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Passive Sampling for Volatile Organic Compounds in Indoor Air – Controlled Laboratory Comparison of Four Sampler Types

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This article describes laboratory testing of four passive diffusive samplers for assessing indoor air concentrations of volatile organic compounds (VOCs), including SKC Ultra II, Radiello®, Waterloo Membrane Sampler (WMS) and Automated Thermal Desorption (ATD) tubes with two different sorbents (Tenax TA and Carbopack B). The testing included 10 VOCs (including chlorinated ethenes, ethanes, and methanes, aromatic and aliphatic hydrocarbons), spanning a range of properties and including some compounds expected to pose challenges (naphthalene, methyl ethyl ketone). Tests were conducted at different temperatures (17 to 30 °C), relative humidities (30 to 90 % RH), face velocities (0.014 to 0.41 m/s), concentrations (1 to 100 parts per billion by volume [ppb_v]) and sampling durations (1 to 7 days). The results show that all of the passive samplers provided data that met the success criteria (relative percent difference [RPD] ≤ 45% of active sample concentrations and coefficient of variation [COV] ≤ 30%) in the majority of cases, but some compounds were problematic for some samplers. The passive sampler uptake rates depend to varying degrees on the sampler, sorbent, target compounds and environmental conditions, so field calibration is advantageous for the highest levels of data quality.

Environmental impact

Passive sampling has been used for indoor air quality monitoring in occupational settings for decades, but the application to monitoring subsurface vapour intrusion to indoor air requires additional effort to assess their capabilities and limitations for lower concentrations and longer exposure durations. This study was commissioned by the United States Department of Defence to provide data needed to demonstrate and validate the use of passive sampling to guide practitioners in the appropriate use and support acceptance where appropriate by regulatory agencies. Several different samplers were tested under a wide range of controlled laboratory conditions with review from leading experts on each sampler type, which provide a unique and valuable new body of data.

Introduction

Subsurface vapor migration to indoor air is an important and challenging component of human health risk assessment for volatile organic compounds (VOCs) in soil and groundwater.[1,2] For sites where vapor intrusion is a potential concern, initial characterization is typically required and long-term monitoring may be warranted for which VOC vapor concentration measurements are usually a primary line of evidence. Conventional methods for air sampling include passivated canisters with analysis by Method TO-15[3] and pumped sorptive tubes with analysis by Method TO-17.[4] However, neither method was designed or could be easily modified for sample durations greater than about 24 hours. Temporal variability in indoor air concentrations is problematic[5-10] and 24-hour samples may not be representative of the longer-term average concentrations considered in human health risk assessment. Longer sampling intervals were adopted by radon researchers to manage temporal variability; a 90-day radon sample is referred to as a "short-term sample" and any sample less than 72 hours is not recommended[11]. Vapor

intrusion for VOCs and radon are not identical, but they are influenced by many of the same processes, so long-term sampling for VOCs warrants consideration. Passive samplers are well-suited to this application.

Passive samplers have been used for industrial hygiene monitoring for decades,[12-28] and their application to the low concentrations of interest for vapor intrusion has been more recently evaluated.[29-32] International standards are available describing the sampling procedure and the sampler performance assessment.[33-52] The objectives of this study were to identify whether and under what conditions the four candidate passive samplers provide accurate and precise measurements of VOC vapor concentrations of interest for human health risk assessment and to document the study findings so that regulatory agencies have strong scientific support for accepting passive sampler data, where appropriate.

Basic Principles of Quantitative Passive Sampling

The basic principles of operation for all of the passive samplers tested in this study are similar. Each device is supplied by the vendor or laboratory as certified clean and sealed in air-tight packing. The sampler is exposed to the air or gas being investigated for a measured amount of time (t), during which VOCs diffuse or permeate into the device from the surrounding atmosphere and a certain mass (M) of each VOC is trapped on the sorptive medium. The device is then re-sealed in an air-tight container and returned to the laboratory, where the mass adsorbed is quantified. The time-weighted average (TWA) concentration (C_o) of a particular analyte in the medium being sampled can be calculated as follows:

$$C_s = \frac{M}{(UR)(t)} \quad (1)$$

The uptake rate (UR) is the key factor controlling the accuracy of the concentration measurement. The mass adsorbed and sample duration can both be measured very accurately. The uptake rate has units of mL min^{-1}, similar to a flow rate, despite the fact that the samplers are designed to operate only by diffusion or permeation. The uptake rate is equal to the flow rate that would be required for a pumped sampler to adsorb the same mass over the same sample duration when exposed to the same concentration.

