

Report #1

The authors characterized organic nitrates at an urban site in south China based on the measurements of aerosol mass spectrometer and volatile organic compounds (VOCs). The ratios of $\text{NO}^+/\text{NO}_2^+$ and positive matrix factorization were used to estimate the concentrations of organic nitrates. The authors found that organic nitrates contribute substantial fractions of total nitrate in spring, summer and autumn, and the reactions between biogenic VOCs and NO_3 radical were the major formation pathway. This manuscript is generally well written, and I have some comments below.

1. Concerning the PMF results, the authors need to show more diagnostic plots to justify the results. For example, previous study by the same group (He et al., 2011) was able to identify four OA factors in autumn at the same site, while the biomass burning OA was not resolved in this study. The spectrum of LO-OOA in autumn (Figure S1) shows clear m/z 60 and 73 signals, suggesting that more factors are needed. In addition, I would suggest the authors checking the changes in NO^+ , NO_2^+ in OA factors across different f_{peak} values, and give an estimation of uncertainties.

REPLY:

According to the diagnostic plots of the PMF analysis shown in Figure S2 to S4 in the supplementary, the same organic factors were obtained in PMF based on only OA spectra and OA spectra combining with NO_x^+ ions. Although the 3-factor solution for OA seemed to have a “mixed factor” problem (Zhu et al., 2018), such as HOA mixed with COA (clear $\text{C}_3\text{H}_3\text{O}^+$ in m/z 55 for spring, summer and autumn) (Mohr et al., 2012) and BBOA mixed with LO-OOA (clear m/z 60 and 73 signals in LO-OOA for autumn) (Cubison et al., 2011), running PMF with more factors would produce unexplained factors but little influence the apportionment between organic nitrate and inorganic nitrate (Table S1). In addition, the uncertainties of NO^+ and NO_2^+ in OA factors across different f_{peak} values (from -1.0 to 1.0) were very small (Table S2). Thus, the 3-factor solution was finally used for quantifying organic nitrates in spring, summer and autumn. We have added the related description in section 2.3.

Table S1. The correlation coefficients (R) of $\text{NO}_{3,\text{org}}$ and $\text{NO}_{3,\text{inorg}}$ in 3- to 5-factors solutions estimated by PMF method with these estimated by NO_x method, respectively.

		3-factor solution		4-factor solution		5-factor solution	
		$\text{NO}_{3,\text{org}}$	$\text{NO}_{3,\text{inorg}}$	$\text{NO}_{3,\text{org}}$	$\text{NO}_{3,\text{inorg}}$	$\text{NO}_{3,\text{org}}$	$\text{NO}_{3,\text{inorg}}$
		(NO_x vs. PMF)	(NO_x vs. PMF)	(NO_x vs. PMF)	(NO_x vs. PMF)	(NO_x vs. PMF)	(NO_x vs. PMF)
Spring	R	0.82	0.92	0.81	0.90	0.80	0.91
	Slope	1.21	0.76	1.15	0.78	1.20	0.82
Summer	R	0.82	0.87	0.82	0.88	0.81	0.90
	Slope	1.53	0.70	1.50	0.65	1.45	0.64
Autumn	R	0.77	0.86	0.75	0.85	0.76	0.83
	Slope	0.81	0.85	0.76	0.82	0.75	0.78

Table S2. The mass fraction of NO⁺ and NO₂⁺ in OA factors when f_{peak} is 0 and the uncertainties of NO⁺ and NO₂⁺ in OA factors across different f_{peak} values (from -1.0 to 1.0)

			HOA	LO-OOA	MO-OOA
Spring	NO ⁺	f _{peak} =0	1.3*10 ⁻²	1.4*10 ⁻²	9.8*10 ⁻³
		uncertainty	3.4%	1.4%	6.8%
	NO ₂ ⁺	f _{peak} =0	1.2*10 ⁻²	1.5*10 ⁻⁴	3.0*10 ⁻⁸
		uncertainty	8.5%	3.8%	4.3%
Summer	NO ⁺	f _{peak} =0	1.5*10 ⁻²	1.0*10 ⁻²	1.2*10 ⁻²
		uncertainty	1.5%	5.1%	3.0%
	NO ₂ ⁺	f _{peak} =0	1.47*10 ⁻⁶	6.7*10 ⁻⁴	1.8*10 ⁻³
		uncertainty	4.8%	6.9%	4.0%
Autumn	NO ⁺	f _{peak} =0	1.1*10 ⁻²	3.1*10 ⁻²	1.0*10 ⁻²
		uncertainty	4.5%	0.5%	1.2%
	NO ₂ ⁺	f _{peak} =0	7.0*10 ⁻⁸	9.8*10 ⁻⁸	2.8*10 ⁻⁷
		uncertainty	0.6%	1.9%	1.2%

2. High NO⁺ signal and NO⁺/NO₂⁺ ratio were also observed in HOA spectrum, are they organic nitrates from direct emissions or some other sources. Please calculate the mass fractions of organic nitrates in three OA factors. A major fraction would be expected in LO-OOA, and not surprisingly, organic nitrates were well correlated with LO-OOA.

REPLY:

The mass fraction of organic nitrates in HOA, LO-OOA and MO-OOA was 31%, 49% and 20%, respectively, in spring; 28%, 52% and 20%, respectively, in summer; 30%, 46% and 24% in HOA, LO-OOA and MO-OOA, respectively, in autumn. We have added this statement in section 3.1.

3. The authors calibrated AMS every two weeks, could the authors show the NO⁺/NO₂⁺ ratio for each calibration to check the stability of the instrument.

REPLY:

In this study, R_{NH₄NO₃} was determined by IE calibration using pure NH₄NO₃ on every two weeks for each campaigns and the results show stable values: In spring, the average R_{NH₄NO₃} was 2.66 for the first IE calibration and 2.94 for the second IE calibration; in summer, the average R_{NH₄NO₃} was 3.05 and 3.34 for the first and second IE calibration, respectively; in autumn, the average R_{NH₄NO₃} was 3.33 and 3.31 for the first and second IE calibration, respectively; in winter, the average R_{NH₄NO₃} was 3.45 and 3.51 for the first and second IE calibration, respectively. We have added this in section 2.3.

4. In the abstract and conclusions, the authors highlight the importance of organic nitrates using its

contribution in total nitrates. I would suggest the authors using the mass fractions of organic nitrates in total OA. In addition, could the authors compare the mass concentrations of organic nitrates with previous studies in Pearl River Delta?

REPLY:

We have amended the description in the abstract and conclusions according to this comment. According to the best of our knowledge, no literature has reported the mass concentrations of organic nitrates in Pearl River Delta region, but we have added section 3.5 to compare the organic nitrates in this study to other similar studies across the world.

5. I suggest the authors adding the time series of non-refractory aerosol species during three seasons in supplementary. This is good for readers to evaluate the sources of organic nitrates. For example, the time series of organic nitrates in spring in Figure 2(a) showed clear plumes, which were very likely from regional transport. Without showing other aerosol species, it is hard to tell.

REPLY:

We have added the time series of non-refractory aerosol species in Figure S1 in the supplementary.

6. A more detailed description of VOC measurements is needed in experimental methods.

REPLY:

We have added the related description in section 2.2.2. “In the spring campaign, ambient VOC concentrations were also measured using an on-line VOC monitoring system (TH-300B, Tianhong Corp.), including an ultralow-temperature preconcentration cold trap and an automated in-situ gas chromatograph (Agilent 7820A) equipped with a mass spectrometer (Agilent 5977E). The system had both a flame ionization detector (FID) gas channel for C2–C5 hydrocarbons and a mass spectrometer (MS) gas channel for C5–C12 hydrocarbons, halo hydrocarbons and oxygenated VOCs. A complete working cycle of the system was one hour and included five steps: sample collection, freeze-trapping, thermal desorption, GC-FID/MS analysis, heating and anti-blowing purification. The sample collection time was 5 min, the sampling flow was 60 ml min⁻¹, and the anti-blowing flow was 200 ml min⁻¹. The calibration of over 100 VOCs was performed using mixed standard gas before and after the campaign. Detection limits for most compounds were near 5pptv. More description of this instrument can be found in Wang et al. (2014).”

7. Spell out “VOCs” in the abstract, and show slopes in Figure 2(b).

REPLY:

We have amended it and the slopes were given in Table S1.

References

Wang, M.; Zeng, L.; Lu, S.; Shao, M.; Liu, X.; Yu, X.; Chen, W.; Yuan, B.; Zhang, Q.; Hu, M.; Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, 6, (23), 9424-9434. Analytical Methods, <https://doi.10.1039/C4AY01855A>, 2014.

Report #2

This study used an HR-ToF-AMS to investigate the particulate organic nitrate (pON) in Shenzhen, China over one-year measurement. The authors applied two methods (i.e., $\text{NO}^+/\text{NO}_2^+$ ratio and PMF analysis including NO^+ and NO_2^+ ions) to estimate the concentration of pON nitrate. The fractions of pON in total nitrate in different seasons are reported. Further, it is concluded that biogenic VOCs+nitrate radical is the major source of pON, even though the sampling site is located in polluted urban area. The topic is of interest to the community. Overall, the results are clearly presented and consistent with previous studies.

1. My major concern is that this paper is scientifically correct, but not obviously a significant advance in the field. This study mirrored the analysis procedure from previous publications, but did not emphasize the unique contribution to our knowledge on pON. One interesting point to expand discussions on, as the authors briefly discussed, is that pON concentration in this study is similar to that in the southeastern U.S., a region with lower NO_x . A deeper investigation on this comparison may reveal whether the pON formation is VOCs- or NO_x -limited across different regions. It is also helpful to contrast to the pON concentration in Europe [Kjendler-Scharr *et al.*, 2016], where the NO_x is likely comparable to that in this study. In addition, the diurnal variation of pON (i.e., the increase near 3am) is another interesting point to explore.

REPLY:

We have added some description in *Introduction* to address the contribution of this paper on organic nitrates studies in detail. “Ng *et al.* (2017) reviewed the nitrate radical chemistry and the abundance of particulate organic nitrates in the United States and Europe, and further concluded that particulate organic nitrates are formed substantially via $\text{NO}_3 + \text{BVOC}$ chemistry, which plays an important role in SOA formation. Unfortunately, relevant Chinese datasets are scarce yet and not included in this review. This was because (1) the contributions of organic nitrates in SOA and total nitrates in Chinese atmosphere remain poorly understood; (2) the anthropogenic and biogenic precursor emissions in China are largely different from those in the United States and Europe, and thus cannot be easily estimated. To our best knowledge, few studies have investigated the concentrations and formation pathways of particulate organic nitrates in China. Xu *et al.* (2017) estimated the mass concentration of organic nitrogen in Beijing using AMS, but in this study they ignored the contribution of NO_x^+ family, which are the major fragments of organic nitrates.” In addition, we added section 3.3 to discuss the size distribution characteristics of organic nitrates. We used the $\text{NO}^+/\text{NO}_2^+$ ratio as an indicator to investigate the size distribution characteristics of organic nitrates. It is clearly found that the $\text{NO}^+/\text{NO}_2^+$ ratio generally increases towards smaller size in spring, summer, and autumn, while the $\text{NO}^+/\text{NO}_2^+$ ratio keep similar to the value of $R_{\text{NH}_4\text{NO}_3}$ throughout the full size range in winter. It should also be noted that in spring, summer, and autumn, the lowest values of $\text{NO}^+/\text{NO}_2^+$ ratio at $> 1\mu\text{m}$ are also approximate to the seasonal values of $R_{\text{NH}_4\text{NO}_3}$. These characteristics clearly indicate that organic nitrates occurred mostly in fresh particles with smaller sizes, and thus should be mainly of local origin. The diurnal trends of size distributions of $\text{NO}^+/\text{NO}_2^+$ ratio show higher values in small size range at night comparing that in the day in spring, summer and autumn, suggesting a dominant nighttime origin of organic nitrates. Furthermore, according to the calculated production potential of organic nitrates from a $\text{NO}_3 + \text{VOC}$ reaction and SOA yields in section 3.4, we find that besides the BVOCs species, anthropogenic styrene plays an important role in nighttime particulate organic nitrate formation in urban atmosphere in China. Finally, we compared this study with other particulate organic nitrate studies in section 3.5 and the results show that the formation of particulate organic nitrate is more likely

NO_x-control than BVOCs-control and high NO_x emissions could promote biogenic SOA formation at night. The detailed reply regarding the diurnal variation of pON can be found in Question 5 below.

2. The diurnal trends of PMF factors should be included. Please add the diurnal trend of LO-OOA in Figure 5.

REPLY:

We have added the diurnal trend of LO-OOA in Figure 6.

3. Cautions are required when using the method in section 3.3 to estimate the pON formation. To investigate the sources of measured pON, what is really required is the reacted amount of VOCs. The calculated pON, on the other hand, is based on the measured VOCs existing in the atmosphere. Thus, the calculated pON is not directly comparable to measured pON. This analysis can only serve as a ballpark estimation. The conclusion that biogenic VOCs + NO₃ is the major source of pON should be toned down.

REPLY:

We have made a lot of modification in the manuscript and tone down the conclusion that biogenic VOCs + NO₃ is the major source of pON. According to the section 3.2 and 3.3, we can conclude the nighttime NO₃+VOCs reactions serve as an important source for organic nitrates, and in section 3.4, further investigation on potential pathway for nighttime particulate organic nitrates formation was performed. We used the NO₃ loss rate at night, which can be calculated as $K_i \cdot [VOC_i]$ in Eq. (9), to roughly judge the production potential of organic nitrates from a NO₃+VOC reaction:

$$[\text{Production Potential}]_{\text{NO}_3+\text{VOC}_i} = K_i \cdot [VOC_i] \cdot [NO_3] \quad (9)$$

Where K_i represents the reaction rate coefficient for NO₃ radical and a VOC, $[VOC_i]$ is the concentration of the specific VOC and $[NO_3]$ is the concentration of NO₃ radical. According to the distribution of production potential, five biogenic VOCs (BVOCs) (i.e., α -pinene, limonene, camphene, β -pinene and isoprene) and one anthropogenic VOC (styrene) were identified as notable VOC precursors with high production potential, while the sum of production potential from the other VOCs was negligible. In addition, the estimated SOA production from NO₃+VOCs reactions using SOA mass yields shows that α -pinene, limonene and styrene were the key VOC precursors for nighttime organic nitrates formation in urban atmosphere in Shenzhen. This result highlights the key role of this anthropogenic VOC precursor in nighttime particulate organic nitrate formation in urban atmosphere in China, and relevant smog chamber studies for anthropogenic VOCs+NO₃ reactions are needed to support parameterization in modeling.

