Response of "The Important Contribution of Secondary Formation and Biomass Burning to Oxidized Organic Nitrogen (OON) in a Polluted Urban Area: Insights from In Situ FIGAERO-CIMS Measurements" in *Atmos. Chem. Phys. Discuss. Doi: 10.5194/acp-2023-8*

Anonymous Referee #2

2.0. The authors performed measurements of gas and particle-phase organic compounds using a FIGAERO-CIMS in a polluted urban location in China, with a particular focus in oxidized organic nitrogen species. Using $C_6H_{10}O_5$ (levoglucosan) as a tracer, they estimated the contribution of biomass burning to the measured gas and particle concentrations. Calculations were done to estimate the contribution of different oxidants and precursors to secondary organic nitrogen production. Broadly, the measurements and analysis presented in this manuscript are useful for helping to understand sources of organic nitrogen gases and particles in urban areas. Before this work is published, I believe there are several major issues that should be addressed. If I understand the experimental setup correctly, I am worried about the impact of sampling through a nafion tube. I think the authors should consider how much that could affect their measurements in light of recent literature on the topic. I also want to see an uncertainty analysis of the measurements, especially of the voltage scanning technique that is still a relatively new method of CIMS quantification. Taken together, I think the authors should carefully discuss the strengths or limits of their conclusions in the context of these uncertainties.

A2.0. We appreciate the reviewer for his/her insightful comments and suggestions, which help us tremendously in improving the quality of our work. Following the reviewer's suggestions, we have carefully revised the manuscript. To facilitate the review process, we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper **(in bold text).**

Comments:

2.1. Line 103: Have the authors investigated any artifacts that could result from sampling the CIMS through a nafion dryer? For instance, have you considered possible particle losses, or losses of compounds with particular functional groups that do not transmit well through nafion? This previous work from Liu et al. 2019 indicates that polar S/IVOCs do not

transmit well through nafion (https://amt.copernicus.org/articles/12/3137/2019/). This could be a critical problem for this work, and needs to be addressed.

A2.1: Thanks for the reviewer's comment. We need to point out that the nafion dryer was only set in the aerosol sampling line, not the gas phase line, thus the gas-phase S/IVOCs shall not be affected. The nafion dryer was necessary in our study due to the high humidity of ambient air (72 ± 17%), which could lead to the water condensation on the sampling filters of FIGAERO-CIMS under room temperatures. Liu et al. 2019 recommended that "Aerosols in equilibrium with S/IVOCs will be perturbed by the removal of the gases by the Nafion, so we recommend installing Nafion dryers or humidifiers at the last possible location before an instrument and to minimize residence time both in the dryer and between the dryer and instrument whenever possible." In our setup, we set up the nafion dryer around 1 meter ahead of the FIGAERO inlet at a flow rate of 5 L min⁻¹ with 1/4-inch stainless tubes. The total residence time of aerosol in the dryer and between the dryer and instrument are ~ 0.12 and 0.23 second respectively. For this time scale, the removal of SVOCs would be around less than two percents based on partitioning delay model (Pagonis et al., 2017). Thus, we believe that the loss of SVOC in aerosol phases in such a short time shall be very small. Also, we added a reminder to the readers that accurate correction for the losses to nafion dryer remains impossible. No loss correction was performed in this study. To clarify this, we revised the relative discussion in line 105-112:

"The sampling flow rate is 3.8 L min⁻¹ for gas sampling line and 5 L min⁻¹ for particle line. A PM₂.₅ cyclone inlet and a nafion dryer (Perma Pure, model PD-07018T-12MSS) were set ahead of the particle sampling inlet of the FIGAERO to keep the filter for aerosol sampling not getting wet due to the high ambient RH (72 ± 17%) in this campaign. Recent studies show that aerosol in equilibrium with semi-/intermediate-volatility organic compounds (S/IVOCs) will be perturbed by the removal of the gases by the nafion (Liu et al. 2019). However, in this study, the retention time for particles through the nafion dryer was ~0.12 s, which might lead to a very small change of S/IVOCs signal on such a timescale (< a few percents) based on the partitioning delay model (Pagonis et al., 2017). In addition, an accurate correction for S/IVOCs loss in nafion dryer is also not available in current (Liu et al. 2019). Thus, no S/IVOCs correction on aerosol phase was performed in this study."

