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Quantitative Passive Soil Vapor Sampling for VOCs: Field Experiments

Todd McAlary[1,2*], *Hester Groenevelt*[1], *Paul Nicholson*[1], *Suresh Seethapathy*[2], *Paolo Sacco*[3], *Derrick Crump*[4], *Michael Tuday*[5], *Heidi Hayes*[7], *Brian Schumacher*[6], *Paul Johnson*[8], *Tadeusz Górecki*[2] *and Ignacio Rivera-Duarte*[9]

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"Passive soil vapor sampling can now be used to quantify concentrations of VOC vapors, no longer just the relative mass"

[*] Corresponding Author - phone: (519) 822-2230 ext 239; fax (519) 822-3151; e-mail: tmcalary@geosyntec.com

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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

Todd McAlary[1,2], Hester Groenevelt[1], Paul Nicholson[1], Suresh Seethapathy[2], Paolo Sacco[3], Derrick Crump[4], Michael Tuday[5], Heidi Hayes[7], Brian Schumacher[6], Paul Johnson[8], Tadeusz Górecki[2] and Ignacio Rivera-Duarte[9]*

[1] Geosyntec Consultants, Inc. 130 Research Lane, #2, Guelph, Ontario, N1G 5G3

[2] University of Waterloo, Waterloo, Ontario Canada

[3]Fondazione Salvatore Maugeri, Padova, Italy

[4]Cranfield University, Cranfield, UK

[5]Columbia Analytical Services, Simi Valley, CA

[6]USEPA, Las Vegas, NV

[7]Eurofins/Air Toxics, Inc. (formerly Air Toxics Ltd.), Folsom, CA

[8]Arizona State University, Tempe, AZ

[9] SPAWAR Systems Center Pacific, San Diego, CA

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

* Corresponding Author - phone: (519) 822-2230 ext 239; fax (519) 822-3151; e-mail: tmcalary@geosyntec.com

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 [2,4,7]. 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 [8,9]. 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")[10].

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/m^3, 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[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™ [11] from SKC, Inc.; Radiello® [12] from Fondazione Salvatore Maugeri; OVM 3500™ [13] from 3M; Waterloo Membrane Sampler™ or WMS™ [14,15] from SiREM Laboratory, and Passive ATD tube samplers[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[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[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[19]) 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_v) 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 $\mu g/m^3$. 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 design[20]). 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 2-factor, one-half fraction, fractional factorial with triplicates at the center-points[20] (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 ppm_v for all three probes, and generally stabilized within about 20 to 30 seconds. Purge rates were about 3 L/min,

178 so the purge volume was typically about 1 to 1.5 liters, which corresponded to about 1 casing
179 volume for the probe pipe.

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

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

191 Sub-slab vapor samples were collected at three locations. It was not possible to drill 5 cm
192 diameter holes through the floor (needed to accommodate the 3M OVM and SKC samplers)
193 because steel reinforcing bars were repeatedly encountered and eventually broke the teeth on the
194 concrete hole-saw. The ATD, WMS and Radiello passive samplers were tested through a 1-inch
195 diameter hammer-drill hole in the floor slab. In each of the three locations, one sample was
196 collected with each type of passive sampler (1 h duration was sufficient because the
197 concentrations were >1,000 $\mu g/m^3$) and one Summa® canister. Immediately after passive sampler
198 deployment, the hole was purged to remove any atmospheric air entrained during drilling or
199 removal of the prior passive sampler using a vacuum chamber and a 1-L Tedlar bag, which was
200 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 $\mu g/m^3$. 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 [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 $\mu g/m^3$ 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 deployed[1] 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 volumes[21] 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 $\mu g/m^3$ and 38%, respectively. The pooled mean concentration and RSD for TCE were 350 $\mu g/m^3$ 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 effect[1] and poor retention[21], 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 $\mu g/m^3$) 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_o = passive concentration / 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[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 ~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.

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REFERENCES

1. T. Górecki and J. Namiesnik, *Trends in Anal. Chem.,* 2002, 21, 276-291.
2. *Environmental Technology Verification Report, Soil Gas Sampling Technology, W. L. Gore & Associates, Inc. GORE-SORBER Screening Survey*, U.S. EPA Office of Research and Development. EPA/600/R-98/095, 1998.
3. Beacon, 2013. http://www.beacon-usa.com/services/passive-soil-gas-surveys/, accessed on December 26, 2013.
4. *Environmental Technology Verification Report, Soil Gas Sampling Technology, Quadrel Services, Inc., EMFLUX Soil Gas System*, U.S. EPA Office of Research and Development. EPA/600/R-98/096, 1998.
5. D.C. Gomes, M. Alarsa, M.C. Salvador and C. Kupferschmid, *Water Sci. Technol.* 1994, 29, 161.

6. M. Anderson and G. Church, *J. Environ. Eng.* 1998, 124, 555.

7. ASTM Standard D7758. *New Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring and Vapor Intrusion Evaluations* ASTM International, West Conshohocken, PA, www.astm.org, 2011.

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.

