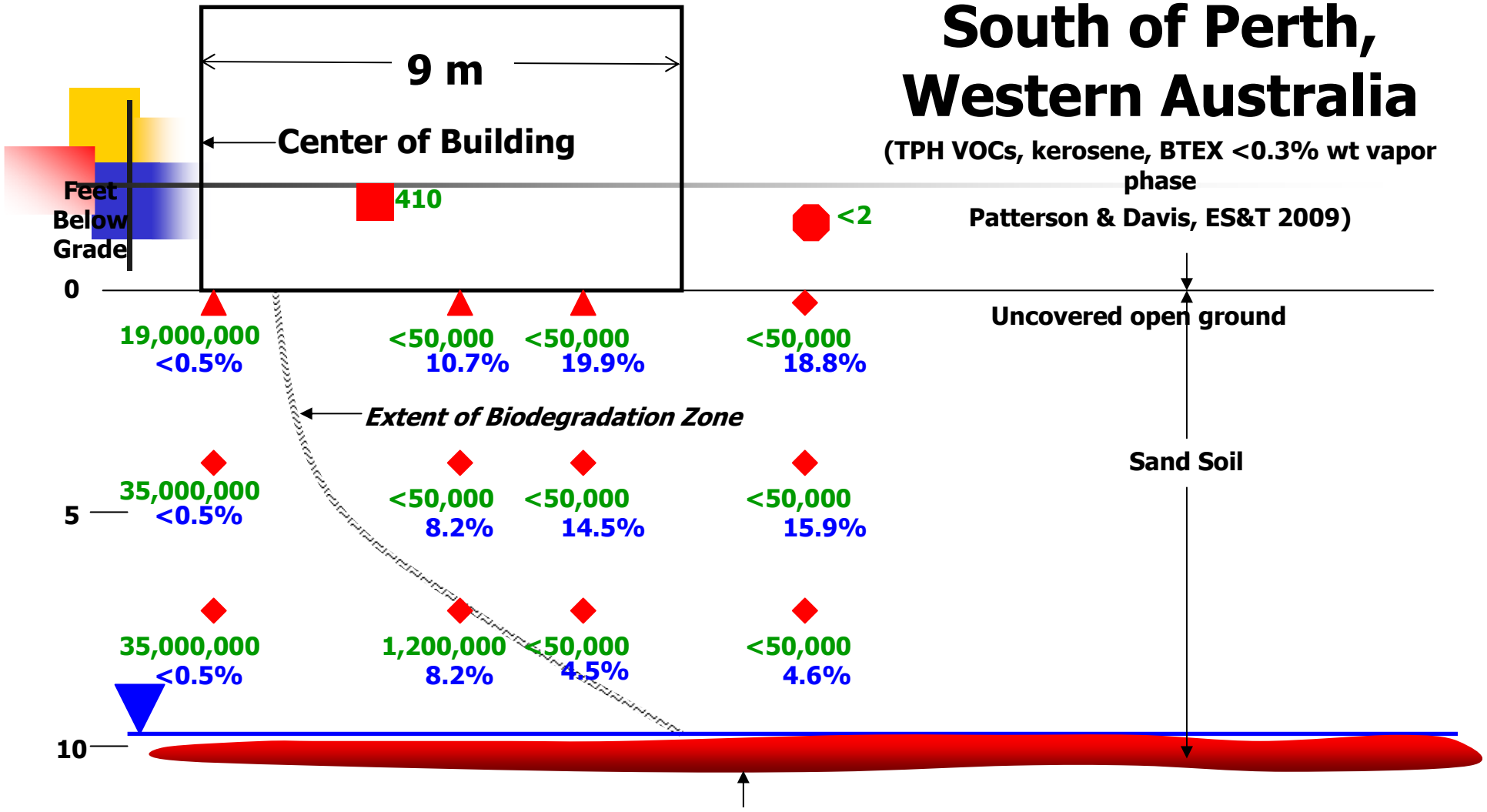


Capping Effect?

South of Perth, Western Australia

(TPH VOCs, kerosene, BTEX <0.3% wt vapor phase

Patterson & Davis, ES&T 2009)



KEY

- Indoor Air measurement
- Outdoor Air measurement
- Sub-Slab (building) Soil Vapor Sample Point
- Subsurface Soil Vapor Sample Point

20,000,000 ug/m3 Petroleum vapor/air concentrations

<1% Oxygen

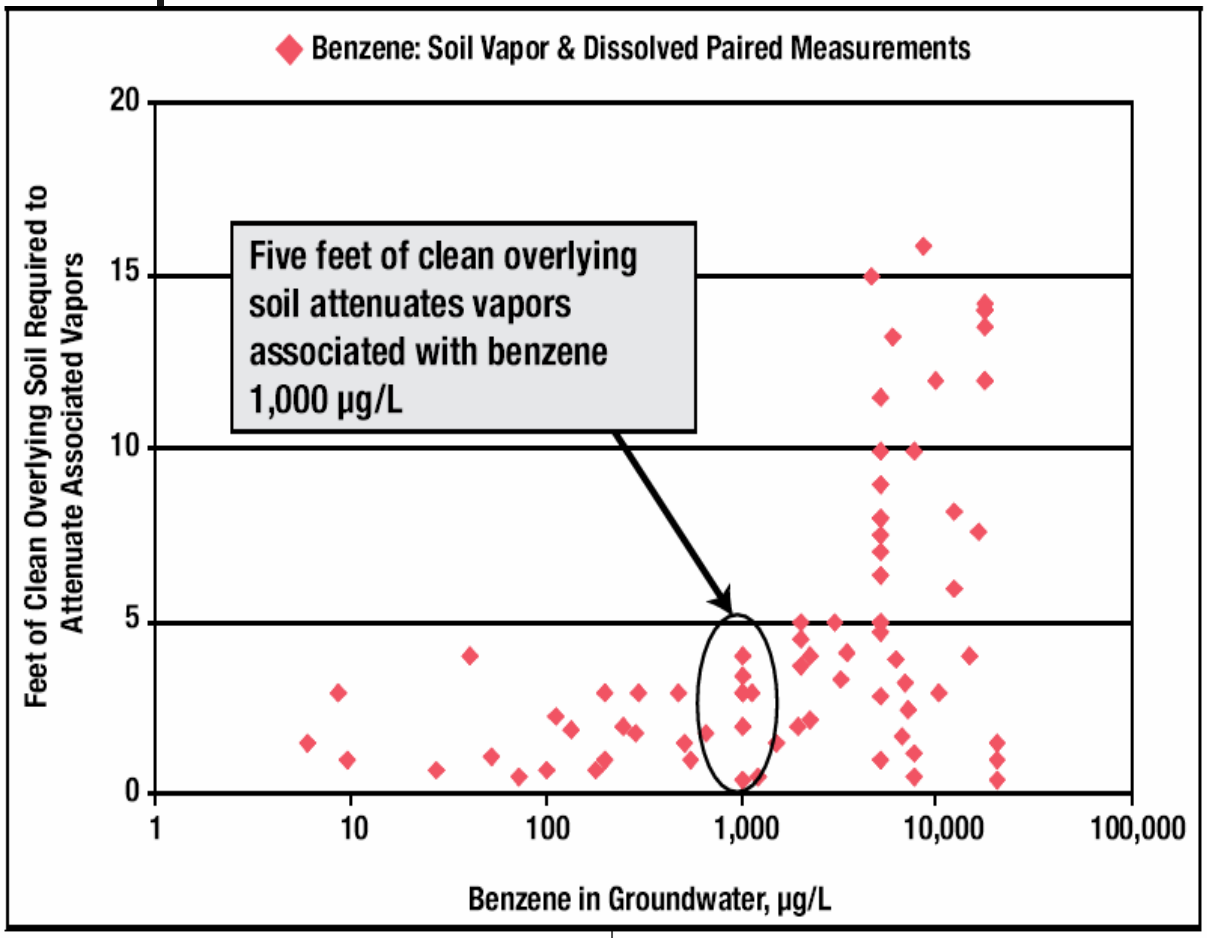
0 — 20

Feet, horizontal

Figure by Robin Davis

Exclusion Criteria – Groundwater to Overlying Soil Vapor Low Source Strength

(courtesy Robin Davis, Utah DEP)



