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# Cost and Performance Report

(ER-200830)

## Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 11DCA | 1,1-dichloroethane |
| 11DCE | 1,1-dichloroethene |
| 111TCA | 1,1,1-trichloroethane |
| 12DCA | 1,2-dichloroethane |
| 124TMB | 1,2,4-trimethylbenzene |
| | |
| ANOVA | a one-way analysis of variance |
| ASTM | ASTM International |
| ASU | Arizona State University |
| ATD | automated thermal desorption |
| | |
| BENZ | Benzene |
| | |
| $C/C_o$ | passive sampler concentration divided by active sampler concentration |
| cDCE | cis-1,2-dichloroethene |
| COC | contaminant of concern |
| COV | coefficient of variation |
| CRREL | Cold Regions Research and Engineering Laboratory |
| $CS_2$ | carbon disulfide |
| CTET | carbon tetrachloride |
| | |
| DoD | Department of Defense |
| | |
| ESTCP | Environmental Security Technology Certification Program |
| | |
| GC | gas chromatograph |
| GC/MS | gas chromatography-mass spectrometry |
| | |
| ITRC | Interstate Technology and Regulatory Council |
| | |
| Koc | organic carbon partitioning coefficient |
| | |
| m/s | meters per second |
| MCAS | Marine Corps Air Station |
| MEK | 2-Butanone |
| $\mu g/m^3$ | micrograms per cubic meter |
| mL/min | milliliters per minute |
| | |
| NAPH | naphthalene |
| NAS JAX | Naval Air Station Jacksonville, Florida |
| NESDI | Navy Environmental Sustainability Development to Integration |
| NHEX | n-Hexane |
| OSWER | (USEPA) Office of Solid Waste and Emergency Response |

| | |
|---|---|
| OTC | Officer Training Command |
| OU | operable unit |
| OVM | Organic Vapor Monitor |
| %RH | percent relative humidity |
| PCE | Tetrachloroethene |
| pg | picograms |
| PID | photoionization detector |
| $ppb_v$ | parts per billion by volume |
| $ppm_v$ | parts per million by volume |
| RMSV | recommended maximum sample volume |
| RPD | relative percent difference |
| SERDP | Strategic Environmental Research and Development Program |
| SSC Pacific | Space and Naval Warfare Systems Center Pacific |
| TCE | trichloroethene |
| TWA | time-weighted average |
| UR | uptake rate |
| USACE | U.S. Army Corps of Engineers |
| USEPA | U.S. Environmental Protection Agency |
| VC | vinyl chloride |
| VI | vapor intrusion |
| VOC | volatile organic compound |
| WMS | Waterloo Membrane Sampler |

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# EXECUTIVE SUMMARY

## OBJECTIVES OF THE DEMONSTRATION

The objectives of this work were to provide data to demonstrate and validate passive diffusive samplers for assessing soil vapor, indoor air, and outdoor air concentrations of volatile organic compounds (VOCs) at sites with potential human health risks. These risks were attributable to subsurface vapor intrusion to indoor air by comparing their accuracy and precision to conventional methods; identifying capabilities and limitations of various sampler types; and providing scientific data to support regulatory review and acceptance where appropriate.

## TECHNOLOGY DESCRIPTION

Passive samplers offer some potential benefits compared to conventional sampling methods and may reduce cost and the implications of temporal variability, which would reduce liabilities for the Department of Defense (DoD). The study team was selected to include individuals highly experienced with passive samplers (in general) and each of the five samplers tested (in particular). The passive samplers tested included: (1) SKC Ultra and Ultra II; (2) Radiello®; (3) Waterloo Membrane Sampler; (4) Automated Thermal Desorption (ATD) tubes; and (5) 3M Organic Vapor Monitor 3500. The full demonstration/validation final report (Environmental Security Technology Certification Program [ESTCP]) contains much more information and is published separately.

## DEMONSTRATION RESULTS

The program included laboratory testing under controlled conditions for 10 VOCs, including chlorinated compounds (ethenes, ethanes, and methanes) and petroleum hydrocarbons (aromatics and aliphatics), spanning a range of properties and including some compounds expected to pose challenges associated with retention and recovery by the sorbents (naphthalene, methyl ethyl ketone). Laboratory tests were performed under conditions of different temperature (17 to 30°C), relative humidity (30 to 90 percent relative humidity [%RH]), sampler face velocity (0.014 to 0.41 meters per second), concentration (1 to 100 parts per billion by volume), and exposure duration (1 to 7 days). These conditions were selected to challenge the samplers across a range of conditions likely to be encountered in indoor and outdoor air field sampling programs. High concentration laboratory tests were also conducted at 1, 10, and 100 parts per million by volume to evaluate concentrations of interest for soil vapor monitoring using the same 10 VOCs and constant test conditions (90 %RH, 30 minutes [min] exposure, 22°C). Inter-laboratory testing was also performed to assess the variance in the analytical results attributable to the differences between several laboratories used in this study.

The program also included field testing of indoor air, outdoor air, sub-slab vapor and deeper soil vapor at several DoD facilities. Indoor and outdoor air samples were collected over durations of 3 to 7 days and Summa canisters were collected over the same durations as an active sample for comparison. Subslab and soil vapor samples were collected with durations ranging from 10 min to 12 days, at depths of about 0.5 (immediately below floor slabs), 4, and 12 feet. Passive samplers were employed with uptake rates ranging from about 0.05 to almost 100 milliliters per minute and analysis by both thermal desorption and solvent extraction. Mathematical modeling was performed to provide theoretical insight into the potential behavior of passive samplers in the subsurface, and

to help select those with uptake rates that would minimize the "starvation effect." The starvation effect refers to a negative bias that occurs when a passive sampler with a high uptake rate removes VOC vapors from the surroundings faster than they are replenished, essentially scrubbing the local atmosphere of VOCs. A flow-through cell apparatus was also tested as an option for sampling existing sub-surface probes that are too small to accommodate a passive sampler.

The results of this demonstration show that all of the passive samplers provided data that met the accuracy, precision, ease of use, and cost success criteria (defined in Section 3) under some or most conditions. Compared to conventional active sampling methods, the passive sampler's precision was generally comparable; ease of use was generally comparable or better; and cost was comparable or better (improving with larger numbers of samples). Accuracy met the success criterion in most cases, and exceptions were attributable to one or more of five possible causes: (a) poor retention of the analytes on the sampler; (b) poor recovery of the analytes from the sorbent; (c) starvation effects, (d) uncertainty in uptake rate for the specific combination of sampler/compound/conditions, or (e) blank contamination. These biases can be prevented in most cases through careful selection of the sampler, as well as sorbent and exposure duration for specific target analytes. Positive biases were less common than negative biases, and attributed either to blank contamination, or to uncertainty in the uptake rates. Most of the passive samplers provided highly reproducible results, which is encouraging because the accuracy can be verified using inter-method duplicate samples (e.g., a limited number of conventional samples collected beside selected passive samples for the same duration as a quality assurance/quality control check), and the field-calibrated uptake rates will be appropriate for other passive samples of the same type collected under similar conditions. This research also demonstrated for the first time the reliable use of passive samplers for quantifying soil vapor concentrations.

## IMPLEMENTATION ISSUES

The overall cost of monitoring with passive samplers is comparable to or lower than monitoring with conventional methods because of the simplicity of the sampling protocols (less time required for sample deployment and collection) and reduced shipping charges. Passive samplers are generally easy to use and minimal training is required for most applications. A modest increase in effort is needed to select the appropriate sampler, sorbent, and exposure duration for the site-specific chemicals of concern and desired reporting limits compared to Summa canisters and U.S. Environmental Protection Agency (USEPA) Method TO-15; however, the level of effort is not much different than the design process for active ATD tube sampling for analysis by USEPA Method TO-17. As the number of samples in a given program increases, the initial cost of sampling design becomes a smaller fraction of the overall total cost, and the passive samplers gain a significant cost advantage. For best results, the selection of the appropriate sampler, sorbent, and exposure duration for a particular set of target chemicals and reporting limits should be reviewed carefully by an experienced professional and the sampling program should include trip-blank samples. Inter-method duplicate samples can also be included to provide field-calibrated uptake rates as an additional accuracy check where needed.

# 1.0 INTRODUCTION

This Cost and Performance Report has been prepared by Geosyntec Consultants, Inc., for the ESTCP review committee and it presents the results of ESTCP project ER-200830: Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion (VI) to Indoor Air using Quantitative Passive Diffusive Adsorptive Sampling Techniques. Dr. Samuel Brock of the Air Force Civil Engineering Center was the U.S. Department of Defense (DoD) Liaison and Dr. Andrea Leeson of ESTCP was the Contracting Officer's Representative.

Additional funding was provided by the Navy Environmental Sustainability Development to Integration (NESDI) Program conducted as part of Project 424 on "Improved Assessment Strategies for Vapor Intrusion." Ms. Leslie Karr was the NESDI Program Manager; Ms. Stacey Curtis was the Space and Naval Warfare Systems Center Pacific (SSC Pacific) representative in the Technology Development Working Group; and Drs. D. Bart Chadwick and Ignacio Rivera-Duarte from SSC Pacific were the project directors.

The ESTCP program provided funding for testing four different passive samplers under both controlled laboratory conditions and field conditions with conventional active sampling and analysis for comparison. The four passive samplers were:

- Passive automated thermal desorption (ATD) tubes;
- Radiello samplers;
- Waterloo Membrane Samplers (WMS); and
- Ultra II badge samplers.

The NESDI research program provided funding to add the 3M Organic Vapor Monitor (OVM) 3500™ sampler for those components of the research where NESDI funding was used to supplement the ESTCP funding.

Passive samplers provide several potential advantages over passivated canister sampling (the current industry standard method for VI assessments), including: (1) simplicity; (2) the ability to collect longer-term integrated samples; (3) smaller size for ease of shipping and handling; and (4) lower overall cost. Prior to this research, each of the five candidate passive sampler technologies had been independently tested and proven to be capable of accurately measuring vapor concentrations in indoor and outdoor air for some chemicals under certain conditions; however, the commercially-available passive samplers had not been rigorously compared with each other. Furthermore, none of the passive samplers were specifically designed for use in soil vapor monitoring, and passive soil vapor sampling has not previously been demonstrated to provide accurate soil vapor concentration data (U.S. Environmental Protection Agency [USEPA], 1998a, b; California Department of Toxic Substance Control, 2011; ASTM International [ASTM] D7758, 2011). This demonstration/validation study was conducted to improve knowledge of the capabilities and limitations of the candidate passive samplers and foster regulatory familiarity, confidence, and acceptance in the future.

## 1.1 BACKGROUND

Subsurface vapor migration to indoor air (VI) has been an important and challenging component of assessing human health risks associated with contaminated soil and groundwater since the late 1990s, during which time regulatory guidance for assessing VI has been issued by at least 41 state agencies, the Interstate Technology and Regulatory Council (ITRC) (2007), and by the USEPA Office of Solid Waste and Emergency Response (OSWER) (USEPA, 2002). Currently, the most common method for collection and analysis of indoor air and sub-slab or soil vapor samples consists of drawing air or soil gas into an evacuated, passivated stainless steel canister (SilcoTek™ or Summa®) through a flow controller followed by shipment to a laboratory for analysis by USEPA Method TO-15 (USEPA, 1996) via gas chromatography-mass spectrometry (GC/MS). The most common alternative to whole-gas sampling is active adsorptive sampling using ATD tubes (USEPA, 1999) (Note: one of the passive samplers included in this study also uses ATD tubes in the passive mode, so this document refers to both active and passive ATD tube samples).

Most volatile organic compound (VOC) VI guidance documents recommend sample durations of 8-hour (commercial) or 24-hour (residential), mostly because conventional sampling for analysis by USEPA Methods TO-15 and TO-17 are not well suited to longer duration samples. Shorter-term samples will inherently show more temporal variability, which makes the results less useful for assessing long-term average exposures. Temporal variability can be managed by collecting a greater number of samples to support a statistical calculation of a representative long-term average concentration (e.g., Johnson et al., 2013; Holton et al., 2012; Luo et al., 2012; Kuehster et al., 2004; Folkes et al., 2009; U.S. EPA, 2012; Johnston, 2013; Johnston and Gibson, 2013); however, this increases cost considerably. Passive samplers may not only be simpler and significantly less expensive, but they are much better suited to longer sampling intervals (i.e., much greater than 24 hours), which is expected to provide data with less variability compared to conventional sampling methods.

## 1.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of the program were to identify whether or not, and under what conditions, passive diffusive samplers provide good quality measurement of VOC vapor concentrations and to document the study findings so that regulatory agencies have strong scientific support for accepting less-expensive alternatives to conventional monitoring methods where applicable. Five different passive samplers were compared to conventional sampling methods to demonstrate the advantages and disadvantages of each under both controlled laboratory conditions and field conditions. None of these passive samplers were specifically designed for soil gas monitoring; however, this is a very useful capability for VI investigations, so the research included development and testing of quantitative passive methods for soil vapor sampling and analysis.

## 1.3 REGULATORY DRIVERS

Regulatory guidance for assessment and management of risks associated with VI has been issued by at least 27 states, USEPA, and ITRC. In most jurisdictions, these documents are only guidance, and are not statutory requirements; however, there are statutory requirements to assess potential human health risks, and this possibility exists where VOCs are present in the subsurface near occupied buildings. Therefore, a screening level assessment is often required, and some amount of

indoor air and soil vapor sampling and analysis is typically expected as a primary line of evidence. VI assessments are also a routine component of 5-year reviews under the Comprehensive Environmental Response, Compensation, and Liability Act, and No Further Action letters have been rescinded to require VI investigations. Furthermore, brownfield redevelopments are required to assess the potential for VI (USEPA, 2002; ASTM E2600-10, 2010), so economic benefits from redevelopment of underutilized properties will provide motivation for VI investigations. For sites where there is unacceptable VI, a long-term monitoring program may be required to demonstrate the effectiveness of mitigation measures, verify the absence of concerns in buildings immediately beyond the mitigated area, or provide a basis for closure upon completion of mitigation activities. There is also an increasing awareness that temporal variability in indoor air concentrations attributable to VI poses a risk of a false-negative conclusion (concluding VI poses no unacceptable risk, when the opposite is the true condition) where sampling is conducted over a relatively short time (e.g., one or a few 24-hour samples over the course of a year or so). Based on the regulatory and sampling issues described, alternatives to the conventional methods are needed.

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# 2.0 TECHNOLOGY

## 2.1 TECHNOLOGY DESCRIPTION

Quantitative passive sampling can be defined as the collection of vapors by diffusion or permeation in response to concentration gradients (rather than pressure gradients, as are used by Summa canisters and pumped ATD tubes) at a known and controlled uptake rate, such that the time-weighted average (TWA) concentration can be calculated from the mass of each analyte collected over a given period of time. The passive sampler acts as a sink for the analytes, which establishes the concentration gradients so no external power source is required; hence, the sampling is termed "passive". There are several different commercially available quantitative passive samplers with different sizes, shapes, materials of construction, sorbents, and protocols. This section describes the quantitative samplers' operating principles, varieties, capabilities, and limitations.

### 2.1.1 Basic Principles of Quantitative Passive Sampling

The basic principles of operation for all five passive samplers tested in this program are similar. Each device is supplied by the vendor or laboratory as certified clean and sealed in air-tight packing. The sampler is exposed to the air or gas being investigated for a measured amount of time (t), during which VOCs diffuse or permeate into the device from the surrounding gas or atmosphere and a certain mass (M) of VOCs will be trapped on the adsorptive medium within the device. The device is re-packed in an air-tight container and returned to the laboratory, where the mass adsorbed is quantified. Once the adsorbed mass has been quantified, the TWA concentration of a particular analyte in the medium being sampled can be calculated as follows:

$$C_o = \frac{M}{(UR)(t)} \tag{1}$$

where:

$C_o$ = TWA concentration in the sampled air (micrograms per cubic meter [$\mu g/m^3$])
$M$ = mass of analyte on the sorbent (picograms [pg])
$UR$ = uptake rate (milliliters per minute [mL/min])
$t$ = sampling time (minute)
(Note: there are two offsetting conversion factors from pg to μg and mL to $m^3$)

The mass adsorbed and exposure duration are both measured very accurately, so the uptake rate is the key factor controlling the accuracy of the concentration measurement. Note that the uptake rate has units of mL/min, similar to a flow rate, despite the fact that the samplers operate by diffusion or permeation; there is ideally no net fluid flow into or through the samplers (the uptake rate is equal to the flow rate that is required for a pumped sorbent tube to absorb the same mass over the same sample duration when exposed to the same concentration).

Most of the passive samplers are available in more than one variety. For example, the uptake rate of a passive sampler can be increased or decreased by design. High uptake rates allow lower concentrations to be quantified for a given exposure duration, which can be an advantage for compounds with very low risk-based screening levels. Lower uptake rates reduce the risk of the

"starvation effect," which occurs when the rate-limiting step during sampling is transport of chemicals to the face of the sampler instead of the uptake rate of the sampler itself. This situation results in a reduction in vapor concentrations near the sampler, and a negative bias in the calculated passive sampler concentrations compared to ideal conditions under which passive sampler uptake rates are typically calibrated. Advection from wind and ventilation during indoor and outdoor air sampling is often sufficient to minimize the starvation effect for all but the highest uptake rate samplers. For soil gas sampling, advection is likely to be minimal and the rate of contaminant vapor replenishment in the gas-filled void space surrounding the sampler is likely to be limited to diffusive transport only; therefore, a much lower uptake rate is required to minimize the starvation effect.

