Impacts of traffic emissions on atmospheric particulate nitrate and organics at a downwind site on the periphery of Guangzhou, China

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1 Abstract:

2 Particulate matter (PM) pollution on the peripheries of Chinese megacities can be as serious as in 3 cities themselves. Given the substantial vehicular emissions in inner-city areas, the direct transport 4 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 5 6 "buffer" zones between cities. To investigate how traffic emissions in inner-city areas impact these 7 adjacent "buffer" zones, a suite of real-time instruments were deployed in Panyu, downwind from 8 central Guangzhou, from November to December 2014. Nitrate mass fraction was higher on high-9 PM days, with the average nitrate-to-sulfate ratio increasing from around 0.35 to 1.5 as the PM 10 mass concentration increased from 10 to 160 μ g/m³. Particulate nitrate was strongly correlated with excess ammonium ($[NH_4^+]/[SO_4^{2-}] - 1.5$) × $[SO_4^{2-}]$), with higher concentrations in December 11 12 than in November due to lower temperatures. The organic mass fraction was the highest across all 13 PM₁ levels throughout the campaign. While organic aerosols (OA) were dominated by secondary 14 organic aerosols (SOA = semi-volatile oxygenated organic aerosols + low-volatility oxygenated 15 organic aerosols) as a campaign average, freshly-emitted hydrocarbon-like organic aerosols (HOA) 16 contributed up to 40% of OA during high-OA periods that typically occurred at nighttime and 17 contributed 23.8% to 28.4% on average. This was due to daytime traffic restrictions on heavy-duty 18 vehicles in Guangzhou, and HOA almost increased linearly with total OA concentration. SOA 19 increased as odd oxygen ($O_x = O_3 + NO_2$) increased during the day due to photochemistry. A 20 combination of nighttime traffic emissions and daytime photochemistry contributed to the buildup 21 of PM in Panyu. The mitigation of PM pollution in inner-city areas by reducing vehicular traffic 22 can potentially improve air quality in peripheral areas.

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24 **1. Introduction:**

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, semivolatile VOCs (SVOCs) and low-volatility VOCs (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).

34 The rapid economic development in the Pearl River Delta (PRD) region has led to a rapid 35 deterioration in air quality, especially due to a sharp increase in PM (Chan and Yao, 2008; Ho et 36 al., 2003; Li et al., 2017). With densely populated cities including two megacities, Guangzhou and 37 Shenzhen, and other smaller cities, the PRD region is developing into a giant city cluster. There 38 are, nevertheless, less populated areas between these cities that can serve as a "buffer" zone in 39 terms of regional air quality. Due to air dispersion patterns and regulatory strategies, air pollutants 40 in highly urbanized regions can greatly influence PM levels in peripheral regions. For example, 41 highly-polluting vehicles such as heavy-duty diesel trucks are banned from the inner areas of many 42 Chinese megacities during the day but are nevertheless active at night and in the early morning, 43 especially on the peripheries of these megacities. This regulatory policy has resulted in nighttime 44 peaks in vehicular pollutants, which have been commonly observed in many Chinese cities (Zhang 45 and Cao, 2015). Although vehicle emissions are substantially reduced relative to the without 46 control scenarios, there was still significantly higher emission density in East China than in 47 developed countries with longer histories of vehicle emission control (Wu et al., 2016). Given the 48 complex and non-linear processes involved in the secondary production of PM such as nitrate and 49 organic aerosols, the impacts of these adjacent "buffer" zones on air quality are crucial. However, 50 relatively little attention has been paid to how air pollutants in major cities affect these adjacent 51 areas.

52 Panyu District lies directly south of central Guangzhou and experiences predominantly 53 northerly/northeasterly winds between September and February (Zou et al., 2015). A campaign 54 with a host of real-time instruments including an Aerodyne HR-ToF-AMS was conducted at a site 55 in Panyu from November to December 2014 and provides a unique opportunity to explore how 56 pollutants from the city center have impacted this adjacent "buffer" zone, especially in terms of 57 nitrate and secondary organic aerosols. As will be shown, the mass fraction of nitrate increased as 58 PM_1 increased, and the organic mass fraction was the highest among PM_1 species across all PM_1 59 levels. A comprehensive analysis of nitrate and organics and their interplay with meteorological 60 parameters will be presented. Primary OA (e.g. HOA) and SOA from traffic-related VOC 61 precursors will also be discussed. Our findings can provide useful information for regional

emission control strategies covering urban and "buffer" areas and improving parameterization inair quality models.

