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Diurnal and day-to-day characteristics of ambient particle mass size distributions from HR-ToF-AMS measurements at an urban site and a suburban site in Hong Kong

Berto P. Lee[1], Hao Wang[2], and Chak K. Chan[1,2*]

[1]School of Energy and Environment, City University of Hong Kong, Hong Kong, China

[2]Division of Environment, Hong Kong University of Science and Technology, Hong Kong, China

Correspondence to: Chak K. Chan (chak.k.chan@cityu.edu.hk)

Abstract. Mass concentration based particle size distributions measured by a high-resolution aerosol mass spectrometer were systematically analyzed to assess long and short-term temporal characteristics of ambient particle size distributions sampled at a typical urban environment close to emission sources and a suburban coastal site representing a regional and local pollution receptor location in Hong Kong. Measured distributions were bimodal and deconvoluted into submodes which were analyzed for day-to-day variations and diurnal variations. Traffic and cooking emissions at the urban site contributed substantially to particle mass in both modes, while notable decreases in mass median diameters were limited to the morning rush hour. Inorganic particle components displayed varying diurnal behavior, including nocturnal nitrate formation and daytime photochemical formation evident in both modes. Suburban particle size distributions exhibited notable seasonal disparities with differing influence of local formation, particularly in spring and summer, and transport which dominated in the fall season leading to notably higher sulfate and organic accumulation mode particle concentrations. Variations in particle mixing state were evaluated by comparison of inter-species mass median diameter trends at both measurement sites. Internal mixing was prevalent in the accumulation mode in spring at the urban site, while greater frequency of time periods with external mixing of particle populations comprising different fractions of organic constituents was observed in summer. At the suburban site, sulfate and nitrate in the accumulation mode more frequently exhibited differing particle size distributions in all seasons signifying a greater extent of external mixing. At the urban site, periods of greater submicron inorganic mass concentrations were more likely to be caused by increases in both Aitken and accumulation mode particle mass in summer, while at the suburban receptor location organic and nitrate Aitken mode particle mass contributed more regularly to higher total submicron species mass concentrations in most seasons (spring, summer and winter).

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1. Introduction

Apart from mass and chemical composition, the size distribution of fine particles represents a vital physical property with important implications for human health and environmental effects of ambient aerosols [*Seinfeld and Pandis*, 2006]. Particle size relates directly to the aerodynamic properties which govern the penetration and deposition of particles in the airways and lungs [*Davidson et al.*, 2005] as well as the scattering and absorption of light which affect the radiative properties and hence ambient visibility [*Ahlquist and Charlson*, 1967; *Bohren and Huffman*, 1983; *Charlson et al.*, 1991; *Schwartz*, 1996; *Seinfeld and Pandis*, 2006]. Hygroscopic growth in response to changes in ambient humidity can alter particle light scattering properties (Seinfeld and Pandis, 2006;Köhler, 1936) and activation of condensation nuclei particles into cloud droplets depend on atmospheric conditions, chemical composition, mixing state as well as the size and morphology of particles (Abbatt et al., 2005;Kerminen et al., 2012;Meng et al., 2014;Westervelt et al., 2013).

Studies into the size distribution of ambient particulate matter in Hong Kong have been largely based on size-segregated filter samples (Yao et al., 2007b;Zheng et al., 2008;Zhuang et al., 1999;Huang et al., 2014;Bian et al., 2014) and measurements by electrostatic classifier instruments (Cheung et al., 2015;Yao et al., 2007a) and were hence either limited in size resolution (offline filter samples) or chemical resolution (total particle count by classification). The majority of measurements in Hong Kong were conducted in suburban environments. Inorganic ammonium and sulfate were mainly found in fine mode particles in condensation and droplet mode size ranges, while nitrate had strong coarse mode contributions (Zhuang et al., 1999). Seasonal differences were evident in solvent-extractable organics and trace metals which were mainly found in $PM_{0.5}$ particles in the wet season and winter whereas in fall a shift to larger particles (0.5–2.5 μm fraction) in fall indicated a possibly stronger influence of aged particle components in the transition period of the Asian monsoon (Zheng et al., 2008). Size distributions acquired by a fast mobility particle sizer at the suburban HKUST supersite were investigated more recently to study the formation and accumulation of ultrafine particles under different air flow regimes. Particle number concentration enhancements during the day were attributed to secondary formation, while evening and nighttime peaks were thought to be related to transport of aged aerosols from upwind locations. Nucleation mode particle peaks were often observed in fall and related to regional pollution influence (Cheung et al., 2015). New particle formation events at the same site occurred as single and two-stage growth processes with organics and sulfuric acid contributing mainly to first stage growth in the daytime while nighttime second stage growth was attributed to ammonium nitrate and organics. Particle size growth into the diameter range of cloud condensation nuclei (CCN) was typically only achieved with the second growth stage (Man et al., 2015).

Investigations into particle size distributions in urban areas of Hong Kong are even scarcer. Yao et al. (Yao et al., 2007a) studied the properties and behavior of particles in vehicle plumes and reported a competing process between ambient background particles and fresh soot particles in the condensation of gaseous precursors and a dependency on temperature with bimodal volume size distributions observed at lower ambient temperatures and unimodal distributions in the lower accumulation size range at higher ambient temperatures.

The Aerodyne aerosol mass spectrometer (Canagaratna et al., 2007) is widely used to determine the chemical composition of major organic and inorganic components of non-refractory submicron particulate matter (NR-PM_1). In contrast to most traditional aerosol sizing instruments, the AMS is capable of resolving main chemical constituents within size distributions through analysis of particle flight times and particle ensemble mass spectra [*Canagaratna et al.*, 2007; *Jayne et al.*, 2000; *Jimenez et al.*, 2003; *Rupakheti et al.*, 2005] and thus yields valuable additional information on differences in composition of submicron particles with the gross of particle mass in the Aitken mode range (D_p ~ 10-100nm) and the accumulation mode range (D_p ~ 100-1000nm) covered by the AMS. Despite the potentially different chemical and physical processes affecting species in different size regions within NR-PM_1, AMS particle size data from ambient measurements are rarely investigated in-depth. Thus, in this work we demonstrate a systematic approach to analyzing AMS species-segregated mass-based particle size distributions and present a detailed discussion of particle size data from HR-ToF-AMS measurements during two field campaigns in Hong Kong in both urban and suburban environments. We aim to evaluate characteristic recurrent changes in size distribution as well as longer term trends in different seasons by analyzing day-to-day variations and diurnal variations of size distributions of submicron organics, sulfate, and nitrate particle mass. Two contrasting sites were chosen representing a typical urban source environment (inner-city, roadside station) close to primary emission sources and a suburban location (coastal, HKUST supersite) which is largely a downwind receptor of varying amounts of local urban, regional and long-range transported pollutants (Li et al., 2015;Huang et al., 2014).

2. Methodology

2.1. Field campaigns

Sampling of ambient submicron non-refractory particulate matter (NR-PM_1) was carried out using an Aerodyne HR-ToF-AMS at the HKUST air quality supersite covering four seasons between May 2011 and February 2012 (spring: 2011-05, summer: 2011-09, fall: 2011-11&12, winter: 2012-02). The HKUST supersite is located on the campus of the Hong Kong University of Science and Technology (22°20'N, 114°16'E), on the east coast of Hong Kong in a suburban area with few primary emission sources in the immediate vicinity. Sampled air was drawn from the rooftop of a pump house building at an approximate height of 25m above ground level. For detailed descriptions of the experimental setup, operating conditions, data treatment, and overall species composition we refer the reader to previous publications (Lee et al., 2013;Li et al., 2015;Li et al., 2013). A further sampling campaign took place between spring 2013 (2013-03 to 2013-05) and summer 2013 (2013-05 to 2013-07) at an inner-city urban location in the densely populated and built-up Kowloon peninsula. Measurements were conducted next to the roadside air quality monitoring station (AQMS) operated by the Environmental Protection Department (EPD) of the HKSAR Government in the Mong Kok (MK) district on a pedestrian crossing at a major road junction. Sampled air was drawn from a height of 3m above ground level. A comprehensive analysis of trends in species concentration and composition identified in this urban campaign has been presented previously (Lee et al., 2015). In both campaigns, particles were sampled through a $PM_{2.5}$ cyclone at a flow rate of 16.67 L/min into a sampling port from which 0.08 L/min was drawn by the AMS and

the remainder drawn by co-sampling instruments and an auxiliary pump. Sample air for the AMS passed through a 1m long diffusion dryer (BMI, San Francisco CA, USA) filled with silica gel to remove bulk gas- and particle-phase water. Additional data from various collocated instruments including meteorological data (wind, temperature, relative humidity, solar irradiation), volatile organic compounds (VOCs) and standard trace gases such as NO_x, SO_2, and O_3 were available and details on employed instrument models and sampling methodologies are discussed in aforementioned studies (Lee et al., 2013, 2015;Li et al., 2015;Li et al., 2013).

