Why the U.S. EPA is Promoting the Collection of Time-Integrated, Passive Indoor Air Samples for Vapor Intrusion Risk Assessments

Presented by:
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REMTECH EXPO

REMTECH Europe

20 September 2019

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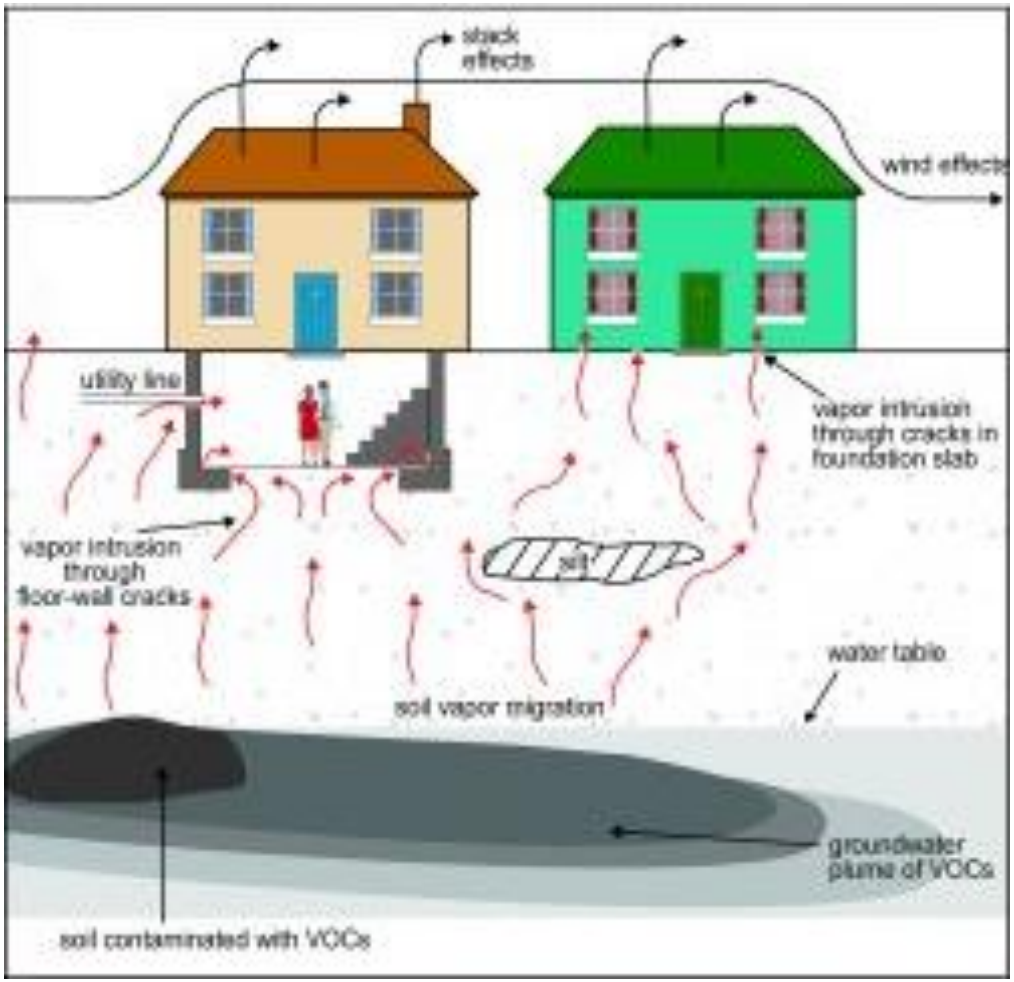
Vapor Intrusion Pathways

The intrusion of contaminants in the vapor phase into buildings presents significant health risks

Exposure Pathway: People breathe on average 10,000 L of air per day



Graphic: U.S. EPA

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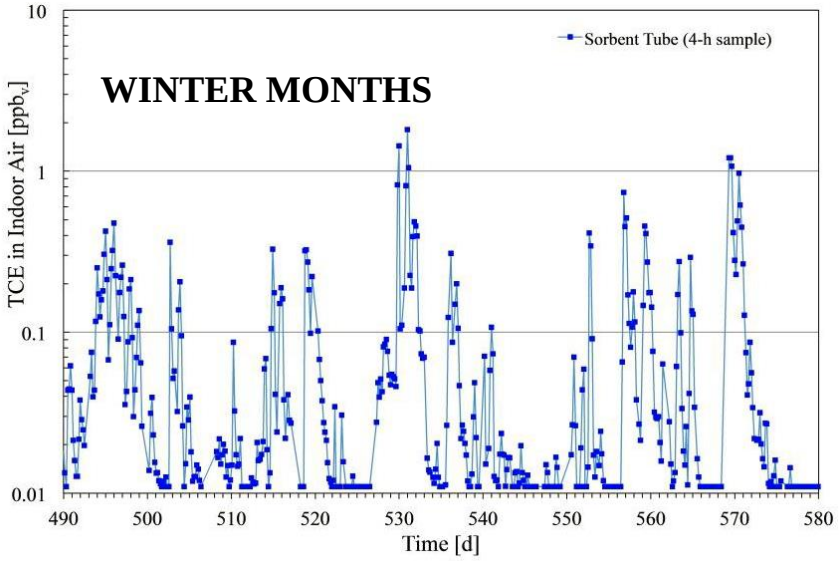
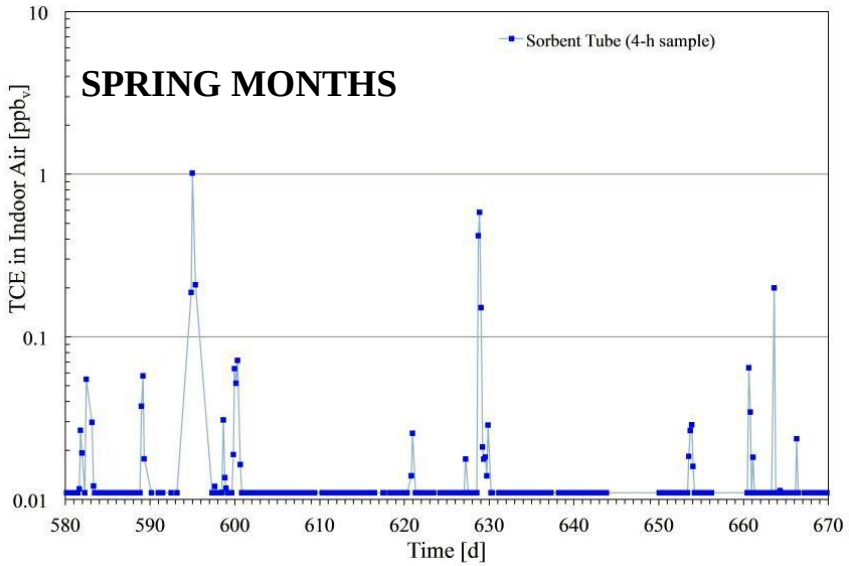
When to Sample – The Challenge

Temporal Variability

Indoor air concentrations can vary daily by orders of magnitude

Vapor intrusion has shown to be episodic – anomalous events occur





Source:

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.

