High abundances of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in fine aerosols ($PM_{2.5}$) in Chengdu, China during wintertime haze pollution

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Abstract

Daytime and nighttime fine aerosol ($PM_{2.5}$) samples were collected during a haze episode in January 2013 within the urban area of Chengdu, southwest China. Aerosol samples were analyzed for low-molecular-weight homologous dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls, as well as organic carbon and elemental carbon. Concentration ranges of diacids, oxoacids, and α-dicarbonyls were 1400–5250 ng m^{-3}, 272–1380 ng m^{-3}, and 88–220 ng m^{-3}, respectively. Molecular distributions of diacids (mean 3388 ± 943 ng m^{-3}) were characterized by a predominance of oxalic acid (C_2; 1373 ± 427 ng m^{-3}), followed by succinic (C_4), terephthalic (tPh), and phthalic (Ph) acids. Such high levels of tPh and Ph were different from those in other Asian cities where malonic acid (C_3) is the second or third highest species, mostly owing to significant emissions from coal combustion and uncontrolled waste incineration. High contents of diacids, oxoacids and α-dicarbonyls were detected on hazy days, suggesting an enhanced emission and/or formation of these organics during such a weather condition. Concentrations of unsaturated aliphatic diacids (e.g., maleic acid) and phthalic acids were higher in nighttime than in daytime. Good positive correlations of C_2 with C_3, C_4, ketomalonic (kC_3), pyruvic (Pyr), and glyoxylic (ωC_2) acids in daytime suggest secondary production of C_2 via the photooxidation of longer-chain diacids and ωC_2. This study demonstrated that both primary emissions and secondary production are important sources of dicarboxylic acids and related compounds in atmospheric aerosols in the Sichuan Basin.

Keywords*:* dicarboxylic acids; oxocarboxylic acids; α-dicarbonyls; urban aerosols; Sichuan Basin

1. Introduction

In recent years, increasing population, industrial and agricultural development, and urbanization have resulted in serious air pollution around the world (Akimoto, 2003; Chen and Kan, 2008; Shah et al., 2013). Fine particulate matters with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) are of particular interest in China because of the frequent severe haze events across the country (Cao et al., 2013; Ho et al., 2011; Sun et al., 2006). These fine particles can easily penetrate a human's lungs causing health problems, and also lead to adverse environmental effects such as visibility deterioration, radiative forcing, and climate change (Huebert et al., 2003; Nel, 2005; Osborne and Lambert, 2014; Wang et al., 2009c), which depend on their chemical components and characteristics (Beckerman et al., 2013; Ebelt et al., 2005; Perrone et al., 2013; Schlesinger, 2007). Although the sulfate, nitrate, and inorganic carbon compounds in aerosols have received much attention, organic compounds including dicarboxylic acids (diacids) and related polar compounds are important components of atmospheric particulate matters (Alier et al., 2014; Kawamura and Sakaguchi, 1999; Nirmalkar et al., 2014).

Diacids and related polar compounds are widely present in the urban, rural, polar and marine aerosols, while their molecular distributions and variable concentrations are critical important to explore their sources and to understand related photochemical reactions (Fu et al., 2013; Ho et al., 2007; Huang et al., 2005; Kawamura and Ikushima, 1993; Kawamura et al., 2013; Kundu et al., 2010; Miyazaki et al., 2009a). Diacids are directly emitted to the atmosphere from natural and anthropogenic primary sources, and/or produced by secondary atmospheric chemical reactions (Kawamura et al., 2013; Narukawa et al., 1999; Warneck, 2003).

Studies on the molecular distributions of diacids have been conducted in urbanized regions of China such as the Yangtze River Delta (Cao et al., 2013; Wang and Kawamura, 2005; Wang et al., 2009b), Beijing-Tianjin-Hebei region, Guanzhong Plain (Cheng et al., 2013; Ho et al., 2010; Huang et al., 2005; Wang et al., 2007; Yang et al., 2011), and Pearl River Delta (Ho et al.,

2011; Li and Yu, 2010; Ma et al., 2010; Miyazaki et al., 2009b); however, little is known about their levels in the Sichuan Basin.

Chengdu, the largest megacity in southwest China, is located in the west of the Sichuan Basin. Owing to its urbanization and the rapid increase in number of vehicles and energy consumption, severe air pollution has occurred in Chengdu (Tao et al., 2011; Wang et al., 2004). The bowl-shaped basin topography with low wind speeds and stable atmospheric conditions makes Chengdu an ideal site, particularly in the winter, for investigating the molecular compositions of diacids during severe haze episodes. In the current study, we report the diurnal variability of diacids, oxocarboxylic acids (oxoacids), and α-dicarbonyls in $PM_{2.5}$ collected in Chengdu during wintertime. Then, we compare their distributions, concentrations and compositions during different weather conditions to examine the sources and transformation mechanisms in a basin region.

2. Material and methods

2.1. Sampling site

Located in the western Sichuan Basin, southwest China, Chengdu City covers a land size of 12,121 km^2 with an urban area of 283.9 km^2, while the population of the city exceeded 11.7 million by the end of 2012 (Fig. 1; http://www.cdstats.chengdu.gov.cn/list.asp?ClassID=020703). The Sichuan Basin is a bowl-shaped basin covering 200,000 km^2 and is completely encircled by mountains that are 1500–4500 m above sea level (Li et al., 2003). The combination of a high evaporation rate and cold wind blowing from the Tibetan Plateau leads to constant production of clouds in the basin and results in overcast days for most of the year. Such clouds also prohibit the exchange of air inside the basin with the ambient atmosphere. Thus, the anthropogenic pollutants emitted into the air tend to remain within the basin (Deng et al., 2012; Lei et al., 1997). Meanwhile, haze episodes in Chengdu are enhanced by the development of an inversion layer

(<1000 m above ground level) and low wind speeds over the Sichuan Basin during the winter, accelerating the accumulation and secondary formation of pollutants emitted from local sources such as heat and power plants, home stoves, and automobiles (Lei et al., 1997). The Chinese government has promoted the auto industry in China, which has become the world's second-largest vehicle market based on unit sales, following the United States. According to Chengdu Economic and Social Development Statistics Bulletin, the number of vehicles in Chengdu exceeded 3.13 million by the end of 2012, which makes Chengdu second to Beijing for the number of vehicles in China.

Because of the basin topography, wind speed rarely exceeded that of a calm wind or breeze in Chengdu City during the sampling period, so wind direction and speed could be ignored (http://www.weather.com.cn/weather/101270101.shtml). Ambient temperatures ranged from 4.0–9.0°C (mean 6.3°C) in daytime, and from 1.0–8.0°C (mean 3.9°C) in nighttime. Relative humidity ranged from 51–86% (mean 72%) in daytime and from 70–90% (mean 83%) in nighttime (http://sc.weather.com.cn/qxfw/index.shtml).

2.2. Sample collection

Fifteen daytime (12 h, 7 a.m. to 7 p.m.) and seventeen nighttime (12 h, 7 p.m. to next day 7 a.m.) $PM_{2.5}$ samples were collected from January 7–23, 2013 in Chengdu (30°40'40"N, 104°08'30"E), southwest China, except during the daytime of January 22 because of an external power outage. A low-volume air sampler (ME-APS100, Beijing, China) was placed on the rooftop (15 m above ground level) of a four-story building on the campus of Chengdu University of Technology, which is located in the northeastern part of Chengdu City (512 m a.s.l., see Fig. 1). The samples were collected onto a pre-baked (450°C for 12 h) quartz fiber filter (Ø47 mm) on a day/night basis with an airflow rate of 16.7 L min^{-1}. Field blanks were collected at the beginning and end of the 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.

2.3. Analytical procedures

Filter samples were analyzed for water-soluble diacids, oxoacids, and α-dicarbonyls using the improved method of Kawamura and Ikushima (1993) and Kawamura (1993). Filter aliquots were extracted under ultrasonication with organic-free pure water (5 ml × 3). The water extracts were adjusted to pH 8.5–9.0 using a 0.05 M KOH solution and then concentrated down to ca. 0.5 ml in a pear-shaped flask by using a rotary evaporator under a vacuum and dried in a nitrogen stream (Mkoma and Kawamura, 2013). The dried samples were then reacted with 14% BF_3/*n*-butanol at 100°C for 30 min. During this procedure, carboxyl functional group was derivatized to butyl ester, and aldehyde and oxo groups were derivatized to dibutoxy acetal (Kawamura, 1993). The derivatives were extracted with 5 ml of *n*-hexane after adding 3 ml of pure water and 0.2 ml of acetonitrile, and the latter made the excess butanol more effectively transfer into the aqueous phase. The hexane layer was further washed with pure water (3 ml × 2). The extracts were dried by using a rotary evaporator and a nitrogen blow-down system, and then dissolved in 50 μl of *n*-hexane.

