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Passive diffusive samplers can be used in a Flow-Through Cell to monitor VOC vapor concentrations during vapor intrusion investigations.

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Soil vapor intrusion to indoor air is an important pathway of potential human exposure to volatile chemicals at contaminated sites, but assessment is challenging using conventional indoor air and soil gas sampling methods because of spatial and temporal variability. This research demonstrates and validates the use of an alternative sampling approach (passive diffusive samplers) for soil vapor monitoring in a flow-through cell. This approach minimizes the starvation effect by maintaining a flow rate greater than the sampler uptake rate and is simpler than conventional pumped sorbent tube sampling because the flow rate need not be as tightly controlled or monitored. Data is presented for a controlled fractional factorial experiment with five different passive samplers, three flow rates and three sample durations for trichloroethene in sub-slab soil vapor.

Quantitative Passive Soil Vapor Sampling for VOCs – Part 4: Flow-Through Cell

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

[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]U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH

ABSTRACT

This paper presents a controlled experiment comparing several quantitative passive samplers for monitoring concentrations of volatile organic compound (VOC) vapors in soil gas using a flow-through cell. This application is simpler than conventional active sampling using adsorptive tubes because the flow rate does not need to be precisely measured and controlled, which is advantageous because the permeability of subsurface materials affects the flow rate and the permeability of geologic materials is highly variable. Using passive samplers in a flow-through

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

cell, the flow rate may not need to be known exactly, as long as it is sufficient to purge the cell in a reasonable time and minimize any negative bias attributable to the starvation effect. An experiment was performed in a 500 mL flow-through cell using a two-factor, one-half fraction fractional factorial test design with flow rates of 80, 670 and 930 mL/min and sample durations of 10, 15 and 20 minutes for each of five different passive samplers (passive Automatic Thermal Desorption Tube, Radiello®, SKC Ultra, Waterloo Membrane Sampler™ and 3M™ OVM 3500). A Summa canister was collected coincident with each passive sampler and analyzed by EPA Method TO-15 to provide a baseline for comparison of the passive sampler concentrations. The passive sampler concentrations were within a factor of 2 of the Summa canister concentrations in 32 of 35 cases. Passive samples collected at the low flow rate and short duration showed low concentrations, which is likely attributable to insufficient purging of the cell after sampler placement.

INTRODUCTION

Subsurface vapor intrusion to indoor air is an important consideration for human health risk assessment at sites with soil or groundwater contamination with volatile organic compounds[1,2]. Conventional sampling and analysis approaches for vapor intrusion investigation yield data with a high degree of spatial and temporal variability[3,4,5], and research is needed to develop alternatives to the conventional approaches[6]. Passive samplers have been used for about 4 decades for indoor air quality monitoring for VOCs in industrial hygiene applications[7,8,9,10], but their use for soil vapor sampling has been hampered by several challenges. One of the earliest attempts to use industrial hygiene samplers for soil gas monitoring[11] showed a negative bias of more than an order of magnitude. This was likely attributable to the starvation effect, which occurs when a passive sampler removes vapors from its surroundings faster than they are replenished, and causes a localized reduction in concentration that leads to a negative bias in the

passive sampler concentration measurements. A possible concentration-dependent humidity effect was also noted. For the past two decades, passive samplers have been used to provide qualitative or semi-quantitative soil vapor data, but the ability to quantify concentration from the mass adsorbed on the sampler has not been established[12,13,14]. Concentrations are needed for comparison to risk-based screening levels when assessing human health risks via vapor intrusion, so many regulatory guidance documents caution that passive soil gas sampling is not quantitative and should only be used as a screening tool[1,15]. Three companion papers provide new insight into passive soil vapor sampling, including theory[16], laboratory testing[17] and field testing[18]. This paper supplements the other three with an alternative strategy to provide flexibility for a wider range of applications.

Temporal variability can be managed by collecting time-weighted average samples over longer time periods, and passive samplers are well suited to this[19,20,21,22]. In much the same way, spatial variability can be managed by collecting samples over larger volumes[22]. The use of passive samplers in a flow-through cell could potentially be used in a variety of applications. For example, sub-slab vapor samples are typically collected with a volume of about 1 L, which represents a very localized measurement of vapor concentrations. A flow-through cell could be used to collect sub-slab vapor concentration measurements over a period of days and draw a large volume of gas (thousands or tens of thousands of liters), which may provide a more representative estimate of the potential for vapor intrusion risks compared to the current "point-measurement" approach. For perspective, risk assessments consider a 25-year exposure scenario, and a default flow rate of soil vapor into a residence is often taken as 5 L/min, which is a total volume of 66 million liters of soil gas entering the building. In that context, a 1L sample seems unlikely to constitute a "representative elemental volume", which is the smallest volume over which a measurement can be made that will yield a value representative of the whole[23].

Other potential applications of passive samplers in a flow-through cell include sampling in high velocity environments, where ordinarily advection and turbulence can cause a positive bias on samplers designed to uptake chemicals only by diffusion. Outdoor sampling programs often need some form of shroud for protection from wind and rain, but a flow-through cell could actually provide a more controlled environment. Vent-pipes in sub-slab mitigation systems, soil vapor extraction systems or building air-supply or exhaust could also be assessed using a flow-through cell to draw a slip-stream under a controlled flow rate, and still achieve the benefit of a longer sample duration to manage temporal variability, compared to what can be achieved with conventional technologies.

The purpose of this paper is to demonstrate the accuracy and precision of five passive samplers in a flow-through cell for monitoring soil vapor and to improve knowledge of the influence of key operational factors (flow rate and sample duration) on the ability of passive samplers to provide quantitative soil vapor concentration data.

EXPERIMENTAL METHODS

The field sampling experiment was designed to assess the performance of five different commercially-available quantitative passive sampling devices compared to conventional sampling and analysis methods (Summa canister and EPA Method TO-15[24]). The effect of the flow rate and sample duration in the cell was also tested in a fractional factorial design.

Sampling Location

Trichloroethene (TCE) was historically used at US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire as a refrigerant to freeze the ground in a test area referred to as the "ice well". Sub-slab soil vapor samples collected in March and June of 2010 at sub-slab probe LB-01 (located just inside the main laboratory building near the former ice well) showed TCE concentrations on the order of

100,000 µg/m^3. The sub-slab probe was constructed of one-half inch diameter (1.27 cm) stainless steel, which is a common diameter for sub-slab probes, however; it is too small to accommodate any of the candidate passive samplers, so direct deployment of the passive samplers in the subsurface would not be possible without installing a larger probe.