2.2. Line 132: I have some questions about the CIMS calibration. I suggest the authors provide the calibrations factors that they determined for the 39 species that were calibrated. Calibrating a CIMS is challenging, but if the authors provide their calibration numbers, then readers can place the resulting concentrations in context of other measurements with possibly different calibration factors (each instrument can be different). I do not see these numbers in Ye et al. 2021 either, but maybe they are published somewhere.

A2.2: The calibration factors for the 39 species were provided in the excel file of the supplement zip package of Ye et al. (2021). We present the introduction picture and the calibration factors of the 39 species in the excel file as Figure A1 below. We also added sentences in line 147-148 to remind readers in the revised main text:

"Their calibration factors were shown in the excel file of the supplement zip package of Ye et al. (2021)."

ion formula	calibration factor (ncps/ppt)	ion formula	calibration factor (ncps/ppt)
m154_IHCN	0.18906	m245_IC4H6O4	165.0587159
m170_IHNCO	0.236	m249_IC4H10O4	14.30139688
m173_ICH2O2	3.715316071	m251_IC7H8O2	22.68495
m187_IC2H4O2	0.053299232	m259_IC5H8O4	44.36595871
m190_IHNO3	28.198	m266_IC6H5NO3	149.04625
m197_ICl2	52.7818	m273_IC6H10O4	12.27945699
m199_IC3H4O2	0.052397933	m279_C5H12IO5	30.66094196
m201_IC3H6O2	0.041353661	m282_IC6H5NO4	92.45548519
m203_IC2H4O3	3.026823	m287_IC7H12O4	48.98198813
m215_IC3H4O3	0.252149667	m289_IC6H10O5	60.11453097
m215_IC4H8O2	0.063134493	m303_C6H8IO6	15.23744638
m217_IC3H6O3	11.3528	m311_IC10H16O3	1.5005
m221_IC6H6O	0.08899	m311_IC6H4N2O5	79.08
m229_IC5H10O2	0.084410205	m315_IC9H16O4	32.56962241
m231_IC3H4O4	87.57454226	m329_C10H18IO4	6.899674479
m235_IC7H8O	0.054	m357_C12H22IO4	7.243826042
m235_IN2O5	16.495	m381_C10H22IO7	1.310960973
m237_IC6H6O2	38.68219875		

Figure A1. The introduction of the excel file and the calibration factors of the 39 species of the supplement zip package of Ye et al. (2021).

2.3. Line 134a: I also would like to see more information about how the voltage scanning procedure was done. I see that there is information given in Ye et al. 2021, but the reader of this paper would benefit from more information included here instead of having to search in other papers for it. Also, it is my understanding that the voltage scanning technique can have relatively high uncertainty.

A2.3: We thank the reviewer for the comment. As the reviewer suggested, we added more information of the voltage scanning method in line 149-160:

" Lopez-Hilfiker et al. (2016) and Iyer et al. (2016) have verified the connections among the binding energy of the iodide-adduct bond, the voltage dissociating iodide adducts and the sensitivity of corresponding species. The relationship between the voltage difference (dV) and signal fraction remaining of an iodide-molecule adduct is established by scanning the dV between the skimmer of the first quadrupole and the entrance to the second quadrupole ion guide of the mass spectrometer. This relationship curve of an individual iodide adduct can be fitted by a sigmoid function and yields two parameters: S_0, the relative signal at the weakest dV compared to the signal under operational dV; dV_{50}, the voltage at which half of the maximum signal is removed (i.e., half the adducts that could be formed are de-clustered). A sigmoidal fit was then applied to the results of all the iodide adducts. An empirical relationship between relative sensitivity ($1/S_0$) and dV_{50} of each ion (includes levoglucosan) based on average values of the entire campaign was obtained. By linking the relative sensitivity of levoglucosan with its absolute sensitivity based on the authentic standard, the absolute sensitivity of all the uncalibrated OON species was determined, after taking into account the relative transmission efficient of all the ions. The detailed data of these response factors can be found in the supporting information of Ye et al. (2021)."