The butyl esters and acetals were determined using an Agilent 6890 gas chromatograph (GC) equipped with a split/splitless injector, a fused silica capillary column (HP-5, 0.2 mm ID × 25 m × 0.52 μm film thickness), and a flame ionization detector (FID). Peaks and GC retention times were compared with those of authentic standards to identify the compounds. Diacids and related compounds were confirmed by mass spectral analysis using a GC-MS system. Recovery experiments were performed by spiking free diacids onto precombusted quartz fiber filters. Results showed that the recoveries were better than 85% for oxalic acid and 90% for malonic, succinic, and adipic acids. Duplicate analysis of the field samples showed that the analytical error of this method was less than 10% for major species. Concentrations of diacids and related compounds reported here were corrected for the blanks but not for recoveries.

Organic carbon (OC) and elemental carbon (EC) concentrations were measured using a Sunset Lab EC/OC Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol. Typically, a 1.54 cm^2 punch (Ø14 mm) of the filter was placed in a quartz tube inside the thermal desorption chamber of the analyzer, and then stepwise heating was applied (Wang and Kawamura, 2005). Duplicate analyses of filter samples for OC and EC showed uncertainties of ±10%.

3. Results and discussion

3.1. Variations of OC and EC in Chengdu aerosols

EC is a product of incomplete combustion of residential coal, motor vehicle fuel, and biomass, while OC results from primary anthropogenic sources and secondary formation via chemical reactions in the atmosphere (Hegde and Kawamura, 2012). Concentration ratios of OC/EC in the Chengdu samples were 2.22±0.51 in daytime, which were slightly higher than those (2.05±0.51) in nighttime, suggesting an enhanced production of OC in daytime. Moreover, the high abundances of EC in nighttime, which may originate from the open burning of municipal wasters including plastics with large emission of terephthalic acid (a point will be discussed later), also contribute to the relative low OC/EC ratios. The OC/EC ratios were similar to those obtained in Beijing (1.9) (Jung et al., 2009b), Guangzhou (2.0, 1.8) (Ho et al., 2011; Jung et al., 2009a), Shanghai (2.3) (Ye et al., 2003), China, and Seoul, Korea (1.8) (Kim et al., 2007). Saarikoski et al. (2008) observed an OC/EC ratio of 6.6 for biomass burning and 0.71 for vehicular emissions, whereas Sandradewi et al. (2008) found values of 7.3 and 1.1 for these two sources, respectively. Cachier et al. (1989) and Watson et al. (2001) also reported that OC/EC ratio is lower for vehicle exhaust (about 1.1), and much higher for the emissions from coal combustion and biomass burning (2.7 and 9.0, respectively). Emissions from coal and biomass burning may contain more organic pollutants that should result in higher OC/EC ratios than vehicular exhausts.

OC/EC ratios in Chengdu are site specific but result from mixed emissions from the

rapidly growing number of automobiles, and burning of coal and biomass. Domestic cooking and heating in the Sichuan Basin can emit a high amount of organic pollutants. The accumulation of pollutants under steady weather conditions may enhance the formation of secondary organic aerosols, resulting in high OC/EC ratios, along with enhanced primary emission from coal and biomass burning, and vehicular exhaust.

3.2. Molecular distributions of diacids and related compounds

A homologous series of α, ω-dicarboxylic acids (C_2–C_{11}), oxocarboxylic acids (ωC_2–ωC_9 and pyruvic acid), and α-dicarbonyls (glyoxal and methylglyoxal) were measured in the $PM_{2.5}$ samples of Chengdu. Their concentrations together with average and median values are summarized in Table 1. Concentrations of total diacids ranged from 1410–5250 ng m^{-3}, with an average of 3450 ± 995 ng m^{-3} in daytime and 3330 ± 920 ng m^{-3} in nighttime, respectively. The average values were higher than those from the Xi'an winter haze sample (2885 ng m^{-3}) (Cheng et al., 2013), New Delhi (2875 ng m^{-3}) (Miyazaki et al., 2009a), Nanjing (1684 ng m^{-3}) (Wang et al., 2002), Hong Kong (1655 ng m^{-3}) (Li and Yu, 2010), Beijing (760 ng m^{-3}) (Ho et al., 2010), Ulaanbaatar (536 ng m^{-3}) (Jung et al., 2010), Chennai (673 ng m^{-3}) (Pavuluri et al., 2010), urban Tokyo (438 ng m^{-3}) (Kawamura and Yasui, 2005), and 3–4 times larger than those reported in 14 Chinese cities (904 ng m^{-3}) (Ho et al., 2007). Because these samples were obtained at urban sites in winter, the highest concentrations of total diacids found in Chengdu would be attributed to serious air pollution associated with specific topography of the Sichuan Basin.

Oxalic acid (C_2) was detected as the most abundant diacid species (1370 ± 427 ng m^{-3}), followed by succinic (C_4, 431 ± 147 ng m^{-3}), and terephthalic acids (tPh, 391 ± 151 ng m^{-3} (Table 1). On average, concentrations of C_2–C_4 diacids accounted for 60% of total diacids. The average concentration of C_2 is lower than those at New Delhi (1430 ± 990 ng m^{-3}) (Miyazaki et al., 2009a) and Xi'an (winter haze time) (1769 ± 450 ng m^{-3}) (Cheng et al., 2013), but substantially higher than those observed at other urban sites in Asia such as Tokyo (270–1350 ng m^{-3}) (Kawamura and

196 Ikushima, 1993; Kawamura and Yasui, 2005), Chennai (435 ng m^{-3}) (Pavuluri et al., 2010),
197 Beijing (449 ng m^{-3}) (Ho et al., 2010), Hong Kong (464 ng m^{-3}) (Ho et al., 2011), and 14 Chinese
198 cities (558 ng m^{-3}) (Ho et al., 2007).

199 Concentrations of total oxoacids ranged from 272–1380 ng m^{-3}, with an average of 750
200 ng m^{-3} (Table 1). Glyoxylic acid (ωC_2) (average: 430 ± 193 ng m^{-3}) was found as a dominant
201 oxoacid, followed by pyruvic acid (Pyr) and 4-oxobutanoic acid (ωC_4). The OH oxidation of
202 glyoxal, glycolic acid, methylglyoxal, and acetic acid use the intermediate, ωC_2, and result in
203 oxalic acid (Kroll et al., 2005). The predominance of ωC_2 in oxoacids was also observed at the
204 Chinese urban sites (Ho et al., 2007). Oxoacids have been regarded as intermediates during the
205 oxidation of monoacids and other precursors in the atmosphere, then resulting in diacids
206 (Kawamura and Ikushima, 1993; Kawamura et al., 1996a).

207 In the present study, average concentrations of two α-dicarbonyls, glyoxal (Gly, 71.1 ng
208 m^{-3}) and methylglyoxal (MeGly, 72.1 ng m^{-3}) were almost the same in Chengdu (Table 1). Their
209 concentrations were similar with those in Xi'an (45 ng m^{-3} and 71 ng m^{-3}) (Cheng et al., 2013)
210 and Hong Kong (35.8 ng m^{-3} and 92.2 ng m^{-3}) (Li and Yu, 2010), but much higher than those
211 reported in 14 urban cities of China (3.02 ng m^{-3} and 14.5 ng m^{-3}) (Ho et al., 2007), and other
212 Asian cities such as New Delhi (18 ng m^{-3} and 25 ng m^{-3}) (Miyazaki et al., 2009a), Ulaanbaatar
213 (14 ng m^{-3} and 20 ng m^{-3}) (Jung et al., 2010), Chennai (5.78 ng m^{-3} and 6.36 ng m^{-3}) (Pavuluri et
214 al., 2010), and urban Tokyo (21.5 ng m^{-3} and 24.1ng m^{-3}) (Kawamura and Yasui, 2005).
215 α-Dicarbonyls (Gly and MeGly) might be the gas-phase oxidation products of volatile organic
216 compounds (VOCs) including benzene, toluene, xylene (Volkamer et al., 2001), ethylene (Ervens
217 et al., 2004), isoprene (Zimmermann and Poppe, 1996), and terpene (Fick et al., 2004), but may
218 act as precursors of secondary organic aerosols via heterogeneous processes (Jang et al., 2002;
219 Kroll et al., 2005; Liggio et al., 2005). In general, these oxoacids and carbonyls are secondarily
220 produced via atmospheric photooxidation of various organic precursors and/or primarily formed

by fossil fuel combustion and biomass burning, and further oxidized into saturated diacids.

