

## 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 with track-changes. Modifications to the manuscript are in *italics*.

### *Reviewer #3*

#### *Comments:*

*The paper reported the on-road mobile measurement results in megacity in China. It is interesting that homogeneous and heterogeneous spatial distributions were observed respectively for haze and clean days. The fine spatial resolution measurement provided a lot of information on localized sources, which is potentially useful for the development of future pollution control strategies. Overall, the paper is well written and logically organized. High-spatial resolution measurements is important yet scarce in China. As one of the pioneering studies in China, I recommend the paper be published subject to minor revision.*

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

#### *Specific comments:*

**1. Line 85, both mass resolution and time resolution of the ToF-ACSM sampling should be provided.**

[R1] We have added those information in Line 93-97 as follows: “Gas pollutants were detected by gas analyzers including NO<sub>2</sub> (Teledyne, T500U), NO-NO<sub>x</sub> (Ecotech, EC9841A), SO<sub>2</sub> (Ecotech, EC9850A), CO (Ecotech, EC9830A), and O<sub>3</sub> (Ecotech, EC9810A) *with a time resolution of 2 s*. The chemical composition of NR-PM<sub>2.5</sub> was measured by an Aerodyne time-of-flight aerosol chemical speciation monitor (TOF-ACSM) with PM<sub>2.5</sub> lens and a capture vaporizer *with a time resolution of 40 s and a mass resolution of about 400* (Zheng et al., 2020)”.

**2. Line 94 and Line 100, I don't think this is a good way to describe how the PMF results were derived and how the instruments were run during the campaign. Although experimental details had been published in the papers from the same group, readers may not have read the other ones and it is not their duty to do so. As an independent submission, at least all the necessary experimental details should be provided in SI to aid understanding of the whole manuscript.**

[R2] We have added Section A as well as Figures S11 and S12 in the Supplement for the experimental details and the PMF analysis. The text in Line 104-106 has also been revised to guide the readers for the supplementary material.

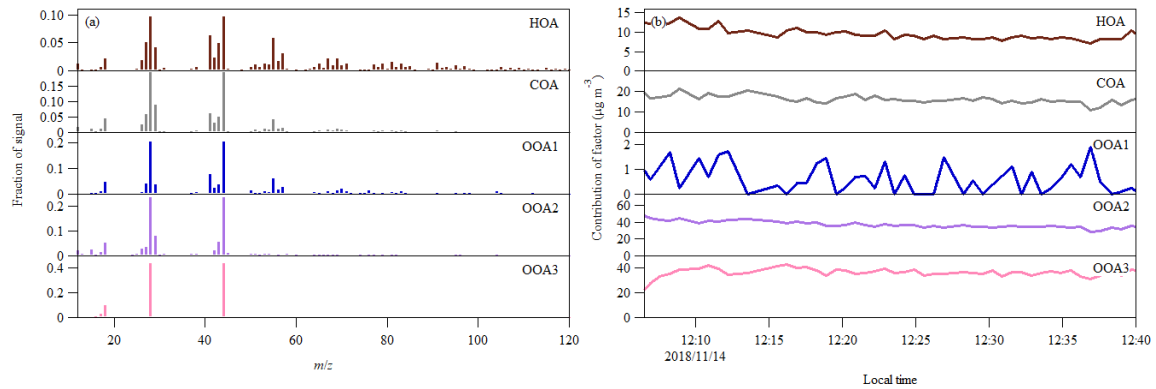


Figure S11. (a) Mass spectra and (b) time series of the OA factors identified by PMF (5-factor solution).

