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# Vertical Screening Distance Criteria to Evaluate Vapor Intrusion Risk from Lead Scavengers

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# Outline

- Background – lead scavengers use, properties and biodegradation
- API study on empirical evaluation of vertical screening distance criteria
- Extract aerobic biodegradation rate constants from existing soil vapor profiles to estimate vertical screening distances
- Conclusions
- Next steps (*companion talk - Hers et al. session E1*)



# Lead scavengers - Use and properties

- Added to leaded gasoline to prevent lead oxide deposits that could foul engines
  - 1925 - Ethylene dibromide (EDB) 1<sup>st</sup> use in leaded gasoline
  - 1940s - Ethylene dichloride (EDC) use started
- Leaded gasoline phase-out - mid 1980's to mid 1990's
  - EDC/EDB in groundwater from gasoline releases >20 years old
- EDC & EDB still used as lead scavenger in aviation gas & racing fuels
- More soluble, less likely to sorb to soil and partition out of water (vs. benzene)

	Water Solubility (mg/L)	Log K <sub>ow</sub> (-)	VP at 25°C (mm Hg)	Henry's Law Constant at 25°C (-)
Benzene	1790	2.13	94.8	0.227
EDB	3910	1.74	11.2	0.027
EDC	8600	1.47	78.9	0.048



# Lead scavengers - Biodegradation

## Aerobic biodegradation

- EDB –  $t_{1/2}$  (days to weeks), aerobic co-metabolism with methane and other alkanes shown to enhance rate
- EDC –  $t_{1/2}$  (days to several months)

## Anaerobic biodegradation – usually via reductive dehalogenation

- EDB –  $t_{1/2}$  (months)
- EDC –  $t_{1/2}$  (months to years)
  
- Biodegradation less understood compared to BTEX



# Empirical evaluation of vertical screening distance criteria

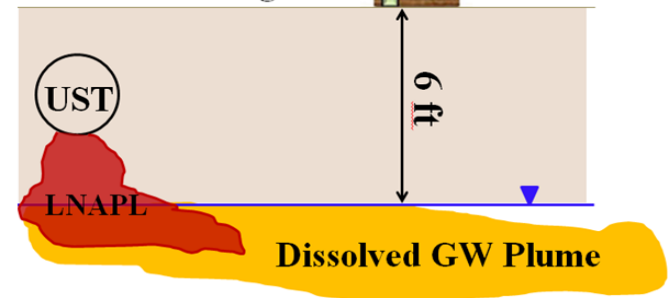
- 2015 EPA OUST PVI guidance established vertical screening distance criteria for benzene (see Figure)
- However, it identified ‘lack of rigorous quantification of EDC and EDB biodegradation’ as a data gap
- Presence of lead scavengers considered a ‘precluding factor’ to apply vertical distance screening approach in EPA, ITRC and 6 states’ VI guidance documents

## Motivation for API study

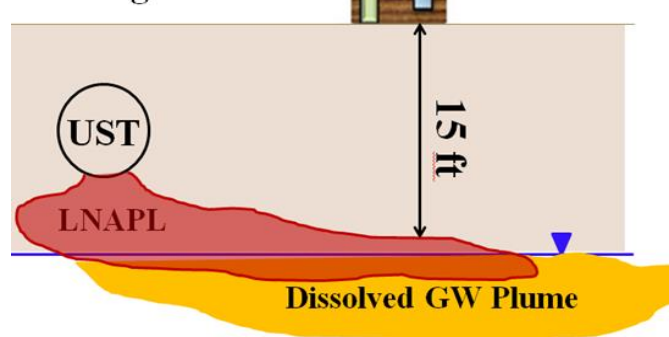
- Determine if vertical screening distance criteria can be established for VI evaluation of lead scavengers
- These criteria could fill the data gap and enable appropriate screening of sites with lead scavengers

