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

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Abstract:
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. NOx 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 µg/m³. Particulate nitrate was strongly correlated with excess ammonium ([NH₄⁺]/[SO₄²⁻] - 1.5) × [SO₄²⁻]), with higher concentrations in December than in November due to lower temperatures. The organic mass fraction was the highest across all PM₁ 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 (Oₓ = O₃ + NO₂) 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.

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 NOₓ, 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 NOₓ, VOCs, semi-volatile 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).

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, there 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.

2. Method

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 7th, 2014 to January 3rd, 2015.

2.2. Measurements
In the HR-ToF-AMS measurements (DeCarlo et al., 2006), ambient air was sampled through a PM$_{2.5}$ cyclone on the rooftop with a flow rate of approximately 0.084 L/min drawn by the AMS and the remainder drawn by an auxiliary pump. A diffusion drier was used to dry the sampled air stream, which reduced the RH of the air to below 30% before entering the HR-ToF-AMS. Other data presented in this work were obtained from collocated instruments including 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. The PM$_{2.5}$ mass concentration as measured with a Grimm 180 was corrected using the daily PM$_{2.5}$ mass concentration through quartz filter measurement (Text S1). Meteorological data (e.g. wind, temperature and RH) were obtained from a weather station located near the sampling site. Solar irradiance data were measured from a station in Nansha District, around 27.5 km from the sampling site. Particle liquid water content (LWC) was estimated with 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.
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 particles were carried out weekly. Ambient air filtered with a HEPA filter was sampled on a daily basis for 30 minutes to obtain background signals. Flow rate was made with a Gilian Gilibrator. PToF size calibrations were made with Nanosphere TM PSL particles (Duke Scientific, Palo Alto, CA, USA) and ammonium nitrate particles in the size range of 178 to 800 nm (selected with a scanning mobility particle sizer). Both flow rate and size calibration were performed before and after the sampling campaign. Gaseous CO$_2$ concentrations were measured with a CO$_2$ monitor (PICARRO 2301) to quantify their contributions to m/z 44 signal intensities.

2.3. Data analysis

AMS data analysis was performed using the SQUIRREL (v1.56D) and PIKA (v1.15D) toolkits written in Igor Pro 6.37A (WaveMetrics Inc., Lake Oswego, OR). Default relative ionization efficiency (RIE) values of 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, and 1.4 for organics were used. The ammonium RIE of 4.7 was chosen as the average from IE calibrations. A particle collection efficiency factor (CE) of 0.7 was used to account for particle losses within the instrument. The influence of RH in this study was minor, as a diffusion drier was used to maintain the sampling line RH consistently below 30%. Under these conditions, Middlebrook’s parameterization suggests a CE of 45–50% based on the measured inorganic constituents (Middlebrook et al., 2012). However, organic compounds, which are less bouncy than inorganics, dominated at the measurement site. They can also hinder the complete efflorescence of particles in the drier and further reduce the particle bounce effect and increase particle collection efficiency. The mass concentrations of PM$_1$ (sum of NR-PM$_1$ and BC) were comparable to those of PM$_{2.5}$ with a slope of 1.1 and Pearson correlation coefficient ($R_p$) of 0.95 (Fig. S2a) when using a CE of 0.7. Furthermore, total AMS organics were also correlated with organic matter (OM) concentrations derived from the OC measurements (Fig. S2b) with a slope of 1.1 and $R_p$ of 0.82. The OC-to-OM conversion was calculated using organic-matter-to-organic-carbon ratio (OM:OC) data from the HR-ToF-AMS elemental analysis. AMS-measured sulfate, nitrate, and ammonium were comparable to those measured with MARGA with slopes of 1.0, 0.9, and 0.7 respectively. These comparisons suggest that a choice of CE = 0.7 is appropriate for the OA-dominating NR-PM$_1$ in this study.
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 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. 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, 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).

