

Responses to review comments-3 (RC3, by the Anonymous Referee #3)

Title: Particulate organic nitrates in eastern China: variation characteristics and effects of anthropogenic activities

Authors: Zhang et al.

The authors analyzed four organic nitrates in ambient PM_{2.5} samples collected at four different sites in eastern China. In combination with other gaseous data, they aim to identify major controlling factors on organic nitrates formation under different atmospheric environments, mainly by examining the correlation relationship between organic nitrates and some gas species and meteorology parameters. Considering the high biogenic and anthropogenic emissions in eastern China, looking at the PNOs formation provides a good chance to explore the influence of human activities on biogenic SOA formation. However, due to limitations on the analyzing method and limited samples collected at each site and the different sampling periods, they are not able to provide a reliable seasonal/spatial/diurnal trend. While the discussion is heavily relying on correlation analysis, the factors controlling the observed PNOs are not sufficiently captured. Therefore, this paper can not be accepted in its current form.

Response: Thanks for the critical comments. It is very difficult to measure the individual organic nitrates and to get accurate measurement results due to the lack of authentic standards. Although the use of surrogate standards will add uncertainty to the absolute concentration, these data can still provide important information on the variation trends. In the revised manuscript, more information has been added to increase the reliability of the analyzing method and 34 additional samples have been supplemented to provide more reliable variation trends. The influences from boundary layer change, air mass transport, and gas-particle partition have been discussed to obtain credible conclusions.

General comments

1. While the topic is on the PNOs in eastern China, the authors only focused on six types of PNOs in the samples. As also mentioned in the discussion that the observed PNOs could be only a small fraction of the total PNOs. I wonder if the measured species here are the dominant PNOs in the samples. Since the authors have conducted HRMS analysis, they should be able to clarify what are the major PNOs formulae in their samples and whether the focused species can represent the variation characteristics of the PNOs.

Response: thanks for the comment. With the assistant of high-resolution mass spectrometry, some other potential organic nitrates are noticed, and the possible molecular formulas include C₅H₉NO₄, C₆H₁₃NO₄, C₇H₁₅NO₄, C₈H₉NO₄, C₉H₁₁NO₄, C₉H₁₉NO₄, and C₁₁H₂₃NO₄. The raw signals of these potential organic nitrates are comparable to or lower than those of the targeted organic nitrates in this study. In addition, a

newly published paper by Shi et al. (2020) has identified dozens of kinds of organic nitrates by using ToF-MS. However, most of the structures have not been confirmed and the approximate concentrations have not been quantified. In our previous unpublished study, we have tried to determine the total organic nitrate by using flourier transform infrared spectroscopy. According to the preliminary results, these six organic nitrates accounted for 15% to 75% of the total organic nitrates in different seasons. With consideration of that the fractions of the six species in total organic nitrates are not very high, the title of this manuscript has changed to “*Monoterpene and oleic acid-derived particulate organic nitrates in eastern China: variation characteristics and effects of anthropogenic activities*”. The relevant sentences in the abstract and the main text have been also changed correspondingly.

2. Several limitations should be considered regarding the analysis method. 1) Employment of surrogates that even don't contain the nitrooxy group would introduce large uncertainty for accurate quantification of PONs. 2) Compare data quantified with different surrogates introduce additional problems in the results and conclusion. As the focused point of this study is to explore the influence of anthropogenic emissions on the BSOA formation, comparison of different PNOs in concentration is not necessary. 3) Formic acid was added to the water only. As the eluent program develops, the formic acid in the mixture of the eluent will change. Formic acid was added to promote the ionization of the analytes. If the concentration of formic acid changes with time, we would expect ionization efficiency changes. This will introduce additional uncertainty in the semi-quantification. For examples, MHN215 and PSON 295 have several isomers which elute at different time. Due to the change in the formic acid concentration in the eluent, the ionization efficiency of different isomers can be different. 4) The authors reported a very low recovery efficiency of 60%. The uncertainty of the data should be evaluated carefully.

Response: 1) Thanks for the comment. The responses of n-pentane and amyl nitrate, isosorbide and isosorbide 5-nitrate in the mass spectrometer have been further determined to estimate the difference in the response caused by the nitrate functional groups. The determination results show that the difference in the response between n-pentane and amyl nitrate is $60.9 \pm 7.17\%$ and that between isosorbide and isosorbide 5-nitrate is $66.6 \pm 2.69\%$. That is, there is indeed an inherent difference between the responses of the nitrate-free surrogate standard and the organic nitrate analyte in the mass spectrometer. However, the discrepancy is below one order of magnitude. In this study, the surrogate standards we selected are quite similar to the organic nitrate analytes in structure and property (indicated by the close retention time), and the nitrate group does not cause an order of magnitude difference. Therefore, the surrogate standards can semi-quantitate the analyte and provide the information on the variation trends.

Line 186–191, “*The difference in the mass spectrum response caused by the nitrate functional group was estimated with n-pentane, amyl nitrate, isosorbide, and isosorbide 5-nitrate. The difference between n-pentane and amyl nitrate was $60.9\% \pm 7.2\%$, and the difference between isosorbide and isosorbide 5-nitrate was $66.6\% \pm 2.7\%$. Indeed, there is an inherent difference in responses of surrogate standards and analytes, and the nitrate group does not cause a difference more than one order of magnitude.*”

Therefore, the concentrations of organic nitrates can be estimated reasonably and further used for exploring the variation characteristics.”

