



1 **Molecular Composition of Oxygenated Nitrogen-Containing Organic**
2 **Compounds Emitted from Combustion of the Three Biomass Macro-**
3 **Components**

4 Hongxing Jiang^{1,2}, Junjie Cai³, Yu Peng,³ Tingting Li⁴, Yanlin Zhang^{*2,5}, Yingjun Chen^{*3,6},
5 Jianmin Chen^{3,6}

6 ¹School of Environmental Science and Engineering, Nanjing University of Information Science and Technology,
7 Nanjing, Jiangsu 210044, China.

8 ²Jiangsu Key Laboratory of Intelligent Atmospheric Environment Monitoring and Carbon-Pollution Co-control,
9 Nanjing University of Information Science and Technology, Nanjing 210044, China.

10 ³Shanghai Key Laboratory of Air Quality and Environmental Health, Department of Environmental Science and
11 Engineering, Fudan University, Shanghai 200433, China.

12 ⁴Oil and Gas Technology Institute of PetroChina Changqing Oilfield Company, Xi'an 710018, China.

13 ⁵School of Ecology and Applied Meteorology, Nanjing University of Information Science and Technology,
14 Nanjing 210044, China.

15 ⁶Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China.

16 *Correspondence to:* Y. Zhang (zhangyanlin@nuist.edu.cn); Y. Chen (yjchenfd@fudan.edu.cn)

17 **Abstract.** Biomass burning is an important source of oxygenated nitrogen-containing organic compounds,
18 but their formation mechanisms remain unclear. CHON compounds in organic aerosols (OAs) from cellulose,
19 hemicellulose, and lignin combustion at three ignition temperatures (IGT) under full-oxygen conditions were
20 characterized by high-resolution mass spectrometry in negative and positive electrospray ionization modes. Our
21 results indicate that CHON[−] and CHON⁺ compounds account for 13–60% and 3.4–32% of OA intensity,
22 respectively, with the composition depending strongly on fuel type and IGT. Lignin-derived CHON compounds
23 had higher aromatic fractions than cellulose- and hemicellulose-derived CHON compounds at low IGT, and all of
24 them had high fractions of reduced-N species with high N contents. With the increasing IGT to 600 °C, the
25 fractions of aromatic CHON increased for OA_{cellulose} and OA_{hemicellulose} but not for OA_{lignin}. However, the molecular
26 overlap of CHON compounds among the three OAs elevated, resulting in high similarity in the composition of
27 nitro-phenolic-like compounds. More reduced-N aromatic compounds were produced at 800 °C for all fuels, but
28 lignin yielded abundant condensed aromatic species. Our findings provide molecular-level insight into CHON
29 chemodiversity across fuel types, and are beneficial for assess the climate and health effects of biomass burning
30 OAs accurately.



31 **Keywords:** NOCs, biomass burning, HR-MS, ignition temperature, fuel types, NACs, condensed aromatic CHON
32 compounds.

33 1 Introduction

34 Nitrogen-containing organic compounds (NOCs) constitute a significant fraction of atmospheric organic
35 aerosol (OA), accounting for up to 10–40% of the OA mass (Yu et al., 2024; Jiang et al., 2023; Liu et al., 2025).
36 Oxygenated NOCs (oxy-NOCs), including organic nitrates and nitroaromatic compounds, are the major
37 components of NOCs. These species not only exert significant impacts on radiative forcing and human health, but
38 also play a crucial role in modulating the nitrogen cycle within ecosystems (Li et al., 2025; Li et al., 2023). For
39 instance, nitroaromatic compounds (NACs) have been identified as an important class of atmospheric brown
40 carbon (BrC) chromophores, contributing over 50% of BrC light absorption in biomass burning (BB) influenced
41 aerosols (Desyaterik et al., 2013; Lin et al., 2017), and thereby affecting regional radiative forcing. Furthermore,
42 NACs are recognized as toxic pollutants in the atmosphere, posing adverse effects on human health (Zhang et al.,
43 2023b; Cao et al., 2025). It was reported that NOCs accounted for up to 20%–80% of total nitrogen deposition
44 globally (Li et al., 2023; Sun et al., 2026). Organic nitrates formed via atmospheric oxidation sequester inorganic
45 nitrogen on one hand, while on the other hand, they can undergo hydrolysis and photolysis to release inorganic
46 nitrogen, thereby acting as a significant secondary source of particulate nitrate (González-Sánchez et al., 2023b).

47 Although atmospheric secondary processes represent major sources of oxy-NOCs, primary emissions,
48 especially from BB, have also been identified as a significant contributing source (Song et al., 2022; Wang et al.,
49 2017b; Tang et al., 2020). For instance, our recent study has shown that anthropogenic sources could contributed
50 89–96% of the total oxy-NOCs signals (Jiang et al., 2023). More notably, the NACs are frequently detected and
51 present high emissions in fresh biomass burning organic aerosols (BBOA) (Wang et al., 2017a; Zhang et al., 2022;
52 Zhang et al., 2023a). Additionally, it has been reported that BB accounts for approximately 78% of global organic
53 nitrogen deposition (Li et al., 2023). However, the substantial variability in the chemical composition of BB-
54 derived NOCs gives rise to an order-of-magnitude spread in the N/C ratio, a key input parameter for nitrogen
55 deposition estimation, thereby introducing significant uncertainty into the assessment (Li et al., 2023; Li et al.,
56 2025). Biomass raw materials, especially straw, are typically rich in alkaloids (Laskin et al., 2009; Wang et al.,
57 2017b). During combustion processes, these alkaloids will undergo pyrolysis and release reduced-nitrogen species
58 or fragments, which further form primary oxy-NOCs. Also, the abundant volatile precursors released from BB



59 can rapidly react with NO_x within the plume atmosphere, forming oxy-NOCs including NACs (Zhang et al., 2022).
60 Consequently, the factors influencing NOC emissions from BB are complex and multifaceted. A recent study
61 demonstrated that emission factors of NACs from residential solid fuel combustion, including BB, are influenced
62 by multiple factors such as fuel type, combustion efficiency, and moisture content, among which fuel type and
63 combustion efficiency are the two most critical parameters (Zhang et al., 2022; Zhang et al., 2023a). Studies also
64 revealed that emission factors of NACs from BB can span multiple orders of magnitude, with their compositional
65 profiles varying substantially with fuel type and combustion conditions (Wang et al., 2017a; Zhang et al., 2022;
66 Zhang et al., 2023a). A recent study based on high-resolution mass spectrometry combined with non-targeted
67 analysis further revealed significant differences in the molecular composition of oxy-NOCs generated from the
68 combustion of wood and straw (Song et al., 2022). Nevertheless, the underlying causes of these compositional
69 discrepancies, as well as the formation mechanisms of NOCs from different biomass fuel types, remain poorly
70 understood.

