



Supplement of

The important contribution of secondary formation and biomass burning to oxidized organic nitrogen (OON) in a polluted urban area: insights from in situ measurements of a chemical ionization mass spectrometer (CIMS)

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Text S1: Intercomparison of AMS-derived organic nitrates based on multiple methods

Nitrate signals (NO^+ , NO_2^+ , HNO_3^+) measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) include both organic nitrates and inorganic nitrates. Many methods were established to separate the total measured nitrates from inorganic nitrates and particle-phase organic nitrates (i.e., the particle-phase nitrate functional group, $\text{pOrgNO}_{3, \text{AMS}}$), i.e., $\text{NO}_2^+/\text{NO}^+$ ratio method (Farmer et al., 2010), Positive Matrix Factorization (PMF) method (Hao et al., 2014; Sun et al., 2012; Xu et al., 2015) and Thermodenuder (TD) method (Xu et al., 2021). In this study, these three methods were applied to quantify $\text{pOrgNO}_{3, \text{AMS}}$. Note that in agreement with Dancy and Reidy (2007), we interpreted the absolute value of the Pearson correlation coefficient as (i) no correlation, if $|r| \leq 0.1$; (ii) weak correlation, if $0.1 < |r| \leq 0.3$; (iii) moderate correlation, if $0.3 < |r| \leq 0.7$; (iv) strong correlation, if $0.7 < |r| \leq 1$; and finally, (v) perfect correlation, if $|r| = 1$.

(1) **$\text{NO}_2^+/\text{NO}^+$ ratio method.** The organic nitrate and inorganic can be detected as NO^+ and NO_2^+ ions in the HR-ToF-AMS. Previous studies have reported much lower $\text{NO}_2^+/\text{NO}^+$ ratios of $\text{pOrgNO}_{3, \text{AMS}}$ (R_{ON}) than that of inorganic nitrates, i.e., NH_4NO_3 ($R_{\text{NH}_4\text{NO}_3}$) (Boyd et al., 2015; Farmer et al., 2010; Fry et al., 2013; Sato et al., 2010). Fry et al. (2013) quantified that the R_{ON} ratio is 2.25 times lower than the $R_{\text{NH}_4\text{NO}_3}$ based on multiple results using different AMSs in chamber studies. Recently, Day et al. (2022) and Fry et al. (2018) summarized more studies and redefined the ratio $R_{\text{NH}_4\text{NO}_3}/R_{\text{ON}}$ to be 2.75. The average $R_{\text{NH}_4\text{NO}_3}$ was estimated to be 0.37 from the standard calibration of NH_4NO_3 , which is quite stable across this entire campaign. Then, the R_{ON} for this study was estimated to be 0.13 based on the $R_{\text{NH}_4\text{NO}_3}/R_{\text{ON}}$ ratio of 2.75.

Thus, the fraction of $\text{pOrgNO}_{3, \text{AMS}}$ in total nitrates (ON_{frac}) measured by the AMS can be calculated as (Farmer et al., 2010):

$$\text{ON}_{\text{frac}} = \frac{(R_{\text{ambient}} - R_{\text{NH}_4\text{NO}_3})(1 + R_{\text{ON}})}{(R_{\text{ON}} - R_{\text{NH}_4\text{NO}_3})(1 + R_{\text{ambient}})} \quad (\text{S1})$$

where R_{ambient} is the $\text{NO}_2^+/\text{NO}^+$ ratio of ambient nitrate. The final concentration of $\text{pOrgNO}_{3, \text{AMS}}$ can be calculated based on total nitrates and ON_{frac} . To calculate the uncertainty of ON_{frac} with the $\text{NO}_2^+/\text{NO}^+$ ratio method, ratios of 2.08 and 4.17 ($R_{\text{ON}} = 0.18$ and 0.09) obtained from isoprene- and monoterpene-derived $\text{pOrgNO}_{3, \text{AMS}}$, were used for calculating the upper (mean $0.85 \mu\text{g m}^{-3}$) and lower (mean $0.53 \mu\text{g m}^{-3}$) bounds of $\text{pOrgNO}_{3, \text{AMS}}$ (Xu et al., 2015; Xu et al., 2021), respectively. Thus, 27% was regarded as the average uncertainty of this method for the estimation $\text{pOrgNO}_{3, \text{AMS}}$ in this study. When the ambient nitrate signal is high in ambient air (e.g., $>5 \mu\text{g m}^{-3}$), the high nitrate signal was mainly contributed by the inorganic ammonium nitrate (Day et al., 2022). This leads to that the $\text{NO}_2^+/\text{NO}^+$ ratio of ambient nitrate is similar to that of pure inorganic ammonium nitrate, thus resulting in a large uncertainty in $\text{pOrgNO}_{3, \text{AMS}}$ estimation. This issue had been fully addressed in the method paper on how

to estimate pOrgNO_{3, AMS} from AMS measurement (Day et al., 2022). The larger uncertainty of estimated pOrgNO_{3, AMS} by AMS
 60 under high nitrate signal periods has also been found in other ambient studies (Yu et al., 2019; Zhu et al., 2016).

(2) **PMF method.** It is well known that the PMF analysis can be used for source appointment and estimation of various
 organic factors, e.g., primary organic aerosol and secondary organic aerosol (SOA). Combining the OA spectral matrix with NO⁺
 and NO₂⁺ ions detected by AMS, different OA factors including organic NO⁺ and NO₂⁺ ions can provide insights regarding the
 relative contributions of pOrgNO_{3, AMS} and inorganic nitrates (Sun et al., 2012; Xu et al., 2015). Therefore, the concentrations of
 65 pOrgNO_{3, AMS} (NO_{org}⁺ and NO_{2,org}⁺) are equal to the sum of NO⁺ and NO₂⁺ via Eqs. (S2) and (S3) (Xu et al., 2015):

$$\text{NO}_{2,\text{org}}^+ = \sum \left([\text{OA factor}]_i \times f_{\text{NO}_2,i} \right) \quad (\text{S2})$$

$$\text{NO}_{\text{org}}^+ = \sum \left([\text{OA factor}]_i \times f_{\text{NO},i} \right) \quad (\text{S3})$$

where [OA factor]_i is the mass concentration of OA factor *i*, *f*_{NO₂,i} and *f*_{NO,i} are the mass fractions of NO₂⁺ and NO⁺ in each factor,
 respectively.

(3) **TD method.** The method was developed for the estimation of pOrgNO_{3, AMS} from the measurement of HR-ToF-AMS
 70 coupled with a thermodenuder based on the difference of volatility between pOrgNO_{3, AMS} (NO_{x,org}⁺) and inorganic nitrates (NO_{x,inorg}⁺)
 in particles (Xu et al., 2021). It is assumed that (I) the remaining mass loading of nitrate fragments was dominated by NO_{x,org}⁺,
 while NO_{x,inorg}⁺ evaporated completely at T = 90°C due to the higher volatility of NO_{x,inorg}⁺ than NO_{x,org}⁺ (Huffman et al., 2008; Ng
 et al., 2017); (II) The C_xH_yN_z⁺ and C_xH_yO_zN_p⁺ ions were supposed to have similar volatility as NO_{x,org}⁺ which dominate the
 75 remaining fragments at T > 90°C (Xu et al., 2021). Combined with the two assumptions, the mass concentration of pOrgNO_{3, AMS}
 ([NO_{3,org}]) in the ambient atmosphere can be determined by Eq. (S4) (Xu et al., 2021):

$$[\text{NO}_{3,\text{org}}] = \frac{[\text{NO}_3]_{T=90^\circ\text{C}}}{\text{MFR}_{\text{CHN}^+ + \text{CHON}^+ T=90^\circ\text{C}}} \quad (\text{S4})$$

The subscript “T = 90°C” denotes the mass concentration or the mass fraction remaining (MFR) of fragments at T = 90°C.

The intercomparison of pOrgNO_{3, AMS} based on these three methods and the particle-phase oxidized organic nitrogen (pOON)
 80 measured by an iodide chemical ionization time-of-flight mass spectrometer installed with a Filter Inlet for Gases and AEROSols
 (FIGAERO-CIMS) in this campaign are presented in Fig. S2. The average concentrations of pOrgNO_{3, AMS} and pOON are shown
 in Table S2. Generally, the pOrgNO_{3, AMS} derived from PMF method increases with total nitrates and is largely overestimated

compared to other methods during the high nitrate periods. The $p\text{OrgNO}_{3,\text{AMS}}$ estimated from the TD method correlates well ($R = 0.73$) with that from $\text{NO}_2^+/\text{NO}^+$ ratio method. However, the former exhibits noisier especially under low nitrate periods probably
 85 due to the large uncertainty of the lower mass remaining fraction for $p\text{OrgNO}_{3,\text{AMS}}$ at higher temperature ($>90^\circ\text{C}$). $T = 90^\circ\text{C}$ was assumed to represent the temperature mentioned above at which inorganic nitrates have been evaporated completely. However, this might not be the case in some environments (Huffman et al., 2008). The drawback of $\text{NO}_2^+/\text{NO}^+$ ratio method is the slightly large uncertainty under high NO_x conditions such as during 25–26 October 2018 (Fig. S2a).

Finally, we chose $\text{NO}_2^+/\text{NO}^+$ ratio method for more analysis in the main text given its smooth profile and relative stable
 90 estimation of total $p\text{OrgNO}_{3,\text{AMS}}$ (Yu et al., 2019). The average mass fraction of $p\text{OrgNO}_{3,\text{AMS}}$ to total nitrates is 15% and that mass fraction increases with decreasing concentration of total nitrates (Fig. S2b), indicating the dominant role of pON chemistry under low nitrate atmospheric environment.

Text S2: The calculation of the production rate of gas-phase organic nitrates

In the presence of NO, the production rate of gas-phase oxidized organic nitrogen (gOON) from hydroxyl radical (OH)
 95 initiated oxidation with volatile organic compounds (VOCs) ($P_{\text{ON}}^{\text{OH}}$) can be calculated following Eq. (S5) (Liebmann et al., 2019):

$$P_{\text{ON}}^{\text{OH}} = [\text{OH}]\beta \sum \alpha_i^{\text{RO}_2} k_i^{\text{OH}} [\text{C}_i] \quad (\text{S5})$$

where $[\text{OH}]$ is the concentration of OH, which was obtained from a box model simulation based on master chemical mechanism v3.3.1 (MCM v3.3.1) (Wang et al., 2020; Wolfe et al., 2016). $[\text{C}_i]$ is the concentration of speciated VOC i . k_i^{OH} is the reaction rate coefficient between OH and VOC i , $\alpha_i^{\text{RO}_2}$ is the formation branching ratio of gOON for speciated VOC i , β represents the fraction
 100 of the peroxy radicals (RO_2) that react with NO which can be estimated by $\beta = \frac{k_{\text{RO}_2+\text{NO}}[\text{NO}]}{k_{\text{RO}_2+\text{NO}}[\text{NO}] + k_{\text{RO}_2+\text{HO}_2}[\text{HO}_2]}$ ($k_{\text{RO}_2+\text{NO}} = 9.0 \times 10^{-12}$ and $k_{\text{RO}_2+\text{HO}_2} = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from MCM v3.3.1) (<http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm>). The estimated values of β were 0.98–1.0 during the campaign, thus $\beta = 1$ was used in this calculation. The VOC species, reaction rate coefficients, yields, and branching ratios used for this calculation can be found in Table 1.

