Vapor Intrusion Risk Pathway: Sampling & Analytical Issues

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This presentation is an excerpt of the vapor intrusion training that Dr. Hartman has been presenting to Federal & State regulatory agencies, DOD facilities, consulting groups, and stakeholders around the country. As of March 2013, this training has been given to over 30 State Regulatory agencies, EPA-OUST, ITRC, Brazil & Australia. Training has also been given to many PRPs such as the major oil companies, DOD, & numerous consulting groups.

Lecture notes are at the bottom of each slide so that if played out as a hard-copy, the presentation can be a useful reference document.

Exclusion Criteria: A PVI Pathway Game Changer

- Step 1: Can Site Be Screened Out?
  - Based upon concentration & depth to source
  - In CA if site is an active fueling station
- Step 2: Can "Screen-Out Data" be Collected?
- Step 3: Do PVI Assessment

VI Assessments Much Simpler & Less Expensive

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So called "exclusion criteria", meaning criteria to eliminate sites from further vapor intrusion assessment based upon source concentration and distance between the source & receptor have fundamentallychanged the process for investigating the VI pathway at petroleum sites.

Table 3 Required Vertical Separation Distance Between Contamination And Building Foundation, Basement, Or Slab.

Media	Benzene	TPH	Vertical Separation Distance (feet)*
Soil (mg/kg)	≤10	≤250	6
	>10 (LNAPL)	>250 (LNAPL)	15**
Groundwater (ug/L)	≤ 5,000	≤30,000	6
	>5,000 (LNAPL)	>30,000 (LNAPL)	15**

The thresholds for LNAPL indicated in this table are indirect evidence of the presence of LNAPL. These thresholds may vary depending on site-specific conditions (e.g., soil type, LNAPL source). Investigators may have different experiences with LNAPL indicators and may use them as appropriate. Direct indicators of LNAPL also apply; these include measurable accumulations of free product, oily sheens, and saturated bulk soil samples.

*Vertical separation distance represents the thickness of clean (TPH ≤ 100 mg/kg), biologically active soil between the source of PHC vapors (LNAPL, residual LNAPL, or dissolved PHCs) and the lowest (deepest) point of a receptor (building foundation, basement, or slab).

** EPA recommends that sub-slab monitoring be used to evaluate the risk of vapor intrusion whenever LNAPL is present in any sample and the vertical separation distance is less than 15 feet. When LNAPL is

EPA-OUST's soon to be released PVI guidance contained exclusion criteria for soil & groundwater contamination and NAPL in the latest draft.

CA Low-Threat Closure Policy

Site Screens Out from VI Pathway:

- If 30’ of Biozone, NAPL screens out
  - Vertically & horizontally
- If 10’ of Biozone, benzene up to 1000 ug/L
- If 5’ of Biozone, benzene up to 100 ug/L

Bioattenuation zone: TPH-soil < 100 mg/kg

Note: O_2 not Required

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California released the low threat closure policy (LTCP) last summer (2012). It contains exclusion criteria similar to, but more conservative, than EPA’s.

Allowable Benzene in GW

1e-6 risk, Residential Scenario

- DTSC VI Guidance:

0.084 ug/m3 / 0.002 = 0.42 ug/L / 0.2 = 0.21 ug/L

~5000x lower than LTCP of 1000 ug/L

- New EPA OSWER Guidance:

0.31 ug/m3/0.001 = 0.31 ug/L/0.2 = 1.55 ug/L

~3300 times lower than EPA-OUST Value of 5000 ug/L

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The screening levels for dissolved benzene contamination in the CA-LTCP are 5000 times higher than CA-EPA levels in their VI guidance.

The screening levels for dissolved benzene contamination in the EPA-OUST draft guidance are 5000 times higher than in the EPA-OSWER VI guidance.

Clearly these new policies have major ramifications on the number of PVI sites requiring VI assessments.

Low-Threat Closure Policy
The Power of Oxygen

CA-LTCP: If oxygen in soil gas >4%:

- Separation distance drops from 10’ to 5’ for benzene up to 1000 ug/L
- Soil gas SLs increase by 1000x!

TPH-soil required for all scenarios but O2 not

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Oxygen plays a key role in some State policies. In CA, the presence of oxygen decreases the separation distance by a factor of 2 and increases soil vapor screening levels by 1000 times!

Soil Gas Allowed Levels

Benzene in Soil Gas, Residential Receptor, 1-6 Risk

	RBSL (ug/m^3)
DTSC Sub-slab	1.6
CHHSL	37
DTSC – Step 5	42
CA Low-Risk Policy: O2<4%	85
CA Low-Risk Policy: O2>4%	85,000

Ambient levels: 1 to 10 ug/m3

This table summarizes the various soil gas screening levels for benzene in CA. Note:

1) The sub-slab value is lower than ambient levels.

2) The presence of oxygen increases soil gas screening values by 1000 times.

NJDEP Gasoline Exclusion Criteria

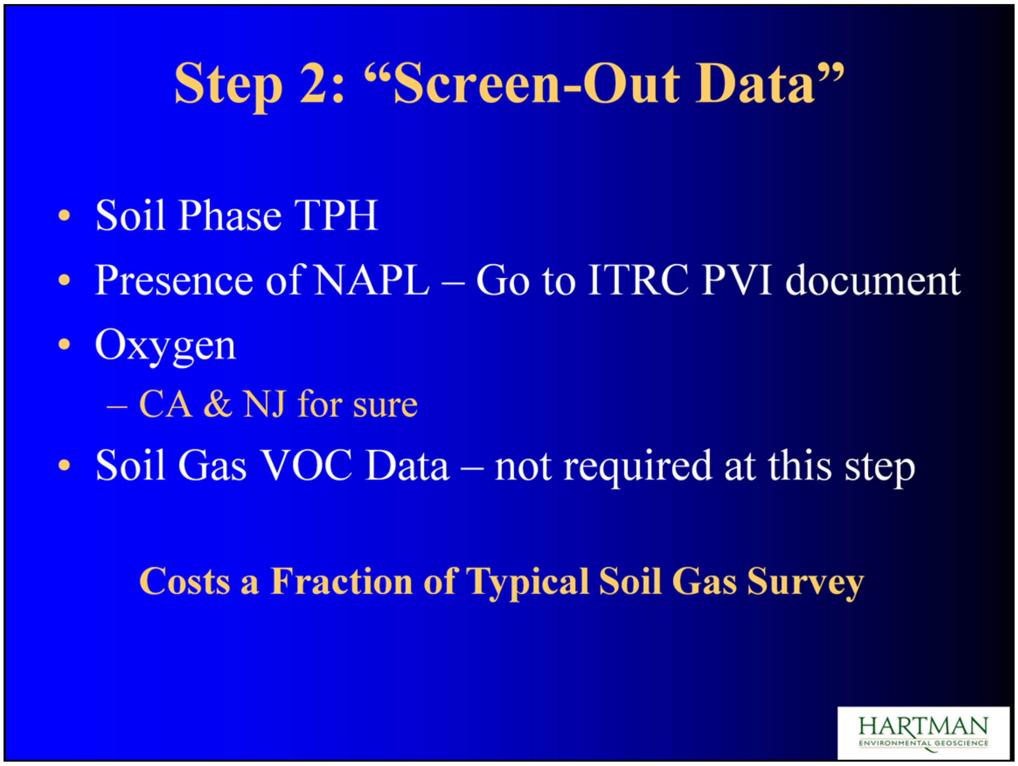
VI Investigation is not required when:

- ≥10 ft between water table and foundation and benzene in GW is ≤1,000 µg/L; or
- ≥5 ft between seasonal high water table and foundation, oxygen levels measured at ≥2% (v/v), and benzene in shallow GW is ≤1,000 µg/L.

O_2 Drops Separation Distance from 10’ to 5’

8

The presence of oxygen drops the separation distance in NJ by a factor of 2.



Some sites may not have the soil phase data or oxygen data to screen out. Rather than perform a full VI investigation, an intermediate and less costly step is to collect the additional data to determine if the site can be screened out. These data will be primarily soil phase data and oxygen data. These data are far less expensive to obtain than typical vapor intrusion VOC data..

Step 3: PVI Specific Sampling Issues

- Soil Gas VOC Analysis
  - Benzene, ethylbenzene & naphthalene
  - TPH??
- Might Need to Sample <5' bgs
  - If samples >5' bgs exceed allowable levels
  - How to know? On-site analysis best
  - If not, collect samples anyway
- Always Collect Oxygen Data

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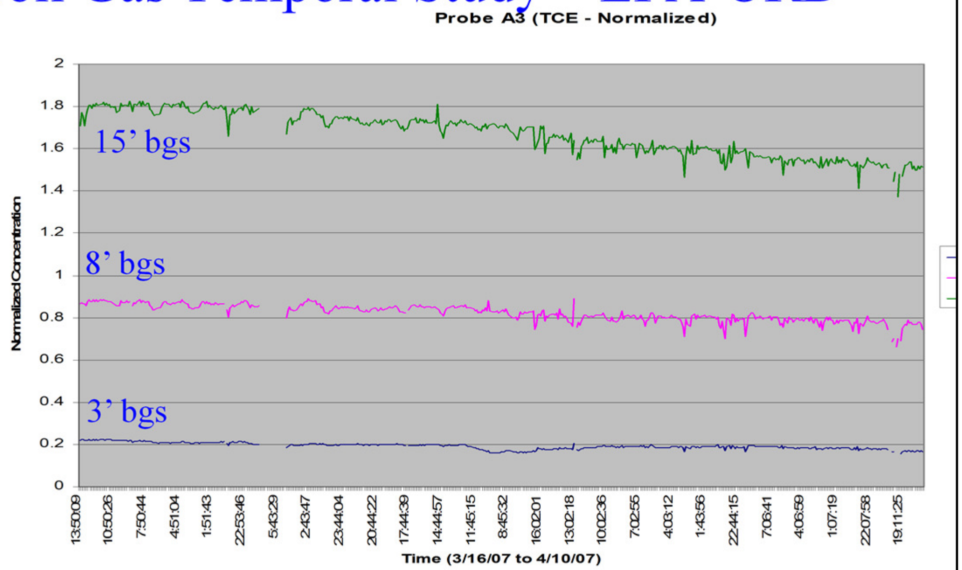
There are some differences in soil gas sampling for petroleum hydrocarbon VOCs than for chlorinated solvents.

The COCs need to be determined and vary from State to State.

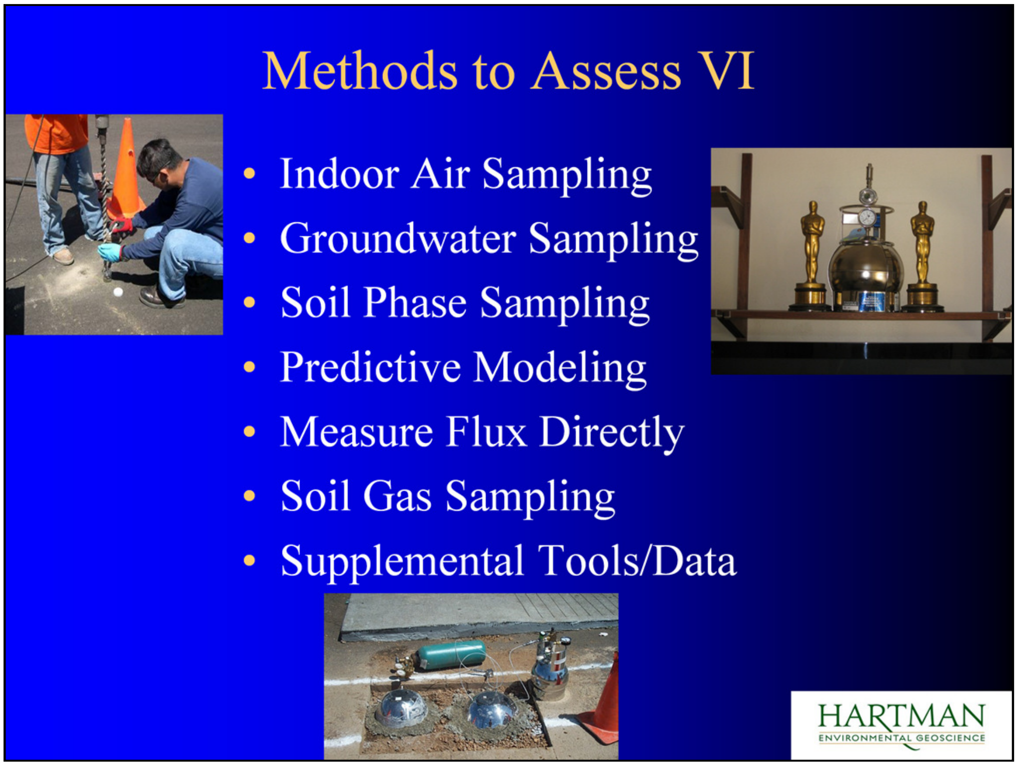
If samples at deeper depths exceed allowable values, shallower samples (<5' bgs) may need to be collected to document the effect of bioattenuation.

