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Quantitative Passive Soil Vapor Sampling for VOCs: Field Experiments

Todd McAlary¹,²*, Hester Groenevelt¹, Paul Nicholson¹, Suresh Seethapathy², Paolo Sacco³,
Derrick Crump⁴, Michael Tuday⁵, Heidi Hayes⁷, Brian Schumacher⁶, Paul Johnson⁸, Tadeusz
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“Passive soil vapor sampling can now be used to quantify concentrations of VOC vapors, no
longer just the relative mass”

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Environmental Impact Statement
To accompany the submission of the draft paper entitled: Quantitative Passive Soil Vapor Sampling for VOCs: Field Experiments
McAlary et al, 2013

Conventional soil vapor sampling for VOC analysis can be impractical in low-permeability soils and time-consuming if quality control measures are implemented to verify the absence of leaks. Passive adsorptive sampling has been an alternative to conventional active sampling for decades, but the uptake rate of the sampler has never been well understood or controlled, so passive sampling has been considered a qualitative or semi-quantitative method. This paper provides the results of a series of controlled field sampling experiments, which demonstrate that passive soil vapor sampling can provide quantitative concentration measurements when the uptake rate is low enough to avoid the starvation effect and the sorbent is strong enough to retain the compounds of interest over the sampling period.
Quantitative Passive Soil Vapor Sampling for VOCs: Field Experiments

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ABSTRACT

Volatile organic compounds (VOCs) are commonly associated with contaminated land and may pose a risk to human health via subsurface vapor intrusion to indoor air. Soil vapor sampling is commonly used to assess the nature and extent of VOC contamination, but can be complicated because of the wide range of geologic material permeability and moisture content conditions that might be encountered, the wide variety of available sampling and analysis methods, and several potential causes of bias and variability, including leaks of atmospheric air, adsorption/desorption interactions, inconsistent sampling protocols and varying levels of experience among sampling.

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personnel. Passive sampling onto adsorbent materials has been available as an alternative to
conventional whole-gas sample collection for decades, but relationships between the mass sorbed
with time and the soil vapor concentration have not been quantitatively established and the
relative merits of various commercially available passive samplers for soil vapor concentration
measurement is unknown. This paper presents the results of field experiments using several
different passive samplers under a wide range of conditions. The results show that properly
designed and deployed quantitative passive soil vapor samplers can be used to measure soil
vapor concentrations with accuracy and precision comparable to conventional active soil vapor
sampling (relative concentrations within a factor of 2 and RSD less than about 80%) where the
uptake rate is low enough to minimize starvation and the exposure duration is not excessive for
weakly retained compounds.

1. INTRODUCTION

Quantitative passive vapor samplers of the kinetic variety provide time-weighted average
concentrations (C) of vapors in the media (usually indoor or outdoor air) to which they are
exposed. C is calculated by dividing the mass of each analyte sorbed (M) by the analyte-specific
uptake rate of the sampler (UR) and the sample time (t)\(^1\). Analyte uptake rates for quantitative
samplers can be determined experimentally or estimated theoretically and they are typically
supplied by the vendor of the passive sampler. This distinguishes the quantitative samplers
tested in this study from qualitative or semi-quantitative passive samplers (e.g., Gore™ Modules
2, Beacon BeSure Passive Soil Gas Technology™ 3, EMFLUX Cartridges™ 4, Petrex tubes™ 5,6
and similar devices) that are not specifically designed to constrain and uniformly control analyte
uptake rates. To date, passive soil vapor samplers have been shown to provide qualitative or
semi-quantitative soil vapor data; however, the ability to quantify soil vapor concentrations from
the mass retained on the sampler has not been established. As a result, many regulatory guidance documents caution that passive soil gas sampling should only be used as a qualitative or semi-quantitative screening tool. Even when a passive sampler is designed in a way that allows the analyte uptake rates to be controlled (e.g. by incorporation of a well-defined diffusion or permeation barrier between the sampled medium and the sorbent), soil gas sampling creates unique challenges. On the one hand, the sampler uptake rate must be high enough to allow quantification of concentrations of concern for an acceptable sampling duration. On the other hand, the uptake rate must be low enough that the sampler itself does not remove analyte vapors faster than they are transported to its face from the surrounding medium, because this would result in a localized reduction in the vapor concentrations near the sampler compared to the surrounding soil, and a low bias in the vapor concentrations (sometimes referred to as the “starvation effect”).