2.2. Data acquisition and treatment

In both campaigns, mass concentration based size distributions in terms of vacuum-aerodynamic particle diameter (dM/$d$logD_{va}) were established by joint acquisition of particle time-of-flight (PToF) measurements and unit mass resolution mass spectra (V-mode) with alternation between modes every 20s for 30 cycles amounting to 5 min of total sampling time. High-resolution mass spectra were acquired for the following 5 min, and thus the overall raw data time resolution for each mode was equal to 10 min. The total particle mass measured in the PToF mode was normalized to the V-mode mass concentration of the same time step. Daily size distributions were generated by averaging over 24h periods (from 0:00 to 23:59). Hourly diurnal size distributions were reconstructed by grouping size distributions within the same hour of the day and establishing representative size distributions based on average, median, 25th and 75th percentile concentration values of each size bin (*referred to as size distribution sets hereinafter*).

At both sampling sites, the seasonally averaged AMS size distributions were bimodal (Lee et al., 2013, 2015;Li et al., 2015) with similar distributions having been observed in other AMS field studies in various parts of the world. (Zhang et al., 2014;Sun et al., 2011;Huang et al., 2011;Aiken et al., 2009;Zhang et al., 2005;Crippa et al., 2013;Docherty et al., 2011;Mohr et al., 2012). Multimodality of size distributions is typical for environments where different sources or formation processes of particles play a role and accordingly such distributions can also be represented as sums of discrete lognormal distributions of the respective constituting submodes (John, 2011).

The measured bimodal size distributions in this work were therefore deconvoluted by fitting two log-normal distributed modes, including one closer to the Aitken size range (*mode diameter ~100nm*) and one in the accumulation size range (*mode diameter ~500nm*), to evaluate differences in trends and formation or transformation processes in the two size regimes. An example of a size distribution fit and associated parameters is depicted in Figure D1 in the Supporting Material. Mode diameter (*i.e.* mass median diameter, MMD), curve width (*i.e.* geometric standard deviation, GSD) and curve area (*equivalent to particle mass concentration within the mode*) are sufficient parameters to completely describe a lognormal distribution and these key variables are used in the following analysis on trends in the fitted species-specific size distributions of organics, nitrate, and sulfate from both HR-AMS sampling campaigns in Hong Kong. Particle diameters are discussed in terms of vacuum-aerodynamic diameter, with detailed discussions on properties and relationships to other size metrics available elsewhere (DeCarlo et al., 2004;Slowik et al., 2004). Further details on PToF data acquisition and size distribution averaging can also be

found in the Supporting Material in Section A and B respectively. While the transmission efficiency of the AMS aerodynamic lens is known to fall off beyond ~1 µm of vacuum-aerodynamic diameter (Liu et al., 2007;Takegawa et al., 2009;Zhang et al., 2004;Bahreini et al., 2008) and may bias measured particle mass in the accumulation mode towards lower concentrations, resolved MMDs at either sampling location were generally well within the upper transmission limit and thus unlikely to have significant effect on the presented analysis.

3. Results and Discussion

3.1. Diurnal size distribution characteristics

Diurnal species variations are predominantly discussed in terms of total mass concentration up to the size cut of the sampling inlet or the instrumental capability, e.g. total species concentrations in NR-PM_1 for AMS-based studies. Utilizing AMS mass-based size distributions and their deconvolution provides complementary insights into the variations of different particle size submodes and their contributions to the overall species variation in NR-PM_1. As previously mentioned, we examined size distributions reconstructed from the average, median, 25th and 75th percentile of hourly grouped size distributions, analogous to commonly reported AMS species diurnal variations, with quantitative analysis focusing on concentrations from the median dataset.

3.2. Urban roadside NR-PM_1

The urban roadside measurements took place between March and July 2013 covering two seasons (Spring 2013: *March to mid-May 2013;* Summer 2013: *mid-May to July 2013*) at a location dominated by the influence of primary emission sources. Organics were the major particulate species in NR-PM_1 of which two-thirds were attributable to traffic and cooking sources. Anthropogenic gas-phase species, including various VOCs, NO_x, CO, and SO_2 were continuously abundant as well (Lee et al., 2015;Sun et al., 2016). Particle size distributions at the urban site exhibited discernible diurnal trends, with Figure 1 depicting the variations in (mass median) diameters of the lognormal fitted Aitken and accumulation modes, corresponding integrated peak areas representing the total mass accounted for by particles in each mode, the geometric standard deviation signifying the spread across particle sizes as well as the total submicron mass (NR-PM_1) diurnal variation for organics, sulfate, and nitrate based on AMS V-mode data. Individual trends are discussed species-wise in the following.

Organics

The diurnal variation of total Aitken and accumulation mode particle mass both largely followed the same trend as total submicron organic mass (lower panels in Figure 1 a,b) affirming that urban sources of organic particulate matter contributed substantially to PM mass across the covered size region. Mass concentrations in both modes were smallest during the the night (*0:00 to 6:00*) and highest during lunch and dinner (*12:00 to 14:00, 19:00 to 21:00*), when the influence of organic aerosol

from cooking (COA - cooking organic aerosol) and from traffic (HOA – hydrocarbon-like organic aerosol) were dominant (Lee et al., 2015). Trends in integrated mode particle mass and MMDs were similar across all size distribution sets (Figure D2 in the Supporting Material), confirming that they occurred persistently throughout the measurement period and making diurnal timescale processes the dominant factor in determining size characteristics of organic-containing particles at this urban roadside location.

Minimum Aitken mode particle mass concentrations (*median values*) amounted to 2.3 µg/m^3 in spring and 1.2 µg/m^3 in summer, accounting for 28-38% of total submicron particulate mass, and were typically reached between 03:00 and 04:00. These concentrations represent the estimated urban background mass of Aitken mode particles carried over from the daytime and not removed by gravitational settling, coagulation or sweep-out as well as contributions from nighttime activity such as residual traffic.

Organic concentrations increased notably between 6:00 and 9:00 during the morning rush hour with traffic-related constituents (*HOA – hydrocarbon-like organic aerosol*) accounting for the largest part (60% in spring, 40% in summer) of this increase (Table A1 in the Supporting Material). In the Aitken mode, particle mass concentrations rose by 1.6 µg m^{-3} (spring) and 0.8 µg m^{-3} (summer) in the same time period. Assuming direct proportionality between the contribution of HOA to total submicron organic mass increase and the increase of particle mass in each submode, 0.9 µg m^{-3} (spring) and 0.3 µg m^{-3} (summer) of particle mass were estimated as traffic-related organic components in the Aitken mode. Significant changes were also evident in the particle size metric (MMD), where a consistent decrease by 20-30% from about 170 nm (spring) or 160 nm (summer) to 130-140 nm (spring) or 120 nm (summer) was evident. This combined shift to smaller particle size and increase in total particle mass denotes a strong increase in the total number concentrations of particles in the Aitken mode range by at least a factor of 4-5 (assuming spherical particles and constant particle density) with significant additional contributions expected from elemental carbon particles and smaller Aitken mode and nucleation mode particles below the cut-off size (<50nm) of the AMS inlet lens.

Beyond 10:00, changes in submicron organic mass concentrations were dominated by variations in cooking-related organic aerosol (COA) components. During the main meal times (12:00 – 14:00 and 19:00 – 21:00) changes in organic submicron mass were almost entirely (>80%) caused by COA in both seasons (Table C1 in the Supporting Material) and daily maximum Aitken mode particle mass concentrations typically occur during these hours (5.5 – 6.2 µg m^{-3} in spring, 3.1 – 3.5 µg m^{-3} in summer) with higher concentrations during the dinner period. Analogous to HOA, considering proportionality between COA fractional contribution and submode particle mass increase, primary cooking emissions accounted for 1.7 - 1.8 µg m^{-3} of organic particle mass in the Aitken mode. Dinner in summer represents a notable exception, where the estimated cooking-related increase only amounted to 0.5 µg m^{-3}. This is mainly due to specific local meteorological and geographical features owing to a greater frequency of easterly surface winds in the warmer season and the geographical distribution of cooking sources predominantly to the east of the sampling site (Sun et al., 2016;Lee et al., 2015), which led to considerably elevated Aitken mode mass concentration throughout the day including the late afternoon period and a correspondingly smaller additional increase during the dinner time. The aforementioned effect is particularly evident in the diurnal trend of the Aitken

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mode particle mass fraction among total organic submicron mass (Figure 3b) which displayed a broad bell-shape during the day in summer with nominal increases of 9-10%, whereas in spring the variation follows a double peak behavior with nominal increases of 4-5% during the meal times which emphasize the more intermittent behavior of cooking-related particle contributions in spring. Cooking emissions had no conspicuous impact on particle size without notable trends in MMDs or the distribution width (GSDs) during the meal time periods (Figure 1a,b - *black lines in lower panels*).

