

Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China

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[1] PM_{2.5} samples from 14 Chinese cities during winter and summer of 2003 were analyzed for 29 water-soluble organic species including diacids, ketoacids and dicarbonyls using a capillary GC and GC/MS. Homologous series of α,ω -dicarboxylic acids (C₂–C₁₂) and ω -oxocarboxylic acids (C₂–C₉) were detected as well as aromatic (phthalic) acid, α -ketoacid (pyruvic acid) and α -dicarbonyls (C₂–C₃). Molecular distributions of diacids demonstrated that oxalic (C₂) acid was the most abundant species followed by C₃ or C₄ diacids. Higher carbon number diacids were less abundant. C₂ diacid constituted 42–74% of total diacids (211–2162 ng m⁻³), corresponding to 0.15–2.83% of PM_{2.5} mass. In winter, the highest concentrations were observed in the southern city of Guangzhou (1886 ng m⁻³), while the lowest concentrations were observed in the northwest city of Jinchang (388 ng m⁻³). In summer, the highest concentrations were found in the northern city of Beijing (1598 ng m⁻³), whereas the lowest concentrations were found in Jinchang (223 ng m⁻³). Spatial variations of water-soluble diacids were characterized by higher concentrations in the south and lower concentrations in the north during winter whereas highest concentrations were observed in the north and midwest during summer. These spatial and seasonal distributions are consistent with photochemical production and the subsequent accumulation under different meteorological conditions.

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1. Introduction

[2] Atmospheric aerosols in China are receiving more attention due to rapid industrialization and urbanization. Anthropogenic aerosols from China may alter the regional atmospheric circulation, leading to an increased summer floods in the south and enhanced drought in the north [Gao and Anderson, 2001; Menon et al., 2002]. Previous studies in China determined mineral constituents and major inorganic ions in the aerosols [e.g., Parrington et al., 1983;

Bergin et al., 2001; Wang et al., 2002; Y. Wang et al., 2006; Duan et al., 2006]. However, studies of carbonaceous aerosols on a molecular level are limited [Liu et al., 2001; Guo et al., 2003; Bi et al., 2005; Wang and Kawamura, 2005; Yang et al., 2005; Zheng et al., 2005; Feng et al., 2006; Huang et al., 2006; Ho et al., 2006]. These measurements were taken in a few megacities located in eastern [Liu et al., 2001; Guo et al., 2003; Wang and Kawamura, 2005; Yang et al., 2005; Zheng et al., 2005] and southern China [Bi et al., 2005; Ho et al., 2006]. Little information is available for urban organic aerosols from middle and western-region China.

[3] Water-soluble organic compounds (WSOC) such as monocarboxylic acids, dicarboxylic acids and aldehydes are important components of atmospheric aerosols [Cautreels and Van Cauwenberghe, 1976; Rogge et al., 1993; Jacobson et al., 2000]. WSOC originate from biomass burning and fossil fuel combustion [Kawamura and Kaplan, 1987; Narukawa et al., 1999], as well as photochemical oxidation of organic precursors from anthropogenic and biogenic sources [Chebbi and Carlier, 1996; Kawamura and Ikushima, 1993; Kawamura et al., 1996a; Kawamura and Sakaguchi, 1999]. Dicarboxylic acids are common in WSOC [Grosjean et al., 1978; Kawamura and Ikushima, 1993; Rogge et al., 1993; Jacobson et al., 2000;

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Table 1. Sampling Site Description and Meteorological Conditions During the 2003 Campaigns

City Name	Code	Population, ^a million	City Description	Location	Sampling Height, m above ground level	Temperature Range	
						Winter	Summer
Southern Cities							
Hong Kong	HK	6	coastal and commercial	22.2°N, 114.1°E	18	10°–19°C	25°–36°C
Guangzhou	GZ	10.2	industrial and commercial	23.1°N, 113.2°E	10	7°–18°C	24°–38°C
Xiamen	XM	2.2	coastal and commercial	24.4°N, 118.1°E	8	8°–17°C	26°–28°C
Chongqing	CQ	5.5	continental and industrial	29.5°N, 106.5°E	10	5°–10°C	25°–40°C
Hangzhou	HZ	7.5	continental	30.2°N, 120.1°E	20	0°–10°C	25°–39°C
Wuhan	WH	8.3	industrial and commercial	30.5°N, 114.2°E	10	2°–10°C	23°–40°C
Shanghai	SH	16.7	industrial and commercial	31.2°N, 121.4°E	8	4°–15°C	24°–37°C
Northern Cities							
Xi'an	XA	7.4	continental and industrial	34.2°N, 108.9°E	10	–4°–5°C	23°–38°C
Qingdao	QD	7.3	coastal	36°N, 120.3°E	10	–4°–5°C	23°–34°C
Yulin	YL	0.4	continental, close to a desert	38.3°N, 109.8°E	10	–22°–6°C	19°–34°C
Jinchang	JC	0.2	Asian dust source regions	38.3°N, 101.1°E	10	–16°–0°C	17°–33°C
Tianjin	TJ	5	industrial	39.1°N, 117.2°E	20	–8°–6°C	21°–36°C
Beijing	BJ	13.8	continental and commercial	39.9°N, 116.4°E	14	–7°–4°C	22°–36°C
Changchun	CC	2.8	continental and industrial	43.9°N, 125.3°E	6	–17°–2°C	15°–33°C

^aPopulation data are from <http://www.cpirc.org.cn>.

Kawamura and Yasui, 2005], are hygroscopic, and play a role in the global radiation balance [Saxena et al., 1995; Facchini et al., 1999; Kerminen, 2001].

[4] Dicarboxylic acids have been found in the urban, rural, and marine atmosphere [Kawamura and Ikushima, 1993; Kawamura et al., 1996b; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Yao et al., 2004; Ho et al., 2006; Huang et al., 2006]. However, knowledge of their detailed composition and secondary formation pathways are limited. Total diacids account for ~1–3% of the total particulate carbon in urban areas and >10% in remote marine environments [Kawamura and Ikushima, 1993; Kawamura et al., 1996b, 1996c; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000]. Oxidative degradation of anthropogenic or biogenic volatile organic compounds (VOCs) by tropospheric oxidants and/or primary traffic emissions have been proposed as origins of dicarboxylic acids [Kawamura and Kaplan, 1987; Kawamura et al., 1996a; Warneck, 2003].

[5] To better understand the current status of air pollution in China, PM_{2.5} (particles with aerodynamic diameters less than 2.5 micrometers) samples were acquired in 14 cities, including several locations in middle and western China, during summer and winter 2003. Molecular compositions of low molecular weight (MW) diacids (C₂–C₁₂), ketoacids (ωC₂–ωC₉, pyruvic acid) and α-dicarbonyls (C₂–C₃) were determined by boron-trifluoride (BF₃)/n-butanol derivatization followed by gas chromatography (GC) and GC/mass spectrometry (MS). Samples were also analyzed for organic carbon (OC), elemental carbon (EC), and water-soluble organic carbon (WSOC). This paper examines the chemical compositions and seasonal and spatial variations of diacids, ketoacids and α-dicarbonyls. G. H. Wang et al. [2006] reported correspondent molecular compositions of solvent extractable organic compound classes, including n-alkanes, PAHs and fatty acids levels.

