



Passive Sampling for Vapor Intrusion Assessment

Purpose

This fact sheet prepared by the Department of Defense (DoD) Tri-Services Environmental Risk Assessment Workgroup (TSERAWG) relates to Sections 3.3.3 and 3.3.4 of the DoD Vapor Intrusion Handbook and reflects application of new technologies for vapor intrusion sampling.

Introduction

Passive sampling is an alternative to USEPA Methods TO-15 and TO-17 for monitoring VOC vapor concentrations and has some potential advantages for vapor intrusion assessments. Recent research sponsored by the Department of Defense (DoD) through the Environmental Security Technology Certification Program (ESTCP) program [\[link to ESTCP 2015 reports\]](#) demonstrated and validated the use of passive samplers for assessing subsurface vapor intrusion to indoor air, including controlled laboratory tests and uncontrolled field tests and demonstrating quantitative passive soil vapor monitoring for the first time. The Naval Facilities Engineering Command (NAVFAC) recently issued a Technical Memorandum [\[link to NAVFAC 2015\]](#) summarizing the research and applications and the United States Environmental Protection Agency (U.S. EPA) issued an Engineering Issues Paper [\[link to EPA 2014\]](#) with detailed information for users. This fact sheet is intended to provide a high-level overview and offer reference to resources that detail the application and analysis of passive sampling for vapor intrusion.

Potential Advantages

- Time-weighted average (TWA) concentrations of volatile organic compounds (VOCs) in indoor air, outdoor air and soil gas that are less subject to the influences of temporal variability
- Simple protocols - reduces the cost of sampling and risk of operator error
- Long track record - three decades of use in industrial hygiene and radon monitoring
- Several commercial samplers and sorbents to choose from - customize to site conditions
- Smaller and lighter – easier and less expensive to ship to sites and labs
- Less obtrusive than conventional samplers

Potential Limitations

- Weakly sorbed chemicals may not be well retained by passive samplers and strongly sorbed chemicals may not be well recovered during analysis, so the sorbent used within the sampler must be selected to suit the compounds of concern.
- The uptake rate of the sampler is calibrated by comparison to concentrations measured using conventional methods. Not all passive samplers have been calibrated for all compounds of

potential concern under all conditions, but field-calibration is always an option and recommended where the highest level of data quality is desired.

- Blank contamination is possible if the samplers are not stored and handled appropriately, so travel blanks are needed as a quality assurance/quality control measure.

Keys to Data Quality

- Routine quality assurance/quality control (QA/QC) plus trip blanks, media blanks, duplicates
- Select a sampler with calibrated uptake rates for the key chemicals of concern that are low enough to avoid the starvation effect, but high enough to achieve desired reporting limits in a reasonable sample duration.
- Select sample duration to achieve desired reporting limit.
- Select sorbents for good retention (safe sample volume > product of uptake rate x sample duration) and recovery (same as EPA Method TO-17).
- Consider field calibration when the highest levels of data quality are desired.

Rationale for Passive Sampling

Vapor intrusion is a pathway of potential human exposure to volatile chemicals below buildings. The U.S. EPA issued guidance in June 2015 [\[link to OSWER 2015\]](#) which provides the guidance for assessment of vapor intrusion at current or potential future occupied buildings near volatile chemicals in the subsurface. Indoor air sampling and analysis by EPA Method TO-15 [\[link to EPA 1999\]](#) is currently the most common method for vapor intrusion assessments, but the method is not designed for samples of a duration longer than a few days at most and is usually used over an 8- or 24-hour period. Temporal variability in the indoor air concentration occurs in response to changes in the wind, barometric pressure, building pressure and ventilation, so any given sample may indicate concentrations that are lower or higher than the longer-term average values. Radon researchers have been aware of this for decades and have developed sampling protocols for short-term (2 days to 90 days) or long-term (>90 days) exposures. Passive samplers can be used to provide TWA samples over a period of a week or potentially longer, which is a practical alternative to collecting a time-series of canister samples. Passive samplers are also smaller, and therefore less expensive to ship than Summa® canisters and the sampling protocols are much easier, both of which reduce cost.

