Field sampling demonstration of portable thermal desorption collection and analysis instrumentation

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Figure S1. Environmental conditions as recorded by the Kestrel 4500 Portable Weather Station. Sites are A) Auto Maintenance; B) Aircraft Hangar #1; C) Bowling Alley; D) Gas Pumps; E) Aircraft Hangar #2; F) Pesticide Storage Unit; G) Animal Housing Facility; H) Biology Laboratory. Measurements were collected using barometric pressure as the reference for each location. Therefore, changes in conditions such as temperature and humidity which affect atmospheric pressure will result in fluctuations of the altitude readout despite the fact that the meter remained in the same physical location.

Table S1. Summary of MultiRae and ppbRae (VOC) Data for Each Sampling Site

		HCN (ppm)	NO ₂ (ppm)	H ₂ S (ppm)	CO (ppm)	SO ₂ (ppm)	CO ₂ (ppm)	VOC (ppb)
TWA		-	0.2	1	25	-	5000	-
STEL		4.7	-	5	-	0.25	30000	-
Auto Maintenance	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	1.000	0.500	0	0	0	500.000	3440.000
	Mean	0.278	0.027	0	0	0	200.209	205.676
	St Dev	0.249	0.087	0	0	0	13.924	481.672
Aircraft Hangar #1	Min	0.000	0.000	0	0	0	0.000	36.000
	Max	0.500	0.300	0	0	0	1800.000	175.000
	Mean	0.312	0.000	0	0	0	204.108	130.727
	St Dev	0.242	0.007	0	0	0	50.901	25.888
Bowling Alley	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	0.500	0.400	0	0	0	300.000	1053.000
	Mean	0.044	0.111	0	0	0	204.992	185.809
	St Dev	0.141	0.095	0	0	0	24.168	61.182
Gas Pumps	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	2.000	0.200	0	0	0.100	300.000	509.000
	Mean	0.435	0.003	0	0	0.002	180.154	1.184
	St Dev	0.417	0.017	0	0	0.014	62.058	10.735
Aircraft Hangar #2	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	0.500	0.200	0	0	0	300.000	0.000
	Mean	0.025	0.002	0	0	0	202.227	0.000
	St Dev	0.110	0.015	0	0	0	18.132	0.000
Pesticide Unit	Min	0.000	0.000	0	0	0	0.000	58.000
	Max	0.500	0.100	0	0	0	500.000	1465.000
	Mean	0.037	0.000	0	0	0	205.376	438.268
	St Dev	0.131	0.005	0	0	0	25.147	322.221
Animal Facility	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	0.500	1.200	0	0	0	300.000	254.000
	Mean	0.045	0.573	0	0	0	205.725	161.436
	St Dev	0.143	0.331	0	0	0	25.495	38.583
Biology Laboratory	Min	0.000	0.000	0	0	0	0.000	0.000
	Max	0.500	2.000	0	0	0	500.000	9404.000
	Mean	0.008	0.291	0	0	0	207.848	29.484
	St Dev	0.063	0.492	0	0	0	30.026	232.256

Time weighted average (TWA) and short-term exposure limit (STEL) values all from Ref [1].

The MultiRae Pro was utilized to detect the presence of common gases at each site. Of the environmental gases detected by the MultiRae Pro (HCN, NO₂, H₂S, CO, SO₂, CO₂; Table S2) or ppbRae (total VOC), NO₂ was the only compound detected above ACGIH TWA/STEL (short-term exposure limit) in the Animal Housing Facility and Biology Laboratory.

Table S2. Detection Events from Field Sampling.

	Benchtop System		HAPSITE [®]	
	Detection Frequency	Events above LOR	Detection Frequency	Events above LOR
1,2,3-trimethylbenzene	ND	ND	6	2
1,2,4-trimethylbenzene	1	1	0	0
1,3,5-trimethylbenzene	1	1	6	1
1,4-dioxane	8	8	7	3
4-Ethyltoluene	2	2	6	3
Acetone	8	8	8	8
Benzene	7	7	8	8
Ethyl Acetate	2	2	ND	ND
Ethylbenzene	3	3	6	3
Heptane	2	2	4	3
Isopropyl Alcohol	6	6	6	6
m,p-xylene	4	3	7	5
n-hexane	3	3	4	3
o-xylene	4	3	4	4
Styrene	2	0	8	1
Tetrahydrofuran	7	5	1	1
Toluene	7	5	8	6
Trichloroethylene	4	1	2	0

