How To Collect Samples over Days or Weeks to Identify Vapor Intrusion Risks

Show of The South
Gatlinburg TN

George Shaw
and
Harry O'Neill
Beacon Environmental Services, Inc.

21 April 2016

TN Department of Environment & Conservation

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Road Map

- Beacon's experience
- EPA guidance documents
- Passive sampler types – benefits and limitations
- Principles of how operate
- Importance of quality control in sampler design and analysis
- Comparison data
- Considerations for where to collect samples
- Questions

Laboratory Accreditation

Beacon is a specialized laboratory focused on providing highly accurate air and soil vapor data

PJLA
Testing
DoD ELAP

Accredited in accordance with:

ISO/IEC 17025:2005

NELAP

U.S. DoD Environmental Laboratory Accreditation Program (ELAP)

Accredited Analytical Methods:

U.S. EPA Methods 8260C, TO-17, and TO-15

Beacon is first laboratory to achieve accreditation for the new EPA Method 325

US EPA GUIDANCE DOCUMENTS

OSWER Technical Guide For Assessing And Mitigating The Vapor Intrusion Pathway From Subsurface Vapor Sources To Indoor Air – June 2015

Time-integrated samples of indoor air over longer periods than one day are also indicated by field observations demonstrating that indoor air concentrations arising from vapor intrusion can be temporally variable within a day and between days and seasons **(EPA 2012f; Holton et al., 2013a).**

Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods – July 2015

US EPA Method 325: Volatile Organic Compounds from Fugitive and Area Sources – September 2015

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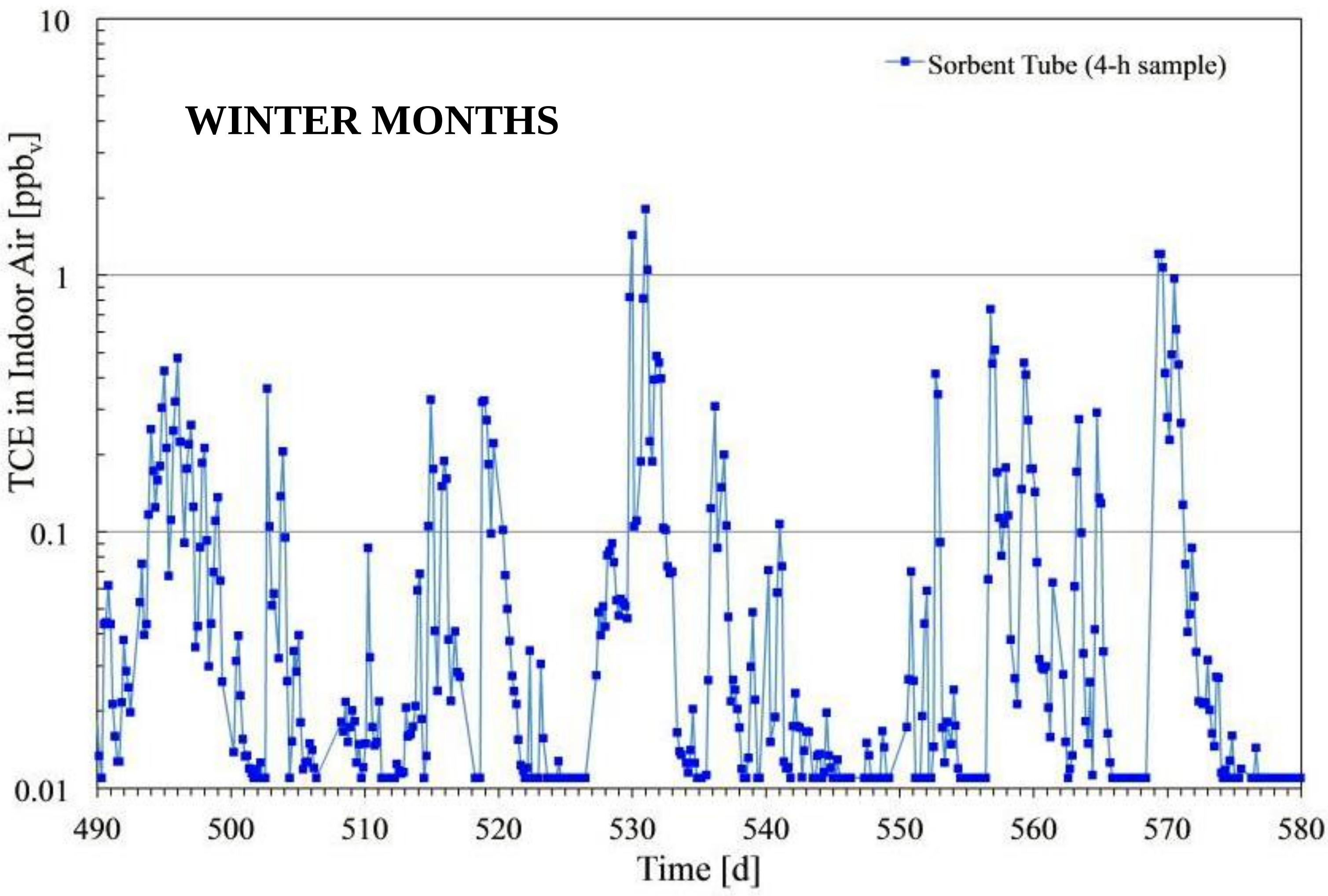
Importance of Long-Duration Sampling



