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Gehui Wang
Chinese Academy of Sciences

Jianjun Li
Central University of Finance and Economics

Junji Cao
Chinese Academy of Sciences

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Atmospheric oxalic acid and related secondary organic aerosols in Qinghai Lake, a continental background site in Tibet Plateau

Jingjing Meng[a], Gehui Wang[a,b,*], Jianjun Li[a], Chunlei Cheng[a], Junji Cao[a]

[a] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China
[b] School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China

HIGHLIGHTS

- Unique molecular characteristics of SOA in remote continental atmosphere.
- Origins and formation mechanisms of SOA in Tibet Plateau.
- Biomass combustion process produces low levels of oxalate, glyoxal and methylglyoxal.

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ABSTRACT

Summertime $PM_{2.5}$ aerosols collected from Qinghai Lake (3200 m a.s.l.), a remote continental site in the northeastern part of Tibetan Plateau, were analyzed for dicarboxylic acids (C_2–C_{11}), ketocarboxylic acids and α-dicarbonyals. Oxalic acid (C_2) is the dominant dicarboxylic acid in the samples, followed by malonic, succinic and azelaic acids. Total dicarboxylic acids (231 ± 119 ng m^{-3}), ketocarboxylic acids (8.4 ± 4.3 ng m^{-3}), and α-dicarbonyls (2.7 ± 2.1 ng m^{-3}) at the Tibetan background site are 2–5 times less than those detected in lowland areas such as 14 Chinese megacities. Compared to those in other urban and marine areas enhancements in relative abundances of C_2/total diacids and diacids-C/WSOC of the $PM_{2.5}$ samples suggest that organic aerosols in the region are more oxidized due to strong solar radiation. Molecular compositions and air mass trajectories demonstrate that the above secondary organic aerosols in the Qinghai Lake atmosphere are largely derived from long-range transport. Ratios of oxalic acid, glyoxal and methylglyoxal to levoglucosan in $PM_{2.5}$ aerosols emitted from household burning of yak dung, a major energy source for Tibetan in the region, are 30–400 times lower than those in the ambient air, which further indicates that primary emission from biomass burning is a negligible source of atmospheric oxalic acid and α-dicarbonyls at this background site.

1. Introduction

Water-soluble organic compounds are important components of tropospheric aerosols, accounting for up to 70% of the total aerosol mass (Jacobson et al., 2000; Sorooshian et al., 2007a; Jung et al., 2010). Water-soluble organic compounds can change the hygroscopic properties of particles and thus influence the atmospheric radiative forcing through acting as cloud condensation nuclei (CCN). Moreover, water-soluble organic compounds such as alcohols and carboxylic acids can act as surfactants, and thus increase the solubility of airborne particulate pollutants in human respiratory tract (Latif and Peter, 2004). Dicarboxylic acids, ketocatboxylic acids and α-dicarbonyls are important classes of water-soluble organic compounds, which are taken as secondary organic aerosols (SOA) because these compounds in the atmosphere are mostly produced from photochemical oxidation. Dicarboxylic acids and related compounds have been found in a wide variety of environments including urban (Wang et al., 2002, 2006b, 2012; Kawamura and Yasui, 2005), suburban (He and Kawamura, 2010; Ho et al., 2010), mountain (Wang et al., 2009; Hegde and Kawamura, 2012), marine (Wang et al., 2006c; Mochida et al., 2003) and free troposphere (Sorooshian et al., 2007b). Most studies have focused on dicarboxylic acids in urban atmosphere. However, information on dicarboxylic acids in high altitude regions is very limited, where dicarboxylic acids and related water-soluble species are easily lofted into clouds and activated as CCN. Tibet Plateau is called as “the roof of the world”, where population is sparse and anthropogenic

* Corresponding author. State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China. Tel.: +86 29 8832 9320; fax: +86 29 8832 0456.
E-mail addresses: wanggh@ieecas.cn, gehuiwang@yahoo.com.cn (G. Wang).

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activity is insignificant. Our previous study on atmospheric aerosols from Qinghai Lake, a remote site in northeast Tibet Plateau, found that atmospheric environment of Qinghai Lake is still pristine (Li et al., 2013). To the best of our knowledge, the current study is the first time to characterize secondary organic aerosols (SOA) in the Tibetan atmosphere. We first explored molecular composition and concentration of airborne particulate dicarboxylic acids and related compounds and then discussed their sources and formation mechanisms by comparing with those in other regions and in biomass burning emissions.

2. Experimental section

2.1. Collection of ambient aerosol

Qinghai Lake, the largest closed interior saline lake in China, is located in the northeastern part of Tibetan Plateau with an altitude of 3200 m (Fig. 1). $PM_{2.5}$ samples were collected on the rooftop (~20 m above ground level) of a tower at the "Bird Island" peninsula (location: 36°58′44″N, 99°54′24″E), which is situated on the northwestern shore of Qinghai Lake (shown in Fig. 1). $PM_{2.5}$ samples were collected for two months each lasting for 24 h from the beginning of July to the end of August 2010 using a high-volume air sampler (Anderson, USA) equipped with prebaked (450 °C, 8 h) quartz fiber filters (Whatman, USA) at an airflow rate of 1.13 $m^3\ min^{-1}$. Field blank samples were also collected for about 10 min without sucking any air before and after sampling by mounting a blank filter onto the sampler. After sampling, each sample was sealed in an aluminum foil bag and stored at −18 °C before analysis. A total of 34 samples collected every other day were analyzed for dicarboxylic acids and related SOA, and the remaining were reserved for a carbon isotope analysis in the future.

