**Water-Soluble Organic Carbon and Oxalate in Aerosols at a Coastal Urban Site in
China: Size Distribution Characteristics, Sources and Formation Mechanisms**

Xiao-Feng Huang ^a, Jian Zhen Yu ^{a,*}, Ling-Yan He ^b, Zibing Yuan ^a

^a Atmospheric, Marine and Coastal Environment Program and Department of Chemistry,

Hong Kong University of Science & Technology,

Clear Water Bay, Kowloon, Hong Kong, China

^b Shenzhen Graduate School, Peking University, Shenzhen, China

*Corresponding author

Phone: 852-2358-7389, Fax: 852-2358-1594, Email: chjianyu@ust.hk

Revision Submitted to

Journal of Geophysical Research

17 June 2006

Abstract:

Water-soluble organic compounds in aerosol contribute a significant fraction to organic aerosol mass and influence interactions of aerosols with water in the atmosphere. Despite their importance, the sources and formation mechanisms of these compounds are not well understood. In this work, we measured the size distributions of water-soluble organic carbon (WSOC) and its most abundant single component, oxalate, in the urban area of Shenzhen, a coastal metropolitan city in southern China. In the cloud condensation nuclei size range, organic compounds were found to constitute a significant fraction (roughly one-half) of the total water-soluble substance mass. The positive matrix factorization (PMF) model was used to resolve the bulk mass size distributions into condensation, droplet, and coarse modes, with their respective modal peak at 0.4 μm , 1.0 μm , and 5.5 μm . Both WSOC and oxalate had a dominant droplet mode, a minor condensation mode, and a minor coarse mode. Approximately one-half of WSOC and two-thirds of oxalate mass was in the droplet mode. The sources and formation mechanisms of oxalate and WSOC were inferred in reference to the well-understood size distribution characteristics of inorganic species (Ca^{2+} , Na^+ , K^+ , and SO_4^{2-}), in conjunction with source identification and contribution estimation by PMF. We found that the droplet mode oxalate was mostly produced from in-cloud aqueous-phase reactions. Among significant sources contributing to the total WSOC were biomass burning, in-cloud processing, soil dust particles, and aged sea salt particles. The first two sources were the major contributors to the droplet WSOC while the latter two were responsible for the coarse mode WSOC. The droplet mode WSOC correlated well with K^+ and sulfate, consistent with the source estimates by PMF. Future work on WSOC is suggested to be directed at characterizing the biomass burning aerosols and elucidating the molecular formation pathways in the aqueous phase.

1. Introduction

Water-soluble organic compounds constitute a substantial fraction of carbonaceous aerosols, typically accounting for 20-80% of particulate organic matter on a carbon mass basis [Saxena and Hildemann, 1996; Zappoli et al., 1999; Krivácsy et al., 2001; Mader et al., 30 2004]. Due to their affinity with water, water-soluble organic compounds play an important role in aerosol-cloud interactions [Novakov and Penner, 1993; Matsumoto et al., 1997; Facchini et al., 1999], wet scavenging of aerosols, and formation of haze [Facchini et al., 2000; Watson, 2002]. Despite their atmospheric abundance and significance, the sources and formation mechanisms of water-soluble organic aerosols are not well understood.

35 Water-soluble organic aerosols can either be directly emitted from sources or be formed in the atmosphere. For example, levoglucosan, a water-soluble monosaccharide anhydride, has long been established as a tracer for biomass burning [Simoneit, 2002]; dicarboxylic acids, a group of known water-soluble aerosol constituents, are present in aerosols emitted from vehicular exhausts [Kawamura and Kaplan, 1987] and biomass burning [Narukawa et al., 1999]. On the other hand, dicarboxylic acids are known products of atmospheric 40 oxidation of many common volatile organic compounds (VOCs) (e.g., aromatic hydrocarbons, cyclohexane) [Kleindienst et al., 1999; Kalberer et al., 2000]. In general, secondary organic aerosol (SOA) constituents are water-soluble since the oxidation reactions leading to their formation impart polar functional groups (e.g., hydroxyl, carbonyl, and carboxyl) to the SOA 45 compounds. Two possible formation mechanisms can be suggested for the secondary water-soluble organic aerosols: homogeneous photooxidation from VOC precursors and heterogeneous oxidation in the presence of clouds/fog. The homogeneous formation pathways have been demonstrated in numerous smog chamber experiments that simulated atmospheric oxidation [Seinfeld and Pandis, 1998 and references therein]. More recently, an 50 increasing number of studies have demonstrated that formation of SOA in cloud/fog droplets is plausible [Blando and Turpin, 2000; Yao et al., 2002; 2003; Warneck, 2003; Crahan et al., 2004; Yu et al., 2005].

Size distributions of aerosol components provide important information about their sources, formation and growth mechanisms [Hinds, 1999]. The typical modes in the mass size distributions of ambient aerosols include nuclei condensation, accumulation, and coarse modes [Whitby, 1978]. Each mode is associated with a specific size range, source, and formation mechanism. Coarse particles are attributed to sea salts or particles generated through abrasion mechanisms (e.g., dust from the wind-driven erosion of soils or released plant fragments). Among fine particles, those arising from condensation and coagulation processes have size distribution peaks at near 0.3 μm in diameter, at which the accumulation of materials by condensation and coagulation is most efficient [Warneck, 2000]; particles arising from in-cloud processing followed by cloud/fog evaporation peak at 0.7 μm [Meng and Seinfeld, 1994; Kerminen and Wexler, 1995]. Primary particles emitted from high-temperature combustion sources appear in the condensation mode as a result of coagulation and vapor condensation after emission [Ondov and Wexler, 1998; Seinfeld and Pandis, 1998].

Most measurements of water-soluble organic carbon (WSOC) were made on bulk aerosol samples (e.g., total suspended particulates, particulate matter less than 10 μm or 2.5 μm). Size distribution measurements have been scarce. To our knowledge, only three papers have reported WSOC size distributions in ambient aerosols [Matsumoto et al., 1998; Li et al., 2000; Yu et al., 2004]. The WSOC size distribution measurements by Matsumoto et al. [1998] were made in a remote marine atmosphere (the Ogasawara Islands in the northwest Pacific Ocean); those by Li et al. [2000] at a remote continental site (the Tibetan Plateau in western China), and those by Yu et al. [2004] at a coastal location (Hong Kong in southern China).

In this study, we measured size distributions of WSOC and the most abundant WSOC species, oxalate, in the range of 0.056-18 μm in Shenzhen, a coastal city in southern China. We also measured the major inorganic compounds in the same sets of size-segregated aerosol samples as an aid in the interpretation of the size distribution characteristics of WSOC and

oxalate. The objective of this work was to investigate the characteristics, sources and
80 formation mechanisms of aerosol WSOC and oxalate in coastal urban environments.