2) The comparisons of PON concentrations quantified with different surrogates have been modified in the modified or removed in the revised manuscript. The revised descriptions are as follows.

Line 202-205: *“Among these monoterpene-derived organic nitrates, MHN215 was the dominant species, with an average concentration of 51.9–212 ng m⁻³, followed by PKN229 (10.0–113 ng m⁻³), HDCN247 (9.5–21.6 ng m⁻³) and PSON295 (3.1–9.6 ng m⁻³). Among the oleic acid-derived organic nitrates, the average concentration of OAKN359 (34.1–146 ng m⁻³) was much higher than OAHN361 (0.7–4.1 ng m⁻³).”*

Line 244-245: *“The large proportion of monoterpene-derived organic nitrates in PONs was also observed in southeastern United States (23–44% in mole) and in East Asia (Ayres et al., 2015; Lin et al., 2012)”*

The following description has been removed from the manuscript.

Line 225–226 in the original manuscript: *“MHN215 constituted the largest fraction of the identified PONs at all four sampling sites, accounting for 35–58%, followed by OAKN359 and PKN229.”*

3) Thank the reviewer’s useful comments. To make clear the difference in the responses of different isomers caused by the change in eluent compositions, we have tested five samples to compare the difference in the response under different eluent conditions. Specifically, formic acid is added in both mobile phases of methanol and water with a concentration of 0.1%, which is close to the concentration of formic acid when MHN215 is eluted in the positive ion mode. In addition, 36% formic acid is also added to the mobile phases, which is similar to the situation when PSON295 is eluted in the negative ion mode.

For the responses of the two isomers of MHN215, the relative mean deviation under the above two eluent conditions is 4.1%–2.9%. Due to the close retention time of the two isomers and the small gradient change when it was eluted, there is no significant difference in the response in the mass spectrometer and thus no obvious uncertainty in the measured concentrations of MHN215. As to PSON 295, the average relative deviation of the response of the first eluted isomer under two test conditions is 29.7±6.7%. The relative mean deviation of the second isomers is 13.4±6.7%. The slightly high difference for the two isomers of PSON 295 may be due to the relative large discrepancy in the elution time. Despite all this, it will not significantly change the relevant results and conclusion in this study, because the concentrations of PSON 295 are very low.

4) The recoveries obtained in this study to some extent depend on the molecular type of the target compounds. In the previous study, the recoveries of some similar compounds, such as pinic acid, pinonic acid, and camphor sulphonic acid, were about 74% (Kristensen and Glasius, 2011). In this study, we

have updated the recoveries for surrogate standards and evaluated the uncertainty based on a large number of recovery experiments. The following information has been updated and added in the revised manuscript.

Line 182–185, “Recoveries of (1R, 2R, 5R)-(+)-2-hydroxy-3-pinane, ricinoleic acid, and (-)-10-camphor sulfonic acid in six spiked samples were $71 \pm 9\%$, $64 \pm 4\%$, and $78 \pm 4\%$, respectively. Based on the uncertainty in the recovery ($\pm 12.7\%$) and the repeatability ($\pm 4.1\%$), the overall uncertainty for the measurements is estimated to be 13.3%.”

3. Though correlation analysis could provide some clues for explaining the observed season/diurnal/spatial trend, the actual atmospheric process should also be considered. The observed concentration of the PNOs in the particles is governed by the production, gas-particle partitioning, the atmospheric loss process, and meteorological conditions. For example, the boundary layer height can play an important role in the observed diurnal trend of PNOs. MHN215, PKN229, and LDK247 seem to be semivolatile organic compounds which will exist in both gas and particle phase. Thus the partitioning effect should be considered in the discussion. PNOs can be partly photolyzed and have relatively short lifetime against hydrolysis. These may also be important in the explanation of the results.

Response: Thanks for the helpful comments. Additional discussion on the boundary layer height change, gas-particle partitioning effect, and the losses processes has been added in the revised manuscript to explain the variation patterns of the observed particulate organic nitrates.

Line 260–264, “To verify whether the diurnal difference was aroused by the change in boundary layer height, the PNOs/PM_{2.5} ratios were also compared (see Fig. S3). The very similar diurnal trends between PNO concentrations and PNOs/PM_{2.5} ratios suggest that the boundary layer change had little influence on the diurnal difference in the concentrations of PNOs. Further cluster analysis (shown in Fig. S4) indicates that the air masses exhibited no significant difference between the daytime and nighttime sampling periods. It means that the diurnal difference was not mainly caused by air mass transport.”

Line 274–278, “At DY site in winter, the emission of BVOCs was not high in cold season and the high production of PNOs was attributed that the organic nitrates readily partition into the particle phase from the gas phase at low temperature. As reported in the previous study, the production of SOA was estimated to increase by more than 20% when the temperature dropped by 10 °C (Sheehan et al., 2001).”

Line 288–298, “On the basis of the observation data, it was difficult to see any apparent effects of photolysis and hydrolysis on the concentrations and variations of PNOs from temperature and humidity. Takeuchi and Ng (2019) comprehensively evaluated the hydrolysis processes of particulate organic nitrates which were generated from the oxidation of α -pinene and β -pinene and the results showed that the hydrolysis lifetime was fast, within 30 min. However, in this study, the concentrations of PNOs and

their ratios to PM_{2.5} in the moist conditions in summer were even higher than those in another season. With consideration of the moderate humidity in northern China, hydrolysis was not considered as the dominant factor that caused the lower concentrations of PONs at nighttime than daytime at the DY site in summer. In addition, the concentrations of PONs and their ratios to PM_{2.5} in summer with intensive solar radiation were not lower than those in other seasons. Furthermore, the organic nitrates produced from different precursors have different photochemical aging behaviors and the photolysis rates of the organic nitrates are relatively small when compared to their production rates (Nah et al., 2016; Luke et al., 1989), so photolysis was not the major factor that governed the diurnal differences of PONs in this study.”

