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# Size-resolved particulate water-soluble organic compounds in the urban, mountain and marine atmosphere

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# Abstract

Primary (i.e., sugars and sugar alcohols) and secondary water-soluble organic compounds (WSOCs) (i.e., dicarboxylic acids and aromatic acids) were characterised on a molecular level in size-segregated aerosols from the urban and mountain atmosphere

- <sup>5</sup> of China and from the marine atmosphere in the outflow region of East Asia. Levoglucosan is the most abundant WSOCs in the urban and mountain atmosphere, whose accumulated concentrations in all stages are 1–3 orders of magnitude higher than those of marine aerosols. In contrast, malic, succinic and phthalic acids are dominant in the marine aerosols, which are 3–6 times more abundant than levoglucosan. This
- <sup>10</sup> suggests that a continuous formation of secondary organic aerosols is occurring in the marine atmosphere during the long-range transport of air mass from inland China to the North Pacific. Sugars and sugar-alcohols, except for levoglucosan, gave a bimodal size distribution in the urban and mountain areas, peaking at 0.7–1.1 µm and >3.3 µm, and a unimodal distribution in the marine region, peaking at >3.3 µm. In contrast, levoglu-
- $_{15}$  cosan and all the secondary WSOCs, except for benzoic and azelaic acids, showed a unimodal size distribution with a peak at 0.7–1.1  $\mu m$ . Geometric mean diameters (GMDs) of the WSOCs in fine particles (<2.1  $\mu m$ ) at the urban site are larger in winter than in spring, due to an enhanced coagulation effect under the development of an inversion layer. However, GMDs of levoglucosan and most of the secondary WSOCs in
- the coarse mode are larger in the mountain and marine air and smaller in the urban air. This is most likely caused by an enhanced hygroscopic growth due to the high humidity of the mountain and marine atmosphere.

#### 1 Introduction

Water-soluble organic compounds (WSOCs) constitute a substantial fraction of atmo spheric organic matter, accounting for 10–90% of organic carbon content in fine ambi ent aerosols depending on the locations (Mader et al., 2004; Ming and Russell, 2004;





Pöschl, 2005; Yu et al., 2004). WSOCs play an important role in global climate change by altering the hygroscopicity of atmospheric aerosols (Cruz and Pandis, 2000; Decesari et al., 2005; Kuwata et al., 2008). WSOCs can also cause a negative effect on human health by increasing the solubility of toxic pollutants (Sorjamaa et al., 2004). Moreover, some of WSOCs are allergens, leading to asthma and other diseases (Franze et al., 2004, 2005).

<sup>1</sup>H NMR (Decesari et al., 2007; Graham et al., 2002) and <sup>13</sup>C NMR (Sannigrahi et al., 2006) analyses indicate that WSOCs are predominantly composed of aliphatic compounds containing carboxyl, carbonyl and hydroxyl groups (carboxylic acids, aldehydes, sugars, alcohols, etc.) with a minor content of aromatic rings bearing carboxylic and phenolic groups. Sugars and sugar-alcohols are an important class of primary WSOCs in the atmospheric aerosol particles. Anhydrosaccharides (e.g., levoglucosan, mannosan and galactosan) are the pyrolysis products of cellulose and hemicellulose (Fraser and Lakshmanan, 2000; Simoneit et al., 2003, 2004a; Wang et al., 2009a, c).

- Other sugars (e.g., glucose, fructose and sucrose) and sugar-alcohols (e.g., arabitol, mannitol, and inositol) are the metabolic products of biota including pollen, spores, fungi, algae and bacteria in soil (Wang et al., 2009b). Sizes of those primary aerosols range from a few tens of nanometers to hundreds of micrometers (Carvalho et al., 2003; Wang et al., 2009c). Dicarboxylic acids and related compounds are another im-
- <sup>20</sup> portant class of WSOCs in the atmosphere, major portion of which results from photooxidation of organic precursors and are, thus, considered, in general, as secondary products (Blando et al., 1998; Claeys et al., 2007; Glasius et al., 2000; Kawamura and Yasui, 2005; Wang et al., 2009b).