4. Figure 3. What is “NO_{3,org1_ratio”?}

REPLY:

The NO₃ estimation based on NO⁺/NO₂⁺ ratio method using the upper bounds of R_{ON}/R_{NH₄NO₃} is denoted as NO_{3,org1_ratio}, Please see the footnote in Table 2.). In order to see it clearly, we changed it to “NO_{3_org_ratio_1” in the text.}

5. Figure 5 and Line 209. What causes the pON increase near 3am?

REPLY:

We have added the detailed discussion in section 3.4 to explain the pON increase near 3am. “Figure 6 shows the average nighttime variations of BC, LO-OOA, NO_{3,org_ratio_1}, NO_{3,org_PMF} and production

potential of the six notable VOCs identified during the spring campaign. The concentrations of BC and LO-OOA generally decreased slowly after sunset till sunshine due to the combined effect of both the planetary boundary layer variation and traffic emissions, while particulate organic nitrates showed a different trend with two clear growth processes (19:00-22:00 and 3:00-6:00) at night, suggesting their unique sources. In contrast, the production potentials of the six notable VOCs with NO₃ had two roughly similar increases at the same periods as those of particulate organic nitrates, which supported the key role of NO₃+VOCs reactions for nighttime organic nitrate formation.”

6. Line 31. Please add reference to support this statement. Replace “recognize” with “recognized”.

REPLY:

We have added the reference and replaced “recognized” with “recognize”.

7. Line 99. NO, NO₂, NO₃, and NO₃, ON need superscript “+”. This should be revised throughout the manuscript.

REPLY:

We have corrected it.

8. Line 131. How is the SA calculated?

REPLY:

SA is calculated from the size-resolved particle number concentrations assuming spherical particles measured by a scanning mobility particle sizer (SMPS) (TSI Inc., USA, 3775 CPC and TSI Inc. 3080 DMA). And 220 μm² cm⁻³ is actually under dry conditions, the ambient (wet) aerosol SA is 475 μm² cm⁻³ by using the hygroscopic growth factor in Liu et al. (2010). We have added and corrected the related description in Text S1 in the supplementary. We have added this description in Text S1 in the supplementary.

9. Line 149. As a sanity check, are NO⁺ and NO₂⁺ exclusively apportioned into NIA in winter?

REPLY:

The NO_x⁺ method is not suitable to estimate the mass concentration of organic nitrates due to more than 50% ambient NO⁺/NO₂⁺ values smaller than R_{NH₄NO₃}. Thus, we use PMF method to estimate the organic nitrates and the result are shown in the figure (added to FigureS6) below. A majority NO⁺ and NO₂⁺ ions are apportioned into NIA and the contribution of organic nitrates in total nitrates is about 4%. We have added some description in Section 3.1. ”It should be noted that the small difference between the average R_{obs} and R_{NH₄NO₃} in winter leads to a large portion of negative data using the NO⁺/NO₂⁺ ratio method (Table 1), and the result from the PMF method shows the contribution of organic nitrates in total nitrates is only 4.2% in winter (Figure S6), suggesting a negligible contribution of organic nitrates. Thus, we will only discuss organic nitrate estimation results in spring, summer and autumn.”

10. Line 197. It should be section 2.4, instead of 2.3.

REPLY:

We have corrected it.

References

- Liu, X.G., Zhang, Y.H., Wen, M.T., Wang, J.L., Jung, J.S., Chang, S.-Y., Hu, M., Zeng, L.M. and Kim, Y.J.: A closure study of aerosol hygroscopic growth factor during the 2006 Pearl River Delta Campaign. *Adv. Atmos. Sci.* 27, 947–956, 2010.
- Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, 17, 2103-2162, <https://doi.org/10.5194/acp-17-2103-2017>, 2017.
- Xu, W., Sun, Y., Wang, Q., Du, W., Zhao, J., Ge, X., Han, T., Zhang, Y., Zhou, W., Li, J., Fu, P., Wang, Z., Worsnop, D.R.: Seasonal Characterization of Organic Nitrogen in Atmospheric Aerosols Using High Resolution Aerosol Mass Spectrometry in Beijing, China. *ACS Earth Sp. Chem.* 1, 673–682. <https://doi.org/10.1021/acsearthspacechem.7b00106>, 2017.

Report #3

1. Some of the methods are reasonably well described and follow on methods developed and described in the literature, although additional details are needed for several aspects. However, overall nothing new seems to be offered in terms of method development nor advancement in understanding of atmospheric science (which Ref #2 recognized as well). The conclusions the authors arrive at are not surprising and have been previously published. Thus, it largely comes across as a data report, where measurements were made, previous methods are applied and the scientific analysis/interpretation is conducted in this case with less rigor than prior publications. Thus the value to the literature essentially amounts a report of measurements and simple calculations conducted in a different location. The results section consists of only a few figures and ~2 pages of 1.5-space text, a reflection of the thin-ness of new content. Importantly, some conclusions are overstated with insufficient evidence or even faulty logic presented, so in present form is in fact misleading.

REPLY:

We have done lots of modification and corrected the mistakes based on each comment to offer more solid and convincing conclusions. Please see the details as below.

2. Text was generally readable but there are lots of grammar errors. A few pervasive errors include the addition or omission of articles (e.g. “the”, “a”) or plurality when not needed or needed. Reviewing by native English speaker BEFORE submission is recommended. Much of the text is written clearly, while in many cases insufficient details were provided to understand exactly what was done.

REPLY:

We have corrected them in the text.

3. I agree with Referee 1 that there is not sufficient detail provided on the PMF (both justification of solutions, as well as summary of results). This should also include the NO_x^+ ratios for each factor, discussion of the meaning and/or possible biases related to the HOA factor containing nitrates and the inorganic factor having a different NO_x^+ ratios than calibrations. Correlations of organic nitrates vs all of the factors should be presented (ideally a version of Fig. 3 for each factor in the supplementary). Simply showing that organic nitrates correlate with LO-OOA does not make a convincing case that they are related since often all concentrations largely increase and decrease at a given sampling site together. Additionally diurnal cycles should be shown for all factors

REPLY:

The key diagnostic plots of chosen factors and the mass spectrum profiles of 3 to 5 factors for spring, summer and autumn are shown in Figure S2 to S4 (in the supplementary). The NO_x^+ ratios for NIAs are given in section 3.1 in the manuscript (2.93 for spring, 3.53 for summer and 3.54 for autumn), and NO_x^+ ratios for OA factors are shown in Table S2 in the supplement. And the uncertainties of NO^+ and NO_2^+ in OA factors across different f_{peak} values are also shown in Table S2. Correlations of organic nitrates vs. all of factors are presented in Figure S7 to S9 in the supplementary. The diurnal cycles for OA factors in each season are shown in Figure S5 and it shows that all OA factors have distinctive variation trends in different seasons.

Table S2. The values of NO^+ and NO_2^+ in OA factors when f_{peak} is 0 and the uncertainties of NO^+ and NO_2^+ in OA factors across different f_{peak} values (from -1.0 to 1.0)

			HOA	LO-OOA	MO-OOA
Spring	NO^+	$f_{\text{peak}}=0$	1.3×10^{-2}	1.4×10^{-2}	9.8×10^{-3}

		uncertainty	3.4%	1.4%	6.8%
	NO ₂ ⁺	fpeak=0	1.2*10 ⁻²	1.5*10 ⁻⁴	3.0*10 ⁻⁸
		uncertainty	8.5%	3.8%	4.3%
Summer	NO ⁺	fpeak=0	1.5*10 ⁻²	1.0*10 ⁻²	1.2*10 ⁻²
		uncertainty	1.5%	5.1%	3.0%
	NO ₂ ⁺	fpeak=0	1.47*10 ⁻⁶	6.7*10 ⁻⁴	1.8*10 ⁻³
		uncertainty	4.8%	6.9%	4.0%
Autumn	NO ⁺	fpeak=0	1.1*10 ⁻²	3.1*10 ⁻²	1.0*10 ⁻²
		uncertainty	4.5%	0.5%	1.2%
	NO ₂ ⁺	fpeak=0	7.0*10 ⁻⁸	9.8*10 ⁻⁸	2.8*10 ⁻⁷
		uncertainty	0.6%	1.9%	1.2%

4. Evidence is thin to install confidence that the methods for separation of organic nitrates is producing meaningful separation. While the methods have been applied before in other papers, the methods may be prone to substantial error and potentially bias when organic nitrates are a small fraction of total nitrate, as is the case here for all seasons except summertime. Diurnal cycles of the total nitrate and inorganic and organic nitrates calculated by the different methods would be helpful. Showing correlations of both the organic AND inorganic nitrate with the PMF factors may also be informative.

REPLY:

We have added more discussion to support that the separation between organic and inorganic nitrates is meaningful in section 3.1. Diurnal cycles of total nitrate and inorganic and organic nitrates calculated by the different methods are given in Figure 2b in the manuscript. The inorganic nitrate (NO_{3_inorg*}) obtained by subtracting NO_{3_org_ratio_1} from total measured nitrates also correlated well with the inorganic nitrate estimated using the PMF method (R=0.92 for spring, 0.87 for summer and 0.86 for autumn). Furthermore, the diurnal trends of organic nitrates obtained by the two methods were also similar in each season, generally with lower concentrations in the daytime and higher concentrations at night, while they were distinctive from those of inorganic nitrate (Figure 2b), supporting that organic nitrates had been well separated from inorganic nitrate in this study.

5. The NO₃ radical concentration calculation is bewildering. The loss in the steady-state calculation is based on only α -pinene and limonene with no justification for this choice (Section 2.4, Table S1). Then the concentrations are neither reported nor shown, it is unclear if they are calculated for only one fixed value or as a time series. What season was this done for? What season does Table S1 pertain to? This is a critical calculation since the conclusion that NO₃ dominates over O₃ for BVOC losses and for the SOA modeling. The calculation that NO₃ accounts for nearly 100% of the BVOC loss at night is a little surprising and also from which major conclusions of this manuscript flow. For the Xu et al. (2015b) study (referenced in the manuscript), they calculated that only 20%/38% of the reacted α/β -pinene was with NO₃ at night. Might the NO₃ calculated here be biased high since only two VOC losses were considered?

REPLY:

Since on-line VOCs measurement was only performed during the spring campaign, the following theoretical analysis of NO₃+VOCs reactions will be just applied to the spring case. Typical nighttime VOC concentrations, their reaction rate coefficients for reacting with NO₃ radical are listed in Table S3. Comparing to five biogenic VOCs (i.e., α -pinene, isoprene, β -pinene, limonene and

camphene)accounting for 99% NO₃ loss in Table S3 in Xu et al. (2015b), one anthropogenic VOC, styrene made the third largest contribution to NO₃ loss, which should not be ignored in the related SOA estimation analysis. But α -pinene and limonene do contribute to nearly 90% of NO₃ loss in our case due to their much higher nighttime concentrations than other BVOCs and rapid reaction rates with NO₃ radical. The nighttime estimated concentration of NO₃ radical in this study is 1.24±0.76pptv, which is about 15 times higher than the nighttime concentration of NO₃ radicals (0.076 pptv) reported in Xu et al. (2015b), this is because that the value of [NO₂]×[O₃] (20ppbv×6.8ppbv) in this case is just about 15 times higher than that value (0.54ppbv for NO₂ and 21 ppbv for O₃) in Xu et al. (2015b). Thus, the nighttime concentration of NO₃ and O₃ is 1.24 pptv and 6.8ppbv, respectively, in this study, while in Xu et al. (2015b), the nighttime concentration of NO₃ and O₃ is 0.076 pptv and 21ppbv, respectively. The much higher NO₃ level and lower O₃ level in this study leads to almost all VOCs reacting with NO₃ radical over O₃ at night.

Table S3. The average campaign concentrations of VOCs measured with an automated in situ gas-chromatography mass spectrometer (GC-MS), their reaction rate coefficients for reacting with NO₃ radical and the production potential from NO₃+VOC in spring.

VOC species	Mean concentration (ppbv)	Rate Coefficient	Production potential (pptv/s)
1,2,3-Trimethylbenzene	0.057	1.90E-15	3.72E-06
1,2,4-Trimethylbenzene	0.177	1.80E-15	1.10E-05
1,3,5-Trimethylbenzene	0.051	8.80E-16	1.54E-06
1,3-Butadiene	0.052	1.00E-13	1.79E-04
1-Butene	0.415	1.32E-14	1.89E-04
1-Hexene	0.022	1.20E-14	9.06E-06
1-Pentene	0.022	1.20E-14	9.27E-06
2,2,4-Trimethylpentane	0.068	9.00E-17	2.10E-07
2,2-Dimethylbutane	0.199	4.40E-16	3.01E-06
2,3,4-Trimethylpentane	0.022	1.90E-16	1.44E-07
2,3-Dimethylbutane	0.299	4.40E-16	4.54E-06
2,3-Dimethylpentane	0.293	1.50E-16	1.51E-06
2-Methylheptane	0.034	1.90E-16	2.20E-07
2-Methylhexane	0.514	1.50E-16	2.66E-06
2-Methylpentane	1.582	1.80E-16	9.81E-06
3-Methylheptane	0.027	1.90E-16	1.74E-07
3-Methylhexane	0.534	1.50E-16	2.76E-06
3-Methylpentane	1.411	2.20E-16	1.07E-05
Acetaldehyde	1.249	2.70E-15	1.16E-04
Acetylene	0.941	5.10E-17	1.65E-06
Acrolein	0.042	3.30E-15	4.73E-06
Benzene	0.599	3.00E-17	6.19E-07
cis-2-Pentene	0.005	3.70E-13	6.57E-05
Cyclohexane	1.164	1.40E-16	5.61E-06
Cyclopentane	0.416	1.40E-16	2.00E-06
Ethane	1.567	1.00E-17	5.40E-07

