

Molecular distributions of diacids, oxoacids and α -dicarbonyls in summer- and winter-time fine aerosols from Tianjin, North China: Emissions from combustion sources and aqueous phase secondary formation

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Key Points:

- We characterized diacids and related compounds in summer- and winter-time fine aerosols (PM_{2.5}) from Tianjin, North China.
- Coal combustion and biomass burning emissions and subsequent secondary processes are the major sources of organic aerosols in North China.
- Aqueous phase secondary processes are the major formation pathways of water-soluble organic aerosols and their loading enhanced in winter.

Abstract

To understand the characteristics and sources of water-soluble organic aerosols (OA) in North China, we studied diacids, oxoacids and α -dicarbonyls in summer- and winter-time fine (PM_{2.5}) aerosols collected from Tianjin. Oxalic (C₂) acid found to be the most abundant diacid species, followed by succinic (C₄), malonic (C₃) and sebacic (C₈) acids, respectively. Glyoxylic (ω C₂) was the most abundant oxoacids followed by pyruvic acid. Concentrations of total diacids, oxoacids and α -dicarbonyls in winter were 2~3 times higher than those in summer, but their mass fractions in PM_{2.5} were exactly the opposite. On average, total diacids carbon accounted for 2.93% in total carbon and 3.31% in organic carbon (OC) in summer and 1.79% and 1.98%, respectively, in winter. Their contribution to water-soluble OC was almost same in both seasons (5.46% and 5.31%, respectively). Molecular distributions, mass ratios of selected diacid (C₃, C₄, M, F C₆, Ph and C₉) species and the linear relations among the selected species (including Σ C₂-C₄ and Σ C₈-C₁₂) and with inorganic markers (K⁺ and SO₄²⁻) implied that the diacids and related compounds are mainly originated from coal combustion and biomass burning emissions and produced in the atmosphere by both *in-situ* photochemical reactions at regional scale in both the seasons and aging during long-range transport, particularly in summer. This study also revealed that diacids and related compounds and WSOC are increased with increasing SO₄²⁻ and they produced in aqueous phase, warranting the need of further reduction in SO₂ and NO_x to control the water-soluble OA loading over North China.

Keywords

Diacids and related compounds, Coal and biomass combustion, Aqueous phase secondary formation, Fine aerosols, North China

1 Introduction

Water-soluble organic aerosols (OA) that make up a substantial fraction of total OA mass; up to 40%, have serious impacts on the Earth's climate system, preferably by indirect radiative forcing (Novakov & Penner, 1993; Ramanathan et al., 2001), and cause adverse effects on human health (Baltensperger et al., 2008), and also play an important role in atmospheric chemistry (Andreae & Crutzen, 1997; Kolb & Worsnop, 2012). Homologues series of dicarboxylic acids, oxoacids and α -dicarbonyls account for a dominant fraction of water-soluble organics (Kawamura & Bikkina, 2016). High abundance of diacids can increase the acidity of aerosols, which could promote the cloud condensation nuclei (CCN) formation and reduce the visibility (Facchini et al., 1999). Because diacids and related compounds are highly water-soluble, their presence on particle surface alters the hygroscopic behavior of the particles (Saxena et al., 1995) and thus, their capacity to act as CCN (Prenni et al., 2001) and regulate microstructure of the clouds (Asa-Awuku et al., 2011). Enhanced CCN number concentrations in the atmosphere should result in the increase of indirect radiative forcing by aerosol, causing a more reflective clouds (Twomey, 1977) and less precipitation (Albrecht, 1989).

53 In addition, diacids and related compounds, which possess low vapor pressure are involved
54 in fog formation and acid precipitation. They participate in various physical and chemical
55 reactions in the atmosphere. *For example*, Folkers et al. (2003) reported that unlike uncoated
56 NH_4HSO_4 particles, the NH_4HSO_4 particles coated with an organic substance containing a
57 diacid have a reduced reaction absorption coefficient for N_2O_5 (one of the main intermediates
58 for NO_x removal in the atmosphere), which increases oxidative capacity of the particles. This
59 indicates that the organic surface inhibits the transfer of N_2O_5 into NH_4HSO_4 core.
60 Consequently, diacids and related compounds play an important role in the climate change.
61 However, studies on the composition and molecular distributions of diacids and related
62 compounds and identification of their secondary formation and transformation pathways are
63 scarce. Therefore, the study of low molecular weight (LMW) diacids and related compounds
64 has become an issue of growing interest in recent times.

65 Diacids and related compounds with high abundance of oxalic (C_2) acid have been
66 recognized as ubiquitous constituents in atmospheric aerosols in various environments such as
67 urban, rural, mountain, polar and marine (Kawamura & Bikkina, 2016). The abundance of total
68 diacids-carbon to total organic carbon (OC) is reported to be 1-3% in urban areas (Kawamura
69 & Ikushima, 1993; Kawamura & Yasui, 2005; Miyazaki et al., 2009; Pavuluri et al., 2010) and
70 up to 16% and 24 % in the remote and tropical marine atmosphere, respectively (Fu et al., 2013;
71 Kawamura & Sakaguchi, 1999). Diacids and related compounds can be emitted directly into
72 the atmosphere from primary sources such as fossil fuel combustion, biomass burning and meat
73 cooking, and formed in the atmosphere by photochemical oxidation of their precursors of both
74 anthropogenic and biogenic origin in gas and liquid phases (Kawamura & Bikkina, 2016;
75 Kawamura et al., 1996). Their relative contributions from primary and secondary sources
76 depend on the types of emissions, meteorology and oxidation capacity of the atmosphere at
77 local scale. In addition, diacids and related compounds are subjected for further photochemical
78 processing (aging) during long-range transport in the atmosphere, resulting multiple
79 generations of more oxygenated species; e.g., carbonyls to carboxylic acids and diacids and
80 long-chain diacids to their lower homologues (Kawamura & Ikushima, 1993; Tilgner &
81 Herrmann, 2010).

82 To understand characteristics, origins and photochemical formation and transformations
83 of OA during long-range atmospheric transport, many observational studies have been carried
84 out over the past two decades, but they are limited to certain regions and not sufficient enough
85 at regional to global scale. In East Asia, high aerosol loadings are common and often suffers
86 from haze events due to enhancing development of urbanization and industrialization in recent
87 times, particularly over China (Carmichael et al., 2009; Huang et al., 2014; Zhang et al., 2012).
88 Despite a great attention has been paid on Chinese aerosol studies through ground-based
89 measurements at different locations and large-scale field experiments, the studies on molecular
90 characterization of OA are very limited (Cao et al., 2007; Fu et al., 2008; Fuzzi et al., 2006;
91 Huang et al., 2014; Nakajima et al., 2007; Wang et al., 2007), and in particular, the studies on
92 more oxygenated species such as diacids and related compounds are sparse (Ho et al., 2007;
93 Wang et al., 2002; Zhang et al., 2016; Zhao et al., 2018). Hence, it is highly necessary to study
94 the characteristics of diacids and related compounds in atmospheric aerosols at different

locations, particularly over North China, where the aerosol loading is much high compared to that in other parts of China.

In this study, we report the molecular distributions of diacids, oxoacids and α -dicarbonyls in fine (PM_{2.5}) summer- and winter-time aerosols collected from Tianjin, North China, which can be considered as an ideal location to collect the air masses originated from the oceanic region in summer and Siberia passing over Mongolia and northern parts of mainland China in winter. We discuss the sources of diacids and related compounds over the North China region including their *in-situ* secondary formation at local scale and photochemical processing (aging) during long-range atmospheric transport, based on mass ratios of selected species and their linear relations with marker ions together with the air mass trajectories.

2 Experimental

2.1 Site Description

Tianjin is a typical metropolis and largest coastal city in North China, located at 39°N and 117°E on the lower reaches of Haihe River and adjacent to the Bohai Sea, with a population of approximately 15 million (<https://en.wikipedia.org/wiki/Tianjin>). The weather is influenced by the East Asian monsoon prevailing with cold and dry air in winter and hot and humid air in summer. Although the consumption of coal for domestic energy has been banned in some cities in North China, its consumption for industrial terminal energy accounts for about 66% to the total energy consumption, which is higher than that in Beijing and Shanghai (Meng et al., 2015). The agricultural activity is significant in northern parts of Tianjin region, and it is also covered with mountains and dense forests. Tianjin is one of the most rapidly developing regions in China and has become an economic center in northern China with an annual growth of GDP at 14.5% (Bian et al., 2007). Furthermore, the East Asian monsoon, which forms as a result of the thermal difference between the Asian continent and the Pacific Ocean, controls the source regions and composition of the air masses transported over to Northeast China. Therefore, Tianjin is considered as an ideal location for collecting the air masses delivered from Siberia, parts of China, and surrounding oceans as well as local emissions.

2.2 Aerosol Sampling

Fine aerosol (PM_{2.5}) sampling was performed at Tianjin University, Nankai district located in central Tianjin. The sampling point is ~ 600 meters away from the road and no industries are located in the immediate vicinity. PM_{2.5} samples were collected on the rooftop of a six-story building (~20 m above ground level (AGL)) using precombusted (at 450°C for 6 hours) quartz fiber filters (Pallflex 2500QAT-UP) and a high-volume sampler (TISCH Environmental TE-6070DX) with a flow rate of 68 m³ h⁻¹ on day- and night-time basis in summer (6-19 July, *n* = 27) and winter (9 November-22 December, *n* = 85) 2016. Before sampling in each season, sampler was calibrated and run for one-day as test period and then actual sampling was started. One blank sample was also collected in each season, placing the filter on filter hood for minutes without turning on the pump. The filter samples were wrapped in aluminum foil and sealed in zip-lock plastic bags and then stored in freezer at -20°C until analysis.

