

2023 Bioremediation Symposium

The Best Method to Assess Whether a Vapor Intrusion Risk is Present and Requires Mitigation The Preference for Passive Samplers

PRESENTED BY

Harry O'Neill

President **Beacon Environmental**



Sixth International Symposium on Bioremediation and Sustainable Environmental Technologies May 09, 2023



Typical Approach -- ≤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









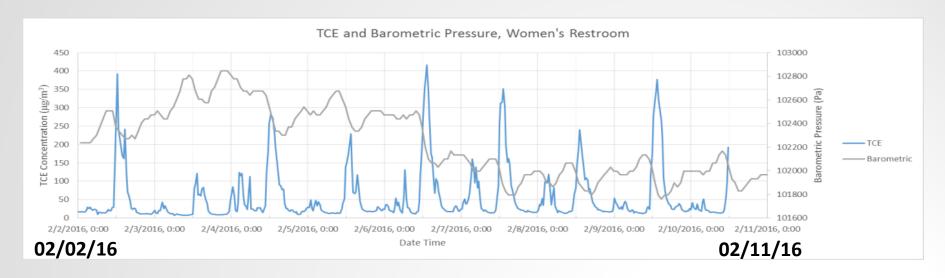
Source: EMS Environmental



Source: H&P Mobile



Temporal Variability Indoor air concentrations change seasonally, weekly, daily, hourly



Data collected by VaporSafe using on-site GC to provide real-time results

"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"

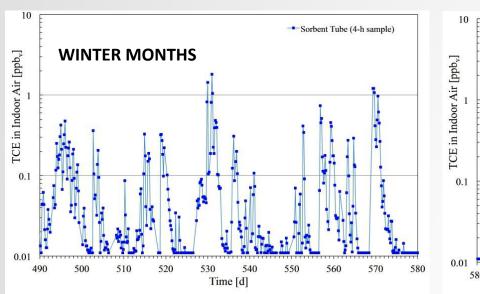
Source: Hosangadi et al, 2017

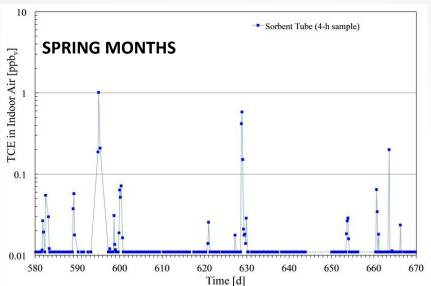


Temporal Variability

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.



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-hr 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 Coin Toss chance of being right

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



The Challenge - Canisters have Carry over Problems





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

Data Source – California GeoTracker Database

Data:

7,000 vapor samples 5,900 groundwater samples

Published 12 September 2018

The Challenge - Canisters have Carry over Problems

"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 of >300%."

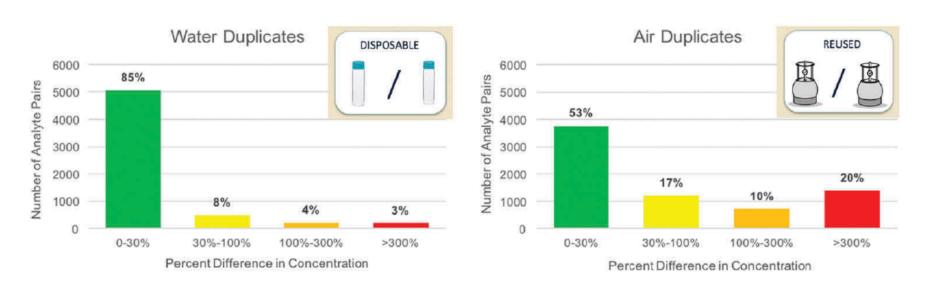


Figure 1. Duplicate variability for water duplicates and air duplicates.