Ethylbenzene	0.563	1.20E-16	2.34E-06
Isoprene	0.032	6.96E-13	7.76E-04
m/p-Xylene	0.602	3.80E-16	7.88E-06
Methacrolein	0.012	3.40E-15	1.44E-06
Methylcyclohexane	0.172	1.40E-16	8.29E-07
Methylcyclopentane	0.673	1.40E-16	3.25E-06
n-Butanal	0.044	1.10E-14	1.68E-05
n-Butane	1.848	4.60E-17	2.93E-06
n-Decane	0.060	2.80E-16	5.74E-07
n-Heptane	0.351	1.50E-16	1.81E-06
n-Hexane	1.916	1.10E-16	7.25E-06
n-Nonane	0.033	2.30E-16	2.59E-07
n-Pentanal	0.128	1.50E-14	6.61E-05
n-Pentane	0.593	8.70E-17	1.78E-06
n-Propylbenzene	0.029	6.00E-16	6.01E-07
Octane	0.064	1.90E-16	4.17E-07
o-Xylene	0.464	3.80E-16	6.06E-06
Propanal	0.144	6.31E-15	3.12E-05
Propane	3.678	7.00E-17	8.86E-06
Propene	0.477	9.54E-15	1.57E-04
Styrene	0.194	1.50E-12	1.00E-02
Toluene	3.120	7.00E-17	7.52E-06
alpha-Piene	0.391	6.21E-12	8.36E-02
beta-Piene	0.013	2.51E-12	1.10E-03
Camphene	0.276	6.20E-13	5.91E-03
Limonene	0.137	1.22E-11	5.77E-02

6. As Referee 2 points out regarding the analysis in Sect. 3.3 on the estimation of pON formation, the sources of measured pON depend on reacted VOCs, not on the amount of VOCs present in the atmosphere. The authors seem to be equating the two. Essentially the authors appear to be calculating the relative amounts of production expected if the sampled airmass was allowed to react to completion with no further emissions. This does not equate to the regional productions since it would systematically underweight more reactive compounds and the two metrics may only be loosely connected. In general, Section 3.3. is highly undersupported and speculative considering the evidence shown. It is not clear what the modeled SOA (blue trace in Fig. 5) even is. Is that the amount produced per unit time from the model? It cannot be the cumulative production since it increases and decreases (and the model does not have dynamics, dilution, mixing, etc.). In any case, the features of organic nitrates and the ambiguous modeled SOA don't match all that well. Also, it seems likely that the day-to-day variability may be of similar or larger magnitude to the variations in the average diurnal cycle (variability bars such as standard deviations would be helpful here). Potentially the very rough similarities may be an averaging artifact? Thus, the diurnal cycle should be supplemented additional evidence, such as time series of the relevant metrics and correlations plots to make a convincing case that the model may be indeed be representing the key processes and explain the measurements. Also, inclusion of inorganic nitrates together with the organic nitrates (diurnal cycle and other relevant plots), would help make a stronger case that the

separation of the organic nitrates is meaningful and robust. Based on this section, the authors conclude (as stated in the abstract) that BVOC + NO₃ at night are the dominant formation pathway of organic nitrates in the polluted atmosphere. This simply has not been demonstrated. Moreover, it appears that the authors are equating boundary layer concentration with overall regional production importance. As the authors note in Sect. 3.3, the boundary layer is expected to be lower during nighttime. Consequently, the concentrations observed represent a smaller volume of air, so equating lower concentrations during daytime with lower overall (column integrated, regional) importance is faulty logic. BL-effects were not considered here nor production during the daytime modeled, thus no conclusions beyond nighttime boundary layer concentrations and production should be drawn based on this analysis. Yet, this manuscript seems to do just that – an example of the vastly overstated implications claimed.

REPLY:

We have accepted this comment and changed the analysis in section 3.4 significantly. First, we used the NO₃ loss rate at night, which can be calculated as $K_i \cdot [VOC_i]$ in Eq. (9), to roughly judge the production potential of organic nitrates from a NO₃+VOC reaction:

$$[\text{Production Potential}]_{\text{NO}_3+\text{VOC}_i} = K_i \cdot [VOC_i] \cdot [NO_3] \quad (9)$$

Where K_i represents the reaction rate coefficient for NO₃ radical and a VOC, $[VOC_i]$ is the concentration of the specific VOC and $[NO_3]$ is the concentration of NO₃ radical. In the spring campaign, the diurnal variations of NO₂, O₃ and estimated NO₃ radical concentrations are shown in Figure S10 (with standard deviations). It was found that the high concentrations of NO₂ (19.93±2.31 ppb) at night led to high yield of NO₃ radical (1.24±0.76 ppt) in Shenzhen.

According to the distribution of production potential, five biogenic VOCs (BVOCs) (i.e., α -pinene, limonene, camphene, β -pinene and isoprene) and one anthropogenic VOC (styrene) were identified as notable VOC precursors with high production potential, while the sum of production potential from the other VOCs was negligible as shown in Figure 5b.

In addition, Figure 6 shows the average nighttime variations of BC, LO-OOA, NO_{3,org_ratio_1}, NO_{3,org_PMF} and production potential of the six notable VOCs identified during the spring campaign. The concentrations of BC and LO-OOA generally decreased slowly after sunset till sunrise due to the combined effect of both the planetary boundary layer variation and traffic emissions, while particulate organic nitrates showed a different trend with two clear growth processes (19:00-22:00 and 3:00-6:00) at night, suggesting their unique sources. In contrast, the production potentials of the six notable VOCs with NO₃ had two roughly similar increases at the same periods as those of particulate organic nitrates, which supported the key role of NO₃+VOCs reactions for nighttime organic nitrate formation.

Finally, based on the production potential evaluation above, we further estimated roughly the nighttime SOA bulk yield of NO₃+the six notable VOC precursors. And the estimated SOA production from NO₃+VOCs reactions using SOA mass yields in the literature was 0-0.33 $\mu\text{g m}^{-3}$ for α -pinene, 0.09-1.28 $\mu\text{g m}^{-3}$ for limonene, 0.24 $\mu\text{g m}^{-3}$ for styrene, 0.004-0.06 $\mu\text{g m}^{-3}$ for β -pinene and 0.002-0.02 $\mu\text{g m}^{-3}$ for isoprene. The SOA yield from camphene is currently unknown in the literature. It is seen that the average observed nighttime concentration of particulate organic nitrates during the spring campaign (0.39-0.83 $\mu\text{g m}^{-3}$, converting NO_{3,org_ratio_1}, NO_{3,org_PMF} in Figure 6 into organic nitrates assuming the average molecular weight of organic nitrates of 200 to 300 g mol^{-1}) was well within the estimated SOA concentration ranges produced by α -pinene, limonene and styrene, indicating that these three VOCs were the key VOC precursors in urban atmosphere in Shenzhen. Considering both the production potentials and SOA yields, the contributions of β -pinene and isoprene to nighttime formation of particulate organic nitrates could be negligible. Besides the BVOCs species, this study

highlights the key role of anthropogenic styrene in nighttime particulate organic nitrate formation in urban atmosphere in China, and relevant smog chamber studies for anthropogenic VOCs+NO₃ reactions are needed to support parameterization in modeling.

7. Kiendler Scharr et al. (2016), Ng et al. (2017), Xu et al. (2015a, 2015b) and others have reported that at many sites throughout the US and Europe, including polluted urban areas, organic nitrates can be substantial fractions of aerosol nitrates and NO₃+BVOC reactions can be an important source. The manuscript fails to make a case for what new information this study from one polluted city provides and how it would add to the body of atmospheric literature.

REPLY:

In the revised manuscript, we have proposed several new information: 1. adding some description in *Introduction* to address the contribution of this paper on organic nitrates studies in detail. “Ng et al. (2017) reviewed the nitrate radical chemistry and the abundance of particulate organic nitrates in the United States and Europe, and further concluded that particulate organic nitrates are formed substantially via NO₃+BVOC chemistry, which plays an important role in SOA formation. Unfortunately, relevant Chinese datasets are scarce yet and not included in this review. This was because (1) the contributions of organic nitrates in SOA and total nitrates in Chinese atmosphere remain poorly understood; (2) the anthropogenic and biogenic precursor emissions in China are largely different from those in the United States and Europe, and thus cannot be easily estimated. To our best knowledge, few studies have investigated the concentrations and formation pathways of particulate organic nitrates in China. Xu et al. (2017) estimated the mass concentration of organic nitrogen in Beijing using AMS, but in this study they ignored the contribution of NO_x⁺ family, which are the major fragments of organic nitrates”; 2. in section 3.3, we discussed the size distribution characteristics of organic nitrates. We used the NO⁺/NO₂⁺ ratio as an indicator to investigate the size distribution characteristics of organic nitrates. It is clearly found that the NO⁺/NO₂⁺ ratio generally increases towards smaller size in spring, summer, and autumn, while the NO⁺/NO₂⁺ ratio keep similar to the value of R_{NH₄NO₃} throughout the full size range in winter. It should also be noted that in spring, summer, and autumn, the lowest values of NO⁺/NO₂⁺ ratio at > 1 μm are also approximate to the seasonal values of R_{NH₄NO₃}. These characteristics clearly indicate that organic nitrates occurred mostly in fresh particles with smaller sizes, and thus should be mainly of local origin. The diurnal trends of size distributions of NO⁺/NO₂⁺ ratio show higher values in small size range at night comparing that in the day in spring, summer and autumn, suggesting a dominant nighttime origin of organic nitrates; 3. according to the analysis in section 3.4, we can find that besides the BVOCs species, anthropogenic styrene plays an important role in nighttime particulate organic nitrate formation in urban atmosphere in China; 4. we compared this study with other particulate organic nitrate studies in section 3.5 and the results show that the formation of particulate organic nitrate is more likely NO_x-control than BVOCs-control and high NO_x emissions could promote biogenic SOA formation at night.

8. The authors broadly refer to their results as pertaining to “South China” which is a large and diverse areas. Unless there is evidence that this site is generally representative of that geographic area, text and conclusions should be limited to just this one urban area. This is an example of overselling the story without providing the supporting analysis.

REPLY:

We have toned down this conclusion and only addressed this case as a typical urban site in South China.

9. L32-3: “Play a larger role” for what? Reference?

REPLY:

We have added the related references.

10. L40-41: The Rollins et al. (2002) paper demonstrated the application of the aerosol-only organic nitrate measurement. The technique for total nitrates was developed and demonstrated a decade earlier (Day et al., 2002).

REPLY:

We have corrected it.

11. L41: “measured” would be better than “obtained”

REPLY:

We have corrected it.

12. L66: “to obtain more representative samples” seems vague. Clarify.

REPLY:

We have deleted “more representative”.

13. L74: “literatures” should not be plural.

REPLY:

We have corrected it.

14. L82-4: state if the RIE of ammonium was calibrated or assumed.

REPLY:

RIE of ammonium was assumed and we have added the statement in section 2.2.1: The relative ionization efficiencies (RIEs) used in the study were 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, 1.4 for organics, and 4.0 for ammonium (Jimenez et al., 2003).

15. L105-6: Site Xu et al. (2015a) since isn't this is exactly what they did?

REPLY:

We have added this reference.

16. L107-8: Stating that negative calculated organic nitrates means that concentrations must be low is not very analytically sound. E.g., can't this just mean the method isn't working well or there are large uncertainties due a variety of possible factors? Please revise to be more precise and inclusive of the possible causes.

REPLY:

We have modified this statement and provided more detailed and precise discussion in section 3.1.

17. L127: Fry et al. 2013 is not the proper reference for heterogeneous N₂O₅ reaction with aerosol. They just performed the calculation.

REPLY:

We have replaced the right literature (Dentener and Crutzen, 1993) with it in the manuscript.

18. L130: Units for velocity are wrong.

REPLY:

We have corrected it.

19. L131: Where did the aerosol surface area concentration for the modeling come from? It does not appear that an aerosol sizing instrument was used in the study.

REPLY:

SA is calculated from the size-resolved particle number concentrations assuming spherical particles measured by a scanning mobility particle sizer (SMPS) (TSI Inc., USA, 3775 CPC and TSI Inc. 3080 DMA). And $220 \mu\text{m}^2 \text{cm}^{-3}$ is actually under dry conditions, the ambient (wet) aerosol SA is $475 \mu\text{m}^2 \text{cm}^{-3}$ by using the hygroscopic growth factor in Liu et al. (2010). We have added and corrected the related description in section 2.2.2 and Text S1.

20. L133-135: Why do the authors include the calculation of the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ gas-phase reaction? The lifetime is 500 years!

REPLY:

We have corrected the value of daily maximum $[\text{H}_2\text{O}]$ ($5.5 \times 10^{17} \text{molecule cm}^{-3}$) and the calculated value of N_2O_5 lifetime with respect to the reaction with H_2O (1470 s).

21. L145: “6.82 and 19.38 ppb”: Too many significant figures. It would be more useful to report averages and standard deviations.

REPLY:

The concentrations of NO_2 and O_3 with their standard deviations are shown in Figure S10 in the supplementary.

22. L159: "may explain" instead? Without any quantitative assessment, it is not justified to say that it does explain it.

REPLY:

We have replace “explain” with “may explain”.

23. L165: “adequate” for what or by what measure? Too vague – needs clarification.

REPLY:

We have replace “adequate” with “good”.

24. L173-4: Statement points out that the organic nitrate is similar to SE US “even though” BC and NO_x are higher in S. China. How is this meaningful? If terpenes are dominantly reacting with NO_3 then the production would be largely controlled by the amount of terpenes present - which appear to be quite modest at this location. Statements like this need more context/discussion to be meaningful. Or remove such comparisons if not informative and making a clear point.

REPLY:

We have deleted this statement.

25. L180: “both organic spectra” should instead read “both OOA spectra”?

REPLY:

We have corrected it

26. L180-2: Unclear. Is this referring to running PMF with and without the NO_x ions? Please clarify.

REPLY:

We have clarified this statement: The mass spectrum profiles and diurnal patterns of each OA factor using PMF based on OA spectra only in spring, summer and autumn are shown in Figure S2-S5.

27. 182-3: Please report these correlations (table?) and show the correlations in the SI (i.e. duplicate Fig. 3 for MO-OOA and HOA).

REPLY:

We have added Figure S7-S9 to show the correlations between organic nitrates with HOA and MO-OOA.

28. L196-198: Limonene and α -pinene shown to account for 90% of NO₃ loss? Assuming the authors are referring to Sect. 2.4 (not 2.3 as written), this is not shown there – or anywhere else. Only 2 compounds were considered according to the text (which references Table S1).

REPLY:

We have added the related information in section 3.4 and table S3.

29. Table 1: “NO₃-“: Is that inorganic nitrate or total nitrate? If total, then the ionic denotation isn’t appropriate.

REPLY:

We have replace “NO₃-” with “total NO₃-”.

30. Figure 5: beta-pinene misspelled.

REPLY:

We have corrected it.

31. Table S1: α -pinene SOA yield: Why was this single reference value picked, considering that there is a substantial range reported in the literature? See Table 2 in Ng et al. (2017). A range would seem more appropriate here unless the authors justify why this particular one is more appropriate for this study.

REPLY:

We have added more references of SOA yield, please see Table 3 in the manuscript.