71 Cellulose (Cel), hemicellulose (Hcel), and lignin(Lign) are the major three macroscale biomass components
72 (TMBCs), displaying substantially different structural features and chemical compositions (Dhyani and Bhaskar,
73 2018; Collard and Blin, 2014). Cellulose and hemicellulose are both polysaccharides, but the degree of
74 polymerization of hemicellulose is much lower than that of cellulose and thus presented lower temperatures for
75 the decomposition rate (Collard and Blin, 2014; Li, 2014). In addition, hemicellulose exhibits a more complex
76 and amorphous composition than cellulose, which varies with plant species (Collard and Blin, 2014; Zhou et al.,
77 2017). Lignin is a complex three-dimensional amorphous polymer built from phenylpropane structural units,
78 typically featuring three types: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) (Kibet et al., 2012; Collard
79 and Blin, 2014; Kawamoto, 2017). The structural and compositional differences among cellulose, hemicellulose,
80 and lignin lead to distinct combustion behaviors and variations in the emitted flue gas composition, which in turn
81 contribute to differences in the profiles of pollutants, such as VOCs (Cheng et al., 2022; Zhu et al., 2022), PAHs
82 and EC (Wang et al., 2023). However, to our knowledge, no study has yet investigated the differences in NOCs
83 emissions from the combustion of the TMBCs.

84 High-resolution mass spectrometry techniques such as Fourier-transform ion cyclotron resonance mass
85 spectrometry and Orbitrap mass spectrometry, coupled with an electrospray ionization (ESI) source and
86 nontargeted analysis, have been successfully employed to characterize the molecular composition of organic
87 aerosols (Tang et al., 2020; Bianco et al., 2018) and their subfractions, including nitrogen- (Wang et al., 2017b;



88 Song et al., 2022; Jiang et al., 2023; Liu et al., 2025; Jiang et al., 2022a) and sulfur-containing organic species
89 (Jiang et al., 2022b; Jiang et al., 2025). In this study, commercial cellulose, hemicellulose, and lignin were selected
90 as fuels and combusted in a laboratory-scale quartz tube furnace at ignition temperature (IGT) of 400, 600, and
91 800 °C under full-oxygen conditions. The molecular composition of oxy-NOCs emitted in the particulate matter
92 was characterized using high-resolution Orbitrap mass spectrometry in both positive and negative ESI (ESI+ and
93 ESI-) modes. Our investigation (1) elucidated the molecular composition of NOCs emitted from the combustion
94 of the three individual biomass components and the differences therein, and (2) revealed the temperature-
95 dependent evolution of NOC molecular profiles during combustion. These findings contribute to a deeper
96 understanding of the molecular characteristics and formation mechanisms of NOCs in biomass combustion
97 emissions.

98 **2 Materials and Methods**

99 **2.1 Combustion Experiments and PM Samples Collection**

100 About 2 g commercial cellulose (purity≥95%, 50 μm, J&K Scientific), hemicellulose (xylan, purity≥95%,
101 50 μm, J&K Scientific) and lignin (alkaline, TCI) were used for the combustion experiments respectively. Details
102 about the structure of TBMCs and the combustion and sample collection system were presented in Figure S1 (Han
103 et al., 2018; Wang et al., 2023). Briefly, the fuels were placed onto a ceramic crucible and heated in a quartz tube
104 furnace combustion at the set temperatures of 400 °C, 600 °C and 800 °C with 20% oxygen contents, respectively.
105 Noted that the IGT represented the furnace temperatures, which means that during the combustion processes, the
106 furnace temperatures will keep in constant. The temperature gradient settings in this study can well simulate the
107 changes in combustion state from the traditional low-efficiency stoves to improved high-efficiency stoves, and
108 could provide reference for understanding the generation of NOC in residential stove combustion. Flue gas from
109 the quartz tube was introduced into a dilution chamber (L=550 mm, Φ=48 mm) and mixed with air (flow of ~5
110 L/min) with the dilution ratio of ~20. The diluted flue gas was subsequently introduced a particle matter sampler
111 (~18 L/min). Each material was combusted three times at a specific IGT to obtain the parallel samples, and the
112 uncertainty of measured OC was within 1%.



113 2.2 HR-MS analysis

114 To minimize the well-known “matrix effects” during the HR-MS analysis processes, a widely used method
115 is adoption the same carbon concentrations for analysis (Jiang et al., 2021; Kellerman et al., 2014). Filters with
116 similar organic carbon (OC) contents (~50 µg C) were punched and extracted with 2 mL methanol/
117 dichloromethane (v:v=1:1) (3 times) under the cold-water bath for 20 minutes. The combined extracts were then
118 filtered with 0.22 µm PTFE membranes, and concentrated to 200 µL. The molecular composition of OA derived
119 from the combustion of cellulose, hemicellulose and lignin (OA_{Cel}, OA_{Hcel} and OA_{Lign}) was analyzed using a high-
120 resolution Q-Exactive Orbitrap mass spectrometer equipped with a heated ESI source (Thermo Electron, Inc.).
121 Analysis was performed in both ESI+ and ESI– modes in this study, as ESI+ mode can provide supplementary
122 information of the reduced NOCs. Detailed information about the instrument setting were described in Text S1
123 (Hoffmann et al., 2011; Jiang et al., 2018; Laskin et al., 2018). Samples were directly injected through a syringe
124 at a flow rate of 5 µL/min, and an average mass spectrum of 5 min detection was obtained. Mass spectra data
125 acquired in all modes was set in the range of m/z 90–800 with a mass resolving power of 140000 at m/z 200.

126 2.3 Peak assignment and data processing

127 All the mass peaks with a signal-to-noise ratio (s/n) higher than 4 were exported using the Xcalibur software
128 (V2.3, Thermo Scientific), and subsequently processed via an open-source R package of MFAssignR to obtain the
129 molecular formula (MF) (Schum et al., 2020). For the mass peaks obtained in the positive modes, [H]⁺ and [Na]⁺
130 adducts were allowed to be present. All the assigned MF detected in ESI– mode can be classified into 4 groups
131 (CHO, CHON, CHOS and CHNOS) based on the elemental composition, and additional groups of CH, CHN,
132 CHS and CHNS are also assigned for the peaks detected in ESI+ mode. Molecules presented in the blank sample
133 were all subtracted from the samples. A series of elemental ratios (e.g., H/C and O/C), DBE, modified aromatic
134 index (AI_{mod}) (Koch and Dittmar, 2016), aromaticity equivalent (Xc) (Yassine et al., 2014) were calculated (details
135 see Text S2).