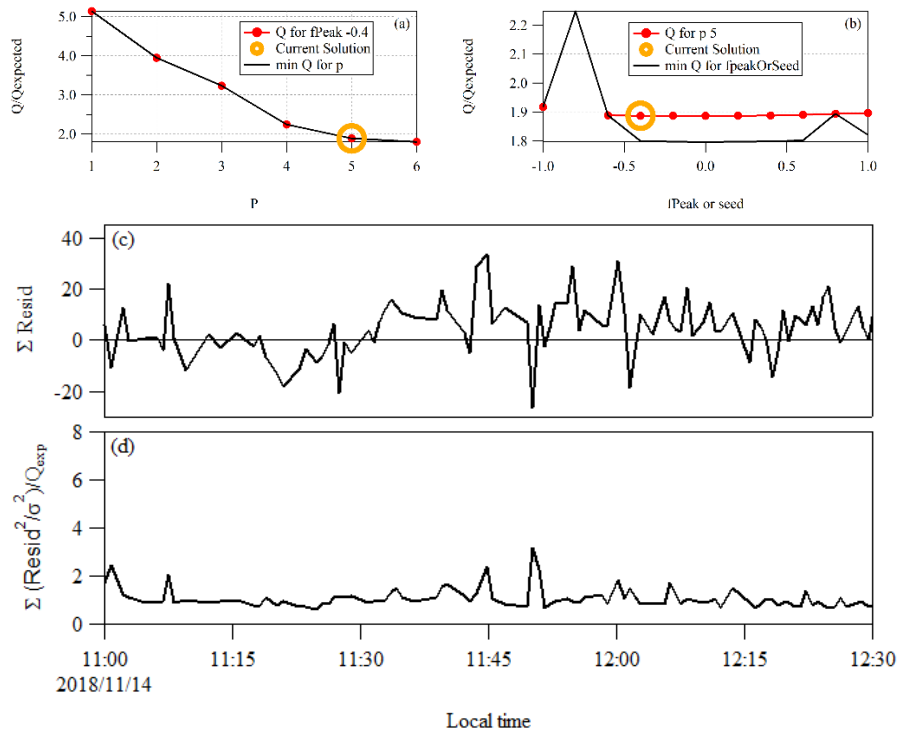


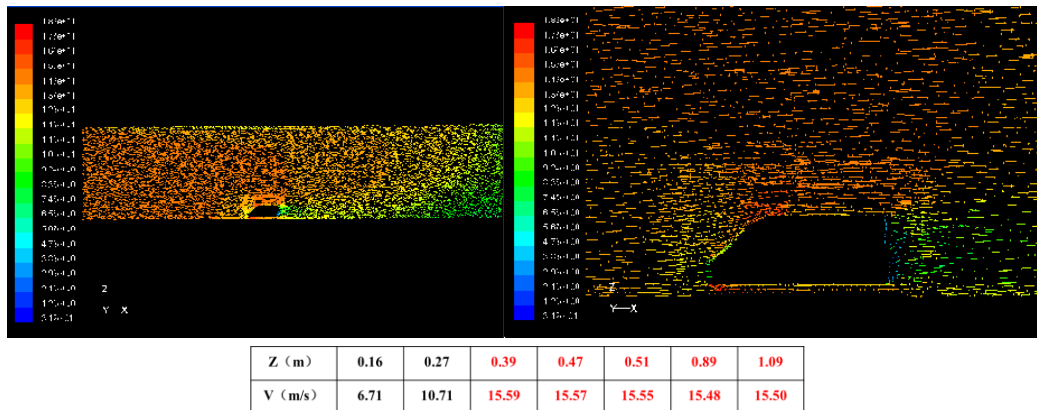
Figure S12. PMF diagnostics for  $Q/Q_{\text{exp}}$ , variance, and residuals. Residuals are shown for the example noon cycle during the haze day.

**3. Line 125: The authors run the mobile lab on the highway, which is largely affected by the on-road vehicle emissions. Although self-contamination from the exhaust of the mobile lab could be eliminated, I'm not sure whether the data could represent the characteristic the specific area as shown on each pie in Figure 1. In another word, if the mobile lab was run on the road several meters away from the highway, would similar composition distributions be derived?**

