



**TECHNICAL MEMORANDUM
TM-NAVFAC EXWC-EV-1503**

**PASSIVE SAMPLING FOR VAPOR INTRUSION
ASSESSMENT**

FINAL

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Table of Contents

Acronyms and Abbreviations.....	v
1.0 Introduction.....	1
2.0 Passive Sampling Basics.....	1
2.1 Passive Sampler Types	3
3.0 Passive Sampler Selection	5
3.1 Comparability to Conventional Methods	6
3.2 Advantages of Passive Samplers Over Conventional Sampling.....	7
3.3 Potential Sources of Bias during Passive Sampling	8
3.4 Considerations for Passive Sampler Deployment.....	9
3.5 Case Studies	11
3.6 Summary.....	12
4.0 References.....	13

List of Figures

Figure 1. Relationship of mass collected versus time for a passive sampler.	2
Figure 2. Axial or tube, badge, and radial sampler types	3
Figure 3. Passive permeation sampler	4
Figure 4. Passive sampler screening matrix. (Source: adapted from U.S. EPA, in press)	6
Figure 5. Correspondence of five types of passive sampler and evacuated canister results for selected chlorinated compounds and petroleum hydrocarbons.....	7

ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
BTEX	benzene, toluene, ethyl benzene and xylenes
COV	coefficient of variation
CRREL	Cold Regions Research and Engineering Lab
DCA	dichloroethane
DCE	dichloroethene
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
MCAS	Marine Corps Air Station
NAVFAC	Naval Facilities Engineering Command
NESDI	Navy's Environmental Sustainability Development to Integration
QA/QC	quality assurance/quality control
RPD	relative percent difference
RPM	Remedial Project Manager
TCE	trichloroethene
USACE	U.S. Army Corps of Engineers
U.S. EPA	United States Environmental Protection Agency
UST	underground storage tank
VI	vapor intrusion
VOC	volatile organic compound

1.0 Introduction

Vapor intrusion (VI) is the migration of volatile chemicals from subsurface soil and/or groundwater into the indoor air of overlying buildings. Volatile organic compounds (VOCs) typically associated with VI are chlorinated solvents and petroleum hydrocarbons. The occurrence of these VOCs in the subsurface generally is due to releases from historic waste disposal practices at industrial sites, dry cleaners, and gasoline stations.

Current approaches for identifying potential VI issues usually involve the comparison of conservative media-specific, risk-based VOC screening levels to concentrations measured in samples of groundwater, indoor air and/or soil vapor. Methods for groundwater sampling are well established. The most common method used for indoor air sampling for VI investigations consists of drawing air into evacuated stainless steel canisters with analysis by United States Environmental Protection Agency (U.S. EPA) Method TO-15. Evacuated canisters are limited to sample durations of 72 hours or less and most often are deployed for 8 to 24 hours. Soil vapor (including sub-slab soil vapor) may be collected in evacuated canisters, inert plastic bags, or glass syringes often with sample durations of 15 minutes or less.

A key concern with indoor air sampling is that the temporal variability of indoor air concentrations leads to uncertainty on whether a canister sample collected over 24 hours or less is representative of the longer-term time-weighted average concentrations on which risk assessments are based. An alternative technique for indoor air and subsurface vapor characterization is passive sampling, which can be implemented over longer durations, thereby minimizing the impacts of temporal variability and obtaining more representative measures of the longer-term average concentrations. This can be much more cost-effective than using sequential 24-hour samples to smooth out temporal variability.

This technical memorandum was prepared for Naval Facilities Engineering Command (NAVFAC) Remedial Project Managers (RPMs), contractors, and other stakeholders to provide an overview of the use of passive samplers for VI applications. It describes the basics of passive sampler theory and design, the available types of passive samplers, the advantages and limitations of passive samplers, and important considerations when implementing a passive sampling program. In addition, the results from two case studies at Department of Defense (DoD) sites are highlighted.

2.0 Passive Sampling Basics

A passive sampler is a device that contains a sorbent in an inert container with an opening of known dimensions that, ideally, allows VOC vapors to pass through at a steady uptake rate. Passive samplers take up VOCs over time according to the general trend shown in Figure 1, assuming the ambient concentration is constant. At early stages (kinetic stage), the rate of mass uptake is constant and the increase in sorbed mass is linear with time. At late stages (equilibrium stage), the mass taken up by the sampler reaches a steady state.

