Vertical Screening Distance Criteria to Evaluate Vapor Intrusion Risk from Lead Scavengers (1,2-DCA and EDB)

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Outline

- Background
- Empirical evaluation of screening distance criteria
  - Data mining of existing data
  - 2017 field pilot
- Soil vapor transport modeling (PVIScreen)
  - Evaluate applicability of 6 ft. and 15 ft. for lead scavengers
  - Next steps – nomograph to screen sites
- Conclusions

What are Lead Scavengers?

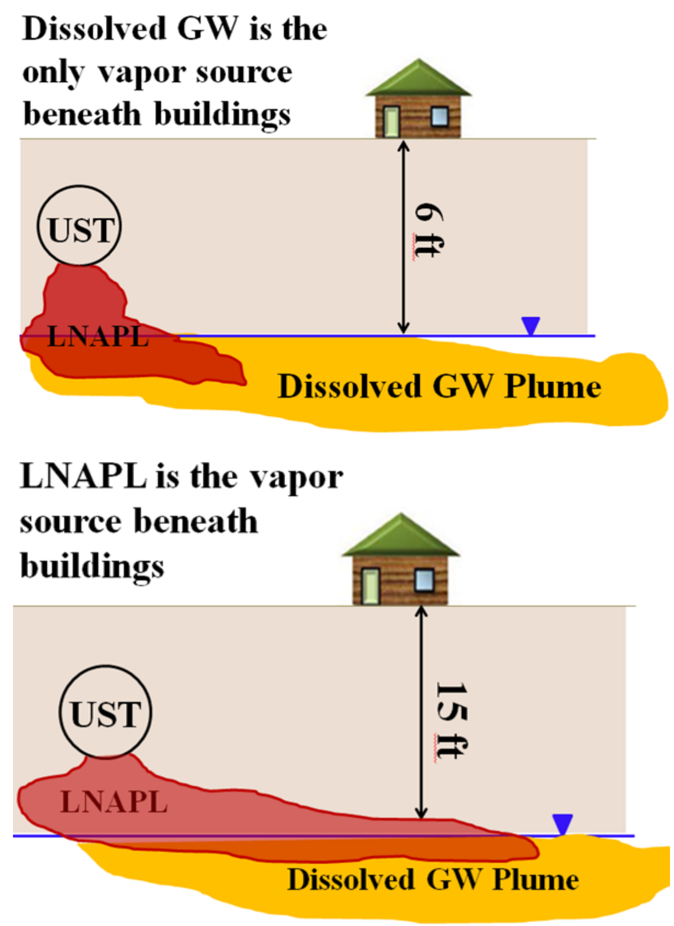
- Additives in leaded gasoline to prevent lead oxide deposits that could foul engines
  - 1925 – Ethylene dibromide (EDB) 1st use in leaded gasoline
  - 1940s – 1,2-Dichloroethane (1,2-DCA) use started
- Leaded gasoline phase-out in the US - mid 1980's to mid 1990's
  - 1,2-DCA and EDB in the subsurface likely over 20 years old
- 1,2-DCA and EDB still used as lead scavenger in aviation gas & racing fuels
- Properties of 1,2-DCA and EDB
  - Compared to benzene: more soluble and less likely to partition out of water, less likely to sorb to soil
  - Known to biodegrade aerobically and anaerobically, but knowledge not as robust as BTEX

Regulatory Context

Vertical screening distance criteria - 2015 EPA OUST[1] PVI[2] guidance

- Additional vapor intrusion (VI) investigation deemed unnecessary at sites that meet these criteria (see schematic).
- ~ 25 states have adopted or referenced this approach in recent VI guidance updates
- However, it identified 'lack of rigorous quantification of 1,2-DCA[3] and EDB[4] biodegradation in soil gas as a data gap.
  - additional VI investigation needed for sites with leaded gasoline releases
  - presence of 1,2-DCA or EDB at the site considered a 'precluding factor' in EPA, ITRC and 6 states' VI guidance documents

Vertical Screening Distance Criteria for Benzene



(1) Office of Underground Storage Tanks
(2) Petroleum Vapor Intrusion
(3) 1,2-DCA – 1,2- Dichloroethane
(4) EDB - Ethylene Dibromide

Mining of Existing PVI Investigation Data

Approach

- Reviewed data from completed PVI investigations at UST sites across the US and Canada
- Extensive filtering for data quality criteria – 144 pairs of 1,2-DCA and 72 pairs of EDB soil gas & groundwater concentration data from 47 sites

Conclusions

1,2-DCA

- Only 9 detections out of 144 data points.
- The large number of ND vapor concentrations at RL < 36 µg/m^3 1,2-DCA suggested significant vadose zone attenuation for 1,2-DCA from both dissolved and LNAPL sources
  - vertical screening distance of 15 ft. is applicable for 1,2-DCA

EDB

- Soil gas analytical reporting limit (2 µg/m^3) > screening level (0.16 µg/m^3)
- This data set was not sufficient to determine vertical screening distance criteria for EDB

Analytical Method to Achieve Lower Reporting Limits for 1,2-DCA and EDB

- Chevron ETC worked with Eurofins Air Toxics who developed a specialized analytical method to achieve reporting limit of 0.16 µg/m^3 EDB in high TPH matrix soil vapor
- Modified EPA TO-15
  - Customized GC equipped with a series of GC columns, Dean Switches, and trapping steps – to enable matrix clean-up and to isolate 1,2-DCA and EDB prior to detection
  - Time-of-Flight Mass Spectrometer (TOF-MS) detector allowed higher sensitivity
- This was the key enabler for the 2017 field pilot
- Method details at https://www.eurofinsus.com/environment-testing/testing-services/air-and-vapor/to-15-hss/ (see schematic)

