FINAL REPORT

Demonstration of a Long-Term Sampling and Novel Analysis Approach for Distinguishing Sources of Volatile Organic Compounds in Indoor Air

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A long-term low flow capillary canister sampling system was demonstrated and validated at Naval Weapons Station (NWS) Yorktown by characterizing VOCs from vapor intrusion (VI) using the innovative low flow sampling system and comparing the results to those from both long term diffusion tube sampling (2 weeks) and consecutive multiple day 24-hour canister sampling. The innovative low flow rate capillary flow controller provides flow rates ranging from 0.1 to 0.5 mL/min, allowing collection of samples over a 1-3 week sampling period. Two locations in each of two large buildings impacted by VI were sampled for six consecutive quarters. Results, focused on TCE which was the highest concentration VOC sampled, demonstrate that the low flow capillary canister system samples collected concentrations over two-week sampling periods that were comparable to average values collected daily over two weeks using the traditional canister sampling approach. TCE concentrations measured using diffusion samplers were significantly different. Seasonal impacts on VOCs concentrations were noted, but did not negatively affect capillary canister performance. Sampling using the capillary canister system required no additional expertise relative to the traditional approach. The capillary canister sampling system controllers are lower cost than traditional flow controllers, and the extended sampling period the approach provides allows for estimation of long-term average exposure, thus allowing for a more robust mitigation decision, which can translate into significant long-term cost savings.

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ACRONYMS AND ABBREVIATIONS

α	Alpha
µg/m^3	microgram per cubic meter
ASTM	American Society for Testing and Materials
bgs	below ground surface
BTEX	Benzene, Toluene, Ethyl Benzene, Xylenes
CARES	Clarkson's Center for Atmospheric Research in Engineering and Science
CIA	Canister Interface Accessory
CO_2	carbon dioxide
DCE	Dichloroethene
DoD	Department of Defense
ESTCP	Environmental Security and Technology Certification Program
EPA	Environmental Protection Agency
GC	Gas Chromatograph
GC/MS	Gas Chromatograph Mass Spectrometry
h	Hours
L	Liter
MEK	Methyl Ethyl Ketone
mL	milliliter
MS	Mass Spectrometry
MTBE	Methyl Tert-butyl Ether
NAVFAC	Naval Facilities Engineering Command
NESDI	Navy's Environmental Sustainability Development to Integration
NIOSH	National Institute for Occupational Safety & Health
NPL	National Priority List
NWS	Naval Weapon Station
O_2	Oxygen
o.d.	Outer Diameter
OSHA	Occupation Safety & Health Administration
PCE	perchloroethylene
PPE	Personal Protective Equipment
ppmv	parts per million by volume

RSL	Risk-Based Screening Level
RI	Remedial Investigation
SERDP	Strategic Environmental Research and Development Program
SOP	Standard Operating Procedure
TCA	trichloroethane
TCE	Trichloroethylene, trichloroethene
TNT	Trinitrotoluene
VI	Vapor Intrusion
VOCs	Volatile Organic Compounds

1.0 INTRODUCTION

1.1 BACKGROUND

The overall goal of this research was to demonstrate and validate a capillary flow controller used for long-term air sampling to characterize chronic indoor air exposures from vapor intrusion (VI). This technology is a potential improvement over current technology which limits the duration of collection of a single Summa^{TM} canister to 24 to 48 hours.

At least 2,151 Department of Defense (DoD) sites have costly groundwater plumes where remediation is driven by chlorinated aliphatic hydrocarbons, 1,307 remediation sites driven by other volatile organic compounds (VOCs), and an additional 1,465 sites with the potential for VI of benzene, toluene, ethyl benzene, xylenes (BTEX/naphthalene) from petroleum sources (EPA 2004). Although some of those sites have reached closure, VI considerations may require even closed sites to be reexamined in some jurisdictions, for example during a 5-year review. The life-cycle cost for these sites is extensive. The costs of sampling and analysis are typically 30 to 70% of life-cycle costs (EPA 2004). The long-term capillary flow controller can substantially reduce these costs by decreasing the number of samples collected over the course of an investigation or long-term monitoring period as a result of minimizing variability. While most sampling strategies currently used in investigations do not involve multiple consecutive day-long samples, regulators and stakeholders are asking for increasing numbers of sampling rounds, driven by the concern with temporal variability that longer sample durations can minimize.

The risk of chronic disease generally depends upon long-term mean exposures received by the individuals over time. Therefore, a sampling strategy that allows for the distribution of individual mean exposures to be characterized across the population at risk is needed. The proposed approach is robust, comparable in cost or less expensive than current methods, allows for long-term sample collection, and requires one sample to capture a full range of analytes and concentrations.

1.2 OBJECTIVES OF THE DEMONSTRATION

This project demonstrated and validated the use of a novel capillary canister sampling system to enable long-term and representative sampling of VOCs in indoor environments impacted by VI. The new canister method provides most of the advantages of both canisters and sorbent samplers and avoids many of their limitations by allowing for long-term (1-3 weeks) sample collection and characterization of VOCs in buildings at risk for VI. Specific demonstration/validation objectives included:

1. Demonstrate, validate, and assess full-scale implementation costs and savings associated with use of evacuated canisters with a novel capillary flow controller for long-term (~2 weeks) collection of VOCs in a single canister.
2. Compare the performance of the long-term capillary-canister sampling system to that of 24- hour canister sampling and passive diffusion sampling methods.
3. Assess seasonal impacts on the performance of the long-term capillary-canister sampling device.

4. Provide data necessary to understand the benefits and limitations of the novel sampling approach.

1.3 REGULATORY DRIVERS

Recent changes to regulatory guidance have been made that could be expected to affect the extent, and ultimately the cost, of VI investigations. First, the U.S. Environmental Protection Agency's (EPA) Region 9 has adopted a short-term exposure limit (accelerated response action level) for trichloroethylene (TCE) of 2 $\mu g/m^3$ in residential indoor air. This new action level requires immediate relocation of residents. This is 60 times lower than any previously published guidance (e.g., California Regional Water Quality Control Board limit of 120 $\mu g/m^3$). Second, the EPA has recently changed VI investigation guidance. They previously recommended a

three-tiered approach for VI investigation including primary screening, secondary screening, and site-specific pathway assessment. In 2013, however, the EPA revised their VI guidance, recommending a detailed site investigation based only on the presence of VOCs in the subsurface and potential for exposure, effectively skipping the "secondary screening" stage of investigation. These changes translate to the potential for many more sites to undergo detailed characterization of VOCs in indoor air and the need for greater understanding of long-term exposure and temporal variability.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Evacuated canisters have been used to collect air samples in both indoor and outdoor air environments for the last three decades. Studies have shown good stability and recovery of many contaminants. However, over- and under-estimations have been reported by several sources depending upon the chemical being sampled (Oliver et al. 1986; Evans et al. 1998; Perrin et al. 1996; Khalil & Rasmussen 1992). EPA procedures TO-14a and TO-15, as well as American Society of Testing Materials (ASTM) D 5466-93, were developed to establish standardized methods to clean, prepare, sample, and analyze low concentrations of VOCs in ambient air using canisters. These methods define the necessary steps to sample VOCs using sub-atmospheric pressures to passively collect a whole air sample in a canister. The airflow into the canister is typically controlled using a diaphragm or critical orifice. These flow devices generally allow for sampling periods from a few minutes to 24-h, depending upon the canister size and contaminant of interest (8-h using 400 mL and up to 24-h using 6 L canisters). The current controllers in practice become tend to be unreliable at durations greater than 24-h (EPA TO-15).

A capillary flow controller (**Figure 1**) was developed to sample at lower flow rates of air into a sampling canister to allow for more reliable long-term sampling (Rossner 2002; 2004; 2005). With the development of this flow control device, the use of evacuated canisters for longer term sampling in typical or smaller canister volumes became possible. The capillary flow controller is a variation on a sharp edge orifice flow controller commonly used to control the flow of air into an air sampling canister. It essentially controls the velocity of the air as a function of the properties of the capillary diameter and length. The longer the capillary is, the slower the flow rate. Typical flow rates used for sampling low levels of VOCs range from 0.1 to 0.5 mL/min. In contrast, the diaphragm flow controller can only sample accurately down to approximately 3.5 mL/min. The low flow rates of the capillary flow controller allow for sampling times as long as 3-4 weeks.

Figure 1. Capillary Flow Controller Coupled with a Standard Air Sampling Canister.

The left side shows the original laboratory system design and the right shows the design currently marketed by Restek.

The initial research conducted by Rossner (2002) focused on the development of the capillary-canister and the evaluation of its ability to collect a representative sample. Recent studies by Rossner et al. (2004; 2005) indicate that representative samples can be effectively collected at extremely low flow rates ranging from 0.05 to 1.0 mL/min in small (400 mL) evacuated canisters.

This research demonstrated that the capillary-canister device collected accurate concentrations of VOCs for hours to weeks when compared to sorbent sampling methods and to an on line gas chromatograph (GC). While long term diffusion sampling offers the advantage of capturing exposures for 1- 3 weeks, there are limitations. Diffusion samplers may not effectively collect all VOCs (such as vinyl chloride), multiple samples must be collected using different sorbents to collect a range of analytes which translates to higher analytical costs, and results can be affected by environmental conditions such as humidity and temperature. Passive samplers also have limited dynamic ranges, thus requiring some estimation of the expected concentrations in order to select the appropriate sampling rate and sampling duration to avoid either overloading or non-detectable results. Also, it is difficult to analyze replicates from the same passive sample collection device. However, the capillary canister sampling system provides for a broader array of analytes, longer sampling times, and is minimally influenced by environmental conditions (Rossner et al., 2004; 2005).

2.2 TECHNOLOGY DEVELOPMENT

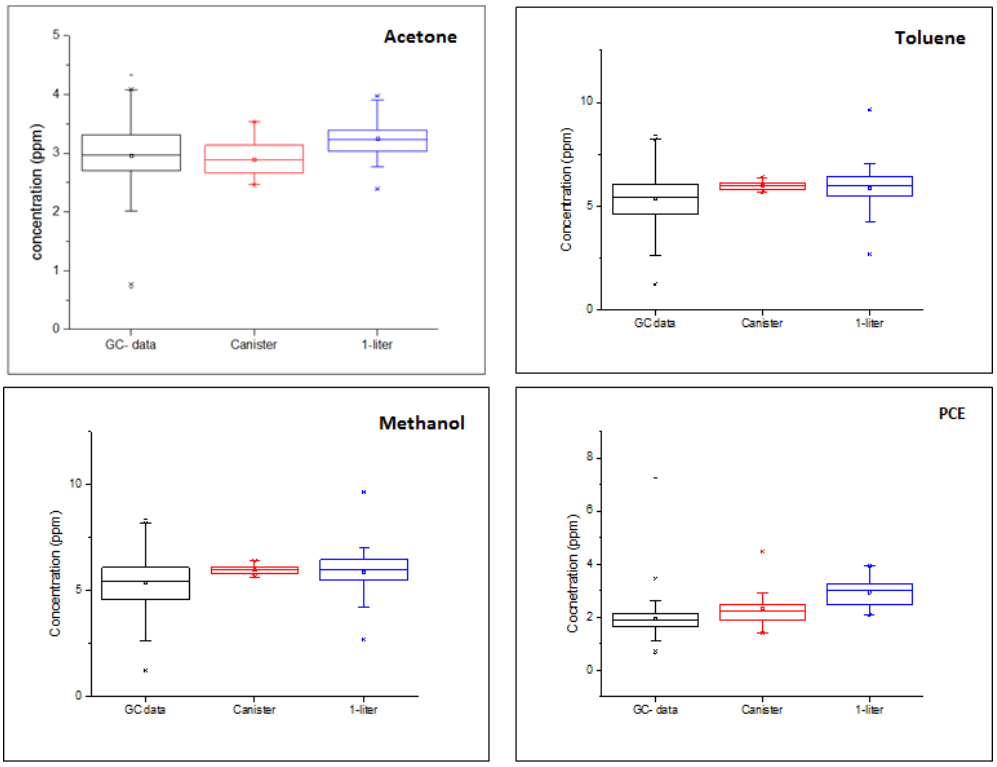
The development of a flow control device occurred in the late 1990s due to an interest in using evacuated canisters for personal breathing zone sampling as an alternative to sorbent samplers. The novel capillary flow controller developed and validated in several laboratory tests (Rossner, 2002; 2004; 2005) offers a distinct advantage over critical orifice or diaphragm flow controllers traditionally used with canisters – it allows for accurate low-flow, longer-term (2-3 weeks vs. up to 1 day) sampling of a broad array of analytes with minimal influence of environmental conditions. Recently, Restek Corporation, a manufacturer of chromatographic supplies and air sampling equipment such as canisters and flow controllers, redesigned the capillary flow controller for ease of use in both occupational and environmental monitoring.

The initial research conducted by Rossner (2002) focused on the development of the capillary-canister and the evaluation of its ability to collect a representative sample. Recent studies by Rossner et al. (2004; 2005) indicate that representative samples can be effectively collected at extremely low flow rates ranging from 0.05 to 1.0 mL/min in small (400 mL) evacuated canisters. This research demonstrated that the capillary-canister device collected accurate concentrations of VOCs for hours to weeks when compared to sorbent sampling methods and to an on line gas chromatograph (GC). While long term diffusion sampling offers the advantage of capturing exposures for 1- 3 weeks, there are limitations. Diffusion samplers may not effectively collect all VOCs (such as vinyl chloride), multiple samples must be collected using different sorbents to collect a range of analytes which translates to higher analytical costs, and results can be affected by environmental conditions such as humidity and temperature. Passive samplers also have limited dynamic ranges, thus requiring some estimation of the expected concentrations in order to select the appropriate sampling rate and sampling duration to avoid either overloading or non-detectable results. Also, it is difficult to analyze replicates from the same passive sample collection device. However, the capillary canister sampling system provides for a broader array of analytes, longer sampling times, and is minimally influenced by environmental conditions (Rossner et al., 2004; 2005).

Recently, chamber studies were conducted for 1-week and 3-week time periods using the capillary flow controller. In the 7-day study, measurements of toluene and perchloroethylene (PCE) were made using the flow-controlled canister system and were compared to those using an online GC (representing the “gold standard”) and those for passive diffusion sorbents.

Six identical 6 L canisters were simultaneously run in a chamber along with 6 diffusion samples (radiellos). The test showed that the VOCs masses collected using the charcoal diffusion tubes (single sorbent) were significantly less than those collected using the online GC standard. The canister systems were observed to sample the same concentrations, statistically, as the online GC standard (Rossner, 2013 *unpublished*).

Figure 2 shows data collected simultaneously from 6 canisters that were each sampled for a three-week period, 21 1-liter canisters sampled daily, and an on-line GC collecting a sample about 8 times per day. Although the sorbent tubes were not used as a comparison point during this set of samples, it is still observed that the canisters can produce reliable data for extended periods of time (Rossner, 2014 unpublished). This is especially significant considering the environmental variability typically associated with long-term sampling.



Note: GC- n=168, 1-liter Canisters -n=21, 6-liter Canisters n=6

Figure 2. Comparison of Daily Samples (1-liter Canisters) to Three Week (6-liter Canister) Samples for four VOCs.

Passive diffusion samplers with single sorbents and multisorbent tubes with calibrated air sampling pumps have been used extensively to characterize VI (e.g., SERDP/ESTCP investments ER-200423, ER-200707, and ER-200830). The choice of sorbent is closely linked to the analytical technique and defines the chemicals that can be quantified (Dewulf, 1999). Regardless of which sorbents are chosen, environmental conditions such as humidity, elevated temperatures, and airborne concentrations present during sampling can significantly affect the sample collection and may limit the effectiveness of the sampling technique. In addition, stability after sampling and adsorption and desorption efficiency may vary widely between VOCs, making it difficult to sample multiple VOCs with one sorbent (Dewulf, 1999).

Hence, sorbents, certainly single sorbents such as those used in diffusion sampler, tend to under-sample (yielding lower concentrations) or omit contaminants entirely when used for indoor air quality assessments (Wang, 2006).

The ability to run wide concentration ranges and multiple analytes is limited and one often must use more than one tube to capture all VOCs of interest. In the absence of detailed information about the expected concentration range at a sampling site, it is possible to either under load or overload a sorbent based method, forcing the analytical laboratory to report the data with flags such as J, J+ or E. Such flagged data tends to be of limited value for decision making or quantitative risk assessment. Active sampling using air sampling pumps has a greater labor and training requirement then either passive sampling or canister methods. The labor and power requirements of active pumping methods often drive sampling costs up substantially for long- term samples.

Canisters lack many of the limitations of solid sorbents for the collection of VOCs. They are not impacted by humidity, temperature, multiple chemicals, or a broad dynamic range of concentration. However, disadvantages of traditional cylinders are their size and sampling duration achievable using a traditional flow controller. Implementation of the capillary flow controller allows for the use of canisters for long durations, weeks as opposed to hours. Evacuated canisters are capable of collecting a whole air sample representative of a wide range of VOCs covering multiple functional groups. Smaller or fewer canisters allow for ease of deployment, are less intrusive to building occupants, reduce labor costs associated with sample collection time, and reduce transportation costs to the lab for analysis.

