



# 1 **Furfural Exhibits Distinct Photooxidation and Secondary Organic** 2 **Aerosol Formation Among Biomass Burning Related Furanoids**

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24 **Abstract.** Furanoids are a major compound class emitted during biomass burning and are highly  
25 reactive toward hydroxyl radicals (OH), suggesting their oxidation may contribute to secondary organic  
26 aerosol (SOA) formation. Previous furanoid studies focused on gas-phase kinetics, leaving SOA



27 formation poorly understood. Here, we investigate the gas-phase oxidation and SOA formation from  
28 furfural, 2-methylfuran, and 3-methylfuran reactions with OH radicals in the presence of nitrogen  
29 oxides at RH<5%. Furfural exhibits distinct oxidation chemistry compared with methylfurans: furfural  
30 alkyl radical preferentially reacts with NO<sub>2</sub>, whereas methylfuran oxidation proceeds via peroxy radical  
31 (RO<sub>2</sub>)+NO channel to form alkoxy radicals. Methylfuran isomers also differ in oxidation product  
32 speciation, with 2-methylfuran generating C<sub>4</sub> and C<sub>5</sub> compounds, whereas 3-methylfuran predominantly  
33 forms C<sub>5</sub> compounds. C<sub>4</sub>H<sub>2</sub>O<sub>3</sub>, potentially maleic anhydride, increases continuously during all furanoid  
34 oxidations, supporting its potential as an aged biomass burning marker. Furfural produces the highest  
35 SOA mass and yield (66.3 μg·m<sup>-3</sup>, 9.8%), followed by 2-methylfuran (10.3 μg·m<sup>-3</sup>, 1.4%) and 3-  
36 methylfuran (7.2 μg·m<sup>-3</sup>, 1.1%). Compared with methylfuran SOA, furfural SOA shows stronger  
37 signatures of lower-volatility oligomers, with higher contributions from large *m/z* fragments, a greater  
38 degree of unsaturation, broader thermograms, and more reduced CHON species (O/N<3). Accordingly,  
39 estimated particulate organic nitrate fraction is highest for 2-methylfuran SOA (~45%), followed by 3-  
40 methylfuran (~36%) and furfural (~11%). These results show that both substituent type and position  
41 should be considered when representing furanoid oxidation in atmospheric models.

## 42 1 Introduction

43 Biomass burning is a significant source of particulate matter (PM) and volatile organic compounds  
44 (VOCs) in the atmosphere (Crutzen and Andreae, 1990; Akagi et al., 2011; Reddington et al., 2016;  
45 Stockwell et al., 2015). It influences air quality, public health, and climate and is expected to increase  
46 due to climate change, affecting broad regions from local to continental scale (Abatzoglou and Williams,  
47 2016; Burke et al., 2023; Joo et al., 2024b). Thousands of different VOCs are released to the atmosphere  
48 from biomass burning. They can react with atmospheric oxidants such as hydroxyl (OH) and nitrate  
49 (NO<sub>3</sub>) radicals to form secondary pollutants such as ozone and secondary organic aerosol (SOA)  
50 (Alvarado et al., 2015; Alvarado and Prinn, 2009), which are reported to have detrimental health effects  
51 (Pye et al., 2021; Liu et al., 2023; Joo et al., 2024b; Pardo et al., 2024; Daellenbach et al., 2020; Zhou  
52 et al., 2019). Recent laboratory combustion studies revealed that SOA formation from biomass burning  
53 VOCs can be substantial (Fang et al., 2017; Lim et al., 2019), and that more than 80% of SOA can come



54 from less-studied precursors (Grieshop et al., 2009). Among the non-traditional VOCs, oxygenated  
55 aromatic compounds (e.g., phenols) and heterocyclic compounds (e.g., furanoids) generally have higher  
56 emissions in smoldering combustion than flaming combustion (Jen et al., 2019) and have been reported  
57 to have high SOA formation potential (Bruns et al., 2016; Hatch et al., 2017; Stefenelli et al., 2019;  
58 Akherati et al., 2020).

59 Furanoids are generated as a result of the pyrolysis of cellulose (Mettler et al., 2012; Romanias et  
60 al., 2024) and their contribution to total VOC emissions and subsequent SOA formation potential is  
61 reported to be particularly significant from combustion of grass- or straw-type fuel (Hatch et al., 2017;  
62 Stefenelli et al., 2019; Akherati et al., 2020). Once released into atmosphere, furanoids are highly  
63 reactive with atmospheric oxidants, contributing 9–25% of total OH radical reactivity among VOCs  
64 emitted from combustion of biomass fuels widely distributed across the United States (Koss et al., 2018;  
65 Gilman et al., 2015; Decker et al., 2021) and 18–23% of total NO<sub>3</sub> radical reactivity for VOCs emitted  
66 from rice straw and ponderosa pine combustion (Decker et al., 2019). The oxidation of furanoids by  
67 atmospheric oxidants can generate multi-functional oxidation products. Specifically, the formation  
68 yield of unsaturated multi-carbonyls has been reported to range from 8 to 75% (Aschmann et al., 2014;  
69 Gómez Alvarez et al., 2009; Bierbach et al., 1995). Such products containing one or more functionalities  
70 have multiple reactive sites that can trigger further accretion reactions to generate semi-volatile or low-  
71 volatility organic compounds (SVOCs or LVOCs) (Kroll and Seinfeld, 2008; Ziemann and Atkinson,  
72 2012; Joo et al., 2019), resulting in the formation of SOA with yields of 0.03–15% (for an OA mass  
73 concentration of 1.0–4900 µg m<sup>-3</sup>) (Romanias et al., 2024; Jiang et al., 2019; Gómez Alvarez et al.,  
74 2009; Strollo and Ziemann, 2013; Colmenar et al., 2020; Tajuelo et al., 2021).

75 Recently, the increasing prevalence of wildfires globally and their significant contributions to  
76 secondary atmospheric chemistry have driven substantial research on the oxidation of furanoids by  
77 various atmospheric oxidants. Despite these efforts, studies on SOA formation from furanoid  
78 photooxidation have thus far lacked continuous, real-time measurements of both gas- and particle-phase  
79 chemical composition (Romanias et al., 2024; Strollo and Ziemann, 2013; Al Ali et al., 2024; Jiang et  
80 al., 2019; Gómez Alvarez et al., 2009; Colmenar et al., 2020; Schueneman et al., 2024; Tajuelo et al.,  
81 2021). This limitation hinders a comprehensive understanding of the detailed gas-phase oxidation



82 chemistry and the corresponding SOA formation potential. Moreover, many investigations have  
83 primarily focused on reaction kinetics and reactivity with atmospheric oxidants (Bierbach et al., 1995;  
84 Zhao and Wang, 2017; Aschmann et al., 2014, 2011; Jiang et al., 2020; Tapia et al., 2011; Yuan et al.,  
85 2017), with relatively few examining the chemical mechanisms and SOA yields (Romanias et al., 2024).

86 In this work, we investigated SOA formation from photooxidation of furanoids in the presence of  
87 nitrogen oxides (NO<sub>x</sub>), focusing on 2-furaldehyde (furfural), 2-methylfuran, and 3-methylfuran, which  
88 together account for 58–67% of furanoids emitted from biomass burning (Hatch et al., 2017; Akagi et  
89 al., 2011; Gilman et al., 2015; Ciccioli et al., 2001). The composition of gas- and particle-phase products  
90 are characterized using online measurements, and the mechanisms for multigenerational gas-phase  
91 oxidation and particle-phase reactions are proposed. The results provide new insights into the  
92 photooxidation chemistry of furanoids and can improve the representation of SOA formation and  
93 evolution in biomass burning plumes in atmospheric models.

