Field sampling demonstration of portable thermal desorption collection and analysis instrumentation

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\textbf{ABSTRACT}

The HAPSITE\textsuperscript{®} (Hazardous Air Pollutants on Site) is a portable gas chromatography-mass spectrometry (GC–MS) unit designed to aid air sampling technicians by identifying and quantifying volatile organic compounds from occupational and environmental sampling. The main goal of the present study was to extend prior laboratory-based work with the portable HAPSITE\textsuperscript{®} ER (extended range model) thermal desorption (TD) capability to real-world field samples from both indoor and outdoor environments using different types of active and passive sampling mechanisms. Understanding the performance of the HAPSITE\textsuperscript{®} ER in a realistic field setting will allow air quality sampling technicians to make improved decisions related to sampling and analysis methods in the field. An important finding was that certain charcoal-based TD sorbents were contraindicated for the HAPSITE\textsuperscript{®} ER because of a substantial hydrocarbon bleed which degraded system performance. A novel time series TD sampler (Logistically Enabled Sampling System-Portable [LESS-P]) was validated using Tenax TA TD tubes against standard active sampling across multiple field sampling sites, and the qualitative analytical trends and compound identities were similar between LESS-P replicates analysed via benchtop GC–MS and HAPSITE\textsuperscript{®} ER. Once validated, the LESS-P was used to determine the reference concentrations for passive sampling calculations. The results confirmed the passive sampling methodology within the benchtop system, but highlighted some systemic sensitivity limitations that must be addressed in order for the HAPSITE\textsuperscript{®} to be accurately applied to passive sampling. We propose that the LESS-P time-series sampler may help to alleviate the requirement for sampling technicians to be on-site during active sampling, allowing for automated sampling throughout the duration of a sampling event.

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Supplemental data for this article can be accessed here.

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1. Introduction

The quality of the ambient environment has a direct impact on the overall health of humans as well as the ability for individuals to perform tasks at an optimal level. Specifically, the air breathed has a significant effect on quality of life, as the average human inhales 13,000 L of air per day [1]. Therefore, the presence of volatile organic compounds (VOCs) in the air can impart a profound influence on health, primarily by capture within the respiratory tract or in the lungs. The VOCs can promote inflammation of the airway or circulatory system enhancing the probability of stroke or heart attack, or cause headache, dizziness, cancer or neurotoxic effects [2]. The susceptibility of an individual to the effects of VOC exposure will vary with a variety of factors including age, gender, activity level etc. Additionally, exposure to indoor or outdoor air will typically vary the probability of encountering certain types of VOCs. The majority of time (87–90%) for most individuals is spent indoors, and indoor air concentrations typically exceed outdoor VOC levels as ventilation rates are too low to adequately clear out pollutants [2,3]. Indoor VOCs may manifest due to cleaning products, cooking, air conditioning or specific occupational hazards, and outdoor air VOCs may present from manufacturing, pesticides and vehicular pollution [3]. However, outdoor air may enter the ventilation system of buildings, and open-air sites are exposed to an uncontrolled environment (temperature, humidity, wind etc.) which may alter chemical reactions or toxicological effects [4]. Therefore, it is important to monitor both indoor and outdoor air for the presence of VOCs to obtain a complete understanding of the exposure profile.

Laboratory-based gas chromatography–mass spectrometry (GC–MS) is a standard method for evaluating VOCs in air [2]. GC–MS can be combined with thermal desorption (TD), a sample collection process designed to capture VOCs by pumping air through a tube containing a sorbent media in the environment where the VOCs are generated. The media in the TD tube will entrain the VOCs until heated in the TD system where they are released and measured using GC-MS. The sampling and analytical process requires no hazardous solvents or any of the relatively complex laboratory procedures that go along with solvent extraction methods for liquid chromatography–MS. Additionally, TD is more sensitive, requires minimal sample preparation and has higher sample recovery than solvent extraction [5]. The process is also non-destructive so the media and tubes can be reconditioned and reused.

Three different types of sampling are possible using TD tubes, each method possessing its own set of advantages (Figure 1). Active sampling (Figure 1(A)) is achieved when air from the sampling site is pumped through the TD tube using a small pump at a specified flow rate for a known time period. Active sampling allows one to get a picture of the VOCs present during a particular time period under a specific set of conditions and detect bolus doses of VOC which may be immediately harmful to health. However, to accurately portray the VOC profile of the sampling environment, samples must be collected during the entire period of human occupancy, in replicate, in multiple different sampling locations [2]. This places a heavy time and cost burden in relation to the sampling technicians and the laboratory personnel who will analyse the TD tubes by GC–MS [6]. Additionally, active sampling may result in breakthrough of lower boiling
Passive sampling is an alternative to active sampling that functions by diffusion of analytes onto the sorbent material according to Fick’s first law of diffusion [2]. Because passive sampling relies on diffusion, longer sampling periods (8 h–2 weeks) are used to obtain adequate compound collection in low-concentration environments. However, the entire sampling period can be captured within a single tube without breakthrough or saturation which may occur during extended periods of active sampling. Passive sampling (Figure 1(B)–(C)) eliminates the need for a calibrated air sample pump, reducing both the logistics tail that goes into maintenance and power for the pumps, and also the need for trained operators to be present during the sampling. For these reasons, the overall cost associated with sampling is reduced compared to active sampling [6]. Passive sampling presents a time-weighted average (TWA) of VOCs detected during the entire sampling event, which may be a more accurate depiction of the long-term effects of the contaminant on the environment than a short-term active measurement [6]. However, short-term increases in VOC concentrations detectable by active sampling which may be detrimental to occupant health will not be represented, long-sampling times may be required to detect low-analyte concentrations and very volatile compounds may not interact sufficiently with the sorbent [6,7].

Passive sampling may be applied in axial (Figure 1(B)) or radial (Figure 1(C)) format. In axial sampling, a TD tube is capped at one end, and a diffusion cap is placed over the sampling end that protects the sorbent material from variations in environmental air flow and provides a specific diffusion path length and surface area for comparison to published data [8]. A variety of sorbent types are available for axial sampling with standard geometries simplifying calculations following GC–MS analysis. Axial format is ideal for applications where reporting a TWA over long-term monitoring (8 h–3 weeks) is desirable. In radial sampling, the air stream interacts with the radial dimension of a sorbent housed within a porous polymer body which is transferred to a TD tube prior to GC–MS evaluation. Radial sampling is beneficial because shorter sampling times are possible due to the fact that the diffusion path is parallel to the radius of the tube,
allowing for a higher surface area (23.6 cm$^2$) and shorter diffusive path length than axial diffusion tubes, resulting in a 100× faster sampling rate. The sampling rate limits the practical volatility range of compounds of interest to those with volatilities less than or equal to benzene due to the high risk of back diffusion of radial samplers. Therefore, stronger sorbents are usually required for radial sampling than for axial or pumped sampling. Additional considerations for radial diffusion include saturation of the sorbent tube due to the higher sampling rate, loss of high boiling point compounds from interaction with the polymer body, fewer published uptake rates (URs) are available, and possible sample loss from transfer of the material to a TD tube. Overall, active as well as axial and radial passive sampling may provide orthogonal data sets with information on different ranges of compounds that can help with completing a total exposure picture for a site.

