Comparison of dicarboxylic acids and related compounds in aerosol samples collected in Xi'an, China during haze and clean periods

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HIGHLIGHTS

- Aerosols were more acidic in haze period.
- Compared to that during clean periods SOA production was enhanced during haze days.
- Mass ratio of glyoxal to methylglyoxal is indicative of aerosol ageing.

ARTICLE INFO

ABSTRACT

PM_{10} aerosols from Xi'an, a mega city of China in winter and summer, 2009 were measured for secondary organic aerosols (SOA) (i.e., dicarboxylic acids (DCA), keto-carboxylic acids, and α-dicarbonyls), water-soluble organic (WSOC) and inorganic carbon (WSIC), elemental carbon (EC) and organic carbon (OC). Molecular compositions of SOA on haze and clean days in both seasons were compared to investigate their sources and formation mechanisms. DCA in the samples were 1843 ± 810 ng m^{-3} in winter and 1259 ± 781 ng m^{-3} in summer, respectively, which is similar and even higher than those measured in 2003. Oxalic acid (C_2, 1162 ± 570 ng m^{-3} in winter and 1907 ± 707 ng m^{-3} in summer) is the predominant species of DCA, followed by t-phthalic (tPh) in winter and phthalic (Ph) in summer. Such a molecular composition is different from those in other Asian cities where succinic acid (C_4) or malonic acid (C_3) is the second highest species, which is mostly due to significant emissions from household combustion of coal and open burning of waste material in Xi'an. Mass ratios of C_2/diacids, diacids/WSOC, WSOC/OC and individual diacid-C/WSOC are higher on the haze days than on the clean days in both seasons, suggesting an enhanced SOA production under the haze condition. We also found that the haze samples are acidic while the clean samples are almost neutral. Such a difference in particle acidity is consistent with the enhanced SOA production, because acid-catalysis is an important aqueous-phase formation pathway of SOA. Gly/mGly mass ratio showed higher values on haze days than on clean day in both seasons. We comprehensively investigated the ratio in literature and found a consistent pattern. Based on our observation results and those documented data we proposed for the first time that concentration ratio of Gly/mGly can be taken as an indicator of aerosol ageing.

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1. Introduction

Water-soluble organic compounds (WSOC) are ubiquitous in the atmosphere from the planetary boundary layer to the free troposphere (Kanakidou et al., 2005), and have received great attention due to their potential abilities to affect climate (Facchini et al., 1999). Dicarboxylic acids and related compounds are an important class of WSOC (Kundu et al., 2010), accounting for 1–3% of the total organic carbon in urban areas and more than 10% of the carbon mass in remote region (Kawamura and Yasui, 2005). An intensive layer of DCA was found over cirrus cloud in Mexico Gulf and Huston region (Sorooshian et al., 2007), suggesting an importance of these compounds as cloud
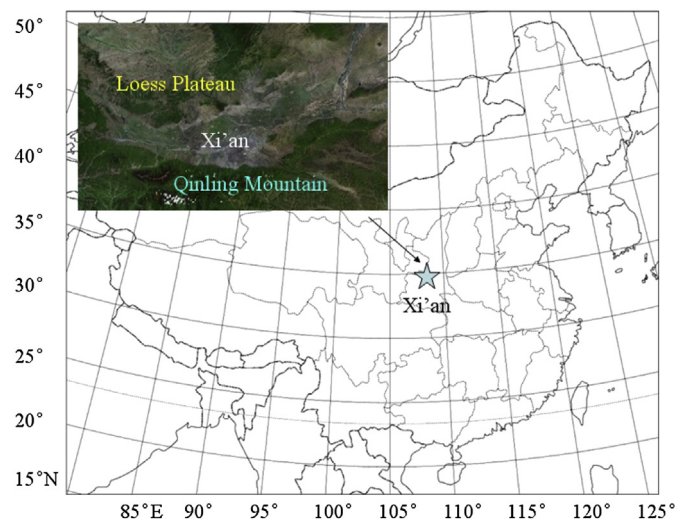
Fig. 1. Location of Xi'an in China.

condensation nuclei (CCN). DCA can be directly emitted from primary sources such as coal and biomass burning, industry activities, cooking and plants emission (Huang and Yu, 2007; Kawamura and Kaplan, 1987; Wang et al., 2011). However, it is believed that DCA in urban area is produced largely from photochemical oxidation (Myriokefalitakis et al., 2011). Oxalic acid (C_2) is the most abundant species of DCA and an end product of many organic compounds during aerosol-phase oxidation processes. Glyoxal (Gly) and methylglyoxal (mGly) are intermediates to produce C_2 (Miyazaki et al., 2009; Warneck, 2003). It was reported recently that atmospheric DCA can react with sea salt (NaCl) and produce HCl (Laskin et al., 2012), which is entirely different from the traditional knowledge. In-cloud process has been taken as a major formation pathway of oxalic acid in the global atmosphere (Warneck, 2003). However, aerosol-phase oxidation may be more important in an urban atmosphere due to cloud-free.