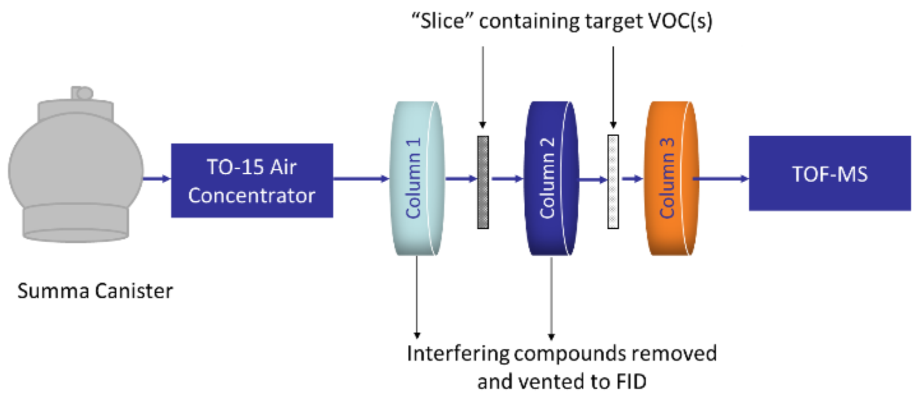


Figure 1. Schematic of modified TO-15 analytical configuration

2017 Field Pilot Activities

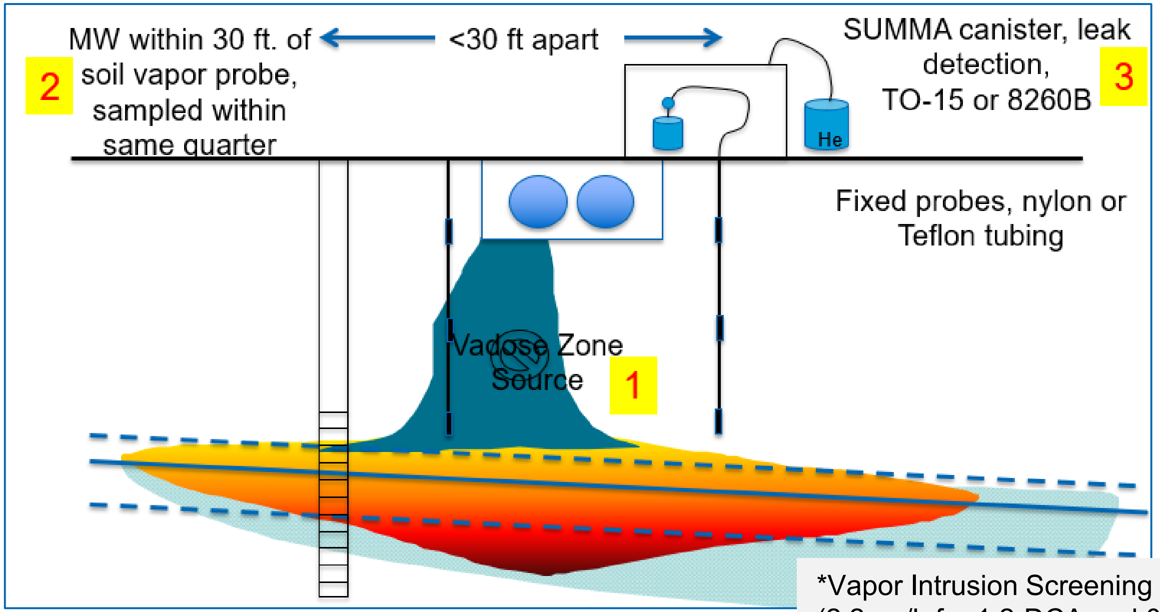
✓Identified 28 candidate sites from 200+ sites

- active regulatory case and
- recent 1,2-DCA/EDB detections above groundwater VISL* (10^{-6} risk level)
- relatively shallow water table

✓Field work planned and attempted on 20 sites in 2H 2017

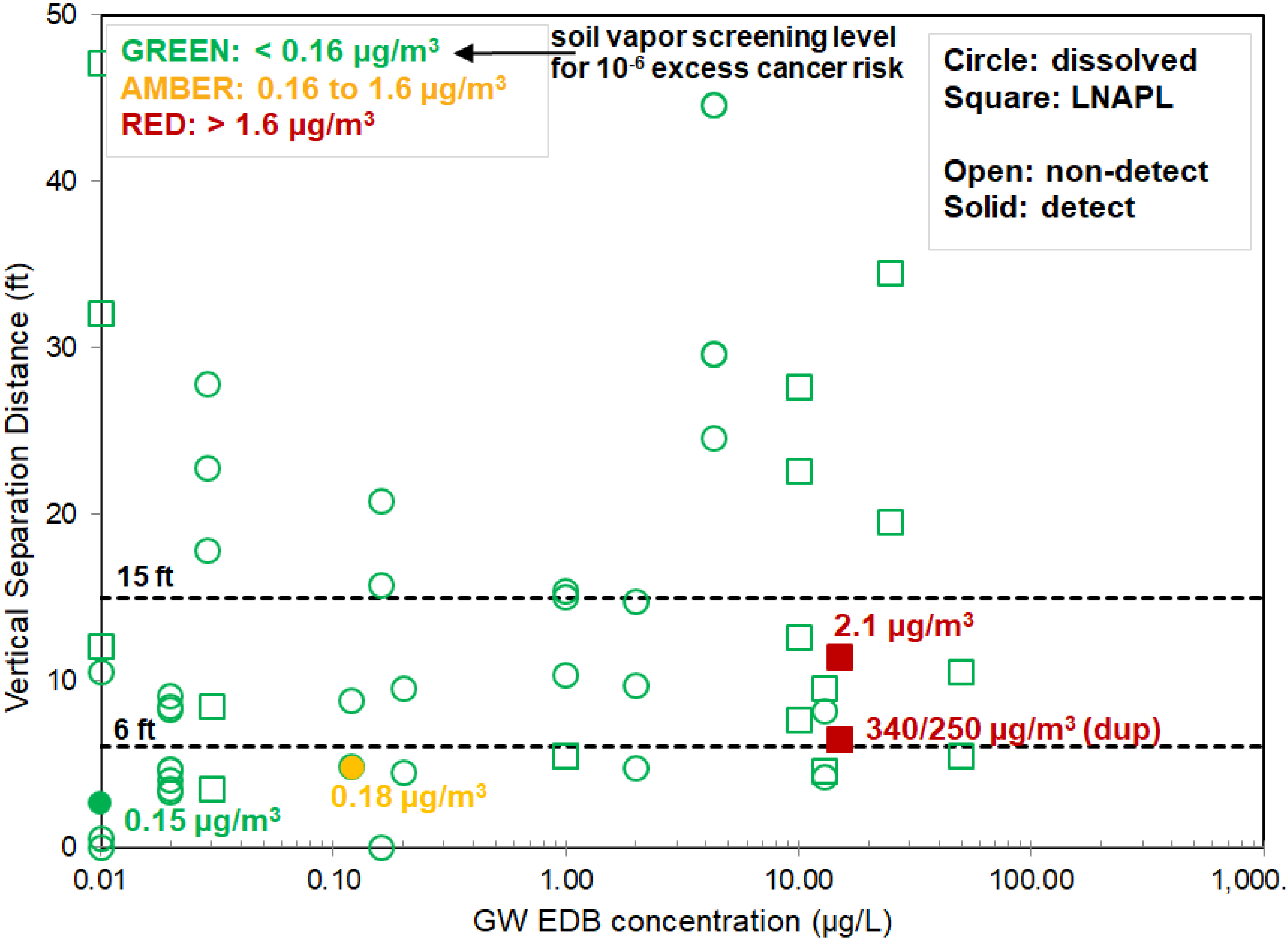
✓<u>14 sites with concurrent soil gas and groundwater data suitable for analysis</u>