References

Liu, X.G., Zhang, Y.H., Wen, M.T., Wang, J.L., Jung, J.S., Chang, S.-Y., Hu, M., Zeng, L.M. and Kim, Y.J.: A closure study of aerosol hygroscopic growth factor during the 2006 Pearl River Delta Campaign. *Adv. Atmos. Sci.* 27, 947–956, 2010.

A list of all relevant changes

1. Line 14-16: Changed to “Based on cross validation of two different data processing methods, organic nitrates were effectively quantified to contribute a notable fraction of organic aerosol (OA): 9-21% in spring, 11-25% in summer and 9-20% in autumn; while organic nitrates were found to little exist in winter.”
2. Line 18-26: Added “The size distribution of organic nitrates also implied that organic nitrates were mainly a local product and could have strong removal during air mass transport. Furthermore, theoretical calculations of nighttime SOA production of NO₃ reactions with volatile organic compounds (VOCs) measured during the spring campaign were performed, resulting in two biogenic VOCs (α -pinene and limonene) and one anthropogenic VOC (styrene) identified as the key VOC precursors for particulate organic nitrates. The comparison with similar studies in the literature implied that nighttime particulate organic nitrates formation could be NO_x-controlled. This study proposes that different from the previous cases in the United States and Europe, modeling nighttime particulate organic nitrate formation should incorporate not only biogenic VOCs but also anthropogenic VOCs with high SOA yield for urban air pollution in China, which call for relevant smog chamber studies to support in future.”
3. Line 35: Changed “recognize” to “recognized” and added references“(Teng et al., 2015, 2017)”.
4. Line 48-56: Added “Ng et al. (2017) reviewed the nitrate radical chemistry and the abundance of particulate organic nitrates in the United States and Europe, and further concluded that particulate organic nitrates are formed substantially via NO₃+BVOC chemistry, which plays an important role in SOA formation. Unfortunately, relevant Chinese datasets are scarce yet and not included in this review. This was because (1) the contributions of organic nitrates in SOA and total nitrates in Chinese atmosphere remain poorly understood; (2) the anthropogenic and biogenic precursor emissions in China are largely different from those in the United States and Europe, and thus cannot be easily estimated. To our best knowledge, few studies have investigated the concentrations and formation pathways of particulate organic nitrates in China. Xu et al. (2017) estimated the mass concentration of organic nitrogen in Beijing using AMS, but in this study they ignored the contribution of NO_x+ family, which are the major fragments of organic nitrates.”
5. Line 69: Deleted “more representative”.

6. Table1: Changed " NO_3^- " to "Total NO_3^- ".
7. Line 83-84: Added "The relative ionization efficiencies (RIEs) used in this study were 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, 1.4 for organics and 4.0 for ammonium, respectively (Jimenez et al., 2003)."
8. Line 92-94: Added "An SMPS system (3775 CPC and 3080 DMA, TSI Inc.) was used to obtain the particle number size distribution in 15–615 nm (mobility diameter) with a time resolution of 5 min."
9. Line 95-103: Added "In the spring campaign, ambient VOC concentrations were also measured using an on-line VOC monitoring system (TH-300B, Tianhong Corp.), including an ultralow-temperature preconcentration cold trap and an automated in-situ gas chromatograph (Agilent 7820A) equipped with a mass spectrometer (Agilent 5977E). The system had both a flame ionization detector (FID) gas channel for C₂–C₅ hydrocarbons and a mass spectrometer (MS) gas channel for C₅–C₁₂ hydrocarbons, halohydrocarbons and oxygenated VOCs. A complete working cycle of the system was one hour and included five steps: sample collection, freeze-trapping, thermal desorption, GC-FID/MS analysis, heating and anti-blowing purification. The sample collection time was 5 min, the sampling flow was 60 ml min⁻¹, and the anti-blowing flow was 200 ml min⁻¹. The calibration of over 100 VOCs was performed using mixed standard gas before and after the campaign. Detection limits for most compounds were near 5 pptv. More description of this instrument can be found in Wang et al. (2014)."
10. Line 108: Corrected to " NO_2^+ " and " NO^+ ".
11. Line 114-117: Added "In spring, the average $R_{\text{NH}_4\text{NO}_3}$ was 2.66 for the first IE calibration and 2.94 for the second one; in summer, the average $R_{\text{NH}_4\text{NO}}$ was 3.05 and 3.34 for the first and second IE calibrations, respectively; in autumn, the average $R_{\text{NH}_4\text{NO}_3}$ was 3.33 and 3.31 for the first and second IE calibrations, respectively; in winter, the average $R_{\text{NH}_4\text{NO}_3}$ was 3.45 and 3.51 for the first and second IE calibrations, respectively."
12. Line 138-144: Added "It should be noted that although the 4-factor solution seemed to have a "mixed factor" problem to some extent (Zhu et al., 2018), such as HOA mixed with COA (clear C₃H₃O⁺ in m/z 55 for spring, summer and autumn) (Mohr et al., 2012) and BBOA mixed with LO-OOA (clear m/z 60 and 73 signals in LO-OOA in autumn) (Cubison et al., 2011), running PMF with more factors would produce unexplained factors but little influence the apportion of NO^+ and NO_2^+ ions between organic nitrates and inorganic nitrate (Table S1). In addition, the uncertainties of NO^+ and NO_2^+ ions in the OA

factors across different f_{peak} values (from -1.0 to 1.0) were very small (Table S2). Therefore, the 4-factor solution was finally used for quantifying organic nitrates in spring, summer and autumn.”

13. Put Section 2.4 to Text S1 in the supplementary.

14 Line 150-151: Added “and the result from the PMF method shows the contribution of organic nitrates in total nitrates is only 4.2% in winter (Figure S6), suggesting a negligible contribution of organic nitrates.”

15. Line 158-159: Added “In the PMF method, the mass fractions of organic nitrates in HOA, LO-OOA and MO-OOA were 31%, 49% and 20%, respectively, in spring; 28%, 52% and 20%, respectively, in summer; 30%, 46% and 24%, respectively, in autumn.”

16. Added “Winter” row in Table 2

17. Line 173-178: Added “The inorganic nitrate ($\text{NO}_3_{\text{inorg}}$) obtained by subtracting $\text{NO}_3_{\text{org_ratio}_1}$ from total measured nitrates also correlated well with the inorganic nitrate estimated using the PMF method ($R=0.92$ for spring, 0.87 for summer and 0.86 for autumn). Furthermore, the diurnal trends of organic nitrates obtained by the two methods were also similar in each season, generally with lower concentrations in the daytime and higher concentrations at night, while they were distinctive from those of inorganic nitrate (Figure 2b), supporting that organic nitrates had been well separated from inorganic nitrate in this study.”

18. Added Figure 2(b) diurnal trends of organic nitrates and NO_3_{org} estimated by the different methods (right panel).

19. Line 187-190: Added “Generally, organic nitrates were indeed found better-correlated with LO-OOA ($R=0.69-0.77$ in Figure 3) than with HOA and MO-OOA ($R=0.03-0.69$ in Figures S6-S8), consistent with the fact that the majority of organic nitrates were associated with LO-OOA in the PMF method.”

20. Line 196-214: Added Section 3.3.

21. Line 217-232: Added “ NO_3+VOCs reactions would yield a large mass of gas- and particle-phase organic nitrates (Rollins et al., 2012; Nah et al., 2016; Boyd et al., 2015, 2017; Xu et al., 2015a, 2015b; Lee et al., 2016). We used the NO_3 loss rate at night, which can be calculated as $K_i \cdot [\text{VOC}_i]$ in Eq. (9), to roughly judge the production potential of organic nitrates from a NO_3+VOC reaction:

$$[\text{Production Potential}]_{\text{NO}_3+\text{VOC}_i} = K_i \cdot [\text{VOC}_i] \cdot [\text{NO}_3] \quad (9)$$

Where K_i represents the reaction rate coefficient for NO_3 radical and a VOC, $[\text{VOC}_i]$ is the concentration of the specific VOC and $[\text{NO}_3]$ is the concentration of NO_3 radical. In the spring

campaign, the diurnal variations of NO₂, O₃ and estimated NO₃ radical concentrations are shown in Figure S10. It was found that the high concentrations of NO₂ (19.93±2.31 ppb) at night led to high yield of NO₃ radical (1.24±0.76 ppt) in Shenzhen, as calculated in Text S1, compared to nighttime NO₃ radical concentrations reported in literature in the United States (Rollins et al., 2012; Xu et al., 2015a). Typical measured nighttime VOC concentrations, their reaction rate coefficients with NO₃ radical and the production potentials calculated are listed in Table S3 and shown in Figure 5. These VOCs were considered based on their higher ambient concentrations and availability for reaction kinetics with NO₃ radical. According to the distribution of production potential, five biogenic VOCs (BVOCs) (i.e., α-pinene, limonene, camphene, β-pinene and isoprene) and one anthropogenic VOC (styrene) were identified as notable VOC precursors with high production potential, while the sum of production potential from the other VOCs was negligible as shown in Figure 5b. ”

22. Added Figure 5(b).

23. Line 237-242: Added “The concentrations of BC and LO-OOA generally decreased slowly after sunset till sunrise due to the combined effect of both the planetary boundary layer variation and traffic emissions, while particulate organic nitrates showed a different trend with two clear growth processes (19:00-22:00 and 3:00-6:00) at night, suggesting their unique sources. In contrast, the production potentials of the six notable VOCs with NO₃ had two roughly similar increases at the same periods as those of particulate organic nitrates, which supported the key role of NO₃+VOCs reactions for nighttime organic nitrate formation. ”

24. Line 246-263: Added “Based on the production potential evaluation above, we further explore SOA yield of NO₃+the six notable VOC precursors according to the analysis method of particulate organic nitrate formation in Xu et al. (2015a). Briefly, NO₃ and ozone are two main oxidants for SOA formation from VOCs at night. Based on the concentrations of oxidants and the reaction rate constants for VOCs with NO₃ and ozone, the branching ratio of each VOC that reacts with NO₃ can be estimated as in Eq. (10). By combining the estimated branching ratios and SOA yields from chamber studies (Table 3), SOA from these VOCs can be calculated as in Eq. (11) (Xu et al., 2015a):

$$branching\ ratio_{species\ i+NO_3} = \frac{k_{[species\ i+NO_3] \times [NO_3]}}{k_{[species\ i+NO_3] \times [NO_3]} + k_{[species\ i+O_3] \times [O_3]}} \quad (10)$$

$$[SOA]_{species,oxidant} = [species] \times branching\ ratio_{species,oxidant} \times yield_{species,oxidant} \quad (11)$$

The results in Table 3 show that all the six notable VOC species were prone to react with NO₃ radical

instead of O₃ at night, and the estimated SOA production from NO₃+VOCs reactions using SOA mass yields in the literature was 0-0.33 μg m⁻³ for α-pinene, 0.09-1.28 μg m⁻³ for limonene, 0.24 μg m⁻³ for styrene, 0.004-0.06 μg m⁻³ for β-pinene and 0.002-0.02 μg m⁻³ for isoprene. The SOA yield from camphene is currently unknown in the literature. It is seen that the average observed nighttime concentration of particulate organic nitrates during the spring campaign (0.39-0.83 μg m⁻³, converting NO_{3.org_ratio_1}, NO_{3.org_PMF} in Figure 6 into organic nitrates assuming the average molecular weight of organic nitrates of 200 to 300 g mol⁻¹) was well within the estimated SOA concentration ranges produced by α-pinene, limonene and styrene in Table 3, indicating that these three VOCs were the key VOC precursors in urban atmosphere in Shenzhen. Considering both the production potentials and SOA yields, the contributions of β-pinene and isoprene to nighttime formation of particulate organic nitrates could be negligible. ”

25. Line 274-283: Added “It should be noted that, all previous studies on nighttime organic nitrate formation in the US and Europe focused on mechanisms of NO₃ reactions with BVOCs (Hallquist et al., 1999; Spittler et al., 2006; Perraud et al., 2010; Fry et al., 2014; Nah et al., 2016; Boyd et al., 2015, 2017). In this study, however, we found that styrene, one of major aromatics derived from anthropogenic emissions (Cabrera-Perez et al., 2016), served as a key VOC precursor for organic nitrate formation in Shenzhen, theoretically with comparable SOA producing ability to those of α-pinene and limonene and much higher ability than those of β-pinene and isoprene. In China, styrene has been actually identified as an important VOC of non-methane hydrocarbons (NMHCs) in urban areas, and has a notable contribution to ozone formation and SOA production (An et al., 2009; Yuan et al., 2013; Zhu et al., 2019). This study further highlights the key role of this anthropogenic VOC precursor in nighttime particulate organic nitrate formation in urban atmosphere in China, and relevant smog chamber studies for anthropogenic VOCs+NO₃ reactions are needed to support parameterization in modeling.”

26. Line 284-302: Added Section 3.5.

27. Line 309-316: Added “The diurnal trend analysis of size distribution of NO⁺/NO₂⁺ ratio further suggested that organic nitrate formation mainly occurred at night, and also presented that organic nitrates concentrated on smaller sizes, suggesting that they were mostly local product. The calculated theoretical nighttime production potential of NO₃ reactions with VOCs measured in spring showed that six VOC species (i.e., α-pinene, limonene, styrene, camphene, β-pinene and isoprene) were notable precursors. The SOA yield analysis further indicated that α-pinene, limonene and styrene contributed mostly to

nighttime formation of particulate organic nitrates in spring in Shenzhen, highlighting the unique contribution of anthropogenic VOCs in comparison with previous studies in the US and Europe. Finally, the comparison of the results in this study with other similar studies implied that nighttime formation of particulate organic nitrates is more likely NO_x-limited than VOCs-limited.”

Characterization of nighttime formation of particulate organic nitrates based on high-resolution aerosol mass spectrometry in an urban atmosphere in China

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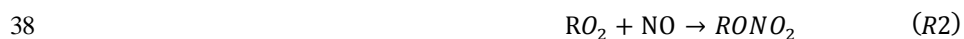
* Authors have equal contribution.

