We thank reviewer#2 for the thorough comments and suggestions to improve the manuscript. Below we reply to the comments point by point. The comments are presented in black, our replies in red and the revised text in green.

General comments:

The manuscript by Qin et al. analyzed an HR-ToF-AMS dataset that was collected a downwind site of Guangzhou along with co-located measurements. Positive matrix factorization (PMF) with ME-2 algorithm was used to identify the major sources of organic aerosols (OA). Particularly, the traffic-related hydrocarbon-like OA was able to be separated and quantified while it cannot be by the unconstrained PMF. The authors then highlighted the importance of traffic emissions in contributing to HOA and nitrate formation at this site. Also, the secondary organic aerosol formation was investigated using SOA vs Ox ratios. While this topic fits within the scope of ACP, this manuscript needs a major revision, particularly, some parts are written hastily and need to be clarified.

We have thoroughly revised the whole manuscript to clarify a number of issues. Please refer to response to Reviewer 1 for the changes in Introduction, and refer to the revised manuscript for the changes in the discussion about the important role of nitrate, HOA and SOA formation. Responses below are for specific comments.

Major comments:

1. The abstract and conclusions claimed a 40% contribution of HOA to organics, which was not discussed in the text at all. Highlighting such a number could be very misleading as Figure 6 shows that the average HOA contributes ~10-30% to OA in both Nov. and Dec.

We thank the reviewer for pointing out this misleading statement. It is meant to be up to 40% contribution of HOA to organics during nighttime. HOA accounted for up to 40% of OA (95th percentile of mass fraction in box-whiskers plot) especially in the evening and at night, likely due to the heavily polluting trucks passing by en route to the downtown area at night (22:00 to 07:00). Change has been made in the abstract and conclusions.

Abstract change to:

Particulate matter (PM) pollution on the peripheries of Chinese megacities can be as serious as in cities themselves. Given the substantial vehicular emissions in inner-city areas, the direct transport of primary PM (e.g. black carbon and primary organics) and effective formation of

secondary PM from precursors (e.g. NO_x and volatile organic compounds) can contribute to PM pollution in "buffer" zones between cities. To investigate how traffic emissions in inner-city areas impact these adjacent "buffer" zones, a suite of real-time instruments were deployed in Panyu, downwind from central Guangzhou, from November to December 2014. Nitrate mass fraction was higher on high-PM days, with the average nitrate-to-sulfate ratio increasing from around 0.35 to 1.5 as the PM mass concentration increased from 10 to 160 $\mu g/m^3$. Particulate nitrate was strongly correlated with excess ammonium ($[NH_4^+]/[SO_4^{2-}]$ - 1.5) × [SO_4^{2-}]), with higher concentrations in December than in November due to lower temperatures. The organic mass fraction was the highest across all PM_1 levels throughout the campaign. While organic aerosols (OA) were dominated by secondary organic aerosols (SOA = semi-volatile oxygenated organic aerosols + low-volatility oxygenated organic aerosols) as a campaign average, freshly-emitted hydrocarbon-like organic aerosols (HOA) contributed up to 40% of OA during high-OA periods that typically occurred at nighttime and contributed 23.8% to 28.4% on average. This was due to daytime traffic restrictions on heavy-duty vehicles in Guangzhou, and HOA almost increased linearly with total OA concentration. SOA increased as odd oxygen ($O_x = O_3 + NO_2$) increased during the day due to photochemistry. A combination of nighttime traffic emissions and daytime photochemistry contributed to the buildup of PM in Panyu. The mitigation of PM pollution in inner-city areas by reducing vehicular traffic can potentially improve air quality in peripheral areas.

Line 276-278 in the original manuscript. Change to:

Fig. 9 shows the monthly average of OA fractions as well as their variations in different ranges of OA concentrations. HOA contributed 23.8% and 28.4% to total OA in November and December respectively. However, HOA increased almost linearly with OA concentration, highlighting the need for traffic control to mitigate high PM concentrations in "buffer" areas. SVOOA and LVOOA remained the dominated OA fractions at OA concentrations below 70 $\mu g/m^3$, which explains the relatively low HOA contribution on a monthly basis.