2. Experimental methods

2.1 Aerosol sampling

Size-segregated aerosol samples were collected in Shenzhen (113.9°E, 22.6°N), a city of
85 six million people situated in the sub-tropics along the southeast coast of China. Shenzhen is
in the southeast corner of the Pearl River Delta (PRD) region, neighboring Hong Kong to the
south. The sampling site was on the roof top of a four-storey building on the campus of
Shenzhen Graduate School, Peking University in the western part of Shenzhen. Under the
influence of the East Asian Monsoon system, Shenzhen has two main seasons, a hot and
90 humid summer from mid-May to mid-September with prevailing southerly wind from the
Pacific Ocean and a cool and dry winter from mid-November to mid-March with prevailing
northerly/northeasterly continental wind. Spring and fall are two short transition seasons
[Chin, 1986]. Air pollutants are typically at higher concentrations in the winter than in the
summer, due to lower mixing height, less removal through wet deposition, and the input of
95 the polluted continental air mass in the winter [HKEPD, 2002].

A ten-stage microorifice uniform deposit impactor (MOUDI, MSP Corp., Shoreview,
MN) was used to collect size-segregated aerosol samples in the range of 0.056–18 μm at a
flow rate of 30 L/min. The collection substrates were 47-mm quartz fiber filters (Whatman,
Maidstone, England). Special quartz fiber spacers of 0.05 inch in thickness (MSP Corp.) were
100 used to compensate for the reduced space between two adjacent impact plates due to the use
of quartz fiber substrates. All the quartz fiber filters were baked at 550°C for 5 h before
sampling to reduce organic residues. Nine sets of samples were collected from July to August
2004 as summer samples, and twelve sets were collected from December 2004 to January
2005 as winter samples. Each sampling event lasted 48 or 72 h. A set of field blank samples

was also collected in each season by loading the sampler for the same sampling duration, but without pulling air through the sampler.

2.2 Chemical analysis

All filter samples were stored at -18°C in a refrigerator before analysis. One quarter of each quartz filter was used to determine the carbon content using a thermal/optical transmittance aerosol carbon analyzer (Sunset Laboratory, OR) [Birch and Cary, 1996]. The temperature program for the thermal analysis was the same as that in the NIOSH method for diesel soot [NIOSH, 1999]. Due to the non-uniform deposition nature of the MOUDI samples, laser correction could not work properly to set the organic carbon (OC) and elemental carbon (EC) split point [Chow et al., 1993]. For lack of a better alternative, we defined OC to be the fraction of carbon that evolved at or below 850°C in a helium atmosphere, and EC to be the fraction of carbon that evolved after 1% oxygen is introduced to the carrier gas during an analytical cycle.

The remaining three quarters of each quartz filter were extracted with 5 ml ultra-pure water ($18.0\text{ m}\Omega$) in an ultrasonic bath for 40 min and filtered with a $0.45\text{ }\mu\text{m}$ Teflon filter (Millipore, Billerica, MA). Part of the resulting solution was used for determination of total WSOC content using a TOC analyzer (Shimadzu, 5000A) [Yang et al., 2003]. The remaining solution was analyzed for ionic species using an ion chromatography (IC) system (DX500, Dionex, Sunnyvale, CA). The anions (i.e., Cl^{-} , NO_3^{-} , SO_4^{2-} , and oxalate) were determined using an AS-11 column and a gradient elution solution of NaOH. The cations (i.e., Na^{+} , NH_4^{+} , K^{+} , Mg^{2+} , and Ca^{2+}) were determined using a CS-12 column and an isocratic elution solution of methanesulfonic acid. The details of the IC methods were given in the paper by Yang et al. [2005].

3. Results and Discussion

3.1 WSOC concentrations

We have considered the sampling artifact issue when designing our sampling strategy. Before commencing field sampling, we investigated the adsorption artifact issue in the following experiment. A 47 mm quartz filter (in a filter holder) was placed upstream of the MOUDI inlet and 72 h sampling was carried out. In such a set-up, the air stream was stripped of particles before entering the MOUDI sampler and consequently only gases entered the MOUDI sampler. The amount of OC on each stage was found in the range of 0.021-0.044 $\mu\text{g}/\text{m}^3$, far lower than the amount of OC obtained in the absence of the pre-filter, which was in the range of 0.15-3.74 $\mu\text{g}/\text{m}^3$. This was an expected result with impactor samplers such as MOUDI. Unlike aerosol collection using filtration, in an impactor sampler, organic vapors have little chance to contact the substrate filters, therefore producing little OC by adsorption. Negative sampling artifact was possible through vaporization of the relatively more volatile aerosol components. However, the WSOC species were likely favorably retained by the polar quartz fibers considering the polar nature of WSOC species.

Figure 1 shows the mean size-segregated chemical compositions of aerosols in the summer and in the winter. In this work, we use 1.8 μm as the split diameter between fine and coarse particles. The reconstructed mass of the measured species had a bimodal distribution in the size range of 0.056–18 μm , with a larger mode for fine particles and a smaller mode for coarse particles. The mass concentrations of both fine and coarse aerosols in the winter were much higher than those in the summer, consistent with the expected seasonal characteristics of air pollutants in this region [HKEPD, 2002]. Total carbon (TC), the sum of organic and elemental carbon, had comparable abundance (40%) to sulfate (30%) in the summer samples while TC was more abundant in the winter samples (43% for TC versus 23% for sulfate). When other elements bound to carbon in organic compounds (e.g., O, N, and S) were considered, the contribution of TC to the total aerosol mass could be even larger. The mean WSOC concentrations were 2.2 $\mu\text{gC}/\text{m}^3$ (summer) and 4.5 $\mu\text{gC}/\text{m}^3$ (winter) in the fine

particles and $1.1 \mu\text{gC}/\text{m}^3$ (summer) and $1.9 \mu\text{gC}/\text{m}^3$ (winter) in the coarse particles. The WSOC concentrations were 70% higher in the winter than in the summer. WSOC constituted a substantial fraction of TC in each size bin, ranging from 21% in the $3.2\text{-}5.6 \mu\text{m}$ size bin to 64% in the $0.056\text{-}0.1 \mu\text{m}$ size bin (Figure 1). The percentage contribution of WSOC to TC had a small seasonal difference, with the winter aerosols containing a slightly higher WSOC fraction. The mean percentages of WSOC in TC were 30% (fine particles) and 24% (coarse particles) in the summer versus 34% (fine particles) and 28% (coarse particles) in the winter.

Table 1 compares the WSOC/TC values in fine particles measured in this work with those in source aerosols from vehicular emissions and biomass burning. Vehicular emissions are major primary carbonaceous aerosol sources in urban areas. There have been no direct source measurements of WSOC/TC in vehicular exhaust. A small number of measurements were made in environments where vehicular emissions are the dominant aerosol source, such as roadside locations [Ruellan and Cachier, 2001; Yu, 2002] and inside a roadway tunnel [Huang, 2006]. Roadside measurements in Hong Kong and in Paris reported WSOC/TC values in the range of 5-19% [Ruellan and Cachier, 2001; Yu, 2002]. The roadside measurements should be regarded as an upper limit for vehicular exhaust aerosols because of the influence of ambient air. The only tunnel measurement, made by our group in Guangzhou, China, reported a WSOC/TC value of 8% [Huang, 2006]. The low WSOC content in vehicular aerosols was consistent with their known hydrophobic characteristic [Weingartner et al., 1995, 1997]. The much higher percentages of WSOC in TC in our ambient aerosols indicated that vehicle emissions were not a significant source of ambient WSOC.

