Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts. This journal is © The Royal Society of Chemistry 2015

Passive Sampling for Volatile Organic 1 **Compounds in Air**– Controlled Laboratory 2 Comparison of Four Sampler Types 3 **Electronic Supplemental Information** 4 5 Todd McAlary^{1,3*}, Hester Groenevelt¹, Stephen Disher², Jason Arnold², Suresh Seethapathy³, 6 Paolo Sacco⁴, Derrick Crump⁵, Brian Schumacher⁶, Heidi Hayes², Paul Johnson⁷, Tadeusz 7 Górecki³ 8 ¹Geosyntec Consultants, Inc. 130 Research Lane, #2, Guelph, Ontario, N1G 5G3 9 ²Eurofins Air Toxics, Inc. (formerly Air Toxics Ltd.), Folsom, CA

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17 Apparatus

18 The apparatus consisted of a system to purify, humidify and control the temperature of a supply of air to which VOCs were added from compressed gas cylinders and delivered to 19 20 exposure chambers containing the passive samplers. The gas cylinders were prepared with concentrations of 10 parts per million by volume (ppm_v) for all of the compounds listed in Table 21 ESI-2, except 1 ppm_v for naphthalene, which has a much lower vapor pressure, and was therefore 22 added at a concentration 10 times lower than the other compounds to prevent it from condensing 23 in the cylinder. The supply gas mixtures were custom-fabricated by Air Liquide America 24 Specialty Gases LLC of Santa Fe Springs, CA. Mass flow controllers were used to mix gas from 25 the cylinders and charcoal-filtered air at flow rates required to achieve the target concentrations 26 of 1, 50 or 100 parts per billion by volume (ppb_y) (0.1, 5 and 10 ppb_y for naphthalene). Humidity 27 28 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 29 piping were heated sufficiently to minimize condensation. 30

31 Three exposure chambers were constructed, each of which consisted of a glass cylinder with 32 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 33 samplers (5 types, each in triplicate) in a circular Teflon manifold designed to be rotated at a 34 constant speed to control the face velocity and allow sufficient distance between the samplers to 35 minimize competition between the samplers. Baffles were installed inside the chambers to 36 minimize the creation of a rotational gas flow inside the chamber (gas rotation in the chamber 37 would reduce the actual face velocity to which the samplers were exposed). The chamber 38 materials were all passivated using the Siltek process by Restek Corporation of Bellefonte, PA to 39

40 coat the surfaces with silicon hydrides and make them as inert as practicable to minimize 41 adsorption and desorption of VOC vapors during the experiments. The design details of the 42 exposure chamber are shown in Figure ESI-1.

43 The mixed and humidified 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 44 negligible compared to the flux through the chamber. The consistency of the vapor 45 46 concentrations inside the chamber was verified by monitoring concentrations at the influent and effluent end of the chamber during the experiments, which were found to have concentrations 47 within analytical error (about 5% relative percent difference [RPD]). The corresponding linear 48 velocity of the gas flow was about 0.002 m/s, which was slow enough to be negligible compared 49 to the face velocity generated via the rotating sampler support frame. The samplers were rotated 50 at 1.0, 18 or 35 rpm using one of three rotisserie motors placed on top of the frame to achieve 51 face velocities of 0.014, 0.23, and 0.41 m/s. Each of the five different types of samplers (A, B, C, 52 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 53 for each chamber. One chamber was dedicated to the 1 ppb_v testing, and was not used for testing 54 at higher concentrations to avoid carry-over (desorption of test compounds from the inner 55 surfaces). 56



58 Figure ESI-1. Design details of the exposure chamber

59 Passive Sampler Uptake Rates

60 Uptake rates used for each of the passive samplers are presented in Table ESI-1. The same uptake rates were used for the ATD tube samplers regardless of whether the sorbent was 61 Carbopack B or Tenax. In most of the samplers, the uptake rate depends on the free-air diffusion 62 coefficient (Table ESI-2), which is closely related to the molecular weight. For these samplers, 63 uptake rates were estimated by linear interpolation from the nearest heavier and lighter molecular 64 weight compounds with vendor-supplied uptake rates. For the WMS sampler, the uptake rate 65 depends on two factors: 1) the distribution coefficient for the compound between air and PDMS 66 (the membrane material), and 2) the permeation rate through PDMS, which has been shown to be 67 strongly correlated with the linear temperature programmed retention index (LTPRI).^{1, 2, 3} Where 68 needed, WMS uptake rates were estimated from the linear regressions and the compound-69 specific retention indices. The SKC Ultra has two sets of published uptake rates: one for air 70 71 velocities of 5 cm/min or higher, and another for 5 cm/min or lower; since the chamber tests were conducted at air velocities of 14 cm/min or higher, the high velocity uptake rates were used. 72

73	Table ESI-1.	Uptal	ke rates	for	the	passive	sampl	lers
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Analyte	WMS ^{1,2}	Radiello ⁴	SKC Ultra ^{5,6}	ATD Tube ⁷
1,1,1-Trichloroethane (TCA)	1.3	62	14	0.50*
1,2,4-Trimethylbenzene				
(124TMB)	13*	50	13*	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	13*	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				

74

75 Properties of the 10 VOCs tested are presented in Table ESI-2.

76 Table ESI-2. Compounds tested and their key properties

Analyte	Koc (mL/g)	Henry's Constant (unitless)	Vapor pressure (atm)	Free Air Diffusion Coefficient (cm ² /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)	43	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

77 *Values drawn from: <u>http://www.epa.gov/superfund/health/conmedia/soil/pdfs/appd_k.pdf</u>

⁷⁸ All other values from http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm

80 Table ESI-3. Inter-laboratory testing scheme

Sampler Type	Home Laboratory	Secondary Laboratories	Number of Samplers to Each Lab
WMS	University of Waterloo	Air Toxics Ltd Airzone One	2
ATD Tubes with Tenax TA	Air Toxics Ltd	Columbia Analytical Services University of Waterloo	2
ATD Tubes with CarboPack B	Air Toxics Ltd	Columbia Analytical Services University of Waterloo	2
SKC Ultra	Columbia Analytical Services	Air Toxics Ltd Airzone One	2
Radiello	Fondazione Salvatore Maugeri	Columbia Analytical Services Air Toxics Ltd	2

81

82 Active Sample Collection and Analysis Methods

83 Chamber concentrations were verified by collecting active thermal desorption tube samples. Clean dual bed sorbent tubes containing 30 mm Tenax GR 35/60 plus 25 mm Carbopack B 60/80 84 with an approximately 350 mg total weight of sorbent were used for sample collection. Two 85 sample pumps were used for sample collection, SKC AirChek 224-PCXR4 and SKC AirChek 86 2000, and were calibrated using a Bios Defender 510 DryCal® primary standard calibrator. A 87 dummy Tenax GC/Carbopack B (GRB) calibration tube was used to set the initial flow rate. 88 The flow rate on the sample tube itself was also recorded immediately prior to sample collection 89 to account for small differences in flow due to tube packing variability. The flow rate after 90 sample collection was also recorded, and the average flow rate was used to calculate sample 91

92 volume. Evaluating all of the calibration flow rates measured for active collection, the flow rate
93 measured at the end of sampling agreed on average within 2% with that measured at the start of
94 the sampling period.