### Vertical Screening Distance Criteria for Benzene

Dissolved GW is the only vapor source beneath buildings



LNAPL is the vapor source beneath buildings



# Limitations of existing soil vapor data

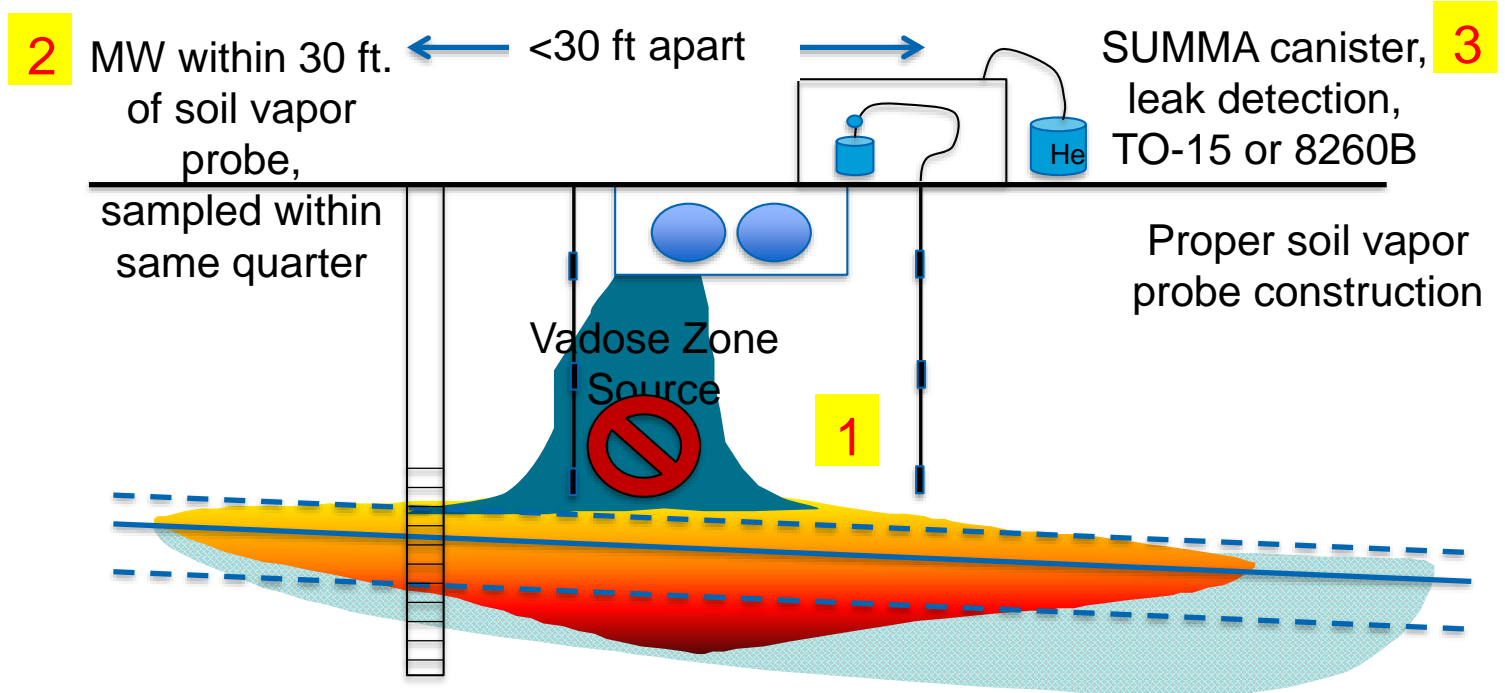
Compound	Soil Vapor Screening Level* ( $\mu\text{g}/\text{m}^3$ )	Soil Vapor Analytical Method Detection Limits (EPA TO-15)		
		Conventional	Low Level	SIM
	$10^{-6}$ excess cancer risk (residential)			
EDC	3.7	2.0	0.40	0.12
EDB	0.16	3.8	0.77	0.23

- Empirical evaluation with existing soil vapor data (with TO-15) is
  - feasible for EDC (TO-15 can achieve soil vapor screening level)
  - not feasible for EDB (TO-15 detection limits not low enough)

