Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in airborne particles during a severe urban haze event caused by wheat straw burning

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ABSTRACT

Molecular compositions and size distributions of water-soluble organic compounds (WSOC, i.e., sugars, sugar-alcohols and carboxylic acids) in particles from urban air of Nanjing, China during a severe haze event caused by field burning of wheat straw were characterized and compared with those in the summer and autumn non-haze periods. During the haze event levoglucosan (4030 ng m^{-3}) was the most abundant compound among the measured WSOC, followed by succinic acid, malic acid, glycerol, arabitol and glucose, being different from those in the non-haze samples, in which sucrose or azelaic acid showed a second highest concentration, although levoglucosan was the highest. The measured WSOC in the haze event were 2–20 times more than those in the non-hazy days. Size distribution results showed that there was no significant change in the compound peaks in coarse mode (>2.1 μm) with respect to the haze and non-haze samples, but a large difference in the fine fraction (<2.1 μm) was found with a sharp increase during the hazy days mostly due to the increased emissions of wheat straw burning. Molecular compositions of organic compounds in the fresh smoke particles from wheat straw burning demonstrate that sharply increased concentrations of glycerol and succinic and malic acids in the fine particles during the haze event were mainly derived from the field burning of wheat straw, although the sources of glucose and related sugar-alcohols whose concentrations significantly increased in the fine haze samples are unclear. Compared to that in the fresh smoke particles of wheat straw burning an increase in relative abundance of succinic acid to levoglucosan during the haze event suggests a significant production of secondary organic aerosols during transport of the smoke plumes.

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1. Introduction

Biomass burning emissions make a significant contribution to particulate organic matter in the troposphere (Crutzen and Andreae, 1990; Mayol-Bracero et al., 2002; Mazzoleni et al., 2007). A major fraction of these organic aerosols are water-soluble, and composed of a highly complex mixture of compounds with difference in molecular compositions and physicochemical properties (Graham et al., 2002). These water-soluble organic compounds (WSOC) have a significant impact on climate effects by altering the cloud condensation nuclei activity of aerosol (Fuzzi et al., 2007; Gao et al., 2003; Koren et al., 2004; Martin et al., 2010); the abundant WSOC within the smoke particles may play an important role in the aqueous phase chemistry occurring within cloud droplet nucleated smoke (Fuzzi et al., 2006; Tuckermann and Cammenga, 2004). Moreover, some of WSOC contained in the smoke are surfactant and have an adverse effect on human health by increasing the solubility of toxic pollutants (Migliaccio et al., 2009; Sorjamaa et al., 2004).

From the end of May to the mid of June is the wheat harvesting and rice planting season in east China. In general, wheat straw is directly burned in the same field during the period. Such a massive biomass burning in rural area releases a huge amount of pollutants, which further diffuse into urban area and mix with the emissions from fossil fuel combustion, resulting in severe haze events under favorable meteorological conditions (Chameides et al., 1999; Fang

et al., 2005; Wang et al., 2009). To understand the impact of the biomass burning on urban air quality, size-resolved particles in the urban atmosphere of Nanjing, a mega-city located in east China, during the haze and non-haze periods were collected and characterized for organic aerosols. Results on water-insoluble organics in the samples have been published elsewhere (Wang et al., 2009). Here, we report the difference in molecular composition and size distribution of WSOC (i.e., sugars, sugar-alcohols and carboxylic acids) in the haze and non-haze samples, and compare with those in fresh smoke particles of wheat straw burning to discuss their sources.

2. Experimental section

2.1. Collection of ambient aerosols

Sampling protocol was described elsewhere (Wang et al., 2009). Briefly, an 8-stage sampler was set up on the rooftop of a three-floor building on the campus of Nanjing University, which is located in the urban center of Nanjing, China. Size-resolved particles were collected onto pre-combusted (450 °C, 6 h) quartz fiber filter (Whatman, Φ 90 mm) with cutoff points as 0.4, 0.7, 1.1, 2.1, 3.3, 4.7, 5.8, 9.0 μm at an airflow rate of 28.3 L min^{-1}. One set of sample collected on June 1−5, 2007 coincided with a severe haze episode occurring on June 1−3, 2007, which was caused by field burning of wheat straw in rural areas around Nanjing city (Wang et al., 2009). Other six sets of samples were collected during the summer and autumn non-haze periods (June 5−17 and Oct. 12−24, 2007). Each set was continuously collected for 4 days. After sampling, the sample was sealed in aluminum foil and stored in a freezer under −20 °C. Field blanks were also collected by mounting filters onto the sampler for about 10 min without sucking any air before and after sampling, and transported into the lab with the real samples. Meteorological conditions during the sampling periods are shown in Table 1.

