ESTCP

FINAL REPORT ADDENDUM

Validation of Passive Samplers for Accurate, Long-Term, Time-Weighted Air Concentrations in Manhole Environments with Potentially Time-Variable Volatile Organic Air Contaminant Concentrations

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14. ABSTRACT

ESTCP projects ER-201505 and ER-201501 suggested manhole air sampling be part of VI assessment but indicated that contaminant concentrations within manholes can be temporally variable and suggested long-term sampling of that environment. Passive samplers offer a cost-effective method for collecting samples and ER-201501 studies indicated the sampler can provide accurate, long-term, time-weighted concentrations for indoor air environments with calibration and validation of the sampler used. The objective of this demonstration was to validate the use of the passive sampler for accurate assessment of volatile organic air contaminant concentrations in manhole environments where temperature, relative humidity, and contaminant concentration can vary with time. Performance was tested against the traditional TO-17 type thermal desorption tube (TD tube) active sampler in two, back-to-back, 8-day sampling events using 5 manholes with a history of contaminant in the vapor phase. Results using the Bland and Altman assessment to determine if the passive sampler was a suitable replacement for the active sampler suggested it was not. However, that method may not have been reasonable given the +/-30% range that is considered acceptable for analytical laboratories. Alternatively, regression analysis indicated the passive sampler was fairly precise, yet lacked accuracy for many analytes. This suggested the sampler could be a viable sampling tool with proper calibration and validation.

15. Subject Terms

Passive Sampler, Alternative VI Pathway, VI, Vapor Intrusion, Chlorinated Solvent Vapor Intrusion, Manhole, Land Drain

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
ASU	Arizona State University
cm	centimeter
cVOC	chlorinated volatile organic compound
CI	confidence interval
d	day
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
ft	foot
g	gram
hr	hour
in	inch
kg	kilogram
LD	Land drain
L	liter
m	meter
µg	microgram
µL	microliter
mg	milligram
ml	milliliter
min	minute
mo	month
ND	non-detect
OU	Operational Unit
Pa	pascal
ppbv	part per billion by volume
QA/QC	Quality assurance/quality control
RH	relative humidity

s	second
SDM	Sun Devil Manor
SERDP	Strategic Environmental Research and Development Program
SS	Sanitary sewer
T	temperature
TCE	trichloroethene/trichloroethylene
TD	thermal desorption
VOA	volatile organic analysis
VOC	volatile organic compound
VI	vapor intrusion
yr	year

ABSTRACT

INTRODUCTION

ESTCP projects ER#201505 and ER#201501 both identified sewers and/or land drains as alternative pathways for vapor intrusion (VI) and suggested manhole air sampling be part of VI assessment. Additionally, ER#201501 indicated that manhole concentrations can be temporally variable and suggested long-term sampling of that environment.

Passive samplers offer a cost-effective method for collecting samples. ESTCP ER#200830 showed that the passive sampler is an effective long-term sampling tool and ER#201501 indicated the passive sampler can provide accurate, long-term, time-weighted concentrations for indoor air environments with time-variable concentrations for up to three weeks with calibration and validation of the sampler used. Passive samplers, however, have not been validated for manhole environments where relative humidity and volatile organic vapor concentrations could be elevated and vapor concentrations, temperature, and relative humidity could each be variable over both the short and long term.

The objective of this demonstration was to validate the use of passive samplers for accurate, long-term, time-weighted volatile organic air concentration measurements in manhole environments. Performance was tested against the traditional TO-17 type thermal desorption tube (TD tube) active sampler.

TECHNOLOGY DESCRIPTION

The passive sampler is a sorbent-based sampler that acts as a sink for analytes, creating a concentration gradient for sample collection and eliminating the need for active collection. The sampler is cost effective, can be easily deployed, can be deployed for an extended period for time-integrated analysis, and requires no support infrastructure. As previously indicated, its use as a sampling tool was validated under ESTCP project ER#200830, and ESTCP ER#201501 showed that passive samplers can provide accurate, long-term, time-weighted concentrations for indoor air monitoring for up to three weeks, however, accurate results required calibration and validation of the sampler used.

PASSIVE SAMPLER PERFORMANCE

Passive sampler performance was tested against the traditional TO-17 type thermal desorption tube (TD tube) active sampler. The demonstration included two, back-to-back, 8-day sampling events in which samplers (passive and active TD tube) were deployed in triplicate in five manholes. Passive sampler validation was based on a comparison of passive vs active sampler concentrations using both linear regression and an assessment of comparability using a method developed by Bland and Altman (1986). Bland and Altman used plots of difference in concentration vs mean concentration for data pairs to evaluate the magnitude of variation.

Assessment of comparability using linear regression indicated that there was a fairly good relationship for all analytes, but for many, that relationship was not 1:1. That suggested the passive sampler was precise but lacked accuracy for many analytes. For those analytes, uptake rates needed to be more effectively calibrated to be suitable for accurate analysis.

Additional assessment of comparability using the Bland and Altman (1986) method suggested the passive sampler was not a suitable replacement for active sampling due to the magnitude of variation between plots of difference in concentration vs mean concentration for passive/active sampler data pairs.

However, use of the Bland and Altman method for assessment may not be reasonable since the acceptable range for lab accreditation and accurate laboratory analysis is inherently large at +/- 30% of the true value. Alternatively, regression analysis suggested that the passive sampler was fairly precise yet lacked accuracy for most analytes, and as such, required proper calibration. This result was consistent with results from ER#201501 for indoor environments. As such, it is believed the passive sampler could be an effective sampling tool with proper calibration and validation.

COST ASSESSMENT

Cost assessment for passive sampler use was based on a per sample assessment or multiples thereof, since it is not possible to estimate how many samplers might be used in manhole deployments across a neighborhood. Cost focused on deployment/retrieval and analytical costs, but did not include preparation, travel, or reporting time. The per sample cost estimate for deployment/retrieval was based on $100/hr for a total of 1 hour and analytical costs of $200, for a total of $300/sample.

PUBLICATIONS

There were no publications associated with this work.

EXECUTIVE SUMMARY

INTRODUCTION

Two ESTCP projects have identified sewers and/or land drains as alternative pathways for vapor intrusion. ER#201505, *Sewers and Utility Tunnels as Preferential Pathways for Volatile Organic Compound Migration into Buildings: Risk Factors and Investigation Protocol* (McHugh and Beckley, 2018), provided a conceptual model for volatile organic compound migration into buildings which included the sewer utility pathway. It also identified a discrete sampling protocol for collecting air samples within sewer manholes. ER#201501, *VI Diagnosis Toolkit for Assessing Vapor Intrusion Pathways and Impacts in Neighborhoods Overlying Dissolved Chlorinated Solvent Plumes* (Johnson, et al., 2020), included sampling of sewer and land-drain manholes as part of "external flux assessment," a preliminary step to determine if contaminant is present at concentrations that could be a concern for vapor intrusion. ER#201501 also indicated that manhole concentrations can be temporally variable and supported long-term sampling of that environment, for which the passive sampler could be an effective tool.

Current sampling technologies require multiple, discrete samples be collected continuously over a sampling period, or equipment/infrastructure to support sampling equipment that allows for continuous collection of single samples over that sampling period (e.g., pumps, timers, electrical, etc.). The passive sampler, on the other hand, is a cost-effective sampler that can be easily deployed, deployed for an extended period for timed integrated analysis, and requires no support infrastructure. ESTCP project ER#200830, *Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques* (McAlary, 2014), showed that the passive sampler is an effective long-term sampling tool and ER#201501 indicated that passive samplers can provide accurate, long-term, time-weighted concentrations for monitoring indoor air environments with time-variable concentrations for up to three weeks with calibration and validation of the sampler used. ER#201501 also suggested that passive samplers could be an effective tool for sampling manhole environments. However, passive samplers have not been validated for manhole environments where relative humidity and volatile organic vapor concentrations could be elevated and vapor concentrations, temperature, and relative humidity could each be variable over both the short and long term. It is those variables that set the manhole environment apart from the indoor environment.

OBJECTIVE

The objective of this demonstration was to validate passive sampler performance against the traditional TO-17 type thermal desorption tube (TD tube) active sampler for accurate assessment of volatile organic air concentrations in manhole environments.

TECHNOLOGY DESCRIPTION

The passive sampler is a sorbent-based sampler that acts as a sink for analytes, creating a concentration gradient for the collection of the sample and eliminating the need for active collection. The sampler is cost effective, can be easily deployed, can be deployed for an extended period for timed integrated analysis, and requires no support infrastructure. Its use as a sampling tool was validated under ESTCP project ER#200830, and ESTCP ER#201501 showed that passive samplers can provide accurate, long-term, time-weighted concentrations for indoor air monitoring for up to three weeks, however, accurate results required calibration and validation of the sampler used.

PERFORMANCE ASSESSMENT

Passive sampler performance was tested against the traditional TO-17 type thermal desorption tube (TD tube) active sampler, the performance objectives for which are shown in Table ES1. The demonstration included two, back-to-back, 8-day sampling events performed March 24 through April 9, 2022, in which samplers (passive and active TD tube) were deployed in triplicate in five manholes with a history of contaminant in the vapor phase. Passive sampler validation was based on a comparison of passive vs active sampler concentrations using both linear regression and an assessment of comparability using a method developed by Bland and Altman (1986). Bland and Altman used plots of the difference in concentration vs the mean concentration for data pairs to evaluate magnitude of variation between data pairs. Plots and basis for evaluation included the mean difference for the entire data set, a 95% confidence interval (CI) for the mean/bias as defined by a *t*-Test using the equation ***CI = mean +/- 2* StdError***, and a 95% CI for the normal Gaussian distribution as defined by the interval ***CI = mean +/- 2*StdDev*** for evaluation.

A brief summary of results is provided in Table ES2 below.

Table ES-1 Performance Objectives

Task [duration]	Performance Objective	Data Requirements	Success Criteria
Validate the use of passive samplers in manhole conditions	Demonstrate that passive samplers provide accurate results for volatile organic contaminant concentrations in manholes where elevated relative humidity is likely and there is the potential for variable vapor concentrations, temperature, and relative humidity over extended sampling periods.	Passive sampler and active TD tube (TO-17) sampler data from seasonal 8-day sampling events.	Strong regression coefficient with 1:1 correlation & Mean difference of concentrations be normally distributed and fall within a 95% confidence interval as follows: • Dmean + 2*s • Dmean - 2*s where Dmean is the mean difference and s is the standard deviation of the differences.

Table ES-2. Summary of Data for Assessment/Comparison of Passive Sampler vs TD Tube Performance.

Results are in ug/m^3 as applicable.

Analyte	Number of usable TD/Passive pairs[1]	R^2 [2]	Slope	Difference Between TD and Passive Sampler Values													
				Mean	Std Dev (SD)	Min	Max	Range	Gaussian Distribution 95% Confidence Interval (CI) for Normal Distribution [3]				t-Test 95% Confidence Interval (CI) Around Mean/bias [4]				
									Range		Values w/in CI		Std Error	CI Range		Values w/in CI	
									Low	High	#	%		Low	High	#	%
TCE	24	0.953	1.15	92.04	81.31	-130	227	357	-70.57	254.65	23	96	16.60	58.85	125.23	10	42
11 DCA	24	0.935	0.75	-1.31	1.64	-5.64	1.14	6.78	-4.59	1.96	23	96	0.33	-1.98	-0.64	9	38
111 TCA	6	0.833	0.34	-11.09	2.74	-14.2	-7.66	6.53	-16.57	-5.61	6	100	1.12	-13.33	-8.85	4	67
11 DCE	21	0.991	2.62	15.12	17.91	1.96	50.2	48.24	-20.70	50.94	21	100	3.91	7.31	22.94	0	0
12 DCA	10	0.939	1.67	1.09	0.75	0.16	2.49	2.33	-0.42	2.60	10	100	0.24	0.61	1.57	5	50
cis 12 DCE	24	0.974	1.41	20.21	19.24	-12.7	60.2	72.9	-18.27	58.70	23	96	3.93	12.36	28.07	5	21
PCE	17	0.959	1.56	11.98	18.16	-1.18	54.8	55.98	-24.33	48.30	16	94	4.40	3.18	20.79	5	29
Trans 12 DCE	23	0.980	1.77	9.11	7.79	-1.85	25.4	27.25	-6.48	24.70	21	91	1.63	5.86	12.36	2	9
VC	9	0.898	2.19	0.93	0.29	0.39	1.39	1.00	0.35	1.50	9	100	0.10	0.74	1.12	6	67

(1) Results based on lab data for which both TD and Passive sampler results were both quantifiable (not ND)

(2) R^2 for linear correlation

(3) 95% confidence interval (CI) for normal distribution about the mean defined by equation CI=Mean +/- 2*StdDev

(4) t-Test - 95% confidence interval (CI) defined by t-test and formula *CI=Mean +/- 2*StdError*

Linear regression analysis using a direct plot of passive sampler concentrations vs active TD tube sampler concentrations indicated R^2 values typically greater than 0.94, suggesting there was a fairly good linear relationship for most analytes. The regression assessment for TCE is shown in Figure ES1, which indicates an R^2 value of 0.95 and a slope of 1.15. However, for many analytes, that relationship was not 1:1. As such, the passive sampler was precise, performing consistently relative to the active sampler, however, results for some analytes were not accurate or representative of actual concentration. For those analytes, uptake rates needed to be more effectively calibrated to be suitable for accurate analysis.

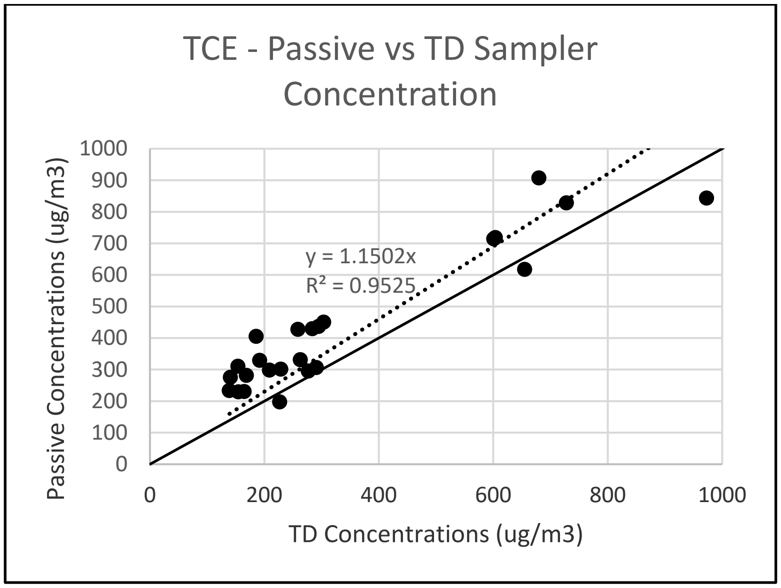


Figure ES-1. Passive Sample Concentration vs TD Tube Sample Concentration.

Slope and R^2 for linear regression shown.

Additional assessment of comparability using the Bland and Altman (1986) method suggested the passive sampler was not a suitable replacement for active sampling due to the magnitude of variation between plots of difference in concentration vs mean concentration for passive/active sampler data pairs.

However, use of the Bland and Altman method for assessment may not be reasonable since the acceptable range for lab accreditation and accurate laboratory analysis is inherently large at +/- 30% of the true value. Alternatively, regression analysis suggested that the passive sampler was fairly precise yet lacked accuracy for most analytes, a shortcoming that could be remedied with effective calibration of uptake rates for analytes of interest. This result was consistent with results from ER#201501 for indoor environments. As such, it is believed the passive sampler could be an effective sampling tool with proper calibration and validation.

COST ASSESSMENT

Since it is difficult to estimate how many samplers might be used in a deployment or with multiple deployments across a neighborhood, costs associated with passive sampler use will focus strictly on deployment, retrieval, and analytical cost on a per sample basis.