Specific comments

1. Line 51-53. I don't get the logic to put this here. This is more related to the influence of SO₂ on BSOA formation rather than PONs production.

Response: one of the compounds studied in Surratt et al. (2008) is nitrooxy organosulfate, i.e., pinene sulfate organic nitrate (PSON295) in our study, so we cited it here in the initial manuscript. Another reference of Han et al. (2016) indicates that particle acidity facilitated the formation of particulate organic nitrates. In the revised manuscript, the former reference has been removed to avoid potential misunderstanding, and the latter reference is retained.

Line 51–52, *“Moreover, laboratory studies have shown that organic nitrates can be formed heterogeneously by acid-catalyzed reactions (Han et al., 2016).”*

2. Line 65-70. Please arrange these sentences. Why put the description of the results in southern California here?

Response: here is an example about the impacts of specific human activities on the ambient concentrations of organic nitrates after giving the general description. The related sentences have been revised.

Line 64–66, *“Day et al. (2010) found that mixed urban fossil fuel combustion was primarily responsible for the high concentrations of PONs in southern California. On the basis of latest observations of PONs in China, large disparity exists and the concentrations of PONs range from below detection limit to several micrograms per cubic meter”.*

3. Line 134. Please clarify how these numbers are determined?

Response: the ratios of SOA to SOC were assumed to be the same with the ratios of organic matters to OC reported in previous studies in the references, which were calculated by the measured OC concentrations and the measured or calculated concentrations of organic matters. The above information has been added in the revised manuscript,

Line 130–134, *“Furthermore, according to the reported ratios of organic matters (OM) to OC based on*

measurements and calculations in previous studies (Turpin and Lim, 2001; Liu et al., 2017), the OM concentrations were estimated from the OC concentrations and the SOA concentrations were estimated from the SOC concentrations by multiplying by a factor to give an estimate, i.e. 2.1, 2.2, 1.8, 1.6 and 1.6 for DY site in winter, DY site in summer, GZ, NJ, and JN sites, respectively.”

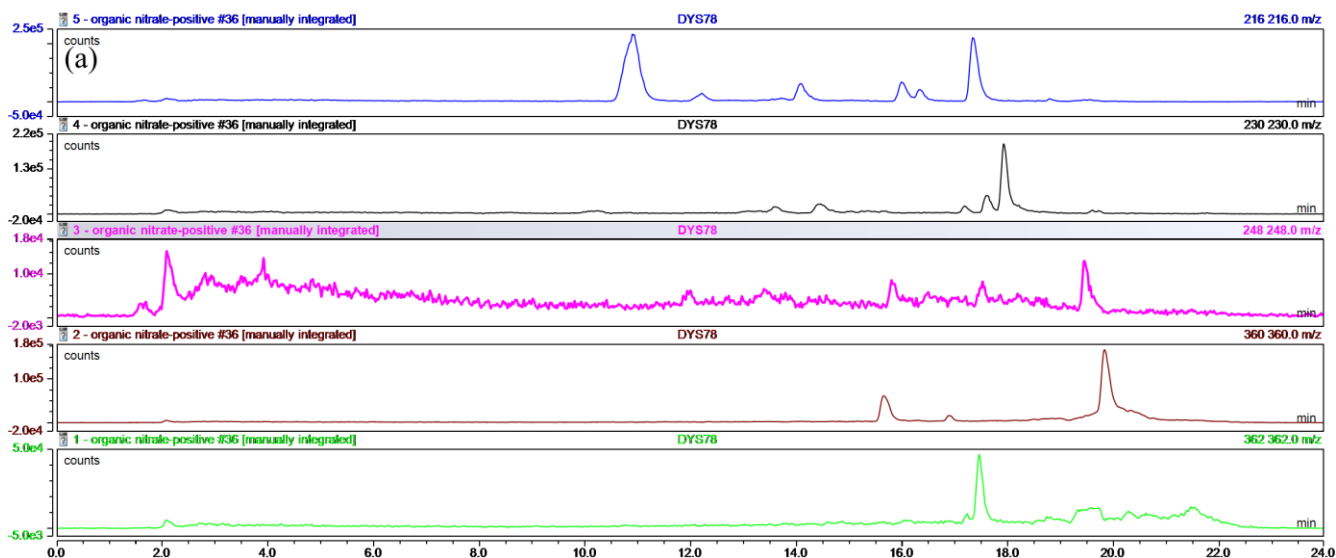
4. Line 161. Previous study by Clafine and Ziemann (2018) found that NO₃ radical oxidation of β-pinene produces di-keto nitrate.

Response: thanks for the reminder. The reference of Clafin and Ziemann (2018) has been added in Table 2 and the name of LDKN 247 has been changed into hydroxydicarbonyl nitrate (HDCN 247) to avoid misleading.

5. It is not convincing by saying “The determination results from both mass spectrometers for the same samples showed good consistency”. Please provide a chromatogram or overall mass spectra from the two instruments of the same sample.

