VI Issues: Lessons Learned & Case Studies

CALIFORNIA UNIFIED PROGRAM ANNUAL TRAINING CONFERENCE

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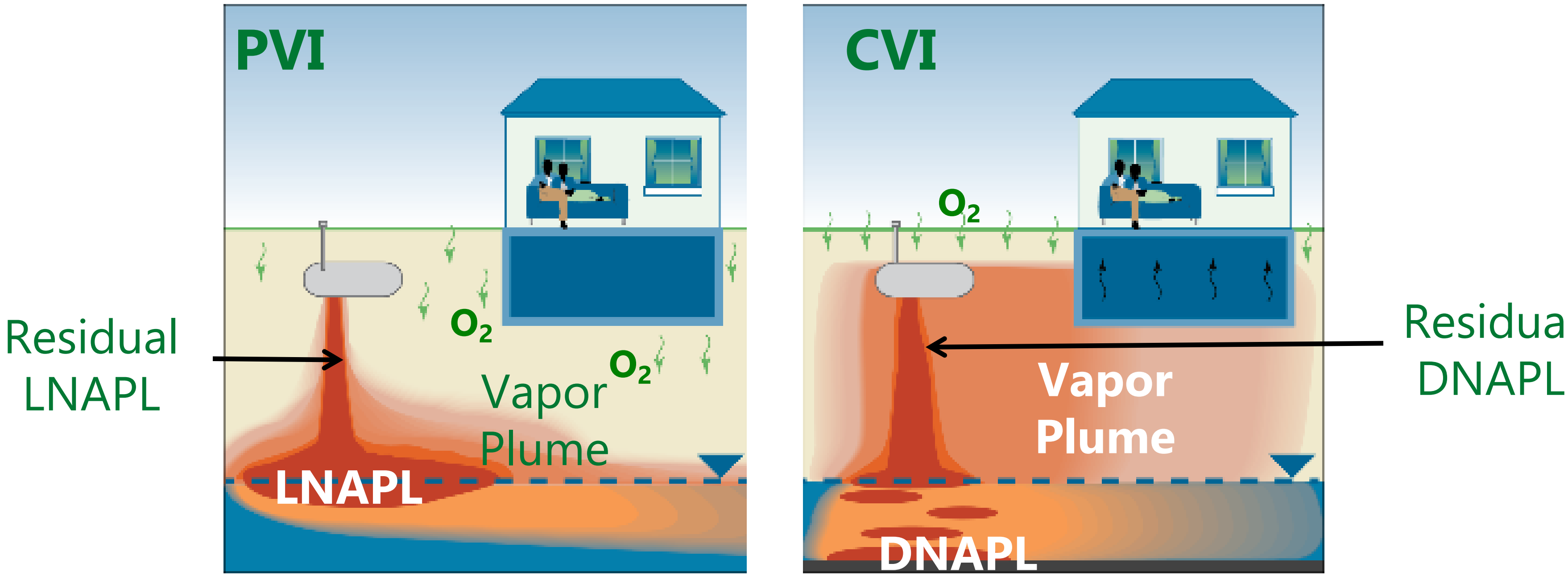
Outline of PVI Lessons Learned Workshop

- Differences between PVI & CVI
- PVI Conceptual Site Model
- Methane & PVI
- Lessons Learned Case Studies
  - Comparisons of field data to modeled data
  - PVI issues associated with development of oil field
  - How not to do a PVI work plan
  - “Top 10” Lessons Learned Summary
  - Examples of sites with PVI problem