Almost all data external building

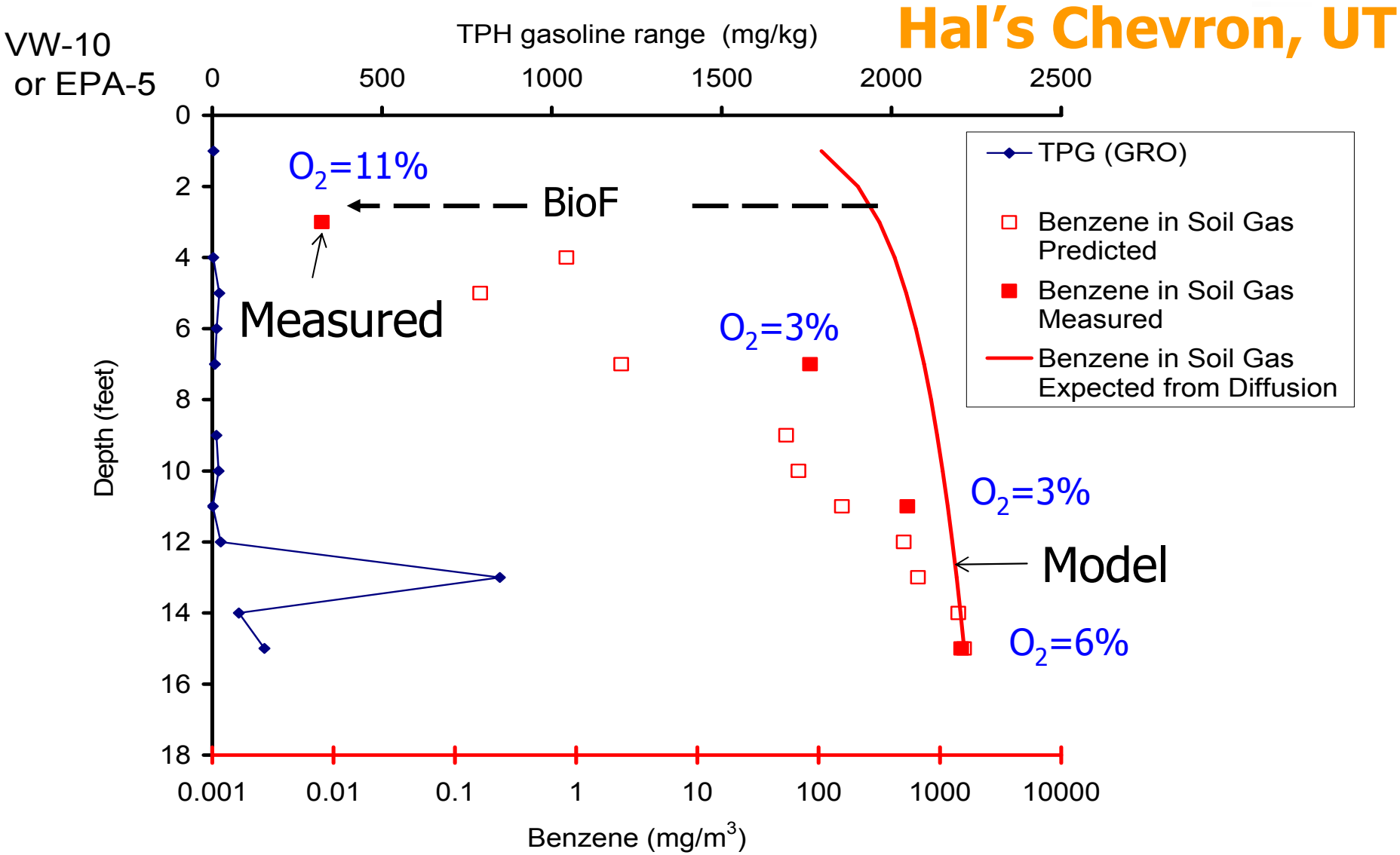
Criteria for Evaluating Data Set

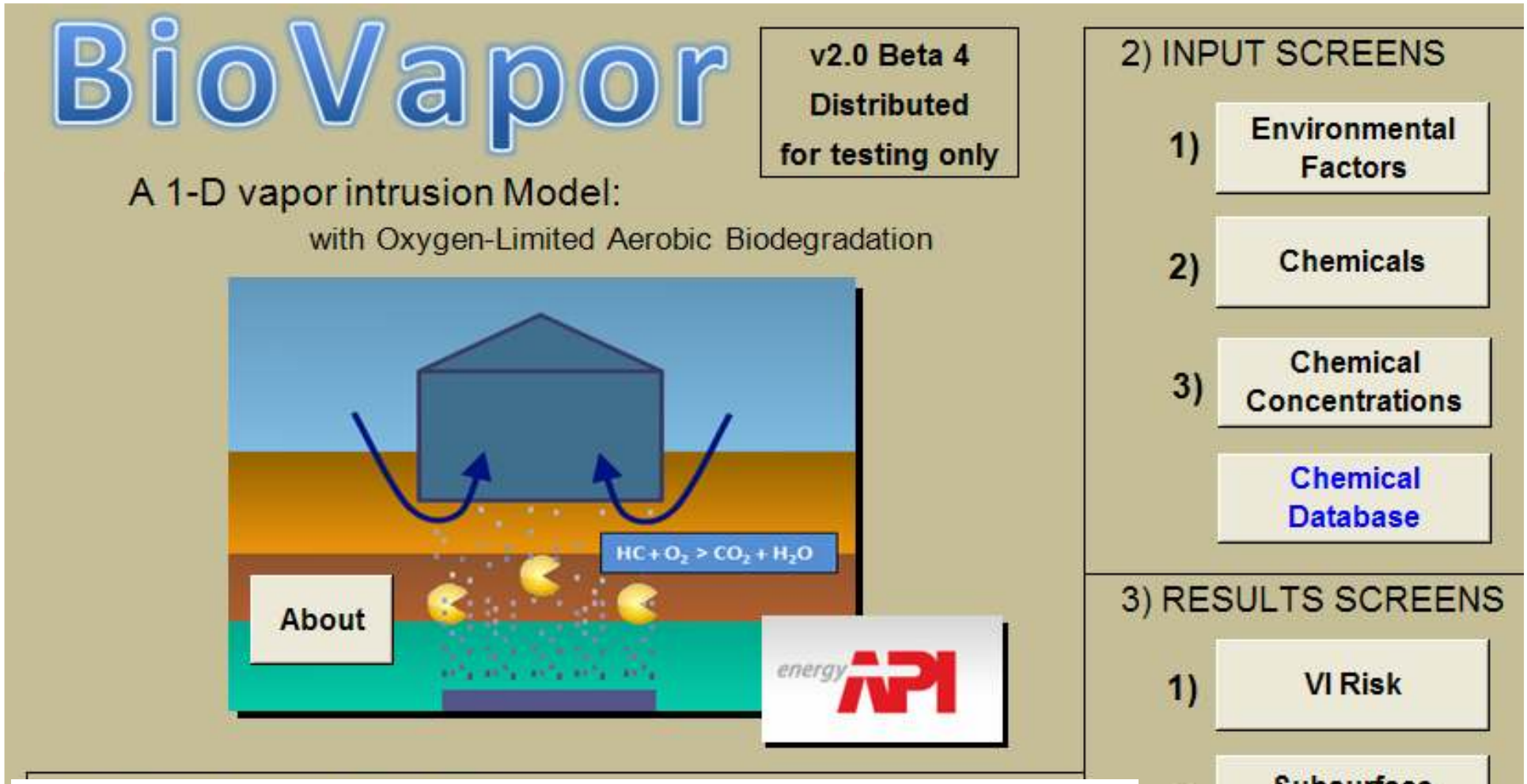
- Dissolved sources at known depth to groundwater
- Clean soil overlies groundwater
- Complete attenuation of soil vapors defined by shallow soil vapors = 0 (which may vary, full attenuation verified by authors)
- Majority of soil vapor measurements from multi-depth soil gas points
- LUST and refinery sites included, but No LNAPL

Robin V. Davis. Evaluating the Vapor Intrusion Pathway: Studies of Natural Attenuation of Subsurface Petroleum Hydrocarbons and Recommended Screening Criteria, 21st Annual National Tanks Conference, Sacramento, CA, VI Workshop and Session, March 30-April 1, 2009.

USEPA ORD Bioreduction Factor

(courtesy Dr. John Wilson, USEPA)





BioVapor model (December 2009) is a user-friendly analytical spreadsheet model developed by George DeVaull, Shell based on J&E framework that incorporates oxygen-limited biodegradation. http://www.api.org/ehs/groundwater/vapor/bio-vapor-intrusion.cfm

Mount Holly, NJ

- UST leaked former gas station
- Shallow water table
- Loamy Sand soils

Golder – NJDEP Research Study

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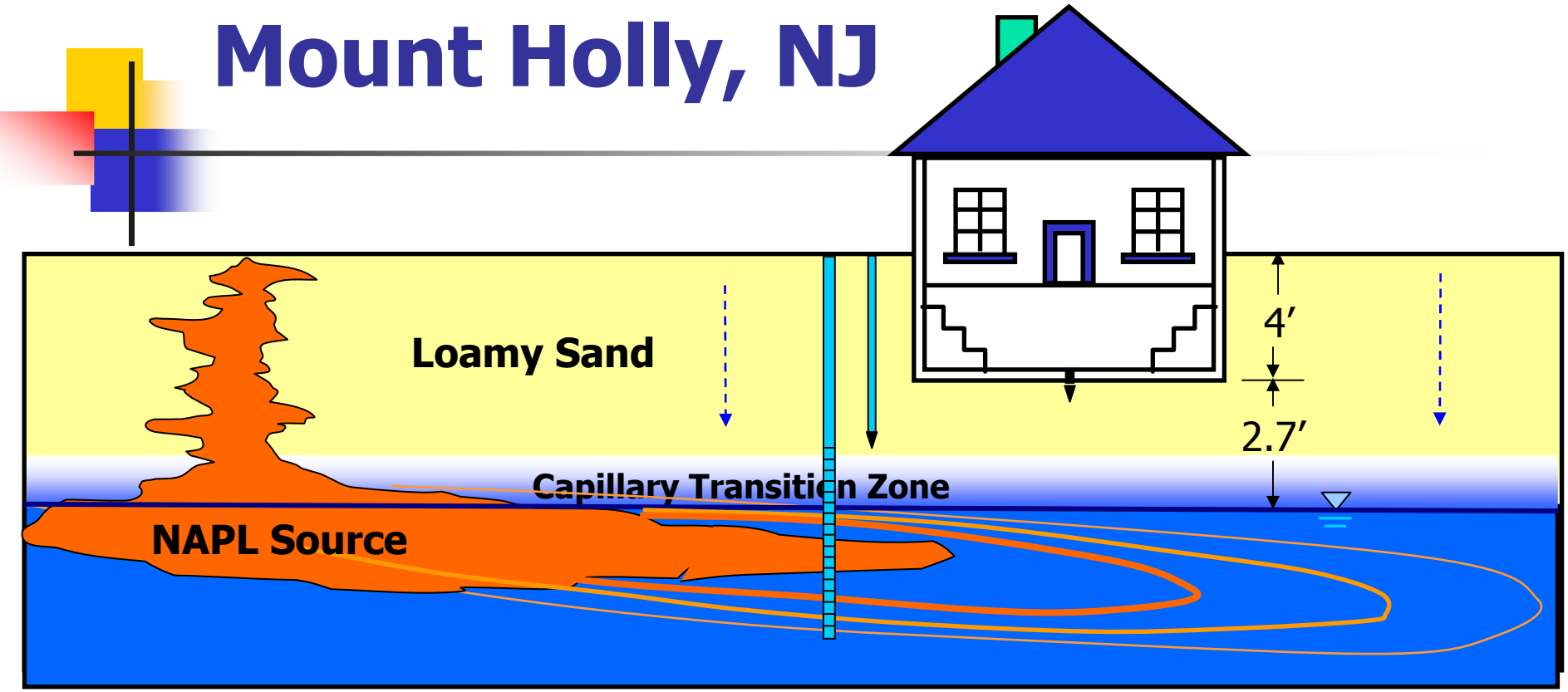
Mount Holly, NJ