Oxygen data should always be collected to the document presence of the aerobic zone.

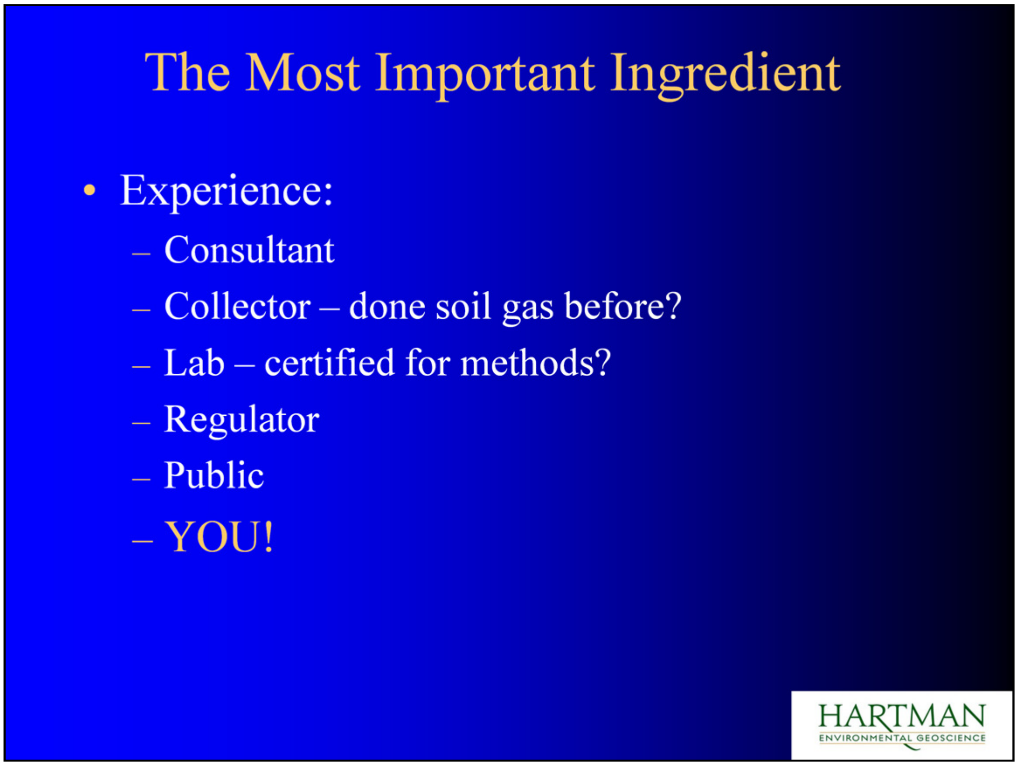
Soil Gas Temporal Study – EPA-ORD



This is a plot of data recently collected for an EPA funded study by an automated instrument at at Vandenberg AFB site from three probes at the same location but at different depth (3', 8, & 17' bgs). This plot consists of over 500 points per probe collected once per hour over a 4 week period from mid March to mid April 2007. The soil gas concentrations varied by less than 10% over these four days even for probes only 3 feet below the surface.

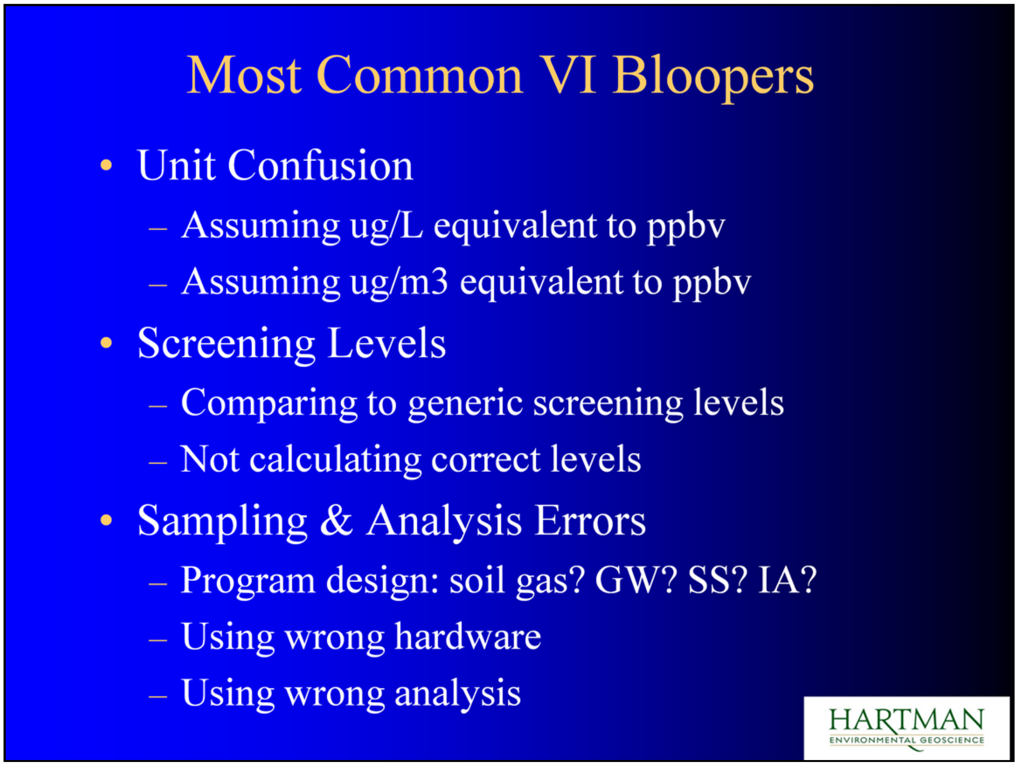


These are the most common methods used in a vapor intrusion assessment.