A further advantage of TD sampling (encompassing both active and passive mechanisms) over legacy processes is that the simplicity of the analysis in terms of minimal sample preparation means that large-scale sample collection and analysis by a deployed health risk assessor could be performed on-site with portable instruments. These instruments may speed up the risk assessment process by obviating the need to transport samples to a laboratory for GC–MS analysis and allow for processing of TD tubes as they are generated on-site. One such option includes the portable GC–MS HAPSITE® (Hazardous Air Pollutants on Site) system, developed by Inficon for emergency responders. The newest version of the HAPSITE® (HAPSITE® ER), contains a TD module which was characterised by this group in a controlled laboratory setting in a previous study [9]. The main goal of the present study was to extend prior laboratory-based work with the portable HAPSITE® ER TD capability to real-world field samples from both indoor and outdoor environments using different types of active and passive sampling mechanisms. An automated time-series sampling system (Logistically Enabled Sampling System-Portable [LESS-P]) was laboratory tested and applied to field sampling in an effort proposed to reduce the logistics burden imparted by traditional active sampling on sampling technicians. This LESS-P data, as well as traditional stand-alone pumped active and passive sampling, was used to compare HAPSITE® ER response to a benchtop GC–MS system to assess capabilities for field sampling. Understanding the performance of the HAPSITE® ER in a realistic setting will allow air quality sampling technicians to make improved decisions related to sampling and analysis methods in the field.

2. Experimental

2.1 Materials

Glass TD tubes are fragile and may pose hazards directly to the sampling technician and instrument periphery. As a result, this study was performed using stainless steel (ss)TD tubes which are a more rugged alternative to glass. The change to ssTD tubes was significant for the HAPSITE® ER, where previous results demonstrated that ssTD tubes only reached ~200°C, despite a set temperature of 300°C, resulting in incomplete desorption of some higher boiling point compounds [9]. Soil vapour intrusion (SVI) tubes were purchased as preconditioned ssTD tubes from Perkin-Elmer (Shelton, CT). Radiello VOCs and BTEX passive samplers (Sigma-Aldrich, Saint Louis, MO) contained
Carbograph 4 sorbent which was manually transferred into ssTD tubes (Markes International, South Wales, UK) for analysis. The Radiello samplers were purchased as pre-packed cartridges (Code 145) with sorbent and designed to fit inside empty 1/4 in. ssTD tubes. The Radiello cartridges were centred in the ssTD tube by the ssTD tube groove, and clips were utilised to keep the cartridges in place.

ssTenax TA TD tubes were purchased from Markes International (South Wales, UK) and were conditioned by using a Markes TC-20 (Markes International, South Wales, UK) supplying 80 mL/min nitrogen flow at 320°C for 2 h. For quantitation, ssTenax TA TD tubes were manually loaded with volumes of 1 ppm (each compound) TO-15 (Restek, Bellefonte, PA) standard gas mix equivalent to different concentrations (ppbv). Loading was performed using a modified Markes Calibration Solution Loading Rig (Markes International, South Wales, UK), backed with constant nitrogen at 124.1 kPa (99.999%) by Gastight syringe (Hamilton Co, Reno, NV, USA). The TO-15 gas mix was injected over a 10-s period with the syringe remaining in the loading rig for an additional 10 s after all the mix had been injected.

2.2 LESS-P and stand-alone active pump sampling

The LESS-P (Signature Science, Austin, TX) time-series TD tube sampling system is a self-contained air pumping system which controls airflow so that sampling can be performed through up to 28 tubes sequentially. Alternatively, two tubes can be simultaneously sampled such that replicates can be obtained from the same time period. Fourteen time-series TD tubes were collected over the entire sampling period so that HAPSITE® ER/benchtop GC–MS comparisons and passive sampling calculations could be accomplished. These data provide the concentration of each compound present in the atmosphere at each sampling site covering the same time period as passive sampling. The BIOS Defender gas flow calibrator was used to calibrate the flow rate of the LESS-P before each sampling event. Four of the first eight tube locations were calibrated using the LESS-P software for both manifolds. Following this, the flow rates of all of the first eight tube locations were measured. If flow for each of the locations was within ±5% of the set point as logged by the LESS-P internal flow meter, the calibration was considered successful according to manufacturer’s instructions. Samples were collected in a pre-programmed time series using the user interface at 30 mL/min for 30 min for a total volume of 900 mL for each TD tube. Two replicates were collected at each 30-min time period; one replicate at each time period was analysed by HAPSITE® ER and the other by benchtop GC–MS. For the laboratory single tube flow tests, the BIOS Defender was used to measure flow every 3 min during the 30-min sampling period. This result was compared to the flow rate logged by the LESS-P system. The dual bank flow reports the flow rate logged by the LESS-P system since the BIOS Defender will measure the total flow entering the system before it splits between the two tubes.

Active sampling was also performed using six stand-alone SidePak SP730 pumps (TSI, Inc., Shoreview, MN) at 30 mL/min for 30 min for a total of 900 mL sample volume. Stand-alone active pump sampling was collected during the same time period as the first LESS-P sample. Triplicate stand-alone active pump samples were analysed in both HAPSITE® ER and the benchtop GC–MS system.
2.3 HAPSITE® ER

