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## Variations in oxygenated and nitrogen-containing primary organic compounds based on the fuel type and burning condition in stove emissions

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Biomass burning emits primary organic gases and particles on a global scale, partly from domestic combustion. While there is growing understanding of the composition and characteristics of these emissions, uncertainties still exist in chemical compositions with respect to different fuel types and burning conditions. However, developments in online instrumentation have allowed for not just detailed chemical characterisation, but also the temporal resolution necessary to separate emissions according to the combustion conditions. Controlled experiments were carried out in the Manchester Aerosol Chamber to chemically characterise the composition of primary or fresh emissions from a domestic stove, using different biomass fuels, by performing controlled dilutor injections into the chamber, employing a combination of online and offline measurements, and comparing results according to different combustion phases (flaming vs. smouldering). A chemical ionization mass spectrometer coupled with a Filter Inlet for GAses and AEROsols inlet (FIGAERO-CIMS) was utilized to investigate the variations in the oxygenated (CHO) and nitrogen-containing (CHON) organic gas and particle-phase compositions, while the aerosol mass spectrometer (AMS) was employed to provide information on the primary aerosol bulk chemical composition. The CHO compounds were more abundant, contributing a higher signal fraction in wood emissions compared to leaves and peat, and with wood smouldering yielding a higher CHO fraction than flaming. The CHON compounds, though of significantly lesser contributions (<20%), were dominated by reduced nitrogen and organonitrogen compounds in the gas and particle phase respectively. The CHON compounds displayed greater aromaticity than the CHO compounds due to their higher double bond equivalent to carbon number (DBE/C) and aromaticity index (AI) values. A greater fraction of CHON compounds resulted in greater aromaticity in wood flaming compared to the smouldering emissions in the particle phase. Leaves exhibited higher aromaticity than wood and peat due to the presence of CHON compounds with greater DBE/C and AI values. Although the results showed differences in primary aerosol composition based on biomass type, the effect of burning conditions on the aerosol particles was only noticeable based on the variations in the AMS  $f_{60}$ , suggesting that the  $f_{60}$  is a useful metric to differentiate emissions from flaming and smouldering burning phases.

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### Environmental significance

Increasing energy prices has led to the proliferation in the use of domestic wood stoves in recent years, and this is projected to increase even further. Across different regions, different biomass fuels are burned to meet residential heating demands. While several studies have attempted to characterise emissions from domestic burners, there are still gaps in knowledge due to the variability in emissions from different biomass fuels and combustion phases. In this study, four different biomass types are burned in a woodstove and the primary emissions are chemically characterised. The results reveal variations in the oxygenated and nitrogen-containing fractions of the emissions based on the fuel type and burning phase and improve our comprehension of fresh stove emissions. The results also provide a foundation for enhancing our understanding of secondary emissions from biomass burning.

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### 1 Introduction

Biomass burning (BB) is a significant source of atmospheric aerosols, contributing two-thirds of the primary organic aerosol



(POA) emitted globally and one-third of the global BC budget and the second-largest source of atmospheric VOCs, after biogenic emissions.<sup>1,2</sup> BB emissions, can upon further reactions in the atmosphere, produce secondary organic aerosols (SOAs).<sup>3</sup> The emissions from the burning of biomass can be influenced by the combustion conditions involving either flaming or smouldering phases, with the smouldering-phase BB producing higher POA emissions than the flaming.<sup>4</sup> While studies have shown that biomass burning emissions are detrimental to human health, air quality and climate,<sup>5</sup> a lot of uncertainty still exists in the understanding of the composition and characteristics of these emissions, which hinders the appreciation and description of consequent SOA formation in the atmosphere.<sup>6</sup>

Within areas such as the UK, there has been a proliferation and utilisation of improved small-scale biomass burners such as wood burning stoves as a low-cost option for meeting residential heating demands. Data provided by the UK National Atmospheric Emissions Inventory (NAEI) indicates that in 2020, residential burning was responsible for 19.8 kt of PM<sub>2.5</sub> emissions, with wood combustion accounting for 17% of that. In addition, the NAEI also estimated a 50% increase every two to three years in domestic stove installations from 2003 onwards.<sup>7</sup> This greatly increases the need to thoroughly characterise the emissions from domestic appliances in order to ascertain their human health and climatic effects.<sup>6</sup>

Previous studies have explored the chemical characteristics of biomass fuels.<sup>6,8,9</sup> Several of these studies focused largely on wood and other fuel types, but peat and leaves were outside their scope. In certain parts of the UK for instance, peat happens to be an important biomass fuel for domestic energy supply<sup>10,11</sup> and its potential as a significant global emission source has been identified.<sup>12</sup> To our knowledge, very few studies have investigated peat and leaf combustion in a wood burning stove, despite the prevalent use of woodstoves to burn peat in certain European countries,<sup>11</sup> and the capabilities of wood burners as a useful tool for understanding emissions from different fuel types. Moreso, while a significant number of studies have attempted to investigate primary emissions from the burning of different fuels using the AMS and proton transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) among others,<sup>8,13,14</sup> not many have utilized the FIGAERO-CIMS in laboratory-controlled burning despite its recent notoriety in atmospheric research studies and recognized high time resolution, selectivity and sensitivity to a wide range of oxygenated and nitrogenated VOCs.<sup>15–17</sup>

While many characterisation studies have focused on individual molecules, complex sources such as wood combustion can deliver a highly complex mixture, which is difficult to interpret. Therefore, to aid interpretation, it is often best to generalise molecular data according to metrics related to carbon number and/or functionality. According to Kroll *et al.*<sup>18</sup> the degree of oxidation (O:C ratio), and the carbon oxidation state (OSc) are critical metrics for characterizing the chemistry of organic aerosols because of their influence on toxicity, hygroscopicity and optical properties.<sup>19</sup> Moreover, studies have also shown that BB emits significant quantities of nitrogen-containing organic aerosols (NOAs), including nitrates, N-

heterocyclic compounds, nitroaromatic compounds (NACs), and amines into the atmosphere.<sup>20</sup> Nitrogen-containing organic compounds such as some N-heterocyclic compounds and NACs contribute to cloud water, light-absorbing organic compounds, also termed brown carbon (BrC),<sup>21</sup> as well as SOAs,<sup>22</sup> hence these compounds significantly affect climate changes and the Earth's radiation balance. NACs are especially known for their adverse human health effects, because of their phytotoxic, carcinogenic and mutagenic properties.<sup>23</sup>

Therefore, this study aims to highlight the differences in composition and chemical properties of conventional fuels (hard and soft wood) *versus* peat and leaves, which will enhance source prediction and the understanding of secondary formation in the atmosphere from these fuels, as well as their potential air quality, health and climatic effects. Specific objectives of the study entail to (1) identify the differences in primary aerosol composition with respect to fuel type and burning conditions; (2) determine the dependencies of the composition and chemical properties in the gas and particle-phase on fuel type and burning phase. The study utilises a CIMS to characterise the oxygenated and nitrogen-containing fraction of primary emissions from the combustion of biomass fuels in a woodburning stove. Additional online measurement techniques were employed to further enhance the understanding of the BBA bulk chemical properties.

