## Response to reviewers

Reviewer comments are in black ***italic*** type. Author responses are indented and in normal font labeled with [R]. Line numbers in the responses correspond to the revised manuscript without track-changes. Modifications to the manuscript are in *italics*.

### *Reviewer #1*

***This paper presents mobile field measurements of fine particle compositions, VOCs, and trace gases on an urban highway road in Beijing. Spatial distributions of different air pollutants under haze and non-haze conditions were investigated. Reference measurement at a fixed station representing the typical urban environment was also conducted to facilitate the analysis of spatial distribution and variability of different pollutants from mobile measurement. This is a revised paper that has been reviewed by two other reviewers. The authors' responses have clearly shown that they have made major changes to the manuscript to address the reviewer's comments. The revised paper is better organized, and the results are presented more clearly. Overall, I support the acceptance of the revised paper after some minor comments are addressed.***

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

***1. The author used the PKU roof site as a reference station for comparing the mobile measurement; however, there is almost no information on the reference station in the methods section.***

[R1] We have added the description about the PKU roof site in section in Line 86-93 as follows: "*Additionally, online measurements of gaseous and particulate pollutants were conducted at a roof station in the PKU campus (39.99 °N, 116.32 °E) as a reference. Temperature, RH, barometric pressure, wind speed, and wind direction were acquired by a Met One weather station (083E, 092, 010C, and 020C). Gas pollutants were measured by Thermo Scientific instruments, including CO (48i-TL), NO-$NO_2$-$NO_x$ (42i-TL), $SO_2$ (43i-TL), and $O_3$ (49i-TL). $PM_{2.5}$ mass concentrations were measured by a tapered element oscillating microbalance monitor (Thermo, TEOM 1400A). Non-refractory chemical components of submicron particles (NR-PM1) were measured by an Aerodyne long time-of-flight aerosol mass spectrometer (LTOF-AMS). The roof site is located between the 4th and the 5th North Ring Roads, representing a typical urban background environment in Beijing (Zheng et al., 2021)*".

***2. Figure 1. Panel d is missing in the figure caption.***

[R2] We have added the description for panel d in the figure caption as follows: "*(d) The average NR-$PM_{2.5}$ composition measured by the TOF-ACSM on the mobile lab on the 4th Ring Road within the distance of 1.5 km from the roof site*".

***3. Line 122-123. It would be better if the corresponding periods of mobile measurement campaigns could be explicitly shown in the time series figure (e.g. Figure S8).***

[R3] We have marked the mobile measurement periods in Figure S8.

***4. Line 130-131 and Figure S8. The wind directions are not clear in the time series figure. It will be clearer if the wind speed and direction can be depicted in the angular arrows.***

[R4] We have revised panel (b) for wind speed and direction in Figure S8.

***5. Line 159 and Line 243. Do you mean the titration of $O_3$ by NO? To consider the titration effects of $O_3$ converting NO to $NO_2$, a better approach is to compare the $O_x$ ($NO_2$+$O_3$) instead of $NO_2$ itself.***

[R5] Yes, we mean the titration of $O_3$ by NO. The mean mixing ratios of on-road $O_x$ (114.1 ppbv) were much greater than the roof-site mean (48.7 ppbv) during the non-haze periods, indicating a possible contribution of direct tailpipe $NO_2$ emissions. However, the roof site was located in the upwind direction and was less affected by urban traffic emissions. The ozone concentration at the roof site might be lower than the on-road level without titration and thus quantitative conclusion is difficult to make. To clarify, we have revised Line 167-174 as follows: "*On-road $NO_2$ can be contributed by direct tailpipe $NO_2$ emissions, NO titration, and urban background. The mean mixing ratios of on-road $O_x$ (114.1 ppbv) were much greater than the roof-site mean ratio (48.7 ppbv) during the non-haze periods, indicating a possible contribution of direct tailpipe $NO_2$ emissions, although tailpipe $NO_2$ emissions for LDGVs of National Stage III to V are expected to be low (Wu et al., 2017). On-road NO titration can also be strong (Yang et al., 2018), considering that the spatial patterns for $O_3$ and NO were anti-correlated (Pearson $r = -0.43$) and the mean mixing ratio of on-road $O_3$ (11.2 ± 2.2 ppbv) were over 2 times lower than the roof-site observations (25.7 ± 12.8 ppbv). Quantitative analysis on their relative contributions to on-road $NO_2$ is however difficult because the site was located in the upwind direction*".

***6. Line 170-176, from Figures 2 and 7, it seems the hydrocarbon showed the greatest spatial variability compared to the acids/anhydrides. Please check and clarify the discussions in this part.***

[R6] Yes, hydrocarbons showed the greatest spatial variability among detected VOCs. We have revised Line 180-183 as follows: "*During the non-haze days, the tentatively-assigned group of hydrocarbons showed the greatest spatial variability (by 21×) among VOCs, whereas the groups of aldehydes/ketones and acids/anhydrides showed less variability (by 4× and 9×, respectively) (Table S2). Secondary production is expected to contribute greatly to the latter two groups (Wang et al., 2021)*".