## 94 **2 Methods**

### 95 **2.1 Environmental Chamber Experiments**

96 Experiments are performed at 22 °C under dry (<5 % RH) conditions in the Georgia Tech  
97 Environmental Chamber (GTEC) facility which consists of two 12 m<sup>3</sup> Teflon chambers (Boyd et al.,  
98 2015). The chamber is cleaned for a day prior to each experiment with pure air (747-14, Aadco, Cleves,  
99 OH) at a rate of 35 L min<sup>-1</sup>. Ammonium sulfate seed aerosol is introduced into the chamber by atomizing  
100 a 0.015M solution for 20 min and passing through a neutralizer. The initial seed particle number and  
101 volume concentrations are ~20000 particles cm<sup>-3</sup> and ~20 μm<sup>3</sup> cm<sup>-3</sup>, respectively. A similar initial  
102 amount of 2-furaldehyde (furfural, 99%, Sigma-Aldrich, St. Louis, MO), 2-methylfuran (99%, Sigma-  
103 Aldrich), or 3-methylfuran (98%, ACROS, Geel, Belgium) is injected into a pure air-flowing glass bulb  
104 for introducing the precursor VOC into the chamber for quantitative comparison of SOA formation.  
105 Nitrous acid (HONO) is injected as an OH source, which has been reported as an important source of  
106 OH in wildfire plumes (Palm et al., 2020; Peng et al., 2020). HONO is generated following the  
107 procedure described in Tuet et al. (2017): adding 10 mL of 1% wt aqueous NaNO<sub>2</sub> (VWR International,



108 Radnor, PA) dropwise into 20 mL of 10% wt H<sub>2</sub>SO<sub>4</sub> (VWR International) in a glass bulb and then  
109 passing zero air over the solution to introduce HONO into the chamber. The HONO injection line is  
110 flushed for 5 min after the injection and then irradiation of UV black lights initiated photooxidation.  
111 Photolysis of HONO yields  $6 \times 10^6$ – $2 \times 10^7$  molecules cm<sup>-3</sup> of OH radicals. NO and NO<sub>2</sub> are also formed  
112 during the HONO synthesis as byproducts. The photolysis rate of NO<sub>2</sub> ( $j_{\text{NO}_2}$ ) in the chamber is  $\sim 0.2$   
113 min<sup>-1</sup>.

## 114 2.2 Instrumentation and data analysis

115 Online bulk aerosol chemical composition is measured using a high-resolution time-of-flight  
116 aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA). HR-ToF-AMS  
117 quantifies organics, nitrate, sulfate, ammonium, and chloride mass concentrations and measures the  
118 bulk elemental composition of organics (e.g., O:C and H:C ratios) (Aiken et al., 2007; Decarlo et al.,  
119 2006; Canagaratna et al., 2015). The data analysis is performed using SQUIRREL v1.57G and PIKA  
120 v1.16G in Igor Pro 6.38B01. Gas- and particle-phase molecular-level compositions are measured and  
121 reported as counts per second using a high-resolution time-of-flight chemical ionization mass  
122 spectrometer (HR-ToF-CIMS, Aerodyne Research Inc.) coupled with a Filter Inlet for Gases and  
123 AEROSol (FIGAERO, Aerodyne Research Inc.) inlet system (Nah et al., 2016a; Lopez-Hilfiker et al.,  
124 2014). Iodide (I<sup>-</sup>) is used as a reagent ion, which selectively measures polar or acidic compounds, and  
125 detected signals are normalized by I<sup>-</sup> (Aljawhary et al., 2013). FIGAERO-CIMS data analysis is  
126 performed in Igor Pro 6.38B01 (WaveMetrics Inc.) using Tofware v2.5.11. The general operation detail  
127 of FIGAERO-CIMS has been described in a previous study (Nah et al., 2016a). Briefly, reagent ions  
128 are introduced into the ion-molecular reaction (IMR) chamber as a mixture of methyl iodide (CH<sub>3</sub>I) and  
129 dry ultrahigh purity (UHP) N<sub>2</sub> (Airgas) that is passed through a <sup>210</sup>Po radioactive source (model P-2021,  
130 NRD, Grand Island, NY). As sensitivity can decrease if the amount of reagent ion depletes substantially  
131 and/or secondary chemistry in IMR occurs (Lee et al., 2014), the gas sampling line is diluted with zero  
132 air before the inlet to keep the fraction of I<sup>-</sup> to the total ions above 80%. To prevent fluctuations in the  
133 sensitivity, we follow the specific setting described in Takeuchi and Ng (2019) that humidify the IMR  
134 with humidified N<sub>2</sub> to minimize variation of the iodide ion chemistry that could arise from difference



135 in water vapor pressure in each experiment (Lee et al., 2014). While measuring gas-phase species,  
136 particles are collected onto a PTFE filter (Pall Corp, Zefluor 25 mm, 2  $\mu\text{m}$  pore-size) in FIGAERO for  
137 20 min and the particle-phase composition is analyzed through thermal desorption cycle (40 min total,  
138 including temperature ramping, soaking, and cooling cycle). We further obtain volatility distribution of  
139 OA as saturation mass concentration ( $C^*$ ,  $\mu\text{g m}^{-3}$ ) via calibration procedure using compounds of known  
140 vapor pressures and matching to their desorption temperature corresponding to the signal peak ( $T_{\text{max}}$ )  
141 (Stark et al., 2017). The estimation of  $C^*$  is detailed in Joo et al. (2019).

142 Offline bulk aerosol composition is analyzed using a liquid chromatography coupled with  
143 electrospray ionization and high-resolution quadrupole time-of-flight tandem mass spectrometry (LC-  
144 ESI-Q-ToF, Agilent 1260 Infinity LC and Agilent 6550 Q-ToF, Agilent, Santa Clara, CA). Additional  
145 chamber experiments (Table S1) with higher initial VOC concentrations are performed to facilitate  
146 collection of sufficient aerosol mass via filter sampling (47 mm Teflon filter, 2  $\mu\text{m}$  pore size, Pall  
147 Corporation) to increase detected ion abundances across a greater range of analytes and thus reduce  
148 analytical uncertainties. Agilent Poroshell 120 SB-Aq reverse-phase column (2.1  $\times$  50 mm, 2.7  $\mu\text{m}$   
149 particle size) is used for LC, and the analysis is performed in both positive and negative modes. Details  
150 of filter extractions, data acquisition, non-targeted data analysis, and QA/QC are discussed previously  
151 (Ditto et al., 2018). Formulas are assigned for the ions in range of  $m/z$  50 – 600 assuming  $[\text{M} + \text{H}]^+$ ,  $[\text{M}$   
152  $+ \text{Na}]^+$ , and  $[\text{M} + \text{NH}_4]^+$  addition in ESI positive mode,  $[\text{M} - \text{H}]^-$  and  $[\text{M} + \text{HCOO}]^-$  or  $[\text{M} + \text{CH}_3\text{COO}]^-$   
153 in negative mode, and also neutral water loss. Ions that surpassed instrument noise (isotope height of  
154 1000 counts and compound height of 5000 counts) and strong peak quality score are assigned with the  
155 following elemental constraints ( $\text{C}_{1-60}\text{H}_{0-120}\text{O}_{0-30}\text{N}_{0-5}\text{S}_{0-1}$ ) in Agilent's MassHunter software.

156 Size-dependent particle number and volume concentrations are monitored using a scanning  
157 mobility particle sizer (SMPS). The SMPS consists of a differential mobility analyzer (DMA) (TSI  
158 3040, TSI Inc., Shoreview, MN) and a condensation particle counter (CPC) (TSI 3775). SMPS is  
159 operated under low-flow mode with sheath flow of 2  $\text{L min}^{-1}$  to scan particles up to 1  $\mu\text{m}$  size range.  
160 Precursor VOC concentration is monitored using a gas chromatograph-flame ionization detector (GC-  
161 FID, Agilent 7890A, Agilent, Santa Clara, CA) with a PLOT-Q column (Agilent). NO, and NO<sub>2</sub> are  
162 monitored using a chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> Analyzer (42C, Thermo Fisher Scientific,



163 Waltham, MA) and a cavity attenuated phase shift NO<sub>2</sub> monitor (CAPS, Aerodyne Research Inc.),  
164 respectively.

## 165 3 Results

### 166 3.1 SOA formation from OH radical oxidation of furanoids

167 Table 1 summarizes furanoid SOA formation experiments that are performed in this study. The  
168 particle wall-loss-corrected SOA yield of furanoid photooxidation range from 1.1% to 9.8% for an  
169 organic aerosol mass concentration ( $\Delta M_o$ ) of 7.2 to 66.3  $\mu\text{g m}^{-3}$ , with the highest SOA yield and  $\Delta M_o$   
170 observed in the furfural+OH experiment among the examined furanoids.  $\Delta M_o$  is estimated by  
171 converting SMPS volume concentration to aerosol mass concentration using the SOA density, which is  
172 determined by performing a series of nucleation experiments. By comparing mobility and aerodynamic  
173 diameters measured by SMPS and HR-ToF-AMS, respectively (Bahreini et al., 2005), the SOA density  
174 for furfural SOA, 2-methylfuran SOA, and 3-methylfuran SOA, is estimated to be 1.35  $\text{g cm}^{-3}$ , 1.42  $\text{g}$   
175  $\text{cm}^{-3}$ , and 1.40  $\text{g cm}^{-3}$ , respectively.

