Emissions of intermediate-volatility and semi-volatile organic compounds from domestic fuels used in Delhi, India

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Abstract

Biomass burning emits significant quantities of intermediate-volatility and semi-volatile volatile organic compounds (I/SVOCs) in a complex mixture, probably containing many thousands of chemical species. These components are significantly more toxic and have poorly understood chemistry compared to volatile organic compounds routinely quantified in ambient air; however, analysis of I/SVOCs presents a difficult analytical challenge.

The gases and particles emitted during the test combustion of a range of domestic solid fuels collected from across Delhi were sampled and analysed. Organic aerosol was collected onto Teflon (PTFE) filters and residual low-volatility gases were adsorbed to the surface of solid-phase extraction (SPE) disks. A new method relying on accelerated solvent extraction (ASE) coupled to comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-ToF-MS) was developed. This highly sensitive and powerful analytical technique enabled over 3000 peaks from I/SVOC species with unique mass spectra to be detected. 15-100 % of gas-phase emissions and 7-100 % of particle-phase emissions were characterised. The method was analysed for suitability to make quantitative measurements of I/SVOCs using SPE disks. Analysis of SPE disks indicated phenolic and furanic compounds were important to gas-phase I/SVOC emissions and levoglucosan to the aerosol phase. Gas-and particle-phase emission factors for 21 polycyclic aromatic hydrocarbons (PAHs) were derived, including 16 compounds listed by the US EPA as priority pollutants. Gas-phase emissions were dominated by smaller PAHs. New emission factors were measured (mg kg^{-1}) for PAHs from combustion of cow dung cake (615), municipal solid waste (1022), crop residue (747), sawdust (1236), fuel wood (247), charcoal (151) and liquefied petroleum gas (56).

The results of this study indicate that cow dung cake and municipal solid waste burning are likely to be significant PAH sources and further study is required to quantify their impact, alongside emissions from fuel wood burning.

1. Introduction

Biomass burning is one of the most important global sources of trace gases and particles to the atmosphere (Simoneit, 2002; Chen et al., 2017; Andreae, 2019), with residential solid fuel combustion and wildfires emitting significant quantities of organic matter (Streets et al., 2003; Barboni et al., 2010; Chen et al., 2017; Liu et al., 2017; Kiely et al., 2019). Emissions of volatile organic compounds (VOCs) and particulate matter (PM) from biomass burning are of interest due to their detrimental impact on air quality. VOCs react to form ozone and secondary organic aerosol (SOA). Intermediate-volatility and semi-volatile organic compounds (I/SVOCs) are also a significant emission from biomass burning (Stockwell et al., 2015; Koss et al., 2018). I/SVOCs are an important class of air pollutant due to their contribution to aerosol formation (Bruns et al., 2016; Lu et al., 2018). I/SVOC emissions are poorly, if at all, represented in regional inventories and chemical transport models. Consequently, their impacts to air quality in developing regions, where solid fuel combustion is a dominant fuel source, are not well understood. Recent studies have shown that the inclusion of I/SVOCs leads to better agreement between modelled and measured values (Ots et al., 2016; Woody et al., 2016; Jathar et al., 2017; Murphy et al., 2017). Global I/SVOC emissions to the atmosphere from biomass burning were estimated to be ~ 54 Tg yr^{-1} from 2005-2008 (Hodzic et al., 2016), with I/SVOCs contributing in the range 8-15.5 Tg yr^{-1} to SOA (Cubison et al., 2011; Hodzic et al., 2016).

SOA formation from biomass burning emissions is poorly understood globally. Important factors include the formation of less volatile products from the oxidation of NMVOCs which partition into the aerosol phase, heterogeneous oxidation of aerosol phase organics, as well as plume dilution followed by evaporation and further gas-phase oxidation (Lim et al., 2019). Ahern et al. (2019) showed that for burning of biomass needles, biogenic VOCs were the dominant class of SOA precursor. This study also found that for wiregrass, furans were the most important SOA precursor. Bruns et al. (2016) showed that SOA formation from combustion of beech fuel wood was dominated by 22 compounds, with phenol, naphthalene and benzene contributing up to 80 % of the observed SOA. SOA formation from biomass burning has been shown to be significant in laboratory studies, with SOA yields from the burning of western U.S. fuels reported to be 24±4 % after 6 h and 56±9 % after 4 d (Lim et al., 2019). However, the effect of atmospheric of aging on I/SVOCs still remains poorly understood (Liu et al., 2017; Decker et al., 2019; Sengupta et al., 2020).

Better understanding of the quantity and composition of I/SVOCs from biomass burning is needed to evaluate their impact on the atmosphere. This is a difficult analytical task, not well suited to conventional analysis with gas chromatography coupled to mass spectrometry (GC-MS). The reason for this is because of the exponential growth of potential isomers with carbon number, which results in a large number of coeluting peaks (Goldstein and Galbally, 2007). The high resolution of two-dimensional gas chromatography (GC×GC) has been demonstrated as an ideal technique to overcome this issue when analysing complex organic samples in both gas (Lewis et al., 2000; Stewart et al., 2021) and particle phases (Hamilton et al., 2004; Lyu et al., 2019). The application of GC×GC to biomass burning emissions has shown hundreds of gaseous I/SVOCs using adsorption-thermal desorption cartridges (Hatch et al., 2015) or solid phase extraction (SPE) disks (Hatch et al., 2018). GC×GC has also been used to analyse the particle phase with samples collected onto PTFE or quartz filters (Hatch et al., 2018; Jen et al., 2019), with the latter study quantifying 149 organic compounds which accounted for 4-37 % of the total mass of organic carbon. The process used by Hatch et al. (2018) demonstrated high recoveries of non-polar species from PTFE filters, with lower recoveries from SPE disks. This study highlighted the need for further evaluation of samples collected onto PTFE filters and SPE disks, ideally improving the method to remove undesirable steps such as trimethylsilylation derivatisation, the use of pyridine and centrifuging which led to high evaporative losses. The need to develop improved sampling and measurement techniques for I/SVOCs has also been highlighted. This is because these species often do not transmit quantitatively through the inlet and tubing when measured using online gas-phase techniques (Pagonis et al., 2017).

Residential combustion, agricultural crop residue burning and open municipal solid waste burning in the developing world are large, poorly characterised pollution sources with the potential to have a significant impact on local and regional air quality, impacting human health (Venkataraman et al., 2005; Jain et al., 2014; Wiedinmyer et al., 2014). Hazardous indoor air pollution from combustion of solid fuels has been shown to be the most important factor from a range of 67 environmental and lifestyle risk factors causing disease in South Asia (Lim et al., 2012). Despite this, nearly 76 % of rural Indian households depend on solid biomass for their cooking needs (Gordon et al., 2018), using biofuels such as fuel wood, cow dung cake and crop residue. Combustion often takes place indoors, without efficient emission controls, which significantly increases the mean household concentration of pollutants, particularly particulate matter with a diameter less than 2.5 μm ($PM_{2.5}$). The health effects from this are significant, with an estimated 3.8 million premature deaths globally due to inefficient indoor combustion from cooking (World Health Organisation, 2018).

Few detailed studies have been conducted examining the composition of I/SVOC emissions from solid-fuel combustion sources from South Asia. Sheesley et al. (2003) used solvent extraction followed by GC-MS to produce emission factors and examine molecular markers from combustion of coconut leaves, rice straw, cow dung cake, biomass briquettes and jackfruit branches collected from Bangladesh. A more recent study extracted $PM_{2.5}$ samples followed by analysis with GC-MS from motorcycles, diesel- and gasoline-generators, agricultural pumps, municipal solid waste burning, cooking fires using fuel wood and cow dung cake, crop residue burning and brick kilns in Nepal (Jayarathne et al., 2018). Lack of knowledge regarding major pollution sources hinders our ability to predict air quality, but also the development of effective mitigation strategies for air pollution which leads to health impacts ranging from respiratory illness to premature death (Brunekreef and Holgate, 2002). This results in many people living with high levels of air pollution (Cohen et al., 2005; Lelieveld et al., 2015) and 13 Indian cities ranking amongst the top 20 cities in the world with the highest levels of ambient $PM_{2.5}$ pollution, based on available data (Gordon et al., 2018).

In this study we develop a more efficient extraction step for the SPE/PTFE technique developed by Hatch et al. (2018), using accelerated solvent extraction into ethyl acetate, which showed high recoveries of non-polar I/SVOCs. Domestic fuels characteristic to Northern India were gathered and organic I/SVOC samples collected onto SPE disks and PTFE filters from controlled laboratory combustion experiments of a variety of fuel woods, cow dung cakes, municipal solid waste samples, crop residues, charcoal and liquefied petroleum gas (LPG). The samples were extracted using this new technique and analysed with GC×GC coupled to time-of-flight mass spectrometry (GC×GC-ToF-MS). Molecular markers were examined from different fuels and the limitations for quantification of the extremely complex samples using a mass spectrometer were examined.