2.2. Collection of fresh smoke particles of wheat straw burning

Fresh smoke particles of wheat straw burning were collected using the same size-segregated sampler as above at the airflow rate of 28.3 L min^{-1}. The sampler was fixed 1 m downwind of the exhaust outlet of a domestic fireplace. The dried wheat straw was burned at a rate of 9.0 kg h^{-1}. Temperature and relative humidity (RH) of the exhaust outlet were 20 °C and 58%, respectively, comparable to the ambient air (14 °C, 37%). The sampling was performed for 30 min to collect enough material. After sampling, the smoke filters were stored together with the above ambient samplers at −20 °C prior to analysis.

2.3. Sample extraction, derivatization and quantification

In the current study, we analyzed 72 size-segregated samples, which are one set haze samples, six sets of non-haze samples and one set for the fresh smoke of wheat straw burning, for various WSOC using following procedure.

An aliquot of the filter was cut in pieces and extracted with a mixture of methanol and dichloromethane (v/v, 2:1), concentrated

to dryness and reacted with BSTFA at 70 °C for 3 h. The derivatives were analyzed by a HP-7890 gas chromatography coupled with a 5975C mass spectrometer using a DB-5MS GC column (30 m × 0.25 mm × 0.25 μm). The GC temperature was programmed from 50 °C (2 min) to 120 °C at 15 °C min^{-1}, and then to 300 °C at 5 °C min^{-1} with a final isothermal hold at 300 °C for 10 min. The sample was injected in a splitless mode at 280 °C and scanned in EI mode at 70 eV from 50 to 650 Da. Response factors of compounds were acquired using authentic standards, which were purchased from Sigma−Aldrich Company. No target compound was found in the field blanks. Of recovery experiment, a few microgram of target compounds dissolved in the methanol/dichloromethane mixture was spiked onto a clean blank filter and dried under ambient conditions, then treated in the same manner as done for real samples (Simoneit et al., 2004c; Wang and Kawamura, 2005). Recoveries of levoglucosan, glucose, sucrose and dicarboxylic acids were better than 80% (Simoneit et al., 2004c; Wang et al., 2009, 2006). Oxalic acid was somewhat depleted due to volatile loss of its trimethylsilyl (TMS) derivatization used in this study and malonic acid in the gas chromatography co-eluted with other unknown compounds (Wang and Kawamura, 2005), thus both were not included in the current study.

3. Results and discussion

3.1. Compositions of sugars, sugar-alcohols and carboxylic acids

3.1.1. Sugars, sugar-alcohols and vanillin

Table 2 shows the ambient concentrations of WSOC, which are the sum of the compound concentration in each stage. A total

Table 1
Meteorological conditions during the sampling period.

Date	Temperature, °C	Relative humidity, %	Visibility, km	Wind speed, m s^{-1}
June 1−5	22 ± 1.7	79 ± 4.9	2.6 ± 0.9	1.0 ± 0.3
June 5−17	24 ± 1.6	66 ± 11	7.0 ± 3.0	6.0 ± 1.7
Oct. 12−24	17 ± 1.6	61 ± 8.5	7.0 ± 1.8	4.0 ± 1.8

Table 2
Ambient concentrations[a] of water-soluble organic compounds during the haze and none-haze days, ng m^{-3}.

	June 1−5	June 5−17	Oct. 12−24
	Haze (n = 1)	None-haze (n = 3)	None-haze (n = 3)
I. Sugars, sugar-alcohols and vanillin			
Levoglucosan	4030	204 ± 129	689 ± 243
Fructose	72	32 ± 2.0	32 ± 13
Glucose	186	49 ± 27	44 ± 8.3
Sucrose	68	177 ± 24	31 ± 19
Trehalose	20	21 ± 0.7	17 ± 1.9
Arabitol	195	16 ± 2.4	21 ± 3.6
Mannitol	123	26 ± 3.9	24 ± 4.2
Inositol	19	4.6 ± 0.3	7.0 ± 2.8
Glycerol	207	41 ± 4.8	44 ± 11
Vanillin	16	0.5 ± 0.2	2.8 ± 0.9
Subtotal	4938	571 ± 125	919 ± 280
II. Carboxylic acids			
Glyceric acid	123	14 ± 3.6	28 ± 6.8
Malic acid	234	68 ± 8.6	56 ± 20
Succinic acid	677	50 ± 5.7	87 ± 22
Glutaric acid	156	23 ± 5.7	40 ± 11
Azelaic acid	112	38 ± 7.8	94 ± 29
Maleic acid	4.3	0.9 ± 0.2	2.2 ± 0.4
Fumaric acid	49	8.3 ± 1.5	27 ± 2.2
Benzoic acid	11	5.8 ± 0.4	10 ± 2.5
o-Phthalic acid	112	42 ± 6.7	69 ± 10
m-Phthalic acid	7.9	2.1 ± 0.4	5.9 ± 1.6
p-Phthalic acid	47	31 ± 10	79 ± 33
m-Salicylic acid	25	1.1 ± 0.2	4.9 ± 1.9
p-Salicylic acid	42	2.4 ± 1.2	13 ± 4.7
Subtotal	1599	288 ± 40	506 ± 124
Total	6536	859 ± 163	1425 ± 404
TSP[b], μg m^{-3}	318	183 ± 17	226 ± 66
Total/TSP, %	2.1	0.5 ± 0.1	0.6 ± 0.0