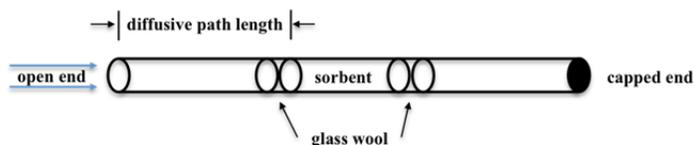
How Passive Samplers Work

There are several generic configurations of passive samplers, as shown in Figure 1. The U.S. EPA Engineering Issues Paper includes a list of commercially available samplers. Passive samplers contain a sorbent (e.g., activated carbon or one of several synthetic alternatives) that acts as a trap for VOCs. The sorbent ideally retains all of the vapors taken up by the sampler over the duration of the sample and releases them with high efficiency during sample preparation prior to analysis. The retention and recovery of VOCs on various sorbents has been well-documented in industry literature because it is critical for accurate sampling using pumped (i.e., active) adsorptive tubes.

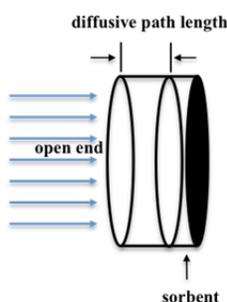
Sorbents fall into two general categories — very strong sorbents requiring solvent extraction and relatively weaker sorbents amenable to thermal desorption. Strong sorbents are not well-suited for highly sorptive compounds (polychlorinated biphenyl [PCB], polycyclic aromatic hydrocarbons [PAHs], and other semi-volatile organic compounds [SVOCs]) and are more appropriate for weakly sorbed

compounds (e.g., vinyl chloride, chloromethane and other low molecular weight, low boiling point compounds such as naphthalene). It is possible that multiple sorbents may be required to sample a range of compounds for a given vapor intrusion investigation, or if there is a short list of probable risk drivers, then the sorbent can be selected to best suit the primary compounds of interest. Analytical chemists familiar with EPA Method TO-17 should be consulted to select the appropriate sorbent for each compound of interest (with preference to the dominant risk drivers).

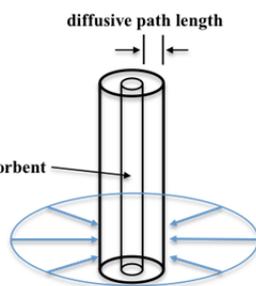
Axial or Tube Sampler



Badge Sampler



Radial Sampler



Membrane Sampler

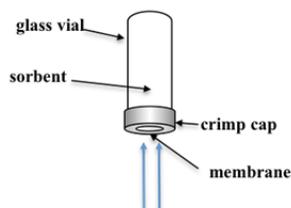


Figure 1: Four generic configurations of passive samplers for VOC vapors (Courtesy of Geosyntec)

The concentration gradient from the surroundings to the sorbent provides the driving force for diffusion of VOC vapors into the sampler. The diffusion rate depends on the concentration gradient, the open area of the face of the sampler, the distance from the face of the sampler to the sorbent and the diffusion coefficient through the medium between the sorbent and the face of the sampler. Diffusion occurs through a medium of air in most cases, but can also occur through a membrane with known permeation rates for the VOCs of interest.

The TWA concentration (C) is calculated from the mass (M) of each VOC (determined by laboratory analysis of the sorbent) divided by the product of the sample duration (t) and the uptake rate (UR):

$$C = \frac{M}{UR t}$$

The sample duration is usually measured with negligible error and the laboratory analysis of the mass sorbed is usually well-controlled, so the key to accurate concentrations with passive sampling is the uptake rate. The uptake rate can vary as a function of temperature, humidity, air velocity or other factors, but fortunately, indoor air is usually climate-controlled for occupant comfort, which limits the impact of these factors. For outdoor air sampling, or where VOCs of interest include compounds for which a particular sampler has not yet been calibrated, a select number of inter-method duplicate samples (e.g., one canister/TO-15 sample for every 10 passive samples) provide field-verified uptake

rates. The reproducibility of passive samplers for a given set of conditions is very good (McAlary et al., 2015), so once the passive sampler is calibrated for a particular compound and/or site conditions, the accuracy is reliable for the batch of samplers.

