

PVI work Group Webinar - July 12, 2011

Progress and Status Report – PVI Database

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U.S. EPA Office of Underground Storage Tanks*





OBJECTIVES AND PURPOSE

- Assemble database of petroleum release sites where pathway has been evaluated via soil gas and groundwater measurements.
- Consolidate & independently check database efforts to date
- Analyze dataset to determine when and under what conditions there is potential for a complete PVI pathway (does not necessarily indicate unacceptable risk)
- Develop data sets that could be used for model comparisons (e.g., BioVapor)
- Develop and support methods and criteria that can be used to exclude (and include) petroleum releases sites from further PVI investigation and concern.



CONTEXT AND PROCESS

- Robin's fall 2010 (updates in 2011) database starting point (great body of work)
- Additional data from ME, MN, IL
- Independent checks conducted – process to ensure completeness and “data of known quality”
- Add data and conduct additional analysis
- Review/add other work (e.g., Chevron database of sites presented at AEHS conference San Diego March 2011, updated Battelle 2011)



ADDED SITE DATA ELEMENTS

- Concentration data
 - BTEX, hexane, heptane, naphthalene concentrations in groundwater & soil vapor (limited number of sites)
 - Aliphatic/Aromatic fractions, MTBE (ME sites only)
 - TPH concentrations in soil
 - Methane concentrations
 - Field headspace PID concentrations
- Analytical methods
 - TPH soil vapor and groundwater (MADEP VPH, APH for ME sites)
 - Fixed gases (field and lab)



ADDED SITE DATA ELEMENTS (cont.)

- City
- Generic soil type (for site), US SCS soil classification, simplified classification (fine, coarse, very coarse)
- Contamination type (gasoline, diesel, BTX)
- Facility type (UST, terminal, refinery, petrochemical)
- Surface cover at soil vapor probe (building, pavement, ground)
- Distance from soil vapor probe to groundwater well
- Building properties: use, foundation type, size
- Flags to link soil vapor probes, wells, and buildings
- For some sites only limited data available or entered



SITES IN CURRENT DATABASE

- Arizona: 1 (in-progress, not yet added to database)
- California: 7
- Maine: 10 (3 in progress)
- Minnesota: 22 (limited data for some sites)
- New Jersey: 3
- Ohio: 4
- South Carolina: 1
- Utah: 4
- Unknown US: 1
- Canada: 2
- Australia: 1



ADDITIONAL SITES

- Maine – groundwater, soil, soil gas, soil data for 13 UST sites
 - Provided by Peter Eremita (ME DEP)
 - Sites in Augusta, Berwick, Gorham, Leeds, Lewiston, Livermore Falls, Milo, North Windham, Portland (2), Saco, Sanford, S. Portland
 - Comprehensive data: O₂, CO₂, CH₄, PID; MADEP VPH and APH
 - DEP's EGAD database provides multiple, consistent formats
 - Great documentation, with maps, aerial photos, boring logs, etc. (over 100 files)
 - Return visits, two SG levels, at several sites
- Minnesota – 22 sites; additional information requested
- Data on possible inclusion sites (e.g., Hartford Illinois (large refinery), Chevron Ohio) not yet obtained



DATA ANALYSIS

- Screening to separate NAPL vs. dissolved sites
- Benzene soil vapor concentration vs. vertical distance above contamination source and conditional probability analysis
- Estimate thickness clean soil for benzene to attenuate below threshold (Robin Davis analysis)
- Oxygen vs. hydrocarbon relationships
- Methane versus vertical distance relationships
- Preliminary analysis aliphatic/aromatic fraction data



SCREENING OVERVIEW

- Hypothesis is behavior is different for LNAPL vs. dissolved phase
- Develop exclusion depth methods for both LNAPL vs. dissolved phase sites (they will likely be different)
- Analyze database to separate dissolved vs. NAPL sites using number of criteria; take into account whether there is NAPL or contamination above water table
- Develop criteria for identifying NAPL vs. dissolved phase sites – this does not necessarily need to be the same as criteria used to screen sites
- Develop inclusion criteria for special cases (just for NAPL sites?)



NAPL vs. DISSOLVED SCREENING INDICATORS - SUMMARY

- Primary
 - Direct indicators of NAPL (sheen, product in well, dye tests, visual evidence)
 - Report or author indicates vapor probe is in contamination or NAPL source zone
 - Inferred from proximity probe to facility (UST nest, dispensers) (within 20 feet)
 - Groundwater concentration indicators
- Secondary
 - Soil concentration indicators
 - Headspace concentrations



NAPL vs. DISSOLVED SCREENING INDICATORS (cont.)

- Groundwater concentration indicators¹
 - Groundwater benzene > 5 mg/L
 - Groundwater TPH > 30 mg/L
- Soil concentration indicators
 - Soil benzene > 10 mg/kg²
 - Soil TPH > 300-500 mg/kg
 - Field headspace vapor concentration > 1,000 ppm
 - In almost all cases, soil concentration indicators didn't affect screening (i.e., there were other factors that indicated NAPL)

1 For limited number of sites (Santa Clara and Jackson's) where there is long dissolved plume (several hundred feet) and where no evidence for LNAPL (and also unlikely for LNAPL body to migrate this far), the above criteria was overridden (i.e., site was designated dissolved)

2. Based on Csat calculation and $foc = 0.006$



BENZENE SOLUBILITY CONSIDERATIONS

- From pure-phase solubility, the calculated benzene concentration for a mole fraction of 0.01 would be 18 mg/L
- But given that mole fraction tends to be less than 0.01, weathering will occur, and non-equilibrium conditions expected, benzene groundwater at many sites with residual NAPL will be closer to 1 mg/L (CAL LUFT manual)

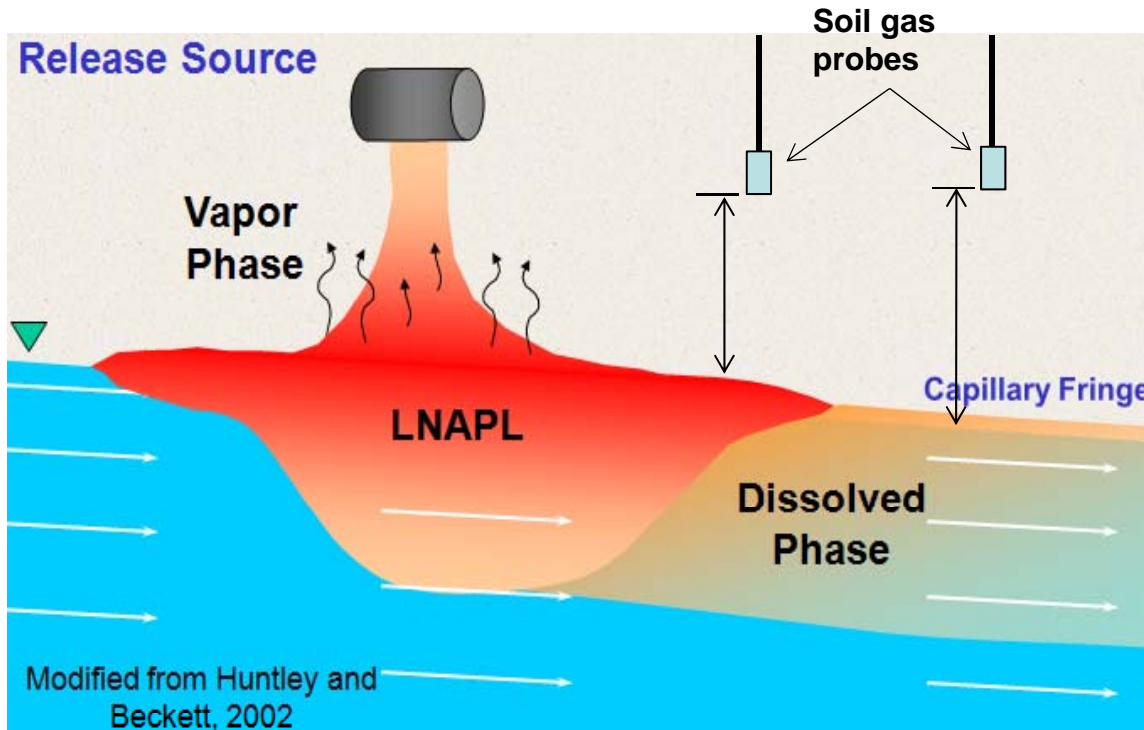


NAPL vs. DISSOLVED SCREENING INDICATORS (cont.)

