

# Demonstration and Validation of the Use of Passive Samplers for Monitoring Soil Vapor Intrusion to Indoor Air

by

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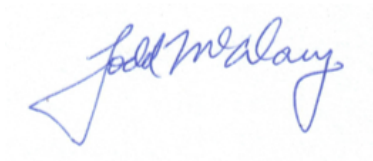
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## AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. Contributions to this research by others are itemized in Section 1.6. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

A handwritten signature in blue ink, reading "Todd McAlary". The signature is written in a cursive style with a large, stylized initial "T" that loops back to the left.

Todd McAlary

## Abstract

This thesis documents a demonstration/validation of passive diffusive samplers for assessing soil vapor, indoor air and outdoor air concentrations of volatile organic compounds (VOCs) at sites with potential human health risks attributable to subsurface vapor intrusion to indoor air. The study was funded by the United States (U.S.) Department of Defense (DoD) and the U.S. Department of the Navy (DoN). The passive samplers tested included: SKC Ultra and Ultra II, Radiello®, Waterloo Membrane Sampler (WMS), Automated Thermal Desorption (ATD) tubes, and 3M OVM 3500. The program included laboratory testing under controlled conditions for 10 VOCs (including chlorinated ethenes, ethanes, and methanes, as well as aromatic and aliphatic hydrocarbons), spanning a range of properties and including some compounds expected to pose challenges (naphthalene, methyl ethyl ketone). Laboratory tests were performed under conditions of different temperature (17 to 30 °C), relative humidity (30 to 90 % RH), face velocity (0.014 to 0.41 m/s), concentration (1 to 100 parts per billion by volume [ppb<sub>v</sub>]) and sample duration (1 to 7 days). These conditions were selected to challenge the samplers across a range of conditions likely to be encountered in indoor and outdoor air field sampling programs. A second set of laboratory tests were also conducted at 1, 10 and 100 parts per million by volume (ppm<sub>v</sub>) to evaluate concentrations of interest for soil vapor monitoring using the same 10 VOCs and constant conditions (80% RH, 30 min exposure, 22 °C). Inter-laboratory testing was performed to assess the variability attributable to the differences between several laboratories used in this study.

The program also included field testing of indoor air, outdoor air, sub-slab vapor and deeper soil vapor at several DoD facilities. Indoor and outdoor air samples were collected over durations of 3 to 7 days, and Summa canister samples were collected over the same durations as the passive samples for comparison. Subslab and soil vapor samples were collected with durations ranging from 10 min to 12 days, at depths of about 15 cm (immediately below floor slabs), 1.2 m and 3.7 m. Passive samplers were employed with uptake rates ranging from about 0.05 to almost 100 mL/min and analysis by both thermal desorption and solvent extraction. Mathematical modeling was performed to provide theoretical insight into the potential behavior of passive samplers in the subsurface, and to help select those with uptake rates that would minimize the risk of a

negative bias from the starvation effect (which occurs when a passive sampler with a high uptake rate removes VOC vapors from the surroundings faster than they are replenished, resulting in biased concentrations). A flow-through cell apparatus was tested as an option for sampling existing sub-surface probes that are too small to accommodate a passive sampler or sampling a slip-stream of a high-velocity gas (e.g., vent-pipes of mitigation systems).

The results of this demonstration show that all of the passive samplers provided data that met the performance criteria for accuracy and precision (relative percent difference less than 45 % for indoor air or 50% for soil vapor compared to conventional active samples and a coefficient of variation less than 30%) under some or most conditions. Exceptions were generally attributable to one or more of five possible causes: poor retention of analytes by the sorbent in the sampler; poor recovery of the analytes from the sorbent; starvation effects, uncertainty in the uptake rate for the specific combination of sampler/compound/conditions, or blank contamination. High (or positive) biases were less common than low biases, and attributed either to blank contamination, or to uncertainty in the uptake rates. Most of the passive samplers provided highly reproducible results throughout the demonstrations. This is encouraging because the accuracy can be established using occasional inter-method verification samples (e.g., conventional samples collected beside the passive samples for the same duration), and the field-calibrated uptake rates will be appropriate for other passive samples collected under similar conditions. Furthermore, this research demonstrated for the first time that passive samplers can be used to quantify soil vapor concentrations with accuracy and precision comparable to conventional methods.

Passive samplers are generally easier to use than conventional methods (Summa canisters and active ATD tubes) and minimal training is required for most applications. A modest increase in effort is needed to select the appropriate sampler, sorbent and sample duration for the site-specific chemicals of concern and desired reporting limits compared to Summa canisters and EPA Method TO-15. As the number of samples in a given program increases, the initial cost of sampling design becomes a smaller fraction of the overall total cost, and the passive samplers gain a significant cost advantage because of the simplicity of the sampling protocols and reduced shipping charges.



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## **Dedication**

I dedicate this thesis to my father Eric Burton McAlary, who taught me to work hard, provide well, and never complain. He also taught me to value higher education, leadership and community service, which I will pursue through ongoing instruction as an Adjunct Professor henceforth. I also dedicate this thesis to his father Burton McAlary, who died of leukemia before I was born. Inhalation of benzene vapors is a known cause of leukemia, and this thesis is focused on monitoring potential inhalation exposures to volatile organic chemicals, including benzene. I hope this work helps reduce health risks for future generations, so grandfathers may meet their grandsons.

# Table of Contents

Abstract.....	iii
Acknowledgments.....	v
List of Tables.....	xi
List of Figures.....	xiii
Abbreviations.....	xviii
1 Introduction.....	1
1.1 Overview of Vapor Intrusion.....	1
1.1.1 Conventional Methods for Monitoring Vapor Intrusion.....	3
1.2 Passive Sampling.....	6
1.2.1 General Principles of Passive Sampler Operation.....	7
1.2.2 Historical Perspective on Passive Sampling.....	11
1.3 Varieties of Passive Samplers.....	18
1.3.1 Candidate Passive Samplers Used in this Study.....	18
1.3.2 Customizing Passive Samplers.....	28
1.3.3 Advantages and Limitations of Passive Sampling.....	30
1.3.4 Standards and Testing for Passive Samplers.....	34
1.4 Prior State-of-the-Art for Passive Soil Vapor Sampling.....	35
1.5 Scope of the Thesis.....	45
1.6 Attribution.....	46
2 Experimental.....	50
2.1 Low Concentration Laboratory Tests.....	50
2.2 High Concentration Laboratory Tests.....	51
2.3 Indoor and Outdoor Field Tests.....	51
2.4 Soil Vapor Field Tests.....	51
2.5 Varieties of Passive Samplers Used.....	52
2.6 Description of Field Test Sites.....	55
2.6.1 Old Town Campus Building 3 (OTC3), San Diego, CA.....	55
2.6.2 SERDP Research House near Hill Air Force Base, Layton, UT.....	56
2.6.3 USACoE Cold Regions Research and Engineering Lab, Hanover, NH.....	58
2.6.4 Marine Corps Air Station (MCAS), Cherry Point, NC.....	59
2.6.5 Naval Air Station (NAS), Jacksonville, FL.....	60

2.7	Performance Objectives .....	62
2.7.1	Accuracy of VOC Vapor Concentrations .....	62
2.7.2	Precision .....	63
2.7.3	Cost.....	63
2.7.4	Ease of Use .....	63
3	Laboratory Chamber Tests (Low Concentration Range) .....	65
3.1	Experimental.....	65
3.1.1	VOCs Included in Laboratory Testing.....	65
3.1.2	Apparatus.....	67
3.1.3	Familiarity Testing .....	70
3.1.4	Intra and Inter-Laboratory Testing .....	71
3.1.5	Center-point Testing (ANOVA testing) .....	72
3.1.6	Fractional Factorial Testing .....	72
3.2	Results and Discussion.....	74
3.2.1	Familiarity Test Results .....	74
3.2.2	Intra and Inter-Laboratory Test Results.....	76
3.2.3	Center-point (ANOVA) Test Results .....	88
3.2.4	Fractional Factorial Test Results .....	92
3.3	Performance Assessment.....	104
3.4	Summary .....	110
4	Indoor and Outdoor Air Testing .....	111
4.1	Experimental.....	111
4.1.1	Sampling Locations and Strategies .....	111
4.1.2	Sample Collection .....	112
4.2	Results and Discussion.....	113
4.2.1	OTC3 .....	113
4.2.2	CRREL .....	116
4.2.3	MCAS Cherry Point .....	118
4.3	Performance Assessment.....	122
4.4	Summary .....	124
5	Mathematical Modeling of Passive Soil Vapor Sampling .....	128
5.1	Conceptual Model for Quantitative Passive Soil Vapor Sampling .....	128
5.2	Mathematical Modeling of Passive Soil Vapor Sampling.....	129

5.2.1	Influence of Soil Moisture on the Effective Diffusion Coefficient in Soil.....	129
5.2.2	Transient Model.....	131
5.2.3	Steady-State Model.....	134
5.3	Results and Discussion .....	134
5.3.1	Transient Model Simulations .....	134
5.3.2	Steady-State Model Simulations.....	141
5.4	Practical Considerations on the Uptake Rate .....	142
5.5	Summary .....	143
6	Laboratory Chamber Tests (High Concentration Range).....	144
6.1	Experimental .....	144
6.1.1	Standard Gas Mixtures .....	144
6.1.2	Varieties of Samplers Used .....	145
6.1.3	Apparatus .....	146
6.1.4	Sample Collection.....	149
6.1.5	Low Uptake Rate Sampler Tests .....	149
6.2	Results and Discussion .....	150
6.3	Summary .....	160
7	Soil Vapor Field Testing .....	161
7.1	Experimental .....	161
7.1.1	Materials and Methods.....	161
7.1.2	Sampling Locations .....	162
7.2	Results and Discussion .....	168
7.3	Summary .....	181
8	Passive Samplers in a Flow-Through Cell.....	182
8.1	Experimental .....	183
8.1.1	Sample Locations.....	183
8.1.2	Apparatus .....	183
8.1.3	Sample Duration .....	184
8.1.4	Flow Rates.....	186
8.1.5	Sampling Procedure.....	186
8.2	Results .....	187
8.3	Summary .....	194
9	Discussion.....	196

9.1	Overall Performance .....	196
9.2	Ease of Use .....	199
9.2.1	3M OVM 3500 .....	200
9.2.2	Radiello .....	200
9.2.3	Waterloo Membrane Sampler .....	200
9.2.4	SKC Ultra and Ultra II .....	201
9.2.5	ATD Tubes .....	201
9.2.6	Comparison to Summa Canisters (TO-15) .....	201
9.2.7	Comparison to Pumped ATD Tubes (TO-17) .....	202
9.3	Cost Assessment .....	202
9.3.1	Cost Model and Cost Analysis .....	202
9.3.2	Cost Drivers .....	207
9.4	Implementation Considerations .....	207
9.4.1	Potential Biases .....	207
9.4.2	Considerations for Sampler Selection .....	209
9.5	Research Needs .....	211
10	References .....	213
11	Appendices .....	232

## List of Tables

<b>Table 1-1:</b> Review Articles on VOC sampling in general and passive sampling in particular .....	12
<b>Table 1-2:</b> Summary of research for passive samplers, sorbents and diffusion/permeation barriers for VOCs and SVOCs in air.....	13
<b>Table 1-3:</b> Select literature demonstrating, validating or applying the SKC Ultra .....	20
<b>Table 1-4:</b> Select literature demonstrating, validating, or applying the Radiello sampler.....	22
<b>Table 1-5:</b> Select literature demonstrating, validating or applying the 3M OVM 3500.....	24
<b>Table 1-6:</b> Select literature demonstrating, validating or applying the ATD tube sampler .....	26
<b>Table 1-7:</b> Calculated uptake rates for the GORE(TM) Module from air .....	40
<b>Table 2-1:</b> Number and varieties of samplers and sorbents used in the field-sampling program .....	54
<b>Table 2-2:</b> Summary of Performance Metrics and Criteria .....	64
<b>Table 3-1:</b> Compounds tested and their key properties .....	66
<b>Table 3-2:</b> Uptake rates for the passive samplers.....	66
<b>Table 3-3:</b> Intra and inter-laboratory testing scheme .....	71
<b>Table 3-4:</b> Fractional factorial testing run scheme.....	73
<b>Table 3-5:</b> Chamber conditions during inter-laboratory testing.....	77
<b>Table 3-6:</b> Concentrations measured during inter-laboratory testing.....	78
<b>Table 3-7:</b> Summary of accuracy and precision in the inter-laboratory test.....	87
<b>Table 3-8:</b> Mean $C/C_0$ values for the low concentration laboratory tests.....	104
<b>Table 3-9:</b> Mean intra-chamber COV values for the low concentration laboratory tests.....	105
<b>Table 3-10:</b> Mean inter-chamber COV values for the low concentration laboratory tests .....	106
<b>Table 3-11:</b> Recommended revised uptake rates for compounds and samplers used in the low concentration laboratory tests .....	107
<b>Table 3-12:</b> Results of ANOVA analysis (p-values) of low concentration lab tests (main effects).....	108
<b>Table 4-1:</b> Indoor and outdoor VOC concentrations with passive and active samples at OTC3 .....	115
<b>Table 4-2:</b> Indoor air VOC concentrations using Summa canisters and passive samplers at CRREL.....	117
<b>Table 4-3:</b> $C/C_0$ and COV for indoor air samples at CRREL .....	123
<b>Table 4-4:</b> $C/C_0$ and COV for indoor air sampling at MCAS 137 .....	125
<b>Table 5-1:</b> Parameter values used in the model simulations (representative of TCE).....	130
<b>Table 5-2:</b> Comparison of time to reach 95% of steady-state concentrations in the void space comparing nominal 1-inch and 4-inch diameter boreholes (total porosity 37.5%).....	136
<b>Table 6-1:</b> Risk-based screening levels <sup>4</sup> .....	144

<b>Table 6-2:</b> Volumes of pure compounds added to humidification vessel for 100 ppm <sub>v</sub> test .....	148
<b>Table 6-3:</b> Concentrations measured in exposure chamber at 1 ppm <sub>v</sub> (NAPH=0.1ppm <sub>v</sub> ) .....	151
<b>Table 6-4:</b> Concentrations measured in exposure chamber at 10 ppm <sub>v</sub> (NAPH=1ppm <sub>v</sub> ) .....	152
<b>Table 6-5:</b> Concentrations measured in the exposure chamber at 100 ppm <sub>v</sub> .....	153
<b>Table 6-6:</b> Average concentrations measured with passive samplers divided by average concentrations measured with Summa canisters (C/C <sub>0</sub> ).....	155
<b>Table 6-7:</b> COV of concentrations measured in test chamber.....	156
<b>Table 6-8:</b> Linear regression parameters for normalized (C/C <sub>0</sub> ) concentration data for 1, 10 and 100 ppm <sub>v</sub> tests at 5 cm/min face velocity and 30 min sample duration.....	157
<b>Table 6-9:</b> Low-uptake rate sampler results (in µg/m <sup>3</sup> ) for three tests: 10 ppm <sub>v</sub> with 5 cm/min velocity, 10 ppm <sub>v</sub> stagnant and 100 ppm <sub>v</sub> stagnant .....	159
<b>Table 7-1:</b> Active and passive soil vapor concentrations in sub-slab samples from Navy OTC3, along with uptake rates (provided by suppliers) for the passive samplers .....	168
<b>Table 7-2:</b> TCE and 11DCE Concentrations measured in active soil gas samples analyzed by the Hapsite transportable GC/MS (H) or Summa® canister and TO-15 (S) at the Layton house, Utah. ....	169
<b>Table 7-3:</b> Passive soil vapor concentrations, average active sampling concentrations and relative concentrations (C/C <sub>0</sub> ) for 1,1-DCE at the Layton House, Utah.....	170
<b>Table 7-4:</b> Passive soil vapor concentrations, average active sampling concentrations and relative concentrations (C/C <sub>0</sub> ) for TCE at the Layton House, Utah .....	171
<b>Table 7-5:</b> TCE and 11DCE concentrations measured in passive samplers at the Layton House, Utah ..	174
<b>Table 7-6:</b> Passive and active soil vapor concentrations for four VOCs in soil gas probes (SG) and sub- slab probes (SSP) at NAS JAX .....	175
<b>Table 8-1:</b> Summary of passive samplers used .....	185
<b>Table 8-2:</b> TCE concentrations measured using passive samplers and Summa canisters.....	188
<b>Table 8-3:</b> Results of ANOVA analysis of flow-through cell test results .....	193
<b>Table 8-4:</b> Summary statistics for all sampler types .....	194
<b>Table 9-1:</b> Cost Comparison for Scenario 1 .....	204
<b>Table 9-2:</b> Cost comparison for Scenario 2.....	205
<b>Table 9-3:</b> Cost comparison for Scenario 3.....	206
<b>Table 9-4:</b> Sample duration required for each of the passive samplers with either solvent extraction or thermal desorption to achieve a reporting limit equal to the residential indoor air screening level corresponding to a 1-in-a-million incremental lifetime cancer risk.....	210



## List of Figures

<b>Figure 1-1:</b> Conceptual model of subsurface vapor intrusion (prepared by the author for U.S.EPA) .....	2
<b>Figure 1-2:</b> Summa canister and pumped ATD tube equipment (different scales; photos courtesy of Columbia Analytical Services, Simi Valley, CA) .....	6
<b>Figure 1-3:</b> Relationship of mass collected versus time for a passive sampler .....	8
<b>Figure 1-4:</b> Concentration profiles for diffusion and permeation passive samplers .....	9
<b>Figure 1-5:</b> Axial, badge, radial and membrane sampler types (blue arrows indicate vapor entry). .....	19
<b>Figure 1-6:</b> SKC Ultra sampler with regular (white) and low-uptake cap (green) (image at left courtesy of SKC).....	20
<b>Figure 1-7:</b> Radiello sampler with regular (white) and low-uptake (yellow) bodies (image at left courtesy of FSM) .....	21
<b>Figure 1-8:</b> 3M OVM 3500 sampler and solid plastic cap used to replace the porous plastic sheet after sampling (image at left courtesy of 3M) .....	23
<b>Figure 1-9:</b> Waterloo Membrane Sampler (WMS), close-up of membrane and protective mesh .....	25
<b>Figure 1-10:</b> ATD tube sampler, regular and low-uptake rate caps, and protective mesh .....	26
<b>Figure 1-11:</b> Photo of two 6L Summa canisters and a 3M OVM 3500 sampler (upper right) .....	32
<b>Figure 1-12:</b> PETREX sampler <sup>50</sup> .....	35
<b>Figure 1-13:</b> The Beacon Be-Sure Sampler (formerly the EMFLUX cartridge) <sup>195</sup> .....	36
<b>Figure 1-14:</b> Mass to concentration relationship for 4 VOCs <sup>193</sup> .....	37
<b>Figure 1-15:</b> Mass to concentration relationship for benzene <sup>196</sup> .....	37
<b>Figure 1-16:</b> Relationship between MtoC correlation and soil gas concentration range for the tie-in points <sup>196</sup> .....	38
<b>Figure 1-17:</b> The GORE(TM) Module <sup>103</sup> .....	39
<b>Figure 1-18:</b> Linear uptake of compounds by the GORE(TM) Module <sup>103</sup> .....	40
<b>Figure 1-19:</b> Correlation between uptake rate and free air diffusion coefficient for GORE(TM) Module 41	
<b>Figure 1-20:</b> Correlation between active soil vapor sampling and analysis by H&P Mobile Geochemistry versus the GORE(TM) Module for a: PCE (top) and b: TCE (bottom) <sup>201</sup> .....	42
<b>Figure 1-21:</b> Correlation between the GORE(TM) Module and active soil vapor sampling <sup>198</sup> .....	43
<b>Figure 1-22:</b> Correlation between the GORE(TM) Module and the Waterloo Membrane Sampler (a.k.a. TWA-PDMS sampler) for PCE (left) and TCE (right) <sup>203</sup> .....	43
<b>Figure 1-23:</b> Correlation between the GORE(TM) Module and the Waterloo Membrane Sampler (a.k.a. TWA-PDMS sampler) for benzene (left) and TPH (right) <sup>203</sup> .....	44

<b>Figure 1-24:</b> Unfiltered comparative data from 5 sites with the GORE(TM) Module <sup>200</sup> .....	44
<b>Figure 2-1:</b> SSC-Pac OTC3 layout and sample locations (courtesy of Geosyntec Consultants, Inc.).....	55
<b>Figure 2-2:</b> Front view of ASU vapor research house in Layton, UT .....	56
<b>Figure 2-3:</b> Locations of passive soil vapor sample at the Layton house (base map courtesy of Arizona State University).....	57
<b>Figure 2-4:</b> CRREL facility and laboratory location (photo courtesy of CRREL).....	58
<b>Figure 2-5:</b> MCAS Cherry Point Building 137 and locations of indoor and outdoor air samples (courtesy Geosyntec) .....	59
<b>Figure 2-6:</b> Southwest corner of Building 103, NAS JAX .....	60
<b>Figure 2-7:</b> NAS JAX Building 103 plan showing locations of previous sub-slab (SS-1, 2 and 3) and soil gas (SG-2) probes installed by GSI, as well as new passive soil gas probes (SGFP-6, -12 and -18) and temporary holes (TH-1, 2 and 3) (modified from GSI <sup>210</sup> ) .....	61
<b>Figure 3-1:</b> Design details of the exposure chamber for the low concentration tests (courtesy of Geosyntec) .....	68
<b>Figure 3-2:</b> Assembled chambers and close-up of the rotating carousel (photos courtesy of Air Toxics Ltd.) .....	69
<b>Figure 3-3:</b> Low concentration test apparatus, including (left to right): compressed gas cylinders containing 10 VOCs, drum of activated carbon for purifying dilution air, humidification vessel, mass flow controllers, exposure chambers (covered with insulation), constant temperature bath, and discharge lines to fumehood (photo courtesy of Air Toxics Ltd.).....	69
<b>Figure 3-4:</b> Active sampling: comparison of results using method TO-15 vs. TO-17 during familiarity tests .....	75
<b>Figure 3-5:</b> Passive sampling: ATD Tenax TA vs. ATD Carbopack B during familiarity tests .....	76
<b>Figure 3-6:</b> Youden plots for each VOC in the inter-laboratory tests.....	84
<b>Figure 3-7:</b> Scatter plot of laboratory 1 vs. laboratory 2 for all VOCs and samplers .....	86
<b>Figure 3-8:</b> Box and whisker plots of center-point test results (with control lines corresponding to +/-25% (inside control lines) and +/-45% (outside control lines)).....	91
<b>Figure 3-9:</b> Coefficient of variation for the initial center-point (ANOVA) testing .....	92
<b>Figure 3-10:</b> ATD tube/Tenax TA results for center-point and fractional factorial tests.....	93
<b>Figure 3-11:</b> ATD tube/Carbopack B results for center-point and fractional factorial tests .....	93
<b>Figure 3-12:</b> SKC Ultra II results for center-point and fractional factorial tests .....	94
<b>Figure 3-13:</b> WMS results for center-point and fractional factorial tests .....	94
<b>Figure 3-14:</b> Radiello results for center-point and fractional factorial tests .....	95

<b>Figure 3-15:</b> ATD Tenax low concentration laboratory test data .....	98
<b>Figure 3-16:</b> ATD Carbopack B low concentration laboratory test data.....	99
<b>Figure 3-17:</b> SKC Ultra II low concentration laboratory test data.....	100
<b>Figure 3-18:</b> WMS low concentration laboratory test data .....	101
<b>Figure 3-19:</b> Radiello low concentration laboratory test data .....	102
<b>Figure 3-20:</b> Active ATD tube low concentration laboratory test data .....	103
<b>Figure 4-1:</b> Typical layout of indoor air sampling array .....	113
<b>Figure 4-2:</b> Stacked bar chart of individual measured concentrations of TCE at each location to the left and average to the right for all indoor samples at OTC3.....	114
<b>Figure 4-3:</b> Passive sampler indoor air concentrations vs. Summa canisters at CRREL .....	116
<b>Figure 4-4:</b> VOCs in indoor air by SKC Ultra II vs Summa canister at MCAS 137 .....	119
<b>Figure 4-5:</b> VOCs in indoor air by Radiello vs. Summa canister at MCAS 137 .....	120
<b>Figure 4-6:</b> VOCs in indoor air by ATD/Carbopack B vs. Summa canister at MCAS 137 .....	120
<b>Figure 4-7:</b> VOCs in indoor air by 3M OVM vs. Summa canister at MCAS 137 .....	121
<b>Figure 4-8:</b> VOCs in indoor air by WMS vs. Summa canister at MCAS 137 .....	121
<b>Figure 5-1:</b> Effective diffusion coefficient versus water-filled porosity for TCE in a soil with 37.5% total porosity, typical of a sandy soil .....	131
<b>Figure 5-2:</b> Schematic of transient mathematical model domain including boundary and initial conditions .....	132
<b>Figure 5-3:</b> Simulated (cumulative) mass delivered by diffusion from surrounding soil to the void space versus time (for a 2.5 cm diameter borehole in a sandy soil with 37.5% total porosity and an initial soil vapor concentration of $100 \mu\text{g}/\text{m}^3$ , assuming no removal of mass by a passive sampler) .....	135
<b>Figure 5-4:</b> Diffusive delivery rate versus time for mass entering the void space (for a 2.5 cm diameter, 10 cm tall void space in a soil with 37.5% total porosity and an initial soil vapor concentration of $100 \mu\text{g}/\text{m}^3$ , assuming no removal of mass by a passive sampler).....	137
<b>Figure 5-5:</b> Relationship between the instantaneous diffusive delivery rate of vapors into the void space versus the percentage of the analyte mass at steady-state ( $100 \times M_t/M_{ss}$ , where $M_t$ is the analyte mass in the borehole at time t, and $M_{ss}$ is the analyte mass at steady state), assuming a 2.5 cm diameter borehole in a soil with 37.5% total porosity, initial soil vapor concentration of $100 \mu\text{g}/\text{m}^3$ , and no removal of mass by a passive sampler. ....	138
<b>Figure 5-6:</b> Superimposed diffusive delivery rates plus uptake rate (for a 10 cm tall and 2.5 cm diameter void space in a soil with 37.5% porosity and an initial soil vapor concentration of $100 \mu\text{g}/\text{m}^3$ containing a passive sampler with an uptake rate of 1 mL/min).....	140

<b>Figure 5-7:</b> Calculated uptake rate corresponding to various values of delta as a function of water-filled porosity (for a 10 cm tall and 2.54 cm diameter void space assuming $r_3 = 1m$ ).....	141
<b>Figure 5-8:</b> Calculated uptake rate corresponding to various $r_3$ values as a function of water-filled porosity (for a 10 cm tall and 2.54 cm diameter void space assuming $\delta = 0.75$ ) .....	142
<b>Figure 6-1:</b> Schematic diagram of experimental apparatus for high concentration laboratory tests .....	147
<b>Figure 7-1:</b> Schematic diagram of the probe for passive vapor sampling at the Layton house, Utah .....	164
<b>Figure 7-2:</b> Schematic diagram of the probe for passive soil vapor sampling at NAS JAX .....	166
<b>Figure 7-3:</b> Relative concentration (passive/active or $C/C_0$ ) at the Layton House for : a) 11DCE, and b) TCE.....	172
<b>Figure 7-4:</b> Correlation between passive samples and Summa canisters at NAS JAX with linear regression and correlation ( $R^2$ ) for soil gas samples .....	176
<b>Figure 7-5:</b> Correlation between passive samples and Summa canisters at NAS JAX with linear regressions and correlation coefficients ( $R^2$ ) for sub-slab samples .....	177
<b>Figure 7-6:</b> Relative concentration (passive/Summa canister) for WMS/low-uptake sampler in temporary open holes at NAS JAX .....	178
<b>Figure 7-7:</b> Relative concentration (passive/active) versus uptake rate for soil gas sampling .....	180
<b>Figure 7-8:</b> Relative concentration (passive/active) versus equivalent sample volume/void volume .....	180
<b>Figure 8-1:</b> Experimental apparatus (schematic) for flow-through cell tests .....	184
<b>Figure 8-2:</b> Reporting limit as a function of sample duration for the passive samplers used in the flow-through cell.....	185
<b>Figure 8-3:</b> TCE concentrations measured with a) Summa canisters, and b) passive samplers in the flow-through cell.....	189
<b>Figure 8-4:</b> Relative TCE concentration ( $C/C_0$ ) for passive samplers in the flow-through cell .....	190
<b>Figure 8-5:</b> Relative concentration of TCE versus number of cell volumes purged through the flow-through cell during the sample period.....	191
<b>Figure 8-6:</b> Relative concentration of TCE versus uptake rate divided by face velocity.....	192
<b>Figure 9-1:</b> Correlations for all passive samplers vs. active samples in the field demonstrations .....	199

## **List of Appendices**

Appendix A: Analytical Methods

Appendix B: Process Flow Diagrams for the Low Concentration Laboratory Test Apparatus

Appendix C: Results of Center-Point (a.k.a. ANOVA) Low Concentration Laboratory Tests

Appendix D: Results of Fractional Factorial Low Concentration Laboratory Tests

Appendix E: Statistical Analysis of the Low Concentration Laboratory Tests

Appendix F: Results of Indoor and Outdoor Air Monitoring at MCAS Cherry Point

Appendix G: Transient Model Derivation for Radial Diffusion to a Passive Soil Vapor Probe

## Abbreviations

11DCA	1,1-dichloroethane
11DCE	1,1-dichloroethene
111TCA	1,1,1-trichloroethane
12DCA	1,2-dichloroethane
112TCA	1,1,2-trichloroethane
1122PCA	1,1,2,2-tetrachloroethane
124TMB	1,2,4-trimethylbenzene
$\mu\text{g}/\text{m}^3$	Micrograms per cubic meter
ACoE	Army Corps of Engineers
AFB	Air Force base
AFCEC	Air Force Center for Civil Engineering
ANOVA	Analysis of Variance
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ASU	Arizona State University
ATD	Automatic Thermal Desorption
ATL	Air Toxics Ltd., Folsom, California (now Eurofins Air Toxics, Inc.)
BENZ	Benzene
BFB	4-Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
BTX	Benzene, Toluene and Xylene
CA	California
C/C <sub>o</sub>	Concentration in passive sampler/concentration in active sampler
CAS	Columbia Analytical Services, Simy Valley, California
CCME	Canadian Council of Ministers of the Environment
CCV	Continuing calibration verification
cDCE	cis-1,2-dichloroethene
CDM	Camp Dresser McKee
CEN	Comité Européen de Normalisation
CH	Czech Republic
CMS	Carbonized Molecular Sieves
COV	Coefficient of Variation (synonymous with relative standard deviation)
CPB	Carbopack B
CRREL	Cold Regions Research and Engineering Laboratory
CTET (or CT)	Carbon tetrachloride
DAI	Direct Aqueous Injection
DCB	Dichlorobenzene
DCE	Dichloroethene
DCM	Dichloromethane
DDR	Diffusive Delivery Rate
DNAPL	Dense, Non-Aqueous Phase Liquid
DoD	Department of Defense

DOL	Department of Labor
STSC	Department of Toxic Substances Control
DoE	Department of Energy
DoN	Department of the Navy
ECD	Electron Capture Detector
EPA	Environmental Protection Agency
EPRI	Electrical Power Research Institute
ER	Environmental Remediation
ESTCP	Environmental Security Technology Certification Program
ETV	Environmental Technology Verification
FID	Flame Ionization Detection
FSM	Fonazione Salvatore Maugeri of Padova, Italy
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
GCB	Graphitized Carbon Black
GC/MS	Gas Chromatography / Mass Spectrometry
Geosyntec	Geosyntec Consultants Inc.
GSA	General Services Administration
GSI	Groundwater Services, Inc.
HEX	Hexane
hr	hour
HVAC	Heating, ventilating and air conditioning
IA	Indoor air
ID	inside diameter
IL	Illinois
ISEA	International Society for the Electronic Arts
ISO	International Standards Organization
ITRC	Interstate Technology and Regulatory Council
K <sub>oc</sub>	Organic carbon partitioning coefficient
LCS	Laboratory Control Spike
LDPE	Low Density Polyethylene
LLE	Liquid-liquid extraction
LNAPL	Light, Non-Aqueous Phase Liquid
LPME	Liquid Phase Microextraction
LTPRI	Linear Temperature Programmed Retention Index
LU	Low-uptake
MACBETH	Monitoring of Atmospheric Concentrations of Benzene in European Towns and Homes
MADEP	Massachusetts Department of Environmental Protection
MCAS	Marine Corps Air Station
MCAS 137	Marine Corps Air Station Cherry Point Building 137, North Carolina
MCRD	Marine Corps Recruit Depot
MDL	Method Detection Limit
MDHS	Methods for the Determination of Hazardous Substances
MEK	Methylethylketone (or 2-Butanone)

MEPS	Microextraction by Packed Sorbent
MESI	Membrane Extraction with a Sorbent Interface
MI	Michigan
MIMS	Membrane Interface Mass Spectrometry
M <sub>RL</sub>	Mass reporting limit
MS	Mass Spectrometer
MTBE	Methyl tert-butyl ether
MW	Molecular weight
NAPH	Naphthalene
NAS	Naval Air Station
NAS JAX	Naval Air Station Jacksonville, Florida
NB	<i>Nota Bene</i>
ND	Not detected
NESDI	Navy Environmental Sustainability Development to Integration
NH	New Hampshire
NHEX	n-Hexane
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NJ	New Jersey
OA	Outdoor Air
OCF	Organichlorine pesticide
ODE	Ordinary differential equation
OH	Ohio
ON	Ontario
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
OTC3	SSC-Pacific Old Town (Campus) Building 3, San Diego, California
OU	Operable Unit
OVM	Organic Vapor Monitor
PA	Pennsylvania
PAH	Polycyclic aromatic hydrocarbon
PDBE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene or perchloroethene
PDE	Partial differential equation
PDMS	Polydimethylsiloxane
PE	Perkin Elmer
PHC	Petroleum Hydrocarbon
PID	Photoionization Detector
POM	Polyoxymethylene
ppm <sub>v</sub>	Parts per million by volume
ppb <sub>v</sub>	Parts per billion by volume
PTFE	Polytetrafluoroethylene
PUF	polyurethane foam
PVC	polyvinyl chloride



QA/QC	Quality Assurance/Quality Control
Qsoil	Volumetric flow rate of soil gas into a building
Qbldg	Volumetric flow rate of air through a building
RAD	Radiello
RH	Relative humidity
RMSV	Recommended Maximum Sample Volume
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SBSE	Stir-Bar Sorptive Extraction
SIM	Selected Ion Monitoring
SPDE	Solid-Phase Dynamic Extraction
SPNTD	Sorbent Packed Needle Trap Device
SPAWAR	Space and Naval Warfare Systems Command
SPME	Solid-Phase Microextraction
SS	Sub-slab
SSC Pacific	SPAWAR Systems Center Pacific
SSP	Sub-slab probe
SSV	Sub-slab vapor
SUM	Summa
SVOC	Semi-Volatile Organic Compound
TCA	Trichloroethane (1,1,1-)
TCE	Trichloroethene
TD	Thermal desorption
tDCE	trans-1,2-dichloroethene
TCE	Trichloroethene
TM	Trademark
TMB	Trimethyl benzene
TO	Toxic Organic
TPH	Total Petroleum Hydrocarbon
TWA	Time-weighted average
UK	United Kingdom
UR	Uptake Rate
U.S. EPA	United States Environmental Protection Agency
UST	Underground Storage Tank
UT	Utah
UW	University of Waterloo
VC	Vinyl chloride
VERAM	Versatile, easy and rapid atmospheric monitor
VI	Vapor Intrusion
VOC	Volatile Organic Compound
VT	Vermont
WMS	Waterloo Membrane Sampler
WMS-LU	Low uptake variety of WMS sampler

# 1 Introduction

## 1.1 Overview of Vapor Intrusion

Subsurface vapor migration to indoor air (vapor intrusion, or VI) for volatile organic compounds (VOCs) is an important component of human health risk assessment and management associated with contaminated soil and groundwater. On average, people inhale about 20,000 L of air every day, so the potential dose via inhalation dominates over other routes of exposure, such as drinking (about 2 L of water per day) or ingestion (a few grams of dust per day). Since the late 1990s, regulatory guidance for assessing vapor intrusion has been issued in several countries, the most influential of which is the United States, where guidance has been issued by at least 27 State Agencies, the Interstate Technology and Regulatory Council,<sup>1</sup> and by the US Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response.<sup>2</sup> Sampling and analysis of indoor air, outdoor air and soil gas are currently the primary lines of evidence for VOC vapor intrusion assessment. For sites where vapor intrusion is a potential concern, long-term monitoring may also be warranted, which will incur significant costs for responsible parties.

The United States Department of Defense (DoD) and related contractors are collectively responsible for environmental compliance at thousands of sites with VOCs in soil or groundwater near occupied buildings, and are required to assess whether and to what extent vapor intrusion poses a potential health concern. The DoD sponsored this research through the Environmental Security and Technology Certification Program (ESTCP) Project ER-0830, “Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques”<sup>3</sup> (GSA Contract #W912HQ-08-C-0046 for \$US 1,040,000) and by the U.S. Navy Environmental Sustainability Development to Integration (NESDI) program Project 424 on “Improved Assessment Strategies for Vapor Intrusion (VI)” (Contract N66001-07-R-0108, TO #0004, Task Order #2 for \$US 117,000). The author of this thesis was the Principal Investigator in both projects.<sup>1</sup>

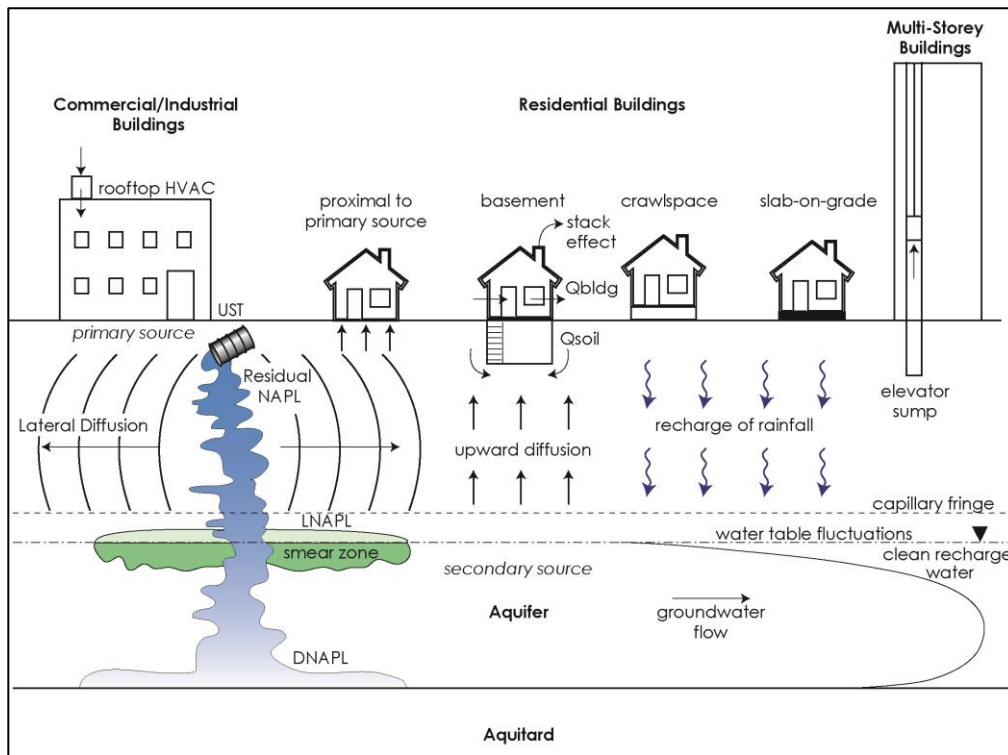
Vapor intrusion occurs because the pressure differential between buildings and the underlying soil fluctuates in response to wind gusts, barometric pressure changes and operation of mechanical fans. The processes are similar to those contributing to radon migration to indoor air. Several different site-specific factors influence the potential for health risks to building occupants, including:

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<sup>1</sup> This Chapter is based partly on the author’s report for ESTCP<sup>3</sup>

- **Source:** Mass, compounds, distribution (localized, such as an underground storage tank [UST] or distributed, such as along a sewer line), depth, age and degree of weathering. Many VOCs are non-aqueous phase liquids (NAPLs), which can be less dense (LNAPL) or more dense (DNAPL) than water and therefore either float on the water table or sink below it;
- **Pathway:** geologic material properties (porosity, texture, moisture, layering, degree of fracturing), driving forces (concentration gradients, barometric pressure cycles, water table fluctuations, pressure gradients resulting from wind load on buildings or thermal gradients), phase transfer (volatilization, sorption, dissolution) and reactions (hydrolysis, biodegradation);
- **Building:** foundation design and integrity, building ventilation rate ( $Q_{bldg}$ ), soil gas flow rate into building ( $Q_{soil}$ ), pressure gradients caused by the heating, ventilating and air conditioning (HVAC) system and thermal gradients that create a stack effect and background sources of chemical vapors (consumer products, building materials, occupants' activities, vehicle emissions and ambient outdoor air quality); and
- **Receptor:** age, frequency and duration of occupancy, sensitivity to chemicals (aged, infirm, pregnant women, asthmatics) and level of exertion (as it relates to respiration rate).

A conceptualization of the variety of vapor intrusion scenarios is depicted in Figure 1-1.



**Figure 1-1:** Conceptual model of subsurface vapor intrusion (prepared by the author for U.S.EPA)

Human health risk assessment considers the toxicity of subsurface contaminants for cancer and non-cancer endpoints. Cancer risks are usually considered acceptable at a level of 1 incremental incident in 1,000,000 receptors over a lifetime of exposure, which is a very protective level and typically results in very low risk-based indoor air screening levels (IASLs).<sup>4</sup> Non-cancer endpoints are usually considered acceptable below a hazardous index of 1.0, over an exposure duration of a year or less.<sup>4</sup> For many common VOCs, the IASLs are on the order of 1  $\mu\text{g}/\text{m}^3$ , so the sampling and analytical methods must have high sensitivity. Indoor air contains many VOCs from consumer products, building materials and occupant's activities, so selectivity is also important. Soil vapor concentrations of concern are higher than the IASLs by a factor that accounts for dilution by the building ventilation rate (referred to as an attenuation factor), so soil vapor screening levels (SVSLs) or sub-slab screening levels (SSSLs) are typically higher than IASLs by a factor of 10 to 1,000, depending on the building size, ventilation rate and regulatory preferences. Soil vapor concentrations in proximity to a subsurface source of VOCs can be several orders of magnitude higher than SSSLs, so a wide dynamic range is also an important consideration for assessment methods.

At the present time, there are varying opinions regarding the reliability of soil vapor sampling for assessing human health risks posed by VOCs. For example, the ITRC vapor intrusion guidance<sup>1</sup> states: "Soil gas data are recommended over other data, specifically soil matrix and groundwater data, because soil gas data represent a direct measurement of the contaminant that can potentially migrate into indoor air". However, the empirical database of soil vapor and indoor air concentrations compiled by the USEPA shows a worse correlation between soil vapor and indoor air concentrations than the corresponding comparison between groundwater and indoor air concentrations.<sup>5</sup> It is not clear what role sampling errors or biases played in the relatively poor correlation between soil vapor and indoor air concentrations. However, soil vapor sampling protocols using passive sampling devices are considerably simpler than active sampling protocols, and simpler protocols are likely to reduce variability attributable to operator error, which provides an incentive to advance the science of passive soil vapor sampling.

### **1.1.1 Conventional Methods for Monitoring Vapor Intrusion**

Currently, the most common method for collection and analysis of indoor air and sub-slab or soil vapor samples during vapor intrusion investigations consists of drawing air or soil gas into an evacuated, passivated stainless steel canister (SilcoTek® or Summa®) with the rate of flow regulated by a flow controller, followed by shipment to a laboratory for analysis by EPA Method TO-15<sup>6</sup> via gas chromatography/mass spectrometry (GC/MS). This is also referred to as "whole-gas" sampling because the container collects all constituents (i.e., typically ~80% nitrogen, ~20% oxygen, and various VOC

vapors). The cost for TO-15 analysis of each Summa canister sample is generally in the range of \$135 to \$180US (depending on the compound list and reporting limit), and includes rental, cleaning and certification for the canister, and flow controller rental in addition to the cost of analysis. Shipping costs are high because of the large size and weight of the canisters. Sampling protocols for canisters are complicated, so labor costs for sample collection are relatively high, and complicated protocols increase the risk of inter-operator errors that may cause data bias and variability.

The OSWER 2002 Draft Vapor Intrusion Guidance<sup>2</sup> lists 114 compounds of potential concern for vapor intrusion, including VOCs, semi-volatile organic compounds (SVOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The California Department of Toxic Substances Control<sup>7</sup> added two polychlorinated biphenyls (PCBs). Of these 116 compounds, only about 46 compounds are included on the standard EPA Method TO-15 analyte list (the TO-15 analyte list is not prescriptive, so it varies from about 65 to 85 compounds between laboratories), and of these, the target indoor air concentrations for an incremental cancer risk of 1 in 1 million are lower than typical analytical reporting limits for several compounds. TO-15 is the most commonly used method for vapor intrusion assessments, and at most sites is the only method used, leaving 70 or more potential compounds of concern for vapor intrusion unquantified. Analysis of an additional 18 polynuclear aromatic hydrocarbons (PAHs) can be accomplished by EPA Method TO-13A, 7 pesticides by EPA Method TO-4A, and 85 VOCs and semi-volatile organic compounds (SVOCs) by TO-17/8270; however, these methods all require different sampling media and analytical methods, so it becomes prohibitively expensive to conduct a comprehensive analysis using current methods. Method TO-15 is typically used for up to about 85 VOCs, of which several are not included in the list of potential compounds of concern for vapor intrusion, and some have reporting limits higher than the IASLs. Consequently, method TO-15 can be used to characterize less than half of the potential compounds of concern for vapor intrusion.

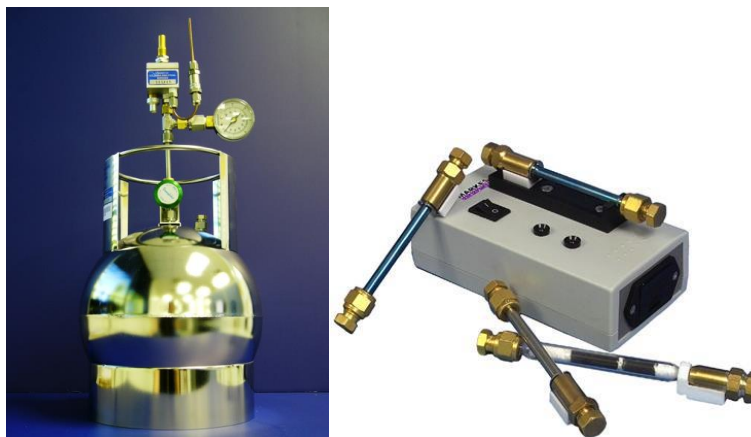
Summa canisters are typically used to collect samples over 8 to 24 hours, and are not well-suited to longer duration samples because the critical orifice or mass flow controllers used to restrict the rate of air flow into the canister becomes difficult to control at very low flow rates. This is particularly problematic because indoor air concentrations fluctuate in response to fluctuations in the building pressure, which are difficult to control. Generally, shorter-duration samples show more temporal variability and larger numbers of samples are required to characterize long-term TWA indoor air concentration with a certain level of confidence compared to longer-duration samples. Passive samplers are better suited to longer sampling durations.

For soil vapor sampling and analysis in particular, there are a wide variety of different methods and guidances available<sup>1,8-14</sup>, but few comparative studies that evaluate the relative performance between various active soil vapor sampling methods.<sup>15</sup> Subsurface gas permeability can vary over many orders of magnitude and care is needed to prevent and document the absence of leaks of atmospheric air into the sample train, especially in low-permeability soils.<sup>16</sup> Leakage can be evaluated using tracer gas and various forms of pneumatic testing, but the complexity of the sampling protocol increases significantly. There are also differing opinions regarding the volume to be purged prior to sample collection, the flow rate and vacuum that should be applied, the potential for adsorption/desorption, reactions with tubing, fittings and containers, and the duration over which the sample should be collected<sup>13</sup>, all of which could potentially be avoided using passive samplers.

The most common alternative to whole-gas sampling is active adsorptive sampling using Automated Thermal Desorption (ATD) tubes (*NB*: one of the passive samplers included in this thesis also uses ATD tubes in the passive mode, so this document refers to both active and passive ATD tube samples). For active adsorptive sampling, the ATD tubes are filled with a selected adsorbent and gas is drawn through the tube at a controlled flow rate for a measured time, from which the total volume of gas constituting the sample can be calculated. The mass of chemicals adsorbed in the tube is determined by laboratory analysis using US EPA Method TO-17,<sup>17</sup> and the concentration is calculated by dividing the measured mass by the volume of gas drawn through the tube. Pumped ATD tube sampling is very commonly used in industrial hygiene applications and tends to be more popular than Summa canister sampling and whole-gas analysis in Europe.

Active adsorptive sampling also faces several practical challenges. For indoor air sampling, the sample duration is usually limited to 24-hours or less to reduce the risk of breakthrough (poorly retained VOCs can migrate chromatographically through the sorbent and be lost from the sample) and because the pumps are often powered by rechargeable batteries with a limited service life. Also, some chemicals have very low risk-based target concentrations for the vapor intrusion pathway and thus require very large volumes of gas to be drawn through the adsorptive media to achieve the required reporting limits. Large sample volumes may exceed practical limits on the flow rate or sample duration and may not be conducive to good retention of weakly sorbed analytes.<sup>18</sup> When collecting active samples in a pumped ATD tube, the potential for breakthrough or poor retention is evaluated by review of the recommended maximum sample volume (RMSV)<sup>19</sup>, which is the volume of air that can be drawn through the ATD tube without unacceptable losses via breakthrough of a particular analyte for a particular sorbent. Verification testing for potential breakthrough can be performed using two ATD tubes in series or distributed pairs of samples (high and low volume), with associated increases in the costs of analyses.

For soil vapor sampling, the concentrations of chemicals in the gas to be sampled are usually unknown in advance, so there is a risk that the concentrations will be higher than expected and the mass adsorbed may exceed the linear range of calibration during analysis. Soil vapor tends to have a relative humidity near 100%, and moisture can interfere with adsorptive sites for activated carbon-based sorbents. The gas permeability of soils is highly variable, and it can be challenging to maintain a constant flow through an ATD tube without imposing excessive vacuum when sampling from probes screened in moderate to low-permeability materials. Despite these drawbacks, the active adsorptive methods are accurate and precise when applied under ideal conditions (unrestricted flow, strongly-retained target compounds, sample duration of several hours or more, concentrations within calibrated range). The choice of the sorbent, sample flow rate, sample duration and analytical method depend on the compounds of interest, target reporting limits and range of anticipated concentrations, which makes active adsorptive sampling more complex than Summa canister sampling. The Summa canister and active ATD tube are shown in Figure 1-2.



**Figure 1-2:** Summa canister and pumped ATD tube equipment (different scales; photos courtesy of Columbia Analytical Services, Simi Valley, CA)

## 1.2 Passive Sampling

A passive sampler collects chemicals via free transport of analyte molecules from the sampled medium to a collecting medium in response to a chemical potential difference.<sup>20</sup> This difference could be due to a concentration gradient or partial pressure gradient; consequently, advective transport into an evacuated canister can be considered passive sampling. This thesis, however, is focused solely on samplers that collect chemicals by diffusion or permeation in response to a concentration gradient.

Passive sampling has several potential advantages over conventional whole-gas sampling, including simpler protocols, smaller size for ease of shipping and handling, and lower overall cost (including the

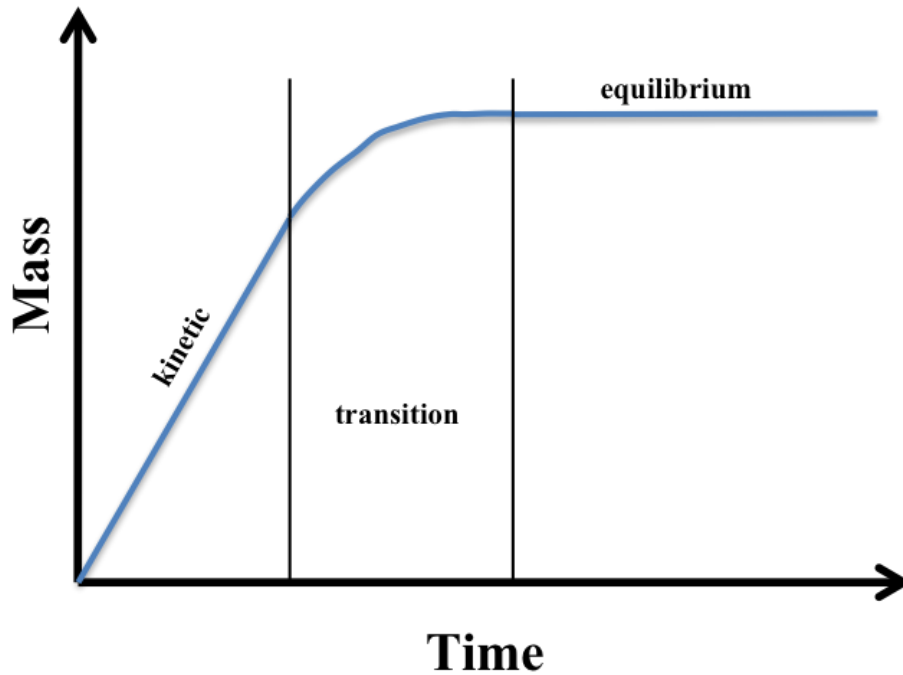
labor cost for sample collection).<sup>21</sup> Much of the early application of passive sampling was focused on industrial hygiene.<sup>22-26</sup> Passive sampling is commonly used for monitoring radon in indoor air,<sup>27</sup> which is similar to subsurface vapor intrusion for VOCs in many ways. Indoor air concentrations of radon vary in response to wind-speed, rainfall, barometric pressure and temperature changes, and there is no reason to believe that indoor air concentrations of VOCs from vapor intrusion would not show some degree of temporal variability attributable to most of the same processes (radon and VOCs have different sources, distributions, and fate mechanisms, so the temporal trends would not likely be identical). The most common methods of radon sample collection (activated carbon badges and electrets) are passive samplers, primarily because of low cost and simplicity, but also because they can be used to collect samples over periods long enough to be more representative of long-term average concentrations. Temporal variability can be managed by collecting a greater number of samples to support statistical calculation of a representative long-term average concentration<sup>28-32</sup>; however, this increases the cost considerably. Passive samplers are better suited to longer sampling intervals (i.e., much greater than 24 hours), which is expected to provide data with less variability compared to conventional shorter duration sampling methods and can characterize long-term time-weighted average exposures with fewer samples than conventional methods.

Passive samplers can potentially assess a wide range of compounds using sorbents selected to provide optimal retention and recovery for selected ranges of compounds (stronger sorbents for low boiling point compounds, and vice-versa). This research tested the applicability of passive samplers under controlled laboratory conditions for a list of 10 common VOCs with a wide range of properties affecting their potential for passive sampling (primarily diffusion coefficient and adsorptive affinity); however, SVOCs, PAHs, PCBs and other very high boiling point compounds were not tested in this program.

### **1.2.1 General Principles of Passive Sampler Operation**

Passive samplers take up analytes over time according to the general trend shown in Figure 1-3. At early stages, the rate of uptake is constant (provided the ambient concentration is constant), and the increase in sorbed mass is linear with time. At late stages, the mass taken up by the sampler reaches a steady state (again, provided the concentration in the environment of the sampler is constant). Passive samplers are of two general varieties depending on the uptake region in which they operate: kinetic (linear region) and equilibrium samplers (steady-state region); the transitional regime between the two is avoided. This thesis deals exclusively with kinetic passive samplers because the focus of this research was human health risk assessment associated with subsurface vapour intrusion to indoor air, where time-weighted average concentrations are preferred.

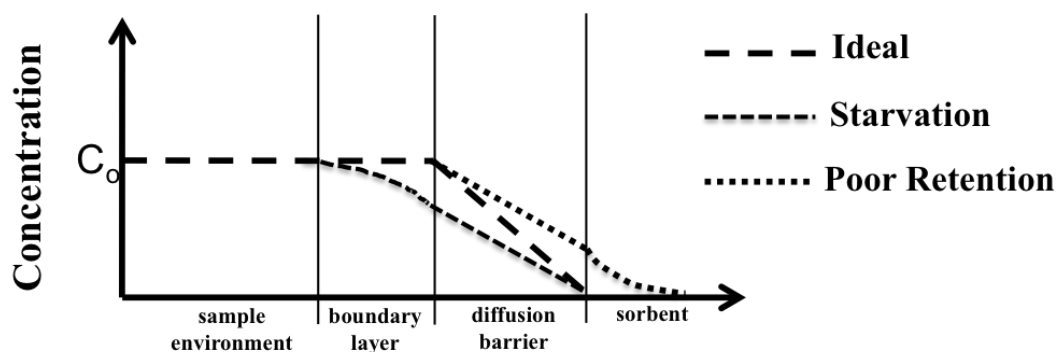




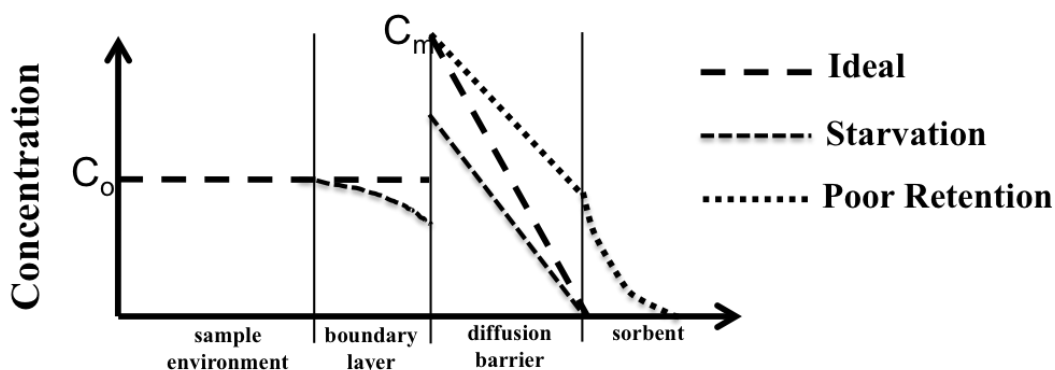
**Figure 1-3:** Relationship of mass collected versus time for a passive sampler

The two general types of kinetic passive samplers operate either by diffusion of molecules through a stagnant layer of air, or permeation through a membrane of various polymer materials. The profile of analyte concentration from the environment being sampled to the sampler is shown schematically for both types of sampler in Figure 1-4. The concentration in the environment ( $C_o$ ) is simplified as being constant as a function of distance from the outer edge of a boundary layer near the sampler, although it can also vary with time. In the ideal case, the rate of transport (by advection and diffusion) of analytes into the boundary layer is equal to or greater than the rate of removal by the sampler, and the concentration remains at  $C_o$  throughout the boundary layer. Ideally, the sorbent completely removes the analyte from the gas phase, reducing the concentration near its surface to effectively zero (i.e., the sorbent acts as a “zero sink”) throughout the sample duration and linear concentration gradient is established across the diffusive barrier or membrane. The concentration at the outer edge of a permeation membrane ( $C_m$ ) may be different than  $C_o$  by a factor equal to the distribution coefficient (also known as partitioning coefficient,  $K = C_m/C_o$ ) for the analyte between the membrane and air.

## Diffusion Passive Sampler



## Permeation Passive Sampler



**Figure 1-4:** Concentration profiles for diffusion and permeation passive samplers

If the velocity of air to which the sampler is exposed is very low (less than about 0.1 to 0.001 m/s depending on the uptake rate of the sampler<sup>33,34</sup>), then the sampler may remove VOC vapors from the air faster than they are replenished, in which case the concentration in the boundary layer decreases, causing a reduction in the concentration gradient, and therefore a reduction in the uptake rate. This causes a negative bias in the concentration reported by the sampler and is commonly referred to as the “starvation effect”. It is generally managed either by increasing the face velocity (rate of air flow past the face of the sampler) using fans or other means or by using passive samplers with lower uptake rates. If the sorbent becomes saturated or a particular analyte is weakly sorbed by a particular sorbent, the sorbent may not act as a perfect zero sink, especially for longer sample durations. This condition is referred to as poor retention, and results in non-zero concentrations of the analyte at the inner edge of the barrier or membrane, which also reduces the concentration gradient and results in negative bias. Both of these potential biases are shown in Figure 1-4.

For kinetic samplers (assuming no starvation), the rate of mass uptake by diffusion is:<sup>23</sup>

$$\frac{M}{t} = DA \frac{(C_o - C_s)}{L} \quad (1-1)$$

where  $C_s$  is the concentration in the gas phase at the inner edge of the diffusive barrier or membrane,  $L$  is the thickness of the diffusive barrier or membrane,  $A$  is the cross sectional area of analyte entry into the sampler and  $D$  is the diffusion coefficient in the diffusive barrier. For permeation samplers,  $D$  is replaced by permeability ( $P$ ), which is equal to the product of the distribution coefficient ( $K$ ) and the diffusion coefficient of the analyte in the membrane ( $D_m$ ). Assuming the sorbent performs as a zero sink as intended, the value of  $C_s$  is essentially zero, so Equation 1-1 becomes:

$$\frac{M}{t} = DA \frac{(C_o)}{L} \quad (1-2)$$

Rearranging:

$$C_o = \frac{M}{t} \frac{L}{DA} \quad (1-3)$$

The second term is referred to as the calibration constant ( $k$ ) because it is the proportionality constant between the parameter of interest ( $C_o$ ) and the two primary measurements ( $M$  and  $t$ ). The reciprocal of the calibration constant is referred to as the uptake rate ( $UR$ ) or sampling rate, which has units of volume/time and is equivalent to the rate of air flow that would be required for an active sampler to take up the same mass over the same sample duration when exposed to the same sample concentration.

Equation 1-3 can also be rearranged to:

$$UR = \frac{DA}{L} = \frac{M}{C_o t} \quad (1-4)$$

Therefore, the uptake rate is sometimes reported in units of mass/concentration/time, according to the third term in Equation 1-4. Note that for permeation samplers, the diffusion coefficient  $D$  in Equation 1-4 is preplaced with permeability  $P$ . The dimensions of the passive sampler calculations reduce to:

$$C_o = \frac{M}{UR t} \quad (1-5)$$

where:

$C_o$  = TWA concentration of a particular analyte in the sampled air [ $\mu\text{g}/\text{m}^3$ ]

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

$UR$  = uptake rate [mL/min]

$t$  = sampling time [min]

(note that there are two offsetting conversion factors from pg to  $\mu\text{g}$  and mL to  $\text{m}^3$ )

The mass adsorbed and the sample duration can both be measured very accurately (commonly within 5% to 15% relative), so the accuracy of the uptake rate is the key factor controlling the accuracy of the calculated concentration. The uptake rates are designed and controlled to the extent possible using a fixed cross-sectional area and thickness for the diffusive barrier or membrane and known diffusion or permeation characteristics for the chemicals of interest. The uptake rates are typically measured in controlled exposure chamber experiments or calculated from first principles based on the free-air diffusion coefficient or permeation rate of the particular compound of interest.

### **1.2.2 Historical Perspective on Passive Sampling**

The earliest passive samplers were developed for occupational hygiene applications, where the sample duration of interest is typically an 8 hour working shift and the target concentrations are generally in the range of about 1 to 100 parts-per-million by volume (ppmv). The earliest description was a colorimetric test-paper for monitoring ozone concentrations<sup>25</sup>, but passive samplers were in more widespread use by the early 1980s<sup>35-38</sup>. The history of development of passive sampling for occupational monitoring from 1988 through 2008 is chronicled in a series of 16 issues of “The Diffusive Monitor” by the UK Health and Safety Executive and in a series of review articles listed in Table 1-1.

A wide variety of different types of passive samplers have been designed and tested over the years, some of which have been designed for different purposes than this research (e.g., different classes of chemicals, occupational hygiene monitoring, etc.). An indication of the diversity of this research is provided in Table 1-2. Acronyms and abbreviations in Tables 1-1 and 1-2 are defined in the List of Abbreviations.

**Table 1-1: Review Articles on VOC sampling in general and passive sampling in particular**

<b>Author(s)</b>	<b>Year</b>	<b>Topic Area</b>	<b>Key findings</b>
Fowler <sup>23</sup>	1982	Fundamentals of Passive Vapor Sampling	Basic theory of diffusive and permeation samplers & factors
Namiesnik et al. <sup>39</sup>	1984	Passive dosimetry for atmospheric pollutants	Exhaustive review of passive sampling devices and theory
Brown <sup>40</sup>	1993	Diffusive samplers for ambient air	Position paper summarizing state-of-the art at the time
Kozdron-Zabiegala et al. <sup>41</sup>	1996	Review of Passive Dosimetry for indoor & outdoor air	Compilation of dosimeters, factors affecting performance & applications
Carmichael <sup>42</sup>	1997	Passive Samplers Role in Global Atmosphere Watch	Recommended for a valuable role in the GAW
Brown <sup>43</sup>	1999	BTX reliability via diffusive samplers	Compilation of uptake rates on PE tube samplers
Brown <sup>44</sup>	1999	Review of Diffusive Samplers	Summary of conditions potentially influencing performance
Brown <sup>45</sup>	2000	Theory and practical considerations for diffusive sampling	Brief overview of passive sampling
Krupa and Legge <sup>46</sup>	2000	Review of passive samplers for ecological monitoring	Recommended co-located active and passive samples at select locations
Górecki and Namiesnik <sup>20</sup>	2002	Passive sampling review	Broad review of passive sampling applications and theory
Namiesnik et al. <sup>21</sup>	2005	Review of passive sampling in environmental analysis	Detailed review of passive sampler theory, devices & applications
Harner et al. <sup>47</sup>	2006	Introductory remarks to the Special Issue	Overview of the reasons for interest in passive sampling for POPs
Bohlin et al. <sup>48</sup>	2007	Review of passive sampling for SVOCs	Overview of different samplers and design considerations
Demeestere et al. <sup>49</sup>	2007	Sample preparation for VOCs in air and water	Review of SPME, MIMS, MESI, DAI, LLE SDME, LPME SBSE and SPDE
Kot-Wasik et al. <sup>50</sup>	2007	Review of passive samplers in environmental studies	Detailed review of passive sampler theory, devices and applications
Ouyang & Pawliszyn <sup>51</sup>	2007	Review of passive samplers and calibration methods	Detailed review of uptake rate calibration for different passive samplers
Partyka et al. <sup>52</sup>	2007	Review of passive sampling for organics in air	Review of the passive sampler designs, sorptive media and analysis methods
Seethapathy et al. <sup>53</sup>	2008	Review of passive sampling in environmental analysis	Comprehensive review of passive sampling from water, air, soil, aerosols
Barro <sup>34</sup>	2009	Review of indoor air sampling and analysis	Detailed review for VOCs carbonyls, PAHs, PCBs
Crump <sup>55</sup>	2009	Application of Diffusive Samplers	Principles, applications and performance summary
Yusa et al. <sup>56</sup>	2009	Review of sampling and analysis for pesticides in air	Passive and active sampling, lab methods and typical concentration ranges
Krol et al. <sup>57</sup>	2010	Review of VOCs air sample collection and preparation	Detailed review of active and passive sample collection and analysis
Woolfenden <sup>58</sup>	2010	Review of sorbent-based air monitoring options (part 1)	Summary-level review of sorbent-based sampling options
Woolfenden <sup>59</sup>	2010	Review of sorbent-based air monitoring options (part 2)	Review of sorbent selection options and factors affecting performance
Zabiegala et al. <sup>60</sup>	2010	Review of passive sampling in environmental monitoring	Detailed review of passive sampler theory, devices & applications
Duan et al. <sup>61</sup>	2011	SPME review	Review of SPME, SBSE, SPDE, MEPS SPNTD for field sampling
Seethapathy et al. <sup>62</sup>	2012	Application of PDMS in analytical chemistry	Comprehensive review of PDMS applications in analytical chemistry
Tuduri et al. <sup>63</sup>	2012	Passive air sampling for SVOCs	Detailed review of sampler designs and theory of uptake kinetics

**Table 1-2:** Summary of research for passive samplers, sorbents and diffusion/permeation barriers for VOCs and SVOCs in air

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Namiesnik et al. <sup>64</sup>	1988	Permeation passive samplers	Silicone polymers appear to be the most suitable membranes	BTX	12 different types of membranes
Bertoni et al. <sup>65</sup>	1990	Double-layer ATD tube sampler	Worked well in chambers and field trials	BTEX	Pyrex tubes with Carbopack C and Carbotrap
Namiesnik et al. <sup>66</sup>	1992	Testing various polyethylenes as membranes	Cryovac EFDX 003 (28 µm) was the most suitable, stable over 9 months	M-xylene, styrene, m-DCB, C-hexanone	Several commercial polyethylene films
Karp <sup>67</sup>	1993	Passive monitoring of USTs	Provides a viable option for leak detection	Hydrocarbons	Glass tube with Carbotrap
Brown et al. <sup>40</sup>	1993	Long-term diffusive sampling	Indications of poor retention for light VOCs after 4 weeks	6 PHCs	PE tube with Tenax
Kelly and Holdren <sup>68</sup>	1995	Summa canisters	Which of 189 VOCs and SVOCs are suitable for use with Summa canisters	VOCs/SVOCs	Summa canisters
Liikala and Evans <sup>69</sup>	1997	Petrex method versus active soil gas survey	Both methods were considered appropriate for screening for gasoline	Gasoline constituents	Petrex method
Otson and Cao <sup>70</sup>	1998	Evaluation of a very low cost passive sampler	Compared well to OVM 3500, but not sensitive enough for outdoor air	25 VOCs	Adsorbent disk in a glass vial versus 3M OVM 3500
Sunesson et al. <sup>71</sup>	1998	Evaluation of 2 sorbents for TD analysis of terpenes	Chromosorb 106 had better retention than Tenax TA	Mono-terpenes	Chromosorb 106 and Tenax TA

**Table 1-2 (cont'd):**

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
ETV Report <sup>72</sup>	1998	EMFLUX Soil Gas Sampling Verification	VOC concentrations were typically 1 to 4 orders of magnitude low	VOCs	EMFLUX
ETV Report <sup>73</sup>	1998	Gore-Sorber Soil Gas Sampling Verification	"Provides only an estimate of the actual concentrations in soil gas"	VOCs	Gore-Sorber
Chandak et al. <sup>74</sup>	1998	Sorption and diffusion of VOCs in PDMS	Detailed theory of VOCs transport through PDMS	VOCs	PDMS
Brancaleoni et al. <sup>75</sup>	1999	Multilayer cartridges with Carbograph 5	Carbograph 5 showed much better retention than Carbograph 1 or 2.	19 VOCs	Carbograph 1, 2 and 5
Krochmal <sup>76</sup>	1999	Workplace monitoring in the 10-1000 mg m <sup>-3</sup> range	Method works well and meets the data quality objectives	Cl-VOCs	Charcoal badge sampler
Uchiyama et al. <sup>77</sup>	1999	PTFE filter and ATD tube sampler for VOCs in air	Sub 0.1 ppbv reporting limits and RSD of 4 to 14 %	15 VOCs	PTFE filter and ATD tube with 6 different sorbents
Olansandan et al. <sup>78</sup>	1999	PTFE tube sampler packed with activated charcoal	50 mL/min uptake rate gave good sensitivity and COV was < ~10%	18 VOCs	PTFE tubing packed with activated charcoal from Shibata Scientific Technology
Qi et al. <sup>79</sup>	2000	Predicting humidity effect on adsorption capacity	Model predicts effect of humidity on sorption of benzene on carbon	Benzene	Activated Carbon
Mabilia et al. <sup>80</sup>	2001	Long-term assessment of benzene via passive sampling	Optimum results were obtained over a 4 to 12 week period	Benzene, toluene, xylenes	Analyst sampler
Zabiegala et al. <sup>81</sup>	2002	Permeation passive sampling vs. ATD charcoal & Tenax	Slight but significant changes in calibration constants over time	BTEX, butyl acetate, styrene, mDCB	Badge sampler (50 µm silicone film with charcoal) vs. ATD tubes (charcoal & Tenax TA)
Yamamoto et al. <sup>82</sup>	2002	Sensitive badge sampler for thermal desorption	Detection limits < 1 ppbv in 2 hours, good correlation to 3M OVM 3500	54 VOCs in the lab, BTEX in the field	Derivative of the 3M badge sampler using Carbopack B

**Table 1-2 (cont'd):**

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Wennrich, Popp & Hafner <sup>83</sup>	2002	Novel sampler for long-term monitoring of SVOCs	Detection limits of $\text{pg}/\text{m}^3$ over durations up to about 1 month	6 SVOCs	LDPE tubing containing PDMS stir bar or silicone tubing
Ochiai et al. <sup>84</sup>	2002	Stabilities of VOCs in passivated canisters	Recovery and degradation varied by compound and humidity	58 VOCs	Summa and fused-filica-lined canisters
Zabiegala et al. <sup>85</sup>	2003	Calibration of silicone membranes vs. analyte properties	Determination of uptake rates vs. MW, carbon number, BP and LTPRI	Aliphatics, aromatics, esters and alcohols	Badge sampler (50 $\mu\text{m}$ silicone film with charcoal)
Laor et al. <sup>86</sup>	2003	Passive sampling of unsaturated zone vapors	50 hour equilibration, good agreement inside and outside well	TCE and naphthalene	Multiple dialysis cells filled with water and closed with membranes
Mayer et al. <sup>87</sup>	2003	Equilibrium passive sampling	Develops the theory for passive sampling of hydrophobic organics	Hydrophobic organic compounds	PDMS-coated glass fibres
DeSantis et al. <sup>88</sup>	2004	Case study around a refinery	Diffusive monitoring is ideally suited to mapping the air quality	$\text{SO}_2$ , $\text{NO}_2$ , $\text{NO}_x$ , $\text{NH}_3$ , BTX	Analyst sampler
Mukerjee et al. <sup>89</sup>	2004	Field comparison in El Paso Texas	Generally good agreement with continuous monitors over 3 to 7 days	$\text{NO}_2$ and BTEX	Ogawa 3300 and 3M OVM 3520
Yamada et al. <sup>90</sup>	2004	Mapping VOCs in outdoor air around Kyoto, Japan	Detection limits of $0.3 \mu\text{g}/\text{m}^3$ and RSD of 3% via $\text{CS}_2$ extraction GC/FID	BTEX	Shibata gas-tube samplers filled with activated carbon
Paschke and Popp <sup>91</sup>	2005	LDPE and silicone vs. PDMS stir bar for SVOCs	Field sampling rates were considerably different than laboratory rates	PAHs	PDMS stir bar and LDPE with silicone polymer sorbent
Jaward et al. <sup>92</sup>	2005	Passive Air Sampling of POPs across Asia	Case study data	PCBs, OCP, PBDEs	PUF disks
Gouin et al. <sup>93</sup>	2005	Assessing POCs in air around the Great Lakes	passive and active samples provided comparable results	pesticide, PCBs and PBDEs	PUF disks vs. high volume sampler



**Table 1-2 (cont'd):**

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Zabiegala et al. <sup>94</sup>	2006	Calibration of silicone membranes vs. LTPRI	Regression equations for uptake vs. LTPRI	aliphatics, aromatics, esters and alcohols	Badge sampler (50 µm silicone film with charcoal)
Larroque et al. <sup>95</sup>	2006	Comparison of two SPME methods for VOCs in air	Competitive sorption was tested using equilibrium vs. non-equilibrium SPME	Acetone, toluene, butyl acetate	Carboxen-coated PDMS SPME fibres
Oury et al. <sup>96</sup>	2006	Comparison of 4 passive samplers over 1 to 14 days	Charcoal samplers performed better for longer sample durations	BTX	GABIE, 3M OVM 3500, ATD tube and Radiello
Thammakhet et al. <sup>97</sup>	2006	Low cost passive sampler verification	Detection limits of less than 1 µg/m <sup>3</sup> and RSD<25%	BTX	Glass bottles with Tenax TA
Hazrati and Harrad <sup>98</sup>	2007	Calibration of PUF disk samplers	Specific environmental conditions affect the sampling rate	PCBs and PBDE	PUF disks
Xiao et al. <sup>99</sup>	2007	Flow-through PUF sampler for SVOCs (wind-driven)	100 m <sup>3</sup> /day sample volume from wind alone (i.e., no power required)	PCB Congeners	PUF
Langlois <sup>100</sup>	2008	GABIE sampler vs. ATD tube sampler comparison	Bias was usually less than 10% with fluctuating concentrations	Toluene, PCE, isoflurane	GABIE and ATD tube
terLaak et al. <sup>101</sup>	2008	PDMS uptake versus surface area and volume	Good linearity and comparison to predictive model with boundary layer	PCBs and PDBEs	PDMS fibres
Zabiegala et al. <sup>102</sup>	2009	VOC outdoor air survey in Gdansk via passive samplers	No significant differences between passive and active samplers	About 20 VOCs	Badge sampler (75 µm silicone film with charcoal) vs. active ATD tubes with Tenax TA
Hodny et al. <sup>103</sup>	2009	Gore-Module concentration estimates	Derived a "soil effectiveness factor" to adjust uptake rate	Cl-VOCs	Gore-Module
Mukerjee et al. <sup>104</sup>	2009	Field comparison in Detroit, Michigan	Generally good agreement with continuous monitors over 7 days	NO <sub>2</sub> and BTEX	Ogawa 3300 and ATD tubes with Carbopack X
Esteve-Turrillas et al. <sup>105</sup>	2009	LDPE lay-flat tube filled with triolein and variants	Activated carbon and Florisil sorbents worked best for BTEX	BTEX	VERAM (versatile, easy and rapid atmospheric monitor)

**Table 1-2 (cont'd):**

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Zabiegala et al. <sup>106</sup>	2010	Permeation sampler vs. Orsa 5 and Radiello Case Study	Statistical analysis showed only minor differences between the methods	About 48 VOCs	Badge sampler (50 µm silicone film with charcoal) vs. Orsa 5 and Radiello
Ly-Verdu et al. <sup>107</sup>	2010	SPME for VOCs in air	Results were comparable to the Radiello passive sampler	26 VOCs	LDPE filled with Triolein
He and Balasubramanian <sup>108</sup>	2010	Comparison of passive vs. active for SVOCs in air	No significant difference (p>0.05) for 68 days for most PAHs and OCPs	PAHs and OCPs	PUF disks vs. high volume sampler
Zabiegala et al. <sup>109</sup>	2011	Permeation sampler vs. Orsa 5 and Radiello Case Study	Additional statistical tests show some differences, but strong correlations	BTEX	Badge sampler (50 µm silicone film with charcoal) vs. Orsa 5 and Radiello
Mason et al. <sup>110</sup>	2011	Evaluating Radiello and Ogawa samplers	Results had comparable accuracy and precision to active sampling	NOx, SO <sub>2</sub> , VOCs, aldehydes, H <sub>2</sub> S	Ogawa for NOx and SO <sub>2</sub> , Radiello for VOCs, aldehydes and H <sub>2</sub> S
ESTCP <sup>111</sup>	2011	SPME Dem/Val Report	Utility of PDMS fibres for monitoring SVOCs in water & sediment	PAHs and PCBs	PDMS-coated fibre
Kwon, Kim and Kim <sup>112</sup>	2012	In-situ solvent extraction sampler	PDMS permeation controlled the sampling rate from water	Caffeine and PAHs	PDMS tubing with acetonitrile as the sorbent
Zhang and Wania <sup>113</sup>	2012	Modeling SVOC uptake on PUF and XAD (both porous)	Mathematical model of uptake, needs more data on kinetics before use	SVOCs	PUF and XAD
Yang et al. <sup>114</sup>	2013	Carbonaceous resin capsule for soil VOCs	Uptake rates were limited by the rate of vapor diffusion through soil	BTEX	Carbonaceous resin capsules
Shetty et al. <sup>115</sup>	2014	In Planta passive sampling for subsurface VOCs	PDMS performed best of all the materials	PCE and TCE	PDMS, LDPE, LLDPE, POM and PVC

### 1.3 Varieties of Passive Samplers

Hundreds of different designs of passive samplers have been developed, some of which have been commercialized and validated for specific applications. Initially, the compounds of interest were NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, and aromatic hydrocarbons (benzene, toluene, xylenes) in air<sup>21</sup>. Over time, the application of passive samplers expanded considerably to include:

- Different media: water, sediment, soil, compost;
- Different families of chemicals: VOCs, SVOCs, PAHs, PCBs, OCPs, mercury;
- Different sorbents: charcoal, porous polymers, carbon molecular sieves, graphitized carbon black, liquid solvents, protein, polyurethane foam and derivitizing agents;
- Different ranges of concentration: workplace > residential > outdoor air; and
- Biomonitoring, using actual plants or animals as the sampler, or triolein-filled membranes designed to mimic the uptake of chemicals by organisms.

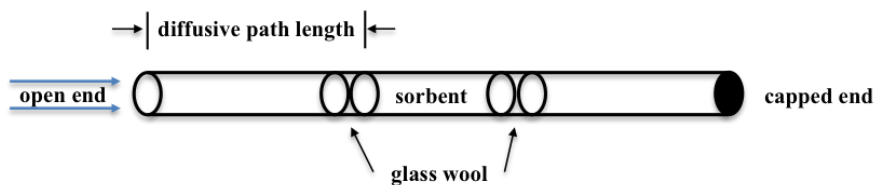
The range of applications is too large to cover in detail, but a summary is provided in Table 1-2.

#### 1.3.1 Candidate Passive Samplers Used in this Study

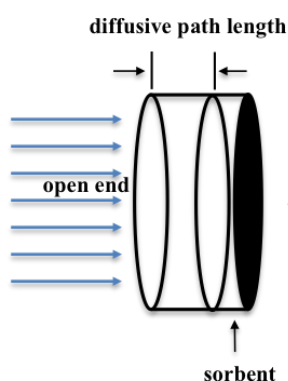
For this thesis, the focus is sampling and analysis of indoor air and soil vapor for the purpose of assessing human health risks for vapor intrusion. For this application, the general types of passive samplers are narrowed considerably to four main types, shown in Figure 1-5. The axial sampler is typically constructed of a standard automated thermal desorption (ATD) tube, of the kind sold by Markes International, Perkin Elmer or other laboratory supply companies. These tubes are also used for active sampling with pumps; however when used in passive mode, the sampler is left open at one end and closed at the other to allow uptake via diffusion through the air-space between the open end and the sorbent. Badge-style samplers generally have a larger cross-sectional area and a shorter diffusive path-length, which increases the uptake rate and provides better sensitivity with shorter sample durations. The larger opening increases the risk of bias from turbulence and advective transport, so a wind-screen is typically added, consisting of porous inert material (e.g., 3M OVM 3500) or hard plastic with small diameter holes (e.g., SKC Ultra). The radial design has an outer cylinder of porous wind-screen and an inner cylinder of sorptive media surrounded by a stainless steel mesh that allows for easy transfer into an ATD tube for analysis by thermal desorption GC/MS. The membrane sampler consists of a thin (25 to 150 μm) membrane of poly(dimethyl)siloxane (PDMS) covering the opening of a small (0.8 to 1.8 mL)

glass vial containing sorbent, which is inverted to maintain contact between the sorbent and the inner surface of the membrane.

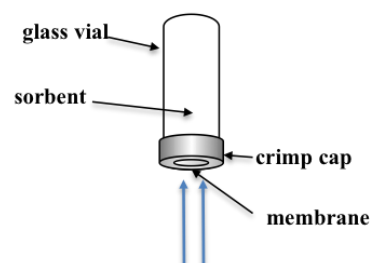
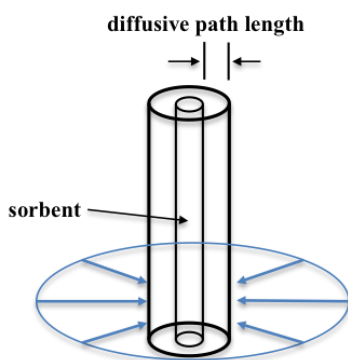
### Axial or Tube Sampler



### Badge Sampler



### Radial Sampler Membrane Sampler



**Figure 1-5:** Axial, badge, radial and membrane sampler types (blue arrows indicate vapor entry).

Prior to this research, each of the five candidate passive sampler technologies had been independently tested by their developers and end-users and proven to be capable of accurately measuring vapor concentrations in indoor and outdoor air for some chemicals under certain conditions; however, the commercially-available passive samplers had not been rigorously compared with each other. The following samplers and configurations were used in this study:

**SKC Ultra™ and Ultra II™**<sup>116-120</sup> are badge-type samplers with options for thermal desorption or solvent extraction, which operate by diffusion through either a plastic cap with ~300 holes, or a low-uptake rate cap with 12 holes (Figure 1-6). These devices have been used for industrial hygiene applications for many years<sup>24,121</sup>, and can provide quantitative VOC analysis of indoor air samples at the ppb<sub>v</sub> level.<sup>122</sup> In the Ultra II sampler, the adsorbent is shipped separately in a sealed vial to retain purity; however, this requires manual transfer of the sorbent from the vial to the sampler and back in the field as well as transfer from the vial into an ATD tube in the laboratory prior to analysis, all of which adds potential for bias and variability. The sampler body establishes a 1-dimensional diffusion profile through a known length and cross-section. Depending on the compounds of interest, this device is

commercially available with various types of sorbent media: Carbopack X, Chromosorb 106, Carbograph 5 and Anasorb GCB1. Columbia Analytical Services (CAS) in Simi Valley, CA is specifically listed by SKC as a specialty provider of the analyses of these devices, and was used for these analyses.



**Figure 1-6:** SKC Ultra sampler with regular (white) and low-uptake cap (green) (image at left courtesy of SKC)

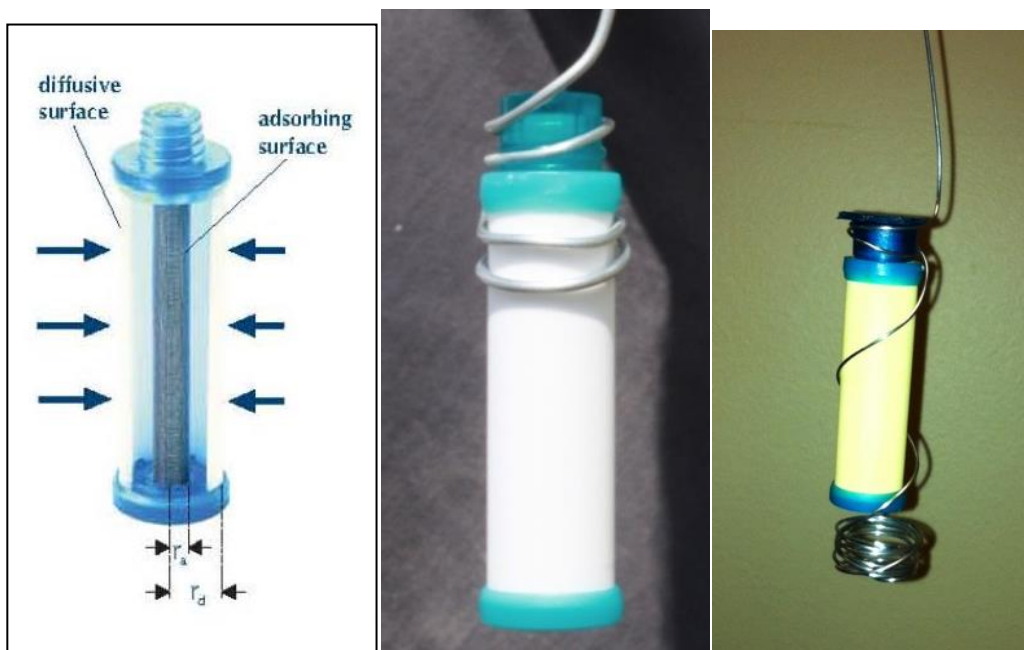
A summary of select literature related to the SKC Ultra sampler is provided in Table 1-3.

**Table 1-3:** Select literature demonstrating, validating or applying the SKC Ultra

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Bergemalm-Rynell et al. <sup>123</sup>	2008	SKC with Anasorb 747 for halogenated anesthetics	validated for ~1ppm and 8 hours	anesthetic gases	SKC 575-002
Strandberg et al. <sup>124</sup>	2005	2 samplers for 1,3-butadiene and benzene	Performance was good over 24 hours, declined somewhat in 7 day samples	Benzene and 1,3-butadiene	SKC Ultra and Radiello with Carbopack X and Carbograph 5
Hendricks <sup>125</sup>	2002	The Marines Project - Personal exposure survey	SKC Ultra generally met OSHA requirements, not Gore-Sorber or ATD	Benzene, ethylbenzene, tetrachloroethane, 135-trimethylbenzene, undecane, etc.	SKC Ultra and Gore-Sorber with some ATD/Tenax

**Radiello®** This sampler has a 2-dimensional (radial) geometry, which has a large exposure area and increases the uptake rate for greater sensitivity (lower reporting limits for a given sample duration) compared to most of the other samplers.<sup>126,127</sup> The sampler is made of two concentric cylinders; the

inner cylinder is a cartridge that contains an adsorbent medium surrounded by a stainless steel mesh. The outer cylinder is made of microporous sintered polyethylene, through which the vapors diffuse. Two different outer cylinders (white and yellow, Figure 1-7) are available, which are manufactured with different wall-thicknesses for adjusting the uptake rates. Calibration constants for the sampler have been determined experimentally and are reported in the user manual for many analytes, or they can be estimated from the uptake rates of similar compounds by comparison of the diffusion or permeation coefficients of the analytes. The inner cylinder can be filled with different sorbents suitable for either solvent extraction or thermal desorption. The cylinders and housings are all the same sizes, so they are interchangeable, and all four combinations (low and high uptake rate, solvent and thermal desorption) are possible. The high uptake rates increase the risk of low bias attributable to starvation in low air velocity settings (especially soil vapor sampling). Radiello is patented by Fondazione Salvatore Maugeri-IRCCS, Centro di Ricerche Ambientali, in Padova, Italy (FSM). The Radiello sampler was used successfully in the Monitoring of Atmospheric Concentration of Benzene in European Towns and Homes (MACBETH) Study<sup>128</sup>, which consisted of sampling and analysis of 3,600 samples, each representative of 5-day exposures, collected on six occasions from about 100 locations in 6 European cities. A summary of select literature related to the Radiello sampler is provided in Table 1-4.

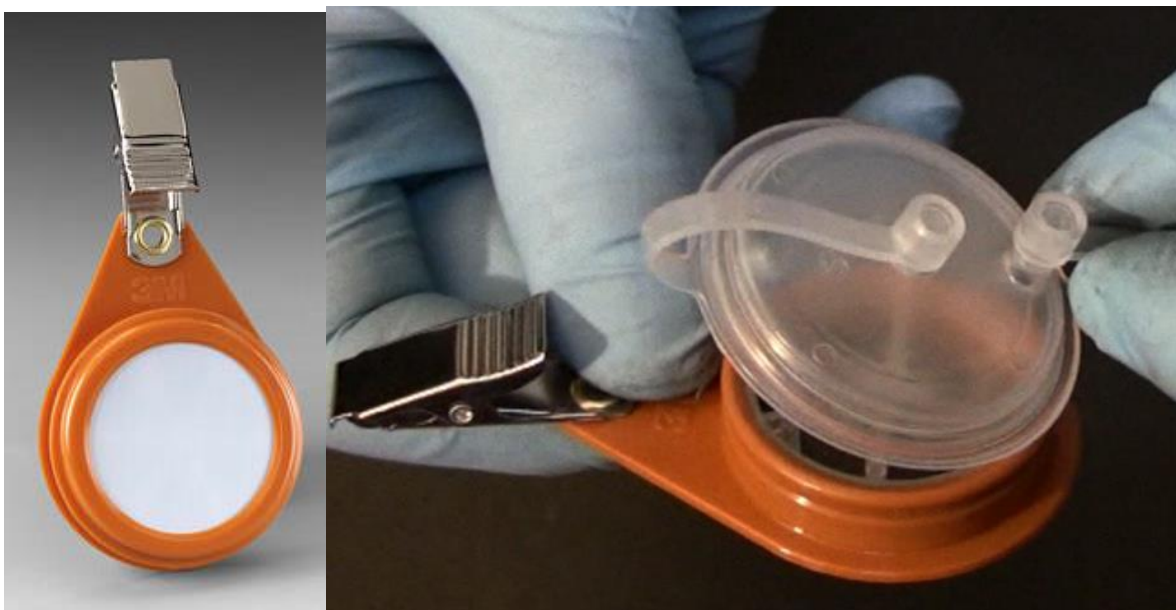


**Figure 1-7:** Radiello sampler with regular (white) and low-uptake (yellow) bodies (image at left courtesy of FSM)

**Table 1-4:** Select literature demonstrating, validating, or applying the Radiello sampler

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Cocheo et al. <sup>126</sup>	1996	Announcing the Radiello Sampler	Provides uptake rates for 32 VOCs for thermal and chemical sorbents	32 VOCs	Radiello with activated charcoal
Bates et al. <sup>129</sup>	1997	High uptake rates and thermal desorption	Saturation and competition required a reduced uptake rate	Benzene, toluene, xylenes	Radiello
Gonzalez-Flesca et al. <sup>128</sup>	2000	MACBETH Programme benzene monitoring	600 samples showed 75% of volunteers with >5 µg m <sup>-3</sup> exposures	Benzene	Radiello/Perkin Elmer with Carbotrap B
Pennequin-Cardinal et al. <sup>130</sup>	2005	Radiello / BTEX at different concentrations & durations	Thermally desorbable sorbent showed decreased retention after 14 days	Benzene, toluene, ethylbenzene, xylenes	Radiello Carbograph 4
Pennequin-Cardinal et al. <sup>131</sup>	2005	Modeling Radiello uptake rates vs. environment factors	Uptake rates for different conc'n, temp., duration, humidity & velocity	Benzene, toluene, ethylbenzene, xylenes	Radiello Carbograph 4
Bruno et al. <sup>132</sup>	2005	Radiello for BTEX using thermal desorption	Good results in 1 to 7 day sampling periods	Benzene, toluene, ethylbenzene, xylenes	Radiello with Carbograph 4
Plaisance et al. <sup>133</sup>	2008	Uncertainty in benzene via Radiello	Temperature and concentration were the main factors for uncertainty	Benzene	Radiello Carbograph 4
Bruno et al. <sup>134</sup>	2008	Radiello for VOCs in non-residential air	Reliable sampling over 24 hour intervals	13 VOCs	Radiello with Carbograph 4
Cocheo et al. <sup>127</sup>	2009	Radiello via chemical and thermal desorption for BTEX	Regression models for BTEX uptake rates for both sorbents	Benzene, toluene, ethylbenzene, xylenes	Radiello with activated charcoal and Carbograph 4
Zabiegala et al. <sup>135</sup>	2010	Outdoor air survey of Gdansk and surrounding areas	Mapped spatial distribution and sources (traffic, industrial emissions)	Benzene, toluene, ethylbenzene, xylenes	Radiello with Carbograph 4
Krol et al. <sup>136</sup>	2010	Review of VOCs air sample collection and preparation	Detailed review of active and passive sample collection and analysis	VOCs	Radiello, ATD tubes, 3M OVM 3500, GABIE, Orsa 5
Gallego et al. <sup>137</sup>	2011	Radiello for VOCs via TD-GC/MS	Assessed effects of concentrations and sample duration	Several VOCs	Radiello Carbograph 4

**3M OVM 3500™** - This device is a badge style sampler originally developed for industrial hygiene monitoring.<sup>138,139</sup> The plastic body snaps together, and holds a white microporous polypropylene sheet as a windscreen at the outer boundary of the diffusive barrier at a fixed distance from a thin film coated with activated carbon (Figure 1-8). Diffusion occurs across the porous barrier and through air to the activated carbon. Solvent extraction of the carbon after a period of exposure is used as the sample preparation, and an aliquot of the extract is injected to a GC/MS to quantify the adsorbed mass of each analyte. The large surface area provides a high uptake rate, which yields good sensitivity with practical sample durations. Conversely, this may exacerbate the starvation effect for passive sampling in low face velocity settings, such as passive soil gas sampling. This sampler is also the largest of the candidate samplers, which is a disadvantage for fitting in passive soil gas probes and flow-through cells. No low-uptake option or thermal desorption option was available at the time of this research. A summary of select literature related to the 3M OVM 3500-series of samplers is provided in Table 1-5.



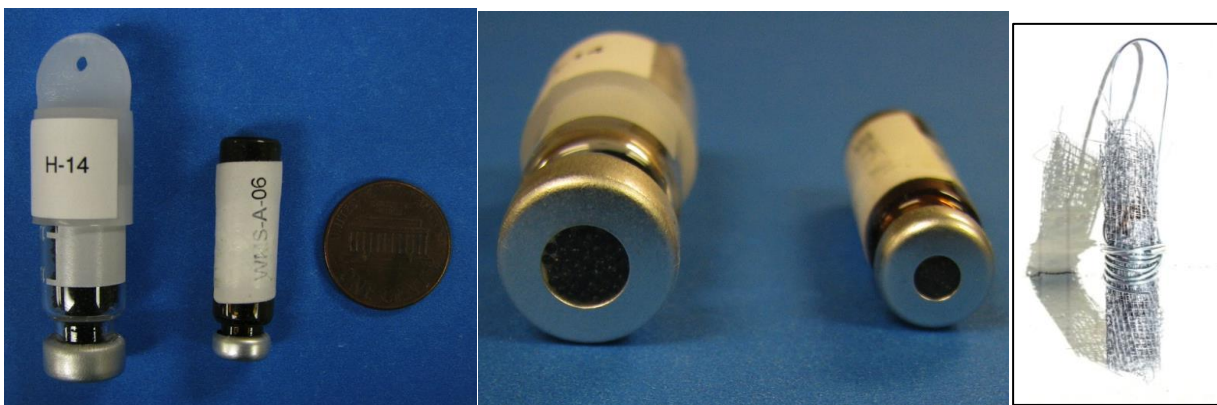
**Figure 1-8:** 3M OVM 3500 sampler and solid plastic cap used to replace the porous plastic sheet after sampling (image at left courtesy of 3M)



**Table 1-5:** Select literature demonstrating, validating or applying the 3M OVM 3500

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Kerfoot and Mayer <sup>140</sup>	1986	Use of Industrial Hygiene sampler for soil gas surveys	Good correlation to active samples, but significant starvation effect	VOCs	3M OVM 3510
Purdham et al. <sup>141</sup>	1994	Charcoal tube versus 3M OVM 3520 badge	Excellent agreement in lab testing, higher variability in field testing	Gasoline vapor	3M OVM 3520
Begerow et al. <sup>142</sup>	1995	Low concentration VOC sampling	Sub $\mu\text{g m}^{-3}$ reporting limits with 4-week samples	Benzene, toluene, ethylbenzene, xylenes, Cl-VOCs	3M OVM 3500
Hori and Tanaka <sup>143</sup>	1996	Effect of Face Velocity on Passive Samplers	Relative concentration by passive sampling increases with face velocity	Toluene	3M OVM 3500 and ProTek Gasbadge
Begerow et al. <sup>144</sup>	1996	Analytical method with GC ECD/FID	Works well for Cl-VOC and PHC mixtures	Benzene, toluene, ethylbenzene, xylenes, Cl-VOCs	3M OVM 3500
Elke et al. <sup>145</sup>	1998	BTEX in indoor air via SPME/HR-GC/FID	Charcoal sorption, $\text{CS}_2$ extraction, reduction by xanthation	VOCs	3M OVM 3500 and Carboxen-PDMS SPME fiber
Chung et al. <sup>146</sup>	1999	Chamber tests of temp. and humidity on 3M OVM(2)	Documented artifacts of concentration, humidity and temperature	9 VOCs	3M OVM 3520
Sexton et al. <sup>147</sup>	2004	Monitoring indoor, outdoor and personal exposures	Indoor air concentrations correlated very strongly to personal monitoring	14 VOCs	3M OVM 3500
Stock et al. <sup>148</sup>	2008	Diffusive samplers for mapping VOCs in Ambient air	OVMs worked well for 72 hour samples, with a slight low bias	19 VOCs	3M OVM 3500
Matysik et al. <sup>149</sup>	2009	Microbial VOCs via charcoal sorbents	Passive sampling of specific VOCs was found to help identify mould	Microbially produced VOCs	3M OVM 3500
Massolo et al. <sup>150</sup>	2010	Mapping VOCs in indoor and outdoor air	Alkanes and aromatics dominated, traffic was a major source	29 VOCs	3M OVM 3500
Herbarth and Matysik <sup>151</sup>	2013	Long-term monitoring study	General trend of falling concentrations of "classical solvents" over time	26 VOCs	3M OVM 3500

**Waterloo Membrane Sampler™**<sup>152,153</sup> The WMS sampler is unique because VOC uptake occurs through a membrane of polydimethylsiloxane (PDMS). VOCs dissolve into the membrane and permeate across it. The membrane excludes water vapor (which can compete for adsorptive sites on some sorbents and interfere with laboratory instruments) and prevents advective uptake by turbulence (so sampling can occur in high air velocity environments without a high or positive bias). The uptake rate is proportional to the linear temperature programmed retention index (LTPRI) of an analyte on a pure PDMS-coated capillary column, so the uptake rates can be estimated with reasonable accuracy for compounds similar to those for which they have been determined in controlled chamber experiments.<sup>94,152</sup> The WMS sampler is manufactured by SiREM Laboratory of Guelph, Ontario and is available from SiREM and through Eurofins Air Toxics of Folsom California. The WMS sampler is available in either a 1.8 mL vial (WMS™) with an exposed membrane surface of about 0.24 cm<sup>2</sup> or a 0.8 mL vial with a smaller membrane area (0.079 cm<sup>2</sup>) and proportionately lower-uptake rates (WMS-LU™), both shown in Figure 1-9. The WMS sampler was used with either solvent extraction (Anasorb 747) or thermal desorption (Carbopack B).



**Figure 1-9:** Waterloo Membrane Sampler (WMS), close-up of membrane and protective mesh

**Passive ATD tube samplers** (from various manufacturers). This sampler consists of a standard Automated Thermal Desorption (ATD) tube (4 mm I.D., 89 mm length) that can be used with a wide variety of adsorbents, depending on the compounds of concern and the target reporting limits and sample durations.<sup>154-158,37,40,55</sup> The ATD tube is shipped with compression-fit end caps and Teflon ferrules on both ends to prevent uptake during shipping. The ATD tube facilitates sample preparation because it can be placed directly on an auto-sampler of a thermal desorption unit for GC/MS analysis by EPA Method TO-17 or equivalent. Therefore, the ATD tube sampler is used almost exclusively with thermally desorbable sorbents (e.g., Tenax TA and Carbopack B). This sampler has either a stainless

steel dust screen (regular uptake) or a cap with a smaller diameter opening (low uptake), as shown in Figure 1-10. A summary of select literature related to the ATD tube sampler is provided in Table 1-6.



