We thank reviewer#1 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:

Qin et al describe measurements of PM composition at a suburban site in the Pearl River Delta, China. The paper is topically relevant to ACP. The data collection methods, analysis, and interpretation all seem appropriate. However, the authors do not clearly articulate what new knowledge is generated by this manuscript, aside from a relatively small (2 month) dataset collected in a city without previously published AMS data. A revised manuscript should place more emphasis on the unique contribution of this work.

We have revised our manuscript significantly to focus on how the pollutants highly urban downtown cities can impact adjacent "buffer" peripheries, especially on nitrate and secondary organic aerosols due to traffic emissions. The manuscript was also significantly revised to highlight the potential impacts of the study, as follows.

The introduction has been changed to highlight the need to understand how urbanized megacities such as Guangzhou affect their peripheral cities. The prevailing wind direction from Guangzhou to Panyu during the campaign provides a unique opportunity for such research. While our study focuses on the PRD area, its findings can potentially be useful to developing control strategies in many city clusters in China.

Introduction change to:

Traffic emissions are one of the main contributors to air quality deterioration in rapidly expanding urban China (Kelly and Zhu, 2016; Zhang et al., 2017). Pollutants emitted from vehicles, such as NO_x, volatile organic compounds (VOCs), black carbon (BC) and other traffic-related particulate matter (PM), have increased over last decades(Wang et al., 2013; Zhang et al., 2012). Apart from the primary PM, the oxidation of traffic-related gaseous pollutants such as NO_x, VOCs, SVOCs and LVOCs leads to the formation of particulate nitrate and secondary organic aerosols (SOA), exacerbating PM pollution. Multiple studies have shown that the concentrations and proportions of nitrate in PM have increased significantly in most Chinese megacities (Pan et al., 2016; Wen et al., 2015; Xue et al., 2014).

The rapid economic development in the Pearl River Delta (PRD) region has led to a rapid deterioration in air quality, especially due to a sharp increase in PM (Chan and Yao, 2008; Ho et al., 2003; Li et al., 2017). With densely populated cities including two megacities,

Guangzhou and Shenzhen, and other smaller cities, the PRD region is developing into a giant city cluster. There are, nevertheless, less populated areas between these cities that can serve as a "buffer" zone in terms of regional air quality. Due to air dispersion patterns and regulatory strategies, air pollutants in highly urbanized regions can greatly influence PM levels in peripheral regions. For example, highly-polluting vehicles such as heavy-duty diesel trucks are banned from the inner areas of many Chinese megacities during the day but are nevertheless active at night and in the early morning, especially on the peripheries of these megacities. This regulatory policy has resulted in nighttime peaks in vehicular pollutants, which have been commonly observed in many Chinese cities (Zhang and Cao, 2015). Although vehicle emissions are substantially reduced relative to the without control scenarios, it was still significantly higher emission density in East China than in developed countries with longer histories of vehicle emission control (Wu et al., 2016). Given the complex and non-linear processes involved in the secondary production of PM such as nitrate and organic aerosols, the impacts of these adjacent "buffer" zones on air quality are crucial. However, relatively little attention has been paid to how air pollutants in major cities affect these adjacent areas.

Panyu District lies directly south of central Guangzhou and experiences predominantly northerly/northeasterly winds between September and February (Zou et al., 2015). A campaign with a host of real-time instruments including an Aerodyne HR-ToF-AMS was conducted at a site in Panyu from November to December 2014 and provides a unique opportunity to explore how pollutants from the city center have impacted this adjacent "buffer" zone, especially in terms of nitrate and secondary organic aerosols. As will be shown, the mass fraction of nitrate increased as PM_1 increased, and the organic mass fraction was the highest among PM_1 species across all PM_1 levels. A comprehensive analysis of nitrate and organics and their interplay with meteorological parameters will be presented. Primary OA (e.g. HOA) and SOA from traffic-related VOC precursors will also be discussed. Our findings can provide useful information for regional emission control strategies covering urban and "buffer" areas and improving parameterization in air quality models.

I have several comments on Section 2.3. Overall, this section seems more like Results than Methods, since much of the section is dedicated to comparing the various constrained versus unconstrained PMF solutions.

Agreed. In order not to dilute the focus of this manuscript, the whole section has been moved to the SI and has been revised according to the specific comments.