9. *Vapor Intrusion Pathway: A Practical Guideline* Interstate Technology and Regulatory Council (ITRC), 2007. http://www.itrcweb.org/Documents/VI-1.pdf

10. T.A. McAlary, X. Wang, A. Unger, H. Groenevelt and T. Górecki, Quantitative Passive Soil Vapor Sampling - Part I: Theory. Submitted to *Env. Sci.: Proc. & Impacts,* DOI:10:1039/C3EM00652B.

11. K. Bergemalm-Rynell, B. Strandberg, E. Andersson and G. Sallsten, *J. Environ. Monit.*, 2008, 10, 1172–1178.

12. V. Cocheo, C. Boaretto and P. Sacco, *Am. Ind. Hyg. Assoc. J.*, 1996, 57, 897-904.

13. J.T. Purdham, A.M. Sass-Kortsak and P.R. Bozek, *Ann. Occup Hyg*. 1994, 38, 721-740.

14. S. Seethapathy and T. Górecki, *J Chromatogr A,* 2011, 1218, 143-155.

15. S. Seethapathy and T. Górecki, *J Chromatogr. A*, 2010, 1217, 7907-7913.

16. S. Batterman, T. Metts and P. Kalliokoski, *J. Environ. Monit.*, 2002, 4, 870–878.

17. V. M. Brown, D.R. Crump and D. Gardiner, *Environ. Technol.*, 1992, 13, 367–375.

18. USEPA On-Line Tool for Site Assessment Calculation – Diffusion Coefficients: http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion.html.

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

Air, Second Edition, Compendium Method TO-15 - Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS), Center for Environmental Research, Information Office of Research and Development, U.S. EPA, Cincinnati, OH, January 1999, EPA/625/R-96/010b

20. D.C. Montgomery, Design and Analysis of Experiments, 7th ed., John Wiley & Sons, Inc., Hoboken, NJ, 2009, 656 pp.

21. *A Tool for Selecting an Adsorbent for Thermal Desorption Applications*: http://www.sigmaaldrich.com/etc/medialib/docs/Supelco/General_Information/t402025.Par.0001.File.tmp/t402025.pdf accessed December 30, 2013.

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

Compound	Sampler	Passive Concentration (ug/m^3)	Active (Summa/TO-15) Concentration (ug/m^3)	C/C_o (Passive / Active)	Sampler Uptake Rate (mL/min)	Uptake rate x sample time (mL)
cis-1,2-DCE Probe SS-2 (120 min sample)	WMS (Anasorb 747)	1,400	13,000	0.11	1.9	228
	3M OVM 3500	130	13,000	0.01	29	3,480
	ATD (Chromosorb 106)	570	13,000	0.04	0.47	56
	Radiello (Charcoal)	<26	13,000	<0.002	64	7,680
	SKC (Chromosorb 106)	57	13,000	<0.01	14	1,680
TCE Probe SS-2 (120 min sample)	WMS (Anasorb 747)	3,800	63,000	0.06	3.3	396
	3M OVM 3500	640	63,000	0.01	31	3,720
	ATD (Chromosorb 106)	2,700	63,000	0.04	0.50	60
	Radiello (Charcoal)	75	63,000	0.001	69	8,280
	SKC (Chromosorb 106)	72	63,000	0.001	15	1,800
TCE Probe SS-5 (15 hr sample)	WMS (Anasorb 747)	<6.6	450	<0.015	3.3	2,970
	3M OVM 3500	8.8	450	0.020	31	27,900
	ATD (Chromosorb 106)	37	450	0.082	.50	450
	Radiello (Anasorb 747)	1.9	450	0.004	69	62,100
	SKC (Chromosorb 106)	8.1	450	0.018	15	13,500

417

418 Table 2: TCE and 11DCE concentrations measured in active soil gas samples analyzed by the
419 Hapsite transportable GC/MS (H) or Summa® canister and TO-15 (S) at the Layton house, Utah.
420 Bold and italics indicate samples suspected of low bias because of incomplete purging.

		Temporal Variability						Spatial Variability		
11DCE (µg/m^3)	*	SGP-1	SGP-2	SGP-3	SGP-4	SGP-5	SGP-6	mean	std.dev.	RSD (%)
21-Jul-10	H	360	350	490	460	160	370	360	110	31
22-Jul-10	S	290	440	480	480	160	240	350	140	39
03-Aug-10	H	***26***	260	210	180	59	66	140	98	72
04-Aug-10	H	310	540	430	120	100	300	300	170	57
05-Aug-10	H	270	480	450	200	100	300	300	140	48
07-Aug-10	H	260	340	280	250	77	230	240	87	37
17-Aug-10	S	110	350	200	110	***16***	80	140	120	81
25-Aug-10	H	200	390	330	180	49	250	230	120	52
02-Sep-10	H	210	230	220	230	56	170	190	68	36
Mean		230	370	340	240	86.6	220	250	120	50
std.dev		100	98	120	140	49.3	100	83		
RSD (%)		46	26	35	56	57	46	33		
TCE (µg/m^3)		SGP-1	SGP-2	SGP-3	SGP-4	SGP-5	SGP-6	mean	std.dev.	RSD (%)
21-Jul-10	H	450	560	480	440	150	370	410	140	35
22-Jul-10	S	290	430	420	320	110	190	290	130	43
03-Aug-10	H	***36***	520	380	240	95	96	230	190	84
04-Aug-10	H	530	570	470	400	140	300	400	160	40
05-Aug-10	H	450	570	530	220	120	280	360	180	50
07-Aug-10	H	450	540	450	320	98	290	360	160	44
17-Aug-10	S	240	520	400	200	***39***	110	250	180	72
25-Aug-10	H	450	890	790	390	100	300	490	300	62
02-Sep-10	H	390	490	470	330	87	220	330	150	46
Mean		370	570	490	320	100	240	350	180	53
std.dev		150	130	120	85	31	91	82		
RSD (%)		42	23	25	27	30	38	24		