Abstract. Organic nitrates are important atmospheric species that significantly affect the cycling of NO_x and ozone production. However, characterization of particulate organic nitrates and their sources in polluted atmosphere is a big challenge and has been little performed in Asia. In this study, an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed at an urban site in China from 2015 to 2016 to characterize particulate organic nitrates in total nitrates with high time resolution. Based on cross validation of two different data processing methods, organic nitrates were effectively quantified to contribute a notable fraction of organic aerosol (OA): 9-21% in spring, 11-25% in summer and 9-20% in autumn; while organic nitrates were found to little exist in winter. The good correlation between organic nitrates and fresh secondary organic aerosol (SOA) at night as well as the diurnal trend of size distribution of organic nitrates indicated a key role of nighttime secondary formation in Shenzhen, which is consistent with what found in the US and Europe. The size distribution of organic nitrates also implied that organic nitrates were mainly a local product and could have strong removal during air mass transport. Furthermore, theoretical calculations of nighttime SOA production of NO₃ reactions with volatile organic compounds (VOCs) measured during the spring campaign were performed, resulting in two biogenic VOCs (α -pinene and limonene) and one anthropogenic VOC (styrene) identified as the key VOC precursors for particulate organic nitrates. The comparison with similar studies in the literature implied that nighttime particulate organic nitrates formation could be NO_x-controlled. This study proposes that different from the previous cases in the United States and Europe, modeling nighttime particulate organic nitrate formation should incorporate not only biogenic VOCs but also anthropogenic VOCs with high SOA yield for urban air pollution in China, which call for relevant smog chamber studies to support in future.

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30 1. Introduction

31 Organic nitrates (ON) in aerosols have an important impact on the fate of NO_x and ozone production (Lelieveld et al., 2016),
32 which can be formed in a minor channel of the reaction between peroxy radicals and NO (R1 and R2) (usually, an increased
33 fraction of this reaction leads to the formation of alkoxy radicals and NO₂ (R3)) or via the NO₃-induced oxidation of unsaturated
34 hydrocarbons (R4). Even though some recent studies have suggested that the formation of organic nitrates from peroxy radicals
35 and NO may play a larger role than previously recognized (Teng et al., 2015, 2017), yields of organic nitrates via NO₃ reacting
36 with alkenes are generally much higher (Fry et al., 2009; Ayres et al., 2015; Boyd et al., 2015, 2017).



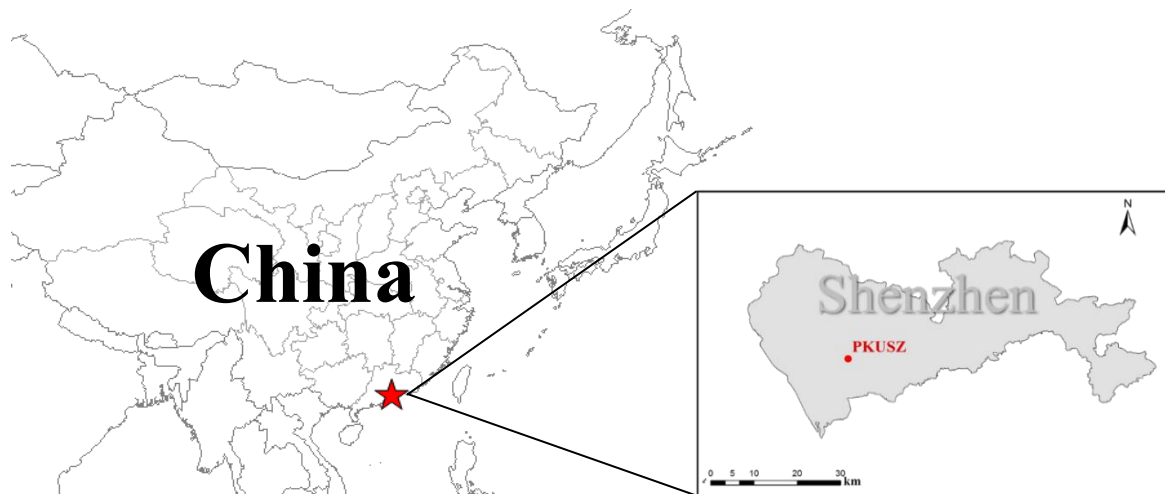
41 Several direct methods have been developed to measure total organic nitrates (gas + particle) in the real atmosphere. For
42 example, Rollins et al. (2012) used a thermal-dissociation laser-induced fluorescence technique (TD-LIF) to observe organic
43 nitrates in the United States; Sobanski et al. (2017) measured organic nitrates in Germany using the thermal dissociation cavity
44 ring-down spectroscopy (TD-CRDS). Field and laboratory studies around the world indicated that particulate organic nitrates
45 could contribute a large portion of secondary organic aerosol (SOA) (Rollins et al., 2012; Xu et al., 2015a; Fry et al., 2013;
46 Ayres et al., 2015; Boyd et al., 2015; Lee et al., 2016). Recently, researchers have proposed some estimation methods for
47 particle-phase organic nitrates based on aerosol mass spectrometry (AMS) with high time resolution (Farmer et al., 2010; Hao
48 et al., 2014; Xu et al., 2015a, 2015b). Ng et al. (2017) reviewed the nitrate radical chemistry and the abundance of particulate
49 organic nitrates in the United States and Europe, and further concluded that particulate organic nitrates are formed substantially
50 via NO₃+BVOC chemistry, which plays an important role in SOA formation. Unfortunately, relevant Chinese datasets are
51 scarce yet and not included in this review. This was because (1) the contributions of organic nitrates in SOA and total nitrates
52 in Chinese atmosphere remain poorly understood; (2) the anthropogenic and biogenic precursor emissions in China are largely
53 different from those in the United States and Europe, and thus cannot be easily estimated. To our best knowledge, few studies
54 have investigated the concentrations and formation pathways of particulate organic nitrates in China. Xu et al. (2017) estimated
55 the mass concentration of organic nitrogen in Beijing using AMS, but in this study they ignored the contribution of NO_x⁺
56 family, which are the major fragments of organic nitrates.

57 Shenzhen is a megacity of China in a subtropical region, where photochemical reactions are very active with high NO_x and
58 both biogenic and anthropogenic VOC emissions (Zhang et al., 2008). To assess the evolution of particulate organic nitrates
59 in a polluted urban atmosphere, we deployed an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-
60 AMS) and other instruments in Shenzhen from 2015 to 2016 in this study. Organic nitrates and their contributions to OA in
61 different seasons were estimated by different methods using the HR-ToF-AMS datasets obtained, based on which, the
62 secondary formation pathway of particulate organic nitrates in Shenzhen was further explored.

63 **2. Experiment methods**

64 **2.1 Sampling site and period**

65 The sampling site (22.6°N, 113.9°E) was on the roof (20 m above ground) of an academic building on the campus of Peking
66 University Shenzhen Graduate School (PKUSZ), which is located in the western urban area in Shenzhen (Figure 1). This site
67 is mostly surrounded by subtropical plants without significant anthropogenic emission sources nearby, except a local road
68 ~100 m from the site. In this study, we used the statistical data from the Meteorological Bureau of Shenzhen Municipality
69 (<http://www.szmb.gov.cn/site/szmb/Esztq/index.html>) as the reference data to determine the sampling periods for four
70 different seasons during 2015-2016, as shown in Table 1.



71

72

Figure 1.The location of the sampling site.

73 **Table 1.**Meteorological conditions, PM₁ species concentrations and relevant parameters for different sampling periods in
74 Shenzhen.

	Sampling period	4.1-4.30, 2016	8.1-8.31, 2015	11.4-11.30, 2015	1.21-2.3, 2016
		Spring	Summer	Autumn	Winter
Meteorology	T (°C)	24.5±2.5	29.0±3.0	23.6±3.7	10.7±4.7
	RH (%)	78.0±12.7	71.2±17.5	68.2±15.8	75.4±18.7
	WS (m s ⁻¹)	1.4±0.8	1.0±0.7	1.2±0.7	1.5±0.8
Species	Org	4.3±3.2	10.0±6.9	7.8±5.9	5.1±3.5
	SO ₄ ²⁻	3.2±1.8	5.8±3.3	2.3±1.5	1.9±1.2
	Total NO ₃	0.96±1.4	0.91±0.90	1.3±1.4	1.6±1.0

$(\mu\text{g m}^{-3})$	NH_4^+	1.4±0.8	2.0±1.1	1.1±0.8	1.2±0.6
	Cl^-	0.14±0.19	0.03±0.05	0.22±0.36	0.64±0.85
	BC	1.9±2.1	2.4±1.6	3.5±2.6	2.4±1.5
	Total	12.0±8.9	15.1±13.8	11.8±9.5	12.2±7.2
ON relevant parameters	$R_{\text{NH}_4\text{NO}_3}$	2.80	3.20	3.32	3.48
	R_{obs}	3.74	6.14	4.30	3.55
	Fraction of positive numbers of $R_{\text{obs}} - R_{\text{NH}_4\text{NO}_3}$	99%	99%	84%	47%

75 2.2 Instrumentation

76 2.2.1 High Resolution Time-of-Flight Aerosol Mass Spectrometer

77 During the sampling periods, chemical composition of non-refractory PM_{10} was measured by an Aerodyne HR-ToF-AMS, and
78 detailed descriptions of this instrument are given in the literature (DeCarlo et al., 2006; Canagaratna et al., 2007). The setup
79 and operation of the HR-ToF-AMS can be found in our previous publications (Huang et al., 2010, 2012; Zhu et al., 2016). To
80 remove coarse particles, a $\text{PM}_{2.5}$ cyclone inlet was installed before the sampling copper tube with a flow rate of 10 l min^{-1} .
81 Before entering the AMS, the sampled air was dried by a nafion dryer (MD-070-12S-4, Perma Pure Inc.) to eliminate the
82 potential influence of relative humidity on particle collection (Matthew et al., 2008). The ionization efficiency (IE) calibrations
83 were performed using pure ammonium nitrate every two weeks. The relative ionization efficiencies (RIEs) used in this study
84 were 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, 1.4 for organics and 4.0 for ammonium, respectively (Jimenez et al., 2003).
85 Composition-dependent collection efficiencies (CEs) were applied to the data according to the method in Middlebrook et al.
86 (2012). The instrument was operated at two ion optical modes with a cycle of 4 min, including 2 min for the mass-sensitive
87 V-mode and 2 min for the high mass resolution W-mode. The HR-ToF-AMS data analysis was performed using the software
88 SQUIRREL (version 1.57) and PIKA (version 1.16) written in Igor Pro 6.37 (Wave Metrics Inc.)
89 (<http://cires1.colorado.edu/jimenezgroup/ToFAMSResources/ToFSoftware/index.html>).

90 2.2.2 Other co-located instruments

91 In addition to the HR-ToF-AMS, other relevant instruments were deployed at the same sampling site. An aethalometer (AE-
92 31, Magee) was used for measurement of refractory black carbon (BC) with a resolution of 5 min. An SMPS system (3775
93 CPC and 3080 DMA, TSI Inc.) was used to obtain the particle number size distribution in 15–615 nm (mobility diameter) with
94 a time resolution of 5 min. Ozone and NO_x were measured by a 49i ozone analyzer and a 42i nitrogen oxide analyzer (Thermo
95 Scientific), respectively. In the spring campaign, ambient VOC concentrations were also measured using an on-line VOC
96 monitoring system (TH-300B, Tianhong Corp.), including an ultralow-temperature preconcentration cold trap and an

97 automated in-situ gas chromatograph (Agilent 7820A) equipped with a mass spectrometer (Agilent 5977E). The system had
 98 both a flame ionization detector (FID) gas channel for C2–C5 hydrocarbons and a mass spectrometer (MS) gas channel for
 99 C5–C12 hydrocarbons, halohydrocarbons and oxygenated VOCs. A complete working cycle of the system was one hour and
 100 included five steps: sample collection, freeze-trapping, thermal desorption, GC-FID/MS analysis, heating and anti-blowing
 101 purification. The sample collection time was 5 min, the sampling flow was 60 ml min⁻¹, and the anti-blowing flow was 200 ml
 102 min⁻¹. The calibration of over 100 VOCs was performed using mixed standard gas before and after the campaign. Detection
 103 limits for most compounds were near 5 pptv. More description of this instrument can be found in Wang et al. (2014).

104 2.3 Organic nitrate estimation methods

105 In this study, we used two independent methods to estimate particulate organic nitrates based on the AMS data, following the
 106 approaches in Xu et al. (2015b). The first method is based on the NO⁺/NO₂⁺ ratio (NO_X⁺ ratio) in the HR-AMS spectrum. Due
 107 to the very different NO_X⁺ ratios of organic nitrates and inorganic nitrate (i.e., R_{ON} and R_{NH₄NO₃}, respectively) (Farmer et al.,
 108 2010; Boyd et al., 2015; Fry et al., 2008; Bruns et al., 2010), the NO₂⁺ and NO⁺ concentrations of organic nitrates (NO_{2,ON} and
 109 NO_{ON}) can be quantified with the HR-AMS data via Eqs. (1) and (2), respectively (Farmer et al., 2010):

$$110 \quad NO_{2,ON}^+ = \frac{NO_{2,obs}^+ \times (R_{obs} - R_{NH_4NO_3})}{R_{ON} - R_{NH_4NO_3}} \quad (1)$$

$$111 \quad NO_{ON}^+ = R_{ON} \times NO_{2,ON} \quad (2)$$

112 where R_{obs} is the NO_X⁺ ratio from the observation. The value of R_{ON} is difficult to determine because it varies between
 113 instruments and precursor VOCs. However, R_{NH₄NO₃} was determined by IE calibration using pure NH₄NO₃ every two weeks
 114 for each campaign and the results showed stable values: In spring, the average R_{NH₄NO₃} was 2.66 for the first IE calibration and
 115 2.94 for the second one; in summer, the average R_{NH₄NO₃} was 3.05 and 3.34 for the first and second IE calibrations, respectively;
 116 in autumn, the average R_{NH₄NO₃} was 3.33 and 3.31 for the first and second IE calibrations, respectively; in winter, the average
 117 R_{NH₄NO₃} was 3.45 and 3.51 for the first and second IE calibrations, respectively. We adopted the R_{ON}/R_{NH₄NO₃} estimation range
 118 (from 2.08 to 3.99) for variation of precursor VOCs in the literature to determine R_{ON} (Farmer et al., 2010; Boyd et al., 2015;
 119 Bruns et al., 2010; Sato et al., 2010; Xu et al., 2015b), and thus two R_{ON} values were calculated for each season to provide the
 120 upper bound (NO_{3,org_ratio_1}) and lower bound (NO_{3,org_ratio_2}) of NO_{3,org} mass concentration.