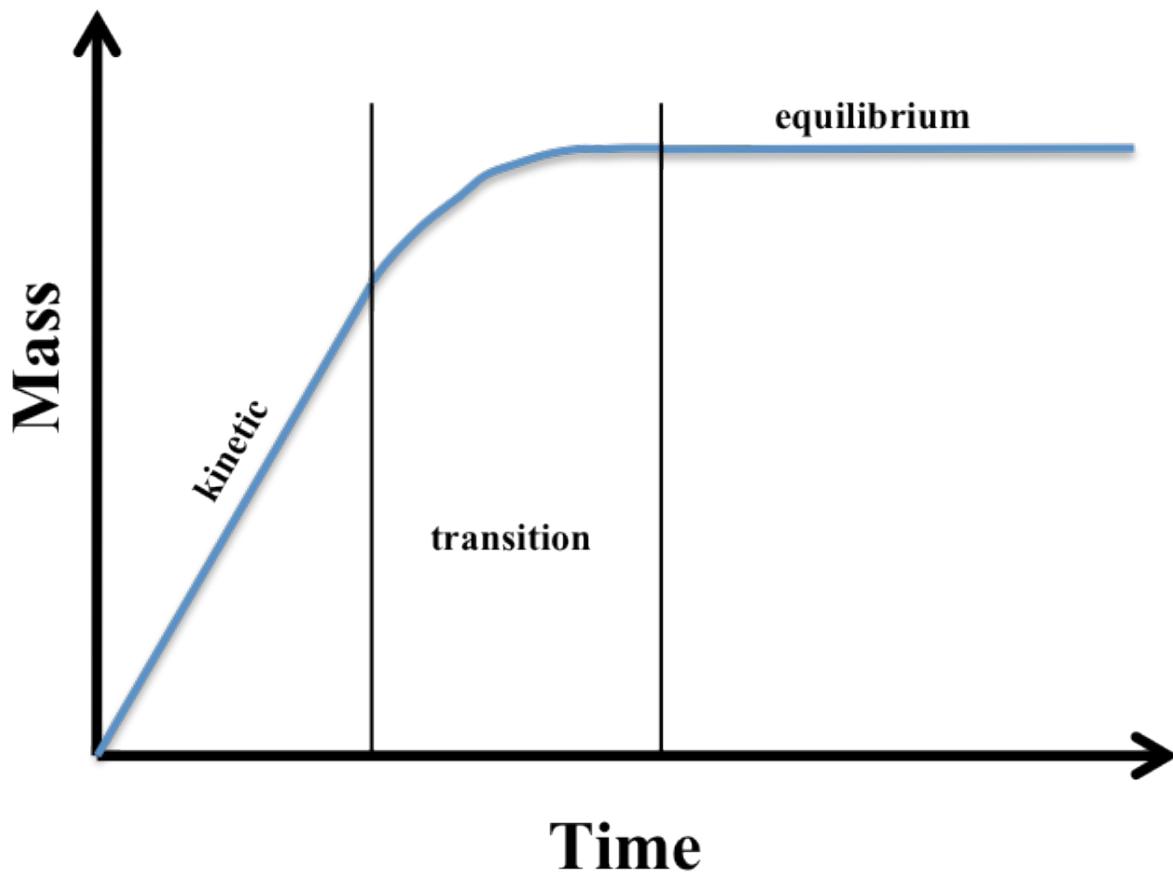


Figure 1. Relationship of mass collected versus time for a passive sampler.

Passive samplers for VI investigations are designed to operate in the kinetic region because they provide time-weighted average concentrations that can be used for human health risk assessments (McAlary et al., 2014a). Passive samplers are analyzed by extracting the VOCs from the sorbent to measure the total mass of each VOC trapped by the sampler during the sampling period. The average concentration (C) over the sampling period can be calculated as the total mass sorbed (M ; reported by the laboratory) divided by the product of the sampling duration (t) and compound-specific uptake rate (UR). The uptake rate has units of volume per unit time (mL/min), and is equal to the flow rate that would be required for a pumped sorptive sampler to trap the same mass over the same sample duration.

$$C = M/(UR \times t)$$

Mass sorbed and sampling duration can be measured with high levels of accuracy, so the uptake rate is the key factor controlling the accuracy of air concentrations determined using passive samplers. The uptake rate is dependent on the geometry of the sampling device, as well as the diffusion coefficient or the permeation constant of the chemical through the region between the sorbent in the passive sampler and the ambient media. The uptake rate may also be dependent on

the sorbent characteristics, which determine VOC retention as well as desorption efficiency. Experimentally derived uptake rates for a range of compounds have been published by the manufacturers for most passive sampler and sorbent configurations.

2.1 Passive Sampler Types

Passive samplers can be classified into two general types based on the method used to control VOC uptake: those that rely on diffusion through a stagnant air region (passive diffusion samplers) and those that rely on permeation through a nonporous membrane (passive permeation samplers), which allow VOCs to partition into and diffuse through the membrane to the sorbent.

Passive diffusion samplers are available in three geometries: axial (or tube), badge, or radial (Figure 2).

