

Point-by-point response to editor's comments

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

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We thank the editor for his comments. Each of these comments has been addressed and detailed in our point-by-point response given below. The exact comment text from the editor 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.

Thanks to the authors for carefully addressing the Reviewers' comments. Both reviewers raised questions regarding the interpolation of PMF results. I believe the additional clarifications and explanations have strengthened the findings. I have a few further suggestions regarding the interpolation of the results:

*1. The authors analyzed the ion balance by considering NH_4^+ , SO_4^{2-} , and NO_3^- to support the assertion that SO_4^{2-} and NO_3^- are fully neutralized. However, If there is no typo in the figure or text, a slope of 1.05 for $n\text{-NH}_4$ vs $(n\text{-SO}_4^{2-} + n\text{-NO}_3^-)$ suggests that they are not fully neutralized. The authors should consider plotting against $2*n\text{-SO}_4 + n\text{-NO}_3$ instead. Additionally, the molar ratio of ammonium to sulfate was 1.8 instead of 2. Does this discrepancy indicate possible amines uptake or just quantification uncertainty?*

Response: Thanks for the careful check. We apologize for the typo. The X axis of Figure S9 should be $2*n\text{-SO}_4^{2-} + n\text{-NO}_3^-$ instead of $n\text{-SO}_4^{2-} + n\text{-NO}_3^-$. We have revised the figure in the revised supporting file.

In the PMF-resolved factor of sulfate formation processes, the molar ratio of $n\text{-NH}_4^+ / n\text{-SO}_4^{2-}$ was 1.8. The measurement results of NH_4^+ , SO_4^{2-} , and NO_3^- , however, revealed that $n\text{-NH}_4^+$ was nearly equal to $2*n\text{-SO}_4^{2-} + n\text{-NO}_3^-$, suggesting 1 molar SO_4^{2-} was typically bound with 2 molar NH_4^+ . The slight discrepancy (1.8 vs 2.0) might be mainly attributed to the uncertainty in the PMF analysis. Overall, our observation results suggested the uptake of amines by sulfate was limited in urban Shanghai due to the abundant presence of ammonia, as stated in the manuscript.

2. Lines 295-304 in the revised manuscript. If we carefully look at the factor profile of the nitrate formation process, we do see isoprene SOA tracers there. Previous studies have already pointed out that traditional isoprene SOA tracers, such as 2-methyltetrol and 2-methylerythritol are formed from NO_x -free oxidation pathway, whereas 2-methylglyceric acid, which often appears

at lower concentrations comes from a NO_x-involved pathway. It would be worthwhile to determine which of these tracers was assigned to this factor. The absence of direct ON contribution from BVOCs may be due to the compounds used for PMF not including typical organic nitrates produced from BVOCs. There are quite a lot of studies focusing on SOA and ON formation from isoprene/monoterpenes via different oxidation pathways. My feeling is that this study is not specifically designed for exploring such objects. I suggest removing the last sentence. Furthermore, the first sentence contradicts the subsequent explanations. The contribution may be assigned to the nitrate formation process factor, as stated.

Response: Thank you for your comment. In the PMF analysis, the isoprene SOA tracer was defined as the sum of 2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol, cis-MTB1, MTB2, and trans-MTB3, as detailed in Table S1 of the supporting file. We concur with the editor that the absence of ON in the BVOC SOA factor could stem from the omission of BVOC-derived organic nitrates as PMF inputs. Instead, ON components generated from BVOC oxidation in the presence of NO_x may have been attributed to the nitrate formation processes. Future studies should prioritize the identification and quantification of ON species with source-specific markers to enhance the source apportionment of ON aerosols.

In the revised manuscript, we have removed the last sentence of the paragraph (Lines 295–304) and modified the opening sentence to:

"Insignificant ON was apportioned to the factor representing SOA formation from isoprene and α -pinene oxidation." (Line 295-296)

3. Line 253, the phrase "through atmospheric reactions between NO_x and catechols" sounds wired. Anyhow, Most VOCs cannot directly react with NO_x. This should be revised for clarity.

Response: We have revised the sentence to "Nitrocatechols are likely formed through the nitration of catechols emitted from biomass burning." (Line 253)