## 2 Experimental methods

### 2.1. Description of experimental design

Laboratory stove experiments were conducted as part of a characterisation study in preparation for the NERC HIP-TOX project,<sup>24</sup> designed to commission and chemically characterise a stove facility and chamber injection protocol for subsequent use in *in vivo* human exposure studies, the results of which will be presented in future publications. These experiments (Table 1) were carried out at the Manchester Aerosol Chamber (MAC) laboratory of the University of Manchester, UK.<sup>6,25,26</sup> A schematic of the experimental setup is illustrated in Fig. 1. The chamber offers the possibility of "holding" the primary emissions, for detailed characterization with a large array of instruments, in a manner similar to Liu *et al.*<sup>27</sup> The biomass smoke from the flue was diluted with compressed dry air at a flow rate of 2 L min<sup>-1</sup>, in order to avoid re-condensation of evaporated materials and coagulation in the  $\frac{1}{2}$  inch stainless steel pipe that was used to channel the smoke from the smokestack to the chamber.<sup>28</sup> This was done continuously for the duration of smoke injection into the chamber. Smoke injection into the MAC was performed by an ejector diluter (eDiluter Pro, Dekati Ltd). The eDiluter was used to control the injection of emissions into the chamber, until  $190.36 \pm 51.18 \mu\text{g m}^{-3}$  (measured using a Scanning Mobility Particle Sizer, SMPS) particle mass concentration was attained.

A description of the MAC has been presented by Shao *et al.*<sup>29</sup> In brief, the MAC is an 18 m<sup>3</sup> fluorinated ethylene propylene (FEP) Teflon bag suspended from a frame comprising a central fixed-frame member and two moving members, all contained within a temperature and relative humidity (RH) controlled



Table 1 Summary of initial experimental conditions for the stove experiments<sup>a</sup>

Experiment	Fuel type	Burning condition	Experiment label	PM concentration ( $\mu\text{g m}^{-3}$ )	OA ( $\mu\text{g m}^{-3}$ )	OA/BC	$\text{NO}_3^-$ ( $\mu\text{g m}^{-3}$ )	$\text{NO}_x$ (ppb)
1	Hardwood (beech)	Flaming	HWFL	256.34	15.88	0.33	2.27	91.84
2	Hardwood (beech)	Smouldering	HWSM	139.03	41.05	4.31	2.97	86.43
3	Softwood (pine)	Flaming	SWFL	149.53	4.66	0.12	0.49	58.20
4	Softwood (pine)	Smouldering	SWSM	111.09	30.31	4.4	1.75	90.69
5	Softwood (pine)	Smouldering	SWSM	215.86	66.11	—	3.13	69.56
6	Leaves (hornbeam)	Smouldering-like	Leaves	226.03	84.96	—	2.57	38.19
7	Leaves (hornbeam)	Smouldering-like	Leaves	222.95	—	—	—	36.66
8	Leaves (hornbeam)	Smouldering-like	Leaves	179.50	60.28	—	2.21	29.52
9	Peat	Smouldering-like	Peat	138.76	64.36	—	0.51	25.09
10	Peat	Smouldering-like	Peat	264.50	112.59	—	0.80	25.23
11	Chamber background experiment			0.10	—	0.10	0	21.73
12	Chamber background experiment			0.19	—	0.19	0	21.81

<sup>a</sup> OA = AMS organics;  $\text{NO}_3^-$  refers to AMS nitrate.

enclosure. Filtered air, *via* a series of fill/flush cycles, is injected into the chamber by passing laboratory air at a flowrate of  $3 \text{ m}^3 \text{ min}^{-1}$  through a combination of Purafil, charcoal, and HEPA filters arranged in series. Chamber conditions during the experiment were controlled at  $25 \pm 1 \text{ }^\circ\text{C}$  and 50–60% RH. The temperature was controlled by using a chamber air conditioning system and the humidity levels were controlled by using an air dryer, which allowed the introduction of dry or humid air.

Biomass burning smoke was injected into the MAC through an Ecodesign wood stove (Esse Model 175F); fitted in a trailer adjacent to the MAC. The major characteristics of this stove in comparison to the conventional stoves in the UK market, is its promise of “precision burning” through its “particulate reburn” technology (serving the same purpose as the “tertiary air” systems), potentially improving its ability to reduce the particulate emissions below the threshold for Ecodesign compliance set out by the EU Commission Regulation.<sup>30</sup> However, the

“clean” or “precision burning” capacity of the wood stove was disabled through the removal of the catalytic filter, to simulate more conventional domestic stove emissions. The biomass types selected for this study were beech wood (hardwood representative of domestic fuels in current use in the UK), softwood (ponderosa pine), peat and leaves (Hornbeam or *Carpinus betulus*). The fuels selected represented components present in domestic burning (wood and peat) as well as wildfires (wood, peat and leaves). Moreover, peat, although not a widely recognized fuel used for domestic burning, is one of the widely used sources of fuels for residential heating purposes in the Republic of Ireland, Finland, and parts of Northern Ireland.<sup>10,11</sup> This study may also be relevant for the understanding of wildfire emissions,<sup>31</sup> although it should be noted that the combustion conditions in a domestic stove are likely to be very different. A summary of the initial experimental conditions is presented in Table 1, and the experiments are hereafter referred

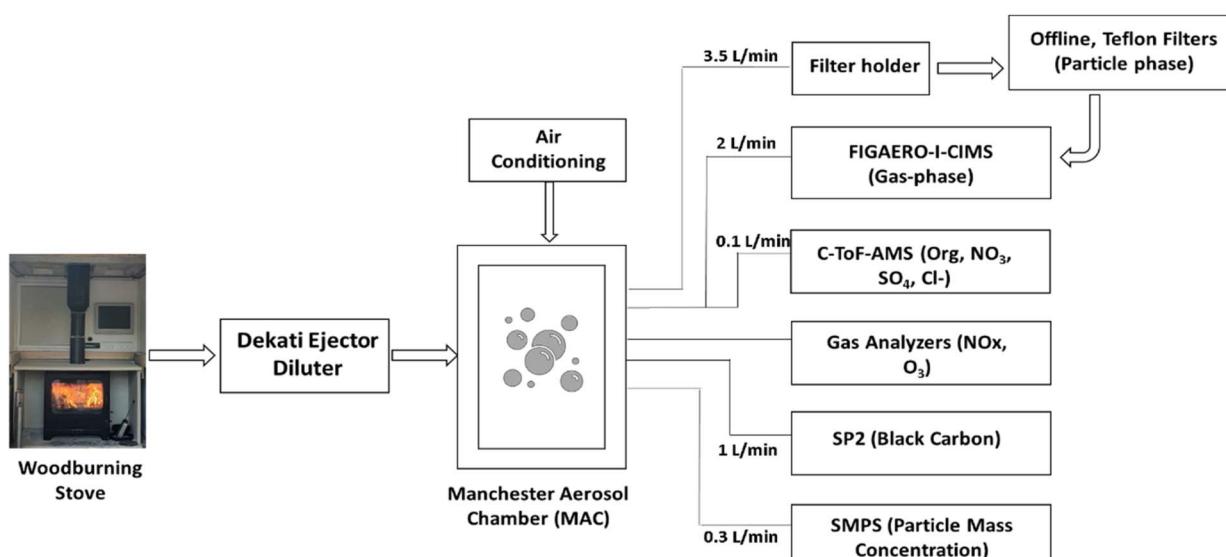


Fig. 1 The schematic of the experimental setup for the biomass burning chamber experiments. C-ToF-AMS: Compact Time of Flight Aerosol Mass Spectrometer; SP2: Single Particle Soot Photometer.



to by their four-letter labels. Moreover, Fig. S1 shows a CIMS gas-phase time-series of selected compounds in the HWFL experiment (Table 1). The time periods before smoke injection, the smoke injection time and periods after smoke injection are shown.