Response: the chromatograms from two instruments have been shown in Fig. S1 in the supporting information.

Line 191–195, “In addition, the extracts of PM_{2.5} samples were analyzed partly by the triple quadrupole tandem mass spectrometer and partly by the Orbitrap mass spectrometer (chromatograms can be seen in Fig. S1). The determination results from both mass spectrometers for the same samples showed good consistency, indicating the reliability of the quantifications of organic nitrates from the low-resolution triple quadrupole tandem mass spectrometer.”



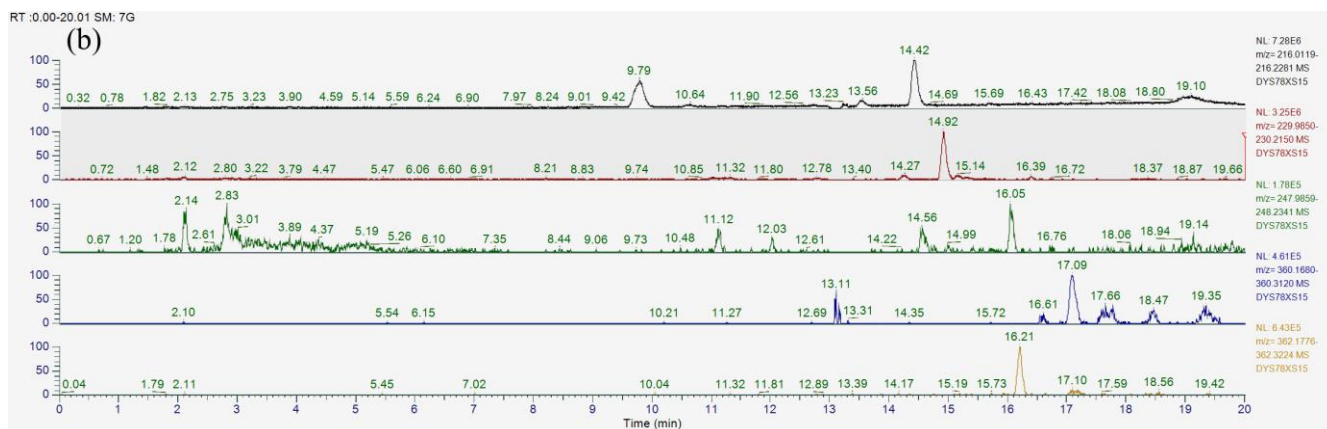


Figure S1. Chromatograms of ambient $PM_{2.5}$ samples for (a) ultra-performance liquid chromatography coupled with electrospray ionization and triple quadrupole tandem mass spectrometry and (b) ultra-high performance liquid chromatography equipped with electrospray ionization and orbitrap mass spectrometry.

6. Line 208–213. Lacking enough supporting for these discussions. First of all, the samples at four sites are collected at a different time of a year. Thus it is hard to obtain an accurate spatial trend. Secondly, as explained in the general comments, PONs are products from the interaction of biogenic and anthropogenic emissions. The emissions of VOCs and NO_x , gas-particle partitioning, environmental conditions, and loss of PNOs should be considered in understanding the spatial and temporary trend.

Response: thanks for the good comments. It has been deleted that “A comparison of different sampling sites shows that elevated PONs concentrations usually appeared at the regions with high vegetation cover.” Instead, the manuscript been revised to try to only explain the reasons why high concentrations of PONs appeared at the GZ site and the DY site in summer. The emissions of precursors, partitioning, hydrolysis and photolysis have been discussed in the revised manuscript as follows.

Line 215–220, “With examination of related pollutants and parameters, an observable increase in the concentration of PONs was noticed with the rising OM concentration at the GZ site and at the DY site in summer. However, the OM concentrations at the two sites were not very high and they did not increase proportionally with the concentration of PONs. With consideration of the high concentrations of BVOCs at the DY site in summer (see Fig. S2) and the intense photochemical activities (71.2 ppb of ozone on average), we attribute the enhanced formation of monoterpene and oleic acid-derived PONs (indicated by elevated ratios of Σ PONs/SOA) at the DY site primarily to the increase of precursors and oxidants.”

Line 221–223, “The high levels of monoterpene and oleic acid-derived PONs and the higher ratios to $PM_{2.5}$ and SOA at GZ site than was primarily ascribed to the intensive emissions of BVOCs in summer from massive broad-leaf trees in the subtropical region (Zheng et al., 2000).”

Line 226–229, “In this study, we did not see obvious evidence that photolysis or hydrolysis affected the concentration of organic nitrates. Nevertheless, the variability of the concentrations of PONs indicates that ambient temperature had non-observable effect and humidity had a positive effect on the

concentrations of PONs at the GZ site, which is not in favor of the hydrolysis loss.”

7. Line 224-232. Due to the limitation of the quantification, discussion on the composition/relative contribution of different PNOs is can hardly provide a concrete conclusion.

Response: the comparisons of the compositions and relative contributions of different PONs have been removed in the revised manuscript. In our view, some conclusion could be drawn from the proportions of the same organic nitrate at different sampling sites. For example, the larger proportion of oleic acid-derived organic nitrates at urban sites was consistent with the effect of cooking on SOA formation. Thus, this part was still retained in the revised manuscript.

