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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Abstract

To understand the characteristics and sources of organic aerosols (OA) in North China, we studied diacids, oxoacids, and α-dicarbonyls in summer- and winter-time fine aerosols (PM$_{2.5}$) collected from Tianjin. Oxalic (C$_2$) acid was found to be the most abundant diacid species, followed by succinic (C$_4$), malonic (C$_3$), and sebacic (C$_8$) acids, respectively. Glyoxyllic (ωC$_2$) was the most abundant oxoacid 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 2.9% in total carbon and 3.3% in organic carbon (OC) in summer and 1.8% and 2.0%, respectively, in winter. Their contributions to water-soluble OC (WSOC) was almost the same in both seasons (5.5% and 5.3%, respectively). Molecular distributions, mass ratios of selected diacid (C$_3$, C$_4$, M, F, C$_6$, Ph, and C$_9$) species, and the linear relations among the selected species (including ∑C$_2$–C$_4$ and ∑C$_6$–C$_12$) and with inorganic markers (K$^+$ and SO$_4^{2-}$) 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 local scale and aging during long-range transport in both summer and winter. This study revealed that diacids and related compounds and WSOC are increased with increasing SO$_4^{2-}$ and they are produced in the aqueous phase, implying that the reduction in NO$_x$ and SO$_2$ emissions could possibly control the water-soluble OA loading over North China.

1. Introduction

Atmospheric fine aerosols (PM$_{2.5}$) 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). In East Asia, high aerosol loadings are common and often suffer from haze events due to enhancing development of urbanization and industrialization in recent times, particularly over China (Carmichael et al., 2009; Huang et al., 2014; Zhang et al., 2012). A great attention has been paid on Chinese aerosol studies through ground-based measurements at different locations and large-scale field experiments focusing on the measurements of inorganic and carbonaceous components, but the studies on molecular characterization of organic aerosols (OA) are limited (Cao et al., 2007; Fu et al., 2008; Fuzzi et al., 2006; Huang et al., 2014; Nakajima et al., 2007; Wang et al., 2007), and, in particular, the studies on more oxygenated species such as dicarboxylic acids and related compounds are scarce, limiting to short-term measurements at some major urban locations and Mt. Tai (Ho et al., 2007; Wang et al., 2002; Zhang et al., 2016; Zhao et al., 2018).

Low-molecular weight (LMW) diacids, oxocarboxylic acids, and α-dicarbonyls are found to be ubiquitous constituents with high abundance of oxalic (C$_2$) acid in atmospheric aerosols in various environments such as urban, rural, mountain, polar, and marine (Cheng et al., 2013; Falkovich et al., 2005; Fisseha et al., 2006; Kawamura & Bikkina, 2016; Meng et al., 2018; Sorathia et al., 2018; Yang et al., 2020) and in atmospheric waters (Sorooshian et al., 2007). Diacids and related compounds can be emitted directly into the atmosphere
from primary sources such as fossil fuel combustion, biomass burning, and meat cooking (primary), and formed in the atmosphere by photochemical oxidation of their precursors of both anthropogenic and biogenic origin in gas and liquid phases (secondary) (Kawamura & Bikkina, 2016; Kawamura et al., 1996; Legrand et al., 2007). In addition, they are subjected for further photochemical processing (aging) in the atmosphere under stagnant conditions at local scale and/or during long-range transport from distant source regions, resulting multiple generations of more oxygenated species; for example, carboxyls to carboxylic acids and diacids and long-chain diacids to their lower homologues (Kawamura & Ikushima, 1993; Tilgner & Herrmann, 2010). Hence, their relative contributions from primary and secondary sources depend on the types of emissions, meteorology, and oxidation capacity of the atmosphere at local to regional scale.

Diacids and related compounds are highly water-soluble and identified as an important group of the water-soluble organic carbon (WSOC) compounds. WSOC species makeup a dominant fraction (up to 80%) of secondary organic aerosol (SOA) mass, which accounts for a substantial fraction (20%–90%) of the PM$_{2.5}$ mass (Hallquist et al., 2009; Kroll & Seinfeld, 2008; Mayol-Bracero et al., 2002; Timonen et al., 2008). The abundance of total diacids-carbon to total organic carbon (OC) is reported to be 1%–3% in urban areas (Kawamura & Ikushima, 1993; Kawamura & Yasui, 2005; Miyazaki et al., 2009; Pavuluri et al., 2010) and up to 16% and 24% in the remote and tropical marine atmosphere, respectively (Fu et al., 2013; Kawamura & Sakaguchi, 1999). Therefore, the characteristics and distributions of diacids and related compounds provide insights on the sources of OA. Because diacids and related compounds can act as surfactants (Latif & Brimblecombe, 2004), their presence on particle surface alters the hygroscopic behavior of the particles (Saxena et al., 1995) and influence the capacity of atmospheric aerosols to act as cloud condensation nuclei (CCN) and ice nuclei (IN) (Peng et al., 2001, 2016; Prenni et al., 2001). As CCN is one of the important parameters that influence the cloud radiative properties (Asa-Awuku et al., 2011), the increase in CCN number concentrations in the atmosphere should impact the indirect radiative forcing by aerosol, possibly resulting a more reflective clouds (Twomey, 1977) and less precipitation (Albrecht, 1989).

Furthermore, diacids and related compounds play a minor role in controlling the pH and free acidity of atmospheric waters (Galloway & Gaudry, 1984), and participate in various physical and chemical reactions in the atmosphere. For example, Folkers et al. (2003) reported that unlike uncoated NH$_4$HSO$_4$ particles, the NH$_4$HSO$_4$ particles coated with an organic substance containing a diacid have a reduced reaction absorption coefficient for N$_2$O$_5$ (one of the main intermediates for NO$_x$ removal in the atmosphere), which increases oxidative capacity of the particles. This indicates that the organic surface inhibits the transfer of N$_2$O$_5$ into NH$_4$HSO$_4$ core. Therefore, the study of LMW diacids and related compounds has become an issue of growing interest in recent times. Many observational studies have been carried out over the past 2 decades on characterization of diacids and related compounds, but they are limited to certain locations and not sufficient enough to fully understand their sources and formation pathways at regional to global scales. Hence, it is highly necessary to study the characteristics of diacids and related compounds in atmospheric aerosols at different locations over the world.

In view of the above, to better understand the characteristics, origins, and secondary formation and transformations of OA, particularly over North China, where the aerosol loading is much high compared to that in other parts of China, summer- and winter-time PM$_{2.5}$ samples were collected in the urban atmosphere of Tianjin, 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. The characteristics of carbonaceous components and stable carbon isotope ratios of total carbon (TC) in the PM$_{2.5}$ have been reported by Wang et al. (2018). Here, we report the molecular composition and distributions of diacids, oxoacids, and α-dicarbonyls in the PM$_{2.5}$. We discuss the sources of diacids and related compounds over the North China region including their secondary formation, but not aged, at local scale (referred as in situ here) and aging at local and/or regional (during the long-range atmospheric transport) scales, based on mass ratios of selected species and their linear relations with marker ions together with the backward air mass trajectories.
2. Experimental

2.1. Site Description

PM$_{2.5}$ sampling was performed at Tianjin University, Nankai district located in central Tianjin, a typical metropolis and largest coastal city in North China, located at 39.11°N and 117.18°E on the lower reaches of Haihe River and adjacent to the Bohai Sea (see Figure S1 in Supporting Information). Tianjin is covered an area of $\sim 11,900$ km$^2$ with a population of $\sim 15$ million (https://en.wikipedia.org/wiki/Tianjin). 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). The energy consumption per capita was 3,001 kg CE (kilogram coal equivalent) in 2002 (Crompton & Wu, 2005) and the consumption is gradually increasing year by year with a growth rate of about 5.7% (Ma et al., 2011). The major industries in Tianjin are the smelting and pressing of ferrous metals, petroleum refining and coking and nuclear fuel processing, chemical raw materials and chemical products manufacturing, electricity and heat production, oil and gas extraction, and nonmetallic mineral products. The industrial energy consumption accounts for more than 70% of the total energy consumption (Zhu et al., 2017), and the energy consumption structure relies mainly on coal, accounting for about 59.4%, followed by oil ($\sim$ 28.5%), electricity (9.8%), and natural gas (2.4%) (Ma et al., 2011). In recent times, the total natural gas consumption is increasing, particularly after the implementation of Coal Replacing Project in 2017, and its annual growth rate in 2017 was 9% in Tianjin (Wang et al., 2019). However, the sampling point is $\sim 600$ m away from the road and no industries are located nearby and, thus, there is no influence of any point source on the composition of PM$_{2.5}$.