The wood fuels were burnt under “flaming” and “smouldering” combustion phases. Similar to the study by Bertrand *et al.*<sup>8</sup> and the protocol used in Allan *et al.*,<sup>32</sup> fire starters and wood kindling were used to ignite the fire. The door of the wood stove was initially kept ajar to aid ignition. The woodstove was then shut after ignition and left until the kindling and starters were completely burnt, before injection of emissions into the chamber commenced. The smoke from the ignition phase was deliberately excluded during smoke injection because it was not indicative of the overall burning of the biomass fuels in the woodstove, due to the presence of the fire starters and kindling.

Furthermore, the burn phases were controlled by varying the air/fuel ratio through the opening and closing of the stove's air restriction valve during burning, to attain flaming or “smouldering” conditions respectively. For the burning phase designated “smouldering” here, fresh wood was added in a manner consistent with the refuelling procedure in the conventional operation of the woodstove in homes, and the smoke injection in the smouldering phase was carried out when there were no more visible flames. It should be noted that the description of ‘smouldering’ used here is for the sake of consistency with other publications from this experiment,<sup>4,25</sup> and it should be noted that the emissions will consist of a combination of emissions from weak combustion of embers from the previous load, and un-combusted pyrolysis emissions from the fresh wood. These pyrolysis emissions have been characterised in previous studies and are known to be chemically and physically distinct from combustion emissions.<sup>33</sup>

## 2.2. Instrumentation

Online and offline CIMS measurements of the gas and particle phases respectively, were carried out by using a FIGAERO-CIMS.<sup>34,35</sup> The instrument was operated with iodide ( $I^-$ ) reagent ions in all the experiments, produced by passing a mix of  $CH_3I$  and ultra-high purity nitrogen over a polonium ( $^{210}Po$ ) radioactive source. This reagent system is useful for the general study of functionalised organic molecules with moderate to high polarity, but it should be noted that it is incapable of detecting non-polar molecules, so pure hydrocarbons are not included in this study. The FIGAERO-CIMS which combines the High-Resolution Time-of-Flight CIMS (HR-ToF-CIMS) coupled with the Filter Inlet for Gases and Aerosols (FIGAERO), was first introduced by Lopez-Hilfiker *et al.*<sup>35</sup> The offline FIGAERO-CIMS filter analysis followed this procedure: the filters were desorbed using dry ultra-high purity nitrogen (UHP  $N_2$ ). The desorption cycle was programmed as follows: 2 min of background measurement (zero), 25 min temperature ramp (from ambient to 200 °C), 15 min temperature soak (where the temperature was kept constant at 200 °C to ensure complete filter desorption); 20 min temperature cool and 2 min of zero.

PTFE filter samples (Mitex™ PTFE, pore size 5.0  $\mu m$ , diam. 47 mm) were collected with a polycarbonate 47-mm in-line filter holder, at a flow rate of 3.5 L  $m^{-1}$ . The Teflon filters were pre-baked at 200 °C for 24 hours prior to sample collection. After collection, they were placed in a Petri dish (Analyslide™, Pall Laboratory, 47 mm diam., Base and Lid: polystyrene), placed inside a tightly locked ziplock bag, and stored frozen until thermal desorption with the FIGAERO-CIMS. Offline filters were sampled during these experiments because the thermocouples of the FIGAERO, responsible for temperature controls during the filter desorption phase, developed a fault just before the commencement of the experimental campaign, and couldn't be replaced in time for the start of the experiments.

The compact time-of-flight aerosol mass spectrometer (C-ToF-AMS) and the SP2 were respectively utilized to explore the composition of the non-refractory (organics, sulfate, nitrate, ammonium, chloride as well as key marker ions) and refractory (black carbon) components in the aerosol particle phase BB emissions, as was previously done.<sup>33</sup> The AMS was calibrated using the standard protocol with ammonium nitrate and the SP2 with Aquadag, using a standard calibration factor of 0.75.<sup>36</sup> The AMS  $f_{43}$ ,  $f_{44}$  and  $f_{60}$  were determined by taking the ratio of these marker peaks divided by the total organic signal.<sup>37</sup> The AMS O : C ratio was also computed as determined by Aiken *et al.*,<sup>38</sup> and is based on the empirical fit between  $f_{44}$  and the AMS O : C ratio.  $NO_x$  measurements were carried out using a chemiluminescent analyzer with a molybdenum converter (Thermo Scientific, model 42i).

**2.2.1. Data processing and analysis.** High-resolution peak fitting of the CIMS data mass spectra was carried out with Igor 7 (WaveMetrics, USA) and Tofware 3.2.3 (Tofwerk AG, Switzerland). Mass calibration of the spectra was carried out using  $I^-$ ,  $I_2^-$ ,  $CH_2O_2I^-$  and  $I_3^-$  ions. The identified peaks considered ranged from  $m/z$  180–500 (excluding the reagent ions,  $I_2^-$ , and  $I_3^-$ ). Identification and assignment of peaks in the mass spectra were primarily assisted by clear identification of compounds confirmed in previous BB studies,<sup>6,17,39</sup> and majority of the peaks identified in this study fell under this category. Secondly for peaks that couldn't be determined from previous studies, assignment of a chemically valid formula as determined from PubChem (<https://pubchem.ncbi.nlm.nih.gov/>) was completed keeping the mass error under  $\pm 10$  ppm. The unassigned fractions in the CIMS measurements (less than 20% of the total fitted signal) represent the peaks that are difficult to identify, caused by either poor signal-to-noise ratios ( $S/N \leq 2$ ) or inaccessible formulae within the trusted error. The signals reported in this study are integrated signals in counts per second (cps), normalized by the sum of the iodide ( $I^-$ ) and water-iodide adduct ( $H_2OI^-$ ) signals. Normalizing individual compound signals to the sum of reagent ions ( $I^- + H_2OI^-$ ) is widely used in CIMS studies,<sup>15,35</sup> and was done to reduce the effects of variations in the reagent ion concentrations and overall instrument sensitivity. The CIMS measurements in both phases were subjected to a two-step subtraction process in order to account for the chamber and filter background and any potential instrument contamination. The method of background subtraction is described in the SI (Fig. S2).

Though previous attempts have been made to constrain the limitations associated with the quantification from FIGAERO-CIMS in both the particle and gas phases,<sup>16</sup> challenges persist due to experimental limitations and a lack of available standards.<sup>40</sup> It should be noted that recent advancements in instrumentation (*e.g.* voltage scanning) has made progress to constrain sensitivities. While standards are available for some compounds detected in this study and these can be calibrated for individually, it is currently implausible to perform calibrations for all compounds identified in CIMS mass spectra with each compound possibly containing multiple isomers that may have different response factors in the CIMS instrument. Hence, we assume uniform sensitivities across the whole range of detected compounds and used normalized signals for the comparisons presented in this study, like previous studies.<sup>6,41,42</sup> Chen *et al.*<sup>42</sup> noted that this assumption was reasonable as they found a good correlation between the total OA measured by the FIGAERO-CIMS and the AMS. However, it should be noted that the uncertainty arising from the assumption of uniform sensitivity may result in an overestimation of the importance of more oxygenated compounds, compared to the less oxygenated, due to their relative affinity to the reagent ions.<sup>15</sup>

Similar to the study of Kong *et al.*<sup>6</sup> who performed an ordinal analysis to determine the most significant masses through ranking before identifying the molecular composition of those masses, this study has applied a ranking system of the normalized signal contribution of the already identified masses in order to ascertain the most influential compounds emitted from each fuel type and burning condition. The top 30 most significant CHO and CHON compounds based on normalized signal contribution have been discussed as fingerprint molecules of the emissions. It should be noted that this study has been limited to organic molecules with two or more carbons, so HCN, HCNO, and HCOOH (formic acid), despite being among the top 30 compounds identified in the gas phase, are not discussed in this study. These compounds are also well reported in BB literature.<sup>17,43</sup> We limited our CIMS analysis to two or more carbons to target higher molecular weight organic compounds which generally make a larger SOA contribution.