Line 240–243, *“It is worth noting that OAKN359 also contributed to a large fraction (16–38%) of the Σ PONs and it was more abundant at urban sites (33–38%) than at rural sites (16–17%). Additionally, PSON295 and OAHN361 only accounted for small proportions of the Σ PONs. It is interesting that the proportion of PSON295 (6%) at the JN sites was markedly higher than those at other sites (<3%)”*

8. Line 234. I don't think in this paper the authors reported PNOs. Instead, the paper by He et al. 2014 and Lin et al. 2012 reported PSON in south China.

Response: the references have been updated in the revised manuscript by removing the reference of Ding et al. 2016 and adding the references of Lin et al 2012.

Line 244–246, *“The large proportion of monoterpene-derived organic nitrates in PONs was also observed in southeastern United States (23–44% in mole) and in East Asia (Ayres et al., 2015; Lin et al., 2012) and was ascribed to the high emissions of monoterpenes together with the relatively high production yields of PONs.”*

9. Line 242-245. These two arguments are not well supported. Since surrogate standard was used, the real concentration of acid-derived organic nitrates is hard to know. Though the oleic acid-derived organic nitrates were quantified with a considerable level, it is hard to estimate the contribution of cooking and oil processing on the SOA production from this single compound. Then you can not state like “significant influence”. For the second argument on PSON295, there is no discussion on the production and loss at all. Thus, no conclusion can be drawn.

Response: thanks for the comment. It will be appropriate to compare the relative concentrations of oleic acid-derived organic nitrate in urban and rural area. The conclusion has been revised as follows.

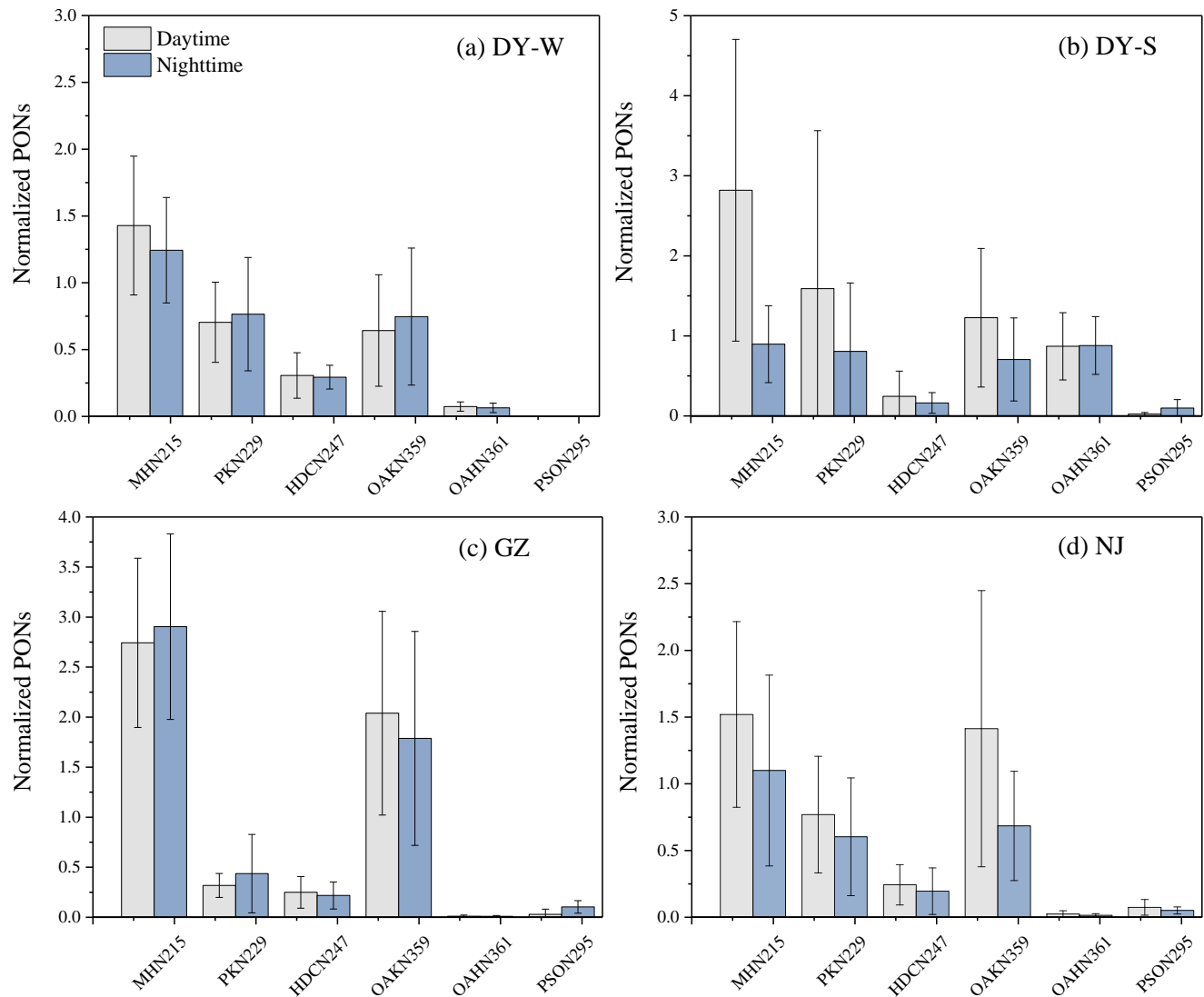
Line 253–255, *“The identification and quantification of oleic acid-derived organic nitrates in this study confirm that the impact of cooking and oil processing on SOA in urban areas is more obvious than that in rural areas in eastern China.”*

The description on PSON295 here, “As for PSON295, the relatively high contribution at urban Jinan is possibly associated with the massive coal-fired industries distributed throughout the city” has been removed, and the influence on PONs concentrations from coal combustion has been discussed in Section

3.3.1.