Researches about DCA have been conducted in many cities of the world (Aggarwal and Kawamura, 2008; Kawamura et al., 2010; Miyazaki et al., 2010), but related works have been performed only in a few cities in China like Beijing (Yao et al., 2003), Nanjing (Wang et al., 2002), Guangzhou (Ho et al., 2011) and Hong Kong (Ho et al., 2006). Several studies have pointed out that atmospheric environment over China especially in the east costal region has been becoming more oxidative due to increasing level of NOx (Wang et al., 2013b). Haze episodes have frequently occurred in many Chinese megacities (Fu et al., 2008a; Sun et al., 2013; Zhang et al., 2012). Aerosol chemistry during haze periods in megacities of China has been given much attention. However, most of which has focused on inorganic components and information on secondary organic aerosols (SOA) during haze period has sparsely been documented (Li et al., 2013; Yang et al., 2012). Xi'an is the largest mega city in northwestern China, which is located in Guanzhong Basin and surrounded by Qinling Mountain and Loess Plateau (Fig. 1). Such topography is favorable for pollutants accumulated in the urban air, frequently resulting in severe haze episodes. In the current study we first identified the seasonality of dicarboxylic acids and relate SOA in the city and then compared their differences in concentrations and compositions during haze and clean periods to investigate the sources and formation mechanisms of SOA in the city.

2. Sample collection and analysis

2.1. Aerosol sampling

PM_{10} samples were collected on 14–22 January and 7–12 February during the winter of 2009 and from 18 July to 13 August during the summer of 2009 in Xi'an. The aerosol sampler was placed on the rooftop of a three-story building within the Institute of Earth Environment, Chinese Academy of Science, which is located in the southwestern part of Xi'an city. PM_{10} samples were collected onto a pre-baked (450 °C for 12 h) quartz fiber filter (Φ90 mm) on a day/night basis for 10 h in each using a mid-volume air sampler (Laoshan Company, China) at an airflow rate of 100 L min^{-1}. Field blank samples were collected at the beginning and the end of the sampling campaign by mounting the blank filter onto the sampler for 10 min without sucking air. After sampling, all the samples were sealed within an aluminum foil bag and stored at −18 °C prior to analysis. Meteorological parameters were simultaneously measured and are shown in Supplement Figure S1.

2.2. Sample analysis

2.2.1. Organic carbon (OC), elemental carbon (EC), and water-soluble organic (WSOC) and inorganic carbon (WSIC)
OC and EC were measured using DRI Model 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2004, 2007). Briefly, a size of 0.53 cm^2 sample filter was put into a quartz boat inside the analyzer and stepwise heated to 140 °C, 280 °C, 480 °C and 580 °C in a non-oxidizing helium (He) atmosphere and to 580 °C, 740 °C and 840 °C in an oxidizing atmosphere of 2% oxygen in helium (Li et al., 2011).

One fourth of filter was cut into pieces, extracted with Milli-Q water for three times and filtered through PTFE filter for removing particles and filter debris. The water-extracts were measured for water-soluble organic and inorganic carbon (WSOC and WSIC) using Shimazdu TOC/TON-5000 Analyzer.

2.2.2. Dicarboxylic acids, keto-carboxylic acids and α-dicarbonyls
PM_{10} samples were analyzed for DCA using a method reported previously (Wang et al., 2012). Briefly, an aliquot of the filter was cut into pieces and ultrasonically extracted with pure water for three times, then concentrated to dryness by a rotary evaporator under a vacuum condition, and reacted with 14% BF$_3$/butanol mixture at 100 °C for 1 h (Wang et al., 2012). After derivatization, n-hexane was added to the products and the derivatives were washed with pure water for 3 times. Finally, the hexane layer was concentrated and quantified by gas chromatography (GC). The GC oven temperature was increased at a rate of 30 °C min^{-1} from 50 °C (2 min) to 120 °C, and then to 300 °C at a rate of 6 °C min^{-1}, finally holding at 300 °C for 10 min (Meng et al., 2013). The target compounds in the derivatives were also confirmed using an Agilent 7890A gas chromatography coupled with a 5975C mass spectrometer. Recoveries of DCA and related compounds were measured, which are 80–85% for C_2 and 92–115% for others. OC, EC, WSOC, WSIC, DCA and related compounds in the field blank samples are all less than 10% of those in the PM_{10} samples. Data reported here were corrected by field blanks but not corrected by the recoveries.