- Geographically distributed across the US (sites in CA, NC, AK, SC, MI, PA and Washington DC)



*Vapor Intrusion Screening Level (for groundwater) (2.2 µg/L for 1,2-DCA and 0.18 µg/L for EDB)

Vertical Transport of EDB Vapors Above Water Table



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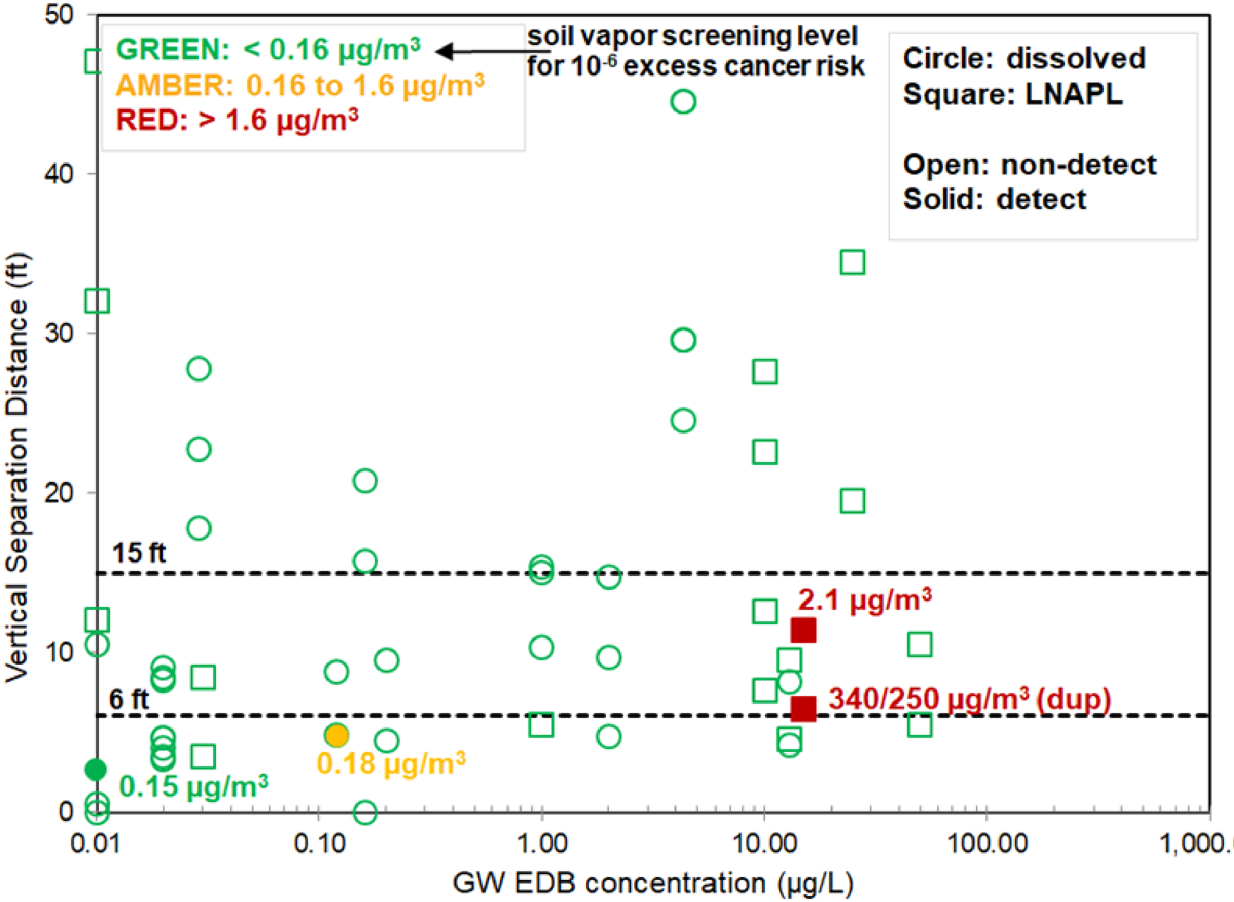
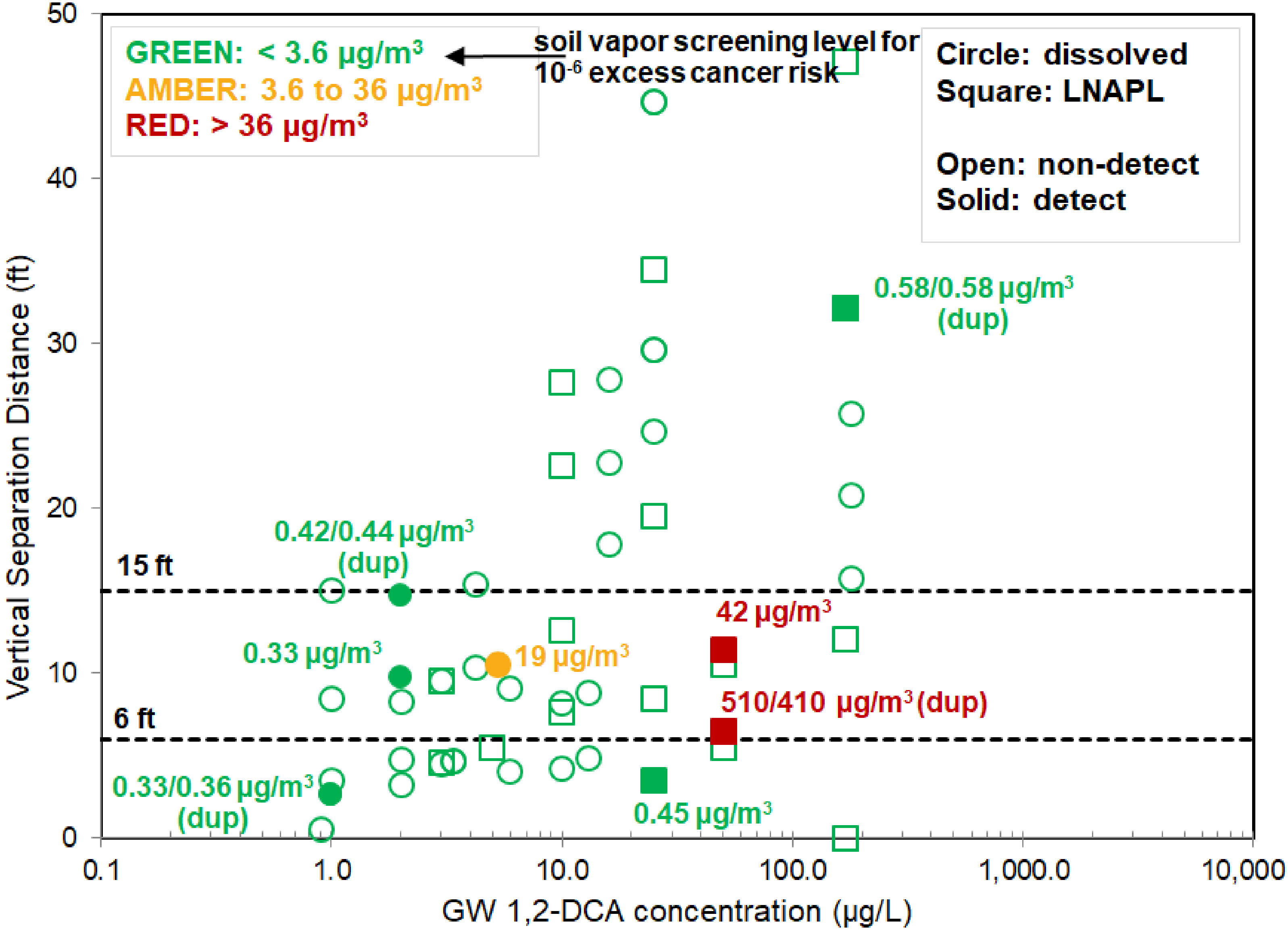
Vertical Transport of EDB Vapors Above Water Table