- Possible Additional Line of Evidence
 - Soil gas composition, i.e., aliphatic vs. aromatic concentrations
 - Dissolved would be expected to have higher aromatic to aliphatic ratio due to faster degradation of aliphatics, consequently the ratio in soil vapor may also be lower.
 - Only limited data available to test this hypothesis (mainly ME sites)
 - May be a future line of evidence



DEPTH TO TOP OF CONTAMINATION



NAPL

- Top of LNAPL smear/soil contamination zone estimated from logs, PID results, historical maximum water table height

DISSOLVED

- Water table measured approximately same time as soil gas



CLEAN SOIL THICKNESS CALCULATION FOR BENZENE ATTENUATION

- For locations where the measured soil gas benzene concentration is less than $< 100 \text{ ug/m}^3$, a clean soil thickness was calculated except when vertical distance between probes is greater than 10 ft. (in sufficient resolution to enable thickness to be calculated)
- Distance to first probe with $C_{\text{vapor}} < 100 \text{ ug/m}^3$ (Method 1)
 - Lower depth = Depth to top of contamination
 - Upper depth = Depth to soil vapor probe with benzene concentration $\leq 100 \text{ ug/m}^3$



CLEAN SOIL THICKNESS CALCULATION FOR BENZENE ATTENUATION

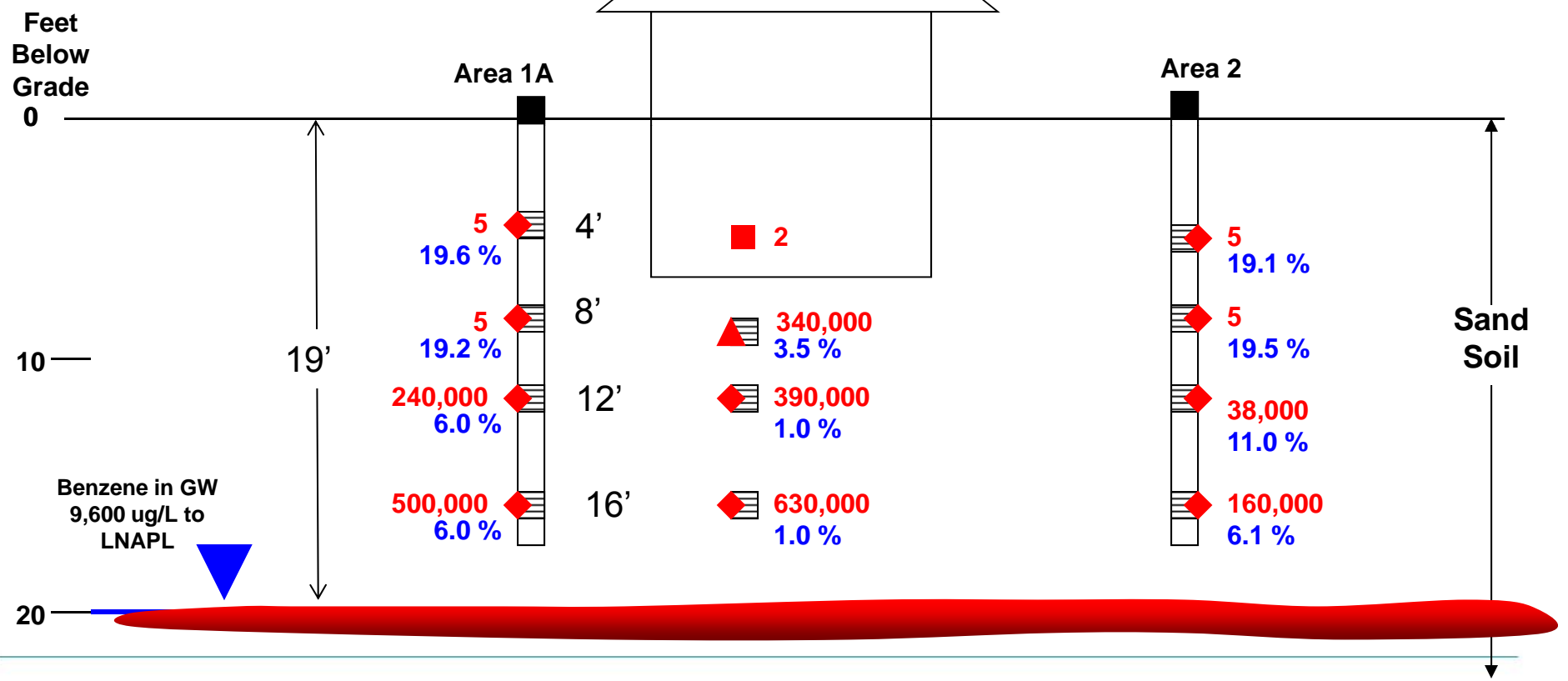
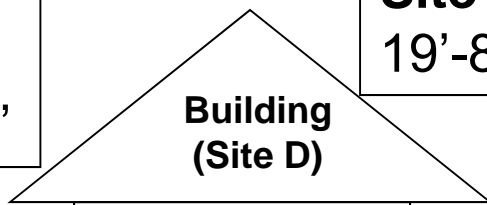
- Interpolated Distance (Method 2)
 - Where benzene attenuates to low concentrations (less than 40 ug/m^3), upper depth is interpolated (half-way) between depths to probes with benzene concentrations $\leq 40 \text{ ug/m}^3$ and $> 100 \text{ ug/m}^3$, subject to minimum thickness of 0.5 ft.
- For locations where the measured soil gas benzene concentration does not attenuate to less than $< 100 \text{ ug/m}^3$, a clean soil thickness can not be calculated, but a minimum thickness (greater than) is calculated equal to distance between shallowest probe and top of contamination



PAULSBORO, NJ (Roggemans, 2002)

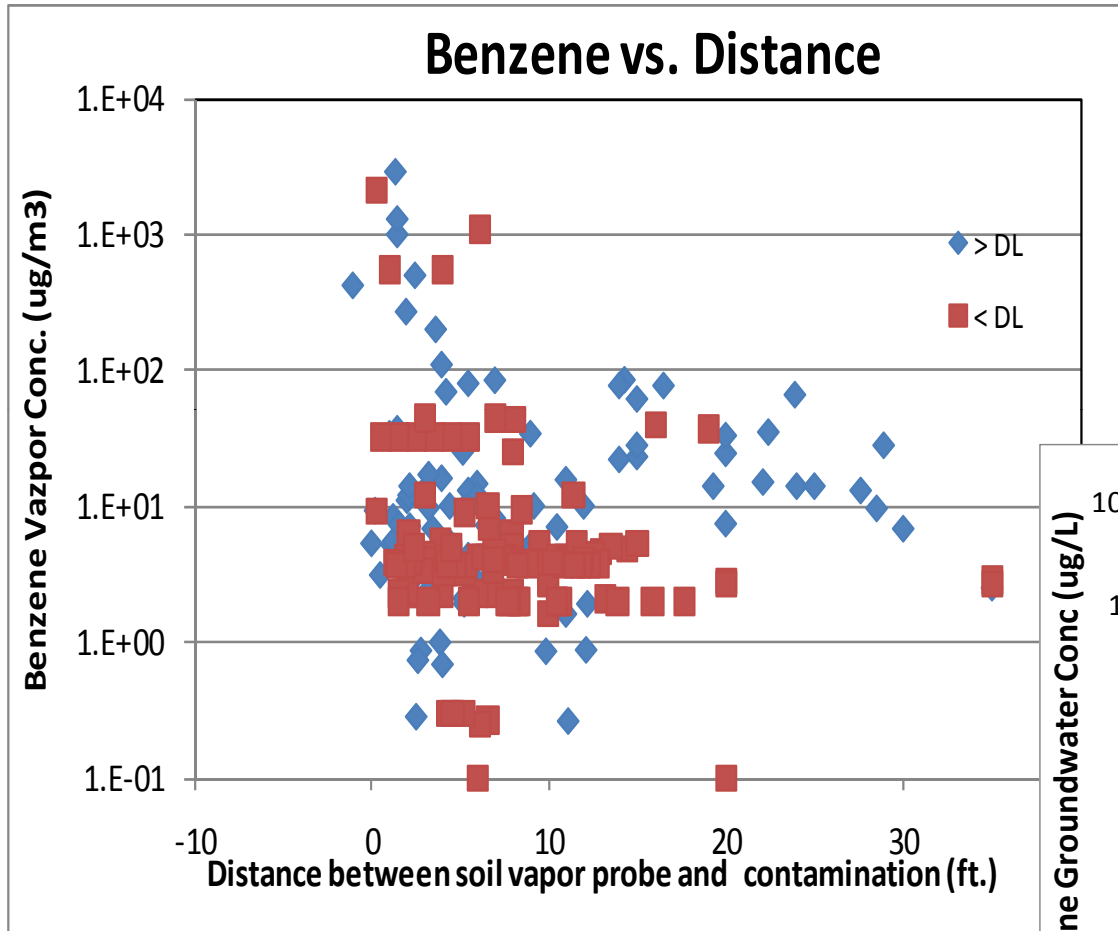
Area 1A
 Method 1: $19' - 8 = 11'$
 Method 2: $19 - (12+8)/2 = 9'$

