

**Vapor Study at Hal's Service Station Site,  
Green River, Utah**

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in partnership with the Utah Dept. of Environmental Quality

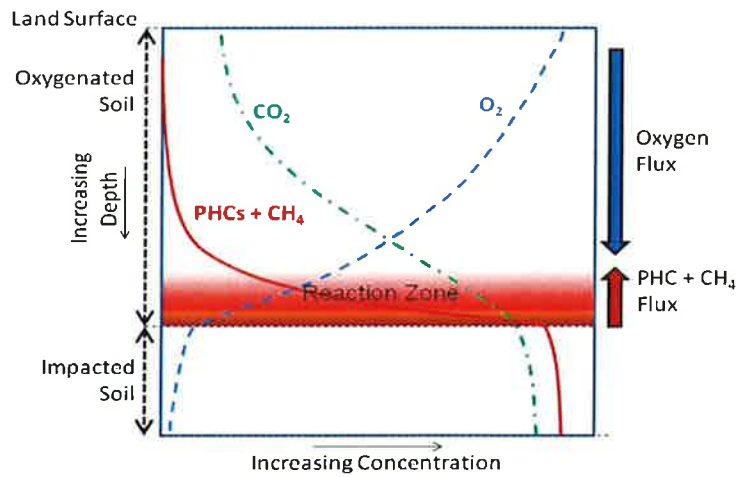
Slide 1 - Study supported by API and carried out in conjunction with Utah Department of Environmental Quality

## Overview

- **Objective 1:** Determine reason soil vapor samples from Hal's site are not consistent with diffusion/biodegradation model used in PVI investigations (EPA, 2013)
  - Coexisting high concentrations of O<sub>2</sub> (> 5%-v), benzene (> 1,000 ug/m<sup>3</sup>) and TPH-v (>10,000 ug/m<sup>3</sup>) in vapor probe samples
- **Objective 2:** Compare methods for collecting vapor samples from groundwater monitoring wells
  - Large purge method (Jewell and Wilson, 2011): used by UDEQ to preview sites for potential PVI risk
  - Small purge method: used in this investigation to collect vapor from near base of screened interval in vadose zone
    - Assumes vapor at base of screened interval is in equilibration with vapor in sand pack/adjacent soil layer

Slide 2 – The approach for objective 1 is to measure soil gas composition as a function of the amount of soil vapor derived from the soil. The approach for objective 2 is to determine whether or not soil vapor at the base of the vadose zone is anaerobic or aerobic.

## How can high O<sub>2</sub> and high TPH samples co-exist?



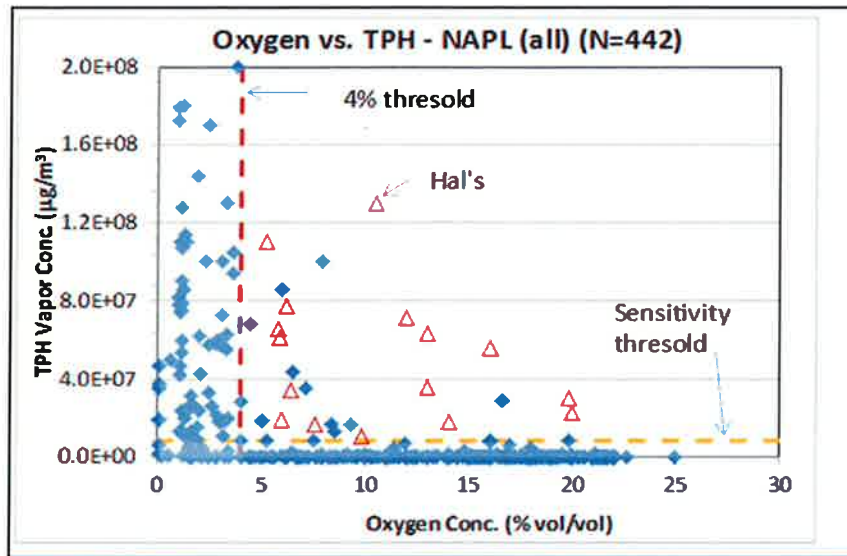
Diffusion/biodegradation model (taken from EPA, 2012):

Above Reaction Zone: O<sub>2</sub> > 5 %-v; benzene < 1,000 ug/m<sup>3</sup>; and TPHV < 10,000 ug/m<sup>3</sup>.