The most important ingredient for cost effective and efficient VI investigations is the experience of the people out in the field. Is the consulting firm experienced at VI investigations? Is it a routine part of their services or an occasional part? Do they put experienced staff in the field who can think or junior staff who aren't experienced?

The same applies to their subcontractors. Does the driller know how to collect soil gas samples? Is the lab experienced at analyzing vapors and does it hold an accreditation?



The 3 most common mistakes made by practitioners in the vapor intrusion arena:

1) Confusing units
2) Using incorrect screening levels
3) Sampling & analysis errors.

Determining Screening Levels

- From Lookup Tables (EPA Table 3)
- From Attenuation Factors (α)
- From J-E Model/Spreadsheets

lower

higher

Levels increase from top to bottom
(less conservative)

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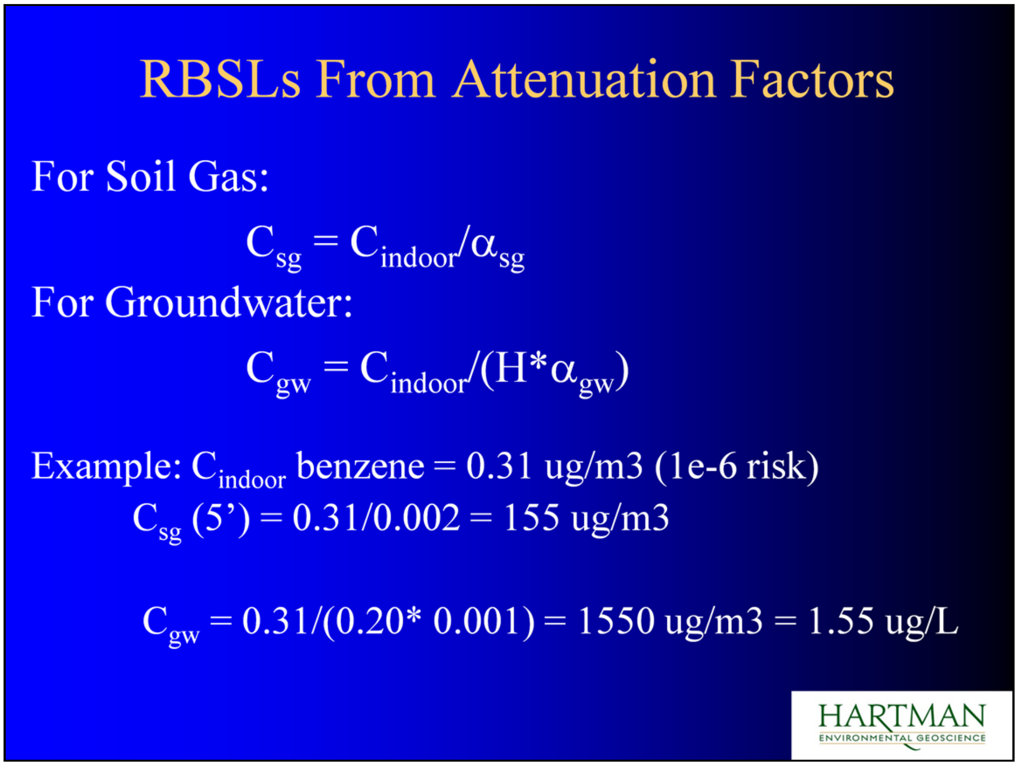
Three methods are typically used to determine screening levels. The first method listed gives the lowest (most conservative) levels. The J-E Model gives the highest (least conservative) levels.



By using attenuation factors, one can calculate target levels for soil gas and groundwater starting from the acceptable indoor air concentration.

This is the method the EPA guidance allows to determine screening levels in the soil gas or groundwater.

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RBSLs from Models

- Johnson-Ettinger Most Common
  - GW, soil, soil gas spreadsheets
  - Least conservative RBSLs
  - No bioattenuation component
- Biovapor
  - J-E model with bioattenuation added
  - In Beta testing by EPA
  - Now available from API

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Several models are available that allow you to calculate screening values for groundwater, soil gas, and even soil phase data. The Johnson-Ettinger model/spreadsheet is the most common. API is releasing a version that includes bioattenuation.

Allowable Soil Gas Levels

(Benzene 1e-6 Risk, residential)

State	Alpha	1/Alpha	Risk Based Level (ug/m^3)
EPA Now	0.002	500	155
EPA 2012?	0.1	10	3.1 (gulp!)
CA	0.002	500	42
NJ	0.05	20	16
MO			118,000
TN	0.0013	780	2,414
CT	0.1	10	192

A summary of the allowable benzene levels in soil gas shows large variation and illustrates the main points: the new EPA guidance is 50x more restrictive and allowable levels are variable from State to State.

Indoor Air Measurement

- Pros:
  - Actual Indoor Concentration
- Cons:
  - Where From?
    - Inside sources (everything!)
    - Outside sources (exhaust)
    - People activities – NO CONTROL!
  - Time-intensive protocols
  - Snapshot, limited data points
  - Expensive!!

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Measuring indoor air might seem to be the most direct and simplest approach, but it has its share of problems. The biggest problem is background sources of contaminants. Many commonly used household products contain some of the target compounds of concern. For example, benzene from consumer products, PCE from dry cleaned clothes, TCE from degreasing cleaners. In addition, the protocols are laborious, intrusive, offer little control, and are expensive. For these reasons, the EPA and many States shy away from this method, especially for PVOCs. However, this method may still be the method of choice if the contaminant of concern is not one commonly found in household products (e.g., 1,1 DCE).

Ahhh or Aaaah?

DRAFT: Volatile Organic Compounds by EPA TO-15

H&P Mobile Geochemistry, Inc.