64 **2. Method**

65 **2.1. Sampling site description**

Guangzhou Panyu Atmospheric Composition Station (GPACS), a China Meteorological Administration site, is located at the summit of Dazhengang (23°00 N, 113°21 E) at an altitude of approximately 150 m (Fig. S1 in the Supplement). The site is approximately 15 km south of the city center and surrounded by residential neighborhoods with no significant industrial sources nearby (Tan et al., 2013; Cheung et al., 2016). Ambient sampling was conducted from November 71 7th, 2014 to January 3rd, 2015.

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73 **2.2. Measurements**

74 In the HR-ToF-AMS measurements (DeCarlo et al., 2006), ambient air was sampled through a 75 PM_{2.5} cyclone on the rooftop with a flow rate of approximately 0.084 L/min drawn by the AMS 76 and the remainder drawn by an auxiliary pump. A diffusion drier was used to dry the sampled air 77 stream, which reduced the RH of the air to below 30% before entering the HR-ToF-AMS. Other 78 data presented in this work were obtained from collocated instruments including a Grimm 180 for 79 PM_{2.5}, a thermo-optical ECOC analyzer (Sunset Laboratory Inc.), a Magee AE33, a dual spot filter-80 based instrument for black carbon (Drinovec et al., 2015), a gas analyzer system (Teledyne 81 Instruments), and a monitor for aerosols and gases in ambient air (MARGA, Metrohm applikon) 82 with a PM_{2.5} cutoff. The PM_{2.5} mass concentration as measured with a Grimm 180 was corrected 83 using the daily PM_{2.5} mass concentration through quartz filter measurement (Text S1). 84 Meteorological data (e.g. wind, temperature and RH) were obtained from a weather station located 85 near the sampling site. Solar irradiance data were measured from a station in Nansha District, 86 around 27.5 km from the sampling site. Particle liquid water content (LWC) was estimated with 87 an aerosol inorganic model (E-AIM II) (Clegg et al., 1998).

The AMS collected five-minute average particle mass spectra spanning from m/z 12 to 300 for the V+ particle time-of-flight (pToF) mode (high sensitivity) and the W mode (high resolution). The high-resolution only analyzed the signals with m/z below 200. AMS calibrations, including ionization efficiency (IE) calibration, flow rate calibration, and size calibration, were used as well

92 as data quality assurance protocols (DeCarlo et al., 2006; Lee et al., 2013; Schurman et al., 2015). IE calibrations with DMA size-selected (mobility diameter, D_m= 400 nm) pure ammonium nitrate 93 94 particles were carried out weekly. Ambient air filtered with a HEPA filter was sampled on a daily 95 basis for 30 minutes to obtain background signals. Flow rate was made with a Gilian Gilibrator. 96 PToF size calibrations were made with Nanosphere TM PSL particles (Duke Scientific, Palo Alto, 97 CA, USA) and ammonium nitrate particles in the size range of 178 to 800 nm (selected with a 98 scanning mobility particle sizer). Both flow rate and size calibration were performed before and 99 after the sampling campaign. Gaseous CO_2 concentrations were measured with a CO_2 monitor 100 (PICARRO 2301) to quantify their contributions to m/z 44 signal intensities.