3.3. Temporal variations of diacids, oxoacids, and α-dicarbonyls

3.3.1. Day and night variations

Concentrations of diacids were higher in daytime than nighttime, except for unsaturated aliphatic diacids (M, F, and mM) and aromatic diacids (Ph, iPh, and tPh) (Figs. 2 and 3). The day- and night-time differences and temporal variations in diacids seem to be closely associated with the sources followed by photochemical oxidation (Hegde and Kawamura, 2012; Miyazaki et al., 2009a). Generally, higher concentrations of most diacids may be attributed to photochemical production of diacids and/or their emissions by fossil fuel combustion and cooking activities, which occurs more frequency in the daytime.

As the dominant species of diacids, oxalic acid (C_2) can be primarily generated by fossil fuel combustion and biomass burning, and secondarily formed by the oxidation of VOCs and other organic precursors in the gas phase and/or aerosol phase (Kawamura et al., 2005; Kawamura et al., 1996b). Higher concentrations and fractions of oxalic acids in daytime than nighttime might result from the differences in net production processes of C_2 between day and night: more effective production of C_2 and/or less significant loss of C_2 in daytime than in nighttime. It is possible that rates of production and loss rates of C_2 are different for daytime and nighttime. During the nighttime, oxidation of organics may be less efficient because of the absence of sunlight and lack of H_2O_2 and OH production (Buxton et al., 1997; Carlton et al., 2007; Charbouillot et al., 2012; Kawamura et al., 1996a; Singh et al., 1985; Suh et al., 2003). Positive correlations between C_2 and precursor compounds such as ωC_2, Pyr, C_3, and C_4 as well as kC_3, were found especially in daytime, implying that secondary production of C_2 occurs through photochemical degradation of its precursors.

Maleic acid (M) may be produced by the ring opening of aromatic hydrocarbons such as toluene and benzene (Kawamura and Sakaguchi, 1999; Kawamura et. al., 1996a). Ho et al. (2006)

reported that high concentrations of toluene observed at Hong Kong were one of the most important sources of methylmaleic acid (mM). It has been suggested that *cis* maleic acid can isomerize to *trans* isomer (fumaric acid) during photochemical transformations (Kawamura and Ikushima, 1993). Higher concentrations of maleic acid than fumaric acid may demonstrate that the Chengdu aerosols contained relatively fresh oxidation products of aromatic hydrocarbons emitted from local pollution sources, and these unsaturated aliphatic diacids were formed in an early stage of photochemical oxidation (Kawamura and Ikushima, 1993). Therefore, the higher concentrations of M, F, and mM in nighttime can be explained by the accumulation of the oxidation products of aromatic hydrocarbons, which are produced during daytime. However, we cannot exclude the possibility that aromatic hydrocarbons are oxidized at night to produce M, F, and mM.

Terephthalic and phthalic acids, which originate from the oxidation of polycyclic aromatic hydrocarbons, were found to be higher in nighttime than in daytime, similar to that of EC. Such a diurnal distribution may be attributed to different precursors and transformation processes of these aromatic diacids in Chengdu aerosols. Unlike the saturated C_2–C_4 diacids, unsaturated and branched-chain diacids are generated via photochemical oxidation of more specific precursors such as aromatic hydrocarbons (Fisseha et al., 2004; Kawamura et al., 1996a) and methylcycloalkenes (Grosjean and Fung, 1984). Singh et al. (1985) reported diurnal variations of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes, and 3- and 4-ethyltoluenes in twelve US cities, with maxima at night and early morning hours and minima in the late morning and early afternoon. In addition, uncontrolled burning of plastic bottles and bags and waste incineration that frequently happened at nighttime would be responsible for high concentrations of tPh during the night (Simoneit et al., 2005; Kawamura and Pavuluri, 2010), while the accumulation of primary emission and secondary product generated during the day also resulted in high Ph in nighttime. Rather, a positive correlation (R^2=0.53,

P<0.05) was observed between tPh and EC at nighttime, suggesting that uncontrolled burning of plastic bottles and bags is a one of the significant sources of EC in Chengdu during nighttime.

3.3.2. Enhanced formation of oxalic acid in hazy days within the Sichuan Basin

Local emissions of diacids and their precursors may be significant in Chengdu because it is a densely populated urban center with many industries including petrochemicals and thermal power plants. Several factors played an important role to form and strengthen the organic acids in Chengdu, such as the special topography of the Sichuan Basin, the height of the planetary boundary layer (PBL), and wind patterns changing infrequently during wintertime. Therefore, relatively high concentrations of total diacids, oxoacids, and α-dicarbonyls were detected in a haze episode during the winter sampling period.

Generally, the air pollution index (API) was higher in haze episodes than other times, and the temporal trend of API was somewhat similar with that of concentrations of total diacids and related compounds (Fig. 4). Aqueous phase chemistry in aerosol/cloud/fog droplets is also important in the production of diacids (Miyazaki et al., 2009a; Warneck, 2003). Since sunlight irradiation was weak and the relative humidity was quite high in hazy days, one possible explanation for the observed increases in the relative concentrations and fractions of C_2 is its secondary formation in the aqueous phase of aerosols. This is supported by high concentrations of pyruvic acid (Pyr) and glyoxylic acid (ωC_2) obtained during the haze episode (Figs. 5 and 6). C_2 is known to be formed in the aqueous phase by OH oxidation of various precursors such as longer-chain diacids, pyruvic acid (Pyr), and glyoxylic acid (ωC_2) (Carlton et al., 2007; Kawamura et al., 1996a).

It was reported that SO_4^{2-} fraction dramatically increased with the pollution level at urban sites in China (Jung et al., 2009b). Previous research observed similarity in size distributions of SO_4^{2-} and C_2, suggesting a common source (Crahan et al., 2004; Guo et al., 2010; Huang et al., 2006; Miyazaki et al., 2010; Wang et al., 2012; Yao et al., 2003). The relationship

between C_2 and SO_4^{2-} and its linear correlation coefficient were adopted to interpret the C_2 formation processes mainly through aqueous phase reactions (Yu et al., 2005). A good correlation between C_2 and SO_4^{2-} was observed at urban cities in East Asia (R^2>0.69) (Yu et al., 2005) and in New Delhi, India (R^2>0.65) (Miyazaki et al., 2009a; Pavuluri et al., 2010), suggesting aqueous phase reactions in cloud/fog as an important pathway for the formation of secondary organic aerosols. In the present study, strong correlations between C_2 and SO_4^{2-} (r = 0.74 in daytime and 0.78 in nighttime; Fig. 7), ωC_2 and SO_4^{2-} (r=0.76 in daytime and 0.89 in nighttime) were observed, suggesting that the photochemical production of C_2 via aqueous phase reactions under high relative humidity conditions was pronounced during the winter in Chengdu. In addition, the slop of the regression line drawn for C_2 and SO_4^{2-} in the daytime samples (14.8) is greater by 14% than that in the nighttime samples (13.1) (Fig. 7). The greater slope together with higher concentrations of C_2 in daytime suggests more effective production of C_2 in daytime.

3.4. Molecular compositions and concentration ratios: Unique features of basin aerosols

3.4.1. High concentrations of selected diacids, C_9, Ph, tPh, and ωC_2

Azelaic acid (C_9): Among C_5 – C_{11} diacids examined in urban $PM_{2.5}$ in Chengdu, azelaic acid (C_9) was much more abundant than others, indicating its unique source (Table 1 and Fig. 3). Azelaic acid was abundant in fine particles from cooking emissions in China (He et al., 2004; Zhao et al., 2007). In addition, degradation of unsaturated fatty acids (from cooking emissions) in the atmosphere can also lead to secondary formation of azelaic acid (Kawamura et al., 1996a; Robinson et al., 2006; Rogge et al., 1991). Therefore, high concentrations of azelaic acid resulted directly and indirectly from cooking emissions in Chengdu.

Terephthalic acid (tPh): Three phthalic acids including *o*-, *m*-, and *p*-isomers were detected. The isomer distribution was characterized by the predominance of terephthalic acid (tPh), followed by phthalic acid, and isophthalic acid. Interestingly, tPh acid in the Chengdu aerosols is as abundant as succinic acid (C_4) in nighttime, and terephthalic and phthalic acids are at higher

concentrations than malonic acid (C_3) in daytime (Table 1). The tPh acid was detected as the third dominant species in the Chengdu aerosols (Table 1 and Fig. 3), while such a high abundance of tPh has rarely been reported in atmospheric aerosols from other regions. The average concentration of tPh acid in Chengdu (391 ng m^{-3}) is higher than that observed in urban Xi'an (250 ng m^{-3}, tPh being the second highest species) (Cheng et al., 2013), Ulaanbaatar (130 ng m^{-3}, tPh being the dominant species) (Jung et al., 2010), about ten times higher than the 45.6 ng m^{-3} reported in wintertime aerosols of Chennai, India (Pavuluri et al., 2010), Beijing (32.4 ng m^{-3}) (Ho et al., 2010), Guangzhou (31.8 ng m^{-3}) (Ho et al., 2011), and Hong Kong (19.9 ng m^{-3}) (Ho et al., 2011). Since tPh is a major chemical component of polyester (polyethylene terephthalate) fiber and plastic bags/bottles, the burning of plastic bottles and shopping bags may emit a significant amount of tPh (Fu et al., 2010; Kawamura and Pavuluri, 2010). In addition, waste incinerators containing plastics frequently occur in open surroundings without any emission control. High concentrations of tPh obtained in Chengdu are different from those in other Asian cities, because they are emitted from uncontrolled burning of waste materials including plastic bottles and bags within the surrounding rural area.