Apparatus

The flow-through cell was constructed of transparent PVC pipe of sufficient length and diameter to fit all of the passive sampler types. The 3M OVM 3500 was the largest passive sampler and required a 2-inch diameter flow-through cell. The top and bottom of the cell consisted of 2-inch diameter stainless steel threaded caps with compression fittings, which were connected to new ¼-inch Nylaflow™ tubing from sub-slab probe LB-01. Soil gas was drawn through the apparatus using a Gast 1H piston pump downstream of the flow-through cell, as shown in **Figure 1**. Three flow controllers (F4, F5, and F6) were assembled in series through a header of stainless steel with compression-fit stainless steel ball-valves at the exhaust end of the flow-through cell to allow simple and rapid changes between high, medium and low flow rates. There were also three different flow controllers (F1, F2, F3) attached to the influent line to allow Summa canister samples to be collected over short, medium and long (10, 15 or 20 minutes) sample durations. Pre-assembly of the flow controllers in manifolds allowed each test to be performed with one new connection (between the Summa canister and one of the three flow controllers F1, F2 or F3) for each successive sampling interval to reduce the risk of leaks. The design of this apparatus was intended to reduce the risk of leaks at the fittings. A shut-in test was performed to verify the absence of leaks by closing the valve at the sub-slab probe, evacuating the entire apparatus with the pump and closing valves at the sub-slab probe and the pump to establish a vacuum of about 100 inches of water column throughout the apparatus. No observable decrease in vacuum occurred over a period of two minutes, so the risk of leakage was considered negligible.

FIGURE 1

Sample Duration

Design calculations were performed to assess the sample duration that would be needed to quantify the TCE concentrations. For passive samplers, the time-weighted average (TWA) concentration (C_o) of a particular analyte can be calculated as follows:

$$C_o = \frac{M}{UR \; x \; t} \qquad (1)$$

where:

C_o = TWA concentration of the analyte in the sampled air or gas [µg/m^3]

M = mass of analyte on the sorbent, blank-corrected as needed [pg]

UR = passive sampler uptake rate [mL/min] (vendor-specified)

t = sample duration [min]

(note that there are two offsetting conversion factors from pg to µg and mL to m^3)

If the laboratory reporting limit (in mass units) is used for M, then the C_0 value will correspond to the reporting limit (in concentration units) for any given sample duration. **Table 1** list the five passive samplers used in this study, the sorbent medium used, the lowest reportable mass (in units of ng) and the vendor-supplied TCE uptake rates[25,26,27,28,29,30,31,32]. The relationship between the analytical reporting limits (in units of µg/m^3) calculated using Equation (1) and the sample duration is shown in **Figure 2**. In theory, all five passive samplers can achieve reporting limits lower than the expected concentration of TCE in sub-slab probe LB-01 (100,000 µg/m^3) within a minute or less. In practice, it takes about 10 to 15 seconds to deploy a passive sampler and retrieve it from the flow-through cell, so the minimum sample duration was set to be 10 minutes to minimize the error related to the duration of sampler deployment and retrieval relative to the sample duration. The maximum sample duration was set to be 20 minutes in order to avoid saturating the sorbent and exceeding the linear range of the laboratory analytical instruments.

The mid-point sample duration was 15 minutes, half-way between the high and low levels for this factor. It is worth noting that samplers with high uptake rates and/or low mass reporting limits are capable of achieving concentration reporting limits as low as common risk-based screening levels for TCE (~100 μg/m^3) within about 30 minutes, which is somewhat longer than typical sampling durations for Summa canisters (5 to 10 min)[33], but still within reason.

TABLE 1

FIGURE 2

Flow Rates

The flow rates for the tests were designed to be sufficient to minimize the starvation effect (i.e., the lowest flow rate was greater than the highest uptake rate of any of the samplers). Flow controllers are adjustable, but the adjustments are quite sensitive, so the actual flow rates were somewhat different than the design flow rates. The goal was to have a low flow rate of 100 mL/min, but the flow meter was actually calibrated to about 80 mL/min. The high flow rate was designed to be 1 L/min, which was fast enough to purge the volume of the flow-through cell in about 30 seconds. This was expected to minimize the period of time during which the passive sampler was exposed to an appreciable percentage of indoor air entrained in the flow-through cell during placement of the passive sampler. The actual high flow rate achieved was 930 mL/min. The mid-point flow rate was designed to be exactly half-way between the high and low flow rates, but was actually 670 mL/min. The cross-sectional area of the cell was about 20 cm^2, so these flow rates correspond to average linear flow velocities of 4, 34 and 47 cm/min. Note that this is considerably lower than the velocities for which passive samplers are typically tested (3,000 to 30,000 cm/min)[34], which further justifies the need for verification of the passive sampler performance under these specific conditions.

Sampling Procedure

166 The sampling procedure consisted of placing one passive sampler in the cell, closing the cell as
167 quickly as possible, drawing sub-slab gas through the cell at the allotted flow rate for the allotted
168 sample duration and removing the passive sampler and replacing with the next sampler to be
169 tested as quickly as possible to minimize the exchange of indoor air with the soil gas in the flow-
170 through cell. Each of the passive samplers was deployed seven times: at all four combinations of
171 high and low levels of sample duration and flow rate, as well as three replicates of the mid-points
172 of the flow rate and sample duration. The order of deployment (sampler type, sample duration
173 and flow rate) was randomized. The faces of the SKC Ultra and OVM3500 samplers were
174 parallel to the flow direction in the cell. The ATD tube and WMS samplers were deployed
175 facing down, toward the influent to the cell. The Radiello was deployed with the long axis
176 vertical in alignment with the flow direction. Trip blanks were included for each passive sampler
177 type (no VOCs were detected).
178 One batch-certified, 1L Summa canister sample was collected to coincide exactly with each
179 passive sample (35 canisters in total). One Summa canister showed a notably low concentration
180 (12,000 $\mu g/m^3$), which was considered likely to have had an un-noticed leak at the fitting to the
181 flow controller and one Summa canister valve was inadvertently left closed throughout the
182 sample period. In these two instances, the Summa canister concentrations used for calculating
183 relative concentrations (passive/Summa) were the average TCE concentration from the two
184 Summa canister samples collected in the preceding and following sample intervals.
185 The Summa canister samples were analyzed by USEPA Method TO-15[24] open scan at Columbia
186 Analytical Services (CAS) of Simi Valley, CA. All the passive samplers were analyzed by
187 GC/MS. The ATD tubes were analyzed by Air Toxics Limited (ATL) of Folsom, CA. The WMS
188 samplers were analyzed by at the University of Waterloo, Ontario Canada. The Radiello
189 samplers were analyzed at the Fondazione Salvatore Maurgeri in Padova, Italy. The SKC

samplers were analyzed at CAS. The 3M OVM 3500, Radiello, WMS and SKC samplers with activated charcoal sorbent were analyzed by CS_2 extraction by adding 1 to 2 mL of low-benzene content carbon disulfide in a closed inert vial and allowing 30 minutes on a shaker. An aliquot of 1 or 2 μL was injected via auto-injector into a GC/MS and the mass of each analyte was determined using an internal standard calibration technique (Radiello and OVM) or external calibration (WMS). The ATD tubes were analyzed using thermal desorption by EPA Method TO-17[35]. For the short-duration and low flow rate conditions, the SKC samplers were used with Carbograph 5 to minimize the risk of a non-detect result. The Carbograph 5 sorbent was transferred into an ATD tube, and analyzed by thermal desorption using EPA Method TO-17.