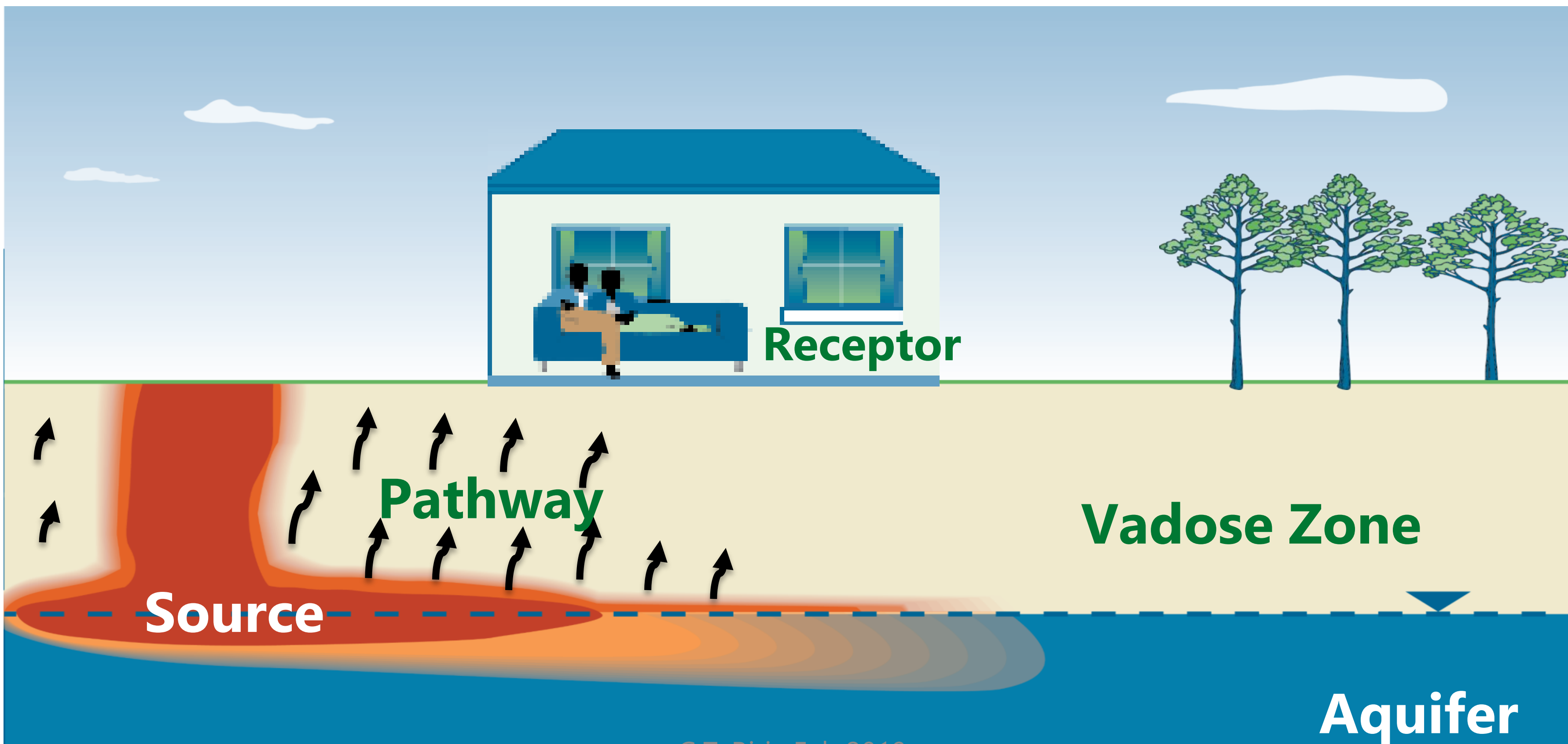
Differences Between PVI and CVI



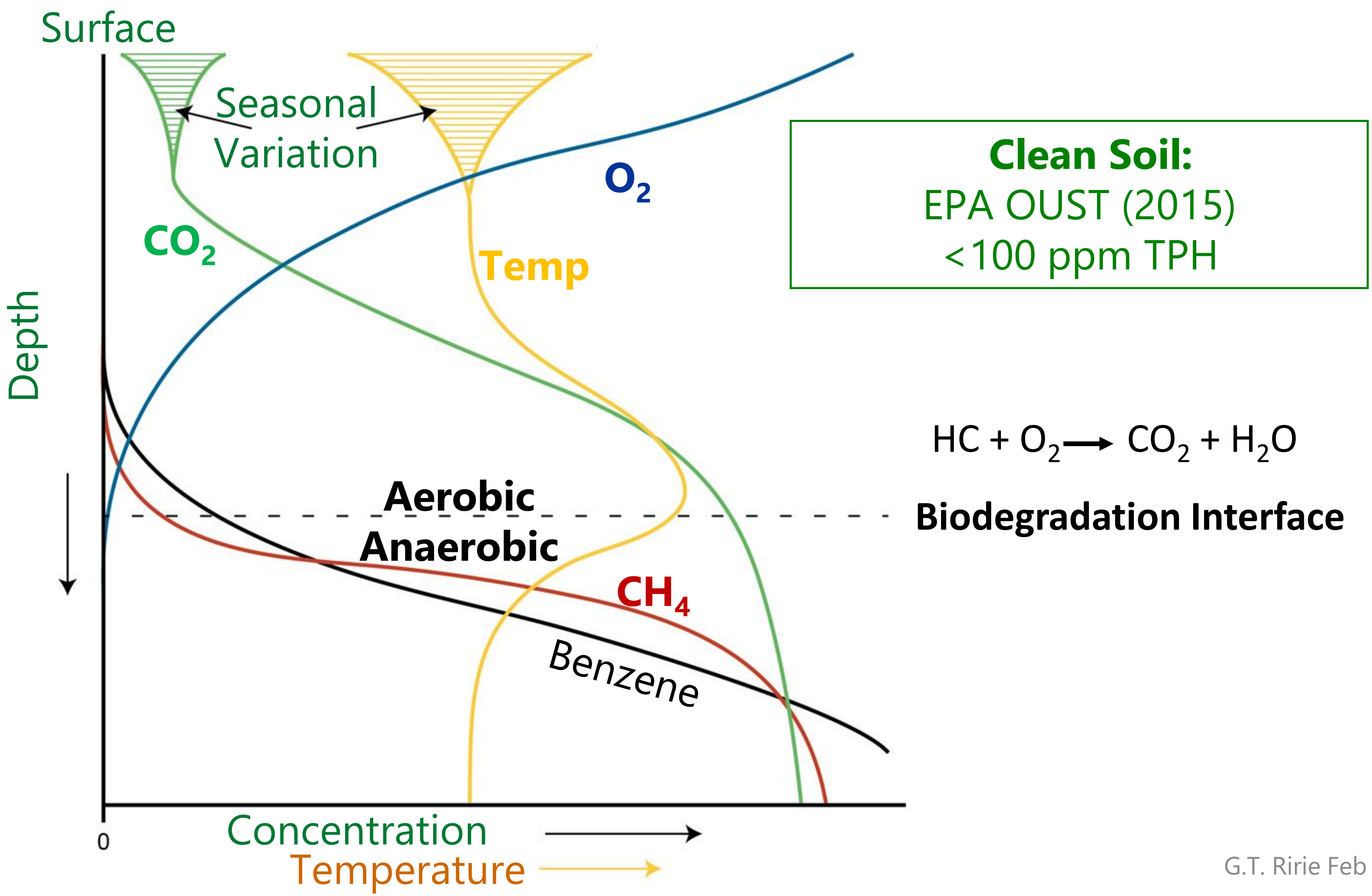
Variable	PVI	CVI
Type of chemical	petroleum hydrocarbon	chlorinated hydrocarbon
Example	benzene	tetrachloroethene (PCE)
Source Type	LNAPL	DNAPL
Aerobic biodegradation	**Consistently very rapid**	consistently very limited
Vapor intrusion potential	low	high
Degradation products	CO_2, H_2O	intermediates

Conceptual Site Model (CSM)

Simplified version (pictures and/or descriptions) of a complex real-world system that approximates its relationships



Petroleum Vapor Intrusion (PVI) Conceptual Site Model – Surrounding Soils are Clean



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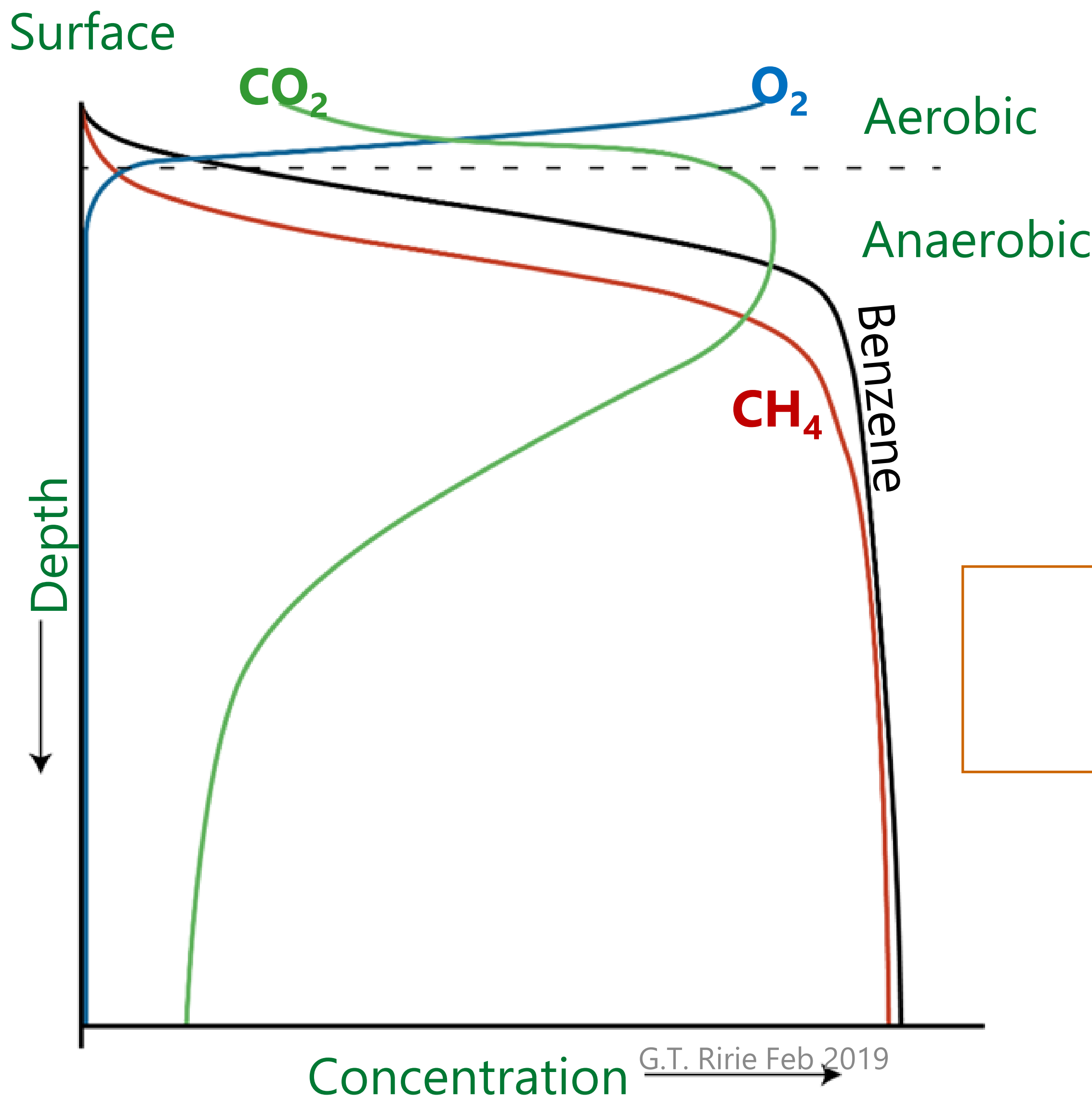
PVI Conceptual Site Model – Surrounding Soils are Dirty



Dirty Soil:
EPA OUST (2015)
>100 ppm TPH

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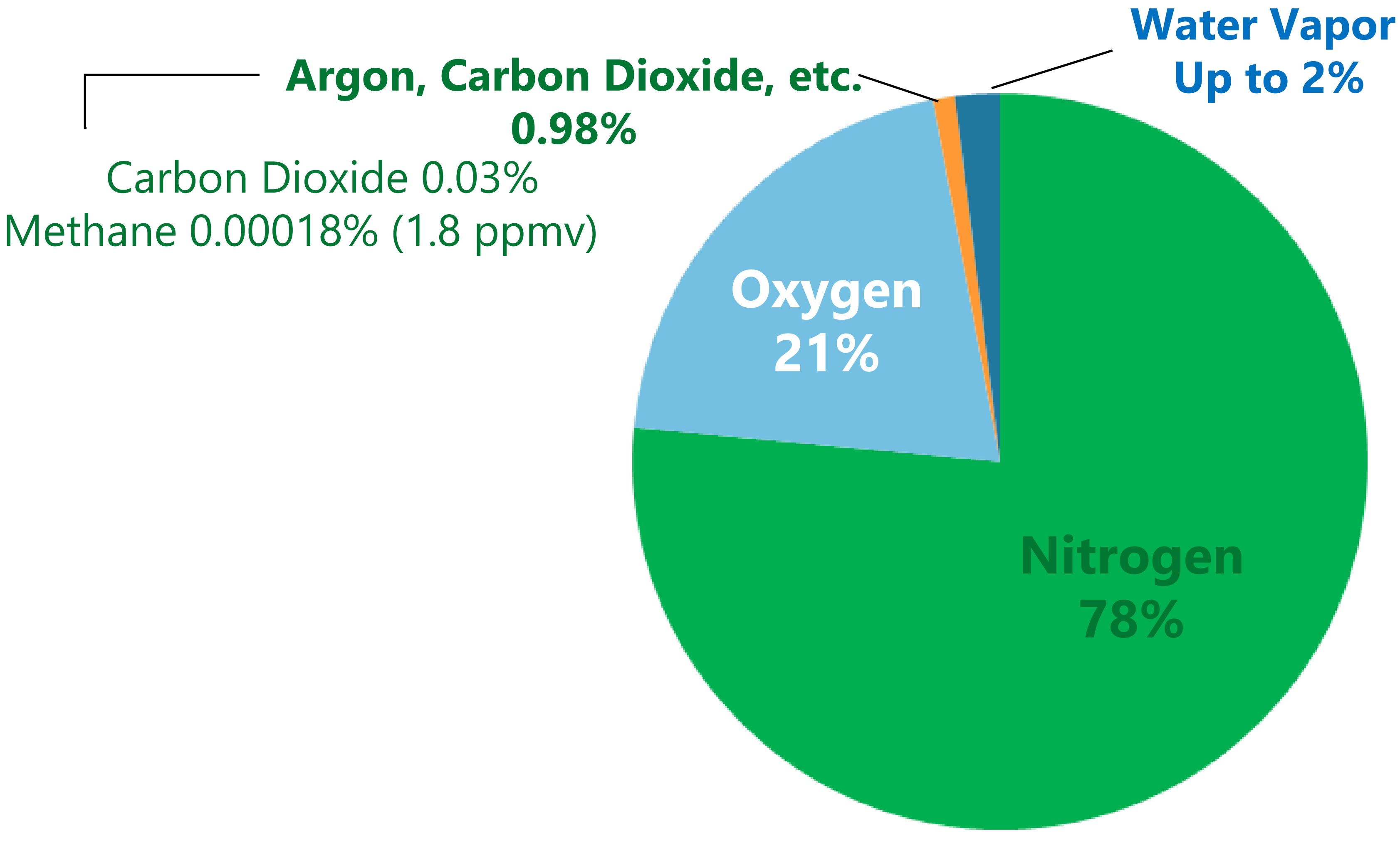
Fixed Air Gases



