Field Pilot to Develop Vertical Screening Distance Criteria to Assess Vapor Intrusion from Lead Scavengers

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Outline

- Background – PVI vs. CVI, lead scavengers
- Empirical evaluation of screening criteria
  - 2015-2016 - Data mining of existing data
  - 2016 – development and validation of analytical method (GC x GC TOF MS)
  - 2017 - concurrent GW and SV sampling with appropriate analytical method
  - 2018 – extraction of first order biodegradation rate constants (to estimate vertical screening distance using API Biovapor model)
- Conclusions

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

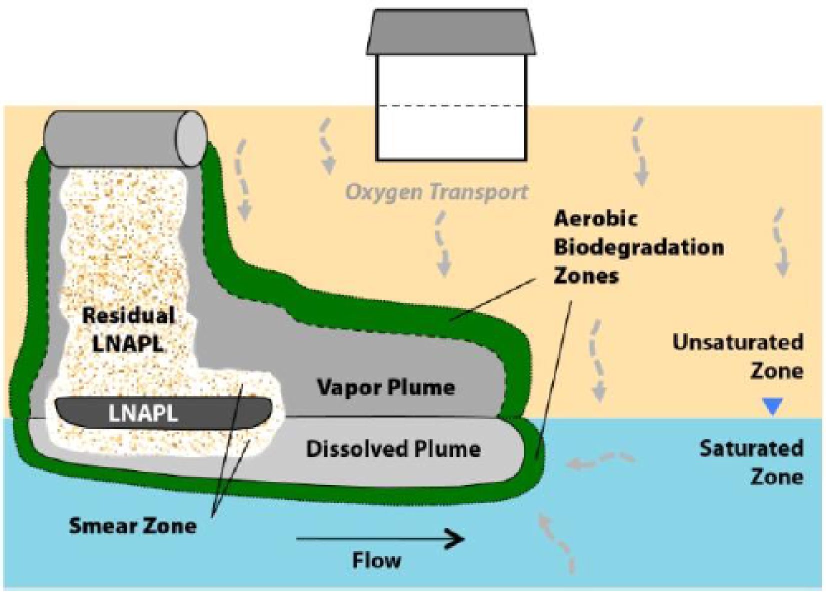

Figure 1. Typical petroleum hydrocarbon transport conceptual scenario

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).

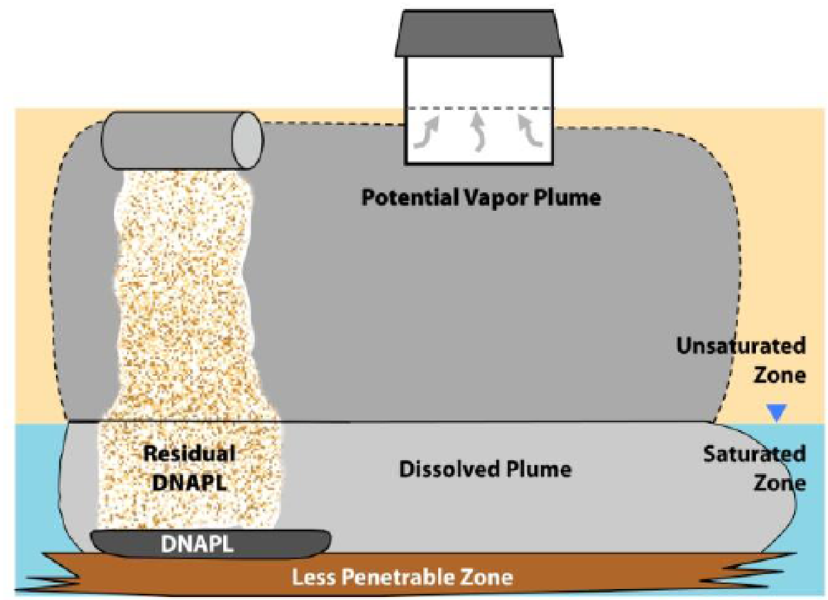

Figure 2. Typical chlorinated solvent transport conceptual scenario

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)

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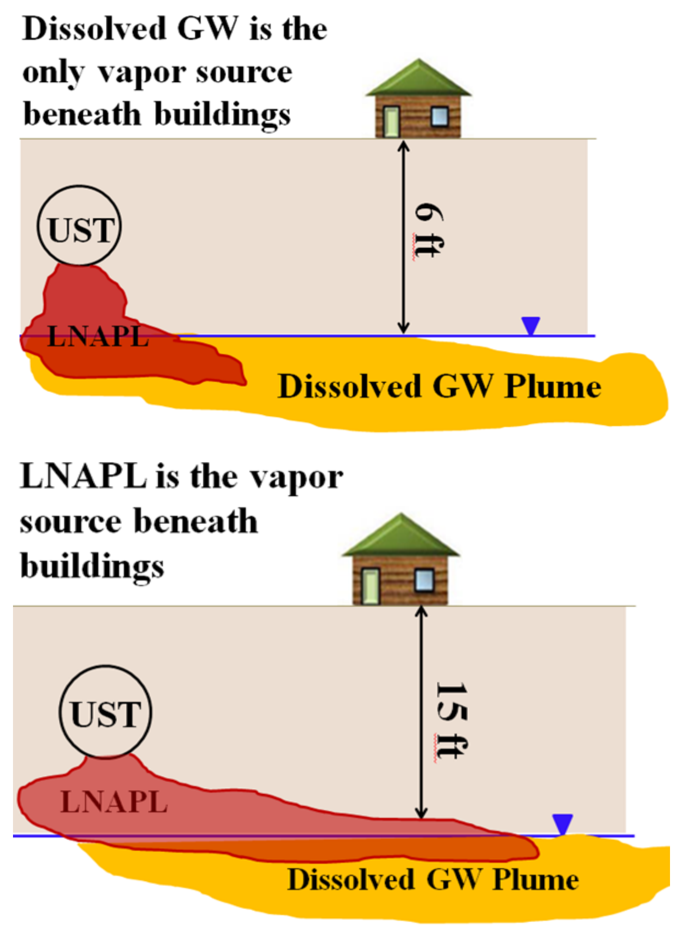
Regulatory Context

2015 EPA OUST PVI guidance established vertical screening distance criteria for benzene (EPA 2015)

- Additional 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* and EDB# biodegradation in soil gas as a data gap and stated *"…vertical separation distances recommended in this guide may not be sufficient for petroleum fuel releases that contain EDB and 1,2-DCA and additional investigation may be necessary to assess their potential for vapor intrusion…"*

Likely presence of 1,2-DCA or EDB at the site considered a 'precluding factor' in ITRC and 6 states' VI guidance documents

Vertical Screening Distance Criteria for Benzene



*1,2-DCA – 1,2- Dichloroethane and #EDB - Ethylene Dibromide (both lead scavengers)

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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/EDB in the subsurface likely over 20 years old
- 1,2-DCA & EDB still used as lead scavenger in aviation gas & racing fuels

- Properties of 1,2-DCA and EDB
  - More soluble, less likely to sorb to soil and partition out of water (vs. benzene)
  - Known to biodegrade aerobically and anaerobically, but knowledge not as robust as BTEX

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Data Mining of Existing PVI Data (2015-2016)