Many of the passive samplers can also be used with more than one type of sorbent. There are two general classes of sorbents, suited either to thermal desorption or solvent extraction as the sample preparation method. Analysis by thermal desorption is typically performed using a method like USEPA Method TO-17 where the ATD tube is heated and flushed with nitrogen or helium into the gas chromatograph (GC). This provides very good sensitivity because all of the mass adsorbed by the sampler is injected into the GC, although there is typically a split ratio at the interface between the injector and the column, so some of the sample may not run through the GC column. Analysis by solvent extraction is typically performed using carbon disulfide ($CS_2$) to extract the target VOCs from the adsorbent; however, only a small aliquot of the total $CS_2$ used is subsequently injected into the GC (e.g., 1 μL injected of 1 mL used for extraction). Consequently, the sampler may need to be exposed for a longer period of time or have a higher uptake rate to achieve comparable reporting limits.

The exposure duration must be long enough to allow the reportable concentrations to be as low as appropriate risk-based target concentrations, or lower. However, longer deployment periods increase the risk of saturation if concentrations are high and poor retention if weaker sorbents are used (Bates et al., 1997). The risk of saturation can be managed with some advance information about expected concentrations, and usually readings with a portable instrument such as a photoionization detector (PID) are sufficient to identify appropriate limits on the exposure duration to avoid saturation (the linear range of analysis for most methods is at least two orders of magnitude, so there is a fair margin for uncertainty in the expected concentrations). Negative biases attributable to poor retention will be most problematic for long exposure durations and combinations of sorbents/compounds that have low recommended maximum sampling volumes (RMSV) (Supelco, 2013).

Different chemicals have different adsorption properties, and a variety of adsorbent media are available, so there are a wide range of options for the selection of the appropriate adsorbent media for a particular compound or list of compounds of interest. The goal is to provide a high degree of retention during sampling and good recovery during analysis. Very volatile and polar compounds (vinyl chloride [VC], chloromethane, and other low molecular weight, low boiling point compounds) require a strong sorbent to be effectively retained during sampling, especially for longer sampling intervals. Less volatile or polar compounds (e.g., naphthalene [NAPH], poly-cyclic aromatic hydrocarbons, polychlorinated biphenyls, and other high molecular weight, high boiling point compounds) do not require a strong sorbent to be effectively retained, and may not be effectively recovered unless a weaker sorbent is used. It may not be practical to select a single

sorbent suitable for the range of compounds of potential interest for VI investigations, in which case two or more samplers are an option. Several publications are available that provide information regarding the effectiveness of various sorbents with various VOCs (Supelco, 2013; ASTM D6196-03, 2009; CEN EN 13528-3, 2003; CEN EN 14412, 2004). For active adsorptive sampling (where air is pumped through a tube of sorbent media), there are RMSVs for combinations of compounds and adsorbents beyond the negative bias in the reported concentrations that is commonly seen, which is attributable to poor retention by the sampler (e.g., attributable to limited sorptive capacity). For passive sampling, there is no specified volume of gas drawn through the adsorbent, but poor retention can still result in negative biases by competition for adsorptive sites (more strongly sorbed compounds can displace less strongly sorbed compounds) causing back-diffusion (diffusion away from the sampler, rather than toward it). The mass loading is proportional to both the sample duration and the analyte concentration, which is increasingly complex when multiple chemicals are present. The selection of the optimum sorbent for a particular set of target compounds can be complicated and should be done in consultation with an experienced analytical chemist.

### 2.1.2 Candidate Passive Samplers Used in this Study

The following samplers and configurations were used in this study:

**SKC Ultra™** and **Ultra II™** (http://www.skcinc.com/prod/590-100.asp) is a badge-type sampler with option for thermal desorption or solvent extraction, which operates by diffusion through either a plastic cap with ~300 holes, or a low-uptake rate cap with 12 holes (Figure 1a). These devices have been used for industrial hygiene applications for many years (Harper and Guild, 1996; OSHA, 2003), and can provide quantitative VOC analysis of indoor air samples at the parts per billion by volume ($ppb_v$) level (Coyne et al., 2002; Bergemalm-Rynell et al., 2008; SKC, 2008; 2012).

**Figure 1a. SKC Ultra sampler with regular (white) and low-uptake cap (green).**

**Radiello® –** This sampler has a 2-dimensional (radial) geometry, which has a large cross-sectional area and increases the uptake rate for greater sensitivity (lower reporting limits for a given exposure duration) compared to most of the other samplers (Cocheo et al., 1996; Cocheo et al., 2009). The sampler is made of two concentric cylinders; the inner cylinder is a cartridge that

contains an adsorbent medium surrounded by a stainless steel mesh (Figure 1b). The outer cylinder is made of microporous sintered polyethylene, through which the vapors diffuse.

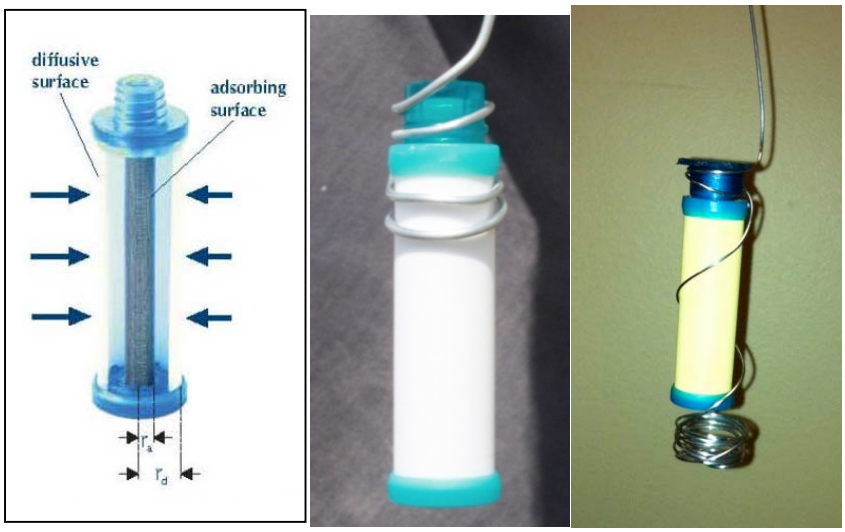


**Figure 1b. Radiello sampler with regular (white) and low-uptake rate (yellow) bodies.**

**3M OVM 3500™ –** This device is a badge style sampler originally developed for industrial hygiene monitoring (Chung et al., 1999; Purdham et al., 1994; Mukerjee et al., 2004). The plastic body snaps together and holds a white porous plastic outer layer (diffusive barrier) at a fixed distance from a thin film coated with activated carbon (Figure 1c). Diffusion occurs across the porous barrier and through air to the activated carbon.

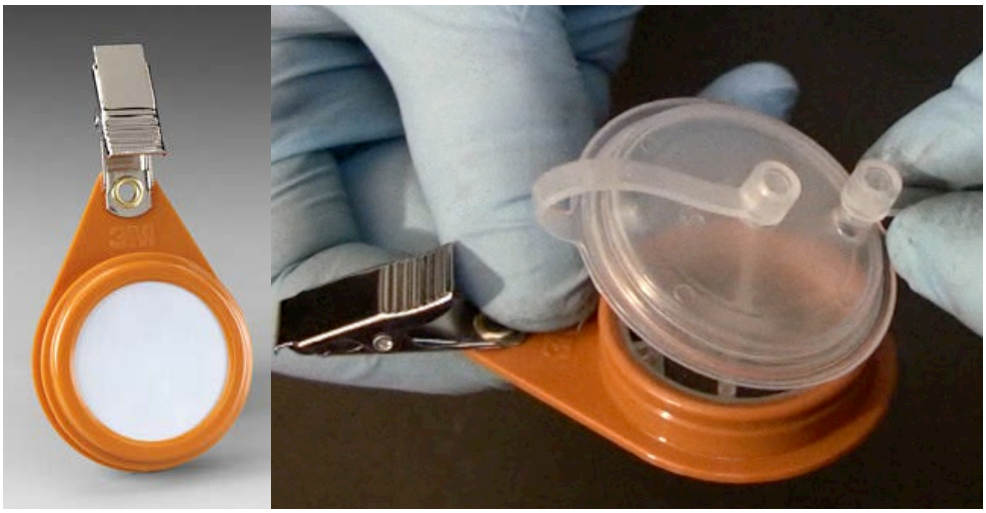

**Figure 1c. 3M OVM 3500 sampler and solid plastic cap used to replace the porous plastic sheet after sampling.**

**Waterloo Membrane Sampler™ –** The WMS sampler (Figure 1d) is unique because VOC uptake occurs through a membrane of polydimethylsiloxane. VOCs dissolve into the membrane and permeate across it (Seethapathy and Gorecki, 2010a; b). The membrane excludes water vapor,

which can compete for adsorptive sites on some sorbents and interfere with laboratory instruments. The membrane also prevents advective uptake by turbulence, so sampling can occur in high air velocity environments without a positive bias.

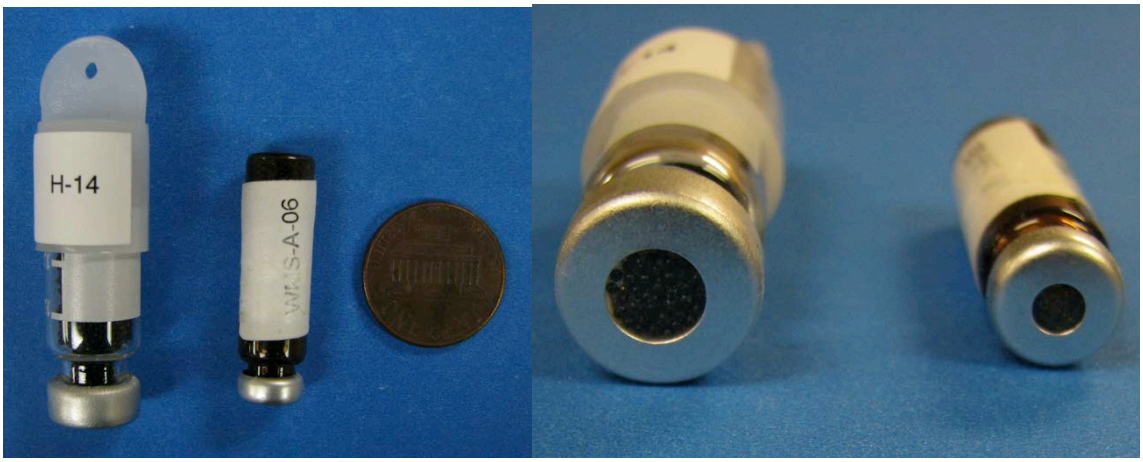


**Figure 1d. WMS and close-up of membrane and adsorbent.**

**Passive ATD tube samplers** (from various manufacturers) **–** This sampler consists of a standard ATD tube (Figure 1e) that can be used with a wide variety of adsorbents, depending on the compounds of concern and the target reporting limits and exposure durations (Cox and Brown, 1984; Batterman et al., 2002; Brown, et al., 1992; Brown, et al., 1993; Brown and Crump, 1998; Crump, 2001; Crump, 2009; Crump et. al., 2004; Sweitzer et al., 2006; Thomas et al., 2011).

**Figure 1e. ATD tube sampler and regular and low-uptake rate caps.**

## 2.2 ADVANTAGES AND LIMITATIONS OF PASSIVE SAMPLING

### 2.2.1 Advantages

Passive diffusive samplers offer at least four potentially significant advantages relative to the current industry standard approach of whole-air sampling with Summa canisters and TO-15 analysis, as described in detail below.

**Lower Cost:** Passive samplers are small in size and shipping charges are minimal in comparison to costs for shipping Summa canisters. Less operator training is required and the labor costs for sampler deployment and retrieval are also lower.

**Simpler Sampling Protocols:** Passive samplers are very similar to devices currently used for monitoring radon, which are most often deployed, retrieved, and shipped by homeowners (i.e., not by technical personnel, which may reduce costs significantly). Simplicity may also help minimize bias and variability attributable to inter-operator errors (differences in the sampling results attributable to operators implementing sampling procedures in different ways), especially for soil vapor sampling.

**Longer-Term Samples:** Passive samplers can be used to collect samples over much longer periods than conventional Summa canister or active ATD tube samplers. This results in measured concentrations that represent a TWA of conditions over the sample collection duration, and minimize short-term temporal variability associated with changes in weather conditions, building ventilation, and occupant's activities.

**Less Obtrusive:** Passive diffusive samplers are small enough to be held in the palm of a hand, and look fairly simple and unobtrusive compared to 6L Summa canisters.

### 2.2.2 Limitations

Passive diffusive samplers have the following potential limitations:

**Starvation Effect:** If the velocity of air to which the sampler is exposed is very low, then the sampler may remove VOC vapors from the air faster than they are replenished, in which case, the sampler itself imposes a localized reduction in the VOC vapor concentrations. This results in a negative bias in the reported concentrations, which is referred to as the "starvation effect."

**Saturation, Competition, Poor Retention, or Poor Recovery:** If passive samplers are exposed to high analyte concentrations for extended periods of time, then the adsorptive sites on the adsorbent media may become occupied with VOCs and the adsorbent performance may diminish (referred to as saturation). If multiple VOCs are present, then more strongly adsorbed compounds may displace less strongly adsorbed compounds (referred to as competition). If long deployment periods are used with weak sorbents, there may also be losses from the sorbent by back-diffusion (referred to as poor retention). If strong sorbent are used with strongly sorbed compounds, the analytes may not be completely released from the sorbent during analysis (referred to as poor recovery). All four processes have the same net effect; a negative bias in the reported concentrations.

**Matching to Target Compounds:** The sampler type and sorbent must be selected with consideration of the compounds of interest and the desired reporting limits. This is similar to challenges of conventional active sampling methods that employ active (pumped) ATD tubes, such as EPA Method TO-17.

**Unplanned Uptake of Chemicals:** The passive samplers can become contaminated by unplanned exposure to chemicals during shipping and storage. The risk is reduced by carefully packing the samplers in clean containers that are impermeable to VOC vapors. The potential can also be evaluated and documented by including field blanks (a.k.a., trip blanks).

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# 3.0 PERFORMANCE OBJECTIVES

The performance objectives are listed in the Table 1 below.

**Table 1. Performance objectives.**

| Performance Objective | Data Requirements | Success Criteria | Results |
|---|---|---|---|
| **Quantitative Performance Objectives** | | | |
| Accuracy of VOC vapor concentration quantization in soil gas, indoor air, and outdoor air. | Concentration measurements using each of the candidate passive samplers and Summa canisters as control, with sufficient samples to assess the effects of the key factors | Accuracy: RPD <25% is typically considered acceptable for duplicate samples analyzed in the same laboratory by the same method. However, the passive samplers were analyzed using different methods and in different laboratories, so the criterion for accuracy was set as an RPD <45% to account for inter-laboratory variability for indoor and outdoor air.<br>For soil gas sampling, spatial variability tends to be greater than in indoor or outdoor air sampling, so a RPD <50% was considered successful. | The accuracy of passive sampling was comparable to conventional methods in most comparisons. Some compounds showed notable biases with certain samplers, which was usually attributable to starvation, poor recovery, or poor retention. Generally, the precision and reproducibility was still acceptable, and instances of poor accuracy could be resolved using more careful selection of sorbents and occasional duplicate samples analyzed by conventional methods, to calculate "field-calibrated" uptake rates. |
| Precision | Replicate sampling to allow calculation of the mean, standard deviation and COV (standard deviation divided by the mean) | COV for passive samplers that is similar to or less than the COV for active samples. USEPA Method TO-15 (USEPA, 1996) specifies a COV of <30% as acceptable. | The COV for the passive samplers varied between tests, but many met the performance objective. Some compounds (MEK, NAPH) and samplers (SKC in low concentration lab tests) showed greater variability than others. |
| Cost | Professional time required for sampling, analytical fees for analysis, material costs, and shipping charges | Cost reduction compared to conventional methods that is sufficient to justify potential costs associated with regulatory acceptance of the passive samplers. | Simpler protocols and lower shipping costs result in savings. The savings are sufficient to off-set the cost of inter-method calibration samples, where the highest level of quality assurance/ quality control is desired. |
| **Qualitative Performance Objectives** | | | |
| Ease of use | Feedback from field personnel with practical experience on usability of technology and time required | Limited training required obtaining high quality data. | SKC Ultra II samples showed some challenges associated with sorbent transfer; otherwise field sampling and analytical methods are easy. Some additional effort is needed to select the sampler, sorbent and exposure duration for a given application compared to conventional methods. |

COV = coefficient of variation
MEK = 2-Butanone
RPD = relative percent difference

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# 4.0 SITE DESCRIPTIONS

The field sampling events were conducted at a total of five locations, some of which were not amenable to sampling of all three media (indoor air, outdoor air, and soil gas). A brief summary of key conditions at each site is provided in this section and the scope of work performed at each site is described in Section 5.

## 4.1 OLD TOWN CAMPUS BUILDING 3, SAN DIEGO, CA

The Annex to Building 3 at SPAWAR Systems Center Pacific Old Town Campus was used for the first field sampling event in March 2010. Processes inside the building are suspected to have produced waste oils, paint sludge, spent acids, plating materials, and degreasing solvents. Previous site assessments (CDM, 2009) identified the presence of VOCs in groundwater and soil vapor samples near the north end of Building 3. This site was developed using dredged bay sediments as backfill and 95% of the site is covered with buildings or pavement. The water table is a few feet below ground surface, consistent with the close proximity to the Pacific Ocean. Passive sub-slab samples were collected through a concrete slab outside of the building.