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EPA OUST: Clean Soil vs Dirty Soil

Table 3. Recommended Vertical Separation Distance Between Contamination And Building Basement Floor, Foundation, Or Crawlspace

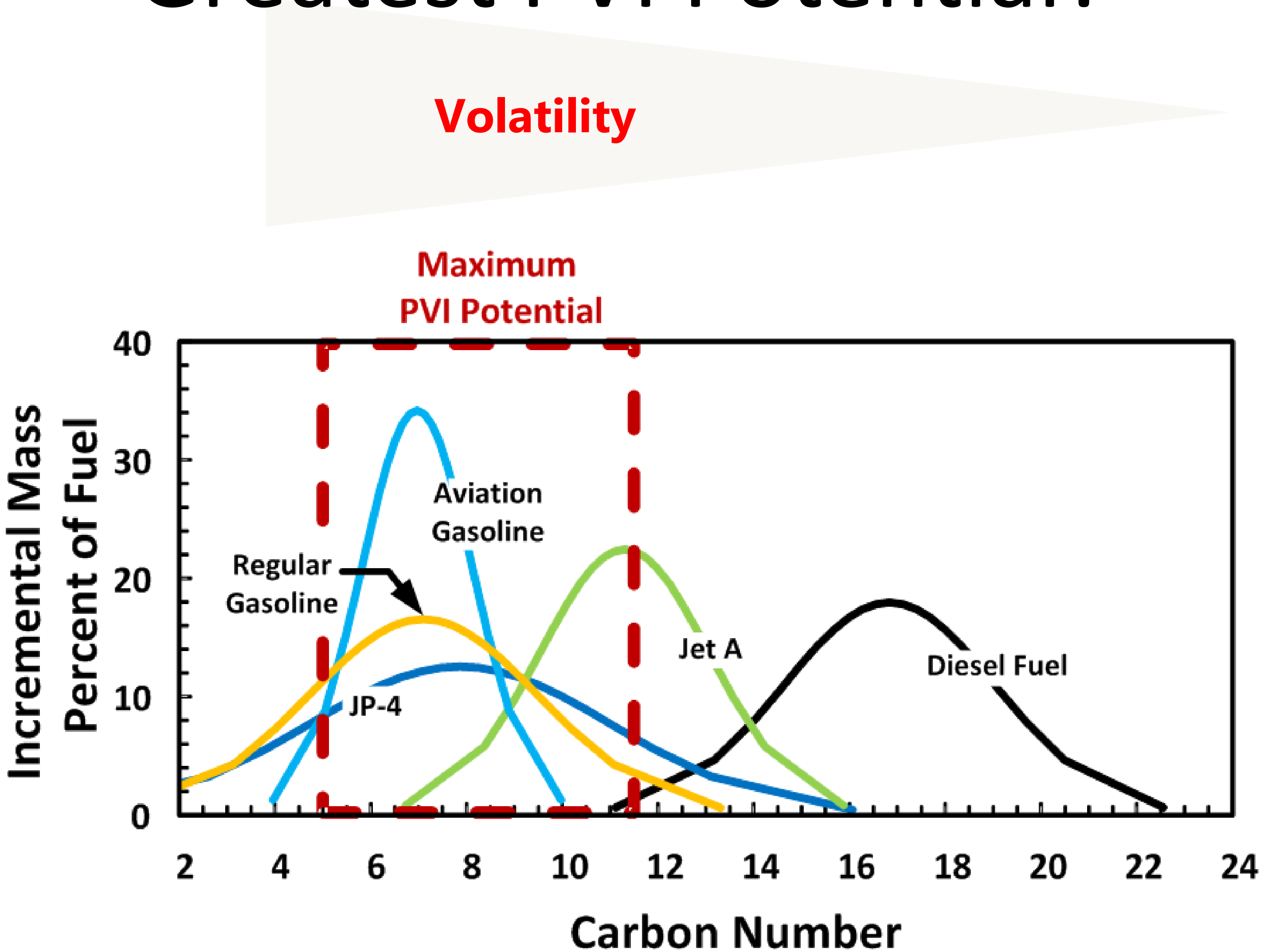
Media	Benzene	TPH	Vertical Separation Distance (feet)*
Soil (mg/Kg)	≤10	≤ 100 (unweathered gasoline), or ≤ 250 (weathered gasoline, diesel)	6
	>10 (LNAPL)	> 100 (unweathered gasoline) >250 (weathered gasoline, diesel)	15
Groundwater (mg/L)	≤5	≤30	6
	>5 (LNAPL)	>30 (LNAPL)	15

Source: EPA OUST PVI Guidance; 510-R-15-001, June 2015

Methane and Petroleum VI - What is the Connection?

- Methane present at virtually all hydrocarbon spills
- Colorless, odorless gas, 1.8 ppmv (1260 µg/m^3) in the atmosphere
- Most abundant organic compound on Earth
- Main component of natural gas (odorant added)
- Methane included in measurement of fixed gases
- Potential safety hazard
  - Upper Explosive Limit (UEL) = 15%
  - Lower Explosive Limit (LEL) = 5% (35 x 10^6 µg/m^3)

Which Petroleum Fuels have the Greatest PVI Potential?



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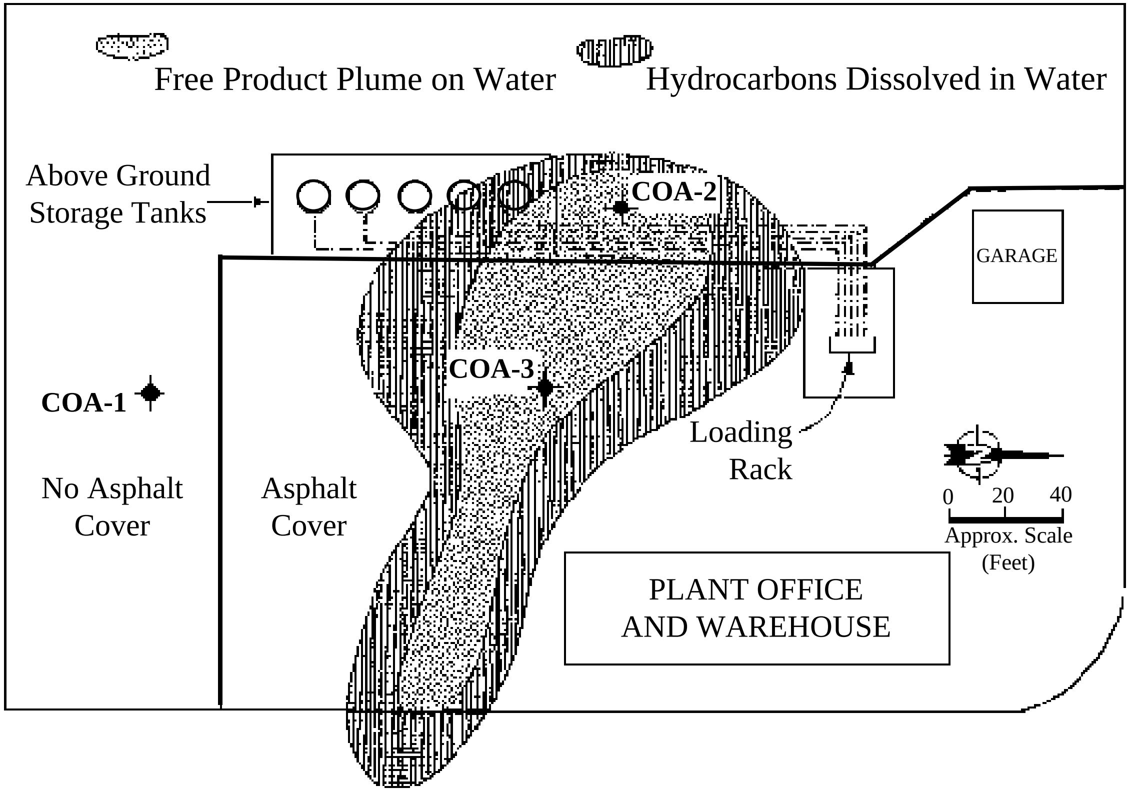
ITRC PVI-1, Figure 2-3