Source: Holton et al., ES&T, 2013, 47, 13347-13354

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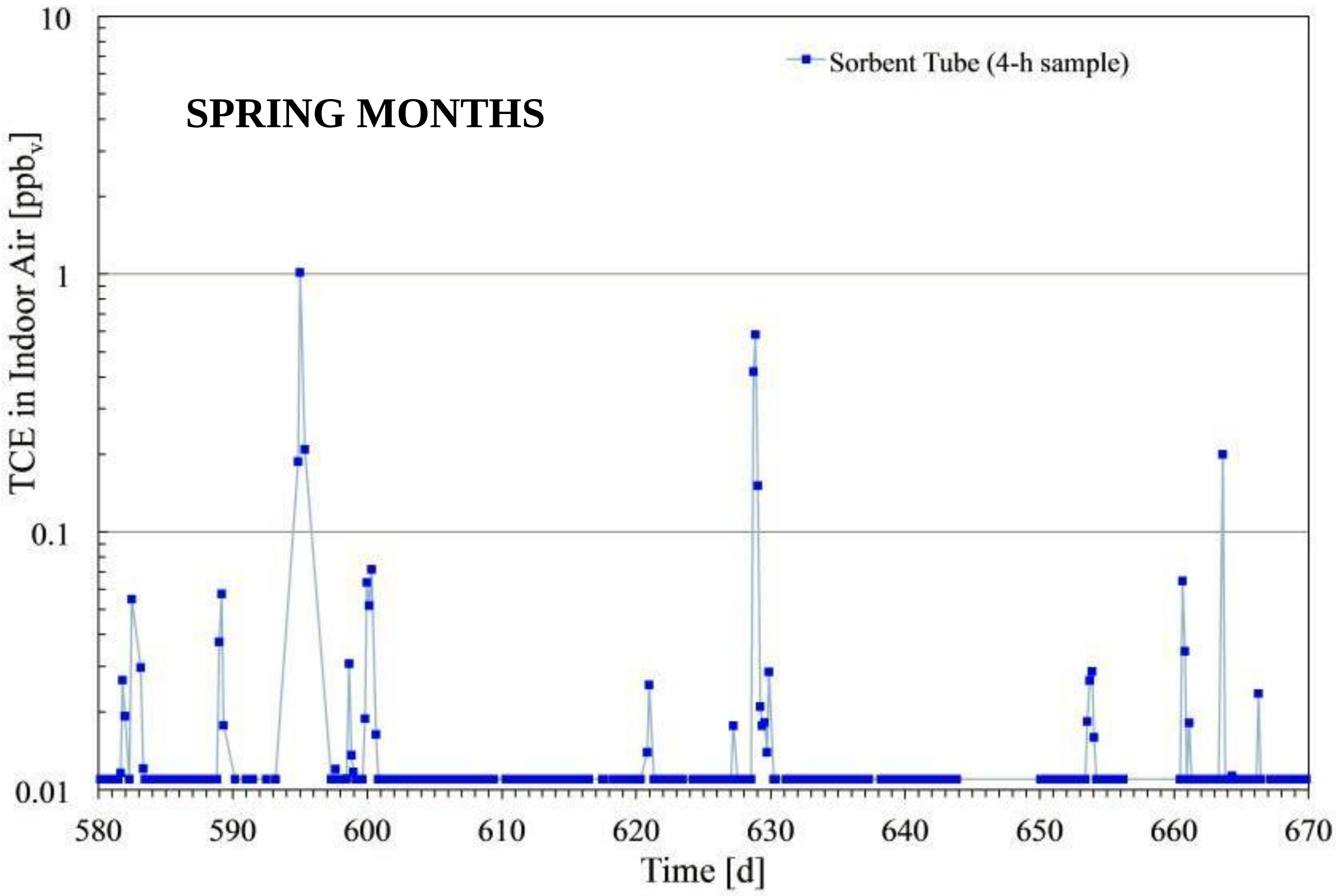
Importance of Long-Duration Sampling



