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## Water-soluble organic compounds in PM<sub>2.5</sub> and size-segregated aerosols over Mount Tai in North China Plain

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[1] Daytime and nighttime PM<sub>2.5</sub> samples were collected at the summit of Mount Tai (1534 m) located in North China Plain during a week in 2006 summer. Size-segregated aerosol particles were also collected using an eight-stage impactor during the same period. Samples were analyzed for various water-soluble organic compounds using GC/FID and GC/MS techniques. Among the species identified in PM<sub>2.5</sub> samples, dicarboxylic acids (C<sub>2</sub>–C<sub>11</sub>) were found as the most abundant compound class, followed by ketocarboxylic acids, saccharides, polyols and polyacids, and dicarbonyls. Daytime concentrations of most compounds were found to be 2–3 times higher than in nighttime. Such a diurnal variation was first interpreted by the depressed transport of pollutants in nighttime from the lowlands to the mountaintop owing to the decreased heights of planetary boundary layer, and second by the photochemical production in daytime. The diurnal variation trends of secondary organic aerosols (SOA) such as diacids at the mountain site are the same as those on lowlands, but the diurnal patterns of primary organic aerosols (POA) on the mountaintop are in contrast to those on lowlands, where POA such as saccharides and polyols are usually higher in nighttime owing to the accumulation within inversion layer developed. The eight-stage impactor samples showed bimodal distributions of diacids and related compounds peaking at size ranges of 0.70–1.1 μm and 5.8–9.0 μm. In the present study, water-soluble organics in the fine mode are largely originated from biomass burning and/or photooxidation of gaseous precursors and the subsequent adsorption on the preexisting particles, whereas those in the coarse mode are mainly derived from suspended soil particles and pollens and in part via the hygroscopic growth of fine particles and formation of cloud/fog droplets.

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### 1. Introduction

[2] Tropospheric aerosols are deeply involved in global radiative balance [Seinfeld and Pandis, 1998] and pollution transport [Akimoto, 2003; Wilkening *et al.*, 2000]. Radiative effects of fine particles in the troposphere are much stronger than coarse particles owing to their more active response to radiation [Seinfeld and Pandis, 1998]. Because water-soluble organic compounds comprise a substantial fraction of the tropospheric organic aerosols, they significantly alter the hygroscopic properties of particles and thus affect the radiative forcing of the atmosphere and climate by acting as

cloud condensation nuclei (CCN) [Hemming and Seinfeld, 2001]. In particular, some water-soluble organics such as carboxylic acids and alcohols can act as surfactants in aerosols [Latif and Brimblecombe, 2004], and have an influence on hygroscopic properties of the particles. They also increase the solubility of toxic pollutants in aerosol particles and fog/rain droplets.

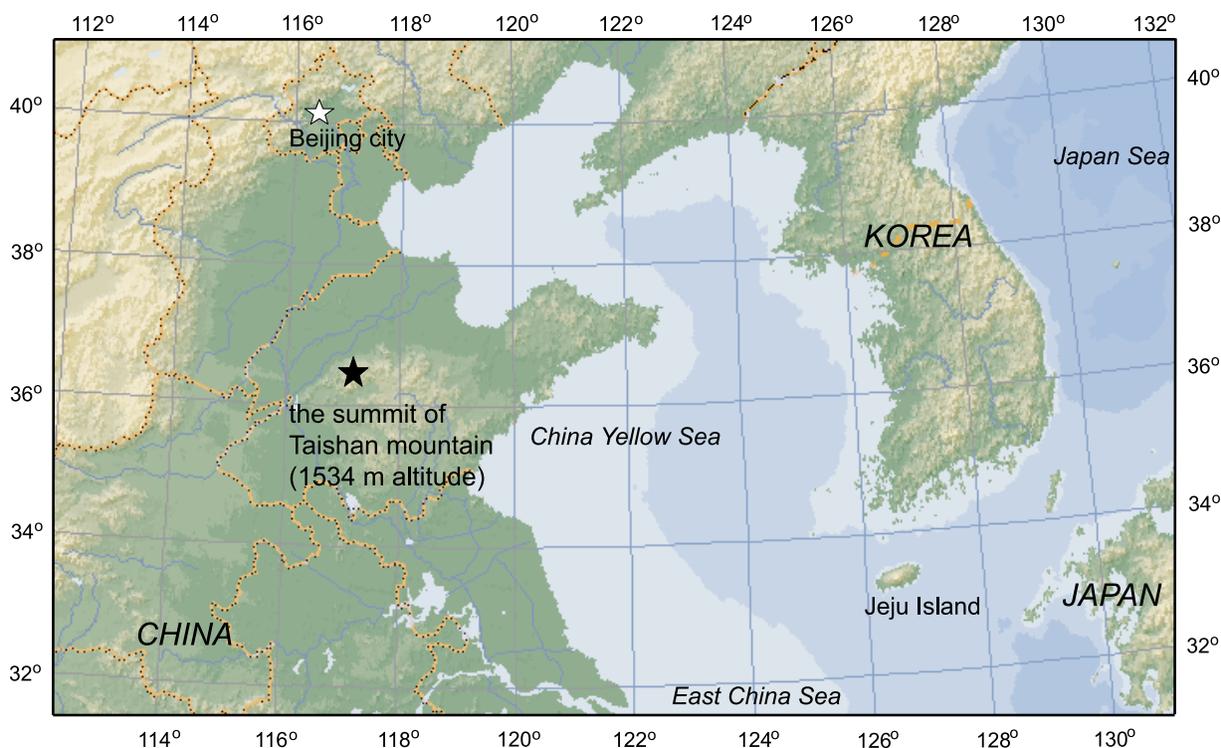
[3] Dicarboxylic acids (DCA) are a major water-soluble organic compound class in the tropospheric aerosols from continental urban sites [Kawamura and Yasui, 2005; Wang *et al.*, 2002; Yao *et al.*, 2004] to remote ocean [Kawamura and Gagosian, 1987; Kawamura and Sakaguchi, 1999]. They can lower the surface tension of water in aerosols [Hyvarinen *et al.*, 2006], and as such enhance the hygroscopic growth of the particles [Zhang *et al.*, 2004]. Although DCAs can be directly emitted from combustion sources [Kawamura and Kaplan, 1987], photochemical oxidation of gaseous organic precursors is more important [Claeys *et al.*, 2004; Kawamura *et al.*, 2005]. Lower molecular weight DCAs ( $\leq C_6$ ) are produced by photooxidation of anthropogenic volatile organic compounds (VOC) whereas higher molecular weight DCAs ( $> C_6$ ) such as azelaic acid (C<sub>9</sub>) are

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**Figure 1.** A map of eastern China and surroundings with a sampling location at Mount Tai ( $36.26^{\circ}\text{N}$ ,  $117.11^{\circ}\text{E}$ ).

produced by oxidation of unsaturated fatty acids from marine and terrestrial plants [Kawamura and Gagosian, 1987; Nepotchaykh and Ariya, 2002] and human cooking activities [Robinson et al., 2006].

