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Atmospheric Measurement Techniques
Discussions

Application of a mobile laboratory using a Selected-Ion Flow-Tube Mass Spectrometer (SIFT-MS) for characterisation of volatile organic compounds and atmospheric trace gases

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Abstract. The importance of emissions source types in urban areas has undergone significant changes over the past two decades. In particular, there has been a considerable reduction in emissions associated with road vehicles. Understanding the role played by different source sectors is important if effective air pollution control is to be achieved. Current atmospheric measurements are made at fixed monitoring sites, most of which do not include the measurement of volatile organic compounds (VOCs) and so our understanding of the temporal and spatial variation of pollutants is limited. Here we describe the application of a mobile laboratory using a selected-ion flow tube mass spectrometer (SIFT-MS) and other trace gas instrumentation to provide on-road, high spatial and temporal resolution measurements of CO_2, CH_4, VOCs and other trace gases. We then present data illustrating the potential of this platform for developing source characterisation methods that account for the similarity in correlation between species. Finally, we consider the benefits of high spatial and temporal resolution measurements in characterising different types of source, which would be difficult or impossible for single species studies.

1 Introduction

Air pollution in many urban areas is a major problem due to a myriad of emissions sources and dense populations leading to increased potential for human exposure. Among important air pollutants, volatile organic compounds (VOCs) are a class of pollutants that can significantly affect the chemistry of the atmosphere and human health. VOCs play an important role in atmospheric chemistry as they react rapidly with hydroxyl radicals and nitrogen oxides in the presence of sunlight to form products such as ozone (O_3) (Zhang et al., 2019) and peroxyacetyl nitrate (PAN) (Roberts, 1990; Roberts et al., 2003). O_3 can cause respiratory irritation (Nuvolone et al., 2018) and damage to ecosystems (Grulke and Heath, 2020). PAN has been shown to have adverse effects on plant growth and human health at high concentrations (Vyskocil et al., 1998). VOCs themselves can undergo gas-to-particle conversions to produce secondary organic aerosol (SOA) (Kourtchev et al., 2016). Also, some VOCs have direct health effects, many can cause acute irritations and damage to internal organs (Shuai et al., 2018) and chronic human exposure to benzene can induce haematological problems and cancer (Kampa and Castanas, 2008).

To combat air quality and health issues in urban areas, it is important that the composition and sources of VOCs are understood. Vehicular emissions of VOCs have historically been of central importance to issues such as ozone and secondary organic aerosol formation. But the composition and sources of these species in urban areas is highly complex and it is difficult to determine the role played by VOCs from road vehicles relative to other sources. While VOC emissions from vehicle exhausts have been aggressively reduced over the past few decades in Europe through the introduction of technologies such as three-way catalysts on gasoline vehicles, they still present an important source of emissions, accounting for 4% of total UK VOC emissions in 2017 (Lewis et al., 2020). Nevertheless, the reduction in vehicular emissions means it is likely that other sources of emissions, for example solvent use, have become more important. This is not reflected in current VOC measurements in the UK, which only measure 13 out of the 20 most significant VOCs (Lewis et al., 2020) due to them being set-up 30 years ago, when road transport was the dominant emissions source of VOCs. The relative contribution of different source types is highly complex and varies both spatially and temporally.

The current understanding of urban air pollution depends on hourly or daily measurements of atmospheric pollutants recorded at stationary monitoring sites. Fixed monitoring sites usually cover a limited amount of species and are unable to fully represent the temporal and spatial variations of pollutants in urban areas. To overcome this problem, mobile laboratories equipped with fast response instruments have been used for high spatial and temporal measurements of pollutants. Several studies have shown the use of on-road mobile laboratories for measurements of gaseous pollutants (Pirjola et al., 2004, 2014; Wu et al., 2013; Bush et al., 2015; Apte et al., 2017; Ars et al., 2020; Vojtisek-Lom et al., 2020) and particles (Pirjola et al., 2004, 2014; Bush et al., 2015; Saarikoski et al., 2017; Popovici et al., 2018; Alas et al., 2019). These studies highlight the use of mobile laboratories for the spatial mapping of pollutants and also mobile measurements such as vehicle plume chase studies. However, these studies focus on measurements of common pollutants such as $\mathrm{CO_2}$, $\mathrm{NO_x}$ and $\mathrm{CH_4}$, which only represent specific emissions sources in urban areas, such as transportation or gas leakages.

VOCs in urban areas are emitted from a much wider range of sources than road transport, including commercial premises such as hairdressers, dry cleaners and many others. To make sure these varied sources are better understood, the number of compounds measured has to be expanded and their spatial emissions in urban areas better resolved. The incorporation of mass spectrometers into a mobile laboratory allows for measurements of dominant VOC species at high spatial resolution.

Previous studies involving mobile measurements using mass spectrometry have used a proton-transfer-reaction mass spectrometer (PTR-MS). Airborne measurements carried out in London using PTR-MS were used to spatially measure benzene and toluene alongside other trace gases to identify dominant emissions sources in the area (Shaw et al., 2015). Early on-road measurements using PTR-MS in a mobile laboratory were carried out by the Aerodyne Research Institute (ARI) targeted acetaldehyde, benzene and toluene in vehicle plume chase experiments (Kolb et al., 2004; Herndon et al., 2005). More recent measurements carried out by the ARI (Knighton et al., 2012; Yacovitch et al., 2015), have focused on spatial mapping of petrochemical emissions and targeted styrene, benzene, toluene and 1,3-butadiene. VOC emissions from the oil and gas industry, such as benzene, toluene and other aromatics have also been investigated using PTR-MS in a mobile laboratory (Warneke et al., 2014; Edie et al., 2020). These studies show that mass spectrometry in a mobile laboratory enhances the applications of mobile measurements as the variety of compounds that can be measured is greatly expanded.