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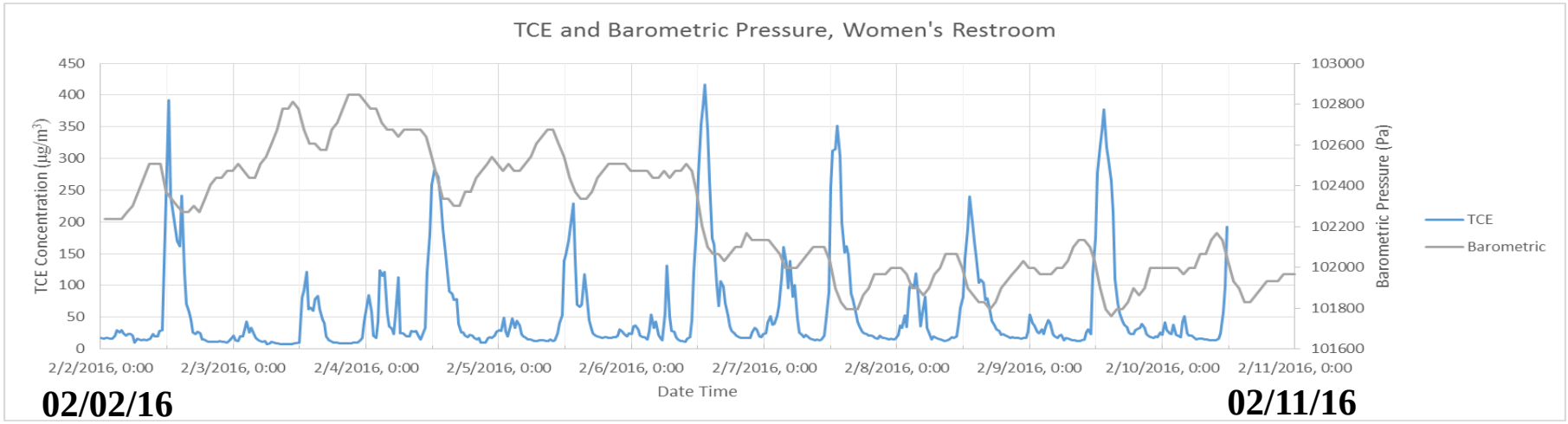
When to Sample – The Challenge



02/02/16 **02/11/16**

"Vapor concentrations can vary in both the subsurface and indoor environments due to barometric pumping, soil moisture dynamics, building ventilation, wind shear, tidal fluctuation, and other environmental and anthropogenic factors"

Source: Hosangadi et al, 2017

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VI Study Results: Analysis of Sampling Outcomes

With 24 hr samples collected:

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

≤24-Hour Average Concentrations

Point in Time Measurement – Typically 8 or 24 hours

US EPA Method TO-15 -- Summa canister

US EPA Method TO-17 -- Sorbent tube and pump

Source: EMS Environmental

Source: H&P Mobile

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Summa Canister – Quality Control Concerns

Taylor & Francis
Taylor & Francis Group

Soil and Sediment Contamination: An International Journal

ISSN: 1532-0383 (Print) 1549-7887 (Online) Journal homepage: http://www.tandfonline.com/loi/bssc20

Evidence of canister contamination causing false positive detections in vapor intrusion investigation results

Thomas E. McHugh, Carlyssa Villarreal, Lila M. Beckley & Sharon R. Rauch

Published 12 September 2018

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Summa Canister – Quality Control Concerns

DATA SOURCE – California GeoTracker Database

- Normal-duplicate vapor sample pairs extracted from California GeoTracker Database

  - 400 sites
  - More than 1,400 samples
  - Timeframe from 2003 – 2016
  - More than 50,000 concentration results

- Working dataset
  - Vapor data: 7,000

- Comparable dataset for groundwater field duplicates compiled
  - Groundwater data: 5,900

Source: McHugh Presentation – Battelle Chlorinated Conference April 2018

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Summa Canister – Quality Control Concerns

"For vapor analyte pairs, 20% of pairs had a percent difference in concentration >300% while, for groundwater analyte pairs, only 3% had a percent difference >300%."

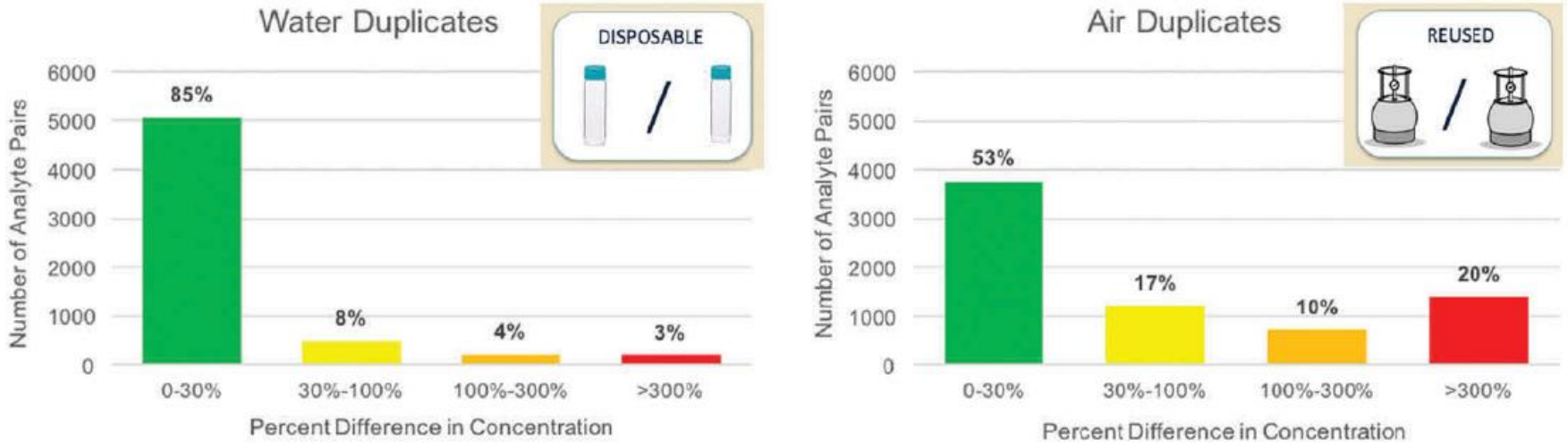

Figure 1. Duplicate variability for water duplicates and air duplicates.