About the question of relative high uncertainty of the voltage scanning method (Isaacman-Vanwertz et al., 2018; Bi et al., 2021). This approach was found to carry high uncertainties for individual analytes (0.5 to 1 order of magnitude) but represents a central tendency that can be used to estimate the sum of analytes with reasonable error ($\sim$30% differences between predicted and measured moles) (Bi et al., 2021). By comparing sensitivity factors if the three nitrogen-containing compounds (in the list of calibrated species) derived from the two methods, an underestimation of 32−56% for the sensitivity from the voltage scanning method was found compared to the method using authentic standard compounds (Figure S3). Finally, an average value of 47% was regarded as the representative uncertainty of the voltage scanning method and the total mass loading of uncalibrated species in this study. To clarify this, we added the description of uncertainty analysis of the voltage scanning method in line 160-168:

"Three OON species which are 4-nitrophenol ($C_6H_5NO_3$), 2,4-dinitrophenol ($C_6H_4N_2O_5$), and 4-nitrocatechol ($C_6H_5NO_4$) were calibrated in both authentic standards and voltage scanning methods. By comparing their sensitivity (Fig. S3), the uncertainty of the voltage scanning method can be roughly estimated. Detailed description of the calibration curves and the application of the calibration curve to estimate the sensitivity can

be refferred to the supporting information text of Ye et al. (2021). In general, the voltage scanning method underestimates (32−56%) the sensitivity of OON in this study compared to the values using the standard compounds as real. This uncertainty was comparable with 30% uncertainty of all analytes in Bi et al. (2021) and 60% uncertainty of total carbon in Isaacman-Vanwertz et al. (2018) measured by the Iodide-CIMS. Finally, an avergae underestimation of 47% on sensitivity was taken as the uncertainty of the whole OON mass loading in this study."

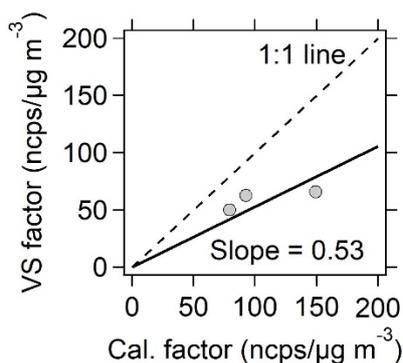



Figure S3. The scatterplot of calibration factors of three nitro-containing compounds (4-nitrophenol, 2,4-dinitrophenol, and 4-nitrocatechol) that derived from voltage scanning method and standard calibration. Based on the slope, 47% was regarded as the uncertainty of the voltage scanning method for OON calibration in this study. The detailed data can be found in the excel file of the supplement zip package of Ye et al. (2021).

2.4. Line 134b: When I look at Fig. S7c of Ye et al. 2021, the sensitivity values calculated from voltage scanning seem larger than I would expect. Perhaps this is normal for the instrument used here, and it would be useful to see the calibration numbers for more common compounds such as many of the 39 directly calibrated species (see my previous question).

A2.4: As the response in A2.2, we provided the calibration factor for all the OON ions used in this study by voltage scanning method and calibration factors of all 39 calibrated species in the excel file of the supplement zip package of Ye et al. (2021) and reminded the readers in line 158-159 in the maintext and caption of Fig. S3.

"The detailed data of these response factors can be found in the supporting information of Ye et al. (2021)."

2.5. Line 134c: My main comment about voltage scanning is that the authors should calculate the uncertainty for voltage scanning calibrations, and apply that uncertainty to the determination of gas and aerosol mass (especially organic nitrogen) measured by the CIMS. Section 3.1 compares AMS and CIMS masses in several ways, but I do not see any analysis of the uncertainties in calibration of the CIMS (or the AMS) and how that affects the comparison. In the Conclusions section Line 472, you say that the CIMS measured 28% of the total pOON, but how well do you know

that number? Is it possible that the CIMS actually measured a much larger fraction, but the calibrations are just really hard to do?

A2.5: Thank you for the reviewer's suggestion. As shown in the response A2.3 above, we added the analysis of uncertainty of the voltage scanning method by the comparison of three OON compounds that were calibrated in both methods. Finally, 47% was used for the OON detection in the CIMS measurement.

To assess the uncertainty of the comparison between the CIMS and the AMS, the error propagation law accounting for the uncertainties in both measurement techniques was applied. We added the detailed information on uncertainty estimation in Text S3. In addition, we revised the discussion of the comparison between CIMS and AMS in the section 3.1 and the conclusion section in the revised main text.