CA Low Threat Closure Policy

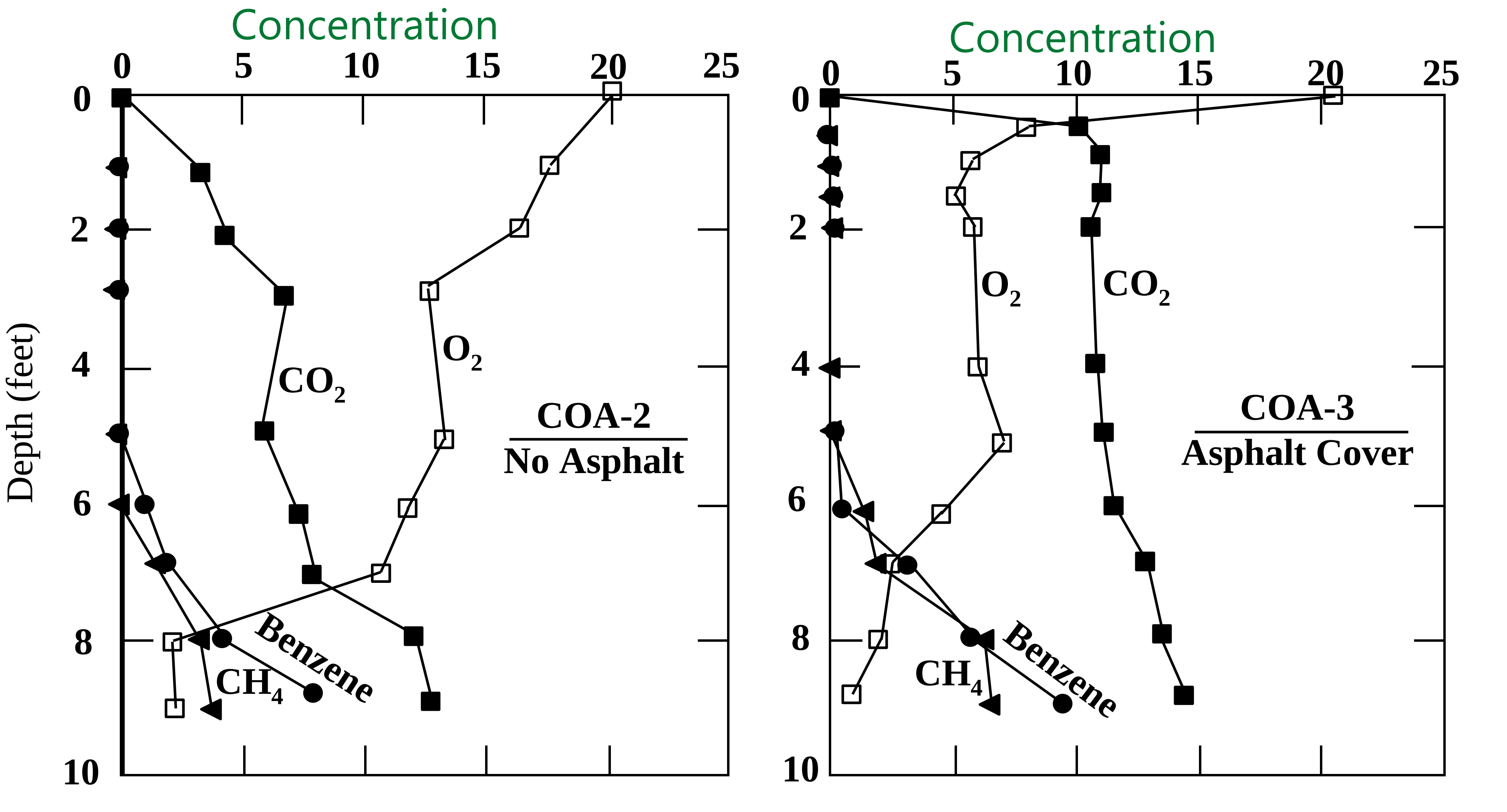
- https://www.waterboards.ca.gov/board_decisions/adopted_orders/resolutions/2012/rs2012_0016atta.pdf

Case Study #1-Comparison of field data to modeled data for benzene



Distribution facility showing free product plume on groundwater and sample locations

Vertical Profile of Soil Gases at Distribution Facility



Free product is at 10 feet

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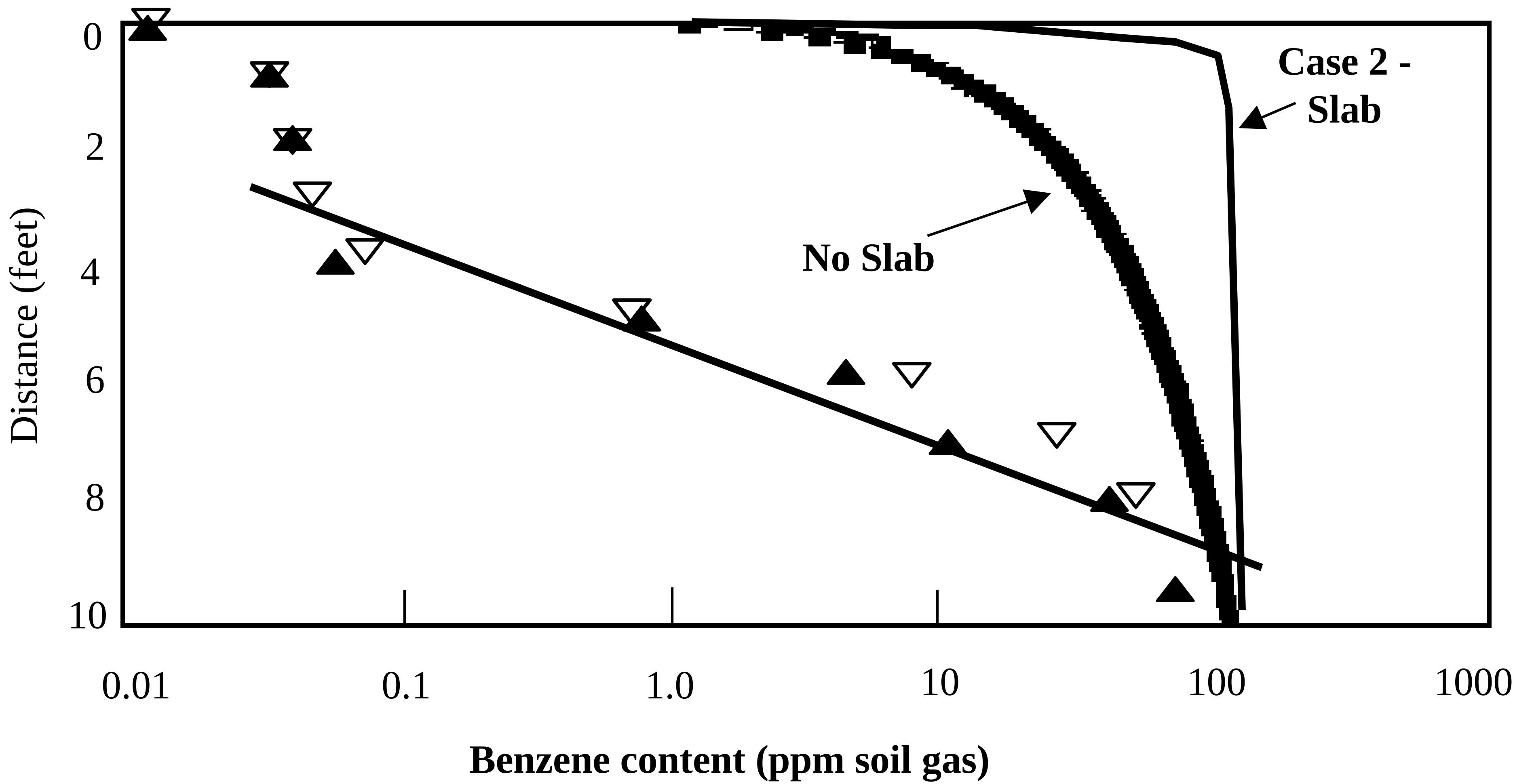
Comparison of J&E model predictions with field data for distribution facility-semi-log plot of data.