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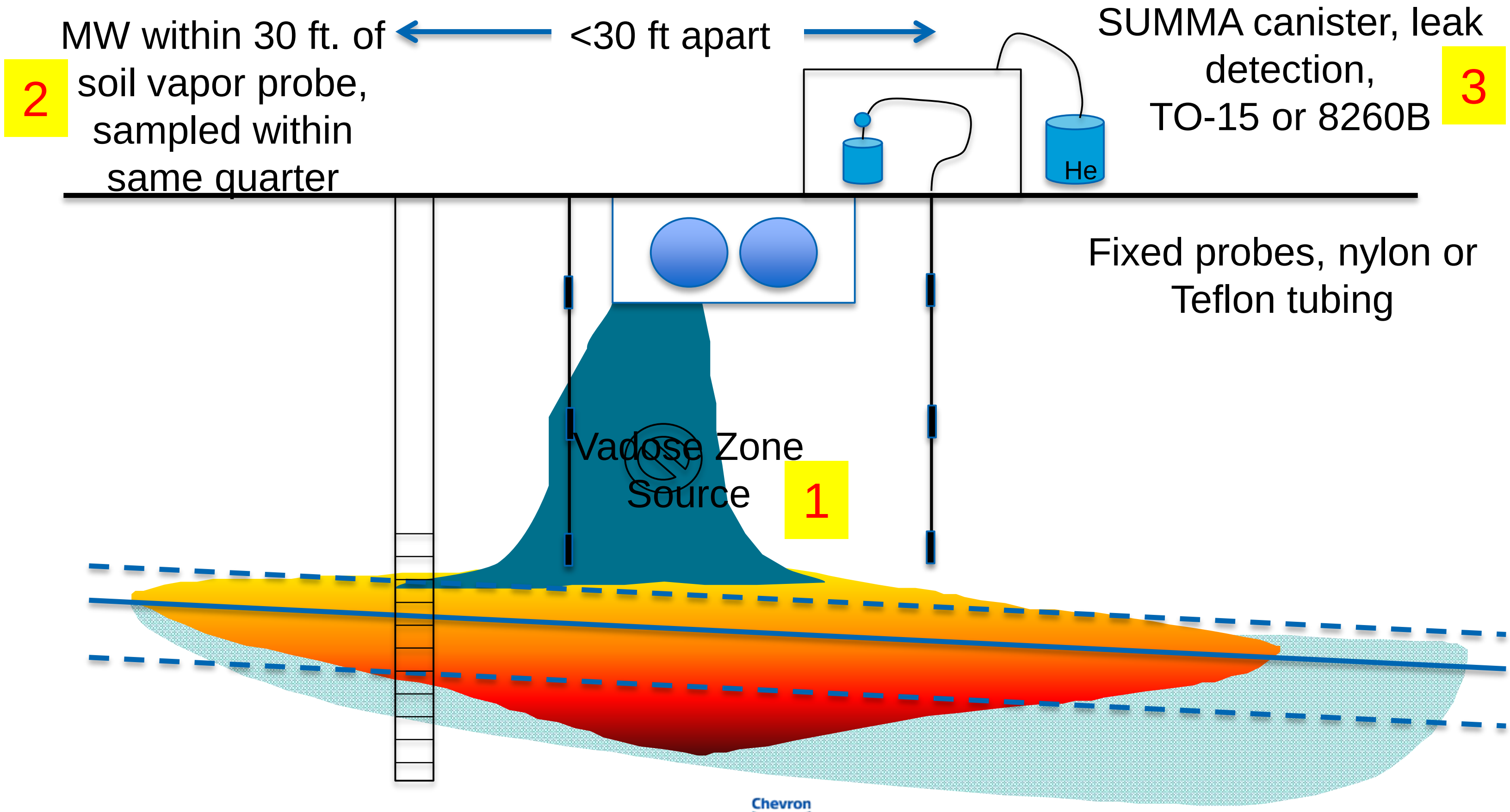
Data Mining of Existing PVI Data to Develop Screening Criteria for 1,2-DCA and EDB (2015-2016)

- Reviewed data from over 140 PVI investigation sites
- Able to obtain 116 pairs of 1,2-DCA and 72 pairs of EDB soil vapor & groundwater concentration data from 26 sites with likely leaded gasoline releases



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Soil Vapor Screening Levels vs. Analytical Capability

- Soil vapor screening level for
  - 1,2-DCA - Achievable with current analytical methods
  - EDB - Not achievable with current analytical methods

Compound	Soil Vapor Screening Level* ($\mu g/m^3$)		Soil Vapor Analytical Reporting Limit (EPA TO-15)
	10^{-6} excess cancer risk (residential)	10^{-5} excess cancer risk (residential)	Conventional
1,2-DCA	3.6	36	2.0
EDB	0.16	1.6	3.8

* Soil vapor screening level - based on Table 8, Technical Guide For Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites (EPA 510-R-15-001), Assumes attenuation factor of 0.03 for soil vapor to indoor air, http://www.epa.gov/vaporintrusion/vapor-intrusion-screening-levels

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Conclusions from 2015-2016 Analysis

1,2-DCA

- Only 6 detections out of 116 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. appeared to be adequate for 1,2-DCA

EDB

- Due to the very low screening level concentration for EDB relative to analytical reporting limits, this data set was not sufficient to determine vertical screening distance criteria for EDB

This work was presented at 2016 AEHS conference - https://iavi.rti.org/attachments/WorkshopsAndConferences/03_Kolhatkar-Lavis_2016_AEHS_screeningcriteria_etal_032316.pdf

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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
  - o 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
  - o Time-of-Flight (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/laboratories/eurofins-air-toxics/services/to-15-hss/ (see schematic)

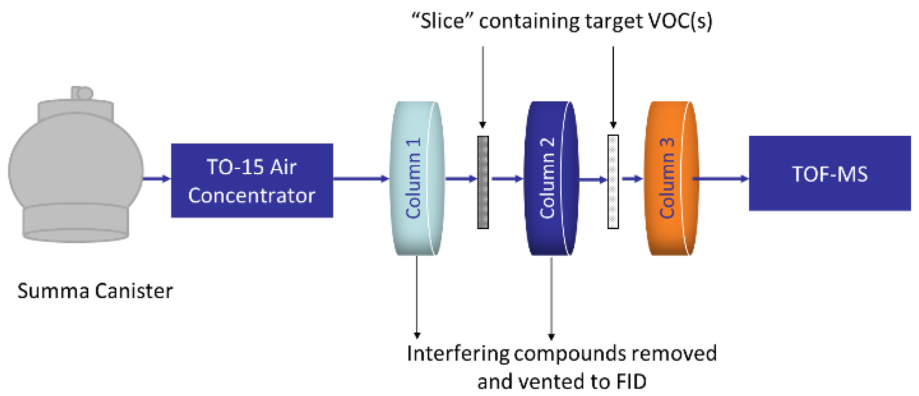

Figure 1. Schematic of modified TO-15 analytical configuration

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2017 Field Pilot

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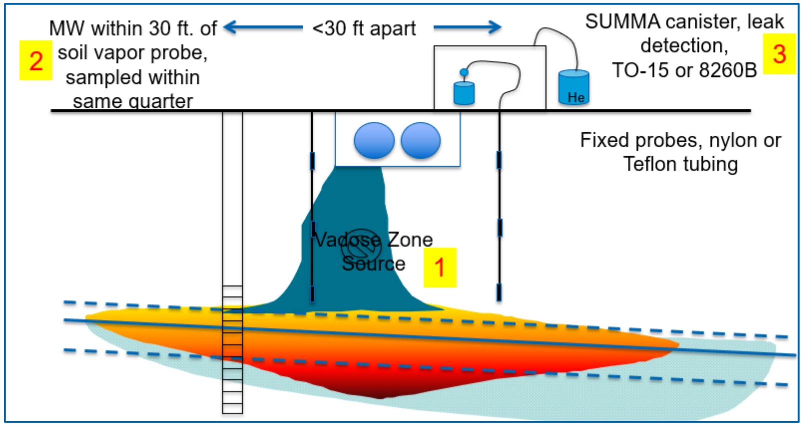
2017 Field Pilot Activities