Previous studies of mobile measurements using PTR-MS were used to target specific compounds, usually emitted from an individual source. The work described here expands on previous studies by using a selected-ion flow-tube mass spectrometer (SIFT-MS) to target 13 compounds at approximately a 2.5 second time resolution. A comparison of SIFT-MS with PTR-MS concluded that SIFT-MS was preferable for analysing samples with complex compound mixtures and varying humidities (Lehnert et al., 2020), which is important for sampling of atmospheric air. SIFT-MS instruments are versatile and have been used to measure VOCs and trace gases across a wide range of applications such as breath analysis (Španěl and Smith, 2008; Castada and Barringer, 2019), consumer products (Langford et al., 2019; Yeoman et al., 2020) and ambient air quality (Prince et al., 2010; Crilley et al., 2019). These studies present successful measurements of varying VOC compounds and atmospheric trace gases, showing that SIFT-MS is suitable for mobile measurements in urban areas.

Here we will describe a mobile laboratory equipped with SIFT-MS and other trace gas instrumentation to provide high spatial and temporal resolution measurements of CO_2, CH_4, VOCs and other trace gases alongside meteorological and geospatial data. We also discuss the steps carried out to assure data quality of these mobile measurements. Examples of data are shown illustrating the potential of this platform for spatial mapping of pollutants and developing source characterisation methods that account for the similarity in correlation between species.

2 Experimental

2.1 Description of the mobile laboratory

The platform used for mobile measurements is the WACL Air Sampling Platform (WASP), which is a Nissan NV400SE L3H2 with interior dimensions of length 3450 mm, width 1650 mm, height 1750 mm and a payload of 1000 kg. The walls and floor in the rear of the van are overlaid and are fitted with 50 mm of insulation. The rear of the van contains an air conditioning system, which can be controlled from the driver cab and maintains the rear of the van at a constant temperature, overcoming any instrumental heating. The instruments are mounted and secured with aircraft-style L-tracks, which are built into the flooring and the ceiling. These allow for ratchet strapping of the SIFT-MS instrument and the instrument rack, where the computer system and the ultra-portable greenhouse gas analyser (UGGA) sit. The power in the van is supplied by two 12VDC 230Ah batteries that are charged whilst driving by a 240VAC inverter. Alternatively they can be charged when stationary by an external mains power port. The total battery life with the instruments and air conditioning running is about 2 hours whilst driving.

The front-facing sample inlet of the van sits at 2.25 m off the ground, at windscreen height of the WASP, and is made from a 6 m length of PTFE tubing with a diameter of 1/2 inch. Sample air is drawn from the outside through the sample inlet by a pump located in the rear at a flow rate of 40 SLPM, and is then fed into the instruments mounted in the rear. Real-time location of the WASP is recorded by a Garmin GPS 18x PC and a measurement of wind speed and direction is measured using a Gill 2D Ultrasonic Wind Sensor, both of which are fitted on the roof of the WASP at a height of 2.5 m. Data outputs of the meteorological sensors and the UGGA are stored on a computer system in the van and the outputs of the SIFT-MS are stored in the internal system of the instrument. Ethernet port connections between the computer system and the SIFT-MS mean that data for all of the instruments can be visualised in real-time in the driver cab whilst measurements are carried out. A schematic

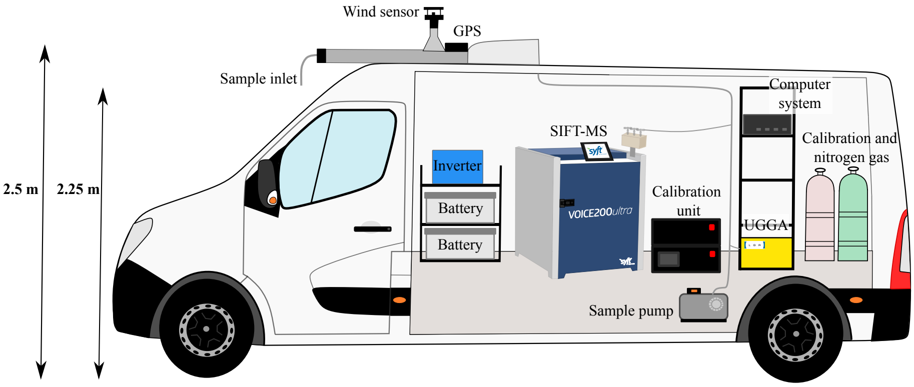

Figure 1. A graphic of the WACL Air Sampling Platform (WASP) used for mobile measurements.

Instrument	**Response time (t90 s)**	**Compounds**	**Power @ 240V (W)**
Voice200 ultra SIFT-MS	2.5	14 organic and inorganic gases	1100
Los Gatos Research UGGA	10	CH_4, CO_2, H_2O	340
Gill 2D Ultrasonic Wind Sensor	1	Wind speed and direction	120
Garmin GPS 18x PC	1	Vehicle speed, direction and location	70

Table 1. Details of the WASP instrumentation.

of the WASP is shown in Figure 1 and further details of the instrumentation are provided in Table 1. Note that the instrument fit in the WASP is flexible and is easily altered due to the relatively large size and payload that the WASP can accommodate.