This paper describes a series of controlled field experiments designed to elucidate the optimal approach to soil gas sampling using kinetic passive samplers. The tests were conducted over a wide range of operating conditions: sample durations from 20 minutes to 11.7 days, concentrations from about 100 to about 60,000 µg/m³, uptake rates from about 0.05 to 80 mL/min, several different chlorinated VOCs, 2.4 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 (solvent extraction and thermal desorption) for each of several different types of commercially-available passive samplers and sorbent media. This provides a previously unavailable set of data with which to assess the capabilities and limitations of passive soil vapor sampling for VOC
concentration measurement. A companion paper\textsuperscript{10} provides theoretical information based on mathematical modeling to support the experimental results provided herein.

2. EXPERIMENTAL

Materials and Methods

The quantitative passive samplers used in this study included: SKC Ultra\textsuperscript{TM} \textsuperscript{11} from SKC, Inc.; Radiello\textsuperscript{®} \textsuperscript{12} from Fondazione Salvatore Maugeri; OVM 3500\textsuperscript{TM} \textsuperscript{13} from 3M; Waterloo Membrane Sampler\textsuperscript{TM} or WMS\textsuperscript{TM} \textsuperscript{14,15} from SiREM Laboratory, and Passive ATD tube samplers\textsuperscript{16,17} from Perkin Elmer. Some of these samplers are available with different sorbents and uptake rates, which allowed different combinations to be evaluated, as described for each test site. The uptake rates used in the study were either supplied by the vendor or estimated from the free-air diffusion coefficients\textsuperscript{18} for diffusive samplers. In the case of the WMS sampler, which uses a polydimethylsiloxane (PDMS) membrane as the rate-limiting barrier, the uptake rates for compounds for which they had not been determined experimentally were estimated from the correlation between the UR and the linear temperature-programmed retention indices of the analytes on PDMS-coated GC columns\textsuperscript{14}. Laboratory analytical methods are described in the Supplemental Information.

Sampling Locations

Samples were collected at: 1) the US Navy San Diego Old Town Campus (OTC), 2) the Arizona State University (ASU) study house in Layton, Utah (near Hill Air Force Base) and 3) Naval Air Station Jacksonville, Florida (NAS JAX), all of which were known to have VOCs in the subsurface near occupied structures, in which case regulatory guidance recommends assessment of potential health risks using lines of evidence including soil vapor concentration measurement.
for individual compounds. Sub-slab samples were collected immediately below concrete slabs at OTC and NAS JAX and deeper soil gas samples were collected at the Layton house and NAS JAX. For vapor intrusion assessments, most regulatory guidance documents recommend that soil gas samples be collected 1.5 m (5 feet) or deeper below ground surface. The experimental designs were as follows:

**Navy OTC:** passive sub-slab samples were collected immediately below the concrete slab-on-grade ground cover 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. Initial screening with a photoionization detector showed total ionizable vapor concentrations in the 0.1 to 10 parts per million v/v (ppm) range. The primary contaminant of concern (COC) was trichloroethene (TCE). Sampler deployment durations were 2 h at location SS-2 where the field screening data showed higher concentrations and 15 h at location SS-5 (where the field screening readings showed lower concentrations) in order to assure that sufficient mass would be collected to provide detectable results, but minimize the risk of overloading the sorptive capacity of the samplers. All five passive samplers were used for sub-slab sampling in configurations (uptake rate and adsorbent) described in Table 1. Samplers were placed in holes drilled or cored through the concrete (depending on the diameter needed to accommodate the sampler), located in a circle of ~1 m diameter, with the Summa canister sample collected in the center of the circle. The volume of the void space in which the samplers were deployed ranged from about 25 mL for the 1-inch diameter drill holes to about 100 mL for the 2-inch diameter coreholes. Immediately after the passive sampler deployment, one liter of soil gas was purged to remove any atmospheric air that may have entered the hole, and the hole was sealed using a rubber stopper wrapped in
aluminum foil to provide a flexible and inert plug. The purged gas was screened to confirm consistent total ionizable vapor concentrations with a Phocheck+™ photoionization detector (PID) from Ionscience (Cambridge, UK), which was field-calibrated according to manufacturer’s instructions.