The nitrate radical (NO_3) concentration was calculated based on measured N_2O_5 by the CIMS assuming temperature
 105 equilibrium between these two species (Brown and Stutz, 2012). Then the gOON production rate from NO_3 initiated oxidation of VOC ($P_{\text{ON}}^{\text{NO}_3}$) can be calculated by Eq. (S6):

$$P_{\text{ON}}^{\text{NO}_3} = \sum \alpha_i k_{\text{NO}_3+\text{C}_i} [\text{C}_i] [\text{NO}_3] \quad (\text{S6})$$

where $[C_i]$ and $[NO_3]$ are the concentrations of speciated VOC i and NO_3 , α_i is the gOON yield, $k_{NO_3+[C_i]}$ is the reaction rate coefficient as shown in Table 1. The reactions between alkanes and NO_3 are very slow accounting for negligible chemical changes in the ambient atmosphere so that alkanes were not included in this calculation. The VOC species of terpenes, aromatics, and alkenes (Table 1) measured during October 2018 were used to calculate the NO_3 loss rate. Only 2% of the NO_3 loss rate was attributed to alkenes. And the NO_3 loss rate attributed to cresol and phenol (30% on average, ranging from 13% to 60%) was three orders of magnitude higher than the other aromatics ($\sim 0.1\%$). Thus, we assumed that the alkanes, alkenes, and the other aromatics (excluding cresol and phenol) contributed little ($<3\%$) to the total gOON production rate, which were not included in this calculation.

The gOON production rate of ozone (O_3) initiated oxidation of VOC ($P_{ON}^{O_3}$) can be calculated by Eq. (S7):

$$P_{ON}^{O_3} = [O_3] \beta \sum \alpha_i^{O_3} k_i^{O_3} [C_i] \alpha_i^{RO_2} \quad (S7)$$

where $[O_3]$ is the concentration of O_3 , $k_i^{O_3}$ is the reaction rate coefficient between O_3 and VOC i , $\alpha_i^{O_3}$ is the yield of RO_2 , and $\alpha_i^{RO_2}$ is the ON yield of the reaction RO_2+NO for speciated VOC (Table 1). β and $[C_i]$ are the same as in Eq. (S5). The short-chain alkenes including propene, butene and pentene yield negligible SOA as well as ON, thus we did not include them in the calculation.

Fig. S4 shows the time series and average diurnal variations of OH, NO_3 , and O_3 used in the calculation above. The average concentration of OH was $1.11 \pm 1.86 \times 10^6$ molecule m^{-3} which peaks at noon (mean $4.20 \pm 2.69 \times 10^6$ molecule m^{-3}). The averaged mixing ratio of NO_3 was 1.14 ± 2.82 ppt which peaks at 18:00 (2.25 ± 3.85 ppt) and night (2.35 ± 5.00 ppt), consistent with other studies in urban areas (Hamilton et al., 2021; Wang et al., 2017). No speciated monoterpene measurement was conducted in this campaign. Thus, we assume that the monoterpenes at this urban site were contributed by limonene and α -pinene with a ratio of 1:1 during this campaign. A recent study found that half of the ambient monoterpenes can be attributed to the VCP-dominated source based on measurements at altitude of 450 m in the Canton Tower in Guangzhou urban area (Li et al., 2022). The other half monoterpenes are mainly from visitor-related emissions since Canton tower is a tourism site. It is consistent with our finding that the ambient monoterpenes in this study is anthropogenic origins. Gkatzelis et al. (2021) found the limonene was the dominant isomer of monoterpenes in VCP emissions. And Coggon et al. (2021) found the α -pinene (19%) and limonene (53%) were the main isomers of monoterpene in the center of megacity New York. Thus, a 1:1 assumption of limonene and α -pinene applied here shall be reasonable. The concentration of sesquiterpenes could be calculated as a function of the monoterpene concentration, as described in Sommers et al. (2022). Since a large fraction of monoterpene in this study was assumed to be anthropogenic, thus, the calculated concentration of sesquiterpenes herein is a high limit. The calculated mass concentration of the sesquiterpenes is only 7% of the monoterpene concentration in this campaign. Omitting the sesquiterpenes in the gOON production rate calculation

should be within the estimated uncertainty of the gOON production rate. In addition, the yield parameters for gOON production rate from sesquiterpenes were missed. Thus, in this study, sesquiterpenes were not accounted for in the final gOON production rate calculation.

Text S3: Uncertainty estimation.

140 **Uncertainty of gOON production rate estimation.** Monte Carlo method was used to estimate the entire uncertainty of the gOON production rate with 10,000 calculations as shown in Fig. S5. During the Monte Carlo method, the kinetic parameter sets were assigned according to Liebmann et al. (2019), which can involve the uncertainties of various parameters, e.g., yields and branch ratios. Then the parameters were allowed to randomly vary within the range and vast number of combinations of input parameters were used to be computed (McKay et al., 2000). During the iteration, we estimated the uncertainty in the term NO₃ pathway of
 145 58%, with 50% from [NO₃], 15% from $k_{\text{NO}_3+\text{C}_i}$, 50% from α_i , and 30% from [C_i]. If 30–50% uncertainties were added to the concentration ratio of α -pinene to limonene, the uncertainty of the term NO₃ pathway increased up to 62–70%. The uncertainty in the term OH pathway was 45%, with 50% from [OH], 15% from k_i^{OH} , 50% from $\alpha_i^{\text{RO}_2}$, 30% from β , and 35% from [C_i]. The uncertainty in the term O₃ pathway was 66%, with contribution of 10% from [O₃], 35% from [C_i], 15% from $k_i^{\text{O}_3}$, 50% from $\alpha_i^{\text{RO}_2}$, 30% from β , and 50% from $\alpha_i^{\text{O}_3}$. An overall uncertainty of 56% was estimated by this method.

150 **Uncertainty for the ratio of pOrgNO₃ measured by CIMS and AMS (pOrgNO_{3,CIMS} vs pOrgNO_{3,AMS}).** This uncertainty estimation was based on the Eq. (S8) below combined with error propagation law.

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

The uncertainty of pOON_{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
 155 weight (MW, 234 ± 7.9 g mol⁻¹), which was obtained with CIMS measurement, was assigned to be 10%. The uncertainty of pOrgNO_{3,AMS} was 30% that was regarded as a low limit due to the measurement uncertainty of AMS. For OON quantification, the uncertainty of the NO₂⁺/NO⁺ ratio method was estimated using the lower and higher NO₂⁺/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,CIMS} can explain 28 ± 18% of pOrgNO_{3,AMS}.

160 **Uncertainty for the source apportionment of OON.** Based on the Eq. (1–2), the uncertainty of the source apportionment of OON was estimated by the 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, ($([OON_{\text{measured}}]/[levo.])_{bb}$), was considered equal to their average standard deviation shown in Table S1, i.e., 20% and 42% for pOON and gOON, respectively. The concentration uncertainties for OON_{bb}

165 were calculated to be 19% and 37% for gas and particle phases, 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 contributions with uncertainties of biomass burning to pOON and gOON are $49 \pm 23\%$ and $24 \pm 25\%$, respectively.

170 **Text S4: The calculation of aromaticity index and seasonal decomposition**

The aromaticity index (AI) is defined for the identification of aromatic and condensed aromatic structures, which was calculated by the Eq. (S9) (Koch and Dittmar, 2016, 2006):

$$AI = \frac{1+c-0.5o-0.5n-0.5h}{c-0.5o-n} \quad (S9)$$

where c, o, n, and h correspond to the number of C, O, N, and H atoms, respectively, in each molecule.

175 A time series usually comprises three components: a long-term trend, seasonal fluctuation, and a remainder component (containing anything else in the time series). A long-term trend is a tendency or state of affairs in which a phenomenon develops and changes continuously over a longer period of time. Seasonal fluctuation is the regular variation caused by seasonal change. The time series decomposition can distill the component of repeatability from complex data. This method is similar to the combination of two filters with large and small bandwidth. The bandwidth can be adjusted for different time resolution. If an additive decomposition was assumed, the Eq. is:

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$$y_t = S_t + T_t + R_t \quad (S10)$$

where y_t is the data, S_t is the seasonal fluctuation, T_t is the long-term trend, and R_t is the remainder component, all at period t . Taking 24 hours as the “season” in the calculation, i.e., adjusting the “bandwidth”, we can get a clearer diurnal variation preventing the trend blurred by the varies intensity between days. The detailed process of the calculation applied in this paper can refer to Hilas et al. (2006).

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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.

Episode	Slope ($\mu\text{g m}^{-3}/\mu\text{g m}^{-3}$)	Episode	Slope ($\mu\text{g m}^{-3}/\mu\text{g m}^{-3}$)
Gas phase			
(06)	5.30 ± 2.10	(28)	3.57 ± 0.72
(20)	1.00 ± 0.18^a	(30)	3.99 ± 0.87
(22)	4.10 ± 1.54	Average	3.95 ± 1.67
(24)	5.75 ± 1.28		
Particle phase			
(06)	6.66 ± 2.28	(25)	5.14 ± 1.76
(07)	3.14 ± 1.05	(28)	5.61 ± 0.69
(13)	5.23 ± 0.26	(30)	4.37 ± 0.42
(20)	5.11 ± 0.40	Average	5.05 ± 1.01
(22)	5.15 ± 0.88		

190 **Note.** ^a The relatively low value from the episode at night on 20 October was also selected for the criteria used here, indicating the special low contribution from biomass burning to gOON during this episode.

Table S2. Summary of average mass concentrations of OON measured or calculated by the CIMS and the AMS, averaged values of gOON production rates, meteorological parameters, and other OON-related parameters during October 2018.

	Average \pm SD		Average \pm SD
pOrgNO_{3,AMS} ($\mu\text{g m}^{-3}$)	--	secondary gOON ($\mu\text{g m}^{-3}$)	0.79 \pm 0.67
<i>NO₂⁺/NO⁺</i>	0.60 \pm 0.46	Total gOON	0.11 \pm 0.11
<i>ratio method</i>		production rate (ppb h⁻¹)	
<i>TD method</i>	1.10 \pm 0.81	<i>OH initiated</i>	0.07 \pm 0.10
<i>PMF method</i>	2.29 \pm 2.38	<i>NO₃ initiated</i>	0.05 \pm 0.07
pOON _{CIMS} ($\mu\text{g m}^{-3}$)	0.66 \pm 0.53	<i>O₃ initiated</i>	0.01 \pm 0.01
gOON _{CIMS} ($\mu\text{g m}^{-3}$)	1.00 \pm 0.67	OA ($\mu\text{g m}^{-3}$)	14.27 \pm 8.20
pC ₄₋₅ N ($\mu\text{g m}^{-3}$)	0.10 \pm 0.07	Nitrate ($\mu\text{g m}^{-3}$)	4.44 \pm 6.05
pC _{6-9_aro} N ($\mu\text{g m}^{-3}$)	0.10 \pm 0.09	pOON _{CIMS} /OA	0.05 \pm 0.02
pC ₈₋₁₀ N ($\mu\text{g m}^{-3}$)	0.27 \pm 0.21	NO (ppb)	9.24 \pm 18.33
pC ₁₁₋₂₀ N ($\mu\text{g m}^{-3}$)	0.09 \pm 0.08	NO ₂ (ppb)	31.17 \pm 18.38
pC _{other} N ($\mu\text{g m}^{-3}$)	0.12 \pm 0.09	O ₃ (ppb)	36.95 \pm 31.21
levoglucosan ($\mu\text{g m}^{-3}$)	0.06 \pm 0.07	wind speed (m s ⁻¹)	4.50 \pm 2.18
BB pOON ($\mu\text{g m}^{-3}$)	0.32 \pm 0.36	temperature (°C)	23.73 \pm 2.92
secondary pOON ($\mu\text{g m}^{-3}$)	0.34 \pm 0.35	RH (%)	71.92 \pm 17.43
BB gOON ($\mu\text{g m}^{-3}$)	0.25 \pm 0.29		