✓Identified 28 candidate sites from 200+ sites
- o active regulatory case and
- o recent 1,2-DCA/EDB detections above groundwater VISL* and
- o relatively shallow water table

✓Field work planned and attempted on 20 sites

✓<u>14 sites with concurrent soil vapor and groundwater data suitable for analysis</u>
- o Geographically distributed across the US (sites in CA, NC, AK, SC, MI, PA and Washington DC)
- o Concurrent sampling of soil vapor and groundwater in 2H 2017



*Vapor Intrusion Screening Level

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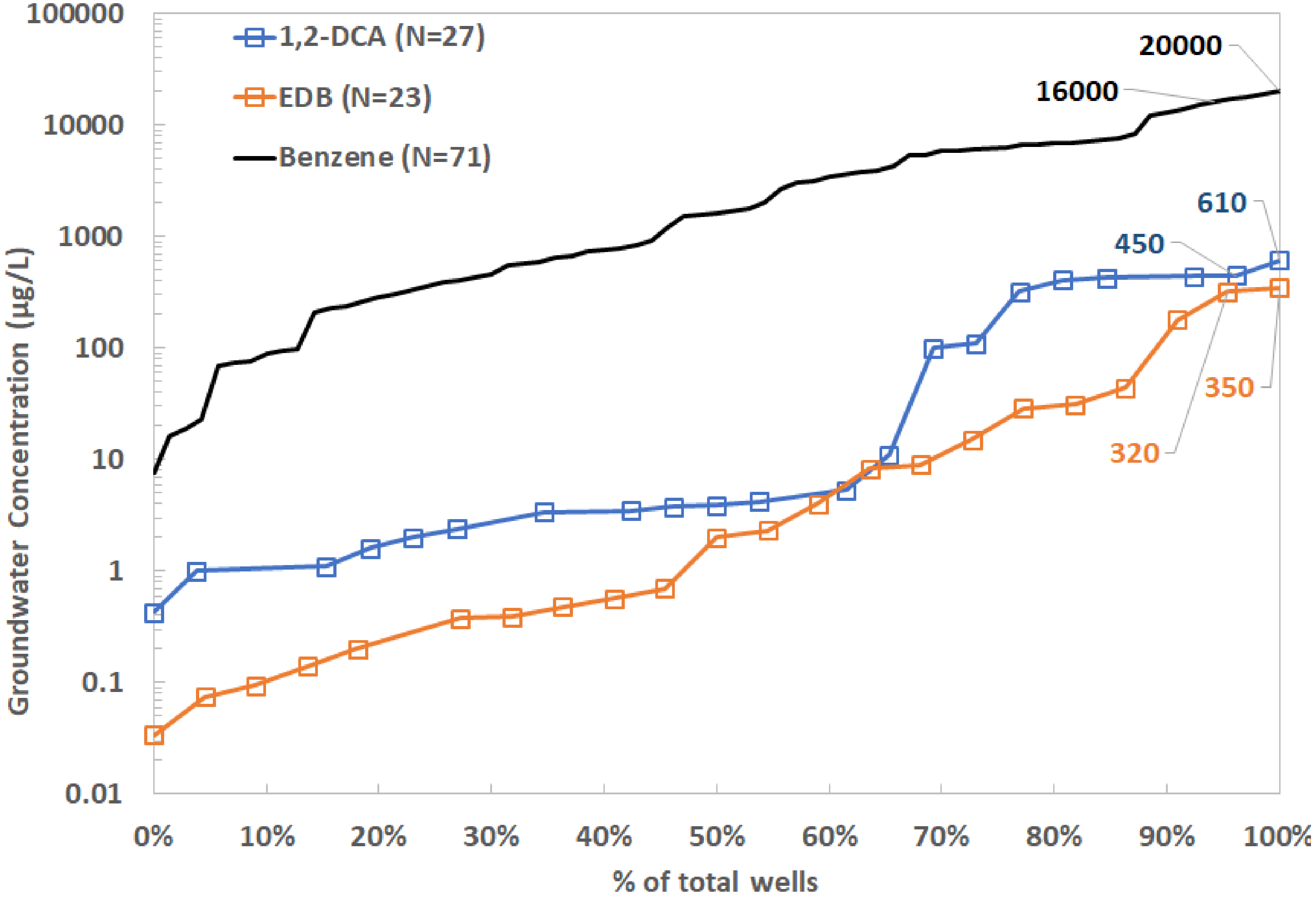
Distribution of 1,2-DCA and EDB Detections in Groundwater at Pilot Sites (2016-17)



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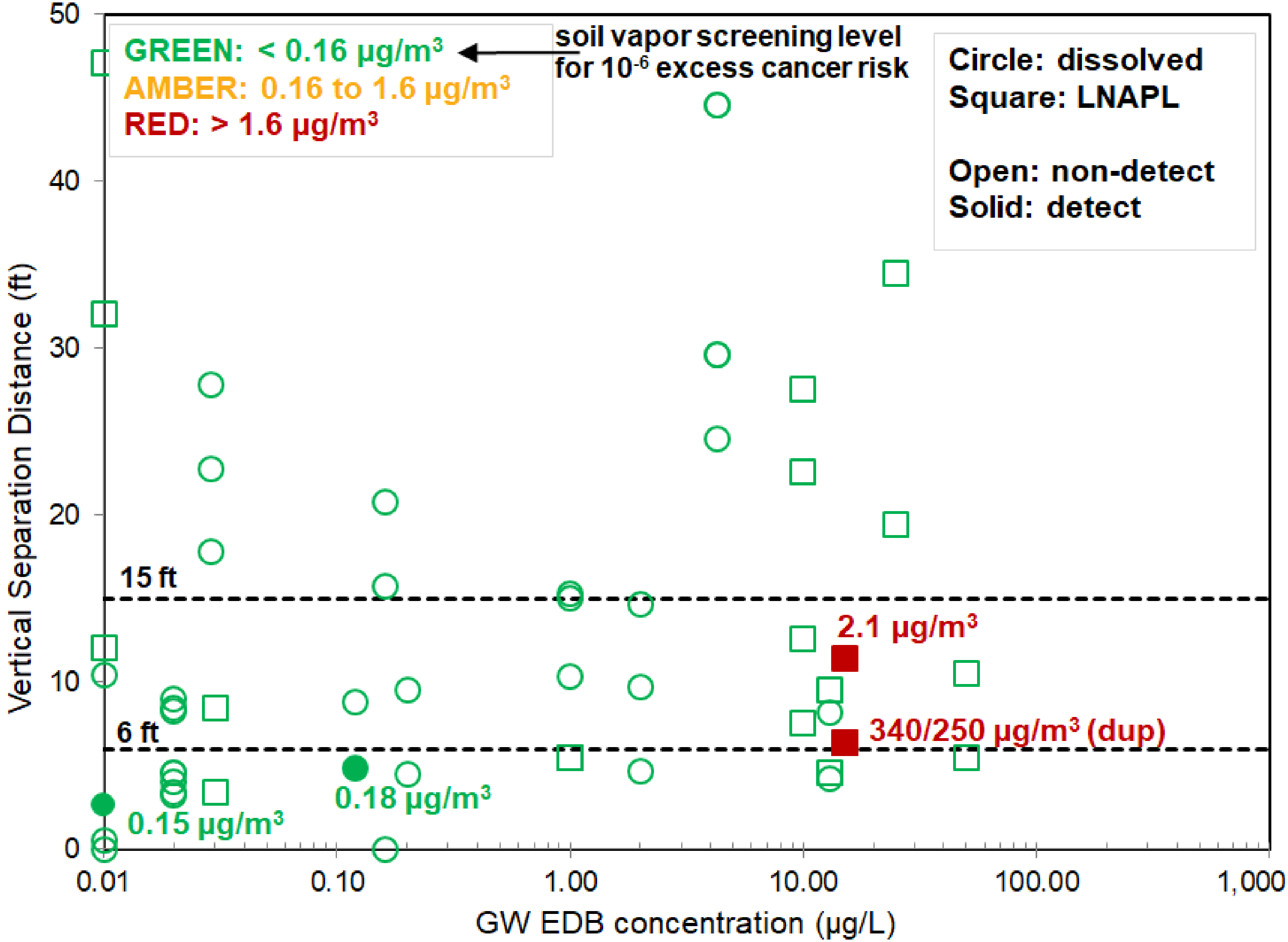
Vertical Transport of EDB Vapors Above Water Table