[4] Saccharides are another important class of water-soluble organic compounds in atmospheric aerosols and are reported from many geographic regions including Amazonia, Brazil [Graham et al., 2002], the western North Pacific [Mochida et al., 2003], and Santiago, Chile [Simoneit et al., 1993]. The dominant saccharides include levoglucosan,  $\alpha$ - and  $\beta$ -glucose,  $\alpha$ - and  $\beta$ -fructose, sucrose, and trehalose, with lesser amount of inositol,  $\alpha$ - and  $\beta$ -mannose,  $\alpha$ - and  $\beta$ -xylose, and  $\alpha$ - and  $\beta$ -galactose. Levoglucosan has been used as a specific biomass burning tracer, which is produced by the pyrolysis of cellulose. In addition, saccharide polyols are also found in the atmosphere [Wang et al., 2006a], including sorbitol, xylitol, mannitol, arabitol, and others. Saccharides and polyols in aerosols are primarily derived from biomass burning [Graham et al., 2002; Simoneit et al., 1999], pollen and fungal metabolism [Simoneit et al., 2004b, 2004c].

[5] Tropospheric chemistry of water-soluble organic compounds is a challenging issue because their temporal and spatial distributions are sometimes region-specific [Huang et al., 2005; Wang et al., 2006a]. Although they have been studied in many regions including the urban [Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987] and remote marine atmosphere [Kawamura and Sakaguchi, 1999], observations of tropospheric aerosols over high mountains were rarely conducted [Decesari et al., 2005; Limbeck and Puxbaum, 1999]. The mountain geography and meteorology may have a strong influence on tropospheric chemistry, which may be different from urban

areas on flat lowlands. In the high mountains, boundary layers become low at night and the mountaintop is often in the free troposphere. Further, ambient temperature significantly drops at night in high mountains and thus relative humidity increases, potentially causing unique behaviors of water-soluble organic compounds.

[6] In this study, we collected summertime tropospheric aerosols at the summit of Mount Tai in North China Plain (NCP), where agricultural activity such as wheat harvest is maximized in early summer and subsequent field burning of agricultural wastes is operated. We analyzed both  $\text{PM}_{2.5}$  aerosols and eight-stage size-segregated particles for various water-soluble organic species using GC and GC/MS. Here we report molecular compositions, concentrations and size distributions of dicarboxylic acids, ketocarboxylic acids,  $\alpha$ -dicarbonyls, sugars, polyols and polyacids in the Mount Tai aerosols. The detailed size distributions of saccharides are, for the first time, reported in the mountain aerosols.

## 2. Experiment

### 2.1. Sampling Site and Procedures

[7] Mount Tai is the highest peak (elevation, 1534 m) in central NCP, which faces to the East China Sea, Korean Peninsula and Japanese Islands (Figure 1). Mount Tai is surrounded by the economically most developed regions in China, where air quality is very poor [Akimoto, 2003; Gao et al., 2005; Richter et al., 2005]. The aerosol sampling was conducted at a meteorological observatory at the mountaintop, which is far away from historical temples and local restaurants on the mountain. Thus, emissions from local sources are minimal [Gao et al., 2005]. Using a high-

**Table 1.** Meteorological Data During the Mount Tai Sampling Period<sup>a</sup>

	Daytime			Nighttime		
	0700–1700 Local Time			1900–0500 Local Time		
	Range	Mean	Std	Range	Mean	Std
Temperature, °C	21.0–35.0	27.7	3.4	19.2–31.5	23.6	2.7
Relative humidity, %	47–96	69	13	40–97	85	12
Pressure, hPa	986–994	991	2.1	987–994	991	1.9
Wind speed, m s <sup>-1</sup>	4–49	22	10	1–65	16	11
Wind direction, deg	72–291	162	63	20–323	184	82

<sup>a</sup>Sampling period is 22–28 June 2006. All the meteorological parameters were measured hourly. Std denotes standard deviation.

volume air sampler (Andersen GM2000, USA, flow rate of air was 1.13 m<sup>3</sup> min<sup>-1</sup>) and prebaked (450°C, 6 h) quartz fiber filters (20 × 25 cm<sup>2</sup>), PM<sub>2.5</sub> aerosol samples were collected on a day/night basis (0700–1700 local time (LT) for daytime and 1900–0500 LT for nighttime) during a week (22–28 June 2006) on the square in front of the Meteorological Station.

[8] An eight-stage impactor sampler (Andersen 20–800, USA, flow rate: 28.3 L min<sup>-1</sup>) was used with glass fiber filters ( $\phi$  90 mm, precombusted at 450°C for 6 h) for size-segregated aerosol sampling. Cutoff sizes of each stage were > 9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.70, 0.7–0.40, and <0.40  $\mu$ m. Particles (>9.0  $\mu$ m) impacted into a pre-separation aluminum vessel were collected from the container using a brush after sampling. However, those particles were not analyzed owing to the potential collection loss by the brush. The size-segregated sampling was continued for 1 week to obtain enough materials.

[9] After the sample collection, filters and field blanks were taken in a prebaked (450°C, 6 h) glass jar with a Teflon-lined screw cap, transported to the laboratory in Sapporo and stored at –20°C prior to analysis. Meteorological parameters, hourly monitored during the campaign, are shown in Table 1.

## 2.2. Sample Extraction, Derivatization, and Determination

[10] In this study, we analyzed 14 PM<sub>2.5</sub> samples and eight size-segregated samples for various organic compounds using two methodologies as follows.

[11] For dicarboxylic acids, an aliquot of the filter was extracted with pure water, and the extracts were filtered through a Pasteur pipette packed with quartz wool to remove filter debris and insoluble particles. The extracts were concentrated to nearly dryness using a rotary evaporator under vacuum, and then reacted with 14% BF<sub>3</sub>/*n*-butanol at 100°C for 30 min to convert the COOH and CHO groups to butyl esters and dibutoxy acetals, respectively. The derivatives were extracted with *n*-hexane and concentrated to 100  $\mu$ L prior to GC injection. Water-extractable diacids, ketocarboxylic acids and dicarbonyls were quantified by GC/FID. More details of sample extraction, derivatization and GC and GC/MS measurements are described elsewhere [Kawamura and Yasui, 2005; Wang et al., 2006a].