2. Methods

2.1 Fuel collection and burning facility

The state of Delhi was gridded (0.05×0.05) and a diverse range of fuel types collected from across the state (see Figure 1). Fuels were stored in a manner akin to local practices prior to combustion, to ensure that the moisture content of fuels were similar to those burnt across the state. A range of solid biomass fuels were collected which included 17 fuel wood species, cow dung cake, charcoal and sawdust (see Table 1). Three crop residue fuel types were collected and consisted of dried stems from vegetable plants such as cabbage (*Brassica spp*) and aubergines (*Solanum melongena*) as well as coconut husk (*Cocos nucifera)*. Municipal solid waste was collected from Bhalaswa, Ghazipur and Okhla landfill sites. A low-cost LPG stove was also purchased to allow direct comparison to other combustion sources.

Fuels were burnt at the CSIR-National Physical Laboratory (NPL), New Delhi, under controlled conditions using a combustion-dilution chamber that has been well described previously (Venkataraman et al., 2002; Saud et al., 2011; Saud et al., 2012; Singh et al., 2013). In summary, 200 g of dry fuel was rapidly heated to spontaneous ignition with emissions driven into a hood and up a flue by convection to allow enough dilution, cooling, and residence time to achieve the quenching of typical indoor environments. This process was designed to replicate the immediate condensational processes that occur in smoke particles approximately 5-20 mins after emission, yet prior to photochemistry which may change composition (Akagi et al., 2011). A low volume sampler (Vayubodhan Pvt.Ltd) was used to collect particulates and low volatility gases passing from the top of the flue through a chamber with a flow rate of 46.7 L min^{-1}. As detailed in Table 1, samples were collected from 30 fuels alongside 8 blank measurements (see the Supplementary Information S1 for an example burn and filter sample). Prior to sample collection, SPE disks (Resprep, C_{18}, 47 mm) were prewashed with 2 × 5 mL acetone (Fisher Scientific analytical reagent grade) and 1 × 5 mL methanol (Sigma-Aldrich HPLC grade), then packed in foil and sealed in airtight bags. Samples were collected onto a PTFE filter (Cole-Parmer, 47 mm, 1.2 μm pore size) placed on top of an SPE disk in a filter holder (Cole-Parmer, 47 mm, PFA) for 30 mins at a flow rate of 6 L min^{-1}, maintained by a mass flow controller (Alicat 0-20 SLM) connected to a pump. Samples were removed from the filter holder immediately after the experiment, wrapped in foil, placed into an airtight bag and stored at – 20 ^{o}C. Samples were transported to the UK for analysis using an insulated container containing dry ice via. air freight and stored at – 20 ^{o}C for around 2 months prior to analysis.

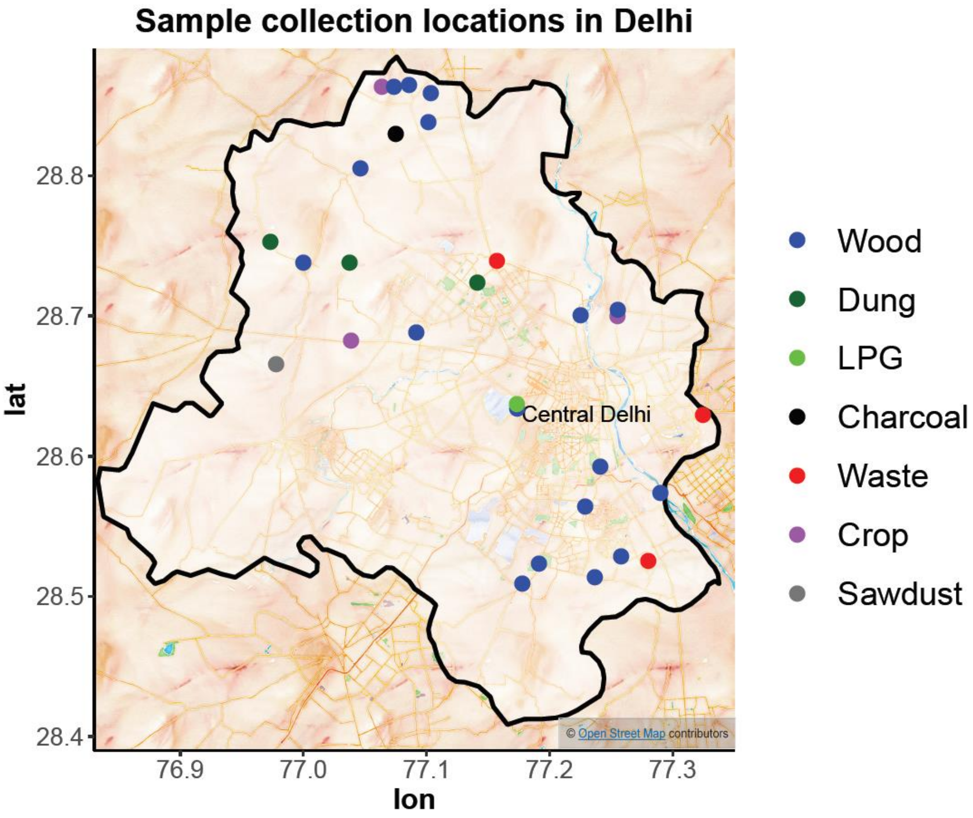

Figure 1. Locations across Delhi used for the local surveys into fuel usage and collection. Map tiles by Stamen Design. Data by © OpenStreetMap contributors 2020. Distributed under a Creative Commons BY-SA License.

Table 1. Types of fuel sampled where *n* = number of burns of a specific fuel type, SPE and PTFE = number of blank corrected peaks detected on SPE disks and PTFE filters, respectively.

Fuel woods	***n***	**SPE**	**PTFE**	**Other**	***n***	**SPE**	**PTFE**
Plywood	1	201	516	Cow dung cake	3	1235	1562
Azadirachta indica	1	557	862	*Cocos nucifera*	1	620	1197
Morus spp	1	805	1132	Charcoal	1	439	280
Shorea spp	1	296	360	Sawdust	1	1112	1486
Ficus religiosa	1	500	712	Waste	3	948	1182
Syzygium spp	1	661	571	LPG	1	-	-
Ficus spp	1	306	292	Blank	8	-	-
Vachellia spp	1	697	800	Cow dung cake mix	1	931	1241
Dalbergia sissoo	1	501	611	*Brassica spp*	1	652	536
Ricinus spp	1	424	271	*Solanum melongena*	1	314	559
Holoptelea spp	1	274	324				
Saraca indica	1	525	484				
Pithecellobium spp	1	525	235				
Eucalyptus spp	1	238	144				
Melia azedarach	1	444	213				
Prosopis spp	1	248	144				
Mangifera indica	1	387	628				

2.2 Extraction

SPE disks and PTFE filters were spiked with an internal standard (50 μL at 20 μg mL^{-1}) containing 6 deuterated PAHs (1,4-Dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}; EPA 8270 Semivolatile Internal Standard Mix, 2000 μg mL^{-1} in DCM) to result in a final internal standard concentration of 1 μg mL^{-1} in solution. The solvent from the internal standard was allowed to evaporate and then SPE disks and PTFE filters were cut and extracted into ethyl acetate (EtOAc) using accelerated solvent extraction (ASE 350, Dionex, ThermoFisher Scientific). Extractions were performed at 80 ^{o}C and 1500 psi for three 5 min cycles. After each cycle, the cell was purged for 60 seconds into a sample collection vial. Samples were then reduced from 15 mL to 0.90 mL over a low flow of N_2 in an ice bath over a period of 6-8 hours (Farren et al., 2015). Samples were then pipetted (glass Pasteur) to sample vials (Sigma-Aldrich, amber glass, 1.5 mL), with ASE vials rinsed with 2 × 50 μL washes of EtOAC, then added to the sample vial and sealed (Agilent 12 mm cap, PTFE/silicone/PTFE). The mass of the sample vial and cap for each sample was measured before and after to determine the exact volume of solvent in each sample. Extracts were frozen prior to analysis to reduce evaporative losses.

2.3 Organic composition analysis

GC×GC-ToF-MS: PTFE samples were analysed using GC×GC-ToF-MS (Leco Pegasus BT 4D) using a splitless injection (1 μL injection, 4mm taper focus liner, SHG 560302). The primary dimension column was a RXI-5SilMS (Restek, 30 m × 0.25 μm × 0.25 mm) connected to a second column of RXI-17SilMS (Restek, 0.25 μm × 0.25 mm, 0.17 m primary GC oven, 0.1 m modulator, 1.42 m secondary oven, 0.31 m transfer line) with a He flow of 1.4 mL min^{-1}. The primary oven was held at 40 ^{o}C for 1 min then ramped at 3 ^{o}C min^{-1} to 322 ^{o}C where it was held for 3 min. The secondary oven was held at 62 ^{o}C for 1 min then ramped at 3.2 ^{o}C min^{-1} to 190 ^{o}C after which it was ramped at 3.6 ^{o}C min^{-1} to 325 ^{o}C and held for 19.5 mins. The inlet was held at 280 ^{o}C and the transfer line at 340 ^{o}C. A 5 s cryogenic modulation was used with a 1.5 s hot pulse and 1 s cool time between stages. Using two separate wash vials, the syringe (10 μL Gerstel) was cleaned prior to injection with two cycles of 3 × 5 μL washes in EtOAc and rinsed post injection with two cycles of 2 × 5 μL washes in EtOAc. Samples with high concentrations of levoglucosan were reanalysed using a faster method, injected split (75:1 and 125:1) with the primary oven held at 40 ^{o}C for 1 min, then ramped at 10 ^{o}C min^{-1} to 220 ^{o}C. The secondary oven was held at 62 ^{o}C for 1 min and then ramped at 10 ^{o}C min^{-1} to 245 ^{o}C.