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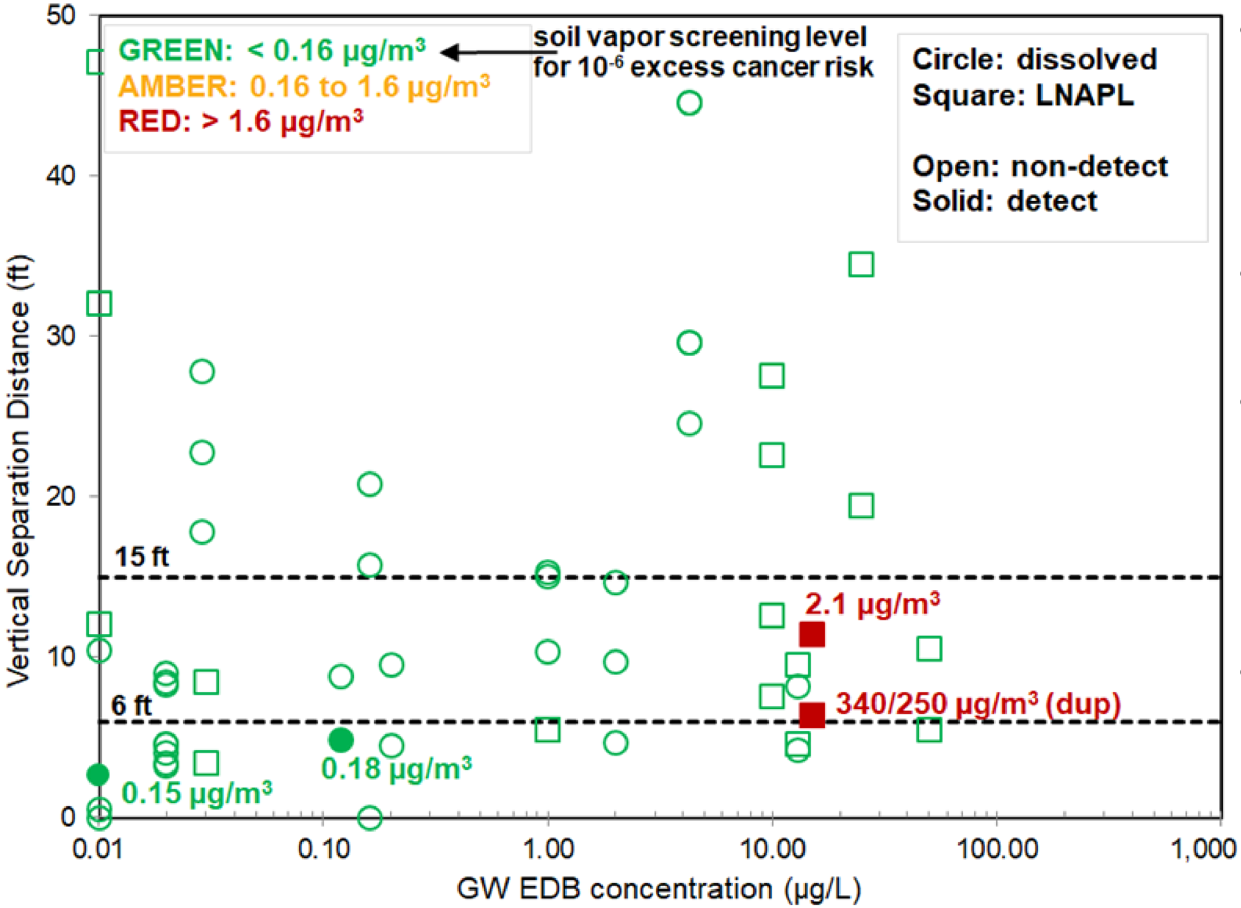
Vertical Transport of EDB Vapors Above Water Table



- Data includes vapors sourced from both dissolved and LNAPL sources at water table
- 55 data pairs [only 4 EDB detections in soil vapor (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)

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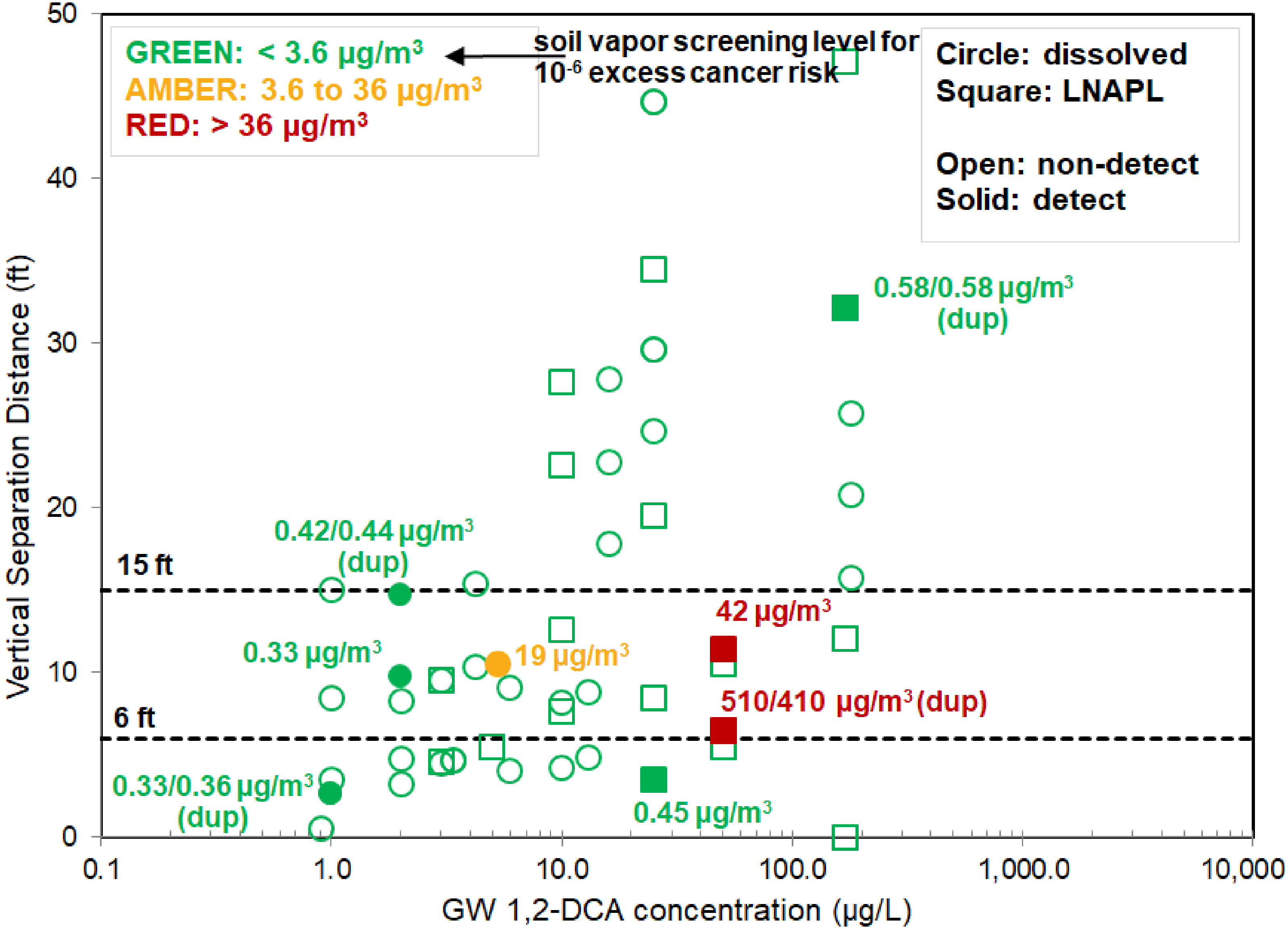
Vertical Transport of 1,2-DCA Vapors Above Water Table