\* 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>



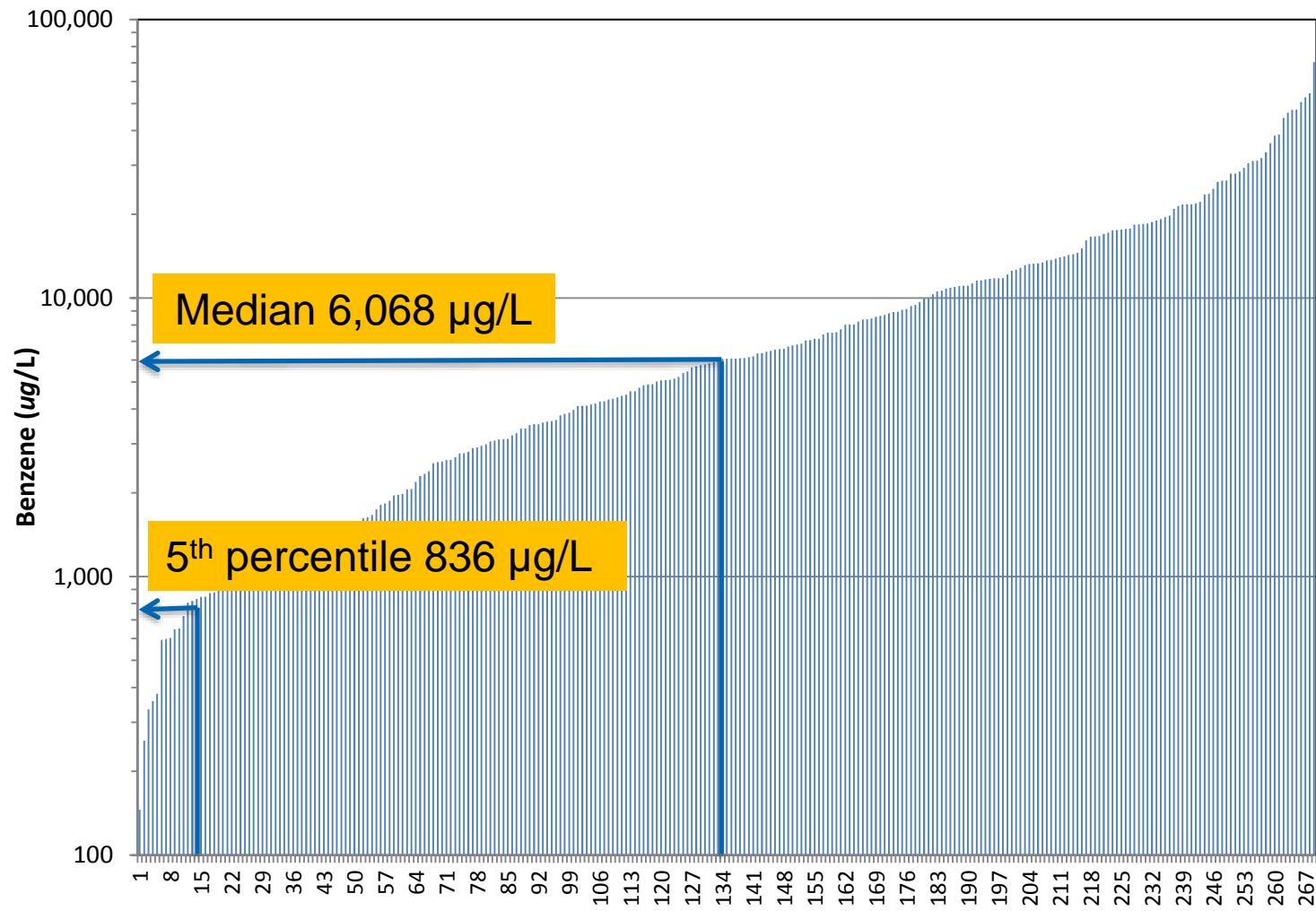
# Three selection criteria for GW and soil vapor data



- Reviewed data from over 140 PVI investigation sites
- Based on these criteria, able to analyze 103 pairs of EDC soil vapor & groundwater concentration data from 26 sites with likely leaded gasoline releases