Source:

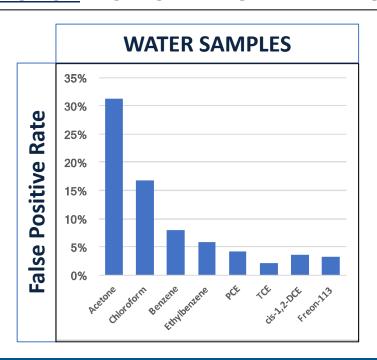
McHugh et al 2018, Evidence of canister contamination causing false positive detections in vapor intrusion investigation results

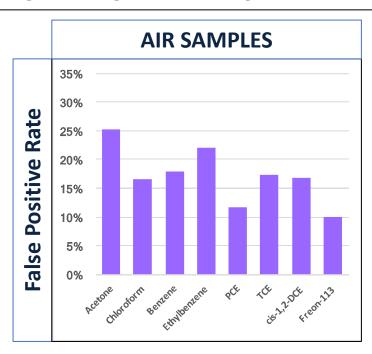


The Challenge - Canisters have Carry over Problems

Study Results

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



The Solution – Long Duration TWA Measurements

Passive Sorbent Samplers



Source: Jim Walden, Wisconsin DNR – AVIP Conference – October 10, 2022



Radial Sampler



Axial Samplers



Passive samplers allow for the collection of samples over days or weeks to measure organic compounds in indoor and ambient air, as well as soil gas. Data are reported as average concentrations (ug/m3 or ppbv) over time and are more representative of both short- and long-term health risks



- Passive samplers are easy to use and rapid to deploy
- Provide time-weighted average concentrations (ug/m³)
- Collect samples over hours, days, or weeks
- No pumps or flow regulators required
- 30-day hold time
- Lightweight easy to ship and transport
- Target broad range of VOCs
- Target concentrations that span orders of magnitude
- Low reporting limits, including in the pptv range









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

- QA/QC requirements identical to Method TO-15 (canisters)
- Analytical results based on minimum of a 5-pt initial calibration
- Internal standards and surrogates included with each analysis
- Daily continuing calibration checks
- LCS/LCSDs
- System daily tunes
- Method blanks
- Detection Limit (MDL) Studies



TD-GC/MS

- Limit of Detection and Quantitation (LOD and LOQ) Studies
- Meets requirements of Level IV data quality objectives
- Reliable identification & quantification



Operates on Fick's 1st Law of Diffusion

Uptake Rate (or Sampling Rate) is expressed as:

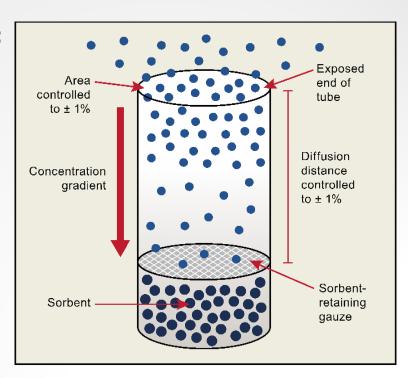
ng/ppbv*min ml/min

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

The sampler does not adsorb compounds from its surrounding environment faster than those compounds can be replenished

There is a 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 ($C_{ads} = 0$)

Axial type samplers



Source: Markes International



Calculate Concentration:

 $C = M / U \times t$

C = Concentration (ug/m³)

M = Mass (nanograms x 1000)

U = Uptake rate (ml/min)

T = time (min)

Theoretical Calculation of Uptake Rate:

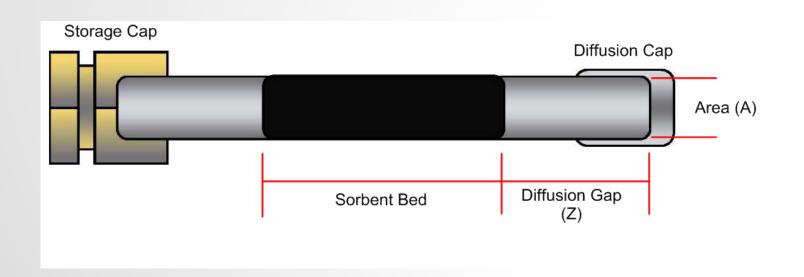
U = D * A/Z

U = Uptake rate (ml/min)

D = Diffusivity coefficient (cm2/sec)

A = Area (cm2)

Z = Diffusion Distance (cm)









Beacon worked with MCBA and the UK Health and Safety Executive (HSE) – the recognized experts in the industry for measuring uptake rates



Test adsorbents in standard axial samplers and Beacon Samplers for range of compounds from Vinyl Chloride to Xylenes

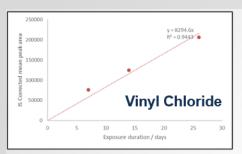


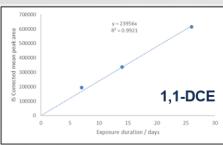


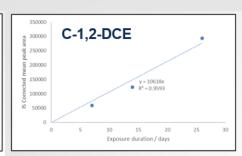


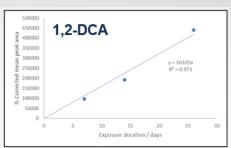
Beacon Funded Study – Axial Tube-Type Samplers

