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Continuous measurements at the urban roadside in an Asian Megacity by Aerosol Chemical Speciation Monitor (ACSM): particulate matter characteristics during fall and winter seasons in Hong Kong

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Abstract

Non-refractory submicron aerosol is characterized using an Aerosol Chemical Speciation Monitor (ACSM) in the fall and winter seasons of 2013 at the roadside in an Asian megacity environment in Hong Kong. Organic aerosol (OA), characterized by appli-

- ⁵ cation of Positive Matrix Factorization (PMF), and sulfate are found dominant. Trafficrelated organic aerosol shows good correlation with other vehicle-related species, and cooking aerosol displays clear meal-time concentration maxima and association with surface winds from restaurant areas. Contributions of individual species and OA factors to high NR-PM₁ are analyzed for hourly data and daily data; while cooking emissions in
- OA contribute to high hourly concentrations, particularly during meal times, secondary organic aerosol components are responsible for episodic events and high day-to-day PM concentrations. Clean periods are either associated with precipitation, which reduces secondary OA with a lesser impact on primary organics, or clean oceanic air masses with reduced long-range transport and better dilution of local pollution. Haze
- events are connected with increases in contribution of secondary organic aerosol, from 30 to 50 % among total non-refractory organics, and influence of continental air masses.

1 Introduction

The Special Administrative Region of Hong Kong (HKSAR) is a global logistics and fi-²⁰ nance center located at the south-eastern edge of the Pearl River Delta Region (PRD), China's largest manufacturing area and one of the world's most densely populated regions. Hong Kong has been plagued by deteriorating air quality, attributed to local emissions from traffic, residential and commercial activity, regional pollution from the PRD and long-range transport (Nie et al., 2013; Wong et al., 2013; Yuan et al., 2013).

²⁵ High-time-resolution online instruments can characterize ambient aerosols quickly and mitigate the influence of changing environmental conditions. Few real-time studies



have been conducted in Hong Kong aside from recent measurement campaigns conducted by high resolution aerosol mass spectrometer (HR-AMS) (Lee et al., 2013; Li et al., 2013, 2015; Huang et al., 2015). Long-term AMS studies tend to be costly and time-consuming due to the complexity of the instrument. The ACSM, whose design is based on the AMS but has been substantially simplified, has seen a growing trend of

⁵ based on the AMS but has been substantially simplified, has seen a growing trend of use due to its comparative ease of operation, robustness, and sufficient time resolution (~20–60 min) for studies spanning months or longer. (Ng et al., 2011; Sun et al., 2012, 2013a, b; Budisulistiorini et al., 2013; Canonaco et al., 2013; Takahama et al., 2013; Bougiatioti et al., 2014; Petit et al., 2015; Ripoll et al., 2015; Tiitta et al., 2014;
¹⁰ Minguillón et al., 2015).

This study presents the first ACSM characterization of particulate matter at a busy urban roadside station in Hong Kong with heavy traffic and commercial and residential activities. It aims to provide long-term characterization of particulate matter sources in a typical inner-city environment, enabling the identification of the relative importance of different sources and typical recurring patterns.

¹⁵ different sources and typical recurrin

2 Experimental

The roadside measurement data were collected from 3 September to 31 December 2013 in Mong Kok (MK), an urban area with dense buildings and population in the Kowloon peninsula as part of a Hong Kong Environmental Protection Department
²⁰ (HKEPD) project (ref.: 13-00986). The sampling site was next to the road-side air quality monitoring station (AQMS) of HKEPD at the junction of the heavily trafficked Nathan Road and Lai Chi Kok Road (22°19′2″ N, 114°10′06″ E). The distribution of businesses in the vicinity varies, with restaurants mainly to the east, commercial buildings to the south and east, small shops for interior decoration, furniture and electrical goods to the south and residential buildings to the north of the sampling location (Lee et al., 2015). The sampling setup is described in detail in the Supplement, Sect. 1.



Non-refractory PM₁ (NR-PM₁) species (sulfate, nitrate, ammonium, chloride, and organics) were measured in-situ by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM, SN: 140–154). Other data including meteorological data (wind, temperature, relative humidity, solar irradiation), volatile organic compounds (VOCs) measured by an online gas-chromatography system (GC955-611 and GC955-811, Synspec BV), and standard criteria pollutants (NO_x, SO₂ and PM_{2.5}) were provided by the HKEPD, with equipment details available from the HKEPD air quality reports (Environmental Protection Department, 2013).

The acquired 20 min-average data were treated according to the general ACSM data analysis protocols established in previous studies (Ng et al., 2011; Sun et al., 2012), using the standard WaveMetrics Igor Pro-based Data Analysis Software (Version 6.3.5.5) and incorporating calibrations for relative ionization efficiency (RIE), collection efficiency (CE) and detection limit (DL). Further details on data treatment can be found in the Supplement, Sect. 2.

- Factors contributing to organic aerosol were explored using PMF (Paatero and Tapper, 1994; Zhang et al., 2011) with the Igor-Pro-based PMF evaluation toolkit (PET) (Ulbrich et al., 2009). In general, PMF can be used to resolve factors as organic aerosol (OA) into hydrocarbon-like OA (HOA), cooking OA (COA), semi-volatile oxygenated OA (SV-OOA), low-volatility oxygenated OA (LV-OOA), and others. The optimal factor num-
- ²⁰ ber was determined by inter-comparing factors' mass spectra and time series, correlations between factors and related tracers, and correlations with standard mass spectra; solutions with 3, 4, and 5 factors at fpeak = 0 were explored, after which the optimal fpeak value was determined by repeating the above analysis with varying fpeak values.

