



VI Issues: Lessons Learned— Including Methane



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VI Issues Encountered, con' t.



- Consultant Issues:

- Using RBSLs for soil gas for sub-slab or vice-versa.
- Using screening levels as clean-up criteria
- Using non-cancer screening levels for carcinogens
- Using wrong exposure times
- Proposing indoor air sampling before evaluating if the VI pathway is complete
- Incorrect construction of soil gas sampling points



- Unit Confusion:

- Assuming ug/L equivalent to ppbv
- Assuming ug/m³ equivalent to ppbv
- Not knowing how to go from ug/m³ to ug/L



“Top Ten” List of VI Issues Encountered

- Reviewer/Agency Issues:

- Requiring soil gas data be acquired even though soil and groundwater is clean enough to screen out site
- Requiring all soil gas samples to be collected in Summa canisters and analyzed by TO-15 when TO-14, 8260 or 8021 ok.
- Using guidance for petroleum hydrocarbon issue that was written for chlorinated hydrocarbons.
- Setting inconsistent clean up levels
- Not permitting SVE systems to be shut off prior to collecting soil gas samples
- Requiring deep soil gas samples



G.T. Ririe, 2013

VI Issues Encountered, con' t.



- Work Plan Issues:

- Work plans submitted for VI work not needed
- Too many samples recommended for
- Not specifying collection of samples in upper part of vadose zone (e.g., 5' bgs) to demonstrate bioattenuation
- Analyzing compounds that were never used at the site.
- Not analyzing for fixed air gases
- Not using correct analytical method to achieve needed detection limits



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VI Issues Encountered, con' t.

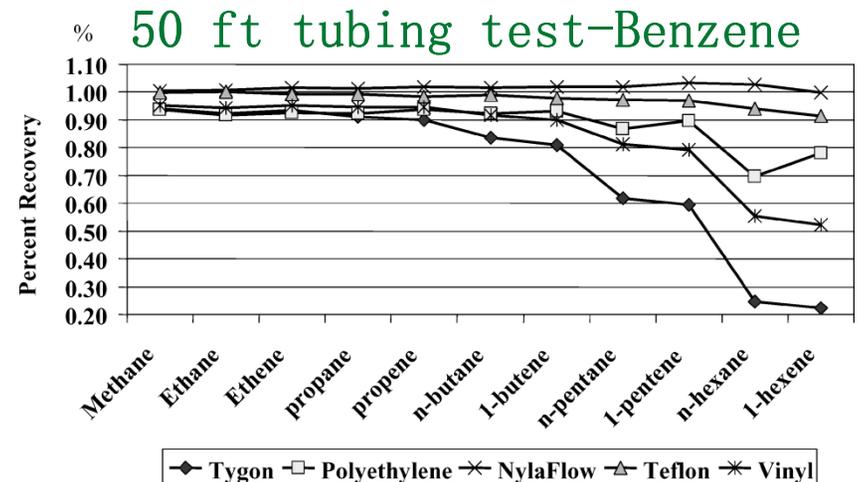


• Soil Gas Probe Installation Issues:

- Using wrong tubing type
- Pinching off tubes incorrect completion
- Not collecting an equipment blank
- Type of tubing used

• Consultant Field Sampling Issues:

- Not opening Summa canisters or Tedlar bags
- No experience with swagelok connectors
- Applying too much liquid tracer
- Returning Summa canisters with 0 pressure
- Lack of attention to chain of custody details
- Bore hole clearance: hand auger/airknife



VI Issues Encountered, con' t.



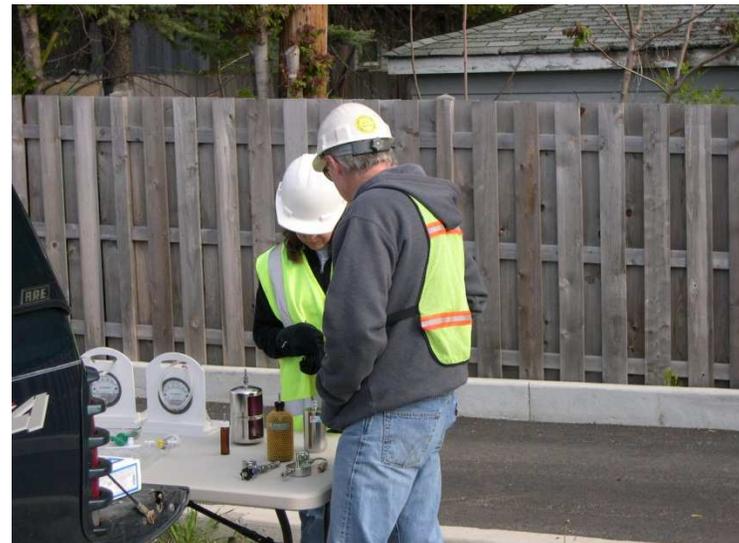
- Probe installation: ground disturbance issues mean no direct push methods can be used
- Avoid air knife
- Sampling open bore holes
- Emergency Response



VI Issues Encountered, con' t.