The whole section has been changed to:

In the main text:

Source apportionment for OA was performed using the newly developed ME-2 and controlled via the SoFi interface coded in Igor Pro (Canonaco et al., 2013). The procedure allows an effective exploration of the solution space, a more objective selection of the optimal solution, and an estimation of the rotational uncertainties (Canonaco et al., 2013; Crippa et al., 2014; Elser et al., 2016; Fröhlich et al., 2015; Paatero and Hopke, 2009). We only considered ions up to m/z 100 due to the low signal-to noise ratios of larger ions. Fully unconstrained runs (PMF) were first explored. However, the three-factor solution suffers from the mixing of the HOA factor with the cooking organic aerosols (COA) factor (Fig. S4) as well as the SVOOA factor with the biomass burning related organic aerosols (BBOA) factor. The four-factor solution splits highly oxidized low-volatile OOA (LVOOA) into two sub-factors (Fig. S5). The inclusion of additional factors still cannot resolve pure primary OA factors (HOA, COA and BBOA) as they may have similar time series or profiles. Zhang et al. (2013) also report that the PCA-resolved HOA can be affected by cooking emissions with a distinct noontime peak in Beijing in spring and summer. However, by introducing a priori information of source profiles for HOA, COA and BBOA, the ME-2 provides additional control over the rotational ambiguity (Canonaco et al., 2013; Paatero and Hopke, 2009). The a value, ranging from zero to unity, stands for the percentage by which each m/z signal of the final solution spectra may differ from the anchor. A value of 0 means no deviation is allowed, while a value of 1 means 100% deviation is allowed. The OA source apportionment was performed by constraining the source profile of HOA, COA and BBOA with a values of 0.1, 0.2, 0.3 for HOA, COA, and BBOA respectively. The HOA source profile was extracted from the data set using a separate PMF run in selected time series with peaks in organic mass concentration. The COA reference was adopted from the Mong Kok campaign in Hong Kong (Lee et al., 2015) while the reference BBOA profile was adopted from MILAGRO (Aiken et al., 2009). A detailed discussion can be found in the supplementary information (Text S2).

In the SI:

Text S2: Source apportionment for OA

Several source profiles from previously reported HR-ToF-AMS data with different a values were explored. However, some ions were missing from the reference source profile when

3

compared with our dataset. For these ions, the signal intensities were estimated based on the unit-mass-resolution (UMR) source profile from the average of multiple ambient data sets (Ng et al., 2011) as follows:

$$I_{m/z} = k * I_{UMR(m/z)} - I_{HRrest(m/z)} \qquad (1);$$

$$k = I_{UMR(total)} / I_{HR(total)} \qquad (2).$$

where $I_{m/z}$ is the signal intensity of the missing ions in the reference profile; k is a correction factor, derived from the ratio of total signal intensities in the UMR and HR profiles, which accounts for the difference in total signal intensity between the profiles; $I_{UMR(m/z)}$ is the total signal intensity at UMR level for the missing ions in the UMR profile; and $I_{HRrest(m/z)}$ is the sum of the signal intensities of the rest of the ions from HR reference profile that shares the same integer m/z as the missing ions. For these ions, whose intensities are derived from the above equation, an a value of 1 (100% deviation) was used.

We used the ME-2 solver with reference mass spectra to tackle the problem of mixing sources in our PMF runs. The HOA the Paris campaign (Crippa et al., 2013) as an input reference however were not fitted in our dataset. The resolved-HOA factor contributed no more than 5% of total OA, and only exhibited a small morning rush peak in the diurnal pattern (Fig. S6). Furthermore, another factor was observed to share similar features with the HOA mass spectrum. This factor exhibited clear rush-hour peaks during the morning and late afternoon, as with traffic-related pollutants (e.g. NO_x and BC). Also, the mass fraction of this factor is 3-4 times higher than the resolved-HOA factor. Alternatively, we directly extracted a local HOA source profile (HOA_{loc}) from the data set using a separate PMF run in selected time series with peaks in organic mass concentration. We selected the high OA events in order to capture some periods with potentially high HOA. As shown in Fig S7, the concentrations of other traffic tracers (for example BC and NOx) were also high. A similar approach of extracting factors in unconstrained PMF and subsequent combination of duplicate factors was also used in a previous study (Fröhlich et al., 2015). (Fröhlich et al., 2015)(Fröhlich et al., 2015) Using the peaks or only one peak yield similar mass spectra for local HOA factors with $R_{uc}=0.99$ (Fig. S7a, S7b). The HOA profiles remained the similar with even more factors (Fig. S7c). We then used the HOA source profile obtained from all of the short peaks as the input HOA source profile (LHOA therein). However, constrained LHOA alone cannot resolved an environmentally reasonable solution either (Fig. S8). We then tried to added other primary OA