Source: McHugh et al 2018

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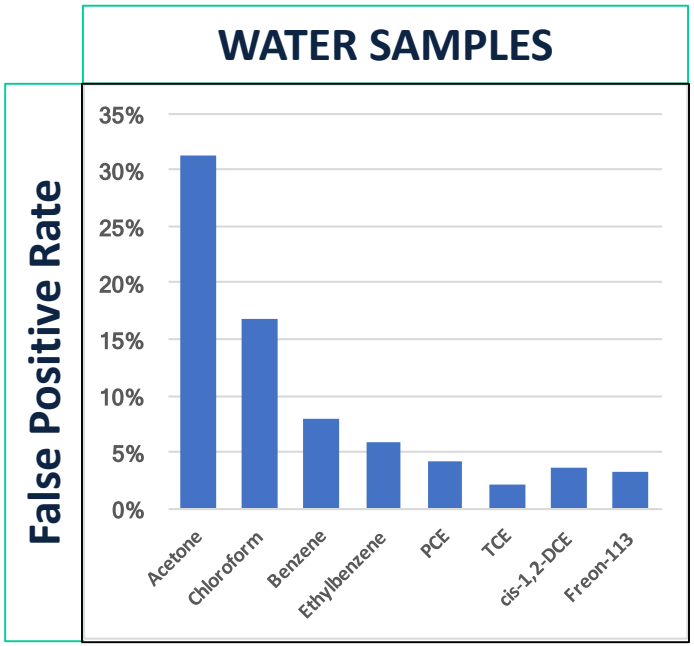
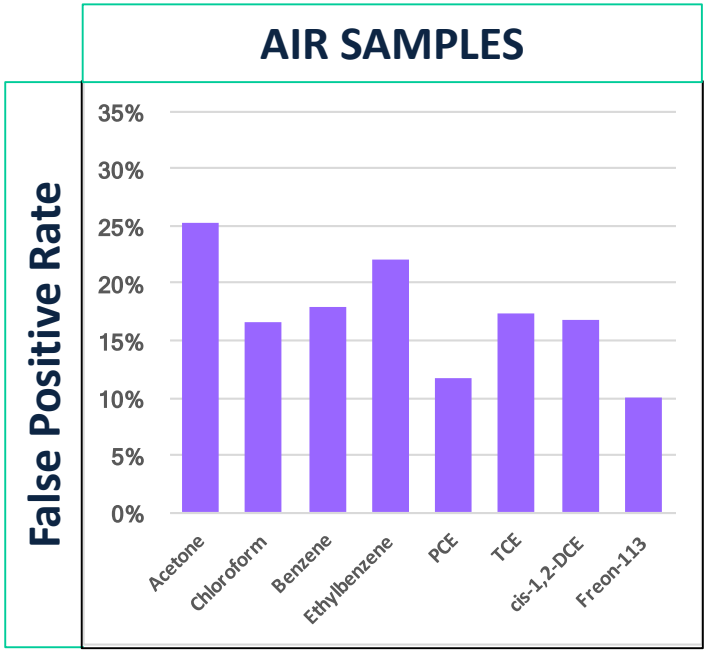
Summa Canister – Quality Control Concerns

RESULTS FROM STUDY

QUESTION: HOW OFTEN IS A DETECTION DUE TO LAB/CONTAINER CONTAMINATION?





KEY POINT: **For air samples, contaminated sample containers are likely a significant source of false positive detections.**

Source: McHugh Presentation – Battelle Chlorinated Conference April 2018

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U.S. EPA Guidance Documents

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

All else being equal, a longer collection period for each individual sample would be expected to yield a more reliable basis for estimating long-term and short term, time-average exposure than would a one-day sample collection period.

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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New EPA 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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Time-Integrated Sampling Strategy - Passive Samplers

Radial Sampler, Badge Sampler, & Axial Samplers

The ability to collect samples over days or weeks provides a better determination of both long term and short term risks to occupants of buildings

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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:

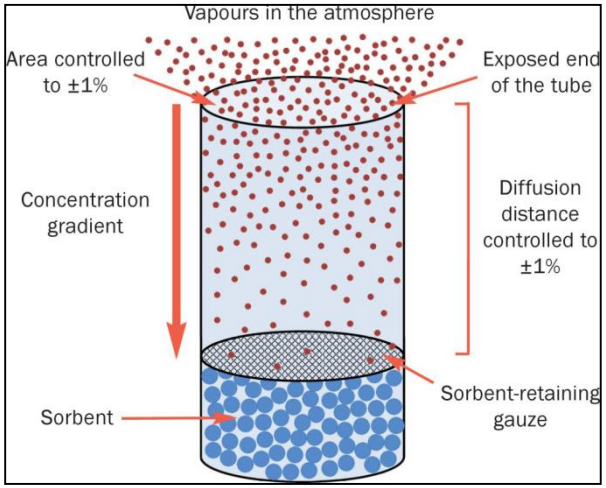
Ambient concentration of the analyte at the surface of the monitor (C_{amb}); that is, does not take matter from its surrounding environment faster than it can be replaced

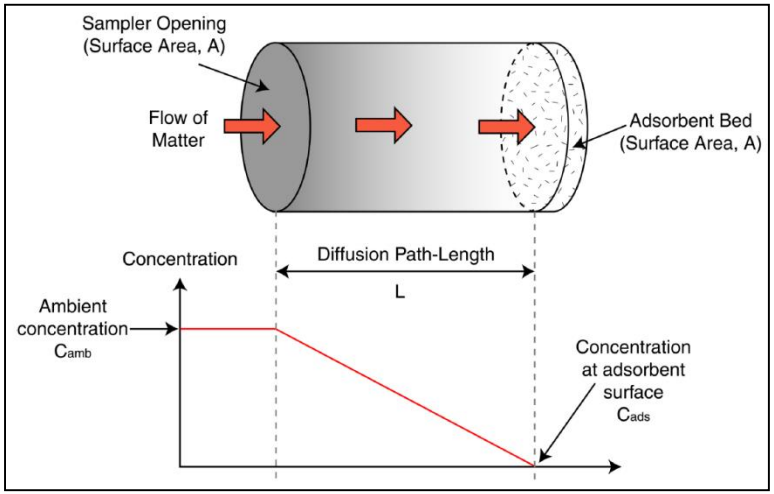
Zero concentration of the analyte at the surface of the sorbent; that is, the adsorbent is a zero sink and therefore there is no saturation of the adsorbent ($C_{ads} = 0$)

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

Source: Markes International

Axial type samplers





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Principles of Passive Sampling

1) **The adsorbent must be compatible with the target VOCs**

2) **The VOCs are retained on the sorbent for the full duration of the sample period – no back diffusion**

3) **Analytical method must completely desorb the VOCs from the adsorbent -- no irreversible sorption**

4) **Air velocity for axial sampler greater than 0.001 m/s (ASTM D6306)**
   Badge samplers require 0.05 to 0.1 m/s

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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Reporting Limits