421

422 Table 3: TCE and 11DCE concentrations measured in passive samplers at the Layton House

Inter-Sampler Variability for 11DCE (μg/m^3)								Spatial and Temporal Variability		
Duration (days)	1	2	2.2	7.9	8.1	9.8	11.7	mean	std.dev.	RSD (%)
ATD CPB	180	280	430	70	15	75	22	150	170	110
Radiello	15	<1.5	17	13	2	49	14	19	18	93
SKC	--	210	99	30	390	130	--	170	140	80
ATD Tenax	110	100	51	79	4	7	3	41	43	100
WMS	350	250	35	250	330	130	360	230	120	55
Mean	110	170	110	75	130	67	83	122	98	89
std.dev	140	110	160	91	180	56	160	89		
RSD (%)	130	68	150	120	150	83	190	73		
Inter-Sampler Variability for TCE (μg/m^3)								**Spatial and Temporal Variability**		
Duration (days)	1	2	2.2	7.9	8.1	9.8	11.7	mean	std.dev.	RSD (%)
ATD CPB	340	610	610	77	100	290	280	330	240	72
Radiello	65	7.0	48	43	22	69	21	35	23	64
SKC	77	540	350	110	730	510	--	450	230	52
ATD Tenax	150	300	320	290	13	63	11	170	150	91
WMS	210	180	53	300	350	220	240	220	100	46
Mean	120	220	190	120	180	150	100	240	150	65
std.dev	110	240	220	120	250	180	120	160		
RSD (%)	93	110	110	100	140	120	120	65		

423

Figure 1: Schematic diagram of the probe for passive soil vapor sampling at the Layton house, Utah

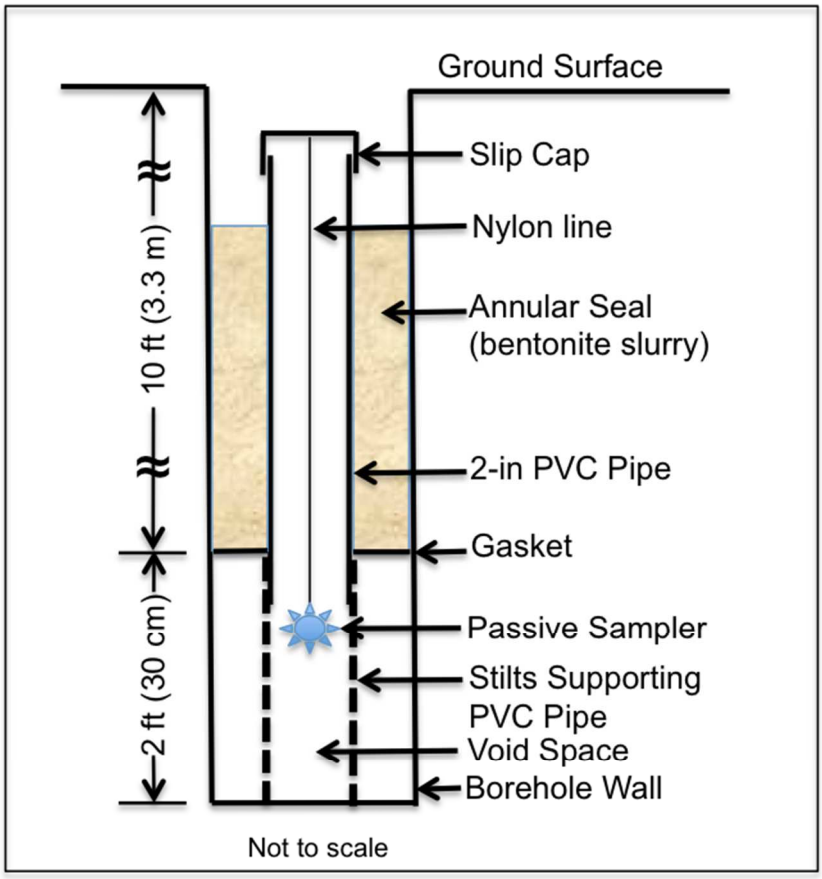
Figure 2: Schematic diagram of the probe for passive soil vapor sampling at NAS Jacksonville