source profiles as constrain. For COA source profile, we chose the COA source profile from the Hong Kong campaign (HK) to constrain our ME-2 runs as cooking styles and ingredients in Guangzhou are similar to those in Hong Kong. For the BBOA factor, we used the reference BBOA profile from MILAGRO (Aiken et al., 2009). The resolved BBOA factor tracked well with its tracer ion ($C_2H_4O_2^+$) and potassium (K^+) in time series.

A four-factor (HOA, COA, BBOA and a free factor) solution had a higher Q/Q_{exp}, while a six-factor (HOA, COA, BBOA and three free factors) solution seemed to split OOA factors without obvious physical meaning. An five-factor solution with a values of 0.1, 0.2, 0.3 for HOA_{local}, COA_{HK}, and $BBOA_{MILAGRO}$, respectively, was finally adopted. The a values for these POA factors were also in line with previous ME-2 studies (Canonaco et al., 2013; Crippa et al., 2014; Fröhlich et al., 2015). We further run the ME-2 with the same conditions with 10 runs to explore the stability of solution. The time series and mass spectra for these 10 runs were quite steady (Fig. S10). The final solution came from results obtained with averaging these ten runs. Two oxygenated organic aerosol factors, SVOOA and LVOOA, were assigned based on their degree of oxygenation.

Specific comments for this section include:

1. The main goal of the text from _line 131-189 is buried. My interpretation is that the authors are describing their efforts to separate an HOA factor from a cooking (COA) factor, and that these two factors do not cleanly "fall out" from unconstrained PMF (e.g., moving from 3 to 4 to 5 unconstrained factors starts splitting OOA factors rather than splitting HOA and COA).
Yes. Because the PMF solutions showed signs of source mixing (viz. HOA mixed with COA, BBOA mixed with OOA), we therefore used ME-2 to constrain the primary OA source. The above statement has been added to this section.

2. I am confused by Lines 167-175. I think the authors performed a separate unconstrained PMF analysis of high concentration events, assumed that the high concentration peaks are dominated by HOA, and used the resulting HOA factor from these high events to constrain the more general HOA mass spectrum. If this is the case, the description is extremely confusing (I had trouble determining if lines 167-175 describe a single PMF solution approach or multiple), and the utility of this approach is not described well. Also, the authors do not describe what evidence they used to attribute the high concentration events to traffic/HOW.

Yes. We performed a separate unconstrained PMF analysis of high OA concentration events to capture a local HOA factor. These high OA events is likely affected by high HOA, so that it is possible to resolve a HOA factor from these high OA peaks by perform a PMF analysis. As shown below, the concentrations of other traffic tracers (for example BC and NOx) were also high, indicating the potential influence by high HOA. A similar approach of extracting factors in unconstrained PMF and subsequent combination of duplicate factors was also used in a previous study (Fröhlich et al., 2015).
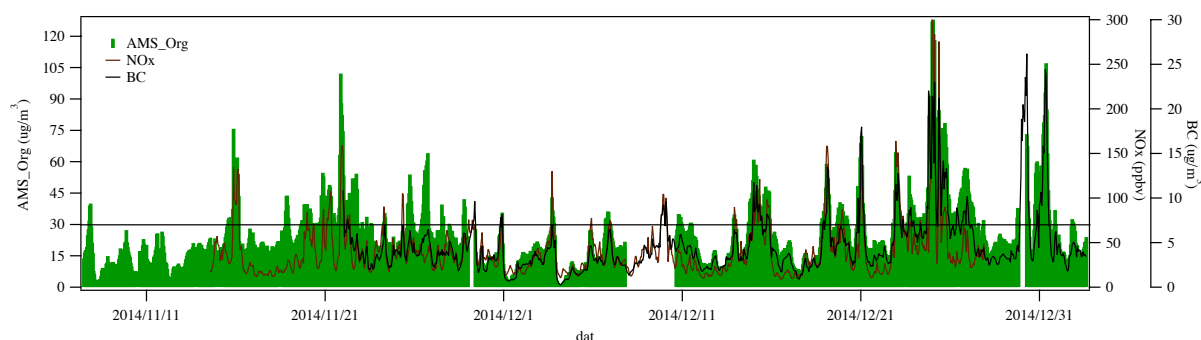
The original text has been change to:

Alternatively, we directly extracted a local HOA source profile (HOA$_{loc}$) from the data set using a separate PMF run in selected time series with peaks in organic mass concentration. We selected the high OA events in order to capture some periods with potentially high HOA. As shown in Fig S7, the concentrations of other traffic tracers (for example BC and NOx) were also high, indicating the potential influence by high HOA. A similar approach of extracting factors in unconstrained PMF and subsequent combination of duplicate factors was also used in a previous study (Fröhlich et al., 2015). (Fröhlich et al., 2015)(Fröhlich et al., 2015) Using the peaks or only one peak yield similar mass spectra for local HOA factors with R$_{uc}$=0.99 (Fig. S7a, S7b). The HOA profiles remained the similar with even more factors (Fig. S7c).

3. Lines 190-201 describe an "optimum" solution (the authors should be careful with this word because their source apportionment was not formally optimized) and compare 10 runs of that optimum solution. What is changing between these 10 runs? It is not explained why the 10 runs might result in different answers.

Changed from "optimal" to "final". The additional ten runs were performed with the same setting as used in the final solution to confirm the stability of the final solution.

4. Does the final PMF solution incorporate the high concentration events, or exclude them? E.g., does the pie chart in Figure 5 include the high concentration events?

Yes. The high concentration events are included in the final solution.

Comments on Section 3.3 - Formation of SOA

1. The main idea of this section seems to be that SOA formation is dominated by gas-phase oxidation chemistry (hence a strong SOA-to-Ox relationship) rather than heterogeneous or aqueous oxidation pathways. This should be stated more clearly.

We have classified the above sentence as suggested.

In line 301-307:

The evolution of AMS OA factors has been used to infer SOA formation via photochemical oxidation in Hong Kong (Lee et al., 2013; Li et al., 2013; Qin et al., 2016). Fig. 11a shows that SOA (SVOOA+LVOOA) increased as O_x increased during the day (7:00 to 18:00) in both November and December. The SOA concentrations do not show clear correlations with temperature or liquid water content in aerosols (Fig 11b, 11c). When taken together, this suggests that SOA formation in our study is dominated by gas-phase oxidation chemistry rather than heterogeneous or aqueous oxidation pathways.

2. The SOA/Ox slope is higher than other locations (Table 2). The humid tropical climate is given as the reason. Can this claim be substantiated more quantitatively? Another possible explanation is that emissions are different in the PRD than the North American cities listed in Table 2. The authors should address possible explanations besides climate.

Agree. The higher emissions in the PRD than the North American cities may also lead to the above results. Liu et al.(2015) and Deng et al.(2017) reported that the emission factor for BC and POA and production factor for SOA under photochemical aging were significantly higher than those studies in Europe and the US and those of light-duty gasoline vehicles.

The above statements have been added to the revised manuscript in Line 313-318.

3. One could argue that Figure 7b shows that SOA formation was essentially independent of temperature for this city over the temperature range sampled in November and December.

Yes. The temperature effect on gas-particle partitioning did not appear to be important in this study. As we stated in the original manuscript:

Higher temperatures should favor the partitioning of SOA to the vapor phase, but higher SOA mass loading was associated with higher temperature in our case (Fig. 7b). In November, LWC stayed in a relatively narrow range (Fig. 7c) when SOA experienced drastic changes. In December, LWC was lower than that in November. Yet, SOA increased as LWC increased. The enhanced LWC may facilitate the SOA formation in December, but such influence was not clear in November. Furthermore, there is no correlation between SOA/OA and LWC in either month.

Other comments

1.   Line 91 - Please provide details for the manufacturer of the MARGA

Metrohm applikon. Added in the revised manuscript line 81.

Other data presented in this work were obtained from collocated instruments, which included a Grimm 180 for $PM_{2.5}$, a thermo-optical ECOC analyzer (Sunset Laboratory Inc.), a Magee AE33, a dual spot filter based instrument for black carbon (Drinovec et al., 2015), a gas analyzer system (Teledyne Instruments), and a monitor for aerosols and gases in ambient air (MARGA, Metrohm applikon) with a $PM_{2.5}$ cutoff.