Experimental Design and Methods

The experimental apparatus consisted of three exposure chambers with a system to supply VOC vapors at controlled levels of concentration, humidity and temperature and is described in detail in the Electronic Supplemental Information (ESI). A schematic of a test chamber is shown in Figure ESI-1.

Samplers and Sorbent Selection

The following samplers and sorbents were used in this study:

- SKC Ultra II™ [22, 53-60] with Carbopack X,
- Radiello® [61, 62] with activated charcoal,
- Waterloo Membrane Sampler™ (WMS) [63, 64] with either Anasorb 747 or Carbopack B, and
- Passive ATD tube samplers [14, 65-73] with both Tenax TA and Carbopack B.

Other passive samplers are or have been commercially-available, including the 3M OVM 3500, the Draeger ORSA 5, the Gas Adsorbent Badge for Individual Exposure (GABIE), the Assay Technologies 521 Badge Sampler, as well as samplers that are not specifically designed to control the uptake rate (Gore Modules and Beacon B-Sure test kits). It was considered impractical to include all types in this testing, so representative samplers of several designs were selected with the expectations that the findings could be generalized to other passive samplers.

Analyses were performed by the laboratories considered by the study team to be most familiar with the respective samplers: Fondazione Salvatore Maugeri in Padova, Italy analyzed the Radiello samplers, the University of Waterloo analyzed the WMS samplers, Columbia Analytical Services of Simi Valley, CA analyzed the SKC Ultra samplers and Air Toxics Ltd. of Folsom, CA analyzed the ATD tube samplers. Details on the analytical methods are provided in the SI. Chamber concentrations were also measured using pumped ATD tubes and Method TO-17 analysis as an active control, as described in the SI.

Uptake rates for a particular compound and sampler can vary by sorbent type, sample duration and air velocity,[44, 56] which were factors that were varied in these experiments. The passive sampler uptake rates selected for use in these experiments were based on vendor-specified values, where available. In some cases, the vendors do not have published uptake rates for a particular VOC. In these instances, an uptake rate was estimated from vendor-specified values for similar compounds. Table ESI-1 provides the uptake rates used and identifies which uptake rates were supplied by the vendors of the passive samplers and which were estimated.

Several publications are available that provide information regarding the effectiveness of various sorbents with various VOCs.[42, 45, 52, 74] For active adsorptive sampling (where air is pumped through a tube of sorbent media), there are recommended maximum sampling volumes (RMSVs) for combinations of compounds and adsorbents beyond which, it is common to observe a low (or negative) bias in the reported concentrations attributable to poor retention by the sorbent. For passive sampling, there is no specified volume of gas drawn through the adsorbent, but poor retention can still result in negative biases by competition for adsorptive sites and back-diffusion (diffusion away from the sampler). The product of the passive sampler uptake rate and the sample duration has units of volume, and is equivalent to the volume of gas that would be required for a pumped sampler to adsorb the same mass as the passive sampler, when exposed to the same concentration. This "equivalent sample volume" was considered as a surrogate for the sample volume for comparison to the RMSV in evaluating the retention of the target analytes for the sorbents used in this study.

VOCs

The analytes included in the experiments were selected to represent commonly occurring VOCs and span a range of properties, as shown in Table ESI-2. The list included chlorinated ethenes, ethanes, and methanes, as well as aromatics, aliphatics and compounds specifically selected because they were expected to be challenging to measure by passive sampling (naphthalene and 2-butanone, or methyl ethyl ketone, MEK). Many other compounds pose a potential concern for vapor intrusion; however, most have

properties within the range represented by these 10 compounds, which makes this list representative for comparison testing purposes. Constant concentrations of 1, 50 or 100 ppb_v were supplied to the test chambers using compressed gas cylinders that were custom-fabricated by Air Liquide America Specialty Gases LLC of Santa Fe Springs, CA, and mass flow controllers to dilute the stock gas as needed (see Electronic Supplemental Information).

Inter-Laboratory Testing

Several laboratories were used in this study so inter-laboratory variances were evaluated by a two-sample inter-laboratory study (a Youden pair experiment).[75, 76] The inter-laboratory testing involved two coincident chambers, each containing triplicates of each of the five passive samplers with all five factors set at their midpoints (duration = 4 days, concentration = 50 ppbv except for naphthalene at 5 ppbv, temperature = 22 °C, humidity = 60% RH and face velocity = 0.23 m/s). Two of each type of passive sampler were analyzed by each of three laboratories according to the scheme in Table ESI-3, which also provided data for assessing intra-laboratory variance.