Design Considerations

For each passive sampling campaign, the sampler type, sorbent and exposure duration should be considered with respect to the data quality objectives. The U.S. EPA Engineering Issues Paper covers this in detail, and an overview is provided here. Field methods for passive soil vapor sampling are described in McAlary et al., 2014c with schematic diagrams of suggested probe designs. The selection process typically includes the following steps:

1. Identify compounds of concern, target concentrations (e.g., risk-based indoor air concentrations or action levels defined for the site), and where possible rank the compounds according to probable contribution to cumulative risk based on the site conceptual model.
2. Select a passive sampler that has calibrated uptake rate values for the key chemicals of concern and other compounds of potential interest to the extent practical. For sub-slab and soil vapor sampling, low uptake rates (~1 mL/min or less) are desired to avoid the starvation effect.
3. Select a minimum sample duration (t_{\min}) sufficient to achieve a concentration reporting limit as low as or lower than the target concentration for each of the key chemicals of concern (t_{\min} = mass reporting limit achievable at the laboratory divided by the product of the target concentration and uptake rate).
4. Select an appropriate sorbent through consultation with the analytical chemist. It is prudent to verify that the sorbent has a recommended safe sample volume larger than the product of the uptake rate and sample duration for each of the key compounds of interest. This can be used to constrain the maximum sample duration (t_{\max}).
5. Select the number and location of samples using building-specific data [\[link to ASTM 2010\]](#).
6. For the highest quality of data, it is prudent to add a certain percentage of inter-method duplicate samples (e.g., one Summa canister sample co-located with a passive sampler for every 10 passive samples collected), which can be used to derive "field-calibrated" uptake rates.

Applications for Passive Samplers

Indoor Air, Outdoor Air, and Soil Gas: Passive samplers can be used to measure VOC vapor concentrations in indoor air, outdoor air and soil gas as part of a multiple lines of evidence assessment of vapor intrusion. Passive samplers can provide indoor air quality data with less uncertainty attributable to temporal variability because they can be collected over a longer duration than methods like TO-15 and TO-17. However, they may not be able to achieve all of the requirements for Level IV data validation, and may need to be supplemented with TO-15 or TO-17 data to meet full target compound list [TCL]/target analyte list [TAL] specifications for definitive data. Passive samplers are simpler to use than TO-15 or TO-17, and can be valuable as an initial screening method to identify locations for TO-15 or TO-17. In many cases, the screening level results provide information that can inform risk management decisions (i.e., if the passive sample results exceed screening levels by a large margin, mitigation decisions could proceed).

Passive soil vapor sampling has been used as an inexpensive option for subsurface VOC plume mapping for decades, but until recently was not considered capable of providing quantitative concentration data

[\[link to CalEPA/DTSC 2011\]](#). McAlary et al. (2014a, b, c) demonstrated that quantitative passive sampling is feasible, as long as the sampler has an uptake rate lower than the rate of vapor diffusion through soil to the face of the sampler, in order to minimize the negative concentrations bias that would occur if the passive sampler withdraws target compounds from the surrounding media faster than they are replenished (called the starvation effect). In soils with relatively high moisture contents, there is a risk that even low-uptake rate passive samplers may suffer from the starvation effect. In these cases, Figure 7 of McAlary et al., 2014a could be used to estimate the uptake rate if the water-filled porosity is known. Otherwise, the void-space could be designed to be relatively large (~1L) and the passive sampler could be deployed only after the void-space has been allowed to equilibrate with the surrounding soil (roughly 1 day).