**Figure 1-10:** ATD tube sampler, regular and low-uptake rate caps, and protective mesh

**Table 1-6:** Select literature demonstrating, validating or applying the ATD tube sampler

Author(s)	Year	Topic Area	Key findings	Compounds	Sampler(s)
Hafkenscheid and Mowrer <sup>159</sup>	1996	Interlaboratory Comparison of Diffusive ATD tubes	RSD of 40 to 50% among 12 laboratories for select hydrocarbons	Hydrocarbons	ATD with various sorbents
Kilic and Ballantine <sup>160</sup>	1998	Comparison of sorbents for long-term passive sampling	Poor retention of low-boiling point VOCs over durations up to 14 days	Acetone, DCM, Toluene and alkanes	ATD tubes with Tenax TA, Chromosorb 106 and Carbotrap
Roche et al. <sup>161</sup>	1999	Performance of ATD tube for very low concentrations	Uptake rates of most volatile compounds decrease with increasing duration and concentration	Aromatic and linear alkanes	ATD tube with Tenax TA
Bates et al. <sup>162</sup>	2000	Ozone-Induced Artefacts	Ozone reactions cause a negative bias	BTX, styrene, aldehydes	ATD/Carbotrap
Tolnai, Gelencser & Hlavay <sup>163</sup>	2001	Theory of non-constant uptake rates for ATD tubes	Mathematical model based on plate theory of uptake rate vs. time	VOCs	ATD tubes and various sorbents
Batterman et al. <sup>164</sup>	2002	Diffusive uptake rate in ATD tubes	Add a needle to prevent diffusive bias at low active rates	VOCs	ATD tubes
ISO 16017-2 <sup>165</sup>	2003	Uptake rates for ATD tubes	Detailed lists of uptake rates for various sorbents	Many VOCs	ATD tube with various sorbents

McClenny et al. <sup>166</sup>	2005	Lab studies of Carbopack X passive sampling	27 VOCs performed well enough to have uptake rates characterized	42 VOCs	ATD tubes with Carbopack X
Jia et al. <sup>18</sup>	2007	Continuous, intermittent and passive air sampling	All three methods are similar (20%) over 3 to 4 days (0.1 to 230 µg/m <sup>3</sup> )	VOCs	ATD tubes with Tenax GR
Demeestere et al. <sup>167</sup>	2008	QA/QC in TD/GC/MS analysis of VOCs	Precision and accuracy factors and improvements	69 VOCs	ATD tubes with Tenax TA
Johnson et al. <sup>168</sup>	2009	Participant-based indoor air sampling	88% of households completed their own passive sampling	VOC, PAHs and NO <sub>2</sub>	ATD tubes, NO <sub>2</sub> badges and PAH sampler
Woolfenden <sup>58</sup>	2010	Review of sorbent-based air monitoring options (part 1)	Summary-level review of sorbent-based sampling options	Wide range	ATD tube and Radiello passive samplers, plus several active samplers
Martin et al. <sup>169</sup>	2010	Verification of diffusive and pumped sampling	14-day uptake rates were measured under a range of humidities	Alkanes and aromatic hydrocarbons	ATD tubes with Carbopack X, Z, B, or Tenax TA
Xian et al. <sup>170</sup>	2011	Use of reference chemical and co-located active samples	Calibration method for passive samplers in field applications	VOCs	ATD tubes with Carbopack B
Walgraeve et al. <sup>171</sup>	2011	Refinement of uptake rates for field sampling	Sorptive efficiency can reduce uptake rates by a factor of up to about 4	25 VOCs	ATD tubes with Tenax TA
Walgraeve et al. <sup>172</sup>	2011	Uptake rates in controlled atmospheres for ATD tubes	Effects of humidity (5 to 80%), time (1,3,7 d) and conc'n (8 to 85 ppbv)	Limonene, toluene, ethyl acetate and hexane	ATD tubes with Tenax TA
Civan et al. <sup>173</sup>	2012	Calculating uptake rates using weather conditions	Regression analysis was used to model uptake rates for 25 VOCs	25 VOCs	ATD tubes with Chromosorb 106
Jia et al. <sup>174</sup>	2012	Variability in Indoor and Outdoor VOCs	Seasonal effects were 50% of variance in indoor air VOCs	VOCs	ATD Tubes with Tenax GR
Johnson and Gibson <sup>175</sup>	2013	Spatiotemporal variability in PCE in indoor air	Statistical analysis of the factors contributing to variability	VOCs	ATD tubes with Chromosorb 106

### 1.3.2 Customizing Passive Samplers

Most of the passive samplers used in this research can be customized for a particular application. For example, the uptake rate of a passive sampler can be increased or decreased by increasing or decreasing the cross sectional area of the face of the sampler (or decreasing or increasing the thickness of the membrane, if present). High uptake rates allow lower concentrations to be quantified for a given sample duration, which can be an advantage for compounds with very low risk-based screening levels or assessment of acute (short-term) exposure risks. Lower uptake rates reduce the risk of the “starvation effect”, and reduce the risk of poor retention for long-duration samples or high vapor concentration settings. Advection from wind and ventilation during indoor and outdoor air sampling is often sufficient to minimize the starvation effect for all but the highest uptake rate samplers. For soil gas sampling, advection is likely to be minimal and the rate of contaminant vapor replenishment in the gas-filled void space surrounding the sampler is likely to be limited to diffusive transport only, so a much lower uptake rate is required to minimize the starvation effect (this is the focus of the mathematical models presented in Chapter 5).

Passive samplers can also be used with more than one type of sorbent. There are two general classes of sorbents, suited either to thermal desorption or solvent extraction as the sample preparation method. Analysis by thermal desorption is typically performed using a method like EPA Method TO-17 where the ATD tube is heated and flushed with nitrogen or helium into the GC. This provides very good sensitivity because a high proportion of the mass adsorbed by the sampler is injected into the GC (there is typically a split at the interface between the TD unit and the column, so some of the sample might not be introduced to the column). Analysis by solvent extraction is typically performed using carbon disulfide (CS<sub>2</sub>) or other strong solvent to extract the target VOCs from the adsorbent; however, only a small aliquot of the total solvent volume is subsequently injected into the GC (e.g., 1 μL injected of 1 mL used for extraction). Consequently, the sampler may need to be exposed for a longer time or have a higher uptake rate to achieve comparable reporting limits. Thermal desorption is used with several types of sorbents, including:

- Porous polymers: e.g., Tenax TA, Chromosorb series, PoraPak Q, N, etc.;
- Graphitized carbon black (GCB): e.g., Carbopack B, X, Carbograph 1 TD, 5 TD, etc.;
- Carbonized molecular sieves (CMS): e.g., UniCarb or Carboxen 1003.

Tenax is very hydrophobic, but does not retain polar analytes or compounds more volatile than n-hexane very well.<sup>59</sup> The Chromosorb and PoraPak series of sorbents have temperature limitations that limit the recovery of less volatile analytes.<sup>59</sup> The GCB and CMS sorbents are compatible with higher desorption

and conditioning temperatures and have low artifact levels while being more hydrophobic than activated carbon or charcoal.<sup>59</sup>

The selection of the preferred sorbent is an important aspect of the passive sampling process. If a weak sorbent is used, the retention of lighter VOCs may be low, especially over longer periods or in areas of high concentrations where the total mass of all VOCs adsorbed becomes large enough that competition for adsorptive sites becomes an issue.

Solvent extraction is usually used with stronger adsorbents (Anasorb 747, activated carbon or charcoal). Stronger sorbents are less likely to show poor retention, but may show low recovery (i.e., less than 100% desorption) for very strongly adsorbed compounds. Several of the passive samplers can be used with different adsorbents and analyzed using either solvent extraction or thermal desorption to provide flexibility for a range of target compounds, reporting limits and expected concentrations (which can range over many orders of magnitude). In pumped ATD tube samplers, multi-bed sorbents are common (weaker to stronger sorbents are used in the direction of flow during sampling) to help retain weakly sorbed compounds without risking poor recovery of strongly-sorbed compounds; however, multi-bed designs are not typically used in passive sampling, and therefore were not attempted in this program.

Different chemicals have different adsorption properties, and a variety of adsorbent media are available, so there are a wide range of options for selection of the appropriate adsorbent media for a particular compound or compounds of interest. The goal is to provide a high degree of retention during sampling and good recovery during analysis. It may not be practical to select a single sorbent suitable for the range of compounds of potential interest for vapor intrusion investigations, in which case two or more samplers are an option. Several publications are available that provide information regarding the effectiveness of various sorbents with various VOCs.<sup>176-178,19</sup> For active adsorptive sampling (where air is pumped through a sorbent tube), there are recommended maximum sampling volumes (RMSVs) for combinations of compounds and adsorbents beyond which low (or negative) bias in the reported concentrations is commonly seen, attributable to poor retention by the sampler. For passive sampling, there is no specified volume of gas drawn through the adsorbent, but the product of the uptake rate and sample duration has units of volume and is equivalent to the volume of gas that would need to be drawn through a pumped sorptive sampler to yield a given mass of analyte for a certain concentration setting. Therefore, the product of the uptake rate and sample duration is referred to here as an “equivalent sample volume” and compared to the RMSV in cases where poor retention appears to be a concern.

The reportable concentration for a passive sample is inversely proportional to the sampling duration, which must be long enough to achieve a reporting limit equal to the risk-based target concentrations or lower for each of the target analytes. However, long deployment periods, high concentrations and

especially the combination of the two increase the risk of poor retention, especially if weaker sorbents are used.<sup>129</sup> The risk of poor retention can be managed with some advance information about expected concentrations using a portable instrument such as a photoionization detector (PID) to identify locations where the sample duration may need to be reduced to minimize the risk of poor retention (the linear range of analysis for most methods is at least two orders of magnitude, so there is a fair margin for uncertainty in the expected concentrations).

### **1.3.3 Advantages and Limitations of Passive Sampling**

#### **1.3.3.1 Advantages**

Passive diffusive samplers offer at least four potentially significant advantages to the current industry standard approach of whole-air sampling with Summa canisters and TO-15 analysis, detailed below.

**Lower Cost:** Summa canisters can cost up to about \$1,000 to purchase, and costs are typically passed along to the end user in the form of a canister rental charge. Flow controllers are required for time-averaged sample collection, and a rental charge is also levied to cover their purchase, cleaning and certification. Summa canisters are large and heavy, and courier charges are based on size and weight, so Summa canisters are much more expensive to ship back and forth to a field site than passive samplers. Summa canisters are re-useable, but they must go through a time-consuming cleaning and certification process, with record keeping of each canister's history by serial number to maintain high levels of QA/QC needed for vapor intrusion investigations, all of which is costly.

Most of the passive samplers are disposable items and are intended for one time use, with the exception of ATD tubes and Radiello housings that are cleaned and reused. They are small in size and shipping charges are minimal in comparison to costs for shipping Summa canisters. Less operator training is required and the labor costs for sampler deployment and retrieval are also lower.

**Simpler Sampling Protocols:** Passive samplers are much easier to deploy than Summa canisters. Indoor air sampling with Summa canisters requires numerous steps: 1) removal of the dust-cap, 2) attachment of the vacuum gauge, 3) opening and closing of the valve, 4) recording vacuum reading to assess whether the canister leaked during shipment from the laboratory, 5) removal of the vacuum gauge, 6) attachment of the flow controller, 7) opening of the valve, 8) recording time, 9) returning at a later time, 10) closing the valve, 11) removing the flow controller, 12) attaching the vacuum gauge, 13) opening and closing of the valve, 14) recording final vacuum to document whether the canister leaks on the return shipment to the laboratory, and 15) replacing the dust cap. Some laboratories provide vacuum gauges integrated with the flow controllers, which eliminates steps 5, 6, 7, 12 and 13. Soil gas sampling adds additional steps for purging prior to sample collection, and this may be complicated in low

permeability soils, where flow rates may not be sufficient for continuous purging and sample collection.<sup>16</sup> Where tracers are used to assess potential leaks, the level of effort in the field sampling activity increases dramatically. By contrast, passive samplers are considerably simpler, typically shipped clean and sealed in air-tight containers which are opened, placed in appropriate locations, left for a specified period, resealed, labeled and returned to the laboratory. For passive soil vapor sampling, a hole must be drilled, and a seal must be placed for the sample duration, or a probe must be installed; however, similar actions are required for active soil vapor sampling. For soil gas sampling, it may not be necessary to purge when using passive samplers, which simplifies the sampling process compared to active sampling. The Radiello and SKC Ultra II samplers require an additional step of placing the sorbent into the housing at the start and removing it at the end of the sampling period. For indoor air monitoring, the passive VOC samplers are very similar to devices currently used for monitoring radon, which are often deployed, retrieved and shipped by homeowners (i.e., not by technical personnel), so much less training is required. Simplicity may help minimize bias and variability attributable to inter-operator errors.

**Longer-Term Samples:** Passive samplers can be used to collect samples over much longer periods than conventional Summa canister or active ATD tube samplers, which results in measured concentrations that represent time-weighted average conditions over the sample collection duration, and minimizes short-term temporal variability associated with changes in weather conditions, building ventilation and occupants' activities. EPA recommends sampling duration of 72-hours or longer for radon in indoor air,<sup>27</sup> and refers to 30-day samples as "short-term" ones. Recent research with high frequency sampling of VOCs in residential properties for vapor intrusion research has shown up to 1,000-fold range in indoor air concentrations.<sup>179,29</sup> In these conditions, the average long-term exposure of occupants to chemicals is dominated by infrequent and relatively short-duration intervals. Conventional samples of 24-hour duration (or shorter) have a high probability missing the infrequent high-concentration events, and therefore are likely to show negative bias compared to the true long-term average indoor air VOC concentrations attributable to vapor intrusion. For vapor intrusion investigations, target concentrations based on 25 to 30 year average exposures are typically the basis for decision-making. Sampling and analytical methods that are affected by short-term temporal variability are undesirable because they either increase uncertainty, or require additional sampling and analysis to characterize the expected degree of variability and support statistical calculations of long-term average concentrations. Summa canisters and active ATD tubes are not well-suited or easily modified for sampling over periods longer than 24 hours.



**Less Obtrusive:** Passive diffusive samplers are small enough to be held in the palm of a hand, and look fairly simple and unobtrusive (Figure 1-11). Summa canisters are much larger (indoor and outdoor air samples typically require a 6 L canister, which is about the size of a bowling ball), and are therefore much more obtrusive. Individuals unfamiliar with Summa canisters have sometimes mistaken them for compressed gas cylinders or explosive devices, which can impose challenges in monitoring within highly-occupied structures or communities or if Summa canisters are to be shipped across international borders.



**Figure 1-11:** Photo of two 6L Summa canisters and a 3M OVM 3500 sampler (upper right)

### 1.3.3.2 Limitations

Passive diffusive samplers have the following potential limitations:

**Starvation Effect:** In indoor and outdoor air sampling, the face velocity is usually high enough to minimize starvation, except perhaps for very high uptake rate samplers. In soil gas sampling, particularly in low-permeability materials, the flow rate of soil gas is very low or nil, which increases the risk of low bias via starvation. Mathematical modeling and sampling using samplers with different uptake rates were included in this study to assess the magnitude of the starvation effect.

**Competition and Poor Retention:** If passive samplers are exposed to high analyte concentrations for extended time, the sorptive sites on the adsorbent media become progressively more fully-occupied with VOCs and the sorbent performance may diminish (referred to as poor retention). If multiple VOCs are present, then more strongly sorbed compounds may displace less strongly sorbed compounds or more abundant compounds could displace less abundant compounds, which could impose low bias on the concentration measurements for the displaced compounds (referred to as competition). If long

deployment periods are used with weak sorbents, there may also be losses from the sorbent by back-diffusion. All three cases have the same net effect of low bias in the reported concentrations.

**Matching to Target Compounds:** The sampler type and sorbent must be selected with consideration of the compounds of interest and the desired reporting limits. This is similar to challenges of conventional active sampling methods that employ active (pumped) ATD tubes, such as EPA Method TO-17. For example, vinyl chloride is weakly retained by adsorbents, and may pose a greater challenge to the samplers than other VOCs. If a very strong adsorbent is used to retain vinyl chloride, then more strongly adsorbed compounds (such as naphthalene) may not be effectively recovered from the sorbent during desorption prior to analysis. In many cases, the compounds of concern for vapor intrusion are limited to a select number of chlorinated ethenes, ethanes, and methanes, many of which are included in the laboratory testing component of this study.

**Unplanned Uptake of Chemicals:** The passive samplers can become contaminated by unplanned exposure to chemicals during shipping and storage. The risk is reduced by carefully packing the samplers in clean containers that are impermeable to VOC vapors. The potential can also be evaluated and documented by including field blanks (a.k.a. trip blanks), which are samplers that travel continuously with the investigative samples, but are not used to collect samples. Trip blanks are also a standard QA/QC component of air monitoring programs using EPA Method TO-17. Field blanks are not required with Summa canisters, because the integrity of the canister during shipping is verified with vacuum measurements before and after each leg of the journey.

**Influence from Environmental Factors:** Stronger sorbents such as charcoal tend to also adsorb water,<sup>180,79</sup> which can be a problem in the analysis and can be limiting for some applications. Weaker adsorbents such as Tenax retain less water, but more volatile compounds are not strongly retained and may be lost from the sampling tube by back diffusion, especially for long sample durations. These types of processes can result in non-ideal behavior of the samplers, where the performance of the sampler in the field may deviate from that expected on the basis of the dimensions of the sampler and the rate of diffusion of the analyte in air. When selecting a method, users often accept compromises on performance, particularly for the study of mixtures of compounds. For example, Carbopack B may be optimal for benzene, but if the intention is to monitor a low volatility compound at the same time (without the additional cost of using a separate sampler) then Tenax might be the preferred choice. This is because while Tenax's performance for determining benzene is compromised to some extent due to back diffusion losses from the tube, giving a lower effective diffusive uptake rate, it can also be used at the same time to determine compounds that would be poorly recovered on heating when using a stronger sorbent, such as Carbopack B.

### 1.3.4 Standards and Testing for Passive Samplers

International standards are available describing the sampling procedure and passive sampler performance assessment.<sup>177,178,181-188</sup> The method for quantification of VOCs in indoor, ambient and workplace air is described in international standard EN ISO 16017-2.<sup>165</sup> This standard provides guidance on the selection of appropriate sorbents for particular purposes where key considerations are the properties of the target analytes, the concentration of interest and the required averaging time of the measurement. The selection of an appropriate sorbent relates predominantly to the volatility of the target analyte(s) and there is a requirement for the sorbent – analyte interaction to be appropriate to allow effective retention of the analyte, but also as efficient release as possible when heat is applied in a flow of gas in the thermal desorber.

EN ISO 16017-2 summarizes the published validation data (available in 2003), as a list of determined diffusive uptake rates for specific sorbent and analyte combinations, identifying the level of validation undertaken. By far most of the validations are for tests appropriate for workplace, with typical concentrations in air near the occupational exposure limit, and exposure periods of 8 hours. The EN ISO 16017-2 standard provides the diffusive uptake rates for passive ATD tubes with over 50 VOCs determined for workplace monitoring including a note on the level of validation of the method. There is also a summary of studies that determined uptake rates for indoor and ambient concentrations using sample periods of between 1 and 4 weeks, with most of the data referring to benzene, toluene, ethylbenzene, and xylene (BTEX), which are volatile aromatic compounds typically found in petroleum, and also data for trimethylbenzene, decane and undecane. The ISO standard also recommends conditions for the thermal desorption of the different sorbents by ATD tubes and GC/MS.

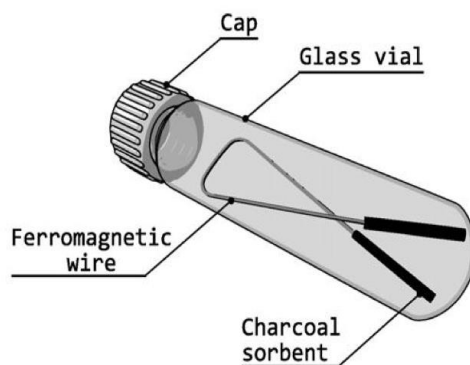
The EN ISO 16017-2 standard also discusses the impact on sampler performance of environmental conditions such as humidity, air velocity, temperature, pressure, and occurrence of transient concentrations. Assuming the correct sorbent is selected, the standard advises that in practical use the three main considerations are air velocity, protection from precipitation and security. For example, the ATD tube sampler has been shown to perform as designed in locations with low air movement (e.g., wind speed of 5 cm/s), but if placed outdoors an appropriate shelter should be used because precipitation, direct solar heating and high wind velocities may adversely affect performance. ISO 16000-5<sup>189</sup> and MADEP<sup>190,191</sup> discuss the strategies for sample locations and options for assessing continuous versus intermittent sources. More information about the impact of environmental factors on the accuracy of the uptake rate for passive samplers is provided by Tolnai et al.<sup>192</sup> and Bohlin et al.,<sup>48</sup>.

The measurement of benzene in ambient air via diffusive sampling is the subject of specific European standards (EN14662-4:2005 for thermal desorption and EN14662-5:2005 for solvent desorption). These

standards describe the sampling and analytical procedure and provide performance data in terms of the expected overall uncertainty of the method. The document was prepared under mandate from the European Commission in order to establish a method appropriate for measuring benzene in ambient air to check compliance with the Air Quality Directive. Unfortunately, the same level of extensive validation is not available for other analytes or for other passive samplers in ambient air. This can be managed to some degree by using inter-method verification samples as a QA/QC measure in a sampling program (for example 1 in 10 passive samples may be verified using a Summa canister/TO-15 sample), which provides information that can be used to derive or check uptake rates for detectable chemicals under the site-specific conditions.

#### 1.4 Prior State-of-the-Art for Passive Soil Vapor Sampling

Passive soil vapor sampling was developed for petroleum resource exploration using the PETREX system (petroleum exploration) and applied for environmental monitoring as early as 1985.<sup>193</sup> The PETREX system consists of charcoal sorbent fused to a ferromagnetic wire that acts like a spring to hold the sorbent inside a glass vial (Figure 1-12). The vial is sealed with a solid screw-cap during shipping and storage, but the cap is removed during sampling, and the vial is placed at a shallow (10 to 30 cm) depth below ground surface, usually for about 2 weeks. High temperature thermal desorption and GC/MS analysis enable a wide range of organics to be identified and the adsorbed mass quantified.



**Figure 1-12:** PETREX sampler<sup>50</sup>

A similar design was initially referred to as the EMFLUX® cartridge by Quadrel, but is now marketed as the Be-Sure™ system by Beacon Environmental Environmental Services, Inc. (Figure 1-13). Rather than having charcoal fused to a wire, the sorbent is contained in a stainless steel mesh packet, and can be selected from a range of available sorbents (typically, thermally desorbable hydrophobic sorbents are used). The EMFLUX system includes a proprietary method of predicting earth tides to identify periods

of expected maximum emissions of soil vapors to the atmosphere, so they typically recommend shorter sample durations of about 3 days.<sup>194</sup>

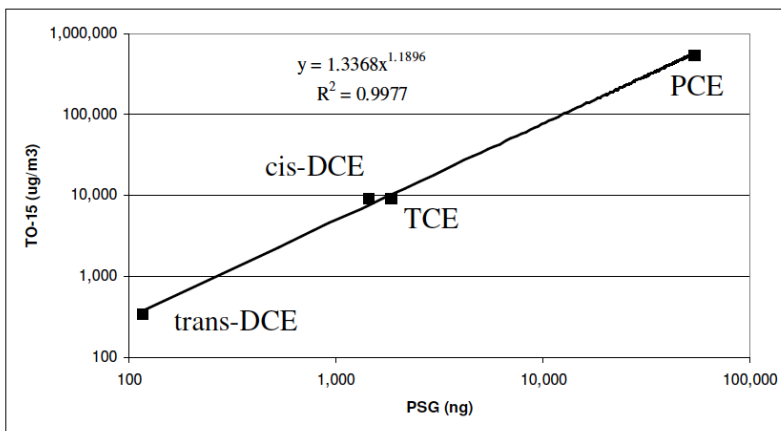


**Figure 1-13:** The Beacon Be-Sure Sampler (formerly the EMFLUX cartridge)<sup>195</sup>

The EMFLUX system has an estimated uptake rate of 1 mL/min,<sup>72</sup> which is within the range of diffusive delivery rates calculated in Chapter 5. However, the EMFLUX uptake rate has no mathematical relationship to the soil properties, which appears to have been the motivation for Beacon to devise an empirical correlation between the sorbed mass and soil vapor concentration they refer to as the “mass to concentration tie-in” [MtoC Tie-in].<sup>196</sup> This “tie-in” is intended to create essentially a calibration curve using a small percentage of locations where a duplicate sample is collected using active sampling and analysis methods. However, the theoretical basis for the empirical relationships is unclear, and many of the relationships are supported by very little data. For example, Figure 1-14 shows a plot of soil vapor concentration versus mass sorbed by the passive sampler for a single sample location from a site in Indiana, which has a regression equation and a high correlation coefficient, but the theoretical basis for why this relationship between concentration and mass sorbed is linear for four different compounds is not explained. In addition, the authors did not describe the soil conditions (porosity and moisture content) on which the empirical relationships depend. These conditions vary both in time and in space. The uptake rates can be calculated from this figure using a version of Equation 1-5, rearranged to solve for UR:

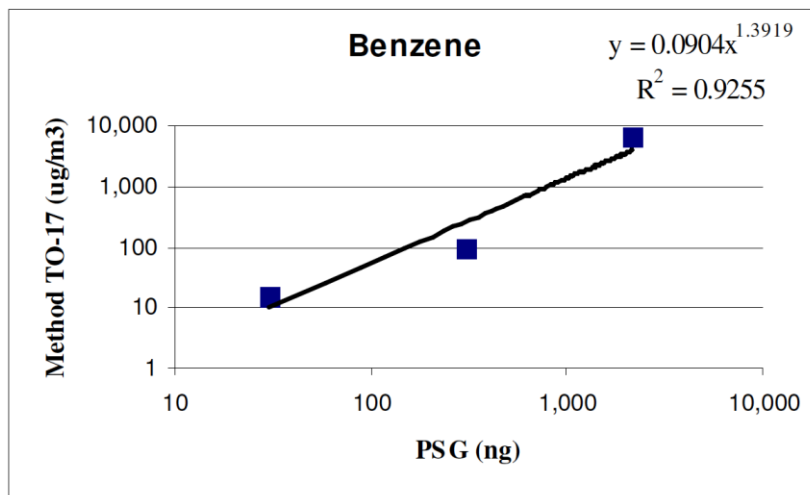
$$UR = \frac{M}{C_0 t} \quad (1-6)$$

The sample duration for the data in Figure 1-14 was 6 days (~8640 minutes), which would yield uptake rates of about 0.04 mL/min for trans-DCE, about 0.02 mL/min for cis-DCE and TCE and about 0.01 mL/min for PCE. Within the uncertainties associated with interpolating numbers from a semi-logarithmic plot, these values are all very similar.



**Figure 1-14:** Mass to concentration relationship for 4 VOCs<sup>193</sup>

Another plot from the same proceedings paper shows the mass to concentration relationship for benzene at a site in northern California (Figure 1-15). The sample duration was 7 days (about 10,080 minutes). The uptake rates for the three data points would be about 0.2, 0.3 and 0.03 mL/min for the low, medium and high concentration samples, respectively (although the authors did not complete this calculation in their paper). This is roughly one order of magnitude range, although it is a very small data set.

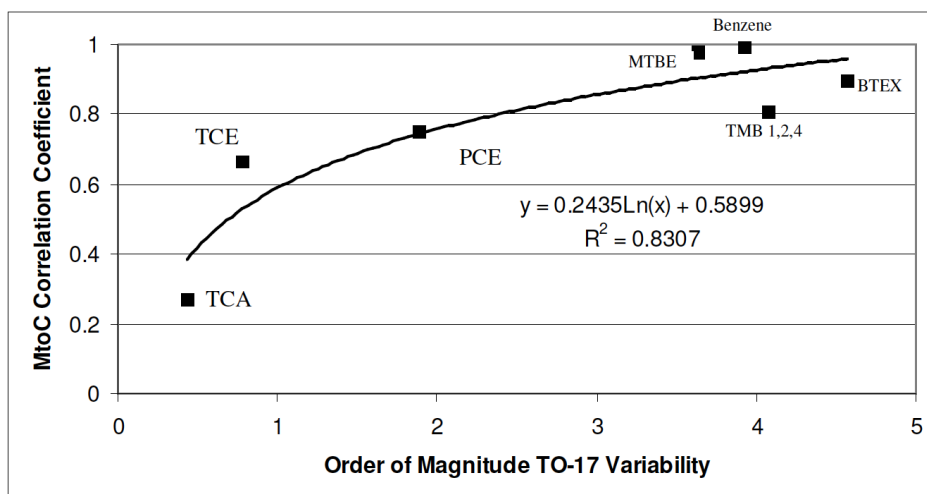


**Figure 1-15:** Mass to concentration relationship for benzene<sup>196</sup>

The uptake rates for PCE from data collected at two different sites and presented on similar plots in their paper are 0.1 mL/min at three sites in the eastern United States and 1.0 mL/min for a site in northern

California, which are not consistent with the value of 0.01 mL/min for the site in Indiana, and collectively, the uptake rates for PCE span two orders of magnitude (100-fold range). Note that the ranges of the uptake rates are within the range of diffusive delivery rates calculated in Chapter 5 of this thesis.

Odenchantz et al.<sup>193</sup> compiled data for seven compounds at the same site (Figure 1-16, below) and stated that “there is clearly a trend between the range of active soil gas concentrations encountered from the tie-in points and the strength of the correlations” for the mass to concentration relationships. They state that “Two orders of magnitude variability in concentration of any compound results in an R-squared of 0.759, which is very strong and significant”, without defining the terms “strong” or “significant” quantitatively. It also appears that they are referring to the range of concentrations when they use the term “variability”.



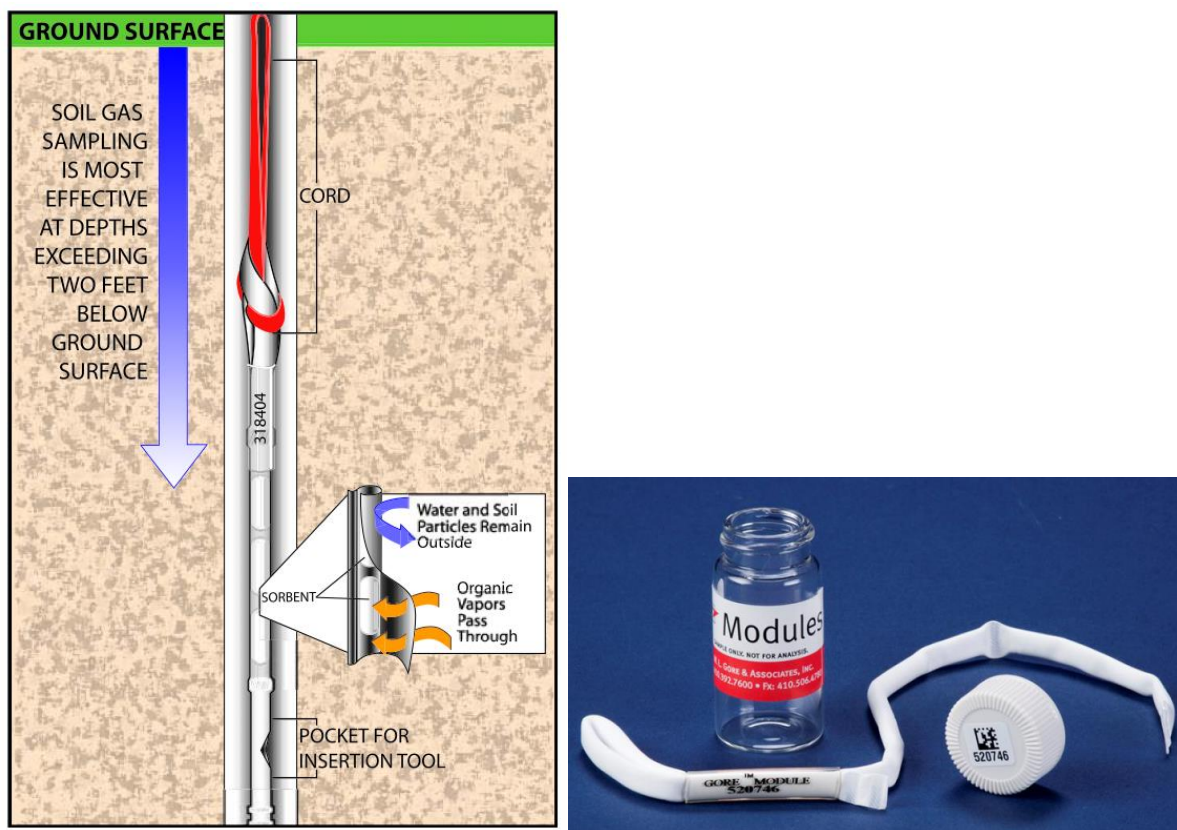
**Figure 1-16:** Relationship between MtoC correlation and soil gas concentration range for the tie-in points<sup>196</sup>

Odenchantz et al.<sup>193</sup> go on to claim that the empirical relationships provide an improvement over any mathematical method for calculating the passive sampler uptake rates because of inherent uncertainties in determining input variables and because of questions related to the underlying assumptions of any mathematical model for calculating the uptake rate. This proceedings paper was issued at the same conference as another proceedings paper by Hodny, Whetzel and Anderson of W.L. Gore and Associates, Inc.,<sup>103</sup> in which they presented a mathematical model to calculate the uptake rate, described below.

The Gore-Sorber (or Gore-Module as it is now known) consists of two packets of a hydrophobic, thermally-desorbable sorbent (which is not identified in their publications or promotional materials, but

is likely Tenax TA or similar) contained within Gore-Tex™ fabric, a water-proof, vapor-permeable microporous material that protects the sorbent from liquid water and soil particles during deployment and provides a strong tether for retrieval at the end of the sample period. The module is shipped in a glass vial with a screw cap for protection from exposure to chemicals in transit and storage, and during emplacement is tethered to a cork at ground surface (Figure 1-17).

Hodny et al.<sup>103</sup> presented a chart to demonstrate the linear uptake of the GORE Module for several VOCs (Figure 1-18). From this graph, the uptake rates for the GORE™ Module from air in units of mL/min can be calculated (see Table 1-7).



**Figure 1-17:** The GORE(TM) Module<sup>103</sup>



TO-15 Compounds 5 ppb  
Expt of 2-28-07

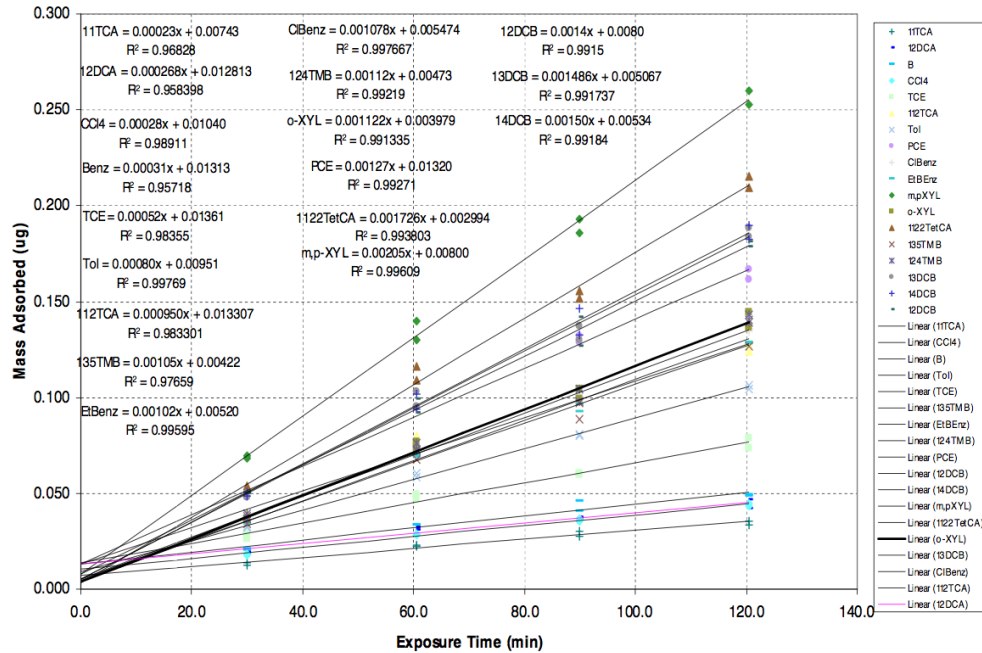


Figure 1-18: Linear uptake of compounds by the GORE(TM) Module<sup>103</sup>

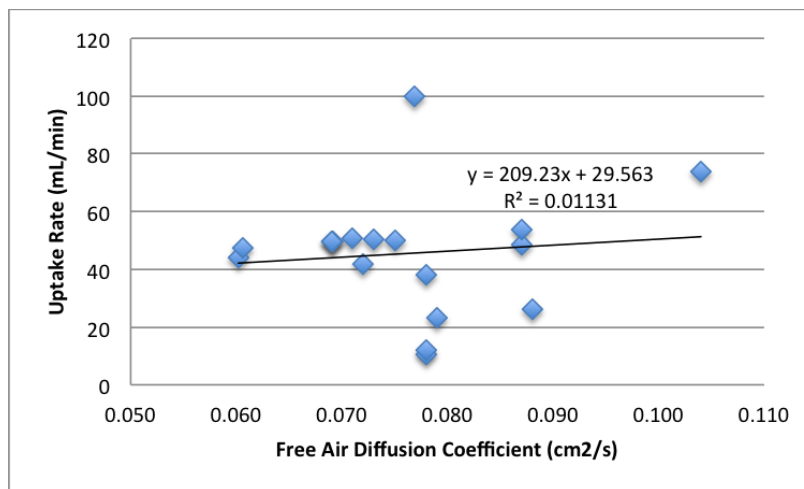
Table 1-7: Calculated uptake rates for the GORE(TM) Module from air

Compound	Concentration ppbv	Concentration ( $\mu\text{g}/\text{m}^3$ )	Sample time (min)	Mass Sorbed ( $\mu\text{g}$ )	Uptake Rate (mL/min)
1,1,1-trichloroethane	5	27	120	0.035	11
1,2-dichloroethane	5	20	120	0.18	74
benzene	5	16	120	0.05	26
carbon tetrachloride	5	32	120	0.045	12
trichloroethene	5	27	120	0.075	23
1,1,2-trichloroethane	5	27	120	0.125	38
toluene	5	19	120	0.11	49
tetrachloroethene	5	34	120	0.17	42
chlorobenzene	5	23	120	0.14	50
ethylbenzene	5	22	120	0.13	50
m,p-xylene	5	22	120	0.26	100
o-xylene	5	22	120	0.14	54
1,1,2,2-tetrachloroethane	5	34	120	0.21	51
1,3,5-trimethylbenzene	5	25	120	0.13	44
1,2,4-trimethylbenzene	5	25	120	0.14	47
1,3-dichlorobenzene	5	30	120	0.18	50
1,4-dichlorobenzene	5	30	120	0.18	50
1,2-dichlorobenzene	5	30	120	0.18	50

These uptake rates are one to two orders of magnitude higher than the EMFLUX or Beacon sampler, which Hodny et al.<sup>103</sup> describe as allowing “greater sensitivity and more accurate contaminant delineation”, but they do not mention that this claim may not be true if the rate-limiting step of analyte uptake by the sampler is slow diffusion of VOC vapors through the soil toward the sampler. They do acknowledge that the soil imposes resistance, and they calculate the effect of this by multiplying their uptake rates by a “soil effectiveness factor” (E), which they define as the ratio of the free air diffusion coefficient ( $D_{air}$ ) to the effective diffusion coefficient in soil ( $D_{eff}$ ) as defined by Johnson and Ettinger<sup>197</sup>, who used the Millington Quirk<sup>198</sup> relationship and assumed that it applies to both the aqueous and gas phases:

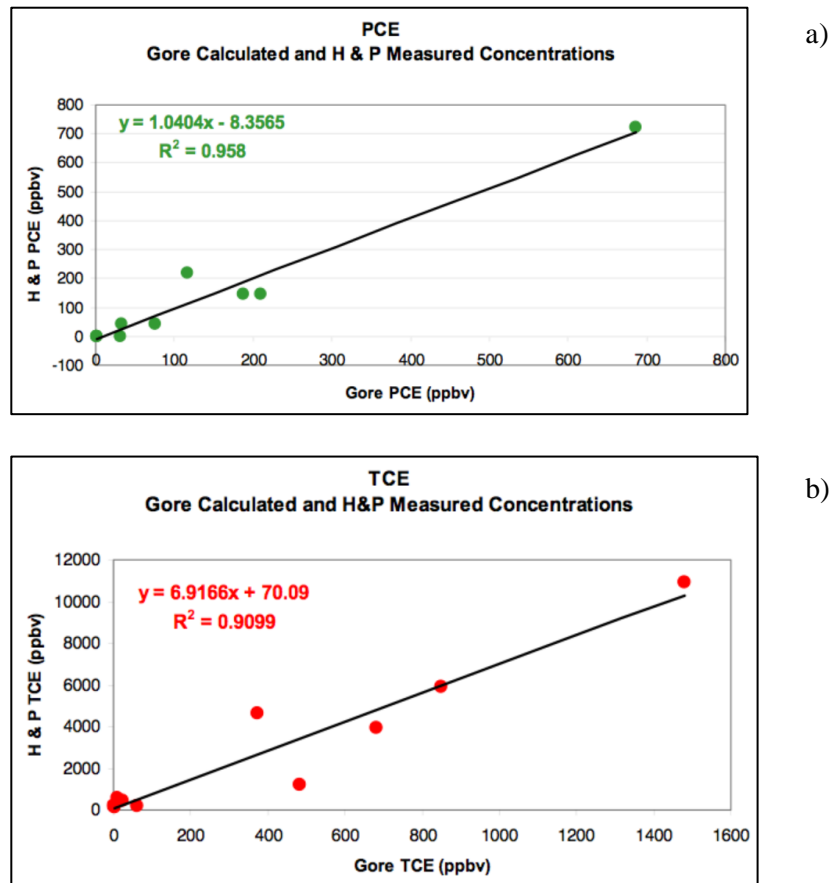
$$E = \theta^{\frac{4}{3}}(1 - \epsilon)^{\frac{10}{3}} \quad (1-7)$$

where  $\theta$  is the soil porosity (volume of voids divided by volume of soil) and  $\epsilon$  is the fraction of pores filled with water (volume of water divided by volume of voids). Soil porosity tends to fall in a fairly narrow range of about 0.25 to about 0.4.<sup>199</sup> A relatively dry soil ( $\epsilon \sim 0.1$ ) would have an effectiveness factor of about 0.1 to 0.2 (within the typical range of porosities). A relatively wet soil ( $\epsilon \sim 0.9$ ) would have an effectiveness factor of about 0.0001 to 0.00001. This adjustment recognizes the importance of the rate of diffusion of vapors through soil, but may not capture all of the processes involved. For example, the inherent assumption that the uptake rate of the sampler is controlled by diffusion is questionable, as shown in Figure 1-19, which shows the correlation between the uptake rates in Table 1-7 and the free air diffusion coefficient.<sup>200</sup> The correlation is very poor ( $r^2 \sim 0.01$ ).



**Figure 1-19:** Correlation between uptake rate and free air diffusion coefficient for GORE(TM) Module. The mathematical model proposed by Hodny et al.<sup>103</sup> yields concentrations that are often up to an order of magnitude different than concentrations measured by active whole-gas sampling and analysis. For

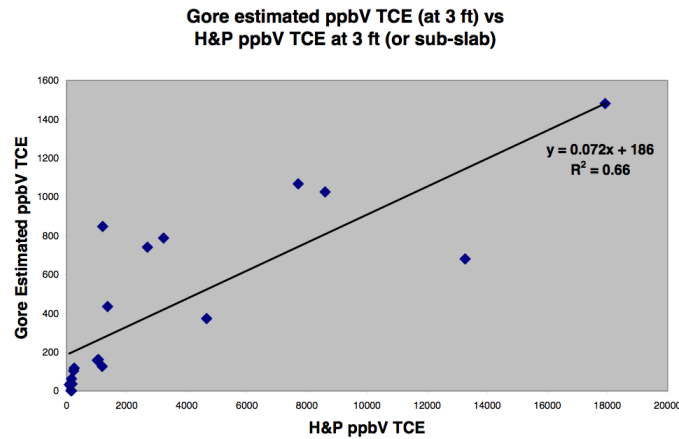
example, Shaw<sup>201</sup> plotted the comparison of concentrations estimated by the GORE team against independent active soil vapor sample data, as shown in Figures 1-20a and 1-20b. The correlation between the GORE™ Module calculations and the active soil vapor concentrations was much better for tetrachloroethene (PCE) (which had a slope of 1.04 and a correlation coefficient of 0.96) than trichloroethene (TCE) (which had a slope of 6.9, indicating the GORE™ Module concentrations were about 7 times lower than the active sample results). The 7-fold difference between PCE and TCE is counter-intuitive and inconsistent with the model in Equation 1-7 because the two compounds have very nearly the same free air diffusion coefficients of 0.072 and 0.079 cm<sup>2</sup>/s, respectively<sup>196</sup> and uptake rates in air for the GORE™ Module that are within a factor of 2 (42 and 23 mL/min, respectively, Table 1-7).



**Figure 1-20:** Correlation between active soil vapor sampling and analysis by H&P Mobile Geochemistry versus the GORE(TM) Module for a: PCE (top) and b: TCE (bottom)<sup>201</sup>

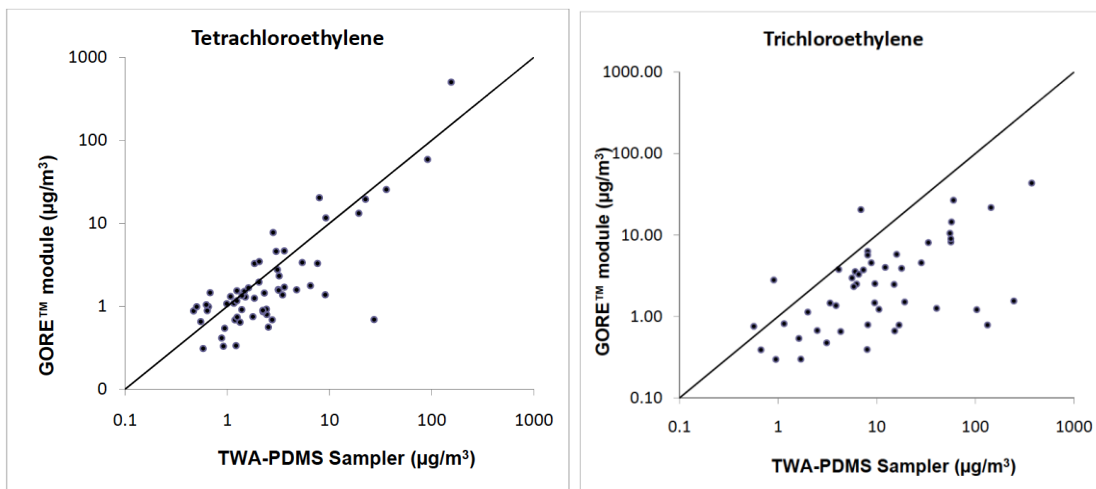
Kurtz<sup>202</sup> plotted the TCE correlation for the GORE™ Module compared to active soil vapor samples collected by H&P Mobile Geochemistry based on data from the same site and time and found a different correlation for TCE ( $R^2 = 0.66$ , as shown in Figure 1-21), which is much lower than the value shown by

Shaw ( $R^2 = 0.9099$ ). The discrepancy appears to be attributable to the selection of different subsets of the data by the two authors.



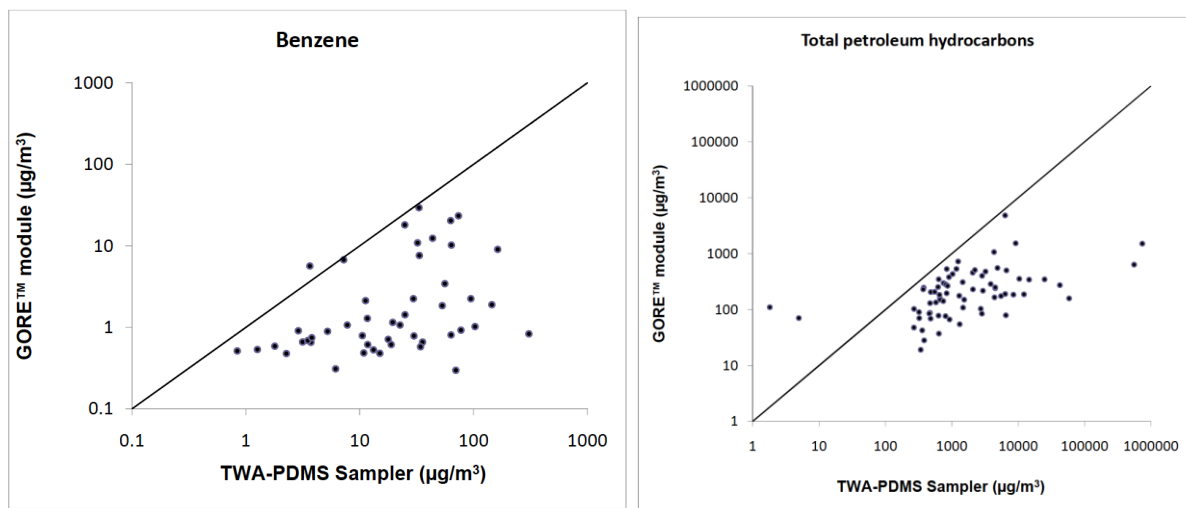
**Figure 1-21:** Correlation between the GORE(TM) Module and active soil vapor sampling<sup>198</sup>

A similar discrepancy between PCE and TCE concentrations estimated by the GORE™ Module was shown by Seethapathy<sup>203</sup> using data from a comparison between the GORE™ Module and the Waterloo Membrane Sampler conducted in Belgium in 2008 (Figure 1-22). The correlation for PCE showed most points centered around the theoretical 1:1 line, whereas TCE showed notably lower concentrations for the GORE™ Module (a linear regression yielded a slope of 0.08).



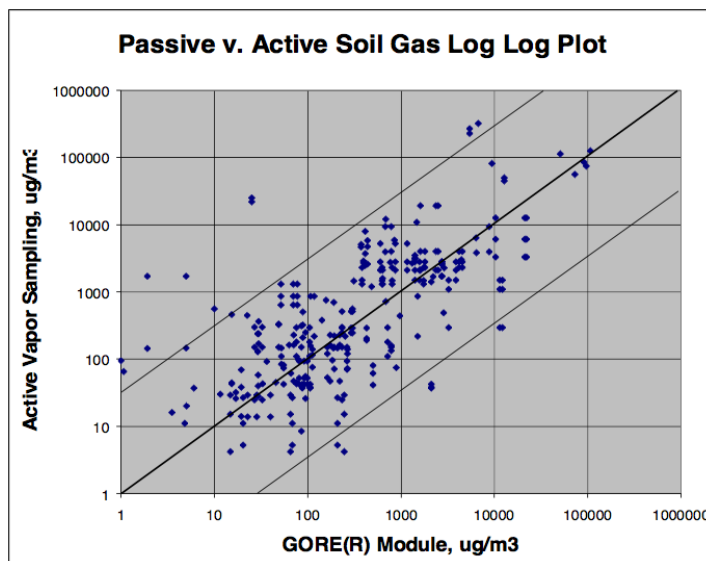
**Figure 1-22:** Correlation between the GORE(TM) Module and the Waterloo Membrane Sampler (a.k.a. TWA-PDMS sampler) for PCE (left) and TCE (right)<sup>203</sup>

The Belgium study also showed an apparent low bias using the GORE™ Module for benzene and total petroleum hydrocarbons (TPH) (Figure 1-23). The magnitude of the apparent low bias for the GORE™ Module was up to about three orders of magnitude.



**Figure 1-23:** Correlation between the GORE(TM) Module and the Waterloo Membrane Sampler (a.k.a. TWA-PDMS sampler) for benzene (left) and TPH (right) <sup>203</sup>

A compilation of the data collected from 5 sites in the midwestern and western United States by Whetzel et al. <sup>204</sup> showed that the GORE™ Module typically provides concentration data within an order of magnitude of adjacent samples collected and analyzed using active soil gas sampling (Figure 1-24).



**Figure 1-24:** Unfiltered comparative data from 5 sites with the GORE(TM) Module <sup>200</sup>

Based on this data, Whetzel et al.<sup>200</sup> concluded that the GORE™ Module “Produces similar soil gas results to established and recognized sampling techniques”, which they claim to be “one order of magnitude variation”, based on data for one compound from one site analyzed by four different active sampling and analysis methods.

The prior state-of-the-art in passive soil vapor sampling was summarized by the California Department of Toxics Substances Control in 2011<sup>14</sup> as follows: “passive soil gas samples cannot be used to measure the contaminant concentration in soil gas or be used to determine the flux of contaminants over a given area. The concentration of volatile chemicals on the adsorbent material in a passive soil gas sample though yielding a contaminant mass value, cannot be directly equated to soil gas concentration.” A similar position was adopted by the Interstate Technology and Regulatory Council (ITRC) in their guidance document for vapor intrusion<sup>1</sup> and by ASTM.<sup>205</sup> The general consensus that passive soil vapor monitoring cannot reliably be used to measure soil vapor concentrations was one of the primary motivations for this research.

## **1.5 Scope of the Thesis**

The use of passive samplers for vapor intrusion assessment depends on their acceptance by regulatory agencies and practitioners in the field. Most of the regulatory guidance documents for vapor intrusion recommend the use of Summa canisters for sample collection and EPA Method TO-15 for analysis. Therefore, a comparison study was needed to show how the passive sampler results compare to the conventional methods. Passive samplers with prior acceptance for industrial hygiene applications are not automatically acceptable for vapor intrusion assessment because the chemicals of concern are not necessarily the same, the target concentrations are in many cases orders of magnitude lower, and the sample durations of interest are generally longer. Furthermore, none of the passive samplers were specifically designed for use in soil vapor monitoring, and passive soil vapor sampling has not previously been demonstrated to provide accurate soil vapor concentration data.<sup>14,73,194,205</sup>

The testing program included both laboratory and field sampling tests. Laboratory tests allow more rigorous control over the factors that might affect the performance, which limits variability and improves the ability to discern statistically significant effects. Field conditions include natural variability that may be important, but difficult to replicate in a realistic way in the laboratory. Both laboratory and field tests were performed with sufficient replication to assess precision and conventional samples as a baseline for comparison to assess accuracy. To the extent possible, the various candidate samplers were tested under virtually identical conditions to provide a fair and unbiased comparison. Peer review by individuals familiar with each of the candidate samplers (as described in Section 1.6)

was included to provide assurance of the objectivity of the experiments. Laboratory experiments were conducted at two ranges of concentration: a low concentration range to represent indoor and outdoor air, and a high concentration range to represent soil vapor, and field sampling was conducted at five DoD facilities.

## 1.6 Attribution

This research was conducted under two contracts with the United States Federal Government totaling \$1,157,000, which is different than some doctoral research programs, and deserves a detailed discussion of the attribution of effort. The author of this thesis was the principal investigator for both research contracts in his capacity as a Principal and the Practice Leader for Vapor Intrusion Services at Geosyntec Consultants, Inc. The author's efforts for the research presented in this thesis included:

- The initial idea that long-term time weighted average samples should be collected for VOC vapor intrusion assessment to manage temporal variability (analogous to the way radon monitoring is performed) and that passive samplers would be better suited to this than the conventional Summa canister and pumped ATD tube devices;
- Securing funding from ESTCP and the Navy as the primary author of both proposals;
- Assembling a team of experts for the Technical Review Panel, including:
  - Dr. Paolo Sacco from Fondazione Salvatore Maugeri in Padova, Italy (Radiello)
  - Dr. Derrick Crump of Cranfield University, UK (passive ATD Tubes)
  - Dr. Tadeusz Górecki, University of Waterloo (U of W), Canada (WMS)
  - Mr. Michael Tuday, CAS labs, Simi Valley USA (SKC Ultra)
  - Dr. John Nocerino, USEPA, Las Vegas, USA (Experimental Design)
  - Dr. Paul Johnson, Arizona State University (vapor intrusion)
  - Dr. Brian Schumacher, USEPA, Las Vegas (soil vapor sampling)
  - Ms. Heidi Hayes, Air Toxics Ltd., Folsom, CA (laboratory analysis)
- Developing the scope of work, including laboratory testing, field testing and mathematical modeling, with input and comment from the internal peer reviewers;
- Primary author of the Demonstration Plan, which specified the scope, methods and execution plan for all laboratory and field testing;
- Field sampling team lead for sampling events at:
  - Navy Old Town Campus (OTC), San Diego
  - Cold Regions Research and Engineering Lab, New Hampshire
  - Naval Air Station, Jacksonville (NAS JAX) Florida;

- Designer, builder and operator of the high concentration test apparatus, including experimental design and execution;
- Designer of the low concentration test apparatus, including the supply gas system, the chamber components, the rotating carousel, and the gas distribution and flow control baffles;
- Calculations of accuracy and precision for all experimental data, including tables and figures;
- Conceptualization of the transient and steady-state mathematical models to simulate the diffusive delivery of VOCs vapors to a passive soil vapor sampler;
- Design of passive soil vapor probes and seals, deployment protocols, selection of sorbents, sample duration and uptake rates;
- Conceptualization and design of the flow-through cell, design of the fractional factorial test design and assembly of apparatus;
- Design of the experimental procedures for the soil vapor sampling tests at OTC, the Layton house and NAS JAX;
- Visited Air Toxics Ltd. (ATL), Columbia Analytical Services (CAS), University of Waterloo (U of W), AirZone One (Airzone) and Fondazione Salvatore Maugeri (FSM) laboratories to meet individually with the lab analysts to communicate the study goals and data quality objectives, review the procedures and apparatus, and review the quality assurance/quality control procedures;
- Literature review;
- Data analysis (except validation and ANOVA), interpretation and reporting;
- Primary author of five journal articles (4 published, one in press) and U.S. Federal Government reports (ESTCP and Navy SPAWAR); and
- Sole author of this thesis (appendices excluded).

The author of this thesis was supported by others for the following efforts:

- The internal peer review team (listed above) was provided an opportunity to review and comment on all of the main deliverables:
  - Proposals
  - Demonstration plans
  - Journal articles (including other co-authors, as listed)
  - ESTCP and SPAWAR reports;
- Advisor Dr. Tadeusz Górecki provided additional review and comment on the thesis;
- Laboratory analysis was contracted to the labs most familiar with each of the passive samplers:
  - Fondazione Salvatore Maugeri or Air Toxics Ltd. (ATL) for the Radiello



- University of Waterloo (Suresh Seethapathy) or ATL for the WMS
- Columbia Analytical Services (CAS) for the SKC Ultra and Ultra II
- AirZone One Limited or ATL for 3M OVM 3500
- ATL for the ATD tubes (active and passive)
- CAS or ATL for Summa canister samples;
- The experimental design for the low concentration laboratory tests was provided by the late John Nocerino of USEPA labs in Las Vegas;
- Data validation, invoicing, progress reports, subcontracting, and scheduling logistics was performed by Hester Groenevelt of Geosyntec Consultants Inc.;
- Electronic database management was performed by Jen Sano of Geosyntec;
- Custom machining of the carousel for the low concentration laboratory tests by the staff of the science department machine shop at the University of Waterloo;
- Fabrication of the flow-through cell by Ryan Brenner of Geosyntec;
- Word processing assistance from Simmy Singh of Geosyntec;
- ANOVA analyses were performed by Cathy Crea of Geosyntec with review by Dr. Ayesha Ali of the University of Guelph and instructional discussion by Fernando Camacho of the University of Waterloo;
- The steady state model was identified in Carslaw and Jaegar's textbook by Robert Ettinger of Geosyntec;
- The transient model was derived by Dr. Andre Unger (U of W) and programmed into Matlab and run by Dr. Xiaomin Wang (U of W), who also ran simulations as directed by the author of this thesis;
- Security clearance and escort for field sampling activities was provided by:
  - Ignacio Rivera-Duarte at the Navy San Diego Site
  - Louise Parker at CRREL
  - Michael Singletary at NAS JAX
  - Jason Williams at MCAS Cherry Point;
- Field sampling support was provided by:
  - David Bertrand and Chris Gale of Geosyntec at the Navy San Diego site
  - David Bertrand and Paul Nicholson of Geosyntec and Quin Bingham of Select Engineering Services at the Layton house
  - Hester Groenevelt and Todd Creamer of Geosyntec and Louise Parker of CRREL at the CRREL site

- Todd Creamer, Lauren Wellborn and Michael Schott of Geosyntec at the MCAS Cherry Point site
- Paul Nicholson and Rachel Klinger of Geosyntec at NAS JAX;
- Hapsite mobile mass spectrometer analyses were performed by Quin Bingham of Select Engineering Services and reviewed by Eric Dettenmeier of Hill Air Force Base;
- The low concentration laboratory chamber tests were performed at ATL by Steven Disher and Jason Arnold, with on-site supervision by Heidi Hayes following the experimental design and methods in the Demonstration Plan.

## 2 Experimental<sup>2</sup>

This section provides a summary of the experimental methods, including the low and high concentration laboratory tests and field sampling. The varieties of samplers used are detailed in Section 2.5, the field test sites are described in Section 2.6 and the performance objectives are discussed in Section 2.7.

### 2.1 Low Concentration Laboratory Tests

The low concentration range (1 to 100 parts per billion by volume [ppbv]) tests were conducted using five passive samplers: WMS (either solvent extraction or thermal desorption), SKC Ultra II (with Carbo-pack X), Radiello (white body and activated charcoal) and two types of ATD tube samplers (one using Carbo-pack B and the other using Tenax TA to compare the two sorbents). Active sampling was conducted using Automatic Thermal Desorption Tubes (ATD Tubes) with analysis by EPA Method TO-17, as described in Appendix A. The low concentration range laboratory studies were designed with assistance by Brian Schumacher and John Nocerino of EPA Research Labs in Las Vegas using Design-Expert 7.1.1. The experimental procedure included 3 steps, starting out with familiarity testing (verifying the degree of control over the experimental conditions), then proceeding to a 1-Way analysis of variance (ANOVA) test, and then to a two-level one-half fraction fractional factorial design, with information from each successive step being used to refine the design of the subsequent steps. Three chambers were custom-fabricated for the low concentration laboratory tests and set up to maintain reasonably constant conditions of 5 independent variables (or “factors”): temperature, humidity, air-flow velocity, concentrations of target compounds and duration. Three of each of the five passive samplers were deployed inside the chamber for the duration of the experiment. The passive sampler concentrations ( $C$ ) were normalized by dividing by the average of the active TO-17 samples for each chamber ( $C_0$ ) to yield relative concentrations ( $C/C_0$ ).

Familiarity testing was conducted to assess the control of the independent variables and understand whether the exposure chambers would perform as intended. The 1-Way ANOVA test was performed to establish the variability that would occur in 6 repeated exposure chamber tests under exactly the same conditions (i.e. to quantify the experimental “noise”). Each of the experimental factors was set at the center of their respective ranges for the 1-Way ANOVA tests, hence, these tests are also referred to here as “Center-Point” tests. Two additional Center-point tests were conducted halfway through the fractional factorial testing to assess the consistency in the results.

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<sup>2</sup> The contents of this Chapter are based on the author’s final reports to ESTCP<sup>3</sup> and the Navy<sup>227</sup>

The two-level one-half fraction fractional factorial test included 16 chambers set at high or low levels of all the factors in strategic combinations such that a small number of exposure chamber experiments could be statistically analyzed to assess the effect of each independent variable compared to the noise. Collectively, the Center-point and fractional factorial tests included 24 chambers, each containing 5 different passive samplers, each in triplicate, which were exposed to 10 VOCs of varying classes (chlorinated ethanes, ethanes, and methanes, aliphatics and aromatics) and physical properties (vapor pressure, solubility and sorption), yielding 3,600 passive sampler measurements. These data were analyzed using analysis of variance (ANOVA) using PROC GLM (SAS version 9.2) by Cathy Crea of Geosyntec Consultants, Inc.

## **2.2 High Concentration Laboratory Tests**

The high concentration range (1 to 100 parts per million by volume [ppmv]) tests were conducted using five passive samplers: WMS, SKC Ultra, Radiello, ATD tube and 3M OVM 3500. For soil gas, humidity and temperature tend to be less variable than indoor or outdoor air, so these parameters were fixed. The face velocity was tested at very low levels to mimic conditions in the subsurface; including some tests at a minimal velocity (5 cm/min) to reduce complications attributable to the starvation effect and some tests at zero velocity (using low-uptake varieties of the samplers designed to minimize starvation regardless of the flow velocity). The exposure durations were 30 minutes to provide detectable mass with minimal risk of sorbent saturation. The same compounds used in the low concentration laboratory tests were also used in the high concentrations laboratory tests for consistency, except the less volatile compounds (naphthalene and 1,2,4-trimethylbenzene), which could not be tested at the highest concentrations.

## **2.3 Indoor and Outdoor Field Tests**

Indoor and outdoor air sampling tests were conducted at three DOD facilities to demonstrate the passive samplers under “real-world” conditions. Samples were collected in triplicate in multiple locations with Summa canister samples for comparison at each of three sites. Each site had different VOCs present and different concentrations, and neither were manipulated from ambient conditions during these tests.

## **2.4 Soil Vapor Field Tests**

A series of controlled field experiments were conducted to elucidate the optimal approach to soil gas sampling using kinetic passive samplers, including a wide range of operating conditions: sample durations from 20 minutes to 11.7 days, concentrations from about 100 to about 60,000  $\mu\text{g}/\text{m}^3$ , 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 at depths of 0.15 to 4.2 m below ground, 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 provided a previously unavailable set of data with which to assess the capabilities and limitations of passive soil vapor sampling for VOC concentration measurement. Information gained during the conduct of the work and mathematical modeling (Chapter 5) was used to guide the evolution of the soil vapor monitoring probe design and passive sampler uptake rates.

## 2.5 Varieties of Passive Samplers Used

Several varieties of each type of passive sampler were used during the field events. Table 2-1 shows the passive samplers used at each of the field sites for each of the media tested, including the number of replicates, the sorbent, and the uptake rate (where more than one uptake rate was available). After each stage of the research, the data were reviewed to assess whether there were indications of data bias or variability attributable to the sorbent selection or choice of uptake rate configurations. In some cases, multiple sorbent types were tested to assess their relative performance (e.g., passive ATD tube samplers were used with both Tenax TA and Carbopack B in both the low concentration laboratory tests and passive soil vapor samples at the Layton house).

The passive sampler uptake rates were based on vendor-specified values, where available. In some cases, the vendors did 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 3-3 provides the uptake rates used and identifies which were supplied by the vendors of the passive samplers, and which were calculated for this study. It should be noted that uptake rates for a particular compound and sampler can vary by sorbent type, sample duration and air velocity,<sup>206</sup> which varied among the laboratory and field experiments. In most of the samplers, the uptake rate depended on the free-air diffusion coefficient,<sup>200</sup> which is closely related to the molecular weight. For these samplers, uptake rates were estimated by linear interpolation from the nearest heavier and lighter molecular weight compounds with vendor-supplied uptake rates. For the WMS sampler, the uptake rate depends on the distribution coefficient for the compound between air and PDMS (the membrane material) and the permeation rate through PDMS; it has been shown to be strongly correlated with the linear temperature programmed retention index (LTPRI) on pure PDMS-coated capillary GC columns.<sup>152,153</sup> Where needed, uptake rates were calculated from the linear regressions and the compound-specific retention indices.

Four of the five passive samplers tested were available with regular and low-uptake rate varieties. The SKC Ultra uses a 12-hole cap to cover the normal 300-hole cover over the sorbent chamber, which was assumed to reduce the uptake rate by a factor of 25 (300/12). The Radiello with the low-uptake yellow body (designed for thermal desorption with Carbograph) has published uptake rates for many compounds and where values were not available, they were calculated using the same interpolation approach as described above for the higher uptake (white body) sampler. The ATD tube sampler can be fitted with a cap that has a small diameter opening (provided courtesy of Nicola Watson of Markes International), but no published uptake rates were available; therefore, they were estimated by dividing the regular uptake rates by a ratio of the inner diameter of the tube versus the opening of the cap (1/10). A few versions of low-uptake WMS samplers were tested with an aluminum shield covering the PDMS membrane with various diameter holes drilled in it, but the fabrication was challenging, so the low-uptake variety was ultimately designed using a smaller vial and crimp-cap (i.e., a 0.8 mL vial instead of the standard 1.8 mL vial).

**Table 2-1:** Number and varieties of samplers and sorbents used in the field-sampling program

Sampler	Uptake Rate	Sorbent	Laboratory Desorption Method	Navy OTC3, San Diego, CA			Hill AFB, Layton, UT	CRREL, Hanover, NH			MCAS, Cherry Point, NC		NAS Jacksonville, FL			
				Indoor Air	Outdoor Air	Passive Sub Slab	Passive Soil Vapor	Indoor Air	Outdoor Air	Flow-Through Sub Slab	Indoor Air	Outdoor Air	Passive Soil Vapor	Temporary Soil Vapor	Passive Sub Slab	
Summa Canister	na	na	TO-15	3 x 3	1 x 3	2 x 1	1 x 9**	3 x 3 <sup>^</sup>	1 x 3 <sup>^</sup>	1 x 3 <sup>6</sup>	3 x 3	1 x 1	2 x 10 & 1 x 15		3 x 1	
3M OVM 3500™	Regular	Charcoal	Solvent	3 x 3	1 x 3	2 x 1		3 x 3	1 x 3	1 x 7	3 x 3	1 x 1	2 x 2 & 1 x 3		NS	
ATD Tube	Regular	Chromosorb 106	Thermal	3 x 3	1 x 3	2 x 1										
		Tenax TA	Thermal				6 x 1									
		Carbopack B	Thermal				6 x 1	3 x 3	1 x 3	1 x 7	3 x 3	1 x 1	2 x 2 & 1 x 3			
	Low uptake rate	Carbopack B	Thermal												3 x 1	
WMST™	Regular	Anasorb 747	Solvent	3 x 3	1 x 3	2 x 1	6 x 1	3 x 3		1 x 7						
		Carbopack B	Thermal						1 x 3		3 x 3	1 x 1				
	Low uptake rate	Anasorb 747	Solvent										2 x 2 & 1 x 3	1 x 6	3 x 1	
SKC Ultra II™	Regular	Charcoal	Solvent					1 x 3; 1 x 2		1 x 1						
		Chromosorb 106	Thermal	3 x 3	1 x 3	2 x 1										
		Carbopack X	Thermal													
		Carbograph 5	Thermal					1 x 1; 1 x 3	1 x 3	1 x 6	3 x 3	1 x 1				
	Low uptake rate	Carbopack X	Thermal													
		Charcoal	Solvent				6 x 1									
		Carbograph 5	Thermal											2 x 2 & 1 x 3		NS
Radiello™	Regular	Charcoal	Solvent	3 x 3	1 x 3	2 x 1	6 x 1			1 x 7						
		Carbograph 4	Thermal					3 x 3	1 x 3							
	Low uptake rate	Carbograph 4	Thermal								3 x 3	1 x 1				
		Charcoal	Solvent											2 x 2 & 1 x 3		3 x 1

*Notes:*

Each cell contains information on the number of locations and number of samples in each location (i.e., 1 x 3 means one location with three samples and 3 x 1 means three locations with one sample each)

na - not applicable

\*\* - conventional active samples included Summa canister/TO-15 analysis and on-site analysis with the Hapsite portable GC/MS

NS - No sample: several attempts were made to core 2-inch diameter holes (large enough to accommodate these samplers), but they were not successful, so these samples were not deployed

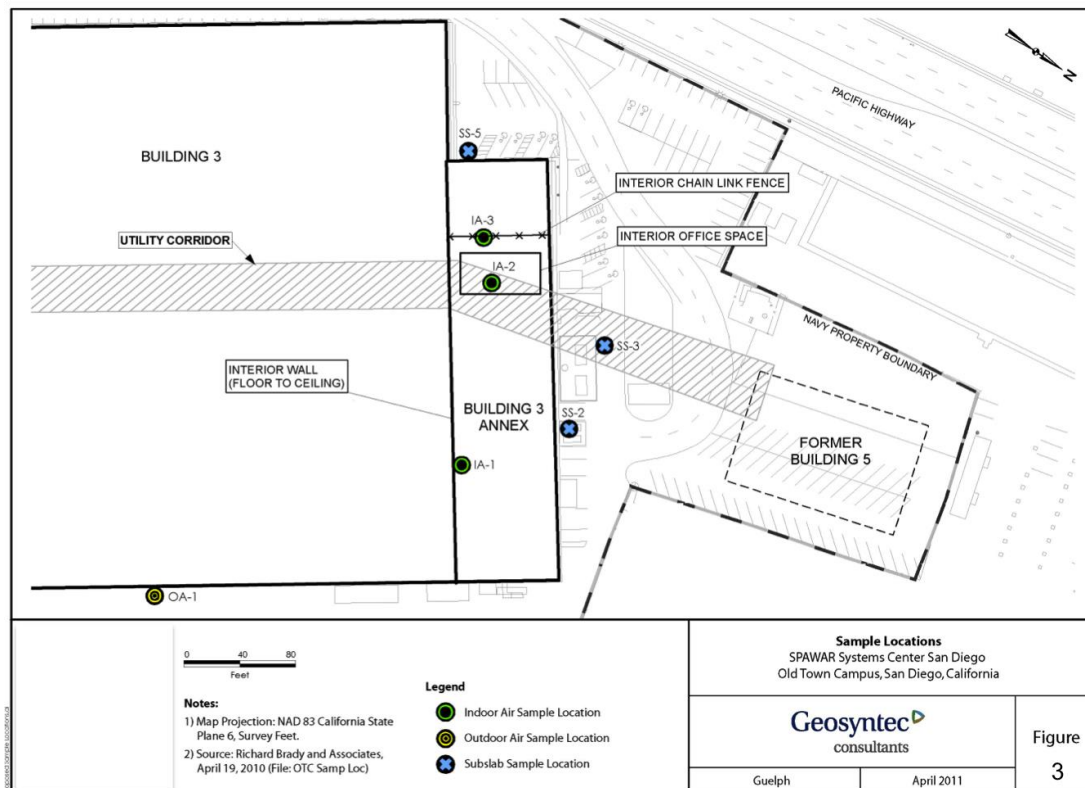
<sup>^</sup> - Flow controllers were set higher than specified, so additional Summa canisters were needed to span the sample period, the results were composited to make triplicate samples

## 2.6 Description of Field Test Sites

The field sampling events were conducted at a total of five locations, some of which were not amenable to sampling of all three media (indoor air, outdoor air and soil gas). A summary of key conditions at each site is provided here and the scope of work performed at each site is described in Chapters 4 and 7.

### 2.6.1 Old Town Campus Building 3 (OTC3), San Diego, CA

The Annex to Building 3 at SPAWAR Systems Center Pacific (SSC-Pac) Old Town Campus (OTC3, Figure 2-1) was used for the first field sampling event in March 2010. Processes inside the building are suspected to have produced waste oils, paint sludge, spent acids, plating materials, and degreasing solvents. Previous site assessments<sup>207</sup> identified the presence of VOCs in groundwater and soil vapor samples near the north end of Building 3. This site was developed using dredged bay sediments as backfill and 95% of the site is covered with buildings or pavement. The water table is a few feet below ground surface, consistent with the close proximity to the Pacific Ocean.



**Figure 2-1:** SSC-Pac OTC3 layout and sample locations (courtesy of Geosyntec Consultants, Inc.)

As an initial verification of the suitability of the site for passive sampler testing, three (3) indoor samples and one (1) outdoor air sample were collected using Waterloo Membrane Samplers (WMS) between December 17, 2009 and January 4, 2010. Trichloroethene (TCE) was detected at concentrations



ranging between 3.3 and 4.6  $\mu\text{g}/\text{m}^3$  in the three indoor air samples, and was not detected above the laboratory reporting limit (0.59  $\mu\text{g}/\text{m}^3$ ) in the outdoor sample.

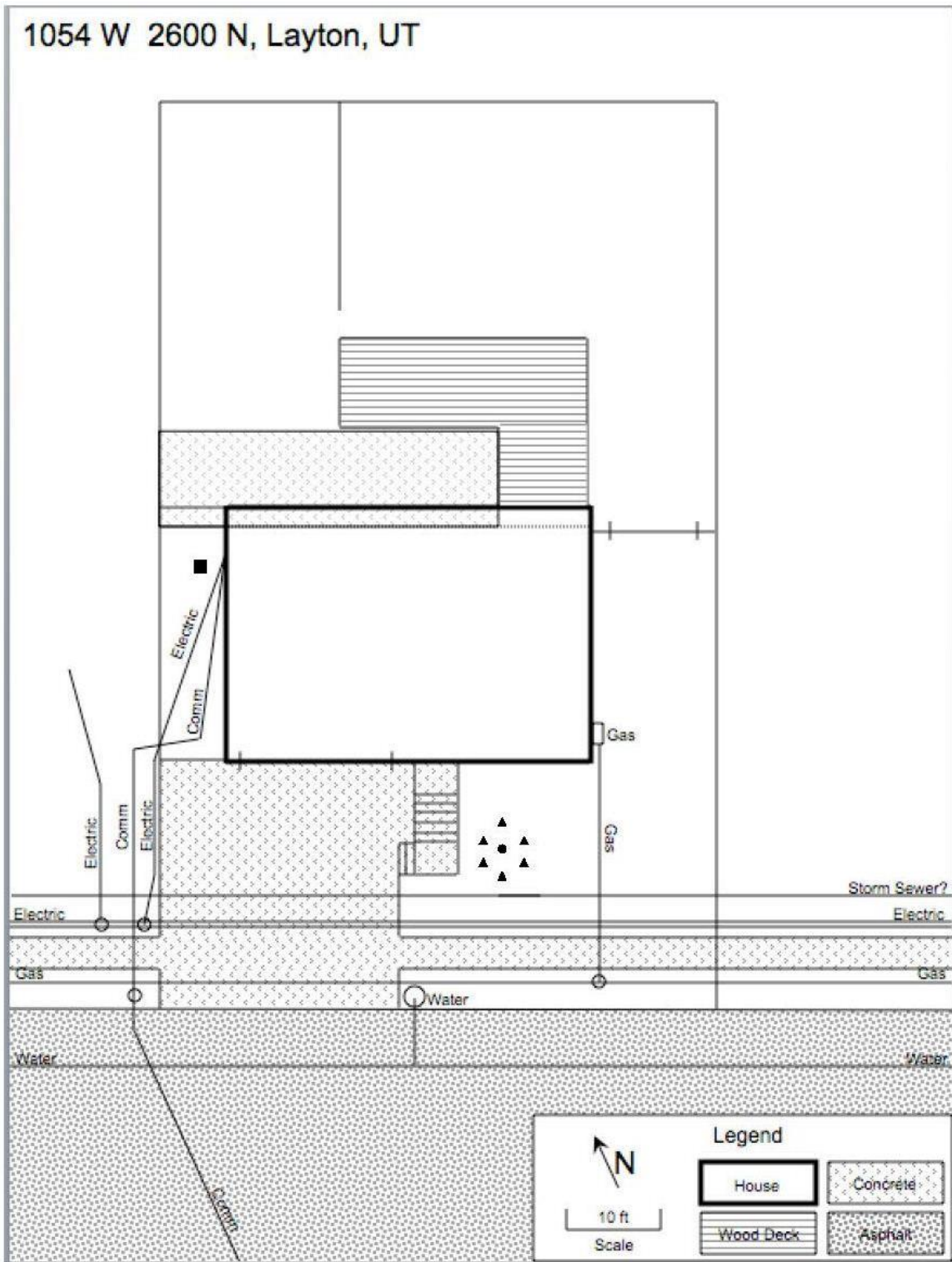
## 2.6.2 SERDP Research House near Hill Air Force Base, Layton, UT

The second field sampling event occurred in July and August 2010 at a residential property currently owned by Arizona State University (ASU) in Layton, Utah, near Hill Air Force Base (Hill AFB) which is being used for vapor intrusion research as part of the Strategic Environmental Research and Development Program (SERDP), Project 1686. For brevity, this is referred to as the Layton house or the Hill AFB site; even though it is actually located hydraulically downgradient of Hill AFB. The building is a single story dwelling with a partially below-grade basement (Figure 2-2). Dissolved TCE and 1,1-dichloroethene (11DCE) are present in groundwater below the building and ASU has confirmed that vapor intrusion of these compounds into the building is occurring.<sup>29</sup> The building is currently uninhabited and is being used for vapor intrusion research. Soil gas data showed a range of VOCs present at concentrations up to 300  $\mu\text{g}/\text{m}^3$  prior to selection of this test site. Passive and active soil gas samples were collected from an array of probes installed in the front yard (Figure 2-3).

The geology of this site and surrounding communities, including Layton, consists of a thin fine sand and silt overburden layer on top of a thick clay layer.<sup>208</sup> This clay layer prevents vertical movement of groundwater and any associated contaminants. The municipal water supplies for the surrounding communities are provided by deep aquifers that are shielded from the shallow contamination by this clay layer and have not reported any issues with water quality related to VOC contamination. Since 1993, investigations have determined that the base's industrial complex had contaminated a large area of groundwater along the southwest boundary and into the communities of Clearfield and Layton.<sup>208</sup> The primary VOCs are TCE and 11DCE. TCE is the most widespread contaminant and occurs in the greatest concentrations.



**Figure 2-2:** Front view of ASU vapor research house in Layton, UT



- conventional soil gas probe location
- ▲ passive soil gas probe locations

**Figure 2-3:** Locations of passive soil vapor sample at the Layton house (base map courtesy of Arizona State University)

### 2.6.3 USACoE Cold Regions Research and Engineering Lab, Hanover, NH

The main Laboratory and Laboratory Addition at the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) facility in Hanover, New Hampshire (Figure 2-4) was the site of the third field sampling event in November 2010. CRREL was established in 1961 by the U.S. Army Corps of Engineers to research and develop equipment and procedures for applications in cold regions. The CRREL site is located in the Connecticut River basin, which is approximately 500 ft wide near the site and fluctuates from 380 to 385 ft above mean sea level.<sup>209</sup> Groundwater flow at the site is controlled by a high permeability esker along the Connecticut River. This esker is surrounded by an area of less permeable lake sediments and the entire area is underlain by irregularly fractured bedrock composed of schistphyllite.<sup>206</sup> The hydraulic conductivity of the esker material based on *in-situ* pumping tests is approximately 283 ft/day, while that of the lake sediments is 57 ft/day.<sup>206</sup>

TCE was used on the site as a refrigerant during the 1960s until the late 1980s. In 1970 a 10,000 gallon underground storage tank (UST) containing TCE near the main laboratory building and laboratory addition released liquid TCE. CRREL has been operating under a New Hampshire Department of Environmental Services (NHDES) Groundwater Management Permit since July 9, 2004. CRREL currently has air strippers at four of its five groundwater production wells, used for non-contact cooling, to treat the water before use in the facility. Previous sampling indicated TCE in indoor air at concentrations ranging from about 10 to about 100  $\mu\text{g}/\text{m}^3$  and in soil gas samples at concentrations several orders of magnitude higher. These concentrations are well within the detection ranges for the candidate passive samplers, therefore making CRREL a viable candidate site for the research conducted, which included indoor and outdoor air monitoring and sub-slab soil vapor sampling in a flow-through cell.

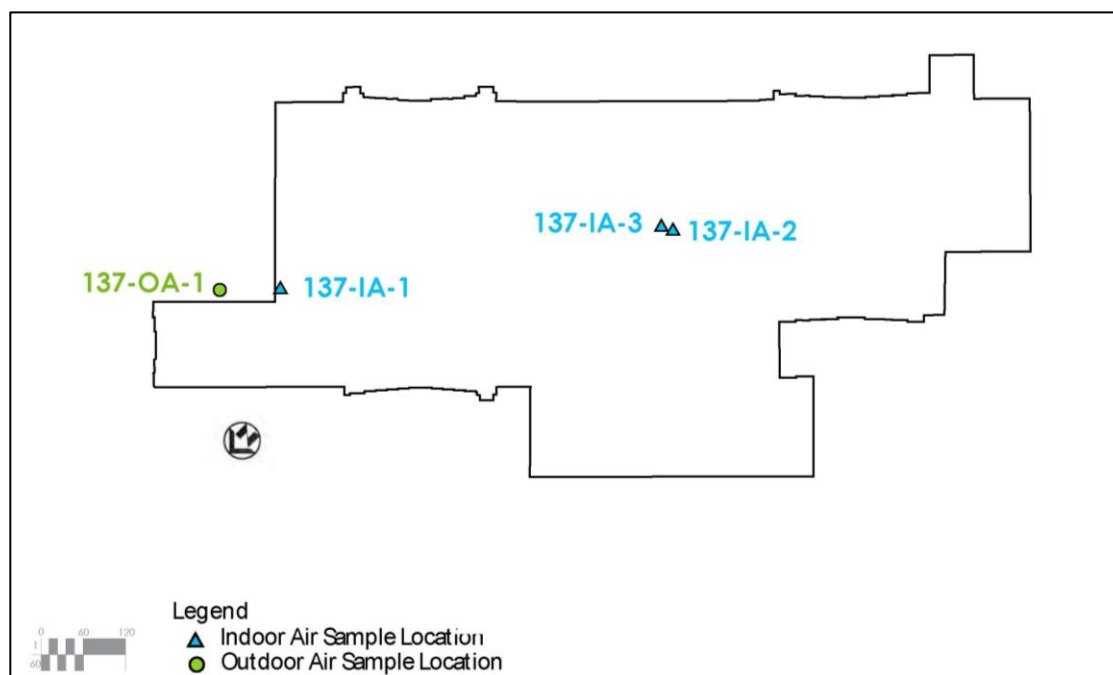


**Figure 2-4:** CRREL facility and laboratory location (photo courtesy of CRREL)

## 2.6.4 Marine Corps Air Station (MCAS), Cherry Point, NC

Building 137 at MCAS Cherry Point (Figure 2-5) was used for the fourth field sampling event in January, 2011. Building 137 is part of Operable Unit (OU) 1 and is referred to as Site 51 under the Federal Facilities Agreement. OU1 is an industrial area in the southern portion of the base and the former plating operations in Building 137 are suspected to have contributed to the OU1 Central Groundwater Plume (a combination of 6 source sites).

The geology of MCAS Cherry Point is primarily composed of Coastal Plain sediments and unconsolidated marine sediments of alternating sands and clays with occasional shell beds and phosphatic sands.<sup>210</sup> Bedrock is encountered at approximately 200 ft below ground surface, while the water table is generally consistent with mean sea level (approximately 15 to 30 ft bgs). The hydraulic conductivity of the clay/silt layers ranges from 0.01 to 0.001 ft/day while that of the sand layers range from 10 to 300 ft/day.<sup>210</sup>



**Figure 2-5:** MCAS Cherry Point Building 137 and locations of indoor and outdoor air samples (courtesy Geosyntec)

Soil and groundwater contamination under Building 137 are primarily attributable to source areas around the building. The most prevalent VOCs with the Central Groundwater plume include TCE, vinyl chloride (VC), cDCE, 11DCA, and 11DCE and less prevalent compounds include PCE, 111TCA, 1122PCA, and 12DCA.<sup>211</sup> There are three distinct plumes of TCE present in OU1 and one is located under Building 137. The plume extends from the upper superficial aquifer to the lower surficial aquifer down gradient from Building 137, where it mixes with another TCE plume.<sup>211</sup>



VOCs were previously detected in soil vapor and groundwater samples during on-going remedial investigations being conducted by the Navy. Two (2) indoor air samples were collected for verification of VOC concentrations using 3M OVM 3500™ samplers between November 3 and 4, 2010 in the northern area of Building 137. TCE, 111TCA, 11DCA, benzene, toluene and xylenes were detected at concentrations ranging between 1.8 to 40  $\mu\text{g}/\text{m}^3$  in the two indoor air samples. Based on these results, the northern corner of Building 137 was identified as a viable field demonstration site for the collection of indoor air samples. No sub-slab or soil vapor samples were collected.

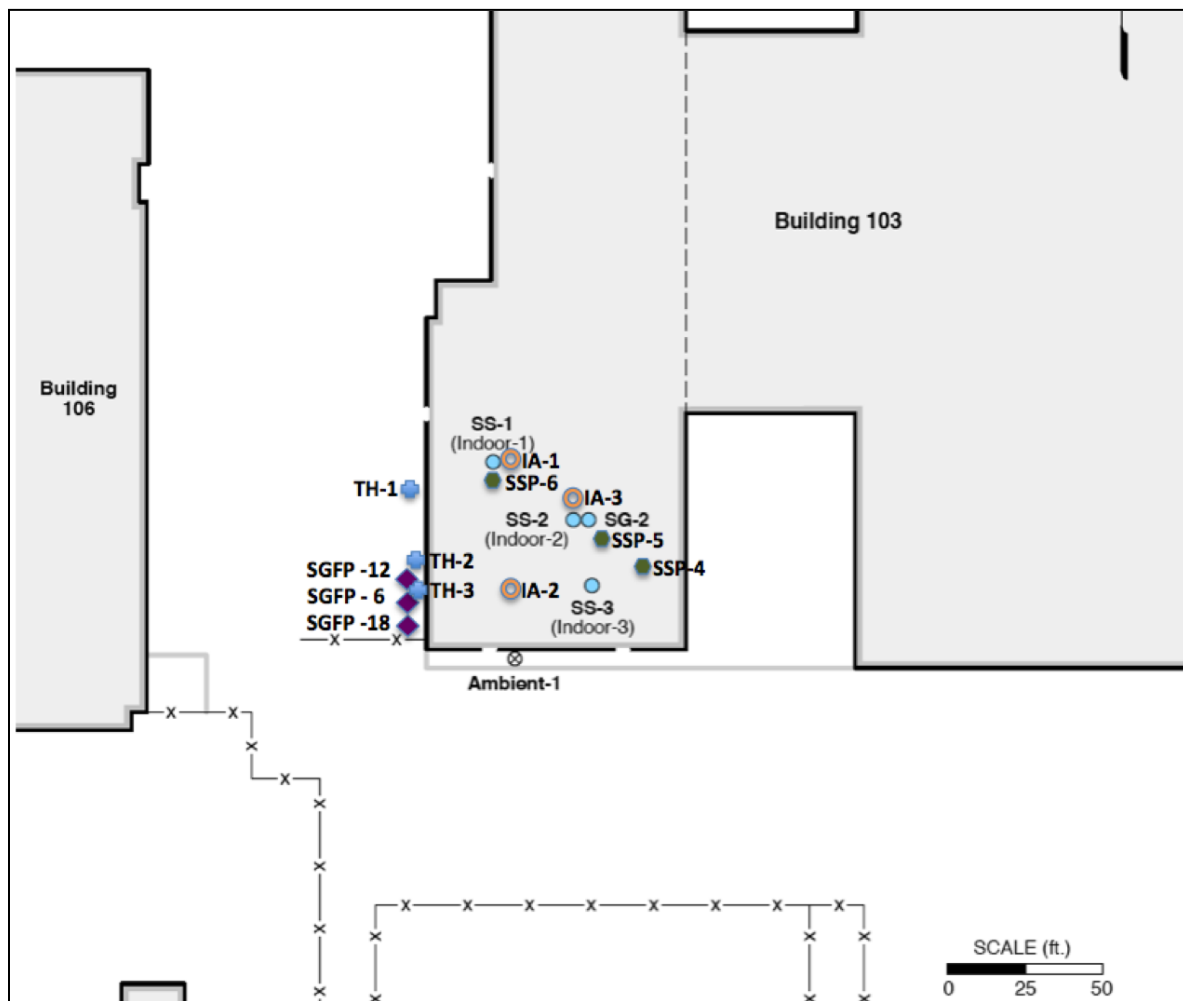
### 2.6.5 Naval Air Station (NAS), Jacksonville, FL

Naval Air Station Jacksonville (NAS JAX), located in Jacksonville, Florida was used for the fifth field sampling event in January 2011. The Five-Year review<sup>212</sup> describes Operable Unit (OU) 3 as a 134-acre site with a former dry cleaner operation. The majority of OU3 was recently re-paved. OU3 is underlain by inter-bedded layers of sand, clayey sand, and clay. The water table at OU3 is located within a few feet of ground surface. Groundwater Services Inc.<sup>213</sup> performed an assessment of soil vapor concentrations and reported elevated VOC concentrations within soil and groundwater in the vicinity of Building 103. The primary contaminants of concern are PCE, TCE, and related degradation products (cDCE and VC).



**Figure 2-6:** Southwest corner of Building 103, NAS JAX

The demonstration was conducted inside and immediately outside the southwest corner of Building 103 (Figure 2-6). Exterior soil gas samples were collected from three probes and one temporary uncased hole within 10 feet (3 m) of the southern corner of the building and within a few feet of the west wall. Sub-slab samples were collected near locations SS-1, SS-2 and SS-3 in Figure 9. No indoor or outdoor air comparison testing was performed. The building is slab-on-grade with a concrete foundation and was constructed in stages beginning in the 1940s. The investigation focused on the southwest corner, which is closest to the areas of TCE, PCE, and degradation products in soil and groundwater. A diagram of NAS JAX Building 103 with sampling locations from a previous assessment by GSI<sup>210</sup> is shown in Figure 2-7.



**Figure 2-7:** NAS JAX Building 103 plan showing locations of previous sub-slab (SS-1, 2 and 3) and soil gas (SG-2) probes installed by GSI, as well as new passive soil gas probes (SGFP-6, -12 and -18) and temporary holes (TH-1, 2 and 3) (modified from GSI<sup>210</sup>)

## 2.7 Performance Objectives

The performance of the passive samplers is primarily defined by their accuracy and precision for VOC vapour concentration measurements. Cost is also an important factor. These three factors are quantitative. Ease of use relative to conventional sampling methods is a qualitative parameter that is also of practical importance. These objectives and the metrics and criteria for evaluating them are described in more detail below and summarized in Table 2-2.

### 2.7.1 Accuracy of VOC Vapor Concentrations

The accuracy of the passive samplers was evaluated by comparing the concentrations of VOCs in indoor air, outdoor air, and soil gas to the results of samples taken by conventional, currently accepted methods (Summa canister sampling and analysis by EPA Method TO-15, as well as pumped ATD tube sampling and analysis by EPA Method TO-17). The two values were compared using the relative percent difference (RPD), which is defined as:

$$RPD = \frac{\text{difference between two numbers}}{\text{average of the two numbers}} \quad (2-1)$$

The generally accepted RPD for TO-15 analysis is <25%, although this is considered fairly generous. An additional margin was added to account for the fact that the passive and active samples were analyzed by different methods and typically at different laboratories than the conventional samples (the average RPD in the inter-laboratory testing program was about 26%). Therefore, the accuracy performance criterion for indoor and outdoor air samples was RPD < 45%. Soil vapor sampling generally shows more spatial variability than indoor air sampling because the vapor distribution in the subsurface is not as well-mixed, so the criterion was relaxed to RPD < 50%.

The concentrations of VOCs were tested over a very wide range so the results were generally presented as normalized or relative concentrations:

$$\frac{C}{C_0} = \frac{\text{passive sampler concentration}}{\text{active sampler concentration}} \quad (2-2)$$

It should be noted that an RPD of +/-45% corresponds to C/C<sub>0</sub> values between 0.63 and 1.58 and an RPD of +/- 50% corresponds to C/C<sub>0</sub> values between 0.5 and 1.67.

Conventional sampling methods for VOC concentrations in indoor air (TO-15 and TO-17) are generally limited to sample durations of 24-hours or less, and available data indicate that 24-hour samples often show temporal variability of up to 10 times compared to long-term average indoor air concentrations.<sup>214,215</sup> Passive samplers are capable of longer sample durations, which can reduce the temporal variability inherent in the data compared to 24-hour samples.<sup>216</sup> Therefore, passive samplers may provide a better representation of long-term average exposure point concentrations than conventional methods even if the accuracy is not within the accuracy performance criterion.

### **2.7.2 Precision**

Precision is a measure of the variation that may be expected within a group of measurements that should ideally be identical. U.S.EPA Method TO-15 specifies a target of < 30% relative standard deviation (RSD, which is also known as the coefficient of variation [COV] and is equal to the standard deviation divided by the mean x 100%) for instrument calibration. The precision performance criterion was therefore set to be a COV < 30% for indoor and outdoor air samples. For soil vapor sampling, the criterion was to have COV for the passive samples similar to the COV of conventional samples and <30% where practical.

### **2.7.3 Cost**

The cost comparison was based on the cost for passive sampler purchase and shipping, laboratory analysis and time spent by trained professionals to deploy and collect a sample. It is also important to consider the extra costs for regulatory agencies to approve sampling with passive samplers as an acceptable investigation method. Regulatory acceptance of new technologies typically requires some comparison to conventional methods until sufficient comparisons are available to provide the agencies with adequate assurance of the performance of the new method. Therefore, the cost estimate for passive sampling included inter-method verification samples using conventional Summa canisters at a frequency of 1 in 10 for all media (indoor and outdoor air and soil vapor). This strategy also provides data to derive field-calibrated uptake rates for the passive samplers under the specific conditions of the sampling event, which would improve the accuracy of the uptake rates compared to vendor-supplied values from chamber tests under potentially different conditions; therefore, it may be a good practice even if not required for regulatory approval.

### **2.7.4 Ease of Use**

Ease of use was evaluated based on a comparison of the passive samplers to the conventional sampling methods, including observations for each sampler type and each sampling medium.



**Table 2-2:** Summary of Performance Metrics and Criteria

Performance Objective	Data Requirements	Performance Criteria
Accuracy of VOC vapor concentration quantitation in soil gas, indoor air and outdoor air.	Concentration measurements using each of the candidate passive samplers and Summa canisters as control, with sufficient samples to assess the effects of the key factors	Assessed using Relative Percent Difference (RPD) compared to a “standard” (e.g., passive sampler compared to Summa canister). Within a single method and lab, an RPD <25% is typically considered acceptable, and this is usually easily achieved. The passive samplers were analyzed using different methods and in different laboratories than the Summa canisters, so an additional margin was needed for the criterion. The inter-laboratory test showed an average RPD of 26% between labs. Therefore, passive sampler concentrations with RPD <45% of the corresponding active sample concentrations were considered valid for indoor and outdoor air. For soil gas sampling, spatial variability tends to be greater than in indoor or outdoor air sampling, so an RPD <50% was considered valid.
Precision	Replicate sampling to allow calculation of the coefficient of variation (COV, standard deviation divided by the mean), a.k.a Relative Standard Deviation (RSD)	Precision: a coefficient of variation (COV) of <30% is considered acceptable for EPA Method TO-15 for instrument calibration. Therefore, COV <30% was considered valid for indoor and outdoor air. For soil vapor sampling, the COV for the passive samplers should be similar to the COV for conventional active samples.
Cost	Professional time required for sampling, analytical fees for analysis, material and shipping charges	Cost reduction compared to conventional methods that is sufficient to justify potential costs associated with additional QA/QC that may be needed to support regulatory acceptance of the passive samplers.
Ease of use	Feedback from field personnel with practical experience on usability of technology	Limited training required for obtaining high quality data. Indoor air sampling no more difficult than a Summa canister. Soil vapor sampling no more difficult than active soil vapor sample collection.

### 3 Laboratory Chamber Tests (Low Concentration Range)<sup>3</sup>

Laboratory testing was conducted to simulate passive sampler performance for indoor and outdoor air sampling. These tests were conducted under controlled conditions for 10 VOCs, including some compounds expected to pose challenges (naphthalene, methyl ethyl ketone). Tests included a range of 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<sub>v</sub>]) and sample durations (1 to 7 days). These conditions were selected to challenge the samplers across a range of conditions likely to be encountered in indoor and outdoor air field sampling programs. The low concentration laboratory tests were performed at Air Toxics Limited in Folsom, CA, under the direction and supervision of the author of this thesis and with review by the Technical Review Panel listed in Section 1.6.

#### 3.1 Experimental

##### 3.1.1 VOCs Included in Laboratory Testing

The list of VOCs included in the low concentration laboratory tests was selected to represent common VOCs and span a range of properties (Table 3-1). The list includes chlorinated ethenes, ethanes, methanes, and aromatics, as well as benzene, naphthalene, hexane, and 2-butanone (or methyl ethyl ketone, MEK). Many other compounds pose a potential concern for vapor intrusion; however, most have properties (vapor pressure, solubility and solid phase partitioning) within the range represented by these 10 compounds, which makes this list representative for comparison testing purposes. The supply gas mixtures were custom-fabricated by Air Liquide America Specialty Gases LLC of Santa Fe Springs, CA, at a concentration of 10 ppm for all of the compounds listed in Table 3-1 except naphthalene, which has a much lower vapor pressure and was therefore present in the mixture at a concentration 10 times lower than the other compounds (1 ppm) to prevent it from condensing in the cylinder.

The uptake rates for the 10 VOCs included in the chamber tests for each of the five passive samplers are shown in Table 3-2. Uptake rate were provided by the passive sampler vendors, except values in italics with an asterisk, which were were calculated from the uptake rates of compounds with similar properties.

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<sup>3</sup> The contents of this Chapter are based on the author's article in submission to ES&T<sup>228</sup>

**Table 3-1:** Compounds tested and their key properties

Analyte	Koc (mL/g)	Henry's Constant @ 25 °C (unitless)	Vapor pressure (atm)	Free Air Diffusion Coefficient (cm <sup>2</sup> /s)	Water solubility (g/L)
1,1,1-Trichloroethane (111TCA)	135*	0.70	0.16	0.078	1.3
1,2,4-Trimethylbenzene (124TMB)	1350	0.25	0.0020	0.061	0.057
1,2-Dichloroethane (12DCA)	38*	0.048	0.11	0.104	8.5
2-Butanone (MEK)	2.3	0.0023	0.10	0.081	220
Benzene (BENZ)	61*	0.23	0.13	0.088	1.8
Carbon tetrachloride (CTET)	152*	1.2	0.15	0.078	0.79
Naphthalene (NAPH)	1540	0.18	0.00012	0.059	0.031
n-Hexane (NHEX)	143	68	0.20	0.20	0.00012
Tetrachloroethene (PCE)	265*	0.75	0.024	0.072	0.20
Trichloroethene (TCE)	94*	0.42	0.095	0.079	1.5

\*Values drawn from: [http://www.epa.gov/superfund/health/conmedia/soil/pdfs/appd\\_k.pdf](http://www.epa.gov/superfund/health/conmedia/soil/pdfs/appd_k.pdf)

All other values from [http://www.epa.gov/oswer/riskassessment/airmodel/johnson\\_ettinger.htm](http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm)

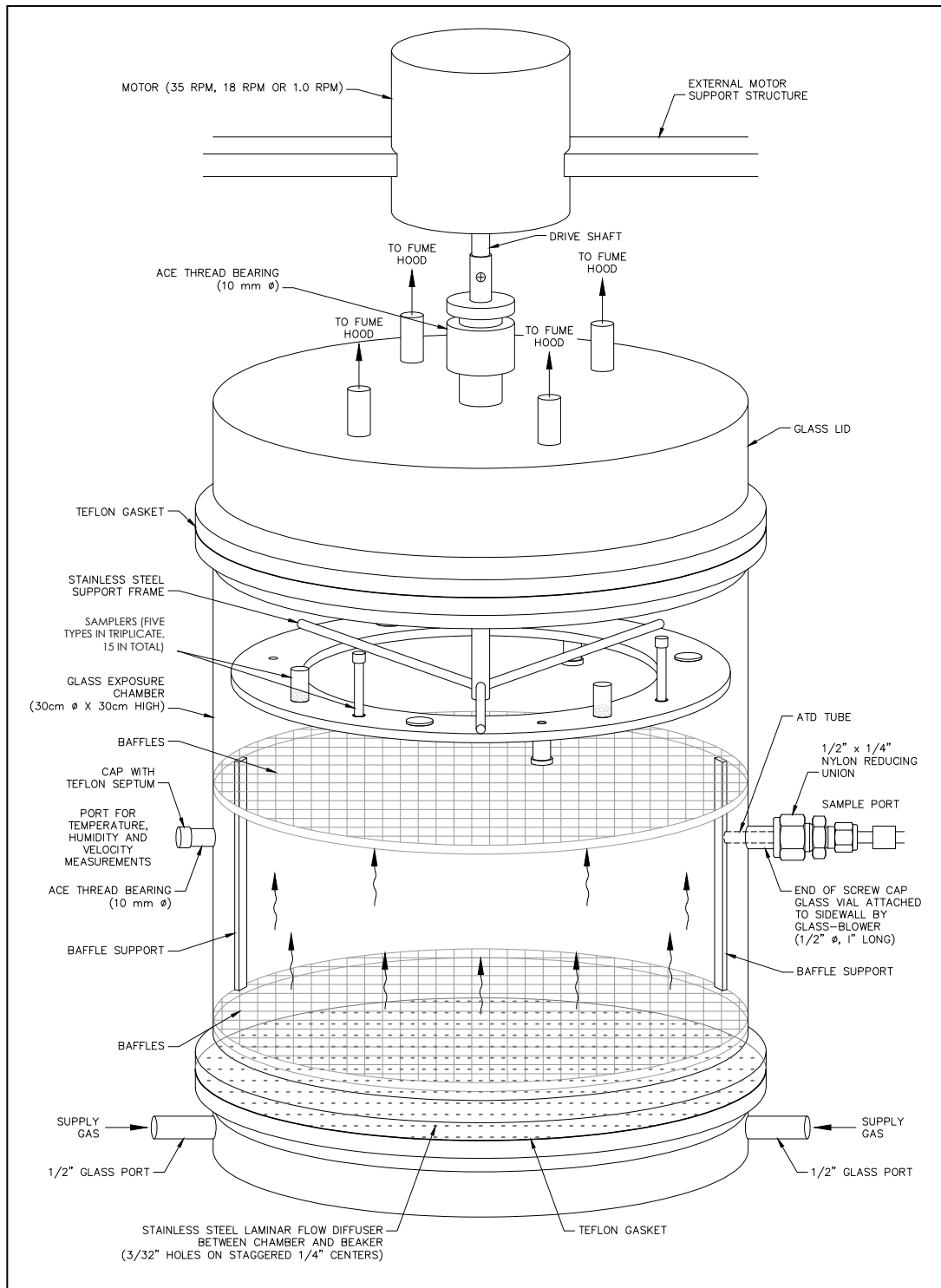
**Table 3-2:** Uptake rates for the passive samplers

Analyte	WMS	Radiello	SKC Ultra	ATD Tube
1,1,1-Trichloroethane (TCA)	1.3	62	14	0.50*
1,2,4-Trimethylbenzene (124TMB)	13*	50	12	0.62
1,2-Dichloroethane (12DCA)	2.6	77	13	0.50*
2-Butanone (MEK)	1.3	79	17	0.50*
Benzene (BENZ)	2.2	80	16	0.35*
Carbon Tetrachloride (CTET)	1.5	67	14	0.50*
n-Hexane (HEX)	1.3*	66	14	0.50
Naphthalene (NAPH)	26*	25	13*	0.50*
Tetrachloroethene (PCE)	5.4	59	13	0.41
Trichloroethene (TCE)	3.3	69	15	0.50*
* - calculated value				

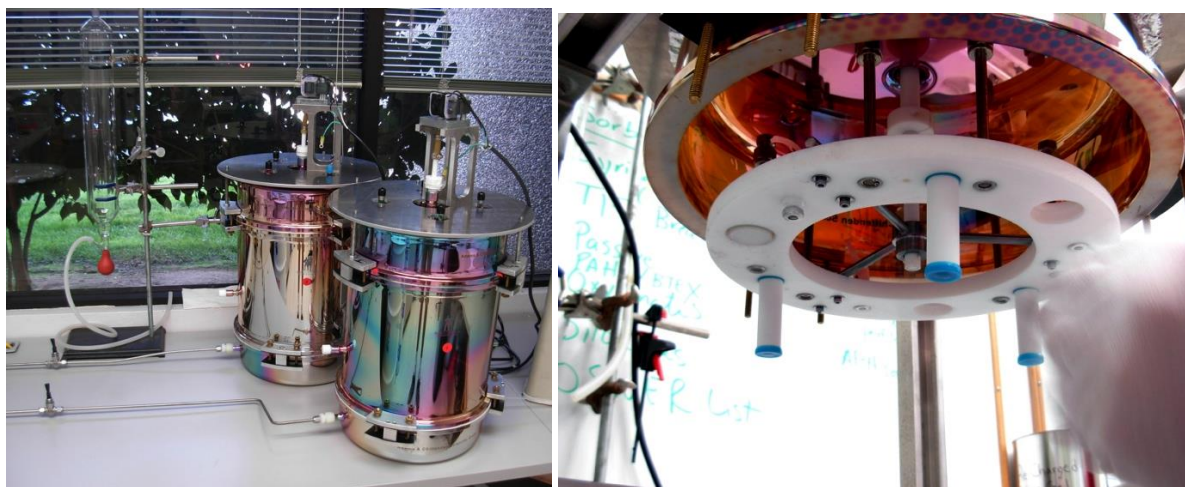
### 3.1.2 Apparatus

The low concentration laboratory testing apparatus consisted of a system to purify, humidify and control the temperature of a supply of up to 40 L/min of air (sufficient for two exposure chambers to operate in parallel at the same time). Activated carbon filtration was used to purify the air inside the laboratory (which was verified by sampling and analysis to contain none of the target VOCs at detectable concentrations) and VOCs were added to the purified air stream from supply gas in compressed gas cylinders. Mass flow controllers were used to deliver the gas from the cylinders and the purified air at flow rates required to achieve the target concentrations of 1, 50 or 100 ppb<sub>v</sub> (0.1, 5 and 10 ppb<sub>v</sub> for naphthalene). Humidity was controlled by passing a portion of the air stream through a glass vessel containing water and a magnetic stir-bar for agitation. For high humidity conditions, the glass vessel and downstream piping were heated slightly to minimize condensation. Process flow diagrams for the apparatus for both conditions are in Appendix B.