## 4.2 OF THE STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM RESEARCH HOUSE NEAR HILL AIR FORCE BASE, LAYTON, UT

The second field sampling event occurred in July and August 2010 at a residential property currently owned by Arizona State University (ASU) in Layton, Utah, near Hill Air Force Base, which is being used for VI research as part of the Strategic Environmental Research and Development Program (SERDP) project ER-1686. The building is a single story dwelling with a partially below-grade basement. Dissolved trichloroethene (TCE) and 1,1-Dichloroethene (11DCE) are present below the building and ASU has confirmed that VI of these compounds into the building is occurring (Johnson et al., 2013). Passive and active soil gas samples were collected from an array of probes installed in the front yard. The primary VOCs are TCE and 11DCE. TCE is the most widespread contaminant and occurs in the greatest concentrations.

## 4.3 THE U.S. ARMY CORPS OF ENGINEERS COLD REGIONS RESEARCH AND ENGINEERING LABORATORY, HANOVER, NH

The main Laboratory and Laboratory Addition at the U.S. Army Corps of Engineers (USACE) Cold Regions Research and Engineering Laboratory (CRREL) facility in Hanover, New Hampshire, was the site of the third field sampling event in November 2010. CRREL was established in 1961 by the USACE to research and develop equipment and procedures for applications in cold regions. TCE was used on the site as a refrigerant during the 1960s until the late 1980s. In 1970, a 10,000 gallon underground storage tank containing TCE near the main laboratory building and laboratory addition released liquid TCE. Previous sampling indicated TCE in indoor air at concentrations ranging from about 10 to about 100 $\mu g/m^3$ and in soil gas samples at concentrations several orders of magnitude higher. These concentrations are well within the detection ranges for the candidate passive samplers, therefore making CRREL a viable candidate site for the proposed research.

## 4.4 MARINE CORPS AIR STATION, CHERRY POINT, NC

Building 137 at the Marine Corps Air Station (MCAS) Cherry Point was used for the fourth field sampling event in January 2011. Building 137 is part of Operable Unit (OU) 1 and is referred to as Site 51 under the Federal Facilities Agreement. OU1 is an industrial area in the southern portion of the base and the former plating operations in Building 137 are suspected to have contributed to the OU1 Central Groundwater Plume (a combination of six source sites).

## 4.5 NAVAL AIR STATION, JACKSONVILLE, FL

Naval Air Station Jacksonville (NAS JAX), located in Jacksonville, Florida was used for the fifth field sampling event in January 2011. The Five-Year review (Tetra Tech, 2005) describes OU3 as a 134-acre site with a former dry cleaner operation. The majority of OU3 was recently re-paved. OU3 is underlain by inter-bedded layers of sand, clayey sand, and clay. The water table at OU3 is located within a few feet of ground surface. Groundwater Services Inc. (GSI, 2009) performed assessment of soil vapor concentrations and reported elevated VOC concentrations within soil and groundwater in the vicinity of Building 103. The primary contaminants of concern (COCs) are Tetrachloroethene (PCE), TCE, and related degradation products (cis-1,2-dichloroethene [cDCE] and VC).

# 5.0 EXPERIMANTAL DESIGN AND METHODS

The research program included laboratory and field-testing to provide data under both controlled conditions and "real-world" sampling conditions. Laboratory testing was divided into low concentration tests (1 to 100 $ppb_v$ range), which were intended to represent the typical range for indoor air monitoring, and high concentration tests (1 to 100 $ppm_v$ range) to represent the typical range of interest for soil vapor monitoring. Field testing was conducted at the five sites described in Section 4.

## 5.1 LIST OF VOLATILE ORGANIC COMPOUNDS INCLUDED IN LABORATORY TESTING

The list of VOCs included in both the low concentration and high concentration laboratory tests was selected to represent common VOCs and span a range of properties (Table 2).

**Table 2. Compounds tested and their key properties.**

| Analyte | Koc (mL/g) | Henry's Constant @ 25 °C (unitless) | Vapor pressure (atm) | Free Air Diffusion Coefficient ($cm^2/s$) | Water solubility (g/L) |
|---|---|---|---|---|---|
| 1,1,1-Trichloroethane (111TCA) | 135* | 0.70 | 0.16 | 0.078 | 1.3 |
| 1,2,4-Trimethylbenzene (124TMB) | 614 | 0.25 | 0.0020 | 0.061 | 0.057 |
| 1,2-Dichloroethane (12DCA) | 38* | 0.048 | 0.11 | 0.104 | 8.6 |
| MEK | 4.5 | 0.0023 | 0.10 | 0.081 | 220 |
| Benzene (BENZ) | 61* | 0.23 | 0.13 | 0.088 | 1.8 |
| Carbon tetrachloride (CTET) | 152* | 1.1 | 0.15 | 0.078 | 0.79 |
| NAPH | 1540 | 0.18 | 0.00012 | 0.059 | 0.031 |
| n-Hexane (NHEX) | 132 | 74 | 0.20 | 0.20 | 0.0095 |
| PCE | 265* | 0.72 | 0.024 | 0.072 | 0.21 |
| TCE | 94* | 0.40 | 0.095 | 0.079 | 1.3 |

*Values drawn from: http://www.epa.gov/superfund/health/conmedia/soil/pdfs/appd_k.pdf
All other values from http://www.epa.gov/region8/r8risk/vi.html
atm = atmosphere
$cm^2/s$ = centimeters squared per second
g/L = grams per liter
Koc - organic carbon partitioning coefficient

## 5.2 VARIETIES OF PASSIVE SAMPLERS USED

Several varieties of each type of passive sampler were used during the field events. Table 3 shows the varieties of each passive sampler used at each of the field sites for each of the media tested, including the number of replicates, the sorbent, and the uptake rate (where more than one uptake rate was available). After each stage of research, the data were reviewed to assess whether there were indications of data bias or variability attributable to the sorbent selection or choice of uptake rate configurations. In some cases, multiple sorbent types were tested to assess their relative performance (e.g., passive ATD tube samplers were used with both Tenax TA and Carbopack B in both the low concentration laboratory tests and passive soil vapor samples at the Layton house). Table 4 provides the uptake rates used and identifies those that were supplied by the vendors of

the passive samplers, and those that were calculated for this study. Where both values are included, the second value is considered more reliable and superseded the first during the course of the study.

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**Table 3. Number and varieties of samplers and sorbents used in the field-sampling program.**

| Sampler | Uptake Rate | Sorbent | Laboratory Desorption Method | Navy OTC3, San Diego, CA | | | Hill AFB, Layton, UT | CRREL, Hanover, NH | | | MCAS, Cherry Point, NC | | NAS Jacksonville, FL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Indoor Air | Outdoor Air | Passive Sub Slab | Passive Soil Vapor | Indoor Air | Outdoor Air | Flow-Through Sub Slab | Indoor Air | Outdoor Air | Passive Soil Vapor | Temporary Soil Vapor | Passive Sub Slab |
| Summa Canister | na | na | TO-15 | 3 x 3 | 1 x 3 | 2 x 1 | 1 x 9** | 3 x 3^ | 1 x 3^ | 1 x 36 | 3 x 3 | 1 x 1 | 2 x 10 & 1 x 15 | | 3 x 1 |
| 3M OVM 3500™ | Regular | Charcoal | Solvent | 3 x 3 | 1 x 3 | 2 x 1 | | 3 x 3 | 1 x 3 | 1 x 7 | 3 x 3 | 1 x 1 | 2 x 2 & 1 x 3 | | NS |
| ATD Tube | Regular | Chromosorb 106 | Thermal | 3 x 3 | 1 x 3 | 2 x 1 | | | | | | | | | |
| | | Tenax TA | Thermal | | | | 6 x 1 | | | | | | | | |
| | | Carbopack B | Thermal | | | | 6 x 1 | 3 x 3 | 1 x 3 | 1 x 7 | 3 x 3 | 1 x 1 | 2 x 2 & 1 x 3 | | |
| | Low uptake rate | Carbopack B | Thermal | | | | | | | | | | | | 3 x 1 |
| WMS™ | Regular | Anasorb 747 | Solvent | 3 x 3 | 1 x 3 | 2 x 1 | 6 x 1 | 3 x 3 | | 1 x 7 | | | | | |
| | | Carbopack B | Thermal | | | | | | 1 x 3 | | 3 x 3 | 1 x 1 | | | |
| | Low uptake rate | Anasorb 747 | Solvent | | | | | | | | | | 2 x 2 & 1 x 3 | 1 x 6 | 3 x 1 |
| SKC Ultra II™ | Regular | Charcoal | Solvent | | | | | 1 x 3; 1 x 2 | | 1 x 1 | | | | | |
| | | Chromosorb 106 | Thermal | 3 x 3 | 1 x 3 | 2 x 1 | | | | | | | | | |
| | | Carbopack X | Thermal | | | | | | | | | | | | |
| | | Carbograph 5 | Thermal | | | | | 1 x 1; 1 x 3 | 1 x 3 | 1 x 6 | 3 x 3 | 1 x 1 | | | |
| | Low uptake rate | Carbopack X | Thermal | | | | | | | | | | | | |
| | | Charcoal | Solvent | | | | 6 x 1 | | | | | | | | |
| | | Carbograph 5 | Thermal | | | | | | | | | | 2 x 2 & 1 x 3 | | NS |
| Radiello™ | Regular | Charcoal | Solvent | 3 x 3 | 1 x 3 | 2 x 1 | 6 x 1 | | | 1 x 7 | | | | | |
| | | Carbograph 4 | Thermal | | | | | 3 x 3 | 1 x 3 | | | | | | |
| | Low uptake rate | Carbograph 4 | Thermal | | | | | | | | 3 x 3 | 1 x 1 | | | |
| | | Charcoal | Solvent | | | | | | | | | | 2 x 2 & 1 x 3 | | 3 x 1 |

*Notes:*

Each cell contains information on the number of locations and number of samples in each location (i.e., 1 x 3 means one location with three samples and 3 x 1 means three locations with one sample each)

na - not applicable

** - conventional active samples included Summa canister/TO-15 analysis and on-site analysis with the Hapsite portable GC/MS

NS - No sample: several attempts were made to core 2-inch diameter holes (large enough to accommodate these samplers), but they were not successful, so these samples were not deployed

^ - Flow controllers were set higher than specified, so additional Summa canisters were needed to span the sample period, the results were composited to make triplicate samples

**Table 4. Uptake rates for the passive samplers (regular and low uptake varieties).**

| Analyte | Uptake Rate (mL/min) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | WMS[1] | | Radiello[2] | | SKC Ultra[3] | | | ATD Tube[4] | | OVM 3500[5] |
| | Regular | Low Uptake -Amber Vial | Regular (white) | Low Uptake (yellow) | Regular | Regular - Zero Velocity | Low Uptake | Regular | Low Uptake | Regular |
| 111TCA | 1.3 | | 62 | 20 | 13; 14 | 9.4 | 0.71 | 0.50 | | 31 |
| 124TMB | 13 | | 50 | | 13 | 9.9 | | 0.62 | | |
| 12DCA | 2.6 | | 77 | 23 | 13 | 12 | | 0.50 | | 33 |
| MEK | 1.3 | | 79 | | 17 | 6.3 | | 0.50 | | |
| BENZ | 2.2 | | 80 | 28 | 16 | 11 | | 0.35 | | 36 |
| CTET | 1.5 | | 67 | | 13 | 10 | | 0.50 | | |
| NHEX | 1.3 | | 66 | | 14 | 9.6 | | 0.50 | | |
| NAPH | 26 | | 25 | | 13 | -- | | 0.50 | | |
| PCE | 5.4 | 1.1 | 59 | 25 | 13 | 10 | 0.55 | 0.41 | 0.041 | 28 |
| TCE | 3.3 | 0.88 | 69 | 27 | 15 | 11 | 0.58 | 0.50 | 0.050 | 31 |
| cis-1,2-Dichloroethene | 1.9 | 0.90; 0.53 | 64 | 32 | 15 | | | 0.47; 0.51 | 0.050 | 29; 35 |
| tDCE | 1.3 | 0.62; 0.51 | 62 | 32 | 15 | | | 0.45; 0.51 | 0.050 | 28; 35 |
| VC | 0.48 | | | | | | | | | 42 |
| 11DCE | 0.82 | | 79 | 32 | 12 | | 1.3 | 0.57 | | 35; 33 |
| 1,1,2-Trichloroethane | 3.3 | | | 20 | 13 | | | 0.50 | | 30 |
| 11DCA | 1.2 | | | 23 | 12 | | | 0.50 | | 33 |
| Toluene | 2.0; 4.2 | | | 30 | 15 | | | 0.32 | 0.032 | 31 |
| Ethylbenzene | 6.6 | | | 26 | 13 | | | 0.30 | | 27 |
| m,p-Xylene | 6.3 | | | 27 | 13 | | | 0.30 | | 27 |
| o-Xylene | 6.2 | | | 25 | 12 | | | 0.30 | | 27 |
| Black - published value | | | | | | | | | | |
| Red - calculated value | | | | | | | | | | |

Sources: 1 – Seethapathy and Górecki, 2010a,b
2 – Fondazione Salvatore Maugeri, 2006
3 – SKC, 2008, 2012 or pers. comm. with Linda Coyne of SKC
4 - Subramanian, 1995; ISO 16017-2, ASTM D6196-03 or pers. comm. Derrick Crump of CU
5 – 3M, 2013a.

tDCE = trans 1,2-Dichloroethene
11DCA = 1,1-Dichloroethane

## 5.3 LOW-CONCENTRATION LABORATORY TESTING

The low concentration laboratory testing (McAlary et al., 2015) consisted of inter-laboratory testing and 24 chamber tests conducted to assess the influence of five factors (temperature, humidity, sample duration, concentration, and face velocity). The design details of the chamber are shown in Figure 2. Several laboratories were used in this study so inter-laboratory and intra-laboratory variances were evaluated by a two-sample inter-laboratory study (a.k.a., a Youden pair experiment) as described by Wernimont and Spendley (1989) and Miller and Miller (1988). The inter-laboratory testing consisted of exposing two duplicate pairs of each of the five passive samplers to VOCs at the midpoints of concentration (about 50 $ppb_v$, except for NAPH at 5 $ppb_v$);

temperature (about 22°C); humidity (about 60 percent relative humidity [%RH]); face velocity (0.23 meters per second [m/s]); and exposure duration (4 days) in the exposure chamber.

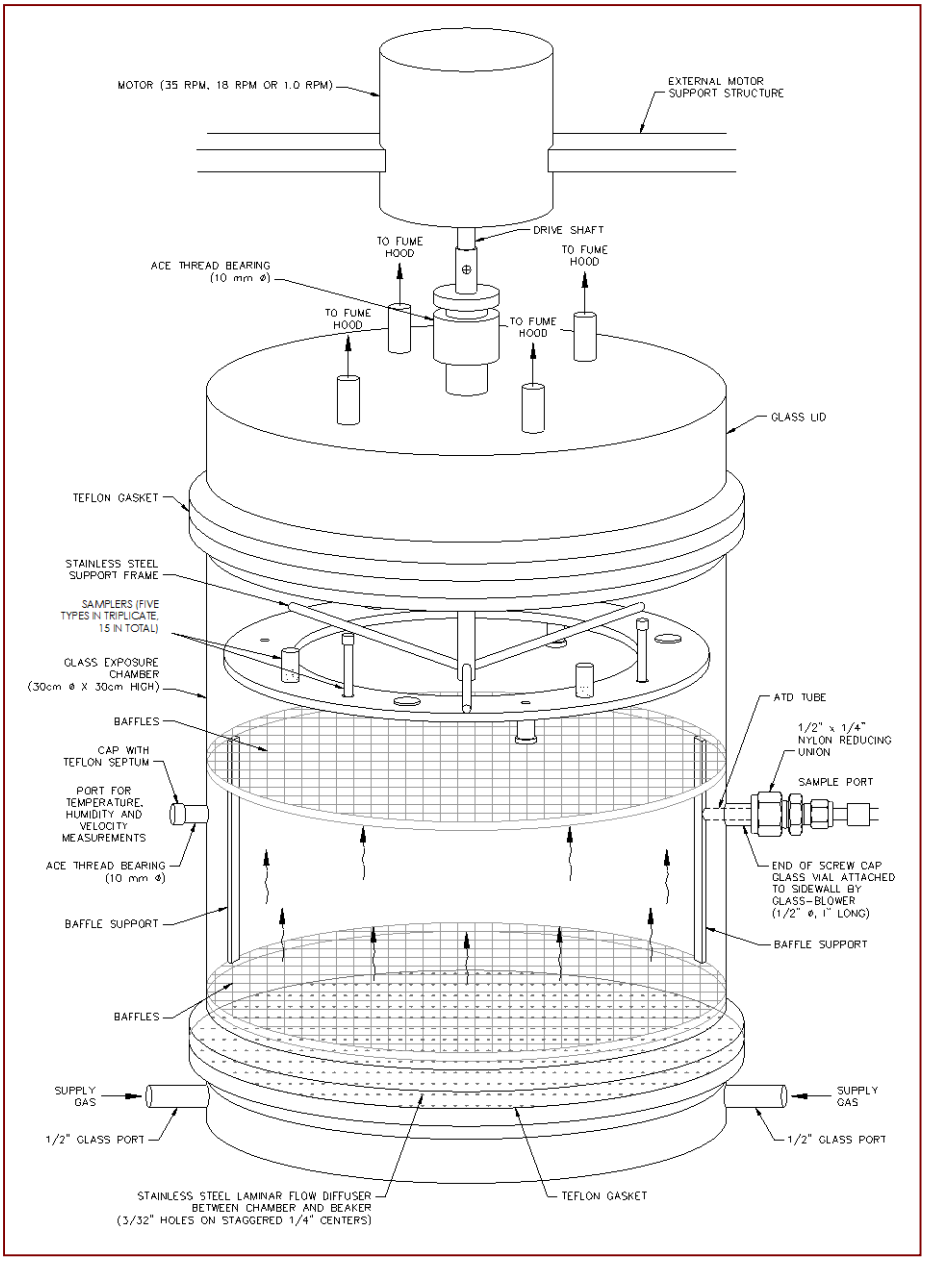



**Figure 2. Design details of the exposure chamber for the low concentration tests.**

Six identical chamber tests were performed to assess the intrinsic (random) variability in the concentrations measured by the passive samplers. This test was used to perform a one-way analysis of variance (ANOVA) to determine the variance that is unavoidable, and not caused by changes in the five key factors; all five factors were held constant at the center points of their respective ranges (duration = 4 days, concentration = 50 $ppb_v$, temperature = 22$^o$C, humidity = 60%RH and face velocity = 0.23 m/s). Each test included all five candidate samplers in triplicate. The

concentrations reported for each of the sampler types were compared to the results of active sampling and analysis by pumped ATD tubes and USEPA Method TO-17 to evaluate whether the passive sampler results were statistically different than the active sample controls for each of the 10 compounds and each of the five samplers. The data were analyzed to assess precision by calculating the COV among replicate samplers (three per chamber for each type) and accuracy by comparing the passive sampler results to active (pumped ATD tube/TO-17) sampler results. Two additional tests were performed at the center-points of all five factors at the middle of the Factorial Testing, to assess whether the experimental results were reproducible over time.

