Responses to the comments from reviewer #2

Major Comment:

The manuscript presented the analysis of the nine nitrated aromatic compounds (NACs) measured in an elevated background station in southeast China. Seasonal variation and source identification of the NACs were detailed in the study, with a particular focus on the precursors and other pollutants' movement that impact the variability of NACs. The primary implication that the authors imparted is the enhanced formation of NACs due to the transport of precursors in a background site. Increasing NO_2 concentration in the background site favored the formation of nitrocatechol (NP) and nitrocatechol (NC).

Understanding the formation of NACs in remote areas is indeed important. However, the findings and relevance of the study should be to justify the publication of such study in ACP. The authors presented several results but minimally contributed new implications that add to up body of knowledge of the formation and transformation of NACs. In particular, a significant portion of the results and discussion was allotted to reiterating prior studies with less effort on understanding further the variability of NACs in the mountainous region. Moreover, the authors indicated that secondary chemistry impact largely the formation of NACs but several statements and results throughout the study indicated otherwise. Quantifying the contribution of primary and secondary emissions to NAC formation will be a valuable addition to this study. The authors have sufficient data (e.g., EC, CO, etc.) to accomplish such task. Analysis of the source using PMF is considerably incoherent based on the identification of factors that overlap with each other. The readability of the manuscript and grammatical issues also limit the conveying of the message of the study, which should be considerably improved in the next versions. Several statements were irrelevant to the discussion, which confuse the readers. Detailed language editing is definitely needed throughout the paper, besides the issues raised in this review. A major revision according to these mentioned comments is consequently required before publication to ACP.

Response: We thank the reviewer's comments. In the revised text, we have made significant changes and improvements to the abstract and conclusion, as well as the discussion section. At the same time, we have re-edited the full text to make it easier for readers to understand. There are indeed different approaches to source apportionment, but this work used the PMF model. Before this, we also tried to use the method recommended by the reviewer, i.e. the EC-tracer method utilized in (Cai et al., 2022), in which CO and levoglucosan were selected as the tracer for combustion and BB, respectively. The results of the two methods were compared and analyzed. Please refer to **Question 12** for details. Furthermore, we renamed the source and provided new evidence. In this work, the model was iterated upon using a variety of combinations of the concentration data set and three to six covariates. Q value and r, which were defined as the agreement between the model fit and the correlation between estimated and measured concentrations, respectively, are used to determine the appropriate factor

number for modeling (Comero et al., 2009). The best solution was determined to be five components based on the Q value and r^2 (Table S2) values. Specific modification content can be seen in the text which has been highlighted and specific answers to the following comments.

Specific comments:

1. Consider shortening and improving the title to attract more readers.

Response: Suggestion taken. We have changed the title into "Contributions of primary emissions and secondary formation to nitrated aromatic compounds in mountain background region of Southeast China".

2. Line 46: Long-range transport of nitration reaction is a vague factor. Does the author mean formation of NACs occurred elsewhere and was transported to the research station? Or plumes containing the precursors (i.e., phenols and catechols) were transported to the site and subsequently oxidized in the site?

Response: We are sorry to cause some trouble to the reviewer. In the revised text, we renamed the source and provided new evidence. There were five source factors identified including biomass burning, coal combustion, secondary formation by nitration reaction, secondary formation by photochemical reaction and other sources. As secondary formation by nitration reaction, it showed high concentrations of NO_3^- (Fig. 5c). This source was much more intense in winter than in other seasons (Fig. 6c). It contributed 10.3% of the total particulate NACs at the summit of Mt. Wuyi during the whole campaign (Fig. 7a). This source may be mainly affected by the transport of pollutants, and NACs were possibly generated during the transmission.

3. Line 110: The exact duration of the measurement is confusing. How many samples were collected per season? Do the measurement days coincide with the days indicated in figure 1 caption 1 (Lines 118-121)? Please clarify. Such information might be presented in the authors' prior study (Ren et al 2019) but it would be more convenient for the readers if such information were available at hand. The reviewer suggests including relevant information in the supplement instead, including the measurement protocols of temperature, relative humidity, SO_2, fossil fuel alkanes, PAHs, and sugars.