The 4-factor solution (HOA, COA, SV-OOA, LV-OOA) is optimal, with $Q/Q_{exp} = 0.8$ and better differentiation between factor time-series ($R_{pr} < 0.6$; Fig. S4). The factors also correlate well with associated inorganics and external tracers (NO₃, SO₄, NH₄, NO_x; Zhang et al., 2005, 2011; Ulbrich et al., 2009), e.g. HOA with NO_x, SV-OOA with NO₃, LV-OOA with SO₄ and NH₄ (Table S4). Furthermore, the resolved mass spectra of four factors exhibit good similarity (all un-centered R (R_{uc}) > 0.80) with reference



source mass spectra from the AMS MS database (Ulbrich, I. M., Lechner, M., and Jimenez, J. L., AMS Spectral Database, url: http://cires.colorado.edu/jimenez-group/ AMSsd; Ulbrich et al., 2009). PMF diagnostic details are shown in the Supplement (Sect. 3) and Fig. S5. We note that m/z 60 and 73 were resolved not only in COA but also in SV-OOA. When PMF was run using only nighttime data (between 00:00 and 06:00 LT), when there is little COA (Fig. S6), these two ions still persist, with similar fractional intensities in SV-OOA as at other times. The time series of m/z 60 and 73 also track well with SV-OOA, with R_{pr} of 0.92 and 0.93 respectively; hence, we believe that their presence in SV-OOA is not the result of artifacts in PMF.

3 Results and discussion

3.1 Mass concentration and chemical composition

Figure 1a and b displays meteorological data (relative humidity, temperature, and precipitation) and mass concentrations of non-refractory PM₁ (NR-PM₁) species and organic aerosol (OA) components, respectively, between September and December 2013. Total NR-PM₁ concentrations vary from 2.1 to 76.4 μ g m⁻³ with an average of 15 $25.9 \pm 13.0 \,\mu\text{g}\,\text{m}^{-3}$. ACSM NR-PM₁ concentrations co-vary with that of PM_{2.5} measured by TEOM ($R^2 = 0.64$, slope = 0.59; Fig. S1); the low slope value may be caused by the different size cuts of ACSM and TEOM and the presence of refractory materials such as elemental carbon (and to a lesser extent mineral dust and sea salt) which the ACSM cannot detect. Overall, daily $PM_{2.5}$ concentrations range from 3.7 to 106.0 μ g m⁻³ and 20 are largely (90.0%) within the 24 h air quality standard of 75 μ gm⁻³ set by the Hong Kong Air Quality Objectives (HKAQO). Days with better air quality ($PM_{2.5} < 35 \mu g m^{-3}$) are mainly observed in the month of September and in rainy periods of other months. The prevailing winds from the ocean in September not only bring in less polluted air mass but also dilute the local air pollutants compared with other seasons (Yuan et al., 25



2006; Li et al., 2015). Precipitation has an obvious impact on total NR-PM₁ concentrations, but as we will discuss, has a lesser effect on primary organics.

Overall, NR-PM₁ is dominated by organics and sulfate with relative contributions of 58.2 and 23.3 % and average concentrations of 15.1 ± 8.1 μg m⁻³ and 6.0 ± 3.5 μg m⁻³,
respectively (Fig. 2a). Other inorganic species (ammonium, nitrate and chloride) amount to approximately 20 % of NR-PM₁. The dominance of organics and sulfate is consistent with previous on-line studies in urban areas (e.g., Salcedo et al., 2006; Aiken et al., 2009; Sun et al., 2012, 2013b) as well as previous filter-based studies in MK (e.g., Louie et al., 2005; Cheng et al., 2010; Huang et al., 2014). The measured composition is consistent with earlier HR-AMS measurements carried out at the same site in spring and summer 2013 (Lee et al., 2015) with very similar overall species distribution, but slightly lower measured concentrations as compared to the ACSM, likely

due to the fact that sampling took place in different time periods (spring-summer 2013 for the AMS campaign, fall-winter 2013 for the ACSM campaign). In the AMS study,

- ¹⁵ 6 PMF aerosol factors were identified (one additional OOA factor and one additional COA factor). A marked difference is observed in the distribution of primary OA (POA) and secondary OA (SOA); whereas in spring and summer (AMS), POA makes up 65% of total organics, the reverse is observed for fall and winter (ACSM) where POA only amounts to 42% overall. A possible reason for this discrepancy is the fact that impacts
- ²⁰ of regional pollution and long-range transport are usually higher during fall and winter (Yuan et al., 2013; Li et al., 2015), thus contributing more SOA.

Elemental carbon (EC) concentrations are significant at the Mong Kok site but not measureable by ACSM due to its high refractory temperature. EC has been discussed extensively in the previously mentioned filter-based studies and a brief comparison

of online ECOC measurements to the results of HR-AMS measurements has been presented in an HR-AMS study (Lee et al., 2015). We therefore do not discuss EC in detail in this work.