Site D
 $19' - 8 = >11'$

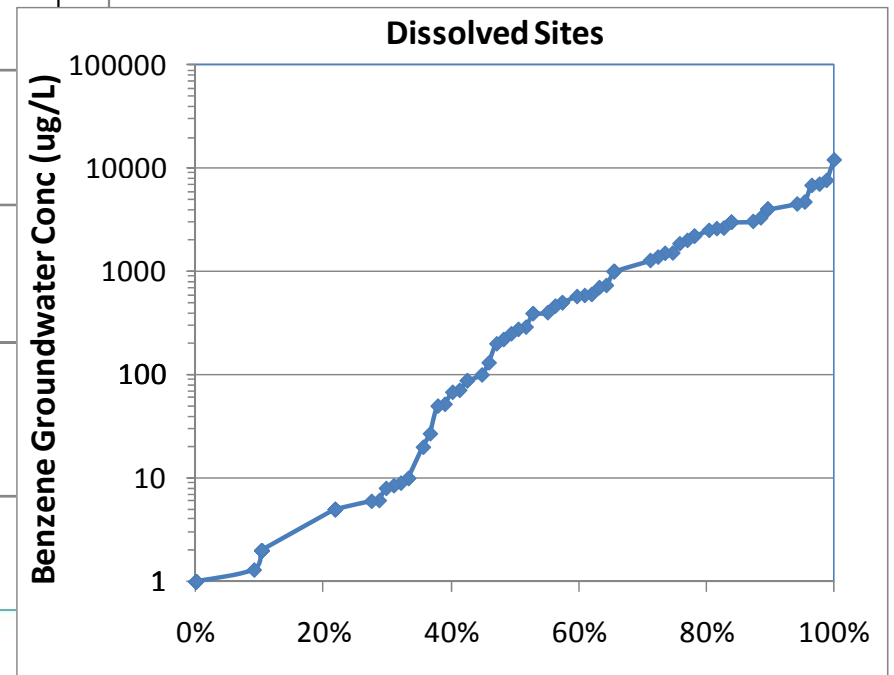




BENZENE – DISSOLVED SITES



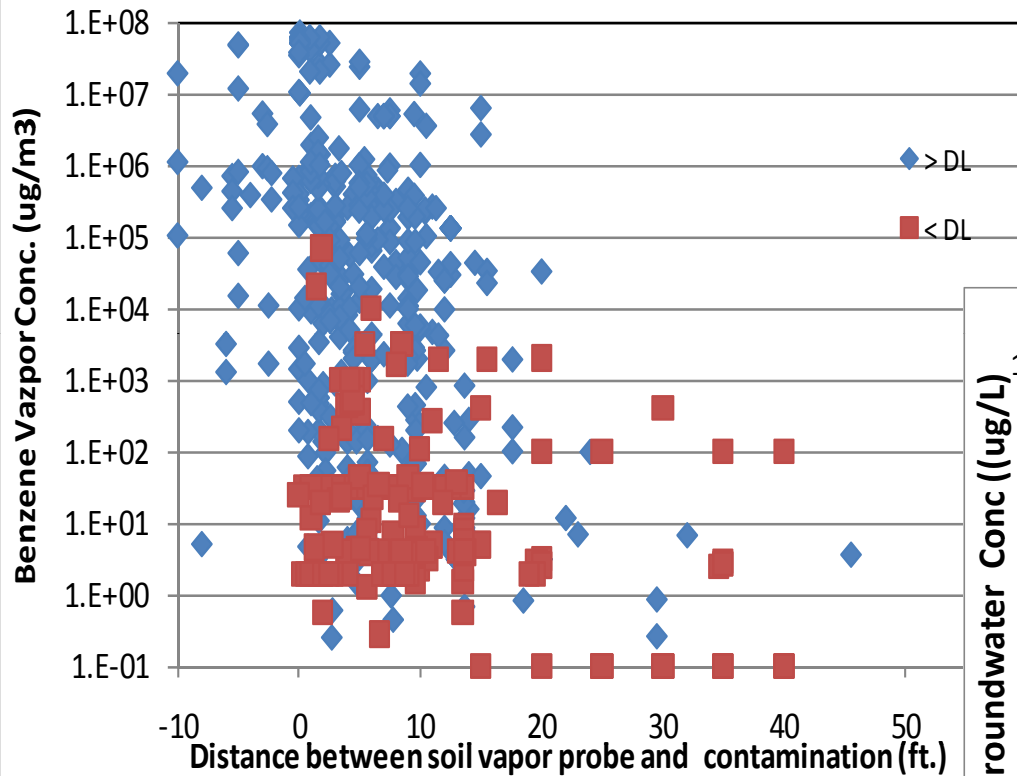
- 32 sites
- 223 data points
- < DL replaced with DL
- 95th percentile = 85 ug/m³





