

Small Purge Sampling of MW's for Evaluating PVI and NSZD

- SAM FALL FORUM-San Diego, CA
- October 11, 2017

G. Todd Ririe

Unocal-Retired

Chevron-Retired

BP-Retired

Presently-Hiking-Biking-Fishing-Consulting....



Bob Sweeney-Environmental & Petroleum Geochemistry

What we are trying to avoid



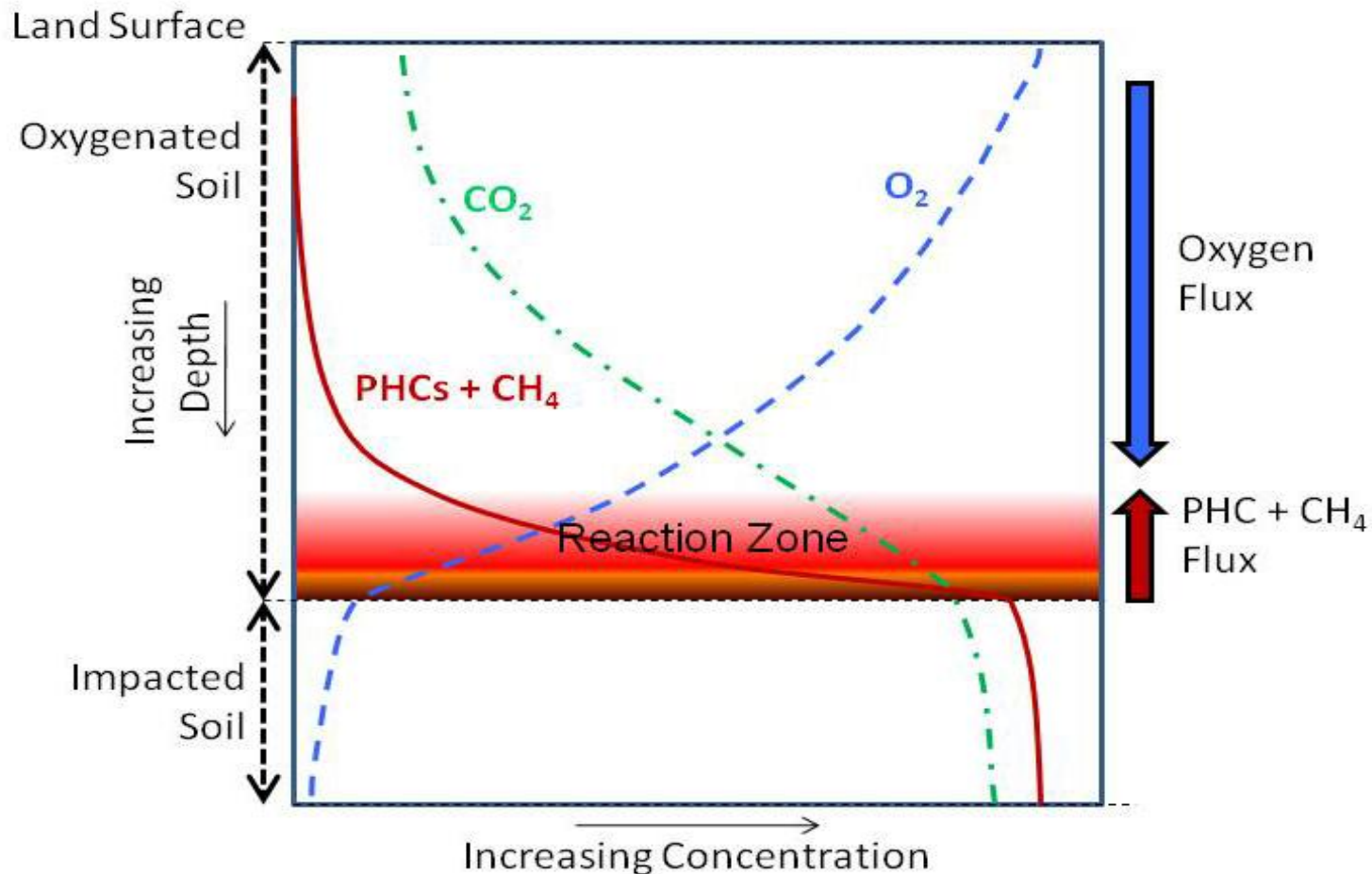
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Objectives

- Present a new method for sampling vapor from existing monitoring wells.
- Determine reason soil vapor samples in EPA data base are not consistent with diffusion/biodegradation model used in PVI investigations.
- Compare methods for collecting vapor samples from groundwater monitoring wells
 - Large purge method (Jewell and Wilson, 2011)
 - Small purge method (Sweeney and Ririe, 2017)



How can high O₂ and high TPH samples co-exist?