Analyte	Result	Reporting Limit	Units	Dilution Factor	Batch	Prepared	Analyzed	Method	Notes
DRAFT: Shaving Cream (E103030-01) Vapor	**Sampled: 03-Mar-11**	**Received: 04-Mar-11**							
Carbon disulfide	**136**	31.5	"	"	"	"	"	"	
trans-1,2-Dichloroethene	ND	40.2	"	"	"	"	"	"	
Methyl tertiary-butyl ether (MTBE)	ND	18.3	"	"	"	"	"	"	
Vinyl acetate	ND	17.8	"	"	"	"	"	"	
1,1-Dichloroethane	ND	20.5	"	"	"	"	"	"	
2-Butanone (MEK)	ND	149	"	"	"	"	"	"	
n-Hexane	**2590**	17.8	"	"					
cis-1,2-Dichloroethene	ND	20.1	"	"					
Diisopropyl ether (DIPE)	ND	21.2	"	"					
Ethyl acetate	ND	91.2	"	"					
Chloroform	ND	24.8	"	"					
2,2-Dichloropropane	ND	23.4	"	"					
Tetrahydrofuran	ND	149	"	"					
Ethyl tert-butyl ether (ETBE)	ND	21.2	"	"					
1,1,1-Trichloroethane	ND	27.6	"	"	"	"	"	"	
1,2-Dichloroethane (EDC)	ND	20.5	"	"	"	"	"	"	
1,1-Dichloropropene	ND	23.0	"	"	"	"	"	"	
Benzene	**389**	16.2	"	"	"	"	"	"	
Carbon tetrachloride	ND	31.9	"	"	"	"	"	"	
Cyclohexane	**469**	87.1	"	"	"	"	"	"	
p-Isopropyltoluene	**37100**	27.8	ug/m3	5	EC10305	04-Mar-11	04-Mar-11	EPA TO-15	E
1,2-Dichlorobenzene	ND	61.0	"	"	"	"	"	"	
n-Butylbenzene	**3000**	27.8	"	"	"	"	"	"	
1,2-Dibromo-3-chloropropane	ND	49.0	"	"	"	"	"	"	
Naphthalene	**104**	26.6	"	"	"	"	"	"	
1,2,4-Trichlorobenzene	**160**	37.6	"	"	"	"	"	"	
1,2,3-Trichlorobenzene	**134**	37.6	"	"	"	"	"	"	
Hexachlorobutadiene	**89.2**	54.1	"	"	"	"	"	"	
Xylenes (total)	ND	22.0	"	"	"	"	"	"	
TPHv (C5 - C11)	**680000**	500	ug/m3	5	EC10305	04-Mar-11	04-Mar-11	EPA TO-15	E