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 x t)/Void Volume



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439 Figure 1

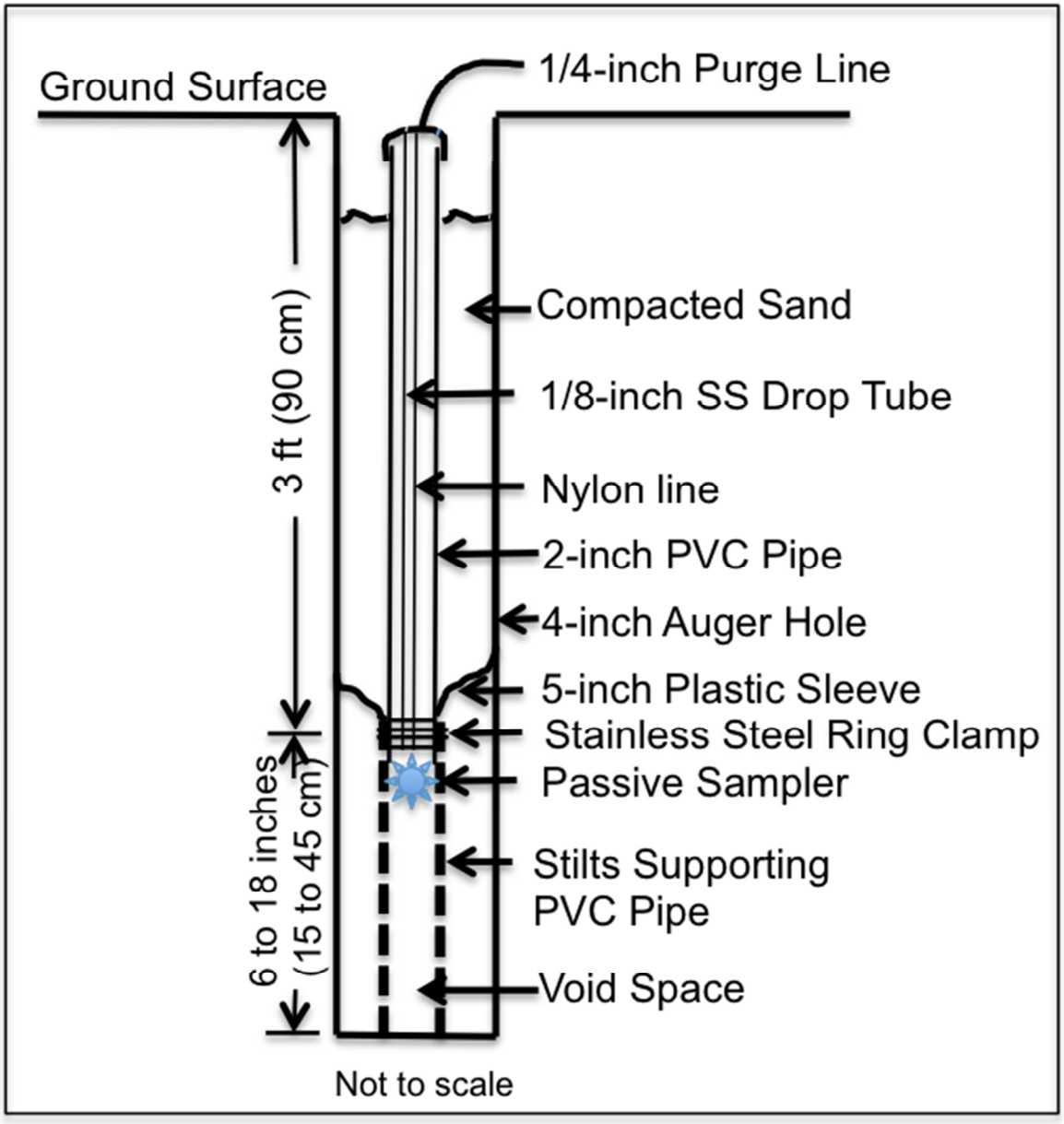

Figure 2