Center-point Testing

Six (6) identical chamber tests were performed to assess the intrinsic (random) variability in the concentrations measured by the passive samplers. All five factors were held constant at the center points of their respective ranges (duration = 4 days, concentration = 50 ppb_v (except for naphthalene at 5 ppb_v), temperature = 22 °C, humidity = 60% RH and face velocity = 0.23 m/s). Each test included all samplers in triplicate and periodic pumped ATD tube samples as a control check (see Table ESI-4). Two additional chamber tests were performed with all factors set at the center-points after half of the factorial testing was conducted, to assess whether the experimental results were reproducible over time. The results of the latter two tests were compared to the results of the initial six center-point tests and the means were within 25% RPD for all compounds and samples (13% on average), indicating reproducibility was acceptable.

Fractional Factorial Testing

A fractional factorial design[77] was used to evaluate the effect of each of the five main factors (temperature, humidity, concentration, face velocity and sample duration). The design of this test was a $2^{(k-1)}$ fractional factorial design The data from the tests were compiled and reviewed in real-time to the extent possible within the time-frame of shipping and analysis. One observation during the conduct of the tests was a high frequency of non-detect results for the WMS sampler in the short-duration (1 day) and low concentration (1 ppbv) tests (i.e., runs 2 and 4 in Table 1), so the sampler was modified to use a thermally-desorbable sorbent for these conditions to increase sensitivity of the analysis. Subsequent low concentration and short duration runs (runs 12 and 18) provided detectable results.

Table 1. Fractional factorial testing run scheme

Run	Conc'n	Temp.	Face	Duration	Humidity
#	(ppb_v)	(°C)	Velocity (m/s)	(days)	(%R.H.)
1	100	17	0.41	1	87
2	1	17	0.014	1	87
3	100	29	0.41	1	33
4	1	29	0.014	1	33
5	100	27	0.41	7	92
6	1	27	0.014	7	92
7	100	17	0.41	7	31
8	1	17	0.014	7	31
9	50	22	0.23	4	63
10	50	22	0.23	4	63
11	100	17	0.014	1	33
12	1	17	0.41	1	33
13	100	17	0.014	7	88
14	1	17	0.41	7	88
15	100	27	0.014	7	32
16	1	27	0.41	7	32
17	100	30	0.014	1	91
18	1	30	0.41	1	91