SPE samples were injected split (10:1) and analysed with a shorter analysis time with the primary oven held at 40 °C for 1 min then ramped at 3 °C min^{-1} to 202 °C where it was held for 4 secs. The secondary oven was held at 62 °C for 1 min then ramped at 3.2 °C min^{-1} to 235 °C. A 75:1 split injection was used for quantitation of concentrations outside of the detector response range for furanics, phenolics, benzaldehydes, naphthalenes and benzonitrile. Peaks were assigned through comparison of retention times with known standards and comparison with the National Institute of Standards and Technology (NIST) mass spectral library. Peaks with no genuine standard available were tentatively identified if the NIST library similarity was > 700. This provides an indication of how similar the mass spectra obtained was to the database mass spectra for the peak, with more details given in Stein, (2011). Peaks with a hit > 900 reflect an excellent match, 800-900 a good match and 700-800 a fair match (Stein, 2011). The uncertainty in this approach has been shown to be low for peaks of hits > 800, with the probability of incorrect identification being around 30 % for hits between 800-900 and 14 % for matches above 900 (Worton et al., 2017). Integration was carried out within the ChromaTOF 5.0 software package (Leko, 2019). Calibration was performed using a 6-point calibration using either a linear or second-order polynomial fit covering the ranges 0.1-2.5 μg ml^{-1} (splitless), 0.5-15 μg ml^{-1} (10:1 split), 15-400 μg ml^{-1} (75:1 split) and 400-800 μg ml^{-1} (125:1 split). Eight blank measurements were made at the beginning and end of the day by passing air from the chamber (6 L min^{-1} for 30 mins) through the filter holder containing PTFE filters and SPE disks (see the Supplementary Information S2 for examples of blank chromatograms). Blank corrections were applied by calculating the average blank value for each compound with blank samples collected using the same sample collection parameters as real samples before and after the relevant burning experiments.

PTR-ToF-MS: Online measurements of naphthalene, methylnaphthalenes and dimethylnaphthalenes were made using a proton transfer reaction-time of flight-mass spectrometer PTR-ToF-MS (PTR 8000; Ionicon Analytik, Innsbruck) and assigned as masses 129.058, 143.08 and 157.097, respectively. Additional details of the PTR-ToF-MS from Physical Research Laboratory (PRL), Ahmedabad used in this study are given in previous papers (Sahu and Saxena, 2015; Sahu et al., 2016). A ¼ inch OD PFA sample line ran from the top of the flue to the instrument which was housed in an air-conditioned laboratory with a sample flow rate of 4.3 L min^{-1}. The sample air was diluted either 5 or 6.25 times into zero air, generated by passing ambient air (1 L min^{-1}) through a heated platinum filament at 550 °C, before entering the instrument with an inlet flow of 250 ml min^{-1}. The instrument was operated with a reduced electric field strength (*E*/*N*, where *N* is the buffer gas density and *E* is the electric field strength) of 120 Td. The drift tube temperature was 60 °C with a pressure of 2.3 mbar and 560 V applied across it.

Calibrations of the PTR-ToF-MS were performed twice a week using a gas calibration unit (Ionicon Analytik, Innsbruck). The calibration gas (Apel-Riemer Environmental Inc., Miami) contained 18 compounds: methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulphide, isoprene, methacrolein, methyl vinyl ketone, 2-butanol, benzene, toluene, 2-hexanone, *m*-xylene, heptanal, α-pinene, 3-octanone and 3-octanol at 1000 ppb (±5 %) and β-caryophyllene at 500 ppb (±5 %). This standard was dynamically diluted into zero air to provide a 6-point calibration. The normalised sensitivity (ncps/ppbv) was then determined for all masses using a transmission curve derived from these standard compounds (Taipale et al., 2008).

Mass calibration and peak fitting of the PTR-ToF-MS data were performed using PTRwid software (Holzinger, 2015). Count rates (cps) of each mass spectral peak were normalised to the primary ion (H_3O^+) and water cluster $(H_3O.H_2O)^+$ peaks and mixing ratios were then determined for each mass using the normalised sensitivity (ncps). Where compounds known to fragment in the PTR-ToF-MS were identified, the mixing ratio of these species was calculated by summing parent ion and fragment ion mixing ratios. Before each burning study, ambient air was sampled to provide a background for the measurement.

2.4 Quantification of recovery and breakthrough

Standards were used for 136 species (see the Supplementary Information S3) including two commercially available standard mixes containing 33 alkanes (C_7-C_{40} saturated alkane standard, certified 1000 μg m^{-1} in hexane, Sigma Aldrich 49452-U) and 64 semi volatiles (EPA CLP Semivolatile Calibration Mix, 1000 μg mL^{-1} in DCM:benzene 3:1, Sigma Aldrich 506508). Further standards were produced in-house, by dissolving high quality standards (> 99 % purity), for a range of additional species also found in samples including nitrogen containing VOCs, furanics, alkyl-substituted monoaromatics, oxygenated aromatics, ketones, aldehydes, methoxy phenols, aromatic acids, PAHs and levoglucosan. Stock solutions of around 1000 μg mL^{-1} were prepared by dissolving 0.01 g into 10 mL EtOAc. Polar components, such as levoglucosan, were dissolved into methanol (MeOH) for stock solutions and those not soluble at room temperature were heated and pipetted using hot pipette tips to make quantitative dilutions.

Six separate PTFE filters and SPE disks were spiked with the standard solution containing 136 compounds (50 μL at 20 μg mL^{-1}), extracted and analysed. Recovery levels were calculated by comparing the signal to direct injection of the diluted standards to the GC×GC-ToF-MS. The recoveries are shown in the Supplementary Information S3. SPE disks showed poor recoveries (S_{rec}) of *n*-nonane to *n*-tridecane and C_2 substituted monoaromatics, likely due to volatilisation of these more-volatile components. Poorer recoveries were also observed of nitroanilines and levoglucosan. Non-polar species showed good recoveries, with high recoveries of C_{14}-C_{20} alkanes, furanics, phenolics, chlorobenzenes and PAHs. PTFE filters demonstrated high recoveries (P_{rec}) of PAHs with more than three rings in their structure (81.6-100 %). Recoveries were low, or zero, for volatile components with boiling points < 200 °C, indicating no retention, which is consistent with the method being well-suited to target the aerosol phase. The recoveries of non-polar species into EtOAc from SPE disks were higher than those reported into MeOH (Hatch et al., 2018).

To quantify the additional effect of breakthrough during sampling, tests were conducted for SPE disks to examine the retention of components adsorbed to their surface when subject to an air flow equivalent to the sample volume. SPE disks were spiked with the calibration mixture containing 96 compounds of interest (50 μL at 20 μg mL^{-1}, $n = 4$) and subject to a purified air flow of 6 L min^{-1} for 30 mins. The samples were extracted and analysed, and the signal compared with 4 × 50 μL spikes directly into 0.95 mL EtOAc. Figure 2 shows the relative enhancement of unpurged over purged samples. For more volatile components a value greater than zero was observed (Figure 2), which indicated breakthrough of the most volatile components and indicated good retention of components with a boiling point of around 225 °C (see the Supplementary Information S4 for breakthrough tests). Concentrations measured for *n*-alkanes on SPE disks were also compared with concurrent measurements made during burning experiments using online thermal-desorption two-dimensional gas chromatography coupled to a flame ionisation detector. The measured concentrations for *n*-alkanes from *n*-nonane to *n*-dodecane were compared using both techniques, with measured concentrations similar for *n*-undecane/*n*-dodecane (bp = 216 °C, see the Supplementary Information S5) but not the smaller alkanes. This was interpreted to indicate little breakthrough for components less volatile than *n*-dodecane. These findings are in line with the US EPA certified methods for Resprep SPE disks (525.1, 506, 550.1, and 549.1), when used to quantitatively analyse drinking water, which show their suitability for quantitative measurement of species with a molecular weight of around naphthalene/acenaphthylene (bp = 218-280 °C). These results indicate that for more volatile species with boiling points below 250 °C, SPE disks can only be used to make qualitative measurements at these sample times and flow rates. Such qualitative information is highly complementary to quantitative measurements using other, less specific, techniques, such as PTR-ToF-MS, where it can assist in identification of the contributors to *m*/*z* ions.