This estimate does not reflect preparation time, travel time, or reporting time. The cost estimate for deployment, retrieval, and analysis of a single passive sampler is shown in the table below.

Table ES-3. Cost Estimate for Deployment, Retrieval, and Analysis of a Single Passive Sampler

Activity		Amount	Unit Cost	Total Cost
Analytical		1	$200	$200
Labor: Consultant	Deployment	0.5 hr	$100/hr	$100
	Retrieval	0.5 hr		
Total				$300

Based on this per sample estimate, costs can be estimated as follows:

- for a single sample deployment in a manhole setting - $300
- for a deployment in 10 manhole settings - $3,000

IMPLEMENTATION ISSUES

Beyond the need for accurate, analyte specific calibration of the passive sampler, deployment in manholes where concentrations might saturate the sorbent-based sampler would be the only implementation issue in terms of understanding actual concentrations within a manhole. However, even if saturation occurs, there is valuable information to be gained in terms of minimum concentrations for analytes of concern and the presence of other analytes present and their relative concentrations. This information can also be used if resampling for more accurate concentrations is necessary.

1.0 INTRODUCTION

Two ESTCP projects have identified sewers and/or land drains as alternative pathways for vapor intrusion. ER#201505, *Sewers and Utility Tunnels as Preferential Pathways for Volatile Organic Compound Migration into Buildings: Risk Factors and Investigation Protocol* (McHugh and Beckley, 2018), provided a conceptual model for volatile organic compound migration into buildings which included the sewer utility pathway. It also identified a discrete sampling protocol for collecting air samples within sewer manholes. ER#201501, *VI Diagnosis Toolkit for Assessing Vapor Intrusion Pathways and Impacts in Neighborhoods Overlying Dissolved Chlorinated Solvent Plumes* (Johnson, et al., 2020), included sampling of sewer and land-drain manholes as part of "external flux assessment," a preliminary step to determine if contaminant is present at concentrations that could be a concern for vapor intrusion. ER#201501 also indicated that manhole concentrations can be temporally variable and supports long-term sampling of that environment.

Current sampling technologies require multiple, discrete samples be collected continuously over a sampling period, or equipment/infrastructure to support sampling equipment that allows for continuous collection of single samples over that sampling period (e.g., pumps, timers, electrical, etc.). The passive sampler, on the other hand, is a cost-effective sampler that can be easily deployed, deployed for an extended period for timed integrated analysis, and requires no support infrastructure. ESTCP project ER#200830 (McAlary, 2014) showed that the passive sampler is an effective long-term sampling tool and ER#201501 (Johnson, et al., 2020) testing showed that passive samplers can provide accurate, long-term, time-weighted concentrations for monitoring indoor air environments with time-variable concentrations for up to three weeks with calibration and validation of the sampler used. ER#201501 also suggested that passive samplers could also be an effective tool for sampling manhole environments. However, passive samplers have not been validated for manhole environments where relative humidity and volatile organic vapor concentrations could be elevated and vapor concentrations, temperature, and relative humidity could each be variable over both the short and long term. While elevated concentration, relative humidity, nor temperature have been identified as problems associated with passive sampler use, it is those variables that set the manhole environment apart from the indoor environment where previous work with passive sampler validation under ER#201501 was performed. The goal of this project was to validate the use of passive samplers against the traditional TO-17 type thermal desorption tube (TD tube) active sampler for accurate, long-term, time-weighted volatile organic air concentration measurements in the manhole environment where relative humidity and volatile contaminant vapor concentrations could be elevated and contaminant vapor concentrations, temperature, and relative humidity could each be variable with time.

This report details the findings of two, back-to-back, 8-day sampling events that were performed from March 24 through April 9, 2022. These events were two of the four events proposed under the Demonstration Plan. Assessment of sampler performance and recommendations that do not support further study under this project are provided.

1.1 OBJECTIVE OF THE DEMONSTRATION

The objective of this demonstration was to validate passive sampler use for long term assessment of chlorinated solvent vapor concentrations in manholes where relative humidity and chlorinated solvent vapor concentrations are likely elevated and contaminant vapor concentrations, temperature, and relative humidity are each potentially variable with time. Passive sampler validation was based on comparison with the TD tube active sampler.

1.2 REGULATORY DRIVERS

While there are no specific regulatory drivers, the success of this demonstration was to validate the use of passive samplers for external VI source mass flux assessments during vapor intrusion investigations, adding to the suite of "tools" available to practitioners and clients with the ER#201501 VI Diagnosis Toolkit. In addition, it was to validate the passive sampler for use in a broader range of conditions.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The passive sampler is a sorbent-based sampler that acts as a sink for analytes, creating a concentration gradient for the collection of sample and eliminating the need for active collection. Its use as a sampling tool was validated under ESTCP project ER#200830 (McAlary, 2014). In addition, ESTCP ER#201501 (Johnson, et al., 2020) showed that passive samplers can provide accurate, long-term, time-weighted concentrations for indoor air monitoring for up to three weeks, however, accurate results required calibration and validation of the sampler used. It also suggested that use of passive samplers could be an effective tool for sampling manhole environments.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantage of the passive sampler is that it is both expedient and cost-effective for sampling: It is effective for long period deployments, easily deployed, and requires no support infrastructure. Limitations of the passive sampler include possible sensitivity to variations in temperature and relative humidity during its deployment and, since it only provides an averaged concentration for the period of deployment, it does not provide maximum contaminant concentrations.

Alternatives to the passive sampler would be the more traditional methods of sampling including summa canisters or the TO-17 method of sampling using actively collected TD tubes.

3.0 PERFORMANCE OBJECTIVE

The performance objective for this project is summarized in Table 1. In brief, passive samplers were to be used in manholes to assess performance, providing accurate time-averaged concentrations over 8-day periods in manhole environments where relative humidity and volatile contaminant vapor concentrations are likely elevated and volatile contaminant vapor concentrations, temperatures, and relative humidity levels could each vary with time. Passive sampler performance would be based on a comparison with traditional TO-17 type TD tube active sampling to validate performance.

Table 1. Performance Objective.

Task [duration]	Performance Objective	Data Requirements	Success Criteria
Validate the use of passive samplers in manhole conditions	Demonstrate that passive samplers provide accurate results for volatile organic contaminant concentrations in manholes where elevated relative humidity is likely and there is the potential for variable vapor concentrations, temperature, and relative humidity over extended sampling periods.	Passive sampler and active TD tube (TO-17) sampler data from seasonal 8-day sampling events.	Strong regression coefficient with 1:1 correlation & Mean difference of concentrations be normally distributed and fall within a 95% confidence interval as follows: • Dmean + 2*s • Dmean - 2*s where Dmean is the mean difference and s is the standard deviation of the differences.

4.0 SITE DESCRIPTION

4.1 SITE SELECTION AND LOCATION

The site selected for work was the Layton, UT neighborhood overlying the dilute dissolved chlorinated solvent plume associated with Hill AFB Operable Unit 8 (OU-8; now OU-15) as shown in Figure 1. This residential area was the primary test site for work under SERDP ER#1686 and ESTCP ER#201501, and was the location of "Sun Devil Manor," the ASU study house. Five manholes within that neighborhood were selected based on their vapor contaminant history from manhole testing that was performed under ER#201501.

4.2 SITE HISTORY AND JUSTIFICATION FOR USE

The residential neighborhood associated with Hill AFB OU-8, Layton, UT was unique because of the extensive historical indoor air, groundwater data, and manhole vapor data sets that have been generated under DoD management of OU-8 and by Arizona State University in association with SERDP ER#1686 and ESTCP ER#201501. In specific, work under ER#201501included extensive investigation of vapor concentrations within 267 manholes across the OU-8 neighborhood, generating data on the spatial distribution of contaminant and seasonal variation in concentration for each location. In addition, a high-density temporal data set from a subset of 15 of those manholes was collected to determine short term variations in concentration.

For effective validation of passive samplers for long-term deployment in manhole environments, both passive and TD-tube samplers should have a quantifiable contaminant load after exposure. To provide an optimal test condition, the manholes selected had historic concentrations that were neither non-detect, nor so high that the sorbent-based samplers (both passive and TD-tube) might risk saturation during long-term deployment.

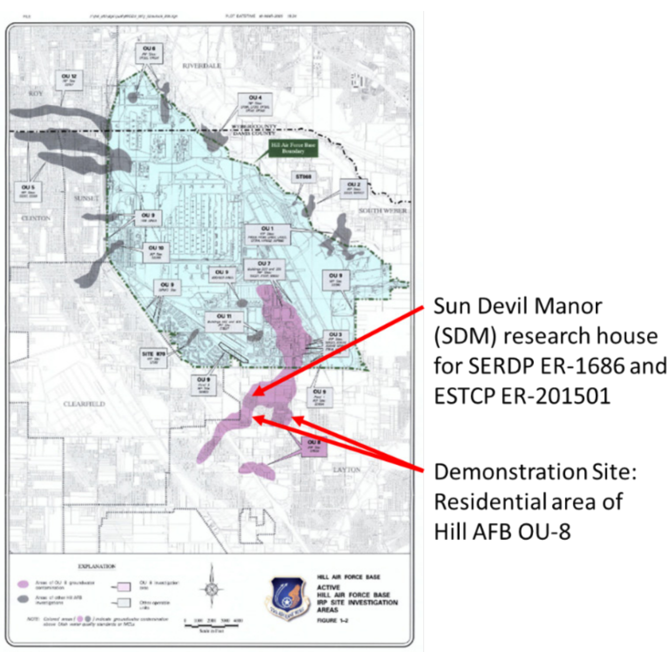


Figure 1. Demonstration Site: Residential Area of Hill AFB OU-8, Layton, UT.

4.3 MANHOLE LOCATIONS UTILIZED FOR SAMPLER DEPLOYMENT

The OU-8 manhole locations utilized for sampling were as follows:

Location 1	Location 2	Location 3	Location 4	Location 5
LD 03 1100W 2600N	LD 08 1150W 2525N	LD 41 2450N 950W	LD 56 650W 2275N	LD 32 2350N 675W

These locations were based on a review of historic manhole air contaminant concentrations from Guo, et.al., 2019. Tricholoroethene (TCE) concentration for locations selected ranged to in excess of 100 ppbv over a span of 3 orders of magnitude. This selection deviated from the originally proposed list of manholes by eliminating one sanitary sewer manhole and replacing it with an adjacent land drain manhole. This was done to avoid potential exposure to Covid.

5.0 EXPERIMENTAL PROCEDURE

As discussed, the focus of this demonstration was the validation of passive sampler performance for long-term, time-weighted assessment of volatile organic air contaminant concentrations in manhole environments. The passive sampler tested was the vial type Beacon Sampler (Beacon Environmental, Forest Hill, Maryland, USA) and its performance was compared to that of TD tubes. The Beacon Sampler was one of several passive samplers tested during indoor, long-term, time weighted testing under ER#201501 and was selected for this study because it was the most effective sampler previously tested in indoor air environments. Data compiled from multiple tests for time-weighted or averaged TCE concentrations for the sampling period showed a 1:1 correlation between 24 hour TO-17 passive sampling and real time GC-ECD analytical, indicating the sampler was both accurate and precise for TCE analyses relative to GC-ECD analytical (Johnson, et al., 2020; Guo, et al., 2021).

The passive sampler involved passive deployment, and as such, no air was actively pumped or pulled through the sampler. The suitability of the sampler for the 8-day deployment was a function of vapor concentration, uptake rate, and mass and characteristic of sorbent(s). The TD tube, on the other hand, was an active sampler, requiring air to be pumped or pulled through it. The suitability of the TD tube for the 8-day deployment was a function of vapor concentration, mass and characteristic of sorbent(s), and the amount of air pulled through the sampler.

5.1 THERMAL DESORPTION (TD) TUBE SAMPLING

TD tube sampling for this project was integrated, timed-interval sampling. To facilitate sampling, a single constant pressure vacuum pump served a manifold, which held three independent flow restrictor orifices, each serving an independent TD tube. Each orifice had a unique flowrate in the range of 35-60 ml/minute and pump runtime determined the total volume of sample collected for each TD tube. To prevent sampler saturation over the 8-day sampling period, active TD tube sample collection was limited to discrete periods equally spaced throughout the sampling period. For this project, sampling was limited to 1 minute "on" followed by 10 min "off," for a total of 1 min sampling per 11 min elapsed time. The timed interval operation reduced contaminant load for the sampler, yet still ensured a time-integrated perspective of concentrations within each manhole. To determine if sampler saturation had occurred, a fourth TD tube was placed downstream in series with one of the primary tubes to determine if there was breakthrough. If contaminant breakthrough had occurred, it would have invalidated all tubes for that location. The integrity of TD tube samples when not being actively collected was ensured via the use of Markes Diff-Lok caps (Markes, LTD, England).

Historical data from the manholes indicated analyte concentrations of up to 100 ppbv for TCE, the dominant cVOC present at each location. Based on that concentration, a sampling flowrate of 60 ml/min, and a total collection runtime of 1048 minutes for 8 days, the sample volume was estimated at 62.8 L and the maximum load for any of the project defined target analytes shown in Table 2 was approximately 42 micrograms. Beacon laboratory empirical data has indicated effective sample volumes greater than two times that mass for single compounds when sampling air or soil gas in complex environments with multiple compounds present. Therefore, it was conservatively estimated that the safe sampling volume was at least twice that proposed for the TD tubes and no breakthrough was anticipated. However, as indicated, a backup tube was placed downstream in series to one of the primary TD tubes at each location and for each sampling event to demonstrate that the safe sampling volume was not exceeded.

Table 2. Target Analyte List.

Sampler Type	Matrix	Analyte	CAS#	Method	Sampler Type	Holding Time
Passive -- Active TD Tube	Air	Vinyl chloride	75-01-4	TO-17	Passive - Vial Active – TD Tube	28 days
		1,1-Dichloroethene	75-35-4			
		trans-1,2-Dichloroethene	156-60-5			
		1,1-Dichloroethane	75-34-3			
		cis-1,2-Dichloroethene	156-59-2			
		1,2-Dichloroethane	107-06-2			
		1,1,1-Trichloroethane	71-55-6			
		1,1,2-Trichloroethane	79-00-5			
		Trichloroethene (TCE)	79-01-6			
		Tetrachloroethene	127-18-7			

5.2 PASSIVE SAMPLING

Per Beacon Environmental analytical laboratory, the sampling rate for the Beacon passive sampler was compound dependent and would vary from 0.33 to 1.0 ml/min (Beacon passive sampler performance is detailed in a report from Beacon (2020) that is provided in Appendix A). That equated to an 8-day sampling volume of 3.8 to 11.5 L, a significantly lower volume and associated mass load of compounds than that estimated for TD tubes. Given an 8-day sampling period, the reporting limit was estimated to be 0.12 ppbv and, with only minor exception, was lower than the lowest historic TCE concentrations reported. Although TCE was the dominant analyte of focus, the capable range for the passive sampler was similar for all analytes shown in Table 2.

Based on the highest historical concentration for TCE for any location and assuming that the 10 analytes considered were equivalent in concentration, the anticipated cumulative mass loading for analytes on the passive sampler for an eight-day exposure was one order of magnitude less than that sorbent capacity of the sampler. As such, a minimum 10x safety factor was built into the test to account for unanticipated concentrations and the presence of other compounds that would consume sorbent capacity. Based on Beacon Environmental's experience with the Beacon sampler and its use in manhole and soil gas environments for chlorinated solvent evaluation, the 10x safety factor was believed to be robust and no exceedances were anticipated.

5.3 EXPERIMENTAL DESIGN

Passive sampler performance was compared to simultaneously, actively collected TD tube samplers. Both passive and active samplers were deployed in triplicate at each sampling location using the sampler shown in Figure 2, the contents of which are detailed in Table 3.