10. Line 250-256. The atmospheric boundary layer height could also play an important role in the diurnal trend, especially for those that nighttime concentrations were higher.

Response: to verify whether the boundary layer height change affected the diurnal patterns of PONs, the daytime and nighttime ratios of PONs to $PM_{2.5}$ are compared (see Fig. S3 in the supporting information). As shown, the diurnal difference in the ratios of PONs to $PM_{2.5}$ are quite similar to those in the concentrations of PONs, confirming that the diurnal variations of PONs observed in this study are not caused by the boundary layer height change.



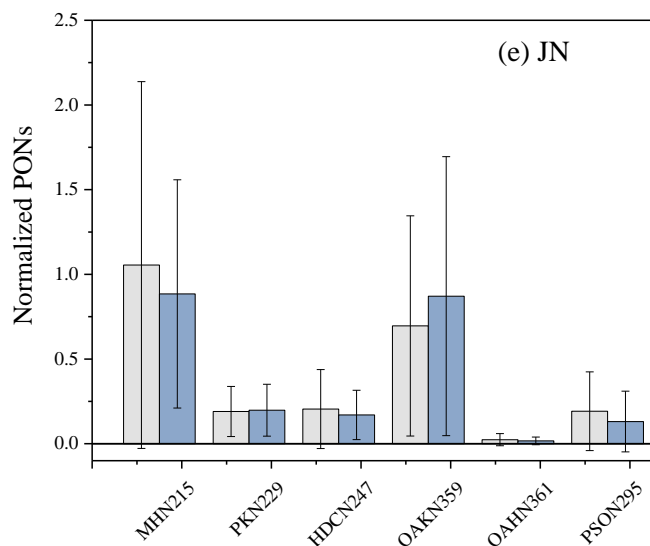


Figure S3. The differences in PONs/PM_{2.5} ratios during daytime and nighttime at different sampling sites.

Line 257–263, “Figure 3 shows the average concentrations of individual PONs during daytime and nighttime at four sampling sites. Generally, the daytime concentrations of PONs were comparable to those at nighttime ($p > 0.1$ for most sites). However, some differences were found between the daytime and nighttime concentrations of individual PONs. Particularly, at the DY site in summer, MHN215 and PKN229 exhibited obviously higher contributions at daytime than those at nighttime ($p < 0.01$). To verify whether the diurnal difference was aroused by the change in boundary layer height, the PONs/PM_{2.5} ratios were also compared (see Fig. S3). The very similar diurnal trends between PON concentrations and PONs/PM_{2.5} ratios suggest that the boundary layer change had little influence on the diurnal difference in the concentrations of PONs.”

11. Line 257-262. When discussing the seasonal trend, production due to emissions and reaction rate change can be important. However, the loss of PNOs due to photolysis and hydrolysis (Nah et al., 2016; Takeuchi and Ng, 2019) can be also different. These should also be considered.

Response: thanks for the comment. We assume that the “seasonal trend” mentioned by the reviewer here meant diurnal difference. Photolysis and hydrolysis have been considered when discussing the seasonal trends in the revised manuscript. Photolysis in the condition of intensive sunlight will reduce the PON concentrations during daytime in summer, while hydrolysis in the condition of high humidity will cause a decrease in the concentrations of PONs particularly at nighttime. Takeuchi and Ng (2019) comprehensively evaluated the hydrolysis processes of particulate organic nitrates which were generated from the oxidation of α -pinene and β -pinene and the results showed that the hydrolysis lifetime was fast, within 30 min. However, in this study, the concentrations of PONs and their ratios to PM_{2.5} in moist conditions in summer were even higher than those in other seasons. With consideration of the moderate humidity in northern China, hydrolysis is not considered as the dominant factor causing the diurnal difference at the DY site in summer. In addition, the concentrations of PONs and their ratios to PM_{2.5} in

summer with intensive solar radiation were not lower than those in other seasons. Furthermore, the particulate organic nitrates produced from different precursors have different photochemical aging behaviors and the photolysis rates of the organic nitrates are relatively small when compared to their production rates (Nah et al., 2016; Luke et al., 1989), so in our view photolysis is not the major factor that governed the diurnal difference of PONs in this study. The following discussion has been added in the revised manuscript.

Line 288–298, *“On the basis of the observation data, it was difficult to see any apparent effects of photolysis and hydrolysis on the concentrations and variations of PONs from temperature and humidity. Takeuchi and Ng (2019) comprehensively evaluated the hydrolysis processes of particulate organic nitrates which were generated from the oxidation of α -pinene and β -pinene and the results showed that the hydrolysis lifetime was fast, within 30 min. However, in this study, the concentrations of PONs and their ratios to $PM_{2.5}$ in the moist conditions in summer were even higher than those in other season. With consideration of the moderate humidity in northern China, hydrolysis was not considered as the dominant factor that caused the lower concentrations of PONs at nighttime than daytime at the DY site in summer. In addition, the concentrations of PONs and their ratios to $PM_{2.5}$ in summer with intensive solar radiation were not lower than those in other seasons. Furthermore, the organic nitrates produced from different precursors have different photochemical aging behaviors and the photolysis rates of the organic nitrates are relatively small when compared to their production rates (Nah et al., 2016; Luke et al., 1989), so photolysis was not the major factor that governed the seasonal differences of PONs in this study.”*

12. Line 289-290. Back trajectory analysis for this day and other sampling days showing different transportation is very helpful to support this argument.