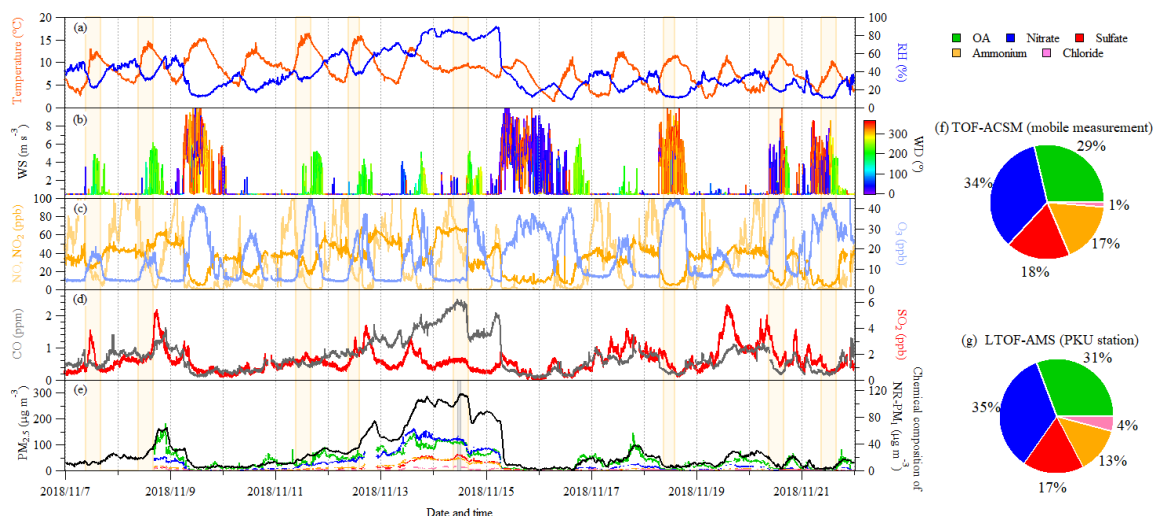
[R3] The sampling inlets were installed at the top front of the vehicle, 3.4 m above the ground (Figure X1). The wind speed was  $0.5\text{-}2\text{ m s}^{-1}$  and sometimes  $4\text{-}6\text{ m s}^{-1}$  during the

measurement period (Fig. S3). When the mobile lab ran for cycles on the 4<sup>th</sup> Ring Road, the PM<sub>2.5</sub> measurements by TOF-ACSM (40 s) may roughly represent a maximum area of 0.16 km<sup>2</sup> upwind (e.g., the wind is persistently perpendicular to the mobile path at a speed of 6 m s<sup>-1</sup>). This means a bigger footprint of our measurements than the stationary measurements on the roadside (e.g., several meters away from the highway). By contrast, the measurements of gas pollutants (2 s) represent a rather small area.

Similar composition distribution between road-side and on-road measurements may be derived for pollutants that are well mixed in the urban background and not affected by vehicle emissions (Gentner et al., 2017). For example, the particle compositions measured on the 4<sup>th</sup> Ring Road were similar to those measured by a long time-of-flight aerosol mass spectrometer (LTOF-AMS) at the PKU roof station (Figure S3). To clarify, we have added some discussion in Line 171-177 as follows: *“The sampling inlets of the PKU mobile lab are located at 3.4 m above the ground, which may sample air from both of urban background and instantaneous plumes. The 40-s PM<sub>2.5</sub> measurements by TOF-ACSM may roughly represent a maximum area of 0.16 km<sup>2</sup> upwind when the mobile laboratory was run on the 4th Ring Road by cycles. The similar chemical composition along the road suggests relatively homogeneous spatial distributions of the mass concentration and composition of NR-PM<sub>2.5</sub> across the city under haze conditions. This is supported by the fact that the particle composition observed at the PKU roof site was similar to our mobile measurements (Figure S3)”*. Figure S3 is also revised with the LTOF-AMS results.