2.2. Collection of fresh aerosol from yak dung burning

Yak dung is the major energy source for Tibetan in the region. To investigate the impact of biomass burning emission on dicarboxylic acids and related compounds in the Qinghai Lake atmosphere, fresh $PM_{2.5}$ aerosols emitted from household yak dung burning were collected using the high-volume sampler above. Three local Tibetan families were randomly selected and the $PM_{2.5}$ sampler was fixed 1 m downwind of the exhaust outlet of the domestic chimney. Each samples was collected for about 15 min and stored together with the above ambient samplers at −18 °C prior to analysis.

2.3. Sample analysis

2.3.1. Dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls

Dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls were determined using the method described by Kawamura and Sakaguchi (1999). Briefly, aliquot of the filter was cut in pieces and extracted with pure Milli-Q water under ultrasonication for three times each in 15 min. The water extracts were subsequently filtrated with quartz wool and concentrated to dryness, followed by a reaction with 14% BF_3/*n*-butanol at 100 °C for 1 h to form butyl esters/dibutoxy acetals. After the reaction the derivatives were dissolved in *n*-hexane and washed with pure water for three times. Finally, the hexane layer was concentrated and analyzed using a capillary gas chromatography (GC; HP 6890) equipped with a split/splitless injector and a flame ionization detector. The GC oven temperature was programmed from 50 (2 min) to 120 °C at 15 °C min^{-1} and then to 300 at 5 °C min^{-1} with a final isothermal hold at 300 °C for 16 min. Peak identification was performed by comparing the GC retention time with that of authentic standards and confirmed by mass spectrum of the sample using a GC–mass spectrometry (GC–MS).

Recovery experiment was performed by spiking the authentic standards onto a blank filter and treated same as the real samples. The recoveries were 75% for oxalic and higher than 85% for other target compounds. The target compounds in the field blanks were less than 4% of those in the ambient samples. Concentrations of all determined compounds reported here were corrected for both field blanks and recoveries.

2.3.2. Inorganic ions, elemental carbon (EC), organic carbon (OC) and water-soluble organic carbon (WSOC)

Analysis details for inorganic ions, EC, OC and WSOC have been reported in our previous paper (Li et al., 2013). Briefly, aliquot of the

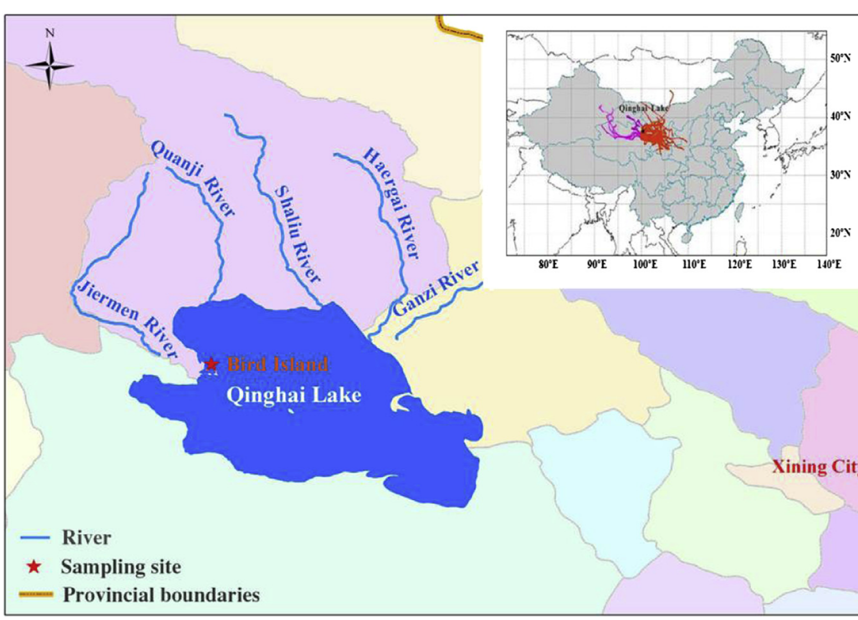

Fig. 1. A map description for the location of the sampling site (Bird Island) and the72-h backward trajectories of air masses arrival at Qinghai Lake during the sampling period (local time, 24 h interval).

$PM_{2.5}$ samples were extracted with Milli-Q water under ultra-sonication for three times, and filtered through PTFE filters, then measured using an ion chromatography (Dionex 600, Dionex, USA). EC and OC in the samples were measured following the IMPROVE thermal reflectance (TOR) protocol using a DRI model 2001 carbon analyzer. As for WSOC in the samples aliquot of the filter was also extracted with pure water and analyzed using Shimadzu TOC-L CPH Total Carbon Analyzer. Data about the inorganic ions, EC, OC, WSOC and levoglucosan have been reported by Li et al. (2013) and cited here to reveal the sources and formation mechanisms of dicarboxylic acids and related secondary organic aerosols (SOA) in the region.

3. Results and discussion

3.1. Molecular characteristics of dicarboxylic acids and related SOA

A series of dicarboxylic acids and related SOA including dicarboxylic acids (C_2–C_{11}), ketocarboxylic acids and α-dicarbonyls in the $PM_{2.5}$ samples were determined. Concentrations of these organic compounds were summarized in Table 1, along with WSOC, EC and OC. Molecular compositions of these SOA are shown in Fig. 2.