Field screening readings were performed to verify the sub-slab vapor concentrations prior to and periodically during the testing program using a MiniRAE™ 2000 photoionization detector (PID) by RAE Systems of San Jose, CA, which was calibrated daily on-site according to manufacturer's instructions.

RESULTS

PID readings on soil vapor samples drawn from sub-slab probe LB-01 were 25 parts per million by volume (ppmv) the night before testing began (November 9, 2010), and virtually identical the morning testing began. The final PID screening reading at the end of the second day of sampling was 19 ppmv, and intermittent reading during the conduct of the test were within this range, which indicated that minimal changes in subsurface conditions occurred during the conduct of the testing. A total volume of about 320 L was purged during the two days of sampling, which is equivalent to the gas contained within a nominal 6-inch thick gravel layer beneath the floor slab with a 35% air-filled porosity within a radial distance of 1.7 m of the sub-slab probe. A PID reading of 25 ppmv corresponds to a TCE concentration of about 80,000 $\mu g/m^3$ (PID response

factor = 0.62, 1 ppmv = 5,400 μg/m^3), which was consistent with expectations from previous sampling.

Active (Summa canister) soil gas samples (**Figure 3a and Table 2**) had TCE concentrations ranging from 20,000 (one outlier excepted) to 55,000 μg/m^3, with a mean of 38,650 μg/m^3 and a relative standard deviation (RSD) of 0.19. The average Summa canister concentration was 38,200 μg/m^3 on November 9 and 39,200 μg/m^3 on November 10, which indicates similar conditions over the two days of testing. Individual Summa canister samples showed differences of up to 20,000 μg/m^3 from one sample to the next, which is a higher degree of variability than expected from experience with similar extended purging studies[22]. The passive sampler data (**Figure 3b**) had TCE concentrations in a similar range to the Summa canister data.

The passive sampler TCE concentrations divided by the coincident Summa canister TCE concentrations are plotted as relative concentrations (C/C_o) in **Figure 4**. The legend numbers are the flow rate in mL/min (first) and the exposure duration in minutes (second). The low flow rate and short sample duration (nominal 100 mL/min for 10 min) showed a low bias for all the passive samplers (except the SKC), which is likely attributable to insufficient purging of the flow through cell during the sampling interval. The relative concentration and bias between the passive sampler and the Summa canister results are presented in **Table 2**. The bias was less than 50% in 31 of 36 cases, which is considered acceptable considering the potential for inter-laboratory variability (which averaged 25% for these samplers in a study yet to be published). A negative bias of 45 to 77% was observed in 4 cases (low flow rate and short duration for ATD, OVM, Radiello and WMS samplers). A positive bias >50 % was observed only at the high flow rate (87% for one ATD sampler and 54% for one Radiello), and may be attributable to advective uptake or uptake via turbulent flow in addition to diffusion. Considering the Summa canisters showed concentration changes of up to 20,000 μg/m^3 in successive samples in some instances,

the variability in the C/C_0 values and the magnitude of the bias cannot be attributed entirely to the passive samplers.

To further explore the root cause of the negative bias in the low flow rate and short duration samples, the results were plotted as relative concentrations (passive/Summa) versus the number of volumes purged through the cell within the sample duration (**Figure 5**). The number of volumes purged was calculated as product of the flow rate and sample duration divided by the volume of the flow-through cell. The samples collected with the smallest number of cell volumes purged (10 minute sample duration and 80 mL/min flow rate, corresponding to only 1.6 purge volumes for the 500 mL cell) showed a low bias for all but one of the samplers (SKC). The low bias is attributable to insufficient purging of indoor air entrained in the flow-through cell at the time of deployment of the sampler, which would dilute the soil vapor TCE concentrations. The SKC Ultra showed a positive bias on the low flow/low duration sample, but this may be attributable to the fact that this sample was analyzed by thermal desorption using EPA Method TO-17, whereas the other SKC samplers were analyzed by solvent extraction. The low bias is no longer apparent for any of the passive samplers in the 20-minute samples collected at the low flow rate, for which the cell was purged 3.2 times in the sample duration.

FIGURE 5

Passive samplers can show a negative bias via the starvation effect when the uptake rate is high compared to the face velocity (velocity of air flow measured at the face of the sampler). This was evaluated by plotting the relative concentration (passive/Summa) versus the ratio of the uptake rate divided by the face velocity (**Figure 6**). With the possible exception of the highest uptake rate samplers in the lowest velocity conditions (OVM 3500 and Radiello at flow rate of 80 mL/min), the average relative concentration was 1.05 (passive sampler concentration 5%

higher than Summa canister concentration), so there is no indication of a starvation effect for the majority of the data collected.

FIGURE 6

A three-way analysis of variance (ANOVA) analysis was run on the concentration values using sampler type, flow rate and sample duration as the three factors of interest (**Table 3**). No interaction terms were included. The data consisted of 72 observations and were run as an unbalanced design using the PROC GLM function in SAS 9.2. The overall F-test was not significant ($F=1.88$, $p = 0.0789$), indicating that there was no statistically significant difference in the TCE concentrations between the Summa canisters and the passive samplers or between the different types of passive samplers at the 5% significance level (alpha =0.05). The analysis of individual factors showed that the sampler type and sample duration was also not significant at the 5% level; however, the flow rate did show a statistically significant effect for the ATD tube sampler. The ATD tube sampler is the only one without a porous plastic or membrane between the sorbent inside the sampler and the medium being monitored, and therefore, may be more susceptible to a positive bias in the uptake rate via convection or turbulence at higher flow rates.

Table 4 shows the mean TCE concentrations measured with each passive sampler and the corresponding Summa canister samples, as well as the RSD for each data set. The RSD values for the ATD, Radiello and OVM samplers were about twice the corresponding Summa canister values, but the RSDs for the WMS and SKC samplers were very similar to the Summa canister data. Table 4 also shows the mean of all seven C/C_0 values calculated for each sampler, which ranged from 0.93 to 1.08, which indicates that on average, the passive sampler result would be expected to very similar to the Summa canister/TO-15 result. The mean bias for each sampler is also included in Table 4, and shows that the bias is in the range of 20% to 40% (some of which

again may be attributable to variability in the Summa canister data and inter-laboratory variability).

CONCLUSION

The flow-through cell tests showed that most of the passive samplers provided measured concentrations within a factor of two of the Summa canister concentration for all conditions tested except the low flow rate and short duration, which showed a negative bias attributable to insufficient purging of indoor air from the cell. The passive samplers showed average accuracy within about 10% of the Summa canisters and a similar range of variability to the Summa canister samples. For soil vapor samples, uncertainty of a factor of 2 in the absolute concentrations is within typical ranges of spatial and temporal variability for risk management decision making.