[a] Ambient concentration is the sum of compound in the 9 size-resolved stages.
[b] TSP: total suspended particles.

of 23 organic compounds were determined with levoglucosan ($204-4030$ ng m^{-3}) being the most abundant for all the samples (Table 2). Concentrations of these organics ($4.3-4030$ ng m^{-3}, Table 2) in the hazy days were one order of magnitude higher those ($0.5-204$ ng m^{-3}) in the summer non-hazy days. In the haze sample, the second highest compound was glycerol (207 ng m^{-3}), followed by arabitol (195 ng m^{-3}), glucose (186 ng m^{-3}) and mannitol (123 ng m^{-3}). In contrast, during the summer non-haze period (i.e., June 5–17) sucrose (177 ± 24 ng m^{-3}) was the second highest, being 2 times higher than in the haze period, followed by glucose, glycerol and fructose. Compared to those in the summer non-hazy days, the higher concentration of levoglucosan (689 ± 243 ng m^{-3}, Table 2) during the autumn non-haze period indicates that the samples were also influenced by biomass burning emissions. However, sucrose decreased in the autumn with other sugars being comparable to those in the summer non-haze time. Sucrose is photosynthesized in leaves of plant, and accumulates in the root cells (Jaeger et al., 1999). Farmland tilling after harvesting wheat causes an enhanced exposure of soil containing wheat root to the air, thus resulting in a sharply increased sucrose during the summer non-haze period. In addition to the sugars and sugar-alcohols, vanillin (16 ng m^{-3}, Table 2) was also much more abundant during the hazy days. Vanillin is a pyrolysis product of lignin-containing materials (Simoneit, 2002), therefore, its sharply increased concentration during the event can be attributed to emissions from the wheat straw burning.

To further investigate seasonal variations in sources of the WSOC above, relative abundances of the target compounds in ambient particles (i.e., total suspended particles, TSP) are plotted in Fig. 1. Compared with that in the haze event, relative concentration of sucrose in the summer non-haze particles was much more enriched (Fig. 1a). Moreover, relative abundances of all primary sugars and sugar-alcohols were higher in the summer non-haze time than in the autumn non-haze time (Fig. 1a). Sugars and sugar-alcohols are the major form of photosynthetically assimilated carbon in the biosphere, and their sources are numerous and include microorganism, plants and animals (Bieleski, 1995; Medeiros et al., 2006). The more abundant of sugars and sugar-alcohols in the summer non-event samples are in agreement with the seasonal variations of saccharide aerosols in Maine (Medeiros et al., 2006) and Texas (Jia et al., 2010) USA, which showed an increase in concentrations of saccharides as growing season progressed and a decrease as it ended, and largely due to more significant biogenic activity in the warm season (Garg et al., 2002; Medeiros et al., 2006). The higher proportion of vanillin in Oct. relative to June shown in Fig. 1a probably suggests other woody material combustion in autumn.

