

Seasonal characteristics of fine particulate matter (PM) based on high resolution time-of-flight aerosol mass spectrometric (HR-ToF-AMS) measurements at the HKUST Supersite in Hong Kong

Y.J. Li^{1,#}, B.P. Lee¹, L. Su², J.C.H. Fung^{1,3} and C.K. Chan^{1,4}

¹Division of Environment, ²Environmental Science Program, ³Department of Mathematics,

⁴Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Hong Kong, China

[#]Now at: School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, U.S.

Manuscript submitted to Atmospheric Chemistry and Physics

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

1 **Abstract**

2 Atmospheric particulate matter (PM) remains poorly understood due to the lack of comprehensive
3 measurements at high time resolution for tracking its dynamic features and the lack of long-term
4 observation for tracking its seasonal variability. Here, we present highly time-resolved and seasonal
5 compositions and characteristics of non-refractory components in PM with diameter less than 1 μm
6 (NR-PM₁) at a suburban site in Hong Kong. The measurements were made with an Aerodyne high-
7 resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) at the Hong Kong University of
8 Science and Technology (HKUST) Air Quality Research Supersite for four months, with one in each
9 season of the year. The average NR-PM₁ concentration of $\sim 15 \mu\text{g}/\text{m}^3$ is higher than those AMS
10 measurements made in South Korea and Japan, but lower than those in North China, the Yangtze River
11 Delta and the nearby Pearl River Delta. The seasonal dependence of the total NR-PM₁ monthly
12 averaged concentrations was small but that of the fractions of the species in NR-PM₁ was significant.
13 Site characteristic plays an important role in the relative fractions of species in NR-PM₁ and our results
14 are generally consistent with measurements at other non-urban sites in this regard. Detailed analyses
15 were conducted on the AMS data in the aspects of (1) species concentrations, (2) size distributions, (3)
16 degree of oxygenation of organics, and (4) positive matrix factorization (PMF)-resolved organic
17 factors in a seasonal context, as well as with air mass origin from back-trajectory analysis. Sulfate had
18 the highest fraction in NR-PM₁ (>40%) and the surrogates of secondary organic species, semi-volatile
19 oxygenated organic aerosol (SVOOA) and low-volatility oxygenated organic aerosol (LVOOA),

1 prevailed (~80%) in the organic portion of NR-PM₁. Local contributions to the organic portion of NR-
2 PM₁ at this suburban site was strongly dependent on season. The hydrocarbon-like organic aerosol
3 (HOA) factor related to local traffic emissions contributed >10% to organic aerosols in spring and
4 summer, but only 6-7% in autumn and winter. The cooking organic aerosol (COA) factor
5 contributed >10% to organic aerosols in winter. With the aid of highly time-resolved data, diurnal
6 patterns of the degree of oxygenation of organic aerosols were used to determine the sources and
7 formation processes of the least understood organic portion of PM. The oxygen-to-carbon atomic ratio
8 (O:C) and average carbon oxidation state (\overline{OS}_C) showed little variation in autumn and winter when the
9 long-range transport of oxidized organics dominated, whereas they peaked in the afternoon in spring
10 and summer when locally produced secondary organic aerosol prevailed. Air mass origin, in contrast,
11 had a strong influence on both NR-PM₁ concentrations and the fractions of species in NR-PM₁. The
12 findings of the current study provide a better understanding of the role of air mass origin in the seasonal
13 characteristics of the PM composition and the relative importance of local vs. transported organic
14 aerosols in this region.

1 **1. Introduction**

2 Particulate matter (PM) remains a serious air quality problem in megacities globally, and it is
3 especially the case in the Pearl River Delta (PRD) economic region in South China (Chan and Yao,
4 2008;Huang et al., 2011), where Hong Kong lies on the southern coastal edge. To understand the PM
5 characteristics, multiple intensive campaigns have been conducted in the PRD region (He et al.,
6 2011;Huang et al., 2011;Xiao et al., 2011;Gong et al., 2012) and in Hong Kong (Lee et al., 2013;Li et
7 al., 2013;Meng et al., 2014;Yeung et al., 2014). Most of these studies, however, were conducted in a
8 particular season of the year and thus can only reflect the chemical characteristics of PM in that short
9 period. In our previous studies at the HKUST Air Quality Research Supersite in spring 2011, PM at
10 this suburban site was found to be influenced by both long-range transport during the hazy period (Lee
11 et al., 2013) and local secondary production during the foggy periods when the air was stagnant (Li et
12 al., 2013). But these findings may not apply in the other seasons of the year because meteorological
13 conditions vary from season to season. Thus high time resolution PM measurements should be made
14 in different seasons to investigate the PM characteristics attributable to meteorological conditions.
15 Hong Kong is influenced by long-range transport to even larger extents in other seasons than in spring,
16 and the organic fractions in PM are higher especially in autumn and winter (Louie et al., 2005),
17 although high PM episodes do not occur frequently (Huang et al., 2009). Aqueous-phase processing
18 may also be less important in the other three seasons when the relative humidity (RH) is much lower.

19 Both primary emission and secondary formation of PM may show seasonal variability. For example,

1 coal-combustion organic aerosol is one of the major PM components in winter in cities in North China
2 like Beijing (Sun et al., 2013). In contrast, secondary organic aerosols (SOA) are anticipated to be
3 more dominant in summer, especially in subtropical areas like Hong Kong (Hu and Yu, 2013). Major
4 air quality problems involving ozone and PM (Li et al., 2012;Wu et al., 2013) in the PRD are also
5 strongly influenced by long-range transport.

6 In this study, we report NR-PM₁ (non-refractory components in PM with diameter less than 1 μm)
7 compositions and characteristics at the HKUST Air Quality Research Supersite in four months, with
8 one in each season of the year. NR-PM₁ was measured with an Aerodyne high-resolution time-of-flight
9 aerosol mass spectrometer (HR-ToF-AMS). Positive matrix factorization (PMF) was performed to
10 resolve different factors of organic aerosols. Seasonal characteristics of NR-PM₁ including (1) species
11 concentrations, (2) size distributions, (3) degree of oxygenation of organics, and (4) PMF-resolved
12 factors are presented. These characteristics are then discussed in conjunction with different air mass
13 origins based on back-trajectory analysis. Finally, the influences of seasonality and air mass origin on
14 NR-PM₁ characteristics are discussed, along with the implications of assessing the long-term
15 variability of such characteristics.

16 **2. Experimental**

17 2.1 Site description

18 The HKUST Supersite is located on the campus of HKUST, which sits on the hill side of Clear
19 Water Bay on the east coast of Hong Kong (Lee et al., 2013;Li et al., 2013). Figure S1 shows the

1 location of the sampling site in the PRD economic zone of South China. Both particle and gas
2 measurements were taken at the HKUST Supersite using a number of online instruments
3 (<http://envr.ust.hk/research/research-facility/background-materials.html>). The Supersite sits on the
4 rooftop of a pump-house on the seafront within a short distance (approximately 30 m) of the sea. The
5 sampling inlets were approximately 20 m above sea level. There is little local emission around the site
6 except for two minor sources. One is the Clear Water Bay Road just outside of campus with mild traffic.
7 The other is a small student canteen within 200 m from the site and it operates only from 18:00 (local
8 time) till midnight.

9 2.2 Measurements

10 NR-PM₁ constituents including sulfate, nitrate, ammonium, chloride, and organics were measured
11 with an Aerodyne HR-ToF-AMS operated under V-MS, pToF, and W-MS modes. The principle behind
12 the instrument has been detailed elsewhere (DeCarlo et al., 2006) and a brief description is provided
13 in Sections 2 and 3 in the Supplementary Information.

14 Gaseous species (CO, CO₂, SO₂, NO, NO₂ and O₃) were measured with standard gas analyzers
15 (Teledyne API). Meteorological parameters were measured by an automatic weather station mounted
16 on a tower right next to the pump-house on which the Supersite sits. The sampling periods were April
17 25th to June 1st, 2011 (spring), September 1st to September 29th, 2011 (summer), October 28th to
18 December 15th, 2011 (autumn), and January 19th to March 1st, 2012 (winter). Note that in this region
19 of a monsoonal climate, prolonged summers and winters and brief autumns and springs are typical

1 (Louie et al., 2005). The definition of seasons above is only approximate as different seasonal
2 characteristics might still be observed within the same period. For example, the chemical composition
3 and hygroscopicity of PM in the first half of September varied dramatically from those in the second
4 half (Yeung et al., 2014), representing mainly summer characteristics but showing some transient
5 behaviors toward autumn. For the current study, the majority of the sampling time lied in the designated
6 season and the seasonality can be captured.

7 2.3 AMS data analysis

8 The AMS unit-mass-resolution (UMR) data and the AMS high-resolution (HR) data were analyzed
9 using the data analysis toolkit SQUIRREL 1.53F and PIKA 1.12F, respectively (Sueper, 2013). The
10 data processing procedures have been detailed in previous studies (Allan et al., 2004; Aiken et al.,
11 2007; Aiken et al., 2008). A collection efficiency (CE) of 0.5, which has been widely used in field
12 studies employing an AMS with a dryer installed in front of its particle inlet (Allan et al., 2003; Aiken
13 et al., 2009), was applied during the whole campaign. Middlebrook et al. (2012) recently suggested
14 that the CE should be composition-dependent with influences of (1) high nitrate content, (2) high
15 relative humidity, and (3) high acidity, implying that the CE should depend on the phase state (liquid
16 or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small
17 amounts of nitrate (see Section 3.1 below). Figure S4 also shows that the aerosol particles were only
18 slightly acidic. At this particular site where the particles have an overwhelmingly dominant sulfate
19 content (see discussion below), a CE of 0.5 would be more appropriate (Li et al., 2013).

1 Size distribution data are presented with the mass concentration ($dM/d\log D_{va}$) as a function of
2 vacuum aerodynamic diameter (D_{va}). The median and mean distribution curves together with the range
3 of the 75th percentile and the 25th percentile, i.e. the interquartile range (IQR), are shown for size
4 distributions in the periods of interest (see Section 3.2 below). The size distributions were as measured
5 and not normalized to average mass concentrations from V-mode.

6 Elemental analysis (Aiken et al., 2007; Aiken et al., 2008) was performed for organics with HR data
7 to obtain the oxygen-to-carbon atomic ratio (O:C), the hydrogen-to-carbon atomic ratio (H:C), and the
8 ratio of organic matter to organic carbon (OM/OC). We reflect the degree of oxygenation of organics
9 in two ways. The first is the O:C directly from elemental analysis (Aiken et al., 2007; Aiken et al., 2008)
10 and the second is the average carbon oxidation state (\overline{OS}_C), which can be approximated by $2 \times O:C -$
11 H:C (Kroll et al., 2011).

12 2.4 Positive matrix factorization (PMF) analysis

13 HR mass spectra of organic components were analyzed by PMF (Paatero and Tapper, 1994; Lanz et
14 al., 2007; Zhang et al., 2011) with a toolkit (version 2.06) based on Igor Pro (Ulbrich et al., 2009). The
15 procedures for PMF analysis using AMS data have been presented elsewhere (Ulbrich et al.,
16 2009; Zhang et al., 2011). In this study, HR mass spectra (m/z 12–150) were used as input for PMF
17 separately for each month, with the error matrix estimated from the sum of electronic and Poisson ion-
18 counting errors for relevant HR ion fragments (Allan et al., 2003; Ulbrich et al., 2009). “Bad” ions with
19 signal-to-noise ratio (SNR) < 0.2 were removed, while “weak” ions ($0.2 < \text{SNR} < 2$) were down-

1 weighted by a factor of 2. Ions (O^+ , HO^+ , H_2O^+ , CO^+ , and CO_2^+) with duplicated information
2 related to the ion CO_2^+ were further down-weighted by a factor equal to the square root of the number
3 of related ions. PMF was first run under the “exploration” mode with the Seed value varying from 0
4 to 100 in steps of 5 (Ulbrich et al., 2009;Zhang et al., 2011). No local minima were shown for the
5 Q/Q_{exp} value, which indicates the results were insensitive to the choice of the Seed value. Therefore,
6 further analysis was proceeded with a Seed value of 0 for all months. Then PMF was run with fPeak
7 varying from -1 to 1 in steps of 0.1 for p (number of factors) from 1 to 10. Solutions with 7 to 8 factors
8 were chosen to minimize residuals and Q values and to resolve a known factor from cooking. Some of
9 those factors were then combined to produce four-factor solutions based on comparison with mass
10 spectra from the literature and a time series of external tracers. The details of the factor combination
11 are shown in Supplementary Information (Section 5). A four-factor solution, with hydrocarbon-like
12 organic aerosols (HOA), cooking organic aerosols (COA), semi-volatile oxygenated organic aerosols
13 (SVOOA) and low-volatility oxygenated organic aerosols (LVOOA), was adopted. The first two
14 factors are considered as locally emitted primary organic aerosols (POA) while the latter two are
15 surrogates of SOA (Jimenez et al., 2009).