In the accumulation mode, residual organic particle mass during the night hours (00:00 – 06:00) was 2.5 times larger in spring (5.5 µg m^{-3}) than in summer (2.0 µg m^{-3}). The mass concentration increase during the morning rush hour was larger in summer (ΔM=3.9 µg m^{-3}) than in spring (ΔM=3.0 µg m^{-3}), which was mainly caused by daytime increases of SOA components in summer (Lee et al., 2015), and consequently led to a lower fractional rush hour increase of traffic related organic constituents. Estimated particle mass contributions of traffic emissions in the accumulation mode amounted to 1.8 µg m^{-3} in spring and 1.6 µg m^{-3} in summer. In terms of particle size, the onset of the rush hour had little conspicuous effects on the accumulation mode without clear trends in MMDs in both seasons. In summer the shift to smaller MMDs was accompanied by a notable narrowing of the Aitken mode, whereas in spring Aitken mode distribution widths remained largely stable throughout the day (Figure 1a,b - *lower panels*).

Maximum accumulation mode particle concentrations during the meal hours reached 10.5 – 12.3 µg m^{-3} in spring and 6.0 – 7.4 µg m^{-3} in summer. Analogous to the Aitken mode, estimated cooking-related particle contributions in the accumulation mode amounted to 2.0 µg m^{-3} (spring) and 1.0 µg m^{-3} (summer) during lunch, and to 2.7 µg m^{-3} (spring) and 2.4 µg m^{-3} (summer) during dinner. Also, distribution widths (GSD) in the accumulation mode were not notably affected by cooking emissions. Seasonal differences were apparent in the mass median diameters of the accumulation mode. In spring, mode diameters remained largely constant (+/- 10nm) apart from a subtle peak during the morning rush hour, indicative of minor condensational growth of traffic-related primary organics or rapidly formed secondary species. In summer, a consistent increase in particle size by 20nm (~5%) during the daytime points to particle growth through secondary formation as a governing factor.

Aitken mode particles contributed larger fractions to the total increase in organic submicron particle mass during the rush hour and mealtimes in spring (33-56%) than in summer (16-38%). These differences were presumably due to seasonal meteorology and associated effects on the formation, accumulation, and dispersion of particles from primary emission sources, as source strengths and characteristics of road traffic and commercial cooking are unlikely to vary with seasons in the inner-city urban areas of Hong Kong. Ambient temperatures and solar irradiation differed substantially with 7°C higher average temperatures (*measured at MK*) and three times higher integrated daily solar irradiation (*measured at HKUST*) in summer compared to spring (Figure D6e,f in the Supporting Material). Lower overall ambient temperatures enhance condensation and nucleation of gas-phase emissions and shift the gas-to-particle partitioning equilibrium of semi-volatile constituents towards the particle-phase. We expect these volatility effects to be a main contributing factor, as sampling took place in direct vicinity of the emission source, i.e. next to the road and thus potential impacts of physical effects such as enhanced near-ground mixing and dispersion through thermally induced convection in summer are expected to be of minor influence. Considering the previously

discussed estimated traffic contributions during the rush hour, the seasonal difference in mass concentration was much more pronounced in the Aitken mode (-67%, 0.6 µg m^{-3}) than the accumulation mode (-12%, 0.2 µg m^{-3}), consistent with the expected stronger impact of reduced nucleation and condensation of more volatile exhaust components on fresher, smaller particles in the warmer season.

Comparing different size distribution sets (Figure D2 in the Supporting Material), the average concentration set in summer yielded notably larger resolved mass median diameters in both modes and greater Aitken mode mass compared to the median, 25^{th}, and 75^{th} percentile concentration sets. This indicates a strong influence of extreme values (i.e. time periods with both larger particle size and larger particle mass concentrations) and thus greater variability in size distributions in the warmer season caused by specific high and low concentration events such as photochemical episodes and precipitation, evident in the greater relative span of organic mass concentrations in summer (See Table A2 in the Supporting Material: ratio of 10th and 90th percentile to median concentration in NR-PM_1). In spring such events masked the diurnal processes to a lesser extent and with consequently greater consistency across different size distribution sets.

Sulfate

Although variations of total submicron sulfate mass concentrations with time of day were generally subtle, distinct trends were notable in MMDs and integrated mode mass concentrations in both Aitken and accumulation mode.

Generally, Aitken mode MMDs were 20% larger in spring (180nm) than in summer (150nm). While in spring fluctuations in Aitken mode MMDs were small throughout the day within a narrow range of +/- 10nm and without apparent regular features, the summertime diurnal variation exhibited a well-defined broad daytime peak with a shift to ~15nm larger particle diameters. A matching trend was evident in the accumulation mode where MMDs increased by ~20nm in summer. Conversely, in spring, a conspicuous nighttime peak in accumulation mode MMDs was observed in the low traffic period between 01:00 and 07:00 which tracked closely with the diurnal variation of O_3 which peaked in the same period with the reduction of the NO_x titration effects at low nighttime traffic volumes. While particulate sulfate production during the day can be achieved through both homogeneous gas-phase oxidation of SO_2 by the OH radical as well as heterogeneous oxidation of SO_2 by dissolved H_2O_2 or O_3 (Seinfeld and Pandis, 2006), nighttime production is limited to the non-photochemical heterogeneous pathway. The apparent increase in accumulation mode particle size was also associated with an increase of integrated submode particle mass by ~0.7 µg/m^3 and thus points to heterogeneous SO_2 oxidation by residual ozone in the cooler and more humid spring season as a local source of particulate sulfate. In the warmer and drier summer season, no corresponding trend was apparent in either accumulation mode MMD or integrated mode concentration. The small magnitude of additionally produced sulfate (< 1 µg/m^3) in spring renders the nighttime production a minor source of particulate sulfate however and affirms that the bulk of the accumulation mode sulfate burden at the urban roadside still originated from regional scale processes in both seasons. In summer, both modes exhibited notable increases in particle mass concentration levels during the daylight hours by ~80% in the Aitken mode and by ~35% in the accumulation mode compared to their respective nighttime “baseline“ concentrations. Integrated over the whole day, the additional sulfate burden above this baseline amounted to 0.4 µg/m^3 and 6 µg/m^3 and thereby

accounted for 34% and 11% of the total daily Aitken and accumulation mode particle mass respectively. This represents a rough estimation of possible local photochemical contributions to the Aitken and accumulation size mode in summer at the urban roadside, excluding possible physical effects, e.g. vertical mixing and advection or dilution laterally through the street canyon. Enhancements in particle mass by photochemical contributions were more pronounced in the Aitken mode, with the median fraction of Aitken mode particle mass among total AMS-measured particle mass (Figure 3) increasing substantially from its nighttime minimum at 4% to a maximum of 7% in the late afternoon in summer, while in spring the fraction remained almost constant at 6% throughout the day.

Considering different size distribution sets (Figure D2 in the Supporting Material), the 75th percentile size distributions and the average size distributions displayed notable increases in Aitken mode particle mass during the nighttime by 20-50% in spring. There was no corresponding trend in the accumulation mode, where changes in integrated mass concentration remained consistently <10%. The skewing of the average and higher percentile data indicates the influence of time periods with significantly elevated nighttime concentrations, likely related to events and atmospheric conditions conducive to the extensive formation of Aitken mode sulfate particles. The accumulation mode showed no notable changes in the average and 75th percentile data during the same time period, thus precluding physical processes such as transport or lowering of the planetary boundary layer as likely influential factors for these observations.

Nitrate

Particulate nitrate mass concentrations in the Aitken and accumulation mode exhibited similar diurnal variations in spring with lower daytime concentrations due to evaporation and higher nighttime concentrations where secondary formation and gas-to-particle partitioning prevailed. Analogous to sulfate, the Aitken mode MMDs for nitrate showed little change (<5%) throughout the day in both seasons. Aitken mode mass concentrations, however, exhibited a twofold increase over the dinner hours accounting for approximately 0.9 µg/m^3 (~16%) of additional particle nitrate mass per day. This may be due to the much higher abundance of small particles from cooking emissions providing additional surface area to facilitate gas-to-particle partitioning of nitrate. Increased signal intensities of oxygenated organic nitrogen ions (see Figure D7 in the Supporting Material) have also been observed during dinner suggesting that organic nitrate or other oxygenated nitrogen-containing organic species that produce nitrate fragments (Farmer et al., 2010) may too have contributed to this observed concentration peak. Accumulation mode nitrate mass increased by almost one-third in the low traffic period (01:00 – 07:00) compared to earlier night concentration levels (22:00 – 00:00) accompanied by a slight increase in MMD by ~10nm in spring. This signifies notable nighttime nitrate production through possibly nitric acid formation by ozone chemistry via the nitrate radical route under influence of organic components or formation of N_2O_5 and subsequent hydrolysis during the night. Local nighttime nitrate production effectively contributed ~3 µg/m^3 (~10%) to the total daily accumulation mode nitrate burden in spring.