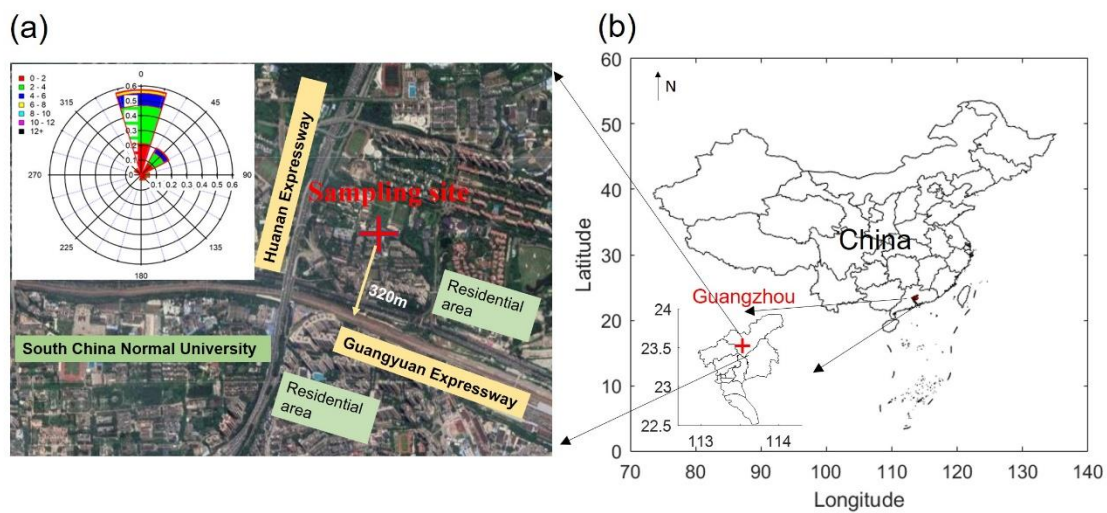
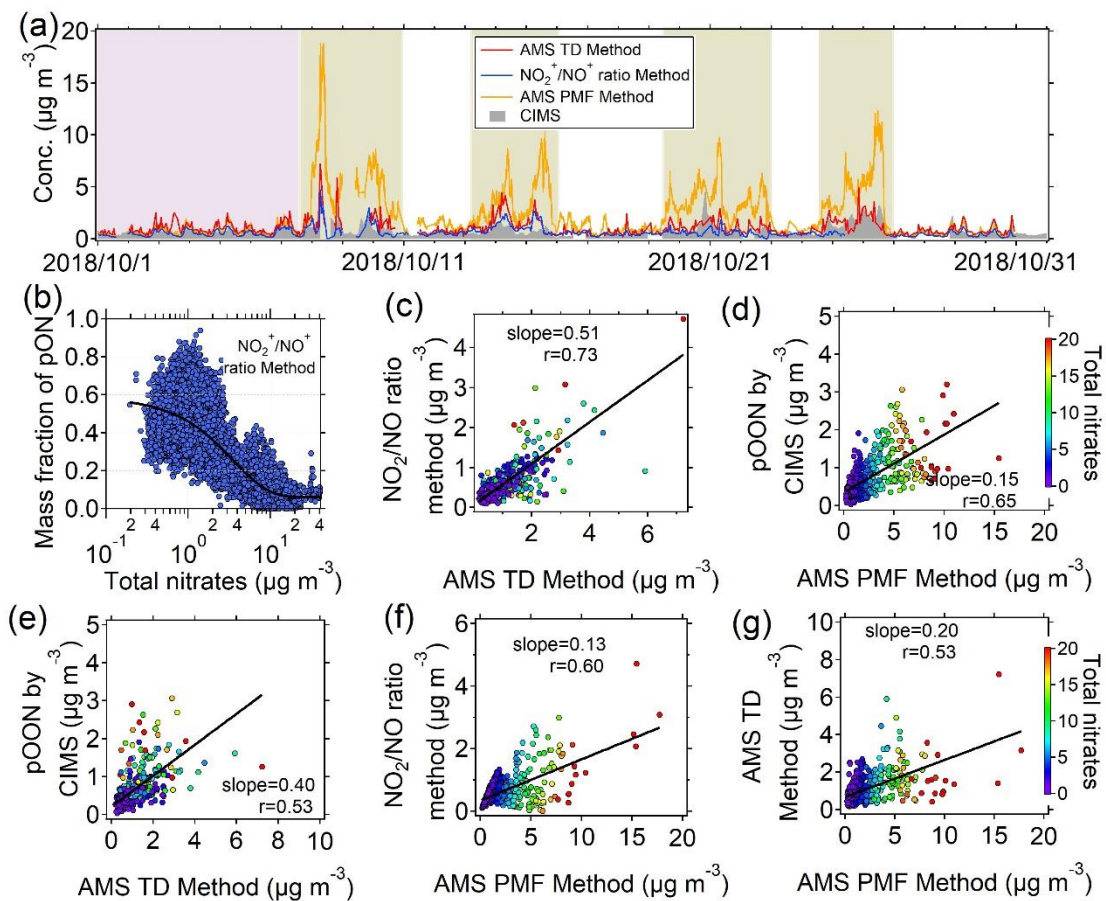
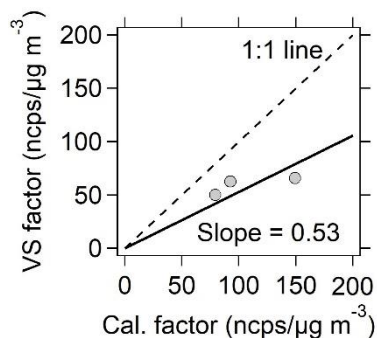


Figure S1. Site descriptions: (a) The satellite view of sampling site in Guangzhou, China. The sampling site is located in the campus of Guangzhou institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). The wind rose plot during the campaign is also shown as insert plot with color represents the wind speed. (b) The location of Guangzhou city in the map of China.

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205 **Figure S2.** (a) Comparison of time series of pOON derived from the CIMS and pOrgNO_{3,AMS} from the AMS based on three methods introduced in Text S1. The tinted backgrounds with light pink and light yellow indicate the period with low and high concentrations of nitrates, respectively. (b) Mass fraction of pOrgNO_{3,AMS} (NO₂⁺/NO⁺ ratio method) to total nitrates as a function of total nitrate signal derived from the AMS. (c–g) Scatterplots of pOON measured by the CIMS and pOrgNO_{3,AMS} calculated by three methods based on the AMS measurement. All the scatters are color-coded by the mass concentration of total nitrate signals measured by the AMS. All the linear fitting are based on the orthogonal distance regression (ODR) algorithm in this study.



210 **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).

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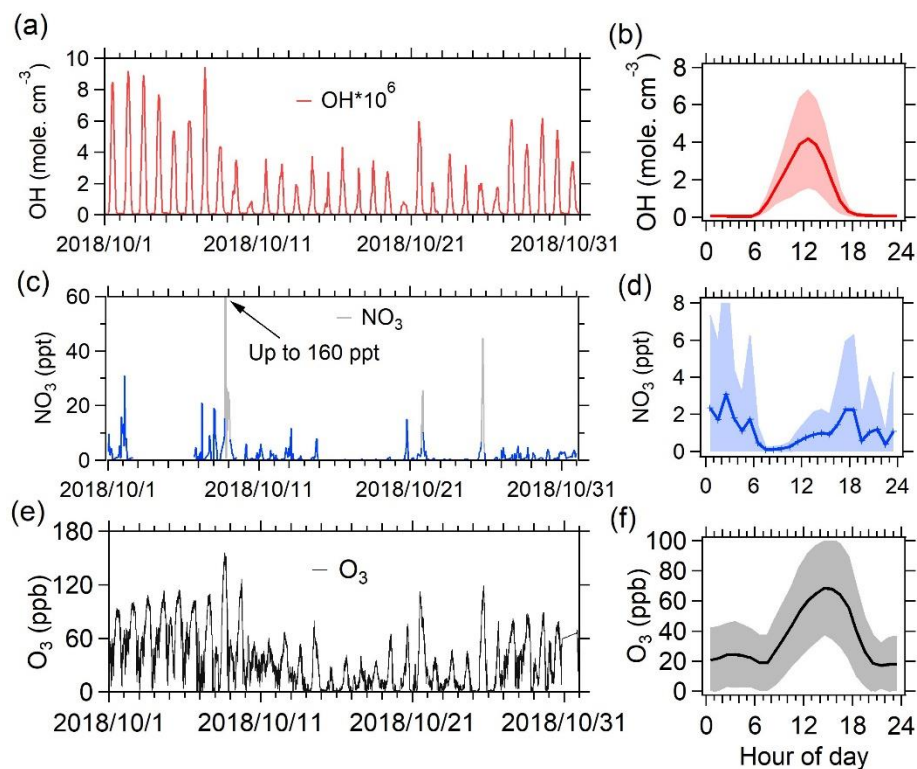
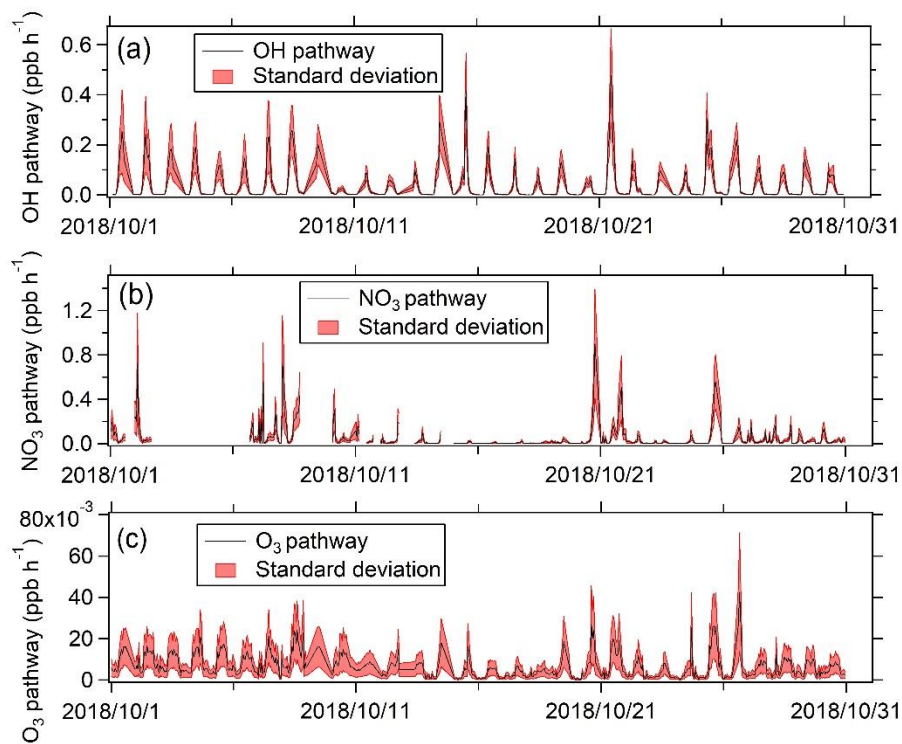


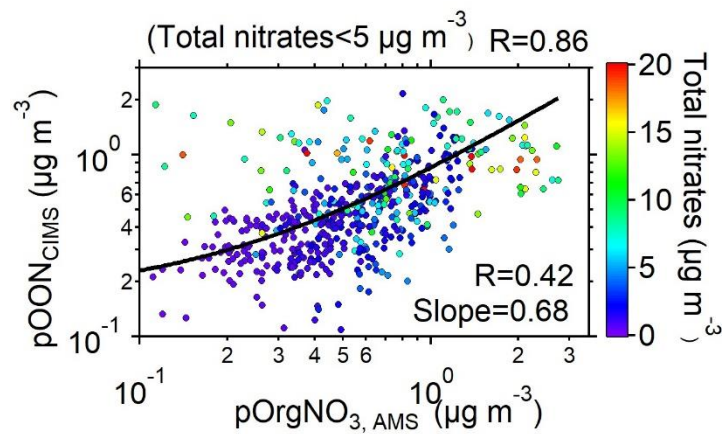
Figure S4. The time series and average diurnal variations of (a, b) OH, (c, d) NO₃ and (e, f) O₃ used in the calculation of the gOON production rate. The shaded areas mean the standard deviations. Based on the on-line measurement of N₂O₅ by the CIMS, extremely high concentration of NO₃ was estimated, which cannot be explained by the box model. To avoid the interferences from extremely high concentration of NO₃, the unexplained peaks color-coded using grey in (c) was not included in the final ON calculation. When such high episodes of measured NO₃ were included in the calculation of gOON production rate, the contribution of gOON production rate from daytime NO₃ oxidation is even larger.