Within/Below Reaction Zone: O<sub>2</sub> is < 5 %-v.

Slide 3 - Conceptual model used to evaluate potential PVI risk. Based on model, high concentrations of benzene and oxygen can only exist within a narrow depth range above the source of TPH vapor.

**Plot of O<sub>2</sub> versus TPH for vapor samples: EPA, 2013**  
**most samples (red triangles) outside model limits are from Hal's**



Aerobic mineralization paradigm

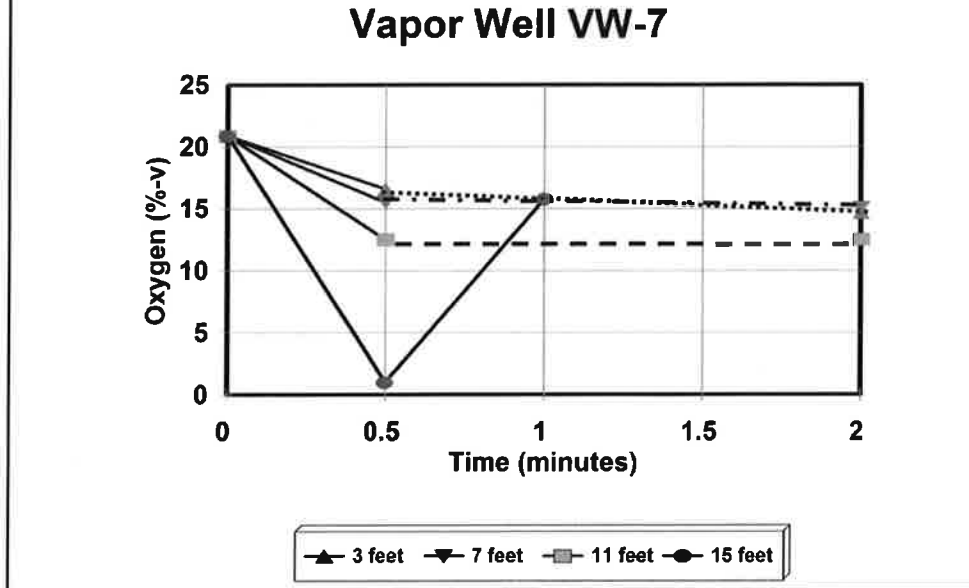
Slide 4 - Measurements with O<sub>2</sub> < 4 % or TPHV < 10,000 ug/m<sup>3</sup> are considered consistent with diffusion/biodegradation model. Most samples falling outside limits for the model are soil vapor samples taken at Hal's site, Green River Utah.

Field set up for collecting and analyzing vapor samples. Measurements of O<sub>2</sub> concentration were continually made on extracted vapor from the wells.