Numerous studies have demonstrated that chemical and physical properties of at-<sup>25</sup> mospheric aerosols are area and location-specific (Greenwald et al., 2007; Pierce and Katz, 1975; Venkataraman et al., 2002; Yoshizumi and Hoshi, 1985). For a better understanding of the relationships between East Asian aerosols and their climate impacts, it is necessary to investigate differences in the chemical and physical characteristics of organic aerosols in the urban, mountain and marine atmosphere over East Asia. In the





current study, we first report the difference in the composition and concentration of the primary and secondary WSOCs in the three types of atmospheric environments, then discuss the difference in their size distributions and sources.

#### 2 Experiment

### 5 2.1 Sample collection

Baoji is a mid-scale city located in central China with a population of 0.75 million (Fig. 1). The sampler was set on the rooftop of a three-floor building at the Environment Monitoring Station of Baoji, which is located in the urban centre. Winter sampling was performed on 11–14 January and 12–20 February 2008, while spring sampling was
conducted on 12–24 April 2008. Size-segregated mountain aerosols were collected on the mountaintop (an elevation of 1534 m a.s.l.) of Mt. Tai located in the central North China Plain, which faces the East China Sea, Korean Peninsula and Japanese Islands (Fig. 1). The mountain sampling was performed for 12 days (12–24 January 2008) in the winter on the square in front of the Meteorological Station located on the mountain-15 top. Size-segregated marine aerosols were collected from 18 March to 12 April 2008

top. Size-segregated marine aerosols were collected from 18 March to 12 April 2008 at Cape Hedo, Okinawa Island, Japan (Fig. 1). There is no major industry on the island and local anthropogenic activities are insignificant.

Size-segregated aerosols at the urban and mountain sites were collected using Andersen 8-stage air sampler (Thermoelectronic Company, USA) with the cutoff points at

- <sup>20</sup> 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4  $\mu$ m at an airflow rate of 28.3 L min<sup>-1</sup> (filter size  $\phi$ 90 mm). On the other hand, the marine size-resolved aerosols were collected on precombusted quartz filters ( $\phi$ 80 mm) by using another type of Andersen 8-stage sampler (Tokyo Dylec Company, Japan) at a flow rate of 100 L min<sup>-1</sup> with cutoff points at 11.3, 7.0, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4  $\mu$ m. All the collected samples were stored at -20 °C
- <sup>25</sup> before analysis. Information including dates, sample numbers, sampling durations and particle concentrations is shown in Table 1.





## 2.2 Sample extraction, derivatization and GC/MS analysis

Detailed methods for extraction, derivatization and gas chromatography/mass spectrometer (GC/MS) analysis are described elsewhere (Wang et al., 2009d). Briefly, aliquots of the sample and blank filter were extracted with a mixture of dichloromethane

<sup>5</sup> and methanol (2:1, v/v) under ultrasonication. The extracts were concentrated to dryness and reacted with BSTFA at 70 °C for 3 h. Finally, the derivatives were diluted with *n*-hexane prior to GC/MS determination.

GC/MS analysis of the derivatized fraction was performed using a Hewlett-Packard 6890 GC coupled to a Hewlett-Packard 5973 MSD. The GC separation was carried out on a DB-5MS fused silica capillary column with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min<sup>-1</sup> and then to 300 °C at 5 °C min<sup>-1</sup> with final isothermal hold at 300 °C for 16 min. The sample was injected in a splitless mode at

- an injector temperature of 280°C, and scanned from 50 to 650 Daltons using electron impact (EI) mode at 70 eV. GC/MS response factors were determined using authentic standards. Average recoveries of the target compounds were better than 80%.
- No serious contamination was found in the field blanks. Here, we focus on chemical compositions and size distributions of water-soluble organic compounds, i.e., sugars, sugar-alcohols, and dicarboxylic and aromatic acids, while those of water-insoluble organic compounds in the samples have been reported in a companion paper (Wang et al., 2009d).