95 The sample tube was inserted in the side port of the chamber located on the side opposite of the calibration gas entrance and immediately below the samplers on the carousel. 96 During the familiarity testing, active samples were collected using the port directly opposite the calibration 97 gas entrance and also immediately below the samplers on the same side as the calibration gas 98 99 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%. 100 101 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 102 103 measurably depleted by the passive samplers. The concentrations measured at the effluent port 104 compared within 5% of the concentrations measured at the side port located below the samplers.

The three concentrations tested (1, 50 and 100 ppbv) required varying flow and duration to insure sufficient mass was collected on the tube for accurate quantification. The typical target flows, duration, and volumes for each concentration are listed in Table ESI-4. On occasion, the flow rate and duration were modified; however, the targeted volume collected was generally kept constant. A minimum of one active sample was collected for each chamber each day of testing.

111 Table ESI-4. Active sample collection parameters

Chamber Concentration	Flow (ml/min)	Duration (min)	Volume (L)
1 ppbv	100	120	12
50 ppbv	25	120	3.0
100 ppbv	25	60	1.5

The '1 ppbv' samples collected under the high humidity and high temperature conditions required an off-line dry purge of dry nitrogen at 50 mL/min for 4 minutes at approximately 21°C to remove excess water prior to sample analysis. No other sample preparation was required.

115 Active and Passive ATD Tube Analysis

116 The active GRB sample tubes and the passive Tenax TA and Carbopack B sample tubes were 117 analyzed following EPA Method TO-17. Sorbent tubes were heated to release adsorbed 118 compounds, which were swept onto a secondary trap for further concentration and removal of 119 moisture. In general, the GRB and Carbopack B tubes were heated to approximately 300°C, and 120 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. 121 The analytical instrumentation used for sample analysis was a Markes Unity/Ultra thermal 122 desorption unit coupled with an Agilent 7890 GC and 5975 MSD. Calibration was achieved by 123 124 injecting and vaporizing methanolic NIST-traceable calibration mixes onto clean sorbent tubes. 125 Since desorption parameters and performance varied slightly for each sorbent type, calibrations 126 were generated for each tube packing. Additionally, the calibration range and the thermal desorption unit operating parameters were optimized for the expected mass loading on each tube. 127 128 The analytical quality control protocols and criteria were based on EPA Method TO-17.

129 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. 130 Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5 were utilized as internal standards, and 4-131 Bromofluorobenzene (BFB) was evaluated as a MS tune check and also monitored as a sample 132 surrogate. The BFB Tune Check was analyzed and evaluated prior to the start of each 24-hour 133 134 analytical clock against the tuning criteria outlined in EPA Method TO-17. The internal 135 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 136 137 active samples collected under conditions of high humidity and high temperature despite the dry-138 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 139 140 evaluated against laboratory limits of 70-130%.

141 The calibration range was optimized for the expected concentration range. The 1 ppby chamber test for 24 hours required the greatest sensitivity and the instrument was configured to 142 cover the range from 0.5 to 10 nanograms. The active samples and the 50 and 100 ppbv passive 143 144 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 145 Carbopack B tubes were analyzed against a calibration with a range from 2000 to 20,000 146 nanograms. In each case, the reporting limit was supported by the lowest calibration level of the 147 initial calibration curve. 148

Overall, linearity was excellent, and the %RSD for each calibration curve was well within TO-150 17 method criterion of less than 30%. Linearity was not always achieved for all of the target 151 compounds at the lower concentrations due to background concentrations from the sorbent 152 packing (e.g. Benzene) or poor analytical response (e.g. Methyl Ethyl Ketone). In several cases, 153 target compounds could not be reliably measured and results were below the linear range and 154 marked as not detected or flagged. Methyl Ethyl Ketone proved to be a poor performing 155 compound throughout the study, specifically with Carbopack B sorbent. Methyl Ethyl Ketone 156 reporting limits were often raised due to linearity issues at the low end of the calibration curve.

Following the daily tune check, a CCV standard 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.

164 Hexane proved to be unstable in the methanolic calibration standard showing gradual loss over 165 Since the second source calibration mix was also prepared in methanol, the discrepancy time 166 was not evident in the daily QC performance until the standard was compared to several NISTvapor phase calibration standards. As part of the laboratory's investigation as to the cause of the 167 higher than expected hexane concentrations measured in the chamber, two independent NIST-168 traceable vapor standards were loaded onto the sorbent tubes and recovered between 150 and 169 170160% demonstrating that the stated hexane concentration in the methanol calibration standard 171 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 172 173 to indicate a positive 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 174

175 indicate which results were biased low as a result of the degraded standard. Unfortunately, this 176 approach did not yield a reliable correction factor. All hexane results generated for the active 177 and passive ATD tubes for Runs 13 through 18 were quantified using freshly prepared 178 methanolic working standards verified with a vapor-phase NIST calibration. When the vapor 179 phase check was analyzed with the daily batch, both the methanolic second source and the vapor 180 phase second source recoveries were reported.

181 Sorbent media cleaning and certification

182 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 183 184 analyzed on the TO-17 unit to insure background concentrations were below the reporting limits. 185 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 186 Carbopack X (60/80 mesh) was transferred to a clean empty ATD tube sleeve with an internal 187 188 support screen to hold the sorbent material. A plug of clean glass wool was used to support 189 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 190 191 analyzed on the TO-17 unit to insure no target compounds were present above the reporting Immediately prior to sample deployment, the sorbent was emptied into a clean 4 mL 192 limit. 193 screw top vial for transfer into the Ultra II badge housing.

194 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_2 and 100 μ L of 197 internal standard solution (2-fluorotoluene) directly in the Radiello glass storage tube without drawing out the cartridge. After 30 min, 2 µL of the CS₂ solution was injected in the 198 gas chromatograph. The GC system (6890N, Agilent Technologies, Wilmington, DE, USA) was 199 equipped with a 50 m column (J&W-PONA, 0.2 mm id, 0.5 µm film thickness) and two 200 detectors, FID and MSD (5975B, Agilent Technologies, Wilmington, DE, USA), connected to 201 202 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 5 203 °C min⁻¹ to 90 °C, followed by 90 °C for 3 min, a second ramp of 10 °C min⁻¹ to 150 °C, and a 204 third ramp of 20 °C min⁻¹ to 250 °C. The total run time was 34 min. The split ratio was 20:1. 205 The carrier gas was nitrogen at 21 psi. The FID temperature was 270 °C. The calibration was 206 performed by the phase equilibrium technique, adding to new, unexposed cartridges 207 208 accurately measured 2 mL aliquots of a series of calibration solutions, prepared by serial dilutions, ranging from 0.82 to 2.04 µg mL⁻¹ (lowest level) and from 3,260 to 8,140 µg 209 mL⁻¹ (highest level), except naphthalene, whose concentrations were about ten times lower (0.14 210 to 555 µg mL⁻¹). Quantitation was made using the FID signal, while MSD was used for 211 compound identity confirmation. 212