The uncertainty estimation added in Text S3:

"Uncertainty for the ratio of pOrgNO$_3$ measured by CIMS and AMS (pOrgNO$_{3,\text{CIMS}}$ vs pOrgNO$_{3,\text{AMS}}$). This uncertainty estimation was based on the Eq. (S8) below combined with error propagation law.

$$\frac{pOrgNO_{3,CIMS}}{pOrgNO_{3,AMS}} = \frac{pOON_{CIMS} \times \frac{MW_{[NO_3]}}{MW_{[pOON]}}}{pOrgNO_{3,AMS}} \qquad \text{(S8)}$$

The uncertainty of pOON$_{\text{CIMS}}$ was 47% according to the uncertainty of OON derived from the comparison of voltage scanning factors and calibration factors (Fig. S3), which was discussed in section 2.2.2 of the main text. The uncertainty of pOON molecular weight (MW, 234 ± 7.9 g mol^{-1}), which was obtained with CIMS measurement, was assigned to be 10%. The uncertainty of pOrgNO$_{3,\text{AMS}}$ was 30% which was obtained based on overall aerosol quantificaiton uncertainty of AMS (Salcedo et al., 2006). For OON quantification, the uncertainty of the NO$_2^+$/NO$^+$ ratio method was estimated using the lower and higher NO$_2^+$/NO$^+$ ratio from ONs (0.18 and 0.09) based on Xu et al. (2015), which was calculated to be 27% as discussed in Text S1. Finally, the total uncertainty of the pOON ratio between CIMS and AMS was 63%. It suggests that the pOrgNO$_{3,\text{CIMS}}$ can explain 28 ± 18% of pOrgNO$_{3,\text{AMS}}$."

The revised discussion of the comparison between the CIMS and the AMS in line 273-276:

"On the other side, if only −ONO$_2$/-NO$_2$ groups are considered to calculate pON$_{\text{CIMS}}$ to be pOrgNO$_{3,\text{CIMS}}$, the calculated pOrgNO$_{3,\text{CIMS}}$ can explain 28 ± 18% of pOrgNO$_{3,\text{AMS}}$, which is consistent with the fraction (23%) of total functionalized OA detected using the CIMS versus total OA measured using the AMS (Ye et al., 2021).

The detailed analysis process on comparison uncertainty between AMS and CIMS can be found in Text S3 of the supporting information.”

The revised conclusion section in line 526-528:

“The good comparison of pOON measured by AMS and FIGAERO-I-CIMS indicates that the CIMS can measure a fraction of 28 ± 18% of total pOON in this study.”

2.6. Line 140: Instead of saying definitively that ONs were the dominant components of OON, I suggest you acknowledge the considerable uncertainty by saying something like this: “Some nitroaromatic signal may be detected as elemental formulas other than those listed above, and some of the signal at the elemental formulas identified here as nitroaromatic may have contributions from ON species. While uncertainty exists, it is likely that ONs dominated the OON observed during this campaign.”

A2.6: We sincerely thank the reviewer for the comment and suggestion on revision. The original sentences were deleted. We added the revised sentences in line 172-175 of the main text suggested by the reviewer:

“**Some nitroaromatic signal may be detected as elemental formulas other than those listed above, and some of the signal at the elemental formulas identified here as nitroaromatics may have contribution from ON species. While uncertainty exists, it is likely that ONs dominated the OON observed during this campaign.**”

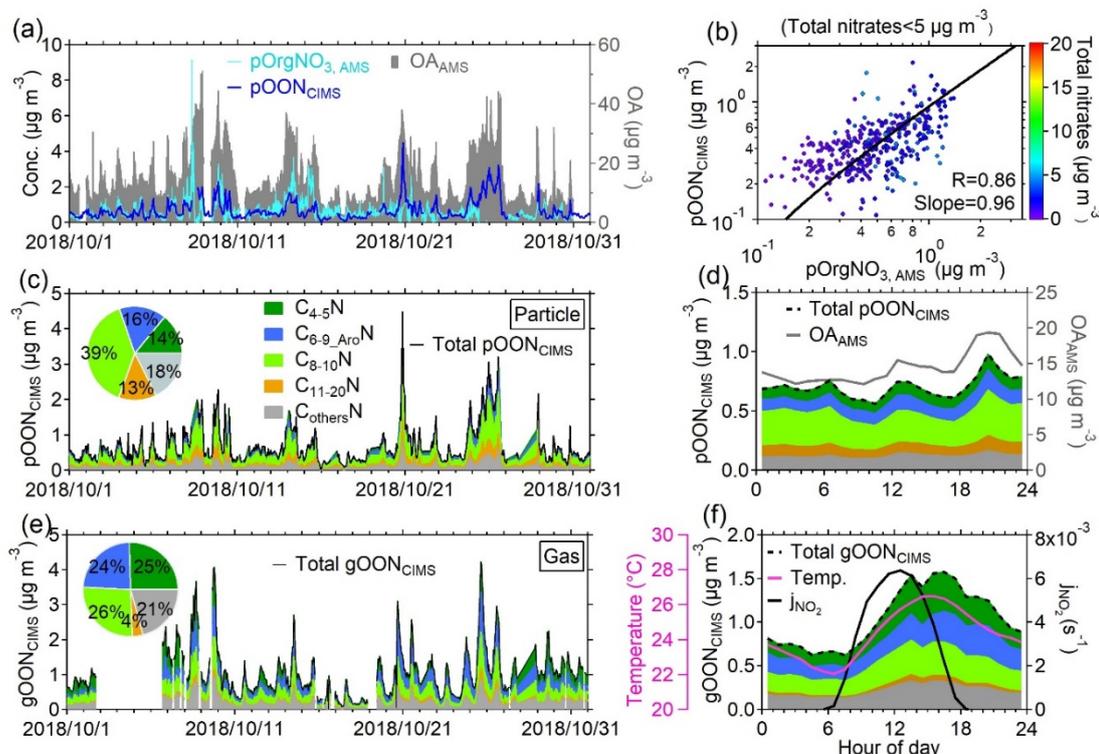
2.7. Line 148: How was this photochemical age determined? Even if it is described in the Chen et al 2021a citation, it would be useful to briefly describe here.