### 2.3. Elemental composition of identified molecules

The identified peaks from the analysis of the CIMS mass spectra were categorized based on their elemental composition. Compounds containing carbon, hydrogen and oxygen only were classed as oxygen-containing compounds or the CHO subgroup while those containing only carbon, hydrogen, oxygen and nitrogen were categorized as the CHON subgroup also referred to as nitrogen-containing organic compounds (NOCs). Moreover, the identified compounds were also subdivided according to the numbers of carbon atoms in their molecular formulae: C<sub>2</sub>–C<sub>5</sub> representing compounds with two to five carbon atoms, C<sub>6</sub>–C<sub>8</sub> representing compounds with six to eight carbon atoms, C<sub>9</sub>–C<sub>11</sub> representing compounds with nine to eleven carbon atoms, C<sub>12</sub>–C<sub>16</sub> representing compounds with twelve to sixteen carbon atoms, >C<sub>16</sub> representing compounds with sixteen carbon atoms greater than sixteen and “Others” representing

CHO and CHON compounds with one carbon atom as well as compounds that are not in the CHO and CHON classes.

### 2.4. Computation of the average carbon oxidation state (OSc), double bond equivalent (DBE) and aromaticity index (AI)

Studies have utilized the carbon oxidation state to characterize the chemical composition of organic molecules.<sup>39,44</sup> Kroll *et al.*<sup>18</sup> established the use of the OSc metric in the evaluation of the degree of oxidation within a complex oxidation reaction. The OSc was computed as described by Du *et al.*<sup>44</sup> using the O : C, H : C, and N : C ratios as shown in eqn (1);

$$\text{OSn} \approx 2 \times \text{O} : \text{C} - \text{H} : \text{C} - (\text{OSn} \times \text{N} : \text{C}) \quad (1)$$

where OSn = 0 if number of N atoms = 0. OSn = +3 if nO < 3 and +5 if nO ≥ 3.

Researchers have also previously characterized the chemical composition of organic aerosols by analysing the degree of unsaturation or the density of C–C double bonds in a molecule, in order to ascertain the existence of aromatic and condensed aromatic moieties in the molecule. This is useful to aid the understanding of potential toxicity effects.<sup>29</sup> In this study, aromaticity was estimated utilizing the double bond equivalent (DBE), and the ratio of double bond equivalent to carbon number (DBE/C). DBE/C is related to the density of double bonds and their aromaticity, with increasing values representing increasing contributions from compounds containing aromatic rings.<sup>45,46</sup> The DBE value was computed as shown in eqn (2);

$$\text{DBE} = \frac{2\text{C} + 2 - \text{H} + \text{N}}{2} \quad (2)$$

where C, H and N represent the number of carbon, hydrogen and nitrogen atoms respectively. Note that DBE is independent of the number of oxygen atoms.

Furthermore, the possibility of double bonds being present in compounds, yet not contributing to aromaticity, condensation or ring formation, makes the DBE/C ratio insufficient to explore the presence of aromatic compounds. They introduced the aromaticity index (AI) which is computed by using eqn (3);

$$\text{AI} = \frac{1 + \text{C} - \text{O} - 0.5 \text{H}}{\text{C} - \text{O} - \text{N}} \quad (3)$$

## 3 Results

### 3.1. Primary aerosol composition and influence of biomass type and burning conditions

The AMS data are presented first, as this provides context for the CIMS results when compared to the extensive previous literature of stove and biomass burning emissions using this instrument. Table S1 shows the mass concentration of organics (OA), nitrate (NO<sub>3</sub><sup>–</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), sulfate (SO<sub>4</sub><sup>2–</sup>), chloride (Cl<sup>–</sup>), black carbon (BC), the mean organic aerosol to black carbon (OA/BC) ratio, the AMS O : C ratio, *f*<sub>43</sub>, *f*<sub>44</sub> and *f*<sub>60</sub> for the different fuels and burning conditions. A plot of *f*<sub>44</sub> and O : C

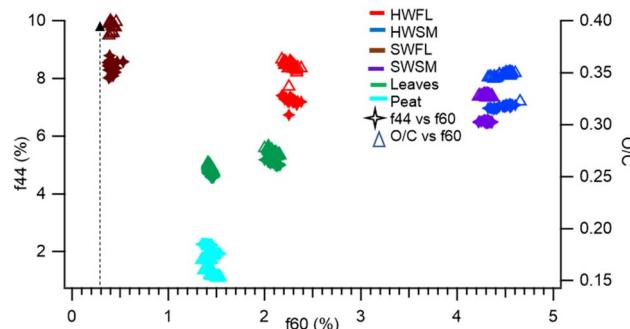


Fig. 2  $f_{44}$  (left-axis) and O:C (right-axis) vs.  $f_{60}$  (bottom-axis). The vertical dashed line represents the Cubison *et al.*<sup>37</sup>  $f_{60}$  background level.

(on the left and right axis respectively) against  $f_{60}$  is presented in Fig. 2 to further elucidate the aerosol chemical properties. The  $f_{44}$  corresponds in behaviour to O:C,<sup>38</sup> and increasing values indicate an increasing degree of oxygenation and the presence of carboxylic acids.<sup>8,9</sup> On the other hand, the  $f_{43}$  represents lesser oxygenation, while the  $f_{60}$  often indicates a signature for biomass burning, representing levoglucosan and similar molecules.<sup>13,38</sup> Hence, the UMR ions  $m/z$  43 ( $\text{C}_2\text{H}_3\text{O}^+$  and  $\text{C}_3\text{H}_7^+$ ),  $m/z$  44 ( $\text{CO}_2^+$ ) and  $m/z$  60 ( $\text{C}_2\text{H}_4\text{O}_2^+$ ), serve as tracer fragments for total OA, OOA and BBOA, respectively.<sup>13</sup>

Fig. 2 indicates variability in the trends among the different biomass types and burning conditions and the observed values were within range of the results of primary BBOA in ambient environments.<sup>37,47</sup> On average, peat emitted the highest fraction of organics, followed by leaves and then wood. Wood fuel types had the largest BC values, with negligible values observed in leaves and peat aerosol. OA and AMS total particulate nitrate were higher in wood smouldering compared to flaming, while BC was higher in flaming compared to smouldering (Fig. S3). Also, nitrate in leaves was comparable to wood, while the lowest concentrations were observed in peat particles. Fig. S3 shows

similarities in the aerosol chemical compositions of repeat experiments for leaves and peat, indicating good repeatable and reproducible chemical characteristics of the organic aerosol in these experiments. Fig. S4 showing repeat experiments for selected CIMS gas-phase markers also demonstrates good repeatability. The highest  $f_{44}$  and O:C values were observed in the wood aerosols. The  $f_{43}$  values were highest in peat and lowest in wood aerosols.