176 There are a few studies to date that have quantified SOA formation from furfural+OH, 2-  
177 methylfuran+OH, and 3-methylfuran+OH (Figure S1). Schueneman et al. (2024) reported an SOA yield  
178 of 16% for  $\Delta M_o = 100 \mu\text{g m}^{-3}$ , and Strollo and Ziemann (2013) reported SOA yields of 12 and 15% for  
179  $\Delta M_o = 2000$  and  $4900 \mu\text{g m}^{-3}$  in furfural and 3-methylfuran photooxidation experiments, respectively.  
180 Meanwhile, Colmenar et al. (2020) reported a substantially lower SOA yield (0.3% for  $\Delta M_o = 90 \mu\text{g m}^{-3}$ )  
181 from the photooxidation of furfural, which could arise from vapor wall loss processes (Nah et al.,  
182 2016b; Zhang et al., 2014) as the experiments were conducted without seed particles. Even within this  
183 limited set of available studies, and despite their varying results, furfural SOA yields are generally  
184 higher than those reported for 3-methylfuran SOA, highlighting the need for systematic comparison of  
185 SOA formation across individual furanoids under controlled experimental conditions to better constrain  
186 their contribution to SOA formation from biomass burning emissions.



## 187 3.2 Chemical composition of gas- and particle-phase components

### 188 3.2.1 Evolution of gas-phase species during photooxidation of furanoids

189 Temporal variations of NO and NO<sub>2</sub> during furanoid+OH reaction are shown in Figure 1a, c, and  
190 e. While 2- and 3-methylfuran experiments show rapid NO decay and depletion of parent VOCs  
191 accompanied by a sharp increase in NO<sub>2</sub> once oxidation is initiated, furfural experiment exhibits a much  
192 slower NO decay and even a slight NO increase at the reaction onset. Temporal profiles of the precursor  
193 VOCs likewise differ by furanoids: 2- and 3-methylfuran are depleted within 50 min of oxidation  
194 (Figure 1d and f), whereas furfural declines steadily until the end of the experiment (Figure 1b). This  
195 behavior is consistent with the slower reaction rate of furfural+OH compared to 2- and 3-  
196 methylfuran+OH (Bierbach et al., 1995; Coggon et al., 2019), although the observed decay could also  
197 reflect differences in effective OH exposure of the parent VOCs.

198 A subset of gas-phase oxidation products that are sensitive to iodide reagent ion is identified using  
199 HR-ToF-CIMS (Figure S2). While the most prominent compound detected during both furfural and 2-  
200 methylfuran experiments share the same *m/z* and molecular formula (*m/z* 100, C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>), the two systems  
201 show distinct product speciation. For OH oxidation of furfural, the dominant gas-phase products are  
202 primarily CHO compounds, whereas the 2-methylfuran system also produces notable CHON species  
203 (i.e., C<sub>4</sub>H<sub>3</sub>NO<sub>5</sub>, C<sub>5</sub>H<sub>5</sub>NO<sub>5</sub>). Overall, CHON species account for a higher fraction of total gas-phase  
204 signal in the 2-methylfuran experiment (20%) compared to the furfural experiment (10%), where 8%  
205 and 2% come from CHON species with O/N ≥ 3 and O/N < 3 in the furfural experiment, respectively.  
206 Meanwhile, the gas-phase signal during the 3-methylfuran experiment is dominated by C<sub>5</sub>H<sub>6</sub>O<sub>3</sub> (*m/z*  
207 114), with the total signal from remaining identified compounds measured at less than 15% of the  
208 C<sub>5</sub>H<sub>6</sub>O<sub>3</sub> signal.

209 Temporal variations of the selected gas-phase oxidation products (Figure 1b, d, and f) can be  
210 grouped into three categories: (1) first-generation product characteristics, showing an immediate  
211 increase at the onset of oxidation; (2) a slower increase compared to first-generation products, reaching  
212 the maximum signal within 200 min after the initiation of oxidation; and (3) compounds that continue  
213 to increase until the end of the experiment. C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> (*m/z* 112) generated during furfural oxidation  
214 (Figure 1b), C<sub>4</sub>H<sub>4</sub>O<sub>3</sub> (*m/z* 100) and C<sub>5</sub>H<sub>6</sub>O<sub>3</sub> (*m/z* 114) generated during 2-methylfuran oxidation (Figure



215 1d), and  $C_5H_6O_3$  ( $m/z$  114) generated during 3-methylfuran oxidation (Figure 1f) can be classified as  
216 the first-generation products. Most of the other detected species fall into the second category, and only  
217  $CH_2O_2$  ( $m/z$  46) shows a continuous increase until the end of the experiment across all systems.

### 218 3.2.2 Chemical composition of furanoid SOA

219 Typical mass spectra of furanoid SOA obtained via HR-ToF-AMS are shown in Figure 2. Furfural  
220 SOA exhibits three distinctive characteristics among furanoid SOA examined in this study. Firstly,  
221 signals at  $m/z$  above 50 are observed to account for 14% of furfural SOA, which is ~3 times higher than  
222 that of 2- and 3-methylfuran SOA. Secondly, fraction of  $m/z$  43 ( $C_2H_3O^+$ ) to OA ( $f_{C_2H_3O^+}$ ) of furfural  
223 SOA is ~5 times lower compared to 2- and 3-methylfuran SOA. In contrast, a well-known organic acid  
224 indicator, the  $m/z$  44 ( $CO_2^+$ ) to OA ( $f_{CO_2^+}$ ) ratio (Alfarra et al., 2004; Ng et al., 2011), remains similar  
225 among all furanoid SOA, ranging from 21 to 25%. Lastly, a prominent signal at  $m/z$  96 ( $C_3H_4O_2^+$ ),  
226 which corresponds to the molecular weight of furfural, is found exclusively in furfural SOA. Given the  
227 absence of enhanced signals at  $m/z$  82 ( $C_5H_6O^+$ , methylfuran parent ion) in 2- and 3-methylfuran SOA,  
228 the oligomers in furfural SOA may retain the structure of the parent compound, unlike the oligomers  
229 that compose 2- and 3-methylfuran SOA.

230 Speciated composition of furanoid SOA identified using FIGAERO-CIMS is shown as mass  
231 spectra at the peak SOA mass concentration in Figure S3.  $C_5H_4O_4$ ,  $C_4H_4O_3$ , and  $C_5H_6O_3$ , which are also  
232 observed with elevated signals in the gas-phase mass spectra (Figure S2), exhibit the strongest signal  
233 levels in furfural, 2-methylfuran, and 3-methylfuran SOA, respectively. Besides these major species,  
234 furfural and 2-methylfuran SOA show higher signal levels across various  $C_{4-5}$  compounds, whereas 3-  
235 methylfuran SOA is dominated by  $C_5$  compounds. These observations are consistent with gas-phase  
236 species speciation (Figure S2), where furfural and 2-methylfuran systems show substantial  
237 contributions from both  $C_4$  and  $C_5$  compounds (e.g.,  $C_4H_4O_3$ ,  $C_5H_4O_4$ ,  $C_5H_6O_3$ ) while the 3-methylfuran  
238 system is dominated by  $C_5H_6O_3$ . Considering that FIGAERO-CIMS uses thermal desorption technique  
239 to probe particle-phase composition, the detected particulate  $C_{4-5}$  compounds may include fragments  
240 produced by thermal decomposition of oligomers.



241 Besides the CHO species that show stronger signal intensity across the furanoid SOA examined in  
242 this study, only a few CHON species such as  $C_5H_3NO_5$ ,  $C_4H_5NO_7$ ,  $C_5H_7NO_7$  show higher signals among  
243 the identified CHON components. Figure 3 summarizes the relative abundances of identified  
244 compounds by carbon number and oxygen number, grouped into CHO and CHON compound classes.  
245  $C_{4-5}$  compounds in furanoid SOA are mostly composed of CHO species with 3 to 6 oxygen atoms.  
246 However, CHON species in 2-methylfuran and 3-methylfuran SOA are dominated by  $C_{4-5}$  compounds  
247 with 7 to 8 oxygen atoms, whereas CHON species in furfural SOA are distributed over a wider range  
248 of carbon number and oxygen number, generally containing fewer than 5 oxygen atoms.