$$136 \quad \text{DBE} = (2n_C + 2 - n_H + n_N) / 2$$

$$137 \quad \text{AI}_{\text{mod}} = (1 + n_C - 0.5n_O - n_S - 0.5n_H) / (n_C - 0.5n_O - n_S - n_N)$$

$$138 \quad \text{Xc} = (3[\text{DBE} - (m \times n_O + n \times n_S)] - 2) / (\text{DBE} - (m \times n_O + n \times n_S)).$$

139 where n_C , n_H , n_O , n_N , and n_S denote the numbers of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms in
140 formula, respectively; m and n correspond to the fraction of oxygen and sulfur involved in the π -bond structure

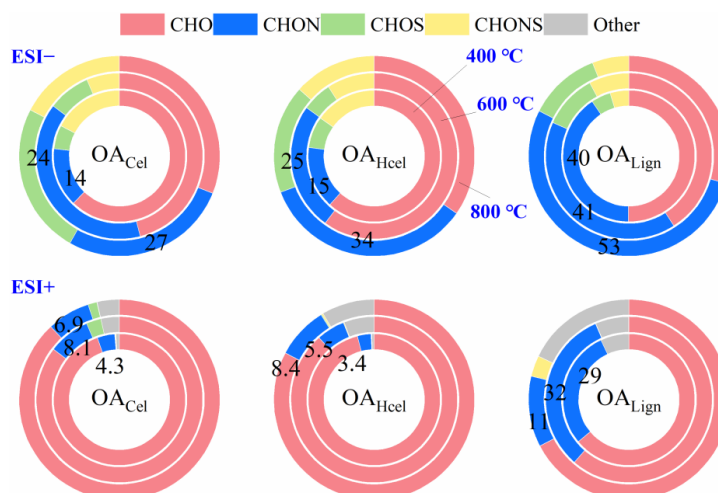


141 of the compound, respectively.

142 **3 Results and Discussion**

143 **3.1 General characteristics and diversity of oxy-NOCs.**

144 Although ESI⁺ and ESI[−] modes exhibit different sensitivities toward CHON compounds, yielding distinct
 145 compositional profiles, both modes confirm that CHON compounds are prevalent in the OA emitted from the
 146 TMBCs. As shown in Figure 1 and Table S1, the formula number of CHON[−] and CHON⁺ were in the range of
 147 327-1042 and 300-1098, accounting for 13-60% and 3.4-32% of total OA intensity in the two separate analytical
 148 mode, respectively. This indicated not only the high diversity of the molecular characteristics but also the
 149 importance of CHON compounds in OA emitted from the TMBCs. As shown in Figure 1, the relative intensity of
 150 CHON compounds varied significantly depending on the fuel types and IGT. The CHON compounds in OA_{Lign}
 151 typically showed higher relative abundance than those in OA_{Cel} and OA_{Hcel} in both analytical modes. However,
 152 the effect of IGT on the relative abundance of CHON compounds varies in two modes. The relative abundances
 153 of CHON[−] compounds in OA₆₀₀ and OA₈₀₀ were clearly higher than that in OA₄₀₀ for all the three biomass fuels.
 154 For CHON⁺ compounds, a similar trend was observed only for OA_{Cel} and OA_{Hcel}, but the relative abundances of
 155 CHON⁺ in OA_{Lign,400} and OA_{Lign,600} were higher than that in OA_{Lign,800}. This might indicate that the formation
 156 mechanisms of CHON compounds varied with compound types, as the two analysis modes target different types
 157 of compounds. The ESI[−] mode has better performance for CHON species with higher oxidation degree, while the
 158 reduced-N substances such as amines, N-heterocycles tend to show high abundance in ESI⁺ mode (Wang et al.,
 159 2018; Song et al., 2022). Thus, an increase in IGT probably is beneficial for the generation of nitro oxygen-
 160 containing species. Meanwhile, the fixed reduced-N in TMBCs (especially lignin, which has a higher content than
 161 that of cellulose and hemicellulose) are released during the combustion process, but the released C-N bonds could
 162 be broken as the temperature increase, resulting in a decrease in the abundance of reduced-N species.



163

164 **Figure 1.** Intensity proportions of elemental formula groups in OA from the combustion of cellulose,
 165 hemicellulose and lignin at 400 °C, 600 °C and 800 °C. Only the percentages (%) of CHON compounds are
 166 presented.

167 Table S2 and S3 presented the intensity-weighted averaged chemical parameters of CHON⁻ and CHON⁺
 168 compounds detected in OA from combustion of the TMBCs, including molecular weight (MW^{*}), element ratios
 169 (e.g., H/C^{*} and O/C^{*}), and indicators characterizing aromaticity and unsaturation of carbon atoms (AI^{*} and
 170 DBE/C^{*}). The MW^{*} of both CHON⁻ and CHON⁺ compounds in OA_{Cel} and OA_{Hcel} gradually decreases as the
 171 IGT increases. Nevertheless, the MW^{*} showed opposite trends along with the IGT for CHON⁻ and CHON⁺
 172 compounds in OA_{Lign}, with its values reaching lowest and highest at 600 °C, respectively. Given that the
 173 combustion efficiency increased with the IGT elevation (Table S1), the increase in IGT usually led to a deeper
 174 degree of fuel pyrolysis. However, due to the presence of benzene ring structure in lignin, a different pyrolysis
 175 phenomenon was presented compared to the two polysaccharide fuels. H/C^{*} ratio, which could reflect the
 176 saturation degree of compounds, showed different trends along with IGT for CHON⁻ and CHON⁺ compounds.
 177 The H/C^{*} value of CHON⁻ compounds displayed a decreasing trend with increasing IGT for all OAs, while an
 178 opposite trend was observed for the CHON⁺ compounds. Similar results can also be found for the index of
 179 DBE/C^{*} and AI^{*} values, and higher aromaticity was observed for lignin derivatives than that of cellulose and
 180 hemicellulose. In OA generated from TMBC combustion at high IGT, CHON⁺ compounds generally presented
 181 lower DBE/C^{*} and AI^{*} values, whereas CHON⁻ compounds exhibited higher DBE/C^{*} and AI^{*} values. These
 182 results not only reflect the effect of increasing IGT on the saturation degree of CHON compound carbon skeleton,