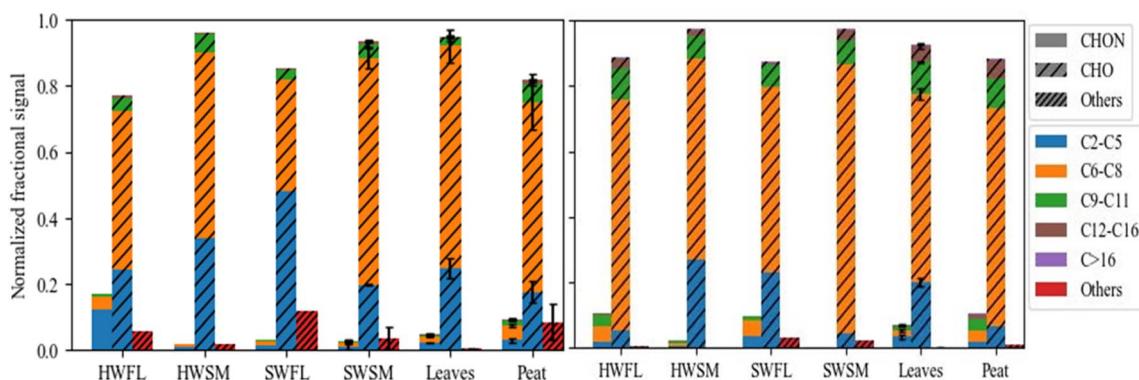
Stove emissions measured here show distinct chemical signatures based on fuel type and burning conditions, with variations in oxygenation ( $f_{44}$ , O:C) and biomass burning tracers ( $f_{60}$ ) influencing their atmospheric behaviour. These differences are critical for improving source apportionment and understanding the health and climate impacts of primary organic aerosols.

### 3.2. FIGAERO-CIMS analysis of gas and particle-phase compounds

**3.2.1. Elemental composition of gas and particle-phase compounds.** The contributions of different functionalities such as the CHO and CHON groups, and the carbon number groups are presented in Fig. 3 for all the compounds identified in this study, and these reveal differences in elemental composition due to fuel type and burning conditions based on the normalized fractional signals.

**3.2.1.1 CHO compounds.** The oxygenated organic aerosols (OOA or CHO) dominated the primary gas and particle phase BB emissions (Fig. 3) across all fuel types and burning conditions. The CHO fraction, on average, was higher in wood followed by leaves and then peat, in both the gas and particle phase. On average, softwood emitted more CHO compounds than hardwood in both gas and particle phases. Smouldering emissions were observed to have a higher fraction of the oxygenated organic compounds compared to the flaming burns in this study. The  $\text{C}_6\text{--C}_8$  fraction was observed to have the highest fractional contribution to the emissions in both the gas and particle phase. This fraction was dominated by  $\text{C}_6\text{H}_6\text{O}_2$ ,

#### A. Gas-phase



#### B. Particle-phase

Fig. 3 Elemental composition of BB (a) gas-phase and (b) particle-phase organics across all experiments. "Others" include non-CHO and non-CHON compounds identified such as nitric acid ( $\text{HNO}_3$ ) as well as C1 compounds (4a). Standard deviations for (A) SWSM ( $n = 2$ ), leaves ( $n = 3$ ) and for peat ( $n = 2$ ); (B) leaves ( $n = 2$ ), are represented by error bars.



$C_7H_8O_2$ ,  $C_8H_{10}O_2$  and  $C_6H_6O_3$  in the gas phase, and the widely established biomass burning tracer  $C_6H_{10}O_5$ , in the particle phase. Higher dominance of the oxygenated  $C_6$ – $C_8$  group was observed in wood smouldering compared to the flaming-phase. The low molecular weight  $C_2$ – $C_5$  compounds were the next most significant fraction and were dominated largely by  $C_2H_4O_2$ ,  $C_3H_6O_3$ ,  $C_5H_8O_3$ , and  $C_5H_8O_4$  in the gas-phase and  $C_2H_4O_3$ ,  $C_4H_6O_4$ ,  $C_5H_6O_4$ , and  $C_5H_8O_4$  in the particle phase. The signal fraction contributed by compounds with  $>C_9$  was comparably higher in the particle phase compared to the gas phase.

**3.2.1.2 CHON compounds.** The nitrogen-containing compounds (CHON or NOCs) contributed  $<20\%$  of the combined signals for all the identified compounds in both the gas and particle phase, across all fuel types and burning conditions. Contributions of gaseous CHON were the highest in hardwood flaming. In the particle phase, the CHON fraction was comparable in wood flaming, leaves and peat emissions. Flaming emissions generally displayed a greater abundance of CHON compounds than smouldering for both wood types. The NOCs were observed to be dominated by the low molecular weight  $C_2$ – $C_5$  compounds. Major contributors in this class of compounds in the gas phase were  $C_2H_3NO$ ,  $C_2H_5NO_3$ ,  $C_3H_3NO_2$ , and  $C_3H_5NO_2$ ;  $C_5H_7NO_3$ ,  $C_5H_9NO_3$ ,  $C_3H_5NO_3$  and  $C_3H_3NO_2$ , were among the top compounds in the particle phase. There was a noticeable, but low contribution from the  $C_6$ – $C_8$  and  $C_9$ – $C_{11}$  classes in the gas and particle phase.

**3.2.2. Chemical characterization of gas and particle-phase compounds.** To evaluate the differences in chemical properties of gas and particle-phase primary emissions from the different fuel types and burning conditions, we present the results from the elemental ratios of H:C and O:C, the OSc, and the aromaticity indices such as DBE, DBE/C and AI for the top 30 gas and particle-phase compounds.

**3.2.2.1 Elemental ratios of the major gas and particle-phase compounds.** The O:C of the 30 most significant oxygenated and nitrogen-containing compounds had very similar ranges in the gas-phase and more variability in the particle phase, across different fuel types. Fig. S6 shows that most of the top 30 gas and particle-phase OOA and NOA compounds occur within the region of O:C  $< 1$  and  $1 < H:C < 2$ . On average, the gas and particle phase O:C of the oxygenated compounds was in the range of 0.55–0.65 and 0.54–0.65 respectively. The nitrogen-containing compounds had relatively lower O:C on average, ranging from 0.40–0.71 and 0.43–0.55 in the gas and particle phase, respectively. The mean H:C of the oxygenated compounds was in the range of 1.40–1.43 and 1.39–1.53 in the gas and particle phase, respectively. The nitrogen-containing compounds had ranges from 1.35–1.57 and 1.26–1.49 in the gas and particle phase, respectively.

Furthermore, most of the top 30 N-containing organic compounds across all experiments in the gas phase exhibited O:N values of  $<3$  except in the hard and soft wood smouldering, which had a significant number O:N  $\geq 3$  (Fig. S7A). More experiments in the particle phase, demonstrated O:N  $\geq 3$  (Fig. S7B).

**3.2.2.2 OSc vs. nC of the major gas and particle-phase compounds.** Fig. S8A and B shows that the OSc has a comparable

ranges across all experiments, with the top 30 CHO and CHON compounds in the gas and particle phase distributed with the region of  $-2 \leq OSc \leq 1$ . It should be noted that OSc for the CHON compounds factors in the oxidation state of nitrogen (OSn), as captured in eqn (1). On average, the OSc of the combined top 30 CHO and CHON species among all burns ranged from  $-0.76$  to  $-1$ , with leaves and peat demonstrating higher mean values than the woodburning emissions. Moreover, the clear separation between the CHO and CHON gas-phase compounds observed in all burns irrespective of fuel type or combustion condition, aligns with the observations in the O:C values, and corroborates the assertions that oxygenated organic compounds are expected to have a higher degree of oxidation than the nitrogen-containing organic compounds.

**3.2.2.3 Aromaticity estimation of the major particle-phase compounds.** To further investigate differences in the chemistry of the emissions from the different fuels and burn phases, the aromaticity of the top 30 most significant compounds in the particle phase was quantified using the DBE, DBE/C ratio and AI, and presented in Fig. 4.