Phthalic acid (Ph): Phthalic acid is one of the most abundant species in the Chengdu samples (Table 1 and Fig. 3), as well as in other Chinese megacities such as Xi'an (Cheng et al., 2013), Guangzhou (Ho et al., 2011), and Beijing (Ho et al., 2010). Organic aerosols in megacities of China might be related to significant emissions from coal combustion, which is not treated effectively in rural areas. Ph is directly emitted from coal combustion and/or generated by atmospheric degradation of aromatic hydrocarbons such as naphthalene (Bunce et al., 1997; Kawamura and Ikushima, 1993). In addition, high concentrations of naphthalene were observed in some cities in China (Lee et al., 2001; Liu et al., 2001; Wang et al., 2009a). The high relative abundances of Ph in total diacids were also reported in urban aerosols in Sapporo (Aggarwal and Kawamura, 2008), in aerosols from fourteen Chinese megacities (Ho et al., 2007), and in primary

346 auto exhaust from near a roadside and tunnel in Hong Kong (Ho et al., 2006). Ph in the Chengdu
347 aerosols was higher than those in other cities, which can be explained by high levels of precursors
348 including PAHs emitted from vehicular exhausts and/or coal burning in the Sichuan Basin.

349 **Glyoxylic acid (ωC_2)**: Concentrations of ωC_2 in the Chengdu aerosols (Table 1 and Fig.
350 6b) were also among the highest in comparison to previous studies; they were approximately three
351 to ten times higher than those from New Delhi (121 ng m^{-3}) (Miyazaki et al., 2009a) and other
352 Chinese sites (37.8 ng m^{-3}) (Ho et al., 2007). C_2 is partly produced via the oxidation of ωC_2 that is
353 derived from MeGly and Gly (Carlton et al., 2007; Cheng et al., 2013; Rinaldi et al., 2011); the
354 levels of these α-dicarbonyls in Chengdu aerosols were also higher than those in other urban
355 regions in China and India (Ho et al., 2007; Miyazaki et al., 2009a). Biogenic and anthropogenic
356 VOCs can react with oxidants to produce MeGly and Gly, which can be hydrated in the aqueous
357 phase and is further oxidized to result in ωC_2, acetic acid, hydrated ωC_2, and oxalic acid (Lim et
358 al., 2005). Such high concentrations of ωC_2 in Chengdu aerosols indicate that ωC_2 is one of the
359 important precursors of oxalic acid.

360 *3.4.2. Correlation analysis and the ratios of C_3/C_4, C_6/C_9, and Ph/C_9*

361 The correlation coefficients of selected species (C_2, C_3, C_4, kC_3, Pyr, ωC_2, and ωC_4) were
362 examined in daytime and nighttime, respectively (Fig. 8). Other than direct vehicular emission,
363 photochemical processes could also control the atmospheric concentrations of these species. For
364 instance, the most abundant oxocarboxylic acid (ωC_2) can be further oxidized to C_2; a good
365 correlation was found between ωC_2 and C_2 ($r = 0.87$, $P < 0.01$ in daytime and $r = 0.80$, $P < 0.01$ in
366 nighttime). Malonic (C_3) and succinic (C_4) acids can be oxidized to C_2 via the breakdown of
367 intermediates such as ketomalonic acid (kC_3) (Kawamura and Ikushima, 1993); thus, strong
368 correlations were often observed among C_2, C_3, and C_4 in this study (Fig. 8).

369 The C_3/C_4 ratio can be used as an indicator of enhanced photochemical formation of
370 diacids in the atmosphere (Kawamura and Ikushima, 1993). Malonic acid (C_3) is derived from the

371 incomplete combustion of fossil fuels or from the secondary atmospheric production. C_3/C_4 ratios
372 (0.25–0.44, average 0.35) observed in vehicular exhaust were lower than those in normal
373 atmospheric aerosol (0.56–2.9, average 1.6), due to C_3 being thermally less stable than C_4 in the
374 high-temperature combustion process (Kawamura and Ikushima, 1993). However, the C_3/C_4 ratios
375 in particles from secondary origin were significantly higher than that range. An average C_3/C_4
376 ratio above 3.0 was detected in the remote Pacific atmosphere, where these diacids mostly
377 resulted from photochemical oxidation of aerosols in which C_3 was abundant (Kawamura and
378 Sakaguchi, 1999). The ratios of C_3/C_4 in Chengdu $PM_{2.5}$ were on average 0.50 ± 0.13, with a
379 range of 0.01– 0.76 (Fig. 9a), which suggests that these diacids mainly originate from the
380 vehicular exhaust. Compared with other megacities (Table 2), the C_3/C_4 ratios in Chengdu
381 aerosols were similar to those in Beijing (0.56) (Ho et al., 2010), Xi'an (0.59) (Cheng et al., 2013),
382 14 Chinese cities (0.51) (Ho et al., 2007), and New Delhi (0.59) (Miyazaki et al., 2009a), but
383 lower than those in Chennai (1.36) (Pavuluri et al., 2010), Hong Kong (1.24) (Ho et al., 2006),
384 and Guangzhou (0.72) (Ho et al., 2011) where secondary marine aerosols are enhanced. The C_3/C_4
385 ratios obtained in this study are lower than or similar to the values reported for direct emissions of
386 vehicular exhaust (Kawamura and Ikushima, 1993), suggesting an important contribution from
387 vehicular emissions in Chengdu.

388 C_6 and Ph are produced by the atmospheric oxidation of anthropogenic cyclic hexene and
389 aromatic hydrocarbons such as naphthalene, respectively (Kawamura and Sakaguchi, 1999),
390 whereas C_9 is derived from biogenic unsaturated fatty acids (e.g., oleic and linoleic acids) which
391 originated from biogenic emissions (marine and terrestrial plants) and/or from anthropogenic
392 cooking activities (Kawamura and Ikushima, 1993; Robinson et al., 2006). Previous studies
393 reported that C_6/C_9 and Ph/C_9 ratios could be used as potential indicators for the source strength of
394 anthropogenic and biogenic precursors transformed to aerosol diacids (Kawamura and Yasui,
395 2005). The mean value of the C_6/C_9 ratio (0.66 for the day and night samples; Table 2; Fig. 9b) in

our study is about 2–3 times lower than that for biomass burning aerosols. However, the C_6/C_9 ratio is similar to that for urban Chinese and Tokyo aerosols (Ho et al., 2007; Kawamura and Yasui, 2005), suggesting that adipic (C_6) acid is less commonly derived from biomass burning and production of C_9 through the oxidation of biogenic unsaturated fatty acids and is possibly higher due to domestic cooking in Chengdu.

We obtained an average Ph/C_9 ratio of 2.36 (Table 2 and Fig. 9c) that is comparable to those (2.23) from urban areas of Chinese megacities (Ho et al., 2010), but higher than those in urban areas of New Delhi and Chennai, India (Miyazaki et al., 2009a; Pavuluri et al., 2010), Ulaanbaatar, Mongolia (Jung et al., 2010), and Tokyo, Japan (Kawamura and Yasui, 2005). This comparison implies that the contribution of Ph from other anthropogenic sources is more significant than from biomass burning. Kawamura and Kaplan (1987) reported that diesel fuel vehicular exhaust showed a Ph/C_6 ratio of 6.58, which was higher than that from gasoline fuel vehicles (2.05). An averaged Ph/C_6 ratio of 3.70 ± 0.9 obtained in this study (Table 2 and Fig. 9d), is higher than those from the urban areas in India (1.38 in New Delhi, 2.92 in Chennai) (Miyazaki et al., 2009a; Pavuluri et al., 2010) and in Japan (1.68 in Tokyo) (Kawamura and Yasui, 2005). Because most passenger cars in Chengdu are gasoline fuel vehicles, this study suggested that naphthalenes and other PAHs from coal burning may be the important source of Ph in Chengdu.