2.2 Instrumentation

2.2.1 Selected-Ion Flow Tube Mass Spectrometer (SIFT-MS)

A Voice200 ultra SIFT-MS manufactured by Syft Technologies (Christchurch, New Zealand), was used to quantify VOCs and inorganic gases. The SIFT-MS principles of operation are discussed in detail elsewhere (Smith and Spanel, 1996; Smith and Španěl, 2005), but a brief outline is included here. The instrument consists of a switchable reagent ion source capable of rapidly switching between multiple reagent ions: H_3O^+, NO^+ and O_2^+, which are generated in a microwave plasma ion source, from a mixture of air and water at a pressure of approximately 440 mTorr. The reagent ions are then extracted into the upstream quadrupole chamber maintained at a pressure of approximately 5×10^{-4} Torr, using a 70 $\mathrm{L\,s^{-1}}$ turbo-molecular pump, and then pass through an array of electrostatic lenses and the upstream quadrupole mass filter. Those not rejected by the mass filter are injected into the flow tube where they are thermalized in a stream of nitrogen prior to selectively ionising target analytes. The product ions then flow into the downstream quadrupole mass filter and the secondary electron multiplier detector, where

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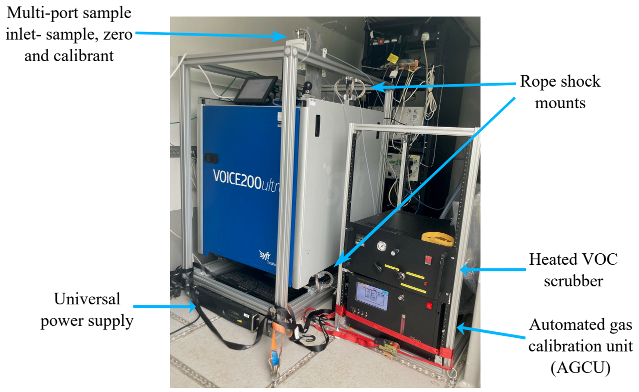

Figure 2. The Voice200 ultra SIFT-MS with in-house built multi-port inlet and heated VOC scrubber, alongside the custom built automated gas calibration unit (AGCU).

the ions are separated by their mass-to-charge ratios (m/z) and the ion counts are measured. The mixing ratios of analyte compounds in the flow tube are calculated using the ion-molecule reactions that take place within the SIFT-MS using Equation 1, where $[A]$ is the analyte mixing ratio, γ is the instrument calibration factor, $[P^+]$ is the product ion, $[R^+]$ is the reagent ion, t_r is the reaction time and k is the rate constant.

$$[A] = \gamma \times \frac{[P^+]}{[R^+] t_r k} \quad (1)$$

Figure 2 shows the SIFT-MS inside the WASP, with an in-house multi-port sample inlet capable of autonomously selecting between sample, zero and calibrant gases using the instrument software (Labsyft 1.6). The multi-port inlet uses 3 PTFE internally coated solenoid valves (12VDC, Gems). The SIFT-MS is suspended in a rope-shock mounted rack, which reduces 3-dimensional vibration the instrument is subjected to during mobile measurements. Whilst driving, the SIFT-MS was operated using a flow tube pressure of 460 mTorr, a nitrogen carrier gas (Research grade, BOC) with a flow rate of 0.6 Torr $\mathrm{L\,s^{-1}}$ and a sample flow rate of 100 SCCM. On the right of Figure 2 is a custom built automated gas calibration unit (AGCU) and a heated VOC zero air generator. The heated VOC scrubber consists of palladium-coated alumina pellets heated to 380°C which produces zero air whilst maintaining the humidity of the sample gas. Mass flow controllers (MFCs) (Alicat) in the AGCU measure and control the flows of diluent zero air and the VOC standard (1ppm certified National Physics Laboratory, UK), and allow for controlled dilution ratios in the ppt-ppm range. Automated step-wise changes to the dilution ratios are made, which generates a multi-point calibration curve for routine external calibration of the SIFT-MS. Figure 3 shows a simplified schematic of the internal gas flow paths in the AGCU and calibration of the compounds is discussed further in Section 3.1.

The SIFT-MS was used to measure 13 different VOCs and inorganic gases during mobile measurements around the city of York, UK. The compounds targeted with the SIFT-MS were chosen to cover a range of emissions sources to help with source apportionment analysis. The compounds measured by the SIFT-MS and the corresponding reagent ions, molecular masses and product ion chemical formulae are shown in Table 2. Only a single product ion was chosen for each compound to minimise

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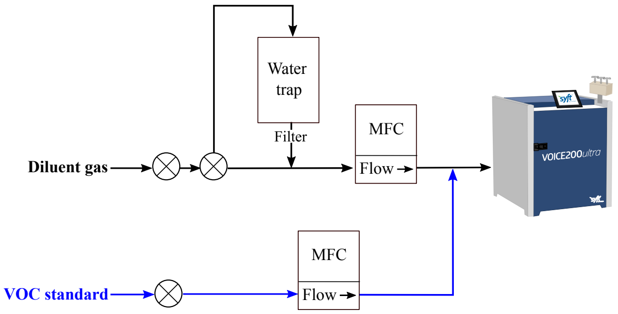

Figure 3. Schematic of the internal gas flow paths in the automated gas calibration unit (AGCU).