	Benzene	Toluene	Xylenes	135-TMB	O_2	CO_2
Groundwater (ug/L)	308	1,150	2,054	-	-	-
Soil Vapor (ug/m^3)	11	2.1	56	98	6.1	8.2
Subslab Vapor (ug/m^3)	0.73	4.9	4.8	<0.98	20.9	-
Indoor Air (ug/m^3)	0.4	3.3	0.87	<0.98	20.9	-
Measured gdw α	<1E-05	<1.9E-05	<2.7E-06	-	-	-

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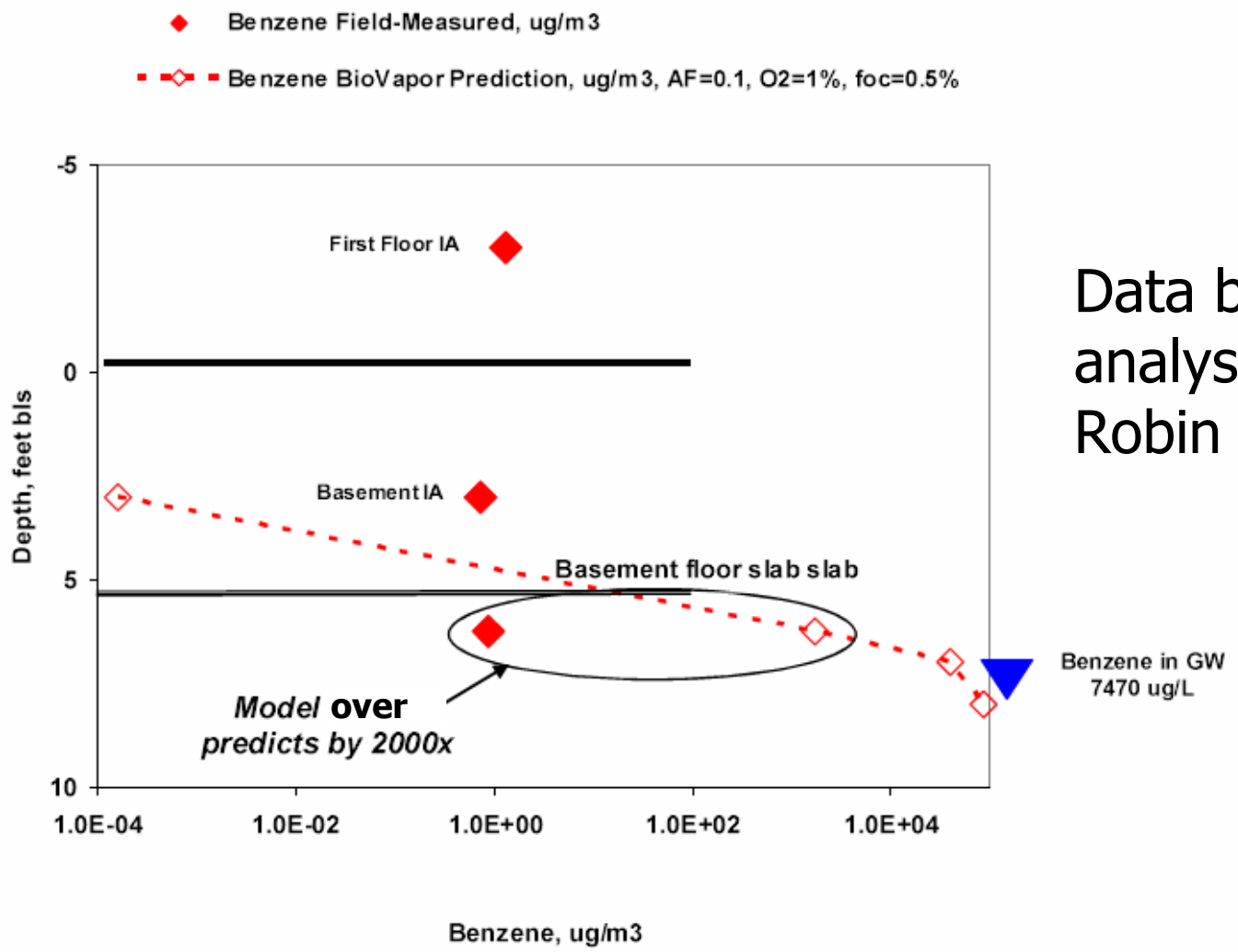
Mt. Holly, NJ, 91 Hulme

Sub-slab vapors & IA above high-strength dissolved source



Data by Golder, analysis by Robin Davis

New Developments for Vapour Intrusion Mitigation

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Mitigation Context

- May be required at sites with VOCs (e.g., chlorinated solvents), radon, methane
- Increased emphasis on pre-emptive mitigation at Brownfield (instead of intensive site characterization and modeling)
- Challenge is no standard practice for design and wide range of options available, costs can be significant [1]

1. Some Guidance: UK CIREA 149 & 665; British Standards 8485:2007; Requirements Los Angeles & San Diego

Mitigation Options

- Below building venting
  - Existing buildings: Active subslab depressurization (SSD) with sealing of building foundation openings
  - New buildings: Passive, provisionally active, venting system typically combined with barrier
- Building HVAC modifications
  - Positively pressurize building (may be difficult to achieve constant positive pressure)
  - Increase ventilation rate
  - Energy cost associated with heating/cooling outdoor air
- Remediate source (e.g., soil vapour extraction)

Radon Mitigation Experience

- Sub-slab depressurization (SSD) combined with sealing of cracks most commonly used technology
- Comprehensive USEPA study[1] compared sub-slab depressurization, slab sealing and house pressurization, found that sub-slab depressurization was most effective method
- SSD often > 90 % reduction in radon concentrations
- Sealing floors alone <= 50 % reduction
- Passive venting alone: Vent connected to stack open to atmosphere: 30% reduction in radon entry[2]

1 Installation & Testing of Indoor Radon Reduction Techniques in 40 Eastern Pennsylvania Houses, EPA Report 600/8-88/002 (400 pg)