	Limit of Quantitation (ug/m3)					
Target Compound	**1 Day**	**3 Days**	**7 Days**	**10 Days**	**14 Days**	**26 Days**
Vinyl Chloride	<1.24	<0.41	<0.18	<0.12	<0.09	<0.05
1,1-Dichloroethene	<1.54	<0.51	<0.22	<0.15	<0.11	<0.06
trans-1,2-Dichloroethene	<0.99	<0.33	<0.14	<0.10	<0.07	<0.04
cis-1,2-Dichloroethene	<0.99	<0.33	<0.14	<0.10	<0.07	<0.04
Trichloroethene	<1.07	<0.36	<0.15	<0.11	<0.08	<0.04
Tetrachloroethene	<1.26	<0.42	<0.18	<0.13	<0.09	<0.05

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Calculate concentration:

$$C = 1000 \times M / (U \times t)$$

C = Concentration ug/m^3

M = Mass (ng)

U = Uptake rate (ml/min)

t = time (min)

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Average reporting limit also indicates that for:

24 Hour Period: TCE conc never exceeded 1.07 ug/m3

8 Hour Period: TCE conc never exceeded 3.21 ug/m3

Note the 24-hr and 8-hr periods do not need to be continuous

Able to both assess short term health risks below screening levels while also measuring long duration, time-weighted average concentrations

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Dr. Paul Johnson Study House:
Time-integrated passive samples collected over 20+ days vs. daily average samples

- **Daily 24 hour samples collected on sorbent tubes with pump (EPA Method TO-17)**

- **Time-integrated samples collected over multiple days using Beacon Passive Samplers (Analysis by EPA Method TO-17)**

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Time-Integrated Beacon Passive Samplers compared to Daily 24-hour average measurements

On going study to compare results of the passive samplers vs. average daily concentrations measured using Method TO-17 with pumped samples

Passive Samplers collected in triplicate; exposed for duration of sampling periods

Pumped samples collected at a flow rate of 10 ml/min with a total volume of 14.4 L

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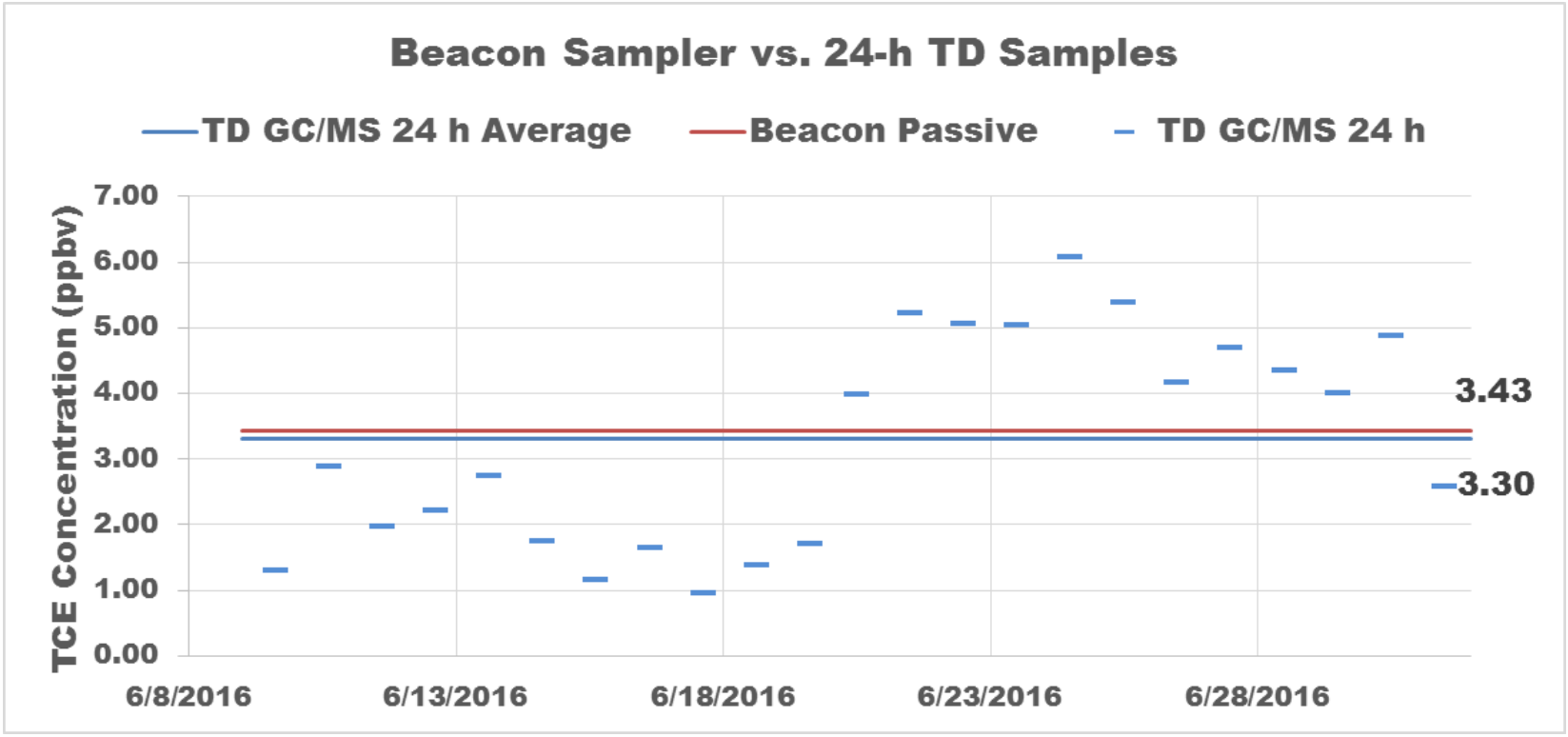
Example of Results

Passive Samplers allow for the collection of samples over longer time periods – days or weeks