2.   Line 89 - what method does the Grimm 180 use for determining PM mass?

The Grimm monitor was based on particle scattering measurements or called optical particle counter. A $PM_{2.5}$ cut-off was placed before the GRIMM 180. We integrated the hourly Grimm 180 data into daily basis, and then compared with the daily $PM_{2.5}$ mass concentration with quartz filter measurement (PQ200 Ambient Air Particulate Sampler with a $PM_{2.5}$ cut-off). Added in the revised SI (Text S1).

3.   Line 92-93 - Please provide more detail on how the Grimm 180 data were corrected with quartz filter data. Did the correction use bare quartz filters only?

Hourly Grimm 180 data was integrated into daily basis, and then compared with quartz filter measurement (PQ200 Ambient Air Particulate Sampler with a $PM_{2.5}$ cut-off). The daily mass concentration by quartz filter sampling was then obtained gravimetrically. The PQ200 and Grimm 180 measurements were in good agreement with R^2 of 0.93, with a slope of PQ200 vs. Grimm 180 data of 1.232. We then used the linearly fitted parameter to correct the hourly

Grimm 180 data to derive the hourly PM$_{2.5}$ mass concentration. Added in the revised SI (Text S1).
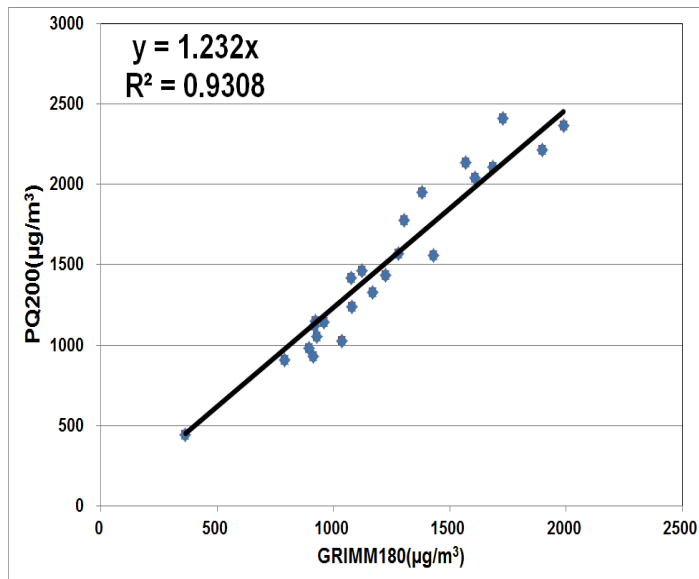
4.   Section 2.2 needs to be broken into multiple paragraphs.

Changed as suggest.

5.   Line 118 - Need citation for the Middlebrook paper

Changed as suggest.

6.   Figure 2b - label says NH3, should be NH4

Changed as suggest.

7.   Line 343 - it is not clear what "this method" and Method 1 refer to, specifically.

"this method" or Method 1 refer to the ON estimation based on NO$^+$ to NO$_2^+$ ratio. Revision in wording has been made.

Change to:

The method using NO$^+$/NO$_2^+$ (Method 1, hereinafter) was adopted in this study to estimate the contributions of inorganic and organic nitrates.

8.   Figure 6 - In December it seems that the mean HOA concentration is often outside of the 75th percentile. Are the diurnal patterns in this month skewed by a few very high concentration days?

Yes. The mean concentrations were greatly affected by a few very high concentration days, especially from 0:00-12:00. There were several significant HOA peaks during December (19 Dec., 21 Dec., 23 Dec, 25 Dec., and 31 Dec., as can be seen from Fig. 4). Furthermore, from Fig. 5c, HOA almost linearly increased with OA concentration, and played a significant contribution to the high OA situation. This observation highlights the importance of traffic control in mitigating the high PM pollution in "buffer" areas.

9. Figure 6 - It looks like the average LVOOA is about 1 ug/m^3 higher in December than November. Given that there is less photochemical activity, does this seem physically reasonable? Or could it be an artifact of the source apportionment?

We analyzed photochemical activities based on locally measured parameters, e.g. O_x etc. Therefore, it is the local photochemical activities that were lower. LVOOA in Dec can be from long range transport.

10. Fig 4 - C3H3O does not seem like a great COA tracer. Is there a scatter plot showing the relationship of COA with this tracer ion?