16 2.5 Back-trajectory analysis

17 In this study, 72-hour back-trajectories were calculated every hour using version 4.8 of the Hybrid
18 Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler and Hess, 1997;Draxler
19 et al., 2012a) for the four sampling periods from 2011 to 2012. The ending location for the trajectories

1 was the HKUST Supersite (latitude: 22.337°N, longitude: 114.263°E) at an elevation of 300 m or 500
2 m above ground level (AGL). The hourly output data of the weather research and forecasting (WRF)
3 model (Wang et al., 2014) were used to drive the HYSPLIT model. When the WRF simulations are
4 finished, the necessary parameters, including 14 surface and 5 upper-level variables, are extracted from
5 hourly WRF outputs, and converted into the compatible format for HYSPLIT (Draxler et al., 2012b).
6 The grid resolution of WRF simulation was 27 km and the total number of vertical layers was 39, with
7 the top level pressure being 50 mb, and 4D-data assimilation (FDDA) was applied to the simulation
8 domain to minimize integration errors. To identify the pollutant characteristics in different
9 predominant transport patterns, back trajectories were clustered into groups with similar patterns. The
10 groups, called clusters hereafter, are represented by their mean trajectories (Draxler et al., 2012b).

11 The solutions with the arrival heights of 300 m and 500 m and with 4, 5, and 6 clusters (Figure S19)
12 were evaluated using four different species concentrations as indicators of (a) transported species
13 (sulfate and LVOOA) and (b) locally emitted species (HOA and COA). The concentrations of these
14 four species in each cluster in a solution are plotted in box-whisker plots in Figures S20 and S21. The
15 rationale is as follows: (1) a larger number of clusters can potentially provide more information and
16 should be attempted; (2) too many clusters may be purely mathematical and makes little physical sense,
17 thus should be avoided; (3) transported species with anthropogenic origins should be associated with
18 long trajectories from the continent; (4) locally emitted species should be associated with short
19 trajectories with calm wind. The optimal number of clusters balancing the first and second points was

1 chosen and an evaluation of the third and fourth points for the same arrival height was conducted to
2 support the choice. More details about the evaluation are shown in Supplementary Information
3 (Section 6). Based on the evaluation, a solution of five clusters with arrival height of 300 m was
4 adopted and was used for further discussion. Figure S22 shows the individual trajectory in each month
5 with trajectories in each cluster color coded for the 300 m arrival height and five-cluster solution. Table
6 1 shows the percentages of time in each measurement month that belong to one of the five clusters.

7 **3. Results and discussion**

8 3.1 Overall characteristics

9 Here we first discuss the overall characteristics of NR-PM₁ in different seasons. *Figure 1* shows the
10 time series, monthly average concentrations and percentages of the five species (sulfate, nitrate,
11 ammonium, chloride, and organics) measured by the HR-ToF-AMS. The total NR-PM₁ concentration
12 showed little seasonal variation, with monthly averages ranging from 14.3 to 15.9 µg/m³. In contrast,
13 the fractions of each species were quite different in the four seasons. Sulfate had the highest portion in
14 NR-PM₁ for all four seasons, accounting for 40–56% by mass. Nitrate remained low (<5%) in spring,
15 summer, and autumn, but it went up to 10% of NR-PM₁ mass in winter. Ammonium accounted for 13–
16 16% of NR-PM₁ mass. The chloride fraction remained very small in all four seasons, but also went up
17 to ~1% in winter (compared with just ~0.1 % in the other three seasons), with a seasonal variability
18 similar to that of nitrate. The contribution of organics varied from 26% in summer to 38% in autumn.

1 Although they still contributed less than sulfate did, organics had quite comparable concentrations to
2 sulfate in autumn and winter.

3 *Table 2* shows the averages and standard deviations, as well as 50th, 25th, and 75th percentiles of
4 meteorological parameters (temperature, RH, and wind speed), gaseous species (CO, NO_x = NO +
5 NO₂, SO₂, O_x = O₃ + NO₂), and NR-PM₁ species. Winter was the only season with average temperature
6 below 20 °C. The observation of high nitrate and chloride concentrations in winter is thus in line with
7 the gas-particle partitioning behavior of ammonium nitrate and ammonium chloride, whose formations
8 are favored at low temperatures (Seinfeld and Pandis, 2006). Wind speed was the lowest in spring
9 which enabled local pollutants such as those from traffic and cooking to accumulate. Together with the
10 high humidity and relatively low temperature, the low wind speed also promotes fog formation and
11 aqueous phase chemistry (Li et al., 2013). CO had the highest concentration in winter and the lowest
12 in summer, a clear indicator for seasonal patterns of air mass origins. Hong Kong is dominated by air
13 masses from the ocean with little anthropogenic sources in summer while it is mostly under the
14 influence of air masses from the north with large combustion-related sources in winter (Yuan et al.,
15 2006). NO_x had the highest concentration in spring, indicating strongest traffic-related influence (Lau
16 et al., 2008) in the season. SO₂ had the highest concentration in autumn, but surprisingly the lowest in
17 winter. O_x had the highest concentrations in autumn and summer, probably because of relatively high
18 photochemical activities in these two seasons.

1 Apart from temporal variations in PM concentration and composition, spatial heterogeneity of PM
2 is also an important aspect to understand the air pollution of a region. For example, Zhang et al.(2012)
3 compared PM₁₀ compositions in 16 sites in various regions in China and their relationship with
4 visibility reduction and identified four major haze areas that coincided with the fast economic
5 development therein. Yang et al. (2011) summarized chemical species measured in PM_{2.5} in China and
6 concluded that not only the PM_{2.5} concentration varied by a factor of six but also the percentages of
7 individual species were substantially different at different sites (e.g., urban vs. rural) and even among
8 the four representative megacities. Herein, we put our all-four-season averages of sulfate, ammonium,
9 nitrate, and organics (SANO) concentrations in NR-PM₁ in comparison with other available AMS
10 measurements in Asia from the literature, as shown in Figure 2. Overall, there is a paucity of AMS
11 measurements in China, given its large geographical coverage and the variability of air pollution and
12 their causes in different cities. This study provides a comprehensive analysis in seasonal characteristics
13 of NR-PM₁ compared to other AMS measurements in this region. For clarity, chloride is excluded
14 from this discussion because its concentration is quite low (<5%) in most of the AMS measurements.
15 The data from the literature and details of the measurements are shown in Table S2. SANO
16 concentrations measured in multiple sites in South Korea and Japan were less than 15 µg/m³, while
17 those measured in North China normally exceeded 40 µg/m³. The highest concentration was found in
18 Beijing and it was an average from five separate measurement campaigns covering a few urban sites
19 and including the strongest episodic event in January 2013 (Zhang et al., 2014). Two measurements in

1 the Yangtze River Delta (YRD) showed SANO concentrations of higher than 25 $\mu\text{g}/\text{m}^3$. Multiple
2 measurements in the PRD region showed SANO concentrations ranging from 30 to 40 $\mu\text{g}/\text{m}^3$. Our
3 suburban site in Hong Kong, as reported in this study, has an average SANO concentration of 15.3
4 $\mu\text{g}/\text{m}^3$. In terms of mass fractions, urban sites (such as Shenzhen, SZC) or sites downwind of urban
5 areas (such as Heshan, HSC) have higher organic and nitrate fractions, while those remote and
6 suburban sites have higher sulfate fractions. For the organic constituents, non-urban sites have much
7 higher fractions of OOA than POA, which is in agreement with what has been reported worldwide
8 (Zhang et al., 2011). This is true for Changdao (CDC), Heshan (HSC), Kaiping (KPC), and Hong Kong
9 (HKC) but Jiaxing (JXC) and Shanghai (SHC) are exceptions. JXC is a suburban site and SHC is an
10 urban site, but their POA and OOA distributions were quite similar. JXC was influenced strongly by
11 biomass burning (BBOA) in the winter campaign (Huang et al., 2013), while only HOA contributed
12 to POA in SHC (Huang et al., 2012). Overall, the fractions of species at our site are in line with those
13 at other non-urban sites and the average SANO concentration is lower than those obtained from the
14 nearby PRD area due to the strong influence of the oceanic air mass in some of the seasons.

15 3.2 Size distributions

16 Size distribution measurements of the HR-ToF-AMS provide additional information to identify the
17 possible sources and processes leading to the PM species formation. The size distributions of sulfate,
18 nitrate and organics are displayed in *Figure 3*. The secondary inorganic species, sulfate and nitrate,
19 both had mass mode diameters (D_{va}) of 500 to 600 nm. The smaller mode at 200 nm was more obvious

1 for organics, especially in spring and summer (*Figure 3*, a-3 and b-3), but the dominant mode for
2 organics was still at ~ 500 nm. These size distributions suggest that PM at this site was generally
3 affected by regional transport of aged particles. Local contribution was minor except for organics in
4 spring and summer.

5 The size distributions of m/z 44, 43, and 57 ions of organics are shown in *Figure 4*. Signals with
6 m/z 43 can be mainly attributed to $C_2H_3O^+$ (>70%), m/z 44 to CO_2^+ (>94%), and m/z 57 to $C_4H_9^+$
7 (>62%), and they only showed marginal seasonal dependence (1 – 11% in their contributions). Ion
8 with m/z 44, which is contributed mainly by carboxylic acids (Ng et al., 2010), had a size distribution
9 similar to that of sulfate, with mass mode diameters peaking at 500 to 600 nm. Carboxylic group
10 formation in organics probably shared similar pathways with sulfate formation, such as gas-phase
11 oxidation or aqueous-phase processes. The m/z 57 ion had a clear peak at a smaller mode with D_{va} of
12 ~ 200 nm, especially in spring. It was mainly attributed to hydrocarbon-like organics that generate
13 $C_4H_9^+$ and its large fraction in a smaller mode at ~ 200 nm indicates a large contribution of
14 hydrocarbon-like organics from primary emissions such as traffic (Canagaratna et al., 2010; Sun et al.,
15 2011). This small mode in the size distribution of m/z 57 was not as obvious in other seasons because
16 of the lower contribution of air mass from the local urban area (see below). The m/z 43 ion has a degree
17 of oxygenation between those of m/z 44 and m/z 57 and its size distribution exhibits the same trend.
18 The size distributions of these ions of different degrees of oxygenation indicate the seasonal
19 dependence of primary and secondary organics at this site.

1 3.3 Degree of oxygenation

2 *Figure 5* shows the results of elemental analysis in two ways. The panels on the left (a-1 through d-
3 1) are the Van Krevelen plots (Heald et al., 2010) for the four months while the ones on the right (a-2
4 through d-2) are the diurnal patterns of average carbon oxidation state (\overline{OS}_C) and oxygen-to-carbon
5 atomic ratio (O:C). The spread of data points in the Van Krevelen plot in spring (May 2011) has been
6 discussed in detail by Li et al. (2013). Briefly, the spring campaign was separated into two foggy
7 periods, one hazy period and the “other” period. Because the chemical processes leading to SOA
8 formation were different in the foggy and hazy periods, the data points clustered in different parts of
9 the Van Krevelen plot, resulting in different slopes and intercepts. Summer (September 2011) had the
10 highest O:C ratio among the four seasons, likely due to higher photochemical activity. This strong
11 influence by photochemistry is also reflected by the higher average O:C ratios in the PMF-resolved
12 SVOOA and LVOOA factors (*Figure 5*, left panels, large blue and red closed squares) in summer than
13 in other seasons. In fact, the overall O:C ratio was so high in summer that it might have some effects
14 on the PMF analysis, resulting in a high CO_2^+ fraction (0.1) and a high O:C ratio (0.25) in the HOA
15 factor in summer. This abnormally high O:C ratio (>0.1) was also observed in other studies in remote
16 or rural areas where highly oxygenated organics dominated the mass spectra (Saarikoski et al.,
17 2012;Hu et al., 2013;Gilardoni et al., 2014). High O_x concentration was associated with high O:C ratio
18 because of the similar secondary nature of the two parameters. The data for autumn and winter (*Figure*
19 5, c-1 and d-1, respectively) are more uniform than those for spring and summer and the slopes and

1 intercepts of the Van Krevelen plots are also quite similar. Since primary contributions to organic
2 aerosol are generally small, these uniform elemental ratio correlations suggest similar processes (most
3 likely during transport) and/or precursors in the oxidation of organics during autumn and winter. It is
4 possible that the original characteristics of the freshly formed SOA were lost by the time they reached
5 Hong Kong.