A fractional factorial design was used to evaluate the effect of each of the five main factors (temperature from 17 to 30°C; humidity from 30 to 90%; concentration from 1 to 100 $ppb_v$; face velocity from 0.014 to 0.4 m/s; and exposure duration from 1 to 7 days). The design of this test was a $2^{(k-1)}$ fractional factorial design (one-half of a full $2^k$ full factorial design, where k is the number of controllable factors). Each analyte relative concentration (passive sampler concentration divided by active sampler concentration [$C/C_o$]) represents a response, of which there were 3,600 in total.

## 5.4 HIGH CONCENTRATION LABORATORY TESTING

Controlled experiments were conducted at concentrations of 1, 10, and 100 parts per million by volume ($ppm_v$) to evaluate the performance of the samplers for concentrations of interest in soil vapor monitoring (McAlary et al., 2014b). Each sampler was deployed for 30 minutes with three randomized replicates. Additional exposure tests were performed using available low uptake rate varieties of the passive samplers at the midpoint concentration (10 $ppm_v$), with the supply gas flow rate held at 100 mL/min for the first test to maintain consistency with the rest of the experiments and with the supply gas shut off for the second test to assess the performance of the samplers in a setting with no net gas flow ("stagnant" conditions), which is a worst-case condition for negative biases attributable to the starvation effect. A schematic diagram of the apparatus is shown in Figure 3.

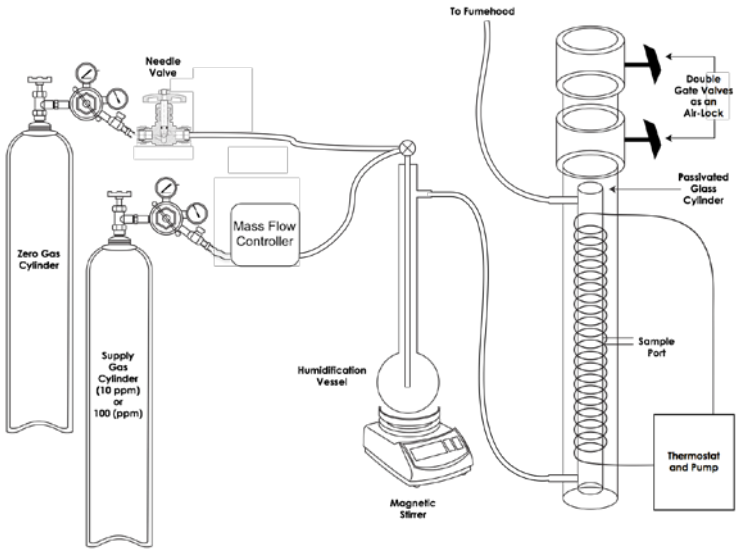



**Figure 3. Schematic diagram of high concentration laboratory experimental apparatus.**

## 5.5 MATHEMATICAL MODELING OF UPTAKE RATES FOR SOIL VAPOR SAMPLING

This research included derivation from first principles of the processes and mechanisms influencing the passive sampling process, and verification through field testing. Two models (transient and steady-state) were used to simulate the passive sampling process (McAlary et al., 2014a). The transient model simulates an empty void space (i.e., no passive sampler), which is a reasonable approximation because a passive sampler with an uptake rate low enough to minimize the starvation effect would only become significant as the concentration inside the void space approached steady-state (i.e., equal to the concentration in the soil at $r_3$, which is far enough away to be unaffected by mass lost to the void space). The transient model also assumes the vertical interval of the void space is small enough that both the soil vapor concentrations and the geologic material are essentially uniform over that interval. The steady-state rate of mass transfer of vapors into the borehole via vapor diffusion through the surrounding soil (M1) is given by Carslaw and Jaeger (1959):

$$M1 = \frac{2\pi D_{eff}(C_{sg} - C_{bh})}{\ln(\frac{r_3}{r_2})} \tag{2}$$

The rate of mass uptake by the sampler (M2) is given by:

$$M2 = C_{bh}\ x\ UR \tag{3}$$

Setting M1 = M2 gives:

$$UR\left[\frac{mL}{min}\right] = \frac{2\pi h[cm]D_{eff}[\frac{cm^2}{s}](1-\delta)}{\ln(\frac{r_3}{r_2})\delta}\ x\ 60[\frac{s}{min}] \tag{4}$$

where:

$$D_{eff} = D_{air}\frac{\theta_a^{10/3}}{\theta_T^2} + \frac{D_w}{H}\frac{\theta_w^{10/3}}{\theta_T^2} \tag{5}$$

Simulations were performed for TCE using the following parameters:

| Parameter name | Symbol | Units | Value |
|---|---|---|---|
| Free air diffusion coefficient | $D_{air}$ | $cm^2/s$ | 0.069 |
| Aqueous diffusion coefficient | $D_w$ | $cm^2/s$ | 0.00001 |
| Henry's Law Constant | H | µg/L air / µg/L water | 0.35 |
| Total porosity | $\theta_T$ | Volume of voids / total volume of soil | 0.375 |
| Water-filled porosity | $\theta_w$ | Volume of water / total volume of soil | 0.01 to 0.36 |
| Air-filled porosity | $\theta_a$ | $\theta_T - \theta_w$ | 0.365 to 0.015 |
| Radius at which soil vapor concentrations are unaffected by the borehole and passive sampler | $r_3$ | cm | 100 |
| Borehole radius | $r_2$ | cm | 1.25 |
| Concentration inside the void space of the borehole | $C_{bh}$ | $\mu g/m^3$ | calculated |
| Concentration in the surrounding soil | $C_{sg}$ | $\mu g/m^3$ | Nominally 100 |

The mathematical modeling (Figure 4) indicated that an uptake rate of 10 mL/min might be acceptable for very dry soil if the data quality objective was to quantify concentrations within a factor of 2 (i.e., $\delta = C_{bh}/C_{sg} = 0.5$). However, an uptake rate of 1 mL/min would be more suitable for soils with a water-filled porosity up to 15% in a soil with total porosity of 37.5%, assuming a more stringent data quality objective of +/-25% (i.e., $\delta = 0.75$). Progressively lower uptake rates would be required to further reduce the low bias or meet typical data quality objectives in very wet soils.

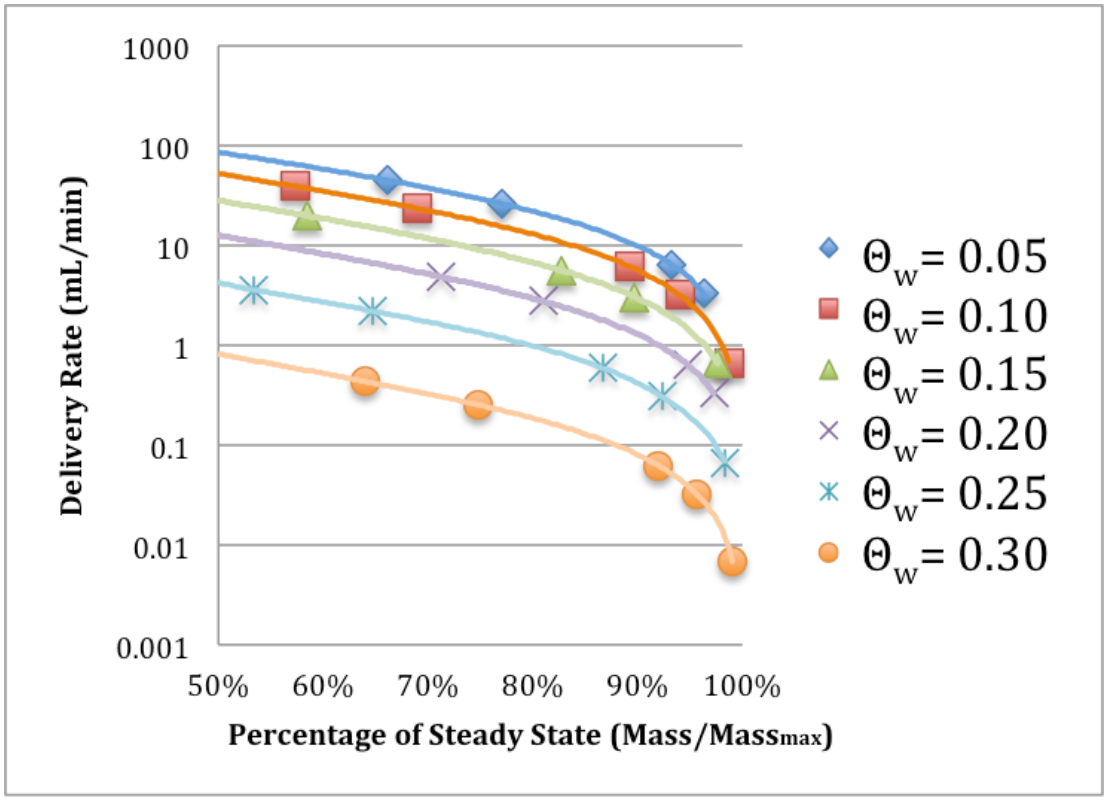



**Figure 4. Relationship between the diffusive delivery rate of TCE vapors into the void space versus the percent of mass entering the void space.**

(where $Mass_{max}$ is the maximum TCE vapor mass in the void space at equilibrium, assuming a 2.5 cm [1-inch] diameter borehole in a soil with 37.5% total porosity, initial soil vapor concentration of 100 µg/m$^3$ and no removal of mass by a passive sampler).

## 5.6 INDOOR AND OUTDOOR AIR FIELD SAMPLING

All indoor and outdoor air samples at each location were collected in reasonably close proximity (i.e., within a few feet, but not so close as to impose interference between them) and about 3 to 5 feet above the floor surface (approximately the breathing zone), as shown in Figure 5. The passive samplers were placed on shelves or hung and secured using thin gauge wire. Summa canisters were placed in close proximity to the passive samplers.

**Figure 5. Typical layout of indoor air sampling array.**

## 5.7 PASSIVE SOIL VAPOR SAMPLING

**Navy Officer Training Command (OTC):** Passive sub-slab samples were collected in two locations with five passive devices and one active sample (Summa canister with analysis by EPA Method TO-15) in each location. Both locations were outside of a building where a concrete slab was accessible for drilling and coring. The primary COC was TCE. Sampler deployment durations were 2 hr at location SS-2 and 15 hr at location SS-5 (longer deployment was required to collect detectable mass of VOCs in the area of lower concentrations, based on the PID screening results of 10 $ppm_v$ and 0.1 $ppm_v$, respectively).

**Layton House:** Six passive soil gas monitoring probes were installed using a 10-cm (4-in) diameter hand-auger to a depth of about 3.6 m (12 ft) in a circular pattern with a radius of about 1 m. Each probe was constructed of a 3 m (10 ft) length of 5 cm (2-in) diameter Schedule 40 PVC pipe, with stilts at the bottom to suspend the pipe 0.6 m (2 ft) above the bottom of the borehole (Figure 6). The deployment durations ranged from 1 to 11.7 days, with each of six sampler types deployed once in each probe, plus one repeat of the first set of samples (a Latin Square design). Active samples were collected after purging at least 6 L from each probe using a vacuum chamber and Tedlar bag at the beginning and end of the experiment, plus at the start of each new deployment period. Field screening was performed using a field-calibrated Phocheck+™ PID to verify steady readings prior to active sample collection. Most of the active samples were analyzed with a Hapsite™ transportable GC/MS (Inficon) and two rounds of active samples were collected in Summa canisters and analyzed by EPA Method TO-15.

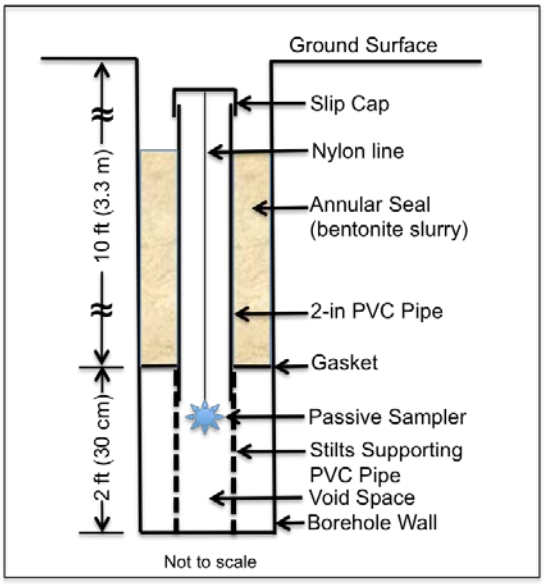



**Figure 6. Schematic diagram of the passive soil vapor probe at the Layton house, Utah.**

**NAS JAX:** Three types of samples were collected at NAS JAX: (1) sub-slab samples inside a single-story, slab-on-grade office building; (2) exterior soil gas samples in cased probes similar to those used at the Layton House; and (3) exterior soil gas samples in an uncased hole. Exterior passive soil gas samples were collected using three 5 cm (2-in) diameter probes in 10 cm (4-in) diameter hand-augered holes. The probes were constructed with void space lengths of about 15, 30, and 45 cm (6, 12, and 18-in) to assess whether the void volume affected the results. The samplers were deployed for 20, 40, and 60 minutes to assess whether the deployment duration affected the results. A total of seven passive samples were collected using each of the five samplers and 35 Summa canister samples were collected for analysis by USEPA Method TO-15 (1:1 ratio). This experimental design is a randomized 2-factor, one-half fraction, fractional factorial with triplicates at the center-points (40 minute exposure in the 30 cm tall void).

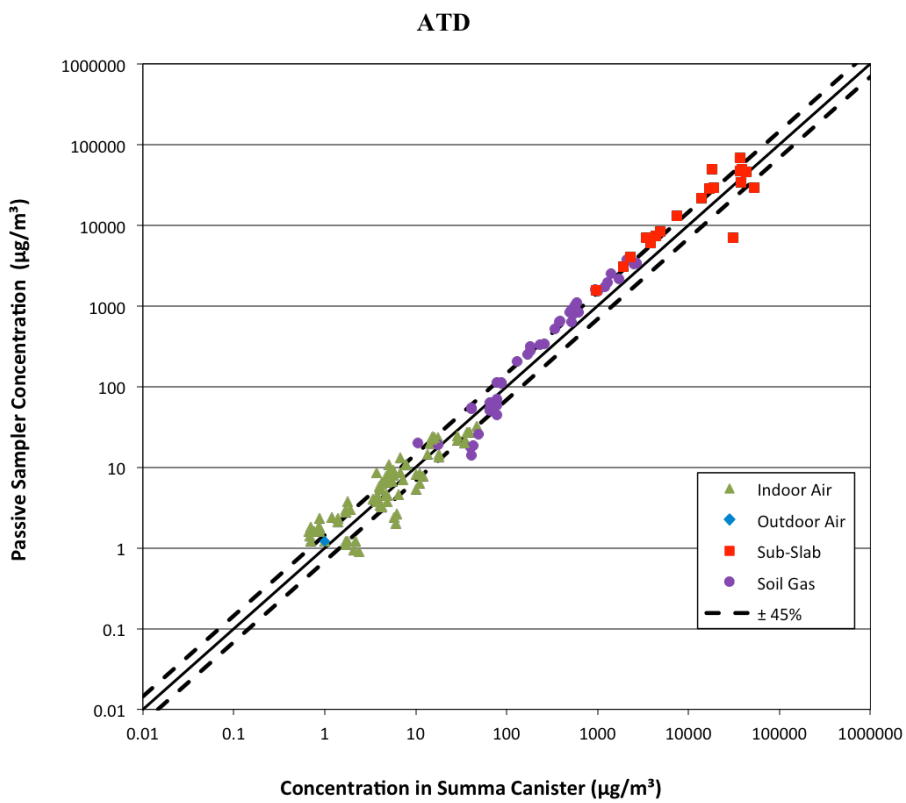
Sub-slab vapor samples were collected at three locations. It was not possible to drill 5 cm diameter holes through the floor (needed to accommodate the 3M OVM and SKC samplers) because steel reinforcing bars were repeatedly encountered and eventually broke the teeth on the concrete hole-saw. The ATD, WMS, and Radiello passive samplers were tested through a 1-inch diameter hammer-drill hole in the floor slab. In each of the three locations, one sample was collected with each type of passive sampler (1 hour duration) and one Summa canister.