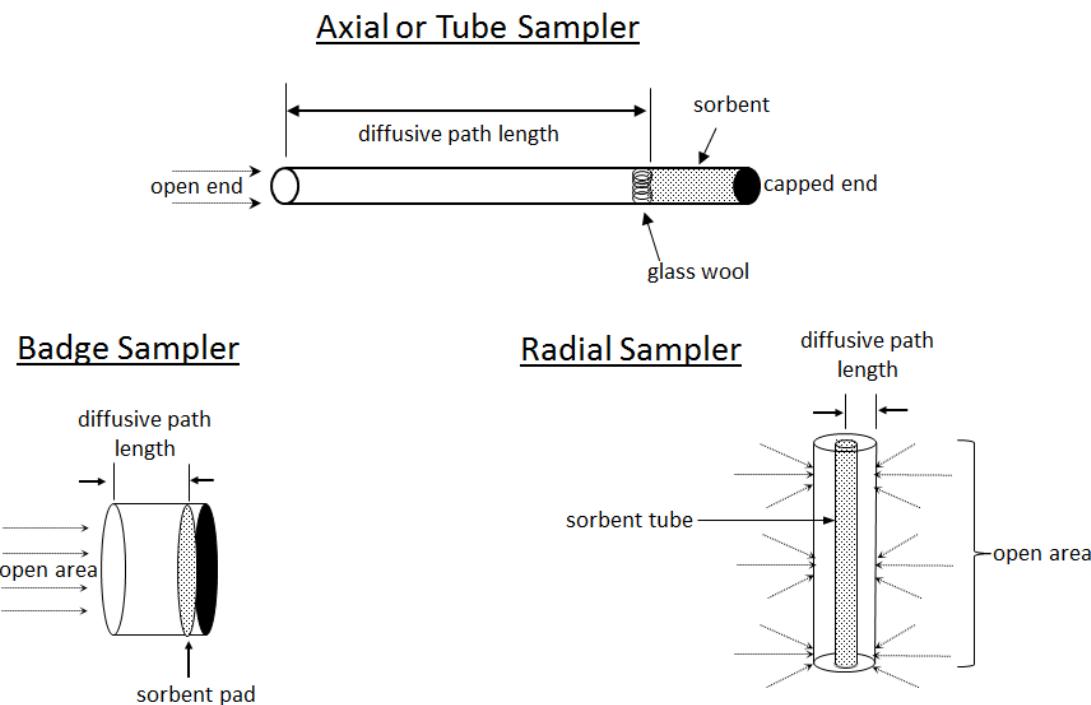


Figure 2. Axial or tube, badge, and radial sampler types (dotted arrows indicate vapor entry). (Source: Geosyntec)

Axial samplers have small cross-sectional surface areas and long diffusive path lengths. The sampler typically is left open at one end and closed at the other to allow uptake via diffusion through the air space between the open end and the sorbent.

Badge samplers have larger cross-sectional surface areas and shorter diffusive path lengths, and therefore have higher uptake rates and better sensitivity with shorter sample durations than tube samplers. The larger opening is typically covered with a porous windscreens to minimize uptake by advection.

Radial samplers have an outer cylinder of porous material that serves as a windscreens and diffusive region and an inner cylinder of stainless steel mesh that houses the sorbent, which provides a very large surface area and a short diffusive path, resulting in generally higher uptake rates than either tube- or badge-style samplers.

Passive permeation samplers (Figure 3) have a thin hydrophobic polymer membrane between the sorbent and ambient media and have uptake rates that depend on the permeation constant for various VOCs.

The passive sampler types described above can be customized for site-specific applications by selecting an appropriate sorbent material for the VOCs of interest and desired sampling duration to achieve a particular reporting limit. There are many different VOCs of interest and many different sorbents, and each compound has a certain affinity for each sorbent.

Sorbents fall into two general categories — very strong sorbents requiring solvent extraction and relatively weaker sorbents amenable to thermal desorption. The goal is to select a sorbent that efficiently retains the VOC mass that enters the sampler, but also releases the VOC mass efficiently during analysis. Compromises between retention and recovery for some of the measured compounds may be required, or sampling can be done with two or more different sorbents in duplicate samples.

Use of thermal sorbents generally results in better analyte sensitivity; however, only a single analysis can be performed because the entire sorbed mass is removed and analyzed, which could lead to estimated results if the calibration range is exceeded or the results are lost if the analytical instrument malfunctions during the analysis. Solvent-extracted sorbents may be a better choice if large ranges of concentrations are expected, because the samples can be diluted to ensure the analyte concentrations are in the calibration range.

It is generally advisable to employ the advice of an experienced analytical chemist to select an appropriate sampler/sorbent combination for the compounds of interest. It is also often useful to screen VOC concentrations prior to sampling with a photoionization detector or flame ionization detector to identify any high VOC concentrations that could result in saturation of the sorbent, in which case, the sample duration could be shortened to maintain an acceptable mass loading on the sampler.

Membrane Sampler

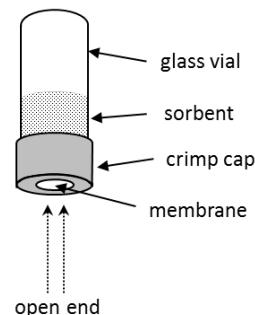


Figure 3. Passive permeation sampler (dotted arrows indicate vapor entry).
(Courtesy: Geosyntec)

3.0 Passive Sampler Selection

Two key questions to consider when selecting passive samplers for a particular application include:

For a particular sampler/sorbent combination, how many of the target compounds have known uptake rates and retention and recovery ranges for the sampling medium of interest?