2. Experiment

2.1. Sampling Sites

[6] Fourteen sites were selected to represent economically developed and developing cities in different geographical

regions (covering 21–44°N, 101–126°E). As described in Table 1, these cities include seven from southern China (i.e., Chongqing (CQ), Guangzhou (GZ), Hong Kong (HK), Hangzhou (HZ), Shanghai (SH), Wuhan (WH), and Xiamen (XM)), and seven from northern China (i.e., Beijing (BJ), Changchun (CC), Jinchang (JC), Qingdao (QD), Tianjin (TJ), Xi'an (XA), and Yulin (YL)).

2.2. Sample Collection

[7] Twenty-four hour PM_{2.5} samples were taken for 2 d in each city for winter and summer 2003 on treated (800°C, 3 h) quartz-fiber filters (47 mm; Pall Corporation, Ann Arbor, MI, USA) using minivolume air samplers (Airmetrics, USA) at a flow rate of 5 L min^{–1}. Winter sampling was simultaneously conducted in 14 cities on 13–14 January 2003, and summer sampling was conducted during June and July 2003 to avoid rain. Filters were stored at –20°C after sampling. Although the filter samples (n = 56) were analyzed separately, averages of the two consecutive samples from each city are reported here.

2.3. OC, EC, and WSOC Analysis

[8] OC and EC were measured on a 0.526 cm² punch from each filter by thermal optical reflectance (TOR) following the IMPROVE protocol on a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) [Chow et al., 1993, 2001, 2004, 2005; Cao et al., 2003]. This produced four OC fractions (OC1, OC2, OC3, and OC4 at 120°C, 250°C, 450°C, and 550°C, respectively, in a helium [He] atmosphere), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen [O₂] was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 at 550°C, 700°C, and 800°C, respectively, in a 2% O₂/98% He atmosphere). IMPROVE OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP, whereas EC is defined as EC1 + EC2 + EC3 – OP.

[9] For WSOC, five punches (0.526 cm²) were taken from each filter and placed into a flat-bottomed screw-capped vial to which 1 mL of distilled deionized water (DDW) was added. Sample vials were heated in an oven at ~95°C for ~0.5 h. Samples were cooled to room temper-

Table 2. Concentrations of Low Molecular Weight Dicarboxylic Acids, Ketocarboxylic Acids, and α Dicarboxyls in PM_{2.5} Samples From 14 Cities of China^a

Compounds, ng m ⁻³	Summer (n = 28)			Winter (n = 28)		
	Range	Average	S.D.	Range	Average	S.D.
Dicarboxylic acids						
Oxalic, C2	88.7–1373	513	285	151–1437	558	351
Malonic, C3	9.40–99.7	50.9	25.1	10.3–111	40.6	24.4
Succinic, C4	15.1–164	71.8	41.2	20.9–195	79.7	50.3
Glutaric, C5	6.46–121	30.0	25.3	9.02–45.1	22.1	10.7
Adipic, C6	7.38–52.9	23.5	12.1	5.18–32.8	15.0	7.81
Pimelic, C7	0.84–29.5	6.34	5.77	1.15–18.5	6.70	5.09
Suberic, C8	MDLs–34.0	9.06	8.48	MDLs–19.9	5.98	5.68
Azelaic, C9	9.02–74.2	31.6	19.7	5.46–77.5	28.9	19.6
Sebacic, C10	MDLs–7.35	2.49	1.94	MDLs–23.1	4.40	5.44
Undecanedioic, C11	1.02–23.3	5.18	4.41	MDLs–12.9	3.80	3.01
Dodecanedioic, C12	MDLs–2.62	0.91	0.78	MDLs–1.95	0.29	0.59
Methylmalonic, iC4	1.13–15.1	3.75	2.84	MDLs–15.7	3.47	3.18
Methylsuccinic, iC5	1.70–24.2	10.3	6.21	5.32–37.3	14.5	8.67
2-Methylglutaric, iC6	0.75–13.9	3.85	2.98	1.22–6.12	3.36	1.25
Maleic, M	0.17–11.8	5.04	3.08	2.61–26.6	7.69	5.46
Fumaric, F	0.26–6.09	2.47	1.63	MDLs–28.3	3.42	6.10
Methylmaleic, mM	0.34–9.99	4.68	2.35	3.18–16.3	6.85	3.13
Phthalic, Ph	30.8–231	102	53.2	29.9–235	78.2	38.8
Isophthalic, iPh	0.50–11.9	4.46	3.01	MDLs–27.8	6.15	7.44
Malic, hC4	0.25–15.7	3.28	3.07	MDLs–15.9	6.41	4.93
Ketomalonic, kC3	MDLs–7.43	2.45	2.05	1.39–16.8	5.58	3.17
4-Ketopimelic, kC7	0.98–14.2	5.74	3.29	MDLs–6.30	2.65	2.04
Total diacids	211–2162	892	457	319–1940	904	480
Ketocarboxylic acids						
Pyruvic	MDLs–6.97	2.63	2.04	MDLs–8.92	3.57	2.16
Glyoxylic, ω C2	2.08–67.2	23.9	16.3	12.3–94.8	37.8	19.5
3-Oxopropanoic, ω C3	0.26–16.4	2.31	3.03	0.35–4.64	1.44	0.89
4-Oxobutanoic, ω C4	MDLs–19.9	5.11	5.39	MDLs–8.07	2.42	2.18
9-Oxononanoic, ω C9	0.15–7.68	2.88	1.82	0.54–33.6	7.08	7.82
Total ketoacids	4.86–114	36.7	23.7	19.8–118	52.3	24.2
α -Dicarboxyls						
Glyoxal, Gly	MDLs–6.77	2.72	2.05	MDLs–9.92	3.02	2.43
Methylglyoxal, MeGly	MDLs–8.50	2.47	2.53	MDLs–54.0	14.5	12.7
Total dicarboxyls	MDLs–15.3	5.17	4.14	0.91–63.9	17.5	13.8
Sum	221–2292	934	483	351–2016	974	499
PM _{2.5} , μ g m ⁻³	20.5–183	86.2	42.8	28.5–506	145	108
OC, μ g m ⁻³	4.74–41.7	16.1	9.08	7.01–125	35.3	31.2
EC, μ g m ⁻³	0.92–13.8	4.00	3.21	1.00–28.1	9.80	7.87
WSOC, μ g m ⁻³	2.16–15.8	7.75	3.47	4.42–43.2	14.4	10.7

^aMDL, method detection limit.

ature and stood for ~48 h. About 0.5 mL of the filter extracts were transferred to another vial by syringe and 20 μ L were taken for WSOC analysis on the DRI Model 2001 Carbon Analyzer. Triplicate analyses showed a precision of $\pm 10\%$.