The volume of the test cell was large enough to accommodate the largest of the passive samplers, but this resulted in a low bias for the low flow rate and short duration tests because of insufficient purging of indoor air entrained during sampler deployment in the cell. This could be resolved either using longer sampling durations, higher flow rates or a flow-through cell that is custom-fit to the passive sampler to reduce the dead volume inside the chamber. The ATD tube appeared to show a positive bias at the high flow rate (960 mL/min), which may be attributable to uptake via turbulence in addition to diffusion because the ATD tube sampler does not have a porous diffusion or non-porous permeation membrane to act as an uptake-rate controlling barrier. The high uptake rate samplers (OVM 3500 and Radiello) appeared to show a slight negative bias at the low flow rate, which may be attributable to the starvation effect because these samplers had the highest uptake rates 31 and 69 mL/min, respectively). This can be managed by selecting a higher flow rate, or using a smaller diameter flow-through cell.

Further testing would be appropriate to assess the performance of other chemicals, different ranges of concentrations and longer sample durations. Some of these conditions have already been evaluated in a companion paper recently published by the same research team[17]. Nevertheless, this should still be considered an emerging technology and comparison testing by conventional active sampling is recommended for applications of this approach until the capabilities and limitations are more fully understood.

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REFERENCES

1. *OSWER Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance),* U.S.EPA, November 29, 2002, EPA530-D-02-004.
2. *Vapor Intrusion Pathway: A Practical Guideline*, Interstate Technology and Regulatory Council (ITRC), 2007, http://www.itrcweb.org/Documents/VI-1.pdf
3. D. Folkes, W. Wertz, J. Kurtz, and T. Kuehster, *Groundwater Monit. Rem.*, 2009, **29**, 70–80.
4. H. Luo, P. Dahlen, P. Johnson, T. Peargin and T. Creamer, *Groundwater Monit. Rem.*, 2009, **29**: 81–91.
5. Y. Yao, R. Shen, K.G. Pennell, and E.M. Suuberg**,** *Environ. Sci. & Tech.,* 2013 **47**(2), 906-913.
6. U.S. Department of Defense, ESTCP Environmental Technologies Solicitation, 2014. http://www.serdp-estcp.org/Funding-Opportunities/ESTCP-Solicitations/Environmental-Technologies-Solicitation.
7. E. D. Palmes and A. F. Gunnison, *Am. Ind. Hyg. Assoc. J*., 1973, **34**, 78–81.
8. ASTM D4597 - *Standard Practice for Sampling Workplace Atmospheres to Collect Gases of Vapors with Solid Sorbent Diffusive Samplers*, ASTM International, West Conshohocken, PA., 2009, www.astm.org.
9. *Workplace Atmospheres - Diffusive Samplers for the Determination of Gases and Vapours - Requirements and Test Methods*, EN 838, Comité Européen de Normalisation, Brussels, Belgium, 1995.

10. ISO 16017-2: *Indoor Ambient and Workplace Air – Sampling and Analysis of Volatile Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography – Part 2: Diffusive Sampling*, International Standards Organization, 2003.

11. *The Use of Industrial Hygiene Samplers for Soil Gas Measurement*, USEPA, Environmental Monitoring Systems Laboratory, Office of Research and Development, EPA/600/4-89/008, 1988.

12. ASTM 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, 2011, www.astm.org.

13. *Environmental Technology Verification Report, Soil Gas Sampling Technology, Quadrel Services, Inc., EMFLUX Soil Gas System*, U.S. EPA, Office of Research and Development. EPA Report No. 600/R-98/096, 1998.

14. *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 Report No. 600/R-98/095, 1998.

15. *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.

16. T. A. McAlary, X. Wang, A. Unger, H. Groenevelt and T. Górecki, *Environ. Sci.: Processes Impacts*, 2014, **16**(3), 482 – 490.

17. T.A. McAlary, H. Groenevelt, S. Seethapathy, P. Sacco, D. Crump, M. Tuday, B. Schumacher, H. Hayes, P. Johnson and T. Górecki, *Environ. Sci.: Processes Impacts*, 2014, **16**(3), 491 – 500.

18. T.A. McAlary, H. Groenevelt, P. Nicholson, S. Seethapathy, P. Sacco, D. Crump, M. Tuday, H. Hayes, B. Schumacher, P. Johnson, T. Górecki and I. Rivera Duarte, *Environ. Sci.: Processes Impacts*, 2014, **16**(3), 501 – 510.

19. T. Górecki and J. Namiesnik, *Trends in Anal. Chem.*, 2002, **21**(4), 276-291.

20. J. Namieśnik, B. Zabiegala, A. Kot-Wasik, M. Partyka, and A. Wasik. *Anal and Bioanal Chem* 2005, **381**, 279-301.

21. S. Seethapathy, T. Górecki, X. Li, *J Chromatogr A.*, 2008, **1184**, 234-253.

22. T.A McAlary, P. Nicholson, L.K. Yik, D. Bertrand, and G. Thrupp, *Groundwater Monit. Rem.*, 2010, **30**(2), 73–85.

23. R. Hill, *J. Mech. and Phys. of Solids,* 1963, **11**(5): 357–372

24. *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)*, U.S. EPA, Center for Environmental Research Information Office of Research and Development Cincinnati, OH, January **1999**, PA/625/R-96/010b.

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

26. G. Subramamian (Ed.), *Quality Assurance in Environmental Monitoring – Instrument Methods, Appendix A*. John Wiley & Sons, 2008, 350p.

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

28. *Performance of SKC Ultra Passive Sampler Containing Carboxen 1016, Carbotrap Z, or Chromosorb 106 When Challenged with a Mixture Containing Twenty of OSHA SLTC's Top Solvent Analytes*, United States Department of Labor Occupational Safety and Health Administration, Washington, D.C., 2003.

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

30, C. Chung, M. Morandi, T. Stock, and M. Afshar, *Environ. Sci. Technol.*, 1999, **33**(20), 3666–3671.

31. S. Seethapathy and T. Górecki, *J. Chromatogr A*. 2011, **1218**(1), 143-155.

32. S. Seethapathy and T. Górecki, *J. Chromatogr A.* 2010, **1217**(50):7907-7913.

33. *Advisory Active Soil Gas Investigations,* California Environmental Protection Agency, Department of Toxic Substances Control, Los Angeles Regional Water Quality Control Board, San Francisco Regional Water Quality Control Board, April 2012.

34. ASTM D6246 – 08, *Standard Practice for Evaluating the Performance of Diffusive Samplers*, ASTM International, West Conshohocken, PA, 2008, http://www.astm.org.

35. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*, U.S. EPA, EPA/625/R-96/010b, 1999.