# 1,000 µg/L benzene in groundwater as a conservative criteria to distinguish LNAPL from dissolved sources



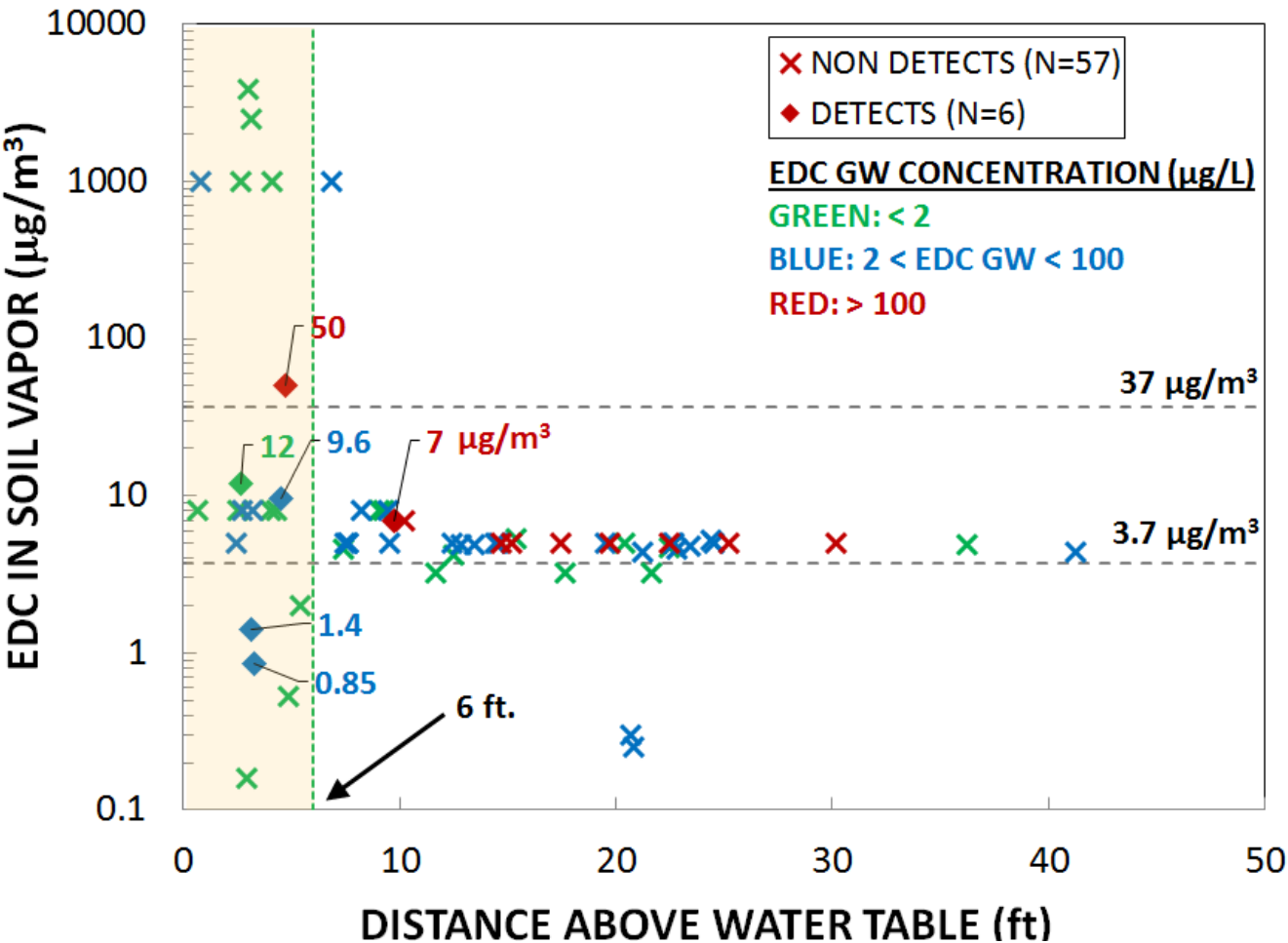
Monitoring Wells



Peargin & Kolhatkar, 2011



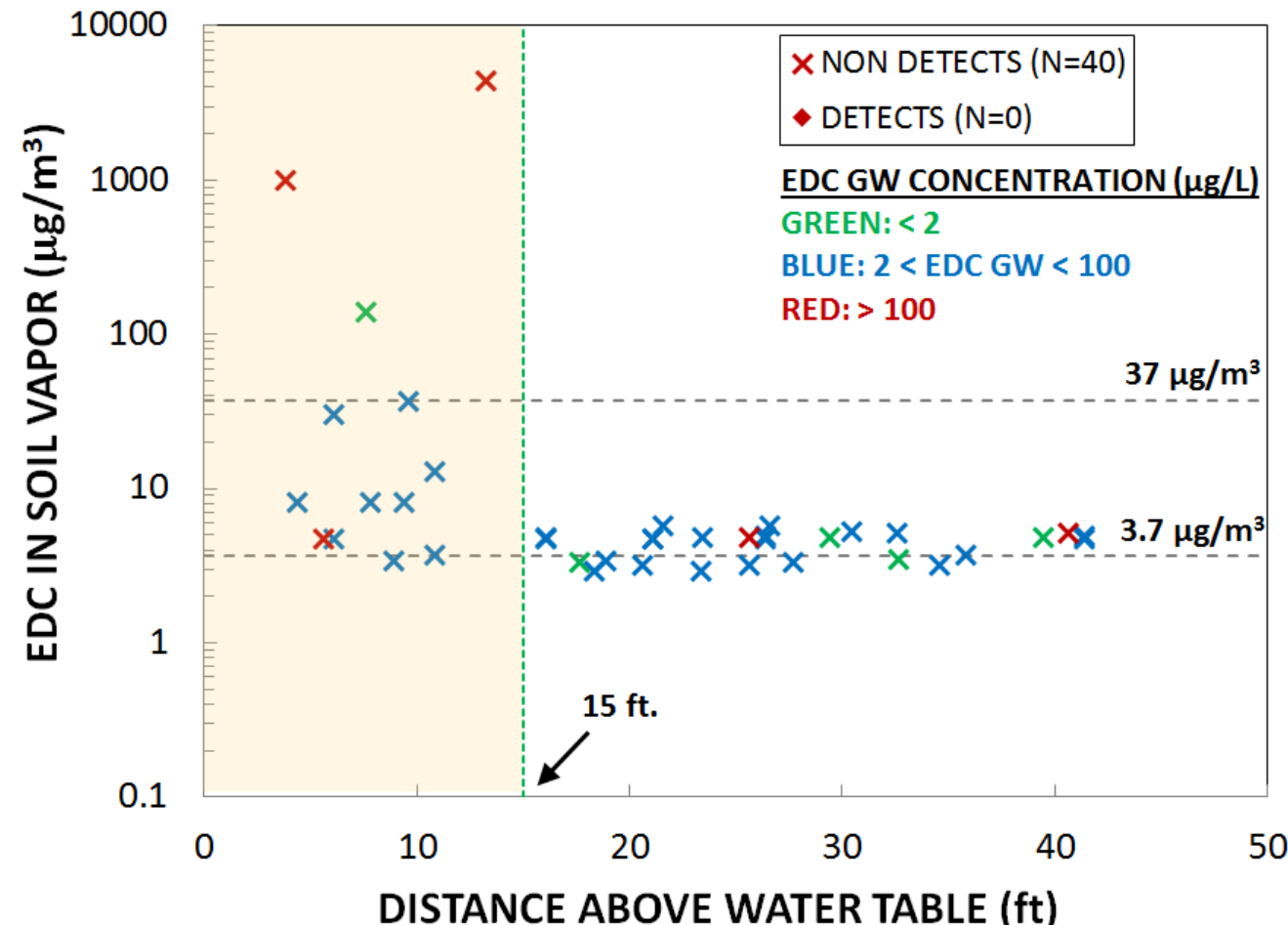
# EDC vapors from dissolved plume (GW benzene < 1000 µg/L)



- Only 6 detections (out of 63 data points) – all within 10 ft. from water table source
- All non detect data at vertical distances > 10 ft. at low (~ 5 µg/m<sup>3</sup>) reporting limits suggesting significant attenuation
- Elevated reporting limits near source (due to interference from other hydrocarbon vapors)



# EDC vapors sourced from LNAPL (defined as GW benzene > 1000 µg/L)



- Very few (40) data points, all ND with low reporting limits (at distances > 15 ft.) suggesting significant attenuation
- Limited data for EDC groundwater concentration > 100 µg/L
- ✓ Vertical screening distance of 15 ft. appears adequate (for GW EDC < 100 µg/L)
- Elevated reporting limits near source (due to interference from other hydrocarbon vapors)



# Conclusions – Empirical Evaluation

- EDC

- For dissolved sources and LNAPL sources with EDC GW < 100 µg/L, vertical screening distance of 15 ft. appears to be adequate
- Current data set is not sufficient to determine criteria for LNAPL sources with EDC GW > 100 µg/L