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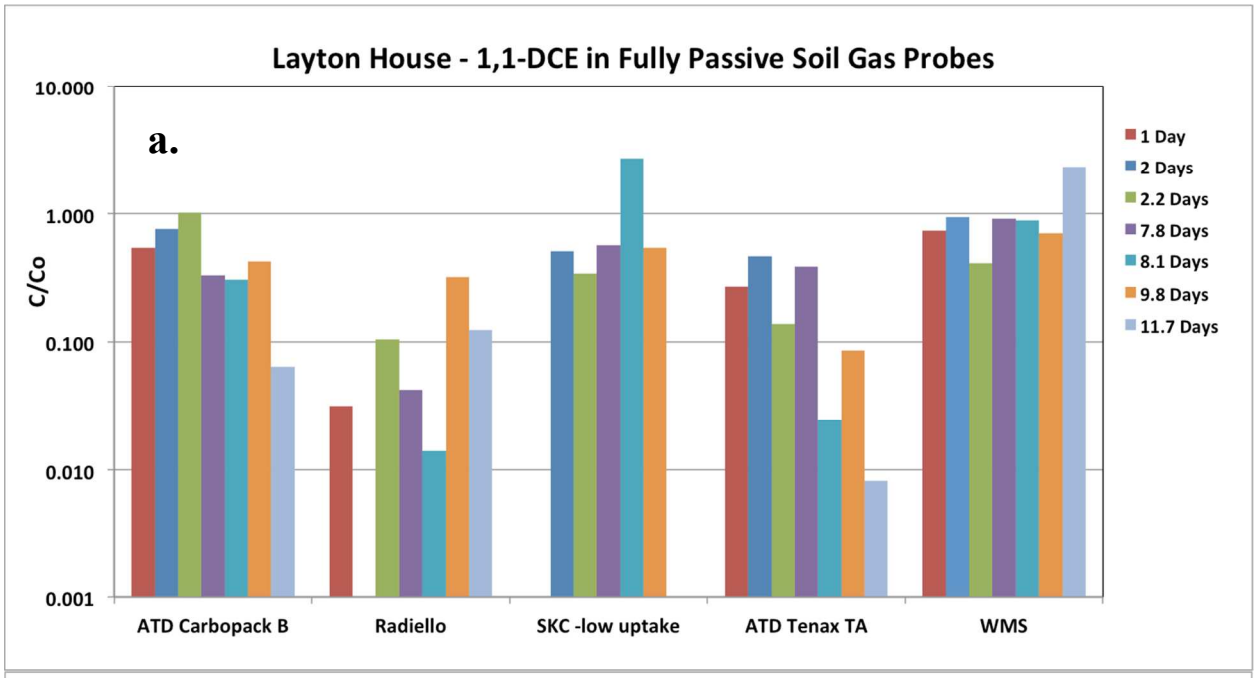

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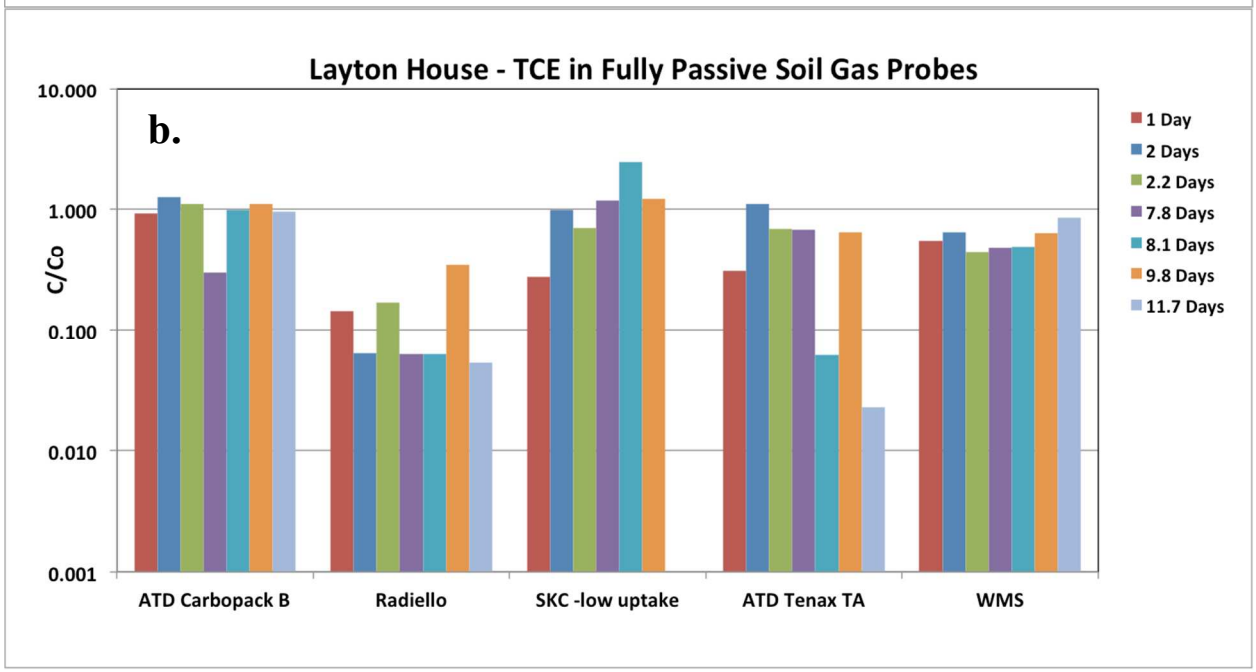