**Layton House:** six passive soil gas monitoring probes were installed to a depth of about 4 m (12 ft) in a circular pattern with a radius of about 1 m using a 10-cm (4-in) diameter hand-auger. Each probe was constructed of 3 m (10 ft) length of 5 cm (2-in) diameter Schedule 40 PVC pipe, with stilts on the bottom to suspend the pipe 0.6 m (2 ft) above the bottom of the borehole. The volume of the void space in which the samplers were deployed was about 5 L. A gasket wrapped in aluminum foil isolated the region above the void space, and the annulus between the PVC pipe and borehole wall above the gasket was filled with a hydrated bentonite slurry (Figure 1). The soil consisted of cohesive brown fine sandy silt with trace clay, with moisture content increasing as the depth approached the water table (~4 m depth). The primary VOCs were trichloroethene (TCE) and 1,1-dichloroethene (1,1-DCE) at concentrations of several hundred µg/m³. To minimize the risk of non-detect results, samples were collected from just above the water table, where soil vapor concentrations were expected to be highest. 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 design²⁰). Active samples were collected after purging at least 6 L from each probe using a vacuum chamber and a 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) via a Tedlar bag and vacuum chamber, and two rounds of active
samples were collected in Summa® canisters and analyzed by EPA Method TO-15.

FIGURE 1

The passive samplers used at the Layton House were customized as follows:

• A 12-hole cap was used with the SKC Ultra Sampler to reduce the uptake rate and
minimize the starvation effect; charcoal was the sorbent.

• The ATD Tube sampler was used with two different sorbents (Carbopack B and Tenax
TA) to assess their relative performance.

• The WMS sampler was also used in two configurations, the regular variety (1.8 mL vial)
and an ultra-low uptake variety for which the membrane was covered with an aluminum
shield with a 1/16” diameter hole drilled through it. The results for the ultra-low uptake
rate variety were below limits of detection for most analytes, so the data are not
presented.

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. The water
table was about 1.5 m (5 ft) below ground surface and the vadose zone was a relatively uniform,
cohesionless, medium-textured sand. To avoid the risk of contact with groundwater, the passive
samplers were deployed just above the water table. The primary VOCs were tetrachloroethene
(PCE), TCE, cis-1,2-dichloroethene (cis-1,2-DCE) and trans-1,2-dichloroethene (trans-1,2-
DCE).
Exterior passive soil gas samples were collected using three 5 cm (2-in) diameter schedule 40 PVC probes in 10 cm (4-in) diameter hand-augered holes with void space lengths of about 15, 30 and 45 cm (6, 12 and 18-in) to assess whether the void volume (1.2 L, 2.4 L and 3.6 L, respectively) 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 5 samplers and 35 Summa® canister samples were collected for analysis by EPA Method TO-15 (1:1 ratio). This experimental design was a randomized two-factor, one-half fraction, fractional factorial with triplicates at the center-points (40 minute sample time in the 30 cm tall void).

The annular seal was constructed by placing fine sand into the annulus between the 2-in PVC well pipe and the 13 cm (5-in) diameter flexible polyethylene sleeve (Figure 2) and tamping the sand with a wooden dowel to cause the plastic sleeve to expand out to the wall of the 10-cm (4-in) diameter borehole. After placing the seal, each probe was purged until PID readings stabilized, then left capped overnight to equilibrate.