The intrusion of chemical vapors from contaminated soils through the subsurface, across foundations, and into buildings and homes has been the focus of many studies and previous SERDP/ESTCP investments. The relationship between subsurface contamination and impacts to indoor air quality has been established in the literature, from the radon exposure work to early VOC vapor intrusion work (Nazaroff, 1985; 1987; Hodgson, 1992; Fischer, 1996; Olson, 2001; Fitzpatrick, 2002; Hers, 2003; Abreu, 2005; Johnson, 2013). One- and six-liter canisters have been used for many years for environmental area sampling of VOCs. The US EPA procedures TO-14a and TO-15, and ASTM D 5466-93 were developed to establish standardized methods to clean, prepare, sample, and analyze low concentrations of VOCs in air using canisters. The canisters have been evaluated by a number of researchers with respect to stability, storage time, recovery, humidity and other parameters (Oliver KD, 1986; McClenny WA, 1991; Pate B, 1992; Coutant RW, 1993; Kelly TJ, 1995; Evans JC, 1998, Wai-mei sin D, 2001).

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Canister sampling is the most common method used in the US for characterization of VOCs in soil gas and indoor air. Canisters lack many of the limitations of solid sorbents for the collection of VOCs. There is limited impact by humidity, temperature, multiple chemicals, or a broad dynamic range of concentration (Coffey et al. 2011; Oliver et al. 1986; Khalil & Rasmussen 1992; Pate et al. 1992; Rossner & Wick 2005; USEPA TO15). However, disadvantages of traditional canister are their size and the limited sampling duration achievable using a traditional flow controller. Implementation of the capillary flow controller allows for the use of canisters for long durations, weeks as opposed to hours. Stainless steel canisters are capable of collecting a whole air sample representative of a wide range of VOCs covering multiple functional groups.

For example, the ability to analyze alcohols and ketones from canister samples can be useful at sites impacted by alternative fuels or petroleum additives (i.e. ethanol, methyl tert-butyl ether (MTBE), methyl ethyl ketone (MEK)) or where these compounds form useful tracers of indoor sources. The same canister sample collected for VOCs can also be used to analyze light hydrocarbons and fixed gasses, such as methane, CO_2 and O_2 that help define the biological zonation in the vadose zone that can be critical for the evaluation of risk from aerobically degradable VOCs, such as BTEX and vinyl chloride. Smaller or fewer canisters allow for ease of deployment, are less intrusive to building occupants, reduce labor costs associated with sample collection time, and reduce transportation costs to the lab for analysis. Disadvantages of canisters include the additional cost for shipping the samples and the potential for leaking canisters during field sampling and/or shipping.

Passive diffusion samplers with single sorbents and multi-sorbent tubes with calibrated air sampling pumps have been used extensively to characterize VOC concentrations in ambient air and are the second most common air sampling technology for VI (e.g., SERDP/ESTCP investments ER-200423, ER-200707, and ER-200830). The choice of sorbent is closely linked to the analytical technique and defines the chemicals that can be quantified. Regardless of which sorbents are chosen, environmental conditions such as humidity, elevated temperatures, and airborne concentrations present during sampling can significantly affect the sample collection and may limit the effectiveness of the sampling technique. In addition, stability after sampling and adsorption and desorption efficiency may vary widely between VOCs, making it difficult to sample multiple VOCs with one sorbent (Dewulf, 1999). Hence, sorbents, certainly single sorbents such as those used in diffusion samplers, tend to under-sample (yielding lower concentrations) or omit contaminants entirely when used for indoor air quality assessments (Wang, 2006). The ability to run wide concentration ranges and multiple analytes is limited and one often must use more than one tube to capture all VOCs of interest. In the absence of detailed information about the expected concentration range at a sampling site, it is possible to either underload or overload a sorbent-based method, forcing the analytical laboratory to report the data with flags. Such flagged data tends to be of limited value for decision-making or quantitative risk assessment. Active sampling using air-sampling pumps has a greater labor and training requirement then either passive sampling or canister methods. The labor and power requirements of active pumping methods often drive sampling costs up substantially for long-term samples.

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3.0 PERFORMANCE OBJECTIVES

The project performance objectives, along with data requirements and criteria have been detailed and grouped by quantitative or qualitative information (**Table 1**).

3.1 PERFORMANCE OBJECTIVE: COMPARE TWO WEEK AND 24-H CANISTER SAMPLE CONCENTRATIONS

The first primary quantitative performance objective is collecting and analyzing VOCs using the two-week low-flow canister approach and comparing those to the *24-h canister approach* in terms of bias (percent difference in time-weighted average concentrations of VOCs) and precision (relative standard deviation of the two approaches). In addition, the flow rate of the two-week low-flow canister approach and the 24-h canister approach will be calculated for all samples, respectively. The temperature will be continuously monitored throughout the project and can be cross-referenced with the flow rate to observe if the parameter has a possible influence on the flow rate. The calculated flow rate the two-week low-flow approach will be compared against the marketed flow rate of ~0.31 mL/min, and the calculated flow rate of the 24-h approach will be compared against its set flow rate.

3.1.1 Data Requirements

Several requirements are necessary for properly demonstrating and evaluating the low-flow canister approach:

- Sub-slab data concentrations and pressures (3-4 locations) using the low-flow approach
- Indoor air data collected under ambient conditions (4 buildings, 2 locations per building) using the low-flow and 24-h canister approaches
- VOCs inventories from sampled buildings
- Ambient air samples
- Above data collected quarterly for two years
- Meteorological data for sampled timeframes as well as indoor temperatures

3.1.2 Success Criteria

Substantial reductions in the variance are possible when extending the averaging time of sampling, hence a week long measurement as opposed to daily measurements will provide a more precise estimate of the actual long-term exposure. Capillary canister sampling will be deemed successful relative to 24-h sampling if the following criteria are met:

- Temporal relationship between the 14-day canisters and the multiple 24-h canisters for each location will be analyzed using a time-weighted average calculation. Statistical analysis will be performed comparing the two sampling methods.
- Low-flow canister approach will not be statistically different with 95% confidence in identification and quantification of indoor air contaminants relative to the 24-h canister method.

- Collocated samples will allow for an analysis of how repeatable (precise) the 14-day method is with respect to the 24-h canister method. Low-flow canister collocated samples will not be statistically different with 95% confidence relative to the 24-h canister method.

Table 1. Performance Objectives

Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
VOCs time-weighted average concentrations are comparable to those from the *24-h canister approach* in terms of bias and precision.	• Indoor air data using the low- flow, 24-hour canister, and diffusion sampler approaches – 4 buildings, 2 locations per building • Sub-slab data • VOCs inventories from sampled buildings • Ambient air samples • Meteorological data • Above data collected quarterly for 1.5 years	• Low-flow canister approach has 95% accuracy in measuring indoor air concentrations relative to the 24-hr canister method and to the diffusion sampler method. • Low-flow canister approach has < 5% difference in standard deviation relative to the 24-h canister method and to the diffusion sampler method.	**MET:** Forty-four of the 48 14-day capillary canister samples' concentrations were within the 95% confidence intervals of 24-hour canister method.
VOCs time-weighted average concentrations are comparable to those from the *diffusion sampler approach* in terms of bias and precision.			**NOT MET:** Sample concentrations for capillary canister and diffusion samplers while in general linear, the diffusion samplers under-estimated the concentration were not comparable.
VOCs identified using the low-flow canister approach are the same as those identified using the *24-h canister approach.*		List of VOCs identified in the low-flow canister approach matches the list identified using the 24-hour canister approach.	**MET:** Only TCE was consistently found in both the capillary canister and 24-hour canister samples. Toluene and PCE were found sporadically in both.
Qualitative Objectives			
Cost-effective	Inventory of costs associated with implementing the low-flow canister sampling and analysis approach, the 24-h canister sampling and analysis approach, and the diffusion sampler sampling and analysis approach.	Costs associated with low-flow canister sampling and analysis approach are lower than or comparable to costs to implement the 24-h canister sampling and analysis approach and the diffusion sampler sampling and analysis approach.	**MET:** The capillary canister sampling system controllers are lower cost than traditional flow controllers. Chemical analyses are the same for both methods. The extended sampling period provides additional data to estimate long-term average exposure, thus allowing for a more robust mitigation decision, which can translate into significant long-term cost savings.
Required expertise	Record of expertise and training necessary to implement the capillary canister approach.	Expertise required to implement capillary canister approach is less than or comparable to expertise required to implement a traditional canister approach and the pressure control approach.	**MET:** No additional expertise is required to implement the capillary canister approach. The only unique required training is on the capillary controller connection to canisters, which is simpler than traditional diaphragm controller connection.

3.2 PERFORMANCE OBJECTIVE: COMPARE TWO WEEK CANISTER DATA AND DIFFUSION SAMPLING DATA

The second objective is to collect and analyze VOCs with the two-week low-flow canister approach and compare those to the *diffusion sampler approach* in terms of bias and precision.

3.2.1 Data Requirements

Several requirements are necessary for properly demonstrating and evaluating the low-flow canister approach:

- Sub-slab data - (3-4 locations) using the low-flow approach
- Indoor air data collected under ambient conditions (4 buildings, 2 locations per building) using the low-flow and diffusion sampler approaches
- VOCs inventories from sampled buildings
- Ambient air samples
- Above data collected quarterly for two years
- Meteorological data for sampled timeframes and indoor temperatures

3.2.2 Success Criteria

Low-flow canister sampling will be considered successful relative to diffusion sampling if the following criteria are met:

- VOCs time-weighted average concentrations measured using the low-flow method will be within the 95% of those measured values using the 24-h canister method.
- Collocated samples will allow for an analysis of how repeatable (precise) the 14-day method is with respect to the 24-h canister method. The relative standard deviation of the low-flow canister method will be <25% different than the standard deviation of the diffusion sampler approach.

3.3 PERFORMANCE OBJECTIVE: COMPARE VOCS DETECTED USING TWO WEEK AND 24-H CANISTERS

The second objective is to compare the identity of VOCs detected using the two different canister sampling approaches.

3.3.1 Data Requirements

The comparison will be made by generating a list of VOCs detected by GC/MS analysis. The list will be compared against a VOCs inventory collected for the sampled buildings.

3.3.2 Success Criteria

The low-flow, long-term canister sampling method will be considered successful relative to diffusion sampling if the lists of VOCs detected for each method matches.

3.4 PERFORMANCE OBJECTIVE: COST EFFECTIVENESS

The low flow canister approach can significantly reduce analysis costs and number of samples collected over the time of a long-term monitoring project. There has been a drive for an increase in number of sampling rounds because of the concern with temporal variability; traditional sampling strategies do not involve sample collections for multiple consecutive days, and the capillary canister approach can address this concern with increasing sampling time. The project aims to demonstrate the robustness and lower cost of capillary canister sampling than current methods because long-term sample collection captures a complete range of analytes and concentrations in a single sample.

3.4.1 Data Requirements

When evaluating the cost-effectiveness of the low flow canister approach, several considerations are taken into account, such as relative cost to 24-h canister and diffusion canister – equipment, labor, shipping, analyses. In addition to previously mentioned costs, inventory of costs associated with implementing the low-flow canister sampling and analysis approach, the 24-h canister sampling and analysis approach, and the diffusion sampler sampling and analysis approach are also accounted for.

3.4.2 Success Criteria

The one success criteria for demonstrating the effectiveness and costs associated with low-flow canister sampling and analysis approach is a lower than or comparable cost to sampling with both the 24-h canister sampling and the diffusion sampler sampling and analysis approach.

3.5 PERFORMANCE OBJECTIVE: REQUIRED EXPERTISE

A variety of factors have the potential to diminish the quality of air samples. Careful handling of the canisters and sorbent tubes can provide the insurance that unwanted air samples won't contaminant the target samples. Therefor it is integral that; sampling, storing, shipping and analyzing are performed by professionals with the expertise for proper implementation to ensure the quality of the air samples.

Indoor air sampling regardless of technology generally requires skills in:

- Selection of appropriate locations for sampling within the indoor environment
- Documentation (filling out sampling forms and chain of custody forms)
- Awareness of clean sampling protocols that must be followed when handling and collecting air samples. This requires care in the shipping, storage, and use of sampling equipment. Cleanliness of personnel who come in contact with the sampling equipment is also important: no smoking, eating, drinking, perfumes, deodorants, dry cleaned clothing, etc.

Summa canister sampling also generally requires skills in properly connecting compression fittings, including Swagelok, operating valves and reading pressure gauges. The capillary flow controllers are equipped with a miniature quick-connect, thus eliminating the skills required for properly connecting a compression fitting.

Sub-slab sampling, regardless of method, requires personnel to be familiar with procedures for conducting leak tests. These sampling skills are typically acquired by environmental scientists and technicians familiar with sampling other media within a few hours of Standard Operating Procedure (SOP) familiarization and on-the-job training.

3.5.1 Data Requirements

There will be a record of expertise and training necessary to implement the capillary canister approach.

3.5.2 Success Criteria

The criterion for success is met when expertise required to implement capillary canister approach is less than or comparable to expertise required to implement a traditional canister approach and the pressure control approach.

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4.0 SITE DESCRIPTION

Based on an initial screening of VI data included in the U.S. Navy's Environmental Sustainability Development to Integration (NESDI) project 476, "A Quantitative Decision Framework for Assessing Navy VI", Naval Weapons Station Yorktown was selected for the demonstration. The site meets key technical project objectives; and offers a broad range of site sampling conditions, including building size, number of rooms per building, room size, insulation from the external environment, and building materials. Selection of the site for the technology demonstration is detailed in the Site Selection Memorandum. Note: originally the demonstration was to take place at both Yorktown and Naval Station Norfolk; however, the opportunity to sample at Norfolk did not become available for logistical reasons during the project period.

4.1 SITE LOCATION AND HISTORY

Located on the Virginia Peninsula in York and James City Counties, Naval Weapons Station (NWS) Yorktown encompasses 10,624 acres. The northwest of the base is bounded by the Cheatham Annex and Kings Creek Commerce Center. York River and the Colonial National Historic Parkway bound the northeast (**Figure 3**). Interstate 64 and the town of Lackey bound the southwest and southeast, respectively. In the early 1900s, NWS Yorktown was originally created to support minelaying in the North Sea for the First World War. For the next 20 years, the depot focused its attention on mines and all related materials. During World War II, the depot expanded its horizons and included trinitrotoluene (TNT) loading plants and overhaul facilities. In the late 1940s, underwater weapon laboratory and research facilities were developed. The NWS Yorktown primary mission today is to provide support and technical services to the armed forces.

NWS Yorktown, Site 31 is a National Priorities List (NPL). Historical groundwater and soil contamination by VOCs at this site has led to measurable VI in buildings throughout. Historically measured VOCs concentrations are included in the NESDI database.

Site 31, Barracks Road Industrial Area, is located in the eastern portion of NWS Yorktown Site 31 and consists of four large buildings (referred to locally as "Sheds" 3 through 6 which are large concrete block buildings) and several smaller buildings (**Figure 4**). Shed 3 and 6, circled in red are the chosen locations for air sampling. The ground surface is generally flat with paved parking lots, loading docks, and multiple industrial buildings. The area to the west of the industrial area slopes down to a ravine containing an intermittent stream that leads to Roosevelt Pond. East of Site 31, the topography is rolling with some ravines containing feeder streams to Ballard Creek.