Source: Holton et al., ES&T, 2013, 47, 13347-13354

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Results: Analysis of Sampling Outcomes

High potential for false negative result concerning VI occurrence

High potential to incorrectly characterize long-term exposure

High potential to incorrectly characterize maximum short-term exposure

- **About half of all 24-h samples would come back non-detect**
- **Only about 50% chance that sample results would have a mean concentration inside a 10X range about the true mean concentration**

Sources:

Johnson, P. Multi-Year Monitoring of a House Overlying a Dilute Chlorinated Hydrocarbon Plume: Implications for Vapor Intrusion Pathway Assessment SERDP & ESTCP Webinar Series, 2014.

Holton et al., ES&T, 2013, 47, 13347-13354

Axial Passive Samplers – The Gold Standard

Tubes: Method TO-17 with Pump

Passive Samplers

Method TO-17

Uses low-flow pumps

Passive Samplers

No pumps required

PJLA Testing DoD ELAP

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Passive Samplers – Principles of Operation

$$J = -D\frac{dC}{dx}$$

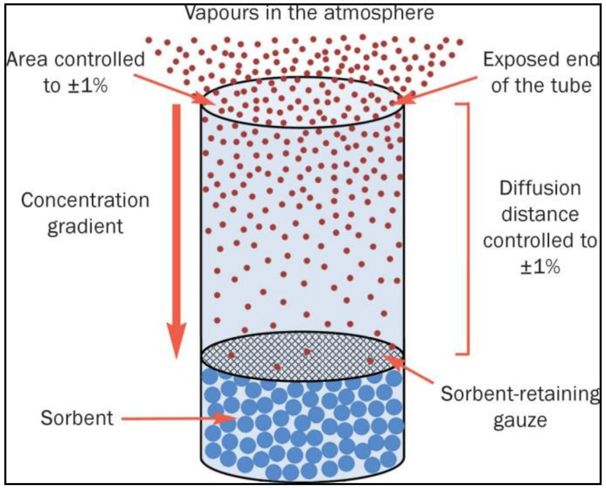
For application of Fick's First Law to a diffusive sampler several simplifying assumptions are necessary:

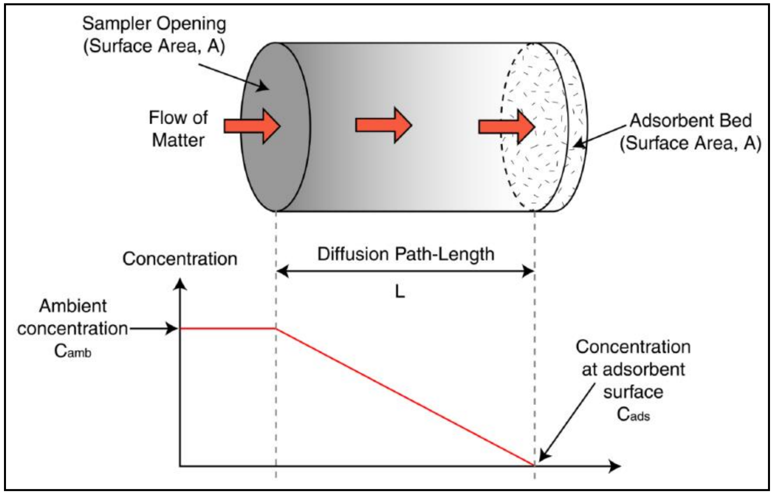
Ambient concentration of the analyte at the surface of the monitor (C_{amb}); that is, does not take matter from its surrounding environment faster than it can be replaced

Zero concentration of the analyte at the surface of the sorbent; that is, the adsorbent is a zero sink and therefore there is no saturation of the adsorbent ($C_{ads} = 0$)

A linear concentration gradient between the two. Steady state conditions always exist

Axial type samplers





Source: Markes International

Sampling with Sorbents – Active and Passive

Active Sampling

Calculate concentration:

ug/m^3 = mass/(flow rate x time)

mass = nanograms
flow rate = ml/min
time = minutes
(e.g., 1000 x ng/ml = ng/L = ug/m^3)

Passive Sampling

Calculate concentration:

$$C = M/U \times t$$

C = Concentration ug/m3
M = Mass (nanograms x 1000)
U = Uptake rate (ml/min)
t = time (min)

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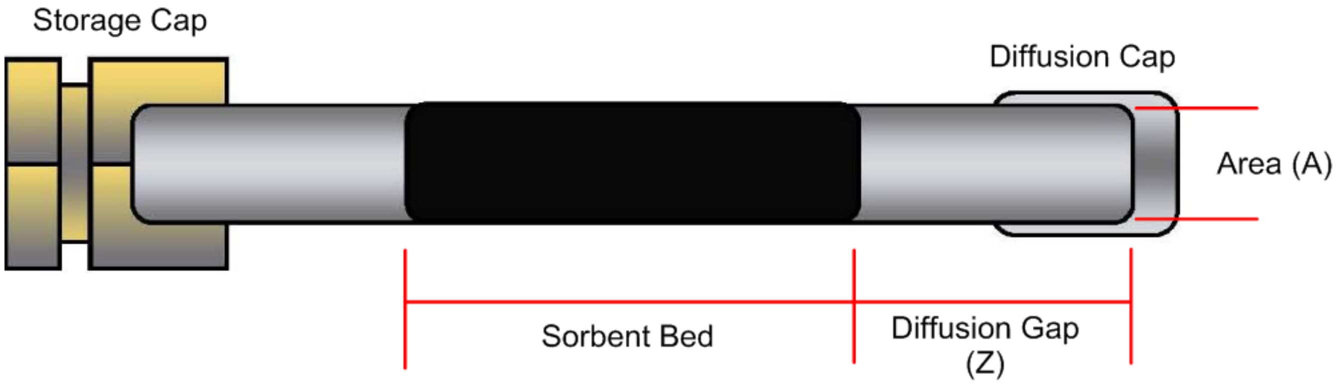
Passive Samplers – Uptake Rates Theoretical



$$U = A/Z \times D$$

uptake rate (U) = ml/min

Area (A) = cm2

Distance (Z) = cm

Diffusivity Coefficient in Air (D) = cm2/sec

(e.g., cm2/cm x cm2/sec x 60 = cm3/min or ml/min)