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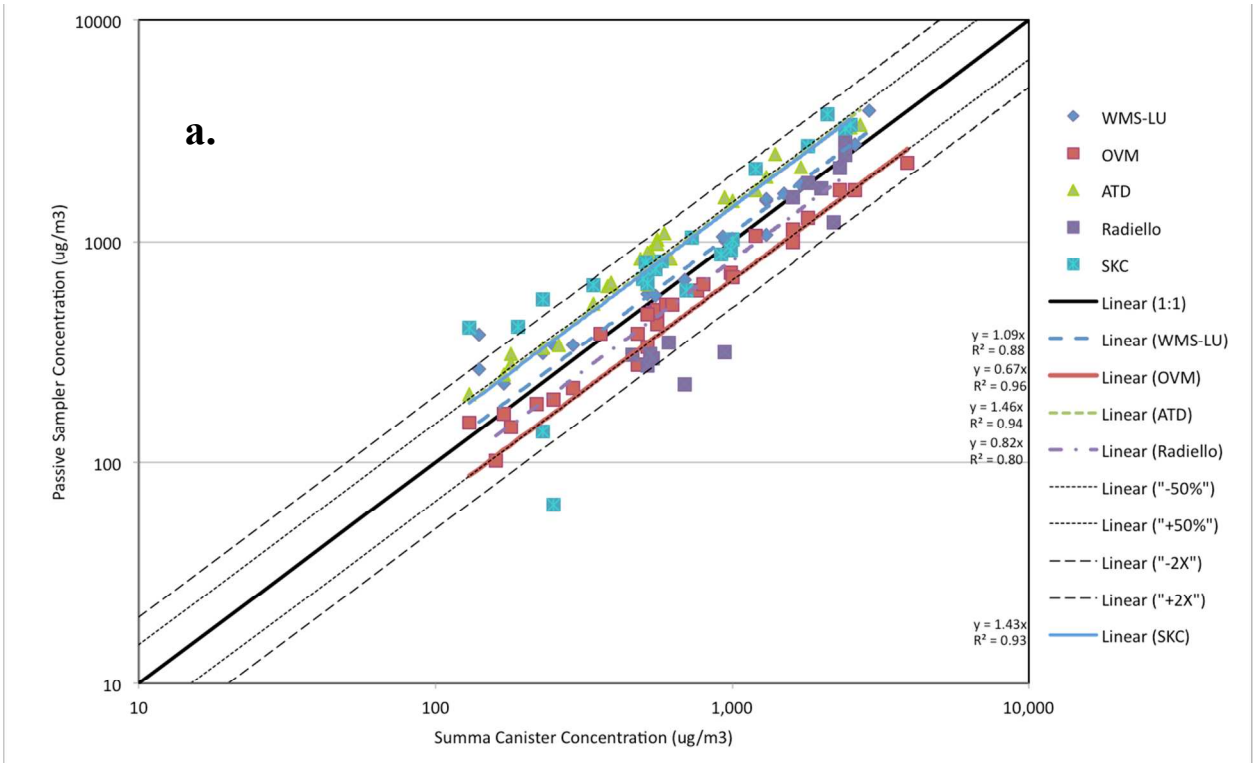

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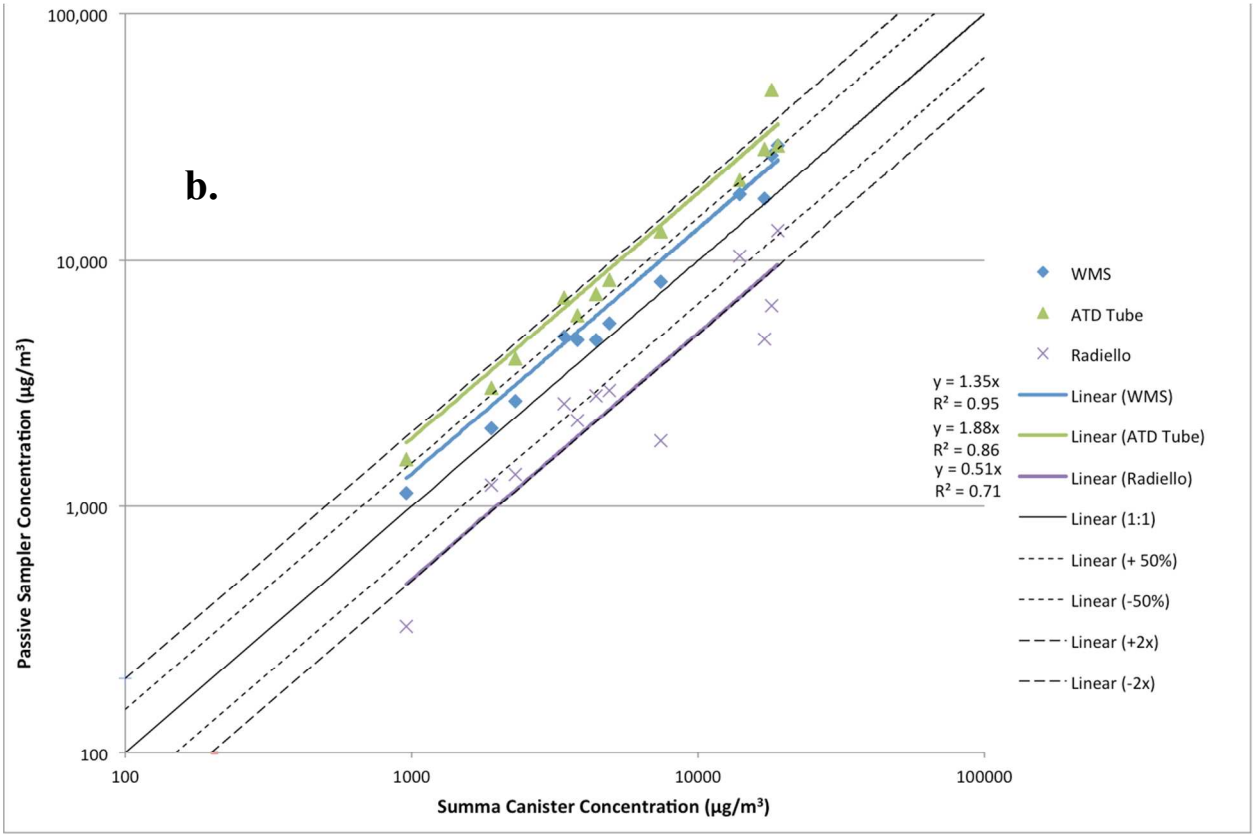