- Smaller samples are better; including Summa canisters
- Flow rate can easily be monitored using hand held syringe
- Tedlar bags have maximum holding time of about 3 days for benzene and 2 days for TEX



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Methane: Potential Safety Hazard



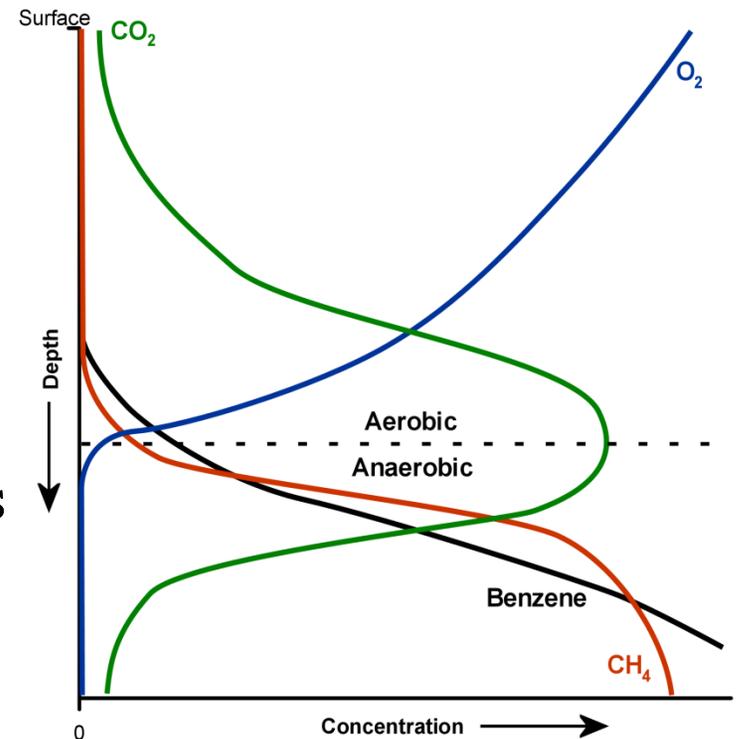
- Colorless-odorless gas: CH₄
- Ubiquitous
- Value in Air: 1.8 ppmv
- Lower Explosive Limit: 50,000 ppmv
- Upper Explosive Limit: 150,000 ppmv
- Main component of natural gas
- Most abundant organic compound on Earth
- Methanogenesis: $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
- Fermentation: Biogas from biodegradable organic matter:
Landfills
- Global Warming: Current Biology publication suggests flatulence from dinosaurs may have warmed the Earth!



Methane: Site Data Required to Assess Hazard and Determine if Action is Needed



- Source concentration
- Volume
- Pressure
- Transport/Preferential Pathways
- Dilution
- Bio-attenuation



The presence of methane in soil gas does not mean there is a hazard

Modified from J. Sepich, 2012

G.T. Ririe, 2013

What Homeowners and Companies Do NOT Want



Soil Gas Sampling Results



Site 1

Sample depth	Methane (ppmv)
1. Subslab 0.5 ft	12
2. Subslab 3 ft	8,300
3. Outside 1ft	1,700
4. Outside 3ft	180,000

Site 2

Sample depth	Methane (ppmv)
1. Subslab 0.5 ft	<10
2. Subslab 3 ft	11,000
3. Outside 1ft	45
4. Outside 5ft	120,000

Isotech Gas Data: High CH₄ Sample

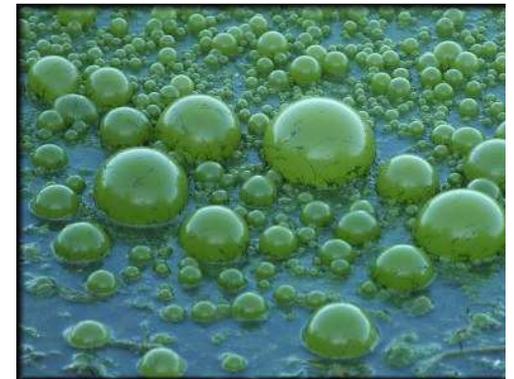


- O₂ = 2.54%
- CO₂ = 35.19%
- N₂ = 38.9%
- C1 = 22.9%
- C2 through C6+ = 0%
- Delta ¹³C1 = -57.18 per mil
- Delta DC1 = -328.4 per mil
- ¹⁴C pMC = 109%