Unlike vehicular exhaust, biomass burning was reported to have a significant fraction of its TC attributable to WSOC. More than 40% of TC in biomass burning aerosols could be water-soluble [Novakov and Corrigan, 1996; Narukawa et al., 1999; Mayol-Bracero et al., 2002]. Biomass burning is common in the form of burning crop residue in China. Duan et al. [2004] estimated that biomass burning aerosols contributed 10-32% of particulate OC at an

urban site in Beijing using an OC/K⁺ ratio derived from regression analysis as an indicator of biomass burning aerosols. Fung et al. [2005] identified biomass burning to be the major cause for a severe air pollution episode in Hong Kong between December 28-30, 1999. As discussion in Section 3.5 shows, biomass burning could be a source for a considerable amount of ambient aerosol WSOC.

In relation to the hygroscopic property of water-soluble organic compounds, it is of interest to compare the relative abundance of WSOC and water-soluble inorganic compounds. Regardless of their chemical nature being organic or inorganic, the affinity of water-soluble compounds for water renders particles containing them to act as effective cloud condensation nuclei (CCN) [Cruz and Pandis, 1997; Corrigan and Novakov, 1999]. Figure 2 plots the mass percentage contribution of organic compounds to the total water-soluble substance mass in different size bins. The mass of water-soluble organic compounds was computed to be 1.6×WSOC. The multiplier of 1.6 was chosen following recommendations given by Turpin and Lim [2001]. The percentage ranged from 20% to 55%. The highest percentage contribution (43% in the summer samples and 55% in the winter samples) occurred in the smallest size bin, 0.056-0.1 μm. It is known that the number distribution of urban aerosols is dominated by particles of <0.1 μm, which accounts for most CCN particles [Seinfeld and Pandis, 1998]. Our results suggest that water-soluble organic and inorganic materials were of similar abundance among CCN particles in the urban atmosphere of Shenzhen. The role of organic compounds, therefore, cannot be overlooked in studying interactions of urban aerosols with water vapor.

3.2 Resolving size distribution modes

Ambient aerosols are known to typically consist of three modes, i.e., condensation, droplet, and coarse modes. The three modes partially overlap [Ondov and Wexler, 1998]. The overlapping of different aerosol modes is analogous to overlapping spectroscopic peaks

arising from a mixture of chemical compounds. Various factor analysis techniques have been
210 successfully used to resolve overlapping spectroscopic peaks [e.g., Malinowski, 1991;
Frenich et al., 2000]. We here use the positive matrix factorization (PMF) model [Paatero,
2000], a variant of factor analysis, on the MOUDI data to resolve the three aerosol modes.
PMF has recently been successfully applied to the resolution of different modes from bulk
aerosol size distributions [Kim et al., 2004; Zhou et al., 2005]. A total of 126 sets of mass size
215 distribution data were generated, with 21 sets of mass distribution data for each of the six
measured species (Ca^{2+} , Na^+ , K^+ , SO_4^{2-} , oxalate, and WSOC). PMF analysis was performed
on these 126 sets of data with the number of factors fixed at three.

Figure 3 shows the three modes as resolved by PMF, with mass medium aerodynamic
diameters (MMADs) at 0.4, 1.0, and 5.5 μm , corresponding to the condensation, droplet, and
220 coarse modes, respectively. The MMADs were determined by fitting the PMF-resolved size
distribution data with log-normal distribution functions using the DISTFIT software (TSI,
USA). The modal characteristics observed in this work were similar to those of the urban
aerosols in the Baltimore/Washington area [Ondov and Wexler, 1998]. The three modes
resolved by PMF explained 95% of the measured total mass in the size range of 0.056-18 μm .
225 The average measured size distribution curves and the PMF-resolved three-modal curves for
the major inorganic species, WSOC and oxalate are shown in Figure 4. The summer and the
winter data were plotted separately to demonstrate seasonal differences (Figure 4). The
seasonal mean concentrations of individual species in the three modes are tabulated in Table
2. The correlation matrix among the measured species in different size modes in the 21 sets of
230 samples is shown in Figure 5. The sources and formation mechanisms of oxalate and WSOC
are discussed below by utilizing their size distribution characteristics and in reference to
those of inorganic compounds.

3.3 Size distributions of inorganic ions

235 A good understanding has been acquired on the size distribution features of inorganic aerosol components (e.g., sulfate, nitrate, and sea salt) in relation to their sources and formation pathways as a result of decades of research. The concurrent measurements of the inorganic species in this work provide convenient references for understanding the sources and formation pathways of WSOC and oxalate. We describe below the size distribution characteristics of the inorganic species measured in this study.

The mass size distributions of both Ca^{2+} and Na^+ showed a predominant coarse mode (Figures 4a-4d). Such size distribution features were well explained by their respective sources. The coarse mode Na^+ was associated with sea salt particles. The coarse mode Ca^{2+} was derived from crustal CaCO_3 followed by its reactions with acidic gases (e.g., HNO_3 and SO_2) [Pakkanen et al., 1996; Zhuang et al., 1999]. This mechanism was consistent with the observation of a high correlation ($R^2 = 0.82$) between the coarse mode Ca^{2+} concentrations and the NO_3^- concentrations in coarse particles. The coarse mode Na^+ and Ca^{2+} have been frequently used as tracers for sea salt particles in coastal environments [Zhuang et al., 1999; Pakkanen et al., 1996; Kerminen et al., 1997] and suspended soil particles.

250 The concentrations of the coarse mode Ca^{2+} were found to be higher than the coarse mode Na^+ , with the mean $[\text{Ca}^{2+}]/[\text{Na}^+]$ equivalent concentration ratios of 2.9 in the summer and 3.4 in the winter. The high abundance of coarse mode Ca^{2+} prompted us to examine the equivalent concentration ratio of $[\text{Ca}^{2+}]/[\text{depleted Cl}^-]$ in the coarse mode, which would reflect the relative preference of reactions of acidic gases with soil particles versus sea salt particles. The equivalent concentration ratio of $[\text{Ca}^{2+}]/[\text{depleted Cl}^-]$ in the coarse mode was 9.1 in the summer samples and 7.8 in the winter samples, suggesting that the heterogeneous reactions between coarse particles and acidic gases mostly occurred on soil particles rather than sea salt particles. Zhuang et al [1999] also reached the same conclusion by examining $[\text{Ca}^{2+}]/[\text{Na}^+]$ ratios in connection with air mass trajectories. It is noted that in comparison with Ca^{2+} , a higher fraction of Na^+ resided in the droplet and condensation modes, especially in the

winter samples. In addition, a moderate correlation ($R^2 = 0.55$) was observed between the droplet mode Na^+ and K^+ , suggesting that biomass burning was likely an important source of Na^+ in fine particles. Ooki et al. [2002] also found that most Na^+ in fine particles in urban Tokyo could not be explained by sea salts and instead originated from anthropogenic sources.