2.3 Measurements of Diacids and Related Compounds

Diacids, oxoacids and α -dicarbonyls in PM_{2.5} were determined following the method reported elsewhere (Kawamura & Ikushima, 1993; Pavuluri et al., 2010). In brief, an aliquot of filter sample (20 mm disc in diameter in winter, 30 mm disc in summer), extracted into Milli-Q water (10 ml) for 3 times under ultrasonication for 10 min each. The extracts were filtered through pasteur pipette loaded with small amount of quartz wool to remove the filter debris and adjusted their pH to 8.4~9.5 using 0.1 M KOH and then concentrated to nearly dryness under rotary evaporation. The diacids and related compounds were derivatized to their corresponding dibutyl esters and/or acetals, by reacting with 14% BF₃/n-butanol at 100°C for one hour. The derivatized species were dissolved in *n*-hexane and washed with Milli Q water and 0.2 ml acetonitrile to remove the unreacted BF₃ and other contents and then concentrated to dryness under rotary evaporation followed by N₂ blow. The derivatized dibutyl esters and/or acetals were finally dissolved into *n*-hexane (100 μ l) and then injected into split/splitless GC/FID (Agilent 7980) equipped with an HP-5 capillary column (0.2 mm \times 25 m, 0.5 μ m film thickness). Identification of various compounds were confirmed by GC/mass spectrometer, whose sampling port temperature and increasing temperature program is same to that of GC-FID. Recoveries of authentic standards of oxalic (C₂), malonic (C₃), succinic (C₄) and adipic (C₆) acids spiked to a pre-combusted quartz fiber filter were 98%, 71%, 85% and 89%, respectively. The analytical errors in duplicate analysis of filter samples was within 5%. The field blank filters were also analyzed following the same procedure and found small peaks for oxalic (C₂), succinic (C₄) and pyruvic (Pyr) acids and glyoxal (Gly), but their concentrations were less than 5% of the actual samples. Final concentrations of the species measured in this study were corrected for the field blanks.

2.4 Inorganic Ions

Inorganic ions were measured using the extract of an aliquot of filter sample extracted into Milli Q water under ultrasonication for 30 minutes and filtered through syringe filter (0.22 μ m) and ion chromatograph (ICS 5000+). A mixture of 1.8 mM Na₂CO₃ and 17 mM NaHCO₃ and 40 mM H₂SO₄ were used as eluent at a flow rate of 1.2 mL min⁻¹ and suppressor, respectively, for anion measurement, respectively. 4 mM H₃PO₄ was used as eluent at a flow rate of 1.0 mL min⁻¹ for cation measurement (Pavuluri et al., 2011). A calibration curve was evaluated for each sequence by the analyses of a set of authentic standards and the analytical errors in duplicate analysis were within 6%. The nss-SO₄²⁻ and nss-K⁺ were calculated using Na⁺ as a reference for sea-salt.

2.5 Meteorology

Weather data such as temperature, humidity, wind and rainfall were monitored using weather station installed beside the sampler during the sampling period and the data were averaged for 12-hours corresponding to each sample period. During the summer campaign, the average temperature was 21.1°C in daytime and 26.3°C in nighttime and the relative humidity (RH) was 45.9% and 70.5%, respectively. They were 6.88°C and 54.7% in daytime and 5.11°C and 61.7% in nighttime, respectively, during the winter campaign. The average wind was

mainly flown from southeast region and the weather was mostly sunny and precipitation was not frequent in summer, whereas the fog formation was significant, visibility was poor, and snowfall often occurred in winter.

2.6 Backward Air Mass Trajectories

Seven-day backward air mass trajectories arriving at 500 m AGL over Tianjin were computed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the National Oceanic and Atmospheric Administration (NOAA). The representative air mass trajectories were provided elsewhere (Wang et al., 2018). In summer, the air masses were originated from the Pacific Ocean and passed over the Bohai Sea and eastern parts of the Chinese mainland. Whereas in winter, they were originated from Eurasia and passed over Siberia, Mongolia and northern parts of China. However, unlike in summer, the air parcels were travelled at very low altitude for most of the time in winter.

3 Results and Discussion

3.1 Molecular Composition and Distributions

A homologous series of saturated normal diacids (C₂-C₁₂) and branched diacids (*iso*C₄-C₆) were detected in both summer- and winter-time Tianjin aerosols (PM_{2.5}). In addition, we found unsaturated aliphatic (maleic (M), fumaric (F) and methylmaleic (mM)) and aromatic (phthalic (Ph), isophthalic (*i*Ph) and terephthalic (*t*Ph)) acids and diacids with an additional functional (carbonyl) group (ketomalonic (kC₃) and 4-ketopimelic (kC₇) acids) in the PM_{2.5}. C₂-C₉ ω -oxoacids, excluding C₆ oxoacid, and an α -oxoacid (Pyr) and α -dicarbonyls (Gly and methylglyoxal (mGly)) were also detected in these samples. Concentrations of individual diacids, oxoacids and α -dicarbonyls and their relative abundances to the total diacids, oxoacids and α -dicarbonyls, respectively, in Tianjin summer- ($n = 27$) and winter-time ($n = 81$) PM_{2.5} are summarized in Table 1. Molecular distributions of diacids and related compounds in day- and night-time in both the seasons are depicted in Fig. 1.

Concentrations of total diacids ranged from 185 ng m⁻³ to 2874 ng m⁻³ with an average of 879 ± 586 ng m⁻³ in the Tianjin PM_{2.5} during the whole campaign ($n = 108$). While those of oxoacids and α -dicarbonyls were 23.8-767 ng m⁻³ (ave. 234 ± 179 ng m⁻³) and 4.39-286 ng m⁻³ (49.4 ± 51.1 ng m⁻³), respectively. Molecular distributions of the measured diacids and related compounds were characterized by a predominance of C₂ diacid followed by glyoxylic (ω C₂), Ph, C₄ and *t*Ph acids, respectively. Pyr was found to be the sixth most abundant species followed by malonic (C₃), oxobutanoic (ω C₄) and azelaic acid (C₉), respectively, during the campaign. Relative abundance of C₂ diacid to total diacids ranged from 10.6% to 58.4% with an average of $38.9 \pm 11.0\%$ followed by Ph (ave. $10.0 \pm 4.49\%$), C₄ ($8.54 \pm 1.94\%$), *t*Ph ($7.68 \pm 5.50\%$), C₃ ($5.42 \pm 1.86\%$) and C₉ ($3.99 \pm 1.84\%$) diacids, respectively, during the whole campaign ($n = 108$). While, on average, ω C₂ acid accounted for $33.1 \pm 15.7\%$ to total oxoacids followed by Pyr ($25.7 \pm 12.0\%$), ω C₄ ($17.7 \pm 7.77\%$) and ω C₃ ($8.35 \pm 4.53\%$) acids, respectively. Both Gly and mGly were almost equally abundant with a relative abundance of $45.1 \pm 20.3\%$ and $54.9 \pm 20.3\%$ to total α -dicarbonyls, respectively.

Table 1

Summary of Concentrations of Diacids, Oxoacids, and α -Dicarbonyls and Their Relative Abundances in Total Diacids, Oxoacids, and α -Dicarbonyls in PM_{2.5} Collected from Tianjin, North China During Winter and Summer, 2016^a.