101 **2.3. Data analysis**

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103 AMS data analysis was performed using the SQUIRREL (v1.56D) and PIKA (v1.15D) toolkits 104 written in Igor Pro 6.37A (WaveMetrics Inc., Lake Oswego, OR). Default relative ionization 105 efficiency (RIE) values of 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, and 1.4 for organics were 106 used. The ammonium RIE of 4.7 was chosen as the average from IE calibrations. A particle 107 collection efficiency factor (CE) of 0.7 was used to account for particle losses within the instrument. 108 The influence of RH in this study was minor, as a diffusion drier was used to maintain the sampling 109 line RH consistently below 30%. Under these conditions, Middlebrook's parameterization 110 suggests a CE of ~45–50% based on the measured inorganic constituents (Middlebrook et al., 111 2012). However, organic compounds, which are less bouncy than inorganics, dominated at the 112 measurement site. They can also hinder the complete efflorescence of particles in the drier and 113 further reduce the particle bounce effect and increase particle collection efficiency. The mass 114 concentrations of PM_1 (sum of nonrefractory- PM_1 and BC) were comparable to those of $PM_{2.5}$ 115 with a slope of 1.1 and Pearson correlation coefficient (R_p) of 0.95 (Fig. S2a) when using a CE of 116 0.7. Furthermore, total AMS organics were also correlated with organic matter (OM) 117 concentrations derived from the OC measurements (Fig. S2b) with a slope of 1.1 and R_p of 0.82. 118 The OC-to-OM conversion was calculated using organic-matter-to-organic-carbon ratio (OM:OC) 119 data from the HR-ToF-AMS elemental analysis. AMS-measured sulfate, nitrate, and ammonium 120 were comparable to those measured with MARGA with slopes of 1.0, 0.9, and 0.7 respectively. 121 These comparisons suggest that a choice of CE = 0.7 is appropriate for the OA-dominating 122 nonrefractory- PM_1 (NR- PM_1) in this study.

123 Source apportionment for OA was performed using the newly developed ME-2 via the SoFi interface coded in Igor Pro (Canonaco et al., 2013). The procedure allows an effective exploration 124 125 of the solution space, a more objective selection of the optimal solution, and an estimation of the 126 rotational uncertainties (Canonaco et al., 2013; Crippa et al., 2014; Elser et al., 2016; Fröhlich et 127 al., 2015; Paatero and Hopke, 2009). We only considered ions up to m/z 100 due to the low signal-128 to noise ratios of larger ions. Fully unconstrained runs (PMF) were first explored. However, the 129 three-factor solution suffers from the mixing of the HOA factor with the cooking organic aerosols 130 (COA) factor (Fig. S4) as well as the SVOOA factor with the biomass burning related organic 131 aerosols (BBOA) factor. The four-factor solution splits highly oxidized low-volatile OOA 132 (LVOOA) into two sub-factors (Fig. S5). The inclusion of additional factors still cannot resolve 133 pure primary OA factors (HOA, COA and BBOA) as they may have similar time series or profiles. 134 Zhang et al. (2013) also report that the principal component analysis--resolved HOA can be 135 affected by cooking emissions with a distinct noontime peak in Beijing in spring and summer. By 136 introducing a priori information of source profiles for HOA, COA and BBOA, the ME-2 provides 137 additional control over the rotational ambiguity (Canonaco et al., 2013; Paatero and Hopke, 2009). 138 The *a* value, ranging from zero to unity, stands for the percentage by which each m/z signal of the 139 final solution spectra may differ from the anchor. A value of 0 means no deviation is allowed, 140 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, and 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).

- 148 **3. Results and Discussion:**
- 149 **3.1. Overall composition**
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151Northerlywindsprevailedthroughouttheentirecampaign152(Text S3). Located south of central Guangzhou, the sampling site was thus severely affected by

153 pollutants transported from the city center. Overall, organics accounted for 46.3 % (or 24.5 μ g/m³) 154 of the PM₁ mass on average. Sulfate, nitrate, ammonium, BC, and chloride accounted for 23.1%, 155 11.2%, 9.1%, 8.3%, and 1.9% of the PM₁ mass respectively (Fig. 1a).Fig. 1b show the variations 156 in species mass fractions in PM_1 species as a function of total PM_1 mass loading (with BC inclusive) 157 and the probability density of PM₁ mass loading respectively. The organic mass fraction was the 158 highest among all PM_1 species across all PM_1 levels. On the contrary, the mass fraction of sulfate 159 decreased from 0.25 to 0.15 as the PM₁ concentration increased from 10 to 160 μ g/m³. The 160 decrease in the sulfate mass fraction was compensated for by the increased mass fraction of nitrate 161 and, to a lesser extent, chloride. The mass ratio of nitrate to sulfate in ambient aerosols can be 162 further used to evaluate the relative importance of stationary and mobile sources (Arimoto, 1996; 163 Tan et al., 2009). In our study, the average nitrate-to-sulfate ratios were around 0.35 when PM₁ levels were lower than 40 μ g/m³. These ratios increased significantly as the PM concentration 164 increased, reaching 1.5 on the highest-PM₁ days (averaging 160 μ g/m³), highlighting the 165 166 substantial contribution of vehicle emission pollutants to PM on high-PM days.