DBE/C and AI values associated with CHON were higher than those associated with the CHO compounds across all biomass types (Fig. 4A and B). Studies show that a threshold DBE/C  $\geq 0.67$  indicates the minimum criterion for the presence of molecules containing condensed aromatic rings; compounds with AI  $> 0.5$  are classified as aromatic, and those with AI  $\geq 0.67$  are classed as condensed aromatic compounds.<sup>46</sup> According to Koch and Dittmar,<sup>46</sup> generally, AI  $> 0.5$  is the minimum criterion for the presence of aromatic species. This therefore means that the top 30 CHO and CHON compounds in the particle phase with a maximum DBE/C of 0.71 and 1.0 respectively and AI values of 0.5 and 1.0 respectively, may contain aromatic and condensed aromatic molecules. It is noteworthy that, although AI is a more conservative approach to aromaticity estimation, it provides more reliable information than the DBE/C metric.<sup>46</sup>

Fig. 4A and B provides information on the aromaticity of the top 30 CHO and CHON compounds in the particle-phase of the different fuel types. As expected, similar behaviour was observed among the CHO compounds in all the fuel types since DBE is independent of oxygen number (Fig. 4A).<sup>46</sup> The DBE/C ratio displayed an inverse relationship *versus* H:C consistent with the observations of Koch and Dittmar,<sup>46</sup> that an increasing number of H atoms in a molecule decreases unsaturation (lower DBE values) and *vice versa*. Fig. 4B (CHON) also shows that aromatic compounds were more prevalent as more nitrogen-containing compounds than oxygenated compounds appear above the aromaticity threshold of DBE/C  $\geq 0.67$  and AI  $> 0.5$ . This suggests that the CHON compounds may contribute more to aromaticity in organic aerosols than CHO compounds, and may also contain larger chromophoric substances.<sup>45</sup> Fig. 4B also reveals a higher number of compounds (and with larger signal intensity) in the aromatic region for hardwood flaming phase emissions compared to their smouldering phases. A similar observation was noted for softwood flaming in comparison to smouldering. In addition, it was also observed that leaves may



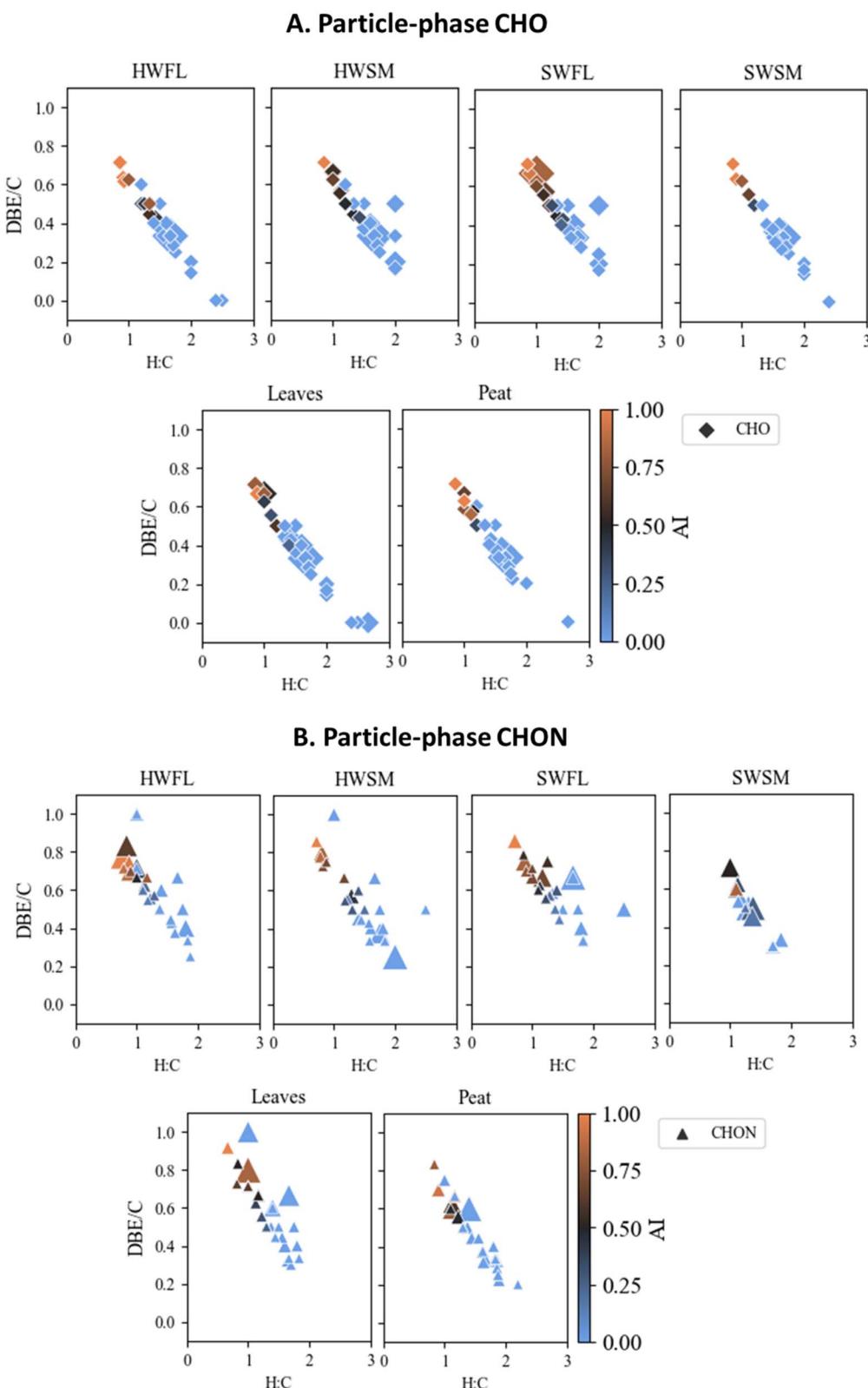


Fig. 4 Particle phase DBE/C vs. H : C ratios in (A) CHO compounds and (B) CHON compounds for different fuel types, coloured-scaled with the aromaticity index.

emit more aromatic compounds in comparison to other fuel types, containing compounds with the highest AI and DBE/C values of 1 in the particle phase.

## 4 Discussion

### 4.1. Insights from primary aerosol composition according to AMS data

**4.1.1. Differences in aerosol composition based on fuel type.** When looking at the AMS data, our results indicate differences in the aerosol composition based on the different fuel types used here. Differences in emissions are likely because of the difference in composition.<sup>13,48</sup> However, the observed higher levels of organic aerosol in peat compared to wood in this study is not consistent with a previous report involving quadrupole-ACSM measurement directly from a stove,<sup>11</sup> probably due to the design and operation of the stove used in their study. The low BC values observed for peat and leaves in this study, compared to wood, are consistent with the findings of Engling *et al.*<sup>49</sup> who explained that the combustion process for peat is akin to a smouldering combustion (characterized by low combustion efficiency); hence peat emissions contain high organic contents but low BC. This is also applicable to leaf burning. In addition, the OA/BC ratios of this study fall within the range observed by McClure *et al.*<sup>9</sup> who reported OA/BC ratios varying between 0.3 and 10 from the laboratory combustion and study of different biomass fuels including softwood, hardwood and peat in their chamber.