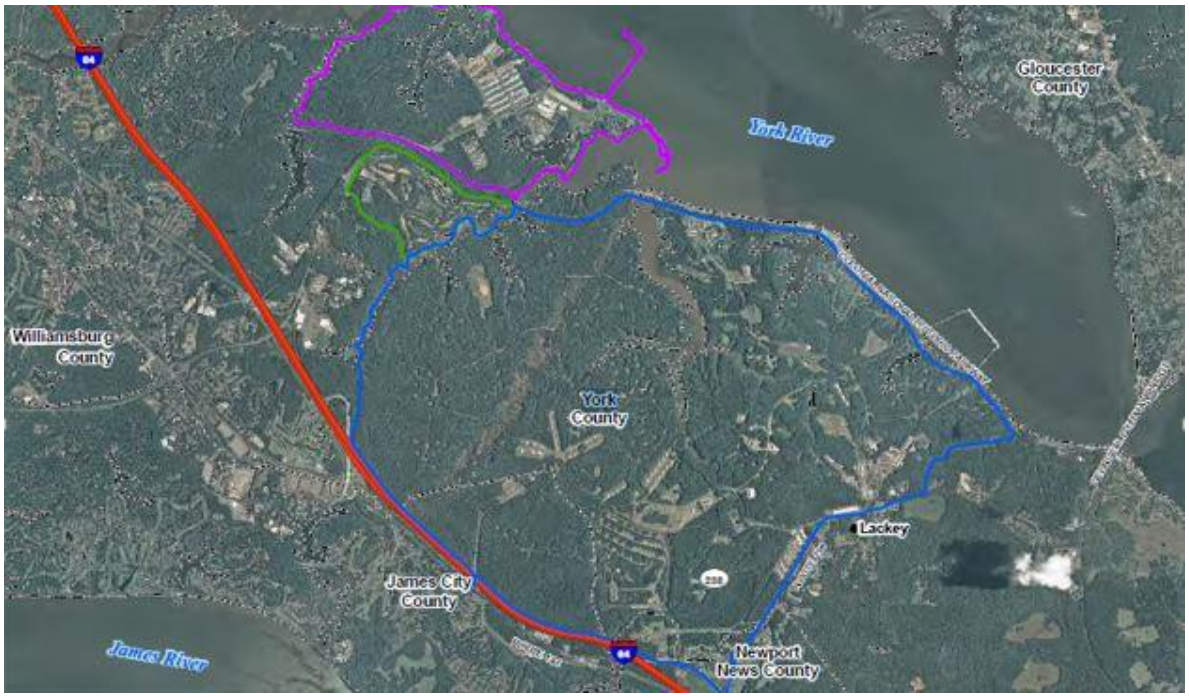

Figure 3. Aerial Photograph Outlining Yorktown Base, Surrounding Counties, Cheatham Annex, and Kings Creek Commerce Park.

Adopted from CH2M HILL Site Management Plan for FY 2014-2015 Naval Weapons Station Yorktown in Yorktown, Virginia.

Figure 4. Close-up Aerial Photograph of Site 31 Building Locations Shed 3, 4, 5, 6 and Building 371

Sampling work will focus on Shed 3 and 6 (circled). Buildings of sampling interest are highlighted in yellow. Reprinted from https://clu-in.org/download/issues/vi/Navy-VI- communication-2014.pdf

4.2 SITE GEOLOGY/HYDROGEOLOGY

Boring data from NWS Yorktown indicate unsaturated sand, silt, and clay, lithologically consistent with the Columbia aquifer, is present from the ground surface to a depth of approximately 25 to 30 feet below ground surface (bgs), where a 15-foot clay layer, lithologically consistent with the Cornwallis Cave confining unit, is encountered. This unit is not continuous across the site, allowing a migration pathway for contaminants into the Cornwallis Cave aquifer, which underlies this clay layer (where present) and represents the shallow aquifer at the site. The Cornwallis Cave aquifer is composed of fine to medium sand and shell fragments. The Yorktown confining unit, which is continuous across the site, lies beneath the Cornwallis Cave aquifer and is composed of greenish gray clay and silt. The Yorktown confining unit also overlies the Yorktown-Eastover aquifer, which consists of fine to coarse sands and shell fragments. Depth to shallow (Cornwallis Cave aquifer) groundwater at the site is between 25 and 40 feet bgs. Site 31 lies on a drainage divide. Surface runoff and groundwater at the site flow to the northeast (to an unnamed tributary to Roosevelt Pond) and the southeast (to Ballard Creek and its tributaries) (CH2M HILL 2012).

4.3 CONTAMINANT DISTRIBUTION

The current nature and extent of contamination in groundwater at NWS Yorktown were evaluated as part of a remedial investigation (RI). Chlorinated VOCs (TCE and its daughter products) and metals are the primary contaminants in groundwater (**Figures 5 and 6**). Based on data collected as part of the RI and discussions with NWS Yorktown personnel and the Navy, Sheds 3 and 6 were selected to be included as part of this study due to the high subslab source strength and documented indoor air concentrations.

Indoor air and sub-slab soil gas samples were collected as part of the initial RI investigation in January 2012. Following the preliminary lab results received in mid-February 2012, the workers in Shed 3 and Shed 6 were evacuated based on the USEPA Region 3 recommendation, as documented in the Site 31 Action Memorandum for the time-critical removal action (Navy, 2012). The maximum concentrations of TCE in indoor air in Shed 3 and Shed 6 were 170 micrograms per cubic meter [$\mu g/m^3$] and 83 $\mu g/m^3$ respectively, which exceeded 26.4 $\mu g/m^3$ (three times the non-cancer risk-based screening level (RSL) of 8.8 $\mu g/m^3$). A contractor was tasked with sealing cracks that were identified as potential pathways. Resampling following this task indicated that indoor air levels for TCE in Sheds 3 and 6 remained above unacceptable levels. These Sheds remain unoccupied. The maximum soil gas concentration for TCE found in Shed 3 were 7,000,000 $\mu g/m^3$ while Shed 6 had a maximum soil gas concentration of 1,500,000 $\mu g/m^3$ (CH2M HILL 2016).

Shed 3 is a very large building (estimated 53,000 sq ft) containing large open areas mainly for equipment use, but also includes work rooms, few offices, a break room, and storage areas. Shed 3 was built in 1919 on an elevated concrete slab. It housed a paint booth, abrasive blast booth, satellite accumulation area for aerosol paint cans, and a parts washer. It was used for wing and fin repair. The building was also historically used as a missile component rework facility and a boiler plant. Shed 6 is a very large building (estimated 50,700 sq ft) containing large open areas mainly for equipment use, but also includes a few offices, a break room, and storage areas. Shed 6 was built in 1941 and was most recently used to support public works and for utilities maintenance.

It was historically used for missile component rework and equipment maintenance. Access to parts of Shed 6 may be limited due to a recent ceiling collapse. VI in Shed 6 was primarily attributed to a block fire wall serving as a preferential pathway.

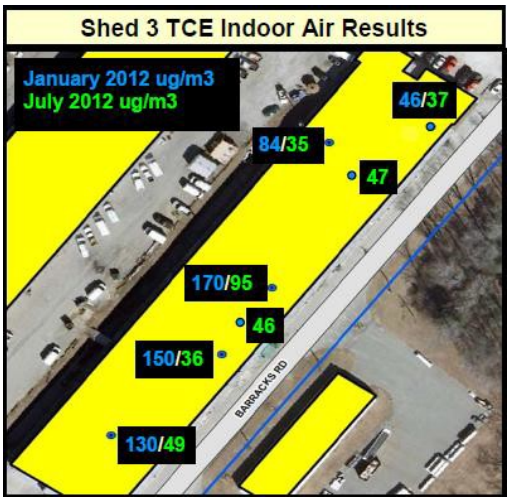

Figure 5. Indoor Air Data from Shed 3.

Indoor air measurements were taken in the winter and summer of 2012 and locations of measurements within Shed 3 are printed. Reprinted from https://clu-in.org/download/issues/vi/Navy-VI-communication-2014.pdf

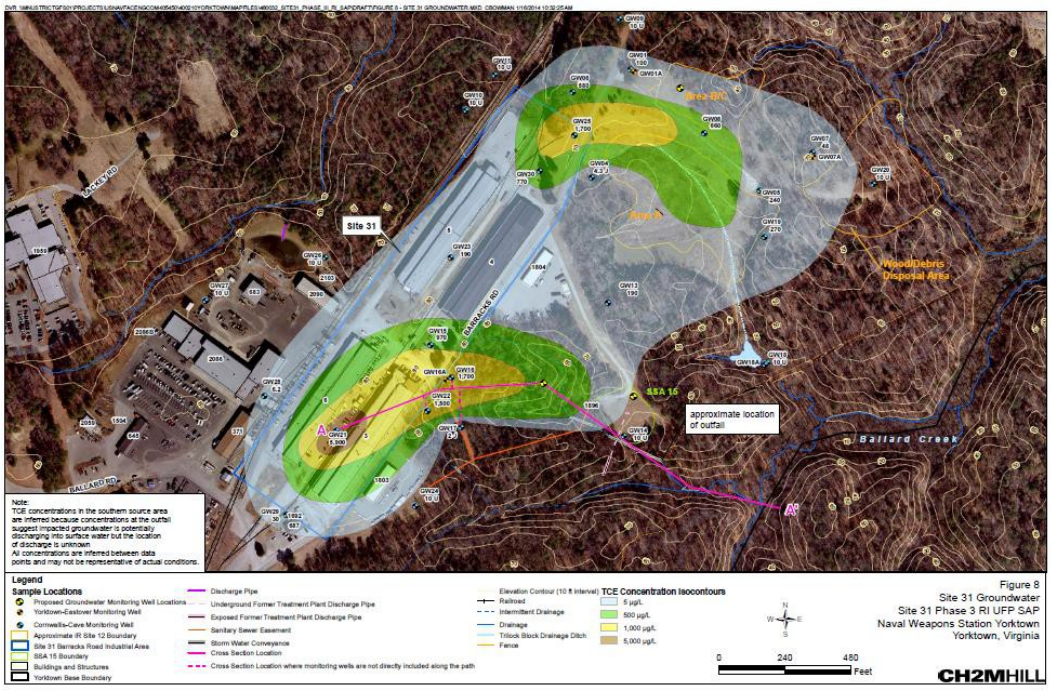

Figure 6. TCE Groundwater Plume as of 2014.

Indoor air concentrations are expected to be highest in the central, west part of Shed 3, and median concentrations in Shed 6, and lowest in Sheds 4 and 5.

5.0 TEST DESIGN

5.1 CONCEPTUAL DESIGN

VOCs baseline indoor air, sub-slab gas, and outdoor ambient air samples were collected at the selected demonstration site. Daily sub-slab samples were collected over 24-h periods using 1-L canisters. Corresponding indoor samples were collected using traditional evacuated Silco coated stainless steel canisters for a period of 24-h, and Carbopack X passive diffusion samplers (7 days). Along with the previously mentioned samples, there were also long-term 14-day capillary controlled samples taken so that a comparison can be made of the results of the 14-day samples to the diffusion tubes, and to the 24-h samples.

Sample collection was repeated quarterly for 18 months to establish long-term temporal variability, demonstrate repeatability, and define the technology's performance under a variety of weather conditions. Analyses were performed using a modified version of TO-15 and TO-17 at Clarkson's Center for Atmospheric Research in Engineering and Science (CARES). CARES is a full service laboratory that supports Clarkson's research initiatives as well as provides external customer analytical services.

5.2 BASELINE CHARACTERIZATION

Baseline information was obtained from NESDI from monitoring performed in 2010 for NWS Yorktown. Additionally, screening (grab) samples were collected from Yorktown in June 2016 using 1-liter canisters to semi-quantitatively identify compounds of concern. Preliminary results from grab samples identified low concentrations (~10 ppb) of VOCs in Shed 3 and very low concentrations (~1-2 ppb) in Shed 6.

Additionally, a series of tests were conducted to assess the air flow rate variability for both the capillary and diaphragm flow controllers. Results indicate that the flow rate for the capillary controllers is approximately $1/10^{th}$ that of the diaphragm controllers. The relative standard deviation of the capillary flow controllers was 5.4%, compared to 2.9% for the diaphragm controller when tested in the laboratory.

5.3 DESIGN & LAYOUT OF TECHNOLOGY COMPONENTS

Four buildings were monitored per sample period (2 weeks). Each test site had one monitoring station. The monitoring station used plastic Rubber Maid^{R} containers with the sampling media on-top (**Figure 7**). This allows for samples to be off the ground, have multiple stages/heights for multiple samples, and canisters can be stored inside Rubber Maid containers between sampling events

Figure 7. Typical Monitoring Station at Each Location with the Additional 1 Quality Control 24-h Canister.

Sample intake will be approximately 3 feet above fixed floor.

5.3.1 Sampling Devices

Silonite®/Silotek® treated Canisters - Used for both 24-h and 14-day samples. Both Silonite/Silcotek are a chemical vapor deposition process that yields a consistent and inert coating layer on the internal stainless steel surface. This coating is typically 400 angstroms thick and prevents analytes from contacting the surface of the canister, thus minimizing loss of collected compounds. The coating is referred to as silco coating hereafter. The internal surface of the canister must be inert to reduce wall loss from adsorption. Using canisters with silco coating increases our ability to analyze the required recovery (100% ±25%). Silonite and Silco is the same technology, just different trademark names used by Entech and Restek, respectively (Cardin & Markle 2014). Silonite/Silco canisters are traditionally manufactured in 400 mL, 1-L, 6-L and 15-L sizes and collect VOCs C2 to C12 (EPA TO-15). These canisters meet the description in method TO-15 "Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces."

Aura™ capillary flow controllers **-** Capillary flow controllers have been researched for Aura™ personal air sampler and are a newly marketed technology that has been designed to meet OSHA and NIOSH criteria required for occupational and environmental sampling (NIOSH 3900). The capillary tube, used to control the flow of air, is a variation on a sharp edge orifice flow controller (**Figure 8**). It essentially controls the velocity of the air as a function of the tube diameter and length. The Aura capillary flow controller is lightweight, easy to use with quick connect that starts and stops the sample flow, no field calibration is required and the systems are quiet because they do not require a sampling pump. The capillary flow controller connected to a canister has the potential to more effectively collect samples when variations in air velocity, temperature and humidity compared to traditional sampling techniques. Typical flow rates for the capillary flow controller are approximately 0.1 and 0.3 mL/min for this application which will enhance the duration of time canisters can be used to collect air samples. Sampling does not require a power source and analysis does not require solvent desorption (Rossner et al 2002).

Figure 8. Capillary Flow Controller Attached to a 6-L Silco Canister.

Silco Canister with CS1200ES -CS1200ES, also known as the diaphragm flow controller, is used for air sample collection up to 24-h. This is a standard canister typically supplied by commercial labs that is coupled with Method TO-15 for sample collection and analysis. Consistent sampling rates ensure accurate and precise analyte recoveries. **Figure 9** displays a CS1200ES passive flow controller attached to a 6 L canister. Diaphragm flow controllers have been used for both environmental and industrial hygiene monitoring for over 15 years (Cardin et al. 2014), and are the standard technology of commercial laboratories.

Figure 9. Silco Coated CS1200ES Flow Controller Attached to a 6-L Silco Canister.

Sorbent tubes - Diffusive monitoring has been used for air monitoring campaigns in industrial hygiene, indoor air studies, VI and large- scale environmental studies. While diffusion samplers are easy to use, they do have several disadvantages. During sampling, diffusive samplers can be influenced by the ambient concentration of the pollutant at the surface of the sampler, the concentration of the pollutant at the surface of the sorbent media, temperature, humidity, and air flow across the diffusion surface. Sources of bias include (1) starvation, which occurs when the sampler absorbs target compounds more quickly they are replenished by the source; (2) poor retention, which can happen if a relatively week sorbent media is selected for chemicals with high volatility; (3) poor recovery of target analytes, which can occur when a stronger sorbent is used for compounds that strongly sorb and when concentrations are underestimated; and (4) blank contamination, which can happen from shipping, handling, storage, and sampler preparation processes, can result in an underestimation of contaminant concentration.

The biases can be avoided through proper sampler type and media selection, proper sampling protocols, and appropriate quality assurance procedures (US EPA 2014a).

Diffusive samplers are governed by Fick's First Law of Diffusion, where the pollutant migrates towards the surface of the sorbent media, at a rate that is dependent on the distance between the sorbent media surface and samplers surface, the cross-sectional area of the sampler, the time the sampler is exposed to the contaminated air, diffusion coefficient of the analyte and the ambient concentration of the pollutant (Equation 1). The uptake rate is the most important variable for calculating the concentration of the target analyte. Additionally, the uptake rate is compound-specific, sorbent media-specific, and also specific to the sampler type.

$$U_{ideal} = 60\ D_1\ \frac{A}{Z} \qquad [1]$$

Where:

U_{ideal} = ideal uptake rate (mL/min)
D_1 = diffusion coefficient (cm^2/s)
A = cross-sectional area (cm^2)
Z = path length (cm)

The industrial standard for axial diffusive samplers consist of a stainless steel sorbent tube (89 mm x ¼" o.d.), prepacked with chosen sorbent. For this project, Carbopack X was used based on the target analytes, known uptake rates, sample time (up to 14 days), and our use of thermal desorption for analysis (USEPA 2015C; Brown and Shirley, 2001). Theoretical and actual uptake rates have been calculated from the manufactures information and academic literature. Actual uptake rates may vary significantly different from the theoretical uptake rate (Markes Int'l 2012; US EPA 2015d; Martin et al. 2010; Brown & Shirley 2001, Walgraeve et al. 2011). While the specifications for the diffusion tubes allow for sampling periods of up to 14 days, two consecutive 7-day samples were also collected for this project due to concern for potential reverse diffusion of some compounds and resulting sample bias.

Temperature and relative humidity instrument, and pressure gauge – Humidity and temperature can impact the uptake rate of passive samplers; barometric pressure can affect the extent of vapor intrusion; and appropriate canister pressure (vacuum) must be maintained prior to sampling to assure proper sample collection. Field gauges were used to measure and verify these conditions. The data from the temperature and relative humidity gauge are continuously logged, and can easily be uploaded onto a computer. The vacuum gauge is calibrated with software to confirm that it is reading pressures to the most precise and accurate degree.