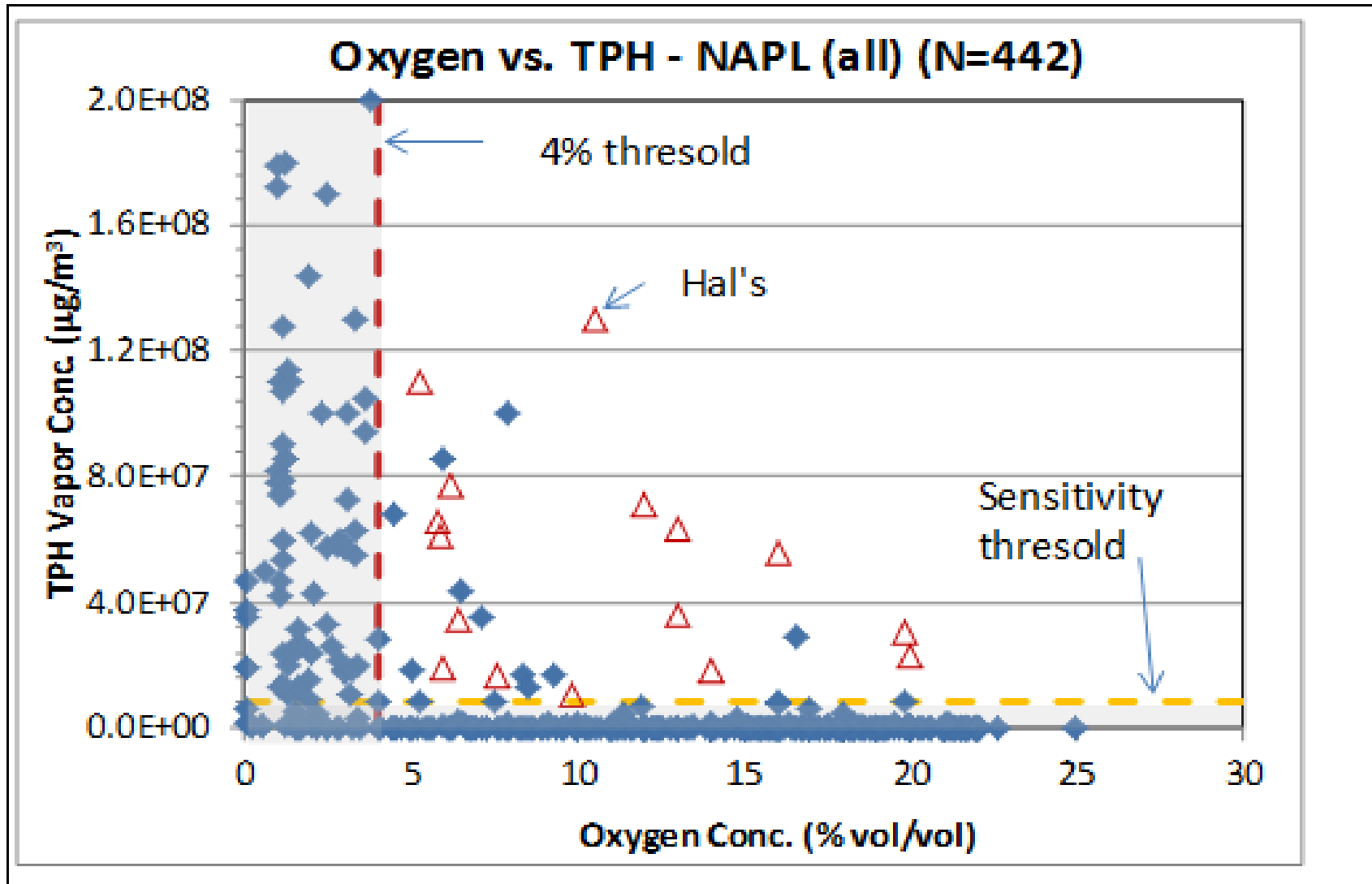
Diffusion/biodegradation model (EPA, 2012)

Above Reaction Zone: O₂ > 5 %-v; benzene < 1,000 ug/m³; TPHV < 10,000 ug/m³.

Within/Below Reaction Zone: O₂ is < 5 %-v.