The  $f_{44}$  (and O : C by extension), as well as  $f_{60}$  values were higher in wood-burning aerosols compared to leaves and peat, excluding the softwood flaming burn which had the lowest  $f_{60}$  (Fig. 2). This indicates that the primary wood aerosols displayed a greater degree of oxygenation compared to leaves and peat, with leaf combustion exhibiting a higher oxygenation compared to peat. While previous studies have compared the differences in oxygenation in wood and peat aerosols,<sup>11</sup> there is little or no information on that of leaves. Chen *et al.*<sup>50</sup> observed similarly low  $f_{44}$  values for peat in their study using a combustion chamber and suggested that primary aerosols from peat are not highly oxygenated. Similar to this study, lower  $f_{60}$  values for peat in comparison with wood have previously been found.<sup>11</sup> This may be because of the lower cellulosic content of peat.<sup>51</sup>  $f_{60}$  is a marker for levoglucosan, a product of the pyrolysis of cellulose and hemicellulose; hence lower levoglucosan levels in peat compared to wood will result in lower  $f_{60}$  values from peat combustion. However, the higher  $f_{43}$  values in peat compared to wood and leaf aerosol particles observed in this study, are consistent with the results of Lin *et al.*,<sup>11</sup> who noted higher levels of  $m/z$  43 in peat than in wood.

**4.1.2. Differences in wood aerosol composition based on burning conditions.** The wood smouldering combustion produced a higher organic aerosol concentration and hence higher OA/BC, while the flaming burns produced the largest BC concentrations and lower higher OA/BC (Table S1), in agreement with previous flaming and smouldering woodstove observations.<sup>28</sup> Similarly, higher total particulate nitrate levels were observed in wood smouldering compared to flaming. The higher OA/BC in smouldering compared to flaming aerosol particles suggests that the smouldering may result in a higher

SOA yield compared to the flaming, previously observed using a wood stove.<sup>28</sup> The flaming burn had higher O : C and slightly higher  $f_{44}$  values than smouldering, both indicating more oxygenated OA. The  $f_{44}$  trend in this study is consistent with observations of Bertrand *et al.*<sup>8</sup> in their wood burning study using a logwood stove and pellet burner. However, Weimer *et al.*<sup>52</sup> using a wood stove and automatic burner to study different wood types, observed higher  $m/z$  44 values in the smouldering phase compared to flaming. While hardwood aerosols had very similar  $f_{44}$  and O : C values irrespective of burning conditions, softwood aerosols exhibited more differences between the burning phases (Fig. 2). The  $f_{43}$  values were comparable in both burning phases (Table S1) and may be limited as a metric to differentiate between burn phases. The inorganic species collectively exhibited a higher dominance in the smouldering phase compared to flaming aerosols.

As shown in Fig. 2, the smouldering conditions displayed higher  $f_{60}$  values than flaming, in consonance with previous flaming and smouldering observations in a woodstove<sup>8</sup> and simulated wildfires.<sup>53</sup> This suggests that  $f_{60}$  may be a useful metric to differentiate between flaming and smouldering burns; however McClure *et al.*<sup>9</sup> differs, stating that  $f_{60}$  is not a useful metric to distinguish between different burn conditions because of their observation of very similar  $f_{60}$  values in both the flaming and smouldering phase, albeit from a wildfire simulation study. Furthermore, Fig. 2 reveals that most of the aerosols are elevated well above the 0.3% of OA  $f_{60}$  background level as expected for BB-impacted air masses.<sup>37</sup> Interestingly, softwood flaming aerosols are positioned very close to the  $f_{60}$  background line, demonstrating a behaviour akin to air masses with negligible BB influence.<sup>54,55</sup> The low  $f_{60}$  values observed in softwood flaming may be attributed to the relatively lower levels of  $C_6H_{10}O_5$  (levoglucosan and levoglucosan-like molecules) in comparison to other experiments (Fig. S5B). Cubison *et al.*<sup>37</sup> reported that  $f_{60}$  is required stay above 0.3% of the OA background line for effective BBOA source prediction analysis using PMF. This therefore implies that it may be difficult to detect an air-mass influenced by softwood flaming aerosols in the atmosphere. This finding supports the notion from previous studies that the use of levoglucosan as a marker of wood burning has high uncertainties.<sup>56</sup>

### 4.2. Differences in FIGAERO-CIMS gas and particle phase composition and characteristics due to fuel type

The dominance of oxygenated compounds (OOAs) irrespective of fuel type observed in this study is consistent with previous observations from a variety of biomass fuels using different appliances.<sup>57,58</sup> Higher mean levels of OOA in softwood than hardwood is probably because softwoods have resin canals that facilitate the storage of volatile terpenes (monoterpenes and sesquiterpenes), unlike hardwoods.<sup>59</sup> OOAs are important because of their significant contribution to SOA formation in the atmosphere due to their high reactivity and wide range of volatility.<sup>39,60</sup>

Among the CHO group,  $C_6H_6O_2$ , an aromatic, phenolic OOA shows dominance by signal fraction (a range of 8.7–39%) across all biomass types in the gas-phase, consistently appearing in the



top 3 most influential compounds by percentage contribution (Fig. S5A).  $C_6H_6O_2$  observed in this study may be attributed to catechol since this isomer has been widely identified in BB studies.<sup>61</sup> The greatest  $C_6H_6O_2$  contribution was observed in leaves followed by peat with the lowest in softwood flaming. Although  $C_6H_6O_2$  is well recognized as a component of POA from BB, to our knowledge, there is little or no information on its dominance in primary BB emissions. The dominance by signal of  $C_6H_6O_2$  in the wood burning emissions observed in this study, may be due to its formation from guaiacol radicals, produced from the breakdown of guaiacol at high temperatures.<sup>6</sup> However, this does not offer an explanation for the high levels of  $C_6H_6O_2$  in leaves and peat which were combusted at much lower temperatures. The high levels of  $C_6H_6O_2$  in leaves and peat in this study could be attributed to their high lignin content, since  $C_6H_6O_2$  is a product of lignin pyrolysis.<sup>62</sup> The observed abundance of  $C_6H_6O_2$  in the solid fuels' emissions of this study (wood and peat) and its potential transformation into nitrocatechol ( $C_6H_5NO_4$ ), suggests possible health implications for domestic solid-fuel burning due to its recognized toxicity, and climate impacts from its contribution to BrC aerosol formation.<sup>63</sup> In a previous laboratory BB study, nitrocatechol emissions had the highest mass among NACs irrespective of the wood type.<sup>64</sup>  $C_6H_{10}O_5$  recognized as levoglucosan and its isomeric derivatives such as mannosan and galactosan have long been established as biomass burning markers.<sup>13,39</sup> Its recognition as the most dominant organic compound in the particle-phase as observed in this study (Fig. S5B) is known.<sup>61</sup> Moreover, its accelerated gas-particle partitioning establishes its relatively low levels in the gas-phase of this study and abundance in the particle phase.<sup>65</sup>

The low emissions of nitrogen-containing compounds in all the different fuel types are dominated by low-molecular weight CHON compounds, and comparable to those in the study of Zhou *et al.*<sup>60</sup> The abundance of  $O:N < 3$  compounds in the gas-phase CHON (Fig. S7A) indicates the presence of reduced nitrogen-containing functional groups such as imides, isocyanates and amines,<sup>53</sup> previously observed in biomass burning emissions.<sup>17</sup> The particle phase displayed a greater number of compounds with  $O:N \geq 3$  across all fuel types (Fig. S7B), possibly indicating considerable presence of compounds with nitro ( $-NO_2$ ) and/or organic nitrates ( $-ONO_2$ ) functional groups. In this study, particulate organic nitrogen (ON) fractions in the primary emissions were observed higher than gaseous ON fractions, similarly reported by Cai *et al.*<sup>66</sup> Moreover, the relatively high fraction of CHON compounds in peat in the gas and particle phase (in comparison with the other fuels) may be a result of the known high nitrogen content of peat fuels.<sup>67</sup> Low contributions from CHON compounds observed in the gas and particle phase BB emissions of this study do not necessarily make them less important because certain classes of these compounds such as the NACs exhibits intense radiative forcing effects as well as detrimental impacts on health even at negligible concentrations which emphasizes the need for continuous investigation of their atmospheric behaviour and sources.<sup>63</sup>