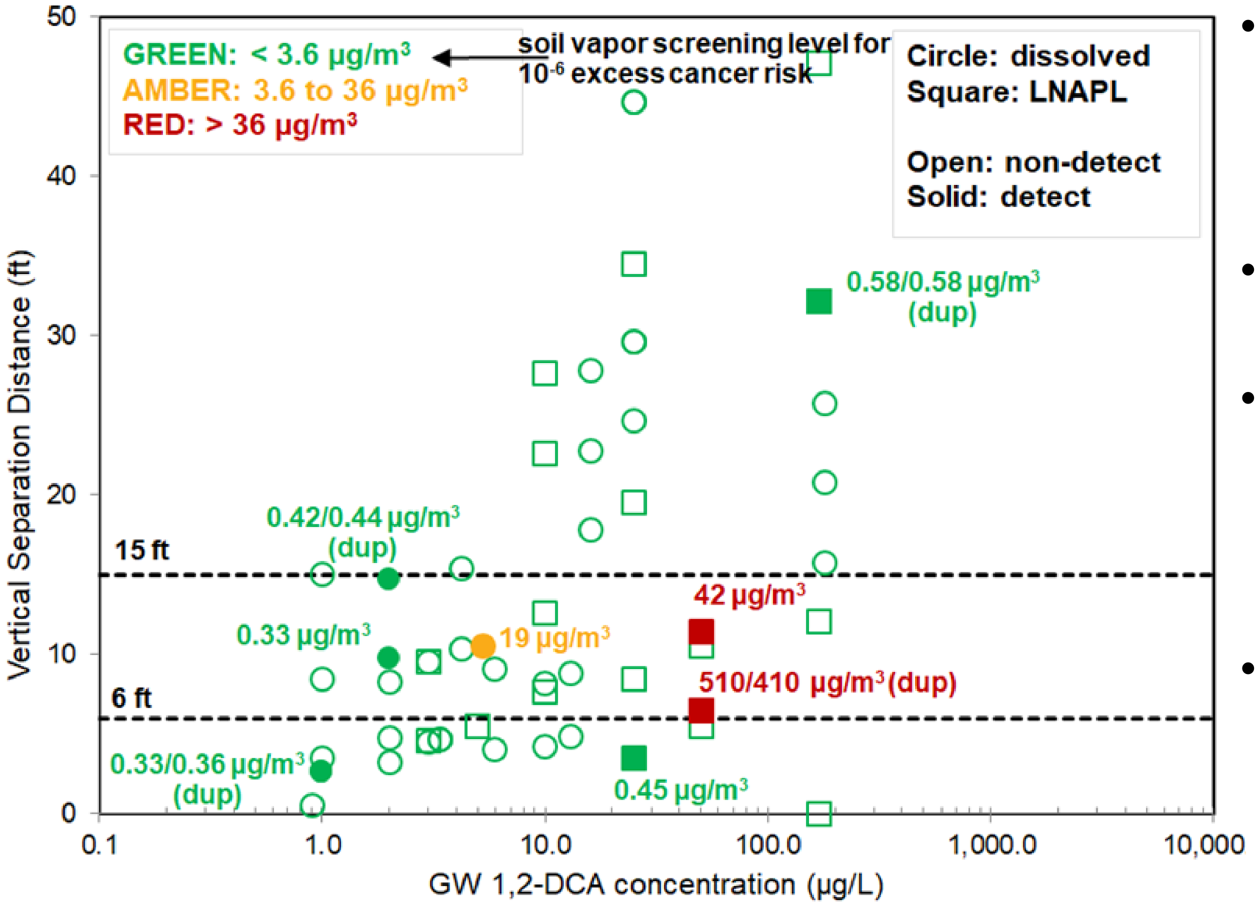
- Data includes vapors sourced from both dissolved-phase and LNAPL sources at the water table
- 55 data pairs [only 4 EDB detections in soil gas (7%)]
- Vertical transport of EDB vapors from:
  - dissolved sources is < 6 ft.
  - LNAPL sources is < 15 ft.
- Vertical screening distances established for benzene (6 ft. and 15 ft.) appear protective for EDB