On the other hand, the agricultural activity is significant in northern parts of Tianjin region, and it is also covered with mountains and dense forests (Figure S1). Furthermore, the weather in Tianjin is influenced by the East Asian monsoon, which forms as a result of the thermal difference between the Asian continent and the Pacific Ocean, prevailing with hot and humid air in summer and cold and dry air in winter. The East Asian monsoon also controls the source regions (oceanic region in summer and continental region in winter), and, thus, 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 northern China, and surrounding oceans as well as local emissions (see Section 2.6).

2.2. Aerosol Sampling

PM$_{2.5}$ samples were collected on the rooftop of a six-story building ($\sim$ 20 m above ground level (AGL) using precombusted (at 450°C for 6 h) quartz fiber filters (Pallflex 2500QAT-UP) and a high-volume sampler (TISCH Environmental TE-6070DX) with a flow rate of 68 m$^3$ h$^{-1}$ in summer (6-19 July, $n = 27$) and winter (10 November to 23 December, $n = 81$) 2016 on day-time (7:30 a.m. to 7:00 p.m. local time and 8:00 a.m. to 7:30 p.m. for summer and winter, respectively) and nighttime (7:30 p.m. to 7:00 a.m. and 7:40 p.m. to 7:40 a.m. for summer and winter, respectively) basis. Before the start of sampling in each season, sampler was calibrated and run for one-day as a test period. One blank sample was also collected in each season, placing the filter on filter hood for several 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 $\alpha$-dicarbonyls in PM$_{2.5}$ were determined following the method reported elsewhere (Kawamura & Ikushima, 1993; Pavuluri et al., 2010, 2018). 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 three times under ultrasonication for 10 min each. The extracts were filtered through Pasteur pipette loaded with a small amount of quartz wool to remove the filter debris and adjusted their pHs 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% BF$_3$/n-butanol at 100°C for 1 hour. The derivatized species were dissolved in n-hexane and washed with Milli-Q water and 0.2 ml acetonitrile to remove the unreacted BF$_3$ and other contents and then concentrated to dryness under rotary evaporation followed by N$_2$ blow. The derivatized dibutyl esters and/or acetals were finally
dissolved into n-hexane (100 μl) and then injected into split/splitless GC-FID (Agilent 7980) equipped with an HP-5 capillary column (0.2 mm × 25 m, 0.5 μm film thickness). Identification of various compounds was confirmed by GC/mass spectrometer, whose sampling port temperature and increasing temperature program is the same to that of GC-FID. Recoveries of authentic standards of only oxalic (C₂), malonic (C₃), succinic (C₄), and adipic (C₆) acids spiked to a precombusted quartz fiber filter were 98%, 71%, 85%, and 89%, respectively. In order to confirm the GC-FID condition and avoid any instrumental measurement errors, we injected a set of authentic standard butylesters of C₂–C₄, maleic (M), fumaric (F), and phthalic (Ph) acids and C₁₈:₀ fatty acid for once on every day of the analysis, before injecting the samples. All the measured compounds were quantified using the concentration of authentic standard butylester of C₄ diacid and its peak area obtained on the day of analysis, because the FID response for all compounds is similar, depending on the number of carbons present in the given compound. Detection limits of this method are about 0.1 ng m⁻³ (Narukawa et al., 2003). 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, but not for recovery.

2.4. PM₂.₅ Mass, Carbonaceous Components, and Inorganic Ions

PM₂.₅ mass in each filter was measured gravimetrically by the mass difference of filters, conditioned in a desiccator for ~48 h, before and after sampling.

Details of the measurements of elemental carbon (EC), OC, and WSOC were described and their data were reported by Wang et al. (2018). Briefly, EC and OC were measured using an aliquot of filter (1.8 cm disc in diameter) and an EC/OC analyzer (Sunset Laboratory Inc., USA) following IMPROVE thermal-optical transmittance protocol and assuming the carbonate carbon to be negligible. WSOC was extracted from an aliquot of filter (4.52 cm²) with organic-free Milli-Q water under ultrasonication and measured using a TOC analyzer (Shimadzu 5000A). The sum of EC and OC was considered as total carbon (TC).

Inorganic ions were measured using the extract of an aliquot of filter sample extracted into Milli-Q water under ultrasonication for 30 min and filtered through syringe filter (0.22 μm) and ion chromatograph (ICS 5000+). A mixture of 1.8 mM Na₂CO₃, 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 ambient temperature, relative humidity (RH), wind speed and direction, and precipitation were monitored using weather station installed beside the sampler during the sampling period and the data were averaged for 12-h corresponding to each sample period. While the hourly gaseous oxidant species (O₃ and NO₂) data were downloaded at http://beijingair.sinaapp.com and averaged corresponding to each sample period. Temporal variations in both meteorology and oxidants are shown in Figure 1. The ambient temperature, RH, and wind speed ranged from 21.1°C to 33.1°C with an average of 29.4 ± 3.4°C, 45.9%–76.6% (ave. 56.8 ± 9.8%) and 1.25–2.43 (1.65 ± 0.33 m sec⁻¹), respectively, in daytime and 22.5–30.2°C (26.3 ± 2.3°C), 60.6%–83.0% (70.5 ± 6.9%) and 0.89–1.88 (1.32 ± 0.30 m sec⁻¹), respectively, in nighttime, during the summer campaign. During the winter campaign, they were −3.25 to 16.8°C (4.63 ± 4.10°C), 19.9%–99.7% (57.1 ± 20.7%), and 0.25–3.66 m sec⁻¹ (1.38 ± 0.70 m sec⁻¹), respectively, in daytime and −2.00 to 9.89°C (3.68 ± 3.20°C), 29.9%–99.9% (60.5 ± 19.2%) and 0.39–3.31 m sec⁻¹ (1.19 ± 0.62 m sec⁻¹), respectively, in nighttime. The winds were mainly flown from southeast (Figure 1a) and no precipitation, except on July 15, 2016 (0.02 cm), occurred in summer, whereas in winter, the winds were mostly from southwest (Figure 1a) and the occurrence of precipitation events were rare and not significant.
2.6. Backward Air Mass Trajectories

Cluster analysis of the air masses arrived over Tianjin at 500 m AGL using 5-day backward air mass trajectories data obtained from Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the National Oceanic and Atmospheric Administration (NOAA) (https://www.ready.noaa.gov/HYSPLIT.php). The computed plots are depicted in Figure 2. In summer, most of the air masses (61%) were originated from

Figure 2. Cluster analysis plots of the 5-day backward air masses trajectories that arrived at 500 m AGL over Tianjin, North China during (a) summer and (b) winter campaign periods, 2016.
the Pacific Ocean and passed over the Bohai Sea and eastern parts of the Chinese mainland, and rest of the air masses were mostly originated from Siberian region and passed over Mongolia and northeastern parts of mainland China (Figure 2a). Whereas in winter, they were originated from Eurasia and passed over Siberia, Mongolia, and northern parts of China (Figure 2b). However, unlike (always above 500 m AGL) in summer, a portion (17%) of the air parcels originated from the mainland of Northwest China were traveled at very low altitude (≤500 m AGL) for most of the time in winter (Figure 2b). Therefore, the contribution of local air masses should be relatively important in winter compared to that in summer.