**FIGURE 2**

Passive soil gas samplers were suspended by nylon lines attached to the bottom of the slip cap and cut to a length just longer than the PVC pipe, so that the samplers were suspended in the open region below the pipe during sampling. Immediately after the passive samplers were deployed and the slip-caps secured, purging was conducted through a 1/4-in compression fitting in the top of the slip-cap. Field screening readings were made by continuously purging each probe and monitoring the effluent with a field-calibrated ppbRAE™ PID by RAE Systems of San Jose, CA. PID readings were consistently within the range of 1.0 to 1.5 ppmv for all three probes, and generally stabilized within about 20 to 30 seconds. Purge rates were about 3 L/min,
so the purge volume was typically about 1 to 1.5 liters, which corresponded to about 1 casing
volume for the probe pipe.

Low-uptake varieties of the Radiello sampler (yellow body), SKC Ultra Sampler (12-hole cap)
and WMS sampler (WMS-LU - 0.8 mL amber vial) were used to minimize the starvation effect.
The ATD tube sampler already has a relatively low uptake rate and was not modified with a low-
uptake cap to avoid having results below the limits of detection. The 3M OVM 3500 sampler
does not have a low-uptake variety.

A 1-L Summa canister sample was collected immediately after purging via a 1/8-in stainless
steel drop-tube (see Figure 2) that extended through a compression-fitting in the slip cap to a
depth just below the bottom of the PVC pipe (i.e., top of the void space), such that the canister
sample was collected below the PVC pipe. The canister was filled quickly (over about 10
seconds) so that the passive sampler would not be biased by advection from the active sample
collection during most of the passive sampling period.

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 h duration was sufficient because the
concentrations were >1,000 µg/m³) and one Summa® canister. Immediately after passive sampler
deployment, the hole was purged to remove any atmospheric air entrained during drilling or
removal of the prior passive sampler using a vacuum chamber and a 1-L Tedlar bag, which was
screened with a field-calibrated ppbRAE® PID to measure the total VOC vapor concentration.
At least two successive purge measurements were made to assure stable PID readings, after which the hole was capped using a foil-covered rubber stopper. The passive samplers were surrounded by a stainless steel wire cage to protect them from direct contact with the soil. The low-uptake rate cap was used for the ATD tube in the sub-slab samples. The WMS and Radiello samplers were the same low-uptake rate configurations used for the external soil gas sampling.

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. The low-uptake WMS sampler was deployed for 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.

3. RESULTS AND DISCUSSION

The results of sampling at the Navy OTC site are shown in Table 1. The compounds detected in the Summa canisters included TCE and cis-1,2-DCE, in the range of 450 to 63,000 µg/m$^3$. The passive sub-slab samplers had a low bias of about 10X to 100X relative to the active samples collected via Summa canister. The magnitude of the low bias generally increased as the uptake rate of the sampler increased, which is consistent with expectations from mathematical modeling\textsuperscript{10}. Based on these results, lower uptake rate samplers were used at the Layton House and NAS JAX.

TABLE 1
At the Layton house, TCE and 1,1-DCE were the primary compounds detected, typically in the range of 100 to 500 µg/m³ in the active samples (Table 2). The average active sample concentrations in Table S1 and S2 (Supplementary Information) were calculated as the mean of the concentrations measured at the beginning and end of the associated passive sampler sample interval, with the exclusion of a few samples that appeared to be biased compared to others from the same probe (shown in bold and italics in Table 2). The concentrations measured with the passive soil vapor samplers (C) were divided by the average active concentration (Co) as shown in Figure 3. These data showed several trends that were consistent with expectations based on transient and steady-state mathematical models of radial vapor diffusion to a borehole in which a passive sampler would be deployed¹ and experience with active (pumped) sorptive sample collection:

- The sampler with the highest uptake rate (Radiello: 79 and 69 mL/min for 1,1-DCE and TCE, respectively) generally showed the lowest concentrations, which is most likely attributable to the starvation effect.