5.3.2 Analytical Instrumentation

MiniRae 2000 - The MiniRae 2000 is a photoionization detector used during sampling. The MiniRae detects VOCs in the concentration range of 0.0 to 99.9 ppmv and can alert the person doing sampling that there are high concentrations of VOCs. The GrayWolf VOC-103 photoionization monitor was used to detect VOCs accurately in the low ppb range.

5.4 FIELD TESTING

Table 2 includes the sampling plan for ambient air, sub-slab, and indoor air samples at NWS Yorktown.

Table 2. Air Sampling Plan

Component	Matrix	Number of samples	Analyte	Location
Diaphragm	Ambient air	14/quarter	BTEX, PCE, TCE, chloroform, TCA, DCE, methylene chloride	Upwind of Sheds 3 and 6
	Sub-slab air	5-14/quarter		Sheds 3 and 6 sub-slab ports
	Indoor air	72/quarter		Shed 3 and 6
Capillary	Ambient air	2/quarter		Upwind of Sheds 3 and 6
	Sub-slab air	14/quarter		Shed 3 and 6 sub-slab ports
	Indoor air	8/quarter		Shed 3 and 6
Diffusion	Ambient air	2/quarter		Upwind of Sheds 3 and 6
	Sub-slab air	Not applicable		Shed 3 and 6 sub-slab ports
	Indoor air	20/quarter		Sheds 3 and 6

5.4.1 Sampling Methods

At each sample location, simultaneously, a 14-day sample, multiple 24-h canister samples, and 2 consecutive 7-day diffusion tube samples were collected at least 3 to 4 feet above the fixed floor (**Figure 10**). Samples were collected, capped, stored and shipped in a manner to prevent any damages, volatilization losses, and tampering. Each sample was labeled to identify the site, location, type of sample, and time of sampling. Samples were shipped either daily or every other day.

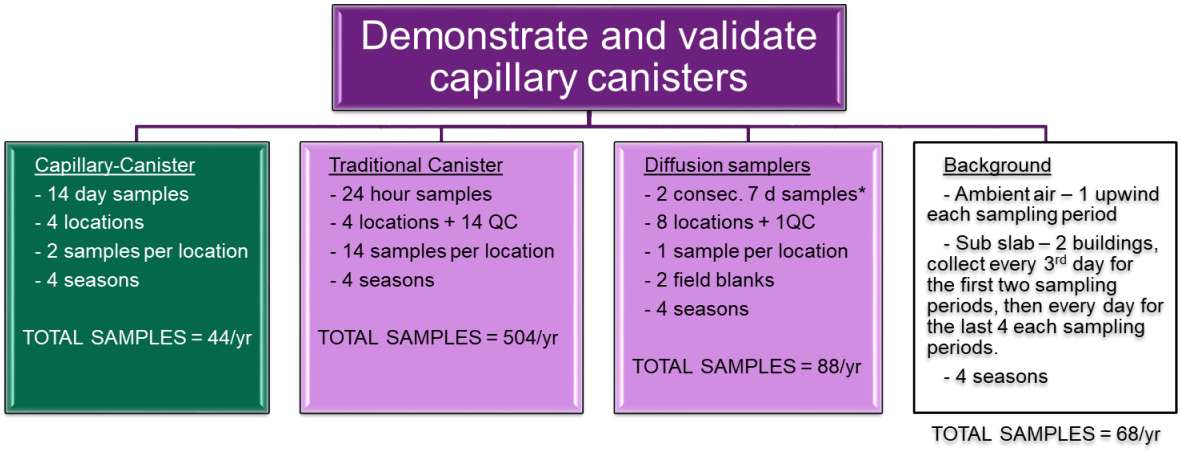

Figure 10. Sampling plan. Sampling methods of all air sampling that will be performed for 1-2 years.

Each location has a specified amount samples to be taken in addition to the number of quality-controlled samples were taken for each sampling event. Approximately, 50 collocated canister samples were collected.

5.4.2 Analytical Methods

Samples were analyzed by Clarkson's CARES full service laboratory, which supports Clarkson's research initiatives and provides external customer analytical services. For canister samples, EPA method TO-15 was used. EPA method TO-17 was used to analyze samples obtained by the diffusion samplers. Samples will be analyzed as quickly upon receipt as possible.

5.4.3 Field Testing Schedule

Table 3 shows the schedule for the setup of sample collection though data analysis. The setup time was a few hours during the first day, sample collection was for 14 days total; sample analysis started two days post field sampling and continued until a few days after sample collection was complete; data analysis was completed thereafter. System start-up was the most time-intensive phase. The field technician arrived at the sampling location with equipment. Pre-screening of VOCs was conducted before entering any contaminated building, wearing proper personal protective equipment (PPE) as per the Site Safety and Health Plan.

Table 3. Schedule for Field Sampling, Sample Analysis and Data Analysis

	2017									2018								
	March			May			Aug			Jan			May			Aug		
Set up																		
Collection																		
Analysis																		
Data analysis																		

During system operation, the canisters with the Aura attached sampled for 14 days. A 6 L canister with diaphragm flow controller collected a sample for 24-h. At each sample site, the 6 L, 24-h sample canister was switched out daily. A 1 L silco with an Aura attached was used for sub-slab sampling, collected every 3rd day initially, then every day for the last 3 sampling events. Ports were purged for at least three port volumes prior to sample collection. Typically, each Markes passive diffusion tube was sampled for 7 days, and then was switched out. Three to four replicate diffusion tubes were placed at each location for each sampling event. The results did not correlate well with the canister samples, hence the protocol was changed in the latter sampling periods August 2017-2018. Thermal desorption tubes were run for 3 days and 7 days to evaluate the performance for shorter time periods. The majority of the instruments used throughout the project did not require external power for performance, hence system shut-down was quite simple and posed limited risk to the field technician's safety. Canisters and diffusion tubes were collected and transported back to the laboratory. Rubber Maid containers and brackets and sample stations were stored in Shed 3 throughout the duration of the study. Temperature and relative humidity probes were retrieved, and data were downloaded after each sample collection period.

5.4.4 Outdoor Ambient Air Samples

One 15 L and one 6 L canisters were used to collect 24-h outdoor concentrations adjacent to the building (up from the prevailing wind direction).

5.4.5 Calibration of Field Instruments

A series of direct reading instruments were used in the field. Each is annually calibrated by a certified laboratory, while monthly calibration is performed in the lab at Clarkson University. The Lascar temperature and relative humidity probes are annually calibrated by Lascar Electronics. GrayWolf VOC 103 and MiniRae 2000 instruments are annually calibrated by the manufacturer, and also prior to each sampling campaign using certified zero gas and isobutelyne. The Ashcroft field vacuum gauge is calibrated by the manufacturer annually and is not calibrated monthly, unless complications arise.

5.4.6 Sample Analysis

Samples were analyzed at Clarkson University's CARES laboratory using standard methods of analysis for canisters (TO-15) and diffusion tubes (TO-17). A Markes CIA ADVANTAGE was used as a pre-concentrator for canister analysis, and a Markes UNITY was used for thermal desorption of the diffusion tubes. Both the UNITY and the CIA are connected to a Thermo GC/MS. The settings on both pre-concentrators and GC/MS were adjusted to optimize the analysis for the chemicals of concern.

5.5 SAMPLING RESULTS

Results displayed in this section are from the six sampling campaigns which occurred over an 18-month period, where each sampling event lasted 14 days. In each sampling campaign canisters with capillary flow controllers collected samples for 14 consecutive days, 24-hour samples were collected with the diaphragm flow controller each day for 14 days. In addition, samples were collected with diffusion tubes for 7 and 14 day intervals. Sub slab samples were collected initially every third day then every day for the last three sampling events. Temperature and relative humidity were monitored continuously at each location within both buildings and compared to outdoor temperatures.

5.5.1 Indoor Air Samples: Canisters

Figures 11-16 show the daily 24-hr TCE measurements using the traditional diaphragm flow controller, along with the 14-day measurements using the capillary flow controller. The bars show daily concentrations. The orange dotted line shows the 14-day sample concentration and the grey line shows the average of the 14 daily samples. Success criteria are met if the 14-day sample falls within the 95% confidence interval of the mean of the 24-hr samples for each location. The confidence interval around the mean of the set of 24 hour samples describes the likelihood that the mean of a separately collected set of fourteen samples (same sample location, same dates and same laboratory) would have a similar mean to the mean calculated for the original set of fourteen samples. **Thus, comparing the result of the capillary controller sample to that confidence interval is a measure of whether the two types of controllers produce equivalent estimates of exposure over a two week period.** It is useful to note in Figures 11 to 16 that many of the fourteen 24-hr samples lie outside the confidence interval around the mean. For example, figure 11 shows for the shed 3 Midway location 8 of the 14 individual 24-hr samples lie outside of the confidence interval around the mean. **Thus, in actual practice, when financial considerations often result in only one or two 24-hour samples being taken during any season; the mean exposure will typically be poorly estimated by the current sampling approach.**

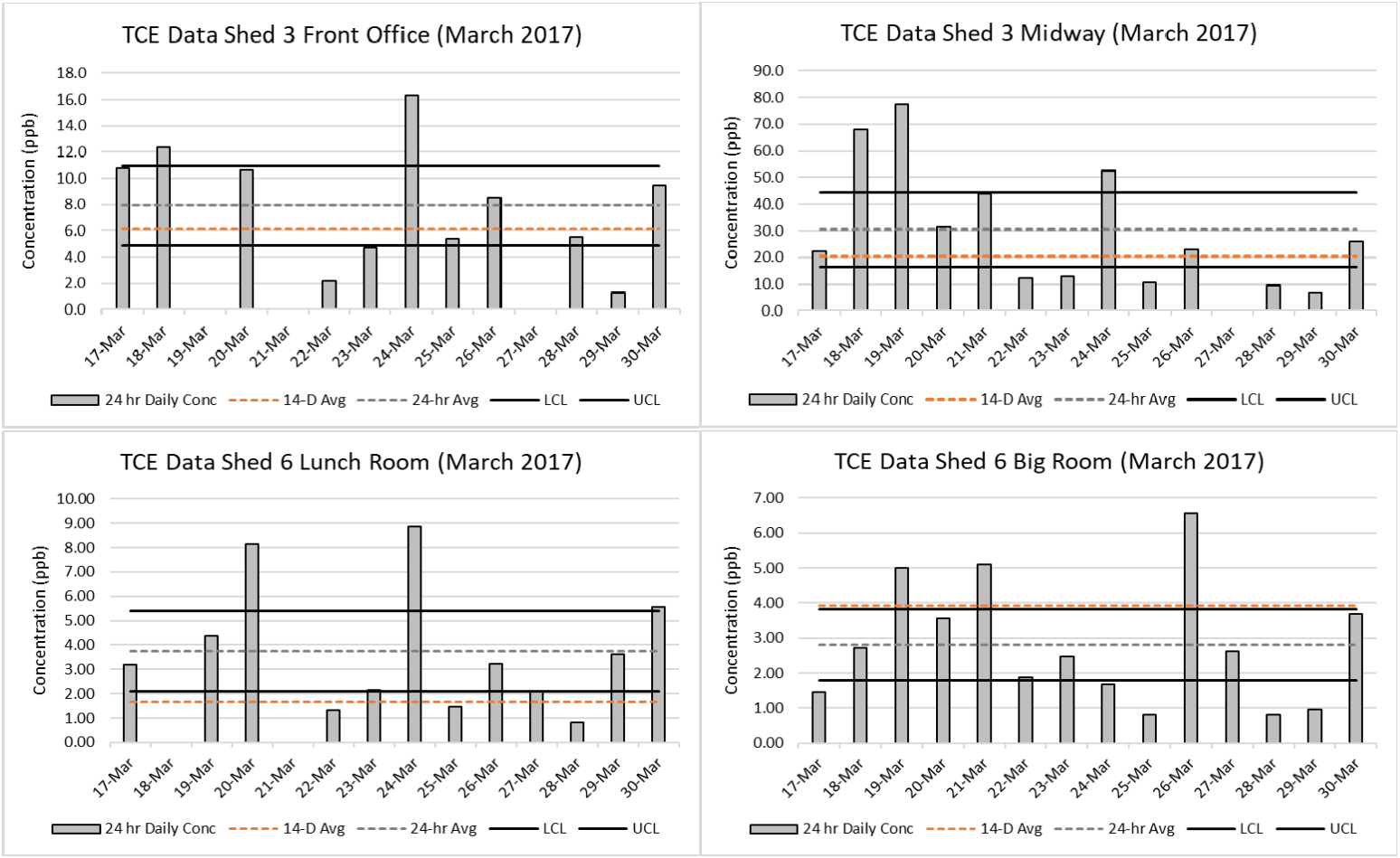

Figure 11. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations During a 2-week Period in March, 2017.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, orange dashed line represents the 14- day sample average. Note: The March sampling event was the first, hence we did experience some analytical difficulties. Several days of data were eliminated due to carry over from the previous samples. The method of analysis was modified and the problem was did not occur on other sampling events.

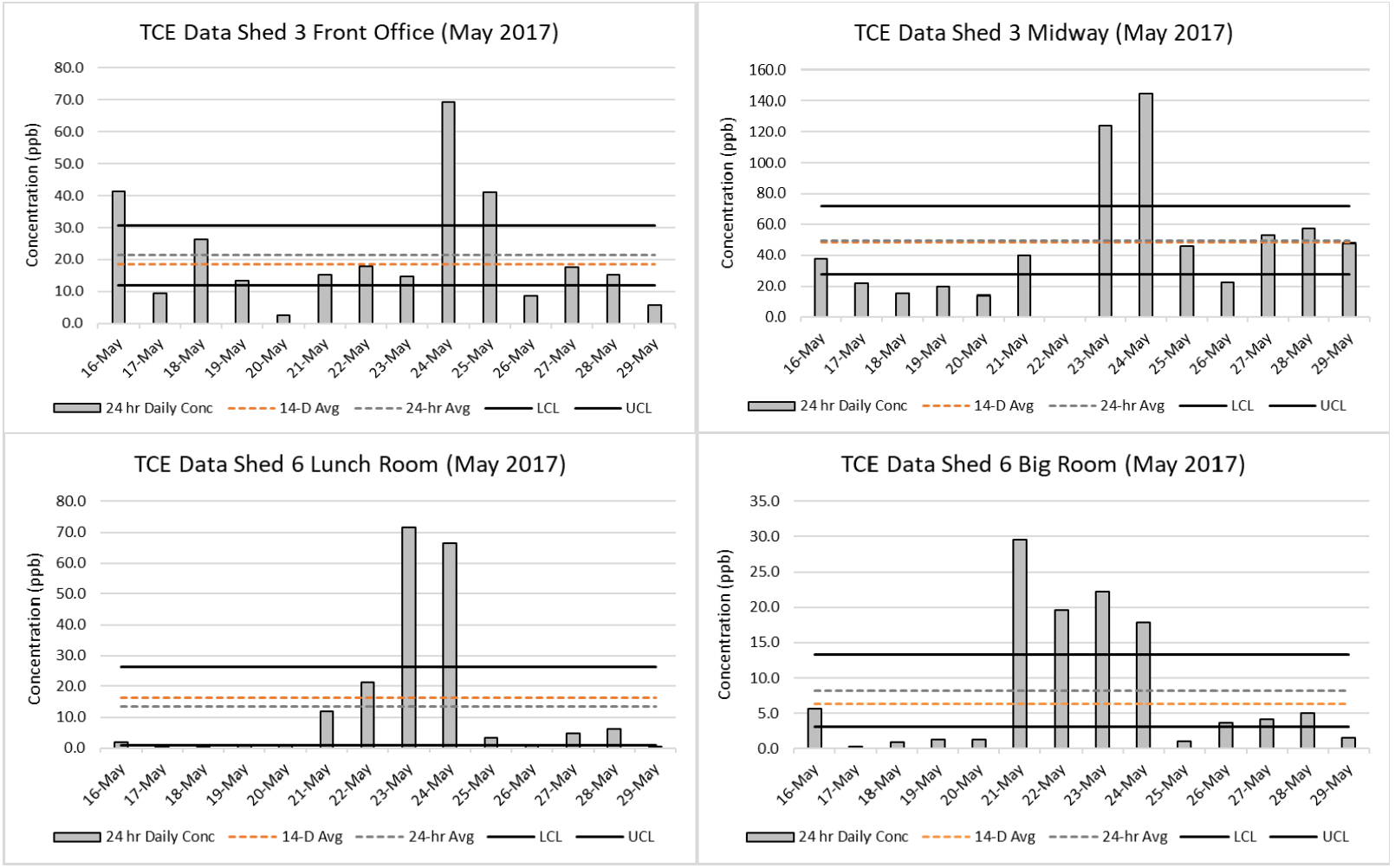

Figure 12. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations during a 2-week Period in May, 2017.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, orange dashed line represents the 14- day sample average