6 In all seasons, both representations of the degree of oxygenation (\overline{OS}_C and O:C) showed an
7 afternoon peak in their diurnal patterns (right panels in *Figure 5*). The peak is most prominent in
8 summer (*Figure 5*, b-2), further supporting that strong photochemistry leads to more oxidized organics.
9 Since \overline{OS}_C is estimated as $2 \times \text{O:C} - \text{H:C}$ (Kroll et al., 2011), H:C can be reflected by the gaps between
10 the red symbols (\overline{OS}_C) and the blue symbols (O:C) in the right panels of *Figure 5*. The largest gap was
11 also observed in summer (*Figure 5*, b-2), which was a result of low H:C in the organics in this particular
12 season (*Figure 5*, b-1). Given the organics were largely secondary, precursors of low H:C in SOA
13 formation such as aromatics or biogenic volatile organic compounds (BVOC) may have led to the
14 observed low H:C ratios. Although it is difficult to distinguish between these two types of precursors
15 from the current dataset, BVOC likely contributed substantially to SOA formation in summer because
16 the site is surrounded by shrubby hills in three directions with relatively little traffic and industrial
17 activities. The relatively high temperature in summer might facilitate more BVOC emission (Guenther
18 et al., 1993) resulting in more SOA with a low H:C ratio. There are only small diurnal variations in the
19 degree of oxygenation in both autumn and winter (*Figure 5*, c-2 and d-2, respectively). The oxidized

1 organics were likely transported to this site rather than locally formed.

2 3.4 PMF factors

3 PMF results were evaluated by time-series correlations of tracer species or ions and by mass-spectra
4 correlations of similar factors (Table S3) from the literature (Zhang et al., 2011). We compared the
5 trends of different species or proxies of species of potentially similar origins and characteristics. For
6 example, as a transported species, LVOOA was compared with another transported species—sulfate.
7 SVOOA was compared with nitrate since both are secondary and semi-volatile. COA was compared
8 with three tracer ions— $C_5H_8O^+$, $C_6H_{10}O^+$, and $C_7H_{12}O^+$ (Sun et al., 2011). HOA was compared
9 with NO_x since both are traffic-related species. HR mass spectra of LVOOA (n = 4), SVOOA (n = 4),
10 COA (n = 2), and HOA (n = 6) from a high resolution AMS spectral database
11 (<http://cires.colorado.edu/jimenez-group/HRAMSsd/>) were averaged and used for correlation analysis
12 with PMF-resolved mass spectra from this study. From the inspection of tracer ions related to
13 levoglucosan ($C_2H_4O_2^+$ and $C_3H_5O_2^+$) (Zhang et al., 2011) or lignin (Li et al., 2011), as well as the MS
14 profiles of the PMF factors, biomass burning organic aerosol was not significant in the current study,
15 although these characteristics might have been lost during aging processes (Hennigan et al., 2010; Li
16 et al., 2014) before they were even transported to the site. COA showed a distinct diurnal pattern with
17 peaks in the early evening, good correlations with the three tracer ions, and good correlations with
18 mass spectra from the literature (panels 3-a through 3-d in Figures S11, S13, S15 and S17). A COA
19 factor was resolved from the single POA factor assigned earlier, namely the HOA factor (Lee et al.,

1 2013;Li et al., 2013). This COA factor is also useful in choosing an initial number of factors. Based on
2 the similarity between the time series or mass spectra of some of the factors and those of tracers and
3 mass spectra in the literature, we believe that both LVOOA and SVOOA were split into two or three
4 “sub-factors”. Such splitting yields “sub-factors” that are not physically meaningful, thus they are
5 combined to produce a single LVOOA or SVOOA factor. Table S3 summarizes the correlation analysis
6 of time series and mass spectra before and after factor combination, with Pearson’s R (R_{Pr}) for time
7 series and un-centered R (R_{UC}) for mass spectra. The results of diagnostics and correlations are shown
8 in Figures S5 to S8 and an example of bootstrapping (May 2011, spring) is shown in Figure S9. The
9 combined four-factor solutions for all seasons are thus used for further analysis. Table S4 shows the
10 elemental analysis results of the four factors in all seasons.

11 Shown in *Figure 6* are the time series (left panels), average concentrations (middle panels), and
12 mass fractions (right panels) of each PMF-resolved factor in the organics in the combined four-factor
13 solutions in each season. Assuming LVOOA and SVOOA can act as surrogates of “aged” and “fresh”
14 SOA respectively (Jimenez et al., 2009), over 80% of the organics in NR-PM₁ were of secondary nature
15 in all four seasons. The relative contributions of LVOOA and SVOOA showed clear seasonal
16 dependence. Summer (*Figure 6*, b-3) had the highest SVOOA fraction of up to 53%. Winter (*Figure*
17 *6*, d-3) had the highest LVOOA fraction of up to 55%, in accordance with our previous discussion that
18 the site was under the influence of long-range transport in this particular season. The COA fractions in
19 both spring and winter were higher than those in the other two seasons, probably due to low wind

1 speed (*Table 2*) which limited dispersion. The fractions of HOA in spring and summer were higher
2 than those in the other months, which can be attributed to the air mass origin to be discussed in the
3 next section. Note that the two POA factors COA and HOA behaved slightly differently because COA
4 was mainly contributed by a student canteen nearby and stagnant air will facilitate the accumulation
5 of this primary emission, while HOA was mainly from the urban area and its contribution was higher
6 when the wind direction was from the south.

7 3.5 Back-trajectory analysis

8 Although the average NR-PM₁ concentration had little dependence on the season, it had a strong
9 dependence on the air mass origin, as shown in *Figure 7*. Continental air masses (Clusters 2, 3, and 5)
10 showed average NR-PM₁ concentrations of 16 – 17 µg/m³. The air masses from South China Sea
11 (Cluster 4) showed the lowest NR-PM₁ concentration (11.2 µg/m³). The air masses from the East China
12 Sea (Cluster 1) showed NR-PM₁ concentration of 14.0 µg/m³.

13 The three clusters with continental air mass origins (Clusters 2, 3, and 5) had similar mass
14 concentrations as well as fractions of species. For example, sulfate and nitrate fractions in all three
15 clusters were 46% and 6% respectively. Ammonium fractions were 14-15% and LVOOA fractions
16 were 15-16%. Cluster 3 had slightly higher POA (HOA and COA) fractions than the other two
17 continental clusters, but a lower SVOOA fraction (10% in Cluster 3 compared with 13% in the other
18 two). Cluster 3 with a short mean trajectory mainly consists of circulating trajectories within the PRD
19 region due to the effect of land-sea breeze in relatively weak background winds. This relatively calm

1 meteorological condition may favor the accumulation of locally emitted air pollutants. In Clusters 1
2 and 4, over 50% of NR-PM₁ mass was sulfate, suggesting that a marine air mass can still transport
3 significant amounts of sulfate to the site, presumably due to oxidation of dimethyl sulfide (Warneck,
4 2000) or residual sulfate accumulating in the ocean after long-range transport. The fraction of HOA in
5 Cluster 4 was the highest among all clusters. The site was downwind of the highly urbanized downtown
6 area. It was more affected by traffic-related emissions in Cluster 4 than in other Clusters. As shown in
7 Table 1, respectively 35% and 17% of the time in spring and summer were associated with Cluster 4.
8 The monthly averaged high HOA fractions in these two seasons (see *Figure 6*, panels a-3 and b-3)
9 were thus clearly affected by the air mass origins represented by Cluster 4.

10 *Figure 8* shows the size distributions of sulfate, organics, and organics with m/z values of 44 (Org44)
11 and 57 (Org57) in all five clusters. As discussed above, the peak at ~200 nm in organics and Org57
12 may be due to primary emissions of vehicular exhausts (Canagaratna et al., 2010; Sun et al., 2011).
13 This peak is clearly observed in Cluster 4, which reinforces our conclusion that traffic-related
14 emissions from the downtown area in the southwest had a strong influence on the organic component
15 in NR-PM₁. Interestingly Cluster 1 is probably also affected by traffic emissions, albeit to a smaller
16 extent, since the same shoulder peak is also observed. Sulfate and Org44 both peak at a larger size of
17 around 500 to 600 nm. A small shoulder peak at around 200 nm for Org44 is observed in Clusters 1,
18 3, and 4, suggesting fresher locally produced oxidized organics are important during the periods of
19 these clusters.

1 From the diurnal patterns of the degree of oxygenation (\overline{OS}_C and O:C) also shown in *Figure 8*.
2 Clusters 1, 3, and 4 had the most obvious diurnal variations, suggesting that more local oxidation of
3 organics may have occurred under the strong photochemical activity near the site. In Clusters 1 and 4,
4 the degree of oxygenation of organics showed sharp decreases in the morning after 6:00 and milder
5 decreases in the evening after 18:00. This observation corresponds to higher emissions of traffic-
6 related HOA, whose degree of oxygenation is low, in these two clusters and is in good agreement with
7 previous analysis showing that the site was strongly affected by local traffic emissions in Clusters 1
8 and 4. Conversion of HOA to SOA during the day resulted in increases in the degree of oxygenation
9 of organics in the two clusters. Without such obvious decreases in rush hours in Cluster 3, the increase
10 in degree of oxygenation at noon in this cluster is significant, with a mean O:C increase of ~ 0.1 from
11 8:00 to 14:00. The calm winds in Cluster 3 can thus facilitate local SOA formation during daytime.
12 Together with the earlier size distribution data analysis, we believe that during the periods of these
13 three clusters, locally formed oxidized organics were more prevalent than transported ones. In contrast,
14 the diurnal variations in the degree of oxygenation in Clusters 2 and 5 are not obvious, suggesting
15 oxidized organics were mostly transported to the site.

16 **4. Conclusions and atmospheric implications**

17 We investigated NR-PM₁ composition with highly time-resolved HR-ToF-AMS measurements in
18 four seasons at the HKUST Supersite. Several major conclusions may be drawn.

19 a) NR-PM₁ at the HKUST Supersite was highly aged with a high sulfate content and highly

1 oxygenated organic components. Monthly average sulfate mass fraction ranged from 40 to 56%
2 and the peak O:C ratio in the diurnal pattern of summer was up to 0.6.

3 b) Seasonal variation in NR-PM₁ concentration was not obvious (14.3 to 15.9 µg/m³) but the
4 relative fractions of different species showed strong seasonal dependence. In terms of percentages
5 of species in the NR-PM₁ mass, sulfate was highest in summer (56%) and lowest in winter (40%).
6 Nitrate was highest in winter (10%) with the low temperatures. Organics were high in autumn
7 (38%) and winter (33%) with the air originating mainly from the continent.

8 c) Both NR-PM₁ concentrations and the relative fractions showed a strong dependence on air
9 mass origin. Averaged NR-PM₁ concentration ranged from 11.2 to 17.3 µg/m³, depending on air
10 mass origin. The diurnal pattern of the degree of oxygenation was more pronounced in the periods
11 when the air masses originated from the ocean, while it varied little in the periods when the air
12 masses originated from the continent with long-range transport.

13 d) Both locally produced and regionally transported organic aerosols contribute to the organic
14 content of PM at this site, and the degree of contribution depends strongly on the season as well as
15 the air mass origin.

16 The last point is of particular interest when trying to identify the source of organics in PM pollution.
17 Traffic-related HOA had a relatively higher fraction in organic aerosols in spring and summer when
18 air masses came mainly from the ocean and they brought local traffic emissions from downtown areas
19 to the site. COA had the highest fraction when the air masses were circulating within the PRD region

1 (Cluster 3). The degree of oxygenation showed the most obvious diurnal patterns in summer and spring
2 and in clusters of less continental influence (Clusters 1, 3, and 4), reflecting the importance of locally
3 produced SOA. Clusters 2 and 5, which are associated mainly with winter and autumn, had little
4 variation in diurnal patterns of degree of oxygenation of organics. This suggests that organic aerosols,
5 most likely dominated by SOA, were transported to the site in autumn and winter.