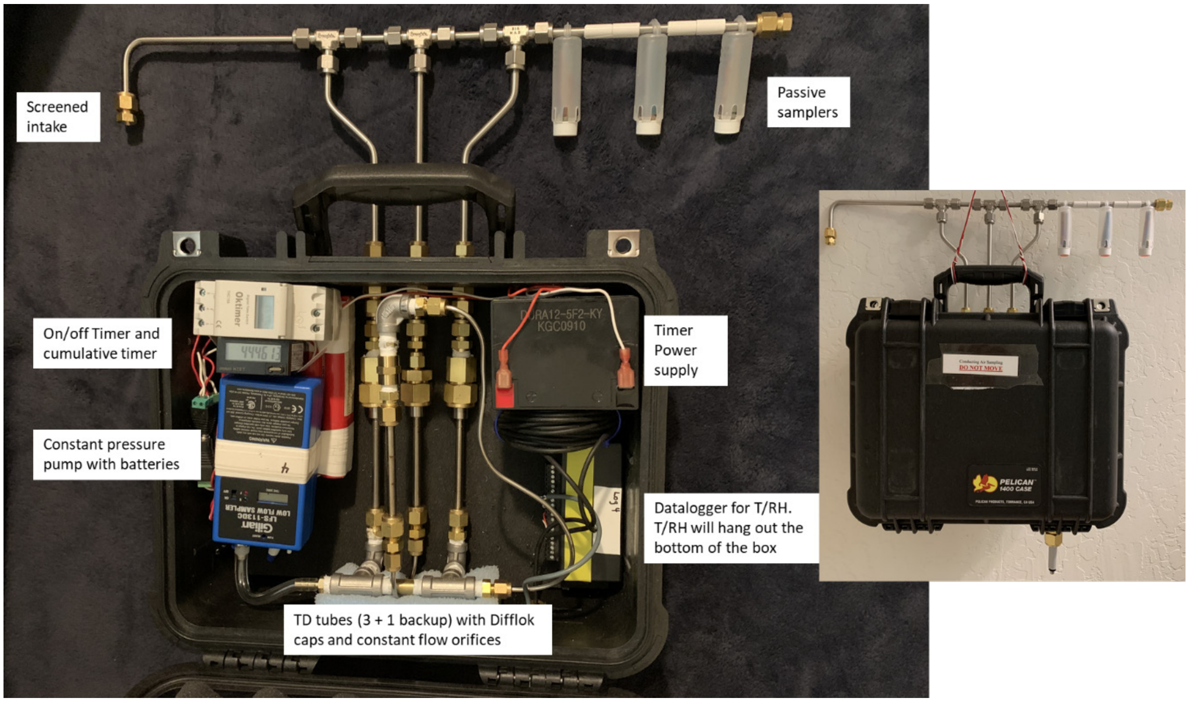


Figure 2. Self-contained Active/Passive Sampler Set for Manhole Deployment.

Table 3. Contents of Each Self-contained Active/Passive Sampler Set.

Item		Number	Description	Comment
Passive Samplers		3	Beacon Sampler	Continuous deployment
Active Samplers - Thermal Desorption (TD) tube sampler and support equipment	Active TD tube sampler	3	TO-17 TD tube type sampler	Continuous deployment. Sampling utilizes timed interval sampling: Timer controlled sampling using a format of 1 minute on vs 10 minutes off. (e.g., 1 min sample collection every 11 minutes for the duration of the sampling event).
	TD tube sampler to determine if there is primary sampler saturation	1	TO-17 TD tube sampler downstream of one primary TD tube samplers to determine if contaminant saturated primary sampler and broke-through to the backup.	
	Constant pressure pump with manifold for 3 TD tube samplers	1	Pump which provides vacuum pressure to manifold holding flow restrictors and samplers	
	Flow restrictor orifices to control TD tube flow	3	Restricts flowrate to between 35-60 ml/min and is independent for each tube. Flowrate will be tested prior to and after each event.	
	Timer	1	Controls pump operation for timed interval sampling	
	Totalizing time clock	1	Meter to cumulate total hours of pump operation	
	DC power	--	Power for pump and timer	
Temperature and Relative Humidity Monitor with Datalogger		1	Monitor ambient manhole conditions that the passive sampler is sensitive to	5-minute logging intervals

Regarding pump exhaust and its potential effect on sampling, sampler operation was as follows:

- exhaust from the constant pressure pump discharged approximately 18" from the TD tube intake or any passive sampler; and
- pump exhaust equated to approximately 150ml per minute or less, and the pump only operated for 1 minute followed by a 10 min quiescent period.

Given sampler design/operation, diffusion, and the likelihood that the manhole environment was not stagnant, there was little concern that pump exhaust had any substantive effect on passive or TD tube samplers.

Two 8-day sampling events were performed back-to-back from March 24 through April 9, 2022. The eight-day event period was slightly greater than the weeklong duration recommended for manhole sampling by Guo et.al. (2019) and was employed to ensure a minimum effective performance period of 7 days.

Within each manhole, samplers were hung from either the manhole cover or from the top manhole ladder rung. Samplers were deployed such that the base of each sampler was approximately 1 ft off the water surface. This provided a consistent deployment between manholes and from one event to the next. Given the circumstances associated with manhole deployment, it was not possible to control lateral placement within a manhole, although the deployment for any specific manhole was consistent from event to event.

Each sampling event included the sampling of the five manholes shown in Section 4.3 above. Sampling detail is highlighted in Table 4.

Table 4. Sampling Event Detail.

Detail	Winter/Spring Event		Comment
	Event 1	Event 2	
Duration of event	8 days	8 days	Replicate winter event would be held immediately following the first winter event.
Manholes per event	5	5	Manhole selection based on knowledge of manhole concentrations from previous sampling.
Passive samplers - Number deployed per manhole	3	3	Sampler used will be the Beacon Sampler, a vial type that was the best performing indoor air sampler in ER-201501 tests.
Active Samplers - Number of TD tubes deployed per manhole	3	3	Does not include a 4th TD tube, plumbed in series with one of the active TD tubes to determine if contaminant breakthrough occurred.
Number of TD tubes per manhole	3	3	Passive sampler performance would be compared to active TD tube sampling. Each sampler set would have 3 passive samplers along with 3 actively sampled TD tubes and 1 backup TD tube to check for contaminant break-through. Beacon Env. provided samplers and analytical.
Number of backup TD tubes per manhole	1	1	
Separate TD tube with unknown concentration spike per manhole	1	1	QA included a blind sample submission consisting of an Absolute Standard PT standard used for lab certification.
Additional monitoring	T, RH	T, RH	Temperature and relative humidity would be continuously monitored/logged during sampling event.

Samples were labeled with the sample location, TD or passive sampler number, date and time of deployment and retrieval, and shipped with chain-of-custody forms via Fedex to Beacon Environmental for analysis. Samples were analyzed for those cVOCs shown in Table 2.

Calibration of equipment: To determine the average flowrate for each TD tube for each event, prior to and after each event the flowrate of each restrictor orifice was measured using a sacrificial TD tube to mimic system resistance and measured using a Gilibrator 2 bubble flowmeter with the low-flow sensor (Sensidyne, Inc., FL). The flowrate was determined as the average flowrate for a minimum three tests. This flowrate was used in conjunction with the pump runtime to determine the volume of sample collected for each TD tube.

Pump runtime verification: The actual runtime for each pump was determined using an inline totalizing hour meter. The totalized runtime was confirmed with an estimate of runtime via calculation for the period of deployment.

Quality assurance: Quality assurance for each sampling location and event included:

- Sampling in triplicate for both passive samplers and TD tubes; and
- QA/QC which consisted of the following:
  - An inline, downstream TD tube for contaminant break-through on TD tubes;
  - A blind sample submission for each sample set using Absolute Standards PT program standards (Absolute Standards, Inc., Hampden, CT) used for lab certification injected onto a TD tube. For the PT program, Absolute Standards send a spiked sample of unknown concentration to the user. The user then analyzes that sample and sends those results to Absolute Standards for verification. Absolute standards provided the verified concentration and whether the analytical was within standards.

6.0 ASSESSING SAMPLER PERFORMANCE

For assessment purposes, data was assessed by two different methods, both of which required relevant pairs of active sampler (TD tube)/passive sampler data for analysis. As such, analytical data was first reduced to data pairs that were detectable for both samplers. Data was initially analyzed by a direct plot of passive sampler concentration vs TD tube sampler concentration for each analyte. Using linear regression, a regression correlation coefficient (R^2) and a slope defining its relationship to a 1:1 agreement were determined.

While the above-mentioned method has its merits, Bland and Altman (1986) argued that while a group of data may suggest a strong correlation, it does not necessarily indicate whether one set of data or method is representative or can be substituted for another. They suggested a plot of the differences between a paired sets of data vs the mean of those data pairs, inclusive of lines identifying the mean difference for the entire set, a 95% confidence interval (CI) for the mean/bias as defined by a *t*-Test using the equation ***CI = mean +/- 2* StdError***, and a 95% CI for the normal Gaussian distribution as defined by the interval ***CI = mean +/- 2*StdDev***. This method provided a better feel for the magnitude of difference between data pairs, providing a greater measure of comparability between samplers.

7.0 RESULTS

7.1 QA/QC

The Absolute Standards PT program for laboratory certification was use for analytical QA/QC. For each event, an unknown PT standard was injected onto 5 separate TD tubes, one for each of the sample location sets. Each unknown was run in concert with a sample set to judge accuracy of TD tube results. Results for all QA/QC samples are shown in Table 5. Results indicated that all unknown samples were within the limits set by the Absolute Standards PT program.

Additional QA/QC involved the use of backup TD tubes to ensure there was no contaminant breakthrough with TD tube sampling. Those results are shown in Tables 6 and 7 for field and analytical data, respectively. Data indicated that there was no breakthrough for any sample.

Based on the results of QA/QC, TD tube sampling data is believed to be accurate and representative of actual concentrations within an acceptable standard of error.

7.2 FIELD AND ANALYTICAL RESULTS

Field and laboratory analytical data for both sampling events is shown in Tables 8 and 9, respectively. Laboratory data is also provided in Appendix B.

7.3 COMPARISON OF PASSIVE SAMPLER PERFORMANCE AS COMPARED TO ACTIVELY SAMPLED TD TUBES

As indicated previously, relevant pairs of TD tube/Passive sampler data were required for analysis, and as such, analytical data was reduced to paired data that were detectable for both samplers. In other words, if a TD tube sample was non-detect, both that ND value and the associated or paired passive sampler data point, whether ND or not, was eliminated, and vice versa. As such, analytical data was reduced to that shown in Table 10, which shows all relevant TD tube/Passive sampler data pairs used for assessment purposes.

Data was assessed by two different methods. The first was a linear regression analysis. This included a plot of passive sampler concentrations vs TD tube sampler concentrations for each analyte, providing a simple comparison of the data and a regression analysis. Plots for this method are shown in Figure 3 and include R^2 values and a 1:1 correlation line for comparison.

Data was also assessed as suggested by Bland and Altman (1986) by plotting the difference between a paired set of data vs the mean of that data pair. In addition, the mean difference is plotted along with 95% confidence interval (*t*-Test) for that mean/bias, and a 95% confidence for a Gaussian normally distributed population. Plots are shown in Figure 4.

Finally, Table 11 provides a summary of the data for both methods of assessment.

Table 5. Results of Absolute Standards PT Sample Concentrations for QA/QC.

QA/QC - AbsoluteGrade PT Program - Concentration (ug/m3)

PT ID	111-TCA					112-TCA					11-DCA				
	PT Evalution			Actual	% of Assigned	PT Evalution			Actual	% of Assigned	PT Evalution			Actual	% of Assigned
	Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit		
PT1#1				9.58	3.79				7.67	-0.90				21.80	9.00
PT1#2				9.36	1.41				7.74	0.00				21.60	8.00
PT1#3	9.23	6.46	12.00	9.49	2.82	7.74	5.42	10.10	7.77	0.39	20.00	14.00	26.00	21.90	9.50
PT1#4				9.73	5.42				7.91	2.20				22.20	11.00
PT1#5				9.57	3.68				7.96	2.84				21.90	9.50
PT2#1				8.85	-23.04				9.32	0.98				18.40	-1.60
PT2#2				9.15	-20.43				9.37	1.52				18.90	1.07
PT2#3	11.50	8.05	15.00	9.26	-19.48	9.23	6.46	12.00	9.52	3.14	18.70	13.10	24.30	19.10	2.14
PT2#4				9.28	-19.30				9.50	2.93				18.60	-0.53
PT2#5				9.20	-20.00				9.36	1.41				18.90	1.07

PT ID	11-DCE					12-DCA					cis 12-DCE				
	PT Evalution			Actual	% of Assigned	PT Evalution			Actual	% of Assigned	T Evalution			Actual	% of
	Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit		
PT1#1				12.40	-0.80				17.50	4.79	18.20	12.70	23.70	17.50	-3.85
PT1#2				12.70	1.60				17.40	4.19				17.60	-3.30
PT1#3	12.50	8.75	16.30	12.40	-0.80	16.70	11.70	21.70	17.40	4.19				17.70	-2.75
PT1#4				12.40	-0.80				17.60	5.39				17.60	-3.30
PT1#5				12.30	-1.60				17.60	5.39				17.80	-2.20
PT2#1				9.29	0.65				5.37	2.48	10.70	7.49	13.90	10.60	-0.93
PT2#2				9.56	3.58				5.61	7.06				10.80	0.93
PT2#3	9.23	6.46	12.00	9.52	3.14	5.24	3.67	6.81	5.69	8.59				10.70	0.00
PT2#4				8.88	-3.79				5.57	6.30				10.70	0.00
PT2#5				9.24	0.11				5.79	10.50				10.80	0.93

PT ID	PCE					trans 12 DCE					TCE				
	PT Evalution			Actual	% of Assigned	PT Evalution			Actual	% of Assigned	PT Evalution			Actual	% of Assigned
	Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit			Assigned Value	Lower Limit	Upper Limit		
PT1#1				17.50	-1.13				10.40	12.68				18.70	0.00
PT1#2				17.20	-2.82				10.40	12.68				18.80	0.53
PT1#3	17.70	12.40	23.00	17.40	-1.69	9.23	6.46	12.00	10.40	12.68	18.70	13.10	24.30	18.70	0.00
PT1#4				17.20	-2.82				10.10	9.43				18.70	0.00
PT1#5				17.00	-3.95				10.30	11.59				18.60	-0.53
PT2#1				18.90	-1.56				20.30	11.54				11.70	0.00
PT2#2				18.80	-2.08				20.00	9.89				11.70	0.00
PT2#3	19.20	13.40	25.00	18.60	-3.12	18.20	12.70	23.70	20.10	10.44	11.70	8.19	15.20	11.70	0.00
PT2#4				19.00	-1.04				20.00	9.89				11.80	0.85
PT2#5				18.90	-1.56				20.40	12.09				11.70	0.00

PT ID	VC				
	PT Evalution			Actual	% of Assigned
	Assigned Value	Lower Limit	Upper Limit		
PT1#1				8.77	-12.30
PT1#2				9.35	-6.50
PT1#3	10.00	7.00	13.00	8.40	-16.00
PT1#4				8.99	-10.10
PT1#5				8.78	-12.20
PT2#1				6.08	-26.21
PT2#2				6.22	-24.51
PT2#3	8.24	5.77	10.70	5.77	-29.98
PT2#4				7.04	-14.56
PT2#5				6.82	-17.23

Table 6. Field Data for QA/QC Backup TD Tubes to Track Contaminant Breakthrough.