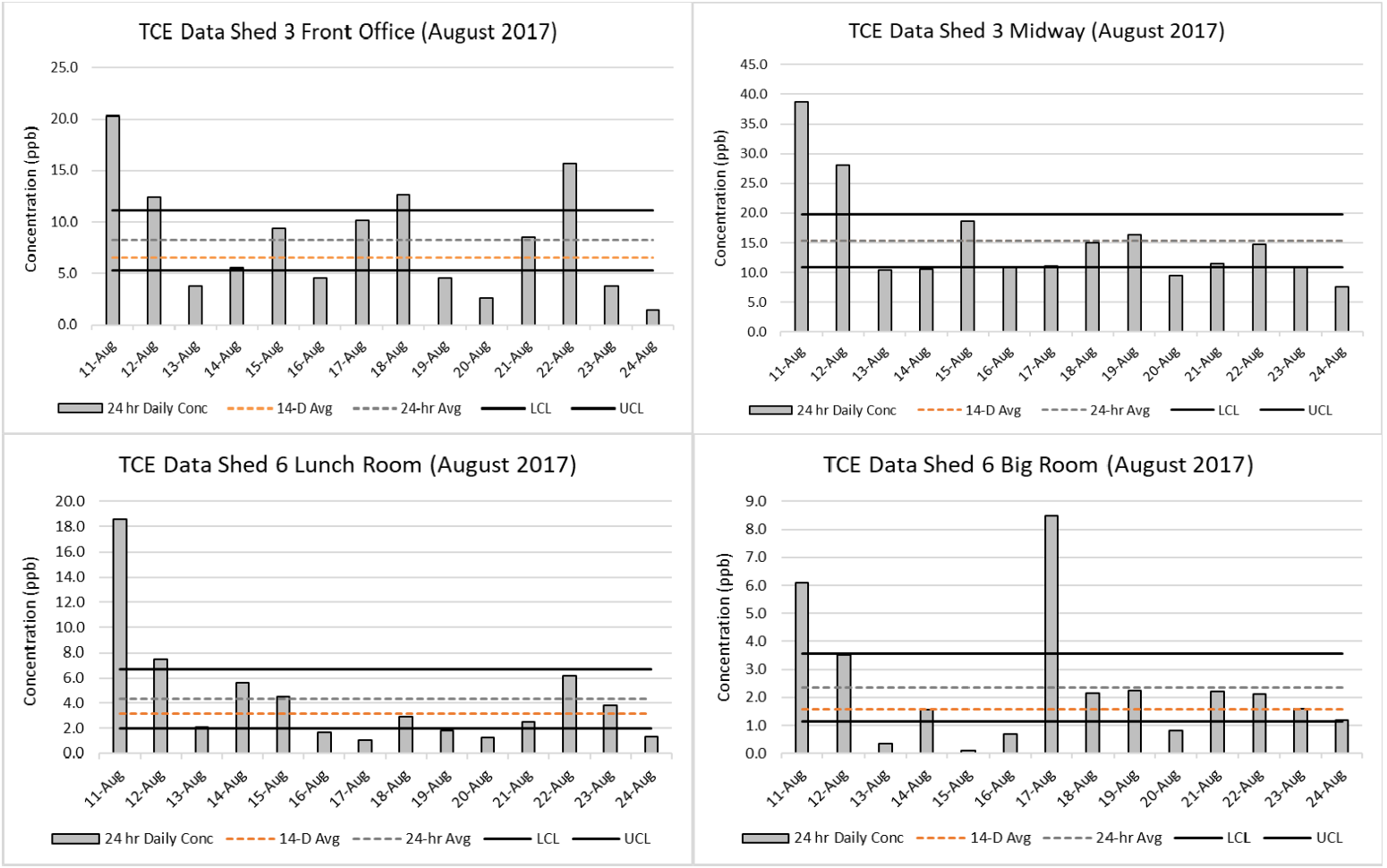

Figure 13. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations During a 2-week Period in August 2017.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, orange dashed line represents the 14- day sample average. Note: In the Midway graph, the orange line is underneath the gray line.

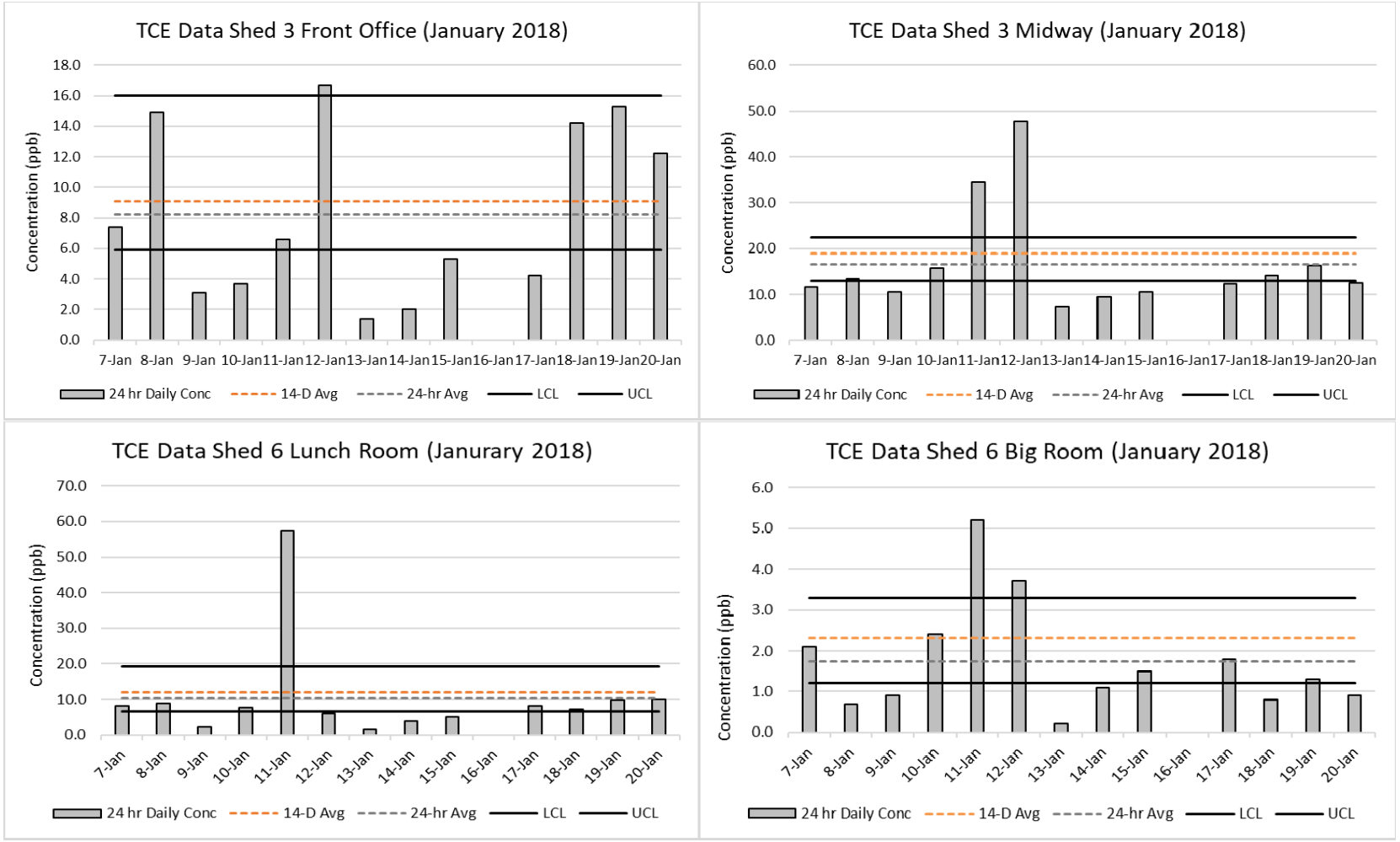

Figure 14. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations During a 2-week Period in January, 2018.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, orange dashed line represents the 14-day sample average.

Figure 15. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations During a 2-week Period in May, 2018.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, green dashed line represents the 14- day sample average.

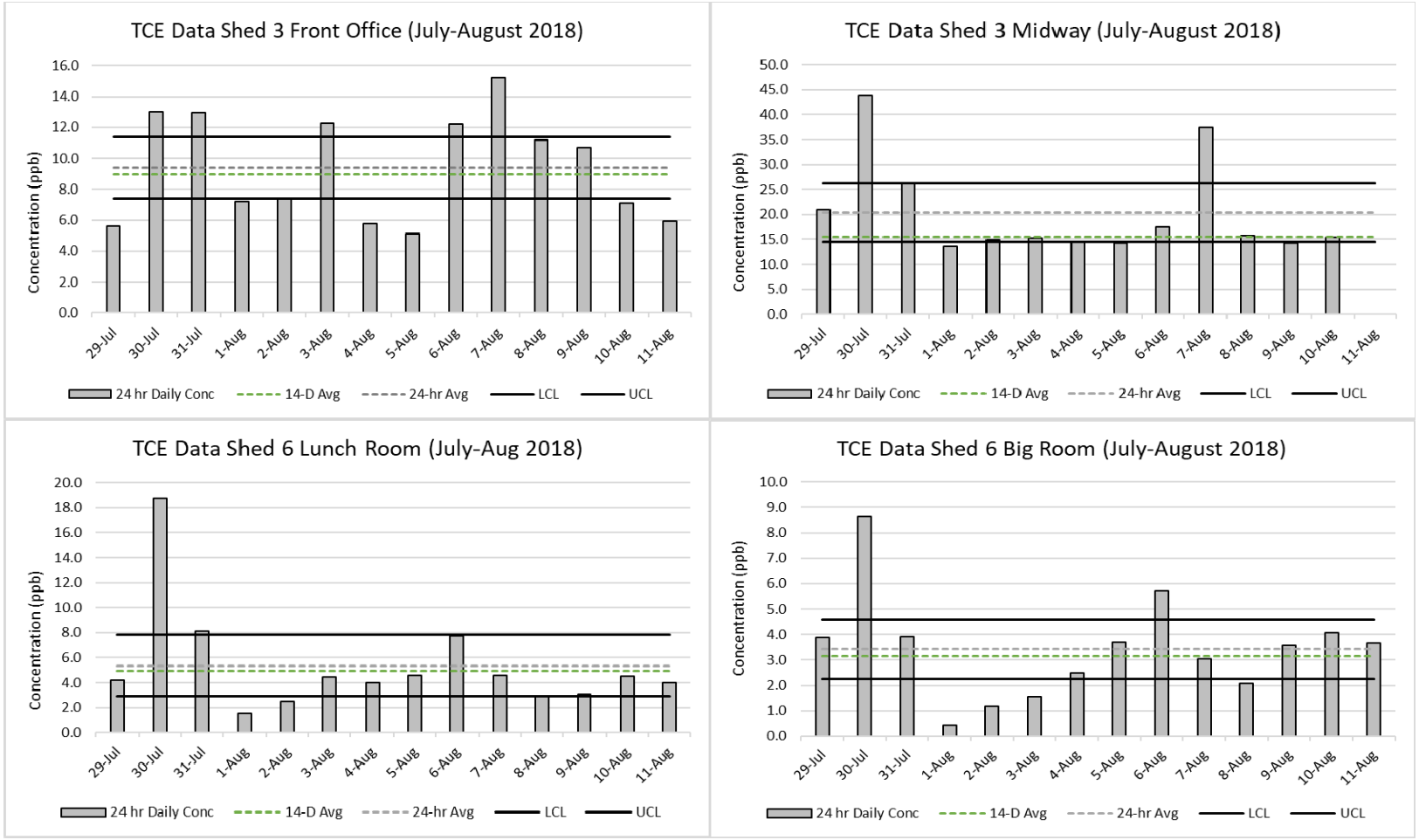

Figure 16. Comparative Analysis of Traditional Diaphragm Daily Samples and Capillary Controller 14-day Samples in Four Locations During a 2-week Period in July, 2018.

Grey bars represent daily concentrations, grey dashed line represents the average of the daily samples, black bars represent the 95% confidence interval for the average of the daily samples, green dashed line represents the 14- day sample average.

Summary statistics of the 24-hr conventional controller samples were calculated for each round and season of the year sampled (tables A- D). The highest concentration at each location was observed in the May 2017 round. At three of the four location the average for the one winter round in January 2018 was below the overall average. This suggests that the indoor air exposure in these buildings is not controlled primarily by stack effect driven soil gas entry rate. Patterns of vapor intrusion seasonal concentrations where the winter does not show the highest concentration have been observed at some other sites (Barnes and McRae, 2017; Johnston and Gibson, 2013).

The air borne concentrations varied by location where Shed 3 Midway>Shed 3 Front Office> Shed 6 Lunch room > Shed 6 Big room, yet this pattern was remained consistent from season to season (See **Tables 4 and 5**).

Table 4. Average Indoor Concentrations of TCE from 24-hr Samples at Each Location for Each Sampling Period

Dates	Shed 3 Midway L1 (ppb)		Shed 3 Front Office L2 (ppb)		Shed 6 Lunch Room L3 (ppb)		Shed 6 Big Room L4 (ppb)	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
March 2017	24.9	18.9	9.1	6.1	4.3	3.7	2.3	1.5
May 2017	49.5	40.7	21.3	18.0	13.7	24.2	8.2	9.7
Aug 2017	15.3	8.5	8.2	5.5	4.3	4.6	2.4	2.3
Jan 2018	16.7	11.5	6.7	5.7	10.5	14.4	1.7	1.4
May 2018	11.6	4.7	4.9	3.2	3.1	2.1	1.8	1.4
August 2018	20.3	9.8	9.4	3.4	5.4	4.3	3.4	2.0
Grand Total	22.8	22.6	10.0	10.0	6.8	12.1	3.3	4.8

Table 5. Average Indoor Air Concentrations at Each Location in Each Season

Dates	Shed 3 Midway L1 (ppb)		Shed 3 Front Office L 2 (ppb)		Shed 6 Lunch Room L 3 (ppb)		Shed 6 Big Room, L 4 (ppb)	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Spring	28.2	29.7	11.8	13.0	7.0	14.7	4.1	6.3
Summer	17.7	9.3	8.8	4.5	4.8	4.4	2.9	2.2
Winter	16.7	11.5	6.7	5.7	10.5	14.4	1.7	1.4
Grand Total	22.8	22.6	10.0	10.0	6.8	12.1	3.3	4.8

5.5.2 Indoor Air Samples: Thermal Desorption Tubes

The Markes Carbopack X diffusion tubes were selected for this project and expected to perform reasonable well with respect to the canisters. The manufacture (Markes) recommended the specific tube for TCE and this recommendation was supported by the literature. However, over the course of the sampling campaign the performance of the thermal desorption tubes was highly variable.

Collocated samples collected for the same amount of time experienced drastic differences in concentrations (3-5 times). The use of the Carbopack X tubes over 7 days had a regression of 0.43 when compared to results from the daily samples taken by the traditional diaphragm flow controllers, and under-sampled relative to the diaphragm flow controllers 70% of the time (**Figure 17a**). Results from the 14-day tubes had higher linearity, but under-sampled 90% of the time (**Figure 17b**). It is possible that the tubes were overloaded and experiencing reverse diffusion. In addition to under sampling, the TD tubes displayed extensive random error associated which one would not expect from co-located samples.

To further investigate the effectiveness of the diffusion tubes, a small laboratory study was conducted to evaluate performance under controlled conditions. Clean, low-humidity air (<10%) was used as a carrier gas throughout the system. Clean air was passed through 3 air filtration devices (Donaldson Ultrafilter, P0035, S0035, A0035). A mass flow meter (Aalborg) was used to indicate the total air flow (LPM) through the system. After air passed through the mass flow meter, the air-line was split and a series of valves were used to direct air into two directions. This was done to help minimize and/or maximize the chamber's humidity levels. Humidity was created by passing air through a volumetric flask filled with deionized water. An aeration device was used at the end of the tigon tubing that was placed directly in the water to help generate bubbles. The humidified air was then introduced back into the dry air path resulting in ~ 50% relative humidity. The air was then directed into the chamber and exhausted out through a lab hood. The system was designed in a manner that allowed for the introduction of a solvent or multiple solvents using a syringe pump. A low flowrate syringe pump (Harvard Apparatus, Holliston, MA) was used to deliver the neat solvents at a constant rate into the air flow. A 25-microliter syringe was used to inject the solvent into the air stream at rates of micro liters per hour. The chamber allow for canister air samples to be collected simultaneously with the TD tubes.