265 K^+ showed a predominant droplet mode and a minor condensation and coarse mode (Figures 4e and 4f). K^+ is one of the most important and enriched nutrient elements of plants. As a result, biomass burning aerosols are enriched with K^+ and in turn K^+ in fine particles can serve as an effective tracer for biomass burning aerosols [Andreae, 1983; Yamasoe et al., 2000; Falkovich et al., 2005]. Fresh biomass burning particles mostly reside in a
270 condensation mode of 0.1-0.5 μm [Remer et al., 1998; Kleeman et al., 1999; Falkovich et al., 2005]. The abundant water-soluble components in biomass burning aerosols make biomass burning aerosols effective CCN [Novakov and Corrigan, 1996; Kaufman and Fraser, 1997]. Once the biomass burning particles are cloud activated, larger particles are subsequently produced due to addition of sulfate, following cloud evaporation. The K^+ in the condensation
275 mode and the droplet mode could be regarded fresh (or slightly aged) and cloud-processed biomass burning aerosols, respectively. The size distribution characteristics of K^+ observed in this work indicated that most of the total K^+ (~80%) at the measurement site was cloud-processed and the relatively fresh biomass burning aerosols only accounted for a small fraction (~10%) (Table 2). K^+ concentrations in both the droplet mode and the condensation
280 mode were 1.9 times higher in the winter samples than in the summer samples, consistent with the fact that biomass burning events were more frequent in the winter in this region. K^+ is also a constituent of soil and sea salt. The coarse mode K^+ was moderately correlated with the coarse mode Ca^{2+} ($R^2 = 0.50$) and the coarse mode Na^+ ($R^2 = 0.47$), confirming that the small coarse mode K^+ could be attributed to soil particles and sea salt particles.

285 Sulfate had a predominant droplet mode, a small condensation mode, and a small coarse mode (Figures 4g and 4h). The size distributions of sulfate have been the subject of numerous

studies in the past few decades because of sulfate's link with acid deposition. As a result, its formation pathways and size distribution characteristics are fairly well understood. The droplet mode SO_4^{2-} is formed through aqueous oxidation of SO_2 in clouds [Meng and Seinfeld 1994; Kerminen and Wexler 1995; Seinfeld and Pandis, 1998]. The condensation mode SO_4^{2-} arises from homogeneous gas-phase photochemical oxidation of SO_2 followed by gas-to-particle conversion [Hering and Friedlander, 1982; John et al., 1990; Seinfeld and Pandis, 1998]. Consistent with the photochemical origin, the condensation mode SO_4^{2-} had a lower concentration in the winter than in the summer (Table 2). The coarse mode SO_4^{2-} could be attributed to a combination of sea salt sulfate and heterogeneous reactions of SO_2 on sea salt and soil particles [Pakkanen et al., 1996; Zhuang et al., 1999].

3.4 Size distributions of oxalate

Oxalic acid is typically the most abundant dicarboxylic acid in atmospheric aerosols. Oxalic acid accounted for 2.9% (summer) and 1.7% (winter) of the fine mode WSOC on a carbon mass basis in our samples. Vehicle emissions [Kawamura and Kaplan, 1987] and biomass burning [Narukawa et al., 1999; Falkovich et al., 2005] are two known primary sources of ambient dicarboxylic acids. The ambient aerosol samples measured in this work had an oxalate/TC ratio in the range of 0.56-0.87%. In comparison, it was found that samples taken in a roadway tunnel in a nearby city, Guangzhou, had an oxalate/TC ratio of 0.13% [Huang, 2006]. The elevated oxalate/TC ratio in ambient samples discounted vehicular emissions as an important source for oxalate.

The size distributions of oxalate were dominated by the large droplet mode while the condensation mode and the coarse mode were both small (Figures 4i and 4j). The droplet mode oxalate and sulfate were found to be highly correlated ($R^2 = 0.92$), a strong indication of a common in-cloud formation mechanism. Good correlations between sulfate and oxalate in fine particles were also found in previous measurements made by our group in various

locations in the East Asian region [Yu et al., 2005]. Model calculations [Warneck, 2003] and aircraft measurements in clouds [Crahan et al., 2004] also supported in-cloud formation as a major formation pathway of aerosol oxalate. Oxalate showed approximately the same moderate correlation with K^+ ($R^2 = 0.75$) as that between sulfate and K^+ ($R^2 = 0.74$). The good correlation of the droplet oxalate with K^+ was likely a result of biomass burning particles acting as effective CCN to promote in-cloud sulfate and oxalate formation.

Biomass burning did not appear to be an important primary source for the condensation mode oxalate, as evidenced by its poor correlation with the condensation mode K^+ ($R^2 = 0.10$). The condensation mode oxalate was most likely photochemically produced in the gas phase followed by condensation onto existing particles in the condensation mode. Smog chamber experiments have established that oxalic acid is a photochemical oxidation product of certain VOCs (e.g., aromatic hydrocarbons and cyclohexene) [Kleindienst et al., 1999; Kalberer et al., 2000]. In our samples, the condensation mode oxalate had similar abundance in the winter and the summer samples (Table 2). The fact that oxalate in the summer samples was not significantly lower than that in the winter samples was in line with being of a photochemical origin after considering the local meteorological characteristics. A few factors would reduce the presence of oxalate in the aerosol phase in the summer relative to the winter. They include higher mixing heights, more removal by wet deposition, and less abundant volatile organic compound precursors in the summer months [Yuan et al., 2006]. It appears that higher production rates of the photochemical formation pathways in the summer compensated for the less favorable factors.

The coarse mode oxalate showed a moderate correlation with the coarse mode Ca^{2+} ($R^2 = 0.56$) and Na^+ ($R^2 = 0.37$), suggesting an association with soil particles and sea salt particles. Similar to the formation mechanism of the coarse mode NO_3^- , oxalic acid and other acidic species in the gas phase could be adsorbed onto alkaline coarse particles [Neusüss et al., 2000; Mochida et al., 2003]. A high correlation coefficient ($R^2 = 0.68$) was found between the

coarse mode NO_3^- and oxalate, supporting the suggestion of coarse oxalate arising from
340 adsorption by coarse particles. In addition, the inorganic cation equivalent concentration was
found to be 1.3 times the inorganic anion equivalent concentration in the coarse particles,
implying an important role of organic anions in the ion balance of the coarse particles.
Alternatively, it was also possible that gas-phase precursors of oxalic acid (e.g., glyoxylic
acid) underwent heterogeneous reactions on coarse particles to produce oxalate [Kerminen et
345 al., 1999; Mochida et al., 2003].