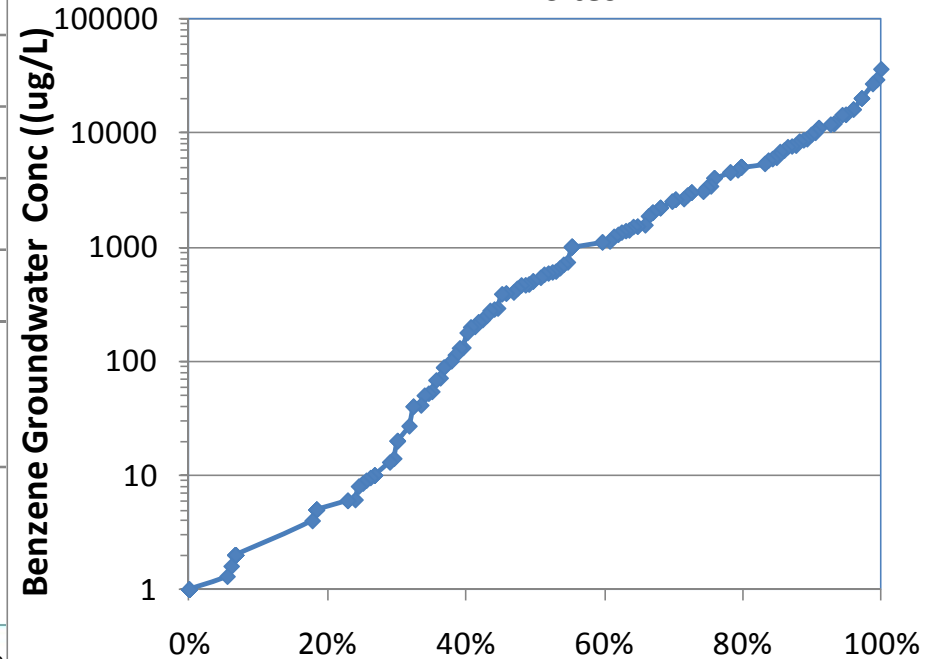
BENZENE – NAPL SITES - ALL

Benzene vs. Distance



- 44 sites
- 545 data points
- < DL replaced with DL

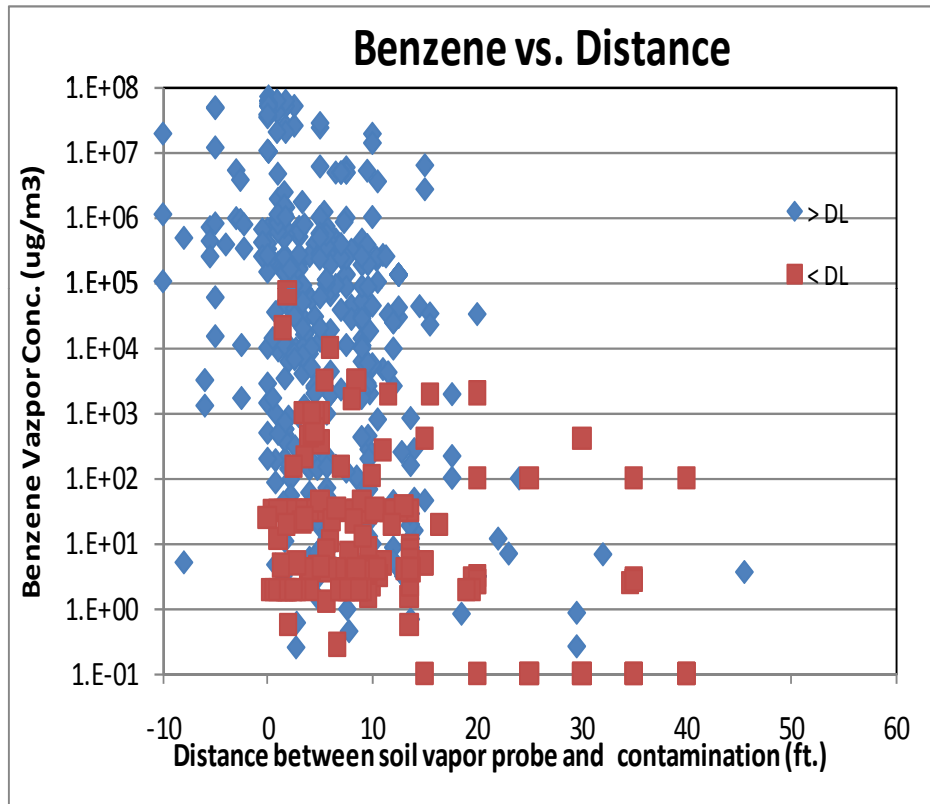
NAPL Sites



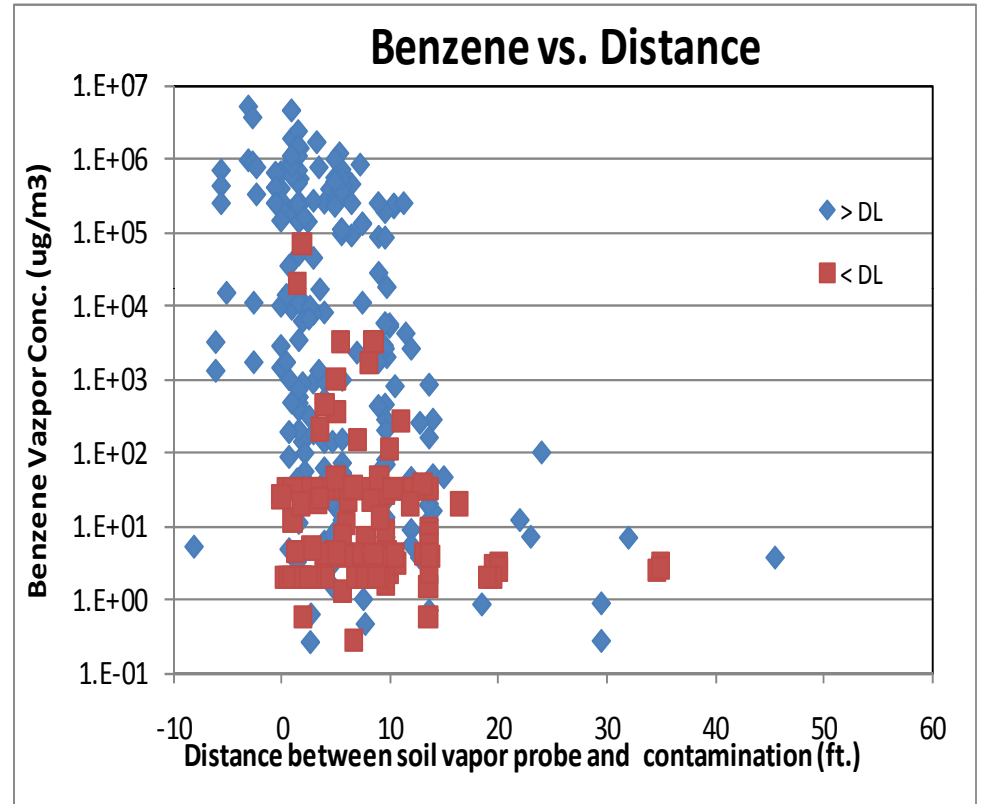


BENZENE – NAPL SITES

UST, Refinery, Terminal



UST Only





CONDITIONAL PROBABILITIES

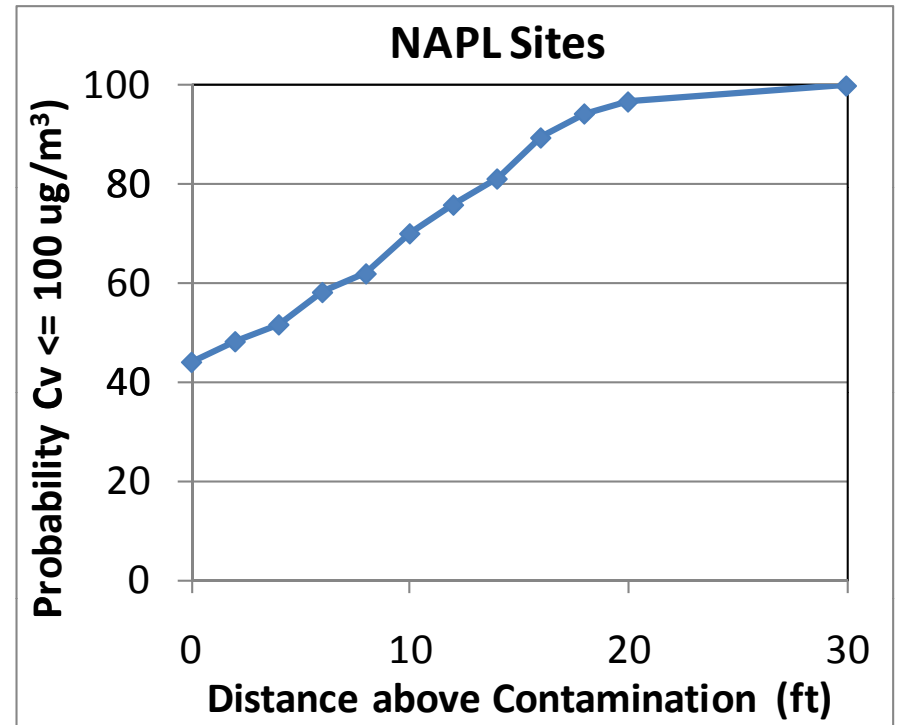
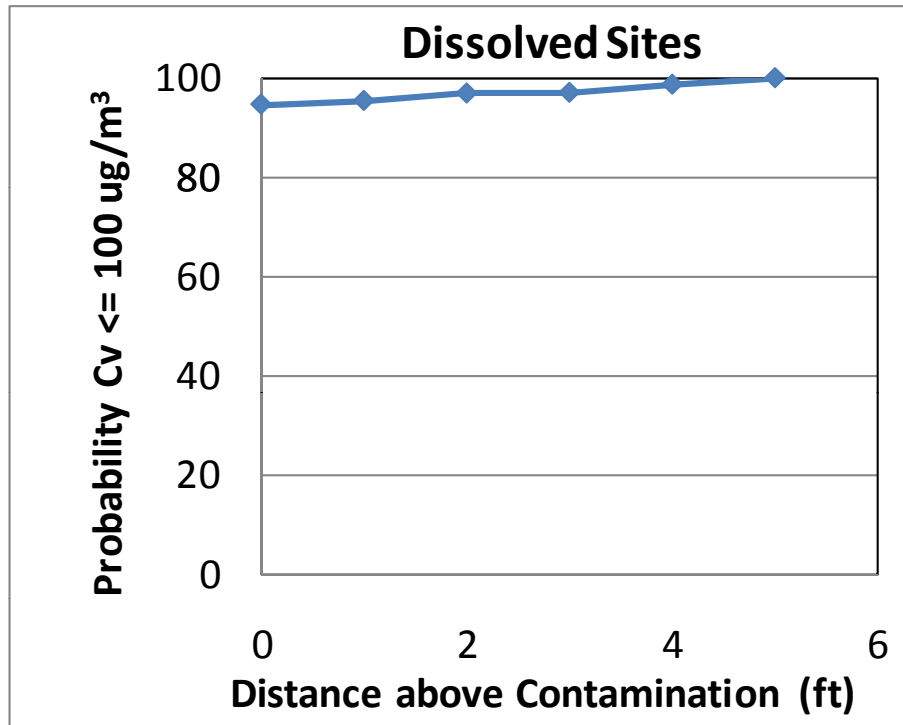
- Evaluate probability for benzene vapor concentration to exceed threshold for varying distances above contamination
- Add additional constraint related to source contamination or groundwater concentrations (simplest dissolved vs. NAPL)

$$P(C_v \leq 100 \text{ ug/m}^3 / z > d, C_g (z=0) < C_{\text{criteria}})$$

- Where z = distance to soil gas probe, d = separation distance, in this case C_{criteria} is NAPL vs. dissolved