Sources of Methane in the Subsurface



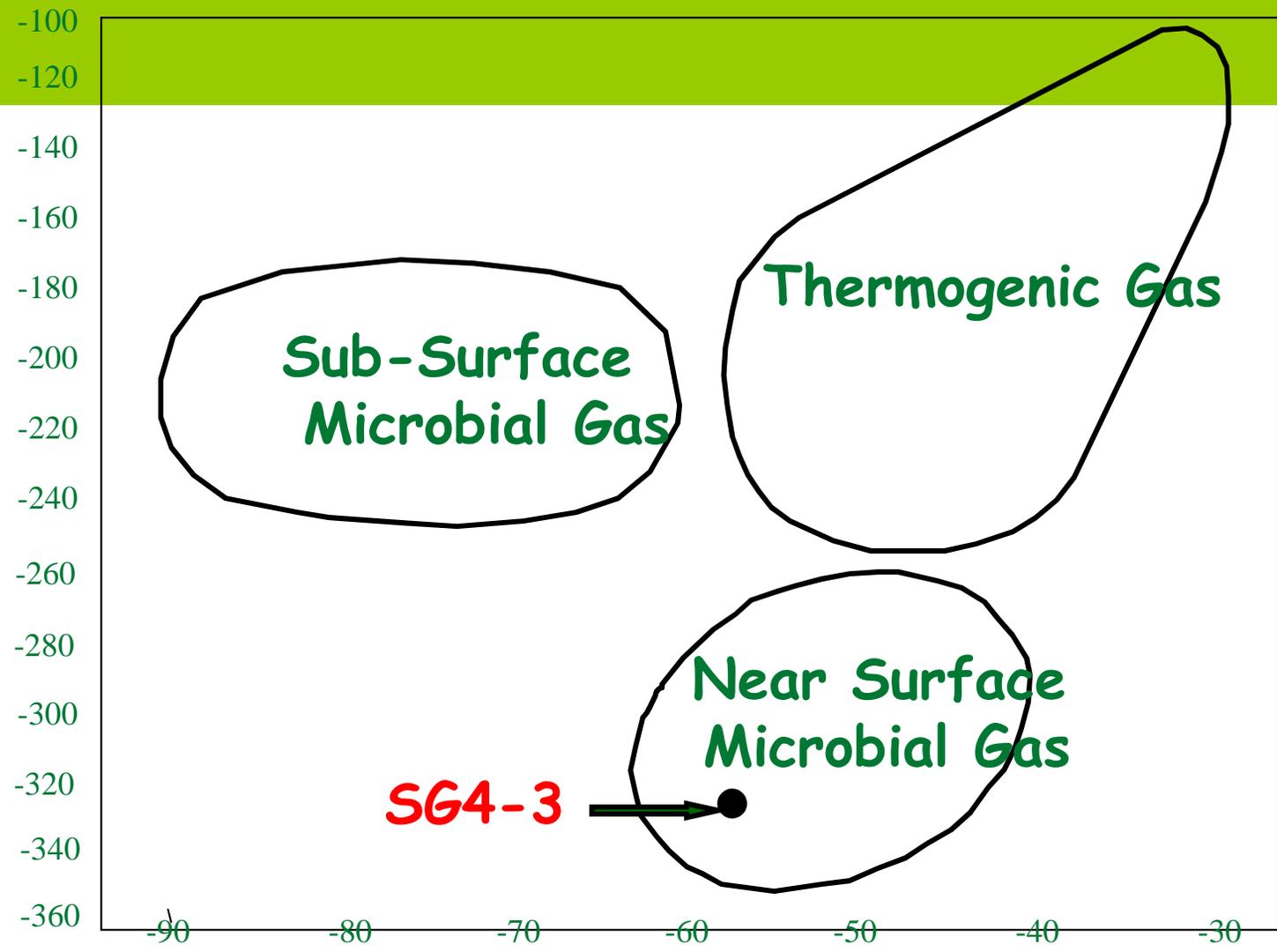
- Methane from biodegradation of petroleum is characterized by:
 - Lack of significant concentrations of ethane and propane
 - CO₂ / methane ratios between 0.3 and 0.6
 - Relationship between carbon isotope ratio of CO₂ & methane concentration
 - C¹⁴ age > 50,000 years old
- ‘Swamp’ gas of poorly identified source can also be distinguished by C-14 age
- Thermogenic methane can be distinguished by molecular composition
 - Geologic considerations and stable isotope ratios may be needed



Modified from R. E. Sweeney, 2011 G. I. Ririe, 2013



Delta D CH₄ per mil



Delta ¹³C CH₄ per mil
Sources of gases as defined in Coleman (1994)

PVI Case Studies



Case Study: How NOT to Do a PVI Investigation!