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3.2. Nitrate formation

169 The increase in the relative contribution of nitrate on highly-polluted days has also been observed 170 in AMS studies at other locations in China, such as Shenzhen (He et al., 2011), Beijing (Huang et 171 al., 2010), and Changdao (Hu et al., 2013). We used the molar concentration of total nitrate 172 $[HNO_3(g) + NO_3(p)]$ to examine the increase in nitrate species, where $HNO_3(g)$ was measured 173 with MARGA and $NO_3(p)$ was measured with HR-ToF-AMS. Organic nitrates can show 174 fragments (NO⁺ and NO₂⁺) similar to inorganic nitrate in HR-ToF-AMS and contribute to the 175 nitrate concentration measured with AMS. Farmer et al. (2010) have used NO⁺-to-NO₂⁺ ratios to 176 estimate organic nitrate concentration from HR-ToF-AMS measurements. Xu et al.(2015) used the 177 NO^+/NO_2^+ values of 5 and 10, which likely correspond to the upper and lower bounds of the ratio 178 from organic nitrates. We adopt the NO^+/NO_2^+ method (hereinafter Method 1) in this study to 179 estimate the contributions of inorganic and organic nitrates. However, the vast array of possible organic nitrate parent compounds in ambient particles and the variations in the NO⁺/NO₂⁺ ratios 180 181 between instruments can lead to biases in the calculations. The organic nitrate concentration can 182 also be estimated using the organic concentration and elemental ratios (OM:OC and N:C) from 183 HR-ToF-AMS measurements (Method 2) (Schurman et al., 2015b). Using these two methods (see

184 details in Text S4), the contribution from organic nitrate ranged from around 10% to 25% of the total AMS-measured nitrate. In Fig. 2, the estimated inorganic nitrate tracked well ($R_p^2 \ge 0.95$, 185 186 0.9<Slope <1) with the total HR-ToF-AMS nitrate concentration, closely followed the 1:1 line, 187 and mostly lay in the range of the 1:1.25 and 1:0.75 lines. Furthermore, as shown in Fig. S2, 188 concentrations of nitrate from AMS were comparable to those from MARGA, with a correlation 189 slope of 0.9 and an R_p of 0.95. The influence of organic nitrates in our calculation of total nitrate 190 is expected to be minor. Given the uncertainties associated with each estimation, we use the HR-191 ToF-AMS nitrate concentration in the following discussions.

192 In Fig. 3, the total (particle + gas) nitrate is closely correlated with NO_x during both daytime and 193 nighttime. At the same NO_x levels, total nitrate increased as O_x increased during the day (Fig. 3a), 194 suggesting the photochemical formation of nitrate. Odd-oxygen (O_x) concentrations are closely 195 linked to the extent of photochemical oxidation in an air mass. We used O_x instead of O_3 to account 196 for the titration of O_3 by freshly emitted NO, which produces NO₂. At night (Fig. 3b), O_x 197 concentrations were relatively low when NO_x concentrations were high. The slope of total nitrate 198 against NO_x during the day is steeper than that at night. The nighttime formation of nitric acid 199 involves the consumption of NO_x and O_3 (Seinfeld and Pandis, 2006). While NO_x can be 200 replenished by primary emissions, O₃ is mainly produced during the day and consumed at night. 201 Thus high total nitrate concentrations were correlated with high NO_x and low O₃ levels at night.