Reagent Ion	**Compound**	**MM**[1]	**Product Ion**
O_2^+	Nitrogen Dioxide	46	NO_2^+
NO^+	Isoprene/Furan	68	$C_5H_8^+$
	Benzene	78	$C_6H_6^+$
	Acetone	88	$(CH_3)_2NO^+$
	Toluene	92	$C_6H_5CH_3^+$
	m-Xylene (C_2-alkyl benzenes)	106	$C_6H_4(CH_3)_2^+$
	Trimethylbenzene (C_3-alkyl benzenes)	120	$C_6H_3(CH_3)_3^+$
	Total Monoterpenes	136	$C_{10}H_{16}^+$
H_3O^+	Methanol	33	CH_3OH^+
	Acetaldehyde	45	CH_3CHO^+
	Ethanol	47	$C_2H_5OH^+$
	Nitrous Acid	48	HNO_2^+
	Butadiene	54	$(C_2H_3)_2^+$

[1] Molar Mass in $\mathrm{g\,mol^{-1}}$

Table 2. The compounds measured by the SIFT-MS and their corresponding reagent ions, molecular masses and product ion chemical formulae.

cycle time and to maximise the number of compounds that could be measured. The sampling method of the SIFT-MS used during the mobile measurements has a 2.5 second cycle time and a 90 ms dwell time.

2.2.2 Ultra-portable Greenhouse Gas Analyser (UGGA)

A Los Gatos Research Ultra-Portable Greenhouse Gas Analyser (UGGA) was used to quantify carbon dioxide (CO_2), methane (CH_4) and water vapour (H_2O). The UGGA instrument uses off-axis integrated-cavity output spectroscopy (off-axis ICOS) to quantify mixing ratios of gaseous species, which has been described in detail previously (Gupta, 2012), but a brief description is included here. Off-axis ICOS uses a laser and an optical cavity in an off-axis configuration (Tan and Long, 2010), which enhances the measured absorption of light by a sample by creating an effective optical path length of several thousands of meters. The measured absorption spectra is recorded and when this is combined with the measured gas temperature and pressure in the cell, effective path length and known line strength, it can be used to determine a quantitative measurement of mixing ratio. The UGGA was used at a 1 Hz time resolution, with a response time of 10 seconds. The precision of the UGGA is < 2 ppb for CH_4, < 300 ppb for CO_2 and < 100 ppm for H_2O. The measurement range of the UGGA is 0.01-100 ppm, 1-20,000 ppm and 500-70,000 ppm for CH_4, CO_2 and H_2O respectively.

2.3 Measurement location

In the summer of 2020, the WASP was used to make measurements around the city of York, UK. Figure 4 shows the measurement route that was driven by the WASP. The route starts at the University of York and then passes into and around the inner ring road of the city and has a total distance of 15.1 kilometers. York has a population of approximately 200,000 people and air pollution in the city is thought to be dominated by vehicle emissions, especially around the inner ring road due to congestion. The measurement route in York was designed to capture a variety of potential emissions sources, such as hairdressers, beauty salons, dry cleaners and eateries, to determine dominant sources. Measurements were carried out for a total of 10 days, between the 30th June 2020 and the 23rd July 2020, during periods of dry weather between the hours of 10:00 and 17:00. The route was driven 31 times in total and the dates and times of each drive are included in the appendix (Table A1). It should be noted that these measurements were made under reduced economic and traffic activity due to Covid-19, which could affect both the concentration and detection of different VOC species.

3 Results

3.1 Calibration and data quality assurance

To ensure accurate measurements, the SIFT-MS was externally calibrated for several compounds using the automated gas calibration unit (AGCU, discussed in Section 2.2.1) and a 1 ppm 14-component VOC gas standard (National Physical Laboratory). These compounds include: acetone, benzene, butadiene, ethanol, isoprene, methanol, m-xylene (C_2-alkyl benzenes), toluene and trimethlybenzene (C_3-alkyl benzenes). Figure 5 shows the multi-point calibration of these compounds that were carried out at the start and end of each day (pre- and post-drive). The calibrations were performed using VOC mixing ratios of 10, 5, 1 and 0 ppb and each of the mixing ratio steps lasted for 3 minutes. Figure 5 shows good agreement between the pre- and post-drive calibrations and also for the left- and right-hand calibration steps. The right-hand steps of the post-drive

Figure 4. Measurement route driven by the WASP for mobile measurements around York (from © Google Maps).

calibrations were used to generate calibration curves for each compound, which were applied to the mixing ratio data obtained during mobile measurements. Additional data from the calibrations, including the coefficient of determination (R^2) values and ion counts per second per ppb (icps ppb $^{-1}$) are included in Table 3. For the compounds where an external calibrant was not available (acetaldehyde, total monoterpenes, NO_2 and HONO), the mixing ratios were dependent on the compound specific rate constant and daily generated instrument calibration factor (ICF, Equation 1). The daily instrument ICF was derived using a 2ppm external gas standard to validate the mass dependent ion transmission of the instrument, details of the gas standard are included in the appendix in Table B1. Table 3 shows the limit of detection, which was calculated using 3 times the standard deviation (σ) of measurements made when sampling from zero air or from nitrogen gas. For each compound there is a limit of detection averaged over 1 minute and 2.5 seconds, which is the amount of time calibration steps were averaged to calculate the slope and the cycle time for the SIFT-MS scanning method respectively.