4. Conclusions

Homologous dicarboxylic acids, oxoacids and α-dicarbonyls (glyoxal and methylglyoxal), as well as OC and EC were detected in aerosol samples collected during winter 2012 at an urban site in Chengdu, Sichuan Basin in southwest China. Average concentrations of oxalic acid (C_2, 1373 ng m^{-3}), terephthalic acid (tPh, 391 ng m^{-3}), glyoxylic acid (ωC_2, 430 ng m^{-3}), and total diacids (3388 ng m^{-3}) were significantly higher than was reported at other urban sites in Asia.

C_2 was the most abundant dicarboxylic acid, followed by succinic, terephthalic, and phthalic acids. The average concentrations and mass fractions of C_2 were higher in daytime (1439 ng m^{-3} and 41.7% of total diacids) than in nighttime (1315 ng m^{-3} and 38.9% of total diacids). Positive correlations of C_2 with C_3, C_4, and ωC_2 were better in daytime than in nighttime, suggesting that significant secondary production of C_2 occurred in daytime via the oxidation of both longer-chain diacids and ωC_2 in the Sichuan Basin during wintertime. An aqueous phase production of C_2 might be important in hazy days under the condition of the basin topography of Chengdu. Relatively low C_3/C_4 ratios (0.50 ± 0.13) and high concentrations of tPh and Ph were found in this study, suggesting that primary emissions from vehicular exhaust, coal combustions and waste incinerations are important emission sources for polar organic compounds in the Sichuan Basin.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 41173022, 41175106), the West Light Foundation of the Chinese Academy of Sciences, and the "Strategic Priority Research Program (B)" of the Chinese Academy of Sciences (Grant No. XDB05030305). This study was also in part supported by Grant-in-aid No. 24221001 from the Japan Society for the Promotion of Science (JSPS). P.F. appreciates the financial support from the "One Hundred Talents" program of the Chinese Academy of Sciences. The authors thank Mr. Lv Long for his help during sample collection. All data presented in this paper are freely available upon request.

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Table 1. Concentrations (ng m^{-3}) of diacids, oxoacids and α-dicarbonyls as well as concentrations (μg m^{-3}) of EC and OC in the $PM_{2.5}$ aerosols collected in Chengdu, China in winter 2012.

Components, abbreviation	Daytime (n=15)				Nighttime (n=17)			
	Min	Max	Mean	Med	Min	Max	Mean	Med
Dicarboxylic acids								
Oxalic, C_2	639	1996	1440	1590	443	2310	1320	1270
Malonic, C_3	85.5	341	227	244	3.49	394	206	222
Succinic, C_4	197	636	436	417	155	683	428	412
Glutaric, C_5	41.2	166	114	124	51.5	163	105	91.6
Adipic, C_6	37.5	156	88.3	92.4	44.4	128	79.0	80.3
Pimelic, C_7	8.27	47.3	34.4	41.9	6.06	51.34	30.5	32.7
Sebacic, C_8	BDL	63.9	8.41	BDL	BDL	BDL	BDL	BDL
Azelaic, C_9	64.0	296	154	150	52.4	191	116	108
Decanedioic, C_{10}	2.66	36.4	21.8	23.7	BDL	35.5	17.5	20.2
Undecanedioic, C_{11}	11.4	75.1	27.7	24.4	11.5	41.3	20.1	16.4
Methylmalonic, iC_4	4.57	17.2	11.0	10.5	3.10	17.6	9.87	8.68
Methylsuccinic, iC_5	30.9	72.5	51.5	50.1	29.8	107	59.3	58.4
2-Methylglutaric, iC_6	3.45	31.7	13.3	9.31	3.66	16.4	8.93	9.05
Maleic, M	22.4	60.2	41.6	42.0	33.1	155	59.5	54.0
Fumaric, F	BDL	17.2	9.00	8.93	BDL	22.8	9.94	8.45
Methylmaleic, mM	14.4	42.1	31.0	31.1	20.8	86.8	38.5	32.6
Phthalic, Ph	147	382	278	274	164	436	304	296
Isophthalic, iPh	4.99	22.8	12.8	13.2	6.37	21.4	14.6	14.1
Terephthalic, tPh	125	571	356	357	200	872	422	400
Malic, hC_4	7.51	18.5	12.1	11.6	6.45	15.0	11.3	11.4
Oxomalonic, kC_3	15.5	154	76.1	69.3	11.5	145	65.4	54.6
4-oxopimelic, kC_7	3.90	17.7	11.8	13.2	2.21	19.2	11.2	11.6
Subtotal	1490	4690	3450	3810	1410	5250	3330	3160
Oxocarboxylic acids								
Pyruvic, Pyr	46.7	176	121	119	41.3	189	114	110
2-Oxoethanoic (Glyoxylic),	178	864	445	412	149	882	416	365
3-Oxopropanoic, ωC_3	9.06	55.9	27.5	21.1	3.63	52.2	24.0	21.1
4-Oxobutanoic, ωC_4	48.6	151	103	93.2	48.4	157	97.1	85.9
5-Oxopentanoic, ωC_5	8.55	28.8	18.4	16.9	6.61	26.3	16.8	16.9
7-Oxoheptanoic, ωC_7	7.30	30.6	21.6	23.2	5.15	34.3	21.4	23.2
8-Oxooctanoic, ωC_8	8.69	42.3	25.8	26.3	7.63	47.5	25.7	25.7
9-Oxononanoic, ωC_9	3.55	22.9	12.0	11.8	5.14	29.0	14.1	14.2
Subtotal	320	1320	774	720	272	1380	729	674
α-Dicarbonyls								
Glyoxal, Gly	44.1	102	69.4	71.1	37.1	130	72.8	61.5
Methylglyoxal, MeGly	34.8	111	75.6	73.5	31.9	118	68.6	65.5
Subtotal	90.0	213	145	144	87.9	215	141	131
OC (μg m^{-3})	28.8	83.5	57.0	57.1	35.1	82.7	57.5	57.6
EC (μg m^{-3})	8.71	42.4	27.5	27.8	11.9	65.6	30.4	27.9

BDL: below detection limit. BDL is ca. 0.01 ng m^{-3}.

678 **Table 2.** Concentrations (ng m^{-3}) and weight ratios of selected diacids and related compounds in the $PM_{2.5}$ aerosols collected in Chengdu, China in winter 2012,
679 along with the literature data for urban aerosols.

Site/Type	Sampling Period	Particle Size	C_2	C_3	C_4	C_6	C_9	Ph	tPh	Total Diacids	ωC_2	C_3/C_4	C_6/C_9	Ph/C_9	C_2/Diacids	Reference
14 Cities, China	Winter 13-14 Jan 2003	$PM_{2.5}$	558	40.6	79.7	15.0	28.9	78.2	–	904	37.8	0.51	0.52	2.71	0.62	Ho et al., 2007
Hong Kong, Yuen Long	Winter Jan 2004	$PM_{2.5}$	1224	100	34.9	16.4	91.1	94.5	–	1655	119	2.86	0.18	1.04	0.74	Li and Yu, 2010
Hong Kong, roadside	Winter Jan + Nov 2003	$PM_{2.5}$	478	89.1	71.9	10.7	16.8	78.0	–	858	43.2	1.24	0.64	4.64	0.56	Ho et al., 2006
Hong Kong, Urban/roadside	Winter Dec 2006~Jan 2007	$PM_{2.5}$	464	26.5	23.2	7.00	24.3	34.1	19.9	644	38.5	1.14	0.29	1.40	0.72	Ho et al., 2011
Guangzhou, China	Winter Dec 2006~Jan 2007	$PM_{2.5}$	182	13.3	18.4	5.39	16.3	91.8	31.8	384	13.0	0.72	0.33	5.63	0.47	Ho et al., 2011
Ulaanbaatar, Mongolia	Winter Nov 2007~Jan 2008	$PM_{2.5}$	107	13.0	63.0	11.0	42.0	54.0	130	536	55.0	0.21	0.26	1.29	0.20	Jung et al., 2010
Beijing, China Urban/PKU	Autumn Aug ~ Sep 2006	$PM_{2.5}$	449	28.1	49.9	17.4	34.8	77.5	32.4	760	25.1	0.56	0.50	2.23	0.59	Ho et al., 2010
Nanjing, China	Winter 15 Feb ~ 1 Mar	$PM_{2.5}$	880	126	195	49.3	102	–	–	1684	–	0.65	0.49	–	0.52	Wang et al., 2002
Chennai, India	Winter Jan ~ Feb 2007	PM_{10}	435	58.7	43.3	5.6	12.6	19.4	45.6	673	41.2	1.36	0.45	1.55	0.65	Pavuluri et al., 2010
Xi'an, China	Winter Jan ~ Feb 2009	PM_{10}	1162	58	98	6.9	15.0	196	250	1843	179	0.59	0.46	13.1	0.63	Chen et al., 2013
Tokyo, Japan	Winter 20-21 Nov 1989	TSP	186	40.5	47.4	14.2	20.6	24.0	–	438	41.5	0.85	0.69	1.17	0.42	Kawamura and Yasui, 2005
New Delhi, India	Sep 2006 ~ Apr 2007 Daytime	TSP	955	181	273	29.0	70	40	5.0	1777	114	0.66	0.41	0.57	0.55	Miyazaki et al., 2009b
New Delhi, India	Sep 2006 ~ Apr 2007 Nighttime	TSP	1906	194	330	32.0	72	45	4.0	2875	128	0.59	0.44	0.63	0.66	Miyazaki et al., 2009b
Chengdu, China	Winter Jan 2013 Daytime	$PM_{2.5}$	1439	227	436	88.3	154	278	356	3454	445	0.53	0.61	1.94	0.42	This study
Chengdu, China	Winter Jan 2013 Nighttime	$PM_{2.5}$	1315	206	428	79.0	116	304	422	3331	416	0.47	0.71	2.72	0.39	This study