6 The AMS NR-PM₁ compositions at this suburban site are similar to those reported in the literature
7 for other non-urban sites in Asia in terms of the fractions of NR-PM₁ species. However, the NR-PM₁
8 concentration is lower than those reported for the nearby PRD area, probably due to the strong
9 influence of the oceanic air mass in some seasons and the low level of locally emitted anthropogenic
10 particles near this suburban site. Sulfate fraction (four-season average 48%) in the current study is even
11 higher than those at remote sites such as Jiju, Korea (JJK, 36%) and Fukue, Japan (FKJ, 40%). The
12 four-season average mass concentration of sulfate of 7.3 $\mu\text{g}/\text{m}^3$ at the suburban site in Hong Kong is
13 close to those measured at four other sites in the PRD region ($\sim 10 \mu\text{g}/\text{m}^3$), but much higher than those
14 measured in JJK and FJK (3 to 4 $\mu\text{g}/\text{m}^3$). Hence, sulfate in the PRD might have a much higher
15 “background” concentration (7 to 10 $\mu\text{g}/\text{m}^3$) than in East Asia. The quality of fossil fuel (especially
16 coal) should be better controlled and the usage of desulfurization technology (Zhao et al., 2010) should
17 be better implemented.

18 In this study, there was a large seasonal effect on the NR-PM₁ species distribution and the chemical
19 characteristics of organic aerosols, but a much weaker one on the overall NR-PM₁ concentration. On

1 the other hand, both NR-PM₁ concentration and chemical characteristics are sensitive to air mass origin.
2 SOA, as indicated by the PMF-resolved OOA factors, had much higher mass fractions (5 times) than
3 did POA (mainly COA and HOA) at this suburban site. This is also reflected by the high degree of
4 oxygenation of the organic components. Therefore, this site is strongly influenced by secondary
5 formation of organic aerosols. By contrast, studies at many other sites in China showed a higher
6 fraction of POA, as shown in *Figure 2*. The HKUST Supersite is thus a suitable location for gaining a
7 better understanding of the processes leading to SOA formation in the region.

8 **5. Acknowledgements**

9 This work was supported by the Environmental Conservation Fund of Hong Kong (project
10 number: ECWW09EG04) and the Research Grants Council of the Hong Kong Special Administrative
11 Region, China (General Research Fund 600413).

1 6. References

- 2 Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron
3 ionization high-resolution mass spectrometry, *Anal. Chem.*, 79, 8350-8358, 2007.
- 4 Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I.
5 M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M.,
6 Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen,
7 J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of
8 primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol
9 mass spectrometry, *Environ. Sci. Technol.*, 42, 4478-4485, 2008.
- 10 Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty,
11 K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A.,
12 Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan,
13 V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P.,
14 Molina, L. T., Sosa, G., and Jimenez, J. L.: Mexico City aerosol analysis during MILAGRO
15 using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine
16 particle composition and organic source apportionment, *Atmos. Chem. Phys.*, 9, 6633-6653,
17 2009.
- 18 Allan, J. D., Alfarra, M. R., Bower, K. N., Williams, P. I., Gallagher, M. W., Jimenez, J. L.,
19 McDonald, A. G., Nemitz, E., Canagaratna, M. R., Jayne, J. T., Coe, H., and Worsnop, D. R.:
20 Quantitative sampling using an Aerodyne aerosol mass spectrometer - 2. Measurements of fine
21 particulate chemical composition in two U.K. cities, *J. Geophys. Res.-Atmos.*, 108, 4091, Doi
22 4010.1029/2002jd002359, 2003.
- 23 Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M.,
24 Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A
25 generalised method for the extraction of chemically resolved mass spectra from aerodyne
26 aerosol mass spectrometer data, *J. Aerosol Sci.*, 35, 909-922, 2004.
- 27 Canagaratna, M. R., Onasch, T. B., Wood, E. C., Herndon, S. C., Jayne, J. T., Cross, E. S., Miake-
28 Lye, R. C., Kolb, C. E., and Worsnop, D. R.: Evolution of Vehicle Exhaust Particles in the
29 Atmosphere, *J. Air Waste Manage. Assoc.*, 60, 1192-1203, 2010.
- 30 Chan, C. K., and Yao, X.: Air pollution in mega cities in China, *Atmos. Environ.*, 42, 1-42, 2008.
- 31 DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M.,
32 Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable,
33 high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281-8289, 2006.
- 34 Draxler, R. R., and Hess, G. D.: Description of the HYSPLIT_4 modeling system, Available at
35 <http://www.arl.noaa.gov/documents/reports/arl-224.pdf>. Accessed Jan., 5th, 2014, NOAA Air
36 Resources Laboratory, Silver Spring, Maryland, USA, 1997.
- 37 Draxler, R. R., Stunder, B., Rolph, G., Stein, A., and Taylor, A.: HYSPLIT_4 User's Guide, Available

1 at http://www.arl.noaa.gov/documents/reports/hysplit_user_guide.pdf. Accessed Jan., 5th,
2 2014, NOAA Air Resources Laboratory, Silver Spring, Maryland, USA, 2012a.

3 Draxler, R. R., Stunder, B., Rolph, G., Stein, A., and Taylor, A.: HYSPLIT tutorial, Available at
4 http://www.arl.noaa.gov/documents/workshop/Spring2011/HYSPLIT_Tutorial.pdf. Accessed
5 Jan., 5th, 2014, NOAA Air Resources Laboratory, Silver Spring, Maryland, USA, 2012b.

6 Gilardoni, S., Massoli, P., Giulianelli, L., Rinaldi, M., Paglione, M., Pollini, F., Lanconelli, C.,
7 Poluzzi, V., Carbone, S., Hillamo, R., Russell, L. M., Facchini, M. C., and Fuzzi, S.: Fog
8 scavenging of organic and inorganic aerosol in the Po Valley, *Atmos. Chem. Phys.*, 14, 6967-
9 6981, 2014.

10 Gong, Z. H., Lan, Z. J., Xue, L., Zeng, L. W., He, L. Y., and Huang, X. F.: Characterization of
11 submicron aerosols in the urban outflow of the central Pearl River Delta region of China,
12 *Front. Env. Sci. Eng.*, 6, 725-733, 2012.

13 Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and
14 Monoterpene Emission Rate Variability - Model Evaluations and Sensitivity Analyses, *J.*
15 *Geophys. Res.-Atmos.*, 98, Doi 10.1029/93jd00527, 12609-12617, 1993.

16 He, L. Y., Huang, X. F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R. Y., and Zhang, Y. H.:
17 Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl
18 River Delta of China using high-resolution aerosol mass spectrometry, *J. Geophys. Res.-*
19 *Atmos.*, 116, Artn D12304, DOI: 10.1029/2010JD014566, 2011.

20 Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen, Q.,
21 Martin, S. T., Farmer, D. K., and Artaxo, P.: A simplified description of the evolution of organic
22 aerosol composition in the atmosphere, *Geophys. Res. Lett.*, 37, L08803, 2010.

23 Hennigan, C. J., Sullivan, A. P., Collett, J. L., Jr., and Robinson, A. L.: Levoglucosan stability in
24 biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, 37, L09806, doi:
25 10.1029/2010gl043088, 2010.

26 Hu, D., and Yu, J. Z.: Secondary organic aerosol tracers and malic acid in Hong Kong: seasonal
27 trends and origins, *Environ. Chem.*, 10, 381-394, 2013.

28 Hu, W. W., Hu, M., Yuan, B., Jimenez, J. L., Tang, Q., Peng, J. F., Hu, W., Shao, M., Wang, M.,
29 Zeng, L. M., Wu, Y. S., Gong, Z. H., Huang, X. F., and He, L. Y.: Insights on organic aerosol
30 aging and the influence of coal combustion at a regional receptor site of central eastern China,
31 *Atmos. Chem. Phys.*, 13, 10095-10112, 2013.

32 Huang, X. F., Yu, J. Z., Yuan, Z. B., Lau, A. K. H., and Louie, P. K. K.: Source analysis of high
33 particulate matter days in Hong Kong, *Atmos. Environ.*, 43, 1196-1203, 2009.

34 Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Kroll, J. H., Ng, N. L., Zhang, Y. H., Lin, Y.,
35 Xue, L., Sun, T. L., Liu, X. G., Shao, M., Jayne, J. T., and Worsnop, D. R.: Characterization of
36 submicron aerosols at a rural site in Pearl River Delta of China using an Aerodyne High-
37 Resolution Aerosol Mass Spectrometer, *Atmos. Chem. Phys.*, 11, 1865-1877, 2011.

38 Huang, X. F., He, L. Y., Xue, L., Sun, T. L., Zeng, L. W., Gong, Z. H., Hu, M., and Zhu, T.: Highly

1 time-resolved chemical characterization of atmospheric fine particles during 2010 Shanghai
2 World Expo, *Atmos. Chem. Phys.*, 12, 4897-4907, 2012.

3 Huang, X. F., Xue, L., Tian, X. D., Shao, W. W., Sun, T. L., Gong, Z. H., Ju, W. W., Jiang, B., Hu,
4 M., and He, L. Y.: Highly time-resolved carbonaceous aerosol characterization in Yangtze
5 River Delta of China: Composition, mixing state and secondary formation, *Atmos. Environ.*,
6 64, 200-207, 2013.

7 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H.,
8 DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M.,
9 Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin,
10 C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M.,
11 Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A.,
12 Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick,
13 F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A.,
14 Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J.
15 R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C.,
16 Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic
17 aerosols in the atmosphere, *Science*, 326, 1525-1529, 2009.

18 Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R.,
19 Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb,
20 C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of
21 atmospheric organic aerosol, *Nature Chem.*, 3, 133-139, 2011.

22 Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prevot, A. S. H.:
23 Source apportionment of submicron organic aerosols at an urban site by factor analytical
24 modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503-1522, 2007.

25 Lau, J., Hung, W. T., Cheung, C. S., and Yuen, D.: Contributions of roadside vehicle emissions to
26 general air quality in Hong Kong, *Transport Res D-Tr E*, 13, 19-26, 2008.

27 Lee, B. Y. L., Li, Y. J., Yu, J. Z., Louie, K. K. P., and Chan, C. K.: Characteristics of ambient aerosol
28 at a suburban site in Hong Kong during springtime, *J. Geophys. Res.-Atmos.*, 118, Doi:
29 10.1002/jgrd.50658, 8625-8639, 2013.

30 Li, Y., Lau, A. K. H., Fung, J. C. H., Zheng, J. Y., Zhong, L. J., and Louie, P. K. K.: Ozone source
31 apportionment (OSAT) to differentiate local regional and super-regional source contributions in
32 the Pearl River Delta region, China, *J. Geophys. Res.-Atmos.*, 117, Artn D15305, Doi
33 10.1029/2011jd017340, 2012.

34 Li, Y. J., Yeung, J. W. T., Leung, T. P. I., Lau, A. P. S., and Chan, C. K.: Characterization of Organic
35 Particles from Incense Burning Using an Aerodyne High-Resolution Time-of-Flight Aerosol
36 Mass Spectrometer, *Aerosol Sci. Technol.*, 46, 654-665, 2011.

37 Li, Y. J., Lee, B. Y. L., Yu, J. Z., Ng, N. L., and Chan, C. K.: Evaluating the degree of oxygenation of
38 organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-of-flight

1 aerosol mass spectrometry (HR-ToF-AMS), *Atmos. Chem. Phys.*, 13, 8739-8753, 2013.

2 Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical
3 oxidation and direct photolysis of vanillin - a model compound of methoxy phenols from
4 biomass burning, *Atmos. Chem. Phys.*, 14, 2871-2885, 2014.

5 Louie, P. K. K., Watson, J. G., Chow, J. C., Chen, A., Sin, D. W. M., and Lau, A. K. H.: Seasonal
6 characteristics and regional transport of PM_{2.5} in Hong Kong, *Atmos. Environ.*, 39, 1695-
7 1710, 2005.

8 Meng, J. W., Yeung, M. C., Li, Y. J., Lee, B. Y. L., and Chan, C. K.: Cloud condensation nuclei
9 (CCN) and HR-ToF-AMS measurements at a coastal site in Hong Kong: Size-resolved CCN
10 activity and closure analysis, *Atmos. Chem. Phys.*, 14, 10267-10282, 2014.

11 Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of
12 Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer
13 using Field Data, *Aerosol Sci. Technol.*, 46, 258-271, 2012.

14 Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H.,
15 Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L.,
16 Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and
17 Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from
18 Aerosol Mass Spectrometry, *Atmos. Chem. Phys.*, 10, 4625-4641, 2010.

19 Paatero, P., and Tapper, U.: Positive Matrix Factorization - a Nonnegative Factor Model with
20 Optimal Utilization of Error-Estimates of Data Values, *Environmetrics*, 5, 111-126, 1994.