Most passive samplers are available with more than one type of sorbent and have a list of published uptake rates for a given number of compounds and sorbents. It is advantageous to select a passive sampler that has vendor-supplied uptake rates for as many of the target compounds as possible. Often, a small number of compounds are the dominant compounds of concern, and the sampler/sorbent selection can focus accordingly. Commercially available passive samplers have uptake rates ranging over two orders of magnitude, which allows flexibility in selecting the optimal sampler configuration to meet project-required reporting limits and/or sample durations.

What target reporting limits are needed and how does that influence the duration of passive sampling?

Reporting limits for each type of passive sampler depend on sample duration as well as lab sensitivity. The minimum sample duration (t_{min}) needed to provide a reporting limit as low as or lower than the screening level for a given VOC can be calculated by dividing the laboratory reporting limit (M_{RL} , in mass units) for each VOC of interest by the product of the uptake rate (UR) and screening level concentration (SL).

$$t_{min} = M_{RL}/(UR \times SL)$$

The chemical with the lowest screening level or uptake rate usually dictates the sample duration. A check on retention is advisable: the product of the uptake rate and sample duration should be less than the recommended safe sample volume for a particular compound/sorbent combination (an analytical chemist can help with this).

Figure 4 provides guidelines for selecting appropriate sampler/sorbent combinations for given types of target compounds, field conditions, and desired reporting limits.

Sampler Type	Uptake Rate	Sampling Duration	Analytical Sensitivity	Target Compounds
Tube (Axial)	Lower	Longer	Lower	Depends on the selected sorbent
Tube (Permeation)				VOCs & SVOCs
Badge (Axial)				
Radial	Higher	Shorter	Higher	

Sorbent Type	Uptake Rate	Sampling Duration	Analytical Sensitivity	Target Compounds
Solvent Extracted	Potentially higher for solvent extracted because samples can be diluted	Longer	Lower	Wide range of compounds
Thermally Desorbable				Depends on the selected sorbent

Figure 4. Passive sampler screening matrix. (Source: adapted from U.S. EPA, in press)

3.1 Comparability to Conventional Methods

As shown in Figure 5, passive samplers yield results that are very similar to those obtained from other established methods of indoor air and soil vapor sampling for many chlorinated solvents and petroleum hydrocarbons under a variety of sampling conditions and for a large range of concentrations (e.g., Lutes et al., 2010; U.S. Navy, 2013; Environmental Security Technology Certification Program [ESTCP], in press). There are, however, compounds or conditions that lead to poor agreement: 1) weakly sorbed (poorly retained) compounds such as polar compounds in high humidity settings or low molecular weight compounds with long sampling durations can be negatively biased (e.g., Lutes et al., 2010), 2) low air velocity settings (e.g., during soil gas or sub-slab sampling) tend to result in negatively biased results for high uptake rate samplers (McAlary et al., 2014a,b,c; McAlary et al., 2015), and 3) turbulence in high air velocity settings tends to result in positively biased results (ESTCP, in press). The conditions showing poor agreement usually can be anticipated and managed by appropriate sorbent selection (there are many sorbents to choose from), sampler type, sample duration, and placement.