183 but also indicate that different types of compounds have different responses to IGT.
184 While the O/C^* and N/C^* ratios of CHON compounds differed between the two analytical modes, their variations
185 with IGT followed similar trends for both CHON⁻ and CHON⁺ compounds. At high IGT, cellulose- and
186 hemicellulose-derived CHON compounds generally had lower O/C^* ratios, while lignin-derived CHON
187 compounds showed the opposite trends. Similar results were also observed for nO_{eff}^* , a metric that excludes
188 oxygen atoms in nitro groups and therefore better reflects the potential carbon oxidation degree (Nie et al., 2022).
189 A plausible explanation for this observation is that the oxygen atoms in cellulose and hemicellulose are
190 predominantly present as hydroxyl ($-OH$) and glycosidic ether ($C-O-C$) groups, whereas those in lignin exist
191 mainly as phenolic hydroxyl and methoxy ($-OCH_3$) groups. With increasing IGT, the oxygen atoms in cellulose
192 and hemicellulose are more readily eliminated compared to those in lignin. In contrast, elevated IGT tend to induce
193 intramolecular rearrangement of oxygen atoms within phenolic hydroxyl and methoxy groups in lignin,
194 accompanied by additional oxidation, which leads to oxygen addition rather than loss (Collard and Blin, 2014;
195 Dhyani and Bhaskar, 2018). The N content of CHON compounds in TMBCs-derived OA varied more complexly
196 with IGT, as it depends on both fuel-bound nitrogen and inorganic nitrogen in the gas atmosphere. The N/C^* ratios
197 of CHON⁻ and CHON⁺ compounds in OA_{Cel} and OA_{Hcel} almost both attained their lowest values at 600 °C,
198 whereas notably higher N/C^* ratios were observed at 400 °C and 800 °C. Nevertheless, lignin-derived CHON still
199 exhibited an increasing N/C^* ratio with rising IGT. Notably, the O/N^* ratios of CHON compounds followed the
200 same temperature-dependent trends as the O/C^* ratios. As the O/N^* ratios can reflect the oxidation state of CHON
201 compounds, our study suggested that reduced-N functional groups (e.g., amides, amines) are preferentially
202 eliminated at intermediate temperatures for cellulose- and hemicellulose-derived CHON, and with increase of IGT,
203 the residual CHON compounds become progressively less oxidized. In contrast, the simultaneous increase of both
204 N/C^* and O/N^* with IGT for lignin-derived CHON indicated that nitrogen incorporation is accompanied by
205 progressive oxidation, likely through reactions of inorganic nitrogen species (e.g., NO_x) with oxidized aromatic
206 structures. These contrasting behaviors highlight that the formation of CHON compounds of BBOA is strongly
207 dependent on the fuel composition.

208 3.2 Molecular Distribution of CHON compounds with N atoms

209 In general, MF with O/N ratios ≥ 3 allow the assignment of nitrooxy ($-ONO_2$) groups, whereas those
210 with relatively lower O/N ratios (<3) are more likely to be reduced-N compounds with other oxygenated
211 functional groups (Wang et al., 2018; Lin et al., 2012). In this study, the CHON⁻ compounds with a higher



O/N ratio (≥ 3) account for 56–96% intensity of overall compounds (Table S4), indicating that the vast majority of CHON[–] species emitted from the combustion of the TMBCs likely contain potential nitrooxy (ONO_2) or nitro (NO_2) groups. For all the TMBCs, the intensity proportion of CHON[–] compounds with O/N ratios ≥ 3 was found to be higher at 600 °C than at 400 °C and 800 °C, indicating that 600 °C is favorable for the formation of nitrooxy or nitro groups. Although CHON⁺ compounds with O/N ratios ≥ 3 dominated in OA_{Cel} and OA_{Hcel} (50–72%), only 20–42% of CHON⁺ compounds in OA_{Lign} exhibited O/N ratios higher than 3. Notably, some CHON compounds with O/N ratios ≥ 3 can be both detected in ESI[–] and ESI⁺ mode. Given that ESI⁺ preferentially ionizes basic functional groups, these common detected species likely represent reduced-N compounds with highly oxygenated functionalities (e.g., amino acid). As shown in Table S4, 2.9–30% of CHON⁺ species having O/N ratio ≥ 3 were identified in both ESI⁺ and ESI[–] modes, which accounted to 1.8–27% intensity of CHON⁺ species. It is obvious that these potential amino acid-like substances showed relatively high proportions at high IGT for OA_{Cel} and OA_{Hcel}, whereas it decreased for lignin-derived CHON⁺ compounds. This result suggested that the formation of these amino acid-like substances was not only temperature-dependent but also influenced by the fuel types.

According to the number of nitrogen and oxygen atoms contained in MF, CHON compounds are classified into N_{1-5}O_1 to $\text{N}_{1-5}\text{O}_{\geq 15}$ subgroups. Both CHON[–] and CHON⁺ compounds were mainly constituted by relatively higher intensity fraction of N_1 group, followed by moderate fraction of N_2 group and lower fraction of N_{3-5} groups. This is consistent with that reported for pine OA in a recent study, differing from the observation that N_2 group accounted for a higher proportion than N_1 in OA derived from straw combustion (Song et al., 2022). As shown in Figure S2, the temperature-dependent variations of CHON[–] distributions were consistent for OAs derived from all fuels. The proportions of N_1 group to CHON[–] intensity was 51%, 68% and 77% in OA_{Cel,400}, OA_{Hcel,400}, and OA_{Lign,400}, and increased significantly to 80%, 84% and 97% in OA_{Cel,600}, OA_{Hcel,600} and OA_{Lign,600}, respectively. Correspondingly, the proportions of CHON[–] compounds with higher N contents (e.g., N_2 and N_{4-5} groups) decreased markedly. When the IGT was further elevated to 800 °C, the N_1 fraction in CHON[–] for OA_{Cel,800}, OA_{Hcel,800} and OA_{Lign,800} dropped back to 53%, 69% and 64%, respectively, while the proportion of N_{2-3} group increased obviously. The most abundant CHON[–] compound groups in OA_{Cel} and OA_{Hcel} shifted from highly oxygenated species ($\text{N}_1\text{O}_{11-14}$ and $\text{N}_1\text{O}_{11-12}$) to less oxygenated species (N_1O_{4-5} and N_1O_4) when the IGT increased from 400 °C to 600 °C (Figure S3), and the dominant species converged to N_1O_{5-6} in OA_{Lign,600}. Also, the highly-intense CHON[–] species become



low oxygen-containing or high N content when the IGT further increased to 800 °C. These results indicate that regardless of fuel type, the effect of IGT on the distribution pattern of CHON⁻ compounds is consistent.