[12] For saccharides, polyols and polyacids, another aliquot of the filter was extracted with a mixture of methanol and dichloromethane (v/v, 1/2) under ultra sonication. The extracts were concentrated to dryness using a

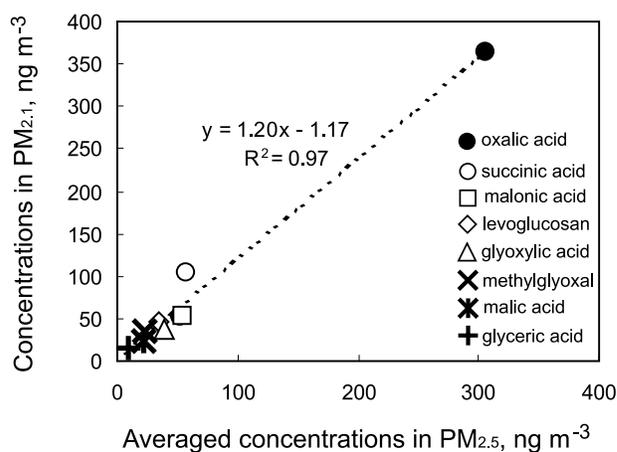
rotary evaporator and nitrogen blow-down system, and then reacted with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) at 70°C for 3 h to convert the OH and COOH groups into trimethylsilyl (TMS) ethers and esters, respectively. Saccharides, polyols and polyacids were determined by GC/MS. More details are described elsewhere [Wang et al., 2006a].

[13] Most of the target compounds were undetectable in the field blanks, except for glycerol and oxalic acid. However, their amounts were less than 2% of the actual samples. Recoveries of all the compounds determined were better than 80%. Data reported here are corrected for the field blanks but not corrected for the recoveries. The mass of aerosol particles with a diameter less than 2.5  $\mu$ m in the size-segregated samples was calculated to be 80  $\mu$ g m<sup>-3</sup> using a standard method described by the sampler manufacturer. It accounts for 80% of the mass collected by the high-volume PM<sub>2.5</sub> sampler, suggesting that particle bounce-off from the upper stage to the lower stage was not serious. A strong linear correlation was found for the major species determined in the PM<sub>2.5</sub> samples and in the summed size fractions (PM<sub>2.1</sub>) of the size-segregated samples (Figure 2). The intercomparison suggests a good consistency between two data sets. But concentrations of the major species obtained in the size-segregated aerosols are 5–20% higher than those obtained by the PM<sub>2.5</sub> samples. Unlike the size-segregated aerosol sampler, the PM<sub>2.5</sub> sampler collect aerosols by filtration, thus compound losses by evaporation may occur owing to the pressure drop in the sampler. Such a negative artifact has been reported [Katz and Chan, 1980; McMurtry, 2000; Peters and Seifert, 1980].

## 3. Results and Discussion

### 3.1. Daytime and Nighttime Concentrations of Organic Compound Classes

[14] Five organic compound classes were determined in the PM<sub>2.5</sub> samples (Table 2), among which DCAs were found



**Figure 2.** An intercomparison of concentrations of the major compounds determined in the PM<sub>2.5</sub> samples and in the PM<sub>2.1</sub> fraction of the eight-stage samples (the PM<sub>2.5</sub> concentrations are the averages of all the day and night samples, while the PM<sub>2.1</sub> concentrations are the sum of the compounds in the stages of < 0.4, 0.4–0.7, 0.7–1.1, and 1.1–2.1  $\mu$ m).

**Table 2.** Concentrations of Water-Soluble Organic Compounds in PM<sub>2.5</sub> Over Mount Tai<sup>a</sup>

	Daytime (n = 7)				Nighttime (n = 7)			
	Min	Max	Mean	Std	Min	Max	Mean	Std
<i>Dicarboxylic Acids</i>								
Oxalic (C <sub>2</sub> )	378	623	455	87	83	284	158	82
Malonic (C <sub>3</sub> )	64	103	77	13	13	43	29	11
Succinic (C <sub>4</sub> )	67	101	84	13	17	48	30	13
Glutaric (C <sub>5</sub> )	18	32	23	6.1	3.7	10	6.8	2.8
Adipic (C <sub>6</sub> )	7.6	13	9.7	1.7	1.5	5.1	3.3	1.3
Pimelic (C <sub>7</sub> )	5.7	14	8.5	2.8	BDL	4.6	2.4	2.1
Suberic (C <sub>8</sub> )	2.9	7.8	5.3	1.8	BDL	2.8	1.7	1.1
Azelaic (C <sub>9</sub> )	9.4	32	21	8.2	1.4	13	6.0	4.1
Decanedioic (C <sub>10</sub> )	0.5	1.8	1.0	0.5	BDL	0.7	0.3	0.3
Undecanedioic (C <sub>11</sub> )	2.2	6.7	4.0	1.4	0.5	4.1	1.9	1.2
Methylsuccinic (iC <sub>5</sub> )	4.9	8.3	7.0	1.2	0.8	3.6	2.1	1.4
Methylglutaric (iC <sub>6</sub> )	1.5	2.4	2.0	0.3	BDL	0.9	0.4	0.4
Maleic (M)	4.1	7.2	5.4	1.2	0.7	5.9	2.8	2.1
Fumaric (F)	2.8	5.0	3.7	0.7	BDL	2.1	1.1	0.9
Methylmaleic (mM)	7.4	18	12	3.3	0.4	8.1	4.1	3.8
Phthalic (Ph)	22	37	28	5.0	5.5	16	11	4.2
Iso-Phthalic (i-Ph)	1.5	2.7	2.0	0.4	0.2	1.3	0.7	0.4
Tere-phthalic (t-Ph)	0.6	1.2	0.9	0.2	BDL	0.3	0.1	0.2
4-Oxopimelic (kC <sub>7</sub> )	BDL	10.7	6.4	3.4	BDL	4.3	1.9	1.7
Subtotal	642	1025	756	139	140	434	263	123
<i>Ketocarboxylic Acids</i>								
Glyoxylic (ωC <sub>2</sub> )	47	84	61	14	6.9	28	17	11
3-Oxopropanoic (ωC <sub>3</sub> )	5.4	14	7.5	2.8	0.9	5.1	2.9	1.8
4-Oxobutanoic (ωC <sub>4</sub> )	4.0	19	9.2	4.8	2.0	6.8	4.0	1.9
9-Oxopelargonic (ωC <sub>9</sub> )	BDL	3.4	2.2	1.1	0.3	1.9	1.0	0.7
Pyruvic (Pyr)	18	43	27	8.3	2.9	14	8.2	5.4
Subtotal	82	163	107	29	13	54	33	21
<i>α-Dicarbonyls</i>								
Methylglyoxal (mGly)	13	47	24	11	0.4	14	7.1	6.4
Glyoxal (Gly)	5.5	18	9.5	4.0	0.7	6.0	3.0	2.4
Subtotal	19	65	33	15	1	20	10	9
<i>Sugars</i>								
Levogluconan	21	123	43	36	1.6	151	36	58
Arabitol	0.9	5.9	3.2	1.9	0.2	1.7	0.8	0.6
Fructose	2.8	6.2	4.7	1.1	0.6	4.6	1.5	1.5
Glucose	7.2	13	9.2	2.1	1.8	4.8	3.2	1.2
Mannitol	1.5	11	6.0	3.6	0.2	2.5	0.9	0.9
Inositol	0.5	2.2	1.5	0.6	0.1	1.8	0.5	0.6
Sucrose	0.9	2.9	1.7	0.7	0.4	5.5	2.2	2.1
Trehalose	1.0	4.4	2.4	1.2	0.3	1.1	0.7	0.3
Subtotal	40	149	72	36	7	160	46	58
<i>Polyols and Polyacids</i>								
Glycerol	8.0	23	17	6.2	8.5	21	14	4.9
Glyceric acid	9.6	17	12	2.4	1.7	6.8	3.7	2.4
Malic acid	3.7	45	28	13	3.5	25	11	9.3
Tartaric acid	1.5	37	7.4	13	BDL	4.9	2.3	2.1
Citric acid	BDL	1.8	0.3	0.7	BDL	1.1	0.4	0.5
Subtotal	54	75	64	9	20	55	32	17

