



PVI Issues: Lessons Learned- Including Methane

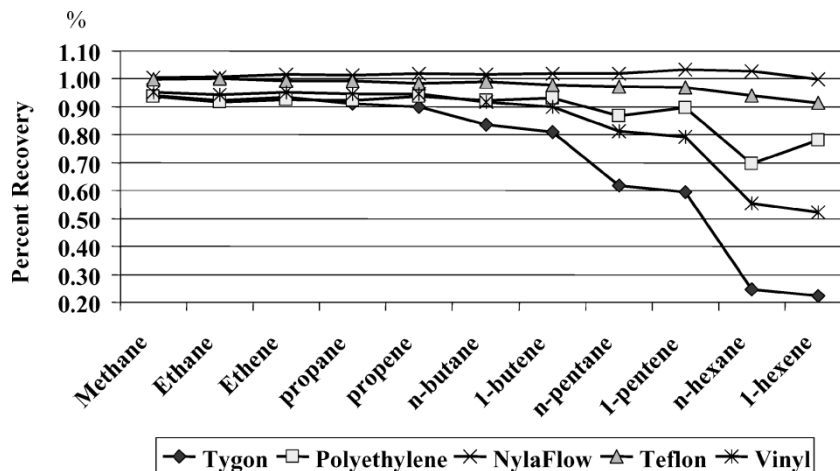


**G. Todd Ririe, BP: La Palma, CA
March 2015**

Top Ten Issues Encountered



- Reports of Odor resulting in PVI investigation
- Bad data resulting in resampling
- Collecting samples not needed to evaluate PVI pathway
- Unit confusion for soil gas sample results
- Using screening criteria for clean up levels



Using wrong tubing

Top Ten Issues Encountered, con't.



- Collecting indoor air samples too early in process
- Analyzing for compounds never used at the site
- Not using correct analytical method for detection levels needed
- Lack of attention to chain of custody details
- Using approaches and guidance for PVI that was intended for CVI

Office indoor air sample: O₂ = 7.5%

Note Negative Vacuums: The cans only filled partially!

Hydrocarbon Odors



“In general, the public does not understand the relationship between odor and risk and believes “if it smells it must be bad”. EPA, 1992



Hydrocarbons usually do not exhibit odors of interest .

Certain cyclic alkenes have been associated with pleasant notes, such as fruity and floral.



Odors are usually complex mixtures.

Sensory responses to separated components of these mixtures can be very different from component to component and from person to person.

Odor Culprits: Sewer Gas vs Natural Gas



Almost always, hydrogen sulfide is the odor culprit- “**rotten egg**” **smell**, although ammonia may be formed in rare cases.



- Odor threshold, the lowest concentration that can be detected with the nose, for hydrogen sulfide is somewhere between .001 and .01 parts per million (ppm). One ppm on a linear scale is one inch in 15.8 miles.
- The first thing to do is make sure the smell is sewer gas—usually a rotten egg smell—and not a **natural gas smell**, which usually smells like a **skunk**.
- Other components of sewer gas may include methane, carbon dioxide, and nitrous oxides.



Detection Limits & Odor Thresholds



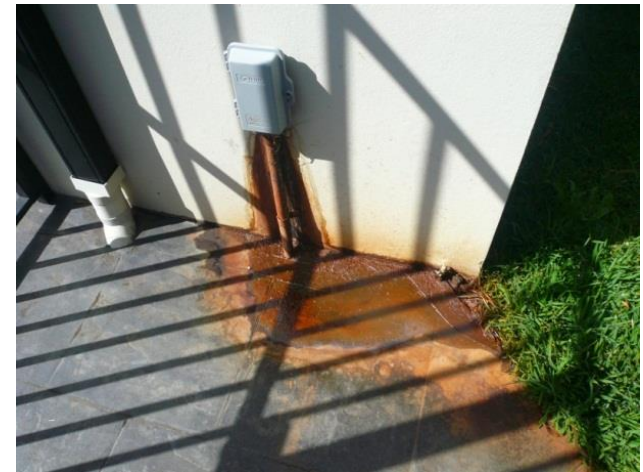
ppbv

COMPOUNDS	ANALYTICAL DETECTION LIMIT *	ODOR THRESHOLD	Ug/m3
Hydrogen Sulfide	0.03	4.7	6.6
Carbonyl Sulfide	0.2	50.	
1-Butene	0.2	1300.	
Butane	1.0	not available	
Methyl Mercaptan	0.02	2.1	4.2
Branched Pentane	0.5	not available	
1-Pentane	0.2	190.	
Pentane	0.5	5000000.	
Ethyl Mercaptan	0.04	3.	
Dimethyl Sulfide	0.03	1.	
Carbon Disulfide	0.5	210.	672
i-Propyl Mercaptan	0.03	not available	
Branched Hexane	0.1	not available	
1-Hexene	0.2	not available	
Hexane	0.1	not available	
n-Propyl Mercaptan	0.03	1.6	9900
Benzene	0.05	3000.	
Cyclohexane	0.2	9500.	
Methylcyclohexane	0.2	not available	
i-Butyl Mercaptan	0.03	not available	
n-Butyl Mercaptan	0.03	6.	
Toluene	0.05	170.	646
Ethylbenzene	0.1	not available	
Xylene	0.1	80.	352