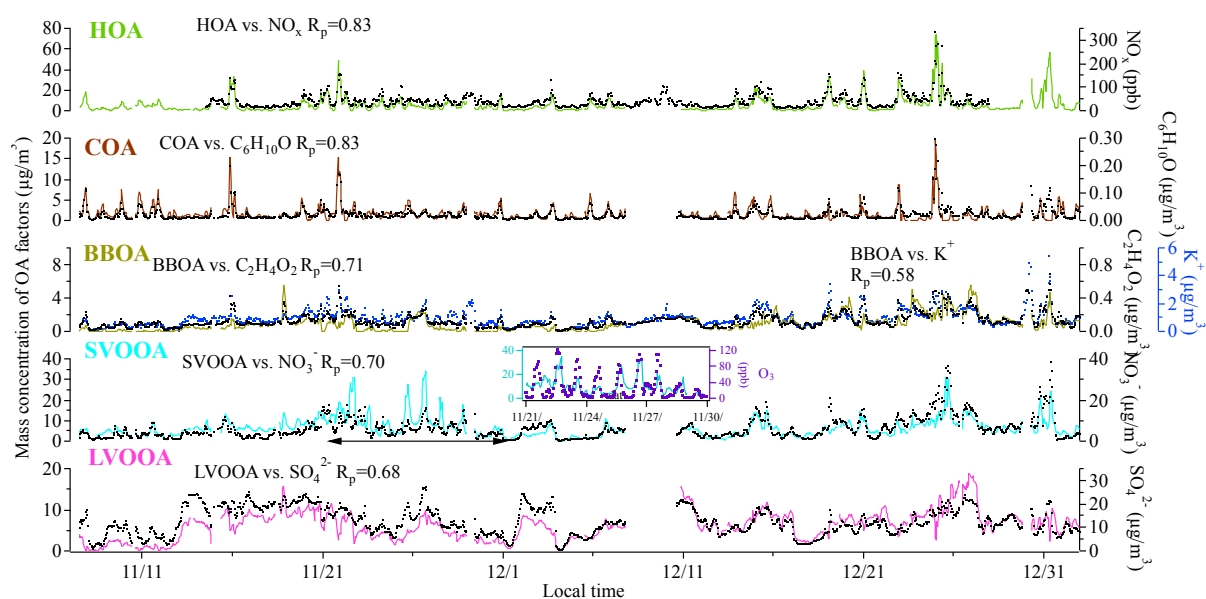Agree. The scatter plot showing the relationship of COA and C_3H_3O and other COA tracer (Sun et al., 2011) is shown as below. Indeed, C_3H_3O does not seem like a great COA tracer. Rather, $C_6H_{10}O$ tracks better with COA.
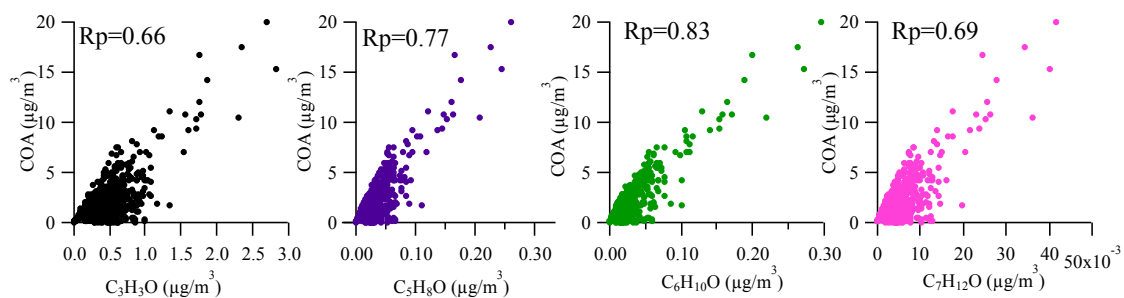
The original text has been change to:

 The time series of COA tracked well with one of its tracer ions, $C_6H_{10}O^+$.

And the time series plot has been changed to:

References:

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty, K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A., Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan, V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P., Molina, L. T., Sosa, G. and Jimenez, J. L.: Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 1: Fine particle composition and organic source apportionment, Atmos. Chem. Phys., 9(17), 6633–6653, doi:10.5194/acp-9-6633-2009, 2009.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U. and Prévôt, A. S. H.: SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6(12), 3649–3661, doi:10.5194/amt-6-3649-2013, 2013.

Chan, C. K. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42(1), 1–42, doi:10.1016/j.atmosenv.2007.09.003, 2008.