3. Results and Discussion

3.1. Molecular Composition and Distributions

A homologous series of saturated linear diacids (C_2–C_12) and branched diacids (isoC_4–C_6) 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 [iPh], and terephthalic [tPh]) acids and diacids with an additional functional (carbonyl) group (ketomalonic (kC_3) and 4-ketopimelic (kC_7) acids) in the PM_{2.5}. C_2–C_9 ω-oxoacids, excluding C_6 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. Averaged molecular distributions of diacids and related compounds in day- and nighttime in both the seasons are depicted in Figure 3.

Concentrations of total diacids ranged from 185 ng m^{-3} to 2,874 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. Averaged molecular distributions of the measured diacids and related compounds were characterized by a predominance of C_2 diacid followed by glyoxylic (ωC_2), Ph, C_4, and tPh acids, respectively. Pyr was found to be the sixth most abundant species followed by C_3 diacid, oxobutanoic (ωC_4), and azelaic acid (C_9), respectively, during the campaign. Relative abundance of C_2 diacid to total diacids ranged from 10.6% to 58.4% with an average of 38.9 ± 11.0% followed by Ph (ave. 10.0% ± 4.5%), C_4 (8.54% ± 1.9%), tPh (7.7% ± 5.5%), C_9 (5.4% ± 1.9%), and C_3 (4.0% ± 1.8%) diacids, respectively, during the whole campaign.

![Figure 3](image-url)
### Table 1
Summary of Concentrations of Diacids, Oxoacids, and α-Dicarbonyls and Their Relative Abundances in Total Diacids, Oxoacids, and α-Dicarbonyls Together With the Concentrations of Inorganic Ions in PM$_{2.5}$ Collected From Tianjin, North China During Winter and Summer 2016

| Compounds        | Concentration (ng m$^{-3}$) | Winter ($n = 81$) | Relative abundance (%) | Concentration (ng m$^{-3}$) | Summer ($n = 27$) | Relative abundance (%) | Diacids |
|------------------|-----------------------------|-------------------|------------------------|-----------------------------|-------------------|------------------------|---------|
|                  | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) |         |
| Oxalic, C$_2$    | 90.5–371 208 213 ± 74.6     | 42.2–1,365 386 405 ± 290 | 35.8 ± 10.4            | 15.6–64.9 33.5 34.5 ± 12.3 | 7.60–157 44.1 48.2 ± 32.0 | 4.6 ± 1.1smiths |
| Malonic, C$_3$   | 8.31–56.6 35.6 34.8 ± 9.94  | 8.3 ± 2.4          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Succinic, C$_4$  | 5.12–22.6 10.6 10.3 ± 3.82  | 8.3 ± 2.4          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Glutaric, C$_5$  | 7.17–30.3 14.7 15.6 ± 5.12  | 8.3 ± 2.4          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Adipic, C$_6$    | 1.93–6.4 2.19 2.32 ± 1.00   | 9.3 ± 2.4          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Pimelic, C$_7$   | 0.99–26.7 3.94 4.73 ± 4.83   | 4.6 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Sebacic, C$_8$   | 1.10–18.0 1.93 3.66 ± 4.37   | 3.6 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |
| Azelaic, C$_9$   | 9.50–193 39.3 ± 11.7         | 3.6 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          | 3.51–35.7 8.03 10.9 ± 7.26 | 2.4 ± 1.1          |

### Oxoacids

| Compounds        | Concentration (ng m$^{-3}$) | Winter ($n = 81$) | Relative abundance (%) | Concentration (ng m$^{-3}$) | Summer ($n = 27$) | Relative abundance (%) | Oxoacids |
|------------------|-----------------------------|-------------------|------------------------|-----------------------------|-------------------|------------------------|---------|
|                  | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) |         |
| Glyoxal, ωC$_2$  | 3.03–44.2 23.8 23.5 ± 10.9  | 26.4 ± 8.1         | 3.03–44.2 23.8 23.5 ± 10.9 | 26.4 ± 8.1         | 3.03–44.2 23.8 23.5 ± 10.9 | 26.4 ± 8.1         |
| Pyruvic, Pyr     | 23.8–188 86.1 86.3 ± 34.7   | –                  | 23.8–188 86.1 86.3 ± 34.7 | –                          | 23.8–188 86.1 86.3 ± 34.7 | –                          |

### α-Dicarbonyls

| Compounds        | Concentration (ng m$^{-3}$) | Winter ($n = 81$) | Relative abundance (%) | Concentration (ng m$^{-3}$) | Summer ($n = 27$) | Relative abundance (%) | α-Dicarbonyls |
|------------------|-----------------------------|-------------------|------------------------|-----------------------------|-------------------|------------------------|---------------|
|                  | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) |               |
| Glyoxal, Gly     | 0.26–11.0 6.64 6.18 ± 2.58  | 42.8 ± 23.9        | 0.26–11.0 6.64 6.18 ± 2.58 | 42.8 ± 23.9        | 0.26–11.0 6.64 6.18 ± 2.58 | 42.8 ± 23.9        |
| Methylglyoxal, mM | 9.85–36.5 8.07 10.8 ± 8.87  | 57.2 ± 23.9        | 0.95–36.5 8.07 10.8 ± 8.87 | 57.2 ± 23.9        | 0.95–36.5 8.07 10.8 ± 8.87 | 57.2 ± 23.9        |
| Total α-dicarbonyls | 6.05–47.6 14.3 17.0 ± 9.5     | –                  | 6.05–47.6 14.3 17.0 ± 9.5     | –                          | 6.05–47.6 14.3 17.0 ± 9.5     | –                          |

### Inorganic Ions

| Compounds        | Concentration (ng m$^{-3}$) | Winter ($n = 81$) | Relative abundance (%) | Concentration (ng m$^{-3}$) | Summer ($n = 27$) | Relative abundance (%) | Inorganic Ions |
|------------------|-----------------------------|-------------------|------------------------|-----------------------------|-------------------|------------------------|----------------|
|                  | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) | Range Med Ave. ± SD         | Range Med Ave. ± SD | Relative abundance (%) |               |
| Potassium, K$^+$ | 3.04–0.53 0.29 0.27 ± 0.10  | –                  | 3.04–0.53 0.29 0.27 ± 0.10 | –                          | 3.04–0.53 0.29 0.27 ± 0.10 | –                          |
ωC₂ acid accounted for 33.1% ± 15.7% to total oxoacids followed by Pyr (25.7% ± 12.0%), ωC₄ (17.7% ± 7.8%) and ωC₃ (8.4% ± 4.5%) acids, respectively. Both Gly and mGly were almost equally abundant with a relative abundance of 45.1% ± 20.3% and 54.9% ± 20.3% to total α-dicarbonyls, respectively.