### 4.3. Differences in composition and characteristics due to combustion conditions

The observed higher fraction of the oxygenated compounds in wood smouldering emissions compared to flaming is consistent with the results of Stefenelli *et al.*<sup>68</sup> in their domestic stove emission study under flaming and smouldering conditions. The higher fraction of oxygenated OA in the smouldering gas and particle phase emissions indicates that the smouldering burn may contribute to higher SOA formation, cloud nucleation and hygroscopicity potential due to the presence of more oxygenated species.<sup>69</sup> The observed CHO contribution in the gas phase in the flaming phase of this study is highly consistent with previous flaming-phase observations.<sup>14,60</sup> However, Evtyugina *et al.*<sup>70</sup> in their study of different wood fuels using a domestic woodstove and fireplace similarly under flaming conditions, observed much lower CHO contribution in their study, probably because they did not consider emissions from lower molecular weight organic gases like acetic acid, which are known to be emitted in large quantities in biomass emissions.<sup>14,58</sup>

The higher fraction of the oxygenated  $C_6-C_8$  group in wood smouldering compared to flaming suggests that smouldering emissions may emit higher levels of oxygenated aromatic compounds.  $C_6H_6O_2$  levels, being one of the most dominant compounds by signal, in the gas-phase were generally observed to be higher under smouldering conditions (associated with lower temperatures) compared to flaming. This is consistent with observations in previous studies and may be because methoxyphenols such as guaiacol are heat-sensitive; hence its decomposition may increase with temperature.<sup>68</sup>

The relatively higher fraction of CHON compounds in hardwood flaming gas-phase emissions may be attributed to the observed higher  $NO_x$  concentrations (Fig. S9). This is supported by the positive correlation between NO (and  $NO_x$ ) and CHON ( $O:N \geq 3$ , organic nitrates) previously observed.<sup>71</sup> However, this offers no explanation for the observed low CHON contributions to hardwood smouldering in the gas-phase, with similarly high  $NO_x$ . The particle-phase CHON fraction was observed to be higher in both hard and soft wood flaming emissions compared to smouldering. In contrast, the particulate organic nitrate (PON) mass estimated from the AMS unit mass resolution (UMR)  $m/z$  30 : 46 ratio (representing the  $NO^+/NO_2^+$  ratio, also referred to as the  $NO_x^+$  ratio)<sup>72</sup> and described in the SI (Fig. S10), was observed to be higher in smouldering aerosol particles compared to flaming (Fig. S10), averaging 75% of the total particulate nitrate mass in both combustion phases. The high percentage of PON in total particulate nitrate corresponds to the results of the CIMS particle phase data, where a large number of compounds with  $O:N \geq 3$  possibly indicating organonitrogen compounds, were observed.

The higher mean  $O:C$  in flaming emissions observed in this study in comparison to smouldering burns is consistent with the observation of Reece *et al.*,<sup>73</sup> who noticed an increase in  $O:C$  and decrease in  $H:C$  with improving combustion efficiency (obtainable in flaming burns) in their characterization of emissions from three different biomass cookstoves. This is consistent with the observations from the AMS data with



similarly higher O:C in the flaming burn aerosol particles compared to smouldering.

Furthermore, the observed higher DBE/C and AI values in wood flaming emissions compared to smouldering indicates that flaming emissions may display greater aromaticity than smouldering emissions, possibly because of a greater abundance of aromatic compounds in the flaming phase of wood than in the smouldering phase.<sup>68</sup> This is consistent with the observations of Kim *et al.*<sup>74</sup> who observed a greater mutagenic and lung toxicity potential in flaming phase emissions compared to smouldering from the combustion of several biomass fuels in a furnace.

## 5 Conclusions and implications

By studying controlled smoke injections into an aerosol chamber using the combined measurements of an iodide FIG-AERO-CIMS and an AMS, we were able to chemically characterise the primary emissions of a stove, while controlling key variables such as fuel type and combustion phase. These experiments offered new insights into primary emissions and provide a chemical basis for subsequent studies on secondary chemistry, toxicology and interpretations of ambient observations. We observed differences in the aerosol particle composition between peat, leaves and wood fuels. However, contrary to the study of McClure *et al.*<sup>9</sup> we found that the AMS  $f_{60}$  is a useful metric to distinguish between burning conditions, displaying higher values in the smouldering phase compared to flaming for both wood types. This is likely because McClure *et al.*<sup>9</sup> studied a laboratory wildfire simulation, unlike this study based on stove emissions. Also, while previous studies establish the usefulness of levoglucosan or the AMS  $f_{60}$  metric in BBOA source apportionment studies, we found that air masses influenced by softwood flaming aerosols in the atmosphere may not be detected as BBOA because of low  $f_{60}$ , below the  $f_{60}$  background level. Trace elements like K<sup>+</sup> and Zn or a combination of levoglucosan and trace elements are recommended to provide more accurate results.

Consistent with previous observations, the oxygenated compounds dominated the stove emissions irrespective of fuel type and burn condition, and were higher in wood compared to leaves and peat. The smouldering burn had a higher oxygenated fraction than flaming in wood emissions, and thus may possess a higher SOA yield.<sup>69</sup> The dominance of the C<sub>6</sub>H<sub>6</sub>O<sub>2</sub> signal in the gas phase was observed in all fuel types and burning conditions along with C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> in the particle phase (excluding softwood flaming). C<sub>6</sub>H<sub>6</sub>O<sub>2</sub> and C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> are products of lignin and cellulose pyrolysis respectively and support the contribution of biomass burning to brown carbon emissions as noted by Ye *et al.*<sup>39</sup> Among the nitrogen-containing compounds, the results of this study indicate a dominance of reduced nitrogen and organo-nitrogen compounds in the gas and particle phase, respectively. The CHON fraction, on average was more pronounced in the particle-phase and contributed more to aromaticity in BB organic emissions than the oxygenated species. Wood flaming emissions displayed greater aromaticity in the particle phase due to a greater CHON fraction, compared to the smouldering phase. The results

also demonstrate that leaf emissions display greater aromaticity than wood and peat because of the presence of CHON compounds with higher DBE/C and AI values.

The photochemical aging effects on the composition and characteristics of fresh smoke from stove emissions and the implication for health will be examined in subsequent publications. Also, insights from this study and aging effects will be explored in source apportionment studies of ambient data, to aid the evaluation of the possible chemical and toxic effects of primary and secondary wood smoke in the atmosphere. Overall, this study enhances our comprehension of POA from a variety of biomass types and burning conditions and provides a critical basis for furthering our understanding of biomass burning related-SOA.

## Author contributions

O. E. O., J. D. A., G. M., A. V., D. H. and P. G. contributed to conceptualization. O. E. O., A. V., D. H., and S. A. S. contributed to investigation. O. E. O., A. V., T. B., S. A. S. and H. W. contributed to formal analysis. O. E. O. wrote the original draft with contributions from A. V., T. J. B. and J. D. A. All authors contributed to reviewing. O. E. O. and J. D. A. contributed to editing.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

The data supporting the findings of this study are partly included in a summarized table in the supplementary information (SI). Additional data can be obtained from the corresponding author upon request.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ea00080g>.

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