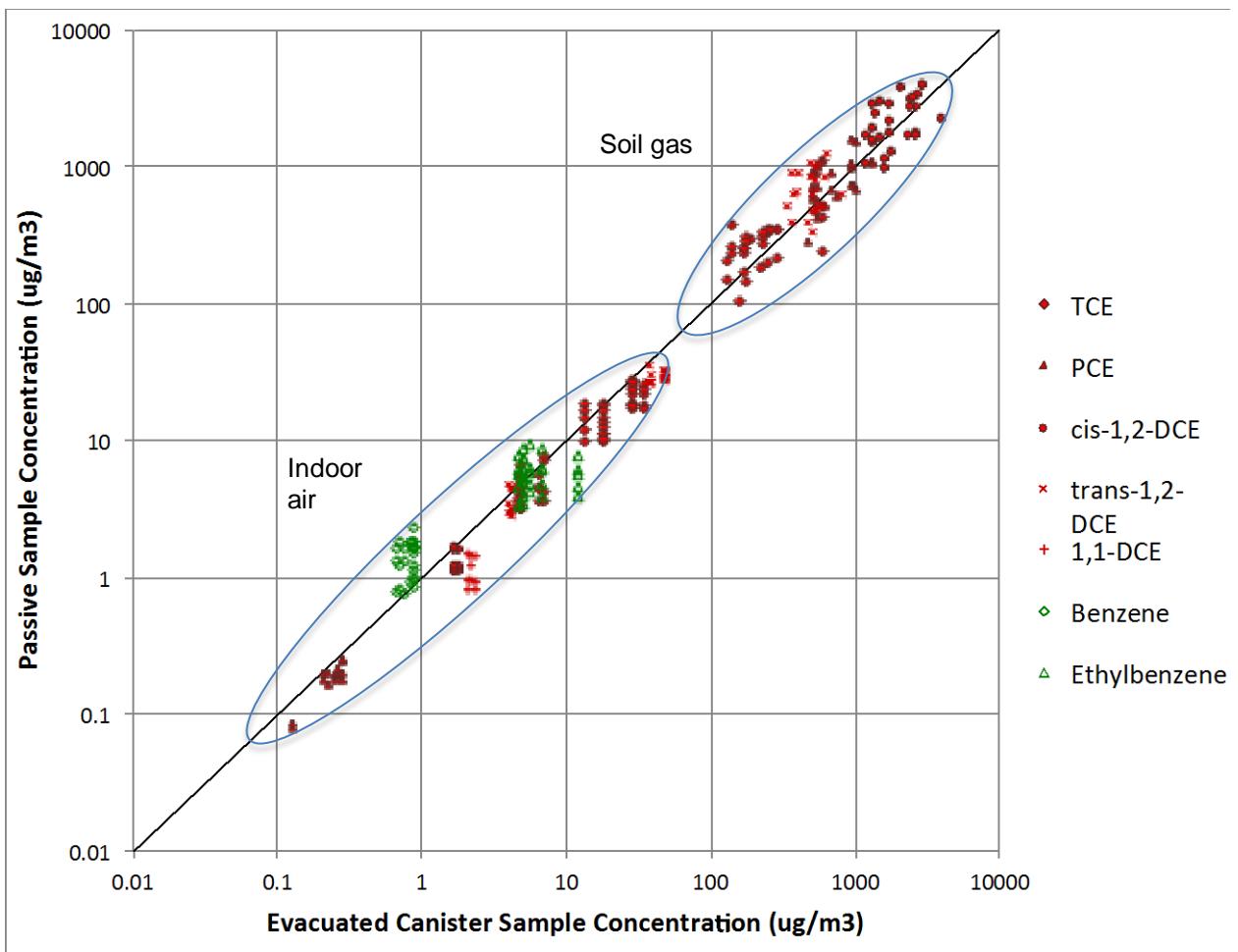


Figure 5. Correspondence of five types of passive sampler and evacuated canister results for selected chlorinated compounds and petroleum hydrocarbons.
 (Source: adapted from ESTCP, in press)

3.2 Advantages of Passive Samplers Over Conventional Sampling

Passive sampling has several potential advantages over conventional evacuated canister sampling, including:

Ease of Use: Passive samplers generally have fairly simple sampling protocols and can be deployed by personnel without specialized training. Passive samplers also are smaller, so they can be placed more discretely during the sampling event than canisters. Additionally, leaks in sampling trains are not an issue for passive samplers as they may be for conventional sampling approaches, especially when collecting soil gas samples.

Analytical Sensitivity: Passive samplers can be configured to provide reporting limits comparable to or lower than those achieved with evacuated canisters by judicious selection of sampler configuration, sorbent, and sample duration. Longer sample durations result in lower reporting limits (better sensitivity) with no change in the cost. For thermally desorbable sorbents, it is prudent to avoid excessively long sample durations for weakly sorbed analytes. A general

guide is to maintain the product of the uptake rate and sample duration at values lower than the recommended safe sample volume for pumped sorptive samplers. An analytical chemist experienced with U.S. EPA Method TO-15 can provide this assurance.

Precision: For a given set of conditions (temperature, humidity, wind speed, etc.), passive samplers provide precision that is comparable to or better than active sampling results (ESTCP, in press). Changes in sampling conditions can affect the uptake rates, in which case, inter-method duplicate samples can provide field-verified uptake rates (e.g., 1 in 10 passive samples are supplemented with a duplicate collected using active sampling methods).

Target Compounds: The conventional canister sampling and analysis method is limited primarily to VOCs with an upper carbon range of approximately C₁₂ (e.g., naphthalene). Given the available variety of sorbents, passive samplers can be configured to collect VOCs in the range of C₁ (except methane) to C₂₆.

Representativeness: Passive samplers can be used to collect longer time-weighted average samples (e.g., several days to several weeks), which provide more representative results if long-term average concentrations are of interest.

Sample Duration: Passive samplers can be used for longer sampling periods than evacuated canisters. Evacuated canisters are largely limited to sampling periods of less than 72 hours in 6-L canisters, but beyond that, maintenance of a constant flow rate becomes increasingly difficult with longer sampling times. Most canister samples are collected over 8 to 24 hours. By contrast, passive samplers can be deployed over periods spanning days to weeks, especially if samplers with strong sorbents and/or low uptake rates are used to avoid analyte loss due to poor retention.

Lower Overall Cost: The simplicity of the sampling protocols and small size of passive samplers means lower labor cost for sample collection and lower shipping cost compared to evacuated canisters.

