Petroleum Vapor Intrusion (PVI)- The Key Role of Natural Attenuation

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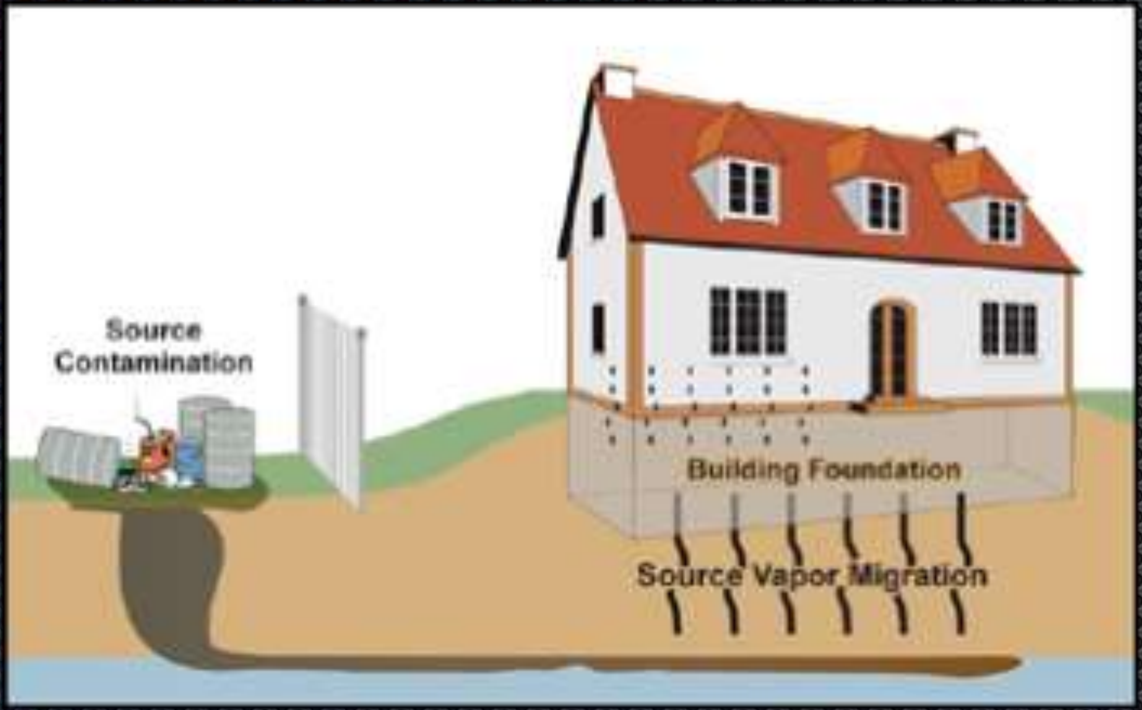


Vapor intrusion involves the migration of chemical vapors in the soil and groundwater to enter buildings through foundation cracks and joints. Sometimes vapor intrusion can result in long-term exposure of contaminants at harmful levels.

- Affects maybe 1/4 of the estimated inventory of 500,000 US brownfields sites.
- New EPA Guidance as of June 2015.
- States regulate, but often very different standards in use.
- Also jurisdictional issues - who is in charge- OSHA? EPA? State?
- No agreement on site investigation practices.
- Limited use of quantitative modeling- very fieldwork based, empirical.

Table 2. Residential screening levels for selected VOCs.

State	Benzene			TCE			PCE		
	Groundwater	Soil Gas	Indoor Air	Groundwater	Soil Gas	Indoor Air	Groundwater	Soil Gas	Indoor Air
Alaska	5	3.1	0.31	5	0.22	0.022	5	8.1	0.81
California	NA	36.2	0.084	NA	528	1.22	NA	180	0.41
Colorado	15	NA	0.23	5	NA	0.016	5	NA	0.31
Connecticut	130	2490	3.3	27	752	1	340	3798	5
Indiana	95-850	250-1400; 25-140[a]	2.5	4.6-700	120-2000; 2-200[a]	1.2-4.1	7.4-1100	320-5200; 32–520[a]	3.2-10
Louisiana	2,900	NA	12	10,000	NA	59	15,000	NA	110
Maine	NA	NA	10[b]	NA	NA	NA	NA	NA	NA
Massachusetts	2000	NA	0.3	30	NA	1.37	50	NA	0.04
Michigan	5600	150	2.9	15,000	700	14	25,000	2100	42
Minnesota	NA	1.3-4.5	1.3-4.5	NA	NA	NA	NA	NA	20
New Hampshire	2000	95	1.9	50	54	1.1	80	68	1.4
New Jersey	15	16	2	1	27	3	1	34	3
New York	NA	NA	NA	NA	NA	5	NA	NA	100
Ohio	14	31	3.1	–	122	12.2	11	81	8.1
Oklahoma	5	3.1	0.27	5	0.17	0.017	5	0.33	0.33
Oregon	160	NA	0.27	6.6	NA	0.018	78	NA	0.34
Pennsylvania	3500	NA	2.7	14,000	NA	12	42,000	NA	36

Notes: Units are μg/L for groundwater and μg/m^3 for soil gas and indoor air. See individual state guidance documents for additional information, including limitations and exceptions. Trigger or action levels for mitigation based on indoor air concentrations may be higher than the screening levels shown. [a]Second range of values shown is for subslab soil gas. [b]Chronic exposure value.

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

Key documents on PVI

EPA United States Environmental Protection Agency

EPA 510-R-15-001

Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites

U.S. Environmental Protection Agency
Office of Underground Storage Tanks
Washington, D.C.

June 2015

ASTM INTERNATIONAL

Designation: E1739 – 95 (Reapproved 2010)ε1

Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites[1]

This standard is issued under the fixed designation E17
original adoption or, in the case of revision, the year of l
superscript epsilon (ε) indicates an editorial change sinc

ε1 NOTE—The units of measurement were editoriall

Petroleum Vapor Intrusion

Fundamentals of Screening, Investigation, and Management

October 2014

Prepared by
The Interstate Technology & Regulatory Council
Petroleum Vapor Intrusion Team

INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC

Petroleum Vapor Intrusion

Fundamentals of Screening, Investigation, and Management

The Opinion of the ITRC

The extent to which this natural biodegradation process restricts PVI, however, is not fully addressed in current guidance documents. Thus, regulatory agencies, consultants, and industry are wasting both money and time on PVI evaluations using traditional VI approaches that in most cases are not necessary and rarely lead to vapor control.