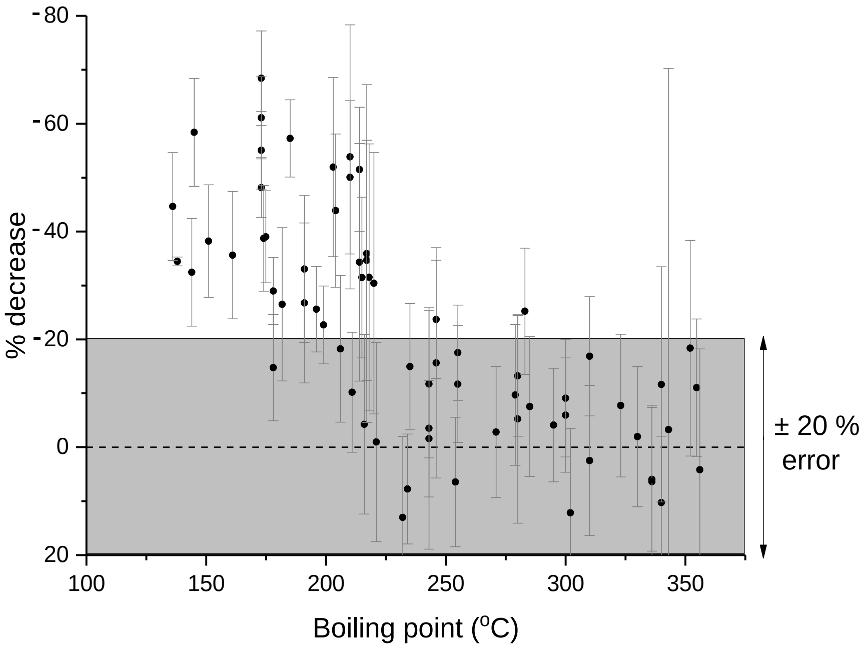

Figure 2. Relative reduction of purged over unpurged samples, presented as a percentage decrease of purged to unpurged signal. The standard deviation of replicate measurements is indicated by the error bars.

3. Results

3.1 Chromatography

Figure 3 shows chromatograms from I/SVOCs in the gas and particle phase from burning a cow dung cake sample collected from SPE disks and PTFE filters during a whole 30-minute burn, after passing through a dilution and cooling chamber. The saturation concentration C_i^* at 298 K is provided as an alternative x-axis and has been calculated for each *n*-alkane, *i*, using:

$$C_i^* = \frac{M_i 10^6 \zeta_i P_{\mathrm{L,i}}^{\mathrm{o}}}{760RT} \qquad \text{E1}$$

where M_i = molecular weight of VOC *i* (g mol^{-1}), ζ_i = activity coefficient of VOC *i* in the condensed phase (assumed to be 1), $P^{o}_{L,i}$ = liquid vapour pressure of VOC *i* in Torr, *R* = gas constant (8.206×10^{-5} m^3 atm mol^{-1} K^{-1}) and *T* = temperature in Kelvin (Lu et al., 2018). The constant 760 Torr has been used to convert between units of atm and Torr where 1 atm = 760 Torr. $P^{o}_{L,i}$ values have been calculated from EPA Estimation Programme Interface Suite data at 298 K (EPA, 2012). The SPE disks showed 1297 peaks with unique mass spectra and captured gaseous VOCs and I/VOCs with C^* ~ 1×10^{8} - 5×10^{2} µg m^{-3} at 298 K. The largest peaks were from alkanes, 1-alkenes, limonene, phenolics, substituted naphthalenes, furanics and substituted pyridines. The PTFE filters captured 1617 I/SVOCs and low and extremely low volatility VOCs (L/ELVOC) with unique mass spectra present in the aerosol phase from C^* ~ 5×10^{6}-1×10^{-5} µg m^{-3} at 298 K. A transition can be seen in the two chromatograms from the gas to the aerosol phase. Species with a saturation vapour concentration less than 5×10^{4} µg m^{-3} at 298 K were predominantly in the aerosol phase after passing though the dilution chamber. A large region of more polar components was present in the I/SVOC region from C^* 5×10^{4}-5×10^{0} µg m^{-3} at 298 K and contained sugar pyrolysis products and highly substituted aromatics such as those with ketone, ether and di and trisubstituted phenol substituents. Many alkanes, from *n*-octadecane to *n*-triatriacontane were present, mainly in the SVOC region. The LVOC region was dominated by a series of sterols and stanols. GC×GC provided extremely high resolution to allow deconvolution of complex samples. The insert in Figure 3 shows how the complexity of the SPE chromatogram can be further resolved by looking at a single ion chromatogram, for example *m*/*z* = 57, which highlighted aliphatic non-polar peaks, with large peaks for alkanes from *n*-nonane to *n*-nonadecane.

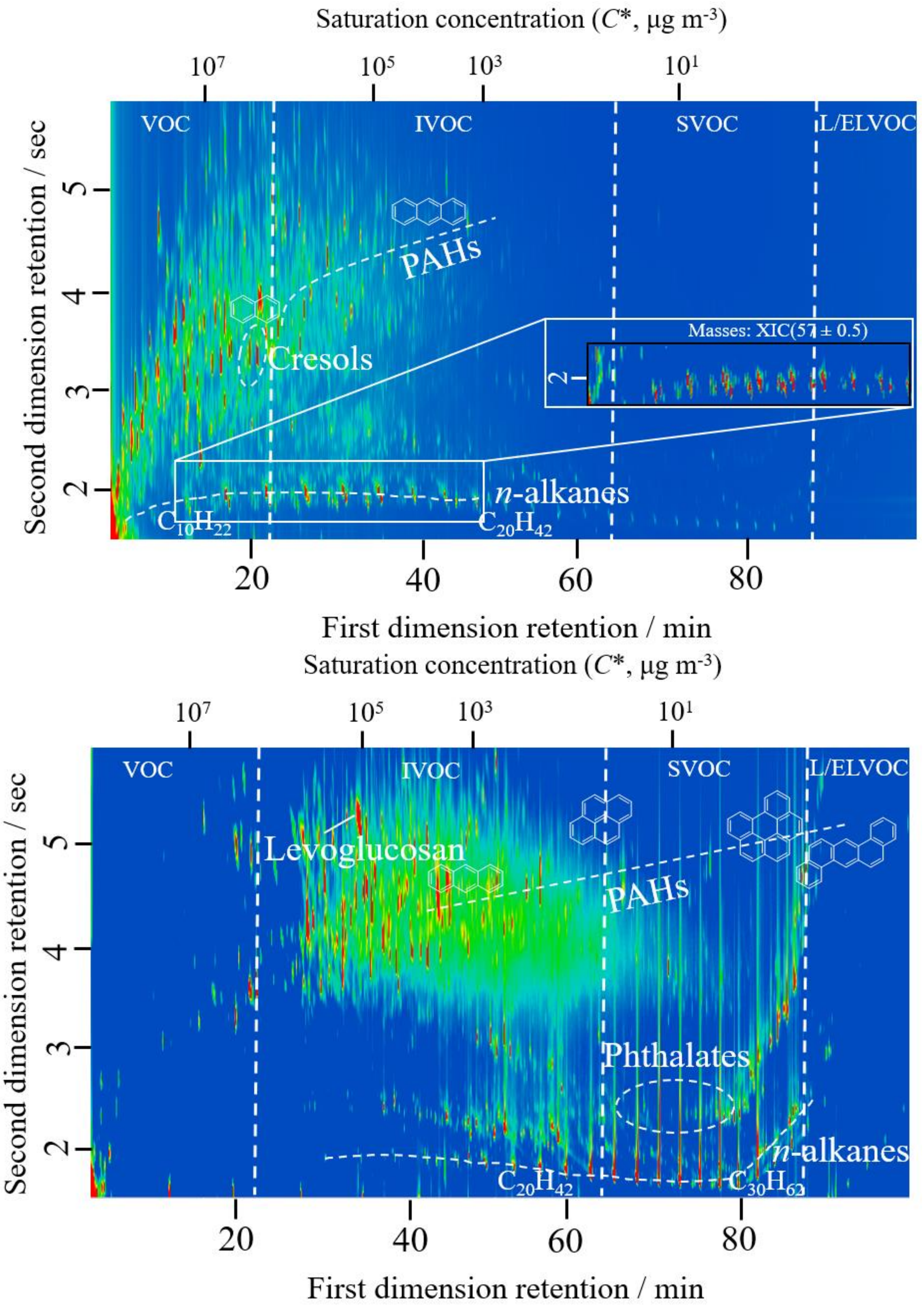

Figure 3. Chromatogram of SPE (top) and PTFE (bottom) extracted samples from the entire burn of cow dung cake. n-Alkane and PAH series are marked on the chromatograms. The saturation concentration scale matches the n-alkane series. See the Supplementary Information S6 for a detailed compositional breakdown by functionality and phase.