Each exposure chamber consisted of a glass cylinder with removable top and bottom glass end caps to allow the chamber to be disassembled for easy cleaning. Each chamber was approximately 30 cm in diameter to accommodate 15 passive samplers (5 types, each in triplicate) in a circular Teflon manifold designed to be rotated at a constant speed to control the face velocity and allow sufficient distance between the samplers to minimize competition between the samplers. Baffles were installed inside the chambers to promote one-dimensional upward flow of gas to the samplers, and minimize the creation of a rotational gas flow inside the chamber (gas rotation in the chamber would reduce the effective face velocity to which the samplers were exposed). The chamber materials were all passivated using the Siltek process by Restek Corporation of Bellefonte, PA to coat the surfaces with silicon hydrides and make them as inert as practicable to minimize adsorption and desorption of VOC vapors during the experiments. The design details of the chamber are shown in Figure 3-1. Photographs of the apparatus are provided in Figures 3-2 and 3-3.



**Figure 3-1:** Design details of the exposure chamber for the low concentration tests (courtesy of Geosyntec)



**Figure 3-2:** Assembled chambers and close-up of the rotating carousel (photos courtesy of Air Toxics Ltd.)



**Figure 3-3:** Low concentration test apparatus, including (left to right): compressed gas cylinders containing 10 VOCs, drum of activated carbon for purifying dilution air, humidification vessel, mass flow controllers, exposure chambers (covered with insulation), constant temperature bath, and discharge lines to fumehood (photo courtesy of Air Toxics Ltd.)

The VOC-fortified and humidified supply gas was fed into the bottom of the chamber and flowed upward through a stainless steel plate with 3/32-inch holes drilled on ¼-inch centers (staggered) to distribute the flow uniformly through the chamber. The cylinder above the diffuser plate was the main body of the chamber and it had two sampling ports added by a glass-blower; one to allow access for measuring the concentration inside the chamber with active sampling methods (pumped ATD tubes), and a second for monitoring temperature and relative humidity. The temperature and relative humidity were monitored with a HygroPalm 1 from Rotronic International of Basserdorf, CH with a SC05 probe. The chamber also had a removable lid, which had an exit manifold in the form of a glass ring around the top, as well as a hole in the middle of the lid, through which the rotating frame supporting the samplers was hung.

The supply gas was fed through the chamber at a rate of about 10 L/min, which was selected to provide sufficient mass flux such that the uptake by the samplers would be negligible compared to the flux through the chamber. This was verified by monitoring concentrations at the influent and effluent end of the chamber during the experiments, which were found to be within about 5%. The corresponding linear velocity of the gas flow was about 0.002 m/s, which was slow enough to be negligible compared to the face velocity generated via the rotating sampler support frame. The samplers were rotated at 1.0, 18 or 35 rpm using one of three rotisserie motors (Models 3M101 and 3M099 by Dayton Electric Motors of Chicago, IL and Master Chef Model 85-1850-8 by Winners Products Engineering, Ltd. of Hong Kong) placed on top of the frame to achieve face velocities of 0.014, 0.23, and 0.41 m/s. Each of the five different types of samplers (A, B, C, D and E) were arranged in triplicate in the order of A, B, C, D, E, A, B, C, D, E, A, B, C, D, E for each chamber. One chamber was dedicated to the 1 ppb<sub>v</sub> testing, and was not used for testing at higher concentrations to avoid carry-over (desorption of test compounds from the inner surfaces).

### **3.1.3 Familiarity Testing**

Familiarity testing (testing to demonstrate control over the experimental equipment and variables) was performed to assess whether the experimental conditions could be controlled to meet the design values of all of the factors (temperature, humidity, face velocity, concentration and sample duration). The face velocity was controlled by the rotisserie motors and the sample duration (1 to 7 days) was controlled by a stopwatch, both of which were easily controlled with no significant variability or bias. The concentrations were controlled by mass flow controllers on the purified air and supply gas tanks, and also showed minimal variability (less than about 10%), which was verified by comparison of successive samples collected using pumped ATD tubes and analyzed by EPA Method TO-17 (described in Appendix A).

During the familiarity testing, some samples were also collected by Summa canister for analysis by EPA Method TO-15 to verify the active ATD tube method. Only two passive sampler types were included during the familiarity testing, which were the ATD samplers with Tenax TA and Carbopack B, to provide initial insight into the differences in performance for the two sorbents for the 10 test compounds.

Temperature and humidity were more challenging to control as they were interdependent. For example, condensation occurred during an attempt to combine 90% humidity with 10 °C temperature. After several days of testing, the temperature range was adjusted from the initial target levels of 10 to 30 °C to a more readily achievable range of 17 to 28 °C. Relative humidity set points were maintained at the initially-planned levels of 30, 60 and 90% RH.

### 3.1.4 Intra and Inter-Laboratory Testing

Several laboratories were used in this study so inter-laboratory and intra-laboratory variances were evaluated by a two-sample inter-laboratory study (a.k.a., a Youden pair experiment) as described by Wernimont and Spendley<sup>217</sup> and Miller and Miller<sup>218</sup>. The inter-laboratory testing consisted of exposing two sets of triplicates of each of the five passive samplers to VOCs at the midpoints of concentration (about 50 ppb<sub>v</sub>, except for naphthalene at 5 ppb<sub>v</sub>), temperature (about 22 °C), humidity (about 60% RH), face velocity (0.23 m/s) and sample duration (4 days) in the exposure chamber and sending two of each sampler to three different laboratories for analysis (Table 3-3).

**Table 3-3:** Intra and inter-laboratory testing scheme

Sampler Type	Primary Laboratory	Secondary Laboratories
WMS	University of Waterloo	Air Toxics Ltd
		Airzone One
ATD Tubes with Tenax TA	Air Toxics Ltd	Columbia Analytical Services
		University of Waterloo
ATD Tubes with CarboPack B	Air Toxics Ltd	Columbia Analytical Services
		University of Waterloo
SKC Ultra	Columbia Analytical Services	Air Toxics Ltd
		Airzone One
Radiello	Fondazione Salvatore Maugeri	Columbia Analytical Services
		Air Toxics Ltd



### 3.1.5 Center-point Testing (ANOVA testing)

Six (6) identical chamber tests were performed to assess the intrinsic (random) variability in the concentrations measured by the passive samplers, and not caused by changes in the 5 key factors, since all five factors were held constant at their central values. Each chamber test included all five candidate samplers in triplicate. Two additional chamber tests were performed with all five 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 these two tests were compared to the results of the initial six center-point tests and the means were within 13% RSD for all compound and samples on average, so the results of all 8 center-point tests were used together in all subsequent statistical analyses.

The concentrations reported for each of the sampler types were compared to the results of active sampling and analysis by pumped ATD tubes and EPA Method TO-17 to evaluate whether the passive sampler results were statistically different than the active sample controls for each of the 10 compounds and each of the 5 samplers using analysis of variance. The data were analyzed to assess precision by calculating the COV among replicate samplers (three per chamber for each type) and accuracy by comparing the passive sampler results to active (pumped ATD tube/TO-17) sampler results.

### 3.1.6 Fractional Factorial Testing

The effect of each of the five main factors (temperature, humidity, concentration, face velocity and sample duration) was evaluated by conducting chamber tests at high and low levels of each factor. The design of this test was a  $2^{(k-1)}$  fractional factorial design (one-half of a full  $2^k$  full factorial design, where  $k$  is the number of controllable factors). This design can be used to assess whether the controllable (main) factors picked for the study (under the conditions specified) have an effect (the main effects) upon the response(s). This design does not resolve interactions between the main effects for the five factors tested. Each analyte relative concentration (passive sampler concentration divided by active sampler concentration, or  $C/C_0$ ) represents a response. Eighteen (18) different chamber tests were performed by systematically changing the key factors to assess the variability for each of the five samplers attributable to each of the five key factors (including two center-point tests in the middle, as described above), following the sequence shown in Table 3-4.

**Table 3-4:** Fractional factorial testing run scheme

Run #	Approximate Concentration (ppbv)	Approximate Temperature (°C)	Face Velocity (m/s)	Duration (days)	Approximate Humidity (%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

The data from these tests were compiled and reviewed as they became available 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, so the sampler was modified to use a thermally-desorbable sorbent (Carbopack B) for these conditions to increase sensitivity and subsequent low concentration/short duration runs (i.e., runs 12 and 18) provided detectable results.

## 3.2 Results and Discussion

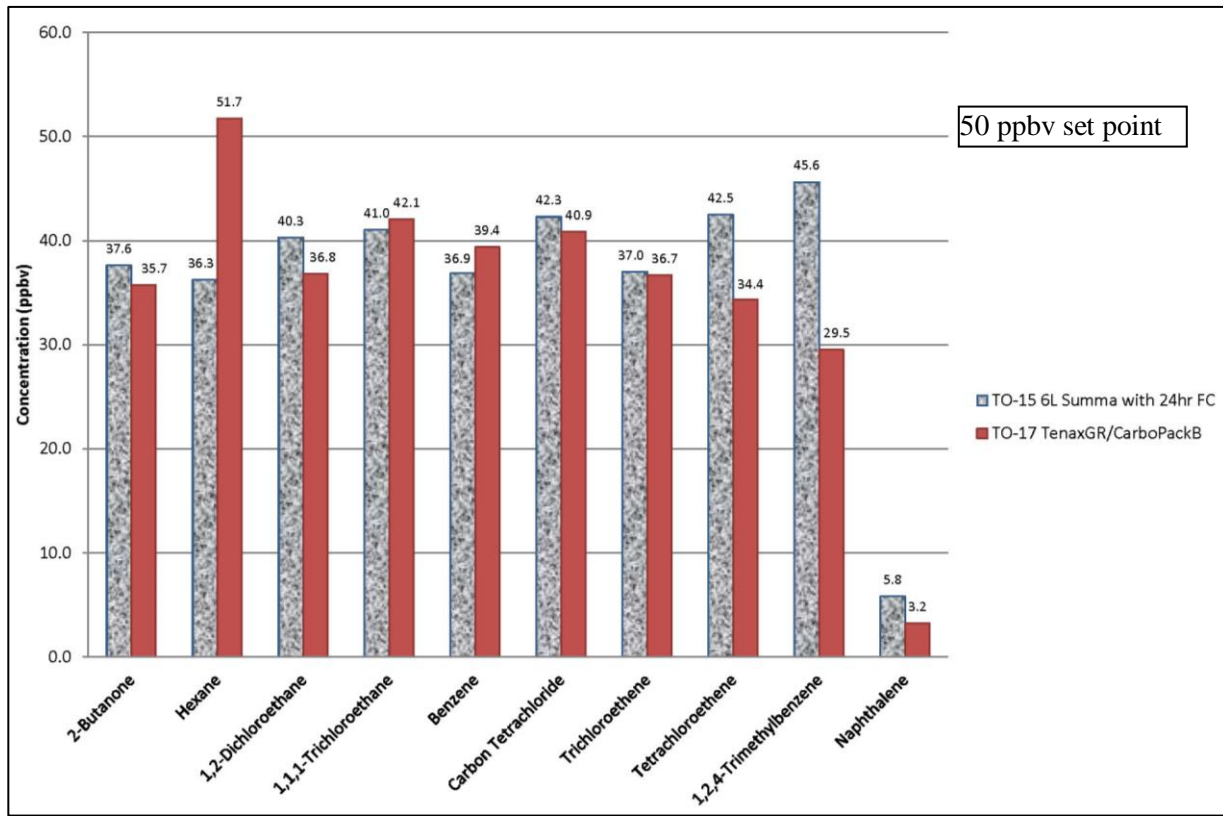
### 3.2.1 Familiarity Test Results

During familiarity testing, relative humidity values ranged from about 68 to 54% with a target value of 60%, which was roughly 10% variation from the set-point of 60% RH. Temperature values ranged from about 22.8 °C to about 19.2 °C, a range of 3.6 °C and an average slightly below the set-point of 22 °C. Additional insulation was added to the experimental apparatus after the familiarity testing to provide better control over the humidity and temperature during the fractional factorial and center-point tests.

During the familiarity testing, active samples were collected using the port directly opposite the calibration gas entrance and also immediately below the samplers on the same side as the calibration gas entrance. The concentrations measured at these three sampling ports confirmed uniform vapor concentrations within the chamber with an average relative standard deviation of less than 5%.

Additionally, active samples were collected above the chamber carousel at the exhaust port during the 1 ppbv and 100 ppbv chamber tests to verify that the target concentrations were not measurably depleted by the passive samplers. The concentrations measured at the effluent port compared within 5% of the concentrations measured at the side port located below the samplers.

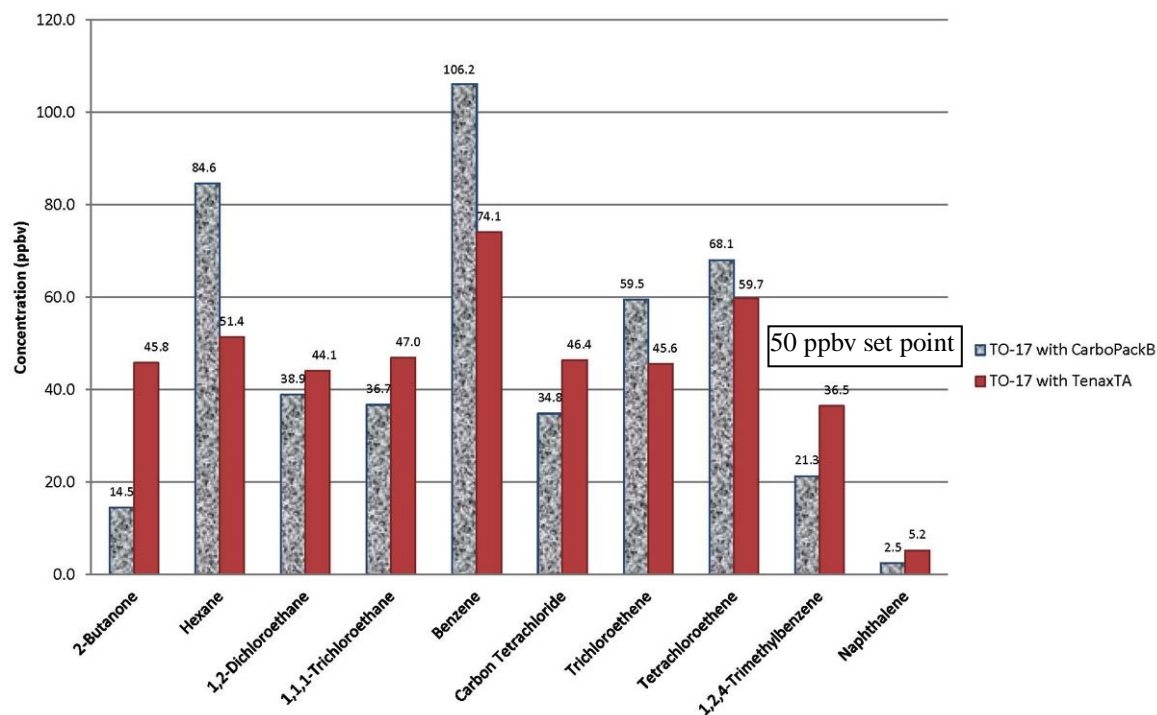
The results for active samples collected from the exposure chamber using Summa canisters and EPA Method TO-15 versus active ATD tubes with a multi-bed sorbent of Tenax GR and Carbopack B analysed by EPA Method TO-17 are shown in Figure 3-4. The concentrations calculated from the mass flow controller settings were 50 ppb<sub>v</sub> for all analytes except naphthalene, which was 5 ppb<sub>v</sub>. Both active sampling methods showed negative or low bias (passive sampler concentrations were lower than expected) for most compounds, likely because the actual concentration in the chamber was lower than planned (~35 to 40 ppbv). This was most likely attributable to imperfect calibration of the mass flow controllers used to blend the stock gas cylinder supply with the purified air. For this reason, all subsequent chamber tests were monitored using active ATD tubes and the passive sampler results were compared to the active ATD tube results, not concentrations calculated from the supply gas dilution. The RPD between the two methods was within the commonly accepted range for duplicates by the same method (+/-25%), except for NAPH (58%), 124TMB (43%) and HEX (35%). All but NAPH met the accuracy performance criterion of 45% RPD for samples collected and analysed by different methods, so the TO-15 and TO-17 results were considered comparable.



**Figure 3-4:** Active sampling: comparison of results using method TO-15 vs. TO-17 during familiarity tests

The results of passive ATD tube sampling inside the exposure chamber during familiarity testing using CarboPack B and Tenax TA are shown in Figure 3-5. Both samplers provided average concentrations close to the set point (52 ppbv for ATD CarboPack and 50 ppbv for ATD Tenax), excluding naphthalene (which was set 10X lower). The RPD between the two methods averaged 42% and met the accuracy performance criterion of +/-45% RPD for all but MEK (104%), HEX (49%), 124TMB (53%) and NAPH (70%). Using the uptake rates in Table 3-3, ATD/CarboPack B showed a high or positive bias (concentrations higher than expected) for benzene and hexane and low bias for MEK, 124TMB and NAPH. The high bias for benzene was most likely attributable to the uptake rate used (0.35 mL/min from Table 3-2). ISO 16071-2 and Subramanian<sup>219</sup> list various uptake rates for benzene on passive ATD samplers in the range of 0.64 to 1.81 mL/min, depending on the sorbent used and sample duration. None of these values match the exact sorbents and duration of this test, but all values are higher than the value used, so the calculated benzene concentration could have been lower by a factor of about 2 or more within

the uncertainty in the uptake rate, which would be closer to the set point. The ATD/Tenax TA results were similar to the active (Summa canister and ATD tube) samples, except for benzene, which also showed high bias, but to a lesser degree. This data demonstrates the sensitivity of the results to the accuracy of the value selected for the uptake rate. The average RPD between the Carbopack B and Tenax samplers was 42%, which was higher than the typical goal for duplicates by the same method (25%). This indicates that even using the same method in the same laboratory, the performance assessment of passive sampling must also consider the effect of sorbent selection.



**Figure 3-5:** Passive sampling: ATD Tenax TA vs. ATD Carbopack B during familiarity tests

### 3.2.2 Intra and Inter-Laboratory Test Results

The chamber conditions monitored during the intra and inter-laboratory testing are presented in Table 3-5. The average flow rates of purified air and supply gas were nearly exactly equal to the set-points of 20 L/min and 100 mL/min, respectively. The average temperature was within 0.2 °C of the set-point of 22 °C and the average relative humidity was within 2% RH of the set-point of 60% RH for both chambers; fluctuations were minimal. Active sampler concentrations averaged 99% of the concentrations calculated from dilution of the supply gas and the precision was good (7% COV). Overall, control over the chamber conditions was excellent.

**Table 3-5:** Chamber conditions during inter-laboratory testing

ESTCP Interlab Performance Testing Chamber Conditions							
Date	Time	Air Flow LPM	Cal Flow ccm	Chamber #1		Chamber #2	
				Temp deg C	humidity %RH	Temp deg C	humidity %RH
11-Mar	1726	-	-	22.6	63.6	-	-
	1830	19.91	101	22.4	64.3	22	65.8
	1945	19.96	101.5	22	62.2	21.5	64
12-Mar	610	20.01	101.3	21.9	62.9	21.9	63.3
	1030	19.95	101.2	21.5	63.1	21.4	63.7
	1100	19.95	101.1	21.7	62.6	21.7	62.8
	1130	20	101.3	21.3	63.5	21.2	64
	1213	20	101.3	21.6	62.3	21.6	62.7
	1253	19.98	101	21.2	63.6	21.1	64.2
	1339	20.01	101	21.5	62.6	21.5	63
	1410	19.95	100.8	21.4	62.5	21	64.3
	1527	19.93	100.7	21.5	62.5	21.3	63.1
	1648	19.93	101	21.3	62.7	20.7	64.7
13-Mar	1753	19.93	101.1	21.2	62.6	21.1	62.9
	954	20.02	101.3	21.8	65.2	21.6	66.1
	1209	20.15	101.5	21.6	63.5	21.5	64
	1428	20.04	101.3	21.8	63.2	21.4	64.8
14-Mar	939	20	101.1	22.2	61.9	22	62.7
	1227	19.97	101.3	22.1	67	21.8	68.3 *
	1249	19.96	101.3	22.4	61.5	22.4	61.9
	1608	19.8	100.5	23.4	59.8	23	61.3
	1720	19.77	100.5	23.5	58.4	23.4	58.9
	1815	19.8	100.5	23.2	58.5	23.1	59.2
15-Mar	2020	19.94	101.3	22.6	59.1	22.5	59.4
	615	20.03	101.1	21.9	60.9	21.7	61.9
	710	19.98	101.3	22.1	60.7	21.9	61.5
	825	20.04	101.1	22.4	59.4	22.4	59.9
	1017	20.05	101.4	21.9	59.9	21.4	61.7
	1121	20.03	101.3	22.1	59.5	21.1	59.8
	1214	20.02	101.4	22	60.3	21.9	61.1
	1306	19.93	101.1	22.8	59	22.7	59.6
	1632	19.83	101.1	23.2	58.5	23	59.5
		Average	19.96	101.12	22.07	61.79	21.83

\*Power outage on 3/14 at 1115 for a period of less than a minute  
 Calibration Cylinder: CC316536

The VOC concentrations measured with the passive samplers during the intra and inter-laboratory tests are shown in Table 3-6 and the Youden plots for each VOC are shown in Figure 3-6 (one plot for each compound). The Youden plots show the results of one duplicate versus the second duplicate sample, where each pair was analyzed by the same sampler, method and laboratory. These data all fell close to the ideal correlation line (1:1 slope, zero intercept) and showed average RSDs of 3 to 10%, which indicated that the intra-laboratory variability was very low for all compounds and all laboratories. Each Youden plot also shows the average concentration measured using pumped ATD tube (active) samples for reference.

**Table 3-6: Concentrations measured during inter-laboratory testing**

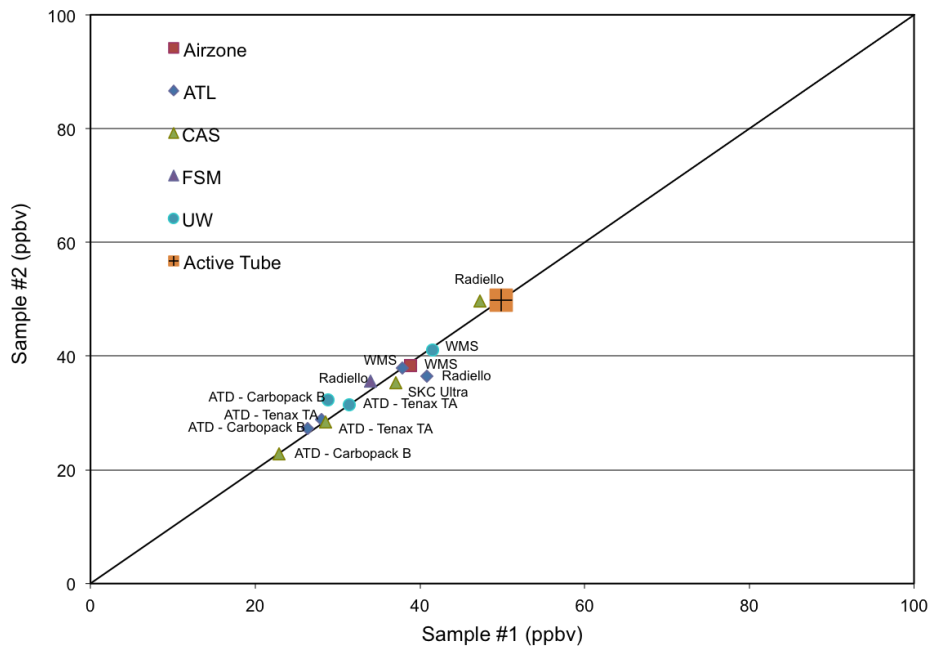
Analyte	Sampler Type	Analytical Laboratory	Sampler #1		Sampler #2	
			ID	Concentration (ppbv)	ID	Concentration (ppbv)
MEK	WMS	UW	PS-C61	46.3	PS-C64	45.2
		ATL	PS-C65	23.3	PS-C66	22.8
		AirZOne	PS-C63	54.6	PS-C62	52.7
	SKC Ultra	CAS	SKC B#2	26.4	SKC B#4	24.8
		ATL	SKC Badge #1	25.0	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarboPackB	ATL	CarboPack B (Chamber 1)	10.6	CarboPack B (Chamber 2)	11.1
		CAS	CarboPack B Chamber 1	4.5	CarboPack B Chamber 2	3.3
		UW	CarboPack B (Chamber 1)	3.6	CarboPack B (Chamber 2)	7.2
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	29.2	Tenax TA (Chamber 2)	29.2
		CAS	Tenax TA Chamber 1	30.2	Tenax TA Chamber 2	30.4
		UW	Tenax TA (Chamber 1)	42.0	Tenax TA (Chamber 2)	40.8
Radiello	FSM	RAD130 #3	13.1	RAD130 #5	12.0	
	ATL	RAD130 #1	11.8	RAD130 #6	11.1	
	CAS	RAD130 #2	13.6	RAD130 #4	13.3	
n-Hexane	WMS	UW	PS-C61	58.9	PS-C64	57.0
		ATL	PS-C65	55.9	PS-C66	52.1
		AirZOne	PS-C63	79.7	PS-C62	60.7
	SKC Ultra	CAS	SKC B#2	44.2	SKC B#4	42.9
		ATL	SKC Badge #1	59.3	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarboPackB	ATL	CarboPack B (Chamber 1)	57.6	CarboPack B (Chamber 2)	56.6
		CAS	CarboPack B Chamber 1	43.3	CarboPack B Chamber 2	41.7
		UW	CarboPack B (Chamber 1)	82.9	CarboPack B (Chamber 2)	83.9
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	31.2	Tenax TA (Chamber 2)	31.2
		CAS	Tenax TA Chamber 1	26.0	Tenax TA Chamber 2	25.8
		UW	Tenax TA (Chamber 1)	41.9	Tenax TA (Chamber 2)	41.9
Radiello	FSM	RAD130 #3	42.8	RAD130 #5	44.7	
	ATL	RAD130 #1	48.3	RAD130 #6	43.6	
	CAS	RAD130 #2	65.5	RAD130 #4	62.0	
1,2-DCA	WMS	UW	PS-C61	41.5	PS-C64	41.0
		ATL	PS-C65	37.9	PS-C66	37.9
		AirZOne	PS-C63	38.9	PS-C62	38.4
	SKC Ultra	CAS	SKC B#2	37.1	SKC B#4	35.3
		ATL	SKC Badge #1	42.5	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarboPackB	ATL	CarboPack B (Chamber 1)	26.4	CarboPack B (Chamber 2)	27.2
		CAS	CarboPack B Chamber 1	22.9	CarboPack B Chamber 2	22.8
		UW	CarboPack B (Chamber 1)	28.9	CarboPack B (Chamber 2)	32.3
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	28.1	Tenax TA (Chamber 2)	28.9
		CAS	Tenax TA Chamber 1	28.5	Tenax TA Chamber 2	28.4
		UW	Tenax TA (Chamber 1)	31.4	Tenax TA (Chamber 2)	31.4
Radiello	FSM	RAD130 #3	34.0	RAD130 #5	35.6	
	ATL	RAD130 #1	40.8	RAD130 #6	36.4	
	CAS	RAD130 #2	47.3	RAD130 #4	49.6	
1,1,1-TCA	WMS	UW	PS-C61	51.6	PS-C64	50.4
		ATL	PS-C65	47.2	PS-C66	44.6
		AirZOne	PS-C63	55.4	PS-C62	48.9
	SKC Ultra	CAS	SKC B#2	29.0	SKC B#4	27.6
		ATL	SKC Badge #1	34.0	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarboPackB	ATL	CarboPack B (Chamber 1)	30.3	CarboPack B (Chamber 2)	30.9
		CAS	CarboPack B Chamber 1	26.8	CarboPack B Chamber 2	25.5
		UW	CarboPack B (Chamber 1)	20.2	CarboPack B (Chamber 2)	23.3
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	32.8	Tenax TA (Chamber 2)	32.8
		CAS	Tenax TA Chamber 1	26.7	Tenax TA Chamber 2	26.4
		UW	Tenax TA (Chamber 1)	44.7	Tenax TA (Chamber 2)	42.8
Radiello	FSM	RAD130 #3	39.1	RAD130 #5	41.3	
	ATL	RAD130 #1	47.8	RAD130 #6	43.2	
	CAS	RAD130 #2	67.2	RAD130 #4	71.8	
Benzene	WMS	UW	PS-C61	48.6	PS-C64	48.8
		ATL	PS-C65	40.1	PS-C66	40.0
		AirZOne	PS-C63	44.6	PS-C62	40.3
	SKC Ultra	CAS	SKC B#2	40.3	SKC B#4	38.2
		ATL	SKC Badge #1	47.1	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarboPackB	ATL	CarboPack B (Chamber 1)	67.7	CarboPack B (Chamber 2)	67.7
		CAS	CarboPack B Chamber 1	62.4	CarboPack B Chamber 2	58.9
		UW	CarboPack B (Chamber 1)	98.4	CarboPack B (Chamber 2)	103.0
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	43.1	Tenax TA (Chamber 2)	43.1
		CAS	Tenax TA Chamber 1	43.0	Tenax TA Chamber 2	42.5
		UW	Tenax TA (Chamber 1)	55.3	Tenax TA (Chamber 2)	53.8
Radiello	FSM	RAD130 #3	40.2	RAD130 #5	42.2	
	ATL	RAD130 #1	38.4	RAD130 #6	35.0	
	CAS	RAD130 #2	48.8	RAD130 #4	50.6	

Analyte	Sampler Type	Analytical Laboratory	Sampler #1		Sampler #2	
			ID	Concentration (ppbv)	ID	Concentration (ppbv)
Carbon Tetrachloride	WMS	UW	PS-C61	54.8	PS-C64	53.8
		ATL	PS-C65	44.8	PS-C66	44.8
		AirZOne	PS-C63	54.4	PS-C62	49.5
	SKC Ultra	CAS	SKC B#2	37.6	SKC B#4	35.7
		ATL	SKC Badge #1	47.2	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarbopackB	ATL	Carbopack B (Chamber 1)	36.8	Carbopack B (Chamber 2)	36.8
		CAS	Carbopack B Chamber 1	33.2	Carbopack B Chamber 2	32.4
		UW	Carbopack B (Chamber 1)	43.2	Carbopack B (Chamber 2)	37.4
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	35.7	Tenax TA (Chamber 2)	36.3
		CAS	Tenax TA Chamber 1	29.6	Tenax TA Chamber 2	29.1
		UW	Tenax TA (Chamber 1)	48.5	Tenax TA (Chamber 2)	46.8
	Radiello	FSM	RAD130 #3	37.1	RAD130 #5	39.3
		ATL	RAD130 #1	43.6	RAD130 #6	39.7
		CAS	RAD130 #2	57.5	RAD130 #4	59.3
TCE	WMS	UW	PS-C61	37.8	PS-C64	38.0
		ATL	PS-C65	38.1	PS-C66	37.1
		AirZOne	PS-C63	31.6	PS-C62	29.3
	SKC Ultra	CAS	SKC B#2	36.9	SKC B#4	34.7
		ATL	SKC Badge #1	44.8	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarbopackB	ATL	Carbopack B (Chamber 1)	50.0	Carbopack B (Chamber 2)	50.0
		CAS	Carbopack B Chamber 1	45.7	Carbopack B Chamber 2	44.0
		UW	Carbopack B (Chamber 1)	64.0	Carbopack B (Chamber 2)	67.1
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	37.5	Tenax TA (Chamber 2)	38.3
		CAS	Tenax TA Chamber 1	35.9	Tenax TA Chamber 2	35.5
		UW	Tenax TA (Chamber 1)	42.1	Tenax TA (Chamber 2)	39.0
	Radiello	FSM	RAD130 #3	39.6	RAD130 #5	41.4
		ATL	RAD130 #1	45.0	RAD130 #6	40.8
		CAS	RAD130 #2	52.4	RAD130 #4	56.0
PCE	WMS	UW	PS-C61	32.5	PS-C64	33.6
		ATL	PS-C65	35.6	PS-C66	33.6
		AirZOne	PS-C63	23.8	PS-C62	21.9
	SKC Ultra	CAS	SKC B#2	42.2	SKC B#4	42.1
		ATL	SKC Badge #1	46.8	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarbopackB	ATL	Carbopack B (Chamber 1)	40.6	Carbopack B (Chamber 2)	39.1
		CAS	Carbopack B Chamber 1	39.0	Carbopack B Chamber 2	35.9
		UW	Carbopack B (Chamber 1)	50.7	Carbopack B (Chamber 2)	55.8
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	35.5	Tenax TA (Chamber 2)	35.0
		CAS	Tenax TA Chamber 1	33.0	Tenax TA Chamber 2	31.8
		UW	Tenax TA (Chamber 1)	39.0	Tenax TA (Chamber 2)	36.5
	Radiello	FSM	RAD130 #3	43.0	RAD130 #5	45.5
		ATL	RAD130 #1	51.6	RAD130 #6	43.0
		CAS	RAD130 #2	51.3	RAD130 #4	54.3
1,2,4-TMB	WMS	UW	PS-C61	19.9	PS-C64	21.3
		ATL	PS-C65	23.5	PS-C66	21.0
		AirZOne	PS-C63	16.8	PS-C62	16.8
	SKC Ultra	CAS	SKC B#2	25.0	SKC B#4	26.0
		ATL	SKC Badge #1	14.3	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarbopackB	ATL	Carbopack B (Chamber 1)	29.9	Carbopack B (Chamber 2)	28.2
		CAS	Carbopack B Chamber 1	26.3	Carbopack B Chamber 2	25.7
		UW	Carbopack B (Chamber 1)	41.2	Carbopack B (Chamber 2)	42.3
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	32.2	Tenax TA (Chamber 2)	31.0
		CAS	Tenax TA Chamber 1	26.6	Tenax TA Chamber 2	26.2
		UW	Tenax TA (Chamber 1)	37.8	Tenax TA (Chamber 2)	35.0
	Radiello	FSM	RAD130 #3	47.9	RAD130 #5	48.7
		ATL	RAD130 #1	46.9	RAD130 #6	42.0
		CAS	RAD130 #2	55.2	RAD130 #4	56.2
Naphthalene	WMS	UW	PS-C61	0.24	PS-C64	0.25
		ATL	PS-C65	0.26	PS-C66	0.22
		AirZOne	PS-C63	0.31	PS-C62	0.31
	SKC Ultra	CAS	SKC B#2	0.93	SKC B#4	0.62
		ATL	SKC Badge #1	0.00	SKC Badge #5	-
		AirZOne	SKC Badge #3	--	SKC Badge #6	--
	ATD - CarbopackB	ATL	Carbopack B (Chamber 1)	3.8	Carbopack B (Chamber 2)	3.5
		CAS	Carbopack B Chamber 1	2.6	Carbopack B Chamber 2	2.7
		UW	Carbopack B (Chamber 1)	1.8	Carbopack B (Chamber 2)	1.2
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	4.9	Tenax TA (Chamber 2)	4.5
		CAS	Tenax TA Chamber 1	3.0	Tenax TA Chamber 2	3.2
		UW	Tenax TA (Chamber 1)	5.6	Tenax TA (Chamber 2)	5.4
	Radiello	FSM	RAD130 #3	9.5	RAD130 #5	9.0
		ATL	RAD130 #1	1.4	RAD130 #6	1.3
		CAS	RAD130 #2	2.6 U	RAD130 #4	2.6 U

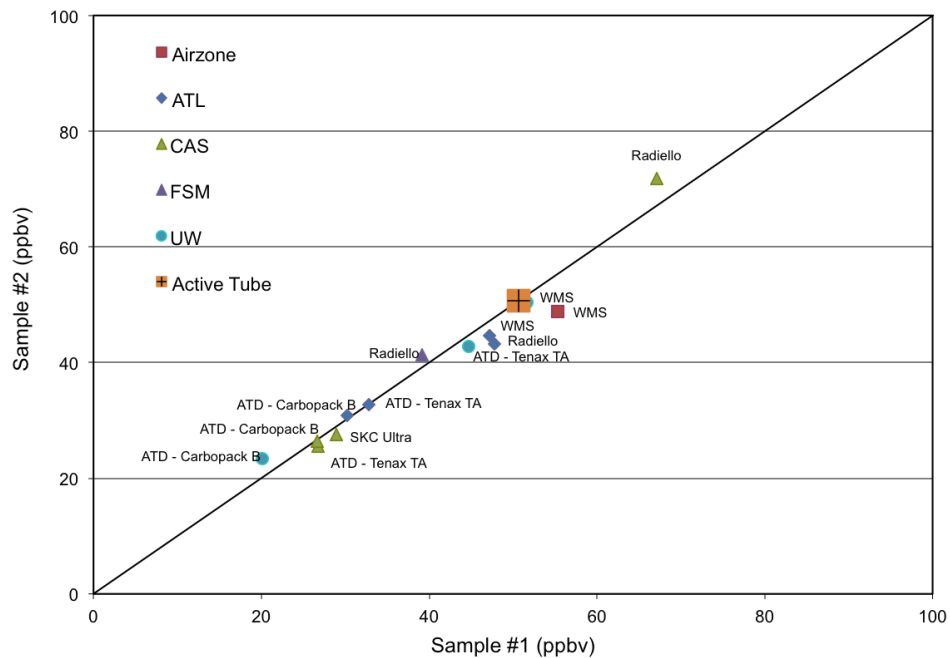
Notes:  
-- results unusable due to unacceptable internal standard recovery  
-- results not quantifiable as mass far exceeded calibration range



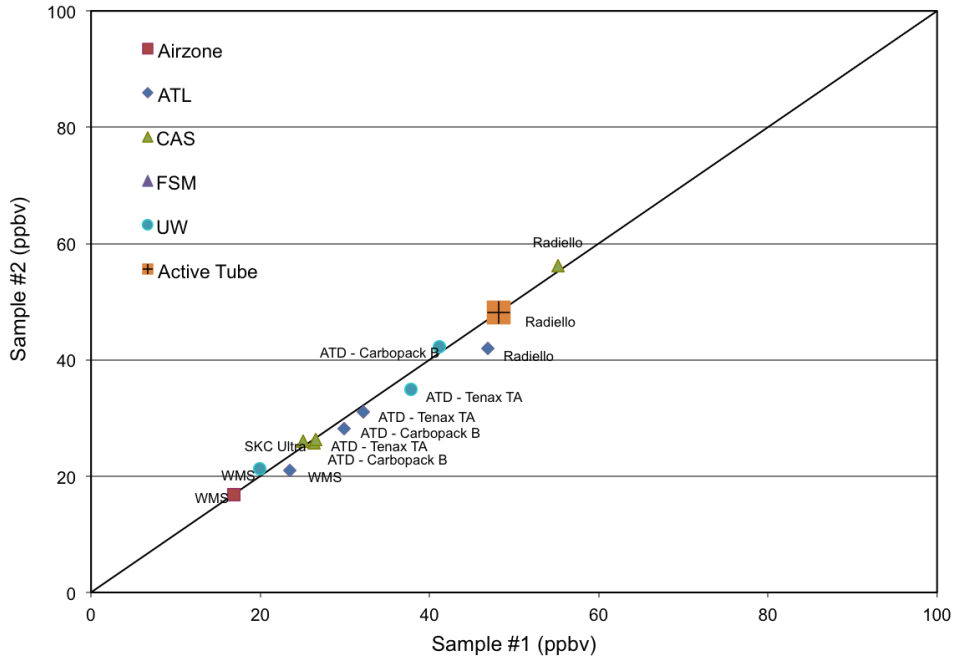
### Youden Plot - 1,2-Dichloroethane



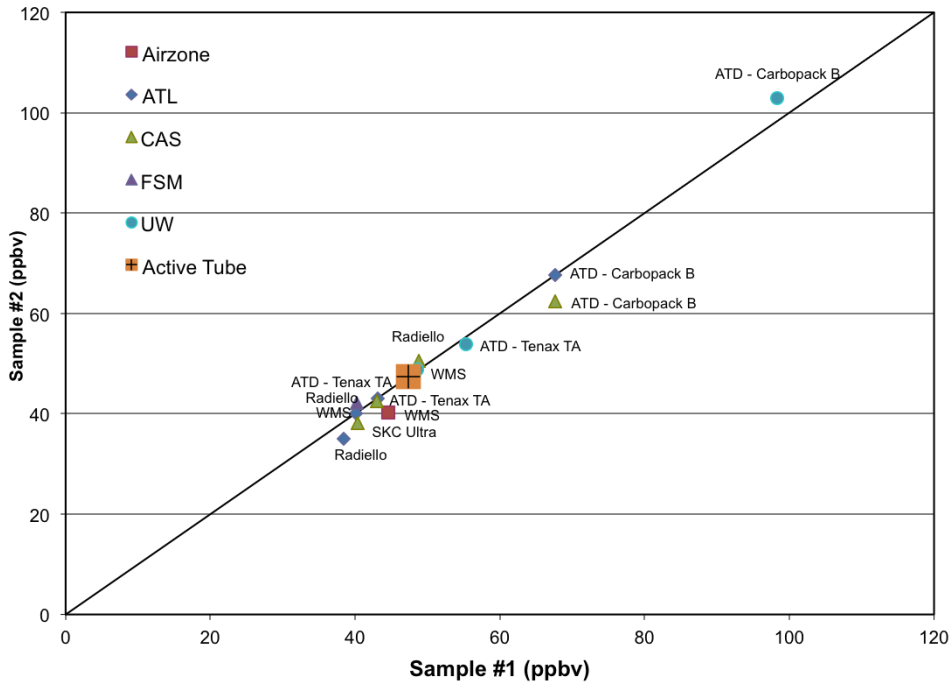
### Youden Plot - 1,1,1-Trichloroethane



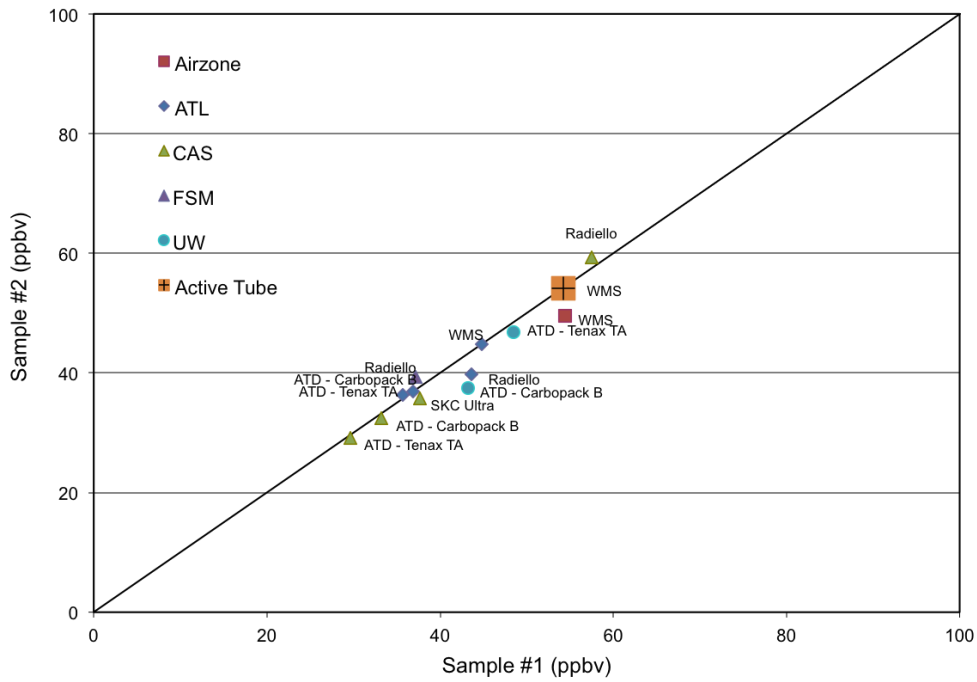
### Youden Plot - 1,2,4-Trimethylbenzene



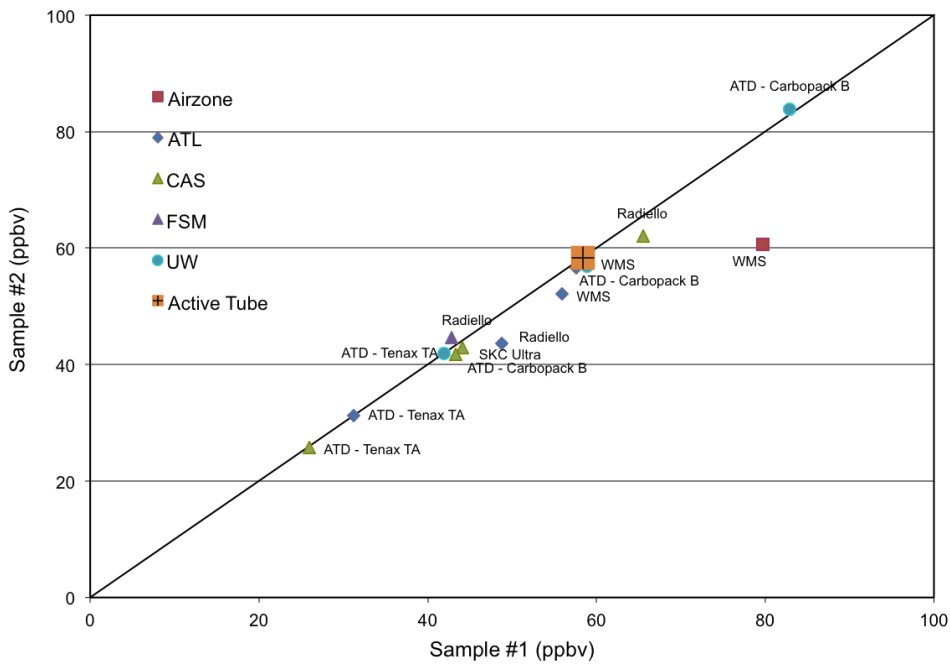
### Youden Plot - Benzene



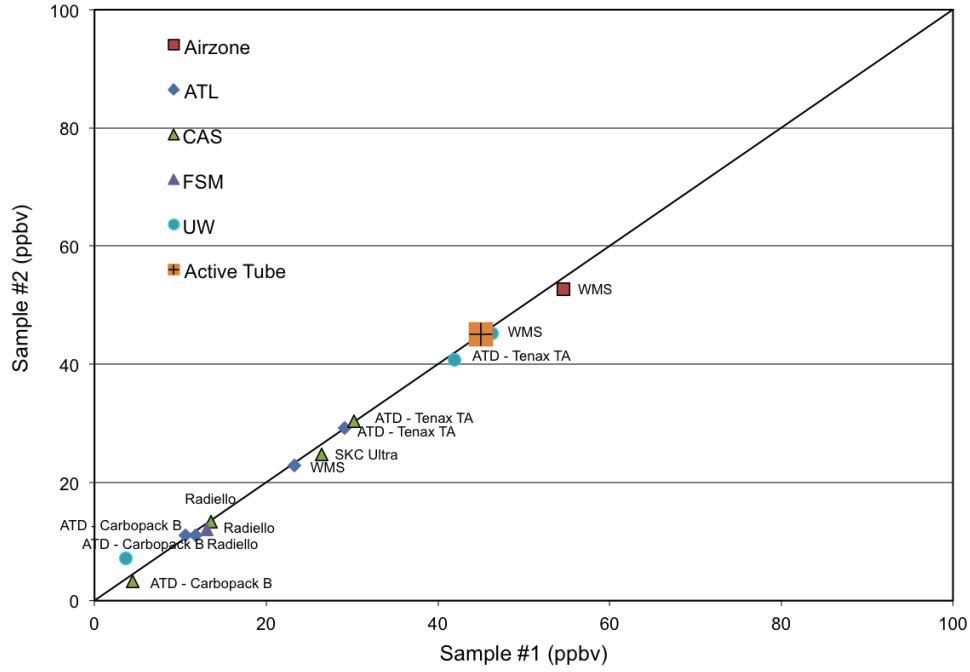
### Youden Plot - Carbon Tetrachloride



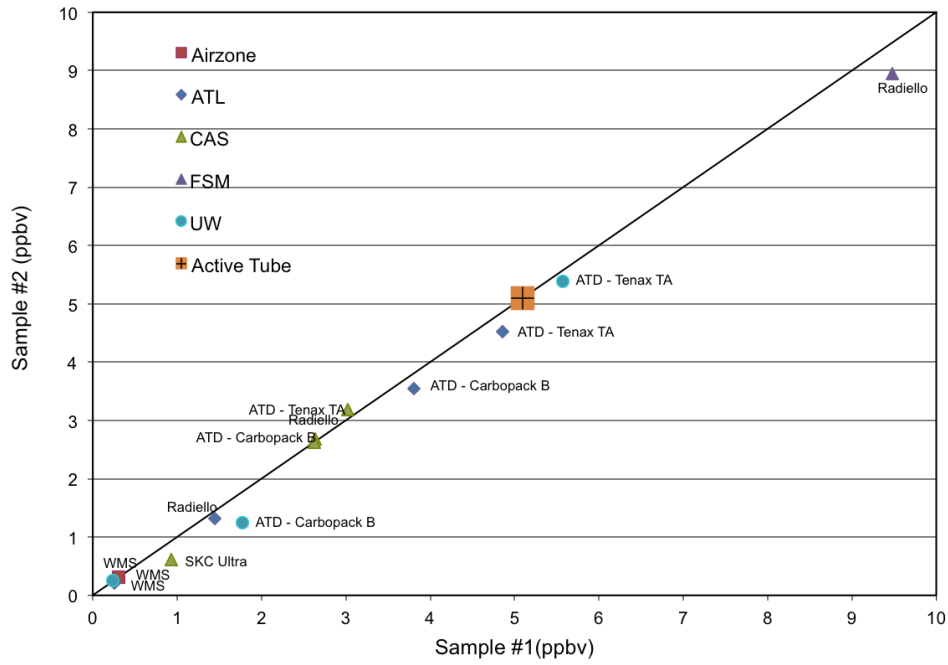
### Youden Plot - Hexane



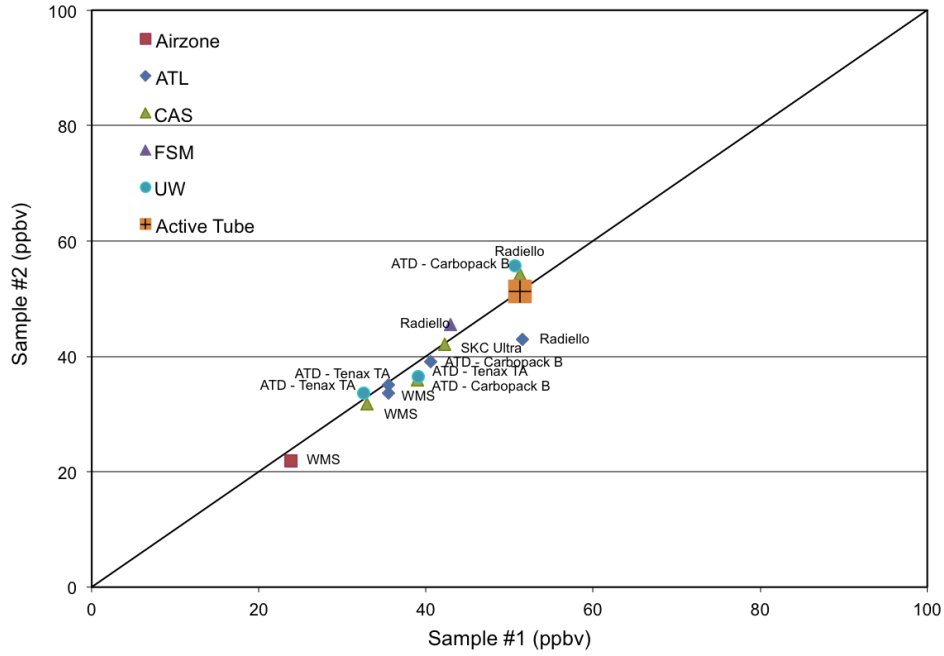
### Youden Plot - Methyleneethyl Ketone



### Youden Plot - Naphthalene



### Youden Plot - Tetrachloroethene



### Youden Plot - Trichloroethene

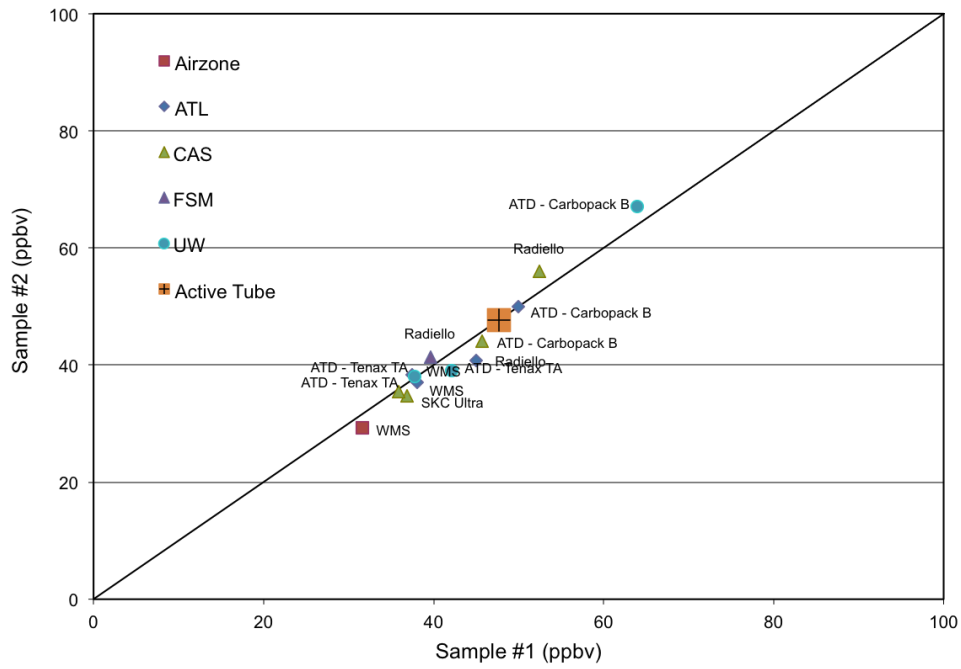
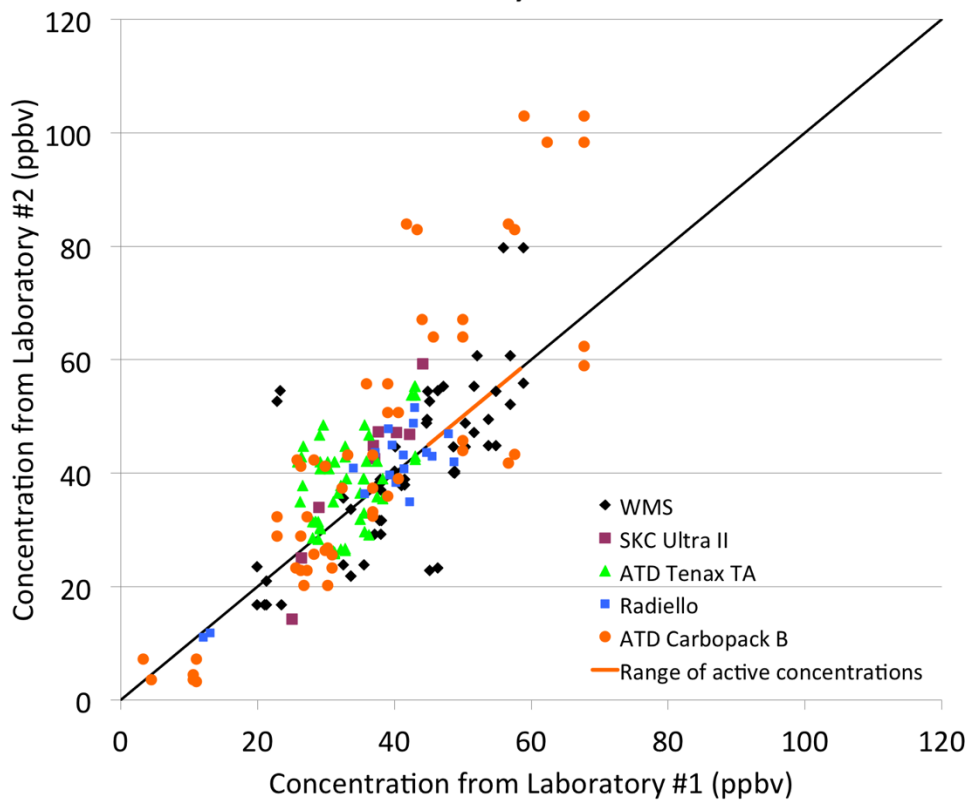


Figure 3-6: Youden plots for each VOC in the inter-laboratory tests

Some compounds showed high or low bias compared to the active controls, especially naphthalene and MEK (both of which were expected to be challenging compounds because of their low volatility and high solubility, respectively). Hexane showed high bias at UW compared to CAS and ATL, which was subsequently attributed to laboratory blank contamination. On average, for all compounds the passive samplers showed relative concentrations ( $C/C_0$ ) of 66% to 80% relative to active sample results, which indicated low (negative) bias.

Figure 3-7 shows the inter-laboratory data plotted as the results from one laboratory versus the second laboratory, where each pair is for the same compound using the same sampler. Note that since three laboratories analyzed each type of sampler, the comparison between one laboratory and another occurs three times for each sampler/compound combination (Lab A:Lab B, Lab B:Lab C, and Lab A:Lab C). For the purpose of Figure 3-7, these were plotted simply as one lab against another, and generically named Lab 1 vs. Lab 2. Comparing Figure 3-6 to Figure 3-7 indicates that the inter-laboratory variability was higher than the intra-laboratory variability, which is common because different laboratories use slightly different equipment and methods. The RPD between one laboratory and another is shown in Table 3-7. The average RPD for all inter-laboratory pairs of concentration measurements was 26%. This was taken into consideration in the performance objectives and accuracy performance criterion in Chapter 2. This degree of variability was consistent with previous studies of inter-laboratory variability for Summa canisters.<sup>220</sup> Table 3-7 contains “R” flags instead of results where the analyses were rejected because they were outside the linear range of the method.



**Figure 3-7:** Scatter plot of laboratory 1 vs. laboratory 2 for all VOCs and samplers

**Table 3-7: Summary of accuracy and precision in the inter-laboratory test**

Sampler type		A		B		C		D		B/A	C/A	D/A	RPD (B:C)	RPD (C:D)	RPD (B:D)	
		(ppbv)		(ppbv)		(ppbv)		(ppbv)								
		TO-17	U of W	Air Toxics	AirZOne					%	%	%	%	%	%	
WMS	MEK	45.2	44.8	46.3	45.2	23.3	22.8	54.6	52.7	102%	51%	119%	66%	80%	16%	
	HEX	59	57.6	58.9	57.0	55.9	52.1	79.7	60.7	99%	93%	120%	7%	26%	19%	
	12DCA	50.3	49.2	41.5	41.0	37.9	37.9	38.9	38.4	83%	76%	78%	9%	2%	7%	
	111TCA	51.0	50.2	51.6	50.4	47.2	44.6	55.4	48.9	101%	91%	103%	10%	13%	2%	
	BENZ	47.8	46.8	48.6	48.8	40.1	40.0	44.6	40.3	103%	85%	90%	19%	6%	14%	
	CT	54.3	54.0	54.8	53.8	44.8	44.8	54.4	49.5	100%	83%	96%	19%	15%	4%	
	TCE	48.0	47.2	37.8	38.0	38.1	37.1	31.6	29.3	80%	79%	64%	1%	21%	22%	
	PCE	51.8	50.6	32.5	33.6	35.6	33.6	23.8	21.9	65%	68%	45%	5%	41%	36%	
	124TMB	48.5	47.8	19.9	21.3	23.5	21.0	16.8	16.8	43%	46%	35%	8%	28%	20%	
	NAPH	5.12	5.06	0.24	0.25	0.26	0.2	0.3	0.3	5%	5%	6%	4%	26%	22%	
		Mean									78%	68%	76%	15%	26%	16%
		TO-17	CAS	Air Toxics	AirZOne											
SKC	MEK	45.2	44.8	26.4	24.8	25.0	R	R	R	57%	R	R	2%	R	R	
Ultra	HEX	59	57.6	44.2	42.9	59.3	R	R	R	75%	R	R	31%	R	R	
	12DCA	50.3	49.2	37.1	35.3	42.5	R	R	R	73%	R	R	16%	R	R	
	111TCA	51.0	50.2	29.0	27.6	34.0	R	R	R	56%	R	R	18%	R	R	
	BENZ	47.8	46.8	40.3	38.2	47.1	R	R	R	83%	R	R	18%	R	R	
	CT	54.3	54.0	37.6	35.7	47.2	R	R	R	68%	R	R	25%	R	R	
	TCE	48.0	47.2	36.9	34.7	44.8	R	R	R	75%	R	R	22%	R	R	
	PCE	51.8	50.6	42.2	42.1	46.8	R	R	R	82%	R	R	11%	R	R	
	124TMB	48.5	47.8	25.0	26.0	14.3	R	R	R	53%	R	R	57%	R	R	
	NAPH	5.12	5.06	0.9	0.6	0.00	R	R	R	15%	R	R		R	R	
		Mean									64%			22%		
		TO-17	Air Toxics	CAS	U of W											
ATD Tube	MEK	45.2	44.8	10.6	11.1	4.5	3.3	3.6	7.2	24%	9%	12%	95%	33%	67%	
Carbopack B	HEX	59	57.6	57.6	56.6	43.3	41.7	82.9	83.9	98%	73%	143%	29%	65%	37%	
	12DCA	50.3	49.2	26.4	27.2	22.9	22.8	28.9	32.3	54%	46%	61%	16%	29%	13%	
	111TCA	51.0	50.2	30.3	30.9	26.8	25.5	20.2	23.3	60%	52%	43%	16%	18%	34%	
	BENZ	47.8	46.8	67.7	67.7	62.4	58.9	98.4	103.0	143%	128%	213%	11%	50%	39%	
	CT	54.3	54.0	36.8	36.8	33.2	32.4	43.2	37.4	68%	61%	74%	12%	21%	9%	
	TCE	48.0	47.2	50.0	50.0	45.7	44.0	64.0	67.1	105%	94%	138%	11%	37%	27%	
	PCE	51.8	50.6	40.6	39.1	39.0	35.9	50.7	55.8	78%	73%	104%	6%	35%	29%	
	124TMB	48.5	47.8	29.9	28.2	26.3	25.7	41.2	42.3	60%	54%	87%	11%	46%	36%	
	NAPH	5.12	5.06	3.81	3.54	2.63	2.7	1.8	1.2	72%	52%	30%	32%	55%	84%	
		Mean									76%	64%	90%	24%	39%	37%
		TO-17	Air Toxics	CAS	U of W											
ATD Tube	MEK	45.2	44.8	29.2	29.2	30.2	30.4	42.0	40.8	65%	67%	92%	4%	31%	35%	
Tenax TA	HEX	59	57.6	31.2	31.2	26.0	25.8	41.9	41.9	54%	44%	72%	19%	47%	29%	
	12DCA	50.3	49.2	28.1	28.9	28.5	28.4	31.4	31.4	57%	57%	63%	0%	10%	10%	
	111TCA	51.0	50.2	32.8	32.8	26.7	26.4	44.7	42.8	65%	52%	87%	21%	49%	29%	
	BENZ	47.8	46.8	43.1	43.1	43.0	42.5	55.3	53.8	91%	90%	115%	1%	24%	24%	
	CT	54.3	54.0	35.7	36.3	29.6	29.1	48.5	46.8	66%	54%	88%	20%	48%	28%	
	TCE	48.0	47.2	37.5	38.3	35.9	35.5	42.1	39.0	80%	75%	85%	6%	13%	7%	
	PCE	51.8	50.6	35.5	35.0	33.0	31.8	39.0	36.5	69%	63%	74%	8%	15%	7%	
	124TMB	48.5	47.8	32.2	31.0	26.6	26.2	37.8	35.0	66%	55%	76%	18%	32%	14%	
	NAPH	5.12	5.06	4.86	4.53	3.03	3.2	5.6	5.4	92%	61%	108%	41%	55%	15%	
		Mean									70%	62%	86%	14%	32%	20%
		TO-17	FSM	Air Toxics	CAS											
Radiello	MEK	45.2	44.8	13.1	12.0	11.8	11.1	13.6	13.3	28%	25%	30%	9%	16%	7%	
	HEX	59	57.6	42.8	44.7	48.8	43.6	65.5	62.0	75%	79%	109%	5%	32%	37%	
	12DCA	50.3	49.2	34.0	35.6	40.8	36.4	47.3	49.6	70%	78%	97%	10%	23%	33%	
	111TCA	51.0	50.2	39.1	41.3	47.8	43.2	67.2	71.8	79%	90%	137%	12%	42%	53%	
	BENZ	47.8	46.8	40.2	42.2	38.4	35.0	48.8	50.6	87%	77%	105%	12%	30%	19%	
	CT	54.3	54.0	37.1	39.3	43.6	39.7	57.5	59.3	71%	77%	108%	9%	33%	42%	
	TCE	48.0	47.2	39.6	41.4	45.0	40.8	52.4	56.0	85%	90%	114%	6%	23%	29%	
	PCE	51.8	50.6	43.0	45.5	51.6	43.0	51.3	54.3	86%	92%	103%	7%	11%	18%	
	124TMB	48.5	47.8	47.9	48.7	46.9	42.0	55.2	56.2	100%	92%	116%	8%	23%	14%	
	NAPH	5.12	5.06	9.5	9.0	1.4	1.3	2.6	2.6	181%	27%	52%	148%	62%	111%	
		Mean									86%	73%	97%	23%	30%	36%



### 3.2.3 Center-point (ANOVA) Test Results

The results of the initial center-point testing are tabulated in Appendix C. The average temperature was within 1 °C of the set-point of 22 °C, and the standard deviation of the temperature was less than 0.5 °C for all six chambers (Table C1). The average relative humidity was within 2% RH of the set-point of 60% RH, and the coefficient of variation was less than 11%. This indicates the chamber conditions were well controlled. The face velocity was controlled at 0.23 m/s by the rotation of the carousel, and the sample duration (4 days) was controlled by a timer, and neither factor had any significant variability.

The chamber concentrations measured with the pumped ATD tubes (Table C2) were generally lower than the concentrations calculated by mass balance and the flow rates of the supply gas and purified air (set point was 50 ppb<sub>v</sub> for all compounds except naphthalene at 5 ppb<sub>v</sub>, achieved by adding 50 mL/min supply gas to 10 L/min purified air). The only compound with an active sample concentration matching the expected concentration calculated from the mass flow controllers was HEX (99% of expected value). The average active ATD tube/TO-17 sample concentrations for the other compounds were generally slightly lower than the set-point, mostly in the range of 33 to 45 ppb<sub>v</sub> and 2.9 to 3.2 ppb<sub>v</sub> for naphthalene. This appears likely to have been attributable to imperfect calibration of the mass flow controllers.

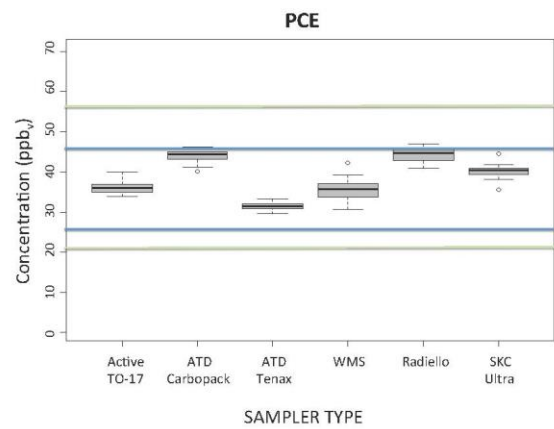
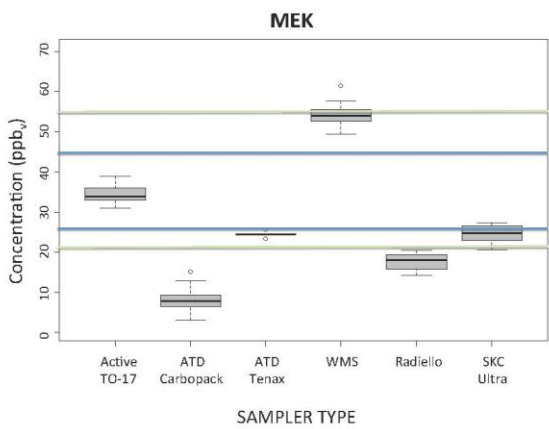
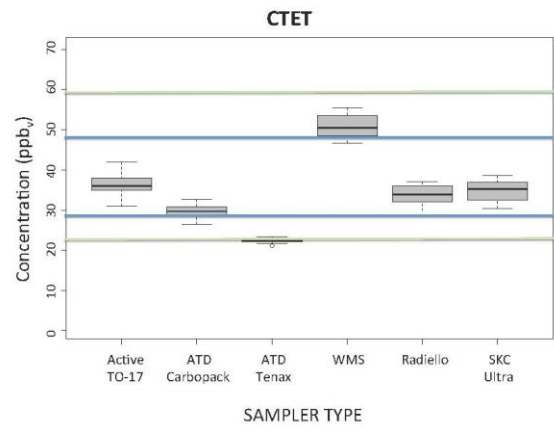
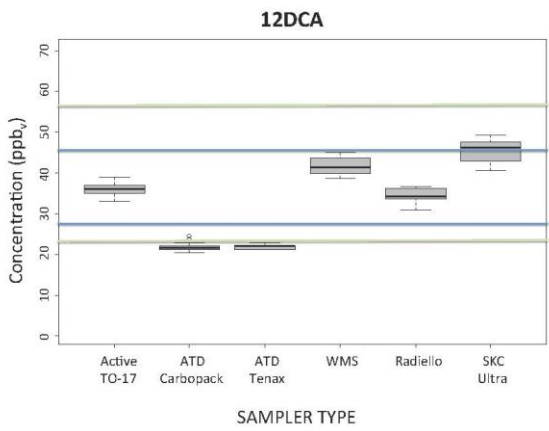
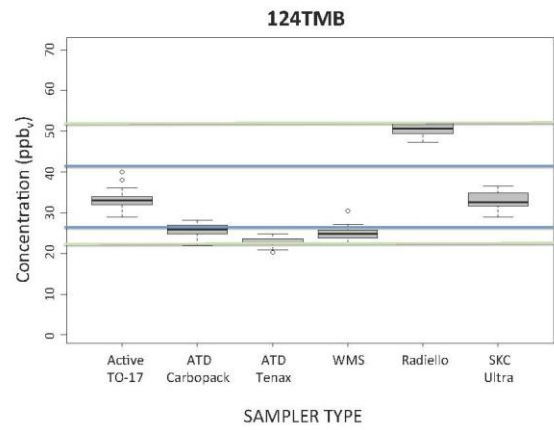
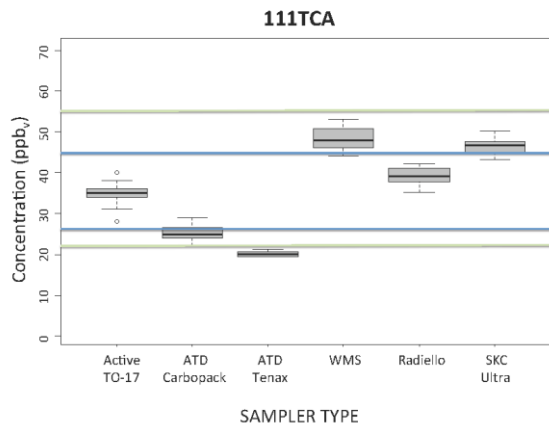
Nevertheless, the active sample results showed minimal variability (COV of 2 to 7%), so the chamber concentrations were reasonably steady for the four-day duration of the center-point tests.

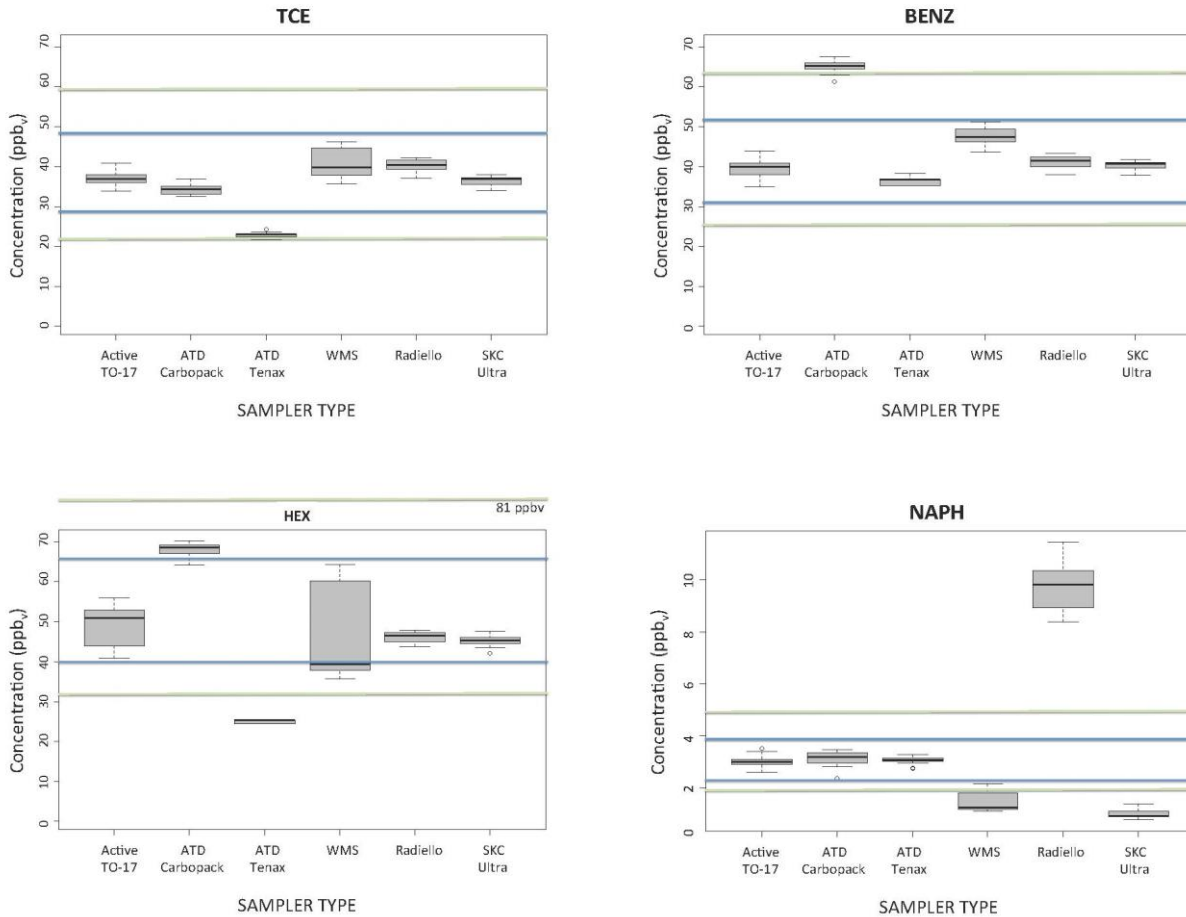
The concentrations measured with passive samplers in the initial center-point tests are presented in Table C3 and summarized in the box and whiskers plots in Figure 3-8. The boxes span the 25<sup>th</sup> to 75<sup>th</sup> percentiles, and the whiskers span the maximum and minimum measured concentrations. Also shown in Figure 3-8 are horizontal lines corresponding to +/-25% and +/-45% RPD of the average active sampler concentration. The passive sampler data showed precision similar to the active ATD tube samples for most of the combinations of sampler/compound, except hexane with the WMS sampler (subsequently attributable to laboratory contamination) and naphthalene with the Radiello sampler. The mean passive sampler concentrations were within the +/- 25% RPD control lines for 24 of the 50 combinations of sampler/compound (roughly half). The mean passive sampler concentrations were outside of +/-45% RPD control lines for only 9 of the 50 sampler/compound combinations:

- ATD tube/Tenax showed low bias for 111TCA, 12DCA and CT. The recommended maximum sample volumes (RMSVs) for 111TCA, 12DCA and CT on Tenax are 0.2, 1 and 0.2 L, respectively (Supelco 2013). The uptake rates for these compounds for the passive ATD tube sampler were all estimated to be 0.5 mL/min (see Table 3-2). The product of the sample duration

(4 days) and the uptake rate was therefore 2.9 L, which was larger than the RMSV for these compounds on Tenax. Carbopack B has a much higher RMSV for 111TCA and CT (20 L for both according to Supelco,<sup>19</sup> and did not show as much low bias for these compounds compared to ATD/Tenax;

- ATD/ Carbopack B showed low bias for 12DCA and MEK and high bias for BENZ. Carbopack B is less hydrophobic than Tenax TA and the two most soluble compounds showed negative bias, so this may be attributable to competition by water vapour. The high bias for BENZ on the ATD/Carbopack B sampler was likely attributable to the uptake rate used being too low, as described for the familiarity testing;
- WMS and SKC showed low bias for NAPH. The WMS and SKC samplers used estimated uptake rates for NAPH, both of which apparently overestimated the true uptake rate for the conditions of the center-point tests by a factor of 2 to 3, which might have also been attributable to low recovery of naphthalene from the (strong) sorbents used (Anasorb 747 and charcoal, respectively);
- Radiello showed high bias for NAPH. This may be attributable to uncertainty in the published uptake rate (25 mL/min). Using the free-air diffusion coefficient for NAPH (0.059 cm<sup>2</sup>/s), and the equation in the Radiello manual,<sup>221</sup> an uptake rate of 50 mL/min could be calculated, which would have resulted in concentrations 2 times lower, hence predominantly within the +/-25% tolerance of the active samples. Naphthalene often shows low recovery, and the published uptake rate of 25 mL/min might be adjusted to partially account for that. The high bias for NAPH on the Radiello analysed by FSM is consistent with the inter-laboratory test data (Table 3-8).





**Figure 3-8:** Box and whisker plots of center-point test results (with control lines corresponding to +/-25% (inside control lines) and +/-45% (outside control lines))

The precision for each passive sampler/compound combination in the center-point tests is shown in Figure 3-9. The precision goal of <30% COV was met for 45 of the 50 sampler/compound combinations (exceptions included MEK and NAPH, which were challenging compounds, and hexane for the WMS, which appeared to be related to laboratory contamination). The COV for the active samples collected from the exposure chamber as controls was in the range of 2 - 7 %.

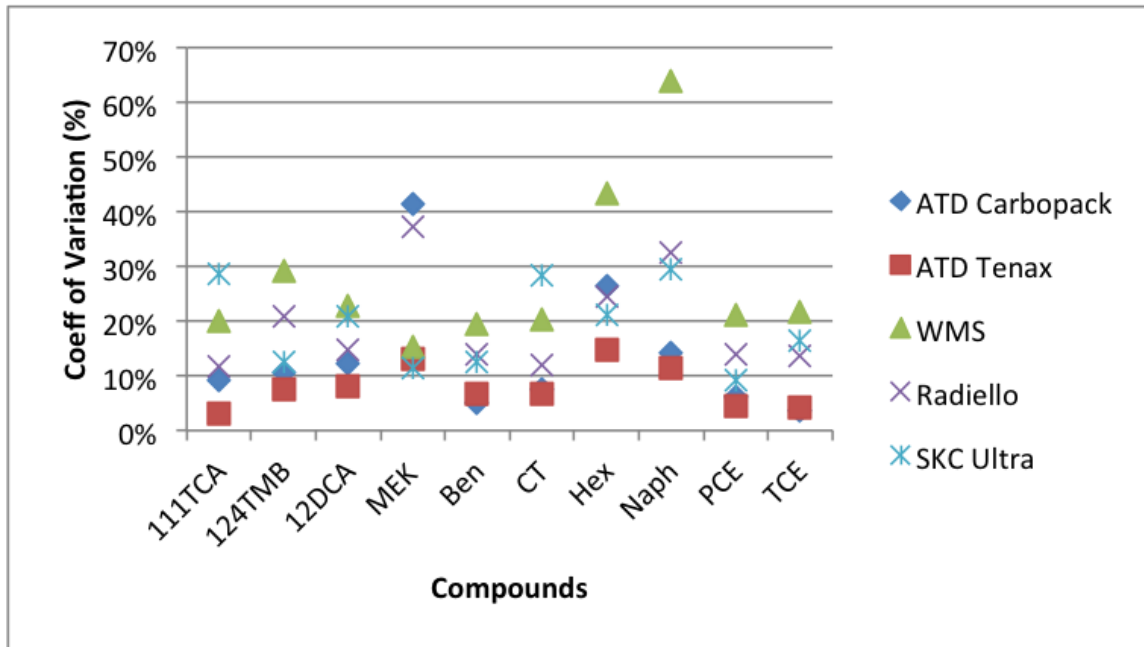


Figure 3-9: Coefficient of variation for the initial center-point (ANOVA) testing

### 3.2.4 Fractional Factorial Test Results

The chamber conditions measured during the fractional factorial testing, the results of analysis of active and passive samples and the relative concentrations (passive/active) are presented in Appendix D. These data were combined with the center-point data and are summarized in two sets of Figures: 3-10 to 3-14 and 3-15 to 3-19. Figures 3-10 to 3-14 have the individual VOCs along the x-axis and the chamber runs in the legend. The latter shows the values of each of the five factors on the x-axis and the compounds in the legend. There were 24 chamber tests, with 10 VOCs and five sampler types, each in triplicate, totalling 3,600 passive concentration measurements. Figures 3-15 to 3-19 show the results of the laboratory chamber tests (center-point and fractional factorial tests) as normalized concentrations ( $C/C_0$ , the passive sampler concentration divided by the chamber concentrations measured using pumped ATD tubes and EPA Method TO-17 analysis) for each compound. The accuracy performance criterion lines (RPD -45% and +45%) are shown for comparison purposes.

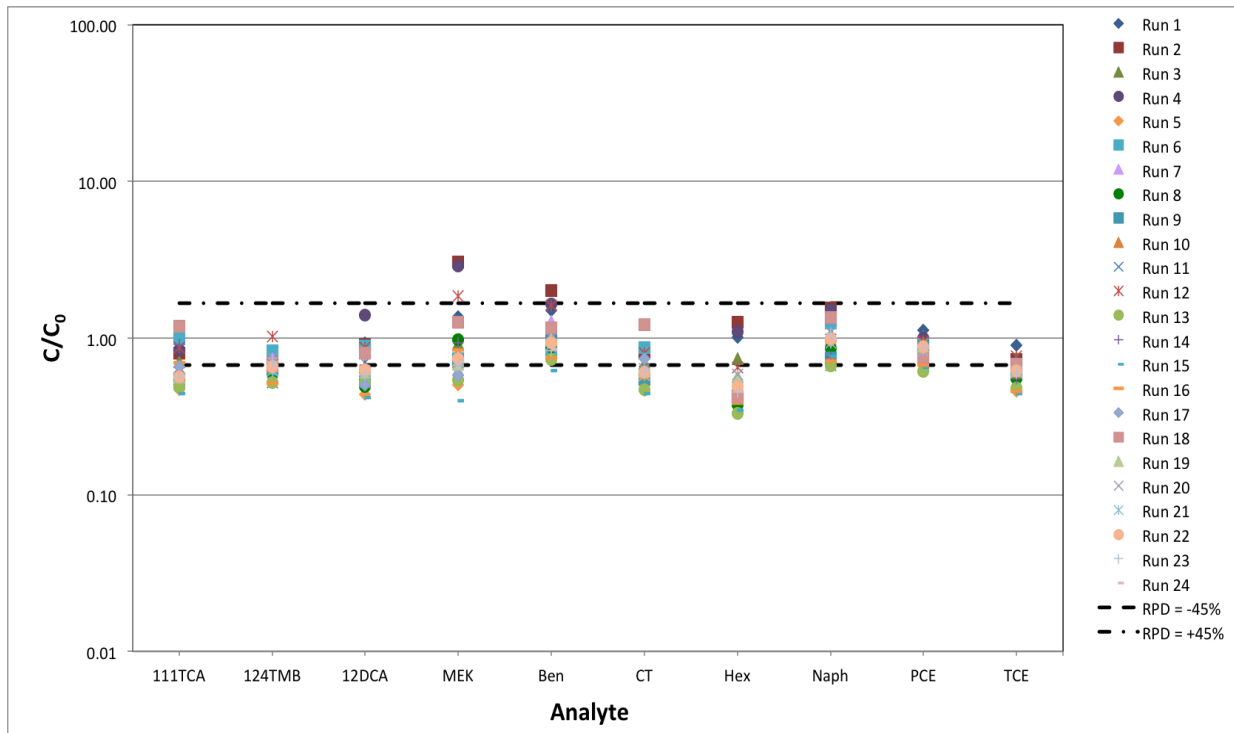


Figure 3-10: ATD tube/Tenax TA results for center-point and fractional factorial tests

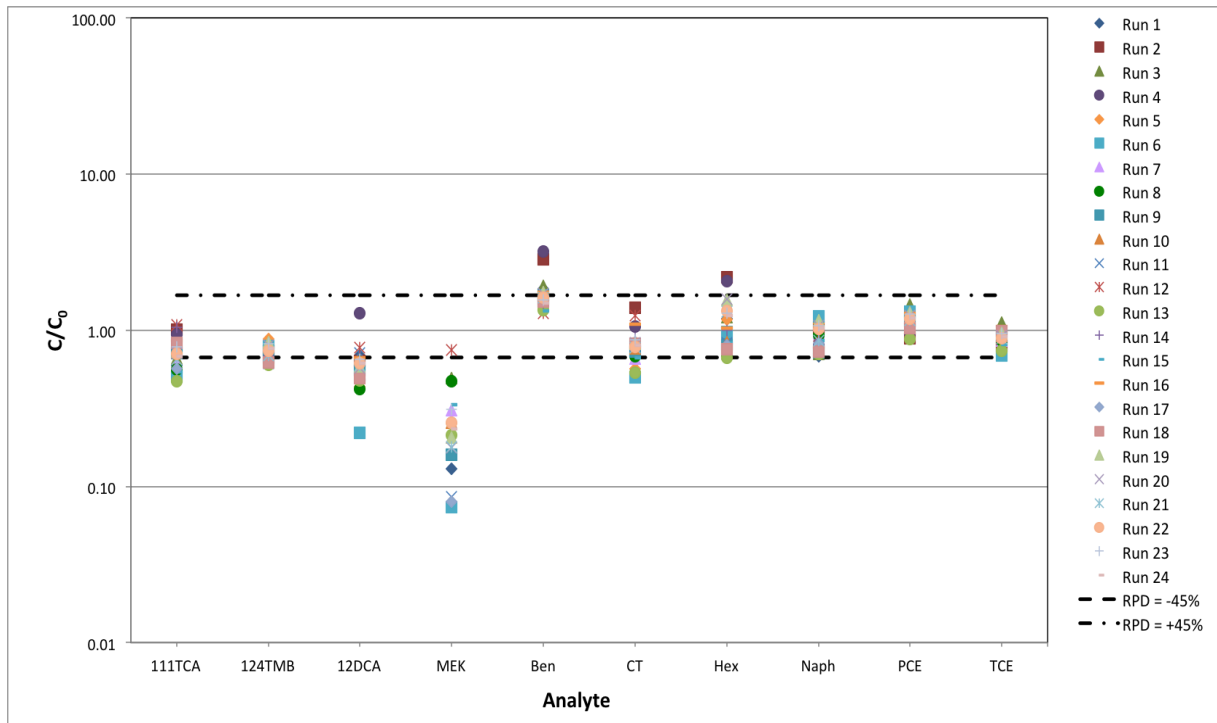


Figure 3-11: ATD tube/Carbopack B results for center-point and fractional factorial tests

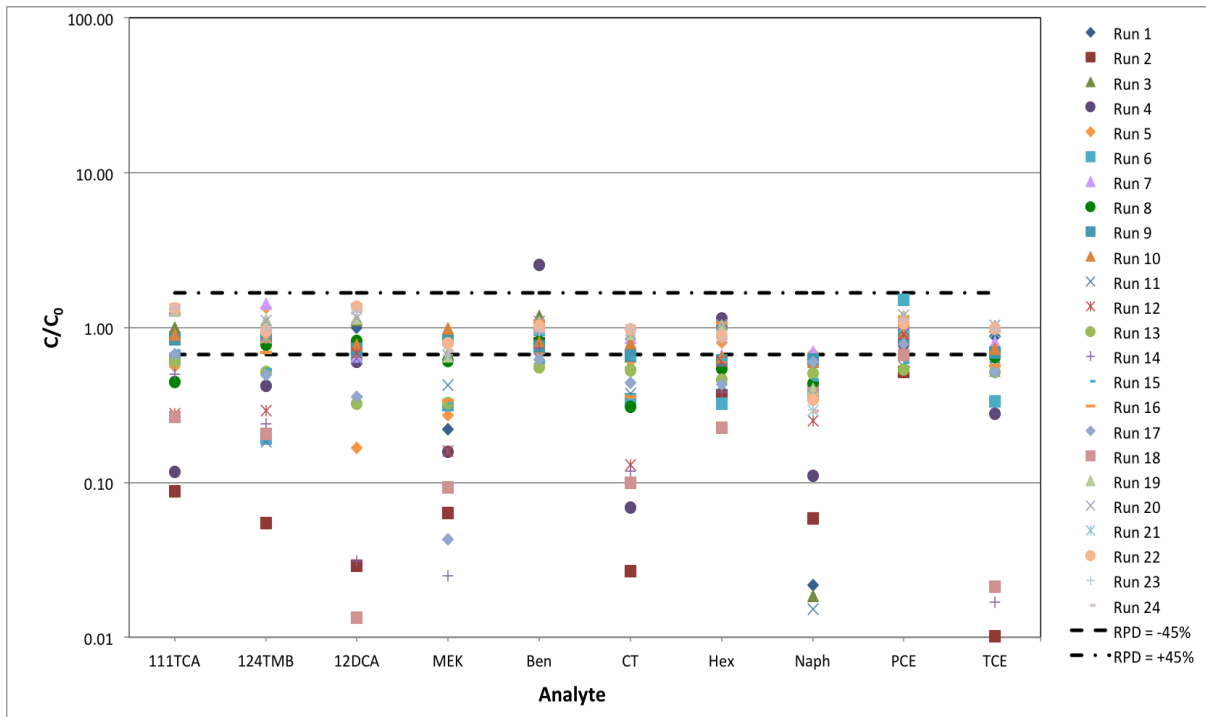


Figure 3-12: SKC Ultra II results for center-point and fractional factorial tests

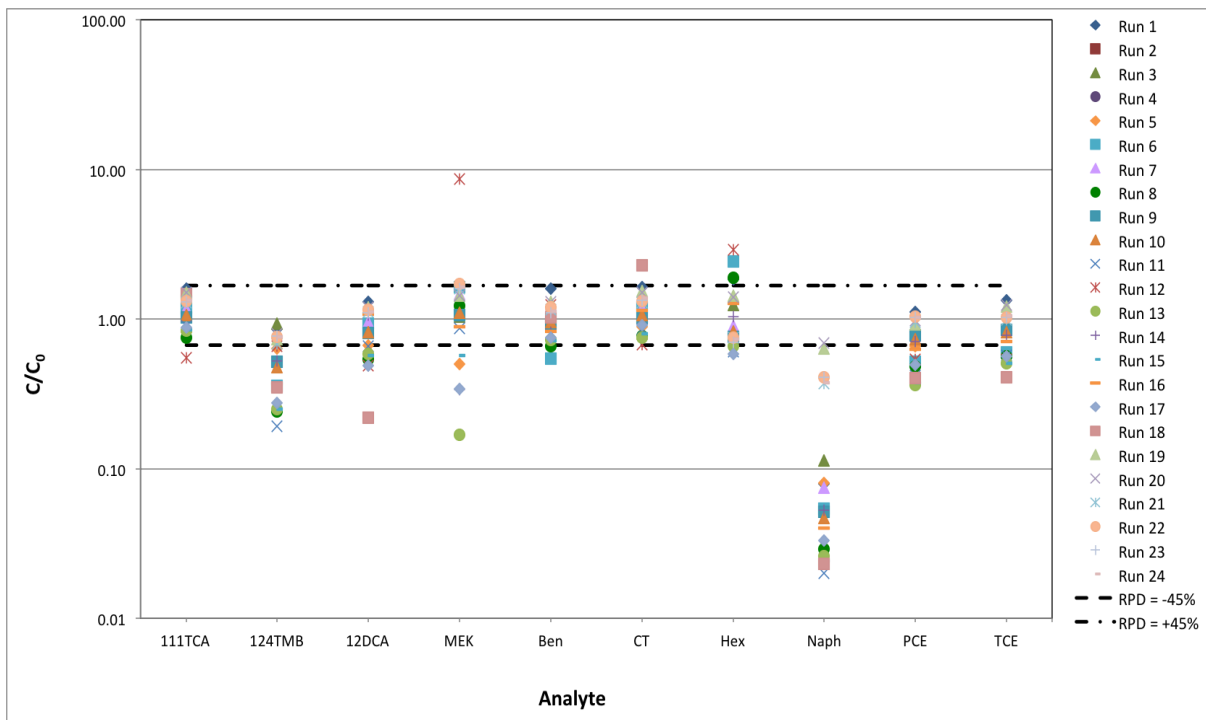
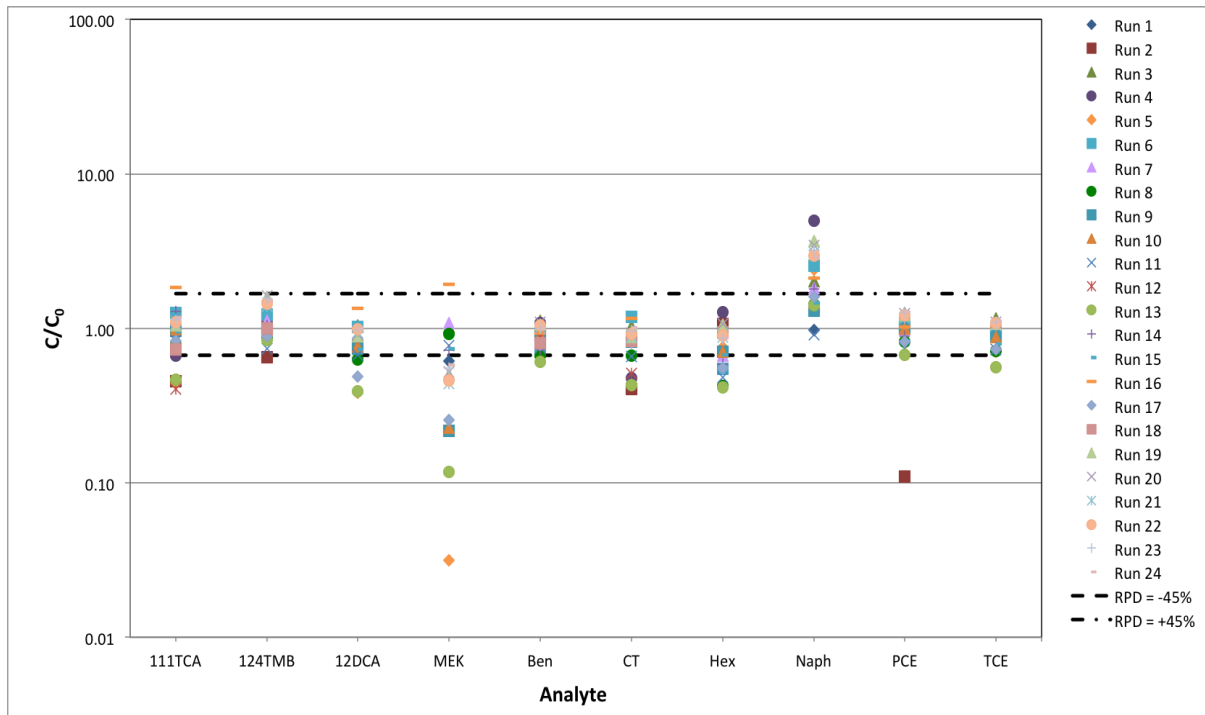


Figure 3-13: WMS results for center-point and fractional factorial tests



**Figure 3-14:** Radiello results for center-point and fractional factorial tests

Some trends are evident in Figures 3-10 to 3-14:

- The ATD Tube sampler with Tenax TA showed low bias for hexane, not observed with the ATD tube with Carboxpack B. The ATD Tube Sampler with Carboxpack B showed low bias for MEK and high bias for benzene, whereas the ATD tube sampler with Tenax TA showed no bias for these compounds. These results demonstrate the importance of proper sorbent selection.
- Both ATD tube samplers showed low bias for 12DCA, which likely meant that the calculated uptake rate of 0.5 mL/min (Table 3-2) was too high (0.3 mL/min would have provided the most accurate results);
- The SKC Ultra II results were biased low (up to 2 orders of magnitude) for some analyses of all compounds excluding benzene and PCE, most commonly for the low concentration and low velocity conditions. The low bias was partly attributable to sample preparation challenges associated with transferring the sorbent from the sampler to the ATD tube prior to analysis by Method TO-17;



- The WMS showed negative bias for NAPH and 124TMB. These two compounds have the highest partitioning coefficients in the PDMS membrane, hence high uptake rates. Consequently, the low bias could be attributable to the starvation effect. Analyte recovery could also be a potential issue with naphthalene, but the recovery from Anasorb 747 by CS<sub>2</sub> extraction was shown to be reasonably good (63-68%) by Seepthapathy.<sup>203</sup> Also, these compounds both had calculated uptake rates (see Table 3-3), and the calculated values may simply have been higher than the actual uptake rates for the chamber conditions (by an average factor of 2 for 124TMB and 6 for NAPH);
- The Radiello results were biased low by a factor of about 1.6 for MEK and high by a factor of about 2.3 for NAPH.

Figures 3-15 to 3-19 show the influence of the exposure chamber conditions on the relative concentrations measured for each of the compounds with each of the samplers (including the Active ATD tube samples in Figure 3-20). Some observations are apparent by inspection of these charts:

- The ATD Tube with Tenax showed very low variability and minimal bias compared to the other methods and the Active ATD tubes, and the only apparent trend was slightly low bias in the 4 and 7 day samples compared to the 1-day samples;
- The ATD Tube with Carbopack B showed similar results to the ATD with Tenax, except for the low bias with MEK and high bias with benzene. This was consistent with the familiarity tests, inter-laboratory tests and center-point tests, and could be corrected in all these tests using a more specific uptake rate for these compounds and sorbent;
- The SKC Ultra sampler showed notably less variability and bias at the center-points compared to the high and low levels of each factor where the results were biased low and highly variable;
- The WMS sampler also showed notably less variability and bias at the center-points compared to the high and low levels of each factor. The WMS showed more variability in the low concentration chamber tests compared to the center-point and high concentrations, which may be attributable to variability between the thermal desorption and solvent extraction methods. Also, the high bias from hexane laboratory contamination was much larger compared to the adsorbed mass from the chamber in the two low concentration/short duration chambers, resulting in C/C<sub>0</sub> values >10. Seethapathy and Górecki<sup>152,153</sup> studied the effect of humidity and temperature on the WMS sampler. They found that humidity had no significant effect, while the uptake rates

decreased with increasing temperature, but only by approximately 20% over the range studied here, so the variability was most likely attributable to other factors;

- The Radiello showed minimal bias and variability and no clear trends attributable to the five factors except for the high bias with naphthalene and the low bias with MEK. The biases for these two compounds were similar in the inter-laboratory and center-point tests, so the accuracy would improve if a more specific uptake rate was used for the compounds and sorbent.