Summertime nitrate production in Hong Kong has been mainly attributed to photochemical activity based on previous measurements of inorganic gas- and particle-phase nitrogen species at the suburban HKUST site (Griffith et al., 2015). Particulate nitrate mass concentrations at the urban Mong Kok site likewise exhibited clear daytime peaks, similar to sulfate

albeit at smaller magnitude with total integrated increases of ~0.3 µg/m^3 and ~0.8 µg/m^3 particulate nitrate per day in the Aitken and accumulation mode respectively. In the Aitken mode, particle mass remained elevated in the early night hours (~19:00 – 22:00), which was likely due to the previously mentioned cooking-related nitrate enhancement analogous to spring. The distribution of total submicron nitrate shifted slightly in favor of the Aitken mode in summer with ~18% of total submicron nitrate found in the Aitken mode compared to ~14% in spring.

Comparing different size distribution sets (Figure D2 in the Supporting Material), the average size distributions displayed notable disparity compared to the remaining sets in both seasons. In summer, integrated particle mass concentrations and MMDs from the average set exhibited consistently larger values than those from the 25th percentile, 75th percentile, and median sets indicating significant influence of time periods with high nitrate concentrations and larger nitrate-containing particles. In spring, the average data exhibited a decrease in MMD in the Aitken mode from night to day, implying prolonged periods of significantly smaller daytime Aitken mode particles.

3.2.1. Suburban coastal NR-PM$_1$

The suburban HKUST site as a downwind receptor of urban and regional pollution was generally dominated by sulfate and oxygenated secondary organic aerosol (SOA) components and much lower fractions of primary organic constituents, which combined typically made up less than a quarter of total organics (Li et al., 2015).

Organics

There were significant seasonal differences with larger fractions (Figure 3a) and concentrations (Figure 4c) of Aitken mode mass in total organic submicron particle mass in spring and summer compared to fall and winter, indicating greater influence of closer-ranged formation sources in the warmer season. Springtime integrated Aitken mode mass concentrations (~0.8 µg/m^3) were twice as high as those in winter (~0.4 µg/m^3). In the accumulation mode highest particle mass loadings were observed in fall (5 µg/m^3) and lowest loadings in spring (3 µg/m^3) following the frequency pattern of continental air mass influence (Figure D8 in the Supporting Material) in each season indicating continental transport of particulate mass or gas-phase precursors. Lowest mass concentrations in the Aitken mode typically occured in the night hours (00:00 – 05:00) in a range of 0.3 – 0.5 µg/m^3 in spring, summer, and winter, while in fall mass loadings of 0.7 - 0.8 µg/m^3 were reached. Diurnal changes were least pronounced in winter with largely constant integrated Aitken mode particle concentrations. In the remaining seasons, varying degrees of daytime changes were apparent with a general increase around 06:00, likely owing to citybound commuter traffic from surrounding roads to the west of the sampling site at 1-2km of lateral distance. This also led to a modest increase in particle polydispersity with a discernible widening of the Aitken mode size distributions (*black solid line, lowest panels in* Figure 2). Daily maxima in spring, summer and fall were reached in the early evening (~21:00) with marked differences in absolute mass concentrations depending on the respective season, from a summer time low of 0.8 µg/m^3 to a fall season high

of 1.4 μg/m^3. Mass median diameters in the Aitken mode were smaller in the night hours and displayed subtle increments during the day in the range of 10-20 nm reaching their maximum typically in the late afternoon, with the exception of the fall season when mass median diameters displayed very little variation with time of day.

Total particle mass in the accumulation mode in spring and summer reached minima during the night hours (2 μg/m^3) and maxima (3 μg/m^3) around noon, remaining stable in the daylight hours thereafter. MMDs increased notably from 440nm at night to 510nm during the day in spring, while in summer a morning rise by ~30nm from 530nm to 560nm was obvious between 06:00 and 10:00 and coincided with the morning rush hour and the associated early morning peak of NO_x and an otherwise stable mode diameter of 530nm for the rest of the day. In fall, the increase in accumulation mode organic mass occurred much earlier, starting in the dark hours at 04:00, with a corresponding trend also evident for nitrate but absent for sulfate, indicating a common source of these organic and nitrate enriched particles. Nighttime MMDs for organics were generally larger (540nm) and decreased to a minimum of 510nm in the early afternoon accompanied by a slight widening of the distribution. In winter, mass concentrations decreased appreciably in the early morning hours and started to increase only beyond 10:00. In the colder seasons (fall, winter), a similar concentration pattern was also observed for gas-phase SO_2 which is considered as a largely regional pollutant with few distinct local sources (Yuan et al., 2013), indicating that changes in boundary layer and mixing with regional background were likely the more dominant processes in winter.

Sulfate

Aitken mode sulfate mass concentrations peaked in the afternoon from spring throughout fall with maximum concentrations reached progressively later in the afternoon (14:00 in spring; 16:00 in fall). Nominal concentrations were highest in spring and summer (0.5-0.6 μg/m^3), slightly lower in fall (0.4 μg/m^3) and reached the lowest levels in winter (0.1 μg/m^3). In addition to the afternoon peak, a conspicuous early morning peak of similar magnitude was evident in spring between 02:00 and 06:00. A greater proportion of southerly winds was evident in said time period compared to the overall seasonal wind frequency distribution (Figure D9a in the Supporting Material) and may indicate transport of sulfate from marine sources in the southern parts of Hong Kong. Diurnal variations in MMDs and GSDs were generally small and without obvious regular trends. Nominal mass median diameters were significantly lower in winter (~170nm) compared to spring and fall (~190nm) and summer (~210nm). Trends in accumulation mode particle mass were more pronounced. In spring, a shallow concentration valley during the late evening and night hours (20:00 to 03:00) with minimum concentrations of 5 μg/m^3 was apparent, while daytime concentrations stayed largely invariant at 6 μg/m^3. The MMDs followed a similar variation with a minimum mode diameter around 550nm in the early hours of the day and slightly larger daytime MMDs around 570nm. Nominal concentrations were larger in summer with a nighttime valley concentration of 7 μg/m^3 and a well-pronounced broad day peak with a maximum of 9.5 μg/m^3 in the early afternoon (14:00-15:00). A prior additional morning peak occurred between 04:00 and 10:00 with particle mass concentrations reaching 8.5 μg/m^3 related to a consistent north-easterly morning wind pattern (Figure D9b in the Supporting Material) and likely associated with transport from north-easterly coastal regions or nighttime fisheries related maritime traffic. The diurnal trend in mass median diameter was similar to that in spring with a night minimum of 570nm and

day maximum of 590nm. In fall, accumulation mode characteristics showed no significant diurnal variability, with a largely stable integrated particle mass of 6 µg/m^3 and only subtle MMD changes (585nm at night; 575nm during the day). In winter, two concentration dips with reductions by ~0.5 µg/m^3 between 06:00 and 10:00 and between 18:00 and 22:00 were evident, while MMDs increased during the day between 10:00 and 15:00 from 520nm, peaking at a size of 540nm.

Nitrate

Nitrate particle mass in the Aitken mode was generally small from spring throughout fall amounting to 0.01 - 0.06 µg/m^3. Winter time concentrations were larger in a range of 0.06 - 0.08 µg/m^3 during the day and 0.10 - 0.12 µg/m^3 in the late evening hours. The latter evening peak centered around 21:00 was evident in most seasons (except spring) and accounted for 12-23% (0.1-0.25 µg/m^3) of total daily Aitken mode nitrate mass burden. Similar to the urban roadside location, these nighttime nitrate peaks coincided with the peak period of organic cooking aerosol concentrations (Figure D10 in the Supporting Material), which were however significantly smaller at the suburban measurement site and mainly attributed to the operation of an on-campus student canteen (Li et al., 2015). Trends in mass median diameters varied between seasons with no discernible trend in winter, a subtle decreasing trend with time of day in spring and broad daytime diameter increases in summer and fall. Solar irradiation in these two seasons was comparatively high (Figure D6b,c in the Supporting Material) indicating that photochemical nitrate production in the Aitken mode may have led to this observed growth in particle size.