<sup>a</sup>Sampling period is 22–28 June 2006. Unit is ng m<sup>-3</sup>. BDL, below detection limit; Min, minimum; Max, maximum; and Std, standard deviation.

as the most abundant compound class (756 ± 139 ng m<sup>-3</sup> in daytime versus 263 ± 123 ng m<sup>-3</sup> in nighttime), followed by ketocarboxylic acids (107 ± 29 versus 33 ± 21 ng m<sup>-3</sup>), saccharides (72 ± 36 versus 46 ± 58 ng m<sup>-3</sup>), polyols and polyacids (64 ± 9 versus 32 ± 17 ng m<sup>-3</sup>), and dicarbonyls (33 ± 15 versus 10 ± 9 ng m<sup>-3</sup>). Interestingly, daytime concentrations are 2–3 times higher than nighttime concentrations for most of the compound classes determined. In particular, photochemical reaction products such as diacids,

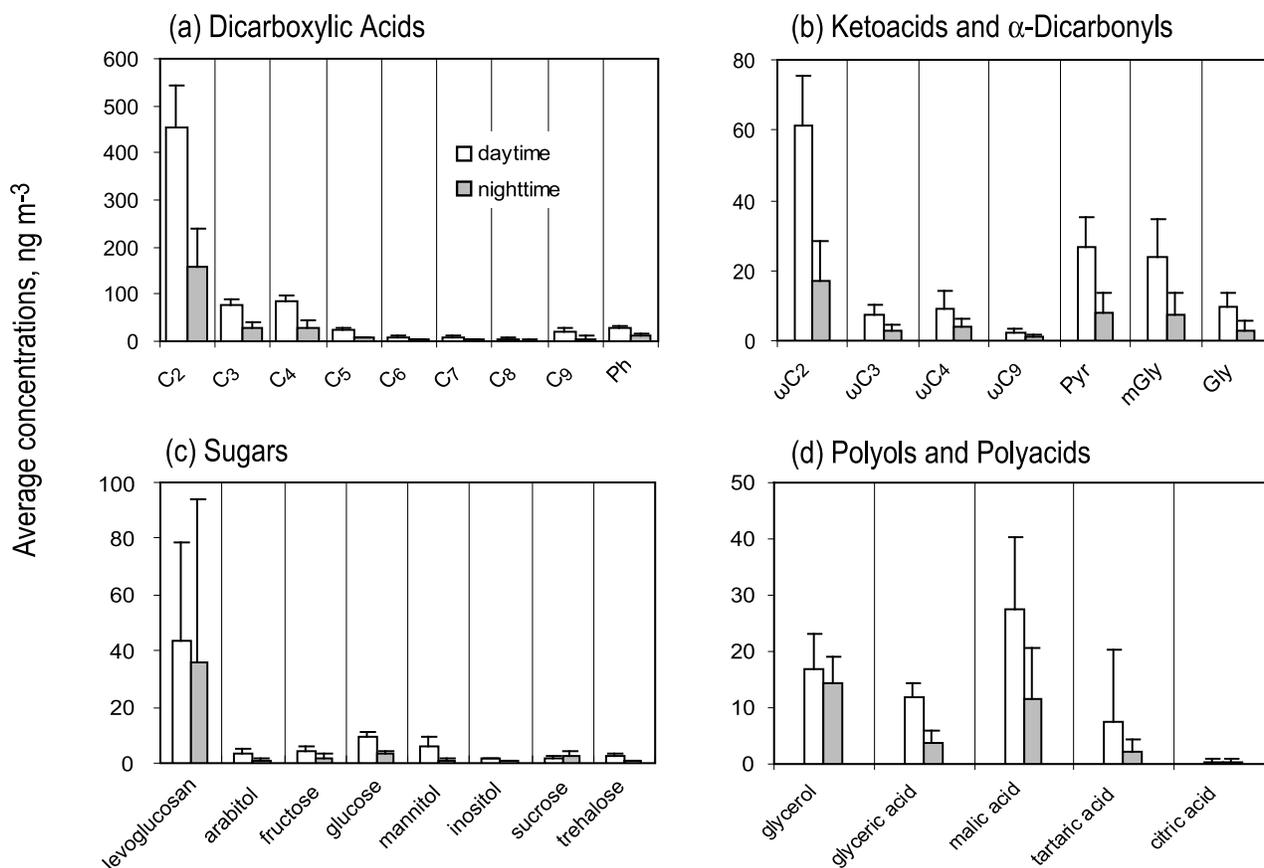
ketoacids and polyacids showed a strong diurnal pattern, suggesting that photochemical process in daytime is an important factor to cause the daytime maxima. This process should be shut down at night, which intensifies the diurnal patterns at the mountaintop.