213 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 ppb_v for 1 day) to the high concentration/ long duration (100 ppb_v for 7 days). The low-level calibration range was approximately 1-500 ng/tube and the high220 level range was approximately 200-50,000 ng/tube. In both cases, internal standards (1,4difluorobenzene and chlorobenzene-d5) and surrogates (toluene-d8 and p-bromofluorobenzene) 221 were added (25 ng or 1000 ng) and a dry purge was performed (2 min @ 50 mL/min or 5 min @ 222 80 mL/min) prior to analysis. Desorption was performed for 15 minutes at 350 °C with a cold 223 224 trap at 25 °C. The inlet was split 2:1 for the low-level method and 20:1 for the high level 225 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 226 2.2.7 60 m x 0.25 mm ID x 1.00 μm film Rxi-1ms (Restek Corp.). The temperature program was the 228 same for both methods: 2 min @ 40C, 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 and the scan range was m/z 33 to 229 230 300. CAS observed background levels of benzene and MEK in these sorbents and were forced to 231 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 232 reporting limits), and even with additional cleaning, background levels of benzene were still 233 observed (in the range of approximately 20-25 ng in 500 mg of sorbent). 234

235 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 (low benzene CS_2) was introduced into the vial, which was then

shaken intermittently over 30 minutes for desorption. After desorption, the vials were centrifuged 243 if necessary, and aliquots of the extract were transferred to 1.8 mL crimp cap vials with 100 µL 244 inserts for GCMS analysis. The injector was set at 275 °C, the split ratio was 1:10 and the 245 injection volume was 1 µL. Helium was the carrier gas, with a flow rate of 2.0 mL/min. The 246 temperature program was 35 °C for 5 min, 5 °C/min to 120 °C, 30 °C/min to 350 °C (held for 3 247 248 minutes). The data acquisition and processing was performed with Chemstation software. The capillary column was a Rxi-1 MS (100% methylsiloxane), 60 m x 0.32 mm with 1.0 µm film 249 thickness. The quantitation mode was Selected Ion Monitoring with three ions for each target 250251 analyte. Multipoint calibration was performed using an external standard.

252 Inter-Laboratory Test Results

The chamber conditions monitored during the intra and inter-laboratory testing are presented in Table ESI-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 setpoint of 60% RH for both chambers and fluctuations were minimal. Active sampler concentrations averaged 99% of the concentrations calculated from dilution of the supply gas with 7% COV.

The VOC concentrations measured with the passive samplers during the intra and interlaboratory tests are shown in Table ESI-6 and the comparisons between the passive and active samples (C/Co) and between laboratories are shown on Table ESI-7. The relative concentrations (C/Co) were generally less than 100% (columns 11, 12 and 13 on Table ESI-7), which indicates a slight low or negative bias for the passive samplers. The relative percent difference between 265 concentrations measured in two different laboratories averaged about 26% (columns 14, 15 and266 16 in Table ESI-7).

267 The intra-laboratory results for each VOC are shown in Figures ESI-2a-j (one plot for each compound), where the results of one duplicate are plotted versus the second duplicate sample, 268 where each pair was analyzed by the same sampler, method and laboratory. Each plot also shows 269 the average concentration measured using pumped ATD tube (active) samples for reference. 270Most compounds showed very low intra-lab variability and concentrations within a factor of 271about 2 of the active samples. Some compounds showed high or negative bias compared to the 272 active samples, especially naphthalene (for WMS, SKC and Radiello) and MEK (for 273 274 ATD/Carbopack B and Radiello), which was not surprising because these two compounds were included in the program specifically because they were expected to be challenging due to their 275 low volatility and high solubility, respectively. Hexane and benzene showed a positive bias in 276the ATD/Carbopack B samplers analyzed at UW compared to CAS and ATL, which was 277 subsequently attributed to laboratory blank contamination. The WMS sampler also showed a 278 negative bias for 124TMB. 279

281	Table ESI-5.	Chamber	conditions	during	inter-	laboratory	testing
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ESTCP Interlab Performance Testing Chamber Conditions													
				Chamb	er #1	Cham	ber #2						
		Air Flow	Cal Flow	Temp	humidity	Temp	humidity						
Date	Time	LPM	ccm	deg C	%RH	deg C	%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						
	1753	19.93	101.1	21.2	62.6	21.1	62.9						
13-Mar	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						
	2020	19.94	101.3	22.6	59.1	22.5	59.4						
15-Mar	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						
		10.00	101.10	<u> </u>	C4 70	24.00	60 F0						
	Average	19.96	101.12	22.07	61.79	21.83	62.58						

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

283 Table ESI-6. Concentrations measured during inter-laboratory testing

-			Sampler #1		Sampler #2	
and the second	Sampler	Analytical		Concentration		Concentration
Analyte	Type	Laboratory	ID DC CC1	(ppbv)	ID DC CC1	(ppbv)
MEK	VVIVIS	ATL	PS-C65	46.3	PS-C64 PS-C66	45.2
in Liv		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	-
	170 0 1 10	AirZOne	SKC Badge #3		SKC Badge #6	-
	AID - CarbopackB		Carbopack B (Chamber 1)	10.6	Carbopack B (Chamber 2)	11.1
		UW	Carbopack B (Chamber 1)	4.5	Carbopack B (Chamber 2)	7.2
	ATD - Tenax TA	ATL	Tenax TA (Chamber 1)	29.2	Tenax TA (Chamber 2)	29.2
	And and the second s	CAS	Tenax TA Chamber 1	30.2	Tenax TA Chamber 2	30.4
	S	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
	M/MAS		RADI30#2	13.0 E9.0	RAD130#4	57.0
n-Hexane	VVIVI3	ATI	PS-C65	55.9	P3-C66	52.1
in the date		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	AIL	Carbopack B (Chamber 1)	57.6	Carbopack B (Chamber 2)	56.6
			Carbonack B (Chamber 1)	43.3	Carbonack B (Chamber 2)	41.7
	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
		AIL	RAD130 #1	48.8	RAD130 #6	43.6
	MAAS		RADISU#2	05.5 41.5	RADISU#4	62.0
1.2-DCA	VVIVI3	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	-
	ATD Cost and all	AirZOne	SKC Badge #3		SKC Badge #6	
	ATD - CarbopackB		Carbopack B (Chamber 1)	26.4	Carbopack B (Chamber 2)	27.2
		UW	Carbonack B (Chamber 1)	28.9	Carbonack 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
		AIL	RAD130 #1	40.8	RAD130 #6	36.4
	MANAS		PS_C51	47.3 51.6	DS_C64	49.8 50.4
1.1.1-TCA	VYIVIJ	ATI	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		Carbopack B (Chamber 1)	30.3	Carbopack B (Chamber 2)	30.9
		UW	Carbopack B (Chamber 1)	20.3	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
			RAD130 #1	47.8	RAD130 #6	43.2
	MAAS		RAD130 #2	67.2	RAD 130 #4	/1.3
Benzene	VVIVI3	ATI	PS-C65	40.1	PS-C66	40.0
beneene		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	AIL	Carbopack B (Chamber 1)	67.7	Carbonack B (Chamber 2)	67.7
		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