3.1.2. Carboxylic acids

Biomass burning emissions are enriched in not only sugars and sugar-alcohols but also carboxylic acids and aldehydes (Nolte et al., 2001; Schauer et al., 1996; Simoneit, 2002). In addition, biomass combustion produces lots of volatile organic compounds (VOC), which can further be converted into secondary organic aerosols (SOA) via photo-oxidation processes (Claeys et al., 2010; Nolte et al., 2001; Schauer et al., 1996; Simoneit, 2002). In the haze samples, much higher concentrations of carboxylic acids were found, which were $2-16$ times higher than those in the summer non-haze samples (Table 2 and Fig. 1b). In the haze sample, succinic acid showed a highest concentration (677 ng m^{-3}, Table 2) among the measured carboxylic acids, followed by malic, glutaric, glyceric, azelaic and o-phthalic acids. On contrast, malic acid (68 ± 8.6 ng m^{-3}) was the most abundant in the summer non-hazy days, followed by succinic, o-phthalic, azelaic, p-phthalic and glutaric acids. The high concentrations of
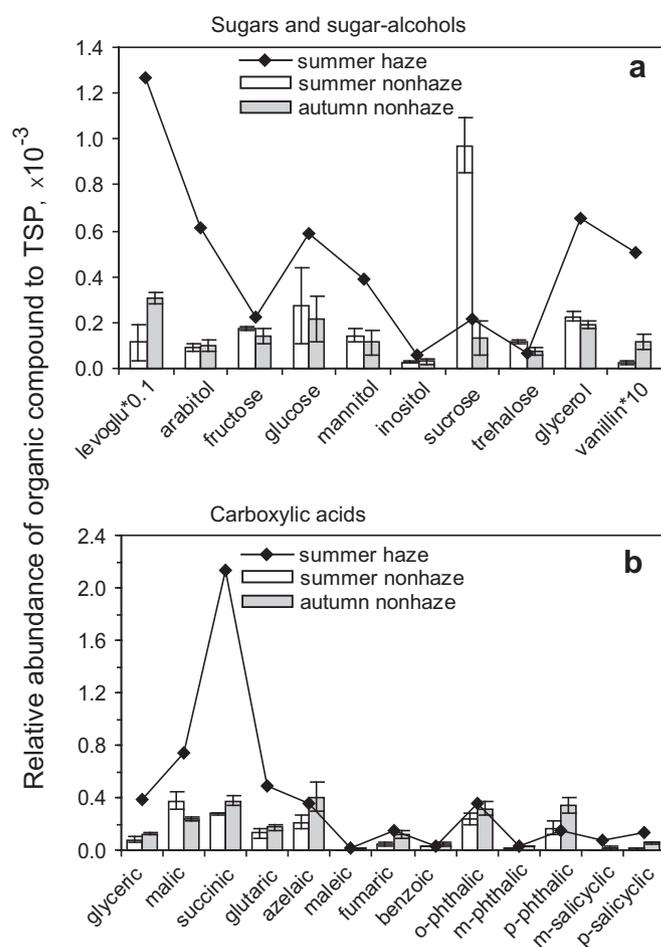
Fig. 1. Relative concentration of compounds to TSP (total suspended particles).

succinic and malic acids indicate that wheat straw burning smoke is enriched in low molecular weight dicarboxylic acids, which is consistent with the results reported by Falkovich et al. (2005) for biomass burning emissions in Rondonia, Brazil. During the autumn non-hazy days concentration (94 ± 29 ng m^{-3}, Table 2) of azelaic acid was the highest, followed by succinic, p-phthalic, o-phthalic, malic and glutaric acids. Lower molecular weight diacids such as oxalic and malonic acids may be more abundant than succinic acid (Falkovich et al., 2005), although both were not quantified because of the limitation of the analytical method used in this study.

Benzoic and o-phthalic acids are not derived from biomass burning emission but secondarily produced by photochemical oxidation of precursors such as toluene, xylene, naphthalene and other anthropogenic pollutants (Seinfeld and Pankow, 2003). Thus, concentration ratio (≈ 2, see Table 2) of the two compounds in the haze time to the summer non-haze time were much lower than other carboxylic acids. Salicylic acids are tracers of smoke from gramineae combustion (Simoneit, 2002), thus their enhanced concentrations in the haze samples can be attributable to the wheat straw burning emissions. Aromatic acids like benzoic and phthalic acids in an urban area are largely produced by photo-oxidation of anthropogenic pollutants (Seinfeld and Pankow, 2003). Thus, compared to those in the summer non-haze time, an increase in relative abundance of these aromatic acids during the autumn non-haze time indicates that the autumn aerosols were more aged (Fig. 1b).

3.2. Size distributions

To further recognize the impact of the wheat straw burning on the urban air quality, size distributions of WSOC except for levoglucosan, which has been described in our previous paper (Wang et al., 2009), during the hazy and non-hazy days are illustrated in Figs. 2 and 3. Geometric mean diameters (GMD) of the compounds in fine ($<$2.1 μm) and coarse ($\geq$2.1 μm) modes of particles are calculated and shown in Table 3.