21 Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L.,
22 Trimborn, A., Facchini, M. C., Fuzzi, S., Hillamo, R., and Worsnop, D.: Chemical
23 characterization of springtime submicrometer aerosol in Po Valley, Italy, *Atmos. Chem. Phys.*,
24 12, 8401-8421, 2012.

25 Seinfeld, J. H., and Pandis, S. N.: *Atmospheric chemistry and physics: From air pollution to climate
26 change*, 2nd ed., Wiley, New Jersey, 2006.

27 Sueper, D.: ToF-AMS data analysis software: [http://cires.colorado.edu/jimenez-](http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html)
28 [group/ToFAMSResources/ToFSoftware/index.html](http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html), access: 1st, December, 2013, 2013.

29 Sun, Y. L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W. N., Bae, M. S., Hung, H. M.,
30 Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y. C.: Characterization of the sources and
31 processes of organic and inorganic aerosols in New York city with a high-resolution time-of-
32 flight aerosol mass spectrometer, *Atmos. Chem. Phys.*, 11, 1581-1602, 2011.

33 Sun, Y. L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., Li, J., and Jia, J. J.: Aerosol
34 composition, sources and processes during wintertime in Beijing, China, *Atmos. Chem. Phys.*,
35 13, 4577-4592, 2013.

36 Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of
37 organic components from Positive Matrix Factorization of aerosol mass spectrometric data,
38 *Atmos. Chem. Phys.*, 9, 2891-2918, 2009.

1 Wang, W., Bruyere, M., Duda, M., Dudhia, J., Gill, D., Kavulich, M., Keene, K., Lin, H.,
2 Michalakes, J., Rizvi, S., and Zhang, X.: Weather Research and Forecasting ARW version 3
3 modeling system user's guide, Available at
4 http://www.mmm.ucar.edu/wrf/users/docs/user_guide_V3/ARWUsersGuideV3.pdf, Mesoscale
5 and Microscale Meteorology Division, National Center for Atmospheric Research, Boulder,
6 CO, U.S.A., 2014.

7 Warneck, P.: Chemistry of the natural atmosphere, 2nd ed., Academic Press, San Diego, CA, 2000.

8 Wu, D., Wu, C., Liao, B., Chen, H., Wu, M., Li, F., Tan, H., Deng, T., Li, H., Jiang, D., and Yu, J. Z.:
9 Black carbon over the South China Sea and in various continental locations in South China,
10 Atmos. Chem. Phys., 13, 12257-12270, 2013.

11 Xiao, R., Takegawa, N., Zheng, M., Kondo, Y., Miyazaki, Y., Miyakawa, T., Hu, M., Shao, M., Zeng,
12 L., Gong, Y., Lu, K., Deng, Z., Zhao, Y., and Zhang, Y. H.: Characterization and source
13 apportionment of submicron aerosol with aerosol mass spectrometer during the PRIDE-PRD
14 2006 campaign, Atmos. Chem. Phys., 11, 6911-6929, 2011.

15 Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G., and Zhao, Q.: Characteristics
16 of PM_{2.5} speciation in representative megacities and across China, Atmos. Chem. Phys., 11,
17 5207-5219, 2011.

18 Yeung, M. C., Lee, B. P., Li, Y. J., and Chan, C. K.: Simultaneous HTDMA and HR-ToF-AMS
19 measurements at the HKUST Supersite in Hong Kong in 2011, J. Geophys. Res. - Atmos., 119,
20 DOI: 10.1002/2013JD021146, 2014.

21 Yuan, Z. B., Yu, J. Z., Lau, A. K. H., Louie, P. K. K., and Fung, J. C. H.: Application of positive
22 matrix factorization in estimating aerosol secondary organic carbon in Hong Kong and its
23 relationship with secondary sulfate, Atmos. Chem. Phys., 6, 25-34, 2006.

24 Zhang, J. K., Sun, Y., Liu, Z. R., Ji, D. S., Hu, B., Liu, Q., and Wang, Y. S.: Characterization of
25 submicron aerosols during a month of serious pollution in Beijing, 2013, Atmos. Chem. Phys.,
26 14, 2887-2903, 2014.

27 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y.
28 L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass
29 spectrometry: a review, Anal. Bioanal. Chem., 401, 3045-3067, 2011.

30 Zhang, X. Y., Wang, Y. Q., Niu, T., Zhang, X. C., Gong, S. L., Zhang, Y. M., and Sun, J. Y.:
31 Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature,
32 regional haze distribution and comparisons with global aerosols, Atmos. Chem. Phys., 12, 779-
33 799, 2012.

34 Zhao, Y., Wang, S. X., Nielsen, C. P., Li, X. H., and Hao, J. M.: Establishment of a database of
35 emission factors for atmospheric pollutants from Chinese coal-fired power plants, Atmos.
36 Environ., 44, 1515-1523, 2010.

37

1 **7. Table**

2 Table 1 Percentages of time split among the five clusters (300 m, 5-cluster solution) in each season.

Season	Cluster					Total
	1	2	3	4	5	
	Marine-east	Coastal	Local	Marin-south	Continental	
201105, spr.	15.6	22.4	26.7	34.5	0.8	100
201109, sum.	34.0	29.5	15.5	17.4	0.8	97
201111, aut.	19.2	41.6	16.5	2.2	20.4	100
201202, win.	8.9	46.1	36.0	2.8	6.1	100

3

1 Table 2 Monthly meteorological conditions, mixing ratios of gaseous species, and mass concentrations
 2 of NR-PM₁ species in the four measurement periods.

		^a Spring: 201105		Summer: 201109		Autumn: 201111		Winter: 201202	
		^e avg±std	^f 50% _{25%} ^{75%}	avg±std	50% _{25%} ^{75%}	avg±std	50% _{25%} ^{75%}	avg±std	50% _{25%} ^{75%}
^b Met	T (°C)	24.3±4.0	24.8 _{23.1} ^{26.3}	27.9±1.9	28.1 _{26.5} ^{29.0}	21.2±3.9	21.7 _{19.2} ^{24.0}	14.5±2.8	14.7 _{12.7} ^{16.3}
	RH (%)	80.3±10.6	82.7 _{75.1} ^{88.2}	78.3±7.6	79.2 _{72.9} ^{83.9}	72.7±12.1	73.6 _{64.8} ^{82.2}	84.0±8.8	84.8 _{79.1} ^{90.2}
	ws (m/s)	1.4±1.0	1.3 _{0.7} ^{2.0}	2.1±1.2	1.9 _{1.3} ^{2.8}	2.3±1.5	1.9 _{1.2} ^{2.9}	1.7±1.2	1.5 _{0.8} ^{2.5}
^c Gas (ppbv)	CO	381±226	378 ₂₀₀ ⁴⁹⁴	302±117	286 ₂₀₃ ³⁸⁶	314±170	287 ₁₈₉ ⁴⁰⁰	438±167	420 ₃₁₈ ⁵⁴⁰
	NO _x	11.0±11.4	7.5 _{5.0} ^{12.6}	6.1±5.9	4.6 _{3.2} ^{7.0}	6.3±5.1	5.0 _{3.3} ^{7.6}	8.6±10.2	6.6 _{4.5} ^{9.6}
	SO ₂	1.8±1.6	1.4 _{0.9} ^{2.1}	2.1±1.3	1.8 _{1.1} ^{2.7}	3.4±1.8	3.0 _{2.1} ^{4.2}	1.6±1.1	1.3 _{0.8} ^{2.0}
	O _x	45.2±26.2	37.6 _{26.3} ^{59.1}	48.4±15.3	47.9 _{37.9} ^{58.0}	49.8±18.3	48.1 _{35.4} ^{62.1}	37.3±13.2	36.5 _{26.8} ^{46.2}
^d NR- PM ₁ (μg/m ³)	SO ₄ ²⁻	7.4±4.5	6.7 _{4.1} ^{9.7}	8.7±3.8	8.9 _{5.9} ^{11.4}	7.1±3.7	6.6 _{4.6} ^{9.7}	6.2±3.2	5.8 _{4.1} ^{7.6}
	NO ₃	0.6±0.7	0.4 _{0.2} ^{0.6}	0.4±0.4	0.2 _{0.1} ^{0.5}	0.7±0.5	0.5 _{0.3} ^{0.9}	1.6±1.4	1.1 _{0.6} ^{2.1}
	NH ₄ ⁺	2.3±1.4	2.1 _{1.3} ^{3.2}	2.4±1.0	2.4 _{1.7} ^{3.2}	2.1±1.1	2.0 _{1.4} ^{2.8}	2.4±1.2	2.3 _{1.7} ^{2.8}
	Cl ⁻	0.02±0.02	0.01 _{<CDL} ^{0.02}	0.01±0.01	0.01 _{0.01} ^{0.02}	0.02±0.02	0.01 _{0.01} ^{0.02}	0.13±0.18	0.07 _{0.03} ^{0.2}
	Org	4.0±3.3	3.2 _{1.8} ^{5.2}	4.1±3.1	3.0 _{1.6} ^{5.5}	6.0±3.5	5.3 _{3.5} ^{8.1}	5.1±2.8	4.7 _{3.2} ^{6.4}
	NR-PM ₁	14.3±3.0	12.7 _{7.7} ^{19.7}	15.6±2.6	15.4 _{10.7} ^{20.8}	15.9±2.7	14.7 _{10.3} ^{21.6}	15.4±2.1	14.5 _{10.8} ^{18.2}

Note:
^a: The measurement periods were April 25 to June 1, 2011 (spring), September 1 to September 29, 2011 (summer), October 28 to December 15, 2011 (autumn), and January 19 to March 1, 2012 (winter).
^b: Meteorological parameters. T is temperature. RH is relative humidity. ws is wind speed.
^c: Mixing ratios of gaseous species in ppbv.
^d: Mass concentrations of five species in NR-PM₁ measured with HR-ToF-AMS.
^e: Average (avg) and standard deviation (std).
^f: Median (50th percentile) and 25th and 75th percentiles. CDL: campaign detection limit as shown in Figure S3.

3

4

5

1 8. Figure Caption

2 Figure 1 Summary of species (sulfate, nitrate, ammonium, chloride, and organics) in NR-PM₁ in the
3 four months. x-1: time series; x-2: monthly mean (dot), median (bar), 25% and 75% percentiles
4 (box), and 10% and 90% percentiles (whiskers), x-3: monthly fraction (x-3), where “x” is “a”
5 for spring (201105), “b” for summer (201109), “c” for autumn (201111), and “d” for winter
6 (201202). Monthly averaged total NR-PM₁ concentrations are shown above the x-2 panels with
7 1 standard deviation. The area of a pie chart is proportional to the NR-PM₁ concentration.

8 Figure 2 Summary of AMS-measured NR-PM₁ compositions in Asia. The green slices represent total
9 organics. Within the green outlines are organics with PMF-resolved factors. The grey slices
10 within the green outlines are the sum of all POA with one or more factors of HOA, COA,
11 BBOA, and CCOA (coal-combustion). The light red slices within the green outlines are the
12 sum of all OOA with one or more factors of SVOOA and LVOOA. The area of a pie chart is
13 proportional to the NR-PM₁ concentration. See Table S2 for the site locations.

14 Figure 3 Size distributions of sulfate (SO₄), nitrate (NO₃), and organics (Org) in the four months. The
15 red, blue and green lines are the means, the black lines are the medians, and the grey areas are
16 the interquartile ranges (IQRs).

17 Figure 4 Size distributions of ions with m/z values of 44, 43, and 57 in organics in the four months.
18 The red, blue and green lines are the means, the black lines are the medians, and the grey areas
19 are the interquartile ranges (IQRs).

20 Figure 5 Summary of the degrees of oxygenation of organics in the four months. The left panels are
21 the Van Krevelen diagrams showing the H:C vs O:C ratios. Small open circles, representing
22 the individual data points, were color-coded by O_x concentration. Large solid squares are the
23 average H:C and O:C ratios of the factors from PMF analysis. S_{ODR} and I_{ODR} are slopes and
24 intercepts from orthogonal distance regression (ODR). There lines with an intercept (I) of 2.0
25 and slopes (S) of -0.5, -1.0, and -2.0 are also added for reference. The right panels are the

1 diurnal patterns of average carbon oxidation state (*OSC*) and the O:C ratio.