			Sampler #1		Sampler #2	
	Sampler	Analytical		Concentration		Concentration
Analyte	Туре	Laboratory	ID	(ppbv)	ID	(ppbv)
	WMS	UW	PS-C61	54.8	PS-C64	53.8
Carbon		ATL	PS-C65	44.8	PS-C66	44.8
Tetrachloride		AirZOne	PS-C63	54.4	PS-C62	49.5
	SKC Ultra	CAS	SKC B#2	37.6	SKC B#4	35.7
		AIL	SKC Badge #1	47.2	SKC Badge #5	-
	ATD CarbonackP	AIIZOne	SKUBadge #3 Carbonack B (Chambor 1)		SKC Badge #6	
	АТО - сагоораско	CAS	Carbonack B (Chamber 1)	22.2	Carbonack B (Chamber 2)	22.4
		UW	Carbonack B (Chamber 1)	43.2	Carbonack B (Chamber 2)	37.4
	ATD - Tenax TA	ATI	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
	WMS	UW	PS-C61	37.8	PS-C64	38.0
TCE		ATL	PS-C65	38.1	PS-C66	37.1
	ave ut	AirZOne	PS-C63	31.6	PS-C62	29.3
	SKC Ultra	CAS	SKC B#2	36.9	SKC B#4	34.7
		AIL Air7One	SKC Badge #1	44.8	SKC Badge #5	
	ATD - CarbonackB		Carbonack B (Chamber 1)	50.0	Carbonack B (Chamber 2)	50.0
	нь савораскь	CAS	Carbonack B Chamber 1	45.7	Carbonack 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
	1	CAS	RAD130 #2	52.4	RAD130 #4	56.0
	WMS	UW	PS-C61	32.5	PS-C64	33.6
PCE		ATL	PS-C65	35.6	PS-C66	33.6
	eve tik	AirZUne	P5-C63	23.8	PS-C62	21.9
	SKC UITra	CAS	SKC B#2	42.2	SKC B#4	42.1
		Air7One	SKC Badge #1	40.0	SKC Badge #5	
	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
		AIL	RAD130 #1	51.6	RAD130 #6	43.0
	14/4.40	CAS	RADI30 #2	51.3	RAD130 #4	54.3
1.3.4.7640	WIVIS	0W	PS-C61	19.9	PS-C64	21.3
1,2,4-11VID		AirZOpo	P3-C05	23.3	P3-C68	16.9
	SKC Ultra	CAS	SKC B#2	25.0	SKC B#4	26.0
	BROOMIN	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
	5	UW	Tenax TA (Chamber 1)	37.8	Tenax TA (Chamber 2)	35.0
	Radiello	FSIVI	RAD130 #3	47.9	RAD130 #5	48.7
		CAS	RAD130 #1	46.9	RAD130 #6	42.0
	A/A/A		DS_C61	0.24	DS-C64	0.25
Nanhthalene	Vervis	ATI	PS-C65	0.24	PS-C66	0.23
rispitchaterie		Air7One	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
	Padiallo	ESAA	renax TA (Chamber 1)	5.6	PAD120 #E	5.4
	Naulellu	ΔΤΙ	RAD130 #3	5.5 1.4	RAD130 #5	5.0
		CAS	RAD130 #2	2.6 U	RAD130 #4	2.6 U
-						

Notes:

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

286 Figure ESI-2 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 287 that since three laboratories analyzed each type of sampler the comparison between one 288 laboratory and another occurs three times for each sampler/compound combination (Lab A:Lab 289 B, Lab B:Lab C, and Lab A:Lab C). For the purpose of Figure ESI-2, these were plotted simply 290 291 as one lab against another, and generically named Lab 1 vs Lab 2. The overall average inter-292 laboratory variability was 26% RPD, which was considered in setting the performance criteria for accuracy. This degree of inter-laboratory variability is consistent with previous studies of 293 294 inter-laboratory variability for Summa canisters⁸.



296 Figure ESI-2. Scatter plot of laboratory 1 versus laboratory 2 for all VOCs and samplers

297	Table ESI-7.	Summary of A	Accuracy and	Precision in	the inter-laborato	ry test
		···· ··	· · · · · · · · · · · · · · · · · · ·			J

Sampler type			A	E	3	(3		D	B/A	C/A	D/A	RPD (B:C)	RPD (C:D)	RPD (B:D)
		(pp	obv)	(pp	ibv)	(pp	bv)	(pj	obv)						
		то	-17	Uο	fW	Air T	oxics	Airz	ZOne	%	%	%	%	%	%
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%
		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%	/9%	64%	1%	21%	22%
	PUE 104TMAD	51.8 AO E	50.6	32.5	33.0	35.0	35.0	16.0	16.0	05%	08%	45%	5%	41%	30%
		40.5	5.06	0.24	0.25	25.5	0.2	10.0	10.0	4570	4070	5570	070 /1%	26%	20%
		0.12	5.00	0.24	0.25	0.20	0.2	0.5	Mean	78%	68%	76%	15%	20%	16%
		ТО	-17	C/	AS	Air T	oxics	Air	7One	7070	00/0	7070	2070	2070	2070
<u> </u>	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
	СТ	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
		-		-		1015			Mean	64%			22%		
		то	-17	Air T	oxics	C,	4S	Uc	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%
	1111CA	51.0	50.2	30.3	30.9	26.8	25.5	20.2	23.3	60%	52%	43%	16%	18%	34%
	BEINZ	47.8	46.8	6/./	6/./	62.4	58.9	98.4	103.0	143%	128%	213%	11%	50%	39%
		10 0	54.0	50.8	50.8	35.2	32.4	43.Z	57.4	105%	01%	1200/	12%	21%	9% 27%
	PCE	51.8	50.6	40.6	30.0	39.0	25.0	50.7	55.8	78%	9470 73%	104%	L170 6%	3770	2770
	124TMB	48.5	47.8	29.9	28.2	26.3	25.7	41.2	42.3	60%	54%	87%	11%	46%	25%
	NAPH	5.12	5.06	3.81	3.54	2.63	2.7	1.8	1.2	72%	52%	30%	32%	55%	84%
		0.22	0.00	0.01	0.0.		1000		Mean	76%	64%	90%	24%	39%	37%
		ТО	-17	Air T	oxics	C,	AS	Ud	ofW						
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%
	СТ	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%
D 1: 11			-1/	FS	IVI	AirT	OXICS		AS	0.001	0.50	0.00		4.000	
Radiello		45.2	44.8	13.1	12.0	11.8	11.1	13.6	13.3	28%	25%	30%	9%	16%	/%
	HEX 12DCA	59	5/.6	42.8	44./	48.8	43.6	65.5	62.0	75%	79%	109%	5%	32%	3/%
	120CA	50.3	49.2	20 1	35.0	40.8	30.4 12 2	41.5	49.0	70%	/8%	9/%	10%	25%	55% E2%
	REN7	170	16.0	39.1 40.2	41.3	201	43.2	100	71.8 50.6	/ 970	90% 770/	1050/	12% 13%	42%	25% 10%
		5/1 2	5/ 0	37 1	30.2	12 6	30.0	40.0 57 5	50.0	0/70 710/	7/70	102%	12% 0%	220/	19%
	TCF	48.0	47.2	30 6	41 /	45.0	40.9	52 /	56.0	25%	9/1/0	11/10/	570	3370 720/	4270 20%
	PCF	51 8	50.6	42.0	45 5	51.6	43.0	51 2	54.3	86%	97%	103%	7%	2370	1.2%
	124TMB	48 5	47.8	47 9	48 7	46 9	42 0	55.2	56.2	100%	92%	116%	8%	73%	14%
	NAPH	5.12	5.06	9.5	9.0	1.4	1.3	2.6	2.6	181%	27%	52%	148%	62%	111%
	1997 (1998 - 1998 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	2005		5.00	- 18	din dan		-15	Mean	86%	73%	97%	23%	30%	36%