- Three data sets showed low bias in the longer-duration samples (ATD with Tenax TA for both 1,1-DCE and TCE, and ATD Carbopack B for 1,1-DCE). These compounds are not strongly retained on these sorbents as evidenced by experimental data reported by Supelco, who report recommended maximum sample volumes²¹ of 0.2, 1.0 and 0.2 L, respectively for these compounds and sorbents. The recommended maximum sample volume is the volume of air that can be drawn through an automatic thermal desorption tube containing a certain mass of a given compound before the compound is liberated from the sorbent and losses become significant via breakthrough. The ATD sampler with Carbopack B showed good retention for TCE, which has a recommended maximum
sample volume of 20 L or more for this sorbent. These data indicate that the low bias is likely attributable to poor retention for the sorbent/analyte combinations with low SSV values and long sample durations.

- The SKC sampler (low uptake cap and charcoal) and WMS sampler (1.8 mL vial and Anasorb 747) showed data very comparable to the active samplers with no apparent lack of retention in the longer-term samples. The SKC and WMS samplers had similar uptake rates to the ATD samplers, so the improved performance in the longer-duration samples is apparently attributable to better retention of 1,1-DCE and TCE by stronger activated carbon-based sorbents.

**FIGURE 3a,b**

The results of the active (Hapsite and Summa) samples at the Layton house showed the ranges of variability that are typically observed with active soil gas sampling (Table 2). Temporal variability can be assessed by comparing the concentrations measured in each probe over 9 events in 6 weeks, while spatial variability can be assessed by comparing the concentrations from 6 probes within one meter of one another. The relative standard deviation (RSD, standard deviation divided by the mean) ranged from 23% to 57% for temporal variability and 31% to 84% for spatial variability. The pooled mean concentration and RSD for 1,1-DCE were 250 µg/m³ and 38%, respectively. The pooled mean concentration and RSD for TCE were 350 µg/m³ and 28%, respectively.

**TABLE 2**

A similar calculation of the mean, standard deviation and relative standard deviation (RSD) for the passive samplers (Table 3) showed that the WMS sampler had an RSD of 40% and 55% for
TCE and 11DCE, respectively. The SKC sampler had RSDs of 52% to 80% for TCE and 11DCE, respectively. The ATD with Carbopack B had an RSD for TCE of 72%. These are all comparable to the active sampler variability, which is encouraging considering the passive samples were collected in different probes, so each set included both spatial and temporal variability. The WMS sampler and SKC Ultra Low-Uptake samplers provided concentrations that were on average within a factor of 2 of the active soil gas sample concentrations. Low biases for the TCE and 11DCE with the Radiello sampler and 11DCE with the ATD tube sampler were consistent with expectations of the starvation effect1 and poor retention21, respectively. As a result, the NAS JAX test used the low-uptake variety of the Radiello (yellow body) and the stronger sorbent (Carbopack B) in the ATD tubes.

**TABLE 3**

The results of passive sampling at NAS JAX (Table S3) showed a broader range of concentrations (~100 to ~30,000 µg/m$^3$) than the previous data sets (Table S2), so the data are presented on x-y scatter plots with the active and passive concentrations as the x and y axes, respectively and logarithmic scales (Figures 4a and 4b). The exterior soil gas passive sampler concentrations (Figure 4a) all yielded regression lines with slopes ranging from 0.67 to 1.46 and correlation coefficient ($R^2$) values of 0.80 to 0.96. The regression lines for the WMS and Radiello samplers fell within the +/-25% range (inner dashed lines in Figure 4a) and the WMS sampler had a better correlation coefficient than the Radiello (0.96 vs. 0.80). Only 8 of the 117 detectable results for all the samplers fell outside the +/- 50% range (outer dotted lines), of which 4 were for TCE in SKC samplers, which may be related to trip blank contamination. Some results fell below the reporting limits (“U-qualified”), including trans-1,2-DCE for the WMS sampler, TCE for the Radiello and some of the PCE and trans-1,2-DCE values for the Radiello.
FIGURE 4a,b

Statistical analysis of the fractional factorial design via analysis of variance (ANOVA) at the 5% level of significance (Table S4) showed that the sampler type was a significant factor for all four compounds detected, sampling duration was not statistically significant, and the void volume was only statistically significant for trans-1,2-DCE and TCE.