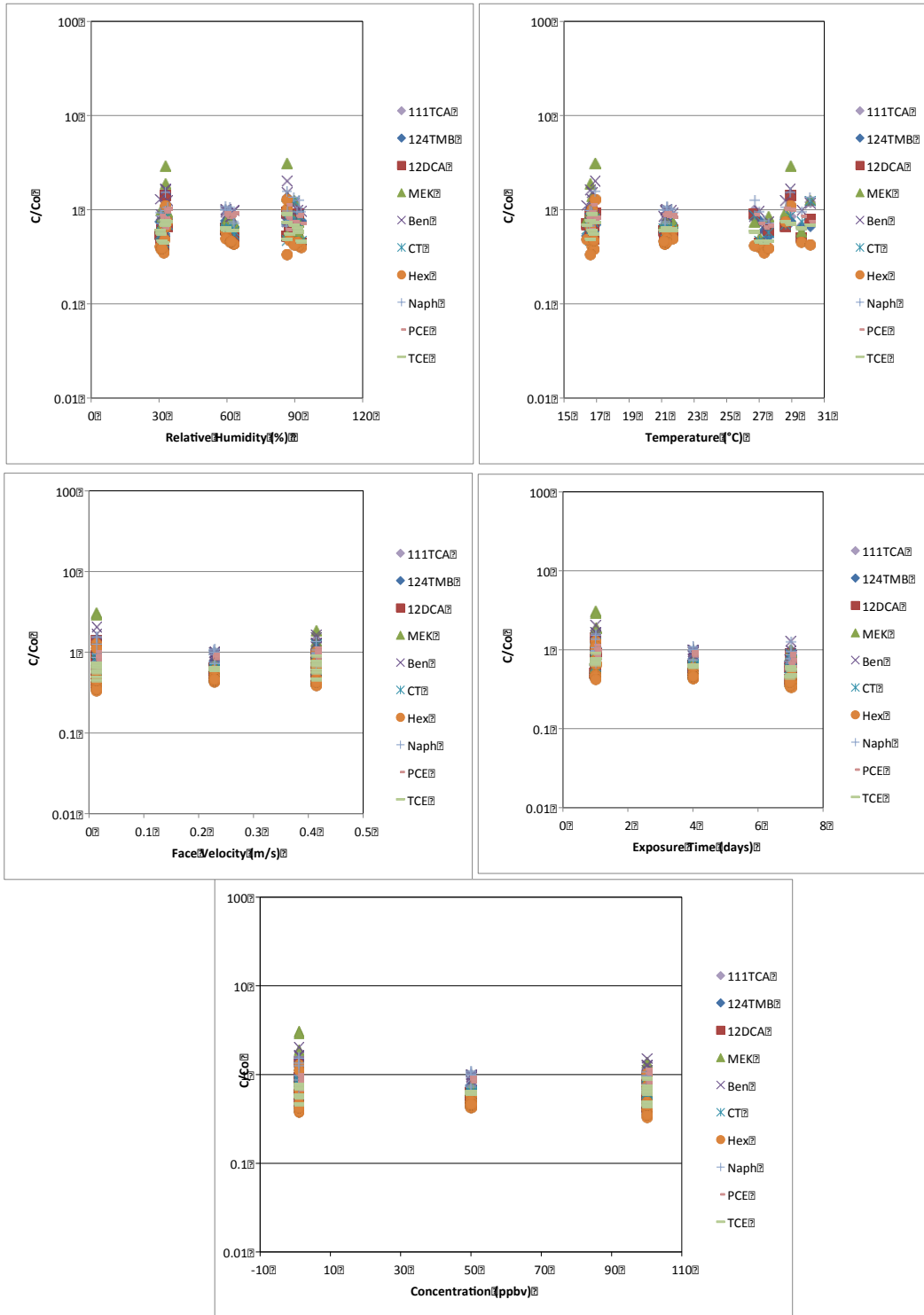


Figure 3-15: ATD Tenax low concentration laboratory test data

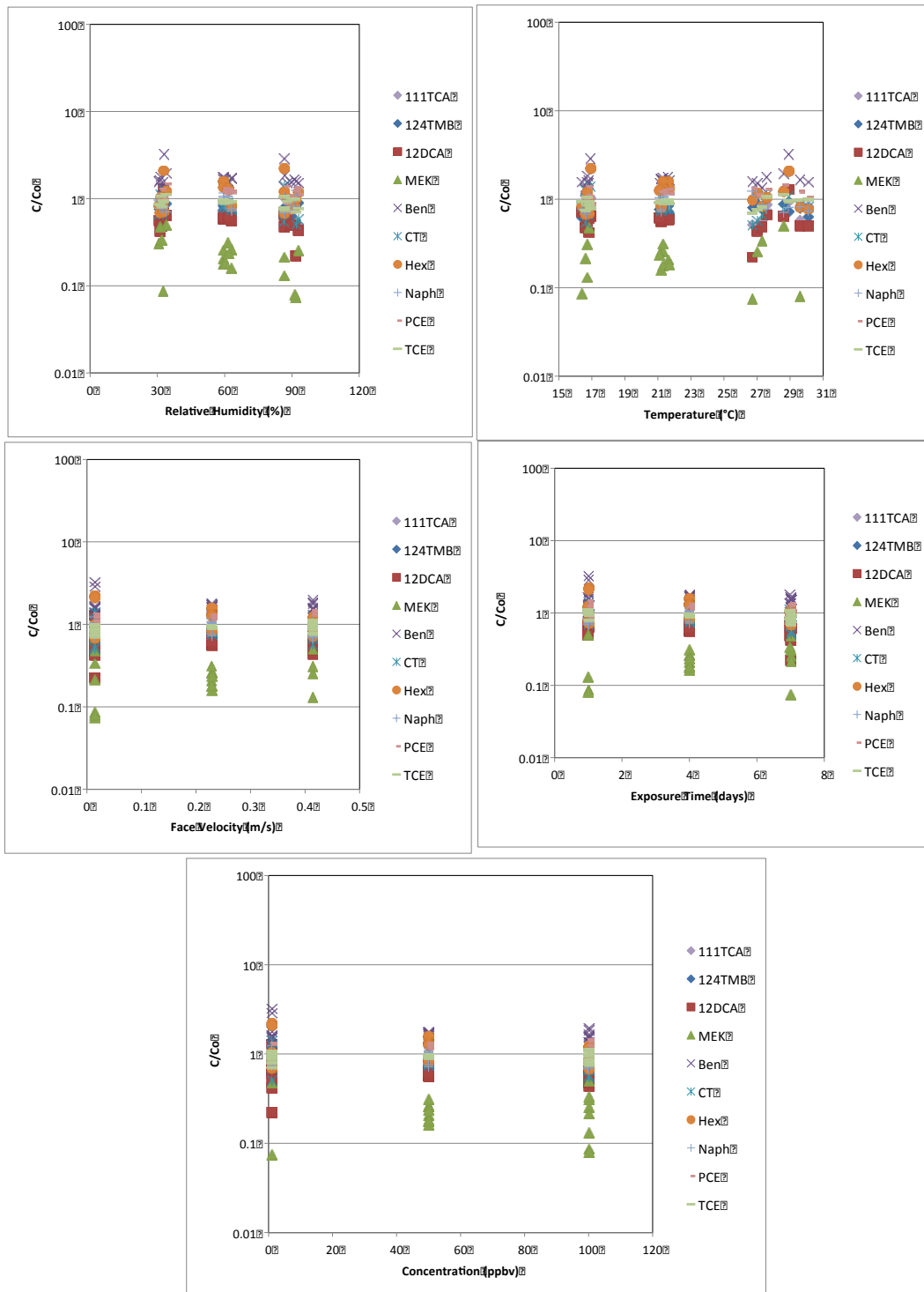


Figure 3-16: ATD Carbopack B low concentration laboratory test data

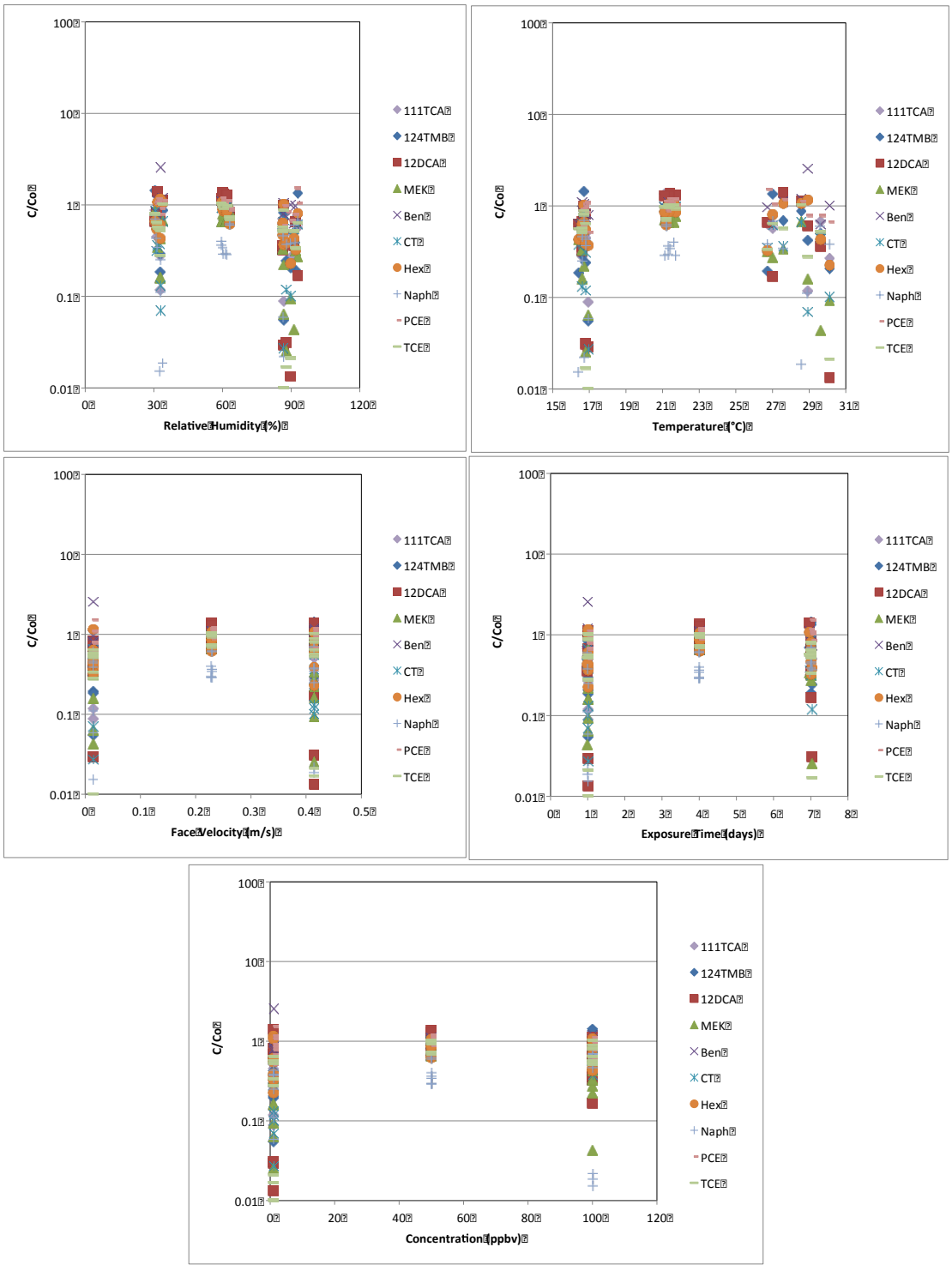


Figure 3-17: SKC Ultra II low concentration laboratory test data

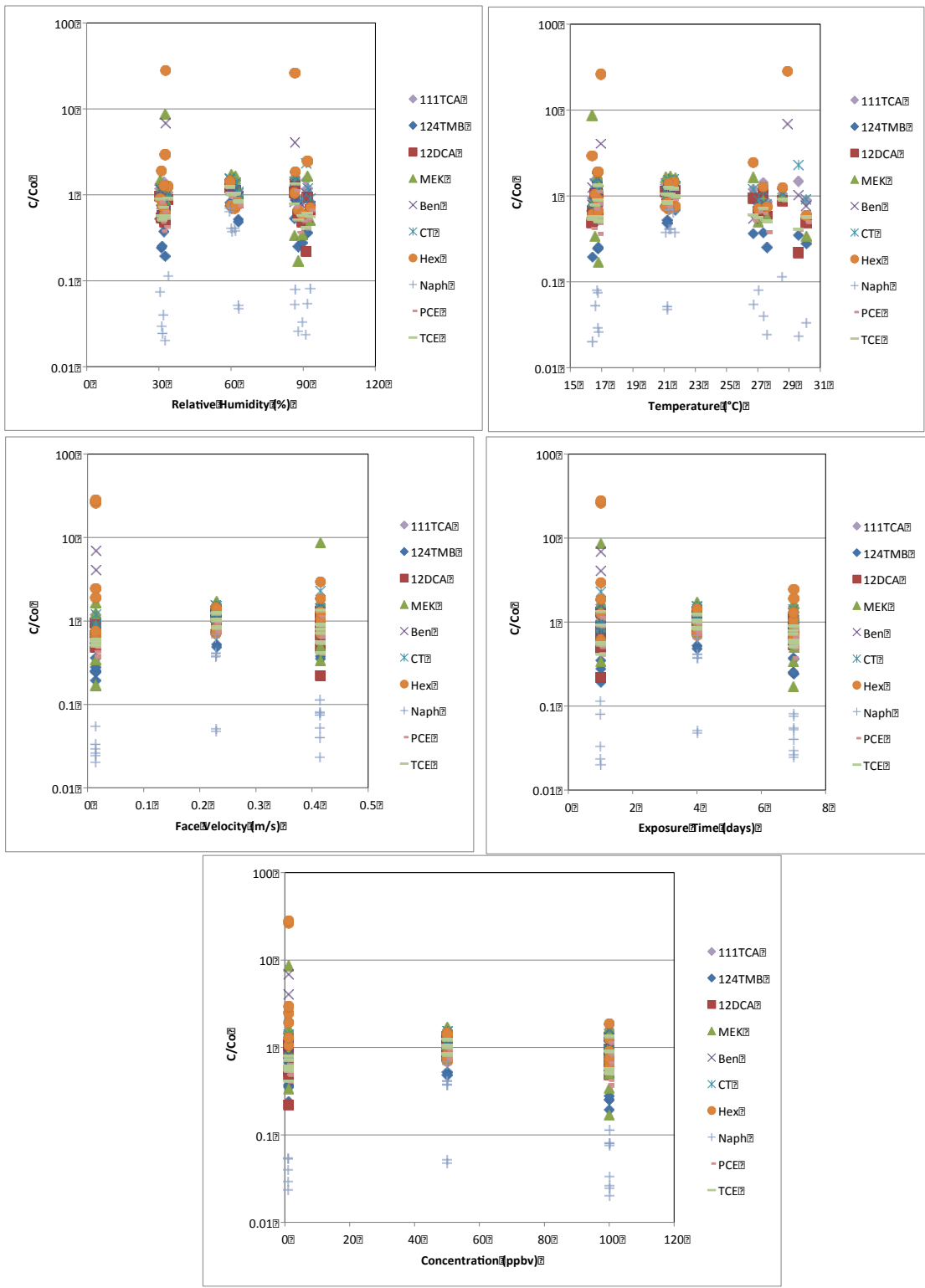


Figure 3-18: WMS low concentration laboratory test data

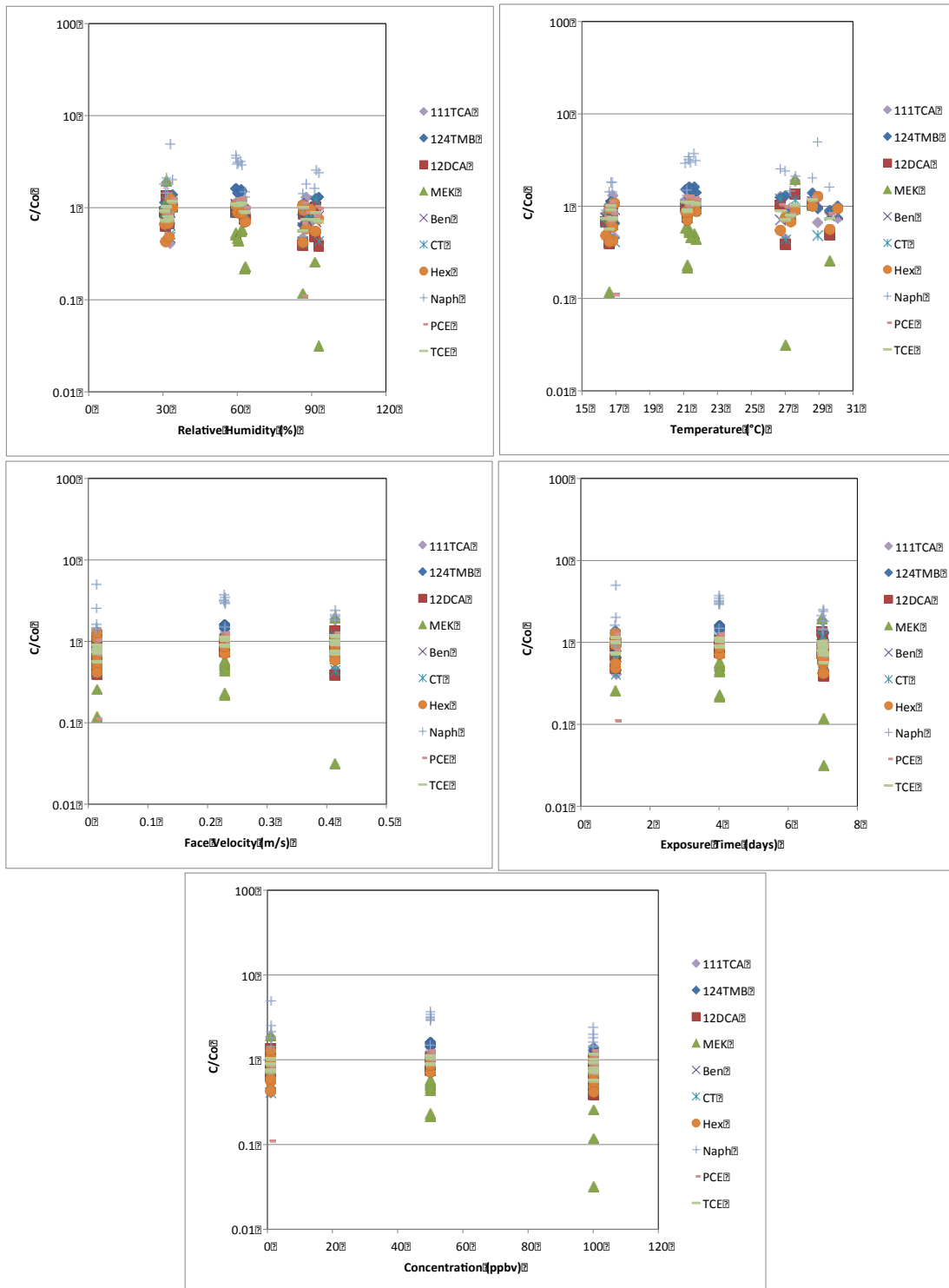


Figure 3-19: Radiello low concentration laboratory test data

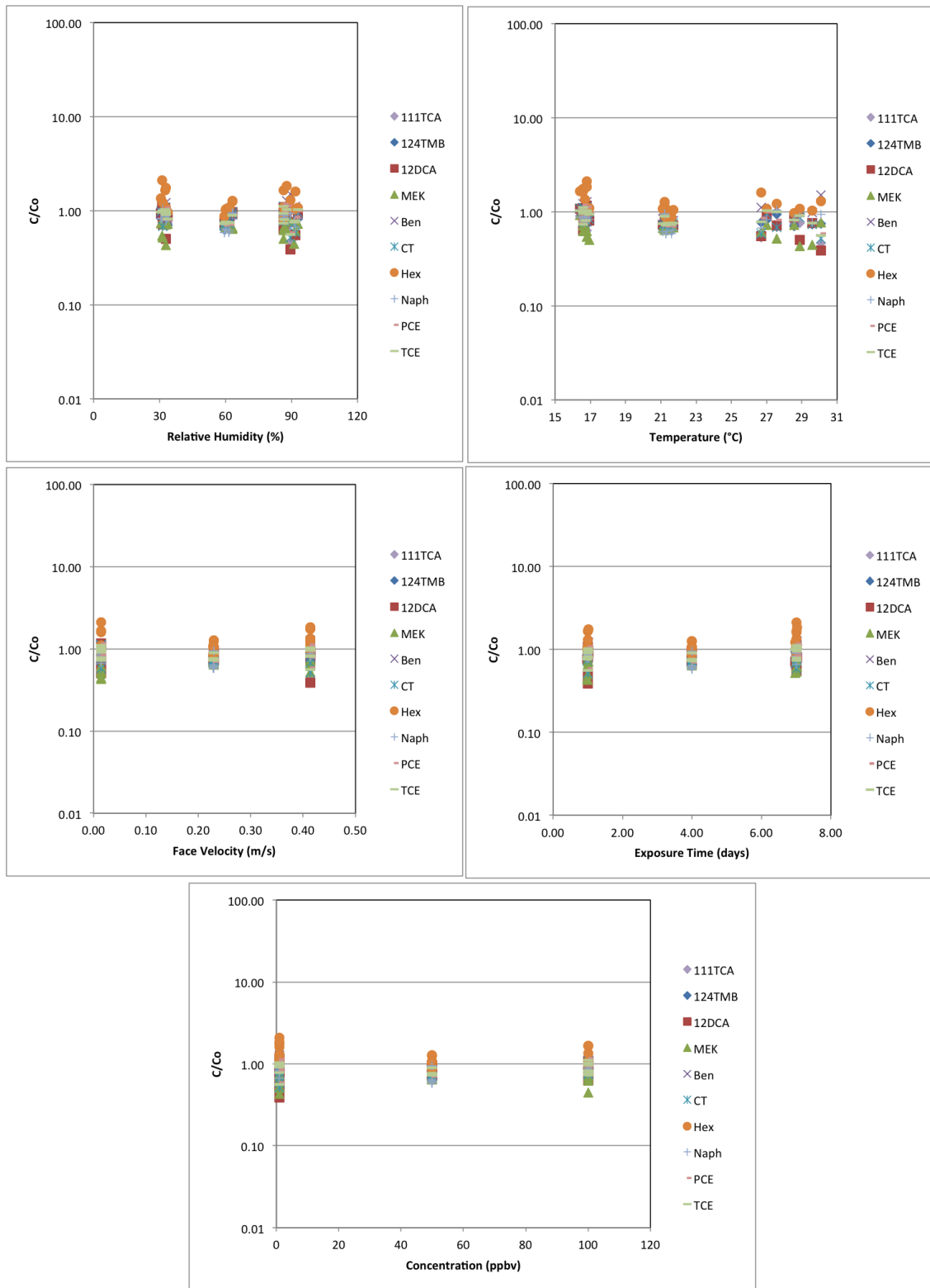


Figure 3-20: Active ATD tube low concentration laboratory test data



### 3.3 Performance Assessment

The overall average accuracy was assessed by calculating the mean  $C/C_0$  (passive concentration/active control) values for all 24 chamber tests (Table 3-8). This included 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. Thus, the mean  $C/C_0$  values represent the average accuracy over a wide range of indoor air monitoring conditions. The accuracy performance criterion (RPD <45%, corresponding to  $C/C_0$  range of 0.63 to 1.58) was met for at least 7 of the 10 compounds for each of the passive samplers (shown using boldface in Table 3-8). Table 3-8 also includes a column comparing the average results of the active ATD tube samples to the concentrations calculated from the mass flow controller measurements. Three of the passive samplers showed low bias for MEK, which could be attributable to high bias in the active sampler results.

**Table 3-8:** Mean  $C/C_0$  values for the low concentration laboratory tests

Compound	Mean $C/C_0$ (passive/active)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active/ Calculated
111TCA	<b>0.72</b>	<b>0.67</b>	<b>1.15</b>	<b>0.95</b>	<b>0.80</b>	0.79
124TMB	<b>0.73</b>	<b>0.69</b>	0.54	<b>1.13</b>	<b>0.69</b>	0.89
12DCA	0.60	<b>0.67</b>	<b>0.86</b>	<b>0.83</b>	<b>0.75</b>	0.87
BEN	1.71	<b>1.07</b>	<b>0.99</b>	<b>0.90</b>	<b>0.95</b>	0.72
CT	<b>0.82</b>	<b>0.67</b>	<b>1.18</b>	<b>0.81</b>	0.55	0.98
HEX	<b>1.12</b>	0.55	<b>1.15</b>	<b>0.80</b>	<b>0.70</b>	0.86
MEK	0.21	<b>1.00</b>	<b>1.12</b>	0.62	0.46	1.33
NAPH	<b>0.90</b>	<b>0.98</b>	0.17	2.26	0.36	0.82
PCE	<b>1.15</b>	<b>0.85</b>	<b>0.72</b>	<b>1.02</b>	<b>0.98</b>	0.94
TCE	<b>0.91</b>	0.62	<b>0.80</b>	<b>0.91</b>	<b>0.87</b>	0.91
Mean $C/C_0$ is the mean of 24 passive/active concentration ratios (one for each chamber test)						
<b>Bold:</b> average $C/C_0$ values within the 0.63 to 1.58 range, meeting the success criterion (RPD < +/-45%)						
Active ATD tube data compared to concentrations calculated from standard gas dilution						

Both intra-chamber and inter-chamber precision were evaluated. The intra-chamber precision was calculated as the average of 24 COV values (one for each of the three replicates within each of the 24 chamber tests), as shown in Table 3-9. 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 negative bias apparently attributable to losses during sample preparation prior to analysis). This result demonstrates that most of the passive samplers were characterized by very good precision and provided very reproducible results under a given set of conditions.

**Table 3-9:** Mean intra-chamber COV values for the low concentration laboratory tests

Compound	Mean Intra-Chamber Coefficient of Variation (COV)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	<b>7%</b>	<b>3%</b>	<b>7%</b>	<b>5%</b>	<b>14%</b>	13%
124TMB	<b>5%</b>	<b>5%</b>	<b>7%</b>	<b>4%</b>	<b>22%</b>	7%
12DCA	<b>8%</b>	<b>3%</b>	<b>6%</b>	<b>4%</b>	<b>12%</b>	9%
MEK	47%	<b>5%</b>	<b>13%</b>	<b>11%</b>	<b>23%</b>	15%
CT	<b>4%</b>	<b>6%</b>	<b>8%</b>	<b>4%</b>	<b>8%</b>	12%
HEX	<b>7%</b>	<b>2%</b>	<b>7%</b>	<b>7%</b>	<b>16%</b>	7%
BENZ	<b>5%</b>	<b>6%</b>	<b>12%</b>	<b>3%</b>	<b>10%</b>	6%
NAPH	<b>6%</b>	<b>12%</b>	<b>7%</b>	<b>6%</b>	<b>16%</b>	7%
PCE	<b>2%</b>	<b>3%</b>	<b>6%</b>	<b>3%</b>	<b>6%</b>	5%
TCE	<b>3%</b>	<b>2%</b>	<b>5%</b>	<b>3%</b>	<b>16%</b>	5%
Mean intra-chamber COV is the average of 24 COV values, from three replicates in each chamber						
<b>Bold:</b> COV value meeting the success criterion (< 30%)						

The inter-chamber precision was calculated considering all 72  $C/C_0$  values for each sampler/compound combination from all 24 chamber tests together as a single population (Table 3-10). 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 3-10:** Mean inter-chamber COV values for the low concentration laboratory tests

Mean inter-chamber COV	Mean Inter-Chamber Coefficient of Variation (COV)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	<b>24%</b>	<b>27%</b>	<b>26%</b>	35%	51%	18%
124TMB	<b>12%</b>	<b>16%</b>	42%	<b>25%</b>	55%	17%
12DCA	31%	32%	35%	<b>28%</b>	61%	23%
MEK	88%	69%	116%	70%	65%	19%
CT	<b>25%</b>	<b>26%</b>	31%	<b>28%</b>	59%	19%
HEX	37%	45%	56%	<b>28%</b>	39%	27%
BENZ	<b>25%</b>	31%	<b>26%</b>	<b>16%</b>	40%	19%
NAPH	<b>18%</b>	<b>25%</b>	128%	46%	58%	17%
PCE	<b>13%</b>	<b>14%</b>	34%	<b>27%</b>	<b>26%</b>	18%
TCE	<b>11%</b>	<b>17%</b>	34%	<b>30%</b>	51%	16%
Inter-chamber COV is the COV of 24 average C/C <sub>0</sub> values, one from each chamber test						
<b>Bold:</b> COV value meeting the success criterion (< 30%)						

The information from the low concentration laboratory chamber tests was used to calculate revised uptake rates for each of the passive sampler/compound combinations. The average C/C<sub>0</sub> values (Table 3-8) were multiplied by the initial uptake rates (Table 3-2) to derive improved uptake rates for the 10 target analytes (Table 3-11). For the center point conditions (temperature of 21 °C, relative humidity of about 60%, 0.23 m/s face velocity, 4 day sample duration, and concentrations of about 50 ppbv), most of the samplers provided data that met the performance criterion for precision (COV<30%, as shown in Figure 3-9), and with better calibrated uptake rates (Table 3-11), the results would meet similar data quality objectives as conventional active Suma canister/TO-15 or active (pumped) ATD tube/TO-17. Combinations of samplers and analytes that did not meet the performance criterion even at the center point conditions (indicated by a double asterisk in Table 3-11) should be supported by inter-method duplicates regardless of the field sampling conditions if the highest level of data quality is needed. 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 3-10 and marked with a single asterisk in Table 3-11) would also benefit from inter-method duplicates when field sampling conditions are not similar to the midpoint levels. For

compounds not listed in Table 3-11, or for other samplers or sorbents, the accuracy will depend on the level of calibration effort for the particular compound and sampler.

**Table 3-11:** Recommended revised uptake rates for compounds and samplers used in the low concentration laboratory tests

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	1.5	59*	11*	0.36	0.34
1,2,4-Trimethylbenzene	7.0*	57	9.0*	0.45	0.43
1,2-Dichloroethane	2.2*	64	9.8*	0.30*	0.34*
2-Butanone (MEK)	1.5*	49**	7.8*	0.11**	0.50*
Benzene	2.2	72	15*	0.60	0.37*
Carbon Tetrachloride	1.8*	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	3.9*	60	13	0.47	0.35
Trichloroethene	2.6*	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°C, 60%RH, 0.2 m/s, 4 days and 50 ppbv, respectively					

Statistical analysis of the low concentration laboratory test data using analysis of variance (ANOVA) is presented in Appendix E and summarized in Table 3-12, which provides the probability (p) that the observed effect is due to random factors only. The highlighted p-values identify the main effects that are statistically significant at the 5% level of significance (i.e.,  $p < 0.05$ ). The fact that the chambers were very well controlled during these experiments resulted in low experimental variability, which increases the probability that a main effect will show a difference that can be statistically resolved when compared to the intrinsic variance.

**Table 3-12:** Results of ANOVA analysis (p-values) of low concentration lab tests (main effects)

Sampler Type	Analyte	Relative Humidity	Temperature	Face Velocity	Exposure Time	Concentration
ATD Carbopack	1,1,1-Trichloroethane	0.0778	0.0281	0.0106	0.0003	<.0001
ATD Carbopack	1,2,4-Trimethylbenzene	0.3181	0.0009	0.1245	0.5664	0.0011
ATD Carbopack	1,2-Dichloroethane	0.0012	0.6819	0.7406	<.0001	0.1371
ATD Carbopack	2-Butanone (MEK)	0.0693	0.4097	0.0603	0.7378	0.0119
ATD Carbopack	Hexane	0.7999	0.2913	0.4002	0.0272	0.1177
ATD Carbopack	Benzene	0.4718	0.2468	0.0547	0.0023	0.0331
ATD Carbopack	Carbon tetrachloride	0.0434	0.2975	0.3501	<.0001	<.0001
ATD Carbopack	Naphthalene	0.2629	0.6088	0.293	0.007	0.0778
ATD Carbopack	Trichloroethene	0.0113	0.2781	0.0002	<.0001	0.9484
ATD Carbopack	Tetrachloroethene	0.8513	0.004	0.0071	0.8484	0.0727
ATD Tenax	1,1,1-Trichloroethane	<.0001	0.2715	0.0021	<.0001	<.0001
ATD Tenax	1,2,4-Trimethylbenzene	0.9169	0.8868	0.0121	0.0296	0.2864
ATD Tenax	1,2-Dichloroethane	0.9154	0.8908	0.4733	<.0001	<.0001
ATD Tenax	2-Butanone (MEK)	0.7719	0.0799	0.1479	<.0001	<.0001
ATD Tenax	Hexane	0.6362	0.21	0.6114	<.0001	0.1148
ATD Tenax	Benzene	0.8106	0.0059	0.438	<.0001	0.0442
ATD Tenax	Carbon tetrachloride	<.0001	0.0229	0.0159	<.0001	<.0001
ATD Tenax	Naphthalene	0.311	0.2147	0.565	0.025	0.0347
ATD Tenax	Trichloroethene	0.5875	0.0002	0.0153	<.0001	0.475
ATD Tenax	Tetrachloroethene	0.3221	0.4522	0.11	<.0001	0.9827
RADIELLO	1,1,1-Trichloroethane	0.1005	0.0261	0.003	0.0899	0.0548
RADIELLO	1,2,4-Trimethylbenzene	0.6688	0.0007	<.0001	0.1133	0.0451
RADIELLO	1,2-Dichloroethane	0.0005	0.054	0.0002	0.0327	<.0001
RADIELLO	2-Butanone (MEK)	<.0001	0.5801	0.0003	0.0738	<.0001
RADIELLO	Hexane	0.1795	0.0066	0.0021	<.0001	0.0035
RADIELLO	Benzene	0.0047	0.0496	0.0012	<.0001	0.6113
RADIELLO	Carbon tetrachloride	0.4994	0.0143	0.0513	0.1724	0.9018
RADIELLO	Naphthalene	0.6635	0.0008	0.933	0.1183	0.0005
RADIELLO	Trichloroethene	0.001	0.0032	<.0001	0.0002	0.0169
RADIELLO	Tetrachloroethene	0.2158	0.0023	<.0001	0.3477	0.9109
SKC	1,1,1-Trichloroethane	0.0906	0.1691	0.0055	0.0096	0.0001
SKC	1,2,4-Trimethylbenzene	0.1362	0.3054	0.0012	0.0004	<.0001
SKC	1,2-Dichloroethane	<.0001	0.5187	0.1033	0.9879	0.6424
SKC	2-Butanone (MEK)	<.0001	0.2819	0.3914	0.0073	0.0028
SKC	Hexane	0.0006	0.0398	0.012	0.4921	0.1584
SKC	Benzene	0.0318	0.0551	0.9085	0.0218	0.0125
SKC	Carbon tetrachloride	0.0223	0.2682	0.032	<.0001	<.0001
SKC	Naphthalene	0.1182	0.1437	0.6579	<.0001	0.1122
SKC	Trichloroethene	<.0001	0.9977	0.0306	0.5618	<.0001
SKC	Tetrachloroethene	0.4868	0.0368	0.018	0.0097	0.1261
WMS	1,1,1-Trichloroethane	0.0224	0.9489	0.0042	0.6355	0.4719
WMS	1,2,4-Trimethylbenzene	0.7716	0.7992	<.0001	0.1467	0.0194
WMS	1,2-Dichloroethane	0.7347	0.1749	0.0054	0.0325	0.1887
WMS	2-Butanone (MEK)	0.5881	0.3369	0.14	0.0319	0.0027
WMS	Hexane	0.6198	0.4942	0.022	0.0003	0.0001
WMS	Benzene	0.5712	0.9017	0.0328	0.0012	0.0099
WMS	Carbon tetrachloride	0.0016	0.3838	0.0035	0.0766	0.0553
WMS	Naphthalene	0.9025	0.4298	<.0001	0.5432	0.006
WMS	Trichloroethene	0.6289	0.0325	0.0006	0.8376	0.0124
WMS	Tetrachloroethene	0.5923	0.1477	<.0001	0.9894	0.0074

red highlighted cells indicate statistical significance when alpha=0.05, therefore, p-value<0.05 = significant

In many cases, the statistically significant effects were consistent with expectations:

- Temperature and humidity showed significant effects less frequently than other factors, but this could be attributable to the fact that these factors were the most challenging to control (higher variability makes it less likely that an effect will show as statistically significant).
- Temperature had a significant effect for 8/10 compounds for the Radiello and no more than 3 compounds for any of the other samplers. The uptake rate for the Radiello depends mostly on the diffusion coefficient of each compound, and the diffusion coefficients change with temperature, so this is not unexpected. The fact that temperature effect was significant for the Radiello more frequently than for other samplers could be related to the fact that the higher uptake rates of this sampler made it more sensitive to changes. The Radiello also showed very low variability, which increased the likelihood that any trends will be significant statistically.
- Humidity had a significant effect for MEK and 12DCA (the two most soluble compounds) in the SKC Ultra and Radiello samplers, but not the WMS (which has a PDMS membrane that reduces water uptake by the sorbent) and ATD-Tenax (Tenax is extremely hydrophobic).
- Sample collection time showed significant effects for the ATD-Tenax sampler for all compounds tested. Tenax has lower recommended maximum sample volumes than Carbo-pack B, so this was most likely attributable to poor retention in the 4-day and 7-day samples. For example, the RMSVs for 111TCA, 12DCA, BENZ, CT and TCE are 0.2, 1, 1, 0.2 and 1 L, respectively.<sup>19</sup> The equivalent sample volume (UR x t) for these compounds for the 7 day samples was 5, 5, 3.5, 5 and 5 L, respectively. RMSVs are not available for MEK, HEX and NAPH, but of the other compounds, 55 of the 64 cases of  $C/C_0 < 0.63$  (i.e., failing the accuracy performance criterion with low bias) had an equivalent sample volume (UR x t) greater than the RMSV. This 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., most strongly sorbed). Sampling time was also significant for 7/10 compounds for the passive ATD sampler with Carbo-pack 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 affected significantly by sampling time, which was consistent with expectations because these samplers both used very strong sorbents (charcoal and Anasorb 747, respectively).

- Face velocity had less of an effect on the ATD tubes than on the other samplers. This may be because they had the lowest uptake rates of the samplers tested, and therefore were less likely to experience low bias from the starvation effect at low air velocities.
- Concentration had a significant effect for MEK on all sampler types, but was otherwise comparable for all samplers and not consistently significant for any other compounds.

### **3.4 Summary**

One general interpretation of the low concentration laboratory test data is that the uptake rates of passive samplers vary in response to the conditions under which testing is performed and the variability is compound-specific. The trends are in many cases consistent with theoretical expectations. The passive samplers show more variability than the pumped ATD tubes due to changes in the temperature, humidity, sample duration, face velocity and concentration; therefore, it is advisable to include some inter-method verification samples in a passive sampling campaign (e.g. collect an active sample beside every 10<sup>th</sup> passive sampler) to provide data that can be used to derive “field-calibrated” uptake rates for a particular set of environmental conditions when the highest level of accuracy is needed. The high precision of the passive samplers under any particular set of conditions (Table 3-9) provides confidence in the consistency of the uptake rates for other passive samplers exposed under the same conditions as the inter-method duplicate.

## 4 Indoor and Outdoor Air Testing

Indoor and outdoor air testing<sup>iv</sup> was performed at three DoD facilities to demonstrate the passive samplers and validate their performance in real settings. Unlike the chamber tests in Chapter 3, field sampling occurs under conditions that are not controlled and are likely to vary over the duration of the sampling event. This provides a different challenge for the passive samplers than the controlled laboratory chamber tests.

### 4.1 Experimental

#### 4.1.1 Sampling Locations and Strategies

At the Navy OTC3 site, the indoor air samples were collected in three locations (2 in the open warehouse area and one in an interior office) with four different types of passive samplers (the OVM 3500 was not included at this stage). Each sampler type was deployed in triplicate at each location. The office was a small room with low (8 foot) ceilings and the warehouse area was a large open area. Outdoor air samples were collected in triplicate in one location adjacent to the warehouse in an area that provided some protection from precipitation, high winds, and direct sunlight. Samplers were deployed on 9 March 2010 and retrieved on 15 March 2010. The active indoor and outdoor air samples at OTC3 were collected over 6 days using a 3-day flow controller by connecting two 6 L Summa canisters via a stainless steel “T-fitting” provided by the laboratory, which allowed for continuous collection of a sample over a 6-day period. One Summa canister was individually certified and one canister was batch certified. Only the individually certified Summa canisters were analyzed; the other canister was needed to provide sufficient volume to allow the connected pair of canisters to continue drawing gas for 6 days.

At CRREL, indoor air samples were collected in three locations, with five sampler types and 3 replicates in each location (similar to the scope at Navy OTC3, but with the addition of the OVM 3500). One outdoor air location was also tested with each of the five sampler types in 3 replicates. Indoor air concentrations at CRREL were expected to be high enough to be detectable with a 3-day deployment of the passive samplers. Outdoor air samples were collected over 7 days using 3-day flow controllers and paired Summa canisters (November 9 to 15, 2010), as described for OTC3. Unfortunately, the flow controllers shipped to CRREL allowed a faster flow rate than intended. Additional Summa canisters were acquired on short notice from TestAmerica (Burlington, VT). For the indoor air samples, a total of 23

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<sup>iv</sup> This Chapter is partly based on the author’s contributions to SPAWAR Report #2018<sup>227</sup>



Summa canisters were used to provide continuous monitoring in triplicate in each of the 3 locations. For the outdoor air samples, two of the paired Summa canister samples were deployed on the first day of the sample period and the third paired set of canisters was deployed on the fourth day in order to obtain outdoor air quality data over the 6 day sampling period (duplicate samples for the first 3 days and a single sample for the next three days). Time-weighted averages of the Summa canister concentrations were then calculated and used as the active control for indoor and outdoor air quality.

At MCAS Cherry Point, indoor air samples were collected in 3 locations with 5 passive sampler types in triplicate in each location. Outdoor air samples were collected in one location with each of five passive sampler types. Outdoor air samples were collected with only one replicate because the results at OTC3 and CRREL were mostly below the limit of detection, and it was not considered a prudent expenditure to continue sampling in triplicate. At MCAS Cherry Point, indoor air samplers were deployed in the break room, warehouse area, and autoclave room. The break room was a small room with low (8 foot) ceilings. The warehouse area was chosen as a sampling location because it was immediately outside the break room and, in contrast to the break room, was a large open area. The autoclave room was chosen as another sampling location because it was a moderately sized space, and was distant from the other two sampling locations. The chosen outdoor air location was beside a one-story shed located immediately outside Building 137. For the active samplers at MCAS CP, 7-day flow controllers provided by Columbia Analytical Services (CAS; Simi Valley, CA) were connected to individually certified 6 L Summa™ canisters. The 7-day flow controllers yielded somewhat inconsistent flow rates, so some of the Summa canister samples had a residual vacuum after 7 days and some did not, indicating some of the samples were shorter than 7 days by an unknown amount. The results of all Summa canister samples were very similar for each location, so all were used as if they were representative of the 7-day average concentrations.

#### **4.1.2 Sample Collection**

Indoor and outdoor air samples were collected over 3 to 7 days and Summa canisters were collected over the same durations as the passive samples for comparison. All indoor and outdoor air samples at each location were collected in reasonably close proximity (i.e., within a few feet, but not so close as to impose interference between them) and about three to five feet above the floor surface (approximately the breathing zone), as shown in Figure 4-1. The passive samplers were placed on shelves or hung and secured using thin gauge wire, then deployed according to the instructions provided in Appendix C. Summa canisters were placed in close proximity to the passive samplers and operated according to the

protocol in Appendix C. The indoor air samples were located in areas that would not be disruptive to building operations and within different sized areas (e.g., enclosed rooms vs. warehouse areas) that would have different building air circulation rates. The outdoor air samples were located in areas that provided some protection from precipitation, high winds, and direct sunlight.



**Figure 4-1:** Typical layout of indoor air sampling array

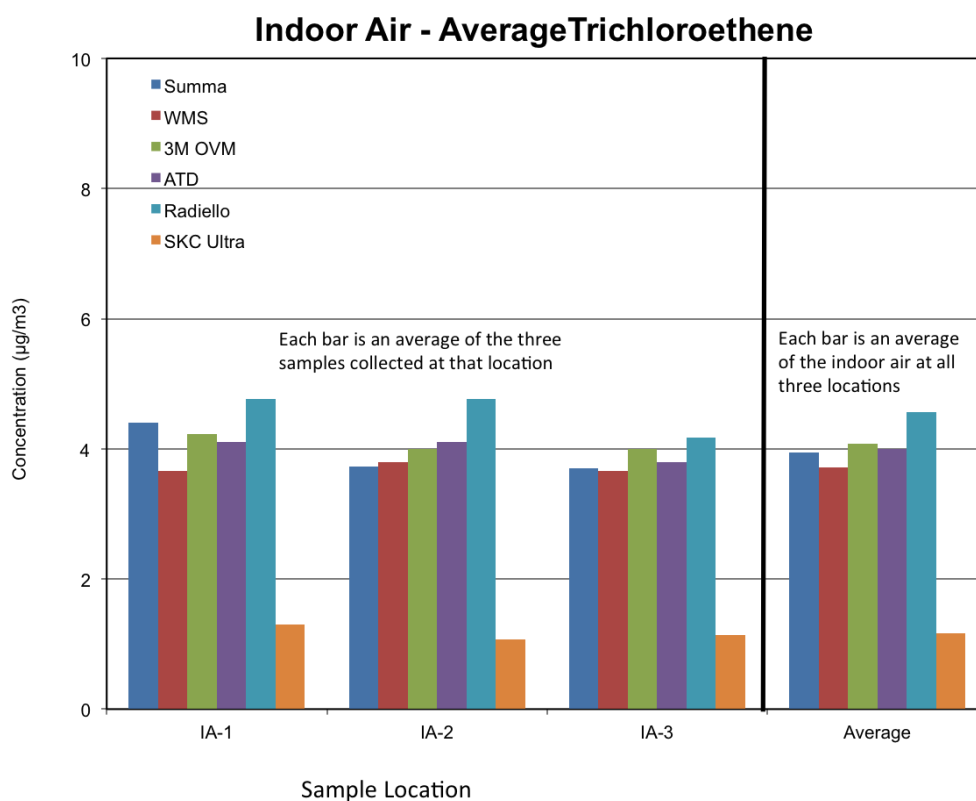
## **4.2 Results and Discussion**

### **4.2.1 OTC3**

Indoor air samples at OTC3 (Table 4-1) showed detectable concentrations of TCE in all samples and cDCE in only those samplers with sufficiently low reporting limits (Radiello, SKC and Summa canister). Outdoor air samples showed no detectable concentrations of VOCs except PCE in the SKC samplers. PCE was detected in all indoor and outdoor samples collected by the SKC samplers at similar concentrations, which were below the reporting limits for all the other samplers, including the Summa canisters.

Figure 4-2 shows stacked bar charts of TCE in indoor air, with the triplicate samples averaged to comprise the individual location bars to the left and all samples combined to comprise the “average” bars

to the right. This chart indicates a strong agreement between all the passive samplers and the Summa canister samples, except for the SKC sampler, which showed negative bias. The SKC Sampler was used with Chromosorb 106 as the adsorbent medium. The RMSV for TCE and cis-1,2-DCE on Chromosorb 106 is less than 5 liters.<sup>19</sup> The uptake rate for the SKC sampler for these compounds is about 15 mL/min and the samplers were deployed for about 7 days. The equivalent sample volume would have been about 150 liters in this instance. The equivalent sampled volume was thus much larger than the recommended maximum sample volume, which indicated that the low bias for the SKC samples was most likely attributable to poor retention. This was an example of a lesson learned from this research because the importance of considering the recommended maximum sample volume was not obvious prior to the OTC3 sampling event.



**Figure 4-2:** Stacked bar chart of individual measured concentrations of TCE at each location to the left and average to the right for all indoor samples at OTC3

**Table 4-1:** Indoor and outdoor VOC concentrations with passive and active samples at OTC3

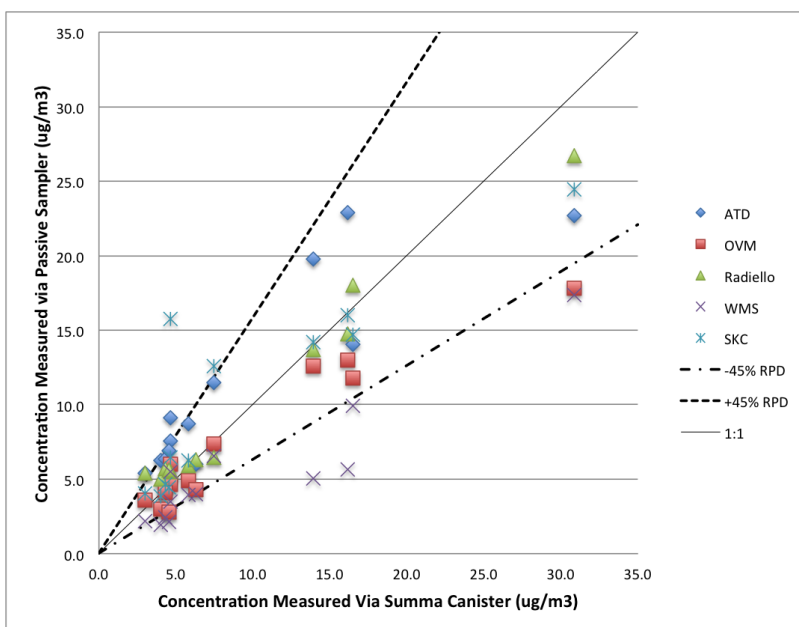
Sampler	VOC ( $\mu\text{g}/\text{m}^3$ )	IA-1			IA-2			IA-3			OA-1		
Summa	cDCE	0.28	0.28	0.30	0.31	0.33	0.31	0.28	0.30	0.30	0.12 U	0.12 U	0.11 U
	PCE	0.18 U	0.19 U	0.18 U	0.19 U	0.19 U	0.42 U	0.22 U	0.18 U	0.18 U	0.21 U	0.21 U	0.18 U
	TCE	4.9	3.7	4.6	3.7	3.8	3.7	3.4	3.8	3.9	0.16 U	0.17 U	0.14 U
WMS	cDCE	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U	6.1 U
	PCE	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U	1.1 U
	TCE	3.2	3.9	3.9	3.2	4.3	3.9	3.9	4.3	2.8	0.71 U	0.71 U	0.71 U
3M OVM 3500	cDCE	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U	0.60 U
	PCE	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U
	TCE	4.5	4.1	4.1	4.1	4.1	3.8	4.1	4.1	3.8	0.28 U	0.28 U	0.28 U
ATD Carbopack B	cDCE	1.3 U	1.3 U	1.3 U	1.3 U	1.3 U	1.3 U	1.3 U	1.3 U	1.3 U	1.2 U	1.2 U	1.2 U
	PCE	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U	1.4 U
	TCE	3.7	4.2	4.4	4.2	4.4	3.7	4	3.7	3.7	1.2 U	1.2 U	1.2 U
Radiello	cDCE	0.36	0.36	0.36 U	0.4	0.38	0.36 U	0.36 U	0.36 U	0.36	0.36 U	0.36 U	0.36 U
	PCE	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U	0.20 U
	TCE	4.7	4.7	4.9	4.6	4.1	3.7	3.7	4.4	4.4	0.17 U	0.17 U	0.17 U
SKC Ultra	cDCE	0.056	0.064	0.07	0.042	0.042	0.042	0.053	0.055	0.051	0.04 U	0.04 U	0.04 U
	PCE	0.052	0.06	0.065	0.059	0.061	0.066	0.059	0.06	0.06	0.05	0.062	0.057
	TCE	1.1	1.4	1.4	1.1	0.93	1.2	1.1	1.2	1.1	0.04 U	0.04 U	0.04 U

U = compound not detected (the value given is the reporting limit)

#### 4.2.2 CRREL

The indoor air sampling data from CRREL generally showed good agreement between the passive samplers and Summa canisters. The measured concentrations are shown in Table 4-2. The average of three replicates for each passive sampler and compound are plotted vs. the average of three Summa canister concentrations in Figure 4-3. Results from the outdoor air samples were generally non-detect or very low, so a comparison to the Summa canister results is not supported.

The indoor air data at CRREL did not show indications of poor retention as observed for the SKC at OTC3. The SKC Ultra was used with charcoal or Carbograph 5 at CRREL, both of which are much stronger sorbents than Chromosorb 106, and the SKC sampler had no results with an unacceptably low bias. The ATD tube used Carboxpack B, which has a recommended maximum sample volume of 20 L for TCE and >100 L for all the other detected analytes. The equivalent sample volumes for the ATD tube sampler were about 5 L, which was less than the recommended maximum sample volumes by a comfortable margin. The ATD tube sampler also had no results with low bias.



**Figure 4-3:** Passive sampler indoor air concentrations vs. Summa canisters at CRREL

The WMS sampler showed low bias for xylenes by a factor of about three (and very consistently for both locations 1 and 2). The SKC sampler showed a positive bias for toluene, also by a factor up to about 3. These biases were most likely attributable to uncertainty in the uptake rate for these particular combinations of sorbent, sampler and analyte.

**Table 4-2: Indoor air VOC concentrations using Summa canisters and passive samplers at CRREL**

Location	Sampler (Subtype/)	TCE ( $\mu\text{g}/\text{m}^3$ )	Toluene ( $\mu\text{g}/\text{m}^3$ )	Ethylbenzene	m,p-Xylene	o-Xylene	1,2,4-TMB ( $\mu\text{g}/\text{m}^3$ )
IA-1	Summa/TO-15	13.4	3.7	4.3	12.4	0.8	4.0
		18.0	5.1	4.7	14.4	4.1	3.9
		18.0	5.2	5.0	15.0	4.1	4.1
	ATD (Regular/Carbopack B)	14.4	8.6	7.6	20.0	5.3	6.3
		14.4	10.8	7.7	20.0	5.6	6.6
		13.4	7.9	7.4	19.3	5.3	5.7
	OVM (Regular/Charcoal)	11.8	7.3	4.5	12.6	3.7	2.8 J
		11.1	5.5	4.5	11.8	3.7	2.6 J
		12.5	5.2	4.9	13.4	3.4	3.6 J
	Radiello (White body/thermal)	18.1	5.7	5.6	13.8	5.4	4.7
		18.2	5.4	5.5	13.7	5.5	5.8
		17.7	5.5	5.3	13.6	5.3	4.4
	WMS (Regular/Anasorb 747)	9.9	6.5	3.8	5.8	2.4	2.2
		9.8	4.5	3.2	4.6	2.0	1.8
		10.1	5.5	3.4	4.8	2.1	1.8
SKC (Regular/mix of char & CG5)	16.4	9.5	6.0	16.0	4.5	4.3	
	16.5	8.8	6.1	16.2	4.5	4.4	
	11.2	28.9	7.3	10.5	3.1	2.8	
IA-2	Summa/TO-15	35.2	7.7	6.7	17.7	4.8	5.1
		28.6	6.7	5.7	15.3	4.2	4.6
		28.8	8.0	5.1	15.4	4.0	4.0
	ATD (Regular/Carbopack B)	21.8	10.8	8.5	23.1	6.9	7.2
		24.5	12.9	9.3	23.9	6.6	7.2
		21.8	10.8	8.5	21.6	5.7	6.2
	OVM (Regular/Charcoal)	17.8	11.0	4.7	12.7	4.1	2.7 J
		17.1	4.9	4.8	12.7	4.0	2.7 J
		18.6	6.1	5.1	13.5	4.2	3.0 J
	Radiello (White body/thermal)	25.6	6.1	6.0	14.6	5.7	5.4
		26.5	6.4	5.7	14.4	5.5	6.0
		28.0	6.8	6.0	15.2	5.9	5.3
	WMS (Regular/Anasorb 747)	16.9	4.9	3.8	5.7	2.5	2.2
		17.6	7.6	4.2	6.0	2.6	2.4
		17.6	7.1	3.8	5.2	2.3	1.8
SKC (Regular/mix of char & CG5)	23.7	10.3	6.3	16.1	4.8	4.6	
	23.1	9.3	6.2	15.9	4.5	4.4	
	26.5	18.2	17 U	34 U	17 U	18 U	
IA-3	Summa/TO-15	7.2	0.75U	0.87U	2.2U	0.87U	0.98U
		6.5	0.75U	0.87U	2.2U	0.87U	0.98U
		5.2	0.75U	0.87U	2.2U	0.87U	0.98U
	ATD (Regular/Carbopack B)	6.9	7.9	1.7 U	1.7 U	1.7 U	2.0 U
		4.5	2.0	1.7 U	1.7 U	1.7 U	2.0 U
		6.5	5.9	1.7 U	1.7 U	1.7 U	2.0 U
	OVM (Regular/Charcoal)	4.2	1.2	0.6 U	0.6 U	0.6 U	0.68 J
		3.6	1.3	0.6 U	0.6 U	0.6 U	0.68 J
		5.1	6.5	0.6 U	0.6 U	0.6 U	0.68 J
	Radiello (White body/thermal)	7.7	0.7	0.2 U	0.4	0.2 U	0.23 U
		5.5	0.7	0.2 U	0.3	0.2 U	0.23 U
		5.7	0.7	0.2 U	0.3	0.2 U	0.23 U
	WMS (Regular/Anasorb 747)	3.6	2.8 U	1.8 U	1.9 U	1.7 U	0.93 U
		4.3	2.8 U	1.8 U	1.9 U	1.7 U	0.93 U
		4.0	8.3	1.8 U	1.9 U	1.7 U	0.93 U
SKC (Regular/mix of char & CG5)	16 U	16 U	17 U	34 U	17 U	18 U	
	16 U	19.5	17 U	34 U	17 U	18 U	
	16 U	16 U	17 U	34 U	17 U	18 U	

U = not detected (value is the reporting limit), J = estimated (>MDL but <RL)

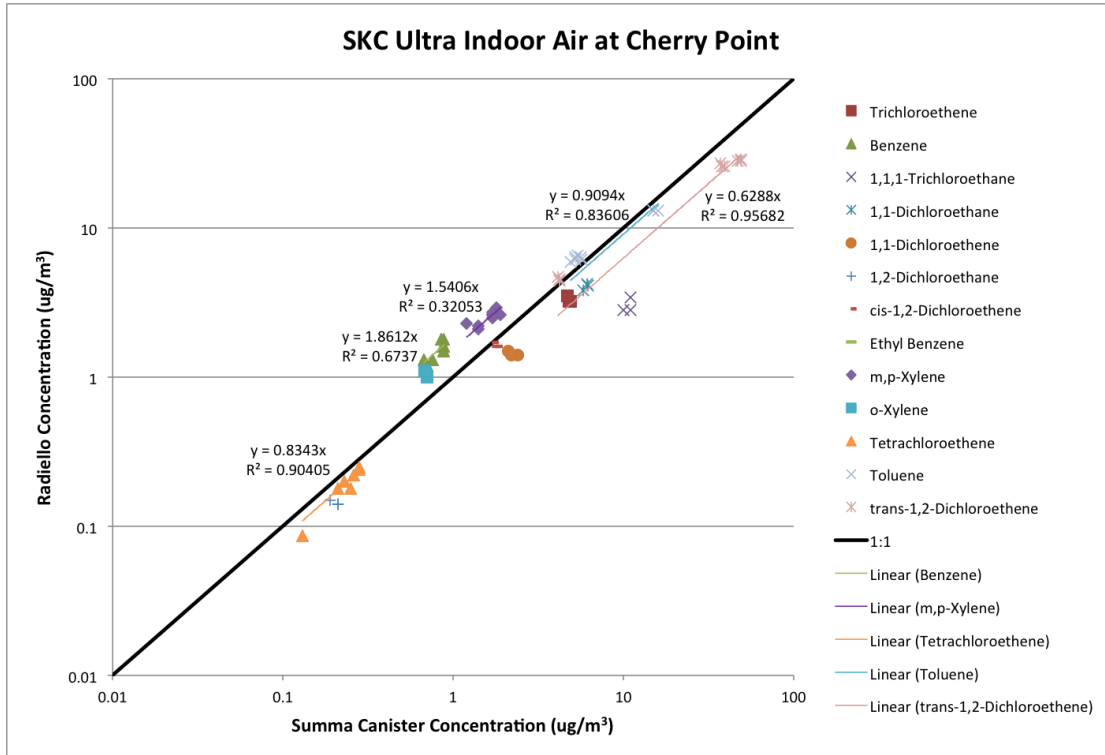
### 4.2.3 MCAS Cherry Point

The results of the MCAS Cherry Point sampling event are presented in Appendix F. Indoor air samples had detectable concentrations of chlorinated VOCs, benzene, toluene, ethyl benzene, and xylenes (BTEX) at the three sample locations. Outdoor air samples had detectable concentrations of VOCs, but generally at concentration less than  $1 \mu\text{g}/\text{m}^3$ .

The concentrations measured at MCAS Building 137 with the passive samplers were plotted against the concentrations measured with the Summa canisters to show the correlations graphically (Figures 4-4 to 4-8) using logarithmic scales to show the data because the numbers spanned a range of almost two orders of magnitude. Where there were sufficient detections in the MCAS indoor air data, a linear regression line was plotted, each with a fixed intercept of zero to focus on the slope and correlation coefficient. The intercept was fixed to zero because a passive sampler should show a zero concentration for any compound that is not present. To assess the significance of the intercept on the correlation, some of the data sets were re-plotted with the intercept not set to zero, but in these comparisons the correlation coefficients and slopes were only marginally different.

The WMS and Radiello samplers showed low bias for cDCE, tDCE, 11DCA (up to one order of magnitude), and 11DCE (up to two orders of magnitude). The uptake rate for these compounds is about 1 to  $2 \text{ mL min}^{-1}$  for the WMS sampler and about 20 to  $30 \text{ mL min}^{-1}$  for the Radiello. When multiplied by the sample duration (about 7 days), this equates to an equivalent sample volume of 10 to 20 liters for the WMS sampler and 200 to 300 liters for the Radiello. The RMSV for these compounds on Carboxograph 4 (used in the Radiello) is less than about 20 liters, and less than 5 liters with Carboxpack B (used in the WMS sampler). The ATD tubes contained the same sorbent (Carboxpack B) as the WMS sampler, but the uptakes rates were lower by up to a factor of 5, so the equivalent sample volume for the ATD tube sampler was about 5 L (similar to the RMSV). For the ATD tubes, cDCE, tDCE, 11DCE and 11DCA were also biased slightly low (to a lesser degree than the Radiello and WMS samplers). The SKC and 3M OVM samplers showed no significant bias for these compounds, presumably because the adsorbent used in these samplers was activated carbon, which retains VOCs more strongly than the thermally-desorbable adsorbents. The MCAS 137 data showed a notable improvement for the SKC Ultra Sampler relative to the results from San Diego OTC3 where Chromosorb 106 (a weaker adsorbent) was used. This improvement in the performance of the SKC sampler again demonstrated the importance of proper selection of the adsorbent for those samplers where the sorbent is interchangeable.

Several other compounds were detected with one or more of the passive samplers with concentrations either higher or lower than the Summa canister values, but with a consistent trend. This was attributable to the uptake rate used to calculate the concentrations being either higher or lower than the actual uptake rates for the compounds and conditions.



**Figure 4-4:** VOCs in indoor air by SKC Ultra II vs Summa canister at MCAS 137



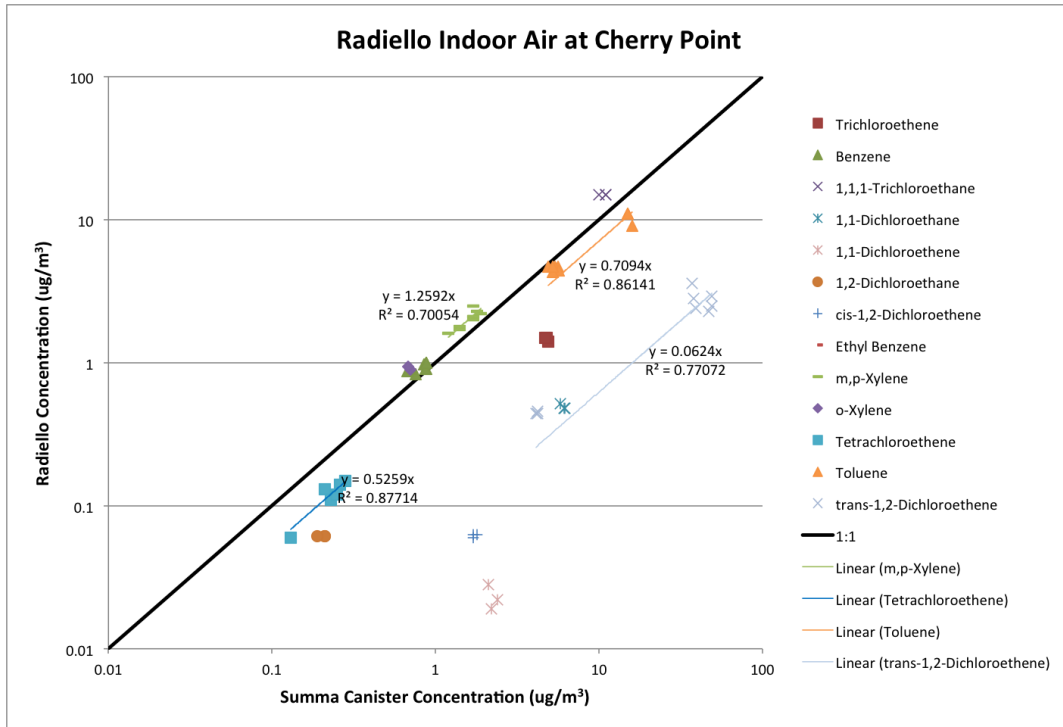


Figure 4-5: VOCs in indoor air by Radiello vs. Summa canister at MCAS 137

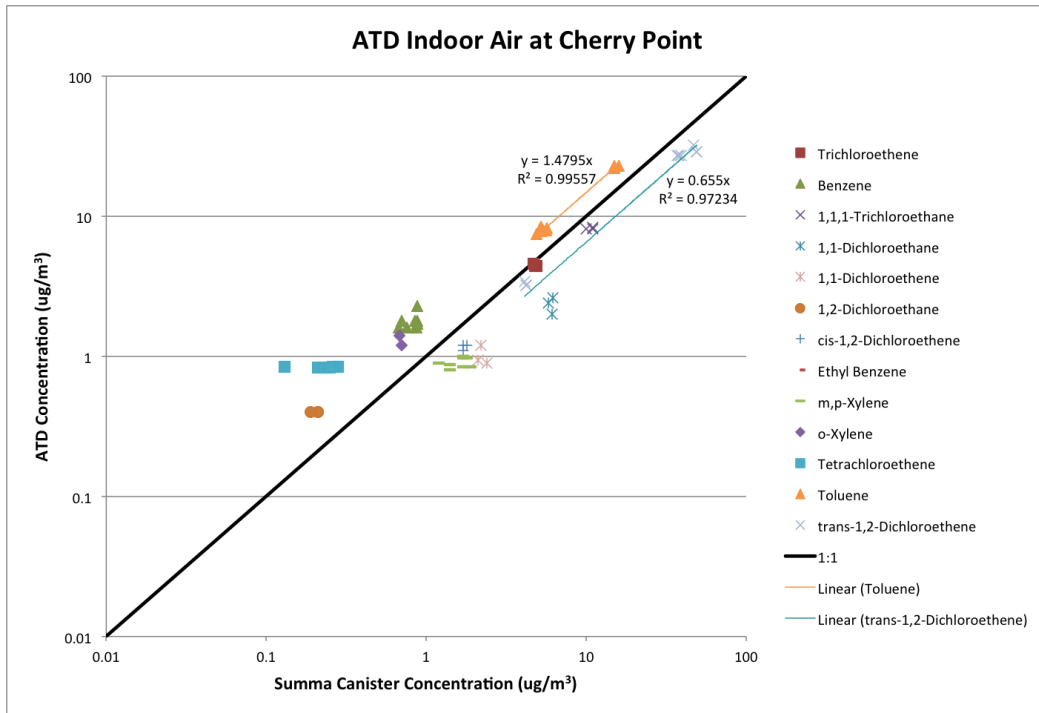


Figure 4-6: VOCs in indoor air by ATD/Carbopack B vs. Summa canister at MCAS 137

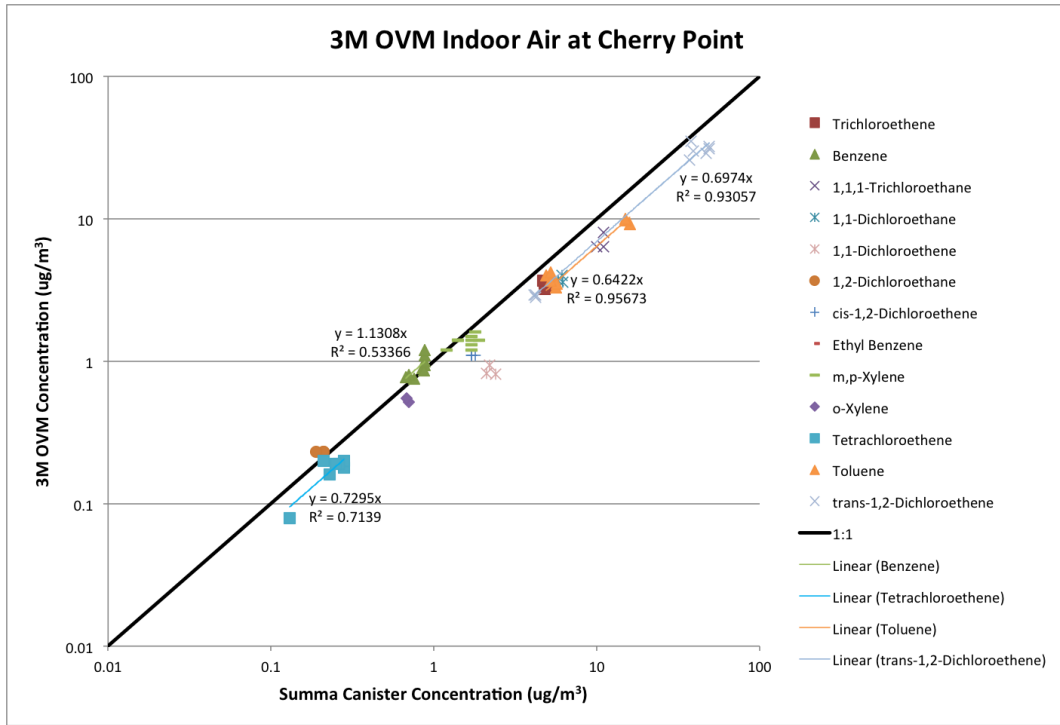


Figure 4-7: VOCs in indoor air by 3M OVM vs. Summa canister at MCAS 137

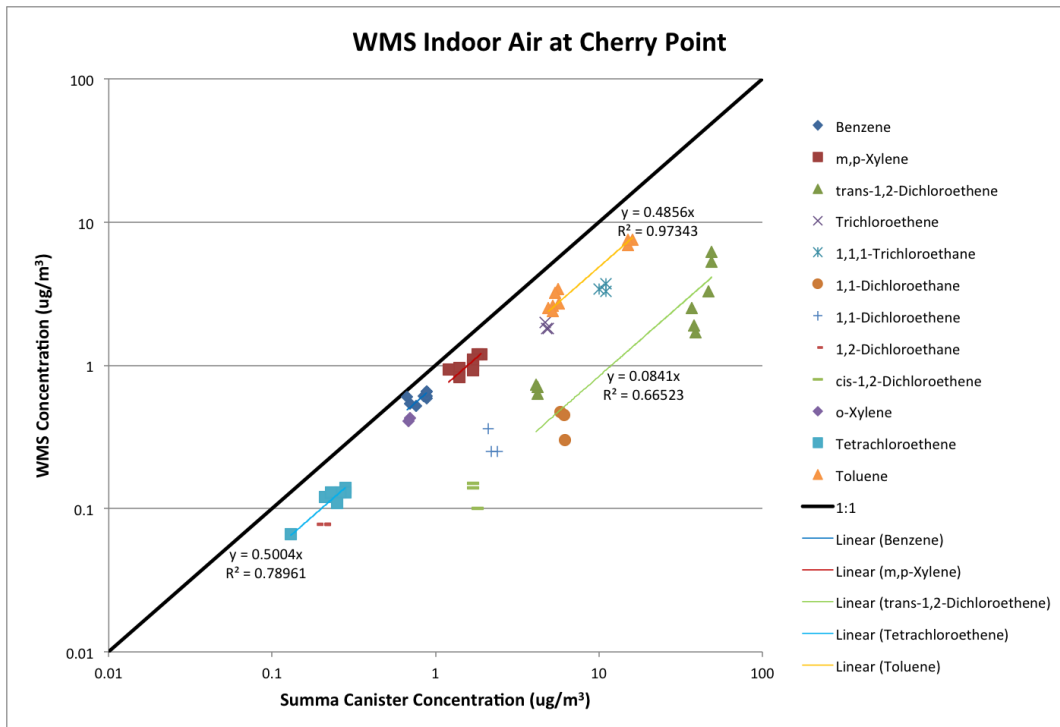


Figure 4-8: VOCs in indoor air by WMS vs. Summa canister at MCAS 137

### 4.3 Performance Assessment

At OTC, most of the indoor and outdoor air concentrations were below the reporting limit, except for TCE in indoor air, which showed excellent accuracy and precision for all of the passive samplers except the SKC Ultra, which showed negative bias attributable to poor retention from an unfortunate selection of a weak sorbent.

At CRREL, the indoor air data met the accuracy performance criterion of  $\pm 45\%$  RPD ( $C/C_0$  between 0.63 and 1.58) in 77% (49/64) of cases. The relative concentrations (average of three replicates by passive sampler divided by average of three replicates by Summa canister) and COV (standard deviation divided by mean for three replicates samples by each sampler for each compound in each location) are shown in Table 4-3. The COV values met the precision performance criterion of 30% or less in 94% (60/64) of cases, and in most cases, the passive samplers had lower COV values than the Summa canisters (SKC excepted). The instances where the passive samplers did not meet the accuracy criterion at CRREL appear to be attributable to inaccuracies in the uptake rates. For example, the  $C/C_0$  values for the WMS sampler for locations 1 and 2 were 0.36 and 0.35 for o-xylene and 0.48 and 0.47 for 124TMB. These results are very consistent. The uptake rates for o-xylene and 124TMB for the WMS sampler were calculated to be 6.2 and 13 mL/min, respectively; however, based on the indoor air sampling results at CRREL, the field-calibrated values would have been 2.2 mL/min for o-xylene and 6.2 for 124TMB. This is an example of the usefulness of some inter-method samples during the conduct of a passive sampling campaign. The uptake rate may be different than expected because of site-specific temperature, humidity, face velocity, sample duration or concentrations, but inter-method samples will allow the uptake rate to be calibrated to the field conditions. Once the site-specific uptake rate is known, the accuracy of all samples collected under similar conditions will be improved because the passive samplers show very good precision.

**Table 4-3: C/C<sub>0</sub> and COV for indoor air samples at CRREL**

Location	Sampler	TCE (C/C <sub>0</sub> )	Toluene (C/C <sub>0</sub> )	Ethyl-benzene (C/C <sub>0</sub> )	m,p-Xylene (C/C <sub>0</sub> )	o-Xylene (C/C <sub>0</sub> )	1,2,4-TMB (C/C <sub>0</sub> )
IA-1	ATD/CPB	<b>0.85</b>	1.95	1.62	<b>1.42</b>	1.8	<b>1.56</b>
	OVM	<b>0.72</b>	<b>1.29</b>	<b>0.99</b>	<b>0.91</b>	<b>1.21</b>	<b>0.75J</b>
	Radiello	<b>1.09</b>	<b>1.18</b>	<b>1.17</b>	<b>0.98</b>	1.81	<b>1.24</b>
	WMS	0.6	<b>1.18</b>	<b>0.75</b>	0.36	<b>0.73</b>	0.48
	SKC	<b>0.89</b>	3.38	<b>1.38</b>	<b>1.02</b>	<b>1.35</b>	<b>0.96</b>
IA-2	ATD/CPB	<b>0.74</b>	<b>1.54</b>	<b>1.5</b>	<b>1.42</b>	<b>1.48</b>	<b>1.51</b>
	OVM	0.58	<b>0.99</b>	<b>0.84</b>	<b>0.8</b>	<b>0.95</b>	0.61J
	Radiello	<b>0.86</b>	<b>0.87</b>	<b>1.01</b>	<b>0.91</b>	<b>1.32</b>	<b>1.22</b>
	WMS	0.56	<b>0.88</b>	<b>0.68</b>	0.35	0.57	0.47
	SKC	<b>0.79</b>	1.69	<b>1.07</b>	<b>0.99</b>	<b>1.08</b>	<b>0.98</b>
IA-3	ATD/CPB	<b>0.95</b>	ND	ND	ND	ND	ND
	OVM	<b>0.68</b>	ND	ND	ND	ND	ND
	Radiello	<b>1</b>	ND	ND	ND	ND	ND
	WMS	<b>0.63</b>	ND	ND	ND	ND	ND
	SKC	ND	ND	ND	ND	ND	ND
boldface: average C/C <sub>0</sub> values of 0.63 to 1.58, which meet the performance criterion: RPD < +/-45%							
Location	Sampler	TCE (COV)	Toluene (COV)	Ethyl-benzene (COV)	m,p-Xylene (COV)	o-Xylene (COV)	1,2,4-TMB (COV)
IA-1	Summa	<b>16%</b>	<b>18%</b>	<b>8%</b>	<b>10%</b>	64%	<b>3%</b>
	ATD/CPB	<b>4%</b>	<b>16%</b>	<b>2%</b>	<b>2%</b>	<b>2%</b>	<b>7%</b>
	OVM	<b>6%</b>	<b>19%</b>	<b>5%</b>	<b>7%</b>	<b>4%</b>	<b>18%</b>
	Radiello	<b>2%</b>	<b>3%</b>	<b>2%</b>	<b>1%</b>	<b>3%</b>	<b>14%</b>
	WMS	<b>1%</b>	<b>18%</b>	<b>9%</b>	<b>12%</b>	<b>10%</b>	<b>13%</b>
	SKC	<b>21%</b>	73%	<b>12%</b>	<b>23%</b>	<b>19%</b>	<b>24%</b>
IA-2	Summa	<b>12%</b>	<b>9%</b>	<b>14%</b>	<b>8%</b>	<b>9%</b>	<b>12%</b>
	ATD/CPB	<b>7%</b>	<b>11%</b>	<b>5%</b>	<b>5%</b>	<b>9%</b>	<b>8%</b>
	OVM	<b>4%</b>	44%	<b>4%</b>	<b>4%</b>	<b>3%</b>	<b>6%</b>
	Radiello	<b>5%</b>	<b>5%</b>	<b>3%</b>	<b>3%</b>	<b>3%</b>	<b>7%</b>
	WMS	<b>2%</b>	<b>23%</b>	<b>5%</b>	<b>7%</b>	<b>7%</b>	<b>13%</b>
	SKC	<b>7%</b>	39%	<b>2%</b>	<b>1%</b>	<b>4%</b>	<b>3%</b>
IA-3	Summa	<b>16%</b>	ND	ND	ND	ND	ND
	ATD/CPB	<b>21%</b>	ND	ND	ND	ND	ND
	OVM	<b>18%</b>	ND	ND	ND	ND	ND
	Radiello	<b>20%</b>	ND	ND	ND	ND	ND
	WMS	<b>10%</b>	ND	ND	ND	ND	ND
	SKC	ND	ND	ND	ND	ND	ND
boldface: COV meets the criterion: < 30%, ND – not detected, J – estimated (>MDL but <RL)							

At MCAS 137, indoor and outdoor air data met the accuracy performance criterion of +/-45% RPD in 62% (56/90) of the available comparisons (Table 4-4), after excluding the data for the WMS and Radiello with poorly retained compounds (cDCE, tDCE, 11DCA, and 11DCE). The excluded compounds all showed negative bias that was likely attributable to poor retention. Where there were sufficient detections, the COV for each compound in each indoor air location for each sampler was calculated and the average of all the COV values was calculated for all five passive samplers and the Summa canisters. The Summa canisters had an average COV of 5% and the passive samplers ranged from 6% to 9%, which was very similar to the conventional method and well within the performance criterion for precision (COV < 30%).

#### **4.4 Summary**

The results of the indoor air field sampling showed that passive samplers are characterized by very good precision, which is consistent with the low concentration laboratory tests. Combinations of compounds and sorbents with low RMSVs showed negative bias that is attributable to poor retention. Combinations of compounds and sorbents with a high RMSV met the accuracy criterion in most cases. The accuracy can be improved if the uptake rates for the particular compounds, sorbents, samplers and environmental conditions are determined through field calibration with occasional duplicates using active samplers.

**Table 4-4: C/C<sub>0</sub> and COV for indoor air sampling at MCAS 137**

Sample Location: Sample Location:	Indoor Air Location #1 137-IA-1 Series																
Sampler Type:	OVM			Radiello			WMS			SKC			ATD Tube			Summa	
Client Sample ID:	137-IA-1A-OVM			137-IA-1A-RAD			137-IA-1A-WMS			137-IA-1A-SKC			137-IA-1A-ATD			137-IA-1A-SUM	
Sampler Type/Sorbent:	Regular/charcoal			Yellow body/Carbograph 4			Regular/Carbopack B			Regular II/Carbograph 5			Regular/Carbopack B			--	
Exposure Duration (min):	9944			9935			9913			9921			9921			--	
Exposure Duration (days):	6.9			6.9			6.9			6.9			6.9			--	
<i>Volatile Organic Compounds</i>	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	COV
( $\mu\text{g}/\text{m}^3$ )																	
1,1,1-Trichloroethane	<b>6.93</b>	<b>0.65</b>	<b>0.13</b>	<b>15.00</b>	<b>1.41</b>		<b>3.47</b>	0.33	<b>0.06</b>	<b>3.00</b>	0.28	<b>0.12</b>	<b>8.17</b>	<b>0.77</b>	<b>0.01</b>	<b>10.67</b>	<b>0.05</b>
1,1,2-Trichloroethane	ND			ND			ND			ND			ND			ND	
1,1-Dichloroethane	<b>3.77</b>	0.62	<b>0.06</b>	<b>0.49</b>	0.08	<b>0.05</b>	<b>0.41</b>	0.07	<b>0.23</b>	<b>4.03</b>	<b>0.67</b>	<b>0.05</b>	<b>2.33</b>	0.39	<b>0.13</b>	<b>6.03</b>	<b>0.03</b>
1,1-Dichloroethene	<b>0.86</b>	0.38	<b>0.08</b>	<b>0.02</b>	0.01	<b>0.20</b>	<b>0.29</b>	0.13	<b>0.22</b>	<b>1.43</b>	<b>0.64</b>	<b>0.04</b>	<b>1.01</b>	0.45	<b>0.16</b>	<b>2.23</b>	<b>0.07</b>
1,2-Dichloroethane	<b>0.23</b>			<b>0.06</b>			ND			<b>0.14</b>		<b>0.04</b>	ND			ND	
Benzene	<b>0.77</b>	<b>1.09</b>	<b>0.03</b>	<b>0.87</b>	<b>1.23</b>	<b>0.05</b>	<b>0.55</b>	<b>0.78</b>	<b>0.08</b>	<b>1.27</b>	1.78	<b>0.05</b>	<b>1.67</b>	2.35	<b>0.07</b>	<b>0.71</b>	<b>0.06</b>
cis-1,2-Dichloroethene	<b>1.10</b>	<b>0.63</b>		<b>0.06</b>	0.04	<b>0.03</b>	<b>0.13</b>	0.08	<b>0.20</b>	<b>1.63</b>	<b>0.94</b>	<b>0.04</b>	<b>1.17</b>	<b>0.67</b>	<b>0.05</b>	<b>1.73</b>	<b>0.03</b>
Ethyl Benzene	<b>0.40</b>		<b>0.03</b>	<b>0.66</b>		<b>0.04</b>	<b>0.28</b>		<b>0.05</b>	<b>0.73</b>		<b>0.04</b>	<b>0.88</b>		<b>0.08</b>	ND	
m,p-Xylene	<b>1.50</b>	<b>0.83</b>	<b>0.07</b>	<b>2.33</b>	<b>1.30</b>	<b>0.07</b>	<b>1.17</b>	<b>0.65</b>	<b>0.05</b>	<b>2.70</b>	<b>1.50</b>	<b>0.06</b>	<b>3.23</b>	1.80	<b>0.12</b>	<b>1.80</b>	<b>0.06</b>
o-Xylene	<b>0.54</b>	<b>0.70</b>	<b>0.03</b>	<b>0.94</b>	<b>1.23</b>	<b>0.04</b>	<b>0.42</b>	0.55	<b>0.02</b>	<b>1.03</b>	<b>1.35</b>	<b>0.06</b>	<b>1.23</b>	1.62	<b>0.12</b>	<b>0.76</b>	<b>0.17</b>
Tetrachloroethene	<b>0.08</b>	0.56	<b>0.03</b>	<b>0.06</b>	0.40	<b>0.02</b>	<b>0.07</b>	0.45	<b>0.03</b>	<b>0.09</b>	<b>0.63</b>	<b>0.08</b>	ND			<b>0.15</b>	<b>0.20</b>
Toluene	<b>9.67</b>	<b>0.63</b>	<b>0.04</b>	<b>10.37</b>	<b>0.68</b>	<b>0.11</b>	<b>7.30</b>	0.48	<b>0.05</b>	<b>13.00</b>	<b>0.85</b>		<b>22.67</b>	1.48	<b>0.03</b>	<b>15.33</b>	<b>0.04</b>
trans-1,2-Dichloroethene	<b>2.87</b>	<b>0.69</b>	<b>0.02</b>	<b>0.45</b>	0.11	<b>0.03</b>	<b>0.69</b>	0.17	<b>0.08</b>	<b>4.53</b>	<b>1.09</b>	<b>0.03</b>	<b>3.27</b>	<b>0.78</b>	<b>0.04</b>	<b>4.17</b>	<b>0.01</b>
Trichloroethene	<b>3.40</b>	<b>0.71</b>	<b>0.08</b>	<b>1.47</b>	0.31	<b>0.04</b>	<b>1.87</b>	0.39	<b>0.06</b>	<b>3.30</b>	<b>0.69</b>	<b>0.05</b>	<b>4.47</b>	<b>0.93</b>	<b>0.03</b>	<b>4.80</b>	<b>0.02</b>
Average		<b>0.68</b>	<b>0.05</b>		0.62	<b>0.06</b>		0.37	<b>0.09</b>		<b>0.95</b>	<b>0.05</b>		<b>1.12</b>	<b>0.08</b>		<b>0.07</b>
Average excluding poor retention					<b>0.93</b>			0.52									
Fraction meeting accuracy criterion		8/11			5/11			2/11			9/11			4/10			

Sample Location: Sample Location:	Indoor Air Location #2 137-IA-2 Series																
Sampler Type:	OVM			Radiello			WMS			SKC			ATD Tube			Summa	
Client Sample ID:	137-IA-2A-OVM			137-IA-2A-RAD Yellow body/Carbograph 4			137-IA-2A-WMS			137-IA-2A-SKC			137-IA-2A-ATD			137-IA-2A-SUM	
Sampler Type/Sorbent:	Regular/charcoal						Regular/Carbopack B			Regular II/Carbograph 5			Regular/Carbopack B			--	
Exposure Duration (min):	9927			9912			9913			9904			9913				
Exposure Duration (days):	6.9			6.9			6.9			6.9			6.9			--	
<i>Volatile Organic Compounds</i>	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	C/C <sub>0</sub>	COV	Average	COV
( $\mu\text{g}/\text{m}^3$ )																	
1,1,1-Trichloroethane	ND			ND			ND			ND			ND			ND	
1,1,2-Trichloroethane	ND			ND			ND			ND			ND			ND	
1,1-Dichloroethane	ND			ND			ND			ND			ND			ND	
1,1-Dichloroethene	<b>0.45</b>			ND			ND			<b>0.03</b>		<b>0.22</b>	ND			ND	
1,2-Dichloroethane	<b>0.23</b>			<b>0.01</b>		<b>0.08</b>	ND			<b>0.06</b>		<b>0.03</b>	ND			ND	
Benzene	<b>0.90</b>	<b>1.04</b>	<b>0.04</b>	<b>0.93</b>	<b>1.08</b>	<b>0.04</b>	<b>0.60</b>	<b>0.70</b>	<b>0.02</b>	<b>1.73</b>	2.00	<b>0.07</b>	<b>1.73</b>	2.00	<b>0.07</b>	<b>0.87</b>	<b>0.02</b>
cis-1,2-Dichloroethene	<b>0.02</b>		<b>0.04</b>	ND			ND			<b>0.16</b>		<b>0.00</b>	ND			ND	
Ethyl Benzene	<b>0.49</b>		<b>0.08</b>	<b>0.77</b>		<b>0.03</b>	<b>0.32</b>		<b>0.08</b>	<b>0.87</b>		<b>0.03</b>	<b>0.99</b>		<b>0.01</b>	ND	
m,p-Xylene	<b>1.30</b>	<b>0.76</b>	<b>0.08</b>	<b>2.07</b>	<b>1.22</b>	<b>0.03</b>	<b>1.01</b>	0.59	<b>0.08</b>	<b>2.60</b>	<b>1.53</b>	<b>0.04</b>	<b>2.80</b>	1.65	<b>0.00</b>	<b>1.70</b>	<b>0</b>
o-Xylene	<b>0.51</b>		<b>0.07</b>	<b>0.87</b>		<b>0.03</b>	<b>0.36</b>		<b>0.06</b>	<b>1.02</b>		<b>0.07</b>	<b>1.10</b>		<b>0.00</b>	ND	
Tetrachloroethene	<b>0.19</b>	<b>0.70</b>	<b>0.05</b>	<b>0.15</b>	0.54	<b>0.04</b>	<b>0.13</b>	0.49	<b>0.04</b>	<b>0.24</b>	<b>0.87</b>	<b>0.06</b>	ND			<b>0.27</b>	
Toluene	<b>3.50</b>	<b>0.63</b>	<b>0.06</b>	<b>4.60</b>	<b>0.83</b>	<b>0.04</b>	<b>3.10</b>	0.56	<b>0.12</b>	<b>6.33</b>	<b>1.14</b>	<b>0.03</b>	<b>8.00</b>	<b>1.44</b>	<b>0.02</b>	<b>5.57</b>	<b>0.03</b>
trans-1,2-Dichloroethene	<b>30.67</b>	<b>0.63</b>	<b>0.05</b>	<b>2.57</b>	0.05	<b>0.12</b>	<b>4.93</b>	0.10	<b>0.30</b>	<b>28.33</b>	0.59	<b>0.02</b>	<b>30.00</b>	0.62	<b>0.06</b>	<b>48.33</b>	<b>0.02</b>
Trichloroethene	<b>0.03</b>		<b>0.04</b>	<b>0.01</b>		<b>0.13</b>	ND			<b>0.03</b>		<b>0.15</b>	ND			ND	
Average		<b>0.75</b>	<b>0.06</b>		<b>0.74</b>	<b>0.06</b>		0.49	<b>0.10</b>		<b>1.22</b>	<b>0.07</b>		<b>1.43</b>	<b>0.03</b>		<b>0.02</b>
Average excluding poor retention					<b>0.91</b>			0.58									
Fraction meeting accuracy criterion		5/5			3/5			1/5			3/5			1/4			

Sample Location: Sample Location:	Indoor Air Location #3 137-IA-3 Series																		
Sampler Type:	OVM			Radiello			WMS			SKC			ATD Tube			Summa			
Client Sample ID:	137-IA-3A-OVM			137-IA-3A-RAD Yellow body/Carbograph 4			137-IA-3A-WMS			137-IA-3A-SKC			137-IA-3A-ATD			137-IA-3A-SUM			
Sampler Type/Sorbent:	Regular/charcoal						Regular/Carbopack B			Regular II/Carbograph 5			Regular/Carbopack B			--			
Exposure Duration (min):	10022			10005			9974			9997			9994						
Exposure Duration (days):	7.0			6.9			6.9			6.9			6.9			--			
<i>Volatile Organic Compounds</i>	Average		C/C <sub>0</sub>	COV	Average		C/C <sub>0</sub>	COV	Average		C/C <sub>0</sub>	COV	Average		C/C <sub>0</sub>	COV	Average		COV
<i>(µg/m<sup>3</sup>)</i>																			
1,1,1-Trichloroethane	ND			ND			ND			ND			ND			ND		ND	
1,1,2-Trichloroethane	ND			ND			ND			ND			ND			ND		ND	
1,1-Dichloroethane	ND			ND			ND			ND			ND			ND		ND	
1,1-Dichloroethene	<b>0.45</b>			ND			ND			<b>0.02</b> <b>0.09</b>			ND			ND		ND	
1,2-Dichloroethane	<b>0.22</b>			<b>0.02</b> <b>0.11</b>			ND			<b>0.06</b> <b>0.05</b>			ND			ND		ND	
Benzene	<b>1.10</b> <b>1.25</b> <b>0.09</b>			<b>1.00</b> <b>1.14</b>			<b>0.64</b> <b>0.73</b> <b>0.04</b>			<b>1.57</b> 1.78 <b>0.04</b>			<b>1.90</b> 2.16 <b>0.18</b>			<b>0.88</b>			
cis-1,2-Dichloroethene	<b>0.02</b> <b>0.13</b>			ND			ND			<b>0.14</b> <b>0.04</b>			ND			ND		ND	
Ethyl Benzene	<b>0.49</b> <b>0.07</b>			<b>0.66</b> <b>0.06</b>			<b>0.30</b> <b>0.09</b>			<b>0.78</b> <b>0.05</b>			<b>0.86</b> <b>0.06</b>			ND		ND	
m,p-Xylene	<b>1.33</b> <b>1.00</b> <b>0.09</b>			<b>1.70</b> <b>1.28</b> <b>0.06</b>			<b>0.91</b> <b>0.68</b> <b>0.08</b>			<b>2.20</b> 1.65 <b>0.05</b>			<b>2.27</b> 1.70 <b>0.07</b>			<b>1.33</b> <b>0.09</b>		ND	
o-Xylene	<b>0.46</b> <b>0.16</b>			<b>0.74</b> <b>0.06</b>			<b>0.35</b> <b>0.08</b>			<b>0.89</b> <b>0.04</b>			<b>1.01</b> <b>0.08</b>			ND		ND	
Tetrachloroethene	<b>0.18</b> <b>0.80</b> <b>0.11</b>			<b>0.12</b> 0.52 <b>0.08</b>			<b>0.12</b> 0.52 <b>0.08</b>			<b>0.19</b> <b>0.81</b> <b>0.06</b>			ND			<b>0.23</b> <b>0.09</b>		ND	
Toluene	<b>3.97</b> <b>0.78</b> <b>0.06</b>			<b>4.57</b> <b>0.90</b> <b>0.05</b>			<b>2.50</b> 0.49 <b>0.04</b>			<b>6.13</b> <b>1.20</b> <b>0.04</b>			<b>7.90</b> <b>1.55</b> <b>0.06</b>			<b>5.10</b> <b>0.03</b>		ND	
trans-1,2-Dichloroethene	<b>30.33</b> <b>0.80</b> <b>0.15</b>			<b>2.93</b> 0.08 <b>0.21</b>			<b>2.03</b> 0.05 <b>0.20</b>			<b>26.33</b> <b>0.69</b> <b>0.02</b>			<b>27.00</b> <b>0.71</b>			<b>38.00</b> <b>0.03</b>		ND	
Trichloroethene	<b>0.02</b> <b>0.05</b>			<b>0.01</b> <b>0.07</b>			ND			ND			ND			ND		ND	
Average	<b>0.92</b> <b>0.10</b>			<b>0.78</b> <b>0.09</b>			0.50 <b>0.09</b>			<b>1.23</b> <b>0.05</b>			<b>1.53</b> <b>0.09</b>			<b>0.06</b>			
Average excluding poor retention				<b>0.96</b>			0.61												
Fraction meeting accuracy criterion	5/5			3/5			2/5			3/5			2/4						

**Notes:** C/C<sub>0</sub> - passive sampler concentration divided by Summa canister concentration (bold where meeting performance criterion)  
COV - Coefficient of variation (bold where meeting performance criterion)  
ND - not detected



## 5 Mathematical Modeling of Passive Soil Vapor Sampling

Passive soil vapor sampling involves transport of vapors through the soil surrounding the drillhole into the void space in which the sampler is deployed, diffusion through the air inside the void-space, and uptake by the sampler. The free-air diffusion coefficients through the air inside the void space are roughly one to several orders of magnitude higher than the effective diffusion coefficient in the surrounding soil, so vapor transport through the air inside the void space is not expected to be the rate-limiting step. This allows the mathematical analysis to focus on two components: the rate of vapor diffusion into the void space (the “diffusive delivery rate”, or DDR) and the rate of vapor uptake by the passive sampler (“passive sampler uptake rate” or UR). Understanding the rate of diffusion of vapors into the void space is necessary to design an uptake rate for the passive sampler that is low enough to minimize the starvation effect. However, the uptake rate must also be high enough to provide adequate sensitivity (ability to meet target reporting limits with an acceptable sampling duration), so both constraints must be considered. This chapter describes mathematical modeling to develop a theoretical basis for meeting both constraints and the accuracy and precision performance criteria<sup>v</sup>.

### 5.1 Conceptual Model for Quantitative Passive Soil Vapor Sampling

Passive soil vapor sampling is usually performed by drilling a hole in the ground, removing soil, placing a passive sampler in the void-space created by drilling, sealing the hole from the atmosphere for the duration of the sample, then retrieving the sampler and backfilling or grouting the hole. A simple conceptual model of this scenario is as follows:

- Immediately after the hole is drilled and the soil is removed, the void space fills with outside air. Assuming atmospheric air can enter the void space with less resistance than gas flowing through the surrounding soil, the initial concentration of vapors inside the void space would be expected to be much lower than the vapor concentration in the surrounding soil, and at worst could be assumed to be essentially zero (if atmospheric air is contaminant-free).
- In most cases, passive samplers are placed in the borehole and the space above the sampler is sealed without purging to remove atmospheric air from the void space around the sampler (purging is feasible during passive soil vapor sampling, but not common).

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<sup>v</sup> This Chapter is based on the authors article: “Quantitative passive soil vapor sampling for VOCs – part 1: theory”<sup>229</sup>

- During the period of sampling, vapors diffuse into the void space from the surrounding soil. If the void space is long relative to its diameter and short enough that the geologic properties and vapor concentrations are relatively uniform over the vertical interval of the void space, then the diffusion will be essentially radially symmetric (this has been assumed for the remainder of this chapter).
- The rate of diffusive mass transport into the void space over time will depend on the concentration gradient and effective diffusion coefficient, and will gradually diminish as the concentration in the void space increases toward equilibration with the surrounding soil. If a passive sampler is present in the void space, the concentration in the void space will remain somewhat below the concentration in the surrounding soil depending on the uptake rate of the passive sampler.
- If the uptake rate of the sampler is small relative to the rate of diffusion into the void space (a goal if the starvation effect is to be small), then the steady-state concentration in the void space will be similar to the concentration in the surrounding soil and passive sampling will be able to provide a quantitative measure of the soil vapor concentration.

## 5.2 Mathematical Modeling of Passive Soil Vapor Sampling

### 5.2.1 Influence of Soil Moisture on the Effective Diffusion Coefficient in Soil

The effective diffusion coefficient depends strongly on the total porosity (volume of pores divided by total volume of soil) and water-filled porosity (volume of water divided by total volume of soil, otherwise known as the volumetric water content). Understanding this relationship is helpful for context in the theory of passive soil gas sampling if diffusion is the main process delivering vapors to the void space in which the sampler is deployed. Johnson and Ettinger<sup>197</sup> adopted the Millington-Quirk<sup>198</sup> equation in their well-known model for assessing the potential for subsurface vapor intrusion to indoor air. Their formulation of the effective diffusion coefficient also includes diffusion in the aqueous phase, assuming the Millington-Quirk empirical relationship is equally valid for both the gas and water phases:

$$D_{eff} = D_{air} \frac{q_a^{10/3}}{q_T^2} + \frac{D_w}{H} \frac{q_w^{10/3}}{q_T^2} \quad (5-1)$$

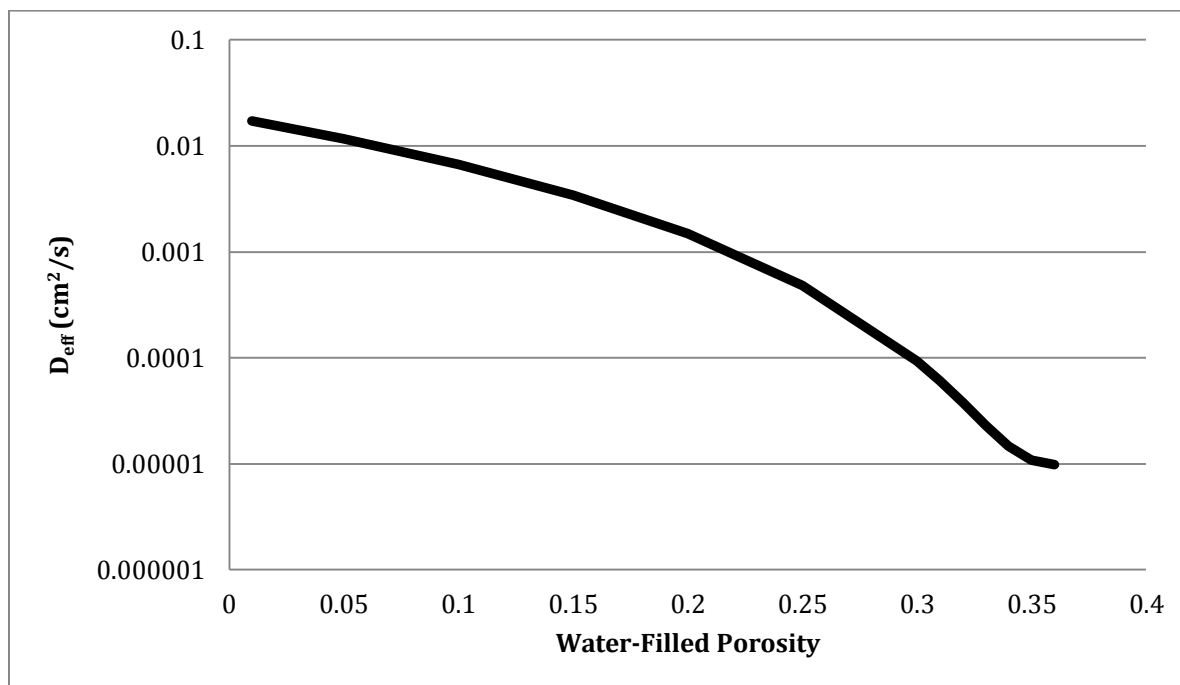
where the parameters are defined in Table 5-1. Parameter values used for all calculations in this chapter were selected to be representative of trichloroethene (TCE), one of the most common VOCs of interest

for human health risk assessment associated with contaminated land. Many other VOCs have similar diffusion coefficients and Henry's Law constants, so the general trend applies for a range of VOCs of interest for human health risk assessments. Equation (5-1) was used to calculate  $D_{\text{eff}}$  for both the transient and steady-state models in this chapter.

**Table 5-1:** Parameter values used in the model simulations (representative of TCE)

Parameter name	Symbol	Units	Value
Free air diffusion coefficient	$D_{\text{air}}$	$\text{cm}^2/\text{s}$	0.069
Aqueous diffusion coefficient	$D_{\text{w}}$	$\text{cm}^2/\text{s}$	0.00001
Henry's Law constant	H	dimensionless	0.35
Total porosity	$\theta_{\text{T}}$	Volume of voids / total volume of soil	0.375
Water-filled porosity	$\theta_{\text{w}}$	Volume of water / total volume of soil	Various values from 0.01 to 0.36
Air-filled porosity	$\theta_{\text{a}}$	$\theta_{\text{T}} - \theta_{\text{w}}$	Various values from 0.365 to 0.015

A series of calculations were performed using Equation (5-1) and the parameter values in Table 5-1 to show the relationship between the effective diffusion coefficient and the water-filled porosity. The calculated  $D_{\text{eff}}$  values span a range from about 0.01 to about 0.00001  $\text{cm}^2/\text{s}$  over a range of water-filled porosities from 1% to 36% in a soil with 37.5% porosity (Figure 5-1). These values are indeed much lower than the free-air diffusion coefficient (0.069  $\text{cm}^2/\text{s}$ ), which supports the assumption that diffusion through the air in the void space in which the sampler is deployed is not rate-limiting.



**Figure 5-1:** Effective diffusion coefficient versus water-filled porosity for TCE in a soil with 37.5% total porosity, typical of a sandy soil

Two models, transient and steady-state, were developed to simulate the passive sampling process, as described below.

### 5.2.2 Transient Model

The conceptualization for a transient mathematical model of radial diffusion of vapors from soil into the void space is shown in Figure 5-2. For simplicity, the transient model simulates an empty void space (i.e., no passive sampler), which is a reasonable approximation because a passive sampler should have a very small influence on the concentration inside the void space, otherwise, the sampler will disturb what it attempts to observe. The concentration profiles are conceptualized as the lines labelled t1, t2 and t3 for early, intermediate and late times, respectively (concentration is plotted on the vertical axis).



$$\bar{c}_g = \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r) \right] \quad (5-4)$$

for  $0 \leq r < r_2$

$$\bar{c}_s = \frac{c_{s_0}}{p} + \kappa \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \frac{\varphi_1\varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r) \right] \quad (5-5)$$

for  $r_2 \leq r < r_3$

Equations (5-6) and (5-7) allow the calculation of the mass in the void space based on the mass flux across the borehole wall from the void side and soil side, respectively.

$$\begin{aligned} \bar{M}(p) &= \frac{D_{air} c_{s_0}}{p^2} q_g \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2) \right] \quad (5-6) \\ &= \frac{D_{air} c_{s_0}}{p^2} q_g \frac{\varphi_2\varphi_1}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}. \end{aligned}$$

$$\begin{aligned} \bar{M}(p) &= \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \frac{\varphi_1\varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2) \right] \quad (5-7) \\ &= \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2\varphi_1\varphi_3}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}. \end{aligned}$$

The inverse Laplace transforms of Equation (5-4), (5-5), (5-6) and (5-7) are computed numerically using the algorithm developed by DeHoog et al.<sup>222</sup> The modified Bessel functions  $I_\alpha$  and  $K_\alpha$  used for Equations (5-4), (5-5), (5-6) and (5-7) are defined by:

$$I_\alpha(x) = i^{-\alpha} J_\alpha(ix) = \sum_{m=0}^{\infty} \frac{1}{m! \Gamma(m + \alpha + 1)} \left(\frac{x}{2}\right)^{2m+\alpha} \quad (5-8)$$

$$K_\alpha(x) = \frac{\pi I_{-\alpha}(x) - I_\alpha(x)}{2 \sin(\alpha\pi)} = \frac{\pi}{2} i^{\alpha+1} H_\alpha^{(1)}(ix) = \frac{\pi}{2} (-i)^{\alpha+1} H_\alpha^{(2)}(-ix) \quad (5-9)$$

The meaning of the symbols in the equations is explained in Appendix D.

### 5.2.3 Steady-State Model

If the duration of passive sampling is long compared to the time required for the vapor concentrations in the void space to approach equilibrium with the surrounding soils, then a steady-state model would also provide insight into the passive sampling mechanisms. For this case, the conceptual model is as follows:

- The vapor concentration in the soil surrounding the void space is uniform at  $c_s$  beyond a radial distance of  $r_3$ ,
- Diffusion occurs in the region between the outer wall of the drillhole (radius =  $r_2$ ) and  $r_3$ , through a cylinder of height  $h$ ,
- The concentration in the gas inside the void space of the borehole ( $c_g$ ) is lower than  $c_s$  by a factor  $\delta = c_g/c_s$  (this value should be close to 1.0 in order for the sampler to be exposed to vapor concentrations very similar to the surrounding soil),
- Radial diffusion occurs from the soil to the void space at a diffusive delivery rate equal to the passive sampler uptake rate for the majority of the sample deployment interval (i.e., the sampling period is long compared to the time required for steady-state diffusion to be established).