### 249 3.3 Volatility of furanoid SOA

250 The 2-D thermograms of furanoid SOA obtained from FIGAERO-CIMS are shown in Figure 4.  
251 These thermograms summarize the signal intensity of identified particle-phase compounds as a function  
252 of desorption temperature, allowing comparison of thermal desorption behavior across the examined  
253 furanoid SOA. Individual species in furfural SOA desorb across a much wider temperature window  
254 ( $\sim 40$  °C to  $180$  °C) compared to 2- and 3-methylfuran SOA, which shows a high-intensity signal band  
255 centered around  $\sim 80$  °C. This trend is well reflected in the signal-weighted-average thermograms (red  
256 lines in Figure 4), where furfural SOA exhibits a higher  $T_{max}$  ( $144.5$  °C) than 2- and 3-methylfuran SOA  
257 ( $T_{max} = 82.6$  °C). The wide thermogram of furfural SOA arises from stronger signals in the lower-  
258 volatility bins ( $C^* = 10^{-4.6}$  and  $10^{-7.8}$   $\mu\text{g m}^{-3}$ ) compared to 2- and 3-methylfuran SOA. In addition to the  
259 higher  $T_{max}$ , the broader signal distribution of furfural SOA suggests a more diverse chemical  
260 composition with a wide range of volatility compared to methylfuran SOA. We note that the signal-  
261 weighted-average thermograms of all furanoid SOA in this study are broader and exhibit higher  $T_{max}$   
262 values ( $82.6$ – $144.5$  °C) than those obtained during single-compound calibrations (e.g., glutaric acid,  
263  $C_5H_8O_4$ ,  $T_{max} = 43$  °C) (Joo et al., 2024a), suggesting the presence of oligomeric species in furanoid SOA  
264 in addition to  $C_5$  monomers.



## 265 4 Discussion

### 266 4.1 Distinct radical chemistry of furfural among furanoids

267 The difference in temporal variations of NO and NO<sub>2</sub> between furfural (Figure 1a) and 2- and 3-  
268 methylfuran (Figure 1c and e) experiments indicates that the radical chemistry following furanoid+OH  
269 reaction can vary depending on the furanoid structure. The initial decrease in NO<sub>2</sub> and concurrent  
270 increase in NO at the onset of furfural photooxidation suggest that radicals such as alkyl radicals (R)  
271 can consume NO<sub>2</sub>, which is converted into NO, instead of undergoing the typical RO<sub>2</sub>+NO channel  
272 observed in the methylfuran experiments. We also note that there could be potential interference in the  
273 observed increase of NO from peroxyacylnitrate (PAN)-like species formed during acyl peroxy radical  
274 reaction pathways. Our results confirm previous theoretical studies that explored photooxidation of  
275 furfural and methylfuran isomers (Yuan et al., 2017; Zhao and Wang, 2017), and the oxidation  
276 mechanism is detailed in Figures 5 (simplified) and S4 (extended). Once photooxidation reactions are  
277 initiated by OH addition at the 2 or 5 position of substituted furanoids, which have lower energy barriers  
278 than OH addition at the 3 or 4 position, hydroxyalkyl radicals generated during furfural+OH (F-R1 and  
279 F-R2) preferentially react with NO<sub>2</sub> (or HO<sub>2</sub>/RO<sub>2</sub>, O<sub>3</sub>) to form hydroxyalkoxyl radicals (F-AR1 and F-  
280 AR2) via R+NO<sub>2</sub> reaction channel (Figure 5a). Although a previous theoretical study suggested that the  
281 typically expected RO<sub>2</sub> (F-PR1) formation pathway can be favored under high NO conditions (Zhao  
282 and Wang, 2017), the elevated NO<sub>2</sub> levels in this study may have limited this pathway. This reaction  
283 channel can be followed by the decomposition pathway to form a heterocyclic hydroxy carbonyl  
284 (R(OH)(O), C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>) or an organic acid (R(O)COOH, C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>), which show the strongest signal  
285 intensity from HR-ToF-CIMS (Figure S2) and can compete with relatively minor reaction pathway that  
286 forms a ring-opened tricarbonyl compound, 4-oxo-2-pentendial (C<sub>5</sub>H<sub>4</sub>O<sub>3</sub>). 4-oxo-2-pentendial is  
287 observed to form more rapidly than C<sub>4</sub>H<sub>4</sub>O<sub>3</sub> (Figure 1b). The effective first-order reaction constant for  
288 the formation of 4-oxo-2-pentendial is estimated to be  $\sim 2 \times 10^4 \text{ s}^{-1}$  via F-R3+O<sub>2</sub> reaction, whereas that  
289 for C<sub>4</sub>H<sub>4</sub>O<sub>3</sub> is estimated to be  $\sim 15 \text{ s}^{-1}$  from F-R1/F-R2, assuming the rate constants of F-R1/F-R2 with  
290 NO<sub>2</sub> are similar to that of a simplified form of alkyl radical (i.e., CH<sub>3</sub> radical) reaction with NO<sub>2</sub>  
291 (Albaladejo et al., 2002; Zhao and Wang, 2017). Additionally, 4-oxo-2-pentendial can form via HO<sub>2</sub>  
292 abstraction of hydroxyperoxy radical (F-PR2), which is formed via ring-opened hydroxyalkyl radical



(F-R3) reaction with  $O_2$ . Unlike F-R1/R2, which are estimated to react slowly with  $O_2$  compared to  $NO_2/HO_2/O_3$ , F-R3 reacts with  $O_2$  sufficiently fast to form a peroxy radical (Zhao and Wang, 2017). Further reaction of 4-oxo-2-pentendial via H-abstraction by OH radical can generate dicarbonyl carboxylic acid ( $R(O)(O)COOH$ ,  $C_5H_4O_4$ ), which is identified as a major product in particle-phase mass spectra (Figure S3).

Because of the presence of aldehyde functionality, unlike 2- and 3-methylfuran, OH oxidation of furfural can proceed through an additional reaction channel besides the OH addition, which is an H-abstraction pathway to form an acyl peroxy radical (Zhao and Wang, 2017). Further reaction of F-PR3 with NO can lead to the formation of an organic acyl nitrate ( $R(O)ONO_2$ ,  $C_5H_3NO_5$ ), which shows the strongest signal among nitrogen-containing compounds in both gas and particle phases (Figure S2 and S3). Beyond the prominent gas-phase species shown in Figure S2, the F-PR3 reaction channel can additionally generate aged biomass burning plume markers such as maleic anhydride ( $C_4H_2O_3$ ) and acyl peroxy nitrate ( $C_5H_3NO_6$ ) (Figure 5a and S4a), which have been reported as fur-PAN (furoyl peroxyxynitrate) in previous studies (Coggon et al., 2019; Roberts et al., 2022).

Meanwhile, the hydroxyalkyl radicals (MF2-R1/R2, and MF3-R1/R2) formed from 2- and 3-methylfuran+OH reactions undergo  $O_2$  addition to form hydroxyperoxy radicals (MF2-PR1/PR2 and MF3-PR1/PR2), which subsequently react with NO via  $RO_2+NO$  channel to produce cyclic hydroxyalkoxy radicals (MF2-AR1/AR2 and MF3-AR1/AR2). The alkoxy radicals subsequently decompose to form cyclic hydroxy carbonyl compounds ( $C_5H_6O_3$  and  $C_4H_4O_3$  from 2-methylfuran+OH, and  $C_5H_6O_3$  from 3-methylfuran+OH reaction (Yuan et al., 2017)) (Figure 5b and c), which are identified as major oxidation products in Figure S2 and show a first-generation product temporal variation in Figure 1d and 1f. Similar to furfural, such reaction channel competes with the formation of dicarbonyl compounds such as 4-oxo-2-pentenal ( $C_5H_6O_2$ ) and 2-methylbutenedial from 2-methylfuran+OH and 3-methylfuran+OH experiments, respectively. The ring-opening pathway is reported to be less favored, particularly for 3-methylfuran oxidation by OH radicals, compared to furfural or 2-methylfuran oxidation (Yuan et al., 2017; Aschmann et al., 2014). Still, these dicarbonyls are observed to form more rapidly compared to other first-generation products (Figure S5), as they are directly generated from alkyl radical (Figure S4b and c). Further reaction of these aldehydes via H-



321 abstraction by OH radicals can explain the formation of major gas-phase CHO species, including  
322  $C_5H_6O_3$  (a carbonyl carboxylic acid, Figure 5b and c), while also providing pathways to CHON species  
323 with prominent signals (Figure S2) such as organic acyl nitrate ( $R(O)ONO_2$ ,  $C_5H_5NO_5$ ). We note that  
324 carboxylic acids commonly found as major oxidation products in HR-ToF-CIMS measurements in this  
325 study can form via Baeyer–Villiger reaction during oligomerization processes (Claflin et al., 2018; Joo  
326 et al., 2019).