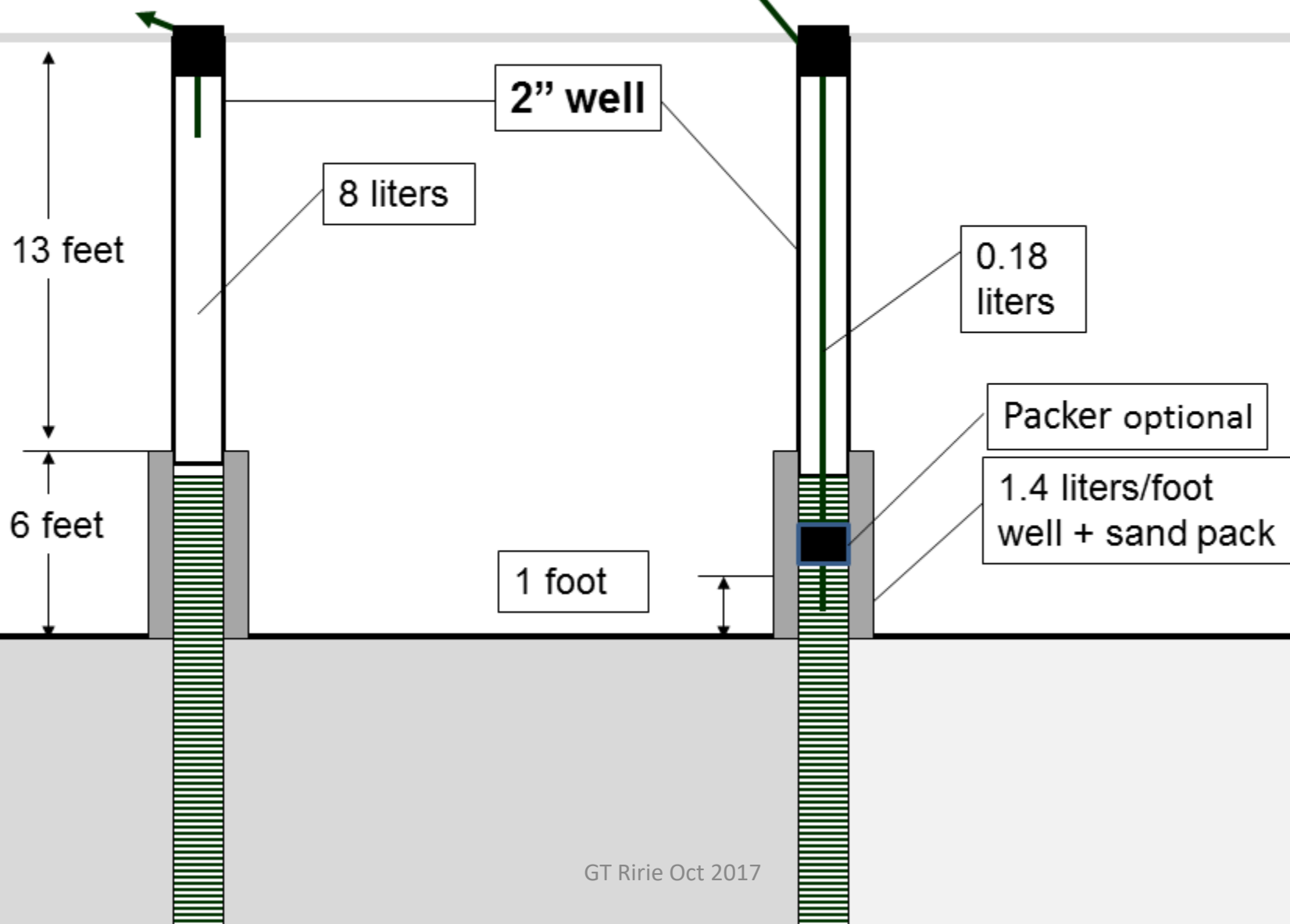
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Plot of O₂ versus TPH for vapor samples: (EPA, 2013)
most samples (red triangles) outside model limits are from Hal's