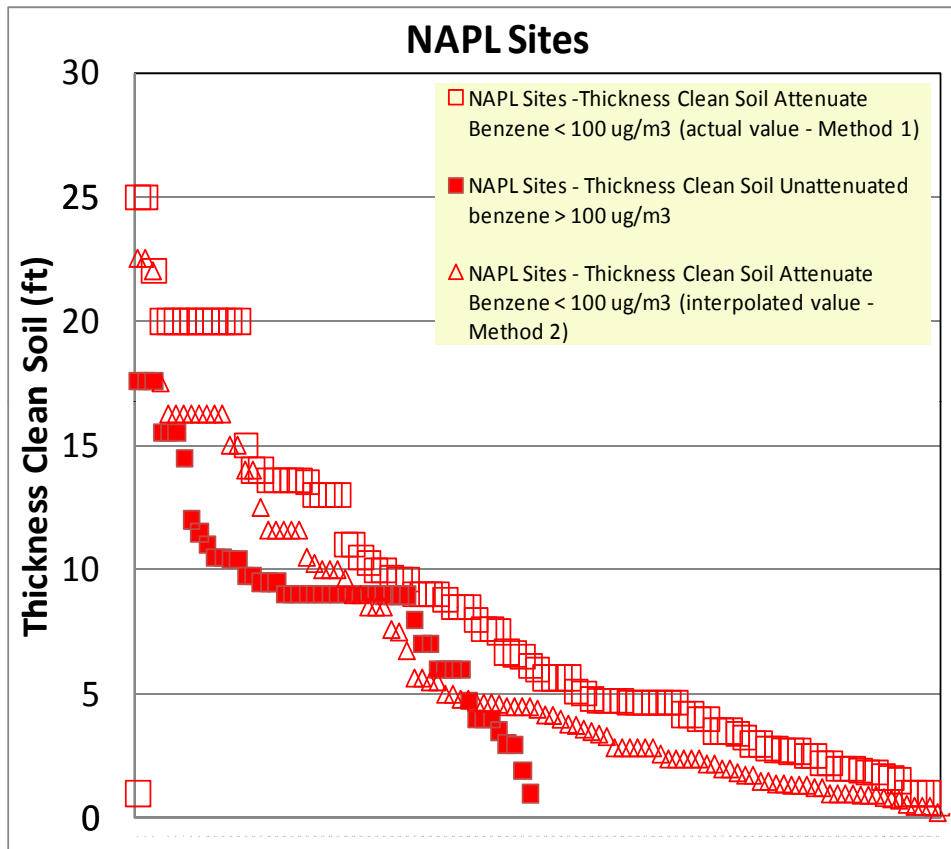
BENZENE - CONDITIONAL PROBABILITIES



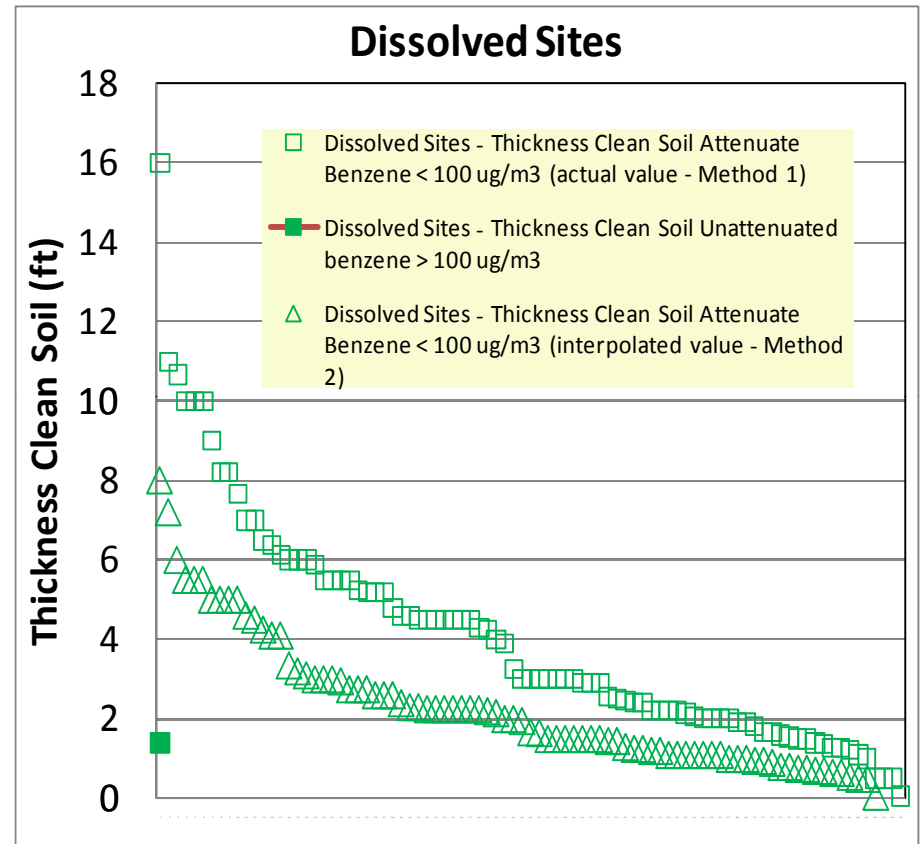
- Possible benzene exclusion distances
 - Dissolved sites ~ 5 ft.
 - NAPL sites ~ 15-20 ft. (consistent with analysis by Matt Lahvis, Shell, Tom Peargin, Chevron)



THICKNESS CLEAN SOIL BENZENE ATTENUATION < 100 ug/m3 (all data)



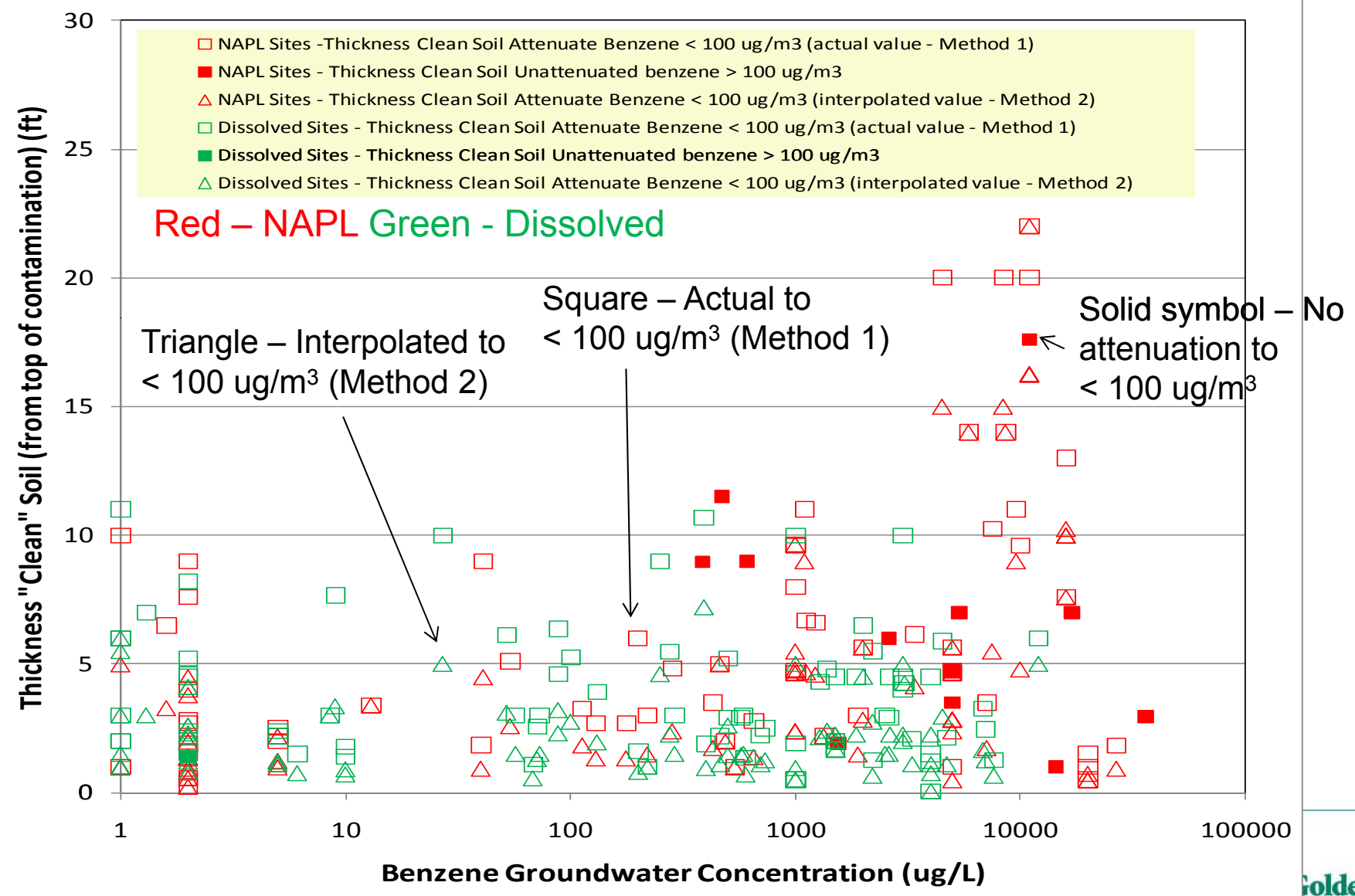
95th percentile Method 1 = 20 ft.