Crippa, M., El Haddad, I., Slowik, J. G., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Sciare, J., Baltensperger, U. and Prévôt, A. S. H.: Identification of marine and continental aerosol sources in Paris using high resolution aerosol mass spectrometry, J. Geophys. Res. Atmos., 118(4), 1950–1963, doi:10.1002/jgrd.50151, 2013.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U. and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14(12), 6159–6176, doi:10.5194/acp-14-6159-2014, 2014.

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.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A. and Hansen, A. D. A.: The "dual-spot" Aethalometer: An improved measurement of aerosol black carbon with real-time loading compensation, Atmos. Meas. Tech., 8(5), 1965–1979, doi:10.5194/amt-8-1965-2015, 2015.

Elser, M., Huang, R.-J., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., Li, G., Bozzetti, C., Daellenbach, K. R., Huang, Y., Zhang, R., Li, Z., Cao, J., Baltensperger, U., El-Haddad, I. and Prévôt, A. S. H.: New insights into PM<sub>2.5</sub> chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry, Atmos. Chem. Phys., 16(5), 3207–3225, doi:10.5194/acp-16-3207-2016, 2016.

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J. and Prévôt, A. S. H.: ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, Atmos. Meas. Tech., 8(6), 2555–2576, doi:10.5194/amt-8-2555-2015, 2015.

Ho, K. ., Lee, S. ., Chan, C. K., Yu, J. C., Chow, J. C. and Yao, X. .: Characterization of chemical species in PM2.5 and PM10 aerosols in Hong Kong, Atmos. Environ., 37(1), 31–39, doi:10.1016/S1352-2310(02)00804-X, 2003.

Kelly, F. J. and Zhu, T.: Transport solutions for cleaner air, Science (80-.)., 352(6288), 934–936, doi:10.1126/science.aaf3420, 2016.

Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K. K. and Chan, C. K.: Physical and chemical characterization of ambient aerosol by HR-ToF-AMS at a suburban site in Hong Kong during springtime 2011, J. Geophys. Res. Atmos., 118(15), 8625–8639, doi:10.1002/jgrd.50658, 2013.

Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K. K. and Chan, C. K.: Journal of Geophysical Research : Atmospheres, , 1–19, doi:10.1002/2015JD023311.Received, 2015.

Li, Y. J., Lee, B. Y. L., Yu, J. Z., Ng, N. L. and Chan, C. K.: Evaluating the degree of oxygenation of organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), Atmos. Chem. Phys., 13(17), 8739–8753, doi:10.5194/acp-13-8739-2013, 2013.

Li, Y. J., Sun, Y., Zhang, Q., Li, X., Li, M., Zhou, Z. and Chan, C. K.: Real-time chemical characterization of atmospheric particulate matter in China : A review, Atmos. Environ., 158, 270–304, doi:10.1016/j.atmosenv.2017.02.027, 2017.

Liu, T., Wang, X., Deng, W., Hu, Q., Ding, X., Zhang, Y., He, Q., Zhang, Z., L??, S., Bi, X., Chen, J. and Yu, J.: Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber, Atmos. Chem. Phys., 15(15), 9049–9062, doi:10.5194/acp-15-9049-2015, 2015.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M. and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, Environ. Sci. Technol., 45(3), 910–916, doi:10.1021/es102951k, 2011.

Paatero, P. and Hopke, P. K.: Rotational tools for factor analytic models, J. Chemom., 23(2), 91–100, doi:10.1002/cem.1197, 2009.

Pan, Y., Wang, Y., Zhang, J., Liu, Z., Wang, L., Tian, S., Tang, G., Gao, W., Ji, D., Song, T. and Wang, Y.: Redefining the importance of nitrate during haze pollution to help optimize an emission control strategy., 2016.

Qin, Y. M., Li, Y. J., Wang, H., Lee, B. P. Y. L., Huang, D. D. and Chan, C. K.: Particulate matter (PM) episodes at a suburban site in Hong Kong: evolution of PM characteristics and role of photochemistry in secondary aerosol formation, Atmos. Chem. Phys., 16(11), 14131–14145, doi:10.5194/acp-2016-414, 2016.

Sun, Y. L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W. N., Bae, M. S., Hung, H. M., Hogrefe, O., Frank, B., Rattigan, O. V. and Lin, Y. C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution

time-of-flight aerosol mass apectrometer, Atmos. Chem. Phys., 11(4), 1581–1602, doi:10.5194/acp-11-1581-2011, 2011.