121 The second method is based on the traditional positive matrix factorization (PMF) analysis of HR organic mass spectra for
 122 resolving different organic factors (Zhang et al., 2011; Ng et al., 2010; Huang et al., 2013), and the same analysis of HR organic
 123 mass spectra, but combined with NO⁺ and NO₂⁺ ions, was performed to separate NO⁺ and NO₂⁺ ions into different organic
 124 factors and an inorganic nitrate factor (Hao et al., 2014; Xu et al., 2015b). The PMF analysis procedures in this study can be
 125 found in our previous publications (Huang et al., 2010; Zhu et al., 2016; He et al., 2011), resulting in three organic factors and
 126 one inorganic factor in spring, summer and autumn: a hydrocarbon-like OA (HOA) characterized by C_nH_{2n+1}⁺ and C_nH_{2n-1}⁺ and
 127 O/C of 0.11 to 0.18, a less-oxidized oxygenated OA (LO-OOA) characterized by C_xH_yO_z⁺ especially C₂H₃O⁺ and O/C of 0.28
 128 to 0.70, a more-oxidized oxygenated OA (MO-OOA) also characterized by C_xH_yO_z⁺ especially CO₂⁺ and O/C of 0.78 to 1.24,

129 and a nitrate inorganic aerosol (NIA) characterized by overwhelming NO^+ and NO_2^+ , as indicated in Fig S6. According to the
130 diagnostic plots of the PMF analysis shown in Figure S2 to S4, the same organic factors as those in the traditional PMF analysis
131 of only organic mass spectra were indeed obtained. The NO^+ and NO_2^+ ions were distributed among different OA factors and
132 the NIA factor; thus the concentrations of nitrate functionality (NO_{org}^+ and $\text{NO}_{2,org}^+$) in organic nitrates ($\text{NO}_{3,org}$) are equal to
133 the sum of NO_2^+ and NO^+ via Eqs. (3) and (4), respectively (Xu et al., 2015b):

$$134 \quad \text{NO}_{2,org}^+ = \sum([\text{OA factor}]_i \times f_{\text{NO}_2,i}) \quad (3)$$

$$135 \quad \text{NO}_{org}^+ = \sum([\text{OA factor}]_i \times f_{\text{NO},i}) \quad (4)$$

136 where $[\text{OA factor}]_i$ represents the mass concentration of OA factor i , and $f_{\text{NO}_2,i}$ and $f_{\text{NO},i}$ represent the mass fractions of NO_2^+
137 and NO^+ , respectively.

138 It should be noted that although the 4-factor solution seemed to have a “mixed factor” problem to some extent (Zhu et al.,
139 2018), such as HOA mixed with COA (clear $\text{C}_3\text{H}_3\text{O}^+$ in m/z 55 for spring, summer and autumn) (Mohr et al., 2012) and BBOA
140 mixed with LO-OOA (clear m/z 60 and 73 signals in LO-OOA in autumn) (Cubison et al., 2011), running PMF with more
141 factors would produce unexplained factors but little influence the apportion of NO^+ and NO_2^+ ions between organic nitrates
142 and inorganic nitrate (Table S1). In addition, the uncertainties of NO^+ and NO_2^+ ions in the OA factors across different peak
143 values (from -1.0 to 1.0) were very small (Table S2). Therefore, the 4-factor solution was finally used for quantifying organic
144 nitrates in spring, summer and autumn.

145 3. Results and discussion

146 3.1 Organic nitrate estimation

147 Table 2 shows the concentrations of nitrate functionality in organic nitrates (i.e., $\text{NO}_{3,org}$), estimated by both the $\text{NO}^+/\text{NO}_2^+$
148 ratio method and PMF method, and their contributions to the total measured nitrate. It should be noted that the small difference
149 between the average R_{obs} and $R_{\text{NH}_4\text{NO}_3}$ in winter leads to a large portion of negative data using the $\text{NO}^+/\text{NO}_2^+$ ratio method
150 (Table 1), and the result from the PMF method shows the contribution of organic nitrates in total nitrates is only 4.2% in winter
151 (Figure S6), suggesting a negligible contribution of organic nitrates. Thus, we will only discuss organic nitrate estimation
152 results in spring, summer and autumn. No matter by the $\text{NO}^+/\text{NO}_2^+$ ratio method or by the PMF method, organic nitrates had
153 the highest ambient concentration ($0.34\text{-}0.53 \mu\text{g m}^{-3}$) and proportion in total nitrates (41-64%) in summer among the different
154 seasons, which is consistent with the finding in the literature (Ng et al., 2017) and presents a different seasonal trend in
155 comparison with that of total nitrates in Table 1. Assuming the average molecular weight of organic nitrates of 200 to 300 g
156 mol^{-1} (Rollins et al., 2012), we found that organic nitrates contributed 9-21% to OA in spring, 11-25% in summer and 9-20%
157 in autumn.

158 In the PMF method, the mass fractions of organic nitrates in HOA, LO-OOA and MO-OOA were 31%, 49% and 20%,
159 respectively, in spring; 28%, 52% and 20%, respectively, in summer; 30%, 46% and 24%, respectively, in autumn. The major

160 fraction of organic nitrates occurring in LO-OOA for the three seasons implied that organic nitrates were mostly related to
 161 fresher secondary OA formation. The NIA factor in all seasons was dominated by NO^+ and NO_2^+ , but also contained some
 162 organic fragments, such as CO_2^+ and $\text{C}_2\text{H}_3\text{O}^+$, which agreed with the findings in the literature (Hao et al., 2014; Xu et al.,
 163 2015b; Sun et al., 2012) and indicated potential interference of organics in the NIA factor. Also note that the $\text{NO}^+/\text{NO}_2^+$ ratios
 164 in NIA (2.93 for spring, 3.53 for summer and 3.54 for autumn) were higher than that for pure NH_4NO_3 (Table 1), indicating
 165 an underestimation of $\text{NO}_{3,\text{org}}$ concentration by the PMF method. This may also explain why the concentration of $\text{NO}_{3,\text{org}}$
 166 estimated using the PMF method was always close to the lower estimation bound of $\text{NO}_{3,\text{org}}$ concentration using the $\text{NO}^+/\text{NO}_2^+$
 167 ratio method in each season in Table 2.

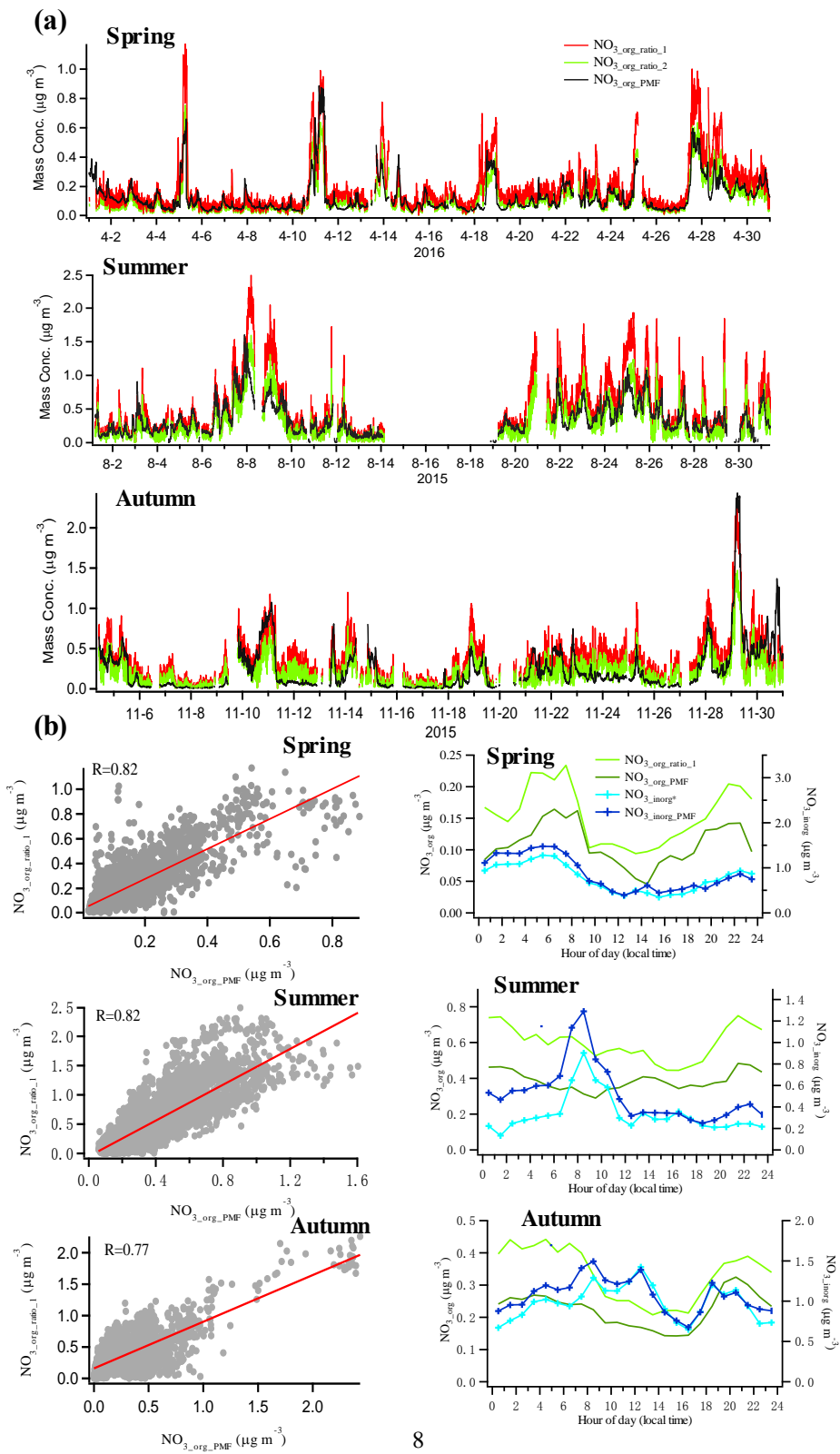
168 **Table 2.** Summary of organic nitrate estimations using the $\text{NO}^+/\text{NO}_2^+$ ratio method and the PMF method

Sampling period	$\text{NO}^+/\text{NO}_2^+$ ratio method				PMF method	
	$\text{NO}_{3,\text{org}}$ ($\mu\text{g m}^{-3}$) ^a		$\text{NO}_{3,\text{org}}/\text{NO}_3$		$\text{NO}_{3,\text{org}}$ ($\mu\text{g m}^{-3}$) ^b	$\text{NO}_{3,\text{org}}/\text{NO}_3$
	lower	upper	lower	upper		
Spring	0.12	0.19	13%	21%	0.12	12%
Summer	0.34	0.53	41%	64%	0.39	43%
Autumn	0.21	0.33	16%	25%	0.21	16%
Winter	∕	∕	∕	∕	0.07	4.2%

169 ^a $\text{NO}_{3,\text{org}}$ for upper bound is denoted as $\text{NO}_{3,\text{org_ratio_1}}$, and $\text{NO}_{3,\text{org}}$ for lower bound is denoted as $\text{NO}_{3,\text{org_ratio_2}}$.

170 ^b $\text{NO}_{3,\text{org}}$ estimated using the PMF method is denoted as $\text{NO}_{3,\text{org_PMF}}$.

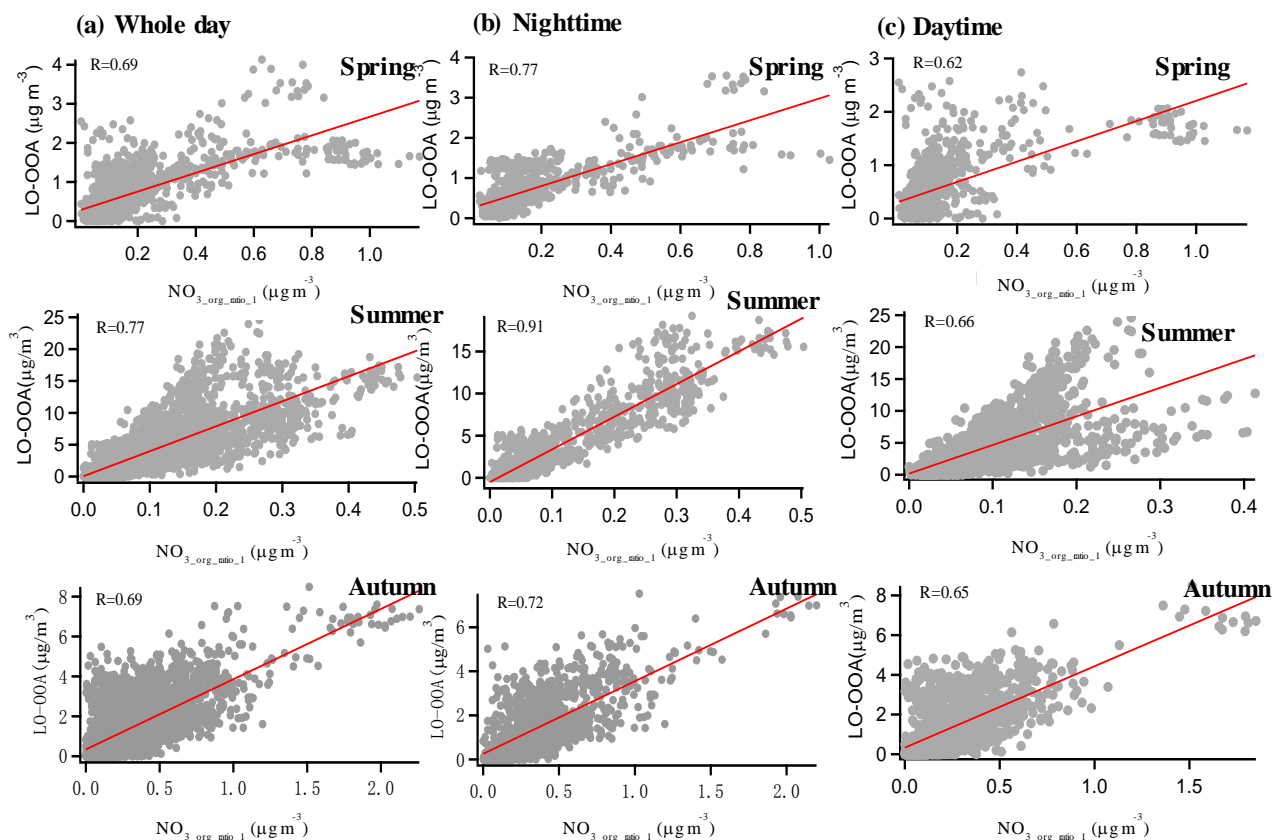
171 To further verify the reliability of the estimated results of organic nitrates, the $\text{NO}_{3,\text{org}}$ concentration time series calculated by
 172 the two methods in each season are shown in Figure 2a, and their correlation coefficient (R) is good (0.82 for spring, 0.82 for
 173 summer and 0.77 for autumn), indicating that similar results were achieved. The inorganic nitrate ($\text{NO}_{3,\text{inorg}}$) obtained by
 174 subtracting $\text{NO}_{3,\text{org_ratio_1}}$ from total measured nitrates also correlated well with the inorganic nitrate estimated using the PMF
 175 method (R=0.92 for spring, 0.87 for summer and 0.86 for autumn). Furthermore, the diurnal trends of organic nitrates obtained
 176 by the two methods were also similar in each season, generally with lower concentrations in the daytime and higher
 177 concentrations at night, while they were distinctive from those of inorganic nitrate (Figure 2b), supporting that organic nitrates
 178 had been well separated from inorganic nitrate in this study.