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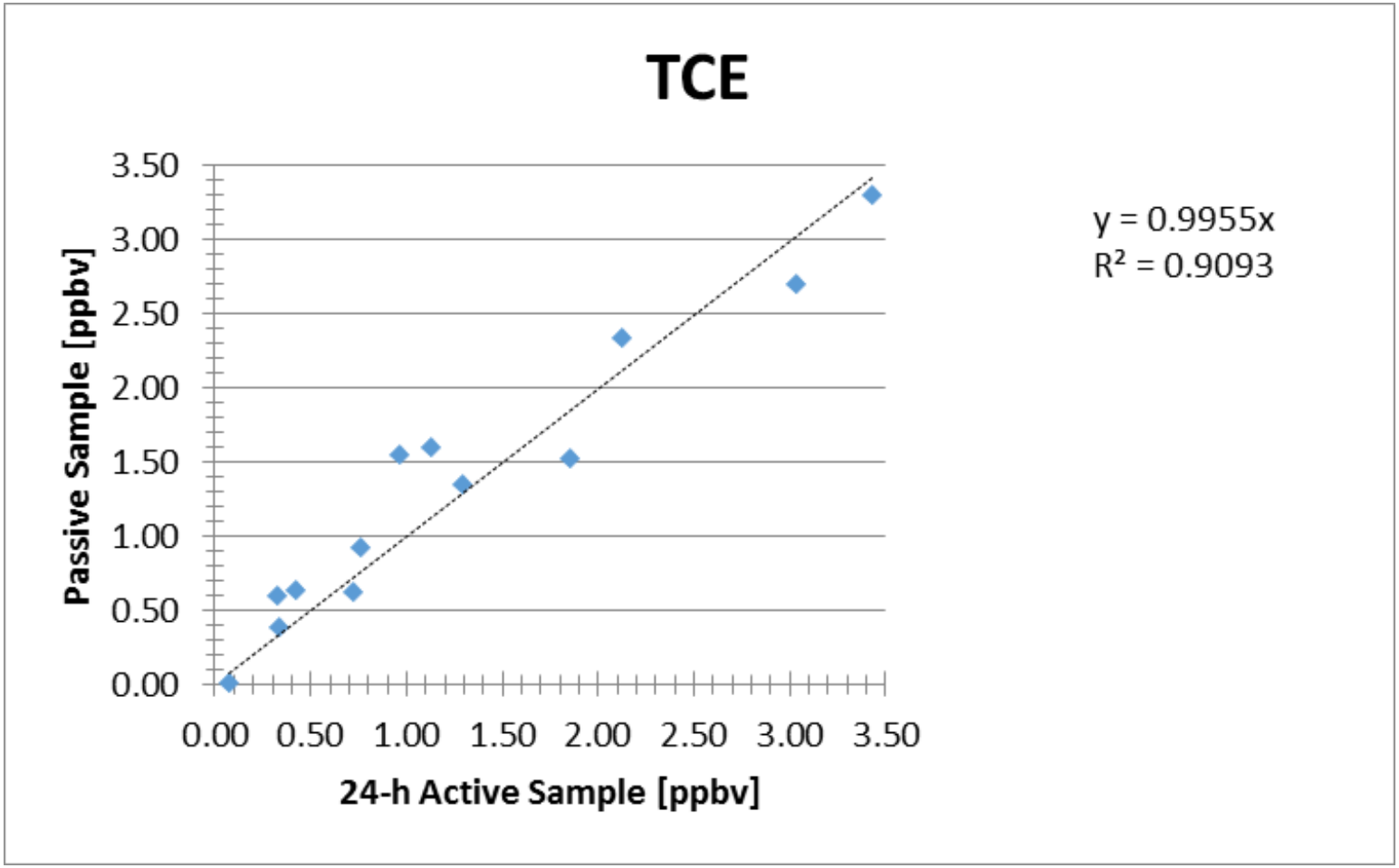
Correlation of Beacon Passive Sampler to Average of 24-hour Active Samples



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Samples Collected in Triplicate
Analysis of Trichloroethene (TCE) Results

Sampling Event	Sampling Days	B-X-01 ppbv	B-X-02 ppbv	B-X-03 ppbv	Average ppbv	Standard Deviation	Coefficient of Variation
1	26	1.41	1.22	1.24	1.29	0.10	0.08
2	23	3.73	3.33	3.22	3.43	0.27	0.08
3	20	3.11	2.84	3.16	3.04	0.17	0.06
4	30	1.95	1.73	1.89	1.86	0.11	0.06
5	52	0.78	0.74	0.63	0.72	0.08	0.11
6	20	1.09	1.28	1.01	1.13	0.14	0.12
7	7	2.39	2.2	1.77	2.12	0.32	0.15
8	7	0.8	0.7	0.78	0.76	0.05	0.07
9	6	0.99	1.03	0.86	0.96	0.09	0.09
10	30	U	U	U			
11	43	0.42	0.25	0.33	0.33	0.09	0.26
12	35	0.41	0.44	0.42	0.42	0.02	0.04
13	36	0.32	0.31	0.34	0.32	0.02	0.05
						AVERAGE	**0.10**

Data Source: Arizona State Univ. Study House
Drs. Paul Johnson, Paul Dahlen, Yuanming Guo

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2,000+ Home Indoor Air Monitoring Program

Passive sorbent samplers are being used to collect samples over 14 to 26 day periods as part of an annual monitoring program of residences overlying a groundwater plume contaminated with chlorinated solvents

Sample during the winter seasons

Previously, summa canisters were collected over 24 hour periods

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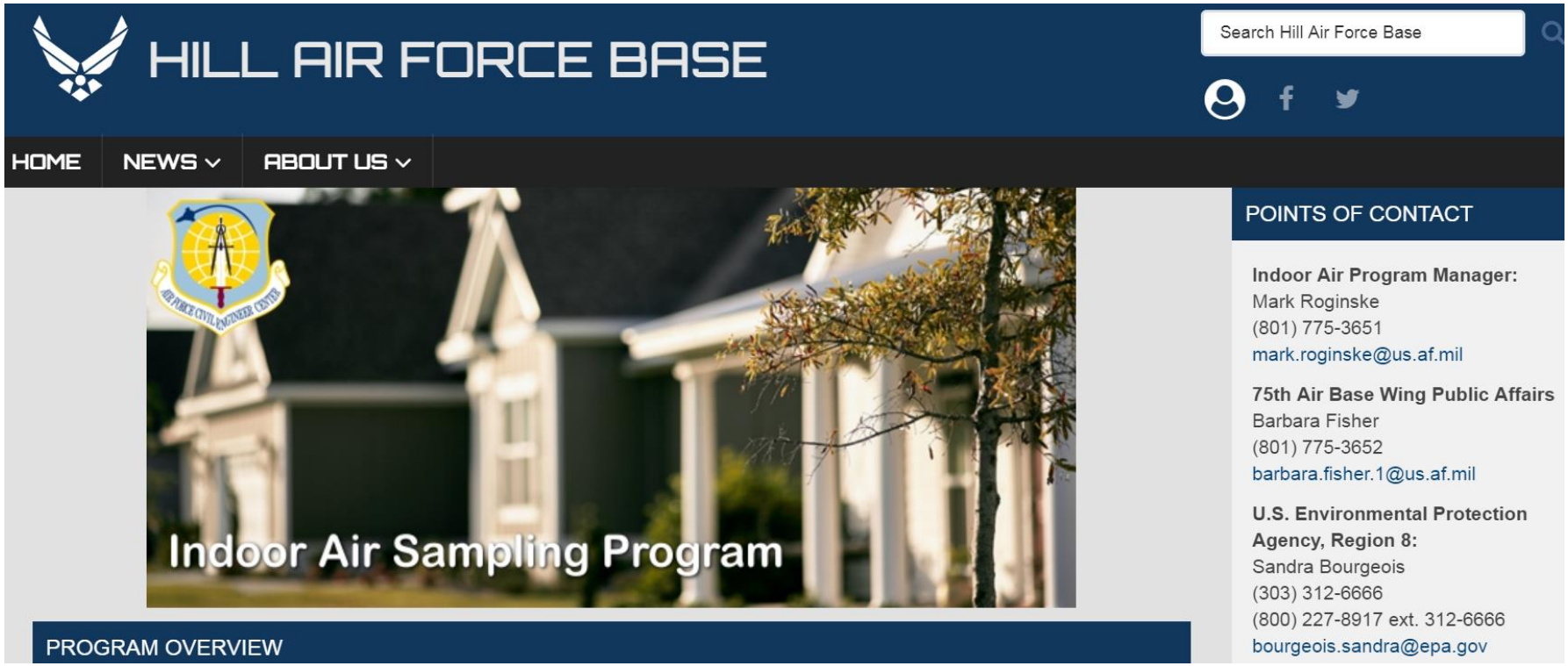
U.S. Department of Defense (DoD) Guidance