Line 280-286 in the original manuscript. Change to:

Figure 10 shows the diurnal patterns in mass concentrations and fractions for the five OA factors. HOA exhibited two typical peaks during both November and December during the morning rush hour at 09:00 and in the evening around 21:00. HOA accounted for up to 40% of OA (95th percentile of mass fraction in a box-whisker plot) especially in the evening and at

night, likely due to heavily polluting trucks passing by en route to the city center at night (22:00 to 07:00). These diurnal variations in HOA correspond to those in the H:C ratio and NO_x as well as BC (Fig. S12), suggesting that vehicle-related pollutants are the main contributor to this OA factor.

2. What the size cutoff for the MARGA measurements? The authors analyzed HR mass spectra below m/z 200, but all mass spectra profiles in the manuscript did not show the signals at m/z > 100. Did the authors use all m/z's or just m/z<100 for PMF analysis? Were V-mode or W-mode spectra used for PMF analysis and elemental analysis?

The size cutoff for MARGA is 2.5 micrometer, i.e. MARGA measured $PM_{2.5}$. The PMF analysis used ions with m/z< 100 in this study. We considered only ions up to m/z 100 due to the low signal-to-noise ratios of larger ions. Both PMF and elemental analysis used the W-mode spectra. We have clarified these in the revised manuscript.

3. The authors used more than two pages to describe PMF-ME2 analysis. Although this analysis is pretty nice, most of which can be moved to the supplementary. Otherwise, this part will dilute the focus of this study.

Changed as suggested.

4. The authors used [NH4+]/[SO42-] to interpret the formation of nitrate, then the authors need to address the largest discrepancies of NH4+ measurements between AMS and MARGA (slope = 0.7, while 0.9-1.0 for sulfate and nitrate), and the potential influences.

Some anions not discussed also neutralized by ammonium, and those anions may have diameter between 1μm to 2.5 μm, which will be captured by MARGA while not by AMS. We have clarified this point in the revised manuscript in line 214.

5. The subtitles of 3.2-3.4 are not appropriate for the discussions below. The descriptions of elemental analysis in section 3.2 are better moved to the section 2.3.

We have re-organized the whole manuscript. However, because the elemental analysis section is more related to the "source and formation of OA" section, we prefer not to move the descriptions of elemental analysis to section 2.3.

6. The mass spectral profiles in Figure 4 are very confusing. The authors need to use ion speciated spectra and add different ion families to each other. The similar figures in supplementary also need to be revised.

We thank the reviewer for the suggestion. We have changed the original mass spectral profiles in the manuscript and the supplementary the ion speciated and add different ion families to each other.

7. One of the focuses of this study is HOA. It is clearly not the important discussions in section 3.2 organics, unfortunately. Also, please check the average contributions of OA in Figure 5. The average contribution of HOA is 26%, which is not consistent with the average diurnal fractions in Nov. and Dec. in Figure 6. In addition, it is better to show two pie charts by comparing the average OA composition between Nov. and Dec.

We focus on the traffic-related pollutants in this study, including but not limiting to the HOA. We also examined the formation of particulate nitrate and secondary organic aerosols (SOA), both of which exacerbate the PM problem. In the revised manuscript, we have made significant changes to highlight the focus of the paper.

In line 159-164:

The mass ratio of nitrate to sulfate in ambient aerosols can be further used to evaluate the relative importance of stationary and mobile sources (Arimoto, 1996; Tan et al., 2009). In our study, the average nitrate-to-sulfate ratios were around 0.35 when PM_1 levels were lower than 40 $\mu g/m^3$. These ratios increased significantly as the PM concentration increased, reaching 1.5 on the highest-PM_1 days (averaging 160 $\mu g/m^3$), highlighting the substantial contribution of vehicle emission pollutants to PM on high-PM days.