To ensure that the VOC mixing ratios measured by the SIFT-MS were independent of instrumental noise, instrument dark counts using the H_3O^+ reagent ion, (m/z 25) were routinely measured during mobile operation, as is shown in figure 6 along with benzene concentration and counts per second (cps) for the benzene product ion (m/z 78). As the figure shows, there was typically minimal instrument noise (0-40 cps for m/z 25) observed during a 45 minute mobile measurement period. Furthermore, significant increases in the mixing ratio of benzene corresponded with large increases in m/z 78 (> 40 cps), therefore showing that these were due to real increases in ambient concentrations. Periods of elevated noise (>100 cps) were routinely removed to improve measurement accuracy. During the 10 days of measurements, a total of approximately 26.5 hours of measurements were made and only 3 minutes of the measurements had to be removed due to excess instrument noise, which may have been due to extreme vibrations or movement when driving. Movement and vibration effects on instrument noise whilst driving were further investigated by sampling the SIFT-MS instrument on nitrogen only, which is shown in the appendix

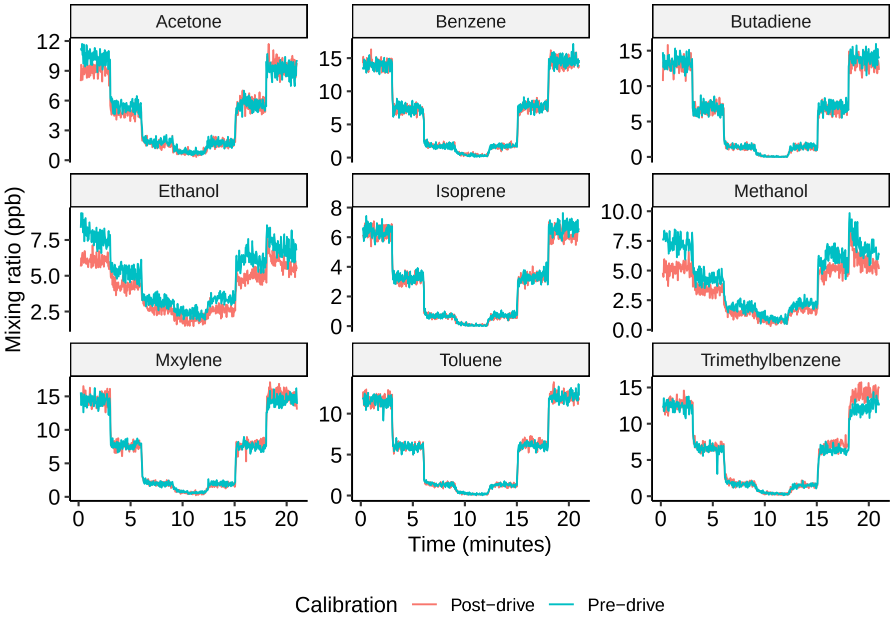

Figure 5. Multi-point calibration for VOC gas standard compounds over 10, 5, 1 and 0 ppb. The blue line shows the calibrations performed pre-drive and the pink line shows the calibration performed post-drive.

(Figure A1). The run did not show any significant changes in instrument noise whilst driving and there were no increases in compound mixing ratios, therefore showing that the driving motion had only a minimal effect on measurement accuracy.

3.2 Spatial distribution of VOCs and inorganic gases

To spatially map the measurements made by the WASP mobile laboratory the data points were "snapped" to the nearest 30 metre segment of road using GPS data (Apte et al., 2017). The points in each 30 metre segment of road were then aggregated to give the median value. The median was selected as it would represent a realistic picture of air pollution on the measurement route and remove any biases that may occur from directly sampling vehicle exhausts. Table 4 contains a statistical summary of the measured compounds, showing the 5th percentile, the median and the 95th percentile of mixing ratios. The majority of the measurements (88.7 %) made by the SIFT-MS significantly exceeded the limits of detection (LOD) calculated for each compound (Table 3) and the 30 metre aggregated median concentrations used for spatial mapping were on average a factor of 15 times higher than the 1 minute average-calculated limit of detection. This provides confidence that the observed compound peaks correspond to real increases in ambient concentrations. The data used to calculate the limit of detection over 1 minute was obtained using 22 data points and the average number of data points per 30 metre section of road was 78, so this further confirms the confidence in the SIFT-MS measurements. The typical spatial distance for the 2.5 seconds recorded by the SIFT-

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Species	**Calibration data**		**Limit of detection**	
	R^2	**cps ppb^{-1}**	**1 minute**	**2.5 seconds**
Acetone	0.98	133	0.05	0.27
Benzene	0.99	215	0.05	0.40
Butadiene	0.99	149	0.02	0.11
Ethanol	0.88	232	0.07	0.22
Isoprene	0.99	205	0.01	0.06
Methanol	0.81	358	0.03	0.21
m-Xylene (C_2-alkyl benzenes)	0.99	473	0.07	0.38
Toluene	0.99	463	0.02	0.13
Trimethylbenzene (C_3-alkyl benzenes)	0.99	449	0.03	0.26
Acetaldehyde	-	-	0.06	0.41
Monoterpenes	-	-	0.02	0.11
Nitrogen Dioxide	-	-	0.88	2.48
Nitrous Acid	-	-	0.26	0.31

Table 3. The coefficient of determination (R^2) and the ion counts per second per ppb (cps ppb^{-1}) calculated from the calibrations. The limit of detection (LOD) of compounds measured by the SIFT-MS (in ppb) averaged over 1 minute and 2.5 seconds (cycle time). Compounds in the upper part of the table were externally calibrated.

MS was 14 metres as the average speed of the mobile laboratory was 20 kilometers per hour during measurements around York.

Figure 7 shows the CO_2 and benzene mixing ratios recorded along the York measurement route, as examples of spatial mapping of compounds using the WASP. The plot shows low mixing ratios on Heslington Lane (blue at the bottom of the map, which represents less than 420 ppm and 0.5 ppb for CO_2 and benzene respectively). The mixing ratios increase around the city centre, where there is higher congestion and emissions may be dominated by vehicles. CO_2 mixing ratios increase to above 450 ppm and elevated levels are seen at road junctions, which is expected as vehicles are a dominant source of CO_2 emissions. Benzene mixing ratios increase to above 0.9 ppb and also shows elevated levels at road junctions. The plots also show some correlation of hotspots (orange and red parts of the maps), especially at junctions with traffic lights where vehicles would be idling.