3. Results and discussion

Although the samples were collected on a day/night basis, most of the target compounds did not show a significant diurnal difference. Therefore, here we discuss the seasonal haze characteristics

Table 1
Concentrations of dicarboxylic acids, keto-carboxylic acids, α-dicarbonyls, WSOC, WSIC, OC, EC in PM_{10} in Xi'an, China during winter and summer.

Compounds	Winter			H/C[a]	Summer			H/C[a]
	Whole period	Haze	Clean		Whole period	Haze	Clean	
	$N = 29$	$N = 5$	$N = 5$		$N = 54$	$N = 5$	$N = 5$	
I. Dicarboxylic acids, ng m^{-3}								
Oxalic, C_2	1162 ± 570	1769 ± 450	523 ± 164	3.4	767 ± 574	1907 ± 707	185 ± 59	10
Malonic, C_3	58 ± 45	127 ± 39	24 ± 16	5.3	82 ± 45	155 ± 38	28 ± 8.5	5.6
Succinic, C_4	98 ± 71	159 ± 42	38 ± 15	4.1	90 ± 49	163 ± 42	35 ± 15	4.6
Glutaric, C_5	21 ± 18	50 ± 18	8.4 ± 3.5	5.9	29 ± 18	50 ± 13	7.6 ± 4.1	6.6
Adipic, C_6	6.9 ± 6.1	17 ± 7.0	3.0 ± 1.2	5.7	19 ± 11	25 ± 11	9.1 ± 4.8	2.7
Pimelic, C_7	2.5 ± 2.7	7.2 ± 3.4	0.8 ± 0.4	8.8	6.2 ± 5.1	6.4 ± 4.0	2.5 ± 1.1	2.6
Suberic, C_8	8.2 ± 7.8	21 ± 9.0	3.4 ± 1.7	6.2	1.2 ± 0.8	1.0 ± 0.4	1.0 ± 0.7	1
Azelaic, C_9	15 ± 16	35 ± 19	16 ± 23	2.2	59 ± 47	68 ± 38	10 ± 2.2	6.8
Undecanedioic, C_{10}	1.6 ± 1.6	4.3 ± 2.2	0.7 ± 0.3	6.2	4.0 ± 3.4	7.3 ± 7.5	2.2 ± 1.5	3.4
Methylsuccinic, iC_5	12 ± 9.7	26 ± 11	5.5 ± 1.7	4.8	12 ± 6.6	19 ± 9.7	4.2 ± 2.1	4.5
Methylglutaric, iC_6	2.2 ± 1.8	5.1 ± 1.6	1.0 ± 0.4	5.3	5.0 ± 3.3	8.8 ± 4.8	2.0 ± 1.1	4.3
Maleic, M	7.0 ± 6.8	17 ± 8.7	2.4 ± 0.7	7.1	8.0 ± 4.5	13 ± 4.3	3.6 ± 1.8	3.6
Fumaric, F	3.0 ± 2.9	7.6 ± 4.0	1.1 ± 0.4	6.9	7.9 ± 5.5	15 ± 6.5	2.0 ± 1.1	7.7
Phthalic, Ph	196 ± 82	237 ± 37	187 ± 53	1.3	103 ± 50	135 ± 24	67 ± 53	2
Isophthalic, iPh	1.2 ± 1.2	3.3 ± 1.2	0.5 ± 0.3	6.3	12 ± 8.5	14 ± 8.1	7.6 ± 4.6	1.8
Terephthalic, tPh	250 ± 118	398 ± 151	167 ± 73	2.4	54 ± 35	74 ± 37	15 ± 8.1	4.9
Subtotal	1843 ± 810	2885 ± 664	982 ± 309	2.9	1259 ± 781	2663 ± 854	378 ± 124	7
II. Keto-carboxylic acids, ng m^{-3}								
Pyruvic, Pyr	56 ± 54	130 ± 81	27 ± 15	4.9	5.0 ± 3.4	9.6 ± 7.4	2.7 ± 1.5	3.5
Glyoxylic, ωC_2	179 ± 111	319 ± 75	97 ± 72	3.3	68 ± 51	171 ± 46	11 ± 5.2	15
3-Oxopropanoic, ωC_3	12 ± 11	30 ± 12	4.2 ± 2.4	7.1	9.5 ± 6.0	15 ± 7.5	3.9 ± 2.6	3.8
Subtotal	247 ± 171	479 ± 167	128 ± 86	3.7	82 ± 57	195 ± 45	18 ± 8.9	11
III. α-Dicarbonyls, ng m^{-3}								
Glyoxal, Gly	45 ± 53	116 ± 57	20 ± 17	5.9	13 ± 9.7	29 ± 10	3.7 ± 3.2	7.9
Methylglyoxal, mGly	71 ± 69	188 ± 63	20 ± 8.4	9.5	24 ± 21	60 ± 30	5.7 ± 3.7	10
Subtotal	116 ± 113	304 ± 108	39 ± 24	7.7	37 ± 28	89 ± 25	9.4 ± 4.5	9.5
Total detected	2207 ± 1044	3668 ± 893	1149 ± 401	3.2	1378 ± 855	2947 ± 858	406 ± 136	7.3
IV. Carbonaceous species, μg m^{-3}								
WSOC	32 ± 12	49 ± 9.6	19 ± 1.8	2.6	9.6 ± 3.1	12 ± 2.7	4.5 ± 0.9	2.7
WSIC	3.7 ± 2.9	2.7 ± 1.0	3.8 ± 1.6	0.7	1.5 ± 1.0	2.1 ± 0.4	2.3 ± 0.5	0.9
OC	59 ± 28	95 ± 35	35 ± 9.5	2.7	12 ± 3.6	13 ± 2.6	7.0 ± 1.5	1.9
EC	19 ± 8.2	27 ± 12	13 ± 6.3	2.1	6.6 ± 2.9	7.3 ± 2.0	2.7 ± 0.8	2.6
PM_{10}	448 ± 138	666 ± 65	258 ± 56	2.6	172 ± 61	281 ± 14	68 ± 8.7	4.1