2.4. Organic Acid Analysis

[10] Water-soluble dicarboxylic acids, ketoacids and dicarboxyls analysis followed the methods of Kawamura and Ikushima [1993] and Kawamura and Yasui [2005]. One quarter of the filter was extracted with pure water (10 mL \times 3), which was made by oxidizing organic impurities of Milli Q water with UV light. The extracts (water soluble organics) were passed through a glass column (Pasteur pipette) packed with a quartz wool to remove solid particles and then concentrated to ~0.1 mL using a rotary evaporator under a vacuum. They were further dried by nitrogen blow down and reacted with 14% BF₃/*n*-butanol at 100°C to convert the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals. The derivatives were extracted with *n*-hexane after adding pure

water and then determined with GC equipped with a split/splitless injector and a HP-5 fused silica capillary column.

[11] Peak identification was performed by comparing GC retention times with those of authentic standards. Ester identification was confirmed by mass spectral analysis using a GC/MS system (Thermo Trace MS) and authentic standards [Kawamura, 1993]. Recoveries of authentic standards spiked on a precombusted quartz-fiber filter were 71% for oxalic acid and better than 80% for malonic, succinic and adipic acids. Recoveries of glyoxylic acid, pyruvic acid and methylglyoxal were 88%, 72% and 47%, respectively. Spiked experiment of diacid standards to the filter sample (QFF 166) showed higher recoveries of oxalic acid (86%) and malonic acid (94%) [Kawamura and Yasui, 2005]. Duplicate analyses of filter sample showed that analytical errors are within 15% for major species. Concentrations of the acids and related compounds reported here are corrected for field blanks, but are not corrected for recovery efficiencies. The blank levels are generally less than 20% of aerosol concentrations for the major species.

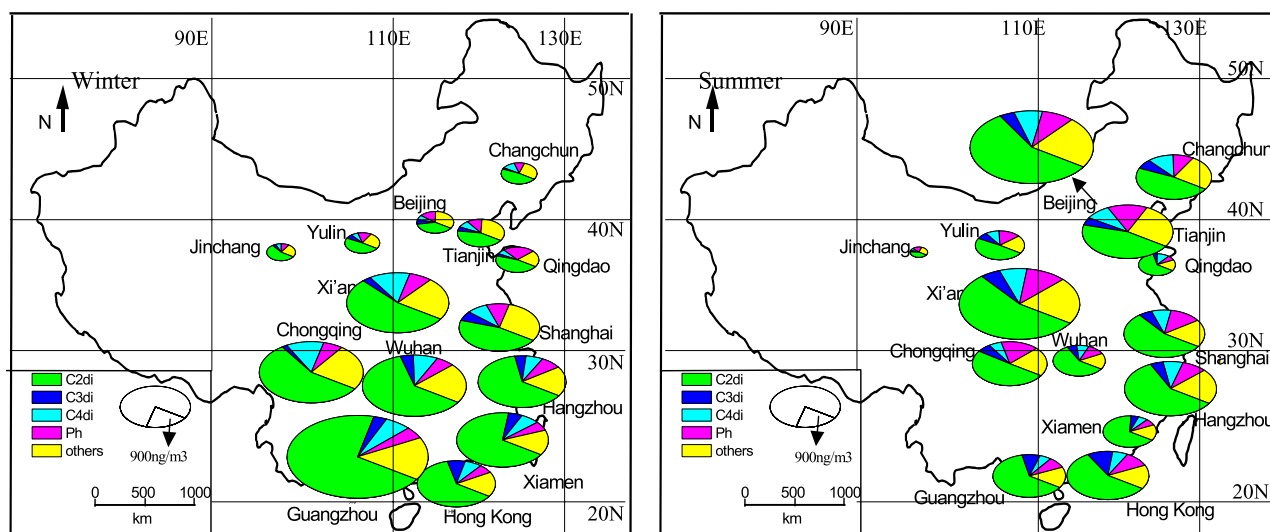


Figure 1. Seasonal and spatial variations of dicarboxylic acids in $\text{PM}_{2.5}$ from 14 Chinese cities (ng m^{-3}).

2.5. Secondary Organic Carbon (SOC) Estimates

[12] The EC enrichment model is used to estimate SOC [Turpin and Huntzicker, 1995]. Primary OC is estimated as:

$$\text{OC}_{\text{pri}} = a + b\text{EC}, \quad (1)$$

where a and b are the intercept and slope estimated from a linear regression for all 56 samples. The product $b\text{EC}$ represents the primary OC associated with combustion sources (coal combustion, traffic). The intercept a , is considered to be the primary OC background concentration originating from noncombustion sources (e.g., biogenic, soil and road resuspended, long-range transport). The SOA is estimated by the difference between the measured OC and primary OC (1):

$$\text{OC}_{\text{secondary}} = \text{OC} - \text{OC}_{\text{pri}} \quad (2)$$

[13] This method assumes that, at a certain location, there is a fixed relationship between primary OC and EC concentrations, i.e., the combustion ratio OC/EC (slope) and the primary OC background concentration (y -intercept) are constant over space and time.

3. Results and Discussion

3.1. Molecular Compositions of Dicarboxylic Acids, Ketoacids, and α -Dicarbonyls in $\text{PM}_{2.5}$

[14] A homologous series of α , ω -dicarboxylic acids (C_2 – C_{12}) and ω -oxocarboxylic acids (C_2 – C_9) were determined. Aromatic (phthalic) diacid and midchain ketodicarboxylic acids (kC_3 , kC_7) were also detected as well as α -ketoacid (pyruvic acid) and α -dicarbonyls (C_2 – C_3), resulting in a total of 29 water-soluble organic species reported in Table 2 and Table S1¹.

[15] Large variations were found among the 14 cities; total diacid concentrations ranged from 319 to 1940 ng m^{-3} (average 904 ng m^{-3}) in winter and from 211 to 2162 ng m^{-3} (average 892 ng m^{-3}) in summer. These values are higher than those (90–1370 ng m^{-3} , average 480 ng m^{-3}) reported in urban Tokyo [Kawamura and Ikushima, 1993], but are closer to the upper range (300–2100 ng m^{-3}) reported in urban Nanjing, China [Wang *et al.*, 2002]. Total ketoacid concentrations ranged from 19.8 to 118 ng m^{-3} (average 52.3 ng m^{-3}) in winter and from 4.86 to 114 ng m^{-3} (average 36.7 ng m^{-3}) in summer, while total dicarbonyl concentrations ranged from 0.91 to 63.9 ng m^{-3} (average 17.5 ng m^{-3}) in winter and from undetectable to 15.3 ng m^{-3} (average 5.17 ng m^{-3}) in summer. These concentrations are similar to those reported (ketoacids: 53 ng m^{-3} ; dicarbonyls: 12 ng m^{-3}) at the Gosan site on Jeju Island, South Korea [Kawamura *et al.*, 2004].