Compounds	Summer (n = 27)				Winter (n = 85)			
	Concentration (ng m ⁻³)			Relative Abundance (%)	Concentration (ng m ⁻³)			Relative Abundance (%)
	Range	Med	Ave. \pm SD	Ave. \pm SD	Range	Med	Ave. \pm SD	Ave. \pm SD
<i>Diacids</i>								
Oxalic, C ₂	90.5–371	208	213 \pm 74.6	48.3 \pm 6.85	42.2–1365	386	405 \pm 290	35.8 \pm 10.4
Malonic, C ₃	15.6–64.9	33.5	34.5 \pm 12.3	7.88 \pm 1.44	7.60–157	44.1	48.2 \pm 32.0	4.60 \pm 1.09
Succinic, C ₄	8.31–56.6	35.6	34.8 \pm 9.94	8.27 \pm 2.35	18.0–275	86.2	89.6 \pm 57.6	8.63 \pm 1.79
Glutaric, C ₅	5.12–22.6	10.6	10.3 \pm 3.82	2.37 \pm 0.70	n.d–416	21.5	31.1 \pm 55.4	2.76 \pm 2.87
Adipic, C ₆	3.51–35.7	8.03	10.9 \pm 7.26	2.44 \pm 1.14	n.d–72.8	21.7	21.8 \pm 13.1	2.19 \pm 0.73
Pimelic, C ₇	0.99–26.7	3.94	4.73 \pm 4.83	1.22 \pm 1.50	n.d–24.2	5.68	6.95 \pm 5.78	0.63 \pm 0.35
Sebacic, C ₈	n.d–17.8	3.23	4.63 \pm 4.75	1.32 \pm 1.72	n.d–154	3.08	11.0 \pm 26.1	1.63 \pm 4.23
Azelaic, C ₉	7.17–30.3	14.7	15.6 \pm 5.12	3.75 \pm 1.33	4.30–193	35.2	39.3 \pm 32.2	4.07 \pm 1.99
Decanedioic, C ₁₀	1.10–18.0	1.93	3.66 \pm 4.37	0.99 \pm 1.37	n.d–363	6.98	32.7 \pm 56.3	3.92 \pm 6.38
Undecanedioic, C ₁₁	1.10–8.36	3.16	3.29 \pm 1.60	0.82 \pm 0.58	n.d–49.8	18.03	18.2 \pm 11.8	2.17 \pm 1.56
Dodecanedioic, C ₁₂	n.d–30.0	5.97	7.22 \pm 7.48	1.86 \pm 1.96	n.d–72.9	9.75	17.0 \pm 17.8	1.83 \pm 2.20
Methylmalonic, iC ₄	0.94–44.0	2.93	5.02 \pm 8.46	1.18 \pm 1.62	n.d–70.3	8.59	12.7 \pm 12.0	1.52 \pm 1.62
Methylsuccinic, iC ₅	1.91–7.25	5.21	4.89 \pm 1.34	1.15 \pm 0.26	n.d–56.6	16.3	18.6 \pm 11.7	1.89 \pm 0.76
2-Methylglutaric, iC ₆	0.45–5.35	1.24	1.64 \pm 1.19	0.37 \pm 0.23	n.d–44.6	5.20	6.09 \pm 5.40	0.73 \pm 0.76
Maleic, M	n.d–4.23	2.19	2.32 \pm 1.00	0.57 \pm 0.31	n.d–71.4	10.1	14.0 \pm 14.2	1.28 \pm 0.65
Fumaric, F	0.68–6.29	1.67	1.92 \pm 1.21	0.47 \pm 0.34	n.d–37.4	7.26	8.85 \pm 7.90	0.78 \pm 0.40
Methylmaleic, mM	n.d–8.58	4.02	4.53 \pm 2.12	1.12 \pm 0.59	3.06–328	14.5	22.9 \pm 37.4	2.22 \pm 2.75
Phthalic, Ph	2.20–128	36.7	35.6 \pm 26.5	7.51 \pm 4.11	8.72–305	94.3	102 \pm 60.8	10.9 \pm 4.31
Isophthalic, i-Ph	n.d–13.3	2.66	3.28 \pm 2.96	0.75 \pm 0.71	n.d–58.6	12.4	14.1 \pm 12.2	1.25 \pm 0.95
Terephthalic, t-Ph	1.81–23.9	13.9	13.9 \pm 5.21	3.20 \pm 1.05	n.d–372	90.0	90.6 \pm 69.4	9.17 \pm 5.57
Ketomalonic, kC ₃	1.13–93.8	3.08	15.6 \pm 24.6	3.07 \pm 4.91	n.d–35.7	9.49	11.9 \pm 8.56	1.15 \pm 0.56
4-Ketopimelic, kC ₇	1.58–15.8	5.94	6.33 \pm 2.95	1.44 \pm 0.46	n.d–49.1	5.12	6.30 \pm 5.83	0.90 \pm 0.96
Total diacids	254–707	416	437 \pm 133		185–2874	1028	1027 \pm 604	
<i>Oxoacids</i>								
Glyoxylic, ω C ₂	7.32–59.1	20.5	24.2 \pm 13.0	27.5 \pm 6.70	6.07–400	83.3	118 \pm 108	34.9 \pm 17.3
3-Oxopropanoic, ω C ₃	1.76–11.7	5.43	5.91 \pm 2.42	6.95 \pm 1.51	n.d–85.3	18.4	23.3 \pm 17.8	8.82 \pm 5.08
4-Oxobutanoic, ω C ₄	1.09–38.4	16.6	16.7 \pm 8.09	18.5 \pm 5.95	n.d–103	51.8	45.4 \pm 25.2	17.5 \pm 8.31
5-Oxopentanoic, ω C ₅	0.41–4.75	1.65	1.68 \pm 0.98	1.96 \pm 0.79	n.d–13.9	3.97	4.16 \pm 2.68	2.04 \pm 2.61
7-Oxoheptanoic, ω C ₇	0.72–12.2	4.31	4.48 \pm 2.29	5.97 \pm 4.30	n.d–16.9	5.60	6.58 \pm 3.74	3.35 \pm 3.19
8-Oxo-octanoic, ω C ₈	3.27–21.2	6.99	7.50 \pm 3.59	9.34 \pm 3.72	n.d–17.9	7.21	7.85 \pm 4.80	4.37 \pm 5.97
9-Oxononanoic, ω C ₉	0.77–4.37	2.27	2.33 \pm 0.91	3.35 \pm 2.67	n.d–47.5	7.30	8.64 \pm 8.33	3.56 \pm 3.92
Pyruvic, Pyr	3.03–44.2	23.8	23.5 \pm 10.9	26.4 \pm 8.11	0.18–216	74.9	71.3 \pm 43.9	25.5 \pm 13.1
Total oxoacids	23.8–188	86.1	86.3 \pm 34.7		30.2–767	249	284 \pm 181	
<i>α-Dicarbonyls</i>								
Gly	0.26–11.0	6.64	6.18 \pm 2.58	42.8 \pm 23.9	1.30–75.8	20.8	24.3 \pm 18.8	45.9 \pm 19.0
mGly	0.95–36.5	8.07	10.8 \pm 8.87	57.2 \pm 23.9	1.88–213	24.8	36.0 \pm 39.1	54.1 \pm 19.0
Total α -dicarbonyls	6.05–47.6	14.3	17.0 \pm 9.58		4.39–286	44.2	60.2 \pm 54.7	

^aAve., average; SD, Standard Deviation; n.d., not detectable.

It is of worthy to note that the high abundance of C₄ diacid than that of C₃ diacid in Tianjin aerosols is a unique feature, because such pattern is generally the opposite to that reported in continental and marine aerosols, particularly in those photochemically aged during long-range atmospheric transport (Kawamura & Bikkina, 2016), but similar to that reported in Beijing aerosols, which were significantly influenced by fossil fuel combustion and waste incineration (Zhao et al., 2018). Unlike most of the previous reports from different locations over the world (Kawamura & Bikkina, 2016), the concentrations of normal saturated diacids did not follow a decreasing trend with increasing carbon chain length, with relatively high loadings of C₁₁ and C₁₂ diacids than their lower homologues, particularly C₇ and C₈ diacids, in both summer and winter (Table 1). Furthermore, average concentrations of total diacids, oxoacids and α -dicarbonyls in Tianjin aerosols were found to be much higher than those (ave. 438 \pm 267, 43.0 \pm 48 and 11.0 \pm 18 ng m⁻³, respectively) reported in Pearl River Delta region, one of the heaviest haze regions in China (Ho et al., 2011) and Jeju Island, Korea (660, 53.0 and 12.4 ng m⁻³,

respectively) (Kawamura et al., 2004), as well as in Arctic aerosols ($\sim 100 \text{ ng m}^{-3}$) (Kawamura et al., 2010) and in Chichijima Island, a remote marine region (range, 6-550 ng m^{-3} ; ave. 130 ng m^{-3}) (Mochida, 2003). However, they were slightly lower than or comparable to those reported in Xi'an fine ($\text{PM}_{2.5}$) aerosols (1350, 167 and 37.0 ng m^{-3} , in summer and 2053, 421, and 120 ng m^{-3} in winter), where high aerosol loading including haze events are common (Wang et al., 2012). Such results and comparisons suggest that the origins of OA in the Tianjin region might be different from other and/or their *in-situ* secondary formation should be more significant.

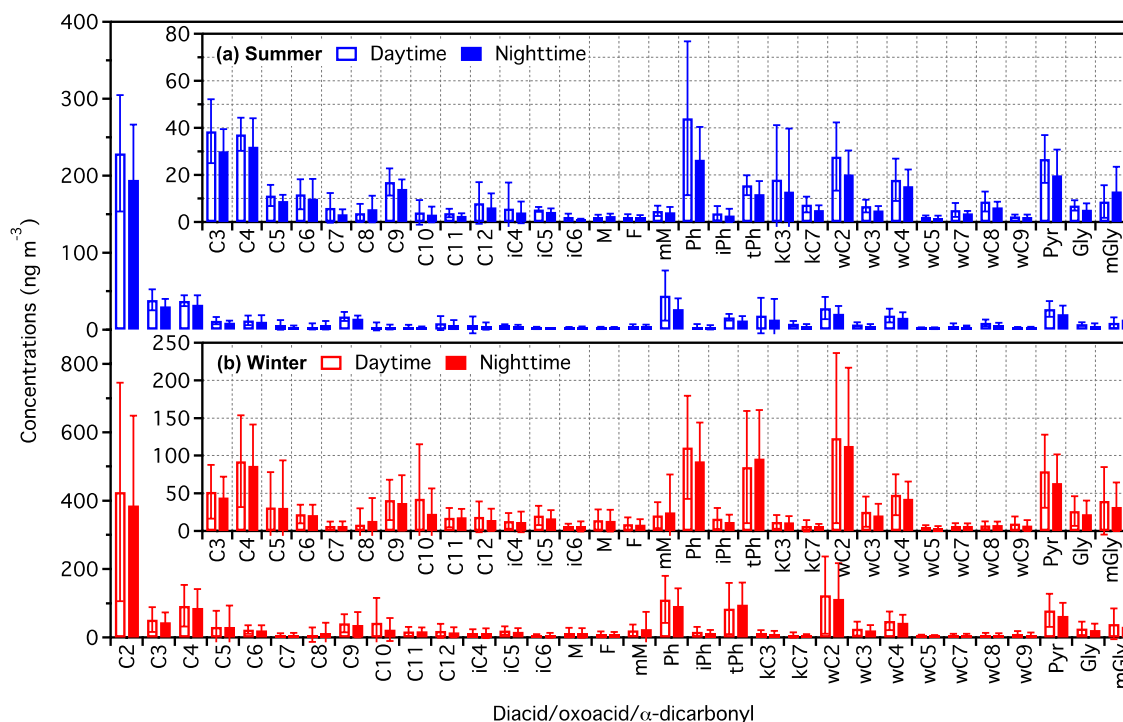


Figure 1. Molecular distributions of diacids, oxoacids, and α -dicarbonyls in $\text{PM}_{2.5}$ collected on day- and night-time basis from Tianjin, North China during (a) summer and (b) winter.

