



# Supplement of

## 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

C. Sun et al.

Correspondence to: C. K. Chan (keckchan@ust.hk)

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#### Supporting Material

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#### 1. Sampling set-up

4 Ambient air was sampled through a PM<sub>2.5</sub> cyclone on the rooftop (approximately 3m above ground level) of an air conditioned sampling shelter at a flow rate of 3.1 L/min, with 0.1 L/min drawn by 5 the ACSM. The sampled air passed through a Nafion dryer (PD-200T-12MSS, Perma Pure LLC) 6 before going into the ACSM. Ionization efficiency (IE) calibrations were performed at least once 7 8 per month during the first three months with DMA-size-selected ( $D_m=350nm$ ) pure ammonium nitrate particles [Jayne et al., 2000; Lee et al., 2015, submitted]. A HEPA filter was installed in-9 10 line before the ACSM for one- to three hours (filter time) per month to determine the detection 11 limits (DL) of the ACSM, which are defined as three times the standard deviations of the 12 concentrations of all species during the filter period. Data points falling below their corresponding detection limit were set to zero in our analysis (Table S1). All mass concentrations were 13 determined at ambient temperature and pressure and presented in local time. 14

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#### 16 2. Data Treatment

The ammonium RIE of 4.57 and sulfate RIE of 1.2 were chosen based on the average from five IE 17 calibrations, while the default RIE values of 1.1 for nitrate, 1.3 for chloride and 1.4 for organics 18 19 were used [Allan et al., 2003; Jimenez et al., 2003]. The influence of RH in this study is considered 20 minor as a Nafion dryer was used to keep the sampling line RH consistently below 30%. Middlebrook et al. [2012] developed an equation based to aerosol composition to estimate the 21 22 collection efficiency (CE). Under the dry conditions used in our sampling, the Middlebrook parameterization suggests a CE of ~45-50% based on the measured inorganic constituents 23 24 (Middlebrook et al., 2012). However, the NR-PM<sub>1</sub> concentration of the majority of data points (~83%), if calculated with a CE of 0.45, would exceed the PM<sub>2.5</sub> concentration measured by TEOM 25 which indicates an underestimation of CE. Therefore, the Middlebrook result does not seem 26 appropriate for this study as the dominance of organic compounds (58.2% of NR-PM<sub>1</sub>) at the 27 measurement site could hinder the complete efflorescence of particles in the drier and reduce the 28 29 particle bounce effect, thus increasing the particle collection efficiency.

A CE of 0.8 was chosen based on the comparison of the NR-PM<sub>1</sub> measurements and PM<sub>2.5</sub> measured independently by HKEPD. The average ratio of NR-PM<sub>1</sub> to PM<sub>2.5</sub> (0.59; Figure S1) is consistent with the results in previous studies that NR-PM<sub>1</sub> contributes 56%-64% of PM<sub>2.5</sub> assuming that NR-PM<sub>1</sub> approximately equals the difference between PM<sub>2.5</sub> and elemental carbon (EC) in PM<sub>2.5</sub> [*Cheng et al.*, 2006; *Lee et al.*, 2006].

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### 3. PMF analysis on Organic Spectra

In this study, PMF input mass spectra were limited to a maximum m/z of 110 because the signal uncertainty at higher m/z values was large due to low ion transmission efficiency and significant interferences from the internal standard of naphthalene at m/z 127-129 [*Ng et al.*, 2011; *Sun et al.*, 2013]. PMF was run in "exploration" mode with fpeak changing from -1 to 1 in steps of 0.2 and the P value (the number of factor) from 1 to 6. PMF analysis procedures followed those in Zhang et al. [2005, 2011].

42 A 4-factor solution is thought to be optimal. First, a 3-factor solution resolves hydrocarbon-like OA (HOA) incorrectly (Figure S2) with excess m/z 44 fractional intensity (f<sub>44</sub>=5%) and a rather 43 poor correlation with NO<sub>x</sub>, with a Pearson's R value ( $R_{pr}$ ) of 0.43 (Table S2). On the other hand, 44 a 5-factor solution resolves one unknown factor (Factor 1) which shows very similar variations in 45 time series as Factor 4 ( $R_{pr}$ =0.80; Figure S3). The 4-factor solution yields Q/Q<sub>exp</sub>=0.8 and better 46 differentiation among the factor time series (R<sub>pr</sub> <0.6; Figure S4). The four factors also correlate 47 48 well with associated inorganics and external tracers [NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub>, NO<sub>x</sub>; Zhang et al., 2005a, 2011; Ulbrich et al., 2009], e.g. HOA with NO<sub>x</sub>, SV-OOA with NO<sub>3</sub>, LV-OOA with SO<sub>4</sub> and NH<sub>4</sub> 49 (Table S4). Furthermore, the mass spectra of the four factors are similar (all un-centered R 50  $(R_{uc}) > 0.80$ ) to corresponding reference mass spectra from the AMS MS database [Ulbrich, I. M., 51 52 Lechner, M., and Jimenez, J. L., AMS Spectral Database, url: http://cires.colorado.edu/jimenezgroup/AMSsd; Ulbrich et al., 2009], as shown in next section. With the 4-factor solution, the 53 54 variation of fpeak had little impact on the value of Q/Qexp, while HOA and low-volatile OOA at 55 fpeak=0 showed the highest correlations with both NO<sub>x</sub> and SO<sub>4</sub>, when compared with solutions using other rotational values (Table S5). Therefore, a 4-factor solution with fpeak=0 was chosen. 56