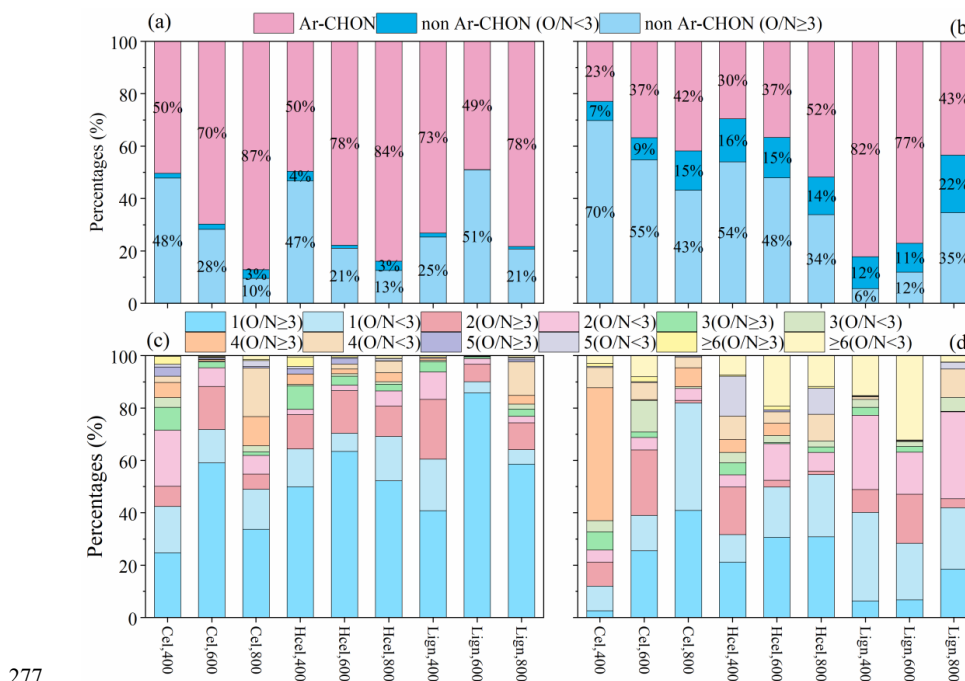
A similar compositional variation of CHON⁺ compounds along with the change of IGT were observed to that of CHON⁻ compounds for OA_{Cel} and OA_{Hcel}, but the temperature-dependent distribution of lignin-derived CHON⁺ compounds was different from that of cellulose and hemicellulose. N₁ species become less important in both OA_{Cel,400} and OA_{Hcel,400} compared to CHON⁻ compounds, and accounted for 41% and 48% of the total CHON⁺ compounds intensity, respectively. At the same time, the contribution of N₃₋₄ group in CHON⁺ compounds showed relatively higher values than that in CHON⁻ compounds for both OA_{Cel,400} and OA_{Hcel,400}. As the IGT increased to 600 °C, the proportions of N₁ group increased but decreased for the N₂ and N₃₋₄ groups. Most important, the major CHON⁺ species also shifted to less oxygenated and low N content species such as N₁O₁ (Figure S4). When the IGT was further elevated to 800 °C, the proportion of N₁₋₂ subgroups in CHON⁺ further increased, with N₁O₅ species being more dominant across the profile, and abundant species in N₂ group having less oxygen atoms (e.g., N₂O₁₋₂). However, in both OA_{Lign,400} and OA_{Lign,600}, the N₁ and N₂ groups dominated the CHON⁺ intensity (97%), but the proportions of N₂ group were notably higher than those in OA_{Cel} and OA_{Hcel}. The situations changed when the IGT increased to 800 °C. The proportions of N₁ and N₃ group increased markedly while the N₂ fraction decreased. Overall, the molecular composition of CHON compounds emitted from the combustion of TMBCs is not only controlled by IGT, but also regulated by the fuel chemical composition. Meanwhile, the types of compounds captured by different ionization modes are different, and their temperature dependence also exhibits differentiated characteristics.

3.3 Structural composition of CHON compounds

As shown in Figure 2, the identified CHON compounds were classified into non-aromatic and aromatic compounds (Ar-CHON) using the combination of AI_{mod} and X_c criteria (Text S2) (Koch and Dittmar, 2016; Yassine et al., 2014). The potential Ar-CHON⁻ compounds accounted for 50% of the total intensity for both OA_{Cel,400} and OA_{Hcel,400}, which was higher than the corresponding proportions observed for CHON⁺ compounds (30% and 23%). High IGT generally accompanied by high proportions of Ar-CHON compounds for both OA_{Cel} and OA_{Hcel}. This is consistent with previous findings that polycyclic aromatic hydrocarbon (PAH) emissions from residential solid fuel combustion increase with IGT, supporting the notion that the formation of Ar-CHON compounds from cellulose and hemicellulose combustion primarily relies on a bottom-up pathway involving small



270 molecular fragments (Wang et al., 2023; Han et al., 2020). In contrast to cellulose and hemicellulose, the
271 proportions of lignin-derived Ar-CHON⁻ compounds displayed a non-monotonic temperature dependence.
272 Specifically, Ar-CHON⁻ compounds constituted 73% of the total CHON⁻ intensity in OA_{Lign,400}, approximately
273 1.5-fold higher than those in OA_{Cel,400} and OA_{Hcel,400}. The ratio then declined markedly to 49% in OA_{Lign,600}, but
274 subsequently rose to 78% in OA_{Lign,800}. For CHON⁺ compounds, the proportion of Ar-CHON⁺ decreased from
275 82% and 80% in OA_{Lign,400} and OA_{Lign,600} to 45% in OA_{Lign,800}. These results suggested the temperature-dependent
276 variations in Ar-CHON compounds emissions were also influenced by fuel types during the combustions.



277 **Figure 2.** Distributions of intensity proportion for (a) Ar-CHON⁻ and (b) Ar-CHON⁺ compounds in OAs
278 derived from the combustion of cellulose, hemicellulose and lignin at the IGT of 400 °C, 600 °C and 800 °C,
279 respectively. Compositional profiles of (c) Ar-CHON⁻ and (d) Ar-CHON⁺ compounds based on the potential
280 number of benzene-rings in formulae.
281

282 The distribution profiles of Ar-CHON⁻ compounds for the TMBCs-derived aerosols suggested that 1-2 ring
283 species were the major fractions across all fuel types (Figure 2c and 2d). Similar variations in the proportions of
284 1-2 ring species with changing IGT were observed for OA derived from all the TMBCs. The fractions of 1-2 ring
285 species to Ar-CHON⁻ compounds were in the range of 72%-94% for OA derived from the TMBCs, with reduced-



286 N species accounted for 16%-39%, respectively. As the IGT increased to 600 °C, the proportion of 1–2 ring species
287 increased markedly (particularly monocyclic NACs), accounting for 89-99% of the total Ar-CHON– intensity.
288 Correspondingly, the proportion of 1–2 ring species with reduced-N decreased clearly for all fuels. Nevertheless,
289 the proportion of 1–2 ring species all declined when the IGT was further elevated to 800 °C, while the proportions
290 of 4-ring Ar-CHON– species (especially reduced-N species) increased notably for all OAs. These results indicate
291 that, despite the structural differences among the TMBCs, the temperature-dependent trends of aromatic Ar-
292 CHON– species composition are consistent, reflecting that temperature may be one of the determining factors in
293 the formation of Ar-CHON– compounds.