As seen in Table 1 total dicarboxylic acids in the Qinghai Lake $PM_{2.5}$ samples ranged from 73 to 573 ng m^{-3} with an average of 231 ± 119 ng m^{-3}, which is about 2 times lower than those in mountain regions such as Mount Tai, east China (day: 756 ± 139 ng m^{-3}; night: 263 ± 123 ng m^{-3}) (Wang et al., 2009) and the central Himalayan in Nainital, India (Hegde and Kawamura, 2012) (day: 480 ± 132 ng m^{-3}; night : 380 ± 107 ng m^{-3}) and 5 times lower than in 14 Chinese megacities (892 ± 457 ng m^{-3} (Ho et al., 2007)) but around 4 times higher than those in the Pacific Ocean areas (e.g. west Pacific Ocean, 60 ng m^{-3} (Wang et al., 2006c); western North Pacific Ocean, 54 ng m^{-3} (Mochida et al., 2003)), indicating that on a global scale atmospheric SOA is much more abundant in a continental background area than in marine regions. Same as those in the above regions, the dominant species in the Qinghai Lake samples is oxalic acid (C_2), whose concentration is 139 ± 82 ng m^{-3} (29–348 ng m^{-3}). Concentrations (14–139 ng m^{-3}, Table S2) of C_2–C_4 in the Qinghai Lake atmosphere

Table 1
Concentrations of dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, WSOC, OC and EC in $PM_{2.5}$ aerosols collected at Qinghai Lake, Tibet Plateau during the summer of 2010.

Compounds	Chemical formula	Concentration		
		Total (n = 34)	Easterly (n = 25)	Westerly (n = 9)
I. Dicarboxylic acids (ng m^{-3})				
Oxalic, C_2	HOOC–COOH	139 ± 82 (29–348)	154 ± 86 (29–348)	98 ± 52 (49–199)
Malonic, C_3	HOOC–CH_2–COOH	25 ± 15 (9.3–78)	28 ± 16 (9.3–78)	17 ± 7.1 (10–31)
Succinic, C_4	HOOC–$(CH_2)_2$–COOH	134 ± 7.8 (3.5–29)	15 ± 8.2 (3.6–29)	11 ± 5.8 (3.5–21)
Glutaric, C_5	HOOC–$(CH_2)_3$–COOH	2.7 ± 1.9 (0.4–6.6)	3.0 ± 2.0 (0.5–6.6)	1.9 ± 1.4 (0.4–4.6)
Adipic, C_6	HOOC–$(CH_2)_4$–COOH	1.1 ± 0.9 (0.2–4.9)	1.2 ± 1.0 (0.2–4.9)	1.0 ± 0.4 (0.4–1.8)
Pimelic, C_7	HOOC–$(CH_2)_5$–COOH	1.2 ± 0.5 (0.2–2.8)	1.2 ± 0.5 (0.2–2.8)	1.4 ± 0.3 (0.9–1.8)
Suberic, C_8	HOOC–$(CH_2)_6$–COOH	0.3 ± 0.2 (0.1–1.4)	0.3 ± 0.3 (0.1–1.4)	0.3 ± 0.2 (0.2–0.6)
Azelaic, C_9	HOOC–$(CH_2)_7$–COOH	10 ± 4.0 (5.0–22)	10 ± 4.2 (5.0–22)	11 ± 3.3 (5.6–5.6)
Sebacic, C_{10}	HOOC–$(CH_2)_8$–COOH	1.6 ± 0.9 (5.7–5.1)	1.6 ± 1.0 (0.7–5.1)	1.4 ± 0.3 (1.0–1.9)
Undecanedioic, C_{11}	HOOC–$(CH_2)_9$–COOH	2.8 ± 2.0 (1.6–13)	2.8 ± 2.3 (1.6–13)	2.9 ± 0.8 (1.6–3.7)
Methylmalonic, iC_4	HOOC–CH(CH_3)–COOH	1.4 ± 2.1 (0.1–12)	1.6 ± 2.4 (0.1–12)	0.8 ± 0.7 (0.1–2.4)
Mehtylsuccinic, iC_5	HOOC–CH(CH_3)–CH_2–COOH	0.9 ± 0.5 (0.2–2.4)	1.0 ± 0.5 (0.3–2.4)	0.7 ± 0.5 (0.2–1.4)
Methyglutaric, iC_6	HOOC–CH(CH_3)–$(CH_2)_2$–COOH	0.7 ± 0.5 (0.1–2.6)	0.8 ± 0.5 (0.1–2.6)	0.6 ± 0.3 (0.2–1.1)
Maleic, M	HOOC–CH = CH–COOH(cis)	4.2 ± 2.0 (1.1–10)	4.4 ± 2.1 (1.1–10)	3.8 ± 1.5 (1.3–5.6)
Fumaric, F	HOOC–CH = CH–COOH(trans)	3.8 ± 3.0 (0.2–14)	4.2 ± 3.3 (0.2–14)	2.7 ± 1.7 (0.5–6.2)
Methylmaleic, mM	HOOC–C(CH_3) = CH–COOH(cis)	4.0 ± 3.3 (1.3–21)	4.1 ± 3.8 (1.3–21)	3.7 ± 1.0 (2.4–5.6)
Phthalic, Ph	HOOC–C_6H_4–COOH(ortho)	6.2 ± 3.6 (2.6–22)	6.2 ± 4.1 (2.6–22)	6.3 ± 1.8 (3.4–8.0)
Isophthalic, iPh	HOOC–C_6H_4–COOH(meta)	1.4 ± 0.7 (0.8–4.4)	1.4 ± 0.8 (0.8–4.4)	1.5 ± 0.4 (0.9–2.1)
Terephthalic, tPh	HOOC–C_6H_4–COOH(para)	1.8 ± 1.1 (0.8–5.3)	1.7 ± 1.0 (0.8–5.1)	2.1 ± 1.3 (0.9–5.3)
Ketomalonic, kC_3	HOOC–HC(O)–COOH	4.4 ± 1.4 (3.0–7.2)	4.2 ± 1.3 (3.0–7.2)	5.2 ± 1.4 (3.1–5.6)
Ketopimelic, kC_7	HOOC$(CH_2)_2$HC(O)$(CH_2)_2$COOH	4.4 ± 1.7 (2.9–9.4)	4.0 ± 1.3 (2.9–7.9)	5.5 ± 2.1 (2.9–9.4)
Subtotal		231 ± 119 (73–573)	250 ± 127 (73–573)	178 ± 75 (109–331)
II. Ketocarboxylic acids (ng m^{-3})				
Pyruvic, Pyr	CH_3–(O)C–COOH	1.0 ± 0.5 (0.2–2.2)	1.0 ± 0.5 (0.2–2.2)	0.9 ± 0.6 (0.4–1.9)
Glyoxylic, ωC_2	OHC–COOH	4.9 ± 3.1 (0.2–11)	5.4 ± 3.3 (0.2–13)	3.4 ± 2.1 (1.3–7.3)
3-Oxopropanoic, ωC_3	OHC–CH_2–COOH	0.6 ± 0.3 (0.1–1.3)	0.6 ± 0.3 (0.1–1.0)	0.6 ± 0.3 (0.2–1.3)
4-Oxobutanoic, ωC_4	OHC–$(CH_2)_2$–COOH	0.9 ± 0.4 (0–1.8)	0.9 ± 0.4 (0.1–1.8)	0.8 ± 0.5 (0–1.6)
7-Oxoheptanoic, ωC_7	OHC–$(CH_2)_5$–COOH	0.7 ± 0.3 (0–1.2)	0.7 ± 0.3 (0.1–1.2)	0.5 ± 0.2 (0.3–1.0)
8-Oxooctanoic, ωC_8	OHC–$(CH_2)_6$–COOH	0.1 ± 0.1 (0–0.5)	0.2 ± 0.1 (0–0.5)	0.1 ± 0.1 (0–0.3)
9-Oxononanoic, ωC_9	OHC–$(CH_2)_7$–COOH	0.3 ± 0.1 (0.1–0.6)	0.3 ± 0.1 (0.1–0.6)	0.2 ± 0.0 (0.2–0.3)
Subtotal		8.4 ± 4.3 (1.9–19)	9.0 ± 4.4 (1.9–19)	6.6 ± 3.3 (2.7–14)
III. α-Dicarbonyls (ng m^{-3})				
Glyoxal, Gly	OHC–CHO	0.9 ± 0.7 (0.1–2.6)	1.0 ± 0.7 (0.1–2.6)	0.6 ± 0.4 (0.2–1.3)
Methyglyoxal, mGly	CH_3–(O)C–CHO	1.8 ± 1.5 (0–5.5)	2.1 ± 1.6 (0–5.5)	1.1 ± 1.0 (0.1–2.8)
Subtotal		2.7 ± 2.1 (0.3–7.9)	3.1 ± 2.2 (0.3–7.0)	1.7 ± 1.4 (0.3–4.1)
Total (all detected species)		242 ± 125 (75–600)	263 ± 133 (75–600)	187 ± 80 (112–349)
WSOC (μg m^{-3})		0.7 ± 0.3 (0.2–1.4)	0.7 ± 0.3 (0.2–1.4)	0.5 ± 0.4 (0.2–1.3)
OC (μg m^{-3})		1.6 ± 0.6 (0.7–2.6)	1.6 ± 0.6 (0.7–2.6)	1.3 ± 0.7 (0.7–2.5)
EC (μg m^{-3})		0.4 ± 0.2 (0.0–0.9)	0.4 ± 0.2 (0.1–0.9)	0.2 ± 0.2 (0.0–0.6)
$PM_{2.5}$ (μg m^{-3})		22 ± 13 (3.8–62)	21 ± 12 (3.8–62)	22 ± 19 (6.2–53)
T (°C)		14 ± 2.8 (9.0–20)	15 ± 2.9 (9.0–20)	13 ± 2.3 (11–17)