1000 µg/L benzene in GW as threshold to distinguish dissolved source from LNAPL (Peargin & Kolhatkar, 2011)

Vertical Transport of 1,2-DCA Vapors Above Water Table



Vertical Transport of 1,2-DCA Vapors Above Water Table



- Data includes vapors sourced from both dissolved-phase and LNAPL sources at the water table
- 55 data pairs [8 detections of 1,2-DCA in soil gas (15%)]
- Vertical transport of 1,2-DCA vapors from:
  - dissolved sources is > 6 ft.
  - LNAPL sources is < 15 ft.
- Vertical screening distance of minimum 15 ft. required for 1,2-DCA

1000 µg/L benzene in GW as threshold to distinguish dissolved source from LNAPL (Peargin & Kolhatkar, 2011)

Comparison of Extracted Rate Constants with Literature Data

Estimated first-order aerobic biodegradation rate constants for 1,2-DCA and EDB are over 100-fold lower than benzene (0.79 1/h) and comparable to those reported by Ma et al. (2016)

Percentile	Dissolved-phase source (1/h)	LNAPL source (1/h)	Range from Ma et al. (2016)
1,2-DCA (19 dissolved-phase, 9 LNAPL)			
0	5.00×10^{-5}	7.00×10^{-5}	5.9×10^{-4} to 5.2×10^{-3}
25	2.26×10^{-4}	7.50×10^{-4}	
50	9.45×10^{-4}	1.03×10^{-3}	
75	1.26×10^{-2}	4.20×10^{-3}	
100	1.40×10^{-1}	1.43×10^{-2}	
EDB (10 dissolved-phase, 5 LNAPL)			
0	8.00×10^{-5}	1.10×10^{-3}	4.1×10^{-4} to 1.8×10^{-2}
25	3.80×10^{-4}	3.50×10^{-3}	
50	7.30×10^{-4}	6.00×10^{-3}	
75	3.00×10^{-3}	1.70×10^{-2}	
100	7.20×10^{-3}	2.40×10^{-2}	

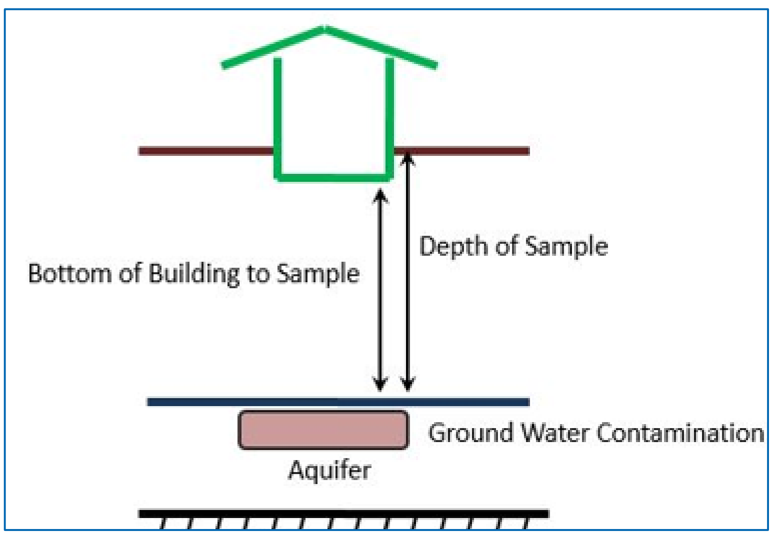
PVIScreen Modeling

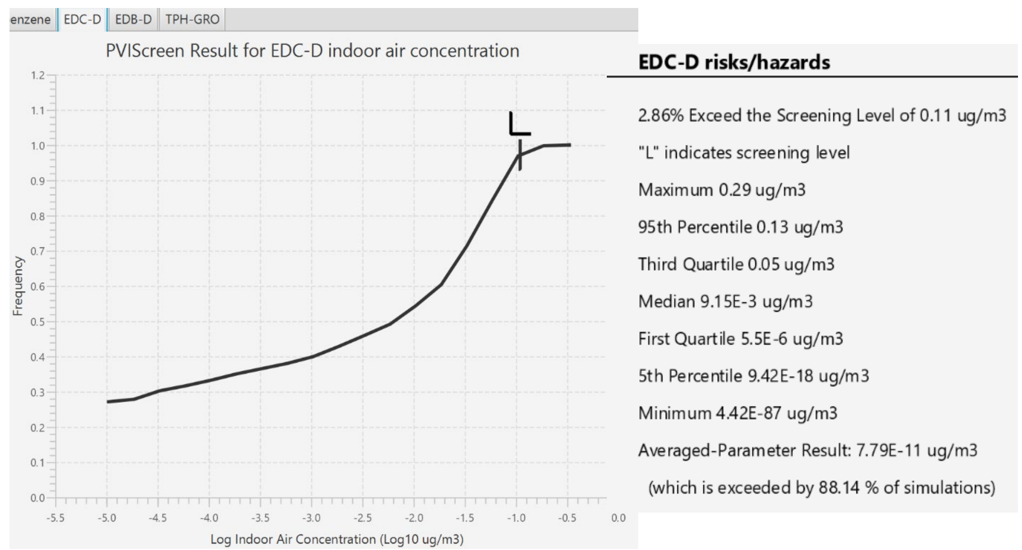
Objective

Use PVIScreen model to evaluate applicability of 6 ft. and 15 ft. as vertical screening distances for 1,2-DCA and EDB