**95th percentile Method 1 = 10 ft.,
Method 2 = 5.5 ft.**



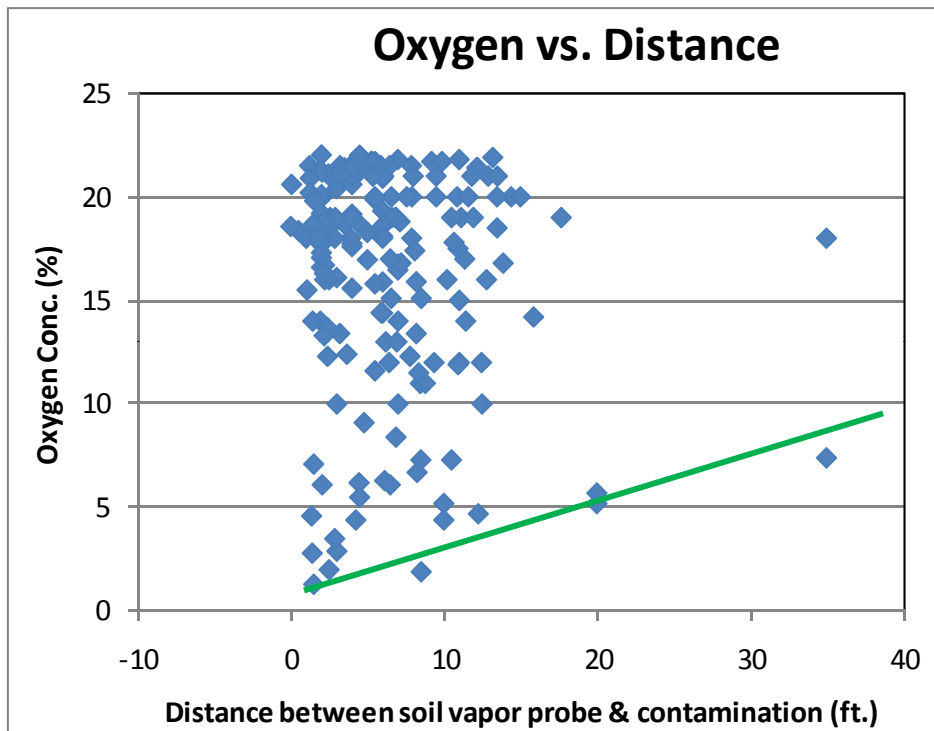
THICKNESS CLEAN SOIL BENZENE ATTENUATION < 100 ug/m³



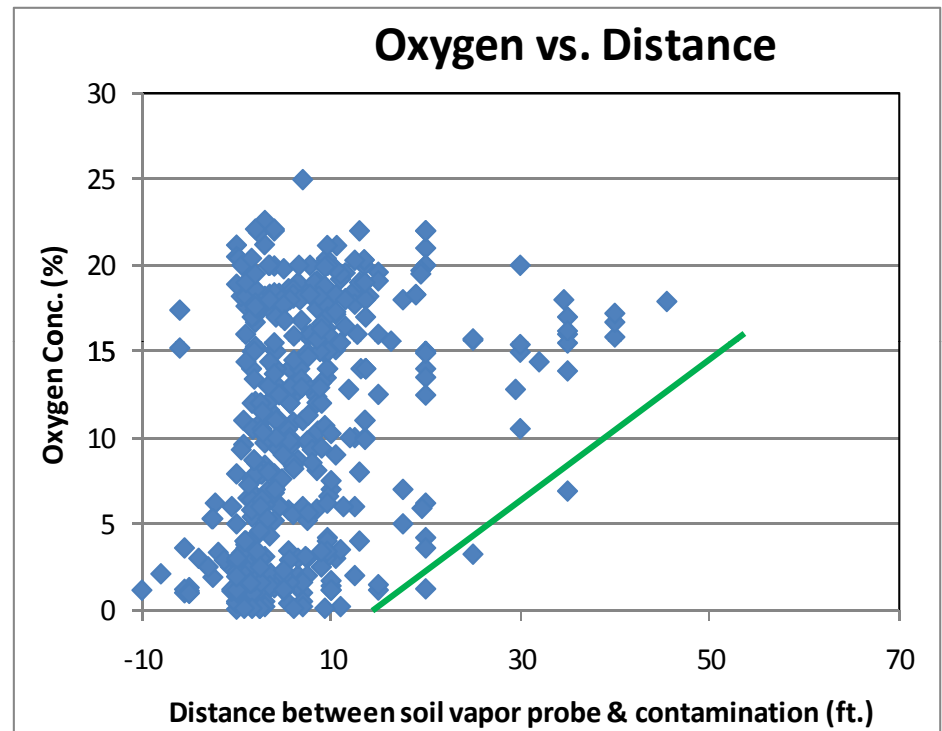


OXYGEN

Dissolved Sites



NAPL Sites

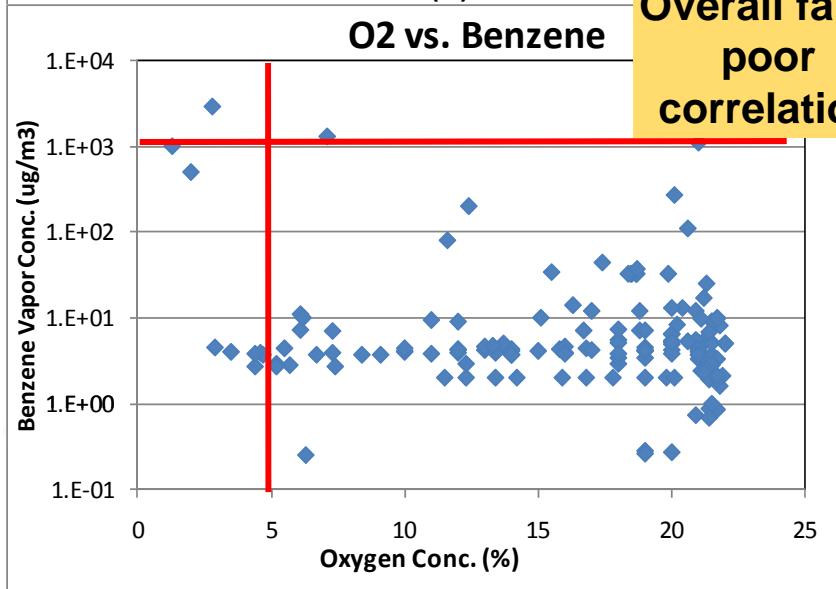
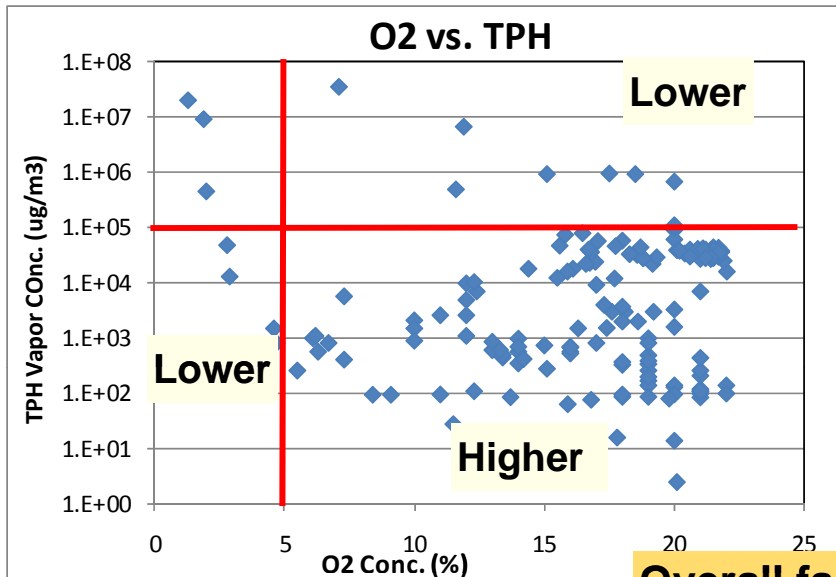


- O₂ trends follow expected behavior for dissolved & NAPL sites
- Dissolved sites: O₂ > 1 % and typically > 5%
- NAPL sites: O₂ depleted until distance > 11 ft.