Vertical Separation Distance for dissolved phase: 5 feet
For LNAPL free product: 15-18 feet
(EPA Guidance 6-15 feet)

Lateral Separation Distance: 30 feet

EPA Screening Model Approach

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

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

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

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

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

Environ. Sci. Technol. 1991, 25, 1445–1452

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

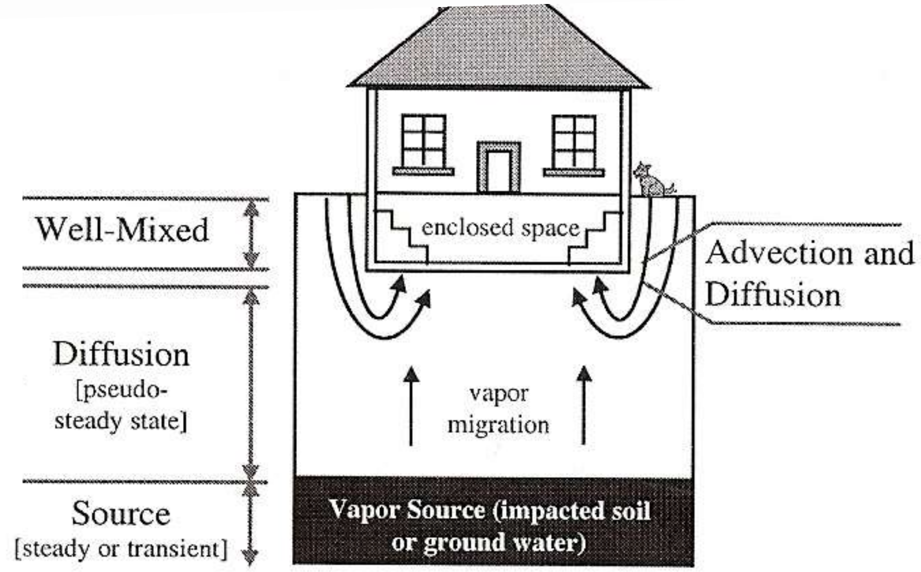
Paul C. Johnson* and Robert A. Ettinger

Shell Development, Westhollow Research Center, Houston, Texas 77251

$Q_{building}$

L_T

D_{eff}



Q_{ck}

A_B

$A_{ck}=L_{ck}w_{ck}$

d_{ck}

D^{ck}

C_{ck}

Attenuation factor depends upon $Q_{building}$

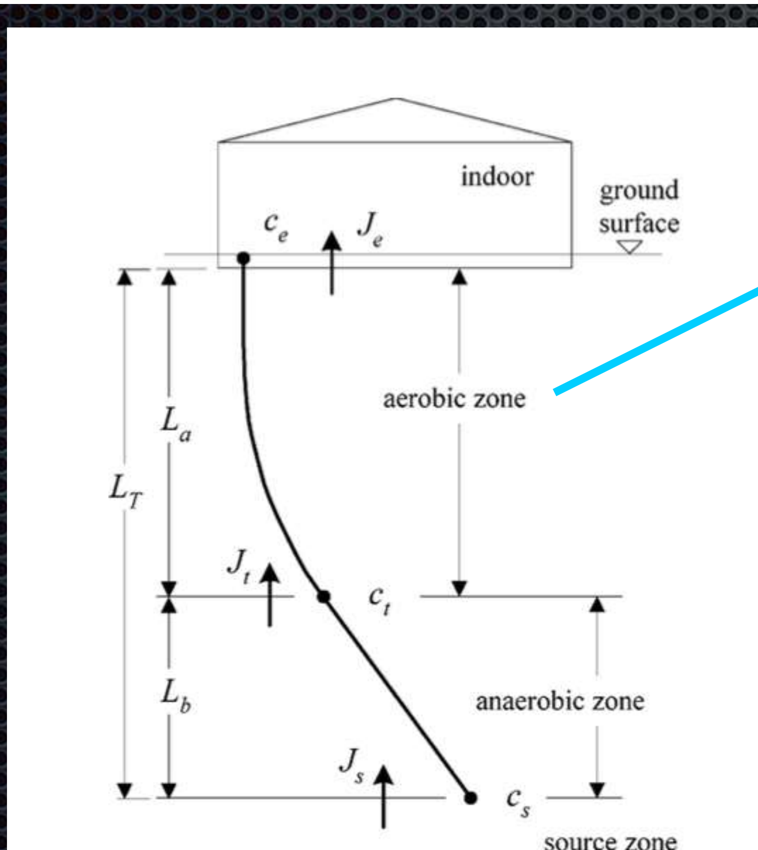
Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source

GEORGE E. DEVAULL*
Shell Global Solution US Inc., Westhollow Technology Center, 3333 Highway Six South, Houston, Texas 77082

Environ. Sci. Technol. 2007, 41, 3241–3248

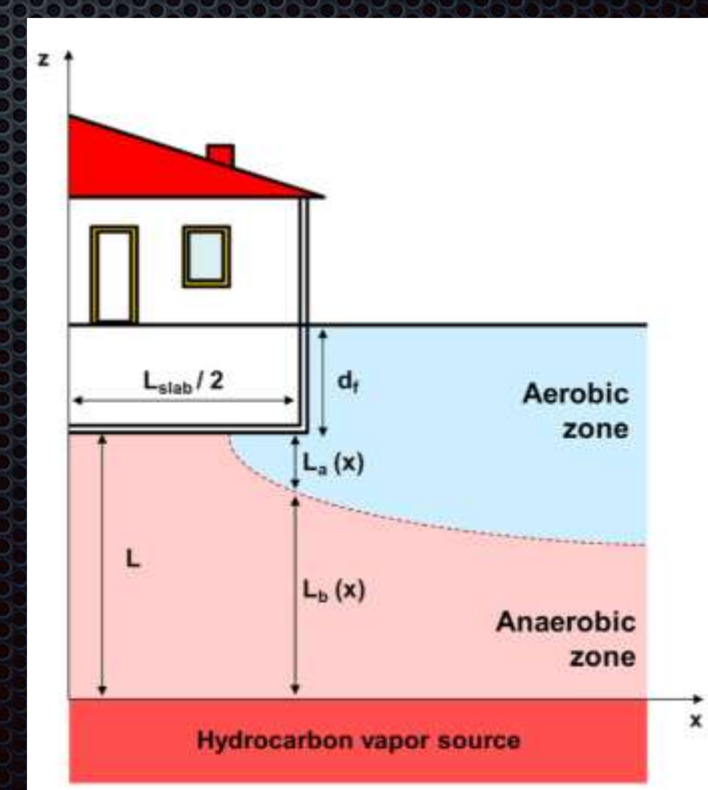
Related approaches include the BioVapor model (API) and PVIScreen from EPA (see Chapter 5 of ITRC Guidance)

