

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.
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- 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.