3.2.1. Sugars, sugar-alcohols and vanillin

During the haze period, glucose, arabitol, and glycerol showed a bimodal size distribution with a major peak in the size range of 0.7–1.1 μm and a minor peak in the size $>$3.3 μm (Fig. 2a–c). In contrast, glucose and arabitol in both non-haze periods showed a bimodal pattern with a small peak in the fine mode ($<$2.1 μm) and a large peak in the coarse mode ($\geq$2.1 μm) (Fig. 2a and b), while glycerol in the two non-haze periods showed two comparable peaks in the fine and coarse ranges (Fig. 2c). Although these sugars and sugar-alcohols are derived from pollen, fungi, bacteria, spores and other biota in soil and enriched in coarse particles (Simoneit et al., 2004a), their high concentrations in fine mode during the haze episode suggest that they should be related to biomass burning emissions. For coarse mode of the sugars and sugar-alcohols, there is no significant difference in the concentration and size distribution between the hazy and the non-hazy days. Such a phenomenon is reasonable, because these coarse modes of organics originate from the natural sources mentioned above rather than biomass burning and fossil fuel combustion.

Vanillin showed a bimodal pattern with two equivalent peaks in the fine and coarse ranges during the haze and non-haze periods (Fig. 2d). Vanillin is a pyrolysis product of lignin and enriched in fine particles. However, the fine mode of vanillin may evaporate into the air due to its relatively high volatility and subsequently condense/adsorb onto the pre-existing particles. Thus, vanillin shifts from fine particles toward larger ones during transport from the rural region to the urban area, resulting in a large fraction in the coarse mode (Herner et al., 2006; Hinds, 1999; Kleeman et al., 2008).

3.2.2. Carboxylic acids

As shown in Fig. 3, most carboxylic acids in the haze sample displayed a unimodal size distribution, peaking at the size 0.7–1.1 μm (Fig. 3a, b and f), in contrast to azelaic (Fig. 3c) and o-phthalic (Fig. 3e) acids, which showed a bimodal pattern with a large peak in the fine mode ($<$2.1 μm) and a minor peak in the coarse mode ($\geq$2.1 μm). During June 5–17 and Oct. 12–24 carboxylic acids except for malic acid showed a bimodal size distribution with a large peak in the fine mode and a small/equivalent peak in the coarse mode. Carboxylic acids are abundantly found in biomass burning emitted fresh smoke, which are pyrolysis products of plant tissue (Falkovich et al., 2005). However, carboxylic acids in the urban atmosphere are mostly produced by photochemical oxidation of organic precursors with ozone, OH radical, NO_x and other oxidants (Kawamura and Yasui, 2005). These primary and secondary acids mainly stay in fine particles, but some of them have high vapor pressure (e.g., benzoic acid) and can be adsorbed onto coarse alkaline particles, leading to a large fraction in the coarse mode (Fig. 3d). The coarse mode of azelaic acid can be explained by a heterogeneous particle-phase oxidation of unsaturated fatty acids in coarse mode (e.g., $C_{18:1}$), which is emitted into the air as coarse particles by wind abrasion with plant surface (Mochida et al., 2007).

As seen in Table 3, all fine mode of WSOC showed a larger GMD in the hazy days than in the summer and autumn non-hazy days. One reason is that the particles emitted from biomass burning are larger than those emitted from fossil fuel combustion (Yang et al., 2006). Another potential reason is an enhanced hygroscopic growth of the airborne particles under relatively higher humidity (RH: 79 ± 4.9%, Table 1) during the event, because biomass burning derived particles are highly water-soluble compared with fossil fuel derived particles (Reid et al., 2005). In addition, the increased concentration of fine particles during the event may also be responsible for the larger GMDs because coagulation effect is a function of particle concentrations (Herner et al., 2006).