Integrated particle mass concentrations in the accumulation mode only exhibited subtle variations from spring throughout fall, with essentially constant diurnal concentrations in spring, a subtle daytime peak in summer which accounted for ~ 15% of total daily accumulation mode nitrate (corresponding to 0.7 µg/m^3) and a conspicuous morning peak between 04:00 and 10:00 in fall accounting for ~ 5% of total daily accumulation mode nitrate (corresponding to 0.5 µg/m^3). Clearer seasonal differences were evident in the trends of MMDs. In spring, MMDs decreased appreciably over the late evening hours (21:00-0:00) with a concurrent widening of the size distribution (increase in GSD). In summer, accumulation mode diameters decreased during the day by ~40nm with a similar trend in accumulation mode organics. Winter time MMDs exhibited a more complex pattern with larger mode diameters in the early hours (04:00 – 10:00) and during the noon-time, and a late-afternoon dip leading to larger spread of intra-day mode diameters ranging from 510nm to 570nm.

In comparison to the urban roadside measurements, diurnal particle size characteristics and mass concentrations in the Aitken and accumulation mode were much more variable for all investigated species at the suburban HKUST site, indicating that longer time scale processes and irregular events (transport patterns, local meteorology) were probably more important in governing particle size distribution characteristics than diurnal processes.

3.3. Day-to-day size distributions

To evaluate the evolution of particle size distributions within seasons, average species-specific size distributions were generated by averaging raw distributions over 24h periods (between 0:00 and 23:59). There was clear long-term variability in

both resolved Aitken and accumulation mode MMDs and integrated submode particle mass concentrations for all species (Figure D11 in the Supporting Material) and overall seasonal differences which have been briefly addressed in the discussion of the diurnal size distribution variations between seasons. Figure 4 depicts the overall average values for all daily fitted MMDs and integrated particle mass concentrations in both the Aitken and accumulation mode at the suburban HKUST and urban MK sites.

3.3.1. Seasonal trends

For the MK roadside station, particle mode diameters were generally larger in spring than in summer for all three investigated species, but with clear differences in the magnitude of changes among individual species. In the Aitken mode, organics and sulfate displayed a moderate decrease in mode diameter by 7-8% each, while nitrate saw a more significant decrease by 25% from spring to summer. In contrast, accumulation mode MMDs for organics exhibited only a subtle decrease by 5% and more substantial decreases for sulfate and nitrate by 20-22% each. Total Aitken mode particle mass decreases varied strongly: -15% for organics, -36% for sulfate and -67% for nitrate. In the accumulation mode, organics and sulfate exhibited similar relative decreases by 40-46%, while nitrate particle mass reduced drastically by 85%.

At the suburban HKUST site, Aitken mode MMDs of nitrate and organics decreased with the progression of seasons from spring to winter with highest mode diameters observed in spring and summer and appreciable decreases in winter by -9% for nitrate and -25% for organics compared to the warmer seasons. Sulfate displayed a similar winter time decrease in MMD (-15%) and an increase of similar magnitude in the summer season (+13%) compared to spring and fall. Variations in sulfate and organic accumulation mode diameters were minor between spring and fall, while wintertime MMDs were 7-12% lower. Nitrate exhibited an overall higher variability in mass median diameters in the accumulation mode in spring (larger standard deviation) and with on average 10% lower MMDs compared to other seasons. In line with the reduction in Aitken mode MMDs in winter, the integrated Aitken mode particle mass decreased as well, by -16% for organics and almost -75% for sulfate, whereas nitrate contributions remained largely stable throughout the seasons. Organic accumulation mode particle mass was significantly higher in the fall and winter season by factors of 1.6 – 2. Diurnal variations in the degree of oxygenation were least pronounced in these seasons (Li et al., 2015) suggesting that influence of transport in autum and winter likely dominated over local formation, thus excerting greater effects on particle mass in the larger size mode. Particulate nitrate concentrations were generally low in the accumulation mode from spring through fall, but increased sharply in winter by factors of 3 – 4. Sulfate accumulation mode mass concentrations remained more stable but saw significant summer time enhancements by ~30% likely due to photochemical activity which also led to high concentrations of Ox and a higher degree of oxygenation of organic aerosol among the four seasons (Li et al., 2015).

Large particles contribute more to particle volume and hence particle mass. Correspondingly, the total submicron concentration of a given species is typically governed by changes in the accumulation mode particle mass and accordingly observed correlation values between integrated accumulation mode particle mass and individual NR-PM_1 species mass concentrations

were generally high (R_{pr}>0.90) at both measurement sites (Figure D12 in the Supporting Material). This applied to both measurement sites regardless of the season. Aitken mode trends were less akin. At the urban roadside station, neither sulfate nor nitrate particle mass in the Aitken mode notably correlated with the respective total submicron species mass concentration in spring (all R_{pr}≤0.20), whereas in summer correlations were more significant with R_{pr}=0.51 for sulfate and R_{pr}=0.80 for nitrate. This signifies that periods of greater species mass concentrations were more likely to be caused by increases in both Aitken and accumulation mode particle mass indicating that particle formation and growth affecting smaller particles was more likely to occur in the warmer season. For organics, Aitken mode particle mass and submicron species mass correlated only weakly (R_{pr} = 0.26 in spring and R_{pr} = 0.38 in summer), i.e. each organic particle submode was governed by largely different dominant souces or formation processes in both seasons at the roadside.

At the suburban background site, Aitken mode particle mass for sulfate showed little correlation with total submicron sulfate concentration (R_{pr}≤0.10) with the exception of the spring season (R_{pr}=0.36) where more frequent wet and foggy conditions may have faciliated sulfate formation in both size modes. For organics and nitrate significantly larger correlation cofficients of submode particle mass to total species concentration ($0.5 \leq R_{pr} \leq 0.7$) were observed in most seasons (spring, summer, winter) indicating significant influence of local or regional formation processes on organic and nitrate Aitken mode particulate mass at the suburban receptor location. In the fall season, much weaker correlations ($0.2 \leq R_{pr} \leq 0.4$) were likely caused by the dominance of continental air mass influence (Figure S8c in the Supporting Material) and greater influence of aged accumulation mode particles on total submicron nitrate mass concentrations.

3.3.2. Inferred changes in mixing state

Shifts in mixing state of ambient particles can be inferred from the inter-species analysis of mass median diameters. Close nominal agreement (i.e. diameter ratios close to 1) infer that particles containing different species were similar in size which thus most likely represents a largely internally mixed particle population, while the spread of data (correlation coefficient) indicates the temporal homogeneity or divergence of resolved mode diameters. A hypothetically perfectly internally mixed particle population over the whole sampling period would, therefore, yield MMD ratios and Pearson's R values of 1 between species, while larger or smaller values are indicative of a greater frequency of heterogeneous (i.e. more externally mixed) particle populations (Figure 5).

At the urban Mong Kok site, changes in accumulation mode mass median diameters for nitrate and sulfate followed similar trends (R_{pr} = 0.88-0.89) and with diameter ratios close to 1 (0.94–0.95) Similarly, fitted accumulation mode diameters of organic constituents predominantly followed that of sulfate in spring nominally (diameter ratio 0.88) and temporally (R_{pr} = 0.80). The nominal agreement of organic and sulfate accumulation mode diameters persisted (diameter ratio 1.03) overall in summer, however, there was significantly more temporal divergence (R_{pr} = 0.65) indicating a greater frequency of time periods with external mixing of particle populations comprising different fractions of organic constituents.

External mixing is more prevalent for freshly formed smaller particles which have typically undergone less condensational growth and coagulation. Indeed, the correlation coefficients of both nitrate and organic Aitken mode MMDs with respect to sulfate were notably lower (0.50 and 0.62) indicating frequent periods of particle populations with different species prevailing in different size regions within the Aitken mode. Sulfate and nitrate were still more likely to occur internally mixed in the Aitken mode in spring with similar diameters (nitrate to sulfate MMD ratio = 1.00), while organic Aitken mode MMDs were consistently lower, indicating greater fractions of organic dominated particles towards the lower end and more inorganic dominated particles towards the upper end of the fitted Aitken mode. In summer, both nitrate and organic MMDs tended to be lower than those of sulfate (diameter ratios of 0.79 – 0.83) but similar to each other, thus implying a shift to externally mixed populations of more nitrate and organic enhanced and internally mixed smaller Aitken mode particles and sulfate dominated larger Aitken mode particles.