294 For aromatic CHON+, the composition varied significantly with IGT among the three fuels. Ar-CHON+
295 compounds derived from the combustion cellulose and hemicellulose at low IGT showed low abundances for 1-
296 ring species, while the species having high potential ring numbers contributed largely to the total Ar-CHON+
297 intensity. Although dominant fractions of 1–2 ring species were observed in lignin-derived Ar-CHON+ at low IGT,
298 reduced-N species accounting for more than 50%. In addition, a high proportion of reduced-N species having 6-
299 ring was also observed in OA_{Lign,400} and OA_{Lign,600}. As noted above, the MCE was relatively low at low IGT, and
300 emissions of CHON+ were mainly formed from large fuel pyrolysis fragments reacting with nitrogen species.
301 However, due to limitations of the X_c and AI_{mod} screening methods used in this study, and the yield of PAHs was
302 generally low at low IGT, some high-ring CHON+ identified are likely biphenyl-like rather than condensed
303 aromatic compounds (Koch and Dittmar, 2016; Yassine et al., 2014). Elevated IGT promoted greater
304 fragmentation of the fuel, intensified oxidation reactions, and enhanced dehydration and decarboxylation
305 processes, resulting in a concurrent increase in the abundance of low-ring oxygenated and reduced-N species (Ma
306 et al., 2022; Leng et al., 2021). And thus, increases in the proportion of 1-ring CHON+ species with IGT were
307 observed at high IGT, correspondingly leading to the total proportion of high-ring CHON+ species decreased for
308 OA_{Cel} and OA_{Hcel}. For lignin-derived CHON+ compounds, the composition of high-ring species at high IGT shifts
309 from 6-ring dominance to 3-4 ring dominance. In summary, our results indicate that fuel-specific pyrolysis
310 pathways and nitrogen reaction mechanisms are different for the TMBCs, but the effect of IGT on building the
311 CHON compound composition is consistent as the elevated IGT universally driving CHON toward lower-ring-
312 number species and increasing the abundance of reduced-N species.

313 3.4 Comparison of CHON compounds emitted from the combustion of TMBCs

314 As shown in Figure 3, the Venn diagrams and Van Krevelen diagrams illustrate the similarities and



315 differences in the molecular composition of CHON compounds emitted from the combustion of the TMBCs at
316 different IGT. The overlap in total CHON (sum of CHON- and CHON+) formulae between $OA_{Cel,400}$ and $OA_{Hcel,400}$
317 accounted for 37% and 28% of the CHON formulae detected in each fuel (Figure S5), and contributed 75% and
318 56% of the total CHON intensity for cellulose and hemicellulose (Figure 3a-c), respectively. In contrast, the
319 similarity between cellulose/hemicellulose and lignin-derived CHON was considerably lower. The CHON
320 formulae shared between $OA_{Cel,400}$ ($OA_{Hcel,400}$) and $OA_{Lign,400}$ accounted for 13% (11%) of the total formulae
321 number, and 1.9% (5.6%) of the total intensity for CHON compounds detected in $OA_{Lign,400}$. Furthermore, the
322 formulae shared by all three fuels accounted for only 3.4–9.3% of the total formulae detected in each fuel, with
323 corresponding intensity contributions of 5.0–15%. The high-abundance lignin-derived CHON compounds were
324 mainly distributed in the region with $(O-2N)/C \leq 0$ and $H/C \geq 0.8$, as well as $0 \leq (O-2N)/C \leq 0.3$ and $0.7 \leq H/C \leq$
325 1.5, which were clearly different with those CHON compounds for $OA_{Cel,400}$ and $OA_{Hcel,400}$. Given that fuel
326 pyrolysis dominates low-temperature combustion processes, the inherent structural disparities among the TMBCs
327 can account for the similarities and disparities in the composition of CHON at low IGT. When the IGT increased
328 to 600 °C, the fractions of common CHON formulae between $OA_{Cel,600}$ and $OA_{Hcel,600}$ increased to 39% and 61%,
329 respectively. Meanwhile, the proportion of formulae shared between $OA_{Cel,600}$ ($OA_{Hcel,600}$) and $OA_{Lign,600}$ increased
330 to 66% (28%) of the total formulae number, and 68% (42%) of the total intensity for CHON compounds detected
331 in $OA_{Lign,600}$. The formulae shared by all three fuels also increased, reaching 40% of the total intensity for $OA_{Lign,600}$.
332 This indicates that the increase in IGT enhanced the overlap in CHON molecular composition among all three
333 fuels. The overlapping CHON formulae among the TMBCs were mainly located in the unsaturated hydrocarbon
334 region and the low-oxidation CRAMs region ($O-2N/C \leq 0.4$). Several NACs such as $C_6H_5NO_4$, $C_7H_7NO_{4-5}$, and
335 $C_8H_9NO_{4-5}$ became the dominant species in $OA_{Lign,600}$, and also exhibited high relative abundances in $OA_{Cel,600}$
336 and $OA_{Hcel,600}$ in addition to alkyl nitrates and amino acid-like CHON compounds (Table S5-S8).

337 However, as the IGT further increased to 800 °C, the overlap in NOC molecular composition among the
338 three fuels did not increase further. For example, the proportion of common CHON formulae between $OA_{Cel,800}$
339 and $OA_{Lign,800}$ decreased markedly compared to that at 600 °C. Importantly, the number and signal intensity
340 fractions of common formulae shared by all the TMBCs also decreased compared to that at 600 °C. The
341 overlapping formulae among the three OAs at 800 °C were still rich in the highly oxidized CRAMs region, and
342 NACs species such as $C_6H_5NO_4$, $C_7H_7NO_{4-5}$, $C_8H_9NO_4$ and $C_9H_9NO_5$ remained high relative abundance across all
343 three fuels (Table S9-S10). Nevertheless, compared to $OA_{Cel,800}$ and $OA_{Hcel,800}$, the number of formulae in the



condensed aromatic region increased obviously in $OA_{Lign,800}$, with highly intense molecules including $C_{12}H_7NO_4$, $C_{16}H_9NO_3$, and $C_{20}H_{10}N_2O_5$. This is consistent with previous study that high IGT promoted the formation of PAHs via free radical reaction pathways during lignin combustion, resulting in higher PAH emissions compared to cellulose and hemicellulose (Wang et al., 2023). However, due to differences in the abundance of precursor compounds formed during fuel fragmentation, the abundances of these common molecules varied among the smoke from different fuels. Thus, a reduction in the overlap among the three fuels at high IGT possibly due to the enhanced fragmentation of fuels and condensed reactions, which generates more diverse and fuel-specific pyrolysis products, thereby reducing the similarity in CHON molecular composition across different biomass fuels.