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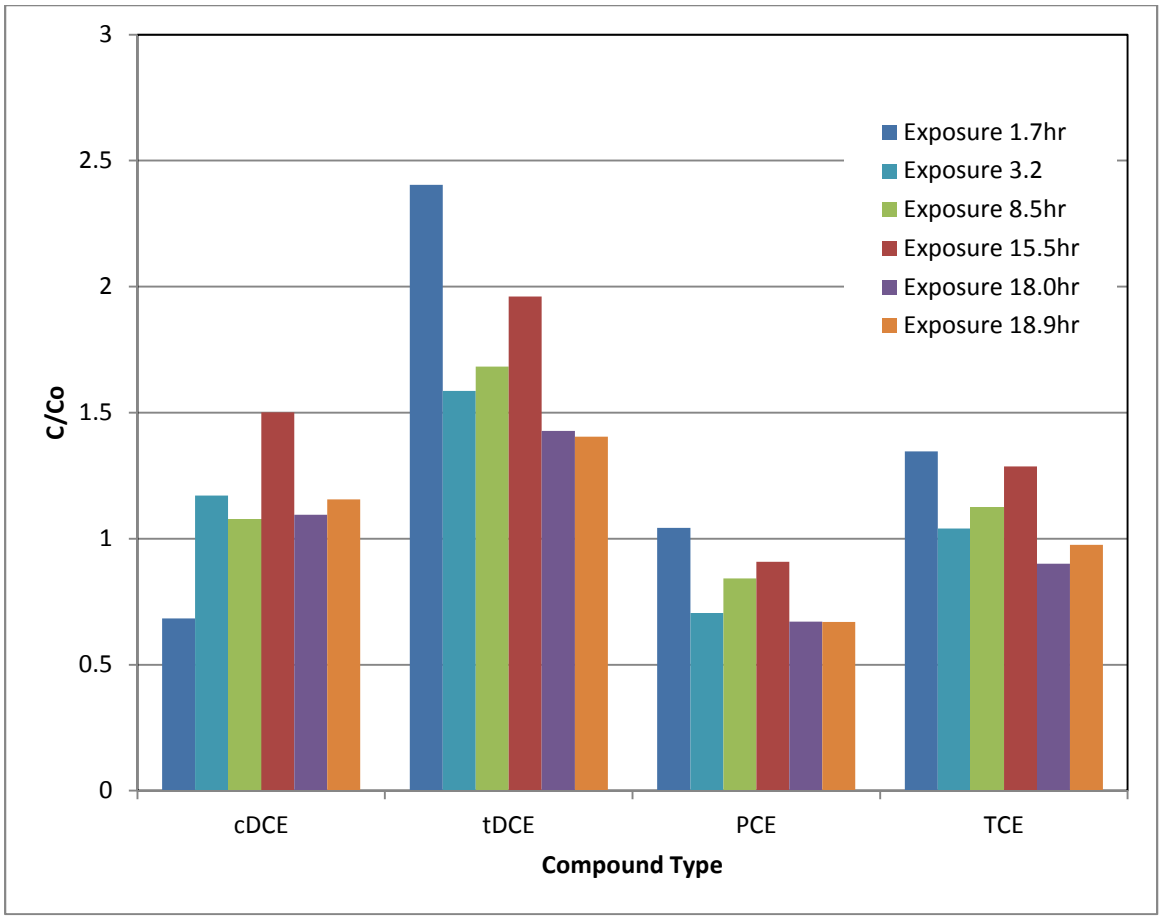