3.2 OA components

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PMF resolved four factors, including two primary OA factors (hydrocarbon-like OA, HOA, from traffic emissions and cooking OA, COA) and two oxygenated OA factors (OOA): highly oxidized low-volatility OOA (LV-OOA) and the less-oxidized semivolatile

OOA (SV-OOA; Aiken et al., 2008; Jimenez et al., 2009; Tiitta et al., 2014). The mass spectra are depicted in Fig. 3. The mass concentration of primary OA factors (HOA and COA), a surrogate of local emissions, constitutes 42% of total organics and is slightly higher than that of LV-OOA (38%; Fig. 2b). SV-OOA contributes approximately 20% to total OA and is associated with both the primary organic aerosol sources and LV-OOA (see Sect. 3.2). 10

3.2.1 Hydrocarbon-like OA (HOA)

HOA has an average concentration of $2.7 \pm 0.98 \,\mu g \,m^{-3}$ (Fig. 1b) and shows strong diurnal variations, including a regular decrease to about $1 \mu g m^{-3}$ during 00:00–05:00 LT (Fig. 4h) which is discussed in Sect. 3.3 in detail. In addition, the temporal variation of HOA displays strong correlations with NO_x ($R_{pr} = 0.69$), CO ($R_{pr} = 0.62$) and several VOCs (Pentane, Toluene, Benzene) as shown in Table S6.

The diurnal patterns of vehicle number, HOA, NO, NO₂, NO₂ and traffic-related VOCs (i-pentane, n-pentane, toluene, octane, benzene, i-butane and n-butane) are depicted in Fig. 5. Vehicle counting on Lai Chi Kok road next to the sampling site spanned 28-

- 31 May 2013 and was provided by HKEPD (Lee et al., 2015). Although these dates 20 are different from our campaign period, they provide a useful reference for the traffic conditions near the site. In general, more gasoline and diesel vehicles are observed during daytime than at night. The decrease of these vehicles during 22:00-04:00 LT is in agreement with the diurnal profile of HOA (Fig. 4h). On the other hand, liquefied petroleum gas (LPG) vehicles, which are usually taxis, show slightly higher numbers 25 during 22:00–04:00 LT at the site. HOA increases sharply from $1.5 \mu g m^{-3}$ at about
- urban roadside in an Discussion Paper ACSM C. Sun et al. **Title Page** Introduction Abstract Discussion Paper Conclusions References Tables **Figures** Back Close **Discussion** Paper Full Screen / Esc Printer-friendly Version Interactive Discussion 06:00 LT to the morning peak of $3.6 \,\mu g m^{-3}$ at 09:00 LT, and then persists at high con-

Discussion

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Continuous

measurements at the

centrations until midnight, including another peak with 3.9 µg m⁻³ at 17:00 LT. The diurnal pattern of HOA is consistent with that of NO_{v} (NO + NO₂), which is almost exclusively from vehicle emissions. These results are consistent with the traffic conditions at MK with heavy traffic continuously after 06:00 LT and rush hours from 07:00 to 11:00 LT and 16:00 to 19:00 LT. NO₂ is the result of direct emission as well as formation from NO, and it increased during daytime to reach a maximum even higher than that of NO at about 17:00 LT. Concentrations of toluene (a fuel additive) and pentane and octane (significant components in exhaust of petrol vehicles; Huang et al., 2011; Wanna et al., 2008) start to increase during the morning rush hour (07:00 LT) and peak between 18:00 and 19:00 LT. HOA and NO_x show a distinct morning peak at \sim 8:00 when 10 a small shoulder is also found in the VOCs. Butane, a constituent of LPG, displays a diurnal pattern different from that of HOA, with higher concentrations between 22:00 and 04:00 LT; LPG-fueled taxis are a major means of transport during the nighttime and early morning, and fuel leakage during refueling may contribute to the observed pattern. Furthermore, the sampling site is near a major junction serving a number of 15 district centers (West Kowloon, Sha Tin, Tsim Sha Tsui) and is therefore frequented by taxis.

3.2.2 Cooking-related OA (COA)

Figure 6a shows COA concentrations sorted by wind direction in MK. The COA concentration reaches up to $12 \,\mu g \,m^{-3}$, contributing ~ 60 % of total organics, when easterly winds dominate, probably due to the large number of restaurants located on the eastern side of the sampling site (Fig. 6a). In general, COA contributes significantly to the total mass of organic aerosol with an average fraction of 24 % ($3.7 \,\mu g \,m^{-3}$), in line with the 16–30 % COA contributions found in several cities including London, Manchester,

²⁵ Barcelona, Beijing, Fresno, and New York (Allen et al., 2010; Huang et al., 2010; Sun et al., 2013b; Mohr et al., 2012; Ge et al., 2012). Figure 7 compares the chemical composition of NR-PM₁ and OA during meal times (lunch, 12:00–02:00 LT, and dinner,



19:00–21:00 LT) and non-meal times (00:00–06:00 LT); the non-meal period is defined by the periods of low concentration ($< 2\mu gm^{-3}$) in the COA diurnal pattern. During dinner time, the average concentration of organics increases by about $11 \,\mu g \,m^{-3}$ and its contributions in total NR-PM₁ increase to 70%, while the concentrations of other species do not change much (Fig. 6b). As shown in Fig. 6c, the increase in organic concentrations results from the increase in COA from 1.7 to 7.8 $\mu g\,m^{-3}$ (~ 360 % increase), and to a lesser extent increases in SV-OOA (from 1.5 to 4.5 μ g m⁻³, a ~ 200 % increase) and in HOA (from 1.4 to $3.2 \,\mu g \,m^{-3}$, a ~ 130 % increase). As shown in Table 1, the average concentration of organics during dinner time is $5 \mu g m^{-3}$ higher than that during lunch, and this increase is attributed to the increase of COA and SV-OOA 10 mass but not of HOA. This is consistent with the expectation that the cooking activities at MK are higher during dinner than during lunch, while traffic during dinner is comparable to or smaller than that during lunch (Fig. 4f and h). The increase of SV-OOA during dinner time may be the result of enhanced cooking emissions and possibly less evaporation due to lower ambient temperature; contributions from traffic emissions are

evaporation due to lower ambient temperature; contributions from traffic emissions ar not likely to be important since there is little increase of HOA during meal time.