202 Gas-to-particle partitioning of nitrate species to form particulate nitrate can be affected by 203 concentrations of ammonium and sulfate. An increase in ammonium or a decrease in sulfate can 204 facilitate the formation of particulate nitrate (Seinfeld and Pandis, 2006). A number of studies have 205 indicated that a molar ratio of ammonium to sulfate of 1.5 demarcates the observation of particulate 206 nitrate (Griffith et al., 2015; Huang et al., 2011a; Liu et al., 2015b; Pathak et al., 2004). Under ammonium-rich (AR, $[NH_4^+]/[SO_4^{2-}] > 1.5$) conditions, additional ammonia is available to transfer 207 HNO₃ to the particle phase. In contrast, under ammonium-poor (AP, $[NH_4^+]/[SO_4^{2-}] < 1.5$) 208 209 conditions, all of the ammonia is used to neutralize H_2SO_4 until letovicite ((NH₄)₃H(SO₄)₂) is 210 formed. AR conditions prevailed throughout the entire campaign. Figure 4 shows that excess ammonium, defined as ([NH₄⁺]/[SO₄²⁻] - 1.5) × [SO₄²⁻]), tracked well with particulate nitrate 211 212 concentration with a slope of 0.93. We also found that excess ammonium tracked better with nitrate than Na⁺ and Ca²⁺ did with MARGA data (Fig. S16) . The slope of nitrate to excess ammonium 213

was less than 1(Fig. 4), indicating that ammonium was sufficient to neutralize the particulate nitrate. Organic acids and other unmeasured anions may account for the extra ammonium not associated with nitrate. The molar concentration of alkali cations was around 7–10 times lower than that of nitrate and their role in stabilizing nitrate was negligible in our study (Fig. S16).

The partitioning of nitrate between the gas and particle phases shows significant differences between November and December (Fig. 5). The average ratio of nitrate to HNO₃ (the slope of the scatter plot) was 3.2 in November and 7.8 in December. NH_3 concentration in the gas phase was not a limiting factor as the concentration of NH_3 was even higher in November than in December (Fig. 5a). Lower temperatures in December shifted the equilibrium toward the particle phase,

- increasing the nitrate concentration in the particle phase (Fig. 5b). Higher RH or particle liquid
- water content favors the formation of nitrate, but the effects were not obvious (Fig. 5c, 5d).
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In summary, the NO_x emissions led to nitrate formation during both daytime and nighttime. The fraction of nitrate increased and compensated for the decrease in the fraction of sulfate as the PM_1 concentration increased. Ammonium-rich conditions prevailed and particulate nitrate tracked well with excess ammonium. Lower temperature in December favors the partitioning of nitrate toward particle phase than in November.

3.3. Organics

Organics contributed most to the PM₁ mass measured in Panyu. 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).

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3.3.1. Elemental analysis of OA

Elemental analysis of OA (ratios of H:C, O:C and OM:OC) provides useful information for assessing OA characteristics and their evolution. Ions in the high-resolution mass spectra were used to calculate the elemental ratios using the Improved-Ambient method (Canagaratna et al., 2015). Results obtained from the Aiken-Ambient (Aiken et al., 2007) protocol are also listed in Table 1 for comparison with elemental ratios reported in the literature. We further used empirical 245 constants (11% for H:C, 27% for O:C, and 9% for OM:OC) from Canagaratna et al. (2015) to estimate the ratios accounting for the possible underestimation of the O:C ratio in earlier studies. 246 247 The average O:C, H:C, and OM:OC ratios showed little variation between the two months, with 248 average values of 0.53, 1.63, and 1.87 respectively in November, and 0.53, 1.65, and 1.87 249 respectively in December. The observed elemental ratios generally agreed with other AMS-based 250 reported values in the PRD (Table 1). The H:C ratio was similar to those at rural sites in Kaiping 251 (1.64) and Heshan (1.65) and slightly higher than that in suburban Hong Kong (1.54 and 1.55) but 252 lower than those at urban sites in Shenzhen (1.81) and Mong Kok in central Hong Kong (1.84). 253 O:C and OM:OC ratios, on the contrary, were higher than those at urban sites (Shenzhen and Mong 254 Kok) and lower than that in Kaiping but similar to those in Heshan and at suburban Hong Kong. 255 Overall, the relatively low H:C ratio and high O:C ratio suggest that OA at this site have a higher 256 degree of oxygenation than those at urban sites (e.g. Shenzhen) but a lower degree than those at 257 rural sites (e.g. Kaiping). Fig. 6 shows that the diurnal variations in H:C, O:C, OM:OC and carbon oxidation state ($\overline{OS}_c \approx 2 \times O:C-H:C$) were similar in November and December. The average H:C 258 259 ratio ranged from 1.6 to 1.7, with a pronounced increase in the late afternoon from 16:00 to 20:00, 260 and remained at a maximum until midnight due to fresh organic sources at night. The O:C and OM:OC ratios and \overline{OS}_{c} increased during the day with afternoon peaks at around 15:00, likely due 261 262 to high photochemical activity and the production of SOA during daylight hours.