PVIScreen - http://www.epa.gov/land-research/pviscreen

- EPA model using BioVapor equations combined with Monte Carlo Analysis
- Allows use of distributions for input parameters (e.g. rate constants and source concentrations) to understand uncertainty in predicted indoor air concentrations





PVIScreen Inputs

- Source concentrations in groundwater: 95th percentile concentration for 1,2-DCA and EDB, variable for benzene (and TPH)

Constituent	Dissolved-Phase Source		LNAPL Source	
	Constant	Variable	Constant	Variable
1,2-DCA	310 µg/L	--	760 µg/L	--
EDB	13 µg/L	--	323 µg/L	--
Benzene	--	DL to 930 µg/L	--	1000 µg/L to 19000 µg/L
TPHg (estimated)	--	DL to 1900 µg/L	--	DL to 40000 µg/L

- Aerobic biodegradation rate constants: range of estimates for 1,2-DCA and EDB
- Building parameters: variable foundation thickness, crack width and air exchange rate
- Soil texture: sand, loam and clay
- Vertical distance between building and vapor source:
  - 6 ft. for dissolved-phase source and 15 ft. for LNAPL source

PVIScreen Modeling Results

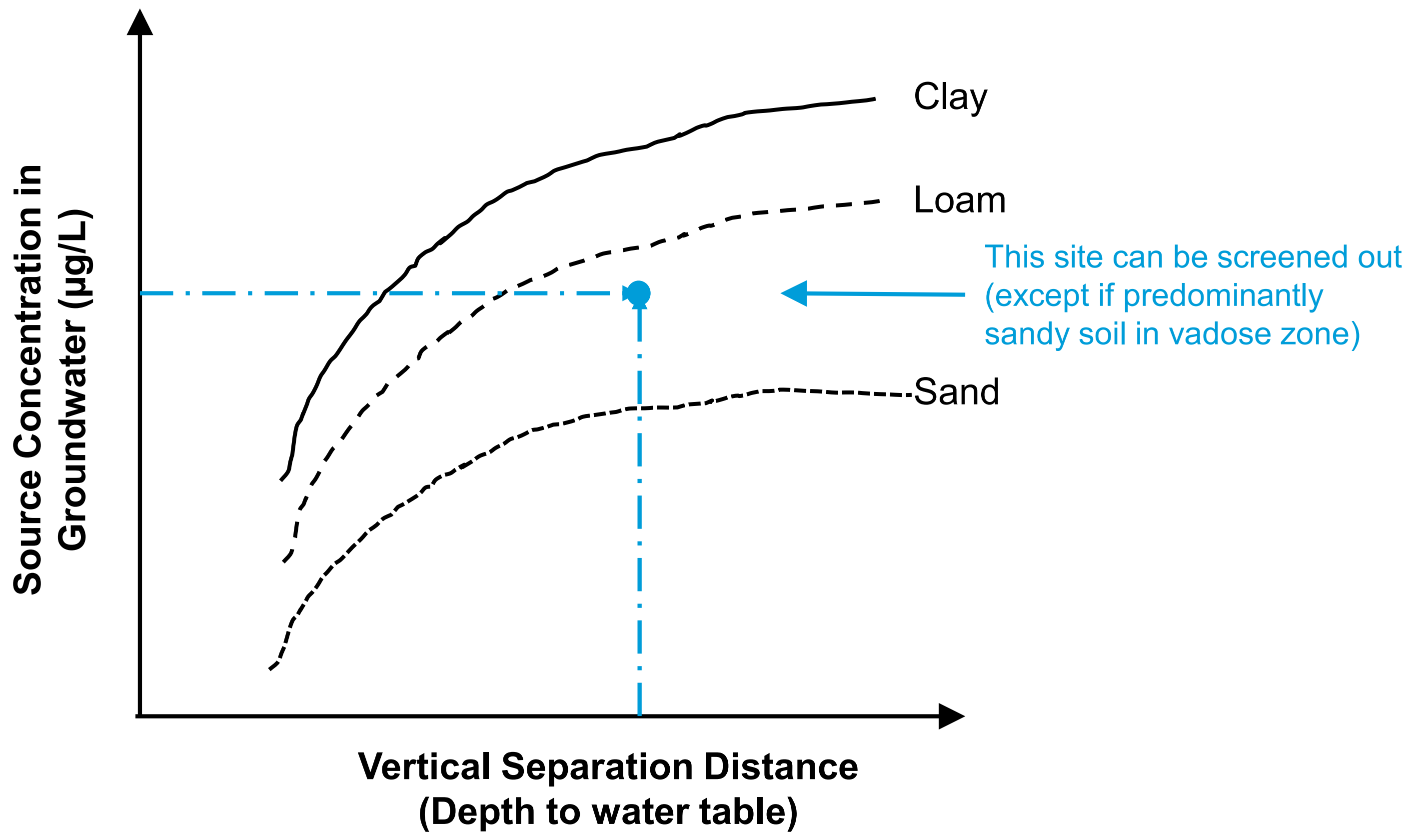
- Used < 5% frequency of exceedance to test applicability (predicted vs. target indoor air concentration)
- Currently established vertical screening distances are applicable
  - except for 1,2-DCA with sand soil texture in vadose zone

Vertical Separation (ft.)	Vapor Source Type	Soil Texture	Frequency at which Predicted Indoor Air Concentration Exceeded Target (%)	
			1,2-DCA*	EDB#
6	Dissolved phase	Sand	46	0
		Loam	7	0
		Clay	0	0
15	LNAPL	Sand	36	2
		Loam	0.6	0
		Clay	0	0

Target Indoor Air Concentration
* 1,2-DCA - 0.11 µg/m^3
\# EDB - 0.0047 µg/m^3

Next Steps

- Given that aerobic rate constants for 1,2-DCA and EDB are ~100-fold lower than benzene, evaluate sensitivity to soil texture and source concentration
- Develop nomographs to compare site specific conditions as a screening tool prior to refined modeling or collection of soil gas data