401 **Table 1:** Summary of passive samplers used

Passive Sampler	**ATD Tube**	**Radiello**	**3M OVM**	**WMS**	**SKC**
Type	Regular uptake	white body	3500	1.8 mL Vial	Ultra
Sorbent	Carbopack B	Charcoal	Charcoal	Anasorb 747	Carbograph 5 or Charcoal
TCE Uptake Rate (mL/min)	0.5	69	31.1	3.28	15
Reporting Limit (ng)	2.7	50	75	50	1000 (charcoal) 50 (Carbograph 5)

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403

404 **Table 2:** TCE Concentrations measured using passive samplers and Summa canisters

Sampler Type	Flow Rate	Sample duration	Passive Sampler TCE Concentration	Summa Canister TCE Concentration	Relative Concentration	Bias
	(mL/min)	(min)	(µg/m^3)	(µg/m^3)	(C/Co)	(%)
ATD Tube	930	20	69,000	37,000	1.9	87
	930	10	47,000	37,000	1.3	28
	80	20	46,000	43,000	1.1	8
	80	10	7,100	31,000	0.23	-77
	670	15	34,000	38,000	0.90	-10
	670	15	29,000	53,000	0.55	-45
	670	15	50,000	39,000	1.3	28
OVM 3500	930	20	27,000	43,000	0.63	-37
	930 dup	20 dup	40,000	34,000	1.2	17
	930	10	51,000	43,000	1.2	18
	80	20	29,000	43,000	0.66	-34
	80	10	19,000	35,000	0.55	-45
	670	15	42,000	39,000	1.1	8
	670	15	38,000	36,000	1.1	6
	670	15	40,000	30,000	1.3	34
Radiello	930	20	49,000	53,000	0.92	-8
	930	10	55,000	36,000	1.5	54
	80	20	32,000	44,000	0.74	-26
	80	10	11,000	36,000	0.30	-70
	670	15	59,000	45,000	1.3	31
	670	15	39,000	29,000	1.3	33
	670	15	33,000	***35,500#***	0.93	-7
SKC Ultra	930	20	34,000	40,000	0.85	-15
	930	10	40,000	44,000	0.92	-8
	80	20	32,000	33,000	0.97	-3
	80*	10*	50,000	42,000	1.2	20
	670	15	42,000	***32,500#***	1.3	30
	670	15	30,000	35,000	0.86	-14
	670	15	44,000	30,000	1.5	48
WMS	930	20	44,000	44,000	0.99	-1
	930	10	39,000	38,000	1.0	3
	80	20	27,000	20,000	1.4	35
	80	10	22,000	51,000	0.42	-58
	670	15	40,000	29,000	1.4	38
	670	15	20,000	34,000	0.58	-42
	670	15	38,000	50,000	0.76	-24

Notes
dup – duplicate
- Summa data are averages of preceding and following samples
* - Carbograph 5 sorbent and thermal desorption used to reduce reporting limit

405 **Table 3: Results of ANOVA analysis of flow-through cell test results**

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	8	1470185958	183773245	1.88	0.0789
Error	63	6156962319	97729561		
Corrected Total	71	7627148277			
Source	**DF**	**Type III SS**	**Mean Square**	**F Value**	**Pr > F**
Sampler Type	5	335354902	67070980	0.69	0.6356
Flow Rate	1	1091813566	1091813566	11.17	**0.0014**
Sample duration	1	45255510	45255510	0.46	0.4987

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408 **Table 4:** Summary statistics for all sampler types

	Mean Passive TCE Concentration	Relative Standard Deviation	Mean Summa TCE Concentration	Relative Standard Deviation	Mean of seven C/Co values	Mean Bias
Sampler	($\mu g/m^3$)	(%)	($\mu g/m^3$)	(%)		(%)
ATD Tube	40,400	48	39,700	17	1.03	40
OVM 3500	35,700	28	37,900	13	0.96	25
Radiello	39,700	41	39,800	20	1.01	33
SKC Ultra	39,100	19	36,600	15	1.08	20
WMS	32,700	30	38,000	30	0.93	29

409

410 **FIGURE CAPTIONS**

411 **Figure 1:** Experimental Apparatus (schematic)

412 **Figure 2:** Reporting limit as a function of sample duration for the passive samplers used in this
413 study

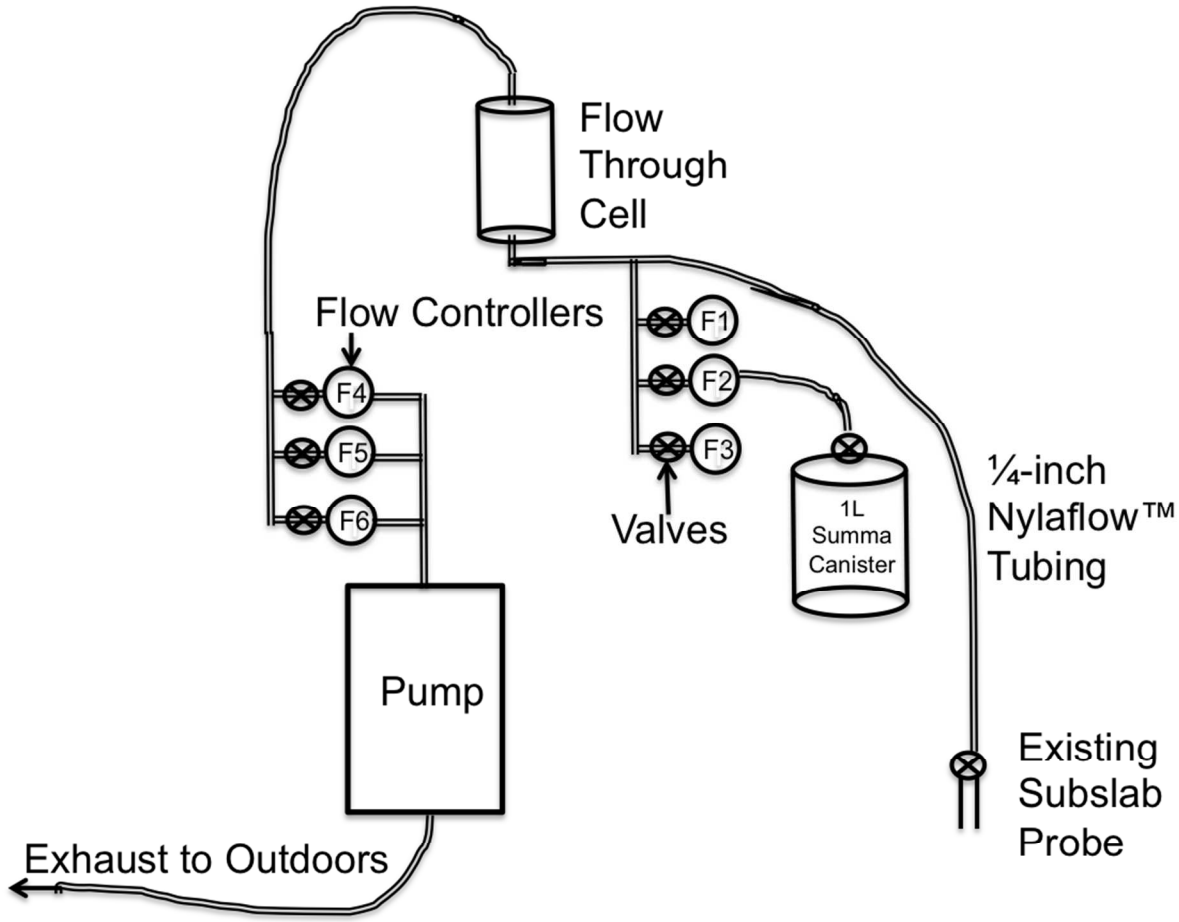
414 **Figure 3:** TCE concentrations measured with Summa canisters (top) and Passive Samplers
415 (bottom) in the flow-through cell

416 **Figure 4:** Relative TCE concentration (C/C_o) for passive samplers in the flow-through cell. In
417 the Legend, the first number is the nominal flow rate (mL/min) and the second number is
418 the sample duration (min), e.g., FT-1000-20 was sampled at 1000 mL/min flow for 20
419 minutes.