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3.3.2. Sources and formation of OA

264 The mass spectra of all OA factors and their mass concentrations obtained through PMF analysis with ME-2, together with the time series of external tracers, are shown in Fig. 7. HOA correlated 265 266 well with NO_x since both are traffic-related species. While the mass spectrum of COA shares 267 spectral similarities with HOA, it is distinguished from that of HOA by a higher contribution of 268 $C_3H_3O^+$ at m/z 55 and a much lower contribution of ions at m/z 57 (He et al., 2010; Mohr et al., 269 2012). The time series of COA tracked well with one of its tracer ions, $C_6H_{10}O^+$. The other primary 270 factor, BBOA, is characterized by the presence of signals at m/z 60 (C₂H₄O₂⁺) and m/z 73 271 (C₃H₅O₂⁺), which are typically associated with levoglucosan (Alfarra et al., 2007; Schneider et al., 272 2006). The time series of COA and BBOA also tracked well with those of its marker ions. The two 273 oxygenated organic aerosol factors (SVOOA and LVOOA) are characterized by oxygenated ions 274 $C_2H_3O^+$ at m/z 43 and CO_2^+ at m/z 44 respectively. The ratio of most-oxidized ions CO_2^+ (m/z 44) to moderately oxygenated ions $C_2H_3O^+$ (m/z 43) is higher in LVOOA than in SVOOA (Jimenez 275

276 et al., 2009). Overall, a strong correlation between concentrations of SVOOA and nitrate was 277 observed. Particulate nitrate also represents semivolatile secondary species, which share similarity 278 with SVOOA in terms of volatility and its partitioning behavior with temperature. Such a 279 correlation is widely used in AMS studies (Crippa et al., 2014; Zhang et al., 2011). From 280 November 21st to December 1st (highlighted by the arrow), SVOOA showed distinct peaks beyond 281 the comparable trend with nitrate. The sharp peaks of SVOOA coincide with those of O_3 , as shown 282 in the inserted panel. Moreover, higher temperatures were also observed during this period (Fig. 283 S5). LVOOA also correlated well with sulfate in time series as both species are regional pollutants. 284 Fig. 8 shows the monthly average of OA fractions as well as their variations in different ranges of 285 OA concentrations. HOA contributed 23.8% and 28.4% to total OA in November and December 286 respectively. However, HOA increased almost linearly with OA concentration, highlighting the 287 need for traffic control to mitigate high PM concentrations in "buffer" areas. SVOOA and LVOOA 288 remained the dominated OA fractions at OA concentrations below 70 μ g/m³, which explains the 289 relatively low HOA contribution on a monthly basis.

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291 Figure 9 shows the diurnal patterns of mass concentrations and fractions for the five OA factors. 292 HOA exhibited two typical peaks during both November and December during the morning rush 293 hour at 09:00 and in the evening around 21:00. HOA accounted for up to 40% of OA (95th 294 percentile of mass fraction in a box-whisker plot) especially in the evening and at night, likely due 295 to heavily polluting trucks passing by *en route* to the city center at night (22:00 to 07:00). These 296 diurnal variations in HOA correspond to those in the H:C ratio and NO_x as well as BC (Fig. S12), 297 further confirming that vehicle-related pollutants are the main contributor to this OA factor. 298 SVOOA had a clear noon-to-afternoon peak in November, consistent with peaks in ozone (Fig. 299 S12), but this peak was less pronounced in December. The noon-to-afternoon peak for SVOOA 300 due to photochemical oxidation processes has been commonly observed worldwide (e.g. Hayes et 301 al., 2013; Qin et al., 2016). It is worthwhile to conduct further study on vehicle-related organic 302 emissions to SVOOA formation. For example, combining radiocarbon and OC/EC measurements 303 with the AMS and organic marker measurements, Zotter et al. (2014) found that the noon-to-304 afternoon SVOOA peak can be attributed to the large increase in fossil OC in the measurements 305 in the Pasadena, California, US. LVOOA showed a relatively flat diurnal pattern, as was found in