Temporary passive soil gas samples were also collected at NAS JAX in a single hole drilled to a depth of 1.6 m (5 ft) with a 2.54-cm (1-in) diameter hammer-drill bit. No PVC pipe was installed in the temporary drilled hole and the sandy soil was sufficiently cohesive to stand open without caving. The low-uptake WMS sampler was deployed for six different sample durations ranging from 1.7 to 18.9 hours (randomized). The hole was sealed during the deployment period using a polyurethane foam plug inside a polyethylene bag of 1-in diameter, which was set to a depth of 1.2 m (4 ft) below ground. The location of the temporary probe was only a few feet from the exterior passive soil gas probes, so the Summa canister data from the nearest exterior passive soil gas probe was used as a baseline for comparison. The field-sampling study is published as McAlary

et al. (2014c). A fractional factorial test using passive samplers in a flow-through cell was also conducted, but not described in this summary report for brevity (it is described in the Final Report and McAlary et al., 2014d).

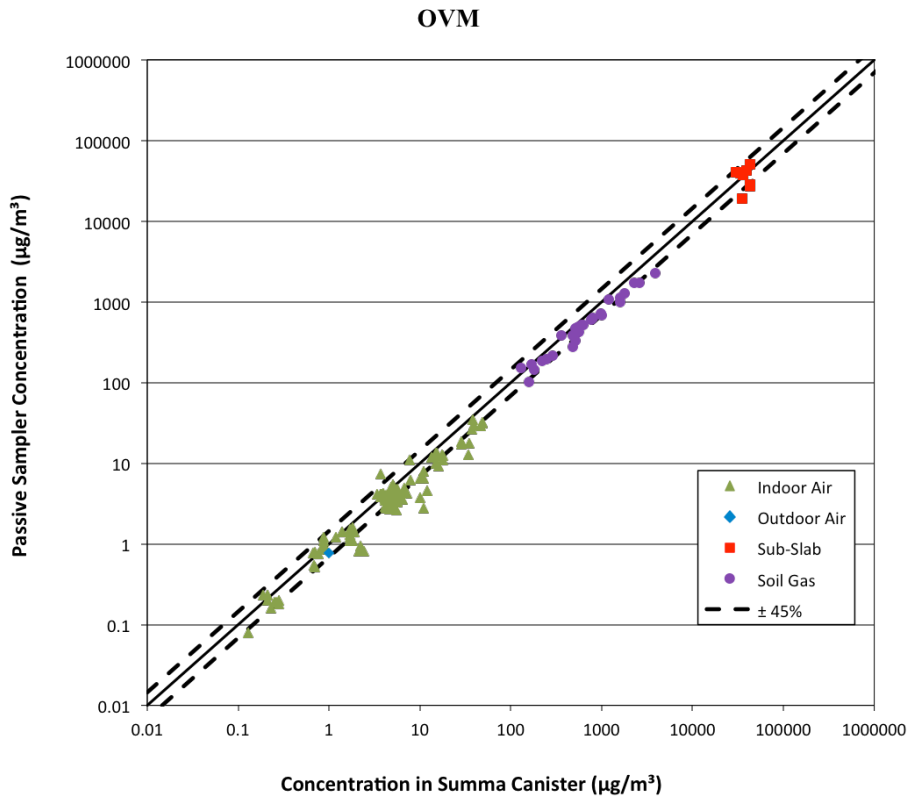
## 5.8 SAMPLING RESULTS

A summary of the correlation between each of the passive samplers and active (TO-15 or TO-17) controls is shown in Figures 7a to e. The data for each sampler type for indoor air, outdoor air, sub-slab gas, and/or soil gas from all five field sites is presented. These plots exclude the results with easily explained biases from: (a) poor retention of the analytes on the sampler (UR x t > RMSV, MEK in high humidity samples with activated carbon); (b) poor recovery of the analytes from the sorbent (e.g., NAPH with activated carbon); (c) starvation effects (samplers with uptake rates higher than a few mL/min in subsurface sampling or UR x t > void volume); or (d) blank contamination. Each of these plots includes a line from the lower left to the upper right corners representing the ideal correlation. There are some outliers in the correlation, which may be attributable to individual compounds for which the uptake rate for a particular sampler may be poorly known or calculated, so there are opportunities for improved data quality over time as more studies are conducted and the uptake rates become supported with more data. Nevertheless, the correlations show generally good agreement over a range of up to seven orders of magnitude in concentration, for sample durations are short as 10 minutes and as long as 12 days for several different VOCs and under a wide range of conditions of temperature, humidity and air velocity.

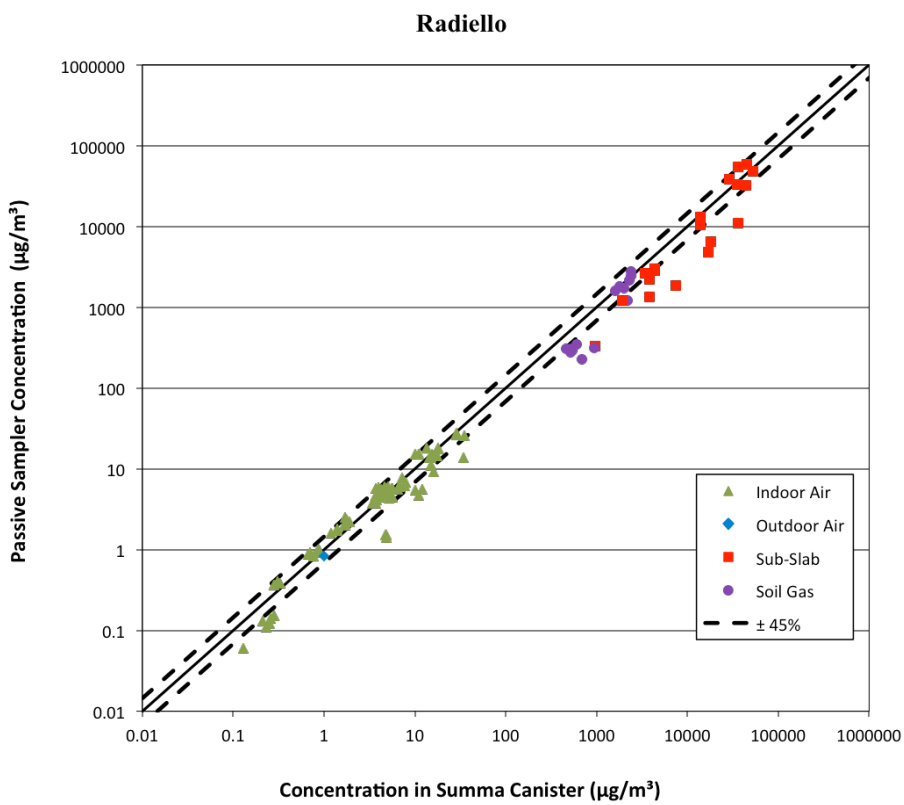



**7a**

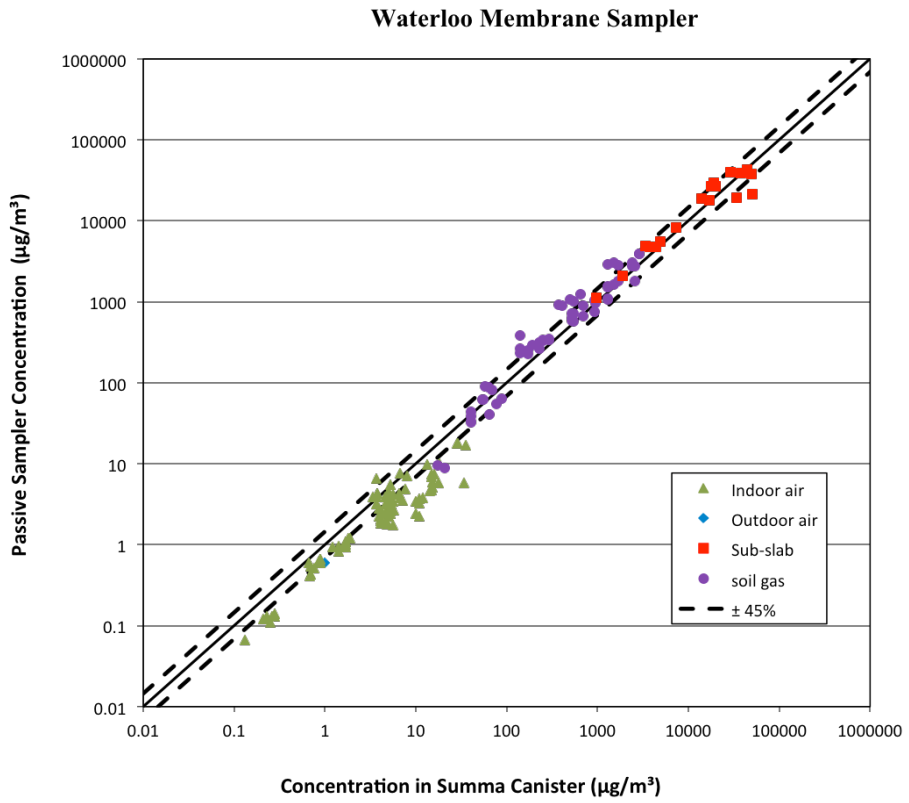
**Figure 7. Correlations for all passive samplers in all field demonstrations (7a through 7e).**


OVM
Passive Sampler Concentration (µg/m³)
Concentration in Summa Canister (µg/m³)
1000000
100000
10000
1000
100
10
1
0.1
0.01
Indoor Air
Outdoor Air
Sub-Slab
Soil Gas
± 45%

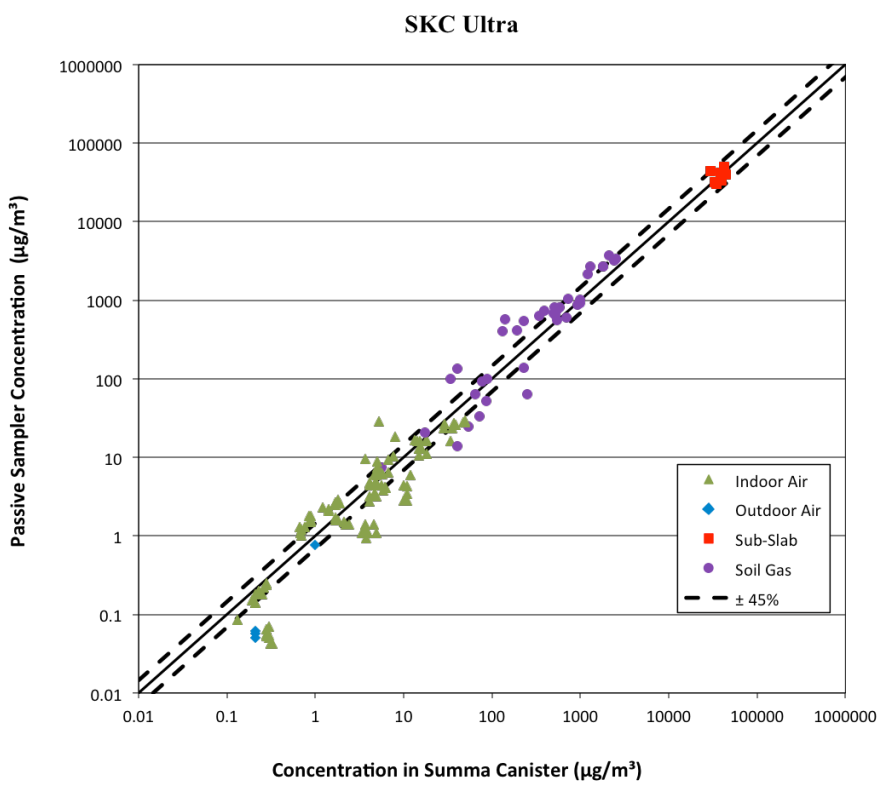
**7b**


Radiello
Passive Sampler Concentration (µg/m³)
Concentration in Summa Canister (µg/m³)
1000000
100000
10000
1000
100
10
1
0.1
0.01
Indoor Air
Outdoor Air
Sub-Slab
Soil Gas
± 45%

**7c**


Waterloo Membrane Sampler
Passive Sampler Concentration (µg/m³)
Concentration in Summa Canister (µg/m³)
1000000
100000
10000
1000
100
10
1
0.1
0.01
Indoor air
Outdoor air
Sub-slab
soil gas
± 45%

**7d**


SKC Ultra
Passive Sampler Concentration (µg/m³)
Concentration in Summa Canister (µg/m³)
1000000
100000
10000
1000
100
10
1
0.1
0.01
Indoor Air
Outdoor Air
Sub-Slab
Soil Gas
± 45%

**7e**

# 6.0 PERFORMANCE ASSESSMENT

## 6.1 LOW CONCENTRATION LABORATORY TESTS

The accuracy performance objective (RPD <45%, corresponding to $C/C_o$ range of 0.63 to 1.58) was met for at least 7 of the 10 compounds for each of the passive samplers in the overall average results of the low concentration laboratory tests (shown using boldface in Table 5). The mean $C/C_o$ (passive concentration/active control) values were calculated for all 24 chamber tests, which included eight tests at the center-points and 16 tests conducted at high and low set points of the exposure duration, face velocity, temperature, humidity, and concentration, so they represent the average accuracy over a wide range of indoor air monitoring conditions. Specific conditions may have different results. In Table 5, a column has been added comparing the average results of the active samples to the concentrations calculated from the mass flow controller measurements. Three of the passive samplers showed a negative bias for MEK, but that may also be attributable to a positive bias in the active sampler results.

**Table 5. Mean $C/C_o$ values for the low concentration laboratory tests.**

| Mean $C/C_o$ (passive/active) | ATD / Carbopack B | ATD / Tenax | WMS | Radiello | SKC | Active/ Calculated |
|---|---|---|---|---|---|---|
| 111TCA | **0.72** | **0.67** | **1.15** | **0.95** | **0.80** | 0.79 |
| 124TMB | **0.73** | **0.69** | 0.54 | **1.13** | **0.69** | 0.89 |
| 12DCA | 0.60 | **0.67** | **0.86** | **0.83** | **0.75** | 0.87 |
| BENZ | 1.71 | **1.07** | **0.99** | **0.90** | **0.95** | 0.72 |
| CTET | **0.82** | **0.67** | **1.18** | **0.81** | 0.55 | 0.98 |
| NHEX | **1.12** | 0.55 | **1.15** | **0.80** | **0.70** | 0.86 |
| MEK | 0.21 | **1.00** | **1.12** | 0.62 | 0.46 | 1.33 |
| NAPH | **0.90** | **0.98** | 0.17 | 2.26 | 0.36 | 0.82 |
| PCE | **1.15** | **0.85** | **0.72** | **1.02** | **0.98** | 0.94 |
| TCE | **0.91** | 0.62 | **0.80** | **0.91** | **0.87** | 0.91 |

Mean $C/C_o$ is the average of 24 passive/active concentration ratios (one for each chamber test)
**boldface**: average $C/C_o$ values of 0.63 to 1.58, which meet the success criteria: RPD < +/-45%
Active ATD tube data was compared to concentrations calculated from mass flow controllers

Precision can be calculated two ways:

1) *Intra-chamber:* calculate the COV of three replicates for each sampler type and each compound within each of 24 chambers, and then take the average (arithmetic mean) of those values across all 24 chambers. This provides a measure of the precision of the samplers that can be expected when they are exposed to a specific set of conditions (Table 6a).

2) *Inter-chamber:* calculate the $C/C_o$ value for each compound and sampler as an average of three replicates within each chamber, and then calculate the COV for all 24 such values measured in each chamber. This provides a measure of the precision of the sampler across a wide range of conditions (Table 6b).