Biodegradation requires oxygen and moisture



Still a 1-D approach, but includes biodegradation

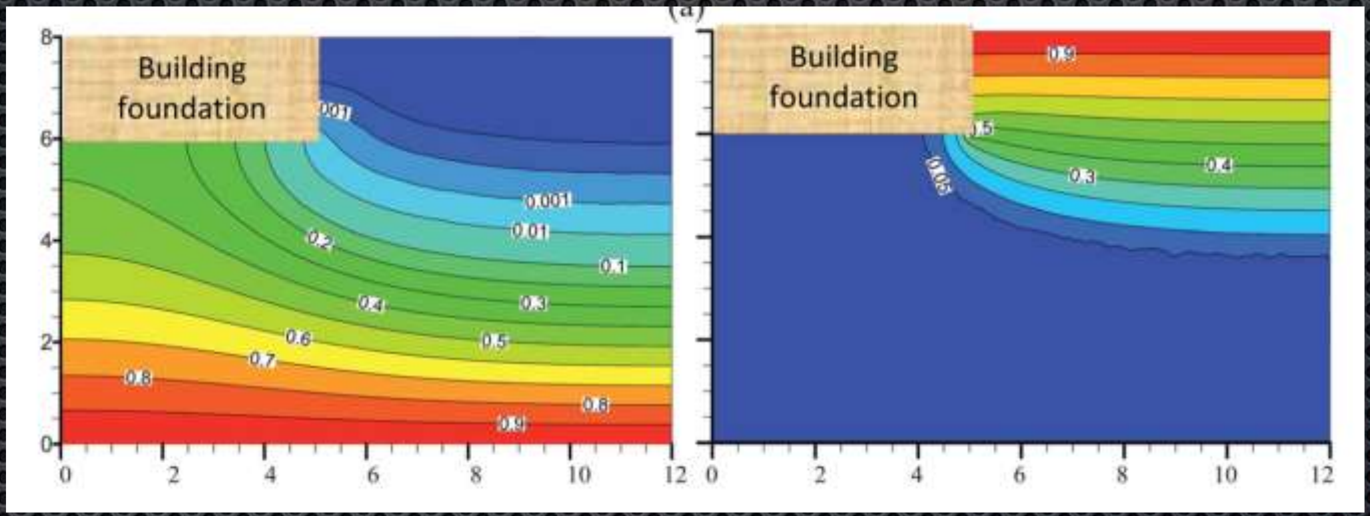
Problem-1D models cannot predict an “oxygen shadow” (see Yao et al. 2014, Verginelli et al.2016 Jl. Haz. Matls.)



Advanced Modeling Approaches

- Abreu and Johnson (2006)- finite element CFD.
- Brown University -a finite element computational package (Comsol) used to describe transport processes.

Hydrocarbon Profiles



Oxygen Profiles

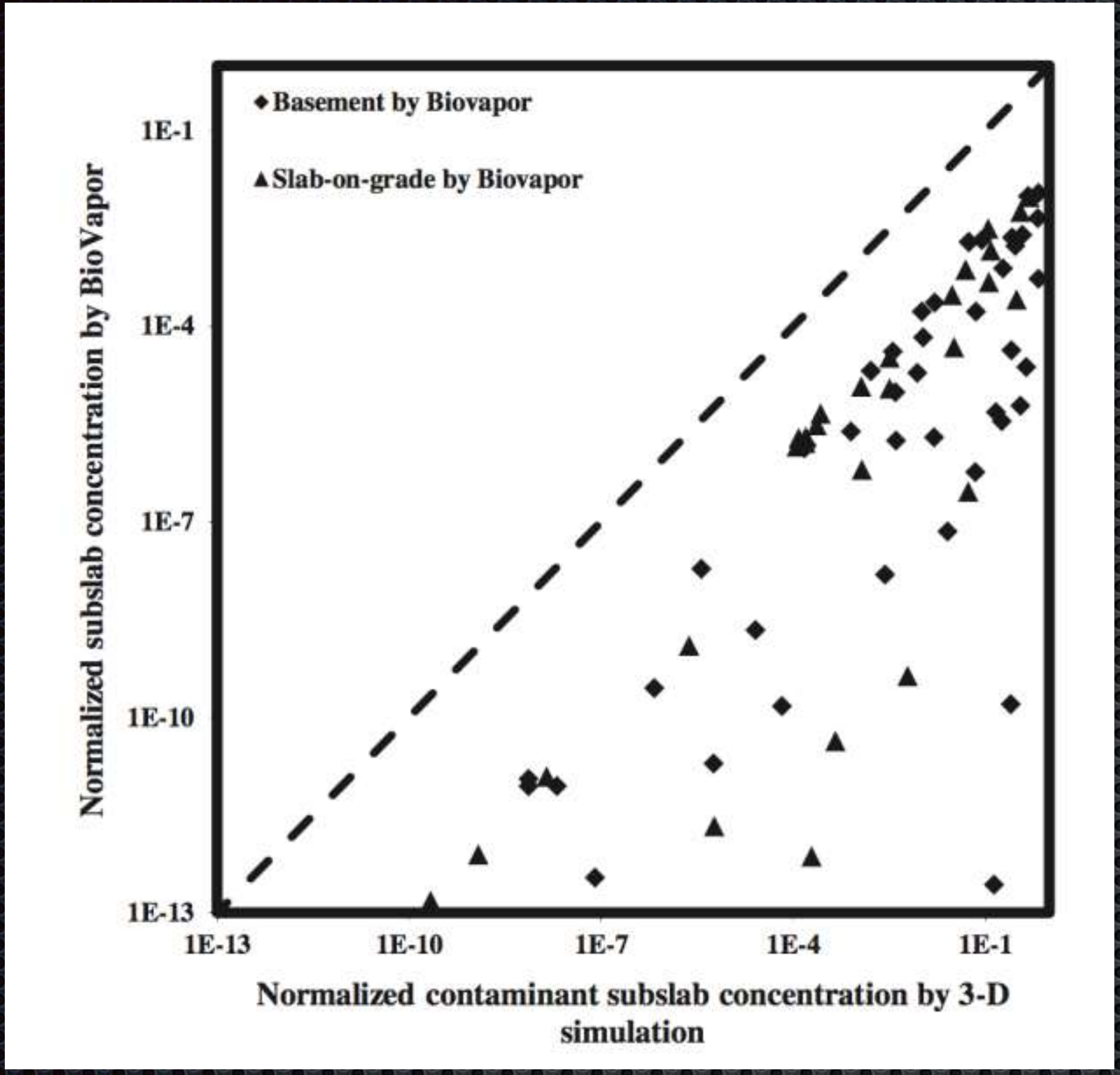
1. Solve for soil gas flow through soil (Darcy's Law).
2. Solve for both oxygen and petroleum species transport via advection and diffusion, including biodegradation
3. Indoor air concentration is calculated using the species flow rate into the structure.