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Passive Samplers – Uptake Rates Theoretical

Chemical	Diffusivity in Air (D) (cm^2/s)	Area (cm2)	Distance (cm)	Uptake Rate (ml/min)
Vinyl Chloride	1.06E-01	0.18857	1.5	0.80
1,1-Dichloroethylene	9.00E-02	0.18857	1.5	0.68
Cis-1,2- Dichloroethylene	8.86E-02	0.18857	1.5	0.67
Trichloroethylene	7.90E-02	0.18857	1.5	0.60
1,1-Dichloroethane	7.42E-02	0.18857	1.5	0.56
Tetrachloroethylene	7.20E-02	0.18857	1.5	0.54
Trans-1,2- Dichloroethylene	7.03E-02	0.18857	1.5	0.53

Uptake Rate

$$U = A/Z \times D$$

Uptake Rates Theoretical vs. Measured

Chemical	Theoretical Uptake Rate (ml/min)	Measured Uptake Rate (ml/min)	Relative Percent Difference (RPD)
Vinyl Chloride	0.80	0.78	2.48%
1,1-Dichloroethylene	0.68	0.57	17.43%
Cis-1,2- Dichloroethylene	0.67	0.58	14.15%
Trichloroethylene	0.60	0.50	17.50%
1,1-Dichloroethane	0.56	0.57	1.83%
Tetrachloroethylene	0.54	0.48	12.33%
Trans-1,2- Dichloroethylene	0.53	0.58	8.96%

Note: t-1,2-DCE measured uptake rate is an estimation based on Graham's Law

Graham's law

$$U_{b\text{-}est} = U_a / \sqrt{(Mb/Ma)}$$

Where M = Molar mass (g/mol)

Need for new uptake rate studies

mcba Consulting

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Adsorbent Types & Properties

Physical Characteristics of Supelco Carbon Adsorbents

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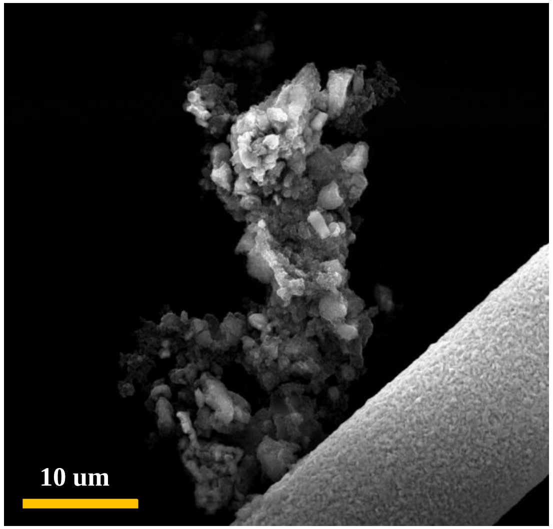
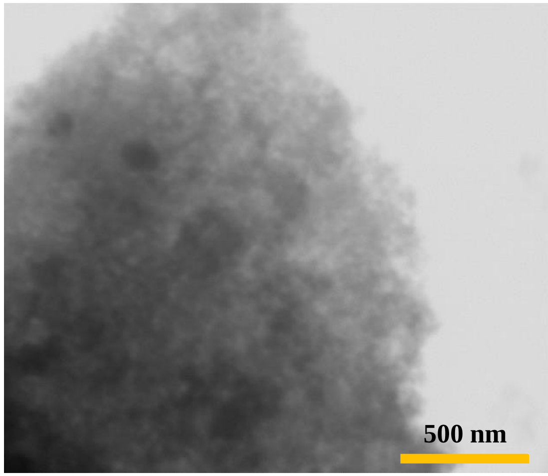
Adsorbent	BET surface area[1] (m^2/g)	Density (g/mL)	Porosity (cc/g)			Micropore Diameter (Å)
			micro-	meso-	macro-	
Carbotrap graphitized carbon black (20/40 mesh)						
Carbotrap F	5	0.69	-	-	-	-
Carbotrap C	10	0.68	-	-	-	-
Carbotrap Y	24	0.45	-	-	-	-
Carbotrap B	100	0.37	-	-	-	-
Carbotrap X	240	0.43	-	0.62	-	100
Carbopack graphitized carbon black (60/80 mesh)						
Carbopack F	5	0.64	-	-	-	-
Carbopack C	10	0.68	-	-	-	-
Carbopack Y	24	0.42	-	-	-	-
Carbopack B	100	0.35	-	-	-	-
Carbopack Z	220	0.18	-	1.73	-	255
Carbopack X	240	0.41	-	0.62	-	100
Carbon Molecular Sieve						
Carboxen-1016	75	0.40	-	0.34	-	-
Carboxen-569	485	0.58	0.20	0.14	0.10	5 - 8
Carboxen- 1021[2]	600	0.62	0.30	-	-	5 - 8
Carboxen-1018[2]	675	0.60	0.35	-	-	6 - 8
Carbosieve S-III[3]	975	0.61	0.35	0.04	-	4 - 11
Carboxen-1003	1000	0.46	0.38	0.26	0.28	5 - 8
Carbosieve G	1160	-	0.49	0.02	-	6 - 15
Carboxen-1000	1200	0.48	0.44	0.16	0.25	10 - 12
Carboxen-1012	1500	0.50	-	0.66	-	19 - 21