Results

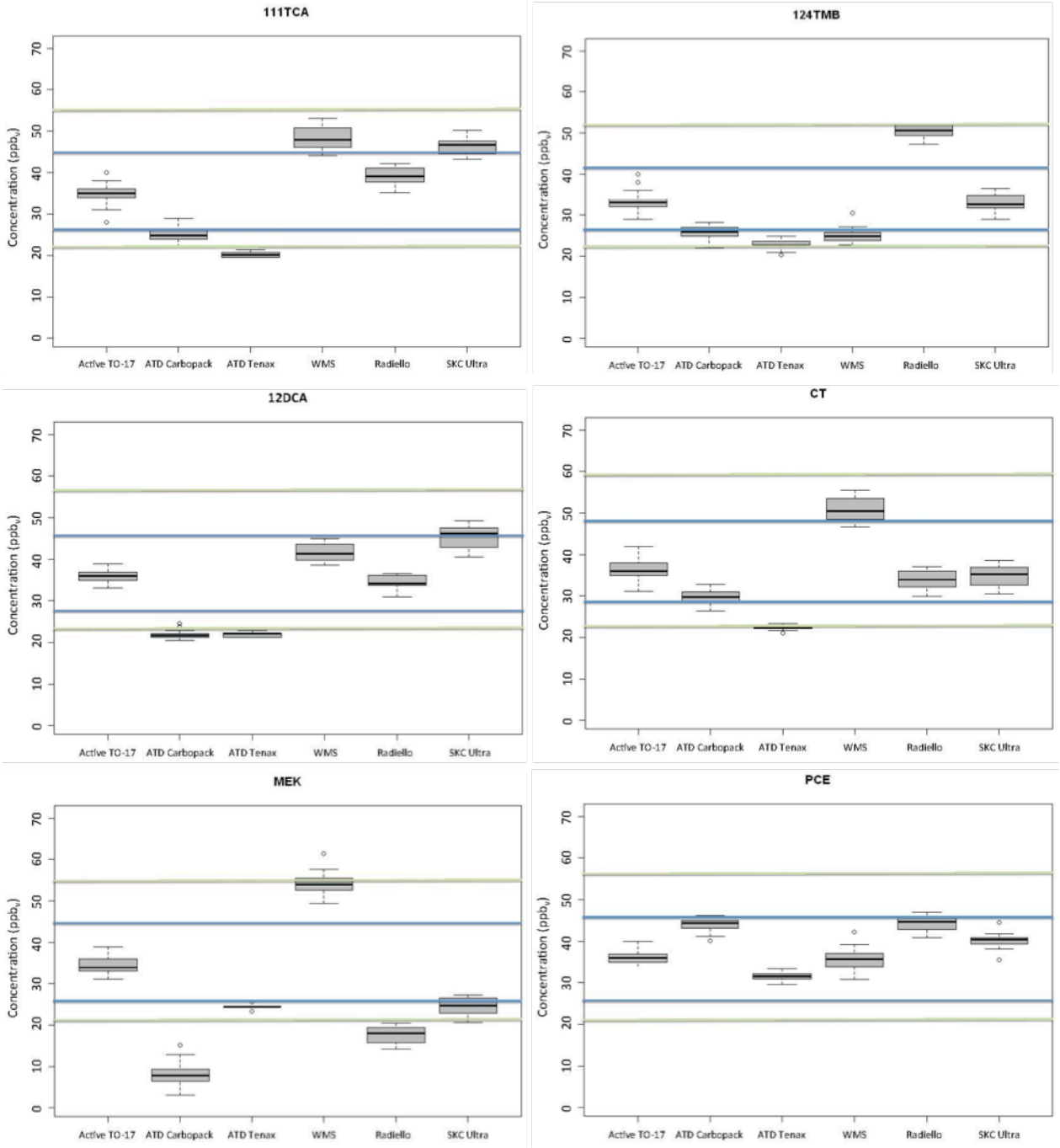
The accuracy of the concentrations reported for each of the sampler types were evaluated by comparing to the results of active sampling and analysis by pumped ATD tubes and EPA Method TO-17 for each of the 10 compounds and each of the 5 samplers in each of the 24 chamber tests. The active samples were collected as a series of samples; however, the data showed that concentrations were held essentially constant, so the relative concentrations were calculated using average values from the active samples for each chamber (typically 3 samples for the 1-day tests, 5 samples for the 4-day tests and 8 samples for the 7-day tests). Precision was evaluated by calculating the coefficient of variation (COV) among replicate samplers (three per chamber for each type) and comparing to a success criterion of COV<30%.

Inter-Laboratory Test Results

The chamber conditions monitored during the inter-laboratory testing are presented in Table ESI-5 and the concentrations measured are presented in Table ESI-6. Figure ESI-2 shows the inter-laboratory variability plotted as the results from one laboratory versus the second laboratory and the calculated inter-laboratory RPD is shown in columns 14, 15 and 16 of Table ESI-7. The average inter-laboratory RPD was 26%. The intra-laboratory variability was very low (3 to 10% RPD between duplicate samples) as shown in Figures ESI-3 a to j. Based on the results of the inter-laboratory test, the success criterion for the accuracy of the passive samplers was adjusted from the conventional value of +/- 25% RPD to +/-45% RPD when comparing results of the passive samplers to the active samplers to account for inter-laboratory variability.

Center-Point Test Results

The chamber conditions monitored during the center-point tests are presented in Table ESI-8 and the VOC concentrations measured with the passive samplers are shown in Table ESI-9 and plotted in Figure 1 (the box spans the 25th to 75th percentiles and the whiskers span the maximum and minimum measured concentrations). The passive sampler data showed precision similar to the active ATD tube samples for most of the combinations of sampler/compound, except: 1) hexane with the WMS sampler (subsequently attributed to laboratory contamination) and 2) naphthalene with the Radiello sampler.