[16] As shown in Figure 1, in winter total dicarboxylic acids were the most abundant in central and southern China (i.e., Guangzhou, Wuhan, Chongqing and Xian), while the lowest concentrations were observed in northern China (Jinchang). While the lowest value was also found in Jinchang during summer, the highest concentrations were found in northern and central China (i.e., Beijing and Xi'an). Local meteorology may contribute to the high loadings of total diacids in western and central China. These cities are located in a basin-like topography with low wind speeds and stable atmospheric conditions. Because Jinchang is located in a low-population desert region, low anthropogenic emissions may result in low loadings.

[17] Oxalic (C_2) acid was the most abundant diacid found in all cities, ranging from 89 ng m^{-3} to 1437 ng m^{-3} with an average of 539 ng m^{-3} , and constituting 42% to 74% (average 58%) of all measured diacids. Oxalic (C_2) acid was also the most abundant diacid at urban [Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Wang *et al.*, 2002; Huang *et al.*, 2006; Ho *et al.*, 2006] and remote

¹Auxiliary materials are available in the HTML. doi:10.1029/2006JD008011.

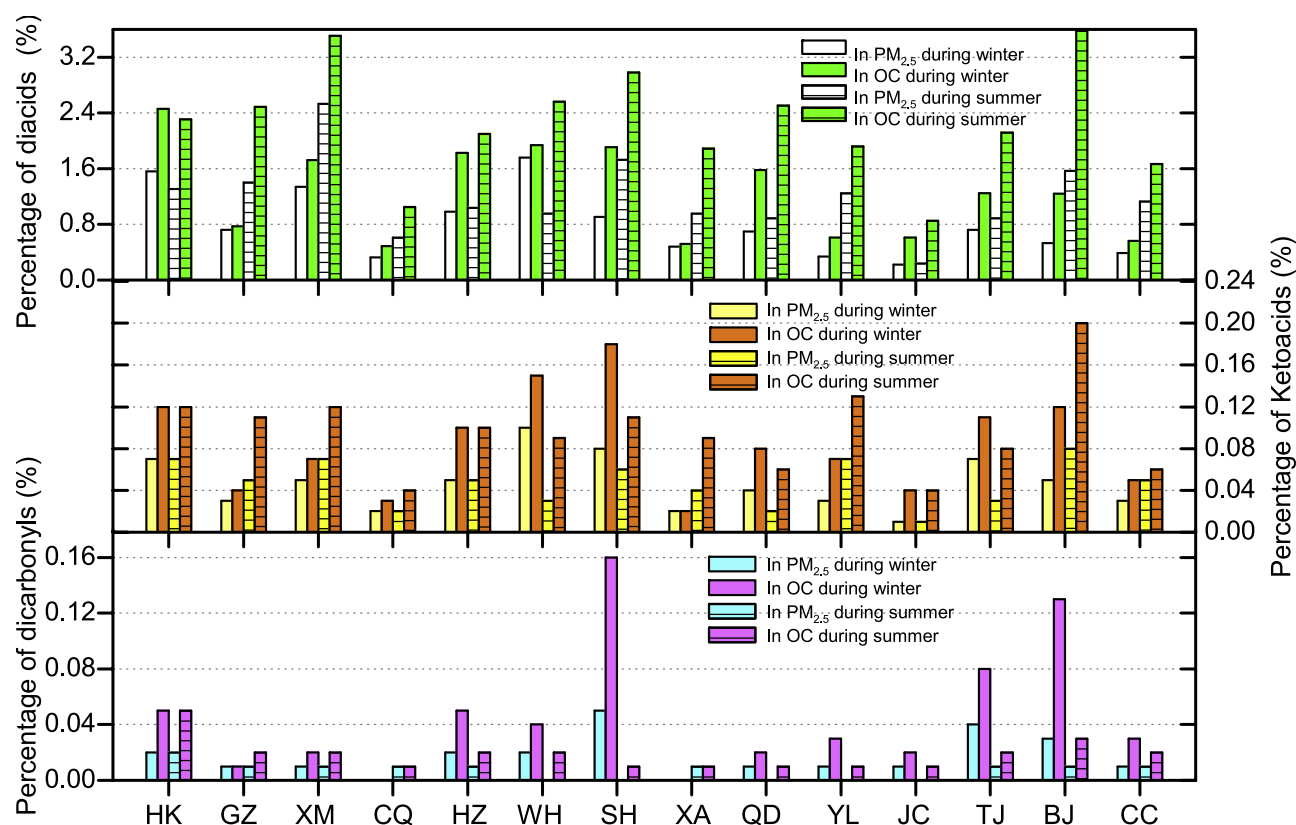


Figure 2. Abundance (%) of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls to $\text{PM}_{2.5}$ and organic carbon (OC) during winter and summer.

marine regions [Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Mochida et al., 2003]. Phthalic (Ph) acid ($30\text{--}235\text{ ng m}^{-3}$, average 90 ng m^{-3}) is the second most abundant diacid, accounting for 5–32% (average 11%) of the total diacid concentration. This is followed by succinic (C_4) acid ($15\text{--}195\text{ ng m}^{-3}$, average 75 ng m^{-3}), accounting for 5–15% (average 8%) of the total diacid concentration. The only exception is for Hong Kong, where the second most abundant diacid was malonic (C_3) acid.

[18] Phthalic acid (aromatic acid) is the second most abundant diacid in 11 cities for summer and in 7 cities for winter. This aromatic acid is directly emitted from combustion sources [Kawamura and Kaplan, 1987] and/or generated by atmospheric degradation of aromatic hydrocarbons such as naphthalene [Kawamura and Ikushima, 1993]. The longer-chain diacids ($\text{C}_5\text{--}\text{C}_{12}$) were less abundant than $\text{C}_2\text{--}\text{C}_4$ species. C_9 diacid is an oxidation product of biogenic unsaturated fatty acids containing a double bond at the C_9 -position (ozone and OH radical oxidation may occur to result in C_9 diacid) [Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Matsunaga et al., 1999]. Ketocarboxylic acids ($5\text{--}118\text{ ng m}^{-3}$, average: 45 ng m^{-3}) and α -dicarbonyls (undetectable– 64 ng m^{-3} , average: 12 ng m^{-3}) were also detected. Glyoxylic acid (ωC_2) is the dominant oxocarboxylic acid; its concentrations are slightly lower than those reported in Tokyo [Kawamura and Yasui, 2005].