Youden Plot - 1,2-Dichloroethane

300 Figure ESI-3a. Intra-laboratory comparison for 12DCA

100 Airzone ATL 80 ▲ CAS Radiello ▲FSM Sample #2 (ppbv) •UW 60 Active Tube WMS WMS Radiello 40 Tenax TA ATD - Tenax TA ATD - Carbopack B ATD - Carbopack B 🖌 SKC Ultra ATD - Carbopack B ATD - Tenax TA 20 0 20 40 0 60 80 100 Sample #1 (ppbv)

Youden Plot - 1,1,1-Trichloroethane

302 Figure ESI-3b. Intra-laboratory comparison for 111TCA



Youden Plot - 1,2,4-Trimethylbenzene

304 Figure ESI-3c. Intra-laboratory comparison for 124TMB



Youden Plot - Benzene

306 Figure ESI-3d. Intra-laboratory comparison for BENZ



Youden Plot - Carbon Tetrachloride

308 Figure ESI-3e. Intra-laboratory comparison for CTET



Youden Plot - Hexane

310 Figure ESI-3f. Intra-laboratory comparison for HEX



Youden Plot - Methylethyl Ketone

312 Figure ESI-3g. Intra-laboratory comparison for MEK



Youden Plot - Naphthalene

314 Figure ESI-3h. Intra-laboratory comparison for NAPH



316 Figure ESI-3i. Intra-laboratory comparison for PCE



Youden Plot - Trichloroethene

318 Figure ESI-3j. Intra-laboratory comparison for TCE

319 Center-Point Tests

The initial six center-point tests had an average temperature within 1°C of the set-point of 22°C (standard deviation of 0.5 °C) and an average relative humidity within 2% RH of the setpoint of 60% RH (standard deviation less than 6.5%), as shown in Table ESI-8. 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 the experimental procedure.

325 The chamber concentrations measured with the pumped ATD tubes (Table ESI-9) were 326 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_y for all compounds except naphthalene at 5 327 ppb_v and was achieved by adding 50 mL/min supply gas to 10 L/min purified air). The only 328 329 compound with an active sample concentration matching the expected concentration calculated 330 from the mass flow controllers was HEX (99% of expected value). The average active ATD 331 tube/TO-17 sample concentrations for the other compounds were generally slightly lower than 332 the set-point, mostly in the range of 33 to 45 ppb_v and 2.9 to 3.2 ppb_v for naphthalene. This appears likely to have been attributable to imperfect calibration of the mass flow controllers. 333 Nevertheless, the passive sampler data were all normalized to active sample concentrations. The 334 active sample results showed minimal variability (COV of 2 to 7%), so the chamber 335 concentrations were reasonably steady and well-characterized for the four-day duration of the 336 center-point tests. 337

339 Table ESI-8. Temperature and Relative Humidity measured during initial Center-Point Tests

ANOVA Rou	ind #1					ANOVA Rou	nd #2				
		Chamber 1		Chamber 2					er 1	Chamber 2	
Date	Time	Temp, °C	RH%	Temp, °C	RH%	Date	Time	Temp. °C	RH%	Temp. °C	RH%
12/18/09	952	21.3	53.3			12/27/09	1403	21.8	59.1		
12/18/09	1005	21.5	59.5	21.2	54.4	12/27/09	1421			21.9	59.1
12/18/09	1005	21.5	58.5	21.5	54.4	12/2//09	1457	22.0	60.0	21.6	60.7
12/18/09	1021			20.8	58.8	12/27/09	1656	21.0	61.9	21.7	61 5
12/18/09	1031			20.8	59.2	12/27/09	1800	21.9	59.9	21.7	59.6
12/18/09	1107			20.8	59.9	12/27/09	1910	22.0	59.6	21.6	60.6
12/18/09	1121			20.6	62.0	12/27/09	2003	22.0	60.7	21.9	60.0
12/18/09	1209			20.6	59.7	12/28/09	739	21.7	61.3	21.7	60.9
12/18/09	1344			21.0	57.4	12/28/09	840	21.7	61.6	21.6	60.4
12/18/09	1407			21.3	57.5	12/28/09	939	21.7	61.6	21.6	60.9
12/18/09	1533			21.0	57.9	12/28/09	1037	21.4	61.6	21.5	60.0
12/18/09	1535			21.4	57.5	12/28/09	1315	21.3	61.8	21.1	60.2
12/18/09	1540			21.3	58.4	12/28/09	1710	21.4	60.7	21.3	61.5
12/18/09	1607	21.8	57.1			12/28/09	1846	21.4	61.0	20.5	60.0
12/18/09	1629			21.2	59.1	12/29/09	747	21.6	61.8	21.4	62.3
12/18/09	1812			20.9	58.5	12/29/09	845	22.0	61.7	22.0	61.4
12/18/09	1916			20.8	57.9	12/29/09	949	21.6	62.5	21.5	62.7
12/18/09	2014			21.0	57.4	12/29/09	1101	21.2	62.3	21.3	60.4
12/18/09	2020	21.0	57.6			12/29/09	1202	(***)		20.8	61.9
12/10/09	876	21.6	59.7			12/29/09	1451	21.2	61.1	21.4	60.8
12/19/09	1020	21.0	50.2			12/29/09	1642	20.9	63.2	20.7	53.1
12/19/09	1031	21.8	58.0			12/29/09	2220	21.5	57.4	20.9	57.9
12/19/09	1247	21.6	58.3	21.6	58.1	12/30/09	814	22.0	49.9	21.8	50.1
12/19/09	1452			21.1	59.2	12/30/09	921	21.7	50.6	21.7	50.6
12/19/09	1657	21.3	58.8	20.9	59.4	12/30/09	1031	21.7	51.2	21.5	51.6
12/20/09	810	21.8	58.4	21.4	59.6	12/30/09	1140	21.7	62.1	21.3	62.6
12/20/09	1022	21.8	58.7	21.5	59.6	12/30/09	1226	21.7	63.5	21.7	62.3
12/20/09	1230	21.9	58.9	21.8	59.5	12/30/09	1247	21.7	61.6	21.3	62.0
12/20/09	1451	21.8	593	21.6	60.1	12/30/09	1346	21.7	61.1	21.7	61.3
12/20/09	1654	21.5	59.0	21.0	59.7	12/30/09	1429	21.9	66.2		
12/20/00	1054	21.5	E0 0	21.4	59.7	12/30/09	1533	22.0	65.8	21.4	65.1
12/20/09	1857	21.8	58.8	21.6	59.4	12/30/09	1640	21.8	65.0		
12/21/09	/16	21.5	59.7	21.6	60.1	12/30/09	1715			21.0	64.3
12/21/09	921	21.4	60.6	21.2	60.9	12/30/09	1824	21.6	64.8	21.0	57.7
12/21/09	1029	21.6	59.9	21.4	60.0	12/30/09	1844	()		21.1	57.8
12/21/09	1135	21.6	60.9	21.4	61.2	12/30/09	1904	21.5	63.7	21.0	60.1
12/21/09	1230	21.9	60.4	21.7	60.7	12/30/09	1927	21.7	59.5	21.3	56.1
12/21/09	1403	21.8	61.6	21.6	61.7	12/31/09	850	21.7	58 5	21.0	59.6
12/21/09	1456	22.0	60.3	21.9	60.2	12/31/09	943	22.1	54.5		
12/21/09	1606	21.6	60.9	21.5	61.1	12/31/09	1012	21.7	58.6	21.5	58.1
12/21/00	1776	21.0	60.5	21.5	60.0	12/31/09	1059	21.6	59.3	21.6	59.4
12/21/09	1/20	21.7	60.7	21.5	60.9	12/31/09	1118	21.4	60.5	21.2	60.5
12/21/09	1927	21.4	61.5	21.2	60.5	12/31/09	1147	21.6	55.9		
12/22/09	712	21.3	63.8	21.4	61.3	12/31/09	1248	21.8	53.3	21.6	52.7
12/22/09	815	21.6	64.9	21.5	62.3	12/31/09	1315	21.8	57.4	21.6	60.5
12/22/09	838	21.7	58.6	21.7	55.6	12/31/09	1353 Mean	22.0	60.2	21./	60.0
12/22/09	933	21.6	57.1				Std. Dev.	0.3	3.8	0.3	3.5
	Mean	21.6	59.4	21.3	59.4		%RSD	1.2	6.4	1.5	5.8
	Std. Dev.	0.23	2.18	0.34	1.69						
	%RSD	1 08	3 67	1.67	7 85	Both Chamb	ers				
	10100	1.00	5.07	1.02	2.00	Zero Air F	low Rate:	10.00 L·min			