3.2.1 Spatial correlation mapping

Spatial mapping is useful as it can highlight hotspots of VOCs and trace gases, but they are insufficient in determining and separating emissions sources in urban areas. A method for source apportionment is to consider the correlation between many

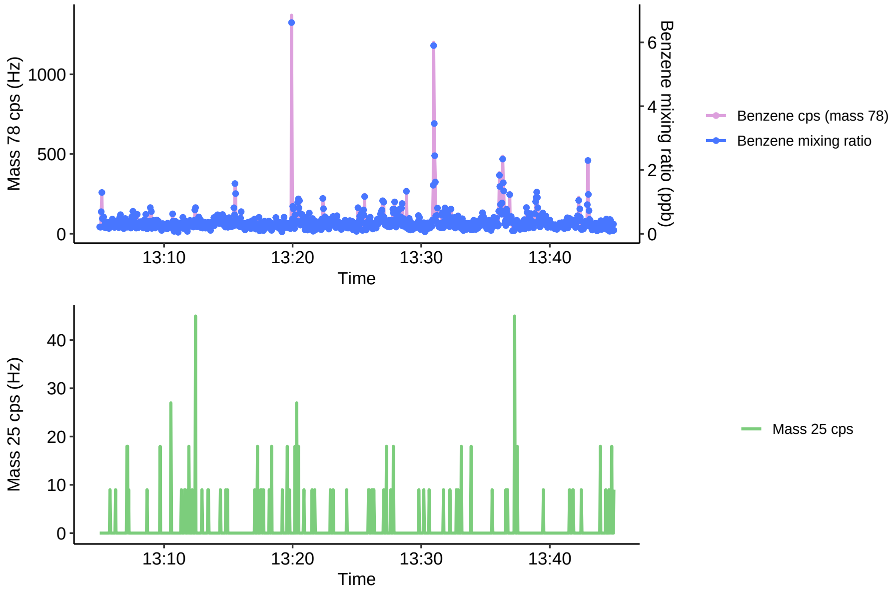

Figure 6. Example of instrument noise during mobile measurements. The blue points show the mixing ratio of benzene and the pink line shows the corresponding counts per second for the benzene ion counts per second (mass 78). The green line shows the variation of mass 25 during mobile measurements, which does not contain any periods of elevated noise.

species over particular roads or areas that measurements have been made. Areas that contain different emissions sources should have different correlations, for example an area dominated by vehicle emissions should show strong correlations with VOCs associated with vehicles such as benzene and toluene and these correlations will be different to other sources, such as evaporative emission of solvents. Figure 8 shows the Spearman correlation of compounds for all of the measurements made by the SIFT-MS and UGGA. Hierarchical clustering is applied to the correlation matrices to group species that are most similar to one another. For example, benzene, toluene, C_2-alkyl benzenes and C_3- alkyl benzenes, appear next to each other in Figure 8 and show a clear cluster, indicating similar behaviour, likely related to their common source from gasoline evaporation. There are other clusters of VOCs which are indicative of different source types - for example commons solvents such as acetone, ethanol and methanol are clustered together in linked urban emissions likely not relating to road transport. Other trace gases associated with tailpipe emissions also appear in a single cluster, e.g NO_2, CO_2 and butadiene. In the future, the aim is to apply this method to smaller spatial scales, where it is expected that spatially varying patterns of correlation may enable specific emissions sources to be identified, potentially at the individual building scale.

3.3 Conclusions and future applications

We have presented some examples of the use of the WASP mobile laboratory with the SIFT-MS that highlight the importance of these measurements. We have demonstrated how the incorporation of the SIFT-MS into the WASP expands the number and

Species	**5th percentile**	**Median**	**95th percentile**
Acetaldehyde	1.70	2.26	3.67
Acetone	0.45	0.83	1.61
Benzene	0.23	0.56	1.42
Butadiene	0.00	0.03	0.22
Ethanol	1.02	1.46	2.78
Isoprene	0.01	0.06	0.14
Methanol	0.66	1.11	1.92
Monoterpenes	0.02	0.09	0.24
m-Xylene (C_2-alkyl benzenes)	0.46	0.89	2.44
Nitrogen Dioxide	5.01	9.39	24.78
Nitrous Acid	0.01	0.09	0.26
Toluene	0.09	0.26	1.21
Trimethylbenzene (C_3-alkyl benzenes)	0.08	0.26	0.87
CH_4	1.84	1.86	1.90
CO_2	400.55	411.26	455.43

Table 4. Summary of measurements made by the SIFT-MS (top of the table, in ppb) and the UGGA (bottom of the table, in ppm) during measurements around York.

variety of compounds measured, meaning that a greater number of emissions sources can be investigated. The SIFT-MS has been used to perform high temporal and spatial measurements of multiple VOCs in an urban area, building on previous work by mobile laboratories which focused on a smaller number of pollutants. The spatial mapping examples highlight the use of the SIFT-MS in the WASP to reveal hotspots of pollutants, which can be further investigated by repeat or stationary measurements at that area. Also, we have demonstrated the spatial correlation method, which shows correlations of compounds dependent on their emissions sources. This method will be further developed in the future for source apportionment and characterisation of different source types, which can be used to increase understanding of air pollution in urban areas and for future emissions regulations.