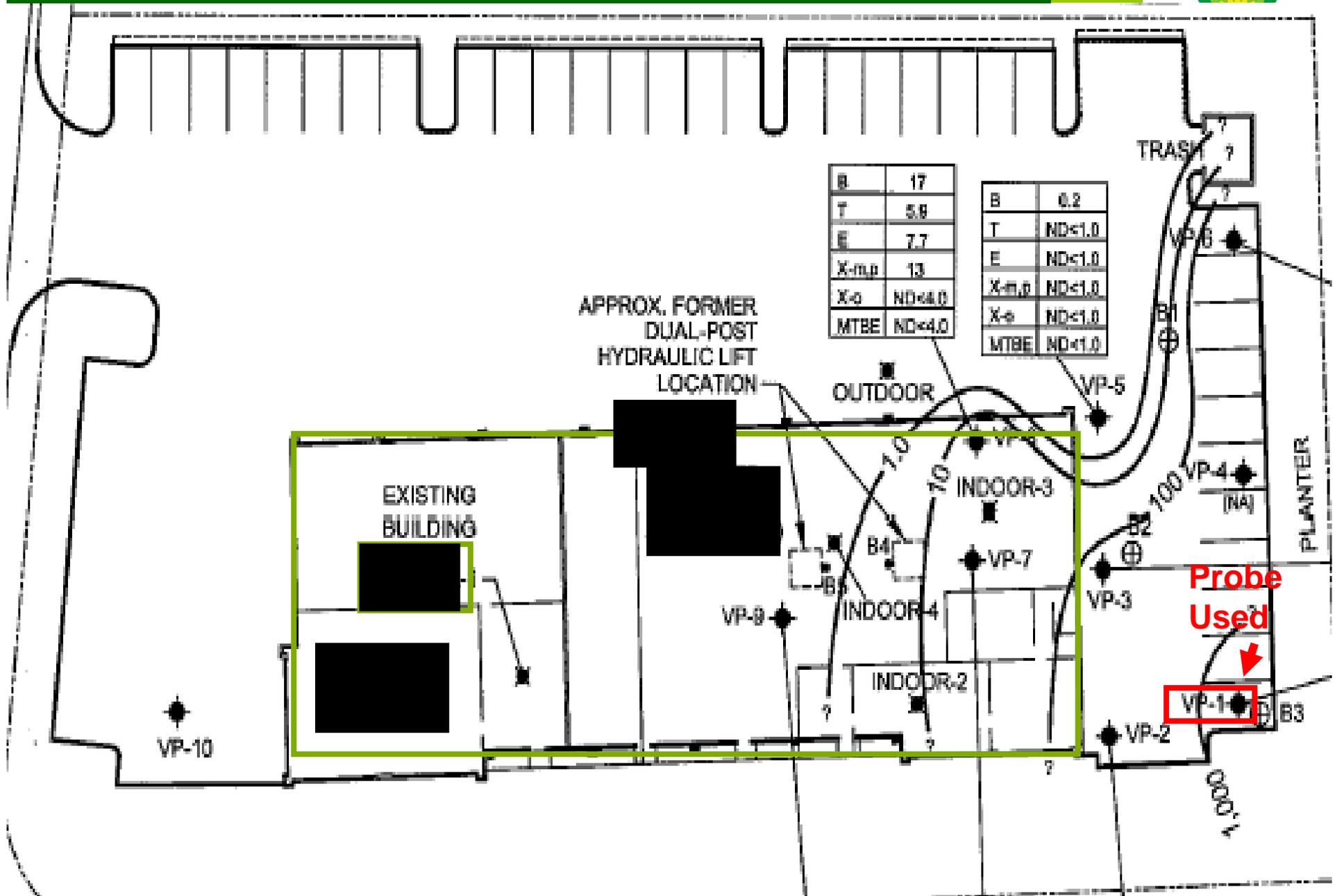


TABLE 1
SOIL GAS SURVEY VAPOR SAMPLE ANALYTICAL RESULTS

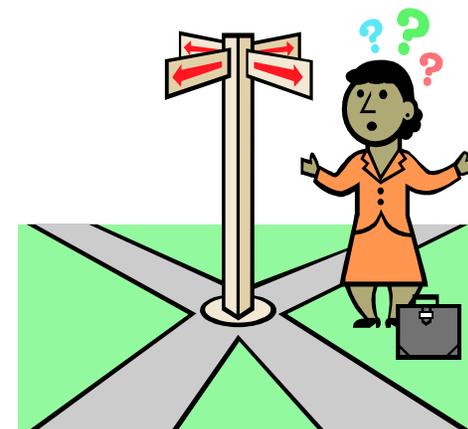
Sample Name	Sample Date	VFH (ug/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	m,p-Xylenes (ug/L)	o-Xylene (ug/L)
VP-1-5	30-Aug-07	ND<200	0.4	ND<1.0	ND<1.0	ND<1.0	ND<1.0
VP-1-15	30-Aug-07	620	4.1	ND<4.0	ND<4.0	ND<4.0	ND<4.0
VP-1-25, 1PV	30-Aug-07	40,000	1200	ND<100	ND<100	110	ND<100
VP-1-25, 3PV	30-Aug-07	13,000	400	ND<100	ND<100	110	ND<100
VP-1-25, 7PV	30-Aug-07	7,800	200	ND<100	ND<100	ND<100	ND<100

Table 5 PRELIMINARY SCREENING EVALUATIONS

Preliminary Screening Evaluations for Soil Gas					
Analyte	Sample Name (sample with the maximum concentration)	Concentration ($\mu\text{g}/\text{m}^3$)	Default Attenuation Factor	Indoor Air Concentration ($\mu\text{g}/\text{m}^3$)	OEHHA Chronic Inhalation RELs ($\mu\text{g}/\text{m}^3$)
Benzene	VP-1-25	1,200	0.001	1.20	60
Toluene	VP-2-25	420	0.001	0.42	300
Ethylbenzene	VP-6-25	30	0.001	0.03	2,000
Xylenes	VP-1-25	110	0.001	0.1	700
MTBE	VP-1-25	170	0.001	0.2	8,000

1200 $\mu\text{g}/\text{L}$ = 1,200,000 $\mu\text{g}/\text{m}^3$

CA-EPA 1 e-5 allowable benzene value: 4.2 $\mu\text{g}/\text{m}^3$

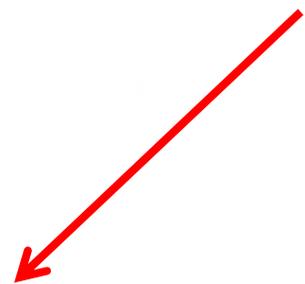


Laboratory analytical results for the vapor samples collected during the soil gas survey indicate that petroleum hydrocarbon vapors are present in the subsurface. The preliminary data was modeled using the advanced version of the Johnson and Ettinger Model (J&E Model). The J&E Model is a fate and transport model that simulates the