[15] However, higher daytime concentrations were also reported for metals [Y. Wang *et al.*, 2007] and black carbon [Liu *et al.*, 2007] in the aerosols from Mount Tai. This may suggest that there is another important factor that also contribute to the diurnal distributions of water-soluble organic compounds. It was found that the heights of boundary layer in the Mount Tai frequently reduced to less than 1000 m at night during the campaign [Takigawa *et al.*, 2007], which keeps the mountaintop (1534 m) in the free troposphere at night. In contrast, the boundary layer came up far above the mountaintop in daytime. This local meteorology of Mount Tai should restrain the upward transport of pollutants from lowland to the summit at night and enhance the transport in daytime. This seems to be supported by the results of levoglucosan (biomass burning tracer and not produced by photochemistry). Concentrations of levoglucosan are similar between day (average 43 ng m<sup>-3</sup>, range 21–123 ng m<sup>-3</sup>) and night samples (average 36 ng m<sup>-3</sup>, range 1.6–151 ng m<sup>-3</sup>), but we can still recognize the lower average concentrations at night, suggesting that decrease in the height of boundary layer at night suppress the upward transport of biomass burning products from the lowland to the mountaintop.

### 3.2. Dicarboxylic and Ketocarboxylic Acids and α-Dicarbonyls

[16] Homologous dicarboxylic acids (DCAs, C<sub>2</sub>–C<sub>11</sub>), together with several ketocarboxylic acids and dicarbonyls, were detected in the PM<sub>2.5</sub> samples with oxalic acid being the dominant species, followed by malonic, succinic, and phthalic acids (Table 2 and Figure 3a). Similar distribution has been reported in East Asian aerosols from the lower troposphere within the boundary layer [Wang *et al.*, 2006b] to the middle troposphere [Kawamura *et al.*, 2003]. Relative abundance of oxalic acid in total DCAs in the Mount Tai samples was 60 ± 1.3% in daytime and 59 ± 3.6% in nighttime. These values are higher than those (49 ± 7.4%) reported from urban Nanjing, China [Wang *et al.*, 2002], but much lower than those (70–75%) reported in the remote marine aerosols from the central Pacific [Kawamura and Sakaguchi, 1999]. Oxalic acid (C<sub>2</sub>) is mostly produced by photooxidation of organic precursors [Kawamura *et al.*, 1996; Limbeck and Puxbaum, 1999], although it is also reported in gasoline and diesel car exhausts as a primary product [Kawamura and Kaplan, 1987]. The higher relative abundance of oxalic acid in the Mount Tai aerosols compared to the flat lowland samples suggests an enhanced photochemical oxidation of organic precursors during the transport from the lower parts of NCP to the mountaintop.

[17] Succinic acid (C<sub>4</sub>) has been suggested as one of the precursors of oxalic (C<sub>2</sub>) and malonic (C<sub>3</sub>) acids [Kawamura *et al.*, 1996]. Adipic acid (C<sub>6</sub>) is believed to be produced from oxidation of anthropogenic cyclic hexene [Grosjean *et al.*, 1978], whereas azelaic acid (C<sub>9</sub>) is a photooxidation product of unsaturated fatty acids (e.g., oleic and linoleic acids) derived from biogenic emissions [Kawamura and Gagosian, 1987] and/or from anthropo-

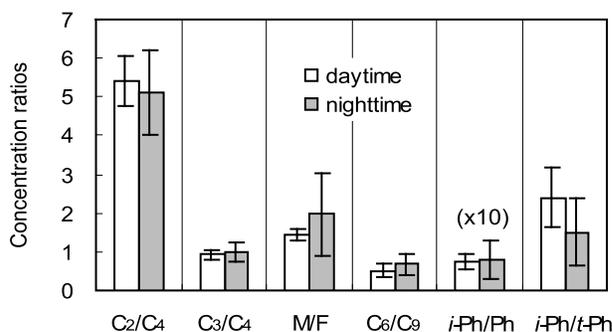


**Figure 3.** Daytime and nighttime molecular compositions of water-soluble organic compound classes in the  $\text{PM}_{2.5}$  aerosols during the campaign at Mount Tai: (a) dicarboxylic acids, (b) ketoacids and  $\alpha$ -dicarbonyls, (c) sugars, and (d) polyols and polyacids. (Bars represent the standard deviations.)

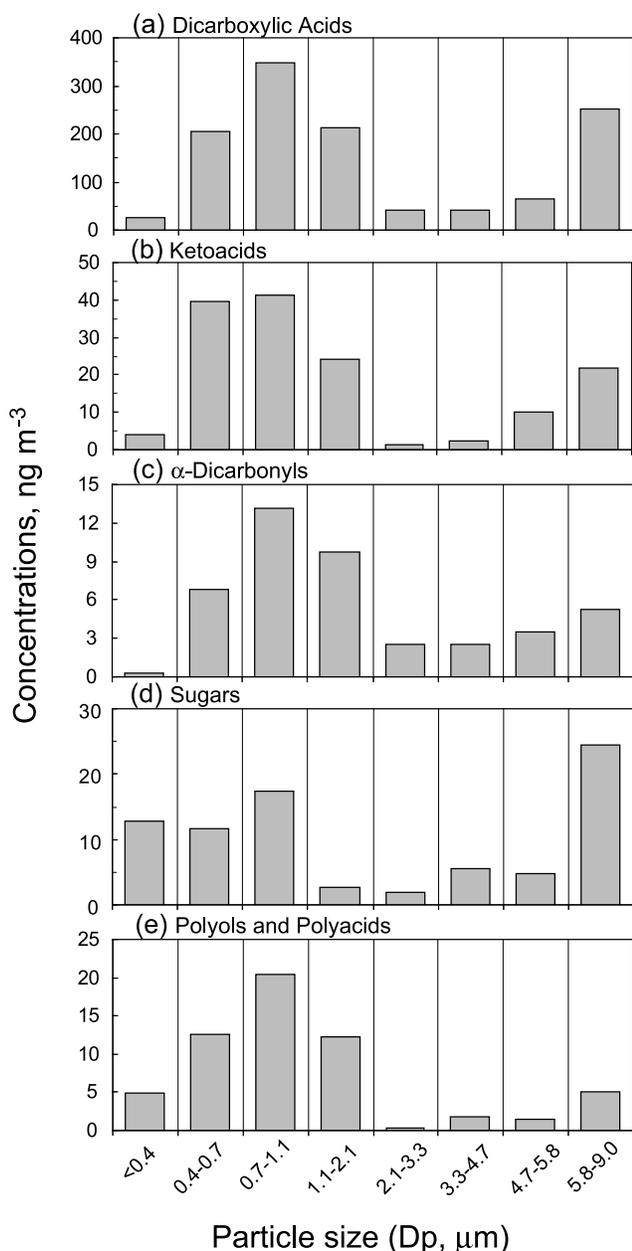
genic cooking activities [Robinson *et al.*, 2006]. Maleic acid (M) can be produced by photooxidation of aromatic hydrocarbons such as benzene and toluene in the atmosphere, and be further isomerized into fumaric acid (F) [Kawamura and Ikushima, 1993]. We found that  $\text{C}_6/\text{C}_9$  and M/F concentration ratios were slightly higher in nighttime than in daytime (Figure 4). This may suggest that oxidative production of  $\text{C}_9$  and M to F isomerization are more significant in daytime. In contrast, *i*-phthalic to *t*-phthalic acid (*i*-Ph/*t*-Ph) ratios were lower in nighttime than in daytime. Such diurnal differences may suggest different origins of air masses over the mountaintop between day and night, although no significant differences were observed for  $\text{C}_2/\text{C}_4$ ,  $\text{C}_3/\text{C}_4$  and *i*-phthalic to phthalic acid (*i*-Ph/Ph) ratios.