420 **Figure 5:** Relative concentration of TCE versus number of pore volumes purged through the
421 flow-through cell during the sample period

422 **Figure 6:** Relative concentration of TCE versus uptake rate divided by face velocity

423



424

425 Figure 1

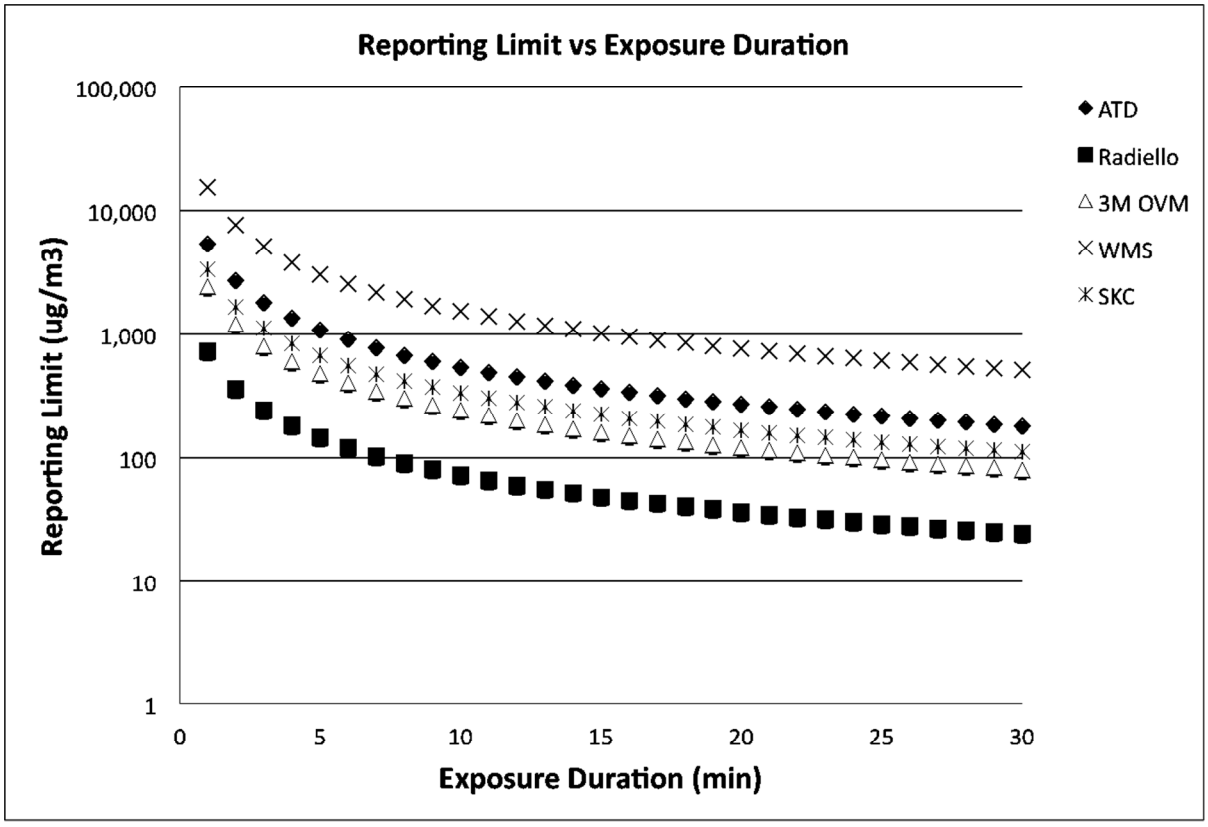
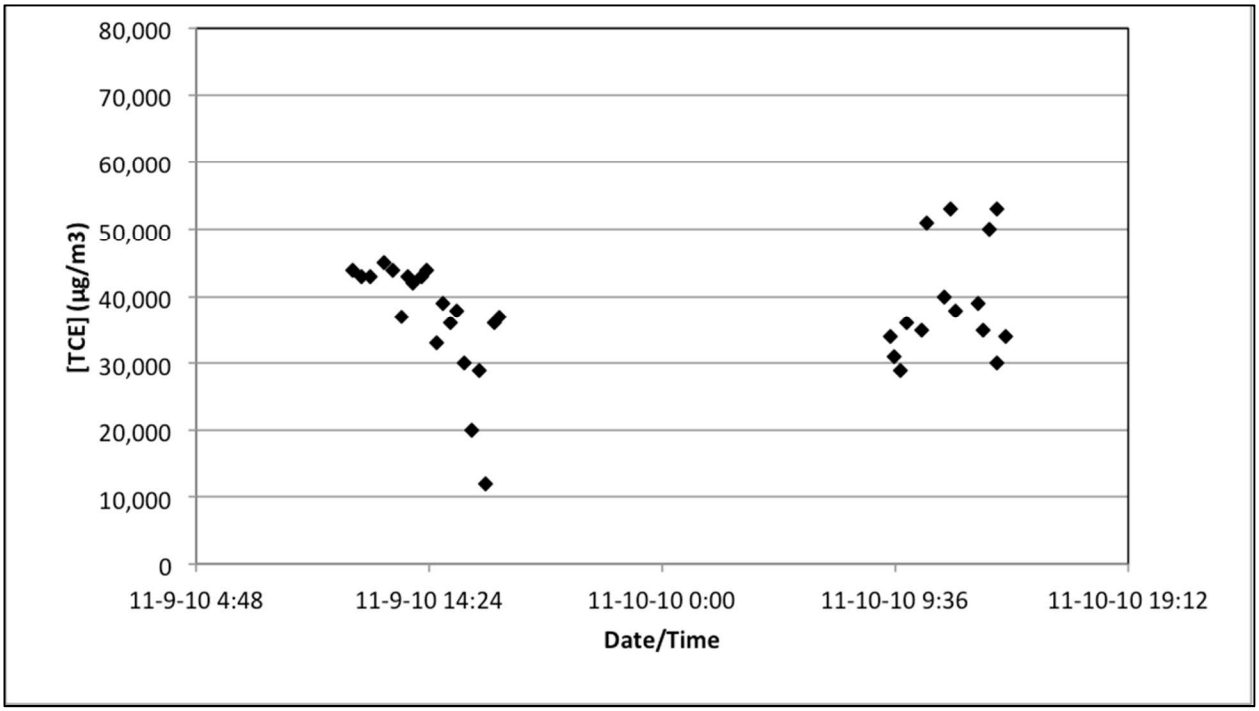
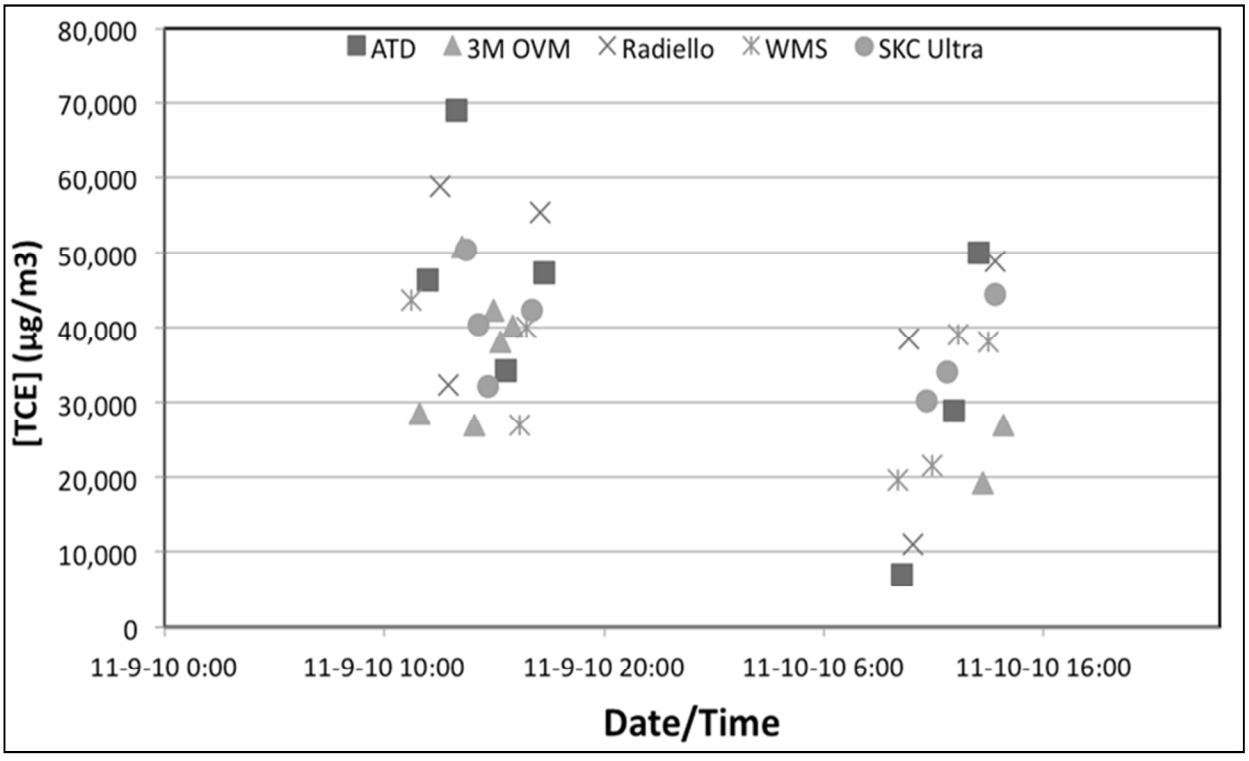