[1] Brunauer, Emmett, Teller (BET) surface area calculations
[2] microporous, monoporous carbon sieve
[3] closed pore structure





Source: Helmich, R., *Air Monitoring Using Passive Sampling Tubes*, EPA Presentation, NEMC Conference, 2014.

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Analysis by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) following EPA Method TO-17

- Analytical results based on 5-point initial calibration
- Internal standards and surrogates included with each analysis
- Daily continuing calibration checks
- Laboratory control samples
- System daily tunes and
- Method blanks
- Method Detection Limit (MDL) Studies
- Limit of Detection and Quantitation (LOD and LOQ) Studies
- Meets requirements of Level III/Level IV data quality objectives

State-of-the-Art Analytical Instruments

Analysis by EPA Method TO-17

Advanced Markes International analytical instrumentation:

Tube placed on AutoSampler with DiffLok® cap to prevent any ingress of tramp air on tubes prior to analysis

Purges sorbent tube of moisture and oxygen prior to desorption

Positive and negative pressure test of sorbent tube prior to analysis

Heated pathways to eliminate cold spots that can cause carry-over and biased results

System recollects sample split for re-analysis

Not a "one-shot deal"

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Beacon Reporting Limits

	14 Day Exposure Period		26 Day Exposure Period	
Target Analyte	Limit of Quantitation (ppbv / ug/m^3)	Limit of Detection (ppbv / ug/m3)	Limit of Quantitation (ppbv / ug/m^3)	Limit of Detection (ppbv / ug/m3)
Vinyl Chloride	0.25 / 0.64	0.12 / 0.32	0.13 / 0.34	0.07 / 0.17
1,1-Dichloroethene	0.22 / 0.87	0.11 / 0.44	0.12 / 0.47	0.06 / 0.23
Trichloroethene	0.18 / 0.99	0.09 / 0.50	0.10 / 0.53	0.05 / 0.27

Note: **Demonstrated LOQ is 10 nanograms (ng)**
Demonstrated LOD is 5 ng
Demonstrated Detection limit (DL) is even less at 2.5 ng

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Summa Canisters compared to Sorbent Tubes