EPA Method
5-10 L/min – 20 min

Small Purge Volume Method
1 L/min – 12 sec purge

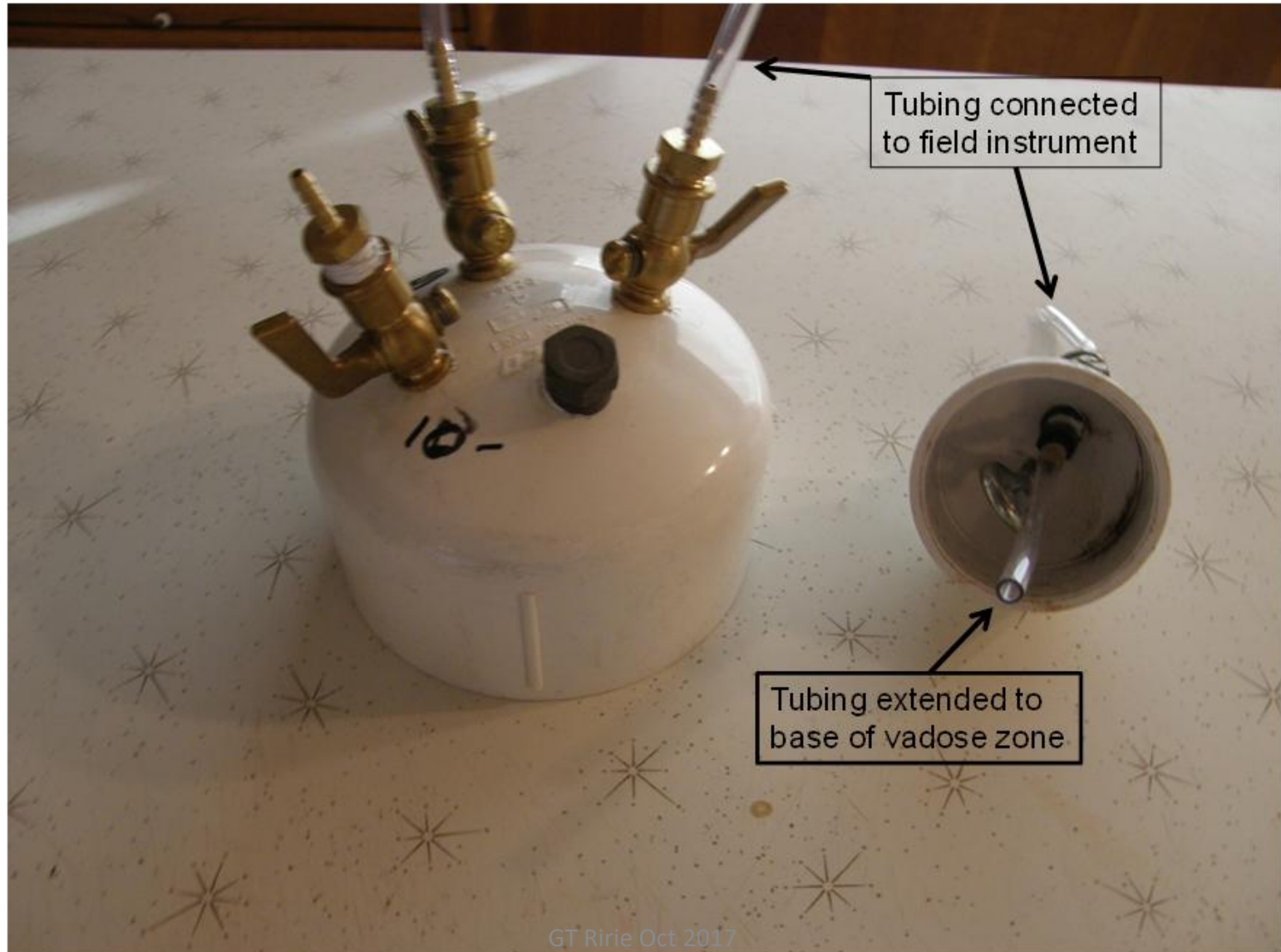


Set up for using Packer: Small Purge Sampling



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Well Caps Modified for Small Purge Sampling



Small Purge Sampling Monitoring Well at LNAPL Site



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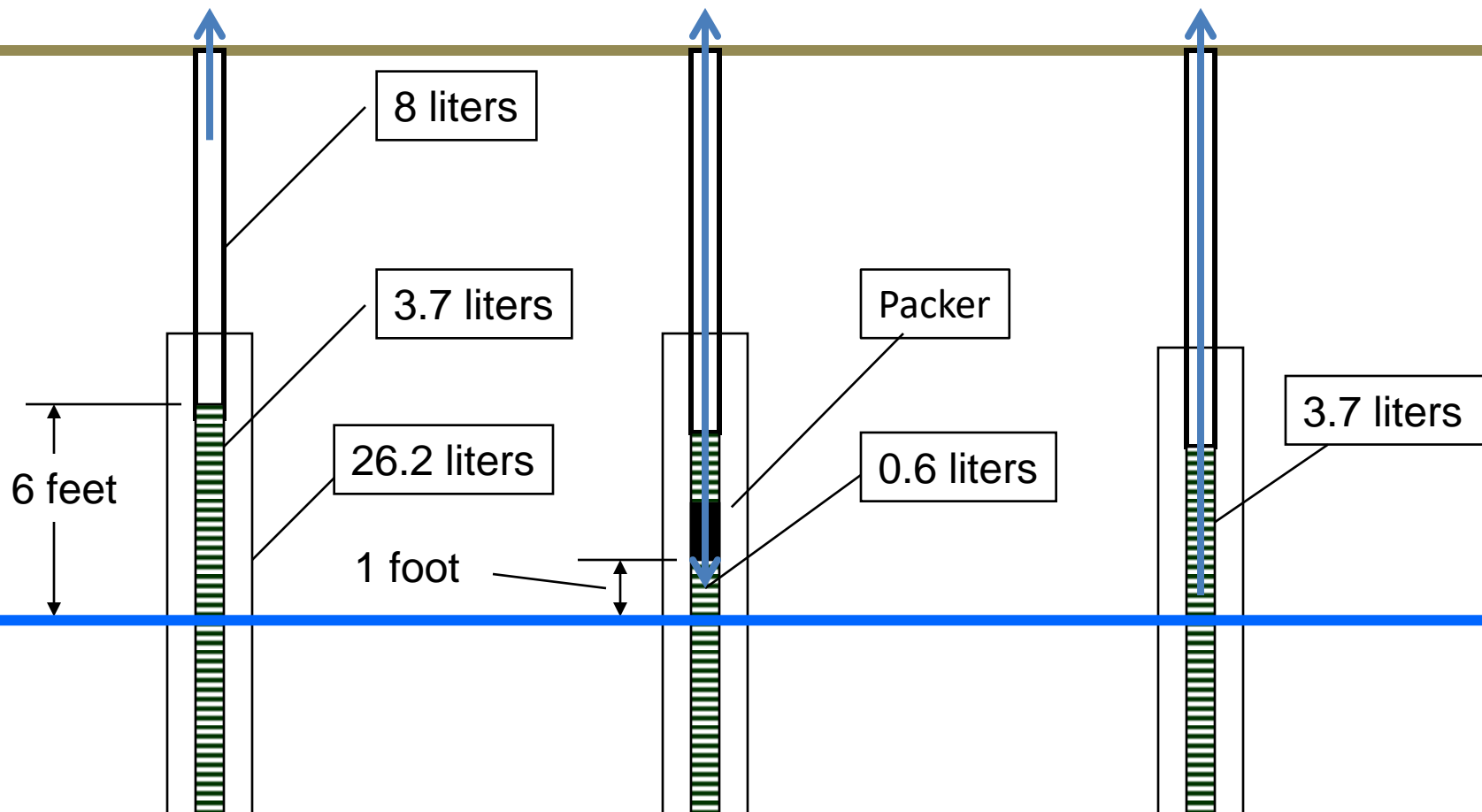
Comparison of Methods for Vapor Sampling from Groundwater Monitoring Wells

Large Purge Method -vapor sample tube below well cap

Purge 5-10 L/min for 20 min

Small Purge Method – vapor sample tube extends to base of vadose zone - extract vapor at 1 L/min