Box	Deploy	Retrieve	TD Tubes											
			Track	Tube ID	Lab ID	Flowrate (ml/min)			Runtime					Volume (L)
						Pre	Post	Avg	Display	hr	min	sec	total min	
1	3/24/22 11:00	4/1/22 11:25	2Bu	1141298	BUTD-0324-1298	49.15	48.74	48.945	172955	17	29	55	1050	51.39
	4/1/22 12:35	4/9/22 10:03	2Bu	1118143	BUTD-0401-8143	48.74	49.34	49.04	171343	17	13	43	1034	50.71
2	3/24/22 13:00	4/1/22 13:08	2Bu	1141500	BUTD-0324-1500	41.11	41.86	41.485	172814	17	28	14	1048	43.48
	4/1/22 13:47	4/9/22 10:28	2Bu	1156606	BUTD-0401-6606	41.8	41.62	41.71	170948	17	9	48	1030	42.96
3	3/24/22 13:53	4/1/22 13:58	2Bu	1078531	BUTD-0324-8531	44.81	44.53	44.67	172823	17	28	23	1048	46.81
	4/1/22 14:40	4/9/22 10:55	2Bu	1156748	BUTD-0401-6748	44.53	44.34	44.435	170718	17	7	18	1027	45.63
4	3/24/22 14:53	4/1/22 14:52	2Bu	1141398	BUTD-0324-1398	38.79	38.99	38.89	172737	17	27	37	1048	40.76
	4/1/22 15:31	4/9/22 11:20	2Bu	1078573	BUTD-0401-8573	38.99	38.5	38.745	170459	17	4	59	1025	39.71
5	3/24/22 16:40	4/1/22 15:40	2Bu	1078855	BUTD-0324-8855	38.67	38.41	38.54	172250	17	22	50	1043	40.20
	4/1/22 16:22	4/9/22 11:46	2Bu	1078601	BUTD-0401-8601	38.41	38.15	38.28	170239	17	2	39	1023	39.16

Table 7. Laboratory Analytical Data for QA/QC backup TD Tubes to Track Contaminant Breakthrough.

Box/ Site	Deploy	Retrieve	TD Tubes												
			Track	Tube ID	Lab ID	Concentration (ug/m3)									
						111-TCA	112-TCA	11-DCA	11-DCE	12-DCA	cis 12-DCE	PCE	trans 12-DCE	TCE	VC
1	3/24/22 11:00	4/1/22 11:25	2Bu	1141298	BUTD-0324-1298	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195
	4/1/22 12:35	4/9/22 10:03	2Bu	1118143	BUTD-0401-8143	<0.197	<0.197	<0.197	<0.197	<0.197	<0.197	<0.197	<0.197	<0.197	<0.197
2	3/24/22 13:00	4/1/22 13:08	2Bu	1141500	BUTD-0324-1500	<0.230	<0.230	<0.230	<0.230	<0.230	<0.230	<0.230	<0.230	<0.230	<0.230
	4/1/22 13:47	4/9/22 10:28	2Bu	1156606	BUTD-0401-6606	<0.233	<0.233	<0.233	<0.233	<0.233	<0.233	<0.233	<0.233	<0.233	<0.233
3	3/24/22 13:53	4/1/22 13:58	2Bu	1078531	BUTD-0324-8531	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214
	4/1/22 14:40	4/9/22 10:55	2Bu	1156748	BUTD-0401-6748	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219
4	3/24/22 14:53	4/1/22 14:52	2Bu	1141398	BUTD-0324-1398	<0.245	<0.245	<0.245	<0.245	<0.245	<0.245	<0.245	<0.245	<0.245	<0.245
	4/1/22 15:31	4/9/22 11:20	2Bu	1078573	BUTD-0401-8573	<0.252	<0.252	<0.252	<0.252	<0.252	<0.252	<0.252	<0.252	<0.252	<0.252
5	3/24/22 16:40	4/1/22 15:40	2Bu	1078855	BUTD-0324-8855	<0.249	<0.249	<0.249	<0.249	<0.249	<0.249	<0.249	<0.249	<0.249	<0.249
	4/1/22 16:22	4/9/22 11:46	2Bu	1078601	BUTD-0401-8601	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255

* Concentrations that show “<” indicate concentrations that are less than the detection limit shown.

Table 8. Field Data for Sampling Events.

Box	Deploy	Retrieve	TD Tubes: Track	Tube ID	Lab ID	Flowrate (ml/min): Pre	Post	Avg	Runtime: Display	hr	min	sec	min	Calc Volume (L)	Passives: Lab ID	Deploy time	Collect Time	Total time: days	min	Temp: Mean	Min	Max	RH: Mean	Min	Max
1	3/24/22 11:00	4/1/22 11:25	1	1118225	TD-0324-8225	37.8	37.24	37.52	172955	17	29	55	1050	39.40	BS-0324-01	3/24/22 11:00	4/1/22 11:25	8.017	11545	11.2	10.8	12.0	98.2	89.4	100
			2	1141241	TD-0324-1241	49.15	48.74	48.945	172955	17	29	55	1050	51.39	BS-0324-07										
			3	1141354	TD-0324-1354	46.18	45.18	45.68	172955	17	29	55	1050	47.96	BS-0324-13										
	4/1/22 12:35	4/9/22 10:03	1	1141313	TD-0401-1313	37.24	37.73	37.485	171343	17	13	43	1034	38.76	BS-0401-01	4/1/22 12:35	4/9/22 10:03	7.894	11368	11.2	10.6	11.5	94.4	34.4	100
			2	1141463	TD-0401-1463	48.74	49.34	49.04	171343	17	13	43	1034	50.71	BS-0401-07										
			3	1118211	TD-0401-8211	45.18	45.93	45.555	171343	17	13	43	1034	47.10	BS-0401-13										
2	3/24/22 13:00	4/1/22 13:08	1	1078615	TD-0324-8615	47.41	47.96	47.685	172814	17	28	14	1048	49.97	BS-0324-03	3/24/22 13:00	4/1/22 13:08	8.006	11528	10.9	10.4	11.2	81.6	66.8	98.3
			2	1118218	TD-0324-8218	41.11	41.86	41.485	172814	17	28	14	1048	43.48	BS-0324-10										
			3	1078589	TD-0324-8589	46.68	46.71	46.695	172814	17	28	14	1048	48.94	BS-0324-14										
	4/1/22 13:47	4/9/22 10:28	1	1156676	TD-0401-6676	47.96	47.83	47.895	170948	17	9	48	1030	49.33	BS-0401-03	4/1/22 13:47	4/9/22 10:28	7.862	11321	11.2	10.3	11.5	75.3	62.2	94.6
			2	1156523	TD-0401-6523	41.8	41.62	41.71	170948	17	9	48	1030	42.96	BS-0401-10										
			3	1141498	TD-0401-1498	46.71	47.05	46.88	170948	17	9	48	1030	48.29	BS-0401-14										
3	3/24/22 13:53	4/1/22 13:58	1	1078796	TD-0324-8796	47.22	46.35	46.785	172823	17	28	23	1048	49.03	BS-0324-05	3/24/22 13:53	4/1/22 13:58	8.003	11525	11.9	11.2	12.4	83.2	75.1	93.9
			2	1141501	TD-0324-1501	44.81	44.53	44.67	172823	17	28	23	1048	46.81	BS-0324-06										
			3	1141471	TD-0324-1471	37.62	37.24	37.43	172823	17	28	23	1048	39.23	BS-0324-15										
	4/1/22 14:40	4/9/22 10:55	1	1078508	TD-0401-8508	46.35	46.28	46.315	170718	17	7	18	1027	47.57	BS-0401-05	4/1/22 14:40	4/9/22 10:55	7.844	11295	12.5	11.8	12.8	79.5	38.1	89.4
			2	1156779	TD-0401-6779	44.53	44.34	44.435	170718	17	7	18	1027	45.63	BS-0401-06										
			3	1156587	TD-0401-6587	37.24	37.47	37.355	170718	17	7	18	1027	38.36	BS-0401-15										
4	3/24/22 14:53	4/1/22 14:52	1	1078620	TD-0324-8620	45.7	46.04	45.87	172737	17	27	37	1048	48.07	BS-0324-11	3/24/22 14:53	4/1/22 14:52	7.999	11519	11.5	10.7	14.2	71.0	30.8	90.1
			2	1118162	TD-0324-8162	38.79	38.99	38.89	172737	17	27	37	1048	40.76	BS-0324-12										
			3	1141446	TD-0324-1446	37.85	37.98	37.915	172737	17	27	37	1048	39.73	BS-0324-04										
	4/1/22 15:31	4/9/22 11:20	1	1078534	TD-0401-8534	46.04	45.22	45.63	170459	17	4	59	1025	46.77	BS-0401-11	4/1/22 15:31	4/9/22 11:20	7.826	11269	11.6	10.3	12.2	70.8	34.3	96.1
			2	1078568	TD-0401-8568	38.99	38.5	38.745	170459	17	4	59	1025	39.71	BS-0401-12										
			3	1078588	TD-0401-8588	37.98	37.61	37.795	170459	17	4	59	1025	38.74	BS-0401-04										
5	3/24/22 16:40	4/1/22 15:40	1	1141419	TD-0324-1419	44.97	45.35	45.16	172250	17	22	50	1043	47.10	BS-0324-08	3/24/22 16:40	4/1/22 15:40	7.958	11460	11.2	10.9	11.6	98.2	91.5	100
			2	1118413	TD-0324-8413	38.67	38.41	38.54	172250	17	22	50	1043	40.20	BS-0324-09										
			3	1117736	TD-0324-7736	42.79	43.19	42.99	172250	17	22	50	1043	44.84	BS-0324-02										
	4/1/22 16:22	4/9/22 11:46	1	1078835	TD-0401-8835	45.35	45.53	45.44	170239	17	2	39	1023	46.49	BS-0401-08	4/1/22 16:22	4/9/22 11:46	7.808	11244	11.5	11.1	11.8	95.7	91.7	98.8
			2	1078664	TD-0401-8664	38.41	38.15	38.28	170239	17	2	39	1023	39.16	BS-0401-09										
			3	1078649	TD-0401-8649	43.19	43.23	43.21	170239	17	2	39	1023	44.20	BS-0401-02										

* Box number correlates with location number as shown in Section 4.3. Locations are not identified here since location has no relevance to the evaluation of the data.

Table 9. Laboratory Analytical Data for Sampling Events.

Box/Site	Deploy	Retrieve	TD Tubes													Passive Samplers - Beacon Sampler										
			Track	Tube ID	Lab ID	Concentration (ug/m3)										Lab ID	Concentration (ug/m3)									
						111-TCA	112-TCA	11-DCA	11-DCE	12-DCA	cis 12-DCE	PCE	trans 12-DCE	TCE	VC		111-TCA	112-TCA	11-DCA	11-DCE	12-DCA	cis 12-DCE	PCE	trans 12-DCE	TCE	VC
1	3/24/22 11:00	4/1/22 11:25	1	1118225	TD-0324-8225	18	<0.254	11	24.6	1.63	9.5	58.3	1.15	154	<0.254	BS-0324-01	9.47	<2.65	10.7	74.8	2.4	14.1	104	2.27	310	<1.08
			2	1141241	TD-0324-1241	16.9	<0.195	10.2	27.9	1.41	10.1	59.3	0.939	165	0.349	BS-0324-07	2.97	<2.65	5.8	69.4	1.57	13.2	70.8	2.23	230	1.74
			3	1141354	TD-0324-1354	17.4	<0.209	10.5	29	1.42	10.4	58.8	0.937	169	0.328	BS-0324-13	7.17	<2.65	9.12	68.4	2.42	13.1	101	2.3	281	<1.08
	4/1/22 12:35	4/9/22 10:03	1	1141313	TD-0401-1313	16.4	0.672	10.3	23.8	1.5	9.83	49.7	0.81	139	0.272	BS-0401-01	4.39	<2.69	7.44	66.4	1.8	13.4	74.2	2.19	233	<1.10
			2	1141463	TD-0401-1463	16	0.665	10.1	24.8	1.28	9.4	51.2	0.794	141	0.314	BS-0401-07	8.34	<2.69	9.72	69.6	2.36	13.6	106	2.15	275	<1.10
			3	1118211	TD-0401-8211	16.6	0.654	10.4	26.2	1.41	9.99	55.2	0.766	155	0.306	BS-0401-13	2.41	<2.69	4.76	62.5	<1.59	11.4	63.3	<2.02	229	1.26
2	3/24/22 13:00	4/1/22 13:08	1	1078615	TD-0324-8615	<0.200	<0.200	2.23	2.25	1.78	58	<0.200	17.9	263	0.566	BS-0324-03	<0.834	<2.66	1.07	5.74	<1.56	89.9	<2.14	31.8	331	1.36
			2	1118218	TD-0324-8218	<0.230	<0.230	2.21	2.45	1.7	64.3	<0.230	17.9	186	0.694	BS-0324-10	<0.834	<2.66	2.32	6.06	3.02	95.4	<2.14	33	405	1.54
			3	1078589	TD-0324-8589	<0.204	<0.204	2.18	2.45	1.63	61.8	<0.204	17.7	295	0.726	BS-0324-14	<0.834	<2.66	3.32	7.67	4.12	122	<2.14	43.1	436	1.96
	4/1/22 13:47	4/9/22 10:28	1	1156676	TD-0401-6676	<0.203	<0.203	2.47	2.64	1.88	69.5	<0.203	19.8	259	0.844	BS-0401-03	<0.849	<2.70	1.64	7.57	2.2	102	<2.17	36.5	427	1.6
			2	1156523	TD-0401-6523	<0.233	<0.233	2.51	2.81	2.05	69.4	<0.233	21.2	284	0.943	BS-0401-10	<0.849	<2.70	2.85	7.89	3.54	108	<2.17	37.2	429	1.97
			3	1141498	TD-0401-1498	<0.207	<0.207	2.41	2.77	1.69	67.7	<0.207	18.1	304	0.981	BS-0401-14	<0.849	<2.70	2.77	7.48	3.65	109	<2.17	38.2	450	1.37
3	3/24/22 13:53	4/1/22 13:58	1	1078796	TD-0324-8796	<0.204	<0.204	<0.204	<0.204	<0.204	<0.204	0.437	<0.204	0.28	<0.204	BS-0324-05	<0.833	<2.65	<1.03	<2.65	<1.56	<1.65	<2.13	<1.99	<2.65	<1.08
			2	1141501	TD-0324-1501	<0.214	<0.214	<0.214	<0.214	<0.214	<0.214	0.431	<0.214	0.294	<0.214	BS-0324-06	<0.833	<2.65	<1.03	<2.65	<1.56	<1.65	<2.13	<1.99	<2.65	<1.08
			3	1141471	TD-0324-1471	<0.255	<0.255	<0.255	<0.255	<0.255	<0.255	0.449	<0.255	<0.255	<0.255	BS-0324-15	<0.833	<2.65	<1.03	<2.65	<1.56	<1.65	<2.13	<1.99	<2.65	<1.08
	4/1/22 14:40	4/9/22 10:55	1	1078508	TD-0401-8508	<0.210	<0.210	<0.210	<0.210	<0.210	<0.210	0.37	<0.210	0.288	<0.210	BS-0401-05	<0.849	<2.70	<1.05	<2.70	<1.59	<1.68	<2.18	<2.03	<2.70	<1.10
			2	1156779	TD-0401-6779	<0.219	<0.219	<0.219	<0.219	<0.219	<0.219	0.349	<0.219	0.299	<0.219	BS-0401-06	<0.849	<2.70	<1.05	<2.70	<1.59	<1.68	<2.18	<2.03	<2.70	<1.10
			3	1156587	TD-0401-6587	<0.261	<0.261	<0.261	<0.261	<0.261	<0.261	0.346	<0.261	0.292	<0.261	BS-0401-15	<0.849	<2.70	<1.05	<2.70	<1.59	<1.68	<2.18	<2.03	<2.70	<1.10
4	3/24/22 14:53	4/1/22 14:52	1	1078620	TD-0324-8620	0.555	<0.208	2.07	0.853	<0.208	42.2	2.27	4.65	291	<0.208	BS-0324-11	<0.834	<2.65	1.43	2.81	<1.56	54.7	3.13	8.32	306	<1.08
			2	1118162	TD-0324-8162	0.577	<0.245	2.22	1.09	<0.245	42.8	2.33	5.04	229	<0.245	BS-0324-12	<0.834	<2.65	1.13	<2.65	<1.56	46.8	2.56	7.52	301	<1.08
			3	1141446	TD-0324-1446	0.544	<0.252	2.13	0.866	<0.252	41.2	2.24	4.9	227	<0.252	BS-0324-04	<0.834	<2.65	1.41	<2.65	<1.56	28.5	<2.14	3.05	197	<1.08
	4/1/22 15:31	4/9/22 11:20	1	1078534	TD-0401-8534	0.466	<0.214	1.89	0.938	<0.214	39.2	2	4.12	277	<0.214	BS-0401-11	<0.853	<2.71	1.65	<2.71	<1.60	44.6	2.95	7.14	295	<1.11
			2	1078568	TD-0401-8568	0.487	<0.252	1.99	0.771	<0.252	42.1	2.1	4.21	209	<0.252	BS-0401-12	<0.853	<2.71	1.42	3.15	<1.60	46.3	2.89	7.33	298	<1.11
			3	1078588	TD-0401-8588	0.422	<0.258	1.77	0.77	<0.258	33.9	2.03	5	192	<0.258	BS-0401-04	<0.853	<2.71	1.59	3.15	<1.60	51.6	3.08	8.28	329	<1.11
5	3/24/22 16:40	4/1/22 15:40	1	1141419	TD-0324-1419	0.844	<0.212	7.51	2.01	0.31	79.4	4.78	21.1	973	0.405	BS-0324-08	<0.839	<2.67	4.37	6.91	<1.57	122	6.41	35.6	843	<1.09
			2	1118413	TD-0324-8413	0.874	<0.249	7.25	2.45	0.348	92.6	4.47	22.3	728	0.517	BS-0324-09	<0.839	<2.67	5.31	7.77	<1.57	130	6.38	35.4	828	<1.09
			3	1117736	TD-0324-7736	0.905	<0.223	7.72	2.43	0.367	103	4.82	23.3	680	0.543	BS-0324-02	<0.839	<2.67	5.4	6.36	<1.57	124	7.69	36.1	907	<1.09
	4/1/22 16:22	4/9/22 11:46	1	1078835	TD-0401-8835	0.732	<0.215	6.4	2.09	0.333	87.8	3.98	19.3	655	0.416	BS-0401-08	<0.855	<2.72	2.53	8.15	<1.60	143	5.96	39.2	617	1.38
			2	1078664	TD-0401-8664	0.711	<0.255	6.11	2.13	0.317	90.3	3.9	19.2	601	0.51	BS-0401-09	<0.855	<2.72	5.13	6.69	<1.60	105	7.44	30.2	714	<1.11
			3	1078649	TD-0401-8649	0.704	<0.226	6.35	2.04	0.345	82.1	4.03	19.6	604	0.454	BS-0401-02	<0.855	<2.72	5.5	6.28	<1.60	110	7.19	30.3	718	<1.11