The HAPSITE® ER system was purchased from Inficon Inc. (East Syracuse, NY, USA) and the performance of a single instrument was evaluated in this study. In this work, we utilised the TD module primarily due to the increased sensitivity and the ability to collect samples on-site and transport them with minimal degradation to the instrument in a stand-off location [9]. The TD module was set to 330°C for 10 min, and desorbed VOCs passed through a heated line (70°C) to a tri-bed concentrator. The concentrator was set to 300°C for an 8-s pre-desorption step, followed by a 30-s desorption. Nitrogen was used as the carrier gas at a constant pressure mode of 88 kPa. A non-polar column (100% polydimethylsiloxane; 15 m × 0.25 mm ID × 1.0 μm df) was utilised in the GC. The GC temperature programme started at 50°C for 2 min, increased at 3°C/min to 80°C, at 12°C/min to 120°C, and at 26°C/min to 200°C where the final temperature was held for 5.6 min. Total GC analysis time was 24 min using a custom method (not Inficon-supplied). A quadrupole MS was utilised as the detector, operated under vacuum provided by a non-evaporative getter and an ion sputter pump [10]. A diffusive polydimethylsiloxane polymeric membrane operated at 80°C was used to interface analytes exiting the GC column and entering MS detector under vacuum operated in the electron impact ionisation mode at 70 eV [10]. The membrane has been shown to pass hydrophobic analytes to the MS ionisation chamber, while polar VOCs are discarded [11]. The mass scan range was \( m/z \) 41–300 and the scan time was 0.78 s. HAPSITE injects known volumes of internal standards bromopentafluorobenzene (BPFP) and 1,3,5-tris(trifluoromethyl)benzene (Tris) (5.44 ppm and 10.83 ppm stock concentrations, respectively) for each analysis from the internal standard canister obtained from Inficon.

Peak heights and compound identities of TO-15 compounds from the field samples were determined using a manual data analysis method so the MS spectrum of each detection event can be evaluated individually rather than relying on the HAPSITE® IQ software for identification and quantitation. Compound identification was aided by NIST Library 11 installed within the HAPSITE® IQ software by matching the retention time and mass spectrum of each compound with those of the TO-15 standards. Quantitation of field samples was performed by comparing TO-15 identified compounds with standard curves. HAPSITE® ER standards were prepared by dilution of 1 ppm initial concentration TO-15 standard mixture (Restek, Bellefonte, PA) to the following equivalent concentrations on ssTenax TA tubes (Markes International, South Wales, UK): 0.5, 1, 2, 5, 25, 50 and 100 ppbv based on a total volume of 400 mL. Several replicates (4–7 total) at each concentration were prepared to obtain a validated calibration curve plotting peak height versus concentration. A validated calibration curve had a relative standard deviation (RSD) <30% for the relative response factor of each compound and meets all other criteria specified by EPA method TO-15 [17]. The concentration of each TO-15 compound identified from the field sampling was calculated by applying the 400-mL calibration curve and multiplying by the correction factor (900/400 = 2.25) to obtain the concentration in 900 mL total sample volume for this study.

2.4 Thermo ISQ GC–MS (‘benchtop system’)

To evaluate and validate the TD capability of HAPSITE® ER, duplicate sorbent tubes were obtained from all field sampling sites: one was analysed by HAPSITE® ER and the other
by Thermo ISQ GC–MS (referred to as ‘benchtop system’ throughout the manuscript). The Thermo ISQ GC–MS utilised a modified version of EPA Method TO-17 for monitoring VOCs via automated, cryogen free TD using a TD-100 TD instrument (Markes International, South Wales, UK) in line with a Trace GC Ultra and ISQ single quadrupole mass spectrometer (Thermo Scientific, Waltham, MA, USA). The TD-100 parameters were as follows: tube desorption temp.: 310°C; tube desorption time: 10 min; flow path temp.: 160°C; trap (U-T15ATA-2S) flow: 50 mL/min; pre-trap fire purge time: 1 min; trap low temp.: 25°C; trap high temp: 315°C for 5 min; trap heating rate: 40°C/s (MAX); Split ratio: 3.5:1 (outlet (trap) split only). A TG-624 column (60 m × 0.32 mm ID × 1.80 μm df; Thermo Scientific, Waltham, MA, USA) was installed into the GC. The GC temperature programme started at 40°C for 1 min and increased at 10°C/min to 240°C where the final temperature was held for 20 min. The total GC analysis time was 41 min. Helium was used as the carrier gas at a constant flow of 2 mL/min. The mass spectrometer was operated in the electron impact ionisation mode at 70 eV. The MS transfer line temperature was 230°C and the ion source temperature was 275°C. The mass scan range was m/z 35–300 and the scan time was 0.154 s.

ssTenax TA tubes were used to prepare the calibration curve using TO-15 standard mixture at 2, 10, 25, 50 and 100 ppbv, 900 mL total volume. TraceFinder software produces a calibration curve automatically for each compound by integrating peak area and plotting the response factor of each compound relative to the internal standard (1,4-difluorobenzene or chlorobenzene-d5) at each concentration. Field sample concentrations were automatically calculated within the TraceFinder software for TO-15 compounds by applying the calibration curves and were reported without further modification.

2.5 Sampling

Passive and stand-alone active pump/LESS-P samples were collected at eight different field sites representing indoor and outdoor environments. All field sites were located in the Dayton, OH area and sampled during the period May–June 2013. All samples were collected in replicate, and replicates were analysed on both HAPSITE® ER and benchtop GC–MS system. A total of 6 passive and 6 stand-alone active pump replicates (3 analysed by HAPSITE® ER and 3 by the benchtop GC–MS) and 28 LESS-P samples (14 analysed by HAPSITE® ER and 14 by benchtop system which were duplicates in time series covering the entire passive sample time) were obtained from each site. The duration of sampling is described in Table 1. A trip blank was collected at each site to provide baseline measurements and aid in passive calculations. The trip blank is a tube that is co-located with the sample tubes, but is briefly opened to mimic the addition of the diffusion cap to sampling tubes, then recapped during the sampling period. This simulates any compound that adsorbs due to the removal of the storage cap in the short time period before the diffusion cap is added. The trip blank also allows for quality assurance related to sample collection, shipment and storage. Active/LESS-P samples were pumped at 30 mL/min for 30 min for a total volume of 900 mL for each TD tube. Environmental conditions were recorded using a Nielsen-Kellerman Kestrel 4500 Portable Weather Station (Boothwyn, PA) and are illustrated in Figure S1.
Rae Systems (San Jose, CA) manufactures a variety of hand-held systems employed by different agencies for environmental gas and VOC monitoring [12]. In particular, the MultiRae Pro and ppbRae models have been widely reported as high sensitivity instruments for exposure detection [13,14] and were incorporated into the present study. A ppbRae (Rae Systems, San Jose, CA) containing a photoionisation detector was used to measure general VOC response for comparison with the HAPSITE® ER. The MultiRae Pro (Rae Systems, San Jose, CA) was used as a detector for light environmental gases including HCN, NO₂, H₂S, CO, SO₂ and CO₂. It was generally used to monitor the sites for conditions which may be harmful to the sampling technicians. A summary table and further discussion can be found in the Supporting Information (Table S1).