3.3. Comparison of the haze samples with fresh smoke aerosols of wheat straw burning

Fresh smoke samples collected by burning wheat straw in a fireplace are found to be enriched in levoglucosan, methoxyphenol, glycerol, and acetic, malic and succinic acids with negligible amount of glucose, arabitol and mannitol (Fig. 4). Glucose, arabitol and mannitol in the atmosphere are mostly derived from ablation of the phyllosphere off fresh leaf surfaces, pollen, spores, fungi and other biota in soil and exist in coarse particles (Medeiros et al., 2006; Simoneit et al., 2004b). Therefore the abundant presence of glucose, arabitol and mannitol in particles with a diameter $<$1 μm during the haze event should have other origins. Table 4 compares the relative abundance of major WSOC in the wheat straw smoke particles with those in the haze aerosols. Levoglucosan-normalized concentrations of fine mode of succinic acid and glucose in the haze samples are much higher than those in the fresh smoke particles. Fossil fuel emissions in the urban area can photochemically produce succinic acid (Kawamura and Yasui, 2005), and thus increase its relative abundance in the aged haze samples. As shown in Table 4, malic acid is much more abundant
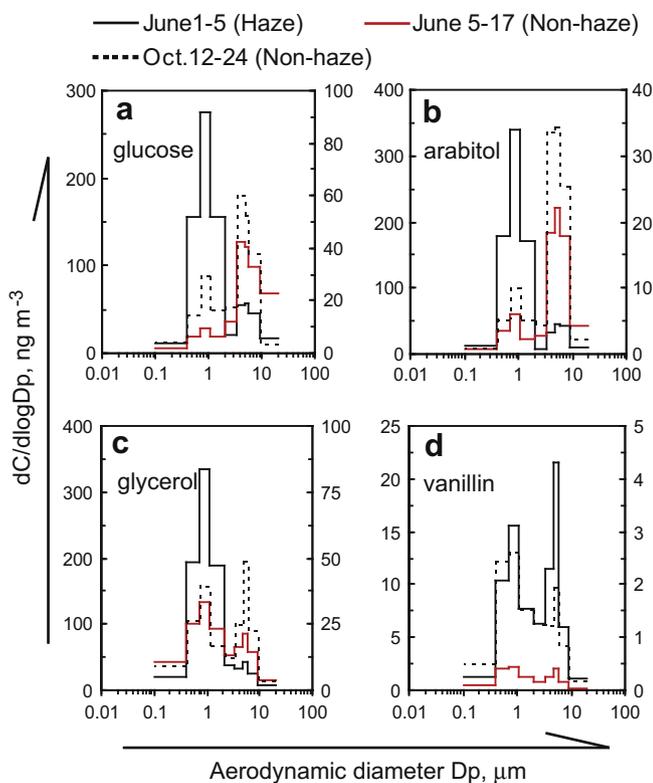
Fig. 2. Size distribution of sugars, sugar-alcohols and vanillin during the haze (June 1–5, refer to left y-axis) and the non-haze (June 5–17 and Oct. 12–24, refer to right y-axis) periods.
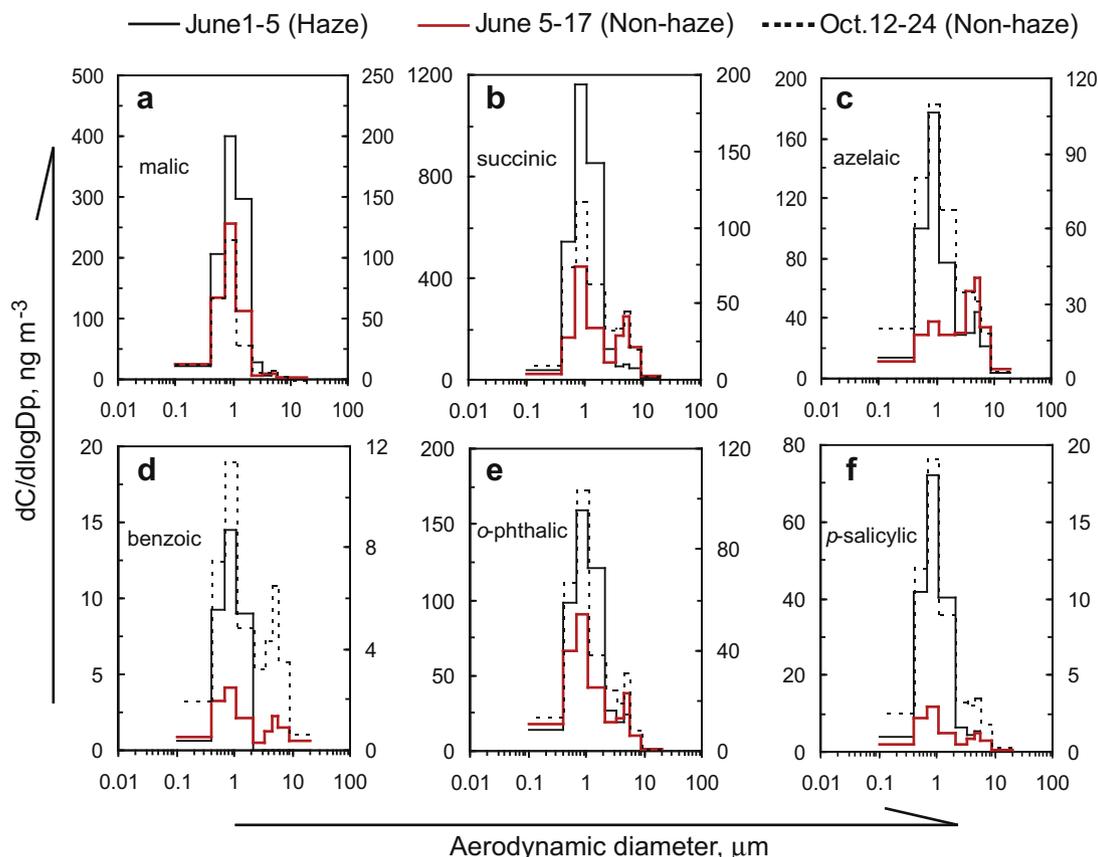
Fig. 3. Size distribution of carboxylic acids during the haze (June 1–5, refer to left y-axis) and the non-haze (June 5–17 and Oct. 12–24, refer to right y-axis) periods.