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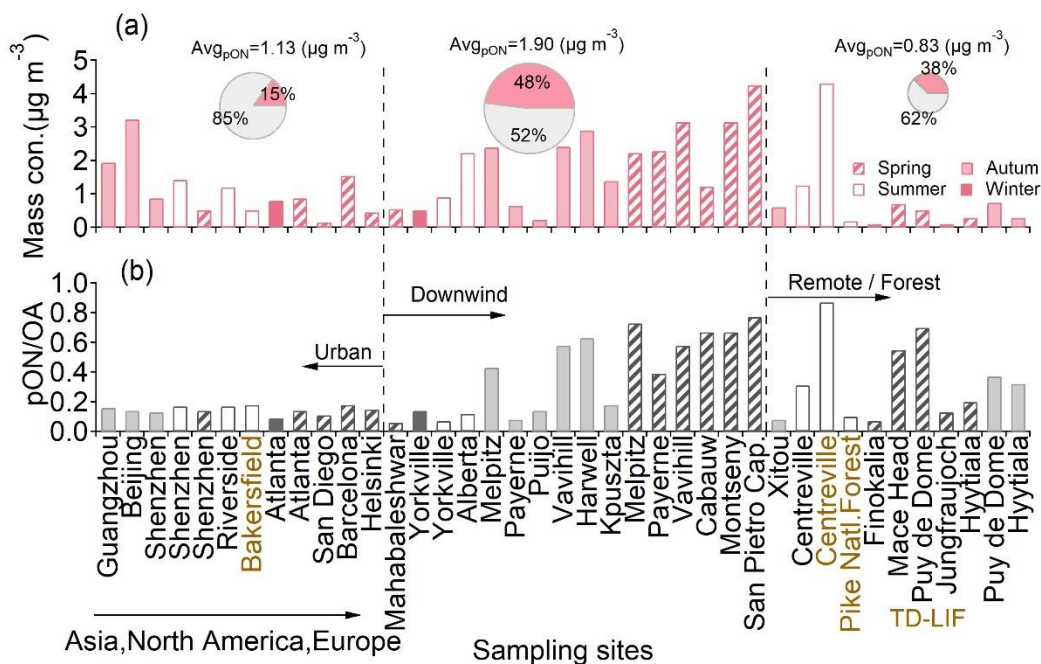
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Figure S5. The uncertainty of gOON production rate of (a) OH, (b) NO₃ and (c) O₃ pathway by Monte Carlo method with 10,000 calculations. The shaded areas mean the standard deviations.

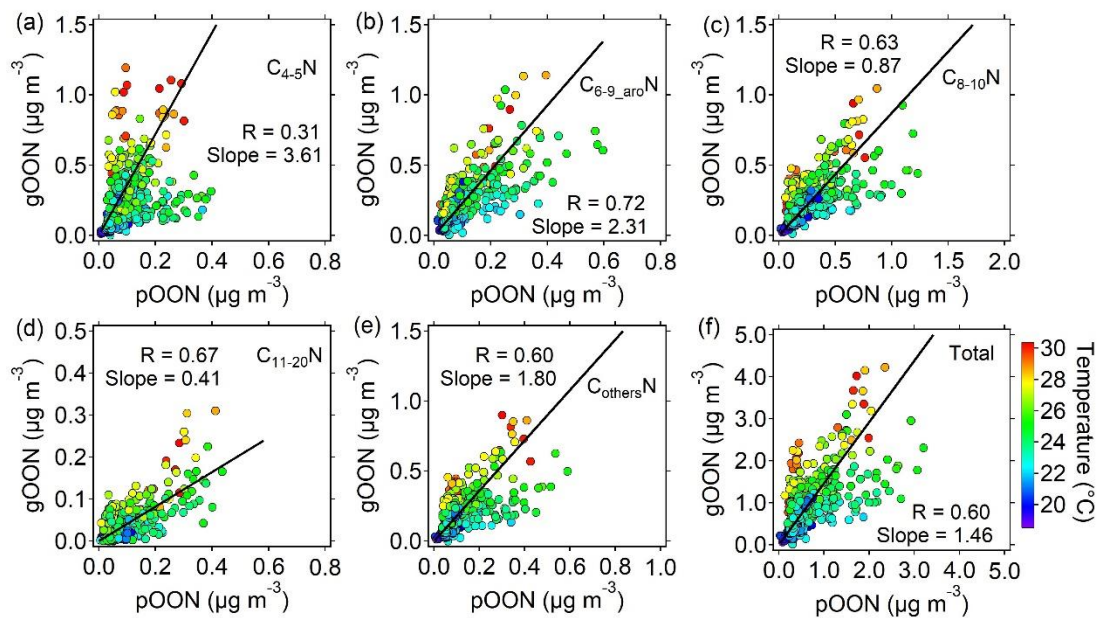


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Figure S6. Scatterplot of $\text{pOON}_{\text{CIMS}}$ versus $\text{pOrgNO}_{3,\text{AMS}}$ during the campaign. The points are color-coded using total nitrates (including inorganic nitrate and organic nitrate) measured by AMS.



235 **Figure S7. (a) Mass concentration pON and (b) its fraction to OA at sites around the world (Ayres et al., 2015; Chen et al.,**
2020; Day et al., 2010; Farmer et al., 2010; Fisher et al., 2016; Fry et al., 2013; Kiendler-Scharr et al., 2016; Lanz et al.,
2010; Lee et al., 2019; Rollins et al., 2012; Salvador et al., 2020; Singla et al., 2019; Xu et al., 2015; Yu et al., 2019) classified
into urban sites, downwind sites (lied downwind of the cities where were influenced by the emissions from the cities), forest
or remote sites with different seasons. The average molecular weight of OON used for all sites is assumed to be 200 g mol^{-1} .
 240 **The inset pies indicate the average fraction of pON (pink) to OA at each type of site. The yellow indicates the data are**
measured by thermal dissociation laser-induced fluorescence instrument (TD-LIF). The method of the $p_{\text{ON}}_{\text{AMS/TD-LIF}}/\text{OA}$
calculation was referred to Takeuchi and Ng (2019).



245 **Figure S8. Scatter plots between gOON and pOON in different categories, i.e., (a) $C_{4-5}N$, (b) $C_{6-9_aro}N$, (c) $C_{8-10}N$, (d) $C_{11-20}N$, (e) $C_{other}N$ and (f) the total values. The plots are color-coded by ambient temperature.**

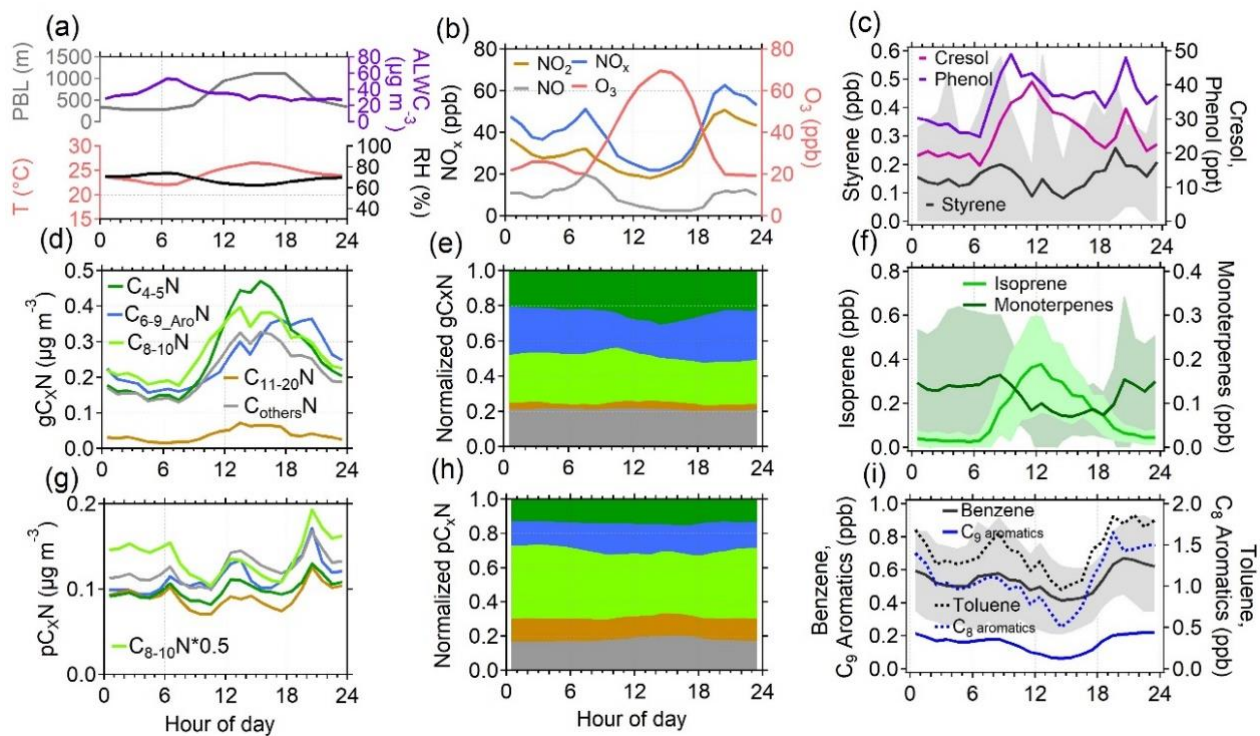


Figure S9. The average diurnal variations of (a) planetary boundary layer height (PBL), aerosol liquid water contents (ALWC), temperature (T) and relative humidity (RH), (b) mixing ratios of nitrogen dioxide (NO_2), nitric oxide (NO), NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$), and ozone (O_3), (c) cresol, phenol, and styrene, (d) gas phase, and (g) particle phase C_xN groups measured by the CIMS, mass fraction of (e) gas- and (h) particle-phase C_xN groups, (f) isoprene and monoterpenes, (i) benzene, toluene, C_8 aromatics, C_9 aromatics during the campaign of October. The shaded areas mean the standard deviations.