[a] H/C= Haze/Clean (Ratio of averaged concentration of haze samples to that of clean samples).

by averaging the day and night data. Five days of each season with the highest and the lowest levels of particle mass were selected respectively to represent the haze and clean days. On the haze days pollutants were accumulated due to the stagnant atmospheric conditions (Supplement Figure S1), while on the clean days higher wind speed and/or wet precipitation diluted or scavenged pollutants. Differences in DCA and related compounds in the haze and clean periods were investigated to further explore the sources and

formation mechanisms of secondary organic aerosols (SOA) in the city.

3.1. Seasonal variations of dicarboxylic acids and related compounds in PM_{10}

Table 1 summarizes the concentrations of DCA, ketocarboxylic acids, α-dicarbonyls, OC, EC, WSOC, and WSIC in the PM_{10} samples. Fig. 2 plots the seasonal variations of DCA and related compounds. Oxalic acid (C_2) is the most abundant DCA, accounting for 62 ± 10% and 58 ± 9% of the total DCA in winter and summer, respectively, followed by t-phthalic (tPh: 14 ± 5%) and phthalic (Ph: 12 ± 6%) acids in winter and phthalic (Ph: 9 ± 5%) and succinic acids (C_4: 7 ± 2%) in summer (Fig. 2). The high concentration of tPh in winter is mostly caused by enhanced burning of waste materials including plastics for house heating in the surrounding rural area (Wang et al., 2012). C_9 is four times higher in summer compared to that in winter, indicating an increase in biogenic SOA production since C_9 is an oxidation product of unsaturated fatty acids that are largely derived from plant emission (Kundu et al., 2010). As shown in Fig. 3 a robust linear correlations ($r^2 = 0.60$ and 0.88 in winter and in summer, respectively) were observed for keto-carboxylic acids and DCA with slopes of 0.18 and 0.07 in winter and summer, respectively. The smaller slope suggests aerosols in summer are more oxidized as keto-carboxylic acids are precursors of DCA (Wang et al., 2012).
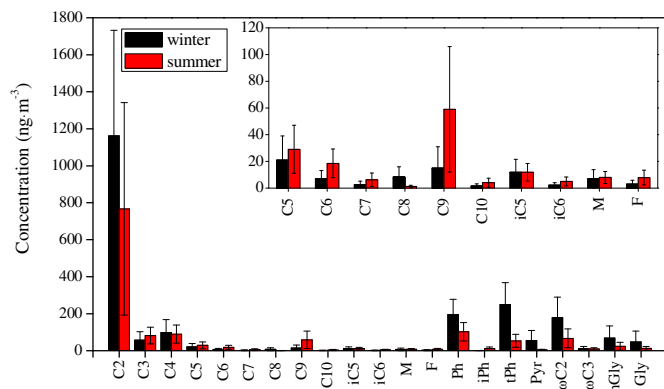