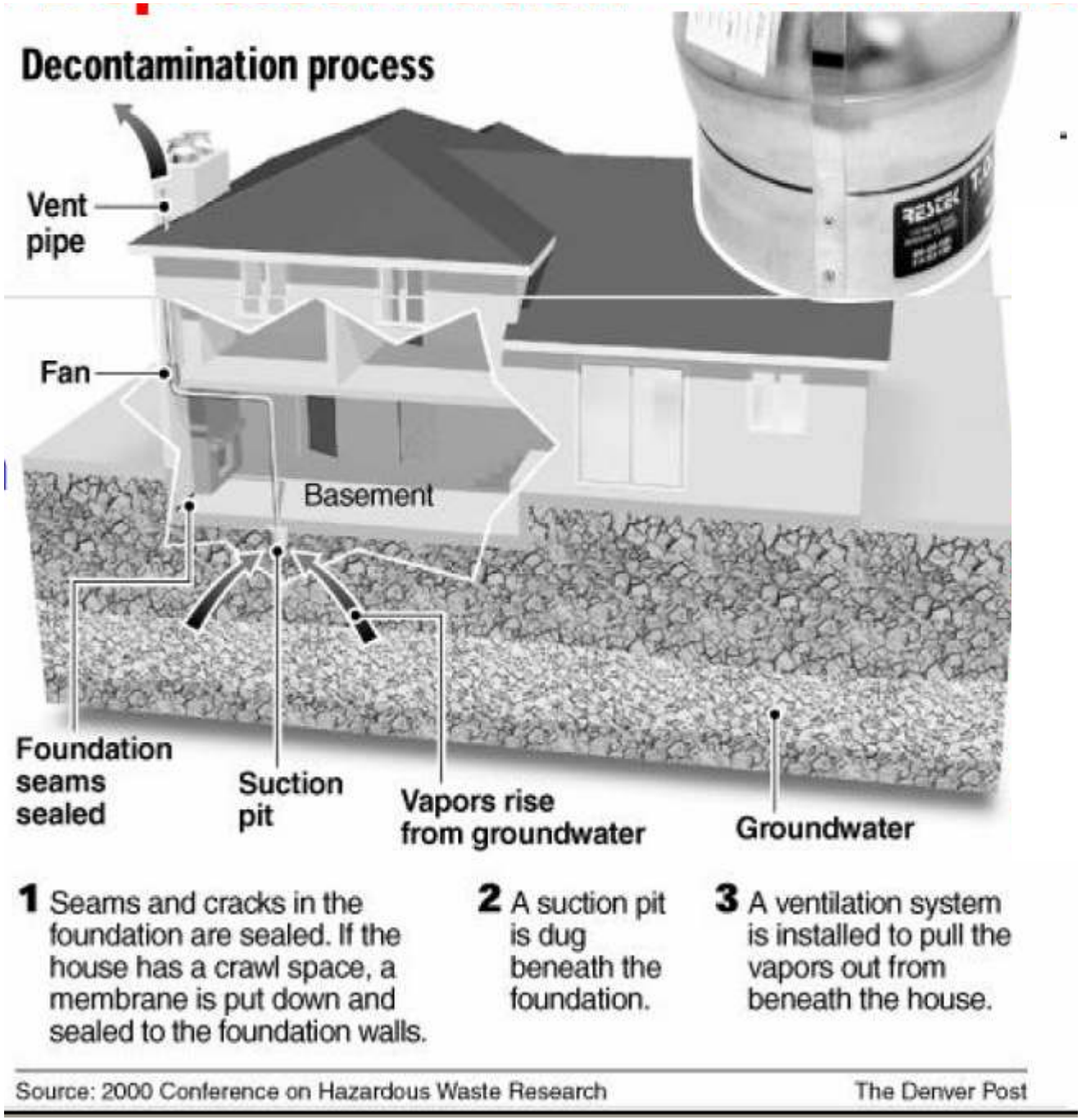
2 Holford, D.J. & Freeman, H.D. Effectiveness of a Passive Subslab Ventilation System in Reducing Radon Concentrations in a Home. Environ. Sci. Technol. 1996, 30, 2914-2920.

SSD Residential/ Small Commercial

Usually 1 to 2 ("radon") sumps

90-150 Watt fans

Work well 80 to 95% reduction typical except shallow water tables



SSD Systems

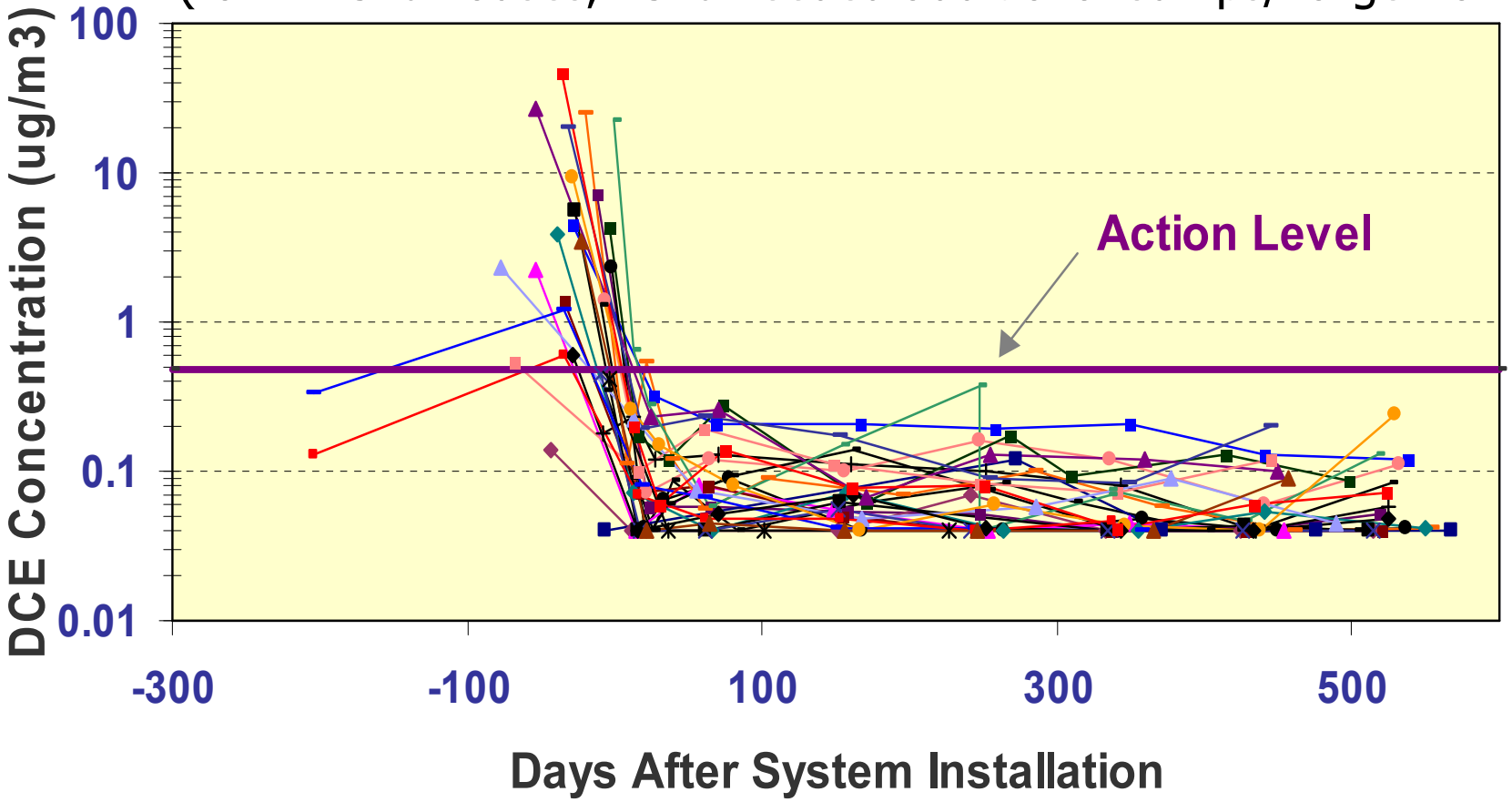
ITRC (2007)

ITRC (2007)

SSD Performance
(Redfield, D.Folkes)

NO MODIFICATIONS REQUIRED

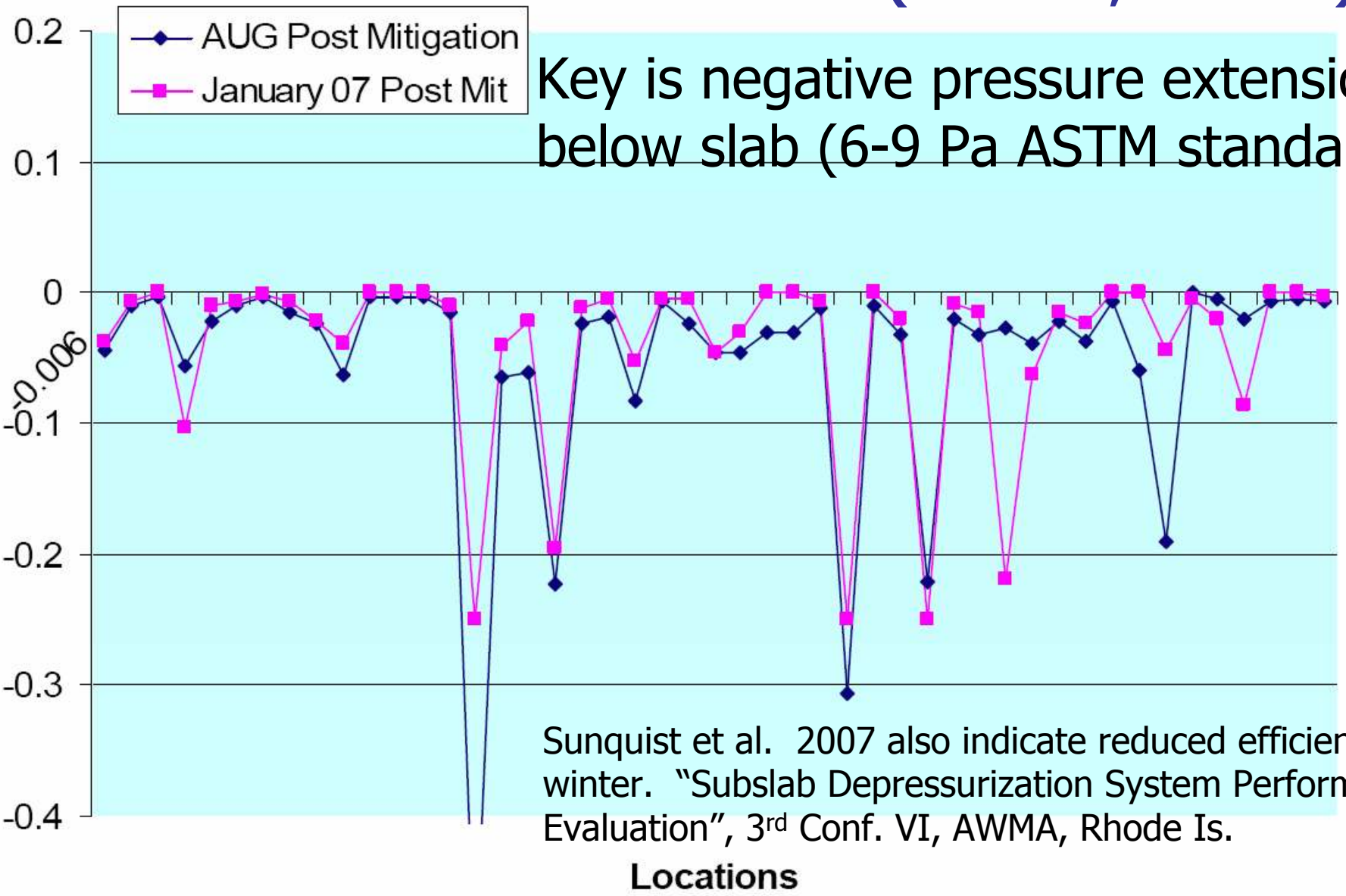
(for ~ 75% houses, 25% needed additional sumps/ larger fans)