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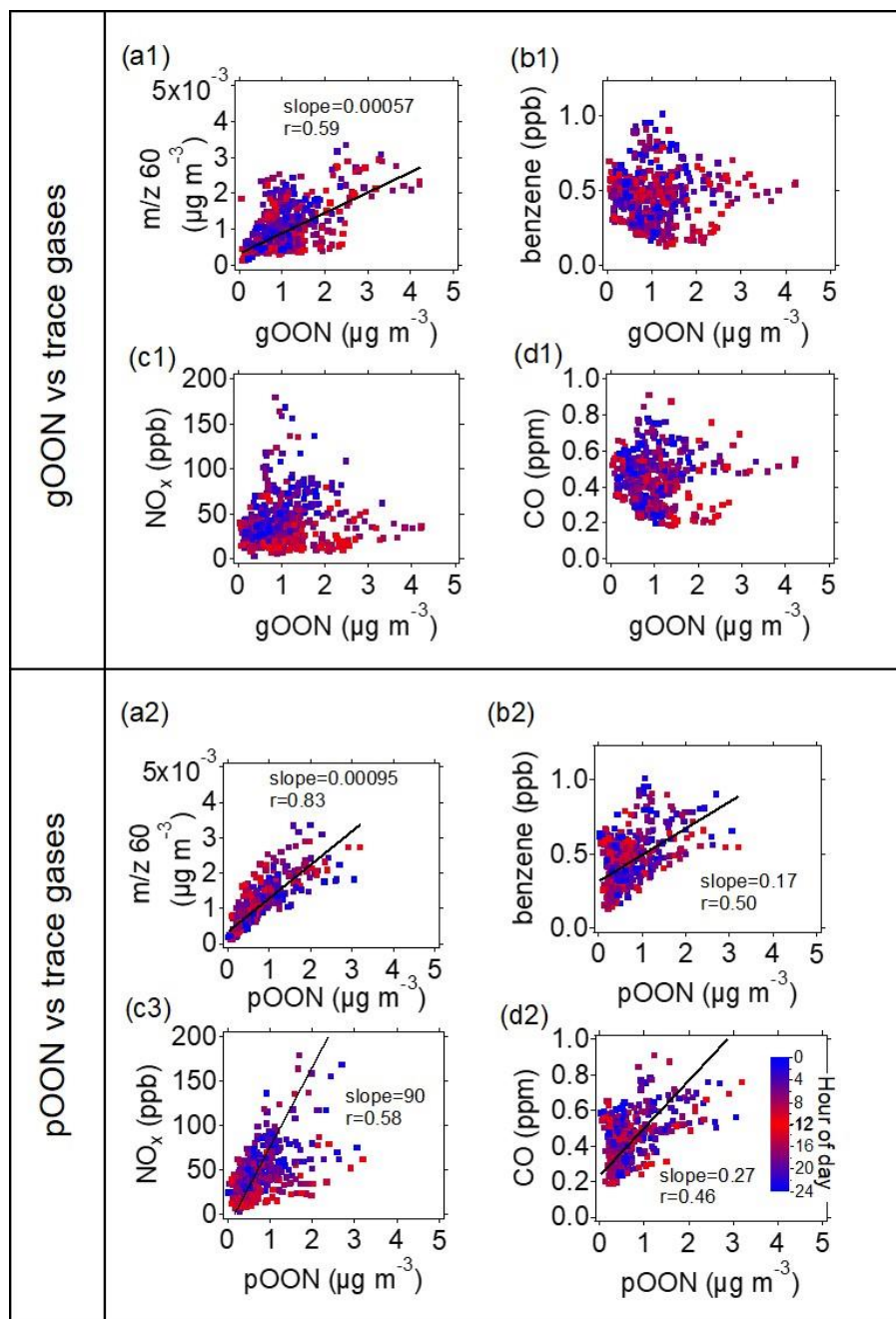


Figure S10. Scatter plots between gOON (up panel) or pOON (down panel) measured by the CIMS and (a1, a2) m/z 60 fragment, (b1, b2) benzene, (c1, c2) NO_x, (d1, d2) carbon monoxide (CO). All scatter plots are color-coded using hour of the day. The HR peak, C₂H₄O₂⁺, representing the levoglucosan, show similar variation as m/z 60.

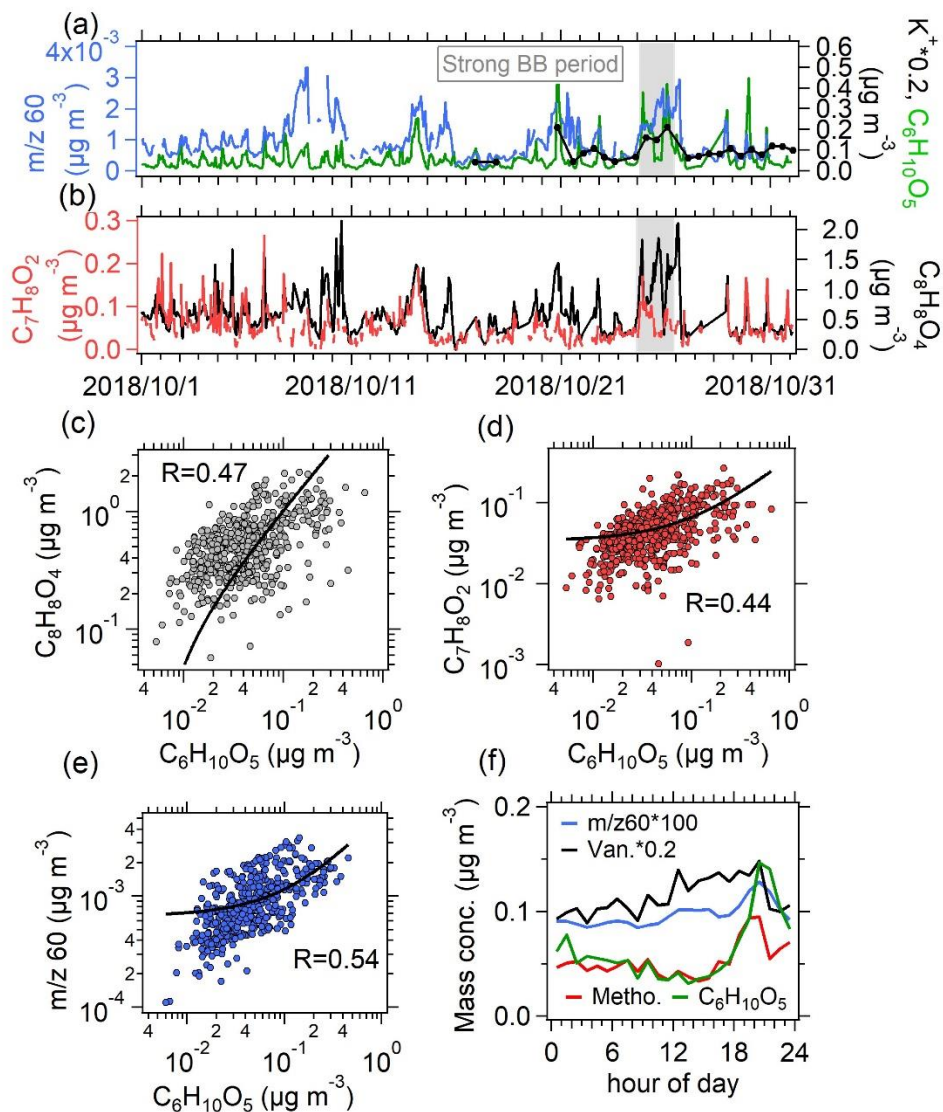


Figure S11. (a) Time series of m/z 60 from the AMS, particulate $C_6H_{10}O_5$ (levoglucosan and its isomers), water-soluble potassium (K^+), (b) $C_7H_8O_2$ (methoxyphenol and its isomers) and $C_8H_8O_4$ (vanillic acid and its isomers) from CIMS. The m/z 60 was found to be a fragment from levoglucosan-like species and supposed to be a tracer of biomass burning (Cubison et al., 2011). Scatter plots of (c) $C_7H_8O_2$ (methoxyphenol and its isomers), (d) $C_8H_8O_4$ (vanillic acid and its isomers), and (e) m/z 60 versus levoglucosan. Moderate agreement between them and $C_6H_{10}O_5$ also demonstrates the existence of biomass burning emissions (Urban et al., 2012). (f) Diurnal variation of the four species.

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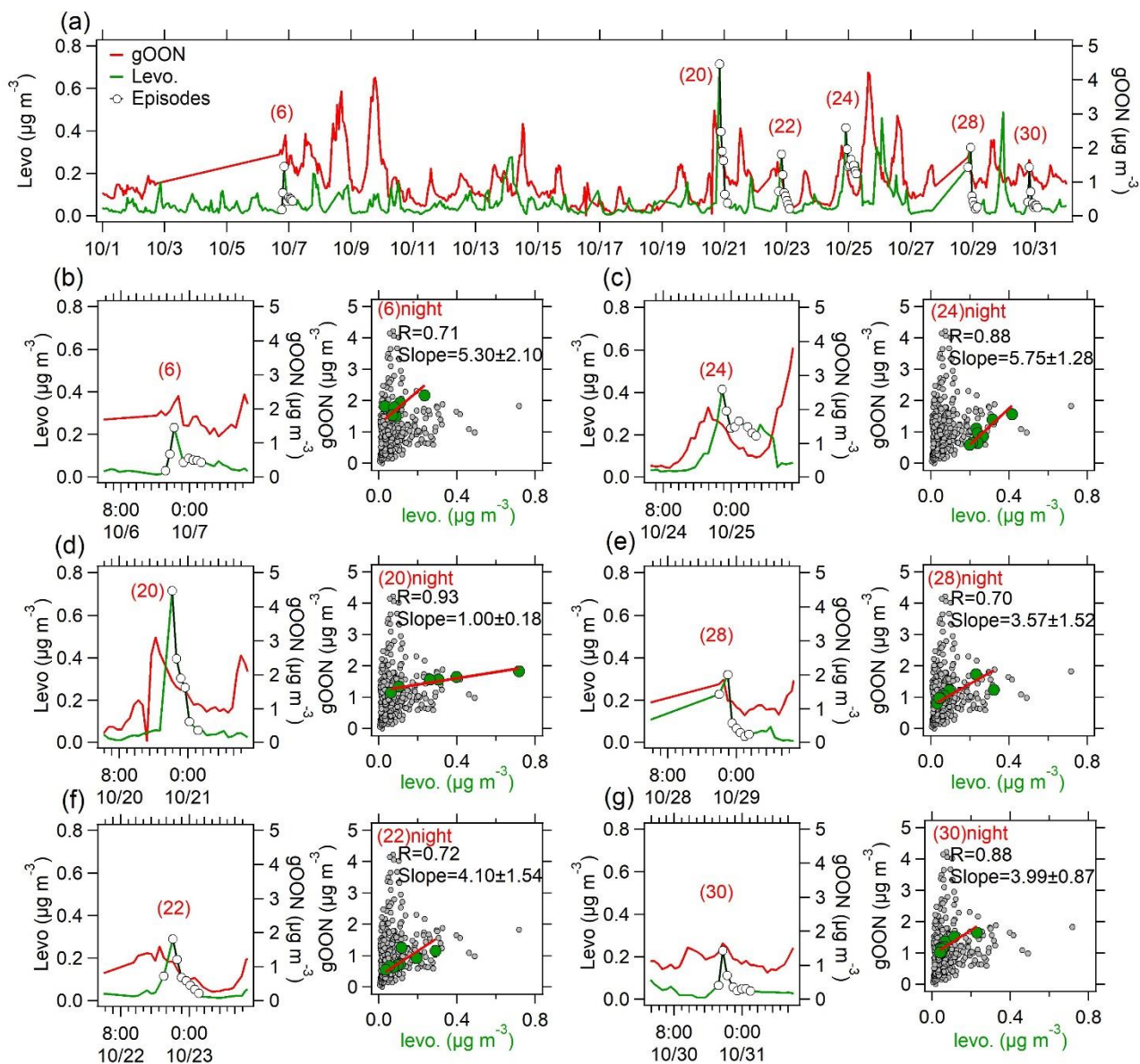


Figure S12. (a) Time series of measured gOON and levoglucosan (levo., particle-phase $\text{C}_6\text{H}_{10}\text{O}_5$) measured by the CIMS. The biomass burning episodes are labeled based on selection criteria as well. (b–f) Six episodes were selected and used for calculating biomass burning ratios between gOON and levoglucosan. The time series and scatter plots during each episode are also shown here.