*ND= Not detected

“Detection Frequency” reports any event where the compound was detected above method detection limit (MDL). The MDL varies for each compound, and is defined as the product of the standard deviation of seven replicate analyses and the students’ t-test for 99% confidence [2]. The MDL was confirmed to be lower than the limit of reporting (LOR) during the quality assurance phase in order to validate instrument performance. One detection event describes the amount of sites a compound was detected at (from 8 total sites) using passive, stand-alone pump, and/or LESS-P sampling; it does not report the total amount of times it was detected from the replicate measurements. Similarly, “Events above LOR” report the number of sites the compound was detected at or above 2 ppbv, which was the lowest concentration used in the calibration curve for the benchtop system. This table shows data before exclusion criteria were applied (shown in Table 2).

Figure S2. Example total ion chromatograms for LESS-P sample 14 at the Pesticide Storage Unit for A) benchtop system and B) HAPSITE[®] ER. Identified peaks are 1) acetone; 2) benzene, 3) toluene, 4) m,p-xylene; 5) 4-ethyltoluene; IS1) 1,4-difluorobenzene; IS2) Chlorobenzene-d₅; IS3) 1,3,5-Tris(trifluoromethyl)benzene; IS4) Bromopentafluorobenzene.

Figure S3. Flow rate testing of LESS-P under controlled laboratory conditions. A) Comparison of flow rate at four different LESS-P positions using either the Defender flow meter or internal LESS-P flow meter as single tubes were sequentially sampled. B) Comparison of the average flow rates for the tubes used for calibration versus the uncalibrated positions for both Defender and internal LESS-P flow meter as single tubes were sequentially sampled. C) Comparison of calibrated and uncalibrated sample locations while two tubes were sampled simultaneously.

The LESS-P contains two independent “banks” of 14 tubes that can be operated in series (Tubes 1-28, sequentially) for individual samples, or parallel (Tubes 1 & 15, 2 & 16, etc.) to obtain duplicate samples during the same time slice. As only half of the tube locations were used for flow rate calibration, we wanted to show: 1) that the locations used for calibration did not differ significantly from those which were uncalibrated; 2) that a standard flow meter (BIOS Defender) measured flow rates close to those logged by the LESS-P; 3) that flow rates were consistent using either series or parallel measurements.

The LESS-P was calibrated by inserting a set of Tenax TA TD tubes into a subset of the total slots. Next, a BIOS Defender flow meter was attached to the inlet port on the LESS-P, and the flow rate was set to 30 mL/min through tube 1 using the manual operation mode of the proprietary software. The settings were adjusted on the LESS-P menu to correct the Defender readings as close to 30 mL/min as possible. These steps were then repeated for positions 3, 5, 7, 15, 17, 19, and 21. For the serial measurements, position 1 was sampled at 30 mL/min for 30 minutes while the BIOS Defender was connected and recorded flow rate every 3 min. The same process was repeated for positions 5, 15, and 21 with the LESS-P. The average flow rates measured for each LESS-P position by the BIOS Defender were compared to the average flow rate reported from the internal LESS-P flow meter (Figure S2A). This experiment is of importance because the BIOS Defender is initially used to standardize the LESS-P internal pumps in the calibration stage. Next, the used TD tubes were replaced with new tubes, and positions 1-8 and 15-22 were serially run with a flow rate of 30 mL/min for 5 minutes each. The Defender was used to record the flow rate of the LESS-P every minute for each tube location. The values for the calibrated positions (1, 3, 5, 7, 15, 17, 19, and 21) were compared to the uncalibrated positions (2, 4, 6, 8, 16, 18, 20, 22) to validate that the flow rate remained constant in each position (Figure S2B). A two-tailed t-test (95% confidence interval) showed that the calibrated and uncalibrated positions did not produce statistically significant differences in flow rate for either the BIOS Defender or LESS-P internal flow meter. Finally, the parallel collection method was set up to sample positions 1 & 15 at 30 mL/min for 5 minutes at the same time. The following pairs of tubes were then collected in

similar fashion: 1 & 15, 2 & 16, 3 & 17, 4 & 18, 5 & 19, 6 & 20, 7 & 21, 8 & 22. In this case, the two banks on the sampling manifold each control flow rate independently, such that external positioning of the BIOS Defender indicates the total flow for two tube locations. Therefore, the Defender was not used in the parallel flow mode and the results are illustrative solely of the flow logged by the internal LESS-P flow meter (Figure S3C). A two-tailed t-test (95% confidence interval) performed in GraphPad Prism5 showed that the calibrated and uncalibrated positions did not produce statistically significant differences in flow rate for the LESS-P internal flow meter. This result in the parallel collection method is particularly important because it replicates the field sampling methodology used in this study.