The interior passive sub-slab samples at NAS JAX also showed strong positive correlations with active sample results (Figure 4b). The passive samplers all yielded regression lines with slopes ranging from 0.51 to 1.88 and $R^2$ values of 0.71 to 0.95. The regression line for the WMS samplers fell within the +/- 25% range, with a correlation coefficient of 0.95. The regression lines for the ATD and Radiello samplers were within the +/-50% range of an ideal (1:1) correlation, with slightly lower correlation coefficients (0.86 and 0.71, respectively) than the WMS sampler.

The exterior passive soil gas samples from a temporary (uncased) hole also showed good correlation to the active (Summa canister) samples (Figure 5), which indicates that uptake rates of 0.5 to 1.1 mL/min for the four compounds detected are low enough to avoid a low bias via starvation for these compounds in a small diameter (2.5 cm) drillhole in sandy soil. This is encouraging because this is consistent with expectations based on mathematical modeling\(^1\) and temporary sampling is a common application of passive soil vapor monitoring because the costs of deployment are much lower compared to the installation of a probe that can be sampled on multiple occasions. Note that the combination of sandy soil and a low-uptake rate sampler were used in this test, which minimizes the risk of a low bias attributable to the starvation effect.

FIGURE 5
The data presented here span a wide range of sample durations, concentrations, uptake rates, several different chlorinated VOCs, void space volumes, ambient temperatures, and methods of sorption and desorption prior to laboratory analysis by several different laboratories using several different samplers and types of sorbent media, which provides unique insight into the capabilities and limitations of passive soil vapor sampling. Three potential challenges were identified:

- **Retention:** combinations of adsorbents and analytes with low recommended maximum sampling volumes (11DCE:Carbopack B, 11DCE:Tenax TA and TCE:Tenax TA at the Layton house, and Chromosorb 106 with TCE and cisDCE at OTC) showed low biases, particularly for longer-term samples. Poor retention can be avoided by selecting adsorbents with higher recommended maximum sampling volumes for the compounds of concern.

- **Starvation:** low biases were more common for samplers with high uptake rates. Figure 6a shows the relative concentration ($C/C_0 = \frac{\text{passive concentration}}{\text{active sample concentration}}$) as a function of the uptake rate. Starvation was minimal on average for samplers with uptake rates of about 1 mL/min or less. Some samplers with higher uptake rates showed good accuracy, which is related to the third challenge.

- **Probe Design:** samplers were deployed in probes with void volumes ranging from 25 mL to 5 L to assess whether this had an effect on the passive sampling results. Figure 6b shows the relative concentration as a function of the ratio of the effective sample volume (UR x t) divided by the void space volume. Low biases were more common for cases where the samplers were deployed in void spaces that were smaller than the effective sample volume (i.e., UR x t/void volume <1), as shown in Figure 6b. In these cases, the mass of vapors in the void-space is not sufficient to satisfy the needs of the sampler and
vapors must diffuse into the void-space from the surrounding soil to avoid starvation, and
this 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\textsuperscript{10}, or 3) using a
short sample duration if the vapor concentrations are high enough to obtain a detectable
result.

FIGURE 6

4. CONCLUSIONS

The passive soil gas concentrations with low uptake rates, strong adsorbents and (UR x t) values
similar to or less than the void volume show a better quantification of soil vapor concentrations
compared to active sampler results than any previously published comparisons that the authors
are aware of.