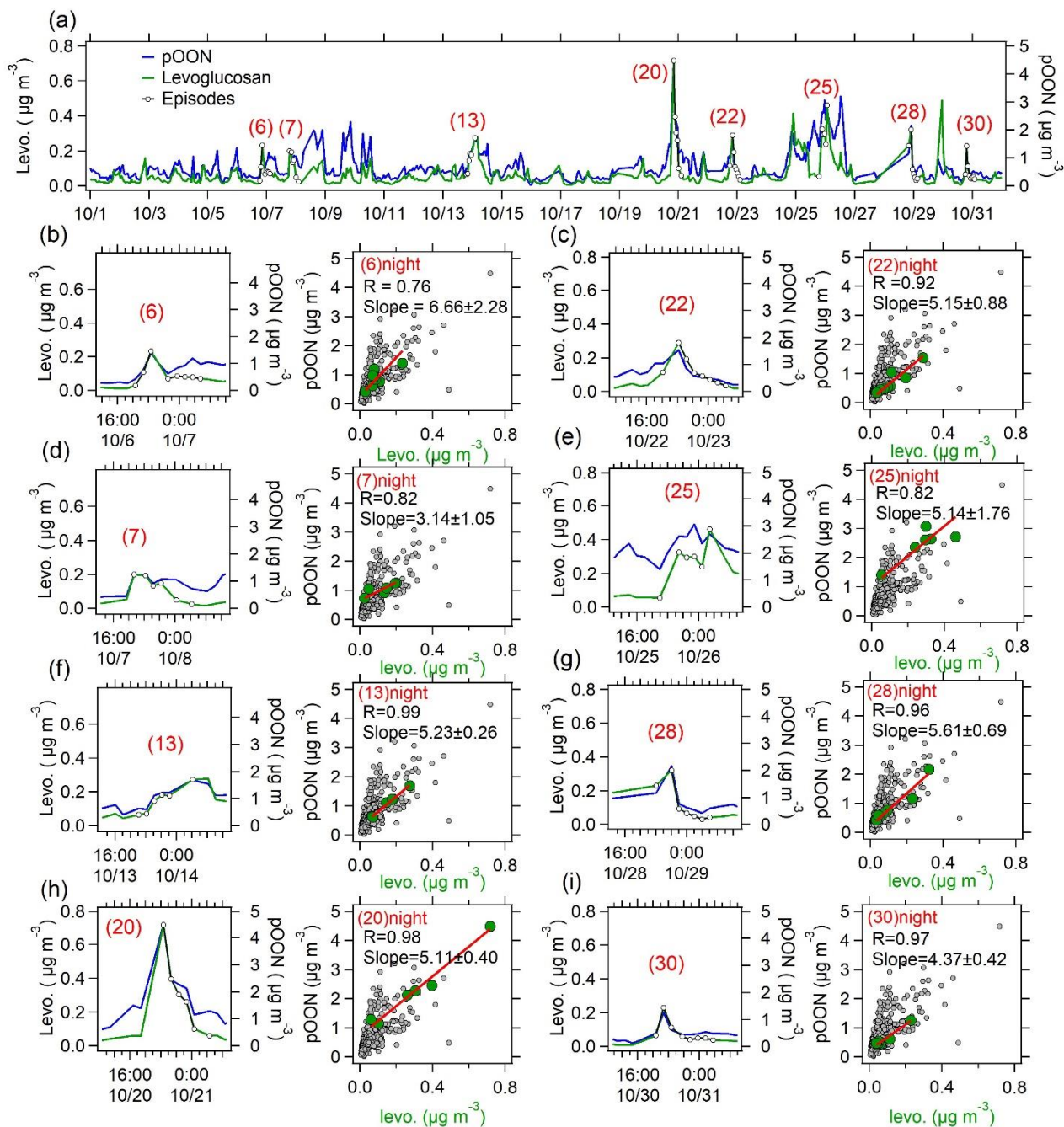
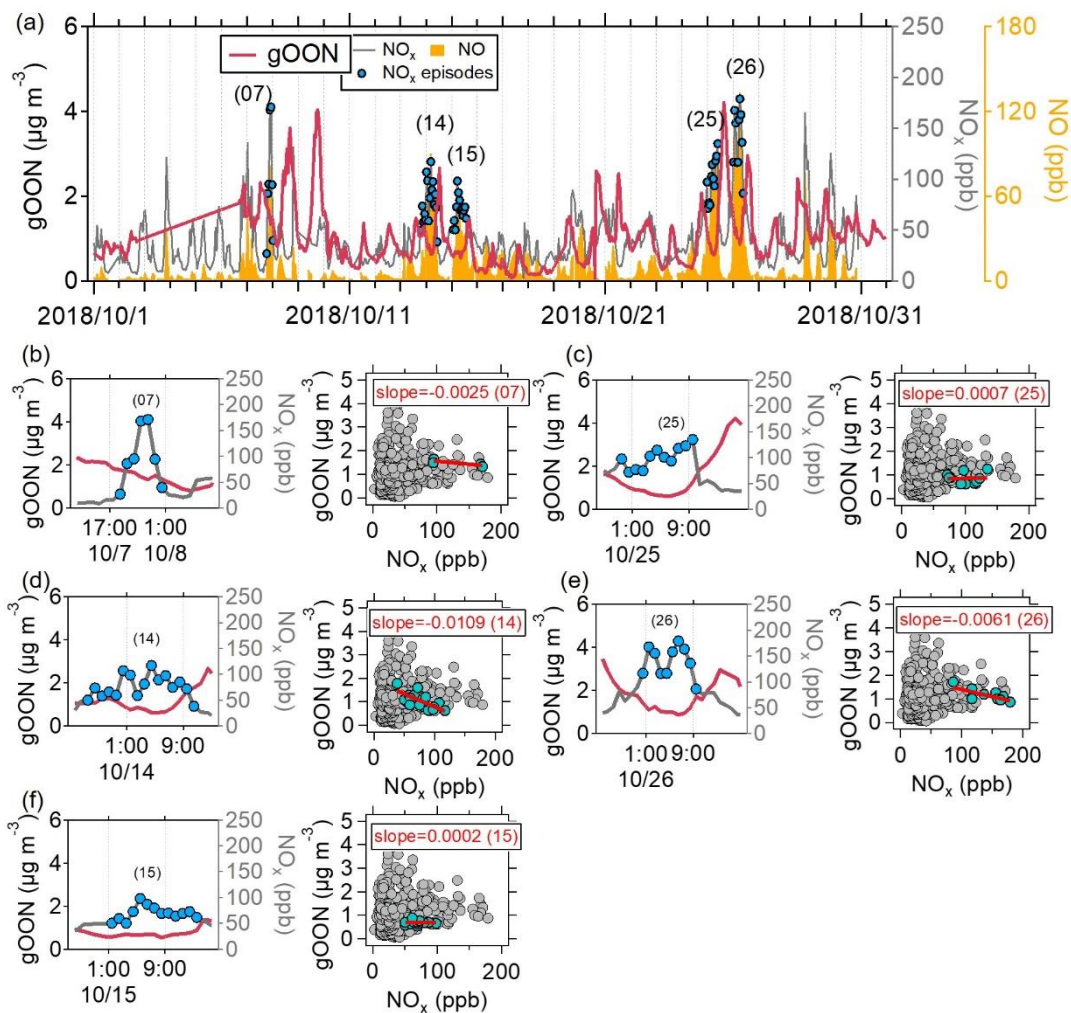


Figure S13. (a) Time series of pOON and levoglucosan (levo.) measured by the CIMS. The biomass burning episodes are labeled based on the selection criteria as well. (b–i) Eight episodes were selected and used for calculating biomass burning ratios between pOON and levoglucosan. The time series and scatter plots during each episode are shown here.



280 **Figure S14. (a)** Time series of gOON measured by the CIMS, and NO/NO_x measured by a NO_x analyzer. The episodes are
 285 labeled based on the high concentration of NO_x. (b–f) Time series and scatter plots of gOON vs NO_x during five selected
 NO_x polluted episodes. NO_x was the tracer for vehicle emissions (Harrison et al., 2003; Krecl et al., 2017). The extremely
 high NO concentrations (100–200 ppb) indicate strong influences from fresh vehicle emissions. No consistent enhancement
 between gOON and NO_x was found during the high NO_x episodes, suggesting the vehicle emission is not an important
 source of gOON in the ambient air.