2.6 Passive sampling calculations

Passive sampling was accomplished with the use of a diffusion cap with a mesh grid (Markes International, South Wales, UK) on the sampling end of ssTenax TA tubes, and the opposite end was sealed with a brass end cap (Markes International, South Wales, UK). The use of the diffusion cap simplifies passive data analysis because all sampling can be considered to occur by diffusion over a single fixed sampling distance, allowing for mass calculations using the well-studied diffusion constant of a compound.

In this work, the mass-on tube was calculated for each detected compound using the ideal gas law in both the sampled tubes and trip blank:

\[ n = \left( \frac{PV}{RT} \right) \times \left( \frac{c_{\text{ppb}}}{1 \times 10^9} \right) \]  

(1)

\( P \) is the pressure in atm (~1 atm), \( V \) is the sampling volume (0.9 L), \( R \) is the ideal gas constant (0.082 L atm/mol/K), \( T \) is the temperature (~298.15 K) and \( c_{\text{ppb}} \) is the concentration (ppbv) reported from the GC–MS data. The moles of each gas (\( n \)) are converted to mass (g) by multiplying by the molar mass (g/mol) for each compound.

One particular challenge with passive sampling lies in converting the mass of VOCs entrained on the TD tube to a concentration value [4] or concrete comparison metric. In this work, UR was used as an estimate of system performance by comparing the experimental UR based on the field sampling to the ideal UR (\( \text{UR}_{\text{ideal}} \)) or UR values published in the literature. The UR describes the amount of VOC interacting with the sorbent per unit time, using the calculated mass-on-tube (from Equation (1)) for a specific analyte. In order to determine the UR, the actual concentration of analyte present during the sampling period must be known. Therefore, \( c \) is the

| Site                          | Time (min) |
|-------------------------------|------------|
| Auto maintenance shop         | 429        |
| Aircraft Hangar no. 1         | 405        |
| Bowling alley                 | 420        |
| Gas pumps                     | 456        |
| Aircraft hangar no. 2         | 423        |
| Pesticide storage unit        | 420        |
| Animal housing facility       | 420        |
| Biology laboratory            | 420        |
background-subtracted average concentration of all LESS-P time-series samples for a compound over the entire time course of the passive measurements (µg/L), estimated using Equation (2):

\[ c = \frac{(m - m_b)}{V} \]  

(2)

where \( m \) is the mass (µg) calculated from the passive diffusion tube following GC–MS analysis (average of triplicate passive measurements at each site and calculated using Equation (1)), \( m_b \) is the calculated mass of the chemical on the trip blank (µg) and \( V \) is the same 0.9-L sampling volume described in Equation (1). This concentration (\( c \), in µg/L) is then inserted into Equation (3) to calculate the experimental UR (mL/min):

\[ UR = \left( \frac{(m - m_b)}{c} \times t^{-1} \right) \times 1000 \]  

(3)

where \( t \) (min) is the passive sampling time (Table 1) period [2].

The ideal URs (mL/min) were calculated according to Equation (4) [15]:

\[ UR_{\text{ideal}} = \frac{60 \times DA}{Z} \]  

(4)

where \( D \) is the diffusion coefficient of the compound in cm²/s [16], \( A \) is the cross sectional area of the sampling tube (0.191 cm² [15]) and \( Z \) is the path length of the air gap (1.5 cm [15]). The UR values for the benchtop system (Table 3) and HAPSITE® ER (Table 4) represent the mean UR value and standard deviation for the triplicate measurements performed at each site the compound was detected. This value is then divided independently by both the \( UR_{\text{ideal}} \) and published UR values and multiplied by 100 to express the ratio as a per cent value. This comparison provides a metric for validation of the passive sampling methodology. Comparisons between the differences of the URs from the ideal/published values between the benchtop system and HAPSITE® ER are reasonable because the results are normalised relative to each system.

### 2.7 Detection criteria

The current study focused on identification and quantitation of EPA Method TO-15 VOCs, a subset of compounds reported as hazardous air pollutants in the Clean Air Act Amendments of 1990 [17]. The study was designed to report the values for compounds present above the limit of reporting (LOR) of 2 ppbv for passive, LESS-P or active stand-alone pump sampling. The LOR was set at 2 ppbv because this was the lowest concentration used to produce the calibration curve for the benchtop system, and therefore the lowest concentration accurately reportable without extrapolation. If a compound was present above the LOR for any single measurement of any of the sampling methods (passive, LESS-P or active stand-alone pump), the reported concentrations of that compound for the other sampling methods were included for comparison even if they were lower than 2 ppbv ('reporting criteria'). A list of compounds detected above LOR along with the detection frequency (number
Table 2. Detection events from all field sampling sites (above LOR) by TD tube.

|                | Auto maintenance | Aircraft hangar no. 1 | Bowling alley | Gas pumps | Aircraft hangar no. 2 | Pesticide storage unit | Animal housing facility | Biology laboratory |
|----------------|------------------|-----------------------|---------------|-----------|-----------------------|------------------------|------------------------|-------------------|
| 1,2,3-Trimethylbenzene | H                |                       |               |           |                       |                        |                        |                   |
| 1,2,4-Trimethylbenzene   | B                |                       |               |           |                       |                        |                        |                   |
| 1,3,5-Trimethylbenzene   | XX               |                       |               |           |                       |                        |                        |                   |
| 1,4-Dioxane              | B                | H                     | H             | H         | H                     |                        |                        |                   |
| 4-Ethyltoluene           | XX               |                       |               |           |                       |                        |                        |                   |
| Acetone                  | XX               | XX                    | XX            | B         | XX                    | XX                     | XX                     | XX                |
| Benzene                  | B                | H                     |               | H         | B                     | H                      |                        |                   |
| Cyclohexane or 3-        | XX               |                       |               |           |                       |                        |                        |                   |
| methylhexane             |                  |                       |               |           |                       |                        |                        |                   |
| Ethyl acetate            |                  |                       |               |           |                       |                        |                        |                   |
| Ethyl benzene            | XX               | B                     |               |           |                       |                        |                        |                   |
| Heptane                  | XX               |                       |               | H         | XX                    |                        |                        |                   |
| Isopropyl alcohol        | XX               | XX                    | XX            |           |                       | XX                     | XX                     | XX                |
| m,p-xylene               | XX               | H                     |               |           | XX                    | XX                     | XX                     | XX                |
| Methyl isobutyl ketone   | XX               |                       |               |           |                       |                        |                        |                   |
| n-Hexane                 | XX               |                       |               |           |                       |                        |                        |                   |
| o-Xylene                 | XX               |                       |               |           |                       |                        |                        |                   |
| Styrene                  | H                |                       |               |           |                       |                        |                        |                   |
| Toluene                  | XX               | XX                    | XX            | XX        | XX                    | XX                     | B                      | XX                |

H indicates compounds detected using HAPSITE® ER only; B signifies compounds detected by the benchtop system only; two Xs (XX) show compounds detected using both systems. The LOR was 2 ppbv for this study, which was the lowest value used in the calibration curve for the benchtop system.
of sites where the compound was detected at any level) is included in Table S2 for
the combination of all of the sampling methods.