At the suburban HKUST site, accumulation mode MMDs of both nitrate and organics were generally quite similar to those of sulfate with diameter ratios of 0.88 – 1.06. Compared to the urban site, correlation coefficients of nitrate and sulfate were consistently lower (0.54 – 0.67) indicating a much greater frequency of time periods where sulfate and nitrate dominated particles in the accumulation exhibited significantly different particle size distributions. In winter, organic MMDs were consistently lower than those of sulfate and nitrate indicating a greater proportion of externally mixed particle populations with organics enriched particles in the lower accumulation size range and inorganic dominated particles in the larger accumulation size range. The least variability in particle size was observed in the summer season where MMDs in both Aitken and accumulation mode displayed variations in relatively narrow ranges between 200-250nm and 500-700nm, whereas in the remaining seasons time periods with particle populations of lower MMD were more frequent, extending to MMDs as low as 100nm in the Aitken mode and 300nm in the accumulation mode. In the Aitken mode, mass median diameters overall were quite similar across species, with diameter ratios of organic and nitrate distributions to those of sulfate in the range of 0.87 – 1.06, indicating that they generally covered a similar size range. The temporal agreement was highly variable with correlation coefficients (R_{pr}) spanning from 0.21 to 0.75 indicating that Aitken mode particle populations at the suburban site were generally more diverse and likely influenced by a greater range of particle formation and growth mechanisms compared to the urban Mong Kok site.

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4. Conclusion

A detailed analysis of AMS mass-based particle size distributions of sulfate, nitrate, and organics in submicron particulate matter measured at two contrasting locations in Hong Kong during two field campaigns has been undertaken. Deconvolution of size distributions into Aitken and accumulation submodes was accomplished by log-normal peak fitting and trends in particle size (mass median diameters), dispersity (geometric standard deviation) and overall particle mass (integrated mode area) were discussed on a diurnal time scale and on a daily basis to evaluate longer-term changes in size distribution characteristics. At the urban roadside location, clear diurnal influences of primary particle and gas-phase species were evident affecting both inorganic and organic component size distributions. Traffic and cooking contributed an estimated 0.3 – 0.9 μg m^{-3} and 0.5 – 1.8 μg m^{-3} of organic component particle mass in the Aitken mode, and 1.6 - 1.8 μg m^{-3} and 1.0 – 2.7 μg m^{-3} respectively in the accumulation mode with concentrations level varying with seasons. Notable changes in Aitken mode mass median diameters of organics were limited to the morning rush hour. Daytime particle concentration maxima of sulfate and nitrate in summer indicated substantial influence of photochemical processes, which also led to increments in mass median diameters in the accumulation mode thus inferring associated particle growth. Nocturnal nitrate formation was apparent in the accumulation mode in spring concurring with the nighttime peak of ozone at the roadside, while in the Aitken mode nitrate particle concentrations were significantly elevated during the dinner hours. Organics-related size distributions were mostly governed by intra-day changes at the urban site with very similar trends across different size distribution sets (i.e. concentration regimes), while disparities in diurnal variations among different size distribution sets were evident for nitrate and sulfate, particularly affecting the average sets, indicating stronger influence of irregular external factors which were not associated with diurnal time scale processes.

Suburban particle size distributions exhibited variable diurnal characteristics, suggesting that irregular processes such as transport and seasonal meteorological conditions were the more dominant processes influencing particle size characteristics. Aitken mode particle mass of organics was significantly larger in spring and summer indicating greater influence of more local formation sources in the warm season. In the accumulation mode, organic particle mass concentrations were highest in fall and lowest in spring, following the frequency pattern of continental air mass influence. For sulfate, Aitken mode mass concentrations mass concentrations peaked in the afternoon from spring throughout fall with highest nominal concentrations in spring and summer and lowest levels in winter, while accumulation mode particle mass was highest in summer and fall and lowest in winter, similar to the trend observed among organic constituents.

Nitrate particle mass in the Aitken mode was generally small in most seasons (0.01 - 0.06 μg m^{-3}), except winter where daytime concentrations reached ~0.1 μg m^{-3}. In both modes, changes in mass median diameters varied temporally and in magnitude with seasons, indicating a stronger influence of specific metereological conditions on the properties of nitrate-containing particles at the surburban site. At the urban site, periods of greater inorganic species mass concentrations were more likely to be caused by increases in both Aitken and accumulation mode particle mass in summer, indicating that particle formation and growth affecting smaller particles was more likely to occur in the warmer season. At the suburban receptor location, significant

correlation of submode particle mass to total species concentration ($0.5 \leq Rpr \leq 0.7$) was observed for organics and nitrate in most seasons (spring, summer, winter) suggesting notable influence of local or regional formation processes on organic and nitrate Aitken mode particulate mass. Variations in particle mixing state were examined by evaluation of inter-species mass median diameter trends at both measurement sites. In the accumulation mode at the urban site, internal mixing appeared to be prevalent in spring, while greater frequency of time periods with external mixing of particle populations comprising different fractions of organic constituents was observed in summer. External mixing was predominant in the Aitken mode at the urban location in both seasons. At the suburban site, sulfate and nitrate in the accumulation mode more frequently exhibited differing particle size distributions in all seasons signifying a greater extent of external mixing. In winter, external mixing of more organics enriched particles in the lower accumulation size range was evident.

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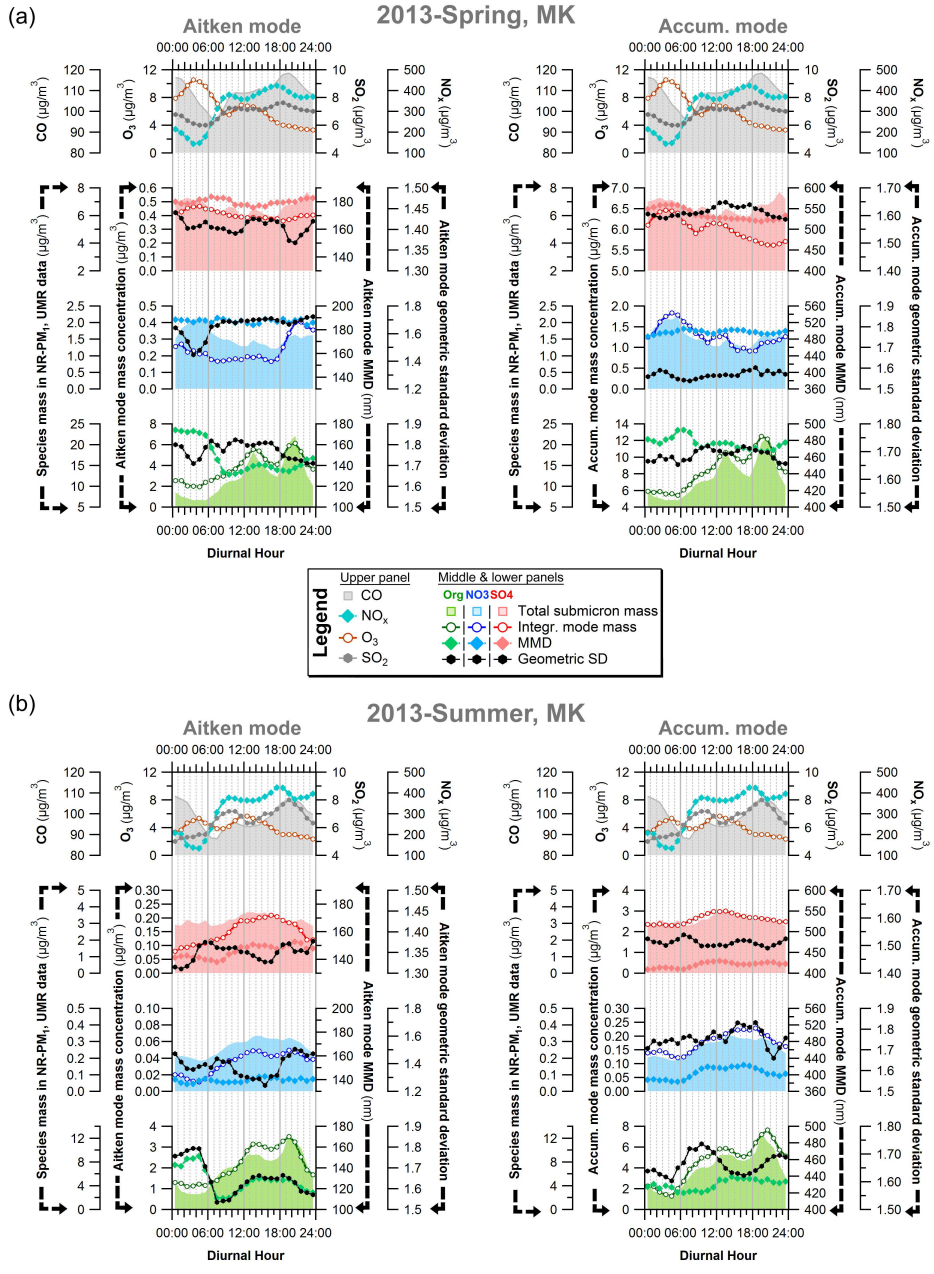