3.2.3 Oxygenated OA (OOA)

The LV-OOA spectrum correlates well with the standard LV-OOA spectrum (Fig. 3), with a $R_{\rm uc}$ of 0.97. The LV-OOA time series is associated with that of SO_4^{2-} with a $R_{\rm pr}$ of 0.86 (Fig. 1), consistent with reports in the literature (DeCarlo et al., 2010; He et al., 2011; Zhang et al., 2014; Tiitta et al., 2014). The LV-OOA diurnal pattern varies little, suggesting that it is part of the background aerosol, possibly resulting from long range transport (Li et al., 2013, 2015).

The mass spectrum of SV-OOA closely resembles that of "standard" SV-OOA (Fig. 3). Some marker fragments of COA and HOA, for example, m/z 41, 43, 55, and 57, are present in the SV-OOA mass spectrum. SV-OOA concentrations are also weakly associated with those of HOA and their co-emitted precursors (benzene and toluene), with $R_{\rm pr}$ of 0.58, 0.65 and 0.51 respectively. In fact, the correlation between



SV-OOA and benzene is better than that of HOA and benzene (0.56). The diurnal pattern of SV-OOA also shows peaks at meal times like COA. Lastly, the fraction of signal at m/z 44 (f44 fraction) of SV-OOA at MK is twice that of the standard measured by Q-AMS (Zhang et al., 2014; Tiitta et al., 2014). Together, these results suggest that SV-

 OOA may be correlated with POA (HOA and COA), possibly due to rapid oxidation of POA to semivolatile gases, which may then form SV-OOA. The variation of the average concentration of SV-OOA as a function of binned LV-OOA concentration in increments and a bin width of 2 μg m⁻³ is shown in Fig. S7. The linear, positive relationship between SV-OOA and LV-OOA suggests that non-local formation and subsequent transport may also contribute to the measured SV-OOA at MK.

Figure 7 displays the concentration of different OA factors (coded by color) as a function of binned O_x concentration (ppb) and binned temperature (°C) with a bin width of 15 ppb and 5 °C, respectively. In general, the concentration of all OA factors increases as O_x increases across all temperatures. While it is understood that LV-OOA and SV-

¹⁵ OOA are correlated with O_x because they all result from similar photochemical activities, the correlation between HOA and O_x is the result of the good correlation (0.78) between HOA and NO₂, which accounts for 84 % of total O_x . NO₂ is partly emitted directly from vehicles and partly formed by secondary oxidation at MK as discussed in Sect. 3.2.1. Increase in ambient temperature is associated with decrease in HOA and SV-OOA, likely due to evaporation effects and partitioning, but it has no obvious correlations with LV-OOA and COA.

To further assess the relative importance of other OA factors to the resolved SV-OOA, ordinary least squares (OLS) regressions were conducted. Considering the potential influence of primary OA on the regression results, the whole dataset was separated into three time periods consisting of: meal time (MT; 12:00–14:00, 19:00–21:00 LT) marked by enhanced COA; background time (BT; 00:00–06:00 LT) marked by low POA; and other time (OT; 06:00–12:00, 14:00–19:00 and 21:00–24:00 LT). The data of each period was further divided into high/low temperature (HTemp, LTem



p = T < 22.5 °C), and high/low O_x (HiO_x, LO_x=O_x < 70 ppb) to reveal impacts of temperature and the degree of oxygenation on the correlations among OA factors.

Tables 2 and 3 show the coefficients of HOA, COA and LV-OOA in the regression equation for the reconstructed SV-OOA and their average concentration during differ-

- ⁵ ent periods under high/low temperature and high/low O_x , respectively. The regression coefficients of HOA and COA during each period under HTemp (Table 2) are much smaller than under LTemp, reflecting a weakening of their relationship with SV-OOA as temperature increases. COA under HTemp during BT does not show relationship with SV-OOA with a coefficient value of 0. The average concentrations of HOA and SV-OOA
- under HTemp are obviously lower than under LTemp for each period but the concentration of COA varied little across different temperatures. These results are consistent with those shown in Fig. 7. The stronger correlations between HOA and SV-OOA than between COA and SV-OOA suggest a closer temperature dependence of HOA and SV-OOA. In contrast, the coefficient of LV-OOA does not change much (0.26 ± 0.02)
 irrespective of temperature ranges and the selected time periods, supporting the idea
- that LV-OOA is the result of transport instead of local formation.

During BT, COA has the lowest concentration (< $2 \mu g m^{-3}$) and shows no correlation with SV-OOA under LO_x. During MT and OT (06:00–24:00 LT) when traffic emission is high, HOA has larger regression coefficients under HiO_x than under LO_x. However,

²⁰ LV-OOA shows a reverse trend with smaller coefficients with SV-OOA. It is probable that HiO_x conditions favor the conversion of SV-OOA to LV-OOA, leading to smaller coefficient of LV-OOA on SV-OOA. In addition, except for the minor increase in the concentrations of COA, the concentrations of HOA, LV-OOA and SV-OOA generally increase by more than 50 % compared with those under LO_x during each period (Fig. 7).

Overall, based on Tables 2 and 3, we can conclude that: (1) the coefficient of HOA is much larger than that of COA over all time periods, and temperature and O_x levels, (2) in the BT periods, the COA concentration is the lowest compared with other periods and had no relationship with SV-OOA under HT or LO_x conditions, (3) COA has the highest average concentration during MT periods but a regression coefficient comparable to



those observed in other periods. Thus, HOA overall has a stronger relationship to SV-OOA than COA has. Cooking emissions reflected by COA are not as important to SV-OOA in the BT periods but they can be important during MT periods. Some SV-OOA might also have converted to LV-OOA under HiO_x , although overall most LV-OOA $_5$ is considered to be from transport.