3.3 Potential Sources of Bias during Passive Sampling

As with any sampling method, care is required to control sources of negative (underestimation) and positive (overestimation) bias. Passive samplers show a very high degree of precision for a given set of sampling conditions (temperature, humidity, air velocity, concentration, and sample duration), but are more susceptible than active samplers to changes in sampling conditions. Field-calibration using a select number of inter-method duplicate samples (e.g., evacuated canister samples) is often valuable to validate the accuracy of (and, if necessary, derive field-calibrated uptake rates for) passive samplers for a given set of conditions. Potential sources of bias for passive samplers include starvation, poor retention, poor recovery, turbulence, high humidity, and blank contamination. Additional information is provided below on these potential issues.

Starvation occurs if the passive sampler withdraws target compounds from the surrounding media faster than they are replenished (e.g., low air velocity settings), causing a negative bias. Usually this is not an issue for indoor and outdoor sampling, but needs to be further considered for soil vapor and sub-slab vapor sampling. Starvation can be minimized either by using low

uptake rate samplers (e.g., tube or membrane samplers) or by maintaining an adequate face velocity (i.e., inducing air movement past the sampling surface with fans or pumps).

Poor retention occurs if a relatively weak sorbent is used to sample highly volatile compounds, especially for long sample durations during which analytes can desorb from the sorbent after initially being adsorbed. Weakly sorbed VOCs (such as low molecular weight compounds or polar compounds in humid settings) can also be displaced through competitive adsorption in the presence of high concentrations of other VOCs or water vapor. The result is a negative bias, as VOCs are lost from the sampler media. The product of the uptake rate and the sample duration should be less than the recommended maximum sample volume for thermally desorbable sorbents (an analytical chemist familiar with U.S. EPA Method TO-17 can help with selection of an appropriate sorbent). Poor retention can be managed by selecting stronger sorbents to minimize analyte loss. Passive permeation samplers or hydrophobic sorbents in passive diffusion samplers can also be used to minimize water vapor uptake because the membrane is hydrophobic.

Poor recovery can occur when stronger sorbents are used with strongly sorbed compounds. Poor recovery results in a negative bias because the sorbed chemical is not completely desorbed from the sorbent during sample analysis. Sorbent selection must balance retention and recovery and consider the range of target analytes and planned sample duration. If recovery rates are known, corrections to the mass measured can be made.

Advection uptake via turbulence in high velocity settings is a source of positive bias since it can lead to greater uptake than anticipated by diffusion alone. This can be avoided by using a wind-screen or using permeation samplers, which have a non-porous membrane and as a result cannot uptake VOCs by advection.

Blank contamination is another source of positive bias and can occur when the sorbents used in passive sampling are inadvertently contaminated during sampler preparation, storage, shipping, or handling and would lead to a positive bias if unidentified. Blank contamination is usually evaluated using media blank, batch certification, and trip blank samples as part of the quality assurance/quality control (QA/QC) program. If VOCs are detected in blanks, the reporting limits may be set at a level equal to the blank concentration divided by the uptake rate and sample duration, or the data might also be blank-corrected (mass measured in blanks is subtracted from mass measured in samples) prior to calculating the time-weighted average concentration.

3.4 Considerations for Passive Sampler Deployment

Several factors should be considered for the deployment of passive samplers including:

Field Preparation: Passive samplers should be stored and transported to and from the field protected from heat and in well-sealed, inert (non-VOC emitting) containers preferably containing scavenger carbon to minimize VOC contamination. The recommended storage condition for most unused passive samplers is generally room temperature. For thermally desorbable sorbents or sampling of polar compounds, storage and transport on ice is recommended. The storage time after manufacture or cleaning/certification and before use is established for each type of sampler and sorbent using shelf-life studies. Manufacturers usually

provide expiration or “use-by” dates. Recertification and recleaning should be performed for samplers that are past their expiration date.

Placing Passive Samplers Indoors for Sampling Ambient Air: Air velocity and humidity should be considered when deploying passive samplers in indoor spaces. Rapid air flow past passive diffusion samplers can result in a positive bias via turbulent uptake, so these samplers should not be placed near areas prone to high air flow such as areas near windows, doors, chimneys, and air vents. Passive permeation samplers are not subject to positive bias in high velocity settings, thus are a better choice in such circumstances. Areas with insufficient air circulation, which can result in a negative bias via starvation, also should be avoided if a high uptake rate passive sampler is used. Humidity can affect the uptake rate of passive diffusion samplers if they are loaded with hydrophilic sorbents (e.g., activated carbon), so high humidity areas such as laundry rooms and bathrooms should be avoided or a hydrophobic sorbent should be used. Alternatively, passive permeation samplers can be deployed as their membranes are hydrophobic, which inhibits uptake of water vapor.

Placing Passive Samplers Outdoors for Sampling Ambient Air: Air velocity, precipitation and temperature need to be considered when deploying passive samplers outdoors. Windy locations should be avoided or a wind shelter should be used to minimize turbulent uptake when using passive diffusion samplers. These samplers should be protected from precipitation and temperature extremes (e.g., avoid direct sunlight) that can speed degradation or release of sorbed chemicals.