$$q = \frac{-\kappa\rho}{\mu}\nabla\phi$$

$$\phi = gz + \int_{P_0}^{P}\frac{dP}{\rho}$$

$$0 = -\nabla\cdot(q_g c_{ig}) + \nabla\cdot(D_i \nabla c_{ig}) - R_i$$

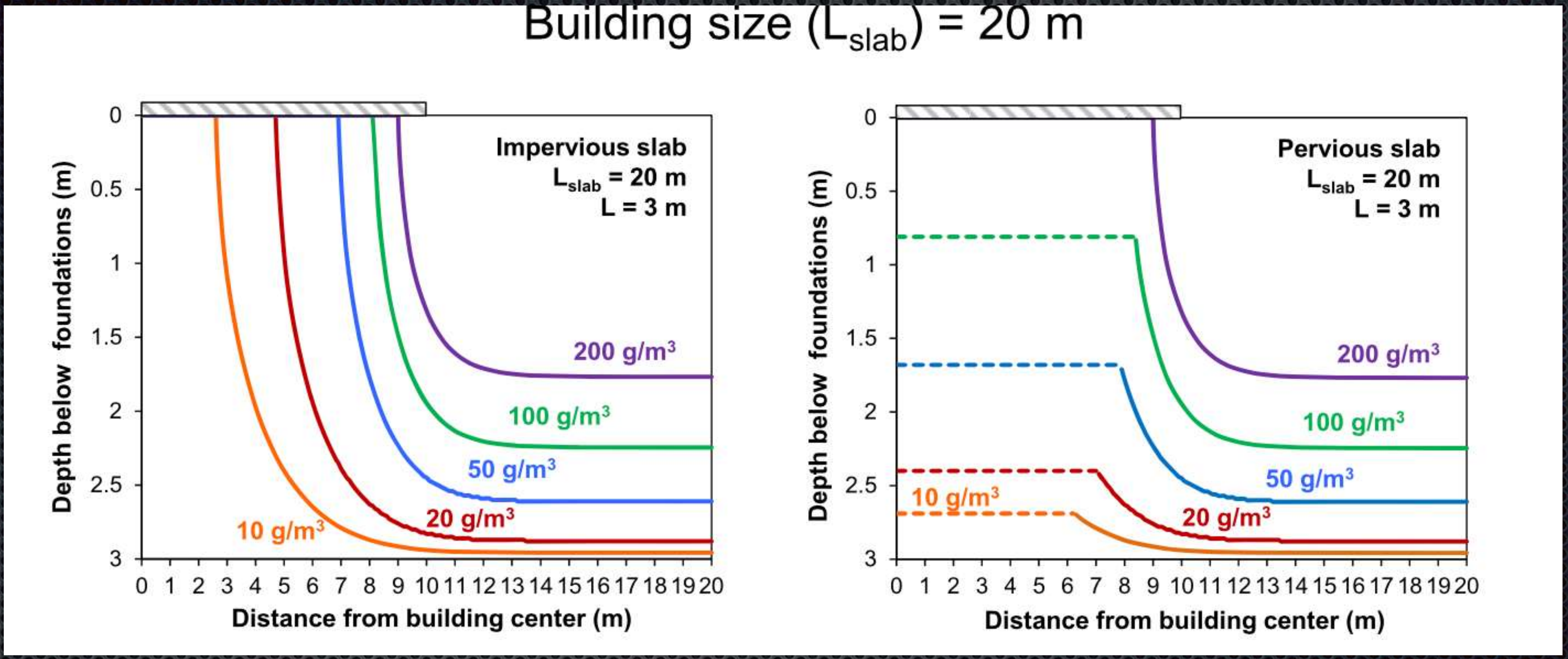
$$C_{indoor} = \frac{J_{Tck}}{A_e \cdot V_b + Q_{ck}}$$



Comparison of BioVapor 1D results to predictions from 3D model of Abreu and Johnson (see Yao et al. 2014, Jl. Haz. Matls.)

1D models overpredict benefit of biodegradation due to neglect of possible oxygen shadow