3.2. Seasonal Variations of Dicarboxylic Acids, Ketoacids, and α -Dicarbonyls in $\text{PM}_{2.5}$

[19] There is no clear winter vs. summer variation for individual dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls, as shown in Table 2. Figure 1 shows that the concentrations in winter are higher in the southern cities than in the northern cities. The latitudinal contrast in winter may be caused by the depressed photochemical oxidation in the north due to the lower ambient temperatures (-14° to 0.5°C). However, these differences were not found in summer. Summer to winter ratios were near or below unity for the southern cities where the temperature and solar radiation are high enough for photochemical oxidation during winter (0° to 19°C). Lower mixing heights, surface inversion layers, and infrequent precipitation in winter may also contribute to higher diacid concentrations [Ho et al., 2006]. High summer to winter ratios (>1) for the northern cities (except for Qingdao and Jinchang) were due to low concentrations of diacids in winter, consistent with depressed photochemical oxidation of organic precursors of both anthropogenic and biogenic origin.

[20] Total dicarboxylic acids, ketocarboxylic acids and dicarbonyl concentrations were normalized to $\text{PM}_{2.5}$ mass and OC to examine seasonal variations (Figure 2). The abundances of total dicarboxylic acids in $\text{PM}_{2.5}$ mass were higher (winter: 0.15–1.94%, average: 0.79%; summer: 0.22–2.83, average: 1.20%) than those of other urban areas (i.e., Tokyo, Japan; 0.46%) [Kawamura and Ikushima, 1993] (Table S2). Higher summer values were found for

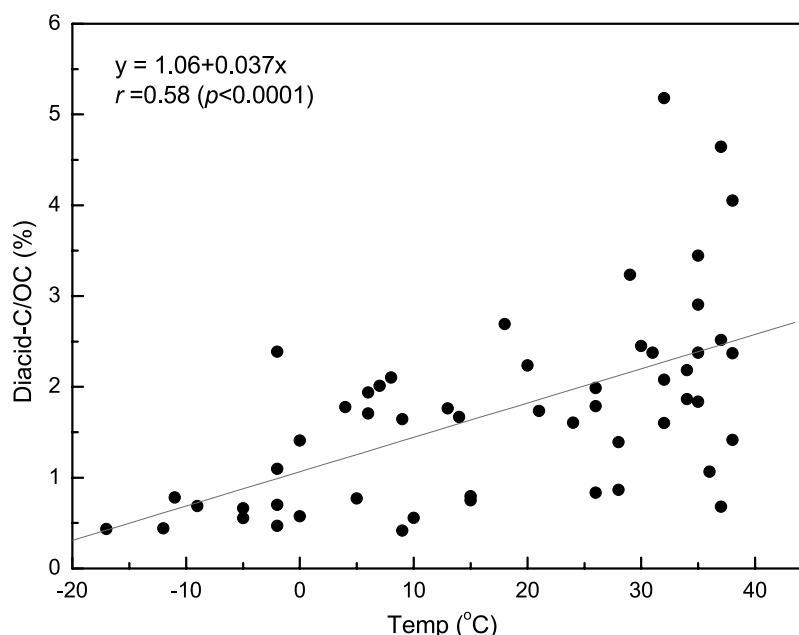


Figure 3. Dependence of the fraction of total dicarboxylic acid in organic carbon (OC) on temperature.

all cities except Hong Kong and Wuhan. Total diacids accounted for 0.49% to 3.58% of OC (winter average: 1.25%; summer average: 2.25%), again being consistent with enhanced secondary production of diacids during warmer weather. Oxalic acid (C_2) carbon relative to OC fluctuated from 0.17 to 2.73% (average 0.77%) with a summer maximum, being consistent with enhanced production during the warm season. Nearly all diacids, ketoacids and dicarbonyls contributed higher fractions of OC during summer than during winter (except for malic, ketomalonic and methylglyoxal). A reasonably good correlation ($r = 0.58-0.63$) was found between total diacid-C/OC and SOC/

OC ratios and ambient temperature (Figures 3 and 4). Abundances of total WSOC were also higher in summer (average 4.9%) than in winter (average 2.8%).

3.3. Comparison With Other Studies

[21] Similar chain length distributions of dicarboxylic acids, with a predominance of oxalic acid, have been observed in several cities. Concentrations of selected diacid species in total suspended particulate (TSP) and $PM_{2.5}$ are compared in Table 3. Average $PM_{2.5}$ concentrations of oxalic acid in Hong Kong, Shanghai and Beijing in this study are higher than those reported in previous studies.

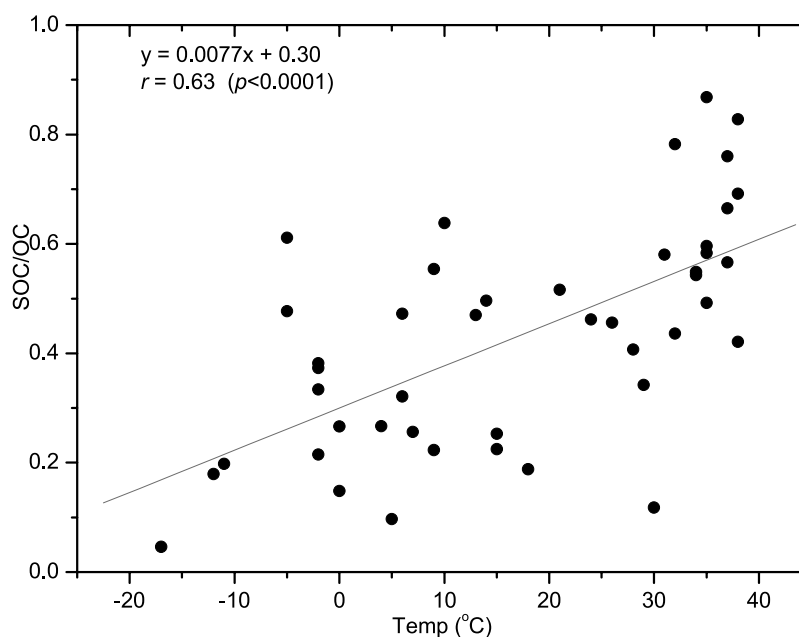


Figure 4. Dependence of the fractions of secondary organic carbon (SOC) in organic carbon (OC) on temperature.