In this work, compounds considered present by the reporting criteria (above 2 ppbv LOR for any of the sampling methods) were not reported as present in Table 2, if one or more of four conditions were met, termed ‘exclusion criteria’. Exclusion criteria were implemented to ensure a level of data quality to discriminate experimental artefacts and increase the probability of a legitimate detection event. First, if the reported concentration of the passive sampling was less than or equal to that of the trip blank, the compound was considered a tube artefact instead of a valid detection. Second, we established a threshold cut-off, where even if one method detected the compound above 2 ppbv, the compound was not reported if the concentration was below 0.05 ppbv. This threshold was used as a subjective cut-off point where instrument operators determined that a compound could no longer be reliably identified from the MS data. Third, data were excluded if the standard deviation of the triplicate passive tubes was greater than the mean. This introduces doubt into the validity of the measurements due to experimental artefacts, especially since only one trip blank was analysed (no standard deviation of trip blank for comparison). Finally, compounds were excluded if the value of the standard deviation subtracted from the mean of the passive was less than that of the trip blank. This implies that at least one of the triplicate samples is in doubt of being a real detection event.

3. Results

3.1 Sorbent compatibility with HAPSITE ER

Prior to field sampling, different types of sorbents were tested for compatibility with the HAPSITE® ER. Tenax TA is a weak sorbent rated for VOCs roughly in the \( C_7 - C_{30} \) volatility range [18], and SVI TD tubes are multi-bed tubes covering the \( C_3 - C_{20} \) volatility range [19] containing a strong carbon-based sorbent. Tenax TA demonstrated a relatively low amount of background bleed (Figure 2(A)), with peaks observed from benzene, toluene, styrene, benzaldehyde, phenol and acetophenone. These products are consistent with artefacts reported in the literature as byproducts of thermal degradation or reaction with atmospheric gases [18,20,21,22]. SVI tubes produced a substantial build-up of hydrocarbons in the HAPSITE® ER instrument (Figure 2(B)) which caused difficulty with data analysis and degraded instrument performance over time. Similarly, the Carbograph 4 sorbent employed in the Radiello also demonstrated a high hydrocarbon background within the HAPSITE® ER (Figure 2(C)) resulting in clogging of the instrument and extensive cleanout of the accessory and system after use. Therefore, despite the potential advantages of radial passive sampling and the wider volatility range covered by SVI tubes, these carbon-based sorbents were not investigated further since they were not compatible with the HAPSITE® ER. Tenax TA was used as the TD sorbent for all subsequent samples due to the relatively low-background matrix.
Figure 2. Blank measurements of sampling media from (A) Tenax TA ssTD tube, (B) SVI ssTD tube, (C) carbograph 4 sorbent from Radiello device transferred to an empty ssTD tube and analyzed by HAPSITE ER.
3.2 Field sampling summary of VOCs identified by TD–GC–MS

Eight sampling sites representing a mix of indoor and outdoor venues (Table 1) were sampled using TD tubes in passive, active stand-alone pumps and LESS-P format. Total detection events prior to application of the exclusion criteria for all compounds detected two or more times and isomers of the same compound are reported in Table S2. Several compounds (1,4-dioxane, acetone, benzene and toluene) were detected at nearly every site using both the benchtop and HAPSITE® systems (Table S2, ‘Detection Frequency’). 1,4-Dioxane is a component of surfactants used in foods, cosmetics and detergents [23]. It is also used as a solvent for greases, lacquers, mineral oils, waxes, metal parts cleaners and paint and varnish strippers, which may explain its presence in the field sampling sites. Benzene and toluene are frequently reported in environmental sampling, from sources such as smoking [24], cooking [25] and automobile emissions [26]. Compounds including ethylbenzene, ethyltoluene, xylenes, trimethylbenzenes, n-alkanes from C₁–C₂₉, various branched alkanes, styrene and acetone have been reported from at least one of these same sources [25,26,27]. Acetone is also a common bioeffluent and component of consumer products widely reported during field sampling [28,29].

After employing the exclusion criteria, 98 total detection events were demonstrated at the eight sampling sites (Table 2). Representative chromatograms for each system are included as Figure S2. A total of 78 (79.6%) compounds were detected using both systems, illustrating that HAPSITE® can detect similar compounds to a reference system from a field sampling environment, despite the design modifications necessary for portability. The HAPSITE® reported a total of 51 detection events with 12 unique detections (the compound was not detected using the benchtop system), while 47 total detection events and 8 unique detections were observed with the benchtop system (Table 2). Of the 20 unique detection events in both systems, 12 were detected by both methods, but were not reported by one of the systems due to the exclusion criteria. 1,4-Dioxane was reported in three sites by the HAPSITE® which were not reported as a detection event by the benchtop system. In each case, 1,4-dioxane was detected above the LOR for the benchtop system (Table S2), but the data were highly variable such that they did not pass the exclusion criteria. For example, the stand alone active pump sampling triplicate measurements for 1,4-dioxane had an average of 56.5% RSD across the eight sites, and 73.2% RSD for the triplicate passive measurements. In comparison, acetone, detected at nearly every site by both types of instrumentation, demonstrated 16.7% RSD for active sampling and 24.0% RSD for passive measurements. Ethyl acetate was detected at two sites by the benchtop system, but was not reported by the HAPSITE® for any field sampling site. Using the same HAPSITE method, previous work has shown that ethyl acetate coelutes with hexane, and that ethyl acetate is observed in one of the lowest intensities of all TO-15 compounds [9]. The intensity at 20 ppbv concentration was 30× lower than that of the internal standard TRIS, which may explain why it was not detected in the HAPSITE® for the present study when only 2–3 ppbv levels were reported in the benchtop system. The remainder (four events) of the unique detection events are anticipated to be a result of a low maximum concentration (~2 ppbv, LOR) of
compound detected by one system which was not discernable by the other instrumentation and identification of different isomers of trimethylbenzene by HAPSITE® or benchtop technology. As a whole, these studies show that the HAPSITE® ER was able to detect similar compounds to those of a laboratory benchtop GC–MS system.