#### 57 <u>Hydrocarbon-like Organic Aerosol (HOA)</u>

58 The mass spectrum of HOA (Figure 4) is dominated by a homologous series of alkyl fragments separated by a CH<sub>2</sub> (m/z 14) unit: the  $C_n H_{2n-1}^+$  ion series (m/z 27, 41, 55, 69, 83, 97), typical of 59 cycloalkanes or unsaturated hydrocarbon, which account for 27% of total peak intensity in the 60 HOA spectrum. The other prominent group is the  $C_nH_{2n+1}^+$  ion series (m/z 29, 43, 57, 71, 85, 99), 61 typical of alkanes and accounting for 26% of the total peak intensity [McLafferty and Turecek, 62 1993; Ng et al., 2011; Li et al., 2012]. This mass spectrum is very similar to the standard HOA 63 spectrum with  $R_{uc}$  of 0.92, and its fractions of  $C_nH_{2n-1}^+$  and  $C_nH_{2n+1}^+$  (27%, 26%) are consistent 64 with standard ones (=28%, 27%) [Ng et al., 2011]. This HOA spectrum is also consistent with that 65 resolved by HR-ToF-AMS at the HKUST Supersite on the dominance of saturated CxHy-type 66 ions, most notably at m/z 43 and 57 [Lee et al., 2013]. 67

#### 68 <u>Cooking Organic Aerosol (COA)</u>

The most prominent ions of the resolved COA profile at MK were m/z 41 (mainly C<sub>2</sub>HO<sup>+</sup>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>) and m/z 55 (mainly C<sub>3</sub>H<sub>3</sub>O<sup>+</sup>, C<sub>4</sub>H<sub>7</sub><sup>+</sup>). Ratios of m/z 41/43 =1.8 and m/z 55/57=2.2, which are distinctly larger than that of HOA at 0.73 and 0.76 respectively (Figure 4); such ratios have been widely reported for COA in AMS and ACSM studies. For example, Lanz et al. [2010] reported ratios of m/z 41/43 and m/z 55/57 of 0.5 and 0.4 in HOA, and 1.2 and 1.2 in COA, respectively, while Sun et.al [2013] reported 0.5 for these two ratios in HOA and 2.3 for those in COA, respectively.

#### 76 Oxygenated Organic Aerosol

LV-OOA is characterized by the prominent m/z 44 ion (mainly CO<sub>2</sub><sup>+</sup>) and minor C<sub>n</sub>H<sub>2n-1</sub> and 77  $C_nH_{2n+1}$  ion series generated by saturated alkanes, alkenes and cycloalkanes. The LVOOA spectra 78 correlated well with the standard spectra of LV-OOA (Figure 4) with a Ruc of 0.97. Furthermore, 79 its time series is comparable to that of  $SO_4^{2-}$  with a  $R_{pr}$  of 0.86 (Figure 1), consistent with reports 80 in the literature [DeCarlo et al., 2010; He et al., 2011; Zhang et al., 2014; Tiitta et al., 2014]. SV-81 82 OOA, which is less oxidized than LV-OOA, is marked by the dominant ions of m/z 43 and m/z 44 mainly contributed by  $C_2H_3O^+$  and  $CO_2^+$ . The mass spectrum of SV-OOA closely resembles that of 83 84 'standard' SV-OOA with a Ruc of 0.87 (Figure 3). Its time series also follows that of nitrate 85  $(R_{pr}=0.63, Figure 1)$ , another secondary and semi-volatile species.

