Point-by-point response to review comments

Manuscript ID: egusphere-2024-4103

Title: "Significant secondary formation of nitrogenous organic aerosols in an urban atmosphere revealed by bihourly measurements of bulk organic nitrogen and comprehensive molecular markers"

Author(s): Xu Yu, Min Zhou, Shuhui Zhu, Liping Qiao, Jinjian Li, Yingge Ma, Zijing Zhang, Kezheng Liao, Hongli Wang, Jian Zhen Yu

We thank the reviewer for his/her constructive comments. Each of these comments has been addressed and detailed in our point-by-point response given below. The exact comment text from the reviewer is in black and italic style while our response text is in blue and normal format in this document. The revised texts are marked in blue in the highlighted manuscript. The line numbers mentioned below refer to those in the revised manuscript.

Comments

This manuscript presents an investigation into the sources and formation mechanisms of nitrogenous organic aerosols (ON) in an urban atmosphere, leveraging a new analytical technique for bulk ON quantification and high-resolution source apportionment. The study's strengths lie in its measurement approach, comprehensive source marker analysis, and identification of secondary ON formation pathways, including nitrate formation, photochemical oxidation, and DCA-associated reduced-N species. Several critical gaps in scientific rigor, data interpretation, and presentation weaken the manuscript's impact. Key concerns include incomplete source apportionment due to unclear presentation in methodology, insufficient mechanistic evidence for DCA_ON formation. Addressing these issues would significantly strengthen the manuscript's contribution to atmospheric chemistry and air quality research.

Response: Thanks for the summary of our work and the overall comments. Please see below for our point-by-point response to your concerns.

1 *The method used for total nitrogen estimation in this study is not commercially available. Additional details regarding the calibration procedure for total nitrogen quantification using this instrument should be provided. The IN and ON datasets should be cross-validated using independent measurements. For instance, it would be important to demonstrate whether water-soluble inorganic nitrate concentrations correlate strongly with the inorganic nitrogen values quantified in this study.*

Response: Please note that the introductions and validations of our new method for quantifying aerosol IN and ON have been detailed in our previous publications. The first paper was published in 2021 (Yu et al., 2021, Simultaneous determination of aerosol inorganic and organic nitrogen by thermal evolution and chemiluminescence detection, Environ Sci Technol, 55, 11579−11589, doi.org/10.1021/acs.est.1c04876). In this paper, the principle of simultaneous determination of aerosol IN and ON has been

elaborated. The accuracy of IN (including NO_3^--N and NH_4^+-N) measurement by the new method has been validated by comparing with ion chromatography (IC) measurements. The results indicated that IN quantities measured by the new method and by IC showed excellent agreement, with both the slope and R-squared value of the linear regression being 0.99, and a negligible intercept. Please refer to Yu et al., 2021 for more details of method characterization and validation. Subsequently, the new analytical approach was applied to online measurements of aerosol IN and ON. Please refer to Li et al. (2022) and Yu et al. (2023). To sum up, we have, in our previous work, demonstrated the robustness of aerosol IN and ON measurement using the new method.

In this study, we have referenced our previous work and briefly introduced the new method as shown in the Methodology section. Nevertheless, we agree with the reviewer that more details on the calibration and cross-validation would be helpful. Accordingly, we have added more descriptions in the revised Methodology section.

> Line 139-144: "4-methyl-imidazole served as the calibration standard for C and N measurements, with systematic calibrations conducted twice monthly. Example calibration curves could be found in Yu et al. (2023) … A comparative analysis of aerosol IN concentrations obtained through the new method and those measured by the Monitor for AeRosols and GAses (MARGA) system was presented in Figure S1."

2 *The terms "Significant" and "significantly" are overused throughout the manuscript (lines 181, 339, 463, 353), yet no quantitative data or statistical evidence (e.g., percentage) are provided to substantiate these claims. For example, when stating that a result is "significant," the authors should clarify how significant it is (e.g., "a 30% increase with 95% confidence") rather than relying on qualitative assertions. Note that the term "significant" carries strong inferential weight in scientific writing; its use in the main text should be reserved for findings supported by rigorous statistical analysis.*

Response: We have read through the manuscript and replaced instances of "significant" with more appropriate expressions where no statistical significance is implied.