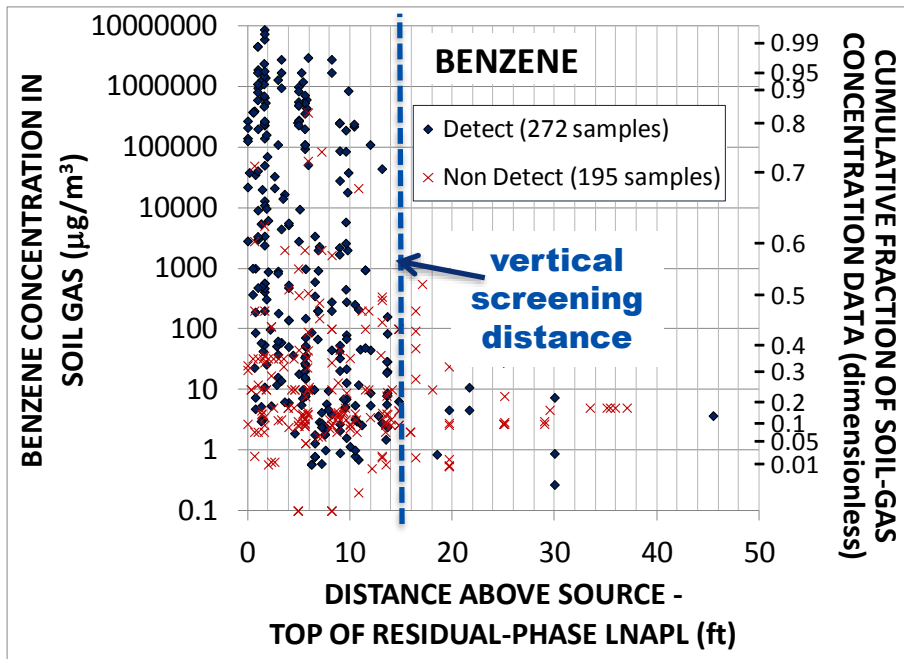
- EDB

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

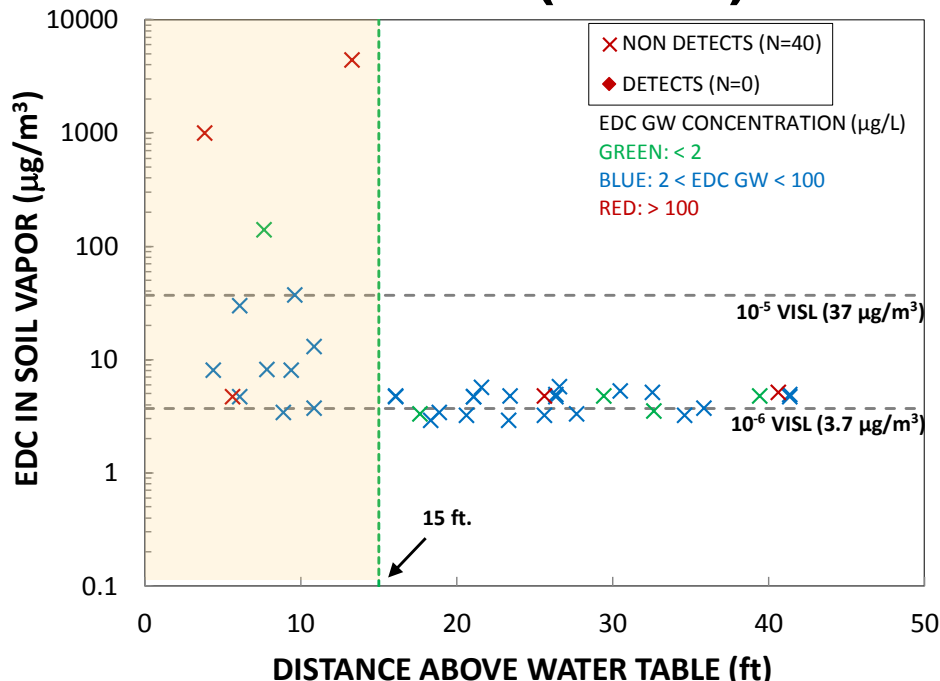


# Modeling: Motivation

## Benzene (NAPL)