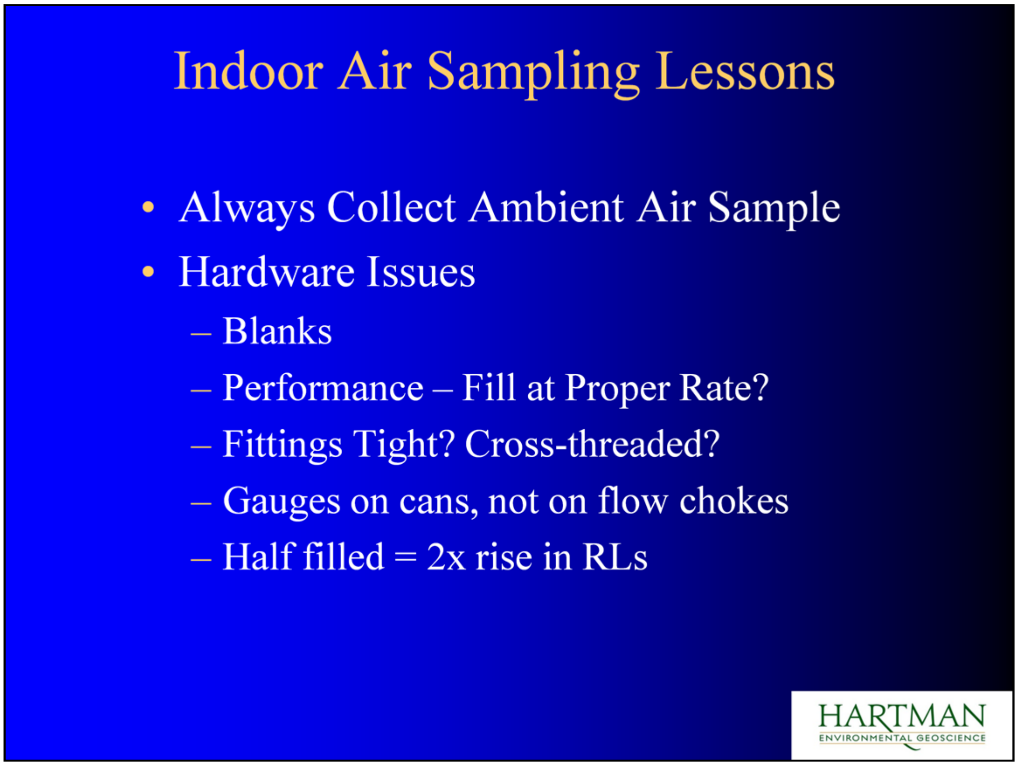
CS2 = 140 ug/m3

Benzene = 389 ug/m3

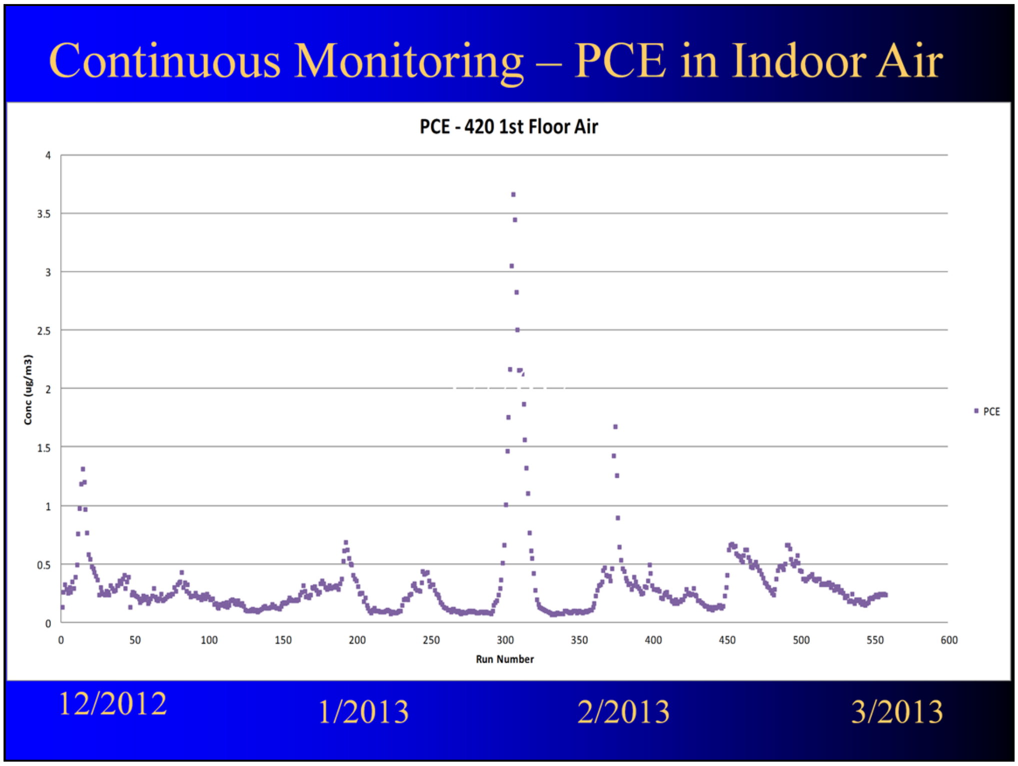
TPH=680,000 ug/m3

An analysis of Barbasol shaving cream: Benzene & TPH at levels 1000x above indoor air screening levels!

The hidden source of benzene & TPH contamination at many structures.

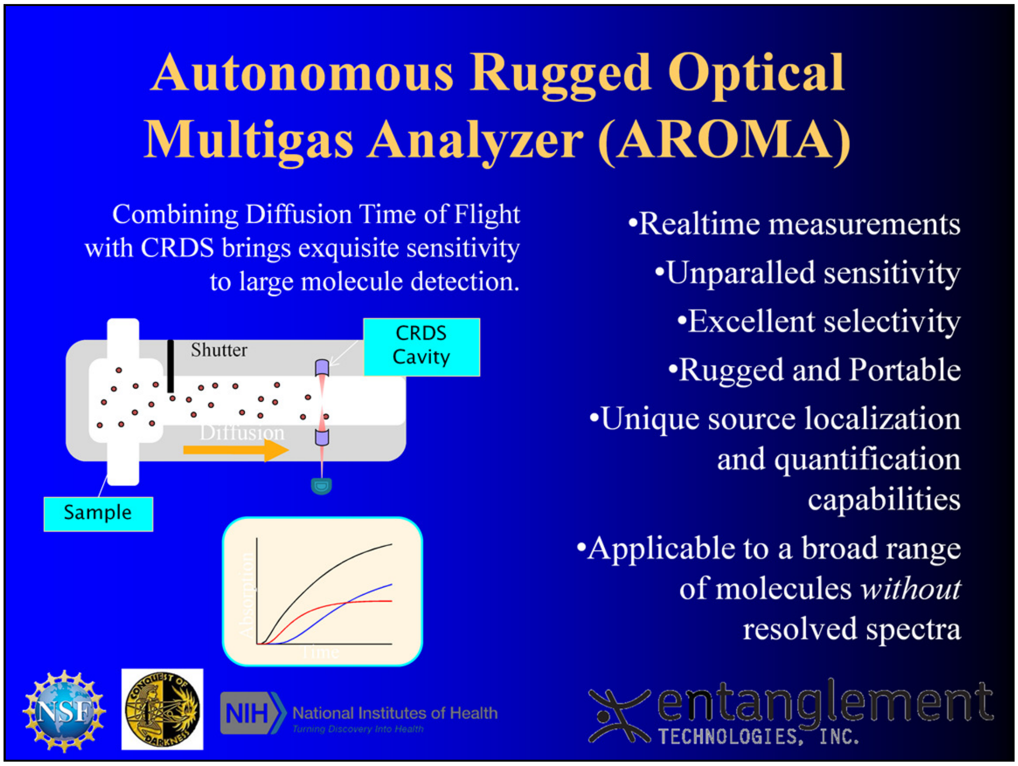


There are issues that need to be considered when sampling indoor air and when interpreting the data. Sampling issues include the hardware, time period for collection, and things as simple as the type of marker used to label the samples.

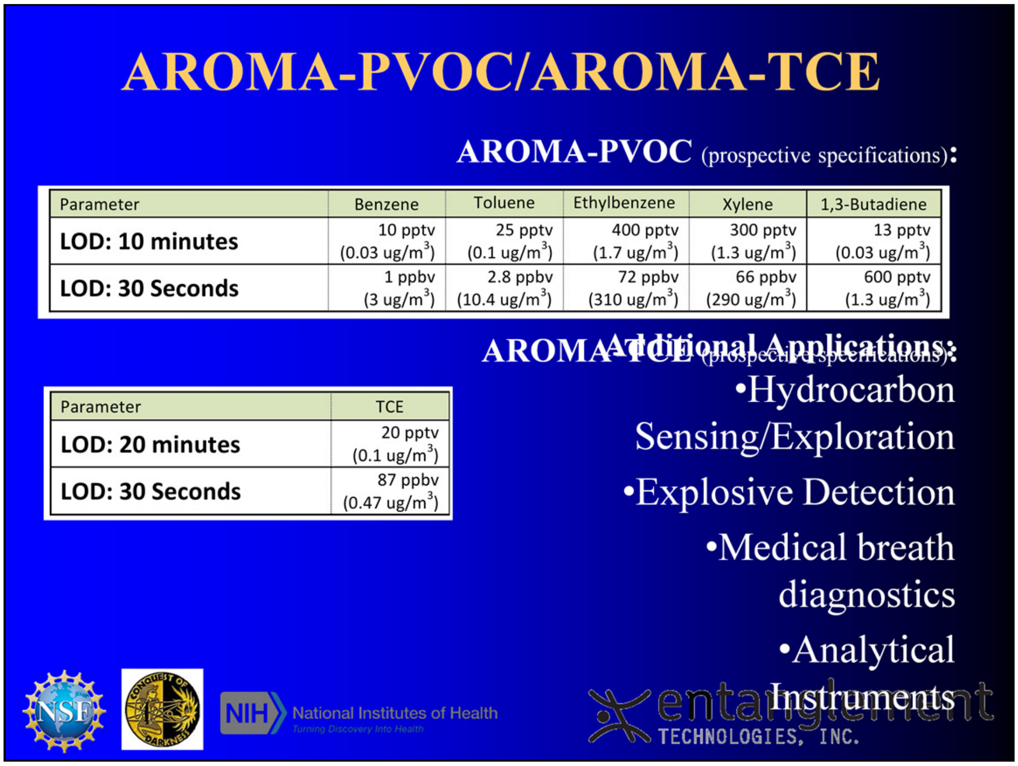


Continuous monitoring data of PCE in indoor air from a house. Sensitive chlorine detectors exist to allow this type of data to be collected.