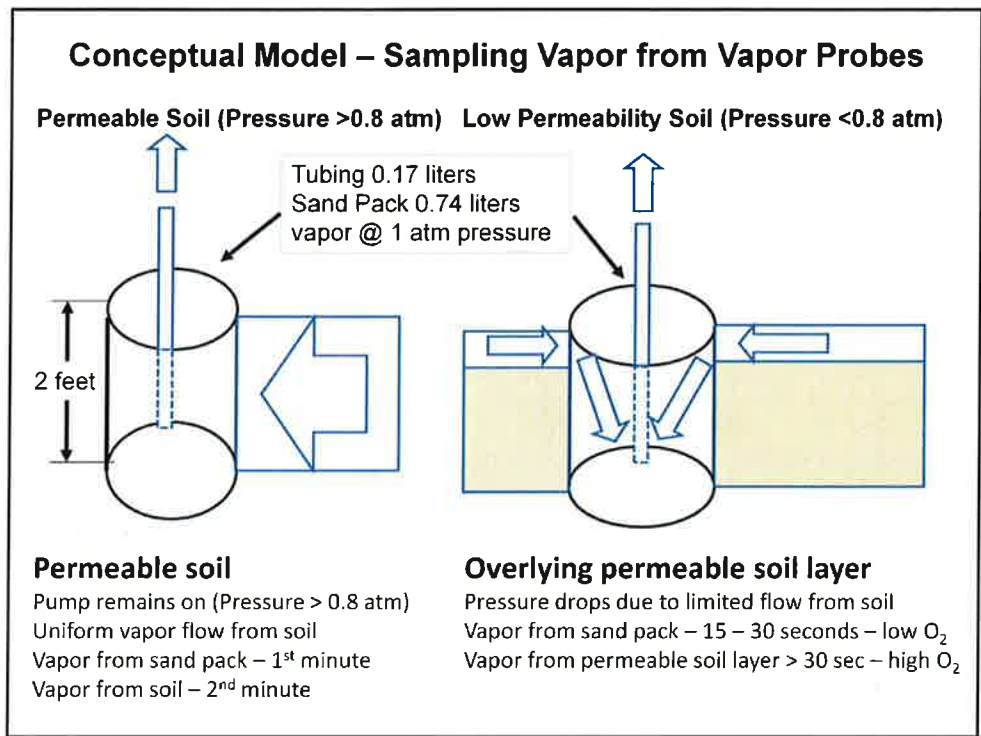
Slide 5 - The approach used to address Objective 1 was to continually monitor gas composition (O<sub>2</sub>/CO<sub>2</sub>) of vapor extracted from soil so that any change in the composition of vapor would be documented. An Eagle field meter was connected to individual vapor probes and soil vapor was extracted at a rate of 1 L/min (or less). The pump on the instrument is set to stop when pressure was reduced to 0.8 atmospheres pressure in tubing (sand pack).

**Oxygen Concentration Trends for Vapor Probes at VW-7**  
Previously 1 liter samples from 15 feet had  $O_2 > 10\% -v$



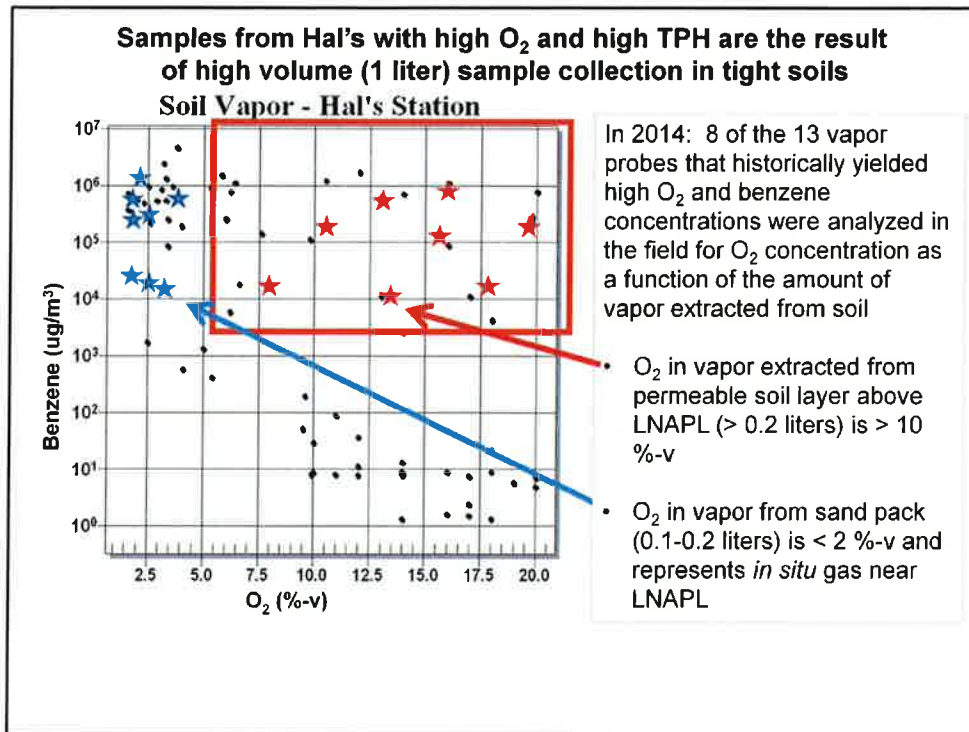
Slide 6 - At depths 3, 7, and 11 feet:  $O_2$  initially decreased (remove air from tube) – then remained relatively constant for 2 minutes.