180 **Figure 2.** (a) Time series of $\text{NO}_{3,\text{org}}$ concentration estimated by the $\text{NO}^+/\text{NO}_2^+$ ratio method and PMF method for each
 181 season; (b) correlations between $\text{NO}_{3,\text{org_ratio_1}}$ and $\text{NO}_{3,\text{org_PMF}}$ (left panel); diurnal trends of organic nitrates and $\text{NO}_{3,\text{org}}$
 182 estimated by the different methods (right panel).

183 3.2 Correlation between organic nitrates and OA factors

184 As indicated by the results in the PMF method, the majority of organic nitrates were associated with LO-OOA in spring,
 185 summer and autumn in the urban atmosphere in Shenzhen, implying a dominant secondary origin of organic nitrates. To further
 186 confirm this relationship, we made the correlation analysis between organic nitrates estimated by the $\text{NO}^+/\text{NO}_2^+$ ratio method
 187 and the three factors resolved by the PMF analysis with only organic mass spectra in the three seasons. Generally, organic
 188 nitrates were indeed found better-correlated with LO-OOA ($R=0.69-0.77$ in Figure 3) than with HOA and MO-OOA ($R=0.03-$
 189 0.69 in Figures S6-S8), consistent with the fact that the majority of organic nitrates were associated with LO-OOA in the PMF
 190 method. However, the moderate correlation between organic nitrates and HOA implied possibility of direct emissions of
 191 organic nitrates. Furthermore, we found a noticeably improved correlation between LO-OOA and organic nitrates at night
 192 (19:00-6:00) and a reduced correlation during the daytime (7:00-18:00) in Figure 3, especially in summer, implying that
 193 organic nitrates formation might be more closely related to secondary formation at night.

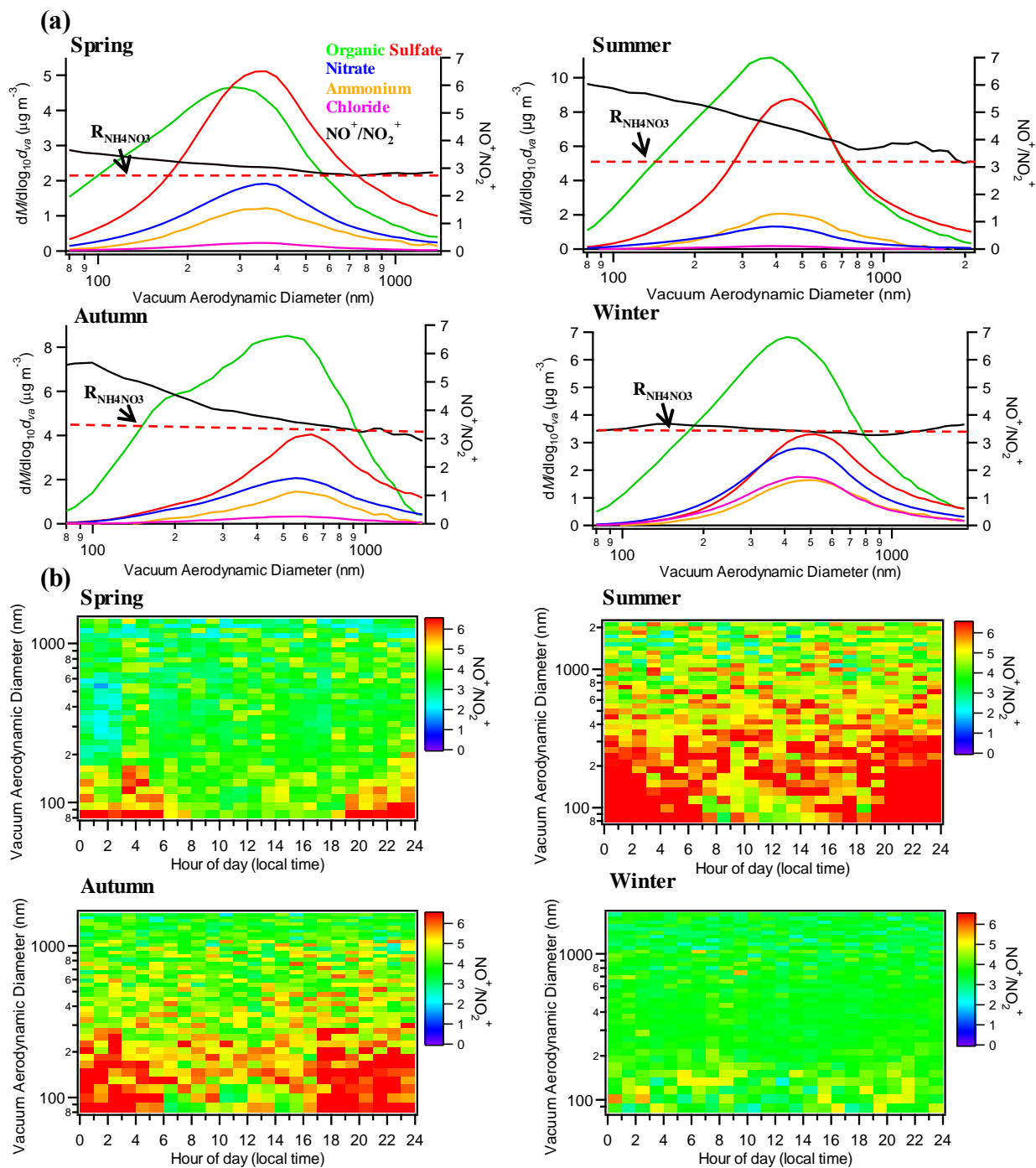


194

195 **Figure 3.**Correlation of $\text{NO}_3\text{-org_ratio}_1$ and LO-OOA in each season for the whole day (a), at night (b) and in the daytime (c).

196 **3.3 Size distribution characteristics of organic nitrates**

197 In this section, we used the $\text{NO}^+/\text{NO}_2^+$ ratio as an indicator to investigate the size distribution characteristics of organic nitrates.
198 The average size distributions of different aerosol species and $\text{NO}^+/\text{NO}_2^+$ ratio in four seasons are shown in Figure 4. It is
199 clearly found that the $\text{NO}^+/\text{NO}_2^+$ ratio generally increased towards smaller size in spring, summer and autumn, while the
200 $\text{NO}^+/\text{NO}_2^+$ ratio kept similar to the value of $R_{\text{NH}_4\text{NO}_3}$ throughout the full size range in winter. It should also be noted that in
201 spring, summer and autumn, the lowest values of $\text{NO}^+/\text{NO}_2^+$ ratio occurring at $>1 \mu\text{m}$ were approximate to the corresponding
202 seasonal values of $R_{\text{NH}_4\text{NO}_3}$. These characteristics clearly indicated that organic nitrates occurred mostly in fresh particles with
203 smaller sizes and thus should be mainly of local origin. Different from the bulk OA and inorganic species, organic nitrates
204 seemed to exist scarcely in larger aged particles, implying that they could be easily removed by deposition and/or chemical
205 degradation during air mass transport. In addition, the diurnal trends of size distribution of $\text{NO}^+/\text{NO}_2^+$ ratio in spring, summer
206 and autumn in Figure 4 show apparent higher values at small sizes at night, suggesting an important nighttime local origin of
207 organic nitrates. Combining with the analysis in section 3.2, local nighttime secondary formation of organic nitrates in warmer
208 seasons in the urban polluted atmosphere in Shenzhen is highlighted. This is well consistent with the previous findings in the
209 US and Europe that the nighttime NO_3+VOCs reactions serve as an important source for particulate organic nitrates (Rollins
210 et al., 2012; Xu et al., 2015a, 2015b; Fry et al., 2013; Lee et al., 2016). We will then explore the nighttime NO_3+VOCs reactions
211 in Shenzhen in the following section.



212

213

214

Figure 4.(a) Average size distributions of aerosol species and $\text{NO}^+/\text{NO}_2^+$ ratio (red dotted line represents $R_{\text{NH}_4\text{NO}_3}$); (b) diurnal trends of size distribution of $\text{NO}^+/\text{NO}_2^+$ ratio.

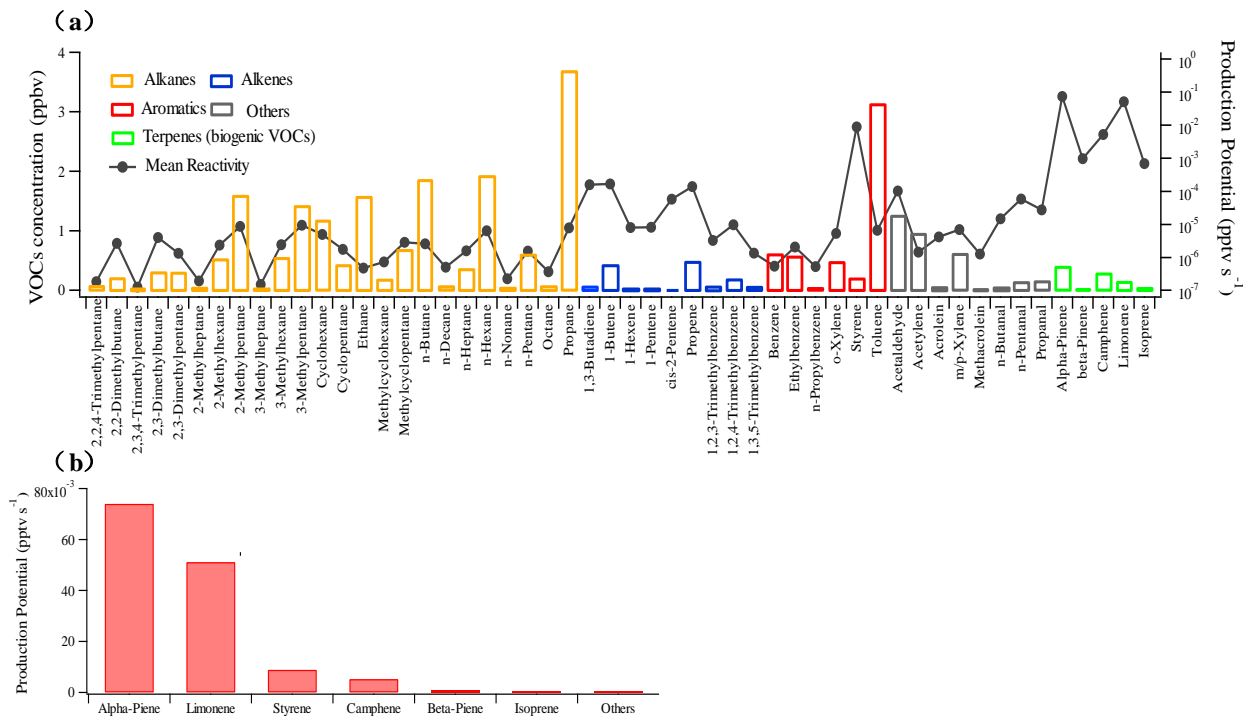
3.4 Nighttime particulate organic nitrate formation via NO₃+VOCs

Since on-line VOCs measurement was only performed during the spring campaign, as described in section 2.2, the following theoretical analysis of NO₃+VOCs reactions will be just applied to the spring case. NO₃+VOCs reactions would yield a large mass of gas- and particle-phase organic nitrates (Rollins et al., 2012; Nah et al., 2016; Boyd et al., 2015, 2017; Xu et al., 2015a, 2015b; Lee et al., 2016). We used the NO₃ loss rate at night, which can be calculated as $K_i \cdot [VOC_i]$ in Eq. (9), to roughly judge the production potential of organic nitrates from a NO₃+VOC reaction:

$$[\text{Production Potential}]_{\text{NO}_3+\text{VOC}_i} = K_i \cdot [VOC_i] \cdot [NO_3] \quad (9)$$

Where K_i represents the reaction rate coefficient for NO₃ radical and a VOC, $[VOC_i]$ is the concentration of the specific VOC and $[NO_3]$ is the concentration of NO₃ radical. In the spring campaign, the diurnal variations of NO₂, O₃ and estimated NO₃ radical concentrations are shown in Figure S10. It was found that the high concentrations of NO₂ (19.93 ± 2.31 ppb) at night led to high yield of NO₃ radical (1.24 ± 0.76 ppt) in Shenzhen, as calculated in Text S1, compared to nighttime NO₃ radical concentrations reported in literature in the United States (Rollins et al., 2012; Xu et al., 2015a).

Typical measured nighttime VOC concentrations, their reaction rate coefficients with NO₃ radical and the production potentials calculated are listed in Table S3 and shown in Figure 5. These VOCs were considered based on their higher ambient concentrations and availability for reaction kinetics with NO₃ radical. According to the distribution of production potential, five biogenic VOCs (BVOCs) (i.e., α -pinene, limonene, camphene, β -pinene and isoprene) and one anthropogenic VOC (styrene) were identified as notable VOC precursors with high production potential, while the sum of production potential from the other VOCs was negligible as shown in Figure 5b.



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Figure 5. (a) Mean concentrations of VOCs and the corresponding calculated production potential of NO_3+VOC at night during the spring campaign; (b) production potential ranking of VOCs at night during the spring campaign.

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Figure 6 shows the average nighttime variations of BC, LO-OOA, $\text{NO}_{3,\text{org_ratio}_1}$, $\text{NO}_{3,\text{org_PMF}}$ and production potential of the six notable VOCs identified during the spring campaign. The concentrations of BC and LO-OOA generally decreased slowly after sunset till sunrise due to the combined effect of both the planetary boundary layer variation and traffic emissions, while particulate organic nitrates showed a different trend with two clear growth processes (19:00-22:00 and 3:00-6:00) at night, suggesting their unique sources. In contrast, the production potentials of the six notable VOCs with NO_3 had two roughly similar increases at the same periods as those of particulate organic nitrates, which supported the key role of NO_3+VOCs reactions for nighttime organic nitrate formation.