TCE concentrations of 100 ppb were maintained in the chamber over test periods ranging from 16 hours to 3 days. Grab samples were collected using 400 mL canisters and analyzed to confirm TCE concentrations within the dynamic dilution system remained constant. As a quality control measure, prior to sampling with each TD tubes, they were analyzed as blanks to validate no residual analytes remained on the sorbent. The TD tubes used for the field sampler were prepared in the same manner. Following the completion of this QC test, they were shipped to the field site for sampling. Upon completion of the sampling, the tubes were analyzed using Markes preconcentrator and the Thermo GC/MS for the analytes of concern. Results are shown in **Figure 18**. Each bar represents 1 sample, excluding the average concentrations. In the lab, TCE concentrations collected onto the tubes were much more consistent as compared to the field samples collected at the four locations (L1-L4). This is primarily because environmental conditions during the sampling period remained constant and controlled. The uptake rates for TD tubes likely remained similar to the uptake rates provided by the manufacturer at 2.68 mL/min, and allowed for an accurate quantitative calculation of sample concentration.

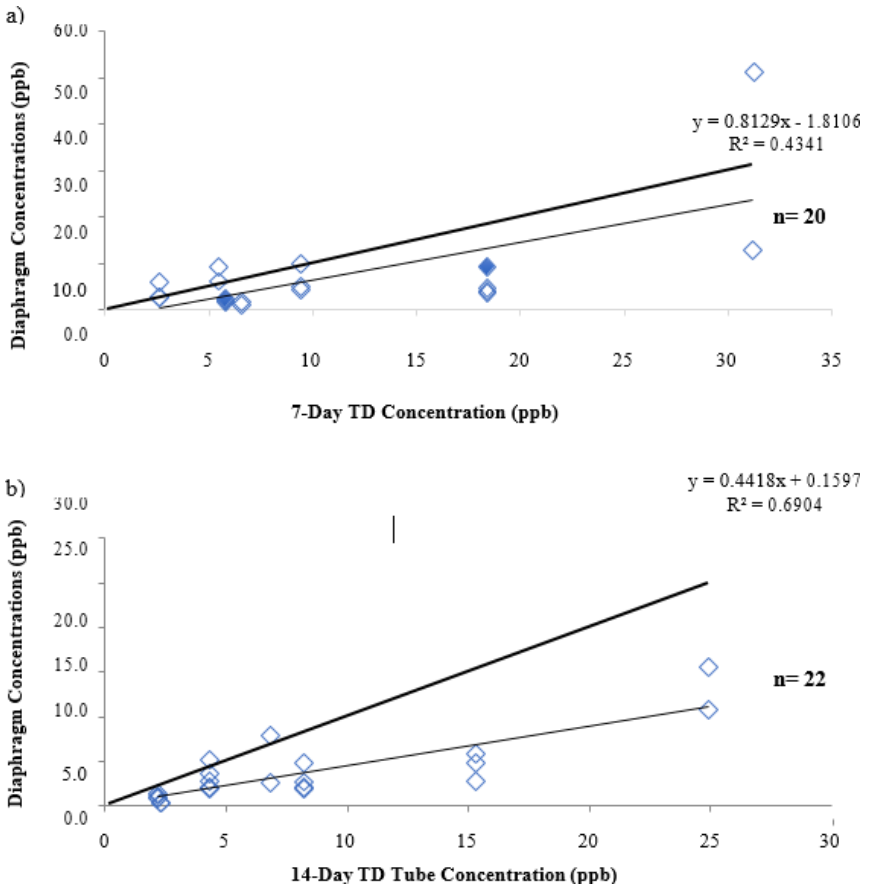

Figure 17. Relationship of Concentrations Collected by Diaphragm (Traditional, Average Daily) and (a.) 7-day Diffusion Samples and (b) 14-day Samples Diffusion Samples.

The dark solid line represents the 1:1 relationship.

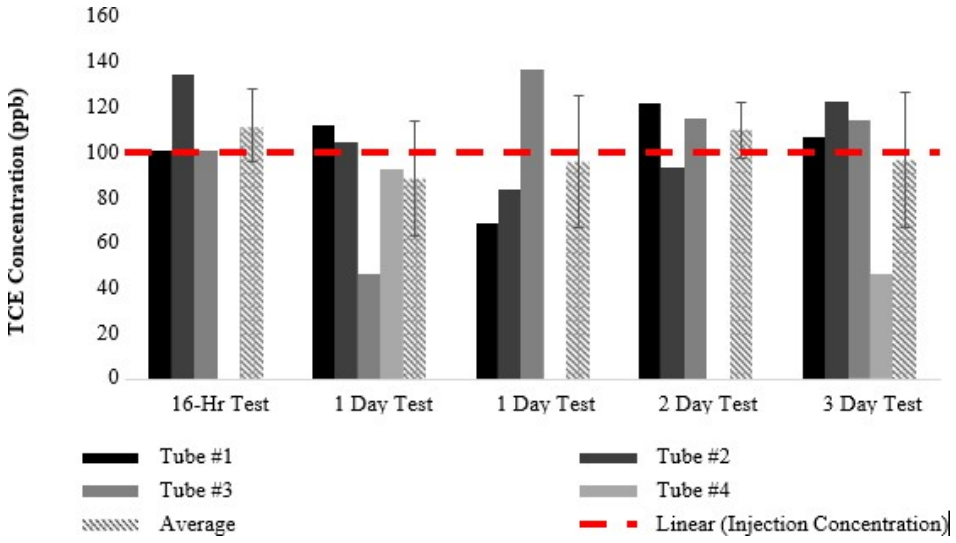

Figure 18. TCE Concentrations Collected onto Thermal Desorption Tubes During Laboratory Tests.

5.5.3 Ambient Air Samples: Outdoor Samples

Concentrations of TCE in outdoor canisters samples (both capillary and diaphragm) were either below the detection limit or below 1 ppb for all sampling events, indicating that no correction was necessary to adjust for outdoor sources.

5.5.4 Indoor and Outdoor Temperature and Humidity Levels

Temperature and humidity were monitored daily at all indoor locations (**Table 6**). Outdoor environmental conditions were obtained from weather underground. **Figure 19** shows indoor and outdoor temperatures during each sampling period.

Table 6. Environmental Conditions Monitored Through all Six Sampling Events

	Mar-17	May-17	Aug-17	Jan-18	May-18	Aug-18
Avg Temp (C).	9.53 ± 5.78	21.2 ± 2.9	25.4 ± 2.3	2.6 ± 7.5	20.4 ± 1.3	26.6 ± 1.9
Temp. Range (C)	-1.11-18.9	13.3-26.1	21.67-30.1	-11.1-19.4	18.3-22.2	24.4-29.4
Avg. Wind (mph)	8.6 ± 1.8	8.2 ± 3.1	5.7 ± 2.2	7.4 ± 2.3	6.6 ± 1.9	4.7 ± 1.6
Avg Precip. per day (in.)	0.1 ± 0.3	0.2 ± 0.2	0.2 ± 0.4	0.1 ± 0.3	0.3 ± 0.8	0.18 ± 0.4
Humidity (%)	69.0 ± 14.6	78.3 ± 11.7	80.5 ± 4.5	68.3 ± 15.0	64.2 ± 16.1	74.9 ± 9.5

5.5.5 Sub-Slab Samples

Sub-slab concentrations were used to calculate attenuation factors for each building, defined as the concentration at the location divided by the sub-slab concentration at the corresponding location. Each air sampling location was correlated with a nearby subslab concentration. **Figure 20** shows the relationship between the indoor and sub-slab concentrations.

5.5.6 Inter-laboratory Comparison of Results

Method TO-15 sets a standard of 25% for single laboratory replicate precision, and 30% for audit accuracy. Typical ranges for inter-laboratory comparisons for method TO-15 in other studies are larger; as large as 2 to 5x (Pearson, 2005, Lutes 2010). Canisters from four of the sample events, May 2017, August 2017, and January 2018, and May 2018 were sent to Centek Laboratory. Their analytical results are shown in **Table 7**. For each inter-lab comparison, 4 to 6 canisters were chosen at random to be analyzed by Centek following EPA TO-15 protocols. The canisters were already analyzed by Clarkson's CARES laboratory using EPA TO - 15. In May 2017, the overall percent difference was low at <8%. In August, the percent difference between the 2 labs was 60% with Centek reporting concentrations between 2 to 3 times higher than Clarkson's CARES laboratory. Upon a later inspection, it was found that a valve on the calibration gas cylinder in the Clarkson lab was loose and likely lead to unwanted atmospheric air entering into the canister, thus diluting the calibration standards. The introduction of atmospheric air explains why Centek had higher reporting values. While this is of concern, it's important to note that all canisters analyzed at the CARES lab were referenced using one calibration standard and it does not affect the overall comparative results between the capillary flow controller and diaphragm flow controller samples.

TD tubes were analyzed separately and a different calibration curve was generated for tubes. The average difference between CARES and Centek for the 4 sampling campaigns was 48%, however if August is not included, this average is approximately 7 %, yet the standard deviation of approximately 27%. (See **Table 7**). Inter laboratory testing often provides a broad range of difference, the analysis by a professional lab seemed to provide a reasonable comparison.

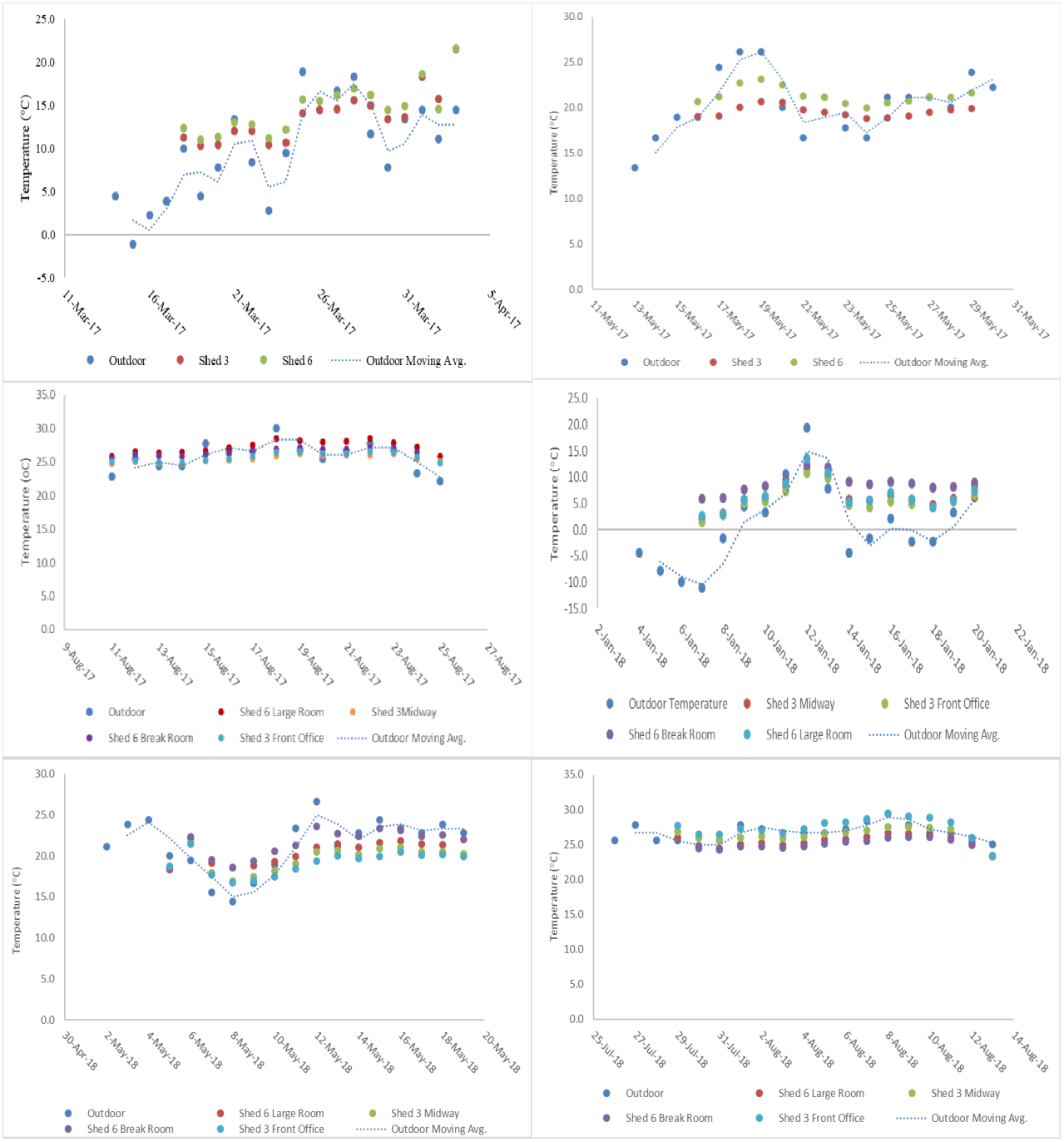

Figure 19. Indoor and Outdoor Temperatures Recorded During each Sampling Event.

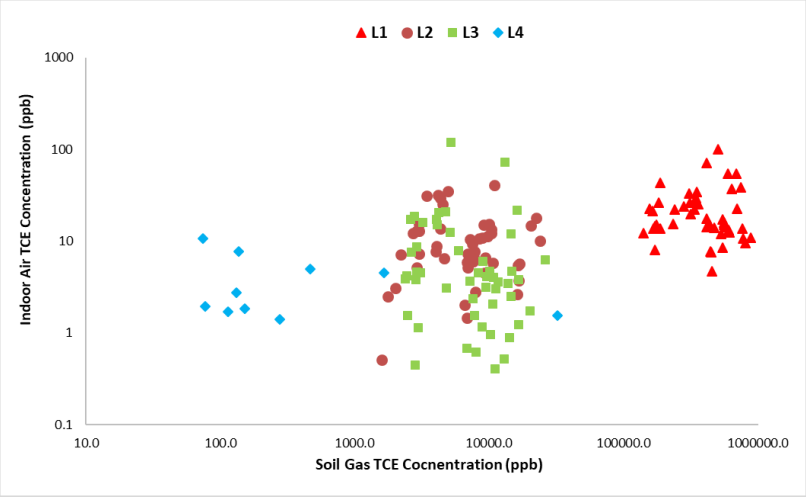

Figure 20. Comparison of Indoor and Sub-slab Sample Concentrations for All Six Sampling Events and All Four Sample Locations (L1-L4).

Table 7. Comparison of Inter-laboratory Results from Clarkson's CARES and Centek Labs

Date	Canister ID	Centek TCE Conc (ppb)	CARES TCE Conc. (ppb)	% Difference
May 2017	11237	46	47.8	-3.8
	4075	43	51	-15.7
	11057	5.5	5.9	-6.8
	4078	5.6	5.7	-1.8
Aug 2017	11240	4.6	1.3	253.8
	4089	28	10.8	159.3
	1002	26	13.3	95.5
	3671	33	16.3	102.5
	1001	21	6.5	223.1
Jan 2018	3671	1.2	0.9	33.3
	4089	9.6	9.8	-2.0
	4050	10	10.7	-6.5
	11240	14	16.9	-17.2
May 2018	1702	7.4	6.54	13.1
	3665	8.5	7.23	17.6
	3648	1.8	1.64	9.8
	7423	2.7	1.44	87.5
	3672	11	13.4	-17.9
	11237	6	5.7	5.3

	All data	Excluding Aug. 2017
Mean of % Difference	48.937	6.78
Median	9.8	-1.9
Standard Dev.	83.0	27.32
Minimum	-17.9	-17.9
Maximum	253.8	87.5
Conf. Level (95%)	40.0	15.8

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6.0 PERFORMANCE ASSESSMENT

6.1 PERFORMANCE OBJECTIVE: COMPARE 2-WEEK AND 24-H CANISTER SAMPLE CONCENTRATIONS

Figure 21 includes a regression analysis for TCE concentrations collected using the diaphragm and capillary flow controllers, which indicates strong correlation between the two, with a slope of 0.95 (with 1.0 indicating a perfect correlation) and a R^2 value of 0.95.