It is worth noting that the high abundance of C₄ diacid than that of C₃ diacid in Tianjin aerosols, particularly in winter (Table 1), is a unique feature, because such pattern is generally the opposite to that reported in continental and marine aerosols, which were considered to be photochemically processed during long-range atmospheric transport (Kawamura & Bikkina, 2016), but similar to that reported in Beijing aerosols, which were 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 linear 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). In order to understand the possible sources of Tianjin aerosols, we examined the concentrations of diacids and related compounds and mass ratios of selected species (see later sections) in Tianjin aerosols with those reported for urban, marine, and polar aerosols from some selected locations in the Asian region and the downwind regions of the Asian continent and Arctic, which were considered to be severely influenced mainly by anthropogenic and/or biogenic emissions and photochemically processed during long-range atmospheric transport. Average concentrations of total diacids, oxoacids, and α-dicarbonyls in Tianjin aerosols were found to be much higher than those (ave. 438 ± 267, 43.0 ± 48, and 11.0 ± 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, 530.0, and 12.4 ng m⁻³, respectively) (Kawamura et al., 2004), as well as in Arctic aerosols (∼100 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 (PM₂.₅) aerosols (1,350, 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 Tianjin region is relatively polluted than remote sites located in downwind regions of East Asia but lesser than other hazy urban locations in China.

### 3.2. Seasonal and Diurnal Variations

#### 3.2.1. Saturated Linear and Branched Diacids

Concentrations of saturated linear 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 C₆, C₇ and C₈ (iC₄;iC₆) diacids were less abundant than their corresponding linear structures in both the seasons (Table 1, Figure 3). Although C₄ diacid was the most abundant species in both the seasons, its relative abundance to total linear C₂–C₁₂ diacids was reduced on average by about 9% from summer to winter (Figure 4). It is also worth to note that C₄ diacid was equally abundant to that of C₃ diacid in summer, whereas in winter, it was higher by a factor of 2 than that of C₃ (Table 1). Their relative abundances to linear diacids were also showed the same seasonal pattern (Figure 4). The high abundance of C₄ than that of C₃ 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 linear C₂–C₁₂ diacids were enhanced by five- and three-folds, respectively, from summer to winter periods, while that of C₅ and C₆ di-
acids were increased by 1% in winter compared to that in summer (Figure 4). In fact, the concentrations of C5 diacid in winter were more than three times higher than that in summer (Table 1).

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 substantially 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 was considered to be the major source of aerosols. It has been reported that oxidation of unsaturated fatty acids produces a homologous series of \(\omega\)-oxoacids and mono- and di-carboxylic acids with C7 diacid being a dominant species in the marine environment (Kawamura & Gagosian, 1987). The C9 diacid was found to be abundant among the long-chain (C8–C12) diacids in atmospheric aerosols in different environments and has been attributed to secondary formation by photochemical oxidation of unsaturated fatty acids (e.g., oleic acid, \(C_{18:1}\)) through the oxidative cleavage of double bond at C9 position (Kawamura & Bikkina, 2016; Kawamura & Gagosian, 1987; Kawamura & Sakaguchi, 1999). In addition, it has been reported that C9 diacid is the dominant product in laboratory photochemical oxidation of authentic oleic acid (Matsunaga et al., 1999; Tedetti et al., 2007). That is why, C9 diacid has been considered as a tracer of OA of biogenic origin such as marine biota and terrestrial plants as well as cooking emissions (Kawamura & Bikkina, 2016). Interestingly, C9 diacid was found to be the fourth most abundant diacids in both summer- and winter-time aerosols in Tianjin (Table 1). Such molecular distributions of C6 and C9 diacids and their seasonal variations suggest that the Tianjin aerosols might have derived from mixed sources in both the seasons.

In fact, most of the air masses arrived in Tianjin in summer were originated from the Pacific Ocean (Figure 2a) that should have been enriched with unsaturated fatty acids of marine biogenic origin. Whereas in winter, they mostly originated from middle east and/or mainland China and passed over Mongolia and partly originated from and/or passed over Siberia (Figure 2b) that should have been enriched with anthropogenic emissions and terrestrial higher plant emissions, respectively. Therefore, the higher relative abundances of C9–C12 diacids in winter than in summer indicate that the OA should have been mainly derived from the enhanced local emissions, probably biomass burning, and subsequent secondary formation in winter. In addition, the long-chain (C8–C12) diacids should have been derived from unsaturated fatty acids of terrestrial biogenic origin that were enriched in the air masses transported from the Siberian region (Figure 2b). The higher levels of NO\(_2\) and lower levels of O\(_3\) in the Tianjin atmosphere (Figure 1b) should have promoted the secondary formation of long-chain diacids from their precursor compounds, rather than
their degradation to short-chain compounds in winter (Kawamura et al., 1996; Pavuluri et al., 2015). High relative abundance of C₂, which has been considered as a measure of the aging of OA (Kawamura & Sackaguchi, 1999), and C₃ diacids in summer than those in winter (Table 1; Figure 4) also indicate that the aging of OA might be more intensive in summer than in winter.

Furthermore, the concentrations of linear diacids found to be generally higher in daytime than that in nighttime (Figures 5a and 5b), except for C₈ diacid in summer and C₇, C₈, and C₉ diacids in winter (Tables S1 and S2). Of course, the diurnal variations were not statistically significant, except for C₁ and C₁₁ diacids (p = 0.04 and 0.03, respectively) in summer (Tables S1 and S2), which is likely because the OA derived from not only local emissions but also from the long-range transported (aged) air masses. However, the general trends of diurnal variations of specific species provide insights on in situ secondary formation and aging of OA. Interestingly, C₂–C₄ diacids showed a substantial differences in their day- and night-time concentrations with higher levels mostly in daytime samples in both the seasons (Figure 5a; Tables S1 and S2). The branched chain diacids, particularly iC₅ and iC₆ diacids, showed a clear diurnal changes, which were statistically significant in summer but not in winter (Tables S1 and S2). Such diurnal variations indicate that in situ photochemical secondary formation of OA was intensive in daytime in the Tianjin atmosphere, associating with intense solar radiation and high loading of O₃ during daytime in summer (Figure 1b). The rarely appeared higher levels of diacids in nighttime than in daytime, mostly in winter (Figure 5), suggest that the in situ secondary formation of OA in the Tianjin atmosphere was significant in nighttime as well. In addition, the significant diurnal variations of branched diacids, unlike their corresponding linear diacids, suggest that they should have been derived from other precursors and/or their secondary formation processes are different from those of the linear diacids. In fact, it has been reported that the branched chain diacids are considered to be generated from the oxidation of methylcycloalkanes by both O₃ and NO₂ (Grosjean & Fung, 1984).

### 3.2.2. Unsaturated and Multifunctional Diacids

Concentrations of both aliphatic unsaturated (M, F, and mM) and aromatic (Ph, iP, and tPh) 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 iP and mM acids. Such pattern is similar to that reported in subtropical Okinawa in the Western Pacific Rim, downwind region of East Asia (Kunwar & Kawamura, 2014) and Xi’an, China (Cheng et al., 2013). The relative abundances of Ph and iP acids to total diacids were higher in winter 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 have 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 was reported to be abundant in some megacities of China. The process of secondary formation of Ph involves its photochemical formation in the gas phase followed by the absorption onto existing particles (Kawamura & Ikushima, 1993). In addition, it can also be directly emitted by automobile exhaust (Kawamura & Kaplan, 1987) and coal combustion (Zhang & Hatakeyama, 2016). 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. Although coal consumption for domestic heating has been substantially reduced in recent years, about 59.4% and 28.5% of the total (domestic plus industrial) energy consumption relies on coal, mainly for industrial terminal, and fuel oil, respectively, in Tianjin (Ma et al., 2011; Zhu et al., 2017). In addition, the air masses that arrived in Tianjin were transported over Mongolia and/or northern Chinese cities in winter (Figure 2b) and should have been enriched with coal combustion emissions due to large consumption of coal for domestic purpose and natural coal and peat fires occurring in Inner Mongolia, China (Liang et al., 2014). The pyrolysis of coal emits a large number of organic compounds including nonaromatic hydrocarbons, carboxylic acids, and aromatic compounds and substantially contribute to atmospheric OA (Wang et al., 2015). Interestingly, the relative abundance of Ph acid in Tianjin aerosols (Table 1) is relatively comparable to that reported from
Figure 5. Temporal variations of selected diacids (a–c), oxoacids (d and e), and α-dicarbonyls (f) and total diacids, oxoacids, and α-dicarbonyls (g) in PM$_{2.5}$ from Tianjin, North China during summer and winter, 2016. Open and close circles and square marks represent day- and nighttime, respectively.