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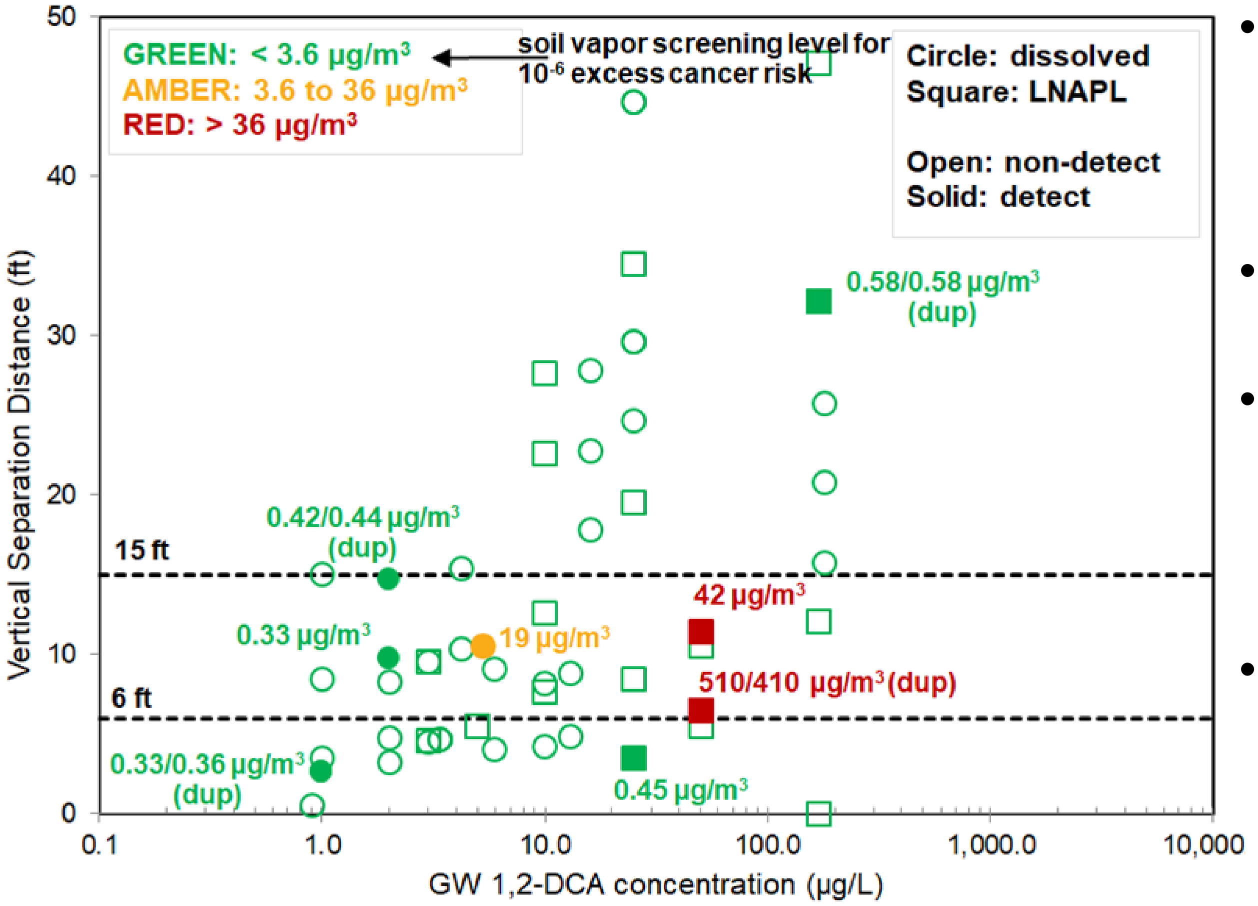
Vertical Transport of 1,2-DCA Vapors Above Water Table



- Data includes vapors sourced from both dissolved and LNAPL sources at water table
- 55 data pairs [8 detections of 1,2-DCA in soil vapor (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)

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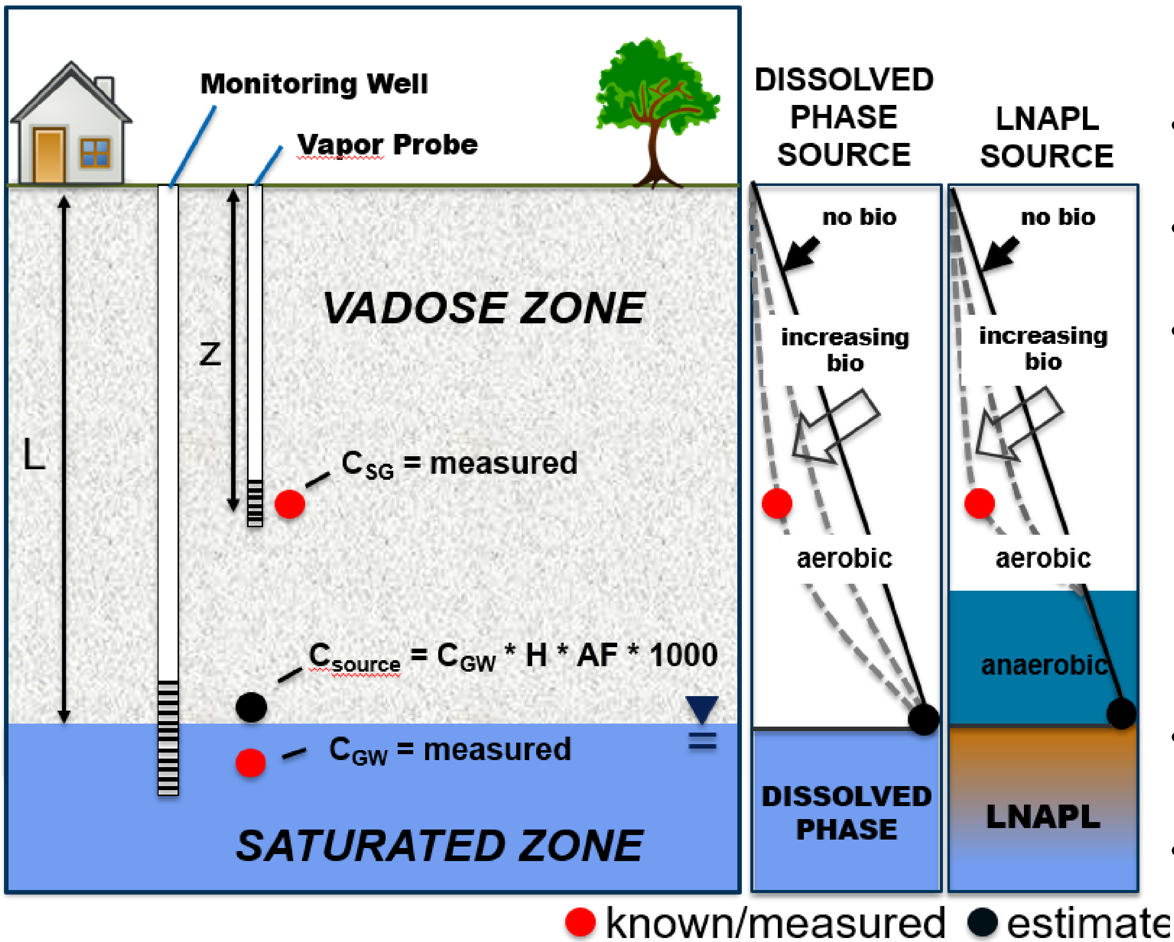
Estimation of First Order Biodegradation Rate Constants for 1,2-DCA and EDB