3.3 Diurnal patterns

The diurnal profiles of NR-PM₁ species and OA components are depicted in Fig. 4. Total organics display a diurnal pattern with two pronounced peaks during 12:00–14:00 and 19:00–21:00 LT, corresponding to the peaks of COA at lunch and dinner time respectively. In addition, organics increase at about 10 a.m., which may be related to the increase of local emissions of HOA and COA by 2.3 and 1.1 μ gm⁻³ respectively from 06:00 to 10:00 LT.

The mass concentration of sulfate (Fig. 4b) does not show any diel variation. It is likely that sulfate, as a regional pollutant, is mainly formed during long-range transport, leading to the lack of a specific diurnal pattern at MK; a similar flat diurnal pattern for sulfate has also been found at the HKUST supersite in Hong Kong (Lee et al., 2013; Li et al., 2015). These results differ significantly from observations in Beijing and Lanzhou in China and Welgegund in South Africa (Sun et al., 2012, 2013b; Xu et al., 2014; Tiitta et al., 2014) where sulfate displays an obvious increase at noon-time in summer and wet seasons due to either photochemical reaction or aqueous oxidation of SO₂. The difference may result from the much lower level of sulfur dioxide (SO₂) with

an average of 4.6 ppb in MK compared to for example, ~ 32 ppb in Beijing, where coal combustion leads to a much higher SO₂ concentration (Lin et al., 2011); sulfate and relative humidity (RH) have almost no correlation ($R^2 = 0.06$) in MK, suggesting that local aqueous processing may not be significant for sulfate observed at Mong Kok.

Nitrate shows a slight dip around noontime, corresponding to the increase of the ambient temperature (Fig. 4j); evaporative loss of particulate nitrate might outweigh the secondary production of nitrate during this time. The diurnal pattern of ammonium



(Fig. 4d) is very similar to that of sulfate, as expected based on their commonly observed association in atmospheric particles. Chloride (Fig. 4e) has rather low concentrations and shows a similar diurnal variation to that of nitrate, likely due to its volatility.

3.4 Day-of-week patterns

⁵ Figure 8a shows the average concentration trends on individual days of the week for NR-PM₁ species and Fig. 8b describes the diurnal patterns of the OA components for weekdays, Saturdays and Sundays, respectively. Because of the small datasets on Saturdays and Sundays, data beyond one standard deviation from the mean (25.9 ± 13.0 µgm⁻³) were removed from the whole dataset to remove the influence of episodic events in this analysis. Overall, total NR-PM₁ concentrations have no obvious variation (average variation less than 5%) from Monday to Saturday, but drop by 16% on Sundays compared to Saturdays. This weekend difference is opposite to the result found in Beijing where higher concentrations occur on Sundays than Saturdays (Sun et al., 2013b). On the other hand, some others such as Lough et al. (2006) and
¹⁵ Rattigan et al. (2010) reported that both Saturdays and Sundays had obvious traffic emissions reduction due to less human activities on weekends in Los Angeles and New York, respectively.

Organics and secondary inorganics (SO₄, NH₄ and NO₃) contributed 54 and 46 % respectively to the concentration difference between Sundays and Saturdays in MK.

- The difference in organics is mainly attributed to the variation of HOA, which shows very similar diurnal variations on Saturdays and weekdays, but has an average decrease of 23 % after 07:00 LT on Sundays. A 37 % reduction of traffic-related carbonaceous aerosol on Sundays compared with weekdays in MK has been reported (Huang et al., 2014). In Hong Kong many people work on Saturday, which leads to a traffic pattern diministration of the second statement of the second statement
- similar to normal weekdays. COA shows nearly the same diurnal patterns on all days, and LV-OOA and SV-OOA do not show obvious variations. Overall, local emissions from traffic contribute most to the day-of-week variations in organics.



3.5 Contributions of individual species and OA factors to high NR-PM₁

Figure 9a–c show the variation in hourly mass concentration of NR-PM₁ species and OA components and their mass fractions as a function of hourly total NR-PM₁ mass loading, respectively. Below 50 μg m⁻³, all aerosol species display a nearly linear in⁵ crease with PM₁ mass loading, with slopes of about 0.5 for organics, 0.25 for sulfate and LV-OOA, and around 0.1 for nitrate, ammonium, COA, HOA and SV-OOA (Fig. 9a). While the fractions of NH₄ and organics remain relatively stable, sulfate exhibits a decrease and then an increase, and NO₃ and chloride show a gradual increase then a decrease respectively as NR-PM₁ increased to 50 μg m⁻³ (Fig. 9b and c). Although the mass concentrations of all organic factors increase as NR-PM₁ increases, SV-OOA is the only factor that increased in mass fraction. Primary OA components (HOA and COA) and transported OA (LV-OOA) show a decrease in fraction and stable contributions respectively as NR-PM₁ increases to 50 μg m⁻³, while the contribution of SV-

- OOA increases sharply from around 5 to 25% of total organic mass. It suggests that $O(2004 \text{ m}^{-3} \text{ m}^{$
- ¹⁵ SV-OOA plays an important role as NR-PM₁ increases to 50 μ g m⁻³ in MK. However, beyond 50 μ g m⁻³, the mass loadings of SO₄ and organics increase, while those of NH₄, NO₃ and LV-OOA remain almost constant, which differs from the observations in Beijing, where NH₄ and NO₃ kept a linear increase from 50 to about 200 μ g m⁻³ (Sun et al., 2013b; Zhang et al., 2014). In terms of fractions, only COA and to a lesser extent
- ²⁰ SV-OOA, increase as NR-PM₁ increases further. In fact, over 80 % of the high hourly NR-PM₁ concentrations (> 50 μ g m⁻³) are observed during the meal-time periods with enhanced cooking activities.