3.2 Seasonal and Diurnal Variations

3.2.1 Saturated Normal and Branched Diacids

Concentrations of saturated normal diacids in winter were twice higher, while the branched diacids were higher by a factor of 3, than those in summer (Table 1). However, branched C_4 , C_5 and C_6 ($i\text{C}_4$ - $i\text{C}_6$) diacids were less abundant than their corresponding normal structures in both the seasons (Table 1, Fig. 1). Although C_2 diacid was the most abundant species in both the seasons, its relative abundance to total normal C_2 - C_{12} diacids was reduced on average by about 9% from summer to winter (Fig. 2). It is also worth to note that C_4 diacid was equally abundant to that of C_3 diacid in summer, whereas in winter, it was higher by a factor of 2 than that of C_3 (Table 1). Their relative abundances to normal diacids were also showed the same seasonal pattern (Fig. 2). The high abundance of C_4 than that of C_3 diacid is consistent with that reported for urban aerosols at 14 megacities over China, in which their

averages were 79.7 ng m⁻³ and 40.6 ng m⁻³ in winter, where fossil fuel combustion and biomass burning were considered as major sources of the aerosols (Ho et al., 2007). However, the relative abundances of C₁₀ and C₁₁ diacids to total normal C₂-C₁₂ diacids were enhanced by 5 and 3 folds, respectively, from summer to winter periods, while that of C₅ and C₉ diacids were increased by 1% in winter compared to that in summer (Fig. 2). In fact, the concentrations of C₅ diacid in winter were more than 3 times higher than that in summer.

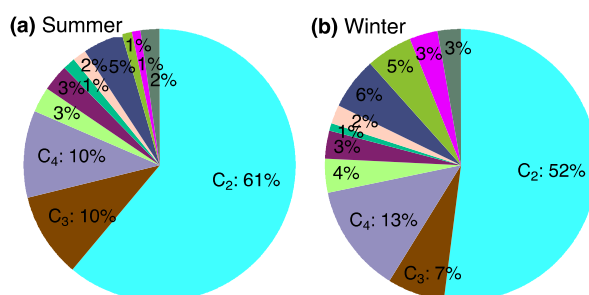


Figure 2. Relative abundances of normal saturated diacids in PM_{2.5} from Tianjin, North China in (a) summer and (b) winter.

It is well established that C₄ diacid is produced by photochemical oxidation of unsaturated fatty acids (Kawamura & Gagosian, 1987) *via* oxoacids as well as by photochemical transformations of higher homologous diacids (Pavuluri et al., 2015; Tilgner & Herrmann, 2010; Yang et al., 2008). While photochemical oxidation of cyclic olefins significantly contributes to C₅ and C₆ diacids (Hatakeyama et al., 1987; Kawamura et al., 1996). In fact, the average concentration of C₆ diacid (Table 1), which has been considered to be a tracer for anthropogenically derived OA (Kawamura & Ikushima, 1993), in summer is comparable to that (12.7 ng m⁻³) reported in Hong Kong road side aerosols, whereas in winter, the average C₆ diacid was much higher than that reported in Hong Kong (10.7 ng m⁻³) (Ho et al., 2006) as well as in Tokyo (ave.14.2 ng m⁻³) (Kawamura & Yasui, 2005), where the input from fossil fuel combustion is the major source of aerosols. In contrast, C₉ diacid, which can be derived from unsaturated fatty acids emitted from marine biota and terrestrial plants as well as cooking emissions and has been considered as a tracer of OA of biogenic origin (Kawamura & Gagosian, 1987), was found to be the fourth most abundant diacids in both summer and winter (Table 1).

Such molecular distributions and their seasonal variations suggest that they might have significantly derived from mixed sources in both the seasons. High relative abundance of C₂ and C₃ diacids in summer than that in winter (Table 1; Fig. 2) indicates that the photochemical processing of OA during long-range atmospheric transport might be significant in summer rather than in winter. Furthermore, the concentrations of straight chain diacids were found to be generally higher in daytime than that in nighttime (Fig. 3a,b), except for C₈ diacid in summer and C₅, C₇ and C₈ diacids in winter (not shown here). Interestingly, C₂-C₄ diacids showed a significant diurnal variation in both the seasons (Fig. 3a), indicating that *in-situ* photochemical oxidation of organics was also more intensive during daytime in the Tianjin atmosphere, associating with intense solar radiation and high ambient temperature (up to 33.1°C) during daytime in summer. However, an enhancement in the relative abundance of C₉ and C₁₂ diacids

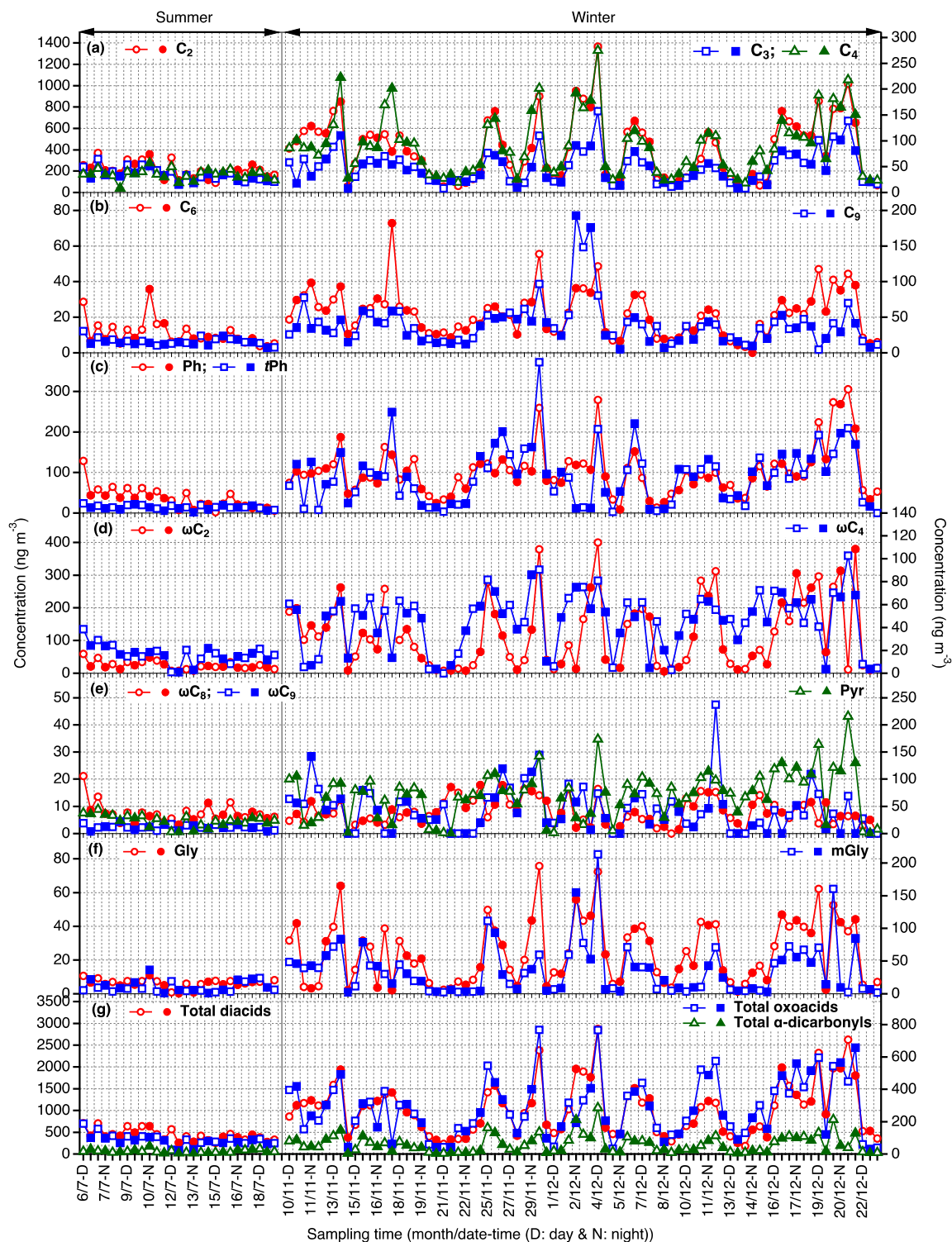
and a large increment in that of C₁₀ and C₁₁ diacids from summer to winter, despite the fact that the air masses arrived in Tianjin were originated from the Pacific Ocean during the summer campaign, indicate that the OA should have been significantly derived from the enhanced local emissions, probably biomass burning, rather than biogenic emissions in winter. Alternatively, they might have derived from terrestrial biogenic VOCs and accumulated in the lower atmosphere due to relatively stagnant weather conditions in winter. The branched chain diacids did not show any diurnal changes, suggesting that they should have been derived from other precursors and/or their photochemical formation process are different from the straight chain diacids. In fact, it has been reported that branched chain diacids are considered to be generated *via* photochemical oxidation of methylcycloalkanes (Grosjean & Fung, 1984).

3.2.2. Unsaturated and Multifunctional Diacids

Concentrations of both aliphatic unsaturated (M, F and mM) and aromatic (Ph, *i*Ph and *t*Ph) diacids measured in this study were ~4 times higher in winter than those in summer. Their distributions were characterized by a predominance of Ph followed by *t*Ph and mM acids. Such pattern is similar to that reported in subtropical Okinawa in the Western Pacific Rim (Kunwar & Kawamura, 2014) and Xi'an, China (Cheng et al., 2013). The relative abundances of Ph and *t*Ph acids to total diacids were higher than those in summer (Table 1). Similarly, those of M and F acids were also showed higher abundances in winter compared to that in summer (Table 1). The average concentration of Ph acid in winter (Table 1) was slightly higher than that (78.0 ng m⁻³) reported in Hong Kong roadside aerosols, where the fossil fuel combustion emissions and their subsequent oxidation has been considered to be the major sources of OA (Ho et al., 2006).