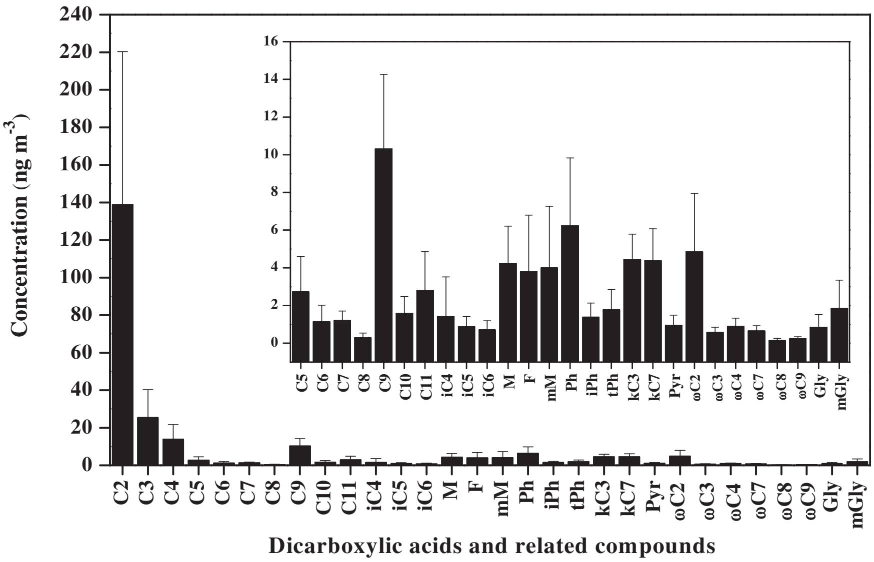

Fig. 2. Molecular composition of dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in $PM_{2.5}$ aerosols collected at Qinghai Lake, Tibet Plateau.