3. Results and Discussion:

3.1. Overall composition

Northerly winds prevailed throughout the entire campaign (Text S3). Located south of central Guangzhou, the sampling site was thus severely affected by
pollutants transported from the city center. Overall, organics accounted for 46.3 % (or 24.5 µg/m³) of the PM₁ mass on average. Sulfate, nitrate, ammonium, BC, and chloride accounted for 23.1%, 11.2%, 9.1%, 8.3%, and 1.9% of the PM₁ mass respectively (Fig. 1a and Fig. 1b show the variations in species mass fractions in PM₁ species as a function of total PM₁ mass loading (with BC inclusive) and the probability density of PM₁ mass loading respectively. The organic mass fraction was the highest among all PM₁ species across all PM₁ levels. On the contrary, the mass fraction of sulfate decreased from 0.25 to 0.15 as the PM₁ concentration increased from 10 to 160 µg/m³. The decrease in the sulfate mass fraction was compensated for by the increased mass fraction of nitrate and, to a lesser extent, chloride. 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 PM₁ levels were lower than 40 µg/m³. These ratios increased significantly as the PM concentration increased, reaching 1.5 on the highest-PM₁ days (averaging 160 µg/m³), highlighting the substantial contribution of vehicle emission pollutants to PM on high-PM days.

3.2. Nitrate formation

The increase in the relative contribution of nitrate on highly-polluted days has also been observed in AMS studies at other locations in China, such as Shenzhen (He et al., 2011), Beijing (Huang et al., 2010), and Changdao (Hu et al., 2013). We used the molar concentration of total nitrate [HNO₃(g) + NO₃(p)] to examine the increase in nitrate species, where HNO₃(g) was measured with MARGA and NO₃(p) was measured with HR-ToF-AMS. Organic nitrates can show fragments (NO⁺ and NO₂⁺) similar to inorganic nitrate in HR-ToF-AMS and contribute to the nitrate concentration measured with AMS. Farmer et al. (2010) have used NO⁺-to-NO₂⁺ ratios to estimate organic nitrate concentration from HR-ToF-AMS measurements. Xu et al.(2015) used the NO⁺/NO₂⁺ values of 5 and 10, which likely correspond to the upper and lower bounds of the ratio from organic nitrates. We adopt the NO⁺/NO₂⁺ method (hereinafter Method 1) in this study to 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 between instruments can lead to biases in the calculations. The organic nitrate concentration can also be estimated using the organic concentration and elemental ratios (OM:OC and N:C) from HR-ToF-AMS measurements (Method 2) (Schurman et al., 2015b). Using these two methods (see
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 ($R_p^2 \geq 0.95, 0.9 < \text{Slope} < 1$) with the total HR-ToF-AMS nitrate concentration, closely followed the 1:1 line, and mostly lay in the range of the 1:1.25 and 1:0.75 lines. Furthermore, as shown in Fig. S2, concentrations of nitrate from AMS were comparable to those from MARGA, with a correlation slope of 0.9 and an $R_p$ of 0.95. The influence of organic nitrates in our calculation of total nitrate is expected to be minor. Given the uncertainties associated with each estimation, we use the HR-ToF-AMS nitrate concentration in the following discussions.

In Fig. 3, the total (particle + gas) nitrate is closely correlated with NO$_x$ during both daytime and nighttime. At the same NO$_x$ levels, total nitrate increased as O$_x$ increased during the day (Fig. 3a), suggesting the photochemical formation of nitrate. Odd-oxygen (O$_x$) concentrations are closely linked to the extent of photochemical oxidation in an air mass. We used O$_x$ instead of O$_3$ to account for the titration of O$_3$ by freshly emitted NO, which produces NO$_2$. At night (Fig. 3b), O$_x$ concentrations were relatively low when NO$_x$ concentrations were high. The slope of total nitrate against NO$_x$ during the day is steeper than that at night. The nighttime formation of nitric acid involves the consumption of NO$_x$ and O$_3$ (Seinfeld and Pandis, 2006). While NO$_x$ can be replenished by primary emissions, O$_3$ is mainly produced during the day and consumed at night. Thus high total nitrate concentrations were correlated with high NO$_x$ and low O$_3$ levels at night.