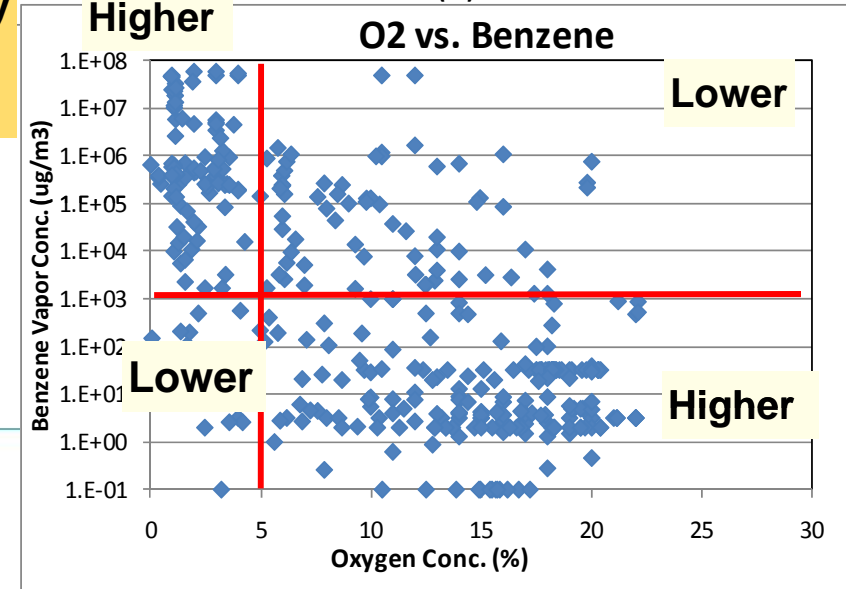
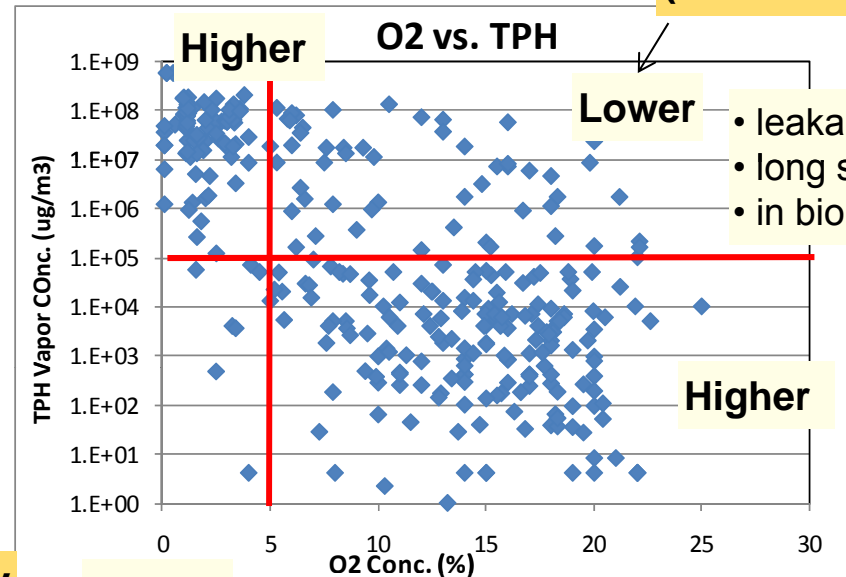
OXYGEN

Dissolved Sites



NAPL Sites

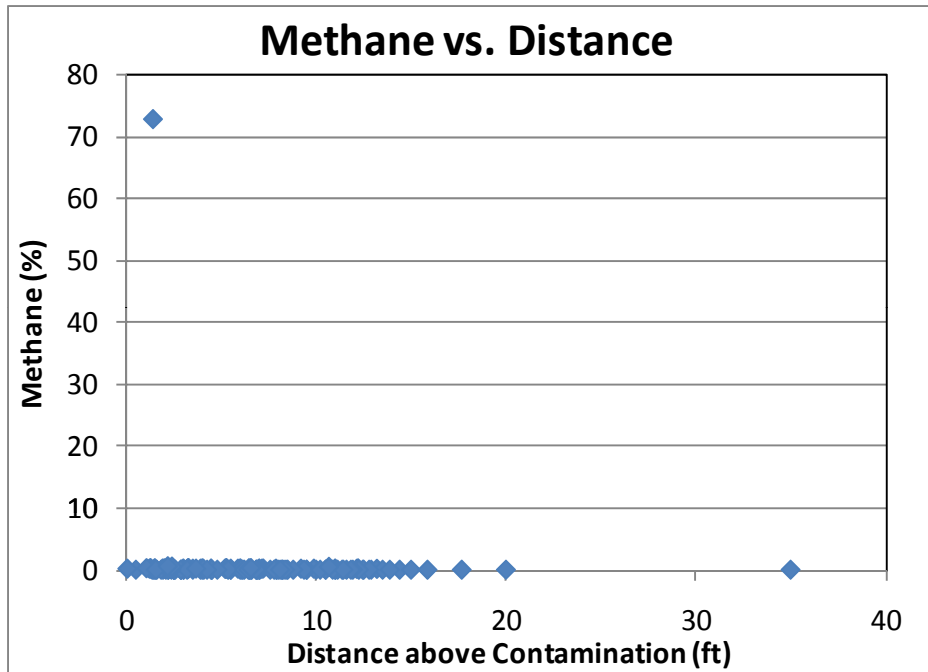
Density (Probability)



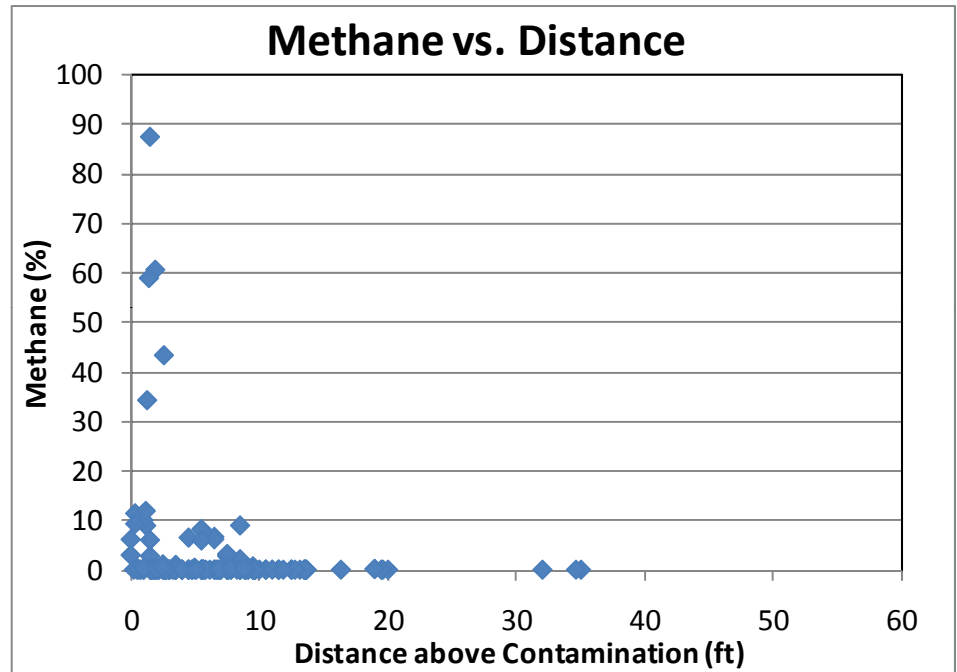


METHANE

Dissolved Sites



NAPL Sites

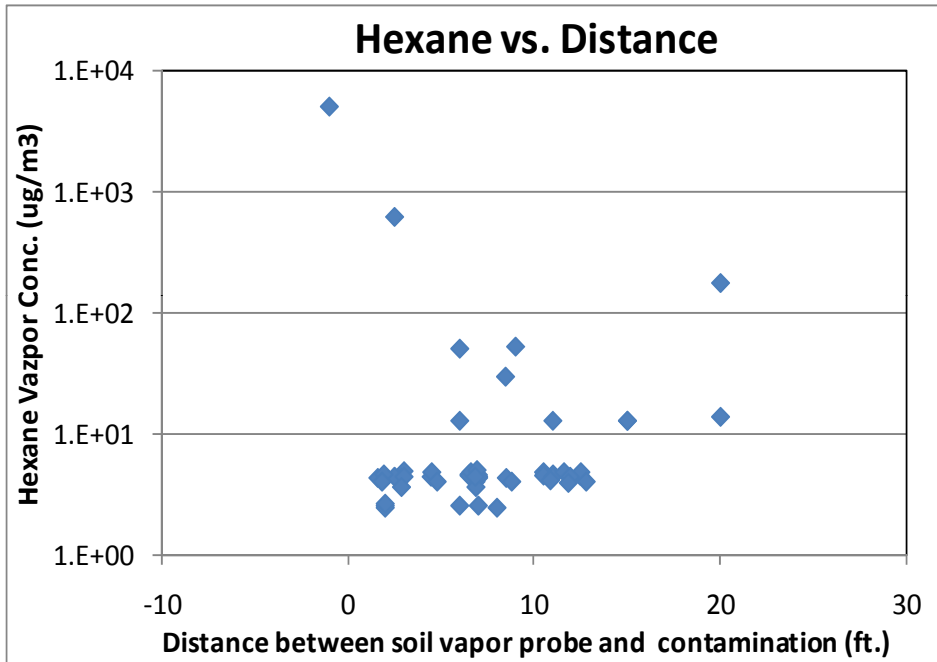


- CH₄ trends follow expected behavior for dissolved & NAPL sites
- CH₄ > 5%: Alameda, Huntingdon, Cumberland Portland ME 1939
- CH₄ = 1 to 5%: Coachella