transport of soil vapors from the subsurface into indoor air. Although the measured vapor concentrations decreased with increasing distance from the vapor source (impacted groundwater), and results for the vapor samples collected from five feet below ground surface (bgs) in each of the vapor probes revealed little to no hydrocarbon vapor concentrations (Table 1), the results of the J&E Model indicated that there was a potential risk of benzene vapor intrusion into indoor air from the concentrations detected at 25 feet bgs in the vapor probes. Therefore, in order to evaluate the potential risk of benzene vapor intrusion into the indoor air of the vacant building at the site, the collection of indoor air samples was proposed. On September 12 and 13, 2007, _____ collected indoor

TABLE 7
J&E MODEL RESULTS

Advanced Soil Gas Screening Model				
Analyte	Sample Name (sample with the maximum concentration)	Concentration (ppmv)	Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
Benzene	VP-1-25	1,200	0.0019	19.0

Benzene is a carcinogen!



Benzene was detected in vapor samples Indoor-1, Indoor-2, and Indoor-3 at concentrations of 0.29, 0.29, and 0.32 ppmv, respectively. Toluene and xylenes were detected in all indoor and outdoor vapor samples. Toluene concentrations ranged from 1.4 to 2.0 ppmv, detected in Indoor-1. Xylenes concentrations ranged from 0.62 to 0.94 ppmv, detected in Indoor-1. Ethylbenzene was detected in Indoor-1 and Indoor-2 at concentrations of 0.29 and 0.22 ppmv, respectively. Indoor air sample analytical results are presented in Table 9.