Packer needed if O₂/CO₂ conc. changes with time



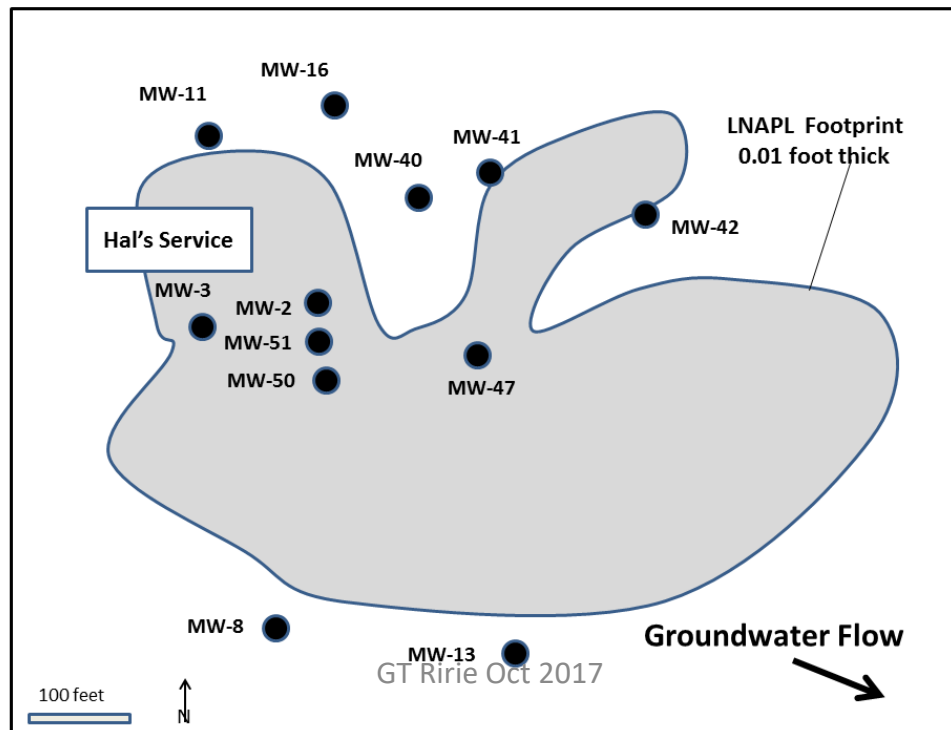
Large purge method – vapor sampled after purging well casing & sand pack