3.5 Size distributions of WSOC

In comparison with the ionic species, WSOC had a more even distribution among the
coarse, droplet, and condensation modes (Figures 4k and 4i), although the droplet mode still
350 contained the most WSOC materials. This was a logical result of aerosol WSOC being a
mixture of numerous constituents that may originate from different primary sources or be
formed via different atmospheric processes. The droplet mode WSOC accounted for 43% (in
summer) and 52% (in winter) of the total WSOC. The droplet mode WSOC had the highest
correlation with the droplet mode K^+ ($R^2 = 0.84$) rather than with the droplet mode sulfate (R^2
355 $= 0.51$), indicating that biomass burning was a significant source, and perhaps a dominant
source, for the droplet mode WSOC during our sampling periods.

Biomass burning could be excluded as an important source of the condensation mode
WSOC on the basis of its poor correlation with the condensation mode K^+ ($R^2 = 0.04$). The
much higher WSOC/ K^+ ratios in the condensation mode (~ 16) than in the droplet mode (~ 3)
360 also suggested the dominance of sources other than biomass burning aerosols for the
condensation mode WSOC. The known possible sources for the condensation mode WSOC
include primary combustion sources and secondary sources. The condensation mode WSOC
had a moderate correlation with the condensation mode Na^+ ($R^2 = 0.64$). The latter was
reported to be associated with combustion processes such as coal burning [Ondov et al., 1989]

365 (see discussion in section 3.3). On the other hand, the condensation mode has long been
recognized to host low vapor-pressure products of homogeneous gas-phase photochemical
oxidation of VOCs [Pandis et al., 1993; Seinfeld and Pandis, 1998]. Our measurements
showed a more abundant condensation mode WSOC in the winter samples than in the
summer samples (Table 2). This seemingly contradicted the expectation of a dominant
370 photochemical origin for this mode. One possible reason for such a contradiction is that the
oxygenated condensable products of gas-phase photochemical reactions are typically
semi-volatile and a higher fraction would partition into the aerosol phase in the winter due to
lower ambient temperatures [Yuan et al., 2006]. Higher contributions from
combustion-derived primary WSOC in the winter could also elevate the condensation mode
375 WSOC.

The coarse mode WSOC showed a moderate correlation with the coarse mode Ca^{2+} (R^2
= 0.36). Unlike the coarse mode oxalate, WSOC had a poor correlation (R^2 = 0.13) with the
coarse mode NO_3^- , implying that most coarse mode WSOC did not come from the gas phase.
Additional measurements such as chemical speciation of the coarse mode WSOC may be
380 necessary in order to gain further insights into the sources and formation mechanisms of
coarse mode WSOC.

We next used PMF to estimate contributions from the major WSOC sources. In the PMF
analysis for source identification and contribution estimation, each size-segregated sample
could be regarded as an independent sample. The concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} ,
385 Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , oxalate, OM, and EC in a total of 210 samples (21 sets $\times$ 10 stages)
were input into the PMF model. We found the profiles of seven sources to be satisfactory and
the derived explained variation (EV) values are shown in Figure 6. Source 1 was identified to
be aged sea salt, indicated by high loadings of Na^+ and Mg^{2+} and low loading of Cl^- ; Source 2

was fresh sea salt, evidenced by high EV loadings of Na^+ , Mg^{2+} , and Cl^- ; Source 3 was
390 associated with vehicular emissions, indicated by prominent EV loadings of OM and EC;
Source 4 was secondary sulfate, indicated by high loadings of NH_4^+ and SO_4^{2-} ; Source 5 was
linked to biomass burning aerosols, evidenced by a high K^+ EV value; Source 6 was soil dust,
suggested by the prominent contribution of Ca^{2+} to EV; Source 7 was secondary nitrate,
indicated by a high EV loading of nitrate. The seven sources explained 97% and 101% of
395 oxalate and WSOC in the size-segregated samples, respectively.

Figure 7a shows the contributions of individual identified sources to the sum of oxalate
and WSOC in all size bins. In-cloud processing, the source that gave rise to secondary sulfate
(i.e., source 4), was the most significant contributor to oxalate (summer: 61%; winter: 56%).
The next two most significant sources were heterogeneous reactions on sea salts (to form
400 aged sea salts, i.e., source 1) (summer: 20%; winter: 14%) and the gas-phase photochemical
reactions (like nitrate, i.e., source 7) (summer: 9%; winter: 17%). It could be inferred from
the co-existence of oxalate and sulfate in source 4 that in-cloud formation was the dominant
source of oxalate. The major source for WSOC was biomass burning (summer: 58%; winter:
76%). Soil particles (summer: 18%; winter: 11%), aged sea salt (summer: 16%; winter: 8%),
405 and in-cloud processing (summer: 8%; winter: 5%) were also important WSOC contributors.
The significant elevation in the contribution of biomass burning from summer to winter was
consistent with more frequent biomass burning in the drier winter months.

The droplet mode oxalate and WSOC were most prominent among the three modes. We
next examined the contributions of individual identified sources to oxalate and WSOC in the
410 size bin of 1.0-1.8 μm , the size bin in the droplet mode that has the least overlap with the

other two modes (Figure 4). The percentage contributions of individual identified sources are shown in Figure 7b. In-cloud processing had a dominant contribution of 79% in the summer and 73% in the winter to oxalate in the size bin of 1.0-1.8 μm . Biomass burning was the most significant contributor to WSOC in this size range in both the summer samples (68%) and the winter samples (87%). In-cloud processing was the next most important contributor to WSOC with a contribution of 14% in the summer samples and 8% in the winter samples.

In summary, the source contribution estimated by PMF results demonstrates that in-cloud processing was the most important source for oxalate and biomass burning was the most important source for WSOC during our sampling periods. This result was consistent with the size distribution characteristics.

4. Conclusions

Size-segregated aerosol sampling was conducted at an urban site in Shenzhen, China in the winter and in the summer of 2004. The results showed that WSOC constituted a substantial fraction of TC, accounting for 30% (summer) and 34% (winter) of TC in the fine particles. Among water-soluble aerosol materials, organic compounds were of comparable abundance to those of inorganic substances (i.e., the sum of the major inorganic ions). The mass fraction of organic compounds in the total water-soluble materials reached the highest value of 55% in the size bin of 0.056-0.1 μm , the size bin for CCN, indicating that the role of water-soluble organic compounds could not be overlooked when considering the interactions of aerosols with water vapor in ambient air. Both oxalate and WSOC had a dominant droplet mode, a minor condensation mode, and a minor coarse mode. The droplet mode was more prominent for oxalate than for WSOC in comparison with the other two modes. Approximately two-thirds of the oxalate mass was in the droplet mode while one-half of the

435 WSOC mass was in the droplet mode. The droplet mode oxalate was mostly produced from
in-cloud aqueous-phase reactions, the condensation mode oxalate had a photochemical origin,
and the coarse mode oxalate was likely a result of adsorption of gas-phase precursors on sea
salt particles. The droplet mode WSOC was found to have a strong correlation with K^+ and
in-cloud processing indicator SO_4^{2-} , suggesting biomass burning and in-cloud processing to
440 be important sources of WSOC in the droplet mode. This finding was verified by the source
estimates using PMF. Of the sources contributing to the total WSOC, soil dust and aged sea
salt particles were the other two significant sources, which mainly contributed to the coarse
mode WSOC.