Conclusions

- The modified EPA TO-15 (HSS) method enabled detecting EDB at the residential VISL in soil gas (reporting limit 0.16 μg/m^3)
- Empirical analysis suggests EPA recommended vertical screening distances are
  - applicable for EDB
  - minimum of 15 ft. vertical screening distance required for 1,2-DCA
- Estimated aerobic biodegradation rate constants for 1,2-DCA and EDB are 100-fold lower than benzene and consistent with literature reported values
- PVIScreen modeling suggests EPA recommended established vertical screening distances are applicable
  - for EDB
  - except for 1,2-DCA with sand in vadose zone

References

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- Interstate Technology & Regulatory Council (ITRC), 2014. Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management. http://www.itrcweb.org/PetroleumVI-Guidance/
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Appendix

Different Conceptual Site Models of Vapor Intrusion from Petroleum (PVI) vs. Chlorinated Solvents (CVI)

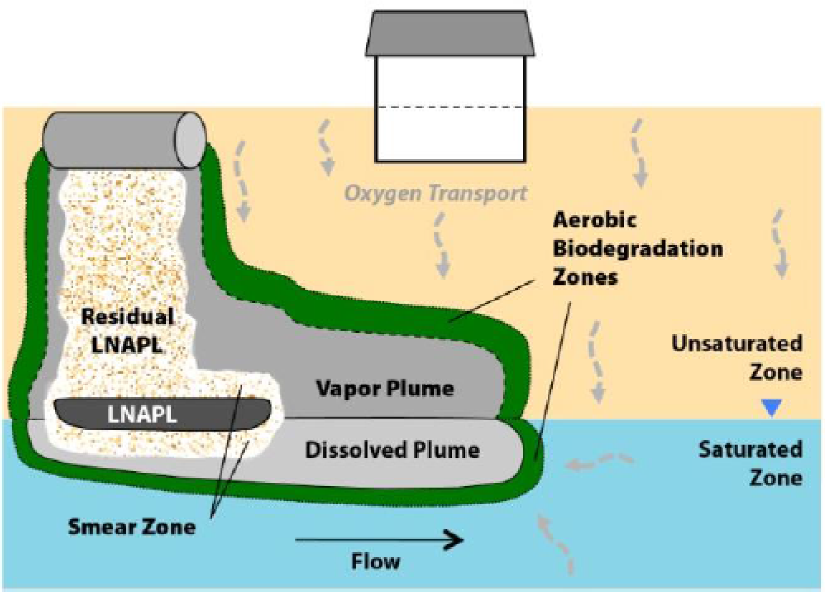


Figure 1. Typical petroleum hydrocarbon transport conceptual scenario

Aerobic biodegradation of PHCs along the perimeter of the vapor and dissolved plumes limits subsurface contaminant spreading. Effective oxygen transport (dashed arrows) maintains aerobic conditions in the biodegradation zone. Petroleum LNAPL (light nonaqueous phase liquid) collects at the groundwater surface (the water table, blue triangle).

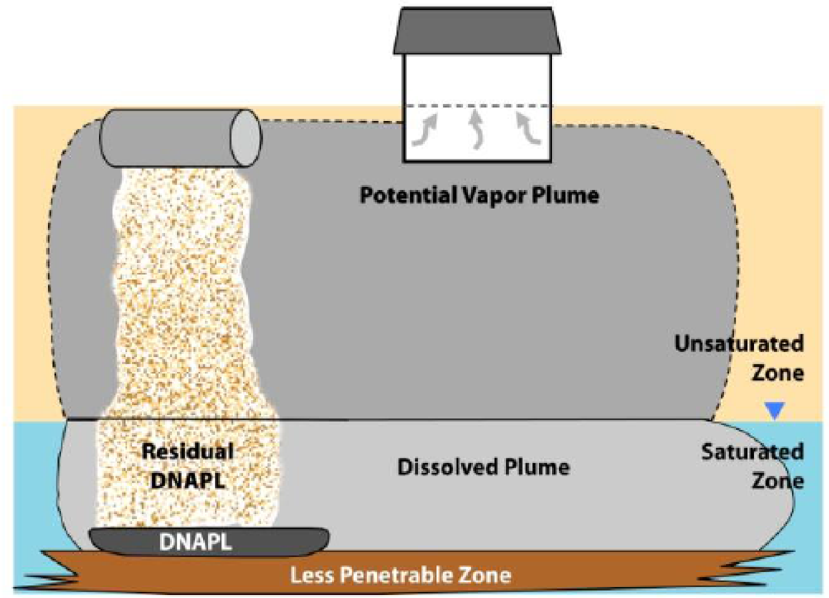
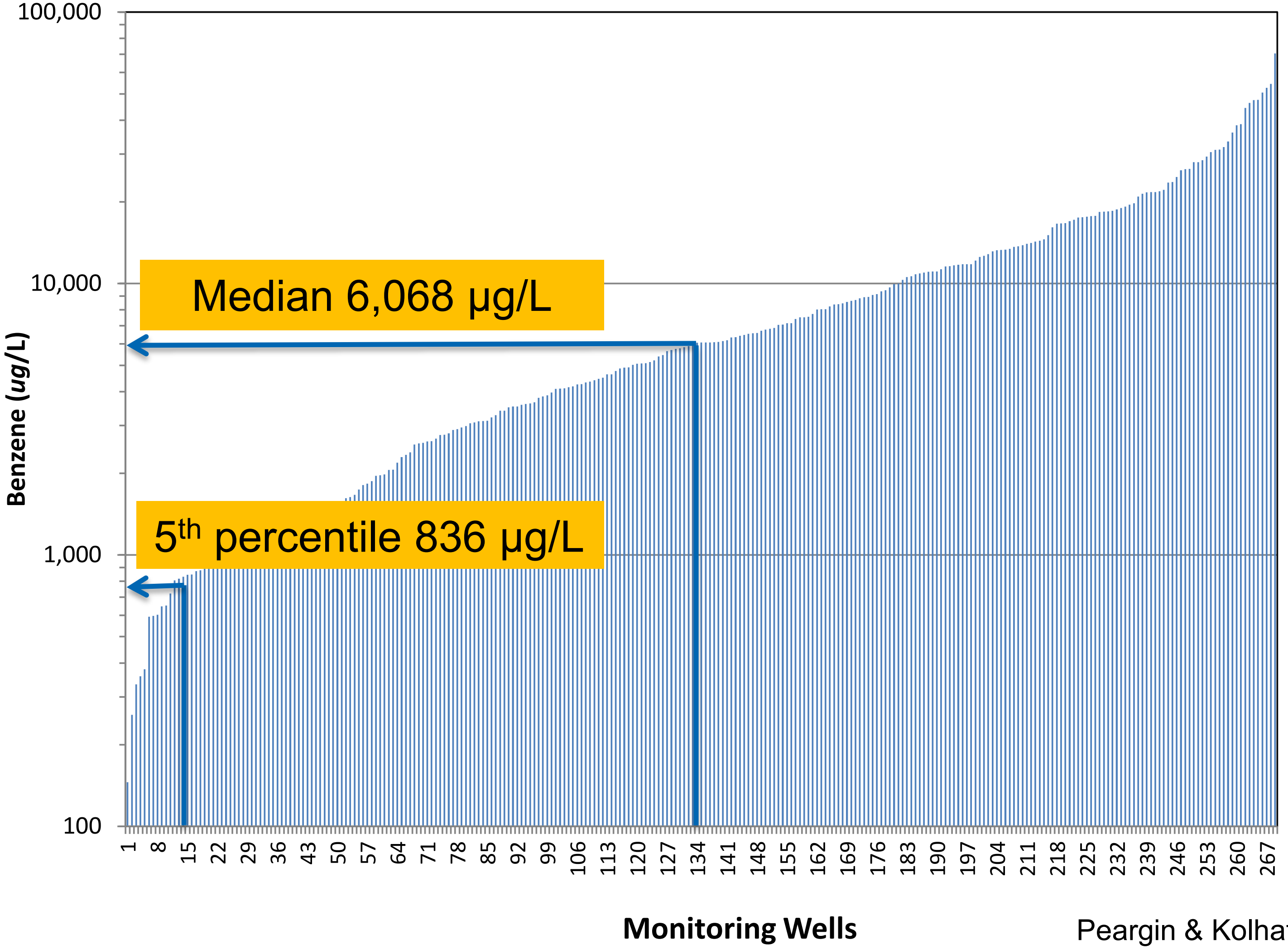