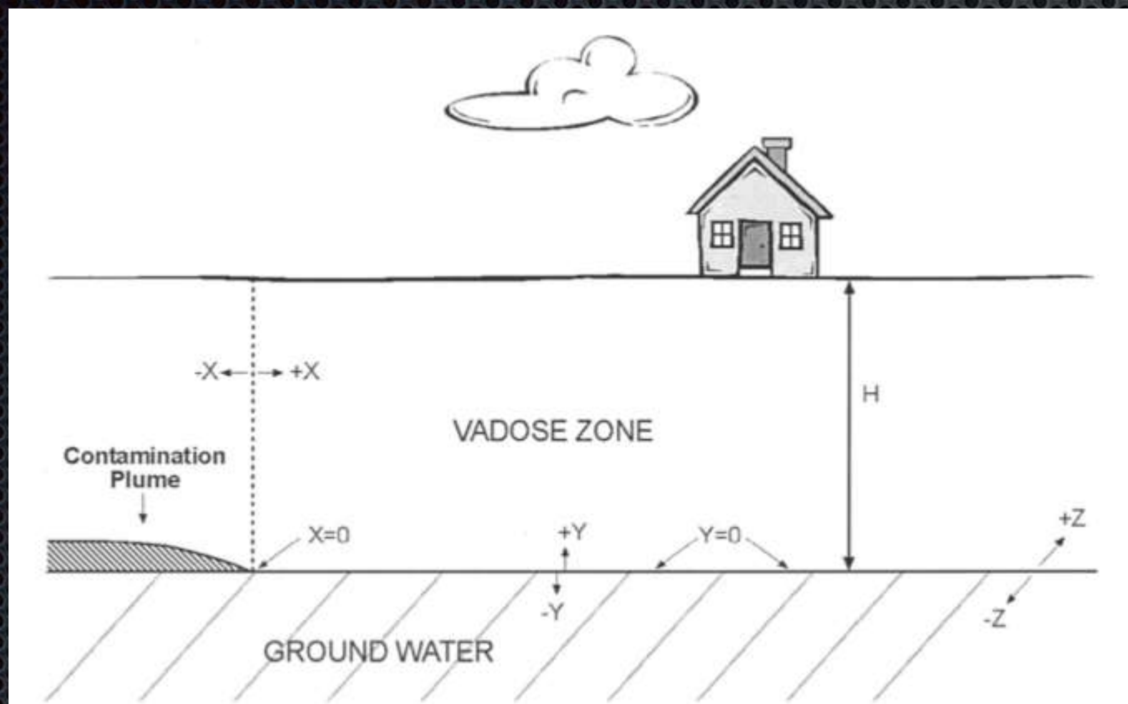
Does not mean 1D screening models necessarily wrong, but need to be careful in establishing conditions.



Predicted location of the aerobic/anaerobic boundary for 20m x 20 m slab-on-grade 3 m above indicated dissolved HC source concentration.

Verginelli et al. Jl. Haz. Matls. 2016

How far is far enough??



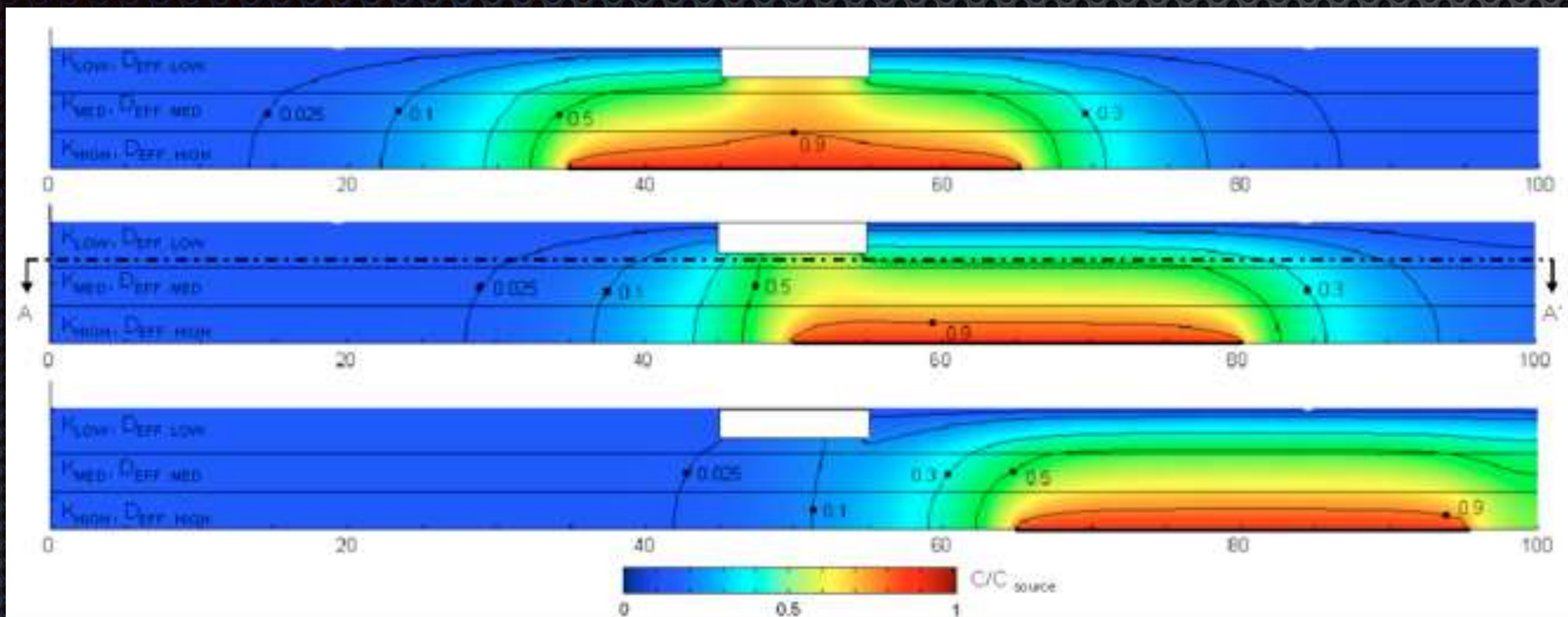
$$D_e\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial C^2}{\partial y^2}\right) = 0$$