Source: https://www.hill.af.mil/IAP/

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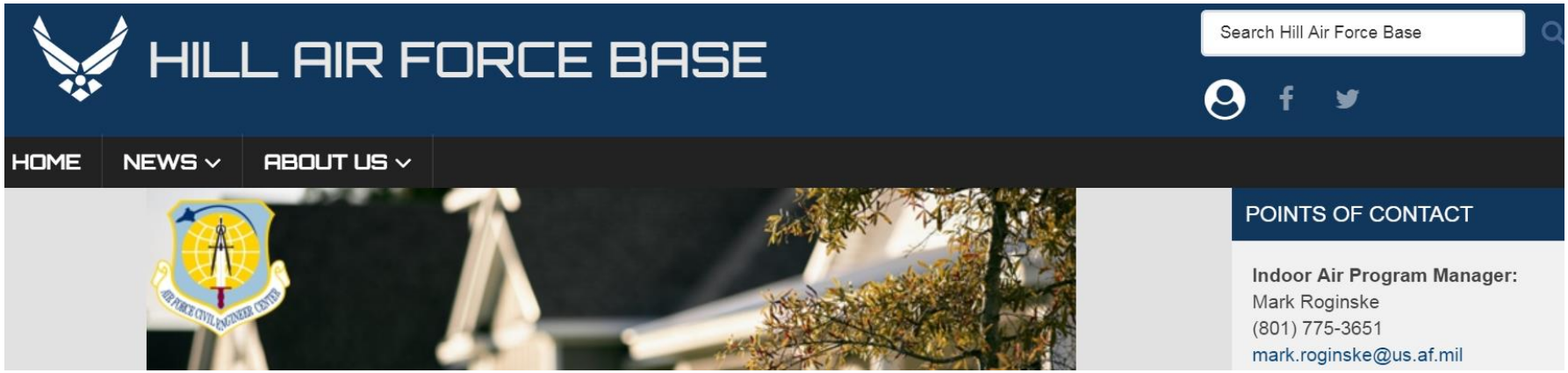
U.S. Department of Defense (DoD) Guidance



"Hill has tested the air in approximately 2,000 homes in communities surrounding the base affected by groundwater contamination. Less than 10 percent of homes tested have had vapor levels above an action level. A vast majority of those homes, however, were tested using a method that could have missed vapor intrusion. Click here for more information about how testing methods have changed to more accurately determine if vapor intrusion is occurring."

Source: https://www.hill.af.mil/IAP/

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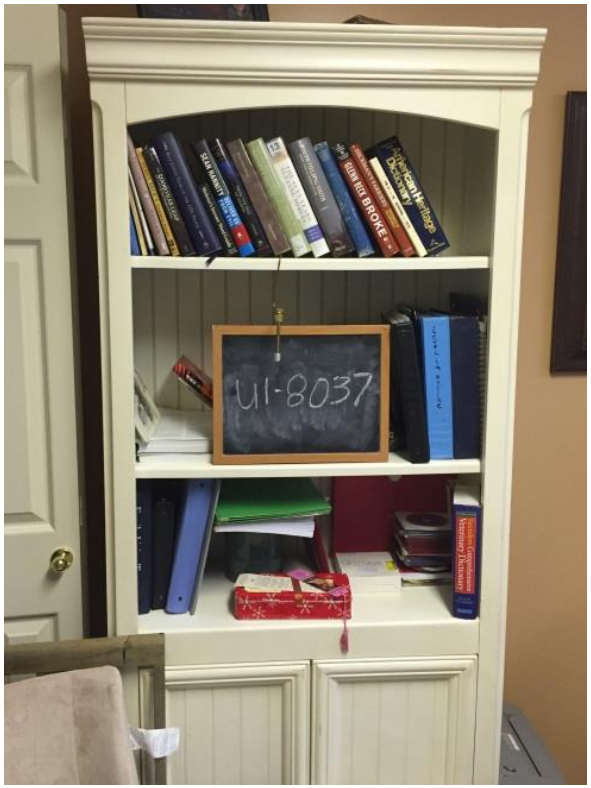
2,000+ Home Indoor Air Monitoring Program

Low-profile and easy to use

Simplified logistics for sampling team

Residents have a very positive response to sorbent samplers being used instead of summa canisters



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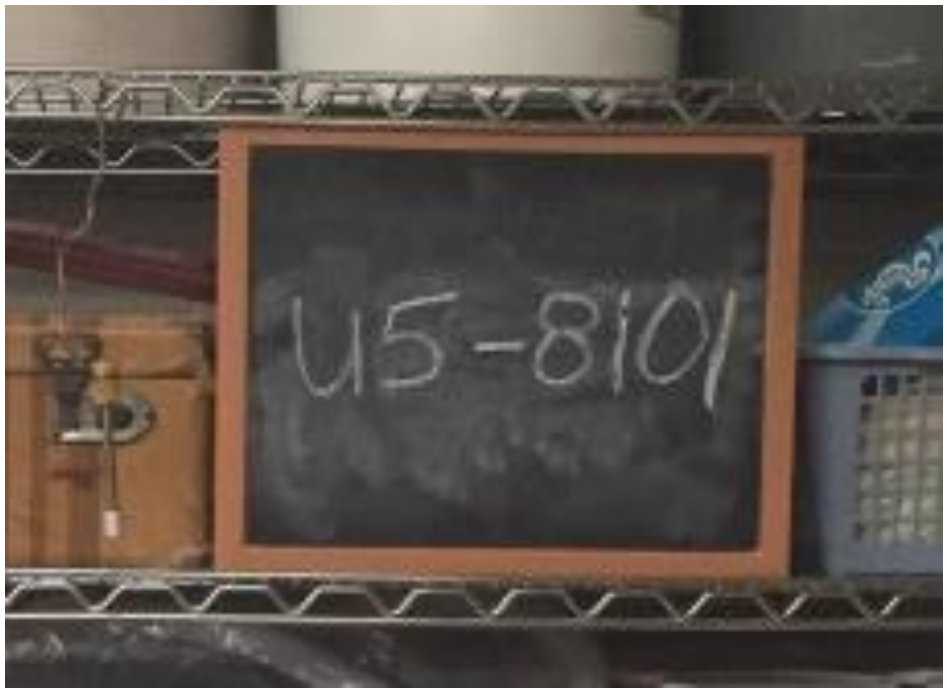