**TABLE 9
INDOOR AIR SAMPLE ANALYTICAL RESULTS**

Sample Name	Sample Date	VFH	Benzene	Toluene	Ethylbenzene	Xylenes	MTBE	DIPE	ETBE	T
Indoor-1	12-Sep-07	ND<1,700	<i>0.29</i>	2.0	<i>0.29</i>	0.94	ND<1.0	ND<1.0	ND<1.0	N
Indoor-2	12-Sep-07	ND<2,000	<i>0.29</i>	1.6	<i>0.22</i>	0.83	ND<1.0	ND<1.0	ND<1.0	N
Indoor-3	12-Sep-07	ND<1,900	0.32	1.7	ND<0.30	0.84	ND<1.0	ND<1.0	ND<1.0	N
Indoor-4	12-Sep-07	ND<2,100	ND<0.30	1.5	ND<0.30	0.62	ND<1.0	ND<1.0	ND<1.0	N
Outdoor-1	12-Sep-07	ND<1,800	ND<0.30	1.4	ND<0.30	0.63	ND<1.0	ND<1.0	ND<1.0	N

NOTES:

VFH = Volatile Fuel Hydrocarbons (C4 - C12)

MTBE = Methyl Tertiary Butyl Ether

DIPE = Di-Isopropyl Ether

ETBE = Ethyl Tertiary Butyl Ether

TAME = Tertiary Amyl Methyl Ether

TBA = Tertiary butanol

ND< = Analyte not detected at or above stated laboratory reporting limit, or method detection limit (MDL), if MDL is specified

All concentrations are in parts per billion by volume (ppbv)

TPH analysis by method EPA-8 TO-15, volatiles analysis by method EPA-2 TO-15

Italics indicates that concentrations are estimated values detected at a level less than the reporting limit and greater than or equal to the MDL

CA allowed
Level for
Benzene:
~1 ppbv

Benzene was detected in vapor samples Indoor-1, Indoor-2, and Indoor-3 at concentrations of 0.29, 0.29, and 0.32 ppmv, respectively. Toluene and xylenes were detected in all indoor and outdoor vapor samples. Toluene concentrations ranged from 1.4 to 2.0 ppmv, detected in Indoor-1. Xylenes concentrations ranged from 0.62 to 0.94 ppmv, detected in Indoor-1. Ethylbenzene was detected in Indoor-1 and Indoor-2 at concentrations of 0.29 and 0.22 ppmv, respectively. Indoor air sample analytical results are presented in Table 9.

Based on the results for the ambient air sample (outdoor sample), there are outside influences on indoor air quality of the investigation building. However, the DTSC recommends a minimum of two indoor air sampling events before making a final risk determination for a site. One indoor air sampling event cannot be reasonably representative of continuous long-term exposure within a building. Multiple sampling events should be conducted to characterize exposure over the long term (DTSC, 2004). In addition,

PVI Assessment Needed-: Former Refinery, Free Product, Odors in Building



1. Odors reported in new bldg 2. Free product on site

3. Sheening present



4. Sampling VI pathways

5. Sampling room with odors

6. Avoided This!

Gasoline Pipeline Spill in Neighborhood



Emergency Response Clean Up



**Field Lab: Basement: 1165; 1st Floor: 122 ppbv/ Cannister: 1st Floor: 470 ppbv
Other homes: at or below ambient (6.4 ppbv measured)**