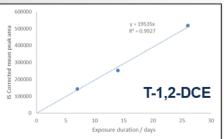
Uptake Rate Linearity with Time

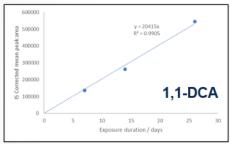


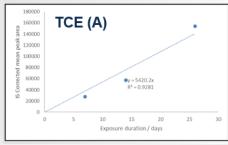


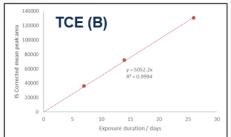




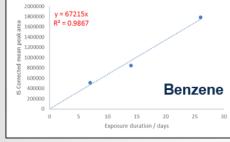


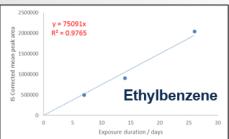


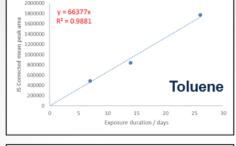


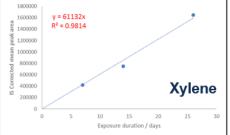










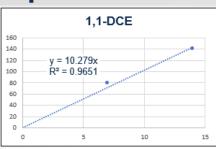


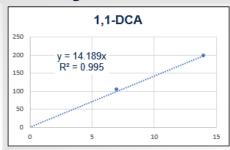


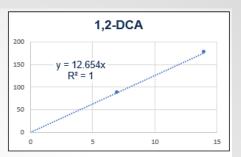
Beacon Funded Study – Beacon Passive Samplers

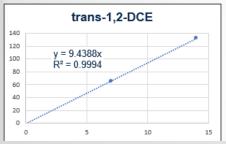
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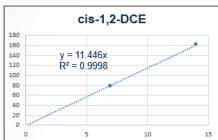


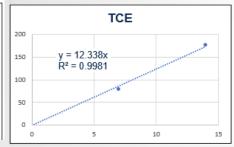


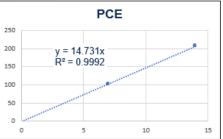




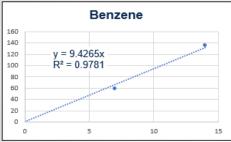


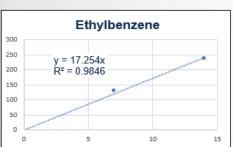


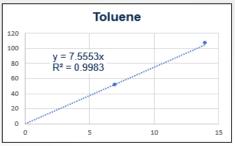


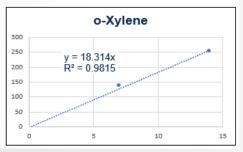
















Time-integrated Passive Samples compared to daily 24-hour average measurements

Robust study performed to compare results of Passive Samplers vs. average daily concentrations measured using Method TO-17 with pumped samples

Passive Samplers collected in triplicate; exposed for the duration of the sampling period

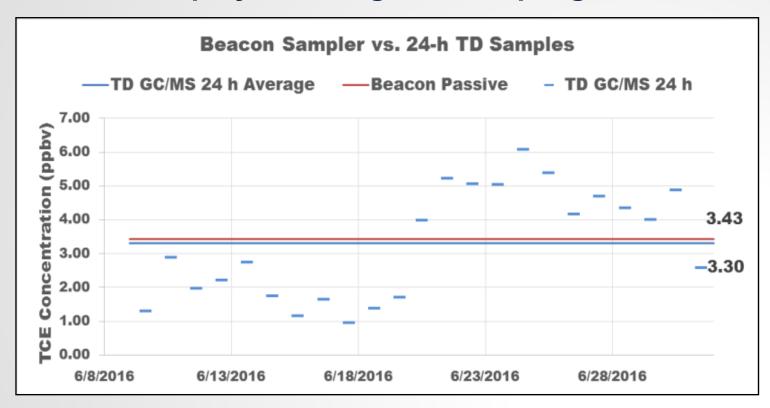
Pumped samples collected at a flow rate of 10 ml/min with a total volume of 14.4 L







Average value of daily measured concentrations compared well to average concentration from passive samplers deployed throughout sampling event