***7. Line 194-195. Is it possible to show a correlation plot on the hot spots of different pollutants with the traffic volume? Any relationship between the HOA with other primary tracers, like CO, NO, or some hydrocarbon?***

[R7] Unfortunately we can't obtain the real-time traffic volume data. The driving speed is not a quantitative indicator and only describes the traffic jam qualitatively. The correlations of HOA with other gaseous species that are related to traffic sources such as CO, NO, and hydrocarbons are weak ($r < 0.2$), although better than the correlations between COA (or OOA) and these gaseous species. Possible reasons for the weak correlations include different dilution or mixing between gas and particulate pollutants, different contributions of urban background, and the influence of other localized sources to some of the pollutants. To clarify, we have revised Line 202-204 as follows: "*The HOA hot spots are generally consistent with the locations where the driving speed was relatively low (i.e., perhaps high traffic volume). We use the driving speed to indicate the traffic volume because the real-time traffic volume data weren't available (Figure S10 in the Supplement)*".

***8. Line 289-292. Do the authors mean the earlier period has fewer vehicle plumes? Please clarify the information here.***

[R8] Yes, there are usually less traffic around noon in Beijing. We have clarified this information in Line 300-304 as follows: "*The traffic volume in Beijing is usually less around noon than in the afternoon (Wu et al., 2017). Consistently, the concentrations of hydrocarbons were greater with larger variations in the afternoon (2:00 p.m. to 4:00 p.m.) than in the earlier period (11:00 a.m. to 2:00 p.m.), indicating more vehicle plumes were captured by the mobile measurements in the afternoon*".

***Reviewer #2:***

***This study utilizes detailed in-situ mobile measurements of aerosol compositions and VOCs to investigate the intracity scale variability of air pollution and its sources in the megacity of Beijing. Distinct spatial variability of air pollutants, sources and chemical processes was found for haze and non-haze conditions. Overall, the manuscript is well organized and clearly written, with the methods and interpretation being solid and convincing. I would like to recommend that it can be accepted after the following minor comments being addressed.***

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

***Line 99-101: BBOA and CCOA were not resolved in the PMF solution. I am wondering whether those primary OA were mixed with HOA, COA, or OOAs. Would the PTR-MS data provide additional information for biomass burning or coal burning tracers (e.g., acetonitrile)?***

[R1] BBOA and CCOA were likely mixed with HOA because of the similarity of their spectra with capture vaporizer (Zheng et al., 2020). Indeed, the PTR-MS data showed low concentrations of acetonitrile (0.15±0.20 ppbv for non-haze periods and 0.60±0.22 ppbv for the haze periods) during the mobile campaign. By comparison, the average concentrations of acetonitrile are usually greater than 0.7-1 ppbv in the winter of Beijing when biomass and coal burning contributes significantly (Huangfu et al., 2021; Shi et al., 2020). We have added this information in Line 108-113.

***Line 147: "in the southeast areas" instead of "in the southeast and lowest areas"?***

[R2] We have revised the text accordingly.

***Line 170-171: The concentration variations of hydrocarbons look more significant than those of acids/anhydrides.***

[R3] Yes. As replied in [R6] for Reviewer #1, we have revised Line 180-183 for clarification.

***Line 207-208: Does non-perfect separation mean inappropriate attribution of POA to SOA or the reverse?***

[R4] As explained in Section A3 in the Supplement, the signal intensity of *m*/*z* 44 is sensitive to the PMF rotation. Therefore, we may overestimate or underestimate SOA because of the rotation choice. The CV-based PMF tends to overestimate the OOA mass comparing with the SV-based analysis, meaning inappropriate attribution of POA to SOA (greater spatial variability in resolved SOA). However, there is a lack of standard methods for quantifying POA and SOA. It is hard to conclude that. To clarify, we have revised this in Line 216-219 as follows: "*Non-perfect separation of POA from SOA by the PMF analysis may also lead to misplaced spatial variability in OOA. For example, the CV-based PMF analysis may overestimate the SOA mass comparing with the traditional AMS analysis (Zheng et al., 2020), which may lead to inappropriate attribution of POA to SOA and thus more spatial variability in SOA. Uncertainty remains in the mass separation of POA and SOA (Sect. A3 of the Supplement)*".

***Line 337: The formula here should be PAN's fragment not PAN itself. How good can this ion represent PAN? Please clarify.***

[R5] Peroxyacetyl nitrate (PAN) can undergo proton transfer reaction with $H_3O^+$ ions, resulting in a protonated signal at *m*/*z* 122.008. Protonated PAN subsequently undergoes a secondary ion-molecule reaction with water to form a product ion $CH_3C(O)OOHH^+$ with *m*/*z* 77.023 (the ion herein) as well as fragment ions at *m*/*z* 43.018 and *m*/*z* 45.993 (Hansel and Wisthaler, 2000; Kaser et al., 2013; Yuan et al., 2017). The signal at *m*/*z* 77.023 correlated well with PAN measured by specific PAN instruments (de Gouw et al., 2003; Kaser et al., 2013). For the high-resolution PTR-QiTOF, possible interferences are protonated peracetic acid ($C_2H_4O_3H^+$) and glycolic acid ($C_2H_4O_3H^+$) while they should have minor contributions in our measurements in Beijing (Yuan et al., 2017). We have revised the text in Line 349-352 to clarify.

## References

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