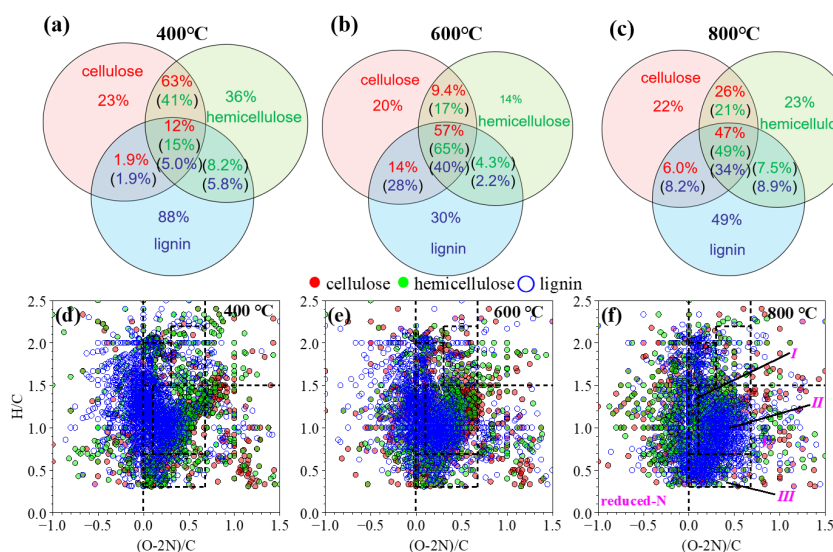


Figure 3. (a-c) Venn diagrams showing the similarity of CHON composition among the OAs from the TMBCs at the IGT of 400 °C, 600 °C and 800 °C, respectively. Percentages in areas of overlap are intensity percentages of CHON compounds that appear in the corresponding samples. (d-e) Van Krevelen diagrams of CHON compounds in OAs from the TMBCs at the three IGT. The identified CHON were also classified into several groups based on the cutoffs described in previous studies (Bianco et al., 2018). The CHON compounds located in regions that marked in figures are reduced-N species, (I) unsaturated hydrocarbons-like, (II) carboxylic-rich alicyclic molecules (CRAMs), (III) condensed aromatics-like compounds. Noted that the CRAMs-like compounds identified in lignin-derived aerosols should be lignin-like or phenolic-like compounds, for ease of expression, we still used the CRAMs-like compound to represent them.

3.5 Mechanism of IGT on the Formation of CHON Molecules.

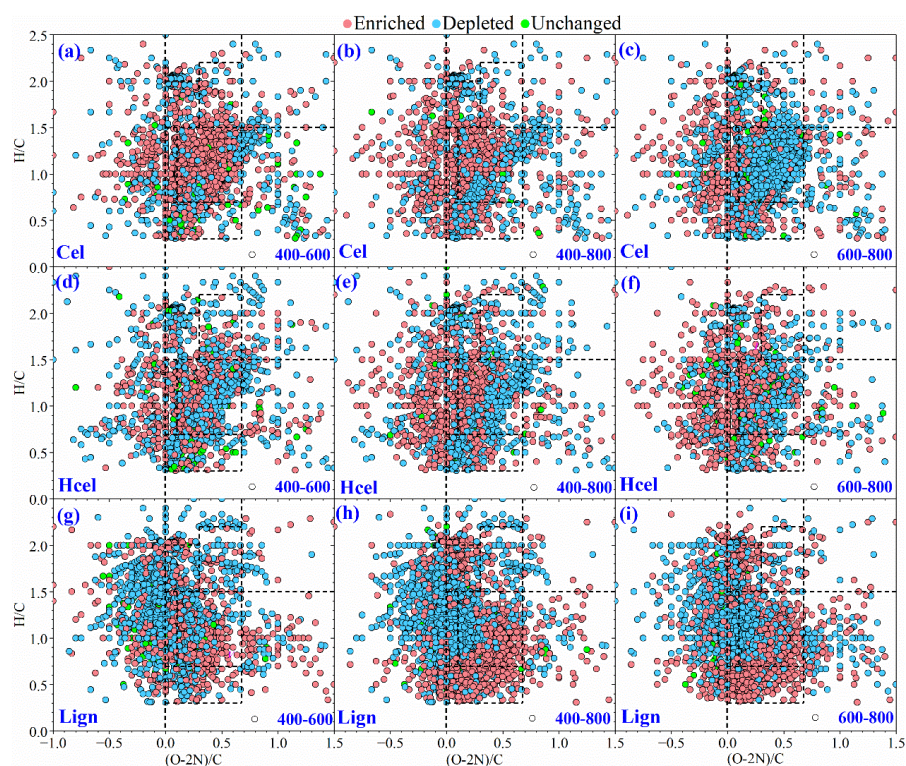


Figure 4 further displayed the changes in the molecular composition of CHON compounds in the combustion emissions of different biomass fuels with IGT. CHON species were classified into three subgroups based on the ratio of their relative abundances in high-temperature versus low-temperature samples: enriched ($RI_{high}/RI_{low} > 1.5$), unchanged ($0.75 \leq RI_{high}/RI_{low} \leq 1.5$) and depleted species ($RI_{high}/RI_{low} < 0.75$). For all the BMTCs, increasing the IGT induced substantial shifts in NOC molecular distributions, with only a small fraction of CHON species remaining unaffected. However, the temperature-dependent trends varied considerably among the fuels. For cellulose and hemicellulose, raising the IGT from 400 °C to 600 °C led to a decrease in the relative abundance of molecules mainly located in the range of (O-2N)/C 0.6–0.9 and H/C 1.2–1.6, while a large number of CRAM-like molecules were enriched. A similar enrichment trend was observed when the IGT was increased from 400 °C to 800 °C, but the enrichment extended to a broader range of reduced-N species with higher unsaturation ($H/C \leq 1.0$). Compared to 600 °C, a large number of CRAMs decreased in relative abundance at 800 °C. However, the number of CRAMs that presented as depleted species were small for hemicellulose than that of cellulose. The contrasting behavior relative to cellulose can be attributed to the smaller structural units of hemicellulose, which require a lower temperature for complete pyrolysis. Lignin-derived CHON compounds displayed a distinct pattern. Increasing IGT from 400 °C to 600 °C decreased the relative abundance of highly saturated reduced-N species, while the CHON compounds that increased in relative abundance were mainly located in the highly oxidized, less saturated CRAM-like region. Only a small subset of highly-oxidized condensed Ar-CHON compounds was enhanced, whereas some low-oxidation-state Ar-CHON compounds diminished. However, when the IGT was further elevated to 800 °C, a notable feature was the marked enrichment of condensed aromatic CHON compounds, which is clearly different from the two polysaccharide fuels.