# 3 Results and discussion

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# 3.1 Compositions and size distributions of primary WSOCs

Concentrations of water-soluble organic compounds in the impactor stages with cutoff points less than 2.1  $\mu$ m and larger than 2.1  $\mu$ m were summed up in Table 2 as fine (<2.1  $\mu$ m) and coarse (≥2.1  $\mu$ m) modes, respectively. Among the sugar and sugar-





alcohol class, levoglucosan shows concentrations to be 1–3 orders of magnitude higher than other compounds in the fine and coarse particles at the urban and mountain sites, accounting for 70–90% of the primary WSOCs. Levoglucosan on the fine mode at the marine site is much more abundant than other sugars and sugar-alcohols, but its

- <sup>5</sup> concentrations on the coarse mode are much less than the primary WSOCs (Table 2). Ambient concentration of levoglucosan in the urban air is around one order of magnitude higher than that in the mountain air and three orders of magnitude higher than that in the marine atmosphere, indicating a dilution process of biomass burning emissions during the transport from the continental sites to the marine region.
- Figure 2 illustrates the size distributions of levoglucosan and glucose in the three types of atmospheric environments. Levoglucosan showed a unimodal distribution with a peak at the size range of 0.7–1.1 µm for all the samples (Fig. 2a–c). Levoglucosan is a dehydrated sugar produced by pyrolysis of cellulose-containing materials. It is initially emitted from the flame as gaseous molecule cluster and subsequently condenses onto
- pre-existing particles as the temperature decreases, thus, it exists mostly in fine particles. In contrast, glucose showed a bimodal size distribution in the urban and mountain air, peaking at 0.7–2.1 and >3.1  $\mu$ m ranges, and a unimodal distribution in the marine atmosphere, peaking at the size >2.1  $\mu$ m (Fig. 2d–f). Other sugars and sugar-alcohols showed a size distribution pattern similar to glucose in the three atmospheric environ-
- <sup>20</sup> ments. Sugars, except for anhydrosaccharides, and sugar-alcohols mostly originate from pollen and metabolic products of biota in soil. Therefore, they are enriched in coarse particles and are more abundant in spring than in winter due to enhanced biological activity and soil resuspension by agricultural practice. We found that sugars (e.g., glucose, Fig. 2d) and sugar-alcohols (e.g., arabitol and mannitol) in the fine mode
- <sup>25</sup> abundantly existed in the urban aerosols, but diminished in the mountain air and almost disappeared in the marine atmosphere. Such a phenomenon on the primary WSOCs that exist abundantly in fine particles has broadly been observed at many locations in the world (Carvalho et al., 2003; Ion et al., 2005; Kourtchv et al., 2008; Yttri et al., 2007).





The origins of glucose and related sugars and sugar-alcohols in fine particles are unclear, but we assume that glucose, arabitol and mannitol in fine particles are probably the hydrolysis products of levoglucosan and other dehydrated saccharides (e.g., galactosan and mannosan). Fraser and Lakshmanan (2000) found that levoglucosan does not undergo acid-catalyzed hydrolysis under typical atmospheric conditions. How-5 ever, we feel that their results may be wrong, because the sulfuric acid concentration  $(0.5 \,\mathrm{g \, L^{-1}})$  they used to simulate the aqueous chemistry of atmospheric droplets is too low. In fact, fine particles especially those with a diameter less than  $1 \mu m$  are very acidic. For example, at 25 °C pure sulfuric acid water droplets (Dp > 100 nm) contain 42.5 wt % H<sub>2</sub>SO<sub>4</sub> under a relative humidity (RH) condition of 50% (Seinfeld and Pan-10 dis, 1998). Helle et al. (2007) found that levoglucosan and cellobiosan can easily be hydrolyzed into glucose by 25 wt % sulfuric acid at 110 °C. Such a hydrolysis probably occurs in an aqueous phase of a fine aerosol under a typical atmospheric condition, resulting in glucose and related sugar-alcohol (e.g., arabitol and mannitol) abundantly in fine mode aerosols, although the fragmentation of aerosols derived from pollen, fungi 15 and other biota can not be ruled out.

# 3.2 Compositions and size distributions of secondary WSOCs

In general, oxalic acid is the dominant aliphatic diacid species in the atmosphere, followed by malonic (C<sub>3</sub>), succinic (C<sub>4</sub>), glutaric (C<sub>5</sub>) and azelaic (C<sub>9</sub>) acids. Oxalic acid
is somewhat depleted because of the volatility of the trimethylsilyl ester derivatized in this study compared to the previous data (Wang et al., 2009b; Wang and Kawamura, 2005). Malonic acid co-eluted with other unknown compounds in the GC-MS analysis (Simoneit et al., 2004b; Wang and Kawamura, 2005). Therefore, the data of both compounds are omitted here. Instead, diacids with a longer carbon chain (i.e., ≥C<sub>4</sub>), hydroxylated acids (i.e., glyceric and malic acids) and aromatic acids were determined. Thirteen organic acids in total were quantified in the size-resolved samples (Table 2).