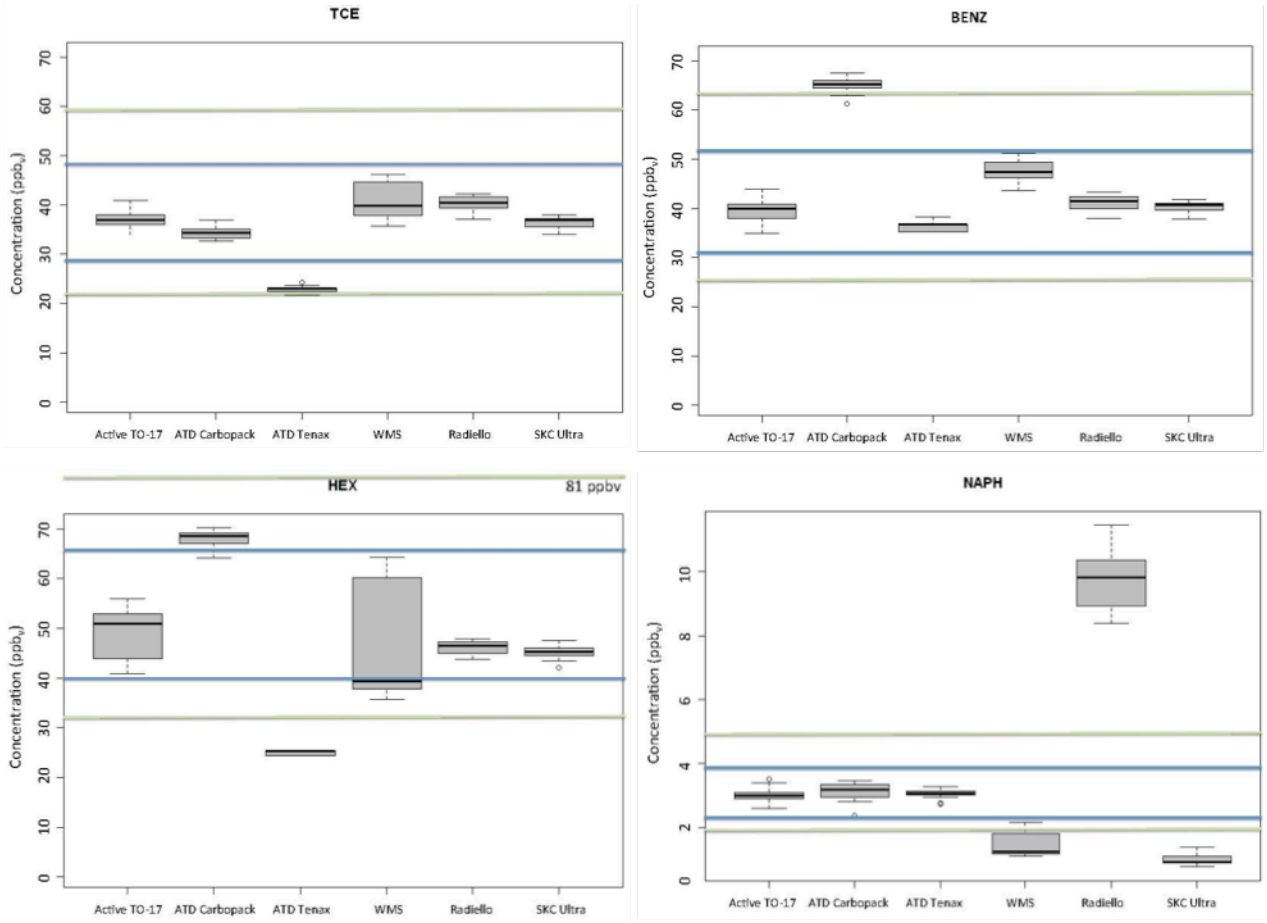


Figure 1. Box and whiskers plots of center-point test results (with control lines corresponding to +/-25% (inside control lines) and +/-45% (outside control lines))

The accuracy was within a C/Co of +/- 25% for 24 of the 50 combinations of sampler/compound, and within +/-45% for 41 of the 50 sampler/compound combinations. Further discussion of results for specific samplers and chemicals is presented in the SI.

The precision for each passive sampler/compound combination in the center-point tests is shown as a plot of the COV in Figure 2. The precision goal of ≤30% COV was met for all but one of the sampler/compound combinations (the only exception was HEX for the WMS, which was related to laboratory contamination). The SKC Ultra showed higher COV values than the other samplers and NAPH and MEK showed higher variability than the other compounds for some samplers. Otherwise, the COV for the passive samplers was similar to the range of COV for the active samples collected from the exposure chamber as controls (2 - 7 %).