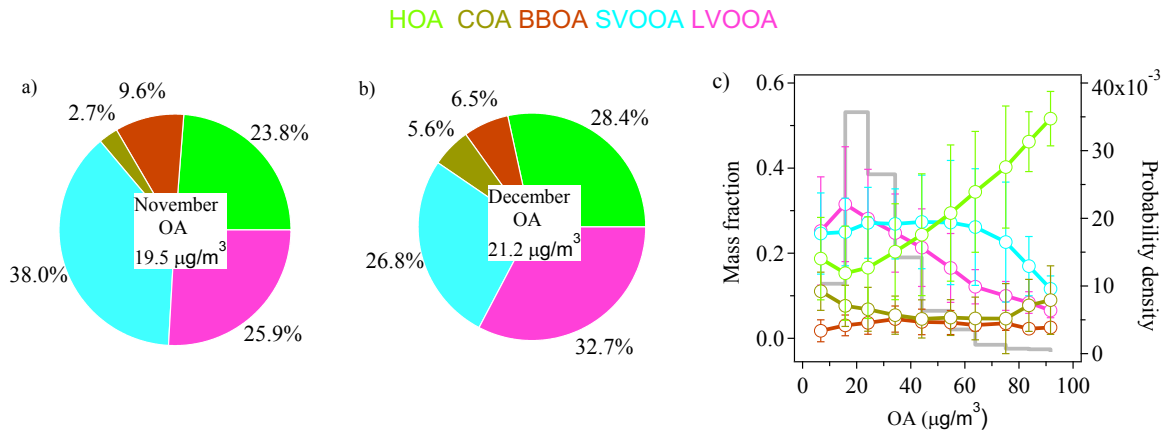
In Line 232-235:

A growing number of studies have shown that vehicle emissions are important sources of both primary and secondary organic aerosols (Deng et al., 2017; Louie et al., 2005; Platt et al., 2014). Reactive tracer gases and the primary organic pollutants can be oxidized to form SOA in urban air outflows (Gentner et al., 2017).

In Section 3.3.2:

In our study, HOA contributed 23.8% to total OA in November, while it contributed to 28.4% of OA in December. However, HOA almost linearly increased with OA concentration, and

played a signiciant role in the high OA situation. This observation highlights the importance of traffic control in mitigating the high PM concentration in such a "buffer" areas. From the probability density distribution, we can see that during the whole campaign, SVOOA and LVOOA were still the dominating OA fractions, which explains the relatively low HOA contribution on a monthly basis. Furthermore, SOA was very likely related to some traffic precursors, such as oxidation of VOCs and HOA, as the overwhelming significance of traffic related POA compared with the other primary sources. Liu et al.(2015) investigated the SOA formation from emissions of light-duty gasoline vehicles operated in China using a smog chamber under idling condition. They found that SOA formation was 12–259 times higher than POA under a conservative OH exposure. Deng et al.(2017) also revealed that the emission factors for BC and POA from major diesel vehicle types in China under idling condition and production factors for SOA under photochemical aging were significantly higher than those studies in Europe and the US and those of light-duty gasoline vehicles in China.



References:

Arimoto, R.: Arimoto et al., 1996.pdf, J. Geophys. Res., 101(d1), 2011–2023, doi:10.1029/95JD01071, 1996.

Deng, W., Hu, Q., Liu, T., Wang, X., Zhang, Y., Song, W., Sun, Y., Bi, X., Yu, J., Yang, W., Huang, X., Zhang, Z., Huang, Z., He, Q., Mellouki, A. and George, C.: Primary particulate emissions and secondary organic aerosol (SOA) formation from idling diesel vehicle exhaust in China, Sci. Total Environ., 593, 462–469, doi:10.1016/j.scitotenv.2017.03.088, 2017.

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.,

Prévôt, 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(3), 1074–1093, doi:10.1021/acs.est.6b04509, 2017.

Louie, P. K. K., Chow, J. C., Chen, L. W. A., Watson, J. G., Leung, G. and Sin, D. W. M.: PM2.5 chemical composition in Hong Kong: Urban and regional variations, Sci. Total Environ., 338(3), 267–281, doi:10.1016/j.scitotenv.2004.07.021, 2005.

Platt, S. M., El Haddad, I., Pieber, S. M., Huang, R.-J., Zardini, A. A., Clairotte, M., Suarez-Bertoa, R., Barmet, P., Pfaffenberger, L., Wolf, R., Slowik, J. G., Fuller, S. J., Kalberer, M., Chirico, R., Dommen, J., Astorga, C., Zimmermann, R., Marchand, N., Hellebust, S., Temime-Roussel, B., Baltensperger, U. and Prévôt, A. S. H.: Two-stroke scooters are a dominant source of air pollution in many cities., Nat. Commun., 5(May), 3749, doi:10.1038/ncomms4749, 2014.

Tan, J. H., Duan, J. C., Chen, D. H., Wang, X. H., Guo, S. J., Bi, X. H., Sheng, G. Y., He, K. Bin and Fu, J. M.: Chemical characteristics of haze during summer and winter in Guangzhou, Atmos. Res., 94(2), 238–245, doi:10.1016/j.atmosres.2009.05.016, 2009.