Gas-to-particle partitioning of nitrate species to form particulate nitrate can be affected by concentrations of ammonium and sulfate. An increase in ammonium or a decrease in sulfate can facilitate the formation of particulate nitrate (Seinfeld and Pandis, 2006). A number of studies have indicated that a molar ratio of ammonium to sulfate of 1.5 demarcates the observation of particulate nitrate (Griffith et al., 2015; Huang et al., 2011a; Liu et al., 2015b; Pathak et al., 2004). Under ammonium-rich (AR, $[\text{NH}_4^+] / [\text{SO}_4^{2-}] > 1.5$) conditions, additional ammonia is available to transfer HNO$_3$ to the particle phase. In contrast, under ammonium-poor (AP, $[\text{NH}_4^+] / [\text{SO}_4^{2-}] < 1.5$) conditions, all of the ammonia is used to neutralize H$_2$SO$_4$ until letovicite ($([\text{NH}_4]_2\text{H(SO}_4)_2$) is formed. AR conditions prevailed throughout the entire campaign. Figure 4 shows that excess ammonium, defined as $([\text{NH}_4^+] / [\text{SO}_4^{2-}] - 1.5) \times [\text{SO}_4^{2-}]$, tracked well with particulate nitrate concentration with a slope of 0.93. Figure 5 shows that excess ammonium tracked better with nitrate than Na$^+$ and Ca$^{2+}$ did (with MARGA data). The slope of nitrate to excess ammonium was
less than 1, 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.

The partitioning of nitrate between the gas and particle phases shows significant differences between November and December (Fig. 6). The average ratio of nitrate to HNO₃ (the slope of the scatter plot) was 3.2 in November and 7.8 in December. NH₃ concentration in the gas phase was not a limiting factor as the concentration of NH₃ was even higher in November than in December (Fig. 6a). Lower temperatures in December shifted the equilibrium toward the particle phase, increasing the nitrate concentration in the particle phase (Fig. 6b). Higher RH or particle liquid water content favors the formation of nitrate, but the effects were not obvious (Fig. 6c, 6d).

In summary, the NOₓ 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 PM₁ 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).

#### 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
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. The average O:C, H:C, and OM:OC ratios showed little variation between the two months, with average values of 0.53, 1.63, and 1.87 respectively in November, and 0.53, 1.65, and 1.87 respectively in December. The observed elemental ratios generally agreed with other AMS-based reported values in the PRD (Table 1). The H:C ratio was similar to those at rural sites in Kaiping (1.64) and Heshan (1.65) and slightly higher than that in suburban Hong Kong (1.54 and 1.55) but lower than those at urban sites in Shenzhen (1.81) and Mong Kok in central Hong Kong (1.84). O:C and OM:OC ratios, on the contrary, were higher than those at urban sites (Shenzhen and Mong Kok) and lower than that in Kaiping but similar to those in Heshan and at suburban Hong Kong. Overall, the relatively low H:C ratio and high O:C ratio suggest that OA at this site have a higher degree of oxygenation than those at urban sites (e.g. Shenzhen) but a lower degree than those at rural sites (e.g. Kaiping). Fig. 7 shows that the diurnal variations in H:C, O:C, OM:OC and carbon oxidation state (\(\overline{\text{OS}}_c \approx 2 \times \text{O:C-H:C}\)) were similar in November and December. The average H:C ratio ranged from 1.6 to 1.7, with a pronounced increase in the late afternoon from 16:00 to 20:00, and remained at a maximum until midnight due to fresh organic sources at night. The O:C and OM:OC ratios and \(\overline{\text{OS}}_c\) increased during the day with afternoon peaks at around 15:00, likely due to high photochemical activity and the production of SOA during daylight hours.