Table 3. Dicarboxylic Acid Concentrations From Different Cities Compared With Levels in the 14 Cities Reported in the Literature^a

Site/Type	Season	Size	Method ^b	Oxalic	Malonic	Succinic	Adipic	Azelaic	Methylmaleic	Phthalic
Tokyo, Japan/urban ^c	1 a average	TSP	GC-FID	270	55	37	16	23	3.8	15
Tokyo, Japan/urban ^d	Jun	TSP	GC-FID	375	71.4	73.4	25.8	15.1	17.5	32.6
Tokyo, Japan/urban ^d	Jul	TSP	GC-FID	157	44	41	13	11	5.7	29
Tokyo, Japan/urban ^d	Nov	TSP	GC-FID	144	29.1	47.3	13.8	19.6	8.2	23.6
Gosan, Jeju Island, Korea/remote ^c	1 a average	TSP	GC-FID	473	67	52	8.4	4.7	5.3	9.8
Shanghai, China/urban ^f	1 a average	PM _{2.5}	IC	500	40/100	200				
Beijing, China/urban ^f	1 a average	PM _{2.5}	IC	300	100	30/20				
Beijing, China/urban ^g	summer and winter	PM _{2.5}	CE	218	39					
Nanjing, China/urban ^h	winter	PM _{2.5}	GC-MS	880	114	146	24	92		
Nanjing, China/urban ^h	spring	PM _{2.5}	GC-MS	440	63	80	49	195		
Nanjing, China/urban ⁱ	summer, daytime	PM _{2.5}	GC-FID			54.6	10.1	19.8		39.2
Nanjing, China/urban ⁱ	summer, nighttime	PM _{2.5}	GC-FID			50.5	2.63	10.4		19.4
Nanjing, China/urban ⁱ	winter, daytime	PM _{2.5}	GC-FID			38.3		32.3		32.4
Nanjing, China/urban ⁱ	winter, nighttime	PM _{2.5}	GC-FID			54.7		43.9		19.9
Hong Kong/urban ^j	summer	PM _{2.5}	IC	90	13	7				
Hong Kong/urban ^j	winter	PM _{2.5}	IC	350	20	50				
Hok Tsui, Hong Kong/remote ^j	summer	PM _{2.5}	IC	40	ND ^k	ND ^k				
Hok Tsui, Hong Kong/remote ^j	winter	PM _{2.5}	IC	370	20	60				
Hong Kong/urban ^l	autumn and winter	TSP	GC-MS	1084	142	118				
Vienna, Austria/urban ^m	summer	TSP	GC-MS/FID	340	244	117	117			
Leipzig, Germany/urban ⁿ	summer	TSP	IC	229	66	35				
Houston, USA/urban ^o	summer	PM _{2.5}	GC-MS		12.5	16.1	6.9	12.5		
This study/urban	winter, 14 cities	PM _{2.5}	GC-MS/FID	558	40.6	79.7	15.0	28.9	6.9	78.2
This study/urban	summer, 14 cities	PM _{2.5}	GC-MS/FID	519	55.0	71.2	22.7	30.2	4.7	101.80

^aUnit is ng m⁻³.^bGC-FID, gas chromatography-flame ionization detector; GC-MS, gas chromatography-mass spectrometry; IC, ion chromatography; CE, capillary electrophoresis.^cKawamura and Ikushima [1993].^dKawamura and Yasui [2005].^eKawamura et al. [2004].^fYao et al. [2004].^gHuang et al. [2005].^hWang et al. [2002].ⁱWang and Kawamura [2005].^jYao et al. [2004].^kND, not detected.^lLi and Yu [2005].^mLimbeck and Puxbaum [1999].ⁿRöhl and Lammel [2002].^oYue and Fraser [2004].

This difference may be partially due to differences in low MW dicarboxylic acid analytical methods. A GC/flame ionization detector (FID) was used in this study as compared to ion chromatography [IC] and capillary electrophoresis [CE] used in other studies. Average PM_{2.5} oxalic acid concentrations are comparable to or slightly higher than those reported for other sites in Asia (Tokyo and Jeju Island) and European cities (Vienna and Leipzig) for TSP samples. Similar to oxalic acid, average concentrations of PM_{2.5} malonic, succinic, adipic and azelaic acids in this study were higher than those in Leipzig (TSP) and Houston (PM_{2.5}), but similar to those in Tokyo (TSP), Vienna (TSP), and some Chinese cities.

[22] Phthalic acid is as abundant as succinic acid in winter and higher than succinic acid in summer. Phthalic acid may be derived from incomplete combustion of aromatic hydrocarbons (e.g., naphthalenes) in vehicular exhaust [Kawamura and Kaplan, 1987] or can be produced by atmospheric oxidation of aromatic hydrocarbons [Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005]. High concentrations of naphthalene were observed in some cities in China [Lee et al., 2001; Liu et al., 2001].

3.4. Correlation Analysis and the Ratios of C₃/C₄, C₆/C₉, and Ph/C₉

[23] Although atmospheric degradation of VOCs including aromatic hydrocarbons has been extensively discussed [e.g., Atkinson and Arey, 2003], formation mechanisms of diacids, including unsaturated species, are poorly understood. Previous studies suggested that low molecular weight diacids are produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons and fatty acids as well as their oxidation products [Kawamura and Sakaguchi, 1999; Kawamura et al., 1996b]. Some saturated diacids such as C₆ and iC₅ may be generated from cyclic olefins via O₃ and OH reactions in gas phase [Grosjean et al., 1978; Hatakeyama et al., 1987]. In contrast, unsaturated and branched-chain diacids have been considered to generate via photochemical oxidation of more specific precursors such as aromatic hydrocarbons [Kawamura et al., 1996a; Fisseha et al., 2004] and methylcycloalkenes [Grosjean and Fung, 1984]. Oxidation of aromatic hydrocarbons is mostly involved with OH radicals rather than O₃ [Finlayson-Pitts and Pitts, 2000]. More recently, oxalic, methylmaleic and pyruvic acids have been reported in the secondary organic

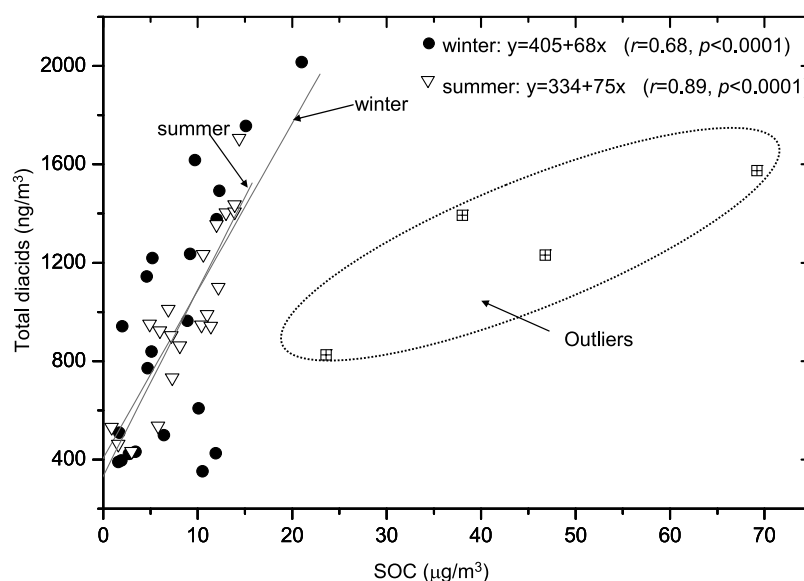


Figure 5. Relationship between the concentrations of total quantified dicarboxylic acids and the secondary organic carbon (SOC).

aerosols produced by the laboratory photo-oxidation of 1,3,5-trimethylbenzene [Fisseha *et al.*, 2004].