- 1st-order aerobic rate constant calibrated to measured soil vapor data (ITRC 2014, Appendix I)
- Vadose zone assumed homogenous/isotropic
- C_{source} based on AF = 0.1 (default value in BioVapor)
- Modeled constituents:
  - 1,2-DCA
  - EDB
  - benzene
  - aliphatics/aromatics: concentrations estimated from benzene concentrations in groundwater (BioVapor Manual)
- No analysis of soil vapor data w/ RLs > Fick's law
- Diffusion-biodegradation model used if the entire soil vapor profile was aerobic

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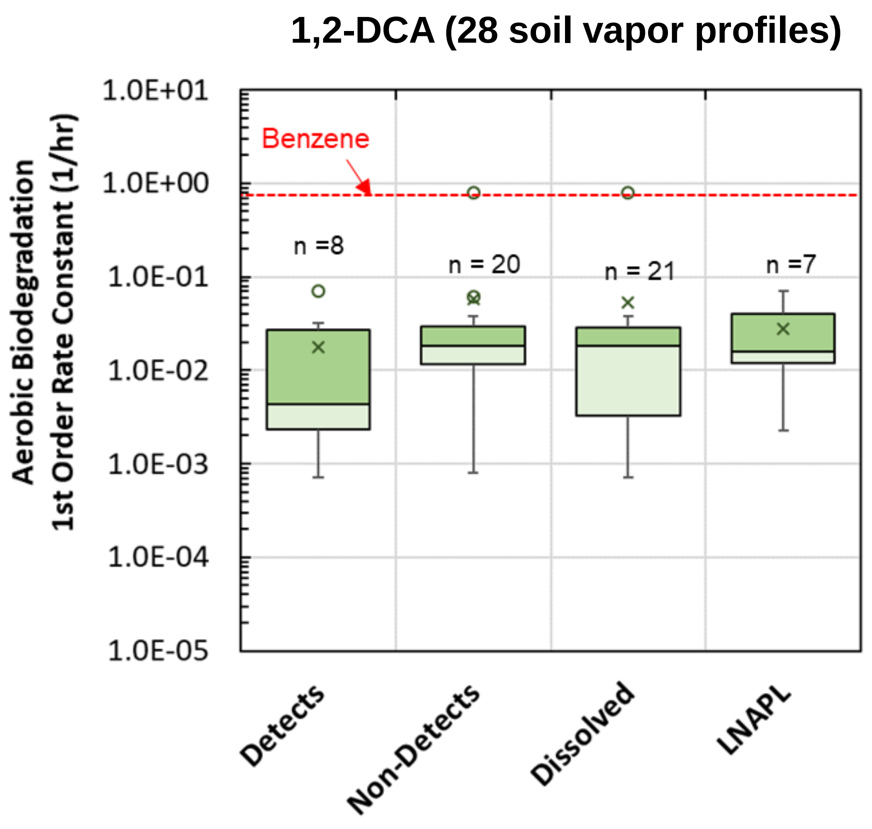
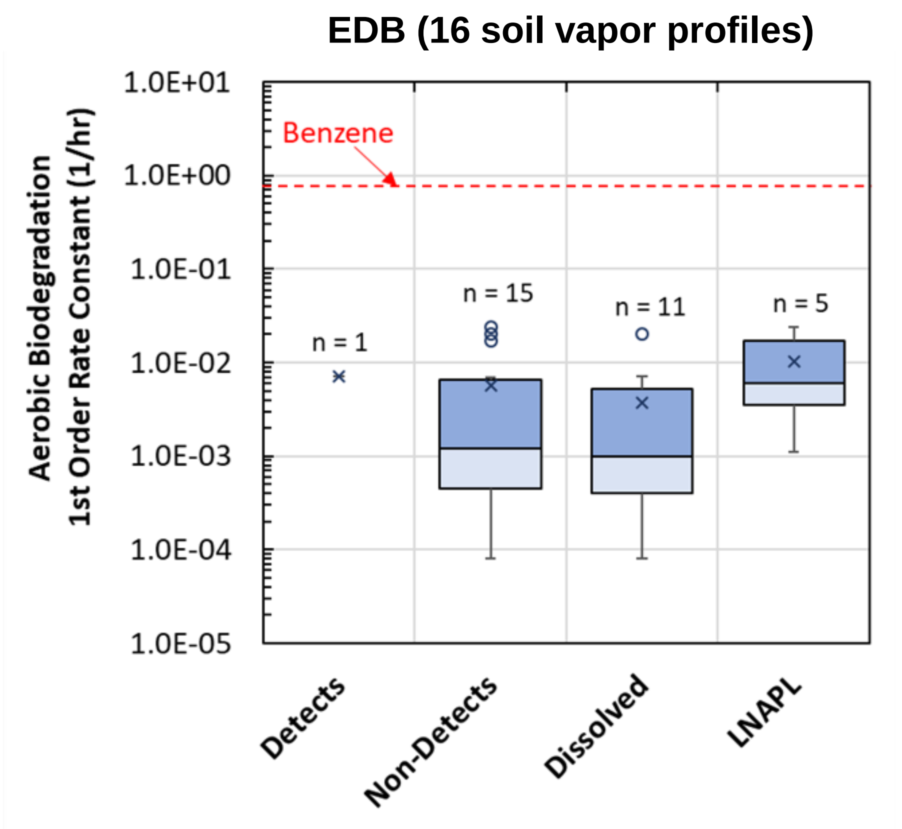
Estimation of First Order Biodegradation Rate Constants for 1,2-DCA and EDB





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Comparison of Rate Constant Estimates with Literature Data

- Estimated aerobic biodegradation rate constants for 1,2-DCA and EDB are over 100-fold lower than benzene and within the range of previous estimates

Source	Median (hr^{-1})	95% Confidence Interval (hr^{-1})
1,2-DCA		
This study (LNAPL)	1.6×10^{-2}	2.3×10^{-3} to 7×10^{-2}
Ma et al. 2016	3×10^{-3}	5.9×10^{-4} to 5.2×10^{-3}
EDB		
This study (LNAPL)	6×10^{-3}	1.1×10^{-3} to 2.4×10^{-2}
Ma et al. 2016	7×10^{-3}	4.1×10^{-4} to 1.8×10^{-2}

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2017 Field Pilot Conclusions

- The modified EPA TO-15 method enabled detecting EDB at the residential VISL in soil vapor (0.16 µg/m3).
- EDB - Vertical separation distances established for benzene (6 ft. for dissolved sources and 15 ft. for LNAPL sources) are protective.
- 1,2-DCA - A minimum of 15 ft. vertical separation distance is required to be protective of VI from 1,2-DCA.
- Estimated first order aerobic biodegradation rate constants are consistent with literature reported values.