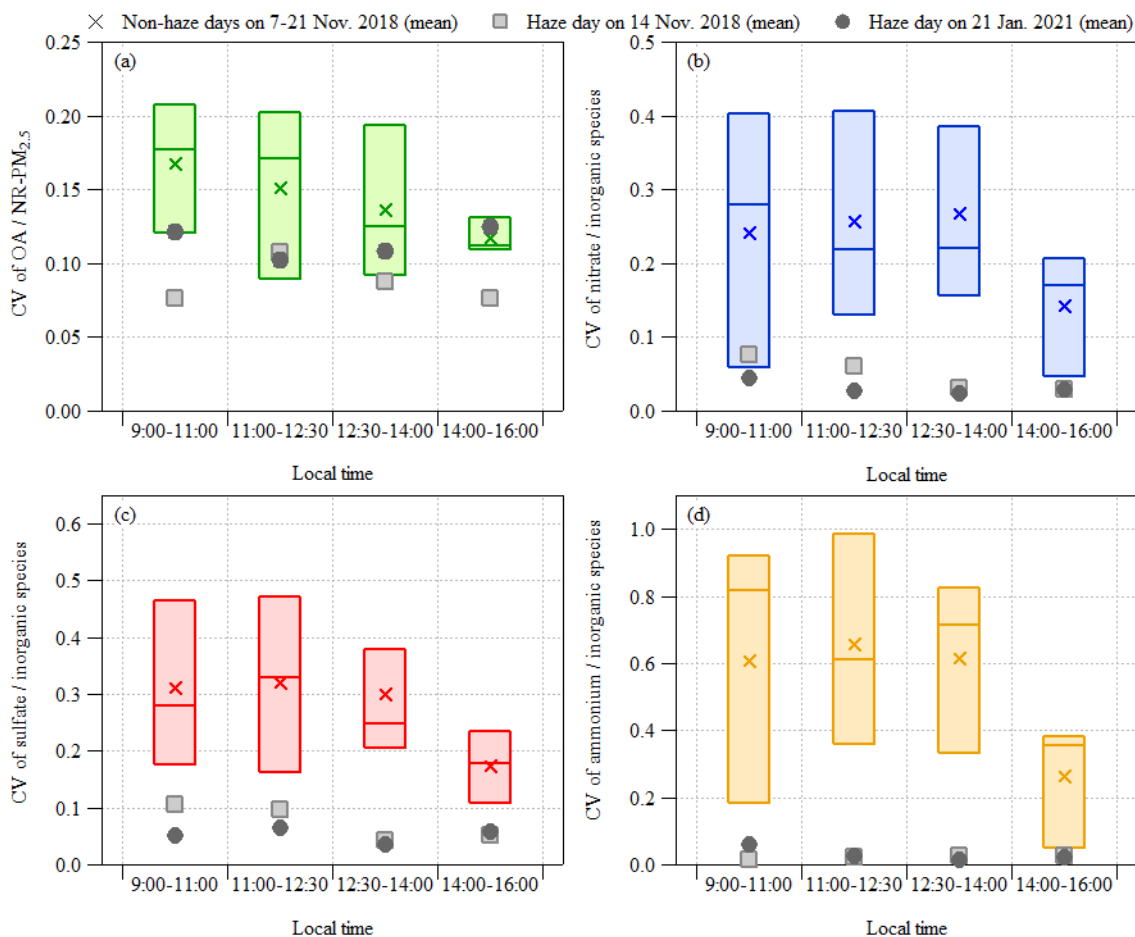
**Figure X1.** The wind field in front of the PKU mobile laboratory at a speed of 50-60 km h<sup>-1</sup> modeled by FLUENT. The sampling height of Z refers to the height above the vehicle. The sampling inlet of PKU mobile laboratory was located at Z=0.4 m.



**Figure S3.** Time series of (a) temperature and relative humidity (RH), (b) wind speed (WS) and wind direction (WD), (c) NO, NO<sub>2</sub>, and O<sub>3</sub>, (d) CO and SO<sub>2</sub>, (e) PM<sub>2.5</sub> mass concentration and chemical composition of NR-PM<sub>1</sub> measured by a long time-of-flight aerosol mass spectrometer (LTOF-AMS) at the PKU campus roof site during the entire mobile campaign in the winter of 2018. (f) and (g) particle composition of NR-PM<sub>2.5</sub> measured by TOF-ACSM in the mobile laboratory and particle composition of NR-PM<sub>1</sub> measured by LTOF-AMS at the PKU campus roof station during the time period of a 4th Ring Road cycle on November 14 (marked in grey in (e)), respectively. The yellow-shaded periods represent the periods having the mobile measurements.