* Concentrations that show "<" indicate concentrations that are less than the detection limit shown.

Table 10. Paired Data Sets for Assessment Purposes.

*All data eliminated for assessment purposes is shown by the shaded areas. Those locations shown with a single * were non-detect. Areas shown with a double ** were associated values that were eliminated since it proved difficult to assess detectable values against non-detectable values.*

Lab ID		Concentration (ug/m3)																			
		111-TCA		112-TCA		11-DCA		11-DCE		12-DCA		cis 12-DCE		PCE		trans 12-DCE		TCE		VC	
TD tube	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive	TD	Passive
TD-0324-8225	BS-0324-01	18	9.47	*	*	11	10.7	24.6	74.8	1.63	2.4	9.5	14.1	58.3	104	1.15	2.27	154	310	*	*
TD-0324-1241	BS-0324-07	16.9	2.97	*	*	10.2	5.8	27.9	69.4	1.41	1.57	10.1	13.2	59.3	70.8	0.939	2.23	165	230	0.349	1.74
TD-0324-1354	BS-0324-13	17.4	7.17	*	*	10.5	9.12	29	68.4	1.42	2.42	10.4	13.1	58.8	101	0.937	2.3	169	281	**	*
TD-0401-1313	BS-0401-01	16.4	4.39	**	*	10.3	7.44	23.8	66.4	1.5	1.8	9.83	13.4	49.7	74.2	0.81	2.19	139	233	**	*
TD-0401-1463	BS-0401-07	16	8.34	**	*	10.1	9.72	24.8	69.6	1.28	2.36	9.4	13.6	51.2	106	0.794	2.15	141	275	**	*
TD-0401-8211	BS-0401-13	16.6	2.41	**	*	10.4	4.76	26.2	62.5	**	*	9.99	11.4	55.2	63.3	**	*	155	229	0.306	1.26
TD-0324-8615	BS-0324-03	*	*	*	*	2.23	1.07	2.25	5.74	**	*	58	89.9	*	*	17.9	31.8	263	331	0.566	1.36
TD-0324-8218	BS-0324-10	*	*	*	*	2.21	2.32	2.45	6.06	1.7	3.02	64.3	95.4	*	*	17.9	33	186	405	0.694	1.54
TD-0324-8589	BS-0324-14	*	*	*	*	2.18	3.32	2.45	7.67	1.63	4.12	61.8	122	*	*	17.7	43.1	295	436	0.726	1.96
TD-0401-6676	BS-0401-03	*	*	*	*	2.47	1.64	2.64	7.57	1.88	2.2	69.5	102	*	*	19.8	36.5	259	427	0.844	1.6
TD-0401-6523	BS-0401-10	*	*	*	*	2.51	2.85	2.81	7.89	2.05	3.54	69.4	108	*	*	21.2	37.2	284	429	0.943	1.97
TD-0401-1498	BS-0401-14	*	*	*	*	2.41	2.77	2.77	7.48	1.69	3.65	67.7	109	*	*	18.1	38.2	304	450	0.981	1.37
TD-0324-8796	BS-0324-05	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	**	*	*	*
TD-0324-1501	BS-0324-06	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	**	*	*	*
TD-0324-1471	BS-0324-15	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	*	*	*	*
TD-0401-8508	BS-0401-05	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	**	*	*	*
TD-0401-6779	BS-0401-06	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	**	*	*	*
TD-0401-6587	BS-0401-15	*	*	*	*	*	*	*	*	*	*	*	*	**	*	*	*	**	*	*	*
TD-0324-8620	BS-0324-11	**	*	*	*	2.07	1.43	0.853	2.81	*	*	42.2	54.7	2.27	1.09	4.65	8.32	291	306	*	*
TD-0324-8162	BS-0324-12	**	*	*	*	2.22	1.13	**	*	*	*	42.8	46.8	2.33	2.56	5.04	7.52	229	301	*	*
TD-0324-1446	BS-0324-04	**	*	*	*	2.13	1.41	**	*	*	*	41.2	28.5	**		4.9	3.05	227	197	*	*
TD-0401-8534	BS-0401-11	**	*	*	*	1.89	1.65	**	*	*	*	39.2	44.6	2	2.95	4.12	7.14	277	295	*	*
TD-0401-8568	BS-0401-12	**	*	*	*	1.99	1.42	0.771	3.15	*	*	42.1	46.3	2.1	2.89	4.21	7.33	209	298	*	*
TD-0401-8588	BS-0401-04	**	*	*	*	1.77	1.59	0.77	3.15	*	*	33.9	51.6	2.03	3.08	5	8.28	192	329	*	*
TD-0324-1419	BS-0324-08	**	*	*	*	7.51	4.37	2.01	6.91	**	*	79.4	122	4.78	6.41	21.1	35.6	973	843	**	*
TD-0324-8413	BS-0324-09	**	*	*	*	7.25	5.31	2.45	7.77	**	*	92.6	130	4.47	6.38	22.3	35.4	728	828	**	*
TD-0324-7736	BS-0324-02	**	*	*	*	7.72	5.4	2.43	6.36	**	*	103	124	4.82	7.69	23.3	36.1	680	907	**	*
TD-0401-8835	BS-0401-08	**	*	*	*	6.4	2.53	2.09	8.15	**	*	87.8	143	3.98	5.96	19.3	39.2	655	617	0.416	1.38
TD-0401-8664	BS-0401-09	**	*	*	*	6.11	5.13	2.13	6.69	**	*	90.3	105	3.9	7.44	19.2	30.2	601	714	**	*
TD-0401-8649	BS-0401-02	**	*	*	*	6.35	5.5	2.04	6.28	**	*	82.1	110	4.03	7.19	19.6	30.3	604	718	**	*

* Shaded cells with "*" were non-detectable values

** Non-shaded cells with "**" were detectable values that were eliminated since associated value was non-detect.

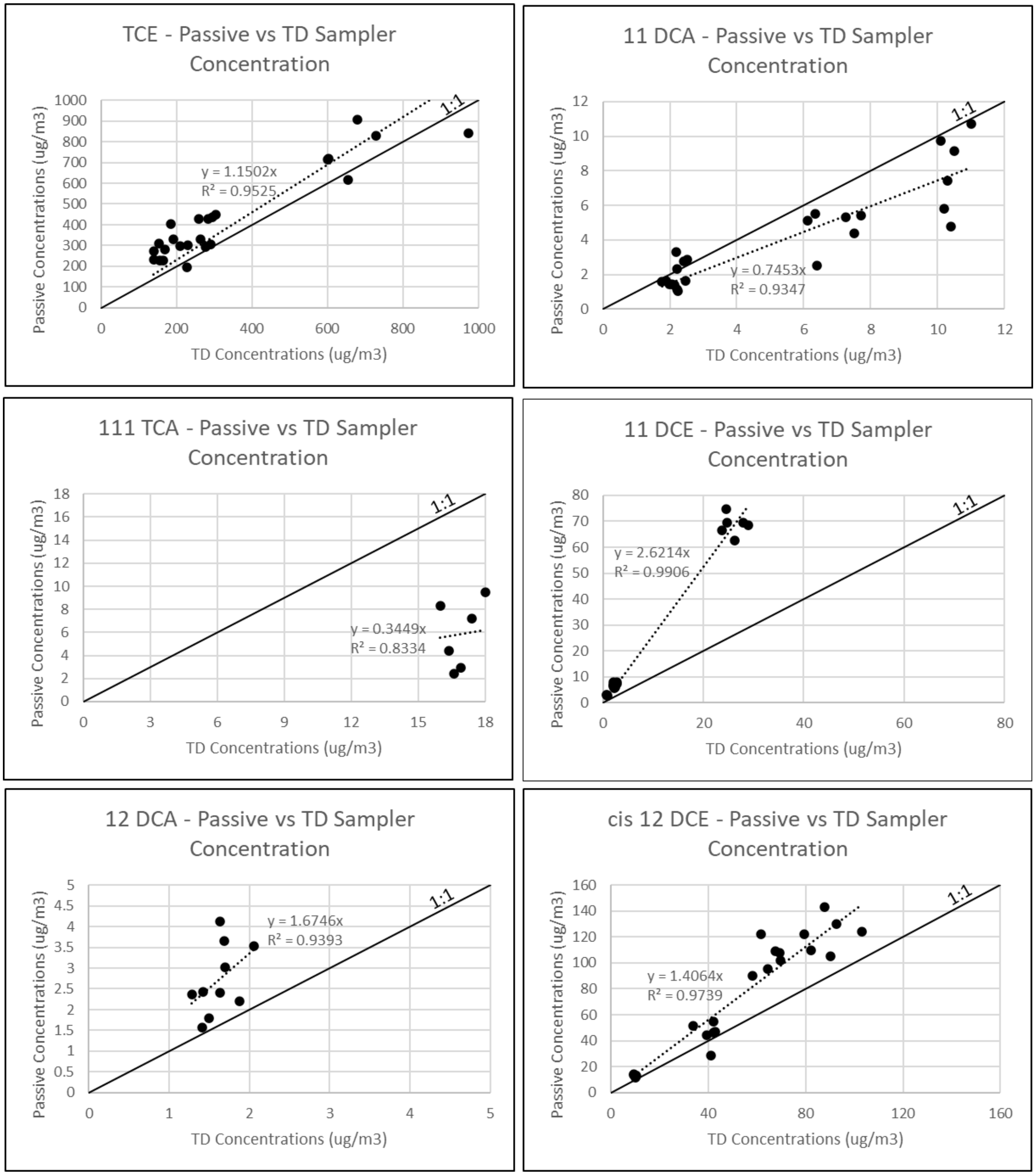
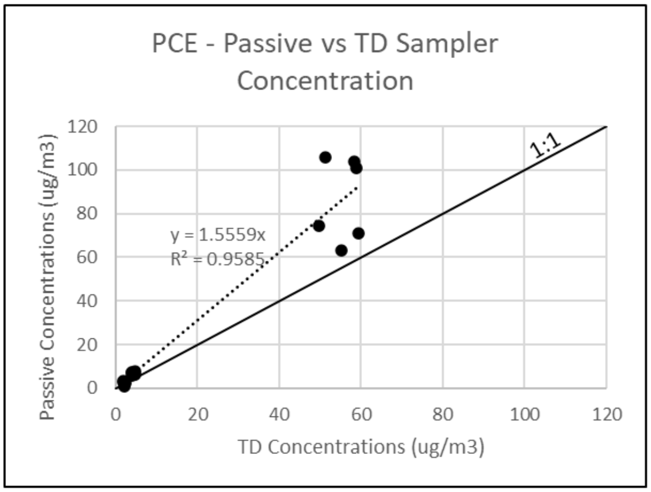
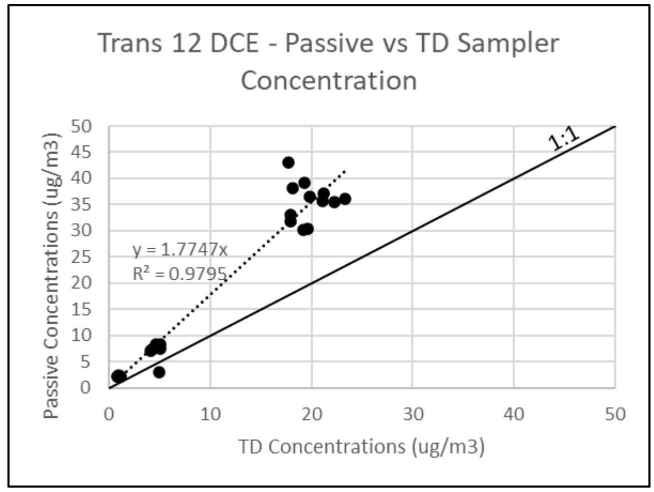


Figure 3. Passive Sample Concentration vs TD Tube Sample Concentration.

Slope and R^2 for linear regression shown.