> Line 222: "significant presence" → "high loadings"
>
> Line 260: "significant" → "considerable"
>
> Line 271: "significant" → "remarkable"
>
> Line 351: "significantly" → "largely"
>
> Line 426: "significant" → "potential"
>
> Line 452: "significant" → "notable"
>
> Line 462: "significant" → "large"

3 *The assertion in line 194 that the primary sources of OC and ON "did not change across seasons" is questionable. For example, biomass burning and coal combustion are known to contribute seasonally variable OC/ON contributions. The authors should provide supplemental data or additional evidence (e.g., time-resolved source apportionment results) to support this claim in this study, particularly given evidence from prior studies demonstrating no seasonal shifts of ON and OC.*

Response: Sorry for causing the confusion. Here, we intend to express that the categories of major primary sources of OC and ON did not change across seasons. As revealed from this and our previous study, vehicle emissions and coal combustion were dominant sources of OC and ON in both summer and fall-winter time in urban Shanghai. However, the absolute contributions of vehicle emissions and coal combustion to OC and ON in fall-winter were much higher than in summer.

Biomass burning might be enhanced during fall-winter time in many regions of China, as revealed by previous studies. In this study, the PMF analysis resolved a primary biomass burning factor and an aged biomass burning factor (i.e., the nitrocatechol formation processes factor). The biomass burning-related ON was apportioned to the aged biomass burning factor. We have discussed the contributions of (aged) biomass burning to ON in the manuscript:

> Line 249-255: "Biomass burning has been recognized as an important source of aerosol ON (Mace et al., 2003; Chen and Chen, 2010; Yu et al., 2017). In this study, we found that a negligible fraction of ON was apportioned to the primary biomass burning factor while a notable presence (7.2%) of ON in the factor of nitrocatechol formation processes (Figure 2). Nitrocatechols are likely formed through atmospheric reactions between NO_x and catechols emitted from biomass burning. This secondary formation pathway was supported by the good correlation between levoglucosan and nitrocatechols (Figure S7)."

In the revised manuscript, we have rephrased the sentence:

> Line 196-197: "Since the categories of major primary sources of OC and ON did not change much at the urban site over seasons, which is discussed below…"

4 *The uncertainty associated with the 18 identified factors requires further verification. (a) The correlation matrix between factors should be presented to evaluate their interdependence.*

Response: We have created a correlation matrix between the resolved factors. The matrix table is displayed below and added as Table S2 in supporting information. We have also added more discussions in text S1 in the supporting information: "There were no strong correlations (R≥0.7) between the resolved factors, indicating that overall, the 18 factors were independent of each other and represented 18 distinct sources."

Table R1. Correlation (R) matrix between the PMF-resolved factors.

	β-caryophyllene SOA formation	Nitrocatechol formation	Phthalic acid formation	Nitrophenol formation	Vehicle emission	Dicarboxylic acid formation	Cooking emission	Residue oil combustion	Photochemical formation	Sea salt emission	Biomass burning	Coal combustion	Industrial emission	Nitrate formation	Sulfate formation	Soil dust	Isoprene&α-pinene SOA formation	Oxygenated cooking OA
β-caryophyllene SOA formation	1.00																	
Nitrocatechol formation	0.29	1.00																
Phthalic acid formation	0.24	0.30	1.00															
Nitrophenol formation	0.07	0.65	0.21	1.00														
Vehicle emission	0.43	0.58	0.12	0.47	1.00													
Dicarboxylic acid formation	0.37	-0.10	0.23	-0.22	-0.08	1.00												
Cooking emission	0.27	0.43	0.16	0.28	0.59	-0.08	1.00											
Residue oil combustion	0.26	0.20	0.01	0.23	0.32	0.26	0.01	1.00										
Photochemical formation	-0.17	-0.41	-0.06	-0.45	-0.63	0.21	-0.37	-0.37	1.00									
Sea salt emission	-0.18	0.12	-0.08	0.32	0.07	-0.26	0.06	-0.06	-0.14	1.00								
Biomass burning	0.35	0.20	0.23	0.03	0.23	0.26	0.06	0.13	-0.40	-0.13	1.00							
Coal combustion	0.22	0.54	0.14	0.50	0.42	-0.01	0.14	0.30	-0.43	0.05	0.37	1.00						
Industrial emission	0.29	0.43	0.12	0.34	0.56	0.03	0.33	0.24	-0.21	0.13	0.00	0.40	1.00					
Nitrate formation	0.32	0.48	0.42	0.32	0.37	0.15	0.23	0.21	-0.22	0.05	0.23	0.44	0.33	1.00				
Sulfate formation	-0.19	0.03	0.19	0.18	-0.16	0.04	-0.18	-0.07	0.07	0.06	-0.02	0.17	-0.02	0.41	1.00			
Soil dust	0.21	0.26	-0.08	-0.02	0.39	-0.05	0.28	-0.01	0.03	-0.16	-0.07	0.10	0.42	0.18	-0.10	1.00		
Isoprene&α-pinene SOA formation	0.46	0.10	0.54	0.00	0.06	0.69	0.06	0.25	0.00	-0.09	0.34	0.08	0.05	0.31	0.07	-0.16	1.00	
Oxygenated cooking OA	0.24	0.14	0.32	0.06	0.23	0.07	0.29	0.06	-0.25	-0.14	0.23	-0.04	0.01	0.21	-0.25	0.21	0.24	1.00