Solved simple 2-D Laplace Equation

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

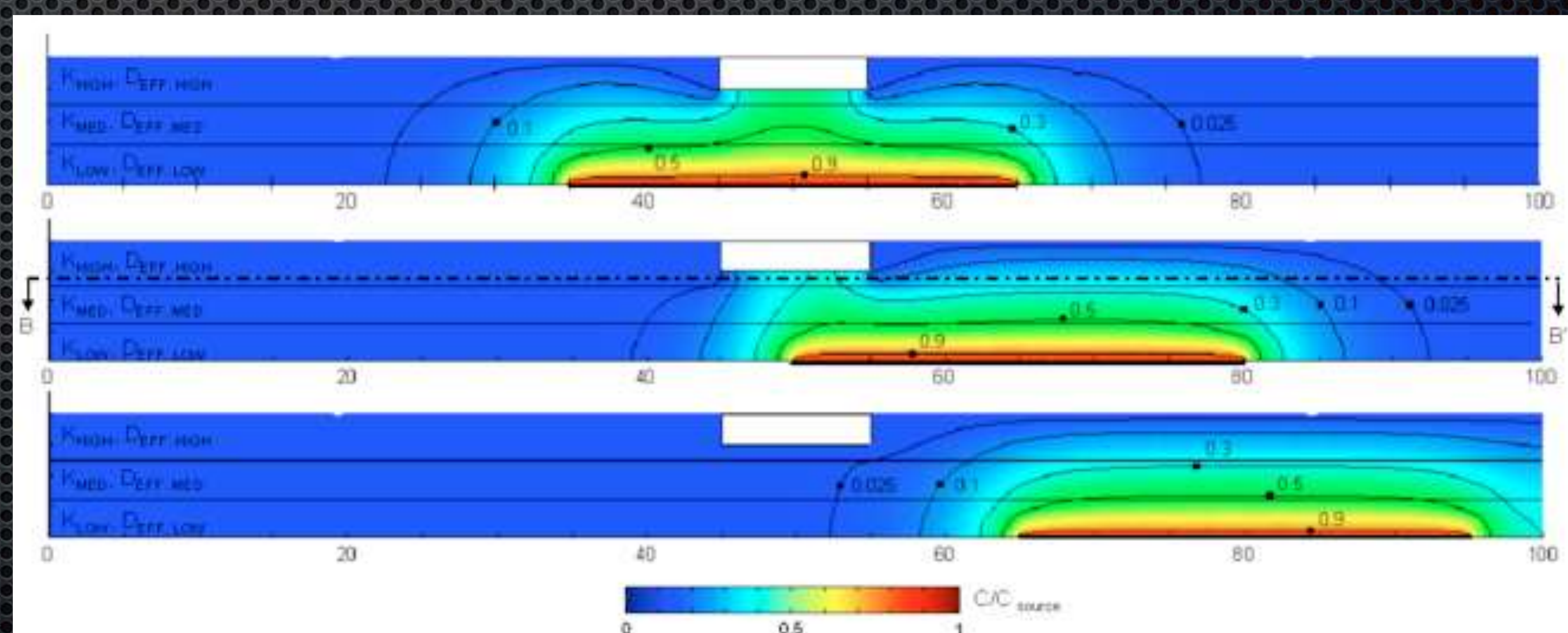
Lowell and Eklund, 2004

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



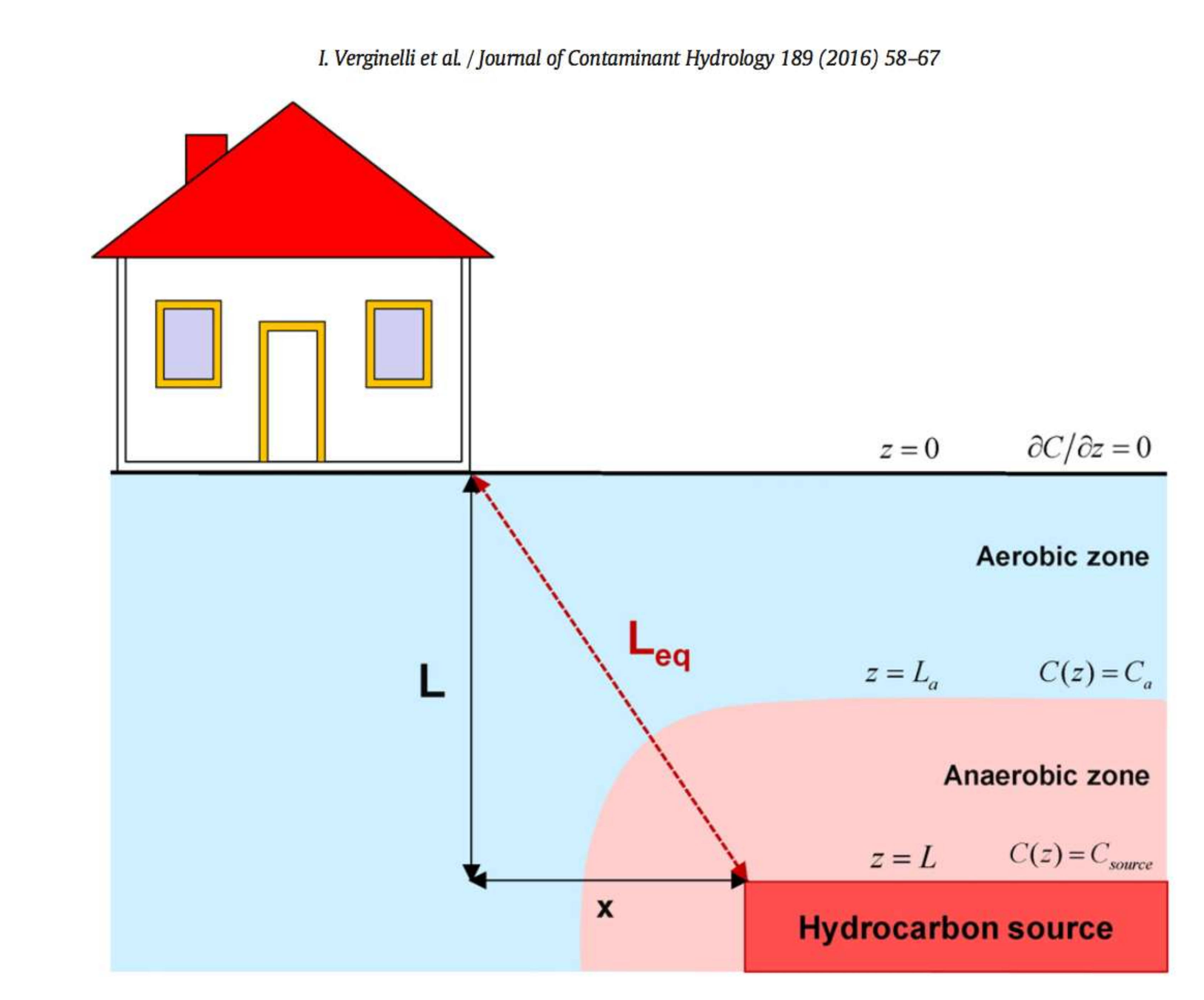
Low permeability top layer
C_{indoor}/C_{source} = 0.0185