Future applications for the WASP and the SIFT-MS include upgrading or including new instruments and the design of the WASP is suited to this as in the rear there is a 5-shelf instrument rack, which currently only holds the UGGA and the computer system. The UGGA will be upgraded to a faster-response version, which will allow for more precise measurements of CO_2 in urban areas and will also be useful for further investigation of vehicle emissions. There will also be an addition of a UV photometric O_3 instrument to monitor the effect of VOCs on air pollution and an ICAD NO_x instrument, which will make for good comparison to the SIFT-MS measured NO_2. Future applications will be to return to measurements around York once activities return to normal, as the current COVID-19 situation will have had an effect on air pollution during the measurement

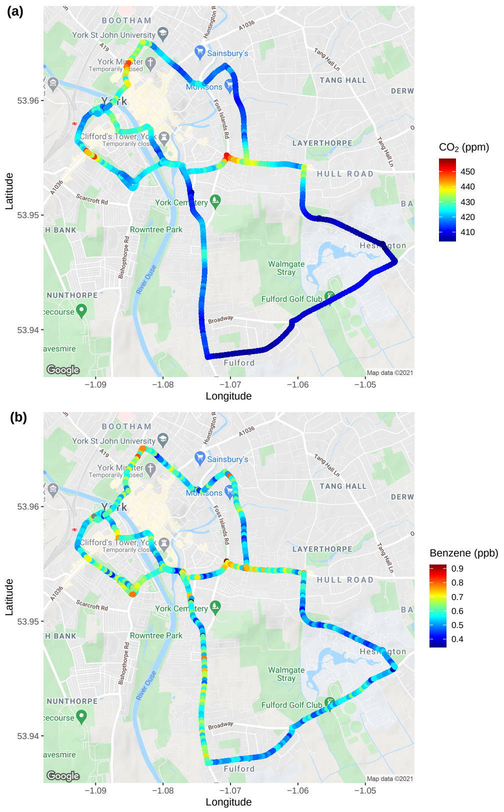

Figure 7. Spatial mapping of median values of (a) CO$_2$ (ppm) and (b) Benzene (ppb) from mobile measurements around York (from © Google Maps).

period due to decreased traffic and closed facilities. The upgrades discussed here also highlight the potential use of the WASP to investigate vehicle emissions as the use of the SIFT-MS means that measurement of currently unregulated compounds can be performed. Future experiments with the WASP and the SIFT-MS to investigate vehicle emissions include plume chase, where the WASP would follow a vehicle and sample the exhaust for a period of time, and point sampling, using the WASP alongside remote sensing instruments by the side of the road and sampling vehicles as they pass. Mobile measurements can also be used alongside this as they are useful for determining the importance of vehicle emissions in urban areas.

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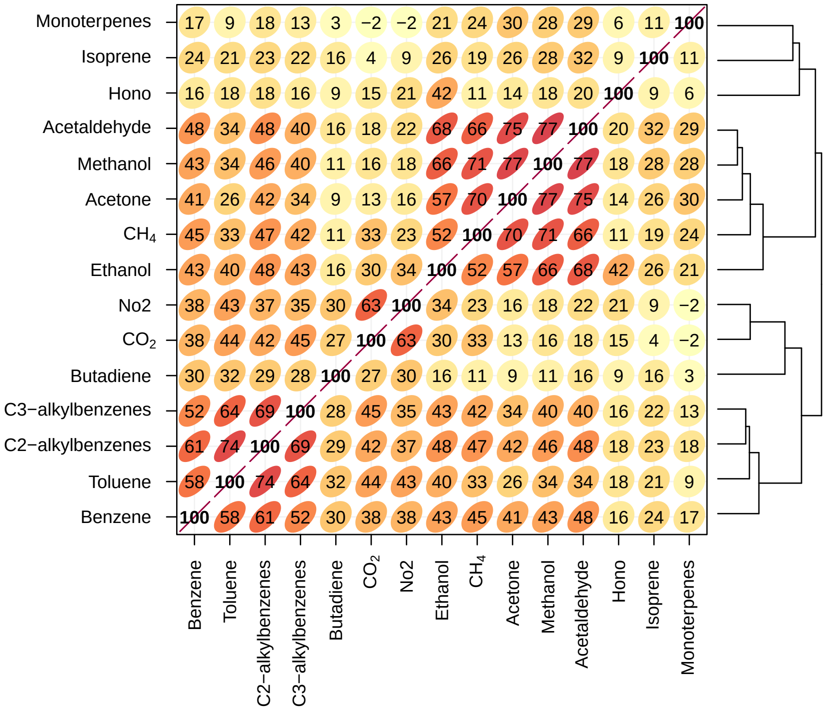

	Benzene	Toluene	C2−alkylbenzenes	C3−alkylbenzenes	Butadiene	CO_2	No2	Ethanol	CH_4	Acetone	Methanol	Acetaldehyde	Hono	Isoprene	Monoterpenes
Monoterpenes	17	9	18	13	3	−2	−2	21	24	30	28	29	6	11	100
Isoprene	24	21	23	22	16	4	9	26	19	26	28	32	9	100	11
Hono	16	18	18	16	9	15	21	42	11	14	18	20	100	9	6
Acetaldehyde	48	34	48	40	16	18	22	68	66	75	77	100	20	32	29
Methanol	43	34	46	40	11	16	18	66	71	77	100	77	18	28	28
Acetone	41	26	42	34	9	13	16	57	70	100	77	75	14	26	30
CH_4	45	33	47	42	11	33	23	52	100	70	71	66	11	19	24
Ethanol	43	40	48	43	16	30	34	100	52	57	66	68	42	26	21
No2	38	43	37	35	30	63	100	34	23	16	18	22	21	9	−2
CO_2	38	44	42	45	27	100	63	30	33	13	16	18	15	4	−2
Butadiene	30	32	29	28	100	27	30	16	11	9	11	16	9	16	3
C3−alkylbenzenes	52	64	69	100	28	45	35	43	42	34	40	40	16	22	13
C2−alkylbenzenes	61	74	100	69	29	42	37	48	47	42	46	48	18	23	18
Toluene	58	100	74	64	32	44	43	40	33	26	34	34	18	21	9
Benzene	100	58	61	52	30	38	38	43	45	41	43	48	16	24	17

Figure 8. Spearman correlation of the compounds measured using the WASP and the SIFT-MS during measurements in York. Note that hierarchical clustering is applied to the correlation matrices to group species that are most similar to one another.