Response: Suggestion taken. In conjunction with the first reviewer's opinion, we have added the descriptions of field observations, measurements of conventional pollutants, and meteorological parameters. The analysis of organics was placed in Sec.2.2, including fossil fuel alkanes, PAHs, sugars and NACs. See line 113, 115-124, 137-138.

4. Line 118-121: The authors should indicate the relevance of using colored (i.e., red and blue) trajectories. I understand that the authors wish to separate the plumes coming from the north and other directions using the colors, but the caption should indicate otherwise.

Response: Suggestion taken. We have added the meanings of different colors to the caption. See line 131-132.

5. Line 185-186: Same problem as comment #3. The abstract and figure 1 caption indicated that sampling occurred between 2014 and 2015. But now the authors indicate March 2013. Please clarify.

Response: We are sorry we made such a mistake, and we have corrected "2013" to "2014". See line 200.

6. Lines 193-197: Irrelevant to the current discussion.

Response: Suggestion taken. We have removed these sentences.

7. Line 203-205: What is the relevance of enhanced BSOA in this section?

Response: The authors cite previous studies to demonstrate that anthropogenic pollutants can be transported to the background points and affect the generation of some SOA species. In the revised version, we have optimized the relevant expression. See line 216-218.

8. Table 1 and the caption should be improved. I assume that the values inside the parenthesis are ranges. Please indicate. Also, reporting the limit of detection (L.O.D.) and blank data are crucial, especially for NACs, to identify whether the reported values are significant. Are these values average for seven days of collection as indicated in line 111? Are the uncertainties presented as standard deviations?

Response: Suggestion taken. We have added annotations in Table 1, i.e. the numbers in the first line indicate mean±std, and the numbers in the second line indicate lowest value-highest value. The concentrations of pollutants in the $PM_{2.5}$ samples in Table 1 are averages, which were taken over for seven days. We have added the information of L.O.D. and concentrations in blank samples of the target compounds in Table S1 in SI.

9. Lines 215-231: The authors listed several studies to compare the NACs concentration in their background station. However, the authors failed to argue why their NAC level is evidently lower than the listed sites. The authors should consider adding a few statements in this section for any justification for observed results.

Response: Suggestion taken. We have explained the differences in NACs levels between urbans, other background sites, abroad and in this work. See line 231-232, 235-240, 242-245.

10. Lines 235-246: The seasonal trends for some NACs are questionable given the minute difference in the values presented in table 1. For instance, the variation of DNP concentration across four seasons is not more than 0.03 ng m^{-3} and the typical standard deviation is 0.03. DNPs are primarily formed through the secondary nitration of nitrophenol, which is usually enhanced during the summer season.

Response: We thank the reviewer's comments. We have added the explanation of 2,4-DNP, and improved the related sentences. See line 248-253.

11. Line 246-247: Such statement is a weak justification of the variability of the NACs across different seasons given the wealth of the data that the authors have. Consider

expounding such statement to properly justify the enhanced NAC concentration during winter. The concentration of Levoglucosan, a biomass-burning tracer, also peaked during winter as indicated in Table 2. Combustion processes severely impact the formation of NACs, which the authors should consider here.

Response: We thank the reviewer's comments. The seasonal variations of the concentrations and compositions of NACs were mainly described in Sec.3.2 and the implied differences in the primary sources and the secondary formation pathways were in the following sections (Sec.3.3). We have changed the related sentences for better understanding. See line 263-266.

12. Lines 268 – 292: The contributions of primary emission and secondary formation to NAC variability are unclear. The authors mentioned that the "connections indicated that burning emissions throughout the year", as well as "probably suggesting that the secondary formation of NACs was also important in the campaign". Quantifying and separating the contribution of each source is essential in assessing the NAC formation. The authors should consider applying the EC-tracer method utilized in (Cai et al., 2022), in which CO and levoglucosan were treated as the markers for primary emissions.