Response: the back trajectory analysis has been added in the supporting information (Fig. S6).

Line 326–328, *“The relatively high levels of SO_2 on 22 and 23 October were ascribed to the transport of plumes from coal-fired industries such as steel plants and thermal power plants in the northeast sector of Jinan City under the influence of northeast winds (see Fig. S6).”*

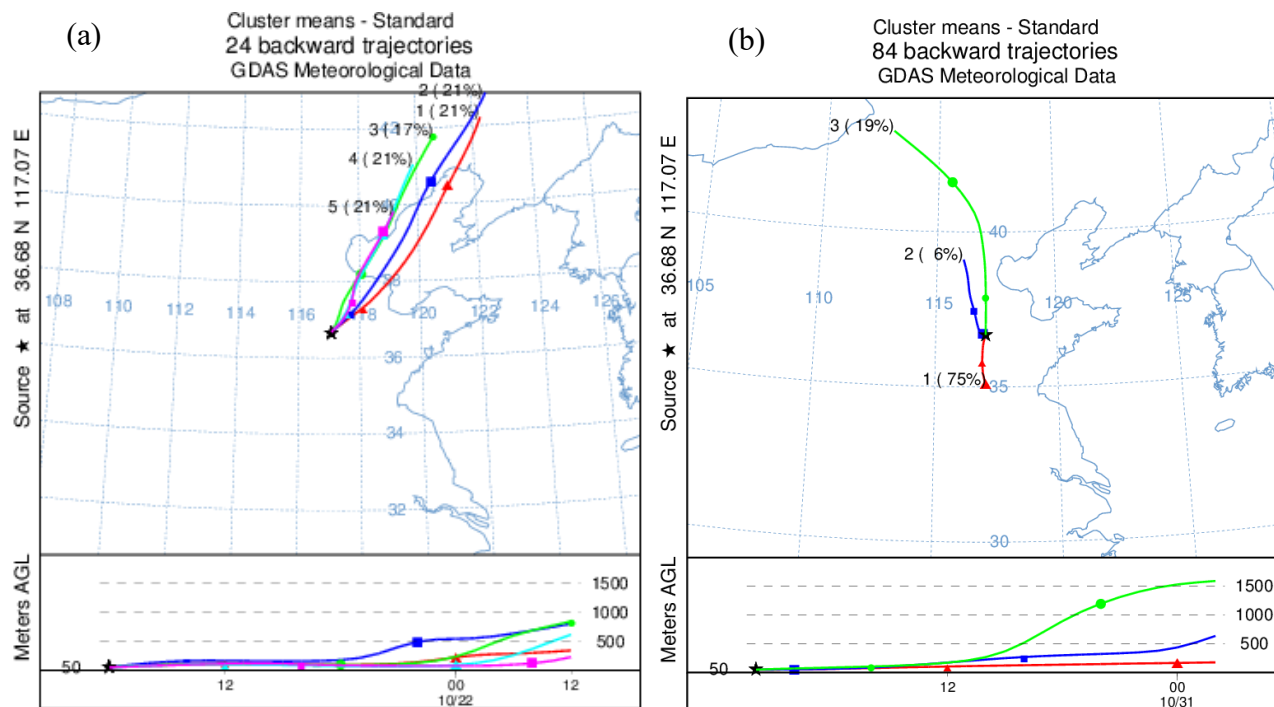


Figure S6. Air masses clusters classified by the 24-h backward trajectories at the JN site (a) on 22 and 23 October and (b) from 25 to 31 October.

13. Line 297-300. While this study focused on the secondary produced PNOs in the atmosphere, it is hard to believe that the NO and NO₂ data has never been shown. For the discussion here, figures showing poor correlations between NO_x and PONs are of equal importance as figures showing good correlation between PNOs and SO₂.

Response: the NO₂ data are shown in Table 3. The NO data are only available at the DY site in summer and thus are not shown in Table 3. The scatter plot showing the correlation between NO₂ and PONs has been added in Figure 6 (see Fig. 6b).

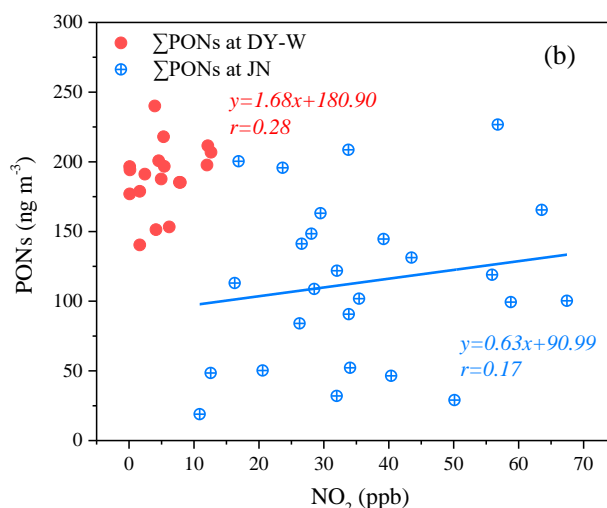


Figure 6b. Correlation plots between PONs and NO₂ at the DY site in winter and at the JN site.