Figure 2





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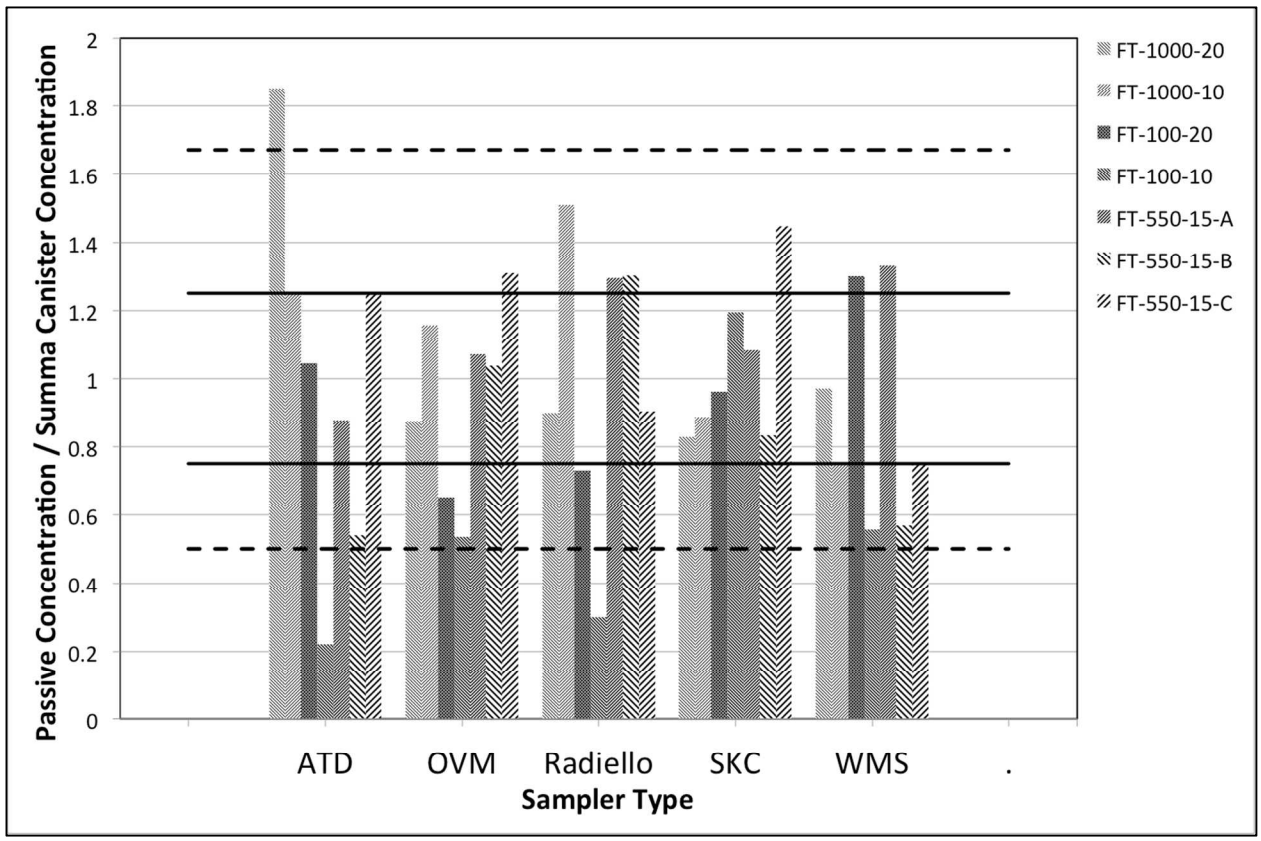