Ph acid is mainly derived from photochemical oxidation of aromatic hydrocarbons such as naphthalene that reported to be abundant in some megacities of China. The process of Ph acid formation mainly involves its photochemical production in gas phase and subsequent absorption onto existing particles (Kawamura & Ikushima, 1993). In addition, it can also be directly emitted by coal combustion and automobile exhaust. The high level of Ph acid in winter in Tianjin aerosols could have been driven by the emission of a large amount of its precursors emitted from coal combustion and/or vehicular exhausts to some extent. In fact, coal consumption, particularly for domestic heating, has been substantially reduced in Tianjin in recent years. However, there are still some localities in northern China, in which coal is the dominant fuel for domestic use. In addition, the air masses were flown from Siberia and pass over Mongolia and most northern Chinese cities in winter (Wang et al., 2018) that should have been enriched with coal combustion emissions. Moreover, the emissions from natural coal and peat fires occurring in Inner Mongolia, China, where the subsurface coal fires are active and one of the more serious fires in the world (Liang et al., 2014), should have been contributed significantly to the atmospheric OA loading in northern China. Interestingly, the relative abundance of Ph acid in Tianjin aerosols (Table 1) is relatively comparable to that reported from Xi'an, China (8.3% in summer and 8.0% in winter), where the emissions from household

325 combustion of coal and plastic burning are significant (Cheng et al., 2013), further supporting
 326 that the contribution from coal combustion to OA is significant over Tianjin.



327 **Figure 3.** Temporal variations of selected diacids (a-c), oxoacids (d,e), and α -dicarbonyls (f) and total
 328 diacids, oxoacids, and α -dicarbonyls (g) in $PM_{2.5}$ from Tianjin, North China during summer and winter, 2016.
 329 Open and close circles and square marks represent day- and night-time, respectively.

*t*Ph is derived from industrial emissions and plastic burning (Kawamura & Pavuluri, 2010). The plastic usage is large in China and the municipal solid waste (MSW), which contains significant amount of plastic, is dumped into open landfills in many towns that often set to fire by residents. The concentration of *t*Ph in Tianjin aerosols was higher in winter by a factor of 2 than that (48.70 ng m⁻³) reported in Beijing (Zhao et al., 2018) and Chennai, India (range, 7.60-168 ng m⁻³; ave. 45.0 ng m⁻³ in winter and 61.3 ng m⁻³ in summer), where MSW that contains significant amount of plastics burning is common (Kawamura & Pavuluri, 2010). Furthermore, the relative abundance of *t*Ph acid in wintertime Tianjin aerosols (Table 1) found to be much higher than that (~4%) reported from Xi'an, China, although it is comparable in summertime (Cheng et al., 2013). Such comparisons with the literature indicate that the plastic burning is an important source of OA over the Tianjin region.

Generally, the measured unsaturated diacids, except for M and F (not shown here), showed higher levels in daytime than in nighttime in summer, although the variations were not significant particularly in the case of *t*Ph acid (Fig. 3c). In winter, mM and *t*Ph also did not show a decrease in winter daytime. However, Ph acid showed high abundance in daytime than in nighttime (Fig. 3c). This result implies that either the input of anthropogenic precursors should be large and/or their secondary formation should be more intensive in daytime in Tianjin.

3.2.3 Oxoacids and α -dicarbonyls

Concentrations of ω -oxoacids, Pyr and α -dicarbonyls were found to be higher by a factor of ~3 in winter than those in summer (Table 1). ω C₂ acid was found to be the most abundant oxoacids followed by Pyr and ω C₄, respectively. The second most abundance of Pyr is different from that in New Delhi, where ω C₄ was the second most abundant oxoacids (Miyazaki et al., 2009), and that in Tokyo as well, where the Pyr was most abundant oxoacid species (Kawamura & Yasui, 2005). ω C₂ accounted for 28% and 35% of total oxoacids in Tianjin aerosols in summer and winter, respectively, with a wide range of concentrations ranging from 6.07 to 400 ng m⁻³ (ave. 24.2 ng m⁻³ in summer and 118.1 ng m⁻³ in winter) that are higher by a factor of ~2 than that reported in Hong Kong roadside aerosols (18.5 ng m⁻³ and 43.2 ng m⁻³, respectively) (Ho et al., 2006). In contrast, Pyr and ω C₄ were 27% and 19%, respectively, in summer, which are higher than that (25% and 16%, respectively) in winter samples (Table 1). Interestingly, total dicarbonyls also showed higher level in winter than in summer. mGly was more abundant than Gly in both summer and winter.

Most of oxoacids and α -dicarbonyls showed relatively high abundance in daytime compared to that in nighttime in winter, whereas in summer, mGly was significantly higher in nighttime (Fig. 3d-f). Gly is largely derived by oxidation of aromatic hydrocarbons, although it can be derived from biogenic and marine emissions for some extent. Therefore, it can be inferred that mGly was produced at night by oxidation of isoprene emitted from terrestrial plants and/or might have extensively transformed to other compounds (e.g., ω C₂) by enhanced photochemical oxidation (Kawamura et al., 1996) during daytime.

However, total diacids, oxoacids and α -dicarbonyls showed a clear diurnal variations with higher levels in daytime in both summer and winter seasons (Fig. 3g), implying that the in-situ photochemical production was always significant in the Tianjin atmosphere.

3.3 Mass Fractions in PM_{2.5}, TC, OC and WSOC

The mass fractions of total diacids, oxoacids and α -dicarbonyls in PM_{2.5} and those of their carbon contents (C) in TC, OC and WSOC in summer and winter are showed in Fig. 4. The mass fractions of diacids-C in TC and WSOC in Tianjin aerosols together with those reported from different locale over the world are given in Table 2. Although the concentrations of most of the diacids and related compounds were higher in winter (Table 1), their fractions in PM_{2.5} were exactly the opposite; that is, higher in summer (Fig. 4). On average, total diacids accounted for 0.60% in PM_{2.5} in winter, whereas in summer, it was almost doubled (1.15%) to that in winter, while the mass fractions of total oxoacids were 0.17% and 0.23%, respectively. Total α -dicarbonyls were accounted for a very minor (0.04% and 0.03%, respectively) fraction in PM_{2.5}, which is likely because the α -dicarbonyls largely present in the gas phase.

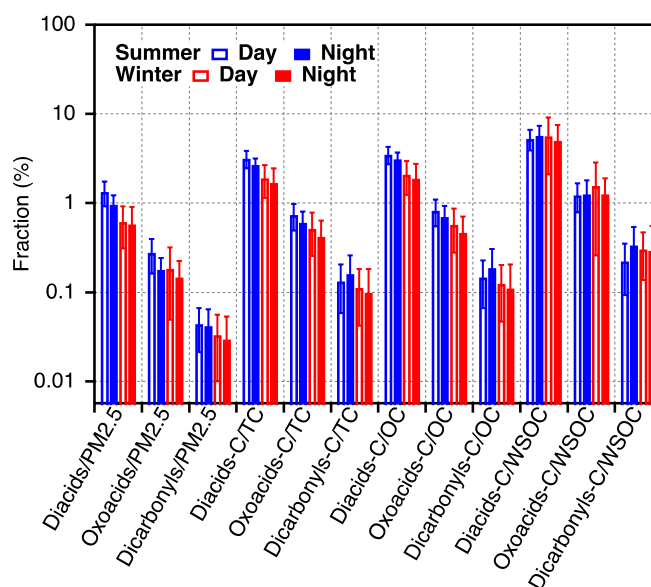


Figure 4. Mass ratios of total diacids, oxoacids, and α -dicarbonyls to PM_{2.5} and their carbon contents (C) to total carbon (TC), organic carbon (OC) and water-soluble OC (WSOC) in the PM_{2.5} from Tianjin, North China.

Total diacids-C accounted for 2.01% to 4.59% (ave. 2.93%) in TC, 2.31-4.97% (3.31%) in OC in Tianjin PM_{2.5} in summer and 0.55-3.87% (1.79%) and 0.63-4.46% (1.98%), respectively, in winter. Such seasonal differences clearly indicate that the secondary formation and transformations of diacids were significantly higher in summer compared to that in winter. The fractions of oxoacids-C and α -dicarbonyls-C in both OC and TC were less than 1% (Fig. 4), but they were higher in summer compared to that in winter, which again support our finding that the aging of OA was more intensive in summer than in winter. In fact, with the enhanced aging of aerosols, diacids-C/TC ratios will increase because diacids are mainly produced in the

atmosphere from photochemical oxidation of precursors, including oxoacids and α -dicarbonyls. The average contribution of total diacids-C to TC in Tianjin in summer is much higher than that reported in urban aerosols from Chennai, India, and Tokyo and Sapporo, Japan as well as in the marine aerosols from the Arctic Ocean in summer (Table 2). However, this ratio is significantly lower than that reported in the remote marine aerosols from the western north and central Pacific and the Arctic aerosols from Alert (Table 2), which were considered to be more aged during the long-range atmospheric transport (Kawamura & Sakaguchi, 1999). These comparisons suggest that the photochemical production of diacids in the Tianjin atmosphere is more intensive than in other regions, and they have been subjected for significant aging, particularly in summer.