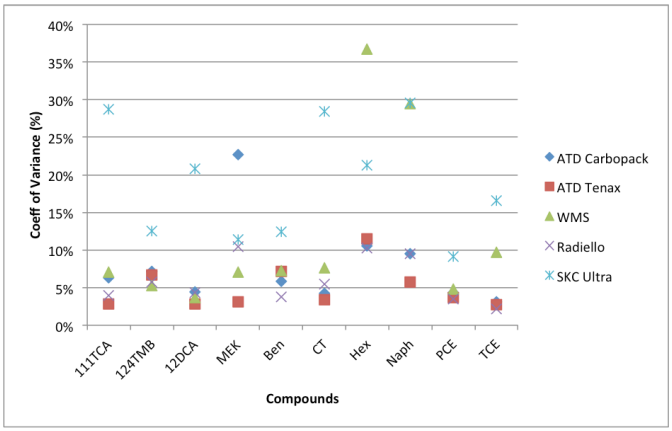


Figure 2. - Coefficient of variation (COV) for the initial six center-point tests

Fractional Factorial Test Results

The fractional factorial test data were combined with the center-point data and are summarized in two sets of figures: Figures ESI-4 a-e and Figures ESI-5 a-f. Specific observations regarding the various samplers, chemicals and chamber conditions are also provided in the SI. The passive sampler performance for all tests are described below.

Performance Assessment

Statistical analysis of the relative concentrations from all 24 chamber tests using analysis of variance (ANOVA) is summarized in Table ESI-10. The highlighted p-values identify the main effects that are statistically significant at the 5% level of significance. The fact that the chambers were very well controlled during these experiments resulted in low experimental variability, which increased the probability that a main effect would show a difference that could be statistically resolved when compared to the intrinsic variance.

Sample duration showed significant effects for the ATD-Tenax sampler for all compounds tested, which is attributable to poor retention in the 4-day and 7-day samples. Tenax has lower recommended maximum sample volumes than Carbopack B for the more volatile compounds. For example, the RMSVs for 111TCA, 12DCA, BENZ, CTET and TCE are 0.2, 1, 1, 0.2 and 1 L, respectively.[74] The product of the uptake rate and the sample duration (the equivalent sample volume) for these compounds for the 7 day samples was 5, 5, 3.5, 5 and 5 L, respectively, all of which are greater than the RMSVs. RMSVs are not available for MEK, HEX and NAPH, but of the other compounds, 55 of the 64 cases where the ATD-Tenax sampler failed the accuracy success criterion with a negative bias (i.e., C/Co<0.63) had an equivalent sample volume (UR x t) greater than the RMSV. This result is further supported by the fact that the only two compounds that had a p value greater than 0.0001 were naphthalene and 124TMB, which were the two compounds with the highest K_{oc} values (i.e., expected to be strongly sorbed). Sampling duration was also significant for 7/10 compounds for the passive ATD sampler with Carbopack B, and the compounds with the lowest p-values (111TCA, 12DCA, CTET and TCE) had the smallest RMSVs (20, 5, 20 and 20 L, respectively). The Radiello and WMS samplers showed the fewest compounds having a significant effect from sample duration, which is likely because these samplers both used very strong sorbents (charcoal and Anasorb 747, respectively). Poor retention in long-duration samples has previousy been observed for the Radiello with Carbotrap, which is a weaker sorbent.[78]

The accuracy success criterion (RPD <45%, corresponding to a C/Co range of 0.63 to 1.58) was met for at least 7 of the 10 compounds for each of the passive samplers in the overall average results of the 24 chamber tests (shown using boldface in Table 2). The mean C/Co (passive concentration/active control) values were calculated for all 24 chamber tests, which includes 8 tests at the center-points and 16 tests conducted at high and low set points of the sample duration, face velocity, temperature, humidity, and concentration; hence, they represent the average accuracy over a wide range of indoor air monitoring conditions. In Table 2, a column has been included comparing the average results of the active ATD tube samples to the concentrations calculated from the mass flow controller measurements. The active ATD tubes met the accuracy criterion for all compounds although MEK showed a somewhat positive bias, which may partly explain the fact that three of the passive samplers showed an apparent negative bias for MEK.

Table 2. Mean C/Co values for the 24 chamber tests

Mean C/Co (passive/active)	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active/ Calculated
111TCA	**0.72**	**0.67**	**1.15**	**0.95**	**0.80**	0.79
124TMB	**0.73**	**0.69**	0.54	**1.13**	**0.69**	0.89
12DCA	0.60	**0.67**	**0.86**	**0.83**	**0.75**	0.87
BEN	1.71	**1.07**	**0.99**	**0.90**	**0.95**	0.72
CT	**0.82**	**0.67**	**1.18**	**0.81**	0.55	0.98
HEX	**1.12**	0.55	**1.15**	**0.80**	**0.70**	0.86
MEK	0.21	**1.00**	**1.12**	0.62	0.46	1.33
NAPH	**0.90**	**0.98**	0.17	2.26	0.36	0.82
PCE	**1.15**	**0.85**	**0.72**	**1.02**	**0.98**	0.94
TCE	**0.91**	0.62	**0.80**	**0.91**	**0.87**	0.91