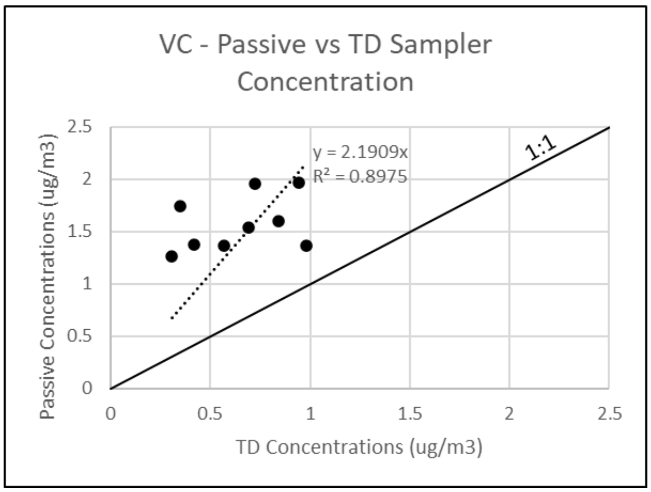
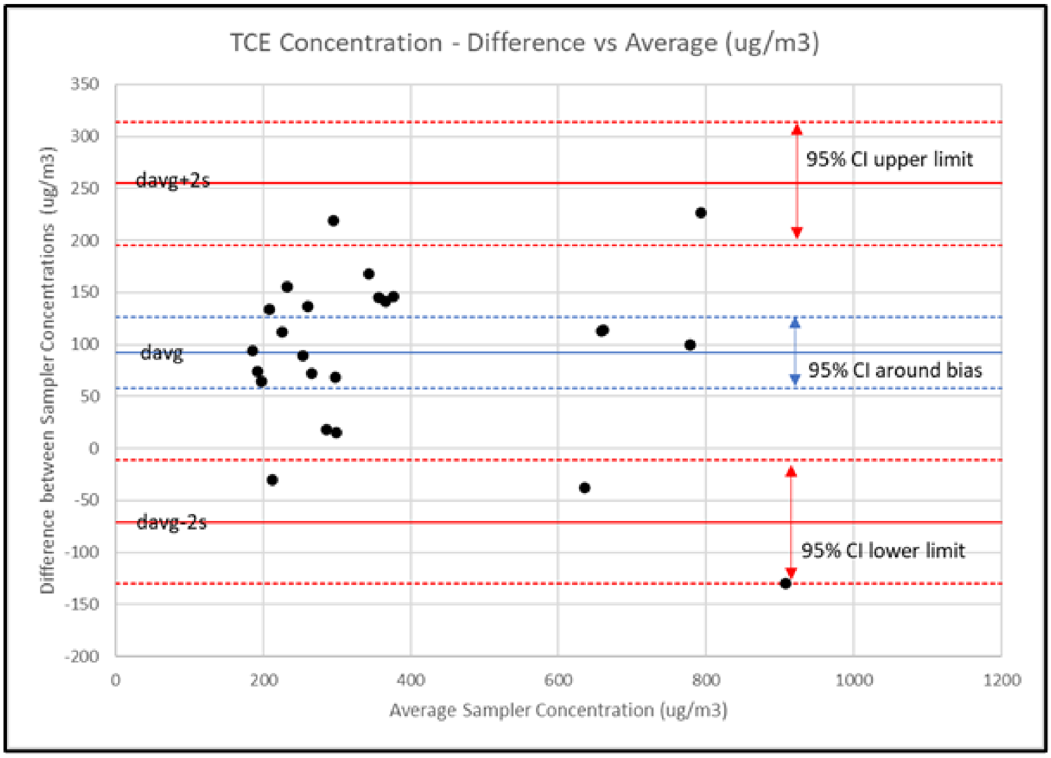


Figure 3. Passive Sample Concentration vs TD Tube Sample Concentration. (Continued)

Slope and R^2 for linear regression shown.



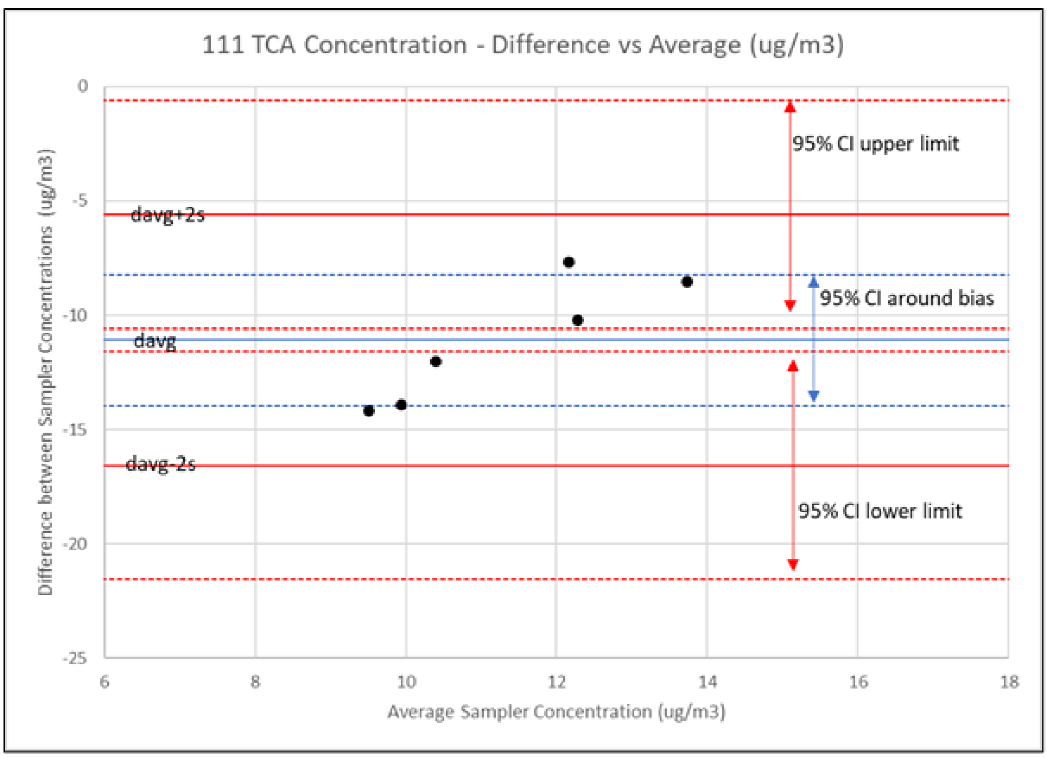
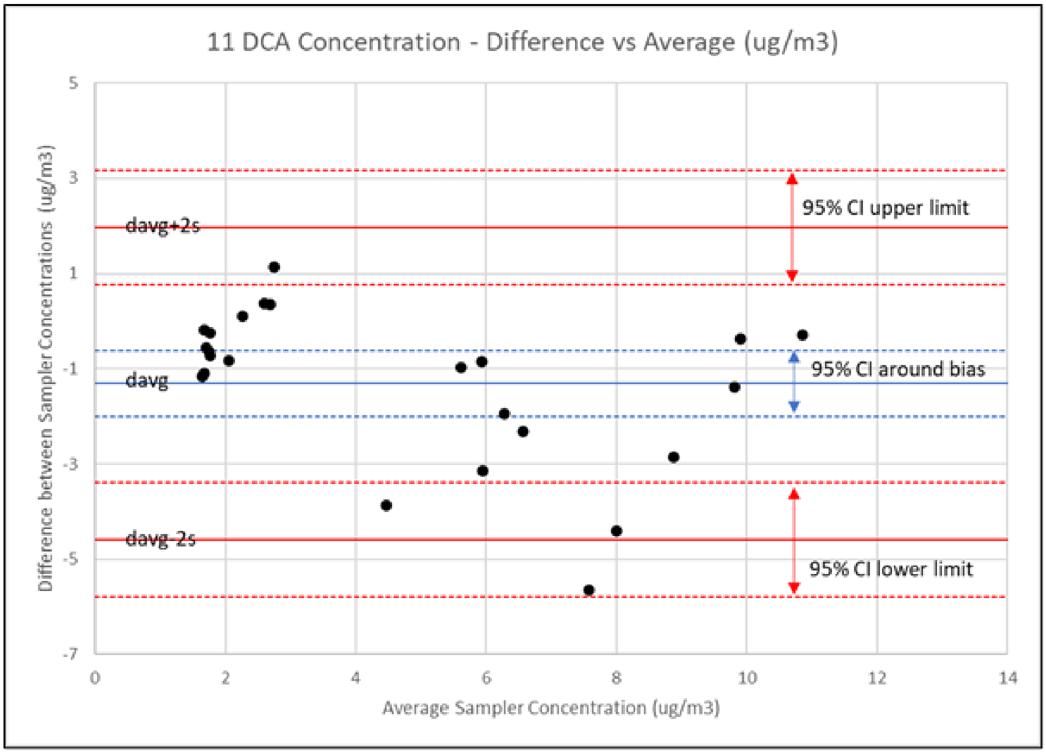


Figure 4. (Pages 18-22) Difference Between Paired Sampler Concentration vs Mean/ Average of that Paired Sampler Concentration for Each Analyte.

Also plotted is the mean difference for all sample pairs, the t-Test based 95% confidence interval for the mean, and the 95% confidence interval for the normal distribution about the mean.



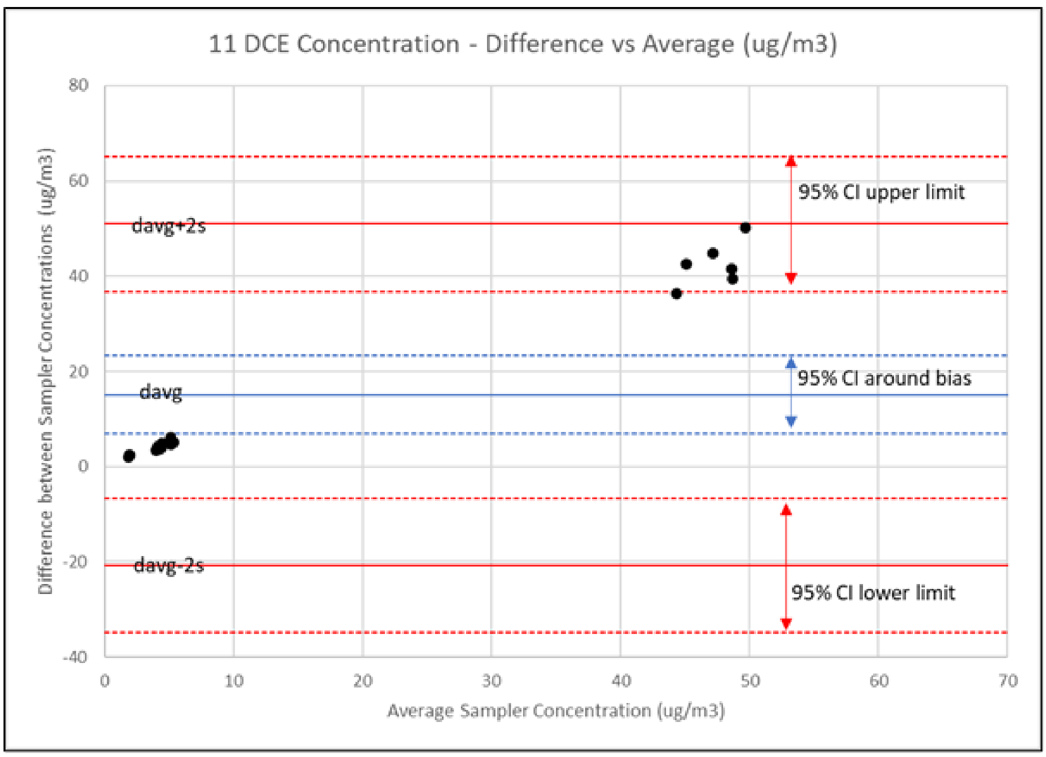
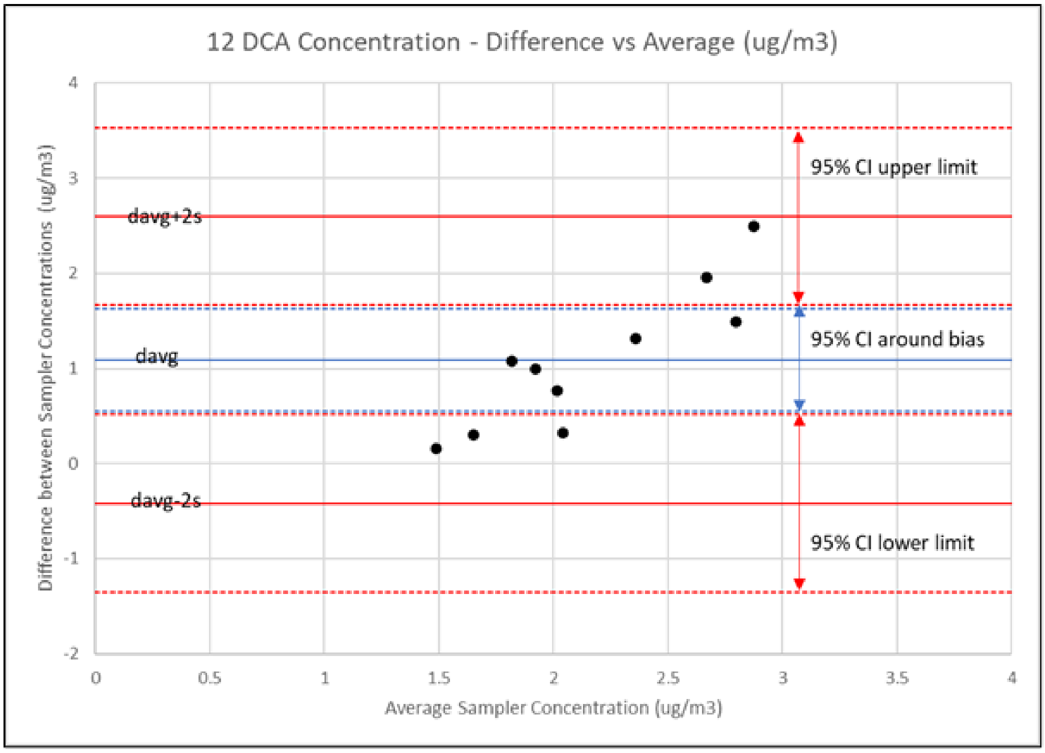


Figure 4. Difference Between Paired Sampler Concentration vs Mean/Average of that Paired Sampler Concentration for Each Analyte. (Continued)

Also plotted is the mean difference for all sample pairs, the t-Test based 95% confidence interval for the mean, and the 95% confidence interval for the normal distribution about the mean.