Small purge method – vapor sampled after O₂/CO₂ concentrations become stable

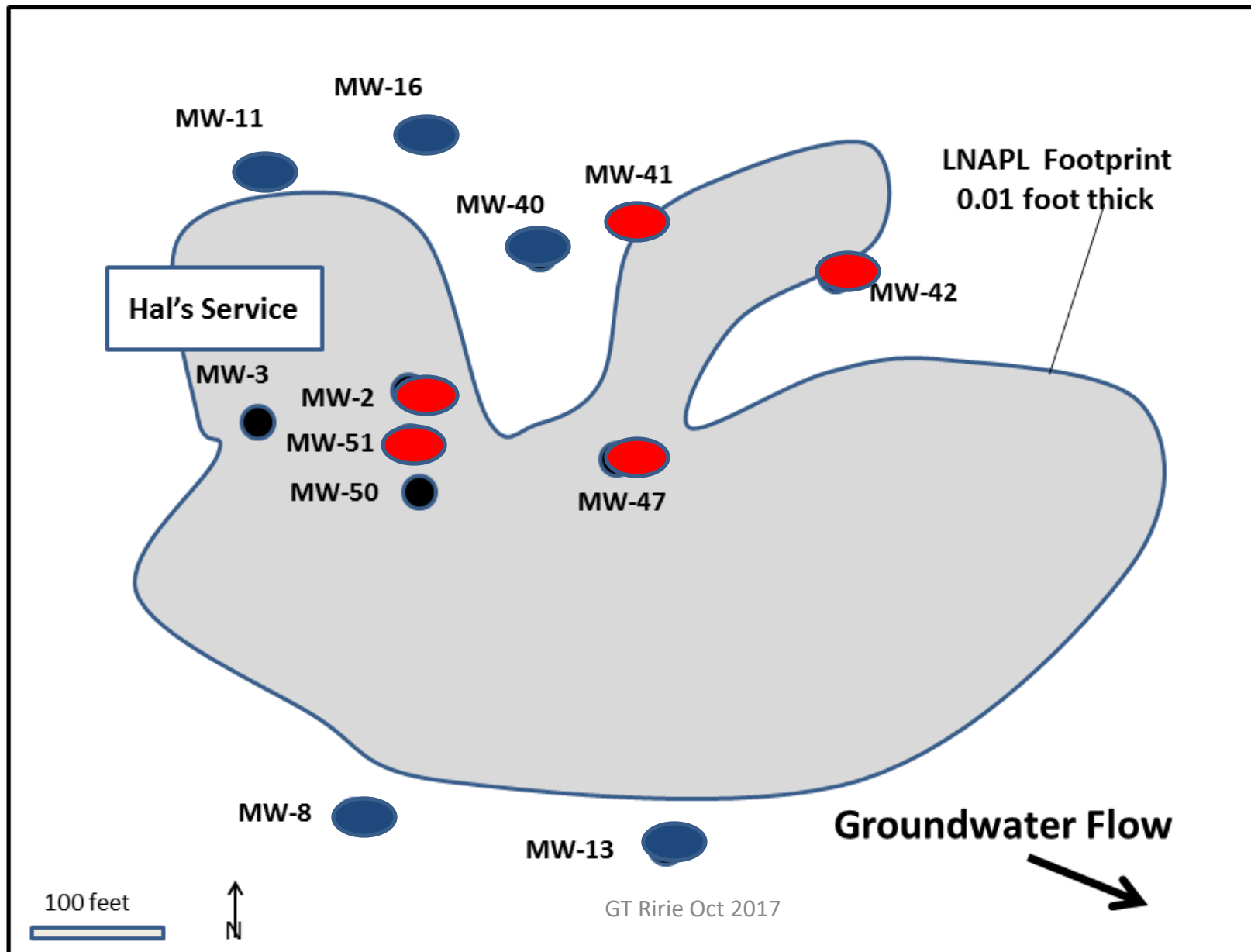
Comparison of Large & Low Flow Sampling

Well	Oxygen (%-v)		CO2 (%-v)
	Large Purge	Small Purge	Small Purge
MW-2	1.36	0 - 1.7	13.5 - 15.5
MW-50/51	18.2	<0.1	14.8 - 15.2
MW-47	17.2	<0.1	12 - 12.1
MW-41	15.4	<0.1	8.5 - 9.6
MW-42	1.63	11.2	1 - 1.2

List of O₂/CO₂ concentrations for vapor from monitoring wells.
The oxygen data for large purge method from Wilson, et al. (2013).



LNAPL Plume Map at Hal's Site, UT

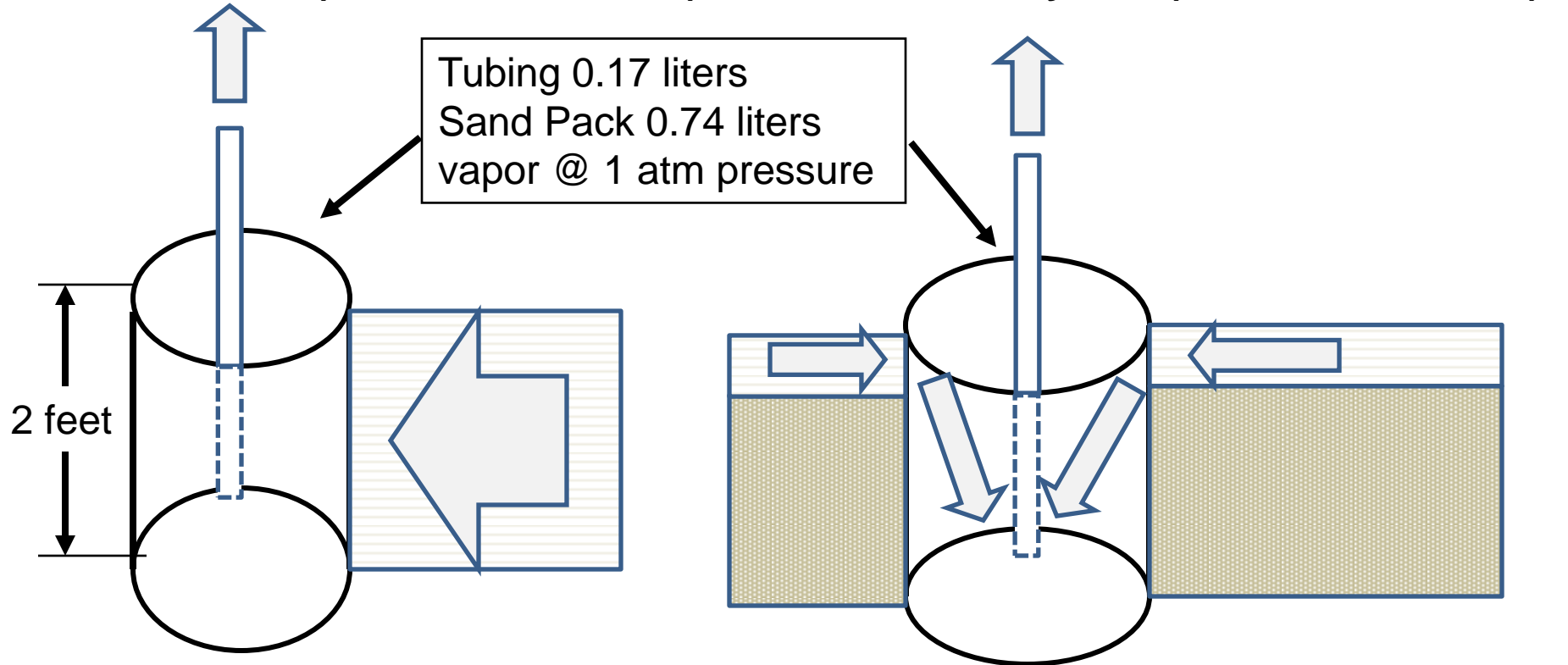


Well Log at Hal's, UT: Small Purge Sampling

Description/Remarks	OVA	Depth (ft)	Well
Asphalt		2	
Silty CLAY	7 ppm	4	
		6	
		8	
Silty fine SAND	500 ppm	10	
		12	
		14	
Clayey SILT/HC odor	2000 ppm	16	
		18	
		20	
		22	
Poorly graded SAND	2000 ppm	24	
		26	
9/6/90		28	
6 feet of product		30	
		32	

Conceptual Model – Sampling Vapor from Vapor Probes

Permeable Soil (Pressure > 0.8 atm) Low Permeability Soil (Pressure < 0.8 atm)



Permeable soil

Pump remains on (Pressure > 0.8 atm)