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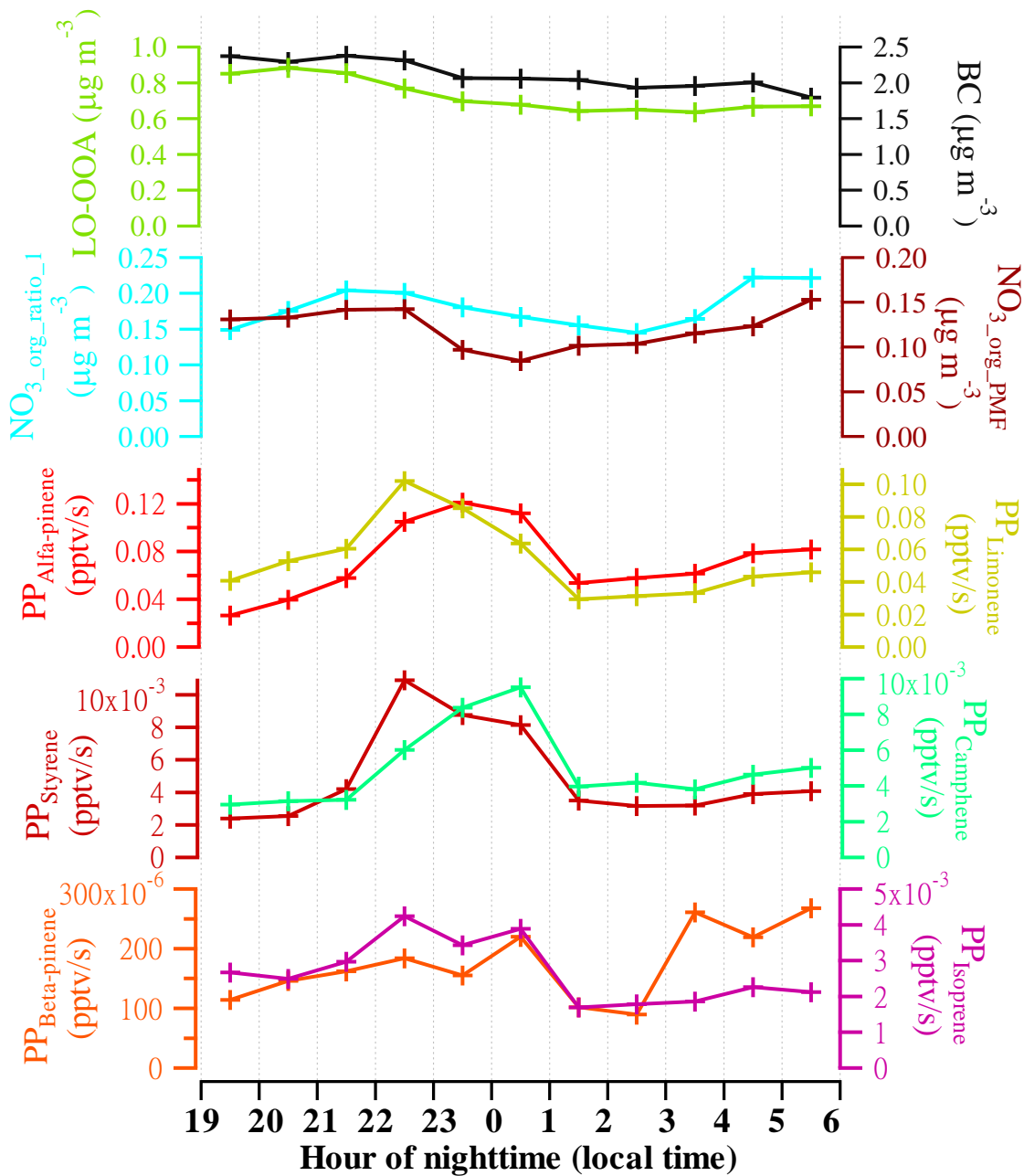
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 244 **Figure 6.** Nighttime variations of BC, LO-OOA, NO₃.org_ratio_1, NO₃.org_PMF and production potential (PP) of six notable VOCs
 245 during the spring campaign.

246 Based on the production potential evaluation above, we further explore SOA yield of NO₃+the six notable VOC precursors
 247 according to the analysis method of particulate organic nitrate formation in Xu et al. (2015a). Briefly, NO₃ and ozone are two
 248 main oxidants for SOA formation from VOCs at night. Based on the concentrations of oxidants and the reaction rate constants

249 for VOCs with NO₃ and ozone, the branching ratio of each VOC that reacts with NO₃ can be estimated as in Eq. (10). By
 250 combining the estimated branching ratios and SOA yields from chamber studies (Table 3), SOA from these VOCs can be
 251 calculated as in Eq. (11) (Xu et al., 2015a):

$$252 \quad \text{branching ratio}_{\text{species} + \text{NO}_3} = \frac{k_{[\text{species} + \text{NO}_3] \times [\text{NO}_3]}}{k_{[\text{species} + \text{NO}_3] \times [\text{NO}_3]} + k_{[\text{species} + \text{O}_3] \times [\text{O}_3]}} \quad (10)$$

$$253 \quad [\text{SOA}]_{\text{species, oxidant}} = [\text{species}] \times \text{branching ratio}_{\text{species, oxidant}} \times \text{yield}_{\text{species, oxidant}} \quad (11)$$

254 The results in Table 3 show that all the six notable VOC species were prone to react with NO₃ radical instead of O₃ at night,
 255 and the estimated SOA production from NO₃+VOCs reactions using SOA mass yields in the literature was 0-0.33 μg m⁻³ for
 256 α-pinene, 0.09-1.28 μg m⁻³ for limonene, 0.24 μg m⁻³ for styrene, 0.004-0.06 μg m⁻³ for β-pinene and 0.002-0.02 μg m⁻³ for
 257 isoprene. The SOA yield from camphene is currently unknown in the literature. It is seen that the average observed nighttime
 258 concentration of particulate organic nitrates during the spring campaign (0.39-0.83 μg m⁻³, converting NO_{3,org_ratio_1}, NO_{3,org_PMF}
 259 in Figure 6 into organic nitrates assuming the average molecular weight of organic nitrates of 200 to 300 g mol⁻¹) was well
 260 within the estimated SOA concentration ranges produced by α-pinene, limonene and styrene in Table 3, indicating that these
 261 three VOCs were the key VOC precursors in urban atmosphere in Shenzhen. Considering both the production potentials and
 262 SOA yields, the contributions of β-pinene and isoprene to nighttime formation of particulate organic nitrates could be
 263 negligible.

264 **Table 3.** Average concentrations, reaction branching and SOA production of α-pinene, limonene, styrene, camphene, β-
 265 pinene and isoprene with respect to different oxidants at night in the spring campaign.

Species	Concentration (ppbv)	Rate coefficient ^a		Branching ratio		SOA yield from the literature (with NO ₃)	SOA from VOCs + NO ₃ (μg m ⁻³)
		NO ₃	O ₃	NO ₃	O ₃		
α-pinene	0.39	6.64E-12	7.2E-17	0.962	0.038	0-0.16 ^b	0-0.33
Limonene	0.14	1.22E-11	1.54E-16	0.957	0.043	0.12-1.74 ^c	0.09-1.28
Styrene	0.19	1.50E-12	1.70E-17	0.941	0.059	0.23 ^d	0.24
Camphene	0.28	6.20E-13	9.0E-19	0.992	0.008	/	/
β-pinene	0.01	2.51E-12	1.50E-17	0.968	0.032	0.07-1.04 ^e	0.004-0.06
Isoprene	0.032	6.96E-13	1.27E-17	0.908	0.091	0.02-0.24 ^f	0.002-0.02

266 ^a Rate coefficients for all species except camphene are from the Master Chemical Mechanism model
 267 (<http://mcm.leeds.ac.uk/MCM/>; under 25 °C), rate coefficients for camphene are from Martínez et al. (1999) and Atkinson et
 268 al. (1990).

269 ^b Hallquist et al. (1999); Spittler et al. (2006); Perraud et al. (2010); Fry et al. (2014); Nah et al. (2016).

270 ^c Fry et al. (2011, 2014); Spittler et al. (2006); Boyd et al. (2017).

271 ^d Cabrera-Perez et al. (2017).

272 ^e Griffin et al. (1999); Fry et al. (2009); Fry et al. (2014); Boyd et al. (2015).

273 ^f Rollins et al. (2009); Ng et al. (2008).

274 It should be noted that, all previous studies on nighttime organic nitrate formation in the US and Europe focused on mechanisms
275 of NO₃ reactions with BVOCs (Hallquist et al., 1999; Spittler et al., 2006; Perraud et al., 2010; Fry et al., 2014; Nah et al., 2016;
276 Boyd et al., 2015, 2017). In this study, however, we found that styrene, one of major aromatics derived from anthropogenic
277 emissions (Cabrera-Perez et al., 2016), served as a key VOC precursor for organic nitrate formation in Shenzhen, theoretically
278 with comparable SOA producing ability to those of α -pinene and limonene and much higher ability than those of β -pinene and
279 isoprene. In China, styrene has been actually identified as an important VOC of non-methane hydrocarbons (NMHCs) in urban
280 areas, and has a notable contribution to ozone formation and SOA production (An et al., 2009; Yuan et al., 2013; Zhu et al.,
281 2019). This study further highlights the key role of this anthropogenic VOC precursor in nighttime particulate organic nitrate
282 formation in urban atmosphere in China, and relevant smog chamber studies for anthropogenic VOCs+NO₃ reactions are
283 needed to support parameterization in modeling.

284 **3.5 Comparison with other similar studies and implications**

285 Table 4 shows the average ambient temperatures, average concentrations of NO, NO₂, monoterpenes, NO_{3,org}, the ratio of
286 NO_{3,org} to NO_{3,total} and the ratio of organic nitrates to total organics in a few similar field campaigns available in the literature,
287 which all found the key role of NO₃+VOCs reactions for nighttime particulate organic nitrate formation. Generally, the
288 concentrations of particulate organic nitrates varied less than an order of magnitude (0.06-0.98 $\mu\text{g}/\text{m}^3$) among the different
289 sites. Higher concentrations of particulate organic nitrates generally corresponded to higher NO_x concentrations rather than
290 BVOC concentrations, implying that the formation of particulate organic nitrates is more likely NO_x-limited than BVOCs-
291 limited. Note that, particulate organic nitrates constituted the major part (86-100%) of total nitrates in the atmosphere scarce
292 of NO_x (in Centreville and Woodland Park), suggesting that NO_x was very quickly consumed to form particulate organic
293 nitrates and thus the formation of particulate organic nitrates should be NO_x-limited. On the other hand, although the BVOC
294 concentrations in Bakersfield were far less than in the other campaigns, the concentration of particulate organic nitrates there
295 showed a medial level among all the campaigns. In the spring campaign of this study, we examined the correlation between
296 organic nitrates and NO₂ or VOCs (by the sum of α -pinene, limonene and styrene) at night (Figure S11) and found a significant
297 correlation of organic nitrates with NO₂ (R=0.40-0.47) rather than with VOCs (R=0.06-0.20), implying a dominant role of
298 NO_x in the organic nitrate formation. Therefore, it is inferred that formation of particulate organic nitrates through BVOC
299 reactions may be indirectly NO_x-controlled, and high NO_x emissions could promote biogenic SOA formation at night.

300 **Table 4.** Average ambient temperatures, average concentrations of monoterpenes, $\text{NO}_{3,\text{total}}$, $\text{NO}_{3,\text{org}}$, $\text{NO}_{3,\text{org}}/\text{NO}_{3,\text{total}}$ and the ratio of organic nitrates to total organics (ON/Org) for different
 301 field campaigns around the world. The ON results at the European and US sites are from Kiendler-Scharr et al. (2016) and Ng et al. (2017).

Sampling site	Site type	Sampling period	Temperature (°C)	NO (ppbv)	NO ₂ (ppbv)	Monoterpenes (ppbv)	NO _{3,org} (µg m ⁻³)	NO _{3,org} /NO _{3,total}	ON/Org	Reference/Note
Bakersfield, US	rural	May-June, 2010	23.0		8.2	0.045 (α-pinene) 0.004 (β-pinene) 0.034 (limonene)	0.16	0.28	0.23	Rollins et al. (2012)/ NO _{3,org} measured by TD-LIF
Woodland Park, US	high attitude	July-August, 2011	15.0		1.2	0.25 (monoterpene)	0.06	0.86	0.09	Fry et al. (2013)/ Use AMS data to estimate NO _{3,org}
Centreville, US	rural	June-July, 2013	24.7	0.1	1.1	0.350 (α-pinene)* 0.312 (β-pinene)* 0.050 (limonene)*	0.08	1.00	0.10	Xu et al. (2015a) Xu et al. (2015b)/ Use AMS data to estimate NO _{3,org}
Barcelona, Spain	urban	March, 2009	13.3	11.0	23.6	0.423 (monoterpene)	0.48	0.13	0.13	Mohr et al. (2012) Pandolfi et al. (2014) / Use AMS data to estimate NO _{3,org}
Shenzhen, China	urban	April, 2016	24.5	8.0	19.4	0.391 (α-pinene)* 0.013 (β-pinene)* 0.137 (limonene)*	0.16	0.17	0.11	This study/ Use AMS data to estimate NO _{3,org}

302 *BVOC concentration at night.

4. Conclusions

An Aerodyne HR-ToF-AMS was deployed in urban Shenzhen for about one month per season during 2015–2016 to characterize particulate organic nitrates with high time resolution. We found that the mass fractions of organic nitrates in total organics were substantial during warmer seasons, including spring (9-21%), summer (11-25%) and autumn (9-20%), while particulate organic nitrates were negligible in winter. The correlation analysis between organic nitrates and each OA factor showed higher correlation ($R=0.77$ in spring, 0.91 in summer and 0.72 in autumn) between organic nitrates and LO-OOA at night. The diurnal trend analysis of size distribution of $\text{NO}^+/\text{NO}_2^+$ ratio further suggested that organic nitrate formation mainly occurred at night, and also presented that organic nitrates concentrated on smaller sizes, suggesting that they were mostly local product. The calculated theoretical nighttime production potential of NO_3 reactions with VOCs measured in spring showed that six VOC species (i.e., α -pinene, limonene, styrene, camphene, β -pinene and isoprene) were notable precursors. The SOA yield analysis further indicated that α -pinene, limonene and styrene contributed mostly to nighttime formation of particulate organic nitrates in spring in Shenzhen, highlighting the unique contribution of anthropogenic VOCs in comparison with previous studies in the US and Europe. Finally, the comparison of the results in this study with other similar studies implied that nighttime formation of particulate organic nitrates is more likely NO_x -limited than VOCs-limited.

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