= field data COA-3 under asphalt

= field data COA-2 no asphalt

Model Case 1 - No slab

Model Case 2 - With Slab

Lessons learned from Case Study #1

- Oxygen concentrations under l the large asphalt slab is higher than anticipated.
- Benzene attenuates more rapidly than methane.
- Both benzene and methane attenuate to zero in short interval when oxygen concentrations are above 4-5%.
- Hydrocarbon gases do not build up under the large asphalt slab.
- Field data do not match J&E model data unless degradation is including into the model.

Case Study #2 -Santa Maria, CA Redevelopment of Oil Field to Homes

- The case study property is within the Santa Maria Valley Oil & Gas field
- Site is near historical oil production well and associated sump
- Remediated to a TPH level < 100 ppm
- Site is now occupied by homes

Site Conditions

- Surficial soils are silty sands, wet at shallow depths from irrigation
- Screened soils were used as backfill on site and contained small < 0.5 inch diameter clasts of asphaltic material
- Soils were compacted to greater than 90% prior to construction
- Topsoil and subsoil were mixed prior to construction of homes

Site Issues

1) Homeowners claim elevated methane levels are killing plants
2) High methane levels in soils may be cause for concern to indoor air
3) Homeowners hire attorney and consultant to collect data and threaten lawsuit

Site Work Plan for Each Property

- Collect vertical soil gas profiles in front and back yard to depth of 10 ft and under slab to depth of 5 ft-analyze for fixed gases and H_2S.
- Collect soil samples from vertical profiles at two locations to depth of 10 ft-analyze for TPH and physical properties.
- Collect soil data necessary to evaluate cause(s) of plant stress
- Collect isotopic data on soil gases to evaluate source and age

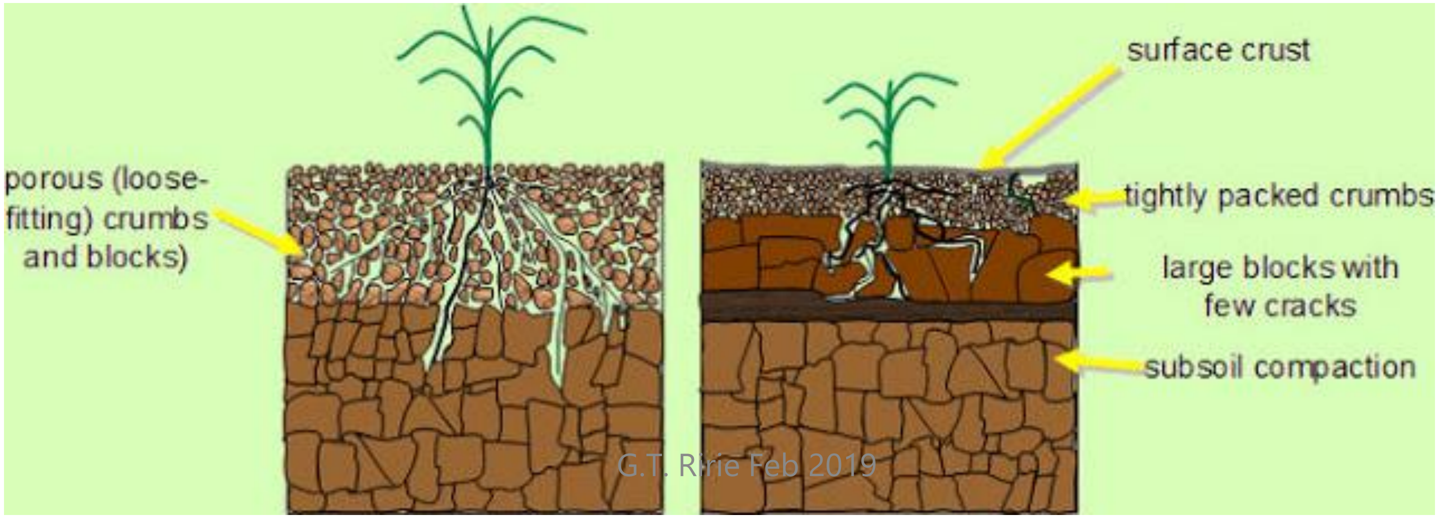
Preparing Soil for Construction

Healthy & Dead Plants

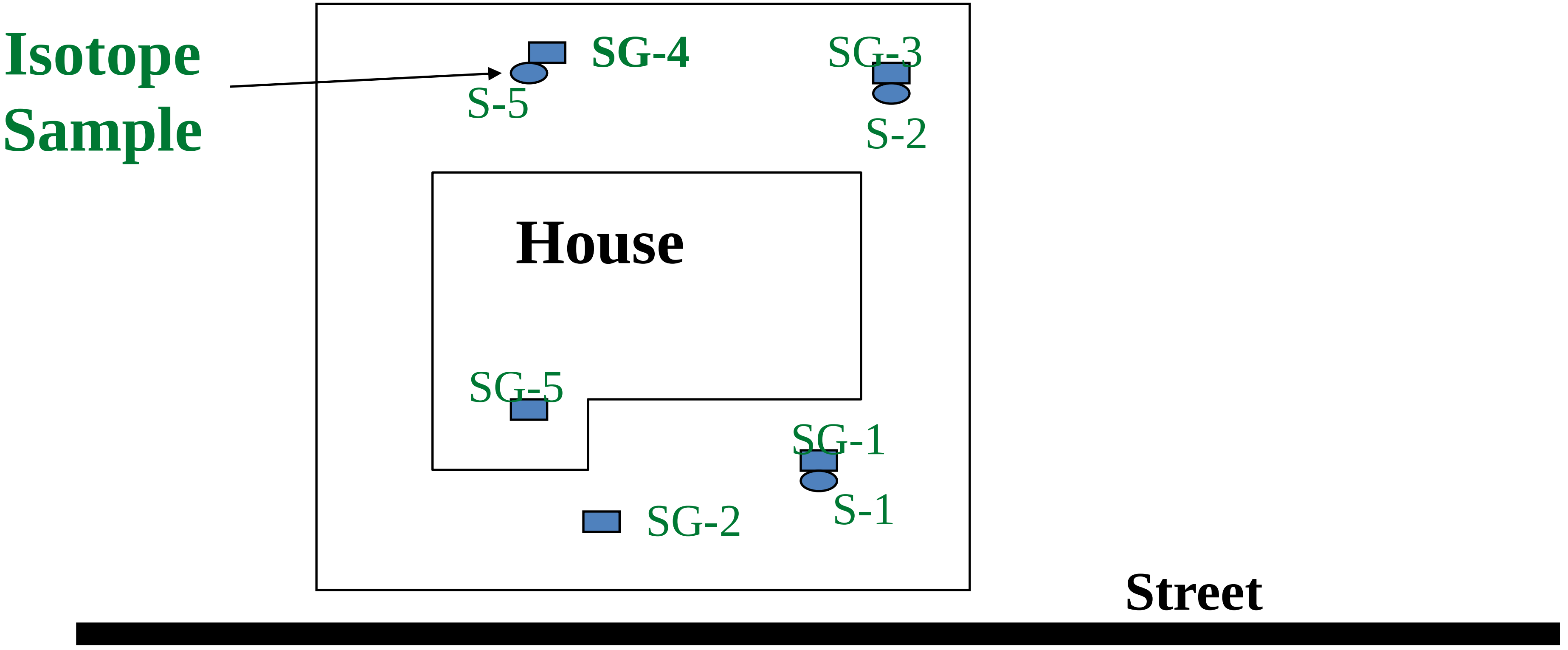
Soil Evaluation-Homeowners plants were stressed

Results of Plant Stress Evaluation

- Tree roots confined to upper 4 inches of soil
- No evidence of topsoil
- Reducing conditions noted below 17 inches
- Penetrometer readings: 3.5-4.5 tons/ft^2 (good garden soil = 0.5 tons/ft^2)
- Percolation rates=152-176 minutes/inch @ 6 inch depth (rate above 60 is too poorly drained for septic leach field)
- All dead shrubs in adjacent park are in wet soils



Direct Push Soil Gas Sampling



Location of soil gas (SG) and soil (S) samples collected at Site 1 in Santa Maria, CA.