Additional testing is warranted to evaluate a wider range of site conditions. In the near term, the
confidence in the accuracy of passive soil vapor sampling can be improved with some on-going
benchmark testing via collection of side-by-side duplicate samples (e.g. one conventional active
soil gas sample for every \textasciitilde 10 passive-diffusive samples). The comparison between the active
sample data and the passive sampler data can be used to derive site-specific and media–specific
uptake rates for the compounds that are detectable in both samples. With proper
calibration/benchmarking, the low variability of the passive samplers is encouraging, and other
benefits such as simplicity, ease of shipping, and lower costs provide sufficient incentive to
justify the calibration/benchmarking effort.
ACKNOWLEDGEMENTS

Funding for this work was provided by the Environmental Security Technology Certification Program (ESTCP) with Sam Brock of the Air Force Civil Engineering Center and Andrea Leeson of ESTCP as the DOD Liaisons and the U.S. Navy SPAWAR Systems Center Pacific under the Improved Assessment Strategies for the Vapor Intrusion project, which is funded by the Navy’s Environmental Sustainability Development to Integration (NESDI) Program under subcontract to Richard Brady and Associates and Computer Sciences Corporation with Bart Chadwick and Ignacio Rivera-Duarte as contracting officers. We gratefully acknowledge Arizona State University and Mike Singletary of Naval Air Station Jacksonville for assistance and site access for sample collection and Caterina Boaretto of Fondazione Salvatore Maugeri for GC analysis of the Radiello samplers.

REFERENCES


8. *Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (Vapor Intrusion Guidance)*, California Environmental Protection Agency/Department of Toxic Substances Control (EPA/DTSC), October 2011.


19. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient*

21. A Tool for Selecting an Adsorbent for Thermal Desorption Applications:


   accessed December 30, 2013.
Table 1: Active and passive soil vapor concentrations in sub-slab samples from Navy OTC, San Diego, along with uptake rates for the passive samplers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sampler</th>
<th>Passive Concentration (ug/m³)</th>
<th>Active (Summa/TO715) Concentration (ug/m³)</th>
<th>C/C₀ (Passive / Active)</th>
<th>Sampler Uptake Rate (mL/min)</th>
<th>Uptake rate x sample time (mL)</th>
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</thead>
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Table 2: TCE and 11DCE concentrations measured in active soil gas samples analyzed by the Hapsite transportable GC/MS (H) or Summa® canister and TO-15 (S) at the Layton house, Utah. Bold and italics indicate samples suspected of low bias because of incomplete purging.

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<th>Spatial Variability</th>
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Table 3: TCE and 11DCE concentrations measured in passive samplers at the Layton House

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<th>8.1</th>
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<th>11.7</th>
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Figure 1: Schematic diagram of the probe for passive soil vapor sampling at the Layton house, Utah.

Figure 2: Schematic diagram of the probe for passive soil vapor sampling at NAS Jacksonville.

Figure 3: Relative concentration (passive/active, or C/Co) at the Layton House, Utah, near Hill AFB for (a) 11DCE and (b) TCE, respectively.

Figure 4: Correlation Between Passive Samples and Summa® Canister Samples at NAS Jacksonville with linear regressions and correlation coefficients ($R^2$) for (a) soil gas and (b) sub-slab samples, respectively, including PCE, TCE, cis-1,2-DCE and trans-1,2-DCE.

Figure 5: Relative Concentration (passive/Summa® canister) for WMS/low-uptake sampler in a 1-inch (2.54 cm) diameter open borehole open from 4 to 5 feet below ground at NAS Jacksonville.

Figure 6: Relative concentration ($C_{passive}/C_{active}$) versus (a) uptake rate, and (b) ($UR \times t$)/Void Volume.
Figure 1
Figure 2
Figure 3

**A.** Layton House - 1,1-DCE in Fully Passive Soil Gas Probes

- **Legend:**
  - 1 Day
  - 2 Days
  - 2.2 Days
  - 7.8 Days
  - 8.1 Days
  - 9.8 Days
  - 11.7 Days

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**B.** Layton House - TCE in Fully Passive Soil Gas Probes

- **Legend:**
  - 1 Day
  - 2 Days
  - 2.2 Days
  - 7.8 Days
  - 8.1 Days
  - 9.8 Days
  - 11.7 Days

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Figure 4

a.

b.
Figure 5
Figure 6

(a) Passive Concentration / Active Concentration (C/Co) vs. Uptake Rate (mL/min)

(b) Passive Concentration / Active Concentration (C/Co) vs. (UR x t) / Void Volume