Dune sands



**Look
Who showed
up!**

Retail Site in Residential Area



Soil Gas (18 inch depth) assessment data



Service Station

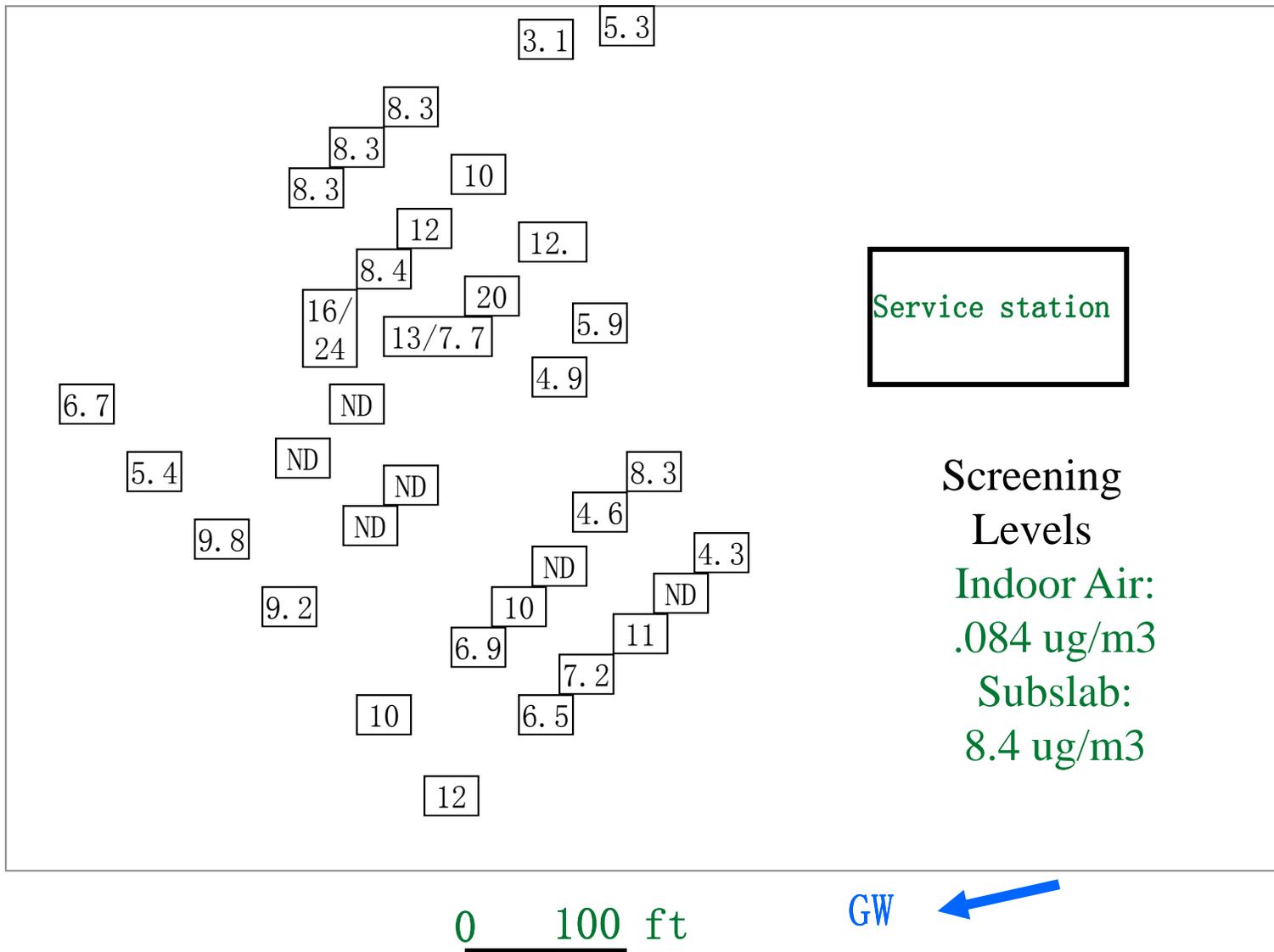
360 Benzene ug/m³

18 inch soil gas sample

Soil Gas Sample Locations (2 ft and 4 ft)



Subslab Soil Gas Data (ug/m3 benzene)



Conclusions: Subslab Soil Gas Sampling



- The results provided statistical evidence that benzene concentrations inside the study area and outside the study area are not significantly different, and that benzene concentrations found in garage samples are higher than those in non-garage samples (primarily collected from living spaces)
- The resulting benzene *background threshold values* range from $12 \mu\text{g}/\text{m}^3$ (for non-garage samples outside the study area) to $15 \mu\text{g}/\text{m}^3$ (for all benzene data). These benzene concentrations correspond to cancer risk estimates ranging from 1×10^{-6} to 2×10^{-6} , respectively, thus providing statistical evidence that background benzene levels in sub-slab are at or above the OCHCA risk management range level of 1×10^{-6}