Soil Gas Sampling Results

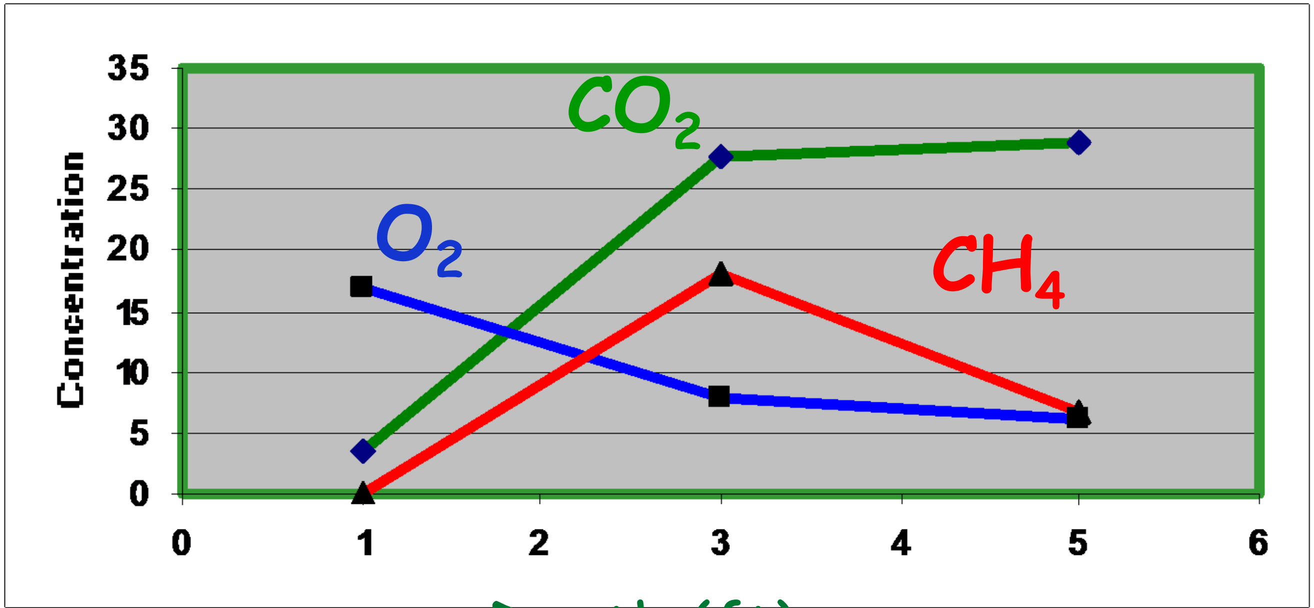
Site 1

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

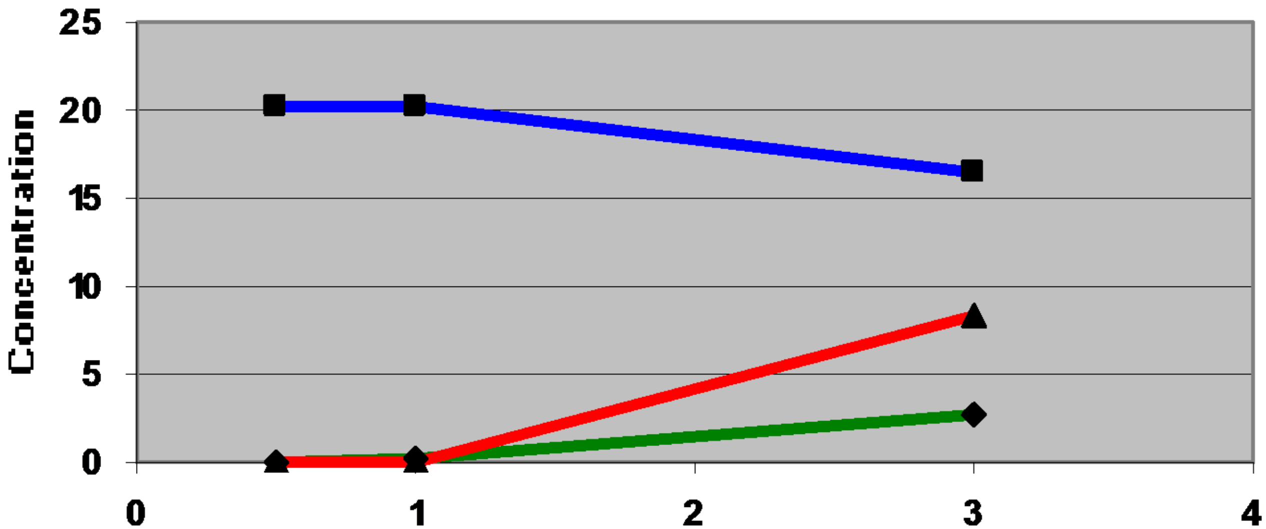
Sample depth	Methane (ppmv)
1. Subslab 0.5 ft	<10
2. Subslab 3 ft	11,000
3. Outside 1ft	45
4. Outside 5ft	120,000

Soil Gas Vertical Profiles



Depth (ft)

Back Yard



Under Slab

Site 1 Santa Maria, CA

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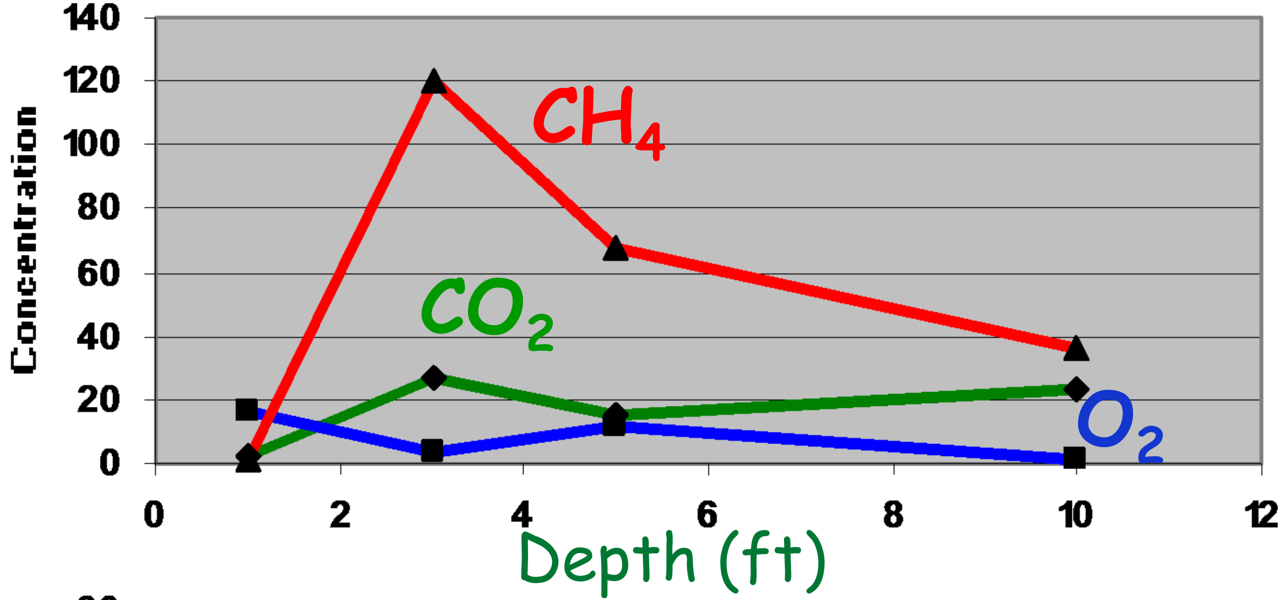
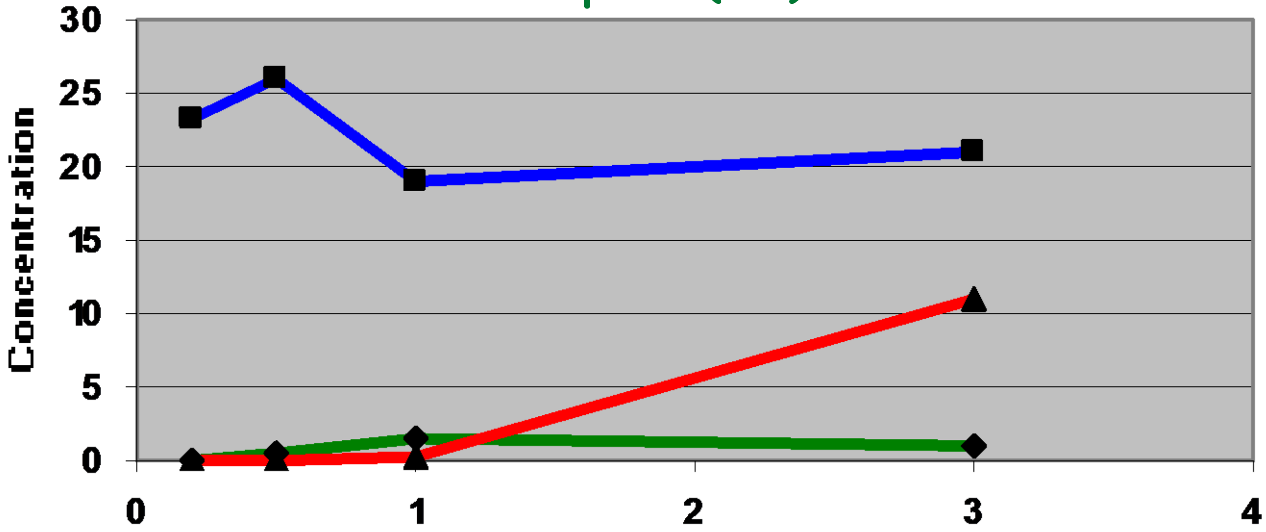
Soil Gas Vertical Profiles