Figure 1. Mode diameter (mass median diameter - MMD, *light colored line and solid marker*), integrated mode mass concentration (*dark colored line and opaque marker*) and width (geometric standard deviation, *black line and black marker*) of the Aitken mode and accumulation mode from diurnal peak fits bimodal of size distributions at the urban Mong Kok site and V-mode AMS species concentrations (*shaded background*) for organics, nitrate and sulfate (*bottom to top*) in (a) Spring 2013 and (b) Summer 2013; The top panel depicts the diurnal variations of relevant gas-phase pollutants (O_3, CO, NO_x, SO_2) measured at the adjacent Mong Kok Air Quality Monitoring Site (MK AQMS); identical plots over each mode

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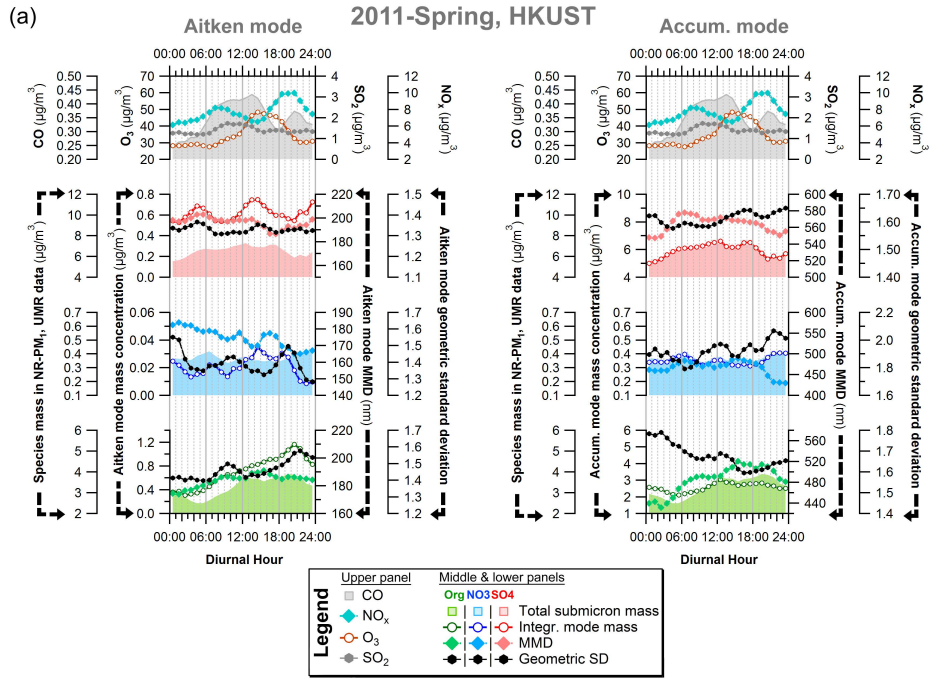

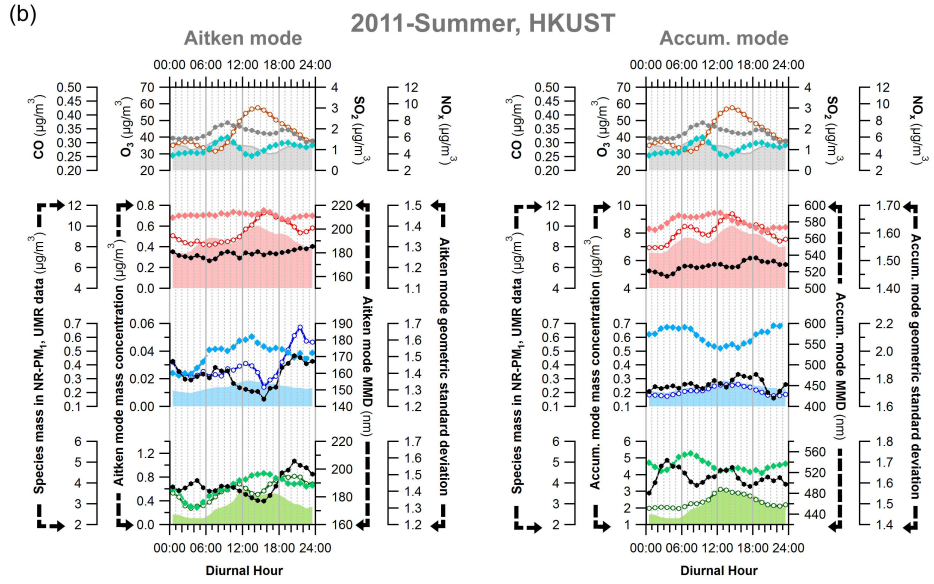

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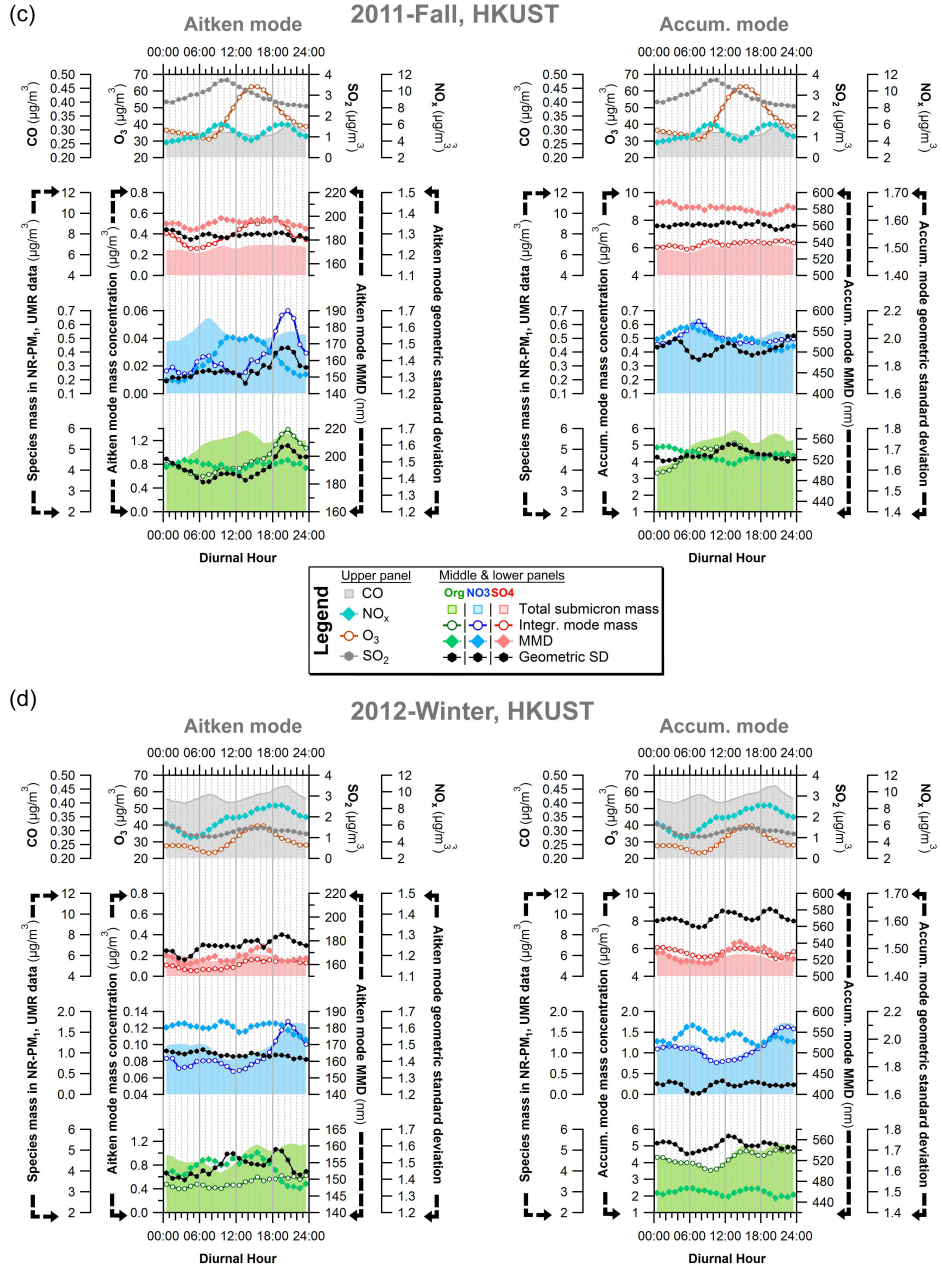