**Table 6a. Intra-Chamber COV values for the low concentration laboratory tests.**

| Mean intra-chamber COV | ATD / Carbopack B | ATD / Tenax | WMS | Radiello | SKC | Active ATD/ Calculated |
|---|---|---|---|---|---|---|
| 111TCA | **7%** | **3%** | **7%** | **5%** | **14%** | **13%** |
| 124TMB | **5%** | **5%** | **7%** | **4%** | **22%** | **7%** |
| 12DCA | **8%** | **3%** | **6%** | **4%** | **12%** | **9%** |
| MEK | 47% | **5%** | **13%** | **11%** | **23%** | **15%** |
| CTET | **4%** | **6%** | **8%** | **4%** | **8%** | **12%** |
| NHEX | **7%** | **2%** | **7%** | **7%** | **16%** | **7%** |
| BENZ | **5%** | **6%** | **12%** | **3%** | **10%** | **6%** |
| NAPH | **6%** | **12%** | **7%** | **6%** | **16%** | **7%** |
| PCE | **2%** | **3%** | **6%** | **3%** | **6%** | **5%** |
| TCE | **3%** | **2%** | **5%** | **3%** | **16%** | **5%** |

Mean intra-chamber COV is the average of 24 COV values, from three replicates in each chamber
**boldface**: COV value meets the success criteria: < 30%

**Table 6b. Inter-Chamber COV values for the low concentration laboratory tests.**

| Mean inter-chamber COV | ATD / Carbopack B | ATD / Tenax | WMS | Radiello | SKC | Active ATD/ Calculated |
|---|---|---|---|---|---|---|
| 111TCA | **24%** | **27%** | **26%** | 35% | 51% | **18%** |
| 124TMB | **12%** | **16%** | 42% | **25%** | 55% | **17%** |
| 12DCA | 31% | 32% | 35% | **28%** | 61% | **23%** |
| MEK | 88% | 69% | 116% | 70% | 65% | **19%** |
| CTET | **25%** | **26%** | 31% | **28%** | 59% | **19%** |
| NHEX | 37% | 45% | 56% | **28%** | 39% | **27%** |
| BENZ | **25%** | 31% | **26%** | **16%** | 40% | **19%** |
| NAPH | **18%** | **25%** | 128% | 46% | 58% | **17%** |
| PCE | **13%** | **14%** | 34% | **27%** | **26%** | **18%** |
| TCE | **11%** | **17%** | 34% | **30%** | 51% | **16%** |

Inter-chamber COV is the COV of 24 average $C/C_o$ values, one from each chamber test
**boldface**: COV value meets the success criteria: < 30%

The intra-chamber precision met the success criteria (COV <30%) for almost all of the passive sampler/compound combinations, except for MEK with the ATD/Carbopack B sampler and the SKC Ultra II was marginal for 124TMB and MEK. The passive samplers had a lower COV than the active control (pumped ATD tubes) in 68% (34/50) cases and 80% of the cases where the SKC Ultra II is not included. This demonstrates that the passive samplers have a high precision and provide very reproducible results under a specific set of conditions.

The inter-chamber comparison showed higher COV values because the high and low values of the test chamber factors (sample duration, face velocity, temperature, humidity, and concentration) caused additional variability. Even the active (pumped) ATD tubes showed an inter-chamber COV that was marginal compared to the success criteria (<30%). The passive samplers showed generally higher COV values and a wider range between compounds, which shows they are more sensitive than the pumped ATD tubes to the test conditions.

Statistical analysis of the low concentration laboratory test data using analysis of variance (ANOVA) showed that the temperature, humidity, face velocity, concentration, and sample

duration had a statistically significant effect on the passive sampler concentrations at the 5% level of significance in 126 of 250 combinations of sampler/compound (i.e., about half of the cases). To account for specific environmental conditions at the time of sampling, some frequency of inter-method verification samples can be included in a passive sampling campaign to provide data that can be used to derive "field-calibrated" uptake rates, for maximum accuracy. For example, in a sampling campaign of 100 passive samplers, 5 or 10 active samples could be collected beside the passive samplers as a calibration check to verify the uptake rates for the site-specific conditions and chemicals. Once calibrated, the high precision of the passive samplers provides confidence in their ability to quantify concentrations for other samples collected under similar conditions. Field-calibration may or may not be necessary or appropriate, depending on whether the data are planned for screening, risk assessment, periodic monitoring, or other uses. I also depends on the degree to which a particular sampler has already been calibrated to a particular compound, which can be resolved in the design stage of the sampling program.

## 6.2 HIGH CONCENTRATION LABORATORY TESTS

The accuracy of the passive samplers in the high concentration tests is summarized in Table 7a, which shows the relative concentration ($C/C_o$), where C is the average passive sampler concentration and $C_0$ is the average Summa canister concentration for each compound, sampler and concentration. The $C/C_o$ values were within the range of 0.6 to 1.7 (which meets the performance criteria for soil gas sampling of an RPD of 50%) in 107 out of 133 (80%) of the sampler/compound/concentration combinations, shown in bold in Table 7a. MEK did not meet the success criteria in 10 of 12 cases and negative bias was common for 124TMB and NAPH.

**Table 7a. Average relative concentrations ($C/C_o$) for high concentration tests.**

| **$C/C_o$ for 1ppm** | **MEK** | **NHEX** | **12DCA** | **111TCA** | **BENZ** | **CTET** | **TCE** | **PCE** | **124TMB** | **NAPH** |
|---|---|---|---|---|---|---|---|---|---|---|
| WMS Anasorb 747 | ND | **1.4** | **0.63** | **0.60** | 0.50 | **0.60** | **0.70** | **0.66** | 0.55 | 0.12 |
| ATD Tenax TA | ND | **1.0** | **0.61** | 0.45 | **1.7** | **0.63** | **1.2** | **0.82** | 0.55 | **1.1** |
| Radiello Charcoal | 0.41 | **0.80** | **0.77** | **0.89** | **0.80** | **0.73** | **0.85** | **0.75** | 0.28 | ND |
| 3M OVM 3500 | 0.21 | **0.65** | **0.60** | **0.64** | **0.83** | **0.62** | **0.73** | **0.82** | **0.63** | ND |
| SKC Carbograph 5 | 1.9 | **0.76** | **0.66** | **0.63** | **0.96** | 0.49 | **0.58** | 0.58 | **0.60** | **1.1** |
| **$C/C_o$ for 10ppm** | **MEK** | **NHEX** | **12DCA** | **111TCA** | **BENZ** | **CTET** | **TCE** | **PCE** | **124TMB** | **NAPH** |
| WMS Anasorb 747 | 0.54 | **0.70** | **0.68** | **0.65** | **0.75** | **0.69** | **0.74** | **0.71** | **0.83** | 0.35 |
| ATD Tenax TA | ND | **1.0** | **0.89** | **0.60** | **1.6** | **0.79** | **1.2** | **0.96** | **0.88** | **1.3** |
| Radiello Charcoal | 0.47 | **0.78** | **0.73** | **0.82** | **0.77** | **0.70** | **0.83** | **0.77** | 0.35 | ND |
| 3M OVM 3500 | 0.22 | **0.70** | **0.68** | **0.68** | **0.68** | **0.74** | **0.85** | **0.96** | **0.95** | 0.46 |
| SKC Charcoal | 0.40 | **1.1** | **1.1** | **1.0** | **0.98** | **0.99** | **1.0** | **1.2** | **1.2** | ND |
| **$C/C_o$ for 100ppm** | **MEK** | **NHEX** | **12DCA** | **111TCA** | **BENZ** | **CTET** | **TCE** | **PCE** | **124TMB** | **NAPH** |
| WMS Anasorb 747 | **0.80** | **0.86** | **0.92** | **0.82** | **1.0** | **0.90** | **1.0** | **1.2** | NT | NT |
| ATD Tenax TA | **1.0** | **1.4** | **1.4** | **1.2** | 2.7 | **1.2** | 2.1 | 1.9 | NT | NT |
| Radiello Charcoal | 0.58 | **1.1** | **1.1** | **1.3** | **1.2** | **1.1** | **1.4** | **1.4** | NT | NT |
| 3M OVM 3500 | 0.30 | **0.86** | **0.88** | **0.94** | **0.86** | **0.96** | **1.2** | **1.4** | NT | NT |
| SKC Charcoal | 0.37 | **1.2** | **1.4** | **1.3** | **1.1** | **1.3** | **1.4** | 1.8 | NT | NT |

The precision of the passive samplers and Summa canisters is summarized in Table 7b, which shows the COV for all the compound and sampler combinations. The COV values for the passive samplers were less than or equal to the COV values for the Summa canister samples in 69% of the cases (91/132). The COV for the passive samplers met the performance objective of 30% or less

in all but one case (NHEX for the WMS sampler). The COV values were generally lower at the 10 and 100 $ppm_v$ levels where the mass was more readily resolved against reporting limits (except for the Radiello, which had the highest COV values at 10 $ppm_v$). The COV for Summa canister analyses averaged over 20% for 124TMB and NAPH.

**Table 7b. COV measured in high concentration tests.**

| COV at 1 ppm | MEK | NHEX | 12DCA | 111TCA | BENZ | CTET | TCE | PCE | 124TMB | NAPH |
|---|---|---|---|---|---|---|---|---|---|---|
| WMS Anasorb 747 | ND | 32% | 3% | 6% | 6% | 5% | 0% | 5% | 6% | 18% |
| ATD Tenax TA | ND | 4% | 7% | 10% | 8% | 13% | 4% | 5% | 15% | NC |
| Radiello Charcoal | 3% | 14% | 9% | 11% | 12% | 9% | 11% | 15% | 19% | ND |
| 3M OVM 3500 | 3% | 9% | 12% | 8% | 20% | 11% | 8% | 9% | 8% | ND |
| SKC Carbograph 5 | 5% | 13% | 16% | 18% | 5% | 21% | 18% | 18% | 19% | 14% |
| Summa Canister | 17% | 15% | 17% | 16% | 18% | 14% | 17% | 20% | 26% | 29% |
| **COV at 10 ppm** | **MEK** | **NHEX** | **12DCA** | **111TCA** | **BENZ** | **CTET** | **TCE** | **PCE** | **124TMB** | **NAPH** |
| WMS Anasorb 747 | 11% | 5% | 4% | 6% | 5% | 4% | 2% | 1% | 4% | 12% |
| ATD Tenax TA | ND | 2% | 0% | 7% | 2% | 7% | 0% | 1% | 2% | 9% |
| Radiello Charcoal | 17% | 14% | 14% | 14% | 14% | 14% | 15% | 15% | 18% | ND |
| 3M OVM 3500 | 4% | 8% | 8% | 6% | 6% | 7% | 8% | 6% | 6% | 7% |
| SKC Charcoal | 18% | 14% | 2% | 4% | 4% | 3% | 4% | 4% | 5% | NC |
| Summa Canister | 6% | 3% | 4% | 3% | 4% | 7% | 6% | 9% | 17% | 22% |
| **COV at 100 ppm** | **MEK** | **NHEX** | **12DCA** | **111TCA** | **BENZ** | **CTET** | **TCE** | **PCE** | **124TMB** | **NAPH** |
| WMS Anasorb 747 | 10% | 9% | 6% | 5% | 9% | 7% | 6% | 6% | NT | NT |
| ATD Tenax TA | 5% | 5% | 4% | 4% | 4% | 4% | 5% | 5% | NT | NT |
| Radiello Charcoal | 14% | 3% | 3% | 3% | 3% | 2% | 3% | 10% | NT | NT |
| 3M OVM 3500 | 1% | 3% | 3% | 2% | 0% | 3% | 6% | 5% | NT | NT |
| SKC Charcoal | 12% | 12% | 9% | 10% | 7% | 9% | 11% | 12% | NT | NT |
| Summa Canister | 11% | 3% | 6% | 3% | 5% | 4% | 6% | 14% | NT | NT |

Notes: NC – Not Calculated (too few detections or two different sorbent)
ND – Not Detected
NT – Not Tested

The results of the high concentration laboratory tests indicate that passive samplers provide comparable accuracy and precision to canister samplers across a broad range of concentrations. These results also show that the uptake rates (which are typically derived for 8 to 24-hour sample durations) provide reasonably accurate results for shorter-term samples (30 minutes), which is important because shorter sample durations are appropriate for higher concentrations commonly of interest in the subsurface. Highly soluble compounds (like MEK) or highly sorptive compounds (like 124TMB and NAPH) appear to be more challenging to quantify accurately than other compounds, which is consistent with observations made during the low concentration laboratory tests.

## 6.3 INDOOR AND OUTDOOR AIR SAMPLING

At OTC, most of the indoor and outdoor air concentrations were below the reporting limit, except for TCE in indoor air, which showed excellent accuracy and precision for all of the passive samplers except the SKC Ultra, which showed a negative bias attributable to poor retention from an unfortunate selection of a weak sorbent (Chromosorb 106).

At CRREL, the indoor air data met the accuracy performance objective of +/-45% RPD in 77% (49/64) cases. The COV values met the precision performance objective of 30% or less in 96% (61/64) of cases. The instances where the passive samplers did not meet the performance objective at CRREL appear to be attributable to inaccuracies in the uptake rate. For example, the $C/C_o$ values for the WMS sampler for locations 1 and 2 were 0.36 and 0.35 for o-xylene and 0.48 and 0.47 for 124TMB. These results are very consistent. The uptake rates for o-xylene and 124TMB for the WMS sampler (Table 3) were calculated to be 6.2 and 13 mL/min, respectively; however, based on the indoor air sampling results at CRREL, the field-calibrated values would have been 2.2 mL/min for o-xylene and 6.2 mL/min for 124TMB. This is an example of the usefulness of some inter-method samples during the conduct of a passive sampling campaign. The uptake rate may be different than expected because of site-specific temperature, humidity, face velocity, exposure duration or concentrations, but inter-method samples will allow the uptake rate to be calibrated to the field conditions. Once the site-specific uptake rate is known, the accuracy of all samples collected under similar conditions will be improved because the passive samplers show very good precision.

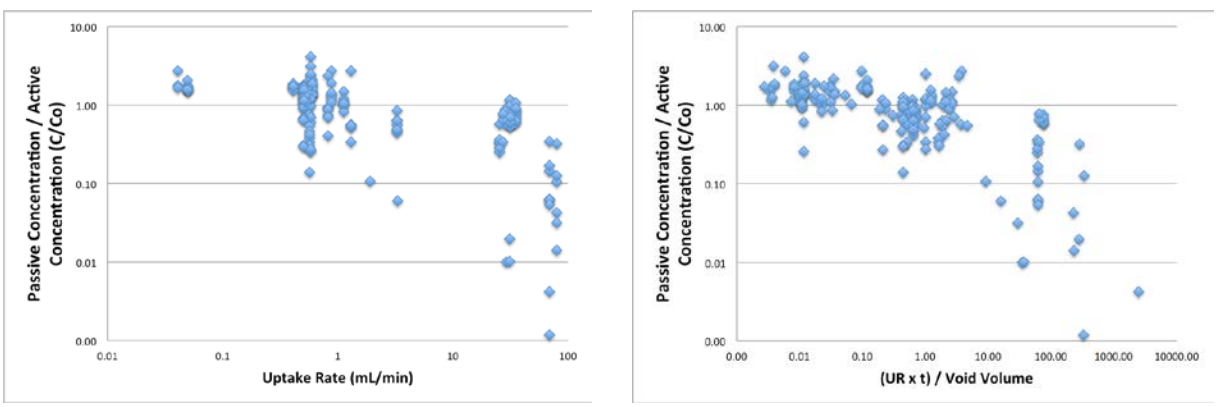
At MCAS 137, indoor and outdoor air data met the accuracy performance objective of +/-45% RPD in 67% (64/96) of the available comparisons, after excluding the data for the WMS and Radiello with poorly retained compounds (cDCE, tDCE, 11DCA, 11DCE, and 12DCA). The excluded compounds all showed negative bias attributable to poor retention (i.e., the uptake rate multiplied by the exposure duration was much greater than the recommended maximum sampling volume). For MCAS 137, the Radiello sampler was used with Crabograph 4 and the WMS was used with Carbopack B, both of which are thermally desorbable sorbents, and have a weaker affinity to the charcoal and Anasorb 747 sorbents used in the Radiello and WMS sampler, respectively, in other tests. If the Summa canister data were used to calculate "field-calibrated" uptake rates, only 9 of 50 uptake rates would have changed by a factor of two or more and only 3 of 50 would have changed by a factor of three or more, so even where the results did not meet the accuracy performance objective, they were within a range that is relatively narrow compared to intrinsic temporal variability in indoor air concentrations. The passive samplers COV ranged from 6% to 9%, which is very similar to the average Summa canister COV of 5% and within the performance criterion for precision.

## 6.4 PASSIVE SOIL VAPOR SAMPLING

The passive soil vapor sampling data collected in this demonstration program span a wide range of operating conditions: sample durations from 20 minutes to 11.7 days; concentrations from about 100 to about 60,000 $\mu g/m^3$; uptake rates from about 0.05 to 80 mL/min; several different chlorinated VOCs; 2.5 to 10 cm (1 to 4 inch) diameter and 2.5 to 46 cm (1 to 18 inch) tall void spaces; ambient temperatures during sample collection from about 15 to about 30°C; analysis by several different laboratories; and different extraction methods for each of several different types of sorbent media. This breadth of testing demonstrated several trends, many of which were consistent with theoretical expectations.