A2.7: The brief description of the determination of the photochemical age was added in line 184-187 of the revised main text:

“**Multiple studies show that levoglucosan might be degraded due to photochemistry (Hennigan et al., 2010; Bai et al., 2013; Lai et al., 2014). We calculated the ambient photochemical age based on the ratios of two hydrocarbons (m+p-xylene and ethylbenzene) that react at different rates with OH radicals (Yuan et al., 2013; Wu et al., 2020; De Gouw et al., 2005). A daily average OH concentration of 1.5×10^6 molecule cm^{-3} was assumed here (Mao et al., 2009; Wang et al., 2020; Chen et al., 2021).**”

2.8. Line 201: Since it makes more sense to compare the AMS pOrgNO3 with CIMS pOON when the AMS total nitrate is less than 5 ug m-3, I suggest you show remove the data points with greater than 5 ug m-3 from Fig. 1b. Then you

can keep Fig. S5a as it is to show all the data. Also, I am not sure I understand the purpose of Fig. S5b and you can probably remove it.

A2.8: We have updated Fig 1b and Fig S5b (now is Fig.S6 in the revised manuscript) as the reviewer suggested.

"Figure 1. Time series and variations of OON during the PRIDE-GBA campaign. (a) Time series of pOON$_{CIMS}$ and pOrgNO$_{3, AMS}$. Time series of total OA detected by the AMS is shown on the right axis. (b) Scatterplot of pOON$_{CIMS}$ versus pOrgNO$_{3, AMS}$ during the campaign. The term "total nitrates <5 μg m^{-3}" indicates the data used in this scatterplot is under the condition that the mass concentration of total nitrates (including organic nitrate and inorganic nitrate) measured by the AMS is lower than 5 μg m^{-3}. The points are color-coded using the total nitrate signals measured by the AMS. The scatterplot from all AMS and CIMS measurement can be found in Fig. S6. The logarithm was applied to both of the axes. Time series of (c) pOON$_{CIMS}$ and (e) gOON$_{CIMS}$, as well as the time series of their C$_x$N groups from the CIMS measurement. The insets show their average mass contributions to total gOON$_{CIMS}$ and pOON$_{CIMS}$ during the campaign, respectively. The average diurnal variations of (d) pOON$_{CIMS}$ and its C$_x$N groups, as well as OA; (f) Average diurnal variations of total gOON$_{CIMS}$ and its C$_x$N groups, photolysis rate of NO$_2$ (j$_{NO2}$), and temperature during the entire campaign. All the diurnal variations calculated throughout the manuscript are based on the average values. All the linear fitting are

based on the orthogonal distance regression (ODR) algorithm in this study. All the acronyms can be found in appendix A."

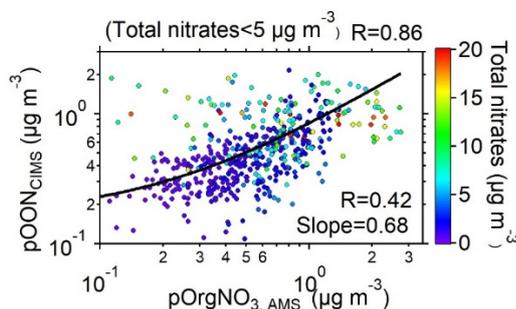



Figure S6. Scatterplot of pOON$_{CIMS}$ versus pOrgNO$_{3, AMS}$ during the campaign. The points are color-coded using total nitrates (including inorganic nitrate and organic nitrate) measured by AMS.