680 Note: Ratios of C_3/C_4, C_6/C_9, and Ph/C_9 were calculated from average values in the references; "–" represents no data or no result.
681

Figure captions:

Fig. 1 Map showing the sampling site in Chengdu within the Sichuan Basin, southwest China.

Fig. 2 Molecular distributions of diacids, oxoacids, and α-dicarbonyls in fine aerosols ($PM_{2.5}$) collected in Chengdu, China in winter. Bars show the standard deviation of the concentrations of each species.

Fig. 3 Pie diagrams of relative abundances (%) of individual diacids in total straight-chain diacids (C_2–C_{11}) and two major aromatic diacids (Ph and tPh) in the fine aerosols.

Fig. 4 Temporal variations (ng m^{-3}) of (a) total diacids, (b) total oxoacids, and (c) total α-dicarbonyls in the aerosol samples, along with API, in winter (open circle for daytime; solid circle for nighttime). API is the "Air Pollution Index".

Fig. 5 Temporal variations (ng m^{-3}) of (a) C_2, (b) C_3, (c) C_4, (d) C_6, (e) C_9, (f) Ph, and (g) tPh acids in the aerosol samples ($PM_{2.5}$) (open circle for daytime; solid circle for nighttime).

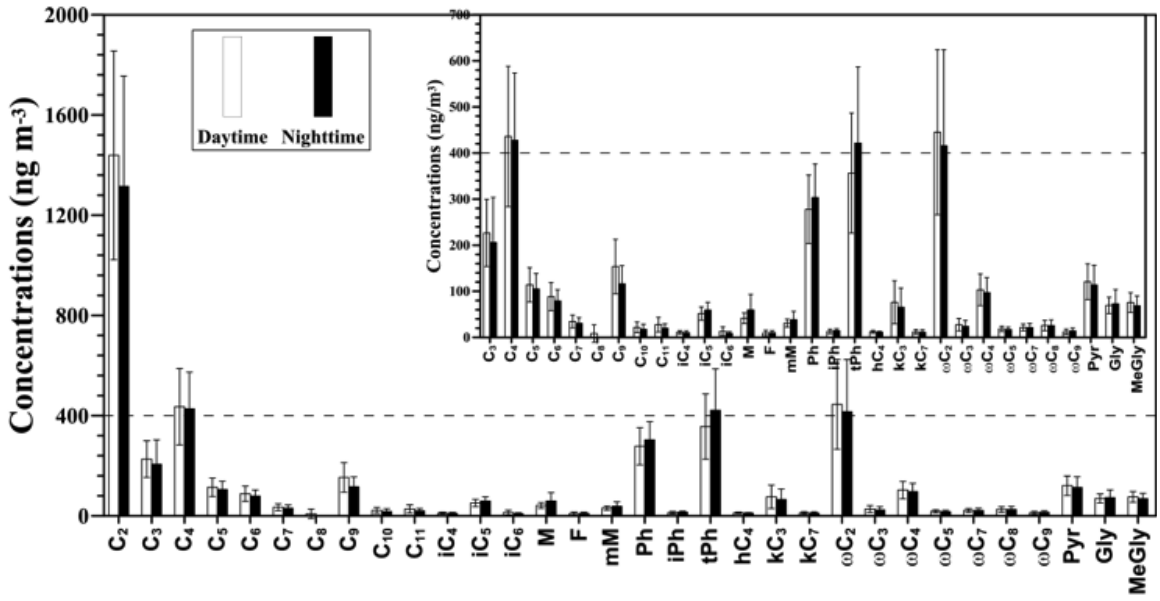
Fig. 6 Temporal variations (ng m^{-3}) of (a) Pyr, (b) ωC_2, (c) Gly, and (d) MeGly in the aerosol samples ($PM_{2.5}$) (open circle for daytime; solid circle for nighttime).

Fig. 7 Correlation plots for the concentrations of oxalic acid (C_2) and sulfate (SO_4^{2-}) in the aerosol samples.

Fig. 8 Scatterplots of (a) C_4, (b) C_3, (c) kC_3, (d) ωC_2, (e) ωC_4, and (f) Pyr with C_2 in the aerosol samples.

Fig. 9 Temporal variations of (a) C_3/C_4, (b) C_6/C_9, (c) Ph/C_9, and (d) Ph/C_6 in the aerosol samples (open circle for daytime; solid circle for nighttime).

Fig. 1 A map showing the sampling site in Chengdu within the Sichuan Basin, Southwest China.



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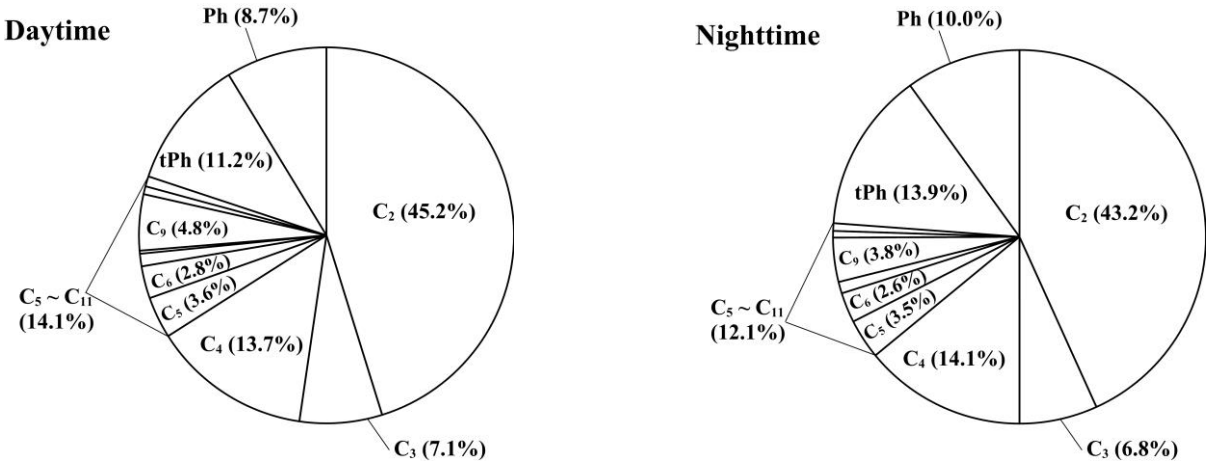
716