Front Yard



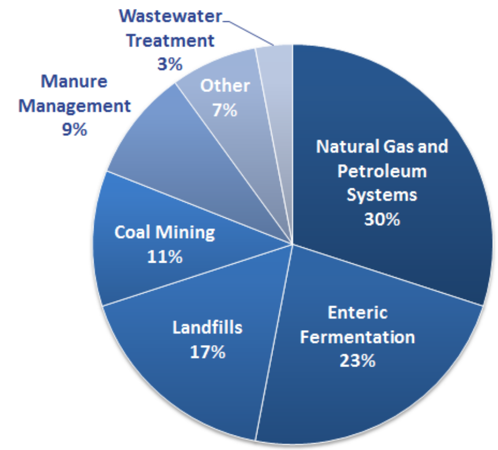
Under Slab

Site 2 Santa Maria, CA

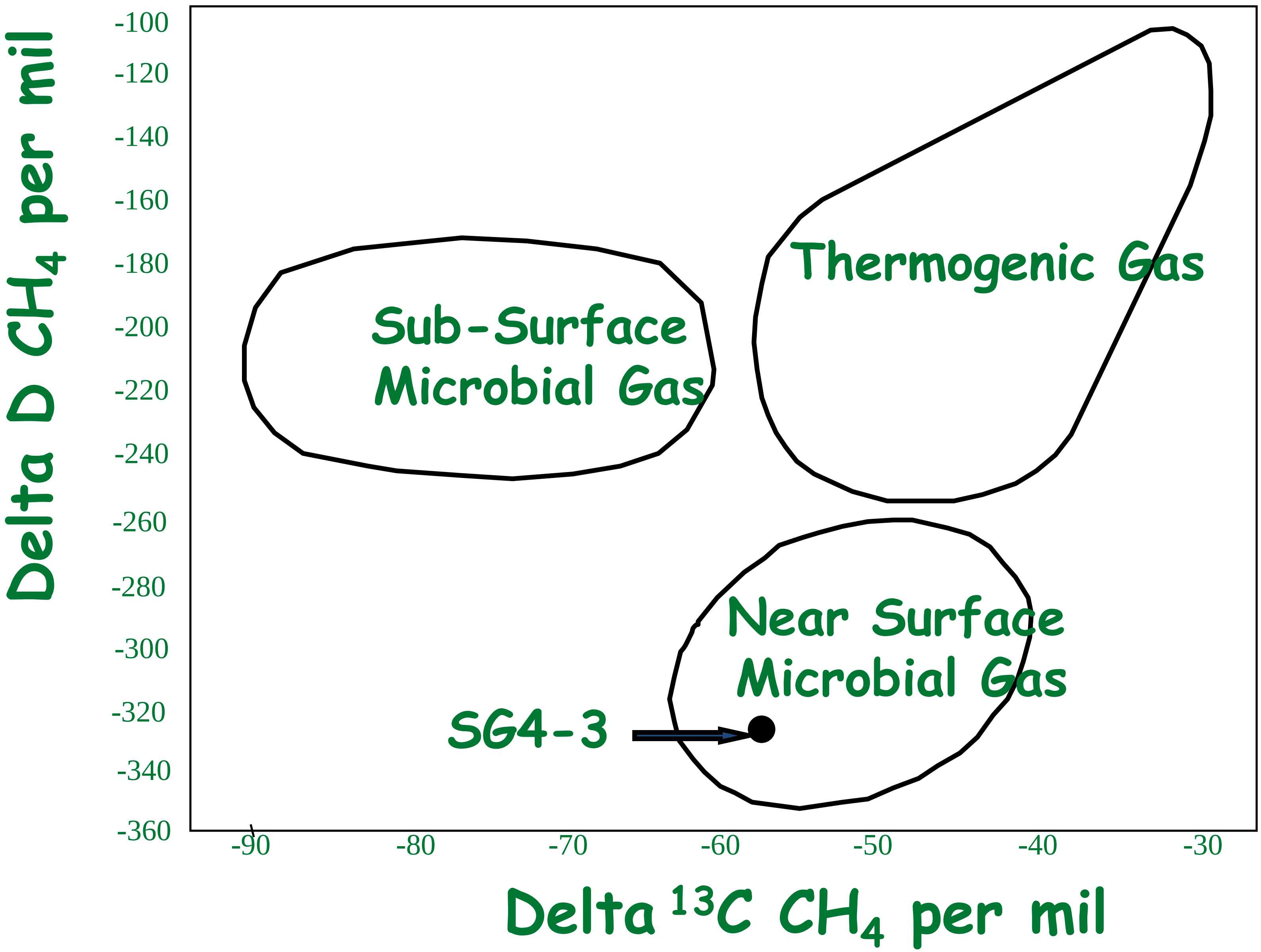
Analysis of Soil Gas Data

- No complete pathway is present -high oxygen concentrations at two feet or less
- High methane trapped under shallow wet soil zone from irrigation.
- Using EPA guidance for estimating vapor intrusion:
  - ✓ Calculated values are 2,000 to 3,000 times below LEL using highest methane below slab
  - ✓ Calculated values are more than 50,000 times below LEL for samples measured directly below the slab

Sources of Methane



Data Suggests Methane is from Natural Organics



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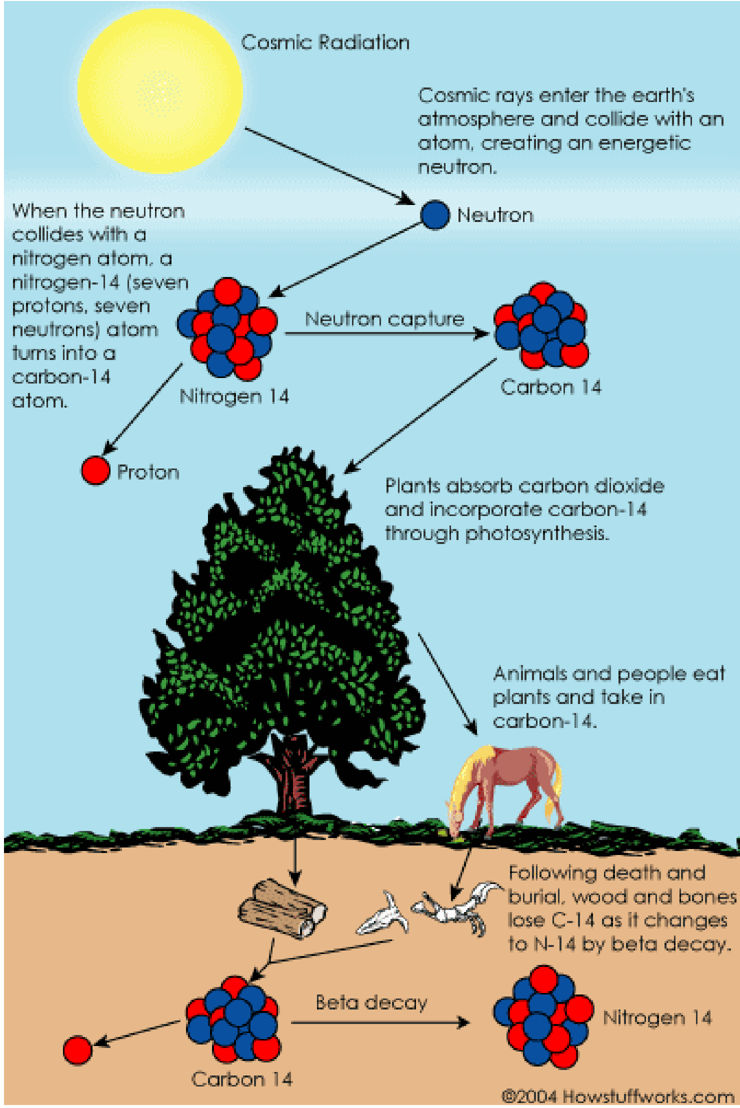
Sources of gases as defined in Coleman (1994)

^{14}C Analysis Confirms Methane is from Young Organic Matter

- O_2 = 2.54%
- CO_2 = 35.19%
- N_2 = 38.9%
- C1 = 22.9%
- C2 through C6+ = 0%
- Delta $^{13}C1$ = -57.18 per mil
- Delta DC1 = -328.4 per mil
- ^{14}C pMC = 109%



Lessons Learned from Case Study #2

- Plant stress is result of highly compacted soils-not methane
- Source of methane can be determined using carbon isotopes-young biogenic gas
- Process driving upward migration of methane is diffusion (no pressure drive)
- No measurable hydrocarbon gases in indoor air-consistent with no complete pathway
- No risk for hydrocarbon gases to accumulate to levels that pose a risk to human health or safety

Case Closed
No Legal Settlements

Discussion Points

- Causes of concern to home owners
- Effect of moisture barriers on methane contents in shallow soils
- High concentration vs low volume
- Under slab vs outside slab soil gas
- Sources of methane

"Top Ten" List of VI Issues Encountered

- **Soil Gas Probe Installation Issues**:
  - Using wrong tubing type
  - Pinching off of tubes due to incorrect surface completion
  - Not collecting an equipment blank
  - Using air knife to clear borehole

- **Field Sampling Issues**:
  - Not opening Summa canisters or Tedlar bags
  - No experience with Swagelok connectors
  - Applying too much liquid tracer

"Top Ten" List of VI Issues Encountered

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
- Vacuum units: inches Hg to inches H_2O

Workplan Issues:

- Work plans submitted for VI work not needed
- Too many samples than what is needed
- Not collecting samples in upper part of vadose zone (e.g., 5' bgs) to demonstrate bioattenuation
- Analyzing compounds that were never used at the site.