The influence of IGT on the emission of pollutants from BB have been widely reported (Peng et al., 2026; Cai et al., 2023; Wang et al., 2023; Peng et al., 2023). The change in IGT provides the energy required for the combustion process, enhances the degree of fuel pyrolysis, and thus affects combustion efficiency (Fawaz et al., 2021). In general, the degree of fuel pyrolysis was incomplete at low IGT, and the oxygen-containing function groups in the polymeric unit (e.g., –OH, C–O–C or –OCH₃) were retained. Given the gas atmosphere was rich in reduced-N radicals (e.g., –C≡N), which mainly originated from the release of basic N in the fuel, the relatively high fractions of reduced-N species with high N atoms were formed from the reactions of reduced-N radicals with the incomplete pyrolytic fragments (section 3.2) (Leng et al., 2021). In addition, some species would also react with NO_x to form nitro/nitrate species including NACs. Since the combustion of lignin can produce substantial



amounts of phenolic species, the OA_{Lign} could contain higher proportions of NACs (Figure 2) (Kibet et al., 2012; Kawamoto, 2017). As the IGT increases to 600 °C, enhanced pyrolysis and oxidation reactions lead to elimination of oxygen atoms and the broken of fuel-released C-N bonds, resulting to the enrichment of CHON species toward N_1 species and low oxygen-containing compounds. Moreover, the formation of non-aromatic CHON compounds may be inhibited at high IGT since nitro/nitrate compounds can undergo hydrolysis or photolysis in ambient environment (Takeuchi and Ng, 2019; Fisher et al., 2016; González-Sánchez et al., 2023a). Also, the increased abundance of small molecular fragments and higher temperatures enhance aromatic-ring synthesis reactions, leading to an increased proportion of aromatic CHON– in cellulose and hemicellulose-derived aerosols. However, the formation rates of polycyclic Ar-CHON compounds are still relatively low due to the low temperature, and the phenolic species start to undergo ring-opening reactions, which lead to the descending in the proportion of lignin-derived Ar-CHON compounds. When the IGT rise to 800 °C, more complete fuel decomposition and stronger deoxygenation reactions occurred, accompanied by enhanced synthesis of polycyclic aromatic CHON– species, leading to the enrichment of Ar-CHON compounds with low oxidation states and high nitrogen content. It is worth noting that, since the flue gas from lignin combustion is rich in aromatic species, and PAHs formation during lignin pyrolysis initiated at 600 °C and accelerates markedly above 700 °C (Kawamoto, 2017; Zhou et al., 2014), the emissions of polycyclic Ar-CHON compounds at high temperatures in $OA_{Lign,800}$ is higher than that in $OA_{Cel,800}$ and $OA_{Hcel,800}$.



409

410 **Figure 4.** Van Krevelen diagrams showing the changes in molecular composition of CHON compounds in OAs
 411 from the combustion of cellulose (Cel), hemicellulose (Hcel) and lignin (Lign) when the IGT changed.

412 4. Conclusion and Atmospheric implications

413 Biomass burning, including residential biomass burning, agricultural open burning and wildfire, has been
 414 considered as one of the most important sources of air pollutants (Chen et al., 2017; Jiang et al., 2024; Jones et
 415 al., 2024; Adam et al., 2021). The impact of BBOA on radiative forcing (Zhong et al., 2024; Yan et al., 2024; Lai
 416 et al., 2024) and health effects (Chen et al., 2024; Shen et al., 2019; Wei et al., 2023; Xu et al., 2023; Yun et al.,
 417 2020; Deng et al., 2021; Bauer et al., 2019; Nawaz and Henze, 2020) has received much attention in recent years.
 418 As one of the main components in BBOA, NOCs have been regarded as an important component that affects the
 419 radiative forcing and health effects of BBOA. However, analysis of OAs emitted from laboratory-simulated
 420 combustion of the TMBCs by ESI+ and ESI- HR-MS revealed that, under full-oxygen conditions, the formation
 421 and emission of CHON compounds in BBOA are governed by not only IGT but also fuel types. Regardless of fuel
 422 type, high IGT led to an increased proportion of CHON- in OA. The proportion of CHON+ in the OA_{Cel} and



423 OA_{Hcell} also increased with elevating IGT, whereas lignin showed the opposite trend. This indicates that emission
424 inventories and source apportionment models must account for combustion temperature and fuel composition to
425 accurately predict the impacts of biomass burning NOCs. Moreover, analysis of temperature-dependent changes
426 in CHON molecular composition suggested that lignin-derived CHON compounds usually constituted higher
427 fractions of Ar-CHON species than that cellulose and hemicellulose at low IGT. However, as the IGT increases,
428 enhanced deoxygenation and C–N cleavage shift CHON toward N₁ and low oxygen-containing compounds,
429 increasing the molecular overlap among the TMBCs, especially the NACs. Although the combustion of lignin at
430 higher IGT could produce more abundant condensed Ar-CHON compounds than cellulose and hemicellulose, the
431 proportion of Ar-CHON species within cellulose- and hemicellulose-derived CHON can be higher than that within
432 lignin. This result indicates that for BB at medium-to-high IGT, the formation of Ar-CHON compounds, including
433 NACs, is less dependent on fuel aromaticity, providing a possible explanation for the higher NAC emissions
434 measured from straw than from wood in previous studies of biomass burning sources. Additionally, since NACs
435 and condensed Ar-CHON are both important BrC chromophores and toxic components, our study achieved a
436 better understanding of the formation and emission of these Ar-CHON compounds, and useful information for
437 developing comprehensive emission reduction strategies.

438 However, this study only examined the combustion of the TMBC at three IGT gradients under full-oxygen
439 conditions, and the results may not fully represent the complexity of real-world BB. A comprehensive
440 investigation of CHON compounds generated under more combustion conditions is therefore required (e.g.,
441 insufficient oxygen supply conditions, different moisture content of fuel). In addition, the formation and emissions
442 of CHON compounds from the TMBCs may be affected by the interactions between the TMBCs (Wu et al., 2016a;
443 Hilbers et al., 2015; Wu et al., 2016b), leading to distinct emission behaviors of CHON compounds for the raw
444 materials of biomasses (e.g., wood and straw). Therefore, it is necessary to investigate whether the interaction
445 between TMBCs affects the formation and emissions of CHON compound during the BB processes.

446 ***Data availability.***

447 The original data used in this study was uploaded on Figshare and can be found in Jiang et al. (2026).

448 ***Supplement.***

449 The supplement related to this paper is available online.

450 ***Author contributions.***



451 H.J., Y.C. and Y.Z. designed the study; H.J., Y.P., and J.C. conducted combustion experiments.; Y.P., J.C. and T.L.
452 helped with the data analysis; Y.J. and J.C supervised this work and help reviewed the manuscript. H.J. prepared
453 the manuscript with contributions from all coauthors.

454 ***Competing interests.***

455 The authors declare that they have no conflict of interest.

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