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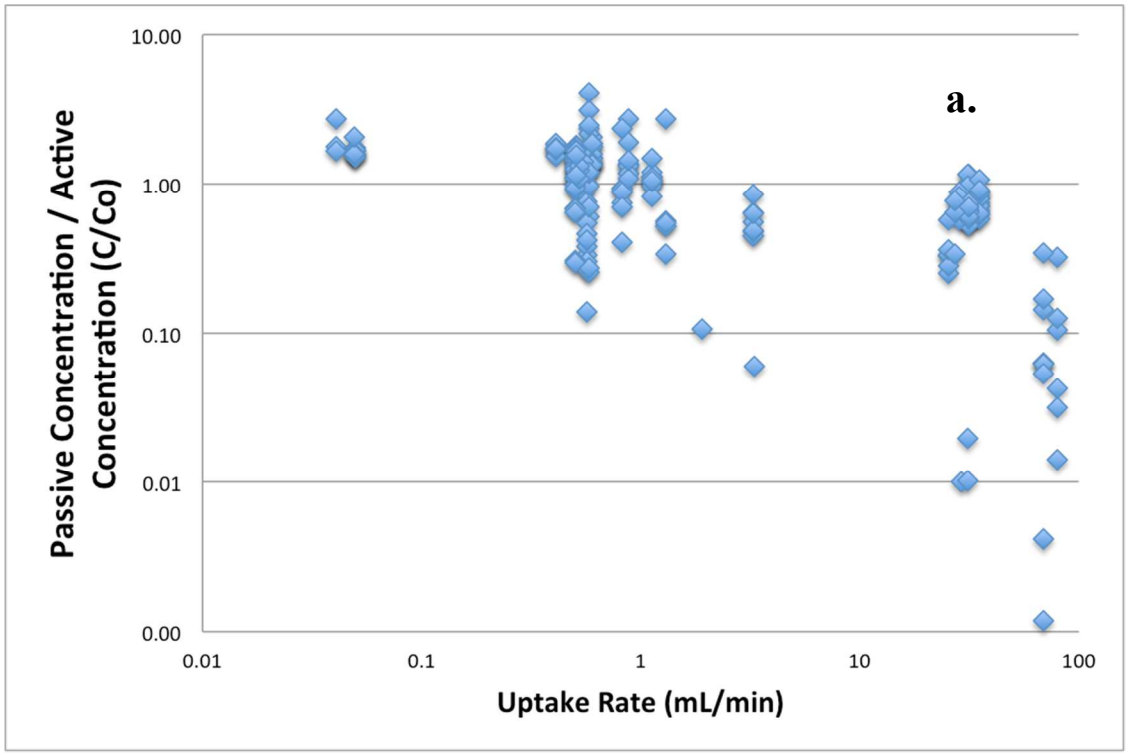
451 Figure 5



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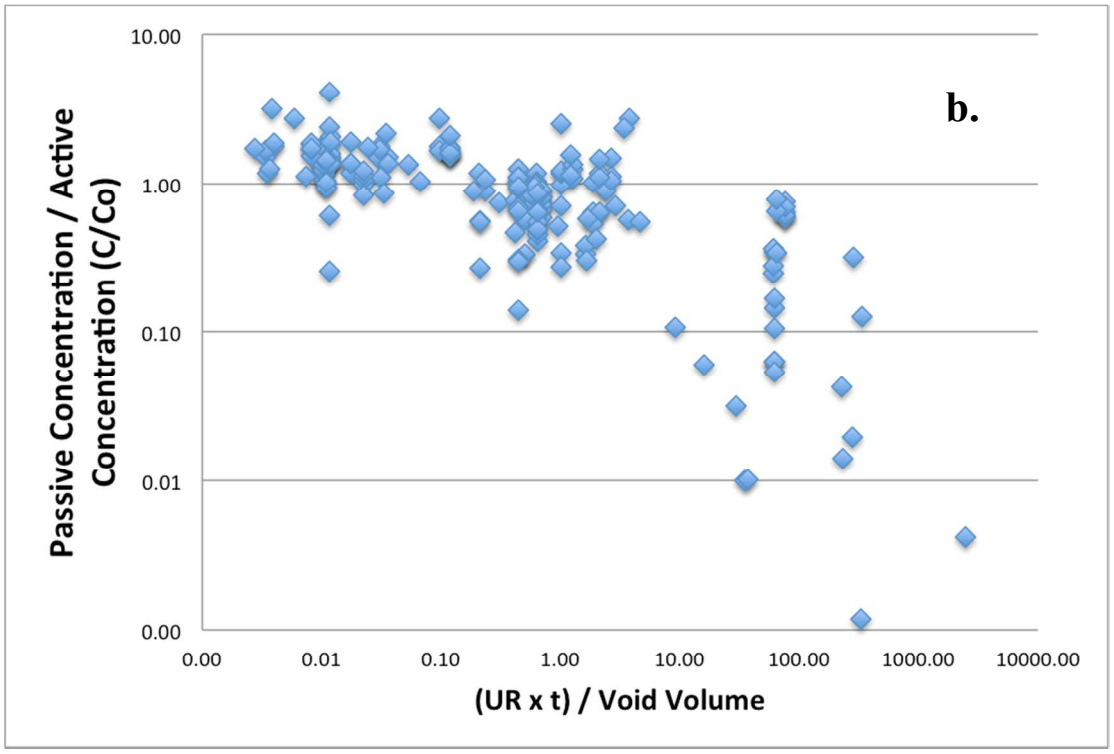

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454 Figure 6