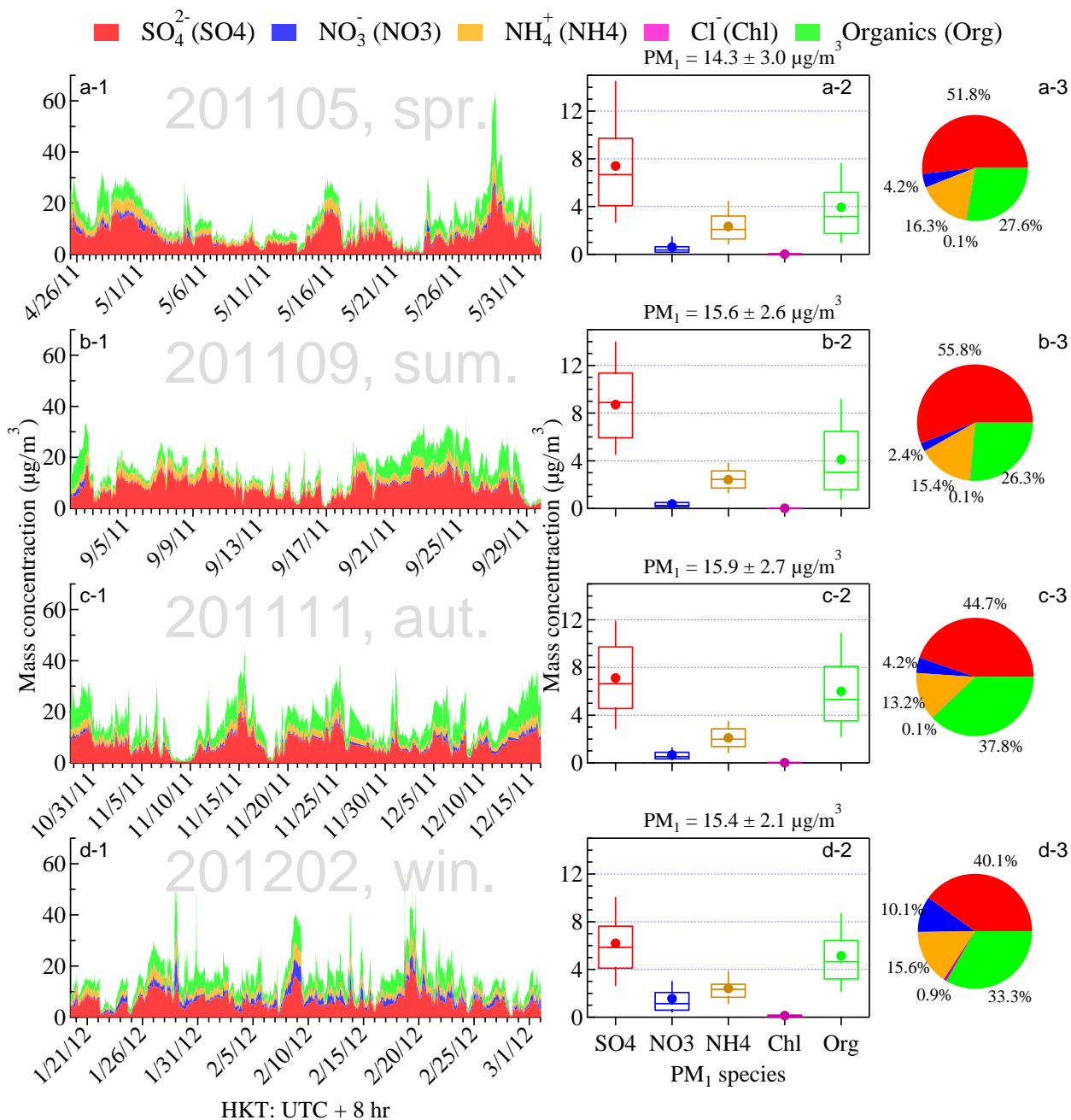
2 Figure 6 Summary of PMF-resolved organic factors (LVOOA, SVOOA, COA, and HOA) in NR-PM₁
3 in the four months. x-1: time series; x-2: monthly mean (dot), median (bar), 25% and 75%
4 percentiles (box), and 10% and 90% percentiles (whiskers); x-3: monthly fraction (x-3), where
5 “x” is “a” for spring (201105), “b” for summer (201109), “c” for autumn (201111), and “d” for
6 winter (201202). Monthly averaged total organic concentrations are shown below the pie charts
7 in x-3 with 1 standard deviation. The area of a pie chart is proportional to the organic
8 concentration.

9 Figure 7 Average fractions of sulfate, ammonium, nitrate and organics with PMF-resolved LVOOA,
10 SVOOA, COA, and HOA in different clusters from the 5-cluster solution at 300 m arrival
11 height (AGL = above ground level). The color lines in the upper panel show the average
12 trajectories and the corresponding color lines in the lower panel show the vertical profiles of
13 those trajectories.

14 Figure 8 Average size distributions of sulfate (SO₄), organics (Org), organics with m/z 44 (Org44) and
15 organics with m/z 57 (Org57), and diurnal patterns of the degree of oxygenation of organics,
16 as represented by average carbon oxidation state (*OSC*) and O:C ratio in different clusters from
17 the 5-cluster solution at 300 m arrival height. For size distributions, the color lines indicate the
18 average size distributions while the grey areas indicate the IQRs. For diurnal patterns of *OSC*
19 and O:C, legends are the same as those in Figure 5 (on top of right panels).

20

1 **9. Figures**



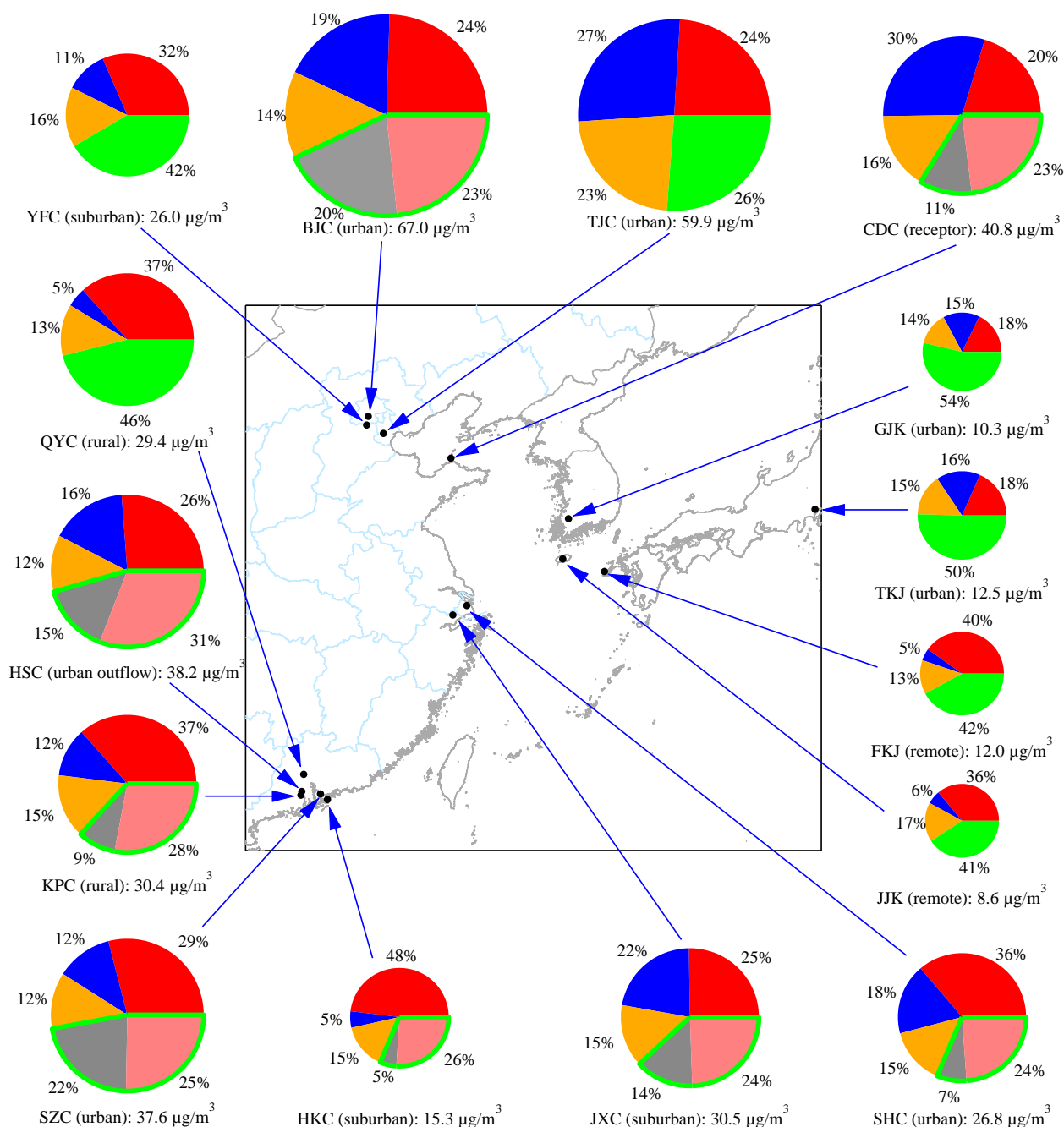
2

3 Figure 1 Summary of species (sulfate, nitrate, ammonium, chloride, and organics) in NR-PM₁ in the
 4 four months. x-1: time series; x-2: monthly mean (dot), median (bar), 25% and 75% percentiles (box),
 5 and 10% and 90% percentiles (whiskers), x-3: monthly fraction (x-3), where “x” is “a” for spring
 6 (201105), “b” for summer (201109), “c” for autumn (201111), and “d” for winter (201202). Monthly
 7 averaged total NR-PM₁ concentrations are shown above the x-2 panels with 1 standard deviation. The
 8 area of a pie chart is proportional to the NR-PM₁ concentration.

9

1

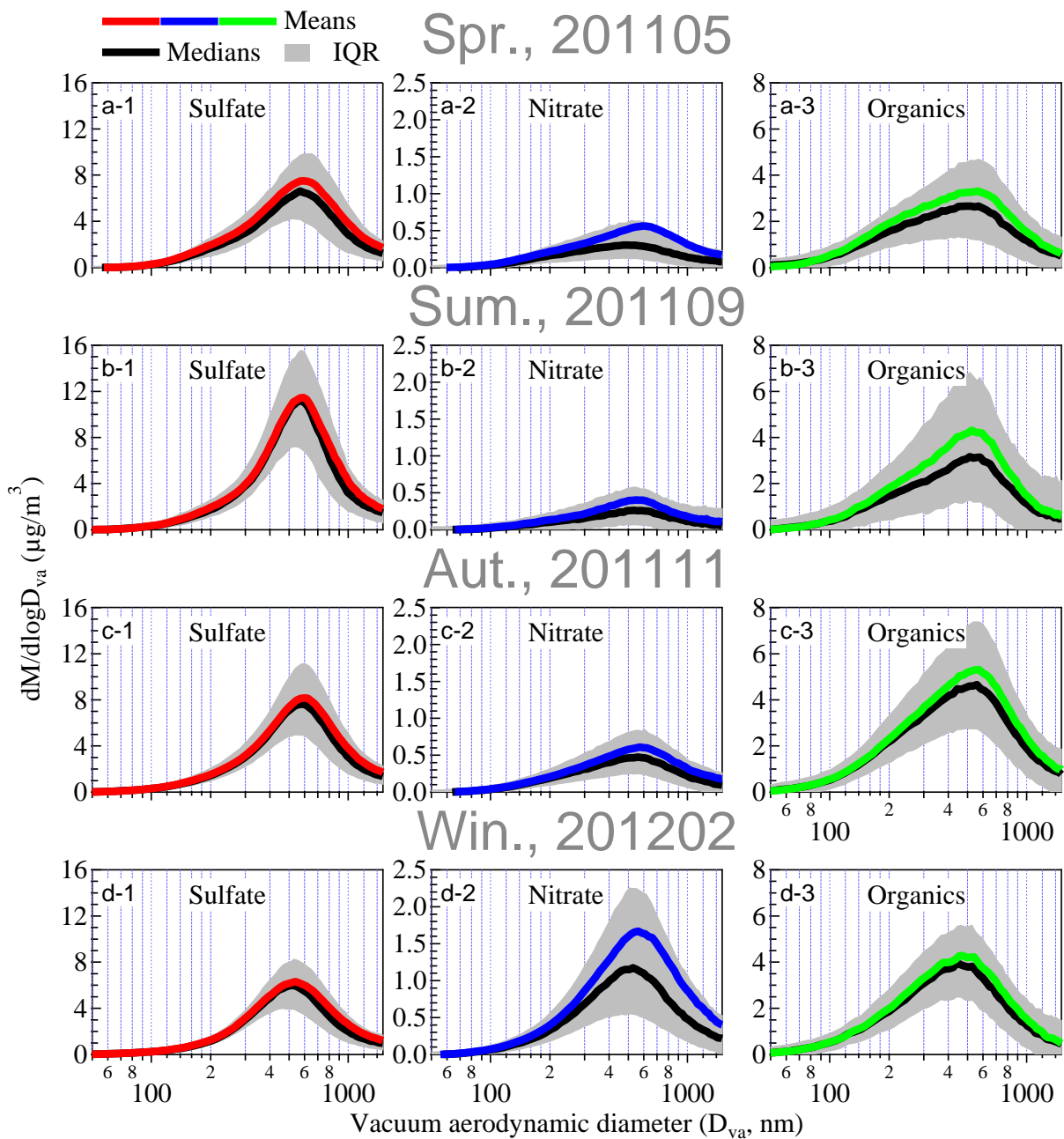
Red: sulfate. Blue: nitrate. Brown: ammonium. Green: organics. Within the green outline: Grey: POA. Light red: OOA.