[24] The correlation coefficients of selected diacids, ketoacids and dicarbonyls in summer were examined. Other than anthropogenic emission, photochemical processes play an important role in controlling their atmospheric concentrations. Therefore fair or good correlations were observed among the selected species, especially in summer. For example, ω C₂, the most abundant ketoacid, may be further oxidized to C₂ diacid; thus a good correlation was found between ω C₂ and C₂ ($r = 0.93$, $P < 0.01$) in summer. Furthermore, C₂ is well correlated with malic acid (hC₄; $r = 0.81$, $P < 0.01$). This is consistent with the atmospheric oxidation process proposed for hC₄ and its degradation to C₂ [Kawamura and Ikushima, 1993]. C₃ and C₄ diacids may be further oxidized to C₂ [Kawamura and Ikushima, 1993], so that good correlations were observed among C₂, C₃ and C₄.

[25] Positive correlation ($r = 0.75$, $P < 0.01$) was also observed between the total quantified dicarboxylic acids and SOC (Figure 5), and the total diacids account for more than 15% (range from 3.3% to 58%) of SOC, suggesting that diacids, ketoacids and dicarbonyls are the major species for SOC in China. Higher correlation coefficient was found in summer ($r = 0.89$, $P < 0.01$) than in winter ($r = 0.68$, $P < 0.01$), consistent with photochemical processes in summer.

[26] It has been suggested that succinic acid (C₄) can serve as a precursor of malonic (C₃) acid [Kawamura *et al.*, 1996a] and that *cis* maleic acid (M) can isomerize to *trans* fumaric acid (F) during photochemical transformations [Kawamura and Ikushima, 1993]. Lower C₃/C₄ ratios (ranging from 0.25–0.44 with an average of 0.35) were observed in vehicular exhaust than those in atmospheric aerosols (0.56–2.9, average 1.6) because malonic acid is thermally less stable than succinic acid in the combustion process, although malonic acid is probably more produced [Kawamura and Ikushima, 1993]. In this study, higher ratios of C₃/C₄ and F/M were found in summer (especially in southern China) than in winter (Table 4), further supporting the importance of secondary formation of diacids. On the other hand, C₆ and phthalic (Ph) acids are produced by the atmospheric oxidation of anthropogenic cyclic hexene and aromatic hydrocarbons such as naphthalene, respectively, whereas C₉ is from biogenic unsaturated fatty acids [Kawamura and Ikushima, 1993]. Thus C₆/C₉ and Ph/C₉ ratios can be used as indicators of source contributions from anthropogenic and biogenic precursors to the aerosol diacids [Kawamura and Yasui, 2005]. Ratios of C₆/C₉ (0.24–2.11, summer: 0.89; winter: 0.62) and Ph/C₉ (1.07–13.3, summer: 4.16; winter: 3.74) were in the same range as those in Tokyo (C₆/C₉ = 0.72; Ph/C₉ = 0.83) but lower than those in Los Angeles in early 1980s (C₆/C₉ = 7.4; Ph/C₉ = 8.0) [Kawamura and Ikushima, 1993; Kawamura and Kaplan,

Table 4. Concentration Ratios of Selected Diacids in PM_{2.5}

Ratio	Malonic/Succinic	Fumaric/Maleic	Adipic/Azelaic	Phthalic/Azelaic
Summer: southern cities	1.12 ± 0.48	0.75 ± 0.61	0.81 ± 0.36	4.32 ± 2.45
Summer: northern cities	0.61 ± 0.17	0.63 ± 0.57	0.98 ± 0.43	4.01 ± 2.45
Average	0.86 ± 0.44	0.69 ± 0.58	0.89 ± 0.40	4.16 ± 2.41
Winter: southern cities	0.63 ± 0.29	0.40 ± 0.22	0.56 ± 0.17	2.57 ± 1.03
Winter: northern cities	0.59 ± 0.36	0.27 ± 0.33	0.69 ± 0.40	4.90 ± 3.53
Average	0.61 ± 0.32	0.33 ± 0.29	0.62 ± 0.31	3.74 ± 2.81