When the hourly averages in Fig. 9 are replaced by daily averages (Fig. 10), the COA concentration varies little and its fraction does not exhibit an increase but instead decreases significantly with increasing daily NR-PM₁. On the other hand, the fractions of SV-OOA and LV-OOA clearly increase. This analysis suggests that while cooking OA is responsible for the hourly high concentrations during meal time and potential



high hourly PM levels, LV-OOA/SV-OOA are responsible for episodic events and high day-to-day PM levels.

To analyze the difference in particle composition and meteorological conditions among episodic periods and clean periods, three heavy polluted episodes (19-22, 5 23-26 October and 10-13 December) and two clean periods (17-18 September and 14–18 December), highlighted in shaded regions in Fig. 1, were analyzed. The average concentrations of these chosen periods are larger than one standard deviation from the average concentration of the campaign $(25.9 \pm 13.0 \,\mu g m^{-3})$. The composition, meteorological features (7 and RH) and oxidation index (O_{y} and f44) of these five events are shown in Table 4. Clean period 1 (C1) is characterized by low NR-PM₁ concentrations 10 (below 13µgm⁻³), prevailing coastal wind (easterly wind), lack of rain, high ambient temperature (~ 28 °C) and high relative humidity (~ 70 %). Another clean period (C2) features continuous precipitation with the coldest and most humid weather condition in the period studied. Haze period 1 (H1) has similar temperature and humidity as C1 but is marked by mixed continental/oceanic winds. From H1 to the following haze period 15 (H2), the observed wind direction shifts to reflect continental transport, with a significant decrease in RH to 36 %. Haze period 3 (H3), just before C2, is also dominated by continental winds but with lower temperatures (~ 19 °C) than during other haze events. The total NR-PM₁ of C1 (12.2 μ gm⁻³) is only 25–30 % of that during haze periods and this is mainly attributed to easterly wind bringing less air pollutants and diluting 20 local air pollutants. HOA, COA and SV-OOA in C1 are lower than in C2 despite the lack of rain during C1; their low concentrations during C1 may be influenced by both particle evaporation during high temperatures, especially for SV-OOA, and dilution of local emissions

²⁵ Compared to the adjacent period H3, precipitation in C2 dramatically reduces the concentration of secondary species such as SO_4 , NH_4 , NO_3 , SV-OOA and LV-OOA, but not primary HOA and COA. The total organic mass reduces by 68 % to an average of 8.1 μ g m⁻³ (Table 4). Precipitation effectively removes secondary particles but is less efficient for primary particles that are continuously generated locally.



The land-sea breeze observed during H1 (Fig. S8) can redistribute PM pollution over the whole PRD region and accumulate air pollutants effectively (Lo et al., 2006; Chan and Yao, 2008; Lee et al., 2013). The pronounced high concentration of LV-OOA and SV-OOA, jointly contributing 70 % of total organics, reflects the oxidation of primary emissions in the PRD under such cycles, which is also observed at the suburban HKUST site (Lee et al., 2013). The periodic nitrate peaks in H1 with low concentration in daytime and high concentration in nighttime coincide with temperature changes. In the adjacent H2 period, the prevailing wind is northwesterly and there is a sharp decrease in relative humidity. It is interesting to note that the dip in RH during H2 coincides with the dip in sulfate, ammonium, nitrate and LV-OOA; this might be caused by decreased aqueous-phase processing, and by decreased gas-particle partitioning associated with water uptake under low RH for secondary aerosol particles (Sun et al., 2013a, b).

The most severe pollution event occurred during the H3 period (10–13 December) with an average NR-PM₁ of 47.7 μg m⁻³. This episode is dominated by persistent northerly wind bringing air masses from the PRD region into Hong Kong and leading to a marked mass increase of secondary species of SO₄, NH₄, NO₃, LV-OOA and SV-OOA. Furthermore, H3 is characterized by the highest mass concentration and relative contribution of nitrate and SV-OOA compared with other haze periods. This is likely due

to the average temperature of H3 being 5–6 $^{\circ}$ C lower than that of other haze events. In addition, although all three haze events have very similar SO₄ mass loading, there is a ~ 50 % increase in NH₄ concentration during the H3 episode, consistent with the increase of nitrate in that period.

The fractions of m/z 44 among total organics (*f* 44) during these three haze occasions are all lower than that at HKUST (Li et al., 2013), which reflects a larger abundance of the less oxygenated POA at the urban MK site. In addition, the POA concentration (HOA + COA) does not change much between clean periods and haze periods. However, its relative contribution decreases from about 50% during clean periods to





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30% during haze events because of the pronounced variation of secondary OA as shown in Fig. 11.