This work has identified that biomass burning and in-cloud processes are important
445 sources for WSOC in fine particles in this region (Southern China). Future work should be
directed at characterizing biomass burning aerosols and elucidating the molecular formation
pathways in the aqueous phase.

Acknowledgements

450 This work was supported by the Research Grants Council of Hong Kong, China (605404) and
the National Basic Research Program from the Ministry of Science & Technology, China
(2005CB422204). X.-F. Huang and Z. B. Yuan acknowledge support from AMCE at HKUST.

References

- 455 Andreae, M. O. (1983), Soot carbon and excess fine potassium - Long range transport of
combustion-derived aerosols, *Science*, 220, 1148–1151.
- Birch, M. E., and R. A. Cary (1996), Black carbon-based method for monitoring occupational
exposures to particulate diesel exhaust, *Aerosol. Sci. Technol.*, 25, 221–241.
- Blando, J. D., and B. J. Turpin (2000), Secondary organic aerosol formation in cloud and fog droplets:
460 a literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623–1632.
- Chin, P. C. (1986) *Climate and weather. In A geography of Hong Kong*; Chiu, T. N., So, C. L., Eds.;
Oxford University Press, New York; pp. 69-85.

- Chow, J. C., J. G. Watson, and L.C. Pritchett (1993), The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. air quality studies, *Atmos. Environ.*, *27A*, 1185–1201.
- Corrigan, C. E., and T. Novakov (1999), Cloud condensation nucleus activity of organic compounds: a laboratory study, *Atmos. Environ.*, *33*, 2661–2668.
- Crahan, K. K., D. Hegg, D. S. Covert, and H. Jonsson (2004), An exploration of aqueous oxalic acid production in the coastal marine atmosphere, *Atmos. Environ.*, *38*, 3757–3764.
- Cruz, C. N., and S. N. Pandis (1997), A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Environ.*, *31*, 2205–2214.
- Duan, F., X. Liu, T. Yu, and H. Cachier (2004), Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing, *Atmos. Environ.*, *38*, 1275–1282.
- Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charison (1999), Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, *401*, 257–259.
- Facchini, M. C., S. Decesari, M. Mircea, S. Fuzzi, and G. Loglio (2000), Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition, *Atmos. Environ.*, *34*, 4853–4857.
- Falkovich, A. H., E. R. Graber, G. Schkolnik, Y. Rudich, W. Maenhaut, and P. Artaxo (2005), Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, *5*, 781–797.
- Frenich, A. G., M. M. Galera, J. L. M. Vidal, D. L. Massart, J. R. Torres-Lapasio, K. De Braekeleer, J.-H. Wang, and P. K. Hopke (2000), Resolution of multicomponent peaks by orthogonal projection approach, positive matrix factorization and alternating least squares, *Anal. Chim. Acta*, *411*, 145–155.
- Fung, J. C. H., A. K. H. Lau, J. S. L. Lam, and Z. Yuan (2005), Observational and modeling analysis of a severe air pollution episode in western Hong Kong, *J. Geophys. Res.*, *110*, D09105, doi:10.1029/2004JD005105.
- Hering, S. V., and S. K. Friedlander (1982), Origins of aerosol sulfur size distributions in the Los Angeles Basin, *Atmos. Environ.*, *16*, 2647–2656.
- Hinds, W. C. (1999), *Aerosol technology: Properties, behavior, and measurement of airborne particles*, 2nd ed., John Wiley & Sons, New York.
- HKEPD (Hong Kong Environmental Protection Department) (2002), *Air quality in Hong Kong 2002*.
- Huang, X.-F. (2006), *Formation mechanisms of water-soluble organic compounds in atmospheric aerosols*, PhD thesis, Hong Kong University of Science & Technology, Hong Kong.
- John, W., S. M. Wall, J. L. Ondo, and W. Winklmayr (1990), Modes in the size distributions of atmospheric inorganic aerosol, *Atmos. Environ.*, *24A*, 2349–2359.
- Kalberer, M., J. Yu, D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (2000), Aerosol formation in the

- cyclohexene-ozone system, *Environ. Sci. Technol.*, **34**, 4894–4901.
- Kaufman, Y. J., and R. S. Fraser (1997), Confirmation of smoke particles effect on clouds and climate forcing, *Science*, **277**, 1636–1639.
- Kawamura, K., and I. R. Kaplan (1987), Motor exhaust emission as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, **21**, 105–110.
- 505 Kerminen, V.-M., and A. S. Wexler (1995), Growth laws for atmospheric aerosol particles: An examination of the bimodality of the accumulation mode. *Atmos. Environ.*, **29**, 3263–3275.
- Kerminen, V.-M., K. Teinilä, R. Hillamo, and T. Mäkelä (1999), Size-segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, **33**, 2089–2100.
- Kerminen, V.-M., T. A. Pakkanen, and R. E. Hillamo (1997), Interactions between inorganic trace
- 510 gases and supermicrometer particles at a coastal site, *Atmos. Environ.*, **31**, 2753–2765.
- Kim, E., P. K. Hopke, T. V. Larson, and D. S. Covert (2004), Analysis of ambient particle size distributions using UNMIX and positive matrix factorization, *Environ. Sci. Technol.*, **38**, 202–209.
- Kleeman, M. J., J. J. Schauer, and G. R. Cass (1999), Fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes, *Environ. Sci. Technol.*, **33**, 3516–3523.
- 515 Kleindienst, T. E., D. F. Smith, W. Li, E. O. Edney, D. J. Driscoll, R. E. Speer, and W. S. Weathers (1999), Secondary organic aerosol formation from the oxidation of aromatic hydrocarbons in the presence of dry submicron ammonium sulfate aerosol, *Atmos. Environ.*, **33**, 3669–3681.
- Krivácsy, Z., A. Gelencsér, G. Kiss, E. Mészáros, Á. Molnár, A. Hoffer, T. Mészáros, Z. Sárvári, D. Temesi, B. Varga, U. Baltensperger, S. Nyeki, and E. Weingartner (2001), Study on the chemical
- 520 character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch, *J. Atmos. Chem.*, **39**, 235–259.
- Li, S. M., J. Tang, H. S. Xue, and D. Toom-Sauntry (2000), Size distribution and estimated optical properties of carbonate, water soluble organic carbon, and sulfate in aerosols at a remote high altitude site in Western China, *Geophys. Res. Lett.*, **27**, 1107–1110.
- 525 Mader, B. T., J. Z. Yu, J. H. Xu, Q. F. Li, W. S. Wu, R. C. Flagan, and J. H. Seinfeld (2004), Molecular composition of the water-soluble fraction of atmospheric carbonaceous aerosols collected during ACE-Asia, *J. Geophys. Res.*, **109**, D06206, doi:10.1029/2003JD004105.
- Malinowski, E. R. (1991), *Factor Analysis in Chemistry*, Wiley, New York.
- Matsumoto, K., H. Tanaka, I. Nagao, and Y. Ishizaka (1997), Contribution of particulate sulfate and
- 530 organic carbon to cloud condensation nuclei in the marine atmosphere, *Geophys. Res. Lett.*, **24**, 655–658.
- Matsumoto, K., I. Nagao, H. Tanaka, H. Miyaji, T. Iida, and Y. Ikebe (1998), Seasonal characteristics of organic and inorganic species and their size distributions in atmospheric aerosols over the northwest Pacific Ocean, *Atmos. Environ.*, **32**, 1931–1946.
- 535 Mayol-Bracero, O. L., P. Guyon, B. Graham, G. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, S. Fuzzi, and P. Artaxo (2002), Water-soluble organic compounds in biomass burning aerosols

over Amazonia 2. Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.* **107**, 8091, doi: 10.1029/2001JD000522.