are comparable to those in Sonnblick (20–76 ng m^{-3}, Table S2), a mountain peak in the central Alps (3106 m a.s.l.) (Legrand et al., 2007), and Chichi-jima Island in North Pacific (1.6–41 ng m^{-3}, Table S2) (Mochida et al., 2003). Relative abundance of oxalic acid to the total diacids in the Qinghai Lake samples is 58 ± 8%, followed by malonic acid (C_3, 11 ± 5.0%), succinic acid (C_4, 6.0 ± 2.0%), azelaic acid (C_9, 5.0 ± 2.0%) and phthalic acid (Ph, 3 ± 1%). Such a molecular composition is similar to that in remote areas such as the western Pacific Ocean and the central Himalayan but different from those in urban regions where phthalic and/or tere-phthalic acids are more abundant than C_9 due to high emissions of anthropogenic precursors (e.g., PAHs and plasticizers) (Wang et al., 2006a; Ho et al., 2007; Cheng et al., 2013). C_9 is mainly produced from the oxidation of biogenic unsaturated fatty acids containing a double bond at the C-9 position (Kawamura and Gagosian, 1987). Relatively higher abundance of C_9 in the Qinghai Lake samples can be attributed to the abundant unsaturated fatty acids emitted from terrestrial plants and subsequent photooxidation (Kawamura and Gagosian, 1987). Averaged ratio of saturated fatty acid $C_{18:0}$ to unsaturated fatty acid $C_{18:1}$ in the $PM_{2.5}$ samples is 8.4 (calculated from the data reported by Li et al. (2013), which is much higher than that in urban area (e.g., 14 Chinese megacities 2.3 ± 0.5) (calculated from the data reported by Wang et al. (2006a)), indicating an enhanced photooxidation in the Tibet Plateau region.

Ketocarboxylic acids and α-dicarbonyls in the $PM_{2.5}$ samples are 8.4 ± 4.3 ng m^{-3} and 2.7 ± 2.1 ng m^{-3}, respectively. Both classes of compounds are the precursors of dicarboxylic acids. As shown in Fig. 2, the most abundant ketocarboxylic acid is glyoxylic acid (ωC_2), comprising 55% of the total, followed by pyruvic acid (Pyr, 12%) and 3-oxobutanoic acid (ωC_4, av. 8.0%). As shown in Table 1, glyoxal (Gly) was less abundant than methylglyoxal (mGly) (0.9 ± 0.7 ng m^{-3} versus 1.8 ± 1.5 ng m^{-3}), because mGly is of a stronger source (Fu et al., 2008) and OH radical oxidation with aerosol-phase mGly is slower compared to Gly (Cheng et al., 2013).

Averaged ratios of total diacid-C to OC (calculated as the ratio of the carbon concentration of all diacids to OC) in the Qinghai Lake samples are 5.1 ± 1.7%, which are about three times higher than that reported for Asian megacities such as 14 Chinese cities (1.4%) (Ho et al., 2007), Tokyo, Japan (0.95%) (Kawamura and Yasui, 2005), Chennai, India (1.6%) (Pavuluri et al., 2010), and remote sites (e.g.: western Pacific, 3.2%; Jeju Island, South Korea, 3.1%) (Sempéré and Kawamura, 2003; Kundu et al., 2010b), again demonstrating more intensive photochemical oxidation nature of the Tibet Plateau atmosphere due to much stronger solar radiation.

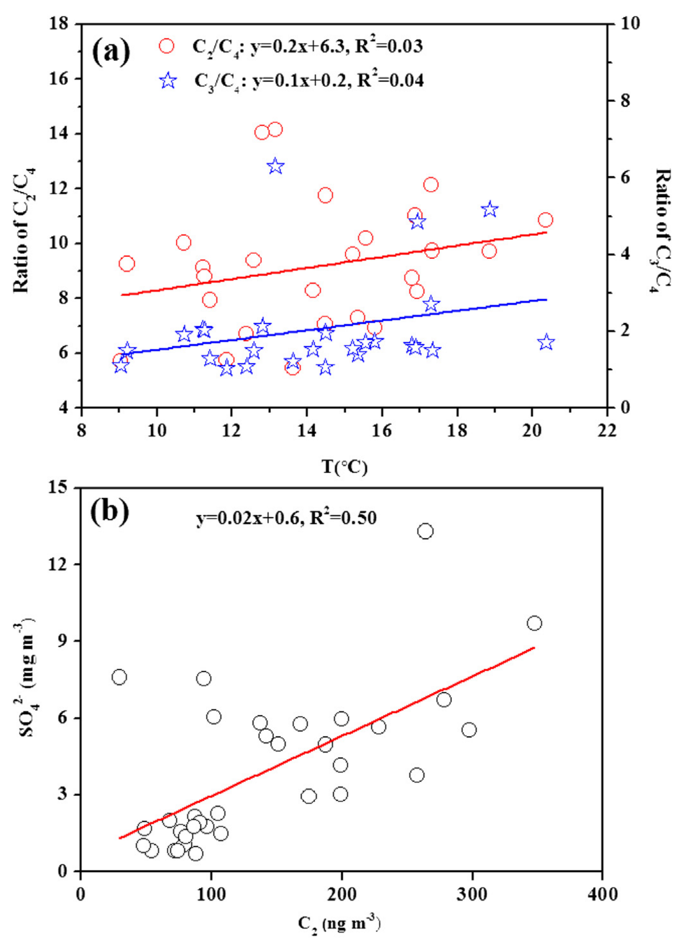

Fig. 3. Linear fit regression for (a) temperature (T) with C_2/C_4 and C_3/C_4 ratios and (b) C_2 with SO_4^{2-} (See the abbreviations in Table 1).