Table 2

Mass Ratios of Total Diacids Carbon to total carbon (TC) and Water-soluble Organic Carbon (WSOC) and Malonic (C₃) to Succinic (C₄) acids in PM_{2.5} from Tianjin and Those at different Locale over the World.

	Sampling period	Total diacids-C/TC (%)			Total diacids-C/WSOC (%)			C ₃ /C ₄		
		Min	Max	Ave	Min	Max	Ave	Min	Max	Ave
Tianjin, China ^a	July 2016	2.01	4.59	2.93	3.13	9.90	5.46	0.65	3.76	1.06
Tianjin, China ^a	Nov-Dec 2016	0.55	3.87	1.79	1.74	19.9	5.31	0.17	1.22	0.55
Automobile exhaust ^a								0.25	0.44	0.35
Tokyo ^b	Apr 1988-Feb 1989	0.18	1.80	0.95				0.56	2.90	1.60
Chennai, India ^d	Jan-Feb & May 2007	0.40	3.00	1.58	4.00	11.0	5.90			
Gosan, Korea ^e	Apr 2001-Mar 2002	0.80	6.20	3.10						
Western Pacific ^f	Aug-Oct 1992	1.10	4.90	3.20	2.10	14.7	8.20			
WN-Central Pacific ^g	Sept-Dec 1990	1.10	15.8	8.80						
Arctic Ocean ^h	Aug 2009	0.28	2.10	0.87						
Arctic (Alert) ⁱ	Feb-Jun 1991	1.50	9.00	4.00						
Sapporo, Japan ^j	Sept 2009-Oct 2010	1.22	3.03	1.95	3.73	16.3	9.20	1.01	5.18	2.08

^aKawamura and Kaplan, 1987; ^bKawamura and Ikushima, 1993; ^cPavuluri et al., 2010; ^dKawamura et al., 2004; ^eSempere and Kawamura, 2003; ^fKawamura and Sakaguchi, 1999; ^gKawamura et al., 2012; ^hKawamura et al., 2010; ⁱPavuluri et al., 2018; ^jthis study.

However, the fraction of diacids-C in WSOC was similar in both the seasons, although the range is quite broad in winter (Fig. 4). On the other hand, there was no clear diurnal trend in the fractions of total diacids-C to TC and WSOC. In fact, WSOC (as well as OC and EC) was increased from summer to winter by a factor of ~3 (Wang et al., 2018) and the concentrations of total diacids were also higher by a factor of ~2 in winter than that in summer (Table 1) and thus, their mass ratios have become almost similar in both the seasons. It indicates that the secondary production of diacids in the Tianjin atmosphere was intensive in winter as well, but the extent of secondary oxidation and/or transformations organics in winter were not as intensive as that in summer. Alternatively, the development of inversion layer might result in accumulation of pollutants including diacids.

In summer, temporal trends of total α -dicarbonyls to TC, OC and WSOC were different from diacids and oxoacids (not shown here). The α -dicarbonyls-C fraction in TC was relatively constant, except for few cases, whereas that in OC showed a diurnal variation, which is opposite to that of total diacids-C/OC in early summer. It is likely because the α -dicarbonyls are first-generation species while the diacids and oxoacids are produced on further oxidation of the α -dicarbonyls. Such trends demonstrate that the OA over Tianjin was significantly aged during the long-range atmospheric transport. Fractions of α -dicarbonyls-C in TC ranged from 0.00 to 0.49% (ave. 0.11%) in summer and 0.01-0.38% (0.11%) in winter. They are similar to

those Mt .Tai (ave: 0.14%) (Kawamura et al., 2013), but higher than that reported in (ave. 0.017%) reported from Arctic Ocean aerosols (Kawamura et al., 2012) and Chennai (0.03%) on the southeast coast of India (Pavuluri et al., 2010). Fractions of α -dicarbonyls-C in WSOC were 0.28% and 0.30% in summer and winter, respectively, and did not show any significant seasonal variation, although their concentrations were increased by a factor of 3 from the summer to winter.

3.4 Implications for Origins and Secondary Processes

3.4.1 Fossil Fuel Combustion and Biomass Burning

It has been well established that C₆ diacid and Ph acid are produced by photochemical oxidation of cyclic alkenes (Hatakeyama et al., 1987) and aromatic hydrocarbons (e.g., naphthalene) of anthropogenic origin (Kawamura & Ikushima, 1993). Whereas C₉ diacid is produced by photochemical oxidation of biogenic unsaturated fatty acids that have a double bond at C-9 position such as oleic acid (Kawamura & Gagosian, 1987). Therefore, the mass ratios of C₆ and Ph acids to C₉ acid have been considered as proxies to evaluate the relative contributions of OA from anthropogenic and biogenic sources (Kawamura et al., 2012). Although average mass ratio of C₆ to C₉ in Tianjin aerosols was almost stable (~0.75) in both the seasons, the average Ph/C₉ (3.65) in winter was significantly higher than that (2.27) in summer. C₆/C₉ ratios in Tianjin are comparable to those reported from 14 cities of China in both winter (ave. 0.62) and summer (0.89) and from Tokyo (0.72) whereas, the Ph/C₉ ratios are comparable to those (3.74) reported from 14 cities of China in winter and lower in summer (4.16) (Ho et al., 2007; Kawamura & Ikushima, 1993). However, both C₆/C₉ and Ph/C₉ ratios are much lower than those reported from Los Angeles (7.4 and 8.0, respectively) (Kawamura & Kaplan, 1987). These results and comparisons suggest that relative contribution of OA from anthropogenic emissions to Tianjin aerosol is similar to that in most of other megacities in China, especially in winter.

Kawamura and Kaplan (1987) reported that Ph/C₆ ratio (6.58) in diesel fueled automobile exhaust is higher by a factor of 3 than that in the gasoline fueled automobile exhaust (2.05). In Tianjin aerosols, average Ph/C₆ ratios were 5.02 (range 1.31-11.0) in winter and 3.38 (0.26-7.15) in summer. In addition, these ratios are comparable or slightly higher than those reported from Chennai, India (2.92), where the influence of anthropogenic emissions are significant, although the biomass burning was considered to be a dominant source (Pavuluri et al., 2010). These indicate that the combustion of diesel fuel should be one of the major sources of OA in Tianjin. In fact, gasoline fuel is a common type of fuel for bus and private vehicles in China. Therefore, such high Ph/C₆ ratios indicate that other fossil fuel such as coal combustion might be a significant source of OA rather than gasoline fuel combustion in the Tianjin region.

However, as discussed earlier, the concentrations of long-chain diacids including C₉ diacid were higher in winter than in summer, indicating the possible enhanced contribution of OA from biomass burning in winter. To confirm such possibility, as shown in Fig. 5, we examined the relations of the sums of short-chain (Σ C₂-C₄) and long-chain (Σ C₈-C₁₂) diacids with potassium ion (K⁺), a tracer for biomass burning (Andreae, 1983). Interestingly, the Σ C₂-

C₄ showed a linear relation with K⁺, although the correlation is weak in summer and strong in winter (Fig. 5), suggesting that the short-chain diacids are significantly derived from biomass burning emissions in both the seasons, particularly in winter. Similarly, the Σ C₈-C₁₂ showed a linear relation with K⁺ in winter, although the correlation is weak due to few exceptional data points, but no relation appeared between them in summer (Fig. 5), suggesting that the contribution of long-chain diacids from biomass burning was significant in winter. In fact, the loading of K⁺ in Tianjin PM_{2.5} was higher by a factor of ~8 in winter than that in summer, confirming that the contribution of biomass burning to the PM_{2.5} was highly significant in winter compared to that in summer.

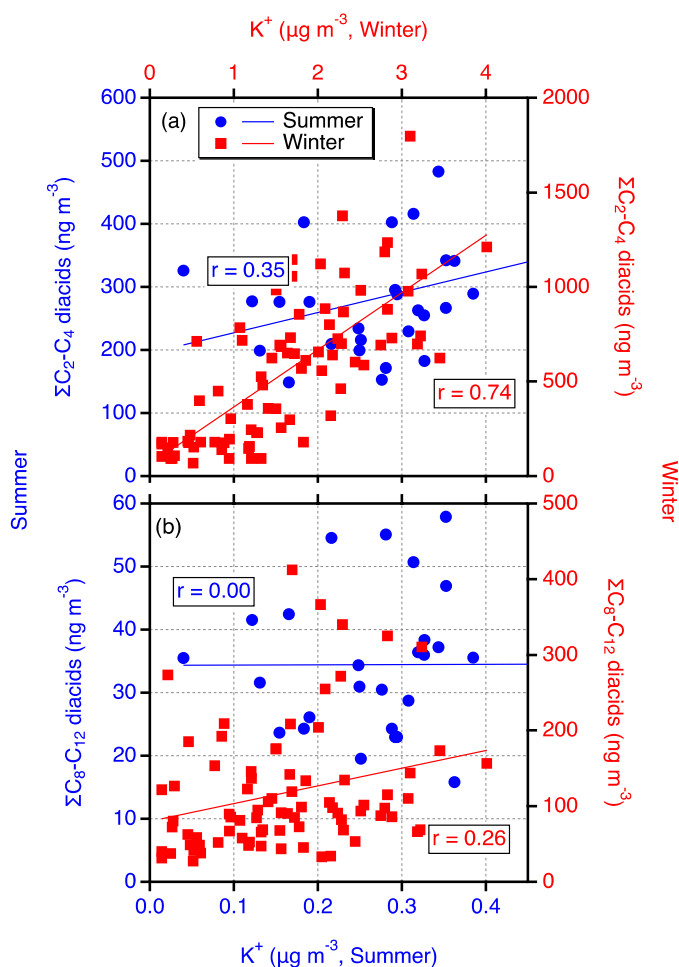


Figure 5. Scatter plots between the sums of (a) short-chain (Σ C₂-C₄) and (b) long-chain (Σ C₈-C₁₂) diacids and potassium ion (K⁺) in PM_{2.5} from Tianjin, North China in summer and winter.