Conclusions 4

- The characteristics and sources of ambient submicron non-refractory particulate matter (NR-PM₁) were investigated in an urban roadside environment in Hong Kong using 5 an Aerodyne ACSM from September to December 2013; these are the first ACSM measurements in Hong Kong. Organics and sulfate dominate total NR-PM₁, making up more than 50 and 20% of measured mass concentration, respectively. PMF analysis of organic aerosol mass spectra vielded four characteristic organic aerosol (OA) factors: hydrocarbon-like organic aerosol (HOA), cooking organic aerosol (COA), semi-volatile 10 oxygenated organic aerosol (SV-OOA) and low-volatility oxygenated organic aerosol (LV-OOA). Primary OA factors (HOA and COA) from fresh emissions contribute 43% of total organics, slightly larger than that of LV-OOA, which is generally a transported pollutant in this study, with about 37% of total organics. SV-OOA contributes about
- 20% of total organics and is variably correlated with HOA, COA and LV-OOA under 15 different conditions and period of a day. While HOA showed a stronger relationship to SV-OOA overall, COA can be an important contributor to SV-OOA during meal times. In addition, the transported pollutants reflected by LV-OOA displays a relatively stable correlation with SV-OOA during the different periods (BT, MT, and OT).
- The mass loadings of traffic related aerosol (HOA) are consistent with expected traffic 20 count data and correlate well with various vehicle-related VOCs and NO_y. Furthermore, HOA, with an average decrease of 23 % after 07:00 LT on Sundays, contributes most to the lower organic concentrations on Sundays when compared with other days. Cooking aerosol (COA) displays a well-defined diurnal variation with lunch- and dinner-time peaks and contributes on average 40% of total organics during mealtimes; COA is 25 clearly associated with local easterly winds, which coincides with the location of nearby restaurants.



The contributions of individual species and OA factors to high NR-PM₁ were analyzed based on hourly data and daily data. It suggests that while cooking is responsible for the hourly high concentrations during meal times, LV-OOA/SV-OOA are responsible for episodic events and high daily PM concentration. Three heavily polluted episodes and two clean periods were recorded during sampling and attributed to different me-

- teorological and circulatory conditions. The analysis of clean periods shows that precipitation has an obvious deposition impact on total NR-PM₁ concentrations, but has a lesser effect on primary organics. Clean ocean wind not only brings in less polluted air mass, but also dilutes the local air pollutants. During this campaign, high-PM events
- ¹⁰ are generally related to continental air mass influence or land-see breeze circulatory conditions, which has less influence on primary emissions but significant effects on secondary particles, with a pronounced increase in the secondary OA contribution during haze events (from 30 to 50 %).

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Table 1. Average concentrations of NR-PM $_1$ and OA components during lunch time, dinner time and non-meal times.

Species $\mu g m^{-3}$	Lunch	Dinner	Non-meal					
Org	18.8	23.7	10.3					
SO ₄	5.8	6.1	6.3					
NH ₄	2.6	2.9	3.0					
NO ₃	1.4	1.8	1.6					
Chl	0.1	0.2	0.2					
Organic aerosol components								
HOA	3.2	3.2	1.4					
COA	6.2	9.6	1.7					
LV-OOA	5.8	5.4	5.6					
SV-OOA	3.6	5.5	1.5					



Table 2. Regression of SV-OOA on HOA, COA and LV-OOA and concentrations of OA factors and O_x under high and low temperature (LT and HT) of the three chosen periods (MT, BT and OT).

Period	Meal time (MT)		Backgrou	und time (BT)	Other time (OT)				
Temperature	LTemp	HTemp	LTemp HTemp		LTemp	HTemp			
Coefficients ^a									
HOA	0.80	0.56	0.70	0.43	0.48	0.23			
COA	0.29	0.15	0.22	0.00	0.31	0.11			
LV-OOA	0.25	0.23	0.23	0.24	0.25	0.28			
Adjusted R ²	0.90	0.81	0.83	0.57	0.85	0.73			
Average Concentration (μ g m ⁻³ , ppb)									
HOA	3.71	2.85	1.60	1.18	3.51	2.88			
COA	7.34	7.40	1.61	1.54	3.50	3.74			
LV-OOA	5.46	5.57	5.91	5.07	5.85	5.99			
SV-OOA	6.30	3.89	2.68	1.44	4.1	2.39			
O_x (ppb)	83.12	85.23	58.71	53.45	75.06	76.77			

^a The coefficient of HOA, COA and LV-OOA in the regression equation reconstructing SV-OOA under LTemp (T < 22.5 °C) and HTemp (T > 22.5 °C) during meal time (12:00–14:00, 19:00–21:00 LT), background time (00:00–06:00 LT) and other time. The average temperature of the whole campaign is 22.5 °C. All entries of coefficients are significant at the 1 % level (two-tailed), except that of HOA/OT, which is significant at the 5 % level.



Table 3. Regression of SV-OOA on HOA, COA and LV-OOA and concentrations of OA factors and Temperature under high and low O_x (HiO_x and LO_x) of three chosen periods (MT, BT and OT).

	Meal time (MT)		Backgro	und time (BT)	Other time (OT)				
	LO_x	HiO_x	LO_x	HiO _x	LO_x	HiO _x			
Coefficients ^a									
HOA	0.50	1.13	0.62	0.64 ^b	0.08 ^b	0.52			
COA	0.13	0.14	0.00	0.15	0.14	0.14			
LV-OOA	0.33	0.10 ^b	0.26	0.18	0.34	0.21			
Adjusted R ²	0.73	0.86	0.73	0.80	0.67	0.78			
Average Concentration (μ g m ⁻³ , ppb)									
HOA	2.24	3.41	1.20	2.03	2.11	3.55			
COA	7.31	7.57	1.59	1.73	2.77	3.71			
LV-OOA	3.50	5.92	5.07	7.22	4.06	6.77			
SV-OOA	3.22	5.29	1.85	2.79	1.8	3.56			
Temp (°C)	23.30	23.80	21.48	20.39	22.01	22.74			

^a The coefficient of HOA, COA and LV-OOA in the regression equation reconstructing SV-OOA under LO_x (O_x < 70 ppb) and HT (O_x > 70 ppb) during meal time (12:00–14:00, 19:00–21:00 LT), background time (00:00–06:00 LT) and other time. 70 ppb is the average O_x of the whole study. All entries of coefficients are significant at 1% level (two-level), except those indicated with ^b, which indicates significance at the 5% level.