The rate of mass transfer ( $R_{MT}$ ) of vapors into the borehole via vapor diffusion through the surrounding soil ( $R_{MT1}$ ) is given by Carslaw and Jaeger<sup>223</sup>:

$$R_{MT1} = \frac{2\pi h D_{eff} (C_s - C_g)}{\ln\left(\frac{r_3}{r_2}\right)} \quad (5-10)$$

The rate of mass uptake by the sampler ( $R_{MT2}$ ) is given by:

$$R_{MT2} = c_g \times UR \quad (5-11)$$

Setting  $R_{MT1} = R_{MT2}$  gives:

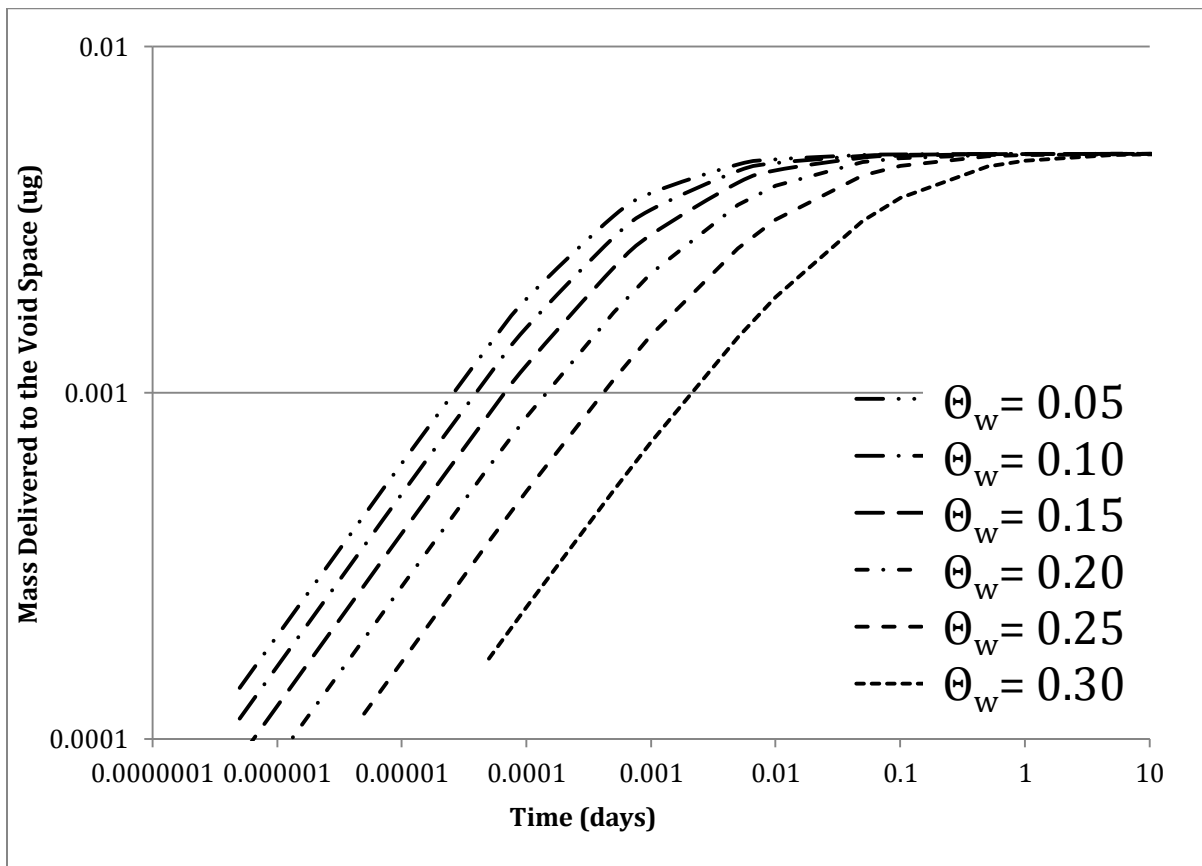
$$UR \left[ \frac{mL}{min} \right] = \frac{2\pi h [cm] D_{eff} \left[ \frac{cm^2}{s} \right] (1-\delta)}{\ln\left(\frac{r_3}{r_2}\right) \delta} \times 60 [s/min] \quad (5-12)$$

## 5.3 Results and Discussion

### 5.3.1 Transient Model Simulations

A series of simulations were performed using the transient model to show the relationship between the mass entering the void space from the surrounding soil and time for a 2.54 cm (1-inch) diameter drillhole,

a soil vapor concentration ( $c_s$ ) of  $100 \mu\text{g}/\text{m}^3$  and a vertical interval of 10 cm. Figure 5-3 shows simulations for a variety of different water-filled porosities ( $\theta_w$ , volume of water divided by total volume of soil) and the corresponding effective diffusion coefficients calculated using Equation 5-1. For all water contents simulated, the mass of TCE in the void space eventually reaches the same steady value as the concentration inside the void space equilibrates with the surrounding soil. These simulations are instructive because they indicate the time required for the void space to equilibrate with the surrounding soil as a function of the moisture content. For relatively dry soils (e.g.,  $\theta_w < 0.1$ ), the void space concentration would be within 10% of the soil vapor concentration in as little as about 10 minutes. For wet soils (e.g.,  $\theta_w = 0.30$ ), a similar level of equilibration may require up to about 1 day.



**Figure 5-3:** Simulated (cumulative) mass delivered by diffusion from surrounding soil to the void space versus time (for a 2.5 cm diameter borehole in a sandy soil with 37.5% total porosity and an initial soil vapor concentration of  $100 \mu\text{g}/\text{m}^3$ , assuming no removal of mass by a passive sampler)



Equilibration occurs more slowly with larger diameter boreholes. A comparison of the equilibration time for a nominal 1-inch and 4-inch diameter voids of 10 cm height are shown in Table 5-2, which shows that the difference in equilibration time is proportional to the difference in the volume of the void space (i.e., varies in proportion to the square of the borehole radius). Most passive samplers can fit within a borehole of 2-inch diameter or less, so the equilibration time would be less than 1 day for most soil moisture contents.

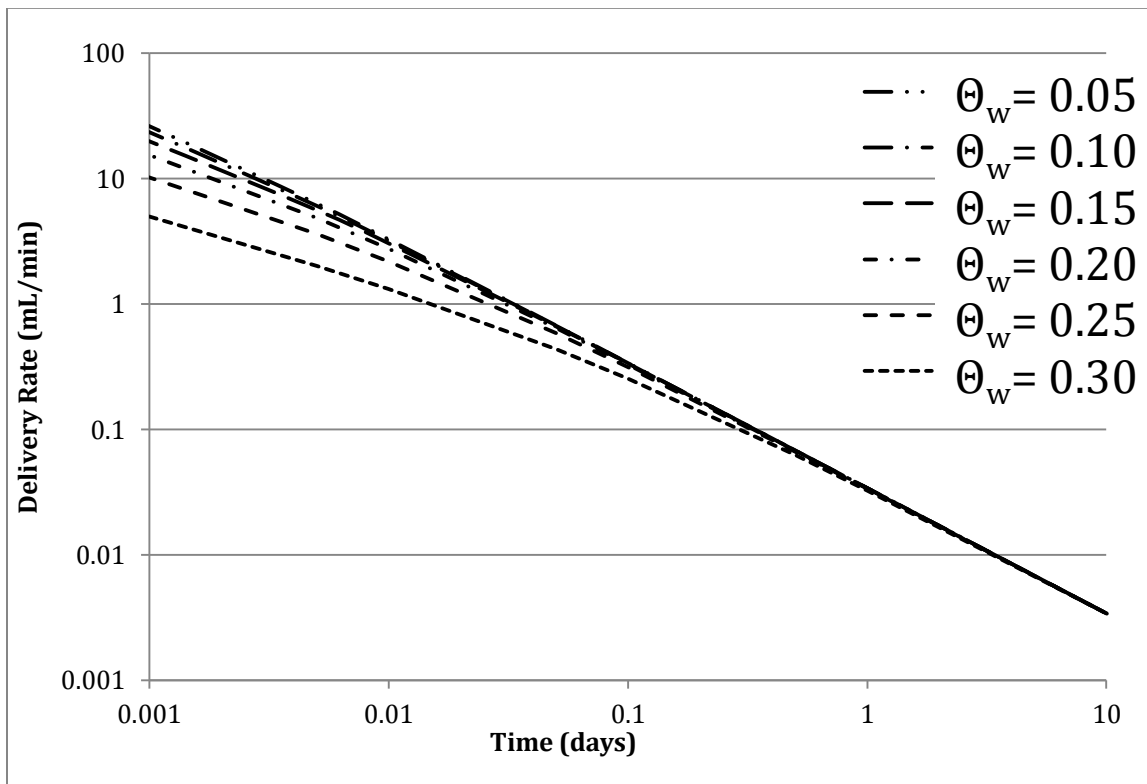
**Table 5-2:** Comparison of time to reach 95% of steady-state concentrations in the void space comparing nominal 1-inch and 4-inch diameter boreholes (total porosity 37.5%)

Water-filled porosity (-)	$D_{\text{eff}}$ ( $m^2/\text{day}$ )	Time to reach 95% $C_{s0}$ (day)		$t_4/t_1$
		$t_1$ ( $r_2 = 0.5\text{inch}$ )	$t_4$ ( $r_2 = 2\text{inch}$ )	
0.01	0.15	0.0048	0.076	16
0.05	0.10	0.0070	0.11	
0.1	0.058	0.012	0.19	
0.15	0.030	0.024	0.38	
0.2	0.013	0.055	0.87	
0.25	0.0042	0.17	2.7	
0.3	0.00080	0.87	13	
0.31	0.00052	1.3	21	
0.32	0.00033	2.1	34	
0.33	0.00020	3.5	56	
0.34	0.00013	5.5	88	
0.35	0.000093	7.5	120	
0.36	0.000084	8.3	130	

The transient model simulations do not account for mass removed by a passive sampler in the borehole, which would draw a small but not insignificant amount of mass from the surrounding soil over time. At steady-state, the uptake rate of the passive sampler (UR) and the diffusive delivery rate from the surrounding soil (DDR) would be equal; therefore, Equation (1-5) can be re-arranged to:

$$DDR = \frac{M}{c t} \quad (5-13)$$

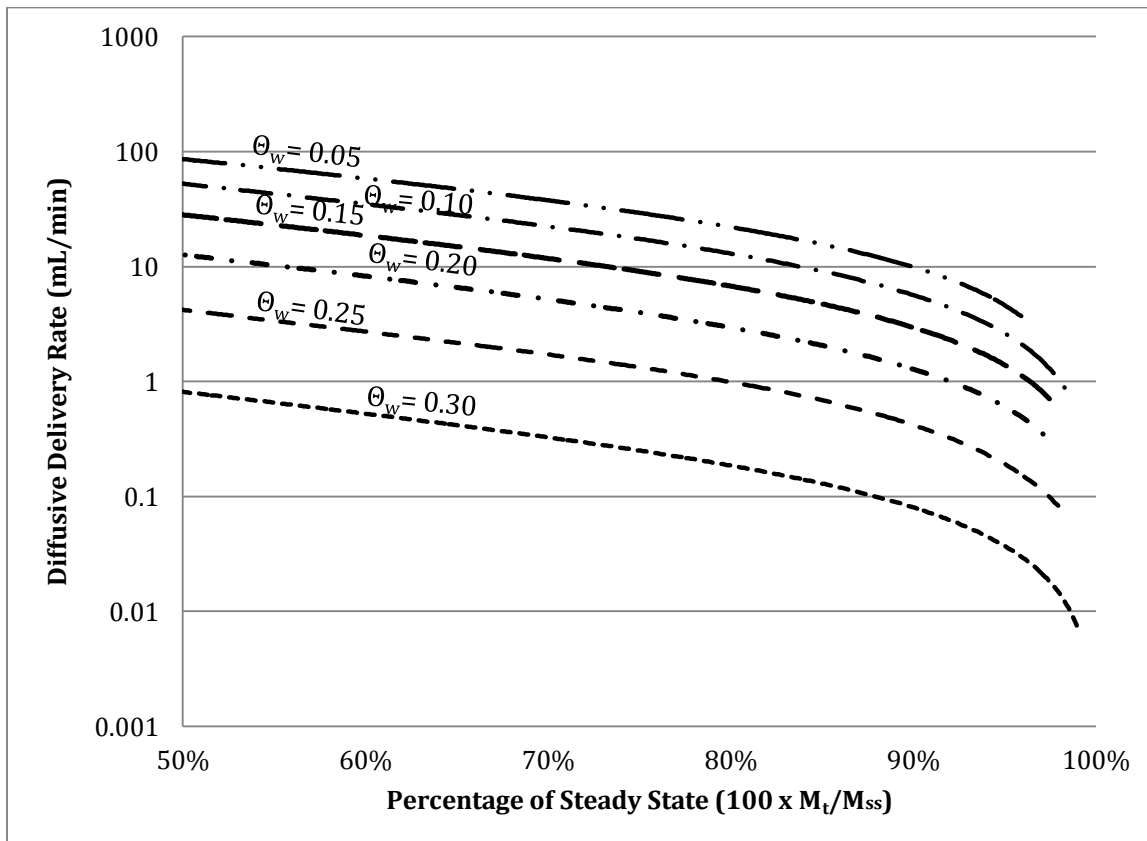
In the period of time before steady-state is achieved, the diffusive delivery rate (DDR) would not be constant and equal to the uptake rate of the sampler, rather, it would be high initially when the concentration gradient is the largest, and gradually slow down as the concentration inside the void space equilibrates with the surrounding soil. Equation 5-13 can be used to calculate DDR values as a function of time where  $M$  is calculated using Equation 5-7 for a given period of time ( $t$ ) and a  $c_s$  value of  $100 \mu\text{g}/\text{m}^3$ , as shown in Figure 5-4. The DDR diminishes to less than about 1 mL/minute within about 30 minutes for all moisture contents. Quantitative passive samplers for indoor air quality monitoring often have uptake rates of 10 to 100 mL/min (Table 3.2), so these simulations demonstrate that a customized sampler with a lower uptake rate would be needed to minimize the starvation effect to enable reliable quantitative soil vapor sampling for all but very short sample durations and dry soils.



**Figure 5-4:** Diffusive delivery rate versus time for mass entering the void space (for a 2.5 cm diameter, 10 cm tall void space in a soil with 37.5% total porosity and an initial soil vapor concentration of  $100 \mu\text{g}/\text{m}^3$ , assuming no removal of mass by a passive sampler)

The DDR decreases as the concentration in the void space approaches equilibrium with the surrounding soil vapor, as shown in Figure 5-5. For very dry soils, the average DDR is greater than 10 mL/min until

about 90% of the mass has entered the void-space (which occurs within 10 minutes according to Figure 5-3). In this scenario, a passive sampler with an uptake rate as high as 10 mL/min may still provide data with an acceptably small starvation effect. In other words, the sampler uptake rate would remain below the diffusive delivery rate from the soil until the mass delivered to the void space is about 90% of the steady-state value, so negative bias of about 10% may be expected, which would meet the data quality objectives typically used for soil vapor monitoring (within 25% RPD). For very wet soils ( $\theta_w = 0.30$ ), the average DDR is about 0.01 mL/min by the time the void space has nearly equilibrated with the surrounding soil (roughly 1 day). For moisture contents typical of most vadose zone soils ( $0.10 < \theta_w < 0.25$ ), Figure 5-5 shows that an uptake rate of about 1 mL/min would be expected to result in an acceptably small starvation effect (i.e., for a water-filled porosity of up to 25% in a soil with 36% porosity, the bias due to the starvation effect for a sampler with an uptake rate of 1 mL/min would be expected be less than -20%).

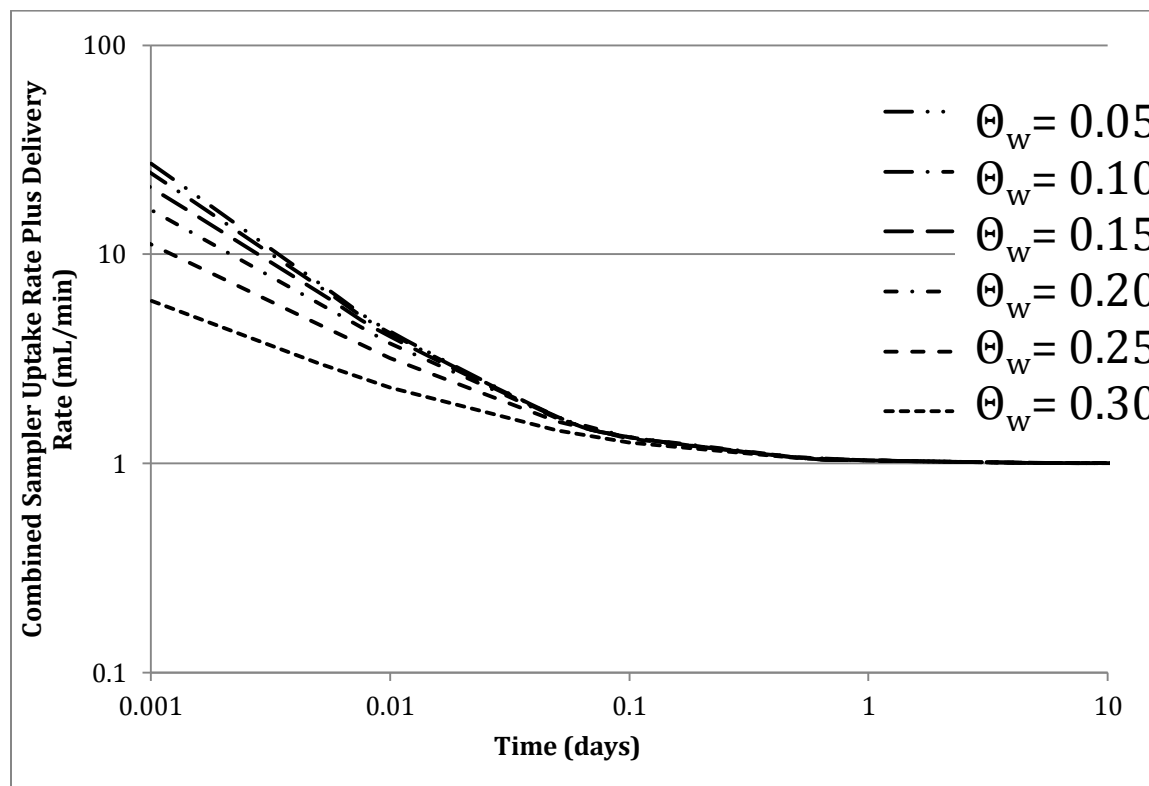


**Figure 5-5:** Relationship between the instantaneous diffusive delivery rate of vapors into the void space versus the percentage of the analyte mass at steady-state ( $100 \times M_t / M_{ss}$ , where  $M_t$  is the analyte mass in the

borehole at time  $t$ , and  $M_{ss}$  is the analyte mass at steady state), assuming a 2.5 cm diameter borehole in a soil with 37.5% total porosity, initial soil vapor concentration of  $100 \mu\text{g}/\text{m}^3$ , and no removal of mass by a passive sampler.

#### 1.3.1.1 Superposition of Diffusive Delivery Rate and Uptake Rate

The transient mathematical model presented above must be processed further to demonstrate the effect of adding a passive sampler to the void space. A mathematical model including 2-dimensional radial diffusion to the void space (diffusive delivery), 3-dimensional diffusion through the void-space to the passive sampler, and uptake by a variety of possible passive sampler designs and geometries is challenging to formulate analytically. However, an approximate model can be derived by adding the diffusive delivery rate (Figure 5-4) and the sampler uptake rate to estimate the effect of both processes occurring at the same time, using the principle of superposition. As long as the uptake rate of the sampler is small, the combined model will differ from the transient analytical model of radial diffusion only after the diffusion into the void space has very nearly attained steady-state, at which time the diffusive delivery rate of vapors into the void space will stabilize at the same value as the uptake rate of the sampler. Figure 5-6 shows an example of the diffusive uptake rate that would be expected if a passive sampler with an uptake rate of 1 mL/min was placed in the void-space simulated in Figures 3, 4 and 5. Within about 1 hour, the delivery rates for all water-filled porosities approach the uptake rate of the sampler (within about a factor of 2). The delivery rate becomes equal to the uptake rate for all soil moisture contents within about 1 day.



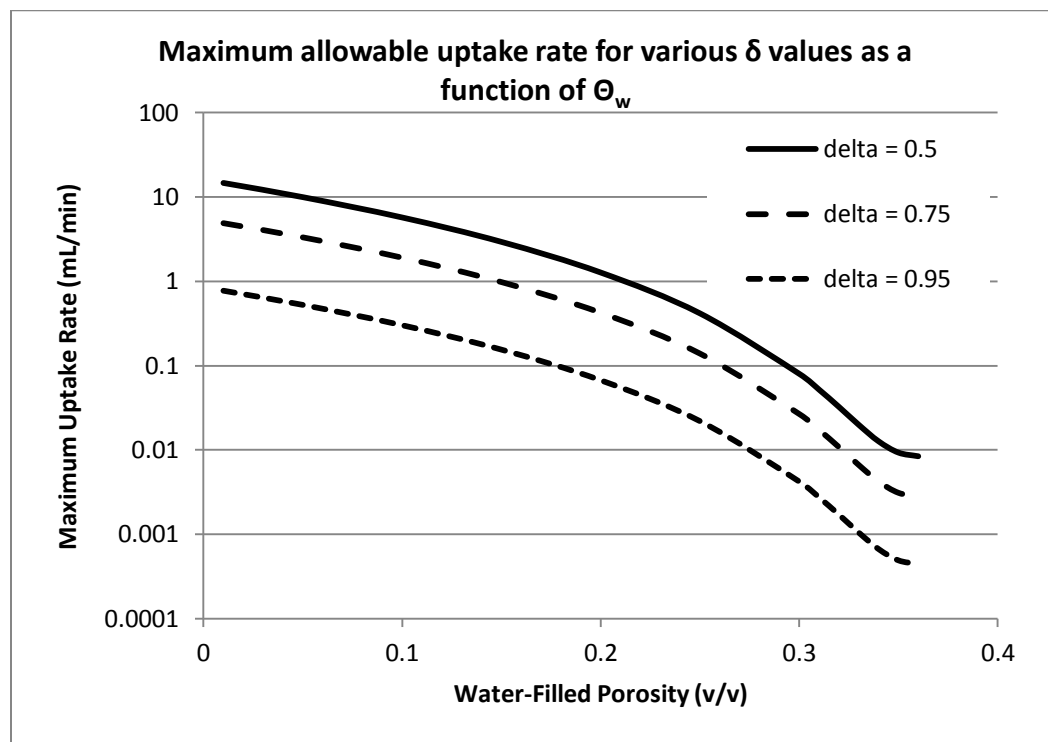
**Figure 5-6:** Superimposed diffusive delivery rates plus uptake rate (for a 10 cm tall and 2.5 cm diameter void space in a soil with 37.5% porosity and an initial soil vapor concentration of  $100 \mu\text{g}/\text{m}^3$  containing a passive sampler with an uptake rate of 1 mL/min)

It should be noted that for very wet soils (water-filled porosity greater than 0.25), the steady-state delivery rate may be less than 1 mL/min, in which case there are two possibilities: 1) a lower uptake rate sampler could be used with a proportionately longer sample duration, or 2) negative bias attributable to starvation may still be experienced. If the negative bias is predictable or acceptably small, the data may still be useful and this may be reasonably evaluated using the models presented here as long as the porosity and moisture content are known or can be reasonably estimated. From a practical perspective, very wet soils have an effective diffusion coefficient about two orders of magnitude lower than dry soils (Figure 5-1), which would reduce the risk to human health from subsurface vapor intrusion to indoor air by a similar amount. Therefore, slight negative bias in the passive sampler result may still result in protective decision-making if the results are compared to screening levels derived to be protective of dry soil conditions. Also, it may be possible to avoid low bias associated with wet soils by design via these routes:

coring the soil and selecting coarse-textured, well-drained intervals for monitoring (if relevant considering the expected contaminant distribution); sampling during dry seasons; or sampling within the rain-shadow below buildings (a.k.a., sub-slab samples).

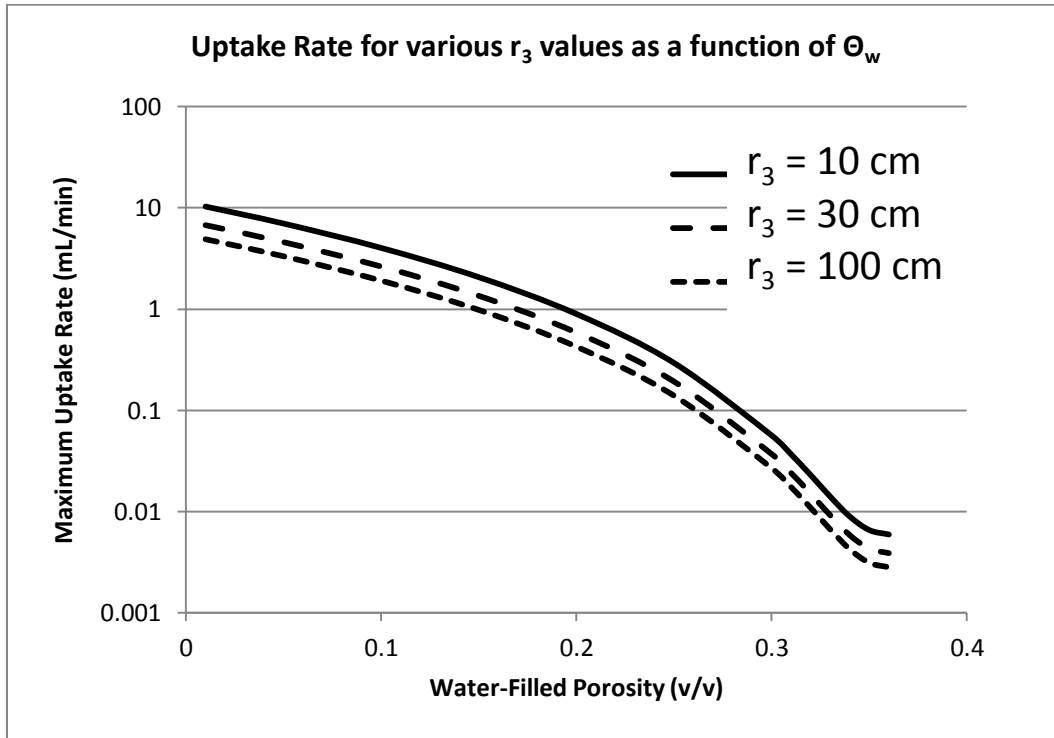
### 5.3.2 Steady-State Model Simulations

For a passive sampler deployed in a borehole with a nominal diameter of 1 inch ( $r_1 = 1.25$  cm) and sealed within a 10 cm void space ( $h = 10$  cm), the uptake rates calculated using Equation (5-12) are shown in Figure 5-7 for  $\delta$  values of 0.5, 0.75 and 0.95. The  $r_3$  value for these calculations was assumed to be 1 m. Figure 5-7 shows that an uptake rate of 10 mL/min might be acceptable for very dry soil if the data quality objective was to quantify concentrations within a factor of 2 (i.e.,  $\delta = 0.5$ ), however; an uptake rate of 1 mL/min would be more suitable for soils with water-filled porosity of up to about 15%, assuming a more stringent data quality objective of  $\pm 25\%$  (i.e.,  $\delta = 0.75$ ). Progressively lower uptake rates would be required to further reduce the negative bias or meet typical data quality objectives in very wet soils.



**Figure 5-7:** Calculated uptake rate corresponding to various values of delta as a function of water-filled porosity (for a 10 cm tall and 2.54 cm diameter void space assuming  $r_3 = 1$  m)

Sensitivity analysis on the  $r_3$  value is shown in Figure 5-8 for the same conditions as in Figure 5-7 and a  $\delta$  value of 0.75. This plot shows that the value assumed for  $r_3$  does not affect the conclusions in a significant way even when it is varied by an order of magnitude.



**Figure 5-8:** Calculated uptake rate corresponding to various  $r_3$  values as a function of water-filled porosity (for a 10 cm tall and 2.54 cm diameter void space assuming  $\delta = 0.75$ )

#### 5.4 Practical Considerations on the Uptake Rate

There is a practical lower limit to the uptake rate for passive sampling, which is imposed by the sample duration needed to achieve a specified reporting limit. Equation (1-5) can be rearranged to calculate the sample duration required to achieve a target reporting limit if the uptake rate of the sampler and the laboratory mass reporting limit ( $M_{RL}$ ) are known:

$$t = \frac{M_{RL}}{c \times UR} \quad (5-13)$$

For example, consider an initial soil vapor concentration of  $100 \mu\text{g}/\text{m}^3$  of TCE and a sampler with an uptake rate of 1 mL/min. A detectable mass of TCE ( $M_{RL} \sim 0.05 \mu\text{g}$  via solvent extraction, GC/MS) would be adsorbed by the sampler in 500 min (0.35 day). This demonstrates that a low-uptake rate

sampler can provide practical sensitivity within a reasonable amount of time and still avoid or minimize the starvation effect. However, if the uptake rate was reduced to 0.1 or 0.01 mL/min, the sample duration would need to increase to 3.5 or 35 days, respectively. There are logistical challenges with long sample durations (costs of return travel to field sites, security, etc.). The sensitivity can be increased using thermal desorption instead of solvent extraction ( $M_{RL} \sim 0.002 \mu\text{g}$ ); however, weaker sorbents are typically used with thermal desorption, hence less-strongly sorbed analytes may not be effectively retained, especially for longer sampling durations. Long duration soil vapor samples also increase the risk of interference by water vapor (competitive sorption or interference with analytical instruments), especially for samplers with charcoal-based sorbents. The PDMS membrane of the WMS sampler is hydrophobic and resists uptake of water in both liquid and vapor forms.

## 5.5 Summary

In order for a kinetic passive sampler to provide quantitative soil vapor concentration data, it must have a known and reliable uptake rate for all of the compounds of interest. The passive sampler uptake rate should be low enough to allow the rate of diffusive delivery of vapors into the void space from the surrounding soil to sustain vapor concentrations in the void space similar to those of the surrounding soil in order to minimize the starvation effect. The uptake rate must also be high enough to provide the ability to detect concentrations at or below risk-based screening levels with acceptable sampling duration. This Chapter demonstrates that kinetic samplers with the uptake rates in the range of  $\sim 0.01$  to  $\sim 10$  mL/min can deliver quantitative passive soil vapor concentration data with only a small bias, depending on the soil moisture, and that an uptake rate of about 1 mL/min provides acceptable accuracy and sensitivity for most commonly-encountered water-filled porosities in unsaturated soils. These conclusions are supported by both transient and steady-state models. The knowledge gained from the mathematical modeling in this chapter allows passive samplers to be modified as needed to achieve uptake rates small enough to minimize starvation and high enough to provide adequate sensitivity, which will simplify and improve the cost-effectiveness of quantitative soil vapor concentration measurement and monitoring for VOCs.



## 6 Laboratory Chamber Tests (High Concentration Range)<sup>vi</sup>

Soil vapor sampling poses different challenges for passive sampling than indoor air or outdoor air. Soil vapor risk-based screening levels for vapor intrusion are higher than indoor air concentrations of concern to account for the magnitude of attenuation that occurs as a result of dilution from the building ventilation system (see Table 6-1). Furthermore, temporal variability is less significant for soil vapor concentrations than indoor air concentrations.<sup>214</sup> For both reasons, the sample duration may be much shorter for passive sampling of soil vapor compared to indoor air. Soil vapor also typically has a high humidity and a very low velocity compared to indoor air. Controlled chamber tests were therefore performed to simulate soil vapor sampling to the extent practicable in a laboratory setting. The same 10 VOCs described in Chapter 3 were used, except the concentration range was 1 to 100 parts per million by volume (ppm<sub>v</sub>).

**Table 6-1:** Risk-based screening levels<sup>4</sup>

Analyte	Residential Indoor Air Screening Level (µg/m <sup>3</sup> )	Residential Soil Vapor Screening Level (µg/m <sup>3</sup> )	Commercial Indoor Air Screening Level (µg/m <sup>3</sup> )	Commercial Soil Vapor Screening Level (µg/m <sup>3</sup> )
1,1,1-Trichloroethane (111TCA)	5,200	170,000	22,000	730,000
1,2,4-Trimethylbenzene (124TMB)	7.3	240	31	1,000
1,2-Dichloroethane (12DCA)	0.094	3.1	0.47	16
2-Butanone (MEK)	5,200	170,000	22,000	730,000
Benzene (BENZ)	0.31	10	1.6	53
Carbon tetrachloride (CTET)	0.41	14	2	67
Naphthalene (NAPH)	0.07	2.3	0.36	12
n-Hexane (NHEX)	730	24,000	3,100	100,000
Tetrachloroethene (PCE)	9.4	310	47	1,600
Trichloroethene (TCE)	0.43	14	3.0	100

### 6.1 Experimental

#### 6.1.1 Standard Gas Mixtures

Two standard J-size cylinders were custom-filled with the compounds listed in Table 3-1 at concentrations of 10 and 100 ppm<sub>v</sub> in N<sub>2</sub> by Air Liquide America Specialty Gases LLC of Santa Fe Springs, CA. NAPH and 124TMB have much lower vapor pressures than the other compounds, and to

<sup>vi</sup> The contents of this Chapter are based on the authors article: “Quantitative passive soil vapor monitoring for VOCs – part 2: laboratory testing”<sup>230</sup>

avoid potential condensation issues, NAPH was added at a concentration of about 1 ppm<sub>v</sub> to the 10 ppm<sub>v</sub> supply gas; neither compound was included in the 100 ppm<sub>v</sub> supply gas mixture. For the test at 1 ppm<sub>v</sub> concentrations, the 10 ppm<sub>v</sub> supply gas was diluted 10:1 with ultra pure nitrogen using a mass flow controller to deliver 9 mL/min of the supply gas and a needle-valve to deliver about 90 mL/min of nitrogen (verified periodically with a soap-bubble flowmeter). For the 10 and 100 ppm<sub>v</sub> tests, the supply gas was delivered at a flow rate of about 100 mL/min, controlled using a mass flow controller and verified using a soap-bubble flow meter.

### 6.1.2 Varieties of Samplers Used

The following samplers were used in this study:

**SKC Ultra™**<sup>123</sup> - The Ultra with activated carbon and solvent extraction analysis was used for the 10 and 100 ppm<sub>v</sub> tests and the Ultra II with Carbograph 5 and thermal desorption analysis was used for the 1 ppm<sub>v</sub> tests to minimize the risk of non-detect results. A cap with 12 holes was used to cover the face of the sampler for the low-uptake rate tests.

**Radiello®**<sup>126</sup> - The yellow body was used with charcoal sorbent and solvent extraction in this experiment to reduce the risk of low bias via starvation and avoid saturation of the adsorbent. The uptake rates were assumed to be the same as those for the thermally desorbable sorbent, which is reasonable if both sorbents act as zero sinks throughout the sample duration. The sample duration was only 30 minutes in this study, so the assumption that the charcoal sorbent acted as a zero sink was considered reasonable.

**3M OVM 3500™**<sup>141</sup> - The OVM is only available in one configuration and was used as supplied.

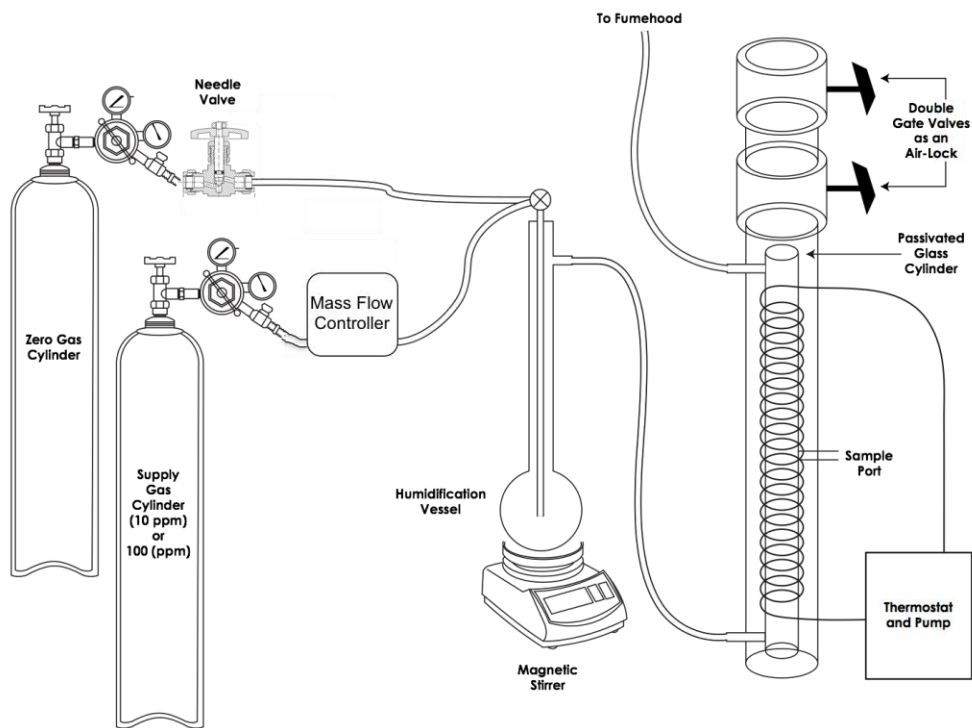
**Waterloo Membrane Sampler™**<sup>152,153</sup> - The WMS sampler was used in the standard configuration (1.8 mL vial with an exposed membrane surface of about 0.24 cm<sup>2</sup> and Anasorb 747 sorbent with analysis by solvent extraction) for the tests at 1, 10 and 100 ppm<sub>v</sub> with 100 mL/min flow. The low-uptake variety (0.8 mL vial with an exposed membrane surface of about 0.079 cm<sup>2</sup> and Anasorb 747 sorbent with analysis by solvent extraction) was used for the low-uptake rate tests.

**Passive ATD tube samplers**<sup>154,164</sup> - The ATD tube sampler is normally used with a dust screen cap that has an opening larger than the tube itself (~4.5 mm I.D.), but can be fitted with a cap (specially designed for this experiment) that has a ~1.4 mm I.D. opening that reduces the uptake rates by a factor of about 10. Tenax TA was used as the sorbent for both regular and low-uptake varieties of the ATD tube sampler, because it is very hydrophobic, and therefore well-suited to sampling in high humidity environments.

### 6.1.3 Apparatus

The laboratory apparatus consisted of a 1-m long x 5-cm diameter glass cylinder with three side ports (influent at the bottom, effluent at the top and a sampling port in the middle). A schematic diagram of the apparatus is shown in **Figure 6-1**. The interior surface of the glass cylinder was passivated using a silanization process. The outer wall of the cylinder was wrapped with 1.6 cm diameter Tygon tubing, which was used to circulate water for temperature control. The cylinder and tubing were placed inside a 10 cm diameter clear acetate tube for structural support and mounted to a frame for stability. Two PVC and stainless steel gate valves were secured to the top of the acetate pipe by friction with Teflon™ tape acting as a seal. The gate valves formed an air-lock, to allow samplers to enter and exit the chamber with minimal disruption to the concentrations inside. A supply of gas containing known concentrations of selected VOCs was humidified and fed through the apparatus. When deployed in the exposure chamber, the badge samplers (3M and SKC) had their face vertical, the WMS and ATD samplers faced down, and the Radiello was aligned near vertical.

Stainless steel and nylon tubing were used to deliver the supply gas to the exposure chamber, with compression fittings used at all connections. All fittings were leak-tested by connecting the apparatus to a 100 mL/min flow of pure helium and monitoring all the fittings with a helium meter. Adjustments were made as necessary until there was no measurable helium in the regions immediately outside of the fittings.



**Figure 6-1:** Schematic diagram of experimental apparatus for high concentration laboratory tests

Three identical humidification vessels were used (one for each concentration) and the water in each vessel was spiked with a mixture containing each of the 10 neat liquid VOCs mixed in proportions such that after dissolving into the water in the humidification vessel, the water would be approximately in equilibrium with the supply gas according to Henry’s Law (Table 6-2). Each humidification vessel contained about 1 L of distilled, deionized water and a Teflon-coated magnetic stir bar. The stir bars operated continuously and the supply gas was delivered to the bottom of the humidification vessel through 1/4-inch glass tubing with a porous ceramic cup at the bottom to generate a large number of small gas bubbles. This apparatus consistently delivered steady source vapor concentrations with a relative humidity of about 80%.

**Table 6-2:** Volumes of pure compounds added to humidification vessel for 100 ppm<sub>v</sub> test

Compound	Molecular Weight	Gas Phase Concentration corresponding to 100 ppm <sub>v</sub> in µg/L	Henry's Constant at 22 °C	Aqueous Concentration (µg/L)	Density of pure liquid (g/mL)	Volume (µL) to dose 1000 mL of water
111TCA	133.41	557	0.65	857	1.320	649
124TMB	120.2	502	0.2	2508	0.876	2863
12DCA	98.96	413	0.059	7001	1.253	5587
MEK	72.11	301	0.004	75244	0.805	93471
BENZ	78.11	326	0.2	1630	0.877	1860
CTET	153.8	642	0.99	648	1.587	409
NAPH	128.2	54 (10 ppm)	0.018	2973	1.140	2608
NHEX	86.18	360	50	7	0.655	11
PCE	165.8	692	0.65	1065	1.622	656
TCE	131.4	548	0.39	1406	1.460	963

All three supply-gas systems were set up simultaneously (Figure 6-1 shows only one for simplicity) and allowed to run continuously for a week at about 100 mL/min prior to the experiments. The temperature and relative humidity were monitored using a RHTemp101A datalogger by Madgetech, Inc. of Warner, NH. Testing was performed starting with the concentrations at 1 ppm<sub>v</sub>, followed by 10 ppm<sub>v</sub> and 100 ppm<sub>v</sub> to reduce potential effects of carryover from one test to the next. At least 60 hrs were allowed for the chamber to equilibrate with each new concentration. At a flow rate of 100 mL/min, more than 700 times the volume of the test chamber passed through the chamber prior to the start of each set of sampling. The sample port at the mid-point of the test chamber was periodically monitored during the stabilization period using the PID to assess the stability of total ionizable vapor concentrations inside the test chamber and verification testing using pumped ATD tubes (50 mL/min for 20 min with Anasorb 747) and solvent extraction GC/MS analysis until concentrations stabilized. NAPH was slower to equilibrate than the other compounds, presumably because of its tendency to adsorb even to inert surfaces.

#### **6.1.4 Sample Collection**

For the 1 ppm<sub>v</sub> test, three replicates of each of the five passive samplers and 1 L Summa canister samples were collected over 30 minutes in random order (denoted using lower case a, b and c in Tables 6-3, 6-4 and 6-5). For the 10 ppm<sub>v</sub> and 100 ppm<sub>v</sub> tests, additional Summa canister samples were collected at the beginning and end for a total of five active samples (denoted a through e). For the 1 and 10 ppm<sub>v</sub> tests, samples were deployed for 30 minutes with no lag between them. PID measurements made after the 10 ppm<sub>v</sub> tests indicated that some of the samplers may have sufficient uptake to influence the concentrations inside the chamber (e.g., 10% lower PID readings after the sample period compared to before for the samplers with higher uptake rates), so a 5 minute interval was allowed for re-equilibration between samples during the 100 ppm<sub>v</sub> tests.

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 and the University of Waterloo analyzed the WMS samplers, both via solvent extraction GC/MS. AirZone One Ltd of Mississauga, Ontario analyzed the OVM 3500 samplers by solvent extraction GC/MS. Columbia Analytical Services of Simi Valley, CA analyzed the SKC Ultra samplers by solvent extraction GC/MS for the Ultra sampler with charcoal and thermal desorption GC/MS for the Ultra II with Carbograph 5 and the Summa canister samples by EPA Method TO-15.<sup>6</sup> Air Toxics Ltd. of Folsom, CA analyzed the ATD tube samplers by thermal desorption GC/MS using a modified version of U.S. EPA Method TO-17.<sup>17</sup> Analytical methods are described in detail in Appendix A.

#### **6.1.5 Low Uptake Rate Sampler Tests**

Additional tests were performed using available low uptake rate varieties of the passive samplers. Two tests were performed at the midpoint concentration (10 ppm<sub>v</sub>) with the supply gas flow velocity held at 5 cm/min (100 mL/min) for the first test to maintain consistency with the rest of the experiments. The second was performed the next day and the supply gas was shut off immediately after deployment of the passive samplers to assess the performance of the samplers in a setting with no net gas flow (“stagnant” conditions), which is a worst-case condition for low biases attributable to the starvation effect. No attempt was made to assess whether thermal convection may have contributed to advection within the column, but the temperature was held as constant as possible. The SKC low-uptake sampler had no detectable concentrations for either of the first two tests, so a third test was performed at 100 ppm<sub>v</sub> under stagnant conditions (only the SKC and ATD tube samplers were used in this test). The low-uptake varieties of passive samplers used for these tests were:

- Radiello – yellow body with charcoal
- SKC Ultra – 12-hole cap with charcoal
- WMS-LU - 0.8 mL vial with Anasorb 747
- ATD tube – Low-uptake cap with Tenax TA

No low-uptake version of the 3M OVM 3500 is available, so it was not included in this set of tests.

## **6.2 Results and Discussion**

The concentrations measured using each of the passive samplers and the Summa canisters are presented in Tables 6-3, 6-4 and 6-5 for the 1, 10 and 100 ppm<sub>v</sub> tests, respectively, along with the uptake rates, individual concentrations measurements, the mean, standard deviation and the relative standard deviation for the three replicates for each sampler at each concentration level.

**Table 6-3:** Concentrations measured in exposure chamber at 1 ppm<sub>v</sub> (NAPH=0.1ppm<sub>v</sub>)

1ppm <sub>v</sub>		Analyte	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH
<b>WMS Anasorb 747</b>	Uptake Rate	(mL/min)	1.3	1.3	2.6	1.3	2.2	1.5	3.3	5.4	13	26
1-WMS-a		(µg/m <sup>3</sup> )	ND	1,650	1,020	1,260	574	1,420	1,320	1,620	960	17
1-WMS-b		(µg/m <sup>3</sup> )	ND	1,650	1,010	1,260	574	1,420	1,320	1,500	853	16
1-WMS-c		(µg/m <sup>3</sup> )	ND	2,800	1,060	1,390	636	1,560	1,320	1,620	880	12
		Mean		2,040	1,030	1,300	594	1,470	1,320	1,580	898	15
		std.dev.		661	27	76	36	77	0	72	56	3
		RSD		0.32	0.03	0.06	0.06	0.05	0.00	0.05	0.06	0.18
<b>ATD Tenax TA</b>	Uptake Rate	(mL/min)	0.50	0.50	0.50	0.50	0.35	0.50	0.41	0.50	0.62	0.50
1-ATD-a		(µg/m <sup>3</sup> )	ND	1,600	1,000	1,000	2,190	1,530	2,280	2,070	1,020	133
1-ATD-b		(µg/m <sup>3</sup> )	ND	1,470	933	867	1,910	1,330	2,110	1,870	753	ND
1-ATD-c		(µg/m <sup>3</sup> )	ND	1,530	1,070	1,070	1,910	1,730	2,200	1,930	914	ND
		Mean		1,530	1,000	978	2,000	1,530	2,200	1,960	896	133
		std.dev.		67	67	102	165	200	81	102	135	
		RSD		0.04	0.07	0.10	0.08	0.13	0.04	0.05	0.15	
<b>Radiello Charcoal</b>	Uptake Rate	(mL/min)	79	66	77	62	80	67	69	59	50	25
1-RAD-a		(µg/m <sup>3</sup> )	611	1,020	1,150	1,730	850	1,610	1,430	1,530	362	ND
1-RAD-b		(µg/m <sup>3</sup> )	637	1,340	1,380	2,170	1,070	1,900	1,790	2,060	530	ND
1-RAD-c		(µg/m <sup>3</sup> )	645	1,190	1,240	1,940	960	1,840	1,600	1,830	476	ND
		Mean	631	1,180	1,260	1,950	961	1,790	1,610	1,810	456	
		std.dev.	18	163	115	222	111	153	177	265	86	
		RSD	0.03	0.14	0.09	0.11	0.12	0.09	0.11	0.15	0.19	
<b>3M OVM 3500</b>	Uptake Rate	(mL/min)	36	32	33	31	36	30	31	28	26	25
1-3M-a		(µg/m <sup>3</sup> )	322	979	964	1,400	1,220	1,550	1,390	2,000	1,030	ND
1-3M-b		(µg/m <sup>3</sup> )	313	865	873	1,290	826	1,330	1,290	1,760	947	ND
1-3M-c		(µg/m <sup>3</sup> )	331	1,040	1,100	1,510	939	1,660	1,500	2,110	1,120	ND
		Mean	322	962	981	1,400	995	1,510	1,390	1,960	1,030	
		std.dev.	9	90	116	108	203	169	107	179	84	
		RSD	0.03	0.09	0.12	0.08	0.20	0.11	0.08	0.09	0.08	
<b>SKC Carbograph 5</b>	Uptake Rate	(mL/min)	17	14	13	13	16	13	15	13	13	13
1-SKC-a		(µg/m <sup>3</sup> )	3,020	1,100	1,010	1,260	1,090	1,050	1,040	1,290	900	125
1-SKC-b		(µg/m <sup>3</sup> )	2,850	1,270	1,284	1,660	1,200	1,470	1,310	1,670	1,180	156
1-SKC-c		(µg/m <sup>3</sup> )	2,770	980	957	1,190	1,150	1,050	938	1,210	842	120
		Mean	2,880	1,120	1,080	1,371	1,150	1,190	1,100	1,390	974	134
		std.dev.	130	145	175	252	56	245	192	249	181	19
		RSD	0.05	0.13	0.16	0.18	0.05	0.21	0.18	0.18	0.19	0.14
1-SUMMA-a		(µg/m <sup>3</sup> )	1,710	1,620	1,810	2,450	1,340	2,580	2,140	2,760	1,950	144
1-SUMMA-b		(µg/m <sup>3</sup> )	1,680	1,580	1,770	2,340	1,300	2,700	2,030	2,560	1,800	139
1-SUMMA-c		(µg/m <sup>3</sup> )	1,230	1,220	1,320	1,780	944	2,040	1,530	1,870	1,150	80
		Mean	1,540	1,470	1,640	2,190	1,190	2,440	1,900	2,400	1,640	121
		std.dev.	269	218	275	357	217	351	321	470	426	36
		RSD	0.17	0.15	0.17	0.16	0.18	0.14	0.17	0.20	0.26	0.29



**Table 6-4:** Concentrations measured in exposure chamber at 10 ppm<sub>v</sub> (NAPH=1ppm<sub>v</sub>)

10 ppm <sub>v</sub>		Analyte	MEK	NHEX	12DC	111TC	BENZ	CTET	TCE	PCE	124TMB	NAPH
<b>WMS Anasorb 747</b>	Uptake Rate	(mL/min)	1.3	1.3	2.6	1.3	2.2	1.5	3.3	5.4	13	26
10-WMS-a		(µg/m <sup>3</sup> )	8,270	20,100	20,700	28,900	17,100	33,300	26,400	29,900	17,300	365
10-WMS-b		(µg/m <sup>3</sup> )	7,730	18,600	19,400	26,000	15,500	31,100	25,400	30,500	18,400	286
10-WMS-c		(µg/m <sup>3</sup> )	9,600	18,600	20,700	26,200	17,100	31,100	25,400	29,900	18,700	339
		Mean	8,530	19,100	20,200	27,000	16,500	31,900	25,700	30,100	18,100	330
		std.dev.	961	881	746	1,597	895	1,283	587	360	706	40
		RSD	0.11	0.05	0.04	0.06	0.05	0.04	0.02	0.01	0.04	0.12
<b>ATD Tenax TA</b>	Uptake Rate	(mL/min)	0.50	0.50	0.50	0.50	0.35	0.50	0.41	0.50	0.62	0.50
10-ATD-a		(µg/m <sup>3</sup> )	ND	26,700	26,700	24,700	34,300	38,700	42,300	40,700	19,400	1,200
10-ATD-b		(µg/m <sup>3</sup> )	ND	28,000	26,700	23,300	35,200	36,700	42,300	40,700	18,800	1,400
10-ATD-c		(µg/m <sup>3</sup> )	ND	27,300	26,700	26,700	35,200	33,300	42,300	41,300	19,400	1,200
		Mean		27,300	26,700	24,889	34,900	36,200	42,300	40,900	19,200	1,270
		std.dev.		667	0	1,678	550	2,694	0	385	310	115
		RSD		0.02	0.00	0.07	0.02	0.07	0.00	0.01	0.02	0.09
<b>Radiello Charcoal</b>	Uptake Rate	(mL/min)	79	66	77	62	80	67	69	59	50	25
10-RAD-a		(µg/m <sup>3</sup> )	8,000	22,700	23,500	36,800	18,100	34,600	31,000	35,000	8,650	ND
10-RAD-b		(µg/m <sup>3</sup> )	5,930	17,700	18,200	28,600	14,000	27,000	24,000	26,800	6,000	ND
10-RAD-c		(µg/m <sup>3</sup> )	8,300	23,100	23,800	37,500	18,400	35,200	31,600	35,700	8,030	ND
		Mean	7,400	21,200	21,800	34,300	16,800	32,200	28,900	32,500	7,560	
		std.dev.	1,280	3,000	3,130	4,920	2,420	4,590	4,230	4,970	1,390	
		RSD	0.17	0.14	0.14	0.14	0.14	0.14	0.15	0.15	0.18	
<b>3M OVM 3500</b>	Uptake Rate	(mL/min)	36	32	33	31	36	30	31	28	26	25
10-3M-a		(µg/m <sup>3</sup> )	3,500	17,700	19,100	27,000	14,100	32,000	27,900	38,700	19,500	420
10-3M-b		(µg/m <sup>3</sup> )	3,320	18,800	20,100	28,000	15,000	33,100	28,900	39,900	20,800	420
10-3M-c		(µg/m <sup>3</sup> )	3,590	20,800	22,100	30,200	16,000	36,400	32,200	43,400	22,000	474
		Mean	3,470	19,100	20,420	28,400	15,000	33,800	29,700	40,700	20,800	438
		std.dev.	141	1,590	1,530	1,650	939	2,300	2,230	2,440	1,300	31
		RSD	0.04	0.08	0.08	0.06	0.06	0.07	0.08	0.06	0.06	0.07
<b>SKC Charcoal</b>	Uptake Rate	(mL/min)	17	14	13	13	16	13	15	13	13	13
10-SKC-a		(µg/m <sup>3</sup> )	6,660	33,700	33,500	44,100	22,200	46,800	37,100	51,000	26,000	ND
10-SKC-b		(µg/m <sup>3</sup> )	5,080	25,700	32,100	40,700	20,500	44,100	34,600	47,300	23,500	ND
10-SKC-c		(µg/m <sup>3</sup> )	7,240	31,300	32,700	41,700	21,600	45,600	36,200	49,300	25,500	ND
		Mean	6,320	30,300	32,800	42,200	21,400	45,500	36,000	49,200	25,000	
		std.dev.	1,120	4,130	719	1,730	868	1,340	1,280	1,850	1,300	
		RSD	0.18	0.14	0.02	0.04	0.04	0.03	0.04	0.04	0.05	
10-SUMMA-a		(µg/m <sup>3</sup> )	14,100	27,300	30,100	41,700	22,100	41,300	35,600	44,200	23,500	1,068
10-SUMMA-b		(µg/m <sup>3</sup> )	15,300	27,300	30,700	41,700	22,100	47,300	35,600	43,500	23,000	961
10-SUMMA-c		(µg/m <sup>3</sup> )	16,500	28,400	31,300	43,400	23,100	49,700	37,200	47,000	26,500	1,230
10-SUMMA-d		(µg/m <sup>3</sup> )	16,200	26,900	28,900	41,800	21,500	46,100	33,400	38,700	17,500	748
10-SUMMA-e		(µg/m <sup>3</sup> )	16,200	26,200	28,500	39,500	21,000	44,900	32,300	38,700	18,500	748
		Mean	15,700	27,200	29,900	41,600	21,900	45,900	34,800	42,400	21,800	951
		std.dev.	983	778	1,220	1,390	849	3,100	1,960	3,640	3,740	208
		RSD	0.06	0.03	0.04	0.03	0.04	0.07	0.06	0.09	0.17	0.22

**Table 6-5:** Concentrations measured in the exposure chamber at 100 ppm<sub>v</sub>

100 ppm <sub>v</sub>			MEK	NHEX	12DCA	11TCA	BENZ	CTET	TCE	PCE
<b>WMS Anasorb 747</b>	Uptake Rate	(mL/min)	1.3	1.3	2.6	1.3	2.2	1.5	3.3	5.4
100-WMS-a		(µg/m <sup>3</sup> )	98,700	181,000	207,000	252,000	171,000	311,000	264,000	324,000
100-WMS-b		(µg/m <sup>3</sup> )	120,000	201,000	220,000	262,000	186,000	333,000	274,000	324,000
100-WMS-c		(µg/m <sup>3</sup> )	107,000	168,000	194,000	236,000	155,000	289,000	244,000	293,000
		Mean	108,000	183,000	207,000	250,000	171,000	311,000	261,000	314,000
		std.dev.	11,000	16,700	12,900	13,200	15,500	22,200	15,500	18,000
		RSD	0.10	0.09	0.06	0.05	0.09	0.07	0.06	0.06
<b>ATD Tenax TA</b>	Uptake Rate	(mL/min)	0.50	0.50	0.50	0.50	0.35	0.50	0.41	0.50
100-ATD-a		(µg/m <sup>3</sup> )	140,000	307,000	320,000	380,000	467,000	440,000	561,000	533,000
100-ATD-b		(µg/m <sup>3</sup> )	133,000	280,000	293,000	353,000	429,000	407,000	512,000	487,000
100-ATD-c		(µg/m <sup>3</sup> )	147,000	300,000	307,000	367,000	457,000	427,000	537,000	513,000
		Mean	140,000	296,000	307,000	367,000	451,000	424,000	537,000	511,000
		std.dev.	6,670	13,900	13,300	13,300	19,800	16,800	24,400	23,400
		RSD	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.05
<b>Radiello Charcoal</b>	Uptake Rate	(mL/min)	79	66	77	62	80	67	69	59
100-RAD-a		(µg/m <sup>3</sup> )	67,200	247,000	260,000	396,000	202,000	386,000	357,000	414,000
100-RAD-b		(µg/m <sup>3</sup> )	78,400	231,000	252,000	382,000	192,000	372,000	338,000	343,000
100-RAD-c		(µg/m <sup>3</sup> )	88,400	236,000	245,000	377,000	190,000	369,000	340,000	410,000
		Mean	78,000	238,000	253,000	385,000	195,000	376,000	345,000	389,000
		std.dev.	10,600	8,140	7,440	9,800	6,260	8,890	10,300	39,600
		RSD	0.14	0.03	0.03	0.03	0.03	0.02	0.03	0.10
<b>3M OVM 3500</b>	Uptake Rate	(mL/min)	36	32	33	31	36	30	31	28
100-3M-a		(µg/m <sup>3</sup> )	40,500	188,000	201,000	280,000	141,000	331,000	300,000	376,000
100-3M-b		(µg/m <sup>3</sup> )	39,600	188,000	201,000	291,000	141,000	342,000	311,000	399,000
100-3M-c		(µg/m <sup>3</sup> )	40,500	177,000	191,000	280,000	141,000	320,000	279,000	364,000
		Mean	40,200	184,000	197,000	284,000	141,000	331,000	297,000	379,000
		std.dev.	532	6,010	5,800	6,230	0	11,040	16,400	18,000
		RSD	0.01	0.03	0.03	0.02	0.00	0.03	0.06	0.05
<b>SKC Charcoal</b>	Uptake Rate	(mL/min)	17	14	13	13	16	13	15	13
1-SKC-a		(µg/m <sup>3</sup> )	43,100	234,000	295,000	382,000	172,000	425,000	334,000	439,000
1-SKC-b		(µg/m <sup>3</sup> )	51,200	258,000	297,000	376,000	165,000	421,000	331,000	443,000
1-SKC-c		(µg/m <sup>3</sup> )	54,200	295,000	346,000	451,000	189,000	489,000	402,000	535,000
		Mean	49,500	262,000	313,000	403,000	175,000	445,000	355,000	473,000
		std.dev.	5,720	31,100	29,300	41,900	12,500	38,100	40,100	54,400
		RSD	0.12	0.12	0.09	0.10	0.07	0.09	0.11	0.12
10-SUMMA-a		(µg/m <sup>3</sup> )	123,000	215,000	231,000	311,000	166,000	354,000	252,000	235,000
10-SUMMA-b		(µg/m <sup>3</sup> )	117,000	205,000	202,000	296,000	153,000	330,000	241,000	276,000
10-SUMMA-c		(µg/m <sup>3</sup> )	138,000	208,000	223,000	295,000	163,000	336,000	252,000	283,000
10-SUMMA-d		(µg/m <sup>3</sup> )	147,000	215,000	231,000	300,000	166,000	342,000	252,000	235,000
10-SUMMA-e		(µg/m <sup>3</sup> )	150,000	223,000	239,000	317,000	176,000	366,000	279,000	325,000
		Mean	135,000	213,000	225,000	304,000	165,000	345,000	255,000	271,000
		std.dev.	14,600	7,000	14,200	9,860	8,170	14,400	14,300	37,700
		RSD	0.11	0.03	0.06	0.03	0.05	0.04	0.06	0.14

The accuracy of the passive samplers is summarized in Table 6-6, which shows the relative concentration ( $C/C_0$ ), where  $C$  is the average passive sampler concentration and  $C_0$  is the average Summa canister concentration for each compound, sampler and concentration. The  $C/C_0$  value was within the range of 0.50 to 1.67 (corresponding to the accuracy performance criterion of 50% RPD) in 84% (113 out of 135) of sampler/compound pairs. The  $C/C_0$  values were generally higher for the 100 ppm<sub>v</sub> tests, which might be attributable to the fact that the chamber was allowed to re-equilibrate for 5 minutes between samples.

MEK showed negative bias on the OVM, Radiello and SKC/charcoal samplers. Charcoal adsorbs water and MEK is the most soluble compound, which might have been the cause of this bias. Note that for the 1 ppm<sub>v</sub> test, the SKC Ultra sampler was used with Carbograph 5 as the sorbent for better sensitivity and the result showed positive bias for MEK, which demonstrates the importance of sorbent selection.

Naphthalene was not detected with the Radiello and showed negative bias for the WMS sampler. 1,2,4-TMB showed negative bias for the Radiello. Naphthalene and 1,2,4-trimethylbenzene were the two compounds with the highest and second highest K<sub>oc</sub> values (Table 3-1), and MEK was the compound with the highest solubility. Less soluble and less sorptive compounds yielded better agreement between the passive samplers and Summa canisters.

**Table 6-6:** Average concentrations measured with passive samplers divided by average concentrations measured with Summa canisters (C/C<sub>0</sub>)

C/C <sub>0</sub> for 1 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	ND	1.38	0.63	0.60	0.50	0.60	0.70	0.66	0.55	0.12	0.64
ATD Tenax TA	ND	1.04	0.61	0.45	1.68	0.63	1.16	0.82	0.55	1.10	0.89
Radiello Charcoal	0.41	0.80	0.77	0.89	0.80	0.73	0.85	0.75	0.28	ND	0.70
3M OVM 3500	0.21	0.65	0.60	0.64	0.83	0.62	0.73	0.82	0.63	ND	0.64
SKC Carbograph 5	1.87	0.76	0.66	0.63	0.96	0.49	0.58	0.58	0.60	1.11	0.82
C/C <sub>0</sub> for 10 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.54	0.70	0.68	0.65	0.75	0.69	0.74	0.71	0.83	0.35	0.66
ATD Tenax TA	ND	1.00	0.89	0.60	1.59	0.79	1.21	0.96	0.88	1.33	1.03
Radiello Charcoal	0.47	0.78	0.73	0.82	0.77	0.70	0.83	0.77	0.35	ND	0.69
3M OVM 3500	0.22	0.70	0.68	0.68	0.68	0.74	0.85	0.96	0.95	0.46	0.69
SKC Charcoal	0.40	1.11	1.10	1.01	0.98	0.99	1.03	1.16	1.15	ND	0.99
C/C <sub>0</sub> for 100 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.80	0.86	0.92	0.82	1.04	0.90	1.02	1.16	NT	NT	0.94
ATD Tenax TA	1.04	1.39	1.36	1.21	2.74	1.23	2.10	1.89	NT	NT	1.62
Radiello Charcoal	0.58	1.12	1.12	1.27	1.18	1.09	1.35	1.44	NT	NT	1.14
3M OVM 3500	0.30	0.86	0.88	0.94	0.86	0.96	1.16	1.40	NT	NT	0.92
SKC Charcoal	0.37	1.23	1.39	1.33	1.07	1.29	1.39	1.75	NT	NT	1.23
Overall Average C/C <sub>0</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.67	0.98	0.74	0.69	0.76	0.73	0.82	0.84	0.69	0.24	0.72
ATD Tenax TA	1.04	1.14	0.96	0.75	2.00	0.88	1.49	1.22	0.71	1.22	1.14
Radiello Charcoal	0.49	0.90	0.87	0.99	0.92	0.84	1.01	0.99	0.31	ND	0.81
3M OVM 3500	0.24	0.74	0.72	0.75	0.79	0.77	0.92	1.06	0.79	0.46	0.72
SKC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notes: NA – Not Available for SKC because two different sorbents were used

ND – Not Detected

NT – Not Tested

The precision of the passive samplers is summarized in Table 6-7, which shows the COV for all the compound and sampler combinations. The COV values for the passive samplers met the performance criterion of <30% in all but one case (126 of 127) and on average were better than the values for the Summa canister samples for all concentration levels.

**Table 6-7: COV of concentrations measured in test chamber**

COV @ 1 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	ND	0.32	0.03	0.06	0.06	0.05	0.00	0.05	0.06	0.18	0.09
ATD Tenax TA	ND	0.04	0.07	0.10	0.08	0.13	0.04	0.05	0.15	NA	0.08
Radiello Charcoal	0.03	0.14	0.09	0.11	0.12	0.09	0.11	0.15	0.19	ND	0.11
3M OVM 3500	0.03	0.09	0.12	0.08	0.20	0.11	0.08	0.09	0.08	ND	0.10
SKC Carbograph 5	0.05	0.13	0.16	0.18	0.05	0.21	0.18	0.18	0.19	0.14	0.15
Summa Canister	0.17	0.15	0.17	0.16	0.18	0.14	0.17	0.20	0.26	0.29	0.19
COV @ 10 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.11	0.05	0.04	0.06	0.05	0.04	0.02	0.01	0.04	0.12	0.05
ATD Tenax TA	ND	0.02	0.00	0.07	0.02	0.07	0.00	0.01	0.02	0.09	0.03
Radiello Charcoal	0.17	0.14	0.14	0.14	0.14	0.14	0.15	0.15	0.18	ND	0.15
3M OVM 3500	0.04	0.08	0.08	0.06	0.06	0.07	0.08	0.06	0.06	0.07	0.07
SKC Charcoal	0.18	0.14	0.02	0.04	0.04	0.03	0.04	0.04	0.05	NA	0.06
Summa Canister	0.06	0.03	0.04	0.03	0.04	0.07	0.06	0.09	0.17	0.22	0.08
COV @ 100 ppm <sub>v</sub>	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.10	0.09	0.06	0.05	0.09	0.07	0.06	0.06	NT	NT	0.07
ATD Tenax TA	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.05	NT	NT	0.04
Radiello Charcoal	0.14	0.03	0.03	0.03	0.03	0.02	0.03	0.10	NT	NT	0.05
3M OVM 3500	0.01	0.03	0.03	0.02	0.00	0.03	0.06	0.05	NT	NT	0.03
SKC Charcoal	0.12	0.12	0.09	0.10	0.07	0.09	0.11	0.12	NT	NT	0.10
Summa Canister	0.11	0.03	0.06	0.03	0.05	0.04	0.06	0.14	NT	NT	0.07
											Overall
Overall Mean COV	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.11	0.15	0.04	0.06	0.07	0.05	0.03	0.04	0.05	0.15	0.07
ATD Tenax TA	0.05	0.04	0.04	0.07	0.05	0.08	0.03	0.04	0.08	0.09	0.06
Radiello Charcoal	0.11	0.10	0.09	0.09	0.10	0.08	0.10	0.13	0.19	NA	0.11
3M OVM 3500	0.03	0.07	0.07	0.05	0.09	0.07	0.07	0.07	0.07	0.07	0.07
SKC	0.11	0.13	0.09	0.11	0.05	0.11	0.11	0.11	0.12	0.14	0.11
Summa Canister	0.11	0.07	0.09	0.08	0.09	0.08	0.09	0.14	0.22	0.26	0.12

Notes: ND – Not Detected

NT – Not Tested

Linear regression analysis was performed to calculate the slope, intercept and correlation coefficient ( $R^2$ ) of the relation between the relative concentration ( $C/C_0$ ) and absolute concentration in the chamber. An ideal correlation would have all  $C/C_0$  values equal to 1.0, which would result in a regression with a slope of zero, an intercept of 1.0 and a correlation coefficient ( $R^2$ ) of 100%. Table 6-8 provides the regression parameters calculated.

**Table 6-8:** Linear regression parameters for normalized ( $C/C_0$ ) concentration data for 1, 10 and 100 ppm<sub>v</sub> tests at 5 cm/min face velocity and 30 min sample duration

Analyte	WMS			ATD			Radiello		
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>
2-Butanone (MEK)	0.01	0.21	0.69	0.01	-0.06	0.99	0.00	0.40	0.98
n-Hexane	0.00	1.07	*	0.01	1.00	0.99	0.01	0.77	0.99
1,2-Dichloroethane	0.00	0.64	1.00	0.01	0.71	0.92	0.00	1.10	0.36
1,1,1-Trichloroethane	0.00	0.62	0.96	0.01	0.49	0.98	0.00	0.85	0.98
Benzene	0.00	0.59	0.87	0.01	1.56	0.97	0.00	0.76	0.97
Carbon Tetrachloride	0.00	0.65	0.89	0.01	0.70	0.94	0.00	0.71	0.99
Trichloroethene	0.00	0.71	0.99	0.01	1.15	1.00	0.01	0.83	1.00
Tetrachloroethene	0.00	0.69	0.99	0.01	0.87	0.99	0.01	0.78	0.99
1,2,4-Trimethylbenzene	0.05	0.50	1.00	-0.01	0.83	0.70	0.00	0.41	0.72
Naphthalene	0.02	0.10	1.00	-0.01	0.84	0.44	0.00	0.04	0.18

Notes: \* - not considered representative because of apparent laboratory contamination in 1 ppm<sub>v</sub> samples

Analyte	3M OVM			SKC		
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>
2-Butanone (MEK)	0.00	0.21	0.98	-0.01	1.21	0.33
n-Hexane	0.00	0.67	1.00	0.01	0.91	0.83
1,2-Dichloroethane	0.00	0.64	0.96	0.00	0.80	0.51
1,1,1-Trichloroethane	0.00	0.67	0.99	0.00	0.79	0.39
Benzene	0.00	0.76	0.27	0.00	0.95	0.97
Carbon Tetrachloride	0.00	0.69	0.87	0.01	0.72	0.63
Trichloroethene	0.00	0.79	0.95	0.01	0.77	0.74
Tetrachloroethene	0.01	0.91	0.92	0.01	0.85	0.75
1,2,4-Trimethylbenzene	0.06	0.58	1.00	-0.01	1.02	0.61
Naphthalene	0.05	-0.05	1.00	-0.01	0.61	0.32

The intercepts were slightly lower than 1 (0.7 mean for 50 observations), which was attributable to the change in procedure for the 100 ppm<sub>v</sub> tests where 5 minutes was allowed between samplers for re-equilibration of the chamber concentrations. This resulted in slightly higher passive sampler concentrations for this test. Otherwise, the slopes were near zero for all but 124TMB and NAPH in the WMS and 3M OVM 3500 samplers. The R<sup>2</sup> values were above 0.85 for all but:

- MEK and NHEX for the WMS,
- 124TMB and NAPH for the ATD,
- 12DCA, 124TMB and NAPH for the Radiello,
- BENZ for the 3M OVM3500 and
- most of the compounds with the SKC Ultra.

This demonstrates that different compounds pose challenges for each of the samplers, which is an area for further research. Also, for those compounds that are well suited for a given sampler, the performance is consistent over the 1 to 100 ppm<sub>v</sub> range with a relatively short (30 min) exposure duration, which is practical for field sampling applications. Soil vapor concentrations show much less temporal variability than indoor air,<sup>214</sup> so long-duration time-weighted average samples are generally not necessary.

The results for the low-uptake rate samplers are provided in Table 6-9. The Radiello sampler (yellow body), WMS-LU (0.8 mL vial) and the ATD tube sampler with the low-uptake rate cap showed average results within a factor of 0.72, 1.08 and 0.72, respectively of the Summa canister results in the 10 ppm<sub>v</sub> test at a flow rate of 100 mL/min, which shows the low uptake rate samplers have accuracy comparable to the regular uptake rate samplers. Under no-flow conditions, the passive samplers showed average C/C<sub>0</sub> values of 0.47, 0.73 and 0.51, respectively, which were lower (by a factor of 0.65, 0.68 and 0.71, respectively) compared to the samples collected with 100 mL/min flow in the chamber. The low bias under no-flow conditions was similar for all three samplers even though they have considerably different uptake rates (about 25 mL/min for the Radiello, about 0.5 mL/min for the WMS-LU and about 0.05 mL/min for the ATD tube). The low-uptake rate Radiello also showed low bias of 100X for 124TMB, and low bias of 5X for tetrachloroethene (PCE) under no flow conditions, which are the compounds with the highest organic carbon partitioning coefficient (K<sub>oc</sub>) values and lowest free air diffusion coefficients (excepting NAPH which was not detected by the Radiello). The ATD tube sampler showed high bias of 2X for BENZ and 9X for NAPH and low bias of about 10X for 1,1,1-trichloroethane (111TCA), carbon tetrachloride (CTET) and 124TMB. The SKC/Charcoal sampler with the low-uptake rate cap showed detectable concentrations for only 3 compounds in the 100 ppm<sub>v</sub> stagnant test, but the concentrations were quantified within a factor of 2 for all three. The WMS-LU sampler showed concentrations within 2X for all compounds under both flowing and stagnant conditions.

**Table 6-9:** Low-uptake rate sampler results (in  $\mu\text{g}/\text{m}^3$ ) for three tests: 10 ppm<sub>v</sub> with 5 cm/min velocity, 10 ppm<sub>v</sub> stagnant and 100 ppm<sub>v</sub> stagnant

<b>10 ppm<sub>v</sub> &amp; 100 mL/min</b>	<b>MEK</b>	<b>NHEX</b>	<b>12DCA</b>	<b>111TCA</b>	<b>BENZ</b>	<b>CTET</b>	<b>TCE</b>	<b>PCE</b>	<b>124TMB</b>	<b>NAPH</b>	<b>Mean</b>
Active Tube Sample #1	14,400	41,900	41,400	55,800	34,400	65,100	51,200	60,500	41,400	1,020	
Active Tube Sample #2	11,600	34,400	38,600	51,200	30,200	60,500	46,500	55,800	36,700	884	
Average Active Tube Concentration	13,000	38,100	40,000	53,500	32,300	62,800	48,800	58,100	39,100	953	
Radiello Yellow Body	12,200	30,800	35,900	61,3400	27,800	44,900	36,800	18,800	230	ND	
Radiello/Active (C/C <sub>0</sub> )	0.94	0.81	0.90	1.15	0.86	0.72	0.75	0.32	0.01		0.72
SKC 12 hole cap	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
WMS 0.8 mL vial #1	17,500	30,100	42,800	57,100	29,900	66,700	50,000	65,500	33,700	1,470	
WMS 0.8 mL vial #2	17,300	30,100	42,800	59,000	29,900	68,200	48,500	59,500	34,100	1,530	
Average WMS (C/C <sub>0</sub> )	1.34	0.79	1.07	1.09	0.92	1.07	1.01	1.08	0.87	1.57	1.08
ATD Low Uptake #1	10,700	18,700	29,300	1,870	81,900	16,700	28,700	30,100	2,260	5,600	
ATD Low Uptake #2	16,000	20,000	30,000	14,000	82,900	20,000	28,700	39,000	2,800	6,400	
Average ATD (C/C <sub>0</sub> )	1.02	0.51	0.74	0.15	2.55	0.29	0.59	0.59	0.06	<b>6.29#</b>	0.72
<b>10 ppm<sub>v</sub> no flow</b>	<b>MEK</b>	<b>NHEX</b>	<b>12DCA</b>	<b>111TCA</b>	<b>BENZ</b>	<b>CTET</b>	<b>TCE</b>	<b>PCE</b>	<b>124TMB</b>	<b>NAPH</b>	
Active Tube Sample	17,500	37,500	37,500	54,200	29,200	61,700	49,200	60,800	38,300	833	
Radiello Yellow	12,800	19,300	21,100	37,300	16,400	27,500	22,700	12,200	1,100	ND	
Radiello (C/C <sub>0</sub> )	0.73	0.52	0.56	0.69	0.56	0.45	0.46	0.20	0.03		0.47
SKC 12 hole cap	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
WMS 0.8 mL vial #1	13,000	24,800	28,900	40,000	21,900	48,100	34,100	39,300	18,300	733	
WMS 0.8 mL vial #2	14,100	20,900	30,800	43,800	22,900	51,200	35,600	42,300	19,800	800	
Average WMS (C/C <sub>0</sub> )	0.77	0.61	0.80	0.77	0.77	0.80	0.71	0.67	0.50	0.92	0.73
ATD Low Uptake #1	13,300	16,000	17,300	9,330	81,900	12,000	17,300	20,300	2,150	9,330	
ATD Low Uptake #2	10,700	6,200	16,700	2,470	53,300	3,130	10,700	8,940	2,690	5,130	
Average ATD (C/C <sub>0</sub> )	0.69	0.30	0.45	0.11	2.32	0.12	0.28	0.24	0.06	<b>8.68#</b>	0.51
<b>100 ppm<sub>v</sub> no flow</b>	<b>MEK</b>	<b>NHEX</b>	<b>12DCA</b>	<b>111TCA</b>	<b>BENZ</b>	<b>CTET</b>	<b>TCE</b>	<b>PCE</b>			
Summa	140,000	240,000	250,000	340,000	180,000	440,000	300,000	380,000			
SKC 12 Hole Cap #1	ND	313,000	440,000	520,000	ND	ND	ND	ND			
SKC 12 Hole Cap #2	ND	321,000	442,000	526,000	ND	ND	ND	ND			
SKC 12 Hole Cap #3	ND	290,000	403,000	487,000	ND	ND	ND	ND			
Average SKC (C/C <sub>0</sub> )		1.28	1.71	1.50							1.50
ATD Low Uptake	260,000	260,000	327,000	480,000	429,000	593,000	327,000	610,000			
ATD/Summa (C/C <sub>0</sub> )	1.86	1.08	1.31	1.41	2.38	1.35	1.09	1.60			1.51

# - Notably different than other results, so these values were not included in the row averages

ND - Not Detected

Notes:



### 6.3 Summary

The results of the high concentration chamber tests indicate that passive samplers can provide vapor concentration measurements in settings similar to those expected to be encountered in passive soil vapor sampling and therefore may be a practical alternative for monitoring soil vapor concentrations for many of the volatile organic compounds of interest for human health risk assessment. Most of the concentrations measured with the passive samplers were within a factor of 2 or less of the concentrations measured with Summa canister/EPA Method TO-15 and the precision of the passive samplers was as good or better than the Summa canisters. This is encouraging considering that the passive samplers and analytical methods are all different and the samples were analyzed in different laboratories, and none of the vendor-supplied uptake rates were derived specifically for short (30 minute) duration, high (80%) humidity, and low (5 cm/min) face velocity settings. Low-uptake rate varieties of four of the samplers yielded similar accuracy to the regular uptake rate samplers, which is encouraging because low uptake rate samplers are likely to be necessary to minimize the starvation effect in passive soil vapor sampling according to the mathematical modeling in Chapter 5. Highly soluble compounds (like MEK) or highly sorptive compounds (like NAPH) appear to be more challenging to quantify accurately than other compounds.

## 7 Soil Vapor Field Testing

This chapter<sup>vii</sup> describes a series of controlled field experiments designed to elucidate the optimal approach to soil gas sampling using kinetic passive samplers. Prior to the conduct of these experiments, it was considered common knowledge that passive soil vapor sampling was a qualitative or semi-quantitative screening method that could be used to map the relative proportions of VOCs and their general distribution, but could not provide reliable measures of soil vapor concentrations.<sup>14,205</sup> The mathematical modeling described in Chapter 5 and the laboratory testing described in Chapter 6 provided unique insight into the design of the samplers and probes needed to achieve soil vapor monitoring data quality that meets the accuracy and precision performance criteria. 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  $\mu\text{g}/\text{m}^3$ , 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.

### 7.1 Experimental

#### 7.1.1 Materials and Methods

The quantitative passive samplers used in these tests included SKC Ultra™, Radiello®, OVM 3500™, Waterloo Membrane Sampler, and Passive ATD tube samplers. 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 and in Table 2-1. The uptake rates used in the study were either supplied by the vendor or estimated from the free-air diffusion coefficients<sup>200</sup> 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.<sup>152</sup> Laboratory analytical methods are described in Appendix A.

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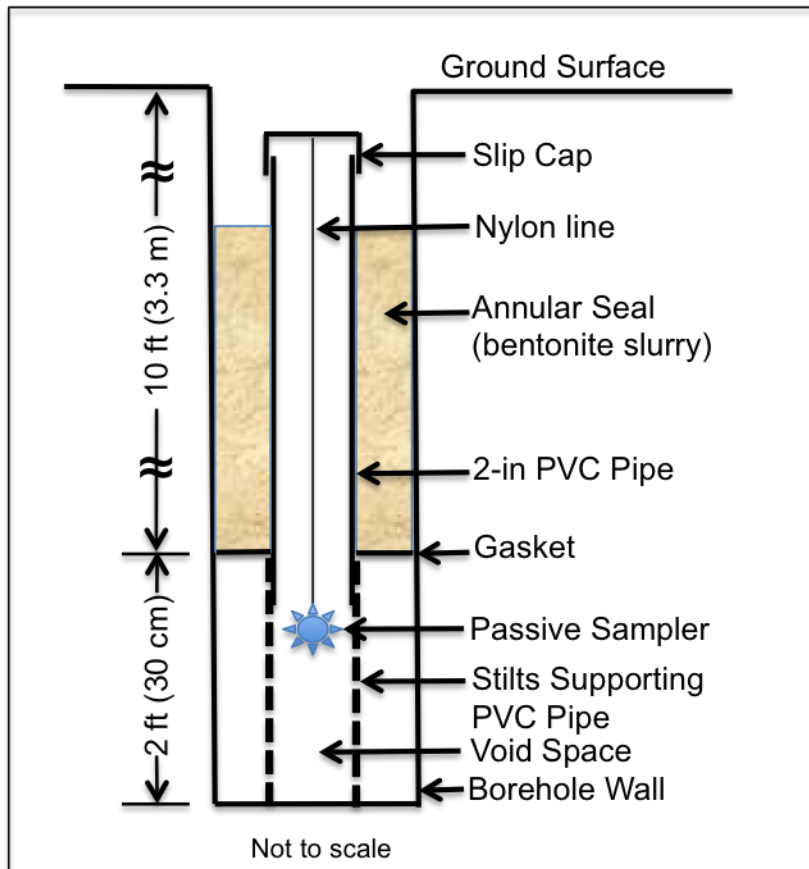
<sup>vii</sup> This Chapter is based on the author's published article "Quantitative passive soil vapor sampling for VOCs – part 3: field experiments"<sup>231</sup>

### 7.1.2 Sampling Locations

Samples were collected at: 1) the US Navy San Diego Old Town Campus (OTC) (see Figure 2-6), 2) the Arizona State University (ASU) study house in Layton, Utah (near Hill Air Force Base) (see Figure 2-8) and 3) Naval Air Station Jacksonville, Florida (NAS JAX) (see Figure 2-12), all of which were known to have VOCs in the subsurface near occupied structures from previous investigations.<sup>208,212,29,207,211,213</sup> 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, except where samples are collected inside a building, in which case, the sample depth is usually immediately below the floor slab. The experimental designs were as follows:

**Navy OTC:** passive sub-slab samples were collected outside of Building 3, immediately below the concrete slab-on-grade ground cover in two locations with five passive devices and one active sample (Summa canister with analysis by EPA Method TO-15) in each location. Both locations were outside of a building where a concrete slab was accessible for drilling and coring. Initial screening with a photoionization detector showed total ionizable vapor concentrations in the 0.1 to 10 ppm<sub>v</sub> range. The primary contaminant of concern 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 exceeding 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 2-1. 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 hydrated bentonite slurry (Figure 7-1). 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). The primary VOCs were trichloroethene (TCE) and 1,1-dichloroethene (1,1-DCE) at concentrations of several hundred  $\mu\text{g}/\text{m}^3$ . 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 the 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).<sup>224</sup> 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 using Summa® canisters and analyzed by EPA Method TO-15.<sup>6</sup>



**Figure 7-1:** Schematic diagram of the probe for passive vapor sampling at the Layton house, Utah

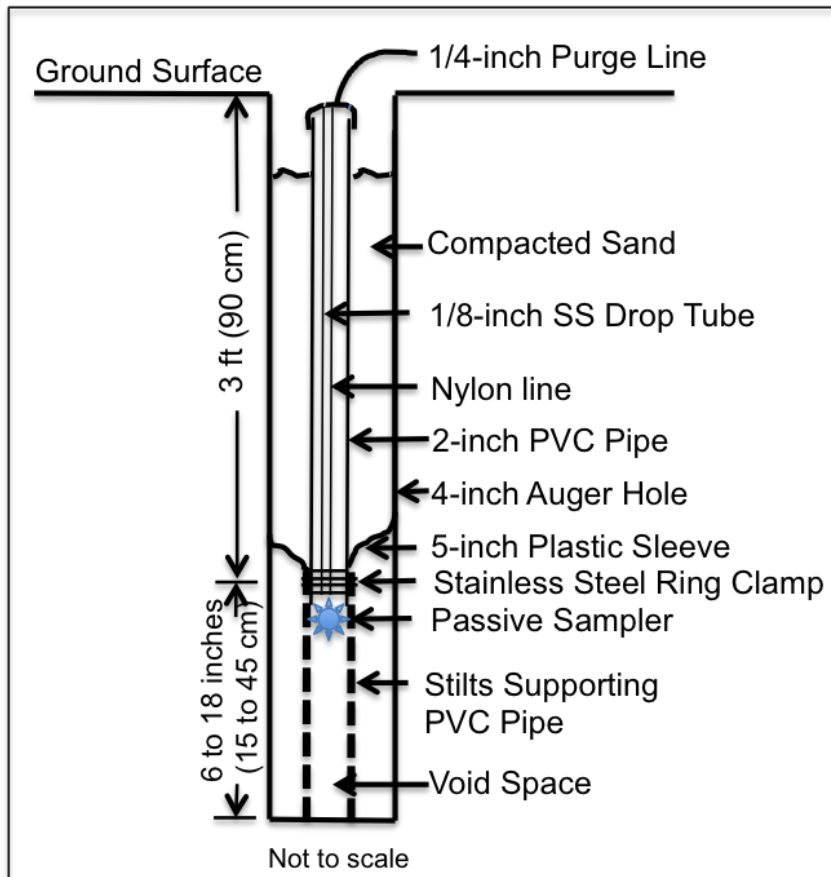
The passive samplers used at the Layton House were customized as follows:

- 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 the effect of the exposure time. Seven passive samples were collected with each of the 5 samplers for a total of 35 passive samples, and 35 Summa<sup>®</sup> 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<sup>224</sup> (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 7-2) 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 7-2:** Schematic diagram of the probe for passive soil vapor sampling at NAS JAX

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<sub>v</sub> for all three probes, and generally stabilized within about 20 to 30 seconds. Purge rates were about 3 L/min, so the purge volume was typically about 1 to 1.5 liters, which corresponded to about 1 casing volume for the probe pipe.

Low-uptake varieties of the Radiello sampler (yellow body), SKC Ultra Sampler (12-hole cap) and WMS sampler (WMS-LU - 0.8 mL) were used to minimize the starvation effect. The ATD tube sampler already

has a relatively low uptake rate and was not modified with a low-uptake cap to avoid results below the limits of detection. The 3M OVM 3500 sampler does not have a low-uptake variety.

A 1 L Summa canister sample was collected immediately after purging via a 1/8-in stainless steel drop-tube (see Figure 7-2) that extended through a compression-fitting in the slip cap to a depth just below the bottom of the PVC pipe (i.e., top of the void space), such that the canister sample was collected below the PVC pipe. The canister was filled quickly (over about 10 seconds) so that the passive sampler would not be biased by advection from the active sample collection during most of the passive sampling period.

Sub-slab vapor samples were collected at three locations. It was not possible to drill 5 cm diameter holes through the floor (needed to accommodate the 3M OVM and SKC samplers) because steel reinforcing bars were repeatedly encountered and eventually broke the teeth on the concrete hole-saw. The ATD, WMS and Radiello passive samplers were tested through a 1-inch diameter hammer-drill hole in the floor slab. In each of the three locations, one sample was collected with each type of passive sampler (1 h duration was sufficient because the concentrations were  $>1,000 \mu\text{g}/\text{m}^3$ ) and one Summa<sup>®</sup> canister. Immediately after passive sampler deployment, the hole was purged to remove any atmospheric air entrained during drilling or removal of the prior passive sampler using a vacuum chamber and a 1 L Tedlar bag, which was screened with a field-calibrated ppbRAE<sup>®</sup> 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.



## 7.2 Results and Discussion

The results of sampling at the Navy OTC site are shown in Table 7-1. The compounds detected in the Summa canisters included TCE and cis-1,2-DCE, in the range of 450 to 63,000  $\mu\text{g}/\text{m}^3$ . The passive sub-slab samplers had 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 presented in Chapter 5. Based on these results, lower uptake rate samplers were used at the Layton House and NAS JAX.

**Table 7-1:** Active and passive soil vapor concentrations in sub-slab samples from Navy OTC3, along with uptake rates (provided by suppliers) for the passive samplers

Compound	Sampler	Passive Concentration ( $\mu\text{g}/\text{m}^3$ )	Active (Summa/TO-15) Concentration ( $\mu\text{g}/\text{m}^3$ )	C/C <sub>0</sub> (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

At the Layton house, TCE and 1,1-DCE were the primary compounds detected, typically in the range of 100 to 500  $\mu\text{g}/\text{m}^3$  in the active samples (Table 7-2). The average active sample concentrations in Table 7-3 and 7-4 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 7-2). The

concentrations measured with the passive soil vapor samplers (C) were divided by the average active concentration ( $C_0$ ) as shown in Figure 7-3.

**Table 7-2:** TCE and 11DCE Concentrations measured in active soil gas samples analyzed by the Hapsite transportable GC/MS (H) or Summa® canister and TO-15 (S) at the Layton house, Utah.

Temporal Variability								Spatial Variability		
11DCE ( $\mu\text{g}/\text{m}^3$ )	*	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	<b>26</b>	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	<b>16</b>	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		
<b>TCE (<math>\mu\text{g}/\text{m}^3</math>)</b>										
		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	<b>36</b>	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	<b>39</b>	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		

Note: Bold and italics indicate samples suspected of low bias because of incomplete purging

**Table 7-3:** Passive soil vapor concentrations, average active sampling concentrations and relative concentrations (C/C<sub>0</sub>) for 1,1-DCE at the Layton House, Utah.

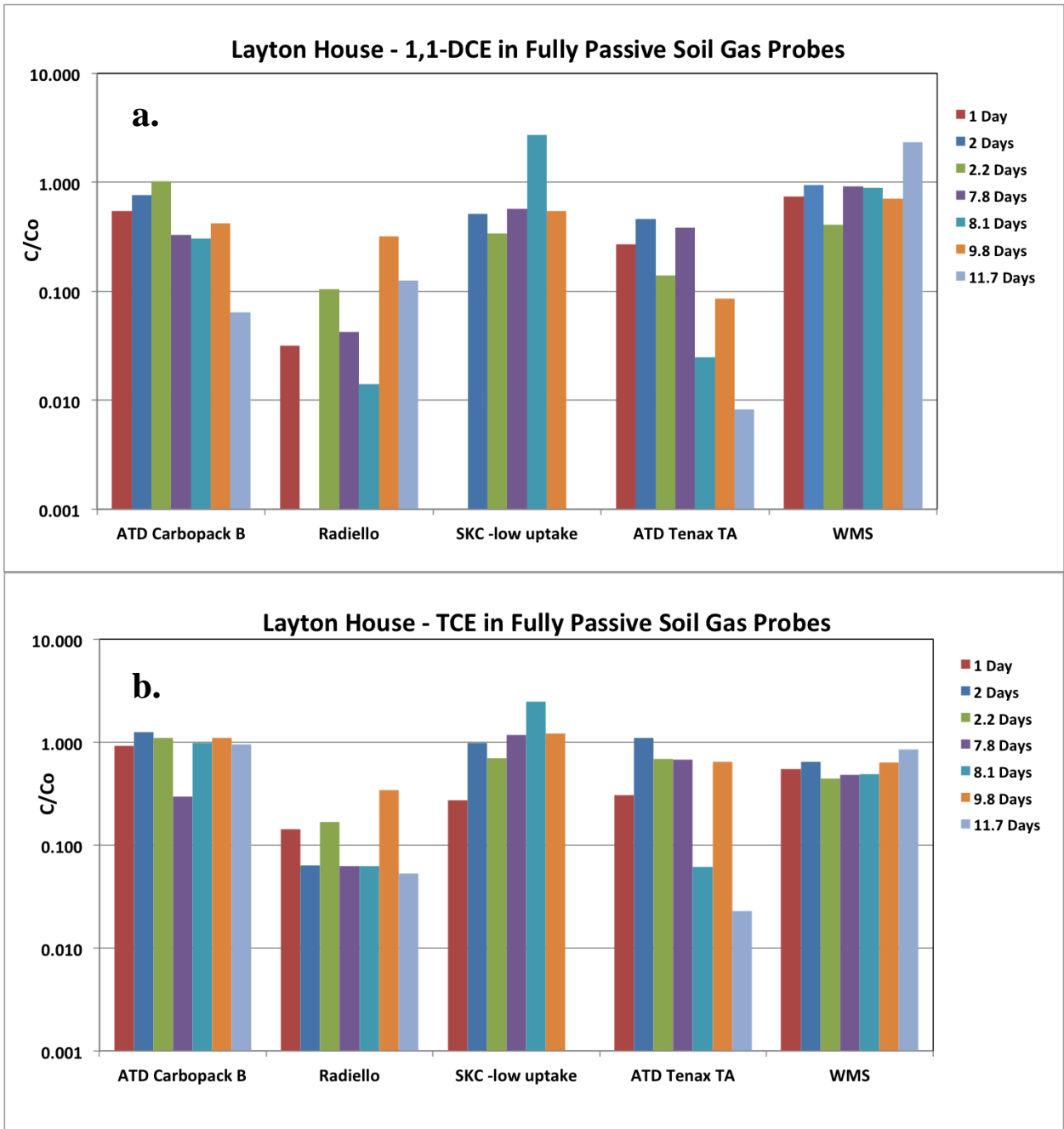
Compound	Sample Time (t) (days)	Sampler	Soil Gas Probe #	Passive Concentration (µg/m <sup>3</sup> )	Average Active Concentration (µg/m <sup>3</sup> )	C/C <sub>0</sub> (Passive / Active)	Uptake Rate (UR) (mL/min)	UR x t (L)
1,1-DCE	1.0	ATD CarbopackB	SGP-1	178	326	0.55	0.57	0.8
		Radiello Charcoal	SGP-3	15	482	0.03	79	119
		SKC Charcoal	SGP-6	--	--	--	1.3	1.9
		ATD Tenax TA	SGP-2	106	393	0.27	0.6	0.8
		WMS Anasorb	SGP-4	348	469	0.74	0.82	1.2
	2.0	ATD CarbopackB	SGP-3	277	365	0.76	0.57	1.7
		Radiello Charcoal	SGP-5	1.51U	89	< 0.02	79	235
		SKC Charcoal	SGP-2	209	406	0.51	1.3	3.8
		ATD Tenax TA	SGP-4	103	221	0.46	0.6	1.7
		WMS Anasorb	SGP-6	250	264	0.94	0.82	2.4
	2.2	ATD CarbopackB	SGP-2	434	425	1.02	0.57	1.8
		Radiello Charcoal	SGP-4	17	165	0.10	79	250
		SKC Charcoal	SGP-1	99	<b>290</b>	0.34	1.3	4.1
		ATD Tenax TA	SGP-3	51	365	0.14	0.6	1.8
		WMS Anasorb	SGP-5	35	87	0.41	0.82	2.6
	7.9	ATD CarbopackB	SGP-6	70	212	0.33	0.57	6.5
		Radiello Charcoal	SGP-2	13	312	0.04	79	910
		SKC Charcoal	SGP-5	30	52	0.57	1.3	14.8
		ATD Tenax TA	SGP-1	79	207	0.38	0.6	6.5
		WMS Anasorb	SGP-3	250	272	0.92	0.82	9.3
	8.1	ATD CarbopackB	SGP-5	15	<b>49</b>	0.30	0.57	6.6
		Radiello Charcoal	SGP-1	2	155	0.01	79	929
		SKC Charcoal	SGP-4	393	144	2.74	1.3	15.1
		ATD Tenax TA	SGP-6	4	166	0.02	0.6	6.6
		WMS Anasorb	SGP-2	327	370	0.88	0.82	9.5
	9.8	ATD CarbopackB	SGP-4	75	177	0.42	0.57	8.1
		Radiello Charcoal	SGP-6	49	154	0.32	79	1,133
		SKC Charcoal	SGP-3	133	243	0.55	1.3	18.4
		ATD Tenax TA	SGP-5	7	<b>77</b>	0.09	0.6	8.1
		WMS Anasorb	SGP-1	130	186	0.70	0.82	11.6
11.7	ATD CarbopackB	SGP-1	22	346	0.06	0.57	9.6	
	Radiello Charcoal	SGP-3	14	109	0.13	79	1,344	
	SKC Charcoal	SGP-6	too wet	351	---	1.3	21.8	
	ATD Tenax TA	SGP-2	3	330	0.01	0.6	9.6	
	WMS Anasorb	SGP-4	363	154	2.35	0.82	13.8	

Note: Bold and italics indicate average active sampling concentrations where one value was not included because of suspected low bias due to incomplete purging.

**Table 7-4:** Passive soil vapor concentrations, average active sampling concentrations and relative concentrations (C/C<sub>0</sub>) for TCE at the Layton House, Utah

Compound	Sample Time (t) (days)	Sampler	Soil Gas Probe #	Passive Concentration (µg/m <sup>3</sup> )	Average Active Concentration (µg/m <sup>3</sup> )	C/C <sub>0</sub> (Passive /Active)	Uptake Rate (UR) (mL/min)	UR x t (L)
TCE	1.0	ATD Carbopack B	SGP-1	342	374	0.91	0.5	0.7
		Radiello Charcoal	SGP-3	65	452	0.14	69	102.5
		SKC Charcoal	SGP-6	77	280	0.27	0.58	0.9
		ATD Tenax TA	SGP-2	151	492	0.31	0.5	0.7
		WMS Anasorb	SGP-4	210	380	0.55	3.28	4.9
	2.0	ATD Carbopack B	SGP-3	611	488	1.25	0.5	1.5
		Radiello Charcoal	SGP-5	7	111	0.06	69	202.9
		SKC Charcoal	SGP-2	541	555	0.98	0.58	1.7
		ATD Tenax TA	SGP-4	300	271	1.11	0.5	1.5
		WMS Anasorb	SGP-6	182	282	0.64	3.28	9.6
	2.2	ATD Carbopack B	SGP-2	611	555	1.10	0.5	1.6
		Radiello Charcoal	SGP-4	48	286	0.17	69	215.3
		SKC Charcoal	SGP-1	345	<b>492</b>	0.70	0.58	1.8
		ATD Tenax TA	SGP-3	319	461	0.69	0.5	1.6
		WMS Anasorb	SGP-5	53	118	0.45	3.28	10.2
	7.9	ATD Carbopack B	SGP-6	77	261	0.30	0.5	5.7
		Radiello Charcoal	SGP-2	43	691	0.06	69	784.9
		SKC Charcoal	SGP-5	113	96	1.18	0.58	6.6
		ATD Tenax TA	SGP-1	286	424	0.68	0.5	5.7
		WMS Anasorb	SGP-3	301	631	0.48	3.28	37.3
	8.1	ATD Carbopack B	SGP-5	103	<b>105</b>	0.99	0.5	5.8
		Radiello Charcoal	SGP-1	22	348	0.06	69	801.1
		SKC Charcoal	SGP-4	728	292	2.49	0.58	6.7
		ATD Tenax TA	SGP-6	13	207	0.06	0.5	5.8
		WMS Anasorb	SGP-2	347	710	0.49	3.28	38.1
	9.8	ATD Carbopack B	SGP-4	287	260	1.10	0.5	7.1
		Radiello Charcoal	SGP-6	69	201	0.34	69	977.0
		SKC Charcoal	SGP-3	511	424	1.21	0.58	8.2
		ATD Tenax TA	SGP-5	63	<b>98</b>	0.64	0.5	7.1
		WMS Anasorb	SGP-1	219	345	0.64	3.28	46.4
11.7	ATD Carbopack B	SGP-1	279	<b>295</b>	0.95	0.5	8.4	
	Radiello Charcoal	SGP-3	21	402	0.05	69	1,159.2	
	SKC Charcoal	SGP-6	too wet	144	---	0.58	9.7	
	ATD Tenax TA	SGP-2	11	476	0.02	0.5	8.4	
	WMS Anasorb	SGP-4	238	280	0.85	3.28	55.1	

Bold and italics indicate average active sample concentrations where one value was not included because of suspected low bias due to incomplete purging.



**Figure 7-3:** Relative concentration (passive/active or C/C<sub>0</sub>) at the Layton House for : a) 1,1-DCE, and b) TCE

These data showed several trends that were consistent with expectations based on transient and steady-state mathematical models in Chapter 5 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 was 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<sup>19</sup> of 0.2, 1.0 and 0.2 L, respectively for these compounds and sorbents. The product of the uptake rate and the sample duration was as high as 9.6 L, which far exceeded the recommended maximum sample volumes. 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 was 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 was apparently attributable to better retention of 1,1-DCE and TCE by stronger sorbents (charcoal and Anasorb 747, respectively).

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 7-2). 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 RSD 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  $\mu\text{g}/\text{m}^3$  and 38%, respectively. The pooled mean concentration and RSD for TCE were 350  $\mu\text{g}/\text{m}^3$  and 28%, respectively.

A similar calculation of the mean, standard deviation and RSD for the passive samplers (Table 7-5) 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 average concentrations that were within the accuracy performance criterion of <50% RPD of the active soil gas sample concentrations and RSD values that were similar to the active samplers (~50%). 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<sup>20</sup> and poor retention<sup>19</sup>, 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 7-5:** TCE and 11DCE concentrations measured in passive samplers at the Layton House, Utah

Passive Sampler Concentrations for 11DCE ( $\mu\text{g}/\text{m}^3$ )								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
Passive Sampler Concentrations for TCE ( $\mu\text{g}/\text{m}^3$ )								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

The results of passive sampling at NAS JAX (Table 7-6) showed a broader range of concentrations (~100 to ~30,000  $\mu\text{g}/\text{m}^3$ ) than the previous data sets (Table 7-5), 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 7-4 and 7-5).