Fig. 2. Molecular compositions of dicarboxylic acids and related compounds in PM_{10} from Xi'an during summer and winter.
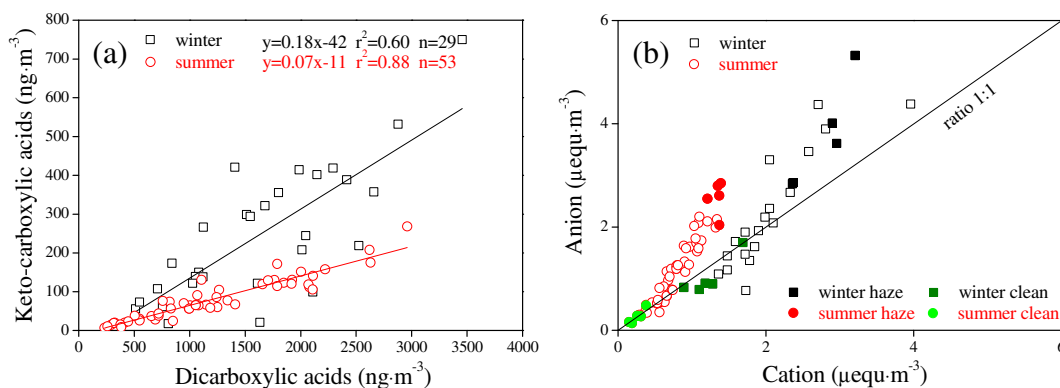
Fig. 3. (a) Linear fit regression for mass concentrations of dicarboxylic acids and keto-carboxylic acids in the PM_{10} samples from Xi'an during winter and summer.(b) Equivalent ratios of anion and cation in the PM_{10} samples from Xi'an during winter and summer.

Table 2
Seasonal difference in concentration ratios of diacids, WSOC, and OC on haze and clean days.

		C_2/Diacids	C_3/C_4	Diacids/WSOC	WSOC/OC
Winter	Haze ($n = 5$)	0.61 ± 0.05	0.80 ± 0.12	0.06 ± 0.01	0.55 ± 0.14
	Clean ($n = 5$)	0.53 ± 0.05	0.59 ± 0.19	0.05 ± 0.02	0.57 ± 0.13
Summer	Haze ($n = 5$)	0.71 ± 0.04	0.98 ± 0.23	0.22 ± 0.05	0.91 ± 0.06
	Clean ($n = 5$)	0.50 ± 0.13	0.85 ± 0.23	0.09 ± 0.04	0.66 ± 0.08

Concentration ratio of OC/EC in the Xi'an samples is 3.1 ± 0.9 in winter and 1.8 ± 0.7 in summer, which is similar to that measured in 2003 (Cao et al., 2005). The higher ratio can be explained by domestic burning coal and biomass that were still the major activity for house heating in Guanzhong Basin, which emitted a high level of organic pollutants (Wang et al., 2013a). Cachier et al. (1989); Watson et al. (2001) also reported that OC/EC ratio is lower for vehicle exhaust, which is about 1.1, and much higher for the emissions from coal combustion biomass burning smokes, which are 2.7 and 9.0, respectively. WSOC accounted for $56 \pm 15\%$ and $78 \pm 16\%$ of OC in winter and summer. Under a typical urban condition, WSOC is thought largely derived from photochemical oxidation (Agarwal et al., 2010; Pathak et al., 2011), thus compared to those in winter the higher ratios of WSOC/OC in summer indicate that aerosols in the warm season are more oxidized.

3.2. Comparison of dicarboxylic acid and related compounds on haze and clean days

As mentioned above five days with the highest and the lowest particle loadings in each season were selected as haze and clean periods, respectively. Differences in concentrations and compositions of the target compounds on both haze and clean periods were identified. As shown in the Figure S1 visibility and mass concentration present opposite variation pattern, which does support this classification. As shown in Table 1, concentrations of DCA and

carbonaceous species except WSIC were 1.0–15 times higher in the haze samples than in the clean samples. During the winter C_2 in the haze samples was 3.4 times higher than that in the clean samples. As for total DCA, ketoacids and α-dicarbonyls, the seasonal differences varied by a factor of 2.9–3.7. Such abundant DCA and related compounds in the haze samples reflect an enhanced SOA production on the haze days. As shown in Table 2, mass ratios of C_2/diacids, C_3/C_4, diacids/WSOC and WSOC/OC are higher for all the haze samples compared to the clean samples, further indicating an increased photochemical oxidation under the haze condition. The relative abundances of DCA in WSOC on a carbon basis (diacids-C/WSOC) are presented in Table 3. The larger percentages of DCA, keto-carboxylic acids, and α-dicarbonyls indicate that WSOC in the haze samples are enriched with SOA. As seen in Fig. 3b, the equivalent ratios of anion to cation in PM_{10} are higher on haze days than on clean days (haze versus clean: 1.3 ± 0.2 versus 0.8 ± 0.1 for winter and 1.9 ± 0.3 versus 1.0 ± 0.2 for summer, respectively). In winter mass ratios of SO_4^{2-} and NO_3^- to PM_{10} increased from 0.16 ± 0.07 on clean days to 0.25 ± 0.10 on haze days, while in summer the ratios increased from 0.18 ± 0.09 to 0.47 ± 0.08. Such facts suggest that haze particles are acidic, which is favorable for acid-catalysis formation of SOA since field measurements (Pathak et al., 2011) and chamber studies (Gao et al., 2004; Jang et al., 2002; Surratt et al., 2007) demonstrated that acidic conditions can enhance SOA yields. Thus, in winter higher OC/EC ratio (3.5 ± 1.0) was observed on haze days in comparison with that (2.7 ± 0.4) on clean days. However, in summer a lower OC/EC ratio (1.9 ± 0.3) was observed in haze periods compared to that (2.6 ± 0.4) in clean periods, which is mostly due to the precipitation scavenging effect on clean days (see Figure S1).