## EDC (NAPL)

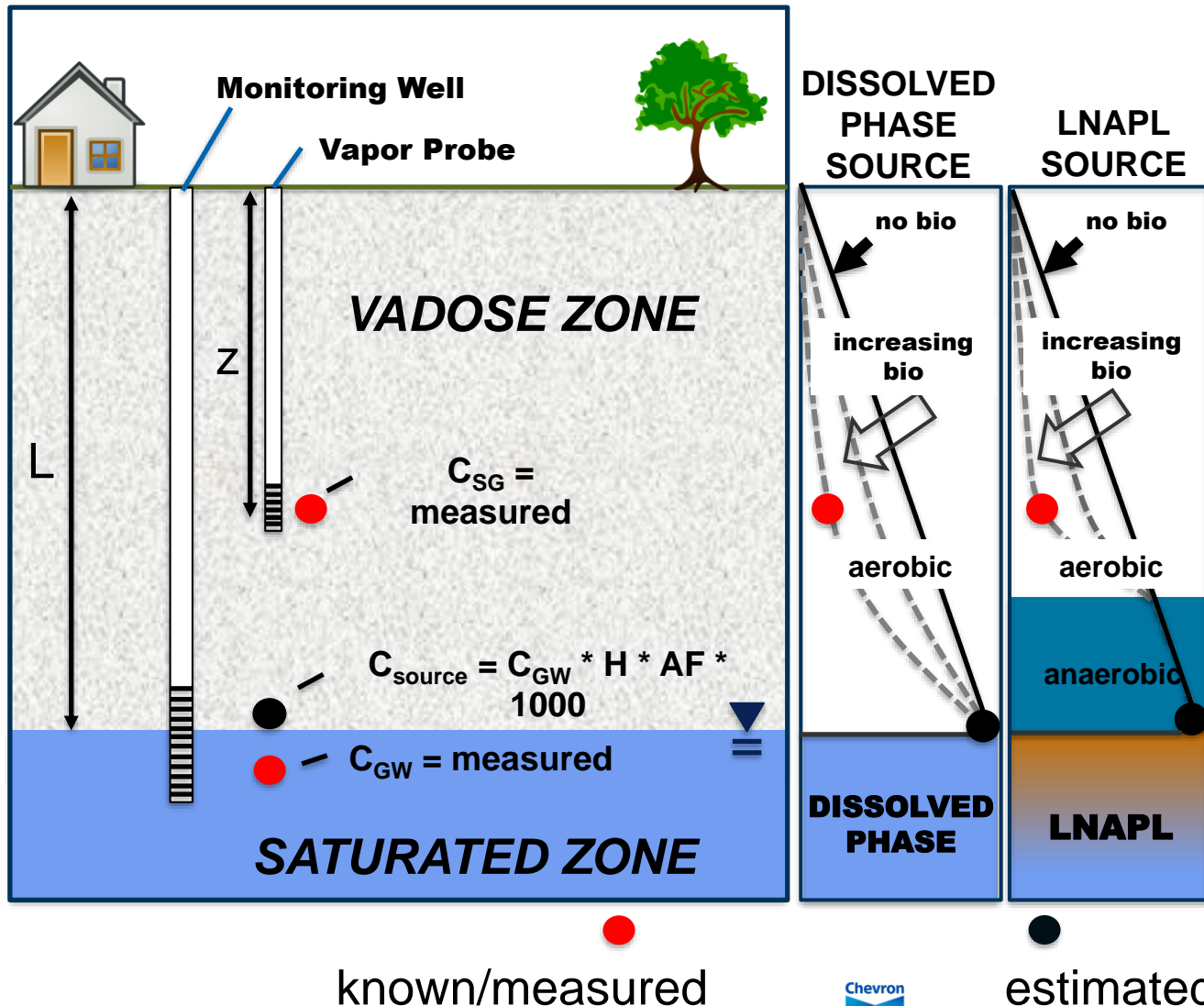


Empirical evaluation of vertical screening distance for EDC is difficult because of large number of non-detects in this dataset