Figure 2. Typical chlorinated solvent transport conceptual scenario

Biodegradation of CHCs is anaerobic and usually slower than PHC biodegradation, so that the vapor and dissolved plumes often migrate farther than PHC plumes. CHC DNAPL (dense nonaqueous-phase liquid), if present, can sink below the water table, collecting in this case on a less penetrable layer.

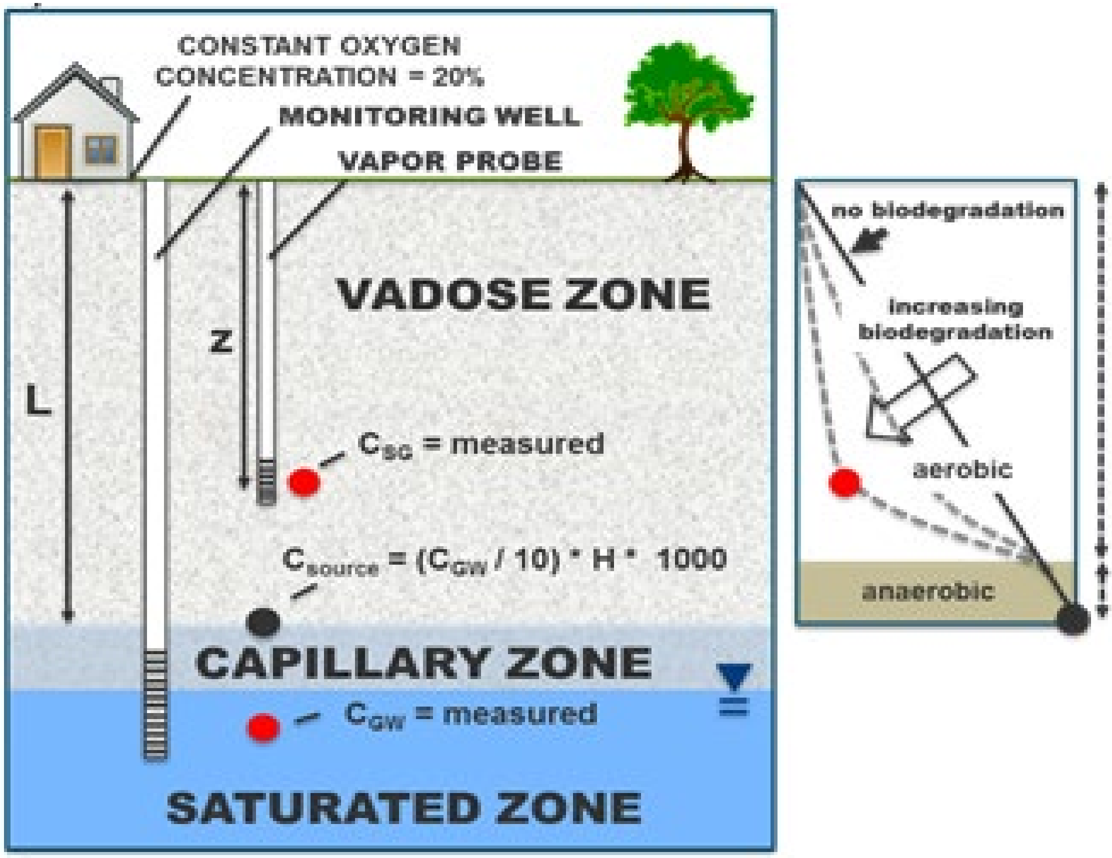
(Source - EPA 2012)

1,000 µg/L Benzene in Groundwater as a Conservative Estimate to Distinguish LNAPL from Dissolved Sources



Peargin & Kolhatkar, 2011

Extracting Aerobic Biodegradation Rate Constants (BioVapor)



- 1st-order aerobic biodegradation rate constant <u>calibrated</u> to measured soil gas data (ITRC 2014, Appendix I)
- Vadose zone assumed homogenous/isotropic
- C_{source} based on AF = 0.1
- Modeled constituents:
  - –1,2-DCA, EDB, benzene
  - –aliphatics/aromatics: concentrations estimated from benzene concentrations in groundwater
- No analysis of soil vapor data w/ RLs > Fick's law