2.9. Fig. 2 Caption: The letters you use in the caption do not match the letters assigned to the figure panels. Please correct this.

A2.9: Corrected.

2.10. Line 278: I strongly recommend that when you refer to CIMS signals, that you always refer to the elemental formula rather than a specific isomer name. For instance, say C7H8O2 instead of methoxyphenol and C8H8O4 instead of vanillic acid. The iodide CIMS signal very likely comes from multiple isomers. Indeed, if you look at Fig. S12 of Palm et al. PNAS 2020, they show that the iodide CIMS signal at C7H8O2 is more likely to be methyl catechol rather than guaiacol. So here in the text, I would suggest changing to "Another two biomass burning tracers, i.e., C7H8O2 (methoxyphenol, methylcatechol, and isomers) and C8H8O4 (vanillic acid and isomers),…" You should also update the text when referring to C6H10O5 (levoglucosan and isomers) and anywhere else that is needed.

A2.10: We agree with the reviewer's suggestion. We updated all the "**levoglucosan**" to be "**C$_6$H$_{10}$O$_5$**" or "**C$_6$H$_{10}$O$_5$ (levoglucosan and its isomer**)" throughout the manuscript. We also revised all the CIMS signals with formula instead of compound names as suggested by the reviewer. I.e., C$_7$H$_8$O$_2$ (methoxyphenol, methylcatechol, and isomers), C$_8$H$_8$O$_4$ (vanillic acid and isomers) and C$_6$H$_5$NO$_3$ (nitrophenol and its isomers).

In addition, the GC-MS analysis based on filter-sampling was also applied to measure the isomers of levoglucosan, mannosan, and galactosan in this campaign, which was reported by Jiang et al. (2023). Based on the analysis, it was found that levoglucosan dominated the mass concentration in its three isomers (>90%), as shown in

Fig. A2 below. To clarify this, the information about the possible contribution of levoglucosan and its isomers to $C_6H_{10}O_5$ was updated in line 179-183:

"In the ambient air, the $C_6H_{10}O_5$ measured in the particle phase using the CIMS was probably composed by levoglucosan and its isomers (mannosan and galactosan) (Ye et al., 2021). The isomer measurement of $C_6H_{10}O_5$ in this campaign have revealed that the levoglucosan contributed 90 ± 2% mass loading of the three isomers of $C_6H_{10}O_5$ (Jiang et al., 2023), thus $C_6H_{10}O_5$ signal in this study can be used as a tracer for biomass burning emission (Bhattarai et al., 2019). The good correlation (R=0.78) between $C_6H_{10}O_5$ and another biomass burning tracer potassium (K^+) (Andreae, 1983; Wang et al., 2017), also supports this statement (Fig. S11a)."

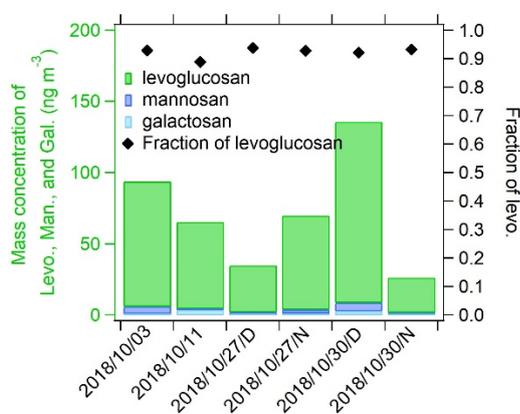



Figure A2. The mass concentration of $C_6H_{10}O_5$ isomers, i.e., levoglucosan, mannosan, and galactosan in this campaign. The mass fraction of levoglucosan to total $C_6H_{10}O_5$ isomer mass loading is also shown.

2.11. Table S1: Please indicate in the table caption that the data that was used to derive these slopes is also shown in Figs. S11 and S12.

A2.11: The caption of Table S1 was updated:

"Table S1. The regression slopes between measured gOON (pOON) vs particle-phase levoglucosan in selected biomass burning emission episodes. The data used to derive these slopes are also shown in Figs. S12 and S13. The average values based on different biomass burning episodes are also shown. "

2.12. Line 316: It seems reasonable to me that OON_bb would be an estimate of primary plus rapidly formed secondary OON from biomass burning emissions. I think that the OON_sec could also include slowly formed (i.e., next day) OON from biomass burning sources in addition to the other sources. That slowly formed OON would not correlate

with the primary C6H10O5 tracer. If the authors agree, please update the text. If not, do you have evidence to suggest otherwise?