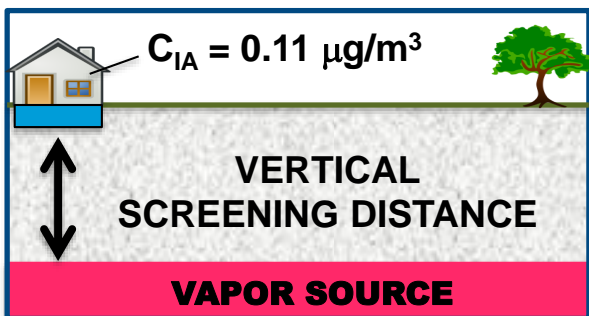
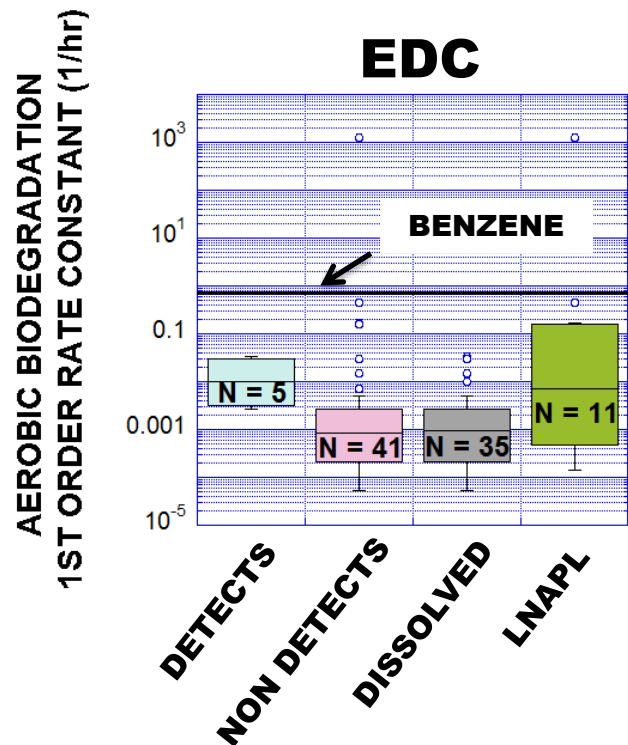
# Modeling (BioVapor\*): EDC

\* <http://www.epa.gov/Environment-Health-and-Safety/Clean-Water/Ground-Water/VaporIntrusion/BioVapor-Form>



- 1<sup>st</sup>-order rate constant (aerobic) calibrated to measured soil-vapor - as defined in ITRC PVI Vapor Intrusion guidance
- $C_{source}$  based on  $AF = 0.1$  (default value in BioVapor)
- no analysis of soil vapor data w/ RLs > Fick's law

# Model estimated vertical screening distance



CONDITION	1 <sup>st</sup> -ORDER AEROBIC DEGRADATION RATE CONSTANT EDC (WATER) (1/hr)	SCREENING DISTANCE EDC in GW (95% concs *) (ft)	SCREENING DISTANCE EDC in GW (max concs **) (ft)
<b>Detects - median (95% CI)</b>	<b>0.010 (0.0022 – 0.043)</b>	<b>6 (3 – 13)</b>	<b>9 (5 – 20)</b>
DeVaul (2015) (95% CI)	0.087 (0.001 – 0.78)	2 (0.7 – 6)	6 (1.1 – 10)
API (2008)	0.0011 - 0.0023	< 13	< 19
LNAPL (median)	> 0.0070	< 8	< 11
Dissolved (median)	> 0.00093	< 19	< 29
Non Detects (median)	> 0.00083	< 20	< 31

\* 95% concentrations of EDC (440 µg/L) and benzene (704 µg/L) in GW

\*\* max concentrations of EDC (1,330 µg/L) and benzene (16,890 µg/L) in GW

- Estimated aerobic biodegradation rate constants are ~ 2 orders of magnitude lower than benzene (consistent with literature)
- **Vertical screening distance for EDC (9 ft.) < for benzene (15 ft.)**



# Conclusions

## Empirical Evaluation

- EDC

- For dissolved sources and LNAPL sources with EDC GW < 100 µg/L, vertical screening distance of 15 ft. appears to be adequate
- Current data set is not sufficient to determine criteria for LNAPL sources with EDC GW > 100 µg/L

- EDB

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

## Modeling

- EDC

- Vertical screening distances derived from modelling of empirical soil vapor/groundwater data for EDC are < 15 ft. (i.e., screening distance of 15 ft. derived for benzene is conservative)



# Next Steps

- Given the large number of non-detects in this limited dataset, additional PVI investigation data are being compiled to broaden the analysis.
- Such empirical analysis is not feasible for EDB due to the limitations of existing soil vapor analytical data (reporting limits > screening level for EDB).
- Sobieski, MN site – Additional soil vapor sampling and analysis for EDB with improved analytical reporting limits (2H 2017).

***Companion talk - “Data Collection and Interpretation to Support Screening Approaches for Vapor Intrusion Risk from Lead Scavengers” by Hers et al. in session E1***





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