Wouldn’t it be nice to be able to do the same for benzene?



A new instrument being developed by a firm in CA may allow continuous monitoring for selected VOCs.



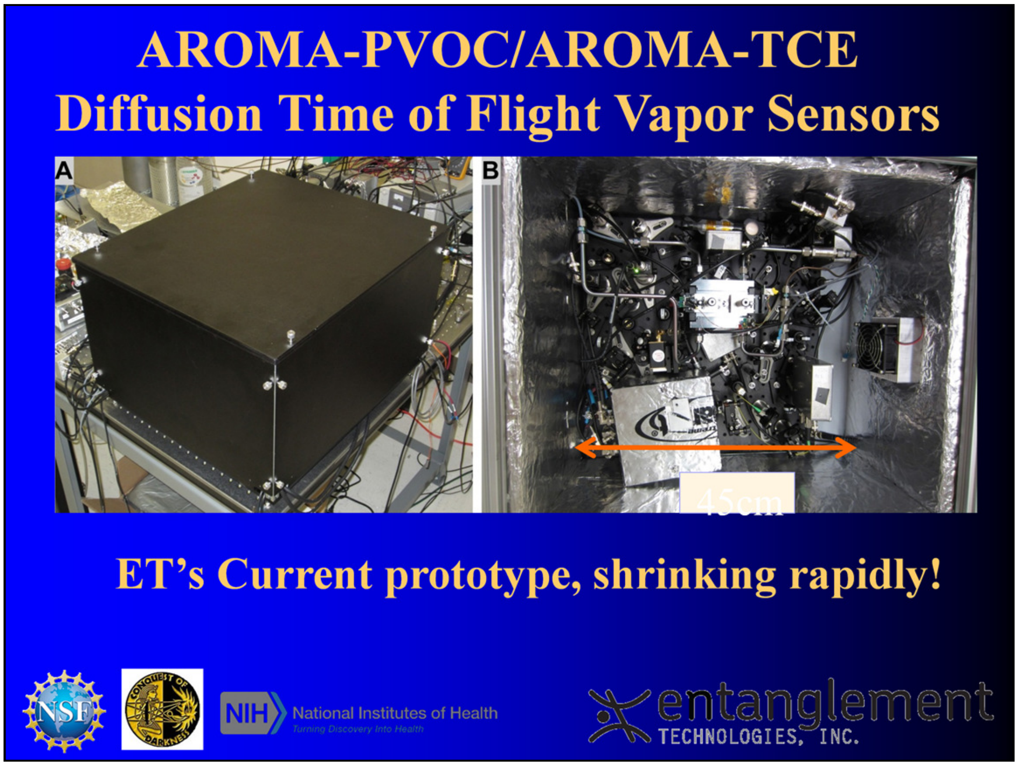
Parameter	Benzene	Toluene	Ethylbenzene	Xylene	1,3-Butadiene
LOD: 10 minutes	10 pptv (0.03 ug/m^3)	25 pptv (0.1 ug/m^3)	400 pptv (1.7 ug/m^3)	300 pptv (1.3 ug/m^3)	13 pptv (0.03 ug/m^3)
LOD: 30 Seconds	1 ppbv (3 ug/m^3)	2.8 ppbv (10.4 ug/m^3)	72 ppbv (310 ug/m^3)	66 ppbv (290 ug/m^3)	600 pptv (1.3 ug/m^3)

Parameter	TCE
LOD: 20 minutes	20 pptv (0.1 ug/m^3)
LOD: 30 Seconds	87 ppbv (0.47 ug/m^3)

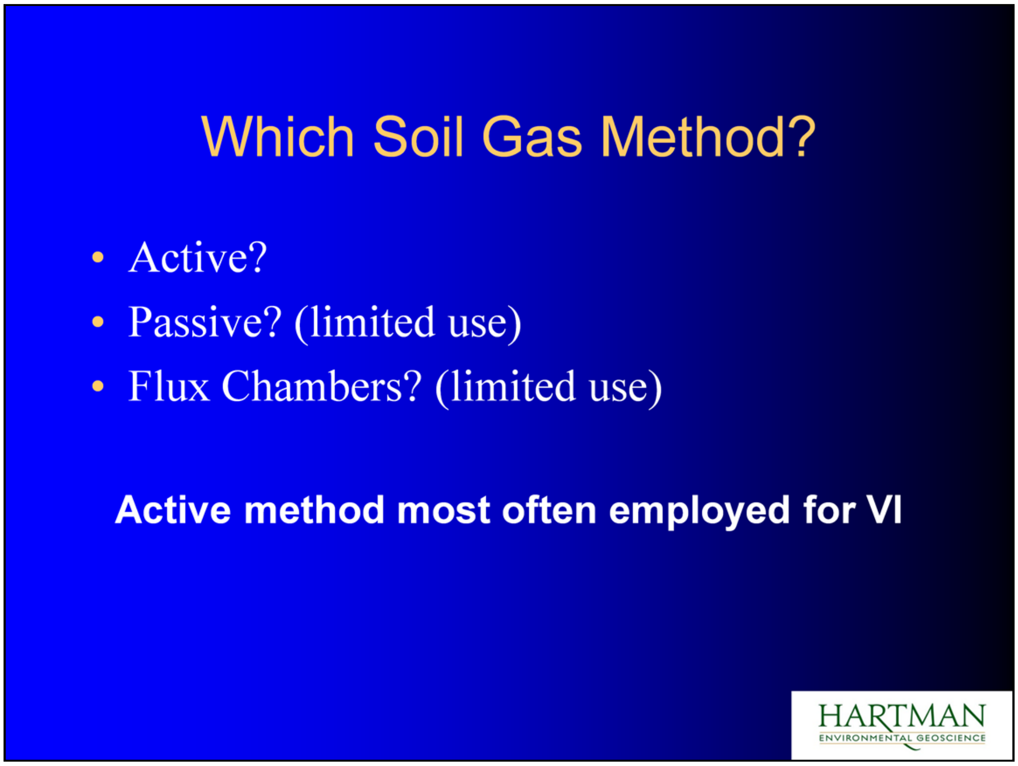
Note the listed specs for benzene and TCE.