These acids are mostly derived from photochemical oxidation of precursor organics in the atmosphere and, thus, grouped as secondary organic compounds (Table 2).





Among the secondary organic aerosols (SOA) in the urban and mountain air, phthalic acid showed the highest concentration during winter and spring, followed by succinic, malic, azelaic and glutaric acids. Phthalic acid is a photo-oxidation product of aromatic compounds such as naphthalene and *o*-xylene (Kawamura and Ikushima, 1993). Such

<sup>5</sup> a molecular compositions of SOA at the urban and mountain sites indicates a significant pollution caused by anthropogenic activities.

However, the SOA composition is different in the marine atmosphere, where malic and succinic acids are dominant; being 2 times more abundant than phthalic acid (Table 2). Succinic and malic acid are believed to originate from the oxidation of unsaturated fatty acids (Kawamura and Ikushima, 1993; Rogge et al., 1993). Therefore, such

- <sup>10</sup> rated fatty acids (Kawamura and Ikushima, 1993; Rogge et al., 1993). Therefore, such a change in the SOA compositions suggests a significant dilution of anthropogenic pollutants and a continuous photochemical oxidation of organic precursors to produce malic and succinic acids during the long-range transport of organic precursor from East Asia to the North Pacific. Glyceric, malic, succinic ( $C_4$ ) and glutaric ( $C_5$ ) acids in all the
- size-segregated samples showed a strong correlation with each other (Fig. 3). Such site- and size-independent linear correlations of glyceric acid with malic acid and  $C_4$ with  $C_5$  imply that they may be produced via similar photochemical pathways.

In a previous study on chemical compositions of smoke particles from wheat straw burning (Wang et al., 2010), we found high concentrations of dicarboxylic acids such as

- <sup>20</sup> succinic, glutaric and azelaic acids in the range of 0.7–2.1 μm with a small amount of malic, maleic and fumaric acids in the smoke particles. Kawamura and Kaplan (1987) also found dicarboxylic acids in vehicular exhausts. However, these primary diacids are relatively minor in the atmosphere, and the major fraction is secondarily formed via photochemical oxidation of gaseous precursors (Kawamura and Yasui, 2005). There-
- fore, it is reasonable that glyceric, malic and succinic acids showed a unimodal size distribution peaking at the range of 0.7–1.1  $\mu$ m for all the samples (Figs. 4 and 5). In contrast, azelaic acid displayed different patterns among the three sample types; the urban samples showed a unimodal distribution with a peak at 0.7–1.1  $\mu$ m, the mountain samples showed a bimodal pattern with a major peak at the range 0.7–1.1  $\mu$ m and a





minor peak at the range  $4.7-5.8 \,\mu$ m, and the marine samples showed a bimodal distribution with two equivalent peaks at the sizes of  $0.7-1.1 \,\mu$ m and  $3.3-4.7 \,\mu$ m (Fig. 5d–f). Other marine aerosol studies also found a similar biomodal distribution pattern for azelaic acid in the North Pacific atmosphere (Miyazaki et al., 2010; Mochida et al., 2007).

- Azelaic acid is believed to be the photo-oxidation product of unsaturated fatty acid C<sub>18:1</sub> (Kawamura and Gagosian, 1987), which enriches in fine particles in urban area mostly due to cooking emissions and in coarse particles (i.e., sea salt) in marine region due to sea wave splashing. Therefore, azelaic acid is much more abundant on coarse mode in the marine samples compared to the urban and mountain samples (Fig. 5d–f).
- Benzoic, phthalic and salicyclic acids are photo-oxidation products of anthropogenic precursors such as toluene, xylene and naphthalene (Kawamura and Ikushima, 1993). These aromatic acids, except for benzoic acid, showed a unimodal size distribution in the urban, mountain and marine aerosols with a peak at 0.7–1.1 μm. Due to the high volatility, benzoic acid in fine particles can evaporate into the air and then condense onto coarse particles that contain alkaline metals such as K, Na and Ca, thus, this acid presented a bimodal size distribution in all the samples (Fig. 6a–c). Such an evaporation/adsorption effect was also observed in our previous study on PAHs in the three types of atmosphere (Wang et al., 2009d).