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References

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Appendix

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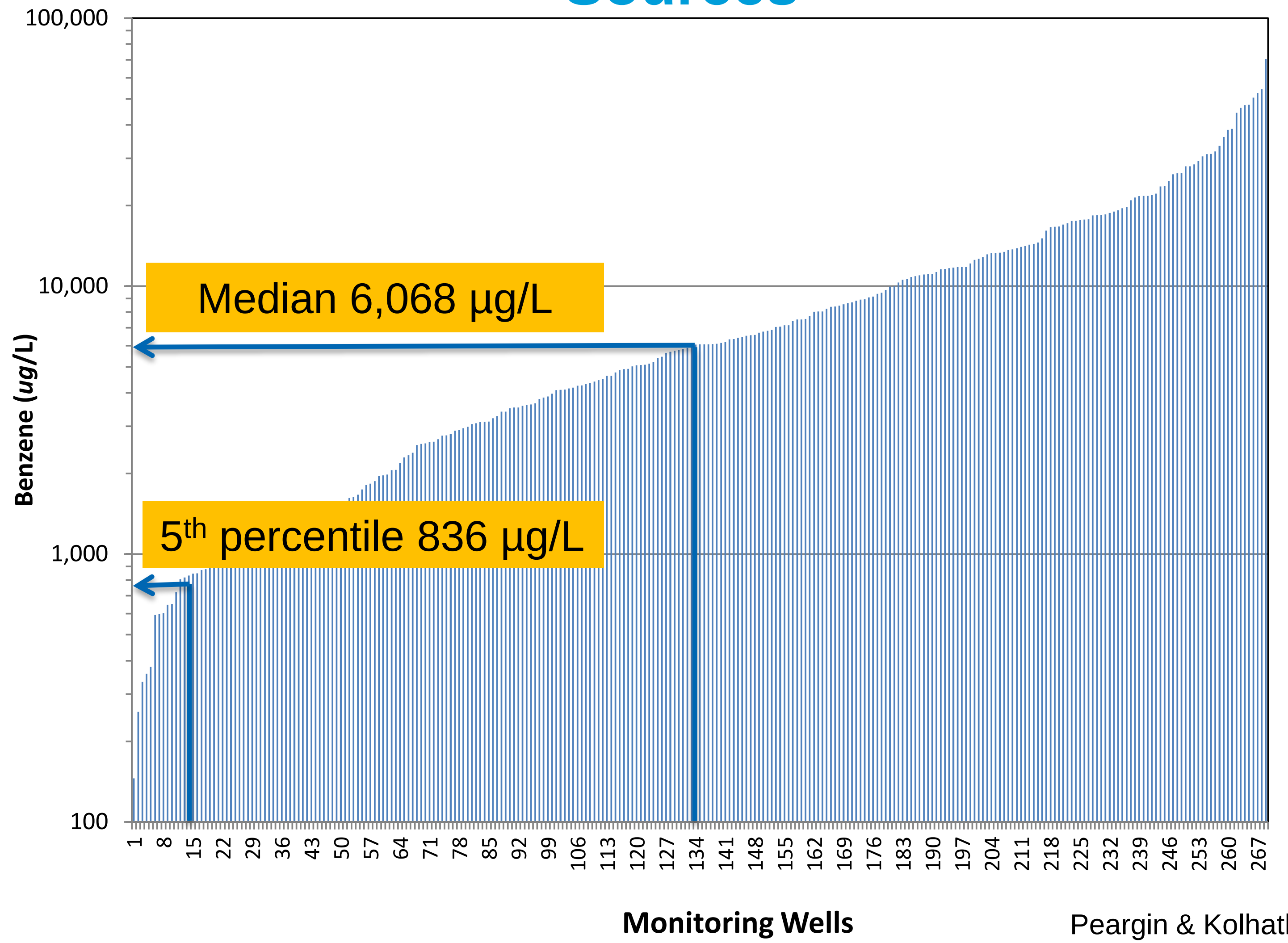
1,000 µg/L Benzene in Groundwater as a Conservative Estimate to Distinguish LNAPL from Dissolved Sources



Peargin & Kolhatkar, 2011

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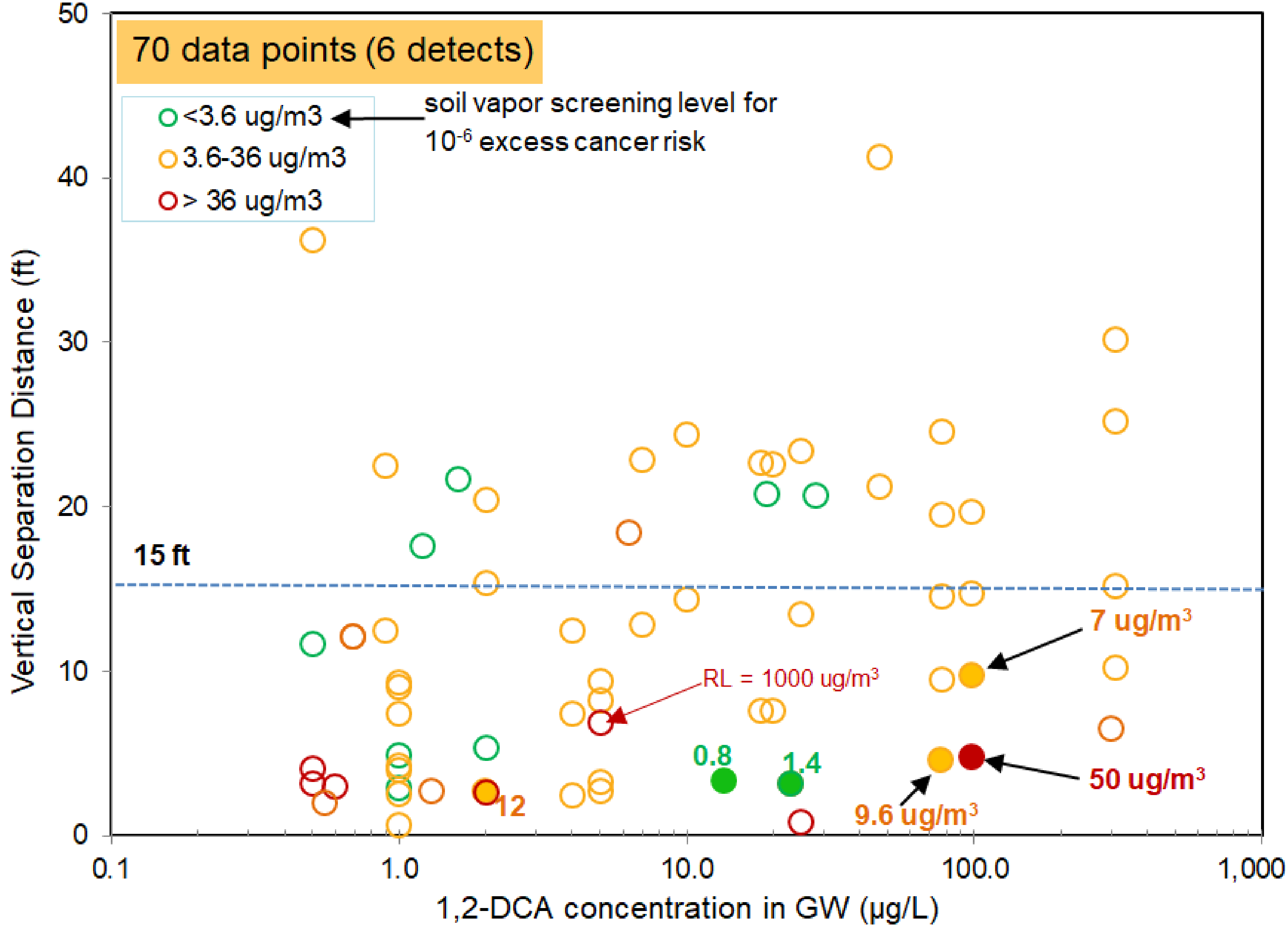
1,2-DCA Vapors from Dissolved Source (2015-16 data mining)