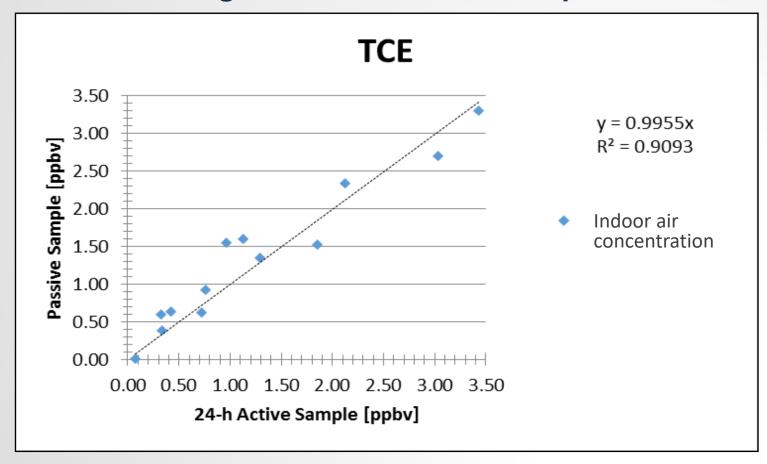




Relative Percent Difference between methods RPD = 3.9%



13 sampling events in study Correlation of passive samplers to average of 24-hour active samples







Samples Collected in Triplicate Analysis of Trichloroethene (TCE) Results

Sampling Event	Sampling Days	B-X-01 B-X-02		B-X-03	Average	Standard	Coefficient
		ppbv	ppbv	ppbv	ppbv	Deviation	of Variation
1	26	1.40	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	0.08	0.07	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
							0.10

The Coefficient of Variation (CV) measures precision [StndDev / Mean]

Source:

Arizona State University Study House
 Drs. Paul Johnson, Paul Dahlen, Yuanming Guo





HILL AIR FORCE BASE



PROGRAM OVERVIEW

In seven communities surrounding Hill AFB, chemicals from historical practices at the base have contaminated areas of shallow groundwater. Since the groundwater is not used for drinking or other household uses, the only way for the public to be exposed to the chemicals in the groundwater is through a process known as vapor intrusion. Vapor intrusion occurs when chemicals from the groundwater evaporate and move into homes or businesses within the affected area. (Click here to see how vapors may move into homes or businesses.)

Vapor intrusion doesn't happen in every home or business within the affected area. Hill AFB's Indoor Air Sampling Program focuses on testing locations most likely to have vapor intrusion—those above or close to areas of shallow groundwater contamination. In cooperation with state and federal regulators, the Air Force has established contaminant levels at which it will recommend taking action to prevent vapors from the groundwater from entering the home or business. These levels are called Risk-Based Action Levels, or RBALs. (Click here for more information about RBALs.) All sampling and mitigation actions will be done at no cost to the resident.

POINTS OF CONTACT

Indoor Air Program Manager

Mark Roginske (801) 775-3651 mark.roginske@us.af.mil

Peifen Tamashiro (801) 775-6981 peifen.tamashiro@us.af.mil

75th Air Base Wing Public Affairs

Barbara Fisher (801) 775-3652 barbara.fisher.1@us.af.mil

U.S. Environmental Protection Agency, Region 8

Sandra Bourgeois (303) 312-6666 (800) 227-8917 ext. 312-6666 bourgeois.sandra@epa.gov

Utah Department of

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



September 2019

Change to Air Sampling Method Improves Sample Accuracy

In 2016, Hill AFB implemented a number of changes to its indoor air sampling program in an effort to improve accuracy and reduce the need for future sampling. The change most noticeable to residents was the method used to obtain the sample. This fact sheet describes the changes made to the sampling method, the rationale for the changes and the effects the changes will have on decisions as the program moves forward.

Device change

The most obvious change is to how the samples are collected. Gone is the large silver Summa canister, which was used to collect a 24-hour sample. It is replaced with a small passive sampling device about the size of a pencil, designed to collect a sample over a 14 to 26-day period. When analyzed, the devices accurately measure an average concentration of chemicals in the air over the entire sampling period.

Recent advances in the science of vapor intrusion have shown that 24-hour samples, such as those collected by the Summa canisters, are not the most effective way to determine whether or not vapor intrusion is occurring in a particular home. Research has shown that the concentrations in a home can vary from day-to-day. This variability is due to changes in weather, outside temperature, furnace use, opening of windows and doors and several other factors, and can affect if contaminant vapors are entering the home.

If a canister were placed in a home during a period of favorable vapor intrusion conditions, then it's likely the chemicals would be detected. However, if a canister were placed in a home when vapor intrusion conditions were unfavorable, then it's unlikely contaminant vapors would

be detected.