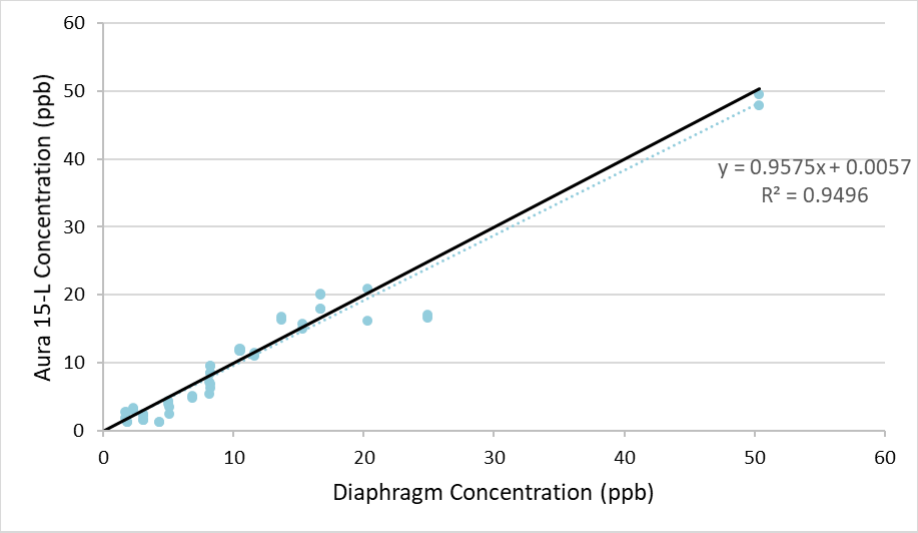

Figure 21. Comparison of TCE Concentrations Collected Using the Diaphragm Controller (x-axis) and the Capillary Controller (y-axis). (Solid Black line is a 1:1 ratio)

To assess the agreement between the two canister methods of measurement beyond the correlation and regression studies, a Bland Altman test was performed. This statistical test was designed to access the agreement between two quantitative methods by examining the differences between mean differences and constructing limits of agreement (LOA). The statistic does not define if the bias is acceptable, only what it is. The Bland Altman test uses the mean and standard deviation of the difference between the two sampling methods. The data set must be normally distributed or if log normal, then the log of differences is used. **Figure 22** is a scatter plot of the log transformed data, the difference of the two paired canister methods is plotted against the mean of the two canister methods. The commonly way to plot the Bland Altman method is to calculate the 95th%, were the data lies within two standard deviations of the mean difference. Only 2 out of 32 (6%) comparative tests were not within the lower and upper LOAs between -0.3 and 0.4 and the average bias was 0.08 ppb. Two comparisons were observed outside the LOA and were likely due to the sequence of samples run on the Markes International GC/MS in March of 2017. Highly concentrated sub slab samples (ranging in the ppm) were analyzed on three separate occasions prior to the analysis of 24 h samples from L2. This analytical sequence may have resulted in carryover of residual TCE to remain on the trap. For this data set, the target value was the idealize difference between the methods and assumed to be 0.0. The greatest difference was observed at the lower concentrations with relatively similar variation for the values above 0.5 for the mean log concentration.

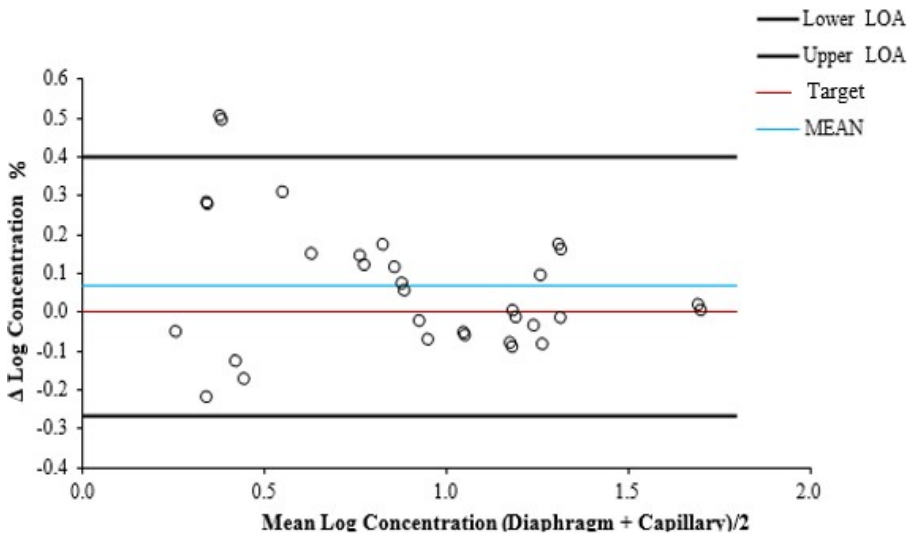

Figure 22. Bland Altman Mean Difference Chart Representing a Comparison of Diaphragm Controller and Capillary Controller Measured TCE Concentration (n=32).

The bias is the difference (~0.8%) between the mean value and target value (the red line).

The objective of the multivariate analysis displayed in **Figures 23 and 24**, was to evaluate if the interaction between parameters impact the capillary flow controller method more than the diaphragm flow controller method. The output variable was concentration. This assessment was not focused on whether the parameters impacted VI, but rather impact on the two canister collection systems. Using Jmp Statistics 9 JMP (13.2) Software (SAS Institute Inc., Cary, NC) key factors evaluated included: sample date or season indoor temperature, indoor relative humidity, interaction of indoor temp and indoor relative humidity, building (location), indoor relative humidity, and location within the building. This is a difficult analysis because of the limited **number of samples in the data set** at each capillary sampling site. **Figure 23** shows that log-transformed concentration data are normal and are thus used as the outcome variable for the assessment of variable interactions. The results of the multivariate analysis (**Figure 24**) suggests association between temperature, relative humidity (RH), and sample date on TCE concentration.

A ratio for the two types of sampling (14 day and 24 hour) was done to allow for statistical analysis. If the average is used, then one has an n=1 or 2 for the 14-day samples and an n=14 for the 24 hour samples, hence a statistical analysis could not be performed on the data set. To resolve the problem of the number of samples, ratios of 24-hour data (diaphragm flow controllers) by capillary flow controller data 14-day data was performed.

A strong correlation was observed between the ratio of the 24 hour (diaphragm flow controller) and 6L and 15L capillary flow controllers) respectively (r = 0.9655). In addition, a reasonable and expected correlation was observed between temperatures and humidity (r=0.6330).

While the relationship between the average of the 24-hour canisters and 14 day canisters is strong as shown in **Figures 11-16** (bars charts), and the regression analysis displayed a strong correlation, further analysis was carried out to examine if an interaction effects between the parameters was impacting the outcome. The parameters studied include the following:

- Temperature – continuous variable
- Product of temperature and relative humidity (RH) – continuous variable
- Relative humidity – categorically variable by low (<58%), mid (58≤x≤78%) and high levels (>78%)
- Time of year – categorically variable by Spring 2017, Spring 2018, Summer 2018, Winter 2017 and Winter 2018
- Locations within buildings
- Buildings

The overall analysis of variance (ANOVA) for the transformed data set (ln 24 hr by 14 day value) accounted for 16% of the variability in the data set (overall adjusted R^2=0.16). While one may hope to account for 30 or 40 percent of the variability in field testing, the 16 percent provide 3 parameters that were the most influential factors (**Table 8)** for the lognormal-transformed data for ratios of 24 hours data by 6 L and 24 hours data by 15 L. Indoor air temperature and relative humidity parameters are related; therefore, the two factors were used together to access both as an interaction factor. The interaction between relative humidity (RH) and temperature parameters is shown in **Table 8** along with the other parameters.

The ANOVA analysis suggest that the time of year, indoor temperature and combined indoor relative humidity & Indoor temperature have the greatest influence on the variability of the two methods. While it is useful to understand the drivers of the variance between the two methods, the conclusions for the data collected in this research did meet the research objectives established in the beginning of the project. The capillary flow controller provides VI data within 95% of the diaphragm flow controllers as defined in Table I – Performance Objectives.

In the end, this analysis did not account for as much variability as one hopes, but the linear regression and agreement between the 14-day average and 24 hour averages suggest the amount of variability between the methods is small. The need to ratio the 24-hour method and capillary method may have tended to normalize the data to seasonal variability and emphasizes the day to day variability.

Table 8. Assessment of the Most Influential Factors

Parameters	Ln (24hoursby 14 6L)	Ln (24hoursby 14 d15L)	Most Influential Factors
Time of the year	p<0.001	p<0.001	1
Indoor Temp (°C)	p=0.004	p<0.001	2
Indoor Temp (°C)*Indoor RH (%)	p=0.053	p=0.010	3
RH category	p=0.090	p=0.274	
Indoor RH (%)	p=0.298	p=0.383	
Building	p=0.766	p=0.392	
Location within building	p=0.829	p=0.948	

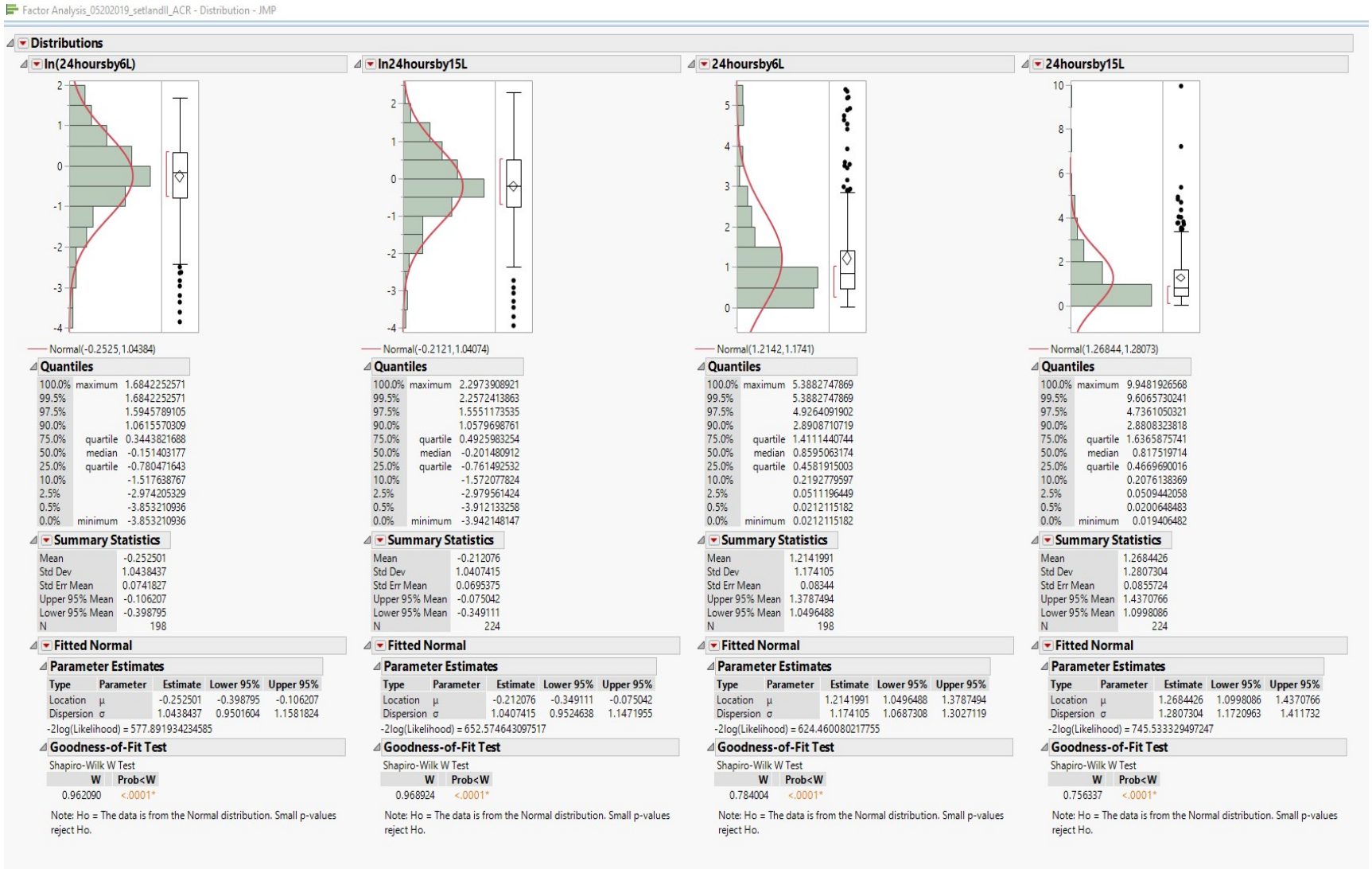

Figure 23. Assessment of Distribution for Normal and Log Transformed Data.

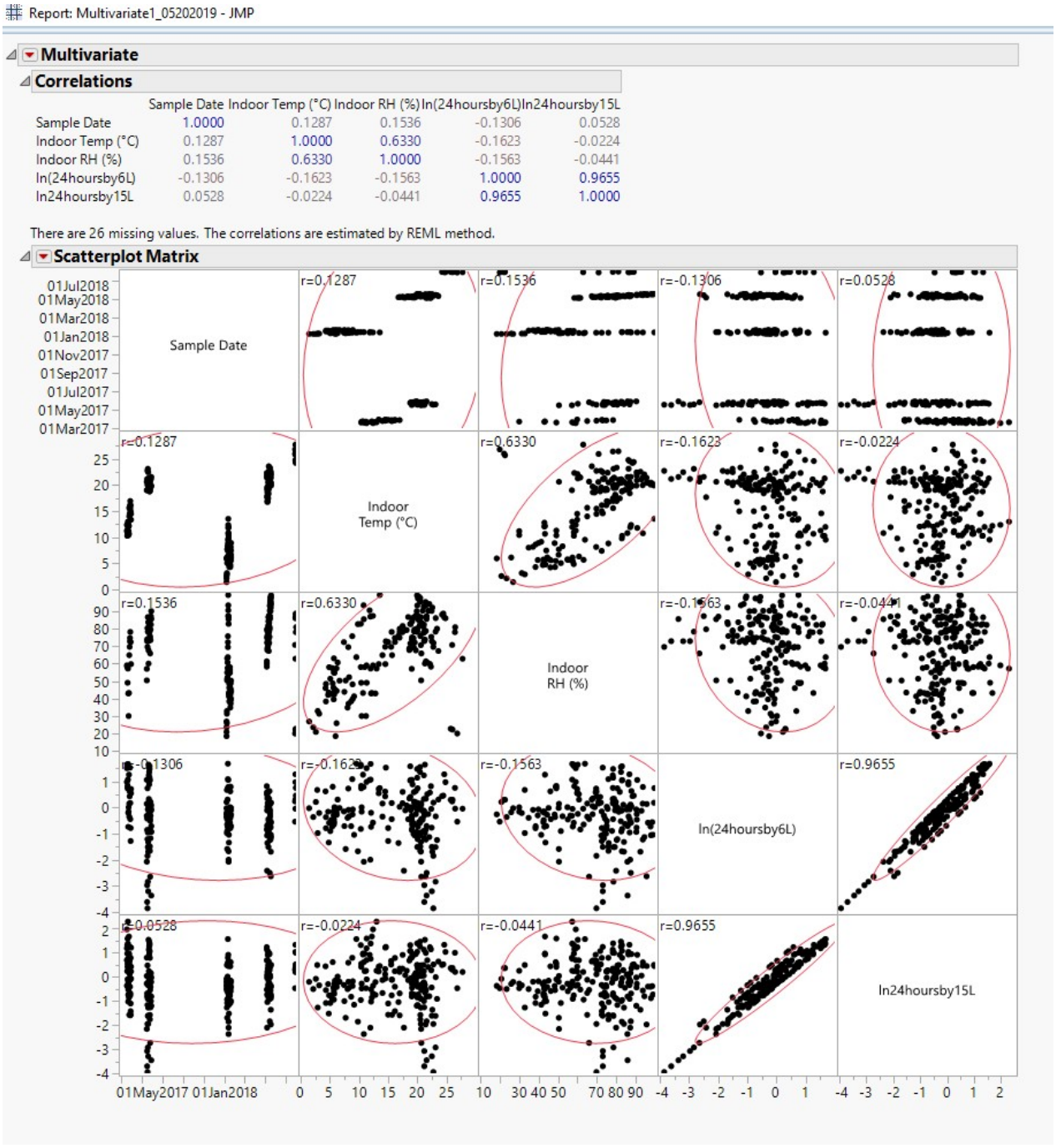

Figure 24. The Scatter Plot Matrix Shows the Correlation Coefficients Between the Variables for the Parameters of the Study.

A strong positive correlation (r) is show for the 24-hour canister sample vs 14-day canisters (r=0.965). A weaker positive correlation is observed between Temperature and %RH (r=0.633).

6.2 PERFORMANCE OBJECTIVE: COMPARE 2-WEEK CANISTER DATA AND DIFFUSION SAMPLING DATA

Figure 17 demonstrates that this performance objective was not met. Concentrations measured by canisters, both with the traditional diaphragm and capillary controllers, are not comparable to those measured by the diffusion samplers used in this project. While disappointing, the under performance of the diffusion samplers may have been a result of over loading, humidity and/or temperature. However, while we did not meet the performance objectives for this study, the passive samplers have been reliable in a number of other studies. The selection of the correct diffusion tube, both the sorbent and the tube types, is critical. In research conducted by Guo et al. during side by side sampling for five different chlorinated compounds, the percent difference between two diffusion tubes was ~ 2x for TCE. The 2 fold difference was similar to some of our sampling result, yet well above the performance standards set for our project. In hind sight, this was an unrealistic target value. Diffusion tubes can be effectively used if one recognizes the variability between tubes and potential for under estimation of concentration depending upon sorbent and chemical of concern, chemical concentration, sample duration, and the influence of environmental factors that may significantly change the uptake rate.

6.3 PERFORMANCE OBJECTIVE: COMPARE VOCS DETECTED USING 2-WEEK AND 24-H CANISTERS

As previously discussed, (**Section 3.0**), only TCE was consistently detected in samples collected by both the traditional diaphragm controller and the low-flow capillary controller. When other contaminants (e.g., toluene, PCE) were occasionally detected and they were found in both sampling systems. The data demonstrates that both canisters systems can detect multiple compounds at a broad range of concentrations, thus meeting our performance objective.