Wang, Y., Zhang, Q. Q., He, K., Zhang, Q. and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: Response to 2000-2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, Atmos. Chem. Phys., 13(5), 2635–2652, doi:10.5194/acp-13-2635-2013, 2013.

Wen, L., Chen, J., Yang, L., Wang, X., Xu, C., Sui, X., Yao, L., Zhu, Y., Zhang, J., Zhu, T. and Wang, W.: Enhanced formation of fine particulate nitrate at a rural site on the North China Plain in summer: The important roles of ammonia and ozone, Atmos. Environ., 101, 294–302, doi:10.1016/j.atmosenv.2014.11.037, 2015.

Wu, X., Wu, Y., Zhang, S., Liu, H., Fu, L. and Hao, J.: Assessment of vehicle emission programs in China during 1998-2013: Achievement, challenges and implications, Environ. Pollut., 214(X), 556–567, doi:10.1016/j.envpol.2016.04.042, 2016.

Xue, J., Yuan, Z., Lau, A. K. H. and Yu, J. Z.: Insights into factors affecting nitrate in $PM_{2.5}$ in a polluted high NO_x environment through hourly observations and size distribution measurements, J. Geophys. Res. Atmos., 119(8), 4888–4902, doi:10.1002/2013JD021108, 2014.

Zhang, Q., Geng, G. N., Wang, S. W., Richter, A. and He, K. Bin: Satellite remote sensing of changes in NO x emissions over China during 1996-2010, Chinese Sci. Bull., 57(22), 2857–2864, doi:10.1007/s11434-012-5015-4, 2012.

Zhang, Y., Cai, J., Wang, S., He, K. and Zheng, M.: Review of receptor-based source apportionment research of fine particulate matter and its challenges in China, Sci. Total Environ., 586, 917–929, doi:10.1016/j.scitotenv.2017.02.071, 2017.

Zhang, Y.-L. and Cao, F.: Fine particulate matter (PM 2.5) in China at a city level., Sci. Rep., 5, 14884, doi:10.1038/srep14884, 2015.

Zou, Y., Deng, X. J., Zhu, D., Gong, D. C., Wang, H., Li, F., Tan, H. B., Deng, T., Mai, B. R., Liu, X. T. and Wang, B. G.: Characteristics of 1 year of observational data of VOCs, NO_x and O_3 at a suburban site in Guangzhou, China, Atmos. Chem. Phys., 15(12), 6625–6636, doi:10.5194/acp-15-6625-2015, 2015.

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 ($[NH_4^+]/[SO_4^{2-}] - 1.5) \times [SO_4^{2-}]$), 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.

HOA COA BBOA SVOOA LVOOA
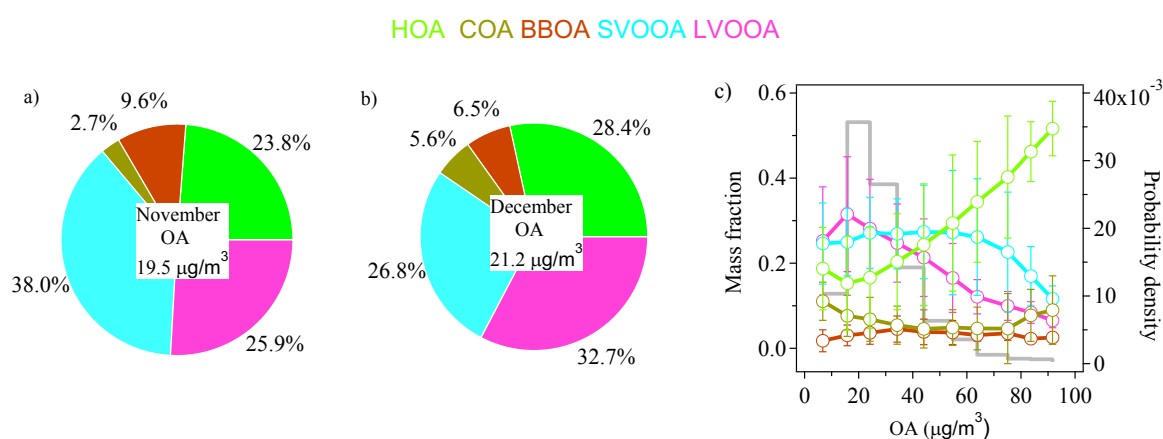
References:

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.