Both Chambers

Zero Air Flow Rate: $10.00 \text{ L} \cdot \text{min}^{-1}$ Standard Flow Rate: $50.0 \text{ mL} \cdot \text{min}^{-1}$

340

 Chamber 1

 Standard Flow Rate:
 50.0 mL·min⁻¹

 Chamber 2

 Standard Flow Rate:
 49.1 mL·min⁻¹

342 Table ESI-8 (cont'd)

ANOVA Round #3

		Chamb	er 1	Chamber 2			
Date	Time	Temp. °C	RH%	Temp. °C	RH%		
1/3/10	1437	21.9	56.8	21.4	57.5		
1/3/10	1555	21.6	55.5	21.5	55.8		
1/3/10	1626	21.7	55.4	21.6	55.3		
1/3/10	1751	21.8	54.6	21.6	54.8		
1/3/10	1823	21.8	56.5	21.8	57.0		
1/3/10	1936	21.9	59.7	21.8	59.4		
1/3/10	2033	21.9	60.6	22.0	60.6		
1/4/10	1137	20.8	54.0	20.6	54.5		
1/4/10	1247	21.0	58.6	20.9	59.0		
1/4/10	1352	21.1	62.0	21.0	61.8		
1/4/10	1425	21.6	60.8	21.2	61.8		
1/4/10	1649	21.8	60.7	21.6			
1/4/10	1738	21.4	59.5	21.2	60.9		
1/4/10	1845	21.4	56.7	21.0	57.9		
1/4/10	2326			21.6	62.3		
1/5/10	1004	21.4	63.7	21.1	64.4		
1/5/10	1047	21.5	62.2	21.5	62.1		
1/5/10	1147	20.7	64.8	20.6	65.0		
1/5/10	1225	20.9	63.7	20.8	63.6		
1/5/10	1337	20.8	63.6	20.3	64.9		
1/5/10	1438	20.9	63.0	21.0	63.0		
1/5/10	1523	20.7	64.2	20.3	65.0		
1/5/10	1649	21.0	63.1	21.0	63.3		
1/5/10	1805	20.8	63.6	20.8	63.9		
1/5/10	2255	21.5	62.9				
1/6/10	1116	20.9	64.4	21.2	63.5		
1/6/10	1244	21.1	63.5	20.9	63.6		
1/6/10	1318	21.2	63.3	21.3	62.9		
1/6/10	1428	21.1	63.2	20.6	65.3		
1/6/10	1527	20.9	64.2	21.0	64.1		
1/6/10	1606	21.0	64.1	20.5	65.6		
1/6/10	1725	21.2	63.3	21.1	63.4		
1/6/10	1806	21.0	64.0	20.9	64.1		
1/6/10	2312	21.6	62.8				
1/7/10	814	21.1	63.3	21.1	63.4		
1/7/10	927	21.1	62.7	21.0	62.9		
1/7/10	956	21.4	61.4	20.9	63.1		
1/7/10	1056	21.0	63.6	20.9	63.8		
1/7/10	1210	21.4	61.9	21.1	62.8		
1/7/10	1326	21.0	63.5	20.9	63.6		
	Mean	21.3	61.4	21.1	61.8		
	Std. Dev.	0.4	3.1	0.4	3.2		
	%RSD	1.7	5.1	1.9	5.1		

Both Chambers

Zero Air Flow Rate: 10.00 L·min⁻¹ **Chamber 1** Standard Flow Rate: 50.0 mL·min⁻¹ **Chamber 2** Standard Flow Rate: 49.1 mL·min⁻¹

344 Table ESI-9. Active Chamber Concentrations for Center-Point Tests

Center-Point (ANOVA) Test #1

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
		Average	34.8	35.4	43.5	37.9	36.6	36.6	35.1	31.6	2.9	35.8
Standard Deviation		1.0	0.5	1.3	1.0	0.7	1.2	1.0	1.8	0.2	1.4	
Coefficient of Variation		of Variation	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	37	36	32	2.9	38
2	21-Dec-09	17:30	34	35	43	38	37	36	35	31	2.8	35
		Average	33.8	35.3	43.3	37.5	36.3	36.4	35.1	31.5	2.9	35.6
	Standa	rd Deviation	2.5	2.0	1.0	1.4	1.6	1.4	1.1	1.7	0.1	1.3
	Coefficient	of Variation	0.074	0.056	0.024	0.038	0.044	0.039	0.032	0.054	0.050	0.037