**Table 7-6: Passive and active soil vapor concentrations for four VOCs in soil gas probes (SG) and sub-slab probes (SSP) at NAS JAX**

Sampler Type (Subtype/Sorbent)	Sample ID	Void Space Volume (L)	Exposure Time (min)	Concentration (µg/m3)							
				cis-1,2-DCE		PCE		trans-1,2-DCE		TCE	
				Passive Sampler	Summa Canister	Passive Sampler	Summa Canister	Passive Sampler	Summa Canister	Passive Sampler	Summa Canister
3M DVM (Regular/ charcoal)	SG-FP-20-1	1	20	1,136	1,600	424	560	384	480	145	180
	SG-FP-20-3	3	20	1,065	1,200	477	540	384	360	151	130
	SG-FP-40-2-A	2	40	1,705	2,300	601	760	490	560	185	220
	SG-FP-40-2-B	2	40	2,273	3,900	724	990	639	800	217	290
	SG-FP-40-2-C	2	40	1,705	2,600	689	1,000	518	600	193	250
	SG-FP-60-1	1	60	994	1,600	277	480	331	520	102	160
	SG-FP-60-3	3	60	1,278	1,800	518	630	469	520	166	170
ATD Tube (Regular/ Carbopack)	SG-FP-20-1	1	20	2,157	1,700	1,024	560	637	520	310	180
	SG-FP-20-3	3	20	1,961	1,300	902	530	627	380	270	140
	SG-FP-40-2-A	2	40	3,775	2,100	1,098	590	833	490	280	180
	SG-FP-40-2-B	2	40	3,382	2,700	1,524	1,000	833	620	340	260
	SG-FP-40-2-C	2	40	3,284	2,500	1,585	940	784	540	330	230
	SG-FP-60-1	1	60	2,484	1,400	976	560	654	390	250	170
	SG-FP-60-3	3	60	1,699	1,200	894	520	523	340	203	130
WMS (0.8µm Amberlite Anasorb 47)	SG-FP-20-1	1	20	1,806	1,700	670	690	9,823	500	162	190
	SG-FP-20-3	3	20	1,521	1,300	580	520	9,823	370	380	140
	SG-FP-40-2-A	2	40	3,897	2,900	1,004	950	4,912	650	340	250
	SG-FP-40-2-B	2	40	2,757	2,600	1,071	1,300	4,912	720	340	290
	SG-FP-40-2-C	2	40	2,757	2,400	1,049	930	4,912	540	312	230
	SG-FP-60-1	1	60	1,648	1,500	565	550	3,274	410	227	170
	SG-FP-60-3	3	60	1,553	1,300	625	520	3,274	380	265	140
Radiello (Yellow Body/ Charcoal)	SG-FP-20-1	1	20	1,730	2,000	295	480	476	580	369	170
	SG-FP-20-3	3	20	1,222	2,200	295	790	476	650	369	220
	SG-FP-40-2-A	2	40	2,794	2,400	148	720	238	580	185	210
	SG-FP-40-2-B	2	40	2,143	2,300	226	690	294	540	185	200
	SG-FP-40-2-C	2	40	2,452	2,400	315	940	310	530	185	220
	SG-FP-60-1	1	60	1,831	1,800	98	650	275	520	123	190
	SG-FP-60-3	3	60	1,582	1,600	348	610	307	460	123	160
SKC* (12-hole cap, Carbograph)	SG-FP-20-1	1	20	2,704	1,800	1,040	730	770	520	*	200
	SG-FP-20-3	3	20	2,129	1,200	648	520	634	340	407	130
	SG-FP-40-2-A	2	40	3,758	2,100	875	920	806	510	546	230
	SG-FP-40-2-B	2	40	3,356	2,500	1,023	1,000	811	580	64	250
	SG-FP-40-2-C	2	40	3,236	2,400	920	990	747	550	139	230
	SG-FP-60-1	1	60	2,693	1,800	603	700	675	500	410	190
	SG-FP-60-3	3	60	2,683	1,300	558	550	734	390	572	140
ATD Tube (Pin-hole/ Carbopack)	SSP-4	--	60	5,998	3,800	13,140	7,400	3,999	2,300	1,549	960
	SSP-5	--	60	7,331	4,400	28,332	17,000	8,331	4,900	3,030	1,900
	SSP-6	--	60	21,328	14,000	49,273	18,000	29,326	19,000	7,071	3,400
WMS (0.8µm Amberlite Anasorb 47)	SSP-4	--	60	4,753	3,800	8,185	7,400	2,679	2,300	1,134	960
	SSP-5	--	60	4,753	4,400	17,857	17,000	5,566	4,900	2,079	1,900
	SSP-6	--	60	18,695	14,000	26,786	18,000	29,470	19,000	4,913	3,400
Radiello (Yellow Body/ Charcoal)	SSP-4	--	60	2,233	3,800	1,850	7,400	1,344	2,300	326	960
	SSP-5	--	60	2,820	4,400	4,770	17,000	2,952	4,900	1,224	1,900
	SSP-6	--	60	10,444	14,000	6,535	18,000	13,233	19,000	2,620	3,400

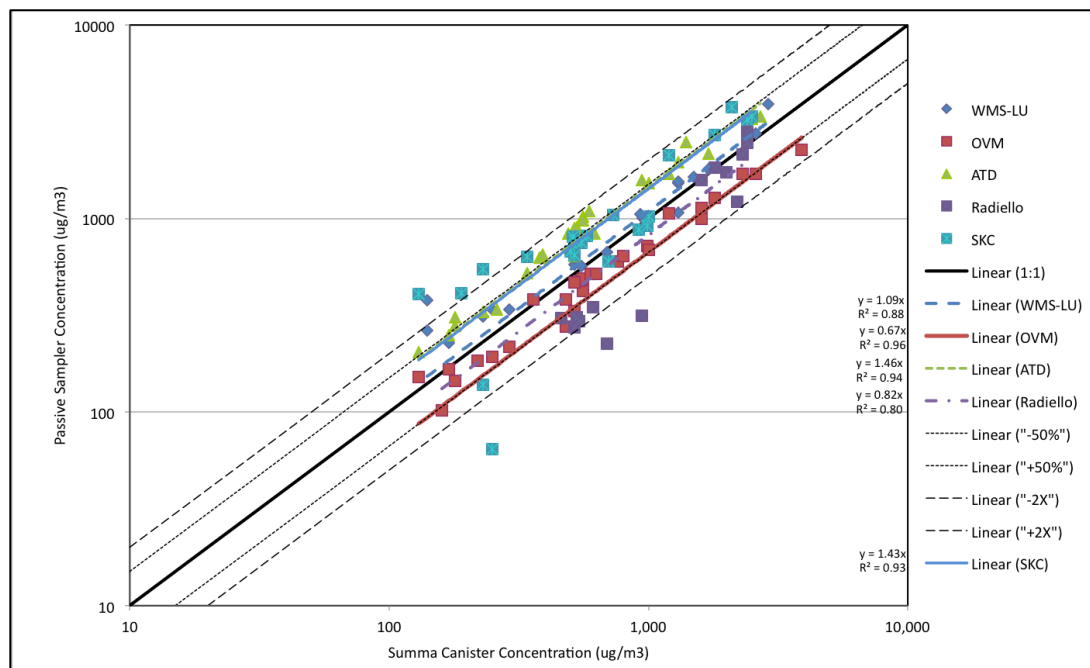
**Notes**

\* The SKC Trip Blank contained a significant level of CE (23.4 ng). This mass was subtracted from the sample masses. Sample SG-FP-20-1-SKCPH had less than 23.4 ng of CE on it, so this result is excluded from the table

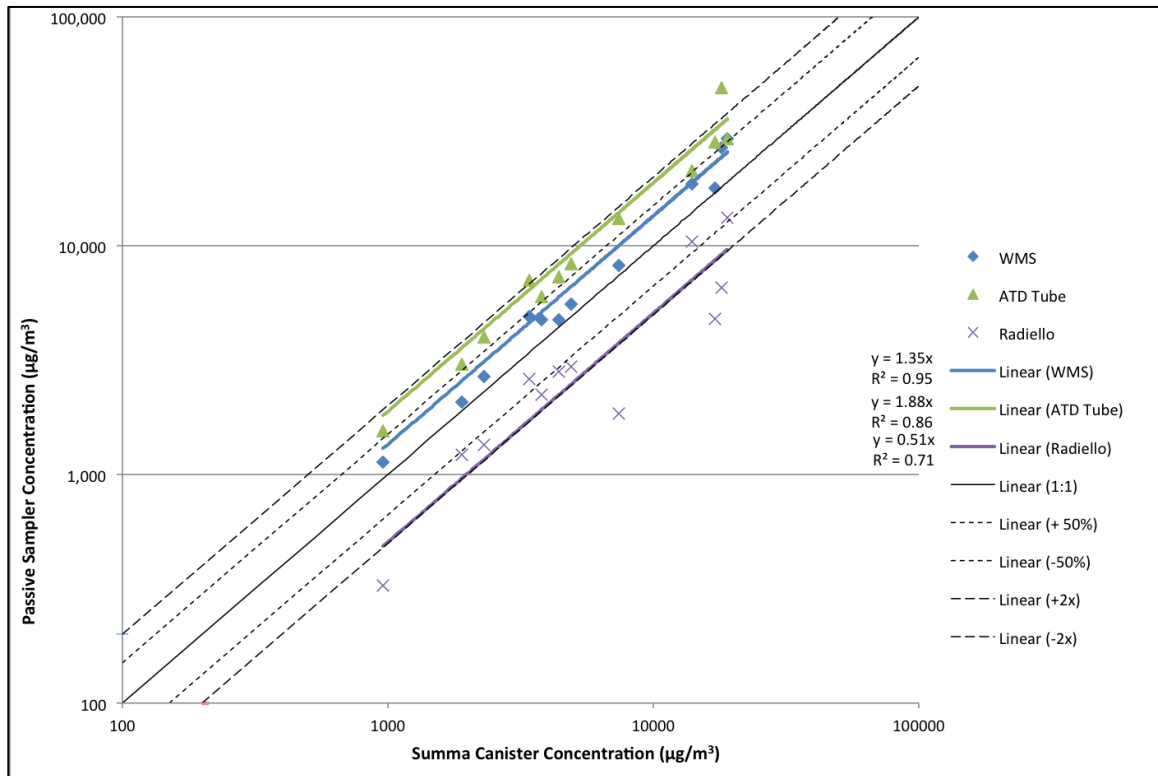


The exterior soil gas passive sampler concentrations (Figure 7-4) all yielded regression lines with slopes ranging from 0.67 to 1.46 and correlation coefficient ( $R^2$ ) values of 0.80 to 0.96. The regression lines for the WMS and Radiello samplers fell within the  $\pm 25\%$  range (inner dashed lines in Figure 7-4) 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  $\pm 50\%$  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.

The interior passive sub-slab samples at NAS JAX also showed strong positive correlations with active sample results (Figure 7-5). 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  $\pm 25\%$  range, with a correlation coefficient of 0.95. The regression lines for the ATD and Radiello samplers were within the  $\pm 50\%$  range of an ideal (1:1) correlation, with slightly lower correlation coefficients (0.86 and 0.71, respectively) than the WMS sampler.



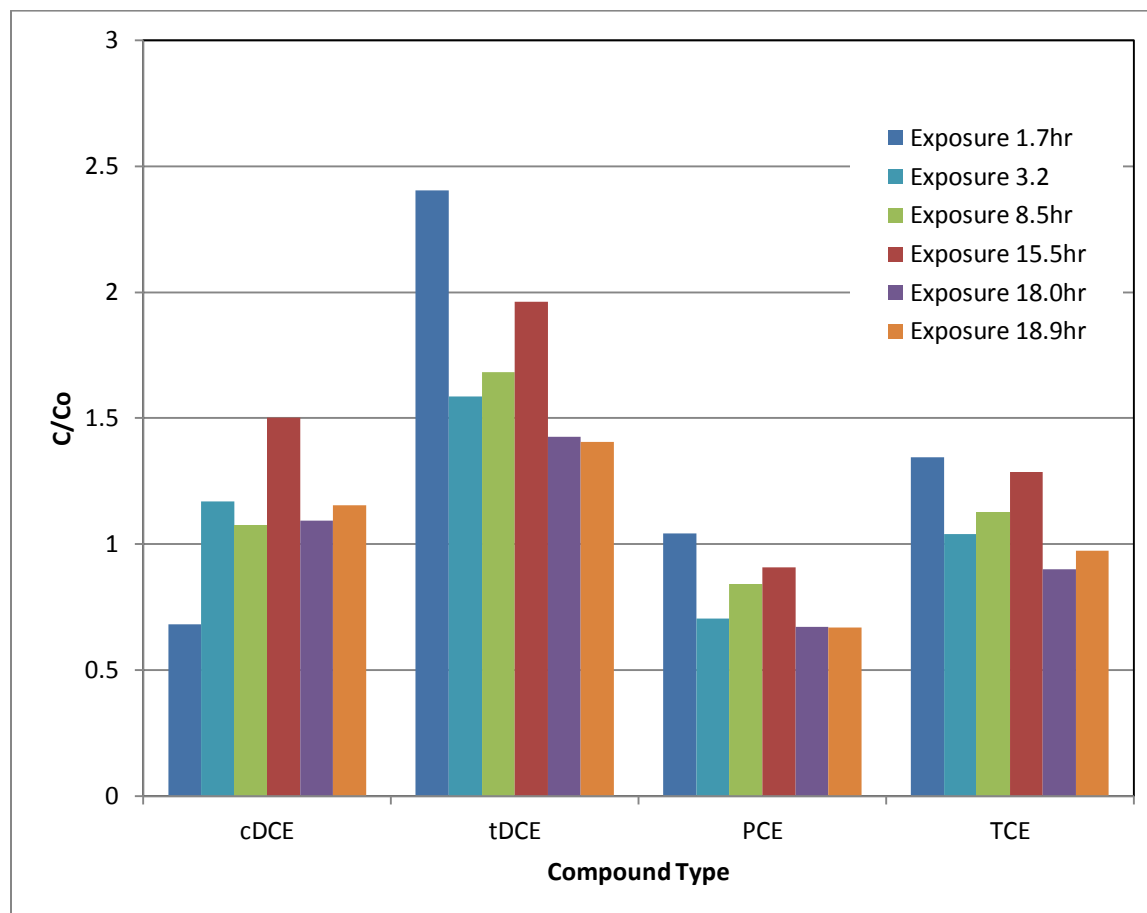
**Figure 7-4:** Correlation between passive samples and Summa canisters at NAS JAX with linear regression and correlation ( $R^2$ ) for soil gas samples



**Figure 7-5:** Correlation between passive samples and Summa canisters at NAS JAX with linear regressions and correlation coefficients ( $R^2$ ) for sub-slab samples

Statistical analysis of the fractional factorial design via analysis of variance (ANOVA) at the 5% level of significance 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 exterior passive soil gas samples from a temporary (uncased) hole also showed good correlation to the active (Summa canister) samples (Figure 7-6), which indicated that uptake rates of 0.5 to 1.1 mL/min for the four compounds detected were low enough to avoid low bias via starvation in a small diameter (2.5 cm) drillhole in sandy soil. This is encouraging because this is consistent with expectations based on mathematical modeling in Chapter 5, 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 low bias attributable to the starvation effect.

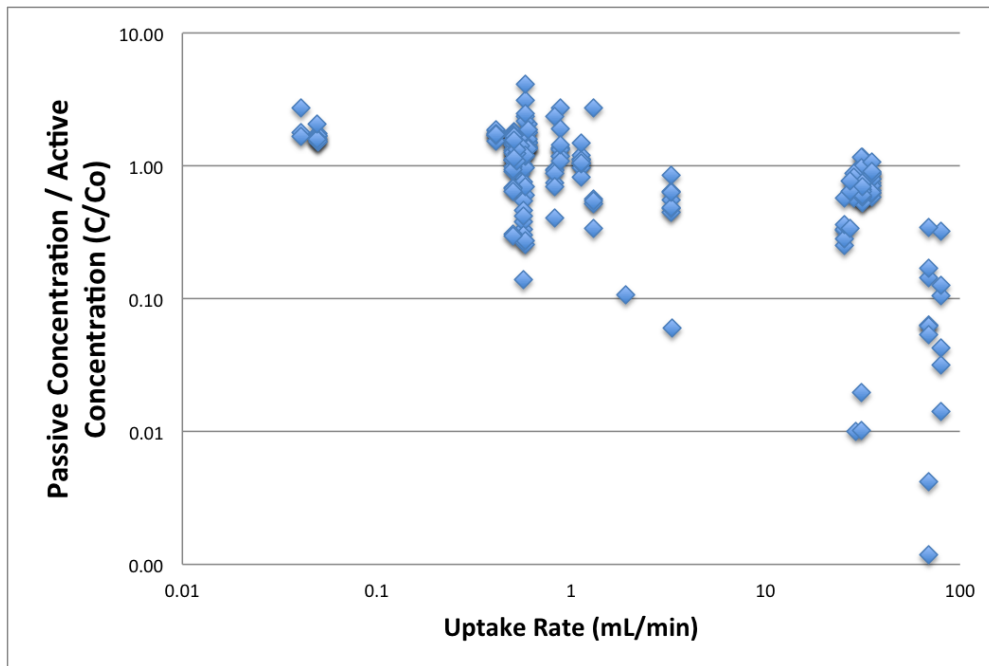


**Figure 7-6:** Relative concentration (passive/Summa canister) for WMS/low-uptake sampler in temporary open holes at NAS JAX

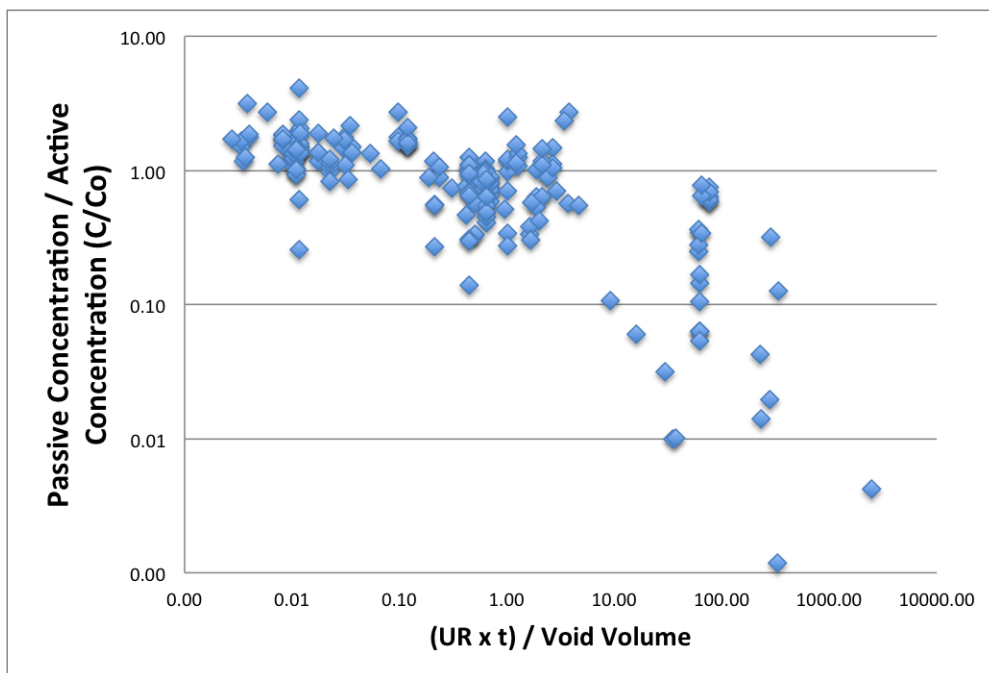
The data presented from the soil vapor field sampling experiments provide previously unavailable insight into the capabilities and limitations of passive soil vapor sampling. Three potential challenges were identified:

- 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 negative 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 7-7 shows the relative concentration ( $C/C_0$  passive concentration / active sample concentration) as a function of the uptake rate. Starvation was generally minimal for samplers with uptake rates of about 1 mL/min or less. Some samplers with higher uptake rates showed good accuracy, which was related to the probe design.
- **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 7-8 shows the relative concentration as a function of the ratio of the effective sample volume ( $UR \times t$ ) 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.,  $UR \times t/\text{void volume} < 1$ ), as shown in Figure 7-8. In these cases, the mass of vapors in the void-space was not sufficient to supply the mass to the passive sampler needed to negate the starvation effect unless vapors continued to diffuse into the void-space from the surrounding soil during the sample period. Diffusion through soil is much slower than diffusion through the air inside the void space and can be very slow in wet soil (see Chapter 5). This challenge can be avoided by designing a void space with a volume larger than the product of UR and t and purging after placement of the passive sampler, by using low-uptake rate samplers that would not induce starvation even if the void-space was small, or by using short sample duration provided the vapor concentrations are high enough to obtain detectable results.



**Figure 7-7:** Relative concentration (passive/active) versus uptake rate for soil gas sampling



**Figure 7-8:** Relative concentration (passive/active) versus equivalent sample volume/void volume

### 7.3 Summary

The passive soil gas concentrations determined using samplers with low uptake rates, strong adsorbents and  $UR \times t$  values similar to or less than the void volume showed better quantification of soil vapor concentrations in comparison to active sampler results than any previously published comparisons (see for example the comparison between Figures 7-4 and 7-5 versus Figure 1-24). This represents a breakthrough for passive soil vapor sampling that has not been accomplished in the 28 years since the earliest applications of the technology.<sup>140</sup>

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 and 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.

## 8 Passive Samplers in a Flow-Through Cell

The use of passive samplers in a flow-through cell<sup>viii</sup> offers potential benefits 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 perform sub-slab vapor concentration measurements over a period of days while drawing a large volume of gas (thousands or tens of thousands of liters), which would 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 results in 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.<sup>225</sup> 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 by diffusion. For example, outdoor sampling programs often need some form of shroud for protection from wind and rain, but a flow-through cell could 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 Chapter is to demonstrate the accuracy and precision of five commercially-available passive samplers in a flow-through cell for monitoring soil vapor compared to conventional sampling and analysis methods (Summa canister and EPA Method TO-15)<sup>6</sup> 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.

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<sup>viii</sup> The contents of this Chapter are based on the author’s article “Quantitative passive soil vapor monitoring for VOCs – part 4: flow-through cell”<sup>232</sup>

## 8.1 Experimental

The field sampling experiment was designed to assess the effect of the flow rate (from 100 to 1,000 mL/min) and sample duration (from 10 to 20 min) in the flow-through cell using a fractional factorial design with three replicates at the center-points, similar to the design used in Chapters 3 and 6.

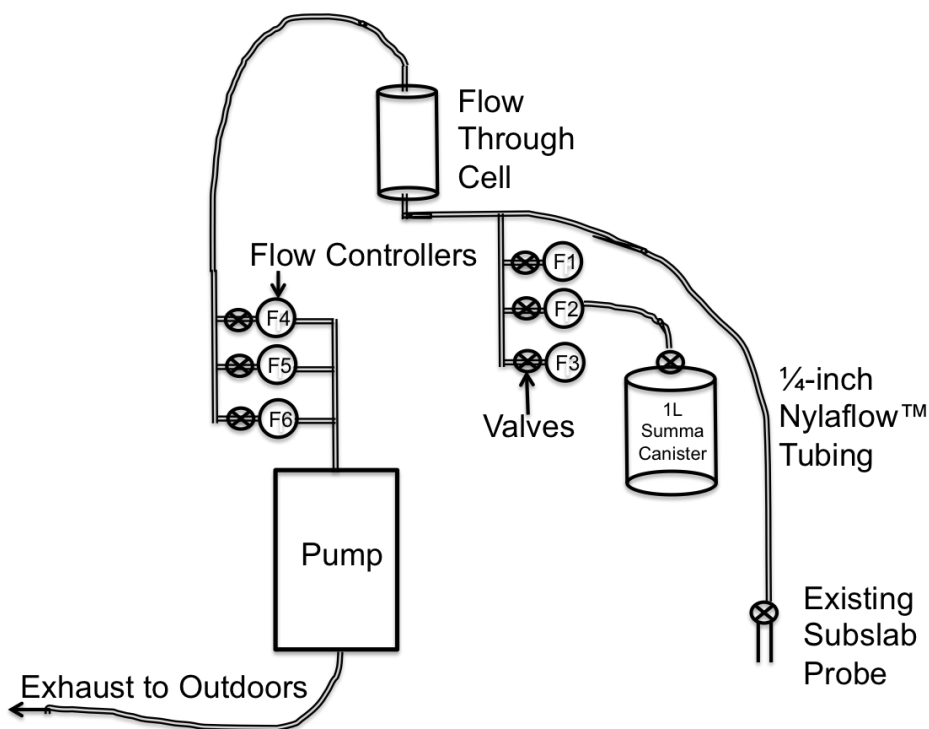
### 8.1.1 Sample Locations

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 shown in Figure 2-4, near the former ice well) showed TCE concentrations on the order of 100,000  $\mu\text{g}/\text{m}^3$ . 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 most of the candidate passive samplers, so direct deployment of the passive samplers in the subsurface would not be possible without installing a larger probe.

### 8.1.2 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 1H piston pump from Gast Manufacturing, Inc. of Benton Harbor, MI downstream of the flow-through cell, as shown in Figure 8-1. 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. 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 0.25 atm (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 8-1:** Experimental apparatus (schematic) for flow-through cell tests

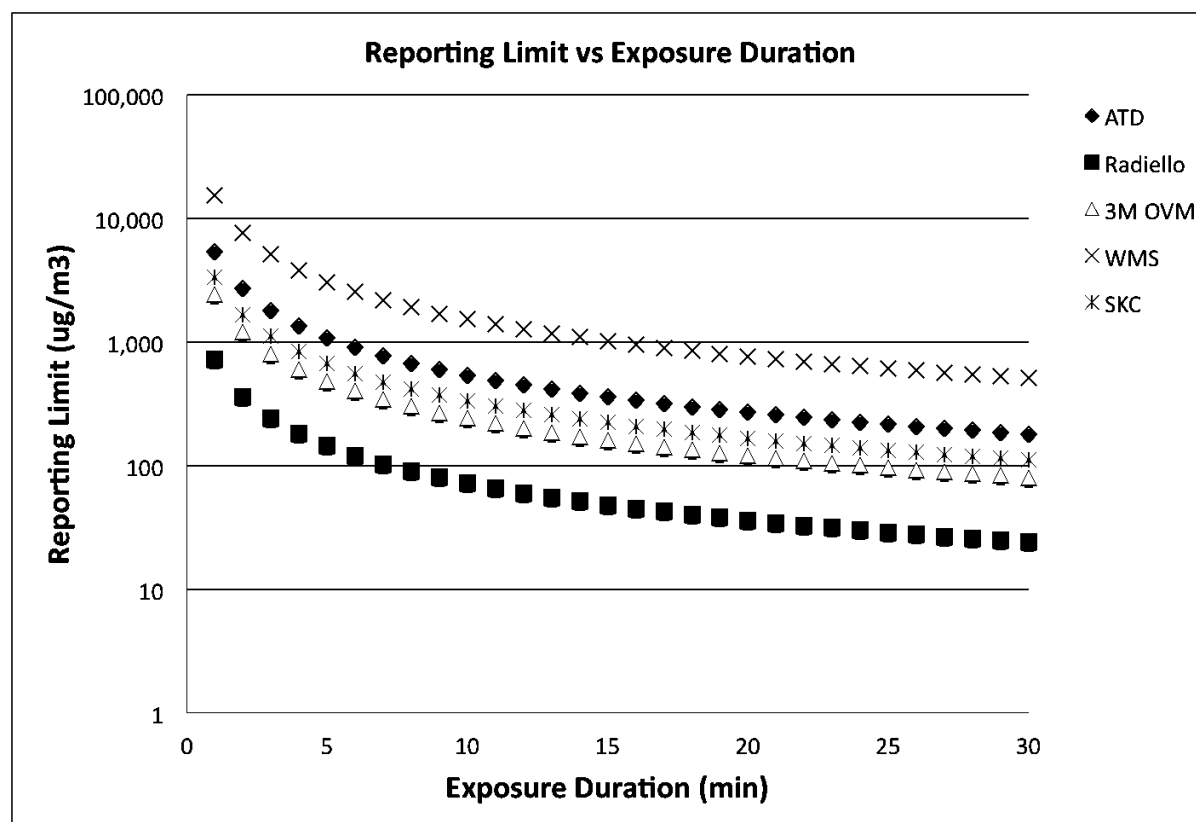
### 8.1.3 Sample Duration

The sample duration needed to quantify the TCE concentrations was calculated by rearranging Equation 1-5 to solve for  $t$  and using the laboratory reporting limit (in mass units) for  $M$ . Table 8-1 list the five passive samplers used in this study, the sorbent used, the lowest reportable mass (in units of ng) and the vendor-supplied TCE uptake rates (Table 3-2). The relationship between the analytical reporting limits (in units of  $\mu\text{g}/\text{m}^3$ ) calculated using Equation (1-5) and the sample duration is shown in Figure 8-2. In theory, all five passive samplers can achieve reporting limits lower than the expected concentration of TCE in sub-slab probe LB-01 ( $100,000 \mu\text{g}/\text{m}^3$ ) 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 poor retention and exceeding the linear range of the laboratory analytical instruments. 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 ( $\sim 100 \mu\text{g}/\text{m}^3$ )

within about 30 minutes, which is somewhat longer than typical sampling durations for Summa canisters (5 to 10 min),<sup>14</sup> but still within reason.

**Table 8-1:** 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)



**Figure 8-2:** Reporting limit as a function of sample duration for the passive samplers used in the flow-through cell

#### 8.1.4 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) and span about an order of magnitude range (100 to 1,000 mL/min). 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 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<sup>2</sup>, 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),<sup>183</sup> which further justifies the need for verification of the passive sampler performance under these specific conditions.

#### 8.1.5 Sampling Procedure

The sampling procedure consisted of placing one passive sampler in the cell, closing the cell as quickly as possible, drawing sub-slab gas through the cell at the allotted flow rate for the allotted sample duration and removing the passive sampler and replacing with the next sampler to be tested as quickly as possible to minimize the exchange of indoor air with the soil gas in the flow-through cell. Each of the passive samplers was deployed seven times: at all four combinations of high and low levels of sample duration and flow rate, as well as three replicates of the mid-points of the flow rate and sample duration. The order of deployment (sampler type, sample duration and flow rate) was randomized. The faces of the SKC Ultra and OVM3500 samplers were parallel to flow in the cell. The ATD tube and WMS samplers were deployed facing down, toward the influent. The Radiello was deployed with the long axis vertical in alignment with flow. Trip blanks were included for each passive sampler type (no VOCs were detected).

One batch-certified, 1L Summa canister sample was collected along with each passive sample (35 canisters total). One canister showed a notably low concentration (12,000 µg/m<sup>3</sup>), and was considered likely to have had an un-noticed leak at the fitting to the flow controller. In addition, one canister valve was inadvertently left closed during the sample period. In these two cases, the Summa canister concentrations used for calculating relative concentrations (passive/Summa) were the average TCE

concentration from the two Summa canister samples collected in the preceding and following sample intervals. These values are flagged in Table 8-2 with a “#” sign.

The Summa canister samples were analyzed by USEPA Method TO-15<sup>6</sup> open scan at Columbia Analytical Services (CAS) of Simi Valley, CA. All the passive samplers were analyzed by GC/MS according to the protocols provided in Appendix A. The ATD tubes were analyzed by Air Toxics Limited (ATL) of Folsom, CA. The WMS samplers were analyzed by at the University of Waterloo, Ontario Canada. The Radiello samplers were analyzed at the Fondazione Salvatore Maurgeri in Padova, Italy. The SKC samplers were analyzed at CAS. For the short-duration and low flow rate conditions, the SKC samplers were used with Carbograph 5 for improved sensitivity. The Carbograph 5 sorbent was transferred into an ATD tube, and analyzed by thermal desorption using EPA Method TO-17 by CAS.

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.

## 8.2 Results

PID readings of soil vapor drawn from sub-slab probe LB-01 were 25 ppm<sub>v</sub> the night before testing (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 ppm<sub>v</sub>, 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 ppm<sub>v</sub> corresponds to a TCE concentration of about 80,000 µg/m<sup>3</sup> (PID response factor = 0.62, 1 ppm<sub>v</sub> = 5,400 µg/m<sup>3</sup>), which was consistent with expectations from previous sampling.

Active (Summa canister) soil gas samples (Figure 8-3a and Table 8-2) had TCE concentrations ranging from 20,000 (one outlier excepted) to 55,000 µg/m<sup>3</sup>, with a mean of 38,650 µg/m<sup>3</sup> and a relative standard deviation (RSD) of 0.19. The average Summa canister concentration was 38,200 µg/m<sup>3</sup> on November 9 and 39,200 µg/m<sup>3</sup> on November 10, which indicates similar conditions over the two days of testing.

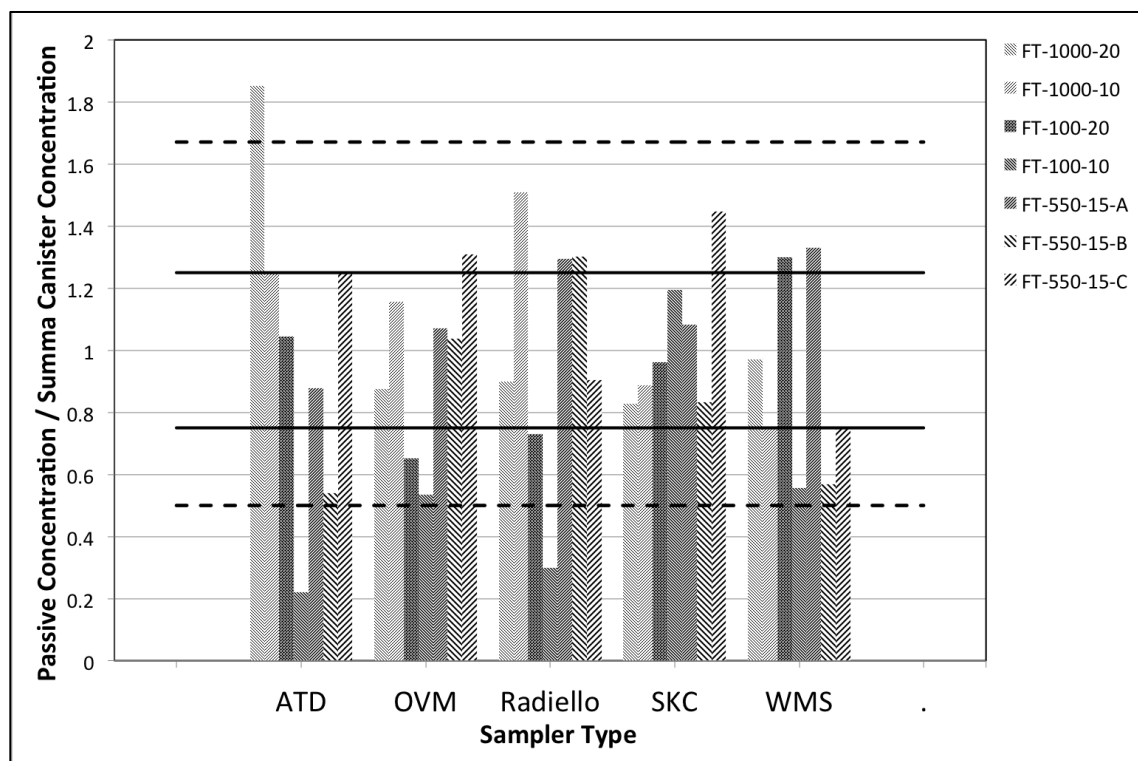
Individual Summa canister samples showed differences of up to 20,000 µg/m<sup>3</sup> from one sample to the next, which is a higher degree of variability than expected from experience with similar extended purging studies.<sup>226</sup> The passive samplers (Figure 8-3b) had similar TCE concentrations to the Summa canisters.

**Table 8-2:** 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)	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $C/C_0$ )	(%)
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	<b>35,500#</b>	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	<b>32,500#</b>	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					

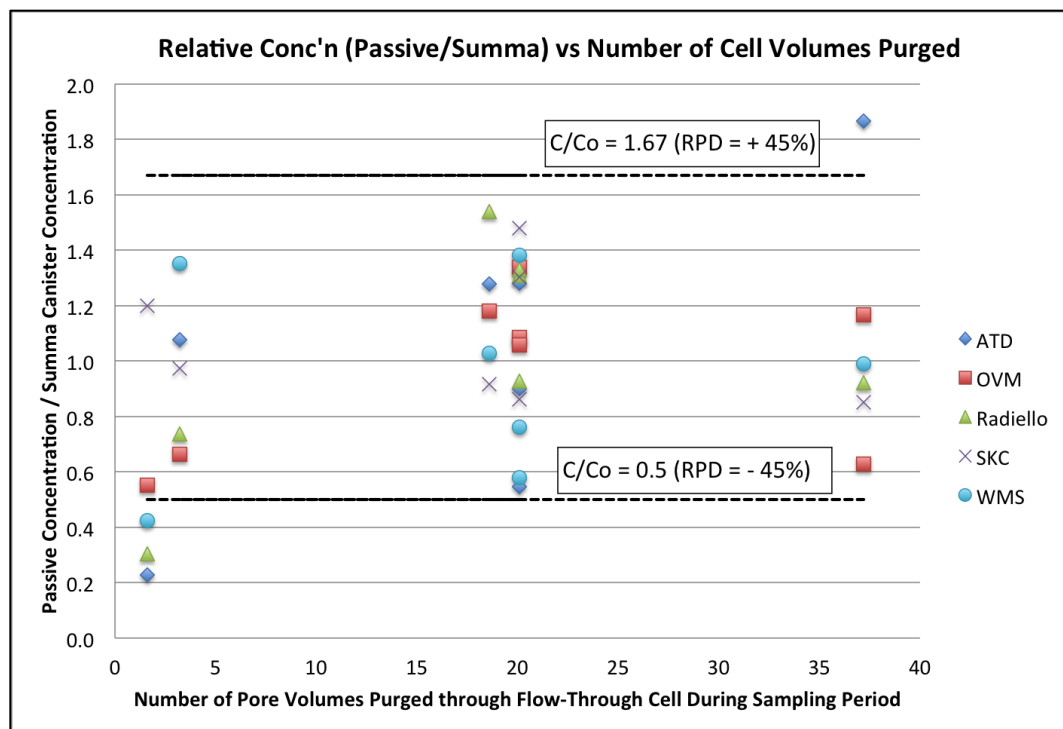


The passive sampler TCE concentrations divided by the coincident Summa canister TCE concentrations are plotted as relative concentrations ( $C/C_0$ ) in Figure 8-4. The legend numbers are the flow rate in mL/min (first) and the exposure duration in minutes (second). The low flow rate and short sample duration (nominal 100 mL/min for 10 min) showed negative bias for all the passive samplers (except the SKC), which was likely attributable to insufficient purging of the cell during the sampling interval. The relative concentration and bias between the passive sampler and the Summa canister results are presented in Table 8-2. The bias was less than 50% in 31 of 36 cases, which is considered acceptable considering the potential for inter-laboratory variability. 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 in addition to diffusion. Considering the Summa canisters showed concentration changes of up to 20,000  $\mu\text{g}/\text{m}^3$  in successive samples in some instances, the variability and bias in the  $C/C_0$  values cannot be attributed entirely to the passive samplers.



**Figure 8-4:** Relative TCE concentration ( $C/C_0$ ) for passive samplers in the flow-through cell

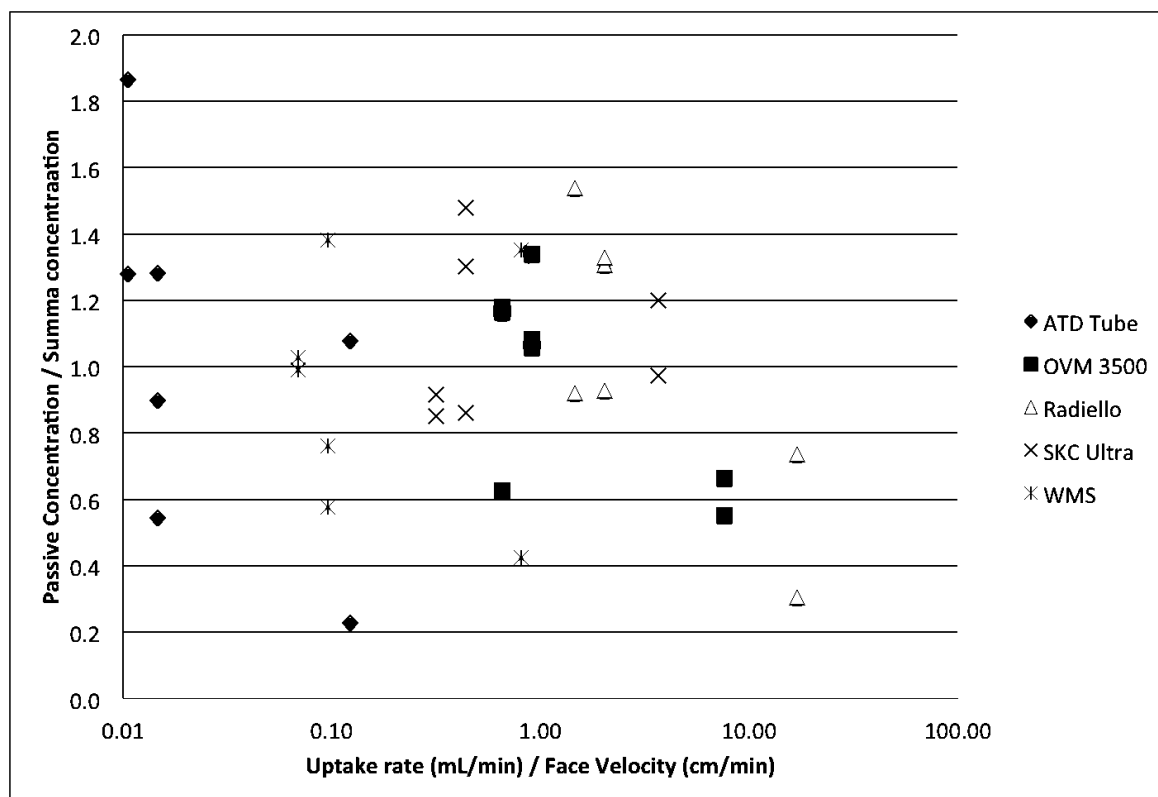
To further explore the root cause of the negative bias in the low flow rate and short duration samples, the results were plotted as relative concentrations (passive/Summa) versus the number of volumes purged through the cell within the sample duration (Figure 8-5). The number of volumes purged was calculated 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 low bias for all but one of the samplers (SKC). The low bias was 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 might 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 was 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 during sampling.



**Figure 8-5:** Relative concentration of TCE versus number of cell volumes purged through the flow-through cell during the sample period



Passive samplers can show 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 8-6). 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 was no indication of a starvation effect for the majority of the data collected.



**Figure 8-6:** Relative concentration of TCE versus uptake rate divided by face velocity

A three-way analysis of variance (ANOVA) was performed on the concentration values using sampler type, flow rate and sample duration as the three factors of interest (Table 8-3). 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 barrier or membrane between the sorbent inside the sampler and the medium being monitored, and therefore, may be more susceptible to positive bias in the uptake rate via convection or turbulence at higher flow rates.

**Table 8-3:** Results of ANOVA analysis of flow-through cell test results

Source	Degrees of Freedom	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	Degrees of Freedom	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	<b>0.0014</b>
Sample duration	1	45255510	45255510	0.46	0.4987

Table 8-4 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 8-4 also shows the mean of all seven  $C/C_0$  values calculated for each sampler. It ranged from 0.93 to 1.08, which indicates that on average, the passive sampler result would be expected to be very similar to the Summa canister/TO-15 result. The difference between the results obtained with the passive samplers versus the Summa canisters was calculated as a bias (absolute value of the difference between the two values divided by the Summa canister concentration, expressed as a percentage) and the mean value of all seven bias measurements for each sampler is included in the far right column of Table 8-4. The bias ranged from 20% to 40% (some of which again might be attributable to variability in the Summa canister data and inter-laboratory variability).

**Table 8-4:** Summary statistics for all sampler types

	<b>Mean Passive TCE Concentration</b>	<b>Relative Standard Deviation</b>	<b>Mean Summa TCE Concentration</b>	<b>Relative Standard Deviation</b>	<b>Mean of seven C/C<sub>0</sub> values</b>	<b>Mean Bias</b>
<b>Sampler</b>	( $\mu\text{g}/\text{m}^3$ )	(%)	( $\mu\text{g}/\text{m}^3$ )	(%)		(%)
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

### 8.3 Summary

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 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 by 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 negative 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 by 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 positive bias at the high flow rate (960 mL/min), which might 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 slight negative biases at the low flow rate, which might be attributable to the starvation effect because these samplers had the highest uptake rates of 31 and 69 mL/min, respectively. This can be managed by selecting a higher flow rate, or using a smaller diameter flow-through cell (velocity is inversely proportional to cross-sectional area for a given flow rate).

Further testing would be appropriate to assess the performance of other chemicals, different ranges of concentrations and longer sample durations. Comparison testing by conventional active sampling is recommended for applications of this approach until the capabilities and limitations are more fully understood.

## 9 Discussion

This Chapter summarizes the results of the research in terms of the performance criteria in Table 2-1<sup>ix</sup>.

### 9.1 Overall Performance

The data for each sampler type for indoor air, outdoor air, sub-slab gas, and/or soil gas from all five field sites were compiled to evaluate the overall performance. These plots (Figure 9-1) exclude the results with easily explained biases, specifically:

- The passive sub-slab samples from OTC were collected before the Study Team understood the importance of using low uptake rates and strong sorbents and all showed negative bias, so they were not included in Figure 57.
- Results for which the equivalent sample volume was much larger than the recommended maximum sample volume showed low bias attributable to poor retention, so they were not included either. This applies to the dichlorinated ethenes and ethanes in indoor air at Cherry point for the Radiello and WMS samplers, the ATD tube with Tenax in soil gas samples at Hill AFB and the ATD with Carbo-pack B for 11DCE only in soil gas samples at Hill AFB, and the cDCE results for indoor air at OTC3 with the SKC,
- Results for which the uptake rate was higher than the expected diffusive delivery rate from the surrounding soil showed a negative bias attributable to starvation and were also not included. This applied to the Radiello sampler at Hill AFB.

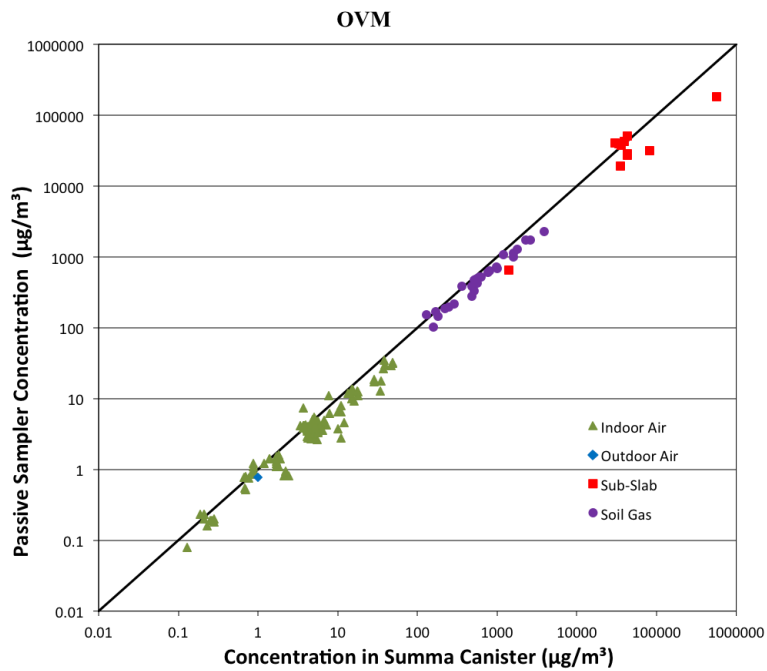
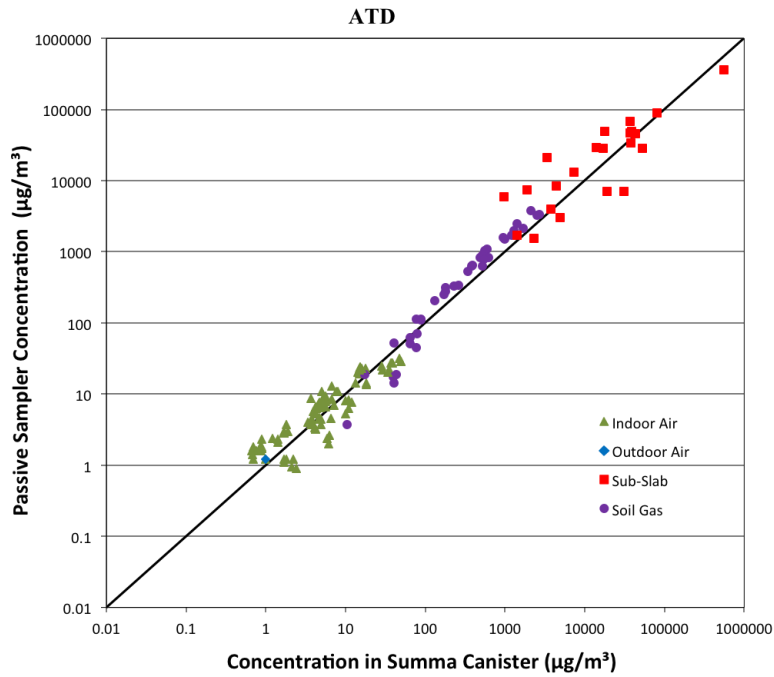
There are some outliers in the correlation, which may be attributable to individual compounds for which the uptake rate for a particular sampler may be poorly known or calculated, so there are opportunities for improved data quality over time as more studies are conducted and the uptake rates become supported with more data.

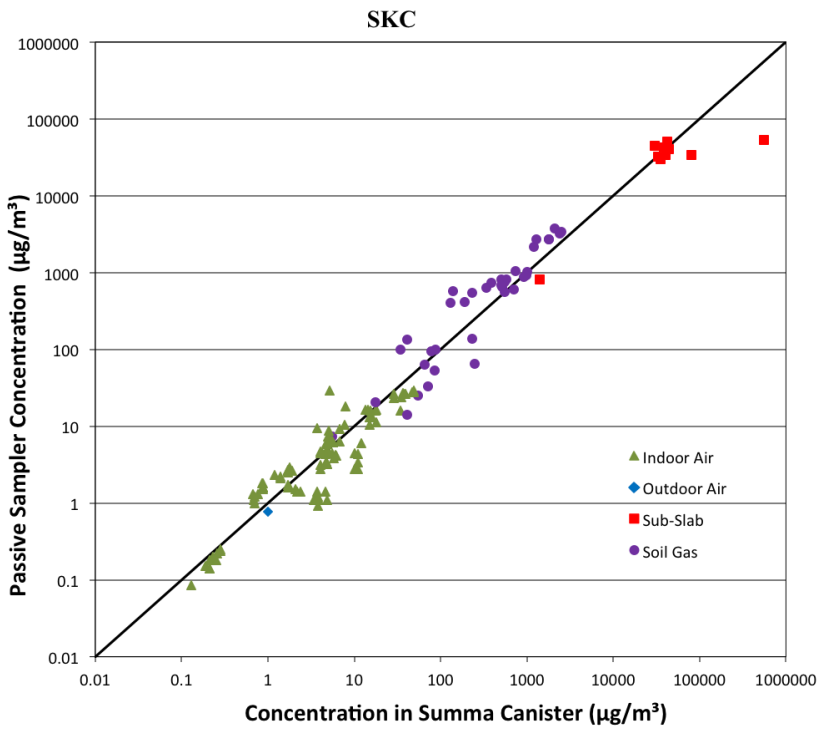
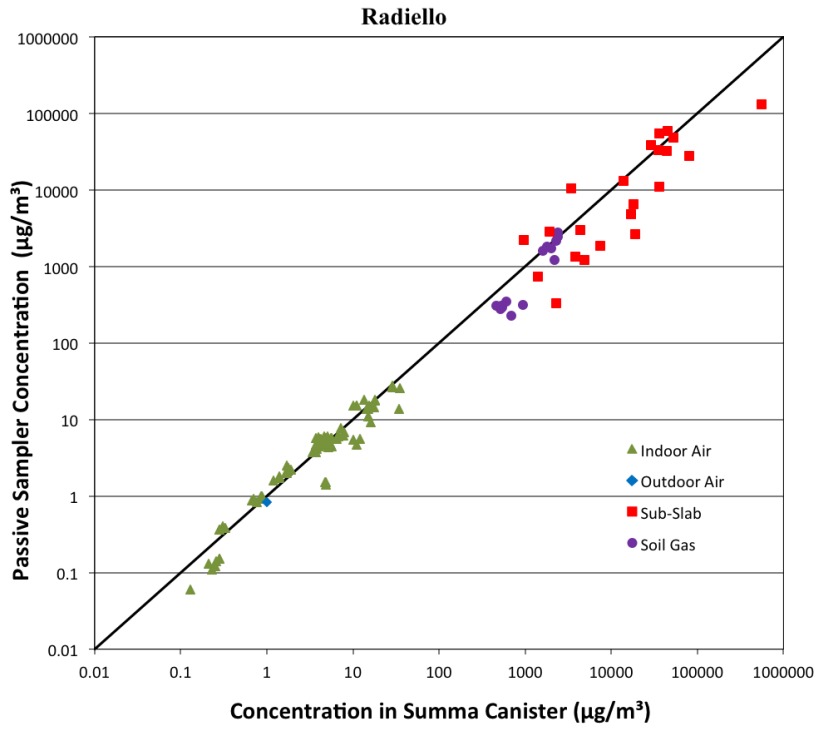
The passive samplers showed precision comparable to or better than conventional Summa canister samples for a given set of conditions, but more sensitivity to changes in the conditions. The precision also varied by compound. For example, NAPH and 124TMB are highly sorptive compounds, which can lead to issues with competitive sorption or poor recovery; whereas 12DCA is weakly sorbed, which can lead to

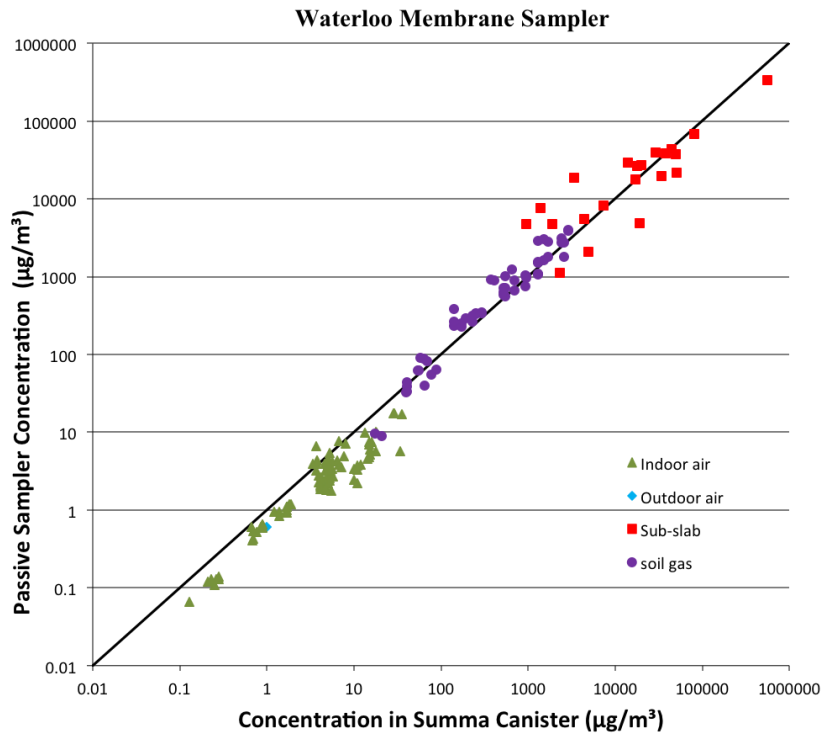
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<sup>ix</sup> This Chapter is based partly on the author's final report to ESTCP<sup>3</sup>

losses in long duration samples with weaker sorbents. MEK was challenging for the less hydrophobic sorbents, apparently because of competition for sorptive sites by water molecules.







**Figure 9-1:** Correlations for all passive samplers vs. active samples in the field demonstrations

## 9.2 Ease of Use

Passive sampling requires some care to select the most appropriate sampler, sorbent, sample duration and method of analysis (solvent extraction vs. thermal desorption) prior to use. The uptake rates should preferably be known for all the target analytes, and this may not be the case for all passive samplers, so it may be necessary to estimate the uptake rates from comparison of diffusion coefficients or permeation constants. The sample duration must be long enough to result in a reporting limit lower than an appropriate target concentration to meet data quality objectives. Where the product of the uptake rate multiplied by the sample duration is greater than the recommended maximum sample volume, it may be appropriate to consider using a stronger adsorbent, or be aware that there may be negative bias from poor retention for the compounds with the lowest recommended maximum sample volumes. A trip blank should be included with each shipment of passive samplers, which is not necessary with Summa canisters because the potential for canister contamination during shipment can be tested with canister vacuum measurements in the field and laboratory before and after shipment in each direction.



Each of the passive samplers has aspects that result in slight differences in their ease of use relative to one another. The ease of use of each of the samplers for indoor air, outdoor air and soil gas sampling is described below, along with any differences or challenges that might influence the selection of one sampler over another.

### **9.2.1 3M OVM 3500**

The 3M OVM 3500 comes in a container that is easily opened and the initiation of sampling is nearly effortless and immediate. At the end of the sample period, the porous plastic cap must be pried off and replaced with a solid plastic cap, which requires a certain amount of force and may be a challenge for individuals with low grip strength. The OVM3500 is also the largest diameter sampler and has only a high uptake rate variety, so it is not well-suited to soil gas or sub-slab sampling because of the extra effort to create a large diameter hole and the increased risk of low bias from the starvation effect. The sorbent (charcoal) retains water much more than some other sorbents, so the 3M OVM 3500 may not be the best selection for sampling in high humidity environments, especially for highly soluble compounds. The high uptake rate is beneficial for outdoor air sampling, but detrimental for soil vapor sampling.

### **9.2.2 Radiello**

The Radiello requires some assembly because the sorbent medium comes separately packaged from the white or yellow body in which it resides during deployment. The operator must be aware that the cylinder of stainless steel mesh should be carefully handled to minimize contamination with skin oil, perfumes, moisturizer, sun-screen, or other potential contaminants. The Radiello requires a shield for outdoor air sampling to protect against wind and rain. The high uptake rate is beneficial for outdoor air sampling, but detrimental for soil vapor sampling.

### **9.2.3 Waterloo Membrane Sampler**

The WMS sampler is easily opened and the initiation of sampling is straightforward. Both the 1.8 mL and 0.8 mL vial sizes are very small and therefore discrete, easy to ship and handle and fit in small diameter holes for soil gas and sub-slab sampling. The operator must be aware not to touch the membrane to avoid contamination, but the membrane is small relative to the rest of the sampler, so this is easily accomplished. The sampler is resistant to water and wind, so protection is not specifically needed for outdoor applications. The sampling rate is low enough for soil vapor sampling with minimal bias attributable to starvation, but this may require long sample duration to achieve adequate sensitivity for outdoor air sampling. High Koc compounds (like NAPH) may require field calibrated uptake rates. The

thermal desorption variety of the WMS sampler requires transfer of the sorbent from the sampler to an ATD tube prior to analysis, which creates a potential for positive bias from compounds adsorbed during transfer or negative bias from sorbent losses during transfer, or desorption of weakly-held compounds during the transfer process.

#### **9.2.4 SKC Ultra and Ultra II**

The SKC Ultra comes pre-loaded with the sorbent media and is simple to use; however, the Ultra II requires the user to transfer the sorbent into the housing at the start of the sampling event, and transfer the sorbent back into the shipping vial at the end; the laboratory then needs to transfer the sorbent into an ATD tube prior to analysis. The additional sorbent transfer steps for the Ultra II creates a potential for positive bias from compounds adsorbed during transfer or negative bias from sorbent losses during transfer, or desorption of weakly-held compounds during the transfer process.

#### **9.2.5 ATD Tubes**

This is the only sampler tested with no membrane or porous plastic barrier to reduce the risk of high bias from turbulent uptake in high face velocity environments, so protection from wind and rain would be appropriate in outdoor sampling. The cost of the tube and fittings is higher than the other passive samplers, so there is a greater risk of loss via theft in outdoor air sampling and security would be prudent. The number of different sorbents available and their influence on the uptake rate for the ATD tube sampler creates a higher level of complexity in the design stage compared to the solvent extraction samplers. The ATD tube samplers have a long history of use and an impressive breadth of published data, which can be used to support their application.

#### **9.2.6 Comparison to Summa Canisters (TO-15)**

Indoor air sampling is slightly more complex with Summa canisters because the canister vacuum must be measured before and after sample collection, the vacuum gauge and flow controller must be attached and detached using compression fitting and wrenches, and the canisters cannot be hung from a thread, they are heavy and generally need to be supported by some piece of furniture (which is not always readily available). Furthermore, long-term time-weighted average sampling (longer than a few days) is challenging.

Sub-slab and soil gas sampling is substantially more complex with Summa canisters because the permeability of the geologic material is often unknown in advance and can vary over 10 or more orders of

magnitude. As a result, the applied vacuum required to sustain the flow-rate of the flow controller (which is usually set in advance and seldom adjusted in the field) is also unknown. If the geologic material has low permeability, a small leak in the probe seal or any of the (usually multiple) fittings can contribute a significant fraction of the total sample drawn by the canister. Tracer tests are often used or required to verify whether any such leak is significant, which involves extra equipment (e.g., shroud, helium cylinder, helium meter, vacuum chamber and pump) and several additional procedural steps, all of which require training and practice to perform with minimal operator bias or error. With passive samplers, the primary process is diffusion, not advection, so leaks and leak testing are not necessary.

### **9.2.7 Comparison to Pumped ATD Tubes (TO-17)**

Active sampling with pumped ATD tubes includes many of the same initial design considerations as passive samplers (sorbent selection, flow rate, sample duration), with the additional consideration of using multiple sorbents in series and a second ATD tube in series to assess the potential for breakthrough. The pumps have a limited battery life (usually 24 hours or less), so it may be necessary to plug them into an electrical socket, which is not always readily available. In dusty environments, the dust may accumulate and impose resistance to flow that could change the flow rate and make it difficult to estimate the total volume of gas drawn through the ATD tube. Therefore, passive samplers are considered to be easier to use than pumped ATD tubes and better suited to long-term passive sampling.

## **9.3 Cost Assessment**

The cost of implementing a site investigation and monitoring using passive samplers was evaluated for three different site investigation scenarios of different scale. The cost drivers for the application of passive samplers were evaluated based on the three scenarios.

### **9.3.1 Cost Model and Cost Analysis**

A cost model was developed to assist remediation professionals in understanding costs associated with passive sampling versus active sampling. The cost model is easiest to understand when compared to active sampling. The cost model identified the major cost elements required to implement passive sampling under three different scenarios:

Scenario 1 – collection of seven (7) sub-slab soil gas samples, seven (7) indoor air samples, and two (2) outdoor air samples at a single building (Table 9-1);

Scenario 2 –collection of fifty (50) sub-slab soil gas samples, fifty (50) indoor air samples, and twelve (12) outdoor air samples at several large buildings (Table 9-2); and

Scenario 3 – a contaminated groundwater plume is migrating beneath a residential community adjacent to a DoD facility. Soil gas probes are installed and sampled to map the subsurface vapor distribution (approximately 100 samples) and the indoor and sub-slab samples are collected in buildings over the areas of elevated soil vapor concentrations (approximately 50 each). Two rounds of sampling are conducted to assess seasonal variations. This scenario assumes that the building occupants are cooperative and willing to watch the passive sampling collection procedures during the first sampling event and deploy their own indoor air and outdoor air samples during the second sampling event (much as is the case with many radon samplers in domestic applications) (Table 9-3).

The cost of using passive samplers in the above scenarios is similar to or less than the cost of using active samplers, as shown in Tables 9-1, 9-2 and 9-3. The costs are similar to conventional methods for small sampling programs because there is an initial effort required to select the appropriate sampler, sorbent and sample duration for a given list of target chemicals and desired reporting limits (this is a “one-time” cost for a given site and set of data quality objectives, and may be trivial if there is only one or a few dominant compounds of interest). For larger sampling programs, the initial effort is more than compensated by the reduced labor costs for sample deployment and reduced shipping costs. Actual costs will depend on the quoted costs of analyses of individual laboratories. Summa canister/TO-15 laboratory fees have decreased in the past few years with increasing competition, and this may occur with passive samplers as the demand increases.

**Table 9-1: Cost Comparison for Scenario 1**

**Scenario 1**

The first cost scenario consists of the collection of seven sub-slab soil gas samples (6 samples and 1 duplicate), seven (7) indoor air samples (6 samples and 1 duplicate), and two (2) outdoor air samples at a single building. The cost comparison between the five passive and one active sampler types are provided below.

Item	Unit Cost	Unit	Number of Units		Conventional Summa/TO-15		WMS		Radiello		ATD		OVM		SKC	
			Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab
<b>LABOR COSTS</b>																
<b>Active (Conventional Summa/TO-15)</b>																
Laboratory coordination, planning	\$125	/hour	2	2	\$250	\$250										
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	4		\$340											
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		9		\$765										
Soil gas sample collection (deployment and retrieval)	\$85	/hour														
<b>Passive</b>																
Laboratory coordination, planning	\$125	/hour	4	4			\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	4				\$340		\$340		\$340		\$340		\$340	
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		3				\$255		\$255		\$255		\$255		\$255
Soil gas sample collection (deployment and retrieval)	\$85	/hour														
<b>LABORATORY COSTS*</b>																
1 Liter Summa Canister (Batch Certified for soil gas/sub-slab)	\$20	/each		8		\$160										
Flow Controller (100 mL/min for soil gas/sub-slab)	\$15	/each		8		\$120										
Modified EPA TO-15 (open scan for soil gas/subslab)	\$140	/each		8		\$1,120										
6 Liter Summa Canister (Individually Certified for indoor/outdoor air)	\$30	/each	9		\$270											
Flow controller (24 hr for indoor/outdoor air)	\$10	/each	9		\$90											
Modified EPA TO-15 SIM and scan (for indoor/outdoor air)	\$180	/each	9		\$1,620											
WMS™ Sampler	\$25	/each	10	8			\$0	\$200								
WMS™ Analysis (solvent extraction for soil gas/sub-slab)	\$150	/each		8				\$1,200								
WMS™ Analysis (thermal desorption for indoor/outdoor air)	\$200	/each	10				\$2,000									
Radiello Sampler	\$30	/each	10	8					\$300	\$240						
Radiello Analysis (modified EPA TO-17)	\$150	/each	10	8					\$1,500	\$1,200						
ATD Tube	\$30	/each	10	8							\$300	\$240				
ATD Tube Analysis (modified EPA TO-17)	\$200	/each	10	8							\$2,000	\$1,600				
3M OVM 3500 Badge	\$20	/each	10	8									\$200	\$160		
3M OVM 3500 Badge Analysis	\$150	/each	10	8									\$1,500	\$1,200		
SKC Ultra II Sampler	\$75	/each	10	8											\$750	\$600
SKC Ultra II Sampler Analysis (modified EPA TO-17)	\$200	/each	10	8											\$2,000	\$1,600
<b>EXPENSES</b>																
Federal Express (Standard Overnight) - 16 Summa canisters (6L)	\$950	/shipment	9		\$534											
Federal Express (Standard Overnight) - 16 Summa canisters (1L)	\$238	/shipment		8		\$119										
Federal Express (Standard Overnight) - 16 passive samplers	\$60	/shipment	10	8			\$38	\$30	\$38	\$30	\$38	\$30	\$38	\$30	\$38	\$30
Concrete coring contractor (SKC and OVM only)	\$500	/day		1									\$500		\$500	
Hammer drill (conventional Summa, WMS, Radiello and ATD only)	\$200	/week		1		\$200		\$200		\$200		\$200				
Helium detector	\$350	/week		1		\$350										
Helium cylinder	\$150	/each		1		\$150										
Sub-slab probe parts (stainless steel) (conventional Summa sampling)	\$25	/each		6		\$150										
1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling)	\$1	/each		6				\$6		\$6		\$6		\$6		\$6
Soil gas probe materials (passive)	\$25	/each														
Soil gas probe materials (active)	\$50	/each														
Subtotal					\$3,104	\$3,384	\$2,878	\$2,391	\$2,678	\$2,431	\$3,178	\$2,831	\$2,578	\$2,651	\$3,628	\$3,491
<b>TOTAL</b>					<b>\$6,488</b>		<b>\$5,269</b>		<b>\$5,109</b>		<b>\$6,009</b>		<b>\$5,229</b>		<b>\$7,119</b>	

**Notes:**

\*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

**Table 9-2: Cost comparison for Scenario 2**

**Scenario 2**

The second cost scenario consists of the collection of fifty (45 samples and 5 duplicates) sub-slab soil gas samples, fifty indoor air samples (45 samples and 5 duplicates), and twelve outdoor air samples (11 samples and 1 duplicate) at several large buildings. The cost comparison between the five passive and one active sampler types are provided below.

Item	Unit Cost	Unit	Number of Units		Conventional Summa/TO-15		WMS		Radiello		ATD		OVM		SKC	
			Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab
<b>LABOR COSTS</b>																
<b>Active (Conventional Summa/TO-15)</b>																
Laboratory coordination, planning	\$125	/hour	2	2	\$250	\$250										
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	29		\$2,465											
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		75		\$6,375										
Soil gas sample collection (deployment and retrieval)	\$85	/hour														
<b>Passive</b>																
Laboratory coordination, planning	\$125	/hour	4	4			\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	29				\$2,465		\$2,465		\$2,465		\$2,465		\$2,465	
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		25				\$2,125		\$2,125		\$2,125		\$2,125		\$2,125
Soil gas sample collection (deployment and retrieval)	\$85	/hour														
<b>LABORATORY COSTS*</b>																
1 Liter Summa Canister (Batch Certified for soil gas/sub-slab)	\$20	/each		50		\$1,000										
Flow Controller (100 mL/min for soil gas/sub-slab)	\$15	/each		50		\$750										
Modified EPA TO-15 (open scan for soil gas/subslab)	\$140	/each		50		\$7,000										
6 Liter Summa Canister (Individually Certified for indoor/outdoor air)	\$30	/each	62		\$1,860											
Flow controller (24 hr for indoor/outdoor air)	\$10	/each	62		\$620											
Modified EPA TO-15 SIM and scan (for indoor/outdoor air)	\$180	/each	62		\$11,160											
WMS™ Sampler	\$25	/each	63	51			\$0	\$1,275								
WMS™ Analysis (solvent extraction for soil gas/sub-slab)	\$150	/each		51				\$7,650								
WMS™ Analysis (thermal desorption for indoor/outdoor air)	\$200	/each	63				\$12,600									
Radiello Sampler	\$30	/each	63	51					\$1,890	\$1,530						
Radiello Analysis (modified EPA TO-17)	\$150	/each	63	51					\$9,450	\$7,650						
ATD Tube	\$30	/each	63	51							\$1,890	\$1,530				
ATD Tube Analysis (modified EPA TO-17)	\$200	/each	63	51							\$12,600	\$10,200				
3M OVM 3500 Badge	\$20	/each	63	51									\$1,260	\$1,020		
3M OVM 3500 Badge Analysis	\$150	/each	63	51									\$9,450	\$7,650		
SKC Ultra II Sampler	\$75	/each	63	51											\$4,725	\$3,825
SKC Ultra II Sampler Analysis (modified EPA TO-17)	\$200	/each	63	51											\$12,600	\$10,200
<b>EXPENSES</b>																
Federal Express (Standard Overnight) - 16 Summa canisters (6L)	\$950	/shipment	62		\$3,681											
Federal Express (Standard Overnight) - 16 Summa canisters (1L)	\$238	/shipment		50		\$742										
Federal Express (Standard Overnight) - 16 passive samplers	\$60	/shipment	63	51			\$236	\$191	\$236	\$191	\$236	\$191	\$236	\$191	\$236	\$191
Concrete coring contractor (SKC and OVM only)	\$500	/day		2										\$1,000		\$1,000
Hammer drill (conventional Summa, WMS, Radiello and ATD only)	\$200	/week		2		\$400		\$400		\$400		\$400				
Helium detector	\$350	/week		2		\$700										
Helium cylinder	\$150	/each		7		\$1,050										
Sub-slab probe parts (stainless steel) (conventional Summa sampling)	\$25	/each		50		\$1,250										
1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling)	\$1	/each		50				\$50		\$50		\$50		\$50		\$50
Soil gas probe materials (passive)	\$25	/each														
Soil gas probe materials (active)	\$50	/each														
Subtotal					\$20,036	\$19,517	\$15,801	\$12,191	\$14,541	\$12,446	\$17,691	\$14,996	\$13,911	\$12,536	\$20,526	\$17,891
<b>TOTAL</b>					<b>\$39,553</b>		<b>\$27,993</b>		<b>\$26,988</b>		<b>\$32,688</b>		<b>\$26,448</b>		<b>\$38,418</b>	

**Notes:**

\*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

**Table 9-3: Cost comparison for Scenario 3**

**Scenario 3**

The third cost scenario represents a site with a contaminated groundwater plume migrating beneath a residential community adjacent to a DOD facility. Soil gas probes are installed and sampled to map the subsurface vapor distribution (approximately 100 samples) and the indoor and sub-slab samples are collected in buildings over the areas of elevated soil gas concentrations (approximately 50 each). Two rounds of sampling are conducted to assess seasonal variations. This scenario assumes that the building occupants are cooperative and willing to watch the passive sampling collection procedures during the first sampling event and deploy their own indoor air and outdoor air samples during the second sampling event (much as is the case with many radon samplers in domestic applications). The cost comparison between the five passive and one active sampler types are provided below.

Item	Unit Cost	Unit	Number of Units		Conventional Summa/TO-15		WMS		Radiello		ATD		OVM		SKC	
			Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab	Indoor & Outdoor	Sub-slab
<b>LABOR COSTS</b>																
<b>Active (Conventional Summa/TO-15)</b>																
Laboratory coordination, planning	\$125	/hour	2	2	\$250	\$250										
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	50		\$4,250											
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		150		\$12,750										
Soil gas sample collection (deployment and retrieval)	\$85	/hour		450		\$38,250										
<b>Passive</b>																
Laboratory coordination, planning	\$125	/hour	4	4			\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500	\$500
Indoor and outdoor sample collection (deployment and retrieval)	\$85	/hour	35				\$2,975		\$2,975		\$2,975		\$2,975		\$2,975	
Sub-slab sample collection (deployment and retrieval)	\$85	/hour		50				\$4,250		\$4,250		\$4,250		\$4,250		\$4,250
Soil gas sample collection (deployment and retrieval)	\$85	/hour		250				\$21,250		\$21,250		\$21,250		\$21,250		\$21,250
<b>LABORATORY COSTS*</b>																
1 Liter Summa Canister (Batch Certified for soil gas/sub-slab)	\$20	/each		300		\$6,000										
Flow Controller (100 mL/min for soil gas/sub-slab)	\$15	/each		300		\$4,500										
Modified EPA TO-15 (open scan for soil gas/subslab)	\$140	/each		300		\$42,000										
6 Liter Summa Canister (Individually Certified for indoor/outdoor air)	\$30	/each	100		\$3,000											
Flow controller (24 hr for indoor/outdoor air)	\$10	/each	100		\$1,000											
Modified EPA TO-15 SIM and scan (for indoor/outdoor air)	\$180	/each	100		\$18,000											
WMS™ Sampler	\$25	/each	100	300			\$0	\$7,500								
WMS™ Analysis (solvent extraction for soil gas/sub-slab)	\$150	/each		300				\$45,000								
WMS™ Analysis (thermal desorption for indoor/outdoor air)	\$200	/each	100				\$20,000									
Radiello Sampler	\$30	/each	100	300					\$3,000	\$9,000						
Radiello Analysis (modified EPA TO-17)	\$150	/each	100	300					\$15,000	\$45,000						
ATD Tube	\$30	/each	100	300							\$3,000	\$9,000				
ATD Tube Analysis (modified EPA TO-17)	\$200	/each	100	300							\$20,000	\$60,000				
3M OVM 3500 Badge	\$20	/each	100	300									\$2,000	\$6,000		
3M OVM 3500 Badge Analysis	\$150	/each	100	300									\$15,000	\$45,000		
SKC Ultra II Sampler	\$75	/each	100	300											\$7,500	\$22,500
SKC Ultra II Sampler Analysis (modified EPA TO-17)	\$200	/each	100	300											\$20,000	\$60,000
<b>EXPENSES</b>																
Federal Express (Standard Overnight) - 16 Summa canisters (6L)	\$950	/shipment	100		\$5,938											
Federal Express (Standard Overnight) - 16 Summa canisters (1L)	\$238	/shipment		300		\$4,453										
Federal Express (Standard Overnight) - 16 passive samplers	\$60	/shipment	100	300			\$375	\$1,125	\$375	\$1,125	\$375	\$1,125	\$375	\$1,125	\$375	\$1,125
Concrete coring contractor (SKC and OVM only)	\$500	/day		10										\$5,000		\$5,000
Hammer drill (conventional Summa, WMS, Radiello and ATD only)	\$200	/week		4		\$800		\$800		\$800		\$800				
Helium detector	\$350	/week		7		\$2,450										
Helium cylinder	\$150	/each		37		\$5,550										
Sub-slab probe parts (stainless steel) (conventional Summa sampling)	\$25	/each		50		\$1,250										
1 inch rubber stoppers, aluminum foil and Teflon tape (passive sampling)	\$1	/each		50				\$50		\$50		\$50		\$50		\$50
Soil gas probe materials (passive)	\$25	/each		100				\$2,500		\$2,500		\$2,500		\$2,500		\$2,500
Soil gas probe materials (active)	\$50	/each		100		\$5,000										
Subtotal					\$32,438	\$123,253	\$23,850	\$82,975	\$21,850	\$84,475	\$26,850	\$99,475	\$20,850	\$85,675	\$31,350	\$117,175
<b>TOTAL</b>					\$155,691		\$106,825		\$106,325		\$126,325		\$106,525		\$148,525	

**Notes:**

\*passive sampler laboratory analytical costs assume an analyte list of 20 compounds or less.

### 9.3.2 Cost Drivers

Passive samplers can reduce costs because the protocols for sampling are simpler, and as a result the costs of training and labor for field personnel are lower than in conventional sampling methods. The passive samplers are also smaller and lighter than Summa canisters, so shipping costs are lower. Passive samplers are capable of collecting samples over a longer period of time than conventional samplers, so fewer samples may be needed to provide data over a given period.

Passive samplers incur more effort in the initial design process because it takes time to select the best sampler, sorbent and sample duration for a given set of target chemicals and target reporting limits. This process can be automated to a significant degree, but should be reviewed by an experienced analytical chemist. Inter-method verification samples are a valuable quality assurance/quality control element that allows uptake rates to be derived or verified for site-specific field sampling conditions, which would add a small increment to the overall cost for sampling campaigns, but add a level of quality control and assurance where the highest level of accuracy is desired.

The cost differential between the various types of passive samplers is relatively small, so the selection between the passive sampling options should be based primarily on technical considerations. One exception is if sub-slab sampling is included, because the larger diameter of the SKC and OVM samplers would require a larger diameter hole, and the cost of coring is higher than the cost of using a hammer-drill to make a smaller diameter hole sufficient to accommodate the ATD, Radiello or WMS samplers.

## 9.4 Implementation Considerations

### 9.4.1 Potential Biases

Most of the passive samplers provided data that met the performance criteria for most compounds under most conditions. Exceptions were generally attributable to one of the following causes:

- Poor retention causes low bias in the passive sampler concentration results. This condition was observed in cases where the sampler uptake rate multiplied by the sample duration (equivalent sample volume) was much larger than the recommended maximum sampling volume (RMSV) for a particular compound and adsorbent. The RMSV is specific for each chemical and adsorbent (Supelco, 2013). To reduce the risk of poor retention, a stronger adsorbent may be selected with a larger RMSV for the compounds of interest. The uptake rate or sample duration may also be reduced to reduce the equivalent sample volume; however, this will increase the reporting limit,



so it is important to verify that the reporting limits are still lower than the applicable risk-based screening levels.

- Poor Recovery causes low bias in the passive sampler results. This condition was not common, but may explain some of the low bias and/or variability for NAPH and 124TMB, the two most strongly sorbed compounds. Laboratories routinely test the recovery of various chemicals from various sorbents, so close communication with the analytical chemist at the sampler and sorbent selection stage can usually assure that recoveries are sufficient.
- Starvation also causes low bias, and occurs when the uptake rate is high relative to the face-velocity of gas in the vicinity of the sampler. Starvation is exacerbated in subsurface (sub-slab and soil gas) sampling, where the face velocity is typically very low. Low uptake rate versions of several passive samplers were developed during the conduct of this research, and tended to minimize this effect. The optimal uptake rate for soil vapor sampling appears to be in the range of about 0.1 to 1 mL/min depending on the rate of transport of vapors through soil, as supported by transient and steady-state models (Chapter 5) as well as empirical data (Chapter 7).
- Uptake Rate Uncertainty can cause high or low bias in the passive sampler results. The uptake rate varies between compounds, samplers, sampling conditions (temperature, humidity, face velocity, sample duration and concentration), and sorbents to varying degrees. For most samplers and most VOCs, the accuracy of the vendor-supplied uptake rates was within a factor of about 2 or 3 for the conditions tested. Considering natural spatial and temporal variability in soil vapor and indoor air quality data, this may be acceptable for many monitoring purposes. Where improved accuracy is required or desired, a field-calibrated uptake rate can be calculated if a selected number of samples are collected using inter-method verification samples (e.g., a select number of conventional Summa canisters beside passive samplers). The comparison between the Summa canister 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. The laboratory and field data both showed that the precision of the passive samplers is generally similar to or better than the active samplers; therefore, with proper calibration/benchmarking, the performance of the passive samplers is expected to be comparable to or better than conventional methods. Some chemicals are more challenging than others, and there are many compounds of potential concern for vapor intrusion that were not evaluated in this study. The laboratory testing program was designed to include chemicals spanning a wide range of properties and to include compounds

expected to be challenging (MEK and NAPH), so the study results indicate that passive samplers are likely to be able to provide good quality (accurate and precise) concentration data for many or most VOCs of concern for vapor intrusion.

- Blank contamination causes high bias and can be identified and corrected using travel blanks, which are recommended for all adsorptive sampling methods.
- The SKC Ultra II showed indications of variability attributable to the transfer of the sorbent into and out of the sampler.

#### 9.4.2 Considerations for Sampler Selection

Selection of the most appropriate sampler for a particular application depends on the:

1. Target compounds: not all sampler types have measured uptake rates for all chemicals;
2. Target concentrations: some samplers have better sensitivity than others for a given sample duration;
3. Ambient gas flow velocities: low uptake rate samplers are preferable in low velocity environments;
4. Desired sample duration: weaker sorbents suffer from poor retention over longer deployment intervals; and
5. Convenience: drilling a 2-inch diameter hole in a concrete slab is much more difficult than drilling a 1-inch diameter or smaller hole, and some sample durations required to meet screening levels may be longer than desired.

With the various combinations of each sampler type (high and low uptake versions, and various types of adsorbents), the selection process requires some specialized knowledge, and should be reviewed carefully by an experienced professional. One important consideration for sampler selection is the reporting limit, which varies inversely with sample duration. Table 9-4 shows an example of how this might affect the selection of a sampler. In Table 9-4, the residential indoor air screening level corresponding to a  $1 \times 10^{-6}$  incremental lifetime cancer risk<sup>4</sup> is listed for comparison and the sample duration required for each of the passive samplers to achieve a reporting limit equal to the screening level is also shown. The sample duration may be longer than practical for compounds with very low screening levels (e.g., chloroform, VC, 1122PCA). There are some blanks in Table 9-4 where the uptake rate is not well known or the specific compound is not suited for use with a specific sorbent.

**Table 9-4:** Sample duration required for each of the passive samplers with either solvent extraction or thermal desorption to achieve a reporting limit equal to the residential indoor air screening level corresponding to a 1-in-a-million incremental lifetime cancer risk

Compound	Residential Indoor Air Screening Level ( $\mu\text{g}/\text{m}^3$ )	WMS		ATD	Radiello		SKC Ultra	3M OVM	
		Solvent Extraction	Thermal Desorption	Thermal Desorption	Solvent Extraction	Thermal Desorption	Solvent Extraction	Thermal Desorption	Solvent Extraction
		Duration (hr)	Duration (hr)	Duration (hr)	Duration (hr)	Duration (hr)	Duration (hr)	Duration (hr)	Duration (hr)
1,1,1-Trichloroethane	5,200	0.13	0.01	0.03	0.01	<0.01	0.03	0.00	0.01
1,1,2,2-Tetrachloroethane	0.042	2800	190						
1,1,2-Trichloroethane	0.15	1700	180	1200			1200	27	280
1,1-Dichloroethane	1.5	470	19	89					25
1,1-Dichloroethene	210	19	0.19	0.56	0.10	<0.01	1.8	0.01	0.36
1,2,4-Trimethylbenzene	7.3	9.1	0.46		4.6	0.23			
1,2-Dichlorobenzene	210	0.27	0.03						0.21
1,2-Dichloroethane	0.094	3400	140	1400	230	4.6	1250	25	400
1,3,5-Trimethylbenzene	--								
1,3-Dichlorobenzene	--								
1,4-Dichlorobenzene	0.22	290	35	140	150				200
2-Butanone	5,200	0.13	0.15	0.14	0.04		0.02	0.01	0.01
4-Methyl-2-pentanone	3,100	0.17	0.03						
Acetone	32,000	0.08	0.01		<0.01		0.01	0.00	0.00
Benzene	0.31	2500	400	130	130	34	670	54	230
Carbon Tetrachloride	0.41	1400	84		61				100
Chlorobenzene	52	3.0	0.14		0.47				0.82
Chloroform	0.11	3900	190		200				340
Chloromethane	94	77							
cis-1,2-Dichloroethene	--								
Cyclohexane	6,300	0.06	0.00	0.01					0.01
Ethylbenzene	0.97	130	5.7	37	253	5.0	130	2.9	47
Heptane	--								
Hexane	730	1.1	0.40				0.16	0.03	0.05
m,p-Xylene	100	1.3	0.06		0.24	0.12	1.3	0.03	
MTBE	9.4	72	2.6		2.7		13	2.3	4.3
Naphthalene	0.072	450	23	45	930				700
o-Xylene	100	1.2	0.05		0.26	0.13	1.4	0.03	
Propylbenzene	1,000	0.09	0.04		0.03				
Styrene	1,000	0.12	0.01	0.04	0.03	0.01	0.16		0.04
Tetrachloroethene	0.41	380	26	100	70	3.4	330	13	
Toluene	5,200	0.04	0.00	0.01	<0.01	0.00	0.02	0.00	0.01
trans-1,2-Dichloroethene	63	20	0.40	2.4	0.43	0.01	3.6	0.04	1.4
Trichloroethene	1.2	210	11	150	20	1.01	93	2.5	33
Vinyl Chloride	0.16	43000	200	400					770

Passive samplers with high uptake rates and/or long sample times should be used for outdoor air, to minimize the risk of non-detect results. It is vital when collecting outdoor air samples with passive samplers that a trip blank be included. The sorbent used in passive sampler fabrication should also be blank-tested to identify any chemicals that might contribute to blank contamination, which is not a requirement for Summa canister sampling and analysis because the canisters are blank-checked and individually or batch-certified by the laboratory before shipment.

## 9.5 Research Needs

Further research is needed to evaluate the performance of passive samplers for other chemicals. 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. Controlled chamber tests with a wider range of compounds would be valuable.

Further research is also needed to evaluate longer-term passive sampling. In the radon field, a 90-day sample is referred to as a “short-term” sample. Controlled chamber tests over a longer duration would be valuable.

Field-calibrated uptake rates would provide insight into the degree of variability from site-to-site. Further testing to assess the limitations of passive soil vapor sampling in wet soil conditions is also warranted. A repository for such information would be valuable and may eventually provide sufficient information to allow better prediction of uptake rates as a function of site-specific conditions, which would reduce or eliminate the need for on-going field calibration.

More than 100 compounds can potentially pose a risk via the vapor intrusion pathway,<sup>2</sup> and they have a wide range of properties that are not all well-suited for a single sorbent. Weakly sorbed compounds like vinyl chloride, chloromethane and other low boiling point, low molecular weight compounds require a strong sorbent to avoid low bias attributable to poor retention, and strongly sorbed compounds like PAHs, PCB, and other SVOCs require a weaker sorbent to avoid low bias attributable to poor recovery. Testing designed to specifically improve the understanding of the ranges of compounds that will yield good retention and good recovery for several different sorbent/sampler combinations would be valuable.

Several compounds of potential concern have very low risk-based screening levels of about 0.1  $\mu\text{g}/\text{m}^3$  or less (e.g., 1,3-butadiene, chloroform, 1,2-dichloroethane, hexachlorobenzene, hexachlorobutadiene, all of the polycyclic aromatic hydrocarbons and polychlorinated biphenyls, 1,1,2,2-tetrachloroethane, 1,1,2-

trichloroethane, and vinyl chloride), so if any of these compounds is a site-specific compound of concern, they will likely dictate the sample duration needed to achieve reporting limits as low as or lower than risk-based screening levels. In some cases, this may result in saturation of the sorbent with compounds that may be more abundant (e.g., limonene, pinene and other terpenes, hydrocarbons and other chemicals from background sources). Further testing to verify the performance of passive samplers at very low reporting limits for these compounds would be valuable.

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## 11 Appendices

## Appendix A

### ANALYTICAL METHODS

For the center-point testing, fractional factorial testing, and high concentration laboratory tests, all samples were analyzed by the laboratories considered most familiar with the sampler: FSM for Radiello, ATL for ATD tubes, UW for WMS, and CAS for SKC. For the field sampling activities, the laboratories that performed the analyses are summarized in Table A-1. One trip blank sample was collected and analyzed for each passive sampler type for each field site. The trip blanks were prepared and shipped with the investigative samples, but were not opened in the field. TCE was detected (23.4 ng) in the SKC blank for the NAS JAX event, while the SKC investigative samples all had values two times or less the value of the trip blank (these samples are discussed further in Section 6). Consequently, the investigative samples were corrected for the blank. All other trip blanks had no detectable or negligible concentrations of target analytes.

The samples were analyzed for the following site-specific target compounds at a minimum:

- Layton House, Utah – TCE, PCE, 111TCA, 11DCE, 11DCA, 12DCA, cDCE, tDCE, VC, carbon tetrachloride, and chloroform.
- CRREL, NH – TCE, benzene, toluene, ethylbenzene, mp-xylene, o-xylene, n-hexane, n-heptane, 2,2,4-trimethylpentane, 1,2,4-trimethylbenzene, methylethylketone, acetone, ethanol, methylene chloride and tetrahydrofuran in indoor and outdoor air and TCE in sub-slab samples.
- OTC3 San Diego– TCE, PCE, cDCE, tDCE, 11DCE, and VC.
- MCAS Cherry point- TCE, PCE, 111TCA, 112TCA, 11DCA, 11DCE, 12DCA, cDCE, tDCE, benzene, ethyl benzene, toluene, and xylenes; and
- NAS Jacksonville – PCE, TCE, cDCE and tDCE.

Table A-1: Laboratories that analyzed the passive samplers in the field-testing program

Sampler	Uptake Rate	Sorbent	Laboratory Description Method	Navy OTC3, San Diego, CA		HHI AFB, Layton		CRRREL, Hanover, NH		MCAS, Cherry Point, NC		NAS Jacksonville, FL	
				Indoor Air	Outdoor Air	Indoor Air	Outdoor Air	Indoor Air	Outdoor Air	Indoor Air	Outdoor Air	Indoor Air	Outdoor Air
Summa Canister	na	na	TO-15	ATL	ATL	ATL	CAS	ATL	ATL	ATL	ATL	CAS	CAS
EM OVM 3500™	Regular	Charcoal	Solvent	ATL	ATL	ATL	CAS	ATL	ATL	ATL	ATL	ATL	NS
ATD Tube	Regular	Chromosorb 106	Thermal	ATL	ATL								
	Regular	Tenax TA	Thermal				ATL						
	Low uptake rate	Carbopack B	Thermal				ATL	ATL	ATL	ATL	ATL	ATL	ATL
	Regular	Carbopack B	Thermal										
WMS™	Regular	Anasorb 747	Solvent	ATL	ATL	ATL	UW	UW	UW	ATL	ATL	ATL	ATL
	Low uptake rate	Carbopack B	Thermal										
	Low uptake rate	Anasorb 747	Solvent										
SKC Ultra II™	Regular	Charcoal	Solvent					CAS				CAS	
	Regular	Chromosorb 106	Thermal	ATL	ATL								
	Regular	Carbopack X	Thermal										
	Regular	Carbopack 5	Thermal				CAS	CAS	CAS	ATL	ATL	ATL	ATL
	Low uptake rate	Carbopack X	Thermal										
	Low uptake rate	Charcoal	Solvent									CAS	NS
	Regular	Carbopack 5	Thermal										
Radcell™	Regular	Charcoal	Solvent	ATL	ATL	ATL	FSM	FSM	FSM				
	Low uptake rate	Carbopack 4	Thermal							ATL	ATL		FSM
	Low uptake rate	Carbopack 4	Thermal										
	Low uptake rate	Charcoal	Solvent										FSM

Notes:  
 ATL - Air Toxics Ltd, Folsom, CA  
 TA - TestAmerica, Burlington, VT  
 FSM - Fondazione Salvatore Maugeri, Padova, Italy  
 UW - University of Waterloo, Waterloo, Canada  
 CAS - Columbia Analytical Services, Simi Valley, CA

### **Summa Canister Analysis**

Summa canister samples were analyzed by EPA Method TO-15 in full scan mode for sub-slab and soil gas samples and EPA Method TO-15 in combine open scan and selected ion monitoring (SIM) mode for all indoor and outdoor air samples.

### **Active and Passive ATD Tube Analysis**

The active and passive ATD tube samples were analyzed following EPA Method TO-17. Sorbent tubes were heated to release adsorbed compounds, which were swept onto a secondary trap for further concentration and removal of moisture. In general, the pumped ATD tubes and passive Carbopack B tubes were heated to approximately 300°C, and the Tenax TA tubes were heated to approximately 265°C. The secondary trap was then heated to 300°C and purged with helium to transfer analytes to the GC/MS for separation and detection. The analytical instrumentation used for sample analysis was a Markes Unity/Ultra thermal desorption unit coupled with an Agilent 7890 GC and 5975 MS. Calibration was achieved by injecting and vaporizing methanolic NIST-traceable calibration mixes onto clean sorbent tubes. Since desorption parameters and performance varied slightly for each sorbent type, calibrations were generated for each tube packing. Additionally, the calibration range and thermal desorption unit operating parameters were optimized for the expected mass loading on each tube. The analytical quality control protocols and criteria were based on EPA Method TO-17.

The internal standards and tune check vapor mix were loaded onto each standard and sample tube using an automated loop prior to the sample desorption. Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5 were utilized as internal standards, and 4-Bromofluorobenzene (BFB) was evaluated as a MS tune check and also monitored as a sample surrogate. The BFB Tune Check was analyzed and evaluated prior to the start of each 24-hour analytical clock against the tuning criteria outlined in EPA Method TO-17. The internal standard recovery was evaluated against the daily continuing calibration verification (CCV). The CCV acceptance criterion was 60-140% recovery. Several exceedances were noted for the active samples collected under conditions of high humidity and high temperature despite the dry-purge step. The target results quantified using the non-compliant internal standards were flagged as estimated values. When monitored as a surrogate for sample analysis, the BFB recovery was evaluated against laboratory limits of 70-130%.

The calibration range was optimized for the expected concentration range. The 1 ppbv chamber test for 24 hours required the greatest sensitivity and the instrument was configured to cover the range from 0.5 to

10 nanograms. The active samples and the 50 and 100 ppbv passive samples were typically analyzed using a calibration range from approximately 5 to 2000 nanograms. Due to the high mass loadings of the 100 ppmv high concentration tests, the passive Carboxpack B tubes were analyzed against a calibration with a range from 2000 to 20,000 nanograms. In each case, the reporting limit was supported by the lowest calibration level of the initial calibration curve.

Overall, linearity was excellent, and the %RSD for each calibration curve was well within TO-17 method criterion of less than 30%. Linearity was not always achieved for all of the target compounds at the lower concentrations due to background concentrations from the sorbent packing (e.g. Benzene) or poor analytical response (e.g. Methyl Ethyl Ketone). In several cases, target compounds could not be reliably measured and results were below the linear range and marked as not detected or flagged. Methyl Ethyl Ketone proved to be a poor performing compound throughout the study, specifically with Carboxpack B sorbent. Methyl Ethyl Ketone reporting limits were often raised due to linearity issues at the low end of the calibration curve.

Following the daily tune check, a CCV was analyzed near the mid-point of the calibration curve. The CCV was evaluated against method recovery limits of 70-130%. A second source standard referred to as the laboratory control spike (LCS) was analyzed after the initial calibration and also after the daily CCV to verify accuracy of the primary standard. The LCS was evaluated against laboratory recovery limits of 70-130%. Recoveries exceeding the CCV or LCS acceptance limits were flagged along with the associated data. The non-compliant QC was also described in the laboratory narrative.

Hexane proved to be unstable in the methanolic calibration standard showing gradual loss over time. Since the second source calibration mix was also prepared in methanol, the discrepancy was not evident in the daily QC performance until the standard was compared to several NIST-vapor phase calibration standards. As part of the laboratory's investigation as to the cause of the higher than expected hexane concentrations measured in the chamber, two independent NIST-traceable vapor standards were loaded onto the sorbent tubes and recovered between 150 and 160% demonstrating that the stated hexane concentration in the methanol calibration standard was no longer accurate. This discrepancy was noted on the data report for Runs 11 and 12 active samples, and the hexane results quantified using the inaccurate initial calibrations were flagged to indicate a high bias. The hexane results generated for the Runs 1 through 10 and runs 11 and 12 passive samples were evaluated to determine if hexane's relative response factor could indicate which results were biased low as a result of the degraded standard.

Unfortunately, this approach did not yield a reliable correction factor. All hexane results generated for

the active and passive ATD tubes for Runs 13 through 18 were quantified using freshly prepared methanolic working standards verified with a vapor-phase NIST calibration. When the vapor phase check was analyzed with the daily batch, both the methanolic second source and the vapor phase second source recoveries were reported.

### **Sorbent media cleaning and certification**

Prior to sample collection, all ATD tubes were cleaned by heating to 300°C for approximately 4 hours with ultra-high purity nitrogen flowing at about 80 mL/min. Each clean tube was analyzed on the TO-17 unit to insure background concentrations were below the reporting limits. Additionally, the Carbopack X sorbent utilized for the SKC Ultra II badges was cleaned and certified prior to sample deployment in the low concentration chamber. An amount of 500 mg Carbopack X (60/80 mesh) was transferred to a clean empty ATD tube sleeve with an internal support screen to hold the sorbent material. A plug of clean glass wool was used to support sorbent bed on the 'fill side' of the tube. The Carbopack X tubes were then cleaned a minimum of 4 hours at 400°C with ultra-purity nitrogen at 80 mL/min flow rate. The cleaned tubes were analyzed on the TO-17 unit to insure no target compounds were present above the reporting limit. Immediately prior to sample deployment, the sorbent was emptied into a clean 4 mL screw top vial for transfer into the Ultra II badge housing.

### **Radiello Sampler Analysis**

Fondazione Salvatore Maugeri analyzed the Radiello samplers. The activated charcoal sorbent in the Radiello sampler was extracted by introducing 2 mL of low-benzene CS<sub>2</sub> and 100 µL of internal standard solution (2-fluorotoluene) directly in the Radiello glass storage tube without drawing out the cartridge. After 30 min, 2 µL of the CS<sub>2</sub> solution was injected in the gas chromatograph. The GC system (6890N, Agilent Technologies, Wilmington, DE, USA) was equipped with a 50 m column (J&W-PONA, 0.2 mm id, 0.5 µm film thickness) and two detectors, FID and MS (5975B, Agilent Technologies, Wilmington, DE, USA), connected to the column via a three-way splitter (flow rate ratio 1:1). The injector temperature was 260 °C and the column temperature program was 40 °C for 5 min followed by a temperature ramp of 5 °C min<sup>-1</sup> to 90 °C, followed by 90 °C for 3 min, a second ramp of 10 °C min<sup>-1</sup> to 150 °C, and a third ramp of 20 °C min<sup>-1</sup> to 250 °C. The total run time was 34 min. The split ratio was 20:1. The carrier gas was nitrogen at 21 psi. The FID temperature was 270 °C. The calibration was performed by the phase equilibrium technique, adding to new, unexposed cartridges accurately measured

2 mL aliquots of a series of calibration solutions, prepared by serial dilutions, ranging from 0.82 to 2.04  $\mu\text{g mL}^{-1}$  (lowest level) and from 3,260 to 8,140  $\mu\text{g mL}^{-1}$  (highest level), except naphthalene, whose concentrations were about ten times lower (0.14 to 555  $\mu\text{g mL}^{-1}$ ). Quantitation was made using the FID signal, while MS was used for compound identity confirmation.

### **SKC Ultra II Sampler Analysis**

Columbia Analytical Services (CAS), Simi Valley California analyzed the SKC Ultra II samplers using a Markes Unity/Ultra Series 2 - Agilent 7890/5975C GC-MS. The sorbent (Carbopack X) was transferred to an automatic thermal desorption (ATD) tube prior to analysis. Two different calibration ranges were used to accommodate the range from the low concentration/short duration tests (1 ppbv for 1 day) to the high concentration/ long duration (100 ppbv for 7 days). The low-level calibration range was approximately 1-500 ng/tube and the high-level range was approximately 200-50,000 ng/tube. In both cases, internal standards (1,4-difluorobenzene and chlorobenzene-d5) and surrogates (toluene-d8 and p-bromofluorobenzene) were added (25 ng or 1000 ng) and a dry purge was performed (2 min @ 50 mL/min or 5 min @ 80 mL/min) prior to analysis. Desorption was performed for 15 minutes at 350 °C with a cold trap at 25 °C. The inlet was split 2:1 for the low-level method and 20:1 for the high level method. Injection occurred over 3 minutes at 290 °C in both cases. The outlet split was 10:1 for the low-level method and 50:1 for the high-level method. The column for both methods was a 60 m x 0.25 mm ID x 1.00  $\mu\text{m}$  film Rxi-1ms (Restek Corp.). The temperature program was the same for both methods: 2 min @ 40 °C, 5 °C/min to 70 °C, 10 °C/min to 120 °C, 20 °C/min to 240 °C. The scan rate was set for both methods to 2.7 scans/sec; scan range was m/z 33 to 300. CAS observed background levels of benzene and MEK in these sorbents and were forced to therefore raise the reporting limit of these compounds. The sorbent media as received from the manufacturer required additional conditioning to meet the objectives of this project (i.e. low reporting limits), and even with additional cleaning, background levels of benzene were still observed (in the range of approximately 20-25 ng in 500 mg of sorbent).

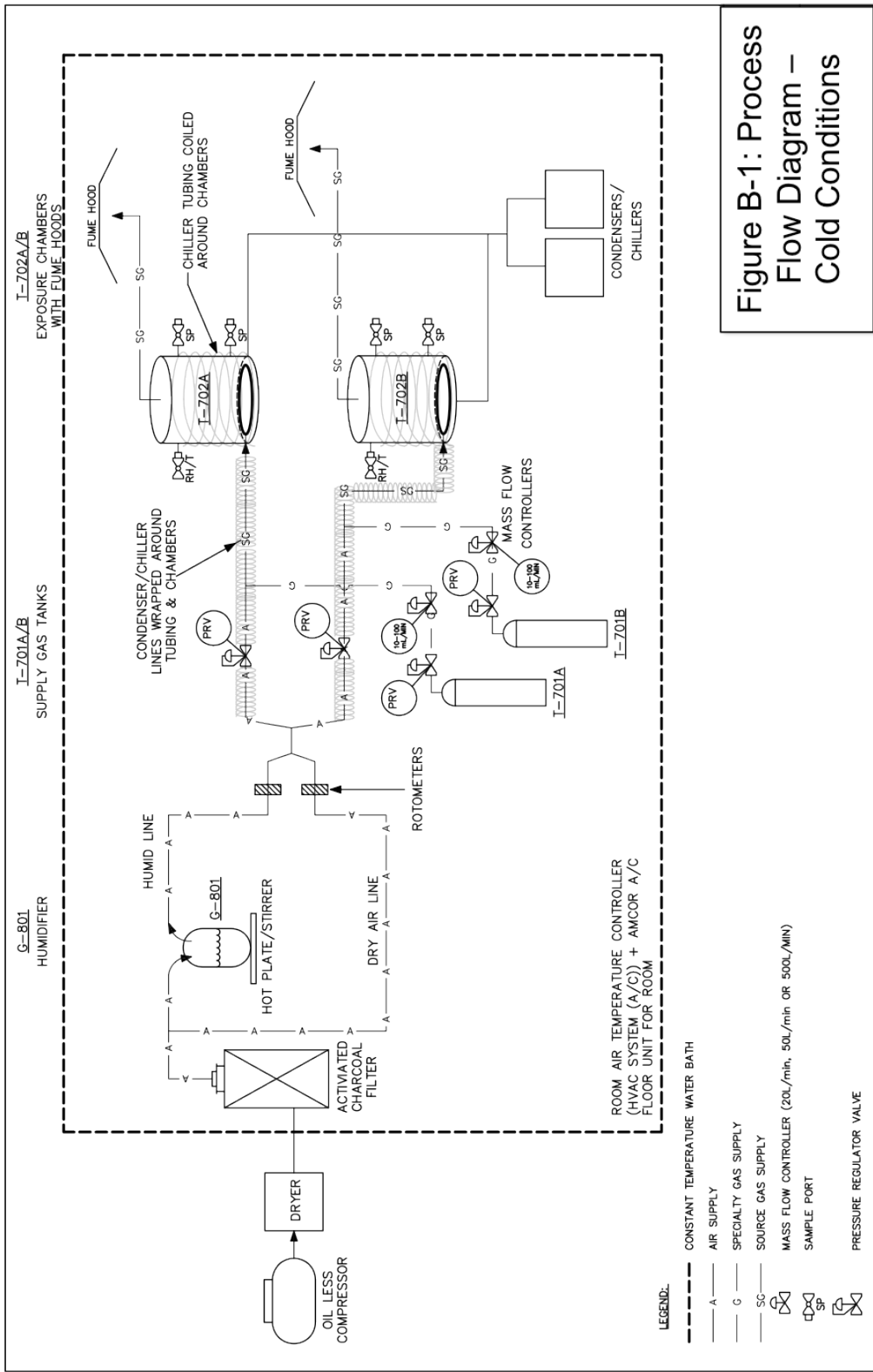
### **Waterloo Membrane Sampler Analysis**

The University of Waterloo (Suresh Seethapathy) analyzed the WMS samples using an Agilent Technologies model 6890 gas chromatograph. The aluminum crimp cap was removed from the sampler with the help of a de-crimper (Chromatographic Specialties Inc., Brockville, ON), and the sorbent along

with the PDMS membrane were transferred to a 4 mL vial for desorption. Since the sorbent tended to stick to the surface of the membrane and it was cumbersome to try to separate them, it was decided to extract the membrane along with the sorbent. A 1 mL aliquot of the desorption solvent was introduced into the vial, which was then shaken intermittently over 30 minutes for desorption. After desorption, the vials were centrifuged if necessary, and aliquots of the extract were transferred to 1.8 mL crimp cap vials with 100  $\mu$ L inserts for GC/MS analysis. The injector was set at 275  $^{\circ}$ C, the split ratio was 1:10 and the injection volume was 1  $\mu$ L. Helium was the carrier gas, with a flow rate of 2.0 mL/min. The temperature program was 35  $^{\circ}$ C for 5 min, 5  $^{\circ}$ C/min to 120  $^{\circ}$ C, 30  $^{\circ}$ C/min to 350  $^{\circ}$ C (held for 3 minutes). The data acquisition and processing was performed with Chemstation software. The capillary column was Rxi-1 MS (100% methylsiloxane), 60 m x 0.32 mm with 1.0  $\mu$ m film thickness. The quantitation mode was Selected Ion Monitoring with three ions for each target analyte. Multipoint calibration was performed using an external standard.