Xi’an, China (8.3% in summer and 8.0% in winter), where the emissions from household combustion of coal are large (Cheng et al., 2013), further supporting that the contribution from coal combustion to OA is important over Tianjin.
In contrast, tPh 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 tPh in Tianjin aerosols was higher in winter by a factor of 2 than that (48.70 ng m\(^{-3}\)) reported in Beijing, China (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 tPh acid in wintertime Tianjin aerosols (Table 1) found to be much higher than that (∼4%) reported from Xi’an, China, where the emissions from plastic burning are important, although it is comparable in summertime (Cheng et al., 2013). Such comparisons with the literature indicate that, in addition to coal combustion, the plastic burning is also an important source of OA over the Tianjin region. However, quantitative identification of the tPh and/or OA from plastic burning needs to be explored in northern and other parts of China, a subject of future research.

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 statistically significant only in the case of Ph (\(p = 0.05\)) and tPh (\(p = 0.03\)) acids (Figure 3c Table S1). In contrast, mM and tPh acids showed a nocturnal distribution with higher levels in nighttime, whereas Ph acid showed the high abundance in daytime than in nighttime in winter, although such variations were not statistically significant (Figure 3c, Table S2). These results imply that their in situ secondary formation should be more intensive in daytime compared to that in nighttime in summer. Whereas in winter, the in situ nighttime chemistry (i.e., oxidation by NO\(_3\) radicals) might played an important role, rather than daytime chemistry (oxidation by O\(_3\)). In addition, the emission of these species, particularly tPh acid, from primary sources (e.g., plastic burning) might higher during nighttime in winter in Tianjin and/or surrounding areas.

### 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). ωC\(_2\) acid was found to be the most abundant oxoacids followed by Pyr and ωC\(_4\) acids, respectively. Such molecular distribution is different from that reported in New Delhi, where the second most abundant oxoacids was ωC\(_4\) acid (Miyazaki et al., 2009), as well as from that reported in Tokyo, where Pyr was the most abundant oxoacids (Kawamura & Yasui, 2005). ωC\(_2\) acid 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). Interestingly, total dicarbonyls also showed higher level in winter than in summer. mM Gly was more abundant than Gly in both summer and winter.

Most of the oxoacids and α-dicarbonyls showed relatively high abundance in daytime compared to that in nighttime in winter, whereas in summer, mGly was higher in nighttime (Figures 3d–3f), but their diurnal variations were insignificant in both the seasons (Tables S1 and S2). Gly is largely derived by oxidation of aromatic hydrocarbons, although it can be derived from biogenic and marine emissions for some extent. The low abundance of mGly in daytime might be due to its extensive transformation into other more oxidized compounds (e.g., ωC\(_3\)) by enhanced photochemical oxidation reactions (Kawamura et al., 1996; Lim et al., 2010).

However, total diacids, oxoacids, and α-dicarbonyls showed a diurnal pattern with higher levels mostly in daytime in summer, whereas in winter, they did not show any systematic diurnal pattern (Figure 3g). Moreover, such variations were statistically significant in the case of diacids (\(p = 0.04\)) and considerable in the case of oxoacids (\(p = 0.06\)) in summer, but not in winter (Tables S1 and S2). These results together with the diurnal variations of individual species imply that their in situ photochemical secondary formation was important in summer, whereas primary emissions and nighttime chemistry were important in winter.

### 3.3. Mass Fractions in PM\(_{2.5}\), TC, OC, and WSOC

As detailed in Section 1, diacids and related compounds are an important group of WSOC compounds and accounts for a substantial fraction to OC (Fu et al., 2013; Kawamura & Sakaguchi, 1999; Pavuluri et al., 2010).
Mass fractions of the concentrations of total diacids, oxoacids, and α-dicarbonyls in PM$_{2.5}$ together with those of their C contents in TC, OC, and WSOC in summer and winter are depicted in Figure 6. In fact, diacids carbon (C) contents showed a linear relationship with good correlation coefficients and statistical significance at 0.01 level with OC ($r = 0.71$ in summer and $r = 0.73$ in winter) and WSOC ($r = 0.55$ and 0.82 in winter and summer, respectively) (Figure S2). Such linear relations suggest that the origins and/or the extent of secondary formation of diacids and OC as well as WSOC might be similar during the campaign. Therefore, the mass fractions of diacid-C in various carbonaceous components and in PM$_{2.5}$ could provide insights on the sources of OA.

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 (Figure 6). On an average, total diacids accounted for 0.60% in PM$_{2.5}$ in winter, whereas in summer, it was almost doubled (1.2%) to that in winter, while the mass fractions of total oxoacids were the same, 0.2%, in both the seasons. Total α-dicarbonyls were accounted for a minor (0.04% and 0.03%, respectively) fraction in PM$_{2.5}$, because we measured only two α-dicarbonyl species, which are partly present in the gas phase (Kawamura et al., 1996; Lim et al., 2005).

Total diacids-C accounted for 2.0%–4.6% (ave. 2.9%) in TC and 2.3%–5.0% (3.3%) in OC in Tianjin PM$_{2.5}$ in summer and 0.6%–3.9% (1.8%) and 0.6%–4.5% (2.0%), respectively, in winter. While the fractions of oxoacids-C and α-dicarbonlys-C in both TC and OC were less than 1% (Figure 6), but they were higher in summer compared to that in winter. In fact, the mass ratios of diacids-C, oxoacids-C, and α-dicarbonyls-C to TC and OC will increase with increasing aging of aerosols, because diacids and related compounds are mainly produced by oxidation reactions of their precursor compounds and then be subjected for further processing in the atmosphere. On the other hand, concentrations of elemental carbon (EC), a tracer for primary carbonaceous aerosols, were found to be lower (ave. 0.66 μg m$^{-3}$) by a factor of ~4 in summer than in winter (2.55 μg m$^{-3}$) (Wang et al., 2018). Such seasonal differences in mass fractions of diacids-C, oxoacids-C, and α-dicarbonlys-C in TC and OC together with the levels of EC imply that the secondary formation and aging of OA were more intensive in summer than in winter, whereas primary emissions were relatively more important in winter.

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. 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 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 secondary formation of diacids in the Tianjin atmosphere is more intensive than in other urban locations, and they have been subjected for considerable aging, particularly in summer.