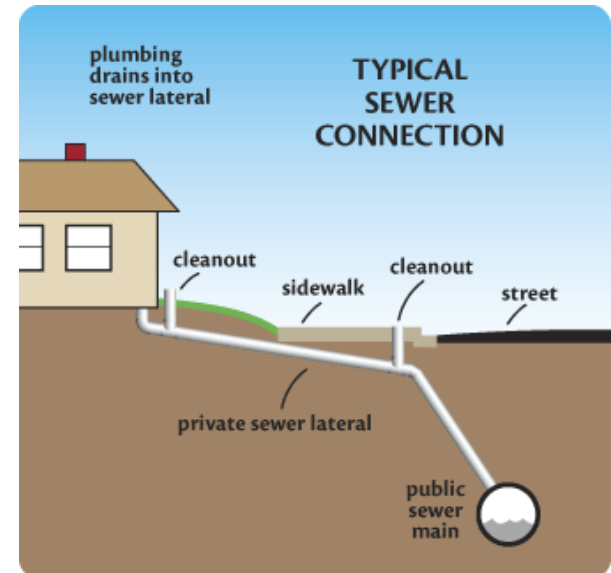
Preferential Pathways



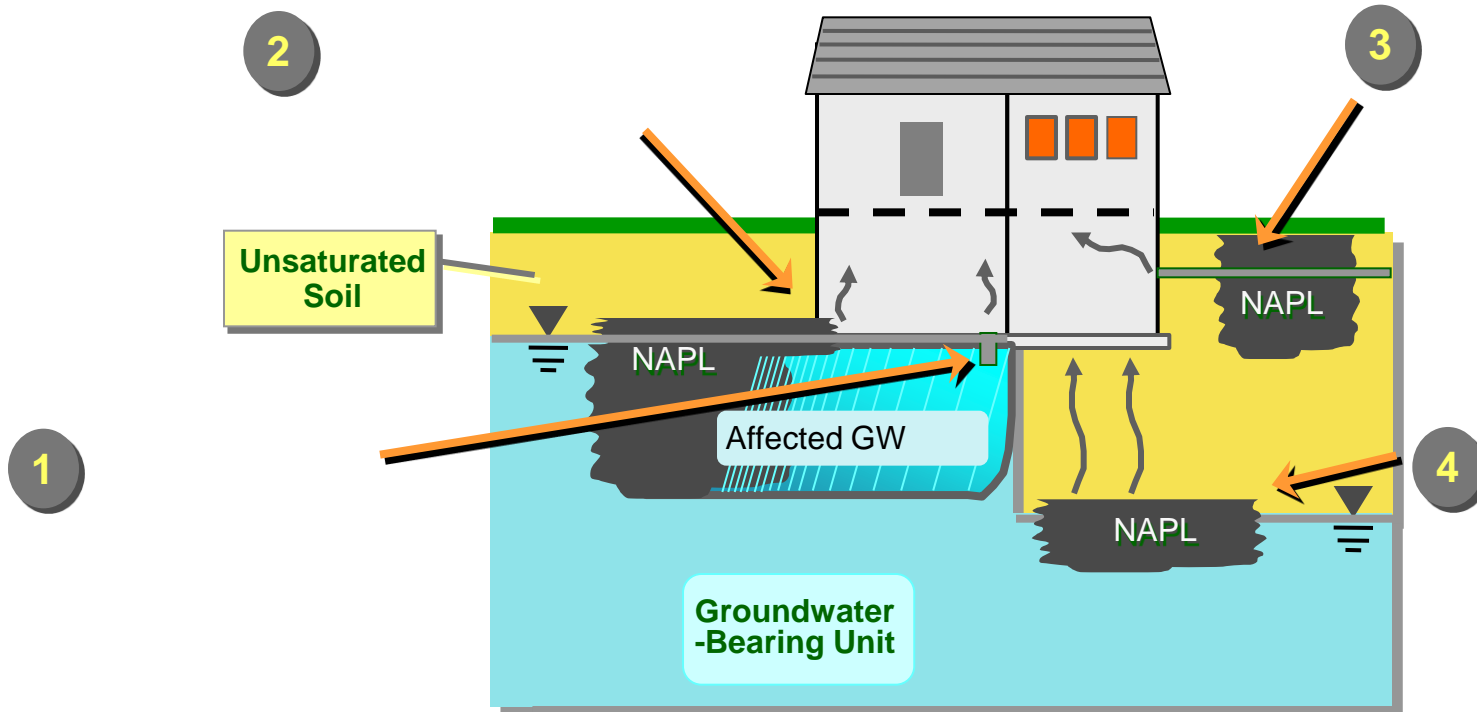
Conduit intersected LNAPL



Sewers



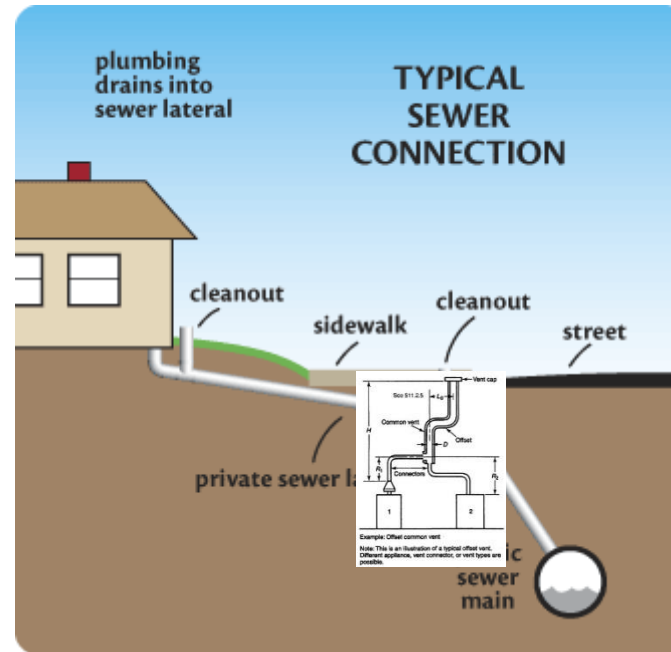
Petroleum Vapor Intrusion: Petroleum Industry Experience



KEY POINT:

- For petroleum sites, vapor intrusion is generally associated with i) direct impacts or ii) NAPL sources, but not diffusion of vapors from dissolved plumes.
- Delineation of vapor sources is important for screening

Sewers & Sewer Gas



- Sewer gas can enter a home through a floor drain, from a leaking or blocked plumbing roof vent, or (if the gases are in soil adjacent to the house) through cracks in foundations.
- Flush floor and sink drains with water to prevent the traps in pipes to the sewer from drying out.
- Occasionally check the roof plumbing vent for blockage from debris such as leaves or bird nests.

Some Sources of Sewer Gas



- The source of the sewer gas can be plumbing fixtures whose **traps have gone dry** or have lost enough water that the water seal within the trap has broken.
- **Cracks** in either plumbing drain lines or vents pipes are the other source of sewer gas leaks. If the crack is in a drain line, you often see an associated water leak. But vent pipe cracks are far more elusive.
- Sewer gas problems can also be caused by plumbing **vent pipes that are clogged**.
- Sewer gas leaks can be quickly discovered by a plumber who owns a very cool machine that generates artificial smoke".
- "...illegal connection in our drain system. The person who installed the condensate drain line from our air conditioner **installed it without a vent line.**"