Figure 4

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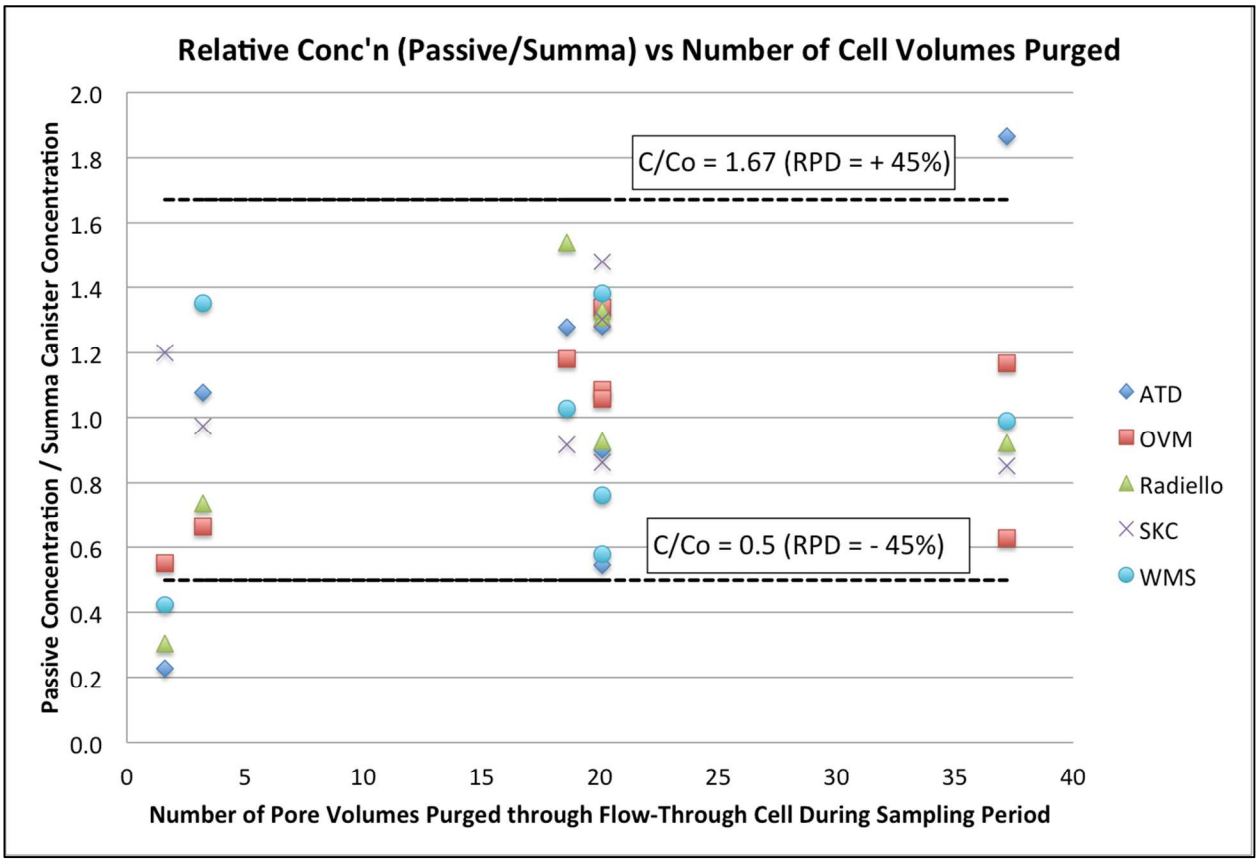

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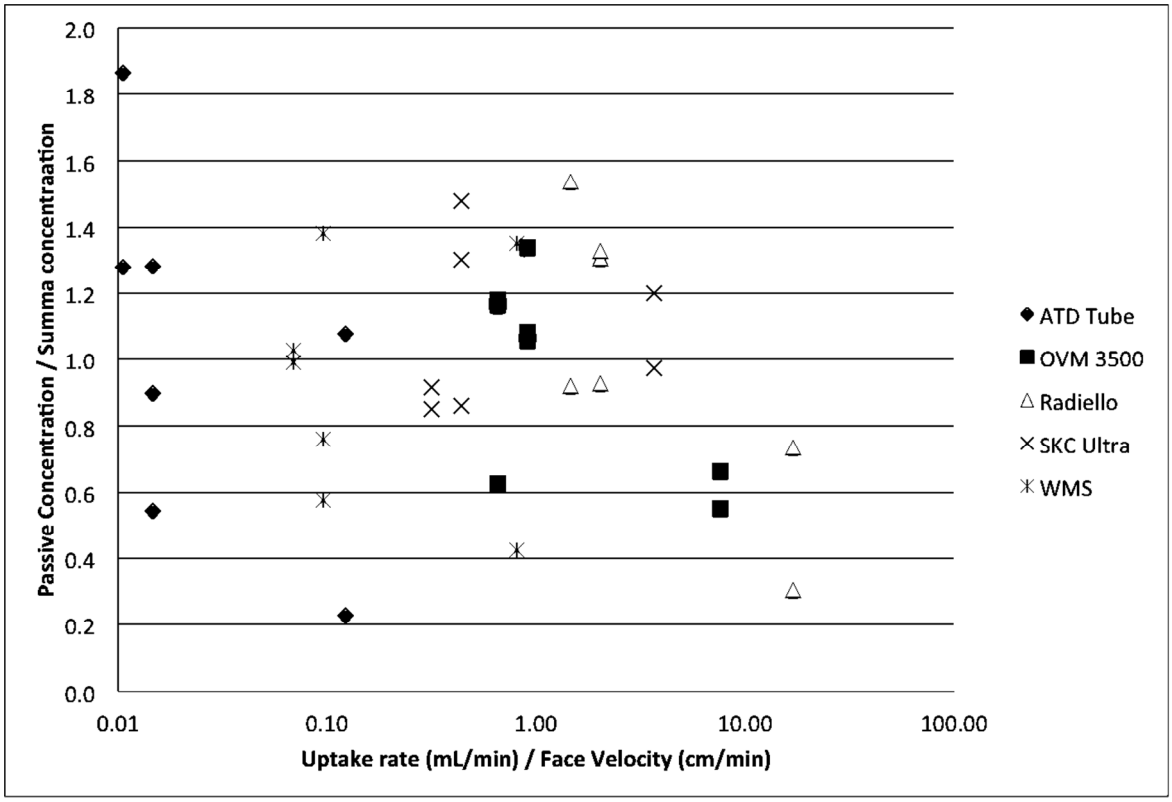
439 Figure 5



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441 Figure 6