3.4.2 Photochemical Secondary Formation and Aging

It has been established that C₃ and C₄ diacids are emitted from primary sources such as fossil fuel combustion and biomass burning, however, the relative contribution of the former is small compared to the latter, because the C₃ is unstable at high temperatures (Kawamura & Ikushima, 1993). However, C₃ can be produced by photochemical breakdown of C₄ diacid (Charbouillot et al., 2012; Kawamura et al., 1996; Pavuluri et al., 2015). Hence, C₃/C₄ ratio has been considered as a measure to assess the extent of aging of OA in the atmosphere (Aggarwal

& Kawamura, 2008; Kawamura & Ikushima, 1993). The C₃/C₄ ratios in Tianjin PM_{2.5} were found to be always higher in summer than those reported for vehicular emissions, whereas in winter, their lower ends were comparable to those of the vehicular emissions (Table 2). Furthermore, the average C₃/C₄ in summer was more than twice to that in winter and comparable to those reported from Tokyo but lower than that reported from Sapporo, Japan and from the remote Pacific, which are considered to be aged (Kawamura & Sakaguchi, 1999). Such results and comparisons suggest that the diacids and related compounds in Tianjin PM_{2.5} are largely produced by secondary formation, particularly in summer but not subjected for more aging, whereas in winter, the emissions from fossil fuel combustion should have also been contributed significantly.

However, the C₃/C₄ ratios found to be higher in daytime (ave. 1.03; range 0.64-1.40) than that (0.88; 0.73-1.10) in nighttime in summer, but such diurnal variations were not appeared in winter. In addition, the C₃/C₄ showed a significant correlation ($r = 0.59$, $p < 0.05$) with ambient temperature in daytime. These results indicate that photochemical aging was intensive under high ambient temperatures and strong solar radiation in daytime in the Tianjin urban atmosphere that promotes the transformation of C₄ to C₃ diacid. Moreover, the C₆/C₉ mass ratios presented a relatively clear diurnal trends with higher values in daytime (ave. 0.64) than those in nighttime (0.59) in summer. Similar diurnal variations were appeared in the case of Ph/C₉ as well. They further support that the aging (breakdown of C₉ to its lower homologues) was more intensive during daytime than in nighttime.

In contrast, averaged mass ratio of M to F acid did not show a significant difference between summer (1.43 ± 0.81) and winter (1.68 ± 0.90). In fact, the transformation of M acid (*cis*-form) to F acid (*trans*-form) increases with aging under strong solar radiation and hence, the M/F ratio is decreased in the more aged OA (Kundu et al., 2010a; Kundu et al., 2010b). Furthermore, the M/F ratios in Tianjin PM_{2.5} are higher by a factor of ~3 than those (ave. 0.56) reported in marine aerosols from the North Pacific (Kawamura & Sakaguchi, 1999) and Chichijima island (Mochida, 2003), which have been considered as more aged, implying that the OA in Tianjin PM_{2.5} are relatively less aged and significantly derived from the sources at a regional scale. However, the relative abundance of C₂ diacid (C₂%) to total diacids, which can be used as a measure of the extent of OA aging, was accounted for up to 63% in summer with relatively high abundance (49%) in nighttime than in daytime (47%). In winter, C₂% was significantly lower than that in summer and did not show any difference between day- and night-time (35.6% and 36%, respectively). Such high C₂% implies that the Tianjin OA were significantly aged and the contributions from long-range transported air masses cannot be precluded.

3.4.3 Possible Secondary Formation in Aqueous Phase

C₂ diacid is produced from photochemical breakdown of its higher homologues: C₃ and C₄ diacids, and oxoacids: ωC₂ and Pyr acids, that derived from α-dicarbonyls in aqueous phase (Carlton et al., 2007; Ervens, 2004; Kawamura & Ikushima, 1993; Kawamura et al., 1996; Warneck, 2003). Recently, Pavuluri et al. (2015) found that the production of C₄ diacid is much higher compared to all other species including C₂ diacid and its production is increased with increasing UV irradiation time in aqueous aerosols until the precursor compounds are

completely oxidized. Thereafter, the concentration of C₄ diacid starts to decrease with UV irradiation due to photochemical breakdown into its lower homologues: C₃ and C₂ diacids (Pavuluri et al., 2015). Kawamura et al. (2012) found high abundance of C₄ diacid than C₂ diacid in some of marine aerosol samples collected under overcast conditions with fog or brume events over the Arctic Ocean. However, they have been attributed the low abundance of the C₂ diacid for its degradation in aqueous phase, preferably in presence of water-soluble iron. In contrast, Miyazaki et al. (2009) found high abundance of C₂ diacid in nighttime, which is consistent with the increase in SO₄²⁻ loading, and attributed to enhanced production in aqueous phase.

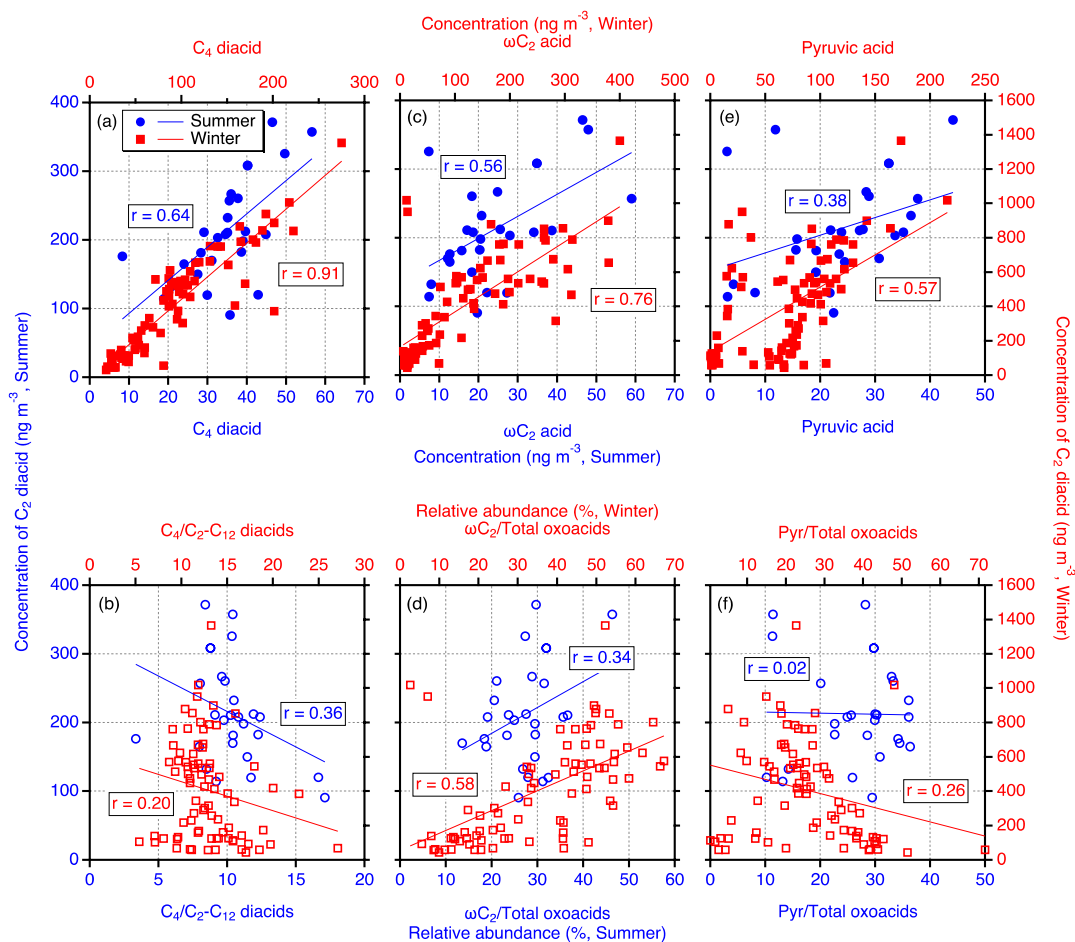


Figure 6. Scatter plots between concentration of C₂ diacid and the concentrations of C₄ diacid (a), ωC₂ acid (b), and pyruvic acid (c), and relative abundance of C₄ diacid in total normal saturated (C₂-C₁₂) diacids (d), the relative abundances of ωC₂ acid (e) and pyruvic acid (f) in total oxoacids in PM_{2.5} from Tianjin, North China in summer and winter. See Table 1 for abbreviations of symbols.

Though the average concentrations of C₂ and C₃ diacids were increased by only about 2.0 and 1.4 folds, respectively, those of C₄ diacid and Pyr acid were increased by ~3 times while that of ωC₂ was increased by a factor of 5 from summer to winter in Tianjin PM_{2.5} (Table 1). Furthermore, the relative abundances of C₂ and C₃ diacids to total diacids were decreased by a factor of about 1.4 and 2, respectively, from summer to winter, whereas that of C₄ diacid to total diacids and those of ωC₂ and Pyr acids to total oxoacids remained almost same in both the seasons (Table 1). Such higher levels and abundances of C₄, ωC₂ and Pyr acids in winter

compared to those of C₂ and C₃ diacids imply that the secondary formation of diacids and related compounds and/or degradation of the C₂ and C₃ diacids in aqueous phase might be significant in the Tianjin atmosphere, particularly in winter, although we do not preclude such possibility in summer as well.