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Analysis by U.S. EPA Method TO-17

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

- Analytical results based on a minimum of a 5-point initial calibration
- Internal standards and surrogates included with each analysis
- Daily continuing calibration checks
- Laboratory control samples (LCS and LCSD)
- System daily tunes
- Method blanks

TD-GC/MS

- Quarterly Limit of Detection and Quantitation (LOD and LOQ) Studies
- US EPA Level III data packages submitted
- Results provided within 5 business days of sample receipt

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Target Compounds

Vinyl Chloride

1,1-Dichloroethene

cis-1,2-Dichloroethene

trans-1,2-Dichloroethene

1,2-Dichloroethane

Trichloroethene

Tetrachloroethene

Benzene

Toluene

Ethylbenzene

o-Xylene

p&m-Xylenes

1,4-Dichlorobenzene

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600+/ year Home Indoor Air Monitoring Program

Good correlation with prior data collected at homes over past decade when summa canister samples were collected

Data for blind duplicate passive samples

Target Compounds included: TCE; trans-1,2-DCE; cis-1,2-DCE; 1,2-DCA; Benzene; Toluene; Ethylbenzene and 1,4 dichlorobenzene*

Season	Passive Sampler ug/m3	Duplicate Passive Sampler ug/m3	%D		Season	Passive Sampler ug/m3	Duplicate Passive Sampler ug/m3	%D
2017-2018	0.06	0.06	0.0		2017-2018	0.33	0.34	3.0
2017-2018	0.18	0.19	5.6		2016-2017	0.12	0.12	0.0
2017-2018	0.01	0.05	400.0	*	2016-2017	0.23	0.23	0.0
2017-2018	0.48	0.54	12.5		2016-2017	0.26	0.26	0.0
2017-2018	0.22	0.21	4.8		2015-2016	0.25	0.24	4.2
2017-2018	1.77	1.78	0.6		2015-2016	0.26	0.26	0.0
2017-2018	0.21	0.22	4.8		2015-2016	0.31	0.37	19.4
2017-2018	1.65	1.64	0.6		2015-2016	0.63	0.61	3.3
2017-2018	1.87	1.91	2.1		2015-2016	1.36	1.32	3.0
2017-2018	0.8	0.84	5.0		2015-2016	2.09	2.24	7.2
2017-2018	6.93	7.79	12.4		2015-2016	2.86	2.52	13.5
2017-2018	0.09	0.07	28.6		2015-2016	8.28	7.8	6.2
2017-2018	0.08	0.07	14.3		2015-2016	10.12	9.97	1.5

*Standard adsorbent tube not well suited for 1,4 DCB. A better option would be the Beacon Sampler

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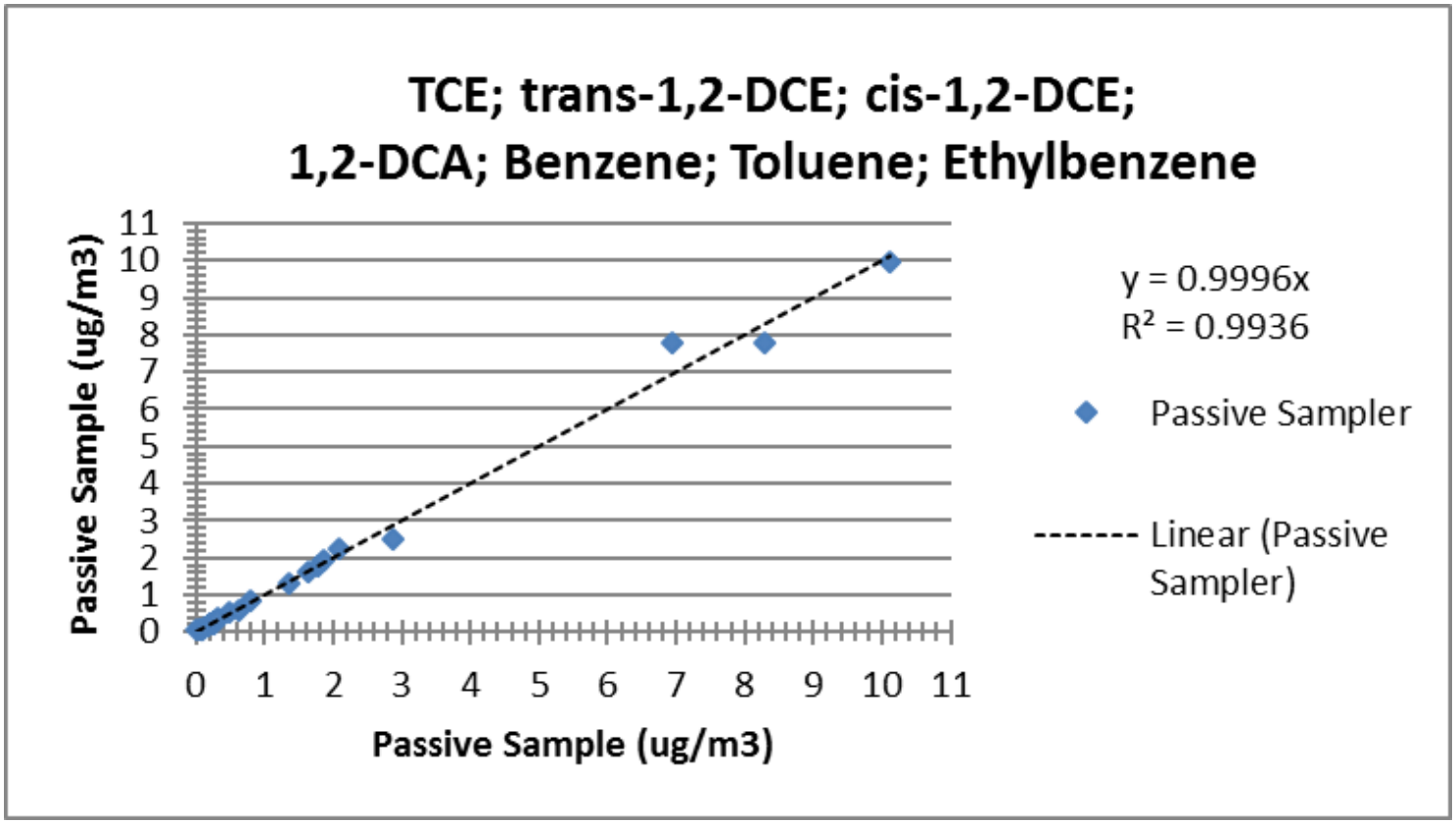
Data for blind duplicate passive samples