*4. Lines 125-145, it is interesting that on clean days great spatial variability of aerosol components was observed. What about the daily variation? I'm curious whether the observed spatial variation can well represent the local emission. Also, why the authors specifically present the results of the noon cycles instead of the average of the whole cycles for one day or during all clean days' sampling since the campaign lasted for around 2 weeks.*

[R4] We have added the results of the chemical composition of non-refractory submicron particles measured by the LTOF-AMS at the PKU roof station to Figure S3. As shown in Figure S3, the day-to-day or diurnal variations of particle composition clearly present. Averaging the data for the whole measurement period or all clean days would smooth out the spatial variability. We therefore only presented the example noon cycles in Figure 1. To support our conclusion that the spatial variability of aerosol composition is greater during the clean days than during the haze day, we have added a new graph as Figure 2. This graph shows the CV (i.e., spatial variability) distributions of all clean-day cycles vs. the haze-day cycles for the mass fractions of major particle components. During the 2018 mobile campaign, we only had one haze-day data. In the revised manuscript, we have added another haze-day data that were collected on 21 January 2021 in Beijing. Despite of the day-to-day variations, the clean-day CV values are significantly greater than the haze-day values for all time periods.



**Figure 2.** The CV values for the inorganic and organic mass fraction in NR-PM<sub>2.5</sub> for all cycles during the mobile campaign. The box plots show the 75th, median, and 25th percentiles.

**5. Line 164: megacity scale? Or the authors meant the regional scale?**

[R5] Yes, we meant megacity scale. The severe winter haze is typically a regional event. But we have only measured in Beijing and have no data to tell whether the particle composition were similar outside urban Beijing. To be clear, we have revised the text as follows: “*The similar particle composition may suggest a chemical homogeneity at least on the megacity scale*” in Line 171.

**6. Line 248: Why hydrocarbons accumulated in the afternoon (12:00pm-14:00pm)? Hydrocarbons should decrease during the noon time because of photochemical consumption as observed from on-site measurements in literature.**

[R6] We agree with the reviewer that photochemical consumption may lead to a noontime valley of hydrocarbon concentrations as observed in urban background site. The on-road measurements of hydrocarbons are however largely affected by instantaneous vehicle plumes. Therefore, the measurements herein do not represent urban background conditions for hydrocarbons. As shown in Figure 4, the median concentrations during 12:00-14:00 are lower than the morning concentrations but the data span in a wide range.

To clarify, we have revised the text in Line 279-290 as follows: “*The on-road measurements of hydrocarbons are largely affected by instantaneous vehicle plumes. The greater concentrations of hydrocarbon 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.) suggest that the mobile measurements captured less vehicle plumes, which is consistent with the less traffic volume on the road. Under non-haze conditions, the spatial variabilities of hydrocarbons vary significantly during the day. Their CV values are high in the morning and low in the afternoon. It is likely that photochemistry and better mixing conditions in the afternoon smooth out some of the spatial variabilities caused by on-road vehicle emissions (Mellouki et al., 2015; Karl et al., 2018). By contrast, their concentrations keep decreasing during the day under haze conditions, and the greater concentrations of  $\Sigma$  hydrocarbons than during the clean days are plausibly driven by the greater contribution of regional transport to on-road air and stagnant meteorological conditions that favour the accumulation of on-road vehicle plumes*”

**7. From the discussion in Section 3.3, it seems variations of VOCs and OVOCs species are predominantly driven by on-road vehicles or high-emitting plumes. The running cycles on the 4th Ring Road cover different regions characterized by different functions, such as industrial area, residential area, etc., yet the VOC characteristics in different regions were not discussed in detail except vehicle emission. Could more information on local sources for different regions be derived from the measurements? After all, mobile emission is not the only emission source.**

[R7] Yes, we agree with the reviewer that local sources can affect the on-road mobile measurements. For example, as we mentioned in Line 246 that the high T/B ratios in the south region of the 4th ring road may be explained by industrial plumes (e.g., from chemical plants, painting processes, or constructions involving evaporation emissions). Cooking exhaust plumes present as well as indicated by the COA hotspot in Figure 1c. We have clarified in Line 250-251 that mobile emissions are not the only source that influence the on-road air.

**8. Line 540: Legend, non-haze and haze days should be denoted in Figure 4.**

[R8] We have revised this figure (now Figure 5) to clarify the non-haze and haze-day results.

## Reference

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prevot, A. S. H., and Robinson, A. L.: Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions, *Environ. Sci. Technol.*, 51, 1074-1093, <https://doi.org/10.1021/acs.est.6b04509>, 2017.