[18] Homologous ketocarboxylic acids ( $\omega\text{C}_2$ – $\omega\text{C}_4$ ,  $\omega\text{C}_9$  and Pyr) and  $\alpha$ -dicarbonyls (mGly and Gly) were detected in the samples with total concentrations of 13–163  $\text{ng m}^{-3}$  (average 70  $\text{ng m}^{-3}$ ) and 1–65  $\text{ng m}^{-3}$  (average 22  $\text{ng m}^{-3}$ ), respectively (Table 2 and Figure 3b). These ketoacids and carbonyls are secondarily produced via atmospheric photooxidation of organic precursors and/or primarily formed by fossil fuel combustion and biomass burning, and further oxidized into saturated DCAs [Chebbi and Carlier, 1996; Kawamura *et al.*, 1996; Volkamer *et al.*, 2006]. Glyoxal, the smallest  $\alpha$ -dicarbonyl, generally originates from the oxidation of anthropogenic and biogenic VOCs and serves as a novel indicator for fast VOC chemistry [Volkamer *et al.*,

2005; Wittrock *et al.*, 2006]. Glyoxal and methylglyoxal concentrations at the summit of Mount Tai are comparable to those in urban areas of coastal China [Wang *et al.*, 2002], but much higher than those reported in Jeju Island, the East China Sea (average 12  $\text{ng m}^{-3}$ ) [Kawamura *et al.*, 2004]. This contrast is consistent with the enhanced concentrations



**Figure 4.** Differences in the mass concentration ratios of selected dicarboxylic acids between the daytime and nighttime samples ( $\text{PM}_{2.5}$ ) collected at Mount Tai. For abbreviations  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_9$ , M, F, Ph, *i*-Ph, and *t*-Ph, see Table 2. Bars represent the standard deviations. The *t* test for the paired samples showed  $p \leq 0.05$ .



**Figure 5.** Size distributions of water-soluble organic compound classes in the atmospheric aerosols over the summit of Mount Tai.

of glyoxal and formaldehyde over the NCP region as reported by satellite observation [Wittrock *et al.*, 2006]. Although Wittrock *et al.* [2006] reported gaseous carbonyls, our study demonstrates that particulate  $\alpha$ -dicarbonyls are also abundant in the atmosphere over NCP.

### 3.3. Sugars, Polyols, and Polyacids

[19] Concentrations of saccharides including levoglucosan and several primary sugars in  $PM_{2.5}$  samples were  $7\text{--}160\text{ ng m}^{-3}$  (average  $59\text{ ng m}^{-3}$ ) (Table 2 and Figure 3c), accounting for 66% of those ( $90 \pm 32\text{ ng m}^{-3}$ ) in total suspended particles (TSP) collected at the same site during the same period [Fu *et al.*, 2008]. Levoglucosan, a tracer for biomass burning, was found as a dominant sugar ( $43 \pm 36$

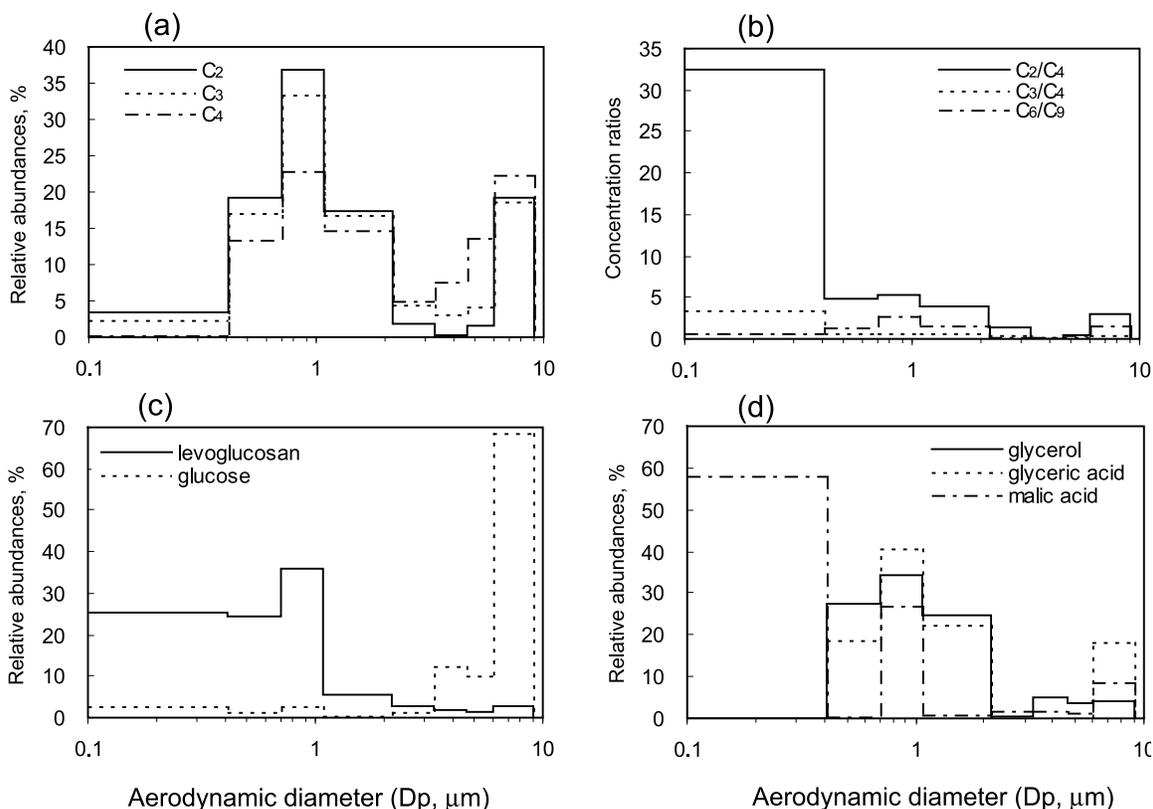
and  $36 \pm 58\text{ ng m}^{-3}$  at day and night, respectively) (Table 2), followed by glucose, sucrose and/or mannitol. The predominance of levoglucosan in the aerosols is consistent with the ground surface samples from Chinese megacities [Wang *et al.*, 2006a]. Although the concentrations of the saccharides at Mount Tai are less than those ( $9.4\text{--}735\text{ ng m}^{-3}$ , average  $132\text{ ng m}^{-3}$ ) on the lowlands in China [Wang *et al.*, 2006a], they are higher than those ( $31 \pm 25\text{ ng m}^{-3}$ ) measured in  $PM_{2.5}$  aerosols collected by aircraft ( $0.5\text{--}3.0\text{ km}$  altitude) over coastal China [G. H. Wang *et al.*, 2007]. Sucrose, a minor species in this group, is a metabolism product of bacteria in soil. Its higher concentrations in nighttime ( $2.2 \pm 2.1\text{ ng m}^{-3}$ ) than in daytime ( $1.7 \pm 0.7\text{ ng m}^{-3}$ ) (Table 2) were probably caused by an enhanced bacteria activity under higher humid conditions at night.