Uniform vapor flow from soil

Vapor from sand pack – 1st minute

Vapor from soil – 2nd minute

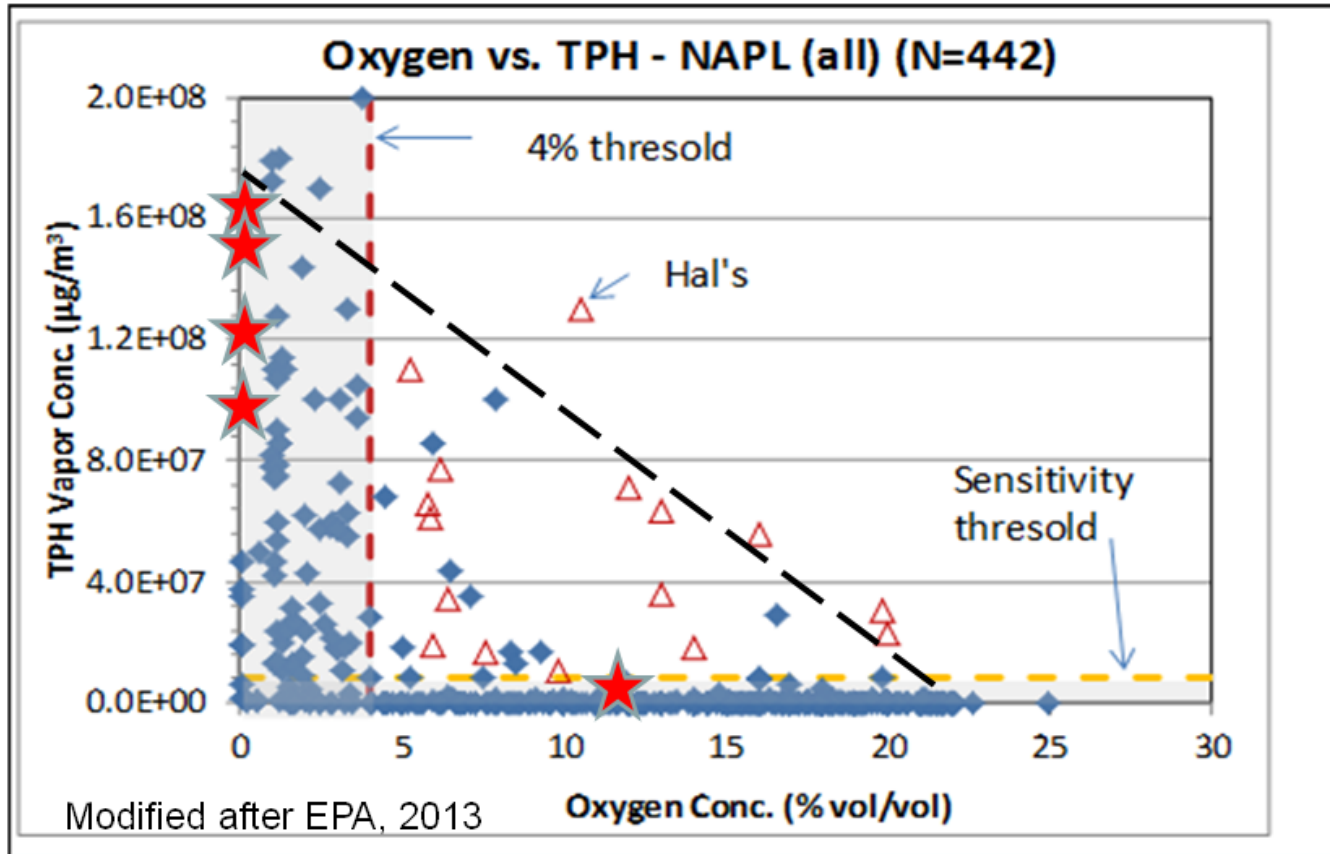
Overlying permeable soil layer

Pressure drops due to limited flow from soil

Vapor from sand pack – 15 – 30 seconds – low O₂

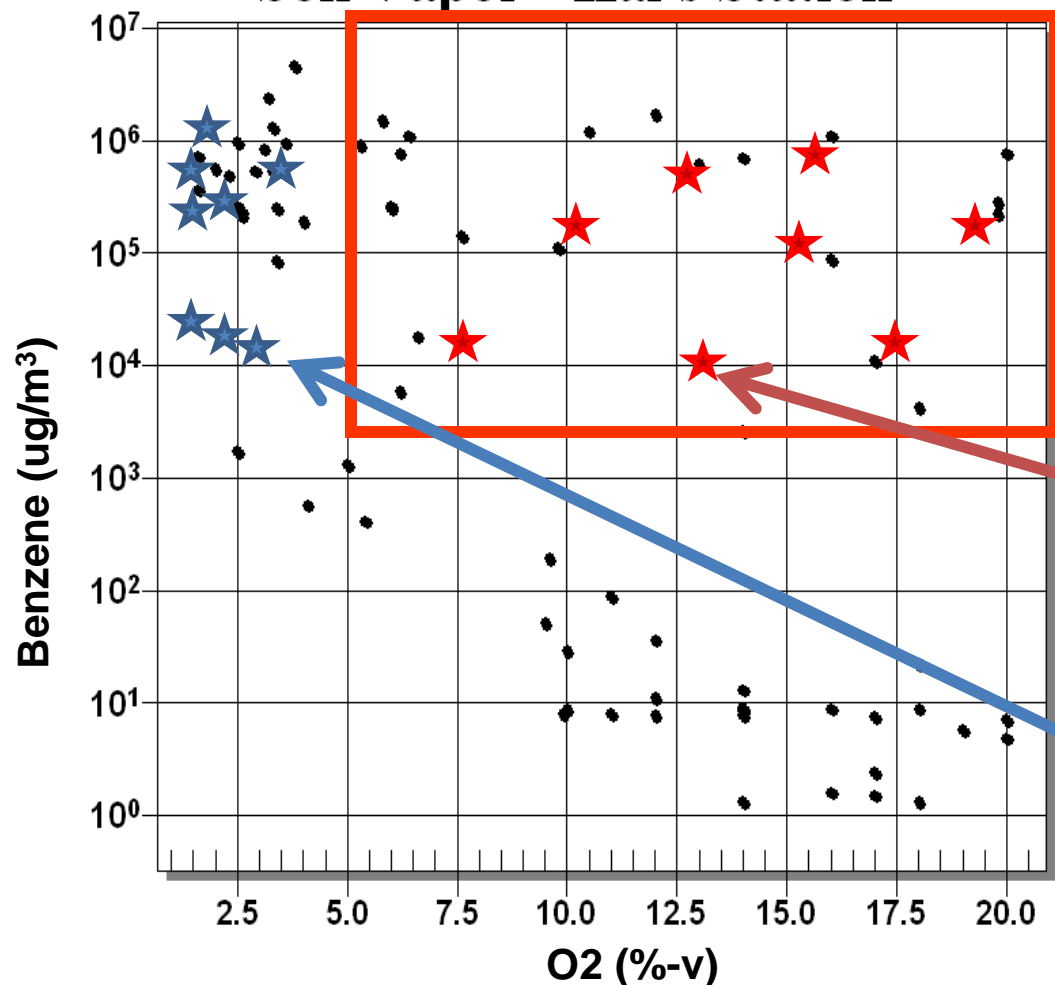
Vapor from permeable soil layer > 30 sec – high O₂

Red Stars-Low Purge Samples; dashed line-trend for mixing fresh gasoline vapor and air



Samples from Hal's with high O₂ and high TPH are the result of high volume (1 liter) sample collection in tight soils

Soil Vapor - Hal's Station



8 of the 13 vapor probes that historically yielded high O₂ and benzene concentrations were analyzed using low purge:

- O₂ in vapor extracted from permeable soil layer above LNAPL (> 0.2 liters) is > 10 %-v
- O₂ in vapor from sand pack (0.1-0.2 liters) is < 2 %-v and represents *in situ* gas near LNAPL

Small purge analyses documents **low O₂** in monitoring wells over LNAPL and **high O₂** in wells not over LNAPL.

		Oxygen (%-v)			Carbon Dioxide (%-v)					
Well	Depth (feet)	Before (%-v)	Lab (%-v)	After (%-v)	Before (%-v)	Lab (%-v)	After (%-v)	Storage	N ₂ (%-v)	CH ₄ (ppm-v)
a) Over LNAPL footprint										
MW-50*	17.5	<0.1	2.0	<0.1	14.8	14.0	15.2	Tedlar	78	2,200
MW-2	17	1.7	2.0	0.9	15.2	14.8	13.5	Tedlar	71.1	3,800
MW-2	17	<0.1	4.9	<0.1	15.5	12.0	14.8	Vial	78	4,090
MW-3	17.5	<0.1	3.5	<0.1	12.3	13.0	15	Tedlar	84	1,900
MW-41	17.5	<0.1	4.0	<0.1	8.5	8.7	9.2	Tedlar	93	ND