3.3 LESS-P validation

The LESS-P was widely used throughout this work for field sampling, but to the best of our knowledge, the instrument has only been utilised in two peer-reviewed manuscripts to date [30,31]. In order to confirm performance of the system for field sampling, a series of controlled sampling evaluations were performed mimicking the conditions related to field use (see Supplementary Information for more details). In the first set of tests, the flow rate was measured for individual tube locations after calibration for half of the tube positions. These results showed that the flow is stable in four LESS-P positions over the 30-min sampling time period (1.11% RSD for all tubes when using the BIOS Defender, 0% RSD from the LESS-P internal flow meter), the average flow rate is within 3% of the set point for the LESS-P internal flow meter (±5% for validation of calibration according to manufacturer’s instructions), and the average flow rate reported by the LESS-P internal flow meter is within ~3 mL/min of the value measured by the BIOS Defender (Figure S3A). The average flow rates between the two banks were similar (32.9 ± 0.8 mL/min for bank 1 tubes by Defender, 32.3 ± 0.2 mL/min for bank 2 tubes by Defender, 29 ± 0.0 mL/min for both banks by internal LESS-P flow meter), and the average flow rates between the calibrated and uncalibrated tubes were not significantly different when all locations were sampled in series (Figure S3B). These tests also demonstrated that the flow rate is accurate in parallel sampling mode (average for all tubes 28.8 ± 0.5 mL/min, within 4% of set point), and did not significantly differ between banks (28.8 ± 0.7 mL/min for bank 1, 28.9 ± 0.4 mL/min for bank 2). Flow rate analysis is a reasonable means of measuring system performance since the amount of VOC deposited on similar tube types should be approximately equal if the same flow rate and sampling time are used. Extending this premise, a representative example from the field sampling showed that the VOC content and quantities of compounds sampled using the LESS-P was similar to that of active stand-alone pump sampling collected during the same time period and analysed using both HAPSITE® and benchtop system (Figure S4). These results, in combination with the flow rate testing, effectively validated the use of LESS-P for field testing. The LESS-P was then applied to the following studies to compare the performance of the HAPSITE® ER to the benchtop system.

3.4 Active (LESS-P and stand-alone pump) field samples analysed using HAPSITE ER and benchtop system

It is well understood that certain performance trade-offs are inevitable when transitioning from a laboratory grade benchtop system to a portable unit. Therefore, it is difficult to directly compare the results of the compounds found in the benchtop GC–MS versus HAPSITE® due to the differences in the systems and methods used for compound detection. For example, HAPSITE® is limited in GC column and desorption temperature
of ssTD tubes compared to the benchtop system (200°C for HAPSITE®), and the mass scan time is slower, resulting in attenuation or elimination of detection capabilities of VOCs with high boiling point or low abundance. The hydrophobic membrane interfacing the HAPSITE® ER GC to the MS has been reported to limit the resolution of certain compounds [11], and different trap desorption programmes are utilised between HAPSITE® and benchtop systems. In addition, the benchtop system employs helium as the carrier gas with a 60 m mid-polar 6% cyanopropylphenyl methylpolysiloxane GC column versus a 15 m non-polar 100% polydimethylsiloxane (PDMS) with nitrogen as the carrier gas in the HAPSITE® ER column. HAPSITE® ER operates in a constant pressure mode that is not user-adjustable, where pressure may be too high for early eluting compounds to separate properly, resulting in coelution of some of the more volatile compounds. In previous studies it was demonstrated that acetone, pentane, isopropanol and ethanol coelute and hexane coelutes with ethyl acetate and similar unidentifiable hydrocarbons in the HAPSITE® ER [9]). Therefore, the benchtop system is used as a reference method to compare the analytical trends of TO-15 compound detection performance of the HAPSITE® rather than a direct comparison metric. Understanding how an optimised HAPSITE® ER method compares to a fully optimised laboratory reference method is critical in understanding the true detection capabilities of the portable unit.

The first set of analyses involved analysing the HAPSITE® ER trends over time, and comparing those trends to the benchtop system and a second portable validated VOC detection technology, the ppbRae. The sum of the total ion chromatograms (TIC) analysed by time-series sampling (LESS-P samples) were plotted for each system and versus total VOC content from the ppbRae. In general, the basic trends from HAPSITE® ER and benchtop systems match closely over time (Figure S5). For example, the benchtop system and HAPSITE® both show an increase from LESS-P10-13 and decrease at sample 14 at the Auto Maintenance Shop (Figure S5A, time period from 14:09 to 15:21). This trend is similar to the results of the ppbRAE, which detects an increase in total VOCs during the same time period. The trends at other sites also were qualitatively similar, showing that the HAPSITE® ER data provide results close to both the benchtop system and the ppbRae.

The results for representative individual compounds sampled using LESS-P also follow similar trends to the TIC values between the two systems (Figure S6). HAPSITE® concentrations for hexane (Figure S6A) and isopropanol (Figure S6B) are higher than in the benchtop system, potentially due to coelution as described above. Also, it was observed that some VOCs (p/m-xylene, isopropanol, toluene and 4-ethyltoluene) showed saturation using the HAPSITE® ER, causing reported compound concentrations to be lower than (Figure S6C) or not mirroring the trends (Figure S6D) of the benchtop system. One potential reason for this saturation is because HAPSITE® does not have an option to split flow for high concentration samples, where the benchtop GC–MS can split flow. In HAPSITE®, saturation occurs when the intensity of any of the mass ions in a compound reaches more than 60,000,000 ion counts. Consequently, accurate quantification was not possible when the level of a VOC was higher than its saturation concentration. Acetone, isopropanol and toluene consistently demonstrated concentrations 3.1, 3.2 and 2.3 times higher in the HAPSITE® ER than the benchtop system across all sites. This is anticipated to be a result of the
coelution of acetone and isopropanol, as well of the presence of toluene as TD tube bleed material in HAPSITE®. While these compounds were difficult to accurately quantitate in HAPSITE® ER, the response between the HAPSITE® and the benchtop system corresponded well over time for the analysis of TD tube sampling using the LESS-P sampling system (Figure S6B). Overall, this simple comparison in this section shows that the HAPSITE® ER reports the same general trends as the benchtop system and ppbRAE across a time series as long as HAPSITE® compound saturation is not observed.

The performance of the stand-alone pump active sampling was also evaluated between HAPSITE® ER and benchtop GC–MS. The analytical trends, in this case, the ratios of the concentrations of compounds for each system, were similar between the two units. For example, toluene is the most abundant compound, and m,p-xylene concentration is lower than heptane, heptane is lower than ethylbenzene etc. for both systems (Figure S7). A summary of the compounds detected above LOR using HAPSITE® ER and benchtop system for both LESS-P and stand-alone pumps is presented as Table S3. The quantitative results were more variable between systems, much like in the LESS-P data (Figure S6). Another similarity to the LESS-P HAPSITE® ER versus benchtop system results was that acetone, isopropanol and toluene concentrations were higher (2.6, 3.4 and 1.5 times, respectively) than the benchtop system results. The similar performance between stand-alone pumps and LESS-P for both HAPSITE® ER and benchtop system demonstrates the potential for LESS-P integration into a sampling toolkit to minimise the burden on sampling technicians.