During the summer C_2 and related compounds on the haze days are much more abundant than on clean days (Haze/Clean ratios ≥ 7.0). In comparison with those in the winter higher ratios of C_2/diacids (0.71 ± 0.04) and WSOC/OC (0.91 ± 0.06) of the summertime haze samples indicate that the summer haze aerosols are more oxidized. As for C_2, ωC_2 and mGly, their relative abundances to WSOC during the summer are about 4 times higher in haze

Table 3
Abundance of dicarboxylic acids and related compounds relative to WSOC on a carbon basis on haze and clean days (%).

|		C_2–C/WSOC	C_3–C/WSOC	C_4–C/WSOC	C_9–C/WSOC	ωC_2–C/WSOC	mGly-C/WSOC	Gly-C/WSOC	Diacids-C/WSOC	Ketoacids-C/WSOC	α-Dicarbonyls-C/WSOC
Winter	Haze ($n = 5$)	0.96 ± 0.13	0.09 ± 0.02	0.13 ± 0.02	0.04 ± 0.02	0.21 ± 0.04	0.18 ± 0.05	0.10 ± 0.05	2.12 ± 0.27	0.34 ± 0.09	0.28 ± 0.06
	Clean ($n = 5$)	0.73 ± 0.24	0.04 ± 0.03	0.08 ± 0.03	0.04 ± 0.06	0.16 ± 0.11	0.06 ± 0.02	0.04 ± 0.04	2.04 ± 0.67	0.22 ± 0.14	0.09 ± 0.05
Summer	Haze ($n = 5$)	4.27 ± 1.23	0.46 ± 0.12	0.57 ± 0.19	0.32 ± 0.18	0.47 ± 0.12	0.29 ± 0.24	0.10 ± 0.03	7.18 ± 1.60	0.72 ± 0.13	0.39 ± 0.24
	Clean ($n = 5$)	1.12 ± 0.37	0.22 ± 0.07	0.34 ± 0.20	0.13 ± 0.29	0.09 ± 0.04	0.06 ± 0.04	0.04 ± 0.04	3.37 ± 1.73	0.27 ± 0.18	0.10 ± 0.06
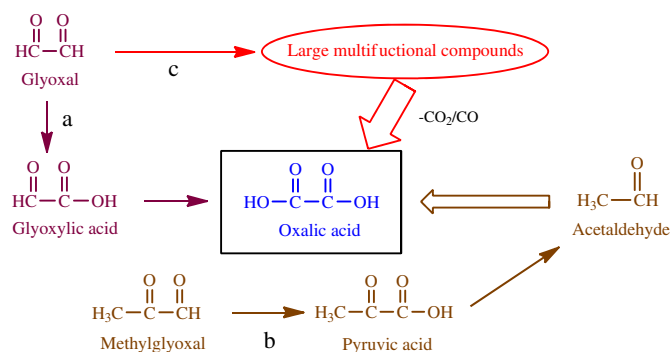
Fig. 4. A diagram of aqueous-phase oxidation pathways of glyoxal (Gly) and methylglyoxal (mGly) (The pathways **a** and **b** were proposed by Ervens et al. (2004) and the pathway **c** was proposed by Carlton et al. (2007)).

Table 4
Concentration ratio of Gly/mGly in PM_{10} from Xi'an on haze and clean days.

	Haze ($n = 5$)	Clean ($n = 5$)
Winter	0.51 ± 0.10	1.02 ± 0.35
Summer	0.33 ± 0.23	0.95 ± 0.05

periods than in clean periods. Such differences between haze and clean days in summer are more pronounced compared to that in winter due to intensive photooxidation. From Fig. 3b it can be seen that haze samples are acidic while clean samples are almost neutral in both seasons, again indicating the importance of acid-catalysis in aerosol aqueous oxidation, especially under summer haze condition.