# 3.3 Geometric mean diameter of WSOCs

To further recognize the difference in the size distributions of the WSOCs in the three environments, we calculated the geometric mean diameter (GMD) of the fine (<2.1 µm) and coarse (≥2.1 µm) modes for all the measured species (Table 3). In the urban atmosphere, concentrations of levoglucosan and the secondary WSOCs at the size of 1.1–2.1 µm are higher in winter than in spring, indicating an enhanced coagulation effect under favourable meteorological conditions in winter (e.g., development of inversion layer) in addition to the difference in their sources, leading to GMD in fine mode to be larger in winter than in spring (Table 3). Such a coagulation effect is more significant in the urban region than in the mountain and marine areas because the coagulation effect.</p>





fect is a function of particle concentration (Hinds, 1999), resulting the fine mode GMDs of most WSOCs to be largest in the urban air and smallest in the marine air during the same season (Table 3).

However, levoglucosn and the secondary WSOCs, except for azelaic and benzoic
acids, showed the largest GMDs values in the coarse mode in the marine aerosols and the smallest values in the urban aerosols, which can be explained by an enhanced hygroscopic growth of the particles due to higher humidity in the mountain and marine environments. Abundance of the secondary WSOCs relative to the primary WSOCs in the urban aerosols are higher in winter than in spring. They are also higher at the marine site than those at the two continental sites, suggesting an enhanced aerosol aging

in the marine atmosphere. Compared to those in the urban and mountain samples, the size distribution patterns of all the WSOCs in the marine samples shifted toward larger size range, which is most likely caused by the hygroscopic growth of particles due to high humidity of the marine atmosphere.

#### 15 4 Summary and conclusion

Molecular compositions and size distributions of primary (i.e., sugars and sugaralcohol) and secondary (i.e., dicarboxlic acids and related compounds) WSOCs were characterised in the urban, mountain and marine aerosols over East Asia. WSOCs in the urban and mountain areas are dominated by levoglucosan. In contrast, WSOCs

- <sup>20</sup> in the marine air are dominated by malic and succinic acids, suggesting a continuous photo-oxidation of organic precursors to produce secondary organic aerosols. Sugars and sugar-alcohols excluding levoglucosan in the urban and mountain atmospheres presented a bimodal size distribution (i.e., accumulation mode and coarse mode) with two peaks at the sizes of 0.7–2.1  $\mu$ m and >3.1  $\mu$ m, whereas a unimodal size distribution
- $_{25}$  tion (i.e., coarse mode) of the WSOCs was found in the marine air with a peak at the range larger than 3.1  $\mu m$ . Primary WSOCs in the coarse mode are largely derived from biogenic origins, whereas those in the fine mode may originate from acid-catalyzed hy-





drolysis of anhydrosaccharides. Levoglucosan and all the secondary WSOCs, except for azelaic and benzoic acids, showed a unimodal distribution with a peak at 0.7–2.1  $\mu m$  in the three types of aerosol samples.

GMDs of fine mode in the urban aerosols are larger than those in the mountain and <sup>5</sup> marine regions, and also larger in winter than in spring, mainly due to an increased coagulation of fine particles in the urban air, especially in winter due to development of inversion layer. However, GMDs of levoglucosan and the secondary WSOCs in the coarse mode are largest in the marine air and smallest in the urban air, which is probably caused by an enhanced hygroscopic growth of the particles due to higher 10 humidity in the marine atmosphere.

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**Table 1.** Sampling information during the 2008 Campaign.

Site	Season	Date	Duration of each sampling	Number of sample sets	TSP <sup>a</sup> μg m <sup>-3</sup>
Urban (Baoji, China)	Winter	01/11-14, 02/12-20	4 days	3	316±76
	Spring	04/12-24	4 days	3	286±150
Mountain (Mt. Tai, China)	Winter	01/12-24	4 days	3	102±60
Marine (Okinawa Is. Japan)	Spring	03/18-04/12	3-5 days	5	ND <sup>b</sup>

<sup>a</sup> TSP: total suspended particles, the sum of particle concentration on all stages of the impactor; <sup>b</sup>ND: not determined.