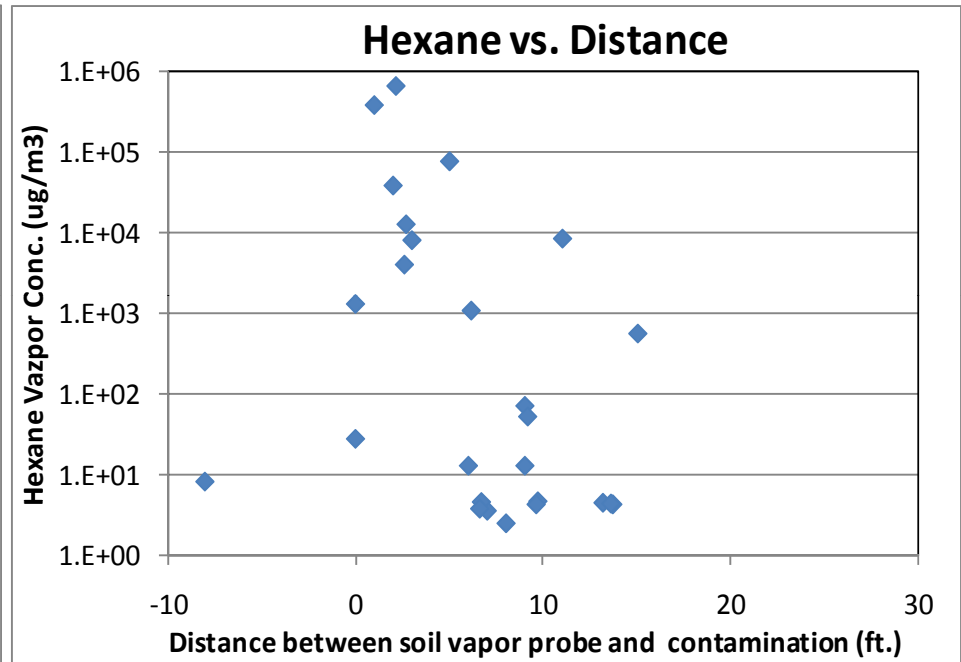


HEXANE

Dissolved Sites



NAPL Sites



- Initial analysis suggests approximately similar trends to benzene
- Appears hexane would likely not be a risk driver, assuming hexane RfC of 200 ug/m3 and approximately 100-fold dilution



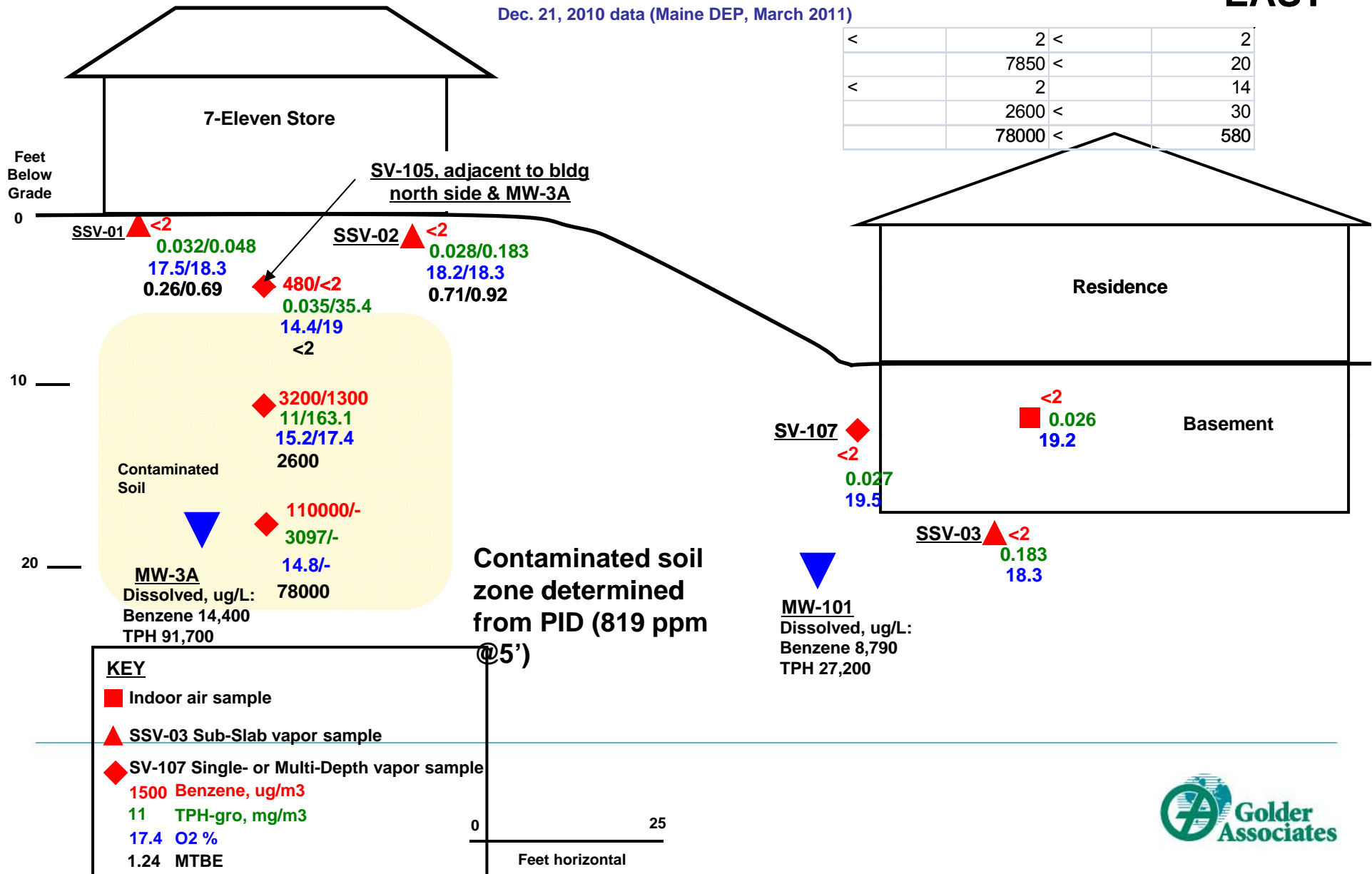
Lewiston, Maine

7-Eleven, 345 Main Street

Dec. 21, 2010 data (Maine DEP, March 2011)

WEST

EAST





DISCUSSION

- Developing exclusion and inclusion criteria – what is needed to develop and technically defend? Initial criteria:
 - Minimum X ft. clean soil between lowest part of building and shallowest impacted site
 - Dissolved contamination, as evidenced by:
 - No LNAPL in wells
 - GW benzene < X mg/L, GW TPH < Y mg/L
 - Continuous soil cores over interval of interest indicating:
 - Absence of NAPL (sheens, staining, strong odours)
 - Testing at 6 inch intervals; Headspace PID < X ppm, TPH soil < Y ppm (no rapid change in PID concentrations), or
 - Oxygen < X %



DISCUSSION

- Implementation – How will exclusion criteria be adopted and implemented by states in the field? What measurements will be needed? What are next steps at “included” sites?
- ‘Closing’ current effort and maintaining database into the future.
- Possible data gaps and additional analysis
 - Aliphatic and aromatic fractions (ME data)
 - Ethanol sites and methane
 - Comparisons to model predictions
 - Inclusion sites



AK GUIDANCE

- Sheens (*NAPL should be expected to be present as residual phase at any locations with historic NAPL occurrence); headspace vapors (PID head space readings of thousands of parts per million (ppm) at recent gasoline spill sites, hundreds of ppm at recent diesel spill sites and old gasoline spill sites, and tens of ppm at old diesel spill sites are likely to indicate the presence of NAPL according to: <http://www.dec.state.ak.us/spar/csp/guidance/hrc/HR C%20User%20Manual.pdf>)?



CA GUIDANCE

LUFT site is assumed to present no unacceptable risk from vapor intrusion if the following site conditions are met:

- 1) *For soil sources and low-strength groundwater sources: 5 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.*
- 2) *For high-strength groundwater sources: 10 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.*
- 3) *For measurable free product on the water table: 30 feet or more of clean soil between the bottom of the building and the water table.*



CA GUIDANCE (cont.)

- A “low-strength groundwater source” is defined as *dissolved-phase benzene groundwater concentrations < 1,000 µg/L & dissolved phase TPH concentrations < 10,000 µg/L*. A “high-strength groundwater source” is defined as dissolved benzene concentrations >1,000 µg/L & *dissolved-phase TPH concentrations > 10,000 µg/L*.
- In the unsaturated zone, clean soil is defined as TPH concentrations < 100 mg/kg PID readings < 10 ppm, or O₂ >4%.



NJDEP Vapor Intrusion Guidance

- 30-foot distance criterion (both horizontal and vertical), for petroleum related ground water contamination based, in part, on 2004 PA VIG; 100-feet for petroleum LNAPL.
- Allows assessment of biodegradation for petroleum hydrocarbons based on subsurface O_2 and depth to ground water.
- Soil gas sampling (e.g., vertical profiling of volatiles, O_2 and CO_2) “usually more relevant” than ground water sampling for evaluating VI when GWSL are exceeded.
- Use of additional 10x ground water to indoor air AF for PHCs assumes a minimum of 4% oxygen exists in the soil
- Recommends collection of sub-slab soil gas samples in lieu of indoor air samples for PHCs.