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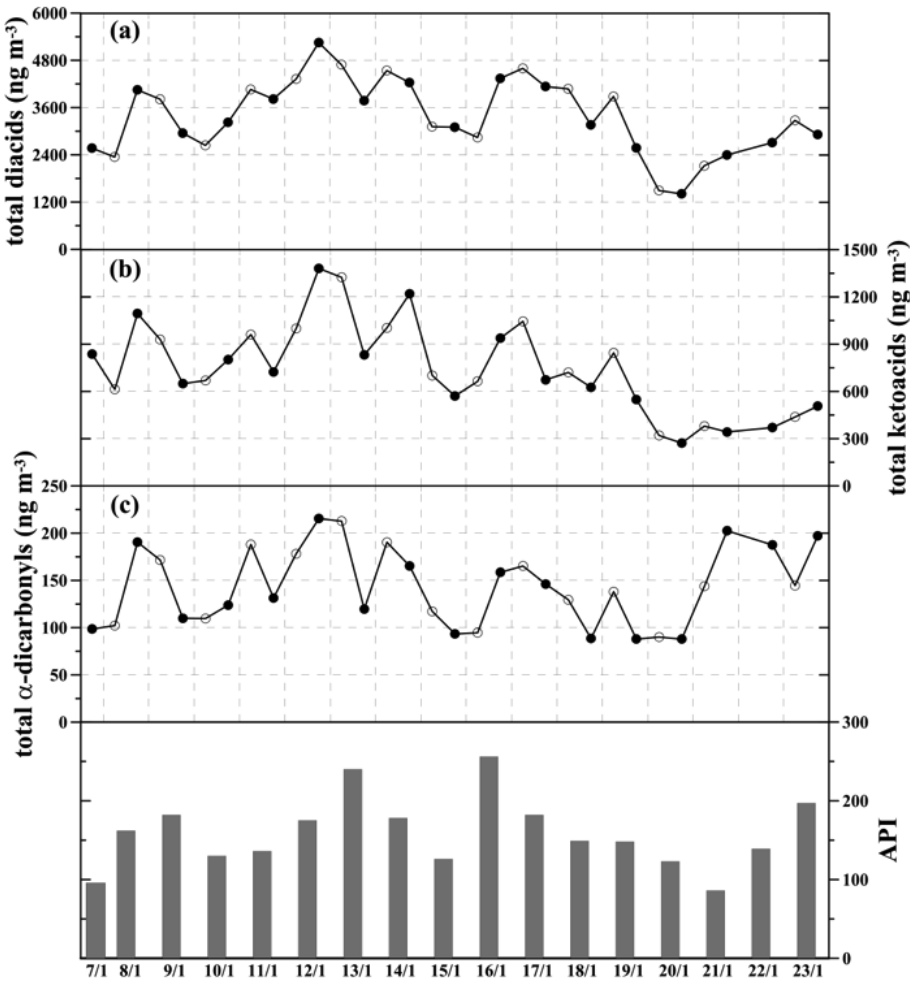

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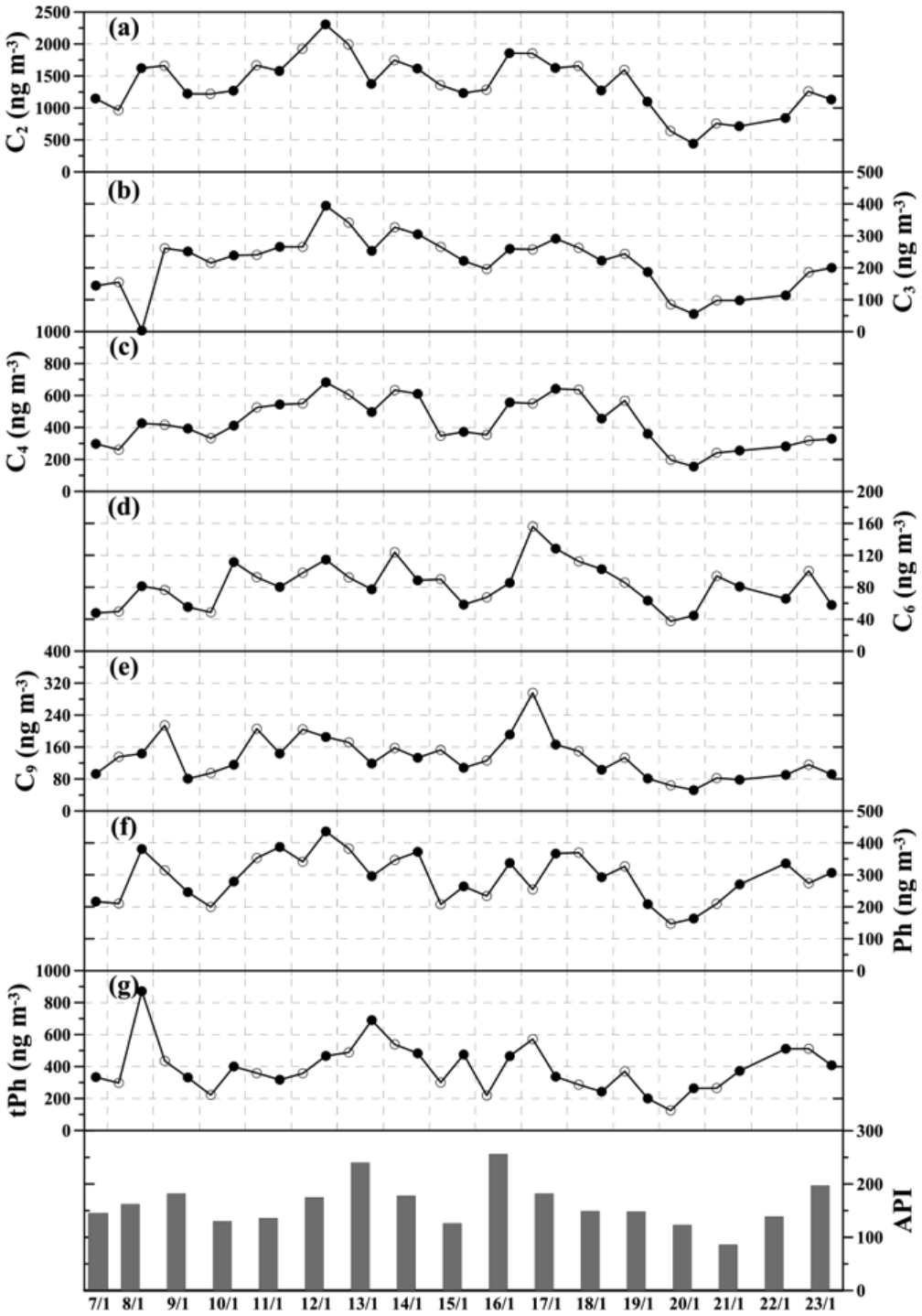

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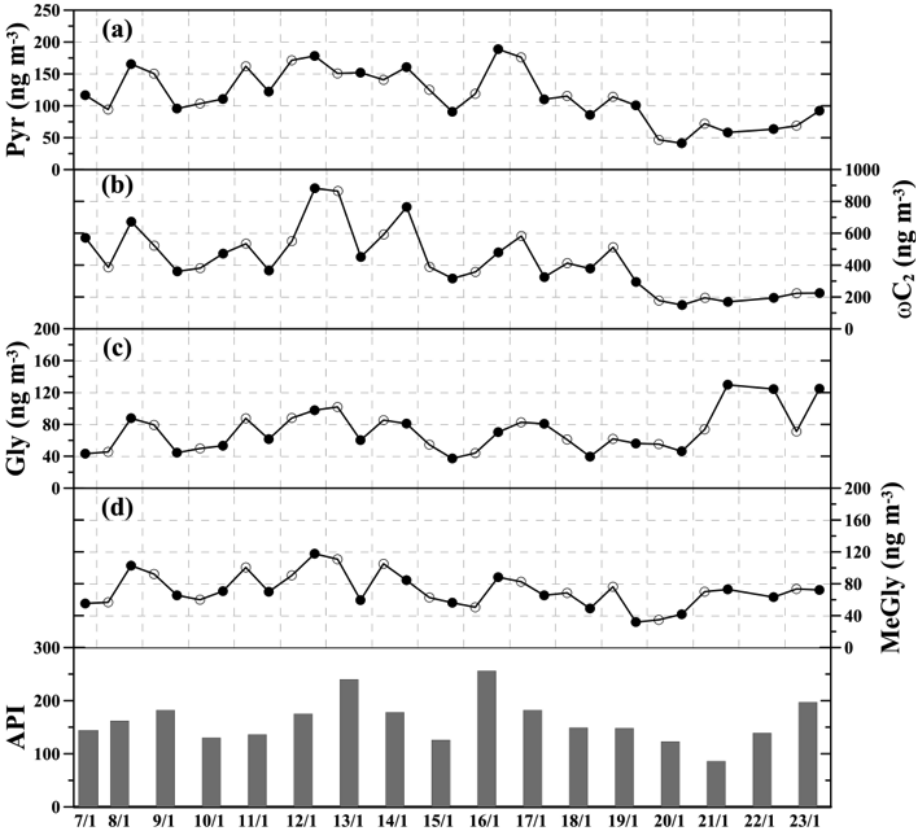