Table 3
Geometric mean diameters (GMD, μm)[a] of neutral and acidic water-soluble organics in the fine (<2.1 μm) and coarse (≥2.1 μm) modes of particles collected during the haze and non-haze periods.

| | June 1–5 (n = 1) | | June 5–17 (n = 3) | | Oct. 12–24 (n = 3) | |
| | Haze | | Non-haze | | Non-haze | |
	Fine	Coarse	Fine	Coarse	Fine	Coarse
I. Sugars, sugar-alcohols and vanillin						
Levoglucosan	0.86	3.42	0.79 ± 0.09	3.79 ± 0.19	0.76 ± 0.03	3.50 ± 0.04
Fructose	0.79	5.12	0.67 ± 0.06	5.59 ± 0.02	0.71 ± 0.04	5.02 ± 0.19
Glucose	0.87	4.85	0.77 ± 0.15	4.88 ± 0.15	0.74 ± 0.08	4.81 ± 0.13
Sucrose	0.82	5.99	0.68 ± 0.08	6.83 ± 0.14	0.84 ± 0.04	5.20 ± 0.17
Trehalose	0.92	5.30	ND[b]	5.47 ± 0.12	1.30 ± 0.49	5.20 ± 0.16
Arabitol	0.86	5.39	0.73 ± 0.14	5.26 ± 0.11	0.79 ± 0.04	5.15 ± 0.20
Mannitol	0.83	5.77	0.70 ± 0.17	5.38 ± 0.10	0.77 ± 0.04	5.32 ± 0.12
Inositol	0.81	4.71	0.62 ± 0.07	5.53 ± 0.06	0.70 ± 0.02	4.68 ± 0.08
Glycerol	0.85	4.20	0.63 ± 0.09	4.58 ± 0.63	0.61 ± 0.15	4.76 ± 0.15
Vanillin	0.78	4.51	0.69 ± 0.05	4.51 ± 0.13	0.74 ± 0.11	4.24 ± 0.16
II. Carboxylic acids						
Glyceric acid	0.91	3.72	0.74 ± 0.07	4.45 ± 0.29	0.71 ± 0.02	4.03 ± 0.11
Malic acid	0.91	3.30	0.77 ± 0.09	4.29 ± 0.10	0.68 ± 0.05	4.04 ± 0.20
Succinic acid	0.95	3.76	0.85 ± 0.08	4.83 ± 0.13	0.82 ± 0.06	4.20 ± 0.13
Glutaric acid	0.96	3.66	0.80 ± 0.10	4.90 ± 0.14	0.81 ± 0.08	4.32 ± 0.07
Azelaic acid	0.78	4.30	0.67 ± 0.08	4.56 ± 0.30	0.77 ± 0.13	4.03 ± 0.08
Maleic acid	0.90	3.95	0.69 ± 0.09	4.15 ± 0.20	0.79 ± 0.12	3.72 ± 0.26
Fumaric acid	0.91	4.32	0.72 ± 0.09	4.40 ± 0.20	0.77 ± 0.11	4.56 ± 0.43
Benzoic acid	0.88	ND[b]	0.66 ± 0.07	4.70 ± 0.09	0.67 ± 0.03	4.49 ± 0.08
o-Phthalic acid	0.85	3.91	0.67 ± 0.04	4.23 ± 0.25	0.69 ± 0.03	3.91 ± 0.25
m-Phthalic acid	0.83	3.76	0.67 ± 0.06	4.43 ± 0.15	0.69 ± 0.05	3.97 ± 0.13
p-Phthalic acid	0.81	3.53	0.79 ± 0.01	3.79 ± 0.16	0.80 ± 0.04	3.58 ± 0.19
m-Salicylic acid	0.88	3.68	0.88 ± 0.31	4.74 ± 0.20	0.79 ± 0.11	4.05 ± 0.02
p-Salicylic acid	0.85	3.93	0.65 ± 0.03	4.63 ± 0.15	0.78 ± 0.11	4.11 ± 0.08