Typical House Subslab Investigation

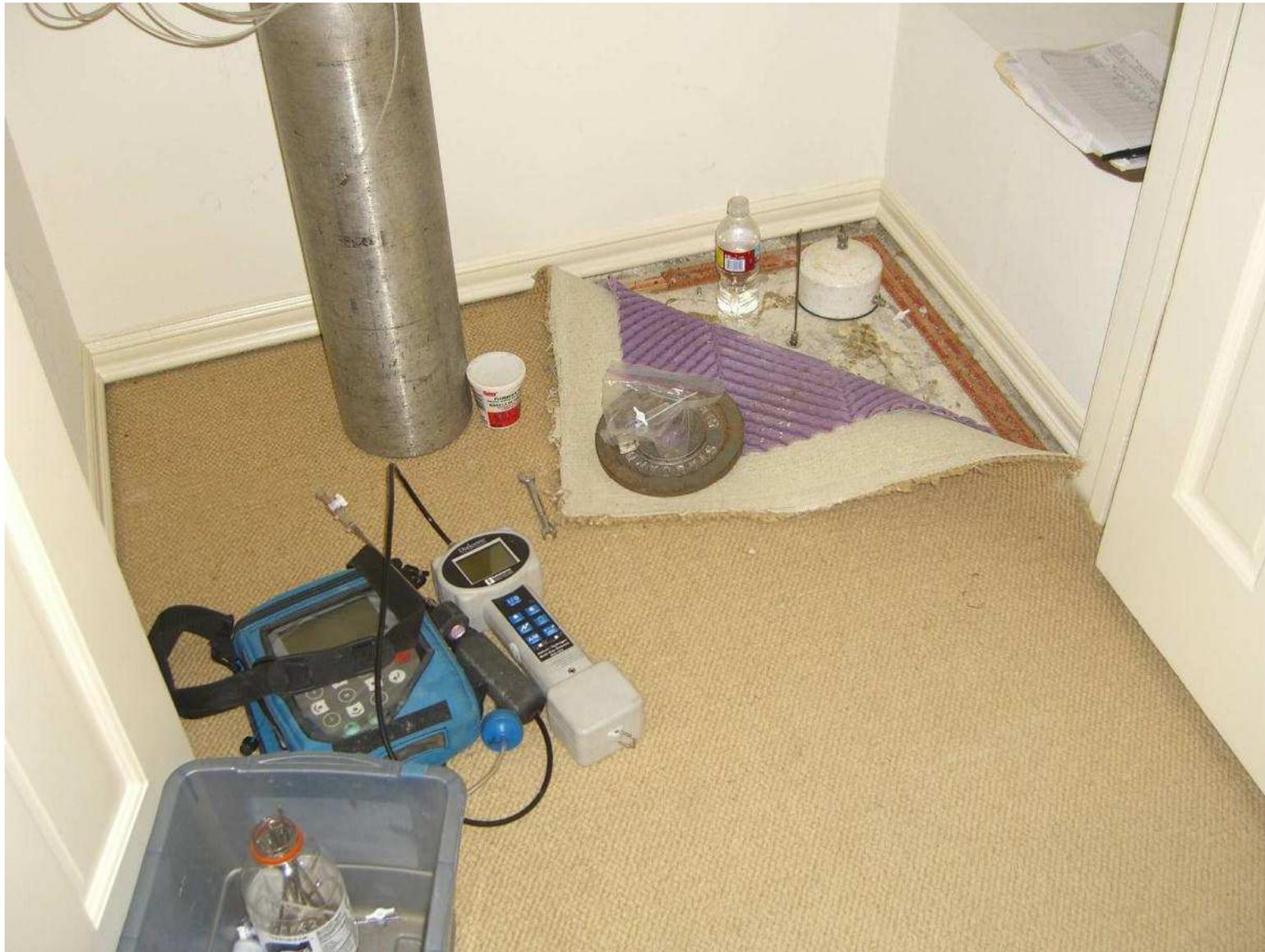


Subslab Sample- Garage



Note bentonite seal
and syringe sample

Subslab Sample- Interior of Home



BBQ Grill With Natural Gas Connection



Subslab Sample Results: Home with Leaking Natural Gas Pipeline



Analyte	BBQ	Garage	Patio	Garage #2	Closet
methane	40%	90%	100%	nd (0.1%)	nd (0.1%)
	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3
n-hexane	1700	2000	10000	nd (15)	nd (15)
cy-hexane	750	5500	12000	nd (20)	21
n-heptane	460	710	3100	nd (50)	nd (50)
benzene	<u>270</u>	<u>340</u>	<u>1900</u>	<u>6.5</u>	<u>7.9</u>
toluene	150	110	120	44	62
xylenes	40	105	177	113	33
tri-methyl benzene	3	85	25	110	nd (10)
tri-methyl pentane	nd (200)	300	nd (200)	nd (20)	nd (20)

The Final Solution?



Excavation within cell



Clean backfill

SVE Prior to Dig



SVE Still Running