[20] Polyols and polyacids, including glycerol and glyceric, malic, tartaric and citric acids, were detected in the  $PM_{2.5}$  aerosols (Table 2 and Figure 3d) with glycerol and glyceric and malic acids being the major species in this group. Concentrations of these compounds in the mountain aerosols ( $9.6 \pm 10.7\text{ ng m}^{-3}$ ) are less than those ( $38 \pm 35\text{ ng m}^{-3}$ ) reported in the lowland aerosols from Chinese megacities [Wang *et al.*, 2006a], but are very close to those ( $7.0 \pm 8.1\text{ ng m}^{-3}$ ) in the summertime tropospheric aerosols collected by aircraft ( $0.5\text{--}3.0\text{ km}$  altitude) over inland China [G. H. Wang *et al.*, 2007]. Glyceric and malic acids are secondary photooxidation products in the atmosphere [Kawamura and Ikushima, 1993; Simoneit *et al.*, 2004c]. The sum of glyceric and malic acids (average  $27\text{ ng m}^{-3}$ ) (Table 2) in the fine particles over Mount Tai is 3 times higher than that (average  $7.5\text{ ng m}^{-3}$ ) reported in the aircraft samples over the North Pacific [Simoneit *et al.*, 2004b]. This may suggest that the mountain aerosols are photochemically aged, to some extent, like marine aerosols, although the aircraft samples are more aged but may be more diluted and/or further subjected to photochemical decomposition during the transport over the Pacific.

[21] Glycerol is a reduced sugar primarily produced by fungal metabolism in soils and is emitted to the atmosphere as wind-blown dusts [Simoneit *et al.*, 2004c]. Its concentration (average  $15\text{ ng m}^{-3}$ , Table 2) in the mountain aerosols is much less than that (average  $38\text{ ng m}^{-3}$ ) of the aircraft aerosols over the North Pacific [Simoneit *et al.*, 2004b]. Such a difference may be associated with the fact that Mount Tai samples are  $PM_{2.5}$  whereas the North Pacific samples are total suspended particles (TSP), and thus soil fungus-derived glycerol that is enriched in coarse particles is less abundant in the  $PM_{2.5}$  samples from Mount Tai. However, it is important to stress that the Mount Tai measurements represent a very limited time period (1 week) and may not be representative of typical concentrations measured at the site.

### 3.4. Size Distributions

[22] Various water-soluble organics were also determined in the eight-stage size-segregated aerosols from Mount Tai. As shown in Figures 5a, 5b, 5c, and 5e, bimodal distributions were found for diacids, ketoacids,  $\alpha$ -dicarbonyls, and polyols and polyacids with two peaks at  $0.70\text{--}1.1$  and  $5.8\text{--}9.0\text{ }\mu\text{m}$  in diameter. Although major diacids ( $C_2$ ,  $C_3$  and  $C_4$ ) maximized at  $0.70\text{--}1.1\text{ }\mu\text{m}$ , some minor diacid species such as  $C_8$ ,  $C_9$  and  $C_{10}$  showed a peak at larger size ( $1.1\text{--}2.2\text{ }\mu\text{m}$ )



**Figure 6.** Relative abundances and concentration ratios of water-soluble organic compounds in size-segregated aerosols collected at Mount Tai (total amount of each compound in the eight stages: C<sub>2</sub>, 471 ng m<sup>-3</sup>; C<sub>3</sub>, 76 ng m<sup>-3</sup>; C<sub>4</sub>, 140 ng m<sup>-3</sup>; levoglucosan, 47 ng m<sup>-3</sup>; glucose, 13 ng m<sup>-3</sup>; glycerol, 30 ng m<sup>-3</sup>; glyceric acid, 16 ng m<sup>-3</sup>; and malic acid, 7.4 ng m<sup>-3</sup>).

(data are not shown here). In contrast, total sugars showed a different pattern with the highest concentration on the coarse mode (5.8–9.0  $\mu\text{m}$ ) (Figure 5d), mainly owing to the high concentration of sucrose. Such a bimodal distribution of dicarboxylic acids was not observed during the summer periods in urban Beijing, where diacids showed unimodal distribution with a peak in the fine mode [Yao *et al.*, 2003]. During the sampling period wind directions varied in a wide range of 20–323° (average 173° ± 74°), but there is no systematic difference in the wind direction between day and night (Table 1). Thus, influence of wind direction on the size distributions of diacids and related compounds may be insignificant. The coarse mode of diacids could in part be derived from biological formation in soil and/or adsorption of gaseous DCAs on alkali soil particles, but the bimodal patterns of the diacids on the mountaintop may be associated with other meteorological conditions of the high mountain regions.

[23] Over Mount Tai, fog or cloud events were often observed in nighttime during the campaign. Sizes of cloud/fog droplets are larger than the aerosol particles, ranging from a few micrometers to several hundreds of micrometers, because the droplets are grown by the condensation of water vapor from the particles that are activated as CCN [Seinfeld and Pandis, 1998]. In addition to the chemical components of aerosols, the cloud/fog droplets further uptake soluble gases via aqueous phase reactions [Blando and Turpin, 2000; Chen *et al.*, 2007]. Those droplets can be collected in the coarse fractions during the impactor sampling. These

situations may cause an enrichment of diacids on the coarse mode of size-segregated aerosols. Unfortunately, the largest fraction (>9  $\mu\text{m}$ ) was not analyzed for the chemical composition as described above. A formation of cloud/fog droplets that may enrich water-soluble compounds including diacids [Raja *et al.*, 2008] and/or hygroscopic growth of particles at night could lead to a decrease in the concentrations of water-soluble organics, to some extent, in PM<sub>2.5</sub>.

