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.

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 PONs 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 wether the focused species can represent the variation characteristics of the PNOs.

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.

3. Though correlation analysis could provide some clues for explaining the observed season/diurnal/spatial trend, the actuall atmospheric process should also be considered.

The observed concentration of the PNOs in the particles is governed by the production, gas-particle portioning, the atmospheric loss process, and meteorological conditions . For example, the boundary layer height can play an important role in the observed diurnal trend of PONs. 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. PONs can be partly photolyzed and have relatively short lifetime against hydrolysis. These may also be important in the explanation of the results.

Specific comments

1. Line 51-53. I don't get the logic to put this here. This is more related to the influence of SO_2 on BSOA formation rather than PONs production.

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

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

4. Line 161. Previous study by Clafine and Ziemann (2018) found that NO_3 radical oxidation of b-pinene produces di-keto nitrate.

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.

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 NOx, gas-particle partitioning, environmental conditions, and loss of PNOs should be considered in understanding the spatial and temporary trend.

7. Line224-232. Due to the limitation of the quantification, discussion on the composition/relative contribution of different PNOs is can hardly provide a concrete conclusion.

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.

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.

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

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.

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

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 NO_2 data has never been shown. For the discussion here, figures showing poor correlations between NOx and PONs are of equal importance as figures showing good correlation between PNOs and SO_2.

14. Line 312-314. If this is the contribution of the CI+SO_2 pathway, I will double that this can affect LDK247 production significantly. 1) in this calculation, lots of parameters are needed, such as NO_3 radical concentration, NO mixing ration, and SO_2 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 SO_2, the author may do the calculation in an alternative way. That is to vary the SO_2 concentration in a reasonable range while fixing other parameters. Then the authors may see how can this pathway contribute to the LSK247 production.

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.

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.

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.

Errors

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

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

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

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

5. Line 304. Delete the space before PNOs

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

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

Reference

Claflin, M. S. and Ziemann, P. J.: Identification and Quantitation of Aerosol Products of the Reaction of β-Pinene with NO3 Radicals and Implications for Gas- and Particle-Phase Reaction Mechanisms, The Journal of Physical Chemistry A, 122, 3640-3652, 2018.

Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in Humic-like Substance Fraction Isolated from Aerosols at Seven Locations in East Asia: A Study by Ultra-High-Resolution Mass Spectrometry, Environ. Sci. Technol., 46, 13118-13127, 2012.

Nah, T., Sanchez, J., Boyd, C. M., and Ng, N. L.: Photochemical Aging of α-pinene and β-pinene Secondary Organic Aerosol formed from Nitrate Radical Oxidation, Environ. Sci. Technol., 50, 222-231, 2016.

Takeuchi, M. and Ng, N. L.: Chemical Composition and Hydrolysis of Organic Nitrate Aerosol Formed from Hydroxyl and Nitrate Radical Oxidation of α-pinene and β-pinene, Atmos. Chem. Phys. Discuss., 2019, 1-39, 2019.