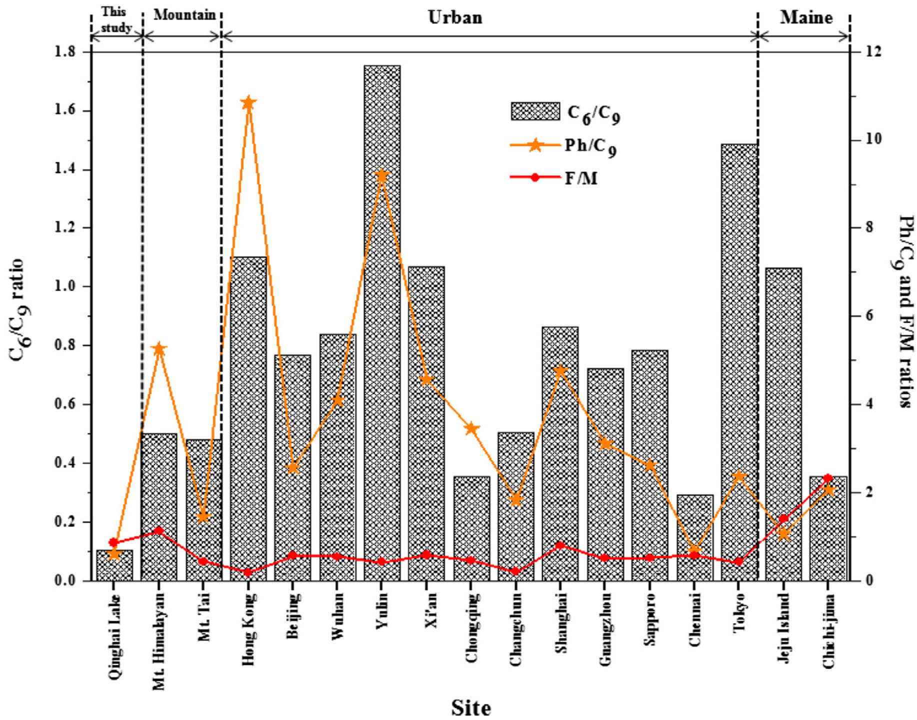

Fig. 4. Comparison of mass ratios of C_6/C_9, Ph/C_9 and F/M in the Qinghai Lake atmosphere with those in other regions (See the abbreviations in Table 1. Data for other regions are calculated from the same documents as those in Fig. 3).

3.2. Concentrations of OC, EC and WSOC

OC and EC in the Qinghai Lake samples ranged from 0.7 to 2.6 μg m^{-3} (ave. 1.6 ± 0.6 μg m^{-3}) and 0.03 to 0.9 μg m^{-3} (ave. 0.6 ± 0.3 μg m^{-3}), respectively, which are about one order of magnitude lower than those reported for 14 Chinese cities (Cao et al., 2007). OC/EC ratio of the Qinghai Lake samples is 6.0 ± 3.9 and about 50% higher than that for Chinese urban aerosols (4.2 ± 1.0) (Cao et al., 2007). Relative abundance of WSOC to OC is 41 ± 13% for the Qinghai Lake aerosols, which is also higher than those observed in the central Himalayan (29%) (Hegde and Kawamura, 2012) and the Northwest Pacific (i.e., Gosan, Korea) (30 ± 12%) (Miyazaki et al., 2007), mostly due to an enhanced photochemical oxidation (Aggarwal and Kawamura, 2009).

Table 2
Principal component analysis for major species in $PM_{2.5}$ aerosols from Qinghai Lake.

Compounds	Component			
	1	2	3	4
C_2	**0.75**	**0.54**	0.23	0.23
C_3	**0.90**	**0.78**	0.16	0.06
C_4	**0.80**	0.36	0.24	0.29
C_5	**0.76**	0.42	0.23	0.20
C_6	**0.91**	0.06	0.30	−0.16
C_9	**0.90**	0.07	0.18	0.15
Pyr	**0.53**	**0.61**	−0.41	0.42
ωC_2	**0.67**	0.43	0.23	0.24
mGly	**0.54**	**0.67**	0.20	0.27
Gly	**0.80**	0.41	0.15	0.33
WSOC	0.38	0.49	0.42	0.44
Levoglucosan	0.12	0.12	0.17	**0.88**
Mg^{2+}	0.41	0.10	**0.82**	0.30
Ca^{2+}	0.29	0.11	**0.86**	0.30
K^+	0.15	0.22	**0.64**	0.18
SO_4^{2-}	0.17	**0.68**	0.28	0.12
NO_3^-	0.16	**0.58**	0.38	0.42
Variance (%)	61	13	8	7

Absolute values higher than 0.5 are highlighted in bold.

3.3. Origins and formation mechanisms of diacids in the Qinghai Lake atmosphere

Several studies proposed that the ratios of C_2/C_4 and C_3/C_4 are indicative of aerosol aging, because they found that C_2, C_3 and C_4 are produced by the photochemical degradation of longer-chain dicarboxylic acids, and the production of C_3 comes from the chemical oxidation of C_4 (Jung et al., 2010; Sorooshian et al., 2007b). C_2/C_4 and C_3/C_4 ratios in the Qinghai Lake samples are 11 ± 7.2 and 2.2 ± 1.3, respectively, higher than those reported for urban aerosols such as 14 Chinese megacities (10 ± 3.1 and 0.9 ± 0.4) (Ho et al., 2007), Sapporo, Japan (3.3 and 1.3) (Aggarwal and Kawamura, 2008), marine aerosols such as Jeju Island, Korea (8.2 and 1.1) (Kundu et al., 2010b) and high alpine site in Austria (0.9 and 1.6)(Legrand et al., 2007) (Fig. S1). Pavuluri et al. (2010) found that C_2/C_4 and C_3/C_4 ratios could have strong correlation with ambient temperatures when local photooxidation is more important than long-range transport. In this study, both ratios of C_2/C_4 ($R^2 = 0.03$) and C_3/C_4 ($R^2 = 0.04$) exhibited very weak correlations with ambient temperatures (Fig. 3a), indicating that dicarboxylic acids and related SOA in the Qinghai Lake atmosphere are largely derived from long-range transport.