306 Shenzhen (He et al., 2011), in contrast to the significant noon-to-afternoon peaks for LVOOA at 307 rural sites in Kaiping (Huang et al., 2011b) and Heshan (Gong et al., 2012).

308 The evolution of AMS OA factors has been used to infer SOA formation via photochemical 309 oxidation in Hong Kong (Lee et al., 2013; Li et al., 2013; Qin et al., 2016b). Fig. 10 shows that 310 SOA (SVOOA+LVOOA) increased as O_x increased during the day (7:00 to 18:00) in both 311 November and December. The SOA concentrations do not show clear correlations with 312 temperature or liquid water content in aerosols (Fig. s17a, s17b). When taken together, these 313 observations suggest that SOA formation in our study was dominated by gas-phase oxidation 314 chemistry rather than heterogeneous or aqueous oxidation pathways. Furthermore, the regression slopes for SOA versus O_x are 0.23 ±0.014 (R_{pr} =0.85) and 0.25 ±0.025 (R_{pr} =0.55) µg /(sm³ ppb) 315 316 for November and December respectively. The volume unit "sm" stands for volume under 317 standard-temperature-pressure conditions. The slopes are higher than those reported in earlier 318 studies during spring and summer in North America (Table 2), and significant production of SOA 319 may be attributed to the photo-oxidation of large amounts of accumulated VOCs between the inner 320 city and this peripheral site in Panyu. Liu et al.(2015) investigated SOA formation from light-duty 321 gasoline vehicles operated in China using a smog chamber under idling conditions. They found 322 that SOA formation was 12–259 times higher than POA under conservative OH exposure. Deng 323 et al.(2017) also revealed that the emission factors for BC and POA from major diesel vehicle 324 types in China under idling conditions and the production factor for SOA under photochemical 325 aging were significantly higher than those in studies in Europe and the US and those on light-duty 326 gasoline vehicles in China.

327 **4. Conclusions**

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PM pollution in both megacities and their peripheries should be considered together. In this study, we have found that PM_1 levels in Panyu, a peripheral area of Guangzhou, were significantly affected by traffic emissions. OA were the overwhelmingly dominant species (> 45%) at all PM_1 levels. A notable increase in the nitrate-to-sulfate ratio was observed with increases in PM concentration, emphasizing the important role of vehicle emission pollutants on high-PM days.

The formation of total nitrate (particulate + gas) was closely correlated with NO_x during both daytime and nighttime with a much steeper slope during daytime than during nighttime. During the day, total nitrate increased as O_x increased at the same NO_x level, suggesting the photochemical formation of nitrate. At night, high total nitrate concentrations were associated with high NO_x but low O_x levels. Ammonium-rich conditions prevailed throughout the campaign and particulate nitrate was closely associated with excess ammonium. The fraction of particle phase nitrate in December was higher than that in November, primarily due to lower temperatures that favored the partitioning of nitrate toward particle phase.

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The nighttime emissions of OA and efficient photochemical production of SOA during the day 343 344 together accounted for continued high OA concentrations. HOA increased almost linearly with 345 OA concentration and contributed up to 40% of the high organic concentrations at night. SOA 346 (SVOOA+LVOOA) played a more important role on monthly averages and during the day. SOA 347 concentrations changed with the photochemical oxidation marker (O_x), and the observed ratios of 348 SOA to O_x were higher than those reported for Pasadena and Mexico City during the summer. This 349 efficient SOA formation was fueled by large sources of SOA precursors (e.g. HOA and VOCs) on 350 the periphery of Guangzhou. PM pollution in both megacities and their peripheries should thus be 351 considered together.