345

Center-Point (ANOVA) Test #2

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

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Center-Point (ANOVA) Test #3

Chamber # Data		Time	Analyte (ppbv)										
Chamber #	Date	Time	111-TCA	СТ	Hexane	Benzene	12-DCA	TCE	PCE	124-TMB	Naphthalene	2-MEK	
1	3-Jan-10	14:35	35	36	56	44	37	40	37	34	3.1	36	
1	4-Jan-10	11:50	34	36	52	41	35	36	34	32	2.9	33	
1	4-Jan-10	16:35	35	35	53	41	35	36	34	30	2.8	34	
1	5-Jan-10	12:30	37	37	55	43	37	37	36	33	3.0	32	
1	6-Jan-10	11:20	34	34	52	41	36	36	34	31	2.8	34	
1	6-Jan-10	15:27	40	42	56	44	39	38	37	32	3.0	37	
1	7-Jan-10	10:26	36	39	54	42	36	38	37	33	3.0	39	
		Average	35.9	37.0	54.0	42.3	36.4	37.3	35.6	32.1	2.9	35.0	
	Standard Deviation		2.1	2.7	1.7	1.4	1.4	1.5	1.5	1.3	0.1	2.4	
	Coefficient of Variation		0.059	0.073	0.032	0.033	0.038	0.040	0.043	0.042	0.039	0.070	
2	3-Jan-10	16:41	36	37	55	43	36	38	36	32	3.0	35	
2	4-Jan-10	13:54	34	36	53	42	35	37	35	33	3.1	33	
2	5-Jan-10	10:26	36	36	53	42	36	36	35	34	3.1	32	
2	5-Jan-10	14:40	34	34	53	41	36	37	36	33	3.0	32	
2	6-Jan-10	13:22	37	38	54	43	37	38	37	34	3.1	34	
2	7-Jan-10	8:21	36	36	55	43	38	38	36	33	3.0	36	
	Average			36.2	53.8	42.3	36.3	37.3	35.8	33.2	3.1	33.7	
	Standa	rd Deviation	1.2	1.3	1.0	0.8	1.0	0.8	0.8	0.8	0.1	1.6	
	Coefficient	of Variation	0.034	0.037	0.018	0.019	0.028	0.022	0.021	0.023	0.018	0.049	

In the Center Point Tests, 41 of 50 Sampler/compound combinations met the accuracy goal of
 +/- 45% RPD. The exceptions were:

• ATD tube/Tenax showed negative bias for 111TCA, 12DCA and CTET;

- ATD/Carbopack B showed negative bias for 12DCA and MEK and positive bias for
 BENZ;
- WMS and SKC showed negative bias for NAPH;

• Radiello showed a positive bias for NAPH.

355 The positive bias for benzene with the ATD/Carbopack B sampler was most likely attributable to the uptake rate used (0.35 mL/min from Table ESI-1). ISO 16017-2 and Subramanian, 1995 356 list various uptake rates for benzene on passive ATD samplers in the range of 0.64 to 1.81 357 mL/min, depending on the sorbent used and sample duration. None of these values match the 358 359 exact sorbents and duration of this test, but all values are higher than the uptake rate used in these tests. The calculated benzene concentration would have been lower by a factor of about 2 360 361 or more (i.e., essentially equal to the set-point) if a different uptake rate within the published range was used instead. 362

The negative bias for 111TCA, 12DCA and CTET on the ATD/Tenax sampler may be attributable to poor retention since Tenax is a weaker sorbent than Carbopack B. The recommended maximum sample volumes (RMSVs) for 111TCA, 12DCA and CTET on Tenax are 0.2, 1 and 0.2 L, respectively (Supelco 2014). The uptake rate for these compounds for the passive ATD tube sampler was estimated to be 0.5 mL/min (see Table ESI-1). The product of the sample duration (4 days) and the uptake rate was therefore 2.9 L, which was larger than the 369 RMSV for these compounds on Tenax. Carbopack B has a much higher RMSV for 111TCA and CTET (20 L for both according to Supelco, 2014), and did not show as much negative bias for 370 these compounds compared to ATD/Tenax. The positive bias for the Radiello/NAPH may be 371 attributable to uncertainty in the published uptake rate (25 mL/min). Using the free-air diffusion 372 coefficient for NAPH (0.059 cm^2/s) and the equation in the Radiello manual,⁴ an uptake rate of 373 374 50 mL/min could be calculated. Such uptake rate would have resulted in concentrations 2 times lower, which would have been within the +/-25% tolerance of the active samples. Naphthalene 375 often shows low recovery when sampled using strong sorbents like charcoal, and the published 376 uptake rate of 25 mL/min may be set as such to partially account for that. The positive bias for 377 NAPH on the Radiello analysed by FSM is consistent with the inter-laboratory test data (Table 378 ESI-6). The WMS and SKC samplers used estimated uptake rates for NAPH, both of which 379 380 apparently overestimated the true uptake rate for the conditions of the center-point tests by a factor of 2 to 3, which may also be attributable to low recovery of naphthalene from the (strong) 381 382 sorbents used (Anasorb 747 and Carbopack X, respectively).

383 Combined Results from Fractional Factorial and Center-Point Tests

384 The fractional factorial test data and the center-point test data were combined and a summarized in two sets of figures: Figures ESI-4 a-e and Figures ESI-5 a-f. The former has the 385 386 individual VOCs along the x-axis and the chamber runs in the legend. The latter shows the 387 values of each of the five factors on the x-axis and the compounds in the legend. Both sets of plots have normalized concentrations (C/Co, the passive sampler concentration divided by the 388 389 chamber concentrations measured using pumped ATD tubes and EPA Method TO-17 analysis) on the vertical axis. The accuracy success criterion lines (RPD = -45% and +45%) are shown in 390 Figures ESI-4 a-e for comparison purposes. Some trends are evident in Figures ESI-4a-e: 391

The ATD Tube Sampler with Tenax TA showed a negative bias for hexane, which was
 not observed with the ATD tube with Carbopack B. The ATD Tube Sampler with
 Carbopack B showed a negative bias for MEK and a positive bias for benzene;
 whereas, the ATD tube sampler with Tenax TA showed no bias for MEK and benzene.

- Both ATD tube samplers showed a negative bias for 12DCA, which likely means the calculated uptake rate of 0.5 mL/min (Table 2) is too high (0.3 mL/min would have provided an accurate result);
- 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 negative 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;
- 404 The WMS showed a negative bias for NAPH and 124TMB. These two compounds 405 have the highest partitioning coefficients in the PDMS membrane, which results in very 406 high permeability, so the negative bias may be attributable to the starvation effect. 407 Recovery is also a potential issue with naphthalene, but the recovery from Anasorb 747 408 by CS_2 extraction has been shown to be reasonably good (63-68%) by Seepthapathy 409 (2009). Also, these compounds both had estimated uptake rates (see Table 2), and the 410 estimates may have been higher than the actual uptake rates for the chamber conditions 411 (by a factor of ~2 for 124TMB and ~6 for NAPH); and
- The Radiello results were biased low by a factor of ~1.6 for MEK and high by a factor
 of ~2.3 for NAPH.