EFFICACY OF SUB-SLAB DEPRESSURIZATION FOR MITIGATION OF VAPOR INTRUSION OF CHLORINATED ORGANIC COMPOUNDS DJ Folkes* and DW Kurz Indoor Air 2002

Post Mitigation PFE

(Endicott, B.Wertz)

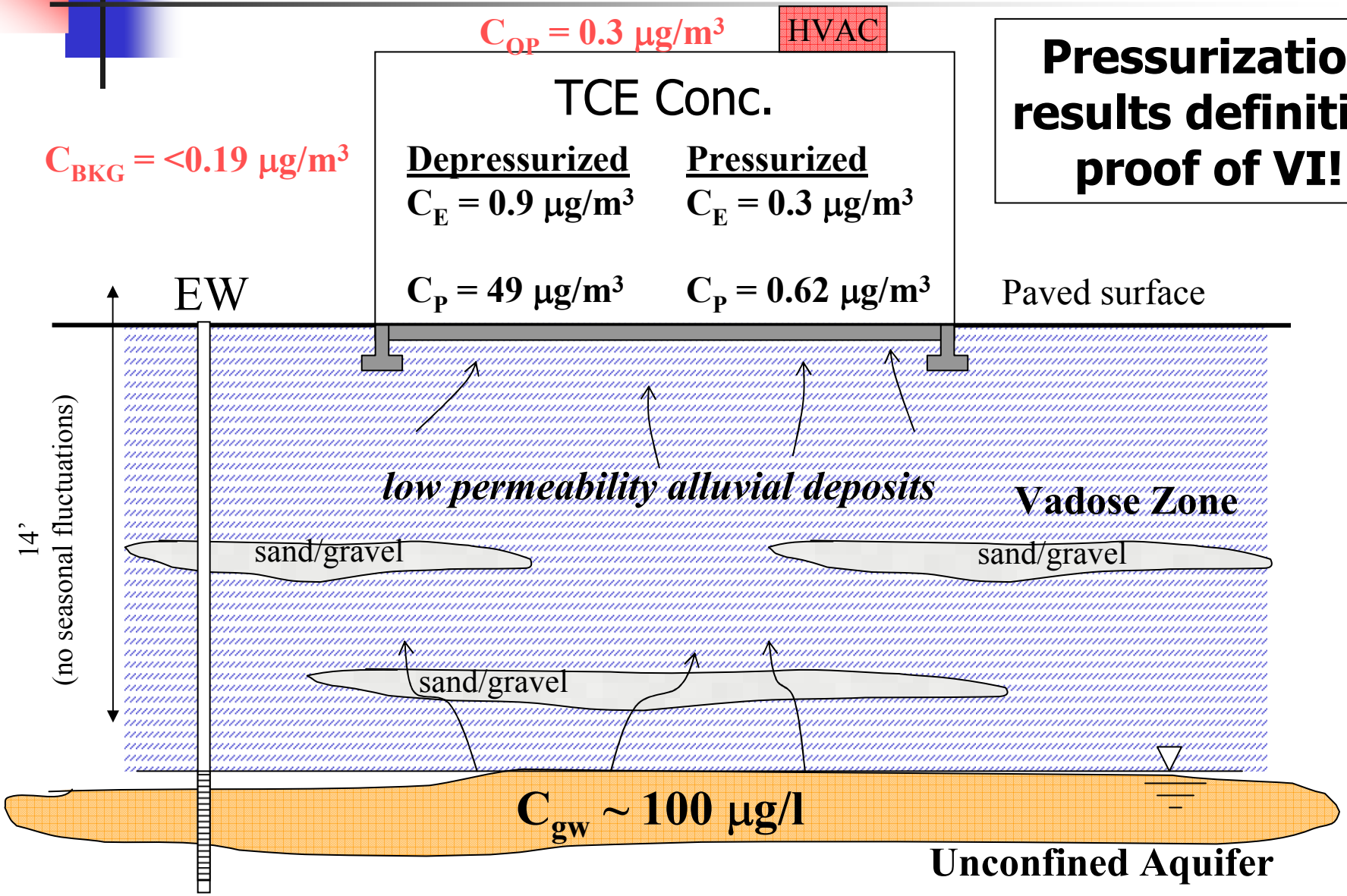


Key is negative pressure extension below slab (6-9 Pa ASTM standard)

Sunquist et al. 2007 also indicate reduced efficiency in winter. "Subslab Depressurization System Performance Evaluation", 3rd Conf. VI, AWMA, Rhode Is.

Commercial Building VI Study
(Wozniak et al., AEHS, 2004)

Pressurization results definitive proof of VI!

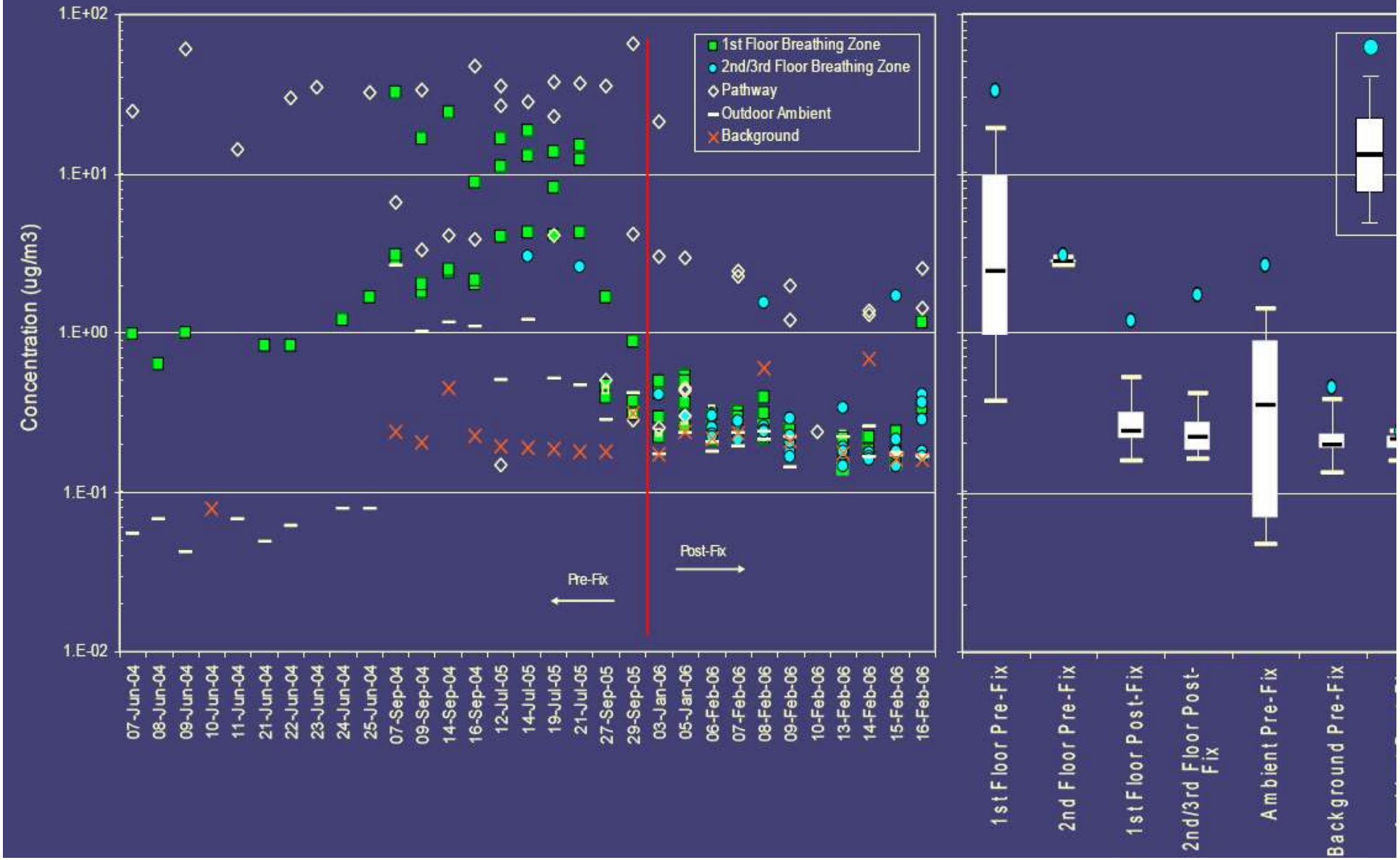


Moffett AFB Hanger
(D. Brenner, AWMA, 2006)