Response: We thank the reviewer's comments. Quantifying and separating the contribution of each source is essential in assessing the NAC formation. In Section 3.3, we discussed the influencing factors and main sources of NACs. Firstly, the possible sources are qualitatively recognized through the correlation with the related factors, then these sources are quantified by PMF. Before this, we also tried to use the method recommended by the reviewer, i.e. the EC-tracer method utilized in (Cai et al., 2022), in which CO and levoglucosan were selected as the tracer for combustion and BB, respectively. The secondary formation of NACs was evaluated via Equation 1,

$$[\mathrm{NACs}]_s = [\mathrm{NACs}]_t - ([\mathrm{NACs}]/[\mathrm{tracer}])_{\mathrm{pri}} \times [\mathrm{tracer}] \quad (1)$$

Where $[NACs]_s$ and $[NACs]_t$ are the concentration of NACs generated from secondary oxidation and the total measured NACs, respectively, $([NACs]/[tracer])_{pri}$ is the primary emission ratio of NACs relative to the tracer, [tracer] is the concentration of tracer. $([NACs]/[tracer])_{pri}$ was estimated from the fitting of the minimum [NACs]/ [tracer] ratio, assuming that the primary source dominated the period with minimal secondary formation. In this work, $([NACs]/[tracer])_{pri}$ was taken the minimum value during the whole sampling period, and the results of BB as tracer were most similar to those of PMF in this paper. The contribution of secondary formation was the greatest in summer, reaching an average of 78%, and ranged from 32% to 51% in other seasons, indicating secondary generation was an important source of NAC in this remote areas during the sampling time. However, the primary [NACs]/ [tracer] ratio varies with time, so a fixed primary [NACs]/[tracer] ratio results in large uncertainties. For example, the minimum value of [NACs]/[BB] in this work were 0.049, 0.146, 0.065, and 0.049 in spring, summer, autumn, and winter, respectively, and there were big differences among them. And this difference may also be related to the small number of samples collected. Synthesize the above reasons, this work used the PMF model. The model was iterated upon using a variety of combinations of the concentration data set and three to six

covariates. Q value and r, which were defined as the agreement between the model fit and the correlation between estimated and measured concentrations, respectively, are used to determine the appropriate factor number for modeling (Comero et al., 2009). The best solution was determined to be five components based on the Q value and r^2 (Table S2) values. Meanwhile, we analyzed the contributions of these sources in different seasons. For ease of understanding, we have modified the title of this section and divided it into two parts. i.e. Changing "3.3 Influence factors and sources of NACs" into "Source apportionment"; adding "3.3.1 Source identification" and "3.3.2 Contributions of sources in different seasons".

13. Table 3 indicates that almost all NACs correlated better with levoglucosan compared to ozone that is an evident tracer of secondary chemistry. This might be an indication of the key source of NACs.

Response: We agree with the reviewer. In this work, we used levoglucosan as the tracer for biomass burning in PMF, and demonstrated that biomass burning was an important source of NACs throughout the year during the campaign.

14. Line 302-319: The identification of the factor profile from PMF is unclear and incoherent. The authors immediately assumed that most of the factors originate from transmission processes without presenting clear evidence. What are the diurnal profiles of the typical gas pollutants such as SO2, CO, NOx, and O3? Do these pollutants show no evident trend similar to local sources? Did the authors consider the contribution of the local mountain-valley breeze that transports pollutants to the elevated site?

Response: We were a bit arbitrary in determining whether the source was transmission or local, so we renamed the source and provided new evidence. There were five source factors identified including biomass burning, coal combustion, secondary formation by nitration reaction, secondary formation by photochemical reaction, and mixed sources. The detailed discussion can be seen line 310-343.

15. Line 302-319: Several factors overlap with each other based on the time series of the contributions shown in figure 6. The naming of each factor is problematic, particularly the long-range transport of nitration reaction. Do the authors mean aged plume, in which the nitration occurred remotely from the site?