3.3. Glyoxal and methylglyoxal on the haze and clean days

Aqueous-phase oxidation of glyoxal (Gly) and methylglyoxal (mGly) are important global and regional sources of SOA including C_2 (Carlton et al., 2007). Model simulation results suggest that on a global scale mGly (140 Tg yr^{-1}) is of stronger sources than Gly (45 Tg yr^{-1}) with 50–80% of them being derived from isoprene oxidation (Fu et al., 2008b). However, in urban area emission sources of Gly and mGly are approximately the same (Guenther et al., 2006). As shown in Table 4, average mass ratio of Gly/mGly in Xi'an is lower in summer than in winter and also lower on haze days than on clean days in both seasons (Table 4), which probably suggests that Gly in aerosol phase is consumed faster than mGly.

Previous studies found that Gly can initially be oxidized to glyoxylic acid (ωC_2) and subsequently be oxidized to C_2 (showed in Fig. 4, reaction route *a*) (Wang et al., 2012; Warneck, 2003), while mGly is firstly oxidized to pyruvic acid (Pyr) and subsequently transformed to the end product, C_2 (showed in Fig. 4, reaction route *b*) (Ervens et al., 2004). However, box experiment conducted by Carlton (Carlton et al., 2007) showed that major fraction of Gly in aerosol phase is oxidized by OH radical to form larger multifunctional compounds rather than ωC_2 (reaction route *c* in Fig. 4) and subsequently degraded into C_2, which is the major formation pathway of C_2. In contrast, C_2 formed through the ωC_2 pathway is less than 1% (Fig. 4, reaction route *a*) (Buxton et al., 1997; Carlton et al., 2007). Aqueous-phase oxidation by OH is faster for Gly (3×10^{10} M^{-1} s^{-1}) than for mGly (1.1×10^9 M^{-1} s^{-1}) (Carlton et al., 2007). Thus, abundance of Gly relative to mGly is an indicator of aerosol ageing. As shown in Table 4, the ratio of Gly/mGly in the Xi'an samples is lower on the haze days compared to that on clean days and also lower in summer than in winter. Such temporal variations are consistent with the box experiment results. Our previous field observations found that aerosols on haze days are narrower to larger sizes compared to the particles on clean days due to longer residence time under the stagnant condition (Wang et al., 2012, 2009a, 2009b) and enriched in sulfate, which accelerates the aqueous phase oxidation.

Ratios of Gly/mGly from other cities are presented in Table 5. All of the ratios are lower in summer than in winter. Gly/mGly from New Delhi, India exhibited a lower ratio in daytime than in night-time. Such seasonal and diurnal differences further support our proposal that aqueous phase transformation rate of Gly is faster than that of mGly and Gly/mGly ratio is indicative of aerosol ageing.

3.4. Comparison of dicarboxylic acid in Xi'an with those in other Asian megacities

Table 6 presents concentrations of DCA and their relative abundances from different Asian cities. DCA in Xi'an are the most abundant among the cities, except for New Delhi, India in winter, with a higher C_2/diacids ratio, suggesting the serious SOA pollution problem in the city. Unlike that in the cities of Japan (Tokyo and Sapporo), India (New Delhi and Chennai) and Mongolia (Ulaan-baatar), Ph in Chinese megacities such as Xi'an, Guangzhou and Beijing are more abundant than C_4. Such a chemical fingerprint of SOA in China megacities is related to high level emissions from coal burning, which is not efficiently controlled especially in rural areas, because Ph is directly emitted from coal combustion and/or generated by atmospheric degradation of aromatic hydrocarbons

Table 5
Mass ratio of Gly/mGly in East Asian cities.

Cities	Location	Particle size	Winter			Summer		
			Gly	mGly	Gly/mGly	Gly	mGly	Gly/mGly
Chennai, India[a]	N 13°05'E 80°18'	PM_{10}	7.4	6.6	1.12	2.9	4.2	0.69
Hong Kong, China[b]	N 22°17'E 114°08'	$PM_{2.5}$	5.3	6.4	0.82	0.19	10	0.02
New Delhi, India[c]	N 28°37'E 77°13'	TSP	12	28	0.43[1]	–	–	–
			24	31	0.77[2]	–	–	–
Jeju island, South Korea[d]	N 33°29'E 126°16'	TSP	9.3	14	0.67	2.0	7.1	0.28
Xi'an, China[e]	N 34°16'E 108°54'	PM_{10}	45 ± 53	71 ± 69	0.68 ± 0.55	13 ± 9.7	24 ± 21	0.60 ± 0.31
Tokyo, Japan[f]	N 35°41'E 139°44'	TSP	22	24	0.89	7.8	14	0.56
Ulaanbaatar, Mongolia[g]	N 47°55'E 106°53'	$PM_{2.5}$	14	20	0.70	–	–	–

[a] Pavuluri et al., 2010.
[b] Ho et al., 2006.
[c] Miyazaki et al., 2009: 1.average concentration in daytime; 2.average concentration in nighttime.
[d] Kundu et al., 2010.
[e] This work.
[f] Kawamura and Yasui, 2005.
[g] Jung et al., 2010.