Table 4. Measured and calculated parameters in four chosen periods (C1, H1, H2, H3 and C2).

	Clean pe	riod 1 (C1) ^a	Haze period 1 (H1)		Haze period 2 (H2)		Haze period 3 (H3)		Clean period 2 (C2)	
RH (%)	7	70.8	65.0		36.4		64.8		84.6	
T (°C)	2	27.6	2	5.0	2	3.8	1	8.7	1	3.2
O_x (ppb)	6	69.6	8	2.0	9	9.5	7	0.4	2	10.9
f 44	0.114		0.118		0.120		0.108		0.057	
Precip(mm)		0		0	0		0		8.9	
(µg m ⁻³ , %)	Conc.	Perc.	Conc.	Perc.	Conc.	Perc.	Conc.	Perc.	Conc.	Perc.
NR-PM ₁	12.2		44.1		39.0		47.7		11.6	
Org	6.7	54.4	25.2	57.2	21.1	54.2	25.1	52.6	8.1	69.6
SO ₄	3.8	31.2	11.8	26.8	12.1	30.9	11.4	23.8	1.5	12.8
NH_4	1.2	9.9	4.4	10.1	4.4	11.3	6.5	13.6	1.1	9.4
NO ₃	0.4	3.5	2.4	5.6	1.3	3.4	4.4	9.2	0.8	7.3
Chl	0.1	1.0	0.2	0.4	0.1	0.2	0.4	0.8	0.1	0.9
HOA	1.2	18.5	3.8	15.1	3.0	14.4	4.2	16.9	2.1	26.2
COA	2.3	34.8	3.7	14.5	3.3	15.5	3.3	13.1	2.6	31.7
LV-OOA	3.0	44.8	11.5	45.4	10.2	48.4	9.9	39.6	1.8	22.0
SV-OOA	0.1	2.0	6.3	25.0	4.5	21.6	7.6	30.4	1.6	20.1

^a Average of data from clean days (C1 and C2) and hazy days (H1, H2 and H3). C: 17–18 September; H1: 19–22 October; H2: 23–26 October; H3: 10–13 December; C2: 14–18 December.

T: temperature; RH: relative humidity; O_x: odd oxygen (O₃ + NO₂) in ppbv; f44: fraction of m/z 44 in organic mass spectra.









Figure 2. Average concentration of each chemical composition of **(a)** NR-PM₁ (Org, SO₄, NO₃, NH₄ and Chl) and **(b)** organic aerosol (LV-OOA, SV-OOA, HOA and COA).





Figure 3. Mass spectra of resolved OA components (HOA, SV-OOA, LV-OOA, COA) and the correlation with standard mass spectral profiles available on the AMS MS database (Ulbrich, I. M., Lechner, M., and Jimenez, J. L., AMS Spectral Database). The x and y axes in the right-hand graphs are mass spectra of resolved factor and the standard, respectively.





Figure 4. Diurnal profiles of NR-PM₁ species, OA components and Temperature for the entire study with 25 and 75 percentile boxes, 10 and 90 percentile whiskers, mean as colored marker and median as black line in the whisker box.











Figure 6. (a) Wind rose plot of COA concentration. The angle and radius present the wind direction and its probability, respectively, while color indicates COA concentration. **(b)** The fractional composition of NR-PM₁ species during meal time (12:00-02:00, 19:00-21:00 LT) and non-meal time (00:00-06:00 LT). **(c)** The fractional composition of OA during meal time and non-meal time, respectively.





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Figure 7. Variation of the average concentration of OA components (HOA, SV-OOA, LV-OOA and COA) coded by color as a function of binned O_x concentration (ppb) and binned temperature (°C).



Figure 8. (a) Day-of-week variations of NR-PM₁ species (standard deviation as vertical line) and **(b)** average diurnal patterns of OA components for weekdays, Saturdays and Sundays.





Figure 9. (a) Variation in mass concentration of NR-PM₁ species and OA components as a function of total NR-PM₁ mass loading, and (b) mass fraction of total NR-PM₁ for NR-PM₁ species, and (c) mass fraction of total organics for OA components, as a function of total NR-PM₁ mass loading. The data were binned by the hourly average NR-PM₁ mass with a range of $7 \,\mu g m^{-3}$, and the vertical lines are the standard deviation.





Figure 10. (a) Variation in mass concentration of NR-PM₁ species and OA components as a function of total NR-PM₁ mass loading, and **(b)** mass fraction of total NR-PM₁ for NR-PM₁ species, and **(c)** mass fraction of total organics for OA components, as a function of total NR-PM₁ mass loading. The data were binned by the *daily average* NR-PM₁ mass with a range of $7 \,\mu g m^{-3}$, and the vertical lines are the standard deviation.





Figure 11. Mass fraction of hydrocarbon-like organic aerosol (HOA), cooking organic aerosol (COA), semi-volatile oxygenated organic aerosol (SV-OOA) and low-volatility oxygenated organic aerosol (LV-OOA) in color, and the mass concentration of POA and SOA marked by triangles and circles, respectively, during five periods: clean periods (C1 and C2), and haze periods (H1, H2 and H3).