Comparison Data
Passive Samplers – 14 Day Sample
Summa Canister – 24 Hour Sample

Sample Location	AI103			AI103P			AI106			AI109		
Compound	TO-17 (14 day)	TO-15	RPD	TO-17 (14 day)	TO-15	RPD	TO-17 (14 day)	TO-15	RPD	TO-17 (14 day)	TO-15	RPD
Tetrachloroethene	3.4	3.4	0%	3.6	3.6	0%	0.45 J	0.43 J	5%	0.82 J	0.73 J	12%
Trichloroethene	1.3	1.2	8%	1.8	1.3	32%	0.11 U	0.46 U	NA	16	13	21%
Samples collected in June 2012												
Units in micrograms/cubic meter (ug/m^3)												

Strong correlation between passive sorbent tubes and summa canister data for the two primary compounds of concern (PCE and TCE)

Project Management:
CH2M – Eric Davis and Kimberly Stokes

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Passive Samplers -- Indoor Air

Duplicate Sample Results

Sample Location	Indoor #1		
Compound	Beacon Passive Diffusion Sampler (14 Days)	Beacon Passive Diffusion Sampler (14 Days)	RPD
Methylene Chloride	0.60	0.59	1.7%
Trichloroethene	0.85	0.87	2.3%
Toluene	34.0	33.8	0.4%
Tetrachloroethene	306.7	305.6	0.4%
Ethylbenzene	4.11	4.01	2.5%
p & m-Xylene	10.98	10.59	3.6%
o-Xylene	2.66	2.64	0.8%

Sample Location	Indoor #2		
Compound	Beacon Passive Diffusion Sampler (14 Days)	Beacon Passive Diffusion Sampler (14 Days)	RPD
1,1,1-Trichloroethane	1.45	1.39	4.2%
Trichloroethene	2.44	2.58	5.6%
Tetrachloroethene	29.24	31.27	6.7%
Ethylbenzene	1.15	1.07	7.2%

Results in ug/m3

Duplicate samples suspended side by side show excellent correlation with a 14-day sampling period.

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Duplicate Comparison Passive Samplers vs. Summas

	BEACON	BEACON		Summ Canister	Summ Canister	
Sample ID:	**SM02-0214IAP**	**SM02-0214IAP Dup**		**SM02-0214IAP**	**SM03-0214IAP**	
Project Number:	2798	2798				
Lab File ID:	C14030506	C14030507				
Received Date:	2/28/14	2/28/14				
Analysis Date:	3/5/14	3/5/14				
Analysis Time:	5:19 PM	6:02 PM				
Matrix:	Air	Air		**TO-15 LL**	**TO-15 LL**	
COMPOUNDS	ug/m3	ug/ms	**RSD %**	ug/m3	ug/m3	**RSD %**
Vinyl Chloride	U	U				
1,1-Dichloroethene	U	U				
Methylene Chloride	U	U		**0.75**	**0.91**	**19.3%**
trans-1,2-Dichloroethene	U	U				
1,1-Dichloroethane	U	U				
cis-1,2-Dichloroethene	U	U				
Chloroform	U	U		**0.11**	**0.12**	**8.7%**
1,1,1-Trichloroethane	**1.45**	**1.39**	**4.2%**	**3.2**	**3.9**	**19.7%**
Benzene	U	U		**1.0**	**1.4**	**33.3%**
Trichloroethene	**2.44**	**2.58**	**5.6%**	**3.5**	**5.2**	**39.1%**
Tetrachloroethene	**29.24**	**31.27**	**6.7%**	**60**	**90**	**40.0%**
Ethylbenzene	**1.15**	**1.07**	**7.2%**	**0.28**	**0.32**	**13.3%**

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Passive Samplers -- Ambient Air (Method 325B)

	Round						
Location	**1**	**2**	**3**	**4**	**Mean**	**Max**	**Std. Dev.**
02-01	6.32	7.36	9.36	3.62	6.67	9.36	2.07
02-02	2.90	3.14	3.40	2.54	3.00	3.40	0.32
02-03	4.49	4.76	5.54	2.92	4.43	5.54	0.95
02-04	2.14	3.87	5.65	2.39	3.51	5.65	1.40
02-05	2.70	2.76	3.35	1.96	2.69	3.35	0.49
02-06	3.05	5.03	6.85	2.74	4.42	6.85	1.66
02-07	--	--	--	1.23	1.23	1.23	--