[a] GMD: logGMD = $(\sum C_i \log Dp_i)/\sum C_i$, where C_i is the concentration of compound in size i and Dp_i is the geometric mean particle diameter collected on stage i (Hinds, 1999).
[b] ND: not detected.
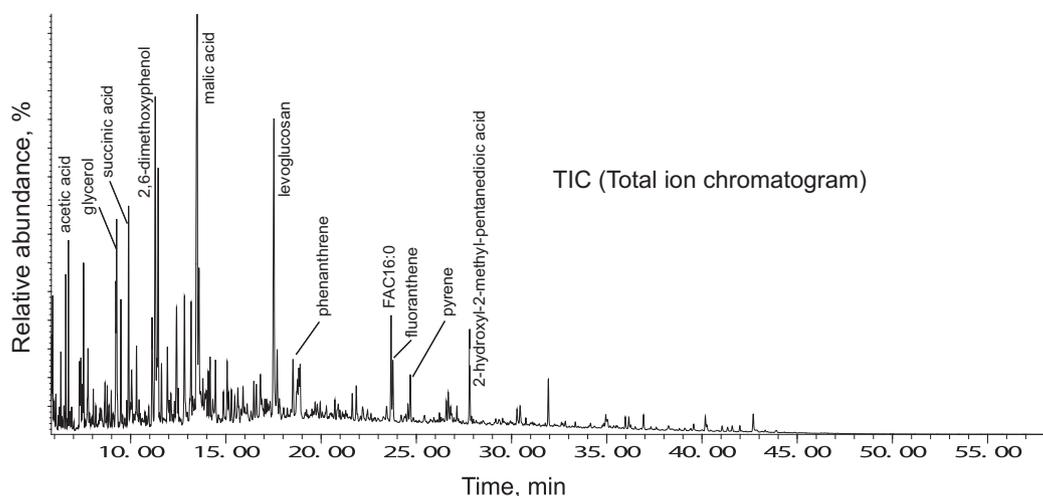
Fig. 4. GC–MS data for a total extract (TMS derivatized) of fresh smoke particles of wheat straw burning (Particle size 0.7–1.1 μm).

Table 4
Abundance of major species normalized by levoglucosan in fine (<2.1 μm) and coarse (≥2.1 μm) modes of fresh smoke particles of wheat straw burning and urban haze aerosols (%).

	Fresh smoke particles		Urban haze aerosols	
	Fine	Coarse	Fine	Coarse
Glucose	0.9	0.8	3.7	28
Glycerol	29	26	4.6	19
Malic acid	105	161	5.8	5
Succinic acid	9.1	17	16	36

change in the analyte peaks of coarse particles (>2.1 μm) with respect to the haze and non-haze samples, but a large difference in the fine fraction was found with a sharp increase during the hazy days mainly due to the increased emissions of wheat straw burning. Compared to both compounds in the fresh wheat straw burning smoke particles more abundant succinic acid than malic acid in the haze aerosols probably indicates that succinic acid is preferably formed via photochemical oxidation of organic precursors during the transport of the biomass burning emissions.

Acknowledgments

than succinic acid in the smoke particles but much less abundant than succinic acid in the haze samples. Both acids showed comparable concentrations in the urban air during the summer non-hazy period (Table 2), thus the increased succinic acid in the haze samples further suggest that during transport succinic acid is preferably formed via oxidation of precursors in the biomass burning smoke and/or more chemically stable than malic acid. In the current stage, we do not know the specific reason why glucose in the fine mode of haze aerosols is so abundant compared to those in the non-haze samples, since glucose and related sugar-alcohols in the fresh smoke samples are negligible. Abundant presence of glucose and arabitol in fine particles have also been found in many other locations in the world (Carvalho et al., 2003; Ion et al., 2005; Kourtchev et al., 2008; Yttri et al., 2007), which are proposed to be produced by secondary pathways (Carvalho et al., 2003; Pun et al., 1999) or from uncombusted biomass materials (Medeiros et al., 2006).

4. Conclusion

Molecular compositions and size distributions of airborne particulate sugars, sugar-alcohols and carboxylic acids in urban area of Nanjing during the wheat straw burning of haze and non-haze periods were characterized. During the haze event levoglucosan was the dominant compound among the measured WSOC, followed by succinic acid, malic acid, glycerol, arabitol and glucose. In contrast, during the summer and autumn non-haze periods levoglucosan was the most abundant, but sucrose or azelaic acid showed a second highest concentration, followed by malic/succinic acid and glucose. Concentrations of the determined WSOC in the hazy days were 2–20 times more abundant than those in the non-hazy days. Size distribution results showed that there was no much

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