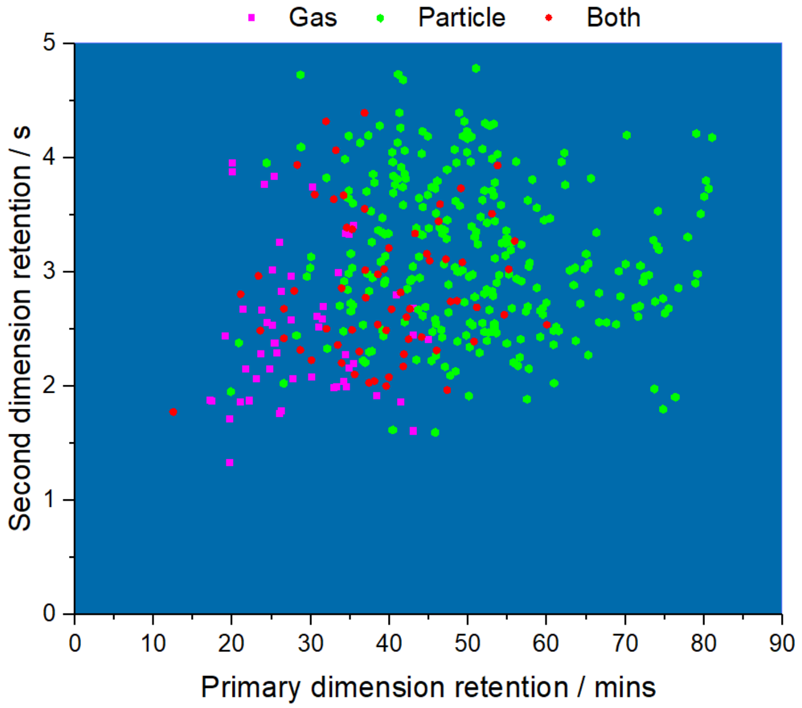

Figure 4. Gas and particle phase composition of PAH emissions from burning cow dung cake.

Figure 4 shows that the complexity of emissions was vast, with almost 400 PAHs forming a group towards the top centre to right of the chromatogram. The most abundant calibrated PAH in the gas phase was naphthalene, followed by methyl and dimethyl naphthalene isomers. A range of methyl, dimethyl, tri and tetramethyl naphthalenes as well as ethyl, propyl, butyl and methyl propyl isomers were detected. Naphthalene isomers substituted with aldehydes, carboxylic acids and nitriles were also released. Biphenyl and a range of methyl, dimethyl and ethyl biphenyls were also released. A range of other PAHs such as acenaphthylene, fluorene, azulene, quinoline, chamazulene, benzophenone, stilbene and benzofurans along with their alkyl substituted isomers were also in the gas phase. A large amount of highly substituted, larger PAHs with more than 3 aromatics rings in their structure were present in the aerosol phase.

Other peaks present on SPE disks and PTFE filters (SPE/PTFE) included alkenes (84/43), mostly towards the bottom of the chromatogram, along with a row of non-cyclic aliphatic (23/35) and cyclic aliphatic species (25/6) (see the Supplementary Information S6 for a figure containing all peaks). Above was a row of substituted aromatics (103/35), carboxylic acids (68/118) and sterols/stanols (1/63) as well as oxygenated hydrocarbons containing a range of ether, alcohol and aldehyde functionalities (229/234). Peaks were also present from oxygenated aromatics (106/145), phenolics (54/122), substituted benzoic acids (15/27), furanic species (72/42), monoterpenes (2/1) and sulphur containing species (13/4).

A wide array of nitrogen containing VOCs were present in the cow dung cake samples, with peaks on SPE disks and PTFE filters (SPE/PTFE) from pyridines and pyrazines (43/35), amines (47/28), amides (38/37), nitriles (42/31), 6-membered heterocycles (13/14), 5-membered heterocycles including aromatics such as pyrroles as well as pyrazolines and pyrrolidines (50/45), 4-membered heterocycles (3/3), 3-membered heterocycles (4/1), nitrogen containing PAHs (14/24), imidazoles (9/12), imines (3/1) and azoles (23/10). The large amount of nitrogen containing VOCs are likely formed from the volatilisation and decomposition of nitrogen-containing compounds within the cow dung cake, such as free amino acids, pyrroline, pyridine and chlorophyll (Leppalahti and Koljonen, 1995; Burling et al., 2010; Ren and Zhao, 2015). Nitrogen containing VOCs are of concern because they can be extremely toxic (Ramírez et al., 2014; Farren et al., 2015) and amines in particular can change the hydrological cycle by leading to the creation of new particles (Smith et al., 2008; Kirkby et al., 2011; Yu and Luo, 2014) which act as cloud condensation nuclei (Kerminen et al., 2005; Laaksonen et al., 2005; Sotiropoulou et al., 2006).

Figure 5 shows a comparison of organic aerosol composition observed from different fuel types (LPG, fuel wood, sawdust and municipal solid waste). The measured emissions had very different compositions, reflecting the variability of organic components produced from different fuel types (see the Supplementary Information S7 and S8 for species observed from different sample types on SPE disks and PTFE filters). Sawdust, municipal solid waste and cow dung cake (shown in Figure 3) emitted a wide range and complexity of species. Particle phase emissions from LPG burning were minimal, with most peaks from the internal standard or contaminants in the solvent. Fuel wood combustion released more organic components into the aerosol phase, with the majority being IVOCs with $C^* \sim 1.2\times10^5$-7×10^1 µg m^{-3} at 298 K. The largest peak belonged to levoglucosan, with other peaks from monoaromatics with several polar substituents such as ethers and phenolics, for example dimethoxyhydrotoluene and syringyl acetone. These were likely from the depolymerisation of lignin (Simoneit et al., 1993; Sekimoto et al., 2018), an amorphous polymer constituting about 25 % of fuel woods (Sjöström, 1993) and formed of randomly linked, high-molecular weight phenolic compounds (Shafizadeh, 1982).

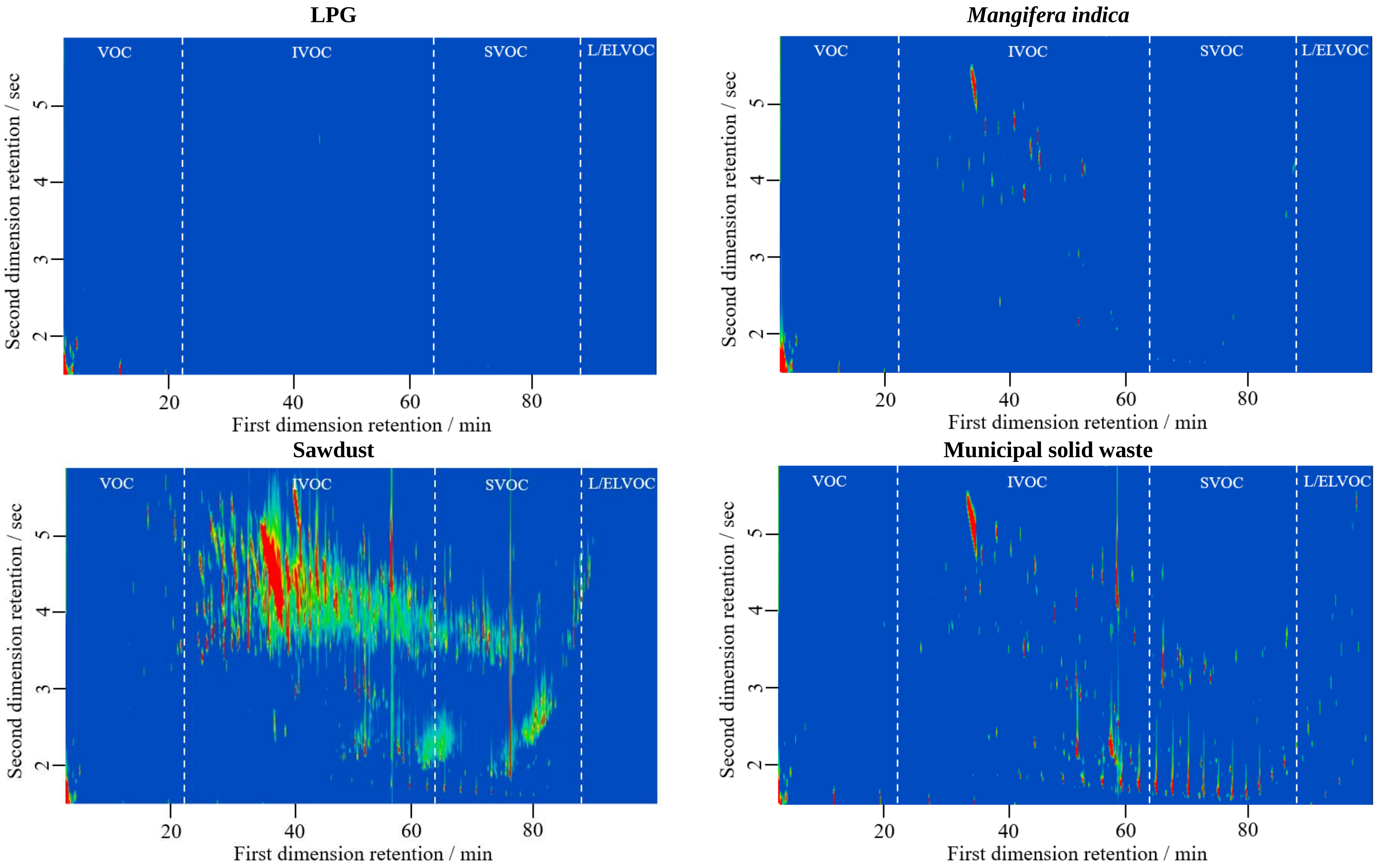

Figure 5. Measurements of organic aerosol from a range of different fuel types, with the contrast at the same scale.