A2.12: We agree with the reviewer's comment and updated the corresponding description in line 363-366 of the revised main text:

"the OON_{bb} herein is referred to as the total primary and rapidly formed secondary OON from biomass burning emissions. OON_{sec} is defined as secondary OON from non-biomass burning sources, e.g., biogenic and non-biomass burning anthropogenic sources and possible OON slowly formed from biomass burning sources (i.e., next day), which shall be minor."

2.13. Section 3.2: I would like to see a discussion at the end of (or throughout) this section of the authors' assessment of the uncertainties of this analysis. For instance, the iodide CIMS C6H10O5 signal is not a perfect representation of primary biomass burning emissions. That signal can have variability due to chemistry, variable emissions, etc. This should be discussed. Also I think a considerable source of uncertainty is that the OON_sec is defined just as the OON that is not biomass burning related, rather than defining OON_sec by some correlation with a secondary chemistry tracer. How could this affect your results?

A2.13: We thank the reviewer's comment. To assess the uncertainty of the calculation in section 3.2, we applied the Monte Carlo method to calculate the uncertainty for the fraction of biomass burning related OON to total OON. The calculation was repeated for 10000 times. In the calculation, the uncertainty of the ratio, $([OON_{measured}]/[levo.])_{bb}$, was derived from their uncertainty which was previously discussed in section 3.2. The uncertainty of the levoglucosan that was regarded as a tracer of biomass burning emissions was 10% considering the mass fraction among its isomers and its standard calibration (Ye et al., 2021), as shown in A2.10. In addition, we also include the standard deviation of source apportionment results at different time points in the final uncertainty calculation. The final results show that the biomass burning emissions accounted for 49 ± 23% of total pOON from CIMS, while the contribution was much lower (24 ± 25%) for gOON. To clarify this, we revised the description in line 372-376 of the main text and add the analysis of uncertainty in Text S3 in supporting information.

The revised section in line 375-378 of the main text:

"On average, biomass burning emissions accounted for 49 ± 23% of total pOON from CIMS, while the contribution was much lower (24 ± 25%) for gOON (Figs. 2b and 2d), indicating that biomass burning is one of the major sources for pOON measured by CIMS, and gOON is predominately from secondary formation

(76 ± 25%) (Huang et al., 2019; Lee et al., 2016). The uncertainty of these ratios representing the error of this source apportionment method, was estimated based on Monte Carlo method. The detailed calculation can be found in Text S3 of the supporting information."

The detailed uncertainty analysis added in Text S3 in supporting information:

"Uncertainty for the source apportionment of OON. Based on the Eq. (1−2), the uncertainty of the source apportionment of OON was estimated by Monte Carlo method with 10,000 calculations. The uncertainty of levoglucosan was 10% considering its standard calibration (Ye et al., 2021) and mass contribution (90 ± 2%) among isomers (referred to section 2.2.2). The uncertainty of the primary ratios of OON vs levoglucosan, $(([OON_{measured}]/[levo.])_{bb})$, was considered equal to their average standard deviation shown in Table S1, i.e., 20% and 42% for pOON and gOON, respectively. After performing the Monte Carlo method, the uncertainties of the OON_{bb} fraction in total OON were around 9% and 11% for aerosol and gas phase, respectively. The standard deviations of averaged OON_{bb} fraction in total OON from the entire campaign were around 22% and 23% for aerosol and gas phase, respectively. By combining the uncertainty from Monte Carlo and standard deviation due to averaging, the final contribution s with uncertainties of biomass burning to pOON and gOON are 49 ± 23% and 24 ±25%, respectively."

About the representativeness of levoglucosan itself as a tracer for biomass burning. We have addressed that the uncertainty might exist due to their photodegradation in the ambient air, as shown below in line 187-191. To account for the emission variability of levoglucosan, we selected the multiple plumes to obtain the primary ratio of OON with levoglucosan for minimizing the uncertainty. The primary ratio uncertainty was finally considered in the source apportionment results as shown above.

"The estimated results show that the average diurnal photochemical age varied from 0.2 days during the night to maximum 0.5 days in the daytime in this campaign (Chen et al., 2021), which was lower than the lifetime of levoglucosan (>1 day −26 days) determined in laboratory and field studies (Hennigan et al., 2010; Hoffmann et al., 2010; Lai et al., 2014; Bai et al., 2013; Bhattarai et al., 2019). It suggests that the levoglucosan observed in this study shall be stable for being the tracer of biomass burning emissions."