(b) *The observation that no organic nitrogen (ON) was attributed to biomass burning or isoprene/α-pinene SOA factors (lines 232-233) is unexpected and conflicts with extensive evidence. Biomass burning is a well-documented source of nitrogen-*

containing organic aerosols (OA) in both rural and urban environments. (Li et al., 2023) Similarly, biogenic VOC (BVOC) oxidation under high-NOx or NO3 radical-dominated conditions has been shown to produce ON (Xu et al., 2014). The authors should reconcile these discrepancies by either (1) re-examining their receptor modeling framework, (2) acknowledging limitations in source apportionment resolution.

Response: We thank the reviewer's comment. We take this opportunity to clarify that in the resolved PMF source factors, two of them are related to biomass burning (BB), a primary BB factor characterized by high loadings of levoglucosan, mannosan, and galactosan, and an aged BB factor indicated by the dominant presence of nitrocatechols. BB-related ON was apportioned to the aged biomass burning factor.

We have revised the discussions on the contribution of biomass burning to ON in the manuscript:

> Line 249-255: "Biomass burning has been recognized as an important source of aerosol ON (Mace et al., 2003; Chen and Chen, 2010; Yu et al., 2017). In this study, we found that a negligible fraction of ON was apportioned to the primary biomass burning factor while a notable presence (7.2%) of ON in the factor of nitrocatechol formation processes (Figure 2). Nitrocatechols are likely formed through atmospheric reactions between NO_x and catechols emitted from biomass burning. This secondary formation pathway was supported by the good correlation between levoglucosan and nitrocatechols (Figure S7)."

The potential contribution to ON aerosol from organic nitrate formation involving the reactions between BVOCs (oxidation products) and NO_x/NO_3 radicals might be reflected by the ON mass associated with nitrate formation processes. In this study, we found a substantial fraction (14%) of ON was distributed in the factor of nitrate formation processes. As we proposed in the manuscript: "The ON associated with nitrate formation processes may indicate the formation of organic nitrates, which share common precursor of NO_x with nitrate." ON had stronger correlations with NO_x (R^2=0.45) and nitrate (R^2=0.39) compared to biogenic SOA tracers (R^2=0.18), which might be the reason that organic nitrate went to the factor of nitrate formation processes rather than biogenic SOA factors when conducting PMF analysis. This result might be linked to the differences in the underlying formation mechanisms of organic nitrates and biogenic SOA tracers, but currently they are not well understood.

We have added more discussions in the manuscript:

> Line 295-304: "SOA formation from isoprene and α-pinene oxidation contributed insignificantly to the observed ON. While it is known that reactions between biogenic volatile organic compounds such as isoprene and α-pinene with NO_x or NO_3 radicals can yield organic nitrates, such contributions may have been captured within the nitrate formation factor, rather than the biogenic SOA factors, in the PMF analysis. This interpretation is supported by correlation analysis, where ON showed stronger associations with NO_x (R^2 = 0.45) and nitrate (R^2 = 0.39) than with isoprene- and α-pinene-derived SOA tracers (R^2 = 0.18–0.19). The apparent allocation of biogenically derived organic nitrates to the nitrate formation factor may reflect differences in the formation mechanisms of organic nitrates versus those of traditional biogenic SOA tracers. However, the specific chemical pathways

governing these processes remain insufficiently understood and warrant further investigation."

We acknowledge uncertainties of PMF modeling in apportioning sources to ON aerosol, despite we tried our best to obtain a "most reasonable" PMF solution. We have acknowledged the uncertainties in the "Conclusion and implications" section in the manuscript.

(c) *The proposed formation pathway for ON from oxidized cooking emissions lacks mechanistic clarity and experimental support. The authors should either (1) provide chemical speciation data (e.g., HRMS) linking cooking-derived organic compounds to ON precursors, (2) reference chamber studies demonstrating this pathway, or (3) propose a plausible reaction mechanism (e.g., radical-induced coupling of cooking-derived VOCs with NOx). Without such evidence, this conclusion remains speculative.*

Response: Thanks for the suggestions. Previous chamber studies have suggested that N_2O_5/NO_3 radicals could effectively react with unsaturated fatty acid particles from cooking emissions, leading to the formation of organic nitrates (Gross et al., 2009; Zhao et al., 2011). In the revised manuscript, we have added more discussions of ON formation associated with cooking oxidation processes.