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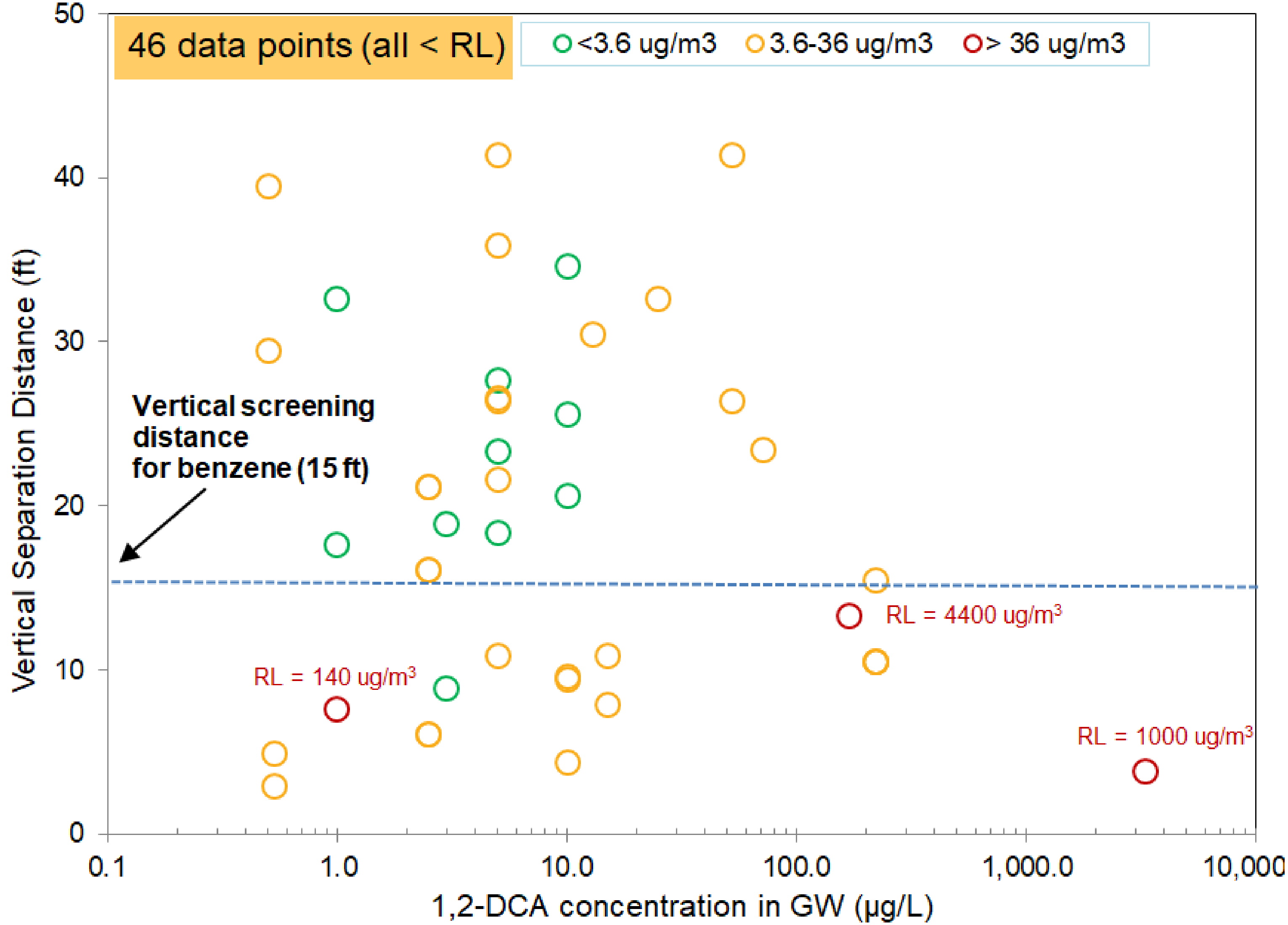
1,2-DCA Vapors from LNAPL (2015-16 data mining)



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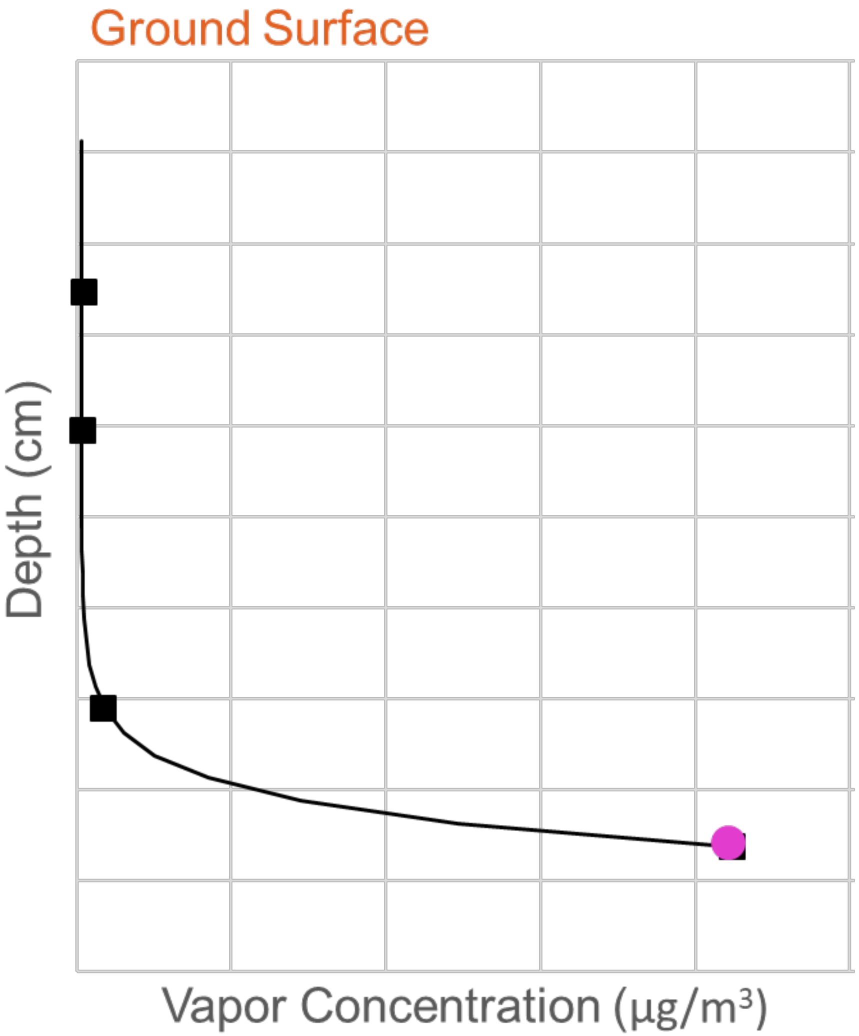
Calibration if all soil vapor data has O_2 > 1%



Criteria:

- Soil vapor data is detect
- Soil vapor data in aerobic zone

Fitting:

- ITRC Manual solution
- Oxygen never limiting
- Source: deepest soil vapor probe

$$C(z) = C(z=0) * \exp\left(-\frac{z}{\sqrt{\frac{D_{eff} * H}{\theta_w * k_w}}}\right)$$

$$D_{\mathrm{eff}} = \left(\frac{\theta_{\mathrm{v}}^{10/3}}{\theta_{\mathrm{T}}^{2}} \cdot D_{\mathrm{v}} + \frac{\theta_{\mathrm{w}}^{10/3}}{\theta_{\mathrm{T}}^{2}} \cdot \frac{D_{\mathrm{w}}}{H}\right)$$

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