We understand the high uncertainty related to the OONsec due to its not being resolved based on secondary chemistry tracer. However, a very good correlation has been found between gas-phase secondary OON (gOONsec) and photooxidation product O_3, supporting its secondary origins. In addition, a good correlation between particle-

phase OONsec (pOONsec) and semi-volatile oxygenated OA (SV-OOA), which were freshly formed SOA, was also found, as shown in Figure S17 below. This also supports the pOONsec were from secondary sources. To clarify this, we added relative discussion and revised the sentence in line 372-374 in the revised main text:

"The particle-phase OON$_{sec}$ also showed consistent variation (R=0.70) to semi-volatile oxygenated OA (SV-OOA), which was treated as freshly formed SOA during the day (Fig. S17) (Chen et al., 2021), supporting the secondary origins of pOON$_{sec}$. These results validated the source apportionment of OON applied herein."

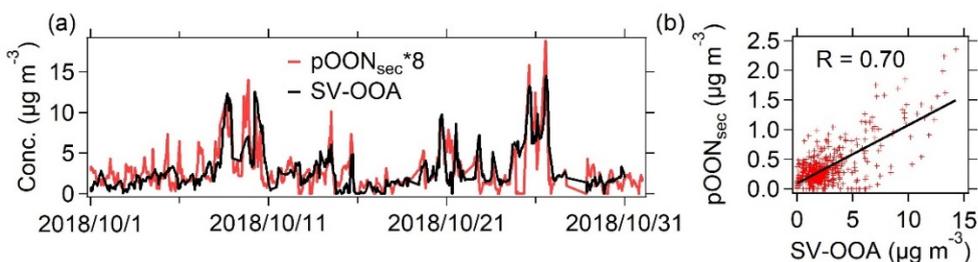



Figure S17. (a) The time series of pOONsec and semi-volatile oxygenated OA (SV-OOA) and (b) their scatterplot. The SV-OOA was treated as freshly formed secondary organic aerosol, which show good correlation with gas-phase oxidation product pentanones. The detailed information of SV-OOA can be found in Chen et al. (2021).

2.14. Line 458: This correlation of $0.52 < R < 0.79$ is not very high, so I would not agree that this means that C10HxNOy (y>=6) "indeed mainly" comes from biomass burning emissions. Correlation does not mean causation, and Fig. 7b shows that these C10 compounds are present during the whole campaign and not just during biomass burning periods. I suggest the authors remove this assertion or follow it up with other analysis such as correlation with a monoterpene SOA tracer.

A2.14: We removed this assertion in the revised main text.

2.15. Line 472: I mentioned this in a comment earlier, but I would like to see what your estimated error bars number of how much pOON the CIMS sampled relative to the AMS. But, if this number is your best estimate, then how does this affect your conclusions? If the CIMS only measures a small fraction of the pOON, then is it justified to conclude that about half of pOON is from biomass burning, or can you really only say that about half of the 28% of measured pOON is from biomass burning emissions? There are some uncertainties here related to not being able to measure most of the organic nitrogen that I believe the authors should explore further.

A2.15: We thank the reviewer's comments and suggestions. As our response in the A2.5, the error bar for the fraction (28%) was 18% that was calculated by the uncertainty from pOON from the CIMS and the AMS. we revised the relative discussion in the conclusion section of the main text in line 526-530:

"The good comparison of pOON measured by AMS and FIGAERO-I-CIMS indicates that the CIMS can measure a fraction of 28 ± 18% of total pOON in this study. Compared to AMS, the missed pOON mass measured by CIMS is probably due to the lack of detection of less-polar OON (keto/alkyl ON) and/or non-nitrogen-containing pOON resulting from the loss of −NO$_2$ group by thermal desorption in CIMS measurement."

We agree with the reviewer that the source apportionment is only applicable to the pOON measured by CIMS and further work focused on the OON which was not detected by the CIMS should attract more attention. To clarify this, we revised the discussion in line 531-535:

"Using C$_6$H$_{10}$O$_5$ (~90% of levoglucosan) as the biomass burning tracer for source apportionment, almost half of the pOON measured by the CIMS is attributed to biomass burning in this study, underscoring the important contribution of biomass burning to pOON in this urban area. Biomass burning is a very common source across the world. The proposed estimation method in this study might help to clarify the exact biomass burning contribution to OON and their potential atmospheric implication. Note that the sources of the undetected pOON from CIMS are still unknown, which shall be further investigated. "

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