Figure 2. Mode diameter (mass median diameter - MMD, *light colored line and solid marker*), integrated mode mass concentration (*dark colored line and opaque marker*) and width (geometric standard deviation, *black line and black marker*) of the Aitken mode and accumulation mode from bimodal peak fits of diurnal size distributions at the suburban HKUST supersite and V-mode AMS species concentrations (*shaded background*) for organics, nitrate and sulfate (*bottom to top*) in (a) spring, (b) summer, (c) fall and (d) winter in 2011-2012; the top panel depicts the diurnal variations of relevant gas-phase pollutants (O_3, CO, NO_x, SO_2) measured at the same site, identical plots over each mode

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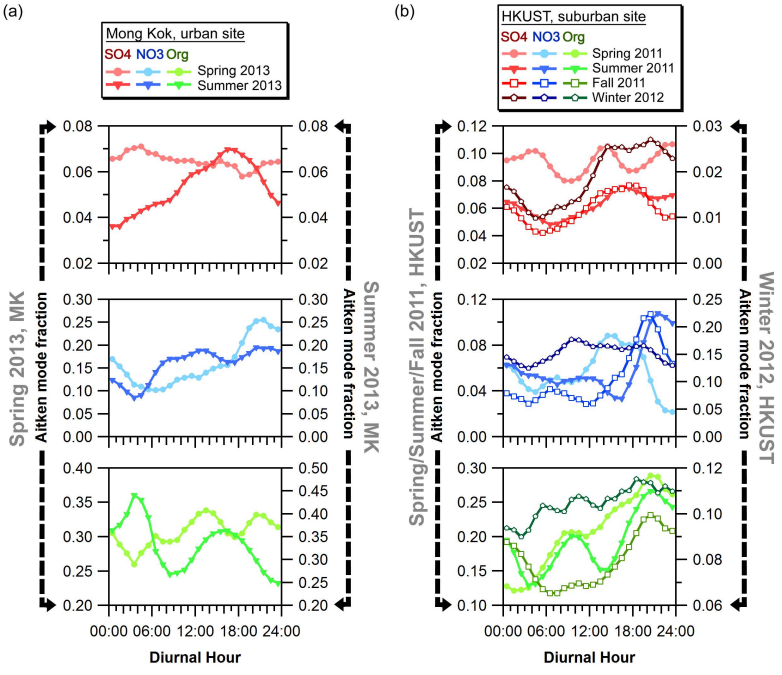

Figure 3. Diurnal variation of the fraction of Aitken mode particle mass among total submicron species mass for organics (*bottom*), nitrate (*middle*) and sulfate (*top*) at the (a) urban Mong Kong site, and (b) suburban HKUST supersite in different seasons; *based on median concentrations, seasons denoted by marker color and type of marker symbol*

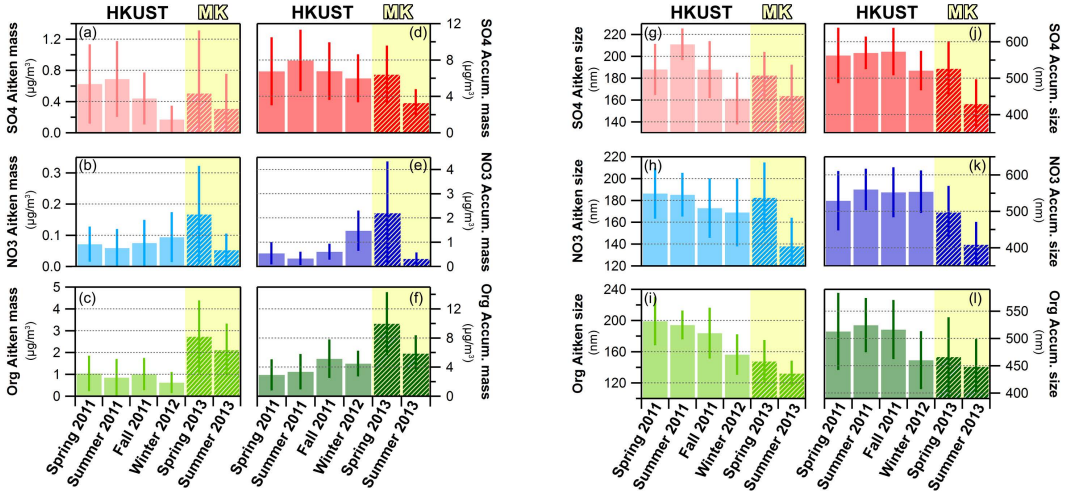

Figure 4. Average and standard deviation of daily fit values of Aitken and accumulation mode particle mass and mass median diameters at the suburban HKUST site (*solid bars*) and urban MK site (*hashed bars*). The integrated particle mass is depicted in (a), (b), (c) for the Aitken mode, and in (d), (e), (f) for the accumulation mode for sulfate, nitrate, and organics respectively. The mass median diameter is depicted in (g), (h), (i) for the Aitken mode and in (j), (k), (l) for the accumulation mode for sulfate, nitrate and organics respectively.

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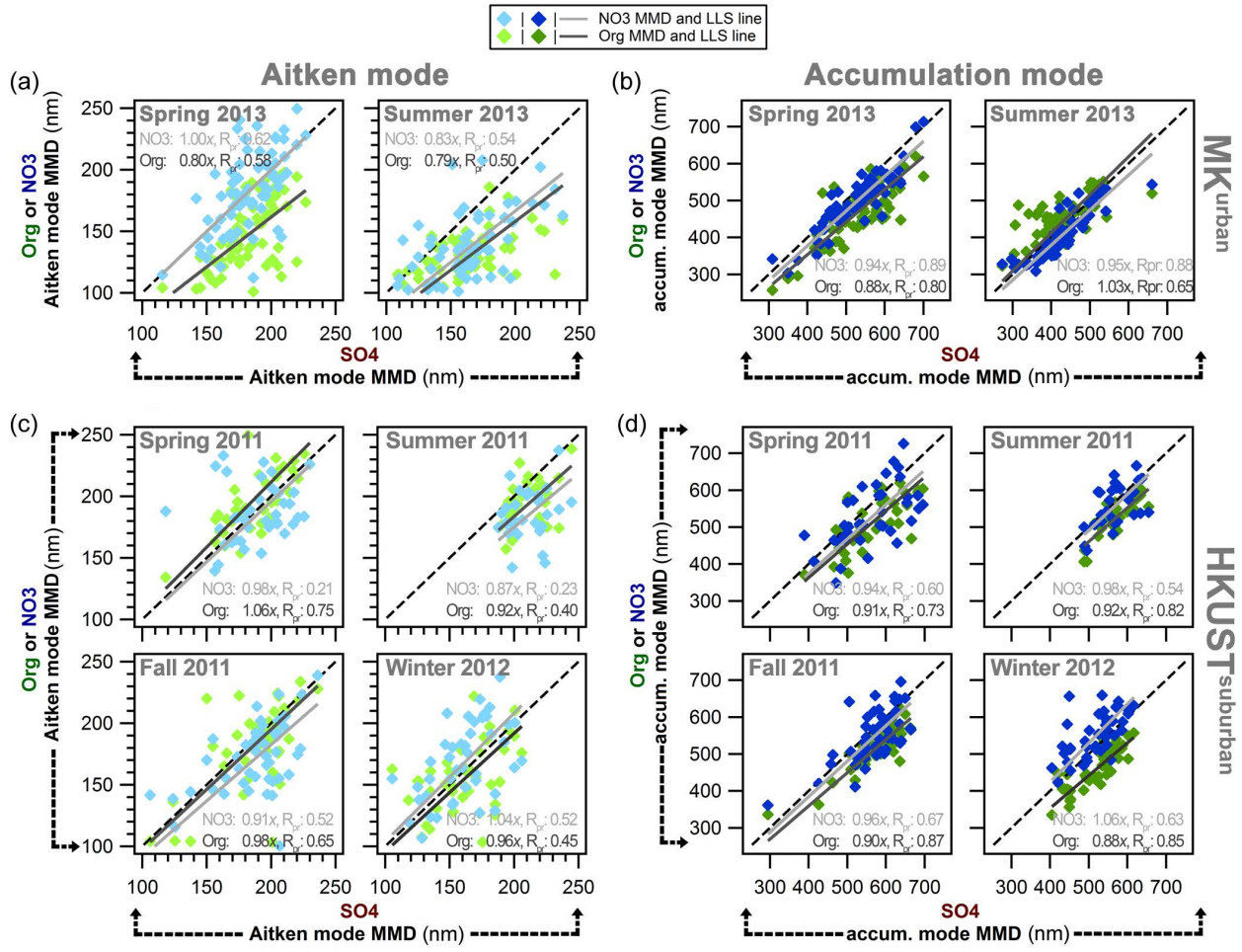

Figure 5. Scatter plots of fitted mass median diameters of organics and nitrate vs. Sulfate for the (a) Aitken mode and (b) accumulation mode at the urban Mong Kok site, and (c) Aitken mode and (d) accumulation mode at the HKUST suburban site