Meng, Z., and J. H. Seinfeld (1994), On the source of the submicrometer droplet mode of urban and regional aerosols, *Aerosol Sci. Technol.*, **20**, 253–265.

Mochida, M., N. Umemoto, K. Kawamura, and M. Uematsu (2003), Bimodal size distribution of C-2-C-4 dicarboxylic acids in the marine aerosols, *Geophys. Res. Lett.*, **30**, 1672–1675.

Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, **26**, 3101–3104.

Neusüss, C., M. Pelzing, A. Plewka, and H. Herrmann (2000), A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: method and first results, *J. Geophys. Res.*, **105**, 4512–4527.

NIOSH (1999). Method 5040 Issue 3: Elemental carbon (diesel exhaust). In *NIOSH Manual of Analytical Methods*, 4th ed.; National Institute of Occupational Safety and Health: Cincinnati, OH.

Novakov, T., and C. E. Corrigan (1996), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, **23**, 2141–2144.

Novakov, T., and J. E. Penner (1993), Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, **365**, 823–826.

Ondov, J. M., and A. S. Wexler (1998), Where do particulate toxins reside? An improved paradigm for the structure and dynamics of the urban mid-Atlantic aerosol, *Environ. Sci. Technol.*, **32**, 2547–2555.

Ondov, J. M., C. E. Choquette, W. H. Zoller, G. E. Gordon, A. H. Biermann, and R. E. Heft (1989), Atmospheric behavior of trace elements on particles emitted from a coal-fired power plant, *Atmos. Environ.*, **23**, 2193–2204.

Ooki, A., M. Uematsu, K. Miura, and S. Nakae (2002), Sources of sodium in atmospheric fine particles, *Atmos. Environ.*, **36**, 4367–4374.

Paatero, P. (2000), *User's guide for positive matrix factorization programs PMF2 and PMF3*, University of Helsinki, Helsinki, Finland.

Pakkanen, T. A., V.-M. Kerminen, R. E. Hillamo, M. Makinen, T. Makela, and A. Virkkula (1996), Distribution of nitrate over sea-salt and soil derived particles—implications from a field study, *J. Atmos. Chem.*, **24**, 189–205.

Pandis, S. N., A. S. Wexler, and J. H. Seinfeld (1993), Secondary organic aerosol formation and transport. 2. Predicting the ambient secondary organic aerosol-size distribution. *Atmos. Environ.*, **27A**, 2403–2416.

Remer, L. A., Y. J. Kaufman, B. N. Holben, A. M. Thompson, and D. McNamara (1998), Biomass burning aerosol size distribution and modeled optical properties, *J. Geophys. Res.*, **103**, 31879–31891.

575 Ruellan, S., and H. Cachier (2001), Characterisation of fresh particulate vehicular exhausts near a
 Paris high flow road, *Atmos. Environ.*, *35*, 453–468.

Saxena, P., and L. M. Hildemann (1996), Water-soluble organics in atmospheric particles: a critical
 review of the literature and application of thermodynamics to identify candidate compounds, *J.*
Atmos. Chem., *24*, 57–109.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to*
 580 *Climate Change*, John Wiley, New York.

Simoneit, B. R. T. (2002), Biomass burning—a review of organic tracers for smoke from incomplete
 combustion, *Appl. Geochem.*, *17*, 129–162.

Turpin, B. J., and H.-J. Lim (2001), Species contributions to PM_{2.5} mass concentrations: Revisiting
 common assumptions for estimating organic mass, *Aerosol Sci. Technol.*, *35*, 602–610.

585 Warneck, P. (2000), *Chemistry of the natural atmosphere*, Academic Press, San Diego.

Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine
 atmosphere, *Atmos. Environ.*, *37*, 2423–2427.

Watson, J. G. (2002), Visibility: Science and regulation, *J. Air Waste Assoc. Manag.*, *52*, 628–713.

Weingartner, E., H. Burtscher, and U. Baltensperger (1997), Hygroscopic properties of carbon and
 590 diesel soot particles, *Atmos. Environ.*, *31*, 2311–2327.

Weingartner, E., U. Baltensperger, and H. Burtscher (1995), Growth and structural change of
 combustion aerosols at high relative humidity, *Environ. Sci. Technol.*, *29*, 2982–2986.

Whitby, K. T. (1978), The physical characteristics of sulfur aerosols, *Atmos. Environ.*, *12*, 135–159.

Yamasoe, M. A., P. Artaxo, A. H. Miguel, and A. G. Allen (2000), Chemical composition of aerosol
 595 particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and
 trace elements, *Atmos. Environ.*, *34*, 1641–1653.

Yang, H., J. Z. Yu, S. S. H. Ho, J. Xu, W.-S. Wu, C. H. Wan, X. Wang, X. Wang, and L. Wang (2005),
 The chemical composition of inorganic and carbonaceous materials in PM_{2.5} in Nanjing, China,
Atmos. Environ., *39*, 3735–3749.

600 Yang, H., Q. Li, and J. Z. Yu (2003), Comparison of two methods for the determination of
 water-soluble organic carbon in atmospheric particles, *Atmos. Environ.*, *37*, 865–870.

Yao, X., A. P. S. Lau, M. Fang, C. K. Chan, and M. Hu (2003), Size distributions and formation of
 ionic species in atmospheric particulate pollutants in Beijing, China: 2. Dicarboxylic acids, *Atmos.*
Environ., *37*, 3001–3007.

605 Yao, X., M. Fang, and C. K. Chan (2002), Size distributions and formation of dicarboxylic acids in
 atmospheric particles, *Atmos. Environ.*, *36*, 2099–2107.

Yu, J. Z. (2002), *Chemical characterization of water-soluble organic compounds in particulate matter*
in Hong Kong, report, Hong Kong Environmental Protection Department, Hong Kong.

Yu, J. Z., H. Yang, H. Zhang, and K. H. Lau (2004), Size distributions of water-soluble organic carbon
 610 in ambient aerosols and its size-resolved thermal characteristics, *Atmos. Environ.*, *38*, 1061–1071.