327 Gas-phase oxidation chemistry of the furanoids explored here shows that the substituent on the  
328 furan ring governs the radical pathways:  $R+NO_2$  is more influential in furfural+OH reaction, whereas  
329  $RO_2+NO$  chemistry dominates 2- and 3-methylfuran+OH reaction. Furthermore, even with the same  
330 substituent, different positional isomers (2- vs. 3-methylfuran) can divert the reaction channels,  
331 producing first-generation products with different carbon numbers ( $C_4$  vs.  $C_5$ ). This disparity in gas-  
332 phase oxidation across furanoid types drives differences in furanoid SOA formation potential and  
333 composition. Although ring-opening pathways are common for furanoids,  $C_5H_6O_2$  and its subsequent  
334 oxidation products retain fewer oxygenated functional groups compared to the ring-opened first-  
335 generation product formed during the furfural+OH reaction ( $C_5H_4O_3$ ), resulting in fewer reactive sites  
336 available for accretion reactions.

## 337 **4.2 Oligomer formation and structural complexity of furfural SOA**

338 Speciated SOA composition measured using FIGAERO-CIMS confirms the presence of  
339 oligomeric compounds in all furanoid SOA examined in this study. The relative abundances of  
340 compounds identified by FIGAERO-CIMS (Figure 3) demonstrate that dimeric species in the  $C_{6-10}$   
341 range comprise a sizable fraction of total detected particle-phase ion abundances (furfural SOA: 15%  
342 & 19%, 2-methylfuran SOA: 13% & 13%, 3-methylfuran SOA: 16% & 17% for CHO & CHON  
343 compounds, respectively). Additionally, the detected  $C_{4-5}$  compounds include fragments produced by  
344 thermal decomposition of oligomers during the thermal desorption process in FIGAERO-CIMS. The  
345 presence of oligomers is further confirmed from offline LC-TOF filter analysis, which provides  
346 additional evidence for a range of  $C_{6+}$  accretion products, extending up to  $C_{32}$  (Figure S6). Furfural SOA  
347 appears to have a higher oligomer contribution with FIGAERO-CIMS thermogram and LC-TOF carbon



number distribution that extend substantially into higher molecular weight species (Figures 4 and S6). In addition to higher contributions from C<sub>6-10</sub> compounds, the fraction of  $m/z > 50$  fragments detected by HR-ToF-AMS is also higher for furfural SOA compared to 2-methylfuran SOA and 3-methylfuran SOA (Figure 2). Accordingly, this is consistent with the higher  $\Delta M_o$  and SOA yield observed for furfural among all furanoids examined in this study (Table 1).

As proposed in Section 4.1, the greater availability of reactive sites for accretion reactions for molecules generated during photooxidation of furfural (Figure S4) suggests that the oxidation products can have molecular structures with more diverse functionalities. Furthermore, the broader high-signal band observed in the 2-D thermogram of furfural SOA (Figure 4) suggests the presence of more chemically diverse particle-phase products. Molecular information on furanoid SOA obtained from FIGAERO-CIMS (Figure 6) further indicates that furfural SOA has a lower but broader C\* distribution and exhibits a higher average degree of unsaturation ( $DU = nC - (nH/2) + (nN/2) + 1$ ) for a similar  $m/z$  range compared to 2- and 3-methylfuran SOA. It is well known that a higher level of DU can be associated with the presence of aromatics or oxygenated functionalities such as carbonyls and carboxylic acids, which may correspond to the higher fraction of C<sub>x</sub>H<sub>y</sub>O<sub>z>1</sub> species and a higher oxidation state ( $OSc = 2 \times O:C - H:C$ ) observed for furfural SOA ( $OSc = 1.32$ ) compared to 2-methylfuran SOA ( $OSc = 1.19$ ) and 3-methylfuran SOA ( $OSc = 0.60$ ) in HR-ToF-AMS (Figure 2). An increase in the abundance of such functionalities can decrease volatility (Pankow and Asher, 2008), thereby facilitating SOA formation. Furthermore, the high DU of furfural SOA may be related to the stronger brown carbon formation reported previously (Joo et al., 2024a), as conjugated bonds that can increase DU are also known to enhance light-absorbing properties besides reduced CHON species that can be associated with amine, imine, or amide functional groups (Chen et al., 2022; Laskin et al., 2015).

#### 4.3 Distinct CHON composition and organic nitrate formation in furanoid SOA

Differences in radical chemistry among furanoids (i.e., R+NO<sub>2</sub> and RO<sub>2</sub>+NO pathways during furfural+OH and methylfuran+OH reactions, respectively) can distinctly influence the composition of CHON species in the particle phase. The products from these pathways differ; RO<sub>2</sub>+NO reactions are known to generate alkoxy radicals (major pathway) and organic nitrate (RONO<sub>2</sub>) (minor pathway)



375 (Perring et al., 2013), whereas  $R+NO_2$  reaction can generate alkoxy radicals (major pathway) and nitro  
376 organics ( $RNO_2$ ) (minor pathway) (Rissanen et al., 2010), which are generally more reduced than  
377 organic nitrate functionalities. Furthermore, furfural oxidation products can interact with  $NH_3/NH_4^+$  at  
378 the particle surface to form reduced nitrogen functionalities such as amine or amide during  
379 photooxidation (Joo et al., 2024a). Results from FIGAERO-CIMS (Figure 3) demonstrate this  
380 difference, showing relatively predominant, less oxygenated CHON ( $C_xH_yN_nO_{\leq 6}$ ) species across a wide  
381 range of carbon number in furfural SOA, whereas CHON species in 2- and 3-methylfuran SOA are  
382 relatively more oxygenated, with signal intensities concentrated at  $C_{4-5}H_yN_nO_7$  compounds. When all  
383 the detected CHON species are lumped into two classes ( $O/N \geq 3$  and  $O/N < 3$ ) (Figure 7), 19.0% of the  
384 furfural SOA signal measured by FIGAERO-CIMS is attributed to CHON species with higher O/N  
385 ratios ( $O/N \geq 3$ ), whereas 8.3% is attributed to CHON species with lower O/N ratios ( $O/N < 3$ ). Compared  
386 to furfural SOA, CHON species with  $O/N \geq 3$  contribute a larger fraction of the total FIGAERO-CIMS  
387 signal in 2-methylfuran and 3-methylfuran SOA, accounting for 35.1% and 24.2%, respectively, while  
388 CHON species with  $O/N < 3$  contribute 0.6% and 0.2%, respectively. The bulk composition analysis by  
389 LC-ESI-Q-ToF further supports these observations (Figure S7), showing a higher relative contribution  
390 of CHON species with  $O/N \geq 3$  in 2- and 3-methylfuran SOA than in furfural SOA.

391 CHON species with  $O/N \geq 3$  are likely associated with the formation of organic nitrate compounds,  
392 especially for species measured using FIGAERO-CIMS, considering their high sensitivity toward  
393 iodide reagent ion (Lee et al., 2014; Takeuchi and Ng, 2019). Accordingly, we estimate the particulate  
394 organic nitrate to organic aerosol ratio ( $pRONO_2/Org$ ) using the method proposed by Takeuchi et al.  
395 (2024), which leverages  $R_{ON}$  ( $NO^+/NO_2^+$  ratio of organic nitrate) and  $R_{AN}$  ( $NO^+/NO_2^+$  ratio of  
396 ammonium nitrate) obtained from HR-ToF-AMS (Table S2), together with molecular weight of CHON  
397 ( $O/N \geq 3$ ) species (furfural:  $137.8 \text{ g mol}^{-1}$  / 2-methylfuran:  $191.3 \text{ g mol}^{-1}$  / 3-methylfuran:  $203.0 \text{ g mol}^{-1}$ )  
398 obtained from FIGAERO-CIMS (Figure 7d). In this study, 2-methylfuran SOA shows the highest  
399  $pRONO_2/Org$  ratio (45%), followed by 3-methylfuran SOA (36%), and furfural SOA (11%), consistent  
400 with the relative fraction of CHON species with  $O/N \geq 3$  observed from both FIGAERO-CIMS and LC-  
401 ESI-Q-ToF measurements. It should also be noted that  $pRONO_2/Org$  values may be influenced by



402 fragmentation of other nitrogen-containing organics in HR-ToF-AMS measurements, particularly nitro  
403 compounds (Xu et al., 2021).