It has been well established that C₄ (and C₃) diacids, ω C₂ acid and Pyr (*via* ω C₂ acid) acid that are mainly produced from their precursors in aqueous phase can easily transformed into C₂ diacid upon further oxidation in the aqueous phase (Carlton et al., 2007; Ervens, 2004; Kawamura et al., 1996; Pavuluri et al., 2015; Warneck, 2003). Hence, the relations of C₄, ω C₂ and Pyr with C₂ diacid could provide better insights to assess the role of aqueous phase reactions in the formation of secondary organic aerosols in the Tianjin atmosphere. As shown in Fig. 6a,c,e, concentrations of C₂ diacid showed a very good, good and modern linear relation with those of C₄ (and C₃, not shown here), ω C₂ acid and Pyr, respectively, in winter and moderate relations in summer. In fact, the relative humidity was high up to 80% in winter, which could promote the aqueous phase oxidation reactions and thus played a significant role in SOA generation in winter in the Tianjin atmosphere compared to that in summer. On the other hand, as discussed earlier, the aging of aerosols should have been more intensive in summer under strong solar radiation and high ambient temperatures that could have promoted the enhanced photochemical transformation of C₄ (and C₃), ω C₂ and Pyr to an ultimate product, C₂ diacid, rather than simultaneous formation of all the species, in summer.

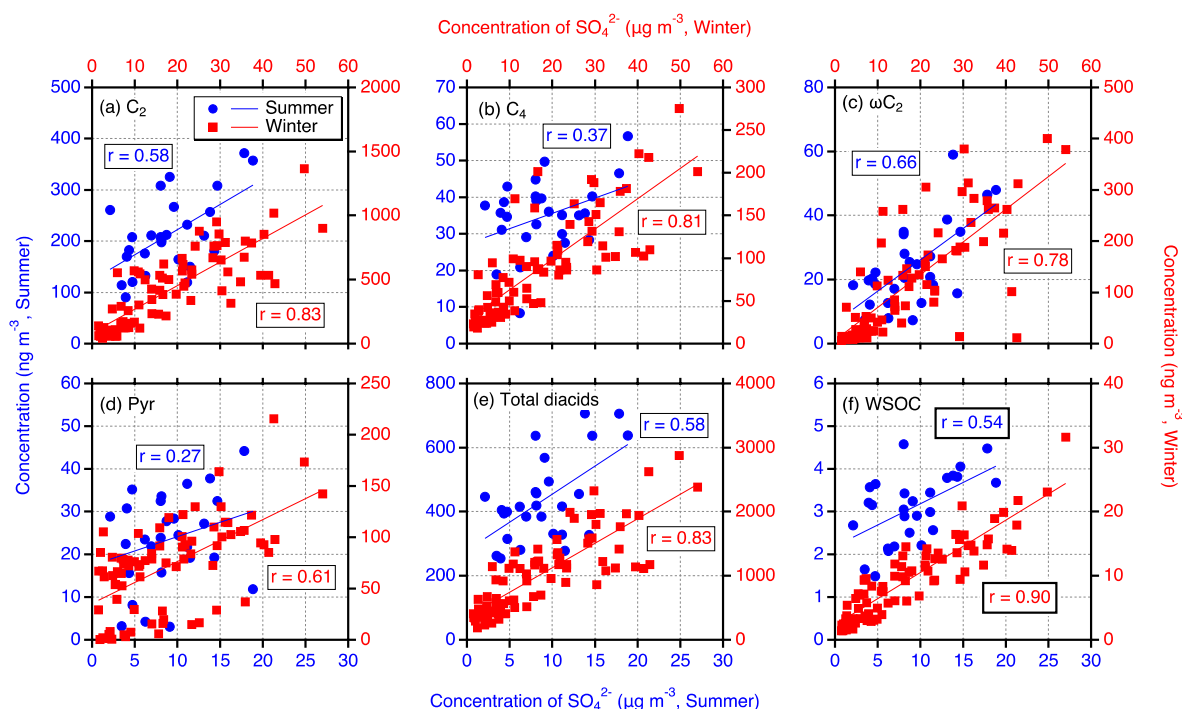


Figure 7. Scatter plots between concentrations of (a) C₂ diacid, (b) C₄ diacid, (c) ω C₂ acid, (d) pyruvic acid, (e) total diacids and (f) water-soluble organic carbon (WSOC) in PM_{2.5} from Tianjin, North China in summer and winter. See Table 1 for abbreviations of symbols. WSOC data is obtained from Wang et al. (2018).

Furthermore, concentrations of C₂ diacid showed an inverse relation with the relative abundance of C₄ diacid (C₄%) to the total normal (Σ C₂-C₁₂) diacids as well as with that of Pyr

to total oxoacids in both the seasons, although the coefficients were weak (Fig. 6b,f). Interestingly, the correlation coefficient between C₂ and C₄% was slightly higher in summer than that in winter, whereas that between C₂ and Pyr% was higher in winter than in summer (Fig. 6b,f). In contrast, C₂ diacid showed a linear relation with the relative abundance of ωC₂ acid (ωC₂%) to total oxoacids in both the seasons, however, the correlation coefficient between them was higher in winter than that in summer (Fig. 6d). These results imply that the formation of C₂ diacid by photochemical breakdown of C₄ (and C₃) diacids should have been dominated in summer whereas in winter, the C₂ diacid should have been mainly produced *via* ωC₂ acid in aqueous phase. The linear relation between C₂ and ωC₂% indicates the formation of the ωC₂ acid from its precursors must be more effective than its transformation to C₂ diacid in aqueous phase. Of course, the degradation of C₂ diacid could also be effective in aqueous phase, if sufficient amount of water-soluble iron available in the liquid aerosol, that can also results the positive relation between C₂ and ωC₂%.

Yu et al. (2005) found very good correlation between SO₄₂₋ and C₂ diacid in atmospheric aerosols from several locations over East Asia and interpreted that the C₂ diacid is highly produced in aqueous aerosols and its loading is increased with the increasing level of the SO₄₂₋. As shown in Fig. 7, C₂ diacid as well as C₄, ωC₂ and Pyr acids, total diacids and total oxoacids (not shown here) showed linear relations with SO₄₂₋ with high and moderate (weak in the case of C₄ and Pyr acids) correlation coefficients in winter and summer, respectively. The correlation coefficient between total oxoacids and SO₄₂₋ was 0.50 in summer and 0.81 in winter. Interestingly, WSOC also showed very strong and moderate linear relationship with the SO₄₂₋ in winter and summer, respectively (Fig. 7f). These linear relations imply that *in-situ* secondary formation of OA including diacids and related compounds in aqueous phase is significant in both the seasons but more intensive and thus the OA are less aged in winter. In summer, particularly the poor correlation between C₄ and Pyr acids, which are mostly first generation species in aqueous phase, and SO₄₂₋ indicates that the aging of OA generated at local scale under strong solar radiation as well as transported from distant source regions in North China was significant. Moreover, the strong correlation of WSOC with the SO₄₂₋ indicate that the water-soluble OA loading is increased with the increasing in SO₄₂₋ levels, probably due to the enhancement in oxidation of OA species in aqueous phase under acidic conditions in the Tianjin atmosphere. Therefore, it is highly necessary to further reduce the emission of oxidant species such as SO₂ and NO_x and thus, the reduction of H₂SO₄ and HNO₃ and subsequently the water-soluble OA in North China.

4 Conclusions

Diacids and related compounds measured in PM_{2.5} samples collected on day- and night-time basis in summer and winter 2016 from Tianjin, North China showed the high abundance of C₂ diacid followed by ωC₂, Ph and *t*Ph acids, respectively. C₄ diacid was the second most abundant diacids followed by C₃ diacid, while Pyr was the second most abundant oxoacids. All diacid, oxoacid and α-dicarbonyl species, except for kC₃ and kC₇, showed a high loading in winter than in summer, but their mass fractions in PM_{2.5} were exactly the opposite; higher in summer than in winter. On average, total diacids-C accounted for 2.93% in TC and 3.31% in

OC in summer and 1.79% and 1.98%, respectively, in winter. Although the diurnal pattern was not systematic, on average, most of the species showed a diurnal pattern. Diacids, oxoacids and α -dicarbonyls are relatively abundant in the Tianjin atmosphere compared to those reported from most of other urban localities over China in winter. Mass ratios of C₆/C₉, Ph/C₉ and Ph/C₆ diacids and their comparison with the literature together with the linear relations of sum of short-chain (Σ C₂-C₄) and long-chain (Σ C₈-C₁₂) diacids with K₊ indicated that anthropogenic emissions, mainly coal combustion, and biomass burning emissions are the major sources in Tianjin region and their contributions are significantly enhanced in winter. The mass ratios of C₃/C₄ and M/F as and the relative abundance of C₂ diacid (C₂%) to total diacids suggested that the diacids and related compounds in Tianjin PM_{2.5} are largely produced by in-situ secondary formation but the aging of OA and the contributions from long-range transported air masses cannot be precluded, particularly in summer. The linear relations between concentrations of C₂ diacid those of C₄, ω C₂ and Pyr acids and with the relative abundance of C₄ diacid (C₄%) to the total normal (Σ C₂-C₁₂) diacids, and that of ω C₂ and Pyr to total oxoacids as well as with SO₄₂₋ implied that the in-situ secondary formation of OA including diacids and related compounds in aqueous phase is significant in both the seasons but more intensive and thus the OA are less aged in winter. In summer, the aging of OA generated at local scale as well as transported from distant source regions was significant in North China. The strong correlation of WSOC with the SO₄₂₋ indicated that the water-soluble OA loading is increased with the increasing in SO₄₂₋ levels and need to reduce the emission of oxidants such as SO₂ and NO_x to control the water-soluble OA loading in North China.

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