Benzene at 0.03 ug/m3 is below 1e-6 risk level.

TCE at 0.47 ug/m3 in 30 seconds is at the 1e-6 risk level.



Currently the size of a microwave, but expected to shrink.



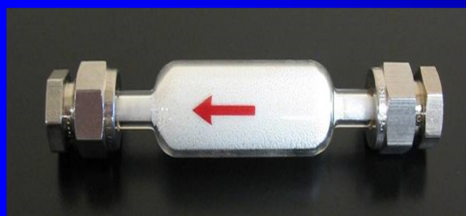
There are three types of soil gas methods. Active refers to actively withdrawing vapor out of the ground. It gives quantitative values. Passive refers to burying an adsorbent in the ground and letting the vapors passively contact and adsorb onto the collector. It does not give quantitative data and hence can not be used for risk applications, except for screening. Surface flux chambers were discussed previously.

The active method is the one most applicable to risk assessments.

Flux Chamber Site

A mobile trailer park with shallow (2’ bgs) ground water. The prefec tsite for flux chambers.

SVOC Sampling



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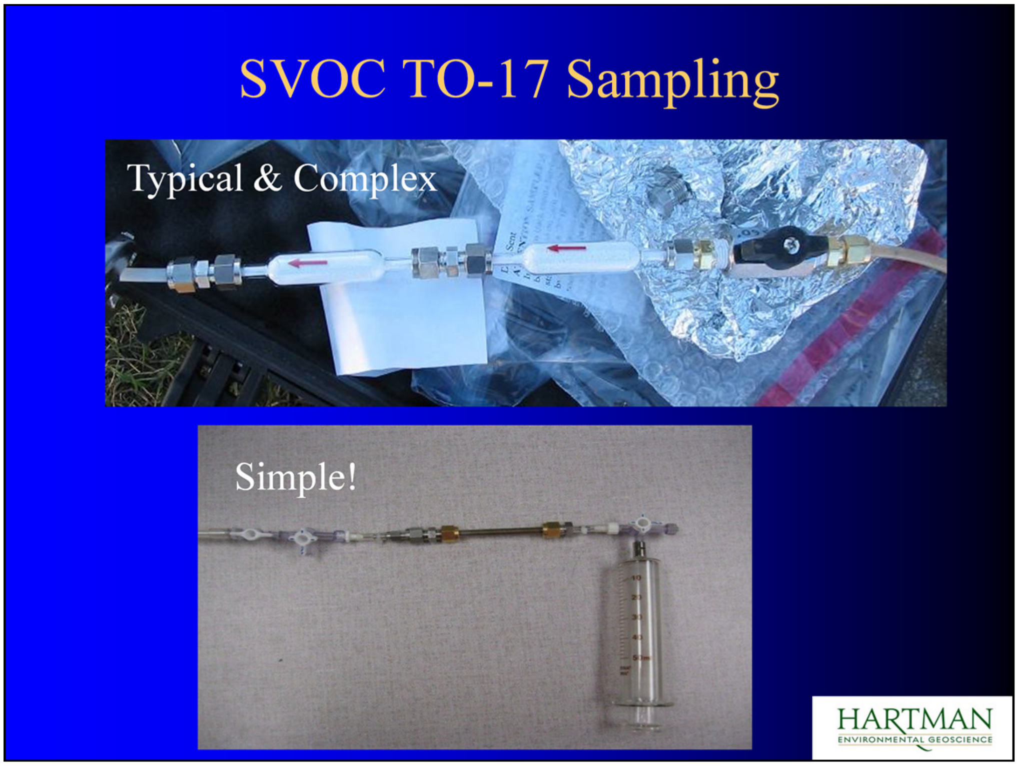
A typical sampling arrangement used for collection of samples on adsorbants. Note the abundance of fittings and the need for duplicate cartridges for breakthrough. A very complicated set-up, prone to leaks.

Canisters vs. Tubes

New style adsorbent tubes are much smaller than bulky canisters and can’t be broken.



Top photo: A typical sampling arrangement used for collection of samples on adsorbants. Note the abundance of fittings and the need for duplicate cartridges for breakthrough. A very complicated set-up, prone to leaks.

Bottom photo: A much simpler sampling arrangement for adsorbent tubes with better control on actual vapor volumes passed through the adsorbent.

TPH Compounds

- Recommended
  - BTEX (BE only drivers)
  - Methane
  - 1-2 dichloroethane (EDC) & 1-2 dibromoethane (EDB)
  - Naphthalene, 2-methyl naphthalene
- Some States:
  - Aliphatics (C5-C8 & C9-C12)
  - Aromatics (C9-C10)
  - TPHg – different from the aliphatics

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Petroleum compounds of concern vary from State to State. Consult the oversight agencies specifications.

Other Analytical Issues

- 1,3 Butadiene
  - False positive caused by i-butylene
  - Must have lab manually read ion chromatogram
  - Not on most agency soil gas target lists
- Naphthalene
  - 8260, TO-15, TO-17 all used, but …

TO-17 gets PVOCs, TPHg, TPHd in same run!!

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Watch out for false detections of 1,3 butadiene.

Also, naphthalene is best analyzed by TO-17.

Parting Thoughts

Upcoming Conferences

- AWMA Annual Conf – Chicago, 6/25/2013
- Cleanup 2013 – Melbourne, Oz 9/16/2013

Looking for a Great PVI Guidance Template?

Look at the Australian PVI Guidance

Upcoming vapor intrusion training.