2

3

4 Figure 2 Summary of AMS-measured NR-PM₁ compositions in Asia. The green slices represent total
 5 organics. Within the green outlines are organics with PMF-resolved factors. The grey slices within the
 6 green outlines are the sum of all POA with one or more factors of HOA, COA, BBOA, and CCOA
 7 (coal-combustion). The light red slices within the green outlines are the sum of all OOA with one or
 8 more factors of SVOOA and LVOOA. The area of a pie chart is proportional to the NR-PM₁
 9 concentration. See Table S2 for the site locations.

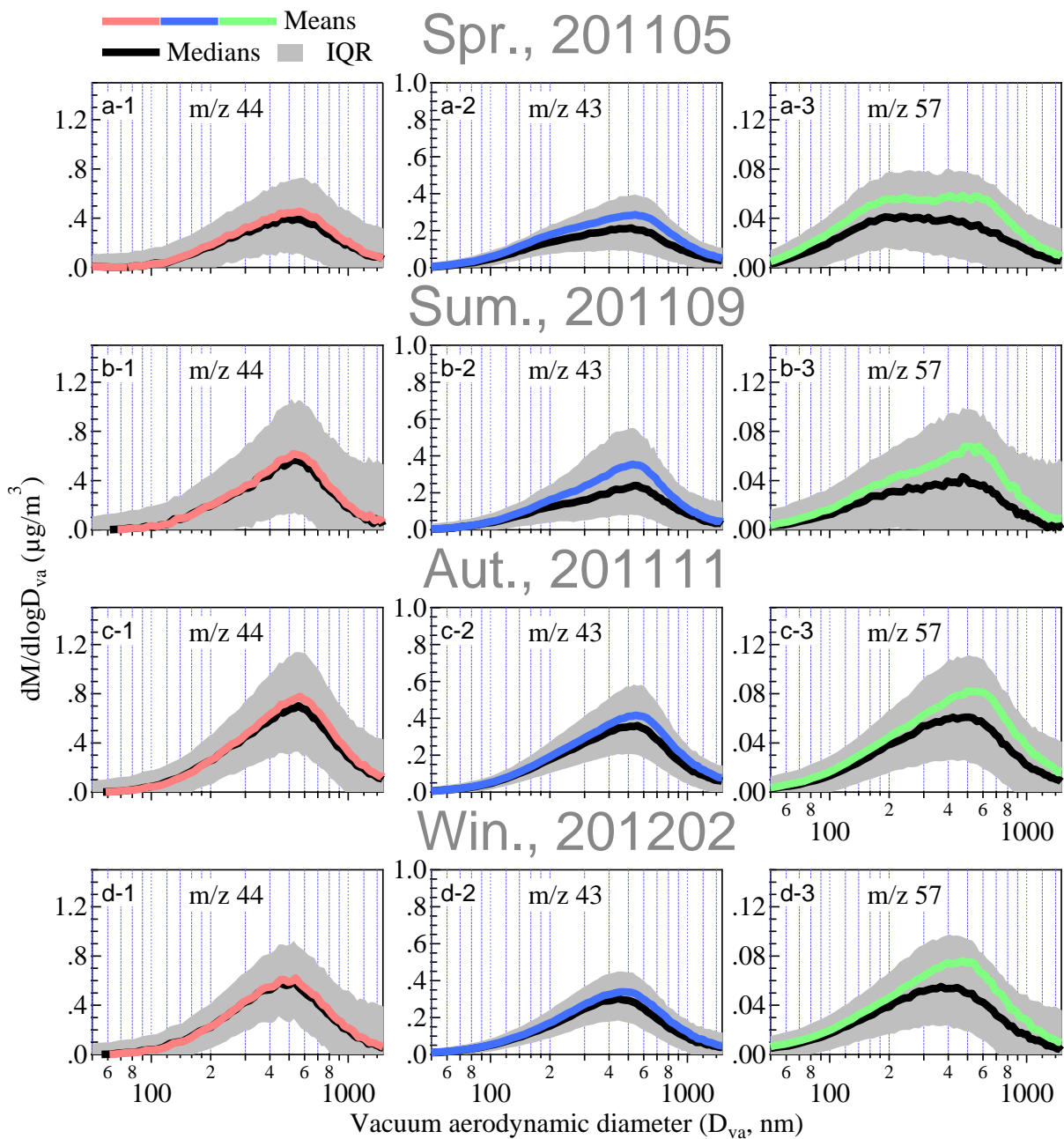


1

2

3 Figure 3 Size distributions of sulfate (SO₄), nitrate (NO₃), and organics (Org) in the four months. The
 4 red, blue and green lines are the means, the black lines are the medians, and the grey areas are the
 5 interquartile ranges (IQRs).

6



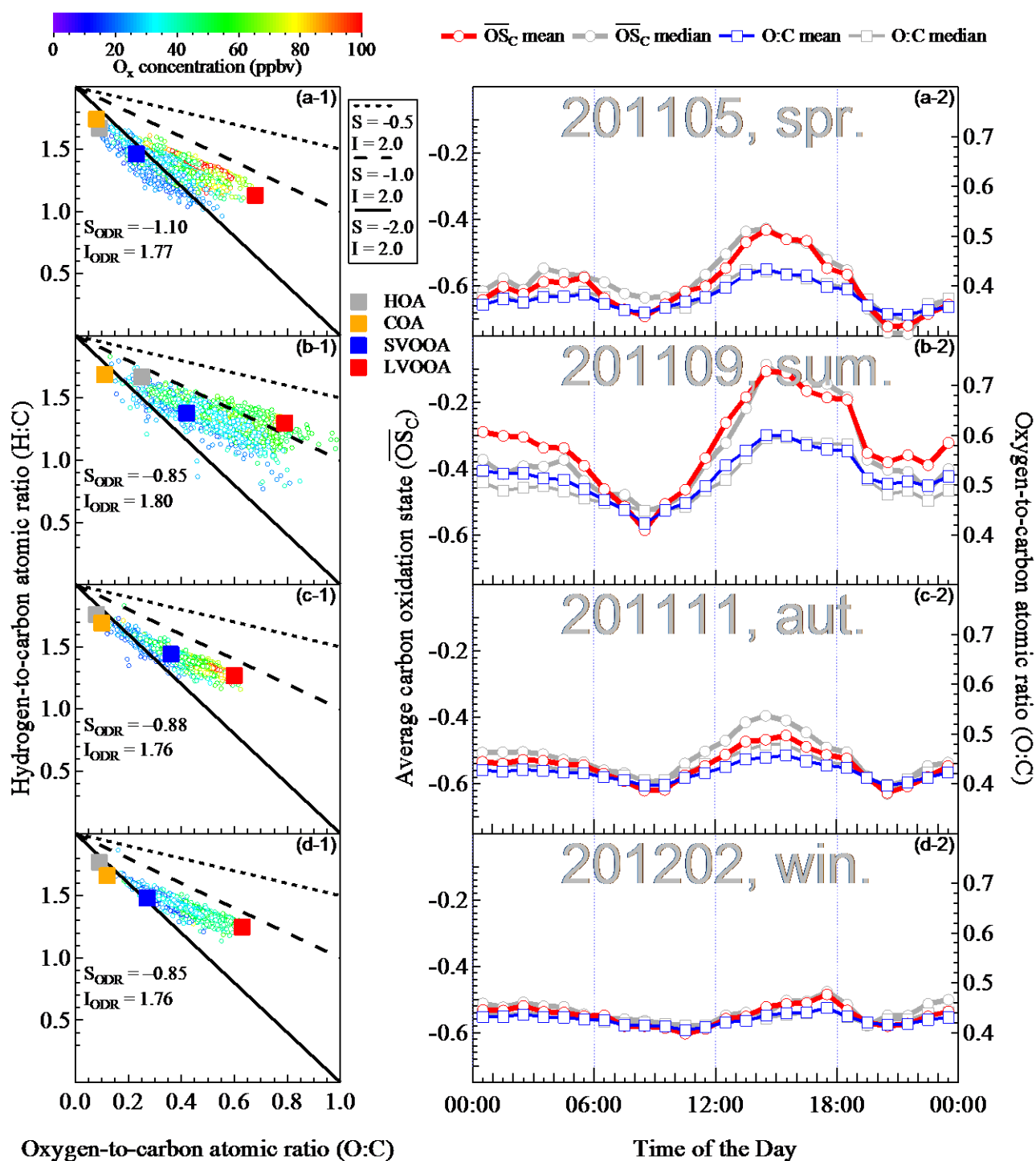
1

2

3 Figure 4 Size distributions of ions with m/z values of 44, 43, and 57 in organics in the four months.

4 The red, blue and green lines are the means, the black lines are the medians, and the grey areas are the
 5 interquartile ranges (IQRs).

6



1 Oxygen-to-carbon atomic ratio (O:C)

2 Figure 5 Summary of the degrees of oxygenation of organics in the four months. The left panels are

3 the Van Krevelen diagrams showing the H:C vs O:C ratios. Small open circles, representing the

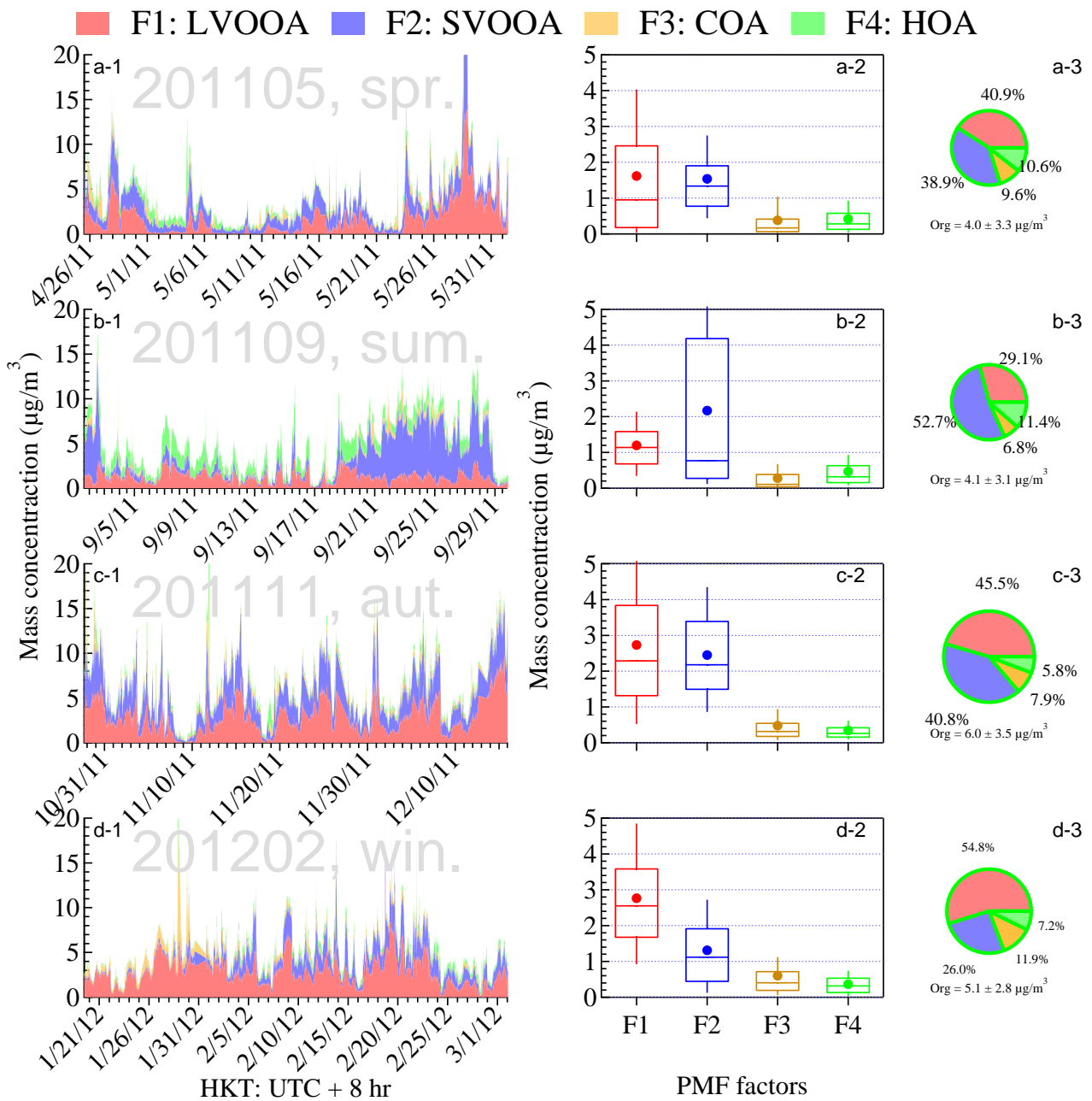
4 individual data points, were color-coded by O_x concentration. Large solid squares are the average H:C