Sawdust, although not a widely used fuel source, released many I/S/L/ELVOC components in the aerosol phase over a much wider range ($C^* \sim 5.8\times10^5 - 1\times10^{-3}$ µg m^{-3} at 298 K). The largest peak was from levoglucosan, with another large peak from squalene. Many peaks were from polar substituted aromatics as well as many PAHs and their substituents, such as 2-methyl-9,10-anthracenedione. The largest peak from municipal solid waste burning was also levoglucosan, but this fuel type released fewer of the polar substituted monoaromatics than other fuels. Municipal solid waste released alkanes and SVOC species such as terphenyls, alkanes and many PAHs.

3.2 Molecular markers for domestic fuels

Cow dung cake combustion emitted a range of sterols/stanols, which have been reported previously (Sheesley et al., 2003). This study suggested that 5β-stigmastanol, coprostanol and cholestanol could be used as tracers for emissions from cow dung cake burning. This is because in higher animals, anaerobic microbial reduction of sitosterol and cholesterol forms the distinctive β configuration of the C-5 proton of 5β-stigmastanol and coprostanol. This contrasts with the α C-5 proton caused by aerobic digestion in aquatic environments. Jayarathne et al. (2018) reported 5β-stigmastanol emissions from hardwood, and Fine et al. (2001) reported 5α-stigmastanol emissions from hardwood. Four fuel wood combustion experiments in our study showed emissions of an isomer of stigmastanol, a result similar to Jayarathne et al. (2018) that 5β-stigmastanol was not unique to cow dung cake burning or the MS measurement method used was unable to distinguish between 5α- and 5β-stigmastanol. Cholestanol and coprostanol were found uniquely during cow dung cake combustion in our study and suggested that they can be used as unique tracers for cow dung cake burning.

Fuel wood combustion generally released fewer organic components into the aerosol phase than fuels such as cow dung cake, MSW and sawdust. Levoglucosan has been traditionally suggested as a tracer for biomass burning emissions, however, emissions of levoglucosan from a range of sources mean that this is of limited use as a unique tracer of woodsmoke emissions in regions with multiple burning sources. This could potentially be resolved in future studies by examining the ratio of levoglucosan to other sugars in different source types. This may differentiate different biomass burning sources as the chemical composition of different sources should determine the emission ratio of levoglucosan to other sugar pyrolysis products (Sheesley et al., 2003).

The presence of a wide range of terphenyls from municipal solid waste combustion in this study was not unique. Jayarathne et al. (2018) suggested that triphenyl benzene was a unique tracer of waste burning emissions. Whilst this study found triphenyl benzene present in one cow dung cake sample and in municipal solid waste samples, the waste combustion emitted on average 19 terphenyls, many more than from cow dung cake combustion (2). Terphenyls have been previously reported from incineration of waste (Tong et al., 1984) and our study suggests that these compounds are good indicators of municipal solid waste burning.

3.3 Total identification

Figure 6A and 6B show a comparison of the relative abundance of peaks identified, defined here as the sum of peak areas identified and calibrated using genuine standards for compounds present in the SPE and PTFE samples compared to the total observed peak area (using the blank subtracted total ion current, TIC).

Figure 6A shows that between 15 and 100 % of the peak area of the TIC in the SPE chromatogram could be identified. The highest proportion of species that could be identified was from fuel wood (67 %), followed by crop residue (57 %), charcoal (48 %), municipal solid waste (46 %), cow dung cake (39 %) and sawdust (16 %). Lower total identification in samples such as cow dung cake was due to increased complexity of emissions, which were not covered by the standards used.

Figure 6B shows that between 7 – 100 % of the organic composition of aerosol released from burning was identified and could be quantified with genuine standards. Generally, a much lower proportion of organic matter within aerosol samples was identified due to a lack of genuine standards available, particularly in complex samples. The lowest mean relative contribution identified from samples was sawdust (9 %), followed by cow dung cake (11 %) and municipal solid waste (16 %). A larger relative contribution was identified from fuel woods (34 %) and charcoal (39 %) due to less complex emissions. A large relative contribution of some fuel woods was identified from *Saraca indica* (91 %) and *Pithecellobium spp* (82 %) due to a low amount of organic matter released from these samples. This also influenced the percentage identification from crop residue which achieved 46 % identification, due to only 3 samples with 98 % identification from *Solanum melongena* but only 26 % from *Cocos nucifera* and 13 % from *Brassica spp*. 100 % of the aerosol released from LPG was quantified due to little being released into the aerosol phase and this was principally composed of PAHs.

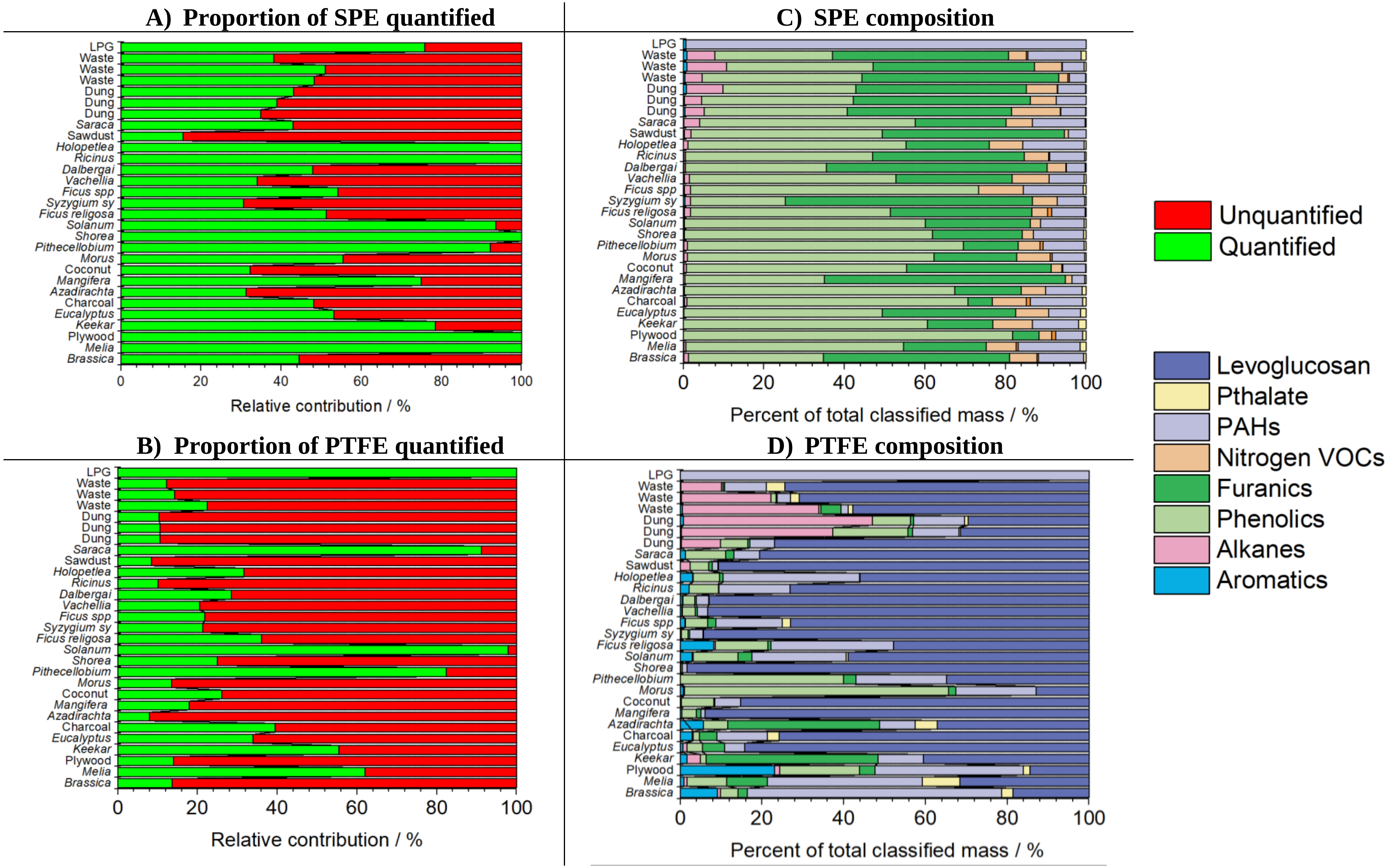

Figure 6. Area of organic matter quantified with genuine standards, as a fraction of total ion current (TIC) (6A and 6B, left panel). Semi-quantitative/quantitative analysis of SPE/PTFE fraction (6C and 6D, right panel).

These low levels of identification of organic aerosol were in line with those reported by Jen et al. (2019), where unknown chemical species represented 35-90 % of the observed organic aerosol mass from biomass burning samples. The percentage identification in this study should not be influenced by the filter sampling media and was low in complex samples due to a lack of genuine standards to allow quantitative detector-response curves for individual analytes.