## 404 **5 Conclusions and implications**

405 This work investigates photooxidation chemistry and SOA formation from reactions of furanoids  
406 with OH radicals. Among the furanoids examined, furfural+OH reaction generates the highest SOA  
407 yield (9.8%) with a corresponding organic mass concentration of  $66.3 \mu\text{g m}^{-3}$ , followed by SOA formed  
408 during 2-methylfuran+OH ( $1.2\%$  at  $8.9 \mu\text{g m}^{-3}$ ) and 3-methylfuran+OH reaction ( $1.0\%$  at  $6.9 \mu\text{g m}^{-3}$ ).  
409 A previous study reported that furanoids can contribute up to 51% of potential SOA depending on the  
410 type of fuel combusted (Hatch et al., 2015). Given the large emissions of furfural from various biomass  
411 burning fuels such as ponderosa pine and rice straw (Ciccioli et al., 2001; Gilman et al., 2015; Hatch et  
412 al., 2015), our findings suggest that furfural can be the most important SOA precursor among furanoids  
413 emitted from the biomass burning across different continents.

414 The difference in the amount of SOA formed can be closely associated with the molecular structure  
415 characteristics of furanoid SOA. Furfural SOA exhibits greater molecular complexity, with a lower but  
416 broader  $C^*$  distribution and a higher average DU within a similar  $m/z$  range compared to 2- and 3-  
417 methylfuran SOA. The molecular complexity of furfural SOA can be relevant to multigenerational  
418 oxidation products generated from the first-generation ring-opened tricarbonyl ( $C_5H_4O_3$ ), which retains  
419 more reactive sites available compared to oxidation products of dicarbonyls ( $C_5H_6O_2$ ) generated during  
420 2- and 3-methylfuran SOA formation. Even among alkyl-substituted furanoids, the distribution of first-  
421 generation oxidation products differs by isomer type. Methyl substitution at the 2-position yields both  
422  $C_4$  and  $C_5$  products, whereas substitution at the 3-position predominantly yields  $C_5$  products. These  
423 differences may have driven variations in SOA composition and volatility between methylfuran isomers.

424 While biomass burning is generally understood to enhance ozone formation (Jin et al.; Xu et al.,  
425 2022), large emissions of furfural during biomass burning can add complexity when detailed radical  
426 reactions are integrated to estimate ozone production. Unlike 2- and 3-methylfuran that undergo typical  
427  $RO_2+NO$  reaction that produces  $NO_2$ , which can form ozone through subsequent photochemical  
428 reactions, furfural oxidation is influenced by the  $R+NO_2$  channel. This radical reaction channel



429 consumes  $\text{NO}_2$  and yields  $\text{NO}$ , which can titrate ozone. In addition, the alkyl radical from furfural+OH  
430 can directly consume ozone, competing with  $\text{NO}_2$  to form alkoxy radical and bypassing the formation  
431 of peroxy radical (Zhao and Wang, 2017). Furthermore, compared to 2- and 3-methylfuran+OH reaction,  
432 furfural+OH reaction forms fewer organic nitrates, which can serve as  $\text{NO}_x$  reservoirs that can affect  
433 ozone formation downwind of the biomass burning plume (Alvarado et al., 2010).

434 Furanoids are often regarded as indicators of fresh biomass burning plumes, but their  
435 concentrations can decrease rapidly once released into the atmosphere owing to their high reactivity  
436 toward OH and  $\text{NO}_3$  radicals. Accordingly, Müller et al. (2016) and Coggon et al. (2019) suggested that  
437 maleic anhydride ( $\text{C}_4\text{H}_2\text{O}_3$ ) can serve as a tracer of aged biomass burning plumes far downwind of the  
438 source, since its lifetime can exceed 5 days at typical tropospheric OH concentration ( $1.5 \times 10^6$  molec.  
439  $\text{cm}^{-3}$ ). Additionally, Roberts et al. (2022) proposed fur-PAN ( $\text{C}_5\text{H}_3\text{NO}_6$ ) as a photochemical biomass  
440 burning tracer, with an order of magnitude enhancement compared to urban background level when  
441 biomass burning plume hit Pasadena, CA. We identified these two compounds in the furfural+OH  
442 reaction, but only maleic anhydride exhibits a continuous increase throughout the experiment (Figure  
443 S5), suggesting that it is more representative of an aged biomass burning plume marker under the  
444 experimental conditions examined in this study. Furthermore, the presence of  $\text{C}_4\text{H}_2\text{O}_3$  and its continuous  
445 increasing temporal trend are also observed in the 2-methylfuran+OH and 3-methylfuran+OH  
446 experiments, indicating that this compound may serve as a robust indicator of aged biomass burning  
447 influences associated with furanoid emissions.

448 Most current atmospheric models treat furanoids as a single compound class, and even those  
449 incorporating furanoid-specific reaction mechanisms often consider only alkyl-substituted variants  
450 while neglecting functionalized species (Romanias et al., 2024). The observed variability in gas phase  
451 photooxidation chemistry, SOA yield, and SOA composition across furanoid types implies that model  
452 parameterization and OH reactivity estimates should account for differences in functionalization. More  
453 importantly, our results suggest that substituent type can substantially influence radical chemistry, SOA  
454 formation, and SOA composition more strongly than isomeric differences among precursor furanoids.  
455 Thus, differentiating furfural from alkyl-substituted furanoids is important for improving our  
456 understanding of the chemical evolution of biomass burning plumes and their impacts on air quality.



## 457 **Data Availability**

458 The chamber experiment data reported in this study will be made available at the time of publication in  
459 the Index of Chamber Atmospheric Research in the United States (ICARUS) database.

## 460 **Author contribution**

461 TJ and NLN designed the environmental chamber experiments conducted in this study with inputs from  
462 MJA. TJ and DP performed chamber experiments, and TJ compiled and analyzed data obtained from  
463 all operated instruments. JEM, TH-M, and DRG analyzed offline filter data via LC-ESI-Q-ToF. JCR  
464 helped develop oxidation mechanisms. TJ and NLN prepared the original manuscript with contributions  
465 from all co-authors.

## 466 **Competing interests**

467 At least one of the (co-)authors is a member of the editorial board of *Atmospheric Chemistry and Physics*.  
468 The authors have no other competing interests to declare.  
469