In addition, samplers should not be placed under or in trees that can evapotranspire VOCs from the subsurface and create a positive bias for ambient samples. Also, placement should not occur near windows, doors, or exhaust fans to minimize the influence of indoor air concentrations on the outdoor samplers.

Using Passive Samplers for Soil Vapor Sampling: During sub-slab or soil probe deployments, the uptake rate for passive soil vapor sampling must be lower than the rate of diffusive transport from the surrounding soil to the sampler, or a negative bias from starvation will occur. Passive samplers should be protected from direct contact with soil, and the sampler should be sealed in place with a seal that is at a depth just above the sampler, not just at ground surface (e.g., McAlary et al., 2014a,b,c; McAlary et al., 2015). Passive permeation samplers are particularly suited to soil vapor sampling as the hydrophobic nature of the membrane limits the uptake of soil moisture.

Quality Assurance/Quality Control: Passive sampling programs employ the same quality controls as any other sorbent-based sampling and analytical method (e.g., U.S. EPA Method TO-17), including media certification, trip blanks, field duplicates and laboratory QA/QC. Where the highest levels of accuracy are desired, it is valuable to add a certain percentage of collocated inter-method duplicate samples using conventional methods to allow site-specific uptake rates to be calculated because passive sampler uptake rates can vary in response to changes in field conditions (temperature, humidity, pressure, wind speed, and sample duration). The reproducibility of passive samplers is generally within 30% relative percent difference (RPD), so limited numbers of collocated inter-method duplicate samples are adequate to provide a high degree of confidence in the accuracy of all passive samplers collected in similar conditions. As

much as possible, the collocated inter-method duplicate samples should sample for the same duration. Pairs of collocated inter-method duplicate samples may also be retrieved at different times during the sampling duration, to support the conclusion that uptake rates are linear over the entire sampling duration.

3.5 Case Studies

Several field studies have been conducted to demonstrate and validate the use of passive samplers for VI applications. These studies have been supported by the DoD ESTCP and the Navy's Environmental Sustainability Development to Integration (NESDI) Program (ESTCP ER-0830, in press and U.S. Navy, 2013). VI pathway samples (indoor air, outdoor air, sub-slab vapor and deeper soil vapor) were collected using a variety of quantitative passive samplers and evacuated canisters at several DoD facilities known to have VOCs in the subsurface. The VI passive sampling results from two field sites are highlighted here for an Army facility in Hanover, New Hampshire tested under ESTCP and for Marine Corps Air Station (MCAS) Cherry Point, North Carolina tested under NESDI.

USACE Cold Regions Research and Engineering Laboratory, Hanover, NH

A passive sampling program was implemented at 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. Trichloroethene (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 (UST) containing TCE near the main laboratory building and laboratory addition released liquid TCE. Air strippers were installed at four of CRREL's five groundwater production wells, which are used for non-contact cooling, to treat the water before use in the facility.

Indoor air samples were collected in three locations, with five passive sampler types each deployed in triplicate at each location. Indoor air concentrations at CRREL were expected to be high enough to be detectable with a three-day deployment of the passive samplers (previous sampling indicated TCE concentrations in indoor air ranged from about 10 to about 100 $\mu\text{g}/\text{m}^3$). Continuous monitoring in triplicate at each of the three locations was also performed using sequential canisters, and time-weighted concentrations were then calculated and used as the active control for indoor air quality.

The indoor air sampling data generally showed good agreement between the passive samplers and evacuated canisters. TCE concentrations ranged from 6.3 to 30.9 $\mu\text{g}/\text{m}^3$ in the canister samplers in the three locations with a coefficient of variation (COV) of 12% to 16% (where the COV is calculated from the triplicate passive samplers and the triplicate continuous canister samples at each location). The passive sampler results for TCE were within a range of 60% to 109% relative concentration (passive sampler concentration divided by canister sample concentration) for each of the five passive samplers with COVs ranging from 4% (permeation sampler) to 14% (badge sampler). Five petroleum hydrocarbons were also detected and compared. The hydrocarbons performed were comparable to TCE.

Marine Corps Air Station, Cherry Point, NC

Under the NESDI Program, a passive sampling study was implemented in an industrial building at MCAS in Cherry Point, North Carolina. Chlorinated VOCs are present in soil and groundwater at this site, including TCE, 1,2-dichloroethene (1,2-DCE), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethane (1,2-DCA) and 1,1-dichloroethane (1,1-DCA).

Indoor air samples were collected over seven days in three locations with five passive sampler types deployed in triplicate in each location. The indoor air samplers were deployed in a break room, a warehouse area, and an autoclave room. The break room is a small room with low (8-foot) ceilings. The warehouse area was chosen as a sampling location because it is immediately outside the break room and, in contrast to the break room, is a large open area. The autoclave room was chosen as another sampling location because it is a moderately sized space and is distant from the other two sampling locations.