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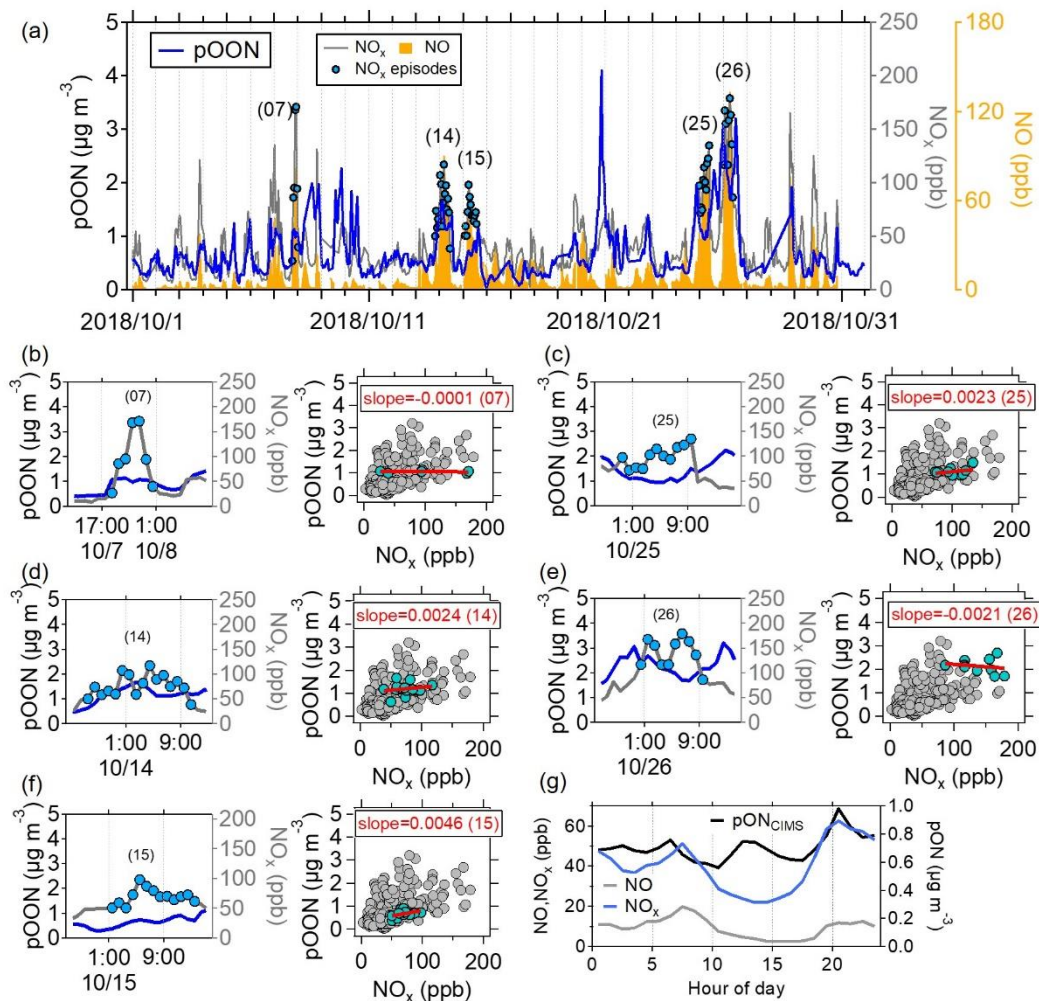
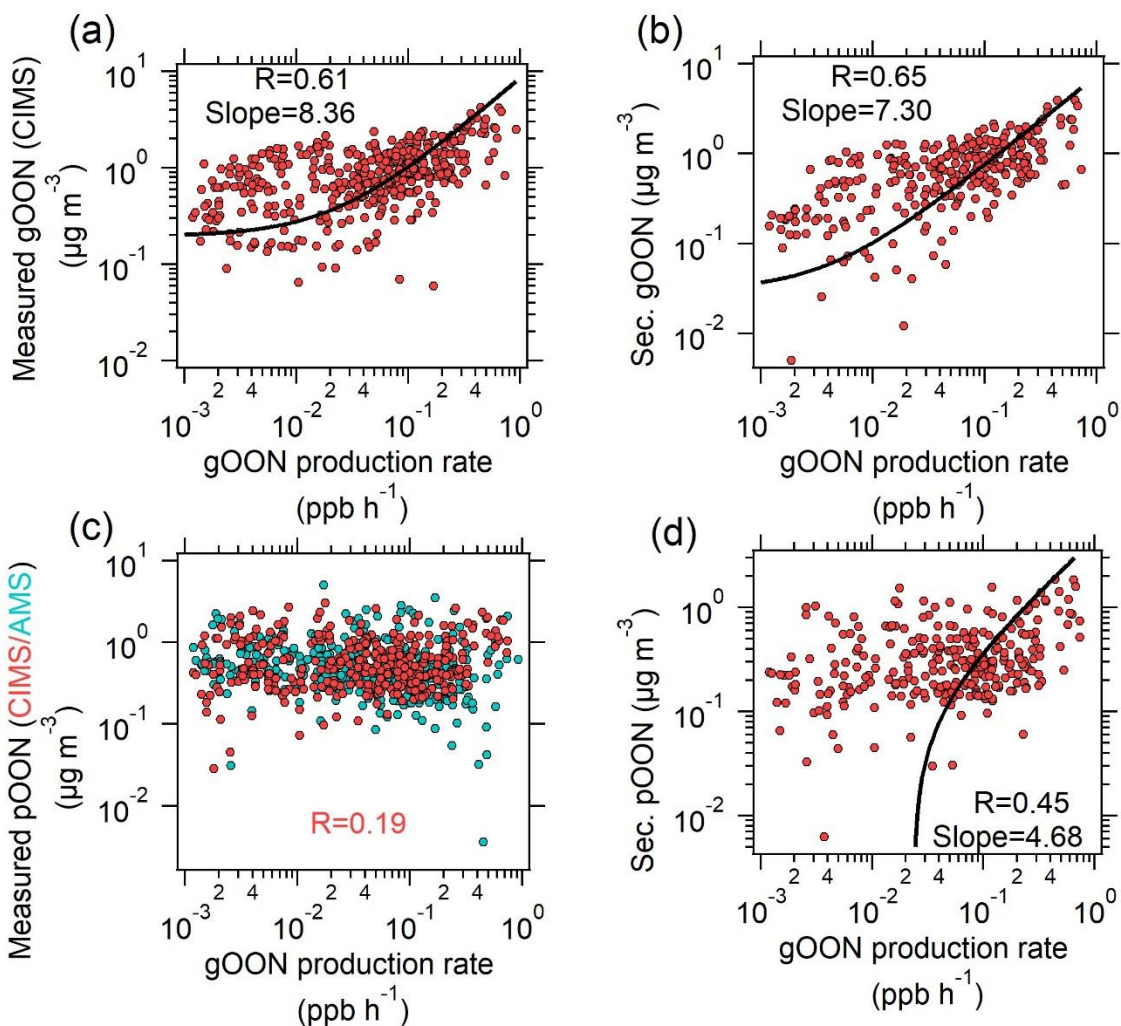


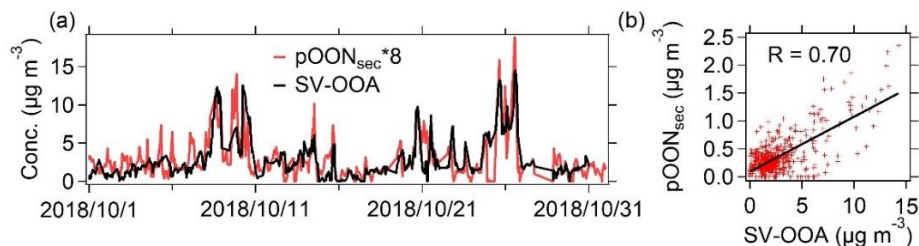
Figure S15. (a) Time series of pOON measured by the CIMS, and NO/NO_x measured by the NO_x analyzer. The episodes are labeled based on the high concentration of NO_x. (b–f) Time series and scatter plots of pOON vs NO_x during five selected NO_x polluted episodes. (g) Diurnal variations of the measured pOON by the CIMS (pOON_{CIMS}), NO and NO_x. NO_x was the tracer for vehicle emissions (Harrison et al., 2003; Krecl et al., 2017). The extremely high NO concentrations (100–200 ppb) indicate strong influence from fresh vehicle emissions during that episode. However, no consistent enhancement between pOON and NO_x was found during these high NO_x episodes, suggesting the vehicle emission is not an important source of pOON in this study.

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Figure S16. Scatter plots between (a) measured gOON and (b) secondary gOON vs total secondary gOON production rate. Scatter plots of (c) measured pOON and (d) secondary pOON vs total secondary gOON production rate. The logarithm is applied for both axes.



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Figure S17. (a) The time series of pOON_{sec} 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).



305 **Figure S18.** The field points of active fires or thermal anomalies from Modis Satellite around the sampling site, Guangzhou Institute of Geochemistry (GIG), in Guangzhou during the strong biomass burning period October 24–26th.

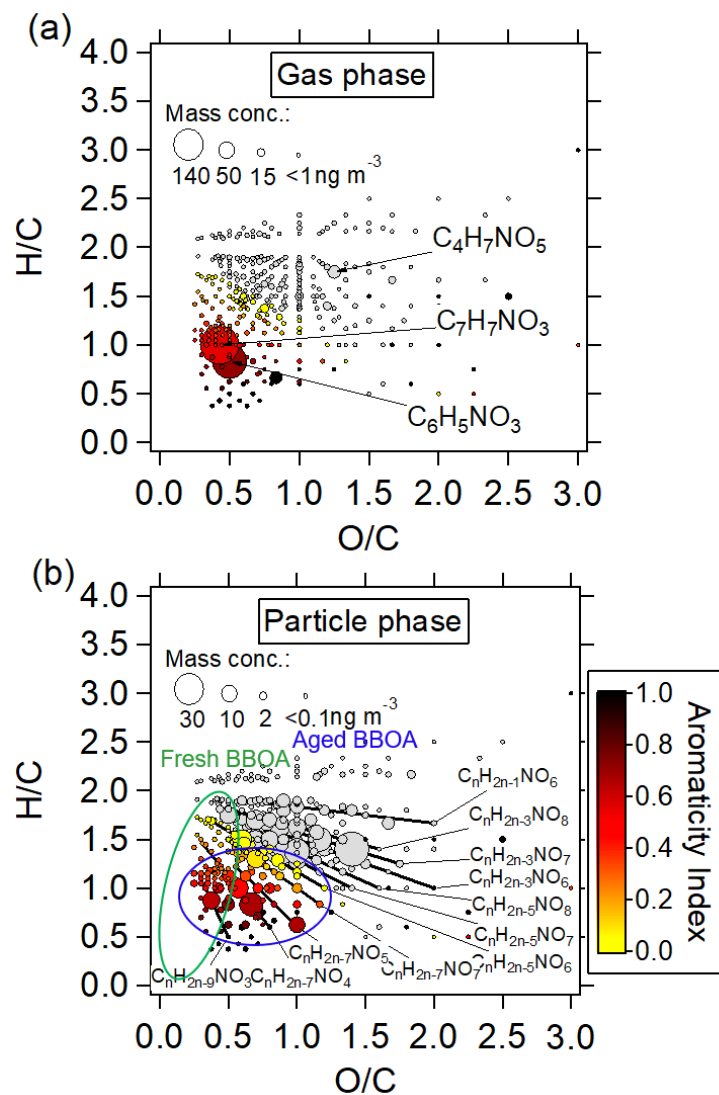


Figure S19. Van Krevelen (VK) diagram of all compounds from (a) gOON and (b) pOON. The size of symbols is proportional to the mean enhanced concentrations at 20:00 on October 22 of each compound. Ions are color-coded with Aromaticity Index between 0 and 1 (Wang et al., 2019). The green and blue ellipse represent OA from freshly emitted and aged biomass burning plumes, respectively, based on orbitrap (ESI⁻) measurement in Wang et al. (2019). During the whole campaign, the most contributive species are C₄H₇NO₅ (7.9%), C₆H₅NO₃ (7.4%) and C₇H₇NO₃ (5.9%) in the gas phase and C₈H₁₁NO₇ (7.9%) in the particle phase. The enhancement concentration of C₄H₇NO₅ is much lower than its mean value, implying secondary formation is its dominant source.