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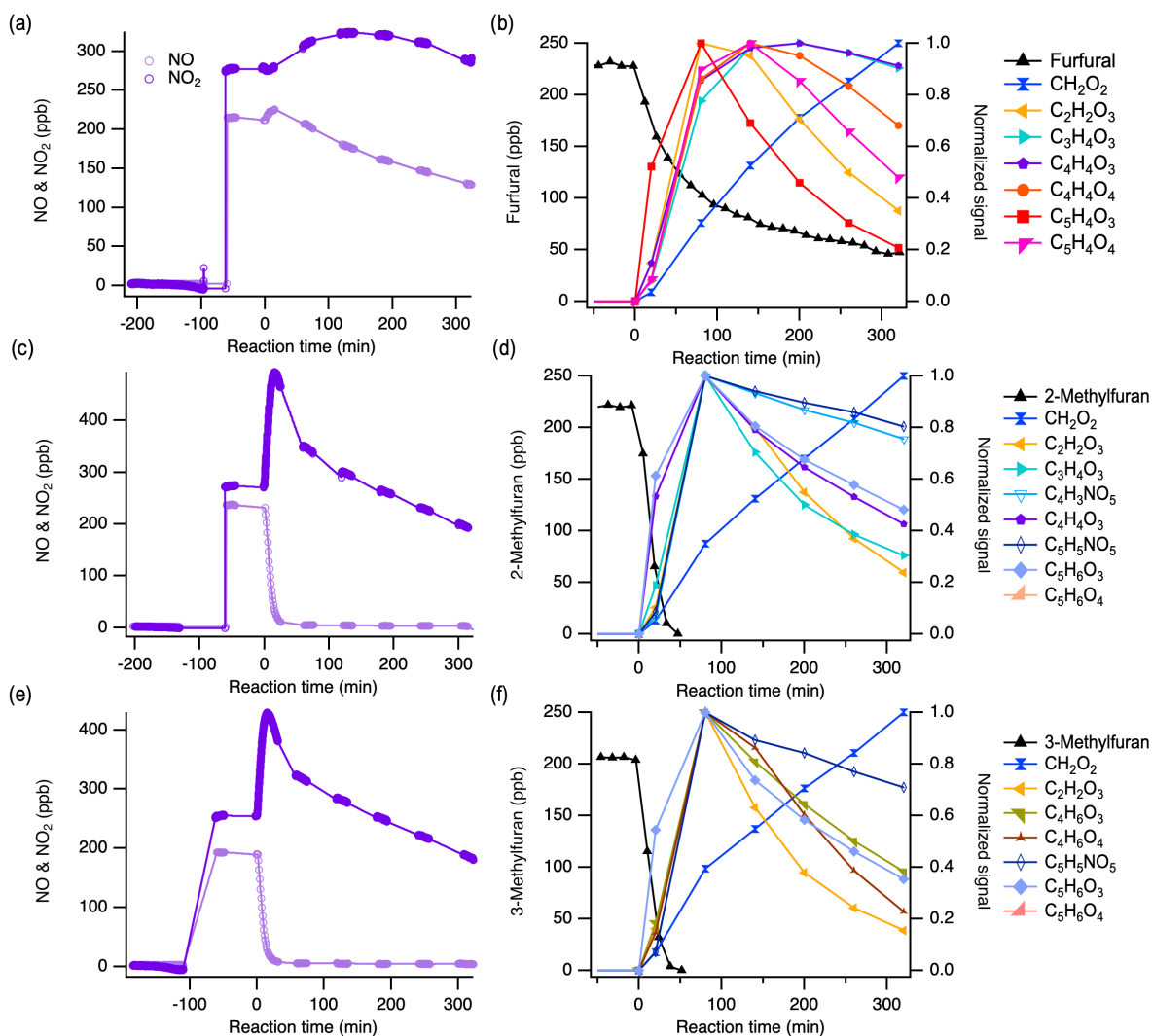
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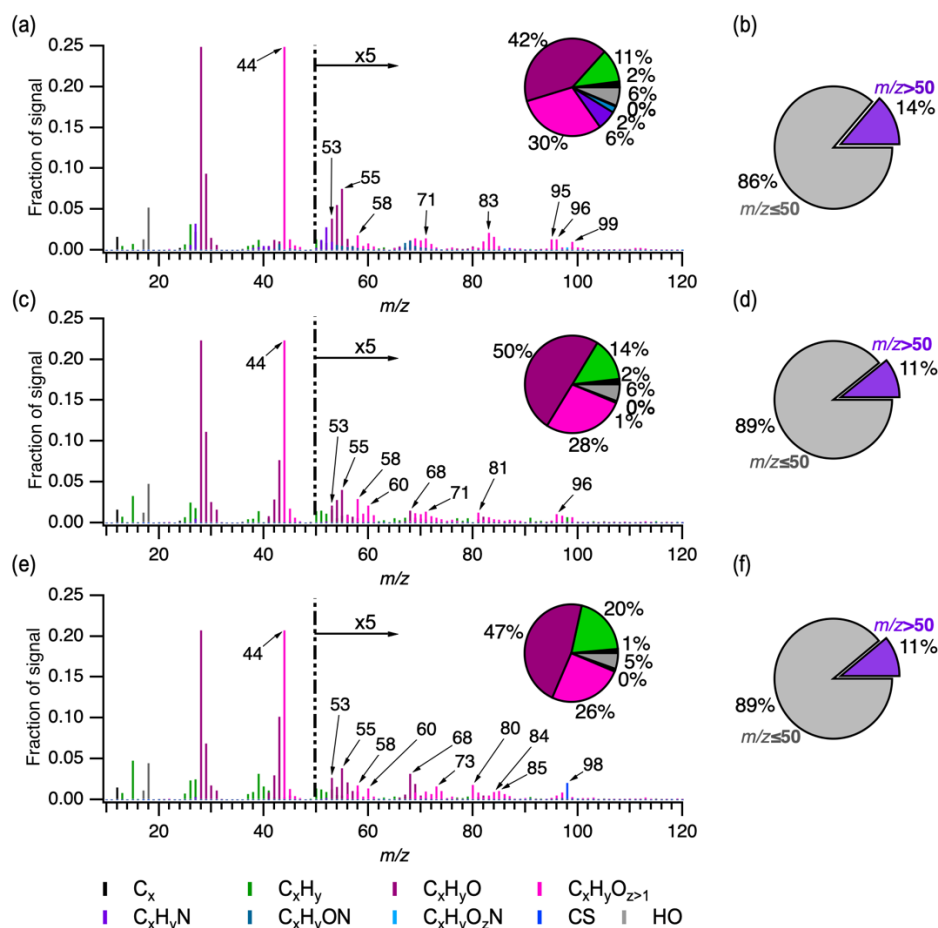
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## 764 Figures and Table



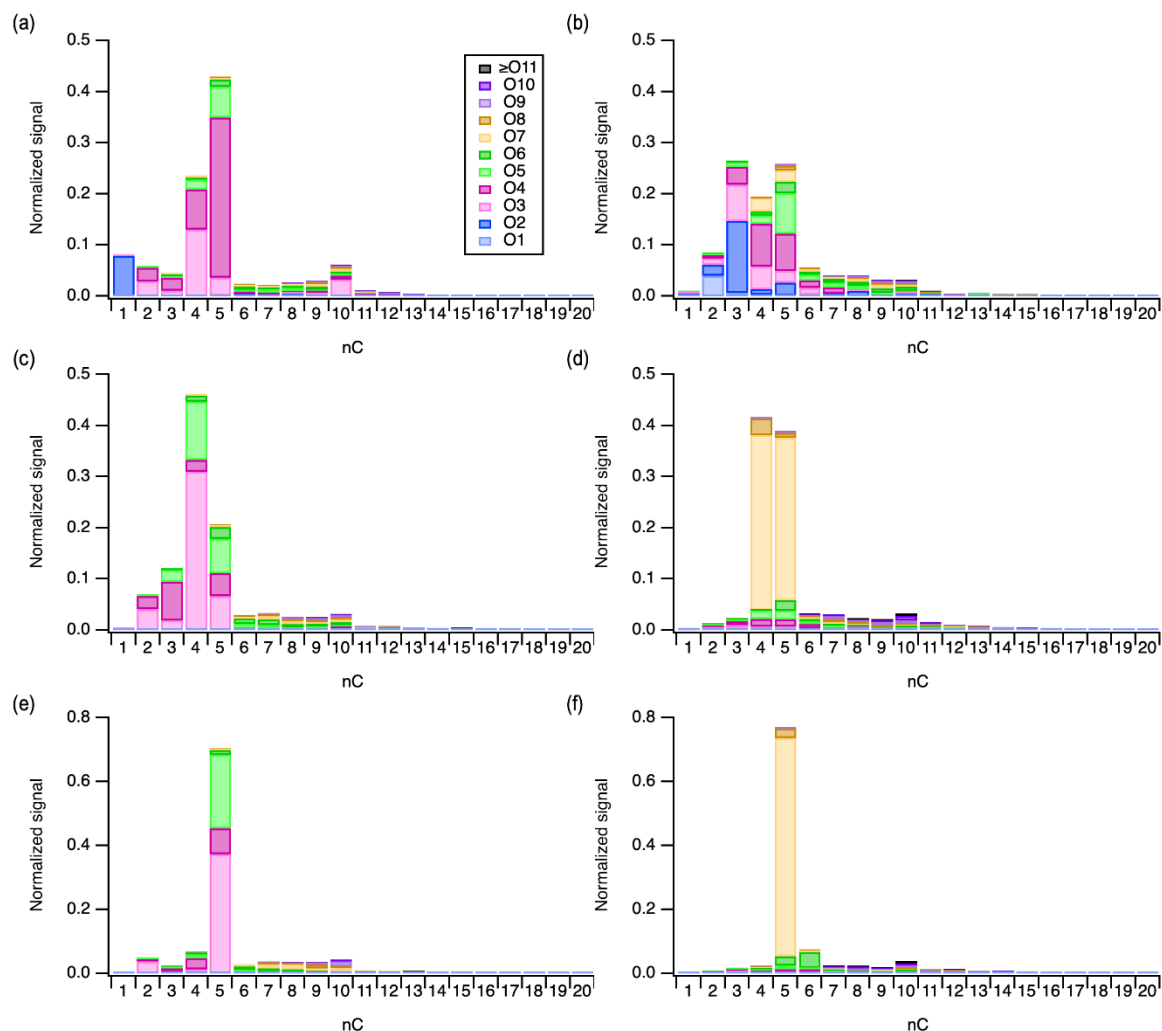
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766 Figure 1. Temporal profiles of NO<sub>x</sub> (a, c, e) and precursor VOCs (b, d, f) with gaseous oxidation  
 767 products during the photooxidation of furfural, 2-methylfuran, and 3-methylfuran, respectively. To  
 768 extend the experimental time, NO and NO<sub>2</sub> monitors sampled 15 mins continuously once every hour  
 769 and data points are interpolated between each measurement period.