3.3.2. Sources and formation of OA
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. 8. HOA correlated well with NO\(_x\) since both are traffic-related species. While the mass spectrum of COA shares spectral similarities with HOA, it is distinguished from that of HOA by a higher contribution of \(\text{C}_3\text{H}_3\text{O}^+\) at m/z 55 and a much lower contribution of ions at m/z 57 (He et al., 2010; Mohr et al., 2012). The time series of COA tracked well with one of its tracer ions, \(\text{C}_6\text{H}_{10}\text{O}^+\). The other primary factor, BBOA, is characterized by the presence of signals at m/z 60 (\(\text{C}_2\text{H}_4\text{O}_2^+\)) and m/z 73 (\(\text{C}_3\text{H}_6\text{O}^+\)), which are typically associated with levoglucosan (Alfarra et al., 2007; Schneider et al., 2006). The time series of COA and BBOA also tracked well with those of its marker ions. The two oxygenated organic aerosol factors (SVOOA and LVOOA) are characterized by oxygenated ions \(\text{C}_2\text{H}_3\text{O}^+\) at m/z 43 and \(\text{CO}_2^+\) at m/z 44 respectively. The ratio of most-oxidized ions \(\text{CO}_2^+\) (m/z 44) to moderately oxygenated ions \(\text{C}_2\text{H}_3\text{O}^+\) (m/z 43) is higher in LVOOA than in SVOOA (Jimenez
et al., 2009). Overall, a strong correlation between concentrations of SVOOA and nitrate, a semi-volatile secondary inorganic species, was observed. From November 21st to December 1st (highlighted by the arrow), SVOOA showed distinct peaks beyond the comparable trend with nitrate. The sharp peaks of SVOOA coincide with those of O₃, as shown in the inserted panel. Moreover, higher temperatures were also observed during this period (Fig. S5). LVOOA also correlated well with sulfate in time series as both species are regional pollutants.

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 µg/m³, which explains the relatively low HOA contribution on a monthly basis.

Figure 10 shows the diurnal patterns of 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 NOₓ as well as BC (Fig. S12), further confirming that vehicle-related pollutants are the main contributor to this OA factor. SVOOA had a clear noon-to-afternoon peak in November, consistent with peaks in ozone (Fig. S12), but this peak was less pronounced in December. The noon-to-afternoon peak for SVOOA due to photochemical oxidation processes has been commonly observed worldwide (Hayes et al., 2013; Qin et al., 2016). Zotter et al. (2014) further suggested that the noon-to-afternoon SVOOA peak can be attributed to the large increase in fossil OC. LVOOA showed a relatively flat diurnal pattern, as was found in Shenzhen (He et al., 2011), in contrast to the significant noon-to-afternoon peaks for LVOOA at rural sites in Kaiping (Huang et al., 2011b) and Heshan (Gong et al., 2012).

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., 2016b). Fig. 11a shows that SOA (SVOOA+LVOOA) increased as O₃ 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, these observations suggest that SOA formation in our study was dominated by gas-phase oxidation chemistry rather than heterogeneous or aqueous oxidation pathways. Furthermore, the regression slopes for SOA versus O\textsubscript{x} are 0.23 ±0.014 (R\textsubscript{pr}=0.85) and 0.25 ±0.025 (R\textsubscript{pr}=0.55) μg /(sm\textsuperscript{3} ppb) for November and December respectively. The volume unit “sm” stands for volume under standard-temperature-pressure conditions. The slopes are higher than those reported in earlier studies during spring and summer in North America (Table 2), and significant production of SOA may be attributed to the photo-oxidation of large amounts of accumulated VOCs between the inner city and this peripheral site in Panyu. Liu et al. (2015) investigated SOA formation from light-duty gasoline vehicles operated in China using a smog chamber under idling conditions. They found that SOA formation was 12–259 times higher than POA under 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 conditions and the production factor for SOA under photochemical aging were significantly higher than those in studies in Europe and the US and those on light-duty gasoline vehicles in China.