Response: We are sorry to cause some trouble to the reviewer. Same as the answer to questions 2 and 14, we renamed the source and provided new evidence. As secondary formation by nitration reaction, it showed high concentrations of NO_3^- (Fig. 5c). This source was much more intense in winter than in other seasons (Fig. 6c). , and may be mainly affected by the transport of pollutants. NACs were possibly generated during the transmission. The detailed discussion can be seen line 310-343.

16. Lines 390-398: These statements should be moved to the introduction instead.

Response: Suggestion taken. We have moved these sentences to the introduction, and polished them as a whole.

17. Lines 398 – 426: The data presented here are quite interesting, however, the author opted to immediately compare their results to prior studies. The authors should have expounded their data. Figure 9 has a lot of implications that the authors can explore. The branching formation of nitrate vs NACs is evidently different during winter and summer, which indicates the impact of primary vs secondary emission in varying atmospheric conditions.

Response: We thank the reviewer's comments. We have made corresponding changes in the revised draft. A description of the relevant content in the reference is added to make a comparative analysis with this paper, e.g. "In general, the mass ratios ranged from 1 to 285 (ng/μg) with average of 73 (ng/μg) during the whole campaign. In previous studies, this ratio was generally between 1 and 14 at urban stations. For example, it was averaged 13.5 (ng/μg) in Beijing during spring and summer (Ren et al., 2022), 1.4 and 2.1 in Jinan during summer and winter, respectively (Wang et al., 2018), and from 1 to 9 (ng/μg) in Shanghai (Cai et al., 2022)". We also explore further into the information covered in Figure 9. See line 419-428, 432-439, 445-458.

18. Line 446-452: The remote site experienced low NO_x condition (<10 μg m^{-3}) all year, yet evident variation of the NAC concentration was shown in figure 2. The secondary chemistry might have a limited contribution to NAC formation in this remote region compared to primary emission. This is consistent with the relationship with biomass-burning tracers.

Response: Many studies have proved that biomass combustion is an important primary source of NACs, and our work also proves this point. Moreover, more and more studies have found that coal burning and traffic are also important sources of them. At the same time, secondary formation is also a non-negligible source of NACs. Wang's previous research has shown that secondary formation is recognized as an important source of particulate nitrated phenols in northern China, especially in the summertime. It was identified as the dominant contributor in the field measurements in rural Yucheng (41 %) and Mt. Tai (42 %). Furthermore, NO_2 played a major role in the formation of nitrated phenols in rural and mountainous areas (Wang et al., 2018). Our results also indicate that secondary formation makes a significant contribution to NAC, on average more than 43% throughout the year and even exceeding 60% in summer. See Fig.7.

19. The Abstract and Conclusion sections did not contribute any new atmospheric insight into NACs formation in remote environments, besides the expected long-range transport of pollutants. The current manuscript appears to be a measurement report and the authors should consider explaining the implications of the study in these sections. These two important sections should not only serve as a summary of the study.

Response: In the revised text, we have made significant changes and improvements to the abstract and conclusion, with adding the new findings and some new thoughts in this paper.

Minor comments:

1. Line 69-71: Add the following references here. These studies impart relevant information regarding the sources and formation of NACs in different atmospheric conditions. The addition of such references to Table 2 is also suggested.
Gaston, C. J., Lopez-Hilfiker, F. D., Whybrew, L. E., Hadley, O., McNair, F., Gao, H., Jaffe, D. A., and Thornton, J. A.: Online molecular characterization of fine particulate matter in Port Angeles, WA: Evidence for a major impact from residential wood smoke, Atmos. Environ., 138, 99–107, https://doi.org/10.1016/j.atmosenv.2016.05.013, 2016.
Salvador, C. M. G., Tang, R., Priestley, M., Li, L., Tsiligiannis, E., Le Breton, M., Zhu, W., Zeng, L., Wang, H., Yu, Y., Hu, M., Guo, S., & Hallquist, M. (2021). Ambient nitro-aromatic compounds – biomass burning versus secondary formation in rural China. Atmos. Chem. Phys., 21(3), 1389-1406, https://doi.org/10.5194/acp-21-1389-2021
Cheng, X., Chen, Q., Li, Y., Huang, G., Liu, Y., Lu, S., Zheng, Y., Qiu, W., Lu, K., Qiu, X., Bianchi, F., Yan, C., Yuan, B., Shao, M., Wang, Z., Canagaratna, M. R., Zhu, T., Wu, Y., & Zeng, L. (2021). Secondary Production of Gaseous Nitrated Phenols in Polluted Urban Environments. Environmental Science & Technology, 55(8), 4410-4419. https://doi.org/10.1021/acs.est.0c07988
Response: Suggestion taken. We have added these related references to the text and Table 2.