Appendix A

Date	No. of routes	Time of routes
30th June 2020	2	13:03–13:42; 13:54–14:37
1st July 2020	3	11:18–11:57; 12:47–13:33; 13:58–14:40
2nd July 2020	3	13:20–14:07; 14:17–15:02; 15:35–16:13
3rd July 2020	4	10:58–11:44; 12:05–12:52; 13:29–14:21; 14:35–15:20
6th July 2020	3	11:40–12:19; 12:41–13:22; 13:42–14:25
8th July 2020	3	11:51–12:35; 13:21–14:07; 14:17–14:59
9th July 2020	4	11:26–12:10; 12:28–13:10; 13:38–14:25; 14:50–15:40
20th July 2020	3	12:00–12:48; 13:00–13:44; 14:32–15:13
21st July 2020	3	11:12–12:41; 12:42–13:30; 13:51–14:45
23rd July 2020	2	11:02–11:47; 12:28–13:17; 13:41–14:32

Table A1. Details of the number of times the route was driven on each day and the times that the drives took place.

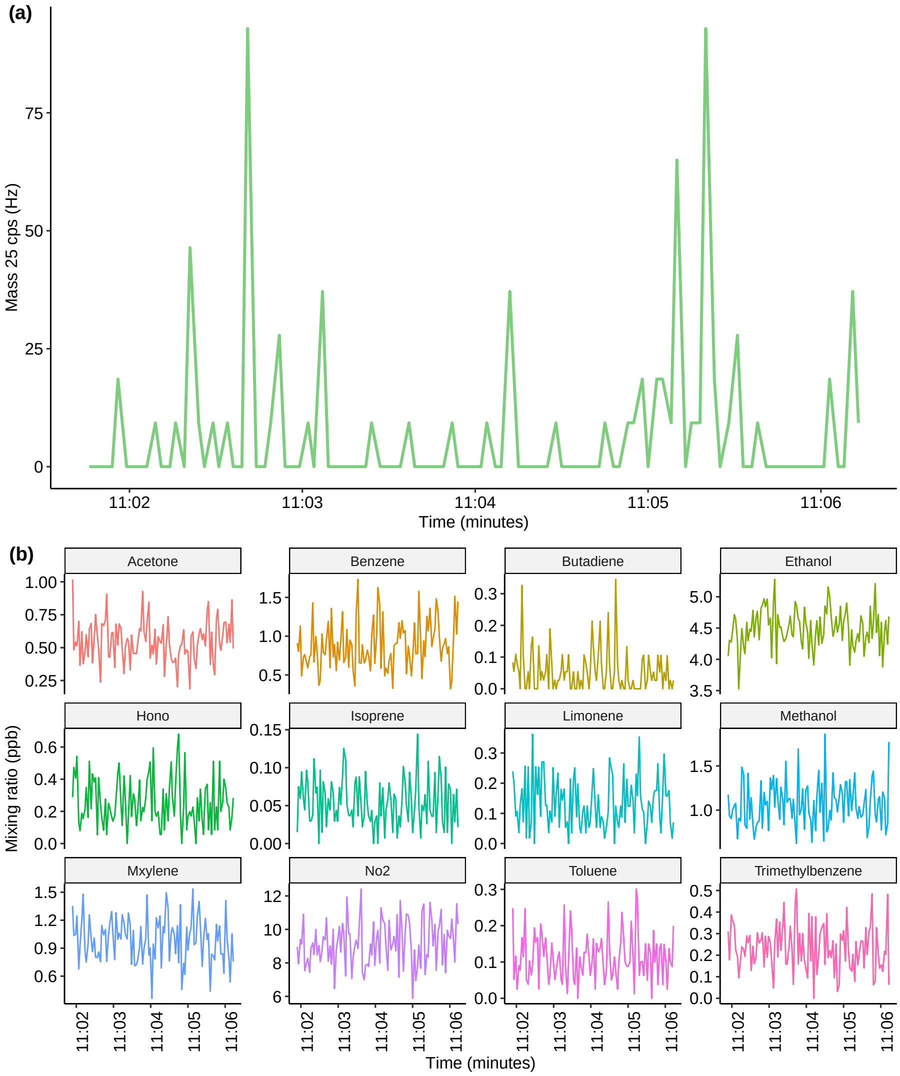

Figure A1. (a) Counts per second of mass 25 which represents instrument noise and (b) mixing ratios of the compounds during a nitrogen-only mobile measurement.

Species	**MM**[1]
Ethylene	28
Isobutane	58
Benzene	78
Toluene	92
Ethylbenzene	106
Tetrafluorobenzene	150
Hexafluorobenzene	186
Octafluorotoluene	236

[1] Molar Mass in $\mathrm{g\,mol^{-1}}$

Table B1. Compounds and their molecular masses in the Syft 2ppm standard gas, which was used to generate the daily instrument calibration factor (ICF).

Author contributions. RW and MS designed and carried out the measurements. AC, JH and SY designed and built the mobile laboratory. RW prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare they have no conflict of interest.

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