3.5 Passive sampling UR calculations for HAPSITE ER and benchtop system

After validating HAPSITE® performance in terms of the identities and trends of compound detection relative to the benchtop system, the next set of experiments was designed to determine whether the system could be applied to passive sampling. The first step involved validating the passive sampling methodology on the benchtop GC–MS. In order to do this, the experimental UR for compounds detected during the field sampling (Table 3) was compared to the ideal uptake rate (Equation (4)), and when possible, reported literature values. The mass on tube for each compound was calculated using Equation (1) (Table S4), and the experimental and ideal uptake rates were calculated from this data using Equations (2) and (4), respectively. For the benchtop system, all experimental uptake rates were within 30% of the ideal uptake rate (Table 3, Expt'/Ideal (%)) with the exceptions of 1,4-dioxane, benzene, ethylbenzene and hexane. Each of these compounds is approaching the cut-off range of C7 recommended for Tenax TA [18]. In particular, benzene is not recommended for Tenax TA because its high volatility can lead to displacement by non-polar high molecular weight compounds [32]. Benzene and toluene are derived from the sorbent material, and variability of both is possible between tubes [20]. Also, the high volatility of hexane and benzene has been reported to result in variable uptake rates due to an exponential relationship between uptake rate and dose at low exposure doses (<40 ppm/min) in tube-type diffusion samplers on Tenax TA [33].

Using the ideal uptake rate as a success metric is known to be problematic for low boiling point VOCs where the experimental uptake rates have been reported to deviate
more from the ideal [3]. Therefore, the experimental uptake rates were also compared to literature values of studies also performing field sampling using Tenax TA (Table 3; Expt’l/Published (%)). In this case, experimental values were all within 30% of the published values with the exception of benzene. The experimental uptake rate values for the two sites benzene was reported at were 3.45 and 0.547 mL/min. The lower value is 81.4% of the ideal uptake rate and 134.4% of the published rate which is within or close to ±30% of the respective value. The second value is several times higher than expected, raising the average experimental uptake rate in Table 3. This high value is anticipated to be due to a level of benzene in the trip blank over an order of magnitude lower than benzene in the six (Table S1) other locations. If this value is falsely lower than what is representative of a blank tube, the $m_b$ (blank mass on tube) term in Equation (2) will be lower than the actual concentration, causing a falsely high calculation of the ambient concentration of the compound, in turn leading to a lower uptake rate calculated by Equation (1). Average experimental uptake rates for all detected compounds (Table 3) were 81.3 ± 11.6% (standard deviation) when compared to the ideal uptake rate for the HAPSITE® ER passive data. Ethylbenzene fell into this window when the published data were compared (Table 4). Similar to the benchtop system, 1,4-dioxane, benzene, ethylbenzene and hexane deviated significantly from

| Compound                 | No. of sites | Avg. uptake expt’l (mL/min) | Ideal uptake (mL/min) | Expt’l/Ideal (%) | Published uptake rate (mL/min) | Expt’l/Published (%) |
|--------------------------|-------------|-----------------------------|-----------------------|-----------------|-------------------------------|----------------------|
| 1,2,4-Trimethylbenzene   | 1           | 0.449 ± ND                  | 0.475                 | 94.6            | 0.482 [34]                    | 93.2                 |
| 1,3,5-Trimethylbenzene   | 1           | 0.452 ± ND                  | 0.474                 | 95.2            | 0.482 [34]                    | 93.7                 |
| 1,4-Dioxane              | 1           | 1.113 ± ND                  | 1.757                 | 63.3            | –                             | ND                   |
| 4-Ethyltoluene           | 2           | 0.510 ± 0.017               | 0.542                 | 94.0            | 0.450 [8]                     | 113.3                |
| Acetone                  | 8           | 0.795 ± 0.226               | 0.947                 | 83.9            | 0.710 [35]                    | 112.0                |
| Benzene                  | 2           | 1.999 ± 2.053               | 0.672                 | 297.3           | 0.407 [34]                    | 491.1                |
| Cyclohexane or 3- methylhexane | 1 | 0.450 ± ND                  | 0.599                 | 75.1            | 0.383/0.361 [8]               | 85.2/80.2 |
| Ethyl acetate            | 2           | 0.415 ± 0.225               | 0.558                 | 74.5            | 0.444 [8]                     | 93.5                 |
| Ethylbenzene             | 3           | 0.369 ± 0.216               | 0.573                 | 64.3            | 0.370 [35]                    | 99.6                 |
| Heptane                  | 2           | 0.415 ± 0.025               | 0.500                 | 83.0            | 0.430 [8]                     | 96.5                 |
| Isopropyl alcohol        | 6           | 0.565 ± 0.199               | 0.733                 | 77.1            | 0.550 [35]                    | 102.6                |
| m,p-Xylene               | 3           | 0.504 ± 0.104               | 0.535                 | 94.3            | 0.419 [34]                    | 120.4                |
| Methyl isobutyl ketone   | 1           | 0.443 ± ND                  | 0.573                 | 77.4            | 0.417 [34]                    | 106.3                |
| n-Hexane                 | 3           | 0.417 ± 0.091               | 0.611                 | 68.3            | 0.496 [33]                    | 84.2                 |
| o-xylene                 | 4           | 0.511 ± 0.144               | 0.665                 | 76.8            | 0.419 [34]                    | 121.9                |
| Toluene                  | 7           | 0.649 ± 0.340               | 0.665                 | 97.7            | 0.512 [36]                    | 126.8                |
the ideal uptake rate (~±50% or greater). The average of all experimental uptake rates (Table 4) were 113.4 ± 107.6% (standard deviation) when compared to the ideal uptake rate (Expt/Ideal (%)), and 123.6 ± 100.4% (Expt/I/Published (%)) when compared to published uptake rates (excluding benzene), showing much higher variability than the benchtop system, despite the fact that measurements for the triplicate values of mass on tube did not demonstrate high standard deviations (Table S4). The %RSD actually averaged lower for all HAPSITE® ER passive triplicates (9.3%) compared to the benchtop system (15.4%), indicating that replicate variability is probably not a major contributor. The values >30% of the ideal uptake rate were contributed by compounds known to be highly variable as described in the benchtop system analysis (toluene, hexane, benzene, 1,4-dioxane, styrene [37,38]) and/or present in single locations (methyl isobutyl ketone, styrene, 1,3,5-trimethylbenzene). Additionally, HAPSITE® appears to report a zero value for any concentration below ~0.1 ppbv in the processed data files. If the value of the trip blank is falsely lower than what should be reported, uptake rates will vary as described above. Most of the trip blank values for all compounds were in the 0.1–1.5 ppbv range, which lie below or in the area of the expected limit of detection of the instrument for many compounds. This characteristic is expected to be a contributor to the deviation of the HAPSITE® uptake rates from the ideal uptake rates, typically trending lower than expected. In fact, Cao and co-workers contend that the main concern with passive sampling is the blank level of the sorbent, which may vary depending on the conditioning level and storage conditions of individual tubes [22]. Further investigation into the tube artefact contribution, detection range for each compound, and employing multiple trip blanks may improve the data variability of passive sampling using the HAPSITE® ER. The effects of saturation and coeluting compounds (both known TO-15 compounds, and currently unidentified analytes from the field samples) are also likely confounding factors for HAPSITE® ER.