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Site/characteristics	Month	Aiken-Ambient (A-A) method			Improved-Ambient (I-A) method			Reference
		0: C	H:C	OM:OC	O: C*	H:C*	OM:OC*	
Panyu/suburban	November	0.42	1.49	1.71	0.53	1.63	1.87	This study
	December	0.41	1.5	1.70	0.53	1.65	1.87	
Kaiping/rural	November	0.47	1.48	1.77	0.60*	1.64*	1.94*	Huang et al., 2011
Shenzhen/urban	November	0.3	1.63	1.57	0.38*	1.81*	1.66*	He et al., 2011
Heshan/rural	November	0.4	1.49	1.72	0.51*	1.65*	1.83*	Gong et al., 2012
HKUST/suburban	February	0.42	1.39	1.71	0.53*	1.54*	1.86*	Li et al.,
	December	0.43	1.4	1.71	0.55*	1.55*	1.87*	2015
Mong Kok/urban	March-mid May	0.25	1.68	1.49	0.32	1.84	1.59	Lee et al., 2015

Table 1. Elemental ratios of organic PM₁ in the PRD

* Improved-Ambient elemental ratios were estimated using the A-A method with empirical constants from M. R. Canagaratna et al. (2015).

Table 2. Comparison of SOA-O_x average ratios

Site	Month	Season	SOA-Ox average	Reference
			ratio	
Panyu, Guangzhou	November	Late autumn	$0.23 \mu g /(sm^3 ppb)^*$	This study
	December	Winter	$0.25 \mu g /(sm^3 ppb)^*$	
Pasadena, CA	May-June (morning)	Late spring-summer	$0.183 \mu g /(sm^3 ppb)^*$	Hayes et al., 2013
	May-June (afternoon)	Late spring-summer	$0.163 \mu g /(sm^3 ppb)^*$	
Riverside, CA	July-August	summer	$0.142 \mu g /(sm^3 ppb)^*$	Docherty et al., 2011
Mexico City	March	spring	$0.156 \mu g /(sm^3 ppb)^*$	Aiken et al., 2009
New York City	July	summer	$0.12 \mu g /(sm^3 ppb)$	Sun et al., 2011

*The volume unit "sm" stands for volume under standard-temperature-pressure conditions.



Organics sufate ammonium nitrate Chloride black carbon

Figure 1. a) Average mass fraction of PM_1 (with BC inclusive) throughout the entire campaign; b) Mass fraction variation among PM_1 species, nitrate to sulfate mass ratio as well as the probability density of PM_1 as a function of total PM_1 mass loading. The probability density distribution describes the relative likelihood of PM_1 mass loading in a range of concentrations.



Figure 2. Scatter plot of estimated inorganic nitrate versa nitrate from HR-ToF-AMS measurement. SL denotes the slope for the linear regression fitting.



Figure 3. Correlations between total nitrate $(HNO_3(g)+NO3(p))$ and $NO_x (NO+NO_2)$. Triangles and circles represent data for November and December respectively. Data are color-coded by O_x during the day and O_3 at night.



Figure 4. Time series of nitrate, excess ammonium and ammonium-to-sulfate molar ratio.



Figure 5. Distribution of nitrate species between $HNO_3(g)$ and $NO_3(p)$, colored by (a)NH₃ concentration (b) temperature, (c) RH, and (d) LWC.



Figure 6. Diurnal variations in H:C, O:C, and OM:OC ratios and carbon oxidation state ($\overline{OS}_c \approx 2 \times O:C-H:C$) during Nov. and Dec. (25th and 75th percentile boxes, 5th and 95th percentile whiskers, median as line in box, and mean as solid colored line).



Figure 7. The mass spectra of all OA factors and the time series of their mass concentrations together with external tracers.

HOA COA BBOA SVOOA LVOOA



Figure 8. Monthly averages of OA fraction as well as variations in OA fractions in different ranges of OA concentration.



Figure 9. Diurnal variations in ME-2 resolved OA factors. Mass concentration of each OA factor (left). Mass fraction of each OA factor (right). 25th and 75th percentile boxes, 5th and 95th percentile whiskers, median as line in box, and mean as solid colored line.



Figure 10. SOA against Ox. The concentration of SOA has been converted to standard temperature-pressure conditions to compare the slope of SOA/O_x with literature values.