Negative bias was observed for combinations of adsorbents and analytes with a small recommended maximum sampling volume, particularly for longer-term exposures, specifically the ATD tube sampler and 11DCE/Carbopack B, 11DCE/Tenax TA, and TCE/Tenax TA at the Layton house. This is attributable to poor retention and can be avoided by selecting adsorbents with higher

recommended maximum sampling volumes for the compounds of concern. Negative bias was more common for samplers with high uptake rates. Figure 8a shows the relative concentration ($C/C_o$ = passive concentration / active sample concentration) as a function of the uptake rate for all the passive soil gas and sub-slab samples in this study. Starvation was minimal on average for samplers with uptake rates of about 1 mL/min or less, which is consistent with expectations from the mathematical modeling (described in more detail in the full report, ESTCP). Some samplers with higher uptake rates showed good accuracy, but only for relatively short exposure durations. Negative bias was more common for cases where the samplers were deployed in void spaces that were smaller than the product of the sampler uptake rate and exposure time (UR x t), as shown in Figure 8b. In these cases, the mass of vapors in the void-space is not sufficient to satisfy the needs of the sampler so vapors must diffuse into the void-space from the surrounding soil during the passive sampling interval to avoid starvation, and diffusion through the surrounding soil is a much slower process than diffusion to the sampler though the air inside the void space. This challenge can be avoided either by: (1) designing a void space larger than (UR x t) and purging after placement of the passive sampler; (2) by using low-uptake rate samplers that will not induce starvation even if the void-space is small; or (3) using a short exposure duration if the vapor concentrations are high enough to obtain a detectable result. The passive soil vapor concentrations that were measured with low uptake rates, strong adsorbents and (UR x t) values similar to or less than the void volume and RMSV show a better correlation to active sampler results than any previously published comparisons that the authors are aware of.




**a** **b**

**Figure 8. Relative concentrations measured with passive samplers in sub-slab and soil vapor samples as a function of the uptake rate (top) and the equivalent sample volume (UR x t) divided by the void volume (bottom).**

## 6.5 EASE OF USE

This section describes the ease of use of each of the samplers for indoor air, outdoor air, and soil gas sampling, along with any differences or challenges that might influence the selection of one sampler over another.

### 6.5.1 3M OVM 3500

The 3M OVM 3500 comes in a container that is easily opened and the initiation of sampling is nearly effortless and immediate. At the end of the sample exposure period, the porous plastic cap

must be pried off and replaced with a solid plastic cap, which may be a challenge for some individuals. The OVM 3500 is also the largest diameter sampler and has only a high uptake rate variety, so it is not well-suited to soil gas or sub-slab sampling.

### 6.5.2 Radiello

The Radiello requires some assembly because the sorbent medium comes separately packaged from the white or yellow body in which it resides during deployment. The operator must be careful to minimize contamination. The Radiello requires a shield for outdoor air sampling to protect against wind and rain.

### 6.5.3 Waterloo Membrane Sampler

The WMS sampler is easily opened and the initiation of sampling is straightforward. Both the 1.8 mL and 0.8 mL vial sizes are very small and therefore discrete, easy to ship and handle and fit in small diameter holes for soil gas and sub-slab sampling. The operator must be aware not to touch the membrane with contaminants. The sampler is resistant to water and wind, so protection is not specifically needed for outdoor applications.

### 6.5.4 SKC Ultra and Ultra II

The SKC Ultra comes pre-loaded with the sorbent media and is simple to use; however, the Ultra II requires the user to transfer the sorbent into the housing at the start of the sampling event, and transfer the sorbent back into the shipping vial at the end and the laboratory then needs to transfer the sorbent into an ATD tube prior to analysis, which can contribute to bias and variability.

### 6.5.5 ATD Tubes

This is the only sampler tested with no membrane or porous plastic barrier to reduce the risk of positive bias from turbulent uptake in high face velocity environments, so protection from wind and rain would be appropriate in outdoor sampling.

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# 7.0 COST ASSESSMENT

This section presents the results of a cost assessment to implement site investigation and monitoring using passive samplers. Section 7.1 describes a cost model that was developed for different scenarios for site investigation and monitoring using passive samplers and an analysis of the cost model. Section 7.2 presents an assessment of the cost drivers for the application of passive samplers.

## 7.1 COST MODEL AND COST ANALYSIS

A cost model was developed to assist remediation professional in understanding costs associated with passive sampling versus active sampling. The cost model is easiest to understand when compared to active sampling. The cost model identified the major cost elements required to implement passive sampling under four different scenarios.

The cost model was developed for the following scenarios:

- *Scenario 1* – collection of seven sub-slab soil gas samples, seven indoor air samples, and two outdoor air samples at a single building (Table 8a);
- *Scenario 2* – the collection of 50 sub-slab soil gas samples, 50 indoor air samples, and 12 outdoor air samples at several large buildings (Table 8b); and
- *Scenario 3* – a contaminated groundwater plume is migrating beneath a residential community adjacent to a DoD facility. Soil gas probes are installed and sampled to map the subsurface vapor distribution (approximately 100 samples) and the indoor and sub-slab samples are collected in buildings over the areas of elevated soil vapor concentrations (approximately 50 each). Two rounds of sampling are conducted to assess seasonal variations. This scenario assumes that the building occupants are cooperative and willing to watch the passive sampling collection procedures during the first sampling event and deploy their own indoor air and outdoor air samples during the second sampling event (much as is the case with many radon samplers in domestic applications) (Table 8c).

The cost of using passive samplers in the above scenarios is similar to or less than the cost of using active samplers, as shown in Table 8a, b, and c. The costs are similar to conventional methods for small sampling programs because there is an initial effort required to select the appropriate sampler, sorbent, and exposure duration for a given list of target chemicals and desired reporting limits. For larger sampling programs, the initial effort is more than compensated by the reduced labor costs for sample deployment and reduced shipping costs. Actual costs will depend on the quoted costs of analyses of individual laboratories. Summa canister/TO-15 laboratory fees have decreased in the past few years with increasing competition, and this may occur with passive samplers as the demand increases.

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# Table 8a. Cost comparison for Scenario 1.

**Scenario 1**

The first cost scenario consists of the collection of seven sub-slab soil gas samples (6 samples and 1 duplicate), seven (7) indoor air samples (6 samples and 1 duplicate), and two (2) outdoor air samples at a single building. The cost comparison between the five passive and one active sampler types are provided below.

| | | | Number of Units | | Conventional Summa/TO-15 | | WMS | | Radiello | | ATD | | OVM | | SKC | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Item** | **Unit Cost** | **Unit** | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab |
| **LABOR COSTS** | | | | | | | | | | | | | | | | |
| **Active (Conventional Summa/TO-15)** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 2 | 2 | $250 | $250 | | | | | | | | | | |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 4 | | $340 | | | | | | | | | | | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 9 | | $765 | | | | | | | | | | |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | | | | | | | | | | | | | |
| **Passive** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 4 | 4 | | | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 4 | | | | $340 | | $340 | | $340 | | $340 | | $340 | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 3 | | | | $255 | | $255 | | $255 | | $255 | | $255 |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | | | | | | | | | | | | | |
| **LABORATORY COSTS*** | | | | | | | | | | | | | | | | |
| 1 Liter Summa Canister (Batch Certified for soil gas/sub-slab) | $20 | /each | | 8 | | $160 | | | | | | | | | | |
| Flow Controller (100 mL/min for soil gas/sub-slab) | $15 | /each | | 8 | | $120 | | | | | | | | | | |
| Modified EPA TO-15 (open scan for soil gas/subslab) | $140 | /each | | 8 | | $1,120 | | | | | | | | | | |
| 6 Liter Summa Canister (Individually Certified for indoor/outdoor air) | $30 | /each | 9 | | $270 | | | | | | | | | | | |
| Flow controller (24 hr for indoor/outdoor air) | $10 | /each | 9 | | $90 | | | | | | | | | | | |
| Modified EPA TO-15 SIM and scan (for indoor/outdoor air) | $180 | /each | 9 | | $1,620 | | | | | | | | | | | |
| WMS™ Sampler | $25 | /each | 10 | 8 | | | $0 | $200 | | | | | | | | |
| WMS™ Analysis (solvent extraction for soil gas/sub-slab) | $150 | /each | | 8 | | | | $1,200 | | | | | | | | |
| WMS™ Analysis (thermal desorption for indoor/outdoor air) | $200 | /each | 10 | | | | $2,000 | | | | | | | | | |
| Radiello Sampler | $30 | /each | 10 | 8 | | | | | $300 | $240 | | | | | | |
| Radiello Analysis (modified EPA TO-17) | $150 | /each | 10 | 8 | | | | | $1,500 | $1,200 | | | | | | |
| ATD Tube | $30 | /each | 10 | 8 | | | | | | | $300 | $240 | | | | |
| ATD Tube Analysis (modified EPA TO-17) | $200 | /each | 10 | 8 | | | | | | | $2,000 | $1,600 | | | | |
| 3M OVM 3500 Badge | $20 | /each | 10 | 8 | | | | | | | | | $200 | $160 | | |
| 3M OVM 3500 Badge Analysis | $150 | /each | 10 | 8 | | | | | | | | | $1,500 | $1,200 | | |
| SKC Ultra II Sampler | $75 | /each | 10 | 8 | | | | | | | | | | | $750 | $600 |
| SKC Ultra II Sampler Analysis (modified EPA TO-17) | $200 | /each | 10 | 8 | | | | | | | | | | | $2,000 | $1,600 |
| **EXPENSES** | | | | | | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (6L) | $950 | /shipment | 9 | | $534 | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (1L) | $238 | /shipment | | 8 | | $119 | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 passive samplers | $60 | /shipment | 10 | 8 | | | $38 | $30 | $38 | $30 | $38 | $30 | $38 | $30 | $38 | $30 |
| Concrete coring contractor (SKC and OVM only) | $500 | /day | | 1 | | | | | | | | | | $500 | | $500 |
| Hammer drill (conventional Summa, WMS, Radiello and ATD only) | $200 | /week | | 1 | | $200 | | $200 | | $200 | | $200 | | | | |
| Helium detector | $350 | /week | | 1 | | $350 | | | | | | | | | | |
| Helium cylinder | $150 | /each | | 1 | | $150 | | | | | | | | | | |
| Sub-slab probe parts (stainless steel) (conventional Summa sampling) | $25 | /each | | 6 | | $150 | | | | | | | | | | |
| 1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling) | $1 | /each | | 6 | | | | $6 | | $6 | | $6 | | $6 | | $6 |
| Soil gas probe materials (passive) | $25 | /each | | | | | | | | | | | | | | |
| Soil gas probe materials (active) | $50 | /each | | | | | | | | | | | | | | |
| Subtotal | | | | | $3,104 | $3,384 | $2,878 | $2,391 | $2,678 | $2,431 | $3,178 | $2,831 | $2,578 | $2,651 | $3,628 | $3,491 |
| **TOTAL** | | | | | $6,488 | | $5,269 | | $5,109 | | $6,009 | | $5,229 | | $7,119 | |

**Notes:**

*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

# Table 8b. Cost comparison for Scenario 2.

**Scenario 2**

The second cost scenario consists of the collection of fifty (45 samples and 5 duplicates) sub-slab soil gas samples, fifty indoor air samples (45 samples and 5 duplicates) , and twelve outdoor air samples (11 samples and 1 duplicate) at several large buildings. The cost comparison between the five passive and one active sampler types are provided below.

| | | | Number of Units | | Conventional Summa/TO-15 | | WMS | | Radiello | | ATD | | OVM | | SKC | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Item** | **Unit Cost** | **Unit** | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab |
| **LABOR COSTS** | | | | | | | | | | | | | | | | |
| **Active (Conventional Summa/TO-15)** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 2 | 2 | $250 | $250 | | | | | | | | | | |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 29 | | $2,465 | | | | | | | | | | | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 75 | | $6,375 | | | | | | | | | | |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | | | | | | | | | | | | | |
| **Passive** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 4 | 4 | | | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 29 | | | | $2,465 | | $2,465 | | $2,465 | | $2,465 | | $2,465 | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 25 | | | | $2,125 | | $2,125 | | $2,125 | | $2,125 | | $2,125 |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | | | | | | | | | | | | | |
| **LABORATORY COSTS*** | | | | | | | | | | | | | | | | |
| 1 Liter Summa Canister (Batch Certified for soil gas/sub-slab) | $20 | /each | | 50 | | $1,000 | | | | | | | | | | |
| Flow Controller (100 mL/min for soil gas/sub-slab) | $15 | /each | | 50 | | $750 | | | | | | | | | | |
| Modified EPA TO-15 (open scan for soil gas/subslab) | $140 | /each | | 50 | | $7,000 | | | | | | | | | | |
| 6 Liter Summa Canister (Individually Certified for indoor/outdoor air) | $30 | /each | 62 | | $1,860 | | | | | | | | | | | |
| Flow controller (24 hr for indoor/outdoor air) | $10 | /each | 62 | | $620 | | | | | | | | | | | |
| Modified EPA TO-15 SIM and scan (for indoor/outdoor air) | $180 | /each | 62 | | $11,160 | | | | | | | | | | | |
| WMS™ Sampler | $25 | /each | 63 | 51 | | | $0 | $1,275 | | | | | | | | |
| WMS™ Analysis (solvent extraction for soil gas/sub-slab) | $150 | /each | | 51 | | | | $7,650 | | | | | | | | |
| WMS™ Analysis (thermal desorption for indoor/outdoor air) | $200 | /each | 63 | | | | $12,600 | | | | | | | | | |
| Radiello Sampler | $30 | /each | 63 | 51 | | | | | $1,890 | $1,530 | | | | | | |
| Radiello Analysis (modified EPA TO-17) | $150 | /each | 63 | 51 | | | | | $9,450 | $7,650 | | | | | | |
| ATD Tube | $30 | /each | 63 | 51 | | | | | | | $1,890 | $1,530 | | | | |
| ATD Tube Analysis (modified EPA TO-17) | $200 | /each | 63 | 51 | | | | | | | $12,600 | $10,200 | | | | |
| 3M OVM 3500 Badge | $20 | /each | 63 | 51 | | | | | | | | | $1,260 | $1,020 | | |
| 3M OVM 3500 Badge Analysis | $150 | /each | 63 | 51 | | | | | | | | | $9,450 | $7,650 | | |
| SKC Ultra II Sampler | $75 | /each | 63 | 51 | | | | | | | | | | | $4,725 | $3,825 |
| SKC Ultra II Sampler Analysis (modified EPA TO-17) | $200 | /each | 63 | 51 | | | | | | | | | | | $12,600 | $10,200 |
| **EXPENSES** | | | | | | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (6L) | $950 | /shipment | 62 | | $3,681 | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (1L) | $238 | /shipment | | 50 | | $742 | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 passive samplers | $60 | /shipment | 63 | 51 | | | $236 | $191 | $236 | $191 | $236 | $191 | $236 | $191 | $236 | $191 |
| Concrete coring contractor (SKC and OVM only) | $500 | /day | | 2 | | | | | | | | | | $1,000 | | $1,000 |
| Hammer drill (conventional Summa, WMS, Radiello and ATD only) | $200 | /week | | 2 | | $400 | | $400 | | $400 | | $400 | | | | |
| Helium detector | $350 | /week | | 2 | | $700 | | | | | | | | | | |
| Helium cylinder | $150 | /each | | 7 | | $1,050 | | | | | | | | | | |
| Sub-slab probe parts (stainless steel) (conventional Summa sampling) | $25 | /each | | 50 | | $1,250 | | | | | | | | | | |
| 1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling) | $1 | /each | | 50 | | | | $50 | | $50 | | $50 | | $50 | | $50 |
| Soil gas probe materials (passive) | $25 | /each | | | | | | | | | | | | | | |
| Soil gas probe materials (active) | $50 | /each | | | | | | | | | | | | | | |
| Subtotal | | | | | $20,036 | $19,517 | $15,801 | $12,191 | $14,541 | $12,446 | $17,691 | $14,996 | $13,911 | $12,536 | $20,526 | $17,891 |
| TOTAL | | | | | $39,553 | | $27,993 | | $26,988 | | $32,688 | | $26,448 | | $38,418 | |

**Notes:**

*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

# Table 8c. Cost comparison for Scenario 3.

**Scenario 3**

The third cost scenario represents a site with a contaminated groundwater plume migrating beneath a residential community adjacent to a DOD facility. Soil gas probes are installed and sampled to map the subsurface vapor distribution (approximately 100 samples) and the indoor and sub-slab samples are collected in buildings over the areas of elevated soil gas concentrations (approximately 50 each). Two rounds of sampling are conducted to assess seasonal variations. This scenario assumes that the building occupants are cooperative and willing to watch the passive sampling collection procedures during the first sampling event and deploy their own indoor air and outdoor air samples during the second sampling event (much as is the case with many radon samplers in domestic applications). The cost comparison between the five passive and one active sampler types are provided below.