Table 3
Comparison of mass ratios of oxalic acid (C_2), methylglyoxal (mGly) and glyoxal to levoglucosan (Lev) in fresh $PM_{2.5}$ aerosols emitted from yak dung burning with those in ambient $PM_{2.5}$ aerosols.

Ratios	Fresh aerosols ($n = 3$)	Ambient aerosols ($n = 34$)
C_2/Lev	0.5 ± 0.3	200 ± 71
mGly/Lev	0.05 ± 0.03	2.3 ± 1.5
Gly/Lev	0.03 ± 0.01	1.1 ± 0.6

Several field observations found a robust correlation between C_2 and SO_4^{2-} and proposed a common formation pathway, i.e., in-cloud (Warneck, 2003) or aqueous-phase formation (Sullivan and Prather, 2007). In this study, we also found a strong correlation between C_2 and SO_4^{2-} ($R^2 = 0.50$) (Fig. 3b), indicating that SOA and sulfate at the continental background site share a common atmospheric process.

Maleic acid (M) can be isomerized to fumaric acid (F) under an intensive radiation (Agarwal et al., 2010). It was reported that the isomerization of M to F is suppressed under haze conditions due to weak sunlight (Hegde and Kawamura, 2012). As shown in Fig. 4, ratio of F/M (0.83 ± 0.46) in the Qinghai Lake atmosphere is higher than that reported in previous studies such as 14 Chinese cities (Ho et al., 2007) and Mt. Tai (Wang et al., 2009), probably indicating an enhanced isomerization of M to F under the Tibet Plateau strong solar radiation condition.

Adipic (C_6) and phthalic (Ph) acids are believed to be produced by the photochemical oxidation of cyclohexene and aromatic hydrocarbons such as naphthalene, which primarily originate from anthropogenic sources (Kawamura and Ikushima, 1993). Conversely, azelaic (C_9) acid is the oxidation product of unsaturated fatty acids emitted from the biogenic sources (Kawamura and Gagosian, 1987). As a result, both ratios of C_6/C_9 and Ph/C_9 can be used to qualitatively assess the strength of anthropogenic source versus biogenic source. As seen in Fig. 4, the values of C_6/C_9 (0.1 ± 0.4) and Ph/C_9 (0.6 ± 0.2) ratios in the Qinghai Lake air are 3–10 times lower than those reported for urban, marine and mountainous atmospheres; on the contrary, C_9 to total diacids ratios of the Qinghai Lake samples are several times higher than those in the northern part of China, again demonstrating that anthropogenic sources are negligible for Qinghai Lake aerosols while biogenic sources are important.

3.4. Principal component analysis

Here we employed principal component analysis (PCA) to further explore the sources and formation mechanisms of diacids and related SOA in the Qinghai Lake atmosphere. Four components

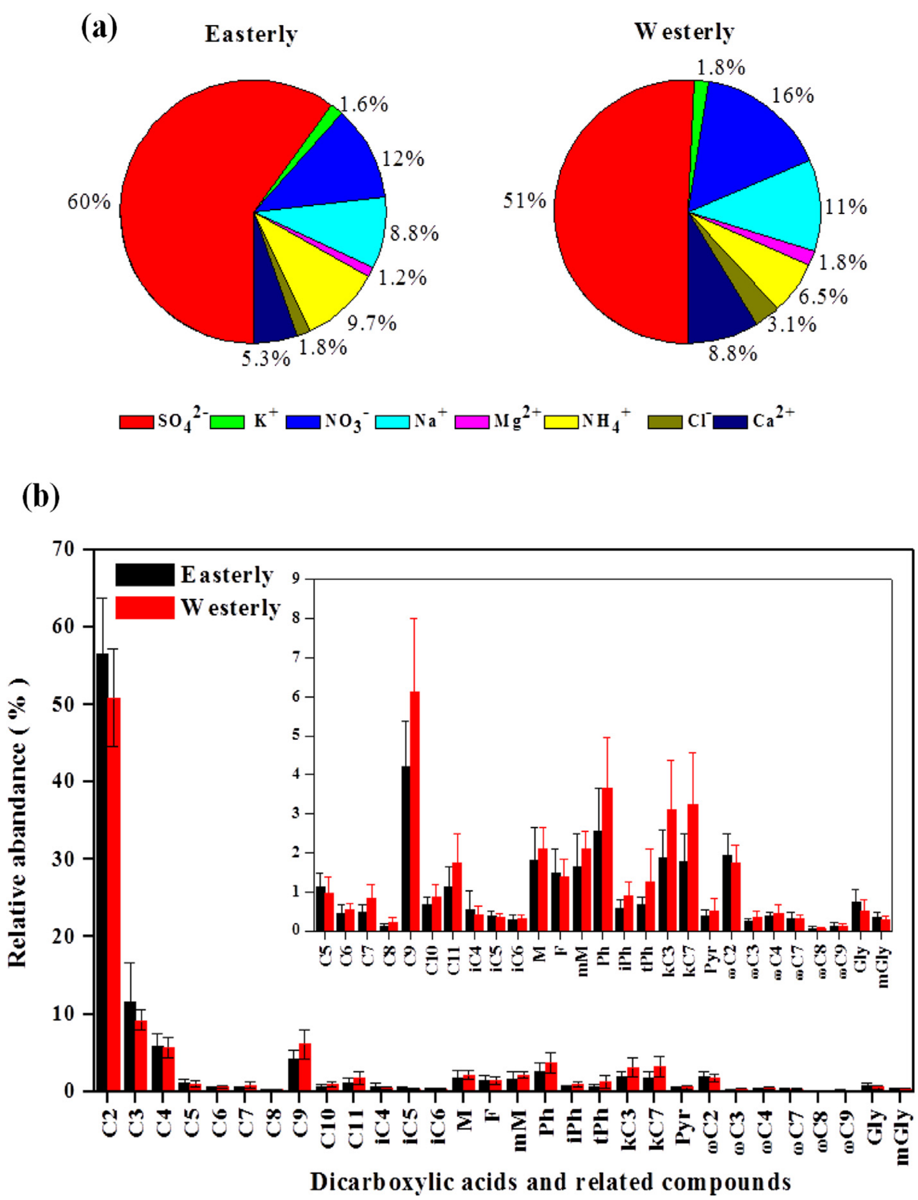

Fig. 5. Difference in compositions of water-soluble species between the easterly samples and the westerly samples ((a) inorganic ions, (b) dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls).