TES

TCE Results

Moffett AFB D. Brenner, AWMA, 2006



New Building Vapour Intrusion Mitigation Matrix

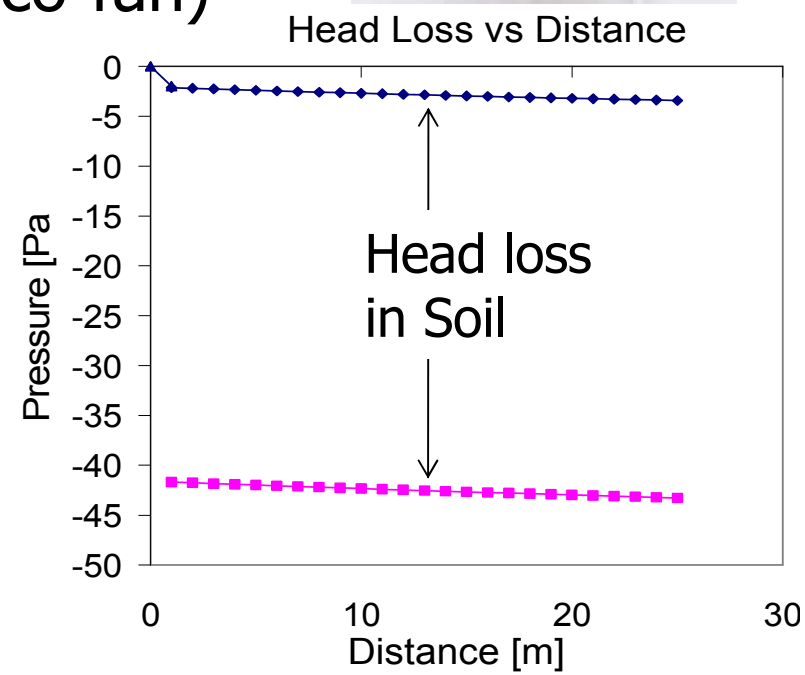
Energy Input	Passive	Low energy – Wind turbines	Higher energy – Electrical fans
Efficiency Assumes pipe losses small	Sand	Gravel	Aerated Floor
Barrier	Concrete Foundation (no additional barrier)	Fine-grained soil	Geomem-brane

Increased Protection

- Mitigation solution depends on contaminant type, concentration, flux and building. Multiple combinations possible and opportunities for optimization

Design Innovations

- Selection of appropriate barrier material
  - **Conventional**: PVC, HDPE
  - **Newer**: PVC alloy, LLDPE with aluminium composite, Liquid boot, GeoSeal
- Wind, Solar-powered turbines (Eco-fan)
  - Golder has developed computer program to optimize design
- Geocomposites
- Aerated floors



More research needed
on sustainable approaches

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Barrier Design

- Important property is permeation rate (not the same as vapor diffusion rate)
- Limited literature (Haxo 1984, Park 1995, Sangan and Rowe, 2002; McWatters 2007, product specifications)
  - Liquid Boot 1.5 mm PCE vapor diffusion rates: 2.7×10^{-14} to 8.1×10^{-14} m^2/sec
  - McWatters (2007) BTEX permeation rates: HDPE 10^{-11} to 3×10^{-10} m^2/sec; PVC 2×10^{-10} to 10^{-9} m^2/sec

Similar to diffusion rate of benzene in water

Be careful if designing system with just barrier (relying on diffusive gradients)

Long diffusive path length

Vancouver, BC Methane Mitigation

Liquid Boot: Single course, high build, polymer modified asphaltic emulsion

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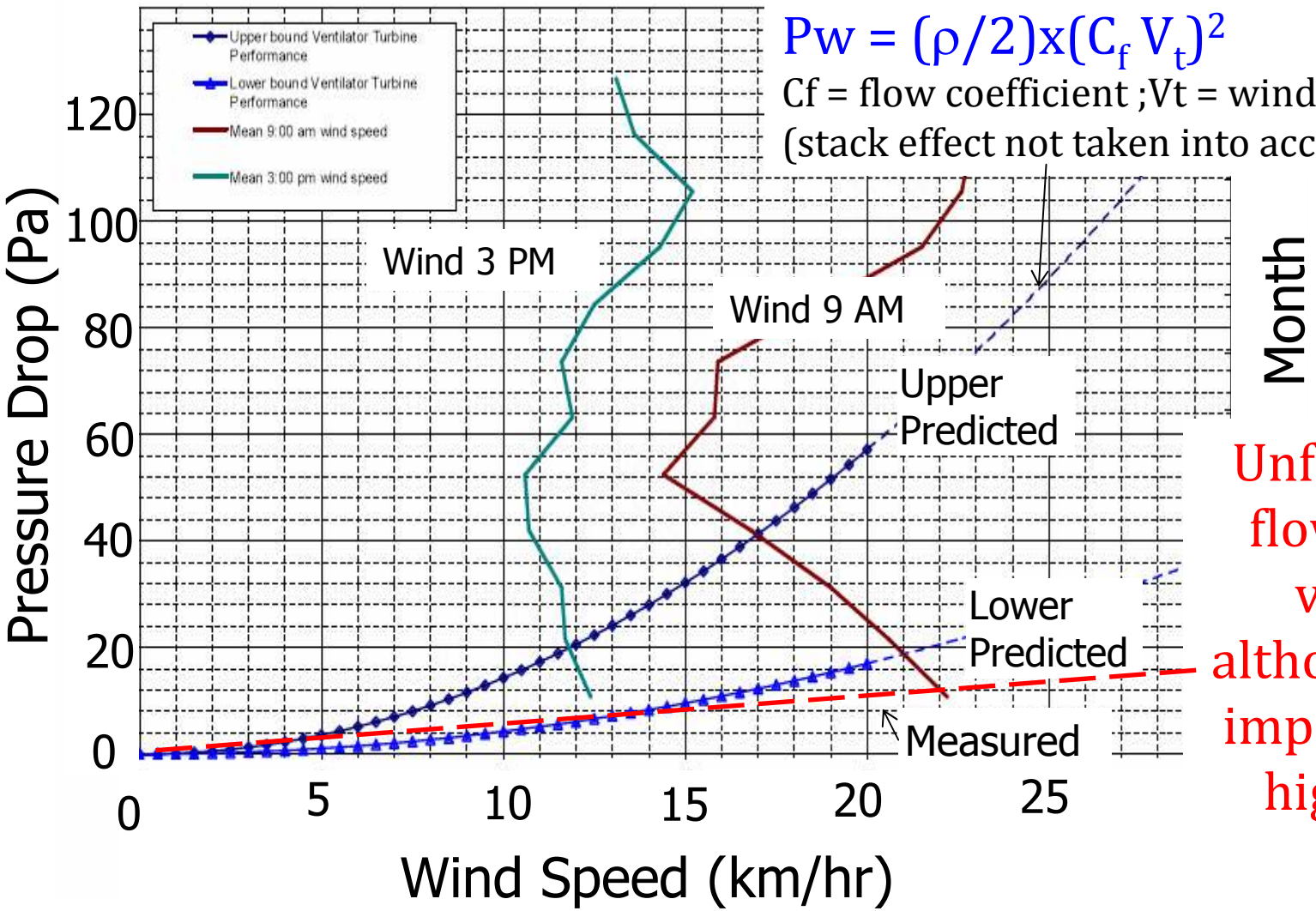
Wind Turbine Performance

Wind Siphoning Pressure (Pw)

$Pw = (\rho/2)x(C_f V_t)^2$

Cf = flow coefficient ;Vt = wind velocity (m/s)
(stack effect not taken into account) (AS 4740)