At depth 15 feet (LNAPL):  $O_2$  decreased to  $< 2\% -v$  (vapor from sand pack) before rapidly increasing to above 15 vol.% when pump would turn off due to pressure  $< 0.8$  atmosphere pressure.



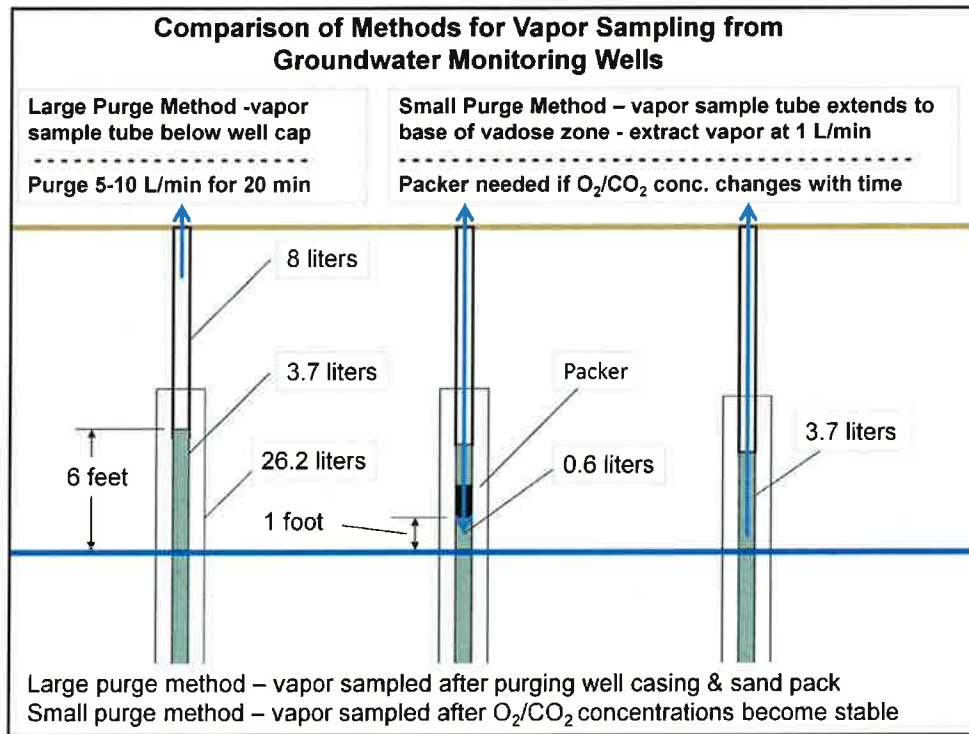
Slide 7 - McAlary, et al. (2009) presents model for sampling vapor from low permeable soil where pressure in sand pack is reduced by removal of vapor during sample collection. With time, vapor will be replenished into sand pack by 'advective' flow due to pressure gradient developed between sand pack and surrounding soil.