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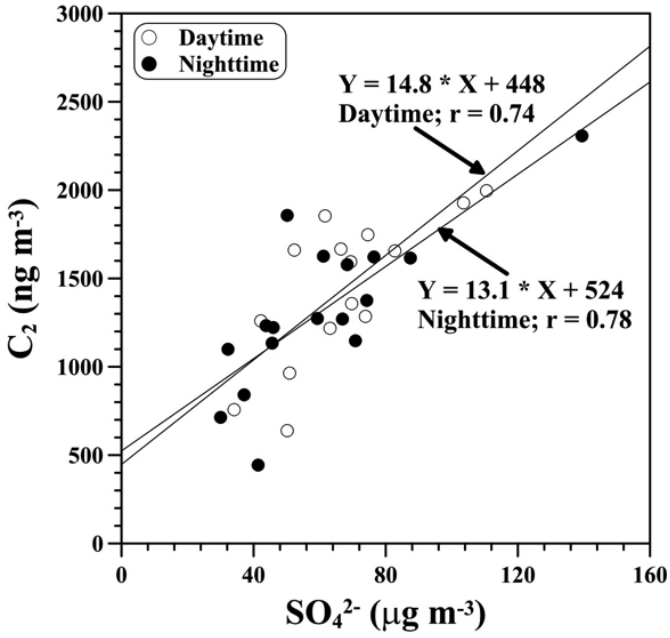

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743
744 **Fig. 7** Correlation plots for the concentrations of oxalic acid (C_2) and sulfate (SO_4^{2-}) in the
745 aerosol samples.
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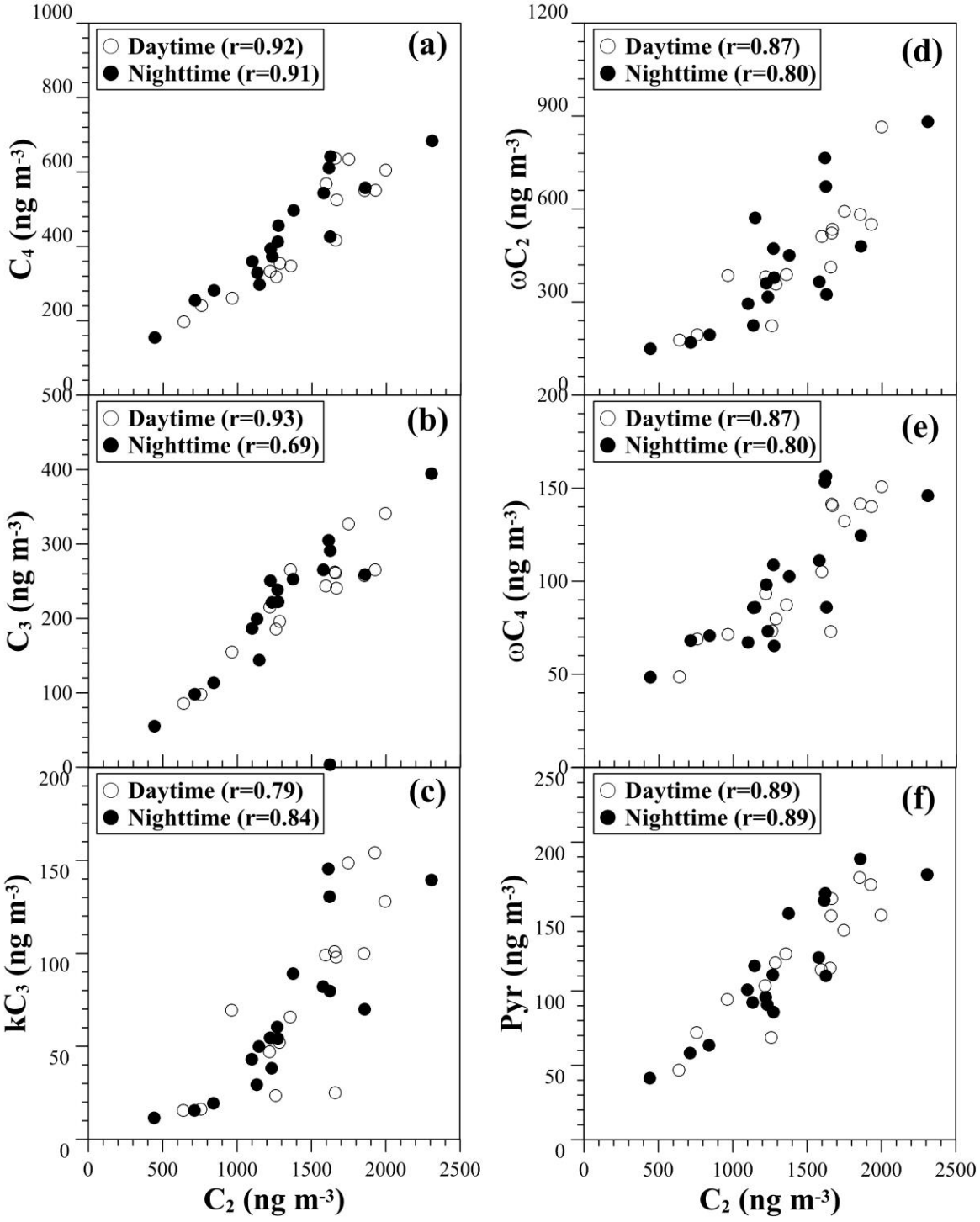

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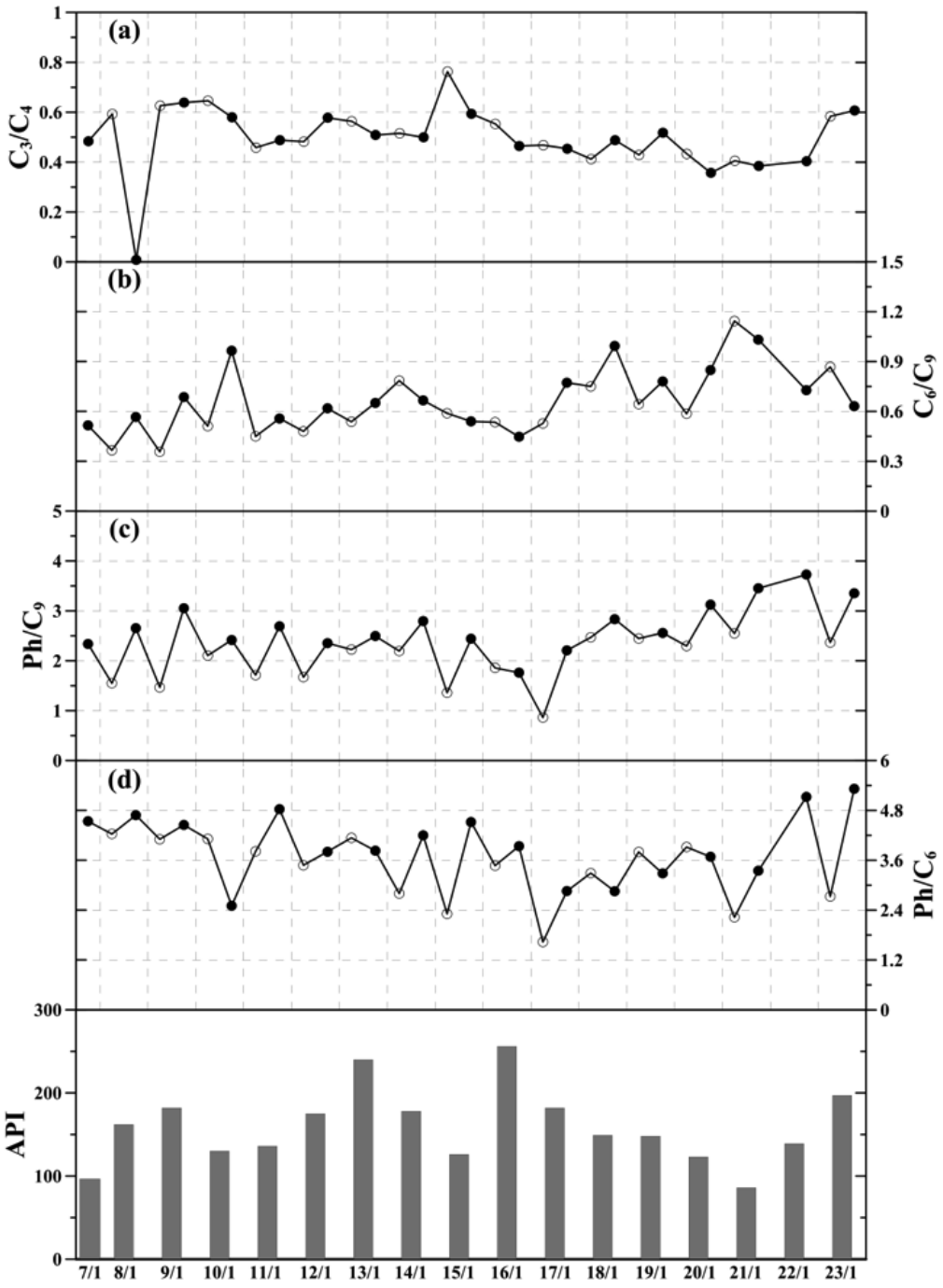

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