MW-41	17.5	<0.1	1.5	<0.1	9.2	10.0	9.6	Vial	83.4	6
MW-42	17.5	11.2	12.3	11.2	1.2	1.7	1	Vial	81.6	9
MW-47*	17.5	<0.1	NA	<0.1	12.1	NA	12	none	NA	NA
b) Not over LNAPL footprint										
MW-8	17.5	5.1	8.8	5.5	7.8	7.2	7.5	Vial	79.5	4
MW-11	17.5	NA	18.0	NA	NA	2.0	NA	Vial	74.8	2
MW-11	17.5	18.6	21.0	18.5	1.5	0.73	1.6	Tedlar	82	ND
MW-11	17.5	13.6	13.8	13.2	3.9	4.7	3.8	Vial	76.8	1
MW-13	17.5	5.6	6.9	5.3	5.3	5.9	5.4	Vial	81.8	131
MW-16	17.5	13.4	13.5	13.5	4.7	5.5	4.6	Vial	75.5	2
MW-40	17.5	15.2	19.0	15.2	3.4	1.7	3.4	Tedlar	82	ND
MW-40	17.5	15.2	15.3	15.4	3.3	4.0	3.1	Vial	76.0	1

Oxygen, carbon dioxide, nitrogen and methane results for monitoring wells sampled without the packer.

Tedlar bags were sent to HP Labs and Evacuated Vials were sent to VaporTech

Field measurements of O₂ and CO₂ were made before and after sample collection for the laboratories

“Before’ field measurements were made after 1 liter of vapor removed from well.
Following collection of sample for lab analysis, the ‘after’ measurement was made.

Conclusions and Lessons Learned

- High O₂ and high TPH concentrations in soil vapor are not representative of *in situ* soil vapor composition above LNAPL.
- The low purge method for sampling vapor from monitoring wells yields results that are consistent with accepted models for hydrocarbon vapor transport.
- The low purge method for sampling vapor from monitoring wells can also be used in NSZD studies.