were deemed to get through the screen test, accounting for 61%, 13%, 8%, and 7% of the variance in each. As shown in Table 2, C_2–C_6, C_9 and Pyr, ωC_2, mGly and Gly showed significant correlations with the first component, while C_2, C_3, Pyr, mGly, $SO_4{}^{2-}$ and $NO_3{}^{-}$ well correlated with the second component. $SO_4{}^{2-}$ and $NO_3{}^{-}$ are regarded as the tracers of secondary aerosols and C_2 is proposed to be formed by hydroxyl radical (OH·) oxidation of various precursors including longer-chain diacids and glyoxylic acid (ωC_2) (Kawamura and Kaplan, 1987; Lim et al., 2005). Thus both components represent photochemical oxidation. However, we cannot distinguish the two components at the current stage. Component 3 presented high loadings with Mg^{2+}, Ca^{2+} and K^{+} (>0.6, Table 3), representing dust source. Levoglucosan, which is a tracer of biomass burning emissions (Fu et al., 2010), had a higher loading (0.88, Table 3) with the fourth component, while all other species presented much lower loadings (<0.42, Table 3), again demonstrating the unimportance of biomass burning emissions as the source of dicarboxylic acids and related compounds at this remote site.

3.5. Backward trajectory analysis

Summertime air masses in Qinghai Lake during the sampling period were largely transported from the easterly and westerly directions (Fig. 1). Therefore, the total samples could be classified as two categories: easterly and westerly. As shown in Fig. 5a, relative abundances of $SO_4{}^{2-}$ and NH_4^+ were lower in air masses transported by the westerly than those by the easterly, but relative abundance of Ca^{2+}, Mg^{2+}, Na^{+} and Cl^{-} were higher in the westerly samples due to the proximity of Qaidam desert in the west. Dicarboxylic acids, ketoacids and α-dicarbonyls in the easterly air masses were more abundant than those in the westerly air masses (Table 1). Moreover, the relative abundances of smaller diacids (C_2–C_5), ωC_2 and α-dicarbonyls were higher in the easterly than in the westerly, indicating that aerosols transported from the westerly are less oxidized (Fig. 5b). The more abundant dicarboxylic acids and related compounds in the easterly samples might suggest that the easterly air masses contain more pollutants, because the eastern part to Qinghai Lake is populated area.

3.6. Comparison with fresh aerosols from yak dung burning

Since abundant C_2, mGly and Gly are found in biomass burning polumes, it has been assumed that biomass combustion can directly produce these compounds (Gao et al., 2003; Falkovich et al., 2005; Fu et al., 2008; Kundu et al., 2010a; Sorooshian et al., 2007b; Narukawa and Kawamura, 1999). Yamasoe et al. (2000) analyzed particles from direct emissions of vegetation fires and found that biomass burning could produce a certain amount of oxalic acid, accounting for $0.07 \pm 0.04\%$ and $0.04 \pm 0.02\%$ of particle mass under flaming and smoldering conditions, respectively. Yak dung is the major energy source for Tibetan in the region, thus we analyzed $PM_{2.5}$ samples collected from the local residential area when burning yak dung for cooking in order to figure out whether biomass burning is an important source of C_2, mGly and Gly. Levoglucosan is a key tracer for biomass burning emission and chemically stable in the atmosphere (Hoffmann et al., 2010), thus the concentration ratios of C_2, mGly and Gly to levoglucosan can be used to evaluate the impact of biomass burning emission on the ambient aerosol composition. As shown in Table 3, ratio of C_2 to levoglucosan in the fresh $PM_{2.5}$ particles is 400 times lower than that in the ambient $PM_{2.5}$ aerosols. Likewise, the ratios of mGly and Gly to levoglucosan are 0.05 ± 0.03 and 0.03 ± 0.01 in the fresh aerosols and 30–40 times less than the ambient samples. Such significant differences between the fresh aerosols and the ambient particles clearly demonstrate that C_2, mGly and Gly in the samples are mostly derived from photochemical oxidation with a negligible amount directly produced from biomass combustion process. Such a result is in agreement with that reported by Carlton et al. (2007), who found that volatile organic precursors emitted from biomass burning (e.g. isoprene, acetone, monoterpenes, acetylene, etc.) could contribute significantly to ambient mGly and Gly through their secondary photo-oxidation products.

4. Summary and conclusion

Dicarboxylic acids and related compounds of $PM_{2.5}$ collected in Qinghai Lake of Tibetan Plateau during summer 2010 were characterized. C_2 is the most abundant species ($58 \pm 8\%$ of total dicarboxylic acids), followed by C_3, C_4 and C_9. Concentrations of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the Qinghai Lake aerosols are 2–5 times lower than those in Chinese urban areas. Molecular compositions and the insignificant correlation of C_3/C_4 and C_2/C_4 ratios with temperatures demonstrate that secondary organic aerosols in the Qinghai Lake atmosphere are largely derived from long-range transport. $PM_{2.5}$ aerosols emitted from yak dung combustion were analyzed for dicarboxylic acids and related compounds, of which results demonstrate that biomass combustion process does not directly produce significant amount of oxalic acid, Gly and mGly and these compounds in the atmosphere are mostly derived from photochemical oxidation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.07.024.

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