However, the fraction of diacids-C in WSOC was similar in both the seasons, although the range is quite broad in winter (Figure 6). It is likely because not only diacids but also WSOC is mostly produced by oxidation reactions of VOCs in the atmosphere, and they both significantly produced from biomass burning emissions (Kundu, Kawamura, Andreae, et al., 2010). 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). Such higher levels of carbonaceous components including EC imply that the contributions of OA including diacids and related compounds from primary emissions might be significant in winter. But the comparable mass fractions of diacids-C in WSOC in winter with that in summer, despite the larger increment in WSOC loading than that of diacids, indicate that the secondary production of diacids in the Tianjin atmosphere was intensive in winter as
well, in addition to primary emissions. Of course, as can be seen from the diacids-C/OC (and TC) ratios, the extent of secondary formation and/or transformations of OA in winter were not as intensive as that in summer. Furthermore, the secondary formation and transformation processes of OA in summer and winter might have varied depending on the availability of oxidants and meteorological conditions. In fact, the loading of O3 was higher in summer, whereas the NO2 was higher in winter, and the ambient temperature and RH were higher in summer and winter, respectively, than in other seasons in the Tianjin atmosphere (Figure 1). Such patterns of seasonal variations in oxidants and meteorological parameters might have prevailed at regional scale and should have promoted the gas phase oxidation reactions of VOCs by O3 under high ambient temperatures in summer and by NO3 radicals in the aqueous phase under high humid conditions in winter over the Tianjin region.

Interestingly, temporal trends of the mass fractions of total α-dicarbonyls in TC, OC, and WSOC were different from those of diacids and oxoacids, particularly in summer (not shown here). The α-dicarbonyls-C fractions in TC were relatively constant, except for few cases, whereas that in OC and WSOC showed a nocturnal distribution, which is opposite to those of total diacids-C in OC and WSOC in early summer. It is well established that α-dicarbonyls convert to oxoacids and then to C2 diacid upon oxidation in the atmosphere (Pavuluri et al., 2015), and, thus, the abundances of α-dicarbonyls are decreased and those of diacids are increased with increasing aging and/or an increase in oxidation capacity of the atmosphere. Therefore, the relatively high mass fractions of α-dicarbonyls in OC (and WSOC) in nighttime than in daytime in summer demonstrate that, in addition to the long-range atmospheric transport from distant source regions (Figure 2), the OA was partially produced by in situ secondary processes in daytime under high solar radiation in the Tianjin atmosphere. On the other hand, since Tianjin is located on the shore of Bohai sea and the sampling point is only about 50 km away from the shore, the mass fractions of diacids and α-dicarbonyls in OC might have been influenced by land-sea breeze circulation that brings the aged pristine air masses that are enriched with the end products such as diacids from sea in daytime and the polluted air masses that are enriched with fresh organics including α-dicarbonyls from land in nighttime (Lu & Turco, 1994).

### 3.4. Implications for Origins and Secondary Processes

#### 3.4.1. Fossil Fuel Combustion and Biomass Burning

As noted earlier, 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 such as oleic acid (C18:1) that have a double bond at C-9 position (Kawamura & Gagosian, 1987). Therefore, the mass ratios of C6 and Ph acids to C9 diacid have been considered as proxies to evaluate the relative contributions of OA from anthropogenic and biogenic sources (Kawamura et al., 2012). Summary of mass ratios of selected marker diacids are provided in Table 3. Although average mass ratio of C6 to C9 in Tianjin aerosols was almost stable in both the seasons, the average Ph/C9 in winter was significantly \( (p = 0.04) \) higher than that in summer (Table 3). C6/C9 ratios in Tianjin are comparable to those reported from 14 cities of China in both winter and summer and from Tokyo whereas, the Ph/C9 ratios are comparable to those reported from 14 cities of China in winter but lower in summer (Table 3). However, both C6/C9 and Ph/C9 ratios are much lower than those reported from Los Angeles (Table 3). 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 in diesel fueled automobile exhaust is higher by a factor of 3 than that in the gasoline fueled automobile exhaust (Table 3). Average Ph/C6 ratios are comparable or slightly higher than those reported from Chennai, India (Table 3), where the influence of anthropogenic emissions are significant, although the biomass burning was considered to be a dominant source (Pavuluri et al., 2010). These results and comparisons 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 again indicate that other fossil fuel such as coal combustion might be an important source of OA, rather than gasoline fuel combustion in Tianjin.

However, as discussed earlier, the concentrations of long-chain diacids including C9 diacid were also higher in winter than in summer, indicating possible enhanced contribution of OA from biomass burning in winter. To confirm such possibility, as shown in Figure 7, we examined the relations of the sums of short-chain (\( \sum C_{2-4} \)) and long-chain (\( \sum C_{8-12} \)) diacids with potassium ion (K\(^+\)), a tracer for biomass burning emissions (Andreae, 1983). Interestingly, the \( \sum C_{2-4} \) showed a linear relation with K\(^+\), although the correlation is weak in summer and strong and statistically significant in winter (Figure 7a), suggesting that the short-chain diacids are mostly derived from biomass burning emissions in both the seasons, particularly in winter. Similarly, the \( \sum C_{8-12} \) showed a linear relation with K\(^+\) in only winter, although the correlation is weak due to few exceptional data points but statistically significant (Figure 7b), suggesting that the contribution of long-chain diacids from biomass burning was important in winter.

| Locale/source | Sampling period | \( C_6/C_9 \) | \( Ph/C_9 \) | \( Ph/C_6 \) | \( C_9/C_4 \) | M/F |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----|
| Tianjin, China\(^a\) | July 2016 | 0.29–2.56 | 0.72 | 0.12–5.28 | 2.27 | 0.26–7.15 | 3.38 | 0.65–3.76 | 1.06 | 0.55–4.22 | 1.49 |
| | November–December 2016 | 0.58–10.9 | 0.75 | 0.35–51.9 | 3.65 | 1.31–11.0 | 5.02 | 0.17–1.22 | 0.55 | 0.13–5.68 | 1.68 |
| Gasoline fueled AE\(^b\) | – | – | 1.87 | – | 3.85 | – | 2.05 | – | 0.33 | – | 2.83 |
| Diesel fueled AE\(^b\) | – | – | 0.64 | – | 4.20 | – | 6.58 | – | 0.59 | – | 7.91 |
| Los Angeles, USA\(^b\) | June, October 1984 | 0.74–40.0 | 14.0 | 3.00–20.0 | 10.7 | 0.13–6.90 | 2.20 | 0.31–0.81 | 0.51 | 0.52–7.33 | 2.14 |
| Tokyo, Japan\(^a\) | April 1988 to February 1989 | 0.30–1.60 | 0.72 | 0.35–1.90 | 0.83 | – | – | 0.56–2.90 | 1.60 | 0.81–3.93 | 1.90 |
| Sapporo, Japan\(^d\) | September 2009 to October 2010 | 0.07–0.42 | 0.21 | 0.09–1.18 | 0.39 | 0.83–3.59 | 1.70 | 1.05–1.58 | 2.08 | 0.73–4.09 | 1.50 |
| 14 Cities, China\(^e\) | January 2003 | – | 0.62 | – | 3.74 | – | – | – | 0.61 | – | – |
| | June–July 2003 | – | 0.89 | – | 4.16 | – | – | – | 0.86 | – | – |
| Chennai, India\(^f\) | January–February 2007 | 0.29–0.90 | 0.51 | 0.58–5.26 | 1.76 | 1.31–8.47 | 3.42 | 0.41–1.17 | 0.74 | 0.82–31.7 | 1.62 |
| | May 2007 | 0.15–0.69 | 0.35 | 0.17–1.17 | 0.74 | 1.06–4.68 | 2.25 | 0.59–1.06 | 0.78 | 0.83–0.94 | 0.53 |

Abbreviations: Ave, average, AE: automobile exhaust.