- Yu, J. Z., J. Xu, and H. Yang (2002), Charring characteristics of atmospheric organic particulate matter in thermal analysis, *Environ. Sci. Technol.*, *36*, 754–761.
- Yu, J. Z., X. F. Huang, J. Xu, and M. Hu (2005), When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, *Environ. Sci. Technol.*, *39*, 128–133.
- 615 Yuan, Z. B., J. Z. Yu, A. K. H. Lau, P. K. K. Louie, and J. C. H. Fung (2006), Application of positive matrix factorization in estimating aerosol secondary organic carbon in Hong Kong and its relationship with secondary sulfate, *Atmos. Chem. Phys.*, *6*, 25–34.
- Zappoli, S., A. Andracchio, S. Fuzzi, M. C. Facchini, A. Gelencsér, G. Kiss, Z. Krivácsy, Á. Molnár, E. Mészáros, H.-C. Hansson, K. Rosman, and Y. Zebühr (1999), Inorganic, organic, and
- 620 macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Environ.*, *33*, 2733–2743.
- Zhou, L., E. Kim, P. K. Hopke, C. Stanier, and S. N. Pandis (2005), Mining airborne particulate size distribution data by positive matrix factorization, *J. Geophys. Res.*, *110*, D07S19, doi:10.1029/2004JD004707.
- 625 Zhuang, H., C. K. Chan, M. Fang, and A. S. Wexler (1999), Formation of nitrate and non-sea-salt sulfate on coarse particles, *Atmos. Environ.*, *33*, 4223–4233.

Tables and Figures

Table 1. Comparison of WSOC/TC ratios in ambient and source fine particles.

Aerosol type	Size	Location	WSOC/TC	Reference
Urban aerosols	PM1.8	Shenzhen, China	30-34%	This work
Roadside	PM2.5	Paris, France	7-19%	Ruellan and Cachier, 2001
Roadside	PM2.5	Hong Kong, China	5-11%	Yu, 2002
Roadway tunnel	PM1.8	Guangzhou, China	8%	Huang, 2006
Under influence of pasture and forest fire	PM2.5	Rondônia, Brazil	41-74%	Mayol-Bracero et al., 2002
Under influence of forest fire	PM2.1	Indonesia	5-32%	Narukawa et al., 1999
Smoldering biomass combustion			>40%	Novakov and Corrigan, 1996

Table 2. Average concentrations of selected species ($\mu\text{g}/\text{m}^3$) in the three size modes.

	Coarse mode		Droplet mode		Condensation mode	
	Summer	Winter	Summer	Winter	Summer	Winter
Ca^{2+}	1.29 $\pm$ 0.51	1.75 $\pm$ 0.73	0.087 $\pm$ 0.053	0.096 $\pm$ 0.059	0.16 $\pm$ 0.04	0.10 $\pm$ 0.04
Na^+	0.51 $\pm$ 0.38	0.59 $\pm$ 0.45	0.10 $\pm$ 0.03	0.17 $\pm$ 0.09	0.11 $\pm$ 0.04	0.18 $\pm$ 0.06
K^+	0.074 $\pm$ 0.030	0.064 $\pm$ 0.041	0.45 $\pm$ 0.47	0.86 $\pm$ 0.36	0.060 $\pm$ 0.051	0.11 $\pm$ 0.06
SO_4^{2-}	0.41 $\pm$ 0.15	0.80 $\pm$ 0.33	6.87 $\pm$ 5.42	8.38 $\pm$ 4.64	1.29 $\pm$ 0.63	0.92 $\pm$ 0.42
Oxalate	0.047 $\pm$ 0.028	0.050 $\pm$ 0.023	0.22 $\pm$ 0.14	0.26 $\pm$ 0.15	0.060 $\pm$ 0.029	0.058 $\pm$ 0.023
WSOC	0.78 $\pm$ 0.17	1.09 $\pm$ 0.41	1.32 $\pm$ 1.35	3.00 $\pm$ 1.53	1.00 $\pm$ 0.37	1.72 $\pm$ 0.42

Figure captions

Figure 1. Average size-segregated chemical composition and percentage contributions of WSOC to TC in the summer samples (top plot) and the winter samples (bottom plot).

Figure 2. Mass percentages of organic compounds in the total water-soluble aerosol mass in different size bins.

Figure 3. The three modes resolved by PMF. (C is the average reconstructed mass sum of the measured species including Ca^{2+} , Na^+ , K^+ , SO_4^{2-} , oxalate, and WSOC.)

Figure 4. Seasonal mean size distributions of four major inorganic species (Ca^{2+} , Na^+ , K^+ and SO_4^{2-}), oxalate and WSOC.

Figure 5. Correlation coefficients (R^2) matrix among the measured species in different size modes.

Figure 6. EV Percentage values for the source profiles derived by PMF.

Figure 7. Percentages of source contributions by the identified sources to oxalate and WSOC in the size range of (a) 0.056-18 μm and (b) 1.0-1.8 μm .

Figure 1. Average size-segregated chemical composition of the summer samples (top plot) and the winter samples (bottom plot).

Figure 2. Mass percentages of organic compounds in the total water-soluble aerosol mass in different size bins.

Figure 3. The three modes resolved by PMF. (C is the average reconstructed mass sum of the measured species including Ca^{2+} , Na^+ , K^+ , SO_4^{2-} , oxalate, and WSOC.)

Figure 4. Seasonal mean size distributions of four major inorganic species (Ca^{2+} , Na^+ , K^+ and SO_4^{2-}), oxalate and WSOC.

Na ⁺ - Coarse	0.25														
Na ⁺ - Droplet		0													
Na ⁺ - Condensation			0.01												
K ⁺ - Coarse	0.5			0.47											
K ⁺ - Droplet		0.11			0.55										
K ⁺ - Condensation			0.27			0.01									
SO ₄ ²⁻ - Coarse	0.38			0.39			0.21								
SO ₄ ²⁻ - Droplet		0.02			0.42			0.74							
SO ₄ ²⁻ - Condensation			0.11			0			0						
oxalate - Coarse	0.56			0.37			0.55			0.24					
oxalate - Droplet		0.03			0.46			0.75			0.92				
oxalate - Condensation			0			0.03			0.1			0.35			
WSOC - Coarse	0.36			0.05			0.1			0.21			0.13		
WSOC - Droplet		0.05			0.5			0.84			0.51			0.57	
WSOC - Condensation			0.01			0.64			0.04			0.02			0.05
R^2 (n=21)	Ca ²⁺ - Coarse	Ca ²⁺ - Droplet	Ca ²⁺ - Condensation	Na ⁺ - Coarse	Na ⁺ - Droplet	Na ⁺ - Condensation	K ⁺ - Coarse	K ⁺ - Droplet	K ⁺ - Condensation	SO ₄ ²⁻ - Coarse	SO ₄ ²⁻ - Droplet	SO ₄ ²⁻ - Condensation	oxalate - Coarse	oxalate - Droplet	oxalate - Condensation

Figure 5. Correlation coefficients (R^2) matrix among the measured species in different size modes.

Figure 6. Percentages of EV values for the source profiles derived by PMF.

Figure 7. Percentages of source contributions of the identified sources to oxalate and WSOC in the size range of (a) 0.056-18 μm and (b) 1.0-1.8 μm .