The sample duration can be adjusted to provide TWA samples over a particular interval of interest. Passive samplers have provided reliable results over sampling time periods ranging up to three months, as long as a strong sorbent is used and the uptake rate is low enough to avoid saturation of the sorbent (see “Design Considerations”). For carcinogenic chemicals, risk-based target concentrations are derived for exposure durations ranging from a few years up to 25 or 30 years, so longer sample durations would generally be preferred. For sub-chronic and acute health risks, shorter sample duration may be more appropriate, in which case a sampler with a higher uptake rate may be preferred. It is critical to understand the toxic endpoint(s) of potential concern in order to ensure the sampling duration is appropriate for the risk analysis. Analytical chemists and risk analysts should be consulted to select the appropriate sample duration for the required screening level.

Workplace Settings: For workplace monitoring, the passive samplers can be sealed in their shipping containers during non-work hours to provide a TWA concentration specific to the working conditions. This is particularly valuable for buildings where the ventilation system operates in a diminished mode when the building is unoccupied, which often reduces the air exchange rate and associated dilution.

Residential Settings: In cases where a large number of residential properties require assessment, passive samplers can provide a relatively unobtrusive initial assessment. A sample can be collected by the resident with minimal instruction, which avoids the resistance of some private property owners to grant access agreements for field sampling crews. The simplicity of passive samplers is particularly valuable for periodic monitoring because a building occupant (homeowner, custodian, etc.) can usually be trained to perform the sampling with minimal effort (the majority of industrial hygiene samples and radon samples are collected this way).

Mitigation Systems: Periodic monitoring of the vent-pipe concentrations of a sub-slab venting system can provide very useful data to support closure of the mitigation system if the mass removal rate falls below the level that would be required to sustain indoor air concentrations above the risk-based target concentration. Membrane samplers are well-suited to monitoring VOC vapor concentrations in vent-pipes because they are not susceptible to advective uptake in a high velocity environment.

Passive samplers should be considered a line of evidence and may not be ideal for all sampling programs. For example, if a rapid assessment of a worst-case condition is desired, it may be preferable to depressurize the building using fans, and collect a grab sample by canister for TO-15 analysis. Some compounds have very low risk-based screening levels (RBSLs) and require long sample durations for passive samplers to be able to achieve concentration reporting limits lower than the RBSL (e.g., 1,1,2,2 tetrachloroethane, 1,2-dichloroethane, chloroform) so sites where these compounds are expected to be risk drivers may be better suited to monitoring by other methods. In some cases, real-time sampling and

analysis may provide unique benefits (e.g., identification of unexpected indoor sources of chemicals) and a mobile laboratory or portable mass spectrometer may be preferable.

Laboratory Selection and QA/QC

Passive samplers should be selected in conjunction with laboratories familiar with their preparation and analysis. The sorbent used should be batch verified or desorbed and certified prior to use. Samplers should be stored away from VOC sources in inert packaging and a shelf-life study should be available to document their expiration date. When sampling is performed, a select number of samples should be included as trip blanks, which accompany the investigative samples during shipping to and from the investigative site, but are never opened – any compounds detected on the trip blanks must be considered in the data validation and interpretation of the investigative samples.

Data Interpretation

Where practical, focus the list of analytes to the primary risk drivers (chemicals present in the subsurface at concentrations that are highest relative to their risk-based screening levels), rather than all analytes that can be quantified by the laboratory to minimize potential confusion attributable to background sources of VOCs.

Consider potential fluctuations in concentration that could occur within the TWA sample, for example: A passive sampler with a 30-day TWA concentration of TCE of $0.1 \mu\text{g}/\text{m}^3$ must have had no 24-hour period $> 3 \mu\text{g}/\text{m}^3$, and no 8-hour period $> 9 \mu\text{g}/\text{m}^3$ and no week-long period $> 0.4 \mu\text{g}/\text{m}^3$.

Cost Comparison

Passive samplers have a similar cost per analysis to conventional sampling; however, the overall program cost can be less for large numbers of samples because the protocols are fast and simple, which results in less labor, and the samplers are small and lightweight, which reduces shipping charges.

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