**Table 2.** Concentrations of water-soluble organic compounds in the fine (<2.1  $\mu$ m) and coarse (≥ 2.1  $\mu$ m) particles from the urban, mountain and marine atmosphere over East Asia, ng m<sup>-3</sup>.

		Url	ban		Mour	ntain	Ма	Marine			
	Winter		Spr	Spring		ter	Sp	Spring			
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse			
I. Primary Water-soluble Organic Compound											
PM <sup>a</sup> , μg m <sup>-3</sup>	203±45	113±35	124±57	162±93	54±38	48±23	NA <sup>b</sup>	NA <sup>b</sup>			
Levoglucosan	729±42	210±37	336±97	51±14	90±42	13±7.7	2.7±1.7	0.8±0.2			
Fructose	$5.0 \pm 4.1$	$5.6 \pm 3.6$	10±4.0	11±2.3	0.6±0.3	1.6±1.5	0.0±0.0	11±6.6			
Glucose	16±2.6	11±6.3	7.9±1.9	25±3.3	1.4±0.7	3.1±2.8	0.2±0.3	17±10			
Sucrose	4.1±1.6	12±9.1	1.5±0.5	43±23	0.2±0.2	1.4±1.0	$0.0 \pm 0.0$	31±7.5			
Trehalose	0.3±0.3	5.7±4.6	0.2±0.2	$11 \pm 4.1$	0.0±0.1	2.5±1.7	$0.0 \pm 0.0$	5.8±2.1			
Arabitol	11±2.1	5.2±2.9	2.2±0.4	$11 \pm 5.0$	0.4±0.2	1.8±1.5	$0.0 \pm 0.0$	3.4±3.1			
Mannitol	3.8±0.9	4.3±2.9	1.1±0.4	$11 \pm 4.1$	$0.0 \pm 0.0$	2.1±2.0	$0.0 \pm 0.0$	4.5±3.1			
Inositol	$4.1 \pm 1.1$	0.8±0.3	3.1±0.8	1.2±0.4	0.2±0.1	0.2±0.2	$0.0 \pm 0.0$	0.4±0.2			
Glycerol	80±21	20±6.7	51±25	22±11	6.1±2.4	4.4±2.0	0.3±0.2	2.2±0.8			
Subtotal	854±69	275±70	413±125	186±50	99±46	30±20	3.3±1.6	75±27			
Subtotal/PM, %	1.8±0.3	1.2±0.1	1.5±0.5	0.7±0.2	$0.9 \pm 0.4$	0.3±0.1	NA <sup>b</sup>	NA <sup>b</sup>			
	II. Secondary Water-Soluble Organic Compounds										
Glyceric acid	31±16	5.0±2.7	16±4.8	3.1±1.9	6.3±4.8	1.0±1.1	2.7±1.2	1.2±0.3			
Malic acid	32±20	3.7±3.4	40±16	3.7±2.3	10±8.8	0.6±0.8	14±5.1	2.1±0.7			
Succinic acid	87±35	24±11	49±5.3	22±10	23±15	10±8.0	8.6±2.6	6.8±1.0			
Glutaric acid	39±17	10±5.6	17±2.2	9.4±3.7	12±8.6	6.9±6.3	1.4±0.5	2.3±0.5			
Azelaic acid	46±17	13±7.0	26±5.1	15±3.1	7.6±5.0	1.8±1.6	0.9±1.2	0.5±0.8			
Maleic acid	2.3±0.7	1.2±0.3	1.5±0.2	0.9±0.2	1.2±0.8	0.6±0.3	0.1±0.0	0.1±0.0			
Fumaric acid	23±7.2	4.4±1.6	8.5±1.5	3.4±1.6	6.2±4.6	2.1±2.0	1.9±0.5	$1.0 \pm 0.1$			
Benzoic acid	10±2.6	5.7±1.2	4.1±1.4	$3.6 \pm 1.5$	5.6±2.9	3.5±1.6	0.3±0.1	0.4±0.2			
Phthalic acid	102±26	47±19	46±8.0	32±14	62±52	26±16	6.0±4.1	1.7±1.0			
Isophthalic acid	7.5±3.5	1.4±0.8	2.8±0.8	0.7±0.5	2.9±2.6	0.7±1.0	0.4±0.3	0.1±0.1			
Terehthalic acid	101±48	52±26	50±13	21±7.1	30±23	8.2±7.4	2.4±1.7	0.6±0.3			
m-Salicyclic acid	14±5.8	3.2±1.6	2.7±0.9	0.9±0.3	1.4±0.7	0.3±0.2	0.1±0.0	$0.0 \pm 0.0$			
p-Salicyclic acid	28±13	19±23	4.7±1.6	2.0±0.5	4.4±2.4	0.8±0.7	0.1±0.1	0.1±0.0			
Subtotal	523±197	190±89	267±52	118±46	173±129	62±47	39±149	17±2.3			
Subtotal/PM, %	0.3±0.1	0.2±0.0	0.2±0.1	0.1±0.0	0.3±0.1	0.1±0.0	NA <sup>b</sup>	NA <sup>b</sup>			