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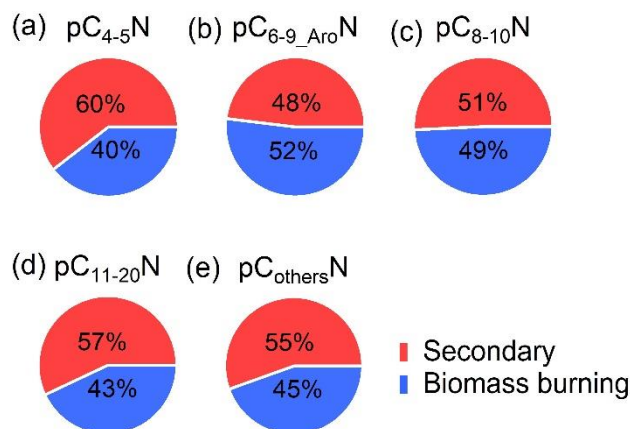
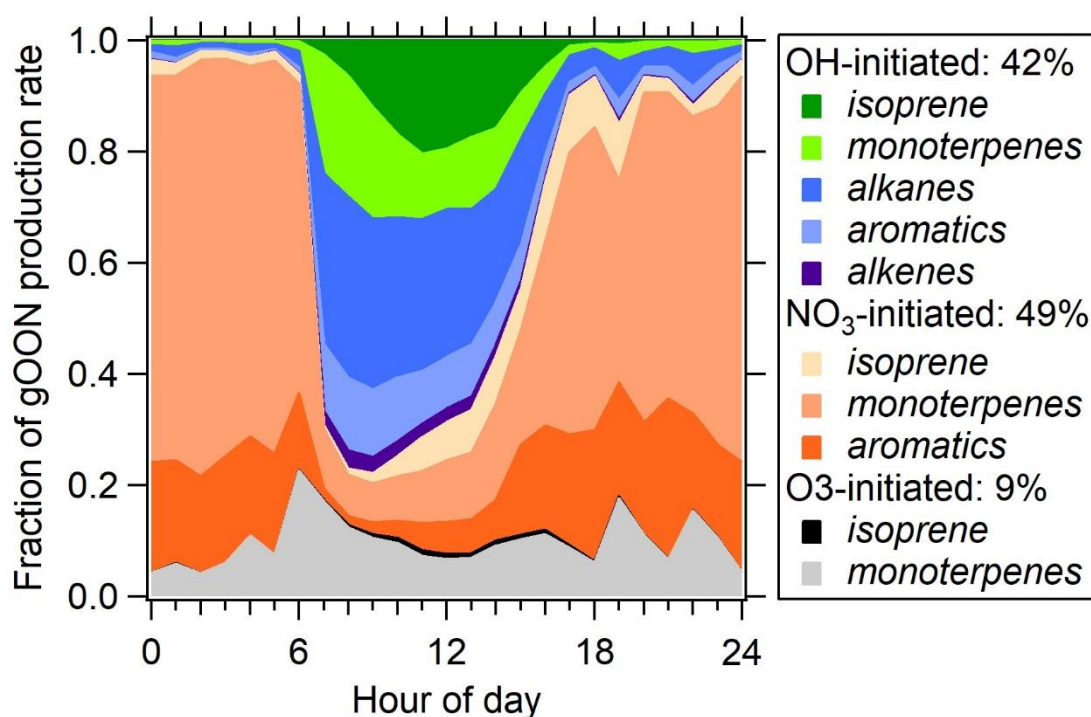
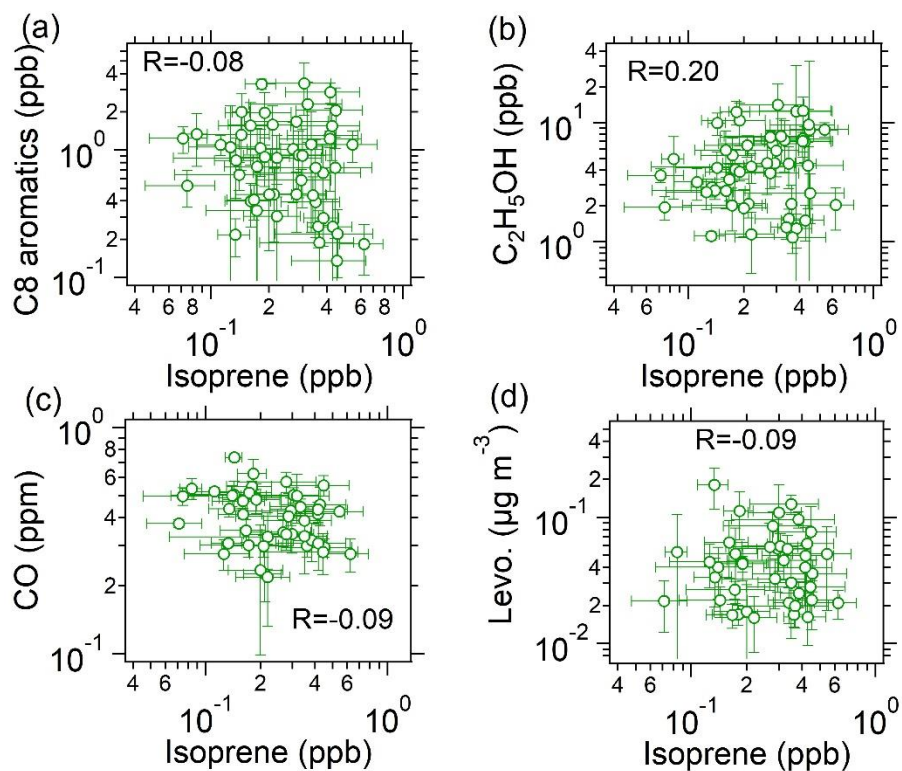


Figure S20. The contributions of biomass burning and secondary formation to each particle-phase C_xN (pC_xN) group following Eqs. (1) and (2) in section 3.2.

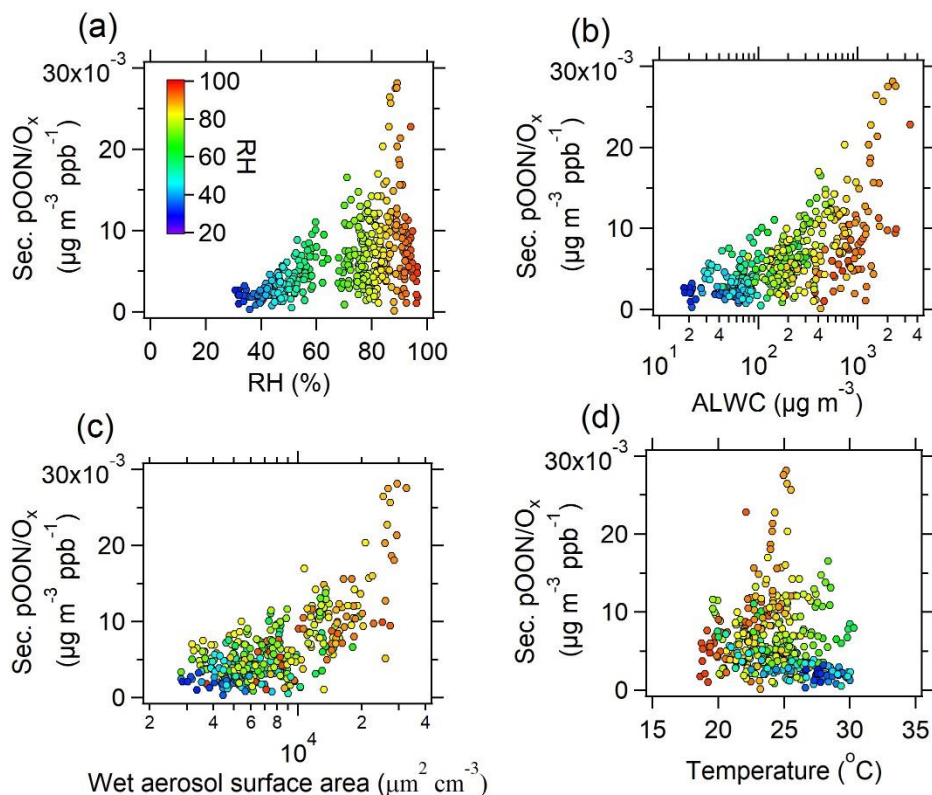


320 Figure S21. Average diurnal variations of the fractions of gOON production rate from OH initiated, NO₃ initiated and O₃ initiated oxidation pathways. For each pathway, contributions from classified VOCs are also shown.

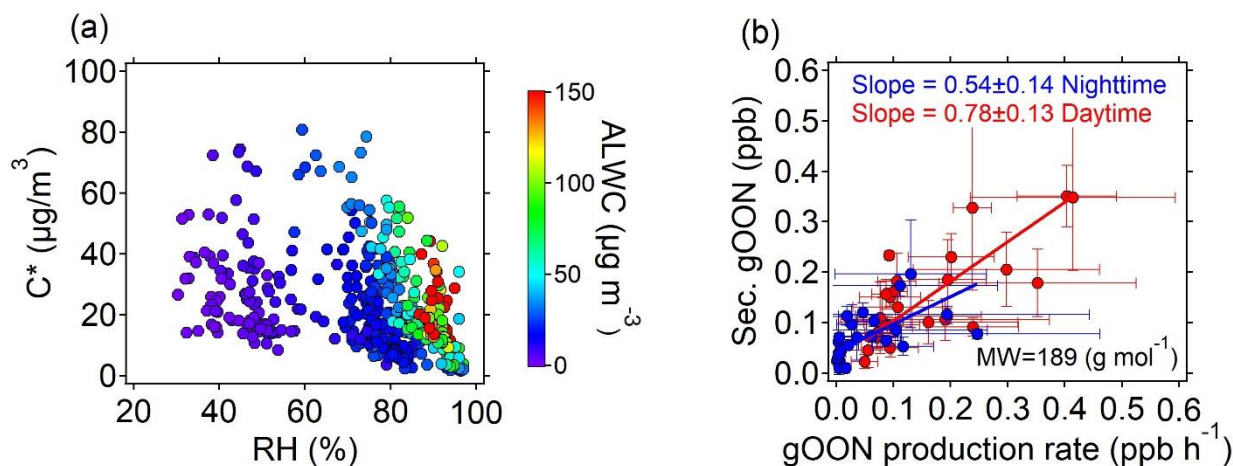


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Figure S22. Scatter plots between the averaged (a) C8 aromatics, (b) ethanol, (c) CO, and (d) levoglucosan vs isoprene during daytime (9:00–18:00) during the entire campaign. The error bars are standard deviations of average values during daytime. The logarithm is applied for both axes.



330 **Figure S23.** The ratio of Secondary (Sec.) pOON to O_x versus the (a) RH, (b) aerosol liquid water content (ALWC), (c) wet
 335 aerosol surface area, and (d) ambient temperature color-coded using the RH during the campaign. Regression slopes
 between pOON and O_x in photochemically processed urban emissions provide a metric to investigate the relative efficiency
 of pOON versus O_3 formation during photochemical oxidation (Wood et al., 2010; Hayes et al., 2013). The different values
 of secondary pOON/ O_x ratio can be attributed to photochemical oxidation from different VOC constituent (Nault et al.,
 2021), heterogenous/aqueous reaction (Zhang et al., 2018; Zhan et al., 2021; Xu et al., 2017; Dai et al., 2019; Hu et al., 2016),
 and mixing with air aloft that contains residual pOON and O_x during boundary layer growth (Wood et al., 2010). The
 secondary pOON/ O_x ratios that positive correlated with ALWC and wet aerosol surface area suggested that partial pOON
 might be formed by heterogenous/aqueous reaction, which can efficiently produce secondary pOON but inefficiently on O_x .



340 **Figure S24.** (a) Scatterplot of saturation mass concentration of total OON ($C^* = 1/(C_p/C_{OA}/C_g)$) versus RH color-coded with
 ALWC. (b) Scatter plot between secondary gOON concentration and gOON production rate. The regression slope can be
 used to estimate the lifetime of gOON following Liebmann et al. (2019).

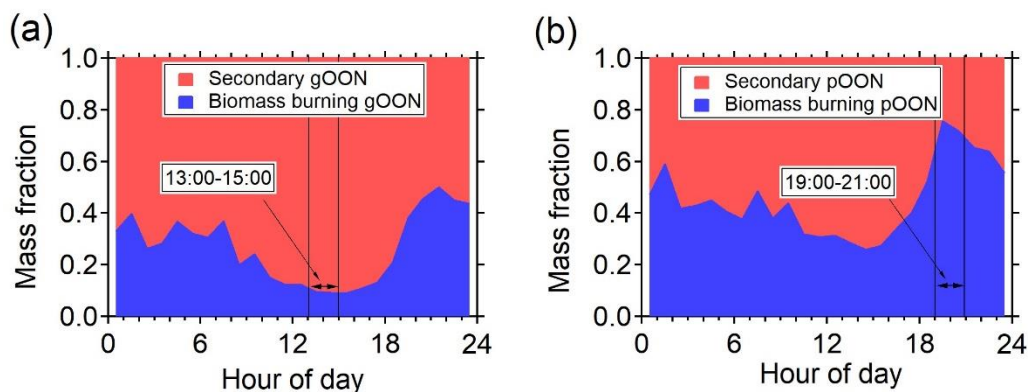


Figure S25. The average diurnal mass fractions of the contributions from secondary formation and biomass burning to (a) gOON and (b) pOON, respectively. The time periods of 13:00–15:00 and 19:00–21:00 represented the secondary formation dominated period and biomass burning dominated period for the particle phase, respectively.

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