**Appendix B**  
**PROCESS FLOW DIAGRAMS**



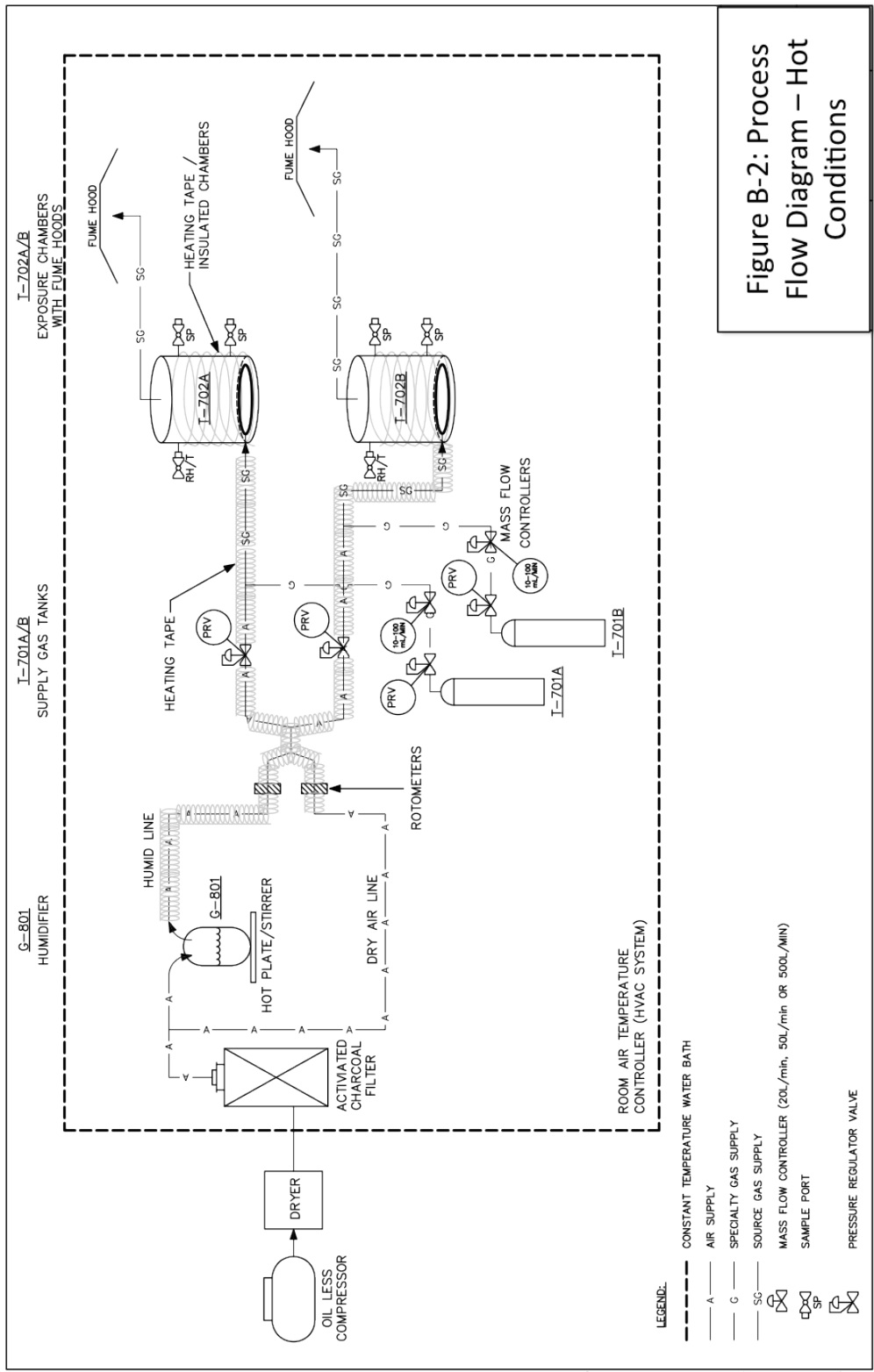


Figure B-2: Process Flow Diagram – Hot Conditions

## **Appendix C**

### **Results of Center-Point Chamber Tests**



**TABLE C2  
Pumped AID Tube Concentrations for Center-Point Chamber Tests**

Chamber #	Date	Time	Analyte (ppbv)									
			111-TCA	CT	Hexane	Benzene	12-DCA	TCE	PCE	124-TMB	Naphthalene	2-MEK
1	18-Dec-09	16:05	36	36	43	38	37	37	35	34	3.0	37
1	19-Dec-09	8:40	36	36	46	40	38	38	37	33	3.1	38
1	19-Dec-09	12:54	35	35	44	38	36	38	36	33	3.0	35
1	20-Dec-09	8:20	33	35	42	37	36	35	34	29	2.6	36
1	20-Dec-09	12:44	35	35	43	37	36	36	35	32	3.0	36
1	21-Dec-09	7:24	34	35	42	37	36	35	34	30	2.8	36
1	21-Dec-09	14:02	34	35	44	38	37	37	35	30	2.8	34
1	22-Dec-09	7:21	35	36	44	38	37	37	35	32	3.0	34
<i>Average</i>			34.8	35.4	43.5	37.9	36.6	36.6	35.1	31.6	2.9	35.8
<i>Standard Deviation</i>			1.0	0.5	1.3	1.0	0.7	1.2	1.0	1.8	0.2	1.4
<i>Coefficient of Variation</i>			0.030	0.015	0.030	0.026	0.020	0.032	0.028	0.056	0.056	0.039
2	18-Dec-09	13:50	33	34	43	36	35	35	34	30	3.0	35
2	18-Dec-09	18:18	28	31	41	35	33	34	34	30	2.8	37
2	19-Dec-09	10:40	35	37	44	39	37	38	36	34	3.1	36
2	19-Dec-09	15:03	34	36	43	37	36	36	34	30	2.7	35
2	20-Dec-09	10:31	35	36	44	38	37	38	37	34	3.1	35
2	20-Dec-09	14:57	35	36	44	38	37	37	35	31	2.9	34
2	21-Dec-09	10:32	36	37	44	39	38	38	36	32	2.9	38
2	21-Dec-09	17:30	34	35	43	38	37	36	35	31	2.8	35
<i>Average</i>			33.8	35.3	43.3	37.5	36.3	36.4	35.1	31.5	2.9	35.6
<i>Standard Deviation</i>			2.5	2.0	1.0	1.4	1.6	1.4	1.1	1.7	0.1	1.3
<i>Coefficient of Variation</i>			0.074	0.056	0.024	0.038	0.044	0.039	0.032	0.054	0.050	0.037

**TABLE C2**  
**Pumped ATD Tube Concentrations for Center-Point Chamber Tests**

Chamber #	Date	Time	Analyte (ppbv)										
			111-TCA	CT	Hexane	Benzene	12-DCA	TCE	PCE	124-TMB	Naphthalene	2-MEK	
1	27-Dec-09	14:45	37	40	56	43	38	41	40	40	35	3.5	35
1	28-Dec-09	7:50	36	38	51	40	35	37	38	38	36	3.2	32
1	28-Dec-09	14:28	34	36	52	40	35	38	38	38	36	3.2	34
1	29-Dec-09	8:01	36	38	51	40	35	38	37	37	36	3.3	34
1	29-Dec-09	14:35	31	33	52	39	35	39	38	38	36	3.2	38
1	30-Dec-09	8:27	38	40	52	41	37	38	38	38	38	3.4	33
1	30-Dec-09	13:51	38	39	51	40	36	37	37	37	34	3.0	33
1	31-Dec-09	11:01	38	39	52	40	36	37	37	37	34	3.0	34
<i>Average</i>			36.0	37.9	52.1	40.4	35.9	38.1	37.9	36.3	36.3	3.2	34.1
<i>Standard Deviation</i>			2.4	2.4	1.6	1.2	1.1	1.4	1.0	2.0	2.0	0.2	1.8
<i>Coefficient of Variation</i>			0.068	0.062	0.032	0.029	0.031	0.036	0.026	0.055	0.055	0.054	0.053
2	27-Dec-09	18:05	37	39	54	42	37	40	38	38	38	3.4	34
2	28-Dec-09	11:31	34	36	50	39	34	36	36	33	33	2.9	33
2	28-Dec-09	16:31	35	37	50	39	35	38	37	34	34	3.0	32
2	29-Dec-09	11:01	37	38	52	40	36	38	38	38	38	3.4	35
2	29-Dec-09	16:38	36	37	50	39	34	36	34	34	34	3.0	32
2	30-Dec-09	10:55	36	38	50	40	35	36	36	33	33	2.9	31
2	30-Dec-09	16:08	38	38	53	41	37	39	39	36	36	3.3	35
2	31-Dec-09	8:58	38	39	52	40	36	38	37	37	34	3.1	34
<i>Average</i>			36.4	37.8	51.4	40.0	35.5	37.6	36.9	35.0	35.0	3.1	33.3
<i>Standard Deviation</i>			1.4	1.0	1.6	1.1	1.2	1.5	1.6	2.1	2.1	0.2	1.5
<i>Coefficient of Variation</i>			0.039	0.027	0.031	0.027	0.034	0.040	0.042	0.059	0.059	0.068	0.045

**TABLE C2**  
**Pumped AID Tube Concentrations for Center-Point Chamber Tests**

Chamber #	Date	Time	Analyte (ppbv)									
			111-TCA	CT	Hexane	Benzene	12-DCA	TCE	PCE	124-TMB	Naphthalene	2-MEK
1	03-Jan-10	14:35	35	36	56	44	37	40	37	34	3.1	36
1	04-Jan-10	11:50	34	36	52	41	35	36	34	32	2.9	33
1	04-Jan-10	16:35	35	35	53	41	35	36	34	30	2.8	34
1	05-Jan-10	12:30	37	37	55	43	37	37	36	33	3.0	32
1	06-Jan-10	11:20	34	34	52	41	36	36	34	31	2.8	34
1	06-Jan-10	15:27	40	42	56	44	39	38	37	32	3.0	37
1	07-Jan-10	10:26	36	39	54	42	36	38	37	33	3.0	39
<i>Average</i>			35.9	37.0	54.0	42.3	36.4	37.3	35.6	32.1	2.9	35.0
<i>Standard Deviation</i>			2.1	2.7	1.7	1.4	1.4	1.5	1.5	1.3	0.1	2.4
<i>Coefficient of Variation</i>			0.059	0.073	0.032	0.033	0.038	0.040	0.043	0.042	0.039	0.070
2	03-Jan-10	16:41	36	37	55	43	36	38	36	32	3.0	35
2	04-Jan-10	13:54	34	36	53	42	35	37	35	33	3.1	33
2	05-Jan-10	10:26	36	36	53	42	36	36	35	34	3.1	32
2	05-Jan-10	14:40	34	34	53	41	36	37	36	33	3.0	32
2	06-Jan-10	13:22	37	38	54	43	37	38	37	34	3.1	34
2	07-Jan-10	8:21	36	36	55	43	38	38	36	33	3.0	36
<i>Average</i>			35.5	36.2	53.8	42.3	36.3	37.3	35.8	33.2	3.1	33.7
<i>Standard Deviation</i>			1.2	1.3	1.0	0.8	1.0	0.8	0.8	0.8	0.1	1.6
<i>Coefficient of Variation</i>			0.034	0.037	0.018	0.019	0.028	0.022	0.021	0.023	0.018	0.049



APPENDIX TABLE C3A  
WMS SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration			
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)		
1	PS-D11 Chamber 1	2-butanone (MEK)	50	1060	5760	1.25	72.12	147	49.4		
		n-hexane	50	1600	5760	1.31	86.18	212	59.5		
		1,2-dichloroethane	50	2640	5760	2.58	98.96	178	43.4		
		1,1,1-trichloroethane	50	2040	5760	1.27	133.41	279	50.6		
		Benzene	50	1870	5760	2.15	78.12	151	46.7		
		Carbon Tetrachloride	50	2740	5760	1.50	143.82	317	53.3		
		Trichloroethene	50	4390	5760	3.28	131.39	232	42.8		
		Tetrachloroethene	50	6500	5760	5.35	165.83	211	30.8		
		1,2,4-Trimethylbenzene	50	8140	5760	12.5	120.19	113	22.7		
		Naphthalene	50	1400	5760	25.6	128.17	9.49	1.8		
		PS-D12 Chamber 2	PS-D12 Chamber 2	2-butanone (MEK)	50	1100	5760	1.25	72.12	153	51.2
				n-hexane	50	1620	5760	1.31	86.18	215	60.2
1,2-dichloroethane	50			2680	5760	2.58	98.96	180	44.0		
1,1,1-trichloroethane	50			2070	5760	1.27	133.41	283	51.2		
Benzene	50			1960	5760	2.15	78.12	158	48.9		
Carbon Tetrachloride	50			2770	5760	1.50	143.82	321	53.9		
Trichloroethene	50			4620	5760	3.28	131.39	245	45.0		
Tetrachloroethene	50			6990	5760	5.35	165.83	227	33.0		
1,2,4-Trimethylbenzene	50			9290	5760	12.5	120.19	129	25.9		
Naphthalene	50			1470	5760	25.6	128.17	9.97	1.9		
PS-D13 Chamber 1	PS-D13 Chamber 1			2-butanone (MEK)	50	1130	5760	1.25	72.12	157	52.6
				n-hexane	50	1730	5760	1.31	86.18	229	64.3
		1,2-dichloroethane	50	2740	5760	2.58	98.96	184	45.1		
		1,1,1-trichloroethane	50	2140	5760	1.27	133.41	293	53.0		
		Benzene	50	2040	5760	2.15	78.12	165	51.0		
		Carbon Tetrachloride	50	2850	5760	1.50	143.82	330	55.5		
		Trichloroethene	50	4750	5760	3.28	131.39	251	46.3		
		Tetrachloroethene	50	7170	5760	5.35	165.83	233	33.9		
		1,2,4-Trimethylbenzene	50	8490	5760	12.5	120.19	118	23.7		
		Naphthalene	50	1420	5760	25.6	128.17	9.63	1.8		
		PS-D14 Chamber 2	PS-D14 Chamber 2	2-butanone (MEK)	50	1070	5760	1.25	72.12	149	49.8
				n-hexane	50	1630	5760	1.31	86.18	216	60.6
1,2-dichloroethane	50			2600	5760	2.58	98.96	175	42.7		
1,1,1-trichloroethane	50			2020	5760	1.27	133.41	276	50.0		
Benzene	50			1940	5760	2.15	78.12	157	48.4		
Carbon Tetrachloride	50			2710	5760	1.50	143.82	314	52.7		
Trichloroethene	50			4590	5760	3.28	131.39	243	44.7		
Tetrachloroethene	50			7130	5760	5.35	165.83	231	33.7		
1,2,4-Trimethylbenzene	50			8700	5760	12.5	120.19	121	24.3		
Naphthalene	50			1690	5760	25.6	128.17	11.46	2.2		
PS-D15 Chamber 1	PS-D15 Chamber 1			2-butanone (MEK)	50	1130	5760	1.25	72.12	157	52.6
				n-hexane	50	1720	5760	1.31	86.18	228	64.0
		1,2-dichloroethane	50	2670	5760	2.58	98.96	180	43.9		
		1,1,1-trichloroethane	50	2120	5760	1.27	133.41	290	52.5		
		Benzene	50	2000	5760	2.15	78.12	161	50.0		
		Carbon Tetrachloride	50	2810	5760	1.50	143.82	325	54.7		
		Trichloroethene	50	4630	5760	3.28	131.39	245	45.1		
		Tetrachloroethene	50	6960	5760	5.35	165.83	226	32.9		
		1,2,4-Trimethylbenzene	50	8440	5760	12.5	120.19	117	23.6		
		Naphthalene	50	1530	5760	25.6	128.17	10.38	2.0		
		PS-D16 Chamber 2	PS-D16 Chamber 2	2-butanone (MEK)	50	1120	5760	1.25	72.12	156	52.1
				n-hexane	50	1620	5760	1.31	86.18	215	60.2
1,2-dichloroethane	50			2670	5760	2.58	98.96	180	43.9		
1,1,1-trichloroethane	50			2050	5760	1.27	133.41	280	50.7		
Benzene	50			1980	5760	2.15	78.12	160	49.4		
Carbon Tetrachloride	50			2750	5760	1.50	143.82	318	53.5		
Trichloroethene	50			4680	5760	3.28	131.39	248	45.5		
Tetrachloroethene	50			7580	5760	5.35	165.83	246	35.8		
1,2,4-Trimethylbenzene	50			9200	5760	12.5	120.19	128	25.7		
Naphthalene	50			1570	5760	25.6	128.17	10.65	2.0		
2	PS-D01			2-butanone (MEK)	50	1160	5760	1.25	72.12	161	54.0
				n-hexane	50	1050	5760	1.31	86.18	139	39.0
		1,2-dichloroethane	50	2420	5760	2.58	98.96	163	39.8		
		1,1,1-trichloroethane	50	1860	5760	1.27	133.41	254	46.0		
		Benzene	50	1850	5760	2.15	78.12	149	46.2		
		Carbon Tetrachloride	50	2490	5760	1.50	143.82	288	48.4		
		Trichloroethene	50	3880	5760	3.28	131.39	205	37.8		
		Tetrachloroethene	50	7510	5760	5.35	165.83	244	35.5		
		1,2,4-Trimethylbenzene	50	8850	5760	12.5	120.19	123	24.7		
		Naphthalene	50	945	5760	25.6	128.17	6.41	1.2		

APPENDIX TABLE C3A  
WMS SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
	PS-D02	2-butanone (MEK)	50	1190	5760	1.25	72.12	165	55.3
		n-hexane	50	1000	5760	1.31	86.18	133	37.1
		1,2-dichloroethane	50	2440	5760	2.58	98.96	164	40.1
		1,1,1-trichloroethane	50	1880	5760	1.27	133.41	257	46.5
		Benzene	50	1860	5760	2.15	78.12	150	46.4
		Carbon Tetrachloride	50	2510	5760	1.50	143.82	291	48.8
		Trichloroethene	50	3920	5760	3.28	131.39	207	38.1
		Tetrachloroethene	50	8950	5760	5.35	165.83	290	42.3
		1,2,4-Trimethylbenzene	50	10900	5760	12.5	120.19	151	30.4
		Naphthalene	50	1150	5760	25.6	128.17	7.80	1.5
	PS-D03	2-butanone (MEK)	50	1170	5760	1.25	72.12	163	54.4
		n-hexane	50	1040	5760	1.31	86.18	138	38.6
		1,2-dichloroethane	50	2430	5760	2.58	98.96	164	39.9
		1,1,1-trichloroethane	50	1860	5760	1.27	133.41	254	46.0
		Benzene	50	1850	5760	2.15	78.12	149	46.2
		Carbon Tetrachloride	50	2480	5760	1.50	143.82	287	48.2
		Trichloroethene	50	3890	5760	3.28	131.39	206	37.9
		Tetrachloroethene	50	7740	5760	5.35	165.83	251	36.6
		1,2,4-Trimethylbenzene	50	9070	5760	12.5	120.19	126	25.3
		Naphthalene	50	979	5760	25.6	128.17	6.64	1.3
	PS-D04	2-butanone (MEK)	50	1160	5760	1.25	72.12	161	53.9
		n-hexane	50	996	5760	1.31	86.18	132	37.0
		1,2-dichloroethane	50	2400	5760	2.58	98.96	161	39.4
		1,1,1-trichloroethane	50	1840	5760	1.27	133.41	252	45.5
		Benzene	50	1820	5760	2.15	78.12	147	45.4
		Carbon Tetrachloride	50	2440	5760	1.50	143.82	282	47.4
		Trichloroethene	50	3810	5760	3.28	131.39	202	37.1
		Tetrachloroethene	50	7370	5760	5.35	165.83	239	34.8
		1,2,4-Trimethylbenzene	50	8960	5760	12.5	120.19	124	25.0
		Naphthalene	50	929	5760	25.6	128.17	6.30	1.2
	PS-D05	2-butanone (MEK)	50	1190	5760	1.25	72.12	165	55.4
		n-hexane	50	1060	5760	1.31	86.18	140	39.4
		1,2-dichloroethane	50	2490	5760	2.58	98.96	168	40.9
		1,1,1-trichloroethane	50	1920	5760	1.27	133.41	262	47.5
		Benzene	50	1880	5760	2.15	78.12	152	46.9
		Carbon Tetrachloride	50	2540	5760	1.50	143.82	294	49.4
Trichloroethene		50	3920	5760	3.28	131.39	207	38.2	
Tetrachloroethene		50	7610	5760	5.35	165.83	247	36.0	
1,2,4-Trimethylbenzene		50	8710	5760	12.5	120.19	121	24.3	
Naphthalene		50	887	5760	25.6	128.17	6.02	1.1	
PS-D06	2-butanone (MEK)	50	1320	5760	1.25	72.12	183	61.4	
	n-hexane	50	1130	5760	1.31	86.18	150	42.0	
	1,2-dichloroethane	50	2660	5760	2.58	98.96	179	43.7	
	1,1,1-trichloroethane	50	2090	5760	1.27	133.41	286	51.7	
	Benzene	50	2050	5760	2.15	78.12	166	51.2	
	Carbon Tetrachloride	50	2760	5760	1.50	143.82	319	53.6	
	Trichloroethene	50	4210	5760	3.28	131.39	223	40.9	
	Tetrachloroethene	50	8070	5760	5.35	165.83	262	38.1	
	1,2,4-Trimethylbenzene	50	8900	5760	12.5	120.19	124	24.8	
	Naphthalene	50	925	5760	25.6	128.17	6.27	1.2	
3	PS-C41	2-butanone (MEK)	50	1160	5760	1.25	72.12	161	54.0
		n-hexane	50	961	5760	1.31	86.18	127	35.8
		1,2-dichloroethane	50	2350	5760	2.58	98.96	158	38.7
		1,1,1-trichloroethane	50	1780	5760	1.27	133.41	243	44.1
		Benzene	50	1750	5760	2.15	78.12	141	43.8
		Carbon Tetrachloride	50	2400	5760	1.50	143.82	278	46.7
		Trichloroethene	50	3680	5760	3.28	131.39	195	35.9
		Tetrachloroethene	50	7310	5760	5.35	165.83	237	34.6
		1,2,4-Trimethylbenzene	50	8170	5760	12.5	120.19	113	22.8
		Naphthalene	50	870	5760	25.6	128.17	5.90	1.1
	PS-C42	2-butanone (MEK)	50	1150	5760	1.25	72.12	160	53.5
		n-hexane	50	1060	5760	1.31	86.18	140	39.4
		1,2-dichloroethane	50	2420	5760	2.58	98.96	163	39.8
		1,1,1-trichloroethane	50	1860	5760	1.27	133.41	254	46.1
		Benzene	50	1830	5760	2.15	78.12	148	45.7
		Carbon Tetrachloride	50	2500	5760	1.50	143.82	289	48.6
		Trichloroethene	50	3860	5760	3.28	131.39	204	37.6
		Tetrachloroethene	50	7870	5760	5.35	165.83	255	37.2
		1,2,4-Trimethylbenzene	50	9080	5760	12.5	120.19	126	25.4
		Naphthalene	50	895	5760	25.6	128.17	6.07	1.1

**APPENDIX TABLE C3A  
WMS SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
--	PS-C43	2-butanone (MEK)	50	1200	5760	1.25	72.12	167	55.9
		n-hexane	50	1020	5760	1.31	86.18	135	37.9
		1,2-dichloroethane	50	2510	5760	2.58	98.96	169	41.3
		1,1,1-trichloroethane	50	1920	5760	1.27	133.41	262	47.6
		Benzene	50	1910	5760	2.15	78.12	154	47.8
		Carbon Tetrachloride	50	2580	5760	1.50	143.82	299	50.2
		Trichloroethene	50	4080	5760	3.28	131.39	216	39.8
		Tetrachloroethene	50	8150	5760	5.35	165.83	264	38.6
		1,2,4-Trimethylbenzene	50	9640	5760	12.5	120.19	134	26.9
		Naphthalene	50	996	5760	25.6	128.17	6.75	1.3
	PS-C44	2-butanone (MEK)	50	1240	5760	1.25	72.12	172	57.7
		n-hexane	50	1130	5760	1.31	86.18	150	42.0
		1,2-dichloroethane	50	2600	5760	2.58	98.96	175	42.7
		1,1,1-trichloroethane	50	2030	5760	1.27	133.41	278	50.3
		Benzene	50	2020	5760	2.15	78.12	163	50.5
		Carbon Tetrachloride	50	2740	5760	1.50	143.82	317	53.3
		Trichloroethene	50	4230	5760	3.28	131.39	224	41.2
		Tetrachloroethene	50	8320	5760	5.35	165.83	270	39.3
		1,2,4-Trimethylbenzene	50	9740	5760	12.5	120.19	135	27.2
		Naphthalene	50	950	5760	25.6	128.17	6.44	1.2
	PS-C45	2-butanone (MEK)	50	1230	5760	1.25	72.12	171	57.3
		n-hexane	50	1060	5760	1.31	86.18	140	39.4
		1,2-dichloroethane	50	2520	5760	2.58	98.96	170	41.5
		1,1,1-trichloroethane	50	1950	5760	1.27	133.41	267	48.3
		Benzene	50	1950	5760	2.15	78.12	157	48.8
		Carbon Tetrachloride	50	2610	5760	1.50	143.82	302	50.8
		Trichloroethene	50	4100	5760	3.28	131.39	217	40.0
		Tetrachloroethene	50	7730	5760	5.35	165.83	251	36.6
		1,2,4-Trimethylbenzene	50	8900	5760	12.5	120.19	124	24.9
		Naphthalene	50	962	5760	25.6	128.17	6.52	1.2
	PS-C48	2-butanone (MEK)	50	1170	5760	1.25	72.12	163	54.5
		n-hexane	50	1010	5760	1.31	86.18	134	37.5
		1,2-dichloroethane	50	2430	5760	2.58	98.96	164	39.9
1,1,1-trichloroethane		50	1870	5760	1.27	133.41	256	46.3	
Benzene		50	1890	5760	2.15	78.12	153	47.2	
Carbon Tetrachloride		50	2520	5760	1.50	143.82	292	49.0	
Trichloroethene		50	3990	5760	3.28	131.39	211	38.8	
Tetrachloroethene		50	7160	5760	5.35	165.83	232	33.9	
1,2,4-Trimethylbenzene		50	8320	5760	12.5	120.19	116	23.2	
Naphthalene		50	862	5760	25.6	128.17	5.85	1.1	
--	PS-D08	2-butanone (MEK)	50		5760	1.25	72.12	0	0.0
		n-hexane	50	140	5760	1.31	86.18	19	5.3
	Trip blank	1,2-dichloroethane	50		5760	2.58	98.96	0	0.0
		1,1,1-trichloroethane	50		5760	1.27	133.41	0	0.0
		Benzene	50		5760	2.15	78.12	0	0.0
		Carbon Tetrachloride	50		5760	1.50	143.82	0	0.0
		Trichloroethene	50		5760	3.28	131.39	0	0.0
		Tetrachloroethene	50		5760	5.35	165.83	0	0.0
		1,2,4-Trimethylbenzene	50		5760	12.5	120.19	0	0.0
		Naphthalene	50		5760	25.6	128.17	0.00	0.00

**Notes:**

ng - nanograms  
min - minutes  
mL/min - millilitres per minute  
g/mol - grams per mole  
 $\mu\text{g}/\text{m}^3$  - micrograms per cubic metre  
ppbv - parts per billion

APPENDIX TABLE C3B  
ATD TENAX SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration		
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)	
1	Chamber 1 TenaxTA (1)	1,1,1-trichloroethane	20	310	5760	0.5	133.41	108	19.5	
		Carbon Tetrachloride	20	370	5760	0.5	143.82	128	21.6	
		n-hexane	50	250	5760	0.5	86.18	90	24.4	
		Benzene	20	240	5760	0.35	78.12	119	36.9	
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.1	
		Trichloroethene	20	350	5760	0.41	131.39	148	27.3	
		Tetrachloroethene	20	490	5760	0.5	165.83	170	24.8	
		1,2,4-Trimethylbenzene	50	370	5760	0.62	120.19	104	20.8	
		Naphthalene	20	42	5760	0.5	128.17	14.58	2.8	
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.5	
		Chamber 1 TenaxTA (2)	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
			Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2
	n-hexane		50	260	5760	0.5	86.18	90	25.3	
	Benzene		20	240	5760	0.35	78.12	119	36.9	
	1,2-dichloroethane		20	260	5760	0.5	98.96	90	22.1	
	Trichloroethene		20	360	5760	0.41	131.39	152	28.1	
	Tetrachloroethene		20	510	5760	0.5	165.83	177	25.8	
	1,2,4-Trimethylbenzene		50	400	5760	0.62	120.19	112	22.5	
	Naphthalene		20	47	5760	0.5	128.17	16.32	3.1	
	2-butanone (MEK)		20	210	5760	0.5	72.12	73	24.5	
	Chamber 1 TenaxTA (3)		1,1,1-trichloroethane	20	310	5760	0.5	133.41	108	19.5
			Carbon Tetrachloride	20	370	5760	0.5	143.82	128	21.6
		n-hexane	50	260	5760	0.5	86.18	90	25.3	
		Benzene	20	240	5760	0.35	78.12	119	36.9	
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.1	
		Trichloroethene	20	360	5760	0.41	131.39	152	28.1	
		Tetrachloroethene	20	520	5760	0.5	165.83	181	26.3	
		1,2,4-Trimethylbenzene	50	410	5760	0.62	120.19	115	23.1	
		Naphthalene	20	46	5760	0.5	128.17	15.97	3.0	
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.5	
		Chamber 2 TenaxTA (1)	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
			Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2
	n-hexane		50	260	5760	0.5	86.18	90	25.3	
	Benzene		20	240	5760	0.35	78.12	119	36.8	
	1,2-dichloroethane		20	260	5760	0.5	98.96	90	22.0	
	Trichloroethene		20	360	5760	0.41	131.39	152	28.0	
	Tetrachloroethene		20	530	5760	0.5	165.83	184	26.8	
	1,2,4-Trimethylbenzene		50	420	5760	0.62	120.19	118	23.6	
	Naphthalene		20	50	5760	0.5	128.17	17.36	3.3	
	2-butanone (MEK)		20	210	5760	0.5	72.12	73	24.4	
	Chamber 2 TenaxTA (2)		1,1,1-trichloroethane	20	330	5760	0.5	133.41	115	20.8
			Carbon Tetrachloride	20	390	5760	0.5	143.82	135	22.7
		n-hexane	50	260	5760	0.5	86.18	90	25.3	
		Benzene	20	250	5760	0.35	78.12	124	38.4	
		1,2-dichloroethane	20	270	5760	0.5	98.96	94	22.9	
		Trichloroethene	20	380	5760	0.41	131.39	161	29.6	
		Tetrachloroethene	20	540	5760	0.5	165.83	188	27.3	
		1,2,4-Trimethylbenzene	50	440	5760	0.62	120.19	123	24.8	
Naphthalene		20	50	5760	0.5	128.17	17.36	3.3		
2-butanone (MEK)		20	220	5760	0.5	72.12	76	25.6		
Chamber 2 TenaxTA (3)		1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1	
		Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2	
	n-hexane	50	260	5760	0.5	86.18	90	25.3		
	Benzene	20	240	5760	0.35	78.12	119	36.8		
	1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0		
	Trichloroethene	20	360	5760	0.41	131.39	152	28.0		
	Tetrachloroethene	20	510	5760	0.5	165.83	177	25.8		
	1,2,4-Trimethylbenzene	50	400	5760	0.62	120.19	112	22.5		
	Naphthalene	20	45	5760	0.5	128.17	15.63	2.9		
	2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.4		
	2	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
			Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2
n-hexane			50	260	5760	0.5	86.18	90	25.3	
Benzene			20	240	5760	0.35	78.12	119	36.9	
1,2-dichloroethane			20	260	5760	0.5	98.96	90	22.1	
Trichloroethene			20	360	5760	0.41	131.39	152	28.1	
Tetrachloroethene			20	500	5760	0.5	165.83	174	25.3	
1,2,4-Trimethylbenzene			50	370	5760	0.62	120.19	104	20.9	
Naphthalene			20	42	5760	0.5	128.17	14.58	2.8	
2-butanone (MEK)			20	210	5760	0.5	72.12	73	24.5	

**APPENDIX TABLE C3B  
ATD TENAX SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	310	5760	0.5	133.41	108	19.5
		Carbon Tetrachloride	20	360	5760	0.5	143.82	125	21.0
		n-hexane	50	260	5760	0.5	86.18	90	25.3
		Benzene	20	240	5760	0.35	78.12	119	36.9
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	360	5760	0.41	131.39	152	28.1
		Tetrachloroethene	20	510	5760	0.5	165.83	177	25.8
		1,2,4-Trimethylbenzene	50	410	5760	0.62	120.19	115	23.1
		Naphthalene	20	47	5760	0.5	128.17	16.32	3.1
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.5
	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
		Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2
		n-hexane	50	260	5760	0.5	86.18	90	25.3
		Benzene	20	240	5760	0.35	78.12	119	36.9
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.1
		Trichloroethene	20	360	5760	0.41	131.39	152	28.1
		Tetrachloroethene	20	510	5760	0.5	165.83	177	25.8
		1,2,4-Trimethylbenzene	50	420	5760	0.62	120.19	118	23.7
		Naphthalene	20	48	5760	0.5	128.17	16.67	3.1
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.5
	Chamber 2 TenaxTA	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
		Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.2
		n-hexane	50	260	5760	0.5	86.18	90	25.3
		Benzene	20	240	5760	0.35	78.12	119	36.8
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0
		Trichloroethene	20	370	5760	0.41	131.39	157	28.8
		Tetrachloroethene	20	520	5760	0.5	165.83	181	26.3
		1,2,4-Trimethylbenzene	50	420	5760	0.62	120.19	118	23.6
Naphthalene		20	48	5760	0.5	128.17	16.67	3.1	
2-butanone (MEK)		20	210	5760	0.5	72.12	73	24.4	
Chamber 2 TenaxTA	1,1,1-trichloroethane	20	340	5760	0.5	133.41	118	21.4	
	Carbon Tetrachloride	20	400	5760	0.5	143.82	139	23.3	
	n-hexane	50	260	5760	0.5	86.18	90	25.3	
	Benzene	20	250	5760	0.35	78.12	124	38.4	
	1,2-dichloroethane	20	270	5760	0.5	98.96	94	22.9	
	Trichloroethene	20	370	5760	0.41	131.39	157	28.8	
	Tetrachloroethene	20	520	5760	0.5	165.83	181	26.3	
	1,2,4-Trimethylbenzene	50	400	5760	0.62	120.19	112	22.5	
	Naphthalene	20	47	5760	0.5	128.17	16.32	3.1	
	2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.4	
Chamber 2 TenaxTA	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1	
	Carbon Tetrachloride	20	390	5760	0.5	143.82	135	22.8	
	n-hexane	50	260	5760	0.5	86.18	90	25.3	
	Benzene	20	240	5760	0.35	78.12	119	36.8	
	1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0	
	Trichloroethene	20	360	5760	0.41	131.39	152	28.0	
	Tetrachloroethene	20	530	5760	0.5	165.83	184	26.8	
	1,2,4-Trimethylbenzene	50	400	5760	0.62	120.19	112	22.5	
	Naphthalene	20	46	5760	0.5	128.17	15.97	3.0	
	2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.4	
3	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	330	5760	0.5	133.41	115	20.8
		Carbon Tetrachloride	20	400	5760	0.5	143.82	139	23.3
		n-hexane	50	250	5760	0.5	86.18	87	24.3
		Benzene	20	230	5760	0.35	78.12	114	35.3
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	340	5760	0.41	131.39	144	26.5
		Tetrachloroethene	20	490	5760	0.5	165.83	170	24.8
		1,2,4-Trimethylbenzene	50	400	5760	0.62	120.19	112	22.5
		Naphthalene	20	48	5760	0.5	128.17	16.67	3.1
		2-butanone (MEK)	20	200	5760	0.5	72.12	69	23.3
	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	310	5760	0.5	133.41	108	19.5
		Carbon Tetrachloride	20	360	5760	0.5	143.82	125	21.0
		n-hexane	50	250	5760	0.5	86.18	87	24.3
		Benzene	20	230	5760	0.35	78.12	114	35.3
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	350	5760	0.41	131.39	148	27.3
		Tetrachloroethene	20	490	5760	0.5	165.83	170	24.8
		1,2,4-Trimethylbenzene	50	390	5760	0.62	120.19	109	22.0
		Naphthalene	20	46	5760	0.5	128.17	15.97	3.0
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.4

APPENDIX TABLE C3B  
ATD TENAX SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
	Chamber 1 TenaxTA	1,1,1-trichloroethane	20	330	5760	0.5	133.41	115	20.8
		Carbon Tetrachloride	20	400	5760	0.5	143.82	139	23.3
		n-hexane	50	250	5760	0.5	86.18	87	24.3
		Benzene	20	230	5760	0.35	78.12	114	35.3
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	360	5760	0.41	131.39	152	28.0
		Tetrachloroethene	20	510	5760	0.5	165.83	177	25.8
		1,2,4-Trimethylbenzene	50	420	5760	0.62	120.19	118	23.6
		Naphthalene	20	50	5760	0.5	128.17	17.36	3.3
		2-butanone (MEK)	20	200	5760	0.5	72.12	69	23.3
	Chamber 2 TenaxTA	1,1,1-trichloroethane	20	310	5760	0.5	133.41	108	19.5
		Carbon Tetrachloride	20	380	5760	0.5	143.82	132	22.1
		n-hexane	50	250	5760	0.5	86.18	87	24.3
		Benzene	20	230	5760	0.35	78.12	114	35.3
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	340	5760	0.41	131.39	144	26.5
		Tetrachloroethene	20	480	5760	0.5	165.83	167	24.3
		1,2,4-Trimethylbenzene	50	360	5760	0.62	120.19	101	20.2
		Naphthalene	20	42	5760	0.5	128.17	14.58	2.7
		2-butanone (MEK)	20	200	5760	0.5	72.12	69	23.2
	Chamber 2 TenaxTA	1,1,1-trichloroethane	20	320	5760	0.5	133.41	111	20.1
		Carbon Tetrachloride	20	390	5760	0.5	143.82	135	22.7
		n-hexane	50	250	5760	0.5	86.18	87	24.3
		Benzene	20	230	5760	0.35	78.12	114	35.3
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	350	5760	0.41	131.39	148	27.2
		Tetrachloroethene	20	510	5760	0.5	165.83	177	25.8
		1,2,4-Trimethylbenzene	50	400	5760	0.62	120.19	112	22.5
		Naphthalene	20	47	5760	0.5	128.17	16.32	3.1
		2-butanone (MEK)	20	200	5760	0.5	72.12	69	23.2
	Chamber 2 TenaxTA	1,1,1-trichloroethane	20	340	5760	0.5	133.41	118	21.4
		Carbon Tetrachloride	20	400	5760	0.5	143.82	139	23.3
		n-hexane	50	260	5760	0.5	86.18	90	25.3
		Benzene	20	240	5760	0.35	78.12	119	36.8
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0
		Trichloroethene	20	370	5760	0.41	131.39	157	28.8
		Tetrachloroethene	20	540	5760	0.5	165.83	188	27.3
		1,2,4-Trimethylbenzene	50	410	5760	0.62	120.19	115	23.1
		Naphthalene	20	49	5760	0.5	128.17	17.01	3.2
		2-butanone (MEK)	20	210	5760	0.5	72.12	73	24.4

**Notes:**

- ng - nanograms
- min - minutes
- mL/min - millilitres per minute
- g/mol - grams per mole
- $\mu\text{g}/\text{m}^3$  - micrograms per cubic metre
- ppbv - parts per billion

APPENDIX TABLE C3C  
ATD CARBOPACK B SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
1	Chamber 1 CarboPack B (1)	1,1,1-trichloroethane	20	400	5760	0.5	133.41	139	25.2
		Carbon Tetrachloride	20	480	5760	0.5	143.82	167	28.0
		n-hexane	20	690	5760	0.5	86.18	240	67.2
		Benzene	20	430	5760	0.35	78.12	213	66.0
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	540	5760	0.41	131.39	229	42.1
		Tetrachloroethene	20	730	5760	0.5	165.83	253	37.0
		1,2,4-Trimethylbenzene	20	480	5760	0.62	120.19	134	27.0
		Naphthalene	20	52	5760	0.5	128.17	18.1	3.4
		2-butanone (MEK)	20	72	5760	0.5	72.12	25.0	8.4
	Chamber 1 CarboPack B (2)	1,1,1-trichloroethane	20	390	5760	0.5	133.41	135	24.5
		Carbon Tetrachloride	20	490	5760	0.5	143.82	170	28.6
		n-hexane	20	700	5760	0.5	86.18	243	68.2
		Benzene	20	430	5760	0.35	78.12	213	66.0
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.1
		Trichloroethene	20	560	5760	0.41	131.39	237	43.6
		Tetrachloroethene	20	740	5760	0.5	165.83	257	37.5
		1,2,4-Trimethylbenzene	20	470	5760	0.62	120.19	132	26.5
		Naphthalene	20	52	5760	0.5	128.17	18.1	3.4
		2-butanone (MEK)	20	55	5760	0.5	72.12	19.1	6.4
	Chamber 1 CarboPack B (3)	1,1,1-trichloroethane	20	420	5760	0.5	133.41	146	26.4
		Carbon Tetrachloride	20	520	5760	0.5	143.82	181	30.4
		n-hexane	20	700	5760	0.5	86.18	243	68.2
		Benzene	20	440	5760	0.35	78.12	218	67.6
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	560	5760	0.41	131.39	237	43.6
		Tetrachloroethene	20	740	5760	0.5	165.83	257	37.5
		1,2,4-Trimethylbenzene	20	460	5760	0.62	120.19	129	25.9
		Naphthalene	20	52	5760	0.5	128.17	18.1	3.4
		2-butanone (MEK)	20	62	5760	0.5	72.12	21.5	7.2
	Chamber 2 CarboPack B (1)	1,1,1-trichloroethane	20	360	5760	0.5	133.41	125	22.6
		Carbon Tetrachloride	20	500	5760	0.5	143.82	174	29.2
		n-hexane	20	700	5760	0.5	86.18	243	68.1
		Benzene	20	420	5760	0.35	78.12	208	64.4
		1,2-dichloroethane	20	240	5760	0.5	98.96	83	20.3
		Trichloroethene	20	510	5760	0.41	131.39	216	39.7
		Tetrachloroethene	20	700	5760	0.5	165.83	243	35.4
		1,2,4-Trimethylbenzene	20	430	5760	0.62	120.19	120	24.2
		Naphthalene	20	47	5760	0.5	128.17	16.3	3.1
		2-butanone (MEK)	20	27	5760	0.5	72.12	9.4	3.1
	Chamber 2 CarboPack B (2)	1,1,1-trichloroethane	20	400	5760	0.5	133.41	139	25.2
		Carbon Tetrachloride	20	490	5760	0.5	143.82	170	28.6
n-hexane		20	720	5760	0.5	86.18	250	70.1	
Benzene		20	420	5760	0.35	78.12	208	64.4	
1,2-dichloroethane		20	260	5760	0.5	98.96	90	22.0	
Trichloroethene		20	530	5760	0.41	131.39	224	41.3	
Tetrachloroethene		20	720	5760	0.5	165.83	250	36.4	
1,2,4-Trimethylbenzene		20	490	5760	0.62	120.19	137	27.6	
Naphthalene		20	51	5760	0.5	128.17	17.7	3.3	
2-butanone (MEK)		20	80	5760	0.5	72.12	27.8	9.3	
Chamber 2 CarboPack B (3)	1,1,1-trichloroethane	20	390	5760	0.5	133.41	135	24.5	
	Carbon Tetrachloride	20	510	5760	0.5	143.82	177	29.7	
	n-hexane	20	680	5760	0.5	86.18	236	66.2	
	Benzene	20	420	5760	0.35	78.12	208	64.4	
	1,2-dichloroethane	20	240	5760	0.5	98.96	83	20.3	
	Trichloroethene	20	530	5760	0.41	131.39	224	41.3	
	Tetrachloroethene	20	700	5760	0.5	165.83	243	35.4	
	1,2,4-Trimethylbenzene	20	430	5760	0.62	120.19	120	24.2	
	Naphthalene	20	44	5760	0.5	128.17	15.3	2.9	
	2-butanone (MEK)	20	55	5760	0.5	72.12	19.1	6.4	
2	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	380	5760	0.5	133.41	132	23.9
		Carbon Tetrachloride	20	520	5760	0.5	143.82	181	30.4
		n-hexane	20	710	5760	0.5	86.18	247	69.2
		Benzene	20	430	5760	0.35	78.12	213	66.1
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	550	5760	0.41	131.39	233	42.9
		Tetrachloroethene	20	730	5760	0.5	165.83	253	37.0
		1,2,4-Trimethylbenzene	20	470	5760	0.62	120.19	132	26.5
		Naphthalene	20	46	5760	0.5	128.17	16.0	3.0
		2-butanone (MEK)	20	35	5760	0.5	72.12	12.2	4.1

APPENDIX TABLE C3C  
ATD CARBOPACK B SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	390	5760	0.5	133.41	135	24.6
		Carbon Tetrachloride	20	530	5760	0.5	143.82	184	31.0
		n-hexane	20	720	5760	0.5	86.18	250	70.2
		Benzene	20	440	5760	0.35	78.12	218	67.6
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	540	5760	0.41	131.39	229	42.1
		Tetrachloroethene	20	740	5760	0.5	165.83	257	37.5
		1,2,4-Trimethylbenzene	20	470	5760	0.62	120.19	132	26.5
		Naphthalene	20	45	5760	0.5	128.17	15.6	2.9
	2-butanone (MEK)	20	37	5760	0.5	72.12	12.8	4.3	
	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	350	5760	0.5	133.41	122	22.0
		Carbon Tetrachloride	20	450	5760	0.5	143.82	156	26.3
		n-hexane	20	670	5760	0.5	86.18	233	65.3
		Benzene	20	410	5760	0.35	78.12	203	63.0
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	510	5760	0.41	131.39	216	39.8
		Tetrachloroethene	20	350	5760	0.5	165.83	122	17.7
		1,2,4-Trimethylbenzene	20	390	5760	0.62	120.19	109	22.0
		Naphthalene	20	36	5760	0.5	128.17	12.5	2.4
	2-butanone (MEK)	20	86	5760	0.5	72.12	29.9	10.0	
	Chamber 2 CarboPack B	1,1,1-trichloroethane	20	440	5760	0.5	133.41	153	27.7
		Carbon Tetrachloride	20	550	5760	0.5	143.82	191	32.1
		n-hexane	20	720	5760	0.5	86.18	250	70.1
		Benzene	20	420	5760	0.35	78.12	208	64.5
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0
		Trichloroethene	20	510	5760	0.41	131.39	216	39.7
		Tetrachloroethene	20	710	5760	0.5	165.83	247	35.9
		1,2,4-Trimethylbenzene	20	450	5760	0.62	120.19	126	25.3
		Naphthalene	20	48	5760	0.5	128.17	16.7	3.1
	2-butanone (MEK)	20	70	5760	0.5	72.12	24.3	8.1	
	Chamber 2 CarboPack B	1,1,1-trichloroethane	20	410	5760	0.5	133.41	142	25.8
		Carbon Tetrachloride	20	490	5760	0.5	143.82	170	28.6
		n-hexane	20	710	5760	0.5	86.18	247	69.1
		Benzene	20	430	5760	0.35	78.12	213	66.0
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0
		Trichloroethene	20	550	5760	0.41	131.39	233	42.8
Tetrachloroethene		20	730	5760	0.5	165.83	253	36.9	
1,2,4-Trimethylbenzene		20	490	5760	0.62	120.19	137	27.6	
Naphthalene		20	50	5760	0.5	128.17	17.4	3.3	
2-butanone (MEK)	20	86	5760	0.5	72.12	29.9	10.0		
Chamber 2 CarboPack B	1,1,1-trichloroethane	20	380	5760	0.5	133.41	132	23.9	
	Carbon Tetrachloride	20	480	5760	0.5	143.82	167	28.0	
	n-hexane	20	680	5760	0.5	86.18	236	66.2	
	Benzene	20	420	5760	0.35	78.12	208	64.5	
	1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2	
	Trichloroethene	20	520	5760	0.41	131.39	220	40.5	
	Tetrachloroethene	20	690	5760	0.5	165.83	240	34.9	
	1,2,4-Trimethylbenzene	20	440	5760	0.62	120.19	123	24.8	
	Naphthalene	20	49	5760	0.5	128.17	17.0	3.2	
2-butanone (MEK)	20	64	5760	0.5	72.12	22.2	7.4		
3	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	430	5760	0.5	133.41	149	27.0
		Carbon Tetrachloride	20	540	5760	0.5	143.82	188	31.5
		n-hexane	20	720	5760	0.5	86.18	250	70.1
		Benzene	20	440	5760	0.35	78.12	218	67.5
		1,2-dichloroethane	20	290	5760	0.5	98.96	101	24.6
		Trichloroethene	20	580	5760	0.41	131.39	246	45.2
		Tetrachloroethene	20	750	5760	0.5	165.83	260	37.9
		1,2,4-Trimethylbenzene	20	500	5760	0.62	120.19	140	28.1
		Naphthalene	20	52	5760	0.5	128.17	18.1	3.4
	2-butanone (MEK)	20	130	5760	0.5	72.12	45.1	15.1	
	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	460	5760	0.5	133.41	160	28.9
		Carbon Tetrachloride	20	560	5760	0.5	143.82	194	32.7
		n-hexane	20	710	5760	0.5	86.18	247	69.1
		Benzene	20	430	5760	0.35	78.12	213	66.0
		1,2-dichloroethane	20	270	5760	0.5	98.96	94	22.9
		Trichloroethene	20	540	5760	0.41	131.39	229	42.0
		Tetrachloroethene	20	720	5760	0.5	165.83	250	36.4
		1,2,4-Trimethylbenzene	20	440	5760	0.62	120.19	123	24.8
Naphthalene		20	45	5760	0.5	128.17	15.6	2.9	
2-butanone (MEK)	20	72	5760	0.5	72.12	25.0	8.4		



APPENDIX TABLE C3C  
ATD CARBOPACK B SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS

ANOVA Test	Sampler ID	Analyte	Reporting limit (ng)	Mass on sampler (ng)	Exposure time (min)	Uptake rate (mL/min)	Molecular Weight (g/mol)	Concentration	
								( $\mu\text{g}/\text{m}^3$ )	(ppbv)
	Chamber 1 CarboPack B	1,1,1-trichloroethane	20	450	5760	0.5	133.41	156	28.3
		Carbon Tetrachloride	20	550	5760	0.5	143.82	191	32.1
		n-hexane	20	710	5760	0.5	86.18	247	69.1
		Benzene	20	430	5760	0.35	78.12	213	66.0
		1,2-dichloroethane	20	280	5760	0.5	98.96	97	23.7
		Trichloroethene	20	540	5760	0.41	131.39	229	42.0
		Tetrachloroethene	20	720	5760	0.5	165.83	250	36.4
		1,2,4-Trimethylbenzene	20	460	5760	0.62	120.19	129	25.9
		Naphthalene	20	47	5760	0.5	128.17	16.3	3.1
		2-butanone (MEK)	20	79	5760	0.5	72.12	27.4	9.2
	Chamber 2 CarboPack B	1,1,1-trichloroethane	20	360	5760	0.5	133.41	125	22.6
		Carbon Tetrachloride	20	470	5760	0.5	143.82	163	27.4
		n-hexane	20	690	5760	0.5	86.18	240	67.1
		Benzene	20	420	5760	0.35	78.12	208	64.4
		1,2-dichloroethane	20	250	5760	0.5	98.96	87	21.2
		Trichloroethene	20	540	5760	0.41	131.39	229	42.0
		Tetrachloroethene	20	700	5760	0.5	165.83	243	35.4
		1,2,4-Trimethylbenzene	20	450	5760	0.62	120.19	126	25.3
		Naphthalene	20	49	5760	0.5	128.17	17.0	3.2
		2-butanone (MEK)	20	34	5760	0.5	72.12	11.8	4.0
	Chamber 2 CarboPack B	1,1,1-trichloroethane	20	400	5760	0.5	133.41	139	25.1
		Carbon Tetrachloride	20	520	5760	0.5	143.82	181	30.3
		n-hexane	20	660	5760	0.5	86.18	229	64.2
		Benzene	20	400	5760	0.35	78.12	198	61.3
		1,2-dichloroethane	20	260	5760	0.5	98.96	90	22.0
		Trichloroethene	20	520	5760	0.41	131.39	220	40.5
		Tetrachloroethene	20	670	5760	0.5	165.83	233	33.9
		1,2,4-Trimethylbenzene	20	420	5760	0.62	120.19	118	23.6
		Naphthalene	20	43	5760	0.5	128.17	14.9	2.8
		2-butanone (MEK)	20	58	5760	0.5	72.12	20.1	6.7
	Chamber 2 CarboPack B	1,1,1-trichloroethane	20	390	5760	0.5	133.41	135	24.5
		Carbon Tetrachloride	20	510	5760	0.5	143.82	177	29.7
		n-hexane	20	710	5760	0.5	86.18	247	69.1
		Benzene	20	420	5760	0.35	78.12	208	64.4
		1,2-dichloroethane	20	280	5760	0.5	98.96	97	23.7
		Trichloroethene	20	540	5760	0.41	131.39	229	42.0
Tetrachloroethene		20	730	5760	0.5	165.83	253	36.9	
1,2,4-Trimethylbenzene		20	480	5760	0.62	120.19	134	27.0	
Naphthalene		20	53	5760	0.5	128.17	18.4	3.5	
2-butanone (MEK)		20	110	5760	0.5	72.12	38.2	12.8	

**Notes:**

ng - nanograms  
min - minutes  
mL/min - millilitres per minute  
g/mol - grams per mole  
 $\mu\text{g}/\text{m}^3$  - micrograms per cubic metre  
ppbv - parts per billion

**APPENDIX TABLE C3D  
SKC SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Mass on sampler (ng)	Exposure Time (min)	Uptake Rate (mL/min)	Molecular Weight (g/mol)	Concentration	
							( $\mu\text{g}/\text{m}^3$ )	(ppbv)
1	ANOVA #2 Chamber 1	2-butanone (MEK)	6523.2	5760	17	72.12	67	22.3
		n-Hexane	12901.7	5760	14	86.18	160	44.9
		1,2-dichloroethane	12718.8	5760	13	98.96	170	41.5
		1,1,1-trichloroethane	18290.8	5760	13	133.41	244	44.3
		Benzene	12251.9	5760	16	78.12	133	41.2
		Carbon Tetrachloride	14405.1	5760	13	143.82	192	32.3
		Trichloroethene	17214.5	5760	15	131.39	199	36.7
		Tetrachloroethene	21513.7	5760	13	165.83	287	41.9
		1,2,4-Trimethylbenzene	13379.4	5760	13	120.19	179	36.0
		Naphthalene	442.0	5760	13	128.17	5.9	1.1
	ANOVA #4 Chamber 1	2-butanone (MEK)	7135.0	5760	17	72.12	73	24.4
		n-Hexane	12880.5	5760	14	86.18	160	44.8
		1,2-dichloroethane	13106.3	5760	13	98.96	175	42.8
		1,1,1-trichloroethane	18371.5	5760	13	133.41	245	44.5
		Benzene	12136.8	5760	16	78.12	132	40.8
		Carbon Tetrachloride	14189.5	5760	13	143.82	189	31.9
		Trichloroethene	17404.5	5760	15	131.39	201	37.1
		Tetrachloroethene	21239.5	5760	13	165.83	284	41.4
		1,2,4-Trimethylbenzene	13110.1	5760	13	120.19	175	35.2
		Naphthalene	478.5	5760	13	128.17	6.4	1.2
	ANOVA #6 Chamber 1	2-butanone (MEK)	6798.0	5760	17	72.12	69	23.3
		n-Hexane	12806.9	5760	14	86.18	159	44.6
		1,2-dichloroethane	12746.2	5760	13	98.96	170	41.6
		1,1,1-trichloroethane	18403.8	5760	13	133.41	246	44.6
		Benzene	12240.7	5760	16	78.12	133	41.1
		Carbon Tetrachloride	14535.2	5760	13	143.82	194	32.6
		Trichloroethene	17729.3	5760	15	131.39	205	37.8
		Tetrachloroethene	21301.7	5760	13	165.83	284	41.5
		1,2,4-Trimethylbenzene	12979.4	5760	13	120.19	173	34.9
		Naphthalene	464.7	5760	13	128.17	6.2	1.2
	ANOVA #3 Chamber 2	2-butanone (MEK)	6692.9	5760	17	72.12	68	22.9
		n-Hexane	13260.6	5760	14	86.18	164	46.1
		1,2-dichloroethane	13195.2	5760	13	98.96	176	43.0
		1,1,1-trichloroethane	19006.2	5760	13	133.41	254	46.0
		Benzene	12401.0	5760	16	78.12	135	41.6
		Carbon Tetrachloride	14553.9	5760	13	143.82	194	32.7
		Trichloroethene	17903.8	5760	15	131.39	207	38.1
		Tetrachloroethene	20901.4	5760	13	165.83	279	40.7
		1,2,4-Trimethylbenzene	13053.1	5760	13	120.19	174	35.0
		Naphthalene	455.2	5760	13	128.17	6.1	1.1
	ANOVA #5 Chamber 2	2-butanone (MEK)	6507.1	5760	17	72.12	66	22.3
		n-Hexane	12793.8	5760	14	86.18	159	44.5
		1,2-dichloroethane	12479.3	5760	13	98.96	167	40.7
		1,1,1-trichloroethane	17847.8	5760	13	133.41	238	43.2
		Benzene	12140.2	5760	16	78.12	132	40.7
		Carbon Tetrachloride	13546.1	5760	13	143.82	181	30.4
		Trichloroethene	17349.9	5760	15	131.39	201	36.9
		Tetrachloroethene	20946.3	5760	13	165.83	280	40.8
		1,2,4-Trimethylbenzene	12439.7	5760	13	120.19	166	33.4
		Naphthalene	414.3	5760	13	128.17	5.5	1.0
	ANOVA #7 Chamber 2	2-butanone (MEK)	7331.6	5760	17	72.12	75	25.1
		n-Hexane	13013.3	5760	14	86.18	161	45.2
		1,2-dichloroethane	13145.6	5760	13	98.96	176	42.9
		1,1,1-trichloroethane	18262.4	5760	13	133.41	244	44.2
		Benzene	12110.6	5760	16	78.12	131	40.6
		Carbon Tetrachloride	14970.0	5760	13	143.82	200	33.6
		Trichloroethene	17421.2	5760	15	131.39	202	37.1
		Tetrachloroethene	22906.8	5760	13	165.83	306	44.6
		1,2,4-Trimethylbenzene	13605.5	5760	13	120.19	182	36.5
		Naphthalene	396.6	5760	13	128.17	5.3	1.0

**APPENDIX TABLE C3D  
SKC SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Mass on sampler (ng)	Exposure Time (min)	Uptake Rate (mL/min)	Molecular Weight (g/mol)	Concentration	
							( $\mu\text{g}/\text{m}^3$ )	(ppbv)
2	ANOVA #12 Chamber 1	2-butanone (MEK)	7951.6	5760	17	72.12	81	27.2
		n-Hexane	13674.2	5760	14	86.18	170	47.6
		1,2-dichloroethane	15117.2	5760	13	98.96	202	49.4
		1,1,1-trichloroethane	19564.3	5760	13	133.41	261	47.4
		Benzene	12336.1	5760	16	78.12	134	41.5
		Carbon Tetrachloride	17142.0	5760	13	143.82	229	38.5
		Trichloroethene	17416.8	5760	15	131.39	202	37.1
		Tetrachloroethene	21003.6	5760	13	165.83	280	40.9
		1,2,4-Trimethylbenzene	12166.1	5760	13	120.19	162	32.7
		Naphthalene	321.5	5760	13	128.17	4.3	0.8
	ANOVA #14 Chamber 1	2-butanone (MEK)	7191.7	5760	17	72.12	73	24.6
		n-Hexane	12115.6	5760	14	86.18	150	42.2
		1,2-dichloroethane	13780.5	5760	13	98.96	184	45.0
		1,1,1-trichloroethane	18540.7	5760	13	133.41	248	44.9
		Benzene	11259.2	5760	16	78.12	122	37.8
		Carbon Tetrachloride	15549.4	5760	13	143.82	208	34.9
		Trichloroethene	15963.2	5760	15	131.39	185	34.0
		Tetrachloroethene	18304.2	5760	13	165.83	244	35.7
		1,2,4-Trimethylbenzene	10739.5	5760	13	120.19	143	28.9
		Naphthalene	352.6	5760	13	128.17	4.7	0.9
	ANOVA #16 Chamber 1	2-butanone (MEK)	7723.9	5760	17	72.12	79	26.5
		n-Hexane	12827.9	5760	14	86.18	159	44.7
		1,2-dichloroethane	14627.3	5760	13	98.96	195	47.8
		1,1,1-trichloroethane	19312.1	5760	13	133.41	258	46.8
		Benzene	11842.6	5760	16	78.12	129	39.8
		Carbon Tetrachloride	15507.5	5760	13	143.82	207	34.8
		Trichloroethene	16855.1	5760	15	131.39	195	35.9
		Tetrachloroethene	20267.0	5760	13	165.83	271	39.5
		1,2,4-Trimethylbenzene	12706.9	5760	13	120.19	170	34.2
		Naphthalene	554.7	5760	13	128.17	7.4	1.4
	ANOVA #13 Chamber 2	2-butanone (MEK)	7743.7	5760	17	72.12	79	26.5
		n-Hexane	12512.6	5760	14	86.18	155	43.5
		1,2-dichloroethane	14500.2	5760	13	98.96	194	47.3
		1,1,1-trichloroethane	19640.0	5760	13	133.41	262	47.5
		Benzene	11722.0	5760	16	78.12	127	39.3
		Carbon Tetrachloride	16194.3	5760	13	143.82	216	36.3
		Trichloroethene	16471.7	5760	15	131.39	191	35.1
		Tetrachloroethene	19590.8	5760	13	165.83	262	38.1
		1,2,4-Trimethylbenzene	11805.1	5760	13	120.19	158	31.7
		Naphthalene	436.3	5760	13	128.17	5.8	1.1
	ANOVA #15 Chamber 2	2-butanone (MEK)	7727.5	5760	17	72.12	79	26.4
		n-Hexane	13036.5	5760	14	86.18	162	45.3
		1,2-dichloroethane	15060.5	5760	13	98.96	201	49.1
		1,1,1-trichloroethane	20289.2	5760	13	133.41	271	49.1
		Benzene	12182.6	5760	16	78.12	132	40.9
		Carbon Tetrachloride	16490.3	5760	13	143.82	220	37.0
		Trichloroethene	17483.6	5760	15	131.39	202	37.2
		Tetrachloroethene	20552.6	5760	13	165.83	274	40.0
		1,2,4-Trimethylbenzene	12070.6	5760	13	120.19	161	32.4
		Naphthalene	357.3	5760	13	128.17	4.8	0.9
	ANOVA #17 Chamber 2	2-butanone (MEK)	7774.1	5760	17	72.12	79	26.6
		n-Hexane	13239.3	5760	14	86.18	164	46.0
		1,2-dichloroethane	15043.1	5760	13	98.96	201	49.1
		1,1,1-trichloroethane	20759.8	5760	13	133.41	277	50.2
		Benzene	12455.9	5760	16	78.12	135	41.8
		Carbon Tetrachloride	17242.0	5760	13	143.82	230	38.7
		Trichloroethene	17723.9	5760	15	131.39	205	37.7
		Tetrachloroethene	20242.0	5760	13	165.83	270	39.4
		1,2,4-Trimethylbenzene	12019.7	5760	13	120.19	161	32.3
		Naphthalene	354.6	5760	13	128.17	4.7	0.9

**APPENDIX TABLE C3D  
SKC SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Mass on sampler (ng)	Exposure Time (min)	Uptake Rate (mL/min)	Molecular Weight (g/mol)	Concentration	
							( $\mu\text{g}/\text{m}^3$ )	(ppbv)
3	ANOVA #22 Chamber 1	2-butanone (MEK)	6972.3	5760	17	72.12	71	23.9
		n-Hexane	13234.3	5760	14	86.18	164	46.0
		1,2-dichloroethane	14553.9	5760	13	98.96	194	47.5
		1,1,1-trichloroethane	20418.7	5760	13	133.41	273	49.4
		Benzene	12268.7	5760	16	78.12	133	41.2
		Carbon Tetrachloride	16512.5	5760	13	143.82	221	37.0
		Trichloroethene	17557.8	5760	15	131.39	203	37.4
		Tetrachloroethene	20517.8	5760	13	165.83	274	39.9
		1,2,4-Trimethylbenzene	11756.6	5760	13	120.19	157	31.6
		Naphthalene	349.5	5760	13	128.17	4.7	0.9
	ANOVA #24 Chamber 1	2-butanone (MEK)	7538.9	5760	17	72.12	77	25.8
		n-Hexane	13312.1	5760	14	86.18	165	46.3
		1,2-dichloroethane	14278.6	5760	13	98.96	191	46.6
		1,1,1-trichloroethane	19440.3	5760	13	133.41	260	47.0
		Benzene	11764.1	5760	16	78.12	128	39.5
		Carbon Tetrachloride	16193.8	5760	13	143.82	216	36.3
		Trichloroethene	16695.9	5760	15	131.39	193	35.5
		Tetrachloroethene	20851.3	5760	13	165.83	278	40.6
		1,2,4-Trimethylbenzene	12099.9	5760	13	120.19	162	32.5
		Naphthalene	375.5	5760	13	128.17	5.0	0.9
	ANOVA #26 Chamber 1	2-butanone (MEK)	6022.1	5760	17	72.12	62	20.6
		n-Hexane	13339.2	5760	14	86.18	165	46.4
		1,2-dichloroethane	14217.4	5760	13	98.96	190	46.4
		1,1,1-trichloroethane	19280.2	5760	13	133.41	257	46.6
		Benzene	11994.2	5760	16	78.12	130	40.2
		Carbon Tetrachloride	15892.5	5760	13	143.82	212	35.7
		Trichloroethene	16734.1	5760	15	131.39	194	35.6
		Tetrachloroethene	20043.9	5760	13	165.83	268	39.0
1,2,4-Trimethylbenzene		11550.6	5760	13	120.19	154	31.0	
Naphthalene		307.0	5760	13	128.17	4.1	0.8	
ANOVA #21 Chamber 2	2-butanone (MEK)	7307.1	5760	17	72.12	75	25.0	
	n-Hexane	13242.8	5760	14	86.18	164	46.0	
	1,2-dichloroethane	14614.8	5760	13	98.96	195	47.6	
	1,1,1-trichloroethane	20277.8	5760	13	133.41	271	49.0	
	Benzene	12191.1	5760	16	78.12	132	40.9	
	Carbon Tetrachloride	16163.7	5760	13	143.82	216	36.2	
	Trichloroethene	17254.8	5760	15	131.39	200	36.7	
	Tetrachloroethene	20903.0	5760	13	165.83	279	40.6	
	1,2,4-Trimethylbenzene	12179.0	5760	13	120.19	163	32.7	
	Naphthalene	353.8	5760	13	128.17	4.7	0.9	
ANOVA #23 Chamber 2	2-butanone (MEK)	7269.6	5760	17	72.12	74	24.9	
	n-Hexane	13176.6	5760	14	86.18	163	45.8	
	1,2-dichloroethane	14077.9	5760	13	98.96	188	45.9	
	1,1,1-trichloroethane	19689.2	5760	13	133.41	263	47.6	
	Benzene	12213.7	5760	16	78.12	133	41.0	
	Carbon Tetrachloride	16472.7	5760	13	143.82	220	36.9	
	Trichloroethene	17402.2	5760	15	131.39	201	37.0	
	Tetrachloroethene	20795.6	5760	13	165.83	278	40.4	
	1,2,4-Trimethylbenzene	11754.1	5760	13	120.19	157	31.5	
	Naphthalene	336.4	5760	13	128.17	4.5	0.8	
ANOVA #25 Chamber 2	2-butanone (MEK)	6225.0	5760	17	72.12	64	21.3	
	n-Hexane	12978.5	5760	14	86.18	161	45.1	
	1,2-dichloroethane	14188.2	5760	13	98.96	189	46.2	
	1,1,1-trichloroethane	19292.1	5760	13	133.41	258	46.6	
	Benzene	11848.3	5760	16	78.12	129	39.7	
	Carbon Tetrachloride	14351.7	5760	13	143.82	192	32.2	
	Trichloroethene	16527.7	5760	15	131.39	191	35.2	
	Tetrachloroethene	20177.0	5760	13	165.83	269	39.2	
	1,2,4-Trimethylbenzene	11833.8	5760	13	120.19	158	31.7	
	Naphthalene	355.7	5760	13	128.17	4.7	0.9	

**Notes:**

- ng - nanograms
- min - minutes
- mL/min - millilitres per minute
- g/mol - grams per mole
- $\mu\text{g}/\text{m}^3$  - micrograms per cubic metre
- ppbv - parts per billion

**APPENDIX TABLE C3E  
RADIELLO SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Concentration	
			( $\mu\text{g}/\text{m}^3$ )	(ppbv)
1	ANOVA 31 Chamber 1	Methylethylketone	25.71	18.95
		n-Hexane	63.61	46.95
		1,2-Dichloroethane	60.05	33.09
		1,1,1-Trichloroethane	72.89	37.00
		Benzene	61.21	41.13
		Carbon tetrachloride	77.83	31.70
		Trichloroethylene	87.28	40.42
		Tetrachloroethylene	102.29	43.90
		1,2,4-Trimethylbenzene	74.97	52.38
		Naphtalene	8.78	11.50
	ANOVA 32 Chamber 1	Methylethylketone	23.09	17.02
		n-Hexane	59.77	44.12
		1,2-Dichloroethane	56.39	31.07
		1,1,1-Trichloroethane	69.51	35.28
		Benzene	56.83	38.18
		Carbon tetrachloride	73.66	30.01
		Trichloroethylene	80.65	37.35
		Tetrachloroethylene	95.73	41.09
		1,2,4-Trimethylbenzene	70.06	48.95
		Naphtalene	7.95	10.41
	ANOVA 33 Chamber 1	Methylethylketone	24.84	18.31
		n-Hexane	63.71	47.03
		1,2-Dichloroethane	61.30	33.78
		1,1,1-Trichloroethane	74.77	37.95
		Benzene	61.76	41.49
		Carbon tetrachloride	79.15	32.24
		Trichloroethylene	87.56	40.55
		Tetrachloroethylene	103.01	44.21
		1,2,4-Trimethylbenzene	74.39	51.98
		Naphtalene	8.07	10.58
	ANOVA 34 Chamber 2	Methylethylketone	24.31	17.90
		n-Hexane	61.26	45.17
		1,2-Dichloroethane	58.81	32.37
		1,1,1-Trichloroethane	72.18	36.60
		Benzene	59.18	39.72
		Carbon tetrachloride	77.77	31.65
		Trichloroethylene	83.51	38.63
		Tetrachloroethylene	99.09	42.49
		1,2,4-Trimethylbenzene	71.11	49.63
		Naphtalene	7.61	9.96
	ANOVA 35 Chamber 2	Methylethylketone	27.82	20.49
		n-Hexane	64.56	47.61
1,2-Dichloroethane		62.32	34.30	
1,1,1-Trichloroethane		77.03	39.06	
Benzene		63.48	42.61	
Carbon tetrachloride		83.05	33.80	
Trichloroethylene		88.81	41.08	
Tetrachloroethylene		105.60	45.28	
1,2,4-Trimethylbenzene		75.07	52.40	
Naphtalene		7.88	10.32	
ANOVA 36 Chamber 2	Methylethylketone	24.44	17.99	
	n-Hexane	62.90	46.39	
	1,2-Dichloroethane	61.52	33.86	
	1,1,1-Trichloroethane	75.82	38.45	
	Benzene	61.48	41.27	
	Carbon tetrachloride	81.74	33.26	
	Trichloroethylene	86.82	40.16	
	Tetrachloroethylene	103.06	44.19	
	1,2,4-Trimethylbenzene	73.27	51.14	
	Naphtalene	7.54	9.87	

**APPENDIX TABLE C3E  
RADIELLO SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Concentration	
			( $\mu\text{g}/\text{m}^3$ )	(ppbv)
2	ANOVA 2 Chamber 1	Methylethylketone	20.34	15.00
		n-Hexane	63.67	47.02
		1,2-Dichloroethane	62.89	34.67
		1,1,1-Trichloroethane	77.72	39.47
		Benzene	62.49	42.00
		Carbon tetrachloride	84.07	34.26
		Trichloroethylene	88.96	41.21
		Tetrachloroethylene	105.66	45.37
		1,2,4-Trimethylbenzene	74.91	52.36
		Naphtalene	8.20	10.75
	ANOVA 2 Chamber 1	Methylethylketone	19.30	14.23
		n-Hexane	59.69	44.08
		1,2-Dichloroethane	59.21	32.64
		1,1,1-Trichloroethane	72.82	36.98
		Benzene	58.51	39.33
		Carbon tetrachloride	78.86	32.14
		Trichloroethylene	81.90	37.94
		Tetrachloroethylene	98.02	42.09
		1,2,4-Trimethylbenzene	69.55	48.61
		Naphtalene	6.83	8.95
	ANOVA 2 Chamber 1	Methylethylketone	21.48	15.84
		n-Hexane	64.21	47.42
		1,2-Dichloroethane	63.32	34.90
		1,1,1-Trichloroethane	78.13	39.67
		Benzene	62.49	42.00
		Carbon tetrachloride	84.81	34.56
		Trichloroethylene	88.29	40.90
		Tetrachloroethylene	104.80	45.00
		1,2,4-Trimethylbenzene	73.87	51.63
		Naphtalene	8.07	10.58
	ANOVA 2 Chamber 2	Methylethylketone	19.88	14.65
		n-Hexane	61.31	45.23
		1,2-Dichloroethane	61.69	33.97
		1,1,1-Trichloroethane	75.82	38.46
		Benzene	59.90	40.22
		Carbon tetrachloride	83.06	33.81
Trichloroethylene		85.68	39.65	
Tetrachloroethylene		100.69	43.19	
1,2,4-Trimethylbenzene		71.20	49.71	
Naphtalene		6.84	8.96	
ANOVA 2 Chamber 2	Methylethylketone	22.09	16.27	
	n-Hexane	64.55	47.62	
	1,2-Dichloroethane	66.01	36.35	
	1,1,1-Trichloroethane	81.31	41.24	
	Benzene	64.52	43.32	
	Carbon tetrachloride	89.22	36.32	
	Trichloroethylene	91.30	42.25	
	Tetrachloroethylene	108.03	46.34	
	1,2,4-Trimethylbenzene	75.32	52.59	
	Naphtalene	7.50	9.82	
ANOVA 2 Chamber 2	Methylethylketone	20.77	15.30	
	n-Hexane	62.31	45.96	
	1,2-Dichloroethane	63.49	34.96	
	1,1,1-Trichloroethane	80.07	40.62	
	Benzene	62.28	41.82	
	Carbon tetrachloride	86.63	35.26	
	Trichloroethylene	87.07	40.30	
	Tetrachloroethylene	105.13	45.09	
	1,2,4-Trimethylbenzene	72.45	50.58	
	Naphtalene	6.95	9.10	

**APPENDIX TABLE C3E  
RADIELLO SAMPLER DATA FOR CENTERPOINT (ANOVA) TESTS**

ANOVA Test	Sampler	Analyte	Concentration	
			( $\mu\text{g}/\text{m}^3$ )	(ppbv)
3	ANOVA 3 Chamber 1	Methylethylketone	26.41	19.46
		n-Hexane	65.31	48.18
		1,2-Dichloroethane	66.30	36.51
		1,1,1-Trichloroethane	83.14	42.17
		Benzene	64.97	43.62
		Carbon tetrachloride	89.74	36.53
		Trichloroethylene	91.82	42.49
		Tetrachloroethylene	110.04	47.20
		1,2,4-Trimethylbenzene	75.03	52.39
		Naphtalene	7.82	10.24
	ANOVA 3 Chamber 1	Methylethylketone	26.88	19.80
		n-Hexane	64.51	47.59
		1,2-Dichloroethane	66.39	36.56
		1,1,1-Trichloroethane	81.86	41.53
		Benzene	64.33	43.19
		Carbon tetrachloride	89.98	36.63
		Trichloroethylene	91.48	42.33
		Tetrachloroethylene	108.59	46.57
		1,2,4-Trimethylbenzene	74.11	51.74
		Naphtalene	7.21	9.44
	ANOVA 3 Chamber 1	Methylethylketone	25.65	18.89
		n-Hexane	60.30	44.48
		1,2-Dichloroethane	61.77	34.01
		1,1,1-Trichloroethane	76.52	38.82
		Benzene	59.48	39.94
		Carbon tetrachloride	83.86	34.14
		Trichloroethylene	83.74	38.76
		Tetrachloroethylene	98.61	42.29
		1,2,4-Trimethylbenzene	68.18	47.60
		Naphtalene	6.59	8.62
	ANOVA 3 Chamber 2	Methylethylketone	26.49	19.51
		n-Hexane	62.52	46.10
		1,2-Dichloroethane	64.69	35.61
		1,1,1-Trichloroethane	80.36	40.75
		Benzene	61.98	41.60
		Carbon tetrachloride	88.65	36.07
		Trichloroethylene	88.17	40.79
		Tetrachloroethylene	104.65	44.87
		1,2,4-Trimethylbenzene	71.76	50.08
		Naphtalene	6.85	8.97
	ANOVA 3 Chamber 2	Methylethylketone	27.41	20.19
		n-Hexane	64.63	47.66
		1,2-Dichloroethane	65.99	36.32
		1,1,1-Trichloroethane	83.39	42.29
		Benzene	63.86	42.87
		Carbon tetrachloride	91.43	37.20
		Trichloroethylene	90.45	41.84
		Tetrachloroethylene	107.43	46.06
1,2,4-Trimethylbenzene		72.76	50.78	
Naphtalene		6.44	8.42	
ANOVA 3 Chamber 2	Methylethylketone	25.76	18.97	
	n-Hexane	63.33	46.70	
	1,2-Dichloroethane	66.91	36.83	
	1,1,1-Trichloroethane	83.38	42.28	
	Benzene	63.47	42.60	
	Carbon tetrachloride	91.79	37.35	
	Trichloroethylene	90.47	41.85	
	Tetrachloroethylene	108.00	46.31	
	1,2,4-Trimethylbenzene	72.39	50.53	
	Naphtalene	6.99	9.15	

**Notes:**

- ng - nanograms
- min - minutes
- mL/min - millilitres per minute
- g/mol - grams per mole
- $\mu\text{g}/\text{m}^3$  - micrograms per cubic metre
- ppbv - parts per billion

## **Appendix D**

### **Results of Fractional Factorial Low Concentration Laboratory Tests**



**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Run Number:		1,440 (1 day)											
	Exposure Time (min):		ATD Tube - CB		ATD Tube - TA		WMS		Radiello		SKC Ultra			
	Replicate		Mass (ng)	Concn (ppbw)	Mass (ng)	Concn (ppbw)	Mass (ng)	Concn (ppbw)	Mass (ng)	Concn (ppbw)	Mass (ng)	Concn (ppbw)		
Methylethylketone	1	15	180	6.9	180	82	106	17	50	935	13			
n-Hexane	1	290	220	111	220	84	161	31	89	6573	90			
1,2-Dichloroethane	1	180	210	60	210	70	104	33	72	6304	81			
1,1,1-Trichloroethane	1	190	270	47	270	67	127	41	83	8108	77			
Benzene	1	240	190	145	190	115	118	32	84	6120	81			
Carbon tetrachloride	1	270	300	62	300	69	130	46	79	5549	49			
Trichloroethene	1	330	290	83	290	73	2600	44	81	8294	70			
Tetrachloroethene	1	460	370	112	370	90	4600	54	91	10087	77			
1,2,4-Trimethylbenzene	1	260	58	250	55	5300	58	31	86	5517	58			
Naphthalene	1	23	31	5.9	31	8.0	0.60	1.9	10	18	0.18			
Methylethylketone	2	1.8	180	0.8	180	82	110	18	53	1248	17			
n-Hexane	2	290	220	111	220	84	1200	31	91	7826	107			
1,2-Dichloroethane	2	170	220	57	220	73	1700	35	76	7329	94			
1,1,1-Trichloroethane	2	200	280	50	280	69	1300	43	85	8517	81			
Benzene	2	240	200	145	200	121	1200	32	86	6779	90			
Carbon tetrachloride	2	220	320	51	320	73	1800	48	82	5503	49			
Trichloroethene	2	330	300	83	300	75	2700	46	84	8965	75			
Tetrachloroethene	2	460	390	112	390	95	4600	56	94	10749	82			
1,2,4-Trimethylbenzene	2	250	260	55	260	58	5100	29	81	5938	63			
Naphthalene	2	21	32	5.4	32	8.2	0.60	1.5	7.8	20	0.20			
Methylethylketone	3	40	240	18	240	110	670	7.1	21	1095	15			
n-Hexane	3	300	310	115	310	119	1300	29	85	6760	93			
1,2-Dichloroethane	3	180	290	60	290	97	1900	32	69	6427	83			
1,1,1-Trichloroethane	3	210	320	52	320	79	1500	40	79	8041	77			
Benzene	3	250	210	151	210	127	1500	30	79	6223	82			
Carbon tetrachloride	3	290	320	67	320	73	2100	46	80	5132	45			
Trichloroethene	3	340	270	85	270	68	3100	42	76	8103	68			
Tetrachloroethene	3	450	370	109	370	90	5400	51	86	9865	76			
1,2,4-Trimethylbenzene	3	250	290	55	290	64	6400	27	73	5237	55			
Naphthalene	3	23	32	5.9	32	8.2	0.81	1.3	6.9	17	0.17			

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Run Number: Exposure Time (min):	1																			
		ATD Tube - CB				ATD Tube - TA				WMS				Radiello				SKC Ultra			
		Mass (ng)	Concn (ppbv)	Replicate	1,440 (1 day)	Mass (ng)	Concn (ppbv)	Replicate	1,440 (1 day)	Mass (ng)	Concn (ppbv)	Replicate	1,440 (1 day)	Mass (ng)	Concn (ppbv)	Replicate	1,440 (1 day)	Mass (ng)	Concn (ppbv)	Replicate	1,440 (1 day)
Methyl ethyl ketone	1	15	6.9	1	180	82	1	580	106	1	17	50	1	935	13	1	1248	53	1	17	
n-Hexane	1	290	111	1	220	84	1	1100	161	1	31	89	1	6573	90	1	7826	91	1	107	
1,2-Dichloroethane	1	180	60	1	210	70	1	1600	104	1	33	72	1	6304	81	1	7329	76	1	94	
1,1,1-Trichloroethane	1	190	47	1	270	67	1	1300	127	1	41	83	1	8108	77	1	8517	85	1	81	
Benzene	1	240	145	1	190	115	1	1200	118	1	32	84	1	6120	81	1	6779	86	1	90	
Carbon tetrachloride	1	270	62	1	300	69	1	1700	130	1	46	79	1	5549	49	1	5503	82	1	75	
Trichloroethene	1	330	83	1	290	73	1	2600	100	1	44	81	1	8294	70	1	8965	84	1	84	
Tetrachloroethene	1	460	112	1	370	90	1	4600	86	1	54	91	1	10087	77	1	10749	94	1	82	
1,2,4-Trimethylbenzene	1	260	58	1	250	55	1	5300	58	1	31	86	1	5517	58	1	5938	81	1	63	
Naphthalene	1	23	5.9	1	31	8.0	1	120	0.60	1	1.9	1.0	1	18	0.18	1	20	0.20	1	0.20	
Methyl ethyl ketone	2	1.8	0.8	2	180	82	2	600	110	2	18	53	2	1248	17	2	1248	53	2	17	
n-Hexane	2	290	111	2	220	84	2	1200	176	2	31	91	2	7826	107	2	7826	91	2	107	
1,2-Dichloroethane	2	170	57	2	220	73	2	1700	110	2	35	76	2	7329	94	2	7329	76	2	94	
1,1,1-Trichloroethane	2	200	50	2	280	69	2	1300	127	2	43	85	2	8517	81	2	8517	85	2	81	
Benzene	2	240	145	2	200	121	2	1200	118	2	32	86	2	6779	90	2	6779	86	2	90	
Carbon tetrachloride	2	220	51	2	320	73	2	1800	138	2	48	82	2	5503	49	2	5503	82	2	49	
Trichloroethene	2	330	83	2	300	75	2	2700	103	2	46	84	2	8965	75	2	8965	84	2	75	
Tetrachloroethene	2	460	112	2	390	95	2	4600	86	2	56	94	2	10749	82	2	10749	94	2	82	
1,2,4-Trimethylbenzene	2	250	55	2	260	58	2	5100	56	2	29	81	2	5938	63	2	5938	81	2	63	
Naphthalene	2	21	5.4	2	32	8.2	2	120	0.60	2	1.5	1.5	2	20	0.20	2	20	1.5	2	0.20	
Methyl ethyl ketone	3	40	18	3	240	110	3	670	123	3	7.1	21	3	1095	15	3	1095	21	3	15	
n-Hexane	3	300	115	3	310	119	3	1300	190	3	29	85	3	6760	93	3	6760	85	3	93	
1,2-Dichloroethane	3	180	60	3	290	97	3	1900	123	3	32	69	3	6427	83	3	6427	69	3	83	
1,1,1-Trichloroethane	3	210	52	3	320	79	3	1500	146	3	40	79	3	8041	77	3	8041	79	3	77	
Benzene	3	250	151	3	210	127	3	1500	148	3	30	79	3	6223	82	3	6223	79	3	82	
Carbon tetrachloride	3	290	67	3	320	73	3	2100	161	3	46	80	3	5132	45	3	5132	79	3	45	
Trichloroethene	3	340	85	3	270	68	3	3100	119	3	42	76	3	8103	68	3	8103	68	3	68	
Tetrachloroethene	3	450	109	3	370	90	3	5400	101	3	51	86	3	9865	76	3	9865	90	3	76	
1,2,4-Trimethylbenzene	3	250	55	3	290	64	3	6400	70	3	27	73	3	5237	55	3	5237	64	3	55	
Naphthalene	3	23	5.9	3	32	8.2	3	160	0.81	3	1.3	6.9	3	17	0.17	3	17	6.9	3	0.17	

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		2											
Exposure Time (min):		1,452 (1 day)											
Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		SKC Ultra			
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methyl ethyl ketone	1	ND	ND	3.4	1.5	ND	ND	ND	ND	2.4	0.032		
n-Hexane	1	7.5	2.9	2.8	1.1	240	35	0.41	1.2	34	0.47		
1,2-Dichloroethane	1	1.5	0.50	2.2	0.73	ND	ND	ND	ND	1.5	0.019		
1,1,1-Trichloroethane	1	3.1	0.76	2.5	0.61	ND	ND	0.18	0.36	9.7	0.09		
Benzene	1	5.2	3.1	3.6	2.2	55	5.4	0.35	0.92	68	0.89		
Carbon tetrachloride	1	4.9	1.1	3.0	0.68	ND	ND	0.20	0.34	3.3	0.029		
Trichloroethene	1	2.9	0.72	2.8	0.70	ND	ND	ND	ND	1.3	0.011		
Tetrachloroethene	1	3.5	0.84	3.2	0.77	ND	ND	ND	ND	75	0.57		
1,2,4-Trimethylbenzene	1	3.4	0.75	2.9	0.64	ND	ND	0.22	0.60	6.9	0.072		
Naphthalene	1	3.5	0.90	9.4	2.4	ND	ND	ND	ND	4.6	0.045		
Methyl ethyl ketone	2	ND	ND	3.6	1.6	ND	ND	ND	ND	0.80	0.011		
n-Hexane	2	5.2	2.0	2.8	1.1	160	23	0.43	1.2	24	0.33		
1,2-Dichloroethane	2	1.6	0.53	2.2	0.73	ND	ND	ND	ND	2.0	0.025		
1,1,1-Trichloroethane	2	3.2	0.79	2.5	0.61	ND	ND	0.17	0.34	6.0	0.057		
Benzene	2	4.2	2.5	3.4	2.0	68	6.6	0.31	0.81	59	0.77		
Carbon tetrachloride	2	5.3	1.2	2.9	0.66	ND	ND	0.21	0.36	2.2	0.019		
Trichloroethene	2	3.0	0.75	2.7	0.67	ND	ND	ND	ND	1.0	0.0083		
Tetrachloroethene	2	3.6	0.87	3.4	0.82	ND	ND	ND	ND	68	0.52		
1,2,4-Trimethylbenzene	2	3.0	0.66	2.8	0.62	ND	ND	0.20	0.55	2.6	0.027		
Naphthalene	2	3.3	0.84	3.5	0.90	ND	ND	ND	ND	4.2	0.041		
Methyl ethyl ketone	3	NA	NA	3.2	1.5	ND	ND	ND	ND	4.0	0.053		
n-Hexane	3	NA	NA	5.4	2.1	190	28	0.38	1.1	30	0.41		
1,2-Dichloroethane	3	NA	NA	2.2	0.73	ND	ND	ND	ND	2.0	0.025		
1,1,1-Trichloroethane	3	NA	NA	2.5	0.61	ND	ND	0.18	0.36	5.6	0.053		
Benzene	3	NA	NA	3.0	1.8	ND	ND	0.37	1.0	54	0.71		
Carbon tetrachloride	3	NA	NA	2.9	0.66	ND	ND	0.19	0.32	2.2	0.02		
Trichloroethene	3	NA	NA	2.7	0.67	ND	ND	ND	ND	1.1	0.0091		
Tetrachloroethene	3	NA	NA	3.3	0.80	ND	ND	0.19	0.32	53	0.41		
1,2,4-Trimethylbenzene	3	NA	NA	3.3	0.73	ND	ND	0.26	0.71	5.4	0.057		
Naphthalene	3	NA	NA	2.4	0.61	ND	ND	ND	ND	6.1	0.060		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		3											
Exposure Time (min):		1,441 (1 day)											
Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		SKC Ultra			
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methylethylketone	1	15	7.1	150	71	400	76	24	72	4876	68		
n-Hexane	1	300	120	200	80	810	123	31	93	6982	99		
1,2-Dichloroethane	1	160	56	150	52	1100	74	39	87	7290	97		
1,1,1-Trichloroethane	1	180	46	230	59	870	88	47	97	7445	74		
Benzene	1	260	163	170	107	870	89	33	90	7249	100		
Carbon tetrachloride	1	280	67	250	60	1200	96	50	89	10371	95		
Trichloroethene	1	350	92	220	58	1900	76	49	93	10044	88		
Tetrachloroethene	1	470	119	280	71	3800	74	56	99	11340	90		
1,2,4-Trimethylbenzene	1	260	60	210	48	6000	69	34	96	4104	45		
Naphthalene	1	21	5.6	27	7.2	200	1.0	3.3	1.7	12	0.12		
Methylethylketone	2	40	19	130	62	450	86	24	73	2731	38		
n-Hexane	2	290	116	170	68	900	137	33	98	7310	104		
1,2-Dichloroethane	2	150	52	170	59	1300	87	41	92	7217	96		
1,1,1-Trichloroethane	2	210	54	230	59	1000	101	50	103	9172	91		
Benzene	2	250	157	160	101	950	97	34	94	7052	97		
Carbon tetrachloride	2	280	67	260	62	1300	104	51	91	4486	41		
Trichloroethene	2	350	92	240	63	2100	84	51	97	9499	83		
Tetrachloroethene	2	450	114	340	86	4000	77	58	101	11281	90		
1,2,4-Trimethylbenzene	2	260	60	250	58	6000	69	34	98	6586	72		
Naphthalene	2	22	5.9	31	8.3	180	0.94	3.0	1.6	20	0		
Methylethylketone	3	170	81	140	67	330	63	25	76	2804	39		
n-Hexane	3	300	120	170	68	680	103	33	98	7316	104		
1,2-Dichloroethane	3	170	59	170	59	970	65	40	90	7275	97		
1,1,1-Trichloroethane	3	260	67	240	62	760	77	50	103	8967	89		
Benzene	3	250	157	160	101	740	76	34	94	6914	95		
Carbon tetrachloride	3	300	72	260	62	1000	80	54	96	4069	37		
Trichloroethene	3	350	92	240	63	1600	64	50	95	9217	80		
Tetrachloroethene	3	460	116	350	88	3200	62	58	101	10852	86		
1,2,4-Trimethylbenzene	3	280	65	260	60	5200	59	35	99	6119	67		
Naphthalene	3	23	6.2	41	11	160	0.84	3.1	1.7	13	0.14		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		4														
Exposure Time (min):		10,099 (7 days)														
Analyte	Replicate	A1D Tube - CB			A1D Tube - TA			WMIS			Radiello			SKC Ultra		
		Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)
Methylethylketone	1	ND	ND	1.3	2.7	1.3	ND	ND	26	ND	ND	ND	ND	6.3	0.088	1.2
n-Hexane	1	4.5	1.8	3.1	3.1	1.2	1.70	1.2	83	1.2	83	1.2	83	1.2	83	1.2
1,2-Dichloroethane	1	2.0	0.69	2.0	2.0	0.69	ND	ND	19	ND	ND	ND	19	0.25	0.25	0.25
1,1,1-Trichloroethane	1	2.7	0.70	2.5	2.5	0.64	ND	ND	11	ND	ND	ND	11	0.11	0.11	0.11
Benzene	1	4.4	2.8	2.9	2.9	1.8	67	6.9	261	1.2	261	1.2	261	3.6	3.6	3.6
Carbon tetrachloride	1	3.8	0.91	3.0	3.0	0.72	ND	ND	3.7	0.48	3.7	0.48	3.7	0.034	0.034	0.034
Trichloroethene	1	3.1	0.81	2.5	2.5	0.65	ND	ND	5.0	ND	5.0	ND	5.0	0.044	0.044	0.044
Tetrachloroethene	1	3.3	0.83	3.7	3.7	0.93	ND	ND	90	ND	90	ND	90	0.71	0.71	0.71
1,2,4-Trimethylbenzene	1	2.6	0.60	3.2	3.2	0.74	ND	ND	49	0.86	49	0.86	49	0.54	0.54	0.54
Naphthalene	1	2.6	0.70	8.9	8.9	2.4	ND	ND	10	0.83	10	0.83	10	0.11	0.11	0.11
Methylethylketone	2	ND	ND	2.4	2.4	1.1	ND	ND	1.0	ND	1.0	ND	1.0	0.014	0.014	0.014
n-Hexane	2	7.5	3.0	2.7	2.7	1.1	210	32	82	1.4	82	1.4	82	1.2	1.2	1.2
1,2-Dichloroethane	2	1.9	0.66	2.0	2.0	0.69	ND	ND	19	ND	19	ND	19	0.25	0.25	0.25
1,1,1-Trichloroethane	2	2.9	0.75	2.4	2.4	0.62	ND	ND	12	0.22	12	0.22	12	0.12	0.12	0.12
Benzene	2	5.3	3.3	2.4	2.4	1.5	63	6.4	70	1.1	70	1.1	70	1.0	1.0	1.0
Carbon tetrachloride	2	4.1	1.0	3.1	3.1	0.74	ND	ND	3.7	0.22	3.7	0.22	3.7	0.034	0.034	0.034
Trichloroethene	2	3.4	0.89	2.4	2.4	0.63	ND	ND	5.0	ND	5.0	ND	5.0	0.044	0.044	0.044
Tetrachloroethene	2	3.6	0.91	3.6	3.6	0.91	ND	ND	84	ND	84	ND	84	0.67	0.67	0.67
1,2,4-Trimethylbenzene	2	2.8	0.65	2.9	2.9	0.67	ND	ND	34	0.30	34	0.30	34	0.37	0.37	0.37
Naphthalene	2	2.4	0.64	3.1	3.1	0.83	ND	ND	8.8	0.77	8.8	0.77	8.8	0.091	0.091	0.091
Methylethylketone	3	ND	ND	2.8	2.8	1.3	ND	ND	7.4	ND	7.4	ND	7.4	0.10	0.10	0.10
n-Hexane	3	4.8	1.9	3.1	3.1	1.2	210	32	95	1.5	95	1.5	95	1.4	1.4	1.4
1,2-Dichloroethane	3	1.7	0.59	2.1	2.1	0.73	ND	ND	31	ND	31	ND	31	0.42	0.42	0.42
1,1,1-Trichloroethane	3	2.7	0.70	2.5	2.5	0.64	ND	ND	3.4	0.26	3.4	0.26	3.4	0.034	0.034	0.034
Benzene	3	5.4	3.4	2.5	2.5	1.6	69	7.1	219	1.0	219	1.0	219	3.0	3.0	3.0
Carbon tetrachloride	3	3.7	0.88	3.2	3.2	0.76	ND	ND	12	0.21	12	0.21	12	0.11	0.11	0.11
Trichloroethene	3	3.4	0.89	2.5	2.5	0.65	ND	ND	77	ND	77	ND	77	0.67	0.67	0.67
Tetrachloroethene	3	3.6	0.91	3.7	3.7	0.93	ND	ND	100	ND	100	ND	100	0.80	0.80	0.80
1,2,4-Trimethylbenzene	3	3.6	0.83	3.2	3.2	0.74	ND	ND	28	0.35	28	0.35	28	0.31	0.31	0.31
Naphthalene	3	2.9	0.78	3.0	3.0	0.80	ND	ND	9.4	0.84	9.4	0.84	9.4	0.10	0.10	0.10

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		5											
Exposure Time (min):		10,099 (7 days)											
Analyte	Replicate	AID Tube - CB		AID Tube - TA		WMS		Radiello		SKC Ultra			
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methyl ethyl ketone	1	150	10	520	35	1400	38	63	2.7	12586	25		
n-Hexane	1	2200	125	720	41	3700	80	191	82	38744	78		
1,2-Dichloroethane	1	810	40	770	38	6700	64	110	35	9456	18		
1,1,1-Trichloroethane	1	1100	40	1000	37	5200	75	131	38	34053	48		
Benzene	1	1600	143	740	66	5100	74	202	79	32054	63		
Carbon tetrachloride	1	1600	54	1200	41	7800	88	162	41	47044	61		
Trichloroethene	1	2100	78	1200	45	10000	57	270	73	53233	66		
Tetrachloroethene	1	3000	108	1900	68	24000	66	396	99	89700	101		
1,2,4-Trimethylbenzene	1	2100	69	1700	56	31000	50	264	107	49962	78		
Naphthalene	1	240	9.1	190	7.2	840	0.62	27	20	2741	4.0		
Methyl ethyl ketone	2	470	32	540	37	1200	32	6.5	2.8	8769	17		
n-Hexane	2	2300	130	750	42	3000	65	188	80	44367	90		
1,2-Dichloroethane	2	850	42	830	41	5600	53	113	36	8571	16		
1,1,1-Trichloroethane	2	1300	48	1200	44	4300	62	133	39	38429	54		
Benzene	2	1600	143	1200	107	4300	62	198	77	35805	70		
Carbon tetrachloride	2	1600	54	1300	44	6500	73	164	41	44323	58		
Trichloroethene	2	2100	78	1300	48	9300	53	264	71	53725	66		
Tetrachloroethene	2	3100	111	2000	72	23000	63	386	96	90777	103		
1,2,4-Trimethylbenzene	2	2200	72	1900	62	31000	50	256	104	76888	120		
Naphthalene	2	240	9.1	210	8.0	890	0.66	25	19	4116	6.0		
Methyl ethyl ketone	3	190	13	550	37	1400	38	3.1	1.3	8304	17		
n-Hexane	3	2200	125	760	43	3800	82	192	82	45570	92		
1,2-Dichloroethane	3	790	39	860	42	7100	68	111	35	6597	13		
1,1,1-Trichloroethane	3	1200	44	1200	44	5500	79	131	39	33428	47		
Benzene	3	1700	152	1200	107	5400	78	202	79	34470	67		
Carbon tetrachloride	3	1600	54	1400	47	8300	94	163	41	42157	55		
Trichloroethene	3	2100	78	1300	48	11000	62	269	72	51765	64		
Tetrachloroethene	3	3200	115	2100	75	25000	69	398	99	94735	107		
1,2,4-Trimethylbenzene	3	2300	75	2000	65	34000	55	265	108	83208	130		
Naphthalene	3	240	9.1	220	8.4	950	0.71	27	20	4689	6.9		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		10,087 (7 days)											
Exposure Time (min):		6											
Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		SKC Ultra			
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methyl ethyl ketone	1	ND	ND	6.7	0.45	33	0.89	ND	ND	1.22	0.24		
n-Hexane	1	27	1.5	11	0.62	150	3.2	2.1	0.88	1.68	0.34		
1,2-Dichloroethane	1	1.5	0.074	10	0.49	52	0.50	1.7	0.53	1.72	0.33		
1,1,1-Trichloroethane	1	6.3	0.23	14	0.51	43	0.62	2.2	0.63	2.34	0.33		
Benzene	1	20	1.8	10	0.87	40	0.58	2.0	0.76	7.07	1.4		
Carbon tetrachloride	1	6.7	0.23	15	0.51	61	0.69	3.0	0.75	1.44	0.19		
Trichloroethene	1	12	0.45	12	0.45	83	0.47	2.7	0.72	2.37	0.29		
Tetrachloroethene	1	31	1.1	21	0.75	160	0.44	3.5	0.87	9.69	1.1		
1,2,4-Trimethylbenzene	1	18	0.59	20	0.65	180	0.29	2.3	0.94	7.7	0.12		
Naphthalene	1	20	0.76	23	0.88	51	0.038	2.3	1.7	1.61	0.24		
Methyl ethyl ketone	2	2.0	0.14	7.4	0.50	78	2.1	ND	ND	86	0.17		
n-Hexane	2	30	1.7	12	0.68	250	5.4	2.0	0.87	4.39	0.89		
1,2-Dichloroethane	2	4.5	0.22	10	0.49	53	0.51	1.7	0.55	2.56	0.49		
1,1,1-Trichloroethane	2	10	0.37	14	0.51	43	0.62	2.6	0.77	3.27	0.46		
Benzene	2	21	1.9	12	1.1	43	0.62	2.1	0.80	5.40	1.1		
Carbon tetrachloride	2	13	0.44	15	0.51	61	0.69	2.9	0.74	2.15	0.28		
Trichloroethene	2	21	0.78	12	0.45	81	0.46	2.8	0.74	2.57	0.32		
Tetrachloroethene	2	32	1.1	21	0.75	160	0.44	3.6	0.90	12.49	1.4		
1,2,4-Trimethylbenzene	2	20	0.65	19	0.62	170	0.28	2.3	0.93	1.85	0.29		
Naphthalene	2	24	0.91	22	0.84	47	0.035	2.2	1.7	2.42	0.35		
Methyl ethyl ketone	3	ND	ND	5.8	0.39	ND	ND	ND	ND	80	0.16		
n-Hexane	3	25	1.4	12	0.68	140	3.0	2.0	0.87	1.58	0.32		
1,2-Dichloroethane	3	1.4	0.069	10	0.49	57	0.54	1.9	0.60	1.49	0.28		
1,1,1-Trichloroethane	3	5.9	0.22	15	0.55	45	0.65	2.1	0.60	1.56	0.22		
Benzene	3	18	1.6	10	0.87	43	0.62	2.1	0.80	4.05	0.79		
Carbon tetrachloride	3	6.2	0.21	15	0.51	63	0.71	2.4	0.60	1.04	0.14		
Trichloroethene	3	11	0.41	13	0.48	86	0.49	2.3	0.63	1.46	0.18		
Tetrachloroethene	3	31	1.1	21	0.75	160	0.44	3.5	0.87	12.11	1.4		
1,2,4-Trimethylbenzene	3	18	0.59	19	0.62	160	0.26	2.3	0.94	2.0	0.030		
Naphthalene	3	21	0.80	21	0.80	48	0.036	2.2	1.7	1.25	0.18		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		SKC Ultra	
		Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)
		Exposure Time (min):		Exposure Time (min):		Exposure Time (min):		Exposure Time (min):		Exposure Time (min):	
		Run Number: 7									
		10,086 (7 days)									
Methyl ethyl ketone	1	110	7.2	710	46	4200	110	203	84	33574	65
n-Hexane	1	2000	109	990	54	5900	123	219	91	44397	87
1,2-Dichloroethane	1	1100	52	1100	52	9900	91	276	85	33068	61
1,1,1-Trichloroethane	1	1600	57	1400	49	8100	113	331	94	57932	79
Benzene	1	1700	147	1400	121	7800	110	230	87	40711	77
Carbon tetrachloride	1	1900	62	1700	56	11000	120	359	88	66334	84
Trichloroethene	1	2300	83	1600	57	16000	88	343	89	62266	74
Tetrachloroethene	1	3000	104	2300	80	28000	74	391	94	88754	97
1,2,4-Trimethylbenzene	1	2100	66	1900	60	27000	42	238	93	78352	118
Naphthalene	1	220	8.1	210	7.7	830	0.60	20	14	4007	5.7
Methyl ethyl ketone	2	420	27	710	46	4000	105	190	79	34627	67
n-Hexane	2	2000	109	980	54	5500	115	210	87	46855	92
1,2-Dichloroethane	2	1100	52	1100	52	9400	87	265	82	34538	63
1,1,1-Trichloroethane	2	1600	57	1400	49	7500	104	318	91	61983	84
Benzene	2	1700	147	1300	112	7400	104	220	83	43009	81
Carbon tetrachloride	2	2000	66	1600	52	10000	109	347	85	69715	88
Trichloroethene	2	2300	83	1600	57	15000	82	328	85	66252	79
Tetrachloroethene	2	2900	101	2400	83	28000	74	375	90	90766	99
1,2,4-Trimethylbenzene	2	2000	63	2000	63	27000	42	230	90	78853	119
Naphthalene	2	210	7.7	210	7.7	870	0.63	20	15	4217	6.0
Methyl ethyl ketone	3	510	33	710	46	4300	112	187	78	31558	61
n-Hexane	3	2100	115	990	54	6000	125	219	91	45590	89
1,2-Dichloroethane	3	1100	52	1000	48	10000	92	274	85	33220	61
1,1,1-Trichloroethane	3	1600	57	1400	49	8200	114	330	94	60301	82
Benzene	3	1700	147	1500	129	7700	108	229	86	41728	79
Carbon tetrachloride	3	2000	66	1600	52	11000	120	364	89	64209	81
Trichloroethene	3	2300	83	1600	57	16000	88	342	89	63951	77
Tetrachloroethene	3	3000	104	2300	80	30000	80	391	94	87016	95
1,2,4-Trimethylbenzene	3	2100	66	1900	60	28000	44	241	95	75820	114
Naphthalene	3	220	8.1	210	7.7	870	0.63	21	16	4036	5.7