Mean C/Co is the mean of 24 passive/active concentration ratios (one for each chamber test)

Bold: average C/Co values of 0.63 to 1.58, which meet the success criterion: RPD < +/-45%

Active ATD tube data were compared to concentrations calculated from mass flow controllers

Precision was evaluated two ways: intra-chamber and inter-chamber. The intra-chamber precision was calculated as the average of 24 COV values (one COV value was calculated for each of the three replicates for each compound and each sampler type within each of the 24 chamber tests), as shown in Table 3. The intra-chamber precision met the success criterion (COV<30%) for all but one of the passive sampler/compound combinations (MEK on ATD/Carbopack B). The passive samplers had a lower COV than the active control (pumped ATD tubes) in 68% (34/50) cases, or 80% of the cases with the SKC Ultra II excluded (the SKC Ultra II had notably more results with a negative bias apparently attributable to losses during sample preparation prior to analysis). This result demonstrates that most of the passive samplers yield very good precision and provide very reproducible results under a given set of conditions.

Table 3. Mean Intra-Chamber COV values for the low concentration laboratory tests

Mean intra-chamber COV	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	**7%**	**3%**	**7%**	**5%**	**14%**	13%
124TMB	**5%**	**5%**	**7%**	**4%**	**22%**	7%
12DCA	**8%**	**3%**	**6%**	**4%**	**12%**	9%
MEK	47%	**5%**	**13%**	**11%**	**23%**	15%
CT	**4%**	**6%**	**8%**	**4%**	**8%**	12%
HEX	**7%**	**2%**	**7%**	**7%**	**16%**	7%
BENZ	**5%**	**6%**	**12%**	**3%**	**10%**	6%
NAPH	**6%**	**12%**	**7%**	**6%**	**16%**	7%
PCE	**2%**	**3%**	**6%**	**3%**	**6%**	5%
TCE	**3%**	**2%**	**5%**	**3%**	**16%**	5%

Mean intra-chamber COV is the average of 24 COV values, from three replicates in each chamber

boldface: COV value meets the success criterion: < 30%

The inter-chamber precision was calculated considering all 72 C/Co values for each passive sampler/compound combination from all 24 chamber tests together as a single population (Table 4). The inter-chamber COV values were higher than the intra-chamber values because the high and low values of the test chamber factors (sample duration, face velocity, temperature, humidity and concentration) caused additional variability in the passive sampler data. Calculated in this way, even the active (pumped) ATD tubes showed a COV that was marginal compared to the success criterion (<30%). The passive samplers showed generally higher COV values than the active samples and a wider range between compounds, which shows they are more sensitive than the pumped ATD tubes to the test conditions.

Table 4. Inter-Chamber COV values for the low concentration laboratory tests

Mean inter-chamber COV	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	**24%**	**27%**	**26%**	35%	51%	18%
124TMB	**12%**	**16%**	42%	**25%**	55%	17%
12DCA	31%	32%	35%	**28%**	61%	23%
MEK	88%	69%	116%	70%	65%	19%
CT	**25%**	**26%**	31%	**28%**	59%	19%
HEX	37%	45%	56%	**28%**	39%	27%
BENZ	**25%**	31%	**26%**	**16%**	40%	19%
NAPH	**18%**	**25%**	128%	46%	58%	17%
PCE	**13%**	**14%**	34%	**27%**	**26%**	18%
TCE	**11%**	**17%**	34%	**30%**	51%	16%

Inter-chamber COV is the COV of 24 average C/Co values, one from each chamber test

boldface: COV value meets the success criterion: < 30%

The chamber test results were used to calculate average uptake rates for each sampler/compound combination. The average C/Co values (Table 2) were multiplied by the initial uptake rates (Table ESI-1) to derive revised uptake rates for the 5 passive samplers and 10 target analytes (Table 5).