2. Line 93: Remove “chief”
Response: Suggestion taken.

3. Line 141: Replace “under’ with “using”
Response: Suggestion taken.

4. Line 201: Replace “sample” with “sampling”
Response: Suggestion taken.

5. Line 263: Replace “interrelation” with “relationship”
Response: Suggestion taken.

6. Line 300: Remove “five styles”
Response: Suggestion taken.

7. Figures 8a and b show similar results. Consider removing one of the plots.
Response: Suggestion taken. See Fig. 8 in the revised text.

References

Cai, D., Wang, X., George, C., Cheng, T., Herrmann, H., Li, X., & Chen, J. (2022). Formation of Secondary Nitroaromatic Compounds in Polluted Urban Environments. Journal of Geophysical Research: Atmospheres, 127(10), e2021JD036167. https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2021JD036167

Cheng, X., Chen, Q., Li, Y., Huang, G., Liu, Y., Lu, S., Zheng, Y., Qiu, W., Lu, K., Qiu, X., Bianchi, F., Yan, C., Yuan, B., Shao, M., Wang, Z., Canagaratna, M. R., Zhu, T., Wu, Y., & Zeng, L. (2021). Secondary Production of Gaseous Nitrated Phenols in Polluted Urban Environments. Environmental Science & Technology, 55(8), 4410-4419.

Comero, S., Capitani, L., and Gawlik, B.: Positive Matrix Factorisation (PMF)–An introduction to the chemometric evaluation of environmental monitoring data using PMF, Office for Official Publications of the European Communities, Luxembourg, 59, 2009.

Gaston, C. J., Lopez-Hilfiker, F. D., Whybrew, L. E., Hadley, O., McNair, F., Gao, H., Jaffe, D. A., and Thornton, J. A.: Online molecular characterization of fine particulate matter in Port Angeles, WA: Evidence for a major impact from residential wood smoke, Atmos. Environ., 138, 99–107, https://doi.org/10.1016/j.atmosenv.2016.05.013, 2016.

Ren, Y., Wei, J., Wang, G., Wu, Z., Ji, Y., and Li, H.: Evolution of aerosol chemistry in Beijing under strong influence of anthropogenic pollutants: Composition, sources, and secondary formation of fine particulate nitrated aromatic compounds, Environ. Res., 204, 111982, https://doi.org/10.1016/j.envres.2021.111982, 2022.

Salvador, C. M. G., Tang, R., Priestley, M., Li, L., Tsiligiannis, E., Le Breton, M., Zhu, W., Zeng, L., Wang, H., Yu, Y., Hu, M., Guo, S., & Hallquist, M. (2021). Ambient nitro-aromatic compounds – biomass burning versus secondary formation in rural China. Atmos. Chem. Phys., 21(3), 1389-1406, https://doi.org/10.5194/acp-21-1389-2021

Wang, L., Wang, X., Gu, R., Wang, H., Yao, L., Wen, L., Zhu, F., Wang, W., Xue, L., Yang, L., Lu, K., Chen, J., Wang, T., Zhang, Y., and Wang, W.: Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation, Atmos. Chem. Phys., 18, 4349-4359, https://doi.org/10.5194/acp-18-4349-2018, 2018.