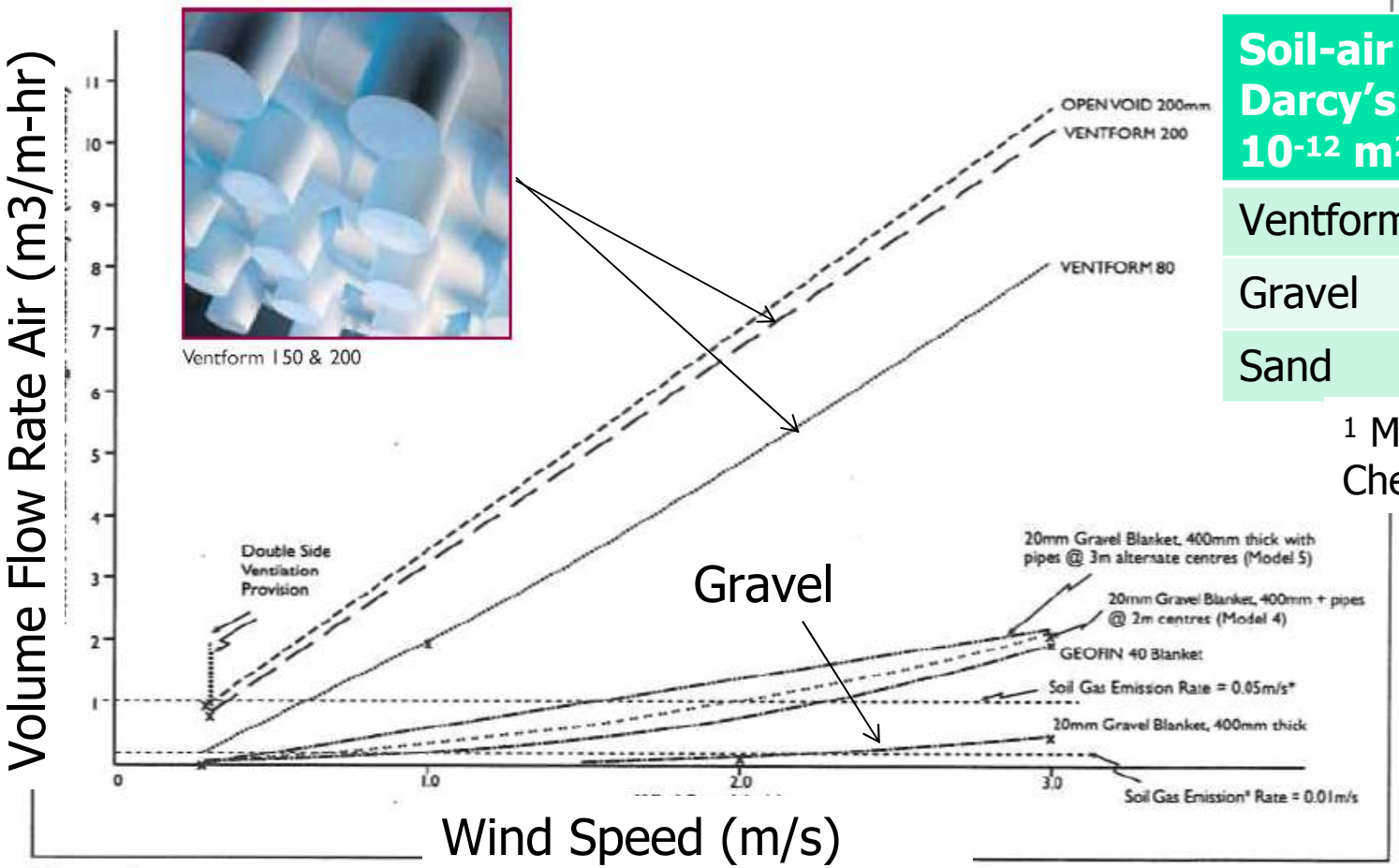


Unfortunately flows will be very low although can be improved with high K vent layers

Pontarolo Cupolex
Aerated Floor Toronto School

UK Research
Passive Venting

Passive Venting of Soil Gases Beneath Buildings Research Report Ove Arup & Partners Sept 1997 – Computational Fluid Dynamics Modeling



Soil-air Permeability Darcy's (1 Darcy = 10^{-12} m^2)	
Ventform	~10^8 +/-
Gravel	~$5x10^4$ +/-[1]
Sand	~10^1 +/-[1]

[1] Mid-point Freeze & Cheery, 1979

Figure 5
Result of CFD Modelling: Volume Flow Rate vs Wind Speed for 30m Wide Foundation

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Mitigation Considerations

- Effective
  - Usually but not always so
- Intrusive
  - Requires sump and piping inside building
- Operation, Maintenance and Monitoring
  - Costs can be significant, therefore emphasis on passive systems
- Performance Monitoring
  - Be careful with VOC measurements since they can lead to incorrect conclusions due to background
  - Recommend pressure and flow measurements

Resources

- **Science Advisory Board Contaminated Sites of British Columbia** (prepared by Golder). Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion. June 2008 (updated version ~Sept 2010)
- **California EPA.** Advisory – Active Soil Gas Investigation. March 2010.
- **U.S.EPA.** *U.S.EPA's Vapor Intrusion Database: Preliminary Evaluation of Attenuation Factors* (March 4, 2008).
- **Interstate Technology and Regulatory Council (ITRC)**. *Vapor Intrusion Pathway: A Practical Guide (VI-1) (January 2007)*. http://www.itrcweb.org/Documents/VI-1.pdf .
- **American Petroleum Institute (API)**. *A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites (November 2005).* http://www.api.org/ehs/groundwater/lnapl/soilgas.cfm

Resources

- **New Jersey Department of Environmental Protection**. *Vapour Intrusion Guidance (October, 2005)*. http://www.state.nj.us/dep/srp/guidance/vaporintrusion/vig.htm
- **Massachusetts Department of Environmental Protection**. *Indoor Air Sampling and Evaluation Guide* (April, 2002). http://www.state.ma.us/dep/ors/orspubs.htm#air

Conclusions

- Vapour intrusion is complex and highly site specific pathway with significant spatial and temporal variability observed
- Appropriate data collection strategy is essential, consider multiple lines of evidence and non-VOC measurements – follow strategic approach
- Proper sampling protocols for soil vapour are essential
- Further research and case studies are needed to better define what types of data are needed
- Aerobic biodegradation of petroleum vapours is a significant process - models should incorporate biodegradation where appropriate
- Variety of mitigation options are available; effectiveness and cost vary

Grazie Mille!

If you have any questions or comments please send email to ihers@golder.com

Thank-you!

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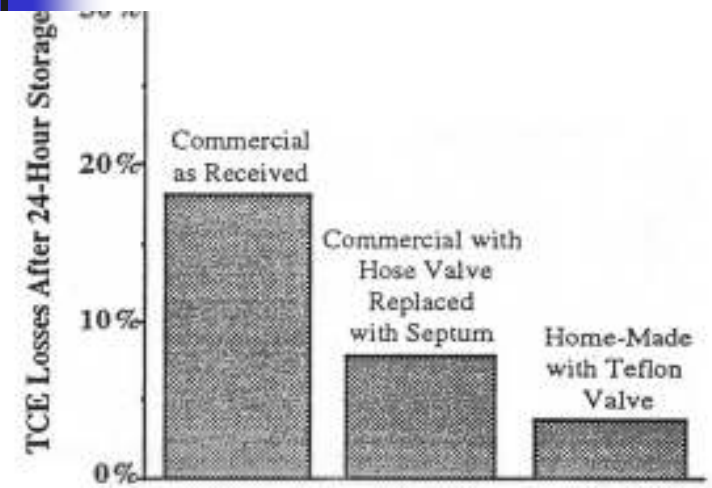
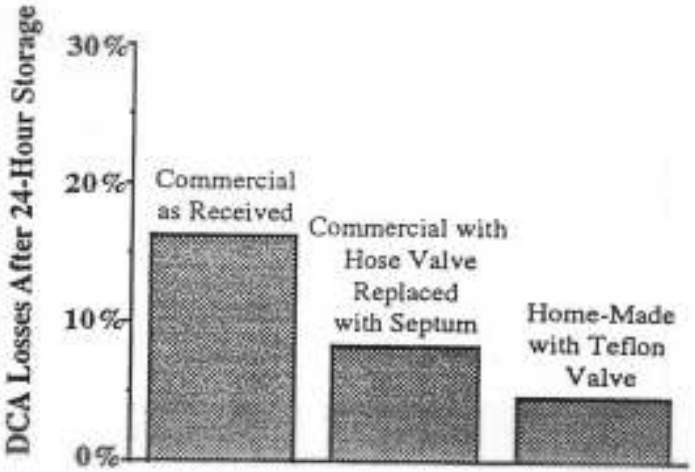
Tedlar Bags

- Proprietary material similar to Teflon
- Bags leak (very short holding times)
- Surface only moderately inert, sorb contaminants (only use new bags for analysis)
- Permeation
- Photo-oxidation concern if not properly stored
- Concern over shipping by air (pressure changes)
- Inexpensive, easy to use
- Not recommended for low-level VOC analysis, but suitable for fixed gases (O2, CO2, CH4) for short holding times

Losses from Tedlar Bags





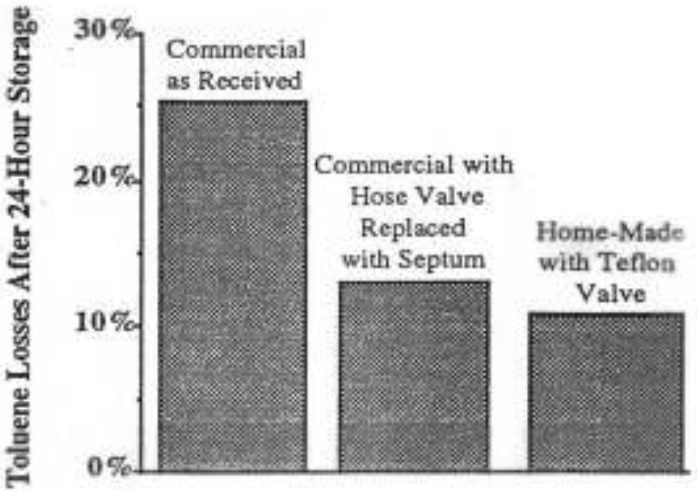


FIGURE 2. Comparisons of VOC losses in each type of bag tested. Commercial as received indicates bags used as received. Commercial with hose valve replaced with septum indicates bags in which the hose valve has been replaced by a Teflon-faced septum. Homemade with Teflon valves refers to bags that were made in the laboratory from Tedlar film and Teflon valves. ES&T 30(10), 1996