<sup>a</sup> PM: particle mass, <sup>b</sup> NA: not available.





**Table 3.** Geometric mean diameter (GMD<sup>*a*</sup>,  $\mu$ m) of water-soluble organic compounds in the fine (<2.1  $\mu$ m) and coarse (≥2.1  $\mu$ m) particles and the whole range of impactor particles size (total) in the urban, mountain and marine atmosphere over East Asia.

	Urban (Baoji, China)					Mountain (Mt. Tai, China)			Marine (Okinawa Is., Japan)			
	Winter (n = 3) Spring (n = 3)		)		Winter $(n = 3)$	)	Spring $(n = 5)$					
	Fine	Coarse	Total	Fine	Coarse	Total	Fine	Coarse	Total	Fine	Coarse	Total
I. Primary water-soluble organic compounds												
Levoglucosan	0.89±0.03	3.46±0.16	$1.21 \pm 0.02$	0.76±0.04	3.52±0.05	0.94±0.09	0.80±0.07	3.72±0.16	0.97±0.14	0.74±0.08	4.05±0.63	1.17±0.23
Fructose	0.63±0.37	6.20±1.01	2.80±1.78	0.68±0.03	8.54±1.05	2.66±0.78	1.04±0.55	7.61±0.99	3.91±1.95	Nd <sup>b</sup>	14.2±0.82	14.2±0.82
Glucose	1.00±0.03	5.74±1.23	2.06±0.55	0.81±0.09	6.47±0.42	3.93±0.68	0.98±0.26	6.67±0.37	3.46±1.12	Nd <sup>b</sup>	9.89±0.60	9.89±0.60
Sucrose	$0.99 \pm 0.04$	7.08±0.49	$3.85 \pm 1.45$	0.82±0.10	$11.0 \pm 0.14$	9.92±0.58	0.69±0.30	7.38±0.21	5.01±1.42	Nd <sup>b</sup>	14.7±0.49	14.7±0.49
Trehalose	Nd <sup>b</sup>	6.01±0.88	5.26±1.77	Nd <sup>b</sup>	5.76±0.51	5.63±0.49	Nd <sup>b</sup>	6.86±0.17	6.69±0.46	Nd <sup>b</sup>	10.7±1.93	10.7±1.93
Arabitol	$1.01 \pm 0.06$	4.72±1.03	1.67±0.31	0.87±0.04	6.20±0.45	4.45±0.59	0.88±0.15	6.78±0.73	4.37±0.95	Nd <sup>b</sup>	7.76±1.20	7.76±1.20
Mannitol	0.97±0.07	5.36±0.96	$2.35 \pm 0.68$	0.81±0.05	5.71±0.14	4.72±0.30	Nd <sup>b</sup>	7.18±1.30	7.18±1.30	Nd <sup>b</sup>	7.65±1.32	7.65±1.32
Inositol	0.82+0.06	$5.15 \pm 0.96$	$1.11 \pm 0.05$	0.67+0.05	7.56+0.44	1.32+0.02	0.89+0.61	6.44+1.06	2.73+1.66	Nd <sup>b</sup>	12.2+0.87	12.2+0.87
Glycerol	0.88±0.05	5.20±1.64	1.25±0.12	0.72±0.05	5.58±0.28	1.39±0.32	0.66±0.06	7.14±0.93	1.77±0.26	1.02±0.52	7.57±1.17	5.76±1.19
				II Sec	ondary water	-soluble organ	nic compounds					
Glyceric acid	$1.04 \pm 0.07$	3.41±0.58	$1.22 \pm 0.10$	0.80±0.05	4.28±0.19	1.05±0.13	0.80±0.20	4.60±1.72	1.04±0.26	0.80±0.10	5.18±0.38	1.52±0.51