High permeability top layer
C_{indoor}/C_{source} = 0.29

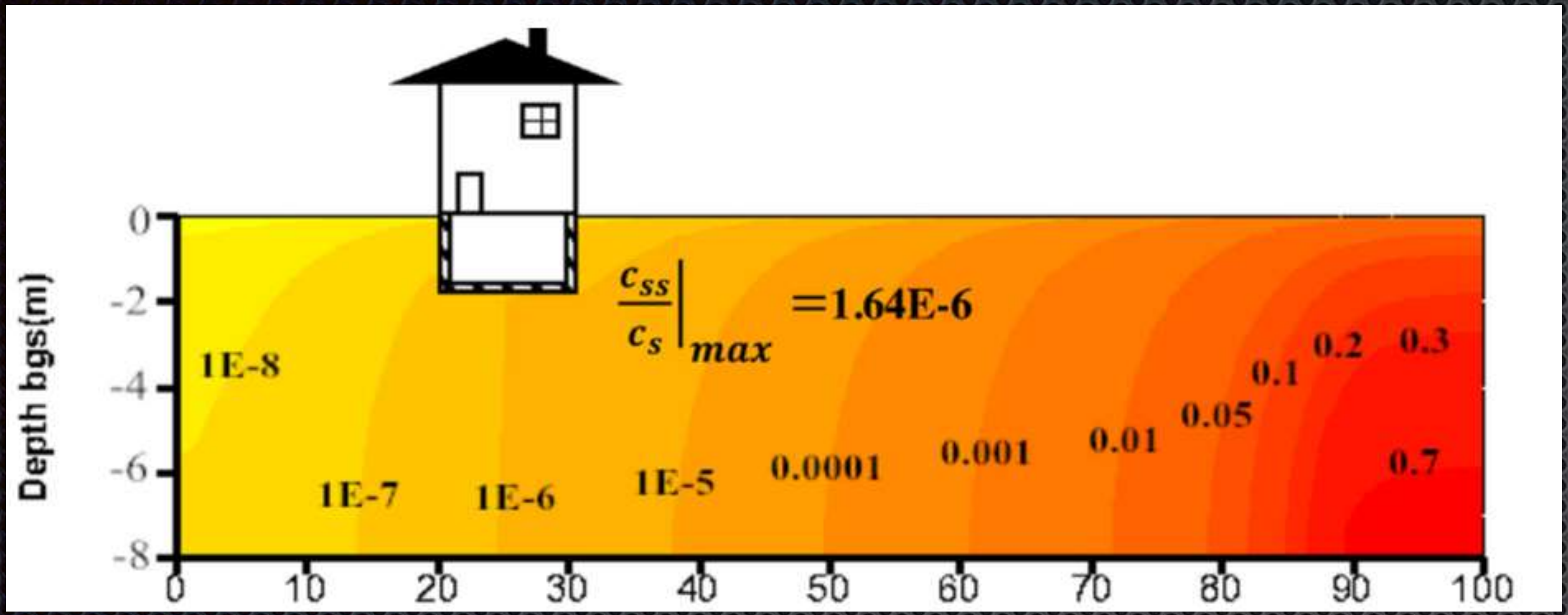


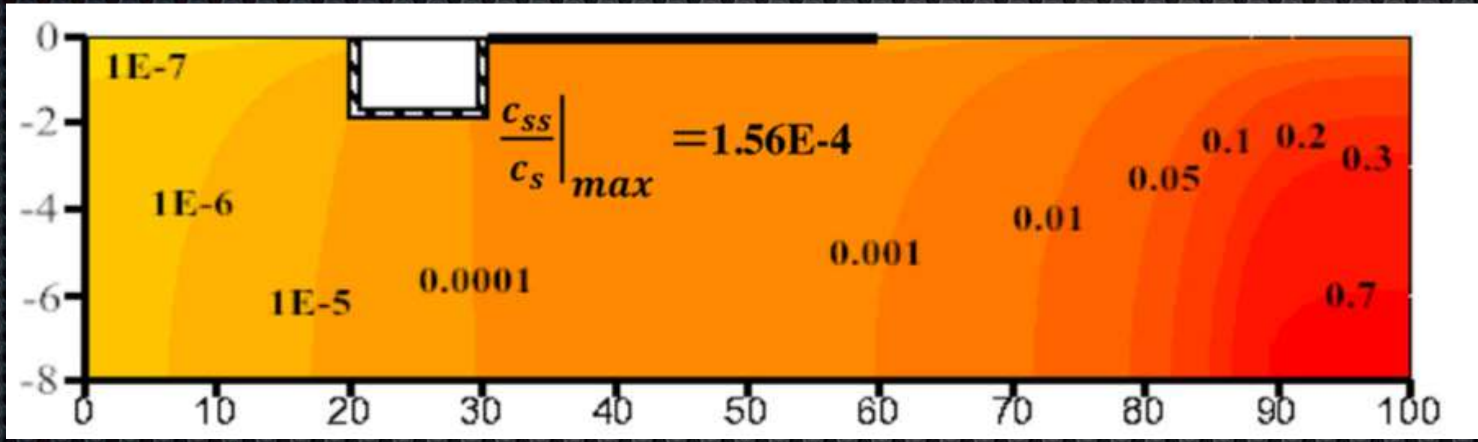
This study showed that 6-7 m lateral separation is sufficient.

In fact for low petroleum GW concentrations (<5 mg/L) virtually no lateral separation is needed.



Note- no surface capping!





Comparison of HC profiles with and without 30 m paved zone around building (no biodeg.)