6.4 PERFORMANCE OBJECTIVE: COST EFFECTIVENESS

At the time we initiated the field portion of this study, we anticipated the need to track personnel time, sampling time, travel cost and shipping cost for the canisters. However, the diaphragm canister system and the capillary flow controller system are prepared, deployed, retrieved and analyzed in the same manner. The only difference is that the capillary flow controller sampling for 14 days will require an additional trip to retrieve the canisters. The sampling events in the project included 14 – 24 hour samples and 2 – 14 day samples per location, yet this is not a realistic situation for a VI assessment. It was done in this project to research the efficacy of the capillary flow controller for VI sampling. Hence, the cost analysis for an actual field project will be based on the number of days that need to be sampled, resulting in the diaphragm being more costly because additional canisters will be needed to collect samples for a multiple days. While the 14 day samples will provide more data with less analysis cost per canister deployed. The deployment and retrieval cost of the 14-day sample may require additional cost depending upon the distance the air sampling technicians needs to travel to retrieve the samples, this assumes an on-site person is not available to turn off the sample and ship it to the lab. In addition, samples could be collected using the capillary canister for fewer days (e.g., 3, 5, 7 days) to optimize cost for the specific sampling strategy necessary for the VI assessment (**Section 7.0**)

6.5 PERFORMANCE OBJECTIVE: REQUIRED EXPERTISE

The two canister sampling systems used in this study are very similar with respect to field application; hence, the required expertise for the capillary flow controller canister system is almost identical to that of the diaphragm canister system. The three Master students who participated in this project, (similar in many ways to an entry level tech), were asked to assess the ease of use of the canisters with both flow controller systems and the TD tubes. The sample prep, canister deployment, shipping and analysis were all very similar in their judgment. However, several advantages are outlined in **Table 9**.

Table 9. Performance Objective: Required Expertise to Perform Sampling

Sampling System	Sample prep	R	Sample set up	R	Shipping	R	Analysis	R
Capillary Canister	Standard canister cleaning per TO-15. The flow controllers can be reused and cleaned with UHP N2 if needed.	1	Lightweight flow controller (few ounces) and the quick connect allow for easy set up. Also, the low flow rate allows for a longer sampling time and/or smaller (1-L) canister can be substituted in for a 6-L. Reduce transportation costs	1	The canister require shipping to and from the sampling location. The size of the shipping boxes with 4 canisters is in convenient. However, smaller canisters can alleviate cost and time to package and ship.	2	Analysis for compounds of interest using TO-15 is very similar for all three methods.	1
Diaphragm Canister	Standard canister cleaning per TO-15. No cross contamination, was not observed in this study.	1	Heavier (1.5 lbs) and bulkier flow controller designed to be connected with a wrench. connected	2	The canister require shipping to and from the sampling location. The size of the shipping boxes with 4 canisters is not convenient to handle.	3	Analysis for compounds of interest using TO-15 is very similar for all three methods.	1
Thermal Desorption Tubes	2-3 times longer to clean the TD tubes.	2	Easy to set up with no tools.	1	Due to the small size the shipping is a fraction of the cost to ship canisters.	1	Analysis for compounds of interest using TO-15 is very similar for all three methods.	2

Note: R=Ranking, where 1 is the best score and 3 is the lowest rating.

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7.0 COST ASSESSMENT

Project Cost are displayed in Table 10 and the actual cost are displayed in Table 11.

Table 10. Cost Model for Capillary Canister Sample Collection and Analysis

Cost Element	Data to be Tracked	Examples/Comments
Material cost	• Unit cost of sampling devices • Unit cost of canisters and diffusion sampling materials • Number of samples	• Capillary flow controllers • Cost of both canister methods
Sampling	• Labor • Travel costs based on number and duration of sampling events • Sample shipment	• Deployment • Sample retrieval • Cost of shipping canisters vs. diffusion samplers
Laboratory analysis	• Number of samples • Per sample analytical laboratory costs	• Costs for EPA TO-15 vs TO-17 • Extraction or desorption costs

7.1 COST ELEMENTS: MATERIAL COST

The primary difference in cost of materials and labor to collect the samples is one cost factor, and a second cost factor is the decision-making processes. The primary cost between the traditional canister sampling approach and the capillary canister approach is the difference in cost between the diaphragm controller and the capillary flow controller. This cost was tracked on a per sample basis, along with the difference in materials costs between capillary canister sampling and sampling using diffusion samplers.

One can develop a variety of scenarios to assess cost depending upon the exposure assessment objectives. Per unit cost for the capillary flow controller system will always be lower if one is considering the additional days of data. If additional data is the primary concern, then the long-term samples will provide a cost-effective means to collect the data. **Table 12** shows examples of the cost of the two methods based on our data collection and unit cost per day of data ($49 vs $519) for Capillary vs Diaphragm, respectively.

Table 11. Sample Collection and Analysis Cost per Sampling Event

Material Cost				
Sampling Equipment	**Unit Cost of Sampling Device**			
Canisters	**Unit Cost**	**Canister + Cap flow Controller**	**Canister + Diaphragm flow Controller**	**Number**
400 mL	$260	$360	$1,110	20
1-L	$375	$475	$1,225	20
6-L	$629	$729	$1,479	40
15-L	$1,050	$1,150	$1,900	10
Flow controllers				
Capillary Flow controllers	$100		na	
Diaphragm Flow controllers	$850		na	
Thermo Desorption Tubes	$123		$123	40
Example Cost of Each Event Sampling Cost Travel and Shipment of Samples				
Food	Fuel	Hotel	Sample Shipping	Supplies
$135	$201	$1,447	$4,683	$474
Total	**$6,939**			
Laboratory Analysis				
	# Samples[1]	**Analytical Lab Cost [2]**		
Canister Indoor & Amb	135	$9,167		
Sub Slab	42			
Thermo Desorption Tube	34			
Total samples per event	**211**			

[1] The number of canister samples were consistent throughout the study, but the number of TD tubes varied due to the results.

[2] The CARES lab was paid a lump sum for the sample analysis. This allow for multiple runs of Calibration standards and QC samples.

Table 12. Cost Analysis Scenarios

			Travel to site a first time			Travel to site a second time [1]							
Type of Canister sample	**Cost to ship 6 canisters to lab**	**Est. Cost to ship 1 canister**	**Travel**	**hotel**	**Per diem**	**Airfare**	**hotel**	**Per diem**	**Analysis**	**Labor at $50/h**	**Total Cost**	**Unit Cost per Day of data**	**Comments**
Capillary	$312.20	$52.03	$50	$110	$62	$350	$110	$62	$1,800	$800	$3,656	**$ 44**	Cost to obtain 14 days of data Cost to obtain 6 - 24-hour samples in 1 day
Diaphragm	$312.20	$52.03	$50	$110	$62	na	na	na	$1,800	$400	$2,734	**$455.70**	
											Total cost differential		$922

Assume the collection of 6 samples using diaphragm Flow Controller for 3 consecutive days (18 total samples) where each sample is collected for 24 hours.

Capillary	$312.20	$52.03	$50	$110	$62	$350	$110	$62	$1,800	$800	$3,656	**$44**	Cost to obtain 14 days of data Cost to obtain 18 – 24-hour samples over 3 day
Diaphragm	$312.20	$52.03	$50	$330	$186	na	na	na	$5,400	$1,200	$7,478	**$415.46**	
											Total cost differential		($3,822)

7.2 THE COST TO MAKE A DECISION

While the cost of materials and labor is fairly straight forward, the risk-based cost is more complicated and likely more significant. The difference in the number of samples required to make the same risk-based decision using traditional 24-h canister sampling versus the capillary canister sampling was tracked for cost assessment purposes as well. **Figure 25** shows a decision process related to selection of capillary canisters, 24-h canisters (traditional canister method), and diffusion samplers. Upon receiving screening-level data from initial indoor air sampling, results are compared to risk-based criteria for deciding the next level of sampling and analysis activity. The 14-day capillary canister approach can offer important advantages over typical 24-h canister sampling where initial screening-level data are near risk-based decision levels. In order to make an appropriate decision regarding building occupancy and remediation, variability in concentrations of VOCs must be well-understood and uncertainty must be minimized. Capillary canisters allow for longer-term sampling than traditional canisters, which become unreliable at durations greater than 24-h. This translates to a need for fewer samples over the course of an investigation or long-term monitoring period as variability is minimized. The regulatory and stakeholder drive for increasing numbers of sampling rounds is driven by the concern over temporal variability that longer sample durations can eliminate.

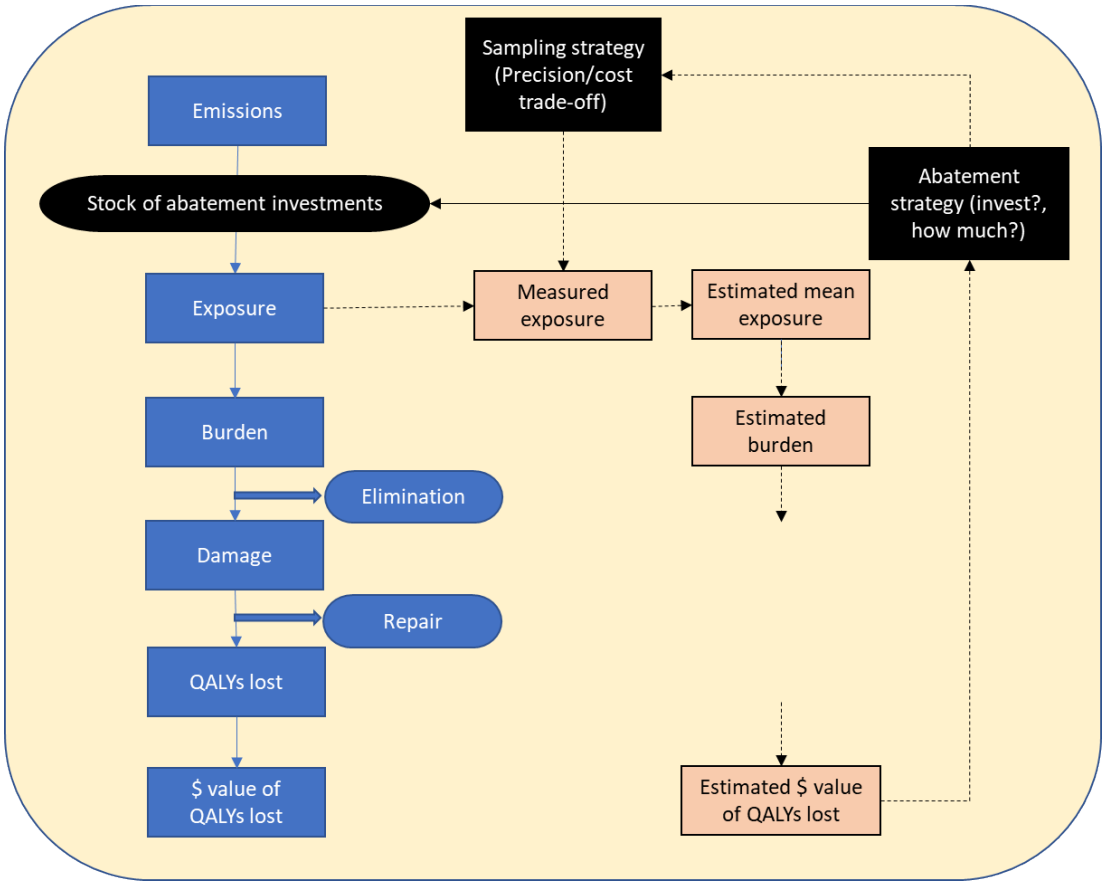

Figure 25. Conceptual Model Adopted from Nocetti et al. 2019 Establishing a Framework for Evaluating the Biological-statistical-economic Considerations for Long-term Exposures to Toxic Substances.

To further explore the optimal numbers of days to be sampled, health benefits and cost, we worked with an economist to develop a decision model for VI dependent upon the number of days of data. The article entitled: *Sampling strategies in the assessment of long-term exposures to toxic substances on air., Diego, N.,, Crimi, M., and Rossner, A.,* was accepted in October of 2019. The scope of the manuscript extends beyond just the sampling methodology, but also includes key factors associated with a decision to remediate or evacuate a building vs deciding that the building is "safe". In particular, characterizing the decision-making process to select an optimal sampling strategy given biological, statistical, and economic considerations. We present a conceptual model **(Figure 25)** and a mathematical representation of the model. Our numerical simulations show that methods that permit the collection of sampling strategy over relatively long periods of time tend to be more accurate (i.e. generating lower Type I and Type II errors) and are more cost-effective than short-term sampling approaches.

The problem for the Decision maker is that he/she does not know with certainty the level of exposure (this may occur because emissions are random or because past abatement investments may stop being effective at a random rate). The Decision maker has an initial estimate of the mean level of exposure, but sampling allows him to generate a more precise estimate. The benefit of a given sampling strategy is then given by the savings generated by the greater precision.

In particular, by reducing the likelihood of Type I errors (invest in abatement when the mean concentration is low) and/or Type II errors (fail to invest in abatement when the mean concentration is high and it would be cost-effective to do so) the Decision Maker is able to reduce health risks in a cost-effective way. The best sampling strategy is the one that maximizes the monetary value of expected health improvements net of expected costs of abatement and sampling.

The mathematical model is not displayed here due to the length and complexity, yet the result is a tool allowing the decision maker to consider the type of sampling needed to make the best decision with respect to health and costs (Nocetti et al., 2019).

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8.0 IMPLEMENTATION ISSUES

In this section, we provide lessons learned and defined a path forward for the capillary flow controller technology. We consider the regulatory issues, and user concerns including procurement and analysis issues.

The long-term flow controller performed well in the field under significant temporal and spatial variation while the low flow rates remained relatively consistent. Data from this project as well as from other VI investigations suggest indoor VOC concentrations can fluctuate by orders of magnitude from one day to another and from season to season. Long term sampling may be more representative of the long-term average concentration within a building, thus relying on one day averages may result in under or over estimation VI contamination. In addition, with shorter sampling times such as 24 hours, the timing of the sampling becomes much more critical and can be a limitation to interpreting the results. The ability to collect an air sample over a long period (weeks) of time can help enhance VI investigations by providing a larger fraction of days sampled vs the traditional 24-hour sample. In addition, the cost per sample is lower for analysis, and shipping costs with respect to the number of days of data collected. The results from this study indicate that the capillary flow controller can be used to generate a better estimate of excess lifetime cancer risks and non-cancer health effects and for risk management decisions.

It is important to note that indoor air sampling is just one step in evaluating buildings impacted by VI. However, it is a critical parameter for assessing VI and health impacts. The long-term air sampling provides a better estimate of chronic exposures as compared to short term sampling. However, long term air sampling may not always be suitable in circumstances where acute health risks need to be assessed. The capillary flow controllers coupled with evacuated canister s was found to be robust, comparable in cost for deployment, but less expensive than current methods for analysis, allows for long-term sample collection (weeks), and requires one sample to capture the full range of analytes and at broad range of concentrations.

8.1 REGULATORY ISSUES

While EPA and many state environmental agencies procedures defined key elements necessary to accompany air sampling (location, spatial, temporal, soil gas, cross slab pressures, questionnaires, chemical inventory, photographs, etc) a specific sampling time is not defined. These agencies, in some cases do however provide recommendations suggest 24-hour samples at multiple seasons and locations within the building (EPA 2015).

The air sampling equipment is very similarly to the 24-hour sampling equipment, hence the addition of a long-term sampling protocol would be relative simple to modify current protocols to adopt the capillary flow controller methodology.

8.2 USER CONCERNS

Current concerns for users should be limited in most areas because the technology is so similar to sampling with the current diaphragm flow controller. The benefit of gaining so much more data, multiple days for the same cost, than 24 hours sample will be useful in the decision-making process.

However, information from the traditional 24-hour sample have been used by regulators and organizations for many years, therefore it may be a concern how well these 14-day samples can be interpreted with respect to the 24-hour samples. The flow controllers should be continued to be used to for demonstration of this technology, including personal air sampling where applicable.

One concern with technology advancement revolves around the analytical labs. They are familiar and have invested in the diaphragm flow controllers and may be reluctant or not have the capillary flow controller available for use. These inventory and logistical issues I believe can be overcome with additional data and technology transfer protocols. As the laboratories gain experience and understanding of the capillary flow controller, I believe they will find it easier to use and maintain than the diaphragm flow controller. In addition, is much easier to replace the capillary flow controller as it is approximately 1/10 the cost of the diaphragm flow controller. In addition, since the onset of this project, NIOSH has approved a protocol for sampling and analysis of canisters with the capillary protocol (NIOSH 3900).

There should be limited concerns with procurement as the flow controllers are commercially available, however, discussions with laboratories will be necessary to ensure they are familiar with the flow controller and will use it.

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