Line 275-277: "The formation of ON compounds associated with oxygenated cooking OA likely involves the reactive uptake of N_2O_5/NO_3 radicals by unsaturated fatty acid particles, leading to the production of organic nitrates (Gross et al., 2009; Zhao et al., 2011)."

5 *The strong correlation between DAC_ON and NH_4^+ (line 324) requires further scrutiny. While demonstrating agreement between these variables is important, the authors must also rule out potential correlations with other PMF factors (e.g., Nitrate_ON) to confirm the specificity of this relationship.*

Response: Ammonia (NH_3), as the most abundant atmospheric base, forms ammonium (NH_4^+), which readily associates with acidic species, both inorganic (e.g., nitrate, sulfate) and organic acids (e.g., dicarboxylic acids, DCAs). Therefore, a positive correlation with NH_4^+ is not expected to be specific to DCAs alone. Accordingly, our intention was not to use the NH_4^+–DCA_ON correlation to suggest a unique or exclusive association, but rather to support the broader hypothesis that DCA-related organic nitrogen (DCA_ON) likely contributes to reduced ON. Additional details addressing this comment are provided below.

We examined the correlations between NH_4^+ and other secondary ON factors identified by PMF. NH_4^+ showed weak correlation with photochemical formation-ON and oxygenated cooking-ON (R^2 < 0.1), a moderate correlation with nitrocatechol formation-ON (R^2 = 0.19), and a strong correlation with nitrate-ON (R^2 = 0.84). The strong NH_4^+–nitrate-ON correlation is primarily attributed to the well-known association between NH_4^+ and nitrate (NO_3^-). Furthermore, since both nitrocatechols and nitrate originate from NO_2, a moderate correlation (R^2 = 0.23) was observed between nitrocatechol and nitrate, which may explain the apparent correlation between nitrocatechol formation-ON and NH_4^+. However, a significant correlation does not

necessarily imply a direct mechanistic contribution. As discussed in the manuscript, nitrocatechol formation-ON and nitrate-ON are more likely associated with oxidized ON species, such as nitroaromatic compounds and organic nitrates. In contrast, the observed association between DCA_ON and NH_4^+ has a more plausible mechanistic basis. Organic acids like DCAs can react with NH_3/NH_4^+ to form organic ammonium salts, which may undergo further reactions, such as dehydration, to produce amides—components commonly classified as reduced ON. This mechanistic pathway motivated our analysis of the DCA_ON–NH_4^+ relationship. We found a clear positive correlation, which provides observational support for the potential formation of reduced ON species involving DCAs.

While we acknowledge that a positive correlation with NH_4^+ is not exclusive to DCA_ON, the combination of observational evidence (detailed in Section 3.3) and mechanistic plausibility strengthens our interpretation that DCA-related ON likely contributes to reduced ON formation.

We have made some modifications to the revised manuscript:

> Lines 361-364: "Overall, while we acknowledge that a positive correlation with NH_4^+ is not exclusive to DCA_ON, the combination of observational evidence described above and mechanistic plausibility strengthens our interpretation that the DCA-related ON likely contributes to reduced ON formation."

6 *The statement in lines 393–396 that higher relative humidity (RH) promotes DCA_ON formation directly contradicts the evidence presented in Figure 3b, which shows that higher pH enhances DCA_ON formation. Higher RH usually leads to higher pH values.*

Response: We apologize for causing this confusion. Here, we have re-examined our results: according to Figure S9 in the supporting information, we found that, overall, the concentrations of DCAs and hDCAs increased with rising RH. However, some extremely high concentrations of DCAs and hDCAs were also observed under moderate RH conditions (50-70%), suggesting the influence of other contributing factors. Figure 3 shows the correlations between DCA_ON and NH_4^+ during periods where DCA_ON exhibited a continuous increase over a few hours. These cases were grouped into higher slope cases and lower slope cases. A higher-slope value indicated a more rapid formation of DCA_ON at a given concentration of NH_4^+. We found that the averaged aerosol liquid water (ALW) content, estimated using the thermodynamic equilibrium model ISORROPIA II with MARGA data, was much lower in higher slope cases (11.3 $\mu g\ m^{-3}$) compared to lower slope cases (49.6 $\mu g\ m^{-3}$). This finding is consistent with the lower pH values in higher slope cases.