Yao et al.
Jl. Haz. Matls. 2015

New Spreadsheet Tool for PVI Screening

PVI2D Toolkit (2015)

The toolkit was developed by Iason Verginelli based on the paper:
"A two-dimensional analytical model of petroleum vapor intrusion"
Yijun Yao, Iason Verginelli and Eric M. Suuberg

Commands: Results | Database

Main Screen

Select Compounds of Concern

Benzene
Ethylbenzene
Styrene
Toluene
Xylenes
Methane
Hexane
Heptane
Naphthalene
Ethanol
Cyclohexane
Methylcyclohexane
MtBE
Other Aliphatic hydrocarbons
Other Aromatic hydrocarbons

Insert >>
Remove <<
Remove All

Inserted Compounds

Benzene

Selected Compounds	Vapor Source Concentration (g/m^3)	Biodegradation constant λ (h^{-1})	Median (Data Range) for λ (h-1) Ref: DeVaull 2011
Benzene	200	0.18	0.27 (0.087–0.78)
Total source concentration	2.00E+02		

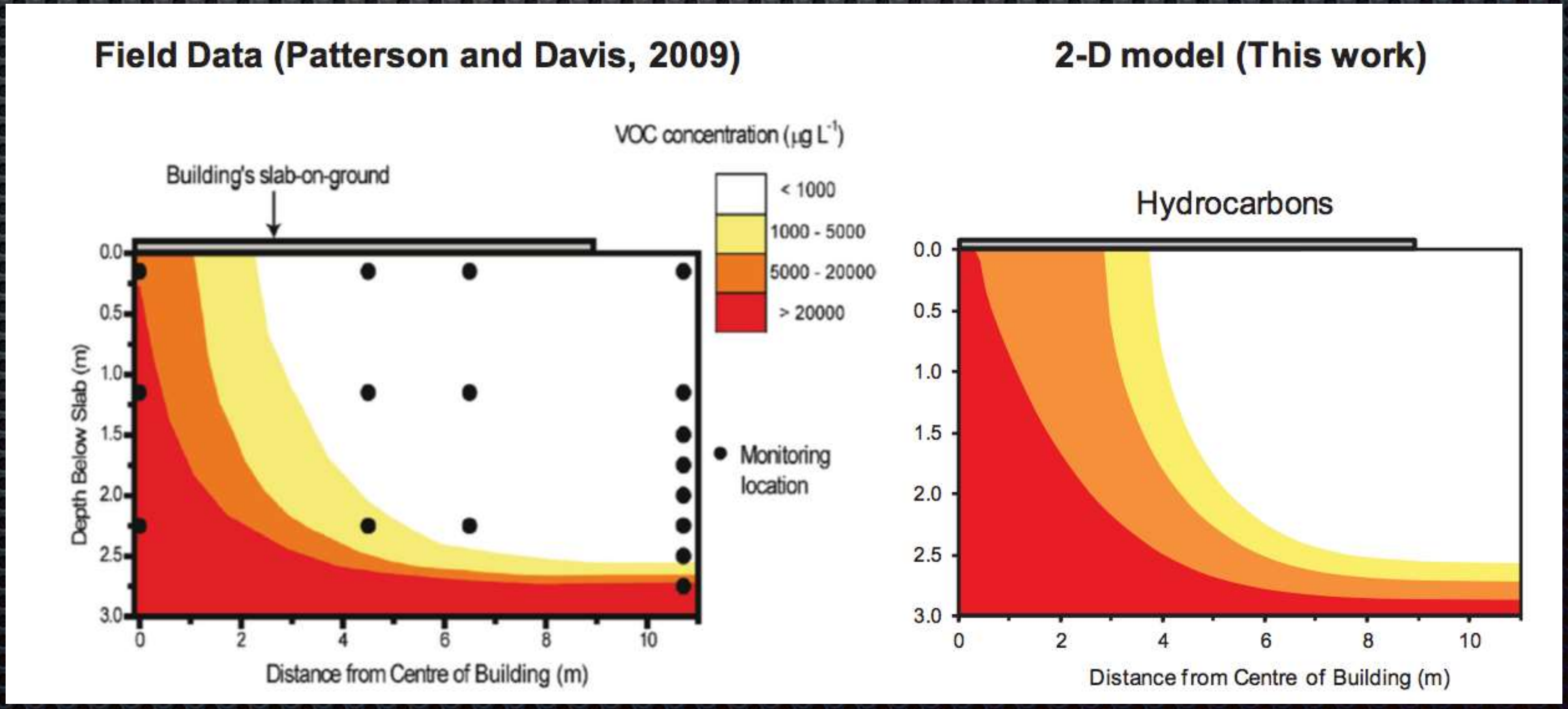
Source Zone			
Source depth below ground surface (d_s)		3	m
Vadose zone	Suggested values	Sand	
Soil Porosity (θ_t)	(0.375)	0.375	m$^3_{voids}$ / m$^3_{soil}$
Moisture-filled porosity of the soil (θ_w)	(0.054)	0.054	m$^3_{water}$ / m$^3_{soil}$
Soil permeability to vapor flow (k_v)	Calculated	9.9E-12	m^2
Oxygen			
O_2 concentration in the atmosphere (c_o^{atm})		279	g/m^3
Minimum O_2 for biodegradation (c_o^{min})		13.7	g/m^3
Outdoor air quality			
Width of source zone area (W)		50	m
Ambient air velocity in the mixing zone (U_{air})		2	m/s
Mixing zone height (δ_{air})		2	m

Building zone			
Foundations depth below ground (d_f)		0	m
Building subslab width (L_{slab})		10	m
Building Area (A_b)		100	m^2
Building volume (V_b)		244	m^3
Foundations perimeter (X_{crack})		40	m
Foundation crack fraction (η)		0.00039	m$^2_{cracks}$ / m$^2_{building}$
Volume air exchanges per unit time (ER)		0.5	h^{-1}
Indoor Disturbance Pressure (Δp)		5	Pa
Foundation thickness (L_{crack})		0.15	m
Air content of the cracks (θ_{acrack})		1	m$^3_{voids}$ / m$^3_{soil}$
Water content of the cracks (θ_{wcrack})		0	m$^3_{water}$ / m$^3_{soil}$
Foundation Airflow Rate (Q_s)	Calculated	7.8	L/min

TOXICANT EXPOSURES IN RHODE ISLAND: Past, Present, and Future

BROWN

PVI2D Toolkit based upon "A Two-Dimensional Analytical Model of Petroleum Vapor Intrusion" by Y. Yao, I. Verginelli and E.M. Suuberg Water Resources Research, 2016



Summary

Well established that biodegradation can play a significant role in reducing the hazard presented by vapor intrusion of petroleum derived contaminants.

Recommended screening distances are based upon large amount of actual field data.

Still, need to be cautious in applying simple rules of thumb where "oxygen shadow" might be possible.

New 3D modeling tools and simple 2D approximations will be more reliable for predicting real situations.