Odors in New Municipal Building; Built on Portion of Former Refinery Site



Odors reported in new bldg



Free product on site



Sheening present



Sampling Sewers



Sampling room with odors

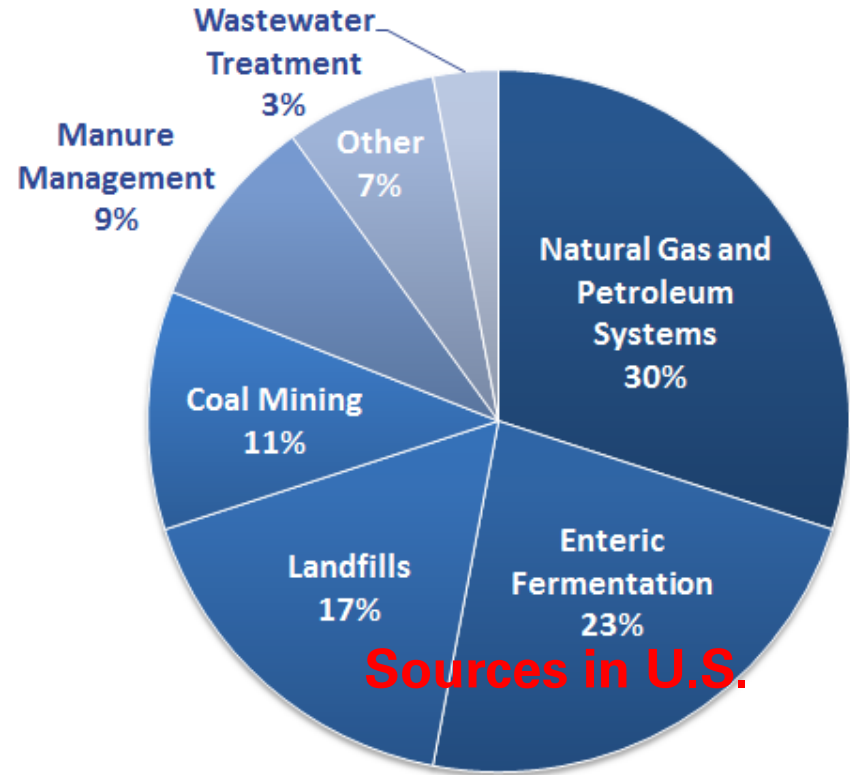


The Culprit???

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**

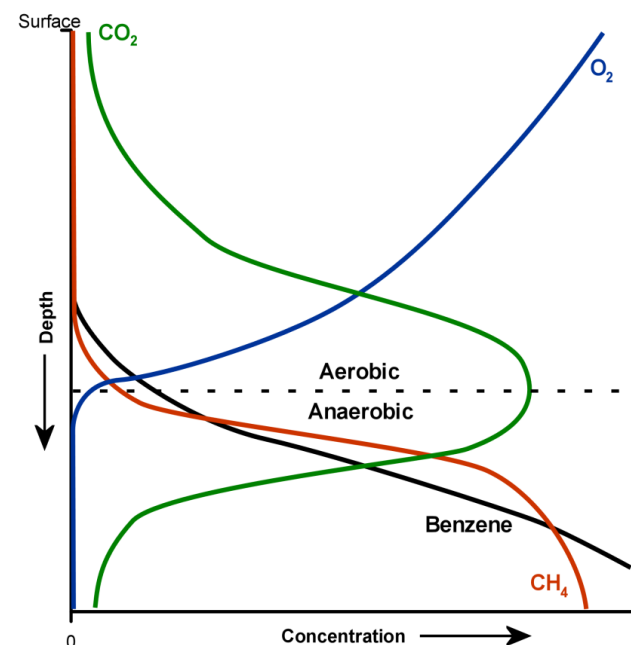


- **Most abundant organic compound on Earth**

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



- Source concentration & displacement of nitrogen and argon
- Volume
- Pressure Differential (>500 Pa [2 in. H₂O])
- Transport
 - Advective-potential problem
 - Pressure Driven- potential problem
 - Diffusion Driven-not a hazard
 - Preferential Pathways
- Dilution
- Bio-attenuation



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

Modified from J. Sepich, 2012

Sources of Methane in the Subsurface



- **Methane from biodegradation of petroleum is characterized by:**

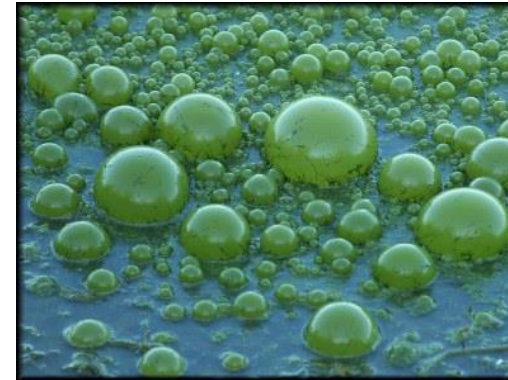
- Lack of significant concentrations of ethane and propane
- CO₂ / methane ratios between 0.3 and 0.6
- C14 age > 50,000 years old



- **'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



What Homeowners and Companies Do NOT Want



Front Yard Sampling for CH₄

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%**

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)

Natural Gas "Impurities" or "Trace Components"



Compound	NG CC	NG NN	NG SB	NG HT	NG EW	Cancer ($\mu\text{g}/\text{m}^3$)	Noncancer ($\mu\text{g}/\text{m}^3$)
Benzene	470	2,200	270	49,000	20	0.310	31.00
Cyclohexane	1,300	1,700	750	42,000	48	n/a	6,300.00
Ethylbenzene	35	160	-	3,500	10	0.970	1,000.00
m,p-Xylene	180	870	36	16,000	40	n/a	100.00
n-Heptane	1,000	5,000	460	51,000	29	n/a	n/a
n-Hexane	3,100	7,600	1,700	76,000	160	n/a	730.00
o-Xylene	56	180	-	3,600	12	n/a	100.00
Propene	21,000	56,000	-	-	-	n/a	3,100.00
Toluene	380	2,600	150	50,000	58	n/a	5,200.00
Methane & TPH	yes	yes	yes	yes	yes	-	-

Gasoline Pipeline Spill in Neighborhood



Emergency Response Clean Up



Basement: 1165 ug/m³
1st Floor: 1551 ug/m³

Other homes: at or below 21 ug/m³



Dune sands



**Look
Who showed
up!**