5 and O:C ratios of the factors from PMF analysis. S_{ODR} and I_{ODR} are slopes and intercepts from

6 orthogonal distance regression (ODR). There lines with an intercept (I) of 2.0 and slopes (S) of -0.5, -

7 1.0, and -2.0 are also added for reference. The right panels are the diurnal patterns of average carbon

8 oxidation state (\overline{OS}_C) and the O:C ratio.

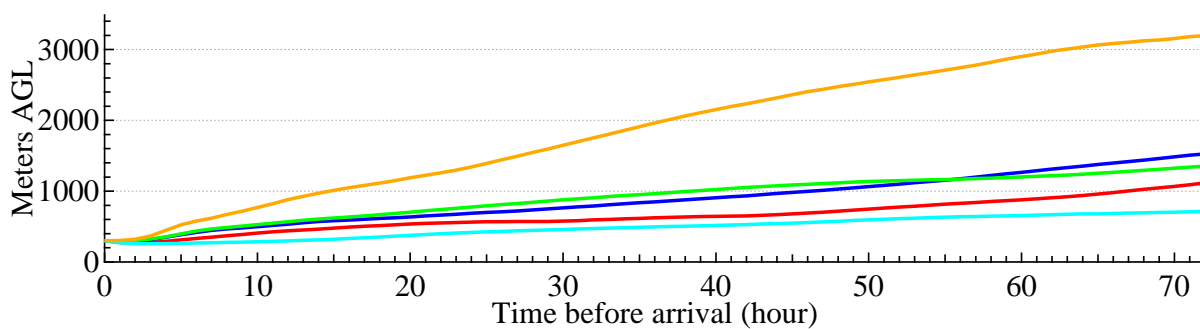
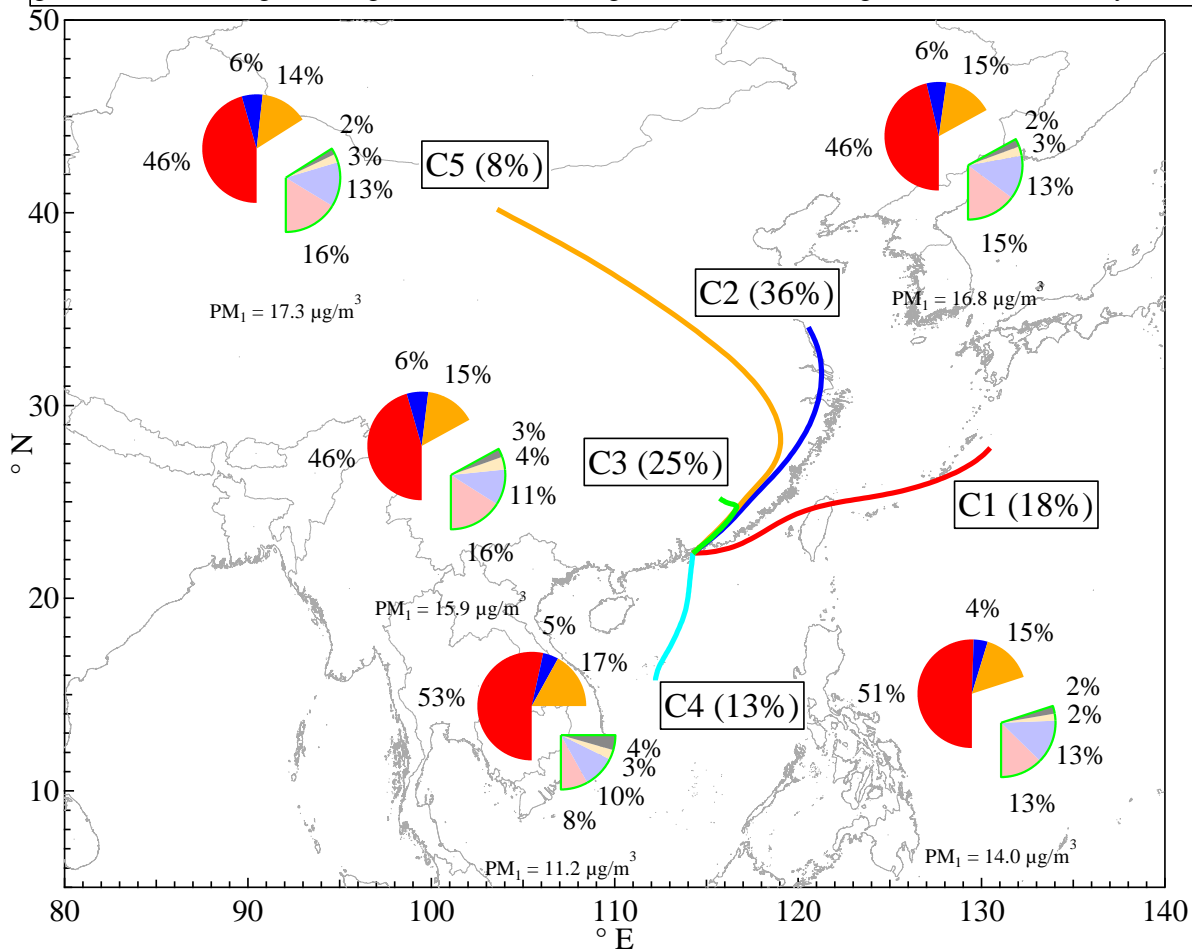


1

2 Figure 6 Summary of PMF-resolved organic factors (LVOOA, SVOOA, COA, and HOA) in NR-PM₁
 3 in the four months. x-1: time series; x-2: monthly mean (dot), median (bar), 25% and 75% percentiles
 4 (box), and 10% and 90% percentiles (whiskers); x-3: monthly fraction (x-3), where “x” is “a” for
 5 spring (201105), “b” for summer (201109), “c” for autumn (201111), and “d” for winter (201202).
 6 Monthly averaged total organic concentrations are shown below the pie charts in x-3 with 1 standard
 7 deviation. The area of a pie chart is proportional to the organic concentration.

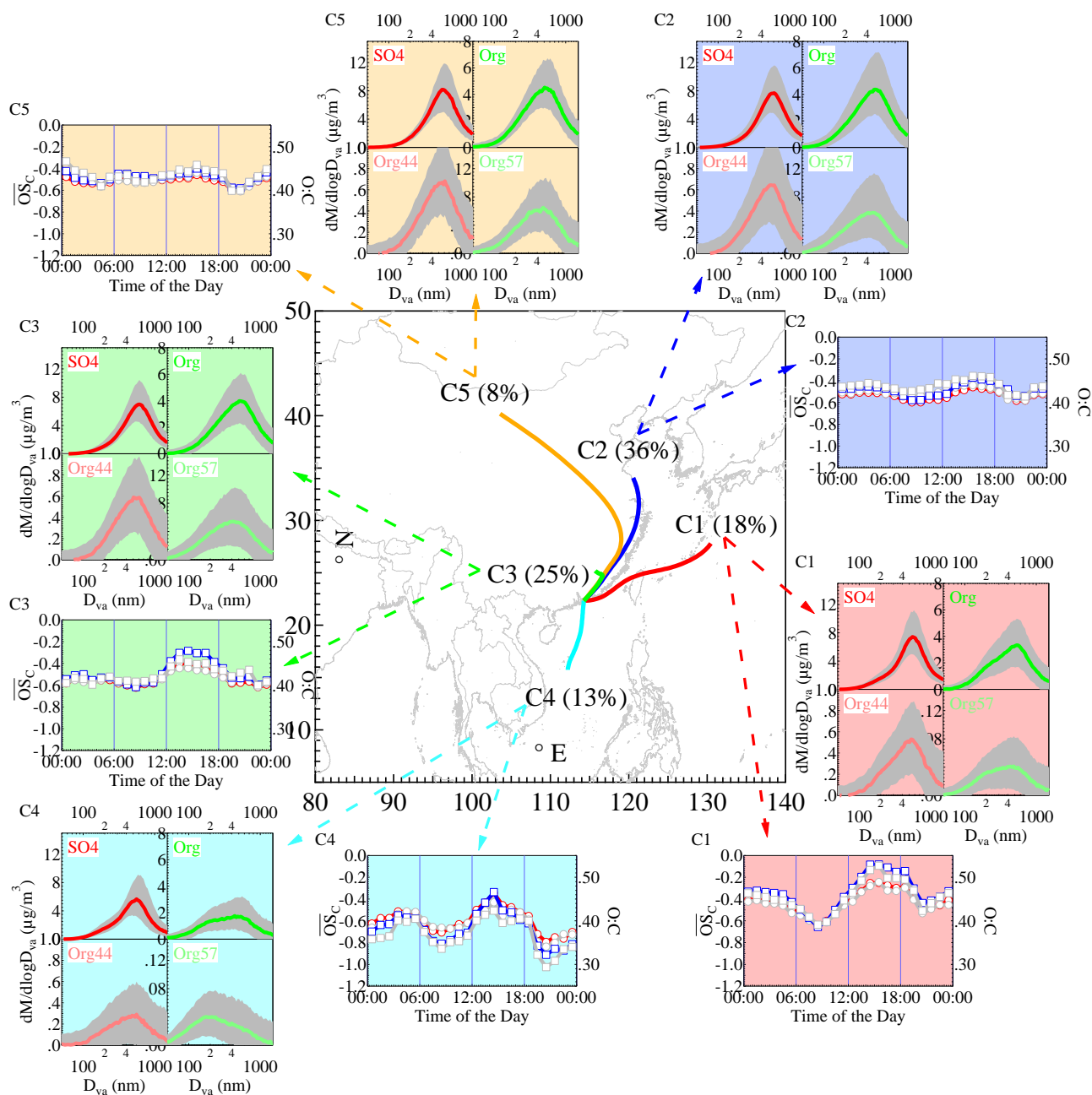
8

The slices without outlines are inorganics: Red = SO₄; Blue = NO₃; Brown = NH₄. The slices within green outlines are organics: Light red = LVOOA; Light blue = SVOOA; Light brown = COA; Grey = HOA



1
2
3
4
5
6

Figure 7 Average fractions of sulfate, ammonium, nitrate and organics with PMF-resolved LVOOA, SVOOA, COA, and HOA in different clusters from the 5-cluster solution at 300 m arrival height (AGL = above ground level). The color lines in the upper panel show the average trajectories and the corresponding color lines in the lower panel show the vertical profiles of those trajectories.



1

2 Figure 8 Average size distributions of sulfate (SO₄), organics (Org), organics with m/z 44 (Org44) and
 3 organics with m/z 57 (Org57), and diurnal patterns of the degree of oxygenation of organics, as
 4 represented by average carbon oxidation state (\overline{OS}_C) and O:C ratio in different clusters from the 5-
 5 cluster solution at 300 m arrival height. For size distributions, the color lines indicate the average size
 6 distributions while the grey areas indicate the IQRs. For diurnal patterns of \overline{OS}_C and O:C, legends are
 7 the same as those in Figure 5 (on top of right panels).