3.4 Composition

Figure 6C provides an indication of I/SVOC composition on SPE disks by mass of quantified species, assuming no compound breakthrough. Phenolic and furanic compounds were the most abundant I/SVOC species released from all fuel types, except for LPG. As a proportion of the total mass of species quantified with genuine standards on SPE disks, phenolics released from fuel woods (22-80 %) represented the largest range, with large amounts released from municipal solid waste (24-37 %), cow dung cake (32-36 %), crop residue (32-57 %) and sawdust (46 %). High emissions of phenolic compounds were of significance because phenolics contribute significantly to SOA production from biomass-burning emissions (Yee et al., 2013; Lauraguais et al., 2014; Gilman et al., 2015; Finewax et al., 2018). A recent study found that, oxygenated aromatic compounds, which included phenols and methoxyphenols, were responsible for just under 60 % of the SOA formed from western U.S. fuels (Akherati et al., 2020).

Large emissions of furanic species were measured from fuel wood (6-59 %), municipal solid waste (35-45 %), cow dung cake (39-42 %), crop residue (25-44 %) and sawdust (43 %). These were important as furans can be toxic and mutagenic (Ravindranath et al., 1984; Peterson, 2006; Monien et al., 2011; WHO, 2016) and have been shown to be some of the species with the highest OH reactivity from biomass burning emissions (Hartikainen et al., 2018; Coggon et al., 2019). Furans have also been shown to result in SOA production (Gómez Alvarez et al., 2009; Strollo and Ziemann, 2013) with 8-15 % of SOA produced from combustion of black spruce, cut grass, Indonesian peat and ponderosa pine estimated to originate from furans and 28-50 % of SOA from rice straw and wiregrass (Hatch et al., 2015). Akherati et al. (2020) found that heterocyclic compounds, which included furans, were responsible for approximately 20 % of SOA from biomass burning emissions from fuels from the western U.S. SOA formation from furanic species remains poorly understood, with a recent study showing an SOA yield of 1.6-2.4 % during the oxidation of 3-methylfuran with the nitrate radical (Joo et al., 2019). Furans from biomass burning emissions are thought to come from low temperature depolymerisation of hemi-cellulose (Sekimoto et al., 2018) and from large alcohols and enols in high-temperature regions of hydrocarbon flames (Johansson et al., 2016).

Emissions of alkanes were most important from combustion of cow dung cake and municipal solid waste (4-9 %), with only small quantities released from combustion of various fuel woods (< 2 %) and crop residues (< 1 %). This reinforced previous studies which found emissions of C_{12}-C_{39} *n*-alkanes from municipal waste incinerators (Karasek and Tong, 1985). PAH emissions represented (3 – 15 %) of the total quantified emission by mass for fuel types other than LPG and have carcinogenic and mutagenic properties (IARC, 1983, 1984; Nisbet and LaGoy, 1992; Lewtas, 2007; Zhang and Tao, 2009; Jia et al., 2011). They can damage cells through the formation of adducts with DNA in many organs such as the kidneys, liver and lungs (Vineis and Husgafvel-Pursiainen, 2005; Xue and Warshawsky, 2005).

Figure 6D shows the quantified aerosol mass was largely dominated by levoglucosan, with a particularly significant contribution in the fuel wood samples (13-98 %). This was similar to a previous study of fuel wood samples from Bangladesh, where levoglucosan was the largest contributor to aerosol mass (Sheesley et al., 2003). Levoglucosan emissions were also large from cow dung cake (30-58 %), which contrasted with the findings of Sheesley et al. (2003). This could be due to differences in the feeding of cows leading to differences in residual undigested organic matter in cow dung cake fuel as well as differences in preparation between samples collected in Bangladesh and those in this study, which had additional dried biogenic material, such as straw, mixed into samples. Levoglucosan emissions were also high from sawdust (91 %), crop residue (19-85 %) and municipal solid waste (58-75 %), with municipal solid waste emissions likely from cellulosic material collected with the fuel.

Levoglucosan emissions from charcoal (76 %) were significant as a proportion of emissions. Emissions from charcoal were low, which meant that a small emission of levoglucosan represented a large proportion of total emissions. It was likely that the fuel collected here may have contained cellulosic organic matter that led to the emission of levoglucosan.

Emissions of alkanes in the gas and particle phases were similar by source type, with particulate alkanes emitted principally during combustion of cow dung cake and municipal solid waste fuels. Emissions of particulate phenolics were large as a proportion of total quantified mass with genuine standards when the total emission of other components was low. For example, phenolics represented a large proportion of emissions from the fuel wood species *Morus spp* and *Pithecellobium spp* with the mass principally from dimethoxyphenols. Emissions from LPG were mainly PAHs and very low.

Whilst SPE samples for these compounds remained semi-quantitative, due to breakthrough, the detection of high emissions of phenolics and furanics in the gas phase from burning was in line with recently published studies (Hatch et al., 2015; Stockwell et al., 2015; Koss et al., 2018). Relatively low levels of total quantified material within the aerosol phase was in line with current literature (Jen et al., 2019), but meant that this analysis was not entirely reflective of the organic fraction for complex samples. It was likely that this study overemphasised the contribution of levoglucosan in complex aerosol samples, relative to other components present at lower levels (Sheesley et al., 2003; Jen et al., 2019). Future instrument development could allow better quantification of complex burning and ambient samples by splitting the eluent between a -MS and -FID. This study suggests that future research uses lower sample volumes, thicker SPE disks and studies the adsorption characteristics of VOCs to SPE disks.

3.5 Development of emission factors

Emission factors have been developed for PAHs (see Figure 7 and the Supplementary Information S9 for table of emission factors by individual fuel type) by calculating the total volume of air convectively drawn up the flue and relating this to the mass of fuel burnt (see the Supplementary Information S10 for details of calculation). Emission factors for sawdust (1240 mg kg^{-1}), municipal solid waste (1020 mg kg^{-1}), crop residue (747 mg kg^{-1}) and cow dung cake (615 mg kg^{-1}) were generally larger than for fuel wood (247 mg kg^{-1}), charcoal (151 mg kg^{-1}) and LPG (56 mg kg^{-1}). The measurement of higher emission factors for cow dung cake than fuel wood was consistent with that observed in other studies (Bhargava et al., 2004; Gadi et al., 2012). Quantitative emission factors of other VOC classes are given in Stewart et al. (2020).

A wide range of emission factors were measured from combustion of fuel woods from 50 mg kg^{-1} for *Prosopis spp* to 907 mg kg^{-1} for *Ficus religosa*. Figure 8 shows that there was large sample to sample variability in emission factors for different fuel wood samples, for which only 1 sample was taken. For this reason, emission factors have been generalised for use in budget estimates to the type of fuel. Mean emission factors are provided for measurements from samples of 17 fuel woods, 3 crop residues, 3 cow dung cakes and 3 different collections of municipal solid waste. Despite this, for LPG and charcoal samples only 1 sample was measured, and this significantly increased the uncertainty in the PAH emission factors from these fuel sources.

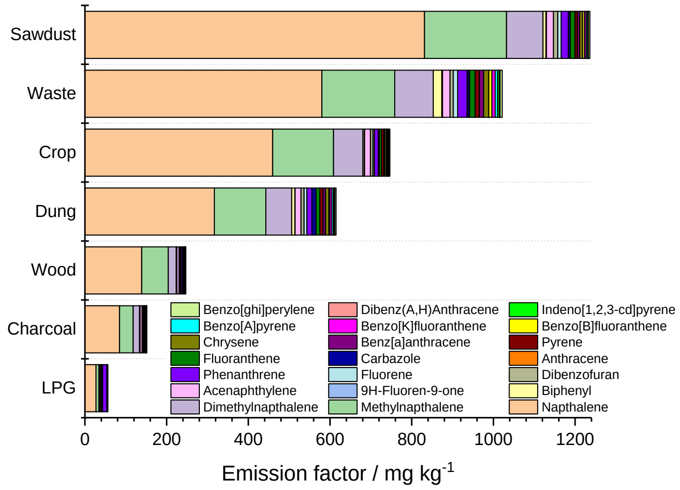

Figure 7. Mean PAH emission factors by fuel type.

For most fuel types, PAH emissions in the gas phase were dominated by naphthalene, methylnaphthalenes and dimethylnaphthalenes, with gas-phase PAHs observed up to pyrene. For fuel wood, crop residue, municipal solid waste, and cow dung cake the percentage of PAHs in the gas phase decreased from 97 %, 96 %, 91 % to 89 %. PAHs from LPG showed the largest fraction in the gas phase (99.9 %) compared to the aerosol phase (0.1 %). Figure 8 shows gas- and particle-phase PAH emissions by individual fuel type, excluding naphthalene as well as C_1- and C_2-substituted naphthalenes. PAHs were present in the aerosol phase from dibenzofuran ($C_{12}H_8O$) to benzo(ghi)perylene ($C_{22}H_{12}$).