The variability in detecting chemical vapors is the primary disadvantage using the 24hour canister method. The passive samplers, technically known as axial type passive samplers, are basically a tube filled with a special material designed to capture specific



Passive diffusion samplers, shown here, replaced Summa canisters. These devices are designed to collect a sample over a period of 14 to 26 days. Research has shown that a long-duration sample is more effective at determining if vapor intrusion is occurring in a home than a 24-hour sample.

chemical vapors. When placed in the home, the tubes are opened to allow air to flow into them. At the conclusion of the sampling timeframe, the tubes are sealed and sent to a laboratory for analysis. The laboratory will report an average concentration of chemicals in the air during the sampling time period.

The Air Force now uses an approximate sampling time period of 26 days. By sampling up to 26 days, the Air Force hopes to be able to determine whether or not vapor intrusion is occurring in the home with a reasonable degree of certainty without requiring sampling the same home multiple times over a period of several years. Recent advances in the science of vapor intrusion have shown that 24-hour samples, such as those collected by the Summa canisters, are not the most effective way to determine whether or not vapor intrusion is occurring in a particular home. Research has shown that the concentrations in a home can vary from day-to-day. This variability is due to changes in weather, outside temperature, furnace use, opening of windows and doors and several other factors, and can affect if contaminant vapors are entering the home.

Source:

https://www.hill.af.mil/Portals/58/documents/Indoor%20Air/AirSampling-Method-FactSheet.pdf?ver=2019-09-04-142302-097



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Source:

https://www.hill.af.mil/Portals/58/documents/Indoor%20Air/AirSampling-Method-FactSheet.pdf?ver=2019-09-04-142302-097



Passive sorbent samplers

26-day sampling periods

Sample during the winter seasons

2,600+ passive samples analyzed to date







Residents continue to have very positive response to sorbent samplers being used instead of 6 L evacuated canisters

They're **low-profile** and **easy-to-use**

Plus for the sampling team... logistically it's much easier to transport samples.







Installation and Retrieval of Beacon Air Sampler

1	On the first day of sampling, a technician will come to your home and hand you a plastic tube with a ready-to-hang Beacon Sampler.	
2	Hang the Sampler on a hook (or the optional tripod that will be provided) at the location pre-designated by the technician.	
3	You will be asked to photograph the location of the Sampler placement with a provided camera. As an option, you may use your mobile phone to e-mail or text the image to the address/number below.	
3	The Sampler will need to remain in place for approx. 30 days. Once in place, do not move it. Leave it until the technician returns. If the Sampler is inadvertently moved, call or email the technician.	2
4	On the last day of testing, a technician will return to retrieve the Sampler. They will provide you with the Sampler's plastic tube. Place the Sampler in the tube and hand it to the technician.	

Resident-based sampling applied last season on limited basis

US EPA has signed off as acceptable sample collection procedure for 2023-2024 season

Sign-up notice to residents will provide option for field tech to collect sample or have resident hang and retrieve sampler



ChloroSorber[™] Sampler Limits of Detection (LODs)

COMPOUND	CAS	Uptake Rate (ml/min)	3 Day LODs (ug/m³)	7 Days LODs (ug/m³)	10 Days LODs (ug/m³)	14 Days LODs (ug/m³)	26 Days LODs (ug/m³)
Vinyl Chloride	75-01-4	0.56	0.207	0.089	0.062	0.044	0.024
1,1-Dichloroethene	75-35-4	0.45	0.257	0.110	0.077	0.055	0.030
trans-1,2-Dichloroethene	156-60-5	0.70	0.165	0.071	0.050	0.035	0.019
1,1-Dichloroethane	75-34-3	0.74	0.156	0.067	0.047	0.034	0.018
cis-1,2-Dichloroethene	156-59-2	0.70	0.165	0.071	0.050	0.035	0.019
Trichloroethene	79-01-6	0.65	0.178	0.076	0.053	0.038	0.021
Tetrachloroethene	127-18-4	0.55	0.210	0.090	0.063	0.045	0.024