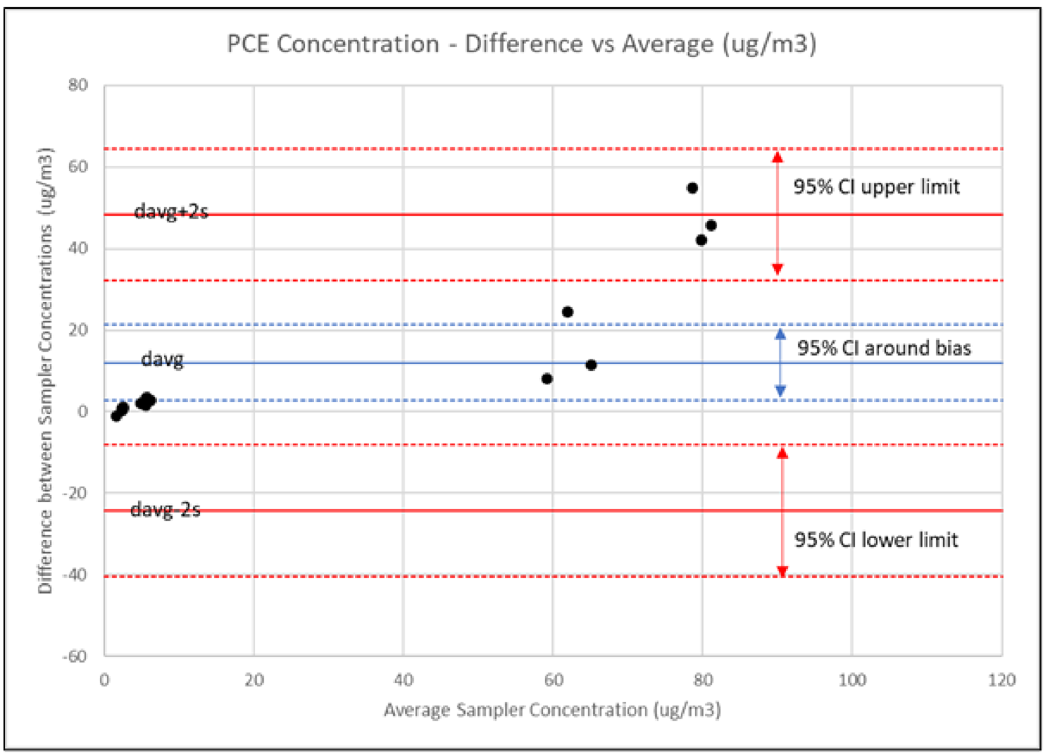
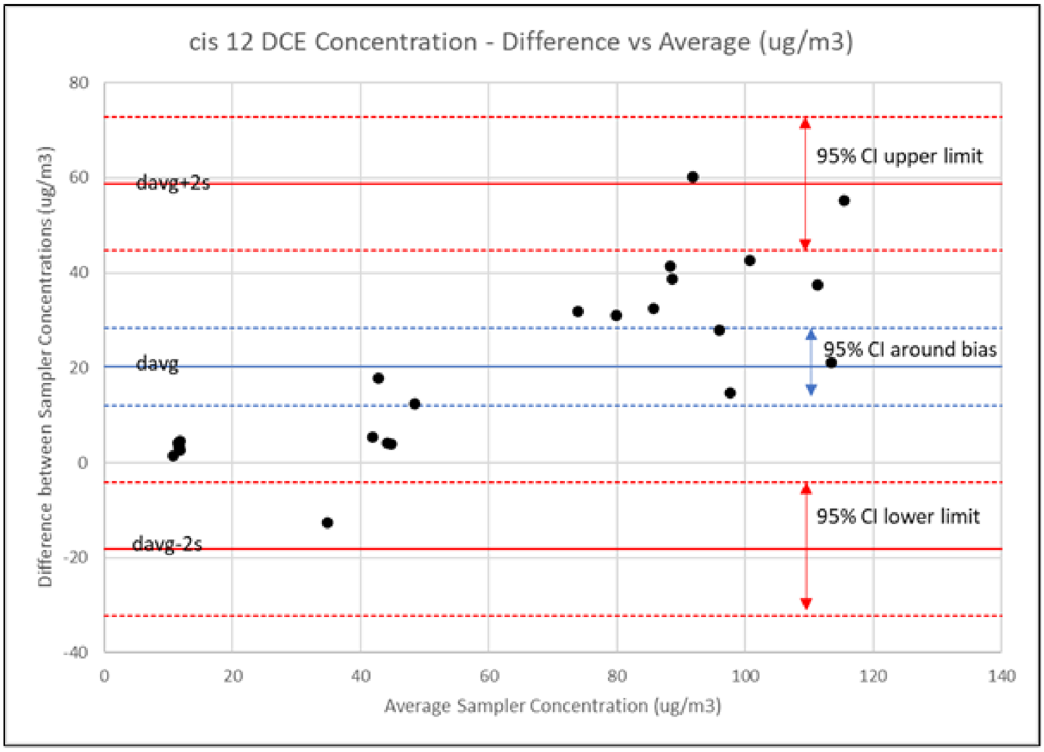


Figure 4. Difference between paired sampler concentration vs mean/average of that Paired Sampler Concentration for Each Analyte. (Continued)

Also plotted is the mean difference for all sample pairs, the t-Test based 95% confidence interval for the mean, and the 95% confidence interval for the normal distribution about the mean.



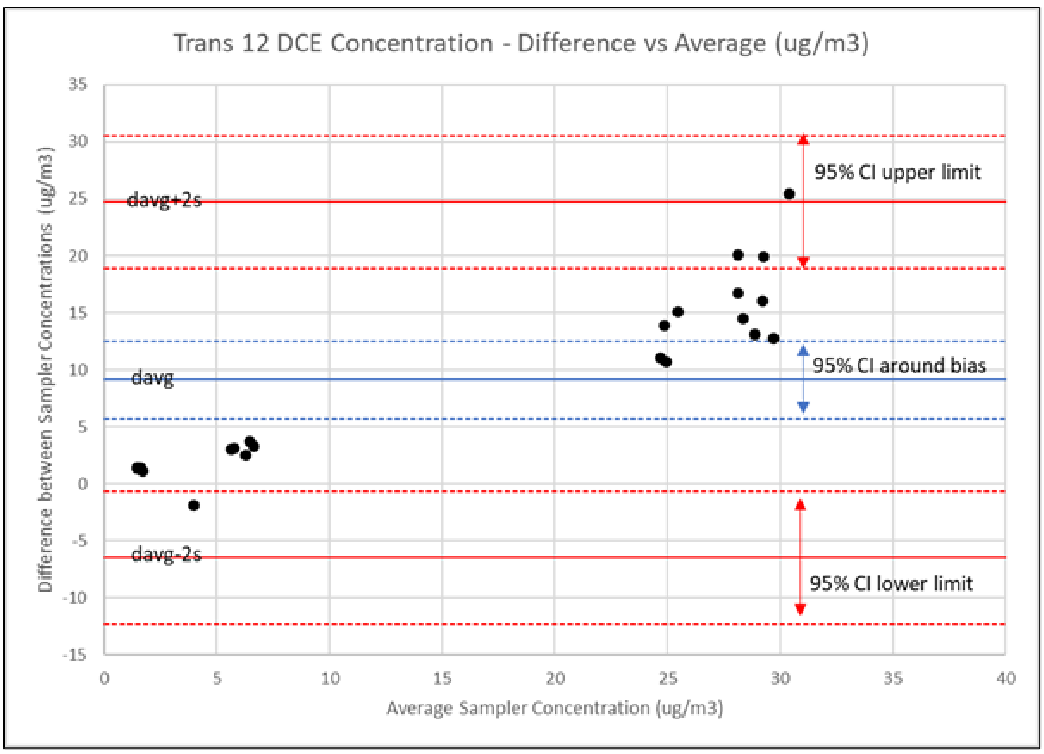


Figure 4. Difference between paired sampler concentration vs mean/average of that Paired Sampler Concentration for Each Analyte. (Continued)

Also plotted is the mean difference for all sample pairs, the t-Test based 95% confidence interval for the mean, and the 95% confidence interval for the normal distribution about the mean.

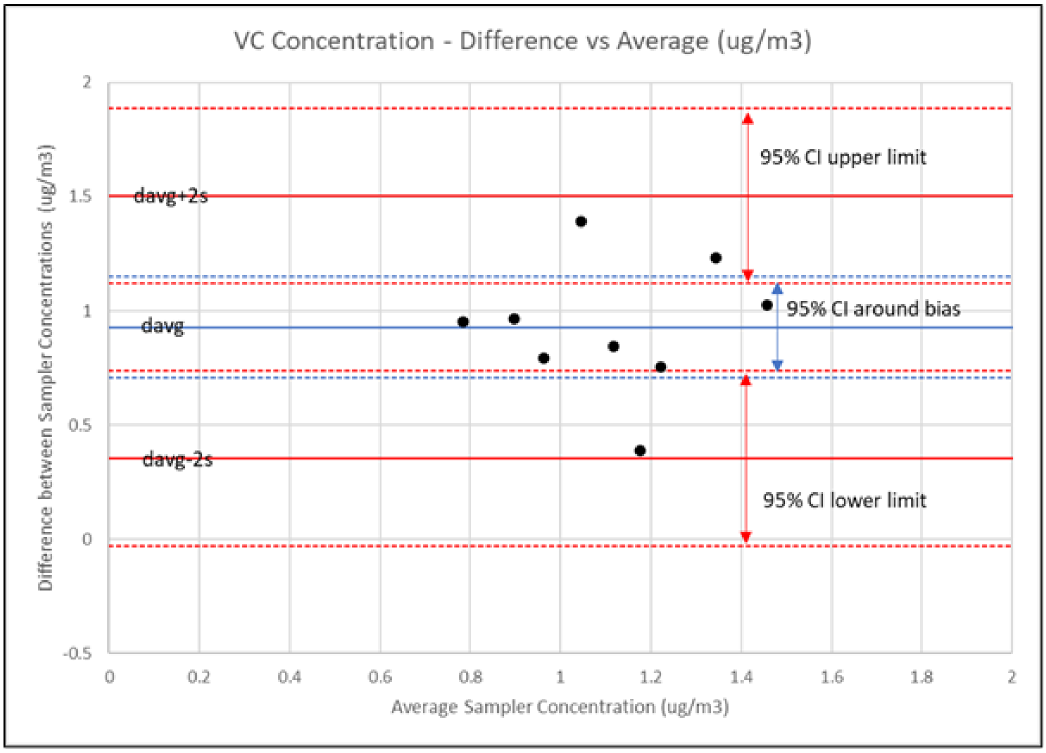


Figure 4 cont. Difference between paired sampler concentration vs mean/average of that Paired Sampler Concentration for Each Analyte.

Also plotted is the mean difference for all sample pairs, the t-Test based 95% confidence interval for the mean, and the 95% confidence interval for the normal distribution about the mean.

Table 11. Summary of Data for Assessment/Comparison of Passive Sampler vs TD Tube Performance.

Results are in ug/m³ as applicable.

Analyte	Number of usable TD/Passive pairs(1)	R^2 (2)	Slope	Difference Between TD and Passive Sampler Values													
				Mean	Std Dev (SD)	Min	Max	Range	Gaussian Distribution 95% Confidence Interval (CI) for Normal Distribution (3)				t-Test 95% Confidence Interval (CI) Around Mean/bias (4)				
									Range		Values w/in CI		Std Error	CI Range		Values w/in CI	
									Low	High	#	%		Low	High	#	%
TCE	24	0.953	1.15	92.04	81.31	-130	227	357	-70.57	254.65	23	96	16.60	58.85	125.23	10	42
11 DCA	24	0.935	0.75	-1.31	1.64	-5.64	1.14	6.78	-4.59	1.96	23	96	0.33	-1.98	-0.64	9	38
111 TCA	6	0.833	0.34	-11.09	2.74	-14.2	-7.66	6.53	-16.57	-5.61	6	100	1.12	-13.33	-8.85	4	67
11 DCE	21	0.991	2.62	15.12	17.91	1.96	50.2	48.24	-20.70	50.94	21	100	3.91	7.31	22.94	0	0
12 DCA	10	0.939	1.67	1.09	0.75	0.16	2.49	2.33	-0.42	2.60	10	100	0.24	0.61	1.57	5	50
cis 12 DCE	24	0.974	1.41	20.21	19.24	-12.7	60.2	72.9	-18.27	58.70	23	96	3.93	12.36	28.07	5	21
PCE	17	0.959	1.56	11.98	18.16	-1.18	54.8	55.98	-24.33	48.30	16	94	4.40	3.18	20.79	5	29
Trans 12 DCE	23	0.980	1.77	9.11	7.79	-1.85	25.4	27.25	-6.48	24.70	21	91	1.63	5.86	12.36	2	9
VC	9	0.898	2.19	0.93	0.29	0.39	1.39	1.00	0.35	1.50	9	100	0.10	0.74	1.12	6	67

(1) Results based on lab data for which both TD and Passive sampler results were both quantifiable (not ND)

(2) R^2 for linear correlation

(3) 95% confidence interval (CI) for normal distribution about the mean defined by equation CI=Mean +/- 2*StdDev

(4) t-Test - 95% confidence interval (CI) defined by t-test and formula *CI=Mean +/- 2*StdError*

Plots of passive sampler concentration vs active TD tube sampler concentration indicated that there is a fairly strong linear relationship between the two with R^2 values for each analyte ranging from 0.83 to 0.98, the majority of values of which were 0.94 or above. However, plots did not indicate a strong 1:1 relationship between the passive and TD tube sampler for most analytes, with relationships (slopes) ranging 0.34 to 2.62. TCE showed the strongest relationship at 1.15.

The results shown above indicated that performance for most analytes was precise or consistent from one analysis to the next yet lacked accuracy relative to TD-tube based concentrations. Since time-weighted concentrations for the passive sampler are analyte specific, calculation based, and are a function of the uptake rate, the lack of accuracy suggested that analyte specific calibration and validation of uptake rates was necessary for effective use. This is the same conclusion that was drawn by Johnson et al. (2020) and Guo et al. (2021).

The secondary assessment (Bland and Altman) using a plot of the difference between a paired set of data vs the mean of that data pair along with 95% confidence intervals for the mean/bias using a standard *t*-Test and for a normally distributed population suggested that data is not that comparable. This was seen in two ways as follows:

- Most data (91% to 100%) within each plot fell within the 95% CI for a normal distribution. However, the plot indicated that the magnitude of intervals was quite large relative to the mean difference. For example, TCE showed a mean difference of 92 ug/m^3, yet the 95% CI of +/- 162 ug/m^3 around that mean.
- A much lower percentage of data within each plot fell within the 95% confidence interval for the mean/bias as determined by the *t*-Test. Those percentages ranged from 0% to 67%. In addition, for 7 of 9 analytes for which usable data was available, the range defined by that 95% CI for each analyte was greater than a +/- 30% range around the mean difference, a range considered acceptable for laboratory analytical.

This secondary analysis suggested that the passive sampler performance does not rank it as a suitable replacement for active sampling.

8.0 COMMENTS – SAMPLER VALIDATION

As indicated, the preliminary assessment of comparability using direct plots of passive sampler concentration vs active TD tube sampler concentration for each analyte and regression analysis suggested that there seemed to be a fairly good linear relationships between analytes, but those relationships were not 1:1. That suggested that while the passive sampler was precise, performing consistently relative to the active sampler, accuracy of the sampler for many analytes was limited and uptake rates for those analytes needed to be more effectively calibrated to be suitable for sampling.

On the other hand, evaluation using the Bland and Altman methodology suggested the passive sampler was not a suitable replacement for active sampling due to the magnitude of variation in results.

Whether the passive sampler is a suitable replacement for the active sampler based on the Bland and Altman assessment, the magnitude of variation suggested it may not be. However, the Absolute Standards PT program (Absolute Standards, Inc, Hamden, CT) for laboratory accreditation/certification uses the acceptable range for accurate analysis as +/- 30%. Based on the magnitude of that acceptable range, conclusions based on the Bland and Altman assessment may not be entirely reasonable.

Based on the regression analysis using data gathered in this study and the results of the regression analysis performed for indoor air sampling under ER #201501, the fairly strong linear relationship with the active sampler indicated the passive sampler was precise, yet that correlation 1:1 indicating accuracy issues. With more effective calibration of uptake rate, it is believed those accuracy issues could be overcome. As such, it is believed that, with additional calibration and validation, the passive sampler could be a viable, cost-effective sampling technology.

Regarding whether two additional sampling events under this project are warranted, it is not believed that two additional sets akin to those produced thus far would alter the outcome or perception of performance.

9.0 COST ASSESSMENT FOR PASSIVE SAMPLER USE

Passive samplers provide a less intrusive, efficient, and cost-effective way to characterize long-term, time-averaged air concentrations.

Since it is difficult to estimate how many samplers might be used in a deployment or with multiple deployments across a neighborhood, costs associated with passive sampler use will focus strictly on deployment, retrieval, and analytical cost on a per sample basis. This estimate does not reflect preparation time, travel time, or reporting time. The cost estimate for deployment, retrieval, and analysis of a single passive sampler is shown in Table 12.

Table 12. Cost Estimate for Deployment, Retrieval, and Analysis of a Single Passive Sampler

<table>
<tr><th colspan="2">Activity</th><th>Amount</th><th>Unit Cost</th><th>Total Cost</th></tr>
<tr><td colspan="2">Analytical</td><td>1</td><td>$200</td><td>$200</td></tr>
<tr><td rowspan="2">Labor: Consultant</td><td>Deployment</td><td>0.5 hr</td><td rowspan="2">$100/hr</td><td rowspan="2">$100</td></tr>
<tr><td>Retrieval</td><td>0.5 hr</td></tr>
<tr><td colspan="4">Total</td><td>$300</td></tr>
</table>

Based on this per sample estimate, costs can be estimated as follows:

- for a single sample deployment in a manhole setting - $300
- for a single sample deployment in 10 manhole settings - $3,000

10.0 IMPLEMENTATION ISSUES

Beyond the need for accurate, analyte specific calibration of the passive sampler, deployment in manholes where concentrations might saturate the sorbent-based sampler would be the only implementation issue in terms of understanding actual concentrations within a manhole. However, even if saturation occurs, there is still valuable information to be gained in terms of minimum concentrations for analytes of concern and the presence of other analytes present and their relative concentrations. This information can also be used if resampling for more accurate concentrations is necessary.