415 Figure ESI-4a. ATD tube/Tenax TA results for center-point and fractional factorial lab tests



417 Figure ESI-4b. ATD tube/Carbopack B results for center-point and fractional factorial lab tests



419 Figure ESI-4c. SKC Ultra II results for center-point and fractional factorial lab tests



421 Figure ESI-4d. WMS results for center-point and fractional factorial lab tests



423 Figure ESI-4e: Radiello results for center-point and fractional factorial lab tests

Figures ESI-5a-f show the influence of the exposure chamber conditions on the relative concentrations measured for each of the compounds with each of the samplers. Figure ESI-5f shows the results for the Active ATD tube samples, where the Co value was taken to be the concentrations calculated from the mass-flow controller settings. 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
negative bias in the 4 and 7 day samples compared to the 1-day sample;

The ATD Tube with Carbopack B showed similar results to the ATD with Tenax,
except for the negative bias with MEK and positive bias with benzene. This is
consistent with the 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
 (except NAPH) compared to the high and low levels of each factor where the results
 were predominantly biased low and highly variable;

439 The WMS sampler also showed notably less variability and bias at the center-points • 440 (except NAPH) compared to the high and low levels of each factor. The WMS sampler 441 had some results below the reporting limit in the first two chamber tests conducted at 442 the low concentration and short sample duration combination of conditions. To avoid 443 non-detect results, the WMS sampler configuration was used with a thermally-444 desorbable sorbent (Carbopack B) and a thermal desorption analysis (Modified TO-17) 445 to increase sensitivity in runs 12 and 18. Consequently, some of the variability for the 446 WMS sampler may be attributable to variability between the thermal desorption and 447 solvent extraction methods. Also, the positive bias from hexane laboratory 448 contamination was much larger compared to the adsorbed mass from the chamber in 449 the two low concentration/short duration chambers, resulting in a C/Co value >10. 450 See thapathy and Górecki² studied the effect of humidity and temperature on the WMS 451 sampler and found humidity had no significant effect and the uptake rates decreased 452 with increasing temperature, but only by a about 20% over the range studied here, so 453 the variability was most likely attributable to other factors; and

The Radiello showed minimal bias and variability and no clear trends attributable to the
 five factors except for the positive bias with NAPH and the negative 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 accurate uptake rate was used for
 the compounds and sorbent.







462 Figure ESI-5b. ATD Carbopack B test data





464 Figure ESI-5c. SKC Ultra II test data





466 Figure ESI-5d. WMS test data





468 Figure ESI-5e. Radiello test data



470 Figure ESI-5f. Active ATD Tube test data (normalized to calculated concentrations)

471 ANOVA Analysis of the Chamber Test Data

The ANOVA analysis of the chamber test data is summarized in Table ESI-10. Specificobservations regarding individual factors, compounds and samplers include:

• <u>Temperature and humidity</u> showed significant effects less frequently than other factors, but this may be attributable to the fact that these factors were the most challenging to control (higher variability makes it less likely that an effect will be statistically significant by comparison).

• <u>Temperature</u> had a significant effect for 8/10 compounds for the Radiello (C/Co increased with temperature for 6 of 8 VOCs) and no more than 3 compounds for any of the other samplers. The diffusion coefficient increases with temperature, so a temperature effect is to be expected. The fact that temperature is significant for the Radiello more frequently than other samplers could be because the Radiello showed very low variability for most compounds (except MEK), which increased the likelihood that any trends would be statistically significant.

Humidity had a significant effect for MEK and 12DCA (the two most soluble compounds) in the SKC Ultra and Radiello samplers (C/Co values decreased with increasing humidity for both compounds in both samplers), but not the WMS (which has a PDMS membrane that inhibits water uptake by the sorbent) and ATD-Tenax (Tenax is extremely hydrophobic).

Face velocity had less effect on the ATD tubes than the other samplers (significant for 3 or 4 of 10 compounds compared to 6 to 9 of 10 compounds for other samplers). This may be because the ATD tube samplers have the lowest uptake rates of the samplers tested,

- and therefore less likely to experience negative bias from the starvation effect at low airvelocities.
- <u>Concentration</u> had a significant effect for MEK on all sampler types (increasing C/Co
 with increasing concentration, except with ATD/Tenax), but was otherwise comparable
 for all samplers and not consistently significant for any other compounds.

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	Nanhthalene	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	Nanhthalene	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)	0.7347	0.3360	0.0034	0.0310	0.0027
WMS	2-Dutatione (MEK)	0.5001	0.3309	0.022	0.0019	0.0027
WMS	Bangana	0.0196	0.4942	0.022	0.0003	0.0001
WMS	Carbon tatrachlorida	0.0712	0.9017	0.0328	0.0012	0.0099
WMS	Nanhthalana	0.0010	0.3838	< 0001	0.0700	0.0333
WMS	Trichloraethere	0.9023	0.4298	0.0001	0.3432	0.000
WMS	Totrachlereathere	0.0289	0.0323	< 0001	0.03/0	0.0124
WINDS	retracmoroetnene	0.3923	0.14//	<0001	0.9894	0.00/4

499 Table ESI-10. Results of ANOVA analysis (p-values) of all 24 chamber tests tests (main effects)

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

501 Participant's Affiliations and Interests

502 This research program included several commercially-available passive samplers. The study 503 team included members that were selected because of their familiarity with various sampler types. Some of the study team members have a commercial interest in the samplers they helped 504 to develop. The study team also included independent parties with no commercial interests in 505 506 any of the samplers (Schumacher, Johnson and Crump). We believe that all samplers were fairly 507 tested and that all members of the research team had equal opportunity to review the study 508 design, results and articles such that there is no bias for or against any of the samplers that might constitute a conflict of interest. The members of the research team and their relationship to the 509 various samplers tested are listed below: 510

Paolo Sacco is employed by Fondazione Salvatore Maugeri (FSM) in Padova, Italy. FSM 511 developed the Radiello[®] sampler and sell it to laboratory supply companies and laboratories 512 513 worldwide. Stephen Disher, Jason Arnold and Heidi Hayes employed by Eurofins/Air Toxics, 514 Inc., which is a commercial laboratory that offers analysis of all of the passive samplers tested. Suresh Seethapathy and Tadeusz Górecki invented the Waterloo Membrane Sampler, and are 515 parties to a license agreement with Geosyntec Consultants, Inc. for commercialization. Todd 516 517 McAlary and Hester Groenevelt are employed by Geosyntec Consultants, Inc., which has a license agreement with Suresh Seethapathy and Tadeusz Górecki and a commercialization 518 519 agreement with Eurofins/Air Toxics, Inc. to produce and sell Waterloo Membrane Samplers 520 through Geosyntec's wholly-owned subsidiary SiREM.

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