| | | | Number of Units | | Conventional Summa/TO-15 | | WMS | | Radiello | | ATD | | OVM | | SKC | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Item | Unit Cost | Unit | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab | Indoor & Outdoor | Sub-slab |
| **LABOR COSTS** | | | | | | | | | | | | | | | | |
| **Active (Conventional Summa/TO-15)** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 2 | 2 | $250 | $250 | | | | | | | | | | |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 50 | | $4,250 | | | | | | | | | | | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 150 | | $12,750 | | | | | | | | | | |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | 450 | | $38,250 | | | | | | | | | | |
| **Passive** | | | | | | | | | | | | | | | | |
| Laboratory coordination, planning | $125 | /hour | 4 | 4 | | | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 | $500 |
| Indoor and outdoor sample collection (deployment and retrieval) | $85 | /hour | 35 | | | | $2,975 | | $2,975 | | $2,975 | | $2,975 | | $2,975 | |
| Sub-slab sample collection (deployment and retrieval) | $85 | /hour | | 50 | | | | $4,250 | | $4,250 | | $4,250 | | $4,250 | | $4,250 |
| Soil gas sample collection (deployment and retrieval) | $85 | /hour | | 250 | | | | $21,250 | | $21,250 | | $21,250 | | $21,250 | | $21,250 |
| **LABORATORY COSTS*** | | | | | | | | | | | | | | | | |
| 1 Liter Summa Canister (Batch Certified for soil gas/sub-slab) | $20 | /each | | 300 | | $6,000 | | | | | | | | | | |
| Flow Controller (100 mL/min for soil gas/sub-slab) | $15 | /each | | 300 | | $4,500 | | | | | | | | | | |
| Modified EPA TO-15 (open scan for soil gas/subslab) | $140 | /each | | 300 | | $42,000 | | | | | | | | | | |
| 6 Liter Summa Canister (Individually Certified for indoor/outdoor air) | $30 | /each | 100 | | $3,000 | | | | | | | | | | | |
| Flow controller (24 hr for indoor/outdoor air) | $10 | /each | 100 | | $1,000 | | | | | | | | | | | |
| Modified EPA TO-15 SIM and scan (for indoor/outdoor air) | $180 | /each | 100 | | $18,000 | | | | | | | | | | | |
| WMS™ Sampler | $25 | /each | 100 | 300 | | | $0 | $7,500 | | | | | | | | |
| WMS™ Analysis (solvent extraction for soil gas/sub-slab) | $150 | /each | | 300 | | | | $45,000 | | | | | | | | |
| WMS™ Analysis (thermal desorption for indoor/outdoor air) | $200 | /each | 100 | | | | $20,000 | | | | | | | | | |
| Radiello Sampler | $30 | /each | 100 | 300 | | | | | $3,000 | $9,000 | | | | | | |
| Radiello Analysis (modified EPA TO-17) | $150 | /each | 100 | 300 | | | | | $15,000 | $45,000 | | | | | | |
| ATD Tube | $30 | /each | 100 | 300 | | | | | | | $3,000 | $9,000 | | | | |
| ATD Tube Analysis (modified EPA TO-17) | $200 | /each | 100 | 300 | | | | | | | $20,000 | $60,000 | | | | |
| 3M OVM 3500 Badge | $20 | /each | 100 | 300 | | | | | | | | | $2,000 | $6,000 | | |
| 3M OVM 3500 Badge Analysis | $150 | /each | 100 | 300 | | | | | | | | | $15,000 | $45,000 | | |
| SKC Ultra II Sampler | $75 | /each | 100 | 300 | | | | | | | | | | | $7,500 | $22,500 |
| SKC Ultra II Sampler Analysis (modified EPA TO-17) | $200 | /each | 100 | 300 | | | | | | | | | | | $20,000 | $60,000 |
| **EXPENSES** | | | | | | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (6L) | $950 | /shipment | 100 | | $5,938 | | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 Summa canisters (1L) | $238 | /shipment | | 300 | | $4,453 | | | | | | | | | | |
| Federal Express (Standard Overnight) - 16 passive samplers | $60 | /shipment | 100 | 300 | | | $375 | $1,125 | $375 | $1,125 | $375 | $1,125 | $375 | $1,125 | $375 | $1,125 |
| Concrete coring contractor (SKC and OVM only) | $500 | /day | | 10 | | | | | | | | | | $5,000 | | $5,000 |
| Hammer drill (conventional Summa, WMS, Radiello and ATD only) | $200 | /week | | 4 | | $800 | | $800 | | $800 | | $800 | | | | |
| Helium detector | $350 | /week | | 7 | | $2,450 | | | | | | | | | | |
| Helium cylinder | $150 | /each | | 37 | | $5,550 | | | | | | | | | | |
| Sub-slab probe parts (stainless steel) (conventional Summa sampling) | $25 | /each | | 50 | | $1,250 | | | | | | | | | | |
| 1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling) | $1 | /each | | 50 | | | | $50 | | $50 | | $50 | | $50 | | $50 |
| Soil gas probe materials (passive) | $25 | /each | | 100 | | | | $2,500 | | $2,500 | | $2,500 | | $2,500 | | $2,500 |
| Soil gas probe materials (active) | $50 | /each | | 100 | | $5,000 | | | | | | | | | | |
| Subtotal | | | | | $32,438 | $123,253 | $23,850 | $82,975 | $21,850 | $84,475 | $26,850 | $99,475 | $20,850 | $85,675 | $31,350 | $117,175 |
| TOTAL | | | | | $155,691 | | $106,825 | | $106,325 | | $126,325 | | $106,525 | | $148,525 | |

**Notes:**

*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

0.686136368

## 7.2 COST DRIVERS

Passive samplers can reduce costs because the protocols for sampling are simpler, and as a result the costs of training and labor for field personnel are lower than in conventional sampling methods. The passive samplers are also smaller and lighter than Summa canisters, so shipping costs are lower. Passive samplers are also capable of collecting samples over a longer period of time than conventional samplers, therefore, fewer samples may be needed to provide data over a given period.

Passive samplers incur more effort in the initial design process because it takes time to select the best sampler, sorbent and exposure duration for a given set of target chemicals and target reporting limits. This process can be automated to a significant degree, but should be reviewed by an experienced analytical chemist. Inter-method verification samples are a valuable quality assurance/quality control element that allows uptake rates to be derived or verified for site-specific field sampling conditions, which would add a small increment to the overall cost for sampling campaigns, but add a level of quality control and assurance where the highest level of accuracy is desired.

The cost differential between the various types of passive samplers is relatively small, so the selection between the passive sampling options should be based primarily on technical considerations. One exception is if sub-slab sampling is included, because the larger diameter of the SKC and OVM samplers would require a larger diameter hole, and the cost of coring is higher than the cost of using a hammer-drill to make a smaller diameter hole sufficient to accommodate the ATD, Radiello, or WMS samplers.

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# 8.0 IMPLEMENTATION ISSUES

## 8.1 POTENTIAL BIASES

Most of the passive samplers provided data that met the success criteria of the performance objectives for most compounds under most conditions. Exceptions were generally attributable to one of the following causes:

*Poor retention* causes a negative bias in the passive sampler concentration results. This condition was observed in cases where the sampler uptake rate multiplied by the exposure duration (referred to here as an "equivalent sample volume") was much larger than the RMSV for a particular compound and adsorbent. The RMSV is specific for each chemical and adsorbent (Supelco, 2013). To reduce the risk of poor retention, a stronger adsorbent may be selected with a larger RMSV for the compounds of interest. The uptake rate or exposure duration may also be reduced to lessen the equivalent sample volume; however, this will increase the reporting limit, so it is important to verify that the reporting limit still meets data quality objectives (typically reporting limits are designed to be lower than risk-based screening levels, and sometimes a margin is added to account for uncertainty).

*Poor recovery* causes a negative bias in the passive sampler results. This condition was not common, but may explain some of the negative bias and/or variability for NAPH and 124TMB, the two most strongly sorbed compounds.

*Starvation* also causes a negative bias, and occurs in cases where the uptake rate is high relative to the face-velocity of gas in the vicinity of the sampler. Starvation is exacerbated in subsurface (sub-slab and soil gas) sampling, where the face velocity is typically very low. Low uptake rate versions of several passive samplers were developed during the course of this research, and tended to minimize this effect. The optimal uptake rate for soil vapor sampling appears to be in the range of about 0.1 to 1 mL/min depending on the rate of transport of vapors through soil, as supported by transient and steady-state models (ESTCP).

*Uptake rate uncertainty* can cause high or negative bias in the passive sampler results. The uptake rate varies between compounds, samplers, sampling conditions (temperature, humidity, face velocity, exposure duration, and concentration), and sorbents to varying degrees. For most samplers and most VOCs, the accuracy of the passive samplers relative to active methods based on vendor-supplied uptake rates was within a factor of about two or three for the conditions tested. Considering natural spatial and temporal variability in soil vapor and indoor air quality data, this may be acceptable for many monitoring purposes. Where improved accuracy is required or desired, a field-calibrated uptake rate can be calculated if a selected number of samples are collected using a inter-method verification samples (e.g., a select number of conventional Summa canisters beside passive samplers). The comparison between the Summa canister data and the passive sample data can be used to derive site-specific and media-specific uptake rates for the compounds that are detectable in both samples. The laboratory and field data both showed that the precision of the passive samplers is generally similar to or better than the active samplers; therefore, with proper calibration/benchmarking, the performance of the passive samplers is expected to be comparable to or better than conventional methods. Some chemicals are more challenging than others, and there are many compounds of potential concern for VI that were not evaluated in this study. The

laboratory testing program was designed to include chemicals spanning a wide range of properties and to include compounds expected to be challenging (MEK and NAPH); the study results indicate that passive samplers are likely to be able to provide good quality (accurate and precise) concentration data for many or most VOCs of concern for the VI pathway.

*Blank contamination* causes a positive bias and can be identified and corrected using travel blanks, which are recommended for all adsorptive sampling methods.

The SKC Ultra II showed indications of variability attributable to the transfer of the sorbent into and out of the sampler.

## 8.2 CONSIDERATIONS FOR SAMPLER SELECTION

Selection of the most appropriate sampler for a particular application depends on the:

- *Target compounds:* not all sampler types have measured uptake rates for all chemicals. This can be managed using inter-method duplicate samples to derive field-calibrated uptake rates.
- *Target concentrations:* some samplers have better sensitivity than others. The reporting limit is proportion to the sample duration, which can be adjusted within limits.
- *Ambient gas flow velocities:* low uptake rate samplers are preferable in low velocity environments. For example, soil gas monitoring should be performed using samplers with uptake rates on the order of 1 mL/min or less.
- *Desired exposure duration:* weaker sorbents suffer from poor retention over longer deployment intervals. This can be assessed by comparing the product of the sampler uptake rate and sample duration to the RMSV for a particular compound/sorbent combination.
- *Convenience:* drilling a 2-inch diameter hole in a concrete slab is much more work than drilling a 1-inch diameter or smaller hole, and some exposure durations required to meet screening levels may be longer than desired.

With the various combinations of each sampler type (high and low uptake versions, and various types of adsorbents), the selection process requires some specialized knowledge and should be reviewed carefully by an experienced professional.

One important consideration for sampler selection is the reporting limit, which varies inversely with exposure duration, as shown in Equation 1. The appropriate sample duration can be calculated by re-arranging Equation 1 to solve for t and using the laboratory's mass reporting limit for M and a compound/sampler-specific uptake rate for UR and a desired concentration limit (such as a risk-based screening level) for $C_o$. Table 9 shows an example of how this might affect the selection of a sampler. In Table 9, the residential indoor air screening level corresponding to a $1\times10^{-6}$ incremental lifetime cancer risk (USEPA, 2013) is listed for comparison and the exposure duration required for each of the passive samplers to achieve a reporting limit equal to the screening level is also shown. The exposure duration may be longer than practical for compounds with very low screening levels (e.g., chloroform, VC, and 1,1,2,2-tetrachloroethane). There are some blanks in

Table 9 where the uptake rate is not well known or the specific compound is not suited for use with a specific sorbent.

The next important consideration is sorbent selection. Thermal desorption may provide lower reporting limits than solvent extraction, but suffers from poor retention of weakly sorbed compounds, especially with longer sample durations. The product of the uptake rate of the compound for a specific sampler and the sample duration calculated above should be less than the recommended sample volume (Supelco, 2013), where possible, to avoid negative bias by poor retention. If activated carbon or Anasorb 747 or similar strong sorbents are used with solvent extraction, re-check the sample duration as described above.

For soil vapor sampling, the uptake rate of the sampler should be lower than the diffusive delivery rate of the surrounding soil. Figure 4 can be used to select an acceptable sampler uptake rate, if the soil moisture is known.

Quality assurance and quality control should include some frequency of the following checks:

1. Media certification: sorbent tested before sampler fabrication to document the mass of target analytes);
2. Trip blanks: samplers that travel to the site and back with investigative samples, but are not exposed to the atmospheres of interest to document the mass of target analytes;
3. Inter-method duplicate samples: co-located samples with a different sampling and analysis method to provide an independent check on the accuracy of the passive samplers, or to provide site-specific uptake rates for the compounds of interest under field conditions. This may not be necessary for combinations of samplers, sorbents and compounds that have extensive data to support the uptake rates for the sample duration and conditions (temperature, humidity and wind speed); and
4. Duplicate samples to assess precision.

Samples of outdoor air should use passive samplers with high uptake rates and/or long exposure times, to minimize the risk of non-detect results. It is vital when collecting outdoor air samples with passive samplers that a trip blank be included. The sorbent used in passive sampler fabrication should also be blank-tested to identify any chemicals that may contribute to blank contamination.

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**Table 9. Exposure duration required for each of the passive samplers with either solvent or thermal analysis to achieve a reporting limit equal to the residential indoor air screening level corresponding to a $1\times10^{-6}$ incremental lifetime cancer risk.**

| Compound | Residential Indoor Air Screening Level (µg/m3) | WMS | | ATD Tube | | Radiello | | SKC Ultra | | 3M OVM |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Solvent Extraction | Thermal Desorption | Tenax TA | Carbopack B | Solvent Extraction | Thermal Desorption | Solvent Extraction | Thermal Desorption | Solvent Extraction |
| | | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) | Exposure Time (hr) |
| 1,1,1-Trichloroethane | 5,200 | 0.13 | 0.01 | 0.03 | 0.03 | 0.01 | <0.01 | 0.03 | 0.00 | 0.01 |
| 1,1,2,2-Tetrachloroethane | 0.042 | 2800 | 190 | | | | | | | |
| 1,1,2-Trichloroethane | 0.15 | 1700 | 180 | 1200 | 1200 | | | 1200 | 27 | 280 |
| 1,1-Dichloroethane | 1.5 | 470 | 19 | 89 | 90 | | | | | 25 |
| 1,1-Dichloroethene | 210 | 19 | 0.19 | 0.56 | 0.56 | 0.10 | <0.01 | 1.8 | 0.01 | 0.36 |
| 1,2,4-Trimethylbenzene | 7.3 | 9.1 | 0.46 | | | 4.6 | 0.23 | | | |
| 1,2-Dichlorobenzene | 210 | 0.27 | 0.03 | | | | | | | 0.21 |
| 1,2-Dichloroethane | 0.094 | 3400 | 140 | 1400 | 1400 | 230 | 4.6 | 1250 | 25 | 400 |
| 1,3,5-Trimethylbenzene | -- | | | | | | | | | |
| 1,3-Dichlorobenzene | -- | | | | | | | | | |
| 1,4-Dichlorobenzene | 0.22 | 290 | 35 | 140 | | 150 | | | | 200 |
| 2-Butanone | 5,200 | 0.13 | 0.15 | 0.14 | | 0.04 | | 0.02 | 0.01 | 0.01 |
| 4-Methyl-2-pentanone | 3,100 | 0.17 | 0.03 | | | | | | | |
| Acetone | 32,000 | 0.08 | 0.01 | | | <0.01 | | 0.01 | 0.00 | 0.00 |
| Benzene | 0.31 | 2500 | 400 | 130 | | 130 | 34 | 670 | 54 | 230 |
| Carbon Tetrachloride | 0.41 | 1400 | 84 | | | 61 | | | | 100 |
| Chlorobenzene | 52 | 3.0 | 0.14 | | | 0.47 | | | | 0.82 |
| Chloroform | 0.11 | 3900 | 190 | | | 200 | | | | 340 |
| Chloromethane | 94 | 77 | | | | | | | | |
| cis-1,2-Dichloroethene | -- | | | | | | | | | |
| Cyclohexane | 6,300 | 0.06 | 0.00 | 0.01 | | | | | | 0.01 |
| Ethylbenzene | 0.97 | 130 | 5.7 | 37 | 250 | 253 | 5.0 | 130 | 2.9 | 47 |
| Heptane | -- | | | | | | | | | |
| Hexane | 730 | 1.1 | 0.40 | | | | | 0.16 | 0.03 | 0.05 |
| m,p-Xylene | 100 | 1.3 | 0.06 | | 2.4 | 0.24 | 0.12 | 1.3 | 0.03 | |
| MTBE | 9.4 | 72 | 2.6 | | | 2.7 | | 13 | 2.3 | 4.3 |
| Naphthalene | 0.072 | 450 | 23 | 45 | | 930 | | | | 700 |
| o-Xylene | 100 | 1.2 | 0.05 | | 2.4 | 0.26 | 0.13 | 1.4 | 0.03 | |
| Propylbenzene | 1,000 | 0.09 | 0.04 | | | 0.03 | | | | |
| Styrene | 1,000 | 0.12 | 0.01 | 0.04 | | 0.03 | 0.01 | 0.16 | | 0.04 |
| Tetrachloroethene | 0.41 | 380 | 26 | 100 | 670 | 70 | 3.4 | 330 | 13 | |
| Toluene | 5,200 | 0.04 | 0.00 | 0.01 | 0.01 | <0.01 | 0.00 | 0.02 | 0.00 | 0.01 |
| trans-1,2-Dichloroethene | 63 | 20 | 0.40 | 2.4 | 2.4 | 0.43 | 0.01 | 3.6 | 0.04 | 1.4 |
| Trichloroethene | 1.2 | 210 | 11 | 150 | 150 | 20 | 1.01 | 93 | 2.5 | 33 |
| Vinyl Chloride | 0.16 | 43000 | 200 | 400 | | | | | | 770 |

Note: Reporting limits depend on laboratory sensitivity, which may change from time-to-time

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# APPENDIX A

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