Reporting Limits of Available Samplers

Beacon Sampler -- Reporting Limits

Compound	Sampling Period (days)	Limit of Quantitation (ug/m3)	Limit of Detection (ug/m3)	Compound	Sampling Period (days)	Limit of Quantitation (ug/m3)	Limit of Detection (ug/m3)
Vinyl Chloride	14	0.61	0.31	1,1,1,2-Tetrachloroethane	14	1.22	0.61
1,1-Dichloroethene	14	1.50	0.75	Chlorobenzene	14	0.58	0.29
Methylene Chloride	14	1.42	0.71	Ethylbenzene	14	1.46	0.58
1,1,2-Trichlorotrifluoroethane (Fr.113)	14	0.56	0.28	p & m-Xylene	14	1.41	0.56
trans-1,2-Dichloroethene	14	1.13	0.56	o-Xylene	14	1.41	0.56
Methyl-t-butyl ether	14	2.48	0.99	1,2,3-Trichloropropane	14	0.66	0.33
1,1-Dichloroethane	14	0.58	0.29	Isopropylbenzene	14	1.49	0.60
cis-1,2-Dichloroethene	14	0.94	0.47	1,3,5-Trimethylbenzene	14	1.49	0.60
Chloroform	14	1.42	0.71	1,2,4-Trimethylbenzene	14	1.49	0.60
1,2-Dichloroethane	14	0.89	0.44	1,3-Dichlorobenzene	14	0.66	0.33
1,1,1-Trichloroethane	14	0.47	0.24	1,4-Dichlorobenzene	14	0.66	0.33
Carbon Tetrachloride	14	1.17	0.58	1,2-Dichlorobenzene	14	0.66	0.33
Benzene	14	2.34	0.94	1,2,4-Trichlorobenzene	14	1.27	0.63
Trichloroethene	14	1.50	0.75	Naphthalene	14	0.62	0.31
1,4-Dioxane	14	1.21	0.60	1,2,3-Trichlorobenzene	14	1.27	0.63
1,1,2-Trichloroethane	14	1.50	0.75	2-Methylnaphthalene	14	0.65	0.33
Toluene	14	3.10	1.24	TPH C4-C9 14 419.56		419.56	419.56
1,2-Dibromoethane (EDB)	14	1.29	0.64	TPH C10-C15 14 359.44		359.44	359.44
Tetrachloroethene	14	1.21	0.60		•		





Radiello 145 Sampler - Reporting Limits

Compound	CAS#	Sampling Period (days)	Limit of Quantitation (ug/m3)	Sampling Period (days)	Limit of Quantitation (ug/m3)
1,1,1-Trichloroethane	71-55-6	1	0.35	3	0.12
1,1-Dichloroethane	75-34-3	1	0.22	3	0.07
1,2,4-Trimethylbenzene	95-63-6	1	0.32	3	0.11
1,2-Dichlorobenzene	95-50-1	1	0.32	3	0.11
1,2-Dichloroethane	107-06-2	1	0.22	3	0.07
1,3,5-Trimethylbenzene	108-67-8	1	0.32	3	0.11
1,4-Dichlorobenzne	106-46-7	1	0.32	3	0.11
Benzene	71-43-2	1	0.25	3	0.08
Carbon Tetrachloride	56-23-5	1	0.26	3	0.09
Chlorobenzene	108-90-7	1	0.28	3	0.09
Chloroform	67-66-3	1	0.24	3	0.08
cis-1,2-Dichloroethene	156-59-2	1	0.22	3	0.07
Ethylbenzene	100-41-4	1	0.27	3	0.09
Isopropylbenzene	98-82-8	1	0.32	3	0.11
Naphthalene	91-20-3	1	0.33	3	0.11
o-Xylene	95-47-6	1	0.28	3	0.09
p & m-Xylene	108-38-3	1	0.26	3	0.09
Styrene	100-42-5	1	0.26	3	0.09
Tetrachloroethene	127-18-4	1	0.27	3	0.09
Toluene	108-88-3	1	0.23	3	0.08
trans-1,2-Dichloroethene	156-60-5	1	0.22	3	0.07
Trichloroethylene	79-01-6	1	0.26	3	0.09





Passive adsorbent samplers are preferred for the following reasons:

- easy to use and relatively unobtrusive
- can sample indoor and ambient air, as well as soil/sewer gas
- target broad list of VOCs and lighter SVOCs at concentrations that span orders of magnitude
- > sample collection periods of hours, days, or weeks
- analytical procedures produce high quality data while achieving low reporting limits
- Easy to 'clean' between uses no carry-over of contamination, which is a documented issue with canisters
- > Sustainable approach for sample collection and analysis
- Allows for the collection of samples over days or weeks to report concentration data that are more representative of the health risks to building occupants – better protection



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