14. Line 312-314. If this is the contribution of the CI+SO₂ pathway, I will double that this can affect LDK247 production significantly. 1) in this calculation, lots of parameters are needed, such as NO₃ radical concentration, NO mixing ratio, and SO₂ mixing ratio. The values being used in this calculation should be clarified, especially for NO which is never shown elsewhere. 2) to show the influence the SO₂, the author may do the calculation in an alternative way. That is to vary the SO₂ concentration in a reasonable range while fixing other parameters. Then the authors may see how can this pathway contribute to the LSK247 production.

Response: Thanks for the comment and suggestion. The data used in the calculation has been clarified. The calculation method has been added in the revised manuscript.

Line 354–358, “*Here, the observed SO₂ concentration at JN site at the daytime (4.9 ppb) and night (4.1 ppb) was used. The NO concentration was assumed to be 5 ppb at daytime and 15 ppb at nighttime, respectively, according to the filed measurements at the same site in late summer/early autumn in 2014 (Wang et al., 2017). The concentration of NO₃ radical was calculated as 0.26 ppt at nighttime using $[NO_3] = [N_2O_5]/(K_{eq}[NO_2])$ (Sander et al. 2006), in which $[N_2O_5]=50$ ppt and $[NO_2]=35$ ppb (Wang et al., 2017).*”

Line 358–360, “*Under the conditions of fixed concentrations of the above species and only the chemical generation being considered, when the SO₂ concentration changed from 0.8 ppb to 8.2 ppb at the JN site, the increase in the contribution of the CIs+SO₂ pathway to the HDCN247 production varied from 0.5% to 15.4%.*”

15. Line 340-341. This is contradictory to the argument by the author that CI+SO₂ have potential influence on PNOs formation. As elevated O₃ concentration would promote CI production.

Response: high levels of ozone can lead to the high concentrations of OH radicals during the daytime, especially in the summer when the solar radiation is intensive. The increase in the OH radical concentration will enhance the formation of organic nitrates. In addition, the elevated concentrations of ozone also promote the production of CIs. The produced CIs are ready to react with not only SO₂ but also NO, NO₂, and CO to form some intermediate products (e.g., 3-isopropenyl-6-oxoheptanal) and finally produce organic nitrates. The contribution of the CIs+SO₂ pathway firstly depends on the SO₂ concentrations of, and secondly relies on the ozone concentrations. At the rural area of DY, during the heating period in winter, a large amount of coal was burned nearby for residential heating and cooking. However, there were rare coal combustion activities near the sampling site, because there was no heating demand. Therefore, CIs+SO₂ pathway did not play an important role in the formation of PONs in summer at the DY site..

Line 385–386, “*Exposed to ozone-rich atmosphere, PONs concentrations were moderately correlated*

with ambient ozone concentrations (Fig. 8, $r = 0.55$, $p < 0.05$.)”

16. As I mentioned before, figures showing good correlation and poor correlation are of equal importance. This comparison provides us a more clear impression of the results.

Response: the scatter plots showing the correlation between PONs and $\text{NO}_2 \cdot \text{O}_3$ at other sites have been added in Fig. 9b.

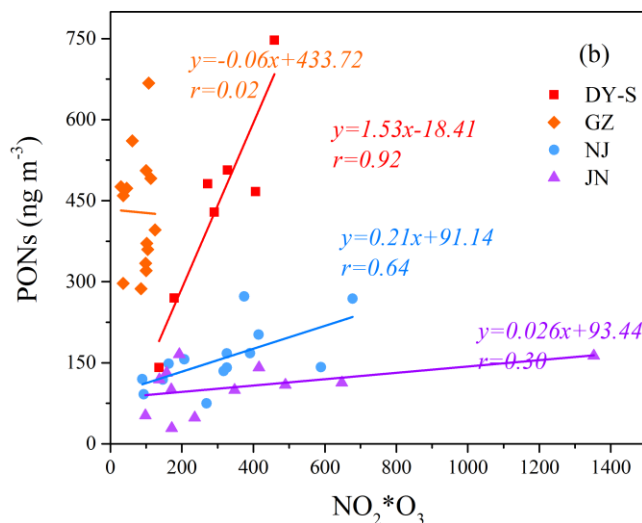


Figure 9b. Scatter plot and the correlations of PONs the concentration product of O₃ and NO₂ at nighttime at the four sites.

17. Line 374-375. Please provide NO data to support this. Since NO is one of the key species in PNOs formation, I suggest the authors to put NO, NO₂ data in table one.

Response: the concentrations of NO₂ are shown in Table 3. However, the NO data are not available at present at most sampling sites, so they are not included in Table 3.

18.

Errors

1. Line 49, replace “higher” with “low”

Response: Thanks for the correction. It has been corrected in the revised manuscript.

2. Line 50. Change “a mechanism catalyzed by aerosol acidity” to “acid-catalyzed reactions”

Response: changed.

3. Line 114. Change “contained” to “shown”

Response: changed.

4. Line 167. Add “with” after “identified”

Response: added.

5. Line 304. Delete the space before PNOs

Response: deleted.

6. Figure 5, “LDKN248” should be “LDKN247”

Response: changed with the new name of HDCN247.

7. Table 2, “(MW = 295, PSON 295” should be “(MW = 295, PSON 295)”

Response: changed.

References:

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