The indoor air sampling data from MCAS showed detectable concentrations of chlorinated VOCs, as well as benzene, toluene, ethyl benzene, and xylenes (BTEX) at the three sample locations. Outdoor air samples had detectable concentrations of VOCs, but generally at concentrations less than $1 \mu\text{g}/\text{m}^3$. Passive samplers with weaker sorbents showed poor retention of weakly sorbed compounds (1,2-DCE, 1,1-DCE, 1,2-DCA and 1,1-DCA). However, passive samplers with stronger sorbents showed good retention and good agreement (within a factor of two) with the evacuated canister results in 84% of cases for chlorinated VOCs and for petroleum hydrocarbons in the range of 0.1 to $10 \mu\text{g}/\text{m}^3$. A more detailed review of the data including graphical comparisons for each passive sampler type versus canister sampling can be found in the NESDI report. Other Navy sites tested under this project include Naval Air Station Jacksonville, Florida and SPAWAR Systems Center Pacific Old Town Annex, California (U.S. Navy, 2013).

3.6 Summary

As demonstrated in the case studies, passive samplers provide an alternative to the conventional methods of sampling air and soil vapor for VI assessment. Because of the advantages over conventional sampling methods described above, passive samplers are valuable tools for VI assessment. Limitations of passive samplers can be managed by proper selection of the sampler and sorbent and proper deployment of the passive samplers. In summary, passive samplers have the following advantageous features:

- Capable of measuring the concentration of a large suite of chlorinated and petroleum hydrocarbon VOCs. The concentration of semivolatile organic compounds may also be measured if the sorbent is properly selected.
- Greater ease of deployment (simple field protocols, lower shipping costs), leading to lower overall costs.
- Capable of deployment over longer timeframes (e.g., weeks to months), which minimizes bias imposed by temporal variability, which can outweigh uncertainties in uptake rates, retention, and recovery.

- Provide reliable, time-averaged sample concentrations with accuracy and precision comparable to conventional methods. Inter-method checks provide assurance of accuracy.

Data from passive samplers are suitable for quantitative risk assessment if, as is the case with all sample collection methods, samples have been collected with appropriate protocols approved by the lead regulatory agency. Approval from site regulators should be obtained prior to collecting passive samples for quantitative risk assessment, and may require collecting active sampler duplicates, typically at a rate of one per 10 passive samplers.

Recent resources that provide information useful for the design and implementation of passive sampling programs are included below.

4.0 References

- American Society for Testing and Materials (ASTM). 2011. D7758 New Practice for Passive Soil Vapor Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring and Vapor Intrusion Evaluations. ASTM International, West Conshohocken, PA.
- American Society for Testing and Materials (ASTM). 2010. D6306-10 Standard Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air. ASTM International, West Conshohocken, PA.
- Environmental Security Technology Certification Program (ESTCP). In press. Project ER-200830. Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques.
- Lutes, C.C., R. Uppencamp, H. Hayes, R. Mosley, and D. Greenwell. 2010. Long-term integrating samplers for indoor air and subslab soil gas at VI sites. Presented at AWMA Specialty Conference: Vapor Intrusion 2010, September 28–30. Chicago, IL.
- McAlary, T.A., X. Wang, A. Unger, H. Groenevelt, and T. Górecki. 2014a. Quantitative passive soil vapor sampling for VOCs—Part 1: theory. *Environ. Sci.: Processes Impacts* 16(3): 482–490.
- McAlary, T.A., H. Groenevelt, S. Seethapathy, P. Sacco, D. Crump, M. Tuday, B. Schumacher, H. Hayes, P. Johnson, and T. Górecki. 2014b. Quantitative passive soil vapor sampling for VOCs—Part 2: laboratory experiments. *Environ. Sci.: Processes Impacts* 16(3): 491–500.
- McAlary, T.A., H. Groenevelt, P. Nicholson, S. Seethapathy, P. Sacco, D. Crump, M. Tuday, H. Hayes, B. Schumacher, P. Johnson, T. Górecki, and I. Rivera Duarte. 2014c. Quantitative passive soil vapor sampling for VOCs—Part 3: field experiments. *Environ. Sci.: Processes Impacts* 16(3): 501–510.

McAlary, T.A., H. Groenevelt, S. Fisher, J. Arnold, S. Seethapathy, P. Sacco, D. Crump, B. Schumacher, H. Hayes, P. Johnson, and T. Górecki. 2015. Passive sampling for volatile organic compounds in indoor air – Controlled laboratory comparison of four sampler types. *Environ. Sci.: Processes Impacts* 17: 896–905.

United States Environmental Protection Agency (U.S. EPA). 2012. Fluctuation of Indoor Radon and VOC Concentrations Due to Seasonal Variations. EPA/600/R-12/673. National Exposure Research Laboratory, Las Vegas, NV. October.

United States Environmental Protection Agency (U.S. EPA). In press. Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods. ORD Engineering Issue Paper.

U.S. Navy, SPAWAR Systems Center Pacific Division. 2013. Improved Assessment Strategies for Vapor Intrusion Passive Samplers and Building Pressure Control. Technical Report 2018. September.