Permeation into Tedlar Bags

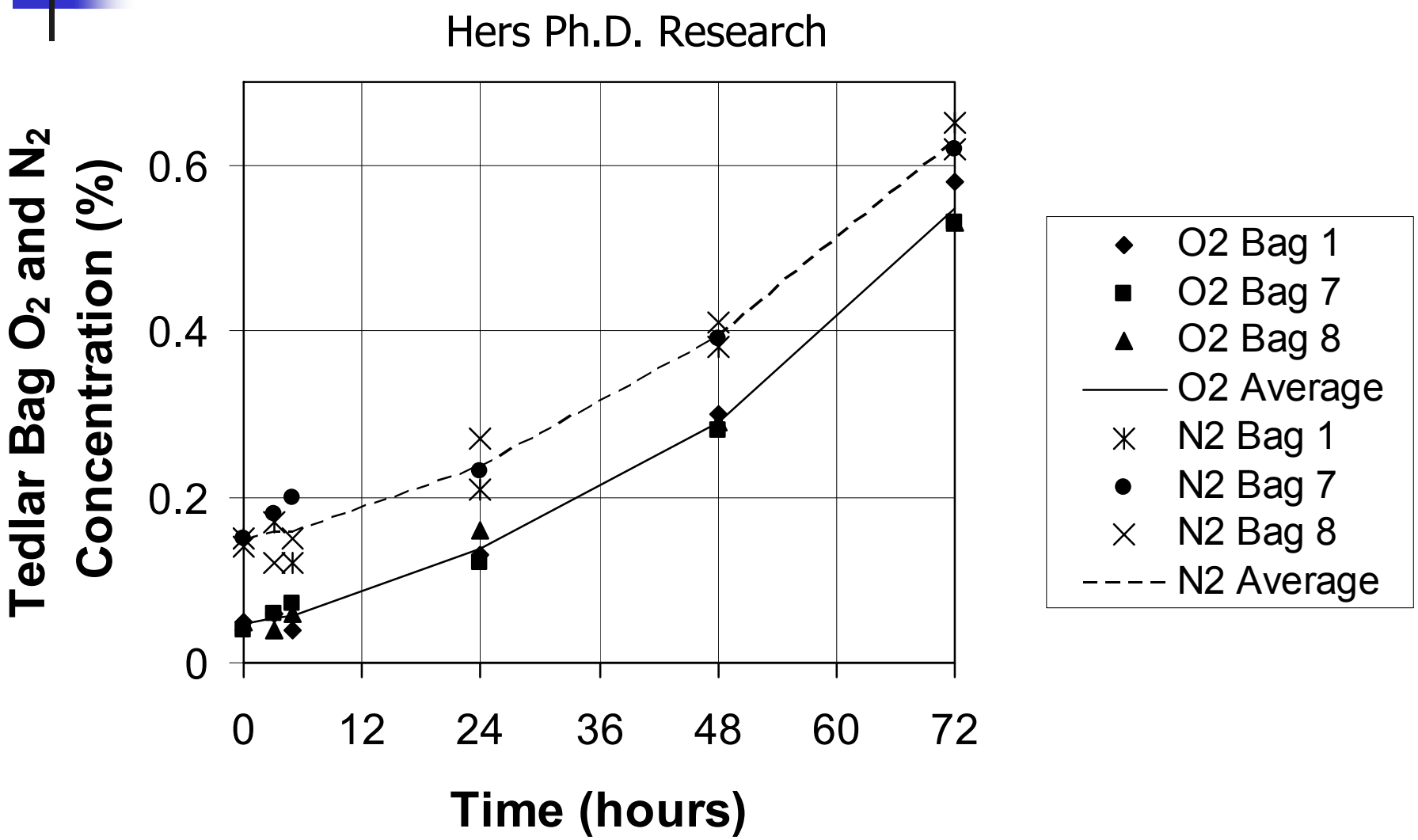


Table 1.2. Comparison of Canisters to Tedlar Bags

	Canisters	Tedlar Bags
Common Volumes	1 and 6 L	1, 3, and 5 L
Type of Sampling	Passive (vacuum)	Active (pump required)
Sample Handling	Room temperature	Room temperature
Media Hold Time	Up to 30 days recommended	Indefinite
Hold Time to Analysis	14-30 days	3 days
Surface Inertness	Excellent	Fair
Cleanliness	10% or 100% certified to ppbv/pptv levels	Some VOCs present at 0.5 to 45 ppbv
Sampling Application	Ambient/indoor air, soil/landfill gas, stationary source	Ambient air (fixed gases only), soil/landfill gas, stationary source
Rule of Thumb	"ppbv device"	"ppmv device"
Advantages	Inertness, hold time, ruggedness, no pump	Purchase/shipping cost, availability, convenience

From Air Toxics

GC/MS

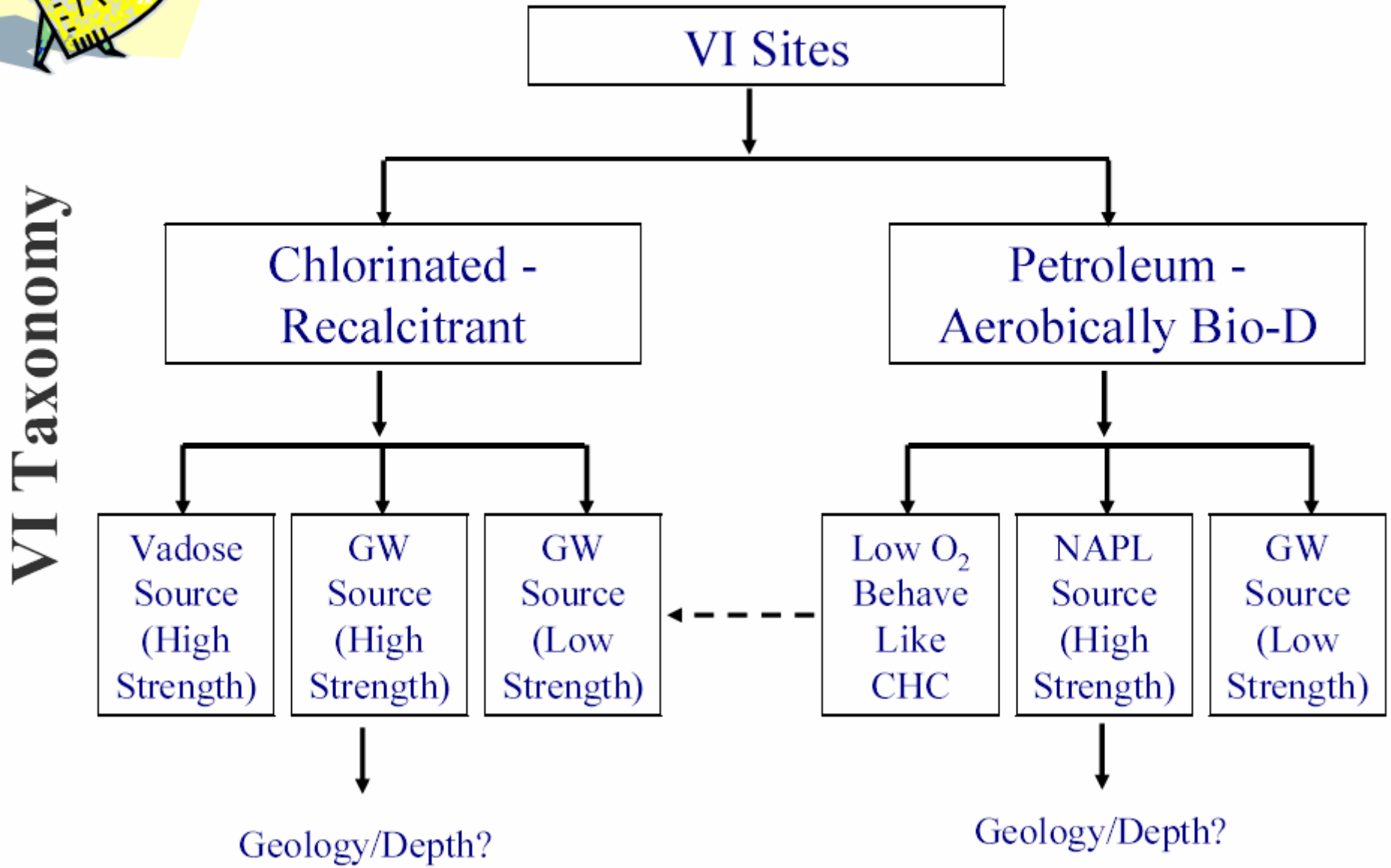
- MS involves electrically charging molecules, accelerating them through magnetic field, breaks molecules into charged fragments creating mass spectrum
- Full scan GC/MS sweeps through 35 to 350 AMU, identification based on retention time complemented by complete mass spectrum, detection limit 0.5 ppbV
- SIM mode increases sensitivity 100X, focuses on 2-3 ions, but no mass spectra
- Co-eluting compounds or interferences may make identification difficult (need skilled analyst)

Definition: Analysis by GC/MS

Gas Chromatography-Mass Spectrometry

- "3-D" analysis
  - (time vs. abundance vs. spectral info)
- Ion fragmentation → chemical mass "fingerprint"
- Allows qualitative and/or semi-quantitative identification of unknowns (i.e. "TICS")

Analysis: Unknowns

- TICs: Tentatively Identified Compounds
  - 10-15 largest *non-target* peaks
- Mass spectral library search
  - NIST library ~120,000 entries
- Compound ID
  - Based on quality of match vs. library reference spectrum
  - ***Interpretation based on expertise of skilled analyst***
- Concentration can be estimated
  - Assumes 1:1 response w/ internal std.

One-Size Fits All?