4. Conclusions

PM pollution in both megacities and their peripheries should be considered together. In this study, we have found that PM\textsubscript{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\textsubscript{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\textsubscript{x} during both daytime and nighttime with a much steeper slope during daytime than during nighttime. During the day, total nitrate increased as O\textsubscript{x} increased at the same NO\textsubscript{x} level, suggesting the photochemical formation of nitrate. At night, high total nitrate concentrations were associated with high NO\textsubscript{x} but low O\textsubscript{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.
The nighttime emissions of OA and efficient photochemical production of SOA during the day together accounted for continued high OA concentrations. HOA increased almost linearly with OA concentration and contributed up to 40% of the high organic concentrations at night. SOA (SVOOA+LVOOA) played a more important role on monthly averages and during the day. SOA concentrations changed with the photochemical oxidation marker (Ox), and the observed ratios of SOA to Ox were higher than those reported for Pasadena and Mexico City during the summer. This efficient SOA formation was fueled by large sources of SOA precursors (e.g. HOA and VOCs) on the periphery of Guangzhou. PM pollution in both megacities and their peripheries should thus be considered together.

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6. References:


Table 1. Elemental ratios of organic PM$_1$ in the PRD

<table>
<thead>
<tr>
<th>Site/characteristics</th>
<th>Month</th>
<th>Aiken-Ambient (A-A) method</th>
<th>Improved-Ambient (I-A) method</th>
<th>Reference</th>
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<td></td>
<td></td>
<td>O:C</td>
<td>H:C</td>
<td>OM:O C</td>
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<td>Panyu/suburban</td>
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<td></td>
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<td>1.48</td>
<td>1.77</td>
</tr>
<tr>
<td>Shenzhen/urban</td>
<td>November</td>
<td>0.3</td>
<td>1.63</td>
<td>1.57</td>
</tr>
<tr>
<td>Heshan/rural</td>
<td>November</td>
<td>0.4</td>
<td>1.49</td>
<td>1.72</td>
</tr>
<tr>
<td>HKUST/suburban</td>
<td>February</td>
<td>0.42</td>
<td>1.39</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>December</td>
<td>0.43</td>
<td>1.4</td>
<td>1.71</td>
</tr>
<tr>
<td>Mong Kok/urban</td>
<td>March-mid</td>
<td>0.25</td>
<td>1.68</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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-Ox average ratios

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

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

<table>
<thead>
<tr>
<th>Organics</th>
<th>sulfate</th>
<th>ammonium</th>
<th>nitrate</th>
<th>Chloride</th>
<th>black carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.3%</td>
<td>23.1%</td>
<td>9.1%</td>
<td>11.2%</td>
<td>1.9%</td>
<td>8.4%</td>
</tr>
</tbody>
</table>

**Total PM$_1$** 55.4 (µg/m$^3$)

**Figure 2.** Scatter plot of estimated inorganic nitrate versus nitrate from HR-ToF-AMS measurement. SL denotes the slope for the linear regression fitting.
Figure 3. Correlations between total nitrate (HNO$_3$(g) + NO$_3$(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. Scatter plots of NO₃ molar concentration from MARGA (PM₂.₅) against those of excess NH₄⁺, Na⁺ and Ca²⁺.
Figure 6. Distribution of nitrate species between $\text{HNO}_3(g)$ and $\text{NO}_3^-(p)$, colored by (a)$\text{NH}_3$ concentration (b) temperature, (c) RH, and (d) LWC.
Figure 7. 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. 8. The mass spectra of all OA factors and the time series of their mass concentrations together with external tracers.
Figure 9. Monthly averages of OA fraction as well as variations in OA fractions in different ranges of OA concentration.
Figure 10. 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 11. (a) SOA against Ox; (b) SOA against temperature; (c) SOA against LWC during the day. The concentration of SOA has been converted to standard temperature-pressure conditions to compare the slope of SOA/Ox with literature values.

\[ y = 0.25x - 1.73; R_p = 0.55 \]
\[ y = 0.23x - 0.66; R_p = 0.85 \]