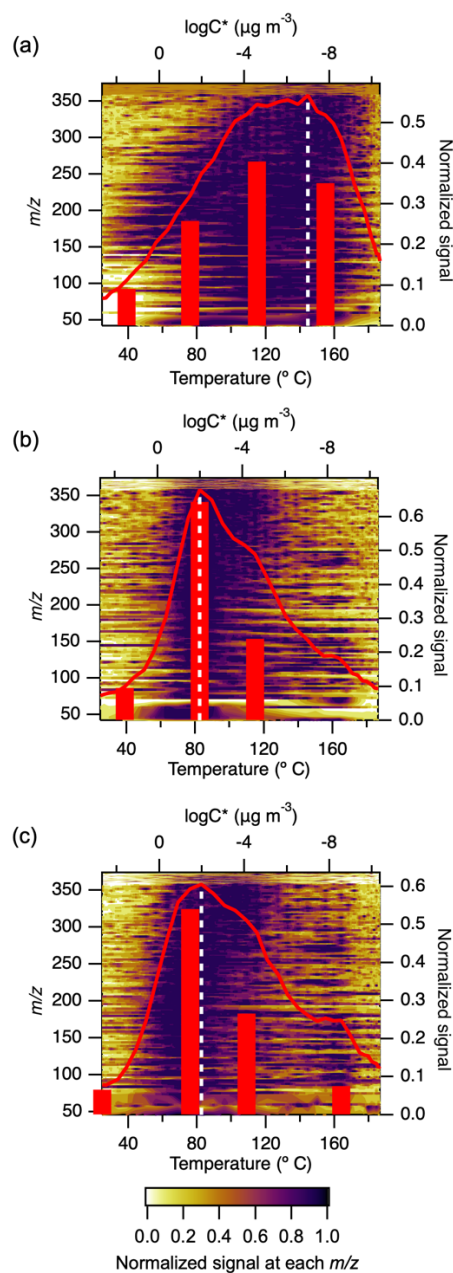
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771 Figure 2. HR-ToF-AMS mass spectra and organic elemental composition of (a) furfural SOA, (c) 2-  
772 methylfuran SOA, and (e) 3-methylfuran SOA. Mass fractions of signals below (grey) and above  
773 (purple)  $m/z$  50 (right panel) are shown for (b) furfural SOA, (d) 2-methylfuran SOA, and (f) 3-  
774 methylfuran SOA.



775

776 Figure 3. CHO (a, c, e) and CHON (b, d, f) compound classes in furfural SOA, 2-methylfuran SOA,  
 777 and 3-methylfuran SOA, respectively, grouped by carbon and oxygen numbers, measured by  
 778 FIGAERO-CIMS.



779

780 Figure 4. 2-D thermograms of (a) furfural SOA, (b) 2-methylfuran SOA, and (c) 3-methylfuran SOA.

781 Solid red lines in 2-D thermograms are signal-weighted average thermograms, and red bars are

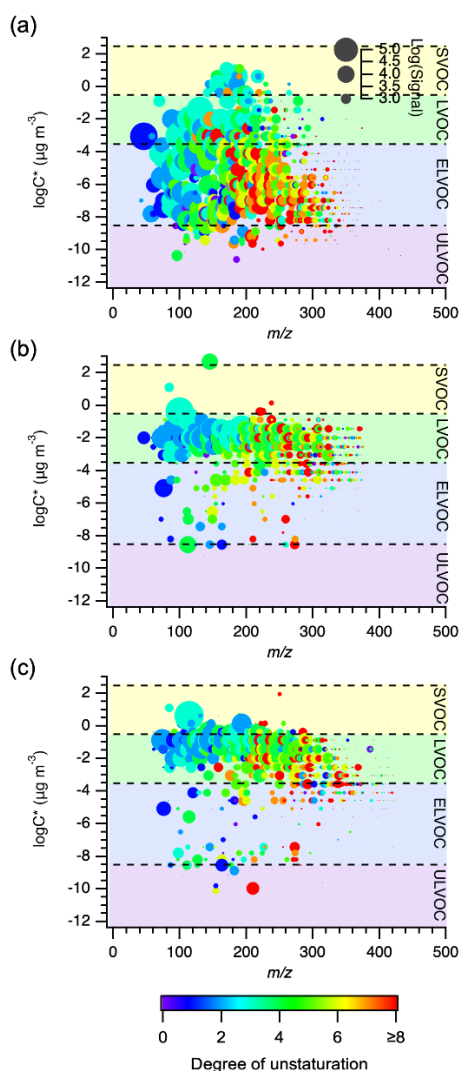
782 estimated  $C^*$  bins.



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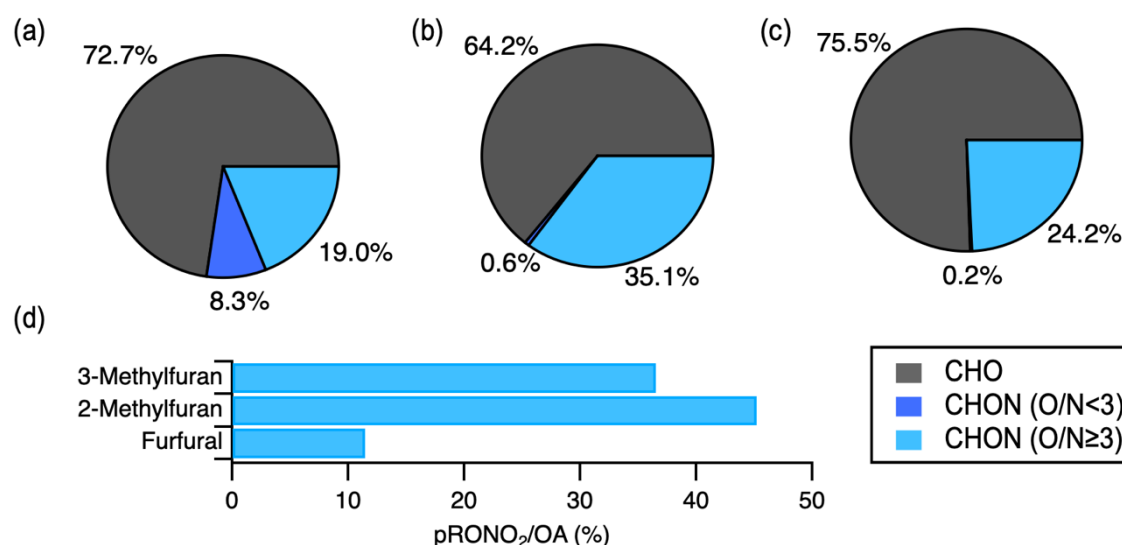


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789 Figure 6. Saturation mass concentration ( $C^*$ ) vs.  $m/z$ , color coded by degree of unsaturation of  
 790 compounds detected in (a) furfural SOA, (b) 2-methylfuran SOA, and (c) 3-methylfuran SOA,  
 791 measured by FIGAERO-CIMS.



792

793 Figure 7. Different compound classes measured by FIGAERO-CIMS, weighted by signal intensity: (a)  
794 furfural SOA, (b) 2-methylfuran SOA, and (c) 3-methylfuran SOA. (d) Percentage of particulate organic  
795 nitrate (pRONO<sub>2</sub>) in organic aerosol (OA) estimated from HR-ToF-AMS measurements with molecular  
796 weight information from FIGAERO-CIMS.

797

798

799 Table 1. Experimental conditions and SOA yields for all experiments.

| Exp. | Precursor     | Initial<br>NO <sub>x</sub><br>(ppb) | RH<br>(%) | Injected<br>VOC<br>(ppb)* | ΔVOC<br>(ppb)* | ΔM <sub>0</sub><br>(μg m <sup>-3</sup> )** | SOA Yield<br>(%) |
|------|---------------|-------------------------------------|-----------|---------------------------|----------------|--------------------------------------------|------------------|
| 1    | Furfural      | 491.4                               | <5        | 228.9±1.8                 | 172.4±1.8      | 66.3±1.0                                   | 9.8±0.05         |
| 2    | 2-methylfuran | 506.1                               | <5        | 220.2±0.3                 | 220.2±0.3      | 10.3±0.5                                   | 1.4±0.06         |
| 3    | 3-methylfuran | 445.3                               | <5        | 205.5±0.3                 | 205.5±0.3      | 7.2±0.5                                    | 1.1±0.07         |

800 \* Uncertainties of VOC and consumed VOC (ΔVOC) are calculated based on the GC-FID calibration error and  
801 1σ of VOC concentrations before onset of the photooxidation.

802 \*\* Uncertainties for ΔM<sub>0</sub> are calculated from 1σ of aerosol volume concentration measured by the SMPS at peak  
803 SOA mass concentration. Uncertainties in the SOA density are also propagated.