Figure S4. Representative comparison of active pumping to LESS-P results for field sampling at the Pesticide Storage Unit. A) Benchtop GC-MS system: The concentration of each detection event for the LESS-P sample is on average $109 \pm 4.2\%$ (standard deviation) of the active measurement, showing that the LESS-P system is consistent with active pumping results. B) HAPSITE[®] ER: The concentration of each detection event for the LESS-P sample is on average $118 \pm 13.7\%$ (standard deviation) of the active measurement, showing that the LESS-P system is consistent with active pumping results. Error bars represent the standard deviation of triplicate tubes collected by active pumping. This was calculated by dividing the concentration from LESS-P sample 1 (collected during the same time period as triplicate active samples) by the mean concentration of the triplicate active measurements and multiplying by 100%.

Figure S5. Qualitative comparison of the response of the LESS-P in either the benchtop or HAPSITE® ER along the right y-axis. Sites are A) Auto Maintenance; B) Aircraft Hangar #1; C) Bowling Alley; D) Gas Pumps; E) Aircraft Hangar #2; F) Pesticide Storage Unit; G) Animal Housing Facility; H) Biology Laboratory. HAPSITE® ER and benchtop system plots were constructed by determining the sum total of all TIC values for each sample, and normalizing against the highest value for each system at each sampling site. Each point on the graph (circle or plus sign) denotes a single sample (ie, LESS-P sample 1, etc.). The response of the ppbRae (green), a generalized VOC detector, is plotted for comparison and is visualized on the left y-axis. Note that the LESS-P values are delayed in respect to the ppbRae measurements due to the 30 min collection time for each LESS-P sample.

Figure S6. Quantitative LESS-P measurements on replicate samples in time series analyzed by benchtop system and HAPSITE[®] ER. A) Hexane; Auto Maintenance Shop, B) Isopropanol; Animal Housing Facility, C) Toluene; Auto Maintenance Shop, D) m,p-Xylene; Animal Housing Facility. Each point on the graph denotes a single sample (ie, LESS-P sample 1, etc.).

Figure S7. Stand-alone pumping comparison between HAPSITE[®] ER and benchtop GC-MS for the Pesticide Storage Unit. Error bars represent the standard deviation of triplicate measurements from three different pumps acquired at the same time and in the same general location. The average of all compounds at this site detected by the HAPSITE[®] ER were $84.8 \pm 42.0\%$ (standard deviation) of the concentration reported by the benchtop system. This average reflects the average of the percentages of the HAPSITE ER concentration measurement divided by the Benchtop measurement for all compounds detected in both systems.

Table S3. Detection Events above LOR from Field Sampling by Sampling Method.

	Benchtop System		HAPSITE® ER	
	Stand-alone Pump Active	LESS-P	Stand-alone Pump Active	LESS-P
1,2,3-trimethylbenzene	0	0	2	2
1,2,4-trimethylbenzene	0	1	0	0
1,3,5-trimethylbenzene	0	1	0	1
1,4-dioxane	3	8	3	3
4-Ethyltoluene	1	2	1	2
Acetone	8	8	8	8
Benzene	3	6	8	8
Ethyl acetate	1	2	0	0
Ethylbenzene	2	3	2	3
Heptane	1	2	4	3
Isopropyl Alcohol	4	6	6	6
m,p -xylene	3	3	2	5
n-hexane	3	4	3	3
o-xylene	1	3	1	4
Styrene	0	0	0	1
Tetrahydrofuran	0	6	2	1
Toluene	4	6	5	6
Trichloroethylene	0	0	0	0

Table S4. Mass on tube calculated from benchtop GC-MS (ng $\pm$ standard deviation)