| Compound                  | No. of sites | Avg. uptake exptl (mL/min) | Ideal uptake (mL/min) | Exptl/Ideal (%) | Published uptake rate (mL/min) | Exptl/I/Published (%) |
|---------------------------|--------------|---------------------------|----------------------|----------------|-----------------------------|---------------------|
| 1,2,3-Trimethylbenzene    | 2            | 0.359 ± 0.114             | 0.474                | 75.8           | 0.482 [34]                  | 74.6                |
| 1,3,5-Trimethylbenzene    | 1            | 1.861 ± ND                | 0.474                | 392.6          | 0.482 [34]                  | 386.0               |
| 1,4-Dioxane               | 3            | 4.598 ± 3.756             | 1.757                | 261.7          | –                           | –                   |
| 4-Ethyltoluene            | 2            | 0.423 ± 0.321             | 0.542                | 78.0           | 0.450 [8]                   | 94.0                |
| Acetone                   | 7            | 0.449 ± 0.211             | 0.947                | 47.9           | 0.710 [35]                  | 63.2                |
| Benzene                   | 3            | 0.954 ± 0.410             | 0.672                | 141.9          | 0.407 [34]                  | 234.4               |
| Cyclohexane or 3-methylhexane | 1          | 0.472 ± ND                | 0.599                | 78.8           | 0.383/0.361 [8]             | 123.2/130.7         |
| Ethylbenzene              | 3            | 0.291 ± 0.025             | 0.573                | 50.9           | 0.370 [35]                  | 78.8                |
| Heptane                   | 3            | 0.208 ± 0.083             | 0.500                | 41.7           | 0.430 [8]                   | 48.4                |
| Isopropyl alcohol         | 6            | 0.537 ± 0.284             | 0.733                | 73.2           | 0.550 [35]                  | 97.6                |
| m,p-Xylene                | 5            | 0.258 ± 0.065             | 0.535                | 35.2           | 0.419 [34]                  | 61.6                |
| Methyl isobutyl ketone    | 1            | 1.056 ± ND                | 0.573                | 197.5          | 0.417 [34]                  | 253.3               |
| n-Hexane                  | 3            | 0.290 ± 0.155             | 0.611                | 50.7           | 0.496 [33]                  | 58.5                |
| α-Xylene                  | 4            | 0.190 ± 0.050             | 0.665                | 31.1           | 0.419 [34]                  | 43.5                |
| Styrene                   | 1            | 1.286 ± ND                | 0.542                | 237.0          | 0.470 [8]                   | 273.5               |
| Toluene                   | 6            | 0.332 ± 0.105             | 0.665                | 50.0           | 0.512 [36]                  | 64.9                |
data. A more comprehensive study is required to determine the characteristic behaviour for each compound on the HAPSITE® ER, particularly those which are commonly found at field sampling sites.

4. Conclusions

A small body of work is building towards demonstrating field-portable HAPSITE® detection capabilities for emergency responders, public health officials and law enforcement professionals [39,40,41,42]. However, only a minimal sampling of literature is available on the newest model, the HAPSITE® ER, which is the first generation of hardware available with a TD module shown to increase sensitivity compared to probe sampling [9,11]. The main goal of this work was to build on previous studies [9] evaluating the HAPSITE® ER TD module in controlled laboratory testing by extending functionality towards field samples. Carbon-based TD sorbents (SVI and Carbograph 4 from Radiello sampler) demonstrated a high background and substantial build-up of hydrocarbons which complicated data analysis and degraded the performance of the HAPSITE® ER system. Tenax TA TD tubes were used for field sampling in this study due to the relatively low artefact levels compared to the carbon-based sorbents. Generally, lower sensitivity, resolution and easier saturation were observed in the HAPSITE® ER compared to the benchtop system, consistent with the design limitations on a portable system. However, the HAPSITE® ER detected ~80% of the same compounds identified by the benchtop GC–MS system, and LESS-P time-series sampling showed that the trends observed over time in the HAPSITE® were similar to the profiles exhibited by a benchtop GC–MS system as well as a well-reported general VOC detector. Feasibility of using the LESS-P time-series sampler as a tool for automated active sampling throughout the study was demonstrated by showing the performance was similar to stand alone active sampling pumps, and helpful in evaluating passive sampling data. Furthermore, a method for passive sampling was validated on the benchtop GC–MS system where all compounds were within ±30% of either the ideal or published uptake rate values with the exception of a single sample. Extension of the same validated passive sampling methodology to HAPSITE® via replicates acquired at identical time points as the benchtop system data resulted in high variability of uptake rates from expected values. We believe that this variability is the product of instrument sensitivity to low levels of compounds in the trip blanks, used to background subtract data for uptake rate calculations. Future efforts are aimed at a complete characterisation of tube artefact and possible trip blank levels, as well as the effect of measuring multiple trip blanks for each location to obtain a more reproducible result within the HAPSITE®. In addition, further characterisation of the behaviour of individual compounds on the HAPSITE® ER compared to the benchtop system may allow for correction factors for more accurate quantitative measurements.

Generally, the combination of passive sampling and LESS-P active sampling is presented as a complimentary package that provides the benefits inherent to each technique without the burden of deploying a trained operator on-site during the entire sampling period. We believe that this body of work adds to the field of portable threat detection by providing trained personnel with further classification of the field sampling
proficiency of the HAPSITE® ER TD module to mitigate residual risk and ensure the proper operation of the HAPSITE® ER within its potential.

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