11.0 REFERENCES

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APPENDIX A BEACON PASSIVE SAMPLERS; REPORTING CONCENTRATION DATA

BEACON ENVIRONMENTAL

Harry O'Neill

TECHNICAL MEMORANDUM

Updated: February 6, 2020

Beacon Passive Samplers Reporting Concentration Data

Uptake Rate

In 2016, Beacon commissioned two consecutive studies at the Health and Safety Laboratory (HSL) in the United Kingdom. The studies set out to experimentally determine and validate the quantitative uptake rates of the Beacon Passive Sampler based on 7-day and 14-day sampling events, which are routine sampling periods used for passive soil gas investigations. Active pumped samplers (reference technique) and conventional, industry-standard, axial passive samplers were included in the studies.

The experiments were carried out in the HSL standard atmosphere generator based upon procedures described in ISO 6145-4:2004. HSL is an internationally recognized center of excellence for VOC sampling, and their methods for the determination of hazardous substances (MDHS) are the source of most of the published uptake rates in the relevant international standard methods (e.g., ISO 16017-2).[1]

Quantitative uptake rates for 13 key chlorinated and aromatic VOCs were determined and verified for the Beacon Passive Sampler for 7- and 14-day exposure periods. In this six-replicate study, the devices showed excellent performance with great linearity and reproducibility. In addition, the uptake rates were within the 0.1 to 1.0 ml/min range, which was confirmed to be the recommended range when sampling for soil gas, as described in the federally funded study ESTCP Report ER-200830.[2] These findings confirmed that the Beacon Passive Sampler is an ideal device for quantitative, time-weighted-average (TWA) concentration determination for the compounds targeted in the study, as well as compounds of similar molecular weight and/or volatility, for both air and soil gas sampling.

Per the requirements of ISO 16017-2, the mass measured (ng) by a passive sampler is converted to a concentration by dividing the mass (ng) by the sampler uptake rate (ml/min) and the sampling period (min), which is then multiplied by a value of 1,000 to convert ng/ml to ug/m³.

The equation used to calculate the time-weighted average concentrations is provided below.

$$C = \frac{1000 \times M}{U \times t}$$

Where:
- C = concentration (ug/m³)
- M = mass (ng)
- U = uptake rate (ml/min)
- t = sampling time (minutes)

The compounds included in the uptake rate study are provided in **Table 1**, which also provides the validated uptake rates.

Table 1: Compounds with Validated Uptake Rates

COMPOUND	Uptake Rate (ml/min)
Vinyl Chloride	0.77
1,1-Dichloroethene	0.33
trans-1,2-Dichloroethene	0.44
1,1-Dichloroethane	0.85
cis-1,2-Dichloroethene	0.54
1,2-Dichloroethane	0.56
1,1,1-Trichloroethane	1.02
Benzene	0.54
Trichloroethene	0.34
Toluene	0.41
Tetrachloroethene	0.41
Ethylbenzene	0.83
o-Xylene	0.86

Graham's Law of gas diffusion is used to calculate the uptake rate for target VOCs that were not included in the uptake rate study. Graham's law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight. In the HSL study, Beacon included a broad range of VOCs from vinyl chloride to o-xylene in order to determine the uptake rates for a wide range of compounds and be able to better estimate uptake rates for other target VOCs. The equation used to calculate the uptake rates based on Graham's Law is provided below:

$$U_c = \frac{U_k}{\sqrt{\frac{MW_c}{MW_k}}}$$

Where: U_c = Uptake rate calculated from known uptake rate (ml/min)

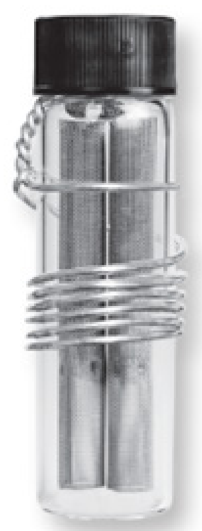
U_k = known uptake rate from study (ml/min)

MW_c = Molecular weight of compound with calculated uptake rate (g/mol)

MW_k = Molecular weight of compound with known uptake rate (g/mol)

Table 2 on the following page provides the known and calculated uptake rates for the list of compounds that are in Beacon's standard list of compounds targeted with EPA Method 8260C or TO-17. Table 2 also provides the molecular weights in g/mol for each of the compounds. The compounds from the uptake rate study used to calculate the other target VOCs were chosen based on similar molecular weights and chemical properties. Note that the calculated uptake rates for the TPH fractions is based on the average uptake rates calculated for each of the individual alkanes within the reported range (e.g., TPH C4-C9 is based on the average of the calculated uptake rates for pentane, hexane, heptane, octane, & nonane).

Table 3 provides the limit of quantitation (LOQ) for each of the compounds in the standard compound list based on 1, 3, 7, and 14 day sampling periods. The LOQ is at or above the low point of the initial calibration curve to ensure data reported are defensible. In addition, results less than the LOQ but greater than the limit of detection (LOD) may be reported as estimates and qualified with a "J" to achieve lower reporting limits. LODs for each compound are provided in **Table 4** ■



The Beacon Passive Soil Gas Sampler

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Table 2: Uptake Rates for Standard Target Compound List

COMPOUND	Uptake Rate (ml/min)	Compound with known uptake rate used to calculate estimated uptake rate	Molecular Weight (g/mol)
Vinyl Chloride	0.77		62.5
1,1-Dichloroethene	0.33		97
1,1,2-Trichlorotrifluoroethane (Fr.113)	0.86	1,1,1-Trichloroethane	187.38
trans-1,2-Dichloroethene	0.44		96.95
Methyl-t-butyl ether	0.51	Benzene	88.17
1,1-Dichloroethane	0.85		99
cis-1,2-Dichloroethene	0.54		96.95
Chloroform	0.36	Trichloroethene	119
1,2-Dichloroethane	0.56		99
1,1,1-Trichloroethane	1.02		133.4
Carbon Tetrachloride	0.43	Tetrachloroethene	153.84
Benzene	0.54		78.11
Trichloroethene	0.34		131.4
1,4-Dioxane	0.42	Toluene	88.11
1,1,2-Trichloroethane	0.34	Trichloroethene	133.4
Toluene	0.41		92
1,2-Dibromoethane (EDB)	0.39	Tetrachloroethene	187.9
Tetrachloroethene	0.41		165.8
1,1,1,2-Tetrachloroethane	0.41	Tetrachloroethene	167.85
Chlorobenzene	0.84	o-Xylene	112.6
Ethylbenzene	0.83		106
p & m-Xylene	0.86	o-Xylene	106.2
1,1,2,2-Tetrachloroethane	0.41	Tetrachloroethene	167.9
o-Xylene	0.86		106.2
1,2,3-Trichloropropane	0.73	o-Xylene	147.43
Isopropylbenzene	0.81	o-Xylene	120.19
1,3,5-Trimethylbenzene	0.81	o-Xylene	120.2
1,2,4-Trimethylbenzene	0.81	o-Xylene	120.2
1,3-Dichlorobenzene	0.73	o-Xylene	147
1,4-Dichlorobenzene	0.73	o-Xylene	147
1,2-Dichlorobenzene	0.73	o-Xylene	147
1,2,4-Trichlorobenzene	0.39	Tetrachloroethene	181.46
Naphthalene	0.78	o-Xylene	128.16
1,2,3-Trichlorobenzene	0.39	Tetrachloroethene	181.45
2-Methylnaphthalene	0.74	o-Xylene	142.2
TPH C4-C9	0.59	Based on the average of the uptake rates calculated for individual alkanes	
TPH C10-C15	0.67		

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Table 3: Limits of Quantitation (LOQs) based on Exposure Periods

COMPOUND	CAS	Uptake Rate (ml/min)	1 Day LOQ (ug/m3)	3 Days LOQ (ug/m3)	7 Days LOQ (ug/m3)	14 Days LOQ (ug/m3)
Vinyl Chloride	75-01-4	0.77	9.02	3.01	1.29	0.64
1,1-Dichloroethene	75-35-4	0.33	21.04	7.01	3.01	1.50
1,1,2-Trichlorotrifluoroethane (Fr.113)	76-13-1	0.86	8.07	2.69	1.15	0.58
trans-1,2-Dichloroethene	156-60-5	0.44	15.78	5.26	2.25	1.13
Methyl-t-butyl ether	1634-04-4	0.51	13.66	4.55	1.95	0.98
1,1-Dichloroethane	75-34-3	0.85	8.17	2.72	1.17	0.58
cis-1,2-Dichloroethene	156-59-2	0.54	12.86	4.29	1.84	0.92
Chloroform	67-66-3	0.36	19.44	6.48	2.78	1.39
1,2-Dichloroethane	107-06-2	0.56	12.40	4.13	1.77	0.89
1,1,1-Trichloroethane	71-55-6	1.02	6.81	2.27	0.97	0.49
Carbon Tetrachloride	56-23-5	0.43	16.32	5.44	2.33	1.17
Benzene	71-43-2	0.54	32.15	10.72	4.59	2.30
Trichloroethene	79-01-6	0.34	20.42	6.81	2.92	1.46
1,4-Dioxane	123-91-1	0.42	41.44	13.81	5.92	2.96
1,1,2-Trichloroethane	79-00-5	0.34	20.58	6.86	2.94	1.47
Toluene	108-88-3	0.41	42.34	14.11	6.05	3.02
1,2-Dibromoethane (EDB)	106-93-4	0.39	18.03	6.01	2.58	1.29
Tetrachloroethene	127-18-4	0.41	16.94	5.65	2.42	1.21
1,1,1,2-Tetrachloroethane	630-20-6	0.41	17.04	5.68	2.43	1.22
Chlorobenzene	108-90-7	0.84	8.31	2.77	1.19	0.59
Ethylbenzene	100-41-4	0.83	20.92	6.97	2.99	1.49
p & m-Xylene	108-38-3	0.86	20.19	6.73	2.88	1.44
1,1,2,2-Tetrachloroethane	79-34-5	0.41	17.04	5.68	2.43	1.22
o-Xylene	95-47-6	0.86	20.19	6.73	2.88	1.44
1,2,3-Trichloropropane	96-18-4	0.73	9.51	3.17	1.36	0.68
Isopropylbenzene	98-82-8	0.81	21.48	7.16	3.07	1.53
1,3,5-Trimethylbenzene	108-67-8	0.81	21.48	7.16	3.07	1.53
1,2,4-Trimethylbenzene	95-63-6	0.81	21.48	7.16	3.07	1.53
1,3-Dichlorobenzene	541-73-1	0.73	9.50	3.17	1.36	0.68
1,4-Dichlorobenzene	106-46-7	0.73	9.50	3.17	1.36	0.68
1,2-Dichlorobenzene	95-50-1	0.73	9.50	3.17	1.36	0.68
1,2,4-Trichlorobenzene	120-82-1	0.39	17.72	5.91	2.53	1.27
Naphthalene	91-20-3	0.78	22.18	7.39	3.17	1.58
1,2,3-Trichlorobenzene	87-61-6	0.39	17.72	5.91	2.53	1.27
2-Methylnaphthalene	91-57-6	0.74	23.36	7.79	3.34	1.67
TPH C4-C9		0.59	5,870	1,960	839	420
TPH C10-C15		0.67	5,180	1,730	740	370

BEACON ENVIRONMENTAL

Table 4: Limits of Detection (LODs) based on Exposure Periods

COMPOUND	CAS	Uptake Rate (ml/min)	1 Day LOD (ug/m3)	3 Days LOD (ug/m3)	7 Days LOD (ug/m3)	14 Days LOD (ug/m3)
Vinyl Chloride	75-01-4	0.77	4.51	1.50	0.64	0.32
1,1-Dichloroethene	75-35-4	0.33	10.52	3.51	1.50	0.75
1,1,2-Trichlorotrifluoroethane (Fr.113)	76-13-1	0.86	4.03	1.34	0.58	0.29
trans-1,2-Dichloroethene	156-60-5	0.44	7.89	2.63	1.13	0.56
Methyl-t-butyl ether	1634-04-4	0.51	6.83	2.28	0.98	0.49
1,1-Dichloroethane	75-34-3	0.85	4.08	1.36	0.58	0.29
cis-1,2-Dichloroethene	156-59-2	0.54	6.43	2.14	0.92	0.46
Chloroform	67-66-3	0.36	9.72	3.24	1.39	0.69
1,2-Dichloroethane	107-06-2	0.56	6.20	2.07	0.89	0.44
1,1,1-Trichloroethane	71-55-6	1.02	3.40	1.13	0.49	0.24
Carbon Tetrachloride	56-23-5	0.43	8.16	2.72	1.17	0.58
Benzene	71-43-2	0.54	6.43	2.14	0.92	0.46
Trichloroethene	79-01-6	0.34	10.21	3.40	1.46	0.73
1,4-Dioxane	123-91-1	0.42	16.58	5.53	2.37	1.18
1,1,2-Trichloroethane	79-00-5	0.34	10.29	3.43	1.47	0.73
Toluene	108-88-3	0.41	16.94	5.65	2.42	1.21
1,2-Dibromoethane (EDB)	106-93-4	0.39	9.02	3.01	1.29	0.64
Tetrachloroethene	127-18-4	0.41	8.47	2.82	1.21	0.60
1,1,1,2-Tetrachloroethane	630-20-6	0.41	8.52	2.84	1.22	0.61
Chlorobenzene	108-90-7	0.84	4.16	1.39	0.59	0.30
Ethylbenzene	100-41-4	0.83	8.37	2.79	1.20	0.60
p & m-Xylene	108-38-3	0.86	8.07	2.69	1.15	0.58
1,1,2,2-Tetrachloroethane	79-34-5	0.41	8.52	2.84	1.22	0.61
o-Xylene	95-47-6	0.86	8.07	2.69	1.15	0.58
1,2,3-Trichloropropane	96-18-4	0.73	4.76	1.59	0.68	0.34
Isopropylbenzene	98-82-8	0.81	8.59	2.86	1.23	0.61
1,3,5-Trimethylbenzene	108-67-8	0.81	8.59	2.86	1.23	0.61
1,2,4-Trimethylbenzene	95-63-6	0.81	8.59	2.86	1.23	0.61
1,3-Dichlorobenzene	541-73-1	0.73	4.75	1.58	0.68	0.34
1,4-Dichlorobenzene	106-46-7	0.73	4.75	1.58	0.68	0.34
1,2-Dichlorobenzene	95-50-1	0.73	4.75	1.58	0.68	0.34
1,2,4-Trichlorobenzene	120-82-1	0.39	8.86	2.95	1.27	0.63
Naphthalene	91-20-3	0.78	8.87	2.96	1.27	0.63
1,2,3-Trichlorobenzene	87-61-6	0.39	8.86	2.95	1.27	0.63
2-Methylnaphthalene	91-57-6	0.74	9.34	3.11	1.33	0.67
TPH C4-C9		0.59	5,874	1,958	839	420
TPH C10-C15		0.67	5,181	1,727	740	370

[1] ESTCP Project ER-200830, Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling, July 2014.
[2] ISO 16017-2, Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 2: Diffusive Sampling, 2003.

APPENDIX B LABORATORY ANALYTICAL DATA

Absolute Standards PT Program Data (QA/QC)
Sample Set 1, Mar 24-Apr 1, 2022
Sample Set 2, Apr 1-Apr 9, 2022