	Auto Maintenance	Aircraft Hangar #1	Bowling Alley	Gas Pumps	Aircraft Hangar #2	Pesticide Storage Unit	Animal Facility	Housing	Biology Laboratory
1,2,3-trimethylbenzene									
1,2,4-trimethylbenzene	2.0 $\pm$ 0.1								
1,3,5-trimethylbenzene	2.6 $\pm$ 0.1								
1,4-dioxane	1.9 $\pm$ 1.3								
4-Ethyltoluene	7.8 $\pm$ 0.7					5.2 $\pm$ 2.8			
Acetone	7.3 $\pm$ 1.4	9.7 $\pm$ 0.8	6.9 $\pm$ 2.0	8.2 $\pm$ 2.6	10.0 $\pm$ 1.9	11.8 $\pm$ 4.5	9.6 $\pm$ 1.1		12.3 $\pm$ 4.0
Benzene	3.9 $\pm$ 0.3						5.8 $\pm$ 0.2		
Cyclohexane or 3- methylhexane	3.8 $\pm$ 0.1								
Ethyl acetate		0.4 $\pm$ 0.0			1.9 $\pm$ 0.6				
Ethylbenzene	5.8 $\pm$ 0.1					2.3 $\pm$ 0.9	9.1 $\pm$ 0.2		
Heptane	6.1 $\pm$ 0.3					1.5 $\pm$ 0.2			
Isopropyl Alcohol	2.6 $\pm$ 0.1	2.2 $\pm$ 0.2	6.2 $\pm$ 0.2			1.5 $\pm$ 0.1	16.4 $\pm$ 0.3		65.5 $\pm$ 2.3
m,p -xylene	22.2 $\pm$ 0.7					9.3 $\pm$ 3.8	36.4 $\pm$ 1.5		
Methyl Isobutyl Ketone	0.8 $\pm$ 0.0								
n-hexane	11.7 $\pm$ 0.3			2.3 $\pm$ 0.2		2.8 $\pm$ 0.3			
o-xylene	7.2 $\pm$ 0.2					2.8 $\pm$ 1.0	5.4 $\pm$ 0.2		0.05 $\pm$ 0.02
Styrene							1.4 $\pm$ 0.8		
Toluene	24.3 $\pm$ 1.0	1.7 $\pm$ 0.1		1.8 $\pm$ 0.2	1.2 $\pm$ 0.2	16.3 $\pm$ 3.2	1.0 $\pm$ 0.1		0.8 $\pm$ 0.3

Table S5. Mass on tube calculated from HAPSITE[®] ER GC-MS (ng $\pm$ standard deviation)

	Auto Maintenance	Aircraft Hangar #1	Bowling Alley	Gas Pumps	Aircraft Hangar #2	Pesticide Storage Unit	Animal Facility	Housing	Biology Laboratory
1,2,3-trimethylbenzene	4.6 $\pm$ 0.0					2.8 $\pm$ 1.2			
1,2,4-trimethylbenzene									
1,3,5-trimethylbenzene	4.0 $\pm$ 0.0								
1,4-dioxane					5.6 $\pm$ 1.6	5.8 $\pm$ 0.1			5.7 $\pm$ 0.1
4-Ethyltoluene	1.2 $\pm$ 0.0					2.9 $\pm$ 0.1			
Acetone	12.4 $\pm$ 2.7	13.3 $\pm$ 2.6	15.3 $\pm$ 1.6		30.4 $\pm$ 19.0	16.2 $\pm$ 2.5	13.2 $\pm$ 1.9		9.2 $\pm$ 0.1
Benzene			8.6 $\pm$ 0.3			8.7 $\pm$ 1.2			8.7 $\pm$ 1.2
Cyclohexane or 3-methylhexane Ethyl acetate	1.1 $\pm$ 0.1								
Ethylbenzene	2.4 $\pm$ 0.0					1.6 $\pm$ 0.1	8.2 $\pm$ 0.1		
Heptane	3.0 $\pm$ 0.0			2.8 $\pm$ 0.0		3.5 $\pm$ 0.1			
Isopropyl Alcohol	19.1 $\pm$ 0.6	65.0 $\pm$ 2.6	7.7 $\pm$ 0.6			0.9 $\pm$ 0.4	74.8 $\pm$ 4.5		84.0 $\pm$ 4.5
m,p -xylene	2.7 $\pm$ 1.7				2.17 $\pm$ 0.2	2.9 $\pm$ 0.1	27.6 $\pm$ 0.5		5.8 $\pm$ 0.2
Methyl Isobutyl Ketone	6.8 $\pm$ 0.1								
n-hexane	10.2 $\pm$ 0.2			3.8 $\pm$ 0.1		4.6 $\pm$ 0.3			
o-xylene	1.4 $\pm$ 0.0					0.8 $\pm$ 0.1	3.0 $\pm$ 0.1		0.8 $\pm$ 0.1
Styrene	2.6 $\pm$ 0.1								
Toluene	11.0 $\pm$ 0.1		5.0 $\pm$ 0.0	7.7 $\pm$ 0.1	5.3 $\pm$ 0.1	13.3 $\pm$ 0.2	4.9 $\pm$ 0.0		13.3 $\pm$ 0.2

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