**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number: 8		10.083 (7 days)													
Exposure Time (min):		AID Tube - CB			AID Tube - TA			WMS			Radiello			WMS	
Analyte	Replicate	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)
Methyl ethyl ketone	1	6.2	0.41	8.6	0.56	28	0.73	190	4.0	1.2	0.51	135	0.26	662	1.3
n-Hexane	1	27	1.5	15	0.82	62	0.57	190	4.0	2.2	0.90	576	1.1	662	1.3
1,2-Dichloroethane	1	12	0.57	12	0.57	62	0.57	62	0.57	2.3	0.71	576	1.1	662	1.3
1,1,1-Trichloroethane	1	19	0.67	17	0.60	58	0.81	58	0.81	3.0	0.86	62	0.084	500	0.94
Benzene	1	22	1.9	11	0.95	52	0.73	52	0.73	2.0	0.77	500	0.94	500	0.94
Carbon tetrachloride	1	25	0.82	18	0.59	75	0.82	75	0.82	3.0	0.72	328	0.41	541	0.65
Trichloroethene	1	24	0.86	15	0.54	100	0.55	100	0.55	2.7	0.71	541	0.65	541	0.65
Tetrachloroethene	1	29	1.0	23	0.80	170	0.45	170	0.45	3.4	0.82	987	1.1	987	1.1
1,2,4-Trimethylbenzene	1	19	0.60	18	0.57	140	0.22	140	0.22	2.1	0.84	153	0.23	267	0.38
Naphthalene	1	20	0.74	19	0.70	32	0.023	32	0.023	1.5	1.1	267	0.38	267	0.38
Methyl ethyl ketone	2	38	0.25	7.6	0.50	24	0.63	24	0.63	1.2	0.51	176	0.34	176	0.34
n-Hexane	2	25	1.4	14	0.77	200	4.2	200	4.2	2.1	0.87	515	1.0	515	1.0
1,2-Dichloroethane	2	10	0.48	12	0.57	69	0.64	69	0.64	2.6	0.80	489	0.90	489	0.90
1,1,1-Trichloroethane	2	17	0.60	16	0.57	57	0.79	57	0.79	3.0	0.85	474	0.64	474	0.64
Benzene	2	21	1.8	11	0.95	53	0.74	53	0.74	1.9	0.73	493	0.93	493	0.93
Carbon tetrachloride	2	23	0.75	18	0.59	80	0.87	80	0.87	3.1	0.76	252	0.32	252	0.32
Trichloroethene	2	23	0.83	15	0.54	100	0.5	100	0.5	2.6	0.68	506	0.61	506	0.61
Tetrachloroethene	2	30	1.0	22	0.76	180	0.48	180	0.48	3.2	0.78	928	1.0	928	1.0
1,2,4-Trimethylbenzene	2	18	0.57	18	0.57	150	0.24	150	0.24	2.1	0.82	662	1.0	662	1.0
Naphthalene	2	22	0.81	19	0.70	30	0.022	30	0.022	1.8	1.3	325	0.46	325	0.46
Methyl ethyl ketone	3	1.7	0.11	7.8	0.51	24	0.63	24	0.63	1.1	0.47	202	0.39	202	0.39
n-Hexane	3	26	1.4	14	0.77	180	3.8	180	3.8	2.1	0.89	566	1.1	566	1.1
1,2-Dichloroethane	3	8.6	0.41	12	0.57	72	0.67	72	0.67	2.2	0.69	494	0.91	494	0.91
1,1,1-Trichloroethane	3	15	0.53	17	0.60	58	0.81	58	0.81	2.9	0.81	517	0.70	517	0.70
Benzene	3	19	1.6	12	0.59	83	0.91	83	0.91	1.9	0.72	440	0.83	440	0.83
Carbon tetrachloride	3	22	0.72	18	0.59	83	0.91	83	0.91	3.1	0.76	246	0.31	246	0.31
Trichloroethene	3	23	0.83	15	0.54	100	0.55	100	0.55	2.7	0.69	516	0.62	516	0.62
Tetrachloroethene	3	30	1.0	23	0.80	180	0.48	180	0.48	3.4	0.81	967	1.1	967	1.1
1,2,4-Trimethylbenzene	3	19	0.60	18	0.57	150	0.24	150	0.24	2.1	0.84	669	1.0	669	1.0
Naphthalene	3	20	0.74	19	0.70	37	0.027	37	0.027	1.5	1.1	156	0.22	156	0.22

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 9											
		Exposure Time (min):						5,758 (4 days)					
		ATD Tube - CB		ATD Tube - TA		WMS		Radiello		WMS			
Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methylethylketone	1	50	5.8	200	23	700	33	10	7	8116	28		
n-Hexane	1	530	52	270	26	1300	48	59	44	11360	39		
1,2-Dichloroethane	1	310	26	300	25	2300	38	63	35	10601	35		
1,1,1-Trichloroethane	1	500	31	380	24	1800	45	82	42	15687	38		
Benzene	1	490	75	280	43	1600	40	60	41	10323	35		
Carbon tetrachloride	1	600	35	450	26	2400	47	98	40	15866	36		
Trichloroethene	1	650	42	420	27	3800	37	85	40	14722	31		
Tetrachloroethene	1	830	51	650	40	7100	34	102	44	21034	41		
1,2,4-Trimethylbenzene	1	550	31	530	30	8300	23	66	46	16414	44		
Naphthalene	1	52	3.4	60	3.9	190	0.24	4.3	5.71	1334	3.4		
Methylethylketone	2	22	2.6	200	23	700	33	10	7	9449	32		
n-Hexane	2	520	51	280	27	1200	45	61	45	11328	39		
1,2-Dichloroethane	2	320	27	300	25	2200	36	65	36	11336	37		
1,1,1-Trichloroethane	2	510	32	390	25	1700	42	84	43	15457	37		
Benzene	2	490	75	290	44	1600	40	61	42	10366	35		
Carbon tetrachloride	2	590	34	450	26	2400	47	96	39	15978	36		
Trichloroethene	2	650	42	430	27	3700	36	88	41	14887	32		
Tetrachloroethene	2	840	52	660	41	7200	34	105	45	20851	41		
1,2,4-Trimethylbenzene	2	550	31	530	30	8900	25	67	47	14800	40		
Naphthalene	2	51	3.3	51	3.3	190	0.24	4.8	6.32	1144	2.9		
Methylethylketone	3	60	7.0	200	23	800	37	8	6	6185	21		
n-Hexane	3	530	52	280	27	1400	52	61	45	11003	38		
1,2-Dichloroethane	3	320	27	300	25	2600	43	66	36	10746	35		
1,1,1-Trichloroethane	3	500	31	390	25	2000	50	85	43	15007	36		
Benzene	3	500	77	290	44	1900	47	62	42	10121	34		
Carbon tetrachloride	3	620	36	450	26	2800	54	95	39	10761	24		
Trichloroethene	3	650	42	430	27	4200	41	88	41	14373	31		
Tetrachloroethene	3	880	54	670	41	7900	37	106	45	19820	39		
1,2,4-Trimethylbenzene	3	580	33	540	30	8900	25	68	47	14259	38		
Naphthalene	3	54	3.5	52	3.4	190	0.24	4.9	6.41	1033	2.6		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number: 10		5,761 (4 days)											
Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		WMS			
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)		
Methyllylketone	1	74	8.6	200	23	870	40	12	9.2	9643	33		
n-Hexane	1	540	53	280	27	1500	56	61	45	11672	41		
1,2-Dichloroethane	1	320	27	300	25	2300	38	67	37	11212	37		
1,1,1-Trichloroethane	1	500	31	390	25	1800	45	85	43	16265	39		
Benzene	1	500	77	300	46	1700	42	61	41	10946	37		
Carbon tetrachloride	1	610	36	460	27	2400	47	96	39	16777	38		
Trichloroethene	1	650	41	430	27	3800	37	87	40	15711	33		
Tetrachloroethene	1	880	54	680	42	6900	33	105	45	20407	40		
1,2,4-Trimethylbenzene	1	580	33	550	31	8100	23	67	47	14676	39		
Naphthalene	1	56	3.7	52	3.4	180	0.23	5.2	6.7	1085	2.7		
Methyllylketone	2	63	7.3	200	23	760	35	8.8	6.5	9476	32		
n-Hexane	2	540	53	280	27	1400	52	59	43	11692	41		
1,2-Dichloroethane	2	310	26	300	25	2400	39	63	35	11288	37		
1,1,1-Trichloroethane	2	460	29	400	25	1900	47	81	41	15389	37		
Benzene	2	500	77	290	44	1800	45	60	40	10851	36		
Carbon tetrachloride	2	570	33	460	27	2600	51	96	39	15684	35		
Trichloroethene	2	650	41	430	27	3800	37	85	39	15463	33		
Tetrachloroethene	2	870	54	670	41	7100	34	102	44	21155	41		
1,2,4-Trimethylbenzene	2	570	32	540	30	8100	23	65	46	15369	41		
Naphthalene	2	54	3.5	51	3.3	170	0.22	5.3	7.0	1213	3.1		
Methyllylketone	3	82	9.5	200	23	730	34	9.4	6.9	9538	33		
n-Hexane	3	550	54	280	27	1300	48	61	45	11657	41		
1,2-Dichloroethane	3	320	27	300	25	2300	38	65	36	11132	36		
1,1,1-Trichloroethane	3	500	31	390	25	1800	45	84	43	15580	38		
Benzene	3	510	78	290	44	1700	42	62	41	10633	36		
Carbon tetrachloride	3	620	36	460	27	2500	49	96	39	16016	36		
Trichloroethene	3	660	42	420	27	3800	37	86	40	15260	32		
Tetrachloroethene	3	880	54	680	42	7000	33	106	45	21893	43		
1,2,4-Trimethylbenzene	3	580	33	540	30	7800	22	68	47	15345	41		
Naphthalene	3	54	3.5	52	3.4	170	0.22	5.5	7.2	1070	2.7		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		WMS	
		Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)
		1,446 (1 days)									
Methyl ethyl ketone	1	12	5.5	160	73	430	78	25	72	2889	39
n-Hexane	1	360	137	210	80	650	95	27	79	5166	70
1,2-Dichloroethane	1	240	80	230	76	1100	71	34	74	5172	66
1,1,1-Trichloroethane	1	310	76	260	64	900	87	40	81	6386	60
Benzene	1	250	150	180	108	770	75	28	74	4794	63
Carbon tetrachloride	1	380	87	300	69	1200	91	43	70	4543	40
Trichloroethene	1	380	95	280	70	1500	57	40	74	6786	57
Tetrachloroethene	1	460	111	370	89	2300	43	48	81	8004	61
1,2,4-Trimethylbenzene	1	280	62	250	55	1700	19	27	76	1975	21
Naphthalene	1	27	6.9	22	5.6	32	0.16	1.5	7.6	15	0.15
Methyl ethyl ketone	2	25	11.4	160	73	450	82	24	71	2849	38
n-Hexane	2	360	137	210	80	710	103	27	80	5128	70
1,2-Dichloroethane	2	220	73	230	76	1100	71	33	73	5242	67
1,1,1-Trichloroethane	2	270	67	260	64	960	93	40	82	6435	61
Benzene	2	260	156	190	114	850	83	28	76	4770	63
Carbon tetrachloride	2	380	87	300	69	1300	99	45	73	4553	40
Trichloroethene	2	380	95	280	70	1600	61	42	77	6771	56
Tetrachloroethene	2	480	116	360	87	2600	48	48	81	7894	60
1,2,4-Trimethylbenzene	2	300	66	250	55	2000	22	28	79	1373	14
Naphthalene	2	25	6.4	24	6.2	39	0.20	1.7	9.0	11	0.11
Methyl ethyl ketone	3	15	6.8	160	73	440	80	24	69	3063	41
n-Hexane	3	360	137	200	76	710	103	27	78	5200	71
1,2-Dichloroethane	3	230	76	220	73	1100	71	33	72	5526	71
1,1,1-Trichloroethane	3	290	71	260	64	890	86	40	81	6744	64
Benzene	3	260	156	180	108	790	77	28	74	4881	64
Carbon tetrachloride	3	390	89	290	66	1200	91	45	73	4991	44
Trichloroethene	3	390	98	280	70	1500	57	41	75	6936	58
Tetrachloroethene	3	460	111	350	85	2400	44	47	80	7955	61
1,2,4-Trimethylbenzene	3	290	64	240	53	1800	20	28	77	2135	22
Naphthalene	3	27	6.9	22	5.6	33	0.17	1.3	6.9	14	0.14

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		12														
Exposure Time (min):		1,460 (1 day)														
Analyte	Replicate	ATD Tube - CB			ATD Tube - TA			WMS			Radiello			WMS		
		Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)
Methyl ethyl ketone	1	0.86	0.39	1.5	3.3	1.5	3.3	1.4	2.5	ND	ND	ND	8.0	0.11	ND	ND
n-Hexane	1	3.3	1.2	1.1	2.8	1.1	1.2	1.2	1.7	0.57	1.7	0.57	77	1.0	1.7	1.0
1,2-Dichloroethane	1	2.0	0.66	0.79	2.4	0.79	6.6	6.6	0.42	ND	ND	ND	42	0.53	ND	ND
1,1,1-Trichloroethane	1	3.6	0.88	0.66	2.7	0.66	4.7	4.7	0.45	ND	ND	ND	20	0.19	ND	ND
Benzene	1	2.6	1.5	2.4	4.1	2.4	1.3	1.3	1.3	0.44	1.2	0.44	89	1.2	1.2	1.2
Carbon tetrachloride	1	5.2	1.2	0.75	3.3	0.75	7.8	7.8	0.59	0.20	0.32	0.20	12	0.1	0.32	0.1
Trichloroethene	1	3.7	0.92	0.74	3.0	0.74	1.2	1.2	0.45	ND	ND	ND	47	0.39	ND	ND
Tetrachloroethene	1	4.3	1.0	1.0	4.1	1.0	27	27	0.50	ND	ND	ND	126	1.0	ND	ND
1,2,4-Trimethylbenzene	1	2.1	0.46	0.92	4.2	0.92	53	53	0.57	0.35	0.96	0.35	1.3	0.54	0.96	0.54
Naphthalene	1	2.2	0.56	0.74	2.9	0.74	ND	ND	ND	ND	ND	ND	19	0.18	ND	ND
Methyl ethyl ketone	2	1.0	0.44	1.3	2.9	1.3	61	61	11	ND	ND	ND	5.6	0.07	11	0.07
n-Hexane	2	3.2	1.2	1.2	3.3	1.2	68	68	10	0.54	1.57	0.54	81	1.1	1.57	1.1
1,2-Dichloroethane	2	2.2	0.72	0.82	2.5	0.82	7.1	7.1	0.45	ND	ND	ND	51	0.64	ND	ND
1,1,1-Trichloroethane	2	3.3	0.81	0.68	2.8	0.68	4.0	4.0	0.38	0.30	0.60	0.30	20	0.19	0.60	0.19
Benzene	2	2.4	1.4	1.8	3.0	1.8	21	21	2.0	0.41	1.1	0.41	120	1.6	1.1	1.6
Carbon tetrachloride	2	4.9	1.1	0.75	3.3	0.75	8.6	8.6	0.65	0.40	0.64	0.40	14	0.12	0.64	0.12
Trichloroethene	2	3.6	0.89	0.74	3.0	0.74	16	16	0.60	ND	ND	ND	69	0.57	ND	ND
Tetrachloroethene	2	4.3	1.0	1.0	4.2	1.0	36	36	0.66	ND	ND	ND	129	1.0	ND	ND
1,2,4-Trimethylbenzene	2	2.8	0.61	1.2	5.4	1.2	64	64	0.69	0.33	0.91	0.33	0.7	0.53	0.91	0.53
Naphthalene	2	3.0	0.76	0.81	3.2	0.81	ND	ND	ND	ND	ND	ND	20	0.20	ND	ND
Methyl ethyl ketone	3	1.7	0.77	1.2	2.6	1.2	27	27	4.9	ND	ND	ND	12	0.16	ND	ND
n-Hexane	3	3.3	1.2	1.1	2.9	1.1	26	26	3.8	0.58	1.7	0.58	77	1.0	1.7	1.0
1,2-Dichloroethane	3	2.2	0.72	0.76	2.3	0.76	7.0	7.0	0.45	ND	ND	ND	53	0.67	ND	ND
1,1,1-Trichloroethane	3	3.4	0.83	0.68	2.8	0.68	4.6	4.6	0.44	0.17	0.34	0.17	28	0.26	0.34	0.26
Benzene	3	2.9	1.7	1.7	2.9	1.7	13	13	1.3	0.37	0.98	0.37	101	1.3	1.3	1.3
Carbon tetrachloride	3	5.0	1.1	0.72	3.2	0.72	8.3	8.3	0.63	0.28	0.45	0.28	16	0.14	0.45	0.14
Trichloroethene	3	3.6	0.89	0.72	2.9	0.72	13	13	0.49	ND	ND	ND	67	0.55	ND	ND
Tetrachloroethene	3	4.3	1.0	1.0	4.2	1.0	29	29	0.53	ND	ND	ND	124	0.94	ND	ND
1,2,4-Trimethylbenzene	3	3.0	0.66	0.74	3.4	0.74	53	53	0.57	0.35	0.96	0.35	50	0.52	0.96	0.52
Naphthalene	3	3.4	0.86	0.76	3.0	0.76	ND	ND	ND	ND	ND	ND	22	0.21	ND	ND

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 13													
		Exposure Time (min): 10,100(7 days)													
		ATD Tube - CB			ATD Tube - TA			WMS			Radiello			WMS	
Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)
Methyl ethyl ketone	1	270	17.6	790	52	620	16	38	16	38	16	16494	32		
n-Hexane	1	2000	109	1000	55	5200	108	165	108	165	69	40667	79		
1,2-Dichloroethane	1	1100	52	1200	57	7000	65	140	65	140	44	19553	36		
1,1,1-Trichloroethane	1	1300	46	1400	49	6000	83	166	83	166	48	46940	64		
Benzene	1	1700	146	920	79	5600	78	175	78	175	67	32741	62		
Carbon tetrachloride	1	1800	59	1600	52	7600	83	208	83	208	48	47819	60		
Trichloroethene	1	2300	82	1500	54	10000	55	241	55	241	64	48966	58		
Tetrachloroethene	1	2900	100	2100	73	16000	42	329	42	329	80	60898	66		
1,2,4-Trimethylbenzene	1	1900	60	1700	54	16000	25	220	25	220	88	35911	54		
Naphthalene	1	170	6.2	160	5.9	340	0.24	18	0.24	18	13	3147	4.4		
Methyl ethyl ketone	2	420	27.4	800	52	640	17	22	17	22	9.4	16242	31		
n-Hexane	2	2100	115	1000	55	5100	106	161	106	161	68	39738	78		
1,2-Dichloroethane	2	1100	52	1200	57	6900	64	137	64	137	43	18832	34		
1,1,1-Trichloroethane	2	1400	49	1400	49	6000	83	164	83	164	48	45482	62		
Benzene	2	1700	146	920	79	5500	77	170	77	170	65	32328	61		
Carbon tetrachloride	2	1800	59	1600	52	7600	83	205	83	205	48	47325	60		
Trichloroethene	2	2300	82	1500	54	10000	55	234	55	234	62	48564	58		
Tetrachloroethene	2	3000	104	2100	73	16000	42	317	42	317	77	56558	62		
1,2,4-Trimethylbenzene	2	2000	63	1700	54	17000	27	211	27	211	84	35084	53		
Naphthalene	2	180	6.6	170	6.2	340	0.24	16	0.24	16	12	3355	4.7		
Methyl ethyl ketone	3	250	16.3	790	52	610	16	20	16	20	8.5	16543	32		
n-Hexane	3	2000	109	1000	55	5400	113	164	113	164	69	37435	73		
1,2-Dichloroethane	3	1100	52	1200	57	7100	65	137	65	137	43	19677	36		
1,1,1-Trichloroethane	3	1400	49	1400	49	6300	88	163	88	163	47	44126	60		
Benzene	3	1700	146	910	78	5800	81	174	81	174	67	30591	58		
Carbon tetrachloride	3	1900	62	1600	52	7800	85	203	85	203	47	44885	57		
Trichloroethene	3	2300	82	1500	54	11000	60	239	60	239	63	46502	56		
Tetrachloroethene	3	3000	104	2000	69	16000	42	326	42	326	80	54577	60		
1,2,4-Trimethylbenzene	3	2000	63	1700	54	16000	25	219	25	219	87	34984	53		
Naphthalene	3	170	6.2	160	5.9	300	0.22	18	0.22	18	13	3199	4.5		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 14													
		ATD Tube - CB		ATD Tube - TA		WMS		Radiello		WMS					
		Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Mass (ng)	Concn (ppbv)				
Methyllylketone	1	ND	ND	8.4	0.55	24	0.6	1.2	0.48	11	0.020				
n-Hexane	1	31	1.7	20	1.1	91	1.9	2.5	1.0	368	0.72				
1,2-Dichloroethane	1	10	0.47	11	0.52	99	0.91	2.4	0.75	12	0.022				
1,1,1-Trichloroethane	1	18	0.63	16	0.56	74	1.0	2.6	0.76	211	0.29				
Benzene	1	22	1.9	12	1.0	78	1.1	2.5	0.93	493	0.93				
Carbon tetrachloride	1	18	0.59	17	0.56	110	1.2	3.0	0.69	57	0.072				
Trichloroethene	1	27	1.0	16	0.57	160	0.87	3.0	0.79	11	0.013				
Tetrachloroethene	1	35	1.2	25	0.86	320	0.85	4.4	1.1	887	1.0				
1,2,4-Trimethylbenzene	1	22	0.69	21	0.66	340	0.53	2.6	1.0	173	0.26				
Naphthalene	1	21	0.77	18	0.66	64	0.05	2.0	1.5	257	0.36				
Methyllylketone	2	ND	ND	8.7	0.57	ND	ND	1.0	0.40	7.1	0.014				
n-Hexane	2	34	1.9	14	0.76	87	1.8	2.8	1.2	366	0.71				
1,2-Dichloroethane	2	10	0.47	11	0.52	87	0.80	2.0	0.62	18	0.033				
1,1,1-Trichloroethane	2	19	0.67	17	0.60	64	0.89	2.9	0.84	254	0.34				
Benzene	2	22	1.9	13	1.1	71	1.0	2.6	1.0	513	1.0				
Carbon tetrachloride	2	22	0.72	18	0.59	110	1.2	2.3	0.52	75	0.094				
Trichloroethene	2	27	1.0	16	0.57	140	0.76	2.6	0.69	14	0.017				
Tetrachloroethene	2	35	1.2	25	0.86	290	0.77	4.1	1.0	883	1.0				
1,2,4-Trimethylbenzene	2	23	0.73	21	0.66	340	0.53	2.9	1.2	167	0.25				
Naphthalene	2	21	0.77	19	0.70	67	0.05	2.2	1.6	256	0.36				
Methyllylketone	3	ND	ND	9.4	0.61	ND	ND	1.1	0.46	6.5	0.013				
n-Hexane	3	36	2.0	13	0.71	98	2.0	2.5	1.0	352	0.69				
1,2-Dichloroethane	3	11	0.52	12	0.57	92	0.85	2.3	0.71	11	0.020				
1,1,1-Trichloroethane	3	19	0.67	16	0.56	68	0.94	3.0	0.86	235	0.32				
Benzene	3	22	1.9	12	1.0	74	1.0	2.3	0.86	488	0.92				
Carbon tetrachloride	3	24	0.78	18	0.59	81	0.88	3.2	0.73	88	0.11				
Trichloroethene	3	26	0.93	16	0.57	145	0.79	3.1	0.82	19	0.022				
Tetrachloroethene	3	35	1.2	24	0.83	300	0.79	3.8	0.93	859	0.94				
1,2,4-Trimethylbenzene	3	22	0.69	20	0.63	340	0.53	2.6	1.0	148	0.22				
Naphthalene	3	21	0.77	18	0.66	64	0.05	2.3	1.7	179	0.25				

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 15																
		Exposure Time (min): 10,046 (7 days)																
		AID Tube - CB			AID Tube - TA			WMS			Raditeilo			WMS				
Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	
Methylethylketone	1	540	36.7	560	38	2200	60	172	73	16494	32							
n-Hexane	1	1800	103	750	43	4300	93	195	82	40667	80							
1,2-Dichloroethane	1	960	48	840	42	6100	59	231	73	19553	36							
1,1,1-Trichloroethane	1	1300	48	1100	40	5300	77	287	83	46940	64							
Benzene	1	1500	135	700	63	5100	75	204	78	32741	62							
Carbon tetrachloride	1	1800	61	1200	41	6700	76	329	77	47819	61							
Trichloroethene	1	2200	82	1200	45	9200	52	302	80	48966	59							
Tetrachloroethene	1	3100	112	1900	69	14000	39	354	87	60898	67							
1,2,4-Trimethylbenzene	1	2400	79	1800	59	15000	25	233	93	35911	54							
Naphthalene	1	220	8.4	210	8.0	320	0.24	19	14	3147	4.5							
Methylethylketone	2	510	34.7	560	38	1700	46	169	71	16242	31							
n-Hexane	2	1800	103	740	42	4000	87	199	84	39738	78							
1,2-Dichloroethane	2	980	49	830	41	5600	54	235	74	18832	35							
1,1,1-Trichloroethane	2	1400	52	1100	40	4900	71	291	85	45482	62							
Benzene	2	1500	135	700	63	4700	69	208	80	32328	61							
Carbon tetrachloride	2	1800	61	1200	41	6200	71	334	78	47325	60							
Trichloroethene	2	2200	82	1200	45	8600	49	307	81	48564	58							
Tetrachloroethene	2	3200	115	1900	69	14000	39	362	89	56558	62							
1,2,4-Trimethylbenzene	2	2400	79	1800	59	15000	25	237	95	35084	53							
Naphthalene	2	230	8.8	200	7.7	320	0.24	19	14	3355	4.8							
Methylethylketone	3	380	25.9	590	40	2200	60	167	70	16543	32							
n-Hexane	3	1800	103	770	44	4300	93	194	82	37435	73							
1,2-Dichloroethane	3	970	48	850	42	6100	59	230	72	19677	36							
1,1,1-Trichloroethane	3	1200	44	1000	37	5300	77	286	83	44126	60							
Benzene	3	1500	135	690	62	5100	75	203	78	30591	58							
Carbon tetrachloride	3	1800	61	1200	41	6600	75	328	77	44885	57							
Trichloroethene	3	2200	82	1200	45	9300	53	299	79	46502	56							
Tetrachloroethene	3	3100	112	1900	69	15000	41	354	87	54577	60							
1,2,4-Trimethylbenzene	3	2300	76	1800	59	16000	26	233	93	34984	53							
Naphthalene	3	220	8.4	190	7.3	330	0.25	20	15	3199	4.5							



**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Run Number:		16											
Exposure Time (min):		10,033 (7 days)											
Analyte	Replicate	ATD Tube - CB		ATD Tube - TA		WMS		Radiello		WMS			
		Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)	Mass (ug)	Concn (ppbv)		
Methyllylketone	1	ND	ND	6.4	0.44	ND	ND	2.4	1.0	22	0.043		
n-Hexane	1	24	1.4	8.9	0.51	72	1.6	2.8	1.2	820	1.7		
1,2-Dichloroethane	1	10	0.50	8.4	0.42	74	0.71	2.7	0.85	562	1.1		
1,1,1-Trichloroethane	1	15	0.55	11	0.41	54	0.78	3.7	1.1	419	0.6		
Benzene	1	22	2.0	10	0.85	59	0.86	2.7	1.0	748	1.5		
Carbon tetrachloride	1	24	0.82	12	0.41	62	0.71	3.7	0.86	163	0.21		
Trichloroethene	1	28	1.0	12	0.45	120	0.68	3.6	0.95	362	0.45		
Tetrachloroethene	1	39	1.4	20	0.72	250	0.69	4.6	1.1	1396	1.6		
1,2,4-Trimethylbenzene	1	25	0.83	20	0.66	300	0.49	3.0	1.2	712	1.1		
Naphthalene	1	23	0.88	20	0.77	62	0.046	3.1	2.3	356	0.53		
Methyllylketone	2	ND	ND	6.4	0.44	24	0.65	2.4	1.0	26	0.053		
n-Hexane	2	23	1.3	8.7	0.50	73	1.6	2.6	1.1	587	1.2		
1,2-Dichloroethane	2	10	0.50	8.3	0.41	78	0.75	3.1	1.0	415	0.79		
1,1,1-Trichloroethane	2	14	0.52	11	0.41	58	0.84	3.5	1.0	431	0.61		
Benzene	2	21	1.9	8.5	0.76	61	0.89	2.5	1.0	523	1.0		
Carbon tetrachloride	2	25	0.86	12	0.41	61	0.70	3.5	0.82	126	0.17		
Trichloroethene	2	27	1.0	12	0.45	115	0.66	3.7	1.0	305	0.38		
Tetrachloroethene	2	38	1.4	21	0.76	230	0.64	4.7	1.2	952	1.1		
1,2,4-Trimethylbenzene	2	25	0.83	20	0.66	260	0.43	2.8	1.1	496	0.78		
Naphthalene	2	21	0.81	21	0.81	54	0.040	3.4	2.6	275	0.41		
Methyllylketone	3	ND	ND	6.1	0.42	26	0.71	2.3	1.0	211	0.42		
n-Hexane	3	23	1.3	8.3	0.47	81	1.8	2.7	1.1	614	1.3		
1,2-Dichloroethane	3	8	0.39	8.7	0.43	81	0.78	3.1	1.0	548	1.0		
1,1,1-Trichloroethane	3	12	0.44	11	0.41	59	0.86	3.9	1.1	663	0.94		
Benzene	3	21	1.9	9.0	0.81	65	0.95	2.7	1.0	558	1.1		
Carbon tetrachloride	3	22	0.75	13	0.44	100	1.14	3.8	0.88	316	0.42		
Trichloroethene	3	28	1.0	12	0.45	130	0.74	4.0	1.1	657	0.82		
Tetrachloroethene	3	39	1.4	20	0.72	260	0.72	4.4	1.1	993	1.1		
1,2,4-Trimethylbenzene	3	26	0.86	20	0.66	310	0.51	3.0	1.2	464	0.73		
Naphthalene	3	23	0.88	21	0.81	62	0.046	2.9	2.2	144	0.21		

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 17 Exposure Time (min): 1,420 (1 day)													
		ATD Tube - CB			ATD Tube - TA			WMS			Radiello			WMS	
		Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)
Methylethylketone	1	17	8.2	140	68	190	37	10	29	364	5.2				
n-Hexane	1	330	134	180	73	540	84	30	91	4790	69				
1,2-Dichloroethane	1	200	71	200	71	930	64	31	69	3700	50				
1,1,1-Trichloroethane	1	180	47	240	63	750	77	40	82	6208	63				
Benzene	1	270	173	160	102	710	74	31	84	4549	64				
Carbon tetrachloride	1	310	75	270	66	950	77	46	76	4058	38				
Trichloroethene	1	400	107	260	69	1400	57	43	81	5870	52				
Tetrachloroethene	1	540	139	360	93	2600	51	54	94	10950	89				
1,2,4-Trimethylbenzene	1	360	85	290	68	2800	33	35	98	4995	56				
Naphthalene	1	25	6.8	33	9.0	54	0.29	2.8	1.5	534	5.6				
Methylethylketone	2	12	5.8	140	68	250	49	11	34	414	5.9				
n-Hexane	2	320	130	180	73	750	116	30	90	4790	69				
1,2-Dichloroethane	2	190	67	200	71	1100	75	31	68	3855	52				
1,1,1-Trichloroethane	2	190	50	240	63	910	94	38	79	6474	65				
Benzene	2	280	179	160	102	870	91	31	84	4695	66				
Carbon tetrachloride	2	310	75	290	71	1200	97	49	81	4419	41				
Trichloroethene	2	410	109	260	69	1700	69	43	81	6697	59				
Tetrachloroethene	2	550	142	390	100	3000	59	54	93	10608	86				
1,2,4-Trimethylbenzene	2	370	87	300	70	3000	35	35	99	4943	55				
Naphthalene	2	29	7.9	32	8.7	57	0.30	2.6	1.4	497	5.2				
Methylethylketone	3	30	14.6	150	73	191	37	10	29	307	4.4				
n-Hexane	3	320	130	180	73	560	87	30	89	4922	71				
1,2-Dichloroethane	3	200	71	200	71	960	66	30	66	3535	48				
1,1,1-Trichloroethane	3	250	66	240	63	770	80	38	78	6611	67				
Benzene	3	270	173	170	109	740	77	30	83	4972	70				
Carbon tetrachloride	3	350	85	290	71	1000	81	43	70	4781	45				
Trichloroethene	3	400	107	270	72	1500	61	43	80	6676	59				
Tetrachloroethene	3	520	134	380	98	2900	57	53	91	11209	91				
1,2,4-Trimethylbenzene	3	370	87	300	70	2000	23	34	96	4507	50				
Naphthalene	3	29	7.9	31	8.5	60	0.32	3.0	1.6	542	5.7				

**APPENDIX D: ANALYTICAL RESULTS OF FRACTIONAL FACTORIAL TESTING**

Analyte	Replicate	Run Number: 18																	
		Exposure Time (min): 1,437 (1 day)																	
		ATD Tube - CB			ATD Tube - TA			WMS			Radiello			WMS					
Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)	Mass (ng)	Concn (ppbv)	Concn (ppbv)		
Methyl/ethylketone	1	ND	ND	3.2	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	0.14			
n-Hexane	1	3.4	1.4	2.1	0.84	ND	ND	ND	0.53	1.6	1.6	11	0.16						
1,2-Dichloroethane	1	0.81	0.28	1.8	0.63	3.3	0.22	ND	ND	ND	ND	0.24	0.0032						
1,1,1-Trichloroethane	1	1.6	0.42	2.2	0.57	9.3	1.0	ND	ND	ND	ND	11	0.11						
Benzene	1	3.5	2.2	2.5	1.58	11	1.1	1.1	0.48	1.3	1.3	118	1.6						
Carbon tetrachloride	1	2.3	0.55	2.6	0.63	15	1.2	1.2	0.35	0.57	0.57	5.0	0.046						
Trichloroethene	1	3.5	0.92	2.5	0.66	10	0.40	0.40	ND	ND	ND	4.0	0.035						
Tetrachloroethene	1	4.9	1.2	3.8	1.0	25	0.49	0.49	ND	ND	ND	91	0.73						
1,2,4-Trimethylbenzene	1	3.1	0.72	3.2	0.74	32	0.37	0.37	0.37	1.0	1.0	7.3	0.081						
Naphthalene	1	2.8	0.76	3.6	1.0	3.3	0.017	0.017	ND	ND	ND	15	0.15						
Methyl/ethylketone	2	ND	ND	2.6	1.2	ND	ND	ND	ND	ND	ND	4.6	0.065						
n-Hexane	2	3.9	1.6	2.0	0.80	ND	ND	ND	0.66	1.9	1.9	46	0.66						
1,2-Dichloroethane	2	1.2	0.42	1.7	0.59	2.2	0.15	0.15	ND	ND	ND	1.6	0.021						
1,1,1-Trichloroethane	2	1.5	0.39	2.3	0.60	5.9	0.60	0.60	0.28	0.57	0.57	16	0.16						
Benzene	2	3.4	2.2	2.4	1.5	15	1.5	1.5	0.33	0.89	0.89	90	1.2						
Carbon tetrachloride	2	1.8	0.43	2.8	0.67	15	1.2	1.2	0.15	0.24	0.24	6.5	0.060						
Trichloroethene	2	3.8	1.0	2.5	0.66	10	0.40	0.40	ND	ND	ND	1.5	0.013						
Tetrachloroethene	2	5.5	1.4	3.7	0.94	28	0.55	0.55	ND	ND	ND	122	0.98						
1,2,4-Trimethylbenzene	2	3.0	0.70	3.2	0.74	39	0.45	0.45	0.42	1.2	1.2	32	0.36						
Naphthalene	2	1.9	0.51	3.5	0.95	4.4	0.023	0.023	ND	ND	ND	33	0.34						
Methyl/ethylketone	3	ND	ND	2.5	1.2	ND	ND	ND	ND	ND	ND	6.6	0.094						
n-Hexane	3	3.9	1.6	2.1	0.84	ND	ND	ND	0.70	2.1	2.1	36	0.52						
1,2-Dichloroethane	3	1.4	0.49	2.0	0.70	2.3	0.16	0.16	0.15	0.00	0.00	0.6	0.01						
1,1,1-Trichloroethane	3	1.7	0.44	2.4	0.62	6.5	0.66	0.66	0.26	0.53	0.53	13	0.13						
Benzene	3	3.1	2.0	2.7	1.7	15	1.5	1.5	0.42	1.1	1.1	92	1.3						
Carbon tetrachloride	3	1.4	0.34	2.8	0.67	16	1.3	1.3	0.32	0.52	0.52	5.9	0.055						
Trichloroethene	3	3.7	1.0	2.6	0.69	10	0.40	0.40	ND	ND	ND	1.6	0.014						
Tetrachloroethene	3	5.1	1.3	3.8	1.0	26	0.51	0.51	ND	ND	ND	106	0.85						
1,2,4-Trimethylbenzene	3	3.3	0.77	3.6	0.84	35	0.40	0.40	0.46	1.29	1.29	26	0.28						
Naphthalene	3	2.4	0.65	6.0	1.6	3.8	0.020	0.020	ND	ND	ND	47	0.49						

**Notes:**

- ND - not detected
- NA - not analyzed. The sample was lost because of an interruption to repair a malfunction in the recollection process
- ng - nanograms
- ppbv - parts per billion by volume
- Concn - concentration

## **Appendix E**

### **Statistical Analysis of the Low Concentration Laboratory Tests**

## Objectives

The objective of the statistical analysis of the low concentration laboratory test data were:

- i) To assess whether the controllable factors (ie. humidity, temperature, face velocity, concentration, exposure time) have a statistically significant effect on the relative concentrations ( $C/C_0$ ), specifically whether the uptake rates change in response to changes in these factors within ranges typically anticipated for indoor air quality monitoring programs.
- ii) To develop to the extent practical a mathematical model to provide a correction factor for the reported concentration of the passive samplers using default uptake rates if the average humidity, temperature, face velocity, concentration, exposure time are known for a particular sampling event.
- iii) To evaluate the accuracy of the passive sampler performance with model developed in (ii).

## Statistical Methods

Only the main effects were analyzed and no interactions. The analyses were run with coded variables (low value of each factor = -1, high value = +1), however, slope estimates for each factor are reported on the original scale (ie. uncoded), so the main effects are values in units of relative concentration ( $C/C_0$ ) divided by the units each factor was measured in (humidity in %RH, temperature in °C, face velocity in m/s, concentration in ppbv, and exposure time in days). Fractional factorial data was used to develop the model and the center point data (the initial six ANOVA runs and the two interspersed runs combined) was used as a test set to validate the model. A correction factor was calculated by dividing the  $C/C_0$  values predicted by the model by observed  $C/C_0$  value from the center point data. This factor was used to assess the accuracy of the predictive model. PROC GLM was used for complete data sets, PROC MIXED was used for data sets with nondetect values (SAS 9.2).

A total of 139 out of 2400 measured concentrations via passive samplers in the fractional factorial tests were nondetect values, all of which were for the lowest concentration chambers (where the target concentrations were 1 ppbv, except naphthalene). Two methods were used to analyze data sets with nondetect values:

- substitution method - a C/Co value of 1 was used for all nondetect results, and
- restricted maximum likelihood (REML) – nondetect values were considered missing values.

## Results

Results from both methods of dealing with the non-detect results (substitution of a value of 1 ppbv and the REML method) rendered similar results: about half of the main effects are statistically significant for the majority of the Sampler Type-Analyte combinations. Table E1a shows the p-values for each sampler/compound/factor combination for the REML method and Table E1b shows the same for the Substitution method. The p-value was less than 0.05 in 126 of 250 cases (almost exactly half) using the REML method and 118 of 250 using the Substitution method. P-values less than 0.05 indicate the effect was greater than would be expected from random variation with 95% confidence. This means the precision of the passive sampler measurements was high enough to allow changes in the uptake rate attributable to changes in the chamber conditions to be determined with statistical confidence. The slope estimates based on the REML model are shown in Table E2. These slope estimates were used to calculate predicted C/Co values for the center point data (Table E3). The relative percent difference (RPD) between the model prediction and the actual average C/Co of the Centerpoint data is shown in the right-hand column of Table E3, and was less than 25% in 30 of 50 cases (which would be considered acceptable as duplicates using typical data quality objectives). The compounds with higher RPDs were generally compounds that were identified as challenging for the various sampler/sorbent combinations in various stages of the testing program.

**Table E1: Main Effects Only Model - REML Method - Summary of Model Statistics and Main Effect P-values**

Sampler Type	Analyte	R-Square	Root MSE	%Rel.Hum.	Temp	Velocity	Exp. Time	Conc'n
ATDC	1,1,1-Trichloroethane	0.65397	0.131494	0.0778	0.0281	0.0106	0.0003	<.0001
ATDC	1,2,4-Trimethylbenzene	0.408658	0.082824	0.3181	0.0009	0.1245	0.5664	0.0011
ATDC	1,2-Dichloroethane	0.457001	0.182717	0.0012	0.6819	0.7406	<.0001	0.1371
ATDC	2-Butanone (MEK)	NA	0.231041122	0.0693	0.4097	0.0603	0.7378	0.0119
ATDC	Hexane	0.190167	0.425402	0.7999	0.2913	0.4002	0.0272	0.1177
ATDC	Benzene	0.339602	0.438782	0.4718	0.2468	0.0547	0.0023	0.0331
ATDC	Carbon tetrachloride	0.556859	0.175896	0.0434	0.2975	0.3501	<.0001	<.0001
ATDC	Naphthalene	0.259426	0.150481	0.2629	0.6088	0.293	0.007	0.0778
ATDC	Trichloroethene	0.540726	0.095064	0.0113	0.2781	0.0002	<.0001	0.9484
ATDC	Tetrachloroethene	0.327887	0.144003	0.8513	0.004	0.0071	0.8484	0.0727
ATDT	1,1,1-Trichloroethane	0.77989	0.097321	<.0001	0.2715	0.0021	<.0001	<.0001
ATDT	1,2,4-Trimethylbenzene	0.238568	0.133566	0.9169	0.8868	0.0121	0.0296	0.2864
ATDT	1,2-Dichloroethane	0.541289	0.181049	0.9154	0.8908	0.4733	<.0001	<.0001
ATDT	2-Butanone (MEK)	0.663055	0.488904	0.7719	0.0799	0.1479	<.0001	<.0001
ATDT	Hexane	0.427453	0.251521	0.6362	0.21	0.6114	<.0001	0.1148
ATDT	Benzene	0.603391	0.265519	0.8106	0.0059	0.438	<.0001	0.0442
ATDT	Carbon tetrachloride	0.795919	0.095384	<.0001	0.0229	0.0159	<.0001	<.0001
ATDT	Naphthalene	0.238298	0.404096	0.311	0.2147	0.565	0.025	0.0347
ATDT	Trichloroethene	0.818063	0.057885	0.5875	0.0002	0.0153	<.0001	0.475
ATDT	Tetrachloroethene	0.426854	0.114163	0.3221	0.4522	0.11	<.0001	0.9827
RADIELLO	1,1,1-Trichloroethane	NA	0.308025973	0.1005	0.0261	0.003	0.0899	0.0548
RADIELLO	1,2,4-Trimethylbenzene	0.552465	0.140001	0.6688	0.0007	<.0001	0.1133	0.0451
RADIELLO	1,2-Dichloroethane	NA	0.171201636	0.0005	0.054	0.0002	0.0327	<.0001
RADIELLO	2-Butanone (MEK)	NA	0.229085137	<.0001	0.5801	0.0003	0.0738	<.0001
RADIELLO	Hexane	0.597975	0.16907	0.1795	0.0066	0.0021	<.0001	0.0035
RADIELLO	Benzene	0.530781	0.110247	0.0047	0.0496	0.0012	<.0001	0.6113
RADIELLO	Carbon tetrachloride	0.235885	0.246583	0.4994	0.0143	0.0513	0.1724	0.9018
RADIELLO	Naphthalene	NA	0.747997326	0.6635	0.0008	0.933	0.1183	0.0005
RADIELLO	Trichloroethene	NA	0.095571962	0.001	0.0032	<.0001	0.0002	0.0169
RADIELLO	Tetrachloroethene	NA	0.125976188	0.2158	0.0023	<.0001	0.3477	0.9109
SKC	1,1,1-Trichloroethane	0.478283	0.251787	0.0906	0.1691	0.0055	0.0096	0.0001
SKC	1,2,4-Trimethylbenzene	0.575654	0.300275	0.1362	0.3054	0.0012	0.0004	<.0001
SKC	1,2-Dichloroethane	0.381462	0.337603	<.0001	0.5187	0.1033	0.9879	0.6424
SKC	2-Butanone (MEK)	0.518151	0.19019	<.0001	0.2819	0.3914	0.0073	0.0028
SKC	Hexane	0.397091	0.247041	0.0006	0.0398	0.012	0.4921	0.1584
SKC	Benzene	0.336701	0.472786	0.0318	0.0551	0.9085	0.0218	0.0125
SKC	Carbon tetrachloride	0.79087	0.124783	0.0223	0.2682	0.032	<.0001	<.0001
SKC	Naphthalene	0.495836	0.180924	0.1182	0.1437	0.6579	<.0001	0.1122
SKC	Trichloroethene	0.619333	0.201723	<.0001	0.9977	0.0306	0.5618	<.0001
SKC	Tetrachloroethene	0.333153	0.242376	0.4868	0.0368	0.018	0.0097	0.1261
WMS	1,1,1-Trichloroethane	NA	0.285236744	0.0224	0.9489	0.0042	0.6355	0.4719
WMS	1,2,4-Trimethylbenzene	NA	0.148761554	0.7716	0.7992	<.0001	0.1467	0.0194
WMS	1,2-Dichloroethane	NA	0.268588905	0.7347	0.1749	0.0054	0.0325	0.1887
WMS	2-Butanone (MEK)	NA	2.203814874	0.5881	0.3369	0.14	0.0319	0.0027
WMS	Hexane	NA	6.668125674	0.6198	0.4942	0.022	0.0003	0.0001
WMS	Benzene	NA	1.503828448	0.5712	0.9017	0.0328	0.0012	0.0099
WMS	Carbon tetrachloride	NA	0.333916157	0.0016	0.3838	0.0035	0.0766	0.0553
WMS	Naphthalene	NA	0.021307276	0.9025	0.4298	<.0001	0.5432	0.006
WMS	Trichloroethene	NA	0.19679939	0.6289	0.0325	0.0006	0.8376	0.0124
WMS	Tetrachloroethene	NA	0.157448404	0.5923	0.1477	<.0001	0.9894	0.0074

red highlighted cells indicate statistical significance when alpha=0.05, therefore, p-value<0.05 = significant

R-Square = 1- SSRResiduals/SSTotal

Root MSE = standard deviation of the model

**Table E1b: Main Effects Only Model - Substitution Method - Summary of Model Statistics and Main Effect P-values**

Sampler Type	Analyte	R-Square	Root MSE	%Rel.Hum.	Temp	Velocity	Exp. Time	Conc'n
ATDC	1,1,1-Trichloroethane	0.65397	0.131494	0.0778	0.0281	0.0106	0.0003	<.0001
ATDC	1,2,4-Trimethylbenzene	0.408658	0.082824	0.3181	0.0009	0.1245	0.5664	0.0011
ATDC	1,2-Dichloroethane	0.457001	0.182717	0.0012	0.6819	0.7406	<.0001	0.1371
ATDC	2-Butanone (MEK)	0.685211	0.237604	0.8292	0.0687	0.0546	0.8199	<.0001
ATDC	Hexane	0.190167	0.425402	0.7999	0.2913	0.4002	0.0272	0.1177
ATDC	Benzene	0.339602	0.438782	0.4718	0.2468	0.0547	0.0023	0.0331
ATDC	Carbon tetrachloride	0.556859	0.175896	0.0434	0.2975	0.3501	<.0001	<.0001
ATDC	Naphthalene	0.259426	0.150481	0.2629	0.6088	0.293	0.007	0.0778
ATDC	Trichloroethene	0.540726	0.095064	0.0113	0.2781	0.0002	<.0001	0.9484
ATDC	Tetrachloroethene	0.327887	0.144003	0.8513	0.004	0.0071	0.8484	0.0727
ATDT	1,1,1-Trichloroethane	0.77989	0.097321	<.0001	0.2715	0.0021	<.0001	<.0001
ATDT	1,2,4-Trimethylbenzene	0.238568	0.133566	0.9169	0.8868	0.0121	0.0296	0.2864
ATDT	1,2-Dichloroethane	0.541289	0.181049	0.9154	0.8908	0.4733	<.0001	<.0001
ATDT	2-Butanone (MEK)	0.663055	0.488904	0.7719	0.0799	0.1479	<.0001	<.0001
ATDT	Hexane	0.427453	0.251521	0.6362	0.21	0.6114	<.0001	0.1148
ATDT	Benzene	0.603391	0.265519	0.8106	0.0059	0.438	<.0001	0.0442
ATDT	Carbon tetrachloride	0.795919	0.095384	<.0001	0.0229	0.0159	<.0001	<.0001
ATDT	Naphthalene	0.238298	0.404096	0.311	0.2147	0.565	0.025	0.0347
ATDT	Trichloroethene	0.818063	0.057885	0.5875	0.0002	0.0153	<.0001	0.475
ATDT	Tetrachloroethene	0.426854	0.114163	0.3221	0.4522	0.11	<.0001	0.9827
RADIELLO	1,1,1-Trichloroethane	0.390998	0.301086	0.0813	0.0214	0.0024	0.0645	0.0522
RADIELLO	1,2,4-Trimethylbenzene	0.552465	0.140001	0.6688	0.0007	<.0001	0.1133	0.0451
RADIELLO	1,2-Dichloroethane	0.62974	0.16889	0.0013	0.0856	0.0006	0.0551	<.0001
RADIELLO	2-Butanone (MEK)	0.661753	0.272766	<.0001	0.2386	0.0145	0.8488	<.0001
RADIELLO	Hexane	0.597975	0.16907	0.1795	0.0066	0.0021	<.0001	0.0035
RADIELLO	Benzene	0.530781	0.110247	0.0047	0.0496	0.0012	<.0001	0.6113
RADIELLO	Carbon tetrachloride	0.235885	0.246583	0.4994	0.0143	0.0513	0.1724	0.9018
RADIELLO	Naphthalene	0.360025	0.827239	0.1301	0.0002	0.2597	0.4227	0.0949
RADIELLO	Trichloroethene	0.669313	0.098347	0.0037	0.01	<.0001	<.0001	0.0016
RADIELLO	Tetrachloroethene	0.512088	0.124381	0.1682	0.0027	<.0001	0.1127	0.6241
SKC	1,1,1-Trichloroethane	0.478283	0.251787	0.0906	0.1691	0.0055	0.0096	0.0001
SKC	1,2,4-Trimethylbenzene	0.575654	0.300275	0.1362	0.3054	0.0012	0.0004	<.0001
SKC	1,2-Dichloroethane	0.381462	0.337603	<.0001	0.5187	0.1033	0.9879	0.6424
SKC	2-Butanone (MEK)	0.518151	0.19019	<.0001	0.2819	0.3914	0.0073	0.0028
SKC	Hexane	0.397091	0.247041	0.0006	0.0398	0.012	0.4921	0.1584
SKC	Benzene	0.336701	0.472786	0.0318	0.0551	0.9085	0.0218	0.0125
SKC	Carbon tetrachloride	0.79087	0.124783	0.0223	0.2682	0.032	<.0001	<.0001
SKC	Naphthalene	0.495836	0.180924	0.1182	0.1437	0.6579	<.0001	0.1122
SKC	Trichloroethene	0.619333	0.201723	<.0001	0.9977	0.0306	0.5618	<.0001
SKC	Tetrachloroethene	0.333153	0.242376	0.4868	0.0368	0.018	0.0097	0.1261
WMS	1,1,1-Trichloroethane	0.308787	0.267216	0.0201	0.6847	0.0016	0.7714	0.2584
WMS	1,2,4-Trimethylbenzene	0.319658	0.247594	0.8852	0.9036	0.0308	0.0006	0.3009
WMS	1,2-Dichloroethane	0.077256	0.293816	0.9017	0.2553	0.1948	0.5741	0.7377
WMS	2-Butanone (MEK)	0.291197	2.063753	0.0869	0.0848	0.0552	0.1272	0.0348
WMS	Hexane	0.446453	6.847496	0.8445	0.9973	0.003	0.0019	0.0008
WMS	Benzene	0.339924	1.520124	0.4382	0.7388	0.052	0.0022	0.0165
WMS	Carbon tetrachloride	0.47662	0.314861	0.001	0.177	0.0002	0.0891	0.0607
WMS	Naphthalene	0.513538	0.277123	0.1442	0.1608	0.2645	<.0001	0.0001
WMS	Trichloroethene	0.196594	0.235807	0.8942	0.0966	0.1389	0.0322	0.6672
WMS	Tetrachloroethene	0.215046	0.228665	0.8315	0.3666	0.0418	0.0174	0.7665

red highlighted cells indicate statistical significance when alpha=0.05



**Table E2: Main Effects Only Model - REML Method - Adjusted Main Effect Slope Estimates**

Sampler Type	Analyte	Intercept	%Rel.Hum.	Temp	Velocity	Exp. Time	Conc'n
ATDC	1,1,1-Trichloroethane	-0.200	0.002	0.009	-0.514	0.051	0.005
ATDC	1,2,4-Trimethylbenzene	1.211	-0.001	-0.009	-0.190	-0.005	-0.002
ATDC	1,2-Dichloroethane	-0.445	0.006	0.002	-0.089	0.078	0.002
ATDC	2-Butanone (MEK)	0.006	0.006	-0.007	-0.841	-0.010	0.006
ATDC	Hexane	0.469	-0.001	-0.013	0.528	0.095	0.004
ATDC	Benzene	0.300	0.003	-0.015	1.267	0.139	0.006
ATDC	Carbon tetrachloride	-0.328	0.004	0.005	-0.243	0.078	0.005
ATDC	Naphthalene	1.087	-0.002	-0.002	0.234	-0.042	0.002
ATDC	Trichloroethene	0.730	0.002	-0.003	-0.570	0.044	0.000
ATDC	Tetrachloroethene	1.697	0.000	-0.013	-0.596	0.003	-0.002
ATDT	1,1,1-Trichloroethane	0.548	-0.004	-0.003	-0.460	0.060	0.005
ATDT	1,2,4-Trimethylbenzene	0.617	0.000	0.001	-0.506	0.029	0.001
ATDT	1,2-Dichloroethane	-0.215	0.000	-0.001	0.189	0.091	0.005
ATDT	2-Butanone (MEK)	-2.851	0.001	0.025	1.040	0.300	0.017
ATDT	Hexane	-0.490	-0.001	0.009	0.186	0.125	0.002
ATDT	Benzene	-0.619	0.001	0.022	-0.300	0.182	0.003
ATDT	Carbon tetrachloride	0.560	-0.004	-0.007	-0.346	0.080	0.004
ATDT	Naphthalene	0.680	-0.004	-0.015	0.338	0.090	0.005
ATDT	Trichloroethene	0.128	0.000	0.007	-0.211	0.072	0.000
ATDT	Tetrachloroethene	0.451	0.001	0.003	-0.269	0.057	0.000
RADIELLO	1,1,1-Trichloroethane	1.516	0.005	-0.021	-1.440	-0.053	0.004
RADIELLO	1,2,4-Trimethylbenzene	2.000	-0.001	-0.015	-1.129	-0.022	-0.002
RADIELLO	1,2-Dichloroethane	0.109	0.007	-0.011	-1.211	0.052	0.007
RADIELLO	2-Butanone (MEK)	-1.399	0.023	-0.005	-1.736	0.058	0.011
RADIELLO	Hexane	0.442	0.002	-0.014	-0.798	0.092	0.003
RADIELLO	Benzene	0.681	0.003	-0.006	-0.553	0.050	0.000
RADIELLO	Carbon tetrachloride	1.470	0.002	-0.018	-0.714	-0.033	0.000
RADIELLO	Naphthalene	1.772	0.004	-0.090	-0.103	0.141	0.021
RADIELLO	Trichloroethene	0.666	0.004	-0.010	-0.933	0.055	0.002
RADIELLO	Tetrachloroethene	1.414	0.002	-0.014	-1.219	0.015	0.000
SKC	1,1,1-Trichloroethane	1.678	0.004	-0.010	-1.064	-0.066	-0.006
SKC	1,2,4-Trimethylbenzene	2.187	0.004	-0.009	-1.512	-0.111	-0.009
SKC	1,2-Dichloroethane	-0.134	0.015	-0.006	-0.811	0.000	-0.001
SKC	2-Butanone (MEK)	0.090	0.009	0.006	-0.238	-0.052	-0.004
SKC	Hexane	0.697	0.009	-0.015	-0.937	0.016	-0.002
SKC	Benzene	-0.249	0.010	-0.027	-0.079	0.108	0.007
SKC	Carbon tetrachloride	1.321	0.003	-0.004	-0.400	-0.059	-0.008
SKC	Naphthalene	1.456	-0.003	-0.008	-0.116	-0.101	-0.002
SKC	Trichloroethene	0.712	0.008	0.000	-0.652	-0.011	-0.008
SKC	Tetrachloroethene	1.576	0.002	-0.015	-0.861	-0.063	0.002
WMS	1,1,1-Trichloroethane	1.989	-0.007	-0.001	-1.408	-0.015	0.001
WMS	1,2,4-Trimethylbenzene	1.010	0.000	0.001	-1.761	0.024	-0.002
WMS	1,2-Dichloroethane	1.400	-0.001	0.012	-1.283	-0.064	-0.002
WMS	2-Butanone (MEK)	-6.487	0.014	0.075	-5.746	0.593	0.056
WMS	Hexane	-23.561	-0.034	-0.139	24.087	2.646	0.172
WMS	Benzene	-5.015	0.008	-0.005	4.852	0.509	0.024
WMS	Carbon tetrachloride	2.056	-0.012	-0.009	-1.683	0.066	0.004
WMS	Naphthalene	0.155	0.000	-0.001	-0.186	-0.002	0.000
WMS	Trichloroethene	0.971	-0.001	0.014	-1.202	0.004	-0.003
WMS	Tetrachloroethene	1.127	-0.001	0.007	-1.514	0.000	-0.003

Table E3: Main Effects Only Model - REML Method - Predicted Values Using ANOVA Data

Sampler Type	Analyte	%Rel.Hum .	Temp	Velocity	Exp. Time	Conc'n	Obs'd C/Co	Predict'd C/Co	Correction Factor	RPD (%)
ATDC	1,1,1-Trichloroethane	60	20	0.23	4.0	50	0.713	0.461	0.646	21.5
ATDC	1,2,4-Trimethylbenzene	60	20	0.23	4.0	50	0.752	0.840	1.117	5.5
ATDC	1,2-Dichloroethane	60	20	0.23	4.0	50	0.595	0.343	0.577	26.8
ATDC	2-Butanone (MEK)	60	20	0.23	4.0	50	1.645	0.260	0.158	72.7
ATDC	Hexane	60	20	0.23	4.0	50	0.796	0.842	1.057	2.8
ATDC	Benzene	60	20	0.23	4.0	50	1.244	1.317	1.058	2.8
ATDC	Carbon tetrachloride	60	20	0.23	4.0	50	0.222	0.507	2.281	39.0
ATDC	Naphthalene	60	20	0.23	4.0	50	0.963	0.910	0.945	2.8
ATDC	Trichloroethene	60	20	0.23	4.0	50	1.215	0.858	0.706	17.2
ATDC	Tetrachloroethene	60	20	0.23	4.0	50	0.922	1.252	1.357	15.2
ATDT	1,1,1-Trichloroethane	60	20	0.23	4.0	50	0.570	0.618	1.084	4.0
ATDT	1,2,4-Trimethylbenzene	60	20	0.23	4.0	50	0.674	0.661	0.982	0.9
ATDT	1,2-Dichloroethane	60	20	0.23	4.0	50	0.587	0.435	0.742	14.8
ATDT	2-Butanone (MEK)	60	20	0.23	4.0	50	0.932	0.039	0.041	92.0
ATDT	Hexane	60	20	0.23	4.0	50	0.600	0.286	0.477	35.4
ATDT	Benzene	60	20	0.23	4.0	50	0.488	0.681	1.394	16.5
ATDT	Carbon tetrachloride	60	20	0.23	4.0	50	0.705	0.601	0.853	7.9
ATDT	Naphthalene	60	20	0.23	4.0	50	0.942	0.843	0.895	5.5
ATDT	Trichloroethene	60	20	0.23	4.0	50	0.886	0.495	0.559	28.3
ATDT	Tetrachloroethene	60	20	0.23	4.0	50	0.613	0.734	1.198	9.0
RADIELLO	1,1,1-Trichloroethane	60	20	0.23	4.0	50	1.293	1.041	0.806	10.8
RADIELLO	1,2,4-Trimethylbenzene	60	20	0.23	4.0	50	0.690	1.236	1.791	28.3
RADIELLO	1,2-Dichloroethane	60	20	0.23	4.0	50	1.067	0.627	0.587	26.0
RADIELLO	2-Butanone (MEK)	60	20	0.23	4.0	50	1.134	0.281	0.248	60.3
RADIELLO	Hexane	60	20	0.23	4.0	50	1.309	0.634	0.484	34.7
RADIELLO	Benzene	60	20	0.23	4.0	50	0.920	0.799	0.868	7.1
RADIELLO	Carbon tetrachloride	60	20	0.23	4.0	50	1.448	0.916	0.633	22.5
RADIELLO	Naphthalene	60	20	0.23	4.0	50	0.375	1.757	4.691	64.9
RADIELLO	Trichloroethene	60	20	0.23	4.0	50	0.933	0.799	0.857	7.7
RADIELLO	Tetrachloroethene	60	20	0.23	4.0	50	1.029	1.030	1.001	0.1
SKC	1,1,1-Trichloroethane	60	20	0.23	4.0	50	1.075	0.911	0.848	8.3
SKC	1,2,4-Trimethylbenzene	60	20	0.23	4.0	50	1.393	1.028	0.738	15.1
SKC	1,2-Dichloroethane	60	20	0.23	4.0	50	0.901	0.433	0.480	35.1
SKC	2-Butanone (MEK)	60	20	0.23	4.0	50	1.001	0.323	0.323	51.2
SKC	Hexane	60	20	0.23	4.0	50	0.909	0.670	0.737	15.2
SKC	Benzene	60	20	0.23	4.0	50	0.879	0.593	0.675	19.4
SKC	Carbon tetrachloride	60	20	0.23	4.0	50	0.438	0.679	1.553	21.7
SKC	Naphthalene	60	20	0.23	4.0	50	2.758	0.617	0.224	63.4
SKC	Trichloroethene	60	20	0.23	4.0	50	1.172	0.628	0.536	30.2
SKC	Tetrachloroethene	60	20	0.23	4.0	50	1.034	1.032	0.998	0.1
WMS	1,1,1-Trichloroethane	60	20	0.23	4.0	50	1.205	1.239	1.028	1.4
WMS	1,2,4-Trimethylbenzene	60	20	0.23	4.0	50	0.964	0.578	0.600	25.0
WMS	1,2-Dichloroethane	60	20	0.23	4.0	50	1.134	0.905	0.798	11.2
WMS	2-Butanone (MEK)	60	20	0.23	4.0	50	0.956	-0.270	-0.283	178.8
WMS	Hexane	60	20	0.23	4.0	50	0.897	-3.629	-4.045	-165.7
WMS	Benzene	60	20	0.23	4.0	50	0.847	-0.272	-0.321	194.7
WMS	Carbon tetrachloride	60	20	0.23	4.0	50	0.760	1.251	1.646	24.4
WMS	Naphthalene	60	20	0.23	4.0	50	0.400	0.074	0.186	68.7
WMS	Trichloroethene	60	20	0.23	4.0	50	1.064	0.756	0.711	16.9
WMS	Tetrachloroethene	60	20	0.23	4.0	50	0.915	0.724	0.792	11.6

red highlights indicate an RPD of >25%

## **Appendix F**

### **Results of Indoor and Outdoor Air Monitoring at MCAS Cherry Point**

TABLE F1  
INDOOR AND OUTDOOR AIR SAMPLING DATA FOR MCAS CHERRY POINT

Matrix: Sample Location: Sampler Type: Sample Location: Client Sample ID: Sampler Type/Solvent: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	Indoor Air												
	Radfield				WMS				SKC				
	137-IA-1A 137-IA-1A-OVM Regular/charcoal 1-6-11 2:17 PM 1-13-11 12:00 PM 9945 6:30 11072606-21A	137-IA-1B 137-IA-1B-OVM Regular/charcoal 1-6-11 2:17 PM 1-13-11 12:00 PM 9945 6:30 11072606-22A	137-IA-1C 137-IA-1C-OVM Regular/charcoal 1-6-11 2:17 PM 1-13-11 12:00 PM 9943 6:30 11072606-23A	137-IA-1A-RAID Yellow body/thermal 1-6-11 2:39 PM 1-13-11 12:06 PM 9935 6:30 11072606-20A	137-IA-1B-RAID Yellow body/thermal 1-6-11 2:39 PM 1-13-11 12:06 PM 9935 6:30 11072606-20A	137-IA-1C-RAID Yellow body/thermal 1-6-11 2:39 PM 1-13-11 12:06 PM 9934 6:30 11072606-20A	137-IA-1A-WMS Regular/Catpack B 1-6-11 2:39 PM 1-13-11 11:52 AM 9913 6:38 11072606-23A	137-IA-1B-WMS Regular/Catpack B 1-6-11 2:39 PM 1-13-11 11:51 AM 9912 6:38 11072606-23A	137-IA-1C-WMS Regular/Catpack B 1-6-11 2:40 PM 1-13-11 11:53 AM 9913 6:38 11072606-23A	137-IA-1A-SKC Regular/Catpack B 1-6-11 2:35 PM 1-13-11 11:55 AM 9920 6:39 11072606-11A	137-IA-1B-SKC Regular/Catpack B 1-6-11 2:36 PM 1-13-11 11:57 AM 9921 6:39 11072606-12A	137-IA-1C-SKC Regular/Catpack B 1-6-11 2:37 PM 1-13-11 11:58 AM 9921 6:39 11072606-13A	137-IA-1A-ATD Regular/Catpack B 11-01-06 11-01-13 9920 6:39 11072606-11A
1,1,1-Trichloroethane	6.4	6.4	8	15 E	15 E	15 E	3.3	3.4	3.7	3.8	3.4	3.4	8.3
1,1,2-Trichloroethane	0.25 U	0.25 U	0.25 U	0.027 U	0.027 U	0.027 U	0.069 U	0.069 U	0.069 U	0.025 U	0.025 U	0.025 U	0.46 U
1,1-Dichloroethane	3.6	3.7	4	0.48	0.52	0.48	0.3	0.47	0.45	0.41	0.42	0.42	2.6
1,1-Dichloroethane	0.81 J	0.82 J	0.94 J	0.019	0.028	0.019	0.25 U	0.36	0.25	1.4	1.5	1.4	0.9
1,2-Dichloroethane	0.23 J	0.23 J	0.23 J	0.061	0.061	0.061	0.078 U	0.078 U	0.078 U	0.14	0.14	0.15	0.40 U
Benzene	0.75	0.8	0.77	0.83	0.91	0.87	0.1	0.54	0.6	1.3	1.2	1.3	1.6
cis-1,2-Dichloroethane	1.1	1.1	1.1	0.63	0.63	0.66	0.1	0.14	0.15	1.6	1.6	1.7	1.2
Ethyl Benzene	0.39	0.41	0.41	0.63	0.67	0.67	0.3	0.27	0.28	0.72	0.71	0.77	0.84
m,p-Xylene	1.4	1.5	1.6	2.2	2.5	2.3	1.2	1.1	1.2	2.6	2.6	2.9	3
o-Xylene	0.52	0.54	0.55	0.9	0.98	0.94	0.43	0.42	0.41	1	1	1.1	1.2
Tetrahalomethane	0.079	0.083	0.083	0.066	0.068	0.068	0.066	0.064 U	0.068	0.086	0.092	0.1	0.84 U
Toluene	9.2	9.8	10	9.1 E	11 E	11 E	7.5	6.9	7.5	13 E	13 E	13 E	23
trans-1,2-Dichloroethane	2.9	2.8	2.9	0.46	0.44	0.44	0.63	0.71	0.73	4.5	4.4	4.7	3.2
Trichloroethane	3.3	3.2	3.7	1.4	1.5	1.5	1.8	1.8	2	3.2	3.2	3.5	4.4

TABLE F1  
INDOOR AND OUTDOOR AIR SAMPLING DATA FOR MCAS CHERRY POINT

Matrix: Sample Location: Sampler Type: Sample Location ID: Sampler ID: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	Indoor Air										Outdoor Air										
	Indoor Air Location #1					Summa					Indoor Air Location #2					WMS					
	137A-1C	137A-1B	137A-1A	137A-1C-SUM	137A-1B-SUM	137A-1A-SUM	137A-1C	137A-1B	137A-1A	137A-1C-SUM	137A-1B-SUM	137A-1A-SUM	137A-2A	137A-2B	137A-2C	137A-2A	137A-2B	137A-2C	137A-2A	137A-2B	137A-2C
1,1,1-Trichloroethane	0.46 U	0.46 U	0.46 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.24 U	0.24 U	0.24 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.18 U
1,1,2-Trichloroethane	2.4	2.4	2.4	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	0.25 U	0.25 U	0.25 U	0.027 U	0.027 U	0.027 U	0.027 U	0.027 U	0.027 U	0.069 U
1,1-Dichloroethane	0.46 U	0.46 U	0.46 U	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.23 U	0.23 U	0.23 U	0.087 U	0.087 U	0.087 U	0.087 U	0.087 U	0.087 U	0.17 U
1,2-Dichloroethane	0.46 U	0.46 U	0.46 U	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.23 U	0.23 U	0.23 U	0.087 U	0.087 U	0.087 U	0.087 U	0.087 U	0.087 U	0.17 U
Benzene	1.8	1.8	1.8	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.91	0.91	0.91	0.091	0.091	0.091	0.091	0.091	0.091	0.078 U
cis-1,2-Dichloroethane	1.1	1.1	1.1	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	0.84	0.84	0.84	0.084	0.084	0.084	0.084	0.084	0.084	0.061
Ethyl Benzene	0.84	0.84	0.84	0.91 U	0.91 U	0.91 U	0.91 U	0.91 U	0.91 U	0.91 U	0.91 U	0.24 U	0.24 U	0.24 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.1 U
m,p-Xylene	3	3	3	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	0.45	0.45	0.45	0.78	0.78	0.78	0.78	0.78	0.78	0.29
o-Xylene	1.1	1.1	1.1	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.2	1.2	1.2	2.1	2.1	2.1	2.1	2.1	2.1	0.93
Tetrachloroethane	0.84 U	0.84 U	0.84 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.13 U	0.47	0.47	0.47	0.86	0.86	0.86	0.86	0.86	0.86	0.34
Toluene	22	22	22	15	15	15	15	15	15	15	15	0.18	0.18	0.18	0.14	0.14	0.14	0.14	0.14	0.14	0.13
trans-1,2-Dichloroethane	3.2	3.2	3.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	2.9	2.9	2.9	4.7 E	4.7 E	4.7 E	4.7 E	4.7 E	4.7 E	2.7
Trichloroethane	4.4	4.4	4.4	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	3.1	3.1	3.1	2.5 E	2.5 E	2.5 E	2.5 E	2.5 E	2.5 E	6.2
				4.8	4.8	4.8	4.7	4.7	4.7	4.7	4.7	0.054	0.054	0.054	0.094	0.094	0.094	0.094	0.094	0.094	0.083 U
												0.035	0.035	0.035	0.073	0.073	0.073	0.073	0.073	0.073	0.088
												0.025	0.025	0.025	0.023	0.023	0.023	0.023	0.023	0.023	0.023
												0.89	0.89	0.89	6.88	6.88	6.88	6.88	6.88	6.88	6.88
												1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296E-2A	1101296D-3A
												1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296E-3A	1101296D-3A

TABLE F1  
INDOOR AND OUTDOOR AIR SAMPLING DATA FOR MCAS CHERRY POINT

Matrix	Indoor Air											
	Indoor Air Location #2											
	Sample Location	SKC	137-IA-2C	137-IA-2A	AID Tube	137-IA-2C	137-IA-2A	Summa	137-IA-2C	137-IA-2A	137-IA-2B	137-IA-2C
Client Sample ID:	137-IA-2A-SKC	137-IA-2B-SKC	137-IA-2C-SKC	137-IA-2A	137-IA-2B-AID	137-IA-2C-AID	137-IA-2A-SUM	137-IA-2B-SUM	137-IA-2C-SUM	137-IA-2A	137-IA-2B	137-IA-2C
Sampler Type/Screen:	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)	Regular (10 Cartridges)
Deployment Date/Time:	1-6-11 1:48 PM	1-6-11 1:50 PM	1-6-11 1:51 PM	1-6-11 1:48 PM	1-6-11 1:50 PM	1-6-11 1:51 PM	1-13-11 10:55 AM	1-13-11 11:18 AM	1-13-11 11:20 AM	1-13-11 11:20 AM	1-13-11 11:20 AM	1-13-11 11:20 AM
Closure Date/Time:	1-13-11 10:55 AM	1-13-11 10:54 AM	1-13-11 10:55 AM	1-13-11 10:54 AM	1-13-11 10:55 AM	1-13-11 10:55 AM	1-13-11 11:25 AM	1-13-11 11:25 AM	1-13-11 11:25 AM	1-13-11 11:25 AM	1-13-11 11:25 AM	1-13-11 11:25 AM
Exposure Duration (days):	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88
Exposure Duration (days):	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88	6.88
Laboratory Sample ID:	1101296B-14A	1101296B-15A	1101296B-16A	1101296E-44A	1101296E-45A	1101296E-46A	1101296C-37A	1101296C-38A	1101296C-39A	1101296C-37A	1101296C-38A	1101296C-39A
Relative Organic Compounds (ppmv)	0.029 U	0.029 U	0.029 U	0.54 U	0.54 U	0.54 U	0.15 U	0.14 U	0.18 U	0.15 U	0.24 U	0.24 U
1,1,1-Trichloroethane	0.025 U	0.025 U	0.025 U	0.46 U	0.46 U	0.46 U	0.15 U	0.14 U	0.18 U	0.15 U	0.24 U	0.24 U
1,1,2-Trichloroethane	0.015 U	0.015 U	0.015 U	0.40 U	0.40 U	0.40 U	0.15 U	0.14 U	0.18 U	0.15 U	0.22 U	0.22 U
1,1-Dichloroethane	0.037	0.037	0.037	0.35 U	0.35 U	0.35 U	0.15 U	0.14 U	0.18 U	0.15 U	0.45 J	0.45 J
1,2-Dichloroethane	0.056	0.056	0.054	0.40 U	0.40 U	0.40 U	0.15 U	0.14 U	0.18 U	0.15 U	0.22 J	0.22 J
Benzene	1.8	1.8	1.6	1.8	1.8	1.6	0.88	0.85	0.87	1.1	1.2	1.2
cis-1,2-Dichloroethene	0.16	0.16	0.16	0.43 U	0.43 U	0.43 U	0.15 U	0.14 U	0.18 U	0.15 U	0.021 U	0.021 U
Ethyl Benzene	0.87	0.9	0.84	1	1	1	0.76 U	0.70 U	0.92 U	0.76 U	0.5	0.52
m,p-Xylene	2.6	2.7	2.5	2.8	2.8	2.8	1.7	1.7	1.7	1.7	1.4	1.4
o-Xylene	1	1.1	0.96	1.1	1.1	1.1	0.76 U	0.70 U	0.92 U	0.76 U	0.52	0.52
Tetrachloroethene	0.24	0.25	0.22	0.84 U	0.84 U	0.84 U	0.28	0.28	0.26	0.28	0.16	0.16
Toluene	6.4	6.5	6.1	7.9	7.9	8.2	5.6	5.4	5.7	4	3.7	4.2
trans-1,2-Dichloroethene	28 E	29 E	28 E	32	29	29	47	49	49	30	26	35
Trichloroethene	0.035	0.031	0.026	0.54 U	0.54 U	0.54 U	0.15 U	0.14 U	0.18 U	0.15 U	0.024	0.026

TABLE F1  
INDOOR AND OUTDOOR AIR SAMPLING DATA FOR MCAS CHERRY POINT

Matrix: Sample Location: Sampler Type: Sample Location: Client Sample ID: Sampler Type/Solvent: Deployment Start Time: Deployment End Time: Exposure Duration (days): Laboratory Sample ID:	Indoor Air						Indoor Air						Summa				
	Radfield			WMS			SKC			ATD Tube			Indoor Air Location #3			Indoor Air Location #3	
	137-IA-3B	137-IA-3C	137-IA-3A	137-IA-3B	137-IA-3C	137-IA-3A	137-IA-3B	137-IA-3C	137-IA-3A	137-IA-3B	137-IA-3C	137-IA-3A	137-IA-3B	137-IA-3C	137-IA-3A	137-IA-3B	137-IA-3C
1,1,1-Trichloroethane	0.13 U	0.13 U	0.18 U	0.18 U	0.18 U	0.18 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U	0.029 U
1,1,2-Trichloroethane	0.027 U	0.027 U	0.069 U	0.069 U	0.069 U	0.069 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U
1,1-Dichloroethane	0.0086 U	0.0086 U	0.17 U	0.17 U	0.17 U	0.17 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U	0.015 U
1,2-Dichloroethane	0.0025 U	0.0025 U	0.24 U	0.24 U	0.24 U	0.24 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U	0.022 U
Benzene	0.02	0.018	0.078 U	0.078 U	0.078 U	0.078 U	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058
1,2-Dichloroethane	0.031 U	0.031 U	0.041 U	0.041 U	0.041 U	0.041 U	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
1,2-Dichloroethane	0.031 U	0.031 U	0.041 U	0.041 U	0.041 U	0.041 U	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
1,2-Dichloroethane	0.62	0.66	0.32	0.32	0.32	0.32	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
1,2-Dichloroethane	1.6	1.7	0.96	0.96	0.96	0.96	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
1,2-Dichloroethane	0.09	0.11	0.12	0.12	0.12	0.12	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
1,2-Dichloroethane	4.3 E	4.7 E	2.5	2.5	2.5	2.5	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
1,2-Dichloroethane	3.6 E	2.8 E	1.7	1.7	1.7	1.7	26 E	26 E	26 E	26 E	26 E	26 E	26 E	26 E	26 E	26 E	26 E
1,2-Dichloroethane	0.0077	0.0077	0.082 U	0.082 U	0.082 U	0.082 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U	0.024 U
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U	0.46 U
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U	0.35 U
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U	0.40 U
1,2-Dichloroethane	0.88	0.88	0.88	0.88	0.88	0.88	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
1,2-Dichloroethane	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U
1,2-Dichloroethane	1.2	1.2	1.2	1.2	1.2	1.2	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
1,2-Dichloroethane	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U	0.83 U
1,2-Dichloroethane	0.23	0.23	0.23	0.23	0.23	0.23	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
1,2-Dichloroethane	5.2	5.2	5.2	5.2	5.2	5.2	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
1,2-Dichloroethane	37	37	37	37	37	37	27	27	27	27	27	27	27	27	27	27	27
1,2-Dichloroethane	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U





APPENDIX F: INDOOR AIR CONCENTRATIONS AND PERFORMANCE STATISTICS FOR MCAS CHERRY POINT

Sample Location: Sample Location:	Indoor Air Location #1																
	137-IA-1 Sites																
	Sample Type: Client Sample ID: Sampler Type/Sovent: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	OVN	Radfield	WMS	SKG	ATD Tube	Summa										
	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV		
<i>Relative Organic Compounds</i>																	
1,1,1-Trichloroethane	6.93	0.65	0.13	15.00	1.41	0	3.47	0.33	0.06	3.00	0.28	0.12	8.17	0.77	0.01	16.07	0.05
1,1,2-Trichloroethane	0.25	--	--	0.03	--	--	0.07	--	--	0.03	--	--	0.46	--	--	0.14	--
1,1-Dichloroethane	3.77	0.62	0.06	0.49	0.08	0.05	0.41	0.07	0.23	4.03	0.67	0.05	2.33	0.39	0.13	6.03	0.03
1,2-Dichloroethane	0.86	0.38	0.08	0.02	0.01	0.20	0.29	0.13	0.22	1.43	0.64	0.04	1.01	0.45	0.16	2.23	0.07
Benzene	0.23	--	0	0.06	--	0	0.08	--	--	0.14	--	0.04	0.40	--	--	0.20	--
cis-1,2-Dichloroethane	0.77	1.09	0.03	0.87	1.23	0.05	0.55	0.78	0.08	1.27	1.78	0.05	1.67	2.35	0.07	0.71	0.06
ethylbenzene	1.10	0.63	0	0.06	0.04	0.03	0.13	0.08	0.20	1.63	0.94	0.04	1.17	0.67	0.05	1.73	0.03
m,p-Xylene	0.40	--	0.05	0.66	0.04	0.04	0.38	--	0.05	0.73	--	0.04	0.88	--	0.08	0.72	--
o-Xylene	1.50	0.83	0.07	2.33	1.30	0.07	1.17	0.65	0.05	2.70	1.50	0.06	3.23	1.80	0.12	1.80	0.06
Tetrachloroethene	0.54	0.70	0.05	0.94	1.23	0.04	0.42	0.55	0.02	1.03	1.35	0.06	1.23	1.62	0.12	0.76	0.17
Toluene	0.08	0.56	0.03	0.06	0.40	0.02	0.07	0.45	0.03	0.09	0.63	0.08	0.84	--	--	0.15	0.20
trans-1,2-Dichloroethene	9.67	0.63	0.04	10.37	0.68	0.11	7.30	0.48	0.05	13.00	0.83	0	22.67	1.48	0.03	15.33	0.04
Trichloroethene	2.87	0.69	0.02	0.45	0.11	0.03	0.69	0.17	0.08	4.53	1.09	0.03	3.27	0.78	0.04	4.17	0.01
	3.40	0.71	0.08	1.47	0.31	0.04	1.87	0.39	0.06	3.30	0.69	0.05	4.47	0.93	0.03	4.80	0.02

**APPENDIX F: INDOOR AIR CONCENTRATIONS AND PERFORMANCE STATISTICS FOR MCAS CHERRY POINT**

Sample Location: Sample Location: Sampler Type: Client Sample ID: Sampler Type/Sorbent: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	Indoor Air Location #1 137-IA-1 Series																
	OVM		Radiello		WMS		SKC		ATD Tube		Summa						
	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	COV			
<i>Volatile Organic Compounds</i> ( <i>µg/m<sup>3</sup></i> )																	
1,1,1-Trichloroethane	6.93	0.65	0.13	15.00	1.41	0	3.47	0.33	0.06	3.00	0.28	0.12	8.17	0.77	0.01	10.67	0.05
1,1,2-Trichloroethane	0.25	--	--	0.03	--	--	0.07	--	--	0.03	--	--	0.46	--	--	0.14	--
1,1-Dichloroethane	3.77	0.62	0.06	0.49	0.08	0.05	0.41	0.07	0.23	4.03	0.67	0.05	2.33	0.39	0.13	6.03	0.03
1,1-Dichloroethene	0.86	0.38	0.08	0.02	0.01	0.20	0.29	0.13	0.22	1.43	0.64	0.04	1.01	0.45	0.16	2.23	0.07
1,2-Dichloroethane	0.23	--	0	0.06	--	0	0.08	--	--	0.14	--	0.04	0.40	--	--	0.20	--
Benzene	0.77	1.09	0.03	0.87	1.23	0.05	0.55	0.78	0.08	1.27	1.78	0.05	1.67	2.35	0.07	0.71	0.06
cis-1,2-Dichloroethene	1.10	0.63	0	0.06	0.04	0.03	0.13	0.08	0.20	1.63	0.94	0.04	1.17	0.67	0.05	1.73	0.03
Ethyl Benzene	0.40	--	0.03	0.66	--	0.04	0.28	--	0.05	0.73	--	0.04	0.88	--	0.08	0.72	--
m,p-Xylene	1.50	0.83	0.07	2.33	1.30	0.07	1.17	0.65	0.05	2.70	1.50	0.06	3.23	1.80	0.12	1.80	0.06
o-Xylene	0.54	0.70	0.03	0.94	1.23	0.04	0.42	0.55	0.02	1.03	1.35	0.06	1.23	1.62	0.12	0.76	0.17
Tetrachloroethene	0.08	0.56	0.03	0.06	0.40	0.02	0.07	0.45	0.03	0.09	0.63	0.08	0.84	--	--	0.15	0.20
Toluene	9.67	0.63	0.04	10.37	0.68	0.11	7.30	0.48	0.05	13.00	0.85	0	22.67	1.48	0.03	15.33	0.04
trans-1,2-Dichloroethene	2.87	0.69	0.02	0.45	0.11	0.03	0.69	0.17	0.08	4.53	1.09	0.03	3.27	0.78	0.04	4.17	0.01
Trichloroethene	3.40	0.71	0.08	1.47	0.31	0.04	1.87	0.39	0.06	3.30	0.69	0.05	4.47	0.93	0.03	4.80	0.02

**APPENDIX F: INDOOR AIR CONCENTRATIONS AND PERFORMANCE STATISTICS FOR MCAS CHERRY POINT**

Sample Location: Sample Location: Sampler Type: Client Sample ID: Sampler Type/Sorbent: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	Indoor Air Location #2 137-IA-2 Series																		
	OVM			Radicle			WMS			SKC			ATD Tube			Summa			
	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	Average	C/Co	COV	
<i>Volatile Organic Compounds (ug/m<sup>3</sup>)</i>																			
1,1,1-Trichloroethane	0.24	--	--	0.14	--	--	0.18	--	--	0.03	--	--	0.54	--	--	0.16	--	--	
1,1,2-Trichloroethane	0.25	--	--	0.03	--	--	0.07	--	--	0.03	--	--	0.46	--	--	0.16	--	--	
1,1-Dichloroethane	0.23	--	--	0.01	--	--	0.17	--	--	0.02	--	--	0.40	--	--	0.16	--	--	
1,1-Dichloroethene	0.45	--	0	0.00	--	--	0.25	--	--	0.03	--	0.22	0.35	--	--	0.16	--	--	
1,2-Dichloroethane	0.23	--	0	0.01	--	0.08	0.08	--	--	0.06	--	0.03	0.40	--	--	0.16	--	--	
Benzene	0.90	1.04	0.04	0.93	1.08	0.04	0.60	0.70	0.02	1.73	2.00	0.07	1.73	2.00	0.07	0.87	0.16	0.02	
cis-1,2-Dichloroethene	0.02	--	0.04	0.00	--	--	0.10	--	--	0.16	--	0.00	0.43	--	--	0.16	--	--	
Ethyl Benzene	0.49	--	0.08	0.77	--	0.03	0.32	--	0.08	0.87	--	0.03	0.99	--	0.01	0.79	--	--	
m,p-Xylene	1.30	0.76	0.08	2.07	1.22	0.03	1.01	0.59	0.08	2.60	1.53	0.04	2.80	1.65	0	1.70	0	0	
o-Xylene	0.51	--	0.07	0.87	--	0.03	0.36	--	0.06	1.02	--	0.07	1.10	--	0	0.79	--	--	
Tetrachloroethene	0.19	0.70	0.05	0.15	0.54	0.04	0.13	0.49	0.04	0.24	0.87	0.06	0.84	3.07	--	0.27	0.04	0.04	
Toluene	3.50	0.63	0.06	4.60	0.83	0.04	3.10	0.56	0.12	6.33	1.14	0.03	8.00	1.44	0.02	5.57	0.80	0.03	
trans-1,2-Dichloroethene	30.67	0.63	0.05	2.57	0.05	0.12	4.93	0.10	0.30	28.33	0.59	0.02	30.00	0.62	0.06	48.33	0.02	0.02	
Trichloroethene	0.03	--	0.04	0.01	--	0.13	0.08	--	--	0.03	--	0.15	0.54	--	--	0.16	--	--	

**APPENDIX F: INDOOR AIR CONCENTRATIONS AND PERFORMANCE STATISTICS FOR MCAS CHERRY POINT**

Sample Location: Sample Location: Sampler Type: Client Sample ID: Sampler Type/Sorbent: Deployment Date/Time: Collection Date/Time: Exposure Duration (min): Exposure Duration (days): Laboratory Sample ID:	Indoor Air Location #3 137-IA-3 Series												
	OVM		Radfield		WMS		SKC		ATD Tube		Summa		
	Average	COV	Average	COV	Average	COV	Average	COV	Average	COV	Average	COV	
<i>Volatile Organic Compounds</i> ( $\mu\text{g}/\text{m}^3$ )													
1,1,1-Trichloroethane	0.24	--	0.13	--	0.18	--	0.03	--	0.54	--	0.14	--	
1,1,2-Trichloroethane	0.25	--	0.03	--	0.07	--	0.02	--	0.46	--	0.14	--	
1,1-Dichloroethane	0.22	--	0.01	--	0.17	--	0.02	--	0.40	--	0.14	--	
1,1-Dichloroethene	<b>0.45</b>	0	0.00	--	0.24	--	<b>0.02</b>	0.09	0.35	--	0.14	--	
1,2-Dichloroethane	<b>0.22</b>	0	<b>0.02</b>	0.11	0.08	--	<b>0.06</b>	0.05	0.40	--	0.14	--	
Benzene	<b>1.10</b>	1.25	<b>1.00</b>	1.14	<b>0.64</b>	0.73	<b>0.14</b>	0.04	<b>1.90</b>	2.16	<b>0.88</b>	0	
cis-1,2-Dichloroethene	<b>0.02</b>	0.13	0.003	--	0.10	--	<b>0.14</b>	0.04	0.43	--	0.14	--	
Ethyl Benzene	<b>0.49</b>	0.07	<b>0.66</b>	--	<b>0.30</b>	--	<b>0.78</b>	0.05	<b>0.86</b>	--	0.68	--	
m,p-Xylene	<b>1.33</b>	1.00	<b>1.70</b>	1.28	<b>0.91</b>	0.68	<b>2.20</b>	1.65	<b>2.27</b>	1.70	<b>1.33</b>	0.09	
o-Xylene	<b>0.46</b>	0.67	<b>0.74</b>	--	<b>0.35</b>	--	<b>0.89</b>	0.04	<b>1.01</b>	--	0.68	--	
Tetrachloroethene	<b>0.18</b>	0.80	<b>0.12</b>	0.52	<b>0.12</b>	0.52	<b>0.19</b>	0.81	<b>0.83</b>	--	<b>0.23</b>	0.09	
Toluene	<b>3.97</b>	0.78	<b>4.57</b>	0.90	<b>2.50</b>	0.49	<b>6.13</b>	1.20	<b>7.90</b>	1.55	<b>5.10</b>	0.03	
trans-1,2-Dichloroethene	<b>30.33</b>	0.80	<b>2.93</b>	0.08	<b>2.03</b>	0.05	<b>26.33</b>	0.69	<b>27.00</b>	0.71	<b>38.00</b>	0.03	
Trichloroethene	<b>0.02</b>	--	<b>0.01</b>	--	<b>0.08</b>	--	<b>0.02</b>	--	<b>0.54</b>	--	<b>0.14</b>	--	

**Notes:**

(1) These calculations include non-detect results using the reporting limit as a surrogate value.

**Bold** - calculations included at least one detected or estimated detection value

-- - All results were non-detect

## Appendix G

### Transient Model Derivation for Radial Diffusion to a Passive Soil Vapor Probe

The transient model derivation is provided below. Dr. Andre Unger originally derived this solution for radial diffusion into a SPME fibre, but the geometry for radial diffusion through two media is analogous for this application as well. In this case the outer medium is soil and the inner medium is the void space within the borehole in which the passive sampler is deployed. The axis of symmetry at  $r = r_1$  was assigned a very small radius ( $10^{-6}$  cm). The radius of the borehole or void space is assigned to be  $r_2$ . Nominal 1-inch (2.54 cm) and 4-inch (10.2 cm) diameter holes were considered because these are common for hand tools used in passive sampler deployment. The radial distance at which concentrations remain essentially unaffected throughout the passive sampling duration ( $r_3$ ) was assigned to be 1 m. A smaller value for  $r_3$  would result in a higher diffusive delivery rate of vapors from the soil to the void space. The sensitivity of this value was evaluated using the steady-state model. Where needed for calculating the volume of the void space, the vertical height of the void space was assumed to be 10 cm. The governing equations are:

Concentration in the gas phase within the void space  $c_g(r, t)$ ;

$$\frac{\partial c_g}{\partial t} - D_{air} \left[ \frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r} \frac{\partial c_g}{\partial r} \right] = 0 \quad 0 \leq r < r_2 \quad (\text{G-1})$$

Concentration in the soil vapor surrounding the void space  $c_s(r, t)$ ;

$$\frac{\partial c_s}{\partial t} - D_{eff} \left[ \frac{\partial^2 c_s}{\partial r^2} + \frac{1}{r} \frac{\partial c_s}{\partial r} \right] = 0 \quad r_2 \leq r < r_3 \quad (\text{G-2})$$

with the following initial and boundary conditions:

$$c_g(r_2, t) = c_s(r_2, t) \quad (\text{G-3})$$

$$c_g(r, 0) = 0 \quad (G-4)$$

$$c_s(r, 0) = c_{s_0} \quad (G-5)$$

$$\frac{\partial c_g}{\partial r}(r_1, t) = 0 \quad (G-6)$$

$$\frac{\partial c_s}{\partial r}(r_3, t) = 0 \quad (G-7)$$

$$D_{air} \frac{\partial c_g}{\partial r}(r_2, t) = D_{eff} \frac{\partial c_s}{\partial r}(r_2, t) \quad (G-8)$$

Applying the Laplace transform to Equation (G-1) to transform the time derivative in order to convert the partial differential equation (PDE) into an ordinary differential equation (ODE):

$$L[c_g(r, t)] = \bar{c}_g(r, p) \quad (G-9)$$

$$L\left[\frac{\partial c_g}{\partial t}\right] = -c_g(r, 0) + p\bar{c}_g(r, p) = p\bar{c}_g(r, p) \quad (G-10)$$

$$D_{air} \left[ \frac{\partial^2 \bar{c}_g}{\partial r^2} + \frac{1}{r} \frac{\partial \bar{c}_g}{\partial r} \right] - p\bar{c}_g = 0 \quad (G-11)$$

where  $p$  is the Laplace transform variable and is complex-valued.

Applying the Laplace transform to Equation (G-2):

$$L[c_s(r, t)] = \bar{c}_s(r, p) \quad (G-12)$$

$$L\left[\frac{\partial c_s}{\partial t}\right] = -c_s(r, 0) + p\bar{c}_s(r, p) = -c_{s_0} + p\bar{c}_s(r, p) \quad (G-13)$$

$$D_{eff} \left[ \frac{\partial^2 \bar{c}_s}{\partial r^2} + \frac{1}{r} \frac{\partial \bar{c}_s}{\partial r} \right] - p\bar{c}_s = -c_{s_0} \quad (G-14)$$

Applying the Laplace transform to initial and boundary Equations (G-3), (G-10), (G-7) and (G-8),

$$\bar{c}_g(r_2, p) = \bar{c}_s(r_2, p) \quad (G-15)$$

$$L \left[ \frac{\partial c_g}{\partial r}(r_1, t) \right] = \int_0^\infty \frac{\partial c_g}{\partial r}(r_1, t) e^{-pt} dt = \frac{\partial}{\partial r} \int_0^\infty c_g(r_1, t) e^{-pt} dt \quad (G-16)$$

$$= \frac{\partial \bar{c}_g}{\partial r}(r_1, p) = 0$$

$$L \left[ \frac{\partial c_s}{\partial r}(r_3, t) \right] = \frac{\partial \bar{c}_s}{\partial r}(r_3, p) = 0 \quad (G-17)$$

$$D_{air} \frac{\partial \bar{c}_g}{\partial r}(r_2, p) = D_{eff} \frac{\partial \bar{c}_s}{\partial r}(r_2, p) \quad (G-18)$$

The transformed governing equation (Equation G-11) is a linear, second-order homogeneous ordinary differential equation (ODE) that has a solution of the general form:

$$\bar{c}_c = AI_0(q_g r) + BK_0(q_g r) \quad (G-19)$$

where  $q_g^2 = \left| -\frac{p}{D_{air}} \right| = \frac{p}{D_{air}}$ , if  $p > 0$ ,  $I_0$  is the modified Bessel function  $I$  of order zero and  $K_0$  is the modified Bessel function of  $K$  of order zero.

Differentiating  $\bar{c}_g$  with respect to  $r$ , we obtain

$$\frac{\partial \bar{c}_g}{\partial r} = q_g AI_1(q_g r) - q_g BK_1(q_g r) \quad (G-20)$$

where  $I_1$  is the modified Bessel function  $I$  of order one and  $K_1$  is the modified Bessel function of  $K$  of order one. Using Equation (G-16),

$$q_g AI_1(q_g r_1) - q_g BK_1(q_g r_1) = 0 \quad (G-21)$$

$$A = \frac{BK_1(q_g r_1)}{I_1(q_g r_1)} \quad (G-22)$$

$$\bar{c}_c = B \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r) \right]. \quad (G-23)$$

The general form solution of Equation (G-14) is

$$\bar{c}_s = \frac{c_{s_0}}{p} + EI_0(q_s r) + FK_0(q_s r) \quad (G-24)$$

where  $q_s^2 = \frac{p}{D_s}$ .

Differentiating  $\bar{c}_s$  with respect to  $r$ , we obtain

$$\frac{\partial \bar{c}_s}{\partial r} = q_s EI_1(q_s r) - q_s FK_1(q_s r) \quad (G-25)$$

and using Equation (G-17),

$$q_s EI_1(q_s r_3) - q_s FK_1(q_s r_3) = 0 \quad (G-26)$$

$$E = \frac{FK_1(q_s r_3)}{I_1(q_s r_3)} \quad (G-27)$$

$$\bar{c}_s = \frac{c_{s_0}}{p} + F \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r) \right]. \quad (G-28)$$

In order to solve the constant  $F$  based on Equation (G-18), differentiate  $\bar{c}_s$  with respect to  $r$  again

$$\frac{\partial \bar{c}_s}{\partial r} = F q_s \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r) - F q_s K_1(q_s r) \quad (G-29)$$

and do the same to Equation (G-23),

$$\frac{\partial \bar{c}_g}{\partial r} = B q_g \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r) - B q_g K_1(q_g r). \quad (G-30)$$

Substituting Equation (G-18) with the two equations above,

$$FD_s q_s \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2) \right] = BD_{air} q_g \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2) \right] \quad (G-31)$$



$$F = B \frac{D_{air} q_g}{D_{eff} q_s} \frac{\overbrace{\left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2) \right]}^{\varphi_1}}{\underbrace{\left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2) \right]}_{\varphi_2}}$$

$$F = B \frac{\varphi_1 \varphi_3}{\varphi_2}$$

$$\therefore \bar{c}_s = \frac{c_{s_0}}{p} + B \frac{\varphi_1 \varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r) \right]. \quad (G-32)$$

In order to determine the constant  $B$  in Equation (G-23) and (G-32), Equation (G-15) is applied:

$$B \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r_2) + K_0(q_g r_2) \right] = \frac{c_{s_0}}{p} + B \frac{\varphi_1 \varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r_2) + K_0(q_s r_2) \right]$$

$$B = \frac{c_{s_0}}{p} \left\{ \underbrace{\left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r_2) + K_0(q_g r_2) \right]}_{\varphi_4} - \frac{\varphi_1 \varphi_3}{\varphi_2} \underbrace{\left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r_2) + K_0(q_s r_2) \right]}_{\varphi_5} \right\}^{-1}$$

$$B = \frac{c_{s_0}}{p} \frac{1}{\varphi_4 - \frac{\varphi_1 \varphi_3 \varphi_5}{\varphi_2}} = \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2 \varphi_4 - \varphi_1 \varphi_3 \varphi_5}. \quad (G-33)$$

Finally, arranging the constant  $B$  into the governing equations, we obtain

$$\bar{c}_g = \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2 \varphi_4 - \varphi_1 \varphi_3 \varphi_5} \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r) \right] \quad (G-34)$$

for  $0 \leq r < r_2$

$$\bar{c}_s = \frac{c_{s_0}}{p} + \kappa \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2 \varphi_4 - \varphi_1 \varphi_3 \varphi_5} \frac{\varphi_1 \varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r) \right] \quad (G-35)$$

for  $r_2 \leq r < r_3$

To find the total mass  $M(t)$  per unit area in the thin film when  $r = r_2$  as a function of time, we have:

$$\text{or } \bar{M}(p) = \frac{D_{eff}}{p} \frac{\partial \bar{c}_s}{\partial r} \Big|_{r=r_2} \quad (\text{G-36})$$

Differentiating Equation (G-34) with respect to  $r$ ,

$$\frac{\partial \bar{c}_g}{\partial r} = \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} q_g I_1(q_g r) - q_g K_1(q_g r) \right] \quad (\text{G-37})$$

And then rearranging the mass function, we obtain,

$$\begin{aligned} \bar{M}(p) &= \frac{D_{air} c_{s_0}}{p^2} q_g \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \left[ \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2) \right] \\ &= \frac{D_{air} c_{s_0}}{p^2} q_g \frac{\varphi_2 \varphi_1}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}. \end{aligned} \quad (\text{G-38})$$

Equation (G-38) allows the calculation of the mass in the void space based on the mass flux across the borehole wall from the void side.

Again, differentiating Equation (G-35) with respect to  $r$ ,

$$\begin{aligned} \frac{\partial \bar{c}_s}{\partial r} &= \frac{c_{s_0}}{p} \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \frac{\varphi_1\varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} q_s I_1(q_s r) - q_s K_1(q_s r) \right] \\ \bar{M}(p) &= \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \frac{\varphi_1\varphi_3}{\varphi_2} \left[ \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2) \right] \\ &= \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2 \varphi_1 \varphi_3}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}. \end{aligned} \quad (\text{G-39})$$

Equation (G-39) allows the calculation of the mass in the void space based on the mass flux across the borehole wall from the soil side.

The inverse Laplace transforms of Equation (G-34), (G-35), (G-38) and (G-39) are computed numerically using the algorithm developed by DeHoog et al.<sup>29</sup>.

## Bessel functions

The modified Bessel functions  $I_\alpha$  and  $K_\alpha$  used for Equations (G-34), (G-35), (G-38) and (G-39) are defined by

$$I_\alpha(x) = i^{-\alpha} J_\alpha(ix) = \sum_{m=0}^{\infty} \frac{1}{m! \Gamma(m + \alpha + 1)} \left(\frac{x}{2}\right)^{2m+\alpha} \quad (\text{G-40})$$

$$K_\alpha(x) = \frac{\pi I_{-\alpha}(x) - I_\alpha(x)}{2 \sin(\alpha\pi)} = \frac{\pi}{2} i^{\alpha+1} H_\alpha^{(1)}(ix) = \frac{\pi}{2} (-i)^{\alpha+1} H_\alpha^{(2)}(-ix) \quad (\text{G-41})$$