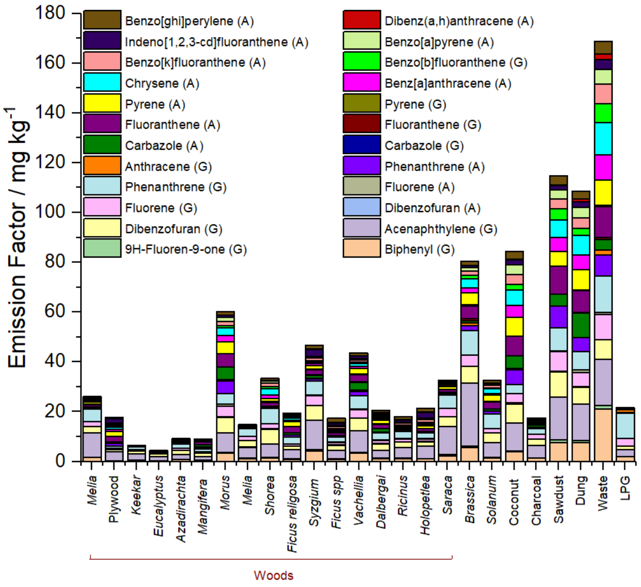

Figure 8. Emission factors of PAHs measured from SPE/PTFE where (G) and (A) represent gas- and aerosol-phase samples, respectively, excluding naphthalene as well as naphthalenes with C_1 and C_2 substituents.

Table 2 shows a comparison of the mean emission factors measured in our study with previous studies. The mean fuel wood total PAH emission factor measured in our study (247 mg kg^{-1}) was a factor 4.7-5.6 larger than those measured by Gadi et al. (2012) and Singh et al. (2013) of 44 and 53 mg kg^{-1}, respectively, for similar fuel woods collected across Delhi and the Indo-Gangetic Plain. The PAH emission factor measured for cow dung cake (615 mg kg^{-1}) was around a factor of 10 larger than those previously measured (60 mg kg^{-1}). The larger total emission factors for fuel wood and cow dung cake was a result of high emissions of gas-phase PAHs measured using PTR-ToF-MS (51-896 mg kg^{-1} for fuel wood and 446-660 mg kg^{-1} for cow dung cake) compared with previous measurements made using PUF plugs (7 mg kg^{-1}). This indicated that either the PTR-ToF-MS was able to better detect and characterise gas-phase emissions than previous methods and suggested either breakthrough or off gassing of smaller gas-phase PAHs from PUF plugs or measurement of significant quantities of other $C_{10}H_8$ isomers on the PTR-ToF-MS. This may highlight an underestimation of 2-ring gas-phase PAH emissions in previous burning studies. Gadi et al. (2012) measured PAH emissions in the particle phase, with the mean emission for fuel wood (44 mg kg^{-1}) greater than our study (9 mg kg^{-1}). Particulate phase emissions of PAHs measured by Singh et al. (2013) from fuel wood (45 mg kg^{-1}) were also larger than our study. By contrast, particle phase PAH emissions from cow dung cake in our study (66 mg kg^{-1}) were comparable to those measured previously of 57-60 mg kg^{-1} (Gadi et al., 2012; Singh et al., 2013). Variability in emission of particulate-phase PAHs in our study compared to literature was likely to be highly influenced by the efficiency of combustion of different fuel types. This may also be explained by measuring only once for many of the fuel types, due to significant burn-to-burn differences in emissions. Although not measured in our study, differences in moisture content between fuel types in our study and literature were likely have a large influence on the total amount of PAHs emitted and may explain the differences in particle-phase emissions.

This study was conducted under controlled laboratory conditions. For some sample types, such as municipal solid waste, the laboratory measurement may not be entirely reflective of real-world conditions. Municipal solid waste combustion may occur under both flaming and smouldering conditions at landfill sites and in backyards, as well as in high-temperature incinerators in more developed countries. All of these are likely to have quite different combustion chemistry, and consequently lead to varying levels of emission.

The particulate phase PAH emission factors from municipal solid waste combustion in our study (14-181 mg kg^{-1}) were much smaller than those of previous studies (1910-8486 mg kg^{-}

^{1}), but the number of samples was limited. Emissions from coconut shell have not been well studied, making comparisons difficult (Gulyurtlu et al., 2003). The emission of particulate phase PAHs from sawdust in our study (62 mg kg^{-1}) was less than that previously reported 259 mg kg^{-1}, but our study found large gas phase PAH emissions (1175 mg kg^{-1}). Particulate PAH emissions from the crop residues burnt in our study (13-53 mg kg^{-1}) fell within the range reported by Kim Oanh et al. (2015) of 0.34-34 mg kg^{-1} for rice straw. Those reported by Wiriya et al. (2016) were smaller (0.47 mg kg^{-1}), but were from fuel dried in an oven at 80 ^{o}C for 24 hours and ignited by an LPG burner and were likely to represent more complete combustion conditions. Emissions of PAHs from charcoal in our study (151 mg kg^{-1}) were larger than those measured for South Asian fuels (25 mg kg^{-1}), caused principally by larger measurement of gas-phase species by PTR-ToF-MS. Both our study and that of Kim Onah et al. (1999) showed charcoal released the least amount of PAH per kg burnt for biofuels. LPG combustion released less particulate PAHs (0.1 mg kg^{-1}) than previous studies (0.8 mg kg^{-1}), but also included a small gas-phase emission (56 mg kg^{-1}). Differences in the distribution of PAHs found in the gas and aerosol phases between our study and literature were also likely to be influenced by the different sample dilutions and gas-to-aerosol partitioning prior to measurement.

Table 2. PAH emission factors measured in our study compared to values from literature for similar fuel types.

Fuel	**PAH emission factor (mg kg^{-1})**			
	Gas	**Particle**	**Total**	**Ref**
Wood	51-896	0.4-34	51-907	Our study
		1-12		(Hosseini et al., 2013)
	22-111	0.4-6	24-114	(Kim Oanh et al., 2005)
	-	44	44	(Gadi et al., 2012)
	7	45	52	(Singh et al., 2013)
		805-7294		(Kakareka et al., 2005)
			43	(Lee et al., 2005)
	66	0.8	67	(Kim Oanh et al., 2002)
	105	4	105	(Kim Oanh et al., 1999)
Dung	446-660	48-98	493-710	Our study
	-	59	-	(Gadi et al., 2012)
	3	57	60	(Singh et al., 2013)
Waste	696-1233	14-181	776-1414	Our study
	-	8486	8486	(Kakareka et al., 2005)
	-	1910	1910	(Young Koo et al., 2013)
Crop	205-1231	13-53	219-1255	Our study
	-	-	5-683	(Jenkins et al., 1996)
	-	-	3-50	(Lu et al., 2009)
	-	-	129-569	(Wei et al., 2014)
	5-230	0.3-34	5-264	(Kim Oanh et al., 2015)
	-	0.47	-	(Wiriya et al., 2016)
Sawdust	1175	62	1236	Our study
		259	261	(Kim Oanh et al., 2002)
Charcoal	147	4	151	Our study
	25	0.1	25	(Kim Oanh et al., 1999)
LPG	56	0.1	56	Our study
	-	0.8	-	(Geng et al., 2014)

4. Conclusions

This paper demonstrated an extraction technique for analysis of I/SVOCs collected onto SPE disks and PTFE filters from combustion of biofuels, which was well suited to the analysis of non-polar species. A range of fuels relevant to burning in India were combusted with organic components collected and analysed, which showed large differences in the composition of organic matter released. The separation power of GC×GC was used to identify an extensive range of I/SVOCs in both gas and particle phases, with 15-100 % of gas-phase emissions and 7-100 % of particle-phase emissions characterised.

The ability to quantify species on SPE disks was assessed and scope for future studies which should assess the adsorption characteristics of IVOCs onto SPE disks was provided. It is recommended that breakthrough of IVOCs collected onto SPE disks at lower sample volumes is evaluated, and better methods for quantification of complex samples are developed. Further characterisation of fuel types from a wider range of sources would enable a better understanding of the drivers of poor air quality in the developing world. This study found that cholestanol and coprostanol were unique to cow dung cake burning samples and these species were therefore suggested as tracers for emissions from cow dung cake burning. Similarly, municipal solid waste burning released many terphenyls, which could act as good indicators of this source. This study found that phenolic and furanic species were the most important gas-phase emissions by mass of I/SVOCs from domestic solid fuel combustion samples collected from the Delhi area of India. New emission factors were developed for US EPA criteria PAHs present in gas and aerosol phases from a large range of fuel types. This suggested that many sources important to air quality in the developing world are larger sources of PAHs than conventional fuel wood burning.

Data Availability: Peaks measured in this study with NIST library hits > 700 are given in the Supplementary Information S7 and S8. Quantitative VOC emission factors measured using PTR-ToF-MS and gas chromatography from the fuel types studied are given in Stewart et al. (2020).

Author contributions. GJS developed the ASE method, GC method, collected samples, organised logistics, extracted/analysed samples and lead the paper. BSN collected samples and assisted with logistics. WJFA measured VOCs by PTR-ToF-MS, supported by CNH, LKS and NT. ARV assisted in running and organising of experiments. NJF, JRH and MWW assisted in

GC×GC-ToF-MS method development. SJS assisted in ASE method development. RA, AM, RJ, SA and LY collected fuels, carried out the burning experiments and measured gas volumes up the flue. SSBMY aided complex sample analysis. EN, NM, RG, SKS and JDL contributed to logistics and data interpretation. TKM and JFH provided overall guidance with setup, conducting, running, and interpreting experiments.

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

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