[24] During the campaign, high-volume air sampling was conducted to collect bulk aerosol (TSP) samples without any particle cutoff. The TSP samples during the sampling period showed similar diurnal trend for diacids (C<sub>2</sub>–C<sub>11</sub>) with higher concentrations in daytime (Kawamura *et al.*, unpublished results, 2007). However, the difference in the TSP samples between day and night is much smaller (<40%) than those (200–300%) found in the PM<sub>2.5</sub> samples. The similar but more distinct trend in PM<sub>2.5</sub> can be explained by selective entrainment of diacids into cloud/fog droplets or hygroscopic growth of fine to coarse particles at night. These processes may cause a significant decrease in the concentrations of diacids in PM<sub>2.5</sub> in nighttime because at least the sizes of fog/cloud particles are much larger (>7  $\mu\text{m}$ ) [Seinfeld and Pandis, 1998] than fine aerosols such as PM<sub>2.5</sub>.

[25] In addition, the normalized abundances of C<sub>2</sub>–C<sub>4</sub> diacids maximized in the fine mode (0.7–1.1  $\mu\text{m}$ ) and, to a lesser extent, in the coarse mode (5.8–9.0  $\mu\text{m}$ ), as shown in Figure 6a. Concentration ratios of diacids (C<sub>2</sub>/C<sub>4</sub> and C<sub>3</sub>/C<sub>4</sub>) maximized in the finest mode (<0.4  $\mu\text{m}$ ) (Figure 6b),

suggesting that oxidative degradation of  $C_4$  to  $C_2$  and  $C_3$  diacids occurred in fine aerosols and/or secondary production in gas phase followed by adsorption on preexisting fine aerosols. A strong linear correlation ( $R^2 = 0.99$ ) was found between the  $C_2/C_4$  and  $C_3/C_4$  ratios among the different stages. This is consistent with the previously reported mechanism that  $C_2$  and  $C_3$  diacids are produced by the oxidation of  $C_4$  in the atmosphere [Kawamura and Ikushima, 1993; Kawamura et al., 1996, 2007].

[26] As shown in Figure 6c, levoglucosan was found to exist mostly in fine particles with a diameter less than  $1.1 \mu\text{m}$ . Levoglucosan is emitted from biomass burning and subsequently aggregates and/or condenses on preexisting particles owing to the higher surface area of fine particles [Simoneit et al., 2004a; Wang et al., 2006b]. Glucose is an important component of pollen and abundantly present in soil microorganisms. This sugar compound can be emitted into the air by wind motion from vegetation and soil systems. Therefore, it is reasonable that soil-derived glucose was found abundantly in coarse particles larger than  $3.0 \mu\text{m}$ , being in contrast to levoglucosan (Figure 6c), whose origin is associated with biomass burning. Recently, CCN efficiencies of saccharides have been reported to be lower than those of organic acids owing to their absence of dissociation in water, and their contributions to cloud formation are less than those of diacids [Ekstrom et al., 2009; Rosenorn et al., 2006; Varga et al., 2007]. Thus, less abundance of levoglucosan on coarse mode (Figure 6c) may mean that cloud/fog formation over the mountaintop does not significantly affect its size distribution.

[27] Glycerol is also derived from soil suspension as discussed above. It was not detected in the particles smaller than  $0.40 \mu\text{m}$  (Figure 6d). Glyceric and malic acids are secondary oxidation products and thus are enriched in the fine mode ( $<2.1 \mu\text{m}$ ), although a significant fraction of both acids was also found on coarse mode ( $5.8\text{--}9.0 \mu\text{m}$ ) (Figure 6d). The peak in the fine mode can be explained by the condensation via photooxidation of gaseous precursors [Kawamura et al., 2007], whereas the second peak in the coarse mode may be attributable to the size shift of aerosols by hygroscopic growth of fine particles, which may occur at night under a high humidity condition. This hygroscopic growth of aerosols occasionally followed by fog/cloud formation may also be responsible for the second peak of diacids and related compounds on coarse mode (Figures 5a–5c). Because the size-segregated sampling was conducted for 7 days at the mountaintop, this process may have often happened in nighttime when ambient temperature decrease and relative humidity increase.

#### 4. Summary and Conclusions

[28] On the basis of the analyses of size-segregated and day/night  $\text{PM}_{2.5}$  aerosol samples, we found diurnal variations of water-soluble organic compounds with daytime maxima and bimodal size distributions for most of the compounds in the Mount Tai atmosphere over North China Plain (NCP). The results are interpreted by long-range atmospheric transport of pollutants and photochemical productions of water-soluble organics during the transport to the mountaintop under unique meteorological conditions of

high mountains (changes in the heights of boundary layer and relative humidity), as follows.

[29] Fine ( $\text{PM}_{2.5}$ ) aerosol samples were collected for 7 days in 2006 summer on a day and night basis at the summit of Mount Tai (1534 m) in NCP and were analyzed for water-soluble organic compounds including dicarboxylic acids, ketocarboxylic acids,  $\alpha$ -dicarbonyls, saccharides, polyols and polyacids using GC and GC/MS. A distinct difference was found in daytime and nighttime concentrations for most of the water-soluble organics. Their daytime concentrations are mostly 2–3 times higher than the nighttime concentrations, which were interpreted by photochemical production of the compounds in daytime and decrease in the heights of the boundary layer at night. Because the heights frequently reduced to less than 1000 m at night in the Mount Tai area, the mountaintop was often in the free troposphere, being isolated from the polluted ambient air of lowland origin at night. This is in contrast to the nighttime maxima generally observed in urban areas owing to the development of inversion layer. Compared with TSP samples,  $\text{PM}_{2.5}$  samples showed more distinct diurnal difference of diacids and related compounds, suggesting the growth of fine particles to larger sizes ( $>2.5 \mu\text{m}$ ) during the formation of cloud/fog droplets at night.

[30] Size-segregated aerosol samples (eight stages from  $<0.4 \mu\text{m}$  to  $9 \mu\text{m}$ ) collected during the campaign showed bimodal distributions of diacids, ketocarboxylic acids, and dicarbonyls with concentration peaks at  $0.70\text{--}1.1 \mu\text{m}$  and  $5.8\text{--}9.0 \mu\text{m}$ . On the other hand, levoglucosan showed a unimodal distribution on a fine mode whereas glucose showed a peak on a coarse mode. The peaks of the water-soluble organics in smaller particles result from the condensations of organics from combustion process and photooxidation products from gaseous precursors. In contrast, the peaks in coarse particles are largely derived from the suspended soils and pollens. However, the peaks of diacids and ketoacids on the coarse mode may also be derived by a hygroscopic growth of fine particles to larger ones at night when relative humidity increases.

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