The occurrences of higher and lower slope cases appeared to be mainly attributed to the differences in atmospheric oxidation capacity, which led to substantial variations in concentration of DCAs–the precursors of DCA_ON. The higher-slope cases corresponded to perods with stronger atmospheric oxidation capacity, as indicated by elevated level of ozone. This enhanced formation of DCAs likely accounted for the more rapid formation of DCA_ON. In comparison, RH and pH did not explicitly facilitate the rapid formation of DCA_ON.

In the revised manuscript, we have re-organized the elaboration. To avoid confusion, we have removed the discussions of influences of RH and pH on DCAs / DCA_ON formation. Specifically, we deleted the sentences of "In this study, the concentration of DCAs increased with rising relative humidity (RH) (Figure S9), suggesting a higher RH could enhance the aqueous formation of DCAs and/or the gas-to-particle partitioning of DCAs" and "Additionally, the higher-slope cases were associated with lower pH values (higher acidity) as calculated using the thermodynamic equilibrium model ISORROPIA II with MARGA data (Figure 3b). The lower pH facilitated the gas-to-particle partitioning of NH_3 and subsequent reactions involving DCAs and NH_3."

We have replaced the comparison of pH between the higher and lower slope cases in Figure 3b with a comparison of ΔDCAs (the differences in DCAs concentrations at the beginning and end of each case) for the two groups. Accordingly, we have added the following discussion to the manuscript:

> Line 355-356: "This argument was supported by the overall greater increase in DCA concentrations observed in the higher-slope cases (Figure 3b)".

7 *Methodology sections switch between past and present tenses (e.g., "We have developed... All measurements were carried out..."). Standardize to past tense for consistency.*

Response: We have revised all present tenses to past tense in the Methodology section when applicable.

References:

Gross, S., Iannone, R., Xiao, S. and Bertram, A. K., Reactive uptake studies of NO_3 and N_2O_5 on alkenoic acid, alkanoate, and polyalcohol substrates to probe nighttime aerosol chemistry, Phys. Chem. Chem. Phys., 11, 7792–7803, 2009.

Huang, D. D., Zhu, S. H., An, J. Y., Wang, Q. Q., Qiao, L. P., Zhou, M., He, X., Ma, Y. G., Sun, Y. L., Huang, C., Yu, J. Z., and Zhang, Q.: Comparative Assessment of Cooking Emission Contributions to Urban Organic Aerosol Using Online Molecular Tracers and Aerosol Mass Spectrometry Measurements, Environ. Sci. Technol., 55, 14526−14535, 2021.

Li, J. J., Yu, X., Li, Q. F., Wang, S., Cheng, Y. Y., and Yu, J. Z.: Online measurement of aerosol inorganic and organic nitrogen based on thermal evolution and chemiluminescent detection, Atmos. Environ., 271, 118905, 2022.

Li, R., Wang, Q. Q., He, X., Zhu, S. H., Zhang, K., Duan, Y. S., Fu, Q. Y., Qiao, L. P., Wang, Y. J., Huang, L., Li, L., and Yu, J. Z.: Source apportionment of $PM_{2.5}$ in Shanghai based on hourly organic molecular markers and other source tracers, Atmos. Chem. Phys., 20, 12047–12061, 2020.

Li, Y., Fu, T.-M., Yu, J. Z., Yu, X., Chen, Q., Miao, R., Zhou, Y., Zhang, A., Ye, J., Yang, X., Tao, S., Liu,H., and Yao, W.: Dissecting the contributions of organic nitrogen aerosols to global atmospheric nitrogen deposition and implications for ecosystems, National Science Review, 10, 10.1093/nsr/nwad244, 2023.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences, 112, 37-42, 10.1073/pnas.1417609112, 2014.

Yu, X., Li, Q. F., Ge, Y., Li, Y. M., Liao, K. Z., Huang, X. H. H., Li, J. J., and Yu, J. Z.: Simultaneous Determination of Aerosol Inorganic and Organic Nitrogen by Thermal Evolution and Chemiluminescence Detection, Environ. Sci. Technol., 55, 11579−11589, 2021.

Yu, X., Zhou, M., Li, J. J., Qiao, L. P., Lou, S. R., Han, W. Y., Zhang, Z. J., Huang, C., and Yu, J. Z.: First Online Observation of Aerosol Total Organic Nitrogen at an Urban Site: Insights Into the Emission

Sources and Formation Pathways of Nitrogenous Organic Aerosols, J. Geophys. Res. Atmos., 128, e2023JD038921, 2023.

Zhao, Z. J., Husainy, S., Stoudemayer, C. T. and Smith, G. D., Reactive uptake of NO_3 radicals by unsaturated fatty acid particles, Phys. Chem. Chem. Phys., 13, 17809–17817, 2011.