Case Study # 3 How Not to Do PVI Investigation!

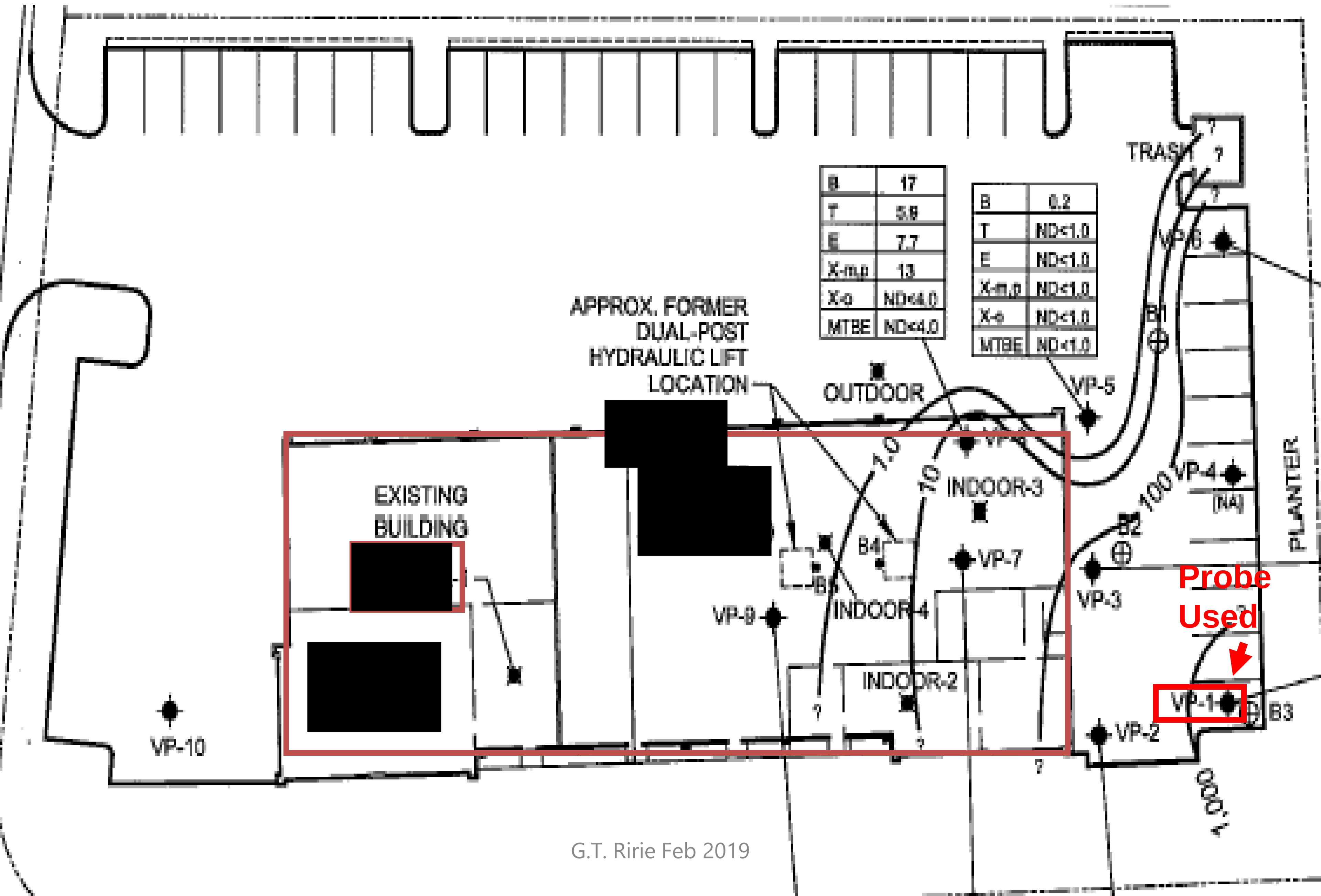


TABLE 1

SOIL GAS SURVEY VAPOR SAMPLE ANALYTICAL RESU

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

STEP 5: PRELIMINARY SCREENING EVALUATION

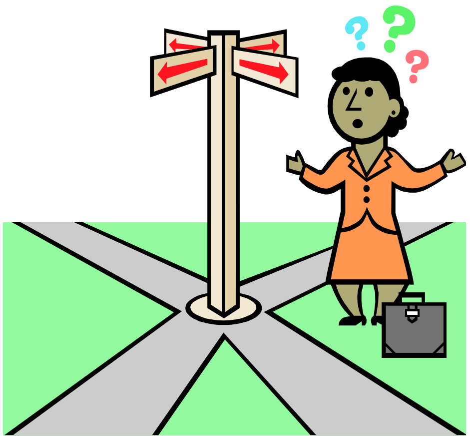
A preliminary screening evaluation was conducted using the default attenuation factors presented in Table 2 of the DTSC/Cal-EPA guidance document. Since the existing building on the site property is for commercial use, the default attenuation factor for the commercial building scenario with a slab-on-grade foundation configuration (0.001) was used along with the maximum detected soil gas BTEX and MTBE concentrations to determine an indoor air concentration. Maximum BTEX and MTBE concentrations were detected in VP-1. The results of the preliminary screening evaluations indicates that indoor air concentrations do not exceed the Office of Environmental Health Hazard Assessment (OEHHA) indoor air screening criteria for chronic inhalation reference exposure levels (RELs) for BTEX and MTBE. The results of the preliminary screening evaluations and the OEHHA chronic

Table 5 PRELIMINARY SCREENING EVALUATIONS

Preliminary Screening Evaluations for Soil Gas					
Analyte	Sample Name (sample with the maximum concentration)	Concentration (µg/m³)	Default Attenuation Factor	Indoor Air Concentration (µg/m³)	OEHHA Chronic Inhalation RELs (µg/m³)
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 ug/L = 1,200,000 ug/m3

CA-EPA 1 e-5 allowable benzene value: 4.2 ug/m3



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 1

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

[redacted]

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, repectively. 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	*0.29*	2.0	*0.29*	0.94	ND<1.0	ND<1.0	ND<1.0	N
Indoor-2	12-Sep-07	ND<2,000	*0.29*	1.6	*0.22*	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)
TPHg analysis by method EPA-2 TO-3, 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 greateer 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, repectively. Indoor air sample analytical results are presented in Table 9.

Case Study #3

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,

Case Study #4 PVI Assessment Needed: Former Refinery, Free Product, Odors in Building

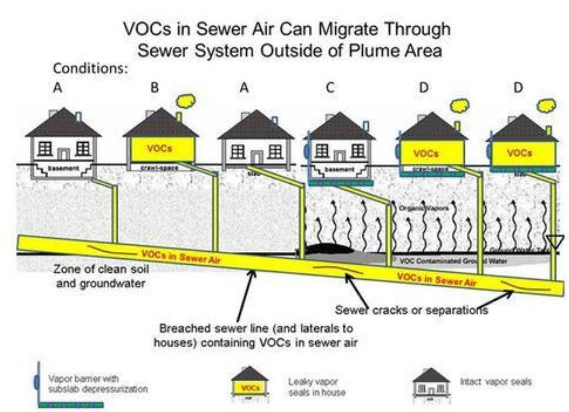
1. Odors reported in new bldg

2. Free product on site

3. Sheening present

4. Sampling VI pathways

5. Sampling room with odors



6. Sewer pathway

Case #5 Gasoline Pipeline Spill in Neighborhood

Emergency Response Clean Up

Field Lab: Basement: 1165; 1st Floor: 122 Canister: 1st Floor: 470

Other homes: at or below ambient (6.4 measured)

All units ppbv

Dune sand in vadose zone

Gasoline Spill in Neighborhood: Emergency Response

TAGA bus

Taga lab

Gas input into GC

Output data quickly

Summary

- Understand the difference between PVI & CVI
- Always use the SCM for evaluating VI issues
- Be aware of Federal, State and Local guidance
- Apply lessons learned
  - Oxygen content key to evaluating PVI pathway
  - Be sure to use correct type of model for PVI
  - Understand sources and issues with methane
  - Use best practices for PVI sampling and analysis
  - Be sure of units, screening levels, background levels
  - Odors good indication of PVI issue, rapid response when needed