Mean	3.60	4.49	5.69	2.49
Std. Dev.	1.41	1.52	2.06	0.70

	1	**2**	**3**	**4**	**Average**
Min	2.14	2.76	3.35	1.23	2.37
Max	6.32	7.36	9.36	3.62	6.67
Difference	4.18	4.60	6.01	2.39	4.30

Field Blanks	**1**	**2**	**3**	**4**
02-07-FB	--	--	--	<0.74

Duplicates	**1**	**2**	**3**	**4**
02-02 DU	2.91	3.03	3.29	2.53
02-02	2.90	3.14	3.40	2.54
Relative Percent Difference	0.34%	3.57%	3.29%	0.39%

Analytical results for Benzene in micrograms per cubic meter (ug/m^3).

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02-03	4.49	4.76	5.54	2.92	4.43	5.54	0.95
02-04	2.14	3.87	5.65	2.39	3.51	5.65	1.40
02-05	2.70	2.76	3.35	1.96	2.69	3.35	0.49
02-06	3.05	5.03	6.85	2.74	4.42	6.85	1.66
02-07	--	--	--	1.23	1.23	1.23	--

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Method 325B – Refinery Fenceline Monitoring

Monitor the emissions of benzene across the perimeter of refineries within the United States.

Final Rule Issued Sept. 2015

Requirement to sample minimum of 12 locations around perimeter of refinery

Continuously sample using passive sorbent tube samplers at each of the sample locations

Two-week sample periods

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Guidance on Passive Samplers

- **ASTM D6306 – 10**, Standard Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air
- **EN ISO 16017**: Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/ capillary gas chromatography. Part 2: Diffusive sampling.
- **MDHS 80**: Volatile organic compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography (August 1995).
- **ASTM D6246 – 08** (2013) Standard Practice for Evaluating the Performance of Diffusive Samplers
- **ASTM D4597** – 10, Standard Practice for Sampling Workplace Atmospheres to Collect Gases or Vapors with Solid Sorbent Diffusive Samplers
- **CEN EN 838**: Workplace atmospheres – Requirements and test methods for diffusive samplers for the determination of gases and vapours.
- Protocol for assessing the performance of a diffusive sampler (Method for the Determination of Hazardous Substances No. 27), UK Health & Safety Executive.

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- CEN EN 838: Workplace atmospheres – Requirements and test methods for diffusive samplers for the determination of gases and vapours.

Guidance on Where to Collect Samples

ASTM D6306-10

- Sample within breathing zone (e.g., approx. 3-5 ft above floor)
- At least lowest level of structure
- Central/unobstructed location; not interfere with normal activity
- Avoid high humidity locations (e.g., bathrooms, laundry rooms)
- Temperature considerations: avoid devices that generate heat/cold
- Not placed in direct sunlight
- Avoid placement near windows, drafty openings, and intake/exhaust vents
- Avoid areas with insufficient air flow (e.g., closets, inside shelves)
- Place at least 20 cm below the ceiling (but not near lighting or air vents), at least 50 cm above the floor, and at least 15 cm from a wall. Locations near outside walls should be avoided, if possible.

Summary

- **Passive samplers are easy to use and less obtrusive than canisters**
- **Quality analytical procedures will produce high quality data while achieving low reporting limits**
- **Sorbent tubes can target concentrations that span orders of magnitude**
- **Passive samplers allow for the collection of samples over several days or weeks to measure organic compounds in indoor and ambient air, which reports an average concentration that may be more representative of health risks**

Any Questions?

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Thank you

Please contact us if you have any questions or to discuss project applications:

PJLA
Testing
DoD ELAP

Thank You

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