## 87 **Tables**

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**Table S1.** Summary for monthly detection limits of NR-PM<sub>1</sub> species (SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Chl and Org)

 Species µg/m <sup>3</sup>	September	October	November	December	
SO4	0.22	0.04	0.05	0.07	
NO <sub>3</sub>	0.04	0.01	0.02	0.05	
NH4	0.07	0.06	0.12	0.11	
Chl	0.02	0.03	0.02	0.02	
Org	0.69	0.17	0.28	0.34	

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91 Table S2. Correlation coefficients (R<sub>pr</sub>) between resolved factors and SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and NO<sub>x</sub> under solution of 3

factors with fPeak=0.

Pearson R	SO <sub>4</sub>	NO <sub>3</sub>	NH4	NO <sub>x</sub>
Factor1	0.80	0.66	0.85	0.25
Factor2	0.07	0.13	0.08	0.55
Factor3	0.40	0.67	0.57	0.43

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94 Table S3. Correlation coefficients (R<sub>pr</sub>) between resolved factors and SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and NO<sub>x</sub> under solution of 5

factors with fPeak=0.

Pearson R	SO4	NO <sub>3</sub>	NH4	NO <sub>x</sub>
Factor1	0.28	0.48	0.38	0.31
Factor2	0.85	0.57	0.86	0.25
Factor3	-0.01	0.13	0.04	0.48
Factor4	0.54	0.71	0.70	0.30
Factor5	0.16	0.33	0.25	0.68

97 Table S4. Correlation coefficients (R<sub>pr</sub>) between resolved factors and SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and NO<sub>x</sub> under solution of 4

factors with fPeak=0.

Pearson R	SO <sub>4</sub>	NO <sub>3</sub>	NH4	NO <sub>x</sub>
LV-OOA	0.86	0.63	0.88	0.21
SV-OOA	0.39	0.63	0.55	0.39
COA	0.05	0.11	0.06	0.42
НОА	0.25	0.48	0.38	0.70
НОА	0.25	0.48	0.38	0.70

100 Table S5. Correlation coefficients between resolved factors and associated tracer (SO<sub>4</sub>, NO<sub>3</sub> and NO<sub>x</sub>) on time series,

101 and corresponding standard mass spectra.

fPeak	-0.4	-0.2	0	+0.2	+0.4
	Corre	lation with associ	ated tracer (R <sub>pr</sub> )		
HOA & NO <sub>x</sub>	0.64	0.65	0.70	0.63	0.63
LV-OOA & SO <sub>4</sub>	0.82	0.85	0.86	0.84	0.80
SV-OOA & NO <sub>3</sub>	0.64	0.63	0.63	0.64	0.64
	Correlat	ion with standar	d mass spectra (R	uc)	
НОА	0.94	0.94	0.92	0.90	0.88
COA	0.77	0.77	0.84	0.76	0.75
LV-OOA	0.98	0.98	0.97	0.97	0.97
SV-OOA	0.83	0.85	0.87	0.78	0.84

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103 Table S6. Correlation coefficients (R<sub>pr</sub>) between HOA concentration and NOx, CO and VOCs (n-Pentane, i-Pentane,

104 Toluene, Benzene).

Gas/VOCs	R <sub>pr</sub> with HOA
NOx	0.69
СО	0.62
n-Pentane	0.61
i-Pentane	0.57
Toluene	0.55
Benzene	0.56

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## **Figures**





**Figure S1.** (y) NR-PM<sub>1</sub> concentration measured by ACSM versus (x) PM<sub>2.5</sub> measured by TEOM during the entire









124 Figure 3S. (a) The mass spectra, time series, and diurnal pattern for 5 factors with fPeak=0, (b) correlation between

- mass spectra profile or time series profiles of each two factors, and (c)  $Q/Q_{exp}$  variation as a function of number of
- 126 factors.



Figure 4S. (a) The mass spectra, time series and diurnal pattern for 4 factors with fPeak=0, (b) correlation between
 mass spectra profile or time series profiles of each two factors, and (c) Q/Qexp variation as a function of number of
 factors.



**Figure 5S**. PMF diagnostics for 4 factors with fPeak=0.



138 Figure S6. The mass spectra and time series resolved by PMF based on data with little COA (0:00 -6:00).



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140 Figure S7. Variation of average concentration of SV-OOA binned by LV-OOA concentration with a step of 2 µg/m<sup>3</sup>

141 as a function of binned LV-OOA concentration.



**Figure S8.** Overview of temporal variation of (**a**) meteorological factors (Relative humidity, Temperature and

145 Precipitation) and (b) non-refractory PM<sub>1</sub> species (Org, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and Chl) and organic aerosol components

146 (LVOOA, SVOOA, HOA and COA) during haze period 1 (H1) and haze period 2 (H2).

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