Table 5. Revised Uptake Rates

Analyte	Revised Uptake Rate (mL/min)				
	WMS	Radiello	SKC Ultra	ATD Tube	ATD Tube
	1.8 mL vial and Anasorb 747	White body and Charcoal	Ultra II and Carbopack X	Carbopack B	Tenax TA
1,1,1-Trichloroethane	2.5	59*	11*	0.36	0.34
1,2,4-Trimethylbenzene	14*	57	9.0*	0.45	0.43
1,2-Dichloroethane	3.5*	64	9.8*	0.30*	0.34*
2-Butanone (MEK)	2.4*	49**	7.8*	0.11**	0.50*
Benzene	3.2	72	15*	0.60	0.37*
Carbon Tetrachloride	2.7*	54	7.2*	0.41	0.34
n-Hexane	2.5*	53	9.8*	0.56*	0.28*
Naphthalene	4.4**	57**	4.7*	0.45	0.49
Tetrachloroethene	6.1*	60	13	0.47	0.35
Trichloroethene	4.1*	63	13*	0.46	0.31

** - Field calibration is recommended

* - consider field calibration if temperature, humidity, velocity, duration or concentration are considerably different than 21^{o}C, 60%RH, 0.2 m/s, 4 days and 50 ppbv, respectively

For the center point conditions (temperature ~ 21 ^{o}C, relative humidity ~ 60%, face velocity = 0.23 m/s, sample duration = 4 day and concentrations ~ 50 ppbv), the passive samplers provided data that met the success criterion for precision (COV<30%) in 49 of 50 cases (Figure 2), and with revised uptake rates for the conditions of sampling tested here (Table 5), the results would meet similar data quality objectives as conventional active samples via Summa canister/TO-15 or active (pumped) ATD tube/TO-17.

Compound/sampler combinations that showed high variability when the chamber conditions were at high or low levels of the 5 factors (not boldfaced in Table 4 and marked with a single asterisk in Table 5) would benefit from inter-method duplicates when field-sampling conditions are not similar to the midpoint levels (e.g., collect one active sample beside every 10th passive sampler to provide data that can be used to derive "field-calibrated" uptake rates for a particular set of environmental conditions). The high precision of the passive samplers under any particular set of conditions (Table 3) provides confidence in the consistency of the uptake rates for other passive samples collected under the same conditions as the inter-method duplicate. Combinations of samplers and analytes that did not meet the success criterion even at the center point conditions (indicated by a double asterisk in Table 5) should be supported by inter-method duplicates regardless of the field sampling conditions if the highest level of data quality is needed (at least until future work reveals the source of the variability or improved prediction of uptake rates as a function of environmental factors).

Discussion

The accuracy and precision of passive samplers should be interpreted in the context of the inherent variability in indoor air concentrations and the value of longer time-weighted average sample durations that can be achieved using passive samplers compared to conventional methods (TO-15 and TO-17). Statistical analysis[83] of recent data collected at an extensively monitored residential duplex[10] showed that three 7-day passive samples yielded concentrations generally within 5X of the long-term average concentration, whereas four 24-hour conventional samples yielded an average concentration generally within about 10X of the long-term average. Therefore, passive samplers can potentially provide data that is more representative of long-term average indoor air concentrations than conventional methods that are limited to shorter sample durations.

Passive samplers will indicate VOC vapors from sources inside the building and outdoor air so forensic analysis is often required to determine the relative contribution of vapors from the subsurface[2,84,85]; however, the same is true for all types of indoor air samples. Quality assurance samples including trip blanks and outdoor air samples should always be included in passive sampling programs.

The VOCs tested were selected to span a wide range of physical properties (Table ESI-2) so the results of this study should be generally informative for most VOCs of interest for vapor intrusion investigations. The 10 VOCs tested in the laboratory clearly showed that there are differences in passive sampler performance attributable to the properties of the chemicals, but the different samplers are not all equally

susceptible to bias and variability for all compounds. Consequently, controlled chamber tests with a wider range of compounds would be valuable.

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Abbreviations

111TCA - 1,1,1-Trichloroethane, 124TMB - 1,2,4-Trimethylbenzene, 12DCA- 1,2-Dichloroethane, MEK - 2-Butanone, BENZ – Benzene, CTET or CT- Carbon Tetrachloride, HEX - n-Hexane, NAPH – Naphthalene, PCE – Tetrachloroethene, TCE – Trichloroethene.

Notes and references

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Electronic Supplementary Information (ESI) available:

- Apparatus
- Passive Sampler Uptake rates
- Chemical properties of the compounds tested
- Analytical methods for all the passive and active samplers
- Chamber conditions and results of the Inter-Laboratory Tests, Centerpoint tests and Fractional Factorial Tests
- Results of the ANOVA Analysis
- Author affiliations and interests

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1 Citations here in the format A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523;

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