Malic acid	1.04±0.07	3.96±0.94	1.18±0.13	0.79±0.02	4.76±0.19	0.93±0.10	0.80±0.23	4.77±1.95	0.90±0.22	0.71±0.06	6.51±0.92	1.03±0.34
Succinic acid	0.99±0.07	4.26±0.20	$1.35 \pm 0.07$	0.90±0.05	4.67±0.31	1.50±0.23	0.88±0.12	5.42±0.37	1.52±0.30	0.88±0.05	5.27±0.27	2.01±0.38
Glutaric acid	1.01±0.07	4.18±0.23	1.34±0.07	0.87±0.06	4.92±0.16	1.61±0.21	0.85±0.13	5.70±0.15	1.64±0.34	0.80±0.22	5.19±0.17	2.57±0.64
Azelaic acid	0.90±0.08	4.01±0.32	1.24±0.05	0.76±0.03	5.13±0.23	1.52±0.06	0.83±0.15	5.48±0.86	1.17±0.31	0.61±0.10	3.54±0.22	1.12±0.15
Maleic acid	0.88±0.07	4.79±0.53	1.59±0.06	0.78±0.05	4.32±0.47	1.53±0.26	0.79±0.17	4.87±0.35	1.46±0.14	0.80±0.10	4.78±0.60	1.80±0.21
Fumaric acid	1.00±0.03	3.91±0.47	1.24±0.07	0.81±0.04	4.52±0.05	1.31±0.18	0.83±0.16	5.61±0.54	1.30±0.31	0.75±0.04	4.99±0.34	1.48±0.40
Benzoic acid	0.85±0.02	5.46±0.55	1.67±0.18	0.72±0.02	6.69±0.70	2.03±0.25	0.78±0.06	5.32±0.25	1.68±0.07	0.67±0.06	6.31±0.11	2.28±0.25
Phthalic acid	0.97±0.04	4.75±0.27	1.59±0.06	0.81±0.07	4.72±0.69	1.67±0.40	0.80±0.10	5.13±0.65	1.57±0.36	0.74±0.03	5.11±0.54	1.24±0.28
Isophthalic acid	1.01±0.03	3.76±0.43	1.23±0.08	0.81±0.09	4.19±0.14	1.14±0.23	0.88±0.13	5.34±0.64	1.23±0.31	0.77±0.03	5.72±1.17	1.59±0.68
Terephthalic acid	1.09±0.05	3.62±0.22	1.64±0.04	0.99±0.05	3.64±0.11	1.46±0.12	0.97±0.11	3.65±0.10	1.29±0.14	0.89±0.07	4.41±0.82	1.32±0.21
m-Salicyclic acid	0.97±0.03	3.61±0.18	1.23±0.03	0.74±0.12	4.41±0.15	1.17±0.11	0.86±0.09	4.55±0.43	1.13±0.20	0.74±0.03	5.18±0.29	1.52±0.44
p-Salicyclic acid	0.98±0.02	3.51±0.52	1.45±0.25	0.73±0.10	4.78±0.08	1.28±0.06	0.84±0.11	4.56±0.46	1.07±0.18	0.73±0.04	6.52±0.48	1.90±0.28

<sup>a</sup> logGMD=( $\sum C_i \log Dp_i$ )/ $C_i$ , where  $C_i$  is the concentration of compound in size *i* and  $Dp_i$  is the geometric mean particle diameter (Hinds, 1999); <sup>b</sup> Nd: not determined.



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Fig. 1. A map description for the sampling sites and surroundings.

























Fig. 5. Size distributions of succinic and azelaic acids in the urban, mountain and marine atmosphere.