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Summa Canister – Quality Control Concerns

Data for the 26 duplicate pairs of Beacon passive samples

Percent Difference (%D)
0 to 30% Range = 96%
30 to 300% Ranges = 0%
>300% = 4%
With Median %D = 4.5%

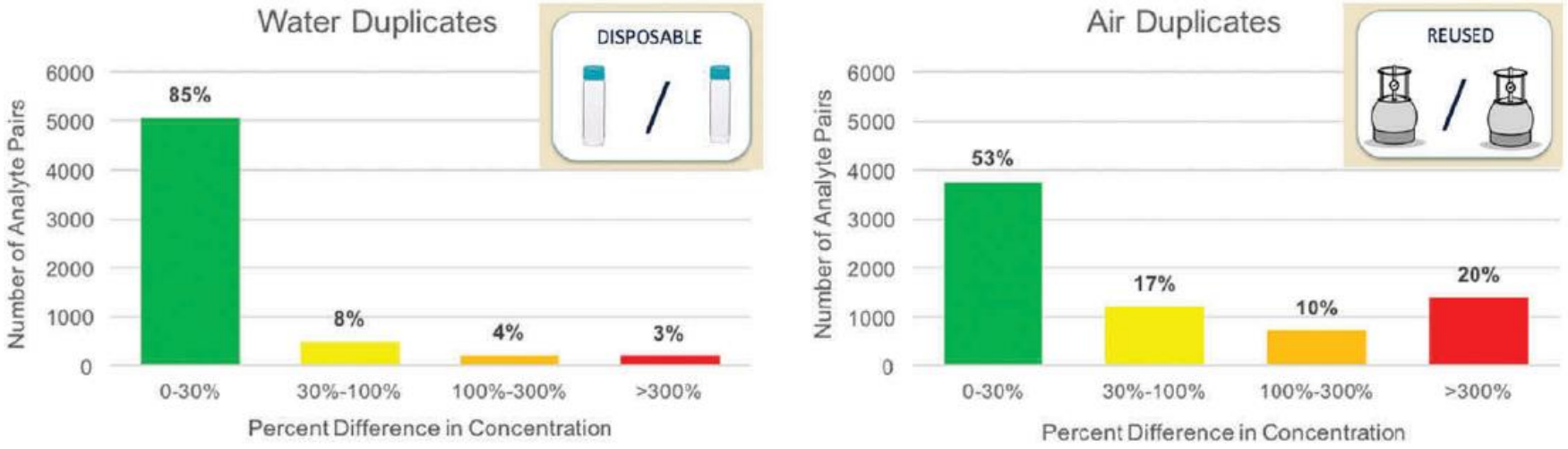

Figure 1. Duplicate variability for water duplicates and air duplicates.

Source: McHugh et al 2018, Evidence of canister contamination causing false positive detections in vapor intrusion investigation results

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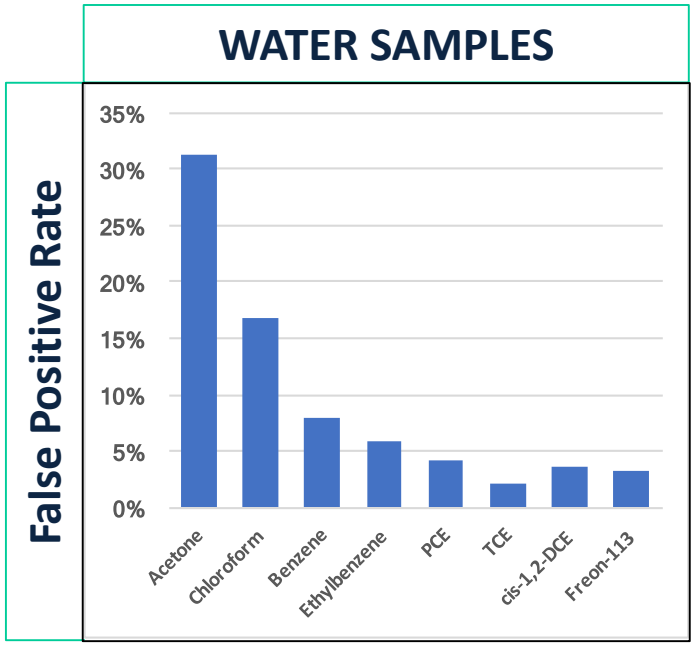
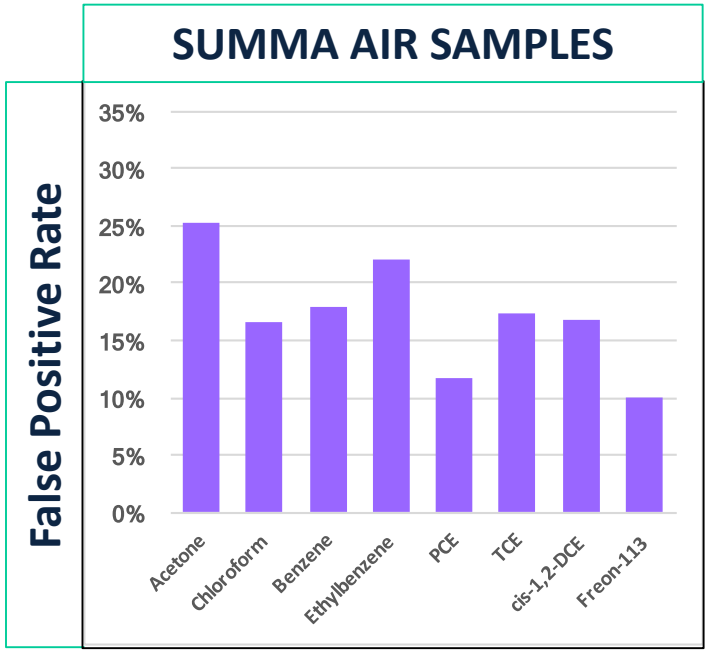
600+ Home Monitoring Program

Data for blind duplicate Beacon passive samples

False Positive Rate = 0 %

QUESTION: HOW OFTEN IS A DETECTION DUE TO LAB/CONTAINER CONTAMINATION?





Source: McHugh Presentation – Battelle Chlorinated Conference April 2018

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Summary – Passive Air Samplers

- **Passive adsorbent samplers are easy to use and less obtrusive than other sampling techniques**
- **Passive sampling methods produce high quality data while achieving low reporting limits**
- **Passive samplers can target concentrations that span orders of magnitude for a wide range of compounds**
- **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 is more representative of the health risks to building occupants than 24-hr samples**

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Grazie!

REMTECH Europe

Beacon… We can be your guide