Table 6
Airborne particulate dicarboxylic acids in Asian megacities.

Season	Cities	Location	Particle size	C_2	C_3	C_4	Ph	Diacids	C_3/C_4	C_6/C_9	Ph/C_9	C_2/Diacids
Winter	Hong Kong, China[a]	N 22°17′ E 114°08′	$PM_{2.5}$	478	89	72	78	822	1.2	0.6	4.6	0.58
	Guangzhou, China[b]	N 23°2′ E 113°3′	$PM_{2.5}$	182	13	18	92	346	0.72	0.33	5.6	0.53
	New Delhi, India[c]	N 28°37′ E 77°13′	TSP	1431	188	302	43	2251	0.6	0.4	0.6	0.64
	Nanjing, China[d]	N 32°03′ E 118°46′	PM_{10}	190	126	195	–[a]	1395	0.65	0.48		0.57
	Tokyo, Japan[e]	N 35°41′ E 139°44′	TSP	186	41	48	24	405	0.8	0.7	1.2	0.46
	Ulaanbaatar, Mongolia[f]	N 47°55′ E 106°53′	$PM_{2.5}$	107	13	63	54	387	0.2	0.3	1.3	0.28
	Xi'an, China[g]	N 34°16′ E 108°54′	PM_{10}	1162	58	98	196	1843	0.69	0.58	25	0.62
Summer	Chennai, India[h]	N 13°05′ E 80°18′	PM_{10}	241	37	28	22	494	1.3	0.3	0.7	0.49
	Hong Kong, China[a]	N 22°17′ E 114°08′	$PM_{2.5}$	268	48	33	90	520	1.4	1.43	9.9	0.51
	Guangzhou, China[b]	N 23°2′ E 113°3′	$PM_{2.5}$	216	19	11	215	523	1.7	0.33	14.3	0.41
	Jeju Island, South Korea[i]	N 33°29′ E 126°16′	TSP	564	73	69	4.9	773	1.1	1.07	1.1	0.73
	Tokyo, Japan[e]	N 35°41′ E 139°44′	TSP	157	44	41	29	350	1.1	1.18	2.6	0.45
	Beijing, China[j]	N 39°55′ E 116°23′	$PM_{2.5}$	449	28	50	77	755	0.6	0.49	2.2	0.59
	Sapporo, Japan[k]	N 43°05′ E 141°21′	TSP	192	77	58	17	403	1.3	0.78	2.6	0.48
	Xi'an, China[g]	N 34°16′ E 108°54′	PM_{10}	767	82	90	103	1259	0.97	0.41	2.3	0.58

[a] Ho et al., 2006.
[b] Ho et al., 2011.
[c] Miyazaki et al., 2009.
[d] Wang et al., 2002.
[e] Kawamura and Yasui, 2005.
[f] Jung et al., 2010.
[g] This work.
[h] Pavuluri et al., 2010.
[i] Kundu et al., 2010.
[j] Ho et al., 2010.
[k] Aggarwal and Kawamura, 2008.

such as naphthalene (Kawamura and Ikushima, 1993). The wintertime ratio of Ph/C_9 (25 ± 17) in Xi'an is much higher than in other cities, which can be explained by high levels of precursors including PAHs emitted from coal burning due to house heating in the city and its surrounding area, i.e., Guanzhong Basin.

4. Conclusions

Summer and winter PM_{10} in Xi'an, inland China was measured for dicarboxylic acids, keto-carboxylic acids, α-dicarbonyls, EC, OC and WSOC, along with a comparison of these components on haze and clean days. High levels of DCA and related compounds were observed in the city, indicating a severe SOA pollution problem. Compared to other cities higher ratio of Ph/C_9 in Chinese megacities including Xi'an suggests that air pollution in China is significantly influenced by coal burning emission, which is not efficiently controlled especially in winter due to house heating. Seasonal variations in compositions of DCA and related compounds in the samples demonstrate that summertime aerosols are much more aged than in winter. Moreover, DCA showed higher concentrations for the haze samples than for the clean samples in both seasons with high relative abundances to particle mass and OC, indicating an increased SOA production under the haze conditions. Inorganic ion equivalents showed that the haze samples are more acidic than the clean samples, suggesting that acid-catalysis probably took an important role in SOA formation during the haze period. Mass concentration of Gly to mGly is lower in summer than in winter and also lower on haze days than on clean days, which can be explained by the higher conversion rate of Gly in aerosol aqueous phase. Our results suggest that the mass ratio of Gly/mGly in urban air is an indicator of aerosol ageing.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.09.013.

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