\(^a\) This study. \(^b\) Kawamura and Kaplan (1987). \(^c\) Kawamura and Ikushima (1993). \(^d\) Pavuluri et al. (2018). \(^e\) Ho et al. (2007). \(^f\) Pavuluri et al. (2010).
To further confirm whether these relations were driven by sources or meteorology, we examined the correlations of all measured individual species with carbonaceous components, marker ions (K⁺ and SO₄²⁻) and PM₂.₅ in summer and winter (see Table S3). Most of the diacids and related compounds showed a significant \((p \leq 0.05)\) correlation with WSOC and OC, but not with EC (except C₆ diacid) and PM₂.₅ (except C₂ and C₄ diacids and mGly), while only C₆, ωC₂, and ωC₃, with K⁺ and C₂, C₃, iC₅, Ph, KCl, and ωC₂ with SO₄²⁻ in summer (Table S3). Whereas in winter, most of the species showed significant correlations with bulk components including EC and PM₂.₅ but their correlation coefficients with SO₄²⁻, WSOC and K⁺ were much higher than those obtained with EC and slightly higher than those obtained with OC (Table S3). Such differences in coefficients confirm that the covariance of diacids and related compounds with carbonaceous components and marker ions was driven by their origins and secondary formation processes, rather than the weather conditions in Tianjin that were not stagnant in winter; the wind speed was comparable to that in summer (Figure 1a). In fact, the loading of K⁺ in Tianjin PM₂.₅ was higher by a factor of \(~8\) in winter than that in summer (Table 1), further confirming that the contribution of biomass burning emissions to the PM₂.₅ was large in winter compared to that in summer in Tianjin.

### 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 diacid is unstable at high temperatures (Kawamura & Ikushima, 1993). However, C₃ diacid 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 PM₂.₅ 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 3). 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 (Table 3) and from the remote Pacific (range 1.01–5.18; ave. 2.08), which were considered to be aged (Kawamura & Sakaguchi, 1999). Such results and comparisons suggest that the diacids and related compounds in Tianjin PM₂.₅ are largely produced by secondary formation, particularly in summer, however, they might have not been severely subjected for subsequent photochemical transformations (i.e., degradation of long-chain diacids to their lower homologues). Whereas in winter, the emissions from fossil fuel combustion should have also been contributed substantially. 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 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.

In contrast, averaged mass ratio of M to F acid did not show a difference between summer and winter (Table 3). 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, Kawamura, Andreae, et al., 2010; Kundu, Kawamura, & Lee, 2010b). Furthermore, the M/F ratios in Tianjin PM₂.₅ are higher by a factor of \(~3\) than those (ave. 0.56) reported in marine aerosols from the North Pacific, which were considered as more aged (Kawamura & Sakaguchi, 1999). However, they are much lower than those.
reported from automobile exhaust and slightly lower than those in Los Angeles and Tokyo aerosols, which were mainly influenced by fossil fuel combustion emissions at local scale (Kawamura & Ikushima, 1993; Kawamura & Kaplan, 1987). On the other hand, the M/F ratios in Tianjin PM$_{2.5}$ are comparable to those reported from Sapporo, Japan and Chennai, India, which were considered to be mainly originated from biogenic and biomass burning emissions, respectively, and potentially aged during long-range atmospheric transport (Pavuluri et al., 2010, 2018). Such comparisons imply that the OA in Tianjin PM$_{2.5}$ were derived from mixed sources and also relatively aged at local to regional scale. Moreover, the relative abundance of C$_2$ diacid (C$_2$%) 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, C$_2$% was lower than that in summer and did not show any difference between day- and nighttime (35.6% and 36%, respectively). Such high C$_2$% implies that the Tianjin OA were aged and substantially contributed from long-range transported air masses from distant source regions (Figure 2) as well, in addition to local sources.

### 3.4.3. Possible Secondary Formation in Aqueous Phase

C$_2$ diacid is produced from photochemical breakdown of its higher homologues: C$_3$ and C$_4$ diacids, and by photooxidation of oxoacids: $\omega$C$_2$ and Pyr acids, that derived from $\alpha$-dicarbonyls in the aqueous phase (Carlton et al., 2007; Ervens, 2004; Kawamura et al., 1996; Kawamura & Ikushima, 1993; Warneck, 2003). Recently, Pavuluri et al. (2015) found that the production of C$_4$ diacid is much higher compared to all other species including C$_2$ diacid until its precursor compounds are completely oxidized, and then the C$_4$ diacid breaks down into its lower homologues: C$_3$ and C$_2$ diacids (Pavuluri et al., 2015). Kawamura et al. (2012) found higher abundance of C$_4$ diacid than C$_2$ diacid in some of marine aerosol samples collected under overcast conditions with fog or brume events over the Arctic Ocean. In contrast, Yu et al. (2005) found very good correlation between SO$_4^{2-}$ and C$_2$ diacid in atmospheric aerosols from several locations over East Asia and Miyazaki et al. (2009) found high abundance of the C$_2$ diacid when the SO$_4^{2-}$ loading was high, and attributed to its enhanced production with increasing level of the SO$_4^{2-}$ in the aqueous phase. Therefore, the molecular distributions of C$_2$–C$_4$ diacids and $\omega$C$_2$ and Pyr acids provide insights on the possible secondary formation of diacids and related compounds in the aqueous phase.

Though the average concentrations of C$_2$ and C$_3$ diacids were increased by only about 2.0- and 1.4-folds, respectively, those of C$_4$ diacid and Pyr were increased by $\sim$3 times while that of $\omega$C$_2$ acid was increased by a factor of 5 from summer to winter in Tianjin PM$_{2.5}$ (Table 1). Furthermore, the relative abundances of C$_2$ and C$_3$ diacids to total diacids were decreased by a factor of about 1.4 and 2, respectively, from summer to winter, whereas that of C$_4$ diacid to total diacids and those of $\omega$C$_2$ and Pyr acids to total oxoacids remained almost same in both the seasons (Table 1). Such higher levels and abundances of C$_4$ diacid and $\omega$C$_2$ and Pyr acids in winter compared to those of C$_2$ and C$_3$ diacids imply that the secondary formation of diacids and related compounds in the aqueous phase might be important in the Tianjin atmosphere, particularly in winter, although we do not preclude such possibility in summer as well. In addition, because the degradation rates of C$_2$ and C$_3$ diacids are high compared their higher homologues (Yang et al., 2008), their degradation might be significant in the aqueous phase, which become more intensive if water-soluble Fe species are present in the aerosol samples due to catalytic oxidation (Pavuluri & Kawamura, 2012).

It has been well established that C$_2$ (and C$_3$) diacids, $\omega$C$_2$ acid, and Pyr ($\text{via} \ \omega$C$_2$ acid) acid that are mainly produced from their precursors such as isoprene, short-chain alkenes and alkynes, dicarbonyls, and aromatic hydrocarbons can be easily transformed into C$_2$ 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 C$_2$ diacid and $\omega$C$_2$, and Pyr with C$_2$ diacid could provide better insights to further assess the role of aqueous phase reactions in the formation of SOA in the Tianjin atmosphere. As shown in Figures 8a, 8c, and 8e, concentrations of C$_2$ diacid showed a very good, good, and moderate linear relations with those of C$_4$ (and C$_3$, not shown here), $\omega$C$_2$ acid, and Pyr, respectively, in winter and moderate relations in summer, and statistically significant in winter. In fact, the relative humidity was high up to 80% in winter, which could promote the aqueous phase oxidation reactions and thus played an important 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), ωC₂, and Pyr to an ultimate product, C₂ diacid, rather than simultaneous formation of all the species, in summer. The scatter plots of $\sum C₂–C₄$ showed a negligible inverse relation with RH in summer, but a significant linear relation ($r = 0.66; p < 0.01$) in winter, and a linear relation with ambient temperature in both the seasons, although correlation coefficients were weak, but significant ($p = 0.04$) in winter (Figure S3). Such relations further confirm that the secondary formation of diacids and related compounds were large in both the seasons, but aqueous phase reactions were more effective in winter.