*McAlary, Todd A., Paul Nicholson, Hester Froenevelt and David Bertrand (2009): A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low Permeability Soils); Ground Water Monitoring & Remediation, 29 #1, pp. 144-152.*



Slide 8 - The 1 liter samples previously collected at Hal's contained a mixture of 'low O<sub>2</sub>/high benzene' vapor from sand pack and 'high O<sub>2</sub>' vapor from permeable soil overlying LNAPL





Slide 9 - Large purge method used by UDEQ to preview sites by measuring benzene concentration in vapor from permeable soil above LNAPL. Small purge method assumes vapor in screened portion of well is in equilibrium with adjacent soil. Packer used when vapor from casing causes change in O<sub>2</sub>/CO<sub>2</sub> concentrations while extracting vapor from base of monitoring well. Large purge method - Jewell, K.P. and J.T. Wilson (2011): *A New Screening Method for Methane in Soil Gas using Existing Groundwater Monitoring Wells; Groundwater Monitoring & Remediation* 31 #3, 82-94.

**Small purge analyses documents low O<sub>2</sub> in monitoring wells over LNAPL and high O<sub>2</sub> in wells not over LNAPL**

Well	Depth (feet)	Oxygen (%-v)			Carbon Dioxide (%-v)			Storage	N <sub>2</sub> (%-v)	CH <sub>4</sub> (ppm-v)
		Before (%-v)	Lab (%-v)	After (%-v)	Before (%-v)	Lab (%-v)	After (%-v)			
<b>a) Over LNAPL footprint</b>										
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>b) Not over LNAPL footprint</b>										
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 O<sub>2</sub> and CO<sub>2</sub> 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.

Slide 10 - At Hal's, long well casing in vadose zone (19 feet) allowed for 3 – 5 liters of vapor to be extracted from monitoring wells without the O<sub>2</sub>/CO<sub>2</sub> composition to change significantly. With the exception of MW-42, vapor at base of vadose zone is anaerobic over LNAPL and aerobic in soil without LNAPL. Atmospheric composition in field – oxygen = 20.9 %-v and carbon dioxide = <0.1 %-v.

**Groundwater monitoring wells can be used to collect viable soil gas data when sampled using low purge method**

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 O<sub>2</sub>/CO<sub>2</sub> concentrations for vapor from monitoring wells.  
The oxygen data for large purge method from Wilson, et al. (2013).

- MW-2 is in source area with hydrocarbon impacted soil throughout the vadose zone – both methods yield equivalent results – soil vapor is anaerobic
- Other wells are at locations where LNAPL exists at top of groundwater
  - With the exception of data from MW-42, vapor sampled by large purge method is aerobic (O<sub>2</sub> >15%-v).
  - With the exception of data from MW-42, vapor sampled by small purge method is anaerobic (O<sub>2</sub><0.1%-v).

Slide 11 - There could have been a problem with small purge sample collection at MW-42 (bad connection?)

## Conclusions and Lessons Learned

- The previously collected measurements of unusual high O<sub>2</sub> and high TPH concentrations in soil vapor at Hal's are not representative of *in situ* soil vapor composition at the site.
  - The measured vapor composition is the result of a mixture of *in situ* anaerobic vapor from hydrocarbon-impacted soil and aerobic vapor extracted from permeable soil layers adjacent to the sand-pack.
  - Because of the presence of fine grained/low permeability soils at the Hal's site, a representative vapor sample from some of the probes can only be collected by using a low volume sampling approach.

## Conclusions and Lessons Learned

- The low purge method for sampling vapor from monitoring wells yields results that are consistent with the presence/absence of a hydrocarbon smear zone at the base of the vadose zone.
  - With one exception, vapor from the smear zone footprint is essentially anaerobic
  - The oxygen concentration upgradient of the smear zone is > 13 %-v.
  - The oxygen concentration downgradient of the smear zone is > 5 %-v.
- The low purge method for sampling vapor from monitoring wells differs from the large purge method described in Jewell and Wilson (2011)
  - The low purge method collects vapor that is representative of adjacent soil
  - The high purge method collects vapor that is representative of permeable soil within the screened interval of the well