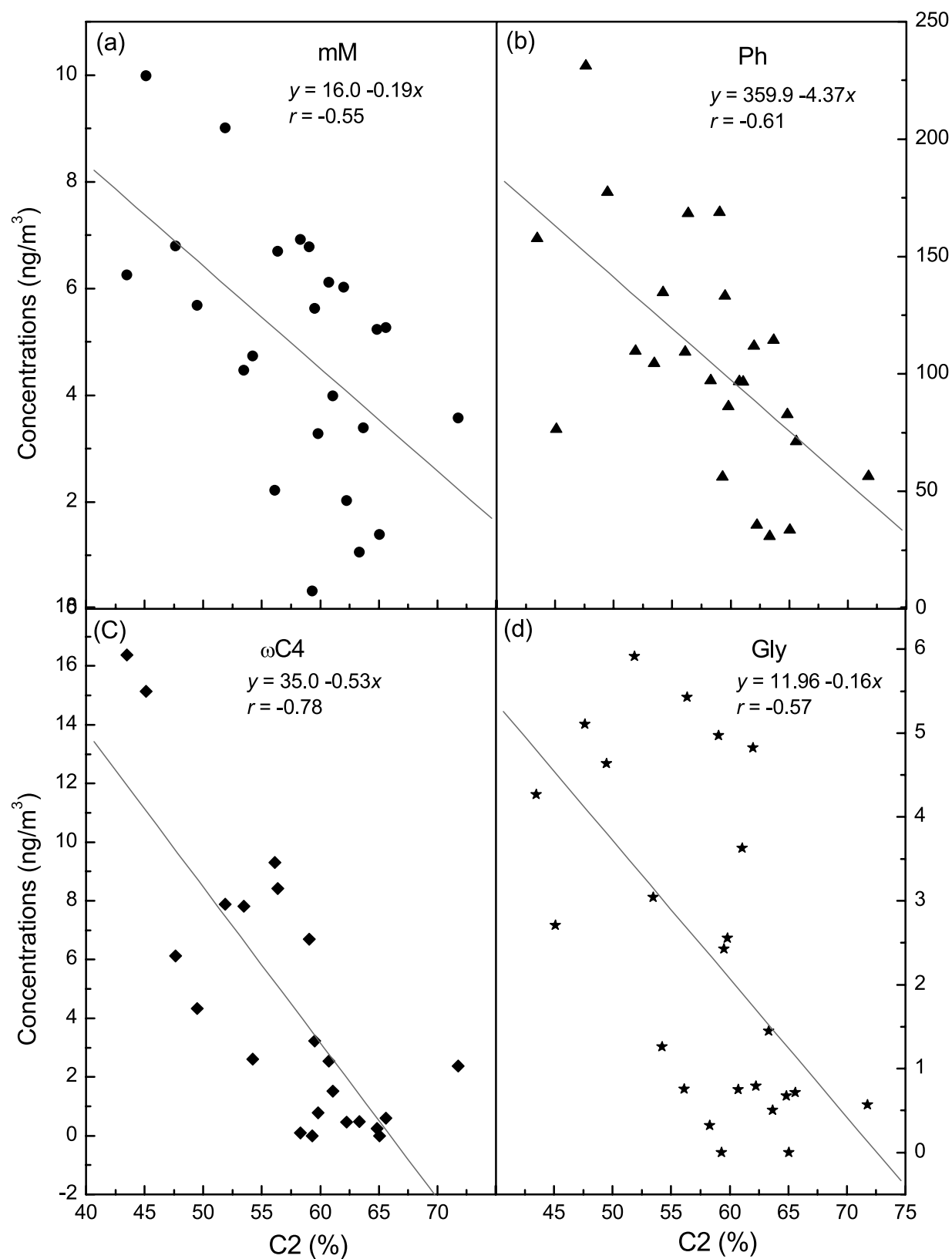


Figure 6. Concentrations of selected compounds: (a) methylmaleic (mM), (b) phthalic (Ph), (c) 4-oxobutanoic acid (ω C4), and (d) glyoxal (Gly) as a function of abundance of oxalic acid relative to total diacids (% C2) for the summer PM_{2.5} samples. Two samples from Jichang are not included.

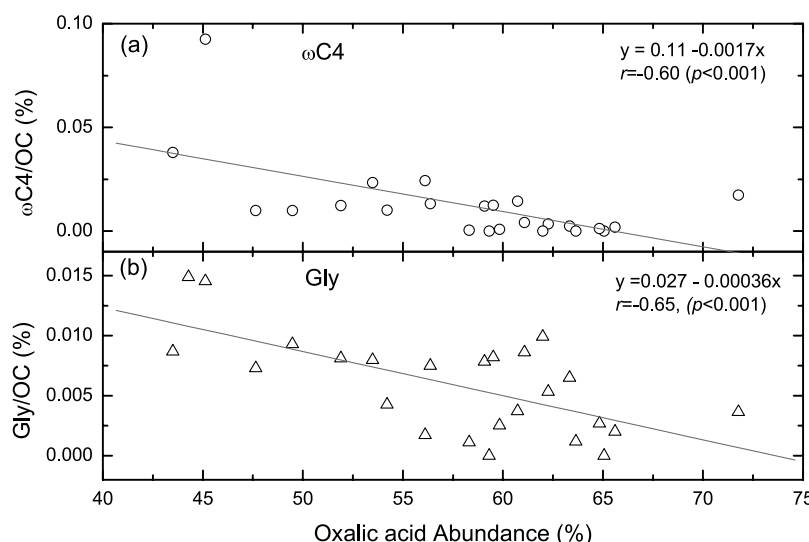


Figure 7. Compounds-C/OC ratios (%) as a function of relative abundance (%) of oxalic acid in total diacids for the summer PM_{2.5} samples: (a) 4-oxobutanoic acid (ω C₄) and (b) glyoxal (Gly). Two samples from Jichang are not included.

1987]. This indicates that anthropogenic contributions in China during 2003 and Tokyo during 1988–1989 are less significant than those of Los Angeles in early 1980s.

[27] This study also suggested that in addition to primary exhaust, secondary formation of particulate diacids by photo-oxidation reaction is also important. Relative abundance of C₂ (%) in total diacids has been proposed as a proxy for photochemical aging of organic aerosols [Kawamura and Sakaguchi, 1999; Kawamura and Yasui, 2005]. Good anticorrelations were observed between C₂ (%) and some water-soluble organic species (Figures 6a–6d); e.g., methylmaleic acid (mM; $r = -0.55$), phthalic acid (Ph; $r = -0.61$), 4-oxobutanoic acids (ω C₄; $r = -0.78$), and glyoxal (Gly; $r = -0.57$) during summer (with the samples from Jinchang removed), suggesting that these unsaturated and saturated diacids are formed in an early stage of the photochemical oxidations. As seen in Figure 7, ω C₄ and Gly species normalized by OC decrease as a function of C₂ (%) in summer with good correlation coefficients; $r = -0.60$ for ω C₄ and -0.66 for glyoxal. Relatively high correlation coefficients for these species demonstrate that saturated diacids and ketoacids are produced in the early stages of photochemical oxidation of aromatic hydrocarbons and cyclic olefins and are further oxidized to oxalic acid by the subsequent reactions. No clear anticorrelation was observed for the winter samples. This again suggests that secondary production of water-soluble organic aerosols is more characteristic to summer season.

4. Summary and Conclusions

[28] Molecular compositions of low molecular weight (MW) diacids (C₂–C₁₂), ketoacids (ω C₂– ω C₉, pyruvic acid) and α -dicarbonyls (C₂–C₃) were studied in the aerosol samples collected from 14 Chinese cities during the winter and summer campaigns of 2003 to better understand their spatial and seasonal variations, and primary and secondary sources. Oxalic (C₂) acid was found as the most

abundant diacid, followed by phthalic (Ph) or succinic (C₄) acids. Wintertime concentrations are higher in the southern cities than in the northern cities, which may be caused by the depressed photochemical oxidation in the north due to the lower ambient temperatures. The total diacids accounted for 0.49% to 3.58% of OC (winter average: 1.25%; summer average: 2.25%), indicating an enhanced secondary production of diacids in the warm season. A good correlation was found between total diacid carbon relative to organic carbon (OC) and the ambient temperature.

[29] Good correlation was also obtained between the total quantified dicarboxylic acid species and the estimated secondary organic carbon (SOC). The total quantified dicarboxylic acids contributed more than 15% of SOC, suggesting that the water-soluble organic species are one of the major contributors of SOC in China. Moreover, higher correlation coefficients in summer indicated that photochemical processes largely control the atmospheric concentrations of diacids and related compounds in the warm season. Higher ratios of C₃/C₄ and fumaric acid/maleic acid were found in summer (especially in southern China) than winter, further supporting the importance of secondary formation of diacids. Good anticorrelations were observed between the abundance of oxalic acid relative to total diacids (C₂,%) and some diacid species; e.g., methylmaleic acid (mM; $r = -0.55$), phthalic acid (Ph; $r = -0.61$), 4-oxobutanoic acids (ω C₄; $r = -0.78$), and glyoxal (Gly; $r = -0.57$) during summer time (with the samples from Jinchang removed), suggesting that these unsaturated and saturated species are formed in an early stage of the photochemical oxidation. No clear anticorrelation was observed for the winter samples. This study clearly demonstrates that secondary production of water-soluble organic aerosols is significant over China during the warm season.

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