Furthermore, concentrations of C₂ diacid showed an inverse relation with the relative abundance of C₄ diacid (C₄%) to the total linear ($\sum C₂–C₁₂$) diacids in both the seasons and with that of Pyr to total oxoacids in winter, although the coefficients were weak and statistically not significant at 95% level in the case of C₄% (Figures 8b and 8f). The correlation coefficient between C₂% and C₄% was slightly higher in summer than that in winter, whereas no relation appeared between C₂% and Pyr% in summer (Figures 8b and 8f). 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 and statistically not significant at 95% level in summer (Figure 8d). These results suggest that the formation of C₂ diacid by photochemical breakdown of C₄ (and C₃) diacids might have been a major pathway in summer whereas in winter, the C₂ diacid should have been mainly produced via ωC₂ acid in the aqueous phase. The linear relation between C₂% and ωC₂% indicates the in situ formation of ωC₂ acid from C₂ diacid.
its precursors must be higher than its subsequent transformation to C₂ diacid in the aqueous phase. In addition, the in situ formation of C₂ diacid via other (oxidation of its higher homologues) pathways might be more effective in the aqueous phase that enhance the concentration of C₂ diacid, resulting a linear relation with ωC₂%.

As shown in Figure 9, C₂ diacid as well as C₄ diacid and ωC₂ acid, total diacids, and total oxoacids (not shown here) showed linear relations with SO₄²⁻ with high and moderate (weak in the case of C₄ diacid and Pyr acid) correlation coefficients in winter and summer, respectively, but statistically significant in both the seasons, except in the case of C₄ and Pyr in summer. The weak correlations of C₄ diacid and Pyr acid, which are the first-generation species in the aqueous phase (Ervens et al., 2004; Lim et al., 2005), and SO₄²⁻ is likely, because the C₄ diacid and Pyr acid are transformed to more oxidized species such as C₃ and C₂ diacids and ωC₂ acid, respectively, upon further oxidation in the aqueous phase (Ervens, 2004; Lim et al., 2005; Pavuluri et al., 2015). In addition, C₄ diacid is produced by photochemical degradation of long-chain diacids that are formed from unsaturated fatty acids and Pyr is produced from α-dicarbonyls in the gas phase with aging (Pavuluri et al., 2015). 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 SO₄²⁻ in winter and summer, respectively (Figure 9f). Such linear relations imply that the secondary formation of OA including diacids and related compounds in the aqueous phase was important in both the seasons, although we do not preclude a substantial contribution of short-chain diacids and related compounds by aging of their higher homologues in aerosol and/or aqueous phase during the long-range atmospheric transport in summer.

Moreover, the strong correlation of WSOC with the SO₄²⁻ indicates that the water-soluble OA loading is increased with the increase in SO₄²⁻ levels, probably due to the enhancement in the oxidation of OA species in the aqueous phase under acidic conditions in the Tianjin atmosphere. Based on observations at four major cities of China (Beijing, Shanghai, Lanzhou, and Guangzhou), it has been reported that the conversion of OC to WSOC and, thus, the fraction of WSOC/OC is increased with increasing aerosol acidity (Pathak et al., 2011), which further supports our hypothesis. However, it is necessary to investigate the role of acidic species on oxidation of organics at molecular level, a subject of future research, to fully understand the
impact of acidic atmospheric conditions on the formation and transformations of OA and, thus, to consider the plausible measures to further reduce the emissions of NO\textsubscript{x} and SO\textsubscript{2} and formation of O\textsubscript{3} and subsequently the water-soluble OA in North China.

4. Conclusions

Diacids and related compounds measured in PM\textsubscript{2.5} samples collected on day- and night-time basis in summer and winter 2016 from Tianjin, North China showed the high abundance of C\textsubscript{2} diacid followed by ωC\textsubscript{2}, Ph, and tPh acids, respectively. C\textsubscript{4} diacid was the second most abundant diacids followed by C\textsubscript{3} diacid, while Pyr was the second most abundant oxoacids. All diacid, oxoacid, and α-dicarbonyl species, except for kC\textsubscript{3} and kC\textsubscript{7}, showed a high loading in winter than in summer, but their mass fractions in PM\textsubscript{2.5} were exactly the opposite; higher in summer than in winter. On an average, total diacids-C accounted for 2.9% in TC and 3.3% in OC in summer and 1.8% and 2.0%, respectively, in winter. Although the diurnal pattern was not systematic, on an average, most of the species showed a diurnal pattern. Diacids, oxoacids, and α-dicarboxyls are relatively abundant in the Tianjin atmosphere compared to those reported from most of other urban localities over China in winter. Mass ratios of C\textsubscript{6}/C\textsubscript{9}, Ph/C\textsubscript{9}, and Ph/C\textsubscript{6} diacids and their comparison with the literature together with the linear relations of sum of short-chain (ΣC\textsubscript{2}–C\textsubscript{4}) and long-chain (ΣC\textsubscript{8}–C\textsubscript{12}) diacids with K\textsuperscript{+} indicated that anthropogenic emissions, mainly coal combustion, and biomass burning emissions are the major sources in Tianjin region and their contributions are enhanced in winter. The mass ratios of C\textsubscript{6}/C\textsubscript{9} and M/F and the relative abundance of C\textsubscript{2} diacid (C\textsubscript{2}%) to total diacids suggested that the diacids and related compounds in Tianjin PM\textsubscript{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 C\textsubscript{2} diacid those of C\textsubscript{4} diacid and ωC\textsubscript{2} and Pyr acids and with the relative abundance of C\textsubscript{6} diacid (C\textsubscript{6}%) to the total linear (ΣC\textsubscript{2}–C\textsubscript{12}) diacids, and that of ωC\textsubscript{2} and Pyr to total oxoacids as well as with SO\textsubscript{4}\textsuperscript{2−} implied that the in situ secondary formation of OA including diacids and related compounds in the aqueous phase is important in both the seasons. Furthermore, the aging of OA, at least WSOC compounds, generated at local scale as well as transported from distant source regions was significant in the Tianjin region, North China. The strong correlation of WSOC with the SO\textsubscript{4}\textsuperscript{2−} indicated that the water-soluble OA loading is increased with the increase in SO\textsubscript{4}\textsuperscript{2−} levels, however, further research is needed to fully understand the impact of acidic atmospheric conditions on the formation and transformations of OA and, thus, to reduce the emissions of NO\textsubscript{x} and SO\textsubscript{2} and the formation of O\textsubscript{3} to control the water-soluble OA loading over North China.

Author Contributions

C. M. Pavuluri: Conceptualization, Methodology, Validation, Formal Analysis, Resources, Writing—Original Draft Preparation, Supervision, Funding Acquisition. S. Wang: Conceptualization, Validation, Formal Analysis, Investigation, Writing—Original Draft Preparation. W. Zhao: Validation. P. Q. Fu: Resources, Writing—Review and Editing. C.-Q. Liu: Writing—Review and Editing. Z. Xu: Project Administration, Writing—Review and Editing.

Data Availability Statement

The data used in this manuscript are listed in tables, figures, and supporting information and Wang et al. (2018). The data can be found online at https://zenodo.org/record/4284173#.X7wJE7NOk2x (DOI: 10.5281/zenodo.4284172).

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